

Supporting Information for

Reactivity Studies on Lanthanum and Cerium Hydrido Metallocenes

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EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ln}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (Ln = La, Ce)¹ were prepared according to the literature method. All other chemicals were purchased from Aldrich Chemical Co. and Energy Chemical Co. and used as received unless otherwise noted. All operations in this procedure should be conducted in a well-ventilated hood. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AV 600 spectrometer at 600 and 150 MHz, respectively. All chemical shifts were reported in δ units with reference to the residual protons of the deuterated solvents, which were internal standards, for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Preparation of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{La}(\mu\text{-OBC}_8\text{H}_{14})(\text{THF})$ (3). A solution of 9-borabicyclo[3.3.1]nonane (9-BBN; 0.0586 g, 0.48 mmol) in THF (1 mL) was slowly added to a toluene (9 mL) solution of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (0.151 g, 0.24 mmol). After stirring at room temperature for 2 h, the solvent was removed under vacuum. THF (2 mL) was added to the residue, and then diffusion of n-hexane into the solution gave colorless crystals of 3. Yield: 0.123 g (73%). M.p.: 72-

74 °C. ^1H NMR (600 MHz, C_6D_6) δ = 6.18 (d, J = 2.5 Hz, 4H, ring CH), 6.12 (t, J = 2.5 Hz, 2H, ring CH), 3.65 (m, 4H, thf), 2.15 (m, 10H, BC_8H_{14}), 1.69 (m, 2H, BC_8H_{14}), 1.38 (s, 36H, $\text{C}(\text{CH}_3)_3$), 1.28 (m, 4H, thf), 1.15 (m, 2H, BC_8H_{14}) $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ = 141.24 (ring C), 108.35 (ring C), 107.26 (ring C), 70.97 (thf), 33.96 (CH), 32.20 ($\text{C}(\text{CH}_3)_3$), 32.07 ($\text{C}(\text{CH}_3)_3$), 24.63(CH_2), 24.03 (CH_2). IR (KBr, cm^{-1}): ν = 2955 (s), 2863 (m), 1659 (m), 1617 (m), 1462 (m), 1406 (s), 1360 (m), 1287 (m), 1251 (m), 1227 (m), 1200 (m), 1161 (m), 1023 (m), 931 (m), 801 (m). Anal. Calcd for $\text{C}_{38}\text{H}_{64}\text{BLaO}_2$: C, 64.96; H, 9.18. Found: C, 64.87; H, 9.15.

The residue was re-extracted with n-hexane, and the solvent/volatiles were removed under vacuum to give the oily $(\text{Me}_2\text{N-}o\text{-C}_6\text{H}_4\text{CH}_2)\text{BC}_8\text{H}_{14}$. By ^1H NMR spectroscopy, $(\text{Me}_2\text{N-}o\text{-C}_6\text{H}_4\text{CH}_2)\text{BC}_8\text{H}_{14}$ is spectroscopically identical to the previous report.²

Preparation of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce}(\mu\text{-OBC}_8\text{H}_{14})(\text{THF})$ (4). This compound was prepared as yellow crystals from the reaction of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (0.150 g, 0.24 mmol) and 9-BBN (0.0586 g, 0.48 mmol) in THF/toluene (10 mL) at room temperature and recrystallization from a THF/n-hexane solution by a procedure similar to that described in the synthesis of **3**. Yield: 0.128 g (76 %). M.p.: 74-76 °C. ^1H NMR (600 MHz, C_6D_6): δ = ^1H NMR (600 MHz, C_6D_6) δ = 12.24 (br, 2H, ring CH), 11.57 (br, 4H, ring CH), 9.17 (br, 4H, thf), 7.13 (br, 2H, BC_8H_{14}), 6.75 (br, 4H, thf), 2.36 (br, 2H, BC_8H_{14}), -2.25 (s, 36H, $\text{C}(\text{CH}_3)_3$), -2.63 (br, 5H, BC_8H_{14}), -3.89 (br, 4H, BC_8H_{14}), -5.14 (br, 1H, BC_8H_{14}). IR (KBr, cm^{-1}): ν = 2954 (m), 2863 (w), 1655 (m), 1616 (m), 1462 (w), 1386 (s), 1361 (m), 1284 (w), 1256 (m), 1200 (w), 1180 (s), 1145 (s), 1077 (s), 1051 (m), 1019 (m), 953 (m) 802 (w). Anal. Calcd for $\text{C}_{38}\text{H}_{64}\text{BCeO}_2$: C, 64.85;

H, 9.17. Found: C, 64.78; H, 9.15.

Preparation of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{La(OC}_6\text{H}_{11}\text{)(THF)}$ (5**).** A solution of 9-BBN (0.0293 g, 0.24 mmol) in toluene (5 mL) was slowly added to a toluene (5 mL) solution of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{La(CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2\text{)}$ (0.151 g, 0.24 mmol) and cyclohexene oxide (0.024 g, 0.24 mmol). After stirring at room temperature for 5 h, the solvent was removed under vacuum. THF (2 mL) was added to the residue, and then diffusion of n-hexane into the solution gave colorless crystals of **5**. Yield: 0.105 g (66 %). M.p.: 106-108 °C. $^1\text{H NMR}$ (600 MHz, C_6D_6) δ = 6.18-6.16 (m, 6H, ring CH), 3.85-3.82 (m, 1H, OCH), 3.65 (t, J = 6.3 Hz, 4H, thf), 2.11-2.04 (m, 2H, CH_2), 1.78 (br, 2H, CH_2), 1.59 (m, 1H, CH_2), 1.40 (s, 36H, $\text{C(CH}_3\text{)}_3$), 1.34-1.31 (m, 8H, thf and CH_2), 1.14 (br, 1H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6) δ = 140.35 (ring C), 107.31 (ring C), 106.99 (ring C), 77.92 (OCH), 69.97 (thf), 39.39 (CH_2), 32.18 ($\text{C(CH}_3\text{)}_3$), 32.07 ($\text{C(CH}_3\text{)}_3$), 26.23 (thf), 25.47 (CH_2), 24.90 (CH_2). IR (KBr, cm^{-1}): ν = 2962 (m), 2854 (m), 1620 (m), 1459 (m), 1385 (m), 1356 (m), 1260 (s), 1199 (m), 1093 (s), 1020 (s), 933 (m), 798 (s). Anal. Calcd for $\text{C}_{36}\text{H}_{61}\text{LaO}_2$: C, 65.04; H, 9.25. Found: C, 64.93; H, 9.22.

Preparation of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce(OC}_6\text{H}_{11}\text{)(THF)}$ (6**).** This compound was prepared as yellow crystals from the reaction of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce(CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2\text{)}$ (0.151 g, 0.24 mmol), cyclohexene oxide (0.024 g, 0.24 mmol) and 9-BBN (0.0293 g, 0.24 mmol) in toluene (10 mL) at room temperature and recrystallization from a THF/n-hexane solution by a procedure similar to that described in the synthesis of **5**. Yield: 0.120 g (75%). M.p.: 110-112 °C. $^1\text{H NMR}$ (600 MHz, C_6D_6): δ = 20.74 (br, 6H, ring CH), 11.01 (br, 2H), 9.38 (br, 2H), 8.53 (m, 1H), 7.50 (m, 1H), -1.44 (br, 4H), -

1.54 (br, 6H), -4.67 (br, 1H), -4.71 (br, 2H), -7.39 (s, 36H, C(CH₃)₃). IR (KBr, cm⁻¹): ν = 2946 (s), 2806 (m), 1547 (m), 1460 (m), 1387 (m), 1359 (m), 1248 (m), 1199 (m), 1162 (m), 1093 (s), 1057 (m), 1025 (m), 932 (m), 801 (s). Anal. Calcd for C₃₆H₆₁CeO₂: C, 64.92; H, 9.23. Found: C, 65.76; H, 9.26.

Preparation of {[η^5 -1,3-(Me₃C)₂C₅H₃]₂LaCl}₂ (7). A solution of 9-BBN (0.0293 g, 0.24 mmol) in toluene (5 mL) was slowly added to a toluene (5 mL) solution of [η^5 -1,3-(Me₃C)₂C₅H₃]₂La(CH₂C₆H₄-*o*-NMe₂) (0.151 g, 0.24 mmol) and Me₃SiCl (0.0261 g, 0.24 mmol). After stirring at room temperature for 2 h, the solvent was removed under vacuum. THF (3 mL) was added to the residue, and then diffusion of n-hexane into the solution gave colorless crystals of **7**. Yield: 0.099 g (78%). M.p.: 70-72 °C. ¹H NMR (600 MHz, C₆D₆) δ = 6.39 (d, *J* = 2.4 Hz, 4H, ring CH), 6.33 (t, *J* = 2.4 Hz, 2H, ring CH), 1.40 (s, 36H, C(CH₃)₃). ¹³C NMR (151 MHz, C₆D₆) δ = 145.03 (ring C), 110.34 (ring C), 108.53 (ring C), 32.67 (C(CH₃)₃), 32.27 (C(CH₃)₃). IR (KBr, cm⁻¹): ν = 2951 (w), 2879 (m), 1564 (s), 1442 (m), 1345 (m), 1316 (m), 1299 (m), 1259 (m), 1102 (s), 1061 (s), 1022 (w), 915 (s), 805 (m). Anal. Calcd for C₅₂H₈₄Cl₂La₂: C, 59.04; H, 8.00. Found: C, 58.95; H, 7.97. By ¹H NMR spectroscopy, Me₃SiH is spectroscopically identical to the previous report.³

Preparation of {[η^5 -1,3-(Me₃C)₂C₅H₃]₂CeCl}₂ (8). This compound was prepared as yellow crystals from the reaction of [η^5 -1,3-(Me₃C)₂C₅H₃]₂Ce(CH₂C₆H₄-*o*-NMe₂) (0.151 g, 0.24 mmol), Me₃SiCl (0.0261 g, 0.24 mmol) and 9-BBN (0.0293 g, 0.24 mmol) in toluene (10 mL) at room temperature and recrystallization from a THF/n-hexane solution by a procedure similar to that described in the synthesis of **5**. Yield: 0.102 g (80 %). The solid-state structure of the complex has been confirmed by single crystal

X-ray diffraction, which is identical to that reported.⁴

Preparation of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{La}(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{12}\text{H}_8\text{N}_2)$ (9**).** A solution of 9-BBN (0.0293 g, 0.24 mmol) in toluene (5 mL) was slowly added to a toluene (5 mL) solution of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{La}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (0.151 g, 0.24 mmol) and phenazine (0.0216 g, 0.12 mmol) with stirring at -20 °C. After stirring at room temperature for 6 h, the solution was filtered. The volume of the filtrate was reduced to 2 mL, the purple crystals of **9** were isolated at room temperature in the glovebox after addition of a few drops of n-hexane. n-Hexane solvated molecules were easily lost upon isolation of the compound as a dry crystalline solid. Yield: 0.087 g (62 %). M.p.: 123-125 °C. ¹H NMR (600 MHz, C₆D₆) δ = 6.45 (br, 4H, ring CH), 6.29 (br, 2H, ring CH), 6.24 (m, 2H, C₁₂N₂H₈), 5.75 (m, 2H, C₁₂N₂H₈), 1.36 (s, 36H, C(CH₃)₃). ¹³C NMR (151 MHz, C₆D₆) δ = 145.10 (C₁₂N₂H₈), 143.33 (ring C), 122.00 (C₁₂N₂H₈), 110.98 (ring C), 108.41 (ring C), 108.13 (C₁₂N₂H₈), 32.42 (C(CH₃)₃), 31.88 (C(CH₃)₃). IR (KBr, cm⁻¹): ν = 2955 (m), 2861 (w), 1643 (m), 1622 (m), 1587 (m), 1509 (m), 1461 (s), 1386 (s), 1359 (m), 1298 (m), 1249 (m), 1198 (m), 1081(s), 1051(s), 1024 (s), 928 (m), 796 (s). A reproducible microanalysis could not be obtained for the compound as the solvent molecule (n-hexane) in the crystal lattice were slowly lost upon isolation of the compound as a dry crystalline solid.

Preparation of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce}(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_{12}\text{H}_8\text{N}_2)\cdot 2\text{C}_6\text{H}_{14}$ (10**·2C₆H₁₄).** This compound was prepared as purple crystals from the reaction of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (0.151 g, 0.24 mmol), phenazine (0.0216 g, 0.12 mmol) and 9-BBN (0.0293 g, 0.24 mmol) in toluene (10 mL) at room temperature and

recrystallization from a toluene/n-hexane solution by a procedure similar to that described in the synthesis of **9**. Yield: 0.081 g (58%). M.p.: 124-126 °C. ¹H NMR (600 MHz, C₆D₆): δ = -4.08 (br, 36H, C(CH₃)₃), -5.03(br, 2H), -5.44(br, 4H). IR (KBr, cm⁻¹): ν = 2959 (m), 2861 (w), 1642 (m), 1618 (m), 1549 (m), 1500 (w), 1462 (m), 1385 (m), 1360 (m), 1259 (m), 1199 (w), 1180 (w), 1145 (m), 1078 (m), 1019 (m), 922 (w), 798 (s). A reproducible microanalysis could not be obtained for the compound as the solvent molecule (n-hexane) in the crystal lattice were slowly lost upon isolation of the compound as a dry crystalline solid.

Preparation of $[\{\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3\}_2\text{La}]_3\text{P}_7\cdot\text{C}_7\text{H}_8$ (11**·C₇H₈).** A solution of 9-BBN (0.0293 g, 0.24 mmol) in toluene (5 mL) was slowly added to a toluene (5 mL) solution of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3\}_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (0.151 g, 0.24 mmol) and P₄ (0.030 g, 0.24 mmol) with stirring at room temperature. After stirring at 40 °C for 12 h, the solution was filtered. The volume of the filtrate was reduced to 2 mL, the light yellow crystals of **11**·C₇H₈ were isolated at room temperature in the glovebox after addition of a few drops of n-hexane. Yield: 0.063 g (44%). M.p.: 198-200 °C (decomposed). ¹H NMR (600 MHz, C₆D₆) δ = 7.14-7.11 (m, 2H, aryl H), 7.05-7.00 (m, 3H, aryl H), 6.52 (br, 12H, ring CH), 6.38 (br, 6H, ring CH), 2.11 (s, 3H, CH₃), 1.50 (s, 108H, C(CH₃)₃). ¹³C NMR (151 MHz, C₆D₆) δ = 143.62 (br, ring C), 137.48 (aryl C), 128.92 (aryl C), 128.15 (aryl C), 125.28 (aryl C), 111.11 (br, ring C), 33.05(C(CH₃)₃), 32.82 (C(CH₃)₃), 21.00 (CH₃). ³¹P NMR (-60°C, 243 MHz, C₄D₈O) δ = -16.79, -27.78, -110.74. IR (KBr, cm⁻¹): ν = 2962 (m), 2862 (m), 1624 (m), 1476 (m), 1383 (m), 1354 (m), 1260 (s), 1243 (m), 1179 (m), 1083 (s), 1023 (s), 923 (w), 800 (m). Anal. Calcd for C₈₅H₁₃₄La₃P₇: C, 57.05; H, 7.55. Found:

C,56.92; H,7.49.

Preparation of $\{[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce}\}_3\text{P}_7\cdot\text{C}_7\text{H}_8$ (12**·**C₇H₈**).** This compound was prepared as brown crystals from the reaction of $[\eta^5\text{-1,3-(Me}_3\text{C)}_2\text{C}_5\text{H}_3]_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$ (0.151 g, 0.24 mmol), P_4 (0.030 g, 0.24 mmol) and 9-BBN (0.0293 g, 0.24 mmol) in toluene (10 mL) at 40 °C and recrystallization from a toluene/n-hexane solution by a procedure similar to that described in the synthesis of **11**. Yield: 0.059 g (41%). M.p.: 198-200 °C (decomposed). ^1H NMR (600 MHz, C_6D_6) δ = 7.15-7.11 (m, 2H, aryl H), 7.05-7.00 (m, 3H, aryl H), 2.11 (s, 3H, toluene CH_3), -0.42 (br, 4H, ring CH), -3.45 (br, 8H, ring CH), -6.90 (br, 108H, $\text{C}(\text{CH}_3)_3$), -11.29 (br, 6H, ring CH). ^{31}P NMR (-60°C, 243 MHz, C_6D_6) δ = -190.48. IR (KBr, cm^{-1}): ν = 2956 (m), 2860 (m), 1652 (w), 1627 (m), 1463 (m), 1385 (m), 1354 (w), 1252 (m), 1198 (m), 1046 (s), 1022 (s), 930 (w), 811 (m). Anal. Calcd for $\text{C}_{85}\text{H}_{134}\text{Ce}_3\text{P}_7$: C, 56.93; H, 7.53. Found: C, 56.78; H, 7.47.

X-ray Crystallography. Single-crystal X-ray diffraction measurements were carried out on an Agilent SuperNova EosS2 diffractometer using graphite monochromated Cu $\text{K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) or Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were kept at 150 (10) K during data collection. The structures were solved by the Superflip⁵ or ShelXT⁶ structure solution program in Olex2⁷ and refined using Full-matrix Least Squares based on F^2 with program SHELXL-2018⁸ within Olex2. Disorder was modelled using standard crystallographic methods including constraints and restraints where necessary. Crystal data and experimental data for **3-7** and **9-12** are summarized in Table S1.

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ORTEP DIAGRAMS

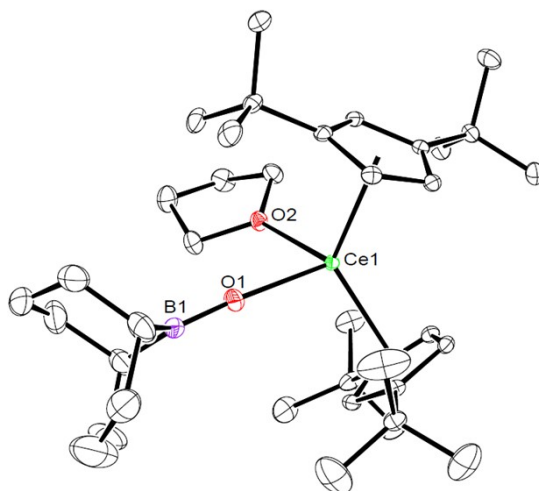


Fig. S1 ORTEP representation of **4**. Displacement ellipsoids are set to 30% probability. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ce(1)-O(1) 2.216(2), Ce(1)-O(2) 2.589(2), Ce(1)-Ct(1) 2.572, Ce(1)-Ct(2) 2.559, Ct(1)-Ce(1)-Ct(2) 124.9, B(1)-O(1)-Ce(1) 175.0(2).

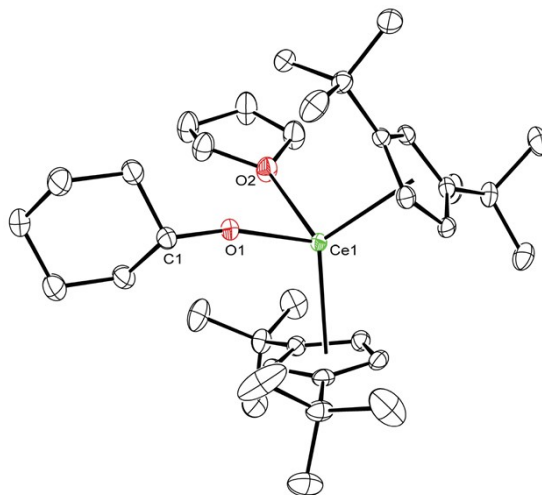


Fig. S2 ORTEP representation of **6**. Displacement ellipsoids are set to 30% probability. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ce(1)-O(1) 2.1477(16), Ce(1)-O(2) 2.5888(17), Ce(1)-Ct(1) 2.594, Ce(1)-Ct(2) 2.591, Ct(1)-Ce(1)-Ct(2) 122.9, C(1)-O(1)-Ce(1) 165.06(15).

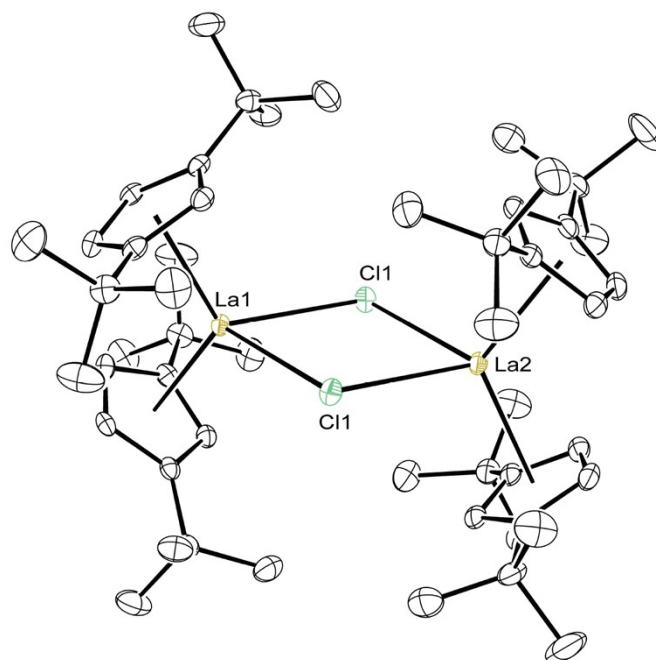


Fig. S3 ORTEP representation of **7**. Displacement ellipsoids are set to 30% probability. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): La(1)-Cl(1) 2.8933(7), La(2)-Cl(1) 2.8918(7), La(1)-Ct(1) 2.557, La(2)-Ct(2) 2.551, Ct(1)-La(1)-Ct(1) 121.6, Ct(2)-La(2)-Ct(2) 120.8

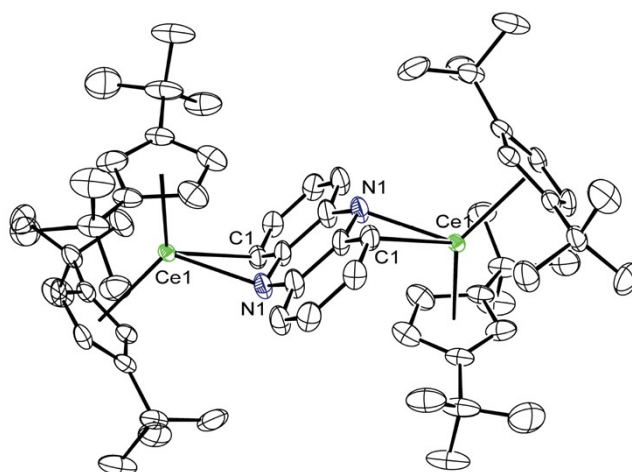


Fig. S4 ORTEP representation of **10**. Displacement ellipsoids are set to 30% probability. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ce(1)-N(1) 2.405(4), Ce(1)-C(2) 2.839(4), Ce(1)-Ct(1) 2.524, Ce(1)-Ct(2) 2.524, Ct(1)-Ce(1)-Ct(2) 134.1.

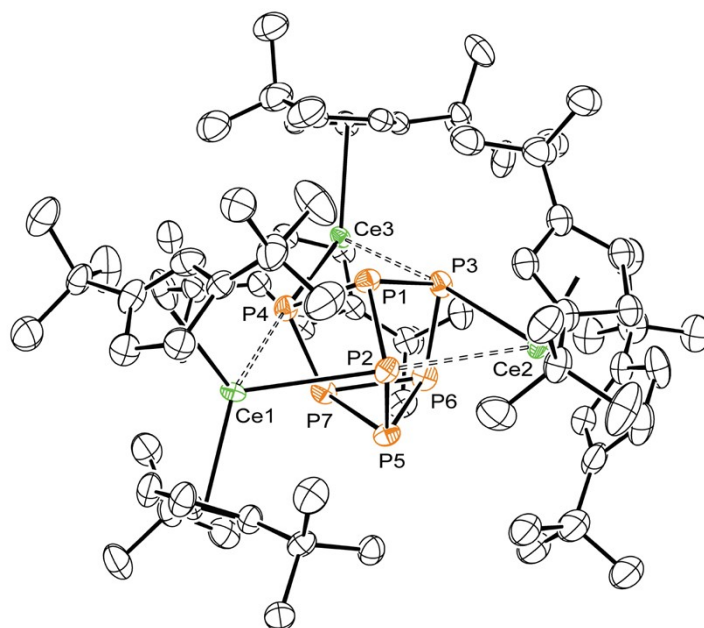


Fig. S5 ORTEP representation of **12**. Displacement ellipsoids are set to 30% probability. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ce(1)-P(2) 3.181(4), Ce(1)-P(4) 3.239(4), Ce(2)-P(3) 3.143(3), Ce(2)-P(2) 3.234(4), Ce(3)-P(3) 3.211(4), Ce(3)-P(4) 3.122(3), Ct(1)-Ce(1) 2.407, Ct(2)-Ce(1) 2.613, Ct(3)-Ce(2) 2.453, Ct(4)-Ce(2) 2.549, Ct(5)-Ce(3) 2.480, Ct(6)-Ce(3) 2.584, Ct(1)-Ce(1)-Ct(2) 117.7, Ct(3)-Ce(2)-Ct(4) 116.2, Ct(5)-Ce(3)-Ct(6) 118.1.

Table S1. Crystal data and experimental parameters for compounds **3-7** and **9-12**

Compound	3	4	5	6	7
Formula	C ₃₈ H ₆₄ BLaO ₂	C ₃₈ H ₆₄ BCeO ₂	C ₃₆ H ₆₁ LaO ₂	C ₃₆ H ₆₁ CeO ₂	C ₅₂ H ₈₄ Cl ₂ La ₂
Fw	702.61	703.82	664.75	665.96	1057.91
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c	Pccn
a/Å	10.53775(16)	10.5206(3)	11.37190(18)	11.36744(17)	12.9548(3)
b/Å	19.3733(3)	19.3399(5)	17.5341(3)	17.5348(3)	16.8937(3)
c/Å	18.2349(3)	18.2318(5)	18.3300(3)	18.2956(3)	24.5878(5)
α/°	90	90.00	90	90	90
β/°	93.1475(14)	93.152(2)	107.0666(19)	107.3342(16)	90
γ/°	90	90.00	90	90	90
Volume/Å ³	3717.05(10)	3703.96(17)	3493.98(11)	3481.16(10)	5381.16(18)
Z	4	4	4	4	4
ρ _{calc} /cm ³	1.256	1.262	1.264	1.271	1.306
μ/mm ⁻¹	1.178	1.258	1.250	1.335	1.695
F(000)	1480.0	1484.0	1400.0	1404.0	2176.0
Crystal size/mm ³	0.2 × 0.2 × 0.05	0.2 × 0.2 × 0.02	0.2 × 0.2 × 0.15	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.05
Radiation	MoKα	MoKα	MoKα	MoKα	MoKα
2θ range (deg)	6.694 to 52.742	7.038 to 52.744	6.776 to 52.744	6.586 to 52.74	6.644 to 52.744
Reflections collected	30964	30589	36244	36097	62442
Independent reflections	7592 [R _{int} = 0.0321]	7563 [R _{int} = 0.0370]	7122 [R _{int} = 0.0311]	7100 [R _{int} = 0.0324]	5501 [R _{int} = 0.0368]
Data/restr/paras	7592/8/401	7563/6/391	7122/44/386	7100/57/395	5501/0/266
GOF	1.052	1.099	1.163	1.073	1.276

R1/wR2 [$I \geq 2\sigma(I)$]	0.0256/0.0554	0.0337/ 0.0746	0.0367 / 0.0839	0.0265 / 0.0604	0.0345/0.0563
R1/wR2 (all data)	0.0340/0.0581	0.0407/ 0.0777	0.0415 / 0.0861	0.0316 / 0.0631	0.0439/0.0594
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.68/-0.40	1.19/-0.76	0.72/-0.84	0.56/-0.36	0.66/-0.68
CCDC	2161841	2161842	2161843	2161844	2161845

Compound	9	10·2C₆H₁₄	11·C₇H₈	12·C₇H₈
Formula	C ₆₄ H ₉₂ La ₂ N ₂	C ₇₆ H ₁₂₀ Ce ₂ N ₂	C ₈₅ H ₁₃₄ La ₃ P ₇	C ₈₅ H ₁₃₄ Ce ₃ P ₇
Fw	1167.21	1341.97	1789.43	1793.06
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a/Å	10.2919(3)	10.5325(2)	14.7718(3)	14.7799(5)
b/Å	11.7807(2)	13.8019(3)	14.8165(5)	14.8493(5)
c/Å	14.5718(5)	14.5653(3)	22.3328(8)	22.4110(9)
α /°	78.604(2)	64.338(2)	74.861(3)	74.202(4)
β /°	76.732(3)	73.743(2)	81.924(2)	81.751(3)
γ /°	70.957(2)	77.473(2)	68.345(3)	68.303(3)
Volume/Å ³	1610.97(8)	1820.95(7)	4379.9(2)	4392.4(3)
Z	1	1	2	2
$\rho_{\text{calc}}/\text{cm}^3$	1.203	1.224	1.357	1.356
μ/mm^{-1}	1.343	1.273	12.593	13.295
F(000)	604.0	706.0	1840.0	1846.0
Crystal size/mm ³	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.15	0.2 × 0.15 × 0.03	0.1 × 0.08 × 0.03

Radiation	MoK α	MoK α	CuK α	CuK α
2 θ range (deg)	6.918 to 52.742	6.59 to 52.742	6.928 to 146.214	6.888 to 143.8
Reflections collected	32522	29781	38478	29866
Independent reflections	6565 [R _{int} = 0.0457]	7428 [R _{int} = 0.0313]	17187 [R _{int} = 0.0325]	16825 [R _{int} = 0.0292]
Data/restr/paras	6565/242/422	7428/35/385	17187/48/861	16825/297/962
GOF	1.189	1.076	1.034	1.033
R1/wR2 [$I \geq 2\sigma(I)$]	0.0597 / 0.1456	0.0393/0.1046	0.0487/0.1254	0.0496/0.1301
R1/wR2 (all data)	0.0624 / 0.1471	0.0442/0.1081	0.0621/0.1341	0.0582/0.1371
Largest diff. peak/hole / e Å ⁻³	1.68/-0.98	1.29/-0.63	1.97/-1.66	1.25/-1.12
CCDC	2161846	2161847	2161848	2161849

NMR Spectra of New Compounds

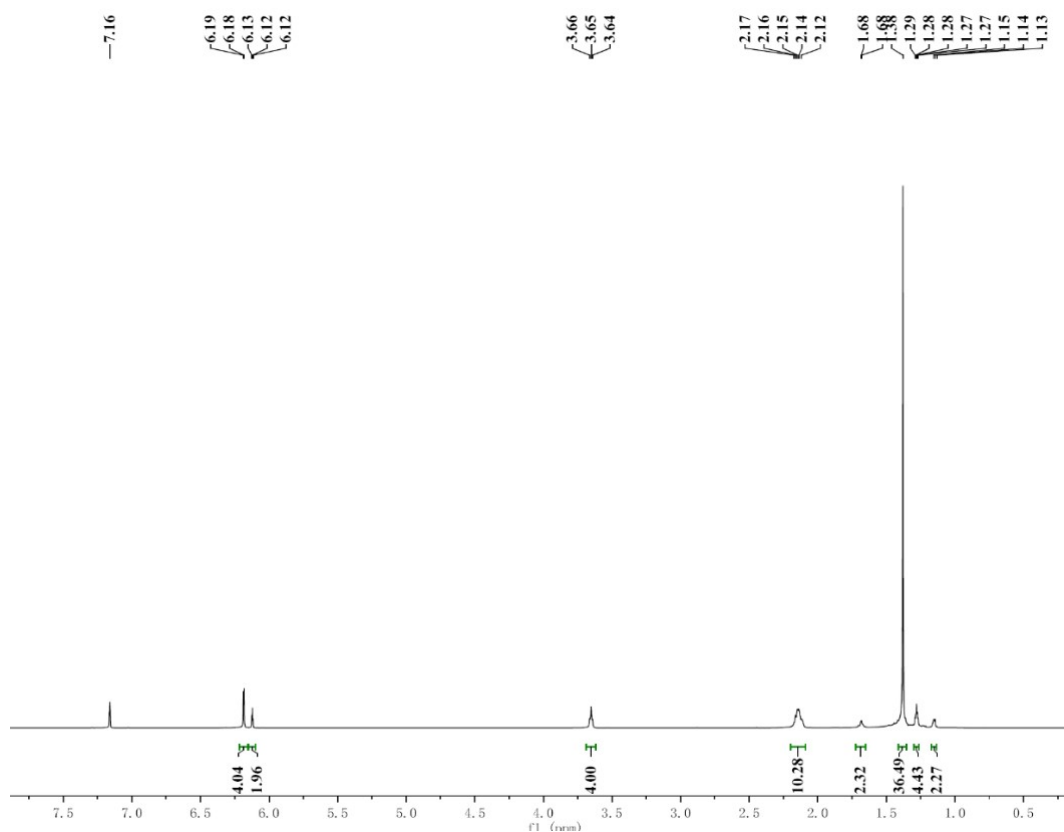


Fig. S6 ¹H NMR Spectrum of **3**

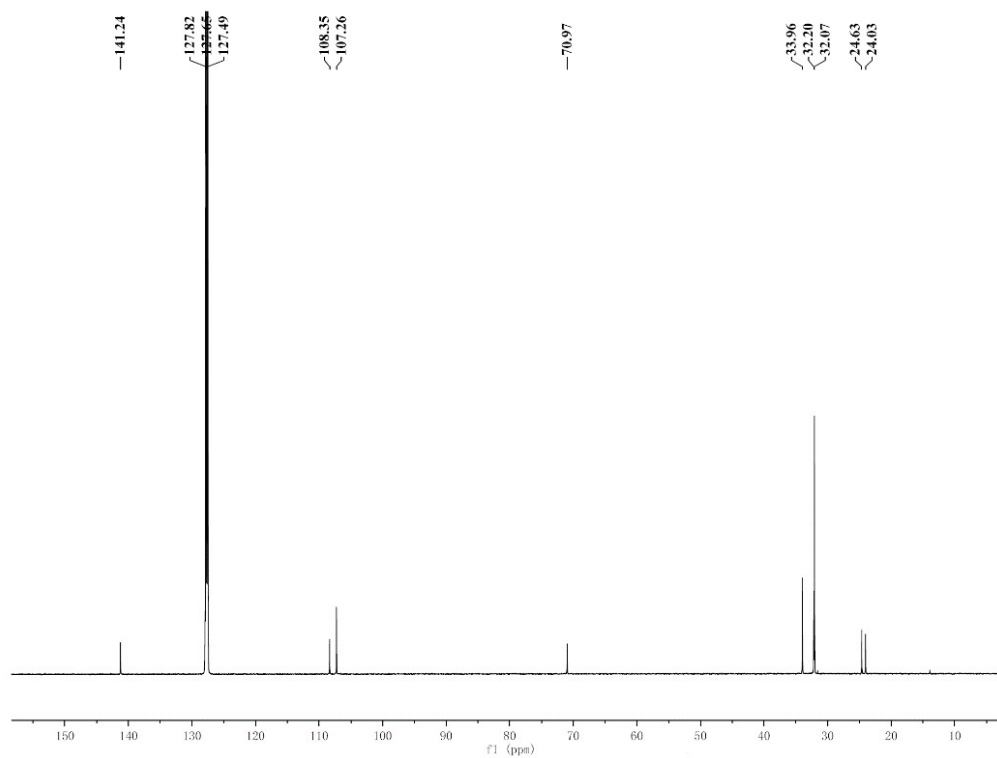


Fig. S7 ¹³C NMR Spectrum of **3**

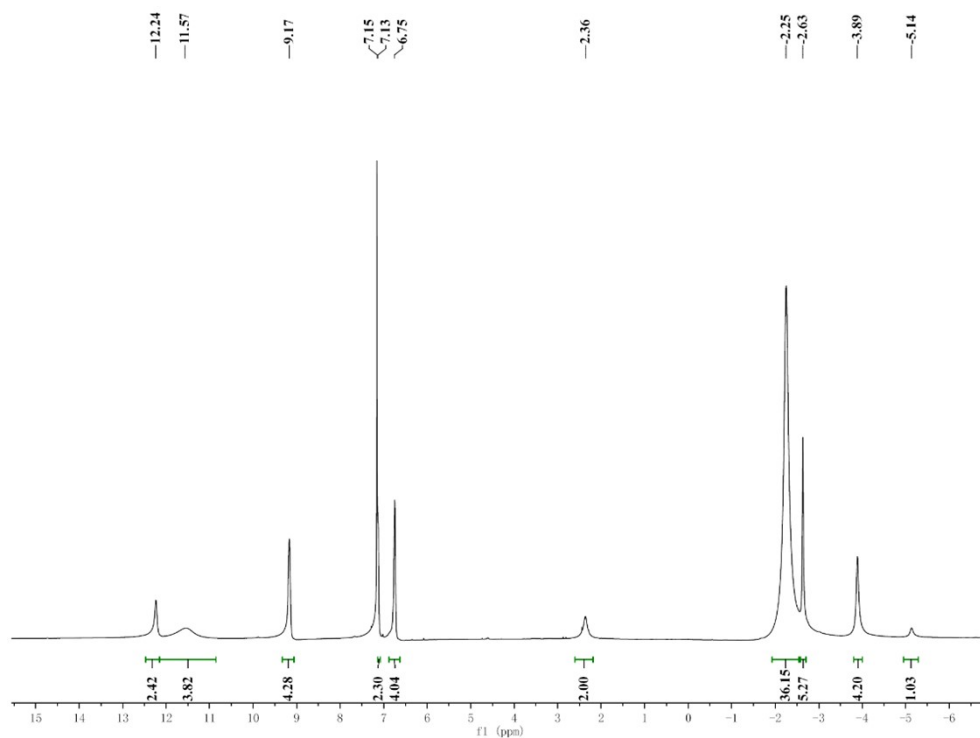


Fig. S8 ^1H NMR Spectrum of 4

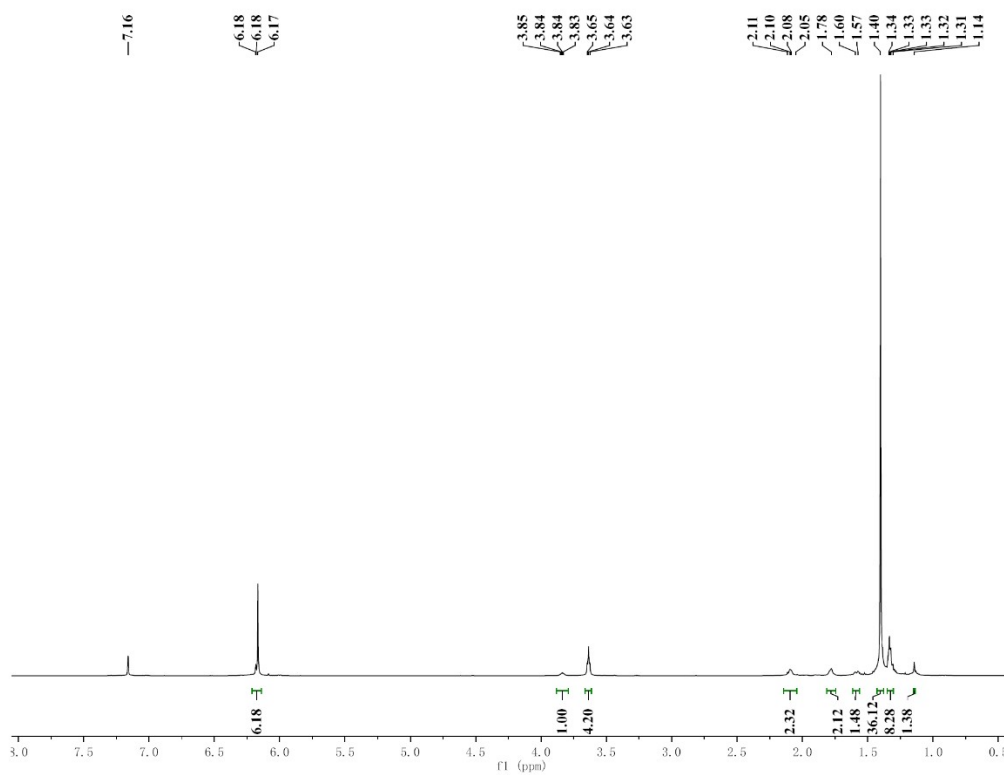


Fig. S9 ^1H NMR Spectrum of 5

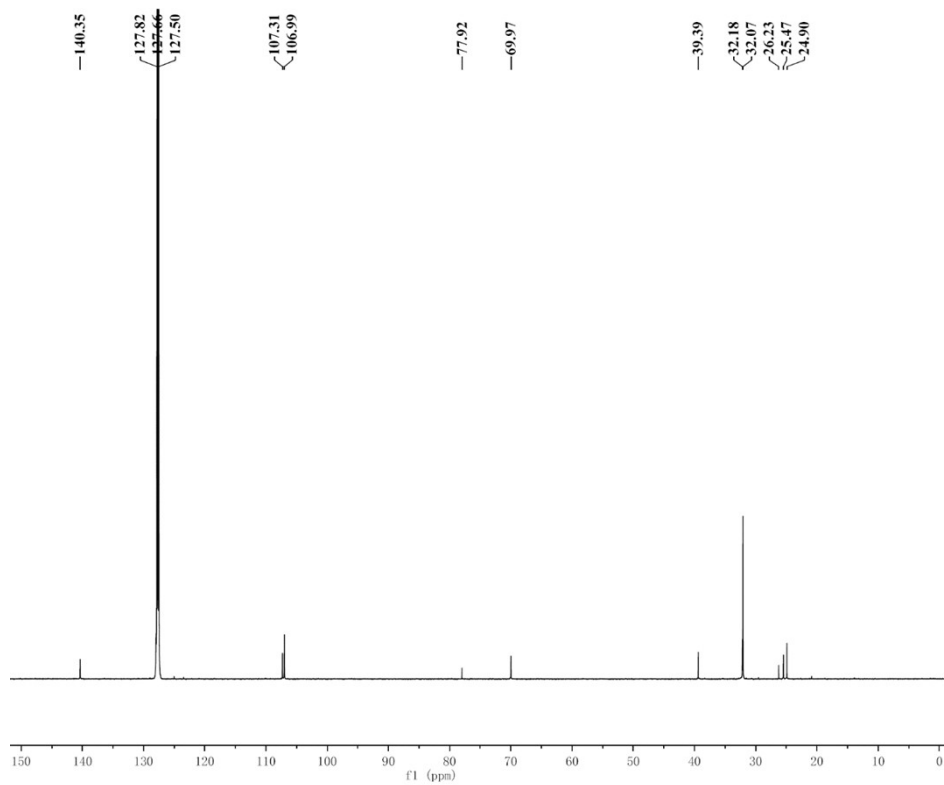


Fig. S10 ^{13}C NMR Spectrum of 5

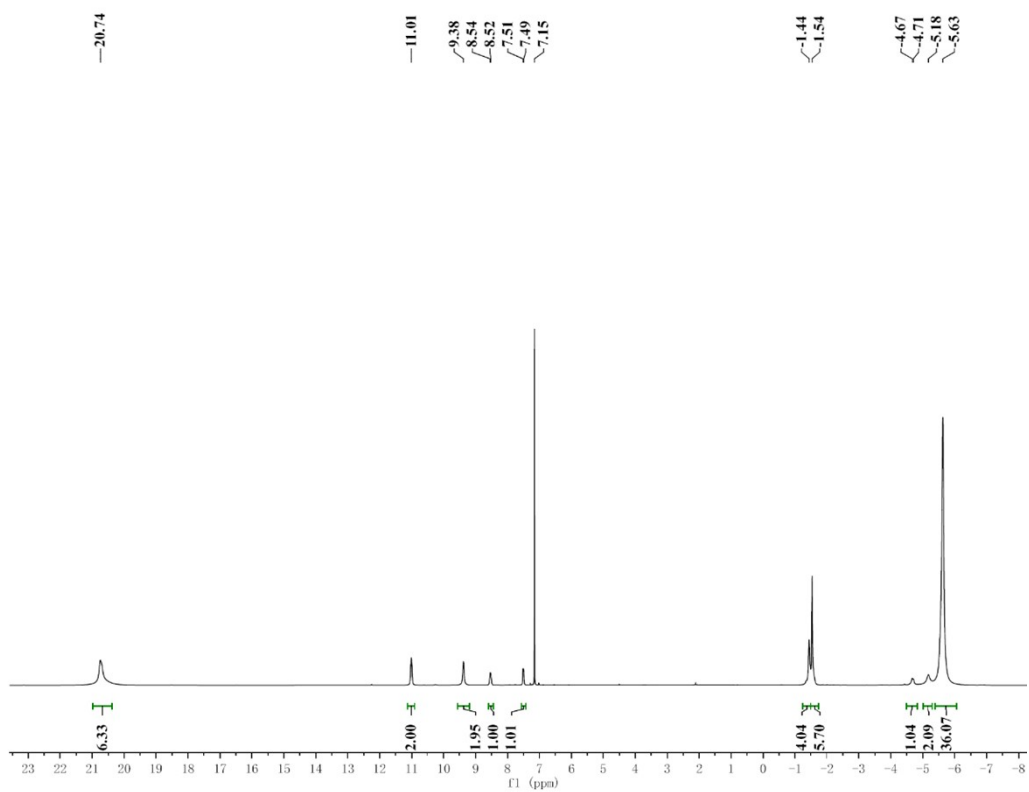


Fig. S11 ^1H NMR Spectrum of 6

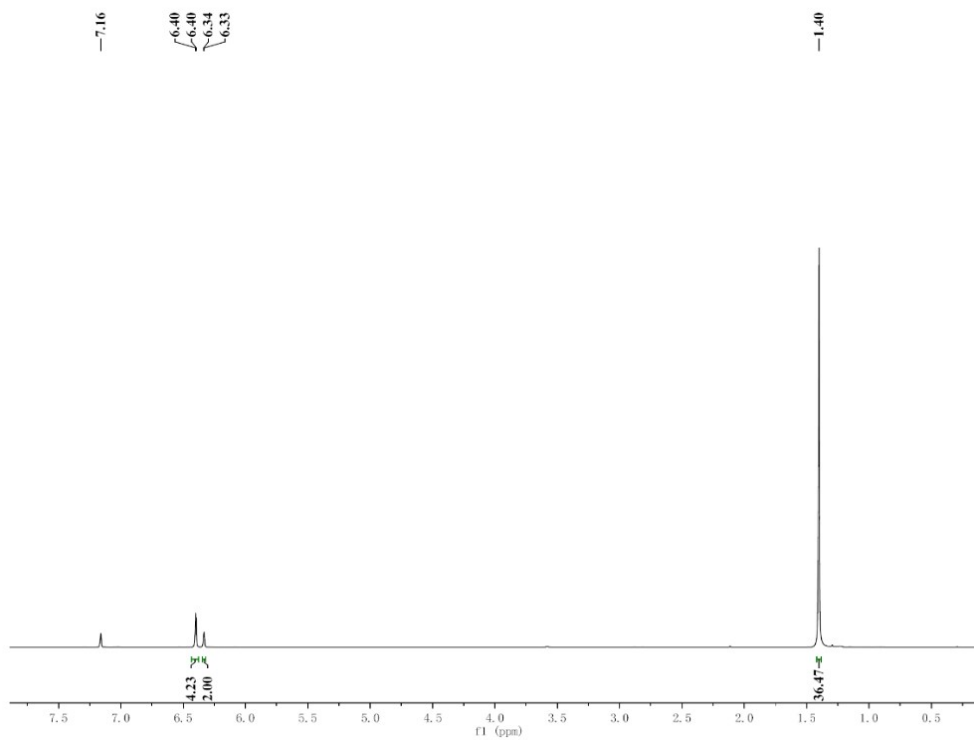


Fig. S12 ^1H NMR Spectrum of **7**

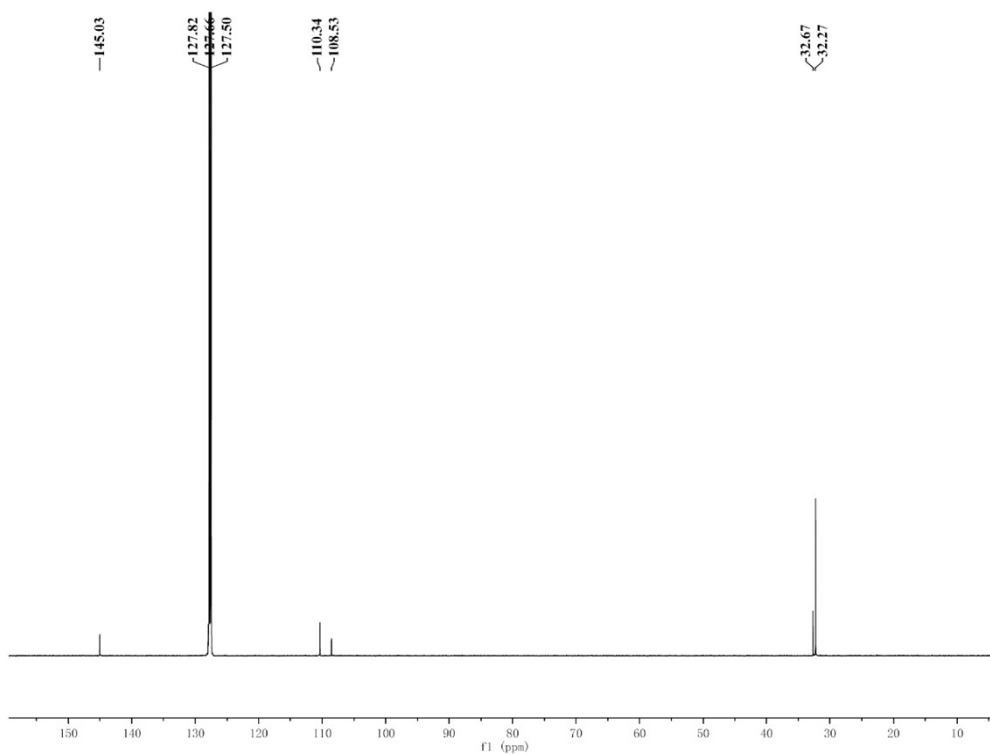


Fig. S13 ^{13}C NMR Spectrum of **7**

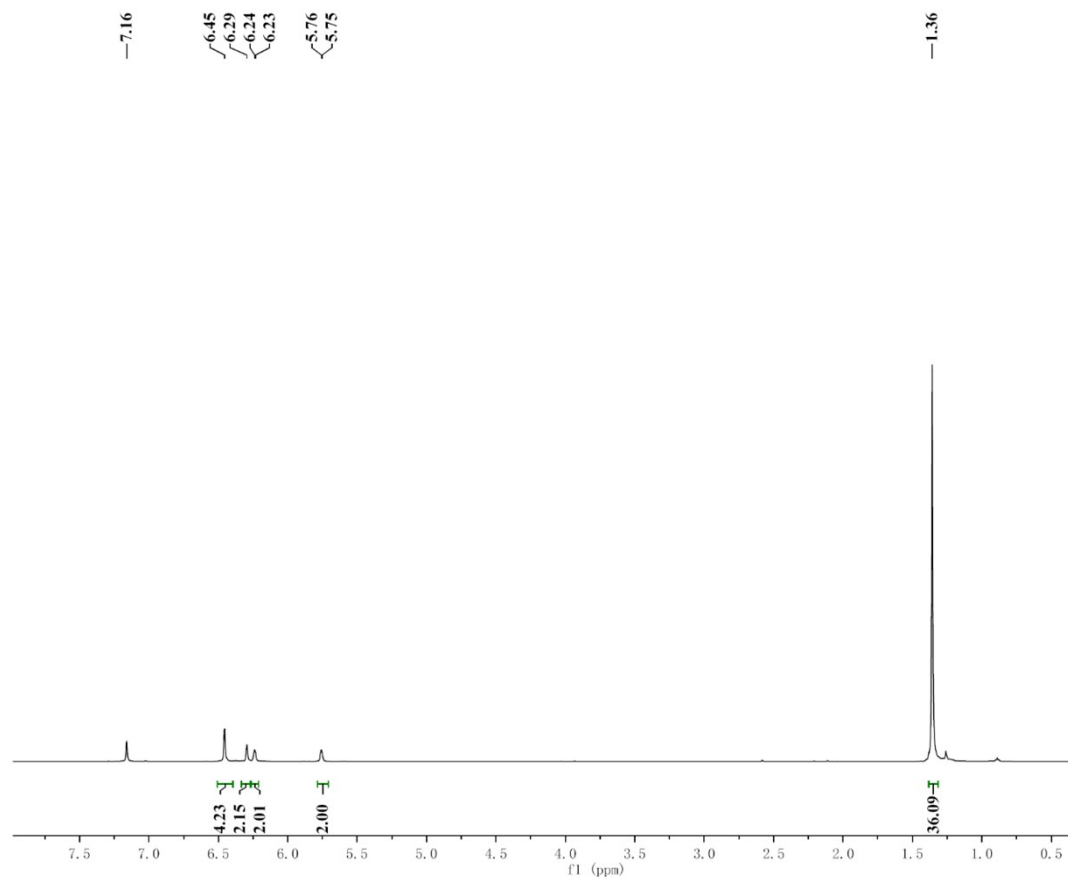


Fig. S14 ^1H NMR Spectrum of **9**

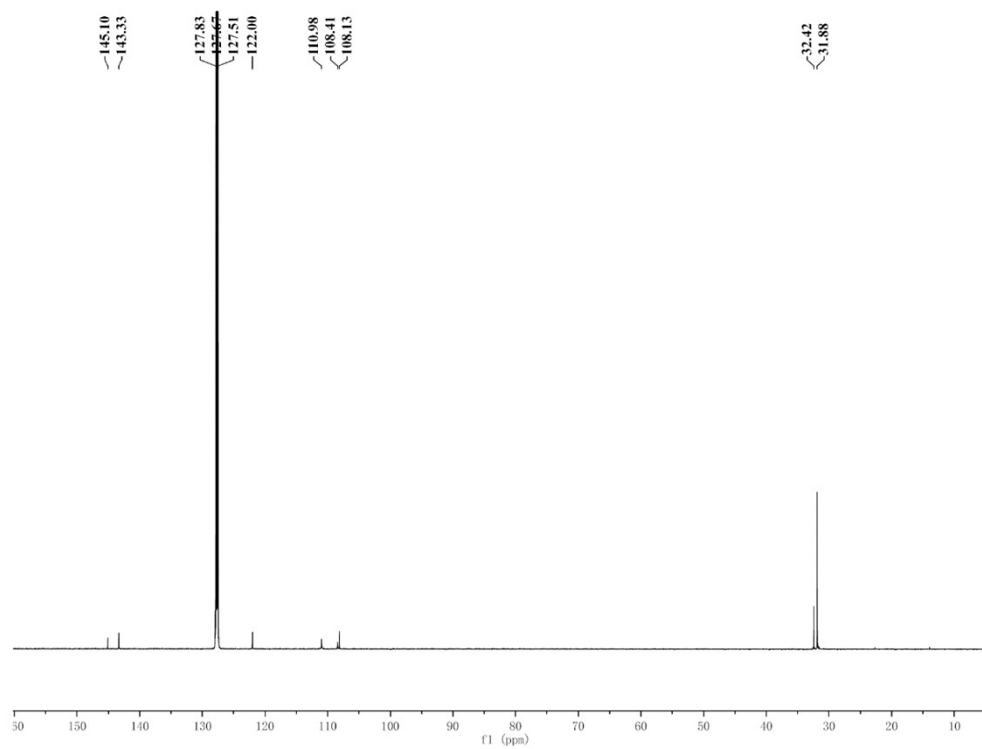


Fig. S15 ^{13}C NMR Spectrum of **9**

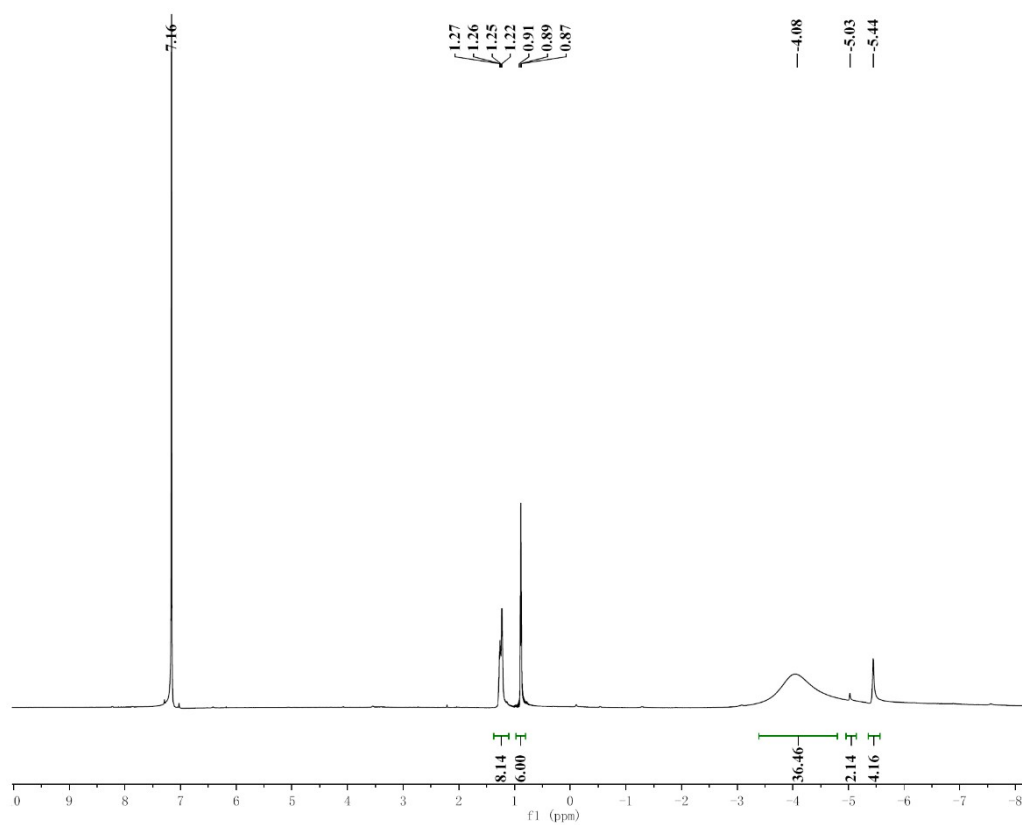


Fig. S16 ^1H NMR Spectrum of **10**

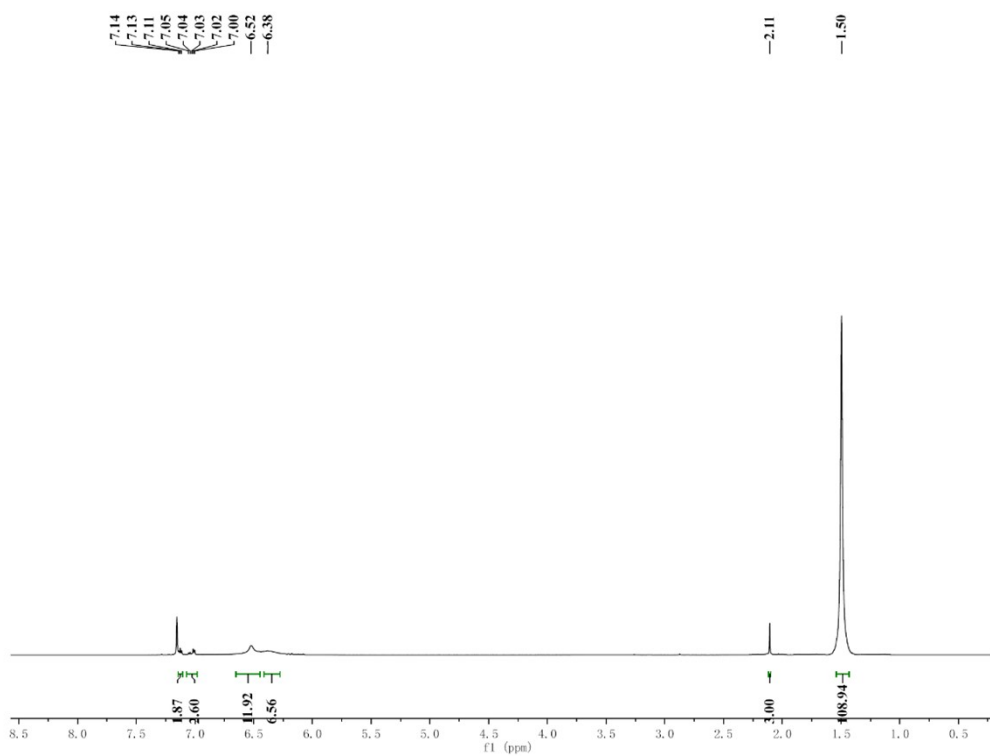


Fig. S17 ^1H NMR Spectrum of **11**

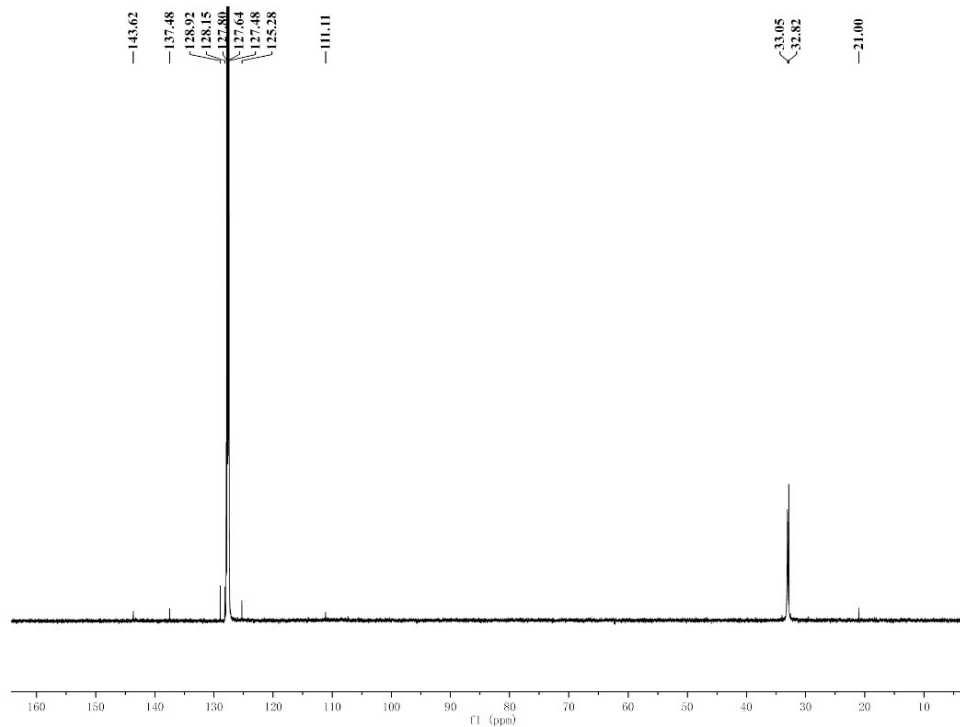


Fig. S18 ^{13}C NMR Spectrum of **11**

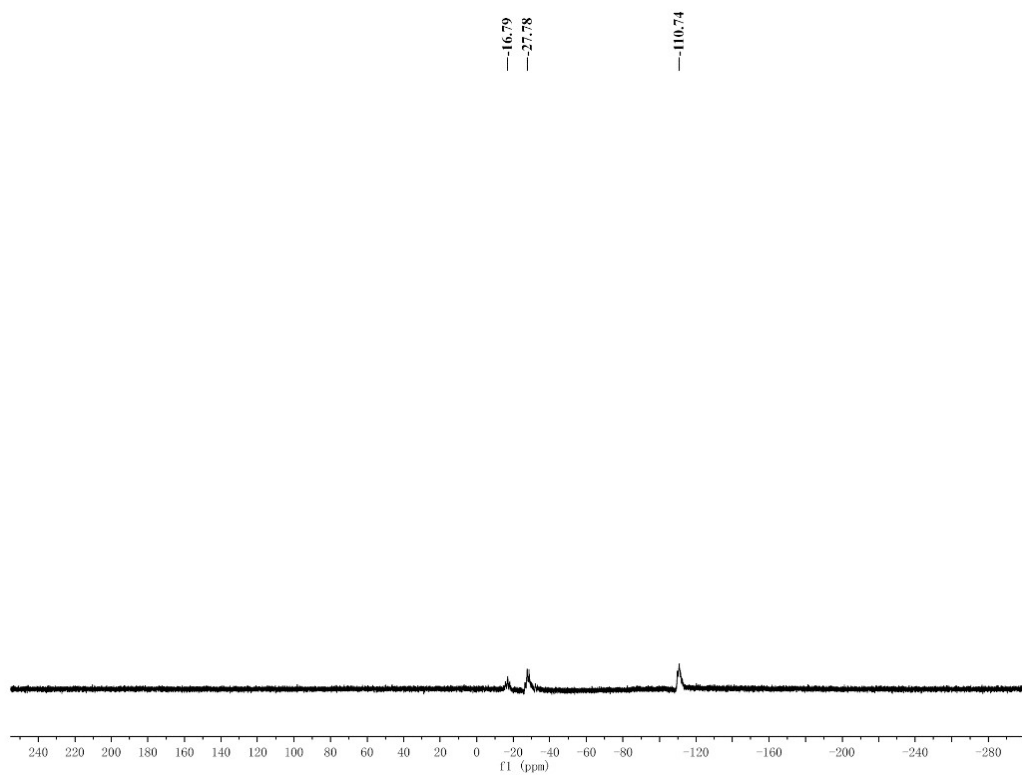


Fig. S19 ^{31}P NMR Spectrum of **11** (-60°C , 243 MHz, $\text{C}_4\text{D}_8\text{O}$)

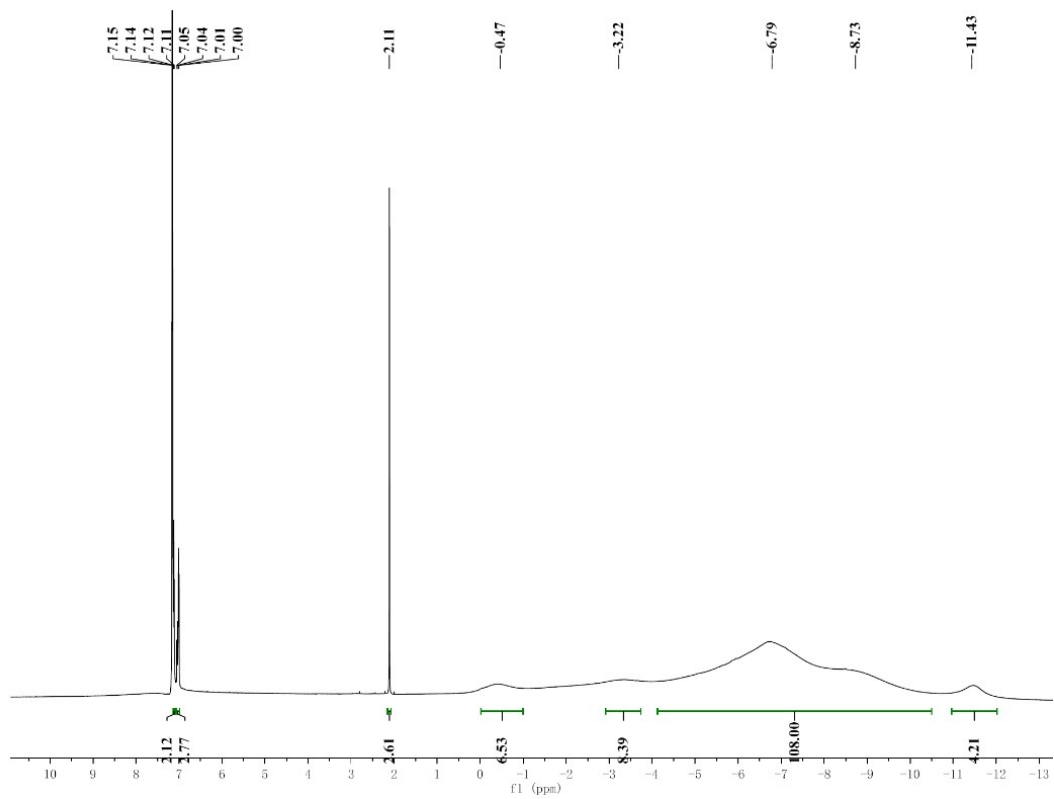


Fig. S20 ^1H NMR Spectrum of **12**

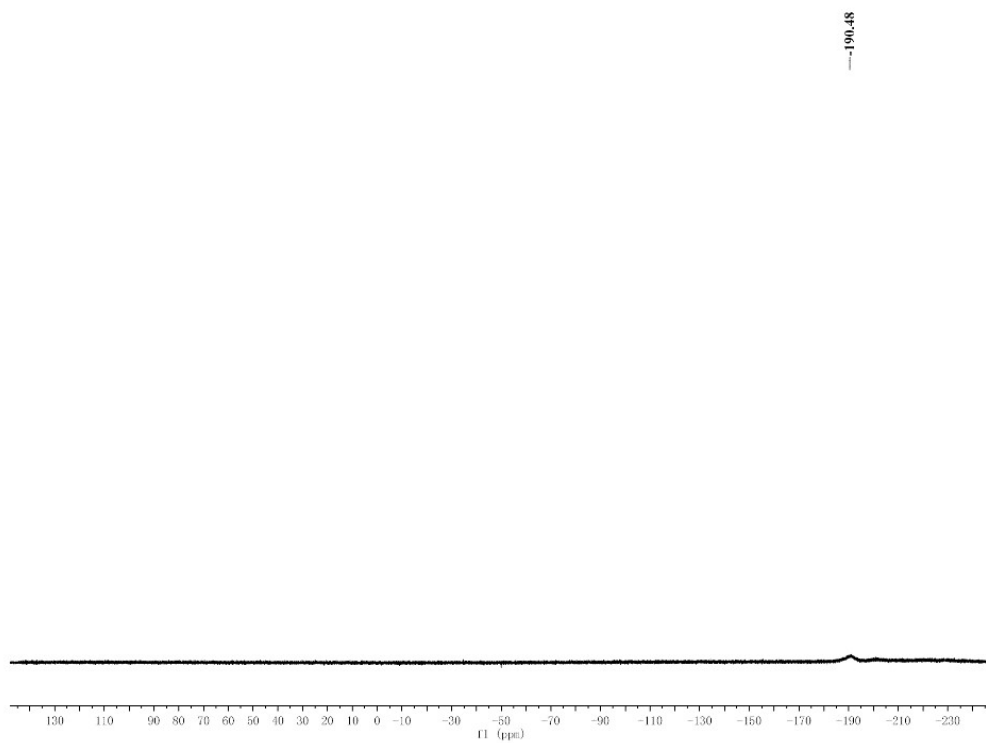


Fig. 21 ^{31}P NMR Spectrum of **12** (25°C, 243 MHz, C_6D_6)