# Supplementary Information

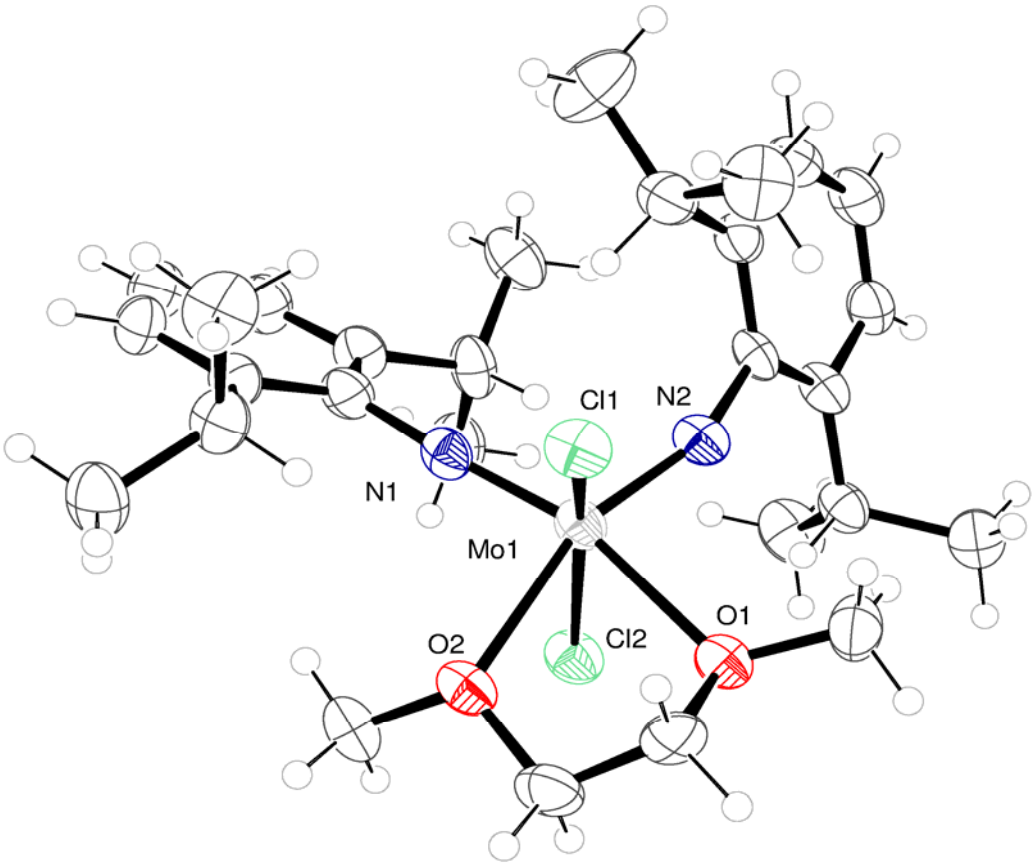
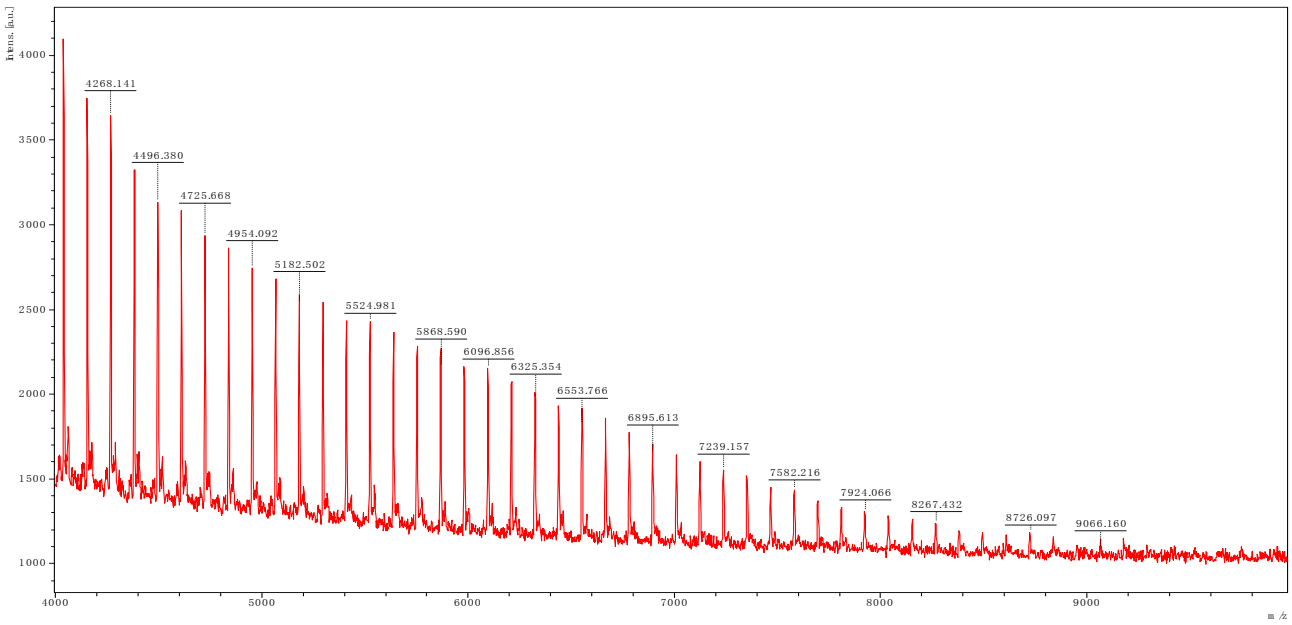
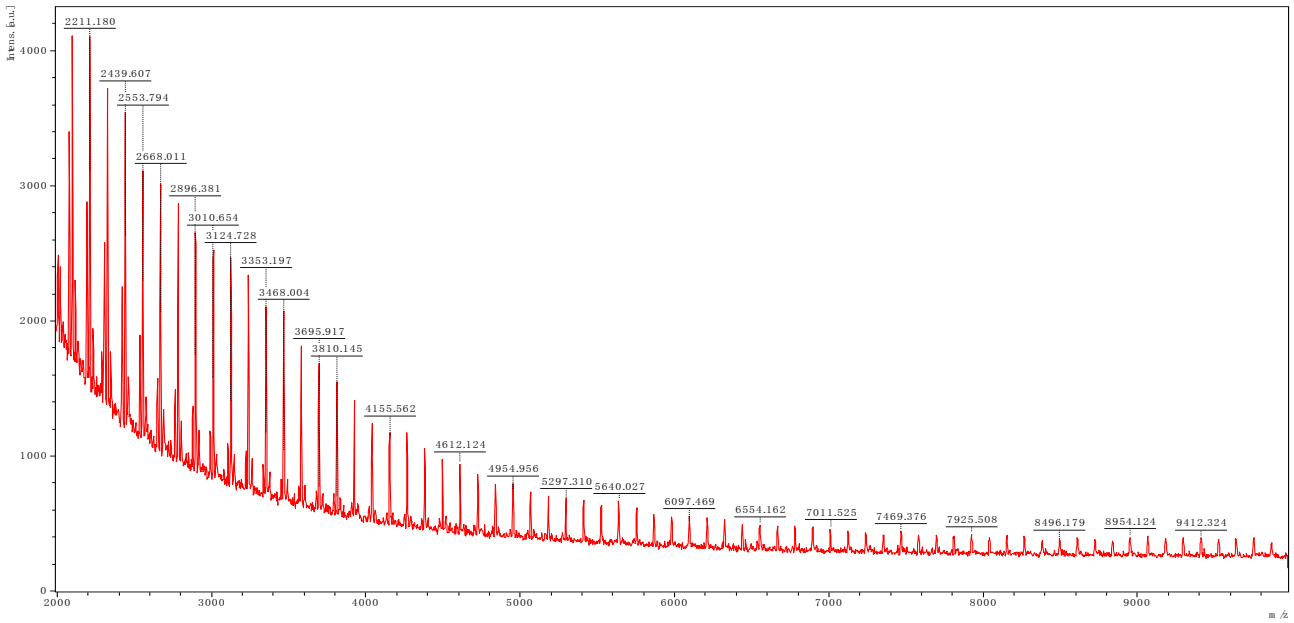



**Figure S1.** Molecular structure of **8**.



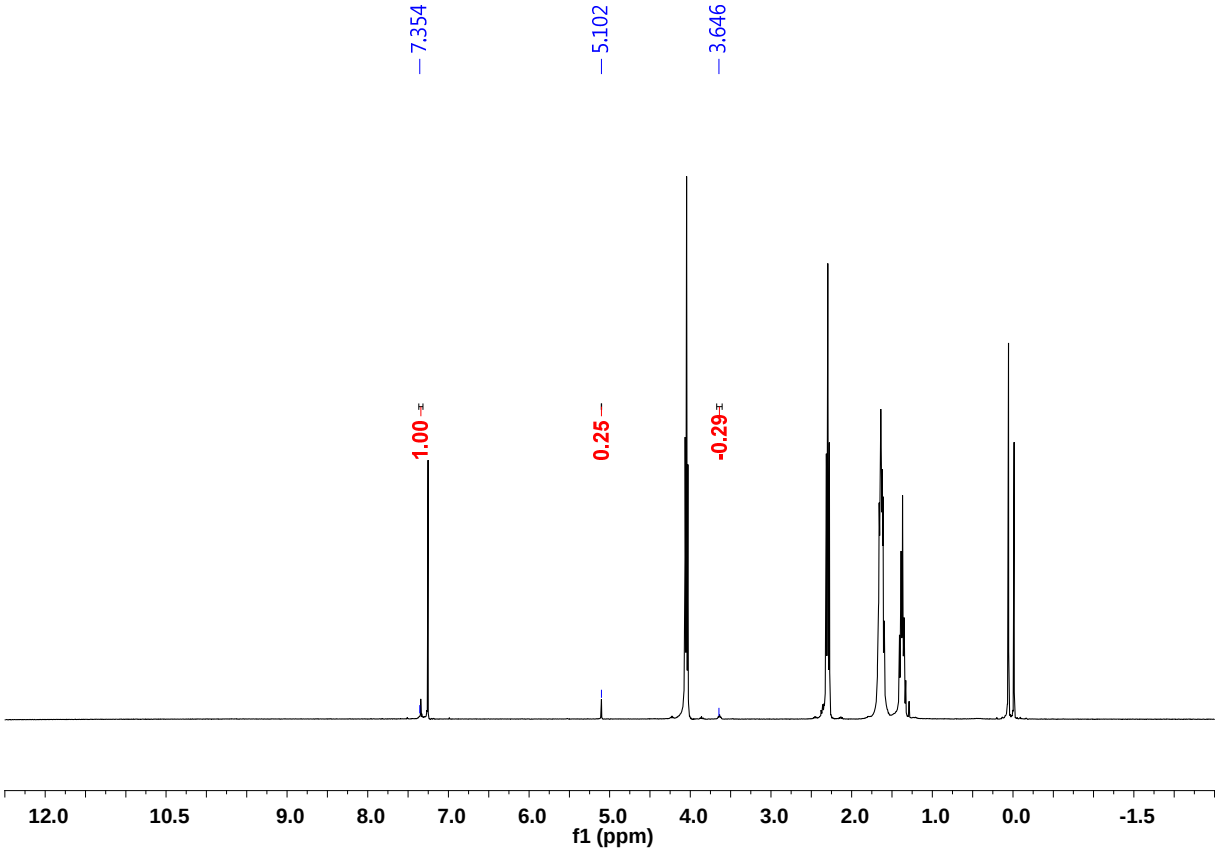

(**a**)

**Figure S2.** *Cont.*



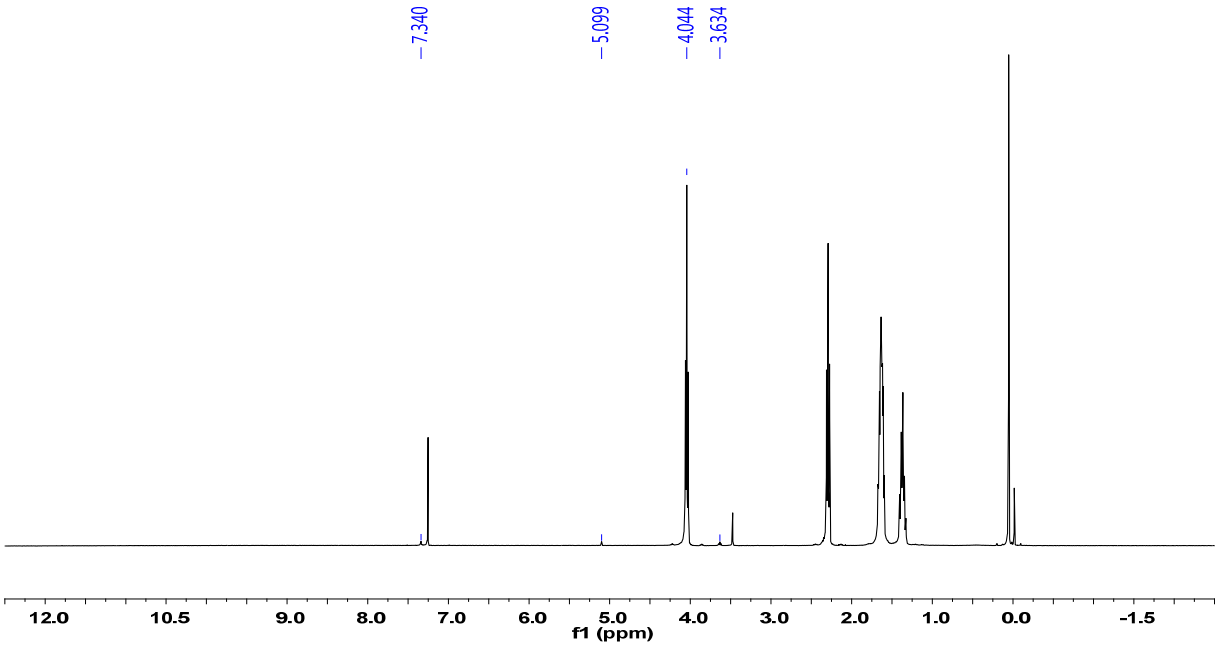

(**b**)

**Figure S2.** MALDI-ToF spectra for PCL from (**a**) **1** and (**b**) **5**.




(**a**)

**Figure S3.** *Cont.*




(**b**)

**Figure S3.** $^{1}$H NMR spectra for PCL from (**a**) **1** and (**b**) **5**.

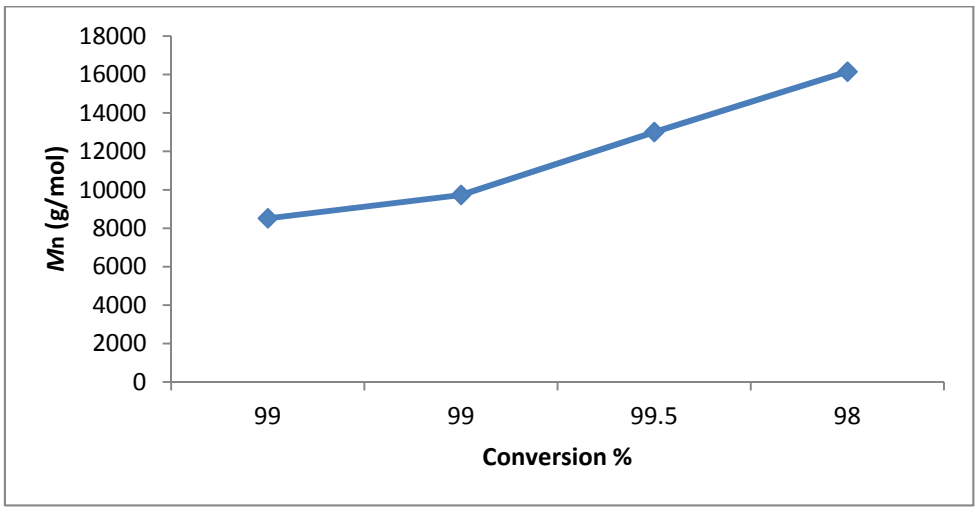



**Figure S4.** Plot of monomer conversion *versus* number average molecular weight for **3**.

**Table S1.** Crystal data for **8**.

| Empirical formula | $C_{28}\ H_{44}\ Cl_2\ Mo\ N_2\ O_2$ |
|---|---|
| Formula weight | 607.49 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | *P*-1 |
| Unit cell dimensions | |
| a = 10.0491(10) Å | α = 92.902(9)° |
| b = 10.6022(11) Å | β = 90.577(9)° |
| c = 15.6133(19) Å | γ = 112.932(8)° |
| Volume | 1529.2(3) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.319 $Mg/m^3$ |
| Absorption coefficient | 0.629 $mm^{-1}$ |
| F(000) | 636 |
| Crystal size | 0.400 × 0.380 × 0.056 $mm^3$ |
| Theta range for data collection | 2.089 to 26.371° |
| Index ranges | $-12 \le h \le 12, -12 \le k \le 13, -19 \le l \le 19$ |
| Reflections collected | 11706 |
| Independent reflections | 6145 (R(int) = 0.0965) |
| Completeness to theta = 25.242° | 98.2% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.981 and 0.855 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6145/0/326 |
| Goodness-of-fit on $F^2$ | 0.893 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0626, wR2 = 0.1356 |
| R indices (all data) | R1 = 0.1214, wR2 = 0.1556 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.547 and −0.948 e.$Å^{-3}$ |

**Table S2.** Bond lengths (Å) and angles (°) for **8**.

| | | | |
|---|---|---|---|
| Mo(1)-N(1) | 1.735(5) | C(12)-H(12B) | 0.9800 |
| Mo(1)-N(2) | 1.754(5) | C(12)-H(12C) | 0.9800 |
| Mo(1)-O(1) | 2.326(4) | C(3)-H(3) | 0.9500 |
| Mo(1)-Cl(1) | 2.4054(16) | O(1)-C(20) | 1.433(8) |
| Mo(1)-O(2) | 2.408(4) | O(1)-C(21) | 1.458(7) |
| Mo(1)-Cl(2) | 2.4099(16) | O(2)-C(23) | 1.449(8) |
| N(1)-C(1) | 1.408(8) | O(2)-C(22) | 1.459(8) |
| C(6)-C(5) | 1.397(9) | C(21)-C(22) | 1.500(9) |
| C(6)-C(1) | 1.412(8) | C(21)-H(21A) | 0.9900 |
| C(6)-C(10) | 1.515(8) | C(21)-H(21B) | 0.9900 |
| C(1)-C(2) | 1.450(8) | C(22)-H(22A) | 0.9900 |
| C(7)-C(2) | 1.520(9) | C(22)-H(22B) | 0.9900 |

**Table S2.** *Cont.*

| | | | |
|---|---|---|---|
| C(7)-C(9) | 1.532(9) | C(20)-H(20A) | 0.9800 |
| C(7)-C(8) | 1.536(10) | C(20)-H(20B) | 0.9800 |
| C(7)-H(7) | 1.0000 | C(20)-H(20C) | 0.9800 |
| C(2)-C(3) | 1.378(9) | C(23)-H(23A) | 0.9800 |
| C(5)-C(4) | 1.392(9) | C(23)-H(23B) | 0.9800 |
| C(5)-H(5) | 0.9500 | C(23)-H(23C) | 0.9800 |
| C(11)-C(10) | 1.542(10) | N(2)-C(31) | 1.413(7) |
| C(11)-H(11A) | 0.9800 | C(32)-C(33) | 1.381(8) |
| C(11)-H(11B) | 0.9800 | C(32)-C(31) | 1.417(8) |
| C(11)-H(11C) | 0.9800 | C(32)-C(37) | 1.513(9) |
| C(10)-C(12) | 1.537(9) | C(36)-C(35) | 1.393(8) |
| C(10)-H(10) | 1.0000 | C(36)-C(31) | 1.422(8) |
| C(4)-C(3) | 1.384(10) | C(36)-C(40) | 1.504(9) |
| C(4)-H(4) | 0.9500 | C(35)-C(34) | 1.391(9) |
| C(9)-H(9A) | 0.9800 | C(35)-H(35) | 0.9500 |
| C(9)-H(9B) | 0.9800 | C(37)-C(38) | 1.517(9) |
| C(9)-H(9C) | 0.9800 | C(37)-C(39) | 1.557(9) |
| C(8)-H(8A) | 0.9800 | C(37)-H(37) | 1.0000 |
| C(8)-H(8B) | 0.9800 | C(40)-C(42) | 1.519(9) |
| C(8)-H(8C) | 0.9800 | C(40)-C(41) | 1.541(10) |
| C(12)-H(12A) | 0.9800 | C(40)-H(40) | 1.0000 |
| C(33)-C(34) | 1.385(10) | N(1)-C(1)-C(2) | 119.1(5) |
| C(33)-H(33) | 0.9500 | C(6)-C(1)-C(2) | 121.7(6) |
| C(34)-H(34) | 0.9500 | C(2)-C(7)-C(9) | 110.5(6) |
| C(39)-H(39A) | 0.9800 | C(2)-C(7)-C(8) | 110.5(5) |
| C(39)-H(39B) | 0.9800 | C(9)-C(7)-C(8) | 111.7(6) |
| C(39)-H(39C) | 0.9800 | C(2)-C(7)-H(7) | 108.0 |
| C(38)-H(38A) | 0.9800 | C(9)-C(7)-H(7) | 108.0 |
| C(38)-H(38B) | 0.9800 | C(8)-C(7)-H(7) | 108.0 |
| C(38)-H(38C) | 0.9800 | C(3)-C(2)-C(1) | 117.3(6) |
| C(41)-H(41A) | 0.9800 | C(3)-C(2)-C(7) | 121.7(6) |
| C(41)-H(41B) | 0.9800 | C(1)-C(2)-C(7) | 121.0(6) |
| C(41)-H(41C) | 0.9800 | C(4)-C(5)-C(6) | 121.6(6) |
| C(42)-H(42A) | 0.9800 | C(4)-C(5)-H(5) | 119.2 |
| C(42)-H(42B) | 0.9800 | C(6)-C(5)-H(5) | 119.2 |
| C(42)-H(42C) | 0.9800 | C(10)-C(11)-H(11A) | 109.5 |
| | | C(10)-C(11)-H(11B) | 109.5 |
| N(1)-Mo(1)-N(2) | 105.2(2) | H(11A)-C(11)-H(11B) | 109.5 |
| N(1)-Mo(1)-O(1) | 163.33(18) | C(10)-C(11)-H(11C) | 109.5 |
| N(2)-Mo(1)-O(1) | 91.47(19) | H(11A)-C(11)-H(11C) | 109.5 |
| N(1)-Mo(1)-Cl(1) | 95.63(17) | H(11B)-C(11)-H(11C) | 109.5 |
| N(2)-Mo(1)-Cl(1) | 98.94(16) | C(6)-C(10)-C(12) | 112.1(6) |
| O(1)-Mo(1)-Cl(1) | 82.01(11) | C(6)-C(10)-C(11) | 109.7(5) |
| N(1)-Mo(1)-O(2) | 93.86(19) | C(12)-C(10)-C(11) | 111.9(6) |
| N(2)-Mo(1)-O(2) | 160.8(2) | C(6)-C(10)-H(10) | 107.6 |
| O(1)-Mo(1)-O(2) | 69.47(15) | C(12)-C(10)-H(10) | 107.6 |

**Table S2.** *Cont.*

| | | | |
|---|---|---|---|
| Cl(1)-Mo(1)-O(2) | 81.09(11) | C(11)-C(10)-H(10) | 107.6 |
| N(1)-Mo(1)-Cl(2) | 94.11(17) | C(3)-C(4)-C(5) | 120.4(6) |
| N(2)-Mo(1)-Cl(2) | 96.86(16) | C(3)-C(4)-H(4) | 119.8 |
| O(1)-Mo(1)-Cl(2) | 83.20(11) | C(5)-C(4)-H(4) | 119.8 |
| Cl(1)-Mo(1)-Cl(2) | 158.57(6) | C(7)-C(9)-H(9A) | 109.5 |
| O(2)-Mo(1)-Cl(2) | 79.24(11) | C(7)-C(9)-H(9B) | 109.5 |
| C(1)-N(1)-Mo(1) | 174.3(4) | H(9A)-C(9)-H(9B) | 109.5 |
| C(5)-C(6)-C(1) | 117.2(5) | C(7)-C(9)-H(9C) | 109.5 |
| C(5)-C(6)-C(10) | 121.5(6) | H(9A)-C(9)-H(9C) | 109.5 |
| C(1)-C(6)-C(10) | 121.2(6) | H(9B)-C(9)-H(9C) | 109.5 |
| N(1)-C(1)-C(6) | 119.1(5) | C(7)-C(8)-H(8A) | 109.5 |
| C(7)-C(8)-H(8B) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 | H(20B)-C(20)-H(20C) | 109.5 |
| C(7)-C(8)-H(8C) | 109.5 | O(2)-C(23)-H(23A) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 | O(2)-C(23)-H(23B) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 | H(23A)-C(23)-H(23B) | 109.5 |
| C(10)-C(12)-H(12A) | 109.5 | O(2)-C(23)-H(23C) | 109.5 |
| C(10)-C(12)-H(12B) | 109.5 | H(23A)-C(23)-H(23C) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 | H(23B)-C(23)-H(23C) | 109.5 |
| C(10)-C(12)-H(12C) | 109.5 | C(31)-N(2)-Mo(1) | 157.8(4) |
| H(12A)-C(12)-H(12C) | 109.5 | C(33)-C(32)-C(31) | 117.2(6) |
| H(12B)-C(12)-H(12C) | 109.5 | C(33)-C(32)-C(37) | 120.4(6) |
| C(2)-C(3)-C(4) | 121.7(6) | C(31)-C(32)-C(37) | 122.4(5) |
| C(2)-C(3)-H(3) | 119.1 | C(35)-C(36)-C(31) | 116.8(6) |
| C(4)-C(3)-H(3) | 119.1 | C(35)-C(36)-C(40) | 121.4(6) |
| C(20)-O(1)-C(21) | 111.4(5) | C(31)-C(36)-C(40) | 121.7(5) |
| C(20)-O(1)-Mo(1) | 120.3(4) | N(2)-C(31)-C(32) | 118.9(5) |
| C(21)-O(1)-Mo(1) | 113.9(3) | N(2)-C(31)-C(36) | 118.9(5) |
| C(23)-O(2)-C(22) | 111.4(5) | C(32)-C(31)-C(36) | 122.3(5) |
| C(23)-O(2)-Mo(1) | 119.9(4) | C(34)-C(35)-C(36) | 121.9(6) |
| C(22)-O(2)-Mo(1) | 113.9(3) | C(34)-C(35)-H(35) | 119.1 |
| O(1)-C(21)-C(22) | 105.4(5) | C(36)-C(35)-H(35) | 119.1 |
| O(1)-C(21)-H(21A) | 110.7 | C(32)-C(37)-C(38) | 111.9(6) |
| C(22)-C(21)-H(21A) | 110.7 | C(32)-C(37)-C(39) | 111.9(5) |
| O(1)-C(21)-H(21B) | 110.7 | C(38)-C(37)-C(39) | 110.9(6) |
| C(22)-C(21)-H(21B) | 110.7 | C(32)-C(37)-H(37) | 107.3 |
| H(21A)-C(21)-H(21B) | 108.8 | C(38)-C(37)-H(37) | 107.3 |
| O(2)-C(22)-C(21) | 107.5(5) | C(39)-C(37)-H(37) | 107.3 |
| O(2)-C(22)-H(22A) | 110.2 | C(36)-C(40)-C(42) | 114.8(6) |
| C(21)-C(22)-H(22A) | 110.2 | C(36)-C(40)-C(41) | 110.6(6) |
| O(2)-C(22)-H(22B) | 110.2 | C(42)-C(40)-C(41) | 109.4(6) |
| C(21)-C(22)-H(22B) | 110.2 | C(36)-C(40)-H(40) | 107.3 |
| H(22A)-C(22)-H(22B) | 108.5 | C(42)-C(40)-H(40) | 107.3 |
| O(1)-C(20)-H(20A) | 109.5 | C(41)-C(40)-H(40) | 107.3 |
| O(1)-C(20)-H(20B) | 109.5 | C(32)-C(33)-C(34) | 122.3(6) |
| H(20A)-C(20)-H(20B) | 109.5 | C(32)-C(33)-H(33) | 118.9 |

**Table S2.** *Cont.*

| | | | |
|---|---|---|---|
| O(1)-C(20)-H(20C) | 109.5 | C(34)-C(33)-H(33) | 118.9 |
| C(33)-C(34)-C(35) | 119.5(6) | H(38A)-C(38)-H(38C) | 109.5 |
| C(33)-C(34)-H(34) | 120.3 | H(38B)-C(38)-H(38C) | 109.5 |
| C(35)-C(34)-H(34) | 120.3 | C(40)-C(41)-H(41A) | 109.5 |
| C(37)-C(39)-H(39A) | 109.5 | C(40)-C(41)-H(41B) | 109.5 |
| C(37)-C(39)-H(39B) | 109.5 | H(41A)-C(41)-H(41B) | 109.5 |
| H(39A)-C(39)-H(39B) | 109.5 | C(40)-C(41)-H(41C) | 109.5 |
| C(37)-C(39)-H(39C) | 109.5 | H(41A)-C(41)-H(41C) | 109.5 |
| H(39A)-C(39)-H(39C) | 109.5 | H(41B)-C(41)-H(41C) | 109.5 |
| H(39B)-C(39)-H(39C) | 109.5 | C(40)-C(42)-H(42A) | 109.5 |
| C(37)-C(38)-H(38A) | 109.5 | C(40)-C(42)-H(42B) | 109.5 |
| C(37)-C(38)-H(38B) | 109.5 | H(42A)-C(42)-H(42B) | 109.5 |
| H(38A)-C(38)-H(38B) | 109.5 | C(40)-C(42)-H(42C) | 109.5 |
| C(37)-C(38)-H(38C) | 109.5 | H(42A)-C(42)-H(42C) | 109.5 |
| H(42B)-C(42)-H(42C) | 109.5 | | |

Symmetry transformations used to generate equivalent atoms.