N-Oxides Amplify Catalyst Reactivity and Isoselectivity in the Ring-Opening Polymerization of *rac*-β-Butyrolactone

Xiang Dong,[a] Alexander M. Brown,[a] Audra J. Woodside,[a] Jerome R. Robinson*[a]

[a] 324 Brook St., Department of Chemistry, Brown University, Providence, RI 02912, United States
Phone: (+1)-401-863-3249; e-mail: jerome_robinson@brown.edu

Supporting Information

1. General Methods.

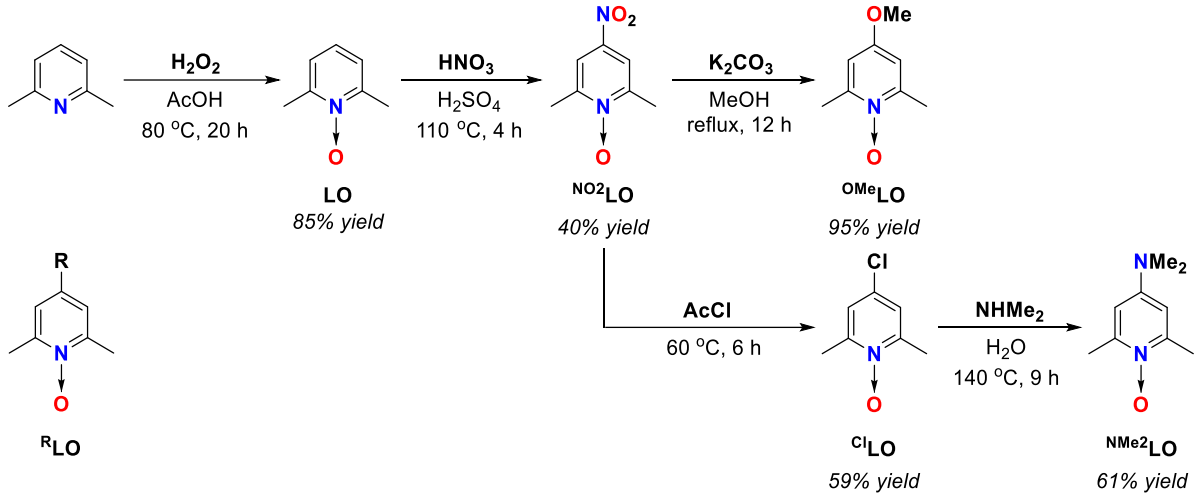
Instruments and measurements: Unless specified, all reactions were performed under inert conditions (N_2) using standard Schlenk techniques or in a MBraun drybox equipped with a standard catalyst purifier and solvent trap. Glassware was oven-dried for at least 2 h at 150 °C prior to use. Celite and 3 Å molecular sieves were heated under reduced pressure at 300 °C for at least 24 h and then cooled under vacuum prior to use. The following spectrometers were used for NMR characterization: Bruker Avance III HD Ascend (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 243 MHz) and a Bruker DRX (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz). ^{1}H- and ^{13}C-NMR shifts are referenced relative to the solvent signal ($CDCl_3$: ^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm; C_6D_6: ^{1}H: 7.16 ppm, ^{13}C: 128.06 ppm), while ^{31}P-NMR shifts are referenced relative to external solution standards (H_3PO_4, 0 ppm). Both instruments were equipped with Z-gradient BBFO probes. Polymer tacticity (P_m, percentage of *meso* diads) was measured using a ^{13}C inverse-gated pulse sequence, followed by integration of the *C*=O resonances (Figure S7).

Gel permeation chromatography (GPC) measurements were performed using an Agilent 1260 equipped with two Poroshell 120 EC-C18 columns heated at 35 °C (4.6 x 100 mm, 2.7 μm) and a UV-vis diode-array detector and refractive detector. The eluent was inhibitor-free THF, and the system was calibrated with standard polystyrene standards ranging from 580 to 1,500,000 Da. Reported molecular weights are those obtained from GPC corrected by a Mark-Houwink factor of 0.54.[1] Unless stated otherwise, all GPC samples were of the quenched crude reaction mixtures (not precipitated or purified polymers). Elemental analyses were performed by CENTC Elemental Analysis Facility at University of Rochester (Rochester, NY) for air-sensitive compounds (**1-RE** and **1-RE(OPPh$_3$)$_2$**) respectively. Samples were shipped in a sealed 2 mL vial that was placed in a 20 mL scintillation vial and sealed, which were then placed in a vacuum-sealed plastic bag.

Materials: Tetrahydrofuran, diethyl ether, toluene, hexanes, and pentane were purchased from Fisher Scientific. Solvents were sparged for 20 min with dry Ar and dried using a commercial two-column solvent purification system (LC Technologies). Solvents were further dried by storing them over 3 Å molecular sieves for at least 48 h prior to use. Ultrapure, deionized water (18.2 MΩ) was obtained from a Millipore Direct-Q 3 UV Water Purification System. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. C_6D_6 was degassed with 3 freeze-pump-thaw cycles and stored over 3 Å molecular sieves for at least 48 h prior to use. Qualitative assessment of moisture-content in these solvents was performed by adding 1 drop of a concentrated solution of a sodium benzophenone radical anion (purple) to 10 mL of solvent where maintenance of a dark blue color for at least 5 minutes was sufficient for use.

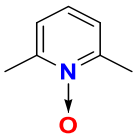
2,6-ditertbutyl phenol (Oakwood Chemical; 99% purity), para-formaldehyde (Alfa Aesar; 97% purity), benzylamine (TCI; 99% purity), triphenylphosphine oxide (Acros; 99% purity), hexamethylphosphoramide (TCI; 98% purity), triphenylphosphate (Sigma-Aldrich; 99% purity), potassium hexamethyldisilazide (Sigma-Aldrich; 95% purity), 1,1,3,3-tetramethyldisilazane (TCI, 97% purity), $LaCl_3$ (Strem; RE = La; 99.9% purity), and acetyl chloride (Acros; 99% purity) were purchased and used as received. Racemic butyrolactone (Sigma-Aldrich; 98% purity) was freshly distilled from CaH_2 under nitrogen and degassed by freeze-pump-thaw cycles prior to use. La[N(SiMe$_3$)$_2$]$_3$,[2] La[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$,[3] **^{Bn}L**, **1-La**, **1-La(OPPh$_3$)$_2$**,[4] were prepared according to reported procedures.

2. Synthetic Details and Characterization.



Scheme S1. Synthesis of 4-substituted lutidine-oxides (**^{R}LO**).

2,6-Lutidine-1-oxide (LO)



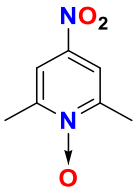
H_2O_2 (20 mL, 174 mmol, 2.0 equiv., 27% in H_2O, 1.10 g/mL; MW = 34.01 g•mol^{-1}) was added to a stirring solution of 2,6-lutidine (9.30 g, 86.8 mmol, 1.0 equiv.; MW = 107.16 g•mol^{-1}) in AcOH (25 mL, 434 mmol, 5.0 equiv., 1.05 g/mL; MW = 60.05 g•mol^{-1}) in a 250 mL round-bottomed flask equipped with a Vigreux condenser. The reaction was heated at 80 °C for 20 h. A saturated $Na_2S_2O_5$ solution (10 mL) was added to the reaction to quench residual peroxide. The reaction was concentrated to ca. 25 mL at 60 °C under reduced pressure (ca. 0.5 Torr). The pH of the mixture was adjusted to 12 with a 25% NaOH solution. The mixture was extracted with CH_2Cl_2 (6 x 20 mL). The combined extraction was dried with Na_2SO_4, filtered, and evaporated under reduced pressure. **2,6-Lutidine-1-oxide** was obtained as a colorless oil. Yield: 9.10 g (20.3 mmol, 85% yield; MW: 123.16 g•mol^{-1}). The ^{1}H-NMR spectrum agrees with the previous report.[5]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.52 (s, 6H; Me), 7.05 (dd, *J* = 8.4, 7.6 Hz, 2H; 3,5-H), 7.12 (d, *J* = 7.6 Hz, 1H; 4-H);

^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 2.31 (s, 6H; Me), 6.28 (t, *J* = 7.6 Hz, 2H; 3,5-H), 6.39 (d, *J* = 7.6 Hz, 1H; 4-H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 18.18 ($\underline{C}H_3$), 122.58 (*m*-$\underline{C}$H), 124.03 (*p*-$\underline{C}$H), 148.47 ($\underline{C}CH_3$).

4-Nitro-2,6-lutidine-1-oxide (^{NO2}LO)



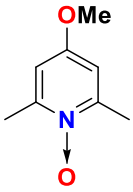
H_2SO_4 (6.2 mL 114 mmol, 3.0 equiv., 98%, 1.84 g/mL; MW = 98.07 g•mol^{-1}) was added to 2,6-lutidine-1-oxide (4.66 g 37.8 mmol, 1.0 equiv.; MW = 123.16 g•mol^{-1}) in a 250 mL round-bottomed flask equipped with a Vigreux condenser. HNO_3 (4.8 mL 76 mmol, 2.0 equiv., 70% in water, 1.41 g/mL; MW = 63.01 g•mol^{-1}) was added dropwise. The reaction was heated at 110 ºC for 4 h and allowed to warm to RT. The flask was then cooled in an ice bath, and water (50 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layer was washed with saturated Na_2CO_3 solution (2 x 25 mL) and water (2 x 25 mL), dried with Na_2SO_4, filtered, and dried under reduced pressure. The resulting solid was washed with pentane (3 x 20 mL) and dried under reduced pressure. **4-Nitro-2,6-lutidine-1-oxide** was obtained as a light-yellow solid. Yield: 2.53 g (15.1 mmol, 40% yield; MW: 168.15 g•mol^{-1}). The ^{1}H-NMR spectrum agrees with the previous report.[5]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.58 (s, 6H; Me), 8.03 (s, 2H; 3,5-H);

^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.92 (s, 6H; Me), 7.14 (s, 2H; 3,5-H).

^{13}C{^{1}H} -NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 18.43 ($\underline{C}H_3$), 117.88 ($\underline{C}H$), 123.93 ($\underline{C}CH_3$), 150.22 ($\underline{C}NO_2$).

4-Methoxy-2,6-lutidine-1-oxide (^{OMe}LO)



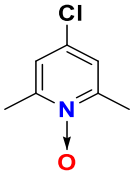
K_2CO_3 (2.38 g 17.3 mmol, 2.0 equiv.; MW = 138.20 g•mol^{-1}) was added to a suspension of 4-nitro-2,6-lutidine-1-oxide (1.45 g 8.62 mmol, 1.0 equiv.; MW = 168.15 g•mol^{-1}) in 15 mL MeOH in a 250 mL round-bottomed flask equipped with a Vigreux condenser. The reaction was heated in an oil bath at 70 ºC for 12 h and allowed to reflux. The mixture was cooled and concentrated to ca. 10 mL under reduced pressure. Water (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined extraction was dried with Na_2SO_4, filtered, and dried under reduced pressure. **4-Methoxy-2,6-lutidine-1-oxide** was obtained as a white solid. Yield: 1.25 g (8.16 mmol, 95% yield; MW: 153.18 g•mol^{-1}). The ^{1}H-NMR spectrum agrees with the previous report.[5]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.53 (s, 6H; ArMe), 3.81 (s, 3H; OMe), 6.69 (s, 2H; 3,5-H).

^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 2.37 (s, 6H; ArMe), 3.01 (s, 3H; OMe), 6.15 (s, 2H; 3,5-H).

^{13}C{^{1}H}-NMR (101 MHz, C_6D_6, 298 K): δ (ppm) = 18.80 ($\underline{C}H_3$), 55.32 (O$\underline{C}H_3$), 109.60 ($\underline{C}$H), 149.09 ($\underline{C}CH_3$), 154.58 ($\underline{C}OCH_3$).

4-Chloro-2,6-lutidine-1-oxide (^{Cl}LO)



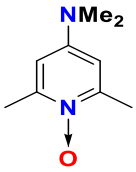
A 250 mL round-bottomed flask was charged with 4-nitro-2,6-lutidine-1-oxide (3.33 g 19.8 mmol, 1.0 equiv.; MW = 168.15 g•mol^{-1}) and AcCl (21 mL, 297 mmol, 15 equiv., 1.10 g/mL; MW = 78.50 g•mol^{-1}) and equipped with a Vigreux condenser. The suspension was heated for 6 h in an oil bath at 60 °C and allowed to reflux. The precipitated solid was isolated by vacuum filtration, washed with acetone (3 x 5 mL), and then dissolved in CH_2Cl_2 (15 mL). The solution was washed with 10% NaOH solution (15 mL) and water (15 mL). The organic layer was dried with Na_2SO_4, filtered, and dried under reduced pressure. **4-Chloro-2,6-lutidine-1-oxide** was obtained as a white solid. Yield: 1.85 g (11.7 mmol, 59% yield; MW: 157.60 g•mol^{-1}). The ^{1}H-NMR spectrum agrees with the previous report.[5]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.49 (s, 6H; ArMe), 7.14 (s, 2H; 3,5-H);

^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 2.10 (s, 6H; ArMe), 6.32 (s, 2H; 3,5-H).

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 18.38 ($\underline{C}H_3$), 124.08 ($\underline{C}$H), 130.30 ($\underline{C}$Cl), 150.09 ($\underline{C}CH_3$).

4-Dimethylamino-2,6-lutidine-1-oxide (^{NMe2}LO)

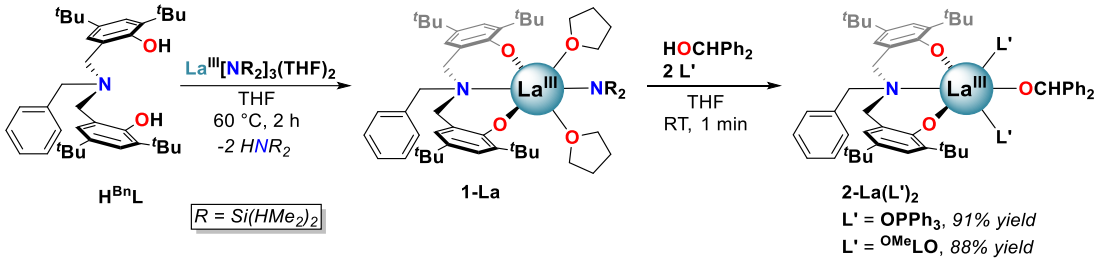


4-Chloro-2,6-lutidine-1-oxide (400 mg, 2.54 mmol, 1.0 equiv.; MW = 157.60 g•mol^{-1}) was added to an aqueous solution of $NHMe_2$ (4.8 mL, 38.1 mmol, 15 equiv., 40% in H_2O, 0.89 g/mL; MW = 45.09 g•mol^{-1}) in a 50 mL sealed vessel. The reaction vessel was heated for 9 h at 140 °C, and then allowed to cool to RT prior to opening. Water (5 mL) was added and the reaction mixture and was extracted with CH_2Cl_2 (9 x 10 mL). The combined extraction was dried with Na_2SO_4, filtered, and evaporated under reduced pressure to yield the crude product as a brown oil. Toluene (5 mL) was added to the crude product, then dried under reduced pressure, followed by CH_2Cl_2 (5 mL). Volatiles were removed under reduced pressure. **4-Dimethylamino-2,6-lutidine-1-oxide** was obtained as a white solid. Yield: 256 mg (1.54 mmol, 61% yield; MW: 166.22 g•mol^{-1}).

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 2.43 (s, 3H; ArMe), 2.92 (s, 6H; NMe_2), 6.30 (s, 2H; 3,5-H);

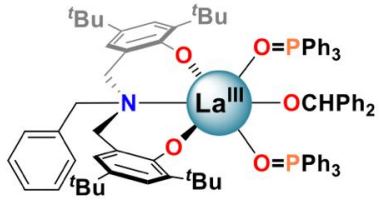
^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 2.18 (s, 3H; NMe_2), 2.53 (s, 6H; ArMe), 5.93 (s, 2H; 3,5-H).

^{13}C{^{1}H}-NMR (101 MHz, C_6D_6, 298 K): δ (ppm) = 18.89 ($\underline{C}H_3$), 38.90 (N$\underline{C}H_3$), 106.72 ($\underline{C}$H), 144.83 ($\underline{C}$N), 147.78 ($\underline{C}CH_3$).



Scheme S2. Synthesis of La complexes.

La(^{Bn}L)(OCHPh$_2$)(OPPh$_3$)$_2$ [2-La(OPPh$_3$)$_2$]



A 20 mL scintillation vial was charged with **H^{Bn}L** (304 mg, 0.56 mmol, 1.0 equiv.; MW: 543.84 g•mol^{-1}), a Teflon-coated stir-bar, and THF (2 mL). To the stirring, clear, and colorless solution, La[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (380 mg, 0.56 mmol, 1.0 equiv.; MW: 680.12 g•mol^{-1}) was added. The solution was heated at 60 °C for 2 h and conversion to **1-La** was confirmed by H-NMR analysis of a reaction aliquot. After the solution was cooled to RT, HOCHPh$_2$ (103 mg, 0.56 mmol, 1.0 equiv.; MW: 184.24 g•mol^{-1}) and OPPh$_3$ (311 mg, 1.12 mmol, 2.0 equiv.; MW: 278.29 g•mol^{-1}) was added. The solution was stirred for 1 min, and then all volatiles were removed under reduced pressure. The resulting solid was triturated with toluene (2 x 2 mL), washed with pentane (2 x 3 mL), and dried under reduced pressure to afford **2-La(OPPh$_3$)$_2$** as a white solid. Yield: 725 mg (0.51 mmol, 91% yield; MW: 1420.54 g•mol^{-1}).

^{1}H-NMR (400 MHz, C_6D_6, 298 K): δ (ppm) = 1.58 (s, 18H; 4-^{t}Bu), 1.71 (s, 18H; 2-^{t}Bu), 3.35 (d, ^{2}J = 12.3 Hz, 2H; N$\underline{CH_2}$ArO), 3.87 (s, 2H; N$\underline{CH_2}$Bn), 4.12 (d, ^{2}J = 12.3 Hz, 2H; N$\underline{CH_2}$ArO), 6.25 (s, 1H; O$\underline{CH}$Ph$_2$), 6.86-6.91 (m, 12H; *m*-H$_{OPPh3}$), 6.97-7.09 (m, 13H; *p*-H$_{OPPh3}$, 5-H$_{ArO}$, H$_{Ph}$), 7.11-7.17 (m, 4H; H$_{Ph}$), 7.21 (d, *J* = 7.3 Hz, H$_{Bn}$), 7.56-7.61 (m, 14H; *o*-H$_{OPPh3}$, 3-H$_{ArO}$), 7.76 (d, *J* = 7.4 Hz, 4H; *o*-H$_{OCHPh2}$);

^{13}C{^{1}H}-NMR (101 MHz, C_6D_6, 298 K): δ (ppm) = 30.6 (C$\underline{Me_3}$), 32.5 (C$\underline{Me_3}$), 34.3 ($\underline{C}$Me$_3$), 35.8 ($\underline{C}$Me$_3$), 51.4 (N$\underline{C}$H$_2$Bn), 59.9 (N$\underline{C}$H$_2$ArO), 82.4 (O$\underline{C}$HPh$_2$), 123.2, 125.2, 125.5, 126.8, 127.5,

127.8, 127.9 128.2, 128.9 (d, $J_{P(31)\text{-}C(13)}$ = 12.6 Hz; *m*-C_{OPPh_3}), 130.6 (d, $J_{P(31)\text{-}C(13)}$ = 106 Hz; C–P), 132.0, 132.3 (d, $J_{P(31)\text{-}C(13)}$ = 2.2 Hz; *p*-C_{OPPh_3}), 132.8 (d, $J_{P(31)\text{-}C(13)}$ = 10.6 Hz; *o*-C_{OPPh_3}, 133.8, 135.6, 136.7, 151.9 (O-CH-$\underline{C}_{OCHPh_2}$), 164.3 (C_{Ar}–O);

$^{31}P\{^{1}H\}$-NMR (162 MHz, C_6D_6, 298 K): δ (ppm) = 33.8 (br);

Elemental Analysis calcd. (%) for $C_{89}H_{92}LaN_2O_5P_2$: C 72.72, H 6.53, N 0.99; found: C 72.55, H 6.87, N 1.00.

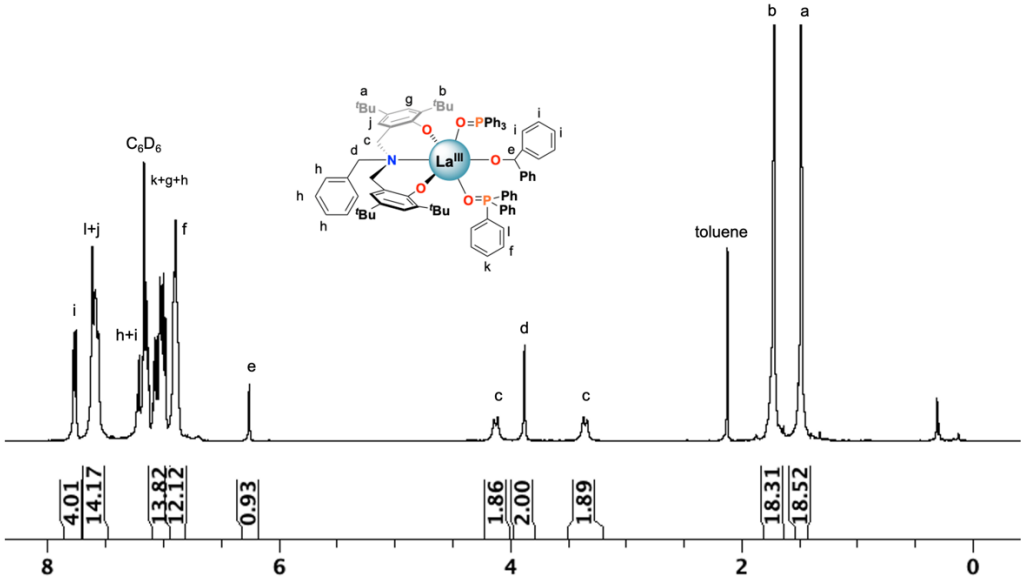


Figure S1a. ^{1}H-NMR (C_6D_6, 400 MHz) spectra of **2-La(OPPh$_3$)$_2$**.

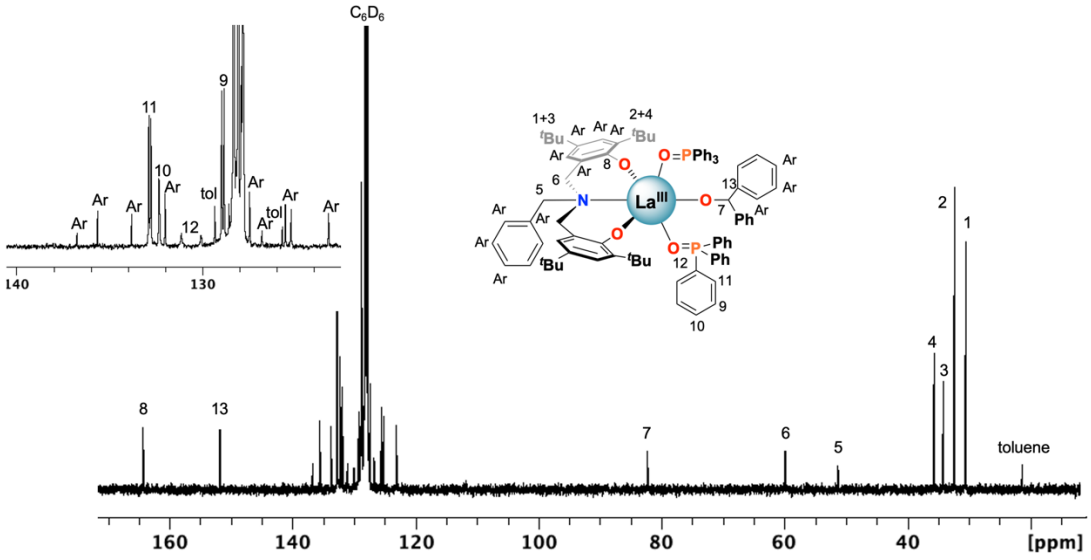


Figure S1b. $^{13}C\{^{1}H\}$- NMR (C_6D_6, 101 MHz) spectra of **2-La(OPPh$_3$)$_2$.**

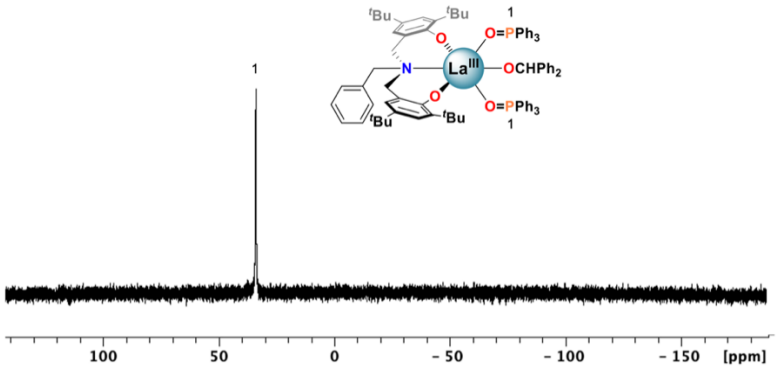
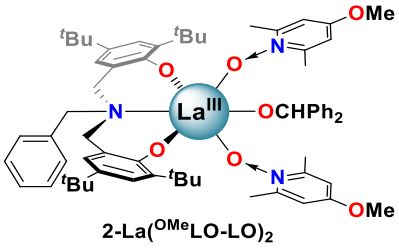


Figure S1c. $^{31}P\{^{1}H\}$-NMR (C_6D_6, 162 MHz) spectra of **2-La(OPPh$_3$)$_2$.**

La(^{Bn}L)(OCHPh$_2$)(^{OMe}LO)$_2$ [2-La(^{OMe}LO)$_2$]



A 20 mL scintillation vial was charged with **H^{Bn}L** (139 mg, 0.26 mmol, 1.0 equiv.; MW: 543.84 g•mol^{-1}), a Teflon-coated stir-bar, and THF (2 mL). To the stirring, clear, and colorless solution, La[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (174 mg, 0.26 mmol, 1.0 equiv.; MW: 680.12 g•mol^{-1}) was added. The solution was heated at 60 °C for 2 h and conversion to **1-La** was confirmed by H-NMR analysis of a reaction aliquot. After the solution was cooled to RT, Ph$_2$CHOH (47 mg, 0.26 mmol, 1.0 equiv.; MW: 184.24 g•mol^{-1}) and 4-MeO-LO (78 mg, 10.51 mmol, 2.0 equiv.; MW: 153.18 g•mol^{-1}) was added. The solution was stirred for 1 min, and then all volatiles were removed under reduced pressure. The resulting solid was washed with cold pentane (2 x 2 mL) and dried under reduced pressure to afford **2-La(^{OMe}LO)$_2$** as a white solid. Yield: 264 mg (0.23 mmol, 88% yield; MW: 1170.32 g•mol^{-1}). **Note**: The product was consistently found to contain ca. 1 equiv. pentane even after drying under reduced pressure (ca. 1 Torr) at RT.

^{1}H-NMR (600 MHz, C_6D_6, 298 K): δ (ppm) = 1.49 (s, 18H; 4-^{t}Bu), 1.91 (s, 18H; 2-^{t}Bu), 2.31 (s, 12H; ArMe$_{OMe-LO}$), 2.85 (s, 6H; OMe), 3.75 (d, ^{2}J = 12.7 Hz, 2H; NC$\underline{H_2}$ArO), 4.26 (s, 2H; NC$\underline{H_2}$Bn), 5.05 (d, br, ^{2}J = 12.7 Hz, 2H; NC$\underline{H_2}$ArO), 5.75 (s, 1H; OC$\underline{H}$Ph$_2$), 5.78 (s, 4H; 3,5-H$_{OMe-LO}$), 6.96 (t, J = 7.2 Hz, 2H; *p*-H$_{OCHPh2}$), 7.10 (t, J = 7.4 Hz, 4H; *m*-H$_{OCHPh2}$), 7.17 (heavily overlapped with C_6D_5H, 1H; *p*-H$_{Bn}$), 7.27 (d, J = 2.4 Hz, 2H; 5-H$_{ArO}$), 7.30 (t, J = 7.2 Hz, 2H; *m*-H$_{Bn}$), 7.45 (d, J = 7.4 Hz, 4H; *o*-H$_{OCHPh2}$), 7.56 (br, 2H; *o*-H$_{Bn}$), 7.67 (d, J = 2.4 Hz, 2H; 3-H$_{ArO}$);

$^{13}C\{^{1}H\}$-NMR (151 MHz, C_6D_6, 298 K): δ (ppm) = 19.38 (Ar$\underline{Me}_{OMe-LO}$), 30.6 (C$\underline{Me_3}$), 32.4 (C$\underline{Me_3}$), 34.3 (C$\underline{Me_3}$), 35.8 (C$\underline{Me_3}$), 50.8 (NC$\underline{H_2}$Bn), 55.0 (OMe), 60.6 (NC$\underline{H_2}$ArO), 81.4 (OC$\underline{H}$Ph$_2$), 109.4 (3,5-C$_{OMe-LO}$), 123.3, 125.3, 125.7, 127.2, 127.3, 127.78 127.81, 128.3, 128.4, 132.5 (2,6-C$_{OMe-LO}$), 134.3, 135.4, 136.6, 150.6 (O-CH-C$_{OCHPh2}$), 158.6 (br, 4-C$_{OMe-LO}$), 164.0 (C$_{Ar}$–O);

Elemental Analysis calcd. (%) for ($C_{66}H_{84}LaN_3O_7$ + C_5H_8): C 68.86, H 7.49, N 3.39; found: C 68.59, H 7.67, N 3.35.

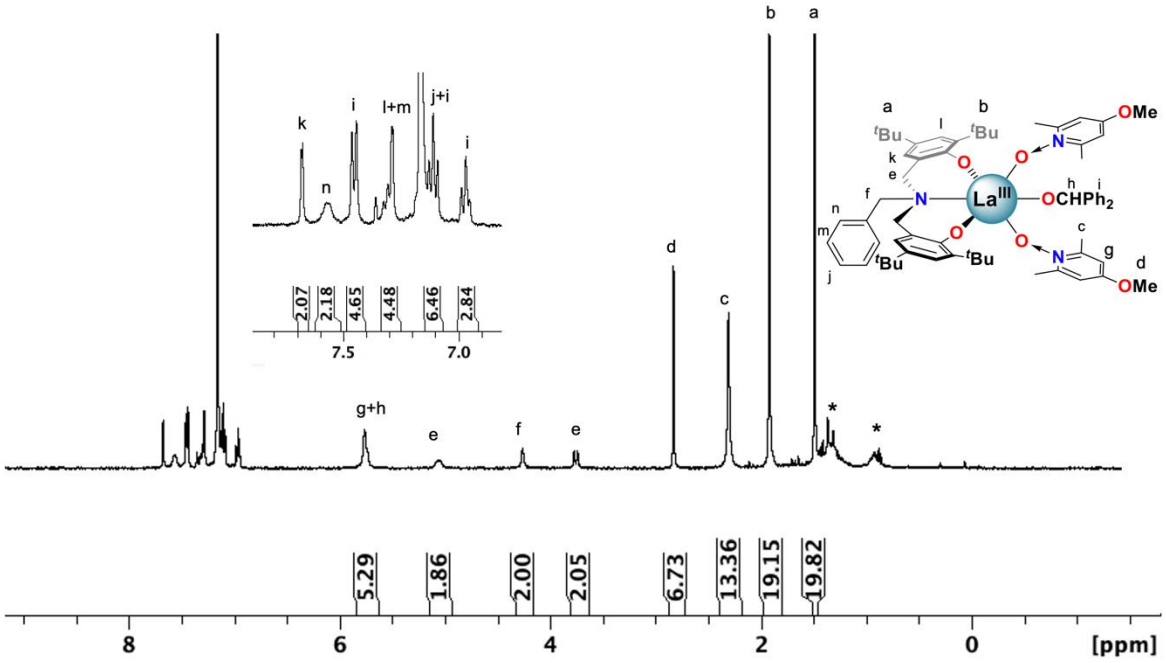


Figure S2a. ^{1}H-NMR (C_6D_6, 600 MHz) spectra of **2-La(^{OMe}LO)$_2$** (*: pentane).

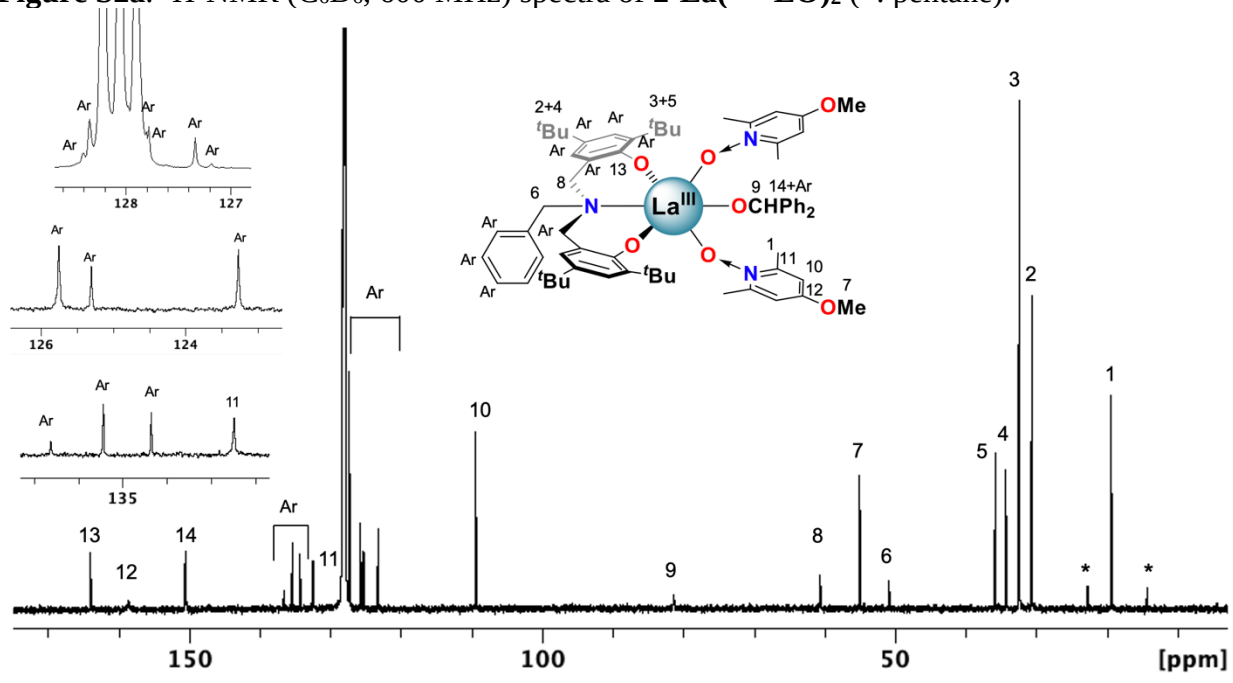


Figure S2b. ^{13}C{^{1}H}-NMR (C_6D_6, 151 MHz) spectra of **2-La(^{OMe}LO)$_2$** (*: pentane)**.**

Table S1. Diffusion coefficients, *D*, and estimated hydrodynamic radii, r_H, measured by ^{1}H DOSY NMR of complexes (**1-La(OPPh$_3$)$_2$, 2-La(OPPh$_3$)$_2$, and 2-La(OMeLO)$_2$**)

Species	D_{Fc} (10^{-10} m^2/s)[a]	D (10^{-10} m^2/s)	D_{Fc}/D	r_H(DOSY)[b] (Å)	r_H(theo.)[c] (Å)
Fc[d]	-	-	-	-	2.166
1-La(OPPh$_3$)$_2$[e]	12.8	4.13	3.10	6.71	6.764
2-La(OPPh$_3$)$_2$	15.3	5.07	3.02	6.54	-
2-La(OMeLO)$_2$	13.5	4.83	2.80	6.05	-

a – DOSY measured diffusion coefficient of ferrocene (Fc) in the experiment of the corresponding complex. DOSY measured diffusion coefficient of the sample *b* – $r_H = D_{Fc}/D_{sample} \cdot r_H$(Fc, theo.). *c* – r_H(theo.) is the average of half lengths of the principal axes of the homogeneous ellipsoid with the same principal moments of inertia of the molecule, which are determined from the crystal structure. *d* – Fc was added to each sample as an internal standard to cancel the fluctuation of temperature and viscosity, of which the diffusion coefficient varies. *e* – From ref. 4. Previously proven to be monomeric in the solid (X-ray diffraction) and solution (DOSY).

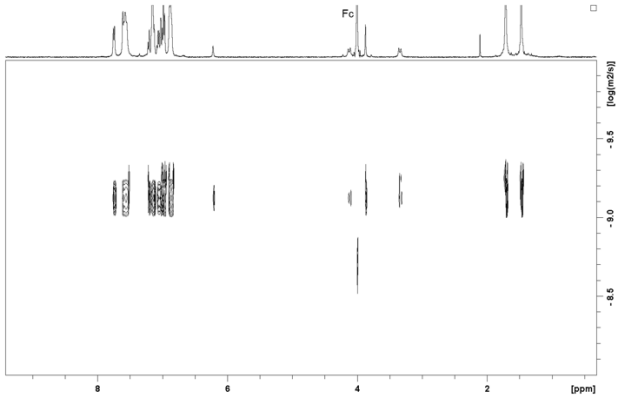


Figure S3. ^{1}H DOSY NMR (400 MHz, C_6D_6) of a mixture of **2-La(OPPh$_3$)$_2$** and ferrocene (Fc). **2-La(OPPh$_3$)$_2$** (14 mg, 0.010 mmol, 1.0 equiv; MW: 1420.54 g•mol^{-1}) and Fc (3.5 mg, 0.019 mmol, 1.9 equiv; MW: 186.04 g•mol^{-1}) were dissolved in 0.5 mL C_6D_6. Diffusion time was (Δ, d20) 100 ms, and the rectangular gradient pulse duration (δ, p30) was 1000 µs.

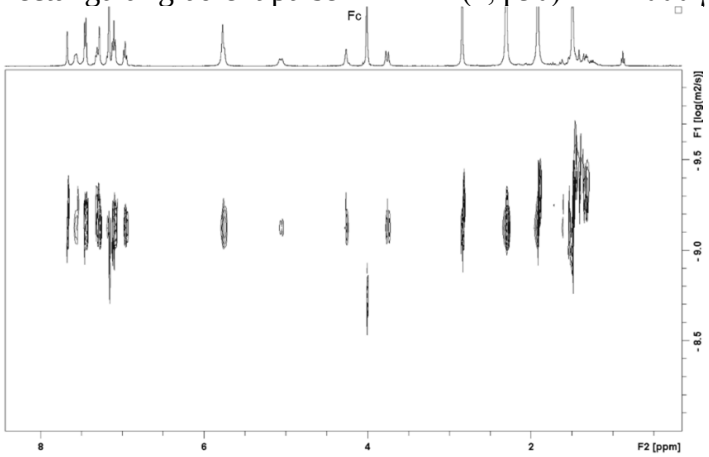


Figure S4. ^{1}H DOSY NMR (400 MHz, C_6D_6) of a mixture of **2-La(OMeLO)$_2$** and ferrocene (Fc). **2-La(OMeLO)$_2$** (12 mg, 0.010 mmol, 1.0 equiv; MW: 1170.32 g•mol^{-1}) and Fc (2.0 mg, 0.011 mmol, 1.1 equiv; MW: 186.04 g•mol^{-1}) were dissolved in 0.5 mL C_6D_6. Diffusion time was (Δ, d20) 100 ms, and the rectangular gradient pulse duration (δ, p30) was 1000 µs.

3. Experimental Procedures
Typical polymerization procedures

Reactions at ambient temperature: In a glovebox, a 2 mL scintillation vial was charged with **1-La** (5.0 mg, 0.0052 mmol, 1.0 equiv.; MW: 957.27 g•mol^{-1}), and toluene (0.382 mL). A toluene solution of $HOCHPh_2$ (2% m/m, 0.055 mL, ρ = 0.867 g/mL; 0.96 mg, 0.0052 mmol, 1.0 equiv.; MW: 184.24 g•mol^{-1}) then a toluene solution of ligand, e.g., **^{OMe}LO** (5% m/m, 0.037 mL, ρ = 0.867 g/mL; 1.6 mg, 0.0105 mmol, 2.0 equiv.; MW: 153.18 g•mol^{-1}) were added to the clear, colorless solution. After approximately one minute, *rac*-BBL (0.085 mL, ρ = 1.06 g/mL, 90 mg, 1.04 mmol, 200 equiv.; MW: 86.09 g•mol^{-1}) was added to the catalyst solution. The conversion was checked by ^{1}H NMR by adding a reaction aliquot to a 0.02 mL of a ca. 5 wt% toluene solution of benzoic acid (BzOH), followed by addition of $CDCl_3$ (~0.5 mL). After the desired conversion and/or time was reached, the reaction was quenched by the addition of a toluene solution of BzOH (5% m/m, ca. 0.1 mL), and volatiles were removed under reduced pressure.

Note: The ROP of *rac*-BBL is exothermic ($\Delta G_p° = –14.1$ kcal•mol^{-1}),[6] and highly active catalysts under the concentrated reaction conditions (2.4 M) can produce a significant exotherm (i.e. reaction is warm to touch). In order to avoid unintended warming of the reaction for the kinetic studies, propagation rates (k_p) were measured under reaction conditions that were diluted 8-fold (0.3 M rather than 2.4 M). The higher solvent volume and slower rates allowed for efficient heat-transfer and stable reaction temperatures.

Reactions at –30 °C: The following modifications to the procedure for the ambient temperature reaction were made: Before addition of *rac*-BBL, both catalyst solution and *rac*-BBL were chilled at –30 °C in the glovebox freezer. After the solution temperatures equilibrated, the *rac*-BBL was added to the catalyst solution and the reaction was run in the freezer.

Sample for end-group analysis: The sample prepared for end-group analysis was isolated from the ROP of *rac*-BBL at –30 °C using [BBL]:[**1-La**]:[**^{OMe}LO**]:[Ph_2CHOH] = 200:1:2:1, [BBL] = 2.4 M. After quenching with BzOH and removing the volatiles, the residue was washed with MeOH (3 x 1 mL) to remove most of the residual free ligand and BzOH. The sample was then dried under reduced pressure to afford the sample used for end-group analysis by NMR.

Procedure for titration experiment with ^{OMe}LO

In a glovebox, a J-Young tube was charged with **1-La** (21.0 mg, 0.022 mmol, 1.0 equiv.; MW: 957.27 g•mol^{-1}) and C_6D_6. After taking a baseline ^{1}H NMR, a solution of **^{OMe}LO** in C_6D_6 (2.2% m/m, ρ = 0.950 g/mL, 0.016 mL, 0.34 mg, 0.0219 mmol, 0.10 equiv.; MW: 153.18 g•mol^{-1}) was added. Subsequent equivalents of **^{OMe}LO** were added in an analogous manner and spectra collected.

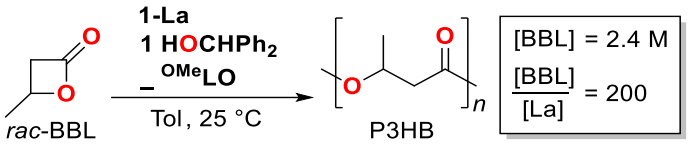
Procedure for Titration experiment with γ-butyrolactone (GBL)

In a glovebox, a J-Young tube was charged with a C_6D_6 solution of **1-La-OCHPh$_2$** (2% m/m, ρ = 0.950 g/mL, 0.325 mL, 6.2 mg, 0.0066 mmol, 1.0 equiv.; MW: 936.06 g•mol^{-1}) and a C_6D_6 solution of **^{OMe}LO** (2% m/m, ρ = 0.950 g/mL, 0.106 mL, 2.0 mg, 0.0132 mmol, 2 equiv.; MW: 153.18 g•mol^{-1}). The total volume was brought to 0.550 mL with C_6D_6. After taking a ^{1}H NMR, the J-

Young tube was returned to the glovebox and γ-butyrolactone (GBL) (5.7 mg, 0.066 mmol, 0.005 mL, 10 equiv.) was added. A ^{1}H NMR was taken. Subsequent equivalents of GBL were added in an analogous manner and spectra collected.

4. Supporting Data and Spectra

Table S2. Impact of ^{OMe}**LO** equivalents on the ROP of *rac*-BBL.



Entry	^{OMe}LO (equiv)	Time (h)	Conv. (%)[a]	$M_{n,calc}$[b] (kg/mol)	$M_{n,exp}$[c] (kg/mol)	$Đ$[c,d]	P_m[e]
1	0	1	20	3.6	2.8	1.05	0.57
2	1	0.1	54	9.5	n.d.	n.d.	n.d.
		1	95	16.5	10.8	1.20	0.67
3	2	0.1	95	16.5	12.5	1.16	0.73
4	3	0.1	96	16.7	12.8	1.14	0.73

a – Determined by ^{1}H-NMR integration of BBL and PHB methine resonances in the crude reaction mixture. *b* – [BBL]/[La]/[HOCHPh$_2$] × Conv. × 0.08609 + 0.18424 kg•mol^{-1}. *c* – Determined by gel permeation chromatography (GPC) at 30 °C in THF using polystyrene standards and corrected by Mark-Houwink factor of 0.54. *d* – M_w/M_n. *e* – Probability of *meso*-linkages between repeat units. Determined by integration of P3HB *C*=O resonances using inverse gated (IG) ^{13}C-NMR.

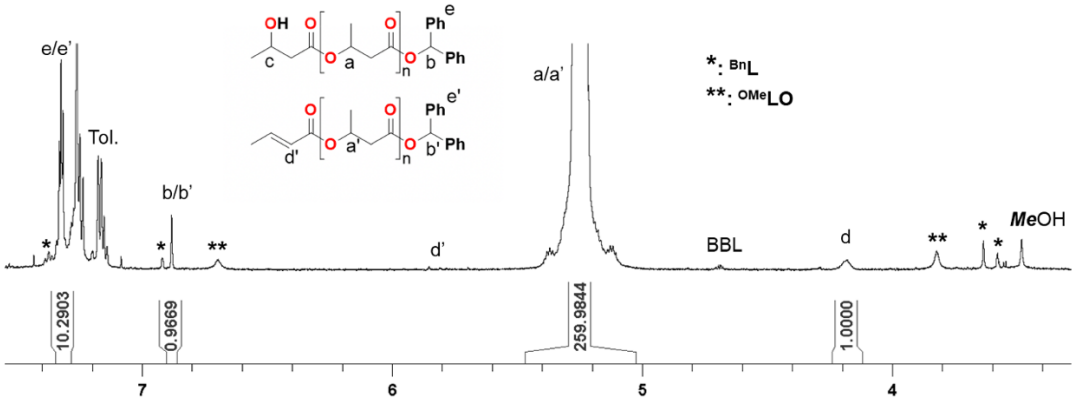


Figure S5. ^{1}H-NMR (600 MHz, $CDCl_3$) of P3HB (Table 1, entry 6). Reaction was performed in toluene at ambient temperature with [BBL]:[**1-La**]:[^{OMe}**LO**]:[Ph_2CHOH] = 200:1:2:1 and [BBL] = 2.4 M within 1 h. The polymer was precipitated from and washed with MeOH. Peaks of Ph_2CH and CH-OH are consistent with those of benzhydryl-3-oxobutanoate.[7]

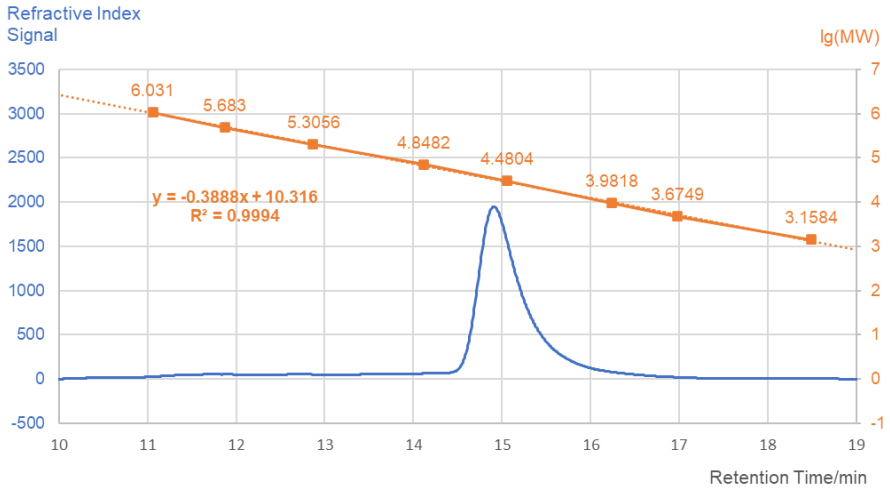


Figure S6. GPC calibration curve using polystyrene standards (orange) and GPC trace (blue) of Table 1, entry 5. The reaction was performed in toluene at ambient temperature for 0.1 h with [BBL]:[**1-La**]:[^{OMe}**LO**]:[HOCHPh$_2$] = 200:1:2:1 and [BBL] = 2.4 M. Conversion = 95%, M_n = 12.5 kg/mol (corrected by Mark-Houwink factor of 0.54), $Đ$ = 1.16

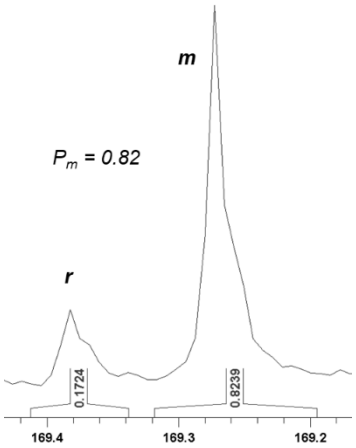


Figure S7. Carbonyl region of IG-^{13}C-NMR (151 MHz, $CDCl_3$) of P3HB with different P_m. Table 1, entry 9. Reaction was performed in toluene at –30 °C for 1 h with [BBL]:[**1-La**]:[^{OMe}**LO**]:[HOCHPh$_2$] = 200:1:2:1 and [BBL] = 2.4 M . Conversion = 99%.

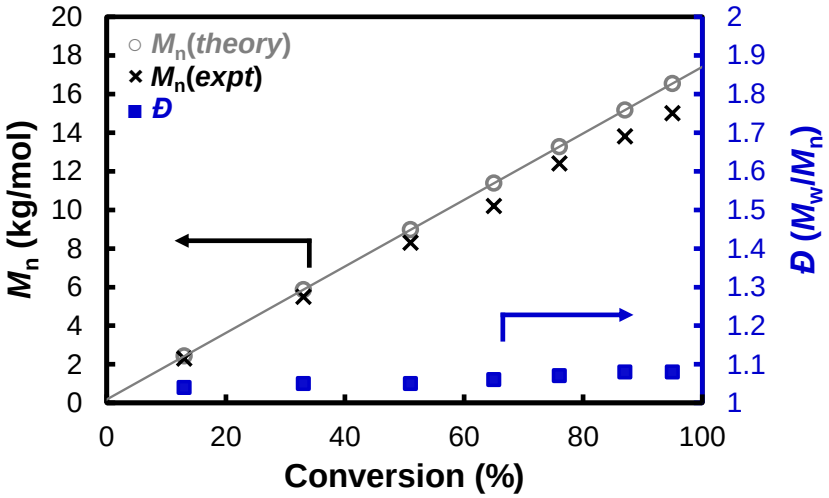


Figure S8. Plot of P3HB M_n and $Đ$ (M_w/M_n) as a function of conversion. **1-La**, $HOCHPh_2$ = 0.5 mol%, ^{OMe}LO = 1 mol%. [*rac*-BBL] = 2.4 M, Tol, –30 °C.

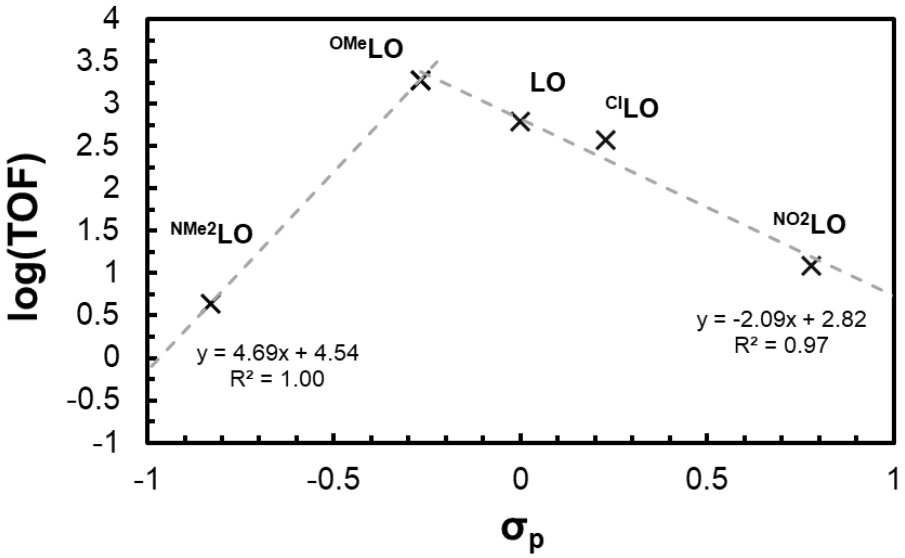
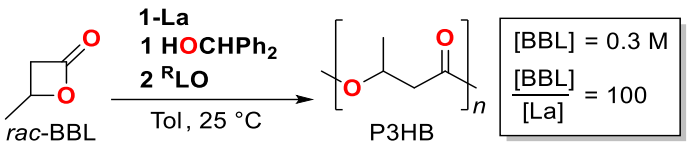


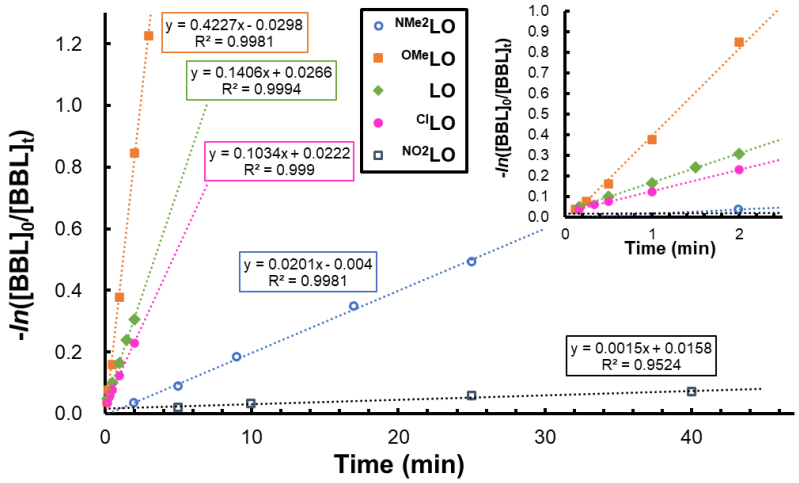
Figure S9. Turnover frequencies (TOF, min^{-1}) plotted versus σ_p (Hammett para-substituent constant) for the ROP of *rac*-BBL with **1-La** + $HOCHPh_2$ + ^{R}**LO**. Reactions were performed in toluene at ambient temperature with [BBL]:[**1-La**]:[^{R}**LO**]:[$HOCHPh_2$] = 200:1:2:1 and [BBL] = 2.4 M.

Table S3. Conversions in early stage of ROP of *rac*-BBL with **1-La** + $HOCHPh_2$ + **^{R}LO**



^{NMe2}LO		^{OMe}LO		LO		^{Cl}LO		^{NO2}LO	
Time (min)	Conv. (%)[a]	Time (min)	Conv. (%)[a]	Time (min)	Conv. (%)[a]	Time (min)	Conv. (%)[a]	Time (min)	Conv. (%)[a]
2	3.4	0.12	3.7	0.17	4.7	0.17	3.6	5	1.8
5	8.5	0.25	7.4	0.5	9.5	0.33	5.7	10	3.3
9	16.8	0.5	14.7	1	15.2	0.5	7.3	25	5.7
17	29.4	1	31.5	1.5	21.3	1	11.6	40	6.9
25	38.8	2	57.1	2	26.4	2	20.5		
		3	70.6						

a – Determined by ^{1}H-NMR integration of BBL and P3HB methine resonances in the crude reaction mixture.

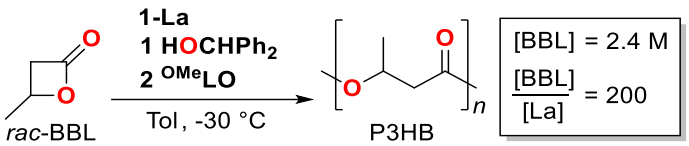


^{R}LO	log(k_p[a])
^{NMe2}LO	0.83
^{OMe}LO	2.15
LO	1.67
^{Cl}LO	1.54
^{NO2}LO	–0.30

a – in $min^{-1}•M^{-1}$

Figure S10. Propagation rate constants (k_p) for the ROP of *rac*-BBL with **1-La** + Ph_2CHOH + **^{R}LO**. Reactions were performed in toluene at ambient temperature with [BBL]:[**1-La**]:[**^{R}LO**]:[$HOCHPh_2$] = 100:1:2:1 and [BBL] = 0.3 M.

Table S4. ROP of *rac*-BBL with **1-La +** $HOCHPh_2$ + 2 ^{OMe}**LO** quenched at different times.



Entry	Time (min)	Conv. (%)[a]	$M_{n,\,calc}$[c] (kg/mol)	$M_{n,\,exp}$[c] (kg/mol)	$Đ$[c,d]
1	1	1	0.4	n.d.	n.d.
2	2	3	0.70	n.d.	n.d.
3	3	6	1.2	n.d.	n.d.
4	5	13	2.4	2.3	1.04
5	10	33	5.9	5.5	1.05
6	15	51	9.0	8.3	1.05
7	20	65	11.4	10.2	1.06
8	25	76	13.3	12.4	1.07
9	30	87	15.2	13.8	1.08
10	40	95	16.5	15.0	1.08

a – Determined by ^{1}H-NMR integration of BBL and PHB methine resonances in the crude reaction mixture. *b* – [BBL]/[La]/[$HOCHPh_2$] × Conv. × 0.08609 + 0.18424 kg•mol^{-1}. *c* – Determined by gel permeation chromatography (GPC) at 30 °C in THF using polystyrene standards and corrected by Mark-Houwink factor of 0.54. d – M_w/M_n.

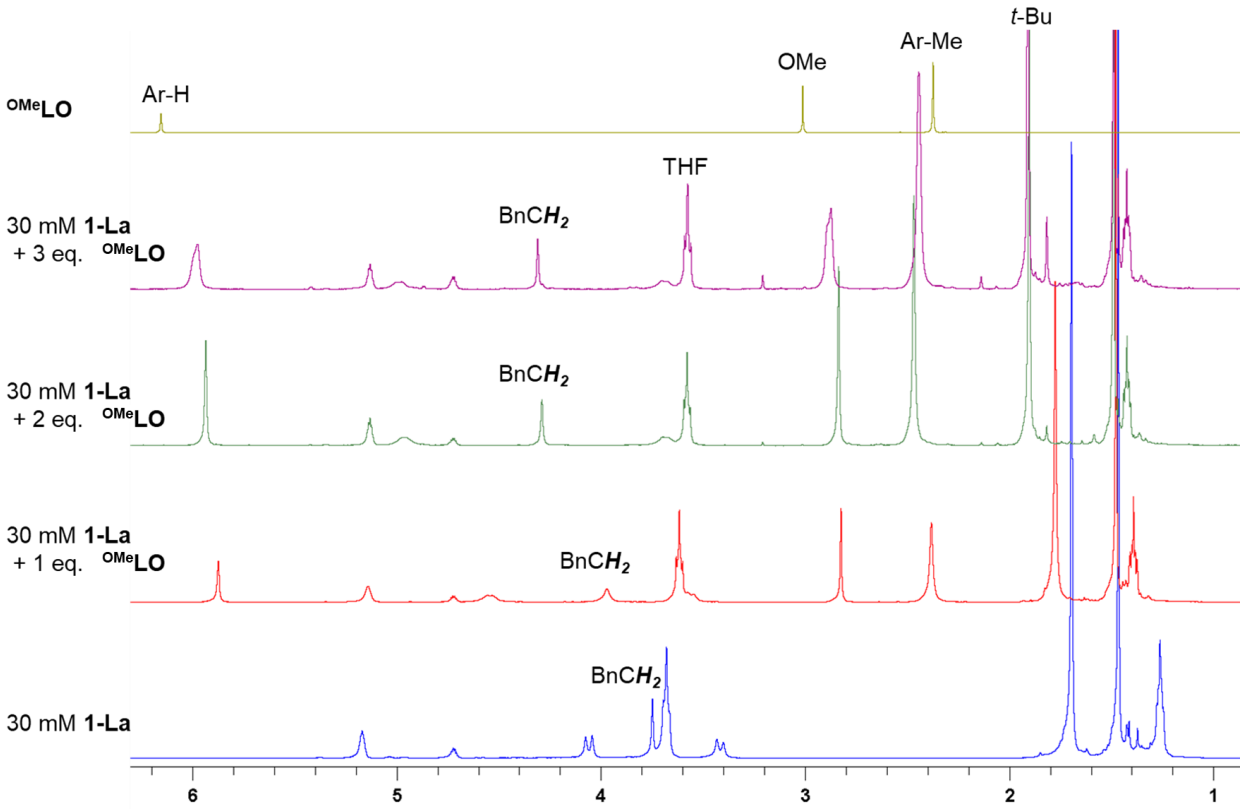
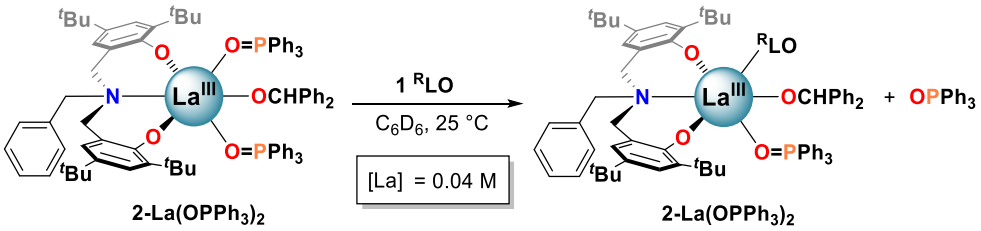


Figure S11. ^{1}H-NMR (400 MHz, C_6D_6, 298 K) of **1-La** (30 mM) in the presence of 0, 1, 2 and 3 equiv of **^{OMe}LO**.

Table S5. Equiv free $OPPh_3$ generated upon addition of 1 equiv **^{R}LO** to **2-La(OPPh$_3$)$_2$ (**C_6D_6 solution, RT, 40 mM).



^{R}LO	^{NMe2}LO	^{OMe}LO	LO	^{Cl}LO	^{NO2}LO
Equiv. free $OPPh_3$[a]	1.32[b]	0.89	0.47	0.37	n.d.[c] (< 0.05)

a – Determined by integration of inverse-gated (IG) ^{31}P-NMR of free (26 ppm) and coordinated (34 ppm) $OPPh_3$ resonances. *b* – The generation of more than one equiv $OPPh_3$ from only one equiv ^{NMe2}LO suggests that a significant amount of another adduct, [La(^{Bn}L)(OCHPh$_2$)(^{NMe2}LO)], must also be formed with this strong donor. *c* – Not determined; no signal for free $OPPh_3$ was observed.

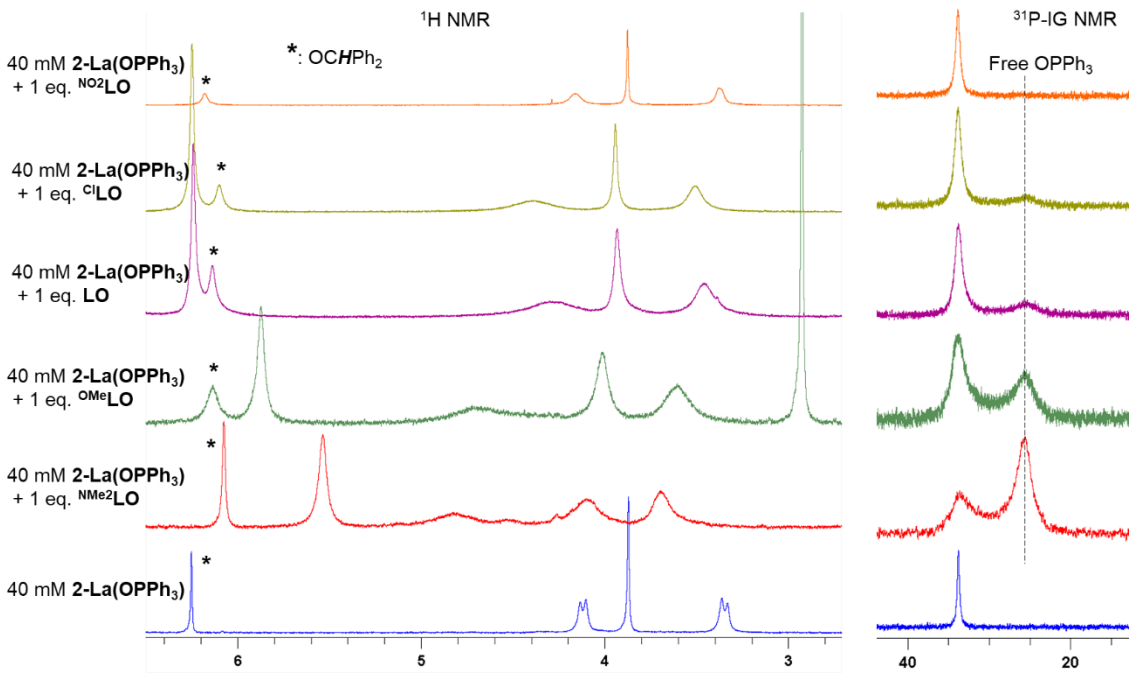


Figure S12. ^{1}H-NMR (400 MHz, C_6D_6, 298 K) and IG-^{31}P-NMR (162 MHz, C_6D_6, 298 K) of **2-La(OPPh$_3$)$_2$** (40 mM) and **2-La(OPPh$_3$)$_2$** (40 mM) in the presence of 1 equiv. of ^{R}**LO**.

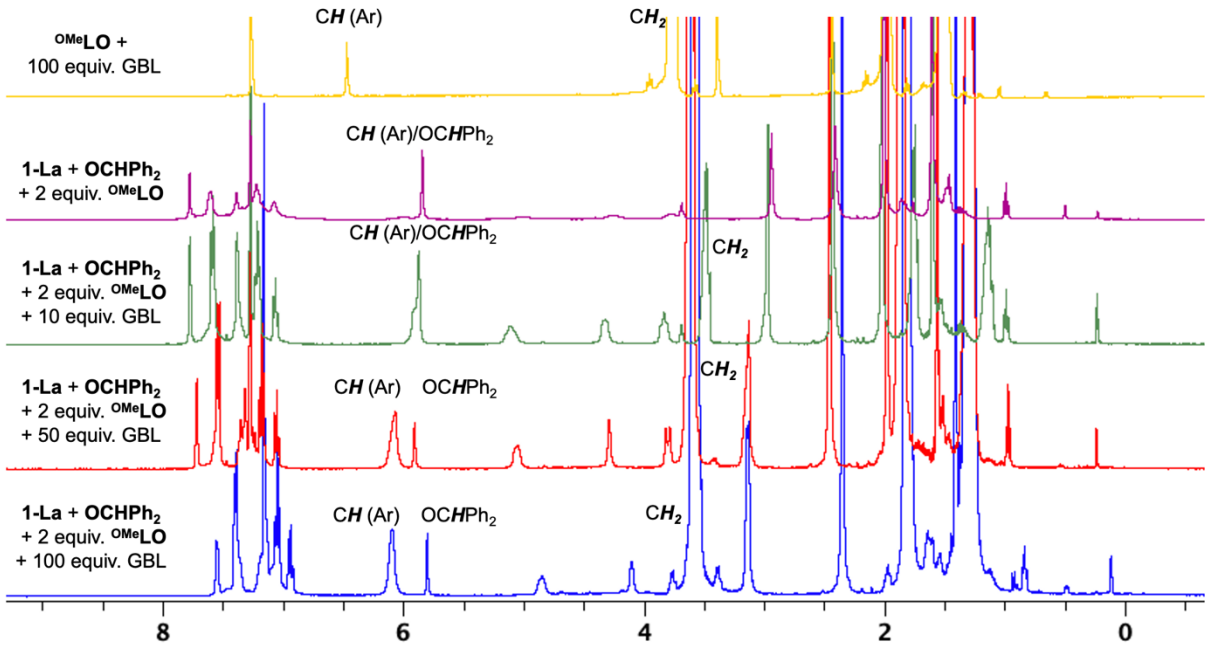


Figure S13. ^{1}H-NMR (400 MHz, C_6D_6) of **1-La**, $OCHPh_2$ + 2 equiv. of ^{OMe}**LO** in the presence of 100 (blue, bottom), 50 (red), 10 (green) and 0 (purple) equiv. of GBL, and ^{OMe}**LO** in the presence of 100 equiv. of GBL (top, yellow). C***H*** (Ar) corresponds to ^{OMe}**LO** and C***H*$_2$** to γ-butyrolactone (GBL).

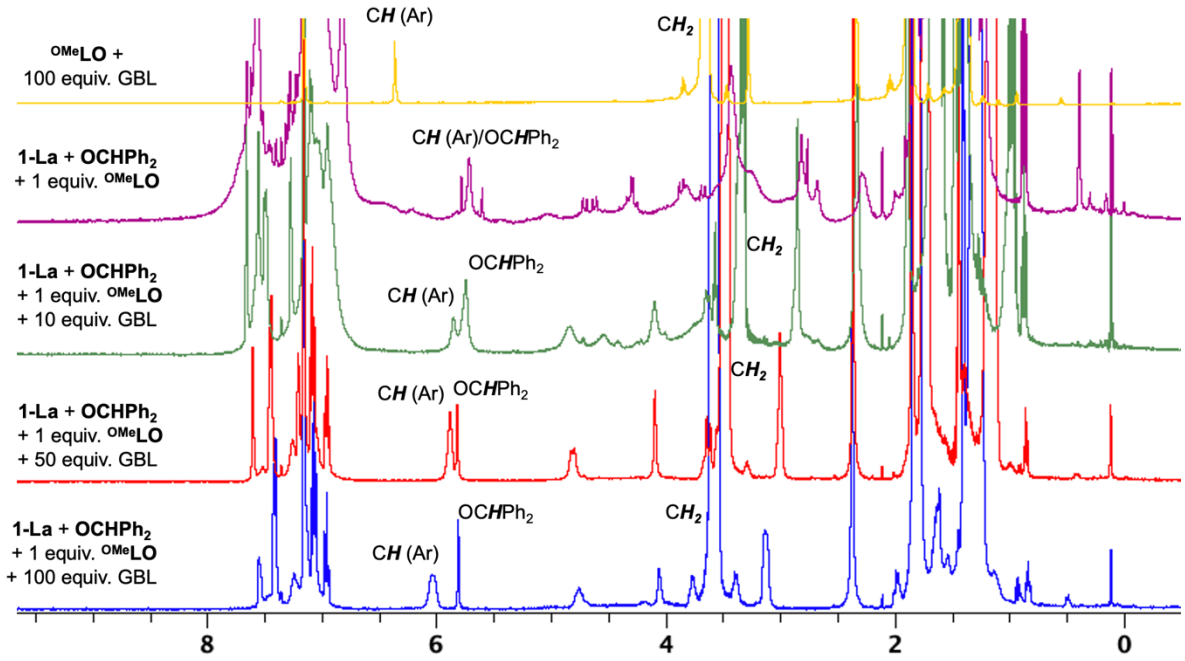


Figure S14. ^{1}H-NMR (400 MHz, C_6D_6) of **1-La**, $OCHPh_2$ + 1 equiv. of **^{OMe}LO** in the presence of 100 (blue, bottom), 50 (red), 10 (green) and 0 (purple) equiv. of GBL, and **^{OMe}LO** in the presence of of 100 equiv. of GBL (top, yellow). C***H*** (Ar) corresponds to **^{OMe}LO** and C***H*$_2$** to γ-butyrolactone (GBL).

5. Computational Studies.

Methods: All calculations were performed employing the Gaussian 09 package (revision D.01).[8]

La complexes: Complexes were optimized at the rM06-L level of theory[9] with Grimme's D3 dispersion correction[10] using the Stuttgart [7s6p5d|5s4p3d][11] ECP46MWB[11-12] contracted pseudopotential basis set on lanthanum and the 6-31G* basis set used on all other atoms.[13] The standard "fine" grid size was used for numerical integrations while a convergence criterion of 10^{-6} was used for all calculations. Optimized geometries were confirmed as minima by frequency analysis (the absence of negative frequencies). To validate the selected methodology, the Mean Unsigned Error (MUE) between the predicted and the experimentally determined (SC-XRD) bond lengths in the primary coordination sphere of **1-La(OPPh$_3$)$_2$** was calculated by the following equation.

$$MUE = \frac{\sum_{i=1}^{n} |y_i - x_i|}{n}$$

BBL binding studies: Eight isomers of **2-La(LO)$_2$** coordinated by BBL were identified by inspection and constructed in Avogadro. Geometry optimization of the complexes were performed in Gaussian 09 using the same level of theory as described above, and the ground state energies were obtained to evaluate the ΔG_{rxn} associated with BBL binding.

Natural Bond Order Analysis: NBO 3.1[14] calculations were performed at the M06-L level of theory using the def2-TZVP basis set.[15] Solvation effects associated with toluene were accounted for in the single point calculations using the SMD continuum solvation model.[16] Input geometries were generated from the crystallographic data or constructed using Avogadro.[17] Wilberg bond orders and natural charges were reported from the constructed output files.

Free ligands (only): For 4-substituted lutidine *N*-oxide (^{R}LO) calculations, structures were optimized at the M06-2X level of theory[18] employing the def2-TZVP basis set.[15] NBO calculations were performed with the same level of theory and basis set.

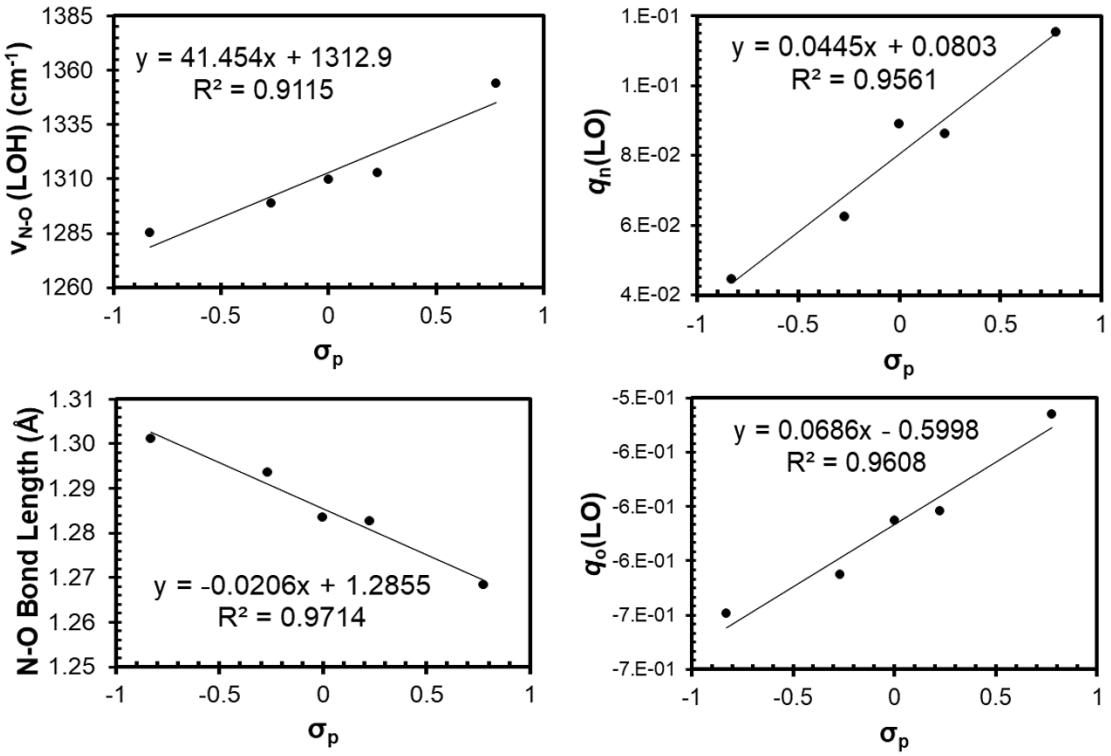


Figure S15. Graphs illustrating N-O Bond length, ν_{N-O}, q_N, and q_O as a function of σ_p for lutidine N-oxide structures.

Table S6. Table of N-O Bond length, ν_{N-O}, q_N, and q_O as a function of σ_p for lutidine N-oxide structures.

R	σ_p	N-O Bond Length (Å)	ν_{N-O} (cm^{-1})	Natural Charge (q_N)	Natural Charge (q_O)
NMe_2	-0.83	1.30116	1285.26	0.04481	-0.65764
OMe	-0.268	1.29356	1298.77	0.06075	-0.62840
H	0	1.28346	1309.54	0.08642	-0.60003
Cl	0.227	1.28273	1312.83	0.08406	-0.59850
NO_2	0.778	1.26381	1354.10	0.11326	-0.54126

Table S7. Cartesian coordinates of **LO** optimized with M06-2X/Def2-TZVP.

Atom	X	Y	Z
N	0	-0.65882	0.00038
C	1.18731	0.01341	0.0001
C	1.18886	1.39543	-0.00005
C	0.00003	2.10448	-0.00003
C	-1.18883	1.39545	-0.00005
C	-1.18732	0.01344	0.00011
C	2.40848	-0.83405	-0.00004
H	2.14324	1.90408	-0.00016
C	-2.40849	-0.83401	-0.00004
H	0.00003	3.18541	-0.00014
H	-2.14319	1.90414	-0.00016
O	-0.00003	-1.94228	-0.00021
H	-3.2983	-0.20907	-0.00021
H	-2.41112	-1.48756	0.87333
H	-2.41087	-1.48761	-0.87338
H	3.2983	-0.20912	-0.00028
H	2.41082	-1.48771	-0.87333
H	2.41113	-1.48752	0.87339

Table S8. Cartesian coordinates of ^{NO2}**LO** optimized with M06-2X/Def2-TZVP.

Atom	X	Y	Z
N	-1.60028	-0.00001	0.00028
C	-1.06449	-1.13601	0.00012
C	0.4103	-1.25428	0.00001
C	1.14876	0.00001	0.00002
C	0.41029	1.25428	0.00002
C	-1.06452	1.13599	0.00009
C	-1.81718	-2.47395	0.00003
H	1.15676	-2.07871	-0.00003
C	-1.81722	2.47393	-0.00007
N	2.60567	0.00001	-0.00002
H	1.15673	2.07872	-0.00004
O	-2.90609	0.00001	-0.00025
O	3.07679	-1.02808	-0.00019
O	3.0768	1.02809	0.0001
H	-0.98448	-3.20718	-0.00004
H	-2.57445	-2.17403	-0.7993
H	-2.57448	-2.17414	0.79933
H	-0.98452	3.20716	-0.0001
H	-2.57459	2.17413	0.79918

H	-2.57442	2.174	-0.79946

Table S9. Cartesian coordinates of ^{MeO}**LO** optimized with M06-2X/Def2-TZVP.

Atom	X	Y	Z
N	-1.4199	0.19516	0.00019
C	-0.50413	1.19459	-0.00039
C	0.85161	0.90647	-0.00087
C	1.28111	-0.41235	-0.00082
C	0.32066	-1.41944	-0.00056
C	-1.01936	-1.1109	-0.00011
C	-1.0536	2.57609	-0.00033
H	1.54289	1.73545	-0.0014
C	-2.10957	-2.1215	0.00032
O	2.57218	-0.80163	-0.00127
H	0.63183	-2.45479	-0.00066
O	-2.68262	0.47596	0.00098
C	3.56264	0.20888	0.00181
H	4.5192	-0.30548	0.00348
H	3.48249	0.83315	0.895
H	3.48657	0.83479	-0.89058
H	-1.69194	-3.12538	-0.00168
H	-2.74943	-1.97892	-0.87138
H	-2.74658	-1.98141	0.87456
H	-0.24607	3.30409	-0.0024
H	-1.6894	2.72406	0.87369
H	-1.69286	2.72267	-0.87202

Table S10. Cartesian coordinates of ^{Cl}**LO** optimized with M06-2X/Def2-TZVP.

Atom	X	Y	Z
N	1.41199	0	0.00008
C	0.73885	-1.18669	0.00001
C	-0.64226	-1.19467	0.00001
C	-1.33725	0.00001	0.00002
C	-0.64226	1.19467	-0.00001
C	0.73886	1.18669	0
C	1.58295	-2.40941	-0.00001
H	-1.16398	-2.14099	-0.00002
C	1.58295	2.40941	0

Cl	-3.06503	0	-0.00001
H	-1.16398	2.141	-0.00004
O	2.69472	-0.00001	-0.00006
H	0.95797	-3.29883	-0.00018
H	2.23605	-2.41004	0.87363
H	2.2363	-2.40984	-0.87345
H	0.95797	3.29883	-0.00017
H	2.23632	2.40985	-0.87343
H	2.23604	2.41002	0.87365

Table S11. Cartesian coordinates of ^{NMe2}**LO**optimized with M06-2X/Def2-TZVP.

Atom	X	Y	Z
N	1.76028	0.00002	0.0001
C	1.0796	-1.17569	-0.00111
C	-0.29866	-1.19107	-0.00517
C	-1.04168	-0.00012	-0.00933
C	-0.29877	1.19091	-0.0052
C	1.07948	1.17566	-0.00116
C	1.9185	-2.40413	0.00247
H	-0.7835	-2.15517	-0.00525
C	1.91826	2.4042	0.00225
N	-2.40596	-0.00006	-0.01764
H	-0.78378	2.15493	-0.00489
O	3.06143	0.00009	0.00422
C	-3.12371	-1.25512	0.00814
C	-3.12333	1.25522	0.00851
H	-2.89351	-1.83362	0.90844
H	-2.88302	-1.87048	-0.86373
H	-4.19115	-1.05508	-0.00374
H	-2.883	1.87058	-0.86347
H	-2.8923	1.83351	0.90875
H	-4.19084	1.05548	-0.00246
H	1.29075	-3.29209	0.0026
H	2.57101	-2.40485	0.87622
H	2.57425	-2.40763	-0.86887
H	1.29042	3.29209	0.00212
H	2.57404	2.40752	-0.86907
H	2.57074	2.40522	0.87602

Table S12. Comparison of natural charges (q) across optimized **1-La(OPPh$_3$)$_2$**, **1-La(LO)$_2$**, **2-La(OPPh$_3$)$_2$**, and **2-La(LO)$_2$** structures. Natural charges were calculated with NBO 3.1 using the M06-L functional and Def2-TZVP basis set (see computational methods).

	1-La(OPPh$_3$)$_2$	**1-La(LO)$_2$**	**2-La(OPPh$_3$)$_2$**	**2-La(LO)$_2$**
$q_{La(1)}$	1.98683	1.92241	2.08173	1.9921
$q_{O(1)}$	-0.91116	-0.92309	-0.90916	-0.88704
$q_{O(2)}$	-0.90204	-0.92832	-0.91293	-0.9271
$q_{O(3)}$	-1.15147	-0.63383	-1.15874	-0.64161
$q_{O(4)}$	-1.15244	-0.61308	-1.14579	-0.61556
$q_{O(5)}$	N/A	N/A	-0.99826	-1.00459
$q_{N(1)}$	-0.46224	-0.46834	-0.47775	-0.47773
$q_{N(2)}$	-1.83539	-1.85027	N/A	N/A
$q_{N(3)}$	N/A	0.06952	N/A	0.07744
$q_{N(4)}$	N/A	0.08294	N/A	0.06423
$q_{P(1)}$	1.98456	N/A	1.98832	N/A
$q_{P(2)}$	1.98683	N/A	1.98017	N/A

Table S13. Comparison of Wilberg bond indices across optimized **1-La(OPPh$_3$)$_2$**, **1-La(LO)$_2$**, **2-La(OPPh$_3$)$_2$**, and **2-La(LO)$_2$** structures. Bond indices were calculated with NBO 3.1 using the M06-L functional and Def2-TZVP basis set (see computational methods).

Bond	**1-La(OPPh$_3$)$_2$**	**1-La(LO)$_2$**	**2-La(OPPh$_3$)$_2$**	**2-La(LO)$_2$**
O(3) - P(1)	1.0196	N/a	1.0272	N/A
O(4) - P(2)	1.0284	N/a	1.0345	N/A
O(3) - N(3)	N/A	1.1461	N/A	1.1485
O(4) - N(4)	N/A	1.1644	N/A	1.1541

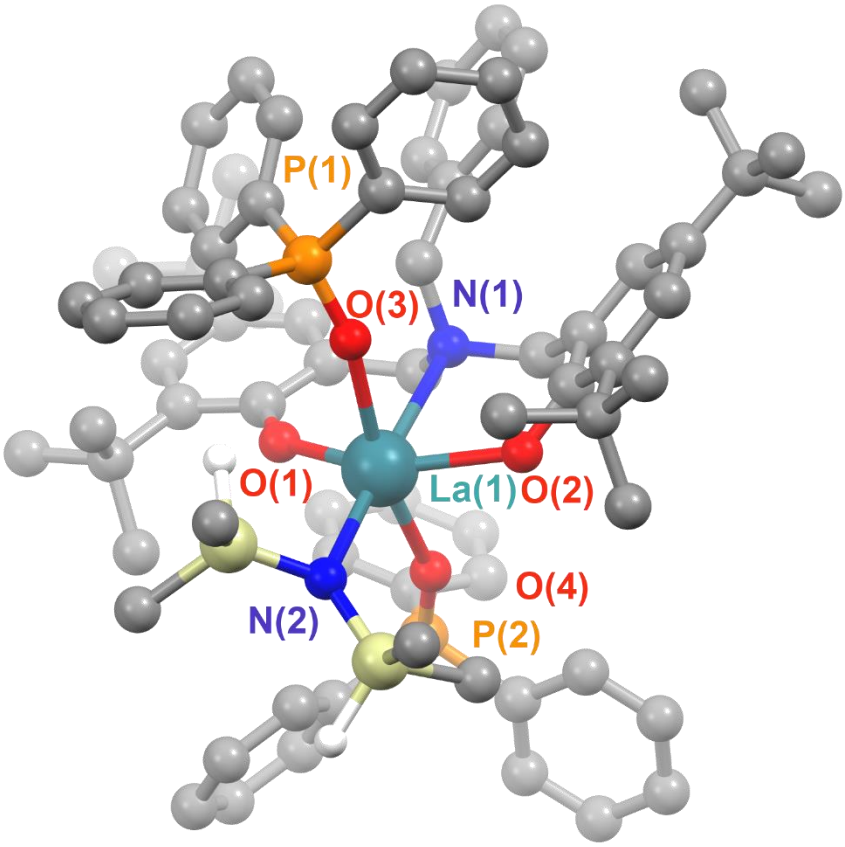


Figure S16. Labeled ball and stick image of DFT-optimized **1-La(OPPh$_3$)$_2$**. H-atoms other than those of the Si–H from the N(SiHMe$_2$)$_2$ group were removed for clarity.

Table S14. Comparison of select bond distances (Å) and metrical parameters of the X-ray / DFT calculated structures of **1-La(OPPh$_3$)$_2$**. The mean unsigned error (MUE) is 0.0465.

Distance (Å)	**X-ray**	**DFT**
La(1)–O(1)	2.276(2)	2.352
La(1)–O(2)	2.267(2)	2.340
La(1)–O(3)	2.482(2)	2.502
La(1)–O(4)	2.457(2)	2.490
La(1)–N(1)	2.828(2)	2.885
La(1)–N(2)	2.459(3)	2.479
Angle (°)		
O(1)–La(1)–O(2)	144.92(8)	143.16
O(1)–La(1)–O(3)	96.74(7)	96.49
O(1)–La(1)–O(4)	84.02(7)	81.62
O(1)–La(1)–N(1)	71.33(7)	71.57
O(1)–La(1)–N(2)	109.07(8)	109.14
O(2)–La(1)–O(3)	85.42(7)	86.13
O(2)–La(1)–O(4)	87.84(7)	85.10

O(2)–La(1)–N(1)	73.92(7)	72.90
O(2)–La(1)–N(2)	105.42(8)	105.88
O(3)–La(1)–O(4)	169.24(7)	165.65
O(3)–La(1)–N(1)	85.97(7)	82.39
O(3)–La(1)–N(2)	96.63(8)	100.31
O(4)–La(1)–N(1)	84.11(7)	83.53
O(4)–La(1)–N(2)	93.24(8)	93.71
N(1)–La(1)–N(2)	177.28(8)	177.05
Angle (°)		
P(1)–O(3)–La(1)	167.6(1)	160.24
P(2)–O(4)–La(1)	163.0(1)	156.94

Table S15. Cartesian coordinates of DFT-optimized **1-La(OPPh$_3$)$_2$**. EM06L = -4695.07004313

Atom	**X**	**Y**	**Z**
La	-0.29981	-1.12441	0.41677
P	-3.74097	-1.48595	-1.45500
P	2.86892	0.44494	2.21830
Si	-0.68865	-2.32960	3.51336
Si	-1.14850	-4.61708	1.53020
O	-1.53853	0.78492	1.01052
O	0.92655	-2.09454	-1.32405
O	1.86782	-0.37776	1.41819
O	-2.27603	-1.50307	-1.05007
N	0.29273	0.97205	-1.47470
N	-0.88206	-2.98133	1.95315
C	-1.90097	2.00475	0.69177
C	-2.68182	2.79876	1.58781
C	-3.21061	2.20371	2.90052
C	-2.06846	1.73578	3.81483
H	-1.48231	0.93847	3.34954
H	-2.47598	1.34691	4.75887
H	-1.39683	2.56965	4.06600
C	-4.12874	1.00989	2.59502
H	-5.01097	1.33205	2.02287
H	-4.49363	0.55516	3.52739
H	-3.60650	0.23436	2.02395
C	-4.03659	3.21514	3.69943
H	-3.44566	4.09286	3.99347
H	-4.40195	2.74214	4.61975

H	-4.91331	3.56853	3.14158
C	-2.98944	4.11350	1.22096
H	-3.55859	4.72400	1.91677
C	-2.60834	4.68217	0.00284
C	-2.91820	6.12510	-0.38782
C	-3.63497	6.88584	0.72586
H	-4.60251	6.43053	0.97328
H	-3.82733	7.92037	0.41444
H	-3.03676	6.92139	1.64535
C	-3.80695	6.14868	-1.63881
H	-3.33988	5.61227	-2.47483
H	-3.99682	7.17976	-1.96774
H	-4.77923	5.67757	-1.43997
C	-1.60302	6.85217	-0.70303
H	-0.92460	6.82899	0.16014
H	-1.78529	7.90346	-0.96541
H	-1.07976	6.38459	-1.54646
C	-1.91934	3.85626	-0.88488
H	-1.68055	4.23038	-1.88418
C	-1.55096	2.54916	-0.57846
C	-0.97878	1.70336	-1.69057
H	-1.71235	0.92442	-1.95735
H	-0.88262	2.34571	-2.58894
C	1.36692	1.80041	-0.89676
H	2.15273	1.10496	-0.57673
H	0.93211	2.23246	0.01047
C	2.02037	2.90614	-1.69463
C	1.37060	4.12081	-1.93938
H	0.35442	4.25854	-1.57668
C	2.02739	5.17353	-2.56952
H	1.50204	6.11228	-2.74321
C	3.35882	5.03836	-2.95459
H	3.87719	5.86387	-3.43991
C	4.02685	3.84392	-2.69802
H	5.07490	3.73169	-2.97403
C	3.36105	2.78997	-2.07716
H	3.89255	1.85886	-1.87022
C	0.67020	0.32745	-2.75881
H	0.75636	1.10505	-3.54257
H	-0.18979	-0.30738	-3.02934
C	1.93172	-0.48819	-2.74119
C	3.01788	-0.09908	-3.52018
H	2.92581	0.82287	-4.10000

C	4.19730	-0.84425	-3.58075
C	5.33998	-0.40032	-4.49338
C	5.73666	1.04749	-4.17858
H	6.07926	1.15358	-3.13887
H	4.89474	1.73610	-4.31860
H	6.55180	1.38091	-4.83621
C	4.87222	-0.47187	-5.95378
H	4.58563	-1.49575	-6.22435
H	5.66750	-0.14729	-6.63970
H	4.00037	0.17210	-6.12303
C	6.58057	-1.27971	-4.34331
H	6.97325	-1.26756	-3.31674
H	7.37903	-0.91846	-5.00394
H	6.37862	-2.32480	-4.60869
C	4.24825	-2.00662	-2.80388
H	5.16424	-2.59086	-2.82028
C	3.19434	-2.45659	-2.00425
C	3.32682	-3.73267	-1.16322
C	4.72751	-4.34167	-1.27227
H	4.97455	-4.63206	-2.30132
H	4.78334	-5.24658	-0.65423
H	5.50514	-3.64978	-0.91949
C	2.32024	-4.78818	-1.64169
H	1.29544	-4.41332	-1.57327
H	2.39773	-5.69940	-1.03110
H	2.51583	-5.06604	-2.68571
C	3.08852	-3.44184	0.32892
H	3.74144	-2.63436	0.68747
H	3.30576	-4.33859	0.92705
H	2.05257	-3.15402	0.53617
C	1.98587	-1.69963	-1.99767
C	0.62807	-3.16939	4.56618
H	1.54563	-3.32598	3.98374
H	0.28825	-4.15504	4.91108
H	0.89244	-2.58202	5.45447
C	-2.26719	-2.15239	4.52899
H	-2.08478	-1.64769	5.48676
H	-2.71239	-3.13102	4.75297
H	-3.01709	-1.56416	3.98423
C	-1.53446	-4.71530	-0.31498
H	-2.52682	-4.31158	-0.55461
H	-1.50155	-5.74646	-0.69006
H	-0.80510	-4.13601	-0.90068

C	0.32003	-5.75244	1.86761
H	1.19714	-5.41979	1.29713
H	0.10879	-6.78798	1.57064
H	0.60877	-5.76494	2.92551
C	-4.00040	-2.71936	-2.74725
C	-2.86971	-3.29317	-3.33878
H	-1.87934	-3.00260	-2.98969
C	-3.02270	-4.23846	-4.34918
H	-2.14189	-4.68758	-4.80379
C	-4.29655	-4.61193	-4.76905
H	-4.41359	-5.35515	-5.55577
C	-5.42497	-4.04182	-4.18097
H	-6.42028	-4.33897	-4.50593
C	-5.27895	-3.09699	-3.17194
H	-6.16263	-2.65867	-2.70671
C	-4.82869	-1.83621	-0.05986
C	-6.18823	-1.49780	-0.08521
H	-6.60729	-0.97653	-0.94669
C	-6.99975	-1.79660	1.00373
H	-8.05343	-1.52520	0.98377
C	-6.45976	-2.43020	2.12197
H	-7.09600	-2.66084	2.97462
C	-5.10725	-2.75796	2.15558
H	-4.67697	-3.24193	3.03033
C	-4.28838	-2.46021	1.06973
H	-3.22135	-2.68740	1.11786
C	-4.27478	0.10418	-2.11753
C	-4.29907	0.34785	-3.49606
H	-4.09539	-0.46261	-4.19579
C	-4.57801	1.62603	-3.96960
H	-4.59462	1.81359	-5.04160
C	-4.83126	2.66366	-3.07378
H	-5.04042	3.66511	-3.44732
C	-4.80995	2.42641	-1.70130
H	-4.97615	3.23708	-0.99323
C	-4.53043	1.15210	-1.22256
H	-4.48753	0.97593	-0.14730
C	2.98406	-0.08995	3.94054
C	3.73558	-1.23458	4.24179
H	4.26388	-1.76125	3.44643
C	3.81077	-1.69789	5.54974
H	4.39605	-2.58687	5.77620
C	3.13052	-1.02927	6.56560

H	3.19013	-1.39314	7.58984
C	2.36904	0.09918	6.27156
H	1.83311	0.61910	7.06299
C	2.29645	0.57123	4.96459
H	1.70652	1.45960	4.74194
C	2.43212	2.19679	2.18403
C	1.09343	2.54843	2.41586
H	0.36187	1.77692	2.66199
C	0.67522	3.86350	2.24034
H	-0.37540	4.11661	2.38307
C	1.58785	4.83315	1.82586
H	1.25505	5.85687	1.66346
C	2.91713	4.49065	1.59374
H	3.62229	5.24009	1.23880
C	3.34121	3.17713	1.77163
H	4.37362	2.91097	1.54973
C	4.52611	0.29168	1.52410
C	4.66537	-0.10391	0.18884
H	3.78866	-0.37614	-0.40197
C	5.93379	-0.18380	-0.38109
H	6.02315	-0.51030	-1.41646
C	7.06066	0.14027	0.36868
H	8.04951	0.07662	-0.08243
C	6.92658	0.53701	1.69894
H	7.80714	0.78405	2.28868
C	5.66426	0.60986	2.27718
H	5.56048	0.90881	3.32104
H	-0.21623	-0.91038	3.26421
H	-2.32449	-5.20212	2.26206

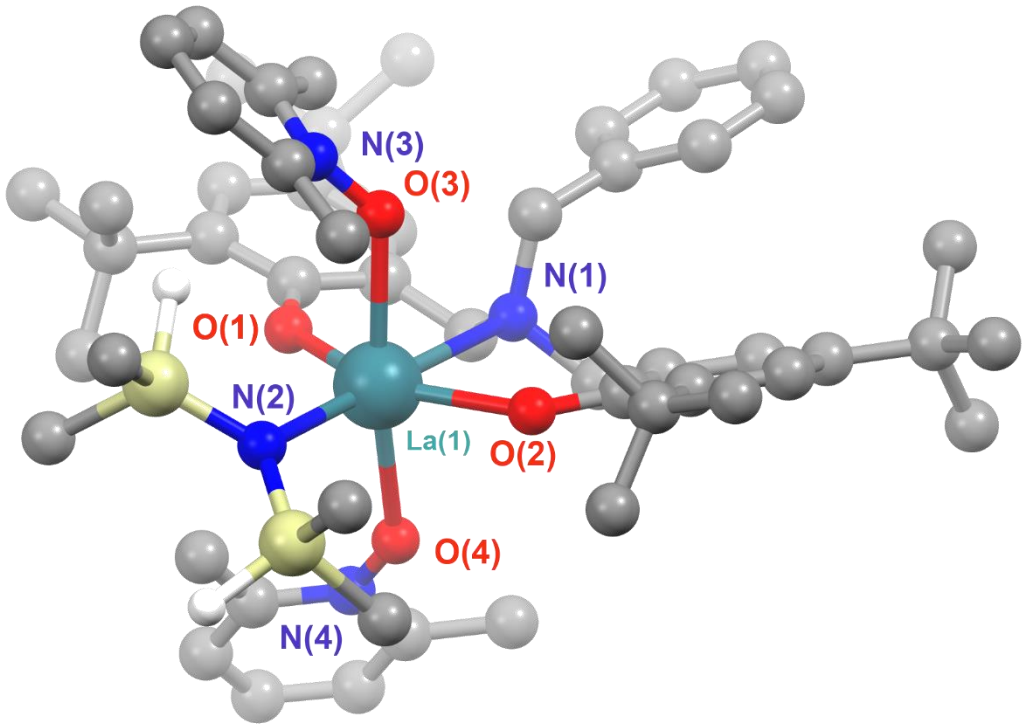


Figure S17. Labeled ball and stick image of DFT-optimized **1-La(LO)$_2$**. H-atoms other than those of the Si–H from the N(SiHMe$_2$)$_2$ group were removed for clarity.

Table S16. Comparison of select bond distances (Å) and metrical parameters for the DFT calculated structures of **1-La(LO)$_2$**.

Distance (Å)	**DFT**
La(1)–O(1)	2.364
La(1)–O(2)	2.321
La(1)–O(3)	2.554
La(1)–O(4)	2.600
La(1)–N(1)	2.825
La(1)–N(2)	2.488
Angle (°)	
O(1)–La(1)–O(2)	90.30
O(1)–La(1)–O(3)	145.24
O(1)–La(1)–O(4)	82.97
O(1)–La(1)–N(1)	73.00
O(1)–La(1)–N(2)	108.28
O(2)–La(1)–O(3)	89.43
O(2)–La(1)–O(4)	89.62
O(2)–La(1)–N(1)	72.29
O(2)–La(1)–N(2)	106.44

O(3)–La(1)–O(4)	86.50
O(3)–La(1)–N(1)	166.72
O(3)–La(1)–N(2)	93.28
O(4)–La(1)–N(1)	80.61
O(4)–La(1)–N(2)	99.68
N(1)–La(1)–N(2)	178.71
Angle (°)	
P(1)–N(3)–La(1)	133.64
P(2)–N(4)–La(1)	141.87

Table S17. Cartesian coordinates of DFT-optimized **1-La(LO)$_2$**. EM06L = -3275.060363

Atom	X	Y	Z
La	0.07843	-1.20463	0.32087
Si	1.94421	-4.12572	-0.59786
Si	-0.35345	-4.70646	1.27474
O	2.10945	-0.00116	0.20647
O	-2.23046	-1.03693	0.48729
O	-0.12494	-1.12983	-2.22397
O	0.28224	-0.68215	2.85979
N	-0.58880	1.54011	0.28184
N	0.61175	-3.63507	0.34972
C	2.64267	1.19912	0.03892
C	3.98987	1.37583	-0.40299
C	4.93021	0.17767	-0.59537
C	4.39014	-0.80937	-1.63679
H	3.38441	-1.15693	-1.38603
H	5.04287	-1.69175	-1.70468
H	4.36147	-0.34518	-2.63258
C	5.09708	-0.53665	0.75309
H	5.53718	0.13881	1.49890
H	5.75884	-1.40880	0.65189
H	4.13039	-0.87692	1.12935
C	6.32732	0.59521	-1.06037
H	6.30350	1.11568	-2.02668
H	6.95043	-0.29980	-1.18348
H	6.83085	1.24817	-0.33631
C	4.47034	2.67753	-0.57384
H	5.48838	2.80568	-0.92914
C	3.72628	3.82429	-0.29203

C	4.27317	5.24190	-0.44200
C	5.66599	5.25922	-1.06958
H	6.40058	4.72965	-0.44976
H	6.01580	6.29319	-1.18254
H	5.66935	4.79575	-2.06448
C	4.35441	5.90355	0.94056
H	3.36979	5.94170	1.42342
H	4.72860	6.93381	0.86218
H	5.02805	5.34725	1.60450
C	3.33407	6.06985	-1.33010
H	3.21557	5.61310	-2.32099
H	3.72582	7.08680	-1.46887
H	2.33526	6.16173	-0.88523
C	2.43206	3.62287	0.18170
H	1.82843	4.48498	0.47507
C	1.86679	2.35702	0.32258
C	0.50922	2.26817	0.96483
H	0.60408	1.75944	1.93923
H	0.17118	3.29887	1.19128
C	-0.82969	1.95383	-1.11883
H	-1.50067	1.19931	-1.55339
H	0.14277	1.85201	-1.61755
C	-1.38931	3.33063	-1.38977
C	-0.56956	4.46342	-1.33849
H	0.48643	4.33983	-1.10523
C	-1.07093	5.72866	-1.62841
H	-0.41243	6.59535	-1.58455
C	-2.40438	5.88151	-1.99864
H	-2.79914	6.86825	-2.23610
C	-3.22419	4.75952	-2.08622
H	-4.26067	4.86483	-2.40306
C	-2.72226	3.49707	-1.78063
H	-3.37045	2.62356	-1.85321
C	-1.77941	1.66867	1.16556
H	-1.90464	2.73420	1.43980
H	-1.49642	1.13505	2.08788
C	-3.09968	1.15190	0.67988
C	-4.19158	2.01543	0.65696
H	-4.01771	3.06677	0.90143
C	-5.47398	1.58423	0.32141
C	-6.64218	2.56830	0.33090
C	-6.35215	3.72190	-0.63636
H	-6.22506	3.35189	-1.66290

H	-5.43516	4.25801	-0.36130
H	-7.17677	4.44829	-0.63784
C	-6.81388	3.13986	1.74467
H	-7.03285	2.34378	2.46740
H	-7.63910	3.86489	1.77665
H	-5.90536	3.65369	2.08253
C	-7.95754	1.91237	-0.08582
H	-7.90400	1.50009	-1.10158
H	-8.76729	2.65305	-0.07123
H	-8.24240	1.09821	0.59275
C	-5.61624	0.23218	-0.00175
H	-6.60305	-0.12700	-0.27845
C	-4.56588	-0.68823	0.01911
C	-4.81044	-2.16047	-0.32136
C	-6.25351	-2.43155	-0.75180
H	-6.97364	-2.21246	0.04681
H	-6.36271	-3.49330	-1.00781
H	-6.53926	-1.84752	-1.63626
C	-4.52208	-3.03989	0.90268
H	-3.48106	-2.94655	1.22155
H	-4.71580	-4.09704	0.67053
H	-5.16543	-2.75743	1.74619
C	-3.90001	-2.58406	-1.47970
H	-4.11611	-1.99775	-2.38391
H	-4.04924	-3.64679	-1.72262
H	-2.85014	-2.43138	-1.21721
C	-3.27175	-0.22515	0.39014
C	1.67160	-5.70898	-1.59503
H	0.75052	-5.68363	-2.18976
H	1.59566	-6.57725	-0.92626
H	2.50656	-5.90237	-2.28131
C	3.57390	-4.35573	0.32949
H	4.33026	-4.82865	-0.31064
H	3.44843	-4.99224	1.21565
H	3.99073	-3.39741	0.66281
C	-1.18411	-3.74906	2.67779
H	-0.47915	-3.46681	3.47058
H	-1.98312	-4.33866	3.14606
H	-1.65655	-2.81851	2.32763
C	-1.70209	-5.53618	0.24938
H	-2.34506	-4.77821	-0.21946
H	-2.35177	-6.18357	0.85236
H	-1.27945	-6.14921	-0.55742

H	2.20239	-3.01558	-1.57518
H	0.45546	-5.80035	1.90947
H	-0.72042	-3.70375	-1.85188
H	-1.80665	-2.99018	-3.03958
C	-0.90151	-3.59742	-2.93255
H	-1.08141	-4.58969	-3.35633
C	0.24445	-2.94869	-3.60445
N	0.55795	-1.67483	-3.20380
H	0.80977	1.02183	-3.52588
H	0.75834	-4.55684	-4.89121
C	1.00866	-3.54004	-4.59891
C	1.55626	-0.94873	-3.80035
C	1.72660	0.44805	-3.34232
C	2.06330	-2.85752	-5.18916
C	2.31903	-1.55315	-4.78832
H	2.66815	-3.32969	-5.95888
H	2.55929	0.92658	-3.86478
H	1.91611	0.49205	-2.26314
H	3.11995	-0.97056	-5.23669
H	-1.23171	0.41083	4.53654
H	-0.60997	1.70374	5.60801
C	-0.42406	1.13413	4.69361
H	-0.46337	1.82577	3.84276
C	0.88831	0.45089	4.77268
N	1.16639	-0.47845	3.79856
H	1.64429	-2.95584	2.77069
H	1.59126	1.42736	6.52135
C	1.82905	0.68427	5.76428
C	2.32584	-1.21474	3.81940
C	2.48355	-2.25011	2.77864
C	3.03310	-0.00626	5.78719
C	3.26382	-0.96282	4.80875
H	3.77115	0.18749	6.56074
H	3.41380	-2.80488	2.92715
H	2.52155	-1.79704	1.77853
H	4.18084	-1.54639	4.79321

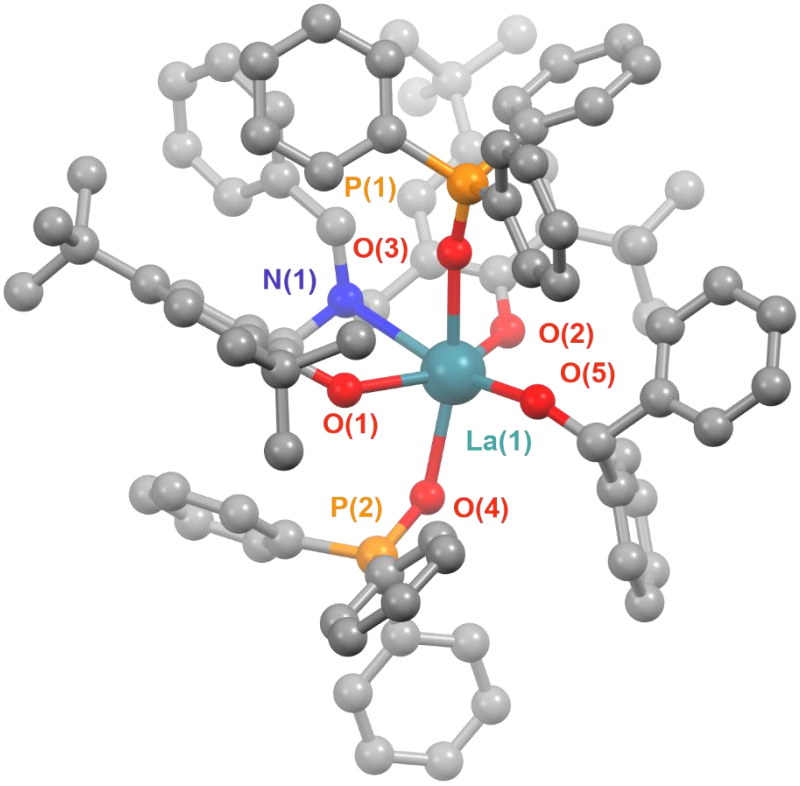


Figure S18. Labeled ball and stick image of DFT-optimized **2-La(OPPh$_3$)$_2$**. H-atoms were removed for clarity.

Table S18. Comparison of select bond distances (Å) and metrical parameters for the DFT calculated structures of **2-La(OPPh$_3$)$_2$**.

Distance (Å)	**DFT**
La(1)–O(1)	2.383
La(1)–O(2)	2.363
La(1)–O(3)	2.494
La(1)–O(4)	2.505
La(1)–O(5)	2.323
La(1)–N(1)	2.871
Angle (°)	
O(1)–La(1)–O(2)	146.63
O(1)–La(1)–O(3)	85.63
O(1)–La(1)–O(4)	80.96
O(1)–La(1)–O(5)	102.29
O(1)–La(1)–N(1)	73.86
O(2)–La(1)–O(3)	93.01
O(2)–La(1)–O(4)	99.13
O(2)–La(1)–O(5)	110.83

O(2)–La(1)–N(1)	73.21
O(3)–La(1)–O(4)	166.51
O(3)–La(1)–O(5)	85.16
O(3)–La(1)–N(1)	78.52
O(4)–La(1)–O(5)	95.91
O(4)–La(1)–N(1)	99.30
O(5)–La(1)–N(1)	163.44
Angle (°)	
P(1)–O(3)–La(1)	169.67
P(2)–O(4)–La(1)	136.72

Table S19. Cartesian coordinates of DFT-optimized **2-La(OPPh$_3$)$_2$**. EM06L = -4476.178651

Atom	**X**	**Y**	**Z**
La	-0.90356	-0.52548	-0.31549
P	-4.05013	1.32622	-1.23408
P	2.21106	-1.16708	2.10906
O	-1.15358	1.59828	0.73636
O	0.05659	-1.74404	-2.09802
O	1.11414	-0.79043	1.12600
O	-3.01434	0.22335	-1.43736
N	0.95972	1.23156	-1.61241
C	-0.40272	2.66937	0.89858
C	-0.27967	3.34613	2.14928
C	-1.06053	2.87147	3.38076
C	-0.74748	1.40636	3.72401
H	-0.90580	0.74166	2.86939
H	-1.39485	1.06329	4.54415
H	0.29065	1.29155	4.06712
C	-2.56274	3.01465	3.10349
H	-2.81766	4.05806	2.86663
H	-3.15122	2.71808	3.98322
H	-2.86772	2.37953	2.26593
C	-0.73594	3.69877	4.62608
H	0.33061	3.64701	4.88539
H	-1.30198	3.30940	5.48190
H	-1.00545	4.75616	4.50674
C	0.55454	4.47034	2.21461
H	0.65789	4.97388	3.17252
C	1.27146	4.97713	1.12531

C	2.18046	6.20085	1.20040
C	2.34833	6.71440	2.62958
H	1.39539	7.03877	3.06672
H	3.02710	7.57669	2.64391
H	2.77505	5.94866	3.29237
C	1.57525	7.32543	0.34804
H	1.45076	7.00897	-0.69574
H	2.21755	8.21723	0.35365
H	0.58693	7.61758	0.72751
C	3.57069	5.85223	0.64737
H	4.03861	5.04015	1.22023
H	4.23638	6.72556	0.69198
H	3.53136	5.51867	-0.39696
C	1.11312	4.31409	-0.09093
H	1.63200	4.67572	-0.98175
C	0.31020	3.18964	-0.21619
C	0.20203	2.50445	-1.53936
H	-0.84998	2.25150	-1.75950
H	0.52279	3.19388	-2.34123
C	2.26341	1.25017	-0.94971
H	2.62372	0.21322	-0.95706
H	2.06684	1.47726	0.10338
C	3.38705	2.14900	-1.41057
C	3.34644	3.02209	-2.50073
H	2.45168	3.08766	-3.11528
C	4.44328	3.82556	-2.81540
H	4.38740	4.49615	-3.67185
C	5.59939	3.77657	-2.04348
H	6.45153	4.40799	-2.28872
C	5.65452	2.90856	-0.95364
H	6.55086	2.85817	-0.33568
C	4.56298	2.10539	-0.64955
H	4.61132	1.42672	0.20490
C	0.97062	0.71827	-3.00430
H	1.33437	1.49358	-3.70158
H	-0.08498	0.53188	-3.26782
C	1.77942	-0.52764	-3.15872
C	3.06272	-0.46861	-3.68764
H	3.44631	0.50552	-4.00331
C	3.86997	-1.60258	-3.78682
C	5.31044	-1.46504	-4.27320
C	6.07145	-0.53956	-3.31133
H	6.06841	-0.94073	-2.28742

H	5.61866	0.45900	-3.26886
H	7.11866	-0.42040	-3.62356
C	5.33490	-0.84718	-5.67703
H	4.80262	-1.48203	-6.39648
H	6.36725	-0.72215	-6.03257
H	4.85877	0.14054	-5.68947
C	6.03733	-2.80755	-4.32935
H	6.09804	-3.28392	-3.34096
H	7.06511	-2.66518	-4.68711
H	5.54252	-3.51318	-5.00875
C	3.30198	-2.81571	-3.38265
H	3.89946	-3.71912	-3.48096
C	2.01647	-2.93584	-2.84594
C	1.44150	-4.29686	-2.44864
C	2.39846	-5.45122	-2.74879
H	2.65221	-5.51389	-3.81492
H	1.92707	-6.40050	-2.46288
H	3.33483	-5.36581	-2.17984
C	0.14951	-4.54480	-3.24064
H	-0.56455	-3.73261	-3.07995
H	-0.31912	-5.48996	-2.93056
H	0.36046	-4.60722	-4.31631
C	1.14279	-4.33872	-0.94449
H	2.07046	-4.31667	-0.35828
H	0.59676	-5.25594	-0.68014
H	0.53122	-3.48340	-0.64124
C	1.24387	-1.75043	-2.67980
C	-5.43415	1.04171	-2.35772
C	-5.63911	-0.25935	-2.82786
H	-4.93536	-1.04584	-2.55742
C	-6.73311	-0.53505	-3.64259
H	-6.88935	-1.54853	-4.00884
C	-7.61996	0.48069	-3.99100
H	-8.47369	0.26154	-4.63001
C	-7.41509	1.77927	-3.52794
H	-8.10271	2.57513	-3.80834
C	-6.32476	2.06132	-2.71202
H	-6.15568	3.08067	-2.36275
C	-4.70479	1.31996	0.44855
C	-5.58907	2.30919	0.89693
H	-5.87614	3.12832	0.23589
C	-6.08983	2.25868	2.19264
H	-6.77070	3.03329	2.54034

C	-5.71353	1.22161	3.04637
H	-6.10149	1.18999	4.06324
C	-4.83573	0.23733	2.60384
H	-4.52256	-0.56571	3.27005
C	-4.33447	0.28076	1.30611
H	-3.63709	-0.48886	0.97709
C	-3.43448	2.98513	-1.58417
C	-3.21488	3.35817	-2.91923
H	-3.53367	2.70020	-3.72823
C	-2.57569	4.55760	-3.21021
H	-2.40029	4.83913	-4.24689
C	-2.14696	5.38999	-2.17558
H	-1.62416	6.31779	-2.40420
C	-2.37208	5.03013	-0.84999
H	-2.01260	5.66014	-0.03725
C	-3.01496	3.83226	-0.55332
H	-3.15842	3.53657	0.48361
C	1.52444	-1.68654	3.69076
C	0.17690	-2.05775	3.74482
H	-0.45191	-2.00278	2.85277
C	-0.36418	-2.49394	4.95221
H	-1.40934	-2.79898	4.98674
C	0.42512	-2.54761	6.09716
H	-0.00325	-2.88848	7.03835
C	1.76586	-2.16471	6.04573
H	2.37983	-2.19757	6.94370
C	2.31734	-1.73464	4.84487
H	3.36345	-1.42728	4.80373
C	3.31162	0.22930	2.43671
C	2.73793	1.50510	2.51644
H	1.67039	1.63866	2.34011
C	3.53121	2.61301	2.78941
H	3.06679	3.59787	2.82806
C	4.90182	2.45677	2.98767
H	5.52364	3.32786	3.19000
C	5.47903	1.19052	2.91543
H	6.55059	1.06805	3.06295
C	4.68809	0.07664	2.63988
H	5.14370	-0.91090	2.56427
C	3.25454	-2.49818	1.47580
C	3.91499	-2.29784	0.25470
H	3.81561	-1.35167	-0.28189
C	4.68481	-3.31452	-0.29656

H	5.17703	-3.15366	-1.25470
C	4.79800	-4.53831	0.36085
H	5.39446	-5.33636	-0.07845
C	4.13737	-4.74716	1.56912
H	4.21595	-5.70689	2.07662
C	3.36662	-3.73074	2.12797
H	2.84274	-3.89708	3.06909
H	-6.66346	-3.56808	-1.35573
H	-4.16901	-4.87773	2.80138
H	-3.21719	-6.93366	3.80917
C	-3.10504	-5.09798	2.69052
C	-2.57226	-6.25348	3.25395
C	-1.21482	-6.53788	3.11280
H	-0.79627	-7.44164	3.55340
C	-0.93696	-4.49844	1.85320
C	-0.39959	-5.65749	2.40623
H	0.66378	-5.86813	2.28585
H	-5.57050	-3.08039	0.82049
C	-5.57590	-3.55584	-1.28579
C	-4.96239	-3.28333	-0.06354
H	-3.68199	-2.59861	2.06544
C	-2.87781	-2.93774	1.37089
C	-4.80028	-3.79468	-2.41740
C	-3.57190	-3.25468	0.04797
H	-5.27541	-4.00894	-3.37426
C	-2.29397	-4.20509	1.98635
C	-2.80252	-3.48745	-1.09806
C	-3.40915	-3.75157	-2.32122
H	-1.71092	-3.47383	-1.03103
H	-2.79263	-3.93354	-3.20038
H	-0.30079	-3.79125	1.32277
O	-1.93245	-1.95287	1.20148

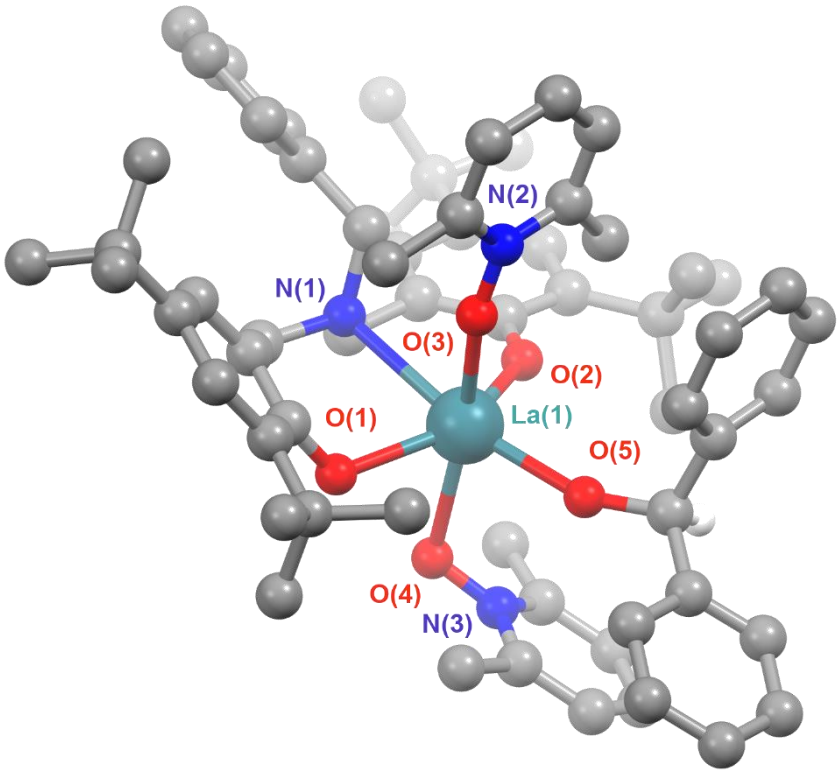


Figure S19. Labeled ball and stick image of DFT-optimized **2-La(LO)$_2$** . H-atoms were removed for clarity.

Table S20. Comparison of select bond distances (Å) and metrical parameters for the DFT calculated structures of **2-La(LO)$_2$**.

Distance (Å)	**DFT**
La(1)–O(1)	2.365
La(1)–O(2)	2.350
La(1)–O(3)	2.509
La(1)–O(4)	2.577
La(1)–O(5)	2.293
La(1)–N(1)	2.775
Angle (°)	
O(1)–La(1)–O(2)	141.86
O(1)–La(1)–O(3)	91.03
O(1)–La(1)–O(4)	76.48
O(1)–La(1)–O(5)	116.54
O(1)–La(1)–N(1)	75.58
O(2)–La(1)–O(3)	104.35
O(2)–La(1)–O(4)	89.74
O(2)–La(1)–O(5)	96.93

O(2)–La(1)–N(1)	72.06
O(3)–La(1)–O(4)	165.81
O(3)–La(1)–O(5)	95.09
O(3)–La(1)–N(1)	82.98
O(4)–La(1)–O(5)	84.76
O(4)–La(1)–N(1)	100.07
O(5)–La(1)–N(1)	167.82
Angle (°)	
P(1)–N(3)–La(1)	156.11
P(2)–N(4)–La(1)	114.07

Table S21. Cartesian coordinates of DFT-optimized **2-La(LO)$_2$**. EM06L (solvent corrected) = -3057.600901 (-3057.607037)

Atom	**X**	**Y**	**Z**
La	0.62347	-0.26391	-0.56337
O	-0.37311	-1.84327	-2.01453
O	0.61844	2.02761	-0.04118
O	-0.43770	-1.35820	1.42989
O	1.67753	0.27209	-2.85264
N	-1.94566	0.70056	-0.97457
C	-1.49352	-2.44740	-1.67503
C	-1.56073	-3.85496	-1.46217
C	-0.30117	-4.71766	-1.61175
C	0.80530	-4.27831	-0.63733
H	1.10466	-3.23734	-0.80066
H	1.70025	-4.90318	-0.77469
H	0.49370	-4.37992	0.41127
C	0.23022	-4.60860	-3.04893
H	-0.50150	-5.00745	-3.76290
H	1.15883	-5.18772	-3.15982
H	0.43241	-3.56693	-3.31126
C	-0.57710	-6.19496	-1.32451
H	-0.94463	-6.35561	-0.30137
H	0.34955	-6.77215	-1.43738
H	-1.31441	-6.61897	-2.01747
C	-2.80138	-4.41834	-1.15239
H	-2.85073	-5.49168	-0.98752
C	-3.98290	-3.67749	-1.02633
C	-5.33262	-4.30868	-0.68824

C	-5.20444	-5.78605	-0.31969
H	-4.81677	-6.38488	-1.15307
H	-6.18685	-6.19481	-0.05091
H	-4.53503	-5.93476	0.53867
C	-6.26819	-4.18626	-1.89845
H	-6.41138	-3.13690	-2.18531
H	-7.25699	-4.61301	-1.67872
H	-5.85610	-4.71382	-2.76768
C	-5.96990	-3.57477	0.50015
H	-5.32199	-3.61119	1.38718
H	-6.93358	-4.02977	0.76787
H	-6.15769	-2.51886	0.26889
C	-3.89171	-2.30010	-1.24167
H	-4.79093	-1.68091	-1.19700
C	-2.68402	-1.67695	-1.54206
C	-2.64451	-0.22295	-1.91269
H	-2.09945	-0.12632	-2.86301
H	-3.67072	0.14916	-2.08329
C	-2.62544	0.83013	0.33185
H	-2.07151	1.60391	0.88477
H	-2.46887	-0.12521	0.85242
C	-4.10347	1.13124	0.34504
C	-4.99682	0.15842	0.80464
H	-4.60348	-0.80516	1.13601
C	-6.36696	0.40042	0.84506
H	-7.04342	-0.36975	1.21421
C	-6.86802	1.62803	0.41930
H	-7.93910	1.82160	0.44586
C	-5.98869	2.61174	-0.02772
H	-6.37072	3.58118	-0.34514
C	-4.61886	2.36746	-0.05924
H	-3.93440	3.15466	-0.37140
C	-1.71896	1.97983	-1.70385
H	-2.64443	2.25935	-2.24182
H	-0.98815	1.72281	-2.49470
C	-1.23458	3.18942	-0.95104
C	-1.91801	4.38950	-1.13113
H	-2.82126	4.37753	-1.74717
C	-1.48366	5.59100	-0.57400
C	-2.29762	6.86567	-0.78527
C	-3.73680	6.64222	-0.29960
H	-3.75876	6.36130	0.76100
H	-4.23480	5.84383	-0.86430

H	-4.33566	7.55481	-0.42365
C	-2.32778	7.21263	-2.27993
H	-1.31587	7.39336	-2.66387
H	-2.92620	8.11624	-2.46114
H	-2.76588	6.39940	-2.87214
C	-1.71525	8.05571	-0.02465
H	-1.67308	7.86746	1.05578
H	-2.33848	8.94478	-0.18351
H	-0.70056	8.30105	-0.36303
C	-0.29092	5.55093	0.15221
H	0.07399	6.47853	0.58255
C	0.46106	4.38886	0.35043
C	1.78460	4.43674	1.12825
C	2.12348	5.85207	1.60149
H	2.22702	6.55625	0.76600
H	3.08023	5.83680	2.13895
H	1.36713	6.25233	2.28879
C	2.95293	3.95028	0.25777
H	2.79899	2.91326	-0.05809
H	3.89352	3.99790	0.82604
H	3.07028	4.57798	-0.63576
C	1.71616	3.53587	2.36733
H	0.83501	3.76623	2.98126
H	2.60973	3.67580	2.99288
H	1.67254	2.48598	2.07064
C	-0.03056	3.16811	-0.19529
H	1.21151	0.29679	2.64334
H	-0.24030	1.20238	2.22588
C	0.25725	0.66502	3.04605
H	0.47528	1.37654	3.84562
C	-0.57076	-0.44620	3.55003
N	-0.89962	-1.42691	2.64950
H	-2.55829	-2.84843	1.06063
H	-0.75136	0.22323	5.55620
C	-1.03459	-0.55605	4.85290
C	-1.72166	-2.47609	2.98055
C	-2.08498	-3.39734	1.88603
C	-1.83216	-1.62443	5.23825
C	-2.17834	-2.57416	4.28594
H	-2.19120	-1.70818	6.26072
H	-2.77026	-4.17186	2.24232
H	-1.20318	-3.87282	1.44176
H	-2.82215	-3.41417	4.53402

H	1.71388	2.80531	-2.07666
H	2.89775	3.80911	-2.95174
C	2.42209	2.82564	-2.91375
H	1.82969	2.66865	-3.82305
C	3.44267	1.75975	-2.77698
N	2.97556	0.47281	-2.81117
H	2.47715	-2.15995	-2.15705
H	5.16752	2.98679	-2.57526
C	4.80770	1.96186	-2.63094
C	3.80831	-0.61571	-2.81344
C	3.16347	-1.93845	-2.98392
C	5.67967	0.88259	-2.55479
C	5.17090	-0.40490	-2.67228
H	6.74649	1.04026	-2.41527
H	3.91923	-2.72817	-3.02214
H	2.55087	-1.95695	-3.89302
H	5.82014	-1.27638	-2.62366
O	2.77877	-0.69251	0.09284
C	3.93752	-0.51099	0.81075
C	5.01412	-1.51538	0.42516
C	6.36684	-1.20886	0.58739
H	6.64423	-0.23944	1.00752
C	7.35417	-2.10999	0.20092
H	8.40540	-1.85141	0.32371
C	6.99798	-3.34058	-0.35059
H	7.76797	-4.04629	-0.65891
C	5.65025	-3.66040	-0.50340
H	5.36209	-4.62163	-0.92956
C	4.66680	-2.75266	-0.11758
H	3.60990	-2.97847	-0.25599
C	3.63231	-0.57969	2.30162
C	3.92059	0.48541	3.15366
H	4.42368	1.36636	2.74948
C	3.54231	0.44945	4.49633
H	3.76221	1.29780	5.14374
C	2.87011	-0.65967	4.99986
H	2.56645	-0.68924	6.04572
C	2.58230	-1.73556	4.15578
H	2.05148	-2.60572	4.54406
C	2.96225	-1.69482	2.81962
H	2.72120	-2.52199	2.14990
H	4.36938	0.49877	0.62280

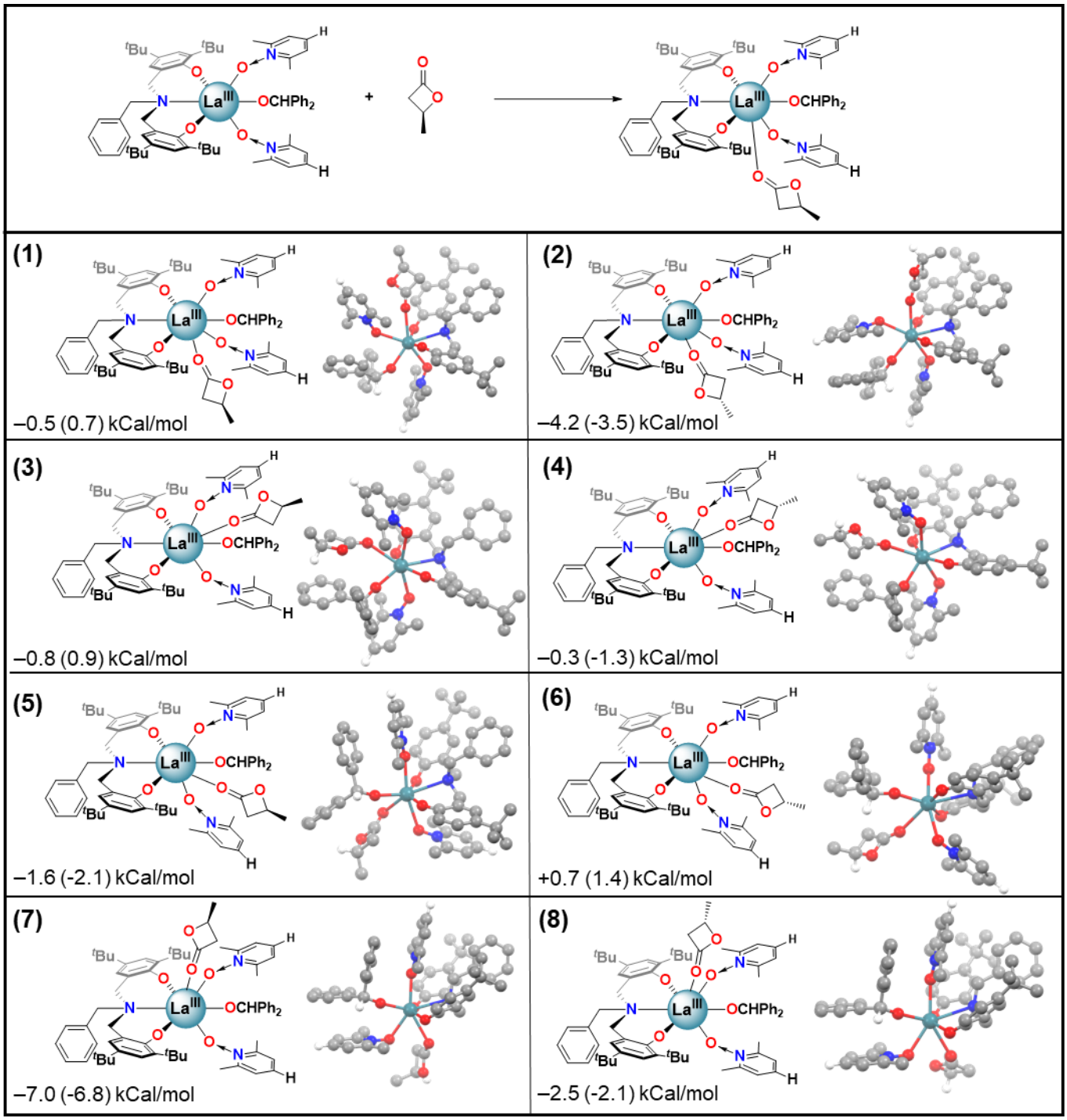


Figure S20. Summary of *in silico* (*S*)-BBL binding studies to **2-La(LO)$_2$**. Hydrogen atoms and ortho tert-butyl groups were removed for clarity. Solvent corrected energies (PCM, toluene) are included in parentheses.

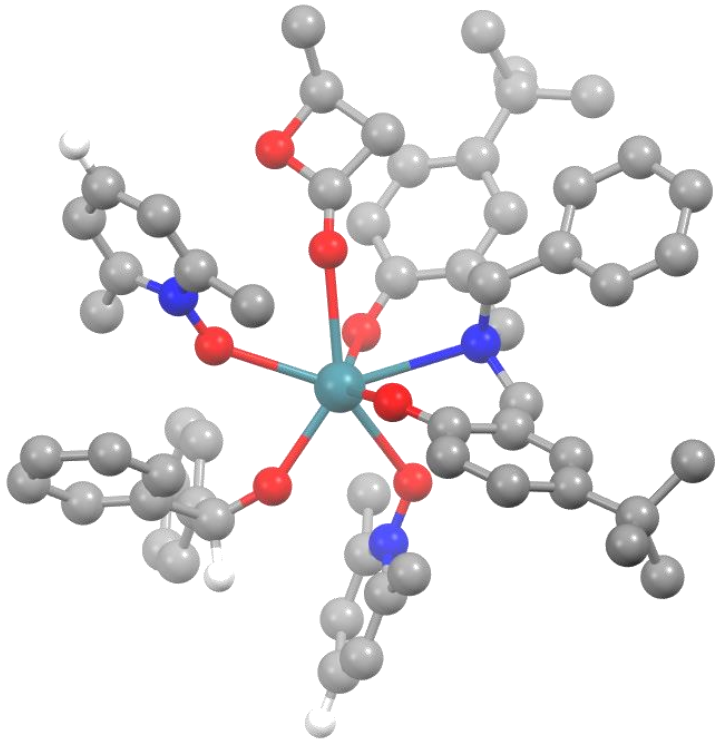


Figure S21. Labeled ball and stick image of **BBL-1** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S22. Cartesian coordinates of **BBL-1**. EM06L (solvent corrected) = -3363.973201 Hartree (-3363.981588)

Atom	**X**	**Y**	**Z**
La	-0.32611	-0.62594	-0.13815
O	-1.23031	1.22590	-1.37503
O	1.67274	-1.28047	0.91556
O	-2.27919	-1.02607	1.51955
O	0.58030	-1.25634	-2.44370
N	1.88741	1.09620	-0.70556
C	-0.97367	2.51120	-1.35039
C	-2.01472	3.49130	-1.21968
C	-3.48673	3.07709	-1.31251
C	-3.88784	2.06848	-0.22923
H	-3.22472	1.19736	-0.22452
H	-4.91754	1.72505	-0.41107
H	-3.86560	2.51441	0.77345
C	-3.71305	2.45261	-2.69854
H	-3.44665	3.16316	-3.49158

H	-4.77135	2.18434	-2.83088
H	-3.10733	1.54992	-2.82618
C	-4.43860	4.26857	-1.18461
H	-4.33155	4.78277	-0.21900
H	-5.47570	3.91598	-1.25232
H	-4.29031	5.00991	-1.97996
C	-1.65673	4.83841	-1.16184
H	-2.44849	5.57658	-1.03837
C	-0.34112	5.30928	-1.27885
C	-0.05009	6.80375	-1.16164
C	-0.90639	7.59656	-2.15760
H	-0.69390	7.28969	-3.18898
H	-0.70193	8.67276	-2.07530
H	-1.97966	7.45197	-1.98399
C	1.41891	7.12279	-1.43537
H	2.08794	6.61604	-0.72743
H	1.59511	8.20207	-1.34384
H	1.71806	6.82051	-2.44680
C	-0.38561	7.26848	0.26364
H	-1.43687	7.06895	0.51380
H	-0.21549	8.34781	0.38048
H	0.24175	6.74986	1.00376
C	0.64626	4.34505	-1.47979
H	1.68389	4.64238	-1.63068
C	0.36452	2.97843	-1.48875
C	1.47214	2.01465	-1.79638
H	1.16705	1.35307	-2.62191
H	2.35467	2.58376	-2.14754
C	2.32032	1.80498	0.52344
H	2.52605	1.01852	1.26364
H	1.44525	2.36158	0.87604
C	3.48282	2.76677	0.42648
C	3.25704	4.14431	0.53132
H	2.23482	4.50384	0.66510
C	4.30542	5.05838	0.47131
H	4.10143	6.12512	0.56192
C	5.61190	4.60770	0.30461
H	6.43525	5.31844	0.25384
C	5.85779	3.23935	0.22314
H	6.87853	2.87306	0.11898
C	4.80689	2.32924	0.29228

H	5.01765	1.26084	0.26996
C	2.95015	0.23276	-1.26223
H	3.74148	0.87554	-1.69615
H	2.48780	-0.28512	-2.11453
C	3.61997	-0.77304	-0.36071
C	4.95714	-1.04908	-0.64601
H	5.43447	-0.46595	-1.43969
C	5.69618	-2.01255	0.03569
C	7.16368	-2.23567	-0.31908
C	7.93288	-0.91771	-0.14689
H	7.86314	-0.55234	0.88610
H	7.53675	-0.13207	-0.80310
H	8.99642	-1.04859	-0.39056
C	7.27733	-2.68933	-1.78036
H	6.74811	-3.63739	-1.94050
H	8.32854	-2.83531	-2.06568
H	6.84584	-1.94920	-2.46555
C	7.81893	-3.29343	0.56702
H	7.78903	-3.01231	1.62738
H	8.87261	-3.41953	0.28678
H	7.33074	-4.27091	0.46457
C	5.03140	-2.70286	1.05168
H	5.58352	-3.45101	1.61371
C	3.69757	-2.47326	1.39291
C	3.05451	-3.21541	2.56770
C	3.99677	-4.23469	3.21071
H	4.30854	-5.01242	2.50152
H	3.48239	-4.73426	4.04199
H	4.90119	-3.76556	3.61842
C	1.80226	-3.98445	2.12339
H	1.08035	-3.32592	1.63323
H	1.31341	-4.45814	2.98832
H	2.06508	-4.78252	1.41565
C	2.69437	-2.18246	3.64535
H	3.60511	-1.74317	4.07341
H	2.12882	-2.65016	4.46521
H	2.09465	-1.37313	3.22144
C	2.95240	-1.49859	0.66102
H	-0.43619	-1.99262	3.01246
H	0.09964	-0.31837	2.91611
C	-0.47104	-1.02497	3.53163

H	0.04967	-1.12378	4.48794
C	-1.86866	-0.58968	3.75298
N	-2.72698	-0.67068	2.68433
H	-4.67577	-0.13137	0.79947
C	-2.36129	-0.15545	4.97443
C	-4.07728	-0.45826	2.82901
C	-4.92143	-0.76920	1.65456
C	-3.70365	0.16012	5.13401
C	-4.55689	-0.02075	4.05348
H	-5.97909	-0.64340	1.90241
H	-4.74088	-1.80228	1.32524
H	1.37700	-3.28381	-0.81932
H	2.26581	-4.54287	-1.70841
C	1.82459	-3.54500	-1.78757
H	2.62246	-2.81457	-1.97013
C	0.79028	-3.52069	-2.84562
N	0.19174	-2.31568	-3.10663
H	-1.80685	-0.47777	-3.19550
C	0.39060	-4.62735	-3.57968
C	-0.81133	-2.17712	-4.02681
C	-1.41022	-0.82867	-4.15737
C	-0.60466	-4.52427	-4.54338
C	-1.20339	-3.29031	-4.75534
H	-2.22531	-0.84322	-4.88687
H	-0.66074	-0.08421	-4.45321
H	-2.00595	-3.16651	-5.47824
O	-1.16105	-2.73795	-0.64482
C	-2.23599	-3.57375	-0.82039
C	-3.29691	-2.94159	-1.71186
C	-3.89859	-3.64624	-2.75528
H	-3.59268	-4.67813	-2.94078
C	-4.86314	-3.04773	-3.56567
H	-5.31323	-3.61308	-4.38150
C	-5.25186	-1.73102	-3.33261
H	-6.00647	-1.26077	-3.96135
C	-4.66680	-1.02028	-2.28479
H	-4.96262	0.00936	-2.08606
C	-3.69489	-1.61994	-1.49265
H	-3.24926	-1.06554	-0.66445
C	-2.84071	-4.02138	0.51704
C	-2.03060	-4.02914	1.65442

H	-0.99424	-3.71525	1.54282
C	-2.53857	-4.38913	2.89741
H	-1.88620	-4.37718	3.77214
C	-3.87730	-4.75792	3.02664
H	-4.28187	-5.03237	4.00006
C	-4.68925	-4.78210	1.89577
H	-5.73554	-5.07463	1.98118
C	-4.17277	-4.42104	0.65114
H	-4.82432	-4.42428	-0.22364
H	-1.91563	-4.50684	-1.34455
O	-2.19920	2.90126	2.48766
H	-2.41561	4.81670	1.67568
O	-0.72369	1.41427	1.57602
C	-1.03439	2.53628	1.90793
C	-1.79195	4.33438	2.43847
H	-0.13709	4.28701	0.91453
H	-2.92135	5.00879	4.14032
C	-0.43093	3.90633	1.89920
C	-1.88714	4.98748	3.78186
H	-1.27498	4.45880	4.52170
H	-1.52909	6.02162	3.71605
H	0.40184	4.01984	2.60416
H	-1.66219	-0.08418	5.80438
H	-5.62529	0.16059	4.14157
H	-4.08381	0.50721	6.09115
H	0.87595	-5.57740	-3.37004
H	-0.91551	-5.39631	-5.11347

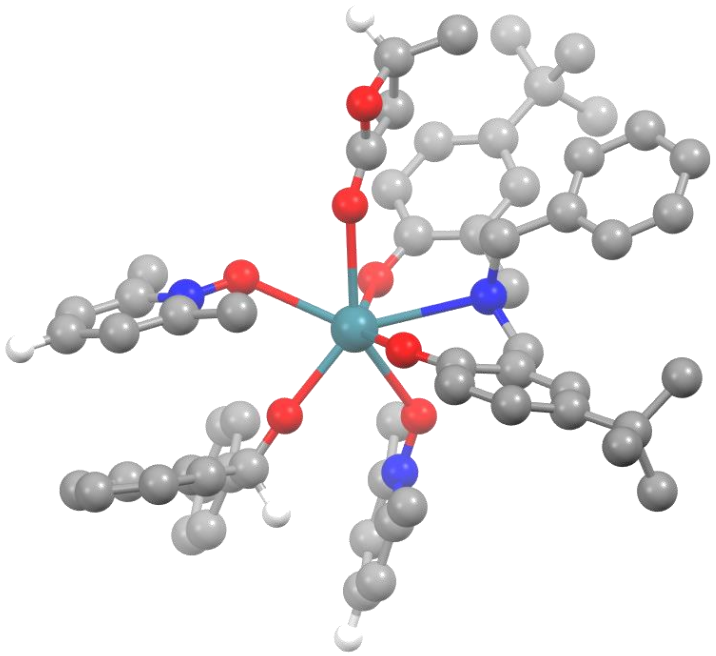


Figure S22. Labeled ball and stick image of **BBL-2** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S23. Cartesian coordinates of **BBL-2**. EM06L (solvent corrected) = -3363.979013 Hartree (-3363.988295)

Atom	**X**	**Y**	**Z**
La	-0.55102	-0.15261	-0.16517
O	0.46320	-2.14622	0.60328
O	-0.04192	2.08142	-0.61283
O	-1.82687	-1.65489	-1.85942
O	-0.51214	0.25360	2.35186
N	2.10524	0.57597	0.67419
C	1.66304	-2.67556	0.66811
C	1.88973	-4.05417	0.37058
C	0.72381	-4.98775	0.02287
C	0.16655	-4.63228	-1.36151
H	-0.15714	-3.58650	-1.41898
H	-0.69467	-5.27290	-1.59964
H	0.91988	-4.81503	-2.14142
C	-0.40816	-4.88713	1.05815
H	-0.03643	-5.09148	2.07170
H	-1.18893	-5.62843	0.83142
H	-0.85840	-3.89121	1.05683
C	1.15582	-6.45647	-0.02344
H	1.88612	-6.65289	-0.81872

H	0.28222	-7.08955	-0.22479
H	1.59562	-6.78550	0.92679
C	3.20294	-4.53204	0.37732
H	3.37342	-5.57500	0.12556
C	4.31294	-3.74906	0.70615
C	5.74258	-4.28590	0.71915
C	5.82779	-5.71621	0.18963
H	5.25904	-6.41771	0.81259
H	6.87174	-6.05436	0.18200
H	5.44440	-5.79290	-0.83653
C	6.28780	-4.26475	2.15347
H	6.28109	-3.25013	2.57043
H	7.32302	-4.63213	2.18617
H	5.68161	-4.89810	2.81290
C	6.63327	-3.39580	-0.15771
H	6.26996	-3.37161	-1.19532
H	7.66801	-3.76547	-0.17234
H	6.65637	-2.36345	0.21305
C	4.05717	-2.42708	1.07508
H	4.88112	-1.78755	1.40091
C	2.77833	-1.87382	1.05574
C	2.58281	-0.48483	1.60037
H	1.82750	-0.51220	2.40018
H	3.53313	-0.15506	2.06287
C	2.98382	0.75595	-0.50454
H	2.48362	1.49493	-1.14640
H	2.96511	-0.20311	-1.02951
C	4.43482	1.12847	-0.29108
C	5.42930	0.15906	-0.46392
H	5.13496	-0.85905	-0.72394
C	6.77908	0.46797	-0.31988
H	7.53155	-0.30535	-0.47270
C	7.16243	1.76602	0.00620
H	8.21632	2.01451	0.12158
C	6.18713	2.74802	0.16229
H	6.47677	3.77272	0.39200
C	4.83979	2.43498	0.00633
H	4.09026	3.21959	0.09073
C	1.97974	1.81681	1.47656
H	2.93722	1.99477	2.00516
H	1.24404	1.57826	2.25784

C	1.60596	3.09395	0.76840
C	2.23786	4.26160	1.19467
H	2.99167	4.17094	1.98264
C	1.97534	5.51230	0.64047
C	2.73806	6.73881	1.13596
C	4.24553	6.51008	0.95363
H	4.49269	6.33523	-0.10189
H	4.59247	5.63863	1.52378
H	4.81944	7.38161	1.29805
C	2.44644	6.95868	2.62611
H	1.37765	7.14148	2.79502
H	3.00372	7.82365	3.01216
H	2.73126	6.08442	3.22444
C	2.35071	8.00682	0.37699
H	2.56507	7.92169	-0.69600
H	2.91816	8.86416	0.76105
H	1.28409	8.23923	0.48937
C	1.02580	5.55536	-0.38420
H	0.81201	6.51351	-0.84939
C	0.33963	4.43002	-0.84190
C	-0.69632	4.53689	-1.96310
C	-0.83006	5.96109	-2.50543
H	-1.15740	6.66968	-1.73360
H	-1.58110	5.97827	-3.30602
H	0.11171	6.33309	-2.92903
C	-2.07542	4.12013	-1.43261
H	-2.04060	3.11392	-1.00534
H	-2.82421	4.12980	-2.23984
H	-2.41841	4.81176	-0.65016
C	-0.28964	3.63763	-3.14052
H	0.67191	3.96346	-3.55813
H	-1.03787	3.69679	-3.94461
H	-0.18879	2.59360	-2.83081
C	0.61153	3.16402	-0.24256
H	-2.32201	1.18637	-1.97163
H	-1.40100	0.40908	-3.28895
C	-2.39681	0.75165	-2.97969
H	-2.71993	1.55686	-3.64630
C	-3.38152	-0.35452	-2.98918
N	-3.01605	-1.53198	-2.38358
H	-2.47329	-4.23347	-2.31678

C	-4.62428	-0.27439	-3.59593
C	-3.85417	-2.61864	-2.35607
C	-3.32001	-3.85175	-1.73381
C	-5.49776	-1.35141	-3.58558
C	-5.09998	-2.52243	-2.95612
H	-4.09603	-4.62050	-1.68274
H	-2.92752	-3.66173	-0.72917
H	-2.01281	2.24135	1.31943
H	-2.50812	3.44630	2.54455
C	-1.87749	2.57156	2.36068
H	-0.82382	2.86346	2.45652
C	-2.23882	1.47321	3.28692
N	-1.51339	0.31455	3.19171
H	-0.81633	-2.21525	2.69631
C	-3.26953	1.52696	4.21539
C	-1.76718	-0.78478	3.97418
C	-0.88764	-1.95768	3.76034
C	-3.56257	0.43596	5.02235
C	-2.79926	-0.71802	4.89583
H	-1.25595	-2.81882	4.32554
H	0.14248	-1.73704	4.07030
H	-3.00508	-1.60005	5.49704
O	-2.80557	0.31209	0.24757
C	-4.05627	0.30017	0.80015
C	-4.36997	-0.98149	1.55808
C	-5.47113	-1.03701	2.42067
H	-6.11256	-0.15822	2.51410
C	-5.74878	-2.18161	3.15929
H	-6.61063	-2.20227	3.82562
C	-4.92075	-3.29958	3.05299
H	-5.13270	-4.19647	3.63320
C	-3.82109	-3.25834	2.20048
H	-3.16174	-4.12271	2.11306
C	-3.55178	-2.10630	1.46118
H	-2.68495	-2.07038	0.79666
C	-5.12337	0.69297	-0.22932
C	-4.93036	1.91708	-0.88218
H	-4.03342	2.49075	-0.64958
C	-5.85620	2.40410	-1.79496
H	-5.68511	3.36599	-2.27906
C	-7.01096	1.67036	-2.07407

H	-7.74925	2.05229	-2.77810
C	-7.21097	0.44920	-1.43922
H	-8.10463	-0.13683	-1.65473
C	-6.27175	-0.03924	-0.52814
H	-6.44437	-1.00039	-0.04391
H	-4.14071	1.10663	1.57218
O	2.34354	-1.02946	-4.07610
H	3.35412	-2.78020	-4.64071
O	0.87020	-0.77156	-2.35752
C	1.82788	-1.31233	-2.86291
C	3.44332	-2.01140	-3.86626
H	2.39400	-3.37838	-2.42396
H	4.97811	-0.86891	-4.84993
C	2.82848	-2.37872	-2.51778
C	4.77521	-1.32320	-3.87487
H	4.81399	-0.53629	-3.11138
H	5.57333	-2.04304	-3.65961
H	3.43222	-2.19300	-1.61930
H	-4.89748	0.66610	-4.06672
H	-5.74797	-3.39493	-2.92214
H	-6.47706	-1.27217	-4.05060
H	-3.84650	2.44659	4.27848
H	-4.37962	0.48194	5.73826

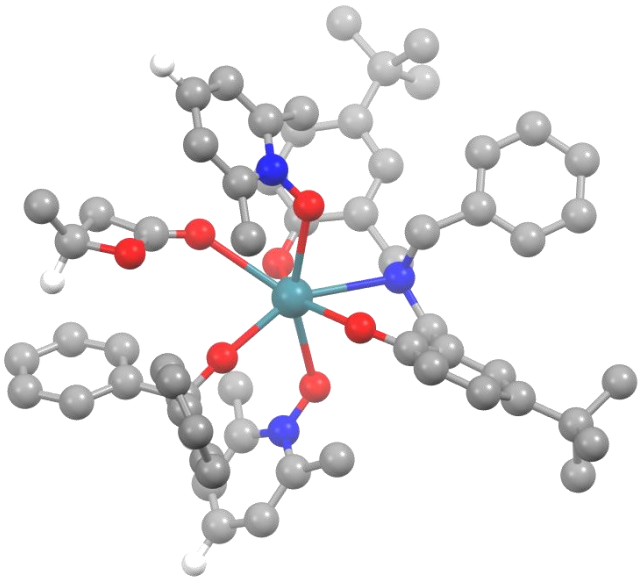


Figure S23. Labeled ball and stick image of **BBL-3** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S24. Cartesian coordinates of **BBL-3**. EM06L (solvent corrected) = -3363.973649 Hartree (-3363.981260)

Atom	**X**	**Y**	**Z**
La	-0.33137	-0.05414	-0.20177
O	-0.27518	1.95514	-1.52422
O	0.97568	-1.84586	0.58132
O	0.29245	0.84094	2.15569
O	-0.01983	-1.08988	-2.55957
N	2.36868	0.33697	-0.71164
C	0.52512	2.99241	-1.36823
C	0.04076	4.33570	-1.31967
C	-1.40847	4.66582	-1.69398
C	-2.40372	4.01359	-0.73088
H	-2.35567	2.92508	-0.79814
H	-3.42770	4.34315	-0.96819
H	-2.19321	4.29518	0.31239
C	-1.69217	4.15090	-3.11364
H	-1.05504	4.65904	-3.84877
H	-2.74027	4.34023	-3.38957
H	-1.50353	3.07563	-3.18158
C	-1.68316	6.17098	-1.68768
H	-1.57149	6.60932	-0.68707
H	-2.71515	6.35522	-2.01381
H	-1.01874	6.71549	-2.37019

C	0.93962	5.35359	-0.98712
H	0.55726	6.36679	-0.90213
C	2.30615	5.14987	-0.77773
C	3.27230	6.27722	-0.41951
C	2.54432	7.58126	-0.09655
H	1.99385	7.97051	-0.96222
H	3.26585	8.35096	0.20591
H	1.82751	7.45181	0.72585
C	4.22574	6.52770	-1.59540
H	4.79790	5.62491	-1.84316
H	4.94412	7.32486	-1.35760
H	3.67147	6.82604	-2.49408
C	4.10189	5.87546	0.80663
H	3.45705	5.65327	1.66836
H	4.78930	6.68237	1.09652
H	4.70579	4.98291	0.60300
C	2.78167	3.85441	-0.98748
H	3.85525	3.65501	-0.94410
C	1.93441	2.78905	-1.27652
C	2.51869	1.46238	-1.66664
H	2.03234	1.11665	-2.59181
H	3.59261	1.59660	-1.89679
C	3.01459	0.60737	0.59439
H	2.83222	-0.27754	1.21687
H	2.44398	1.42828	1.04723
C	4.47733	0.98371	0.61786
C	4.84687	2.24455	1.09732
H	4.06386	2.93579	1.41376
C	6.18208	2.62933	1.17820
H	6.43893	3.61591	1.56357
C	7.18287	1.75124	0.77082
H	8.22935	2.04662	0.82694
C	6.83377	0.48561	0.30693
H	7.60931	-0.21880	0.00763
C	5.49718	0.10191	0.23881
H	5.24552	-0.90864	-0.07712
C	2.86589	-0.88050	-1.39995
H	3.84469	-0.65500	-1.86529
H	2.16895	-1.04242	-2.23557
C	3.01754	-2.13993	-0.59255
C	4.12106	-2.94377	-0.86978

H	4.82462	-2.59570	-1.63258
C	4.36434	-4.14610	-0.20872
C	5.60758	-4.96252	-0.55201
C	6.85954	-4.10163	-0.32815
H	6.92423	-3.76469	0.71462
H	6.85337	-3.20680	-0.96373
H	7.77248	-4.66717	-0.56150
C	5.55295	-5.38711	-2.02540
H	4.67600	-6.01752	-2.22049
H	6.44994	-5.95752	-2.30464
H	5.48985	-4.51776	-2.69175
C	5.73158	-6.21910	0.30773
H	5.80711	-5.97604	1.37520
H	6.63425	-6.77886	0.03078
H	4.87281	-6.88975	0.17596
C	3.45131	-4.50810	0.78584
H	3.63330	-5.42162	1.34535
C	2.32415	-3.74964	1.10996
C	1.41550	-4.13373	2.28030
C	1.85911	-5.43232	2.95777
H	1.82157	-6.28844	2.27120
H	1.18872	-5.65468	3.79816
H	2.87863	-5.36486	3.35861
C	-0.04242	-4.33248	1.83816
H	-0.47153	-3.42262	1.40913
H	-0.66263	-4.62960	2.69636
H	-0.11942	-5.13201	1.08804
C	1.49399	-3.01577	3.33279
H	2.50705	-2.94864	3.75119
H	0.80090	-3.21589	4.16392
H	1.24617	-2.04400	2.89174
C	2.06540	-2.55568	0.37439
H	-0.53621	-1.21640	3.51913
H	-2.24193	-1.18442	4.05602
C	-1.49910	-0.70571	3.41135
H	-1.82509	-0.86271	2.37019
C	-1.39755	0.73941	3.72161
N	-0.46555	1.46036	3.01597
H	1.66457	3.06097	2.42935
C	-2.21089	1.41078	4.62235
C	-0.33615	2.82035	3.14871

C	0.66257	3.48188	2.27879
C	-2.10373	2.78551	4.79479
C	-1.16229	3.48099	4.04580
H	0.69145	4.55817	2.47360
H	0.42529	3.33375	1.21445
H	-0.18366	-3.27805	-1.00812
H	-0.12934	-4.79715	-1.94365
C	-0.01986	-3.71059	-2.00652
H	1.01652	-3.46397	-2.26938
C	-0.98450	-3.14634	-2.97499
N	-0.94608	-1.78720	-3.15972
H	-1.70433	0.81216	-3.06502
C	-1.92952	-3.88180	-3.67787
C	-1.84412	-1.13189	-3.96266
C	-1.68953	0.33742	-4.05441
C	-2.84787	-3.25725	-4.51163
C	-2.80351	-1.87413	-4.63509
H	-2.47979	0.76916	-4.67560
H	-0.70926	0.60511	-4.46884
H	-3.51431	-1.33914	-5.26027
O	-2.29466	-1.20591	-0.54168
C	-3.41392	-1.94994	-0.82606
C	-4.64386	-1.06709	-1.02889
C	-5.94777	-1.53560	-0.84250
H	-6.10046	-2.54342	-0.45542
C	-7.04704	-0.73322	-1.14554
H	-8.05465	-1.11760	-0.99004
C	-6.86276	0.55235	-1.65367
H	-7.72173	1.17301	-1.90413
C	-5.56639	1.02979	-1.84421
H	-5.40218	2.03036	-2.24898
C	-4.47192	0.23090	-1.52190
H	-3.45481	0.60218	-1.65497
C	-3.59547	-3.05873	0.19799
C	-3.33063	-4.38377	-0.14983
H	-3.06196	-4.61212	-1.18349
C	-3.39588	-5.40469	0.79670
H	-3.17600	-6.43126	0.50599
C	-3.73289	-5.10960	2.11373
H	-3.78144	-5.90251	2.85860
C	-4.00571	-3.78989	2.47300

H	-4.27409	-3.55186	3.50253
C	-3.93853	-2.77523	1.52440
H	-4.14793	-1.74488	1.80821
H	-3.29394	-2.47085	-1.80482
O	-4.17385	0.51224	1.95504
H	-6.04062	0.74785	1.04185
O	-2.28676	1.39246	1.01135
C	-3.45979	1.44716	1.29510
C	-5.42591	1.29717	1.76566
H	-4.82976	2.69487	0.10401
H	-6.42785	0.59903	3.53383
C	-4.59755	2.41252	1.13276
C	-6.11510	1.54161	3.07267
H	-5.45513	2.06902	3.77206
H	-7.00996	2.15436	2.91712
H	-4.48313	3.31287	1.74766
H	-2.94596	0.82812	5.17333
H	-1.05111	4.55841	4.13920
H	-2.74623	3.30749	5.50000
H	-1.93769	-4.96043	-3.53758
H	-3.59456	-3.83735	-5.04776

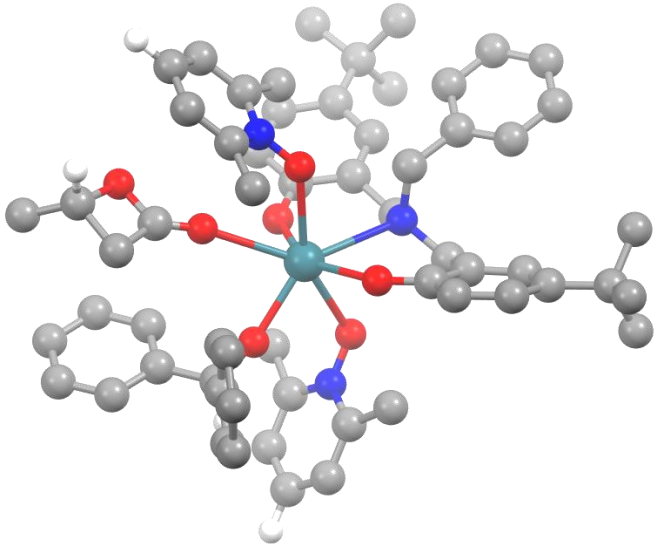


Figure S24. Labeled ball and stick image of **BBL-4** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S25. Cartesian coordinates of **BBL-4**. EM06L (solvent corrected) = -3363.97282 Hartree (-3363.984779)

Atom	**X**	**Y**	**Z**
La	-0.36139	-0.31032	-0.16423
O	-0.60748	1.93262	-0.82440
O	1.15391	-2.01340	0.32010
O	0.01099	0.32234	2.39375
O	0.38867	-0.63828	-2.66658
N	2.23166	0.62398	-0.56795
C	0.06697	3.06129	-0.94023
C	-0.58460	4.32569	-0.83248
C	-2.11253	4.41430	-0.71793
C	-2.61757	3.76230	0.57590
H	-2.28271	2.72449	0.65978
H	-3.71714	3.76303	0.60384
H	-2.26867	4.31477	1.46038
C	-2.76992	3.70776	-1.91360
H	-2.38226	4.09523	-2.86528
H	-3.85704	3.87353	-1.90191
H	-2.58461	2.63095	-1.88264
C	-2.60829	5.86236	-0.72043
H	-2.22046	6.43537	0.13185
H	-3.70375	5.87352	-0.65032
H	-2.32943	6.39411	-1.63924

C	0.19764	5.48291	-0.87324
H	-0.29954	6.44340	-0.77329
C	1.58334	5.47391	-1.04896
C	2.43021	6.74315	-1.10235
C	1.60803	8.00154	-0.82795
H	0.82268	8.15003	-1.57983
H	2.25617	8.88691	-0.85012
H	1.12654	7.96643	0.15804
C	3.06746	6.87488	-2.49234
H	3.69533	6.00712	-2.72876
H	3.70011	7.77160	-2.55157
H	2.29864	6.94994	-3.27160
C	3.54734	6.65755	-0.05412
H	3.13344	6.54612	0.95745
H	4.17112	7.56221	-0.06832
H	4.20386	5.79849	-0.24034
C	2.18478	4.22709	-1.21469
H	3.26123	4.16667	-1.39449
C	1.47288	3.03118	-1.16032
C	2.20631	1.76489	-1.52342
H	1.77578	1.34176	-2.44382
H	3.25102	2.04154	-1.76265
C	2.69218	1.00188	0.78887
H	2.64266	0.08298	1.38978
H	1.93212	1.68474	1.18444
C	4.05184	1.64549	0.93038
C	4.16848	3.03091	1.09064
H	3.26603	3.64375	1.09030
C	5.41511	3.63150	1.24868
H	5.48187	4.71042	1.38414
C	6.57080	2.85454	1.24806
H	7.54594	3.32326	1.37140
C	6.46835	1.47278	1.10812
H	7.36401	0.85318	1.13031
C	5.22032	0.87520	0.95903
H	5.14358	-0.20881	0.88661
C	3.07788	-0.42484	-1.19415
H	4.04428	0.03206	-1.48290
H	2.56506	-0.67204	-2.13469
C	3.38539	-1.68419	-0.42320
C	4.69039	-2.16926	-0.49991

H	5.42244	-1.56952	-1.04840
C	5.09422	-3.35984	0.10064
C	6.55184	-3.80367	0.00241
C	7.46288	-2.69800	0.55513
H	7.21818	-2.46953	1.60086
H	7.36224	-1.76839	-0.01924
H	8.51819	-3.00124	0.51066
C	6.91533	-4.05433	-1.46721
H	6.29441	-4.85120	-1.89590
H	7.96833	-4.35339	-1.56656
H	6.76539	-3.15416	-2.07618
C	6.82099	-5.08420	0.79089
H	6.59337	-4.96101	1.85753
H	7.87923	-5.36299	0.70647
H	6.22666	-5.92717	0.41600
C	4.11179	-4.08337	0.78163
H	4.39689	-5.01655	1.25956
C	2.78197	-3.66996	0.87746
C	1.73776	-4.52684	1.59964
C	2.34170	-5.79787	2.20029
H	2.76756	-6.45655	1.43235
H	1.55807	-6.36384	2.72069
H	3.13024	-5.57637	2.93112
C	0.64079	-4.96697	0.61743
H	0.09193	-4.11095	0.21348
H	-0.08271	-5.62412	1.11995
H	1.07482	-5.52690	-0.22218
C	1.10668	-3.72987	2.75004
H	1.84859	-3.52451	3.53410
H	0.28175	-4.29882	3.20679
H	0.71711	-2.77510	2.38665
C	2.40020	-2.43947	0.26629
H	-1.56939	-1.70953	2.82784
H	-0.31666	-1.73266	4.04458
C	-1.35516	-1.43126	3.86796
H	-2.01119	-1.99989	4.53441
C	-1.52812	0.02266	4.08362
N	-0.76960	0.85152	3.29256
H	-0.05818	4.07728	2.72575
C	-2.37918	0.58099	5.02495
C	-0.81058	2.21747	3.43590

C	0.09235	3.00557	2.56937
C	-2.46683	1.95918	5.17853
C	-1.66890	2.76510	4.37878
H	-0.07787	2.78267	1.50882
H	1.13990	2.75876	2.78336
H	0.58121	-3.07330	-1.69693
H	0.81505	-4.35847	-2.91591
C	0.79207	-3.27698	-2.75567
H	1.79273	-2.86495	-2.93800
C	-0.22436	-2.64419	-3.62387
N	-0.37214	-1.28745	-3.50537
H	-1.53027	1.04848	-2.86415
C	-1.03100	-3.32498	-4.52434
C	-1.31887	-0.59179	-4.21007
C	-1.40212	0.86018	-3.93816
C	-1.98510	-2.65208	-5.27653
C	-2.12415	-1.28033	-5.10473
H	-2.23492	1.30870	-4.48759
H	-0.47051	1.37491	-4.20714
H	-2.87073	-0.71516	-5.65746
O	-2.02386	-1.42640	-1.30067
C	-3.14221	-2.17149	-1.53138
C	-4.42081	-1.33766	-1.40248
C	-5.68648	-1.93128	-1.33907
H	-5.76735	-3.01954	-1.34951
C	-6.83785	-1.15133	-1.25338
H	-7.81512	-1.63081	-1.20513
C	-6.74103	0.23977	-1.22917
H	-7.64100	0.85106	-1.16852
C	-5.48423	0.84122	-1.28605
H	-5.39082	1.92749	-1.25716
C	-4.33728	0.05620	-1.37757
H	-3.35027	0.51701	-1.41294
C	-3.17505	-3.39795	-0.62955
C	-3.37534	-4.68043	-1.13646
H	-3.52834	-4.80728	-2.21030
C	-3.36624	-5.79269	-0.29403
H	-3.51328	-6.78869	-0.70954
C	-3.15751	-5.63278	1.07205
H	-3.14173	-6.50019	1.72982
C	-2.94900	-4.35374	1.59053

H	-2.76755	-4.22181	2.65835
C	-2.95543	-3.25279	0.74359
H	-2.77375	-2.24835	1.13087
H	-3.15166	-2.56026	-2.57810
O	-4.28466	1.40628	2.24364
H	-5.32593	0.62035	3.87331
O	-2.59996	0.21903	1.25747
C	-3.69749	0.29211	1.76055
C	-5.41857	0.60521	2.78053
H	-4.53884	-1.48054	2.78040
H	-6.90844	2.14559	2.66178
C	-4.81255	-0.64012	2.13355
C	-6.73971	1.12365	2.30678
H	-6.78710	1.11520	1.21275
H	-7.54844	0.49116	2.69064
H	-5.35410	-1.02134	1.25721
H	-2.96806	-0.09553	5.64131
H	-1.69588	3.84845	4.46539
H	-3.13840	2.39596	5.91319
H	-0.89766	-4.40060	-4.61259
H	-2.61811	-3.18952	-5.97841

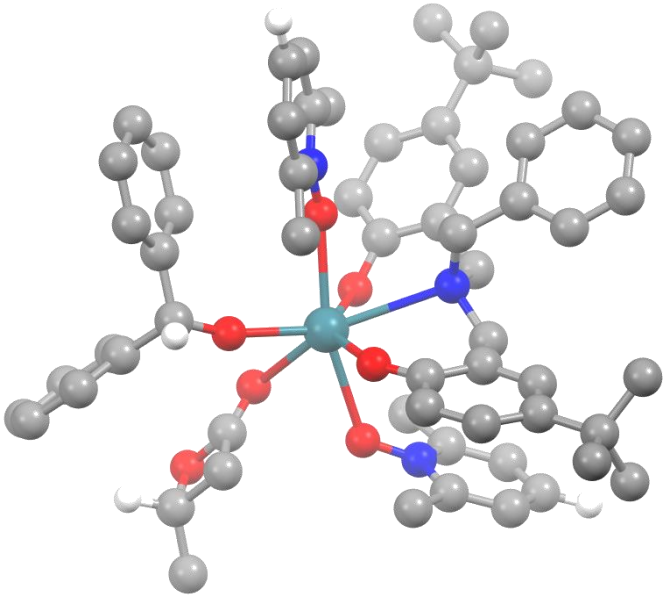


Figure S25. Labeled ball and stick image of **BBL-5** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S26. Cartesian coordinates of **BBL-5**. EM06L (solvent corrected) = -3363.974963 Hartree (-3363.986073)

Atom	**X**	**Y**	**Z**
La	-0.62172	-0.60401	-0.39980
O	-0.92977	1.24507	-1.84392
O	1.15044	-1.75165	0.65454
O	-1.02147	1.24602	1.32501
O	0.22822	-1.96040	-2.56292
N	1.78410	1.01578	-0.34426
C	-0.74330	2.54023	-1.71305
C	-1.78943	3.47829	-1.93541
C	-3.16462	3.00136	-2.41742
C	-3.83393	2.07963	-1.38637
H	-3.19817	1.22288	-1.14259
H	-4.78215	1.68753	-1.78107
H	-4.06675	2.62122	-0.45883
C	-3.01021	2.23230	-3.73956
H	-2.51726	2.85625	-4.49727
H	-3.99684	1.94566	-4.12949
H	-2.42053	1.32331	-3.59572
C	-4.12127	4.16900	-2.66620
H	-4.31433	4.74742	-1.75250
H	-5.08579	3.78420	-3.02104

H	-3.74002	4.86020	-3.42898
C	-1.51039	4.83329	-1.73601
H	-2.31661	5.54879	-1.87691
C	-0.25108	5.32114	-1.36701
C	0.03769	6.80264	-1.13230
C	-1.22923	7.65449	-1.19352
H	-1.70311	7.61331	-2.18208
H	-0.98913	8.70515	-0.98638
H	-1.97216	7.32960	-0.45266
C	1.02026	7.31014	-2.19604
H	1.96044	6.74489	-2.17200
H	1.26241	8.37023	-2.03567
H	0.59664	7.20692	-3.20287
C	0.67377	6.98950	0.25269
H	0.01546	6.61252	1.04745
H	0.87185	8.05162	0.45334
H	1.62932	6.45540	0.33131
C	0.77688	4.38432	-1.23601
H	1.79464	4.71796	-1.01987
C	0.55332	3.01883	-1.38525
C	1.70194	2.05693	-1.40785
H	1.65619	1.48694	-2.35070
H	2.65293	2.62175	-1.42740
C	2.01132	1.59852	0.99904
H	2.12960	0.74452	1.68118
H	1.07864	2.10806	1.26058
C	3.15180	2.57173	1.16734
C	2.86419	3.93011	1.33920
H	1.82009	4.24928	1.34478
C	3.87896	4.86811	1.50296
H	3.62930	5.91972	1.64196
C	5.20983	4.45811	1.50002
H	6.00792	5.18775	1.62700
C	5.51183	3.10600	1.35410
H	6.54895	2.77320	1.37604
C	4.49245	2.17060	1.19520
H	4.73519	1.11062	1.12134
C	2.86717	0.09599	-0.76950
H	3.75338	0.69090	-1.06808
H	2.50053	-0.34206	-1.71069
C	3.34026	-0.99927	0.14848

C	4.71467	-1.21973	0.20928
H	5.36451	-0.53049	-0.33876
C	5.27706	-2.28194	0.91363
C	6.79195	-2.46860	0.92071
C	7.46992	-1.19076	1.43438
H	7.13561	-0.94781	2.45108
H	7.24337	-0.32689	0.79660
H	8.56219	-1.30785	1.45453
C	7.27104	-2.74499	-0.51169
H	6.81648	-3.66388	-0.90617
H	8.36269	-2.86561	-0.54775
H	7.00352	-1.92359	-1.18908
C	7.22860	-3.63406	1.80649
H	6.92096	-3.49016	2.84997
H	8.32170	-3.72922	1.79236
H	6.81056	-4.58819	1.46136
C	4.38848	-3.13937	1.56881
H	4.80281	-3.97259	2.12895
C	2.99926	-2.99209	1.53325
C	2.08597	-4.01769	2.22358
C	2.88358	-5.05216	3.02031
H	3.54493	-5.65243	2.38231
H	2.19036	-5.74406	3.51492
H	3.49853	-4.58460	3.79998
C	1.24256	-4.78159	1.19073
H	0.58287	-4.10148	0.64115
H	0.61241	-5.52635	1.69725
H	1.87764	-5.31661	0.47166
C	1.12460	-3.32364	3.19521
H	1.66911	-2.70622	3.92262
H	0.54298	-4.07067	3.75437
H	0.42936	-2.68587	2.64660
C	2.45100	-1.89883	0.79685
H	-1.09941	-0.96775	2.67600
H	0.55426	-0.41196	2.83576
C	-0.41843	-0.42899	3.34722
H	-0.31164	-0.99135	4.27871
C	-0.90226	0.93824	3.61820
N	-1.16216	1.72827	2.52776
H	-0.86613	3.83973	0.80381
C	-1.07149	1.47086	4.88742

C	-1.55852	3.03672	2.66316
C	-1.77878	3.79097	1.41354
C	-1.48481	2.78355	5.06402
C	-1.71995	3.55904	3.93735
H	-2.11925	4.80831	1.62928
H	-2.51537	3.28754	0.77682
H	-0.17278	0.46255	-3.63408
H	0.34752	0.57024	-5.34310
C	0.18458	-0.11167	-4.50358
H	-0.62955	-0.80476	-4.74847
C	1.42811	-0.85270	-4.19836
N	1.35321	-1.81408	-3.21753
H	1.66375	-3.27563	-1.03505
C	2.65161	-0.63468	-4.81755
C	2.42121	-2.62305	-2.91025
C	2.17925	-3.68310	-1.90870
C	3.77288	-1.37999	-4.47557
C	3.63987	-2.38615	-3.52796
H	3.12222	-4.13972	-1.59380
H	1.52484	-4.46394	-2.32123
O	-2.22148	-1.77655	0.79738
C	-3.15706	-2.20337	1.70887
C	-4.31353	-2.92318	1.02198
C	-4.76892	-4.16315	1.47086
H	-4.28463	-4.62551	2.33326
C	-5.82364	-4.81326	0.83056
H	-6.16546	-5.78164	1.19427
C	-6.43629	-4.22610	-0.27357
H	-7.26007	-4.73033	-0.77666
C	-5.98576	-2.98736	-0.73278
H	-6.45017	-2.52426	-1.60261
C	-4.93430	-2.34318	-0.08934
H	-4.57850	-1.37796	-0.45119
C	-3.70946	-1.06034	2.55821
C	-3.99620	-1.24242	3.91213
H	-3.80993	-2.21775	4.36683
C	-4.50224	-0.19865	4.68368
H	-4.70981	-0.35639	5.74164
C	-4.73489	1.04658	4.10383
H	-5.12210	1.86863	4.70471
C	-4.45900	1.23655	2.75067

H	-4.64314	2.20717	2.28879
C	-3.94654	0.19249	1.98680
H	-3.70485	0.34869	0.93552
H	-2.71190	-2.93463	2.42314
O	-3.60581	-3.15537	-3.10334
H	-4.16100	-4.80216	-1.93676
O	-2.47851	-1.36878	-2.22723
C	-2.69822	-2.55836	-2.30326
C	-3.28284	-4.48324	-2.51052
H	-2.31922	-3.83103	-0.57301
H	-3.69240	-5.65080	-4.27133
C	-2.20331	-3.81946	-1.66024
C	-2.87470	-5.46359	-3.56766
H	-2.01167	-5.09200	-4.13273
H	-2.59811	-6.41887	-3.10689
H	-1.16938	-4.06111	-1.93220
H	2.70231	0.14371	-5.57492
H	4.48410	-3.00643	-3.23615
H	4.73192	-1.18840	-4.94983
H	-2.03578	4.59619	4.01993
H	-1.61622	3.19638	6.06085
H	-0.86633	0.82286	5.73590

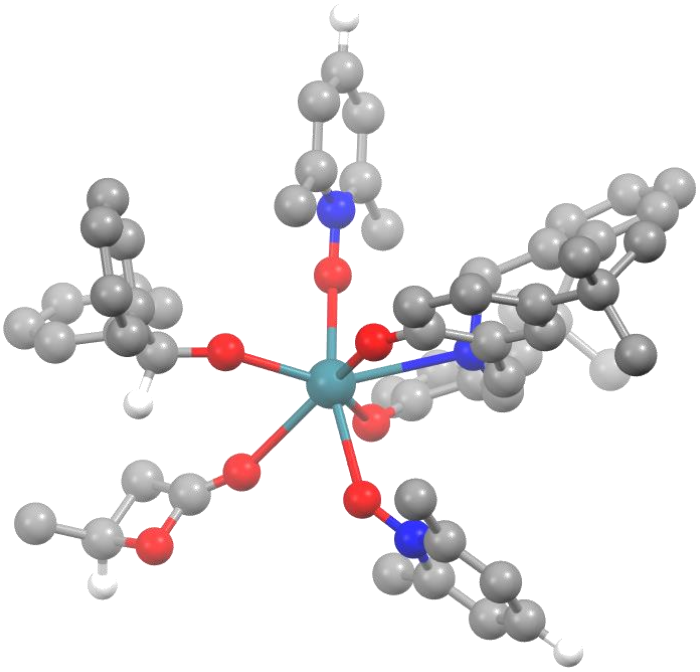


Figure S26. Labeled ball and stick image of **BBL-6** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S27. Cartesian coordinates of **BBL-6**. EM06L (solvent corrected) = -3363.971269 Hartree (-3363.980546)

Atom	**X**	**Y**	**Z**
La	0.60113	-0.54060	0.59402
O	1.20136	1.66181	1.29911
O	-1.33108	-1.76476	0.08399
O	0.97783	0.72628	-1.65923
O	-0.00653	-1.00315	3.04258
N	-1.75637	1.15380	0.36872
C	0.94871	2.88414	0.89396
C	1.99029	3.82781	0.65417
C	3.45435	3.45082	0.90900
C	3.89757	2.30984	-0.01693
H	3.27577	1.41856	0.11348
H	4.94382	2.03381	0.18428
H	3.84899	2.61102	-1.07213
C	3.64203	3.00176	2.36695
H	3.28738	3.77144	3.06541
H	4.70995	2.83362	2.57526
H	3.09403	2.07700	2.56528
C	4.40325	4.62688	0.66667

H	4.37098	4.97871	-0.37291
H	5.43517	4.31471	0.87409
H	4.17875	5.48066	1.31877
C	1.64047	5.09961	0.19492
H	2.43784	5.80870	-0.00901
C	0.32086	5.51755	-0.01115
C	-0.04204	6.91828	-0.50086
C	1.18810	7.71705	-0.92954
H	1.87706	7.89194	-0.09385
H	0.88473	8.69842	-1.31589
H	1.74743	7.20362	-1.72323
C	-0.75626	7.68349	0.62132
H	-1.66497	7.15937	0.94295
H	-1.04927	8.68942	0.28905
H	-0.10709	7.79168	1.49924
C	-0.98835	6.82149	-1.70508
H	-0.52704	6.26289	-2.53144
H	-1.24795	7.82194	-2.07878
H	-1.92508	6.31476	-1.44346
C	-0.68361	4.59643	0.29261
H	-1.73417	4.88380	0.20270
C	-0.39989	3.30156	0.71851
C	-1.52039	2.40014	1.14425
H	-1.33295	2.05480	2.17596
H	-2.45889	2.98714	1.17572
C	-2.02604	1.40509	-1.06388
H	-2.17481	0.41311	-1.51655
H	-1.09358	1.81396	-1.46373
C	-3.15236	2.33417	-1.45472
C	-2.84971	3.59094	-1.99019
H	-1.80354	3.88908	-2.08187
C	-3.85429	4.45863	-2.40931
H	-3.59048	5.42685	-2.83400
C	-5.19031	4.08300	-2.29726
H	-5.97928	4.75864	-2.62415
C	-5.50768	2.82827	-1.78352
H	-6.54829	2.51276	-1.71632
C	-4.49871	1.96082	-1.37454
H	-4.75515	0.96383	-1.02191
C	-2.85472	0.43841	1.06434
H	-3.67980	1.15044	1.26621

H	-2.43670	0.19000	2.05733
C	-3.45132	-0.79917	0.45465
C	-4.83763	-0.93261	0.45878
H	-5.43327	-0.08189	0.80243
C	-5.47760	-2.09876	0.04281
C	-7.00355	-2.15481	0.01181
C	-7.53910	-1.00527	-0.85441
H	-7.14466	-1.06350	-1.87722
H	-7.25613	-0.02667	-0.44556
H	-8.63614	-1.03482	-0.91006
C	-7.55334	-1.99739	1.43573
H	-7.20904	-2.81441	2.08271
H	-8.65236	-2.00406	1.43728
H	-7.22506	-1.05328	1.88831
C	-7.52364	-3.47039	-0.56534
H	-7.16319	-3.63516	-1.58872
H	-8.62068	-3.46016	-0.59532
H	-7.21923	-4.33329	0.04035
C	-4.65762	-3.17229	-0.32029
H	-5.13488	-4.10065	-0.62071
C	-3.26139	-3.12083	-0.30605
C	-2.41546	-4.37131	-0.58008
C	-3.28264	-5.57357	-0.96117
H	-3.98905	-5.84788	-0.16684
H	-2.63768	-6.44281	-1.14249
H	-3.85914	-5.39280	-1.87819
C	-1.63260	-4.74796	0.68823
H	-0.93527	-3.95101	0.96943
H	-1.04567	-5.66075	0.51304
H	-2.31240	-4.94058	1.53026
C	-1.40872	-4.14503	-1.71646
H	-1.90033	-3.71860	-2.60193
H	-0.94907	-5.09780	-2.01303
H	-0.60422	-3.47643	-1.39983
C	-2.63822	-1.89000	0.05243
H	1.05456	-1.79959	-2.34487
H	-0.64452	-1.42454	-2.22191
C	0.18033	-1.51240	-2.94605
H	-0.06148	-2.32707	-3.63374
C	0.37115	-0.24779	-3.67705
N	0.74674	0.84871	-2.93951

H	0.50089	3.32525	-1.79656
C	0.15697	-0.09550	-5.03960
C	0.86764	2.09467	-3.50982
C	1.22928	3.21047	-2.61076
C	0.29351	1.14081	-5.65390
C	0.64216	2.23288	-4.87104
H	1.29214	4.14834	-3.17055
H	2.18416	3.02550	-2.10633
H	0.91475	1.47072	3.36950
H	1.08047	1.95444	5.08803
C	0.87335	1.12001	4.41206
H	1.67114	0.37117	4.49688
C	-0.43834	0.51567	4.72692
N	-0.80218	-0.58470	3.98851
H	-2.15719	-2.25753	2.34688
C	-1.31094	0.97717	5.70213
C	-1.96457	-1.27628	4.23423
C	-2.20015	-2.48589	3.41656
C	-2.51588	0.33273	5.94852
C	-2.82540	-0.80429	5.21382
H	-3.17442	-2.92530	3.64869
H	-1.41432	-3.23185	3.58924
O	1.84675	-2.27930	-0.28153
C	2.94878	-3.06887	-0.47407
C	4.13244	-2.31153	-1.06684
C	5.39803	-2.90763	-1.11263
H	5.51080	-3.93654	-0.76304
C	6.50388	-2.21031	-1.58876
H	7.48314	-2.68865	-1.60276
C	6.35870	-0.90000	-2.04861
H	7.22235	-0.34958	-2.41875
C	5.09893	-0.30762	-2.03401
H	4.96966	0.71252	-2.39569
C	3.99573	-1.00778	-1.54472
H	3.01424	-0.53218	-1.52028
C	2.56524	-4.28219	-1.31535
C	2.08021	-5.42951	-0.68466
H	2.05432	-5.46043	0.40604
C	1.61965	-6.51384	-1.42610
H	1.24410	-7.40098	-0.91627
C	1.63593	-6.46312	-2.81830

H	1.27795	-7.30985	-3.40220
C	2.11563	-5.32242	-3.45903
H	2.13587	-5.27677	-4.54755
C	2.57977	-4.24354	-2.71170
H	2.96570	-3.35546	-3.21570
H	3.31308	-3.47647	0.50129
O	4.55128	-1.73298	3.17917
H	6.42738	-0.91483	3.63427
O	2.90110	-0.70423	1.97920
C	4.06433	-0.91151	2.21964
C	5.94705	-1.40992	2.78327
H	5.59595	0.60525	1.86569
H	6.78274	-3.35722	3.15936
C	5.40580	-0.46212	1.71568
C	6.67711	-2.64088	2.33818
H	6.14177	-3.12662	1.51398
H	7.67890	-2.37618	1.97996
H	5.61572	-0.72497	0.67208
H	-1.01672	1.85755	6.26788
H	-3.74889	-1.35244	5.38283
H	-3.19814	0.70453	6.70862
H	0.74534	3.22617	-5.30047
H	0.12109	1.25415	-6.72109
H	-0.13382	-0.97798	-5.60351

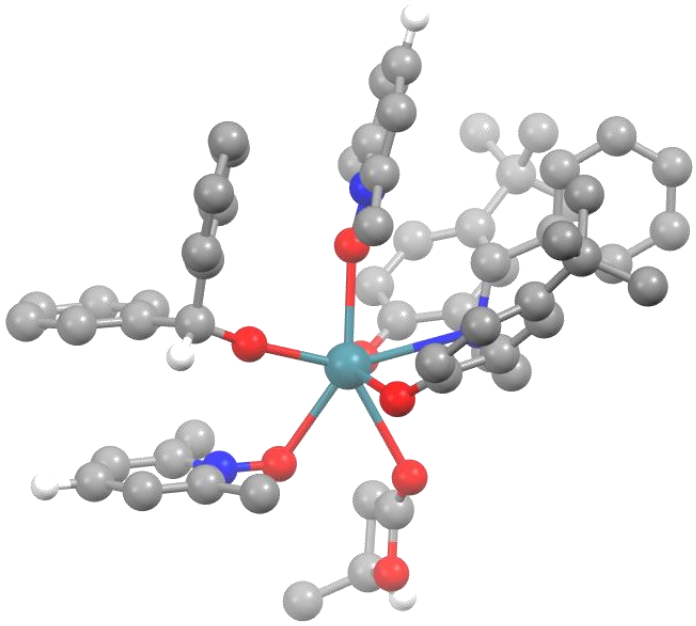


Figure S27. Labeled ball and stick image of **BBL-7** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S28. Cartesian coordinates of **BBL-7**. EM06L (solvent corrected) = -3363.983569 Hartree (-3363.993457)

Atom	**X**	**Y**	**Z**
La	-0.86225	-0.15962	-0.76006
O	-0.92873	2.25396	-0.89238
O	0.04251	-2.09498	-1.76029
O	0.41963	0.07979	1.42867
O	-3.20018	0.07178	-1.90355
N	1.83806	0.55414	-1.43821
C	-0.00776	3.15389	-0.59907
C	-0.27829	4.30047	0.20924
C	-1.71065	4.63138	0.63813
C	-2.27639	3.52967	1.54473
H	-2.14296	2.54094	1.09371
H	-3.35017	3.68917	1.72445
H	-1.77765	3.53177	2.52310
C	-2.59674	4.77505	-0.60745
H	-2.23540	5.58898	-1.24991
H	-3.63293	5.00687	-0.32020
H	-2.59666	3.85173	-1.19169
C	-1.80327	5.94687	1.41337
H	-1.24371	5.91248	2.35724

H	-2.85209	6.15307	1.66355
H	-1.42799	6.79662	0.82887
C	0.79701	5.09661	0.61806
H	0.59175	5.93231	1.28260
C	2.12432	4.86297	0.24310
C	3.31475	5.64691	0.78794
C	2.90026	6.64162	1.87062
H	2.21579	7.40751	1.48439
H	3.78254	7.15947	2.26794
H	2.40169	6.13958	2.71093
C	4.00066	6.41453	-0.34923
H	4.34068	5.73467	-1.14068
H	4.87899	6.96278	0.01900
H	3.31448	7.13938	-0.80500
C	4.32274	4.65911	1.39652
H	3.85689	4.05256	2.18662
H	5.17698	5.19220	1.83636
H	4.71678	3.96299	0.64532
C	2.34092	3.82737	-0.66436
H	3.34965	3.63641	-1.04061
C	1.31703	2.98991	-1.09190
C	1.62767	1.89020	-2.05992
H	0.79675	1.75727	-2.76554
H	2.50813	2.17561	-2.66069
C	2.76446	0.56543	-0.30415
H	2.68670	-0.42149	0.16879
H	2.35627	1.28046	0.42024
C	4.24251	0.86633	-0.44540
C	4.99421	0.70456	0.72737
H	4.48480	0.35859	1.63065
C	6.35717	0.96536	0.76160
H	6.91223	0.82741	1.68855
C	7.01161	1.39498	-0.39214
H	8.08078	1.59826	-0.37561
C	6.28335	1.56002	-1.56436
H	6.78097	1.89413	-2.47349
C	4.91201	1.30139	-1.59219
H	4.37235	1.44329	-2.52478
C	2.19477	-0.44692	-2.48141
H	3.10836	-0.13136	-3.01324
H	1.37365	-0.42652	-3.20972

C	2.38327	-1.83774	-1.95896
C	3.65924	-2.32986	-1.71031
H	4.51046	-1.66384	-1.87870
C	3.87135	-3.62236	-1.22933
C	5.28141	-4.05386	-0.83788
C	5.80915	-3.08405	0.23080
H	5.14148	-3.06345	1.10471
H	5.87633	-2.05773	-0.15205
H	6.81085	-3.37966	0.57376
C	6.20829	-3.99688	-2.05854
H	5.86840	-4.68412	-2.84349
H	7.23607	-4.27368	-1.78508
H	6.23918	-2.98879	-2.49053
C	5.31577	-5.46890	-0.26461
H	4.68227	-5.56007	0.62764
H	6.34022	-5.73427	0.02652
H	4.97569	-6.21488	-0.99415
C	2.74472	-4.44313	-1.10737
H	2.88974	-5.47220	-0.78668
C	1.43879	-4.01003	-1.35662
C	0.24121	-4.95567	-1.23667
C	0.67144	-6.40365	-0.99420
H	1.33031	-6.77601	-1.78936
H	-0.21493	-7.05075	-0.96554
H	1.19469	-6.52528	-0.03661
C	-0.56385	-4.92906	-2.54457
H	-0.89559	-3.91562	-2.78651
H	-1.44657	-5.58011	-2.46189
H	0.04476	-5.29670	-3.38091
C	-0.65978	-4.54960	-0.06152
H	-0.13836	-4.69074	0.89508
H	-1.56329	-5.17902	-0.03695
H	-0.97757	-3.50187	-0.11815
C	1.24102	-2.64206	-1.70234
H	0.32900	-2.45191	1.71671
H	1.73833	-2.27116	0.67082
C	1.42591	-2.39997	1.71690
H	1.83519	-3.35188	2.06826
C	1.89760	-1.28744	2.56437
N	1.32622	-0.05647	2.35029
H	1.21302	2.61844	1.71145

C	2.87010	-1.40698	3.54805
C	1.68837	1.04885	3.08327
C	0.99839	2.31093	2.74386
C	3.26507	-0.31293	4.30513
C	2.66189	0.91518	4.06160
H	1.30461	3.11719	3.41727
H	-0.08933	2.18261	2.79190
H	-2.50629	-2.61296	-1.51250
H	-3.75632	-3.63226	-2.24252
C	-3.42689	-2.59714	-2.11302
H	-3.15421	-2.17331	-3.08690
C	-4.48018	-1.79814	-1.44649
N	-4.28471	-0.44385	-1.37440
H	-3.79099	1.95484	-0.33777
C	-5.64212	-2.32650	-0.90459
C	-5.18345	0.39360	-0.77031
C	-4.81502	1.82808	-0.71283
C	-6.58491	-1.50714	-0.29669
C	-6.34590	-0.14208	-0.23870
H	-5.50484	2.37374	-0.06213
H	-4.83198	2.29216	-1.70870
O	-2.30739	-1.21993	0.69345
C	-3.00765	-1.89429	1.65983
C	-4.14901	-1.06655	2.23911
C	-5.27100	-1.68327	2.79651
H	-5.33037	-2.77408	2.79684
C	-6.30950	-0.92770	3.33284
H	-7.18274	-1.42492	3.75467
C	-6.23271	0.46476	3.33210
H	-7.04189	1.05844	3.75550
C	-5.11023	1.08970	2.79206
H	-5.03520	2.17750	2.79482
C	-4.08015	0.32651	2.24811
H	-3.21086	0.80277	1.79251
C	-2.09188	-2.34727	2.79296
C	-1.84642	-3.69893	3.02840
H	-2.34905	-4.44373	2.40932
C	-0.94945	-4.10367	4.01746
H	-0.75900	-5.16467	4.17599
C	-0.29809	-3.15244	4.79589
H	0.40513	-3.46166	5.56861

C	-0.55452	-1.79616	4.58388
H	-0.05297	-1.04493	5.19524
C	-1.44068	-1.39896	3.59051
H	-1.63123	-0.33886	3.41585
H	-3.46849	-2.82085	1.23916
O	-2.35672	0.87108	-5.12036
H	-2.70442	2.83489	-5.77745
O	-0.91310	0.21749	-3.47525
C	-1.66975	1.02414	-3.96876
C	-3.00170	2.19851	-4.93734
H	-2.76038	2.41918	-2.71951
H	-4.92941	1.65952	-5.73691
C	-2.19602	2.39150	-3.65521
C	-4.48907	2.04899	-4.81330
H	-4.72950	1.35919	-3.99555
H	-4.94992	3.02004	-4.59688
H	-1.44141	3.18407	-3.63793
H	-5.78506	-3.40278	-0.96467
H	-7.03649	0.53139	0.26248
H	-7.48687	-1.92827	0.14033
H	2.93857	1.80361	4.62406
H	4.02889	-0.41483	5.07160
H	3.30511	-2.39088	3.70544

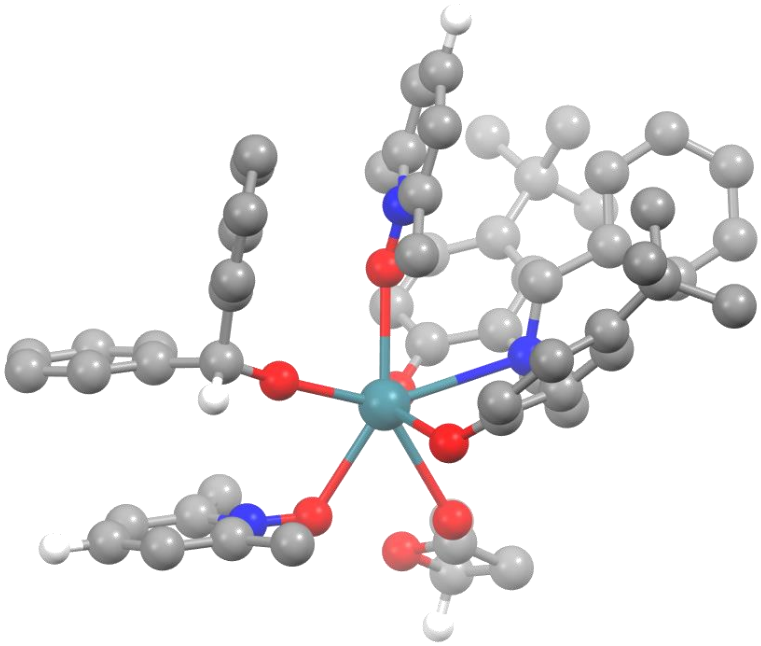


Figure S28. Labeled ball and stick image of **BBL-8** . Hydrogen atoms and tert-butyl groups were removed for clarity.

Table S29. Cartesian coordinates of **BBL-8**. EM06L (solvent corrected) = -3363.976264 Hartree (-3363.986002)

Atom	**X**	**Y**	**Z**
La	0.92660	0.03546	-0.87398
O	0.37231	-2.29660	-0.91831
O	0.35432	2.06887	-1.93795
O	-0.25227	0.03644	1.44161
O	3.06815	-0.41094	-2.20099
N	-1.96901	-0.17531	-1.29906
C	-0.63463	-2.99530	-0.44017
C	-0.44849	-4.11553	0.42500
C	0.96454	-4.60191	0.75975
C	1.75286	-3.51777	1.51019
H	1.68264	-2.54795	1.00585
H	2.81565	-3.79277	1.58260
H	1.38000	-3.39442	2.53591
C	1.69823	-4.96594	-0.53992
H	1.19255	-5.80594	-1.03511
H	2.73011	-5.28020	-0.32410
H	1.72498	-4.11815	-1.23225
C	0.96148	-5.84759	1.64689
H	0.48338	-5.66153	2.61767

H	1.99493	-6.16071	1.84467
H	0.44479	-6.69095	1.17101
C	-1.57940	-4.74320	0.95419
H	-1.42948	-5.57420	1.63894
C	-2.89260	-4.35121	0.67009
C	-4.11827	-5.00943	1.29866
C	-3.73758	-6.05234	2.34847
H	-3.15857	-6.87849	1.91664
H	-4.64127	-6.48329	2.79819
H	-3.13991	-5.61233	3.15828
C	-4.95103	-5.69445	0.20737
H	-5.27342	-4.97553	-0.55631
H	-5.85273	-6.15803	0.63174
H	-4.37193	-6.47837	-0.29714
C	-4.98430	-3.93830	1.97667
H	-4.41919	-3.39940	2.75060
H	-5.86321	-4.39264	2.45538
H	-5.34600	-3.19238	1.25833
C	-3.05249	-3.30565	-0.24169
H	-4.05667	-2.97957	-0.52886
C	-1.96525	-2.64142	-0.80174
C	-2.18753	-1.55113	-1.80850
H	-1.49128	-1.66404	-2.64886
H	-3.20868	-1.64108	-2.22255
C	-2.79489	0.08997	-0.11585
H	-2.57285	1.11680	0.20692
H	-2.40646	-0.56917	0.66537
C	-4.29972	-0.08784	-0.11845
C	-4.89336	-0.24685	1.14126
H	-4.24928	-0.28343	2.02335
C	-6.26946	-0.36604	1.28847
H	-6.69880	-0.49151	2.28166
C	-7.09405	-0.34705	0.16527
H	-8.17244	-0.44837	0.27234
C	-6.52297	-0.20221	-1.09427
H	-7.15361	-0.19043	-1.98169
C	-5.14169	-0.06879	-1.23479
H	-4.72643	0.04491	-2.23201
C	-2.11611	0.81374	-2.40722
H	-3.07064	0.66269	-2.93851
H	-1.31856	0.57662	-3.12444

C	-2.00543	2.24138	-1.97169
C	-3.14973	2.96871	-1.66332
H	-4.11696	2.46392	-1.73906
C	-3.08910	4.28792	-1.21743
C	-4.36029	4.97072	-0.72156
C	-4.92249	4.15386	0.45393
H	-4.17677	4.05694	1.25587
H	-5.20365	3.13838	0.14464
H	-5.81731	4.63228	0.87693
C	-5.41090	5.01910	-1.83720
H	-5.05021	5.60018	-2.69521
H	-6.34112	5.48240	-1.47976
H	-5.66039	4.01333	-2.19773
C	-4.09860	6.39474	-0.23615
H	-3.37593	6.41435	0.59021
H	-5.03007	6.84842	0.12594
H	-3.70765	7.03444	-1.03769
C	-1.82522	4.88967	-1.20250
H	-1.75930	5.93477	-0.90953
C	-0.64184	4.21804	-1.52194
C	0.71418	4.92907	-1.50007
C	0.57038	6.44028	-1.30840
H	-0.05483	6.89509	-2.08762
H	1.55996	6.91321	-1.35696
H	0.13540	6.69592	-0.33331
C	1.43059	4.70661	-2.84032
H	1.55845	3.64204	-3.05200
H	2.42020	5.18618	-2.82821
H	0.85498	5.15199	-3.66226
C	1.58123	4.40815	-0.34345
H	1.15166	4.70023	0.62462
H	2.59237	4.84095	-0.39619
H	1.67986	3.31628	-0.34826
C	-0.71987	2.82704	-1.82669
H	0.45905	2.52483	1.59259
H	-0.97429	2.52546	0.56105
C	-0.62628	2.69316	1.58993
H	-0.83110	3.73761	1.84294
C	-1.29621	1.78408	2.53870
N	-1.03689	0.44259	2.39510
H	-1.68419	-2.20615	1.94773

C	-2.15811	2.19549	3.54515
C	-1.60879	-0.49430	3.22447
C	-1.29449	-1.90860	2.93227
C	-2.74347	1.28035	4.40834
C	-2.45509	-0.06794	4.23710
H	-1.72737	-2.56758	3.69091
H	-0.21205	-2.06863	2.87907
H	3.00706	2.23133	-1.68788
H	4.42779	3.09012	-2.32708
C	3.90707	2.12809	-2.30836
H	3.55204	1.88395	-3.31658
C	4.79127	1.06796	-1.77528
N	4.27513	-0.20105	-1.73936
H	3.36840	-2.48976	-0.59388
C	6.08498	1.26994	-1.32151
C	4.98599	-1.26429	-1.25300
C	4.27400	-2.56193	-1.21352
C	6.84450	0.21251	-0.83607
C	6.28306	-1.05547	-0.81000
H	4.92000	-3.34102	-0.79710
H	3.92092	-2.86072	-2.20724
O	2.61262	0.81805	0.49587
C	3.50573	1.40614	1.35356
C	4.57671	0.44229	1.85035
C	5.81356	0.91507	2.29386
H	6.01825	1.98734	2.24877
C	6.78079	0.03962	2.77887
H	7.74388	0.42422	3.11356
C	6.51732	-1.32872	2.83731
H	7.27080	-2.01609	3.21960
C	5.28164	-1.80858	2.40793
H	5.06407	-2.87635	2.45374
C	4.32158	-0.92664	1.91734
H	3.36033	-1.28866	1.55367
C	2.78924	2.01274	2.55567
C	2.81442	3.38478	2.79926
H	3.38970	4.02954	2.13260
C	2.09591	3.93769	3.85993
H	2.11612	5.01420	4.02689
C	1.35202	3.11386	4.69831
H	0.78622	3.53931	5.52647

C	1.33455	1.73547	4.47293
H	0.75233	1.08572	5.12740
C	2.04387	1.19111	3.40957
H	2.01873	0.11592	3.22244
H	4.04237	2.24808	0.85330
O	1.58627	-2.80658	-3.74223
H	1.46962	-4.06126	-5.42298
O	0.66544	-0.71194	-3.48779
C	0.69924	-1.81751	-3.97416
C	0.81461	-3.73838	-4.60704
H	-0.09106	-2.21551	-5.97632
H	1.06323	-5.51292	-3.41734
C	-0.13650	-2.59569	-4.95168
C	0.26108	-4.87882	-3.80688
H	-0.32165	-4.50765	-2.95328
H	-0.39111	-5.49653	-4.43513
H	-1.18369	-2.72616	-4.65833
H	6.48038	2.28287	-1.34935
H	6.82762	-1.90457	-0.40494
H	7.85261	0.37791	-0.46450
H	-2.89571	-0.82720	4.87928
H	-3.41465	1.61023	5.19703
H	-2.34893	3.26218	3.63625

6. Buried Volume (%V_{bur}) Calculations

All buried volume calculations of the free ligands and metal complexes were performed using SambVca 2.1.[19] Abbreviations for tabulated values are provided within SambVca 2.1, but several are provided again below for convenience.

Free ligands: Structures of the free ligands, $OPPh_3$, PyO, and LO, were obtained from the deposited X-ray structures found in the Cambridge Structural Database (CSD; Structure codes: $OPPh_3$ = TPEPHO,[20] PyO = PYRDNO11,[21] LO = ACOHAC[22]). In the case of LO, the interstitial water molecule was removed. These coordinates were then uploaded via the web applet, and the oxygen of the oxide donor was selected as the center of the sphere. The *z*-axis and *xz*-plane were defined as follows: *z*-axis = O_{PyO} & N_{PyO}, O_{LO} & N_{LO}, O_{OPPh3} & P_{OPPh3} // *xz*-plane = $OPPh_3$: P & C_{OPPh3} (2-Ar), PyO: C (2,6-Ar), LO: C (2,6-Me_2). The distance of the coordination point from the center of the sphere was chosen to be 2.28 Å, with a scaling of 1.17 for all bond radii, and a sphere radius of 3.5 Å.

Metal complexes: Structures of the metal complexes, **1-La($OPPh_3$)$_2$**, **1-La(LO)$_2$**, **2-La($OPPh_3$)$_2$**, **2-La(LO)$_2$**, were obtained from the DFT optimized structures (SI, section 5). La was selected as the center of the sphere, and the *z*-axis and *xz*-plane were defined as follows: *z*-axis = La & ^{Bn}N // *xz*-plane = O_{Ar} & O_{Ar}. Bond radii were scaled to 1.17 and two sphere radii were used to capture the %V_{bur} related to the primary (3.5 Å) and secondary (6.5 Å) coordination spheres. **Note**: La and the N($SiHMe_2$)$_2$ / $OCHPh_2$ groups were excluded from the volume calculations.

Table S30. %V_{bur}($r_{3.5}$) of $OPPh_3$ (CSD: TPEPHO)

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	36.2	8.7	44.9	80.7	19.3
NW	36.4	8.4	44.9	81.2	18.8
NE	38.5	6.3	44.9	85.9	14.1
SE	39	5.9	44.9	86.9	13.1

%V_{free} = 83.7% // %V_{bur} = 16.3%

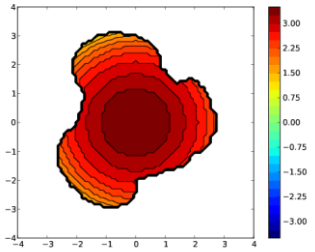


Table S31. %V_{bur}($r_{3.5}$) of PyO (CSD: ACOHAC)

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	39.3	5.5	44.9	87.7	12.3
NW	39.2	5.6	44.9	87.4	12.6
NE	39.3	5.5	44.9	87.7	12.3
SE	39.2	5.6	44.9	87.4	12.6

%V_{free} = 87.6% // %V_{bur} = 12.4%

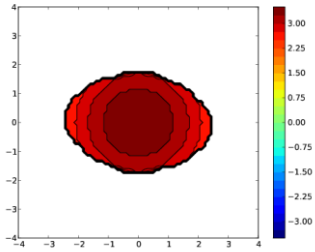


Table S32. %V_{bur}($r_{3.5}$) of LO (CSD: PYRDNO11)

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	37.9	7	44.9	84.4	15.6
NW	37.7	7.2	44.9	84	16
NE	37.8	7.1	44.9	84.2	15.8
SE	37.6	7.3	44.9	83.8	16.2

%V_{free} = 84.1% // %V_{bur} = 15.9%

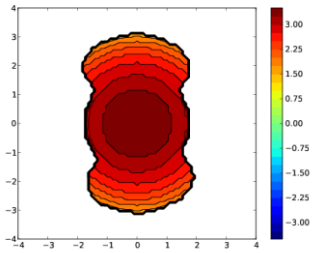


Table S33a. $\%V_{bur}(r_{3.5})$ of **1-La(OPPh$_3$)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	$\%V_{free}$	$\%V_{bur}$
SW	10.8	34	44.9	24.2	75.8
NW	16.5	28.4	44.9	36.8	63.2
NE	11.8	33	44.9	26.4	73.6
SE	16.9	27.9	44.9	37.7	62.3

$\%V_{free}$ = 31.3% // $\%V_{bur}$ = 68.7%

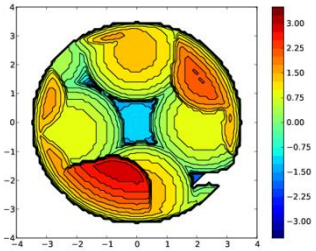


Table S33b. $\%V_{bur}(r_{6.5})$ of **1-La(OPPh$_3$)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	$\%V_{free}$	$\%V_{bur}$
SW	63.4	223.9	287.4	22.1	77.9
NW	91.5	195.8	287.4	31.9	68.1
NE	87.7	199.6	287.4	30.5	69.5
SE	174.2	113.2	287.4	60.6	39.4

$\%V_{free}$ = 36.3% // $\%V_{bur}$ = 63.7%

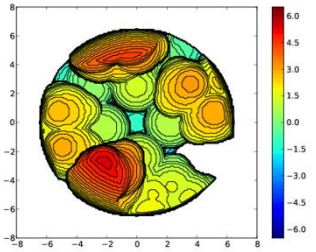


Table S34a. $\%V_{bur}(r_{3.5})$ of **2-La(OPPh$_3$)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	$\%V_{free}$	$\%V_{bur}$
SW	4.7	40.2	44.9	10.4	89.6
NW	11.3	33.5	44.9	25.2	74.8
NE	15.6	29.3	44.9	34.7	65.3
SE	20	24.8	44.9	44.7	55.3

$\%V_{free}$ = 28.8% // $\%V_{bur}$ = 71.2%

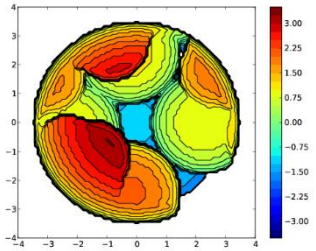


Table S34b. $\%V_{bur}(r_{6.5})$ of **2-La(OPPh$_3$)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	$\%V_{free}$	$\%V_{bur}$
SW	49.6	237.8	287.4	17.3	82.7
NW	64.2	223.2	287.4	22.3	77.7
NE	94	193.4	287.4	32.7	67.3
SE	200.9	86.4	287.4	69.9	30.1

$\%V_{free}$ = 35.6% // $\%V_{bur}$ = 64.4%

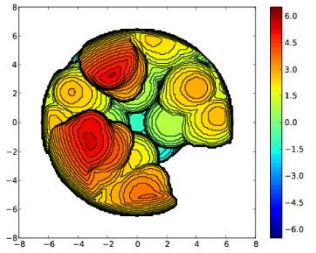


Table S35a. %V_{bur}($r_{3.5}$) of **1-La(LO)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	8.1	36.8	44.9	18	82
NW	13.5	31.4	44.9	30.1	69.9
NE	11.1	33.8	44.9	24.7	75.3
SE	18.7	26.2	44.9	41.6	58.4

%V_{free} = 28.6% // %V_{bur} = 71.4%

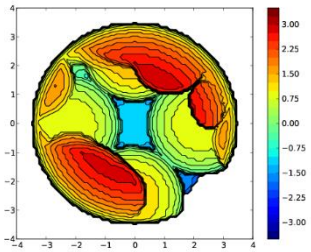


Table S35b. %V_{bur}($r_{6.5}$) of **1-La(LO)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	117.4	169.9	287.4	40.9	59.1
NW	106.1	181.3	287.4	36.9	63.1
NE	125.9	161.4	287.4	43.8	56.2
SE	185.6	101.7	287.4	64.6	35.4

%V_{free} = 46.5% // %V_{bur} = 53.5%

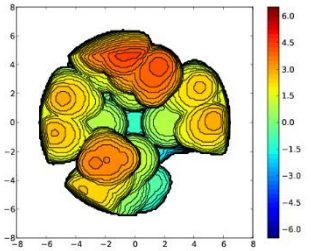


Table S36a. %V_{bur}($r_{3.5}$) of **2-La(LO)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	7	37.8	44.9	15.6	84.4
NW	11.3	33.6	44.9	25.2	74.8
NE	14.4	30.5	44.9	32.1	67.9
SE	9.3	35.5	44.9	20.8	79.2

%V_{free} = 23.4% // %V_{bur} = 76.6%

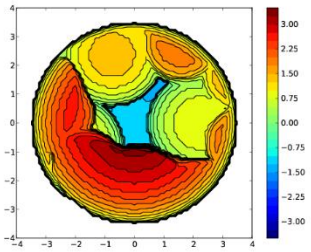
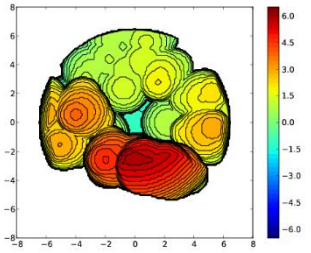


Table S36b. %V_{bur}($r_{6.5}$) of **2-La(LO)$_2$**

Quadrant	V_{free}	V_{bur}	V_{total}	%V_{free}	%V_{bur}
SW	156.7	130.7	287.4	54.5	45.5
NW	105.2	182.2	287.4	36.6	63.4
NE	143.2	144.2	287.4	49.8	50.2
SE	104.7	182.6	287.4	36.4	63.6

%V_{free} = 44.4% // %V_{bur} = 55.6%



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