Supporting information

Subtle Dihedral Angle Effect of Cycloalkyl-Bridged PCCP Diphosphine Ligands on Activity in Chromium-catalyzed Ethylene Tri-/tetramerization

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1. Experimental Section

1.1 General Information

Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of nitrogen using standard Schenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. MMAO-3A (modified methylaluminoxane) (7 wt % in heptane solution) was purchased from Akzo-Nobel. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm; ^{13}C NMR $CDCl_3$: 77.0 ppm). Elemental analysis were performed by microanalytical laboratory in house. Quantitative gas chromatographic analysis of the products of oligomerization was performed on an Agilent 6890 series GC instrument with a J&W DB-1HT column working at 38 ^{o}C for 10 min and then heating at 10 ^{o}C min^{-1} until 250 ^{o}C. *n*-Nonane was used as an internal standard. Mass spectra were recorded on the XEVO G2 TOF instrument by ESI methods. IR spectra were recorded on the Nicolet Magna-IR 550 spectrometer.

$CrCl_3(THF)_3$ was prepared by literature method [1] and its purity verified by elemental analysis. Known compounds **1b~3b** [2], **1c~3c** were prepared according to the literature methods and the purity assessed by ^{1}H and ^{31}P NMR spectroscopy.

1.2 Preparation and characterization of 1~4

Cyclooct-1-enyldiphenylphosphine oxide (4b) 4b was prepared according to literature method [2]. Into a flame-dried 25 mL schlenk tube filled with argon CuI (0.038 g, 0.20 mmol) was flushed with dioxane (5 mL). Then DMEDA (64 μL, 0.60 mmol) was added and the mixture was stirred vigorously for 1 min. Then 1-bromocyclooctene (**4a**) (0.378 g, 2.0 mmol) was added, the mixture was stirred for 0.5 min. followed by the addition of NaI (0.449 g, 3.0 mmol) and Cs_2CO_3 (1.303 g, 4.0 mmol), after stirring for 0.5 min. $Ph_2P(O)H$ (0.404 g, 2.00 mmol) was added neat as a solid and the walls of the vial were rinsed with dioxane (3 mL). The vial was then placed into oil bath pre-heated to 110 ^{o}C and the mixture was stirred for 20 h. After cooling to room temperature , the contents of the vial were filtered through a Celite pad which was then washed with DCM (8×5 mL). The solvents were evaporated under reduced pressure and the crude product was purified using column chromatography (PE/EA = 4/1) to give the pure product as white solid (0.528 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75–7.62 (m, 4H), 7.55–7.47 (m, 2H), 7.46–7.39 (m, 4H), 6.42 (dt, *J* = 20.9, 8.2 Hz, 1H), 2.49–2.37

(m, 2H), 2.38–2.23 (m, 2H), 1.60–1.51 (m, 2H), 1.47–1.36 (m, 4H), 1.30–1.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.73, 146.57, 146.47, 134.67, 133.71, 132.32, 132.01, 131.74, 131.32, 128.49, 128.38, 121.64, 30.55, 29.58, 28.29, 27.09, 26.94, 26.43, 26.32, 25.97, 25.89, 21.97, 19.18. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 32.40 (s).

***Trans*-cyclooctane-1,2-diyl)bis(diphenylphosphine oxide) (4c) 4c** was prepared according to literature method [2]. Into a flame-dried 25 mL Schlenk tube filled with argon **4b** (0.310 g, 1.0 mmol) and diphenylphosphine oxide (0.202 g, 1.0 mmol) were dissolved in dioxane (10 mL) and LiO^tBu was added (0.016 g, 0.20 mmol). The vial was placed into a heating block preheated to 110 °C and the mixture was stirred for 20 h. After cooling to room temperature water (4 mL) was added dropwise and the mixture was stirred vigorously for 1 min., then ethyl acetate (6 mL) and saturated aq. NaCl solution (6 mL) were added and the mixture was stirred vigorously for 5 min. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (4 ×6 mL). The combined organic extracts were dried with $MgSO_4$, filtered and evaporated on a rotary evaporator. The crude product was purified using column chromatography (PE/EA = 3/1) to give the pure product as white solid (0.475 g, 92.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82–7.62 (m, 4H), 7.55–7.39 (m, 12H), 7.35–7.24 (m, 4H), 3.02 (s, 2H), 2.67–2.48 (m, 2H), 2.15–1.98 (m, 4H), 1.84–1.74 (m, 2H), 1.53–1.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 132.31, 132.08, 131.86, 131.61, 131.38, 131.14, 130.91, 130.69, 130.44, 130.22, 129.94, 129.89, 129.84, 129.79, 127.73, 127.68, 127.62, 127.57, 127.52, 127.46, 35.07, 34.77, 34.45, 34.12, 33.82, 27.05, 23.70, 22.05, 22.02, 21.99. ^{31}P NMR (162 MHz, $CDCl_3$) δ = 35.39 (s).

***Trans*-1,2-bis(diphenylphosphaneyl)cyclopentane (1)** In a 50 mL Schlenk flask, **1c** (0.235 g, 0.5 mmol), Ti(O^iPr)$_4$ (83 μL, 0.28 mmol) and $(EtO)_2MeSiH$ (0.48 mL, 3.0 mmol) were dissolved in 20 mL of toluene under argon atmosphere. The resulting solution was heated to reflux for 60 min and dried under reduced pressure. The crude product was purified by flash chromatography on silica gel (PE/EA = 50/1) under argon atmosphere to give the pure product as white solid (0.198 g, 90.3%). *The product was highly reactive with oxygen, so an oxygen-free environment was needed for purification process.* ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.37–7.29 (m, 4H), 7.23–7.17 (m, 6H), 7.16–7.12 (m, 2H), 7.09–6.99 (m, 8H), 2.75–2.60 (m, 2H), 2.26–2.08 (m, 2H), 1.85–1.72 (m, 2H), 1.62–1.50 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 136.76, 136.73, 136.69, 136.66, 136.54, 136.53, 136.48, 136.46, 132.79, 132.76, 132.68, 132.62, 132.55, 132.51, 127.61, 127.48, 127.27, 127.24, 38.68, 38.55, 38.54, 38.51, 38.41, 28.03, 27.97, 27.91, 23.18, 23.16, 23.14. ^{31}P NMR (243 MHz, $CDCl_3$) δ = -7.98 (s). HRMS (EI): m/z

$[M]^+$ calcd. for $C_{29}H_{28}P_2^+$: 438.1666, found: 438.1671.

***Trans*-bis(diphenylphosphaneyl)cyclohexane (2) 2** was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using **2c** (0.242 g, 0.5 mmol), $Ti(O^iPr)_4$ (83 μL, 0.28 mmol), $(EtO)_2MeSiH$ (0.48 mL, 3.0 mmol). **2** was obtained as white powder (0.198 g, 87.6%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.27 (m, 4H), 7.24–7.21 (m, 2H), 7.19–7.17 (m, 6H), 7.16–7.12 (m, 4H), 7.07–7.02 (m, 4H), 2.43 (s, 2H), 2.36–2.23 (m, 2H), 1.95–1.84 (m, 2H), 1.54–1.43 (m, 2H), 1.42–1.32 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 136.21, 136.18, 136.15, 136.12, 135.40, 135.38, 135.34, 135.31, 133.06, 133.02, 132.97, 132.95, 132.89, 132.83, 132.78, 132.76, 132.71, 127.89, 127.74, 127.67, 127.53, 127.51, 127.46, 127.37, 127.35, 127.33, 127.29, 127.27, 127.24, 127.16, 33.21, 33.07, 32.93, 23.13, 23.07, 23.00, 21.82, 21.73, 21.72, 21.69, 21.61. ^{31}P NMR (243 MHz, $CDCl_3$) δ = -14.68 (s). HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{30}H_{30}P_2^+$: 452.1823, found: 452.1820.

***Trans*-bis(diphenylphosphaneyl)cycloheptane (3) 3** was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using **3c** (0.249 g, 0.5 mmol), $Ti(O^iPr)_4$ (83 μL, 0.28 mmol), $(EtO)_2MeSiH$ (0.48 mL, 3.0 mmol). **3** was obtained as white powder (0.212 g, 90.9%).^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.35–7.30 (m, 4H), 7.22–7.14 (m, 9H), 7.13–7.08 (m, 7H), 2.60–2.52 (m, 2H), 2.17–2.11 (m, 2H), 1.83–1.74 (m, 2H), 1.70–1.63 (m, 2H), 1.58–1.46 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 136.30, 136.27, 136.22, 136.19, 135.25, 135.22, 135.18, 135.15, 133.13, 133.08, 133.01, 132.94, 132.89, 132.83, 132.66, 132.58, 132.54, 132.45, 127.92, 127.60, 127.51, 127.47, 127.39, 127.29, 127.26, 127.24, 127.20, 127.18, 127.16, 127.08, 35.57, 35.45, 35.43, 35.40, 35.29, 27.68, 26.50, 26.44, 26.37, 26.24, 26.23, 22.82, 22.77, 22.73. ^{31}P NMR (243 MHz, $CDCl_3$) δ = -10.28 (s). HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{31}H_{32}P_2^+$: 466.1979, found: 466.1981.

***Trans*-bis(diphenylphosphaneyl)cyclooctane (4) 4** was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using **4c** (0.256 g, 0.5 mmol), $Ti(O^iPr)_4$ (83 μL, 0.28 mmol), $(EtO)_2MeSiH$ (0.48 mL, 3.0 mmol). **4** was obtained as white powder (0.214 g, 88.9%).^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36–7.30 (m, 4H), 7.21–7.17 (m, 3H), 7.16–7.07 (m, 13H), 2.63–2.50 (m, 2H), 2.22 (dd, *J* = 22.9, 13.2 Hz, 2H), 1.86–1.73 (m, 4H), 1.64–1.55 (m, 2H), 1.48–1.31 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.44, 136.41, 136.37, 136.34, 135.10, 135.07, 135.04, 135.01, 133.22, 133.15, 133.11, 133.08, 133.04, 133.01, 132.97, 132.93, 132.90, 127.93, 127.59, 127.46, 127.38, 127.35, 127.27, 127.25, 127.22, 127.20, 127.18, 127.15, 35.51,

35.35, 35.20, 26.16, 23.92, 23.86, 23.80, 22.90, 22.82, 22.77, 22.72, 22.64.^{31}P NMR (243 MHz, $CDCl_3$) δ = -11.64 (s). HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{32}H_{34}P_2^+$: 480.2136, found: 480.2139.

2. NMR Spectra of compound 4b, 4c and 1~4.

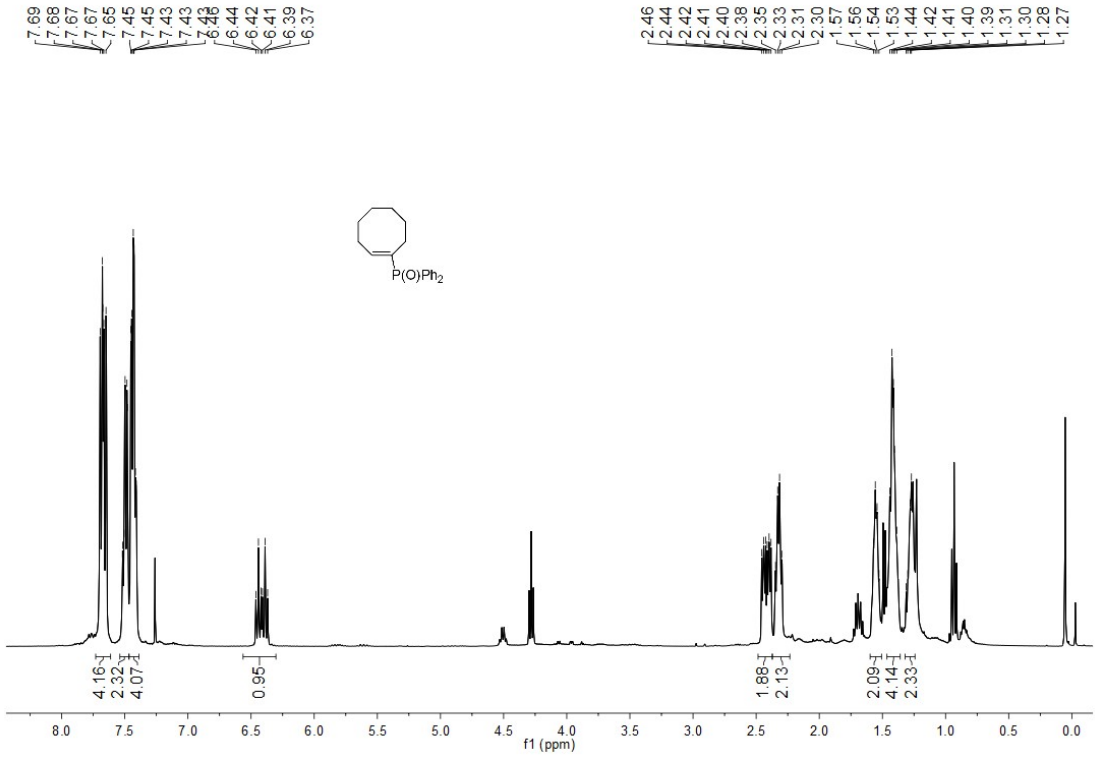

Fig. S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**

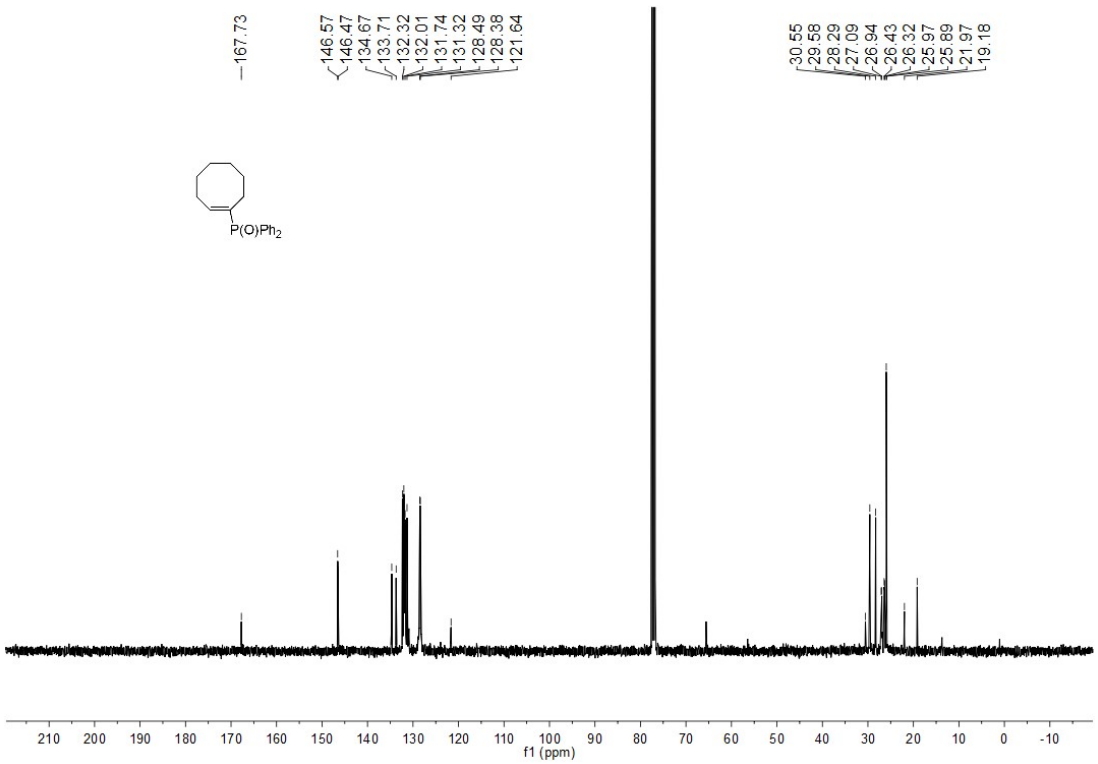

Fig. S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4b**

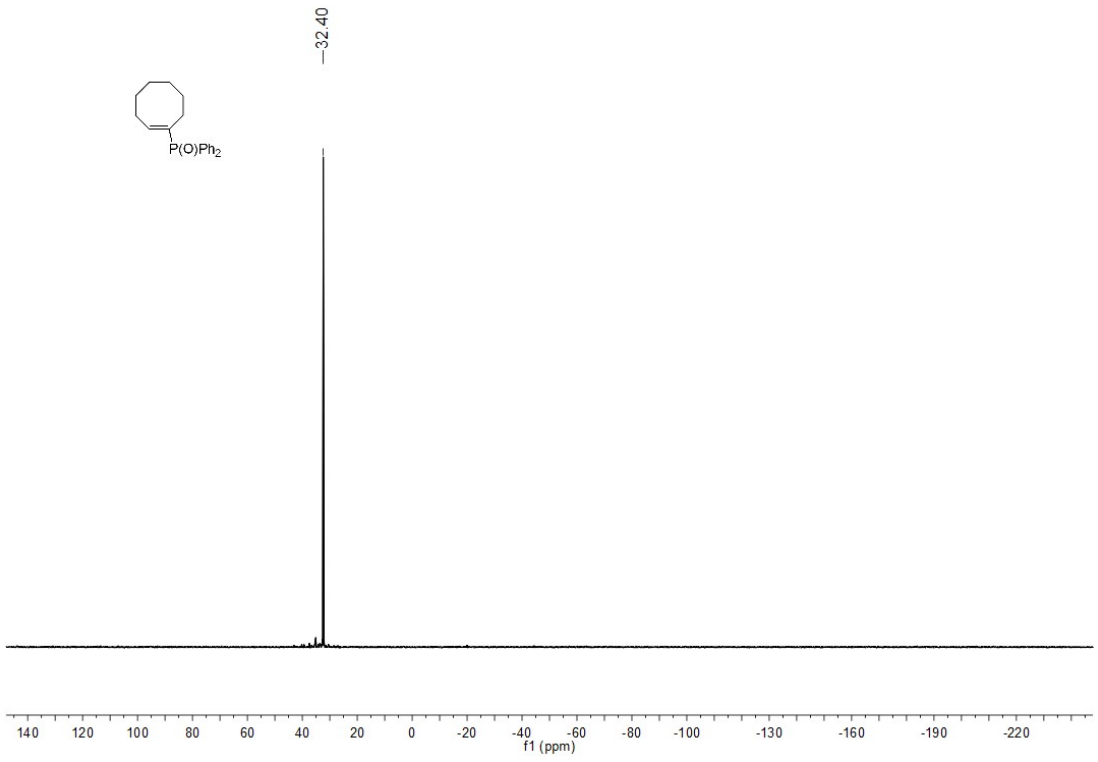

Fig. S3. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4b**

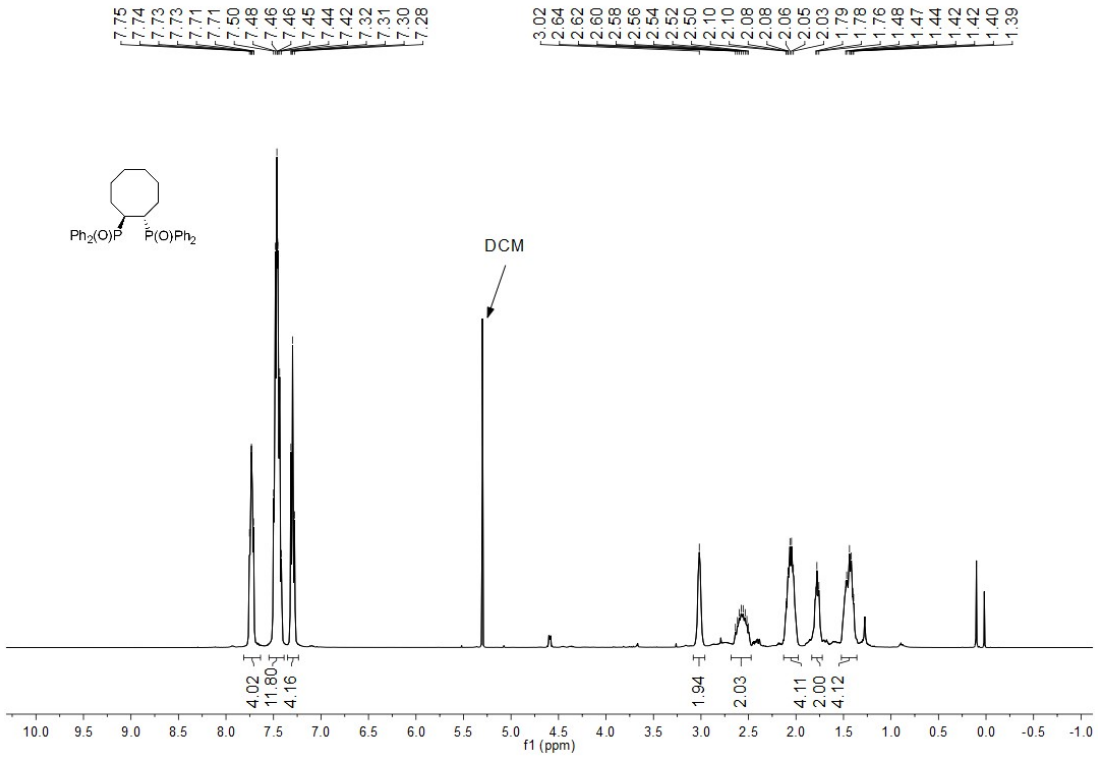

Fig. S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4c**

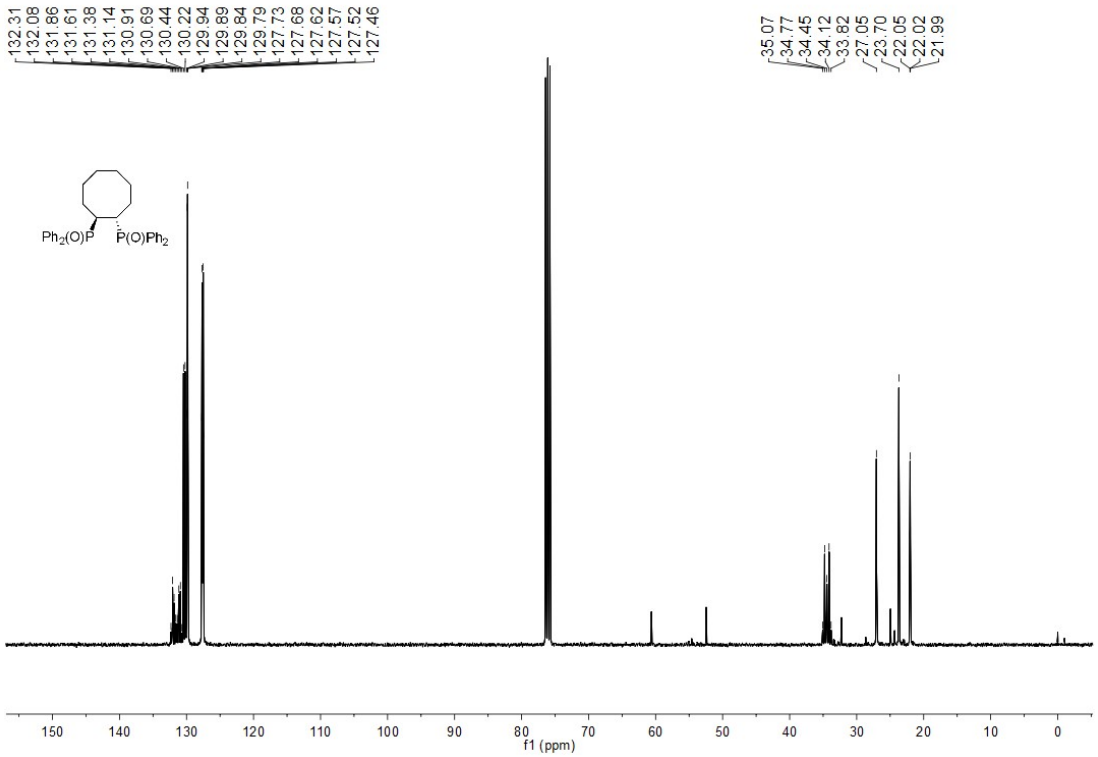

Fig. S5. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4c**

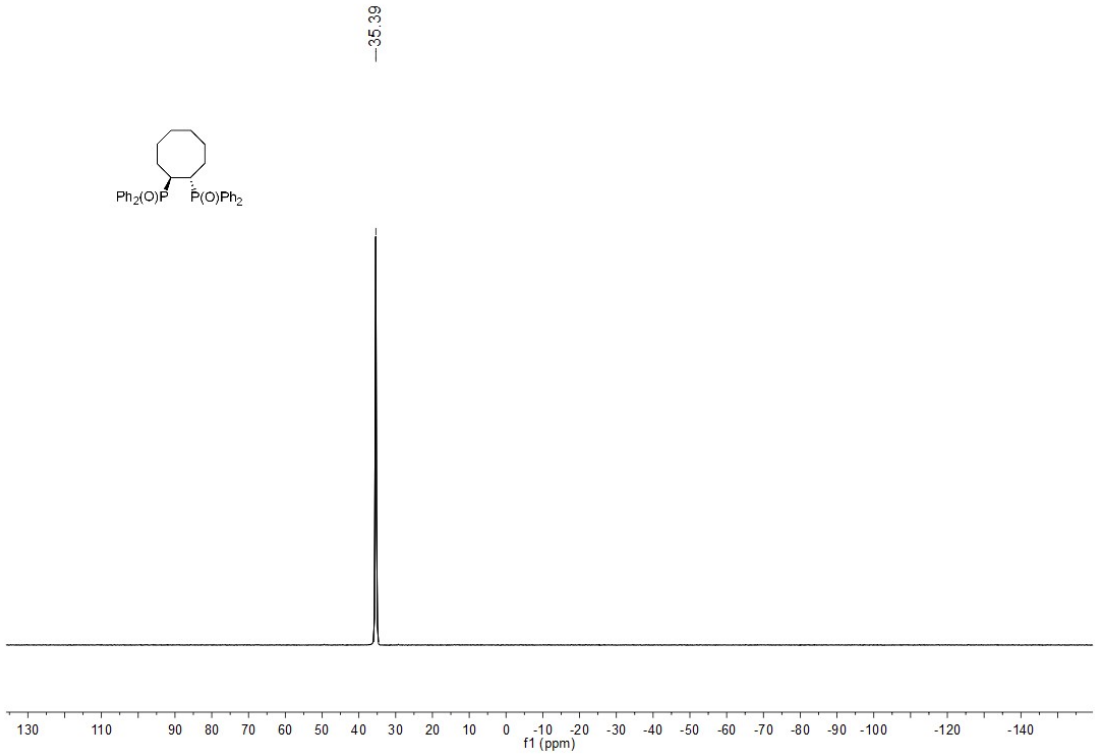

Fig. S6. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4c**

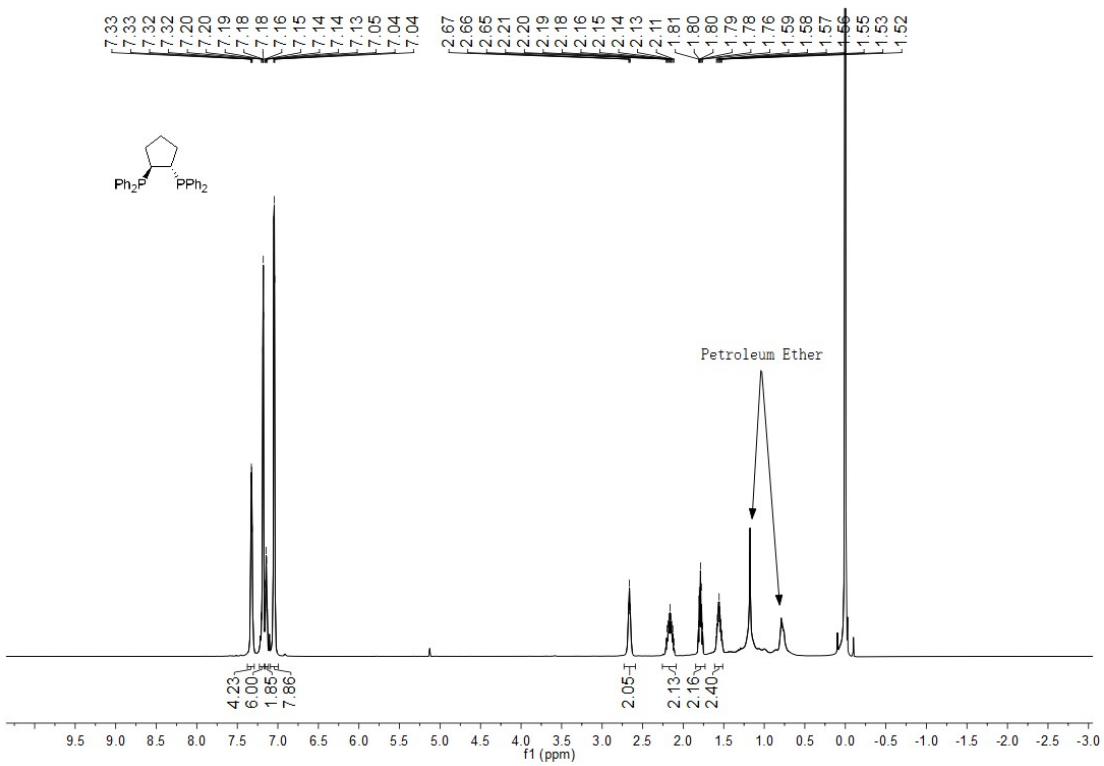

Fig. S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **1**

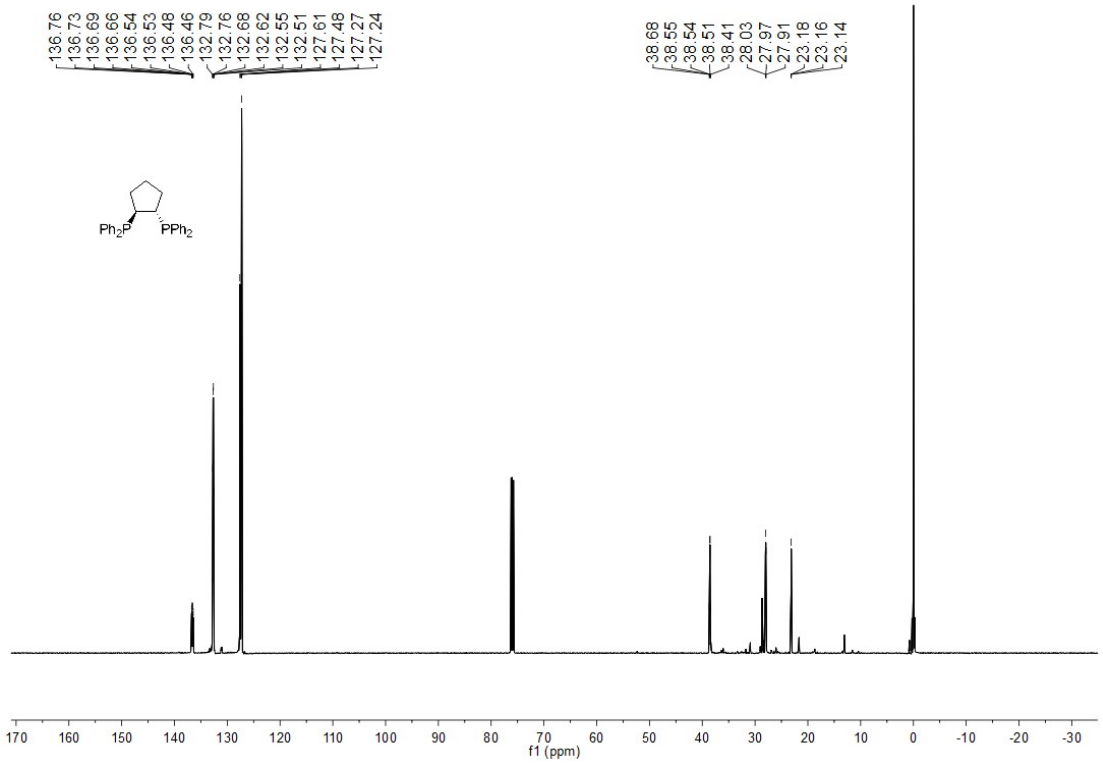

Fig. S8. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **1**

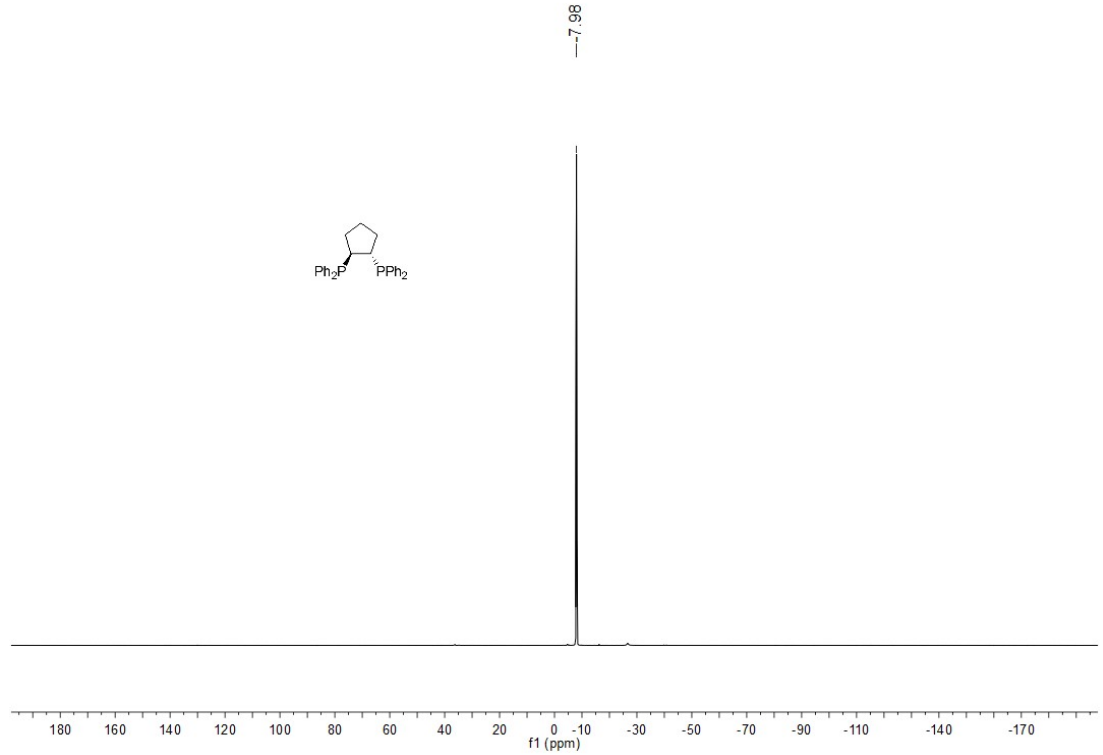

Fig. S9. ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **1**

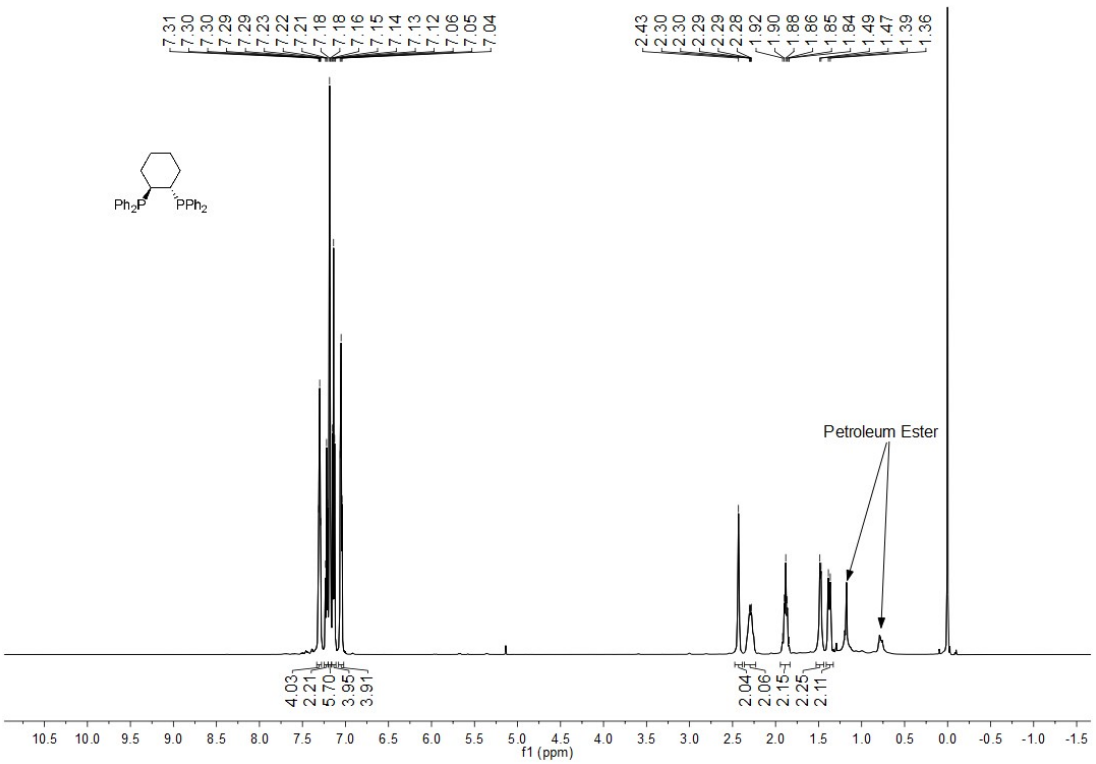

Fig. S10. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **2**

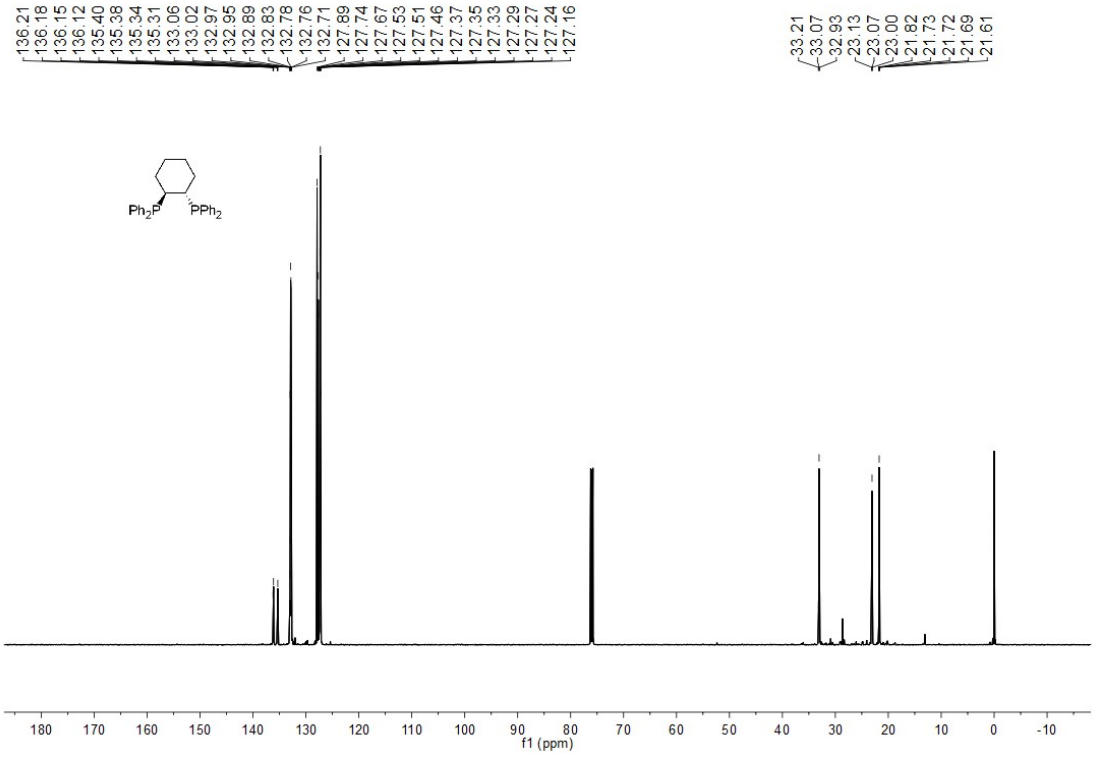

Fig. S11. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **2**

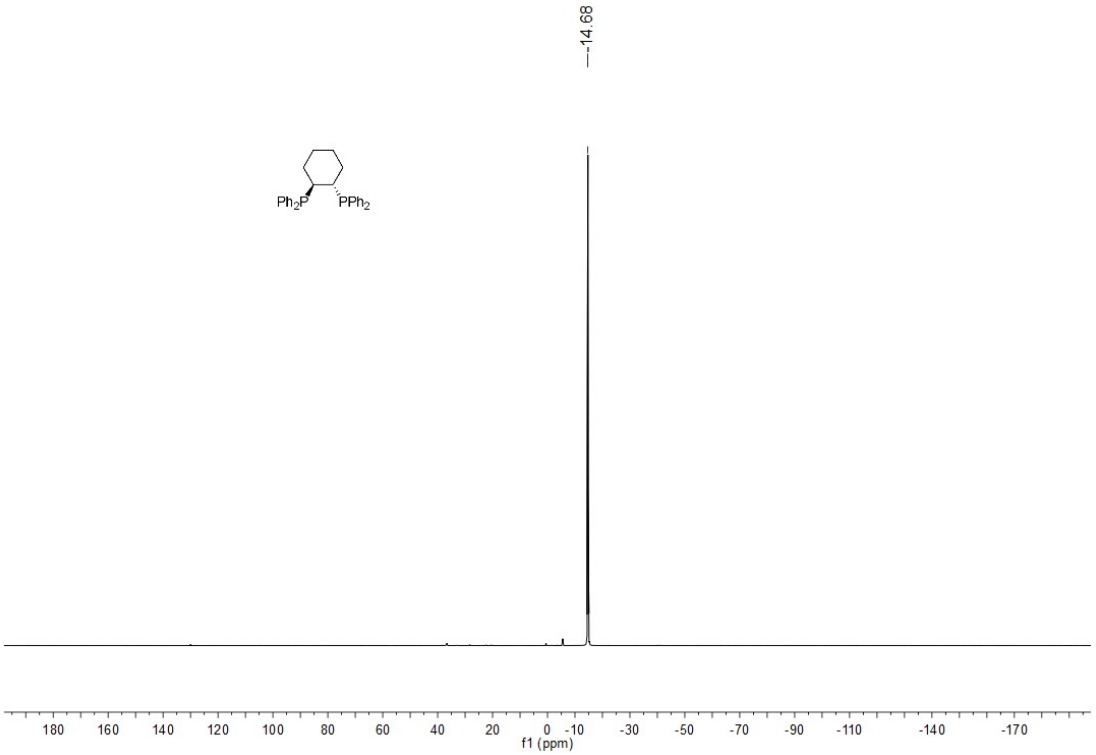

Fig. S12. ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **2**

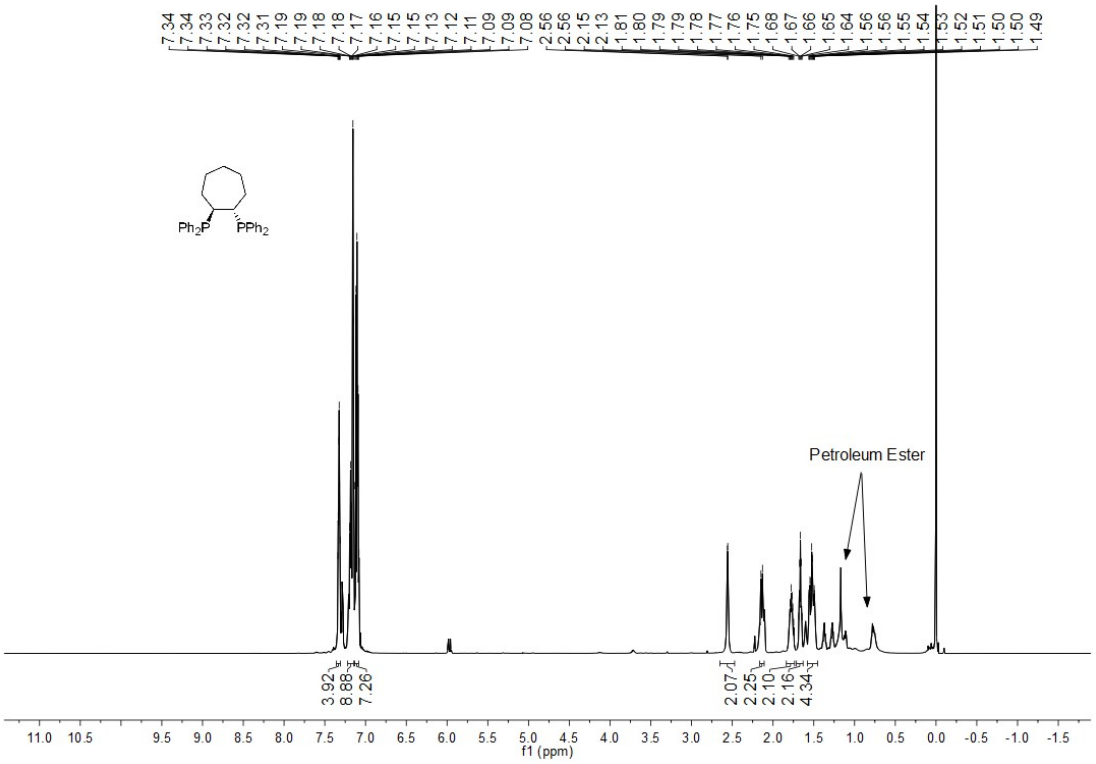

Fig. S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3**

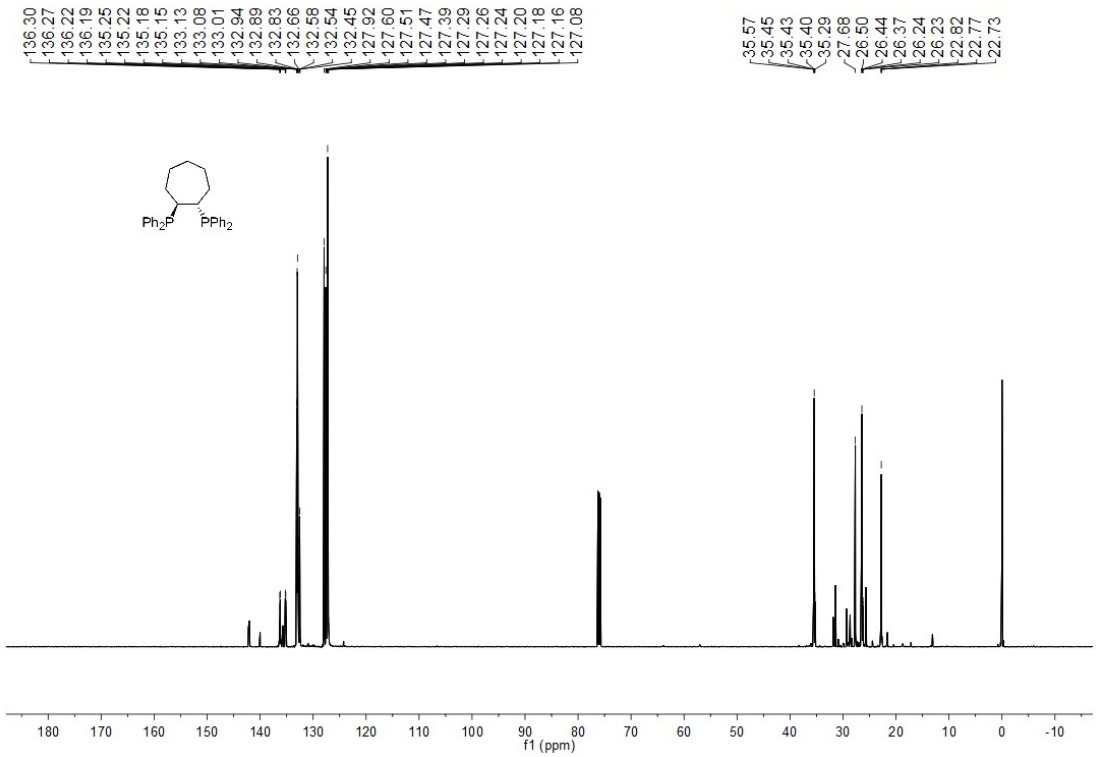

Fig. S14. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3**

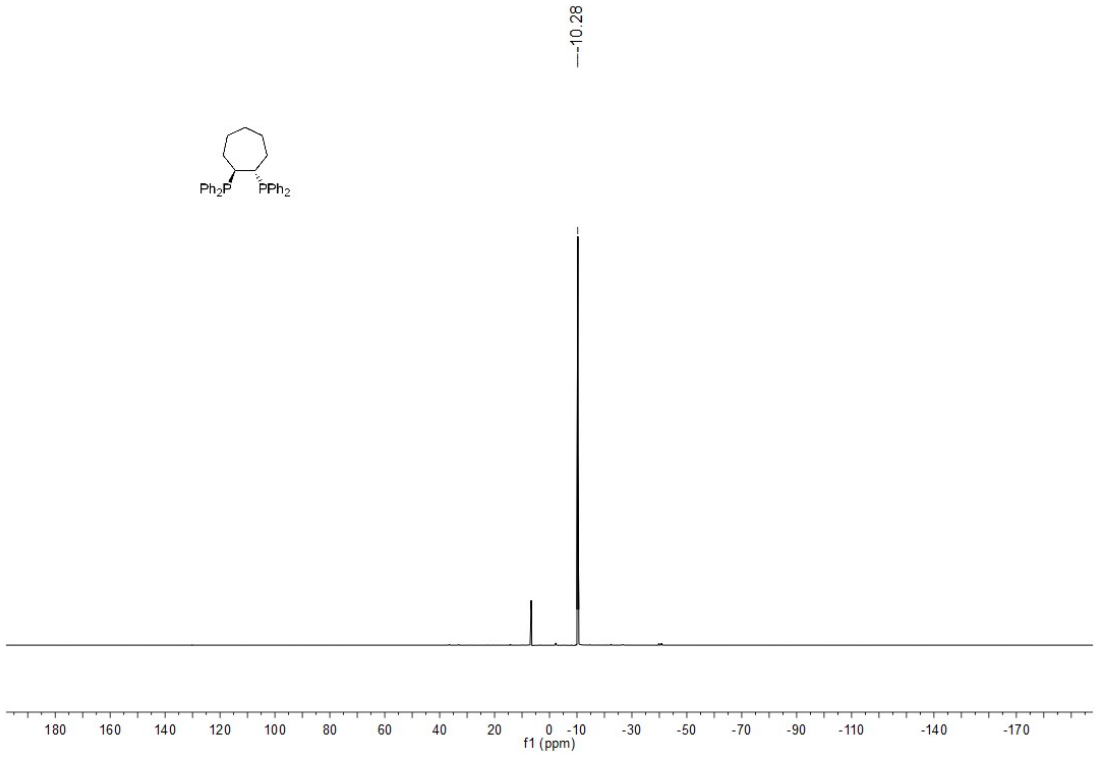

Fig. S15. ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **3**

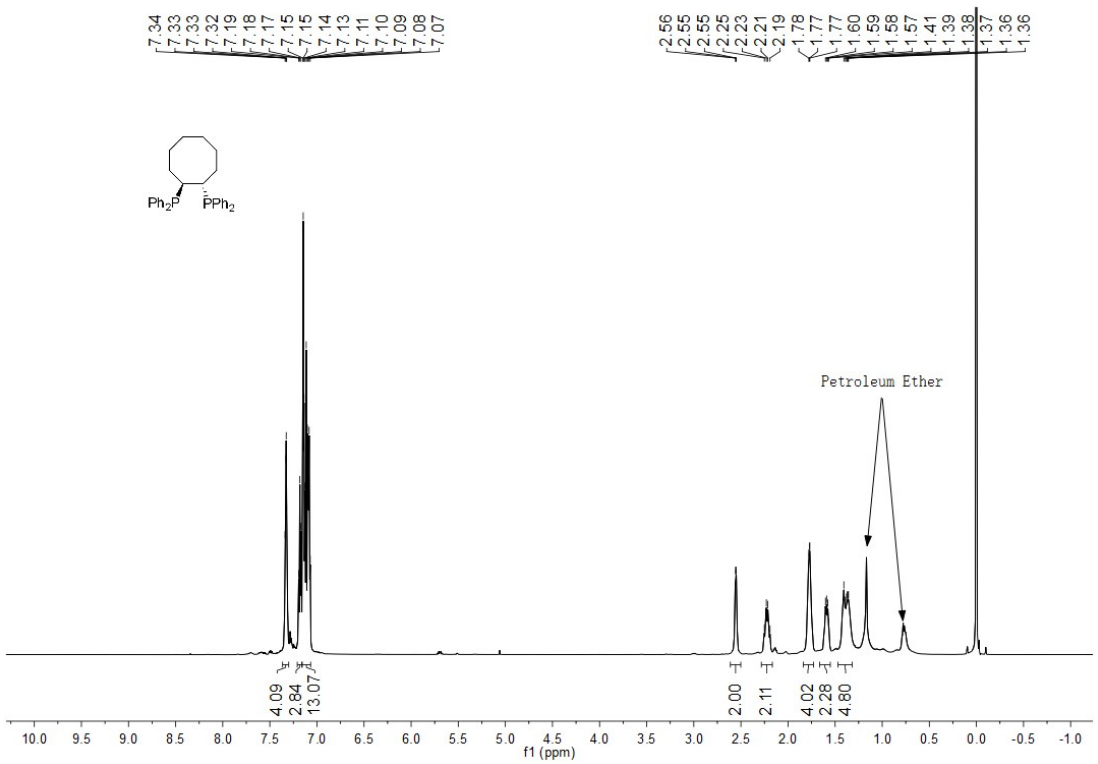

Fig. S16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4**

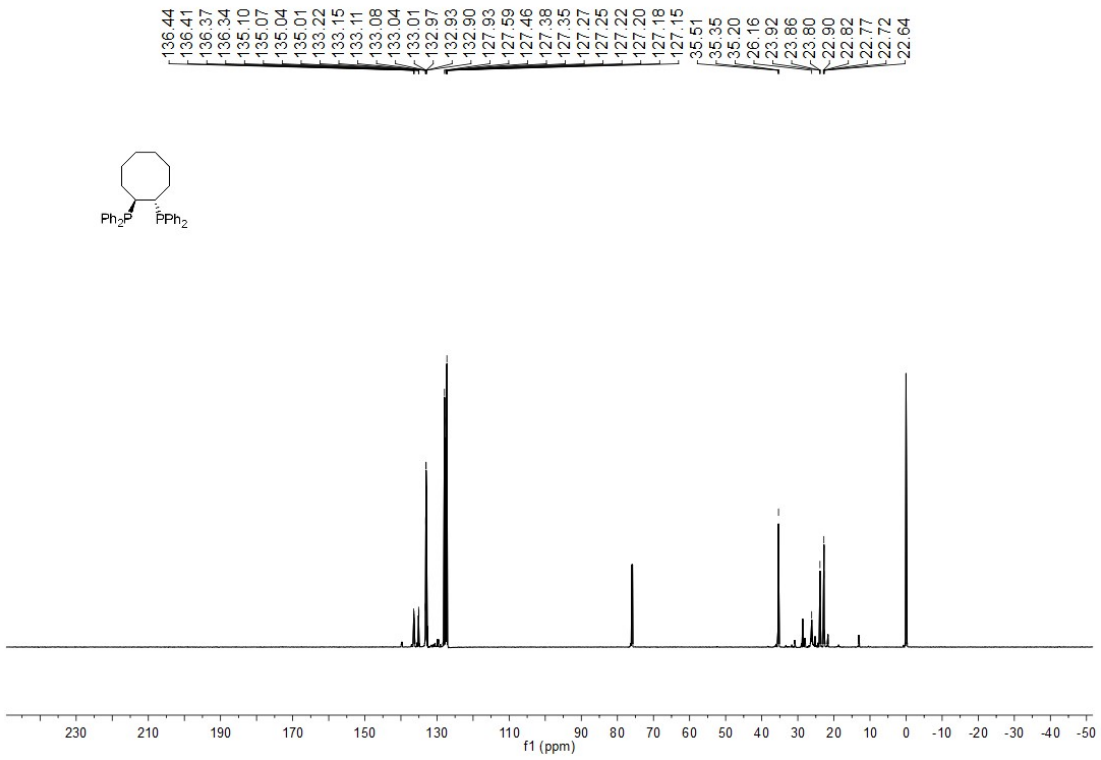

Fig. S17. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4**

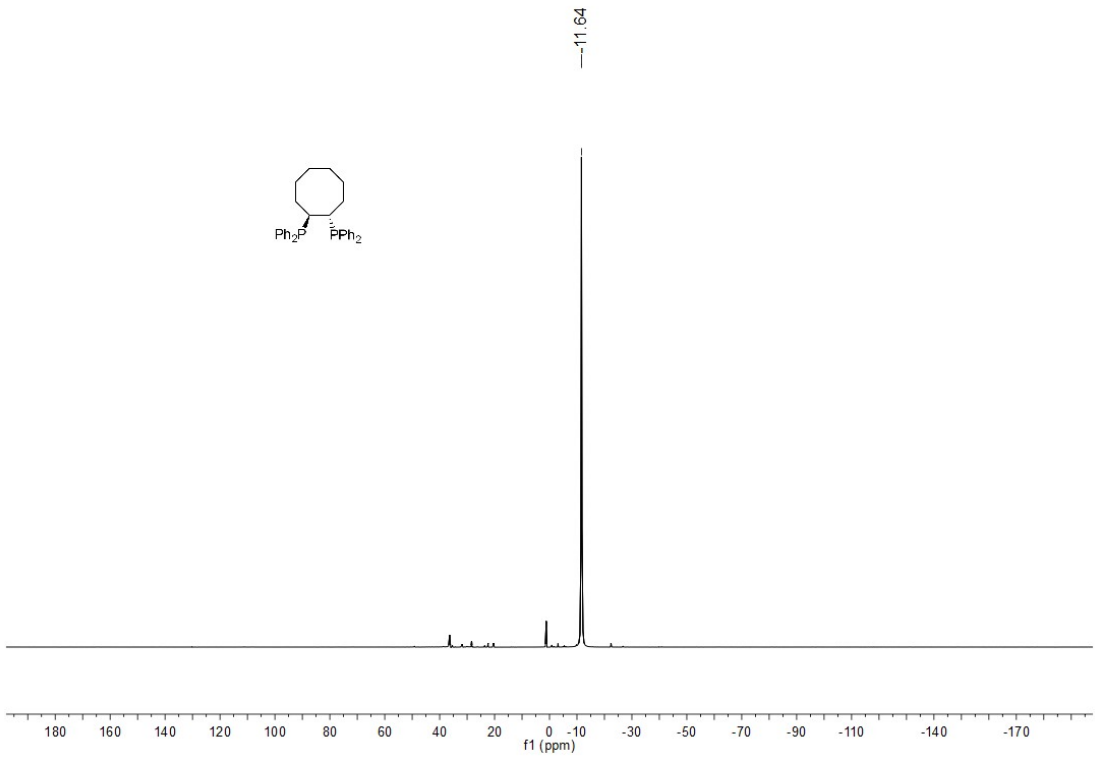

Fig. S18. ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **4**

3. Computational Studies

All geometric optimizations have been carried out by density functional theory using the B3LYP hybrid functional [3] with Grimme's dispersion correction of D3 version (Becke-Johnson damping) [4]. The def2-SVP basis set [5-6] for all atoms was used. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies). Approximate solvent effects were taken into consideration based on the SMD continuum solvation model [7] in the above calculations (solvent=methylcyclohexane). All the above calculations were carried out by Gaussian 16 programs [8].

4. Reference

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