Supplementary Material for:

A synthetic cycle for iminophosphorane synthesis involving directly intermolecular N=P bond formation on N_2-derived molybdenum nitride

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General considerations: NMR spectra were measured on a Bruker 400 MHz spectrometer. ^{31}P chemical shifts were referenced to a phosphoric acid external standard at 25°C. IR spectra were recorded on IRTracer-100 from SHIMADZU. MALDI-TOF measurements were performed on a Bruker ultrafleXtreme equipped with a 355 nm nitrogen laser. HRMS measurements were performed on a Synapt G2-Si HDMS from Waters. EA was measured on UNICUBE from ELEMENTAR. CV spectra were recorded on a CHI660E electrochemical workstation, in a 0.1 M [^{n}Bu$_4$N][OTf]-solution, with a glassy carbon working electrode, a Pt wire as counter electrode and a Ag wire as reference electrode. All potentials were referenced to the redox couple of ferrocene. Reactions were carried out in a glovebox under N_2 unless stated. Sodium metals were washed with hexane and then with THF, and were stored in the glovebox. THF, THF-d_8, 2-MeTHF, toluene and Et_2O were distilled from sodium and other extra dry solvents were commercially available and used without further purification. (PNCNP)Mo(N)I (**1**),[1] 2,6-lutidinium iodide (LutHI)[2] were prepared according to the corresponding

literature. Mercury was degassed before use. ^{n}BuLi, trimethylamine (NEt_3), PBu_3, PMe_3, $PPhMe_2$, PPh_2Me, PPh_3, I_2, Sn and chlorodiisopropylphosphine ($^{i}Pr_2PCl$), 15-crown-5, 1,10-phenanthroline (1,10-phen) were commercially available, and used as purchased. NMR yield was measured by integration vs an internal standard, PPh_3, in a capillary.

X-Ray diffraction The crystal data of complex **2a**, **2b, 3b** was collected using MoKα radiation (wavelength = 0.71073 Å) on Bruker Smart APEXII diffractometer. The crystal data of complexes **2c**, **4**, **6** were collected using CuKα radiation (wavelength = 1.54178 Å) on XtaLAB Synergy-R HyPix diffractometer. Crystals of **2a**, **2b, 4** and **6** were mounted in inert oil and crystal structure determinations were effected at low temperature. Crystals of **2c** and **3b** were effected at ambient temperature. An empirical absorption correction with SADABS was applied.[3] The structures were solved using intrinsic phasing method (ShelXT)[4] and refined using the least-squares method on F^2 (ShelXL).[5] All non-H atoms were refined with anisotropic displacement parameters. X-ray crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/) with reference numbers: 2255256 (**2a**), 2255257 (**2b**), 2255258 (**2c**), 2255259 (**3b**), 2255260 (**4**), 2255261 (**6**).

Synthesis of [(PNCNP)Mo(N=PBu$_3$)I]I (2a)

A mixture of PBu_3 (23 μL, 0.093 mmol) and I_2 (11.7 mg, 0.046 mmol) was added dropwise to (PNCNP)Mo(N)I (**1**) (54 mg, 0.093 mmol) in DCM (~5 mL), affording a deep red solution immediately. After overnight at room temperature, the formation of **2a** was observed by *in situ* NMR of the solution. NMR yield: 69%. Solvent was removed under vacuum, the oily product was washed with toluene and 1,4-dioxane. Red crystals of **2a** were obtained by diffusion of *n*-hexane into its DCM solution. Isolated yield: 46.1 mg, 50%. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.08 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, Ar-$H^{PNCNP\ ligand}$), 6.50 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, Ar-$H^{PNCNP\ ligand}$), 6.26 (s, 2H, N*H*), 2.82 (pseudo p, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, P(C*H*$(CH_3)_2)_2$), 2.52-2.46 (m, 2H, P(C*H*$(CH_3)_2)_2$),

1.81-1.74 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.66-1.55 (m, 12H, P(CH(CH_3)$_2$)$_2$), 1.29-1.21 (m, 18H, P(CH_2CH_2CH_2CH$_3$)$_3$), 0.83 (pseudo t, $^3J_{H\text{-}H}$ = 6.5 Hz, 9H, P(CH$_2$CH$_2$CH$_2$CH_3)$_3$), 0.75 (q, $^3J_{P\text{-}H}$ = 14.6 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz, 6H, P(CH(CH_3)$_2$)$_2$) ppm (Figure S1); ^{31}P{H} NMR (162 MHz, CD$_3$CN): δ = 140.6 (s, 2P), 57.8 (s, 1P) ppm (Figure S2). MS (MALDI-TOF, *m/z*): 780.2 [Cation]$^+$. Anal: calcd for $C_{30}H_{60}N_3I_2P_3Mo$: C 39.79, H 6.68, N 4.64; found: C 39.78, H 6.74, N 4.64.

Synthesis of [(PNCNP)Mo(N=PPhMe$_2$)I]I (2b)

A mixture of PPhMe$_2$ (8.1 μL, 0.057 mmol) and I$_2$ (7.1 mg, 0.028 mmol) was added dropwise to the DCM (~4 mL) solution of (PNCNP)Mo(N)I (**1**) (33 mg, 0.057 mmol), producing a red precipitate immediately. After overnight, the supernatant was removed, and the red powder of [(PNCNP)Mo(N=PPhMe$_2$)I]I (**2b**) was washed with Et$_2$O and then dried. Isolated yield: 27.4 mg, 57%. Single crystals of complex **2b** suitable for X-ray diffraction were obtained by vapor diffusion of *n*-hexane into its DCM solution at room temperature. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 7.69-7.65 (m, 1H, CH^{Ph}), 7.55-7.46 (m, 4H, CH^{Ph}), 7.08 (t, $^3J_{H\text{-}H}$ = 7.9 Hz, 1H, Ar-$H^{PNCNP\ ligand}$), 6.50 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, Ar-$H^{PNCNP\ ligand}$), 6.02 (s, 2H, N*H*), 2.79-2.70 (m, 2H, P(C*H*(CH$_3$)$_2$)$_2$), 2.13-2.03 (m, 2H, P(C*H*(CH$_3$)$_2$)$_2$), 2.05 (d, $^2J_{P\text{-}H}$ = 13.7 Hz, 6H, P(CH_3)$_2$), 1.36-1.24 (m, 18H, P(CH(CH_3)$_2$)$_2$), 1.03-0.98 (m, 6H, P(CH(CH_3)$_2$)$_2$) ppm (Figure S3); ^{31}P{H} NMR (162 MHz, CD$_3$CN): δ = 136.8 (s, 2P), 38.2 (s, 1P) ppm (Figure S4). MS (MALDI-TOF, *m/z*): 716.1 [Cation]$^+$. Anal: calcd for $C_{26}H_{44}N_3I_2P_3Mo$: C 37.12, H 5.27, N 4.99; found: C 37.06, H 5.29, N 4.99.

Synthesis of [(PNCNP)Mo(N=PPh$_2$Me)I]I (2c)

Following the procedure of complex **2a**, complex **2c** was synthesized by the reaction of PPh$_2$Me (17 μL, 0.093 mmol), I$_2$ (12 mg, 0.046 mmol) and (PNCNP)Mo(N)I (**1**) (54 mg, 0.093 mmol) in DCM (~5 mL). NMR yield: 60%. Single crystals of complex **2c** suitable for X-ray diffraction were obtained by diffusion *n*-hexane into DCM solution at room temperature. Isolated yield: 26.3 mg, 31%. ^{1}H NMR (400 MHz, CD$_3$CN): δ =

7.70 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 1H, CH^{Ph}), 7.70 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 1H, CH^{Ph}), 7.51 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, CH^{Ph}), 7.50 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, CH^{Ph}), 7.45 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, CH^{Ph}), 7.41 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, CH^{Ph}), 7.14 (t, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 1H, Ar-$H^{PNCNP\ ligand}$), 6.56 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, Ar-$H^{PNCNP\ ligand}$), 6.10 (s, 2H, N*H*), 2.78-2.70 (m, 2H, PC*H*(CH_3)$_2$), 2.39 (d, $^{2}J_{P\text{-}H}$ = 13.4 Hz, 3H, PCH_3), 1.95-1.85 (m, 2H, PC*H*(CH_3)$_2$), 1.26 (q, $^{3}J_{P\text{-}H}$ = 14.4 Hz, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 6H, P(CH(CH_3)$_2$)$_2$), 1.19-1.09 (m, 12H, P(CH(CH_3)$_2$)$_2$), 0.91 (q, $^{3}J_{P\text{-}H}$ = 14.4 Hz, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 6H, P(CH(CH_3)$_2$)$_2$)) ppm (Figure S5); ^{31}P{H} NMR (162 MHz, CD_3CN): δ = 137.3 (s, 2P), 32.2 (s, 1P) ppm (Figure S6). MS (MALDI-TOF, *m/z*): 778.1 [Cation]$^{+}$. Anal: calcd for $C_{31}H_{46}N_3I_2P_3Mo$: C 41.21, H 5.13, N 4.65; found: C 41.25, H 5.23, N 4.85.

Synthesis of [(PNCNP)Mo(N=PMe$_3$)I]I (2d)

Following the procedure of complex **2a**, complex **2d** was synthesized by the reaction of PMe_3 (20.6 μL, 0.20 mmol), I_2 (25.4 mg, 0.10 mmol) and (PNCNP)Mo(N)I (**1**) (116 mg, 0.20 mmol) in DCM (~6 mL). Crystals of complex **2d** were obtained by diffusion *n*-hexane into DCM solution at room temperature. Isolated yield: 73.6 mg, 47%. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.04 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1H, Ar-$H^{PNCNP\ ligand}$), 6.47 (d, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 2H, Ar-$H^{PNCNP\ ligand}$), 5.98 (s, 2H, N*H*), 2.80 (br s, 2H, PC*H*(CH_3)$_2$), 2.47 (br s, 2H, PC*H*(CH_3)$_2$), 1.80 (d, $^{2}J_{P\text{-}H}$ = 13.8 Hz, 9H, P(CH_3)$_3$), 1.50-1.45 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.42-1.37 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.30-1.24 (m, 6H, P(CH(CH_3)$_2$)$_2$), 1.06-1.00 (m, 6H, P(CH(CH_3)$_2$)$_2$) ppm (Figure S7); ^{31}P{H} NMR (162 MHz, CD_3CN): δ = 137.0 (s, 2P), 44.6 (s, 1P) ppm (Figure S8). MS (MALDI-TOF, *m/z*): 654.1 [Cation]$^{+}$. Anal: calcd for $C_{21}H_{42}N_3I_2P_3Mo$: C 32.37, H 5.43, N 5.39; found: C 32.29, H 5.35, N 5.53.

Synthesis of [Me$_2$PhP=NH$_2$]I (3b) and (PNCNP)Mo(CO)$_3$I (4) from 2b

Sn (18 mg, 0.15 mmol) powder and LutHI (14 mg, 0.06 mmol) were added to the suspension of [(PNCNP)Mo(N=PPhMe$_2$)I]I (**2b**) (25 mg, 0.03 mmol) in DCM (2 mL) at room temperature. CO was bubbled into the suspension then the mixture was stirred

vigorously for 6 h, resulting in a dark red clear solution. Formation of [$Me_2PhP{=}NH_2$]I (**3b**) and (PNCNP)Mo(CO)$_3$I (**4**) were observed and quantified by $^{31}P\{H\}$ NMR in 64% yield and 85% yield respectively. After the solvent was removed under vacuum, the residues were extracted with toluene. The toluene extraction containing complex **4** was taken to dryness. Crystals of **4** were obtained by diffusion of *n*-hexane into its DCM solution. To the above residues that insoluble in toluene, DCM and 1,10-phen (0.03 mmol, 5.4 mg) was added. Red precipitate was separated and the filtrate was dried under vacuum to give **3b** as an oil which could be recrystallized in hot toluene.

(PNCNP)Mo(CO)$_3$I (4):

Isolated yield: 5.8 mg, 30%. ^1H NMR (400 MHz, THF-d_8): δ = 6.60 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, Ar-$H^{PNCNP\ ligand}$), 6.18 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, Ar-$H^{PNCNP\ ligand}$), 5.61 (s, 2H, N*H*), 2.74-2.65 (m, 4H, P(C*H*(CH$_3$)$_2$)$_2$), 1.35 (dd, $^3J_{P\text{-}H}$ = 15.6 Hz, $^3J_{H\text{-}H}$ = 7.1 Hz, 12H, P(CH(C*H*$_3$)$_2$)$_2$), 1.24 (dd, $^3J_{P\text{-}H}$ = 13.0 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz, 12H, P(CH(C*H*$_3$)$_2$)$_2$) ppm (Figure S9); $^{31}P\{H\}$ NMR (162 MHz, THF-d_8): δ = 120.7 ppm (Figure S10). IR (in DCM): 2018, 1948, 1913 cm^{-1} (ν_{CO}). Anal: calcd for $C_{21}H_{33}N_2O_3IMoP_2$: C 39.03, H 5.15, N 4.33; found: C 38.91, H 5.11, N 4.32.

[$Me_2PhP{=}NH_2$]I (3b):

Isolated yiled: 4.7 mg, 56%. ^1H NMR (400 MHz, CD_3CN): δ = 7.95-7.89 (m, 2H, CH^{Ph}), 7.79-7.74 (m, 1H, CH^{Ph}), 7.70-7.64 (m, 2H, CH^{Ph}), 4.43 (s, 2H, NH_2), 2.17 (d, $^2J_{P\text{-}H}$ = 14.4 Hz, 6H, P(CH_3)$_2$) ppm (Figure S11); $^{13}C\{H\}$ NMR (100.63 MHz, CD_3CN): δ = 135.2 (s, PC^{Ph}), 131.8 (d, $^3J_{P\text{-}C}$ = 11.6 Hz, PC^{Ph}), 130.4 (d, $^2J_{P\text{-}C}$ = 13.3 Hz, PC^{Ph}), 126.6 (d, $^1J_{P\text{-}C}$ = 97.5 Hz, PC^{Ph}), 13.51 (d, $^1J_{P\text{-}C}$ = 68.2 Hz, P(*C*H$_3$)$_2$) ppm (Figure S12); $^{31}P\{H\}$ NMR (162 MHz, CD_3CN): δ = 45.5 (s, 1P) ppm (Figure S13). HRMS (ESI, *m/z*): calcd for $C_8H_{13}NP$: 154.0786 [Cation]$^+$; found: 154.0778. Anal: calcd for $C_8H_{13}NIP$: C 34.19, H 4.66, N 4.98; found: C 34.37, H 4.62, N 4.73.

Synthesis of [$Bu_3P{=}NH_2$]I (3a) from 2a

Sn (9 mg, 0.075 mmol) and LutHI (7 mg, 0.03 mmol) were added into the DCM (1 mL) solution of [(PNCNP)Mo(N=PBu$_3$)I]I (**2a**) (14 mg, 0.015 mmol) at room temperature.

CO was bubbled into the solution then the mixture was stirred vigorously for 6 h. Formation of [$Bu_3P{=}NH_2$]I (**3a**) and (PNCNP)Mo$(CO)_3$I (**4**) were observed and quantified by $^{31}P\{H\}$ NMR in 50% and 88% yield respectively. After the solvent was removed under vacuum, the residues were extracted with toluene. [$Bu_3P{=}NH_2$]I (**3a**) was obtained from column chromatography on neutral Al_2O_3 with MeOH as eluent, as colorless oil. Isolated yield: 2.1 mg, 43%. ^1H NMR (400 MHz, CD_3CN): δ = 4.09 (s, 2H, NH_2), 2.18-2.11 (m, 6H, P(C$H_2$$(CH_2)_2CH_3)_3$), 1.61-1.51 (m, 6H, P($CH_2CH_2$$CH_2CH_3)_3$), 1.44 (sextet, $^3J_{H\text{-}H}$ = 7.2 Hz, 6H, P($(CH_2)_2$C$H_2$$CH_3)_3$), 0.93 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 9H, P($(CH_2)_3$C$H_3)_3$) ppm (Figure S14); $^{13}C\{H\}$ NMR (100.63 MHz, CD_3CN): δ = 24.2 (d, $^3J_{P\text{-}C}$ = 16.1 Hz, P($(CH_2)_2$C$H_2$$CH_3)_3$), 23.6 (d, $^1J_{P\text{-}C}$ = 59.5 Hz, P(C$H_2$$(CH_2)_2CH_3)_3$), 23.5 (d, $^2J_{P\text{-}C}$ = 3.9 Hz, P(CH_2C$H_2$$CH_2CH_3)_3$), 13.6 (s, P($(CH_2)_3CH_3)_3$) ppm (Figure S15); $^{31}P\{H\}$ NMR (162 MHz, CD_3CN): δ = 58.0 (s, 1P) ppm (Figure S16). HRMS (ESI, *m/z*): calcd for $C_{12}H_{29}NP$: 218.2038 $[Cation]^+$; found: 218.2029. Anal: calcd for $C_{12}H_{29}NIP$: C 41.75, H 8.47, N 4.06; found: C 41.56, H 8.39, N 4.03.

Synthesis of [$MePh_2P{=}NH_2$]I (3c) from 2c

Sn (18 mg, 0.15 mmol) and LutHI (14 mg, 0.06 mmol) were added into the DCM (2 mL) solution of[(PNCNP)Mo(N=PPh_2Me)I]I (**2c**) (27 mg, 0.03 mmol) at room temperature. CO was bubbled into the solution then the mixture was stirred vigorously for 6 h. Formation of [$MePh_2P{=}NH_2$]I (**3c**) and (PNCNP)Mo$(CO)_3$I (**4**) were observed and quantified by $^{31}P\{H\}$ NMR in 64% and 86% yield respectively. Following the work-up procedure of **3b**, [$MePh_2P{=}NH_2$]I (**3c**) was isolated as white powder. Isolated yield: 6.0 mg, 58%. ^1H NMR (400 MHz, CD_3CN): δ = 7.85-7.79 (m, 6H, CH^{Ph}), 7.70-7.65 (m, 4H, CH^{Ph}), 4.72 (s, 2H, NH_2), 2.47 (d, $^2J_{P\text{-}H}$ = 14.2 Hz, 3H, PCH_3) ppm (Figure S17); $^{13}C\{H\}$ NMR (100.63 MHz, CD_3CN): δ = 135.6 (d, $^4J_{P\text{-}C}$ = 3.1 Hz, PC^{Ph}), 132.9 (d, $^3J_{P\text{-}C}$ = 11.6 Hz, PC^{Ph}), 130.5 (d, $^2J_{P\text{-}C}$ = 13.4 Hz, PC^{Ph}), 124.9 (d, $^1J_{P\text{-}C}$ = 101.3 Hz, PC^{Ph}), 12.8 (d, $^1J_{P\text{-}C}$ = 69.7 Hz, PCH_3) ppm (Figure S18); $^{31}P\{H\}$ NMR (162 MHz, CD_3CN): δ = 40.4 (s, 1P) ppm (Figure S19). HRMS (ESI, *m/z*): calcd for $C_{13}H_{15}NP$:

216.0942 [Cation]$^+$; found: 216.0935. Anal: calcd for $C_{13}H_{15}NIP$: C 45.50, H 4.41, N 4.08; found: C 45.51, H 4.43, N 4.07.

Synthesis of [$Me_3P=NH_2$]I (3d)[6] from 2d

Sn (18 mg, 0.15 mmol) and LutHI (14 mg, 0.06 mmol) were added into the DCM (2 mL) solution of[(PNCNP)Mo(N=PMe_3)I]I (**2d**) (23 mg, 0.03 mmol) at room temperature. CO was bubbled into the solution then the mixture was stirred vigorously for 6 h. The formation of (PNCNP)Mo$(CO)_3$I (**4**) were observed and quantified by $^{31}P\{H\}$ NMR in 87% yield. Following the work-up procedure of **3b**, [$Me_3P=NH_2$]I (**3d**) was isolated as white powder. Isolated yield: 5.5 mg, 84%. ^1H NMR (400 MHz, CD_3CN): δ = 3.99 (s, 2H, NH_2), 1.89 (d, $^2J_{P\text{-}H}$ = 14.6 Hz, 9H, P(CH_3)$_3$) ppm (Figure S20); $^{13}C\{H\}$ NMR (100.63 MHz, CD_3CN): δ = 14.1 (d, $^1J_{P\text{-}C}$ = 66.1 Hz, P(CH$_3$)$_3$) ppm (Figure S21); $^{31}P\{H\}$ NMR (162 MHz, CD_3CN): δ = 51.9 (s, 1P) ppm (Figure S22). HRMS (ESI, *m/z*): calcd for $C_3H_{11}NP$: 92.0629 [Cation]$^+$; found: 92.0622.

Synthesis of (PNCNP)MoI_3 (5) from decarbonylation of 4

To the solution of (PNCNP)Mo$(CO)_3$I (**4**) (26 mg, 0.04 mmol) in Et_2O (8 mL) was added I_2 (10 mg, 0.04 mmol). The mixture was stirred for 5 min at room temperature. The resulted brown cloudy suspension was irradiated with LED (365 nm) under reduced pressure, affording dark purple precipitate within 5 min. The precipitate was collected and washed with Et_2O, then dried under vacuum. This powder of complex (PNCNP)MoI_3 (**5**) was essentially pure for both EA and further reaction. Crystals of **5** was obtained from concentrated DCM solution under -30 °C.[1] Isolated yield: 16.0 mg, 49%. MS (MALDI-TOF, *m/z*): 691.0 [M-I]$^+$. Anal: calcd for $C_{18}H_{33}I_3MoN_2P_2$: C 26.49, H 4.08, N 3.43; found: C 26.48, H 4.08, N 3.27.

Synthesis of [Na(15-crown-5)(THF)][(PNCNP)MoI_3] (6)

To a deep violet solution of (PNCNP)MoI_3 (**5**) (16 mg, 0.019 mmol) in 2-MeTHF (1 mL) at 0 °C was added 15-crown-5 (4 μL, 0.019 mmol) and freshly prepared sodium

amalgam (44 mg, 1 wt%, 0.019 mmol). The mixture was stirred vigorously for 30 min, producing a yellow precipitate and an orange-red supernatant. The precipitate was separated, washed with Et_2O and dried under vacuum. Isolated yield: 20 mg, 88%. Single crystals of complex **6** suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into the THF solution. MS (MALDI-TOF, *m/z*): 690.1 $[Anion\text{-}I]^+$. Anal: calcd for $C_{32}H_{61}I_3MoN_2NaO_6P_2$: C 33.97, H 5.43, N 2.48; found: C 33.88, H 5.49, N 2.30.

Synthesis of [(PNCNP)MoI]$_2$(μ-N$_2$) (7) from complex 6

To the 2-MeTHF suspension of complex **6** (11.3 mg, 0.01 mmol) was added freshly prepared sodium amalgam (23 mg, 1 wt%, 0.01 mmol). The mixture was stirred vigorously for 1 h at 18 °C, gradually forming a deep red solution. $^{31}P\{H\}$ NMR recorded in situ showed the production of the N_2 coordinated complex **7**[1] (53% based on complex **6**). $^{31}P\{H\}$ NMR (162 MHz, 2-MeTHF): δ = 131.7 (d, AB, $^2J_{P\text{-}P}$ = 124.8 Hz, 2P), 131.1 (d, AB, $^2J_{P\text{-}P}$ = 124.4 Hz, 2P) ppm. Single crystals of **7** could be obtained by diffusion of Et_2O into its 2-MeTHF solution.

References

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NMR spectra

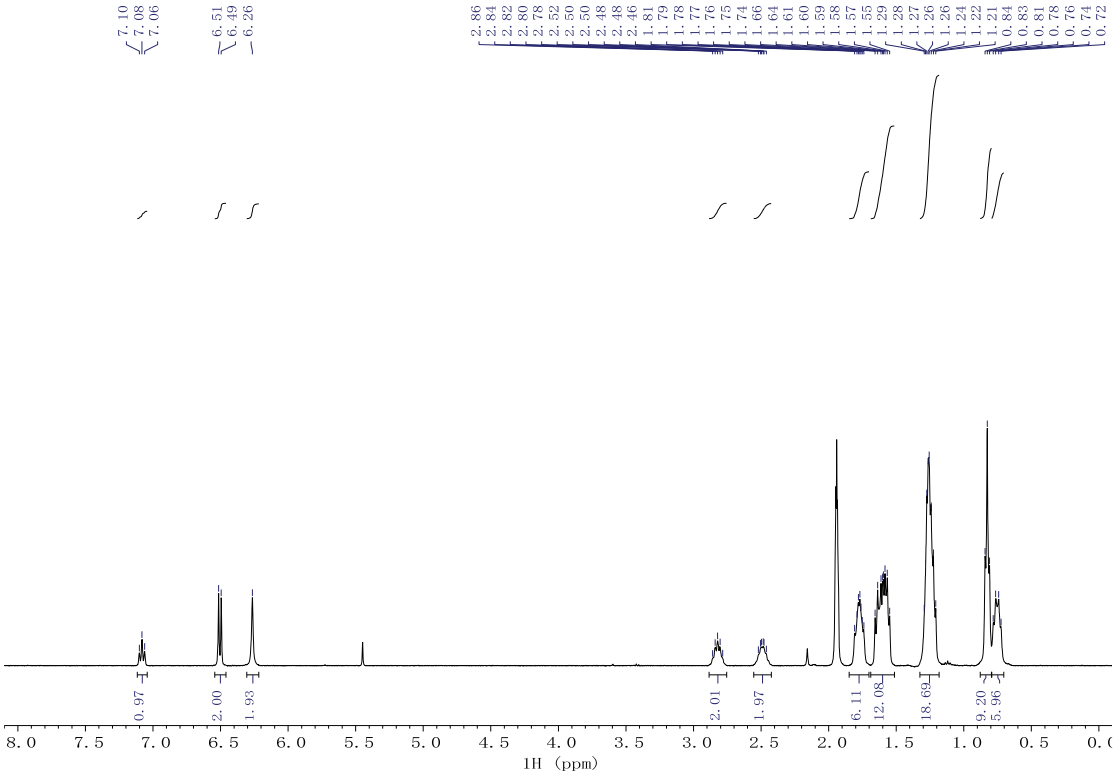


Figure S1. ^{1}H NMR spectrum of [(PNCNP)Mo(N=PBu$_3$)I]I (**2a**) in CD$_3$CN

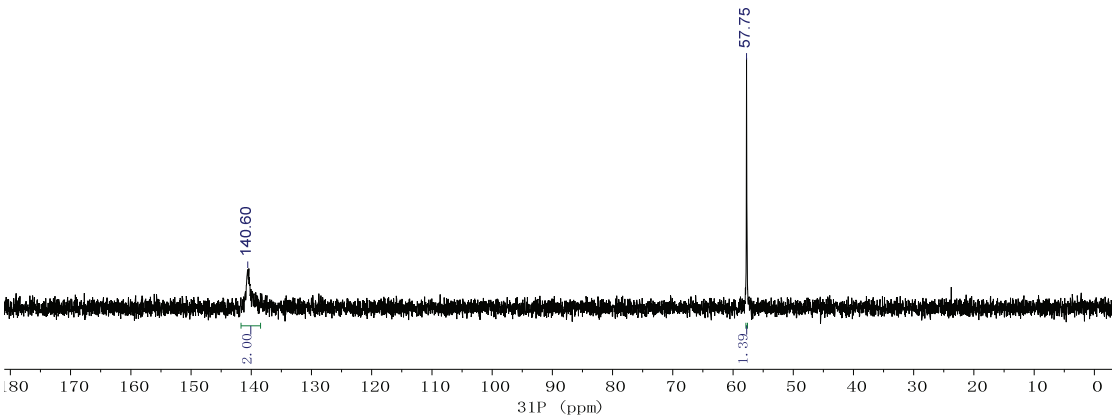


Figure S2. ^{31}P{H} NMR spectrum of [(PNCNP)Mo(N=PBu$_3$)I]I (**2a**) in CD$_3$CN

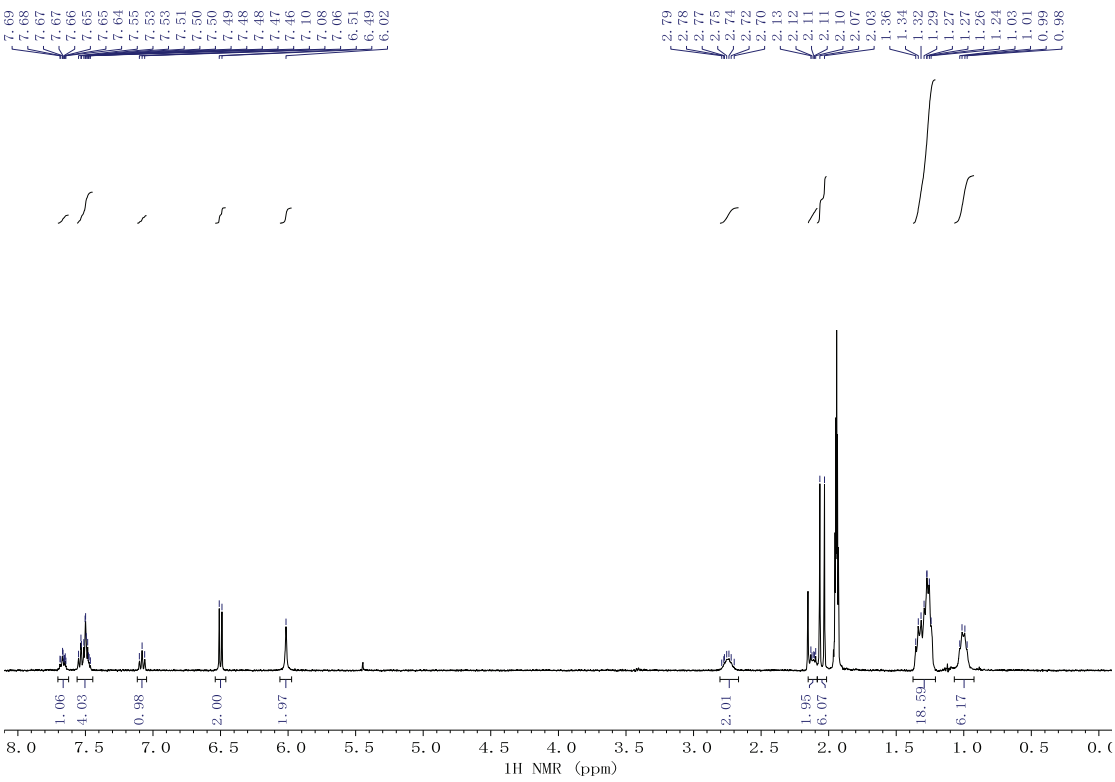


Figure S3. ^{1}H NMR spectrum of [(PNCNP)Mo(N=PPhMe$_2$)I]I (**2b**) in CD$_3$CN

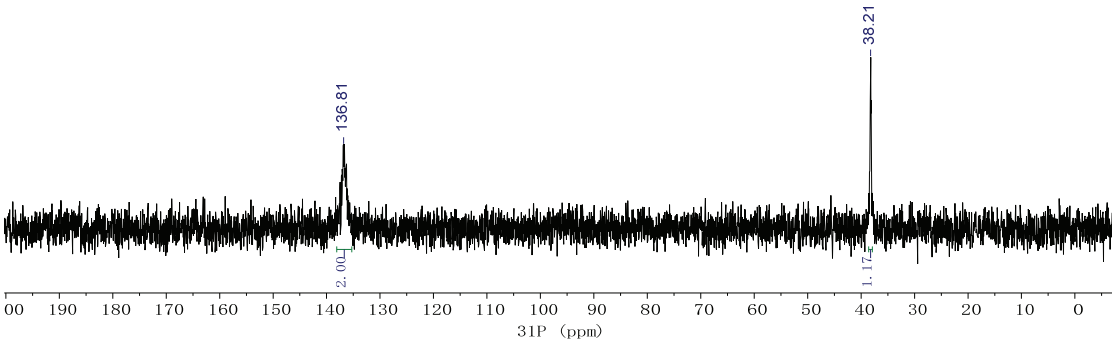


Figure S4. ^{31}P{H} NMR spectrum of [(PNCNP)Mo(N=PPhMe$_2$)I]I (**2b**) in CD$_3$CN

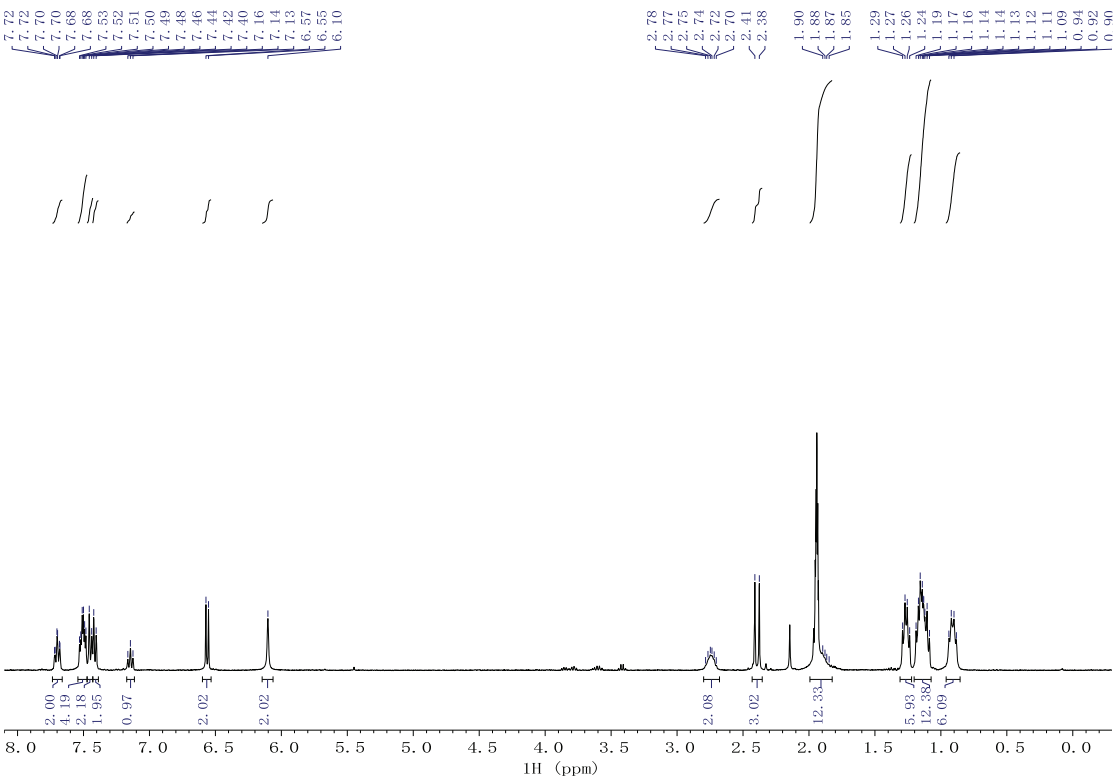


Figure S5. ^{1}H NMR spectrum of [(PNCNP)Mo(N=PPh$_2$Me)I]I (**2c**) in CD$_3$CN

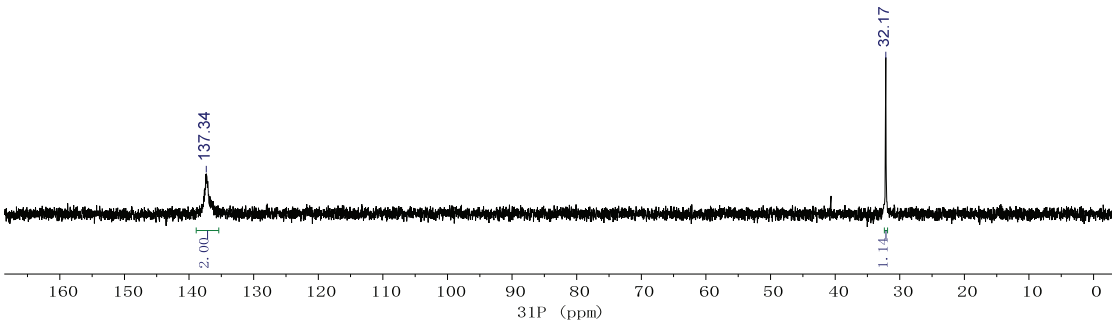


Figure S6. ^{31}P{H} NMR spectrum of [(PNCNP)Mo(N=PPh$_2$Me)I]I (**2c**) in CD$_3$CN

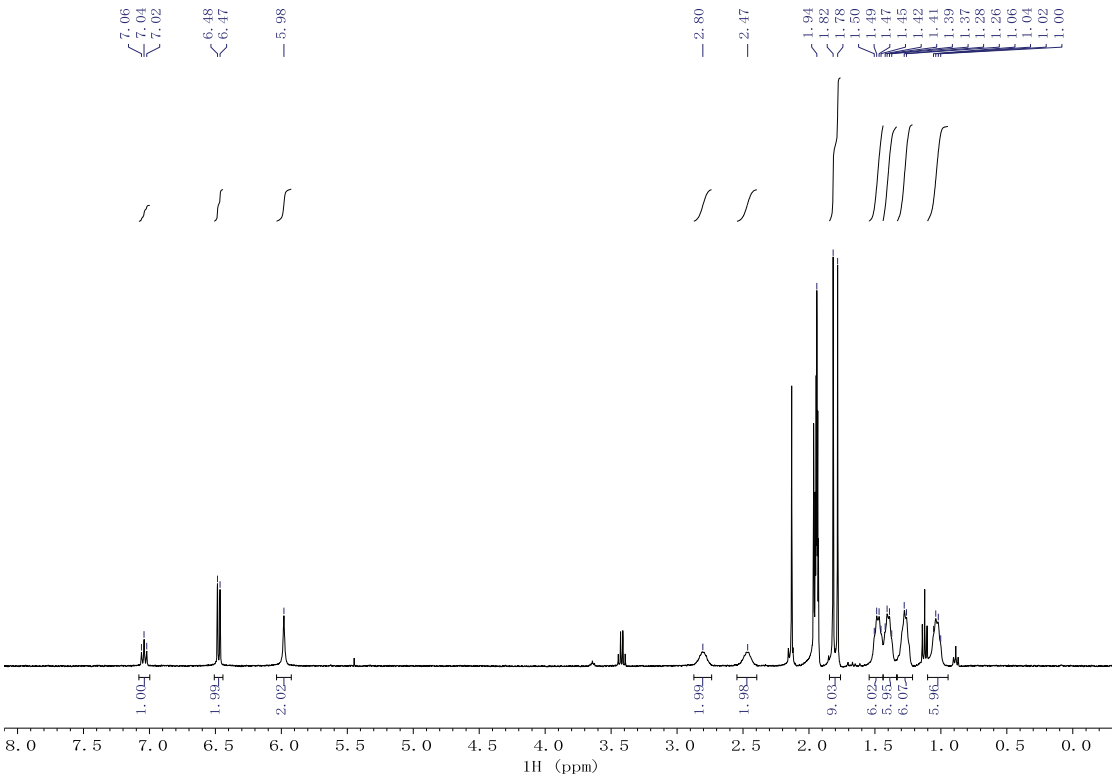


Figure S7. ^{1}H NMR spectrum of [(PNCNP)Mo(N=PMe$_3$)I]I (**2d**) in CD$_3$CN

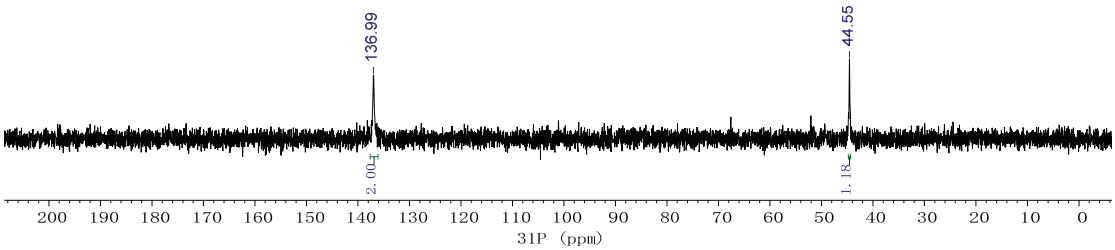


Figure S8. ^{31}P{H} NMR spectrum of [(PNCNP)Mo(N=PMe$_3$)I]I (**2d**) in CD$_3$CN

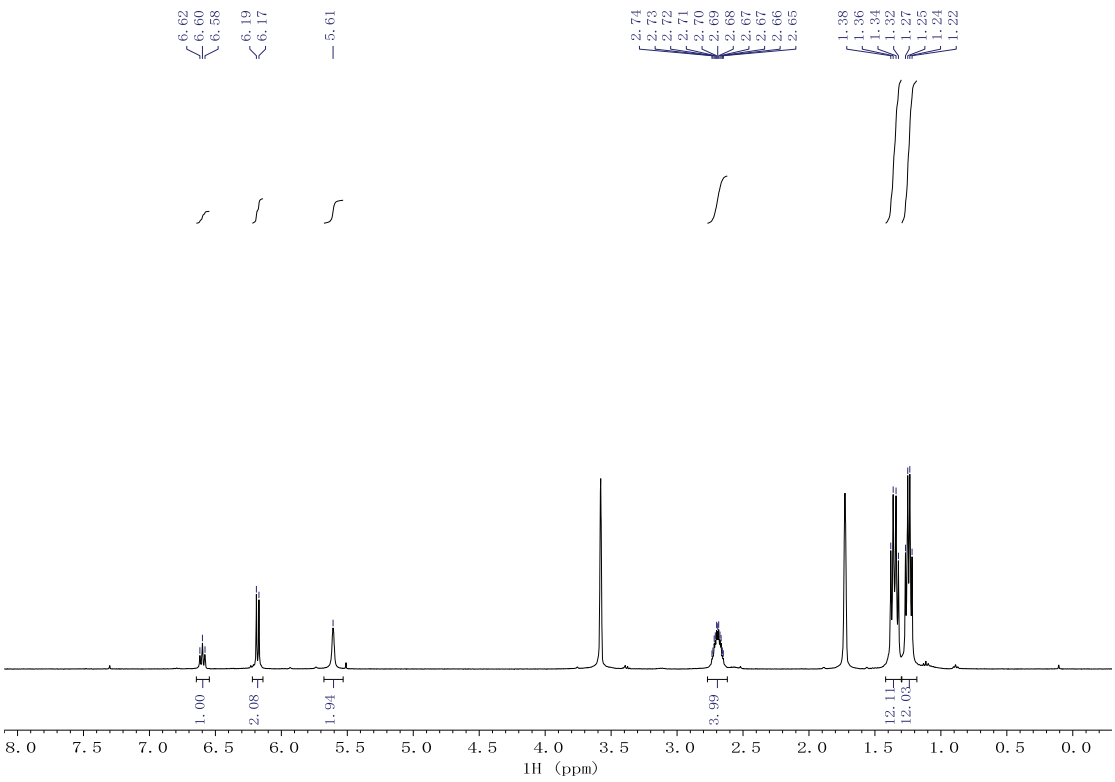


Figure S9. ^{1}H NMR spectrum of (PNCNP)Mo(CO)$_3$I (**4**) in THF-d_8

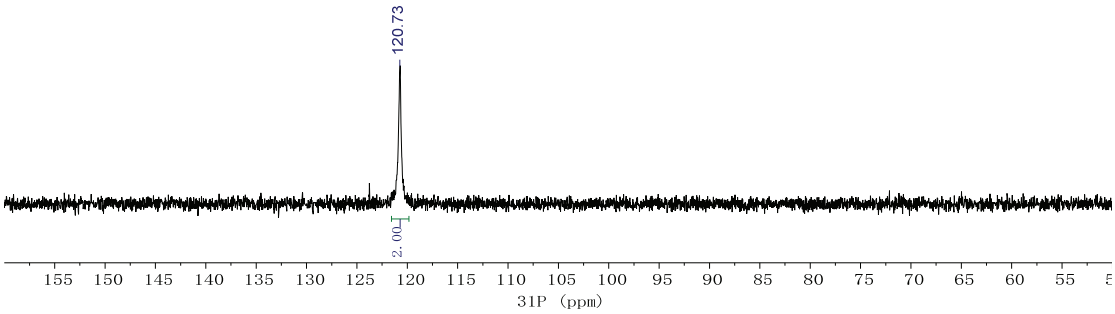


Figure S10. ^{31}P{H} NMR spectrum of (PNCNP)Mo(CO)$_3$I (**4**) in THF-d_8

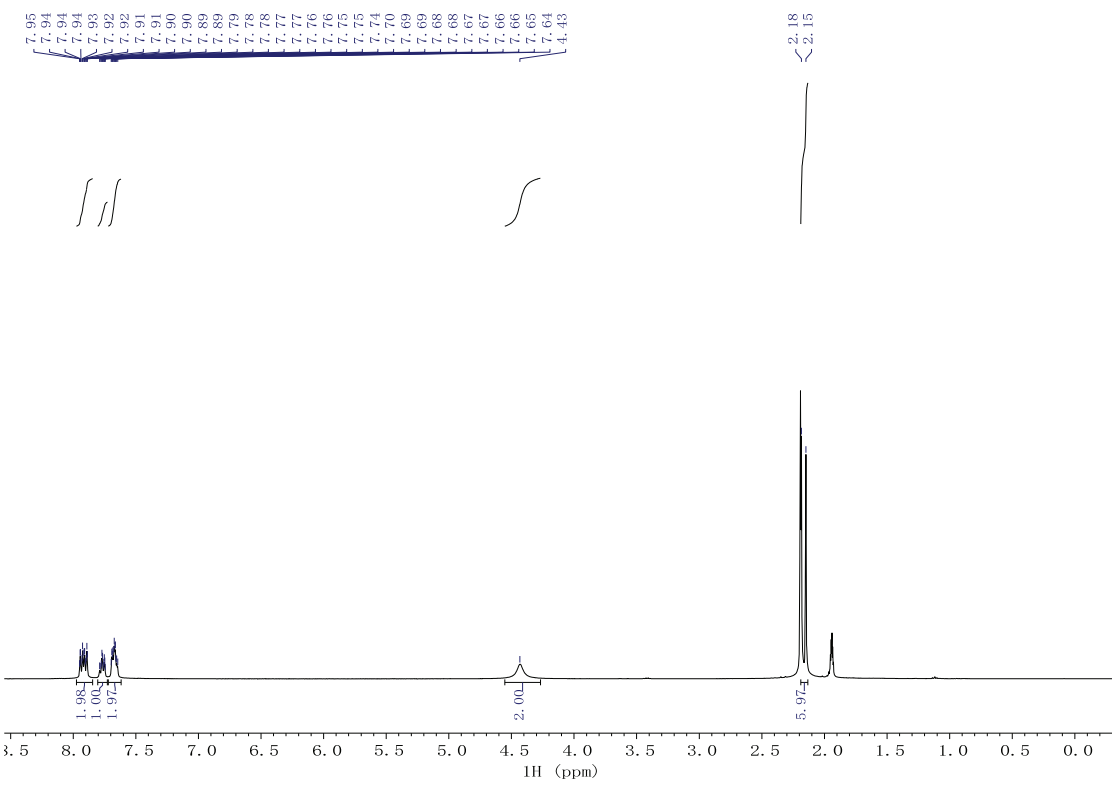


Figure S11. ^{1}H NMR spectrum of [$Me_2PhP{=}NH_2$]I (**3b**) in CD_3CN

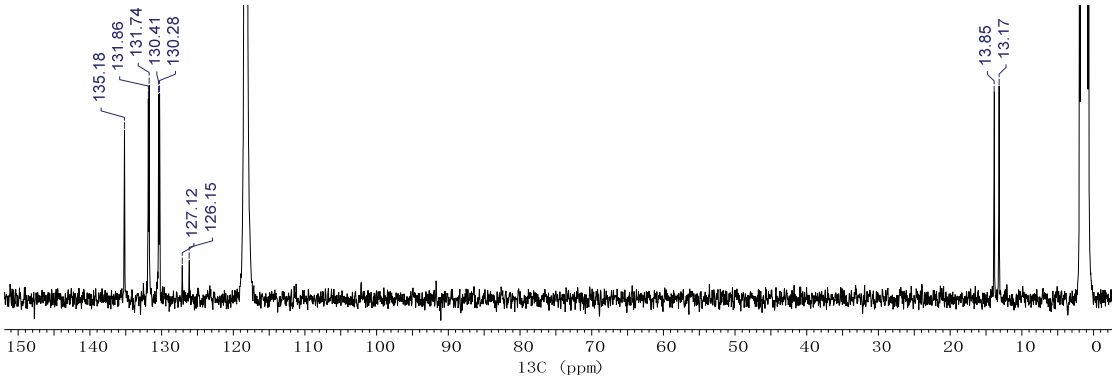


Figure S12. ^{13}C{H} NMR spectrum of [$Me_2PhP{=}NH_2$]I (**3b**) in CD_3CN

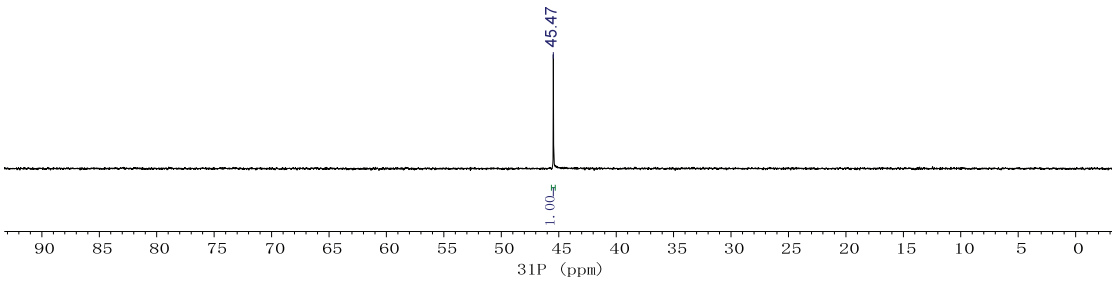


Figure S13. ^{31}P{H} NMR spectrum of [$Me_2PhP{=}NH_2$]I (**3b**) in CD_3CN

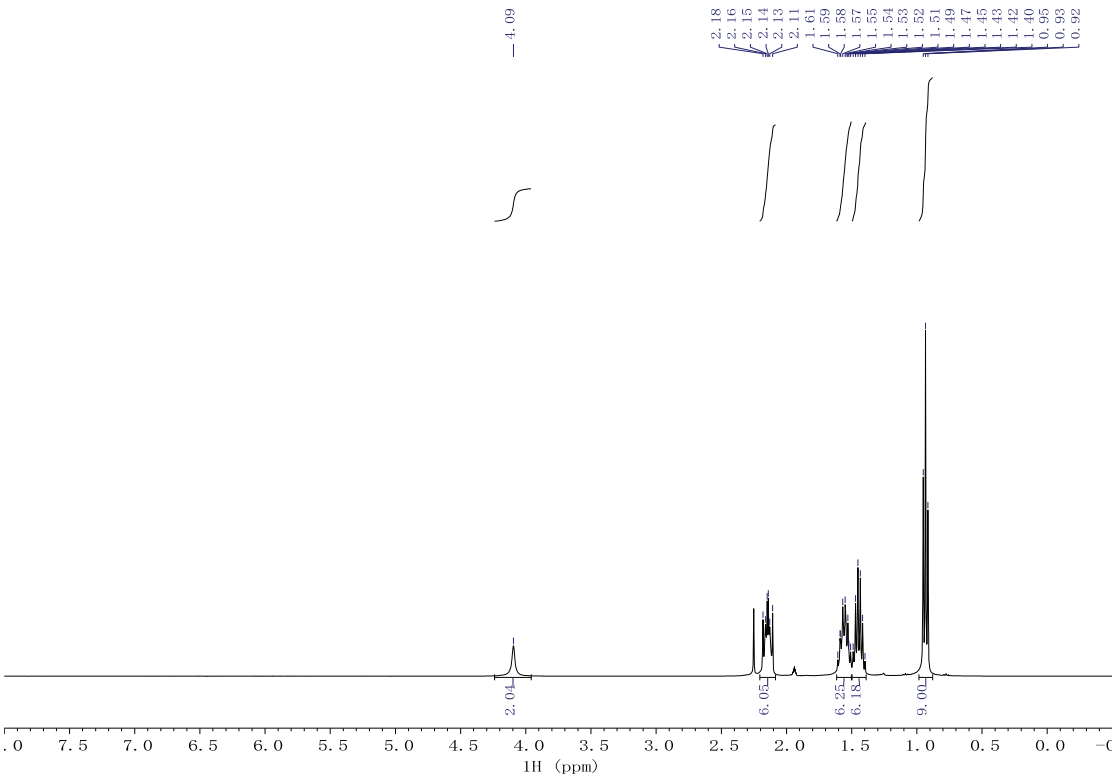


Figure S14. ^{1}H NMR spectrum of [$Bu_3P{=}NH_2$]I (**3a**) in CD_3CN

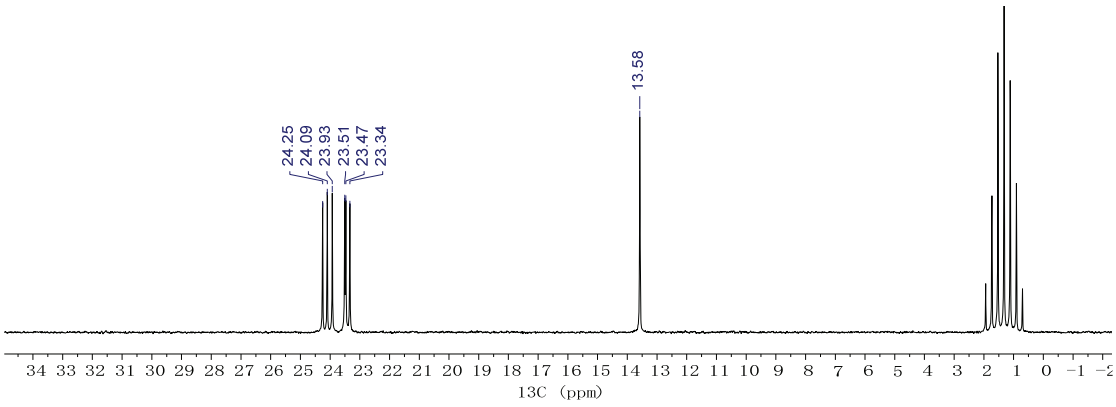


Figure S15. ^{13}C{H} NMR spectrum of [$Bu_3P{=}NH_2$]I (**3a**) in CD_3CN

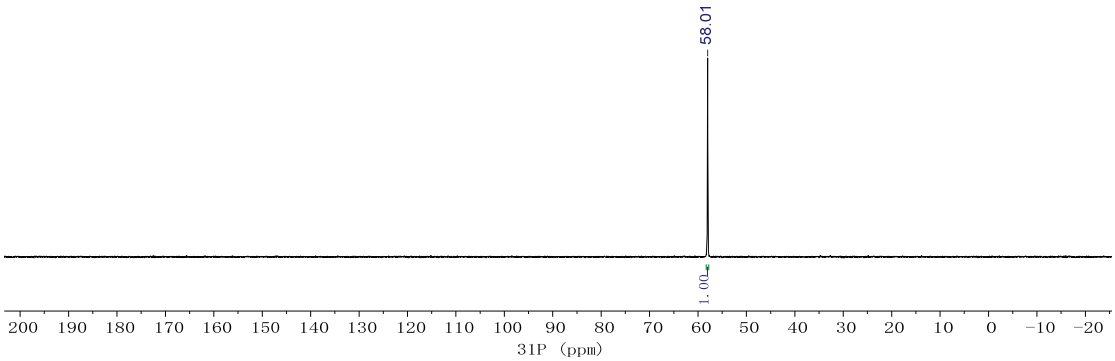


Figure S16. ^{31}P{H} NMR spectrum of [$Bu_3P{=}NH_2$]I (**3a**) in CD_3CN

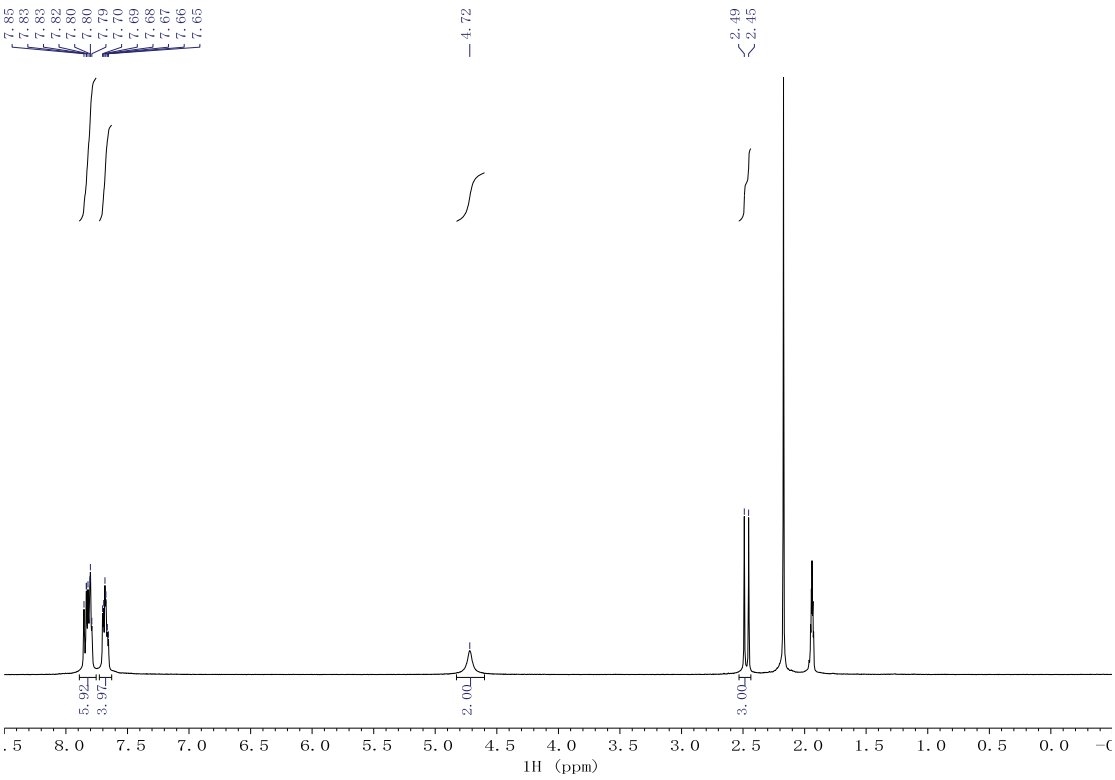


Figure S17. ^{1}H NMR spectrum of [$MePh_2P{=}NH_2$]I (**3c**) in CD_3CN

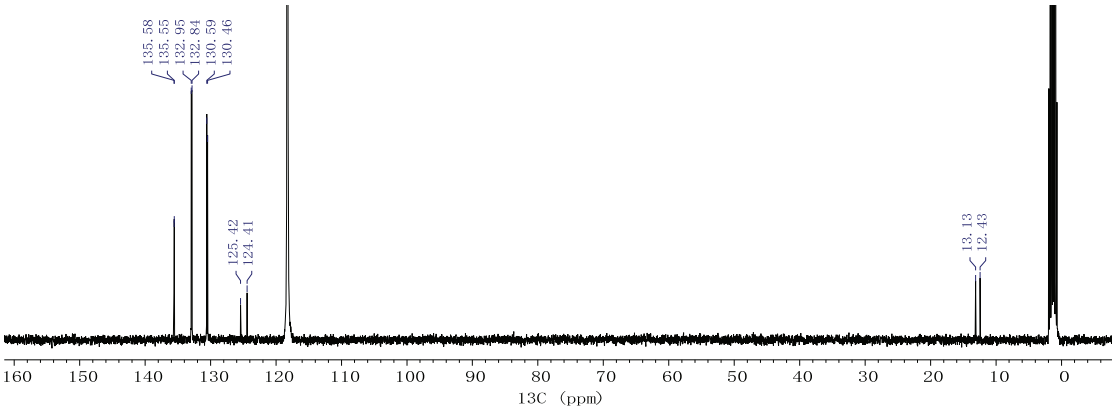


Figure S18. $^{13}C\{H\}$ NMR spectrum of [$MePh_2P{=}NH_2$]I (**3c**) in CD_3CN

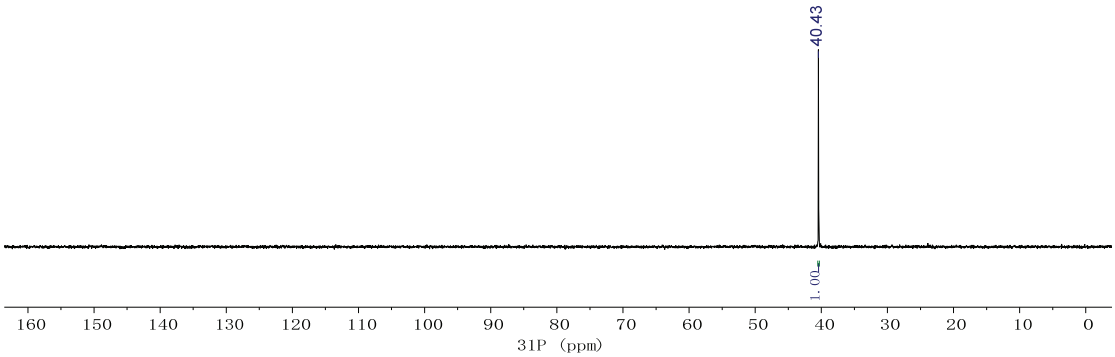


Figure S19. $^{31}P\{H\}$ NMR spectrum of [$MePh_2P{=}NH_2$]I (**3c**) in CD_3CN

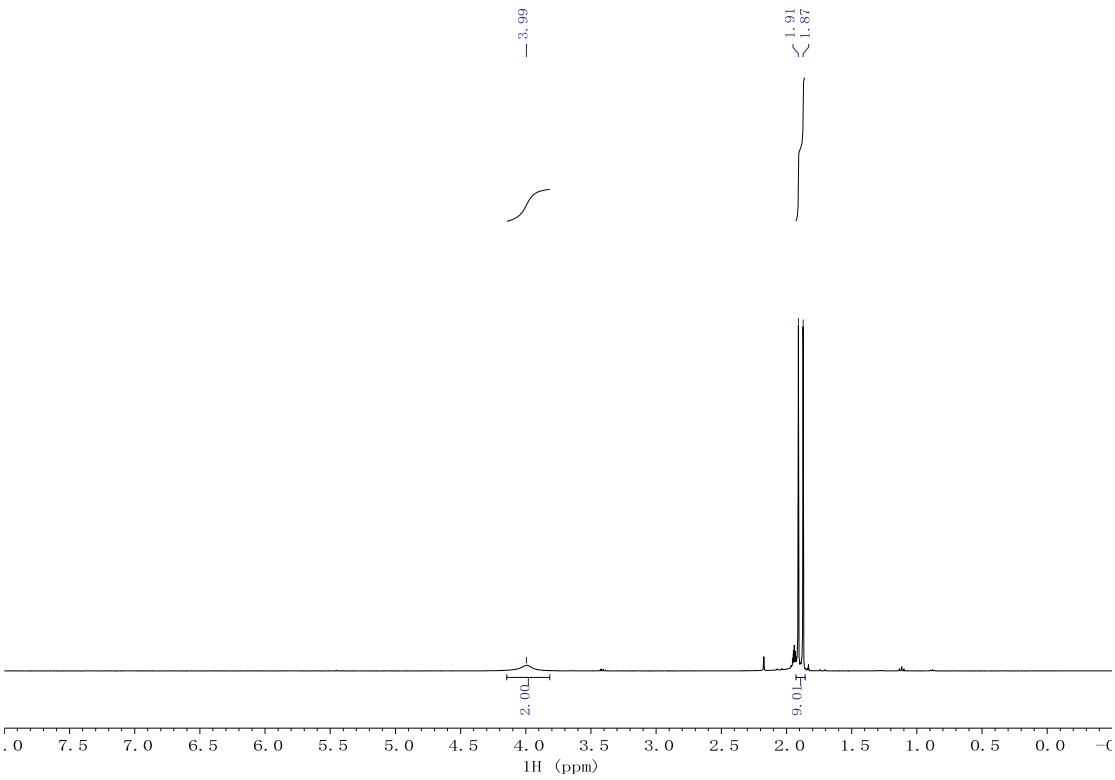


Figure S20. ^{1}H NMR spectrum of $[Me_3P{=}NH_2]I$ (**3d**) in CD_3CN

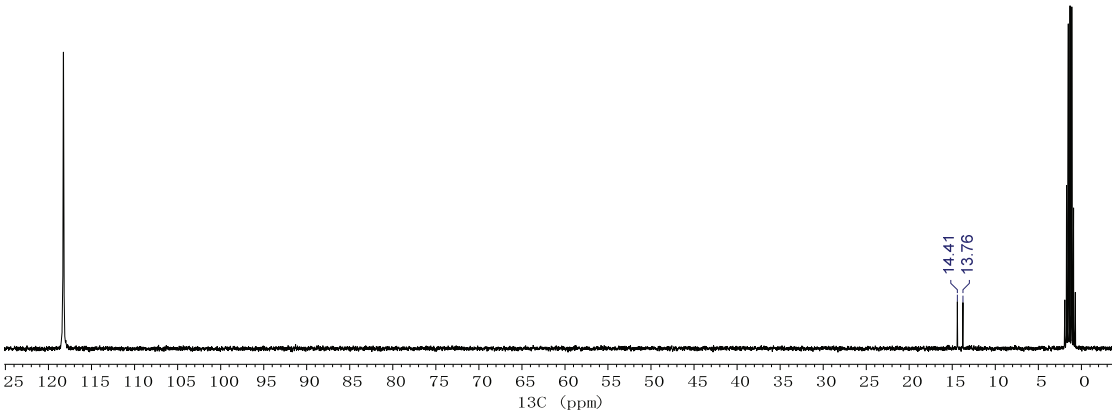


Figure S21. $^{13}C\{H\}$ NMR spectrum of $[Me_3P{=}NH_2]I$ (**3d**) in CD_3CN

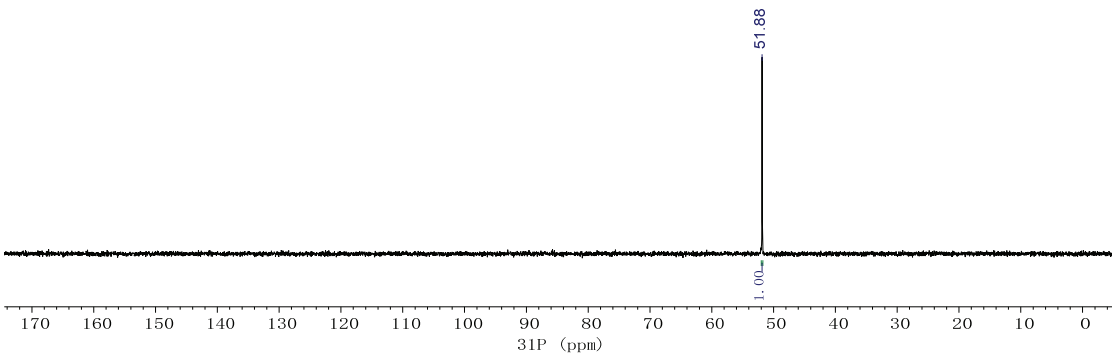
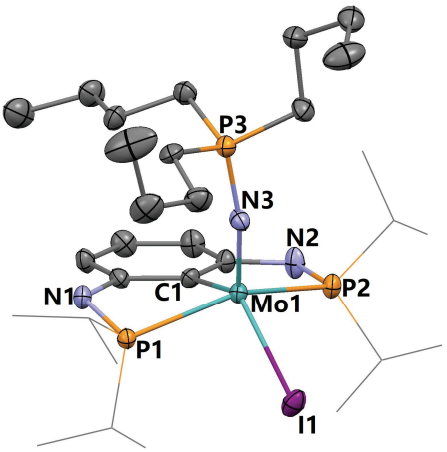


Figure S22. $^{31}P\{H\}$ NMR spectrum of $[Me_3P{=}NH_2]I$ (**3d**) in CD_3CN

Table S1. [(PNCNP)Mo(N=PBu$_3$)I]I (2a)

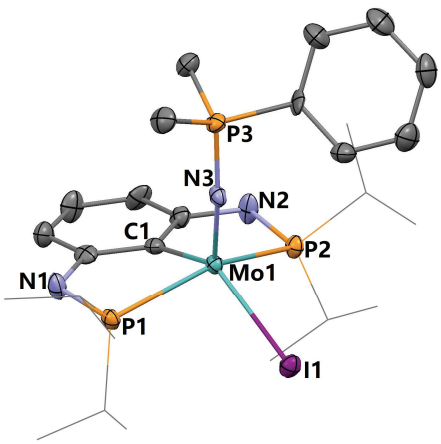
Molecular formula	$C_{30}H_{60}I_2MoN_3P_3$	
Formula weight	905.46	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal size	0.686 × 0.153 × 0.053 mm	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell parameters	*a* = 11.2557(8) Å	α = 90°
	b = 20.5955(16) Å	β = 101.483(3)°
	c = 17.0359(13) Å	γ = 90°
	V = 3870.2(5) Å^3	
Z	4	
F(000)	1816	
Density (calcd)	1.554 g/cm^3	
Absorption coefficient	2.081 mm^{-1}	
Theta range for data collection	2.094 to 25.082°	
Limiting indices	-13<=h<= 13, -24<=k<= 24, -20<=l<= 18	
Reflections collected / unique	28227 / 6841 [R(int) = 0.0798]	
Completeness to theta = 25.082°	99.5%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6841 / 0 / 352	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0425, wR2 = 0.1049	
R indices (all data)	R1 = 0.0493, wR2 = 0.1097	
Largest diff. peak and hole	1.605 and -1.275 eÅ^{-3}	



Selected bond lengths (Å) and angles (°): Mo1-I1 2.7421(5), Mo1-P1 2.4400(12), Mo1-P2 2.4612(12), Mo1-C1 2.117(4), Mo1-N3 1.771(3), P3-N3 1.631(4), N3-Mo1-I1 114.33(12), P1-Mo1-I1 90.36(3), P2-Mo1-I1 91.07(3), C1-Mo1-I1 132.56(11), C1-Mo1-P1 75.66(12), P1-Mo1-P2 143.24(4), N3-Mo1-P1 104.38(12), C1-Mo1-P2 76.51(12), N3-Mo1-P2 108.36(12), N3-Mo1-C1 113.04(16), P3-N3-Mo1 165.0(3).

Table S2. [(PNCNP)Mo(N=PPhMe$_2$)I]I (2b)

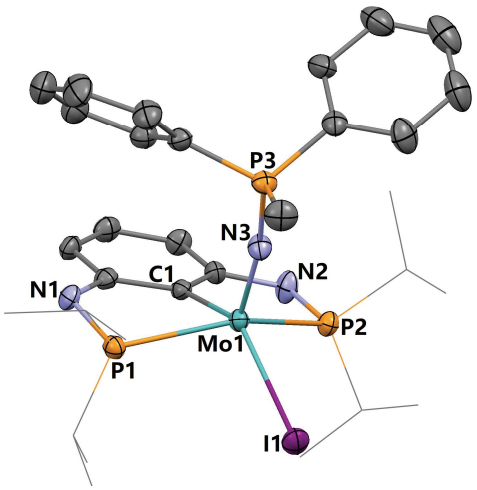
Molecular formula	$C_{26}H_{44}I_2MoN_3P_3$	
Formula weight	841.29	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal size	0.166 × 0.097 × 0.036 mm	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell parameters	a = 17.0447(19) Å	α = 90°
	b = 12.5657(13) Å	β = 105.891(2)°
	c = 16.0127(17) Å	γ = 90°
	V = 3298.5(6) Å^3	
Z	4	
F(000)	1656	
Density (calcd)	1.694 g/cm^3	
Absorption coefficient	2.434 mm^{-1}	
Theta range for data collection	2.240 to 24.414°	
Limiting indices	-19<=h<= 19, -14<=k<= 14, -18<=l<= 18	
Reflections collected / unique	25483 / 5427 [R(int) = 0.0991]	
Completeness to theta = 24.414°	99.6%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5427 / 0 / 316	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1123	
R indices (all data)	R1 = 0.0745, wR2 = 0.1261	
Largest diff. peak and hole	0.799 and -0.892 eÅ^{-3}	



Selected bond lengths (Å) and angles (°): Mo1-I1 2.7600(8), Mo1-P1 2.443(2), Mo1-P2 2.469(2), Mo1-C1 2.129(7), Mo1-N3 1.774(6), P3-N3 1.621(6), N3-Mo1-I1 110.0(2), P1-Mo1-I1 92.98(5), P2-Mo1-I1 90.51(5), C1-Mo1-I1 137.34(19), C1-Mo1-P1 76.8(2), P1-Mo1-P2 142.74(7), N3-Mo1-P1 104.82(19), C1-Mo1-P2 75.7(2), N3-Mo1-P2 108.72(19), N3-Mo1-C1 112.7(3), P3-N3-Mo1 165.3(4).

Table S3. [(PNCNP)Mo(N=PPh$_2$Me)I]I (2c)

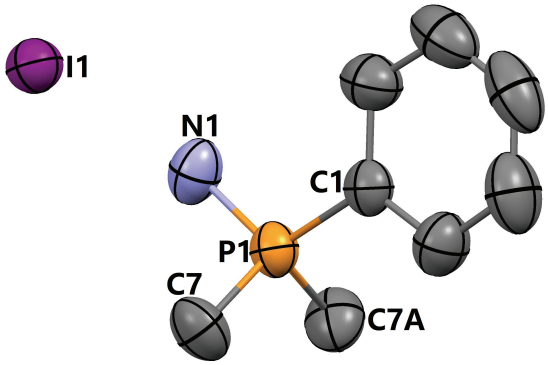
Molecular formula	$C_{31}H_{46}I_2MoN_3P_3$	
Formula weight	903.36	
Temperature	300(2) K	
Wavelength	1.54178 Å	
Crystal size	0.228 × 0.202 × 0.031 mm	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell parameters	a = 32.1147(11) Å	α = 90°
	b = 12.0242(4) Å	β = 103.547(2)°
	c = 19.6739(7) Å	γ = 90°
	V = 3298.5(6) Å^3	
Z	8	
F(000)	3568	
Density (calcd)	1.625 g/cm^3	
Absorption coefficient	17.436 mm^{-1}	
Theta range for data collection	3.939 to 63.015°	
Limiting indices	-35<=h<= 36, -13<=k<= 13, -22<=l<= 20	
Reflections collected / unique	32171 / 5755 [R(int) = 0.0639]	
Completeness to theta = 63.015°	96.3%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5755 / 48 / 361	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1643	
R indices (all data)	R1 = 0.0840, wR2 = 0.1896	
Largest diff. peak and hole	1.385and -1.234 eÅ^{-3}	



Selected bond lengths (Å) and angles (°): Mo1-I1 2.7484(9), Mo1-P1 2.461(2), Mo1-P2 2.454(2), Mo1-C1 2.125(9), Mo1-N3 1.766(7), P3-N3 1.613(8), N3-Mo1-I1 108.8(3), P1-Mo1-I1 96.19(6), P2-Mo1-I1 90.32(6), C1-Mo1-I1 138.7(2), C1-Mo1-P1 76.0(2), P2-Mo1-P1 144.30(8), N3-Mo1-P1 103.9(2), C1-Mo1-P2 76.1(2), N3-Mo1-P2 107.0(3), N3-Mo1-C1 112.4(3), P3-N3-Mo1 169.2(5).

Table S4. [$Me_2PhP{=}NH_2$]I (3b)

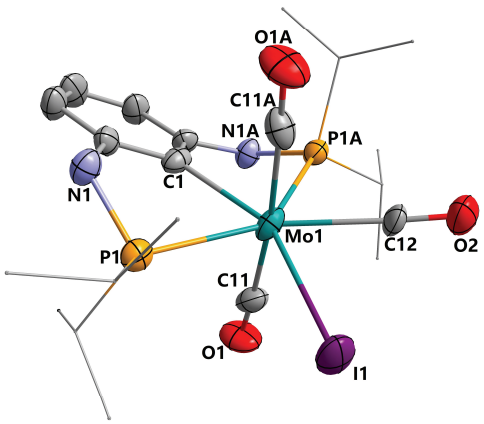
Molecular formula	$C_8H_{13}INP$	
Formula weight	281.06	
Temperature	274(2) K	
Wavelength	0.71073 Å	
Crystal size	0.656 × 0.098 × 0.087 mm	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell parameters	a = 12.818(7) Å	α = 90°
	b = 6.815(3) Å	β = 90°
	c = 12.453(5) Å	γ = 90°
	V = 1093.6(9) Å^3	
Z	4	
F(000)	544	
Density (calcd)	1.707 g/cm^3	
Absorption coefficient	3.021 mm^{-1}	
Theta range for data collection	3.179 to 24.468°	
Limiting indices	-14<=h<= 14, -7<=k<= 7, -14<=l<= 14	
Reflections collected / unique	4626 / 966 [R(int) = 0.0658]	
Completeness to theta = 24.468°	98.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	966 / 1 / 69	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0843	
R indices (all data)	R1 = 0.0444, wR2 = 0.0907	
Largest diff. peak and hole	0.919 and -0.559 eÅ^{-3}	



Selected bond lengths (Å) and angles (°): P1-N1 1.631(6), P1-C1 1.774(6), P1-C7 1.766(5), N1-P1-C1 114.0(3), N1-P1-C7 106.6(2), C1-P1-C7 108.9(2), C7-P1-C7A 111.9(4).

Table S5. (PNCNP)Mo(CO)$_3$I (4)

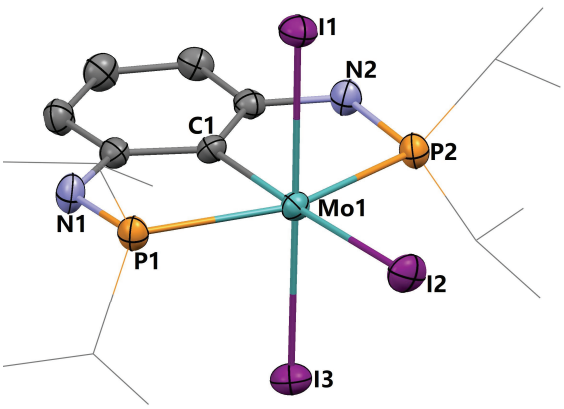
Molecular formula	$C_{21}H_{33}IMoN_2O_3P_2$	
Formula weight	646.27	
Temperature	170(2) K	
Wavelength	1.54178 Å	
Crystal size	0.150 × 0.120 × 0.100 mm	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell parameters	*a* = 25.9591(3) Å	α = 90°
	b = 13.17384(15) Å	β = 90°
	c = 14.86566(17) Å	γ = 90°
	V = 5083.77(10) Å^3	
Z	8	
F(000)	2576	
Density (calcd)	1.689 g/cm^3	
Absorption coefficient	15.143 mm^{-1}	
Theta range for data collection	4.798 to 75.437°	
Limiting indices	-32<=h<= 25, -16<=k<= 16, -18<=l<= 18	
Reflections collected / unique	14290 / 2568 [R(int) = 0.0606]	
Completeness to theta = 67.679°	99.8%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2568 / 1 / 151	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.1007	
R indices (all data)	R1 = 0.0378, wR2 = 0.1010	
Largest diff. peak and hole	0.966 and -0.743 eÅ^{-3}	



Selected bond lengths (Å) and angles (°): Mo1-I1 2.8583(10), Mo1-C1 2.271(9), Mo1-C11 2.027(7), Mo1-C12 2.128(12), Mo1-P1 2.5215(16), C11-O1 1.143(9), C12-O2 1.145(17) I1-Mo1-C11 89.5(2), I1-Mo1-C11A 96.3(2), I1-Mo1-C1 151.89(2), I1-Mo1-P1 137.01(4), I1-Mo1-P1A 82.11(4), I1-Mo1-C12 69.4(3), P1-Mo1-C1 70.32(4), P1-Mo1-C11 84.61(16), P1-Mo1-C11A 93.19(17), P1-Mo1-C12 70.4(3), P1-Mo1-P1A 140.63(7), C1-Mo1-C11 86.8(2), C1-Mo1-C12 138.5(3), P1A-Mo1-C12 147.2(3), C11-Mo1-C11A 173.5(4), C11-Mo1-C12 102.2(4), C11A-Mo1-C12 82.7(4).

Table S6. [Na(15-crown-5)(THF)][(PNCNP)MoI$_3$] (6)

Molecular formula	$C_{18}H_{33}I_3MoN_2P_2 \cdot Na(C_{14}H_{28}O_6) \cdot C_4H_8O$
Formula weight	1203.50
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal size	0.120 × 0.100 × 0.080 mm
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell parameters	a = 11.1871(3) Å α = 90°
	b = 18.9167(5) Å β = 90°
	c = 22.6936(6) Å γ = 90°
	V = 4802.5(2) Å^3
Z	4
F(000)	2388
Density (calcd)	1.665 g/cm^3
Absorption coefficient	18.437 mm^{-1}
Theta range for data collection	3.041 to 66.598°
Limiting indices	-13<=h<= 13, -21<=k<= 22, -27<=l<= 27
Reflections collected / unique	73210 / 8405 [R(int) = 0.0619]
Completeness to theta = 66.598°	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8405 / 183 / 507
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0557
R indices (all data)	R1 = 0.0230, wR2 = 0.0561
Largest diff. peak and hole	0.832 and -0.709 eÅ^{-3}



Selected bond lengths (Å) and angles (°): Mo1-I1 2.7834(5), Mo1-I2 2.8808(5), Mo1-I3 2.7910(5), Mo1-C1 2.159(4), Mo1-P1 2.5375(12), Mo1-P2 2.5391(12), I1-Mo1-I2 89.385(13), I1-Mo1-I3 179.129(17), I1-Mo1-P1 90.91(3), I1-Mo1-P2 88.55(3), I1-Mo1-C1 87.76(12), I2-Mo1-I3 91.486(14) I2-Mo1-P1 102.38(3), I2-Mo1-P2 102.88(3), I2-Mo1-C1 177.14(12), I3-Mo1-P1 88.91(3), I3-Mo1-P2 91.24(3), I3-Mo1-C1 91.37(12), C1-Mo1-P1 77.47(13), C1-Mo1-P2 77.27(13), P2-Mo1-P1 154.73(4).