

Electronic Supplementary Information

Ruthenium Complexes with *N*-Functionalized Secondary Amino Ligands: A New Class of Catalysts toward Efficient Hydrogenation of Esters

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I. General information

Unless otherwise stated, all manipulations were carried out under a dry Ar or N₂ atmosphere by using Schlenk line and glovebox techniques. Organic solvents as toluene, *n*-hexane, diethyl ether and tetrahydrofuran (THF) were dried by refluxing with sodium/potassium benzophenone under N₂ prior to use. 1,4-Dioxane was distilled from CaH₂ and kept in the glovebox for use. Ligands as (CH₂NH₂)₂, (CH₂NHMe)₂, (CH₂NHEt)₂, and (CH₂NH*i*Pr)₂ were purchased from J&K Chemical Co. and used as received. Compounds *o*-PPh₂C₆H₄NH₂,^[1] *o*-PPh₂C₆H₄NHMe,^[2] *o*-PPh₂C₆H₄NEt,^[3] *o*-PPh₂C₆H₄NHCH₂Ph,^[4] and RuCl₂(PPh₃)₃^[5] were prepared according to procedure reported in literatures. ¹H (500 MHz), ¹³C{¹H} (125 MHz), and ³¹P{¹H} (202 MHz) NMR spectra were measured on a Bruker AVIII-500 spectrometer. Solid state ³¹P (162 MHz) NMR spectra were measured on a Bruker AVIII SS-400 spectrometer. Infrared (IR) spectra were recorded using a Nicolet FT-IR 330 spectrometer. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument.

II. General procedure for the catalytic hydrogenation

In a glovebox, ruthenium complex, THF solvent, ester substrate, and NaOMe were charged into a 100 mL Teflon-lined Parr stainless-steel reactor equipped with a stirrer bar. The autoclave was carefully pressurization/venting with H₂ (10 bar) for three times. Then, the autoclave was pressurized with H₂ (50 bar) and heated at 100 °C for 1 h. Afterwards, the autoclave was quickly cooled to ca. 5 °C and depressurized slowly. The mixture was analyzed by gas chromatograph (GC, FULI company, 9790II) equipped with a KB-Wax column (60 m × 0.32 mm × 0.33 μm) after purification through a short, silica-filled column. The conversion of ester and the yield of alcohol were calculated by using *p*-xylene as an internal standard.

III. Synthetic details

Synthesis of (*o*-PPh₂C₆H₄NHMe)₂RuCl₂ (3**)** A mixture of (Ph₃P)₃RuCl₂ (0.48 g, 0.5 mmol) and *o*-PPh₂C₆H₄NHMe (0.29 g, 1.0 mmol) in toluene (40 mL) was allowed to heat to 100 °C and stayed at this temperature for 48 h. During the reaction, an orange solid was gradually formed. After the reaction and cooling to room temperature, the orange solid of compound **3** was collected by filtration and washed with *n*-hexane (2 mL). Yield: 0.34 g, 90%.

¹H NMR (500 MHz, CDCl₃, 298 K, ppm): δ = 3.15 (d, *J*_{HH} = 5.0 Hz, CH₃), 3.21 (d, *J*_{HH} = 5.0 Hz, CH₃), 5.73 (br, NH), 5.94 (br, NH), 6.99-7.04 (m), 7.07 (t, *J*_{HH} = 7.5 Hz), 7.10 (s), 7.13 (t, *J*_{HH} = 7.5 Hz), 7.17 (br), 7.18 (s), 7.20 (s), 7.22-7.36 (m) (C₆H₄ and Ph).

¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K, ppm): δ = 39.85 (s, CH₃), 41.04 (s, CH₃), 123.10 (t, *J*_{PC} = 5.0 Hz), 124.46 (t, *J*_{PC} = 5.0 Hz), 125.79 (s), 126.51 (s), 127.13 (t, *J*_{PC} = 5.0 Hz), 127.23 (d, *J*_{PC} = 3.1 Hz), 127.30 (t, *J*_{PC} = 5.0 Hz), 128.86 (d, *J*_{PC} = 8.1 Hz), 129.10 (d, *J*_{PC} = 11.2 Hz), 130.64 (s), 130.77 (s), 132.96 (s), 133.60 (s), 133.84 (t, *J*_{PC} = 5.0 Hz), 133.98 (t, *J*_{PC} = 2.5 Hz), 134.30 (t, *J*_{PC} = 5.0 Hz), 155.30 (t, *J*_{PC} = 6.3 Hz) (C₆H₄ and Ph).

³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, ppm): δ = 57.61 (s), 61.86 (s).

³¹P NMR (162 MHz, in solid, 298 K, ppm): δ = 58.04 (br).

IR (Nujol mull, KBr, cm⁻¹): ν = 3181, 3245 (N–H).

Anal. Calcd (%) for RuCl₂C₃₈H₃₆N₂P₂ (*M*_r = 754.6): C 60.48, N 3.71, H 4.81; found: C 59.94, N 3.63, H 4.99.

Synthesis of (*o*-PPh₂C₆H₄NHEt)₂RuCl₂ (4**)** A mixture of (Ph₃P)₃RuCl₂ (0.29 g, 0.3 mmol) and *o*-PPh₂C₆H₄NHEt (0.18 g, 0.6 mmol) in toluene (40 mL) was allowed to heat to 65 °C and stayed at this temperature for 4 d. The solution color change from green to brown was observed. After the reaction, the solution was cooled to room temperature. After concentration to ca. 1 mL, addition of *n*-hexane (5 mL) led to precipitation of the light-orange solid from the solution. The solid was collected by filtration and was subject to recrystallization in a THF/*n*-hexane (1 mL/5 mL) solvent mixture at –20 °C. After 3 d, the pure crystalline solid of compound **4** was formed, which was collected by filtration and dried *in vacuo*. Yield: 0.16 g, 68%.

¹H NMR plus ¹H-¹³C HSQC (500 MHz, CDCl₃, 298 K, ppm): δ = 1.13 (t, *J*_{HH} = 5.0 Hz, CH₃), 1.29 (t, *J*_{HH} = 5.0 Hz, CH₃), 3.36 (br, CH₂), 3.47 (br, CH₂), 3.78 (br, CH₂), 5.72 (br, NH), 5.83 (br, NH), 6.78 (br), 6.98-7.34 (m), 7.41 (d, *J*_{HH} = 5.0 Hz), 7.44 (t, *J*_{HH} = 5.0 Hz), 7.55 (d, *J*_{HH} = 5.0 Hz), 7.65 (d, *J*_{HH} = 5.0 Hz) (C₆H₄ and Ph).

¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K, ppm): δ = 14.69 (s, CH₃), 15.07 (s, CH₃), 46.89 (s, CH₂), 48.92 (s, CH₂), 123.87 (s), 125.23 (s), 125.30 (s), 126.13 (s), 127.00 (s), 127.25 (s), 128.22 (s), 128.83 (s), 129.02 (d, *J*_{PC} = 1.9 Hz), 130.14 (s), 130.36 (s), 133.82 (d, *J*_{PC} = 25.0 Hz), 134.04 (d, *J*_{PC} = 30.0 Hz), 134.34 (s), 154.25 (s) (C₆H₄ and Ph).

³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, ppm): δ = 56.67 (s), 60.03 (s).

³¹P NMR (162 MHz, in solid, 298 K, ppm): δ = 61.61 (br).

IR (Nujol mull, KBr, cm⁻¹): ν = 3240 (N–H).

Anal. Calcd (%) for RuCl₂C₄₀H₄₀N₂P₂ (*M*_r = 782.7): C 61.38, N 3.58, H 5.15; found: C 60.29, N 3.23, H 5.25.

Synthesis of (*o*-PPh₂C₆H₄NHCH₂Ph)₂RuCl₂ (5**)** A mixture of (Ph₃P)₃RuCl₂ (0.29 g, 0.3 mmol) and *o*-PPh₂C₆H₄NHCH₂Ph (0.22 g, 0.6 mmol) in toluene (40 mL) was allowed to heat at 100 °C for 48 h. After the reaction a yellow solution was developed. The solution was cooled to room temperature and then concentrated to ca. 1 mL. Addition of *n*-hexane (5 mL) led to precipitation of the brick-red solid from the solution. The solid was collected by filtration and was subject to recrystallization in a THF/*n*-hexane (1 mL/5 mL) solvent mixture at –20 °C. After 3 d, the pure crystalline solid of compound **5** was obtained, which was collected by filtration and dried *in vacuo*. Yield: 0.25 g, 93%.

¹H NMR plus ¹H-¹³C HSQC (500 MHz, CDCl₃, 298 K, ppm): δ = 3.86 (dd, *J*_{HH} = 5.0, 15.0 Hz, CH₂), 4.21 (dd, *J*_{HH} = 10.0, 15.0 Hz, CH₂), 4.93 (dd, *J*_{HH} = 5.0, 15.0 Hz, CH₂), 5.20 (d, *J*_{HH} = 15.0 Hz, CH₂), 5.70 (t, *J*_{HH} = 5.0 Hz, NH), 6.18 (d, *J*_{HH} = 5.0 Hz, NH), 6.89 (d, *J*_{HH} = 10.0 Hz), 7.08 (t, *J*_{HH} = 10.0 Hz), 7.11-7.36 (m), 7.61 (d, *J*_{HH} = 10.0 Hz) (C₆H₄ and Ph).

¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K, ppm): δ = 58.33 (s, CH₂), 59.60 (s, CH₂), 125.53 (d, *J*_{PC} = 7.5 Hz), 125.96 (s), 127.13 (t, *J*_{PC} = 5.0 Hz), 127.26 (t, *J*_{PC} = 5.0 Hz), 127.71 (s), 128.02 (s), 128.74 (s), 129.01 (d, *J*_{PC} = 13.8 Hz), 129.72 (s), 129.90 (s), 133.10 (s), 133.39 (s), 134.15 (d, *J*_{PC} = 10.0 Hz), 138.50 (s), 155.11 (t, *J*_{PC} = 7.5 Hz) (C₆H₄ and Ph).

³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, ppm): δ = 57.66 (s), 59.30 (s).

³¹P NMR (162 MHz, in solid, 298 K, ppm): δ = 57.59 (br).

IR (Nujol mull, KBr, cm⁻¹): ν = 3128, 3192 (N–H).

Anal. Calcd (%) for RuCl₂C₅₀H₄₄N₂P₂ (*M*_r = 906.8): C 66.22, N 3.09, H 4.89; found: C 66.30, N 2.85, H 5.08.

Synthesis of (*o*-PPh₂C₆H₄NH₂)[NH₂(CH₂)₂NH₂]RuCl₂ (6) A mixture of [(Ph₃P)(*o*-PPh₂C₆H₄NH₂)RuCl₂]₂ (**1**, 0.28 g, 0.2 mmol) and (CH₂NH₂)₂ (24.1 mg, 0.4 mmol) in toluene (30 mL) was well-sealed in a high pressure bottle and heated at 130 °C for 4 d. After cooling to room temperature, the light yellow-green solid of compound **6** was formed, which was collected by filtration and washed with *n*-hexane (2 mL). Yield: 0.18 g, 88%. During to insolubility in organic solvent, the solid state ³¹P NMR and IR spectra were recorded.

³¹P NMR (162 MHz, in solid, 298 K, ppm): $\delta = 69.41$ (br).

IR (Nujol mull, KBr, cm⁻¹): $\nu = 3071, 3125, 3209, 3287$ (N-H).

Anal. Calcd (%) for RuCl₂C₂₀H₂₄N₃P ($M_r = 509.1$): C 47.18, N 8.26, H 4.75; found: C 47.42, N 7.88, H 4.56.

Synthesis of (*o*-PPh₂C₆H₄NH₂)[MeNH(CH₂)₂NHMe]RuCl₂ (7) A mixture of [(Ph₃P)(*o*-PPh₂C₆H₄NH₂)RuCl₂]₂ (**1**, 0.28 g, 0.2 mmol) and (CH₂NHMe)₂ (35.3 mg, 0.4 mmol) in THF (30 mL) was heated at 60 °C for 48 h. After the reaction, a yellow solution was developed. The solution was cooled to room temperature and then concentrated to ca. 1 mL. Addition of *n*-hexane (5 mL) led to precipitation of the light-yellow solid from the solution. The solid was collected by filtration and was subject to recrystallization in a THF/*n*-hexane (1 mL/5 mL) solvent mixture at 20 °C. After 4 d, the pure crystalline solid of compound **7** was obtained, which was collected by filtration and dried *in vacuo*. Yield: 96.7 mg, 45%.

¹H NMR plus ¹H-¹³C HSQC (500 MHz, CDCl₃, 298 K, ppm): δ = 1.27 (d, *J*_{HH} = 20.0 Hz, 1 H, NH), 1.59 (dd, *J*_{HH} = 10.0, 20.0 Hz, 1 H, CH₂), 1.90 (d, *J*_{HH} = 10.0 Hz, 1 H, CH₂), 2.16 (d, *J*_{HH} = 10.0 Hz, 3 H, CH₃), 2.82 (d, *J*_{HH} = 5.0 Hz, 3 H, CH₃), 2.84 (d, *J*_{HH} = 15.0 Hz, 1 H, CH₂), 3.16 (dd, *J*_{HH} = 10.0, 20.0 Hz, 1 H, CH₂), 4.65 (br, 1 H, NH), 4.92 (d, *J*_{HH} = 10.0 Hz, 1 H, NH), 5.74 (d, *J*_{HH} = 15.0 Hz, 1 H, NH), 7.04 (t, *J*_{HH} = 10.0 Hz), 7.23 (d, *J*_{HH} = 5.0 Hz), 7.34 (t, *J*_{HH} = 10.0 Hz), 7.40 (br), 7.43 (d, *J*_{HH} = 5.0 Hz), 7.63 (d, *J*_{HH} = 10.0 Hz), 8.51 (t, *J*_{HH} = 10.0 Hz) (14 H, C₆H₄ and Ph).

¹³C{¹H} NMR (125 MHz, CDCl₃, 298 K, ppm): δ = 40.07 (s, 1 C, CH₃), 46.11 (s, 1 C, CH₃), 53.81 (s, 1 C, CH₂), 56.52 (s, 1 C, CH₂), 125.91 (d, *J*_{PC} = 10.0 Hz), 127.54 (d, *J*_{PC} = 5.0 Hz), 128.06 (d, *J*_{PC} = 8.8 Hz), 128.21 (s), 128.96 (s), 129.02 (s), 129.65 (s), 130.38 (d, *J*_{PC} = 18.8 Hz), 131.30 (s), 131.37 (s), 134.07 (d, *J*_{PC} = 37.5 Hz), 135.65 (d, *J*_{PC} = 11.3 Hz), 136.92 (d, *J*_{PC} = 5.0 Hz), 137.24 (s) 149.67 (d, *J*_{PC} = 18.8 Hz) (18 C, C₆H₄ and Ph).

³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K, ppm): δ = 71.35 (s).

IR (Nujol mull, KBr, cm⁻¹): ν = 3146, 3158, 3204, 3267 (N-H).

Anal. Calcd (%) for RuCl₂C₂₂H₂₈N₃P (*M*_r = 537.4): C 49.17, N 7.82, H 5.25; found: C 50.34, N 7.49, H 5.44.

Synthesis of (*o*-PPh₂C₆H₄NH₂)[EtNH(CH₂)₂NHEt]RuCl₂ (8**)** A mixture of [(Ph₃P)(*o*-PPh₂C₆H₄NH₂)RuCl₂]₂ (**1**, 0.28 g, 0.2 mmol) and (CH₂NHEt)₂ (46.5 mg, 0.4 mmol) in toluene (30 mL) was heated at 100 °C for 48 h. After the reaction a light-yellow solution was developed. The solution was slowly cooled to room temperature, and the crystalline solid of compound **8** was collected by filtration and dried *in vacuo*. Yield: 0.19 g, 83%.

¹H NMR plus ¹H-¹³C HSQC (500 MHz, CDCl₃, 298 K, ppm): δ = 0.51 (t, *J*_{HH} = 7.0 Hz, 3 H, CH₃), 1.02 (t, *J*_{HH} = 7.0 Hz, 1 H, NH), 1.11 (t, *J*_{HH} = 7.0 Hz, 3 H, CH₃), 1.45 (m, 1H, CH₂), 1.98 (m, 1 H, CH₂), 2.17 (d, *J*_{HH} = 11.0 Hz, 1 H, CH₂), 2.36 (m, 1 H, CH₂), 3.01 (m, 1 H, CH₂), 3.07-3.18 (m, 2 H, CH₂), 3.98 (m, 1 H, CH₂), 4.31 (t, *J*_{HH} = 8.5 Hz, 1 H, NH), 4.75 (t, *J*_{HH} = 13.0 Hz, 1 H, NH), 5.74 (t, *J*_{HH} = 15.0 Hz, 1 H, NH), 7.04 (t, *J*_{HH} = 8.5 Hz), 7.23 (t, *J*_{HH} = 7.0 Hz), 7.33 (t, *J*_{HH} = 7.5 Hz), 7.36-7.44 (m), 7.58 (m), 8.45 (t, *J*_{HH} = 8.5 Hz) (14 H, C₆H₄ and Ph).

¹³C {¹H} NMR (125 MHz, CDCl₃, 298 K, ppm): δ = 13.26 (s, 1 C, CH₃), 14.46 (s, 1 C, CH₃), 47.14 (s, 1 C, CH₂), 49.23 (s, 1 C, CH₂), 52.52 (s, 1 C, CH₂), 53.55 (s, 1 C, CH₂), 125.89 (d, *J*_{PC} = 9.1 Hz), 127.55 (d, *J*_{PC} = 4.5 Hz), 128.06 (d, *J*_{PC} = 9.6 Hz), 129.03 (d, *J*_{PC} = 8.3 Hz), 129.57 (s), 130.18 (d, *J*_{PC} = 1.4 Hz), 130.44 (s), 131.56 (s), 131.62 (s), 134.43 (d, *J*_{PC} = 37.0 Hz), 135.47 (d, *J*_{PC} = 10.0 Hz), 137.09 (d, *J*_{PC} = 11.8 Hz), 137.11 (d, *J*_{PC} = 67.8 Hz), 149.34 (d, *J*_{PC} = 18.1 Hz) (18 C, C₆H₄ and Ph).

³¹P {¹H} NMR (202 MHz, CDCl₃, 298 K, ppm): δ = 70.75 (s).

IR (Nujol mull, KBr, cm⁻¹): ν = 3128, 3167, 3200, 3245 (N-H).

Anal. Calcd (%) for RuCl₂C₂₄H₃₂N₃P (*M*_r = 565.5): C 50.97, N 7.43, H 5.70; found: C 51.34, N 7.07, H 5.71.

Synthesis of (*o*-PPh₂C₆H₄NH₂)[*i*PrNH(CH₂)₂NH*i*Pr]RuCl₂ (9) A mixture of [(Ph₃P)(*o*-PPh₂C₆H₄NH₂)RuCl₂]₂ (**1**, 0.28 g, 0.2 mmol) and (CH₂NH*i*Pr)₂ (57.7 mg, 0.4 mmol) in 1,4-dioxane (15 mL) was heated at 101 °C for 18 d. During the reaction, a light-yellow solid was gradually formed. After the reaction and cooling to room temperature, the solid of compound **9** was collected by filtration and washed with *n*-hexane (2 mL). Yield: 0.14 g, 59%.

¹H NMR plus ¹H-¹³C HSQC (500 MHz, CDCl₃, 298 K, ppm): δ = 0.87 (d, *J*_{HH} = 5.0 Hz, 3 H, CH₃), 0.88 (unknown, 1 H, NH), 1.10 (d, *J*_{HH} = 10.0 Hz, 3 H, CH₃), 1.49 (dd, *J*_{HH} = 3.5, 6.5 Hz, 6 H, CH₃), 2.63 (dd, *J*_{HH} = 15.0, 25.0 Hz, 1 H, CH), 2.78 (d, *J*_{HH} = 15.0 Hz, 1 H, CH), 3.20 (d, *J*_{HH} = 10.0 Hz, 1 H, NH), 3.23 (s, 1 H, CH), 3.60 (m, 1 H, CH), 3.81 (m, 2 H, CH₂), 4.81 (d, *J*_{HH} = 30.0 Hz, 2 H, NH₂), 7.22-7.32 (m), 7.36 (d, *J*_{HH} = 5.0 Hz), 7.39 (s), 7.49 (t, *J*_{HH} = 5.0 Hz), 7.73 (t, *J*_{HH} = 5.0 Hz) (14 H, C₆H₄ and Ph).

¹³C {¹H} NMR (125 MHz, CDCl₃, 298 K, ppm): δ = 17.83 (s, 1 C, CH), 20.93 (s, 1 C, CH₂), 22.76 (s, 1 C, CH), 23.81 (s, 1 C, CH₂), 41.51 (s, 1 C, CH₃), 45.34 (s, 1 C, CH₃), 50.81 (s, 1 C, CH₃), 57.77 (s, 1 C, CH₃), 127.07 (s), 127.41 (d, *J*_{PC} = 8.8 Hz), 127.70 (d, *J*_{PC} = 7.5 Hz), 128.82 (s), 129.32 (s), 129.88 (s), 132.30 (s), 133.60 (d, *J*_{PC} = 8.8 Hz), 134.11 (d, *J*_{PC} = 8.8 Hz) (18 C, C₆H₄ and Ph).

³¹P {¹H} NMR (202 MHz, CDCl₃, 298 K, ppm): δ = 66.45 (s).

IR (Nujol mull, KBr, cm⁻¹): ν = 3142, 3201, 3254 (N-H).

Anal. Calcd (%) for RuCl₂C₂₆H₃₆N₃P (*M*_r = 593.5): C 52.61, N 7.08, H 6.11; found: C 51.36, N 7.25, H 5.98.

IV. X-ray crystallographic analysis

X-ray crystallographic analysis of 3: Crystallographic data for **3** was collected at 173 K on an Agilent Super Nova system using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Intensity measurements were performed on a rapidly cooled crystal with dimensions of $0.10 \times 0.05 \times 0.05 \text{ mm}^3$ in the range $4.05^\circ < \theta < 73.73^\circ$. The data completeness collected was 96.9%. Absorption correction was applied using the spherical harmonic program (multi-scan type). The structure was solved by direct method (SHELXS-96)^[6] and refined against F^2 using SHELXL-97 program.^[7] In general, non-hydrogen atoms were located from different Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding mode with U_{iso} tied to the U_{iso} of the parent atom unless otherwise specified. Hydrogen atoms H(1) (at N(1)) and H(2) (at N(2)) were located from different Fourier synthesis and refined isotropically. Crystal data for **3**: $\text{C}_{38}\text{H}_{36}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$, $M_r = 754.60$, monoclinic, space group $P2(1)/n$, $a = 18.1403(6)$, $b = 10.3239(3)$, $c = 18.5086(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 106.797(3)^\circ$, $\gamma = 90^\circ$, $V = 3318.38(18) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.510 \text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{Cu}_{K\alpha}) = 6.452 \text{ mm}^{-1}$, $F(000) = 1544$; 12395 measured reflections, 6494 independent ($R_{\text{int}} = 0.0281$). The final refinements converged at $R_1 = 0.0314$ and $wR_2 = 0.0843$ for $I > 2\sigma(I)$ and $R_1 = 0.0330$ and $wR_2 = 0.0857$ for all data. The goodness of fit (GOF) is 1.038. Fourier synthesis gave a min/max residual electron density $-0.950/1.362 \text{ e \AA}^{-3}$. CCDC-1884112 contains the supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray crystallographic analysis of 8: Crystallographic data for **8** was collected at 100 K on an Agilent Super Nova system using graphite-monochromated Mo-K α radiation ($\lambda = 0.71000 \text{ \AA}$). Intensity measurements were performed on a rapidly cooled crystal with dimensions of $0.04 \times 0.04 \times 0.03 \text{ mm}^3$ in the range $1.80^\circ < \theta < 26.41^\circ$. The data completeness collected was 96.9%. Absorption correction was applied using the spherical harmonic program (multi-scan type). The structure was solved by direct method (SHELXS-96)^[6] and refined against F^2 using SHELXL-97 program.^[7] In general, non-hydrogen atoms were located from different Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding mode with U_{iso} tied to the U_{iso} of the parent atom unless otherwise specified. The hydrogen atom(s) at the nitrogen atom (H(1) at the N(1) and H(3A) and H(3B) at the N(3)) were located from different Fourier synthesis and refined isotropically. The ethyl group at N(1) was disordered and treated in PART method. The final refinement gave occupations of 0.69711 and 0.30289 for C(19)C(20) and C(19A)C(20A), respectively. Similar disorder was also observed for the ethyl group at N(2) (C(23)C(24) 0.71166 and C(23A)C(24A)

0.28834). Crystal data for **8**: C₂₄H₃₂Cl₂N₃PRu, $M_r = 565.47$, monoclinic, space group $P2(1)/n$, $a = 12.7575(4)$, $b = 11.4706(4)$, $c = 16.9277(7)$ Å, $\alpha = 90^\circ$, $\beta = 104.391(4)^\circ$, $\gamma = 90^\circ$, $V = 2399.41(15)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.565$ g·cm⁻³, $\mu(\text{MoK}\alpha) = 0.960$ mm⁻¹, $F(000) = 1160$; 9274 measured reflections, 4781 independent ($R_{\text{int}} = 0.0529$). The final refinements converged at $R_1 = 0.0539$ and $wR_2 = 0.1392$ for $I > 2\sigma(I)$ and $R_1 = 0.0641$ and $wR_2 = 0.1502$ for all data. The goodness of fit (GOF) is 1.035. Fourier synthesis gave a min/max residual electron density $-1.144/1.042$ e Å³. CCDC-1884111 contains the supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

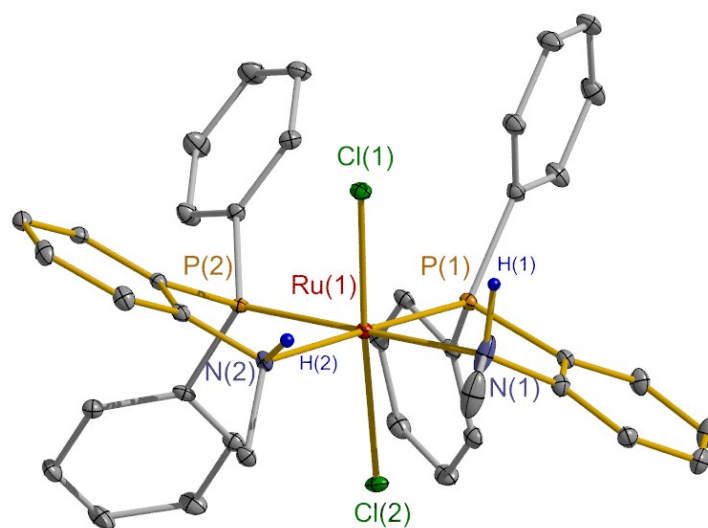


Fig. S1 X-ray crystal structure of **3** with thermal ellipsoids at 30% probability level. Hydrogen atoms except for H(1) and H(2) are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$] for **3**: Ru(1)–P(1) 2.2636(5), Ru(1)–P(2) 2.2411(5), Ru(1)–N(1) 2.225(2), Ru(1)–N(2) 2.2476(18), Ru(1)–Cl(1) 2.4282(5), Ru(1)–Cl(2) 2.3958(5); P(1)–Ru(1)–N(1) 80.94(6), P(2)–Ru(1)–N(2) 80.90(5).

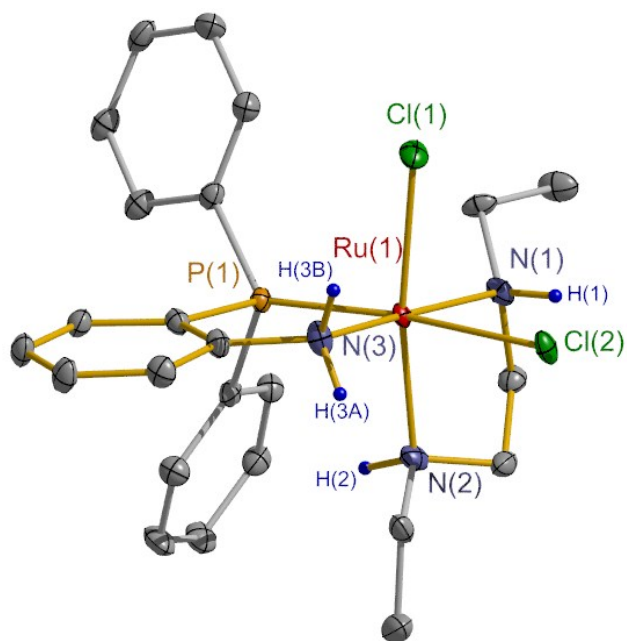


Fig. S2 X-ray crystal structure of **8** with thermal ellipsoids at 30% probability level. Hydrogen atoms except for H(1), H(2), H(3A) and H(3B) are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$] for **8**: Ru(1)–P(1) 2.2205(11), Ru(1)–N(1) 2.135(4), Ru(1)–N(2) 2.136(4), Ru(1)–N(3) 2.140(4), Ru(1)–Cl(1) 2.4280(13), Ru(1)–Cl(2) 2.5072(11); P(1)–Ru(1)–N(3) 83.47(11), N(1)–Ru(1)–N(2) 81.60(16).

V. Activity tests

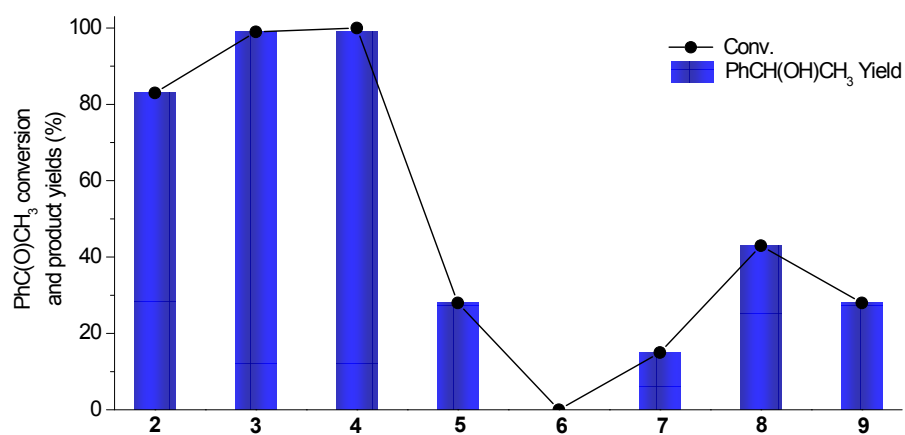


Fig. S3 Catalytic performance of **2-9** for hydrogenation of acetophenone into 1-phenylethanol. Reaction conditions: 13.72 mmol acetophenone, 0.02 mol% ruthenium, 0.2 mol% NaOMe, 10 mL isopropanol, 10 bar H₂; room temperature; 1 h reaction time. The conversion of acetophenone and yield of 1-phenylethanol were analyzed by gas chromatograph (GC) using *p*-xylene as an internal standard.

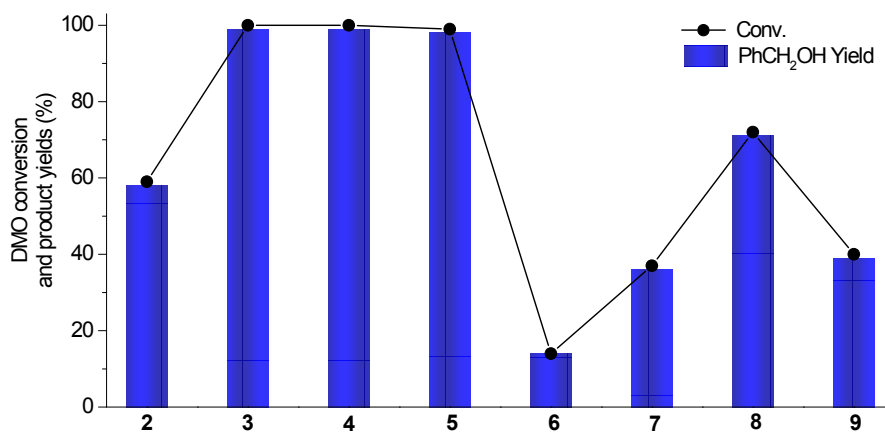
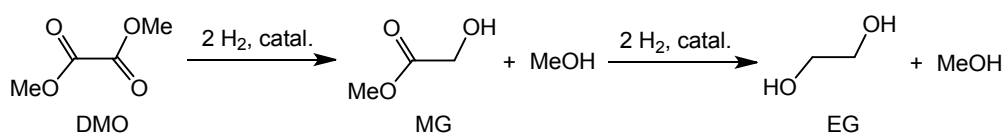


Fig. S4 Catalytic performance of **2-9** for hydrogenation of benzaldehyde into benzyl alcohol. Reaction conditions: 13.72 mmol benzaldehyde, 0.02 mol% ruthenium, 0.2 mol% NaOMe, 10 mL isopropanol, 10 bar H₂; room temperature; 1 h reaction time. The conversion of benzaldehyde and yield of benzyl alcohol were analyzed by gas chromatograph (GC) using *p*-xylene as an internal standard.

Table S1 Hydrogenation of DMO into MG (and/or EG) catalyzed by ruthenium complexes **1-9**.

Entry	Ru complex	Conv. (%)	Yield of MG (%)	Yield of EG (%)	TOF (h ⁻¹)
1	1	7	7	0	140
2	2	8	8	0	160
3	3	77	76	0	1520
4	4	27	27	0	540
5	5	24	24	0	480
6	6	0	0	0	0
7	7	36	36	0	720
8	8	100	98	1	2000
9	9	6	6	0	120

Reaction conditions: 11.35 mmol DMO, 0.05 mol% ruthenium, 0.5 mol% NaOMe, 10 mL THF, 50 bar H₂; 100 °C; 1 h reaction time. The conversion of DMO and yield of alcohols were determined by GC using *p*-xylene as an internal standard.

VI. NMR spectra

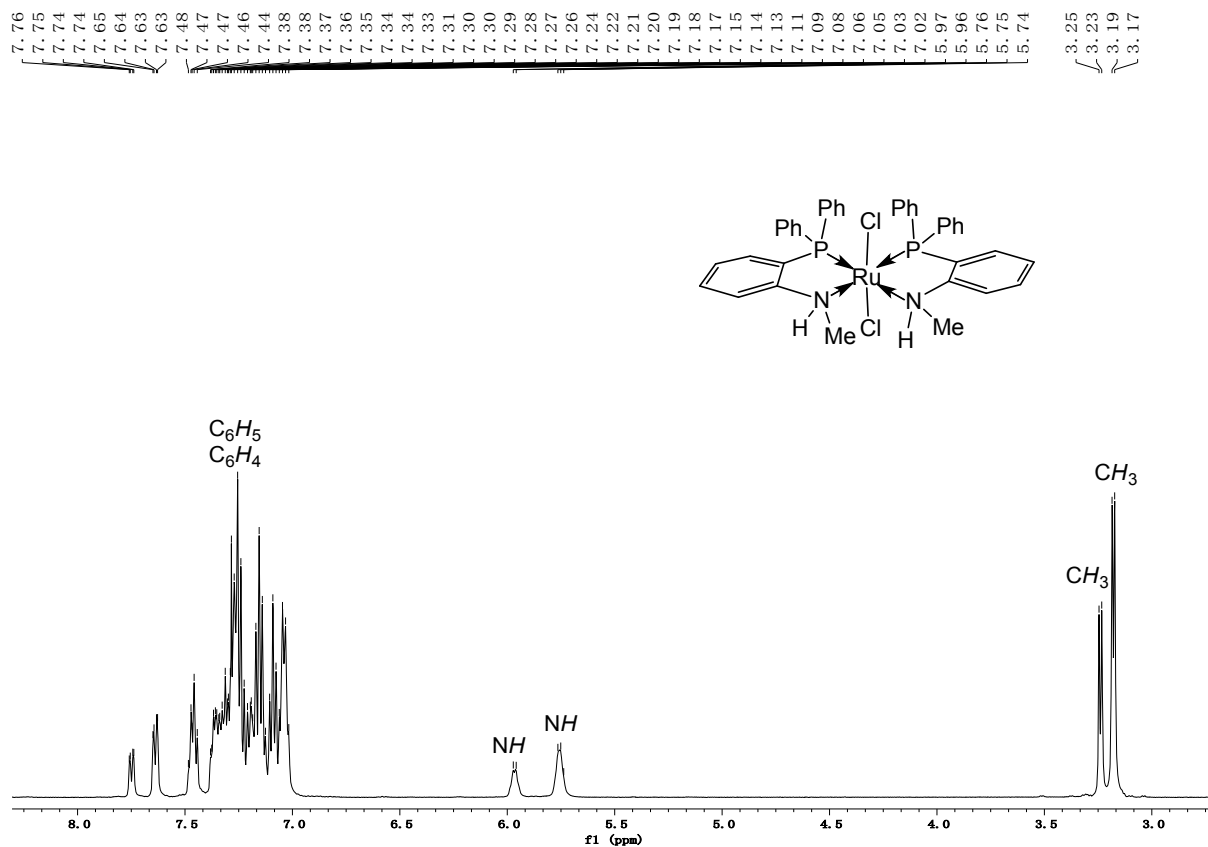


Fig. S5 ^1H NMR spectrum of **3** in CDCl_3 .

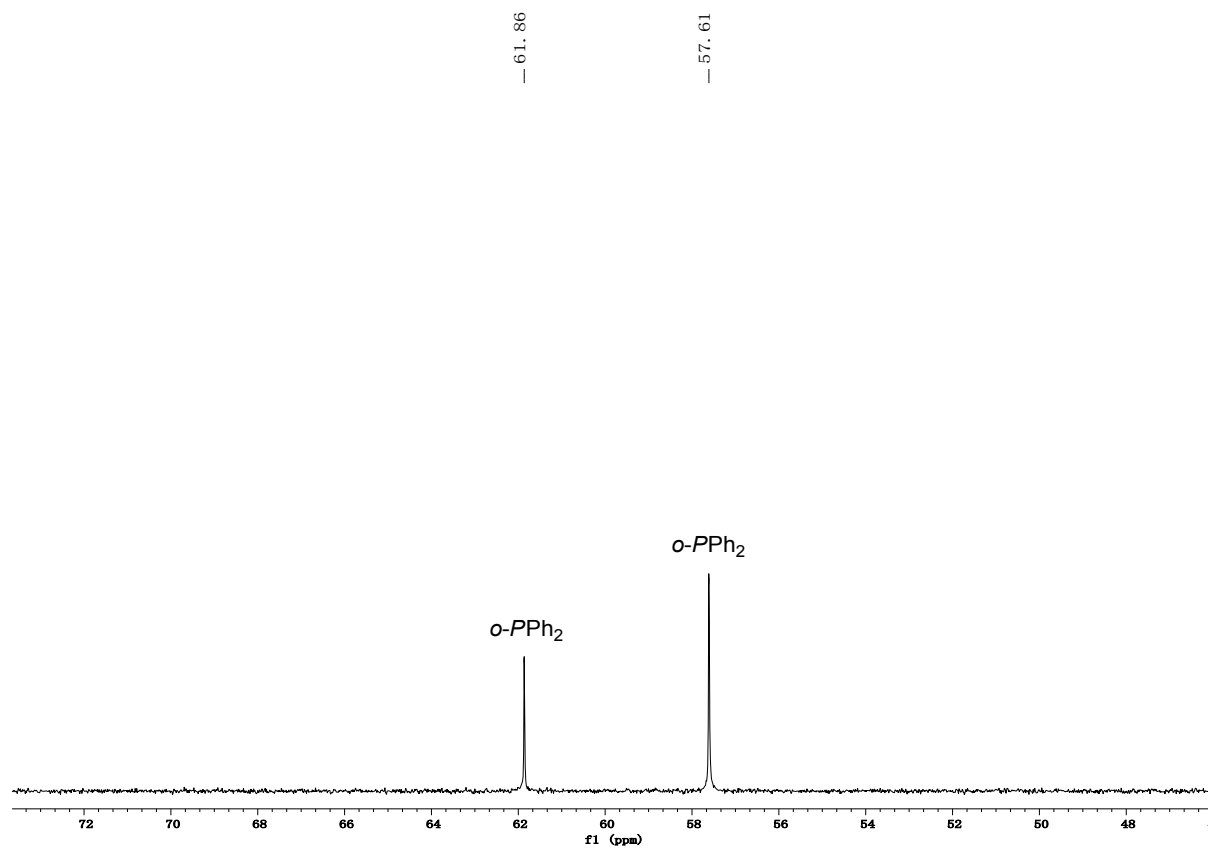


Fig. S6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** in CDCl_3 .

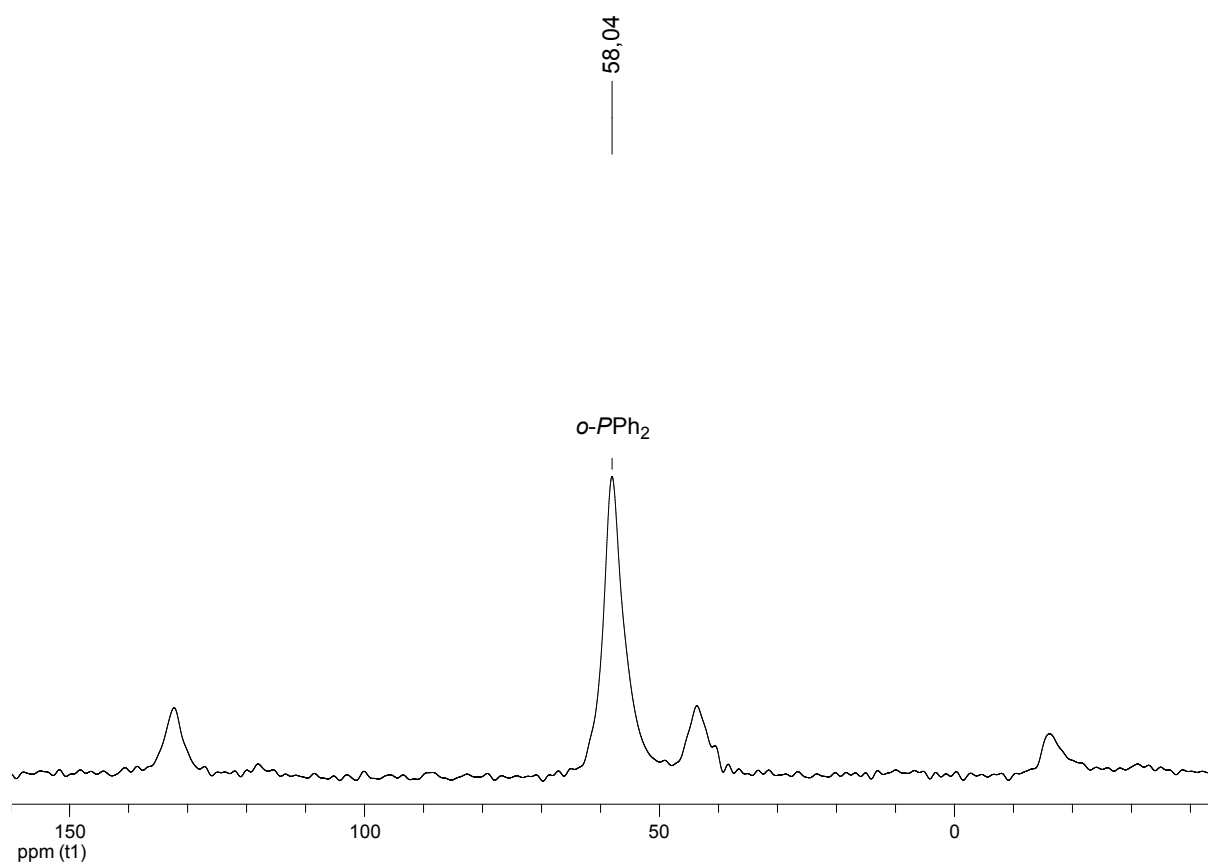


Fig. S7 Solid state ³¹P NMR spectrum of **3**.

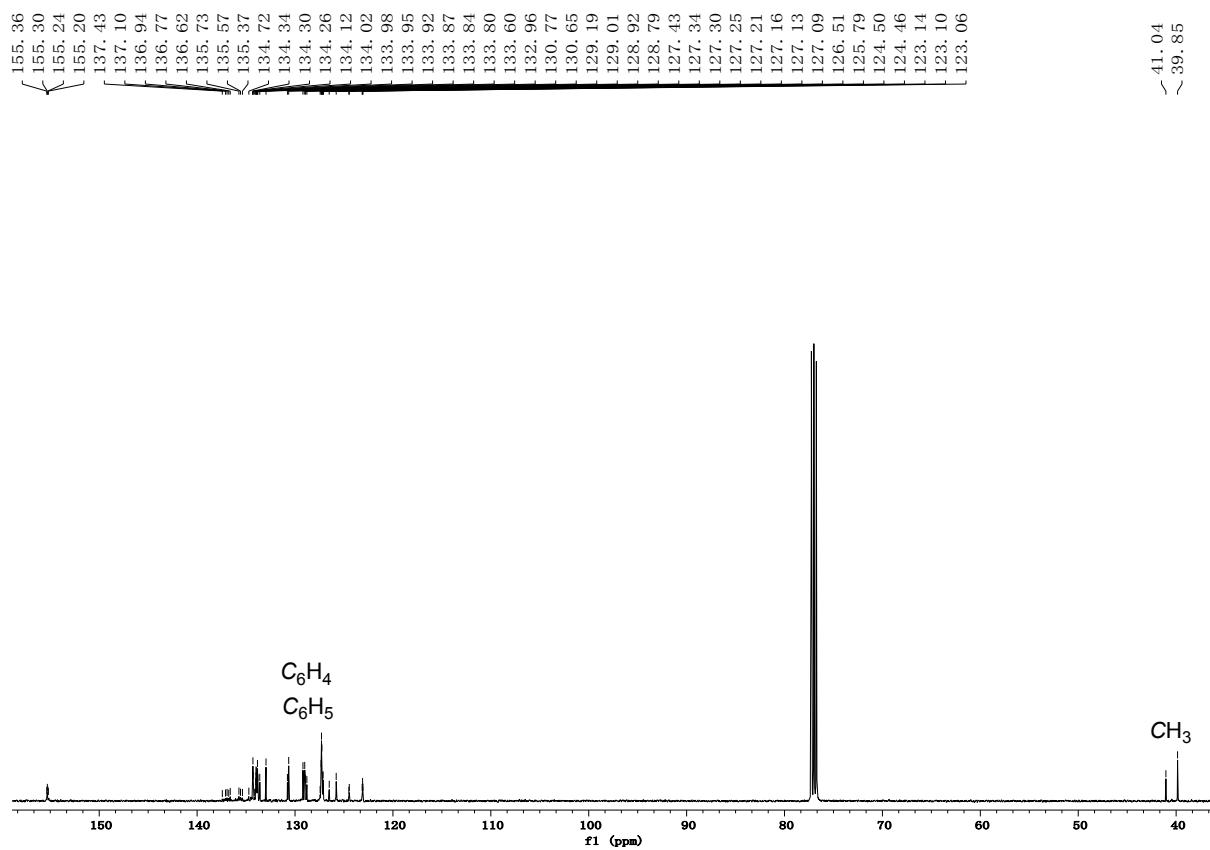


Fig. S8 ¹³C{¹H} NMR spectrum of **3** in CDCl₃.

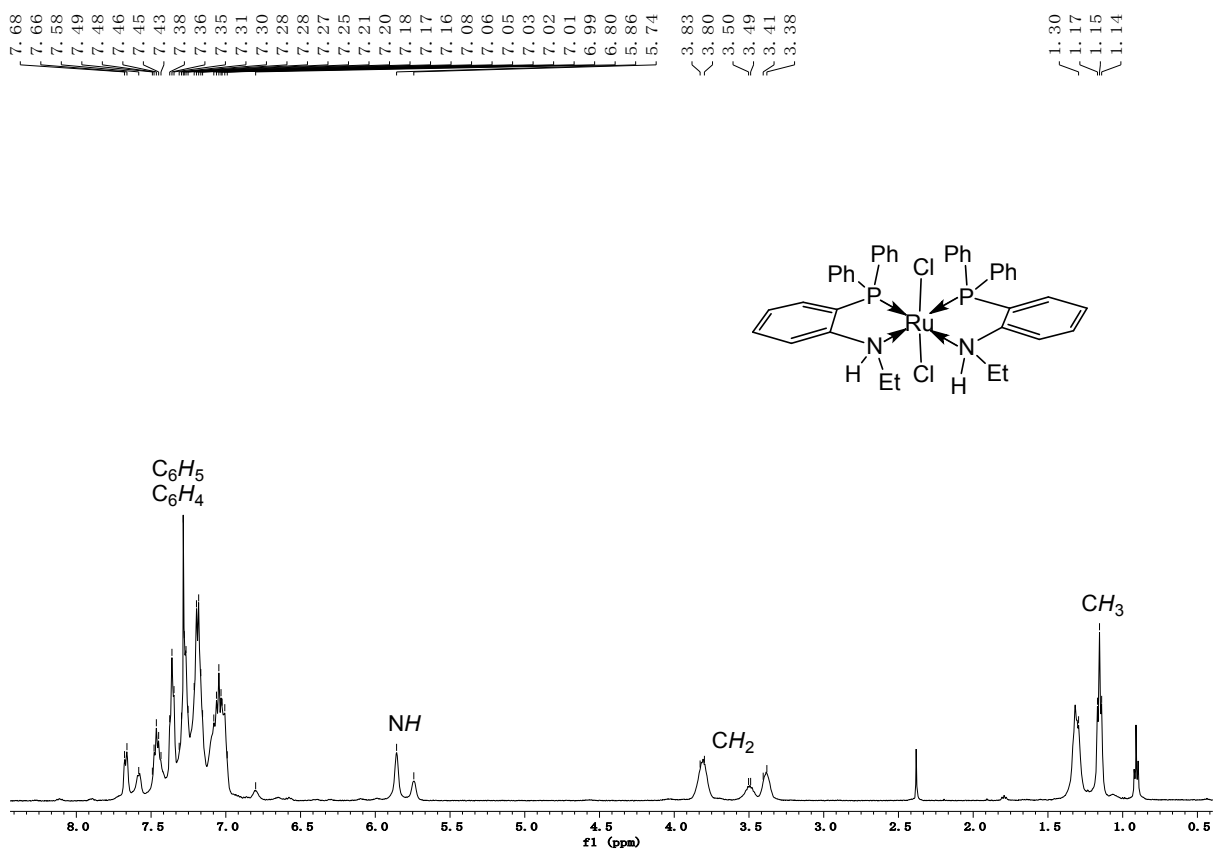


Fig. S9 ^1H NMR spectrum of **4** in CDCl_3 .

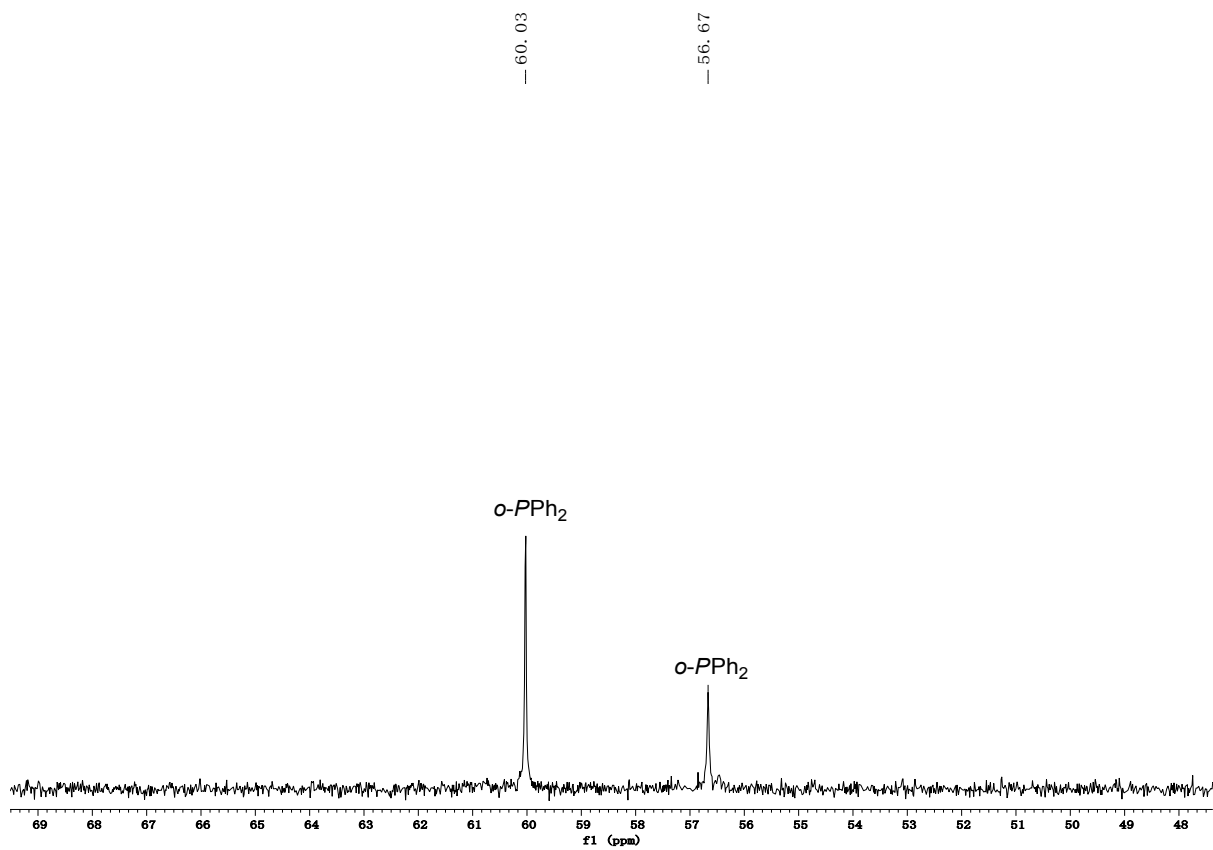


Fig. S10 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** in CDCl_3 .

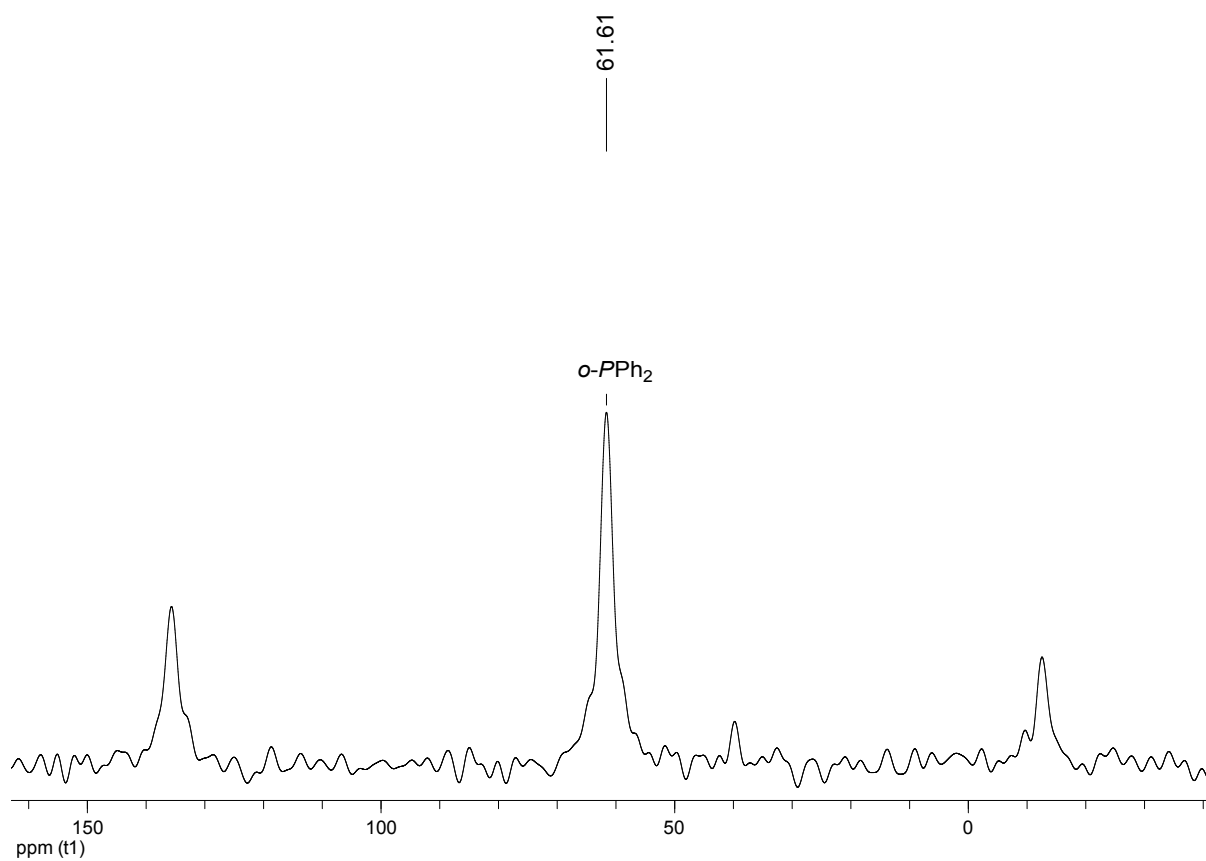


Fig. S11 Solid state ³¹P NMR spectrum of **4**.

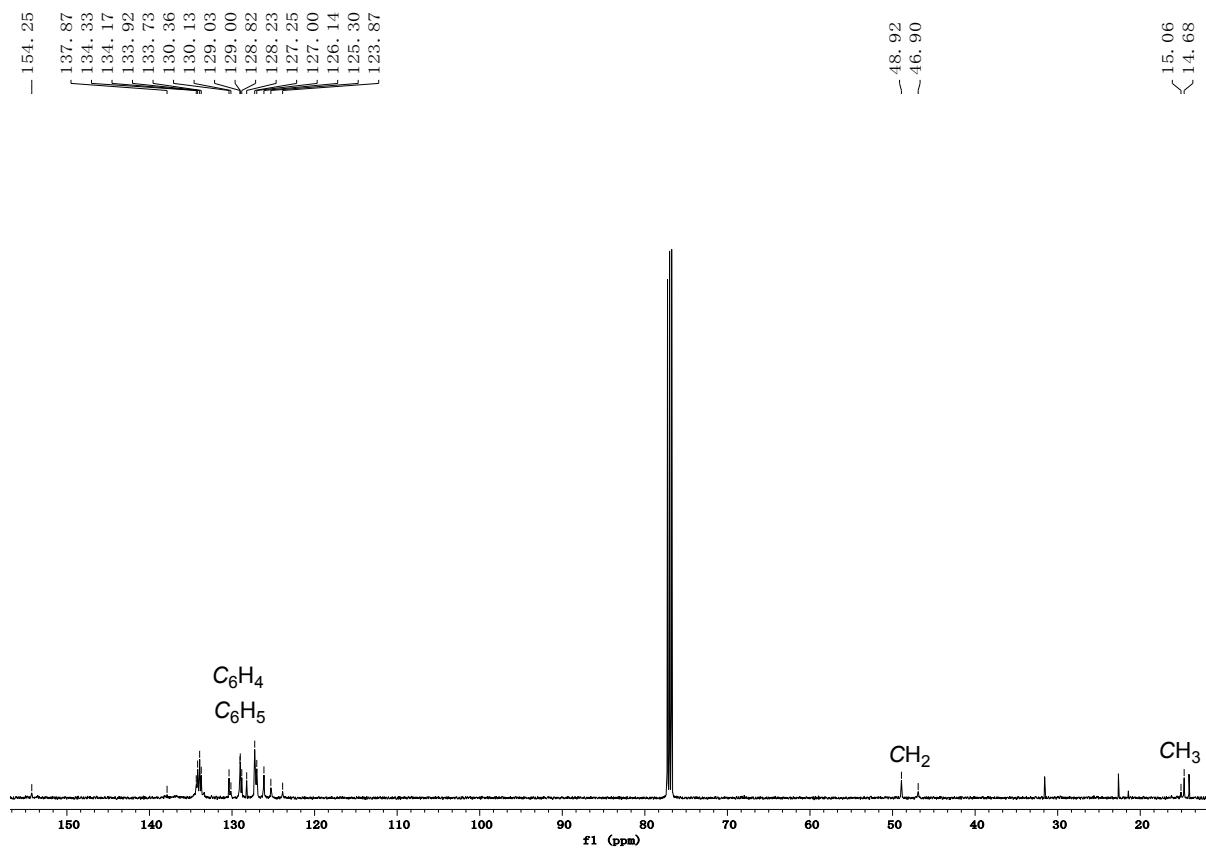


Fig. S12 ¹³C {¹H} NMR spectrum of **4** in CDCl₃.

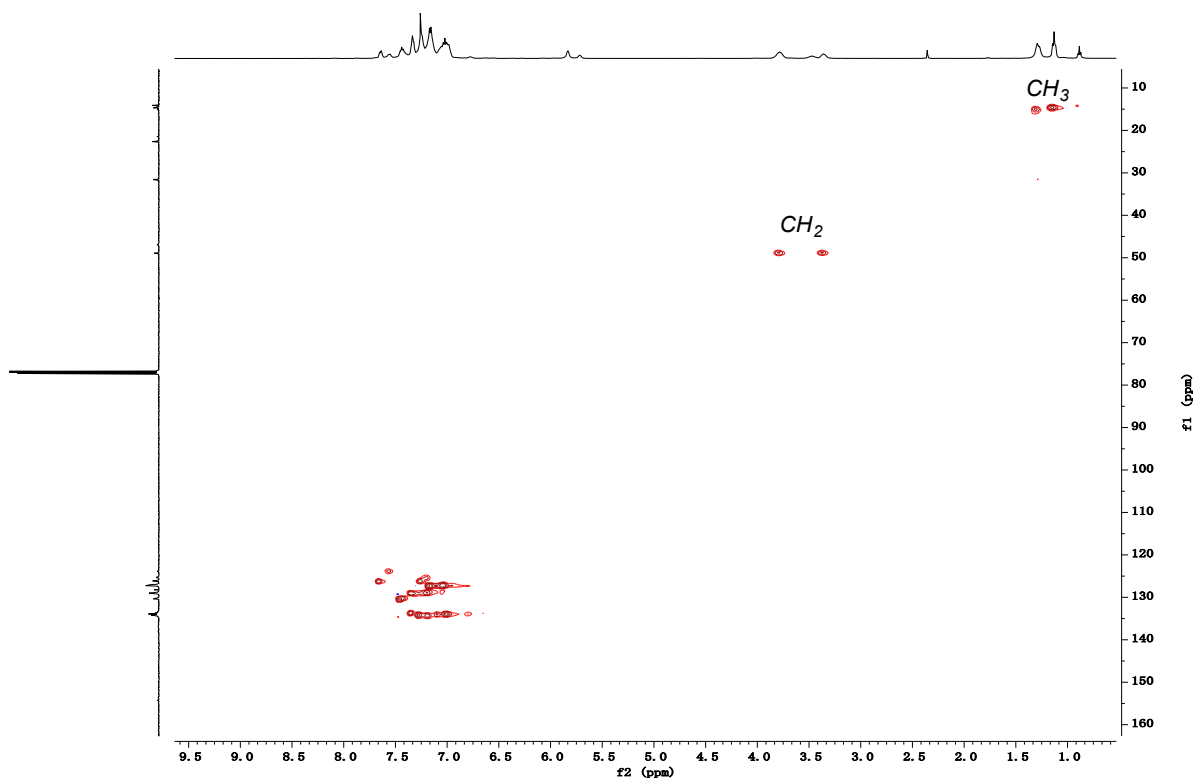


Fig. S13 ^1H - ^{13}C HSQC NMR spectrum of **4** in CDCl_3 .

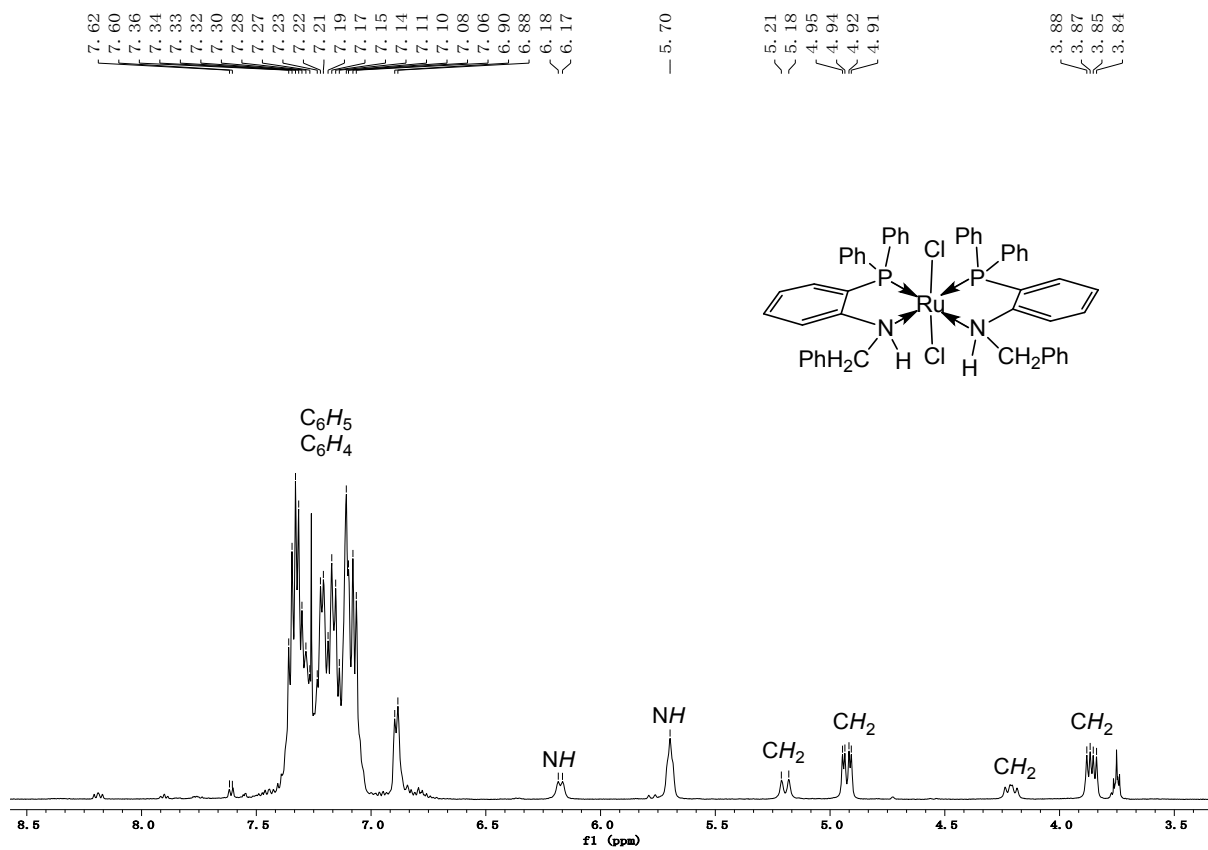


Fig. S14 ^1H NMR spectrum of **5** in CDCl_3 .

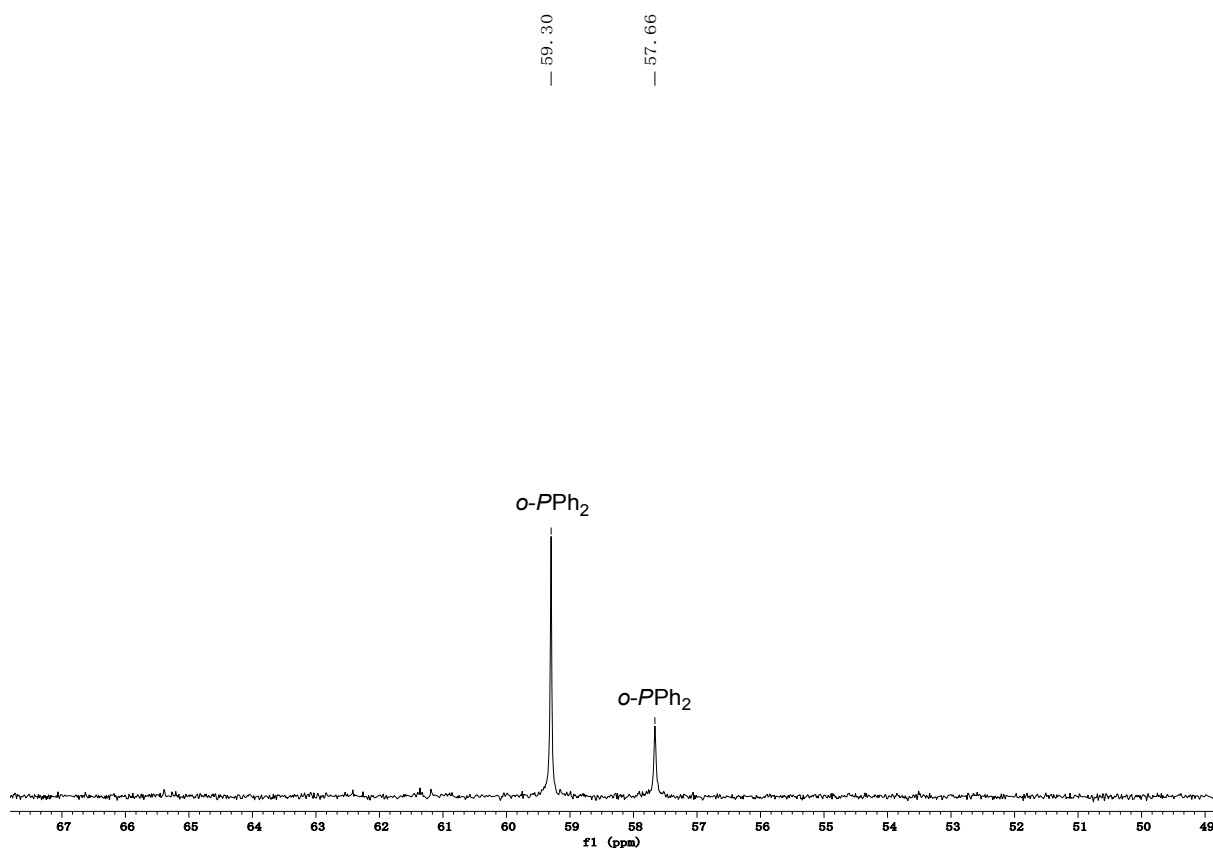


Fig. S15 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** in CDCl_3 .

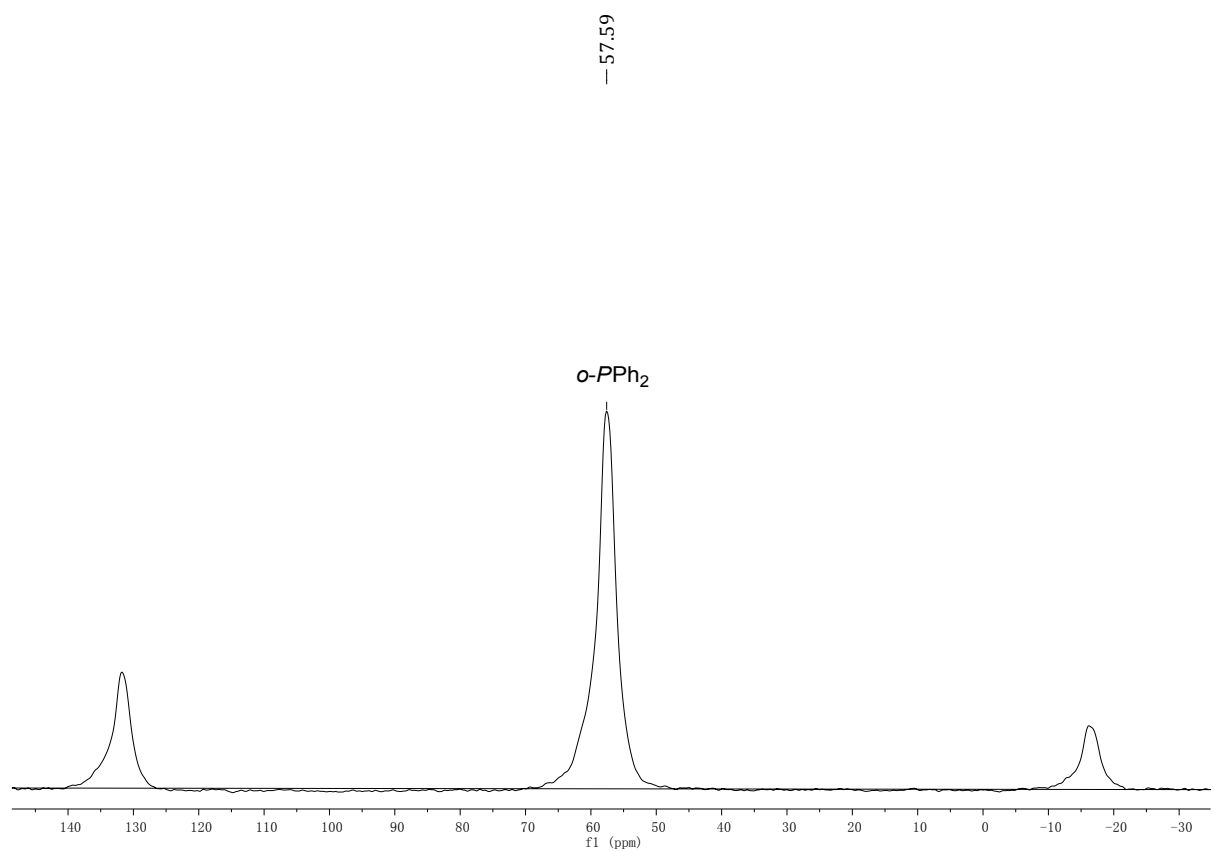


Fig. S16 Solid state ^{31}P NMR spectrum of **5**.

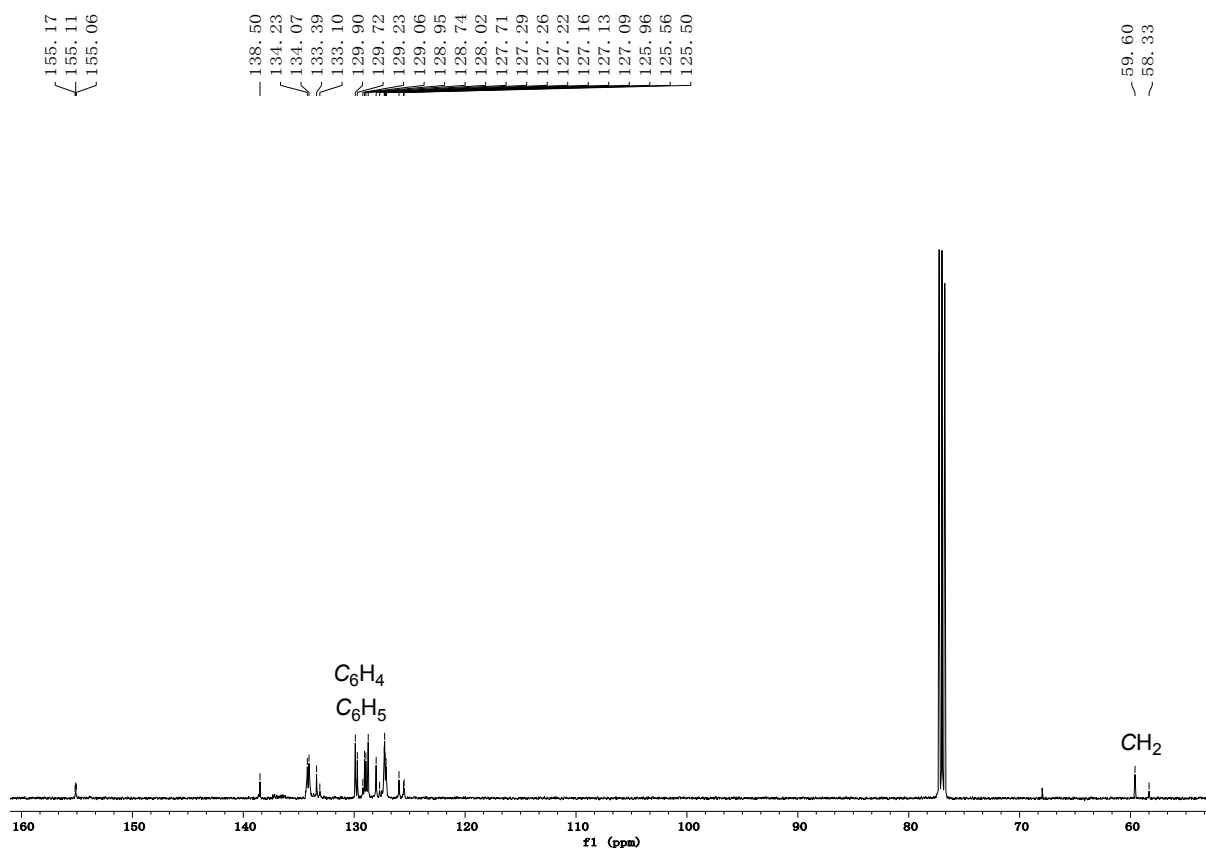


Fig. S17 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in CDCl_3 .

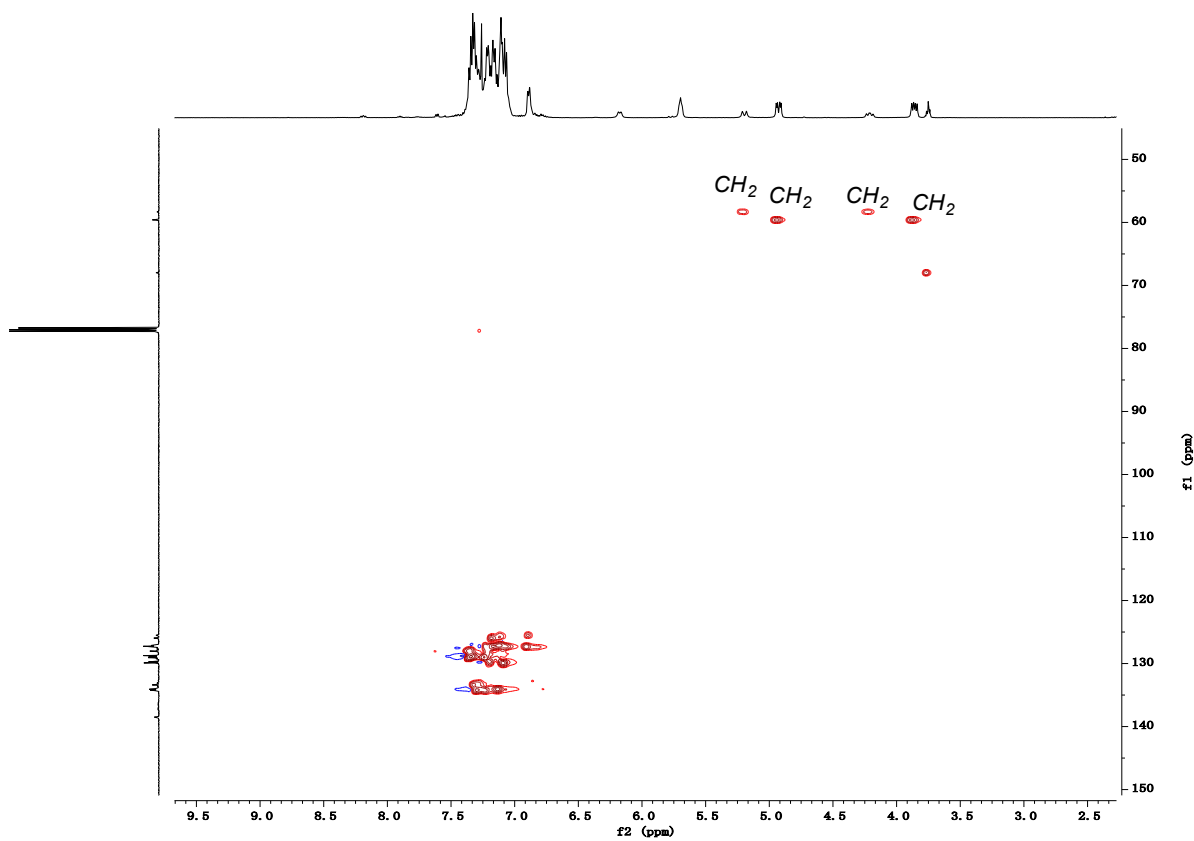


Fig. S18 ^1H - ^{13}C HSQC NMR spectrum of **5** in CDCl_3 .

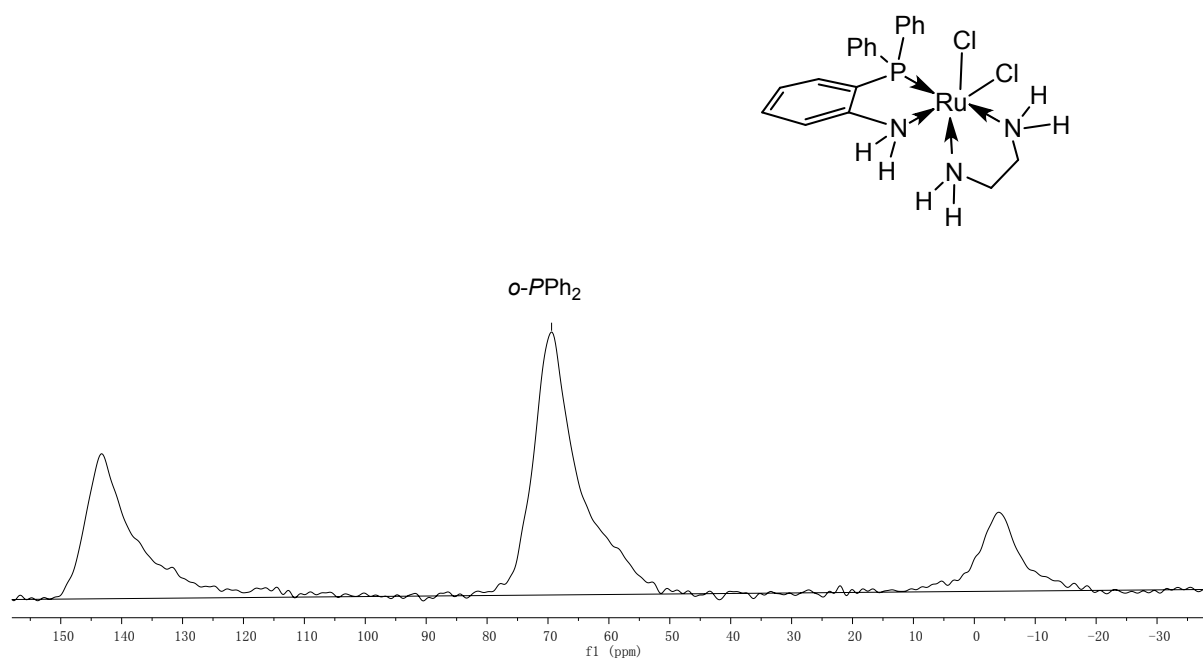


Fig. S19 Solid state ³¹P NMR spectrum of **6**.

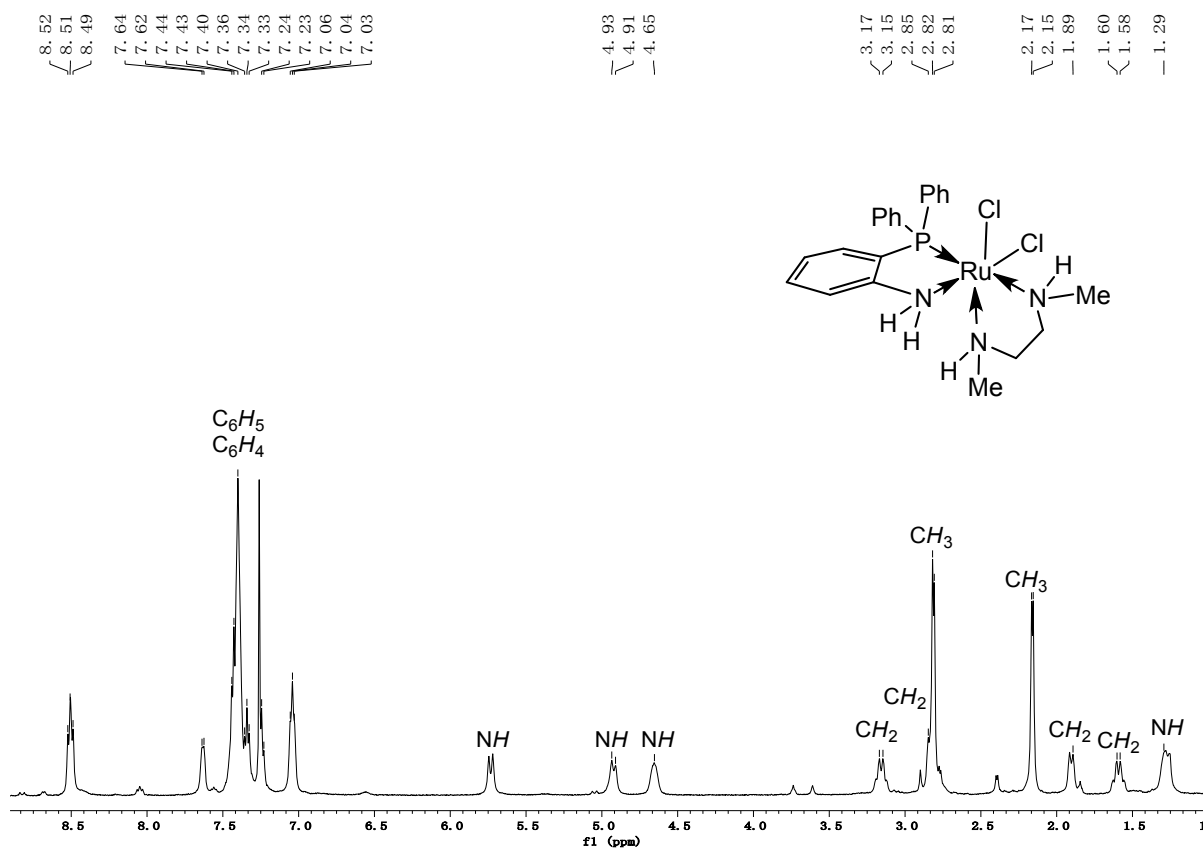


Fig. S20 ¹H NMR spectrum of **7** in CDCl₃.

- 71.35

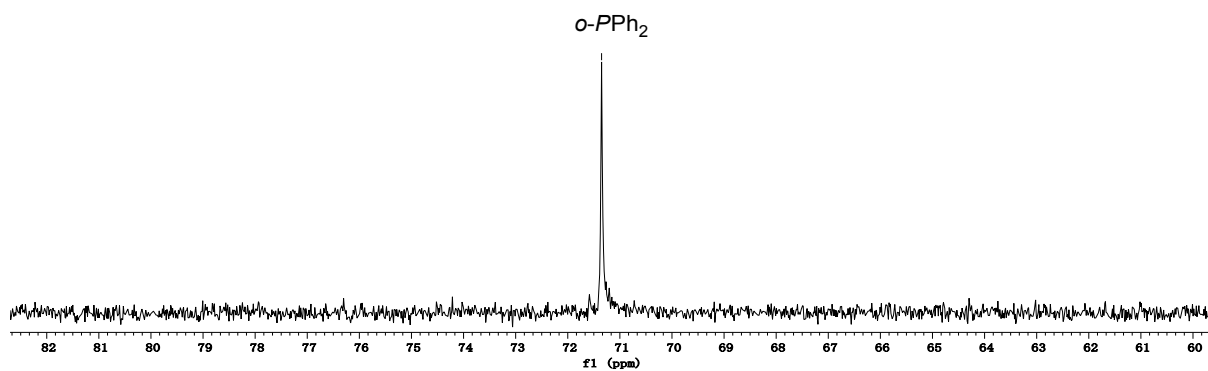


Fig. S21 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 .

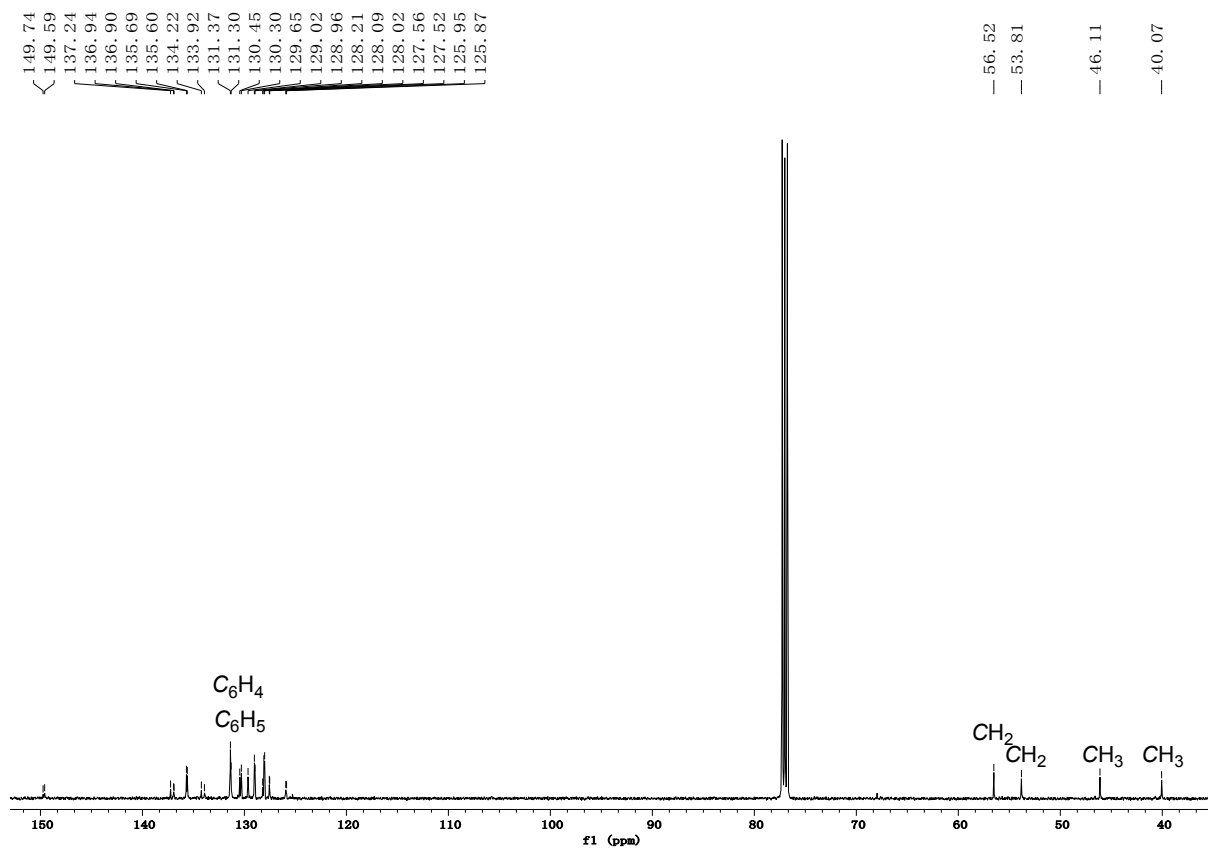


Fig. S22 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in CDCl_3 .

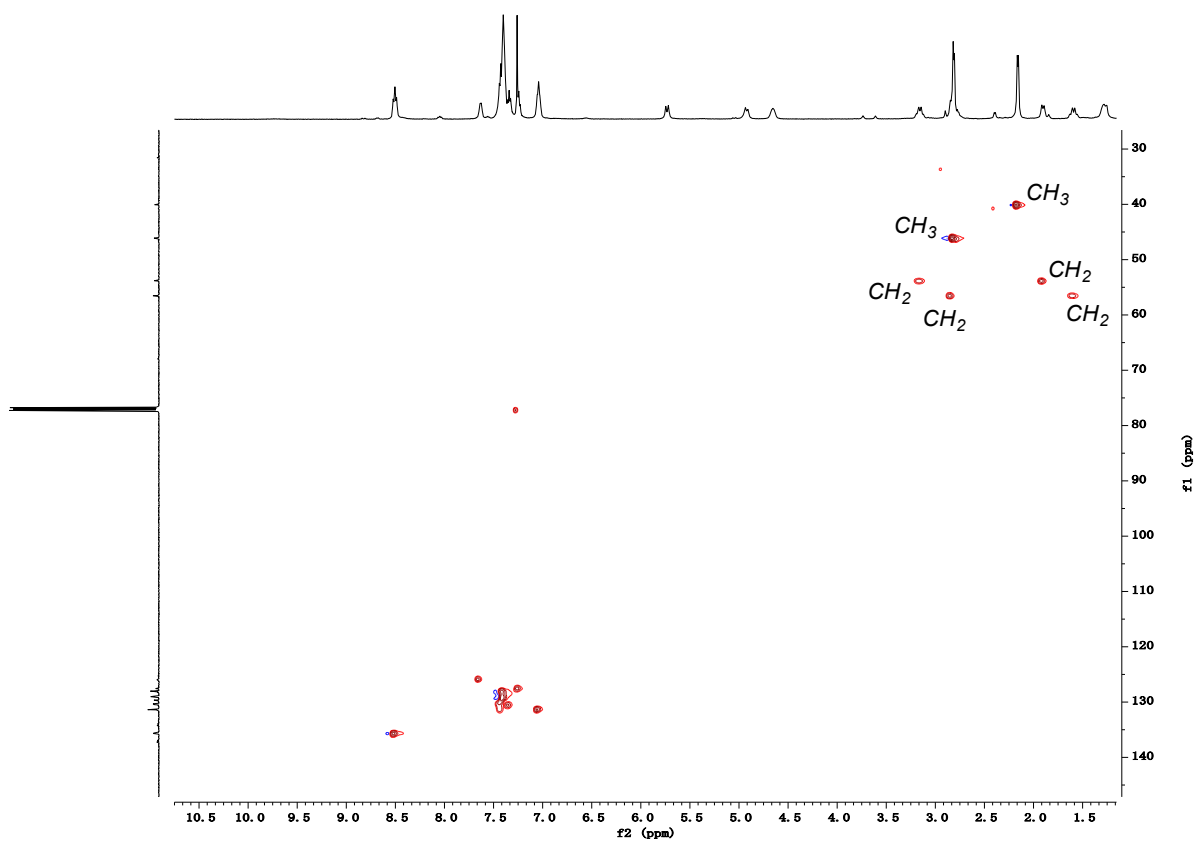


Fig. S23 ^1H - ^{13}C HSQC NMR spectrum of **7** in CDCl_3 .

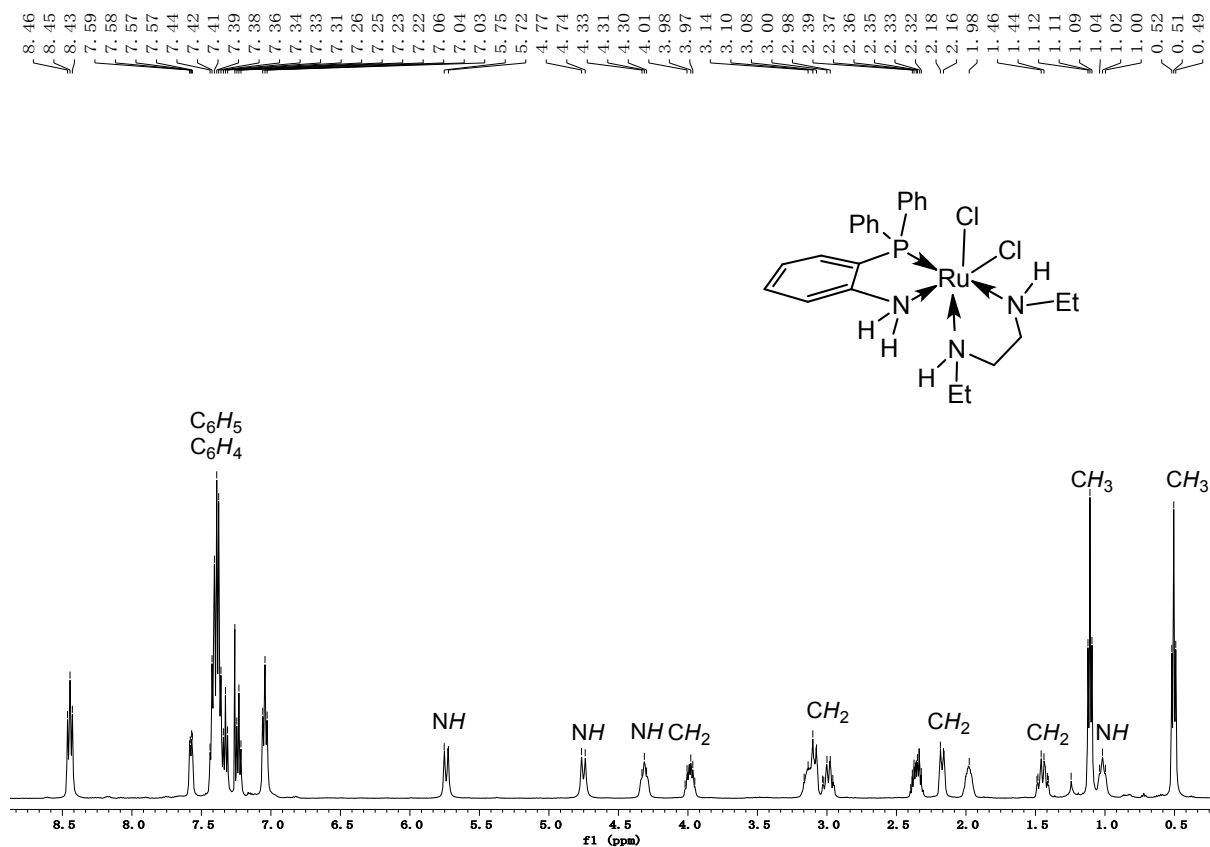


Fig. S24 ^1H NMR spectrum of **8** in CDCl_3 .

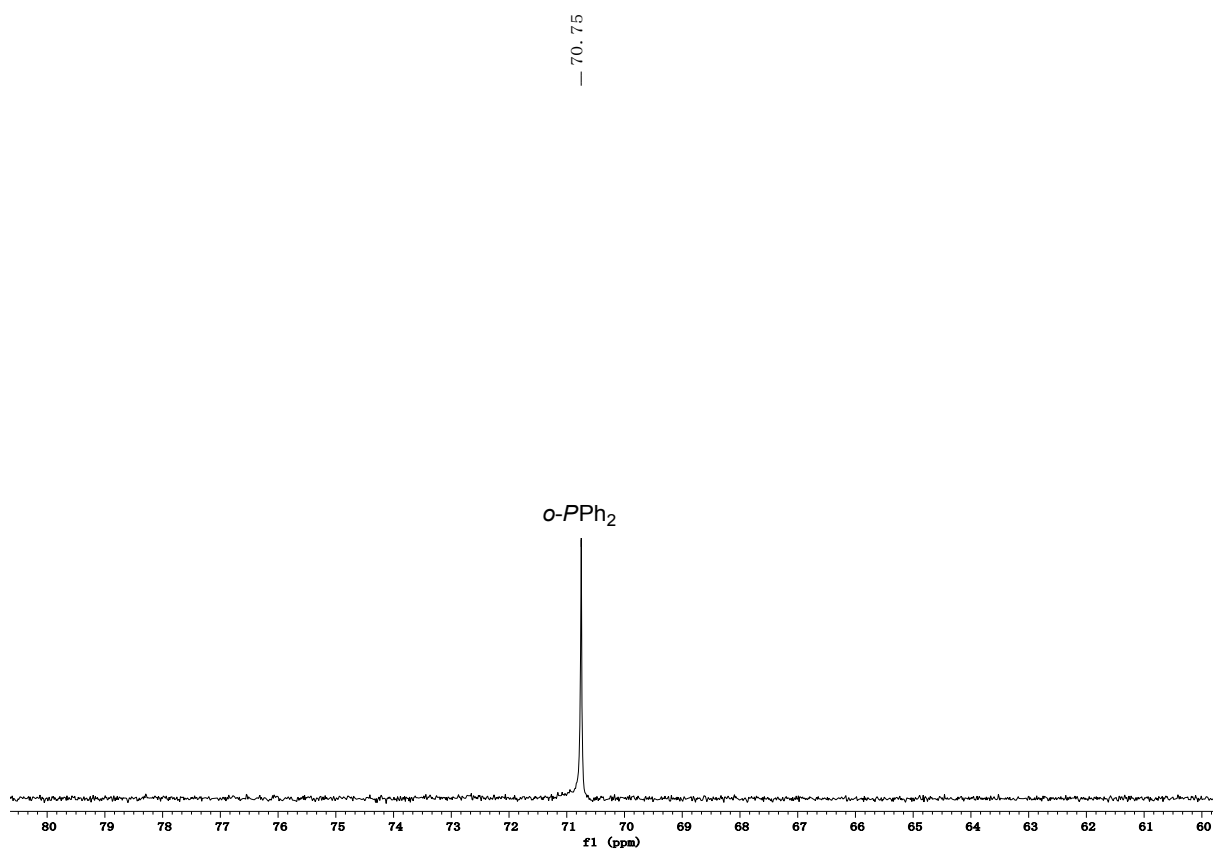


Fig. S25 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 .

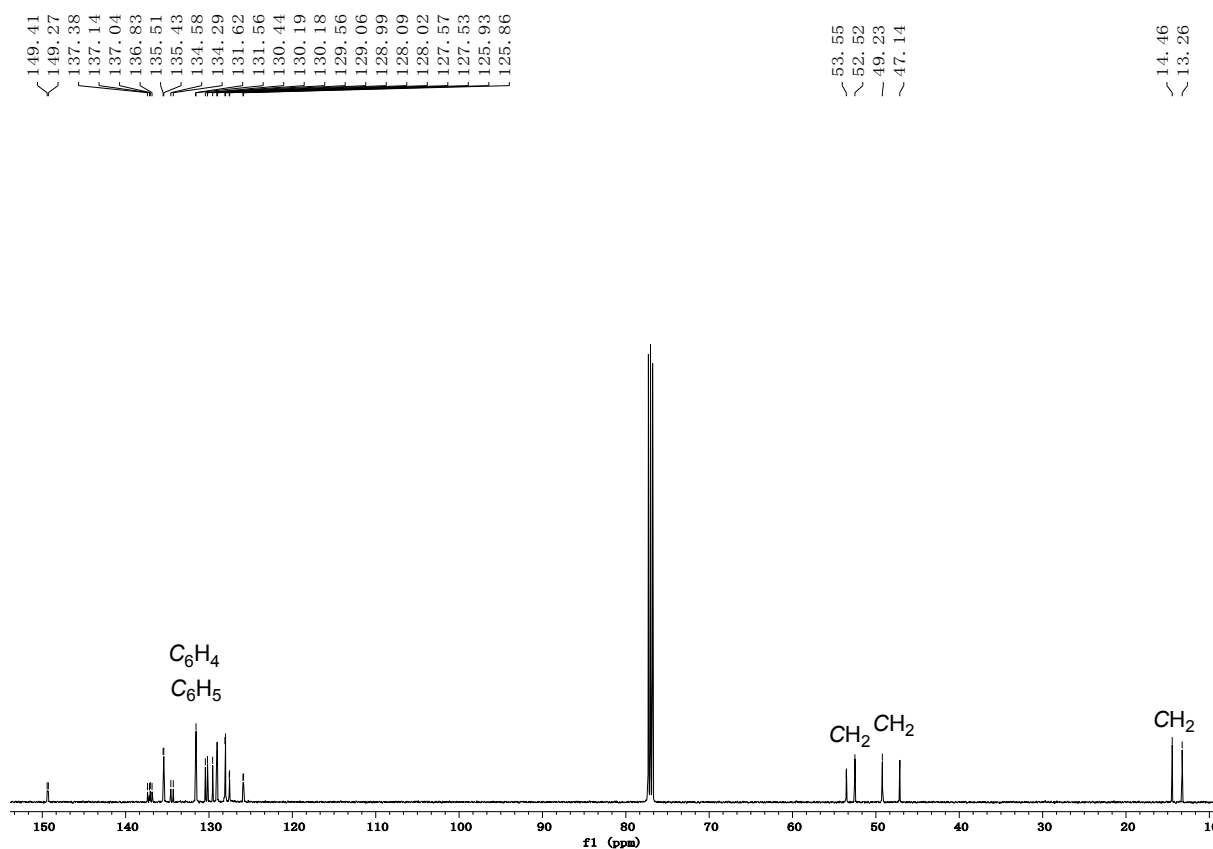


Fig. S26 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in CDCl_3 .

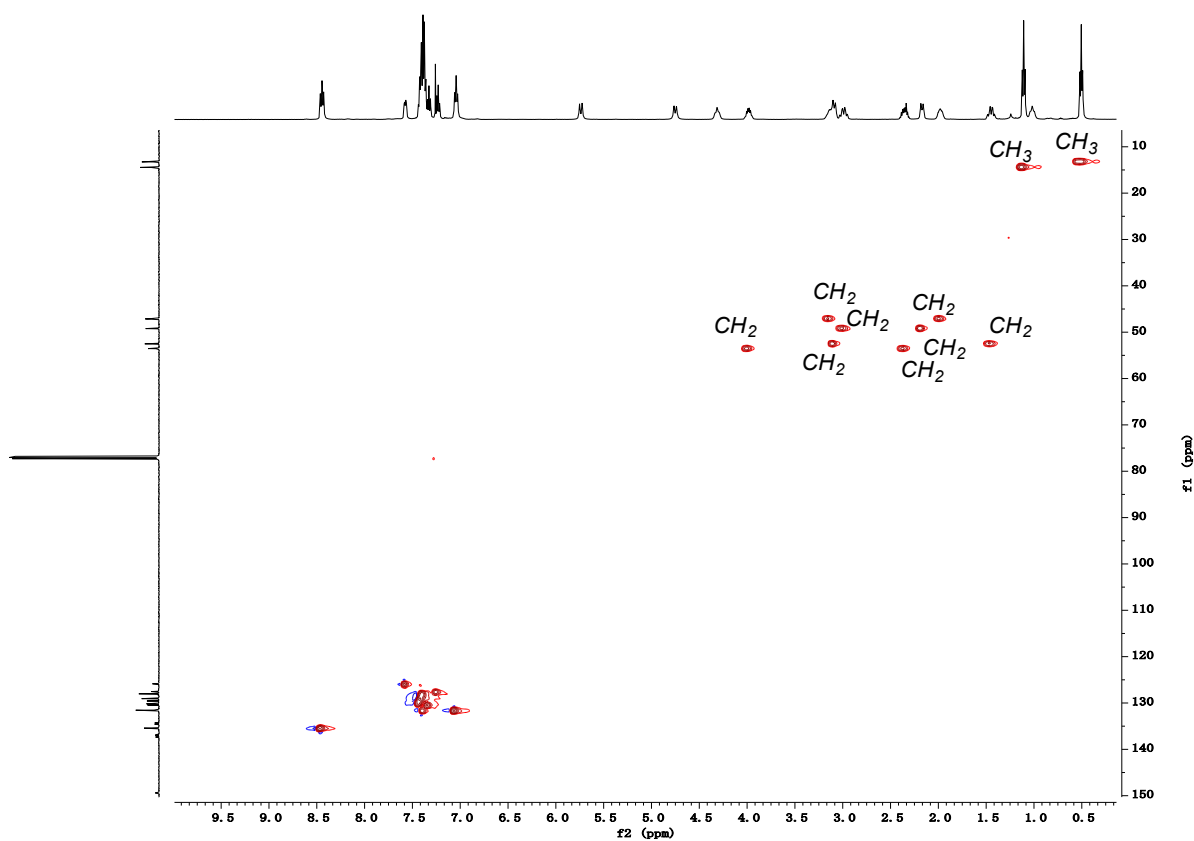


Fig. S27 ^1H - ^{13}C HSQC NMR spectrum of **8** in CDCl_3 .

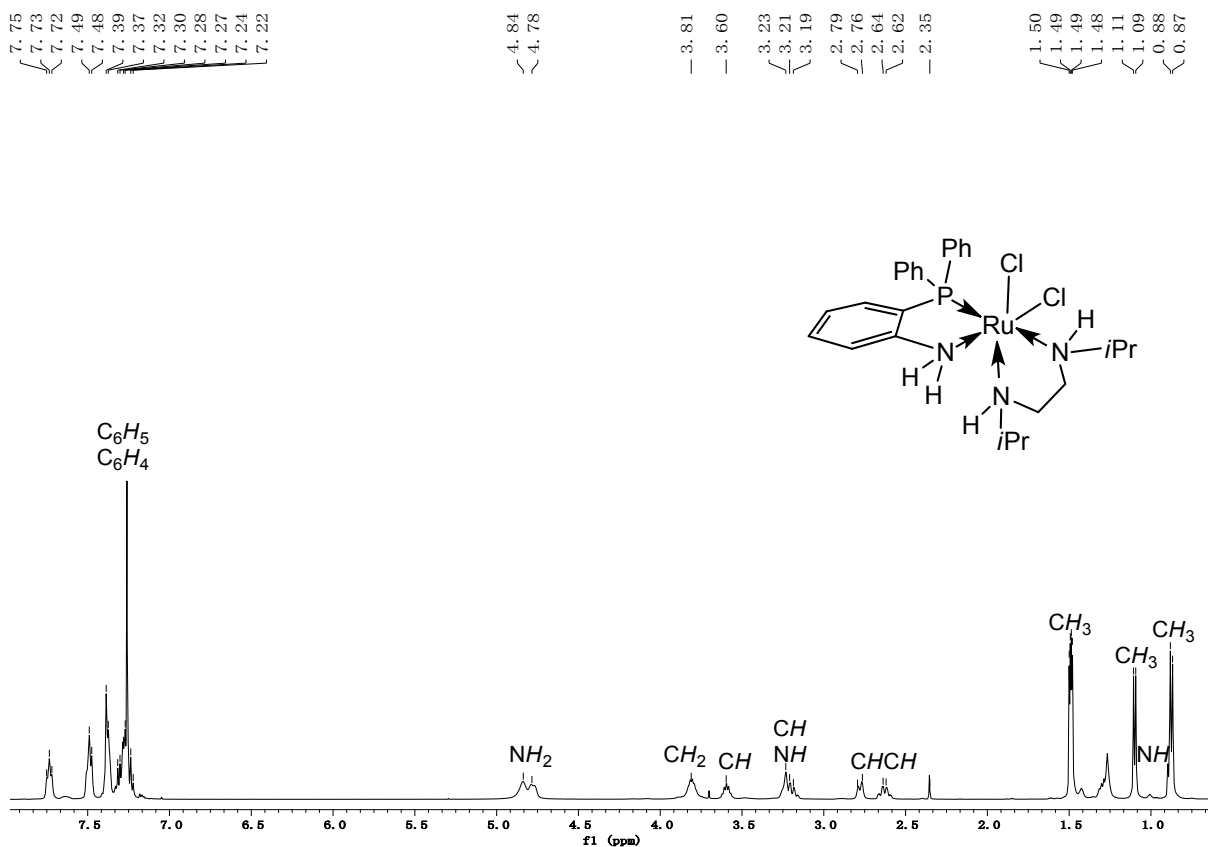


Fig. S28 ^1H NMR spectrum of **9** in CDCl_3 .

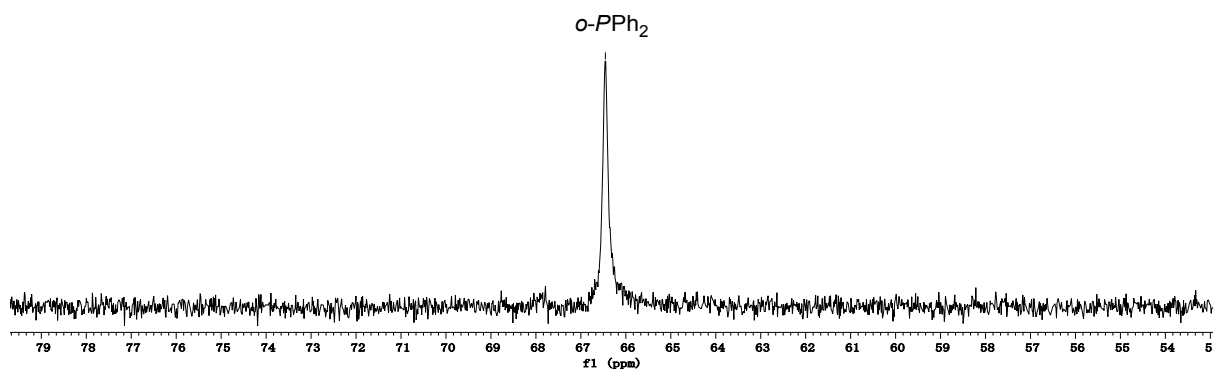


Fig. S29 ³¹P{¹H} NMR spectrum of **9** in CDCl₃.

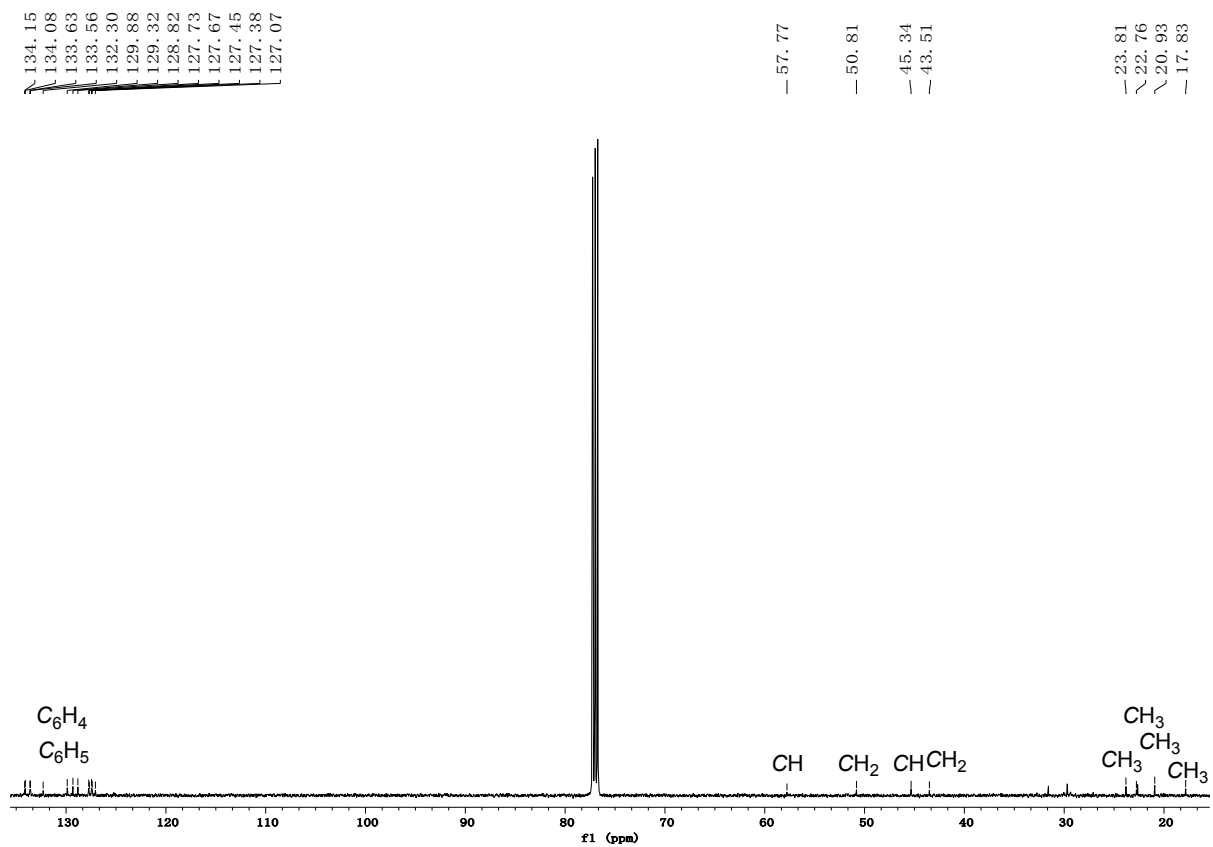


Fig. S30 ¹³C{¹H} NMR spectrum of **9** in CDCl₃.

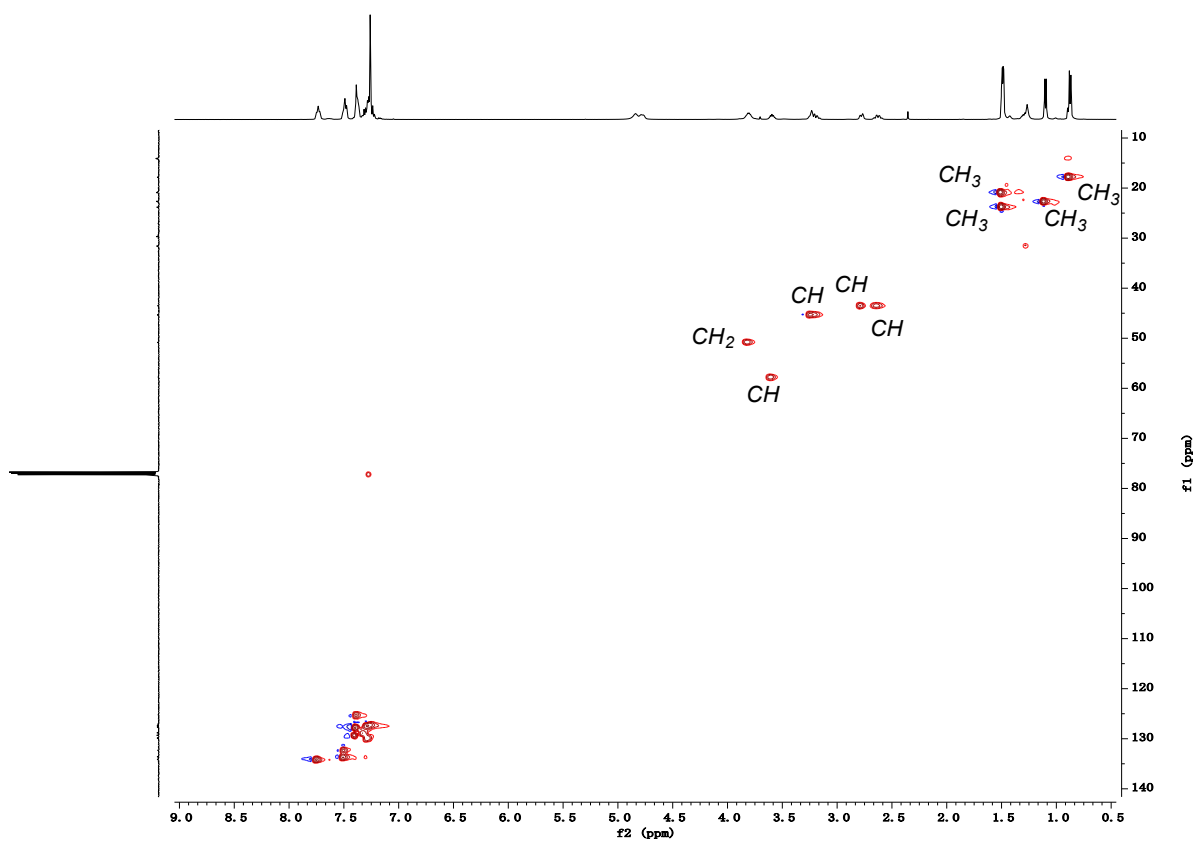


Fig. S31 ^1H - ^{13}C HSQC NMR spectrum of **9** in CDCl_3 .

VII. References

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