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Highly active aluminium catalysts for room temperature ring-opening polymerisation of *rac*-lactide.

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FAIR Data are available from DOI: 10.14469/hpc/4037, as per funding council guidelines.[1]

Materials and methods:
All reagents were obtained from Sigma-Aldrich and Fluorochem. THF was dried over sodium / benzophenone and stored under nitrogen over activated molecular sieve (3 Å) in a glove box. Pentane and toluene were obtained from a solvent purification system and stored under nitrogen over activated molecular sieve (3 Å) in a glove box. All manipulations for complex synthesis and polymerisation reactions were performed using Schlenk techniques or using an MBraun glovebox under nitrogen.

Characterizations:
NMR spectra were recorded on Bruker AVIII-400 and AVIII-500 spectrometers. All chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated *vs.* SiMe4.

Elemental analysis were carried out by Stephen Boyer at London Metropolitan University.

MALDI-ToF spectrometry measurements were performed on Waters/Micromass MALDI micro MX spectrometer using positive ionisation. Polymers were dissolved in THF at a concentration of 10 mg/mL. Dithranol was used as matrix (10 mg/mL in THF).Potassium trifluoroacetate (KTFA) was used as cationizing agent (10 mg/mL in THF). The solutions of polymer, matrix and salt were mixed in a ratio of 1/1/1 (v/v/v), respectively. The mixed solution was spotted on a stainless steel MALDI plate and left to dry for a couple of hours. The spectra were recorded using reflectron mode.

Size Exclusion Chromatography (SEC) measurements were performed on a Waters 1515 equipped with a set of Styragel® HR 5E columns (one 4.6 x 30mm guard column and two 4.6 x 300mm columns) using GPC grade THF (Fischer) as eluent at 0.3 mL/min and 40 °C. RID detection was used using an external Waters 2414 RID at 40 °C. Polystyrene standards (Agilent) were used for calibration.

The pro-ligand $H_2{}^{\mathbf{H2}}\mathbf{L}$ was synthesised according to the literature procedure using 3,5-di-*tert*--butylcatechol and 1,2-ethanediamine.[2]

Synthesis of aluminium complexes (NMR data available here: 10.14469/hpc/4038)

*Synthesis of ^{H2}LAl(Et) (**1**):* A pre-cooled solution (-40 °C) of $AlEt_3$ (61 mg; 0.53 mmol) in THF (2 mL) is added to a pre-cooled solution (-40 °C) of $H_2{}^{\mathbf{H2}}\mathbf{L}$ (250 mg; 0.53 mmol) in THF (5 mL). The solution was allowed to warm to room temperature and stirred for 4 hours. The solvent was evaporated off to yield the crude compound ^{H2}**L**Al(Et) (quantitative yield) as determined by NMR spectroscopy (see below). All attempts to purify the complex using pentane or mixtures pentane/THF at different temperatures (-40 °C and r.t.) led to isolate **2**.

^{1}H NMR (500 MHz, C_6D_6) δ_{1H} (ppm): 7.41 (d, *^4J = 2.3 Hz*, 2H, Ar-H), 6.61 (d, *^4J = 2.3 Hz*, 2H, Ar-H), 2.36 (m, 2H, N-H), 2.00 (m, *^3J = 5.02 Hz*, 2H, $-CH_2-$), 1.84 (m, 2H, $-CH_2-$), 1.69 (s, 18H, ^{t}Bu), 1.48 (t, *^3J = 8.0 Hz*, 3H, $Al-CH_2-CH_3$), 1.39 (s, 18H, ^{t}Bu), 0.24 (q, *^3J = 8.0 Hz*, 2H, $Al-CH_2$). ^{13}C NMR (125 MHz, C_6D_6) δ_{13C} (ppm): 156.7 (C_{quat}, Ar), 137.7 (C_{quat}, Ar), 137.0 (C_{quat}, Ar), 129.4 (C_{quat}, Ar), 122.6 (CH, Ar-H), 116.6 (CH, Ar-H), 46.6 (CH_2, $N-CH_2$), 35.2 (C_{quat}, ^{t}Bu), 34.1 (C_{quat}, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 29.3 (CH_3, ^{t}Bu), 10.4 (CH_3, $Al-CH_2-CH_3$), 1.1 (CH_2, $Al-CH_2$). EA attempted but a low carbon contain was found, possibly due to the air- and moisture-sensitivity of **1** as well as the presence of residual aluminium contaminants (as aforementioned, all purification attempts of **1** led to isolate **2**).

*Synthesis of ^{H}LAl (**2**):* **1** (277 mg; 0.53 mmol) was stirred in pentane overnight to lead to formation of a white precipitate. Subsequent filtration and washing with pentane afford **2** as white powder (198 mg, 76% yield).

^{1}H NMR (500 MHz, C_6D_6) δ_{1H} (ppm): 7.30 (d, *^4J = 2.0 Hz*, 1H, Ar-H), 7.09 (d, *^4J = 2.0 Hz*, 1H, Ar-H), 7.01 (d, *^4J = 2.0 Hz*, 1H, Ar-H), 6.48 (d, *^4J = 2.0 Hz*, 1H, Ar-H), 3.89 (td, 1H, $N-CH_aH$), 3.31 (dd, 1H, N-H), 2.92 (dd, 1H, $N-CH_bH$), 2.28 (m, 1H, $N-CH_cH$), 1.82 (s, 9H, ^{t}Bu), 1.72 (s, 9H, ^{t}Bu), 1.22 (s, 9H, ^{t}Bu), 1.19 (s, 9H, ^{t}Bu). ^{13}C NMR (125 MHz, C_6D_6) δ_{13C}: 154.9 (C_{quat}, Ar), 151.6 (C_{quat}, Ar), 140.8 (C_{quat}, ^{t}Bu), 138.4 (C_{quat}, ^{t}Bu), 136.9 (C_{quat}, ^{t}Bu), 135.6 (C_{quat}, ^{t}Bu), 122.8 (CH, Ar-H), 118.7 (CH, Ar-H), 117.0 (CH, Ar-H), 116.8 (CH, Ar-H), 49.5 (CH_2, $N-CH_2$), 48.7 (CH_2, $N-CH_2$), 31.9 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 29.8 (CH_3, ^{t}Bu). EA: Found: C, 72.97; H, 9.35; N, 5.59, Calc. for $C_{30}H_{45}AlN_2O_2$: C, 73.14; H, 9.21; N, 5.69.

*Synthesis of ^{H2}LAl(OBn) (**3**):* To a solution of **2** (153 mg, 0.31 mmol) in toluene (3 mL) was added 1 equivalent of BnOH (33.8 mg, 32.4 µL, 0.31 mmol). The mixture was allowed to stir at room temperature overnight. Evaporation of the volatile and subsequent washing with pentane afford pure **3** as a white powder (148 mg, 79 % yield).

^{1}H NMR (400 MHz, C_6D_6) δ_{1H} (ppm): 7.53 (d, *^4J = 2.3 Hz*, 1H, Ar-H), 7.26 (d, 2H, Benzyloxy Ar-H) 7.22 (d, *^4J = 2.3 Hz*, 1H, Ar-H), 7.07 (m, 3H, Ar-H + 2 x Benzyloxy Ar-H), 6.94 (t, 1H, Benzyloxy Ar-H), 6.65 (d, *^4J = 2.3 Hz*, 1H, Ar-H), 4.83 (m, 2H, N-H + Benzyloxy CH_2), 4.55 (d, 1H, Benzyloxy CH_2), 3.49 (dd, *^3J = 11.2 Hz, 5.1 Hz*, 1H, N-H), 2.40 (m, 1H, $N-CH_aH-$), 2.26 (m, 2H, $N-CH_bH-$ + $N-CH_cH-$), 2.09 (s, 10H, $N-CH_dH-$ + 9 x ^{t}Bu), 1.39 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.20 (s, 9H, ^{t}Bu). ^{13}C NMR (125 MHz, C_6D_6) δ_{13C}: 158.1 (C_{quat}, Ar), 157.7 (C_{quat}, Ar), 142.3 (C_{quat}, BnO- Ar), 137.5 (C_{quat}, Ar), 136.9 (C_{quat}, Ar), 136.4 (C_{quat}, Ar), 136.3 (C_{quat}, Ar), 132.7 (C_{quat}, Ar), 131.9 (C_{quat}, Ar), 128.8 (CH, BnO- Ar-H), 127.4 (CH, BnO- Ar-H), 127.3 (CH, BnO- Ar-H), 122.5 (CH, Ar-H), 121.8 (CH, Ar-H), 117.7 (CH, Ar-H), 115.6 (CH, Ar-H), 65.1 (CH_2, BnO- $Ar-CH_2-$), 51.8 (CH_2, $N-CH_2$), 42.2 (CH_2, $N-CH_2$), 35.7 (C_{quat}, ^{t}Bu), 35.0 (C_{quat}, ^{t}Bu), 34.5 (C_{quat}, ^{t}Bu), 34.4 (C_{quat}, ^{t}Bu), 32.1 (CH3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 30.6 (CH_3, ^{t}Bu), 29.3 (CH_3, ^{t}Bu). EA: Found: C, 73.84; H, 9.02; N, 4.56, Calc. for $C_{37}H_{53}AlN_2O_3$: C, 73.97; H, 8.89; N, 4.66.

General procedure for polymerisation reactions:

Reaction in solvent: In a glovebox, *rac*-LA was mixed with the desired solvent to reach $[LA]_0$ = 1M. The resulting solution was added to the studied catalyst (10 mg; 0.017 mmol) in a vial equipped with an air-tight PTFE lid. For kinetic studies, aliquots (0.1 mL) were periodically taken for analysis and quenched with *n*-pentane to stop any further reaction. Samples were analysed by ^{1}H NMR spectroscopy to determine conversion by relative integration of signals at 5.06 ppm (monomer) and 5.20 ppm (polymer).

Reaction in bulk: In a glovebox, *rac*-LA (600 mg; 4.16 mmol) was added to a vial equipped with an air-tight PTFE lid and containing the desired amount of catalyst (10mg, 0.017 mmol). The vial was heated at 130 °C in an oil bath and the time recorded. The polymerization was stopped once the mixture became too viscous to stir, upon which a sample was taken and quenched in pentane.

Polymerisation reactions with in-situ generation of the initiator: A solution of $Al(Et)_3$ in THF (1 mL, 0.019 M) was added to vial containing $H_4^{\mathbf{H}}\mathbf{L}$ (9 mg; 0.019 mmol) and let to stir at room temperature for 15 minutes. In a separate vial, *rac*-LA (275.7 mg; 1.9 mmol) was dissolved in THF (0.9 mL) to form a 2.1 M solution, to which BnOH (2 µL; 0.019 mmol) was added using a Gilson pipette. Both vials were combined to start the polymerisation, which was run for a total of 90 minutes. Aliquots were taken and analysed by NMR and GPC.

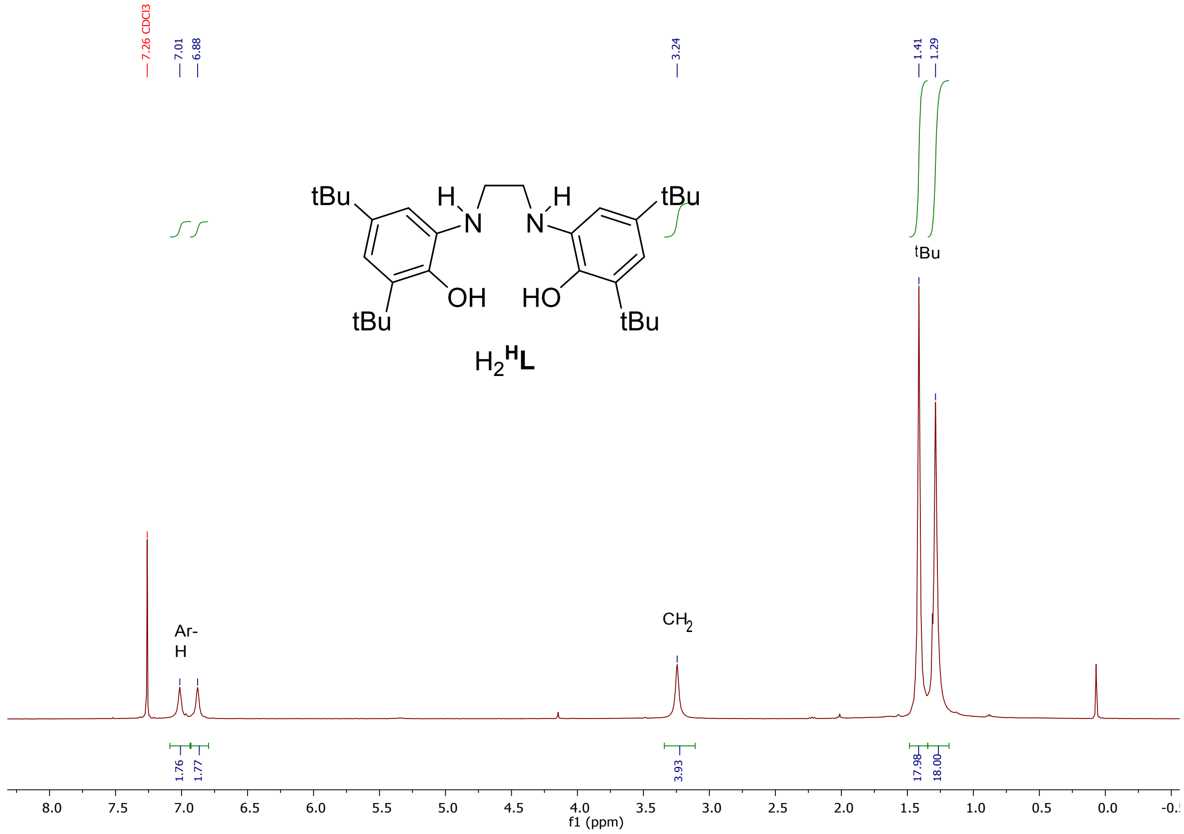


Figure S1. ^{1}H *NMR spectrum* ($CDCl_3$, *24 °C*) *of* $H_2^{\mathbf{H2}}\mathbf{L}$.

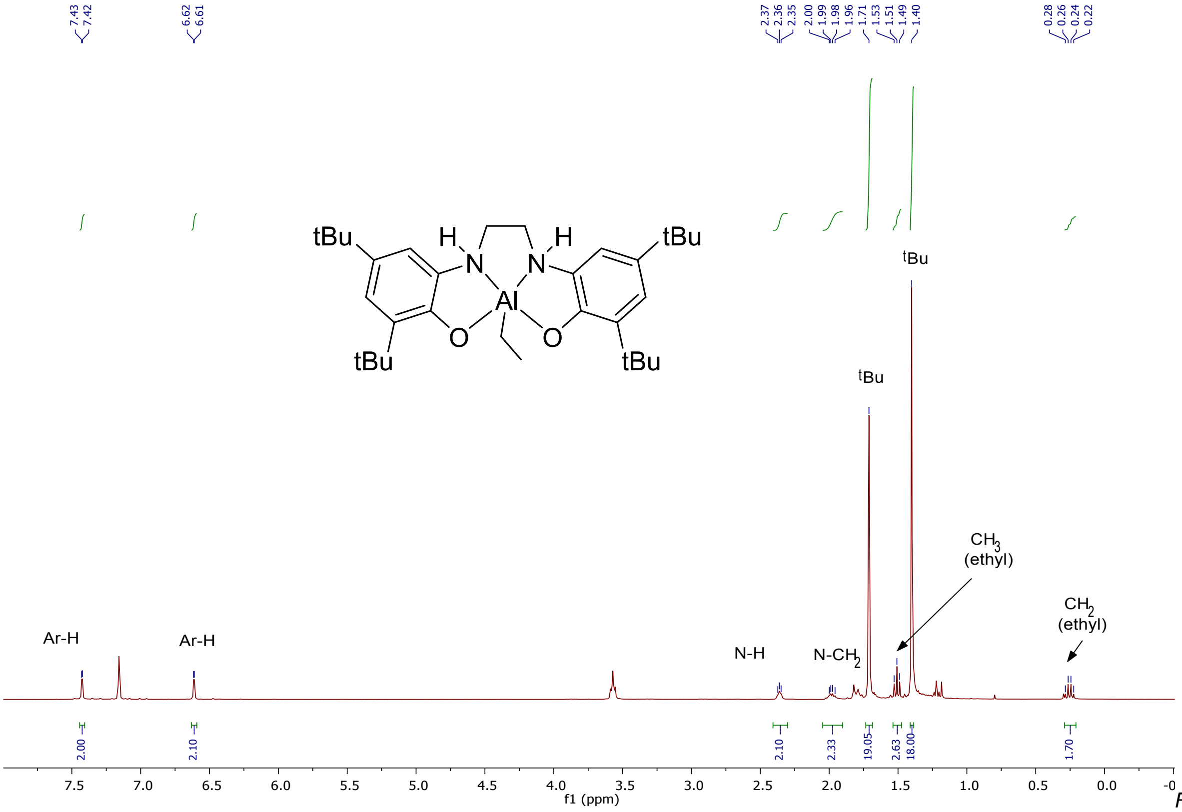


*Figure S2. ^{1}H NMR spectrum (C_6D_6, 24 °C) of **1** (data availbale here DOI: 10.14469/hpc/4038).*

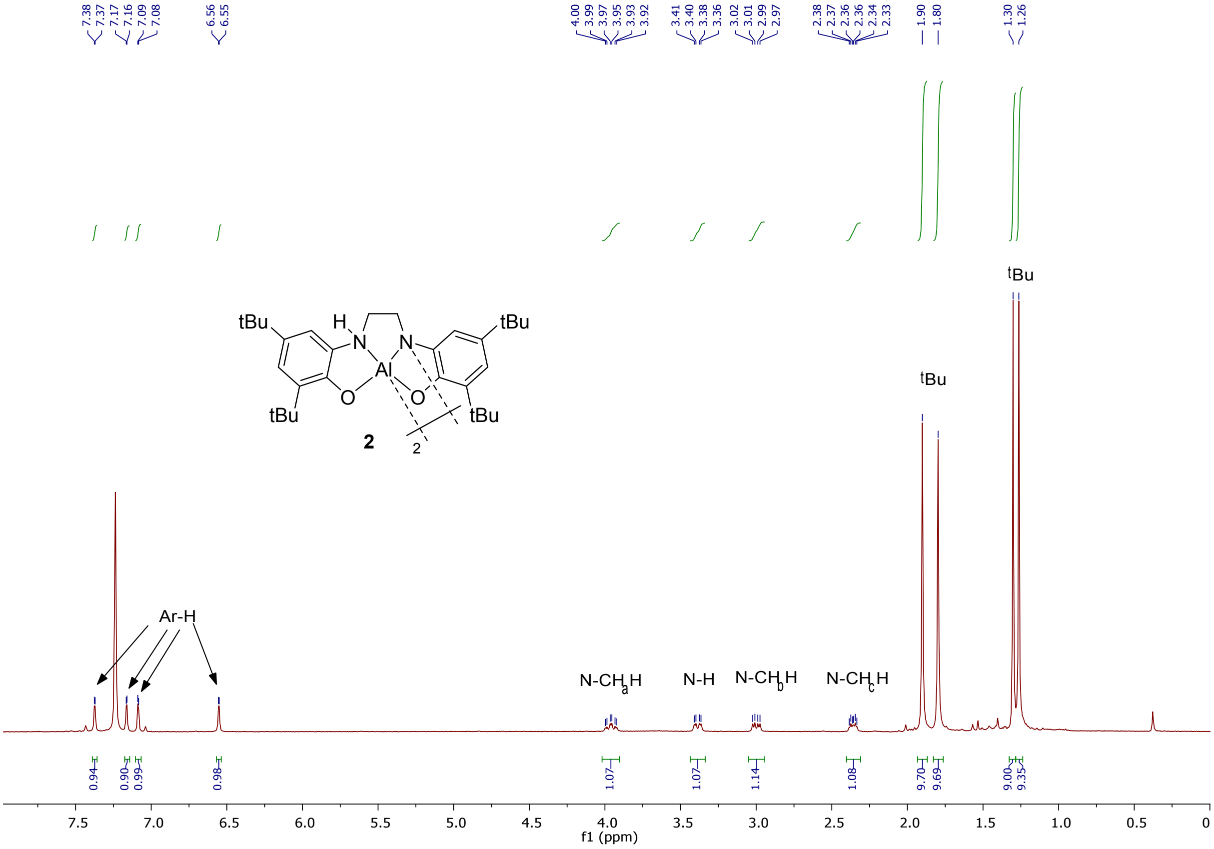


*Figure S3. ^{1}H NMR spectrum (C_6D_6, 24 °C) of **2** (data availbale here, DOI: 10.14469/hpc/4038).*

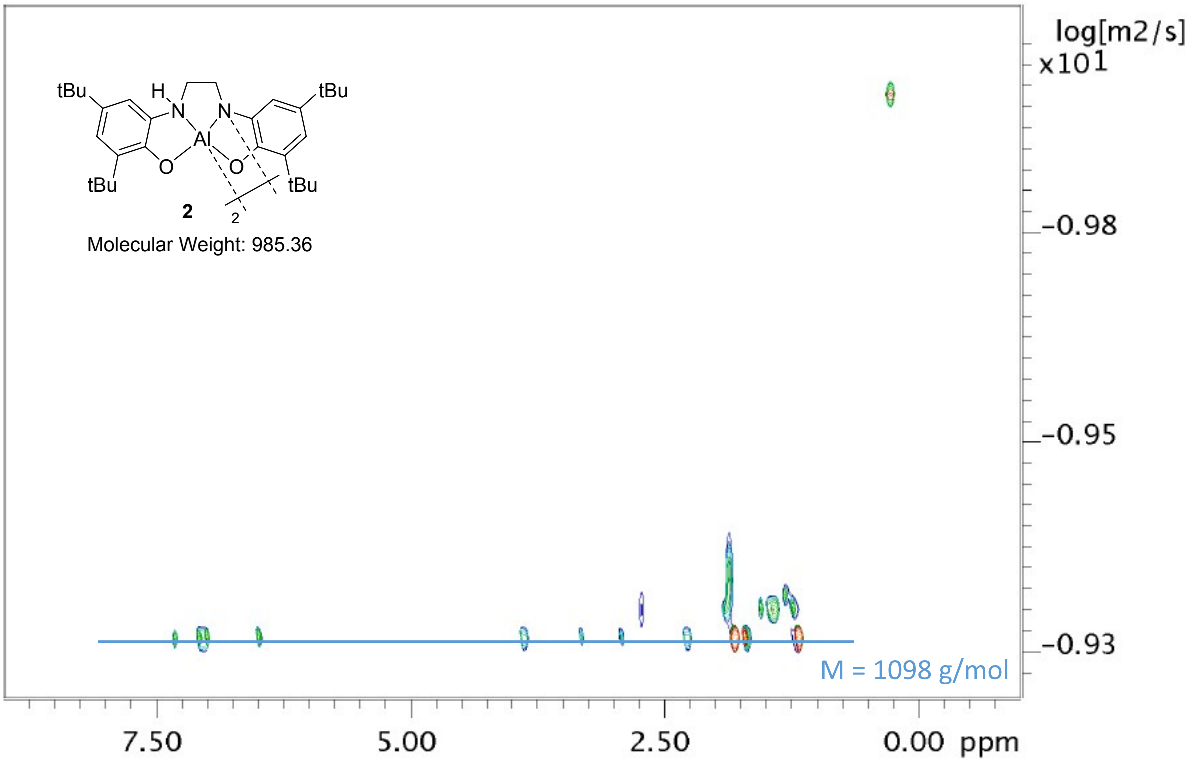


*Figure S4: DOSY NMR spectrum of **2** in C_6D_6 showing a dinuclear structure in solution using an in-house external calibration (data availbale here, DOI: 10.14469/hpc/4038).*

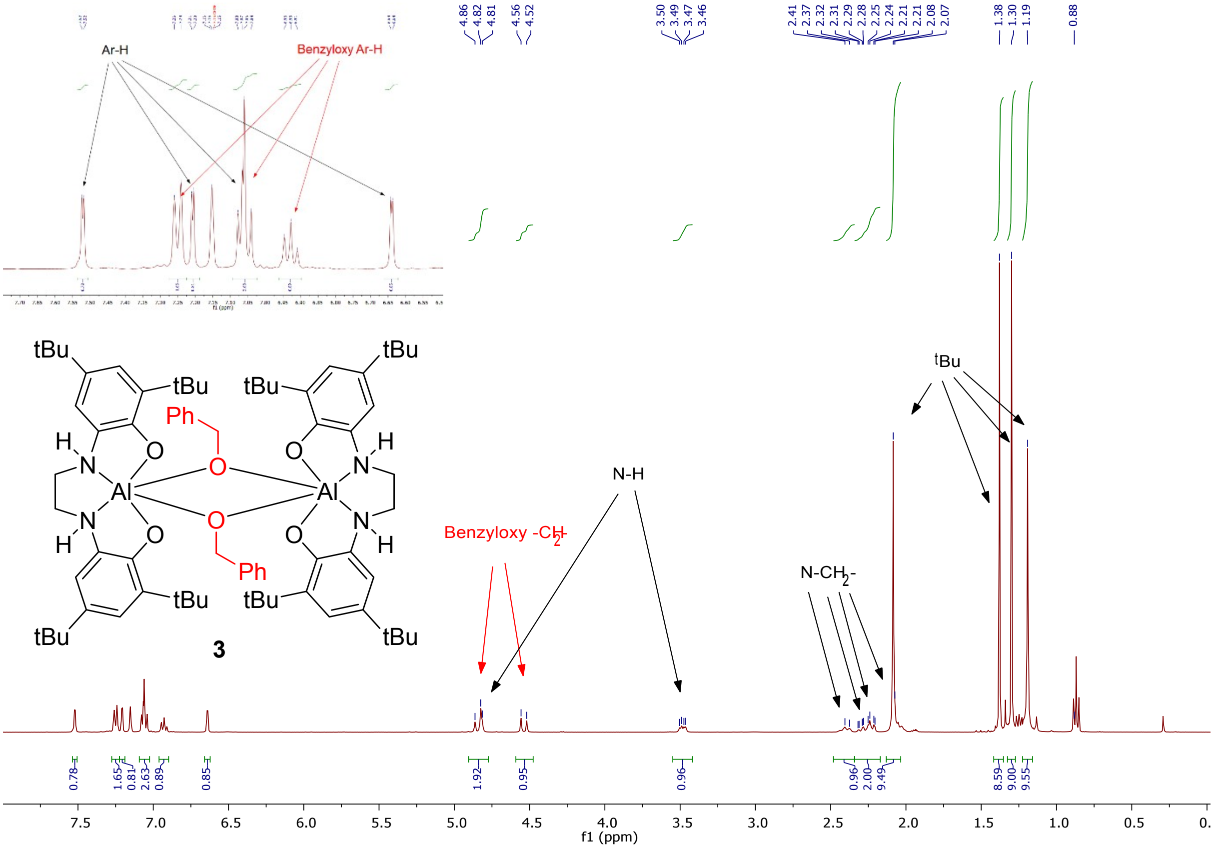


*Figure S5. ^{1}H NMR spectrum (C_6D_6, 24 °C) of **3** (data availbale here, DOI: 10.14469/hpc/4038).*

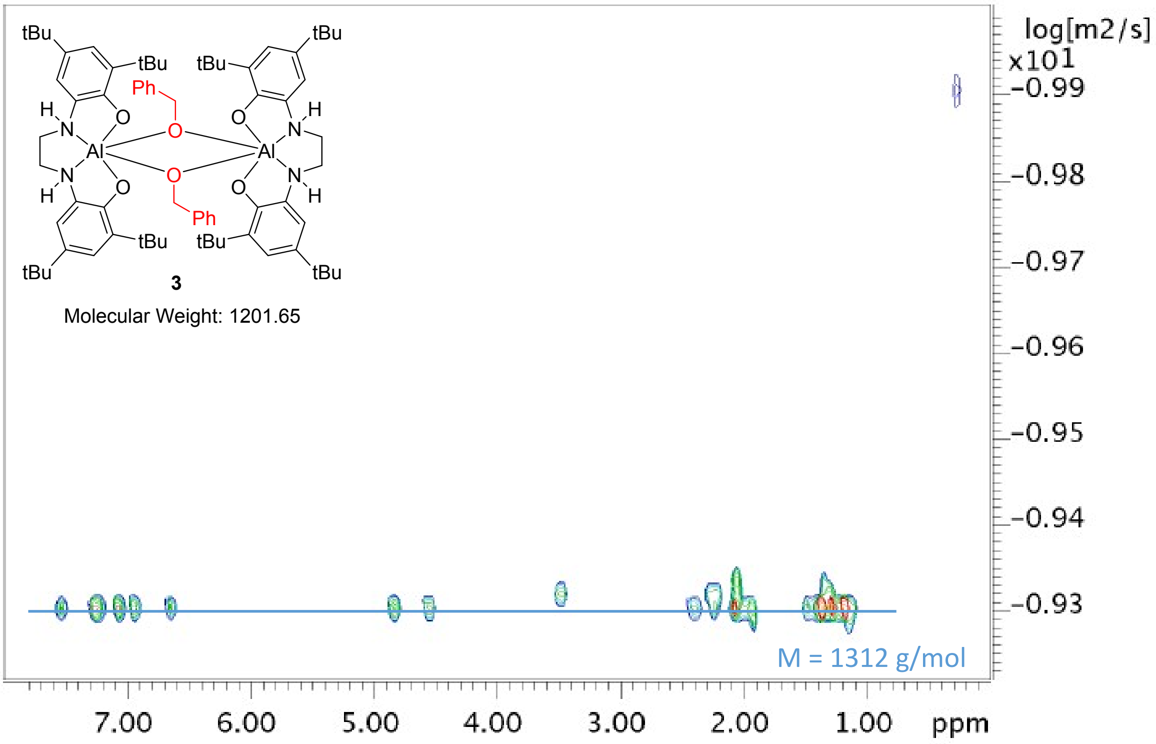


*Figure S6: DOSY NMR spectrum of **3** in C_6D_6 showing a dinuclear structure in solution using an in-house external calibration (data availbale here, DOI: 10.14469/hpc/4038).*

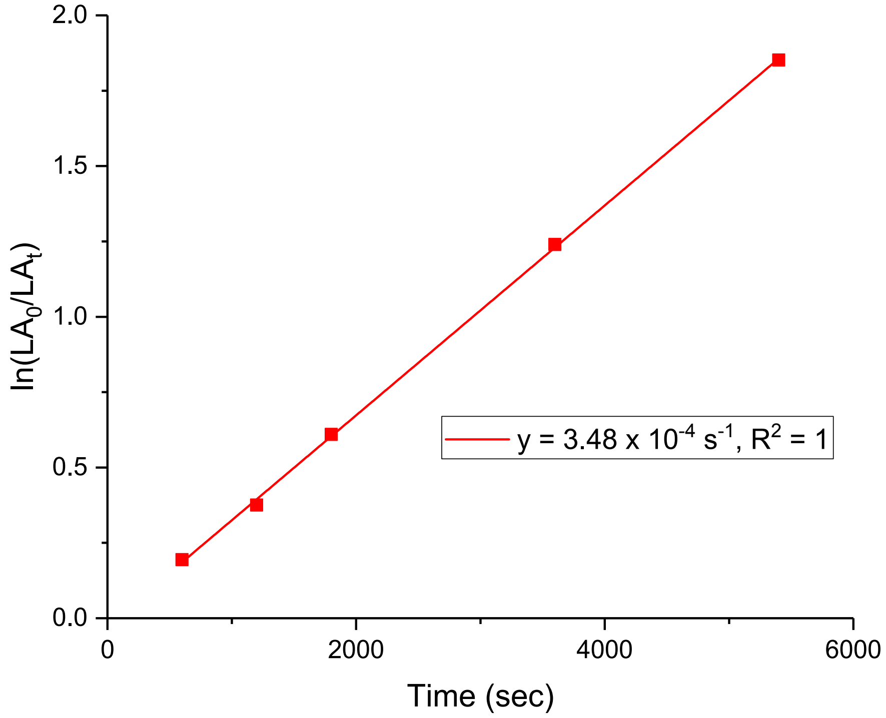


*Figure S7. First-order plot (linear fit) for rac-LA ROP initiated by **1** as per conditions in Table 1, entry 1.*

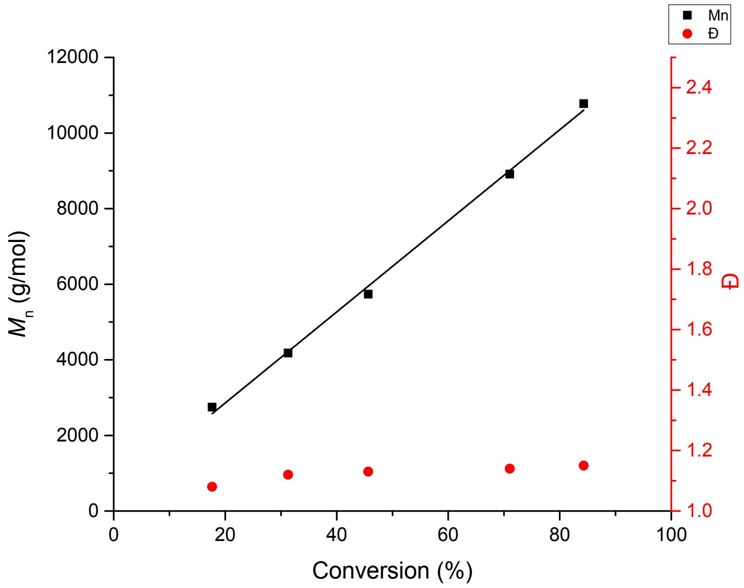


*Figure S8. Plot of M_n vs rac-lactide conversion for rac-La ROP initiated by **1**, as per conditions in Table 1, entry 1.*

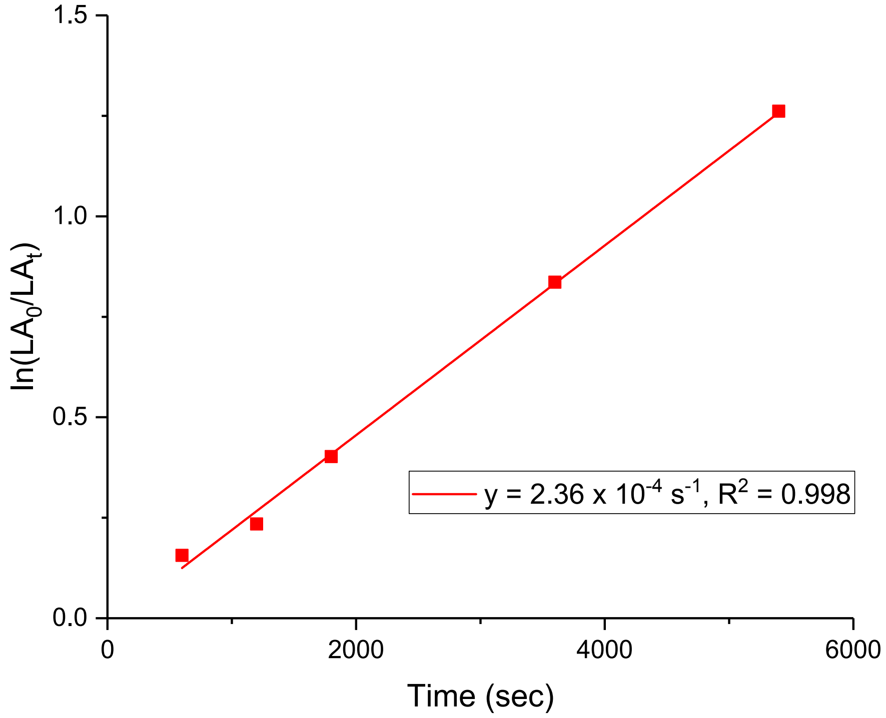


*Figure S9. First-order plot (linear fit) for rac-LA ROP initiated by **1** as per conditions in Table 1, entry 2.*

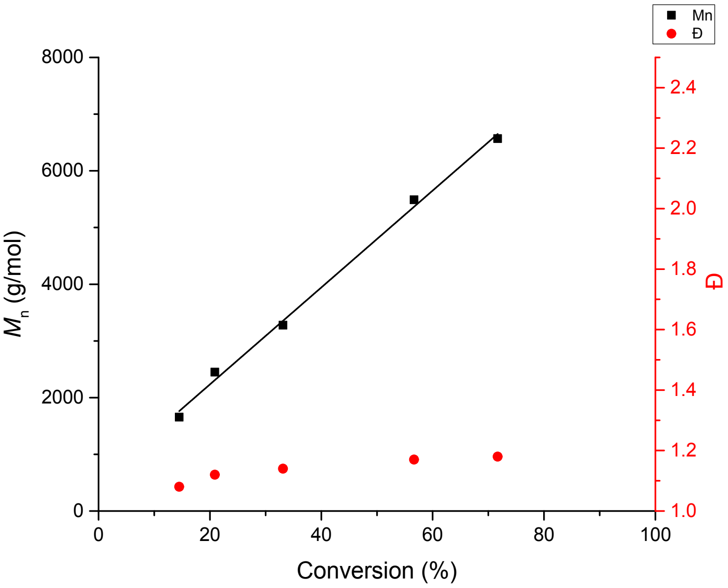


*Figure S10. Plot of M_n vs rac-lactide conversion for rac-La ROP initiated by **1**, as per conditions in Table 1, entry 2.*

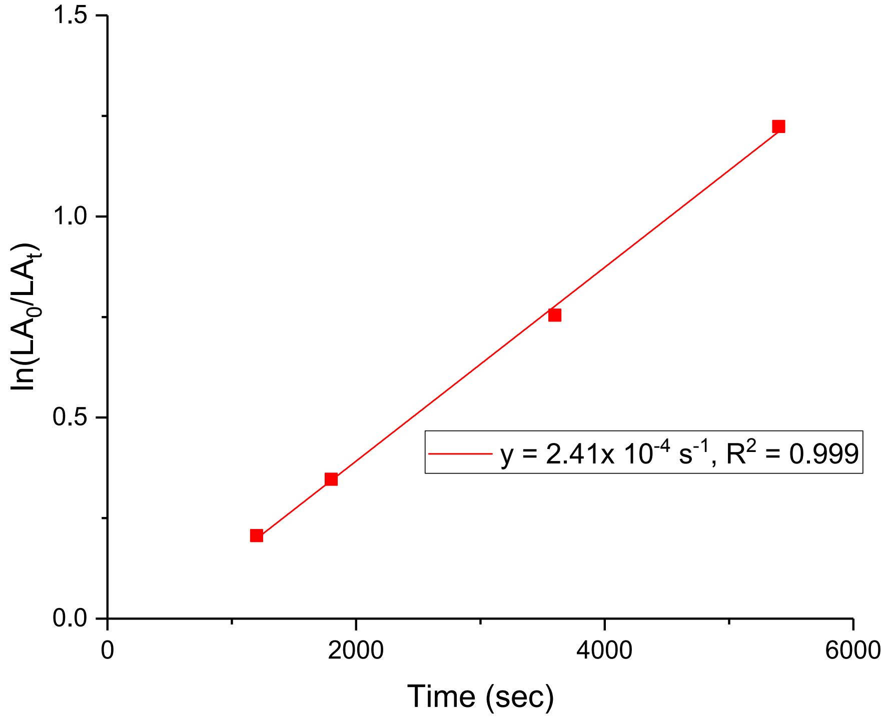


*Figure S11. First-order plot (linear fit) for rac-LA ROP initiated by **2** as per conditions in Table 1, entry 3.*

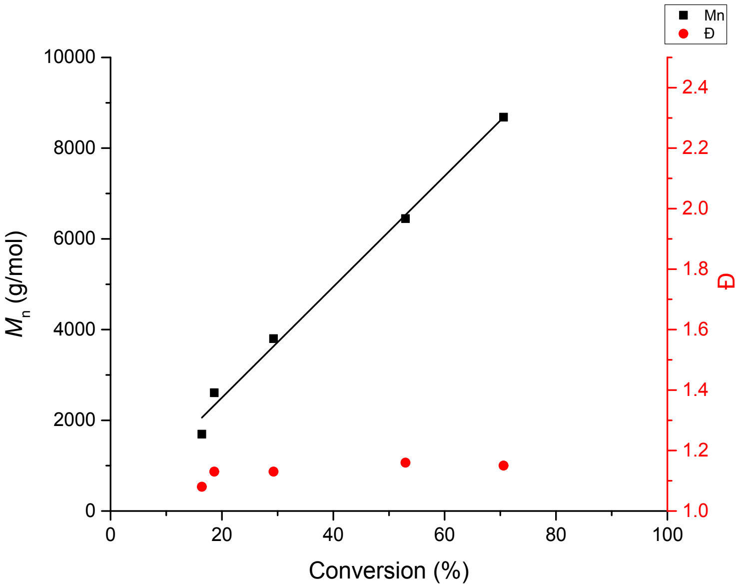


*Figure S12. Plot of M_n vs rac-lactide conversion for rac-La ROP initiated by **2**, as per conditions in Table 1, entry 3.*

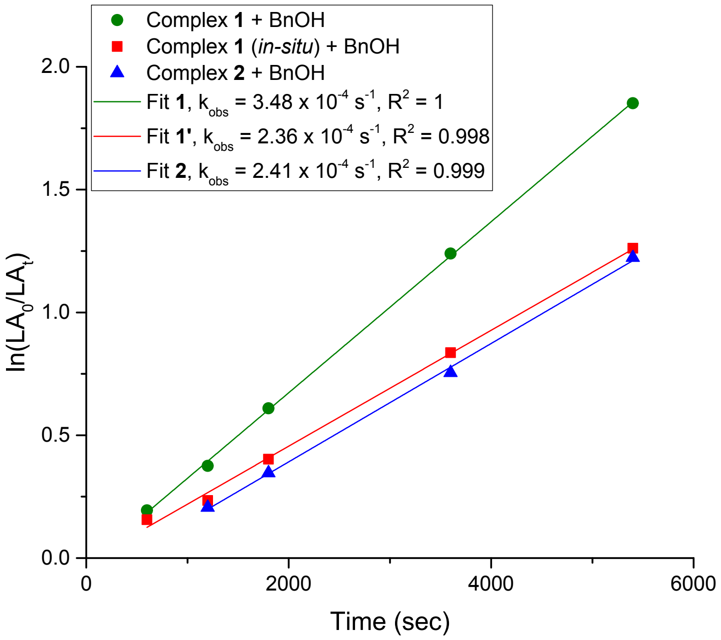


*Figure S13: Overlay of Figure S7 (green dot , Table 1, Entry 1), Figure S9 (red square Table 1, Entry 2) and Figure S10 (blue triangle, Table1, Entry 3) showing similar activities of complexes **1** and **2** in rac-LA ROP when reacted with BnOH.*

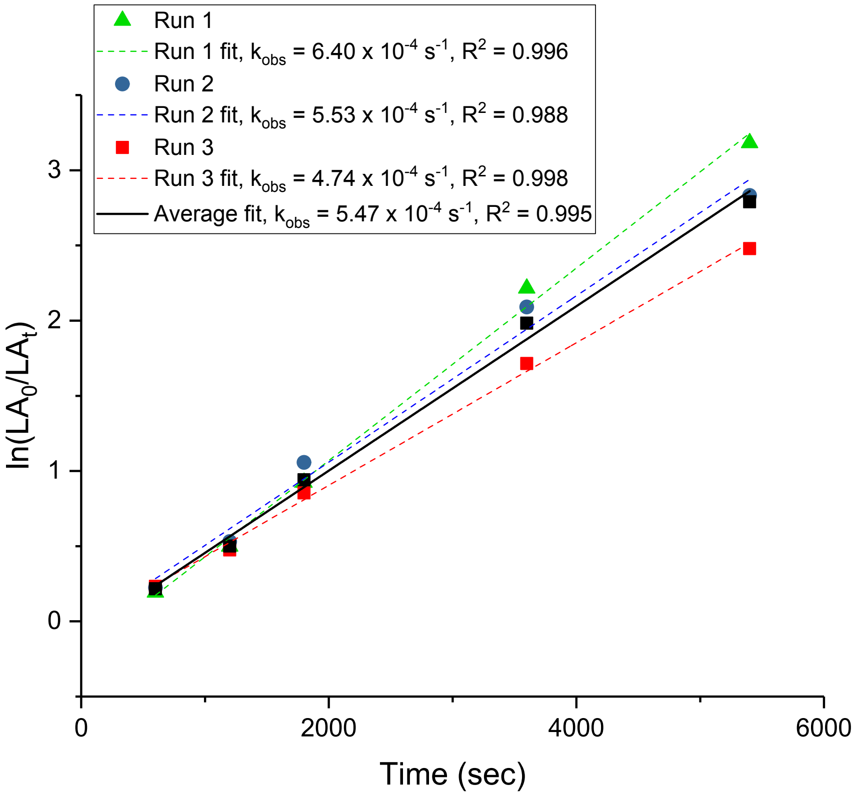


*Figure S14. Overlay of first-order plots (linear fit) for three repeated rac-lactide ROP (dash lines) initiated by **3** as per conditions in Table 1, entry 4 (black squares/plain line = average from the three values).*

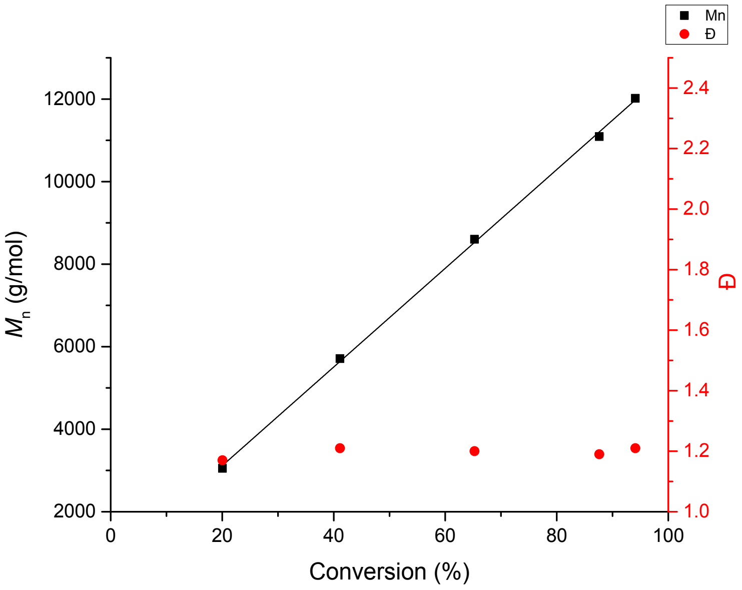
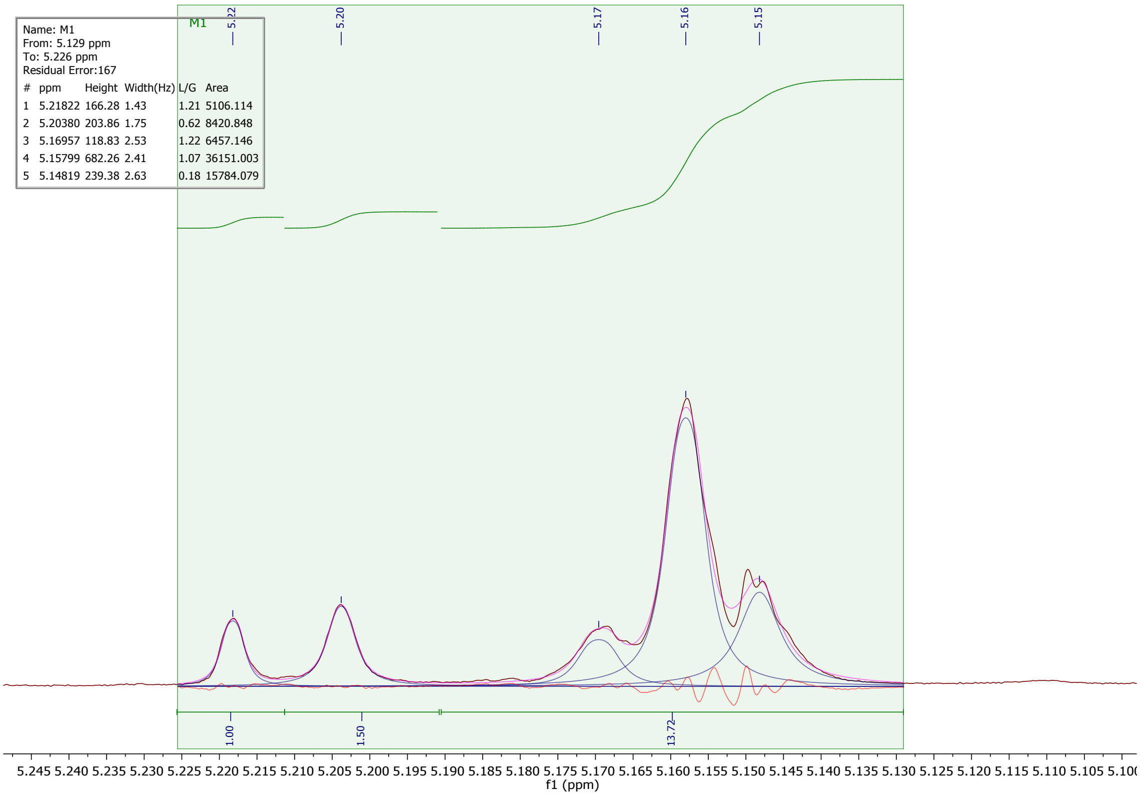


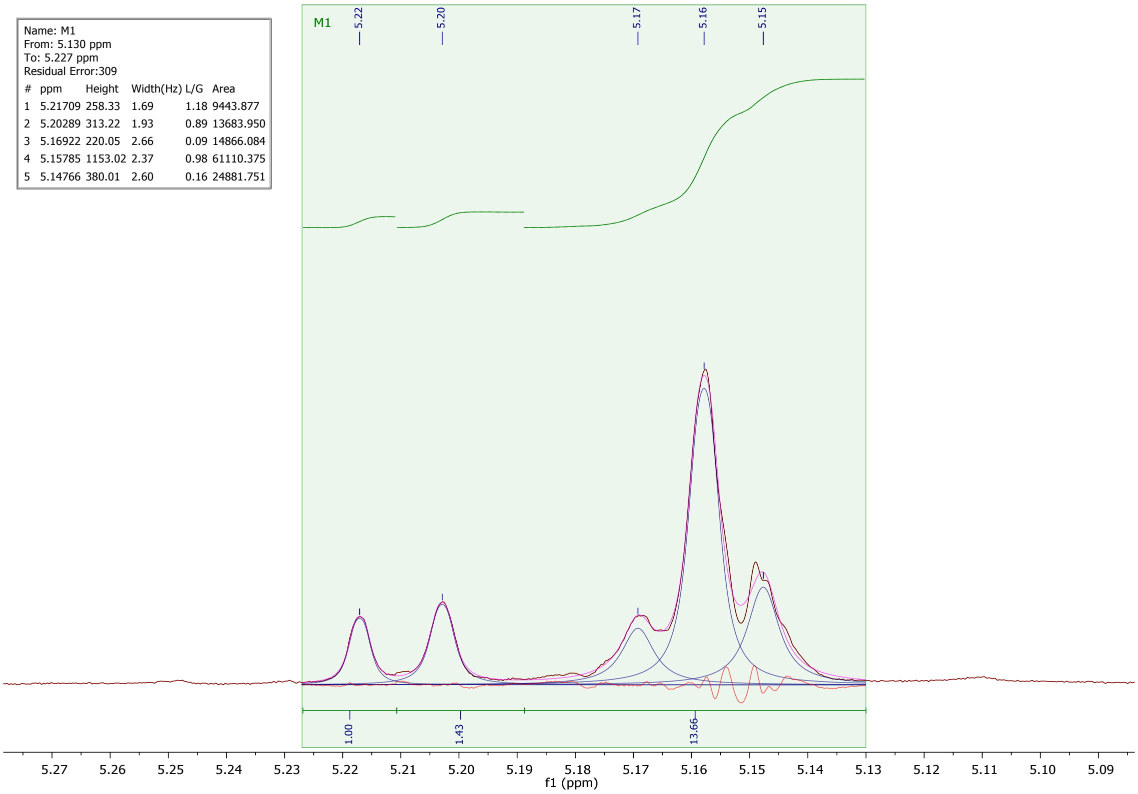
*Figure S15. Plot of M_n vs rac-lactide conversion for rac-La ROP initiated by **3**, as per conditions in Table 1, entry 4.*



Name: M1
From: 5.129 ppm
To: 5.226 ppm
Residual Error:167

#	ppm	Height	Width(Hz)	L/G	Area
1	5.21822	166.28	1.43	1.21	5106.114
2	5.20380	203.86	1.75	0.62	8420.848
3	5.16957	118.83	2.53	1.22	6457.146
4	5.15799	682.26	2.41	1.07	36151.003
5	5.14819	239.38	2.63	0.18	15784.079

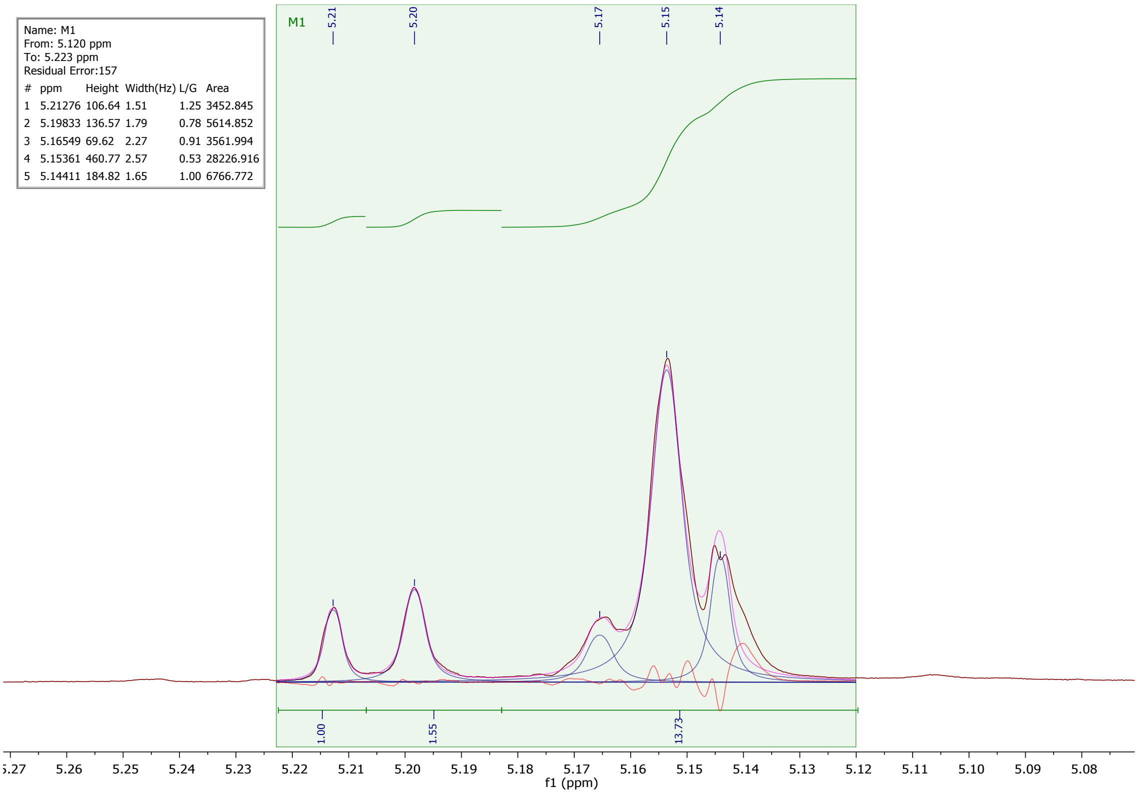
*Figure S16. Methine region of the homonuclear decoupled $^1H\{^1H\}$ NMR spectrum for rac-LA ROP initiated by **1** showing P_m = 0.62 (reaction conditions as per Table 1, entry 1), data available here, DOI: [10.14469/hpc/4040](10.14469/hpc/4040).*



Name: M1
From: 5.130 ppm
To: 5.227 ppm
Residual Error:309

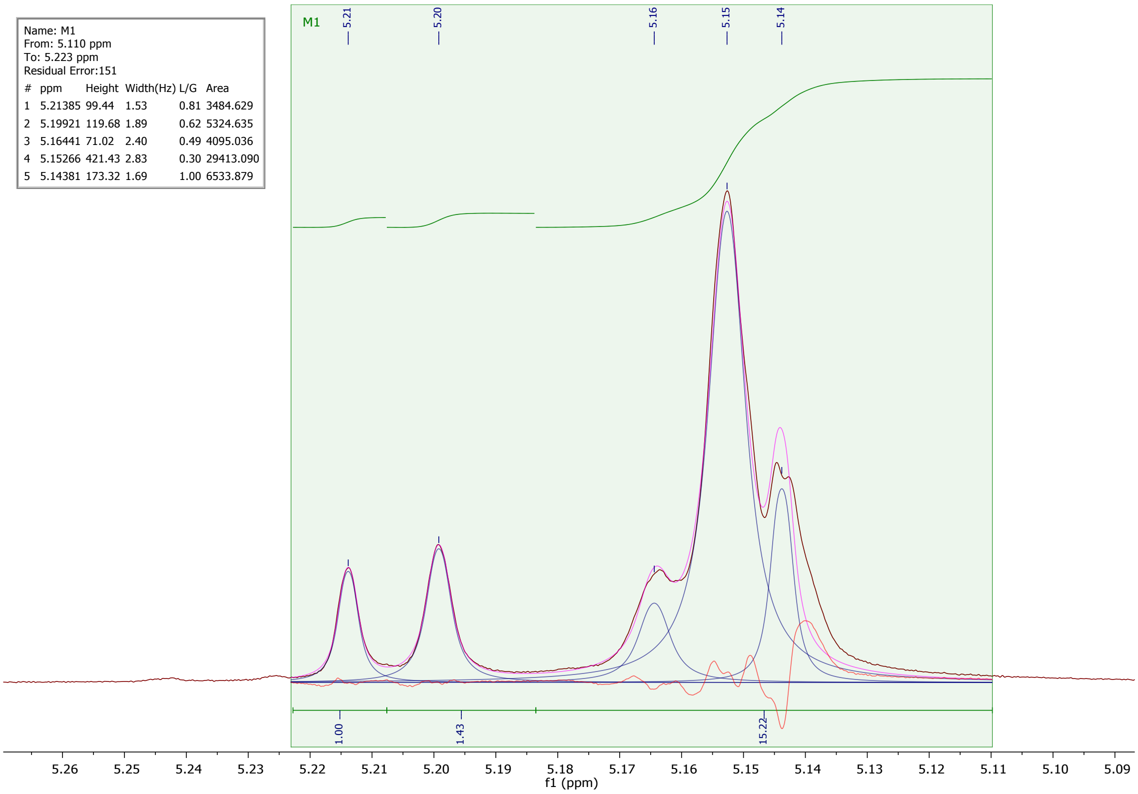
#	ppm	Height	Width(Hz)	L/G	Area
1	5.21709	258.33	1.69	1.18	9443.877
2	5.20289	313.22	1.93	0.89	13683.950
3	5.16922	220.05	2.66	0.09	14866.084
4	5.15785	1153.02	2.37	0.98	61110.375
5	5.14766	380.01	2.60	0.16	24881.751

*Figure S17. Methine region of the homonuclear decoupled $^1H\{^1H\}$ NMR spectrum for rac-LA ROP initiated by **1** showing P_m = 0.59 (reaction conditions as per Table 1, entry 2), data available here, DOI: [10.14469/hpc/4040](10.14469/hpc/4040).*



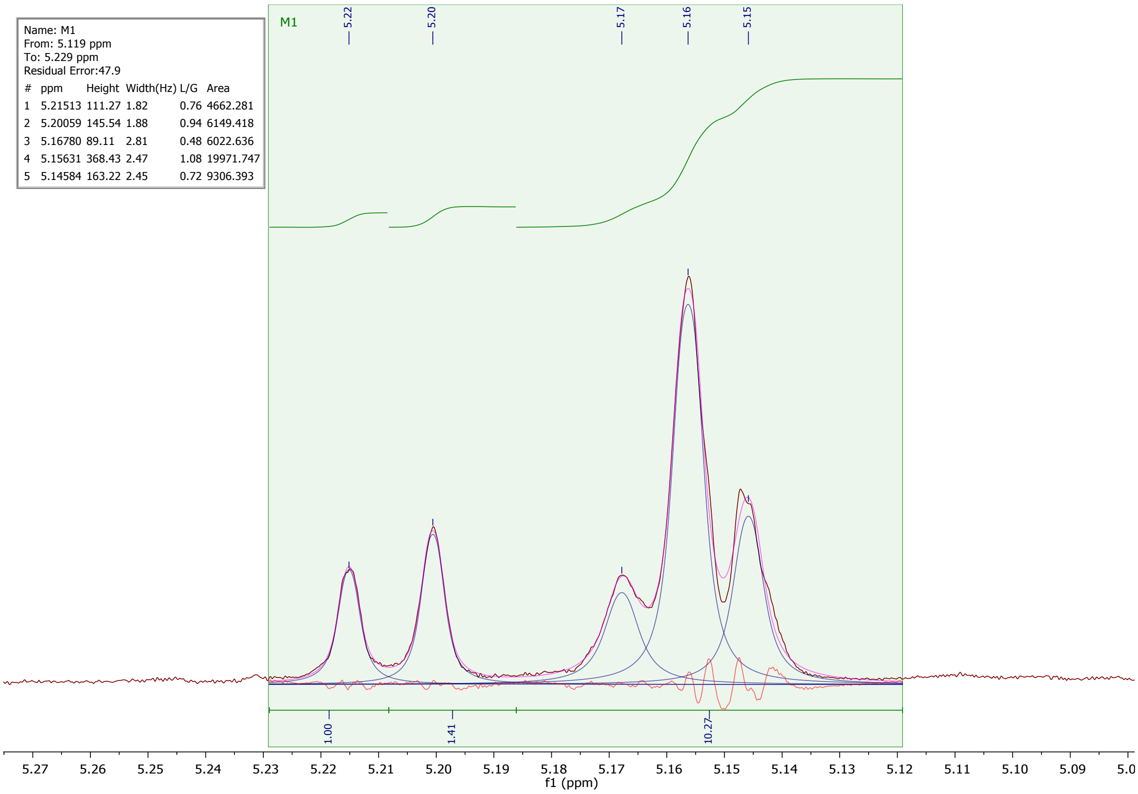
```
Name: M1
From: 5.120 ppm
To: 5.223 ppm
Residual Error:157
#  ppm      Height  Width(Hz) L/G   Area
1  5.21276  106.64  1.51      1.25  3452.845
2  5.19833  136.57  1.79      0.78  5614.852
3  5.16549  69.62   2.27      0.91  3561.994
4  5.15361  460.77  2.57      0.53  28226.916
5  5.14411  184.82  1.65      1.00  6766.772
```

*Figure S18. Methine region of the homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectrum for rac-LA ROP initiated by **2** showing P_m = 0.62 (reaction conditions as per Table 1, entry 3), data available here, DOI: [10.14469/hpc/4040](https://doi.org/10.14469/hpc/4040).*



```
Name: M1
From: 5.110 ppm
To: 5.223 ppm
Residual Error:151
#  ppm      Height  Width(Hz) L/G   Area
1  5.21385  99.44   1.53      0.81  3484.629
2  5.19921  119.68  1.89      0.62  5324.635
3  5.16441  71.02   2.40      0.49  4095.036
4  5.15266  421.43  2.83      0.30  29413.090
5  5.14381  173.32  1.69      1.00  6533.879
```

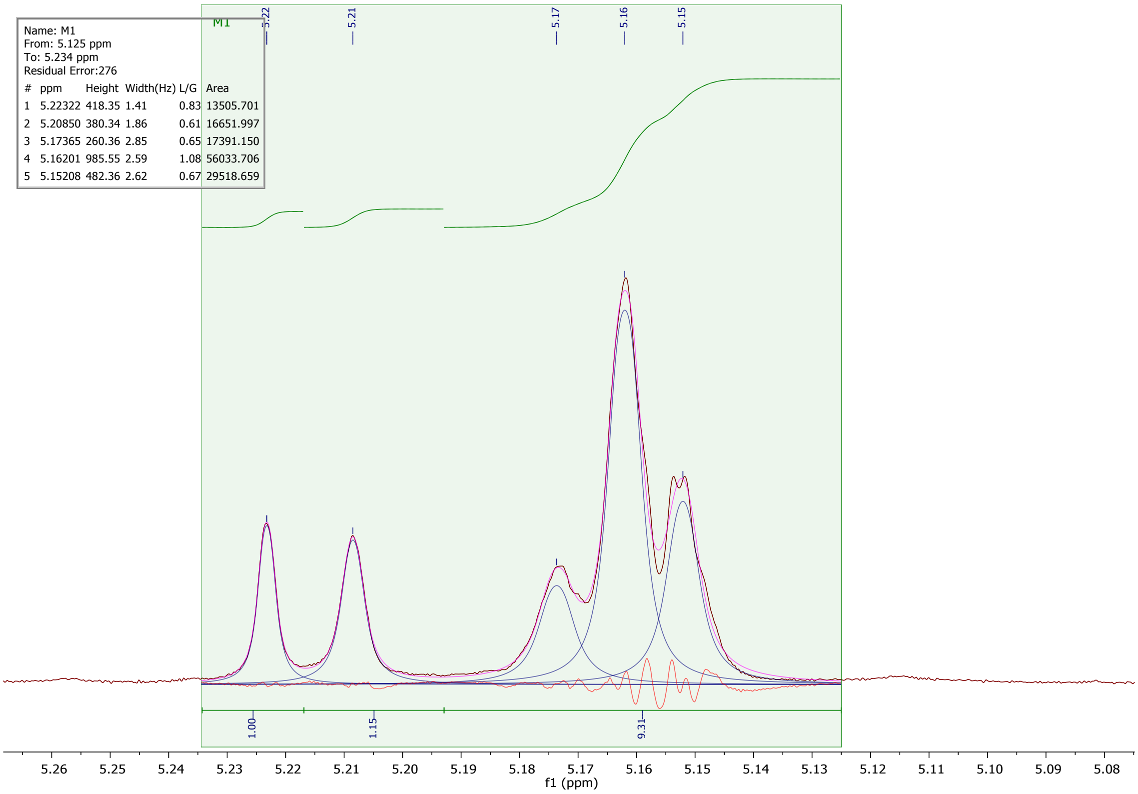
*Figure S19. Methine region of the homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectrum for rac-LA ROP initiated by **3** showing P_m = 0.60 (reaction conditions as per Table 1, entry 4), data available here, DOI: [10.14469/hpc/4040](https://doi.org/10.14469/hpc/4040).*



Name: M1
From: 5.119 ppm
To: 5.229 ppm
Residual Error:47.9

#	ppm	Height	Width(Hz)	L/G	Area
1	5.21513	111.27	1.82	0.76	4662.281
2	5.20059	145.54	1.88	0.94	6149.418
3	5.16780	89.11	2.81	0.48	6022.636
4	5.15631	368.43	2.47	1.08	19971.747
5	5.14584	163.22	2.45	0.72	9306.393

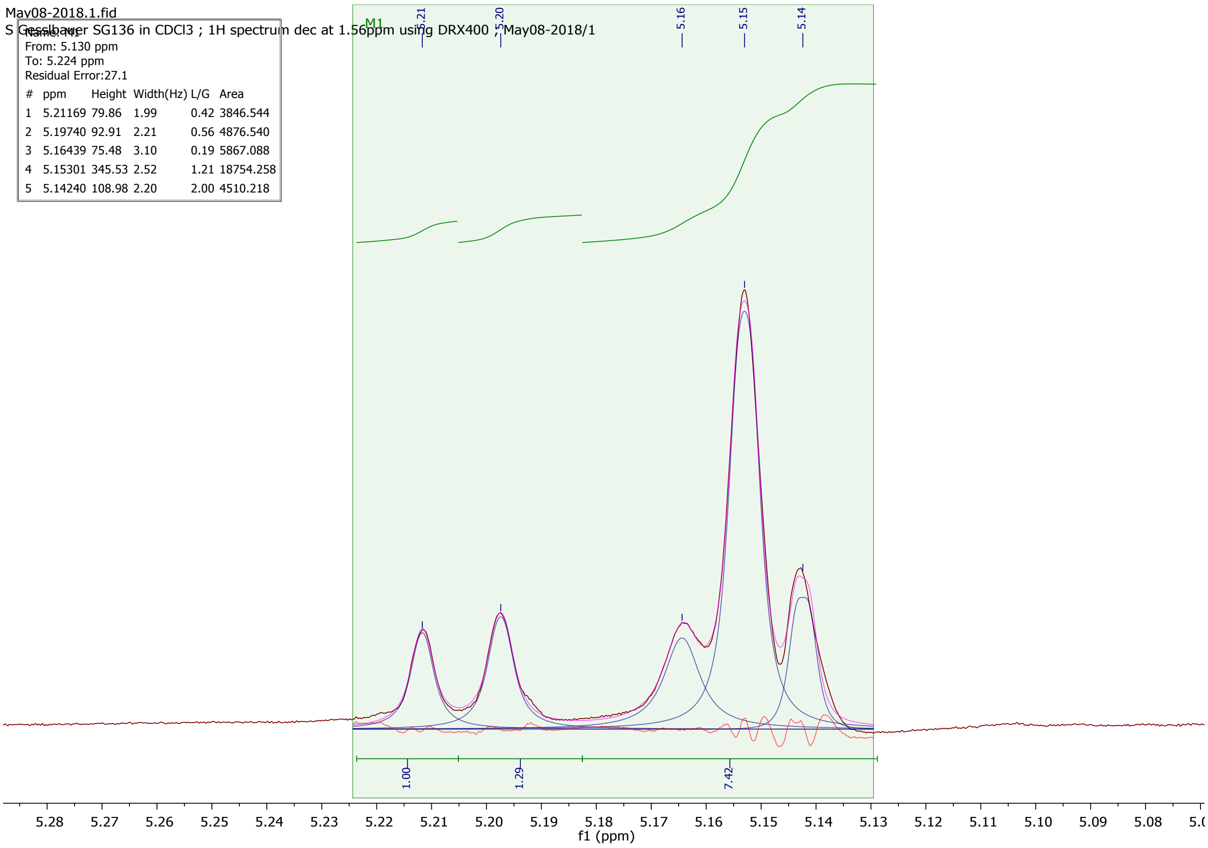
*Figure S20. Methine region of the homonuclear decoupled $^1H\{^1H\}$ NMR spectrum for rac-LA ROP initiated by **3** showing P_m = 0.57 (reaction conditions as per Table 1, entry 5), data available here, DOI: 10.14469/hpc/4040.*



Name: M1
From: 5.125 ppm
To: 5.234 ppm
Residual Error:276

#	ppm	Height	Width(Hz)	L/G	Area
1	5.22322	418.35	1.41	0.83	13505.701
2	5.20850	380.34	1.86	0.61	16651.997
3	5.17365	260.36	2.85	0.65	17391.150
4	5.16201	985.55	2.59	1.08	56033.706
5	5.15208	482.36	2.62	0.67	29518.659

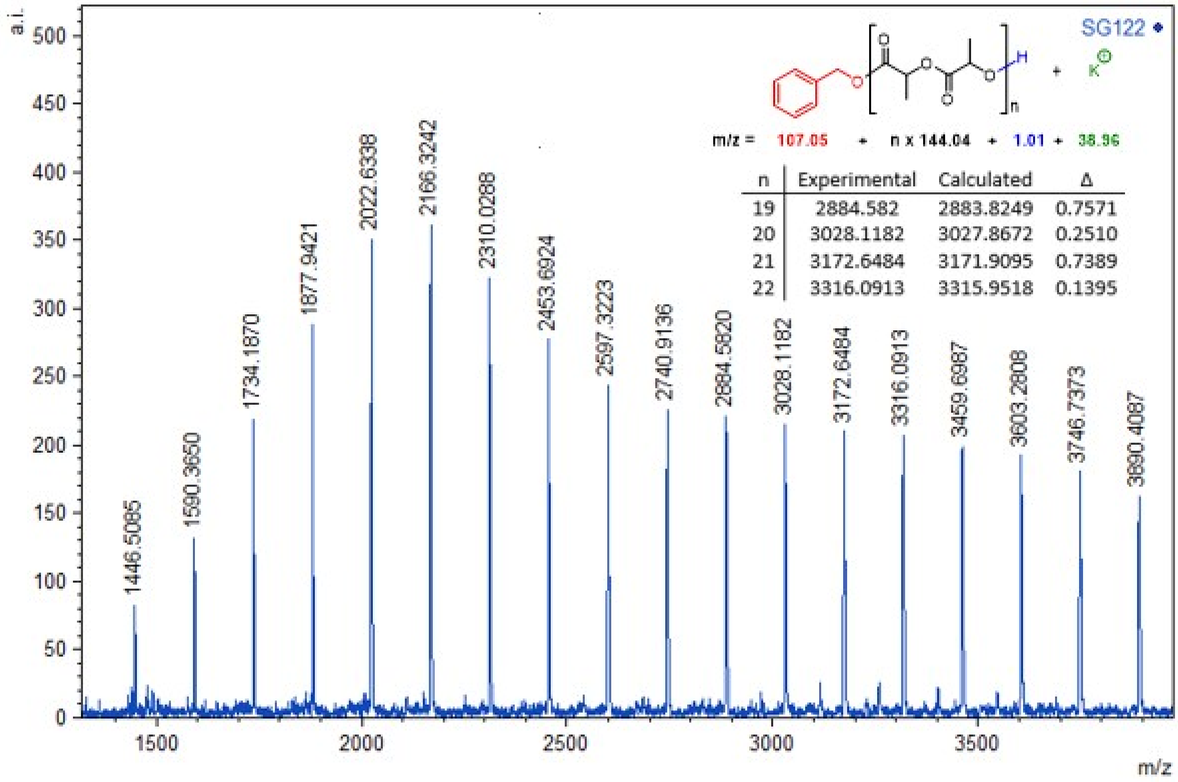
*Figure S21. Methine region of the homonuclear decoupled $^1H\{^1H\}$ NMR spectrum for rac-LA ROP initiated by **3** showing P_m = 0.55 (reaction conditions as per Table 1, entry 8), data available here, DOI: 10.14469/hpc/4040.*



Name: M1
From: 5.130 ppm
To: 5.224 ppm
Residual Error:27.1

#	ppm	Height	Width(Hz)	L/G	Area
1	5.21169	79.86	1.99	0.42	3846.544
2	5.19740	92.91	2.21	0.56	4876.540
3	5.16439	75.48	3.10	0.19	5867.088
4	5.15301	345.53	2.52	1.21	18754.258
5	5.14240	108.98	2.20	2.00	4510.218

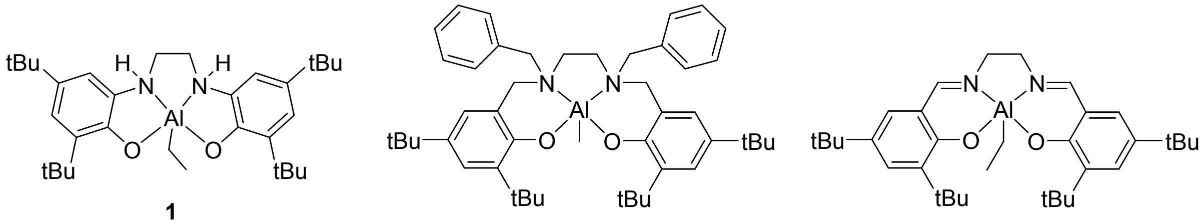
*Figure 22: Methine region of the homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectrum for rac-LA ROP initiated by **3** showing P_m = 0.56 (reaction conditions as per Table 1, entry 9), data available here, DOI: 10.14469/hpc/4040.*



m/z = 107.05 + n x 144.04 + 1.01 + 38.96

n	Experimental	Calculated	Δ
19	2884.582	2883.8249	0.7571
20	3028.1182	3027.8672	0.2510
21	3172.6484	3171.9095	0.7389
22	3316.0913	3315.9518	0.1395

*Figure S23. MALDI-ToF spectrum of PLA obtained using **3**, data available here, DOI: 10.14469/hpc/4039.*



1
(this work)

1-salan

1-salen

*Figure S24: Selected Al salan and Al salen complexes for comparison with **1** in rac-LA ROP as per Table 1, entry 10-11.*[3]

X-Ray crystallography data:

Crystal data for **2**: $C_{60}H_{90}Al_2N_4O_4$, M = 985.31, triclinic, P-1 (no. 2), a = 10.3044(5), b = 10.5110(4), c = 14.5467(9) Å, α = 80.997(4), β = 72.376(5), γ = 83.181(4)°, V = 1478.84(14) Å^3, Z = 1 [C_i symmetry], D_c = 1.106 g cm^{-3}, μ(Cu-Kα) = 0.798 mm^{-1}, T = 173 K, colourless tablets, Agilent Xcalibur PX Ultra A diffractometer; 5645 independent measured reflections (R_{int} = 0.0234), F^2 refinement,[4] R_1(obs) = 0.0416, wR_2(all) = 0.1142, 4579 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(67.7°) = 98.4%], 332 parameters. CCDC 1836017.

The unique N–H hydrogen atom on N7 in the structure of **2** was located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å. The structure sits across a centre of symmetry at the middle of the Al_2N_2 ring.

Crystal data for **2·benzene**: $C_{60}H_{90}Al_2N_4O_4 \cdot C_6H_6$, M = 1063.42, triclinic, P-1 (no. 2), a = 9.7297(4), b = 11.1101(4), c = 30.5073(14) Å, α = 90.706(3), β = 90.073(4), γ = 95.931(3)°, V = 3279.9(2) Å^3, Z = 2, D_c = 1.077 g cm^{-3}, μ(Mo-Kα) = 0.091 mm^{-1}, T = 173 K, colourless plates, Agilent Xcalibur 3 E diffractometer; 12959 independent measured reflections (R_{int} = 0.0306), F^2 refinement,[4] R_1(obs) = 0.0668, wR_2(all) = 0.1847, 8943 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.7%], 717 parameters. CCDC 1836018.

The N–H hydrogen atoms on N7 and N47 in the structure of **2·benzene** were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å.

Crystal data for **3**: $C_{74}H_{106}Al_2N_4O_6 \cdot 4(C_6H_6)$, M = 1514.01, monoclinic, $P2_1/c$ (no. 14), a = 13.4292(4), b = 15.4213(4), c = 22.2668(5) Å, β = 93.350(2)°, V = 4603.5(2) Å^3, Z = 2 [C_i symmetry], D_c = 1.092 g cm^{-3}, μ(Mo-Kα) = 0.084 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3 E diffractometer; 9164 independent measured reflections (R_{int} = 0.0225), F^2 refinement,[4] R_1(obs) = 0.0480, wR_2(all) = 0.1114, 6643 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.7%], 517 parameters. CCDC 1836019.

The unique N–H hydrogen atoms on N7 and N10 in the structure of **3** were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å. The structure sits across a centre of symmetry at the middle of the Al_2O_2 ring. The C61-based included benzene solvent molecule was found to be disordered. Two orientations were identified of *ca*. 73 and 27% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

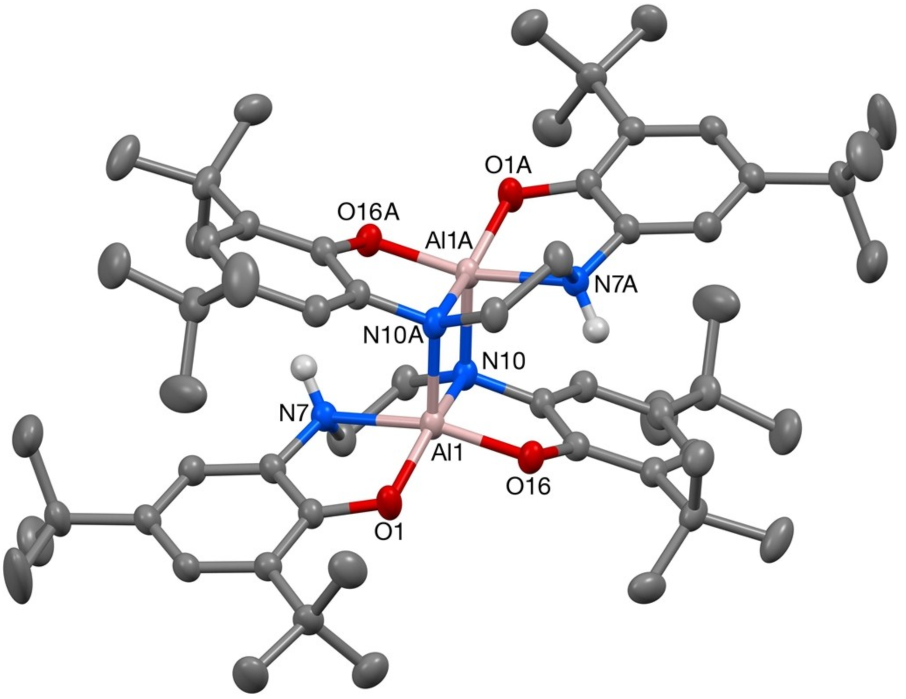


Figure S25: The crystal structure of the C_i-symmetric complex ***2****..*

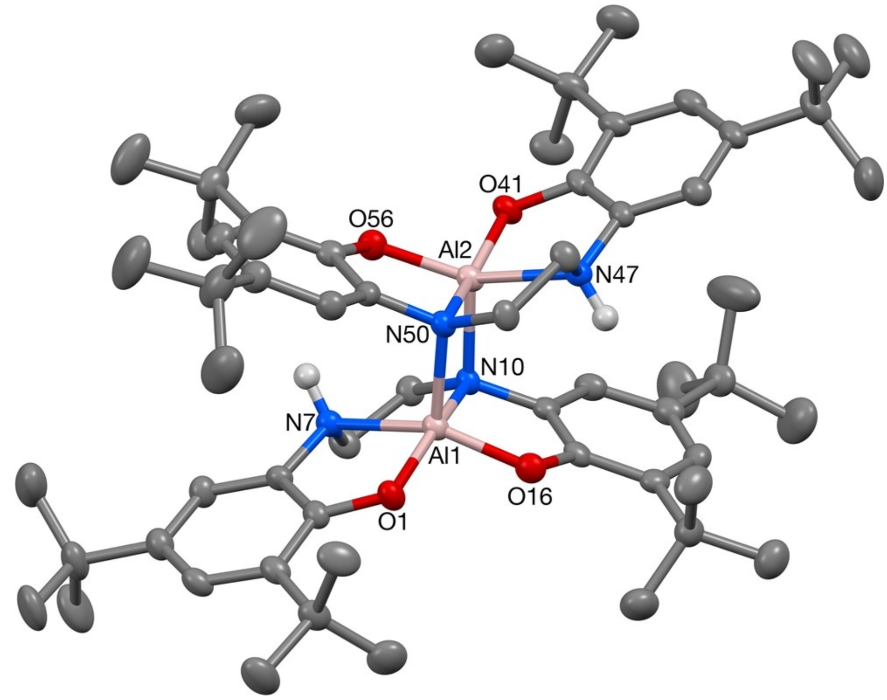


Figure S26: The crystal structure of ***2·benzene****..*

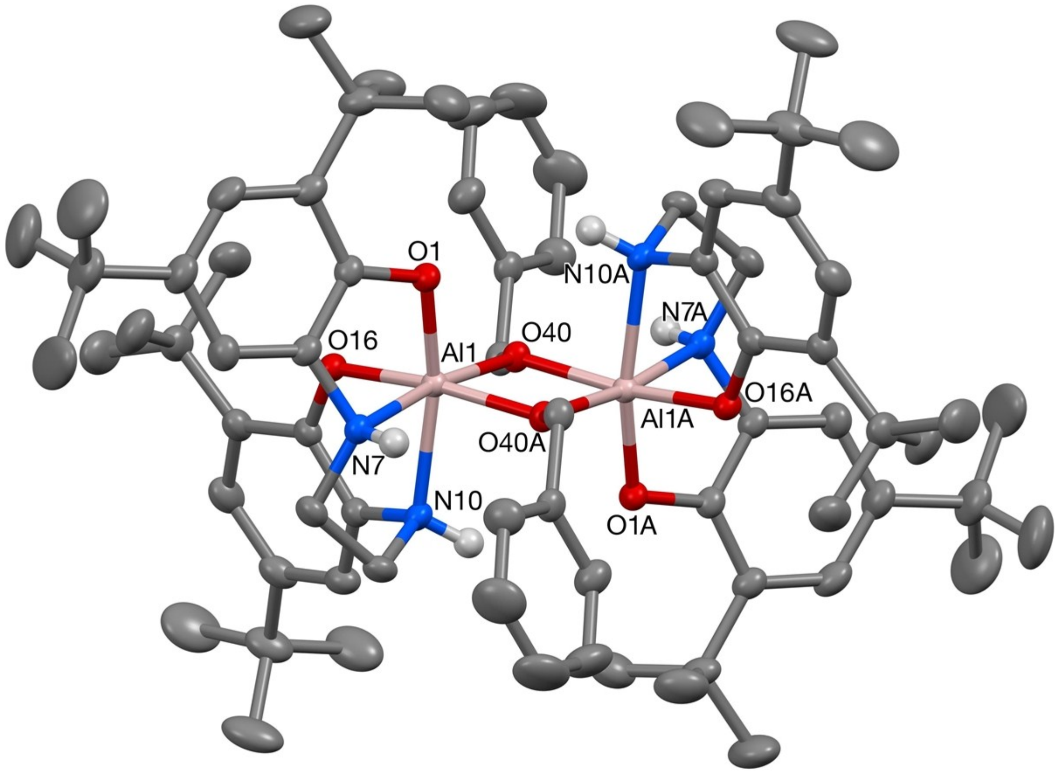


*Figure S27: The crystal structure of the C_i-symmetric complex **3**.*

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