

Ring Opening Polymerization of rac-Lactide by Group 4 Tetracarbamato Complexes:
Activation, Propagation and Role of The Metal

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Supplementary Material

NMR Experiments

A) From **1b** (0.457 mmol) and lactide (0.430 mmol), lactide / Zr molar ratio = 0.95.

Before heating: ^1H NMR (d^8 -toluene) δ = 5.53 (q, 2 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH), 2.98 (q, 16 H, $^3J_{\text{HH}}$ = 6.81 Hz, CH_2CH_3), 1.45 (d, 6 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH_3), 0.83 ppm (t, 24 H, $^3J_{\text{HH}}$ = 6.81 Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (d^8 -toluene) δ = 169.4 (O_2CN), 168.6 (lactide CO), 72.6 (lactide CH), 39.8 (CH_2CH_3), 15.9 (lactide CH_3), 13.6 ppm (CH_2CH_3). After heating (2 h): benzene / oligomer / NHEt_2 = 10 : 7 : 1.

B) From **1b** (0.176 mmol) and lactide (0.375 mmol), lactide / Zr molar ratio = 2.1.

Before heating: ^1H NMR (d^8 -toluene) δ = 5.44 (q, 2 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH), 1.42 ppm (d, 6 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH_3). After heating (2 h): benzene / oligomer / NHEt_2 ratio = 10 : 14 : 1.

C) From **1b** (85.0 μmol) and lactide (0.881 mmol), lactide / Zr molar ratio = 10.

Before heating: ^1H NMR (d^8 -toluene) δ = 5.00 (q, 2 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH), 1.37 ppm (d, 6 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH_3). After heating (2 h): benzene / oligomer / NHEt_2 ratio = 10 : 64 : 3.

D) From **1c** (0.216 mmol) and lactide (0.208 mmol), lactide / Zr molar ratio = 0.96.

Before heating: ^1H NMR (d^8 -toluene) δ = 5.57 (q, 2 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH), 3.73 (m, 8 H, $^3J_{\text{HH}}$ = 6.58 Hz, CHCH_3), 1.48 (d, 6 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH_3), 1.03 ppm (d, 48 H, $^3J_{\text{HH}}$ = 6.58 Hz, CHCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (d^8 -toluene) δ = 169.6 (O_2CN), 168.6 (lactide CO), 72.6 (lactide CH), 45.1 (CHCH_3), 20.8 (CHCH_3), 16.0 ppm (lactide CH_3). After heating (2 h): benzene / oligomer / NH^iPr_2 ratio = 10 : 8 : 1.

E) From **1c** (0.178 mmol) and lactide (0.361 mmol), lactide / Zr molar ratio = 2.

Before heating: ^1H NMR (d^8 -toluene) δ = 5.36 (q, 2 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH), 1.42 ppm (d, 6 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH_3). After heating (2 h): benzene / oligomer / NH^iPr_2 ratio = 10 : 15 : 1.

F) From **1c** (0.072 mmol) and lactide (0.729 mmol), lactide / Zr molar ratio = 10.

Before heating: ^1H NMR (d^8 -toluene) δ = 4.74 (q, 2 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH), 1.33 ppm (d, 6 H, $^3J_{\text{HH}}$ = 6.58 Hz, lactide CH_3). After heating (2 h): benzene / oligomer / NH^iPr_2 ratio = 5 : 20 : 1.

G) From **1d** (0.42 mmol) and lactide (0.38 mmol), lactide / Hf molar ratio = 1.

Before heating: ^1H NMR (d^8 -toluene) δ = 5.37 (q, 2 H, $^3J_{\text{HH}}$ = Hz, lactide CH), 2.99 (q,

16 H, $^3J_{\text{HH}} = 6.96$ Hz, CH_2CH_3), 1.43 (d, 6 H, $^3J_{\text{HH}} = \text{Hz}$, lactide CH_3), 0.86 ppm (t, 24 H, $^3J_{\text{HH}} = 6.96$ Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (d^8 -toluene) $\delta = 169.0$ (O_2CN), 168.4 (lactide CO), 72.5 (lactide CH), 39.9 (CH_2CH_3), 15.8 (lactide CH_3), 13.7 ppm (CH_2CH_3). After heating (5 h): benzene / oligomer / NHET_2 ratio = 10 : 8 : 1.

H) From 1d (0.093 mmol) and lactide (0.34 mmol), lactide / Hf molar ratio = 3.5.

Before heating: ^1H NMR (d^8 -toluene) $\delta = 4.69$ (q, 2 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH), 1.43 ppm (d, 6 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH_3). After heating (2 h): benzene / oligomer / NHET_2 ratio = 10 : 28 : 1.

I) From 1d (7.8 μmol) and lactide (0.38 mmol), lactide / Hf molar ratio = 50. Before

heating: ^1H NMR (d^8 -toluene) $\delta = 3.88$ (q, 2 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH), 1.18 ppm (d, 6 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH_3). After heating (6 h): benzene / oligomer / NHET_2 ratio = 2 : 80 : 1.

J) From 1a (0.045 mmol) and lactide (0.45 mmol), lactide / Ti molar ratio = 10.

Before heating: ^1H NMR (d^8 -toluene) $\delta = 5.15$ (br, 1 H, OH), 4.80 (q, 2 H, $^3J_{\text{HH}} = 6.59$ Hz, lactide CH), 3.09 (q, 16 H, $^3J_{\text{HH}} = 7.33$ Hz, CH_2CH_3), 1.42 (d, 6 H, $^3J_{\text{HH}} = 6.59$ Hz, lactide CH_3), 0.98 ppm (t, 24 H, $^3J_{\text{HH}} = 7.33$ Hz, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (d^8 -toluene) $\delta = 169.4$ (lactide CO), 167.6 (O_2CN), 72.2 (lactide CH), 39.5 (CH_2CH_3), 15.6 (lactide CH_3), 13.8 ppm (CH_2CH_3). After heating (6 h): benzene / oligomer ratio = 1 : 3.

K) Reaction of $\text{Hf}(\text{O}_2^{13}\text{CN}^i\text{Pr}_2)_4$ with *rac*-lactide: $\text{Hf}(\text{O}_2^{13}\text{CN}^i\text{Pr}_2)_4$ (0.023 mmol) and *rac*-lactide (0.486 mmol) were mixed in d^8 -toluene (0.70 mL) in a NMR tube. The tube was sealed and heated at *ca.* 100°C up to maximum conversion (6 hours). The following NMR spectra were recorded at 298K. ^1H NMR (d^8 -toluene, before heating) $\delta = 4.12$ (q, 2 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH), 3.73 (m, 8 H, CHMe_2), 1.22 (d, 6 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH_3), 1.06 ppm (d, 48 H, CHMe_2). ^1H NMR (d^8 -toluene, after heating) $\delta = 5.00$ (m-br, polymer CH), 4.54 (q, 2 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH), 3.73 (m, 8 H, CHMe_2), 1.34 (br, polymer CH_3), 1.30 (d, 6 H, $^3J_{\text{HH}} = 6.58$ Hz, lactide CH_3), 1.06 ppm (d, 48 H, $^3J_{\text{HH}} = 6.58$ Hz, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d^8 -toluene, after heating) $\delta = 169.7\div 169.5$ (polymer $\text{C}=\text{O}$), 169.2 (O_2^{13}CN), 166.6 (lactide $\text{C}=\text{O}$), 72.2 (lactide CH), 69.2 (polymer CH), 45.1 (CHMe_2), 20.7 (CHMe_2), 16.5 (polymer CH_3), 15.6 ppm (lactide CH_3). ^{13}C NMR (d^8 -toluene, after heating, 213K) $\delta = 168.6$ (O_2^{13}CN), 124.8 ppm ($^{13}\text{CO}_2$, see M. Aresta and A. Di Benedetto, *Dalton Trans.* 2007, 2975-2992).

Figure S1. ^{13}C -NMR spectrum (CDCl_3 , 298 K) of polylactide obtained with $\text{Zr}(\text{O}_2\text{CNEt}_2)_4$ as catalyst.

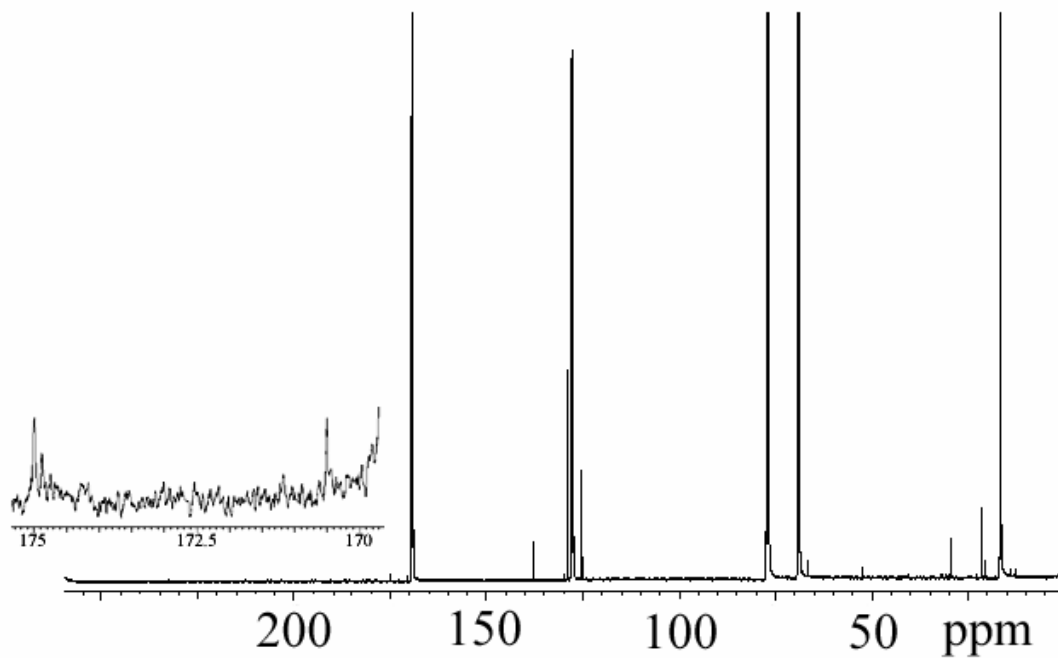


Figure S2. ^1H NMR spectra (CDCl_3 , 298 K) of *rac*-lactide polymer after treatment with MeOH/HCl. The polymer (run 3, Table 2) was prepared by catalyst system $\text{Hf}(\text{O}_2\text{CN}^i\text{Pr}_2)_4$ with 4 equivalent $^i\text{PrOH}$ in toluene at 100 °C.

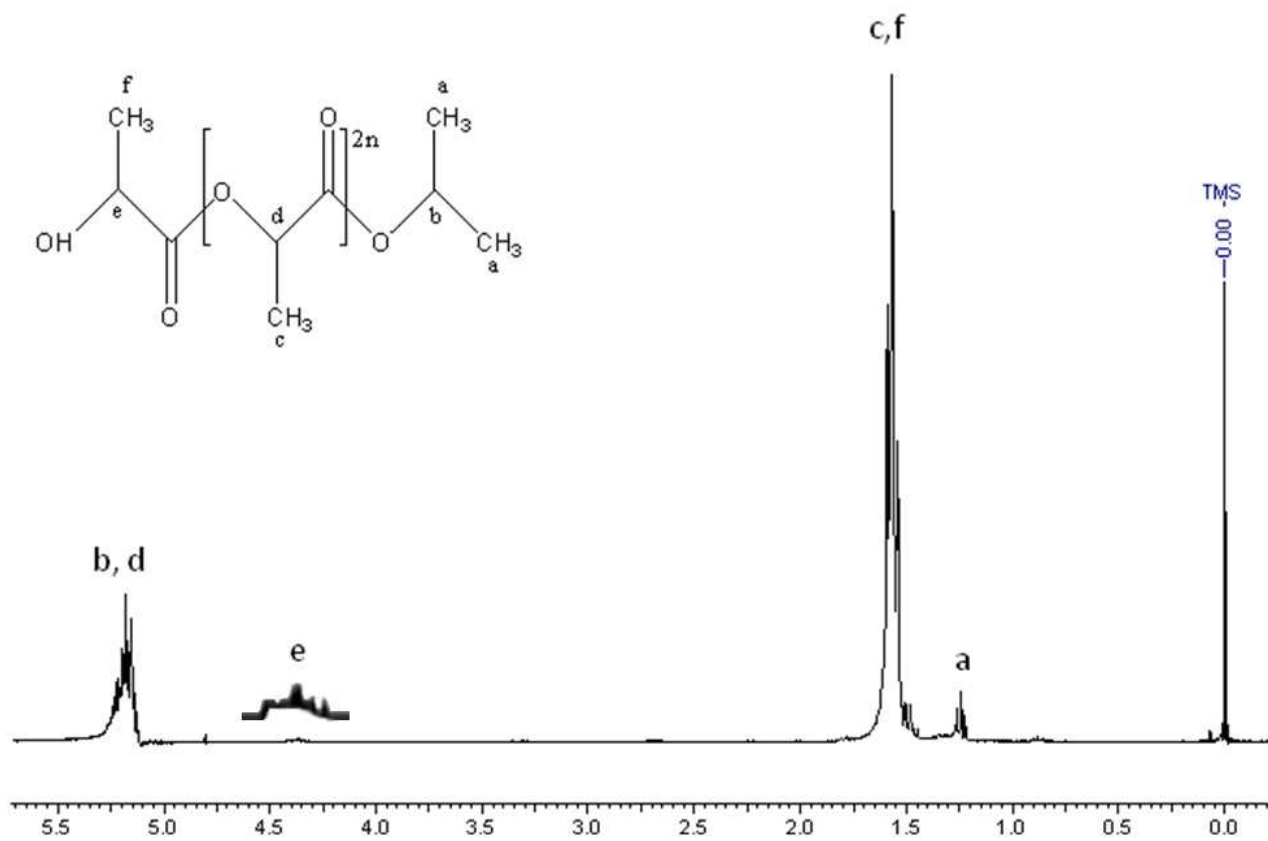


Figure S3. DFT calculated structure of stage A, Figure 3.

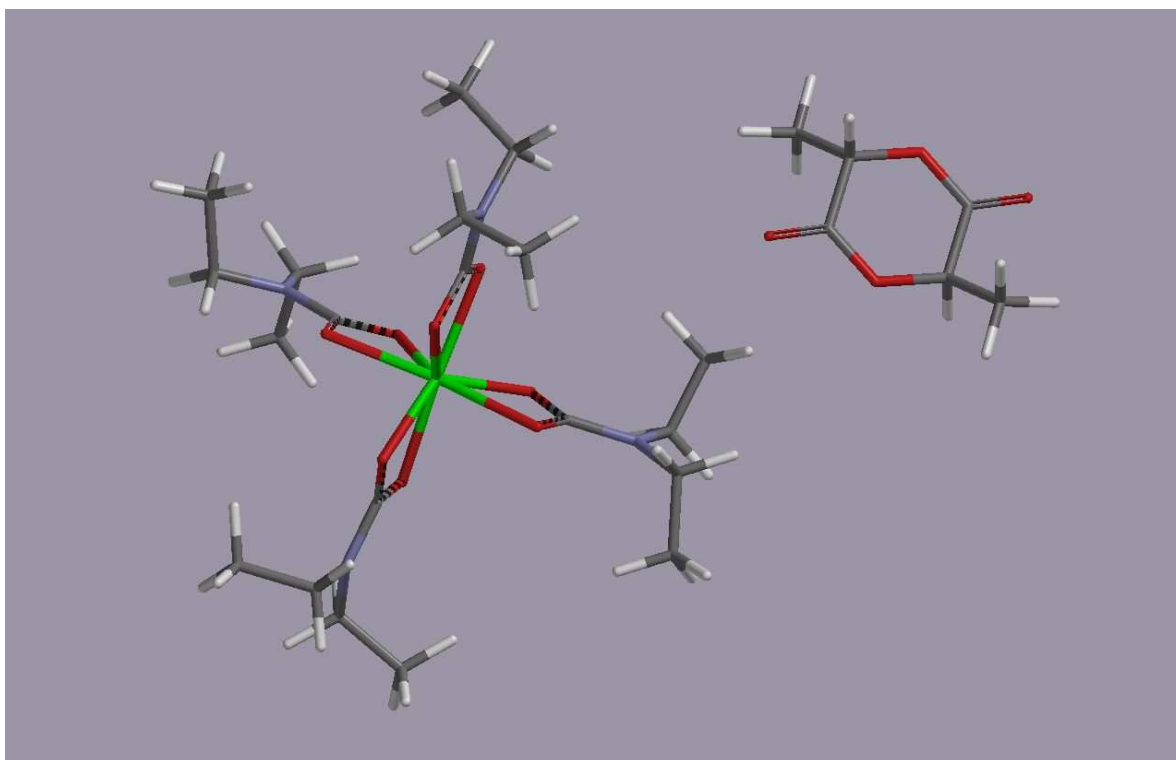


Figure S4. DFT calculated structure of stage B, Figure 3.

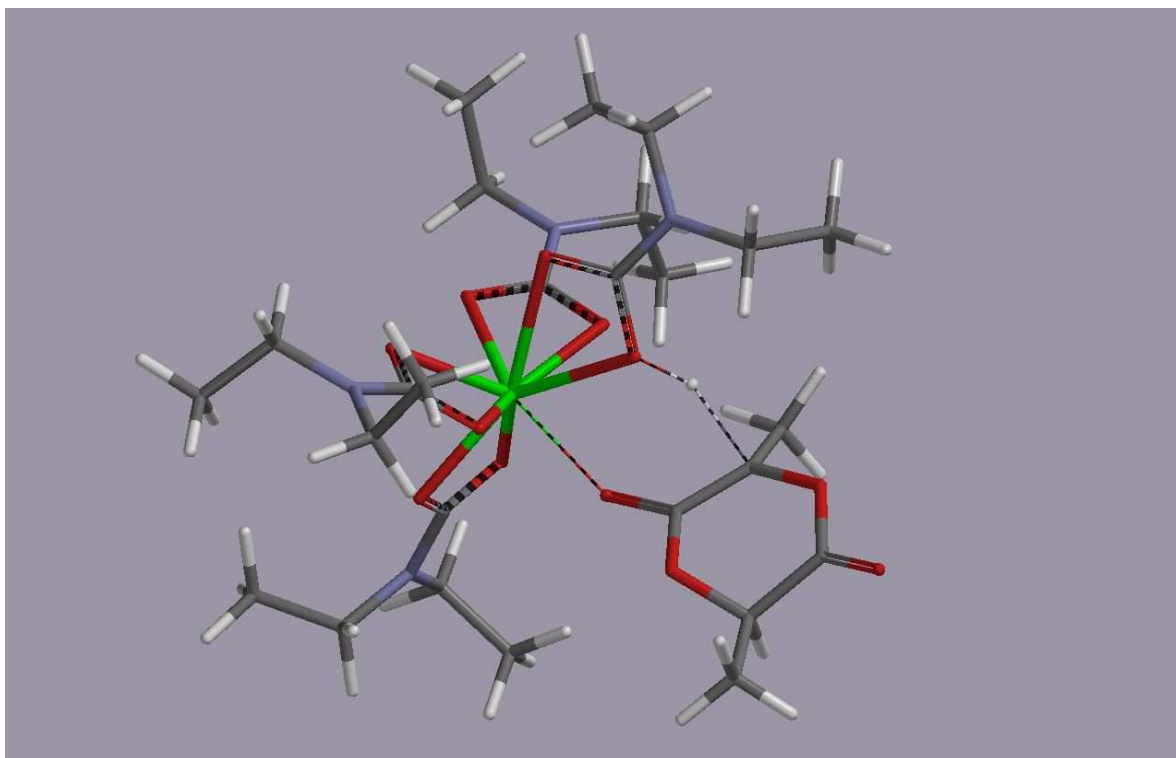


Figure S5. DFT calculated structure of stage C, Figure 3.

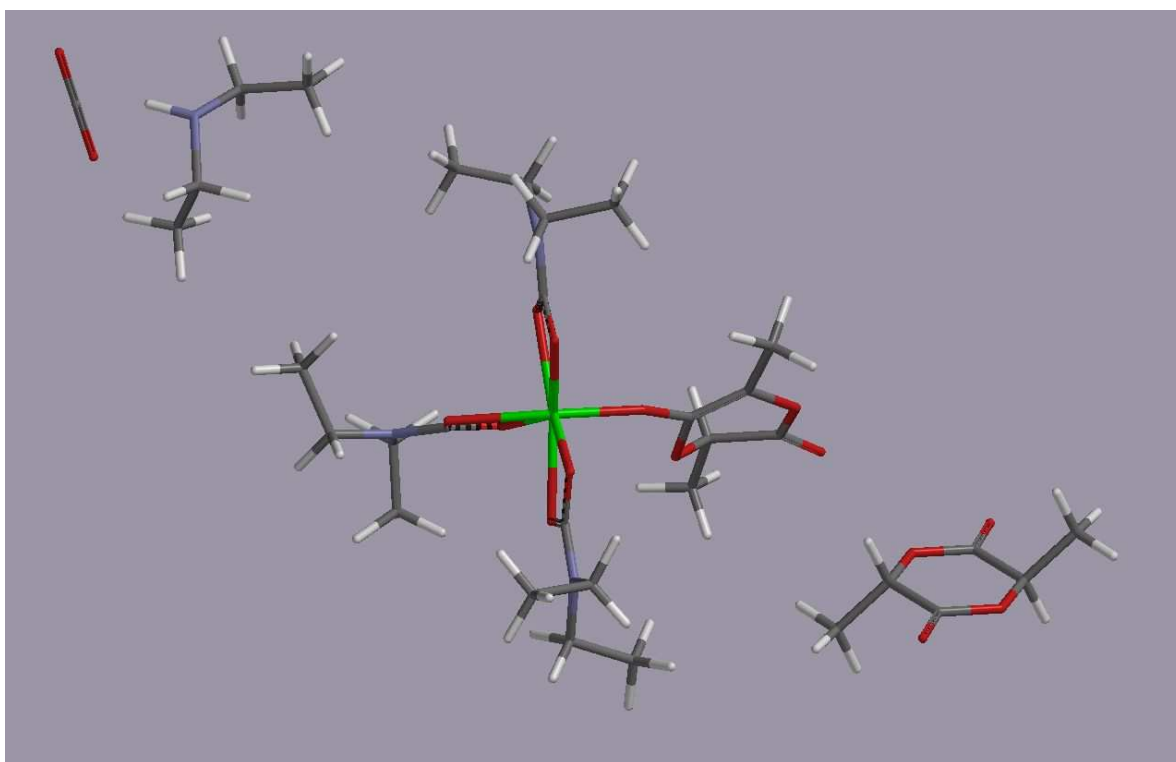


Figure S6. DFT calculated structure of stage D, Figure 3.

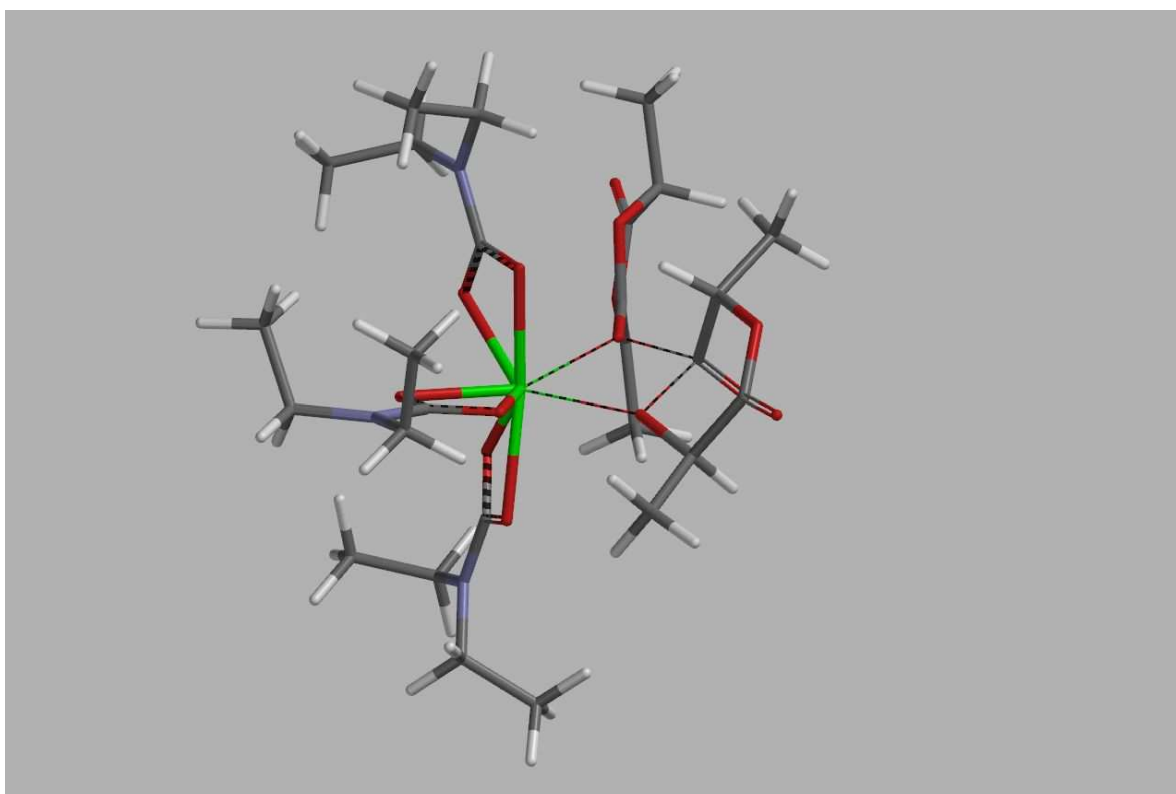


Figure S7. DFT calculated structure of stage E, Figure 3.

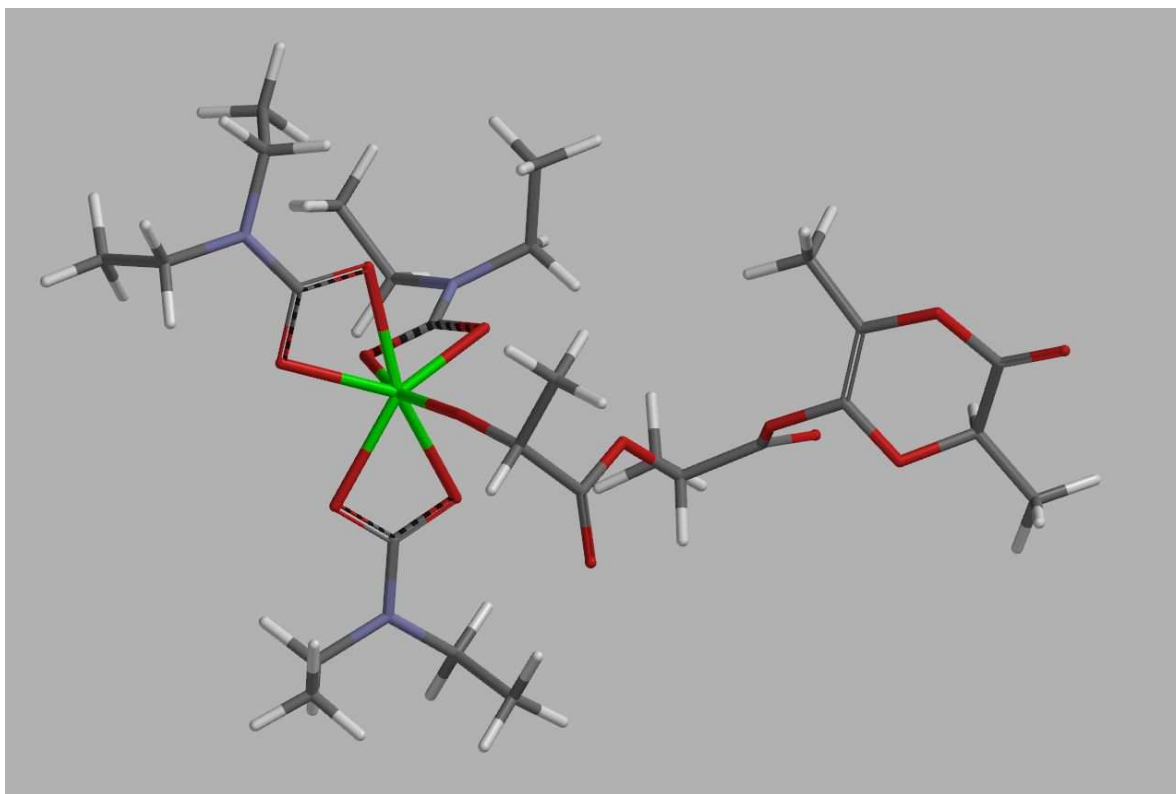


Figure S8. DFT calculated Spin density surface of the radical formed by coupling of two lactide units promoted by **1a**. Positive spin density (0.0004 electron/au³).

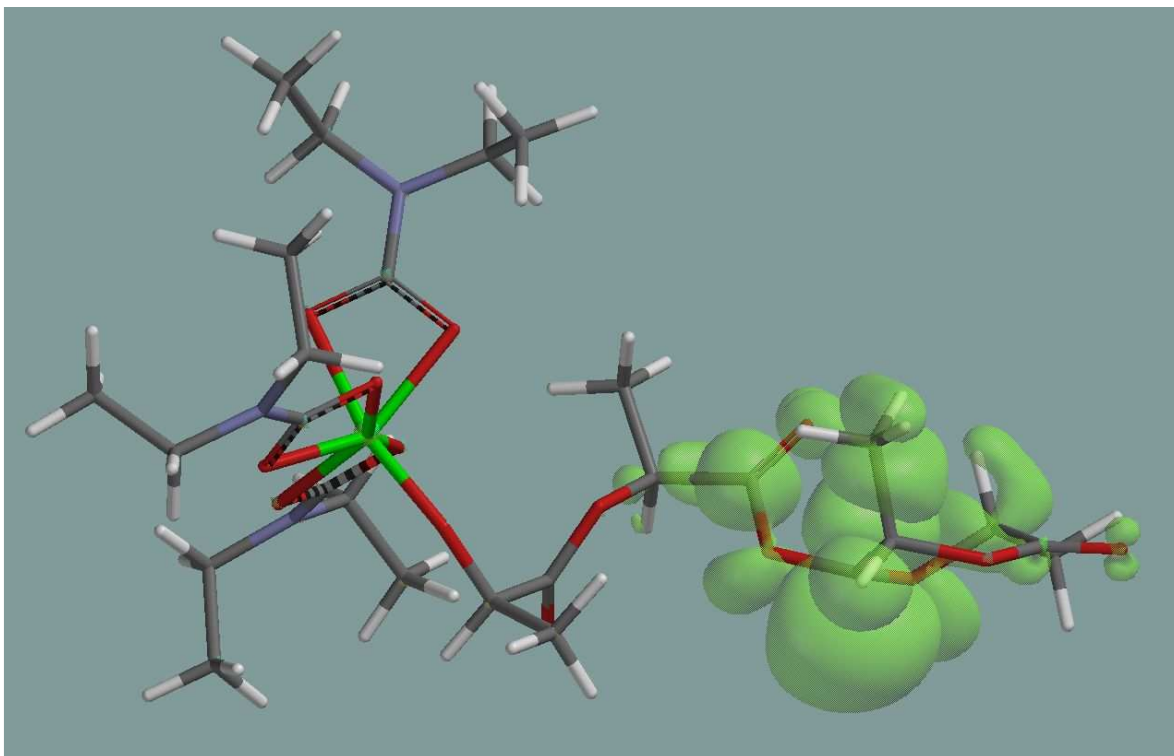


Figure S9. DFT calculated structure of stage A, Figure 5.

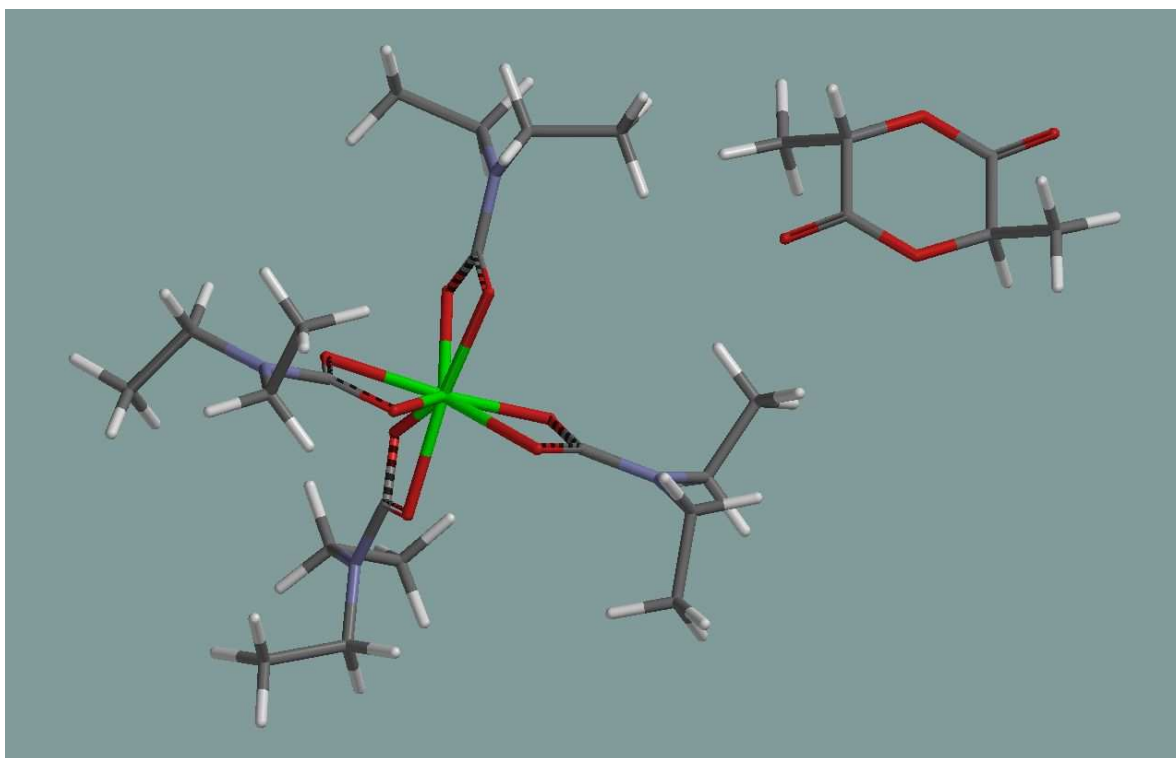


Figure S10. DFT calculated structure of stage B, Figure 5.

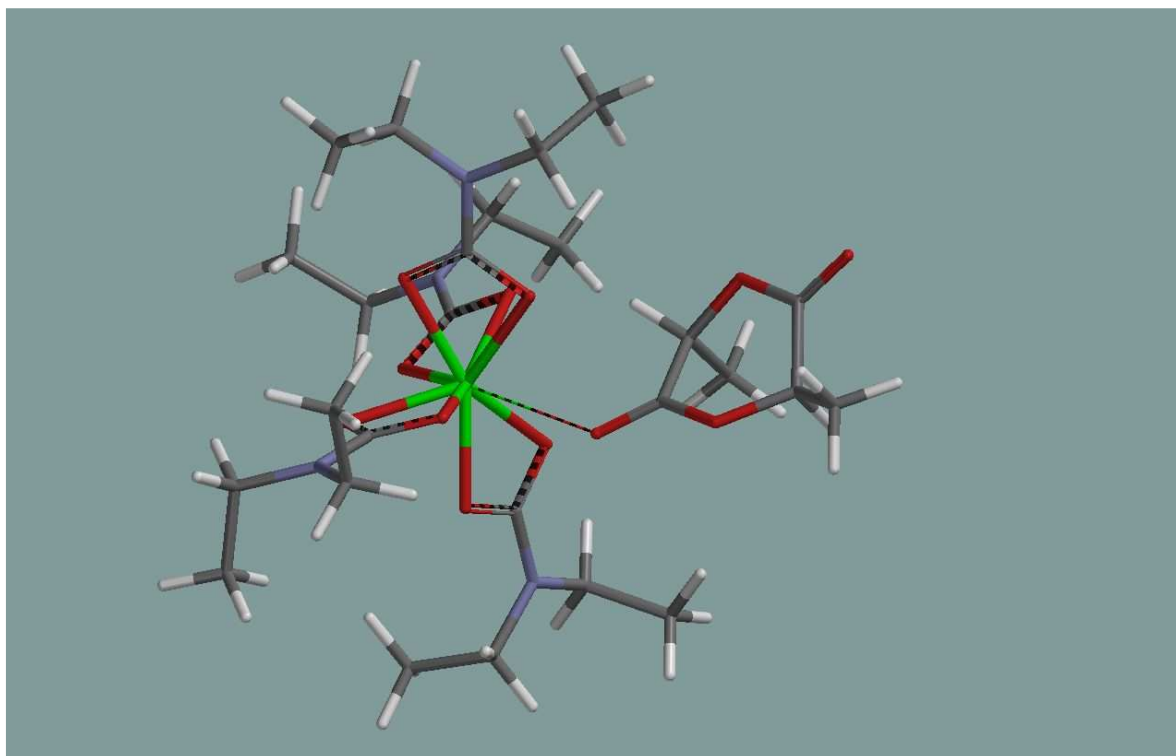


Figure S11. DFT calculated structure of stage C, Figure 5.

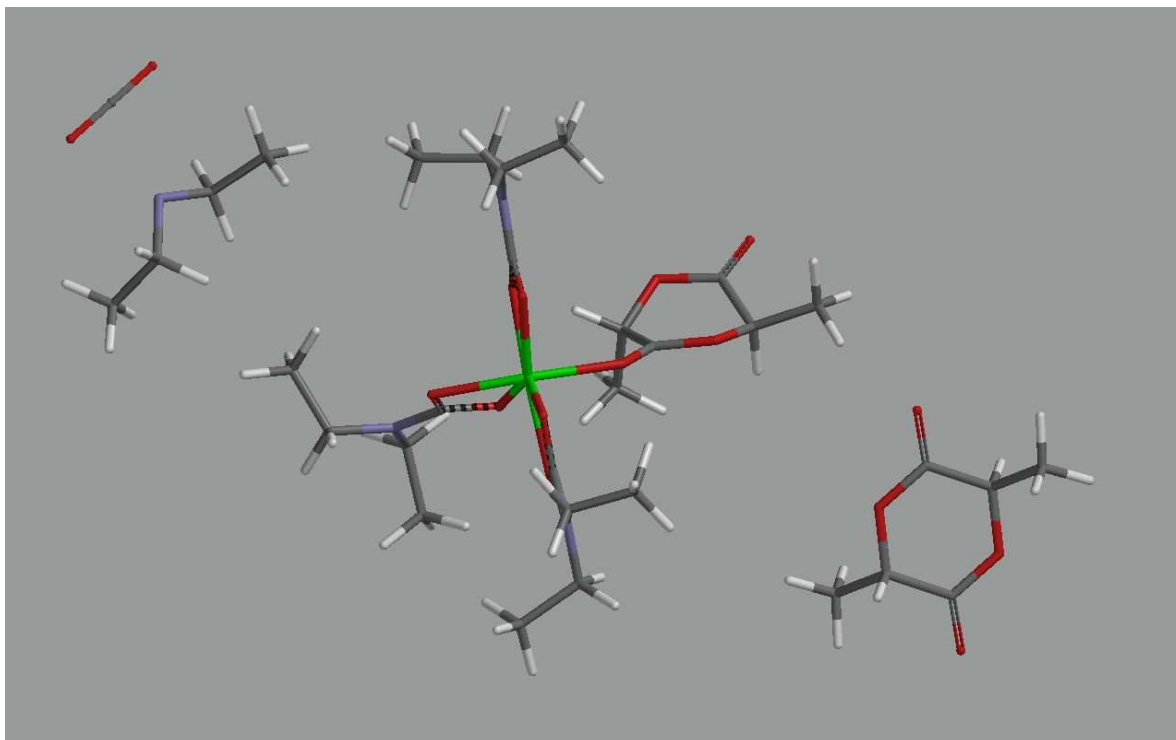


Figure S12. DFT calculated structure of stage D, Figure 5.

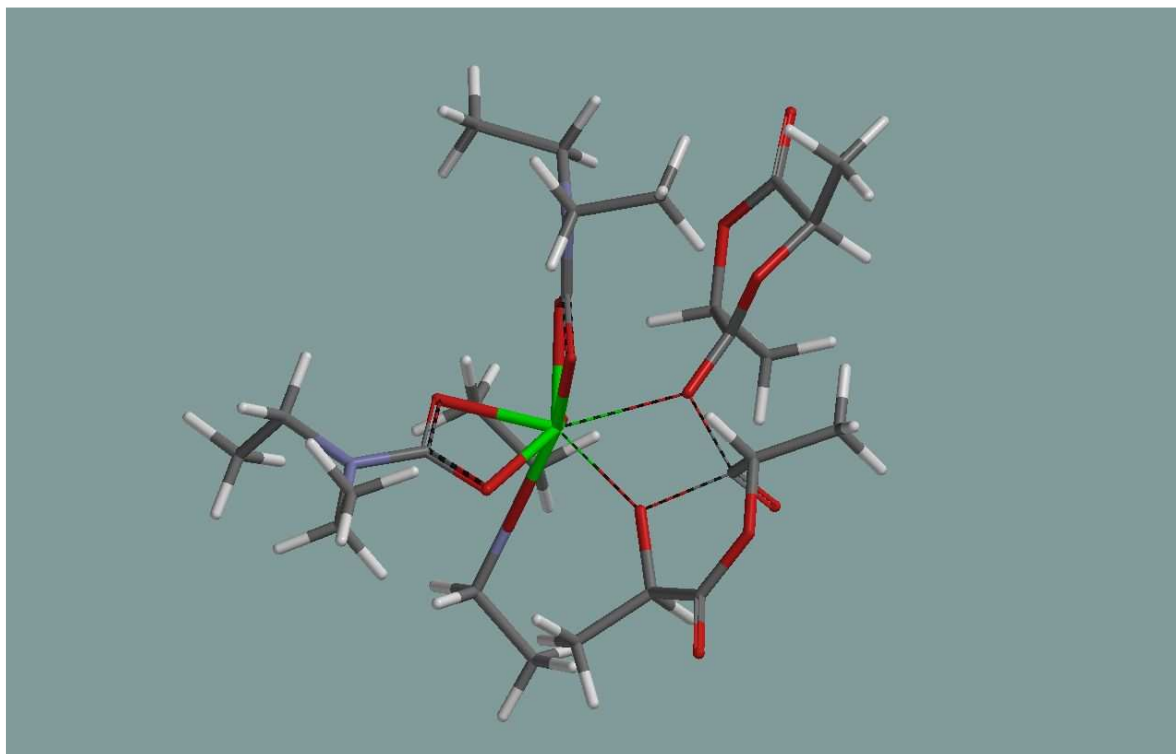


Figure S13. DFT calculated structure of stage E, Figure 5.

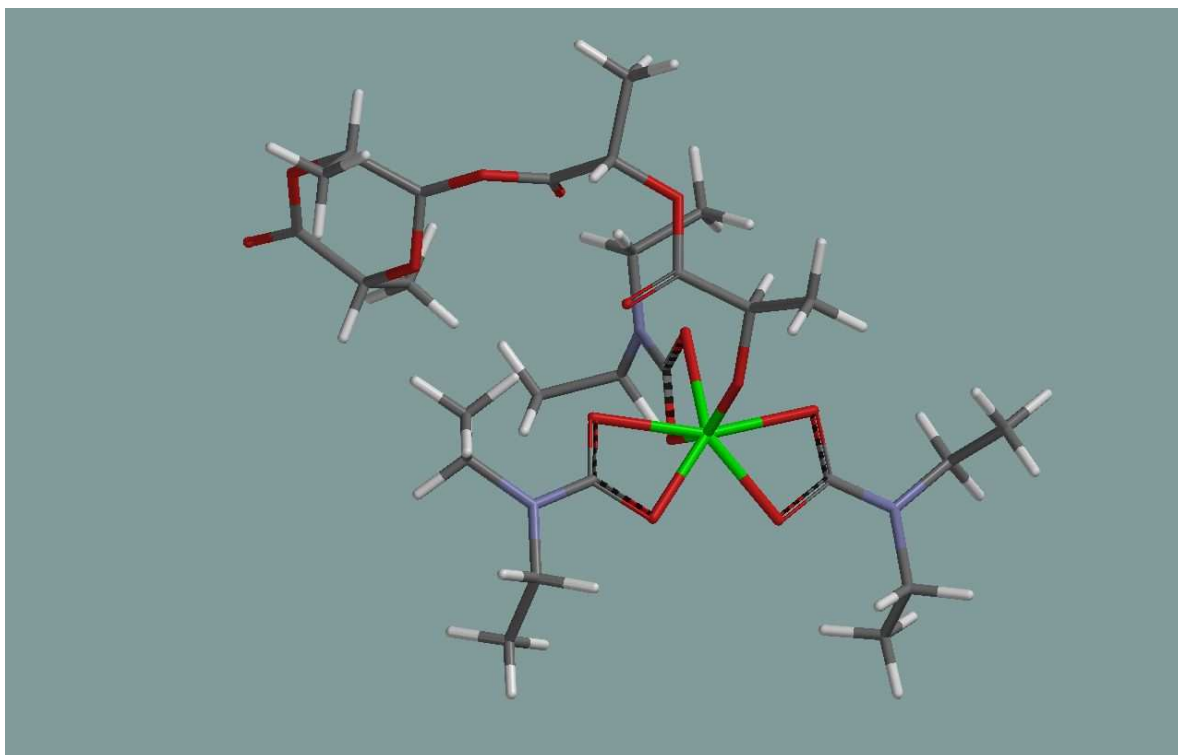
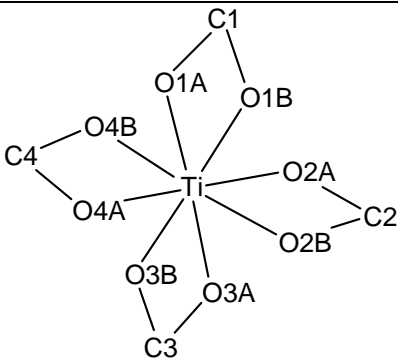


Table S1. Comparison of experimental ^a and calculated ^a bond distances (Å) and angles (deg) for Ti(O₂CNEt₂)₄

	Experimental	Calculated
Ti—O1A	2.0851(16)	2.107
Ti—O1B	2.0562 (15)	2.069
Ti—O2A	2.0561 (16)	2.069
Ti—O2B	2.1087 (16)	2.107
Ti—O3A	2.1013 (16)	2.107
Ti—O3B	2.0663 (16)	2.069
Ti—O4A	2.0530 (15)	2.069
Ti—O4B	2.0897 (15)	2.107
C1—O1A	1.269 (3)	1.276
C1—O1B	1.287 (3)	1.292
C2—O2A	1.281 (3)	1.292
C2—O2B	1.267 (3)	1.276
C3—O3A	1.269 (3)	1.276
C3—O3B	1.281 (3)	1.292
C4—O4A	1.272 (3)	1.276
C4—O4B	1.271 (3)	1.292
O1A—Ti—O1B	62.86 (6)	62.90
O2A—Ti—O2B	62.63(7)	62.89
O3A—Ti—O3B	62.76(6)	62.88
O4A—Ti—O4B	62.76(6)	62.89

^a Solid state (X-ray). Straessler, N. A.; Caudle, M. T.; Groy, T. L. *Acta Crystallogr. Sect. E* **2008**, *64*, m48. ^b Gas-phase (DFT).