

Group 3 Metal Complexes Supported by Tridentate Pyridine- and Thiophene-Linked Bis(naphtolate) Ligands: Synthesis, Structure, and Use in Stereoselective Ring-Opening Polymerization of Racemic Lactide and β -Butyrolactone

Ekaterina Grunova, Evgueni Kirillov,* Thierry Roisnel, and Jean-François Carpentier*

Figure S1. Homodecoupled ^1H NMR spectrum (500 MHz, 293K, CDCl_3) of an heterotactic-enriched PLA ($P_r = 0.88$) obtained with $\{\text{ONO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**3**) (Table 3, entry 5)

Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, 293K, CDCl_3) of a syndiotactic-enriched PHB ($P_r = 0.86$) obtained with $\{\text{ONO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**3**) (Table 4, entry 9)

Figure S3. ^1H NMR spectrum (500 MHz, 293K, CDCl_3) of a syndiotactic-enriched PHB ($P_r = 0.86$) obtained with $\{\text{ONO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**3**) (Table 4, entry 9)

Figure S4. ORTEP drawings of the structure of $\{\text{ONO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**3**) with selected bond lengths (Å) and angles (deg.)

Figure S5. ORTEP drawings of the structure of $\{\text{ONO}^{\text{Si}^i\text{BuMe}_2}\}\text{Y}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**5**) with selected bond lengths (Å) and angles (deg.)

Figure S6. ORTEP drawing of the structure of $\{\text{OSO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**9**) with selected bond lengths (Å) and angles (deg.)

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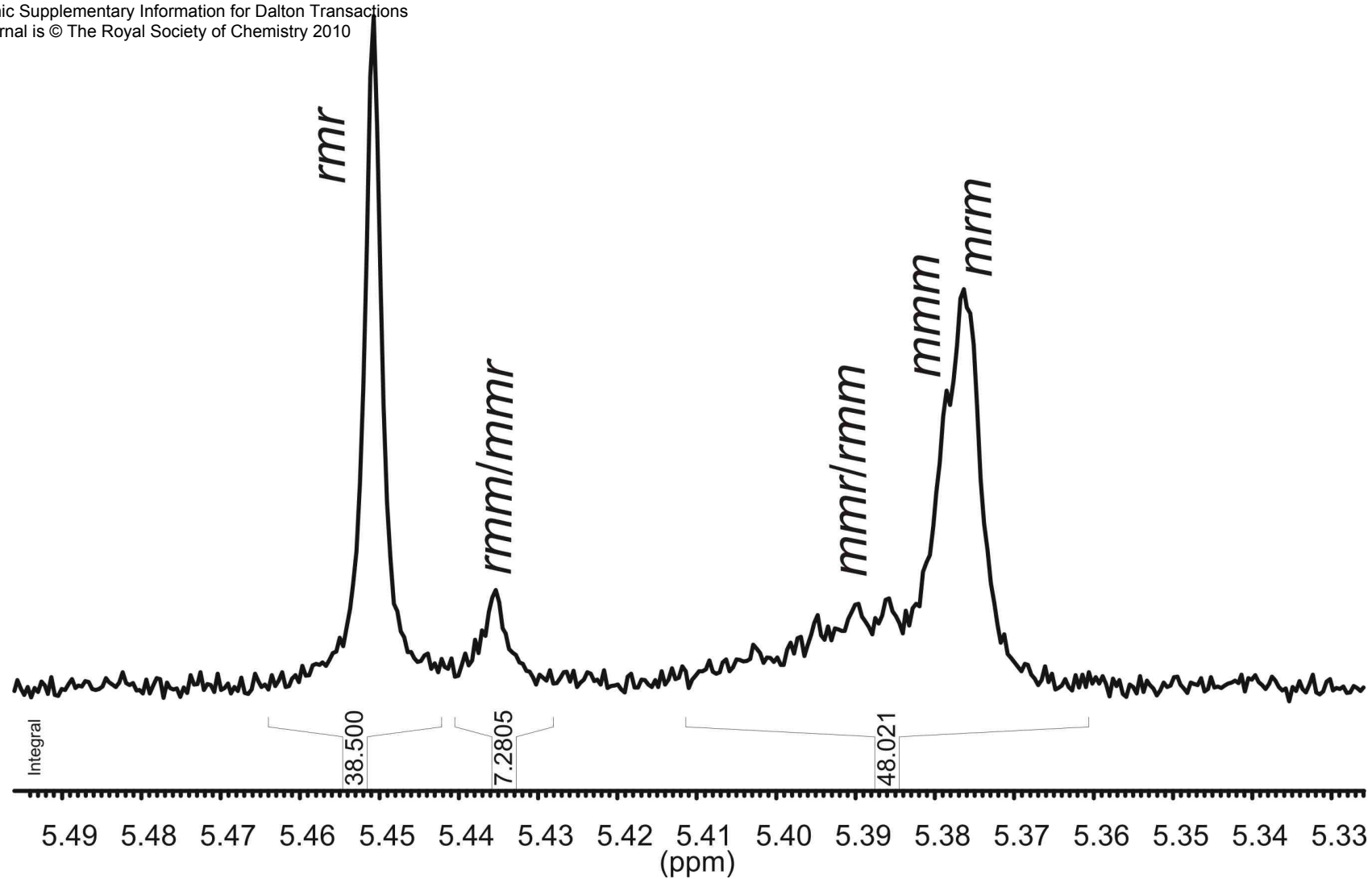


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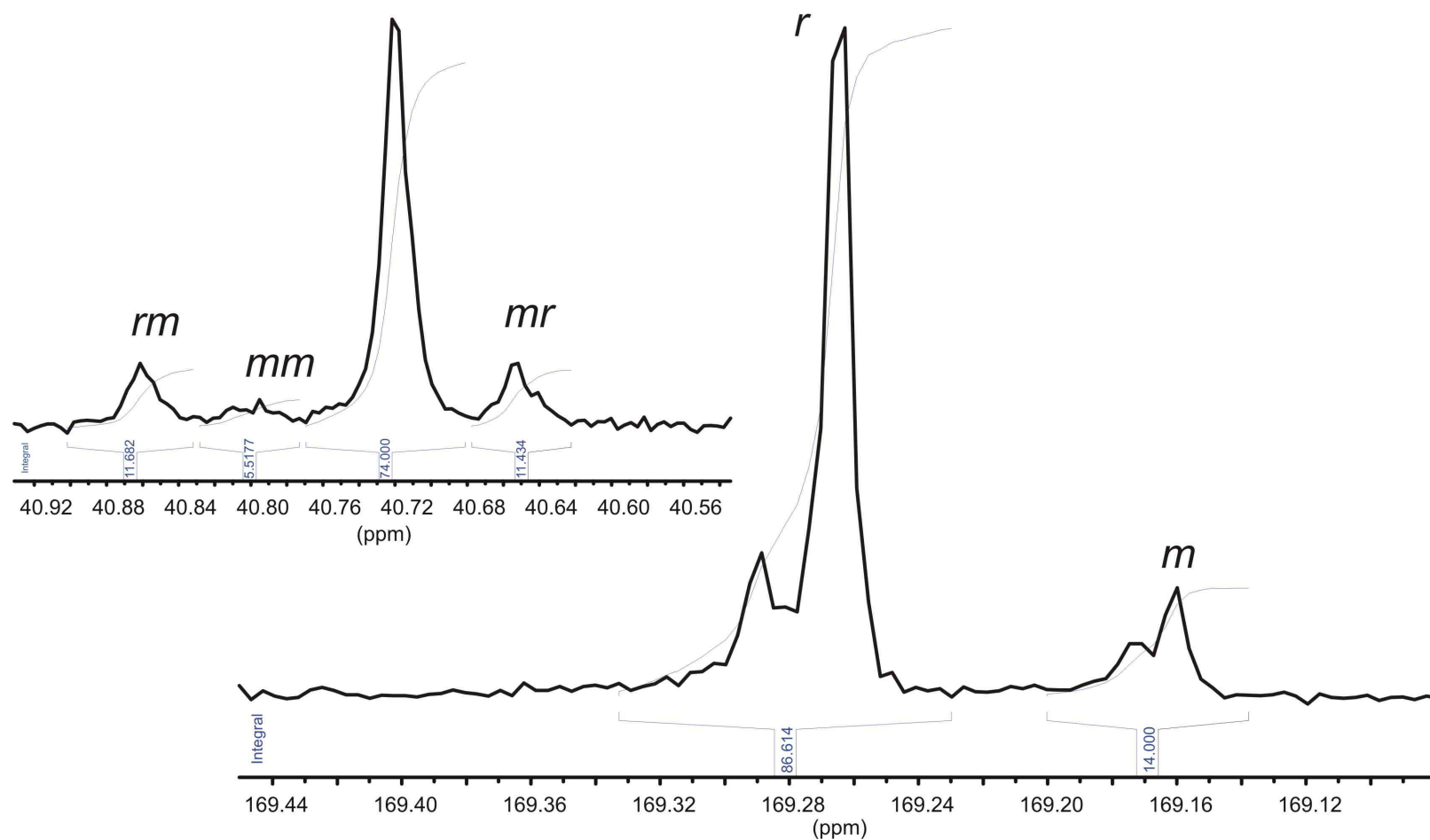


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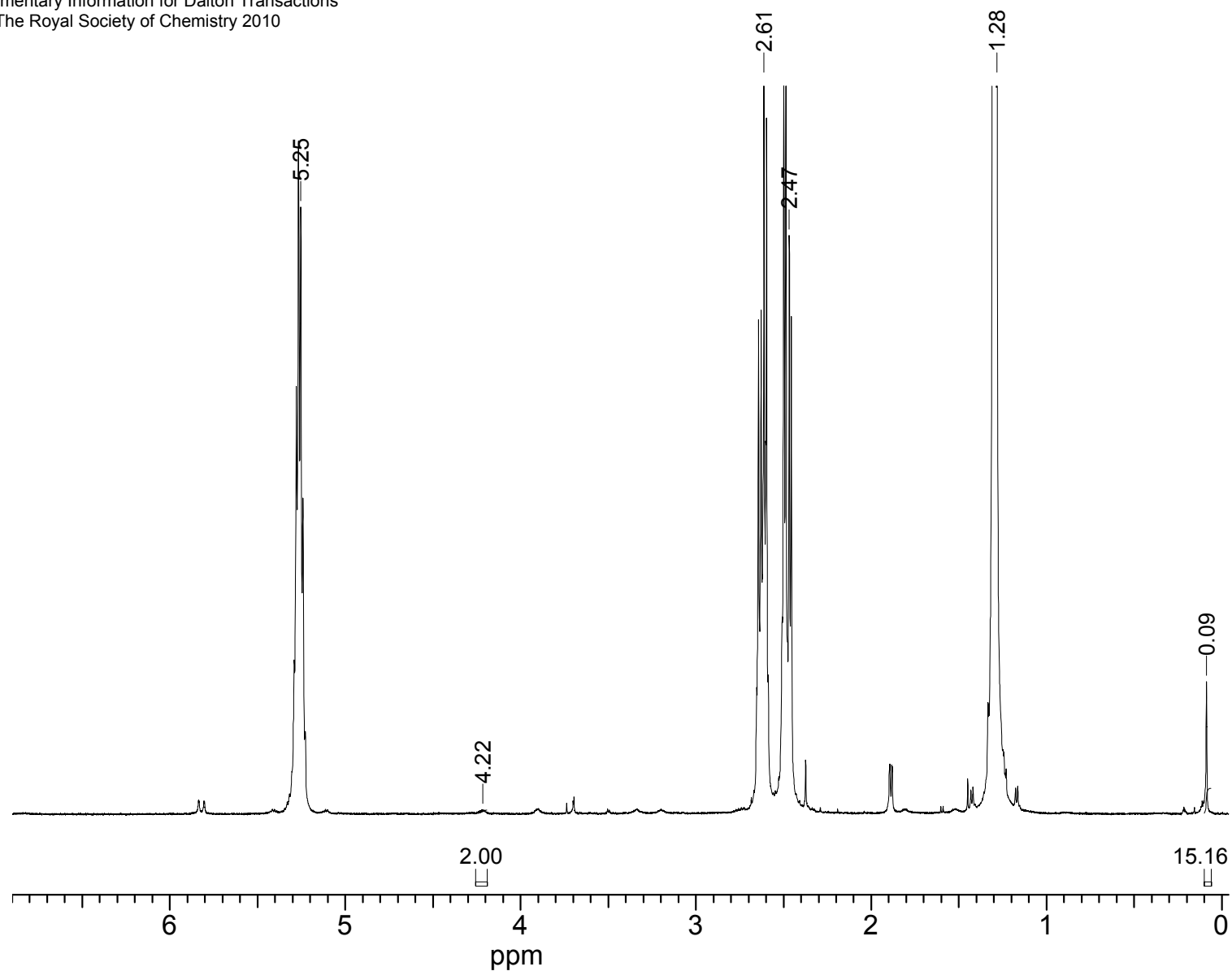


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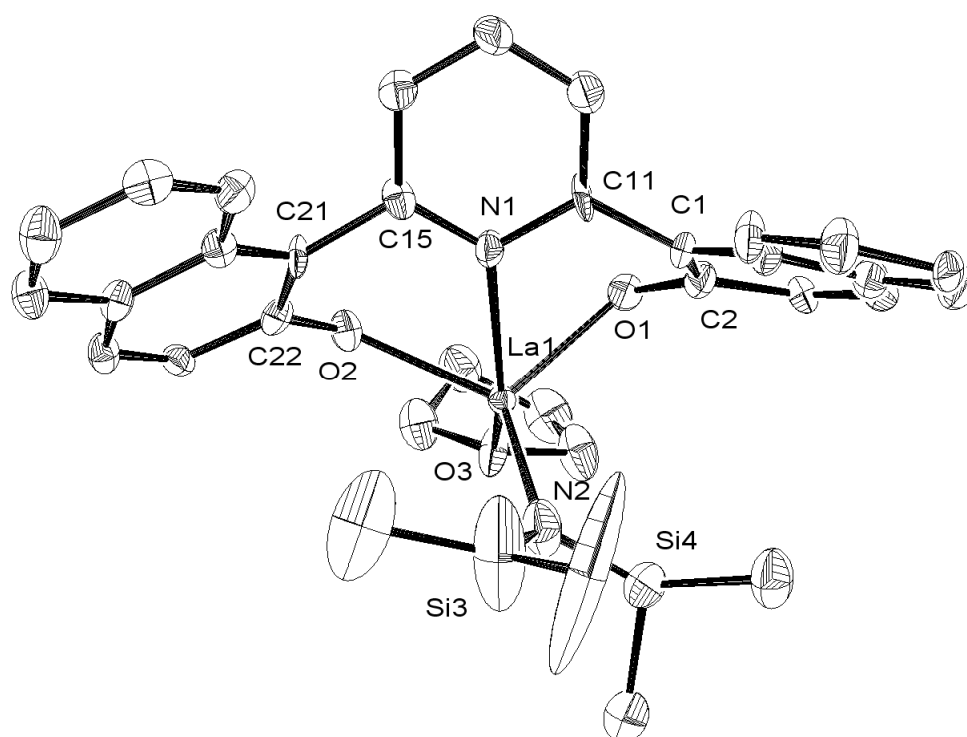


Figure S4. ORTEP drawings of the structure of $\{\text{ONO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**3**) (50% ellipsoid probability; H atoms are omitted for clarity, as well as SiPh_3 groups in the bottom drawing). Selected bond lengths (Å) and angles (deg.): La(1)–O(1), 2.347(8); La(1)–O(2), 2.310(7); La(1)–O(3), 2.545(8); La(1)–N(1), 2.622(9); La(1)–N(2), 2.374(11); O(2)–La(1)–O(1), 112.2(3); O(2)–La(1)–N(2), 122.1(3); O(1)–La(1)–N(2), 118.5(3); O(2)–La(1)–O(3), 90.6(2); O(1)–La(1)–O(3), 86.5(3); N(2)–La(1)–O(3), 117.6(4); O(2)–La(1)–N(1), 71.7(3); O(1)–La(1)–N(1), 76.5(3); N(2)–La(1)–N(1), 94.3(4); O(3)–La(1)–N(1), 148.0(3).

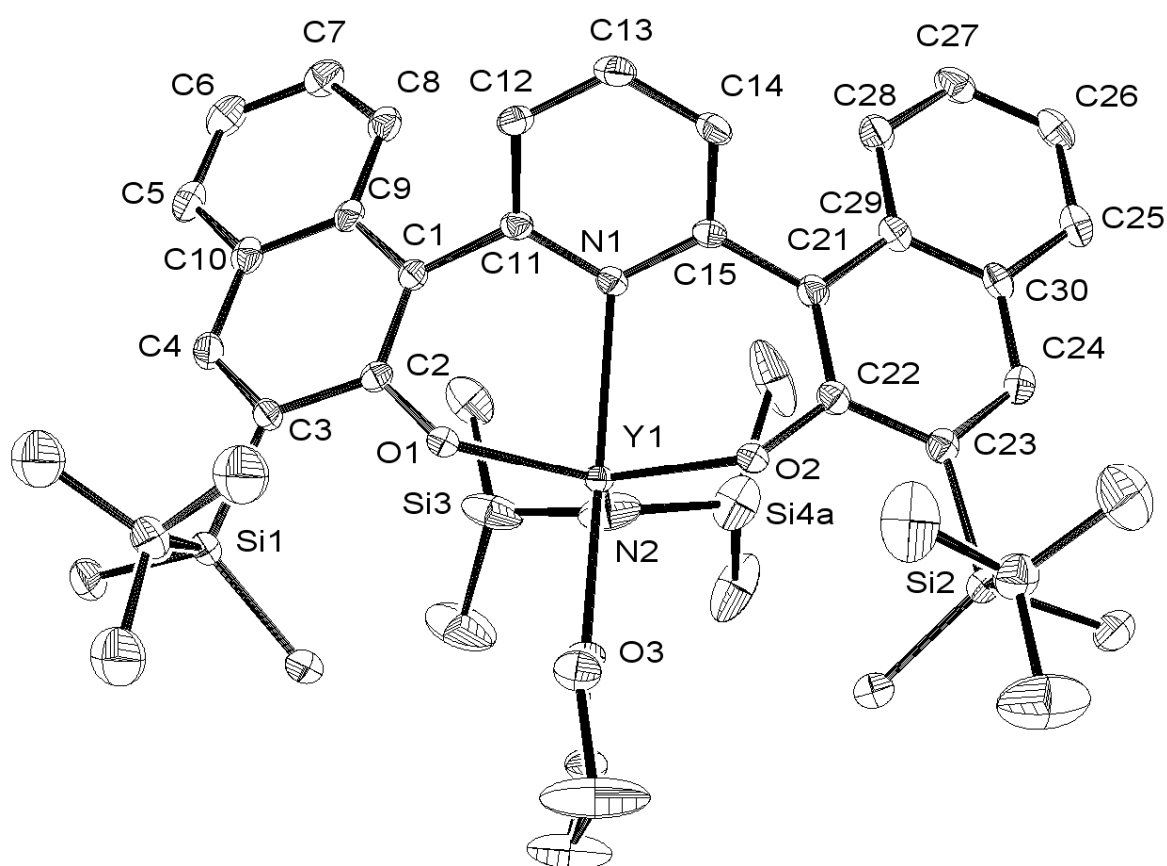


Figure S5. ORTEP drawings of the structure of $\{\text{ONO}^{\text{Si}^t\text{BuMe}_2}\}\text{Y}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**5**) (50% ellipsoid probability; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg.): Y(1)–O(1), 2.1705(15); Y(1)–O(2), 2.1535(15); Y(1)–O(3), 2.3264(15); Y(1)–N(1), 2.4385(17); Y(1)–N(2), 2.210(2); O(2)–Y(1)–O(1), 118.65(6); O(2)–Y(1)–N(2), 117.51(8); O(1)–Y(1)–N(2), 123.24(8); O(2)–Y(1)–O(3), 88.07(5); O(1)–Y(1)–O(3), 87.14(5); N(2)–Y(1)–O(3), 102.37(7); O(2)–Y(1)–N(1), 78.61(6); O(1)–Y(1)–N(1), 80.03(6); N(2)–Y(1)–N(1), 103.57(7); O(3)–Y(1)–N(1), 154.01(6).

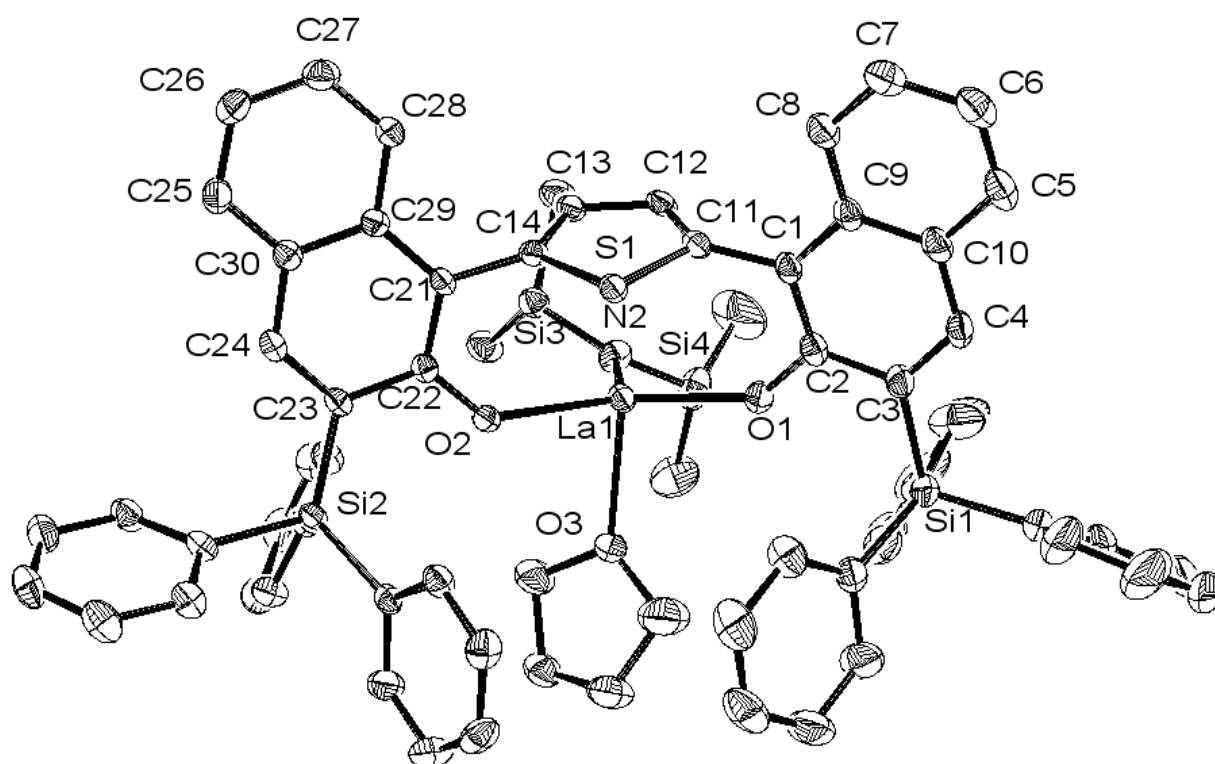


Figure S6. ORTEP drawing of the structure of $\{\text{OSO}^{\text{SiPh}_3}\}\text{La}[\text{N}(\text{SiHMe}_2)_2](\text{THF})$ (**9**) (50% ellipsoid probability; H atoms and La-S bond are omitted for clarity). Selected bond lengths (Å) and angles (deg.): La(1)–O(1), 2.305(2); La(1)–O(2), 2.333(2); La(1)–O(3), 2.477(2); La(1)–N(2), 2.344(3); La(1)–S(1), 3.1715(8); La(1)–C(11), 3.076(3); La(1)–C(12), 3.154(2); La(1)–C(13), 3.195(2); La(1)–C(14), 3.168(2); O(1)–La(1)–O(2), 135.64(7); O(1)–La(1)–N(2), 112.21(9); O(2)–La(1)–N(2), 111.77(9); O(1)–La(1)–O(3), 99.15(7); O(2)–La(1)–O(3), 83.88(7); N(2)–La(1)–O(3), 93.26(8); O(1)–La(1)–S(1), 74.72(5); O(2)–La(1)–S(1), 72.61(5); N(2)–La(1)–S(1), 130.81(7); O(3)–La(1)–S(1), 135.01(6).