Synthesis and *rac*-lactide ring-opening polymerisation studies of new alkaline earth tetrahydroborate complexes

Richard A. Collins, Junjuda Unruangsri and Philip Mountford

SUPPORTING INFORMATION

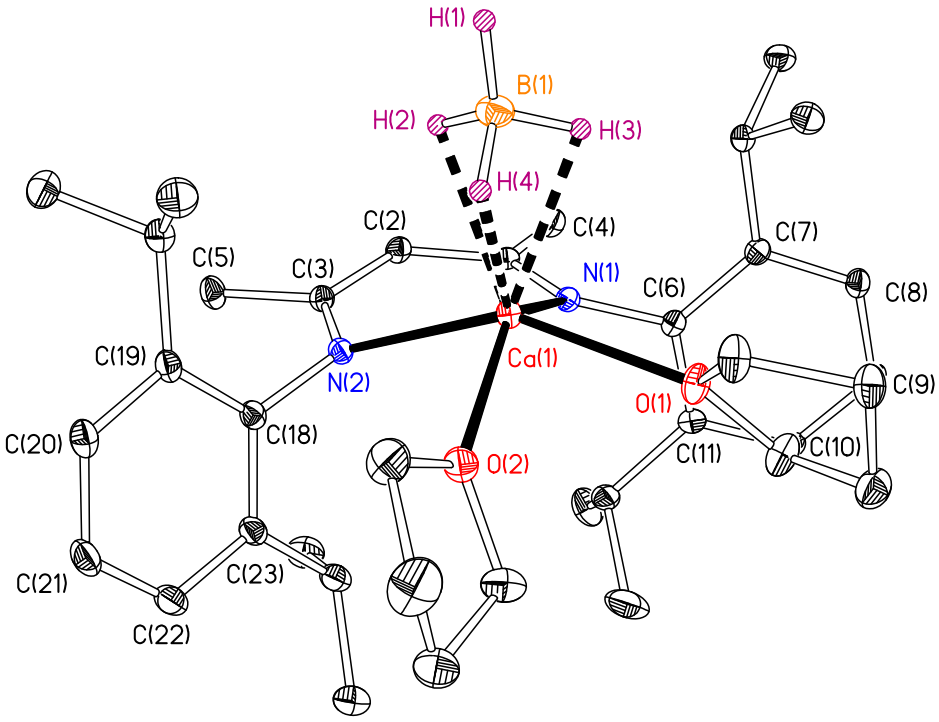

Figure S1. Displacement ellipsoid plot (20% probability) of Ca{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**2**, one of two crystallographically-independent molecules). C-bound H atoms omitted for clarity, and other H atoms drawn as spheres of an arbitrary radius.

Table S1. Further details of the ROP of *rac*-LA using Mg{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF) (**1**).

Equivs *rac*-LA	Time (mins)	Conversion (%)	M_n (GPC)[a]	M_n (calcd.)[b]	PDI	P_r
20	1	90	4,380	2,600	1.43	
20	5	93	4,200	2,680	1.46	0.86
50	1	76	7,870	5,480	1.70	
50	5	93	7,540	6,680	1.74	0.83
100	1	73	13,070	10,530	1.65	
100	5	88	13,070	12,750	1.70	
100	30	92	12,940	13,270	1.75	0.82
150	1	70	17,180	15,060	1.65	
150	5	90	18,500	19,390	1.63	
150	30	94	15,950	20,400	1.81	0.80
200	1	74	22,330	21,270	1.46	
200	5	87	23,250	25,060	1.58	
200	30	91	22,970	26,370	1.62	0.76
250	1	69	23,660	24,850	1.47	
250	5	91	25,550	32,810	1.55	
250	30	92	26,160	33,200	1.64	0.74
300	1	60	22,720	26,150	1.47	
300	5	86	26,670	37,240	1.59	
300	30	91	28,370	39,350	1.55	0.77

Conditions: [*rac*-LA]$_0$:[**1**]$_0$ = 20, 50, 100, 150, 200, 250, 300, 6 mL THF at 23 °C, [*rac*-LA]$_0$ = 0.5 M. [a] Molecular weights (g mol^{-1}) determined from GPC using the appropriate Mark-Houwink corrections. [b] Expected M_n (g mol^{-1}) for 1 chain growing per metal centre at maximum percentage conversion determined by NMR spectroscopy.

Table S2. Further details of the ROP of *rac*-LA using Ca{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**2**).

Time (mins)	Conversion (%)	M_n (GPC)[a]	M_n (calcd.)[b]	PDI
0.5	22	2,160	3,110	1.15
1	24	2,520	3,500	1.18
2	29	2,810	4,230	1.21
4	36	3,230	5,250	1.21
6	40	3,600	5,800	1.28
8	46	3,940	6,560	1.29
12	52	4,200	7,530	1.36
16	56	4,660	8,130	1.37
20	62	4,760	9,010	1.32
30	74	4,990	10,590	1.56
50	82	5,100	11,850	1.72
70	88	5,230	12,650	1.79
90	91	5,350	13,160	1.79

Conditions: [*rac*-LA]$_0$:[**2**]$_0$ = 100:1, 6 mL THF at 23 °C, [*rac*-LA]$_0$ = 0.5 M. [a] Molecular weights (g mol^{-1}) determined from GPC using the appropriate Mark-Houwink corrections. [b] Expected M_n (g mol^{-1}) for 1 chain growing per metal centre at maximum percentage conversion determined by NMR spectroscopy.

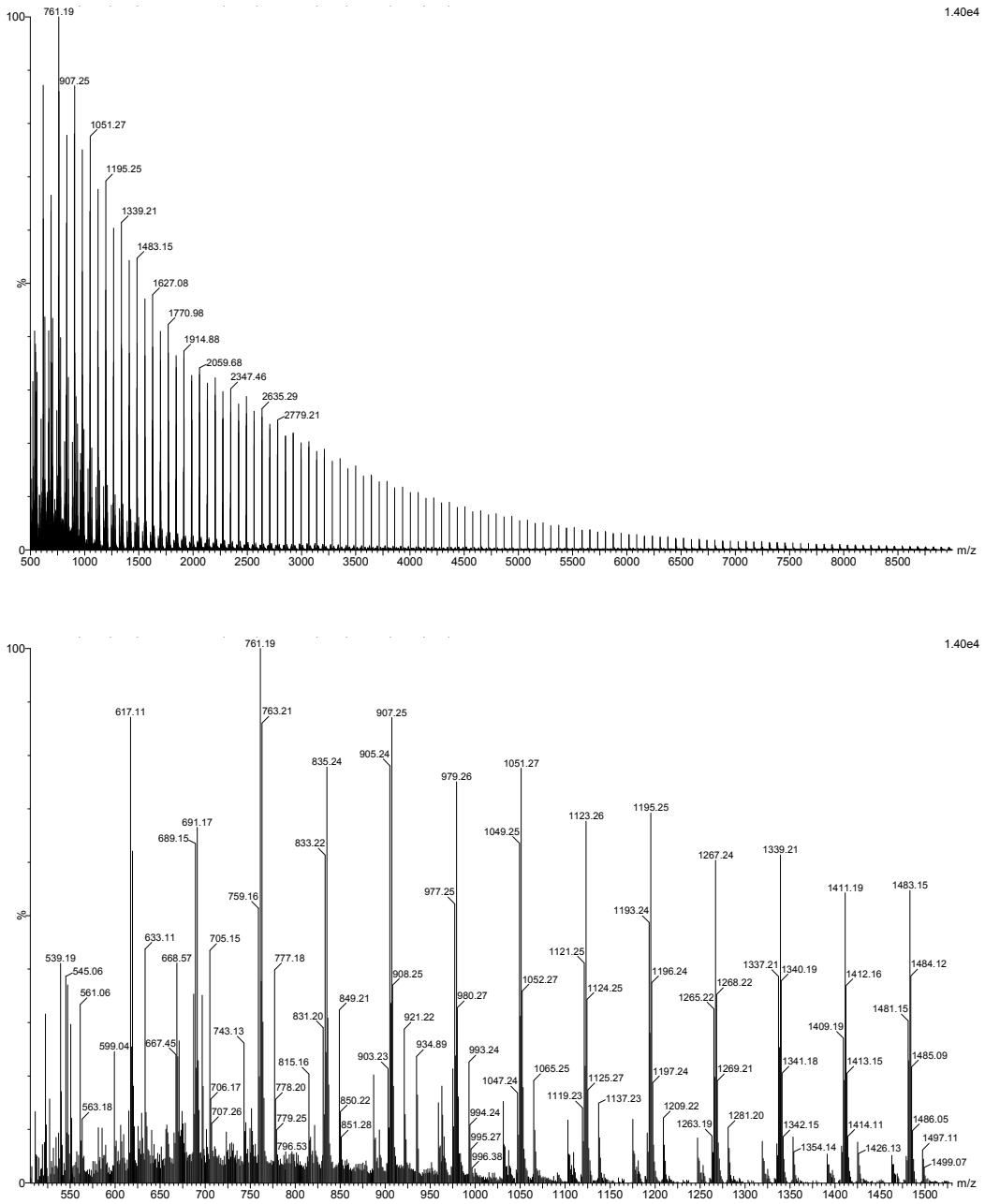

Figure S2. MALDI-ToF mass spectra of the PLA formed with Mg{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF) (**1**). The cationization agent was potassium trifluoroacetate.

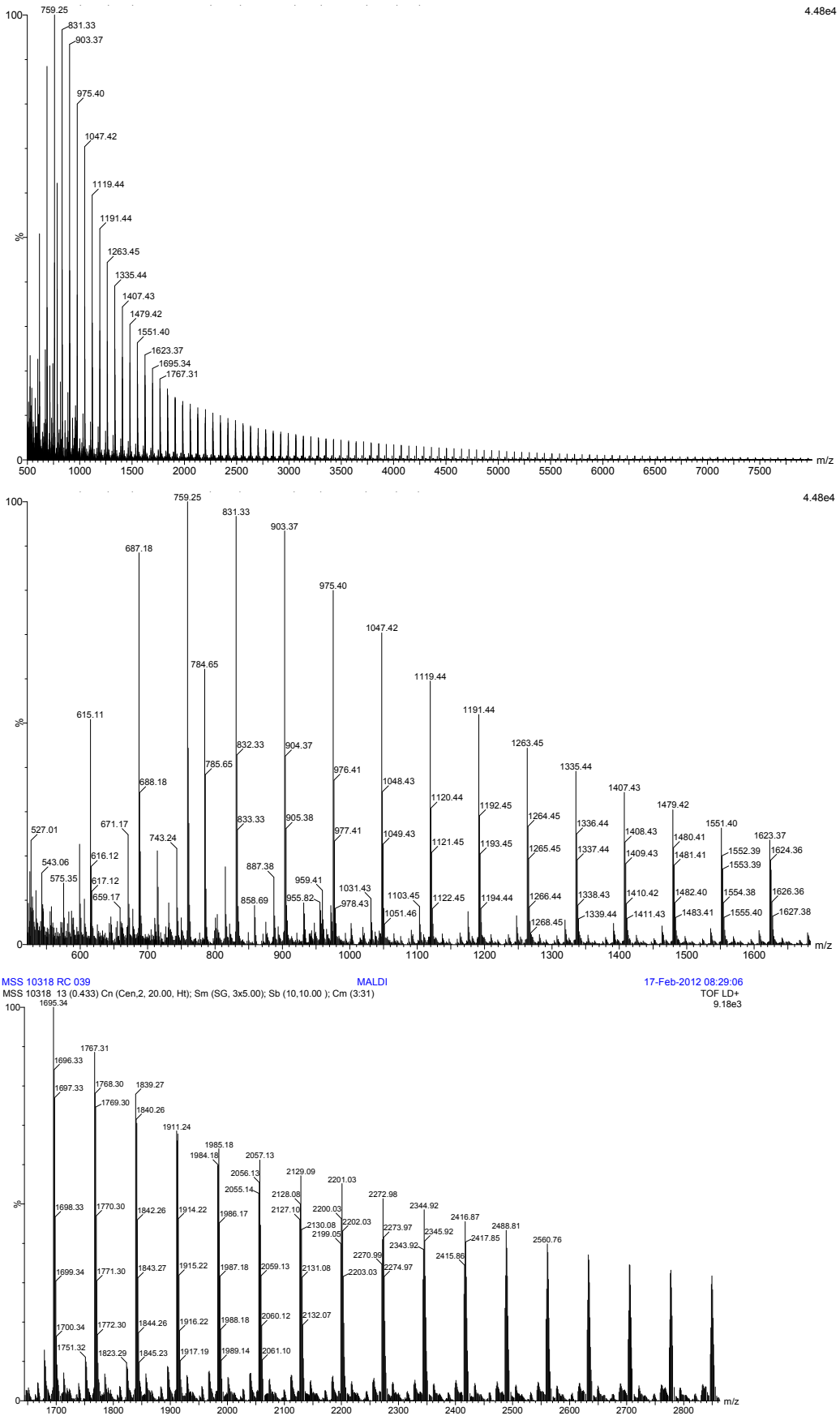

Figure S3. MALDI-ToF mass spectra of the PLA formed with Ca{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**2**). The cationization agent was potassium trifluoroacetate.

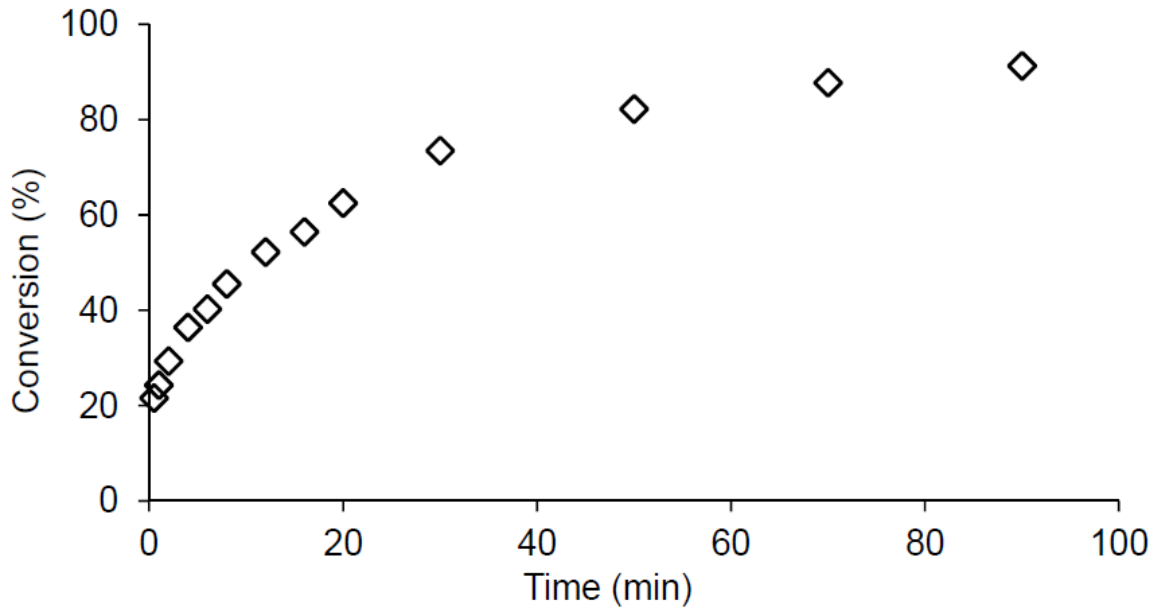

Figure S4. Conversion of *rac*-LA *vs* time using Ca{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**2**). Conditions: 6 mL THF, RT, [*rac*-LA]$_0$:[**2**]$_0$ = 100.

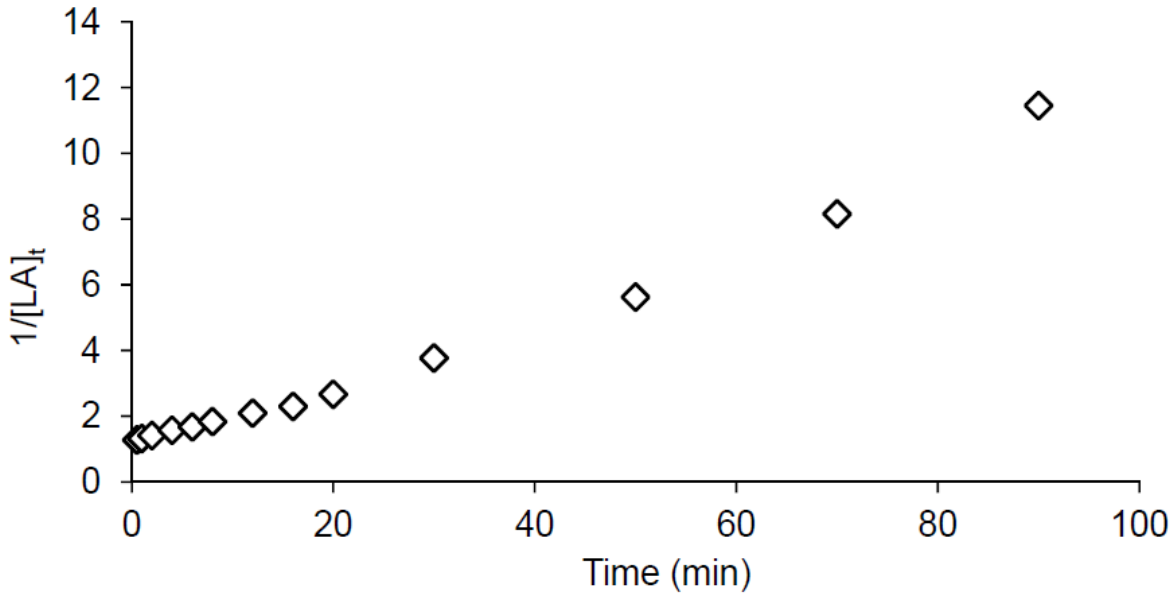

Figure S5. Non-linear 2nd order kinetics plot for the polymerisation of *rac*-LA Ca{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**2**). Conditions: 6 mL THF, RT, [*rac*-LA]$_0$:[**2**]$_0$ = 100. The corresponding 1st order ln plot was also non-linear.

Table S3. Further details of the ROP of *rac*-LA using Mg{HC(P(Ph$_2$)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**4**).

Time (mins)	Conversion (%)	M_n (GPC)[a]	M_n (calcd.)[b]	PDI
30	26	2,390	3,780	1.33
60	39	2,400	5,630	1.27
90	47	2,750	6,790	1.28
120	54	3,120	7,780	1.27
150	60	3,420	8,720	1.29
180	65	3,690	9,360	1.27
210	70	3,850	10,150	1.28
240	76	4,140	10,960	1.29
270	78	4,220	11,270	1.30
300	83	4,350	11,910	1.30
330	83	4,520	11,970	1.27
360	87	4,570	12,470	1.29
390	88	4,610	12,720	1.25
420	90	4,630	12,910	1.31
450	90	4,510	12,990	1.27

Conditions: [*rac*-LA]:[**4**] = 100:1, 6 mL THF at 23 °C, [*rac*-LA]$_0$ = 0.5 M. [a] Molecular weights (g mol^{-1}) determined from GPC using the appropriate Mark-Houwink corrections. [b] Expected M_n (g mol^{-1}) for 1 chain growing per metal centre at the given conversion.

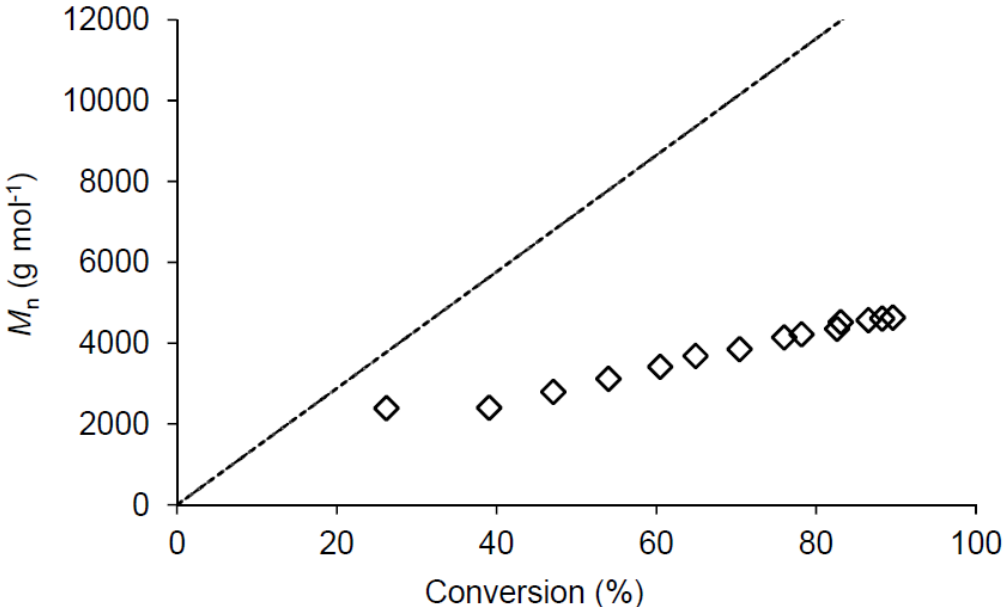

Figure S6. M_n (GPC) *vs.* equivalents *rac*-LA converted using Mg{HC(P(Ph$_2$)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**4**). The dotted line is that expected for 1 PLA chain per metal centre. Conditions: 6 mL THF, RT, [*rac*-LA]$_0$:[**4**]$_0$ = 100.

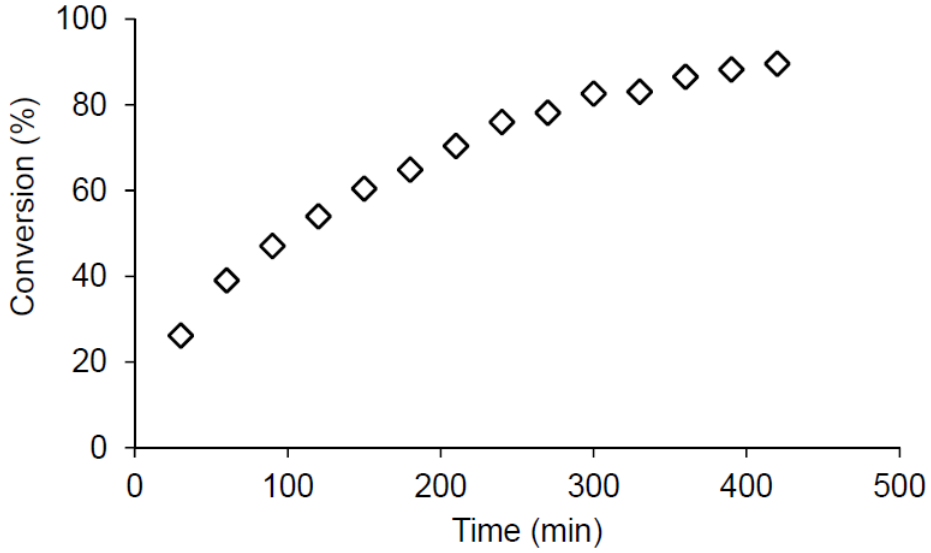

Figure S7. Conversion of *rac*-LA *vs* time using Mg{HC(P(Ph$_2$)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**4**). Conditions: 6 mL THF, RT, [*rac*-LA]$_0$:[**4**]$_0$ = 100.

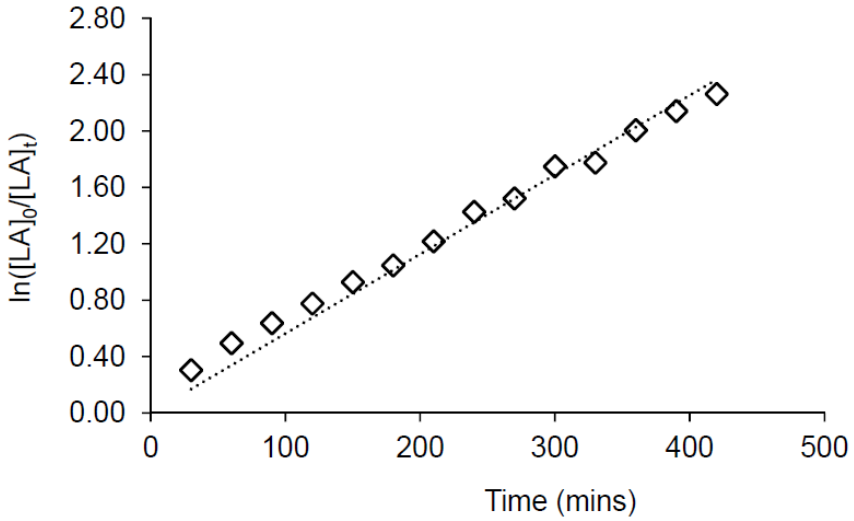

Figure S8. First order ln plot for consumption of *rac*-LA using Mg{HC(P(Ph$_2$)NAr′)$_2$}(BH$_4$)(THF)$_2$ (**4**). R^2 = 0.979, k_{app} = 0.34(2) h^{-1}. Conditions: 6 mL THF, RT, [*rac*-LA]$_0$:[**4**]$_0$ = 100.

Table S4. X-ray data collection and processing parameters for Mg{HC(C(Me)NAr′)$_2$}(BH$_4$)-(THF) (**1**) and M{HC(C(Me)NAr′)$_2$}(BH$_4$)(THF)$_2$ (M = Ca (**2**) or Sr (**3**)).

compound	**1**	**2**	**3**
empirical formula	$C_{33}H_{53}BMgN_2O$	$C_{37}H_{61}BCaN_2O_2$	$C_{37}H_{61}BN_2O_2Sr$
fw	528.91	616.79	664.33
temp / K	150	150	150
wavelength / Å	1.54180	0.71073	1.54180
space group	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$
a / Å	8.9350(6)	14.6535(2)	14.6050(4)
b / Å	16.6750(12)	15.6432(2)	15.7037(4)
c / Å	22.6408(15)	17.6883(3)	17.8465(3)
α / deg	79.081(6)	75.6264(6)	76.402(2)
β / deg	90.008(5)	81.3505(6)	81.680(2)
γ / deg	82.717(6)	70.8144(7)	70.540(2)
V / Å^3	3284.5(4)	3699.07(10)	3741.29(16)
Z	4	4	4
d (calcd) / Mg m^{-3}	1.070	1.107	1.179
abs coeff / mm^{-1}	0.646	0.202	2.230
R indices:[a] R_1 =	0.0496	0.0424	0.0326
R_w =	0.0551	0.0407	0.0399

[a] $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w (|F_o|-|F_c|)^2 / \Sigma w|F_o|^2\}}$ for data with $I > 3\sigma(I)$.