Electronic Supporting Information (ESI) for

Cleavage of Dinitrogen to Yield a (*t*-BuPOCOP)Molybdenum(IV) Nitride

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General. All manipulations of air and moisture sensitive compounds were carried out using standard Schlenk and glovebox techniques under an atmosphere of nitrogen using oven dried glassware. Diethyl ether, pentane, THF, benzene and toluene were purged with nitrogen and passed through activated alumina columns. Heptane, C_6D_6, and THF-d_8 were distilled from dark-purple Na/benzophenone ketyl solutions. All dried and deoxygenated solvents were stored over 4 Å Linde-type molecular sieves prior to use. NMR spectra were recorded at room temperature (293 ± 2 K) on a Varian Inova 500 spectrometer. ^1H NMR shifts are reported relative to residual resonances of the solvent: C_6D_6 (7.16 ppm), THF-d_8 (1.73 ppm). ^{31}P NMR shifts are reported relative to an external sample of 85% $H_3PO_{4(aq)}$ (0.00 ppm). ^{15}N NMR shifts are referenced to an external sample of neat $CH_3C^{15}N$ (+245.5 ppm).[1]

Deuterated solvents and $^{15}N_2$ were obtained from Cambridge Isotope Laboratories, Inc. Li-*n*-Bu solution (titrated immediately prior to use), and trimethylsilyliodide (degassed and stored over Cu) were obtained from Sigma-Aldrich. Sodium, mercury, decamethylchromocene (sublimed), cobaltocene (sublimed) and 15-Crown-5 were obtained from Strem Chemicals, Inc. Sodium amalgam was prepared by adding small pieces of freshly cut sodium metal to filtered mercury (*caution, exothermic!*). Celite 545 was obtained from VWR International, LLC and was stored in a 150 °C oven overnight and cooled under vacuum prior to use. (*t*-BuPOCOP)I,[2] $MoI_3(THF)_3$, $MoBr_3(THF)_3$,[3] $MoCl_3(THF)_3$,[4] and $[Et_3NH][BAr'_4]$[5] were synthesized according to literature procedures. Catalytic activity was assessed using a previously described apparatus.[6] Conditions employed were as previously described by Schrock and coworkers[6] or Nishibayashi and coworkers[7] replacing the respective catalysts with [(*t*-BuPOCOP)Mo(I)(N)][Na(15-crown-5)]. The quantity of NH_3 produced was determined using Berthelot's indophenol method.[8] Mass spectrometry was performed at the Massachusetts Institute of Technology's Department of Chemistry Instrumentation Facility using Q-TOF micro (Waters Corporation) with ESI source in positive mode. Samples were dissolved in O_2 and H_2O free acetonitrile and stored in septum sealed vials prior to sampling. The syringe pump was used at an injection rate of 5 µL/min. The ESI source temperature was 100 °C, the desolvation gas temperature was 150 °C, and desolvation gas flow rate was 360 L/hr. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN.

(*t*-BuPOCOP)MoI$_2$ (1). (*t*-BuPOCOP)I (4.821 g, 9.193 mmol) was dissolved in Et_2O (180 mL) and stored at −30 °C for 1 h. The flask was removed and immediately *n*BuLi (2.54 M in hexanes, 3.7 mL, 9.4 mmol) was added to give a pale yellow solution. After stirring 10 m this solution was transferred to a 250 mL round bottom flask containing a vigorously stirring slurry of freshly prepared $MoI_3(THF)_3$ (6.497 g, 9.376 mmol) in Et_2O (20 mL). The dark red-brown slurry was stirred 15 h at room temperature. Unreacted $MoI_3(THF)_3$ was removed by filtering the slurry through a glass frit and rinsing the solid with Et_2O until the filtrate was nearly colorless. Volatile components of the filtrate were removed under vacuum. Pentane (30 mL) was added to the dark brown tacky solid and the mixture was stirred vigorously several hours before the solid was collected on a fritted glass filter. The brown solid was rinsed with pentane until the filtrate was nearly colorless, then transferred to a Schlenk bomb and heated to 120 °C overnight under dynamic vacuum (10^{-2} Torr). The brown solid was then dissolved in benzene and remaining solid was removed by filtration over Celite. The filtrate was frozen and then sublimed under vacuum to obtain the product as a brown solid. This material was a mixture of (*t*-BuPOCOP)MoI$_2$ and (*t*-BuPOCOP)Mo(I)(O) in an approximate 9:1 ratio. Yield: 3.17 g (4.24 mmol, 46%). ^{1}H NMR (500 MHz, C_6D_6) δ ppm −181.0 (br s, 1H, *p*-H), 18.1 (br s, 36H, C(CH_3)$_3$), 96.9 (br s, 2H, *m*-H). ^{1}H NMR (500 MHz, THF-d_8) δ ppm −180.2 (br s, 1H, *p*-H), 18.0 (br s, 36H, C(CH_3)$_3$), 96.7 (br s, 2H, *m*-H). Anal. calcd.(found) for $C_{22}H_{39}I_{1.9}MoO_{2.1}P_2$ (%): C, 35.89(35.99); H, 5.34(5.33).

(*t*-BuPOCOP)Mo(I)(O) (2). This material was obtained as a mixture of (*t*-BuPOCOP)MoI_2 and (*t*-BuPOCOP)Mo(I)(O) in an approximate 9:1 ratio. ^1H NMR (500 MHz, C_6D_6) δ ppm 1.12 (vt, apparent $J = 7$ Hz, 18H, $C(CH_3)_3$), 1.47 (vt, apparent $J = 7$ Hz, 18H, $C(CH_3)_3$), 6.95 (d, $J = 8$ Hz, 2H, *m*-H), (*p*-H, not located). ^1H NMR (500 MHz, THF-d_8) δ ppm 1.21 (vt, apparent $J = 7$ Hz, 18H, $C(CH_3)_3$), 1.58 (vt, apparent $J = 7$ Hz, 18H, $C(CH_3)_3$), 6.91 (d, $J = 8$ Hz, 2H, *m*-H), 7.37 (t, $J = 8$ Hz, 1H, *p*-H). Anal. calcd.(found) for $C_{22}H_{39}I_{1.9}MoO_{2.1}P_2$ (%): C, 35.89(35.99); H, 5.34(5.33).

Reaction of (*t*-BuPOCOP)MoX_2 and TMSI. The mixture (*t*-BuPOCOP)MoX_2 (X = Cl, I) was synthesized in a manner similar to (*t*-BuPOCOP)MoI_2 using $MoCl_3(THF)_3$ in place of $MoI_3(THF)_3$. The ^1H NMR spectrum indicated a four component mixture in an approximate 5:5:5:1 ratio, the minor component of which corresponds to (*t*-BuPOCOP)MoI_2. The molecular formula of this mixture is estimated to be $C_{22}H_{39}Cl_{1.25}I_{0.75}MoO_2P_2$ (633 g/mol) excluding a small amount of Mo=O species also present. This mixture (149 mg, 235 μmol) was weighed into a Schlenk bomb flask, dissolved in toluene (5 mL) and cooled in a dry ice/acetone bath. Under a counterflow of N_2 gas, trimethylsilyliodide (0.2 mL, 1.4 mmol) was added by syringe. The flask was closed and after brief stirring the flask was warmed to RT and stirred 15 h. Volatile components of the mixture were removed under vacuum while heating the flask to 70 °C for several hours. The crude solid was dissolved in benzene and filtered over Celite. The filtrate was frozen and sublimed to give mixture of (*t*-BuPOCOP)MoI_2 (major component) and (*t*-BuPOCOP)Mo(I)(O) (minor component). Yield: 115 mg (154 mmol, 65%). ^1H NMR spectra were identical to those obtained previously.

[(*t*-BuPOCOP)Mo(I)(N)][Na(15-crown-5)] (3). (*t*BuPOCOP)$Mo(I)_2$ (202 mg, 270 μmol) was dissolved in Et_2O (15 mL) and transferred to a vial containing Na amalgam (7.9 g, 0.5 w% Na in Hg, 1.7 mmol). The mixture was stirred vigorously 13 h and then the green-brown mixture was removed from the amalgam and filtered through Celite. 15-Crown-5 (60. μL, 0.30 μmol) was added and the solution was stirred 0.5 h. Volatile components were removed under vacuum. The dark solid was dissolved in THF (2 mL) and pentane (16 mL) was added slowly while vigorously stirring. The flask was stored at −30 °C to complete precipitation of the product. The green-brown solid was collected on a fritted glass filter, washed with a small portion of pentane and dried under vacuum. Yield: 136 mg (155 μmol, 57%). ^{1}H NMR (500 MHz, THF-d_8) δ ppm 6.83 (t, 1H, *J* = 8 Hz, *p*-H), 6.55 (d, 2H, *J* = 8 Hz, *m*-H), 3.65 (s, 20H, 15-crown-5), 1.58 (vt, 18H, apparent *J* = 6 Hz, *t*Bu), 1.12 (vt, 18H, apparent *J* = 6 Hz, *t*Bu). ^{31}P{^{1}H} NMR (202.5 MHz, THF-d_8) δ ppm 235.85 (s). Anal. calcd.(found) for $C_{32}H_{59}IMoNNaO_7P_2$ (%): C, 43.79(43.59); H, 6.78(6.65); N, 1.60(1.63).

[(*t*-BuPOCOP)Mo(I)(^{15}N)][Na(15-crown-5)] (3-^{15}N). (*t*BuPOCOP)Mo(I)$_2$ (98 mg, 131 μmol) and 15-crown-5 (28 μL, 141 μmol) were dissolved in THF (5 mL) and transferred to a 25 mL RB Schlenk bomb, closed, and removed from the N_2 box. The flask was attached to a gas transfer bridge and then degassed (freeze-pump-thaw ×3) and frozen again. Under a counterflow of N_2, Na amalgam (3.34 g, 0.5 w% Na in Hg, 726 μmol) was added to the flask using a syringe. The flask was closed and degassed by two cycles of freezing at 77 K, thawing to 195 K and evacuating. The headspace was then filled with $^{15}N_2$ gas (20 mL, 1 atm, 77 K, 3.2 mmol) before the flask was sealed. The reaction mixture was warmed to room temperature and stirred vigorously 16 h. The dark brown slurry was removed from the amalgam and filtered through Celite, and solvent was removed from the filtrate under vacuum. Benzene (5 mL) was added and the mixture stirred vigorously 2 h before filtering through Celite. The benzene was removed under vacuum to give product of satisfactory purity. Yield: 53 mg (60. μmol, 46%). ^{1}H and ^{31}P{^{1}H} NMR spectra were identical to those obtained for the unenriched complex. ^{15}N NMR (50.71 MHz, THF-d_8) δ ppm 801.1 (s).

(*t*-BuPOCOP)Mo(I)(N)(H) (4). [(*t*BuPOCOP)Mo(I)(N)][Na(15-crown-5)] (119 mg, 136 μmol) was dissolved in Et_2O (5 mL). [Et_3NH][BAr′$_4$] (142 mg, 144 μmol) was dissolved in Et_2O (2 mL) and the two solutions were combined and stirred. After 10 m the dark brown solution lightened and a precipitate formed. After 3 h the reaction flask was moved to a −30 °C freezer and stored overnight. The precipitate was collected on a fritted glass filter and washed with cold Et_2O, then dried under vacuum to give a yellow solid. Yield: 55 mg (87 μmol, 64%). ^{1}H NMR (500 MHz, C_6D_6) δ ppm 7.05 (t, 1H, *J* = 8 Hz, *p*-H), 6.88 (d, 1H, *J* = 8 Hz, *m*-H), 6.85 (d, 1H, *J* = 8 Hz, *m*-H), 3.94 (dd, 1H, J_{HP} = 6, 133 Hz, P*H*Mo), 1.68 (d, 9H, *J* = 14 Hz, *t*Bu), 1.34 (d, 9H, *J* = 15 Hz, *t*Bu), 1.28 (d, 9H, *J* = 14 Hz, *t*Bu), 0.98 (d, 9H, *J* = 15 Hz, *t*Bu). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6) δ ppm

206.4 (d, $J = 20$ Hz), 161.9 (d, $J = 20$ Hz). Anal. calcd.(found) for $C_{22}H_{40}IMoNO_2P_2$ (%): C, 41.59(41.39); H, 6.35(6.33); N, 2.20(2.23).

(*t*-BuPOCOP)Mo(I)(^{15}N)(H) (4-^{15}N). This compound was synthesized as (*t*BuPOCOP)Mo(I)(N)(H), using [(*t*BuPOCOP)Mo(I)(^{15}N)][Na(15-crown-5)] in place of [(*t*BuPOCOP)Mo(I)(N)][Na(15-crown-5)]. ^{1}H NMR (500 MHz, C_6D_6) δ ppm 7.05 (t, 1H, $J = 8$ Hz, *p*-H), 6.88 (d, 1H, $J = 8$ Hz, *m*-H), 6.85 (d, 1H, $J = 8$ Hz, *m*-H), 3.94 (ddd, 1H, $J_{HP} = 6, 133$ Hz, $J_{HN} = 2.5$ Hz, P*H*Mo), 1.68 (d, 9H, $J = 14$ Hz, *t*Bu), 1.34 (d, 9H, $J = 15$ Hz, *t*Bu), 1.28 (d, 9H, $J = 14$ Hz, *t*Bu), 0.98 (d, 9H, $J = 15$ Hz, *t*Bu). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6) δ ppm 206.4 (dd, $J_{PP} = 20$ Hz, $J_{NP} = 4$ Hz), 161.9 (d, $J = 20$ Hz). ^{15}N NMR (50.71 MHz, C_6D_6) δ ppm 945.0 (br s).

(*t*-BuPOCOP)MoBr$_2$. (*t*-BuPOCOP)I (255 mg, 486 μmol) was dissolved in Et_2O (20 mL) and stored at −30 °C for 1 h. The flask was removed and immediately *n*BuLi (2.5 M in hexanes, 0.20 mL, 0.50 mmol) was added to give a pale yellow solution. After stirring 5 m this solution was transferred to a 100 mL round bottom flask containing a vigorously stirring slurry of freshly prepared $MoBr_3(THF)_3$ (327 mg, 592 μmol) in Et_2O (20 mL). The dark red-brown slurry was stirred 16 h at room temperature. Unreacted $MoBr_3(THF)_3$ was removed by filtering the slurry through a glass frit and rinsing the solid with Et_2O until the filtrate was nearly colorless. Volatile components of the filtrate were removed under vacuum. The brown solid was transferred to a Schlenk bomb and heated to 120 °C overnight under dynamic vacuum (10^{-2} Torr). The brown solid was then dissolved in benzene and remaining red solid was removed by filtration over Celite. The filtrate was frozen and then benzene sublimed under vacuum to obtain a mixture of products as a green solid. This material contained predominantly (*t*-BuPOCOP)MoBr$_2$ with (*t*-BuPOCOP)Mo(Br)(O) and two isomers of (*t*-BuPOCOP)Mo(Br)(I) as minor components in an approximate 8:1:1 ratio. Yield: 251 mg (384 mmol, 79%). ^{1}H NMR (500 MHz, C_6D_6) δ ppm −197.5 (br s, 1H, *p*-H), 20.8 (br s, 36H, C(CH_3)$_3$), 97.9 (br s, 2H, *m*-H). ^{1}H NMR (500 MHz, THF-d_8) δ ppm −196.7 (br s, 1H, *p*-H), 20.5 (br s, 36H, C(CH_3)$_3$), 97.2 (br s, 2H, *m*-H).

(*t*-BuPOCOP)Mo(Br)(O). This material was obtained as a mixture of (*t*-BuPOCOP)MoBr$_2$ and (*t*-BuPOCOP)Mo(Br)(O). ^{1}H NMR (500 MHz, THF-d_8) δ ppm

1.21 (vt, apparent $J = 7$ Hz, 18H, C(CH_3)$_3$), 1.55 (vt, apparent $J = 7$ Hz, 18H, C(CH_3)$_3$), 6.89 (d, $J = 8$ Hz, 2H, *m*-H), 7.35 (t, $J = 8$ Hz, 1H, *p*-H).

The fact that (*t*-BuPOCOP)MoI_2 cannot be isolated from (*t*-BuPOCOP)Mo(I)(O) presents some problems in obtaining definitive characterization. ^{1}H NMR data alone is insufficient and other methods which could support the assignment of this complex (e.g. elemental analysis) are not useful in the absence of pure compound. Several synthetic methods were attempted but the product mixtures obtained were never of high enough purity. The oxophilicity of the MoI_3(THF)$_3$ is likely to blame and the extreme insolubility of this starting material prevents purification to exclude possible oxo containing products. Several attempts were made at chemically differentiating the two species without success. Various conditions were employed to obtain crystals suitable for X-ray diffraction. In two instances X-ray data were collected and in both cases the data were consistent with the proposed molecules. However one of the two determined Mo-I bond distances (2.57 Å) was too short for iodine and the U_{eq} of the corresponding iodine atom refined to a slightly larger value than expected, thus suggesting Br rather than I as the second halide. To ensure bromine was not present in the sample submitted for X-ray diffraction analysis an authentic sample of (*t*-BuPOCOP)MoBr_2 was synthesized. (An oxo containing species was observed in this sample as well in a similar ratio as observed previously.) A comparison of a selected region of the ^{1}H NMR spectra of all three halogen containing species ((*t*-BuPOCOP)MoX_2 where X = some combination of Cl, Br, I) appears below. Mass spectrometry was employed to compare to two complexes, however the sample containing (*t*-BuPOCOP)MoI_2 was not stable under the sampling conditions. Fragments were observed showing an isotopic distribution consistent with fragments containing only the elements C, H, I, Mo, O, P. This experiment was repeated with a sample of (*t*-BuPOCOP)MoBr_2 which proved to be more stable to the sampling conditions. A peak located at 656.1124 m/z was observed which displayed an isotopic distribution consistent with the empirical formula for $[C_{22}H_{40}Br_2Mo_1O_2P_2]^+$ (calcd 655.99 m/z).

In spite of our efforts to characterize (*t*-BuPOCOP)MoI_2 we are aware that definitive evidence was not obtained; however, we feel that the evidence provided along with the fact that the material was carried on to yield expected products which were definitively characterized gives us reasonable confidence our assignment.

X-Ray Structure Determination. Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo K_α radiation (λ = 0.71073 Å). All structures were solved by direct methods using SHELXS[9] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[10] using established refinement techniques.[11] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disorders were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The crown ether is heavily disordered; three discrete positions could be modeled. Occupancies of the three disorder components were refined freely, but were restrained to sum up to unity. They converged at 0.484(3), 0.300(4), and 0.216(4), respectively. The anisotropic displacement parameters are elongated in a direction sensible for a rotation of the ether.

Compound **4** crystallizes in the tetragonal space group I-4 with one molecule in the asymmetric unit. The structure was refined as a merohedral and racemic twin and the twin ratios refined to 0.33(1), 0.14(2), and 0.15(1), respectively. The structure was also fully disordered over at least two positions and the occupancy of the two components was refined freely and converged at 0.8372(8). A third position was faintly visible in the difference Fourier synthesis but refinement was not stable. The oxygen atoms and aromatic ring were restrained to be flat for each component. The anisotropic displacement parameters for equivalent atoms in both components were constrained to be equivalent.

Table S1.
Crystal data and structure refinement for [(*t*-BuPOCOP)Mo(I)(N)][Na(15-crown-5)] (**3**).

CCDC Deposition Code	856986	
Empirical formula	$C_{32} H_{59} I Mo N Na O_7 P_2$	
Formula weight	877.57	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.1382(9) Å	a= 90°.
	b = 18.3038(15) Å	b= 90.287(2)°.
	c = 19.6708(16) Å	g = 90°.
Volume	4010.3(6) Å^3	
Z	4	
Density (calculated)	1.454 Mg/m^3	
Absorption coefficient	1.229 mm^{-1}	
F(000)	1800	
Crystal size	0.20 x 0.15 x 0.03 mm^3	
Theta range for data collection	1.52 to 30.32°.	
Index ranges	$-15<=h<=15$, $-25<=k<=25$, $-27<=l<=24$	
Reflections collected	91396	
Independent reflections	12017 [R_{int} = 0.0569]	
Completeness to theta = 30.32°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9641 and 0.7912	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12017 / 2701 / 691	
Goodness-of-fit on F^2	1.011	
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0375$, $wR2 = 0.0789$	
R indices (all data)	$R1 = 0.0612$, $wR2 = 0.0889$	
Largest diff. peak and hole	1.569 and -1.082 e.Å^{-3}	

Table S2.
Crystal data and structure refinement for (*t*-BuPOCOP)Mo(I)(N)(H) (**4**).

CCDC Deposition Code	856987	
Empirical formula	$C_{22} H_{39} I Mo N O_2 P_2$	
Formula weight	634.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	*I*-4	
Unit cell dimensions	a = 14.3739(7) Å	a= 90°.
	b = 14.3739(7) Å	b= 90°.
	c = 25.6082(13) Å	g = 90°.
Volume	5290.9(5) $Å^3$	
Z	8	
Density (calculated)	1.593 Mg/m^3	
Absorption coefficient	1.801 mm^{-1}	
F(000)	2552	
Crystal size	0.15 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.62 to 30.30°.	
Index ranges	-18<=h<=20, -20<=k<=20, -36<=l<=36	
Reflections collected	31568	
Independent reflections	7952 [R*int* = 0.0394]	
Completeness to theta = 30.30°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7739 and 0.7739	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7952 / 1535 / 365	
Goodness-of-fit on F^2	1.051	
Final *R* indices [$I>2\sigma(I)$]	R*1* = 0.0362, *w*R2 = 0.0845	
R indices (all data)	*R*1 = 0.0377, *w*R2 = 0.0858	
Largest diff. peak and hole	2.722 and -0.982 e.$Å^{-3}$	

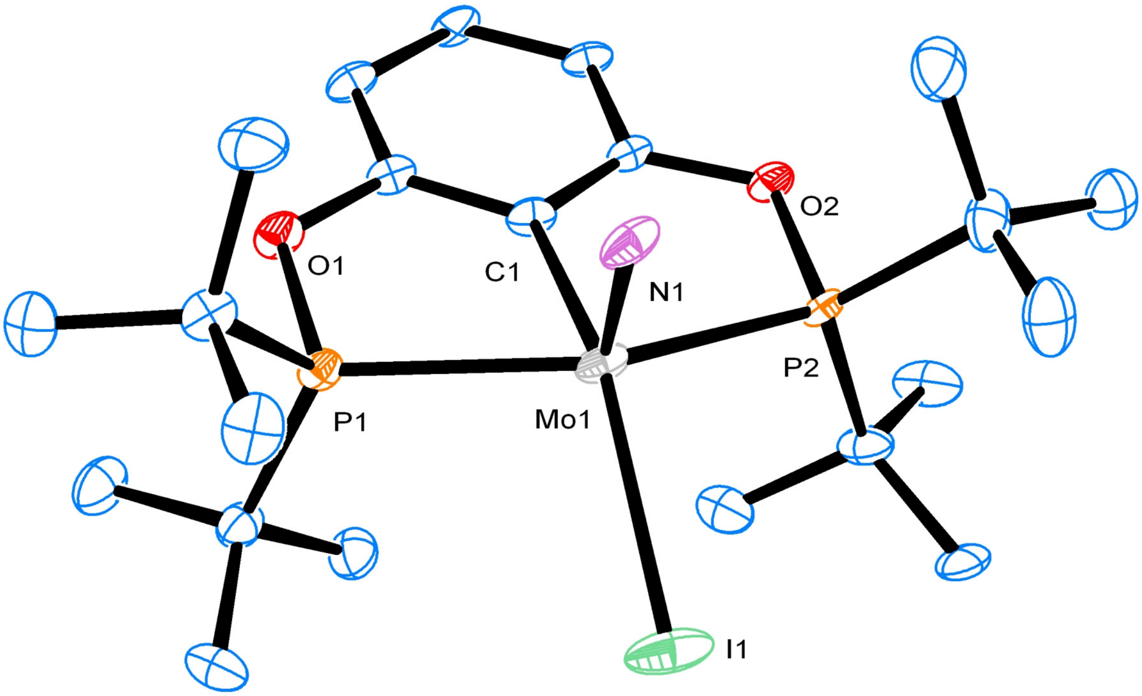

Figure S1. Thermal ellipsoid representation of (*t*-BuPOCOP)Mo(I)(N)(H) (**4**) at 50% probability level. H atoms and whole molecule disorder are omitted. Selected bond distances (Å) and angles (°): Mo1−C1 2.204(4), Mo1−P1 2.529(2), Mo1−P2 2.525(2), Mo1−I1 2.7537(6), Mo1−N1 1.643(3), C1−Mo1−I1 152.44(10), P1−Mo1−P2 145.30(9), I1−Mo1−N1 105.75(14).

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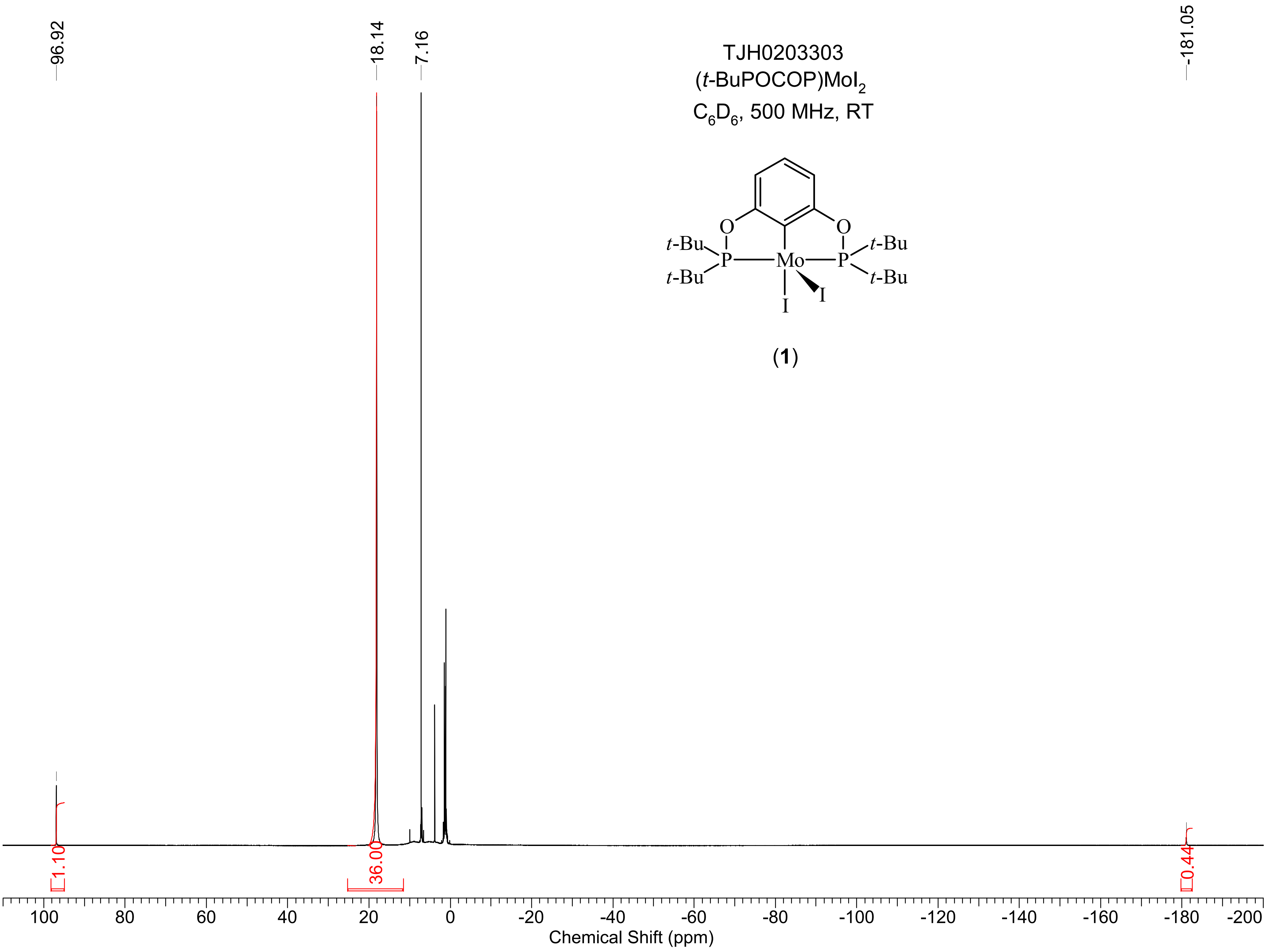
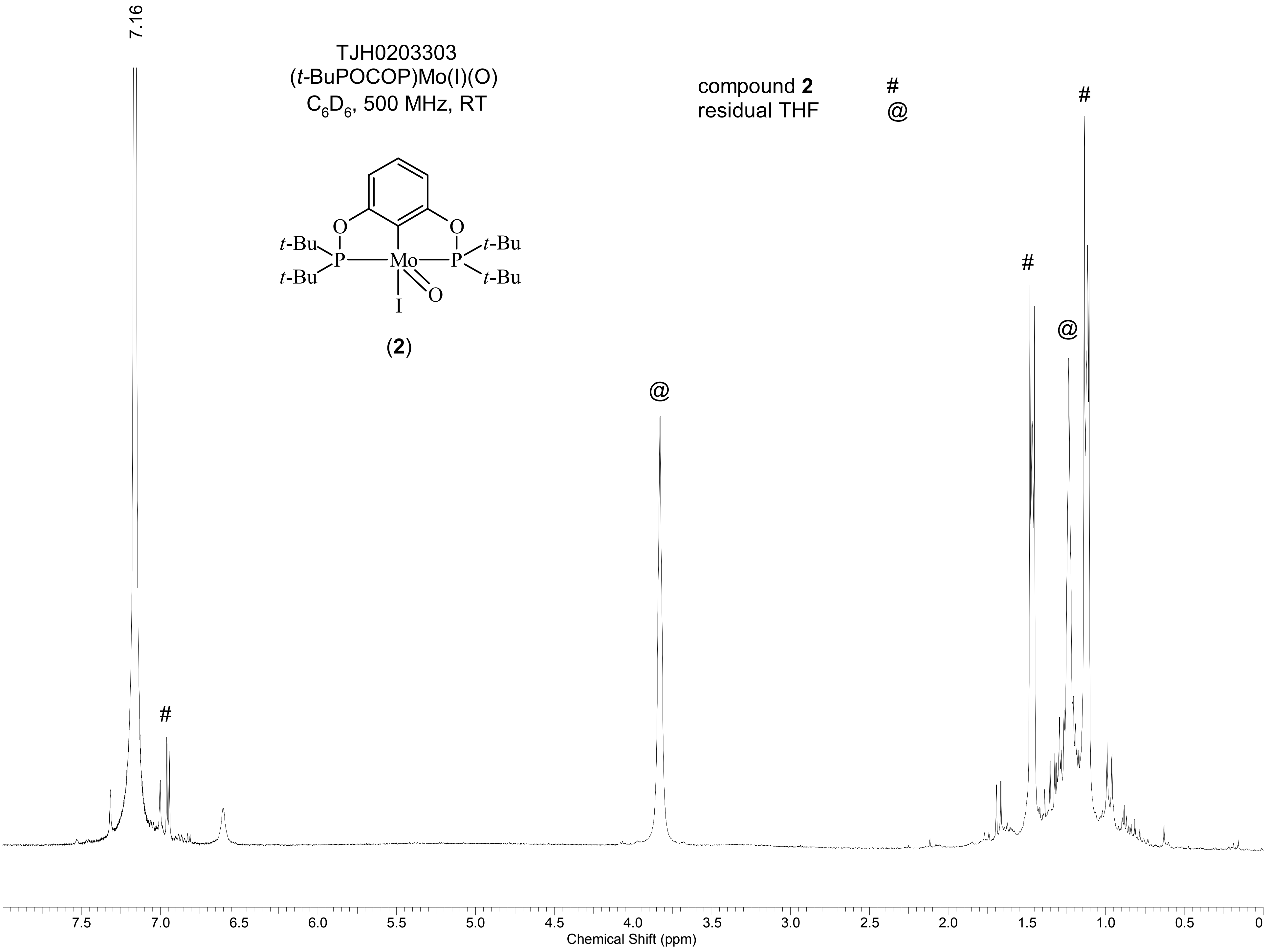

96.92
18.14
7.16
-181.05
TJH0203303
(t-BuPOCOP)MoI2
C6D6, 500 MHz, RT
t-Bu
t-Bu
O
P
Mo
I
I
O
P
t-Bu
t-Bu
(1)
1.10
36.00
0.44
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)


7.16
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C6D6, 500 MHz, RT
O
O
t-Bu
t-Bu
P
Mo
P
t-Bu
t-Bu
O
I
(2)
compound 2 #
residual THF @
#
#
@
@
#
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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2.0
1.5
1.0
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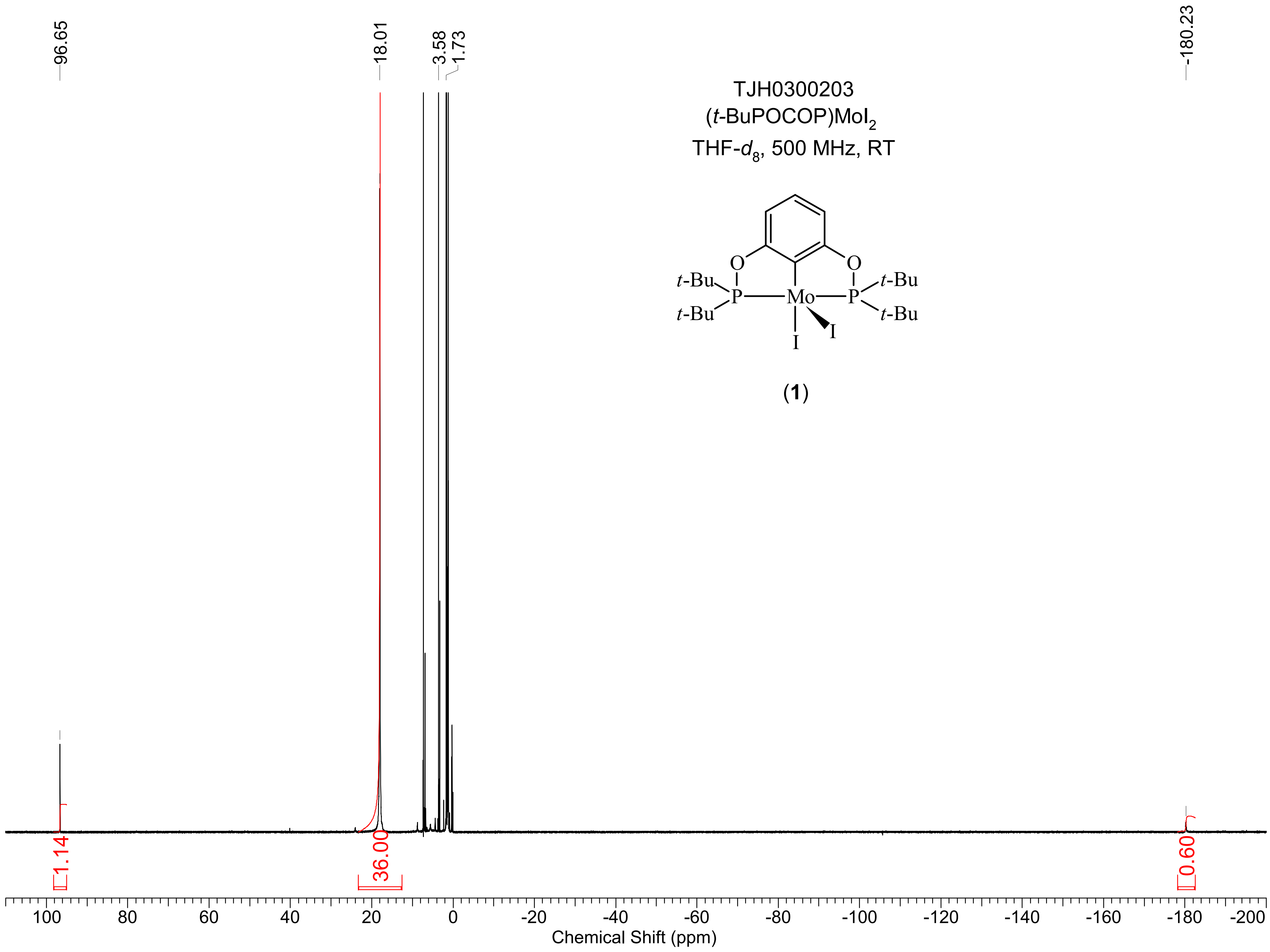
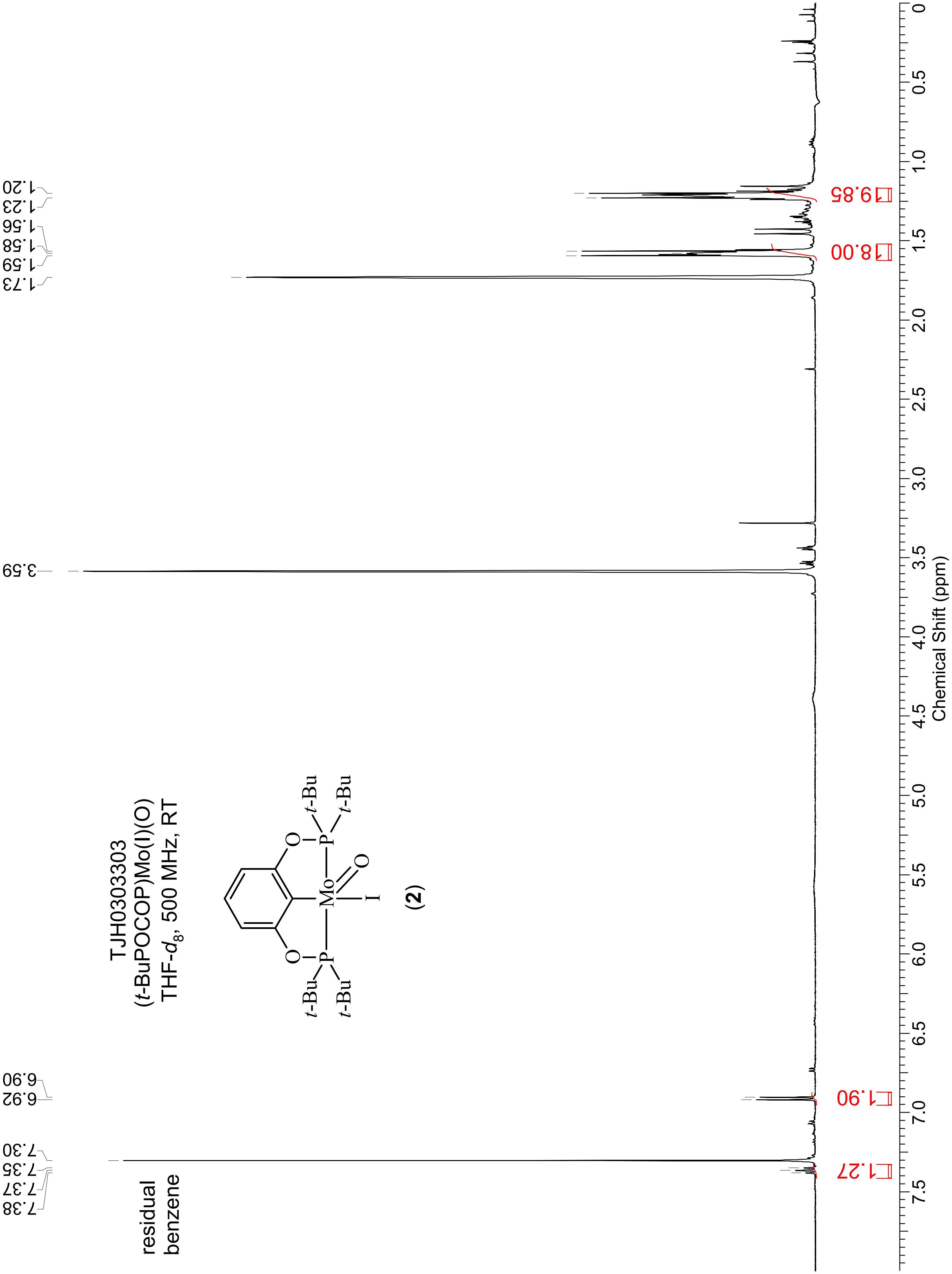
Chemical Shift (ppm)

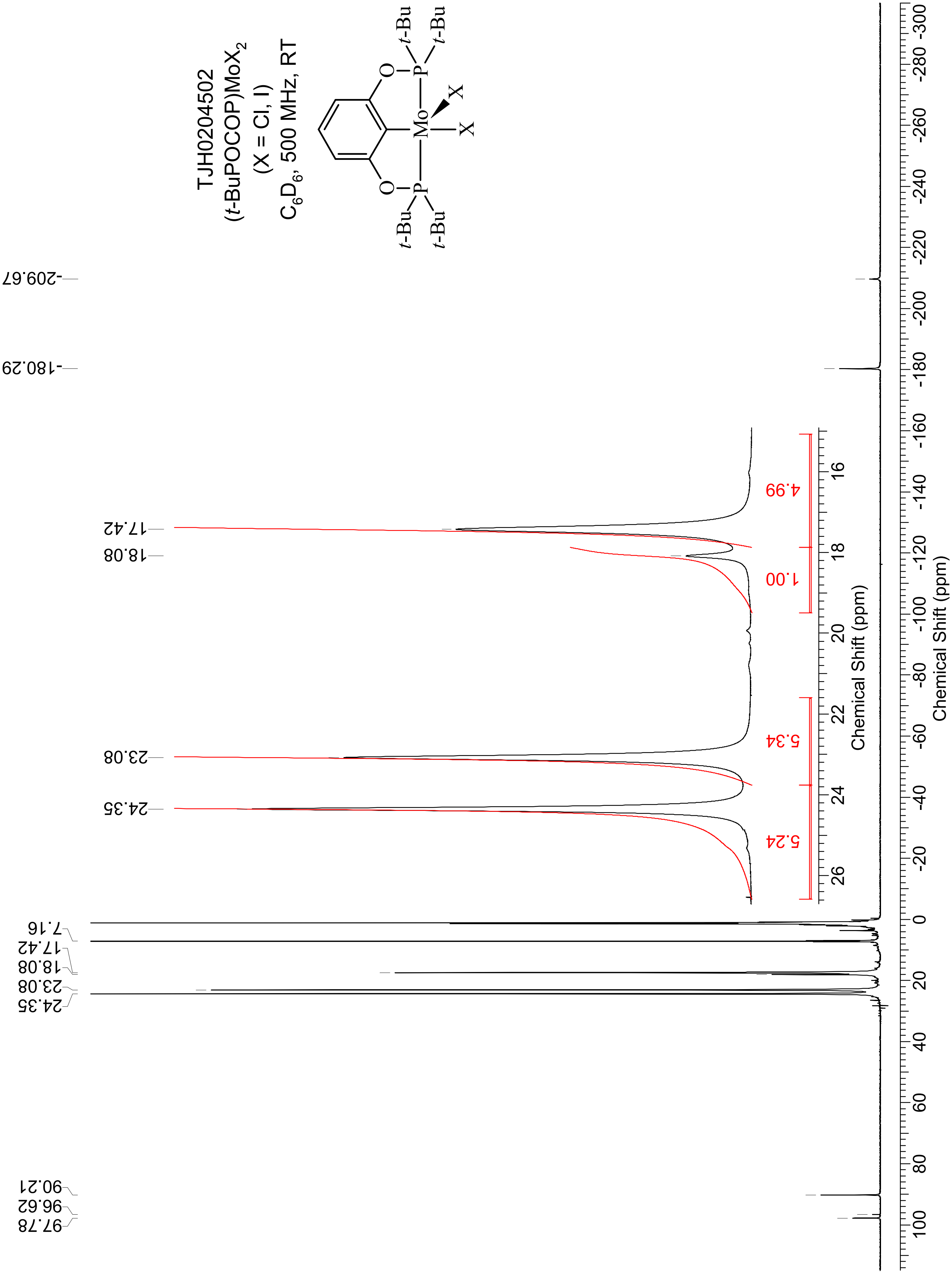


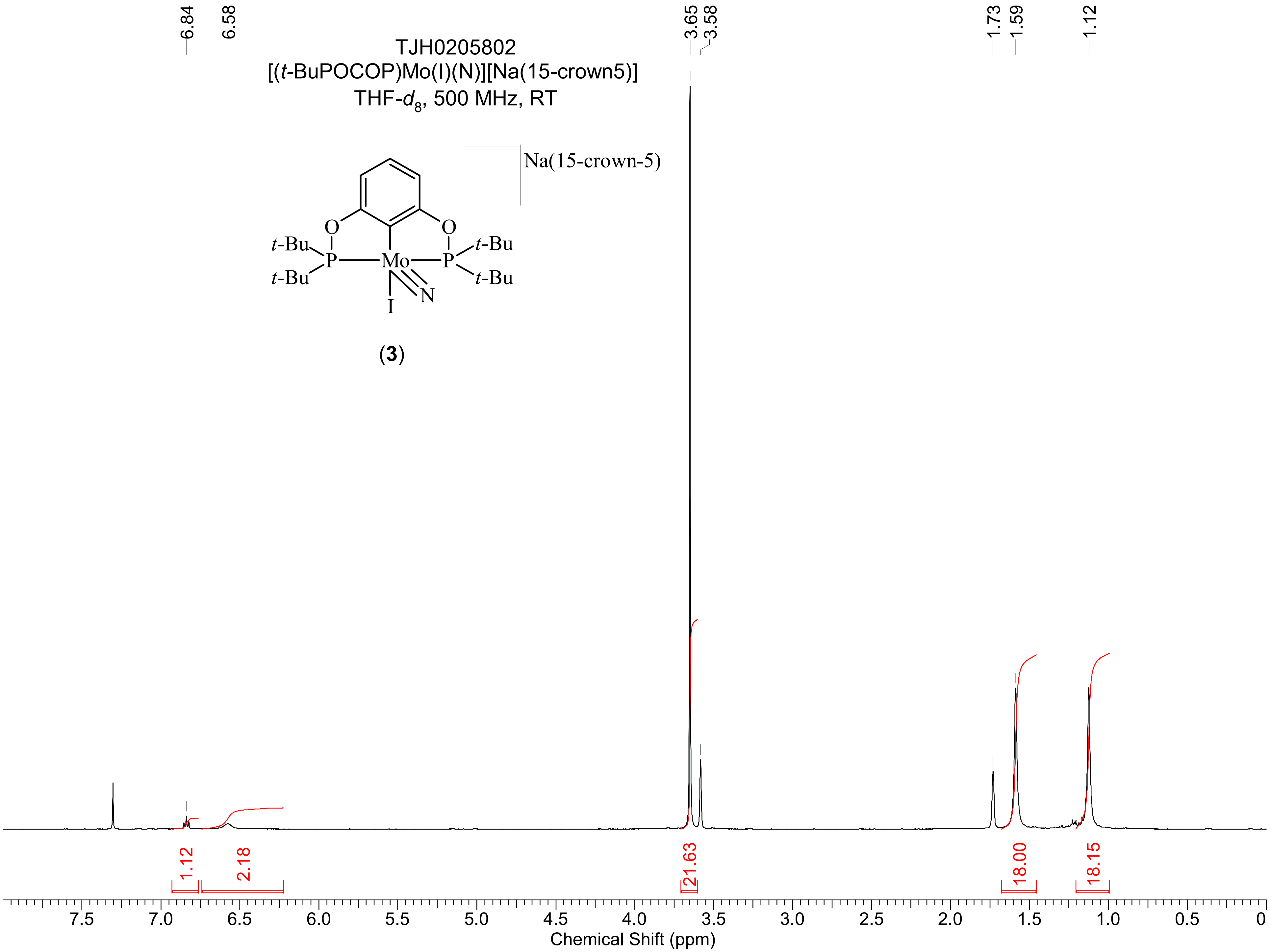
TJH0300203
(t-BuPOCOP)MoI$_2$
THF-d_8, 500 MHz, RT

(**1**)

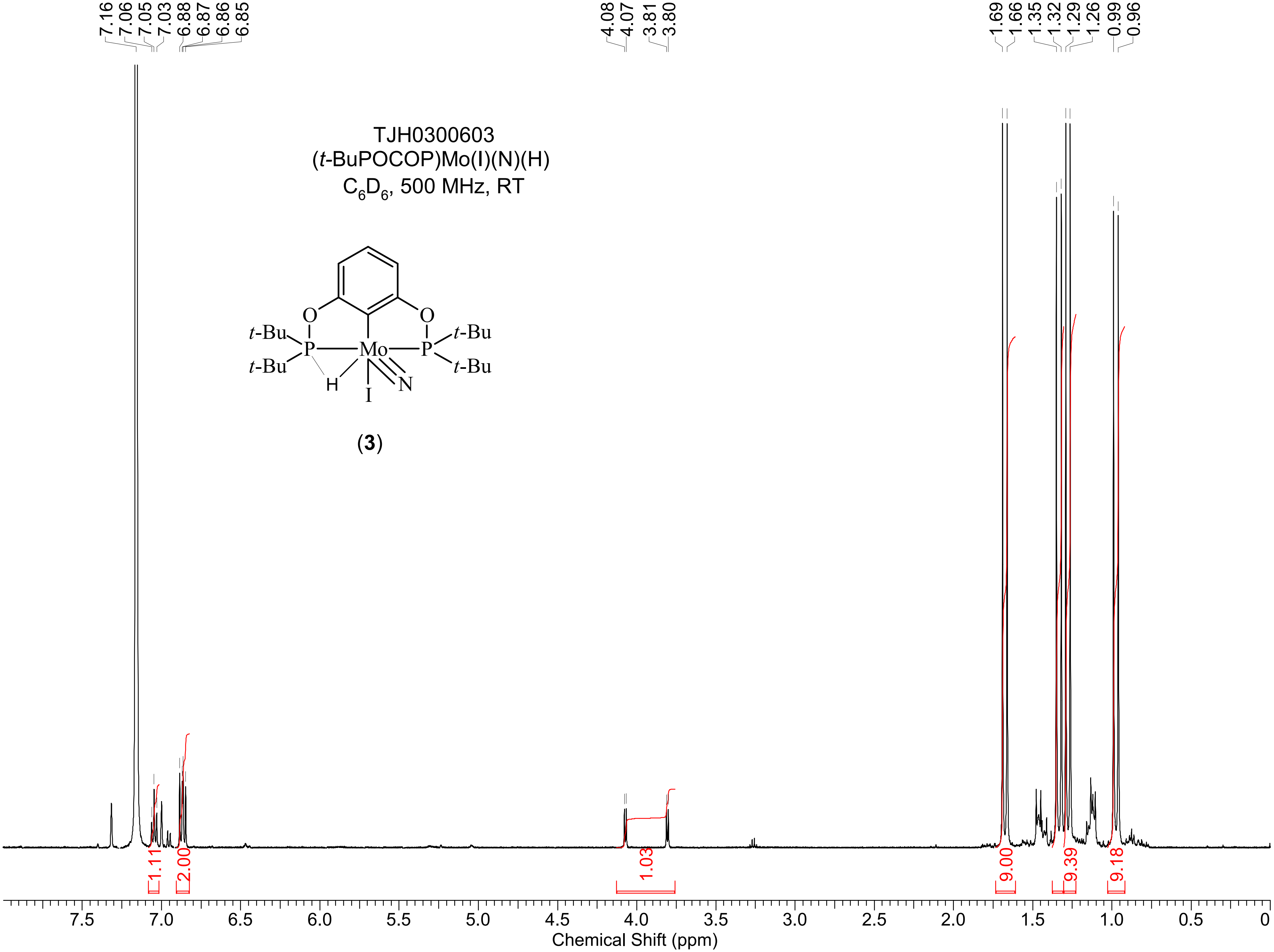

TJH0303303
(t-BuPOCOP)Mo(I)(O)
THF-d_8, 500 MHz, RT
residual
benzene
1.20
1.23
1.56
1.58
1.59
1.73
3.59
6.90
6.92
7.30
7.35
7.37
7.38
19.85
18.00
1.90
1.27
t-Bu
t-Bu
t-Bu
t-Bu
O
O
P
P
Mo
O
I
Chemical Shift (ppm)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

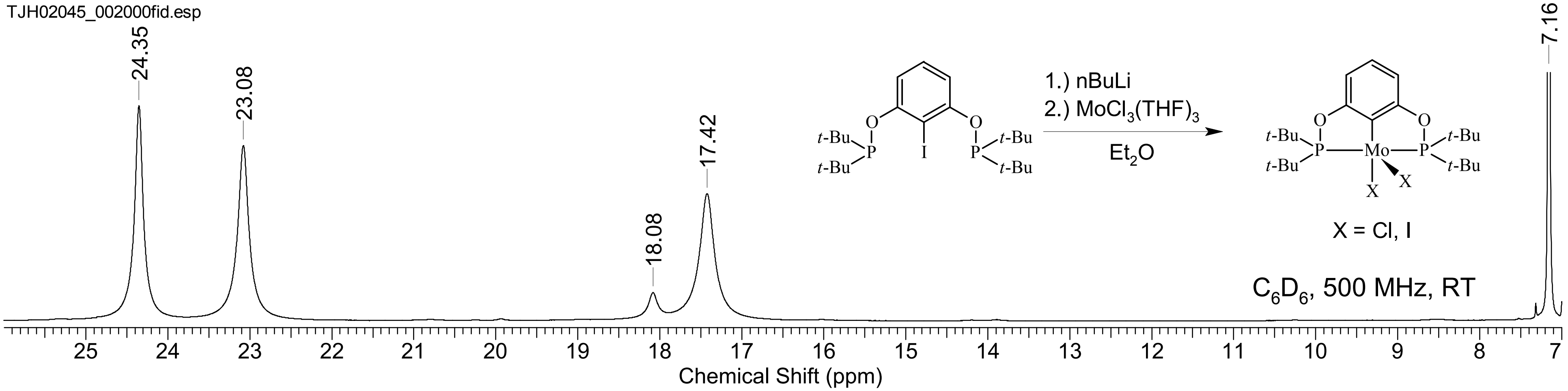
(2)

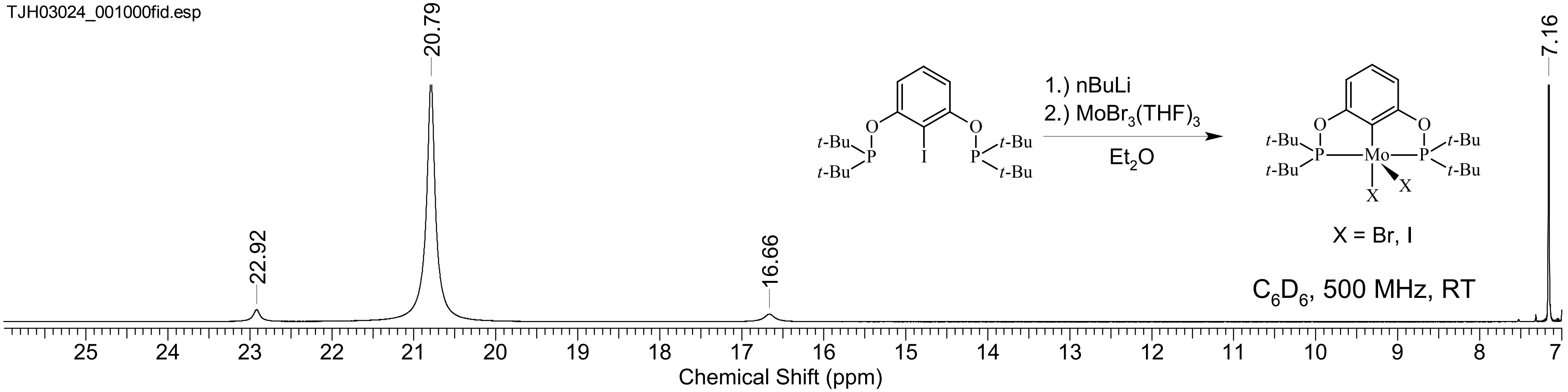

TJH0204502
(t-BuPOCOP)MoX$_2$
(X = Cl, I)
C$_6$D$_6$, 500 MHz, RT
t-Bu
t-Bu
O
P
Mo
X
X
-209.67
-180.29
17.42
18.08
23.08
24.35
7.16
17.42
18.08
23.08
24.35
90.21
96.62
97.78
4.99
1.00
5.34
5.24
16
18
20
22
24
26
Chemical Shift (ppm)
-300
-280
-260
-240
-220
-200
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
Chemical Shift (ppm)

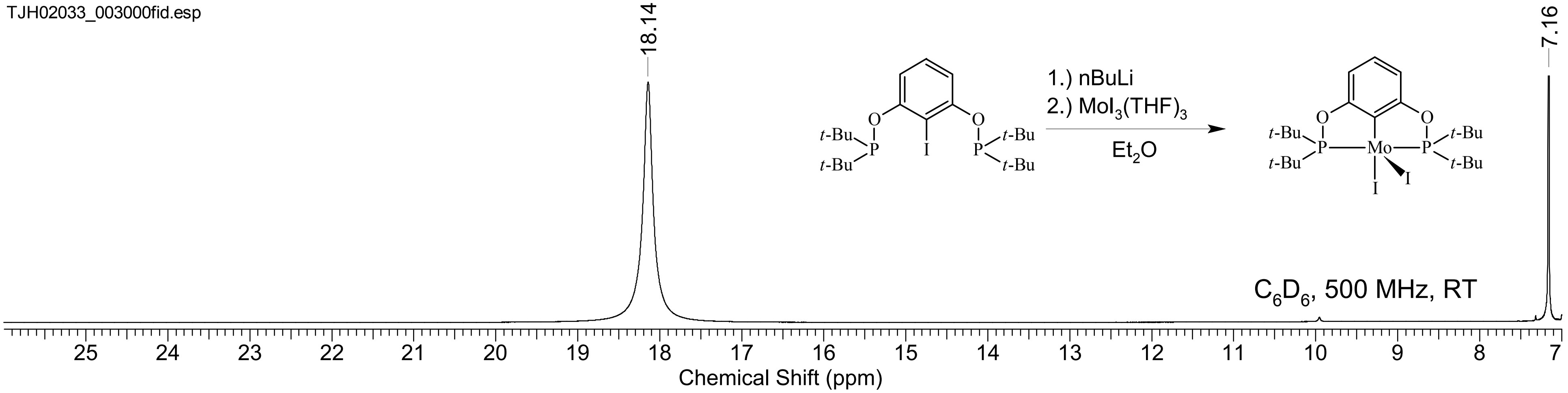

TJH0205802
[(t-BuPOCOP)Mo(I)(N)][Na(15-crown5)]
THF-d_8, 500 MHz, RT
Na(15-crown-5)
O
O
t-Bu
t-Bu
t-Bu
t-Bu
P
P
Mo
N
I
6.84
6.58
3.65
3.58
1.73
1.59
1.12
1.12
2.18
21.63
18.00
18.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

(**3**)


TJH0300603
(*t*-BuPOCOP)Mo(I)(N)(H)
C_6D_6, 500 MHz, RT
(**3**)
t-Bu
t-Bu
t-Bu
t-Bu
O
O
P
P
Mo
H
I
N
7.16
7.06
7.05
7.03
6.88
6.87
6.86
6.85
4.08
4.07
3.81
3.80
1.69
1.66
1.35
1.32
1.29
1.26
0.99
0.96
1.11
2.00
1.03
9.00
9.39
9.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


TJH02045_002000fid.esp
24.35
23.08
18.08
17.42
7.16
1.) nBuLi
2.) $MoCl_3(THF)_3$
Et_2O
t-Bu
P
O
I
Mo
X
X = Cl, I
C_6D_6, 500 MHz, RT
25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7
Chemical Shift (ppm)


TJH03024_001000fid.esp
22.92
20.79
16.66
7.16
1.) nBuLi
2.) $MoBr_3(THF)_3$
Et_2O
t-Bu
P
O
I
Mo
X
X = Br, I
C_6D_6, 500 MHz, RT
25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7
Chemical Shift (ppm)


TJH02033_003000fid.esp
18.14
7.16
1.) nBuLi
2.) $MoI_3(THF)_3$
Et_2O
t-Bu
P
O
I
Mo
C_6D_6, 500 MHz, RT
25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7
Chemical Shift (ppm)