Supporting Information

Salt additives as activity boosters: a simple strategy to access heterometallic cooperativity in lactide polymerisation

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General experimental details

All manipulations requiring inert conditions were performed under an argon atmosphere using standard Schlenk techniques or in a glove box. $Ca(HMDS)_2(THF)_2$,[1] complexes **1**-**2**,[2] and **8**-**9**[3] were synthesised using previously reported procedures and were based on a commercially available (*S,S*)-(+)-2,6-bis[2-(hydroxydiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol (Trost ProPhenol) ligand, developed by Trost *et al.*[4] All reagents and solvents were obtained from Sigma-Aldrich, Fischer Scientific, Honeywell or Acros Organics and were used without further purification unless described otherwise. Dry THF, toluene and hexane were collected from a solvent purification system (Innovative Technologies), dried over activated 4 Å molecular sieves and stored under argon. THF-d_8 and toluene-d_8 NMR solvents for NMR were degassed by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves under an argon atmosphere. *Rac*-lactide (*rac*-LA) was purified by double recrystallisation from toluene and sublimation. Benzyl alcohol (BnOH) was dried over CaH_2 and distilled under reduced pressure prior to use. ^1H, ^{13}C and 2D NMR (COSY, HSQC and DOSY) spectra were recorded on Bruker AVA400, PRO500, AVA500 and AVA600 spectrometers at 298 K at 400 MHz, 500 MHz and 600 MHz and referenced to the residual solvent peaks (^1H: δ 3.58 for THF-d_8 and δ 2.08 for toluene-d_8, ^{13}C: δ 67.21 for THF-d_8 and δ 137.48 for toluene-d_8). ^1H and ^{13}C NMR spectra were assigned on the basis of 2D COSY and HSQC data. The reported DOSY masses (to the nearest whole number) and aggregation states were determined by comparison to a calibration plot made with a range of standards (hexamethyldisilazane (HMDSH), $Zn(HMDS)_2$, β-diketiminate ligand (BDIH) and (BDI)Zn(HMDS)) with molecular weights varying from 161.4 to 643.4 g mol^{-1} in THF-d_8.[5] APPI-MS analysis was performed using a Bruker Daltonics 12T SolariX Fourier Transform Ion Cyclotron Resonance Mass Spectrometer using atmospheric pressure photoionisation (APPI). SEC analyses of the filtered polymer samples were carried out in GPC grade THF at a flow rate of 1 mL min^{-1} at 35 °C on a 1260 Infinity II GPC/SEC single detection system with mixed bed C PLgel columns (300 x 7.5 mm). MALDI-ToF MS analyses were performed using a Bruker Daltonics UltrafleXtreme™ MALDI-ToF/ToF MS instrument. The sample to be analysed, dithranol matrix and KI (cationising agent) were dissolved in THF at 10 mg mL^{-1} and the solutions were mixed in a 2:2:1 volume ratio, respectively. A droplet (2 µL) of the resultant mixture was spotted on to the sample plate and submitted for MALDI-ToF MS analysis.

Synthesis and characterisation of complex 3

Complex **2** (250 mg, 0.31 mmol) was weighed into a Schlenk flask and dissolved in dry THF (6 mL) in the glove box. $Mg(HMDS)_2$ (105.2 mg, 0.31 mmol) was slowly added into the solution of complex **2**. The resulting mixture was stirred for 1 h at ambient temperature under an argon atmosphere in the glove box. THF was subsequently removed *in vacuo* resulting in a pale yellow powder (137.2 mg, 25% yield out of maximum of 50% due to the dimeric nature of **3**).

Solution-state characterisation of **3** in THF-d_8 was challenging due to the broad ^{1}H NMR resonances, attributed to dynamic equilibria in solution (Fig. S2). However, the NMR spectra of **3** were better resolved in toluene-d_8 (Fig. S1), with DOSY analysis indicating that **3** is dimeric in both THF-d_8 (Fig. S3) and toluene-d_8 (Fig. S4).

^{1}H NMR (500 MHz, toluene-d_8, refer to Fig. S1 for assignment) δ 7.71 (dd, 4 H), 7.43 (d, 4 H), 7.30 (t, 8 H), 7.21-7.25 (m, 8 H), 6.93-6.94 (m, 7 H), 6.73-6.76 (m, 4 H), 6.67-6.70 (m, 5 H), 6.64 (s, 2 H), 6.52 (s, 2 H), 4.47 (d, 2 H), 3.97 (d, 2 H), 3.78-3.81 (m, 2 H), 3.58 (d, 2 H), 2.76-2.84 (m, 4 H), 2.51-2.56 (m, 2 H), 2.39 (s, 3 H), 2.27 (s, 3 H), 2.11-2.21 (m, 6 H), 2.00-2.04 (m, 2 H), 1.97 (d, 2 H), 1.48-1.59 (m, 6 H), 1.26-1.34 (m, 4 H), 0.49-0.55 (m, 2 H).

^{13}C NMR (126 MHz, toluene-d_8, see Fig. S1 for labelling) δ 160.59 (C11), 160.16 (C11), 157.51 (C12), 155.60 (C12), 154.66 (C12), 153.82 (C12), 131.49 (C2), 129.50 (C8), 128.79 (C2), 128.80 (C8 + C9), 127.99 (C8 + C9), 127.51 (C8 + C9), 127.33 (C8 + C9), 127.29 (C8 + C9), 127.09 (C8 + C9), 126.81 (C10), 125.28 (C10), 125.25 (C10), 124.93 (C10), 85.05 (C4), 82.88 (C13), 81.62 (C13), 80.42 (C4), 65.30 (C3), 63.36 (C3), 56.11 (C7), 50.80 (C7), 29.89 (C6), 26.99 (C5), 24.06 (C6), 21.29 (C1), 21.17 (C5), 20.61 (C1).

Elemental analysis: calculated for **$[LKMg(HMDSH)]_2$**: C, 68.38; H, 7.26; N, 4.88%. Found: C, 68.71; H, 6.71; N, 4.24%; *m/z* (APPI-MS): 1397.56 $[(LKMg)_2 + H]^+$ (calc: 1397.57)

Synthesis and characterisation of complex 4

Complex **1** (245.4 mg, 0.31 mmol) was weighed into a Schlenk flask and dissolved in dry THF (6 mL) in the glove box. $Ca(HMDS)_2(THF)_2$ (153.8 mg, 0.31 mmol) was slowly added into the solution of complex **1**. The resulting mixture was stirred for 1 h at ambient temperature under an argon atmosphere in the glove box. THF was subsequently removed *in vacuo* resulting in a pale yellow powder (138.3 mg, 24% yield out of maximum of 50% due to the dimeric nature of **4**).

^{1}H NMR (500 MHz, THF-d_8, refer to Fig. S6 for assignment) δ 7.51 (d, 8 H), 7.47 (d, 8 H), 6.84 (s, 4 H), 6.77-6.81 (m, 16 H), 6.68 (dt, 8 H), 4.12 (d, 4 H), 3.80 (t, 4 H), 3.04-3.09 (m, 4 H), 2.74 (d, 4 H), 2.41 (dt, 4 H), 2.18 (s, 6 H), 1.64-1.67 (m, 4 H), 1.52-1.59 (m, 6 H), 1.35-1.41 (m, 6 H).

^{13}C NMR (126 MHz, THF-d_8, see Fig. S6 for labelling) δ 163.06 (C11), 157.95 (C12), 157.54 (C12), 132.46 (C2), 128.02 (C9), 127.84 (C8), 126.65 (C9), 126.62 (C8), 125.35 (C10), 124.08 (C10), 81.25 (C13), 78.01 (C4), 61.46 (C3), 54.87 (C7), 30.08 (C5), 22.15 (C6), 20.60 (C1).

Elemental analysis: calculated for **[LNaCa(THF)(HMDSH)]$_2$**: C, 68.27; H, 7.57; N, 4.51%. Found: C, 68.20; H, 7.27; N, 4.08%; *m/z* (APPI-MS): 1397.57 [(LNaCa)$_2$ + H]$^+$ (calc: 1397.57)

Synthesis and characterisation of complex 5

Complex **2** (250 mg, 0.31 mmol) was weighed into a Schlenk flask and dissolved in dry THF (6 mL) in the glove box. Ca(HMDS)$_2$(THF)$_2$ (153.8 mg, 0.31 mmol) was slowly added into the solution of complex **2**. The resulting mixture was stirred for 1 h at ambient temperature under an argon atmosphere in the glove box. THF was subsequently removed *in vacuo* resulting in a pale yellow powder (139 mg, 28% yield out of maximum of 50% due to the dimeric nature of **5**).

^{1}H NMR (500 MHz, THF-d_8, refer to Fig. S9 for assignment) δ 7.61 (d, 8 H), 7.56 (d, 8 H), 6.88 (s, 4 H), 6.87 (t, 8 H), 6.78 (t, 8 H), 6.72 (t, 4 H), 6.65 (t, 4 H), 4.26 (d, 4 H), 3.87 (t, 4 H), 2.94 (m, 4 H), 2.80 (d, 4 H), 2.38 (q, 4 H), 2.17 (s, 6 H), 1.81-1.88 (m, 8 H), 1.38-1.44 (m, 4 H).

^{13}C NMR (126 MHz, THF-d_8, for labelling see Fig. S9) δ 164.12 (C11), 158.24 (C12), 157.70 (C12), 132.92 (C2), 128.20 (C8), 127.63 (C9), 127.02 (C8), 126.63 (C9), 125.57 (C10), 124.15 (C10), 81.62 (C13), 78.94 (C4), 61.05 (C3), 54.66 (C7), 29.66 (C5), 21.94 (C6), 20.42 (C1).

Elemental analysis: calculated for **[LKCa(HMDSH)]$_2$**: C, 67.15; H, 7.13; N, 4.46%. Found: C, 66.44; H, 6.76; N, 4.42%; *m/z* (APPI-MS): 1429.52 [(LKCa)$_2$ + H]$^+$ (calc: 1429.51)

Synthesis and characterisation of Mg(OBn)$_2$

BnOH (20.6 µL, 0.20 mmol) was dissolved in dry THF (2.5 mL) in a Schlenk flask. Mg(HMDS)$_2$ (34.2 mg, 0.10 mmol) was slowly added into the BnOH solution. The resulting mixture was stirred for 16 h at ambient temperature under an argon atmosphere in the glove box with the Schlenk tap open to allow H_2 gas evolution. THF was subsequently removed *in vacuo* resulting in an off-white sticky solid, which was used directly in preparation of a stock solution for polymerisation studies.

^{1}H NMR (500 MHz, THF-d_8) δ 6.99 (br. m, 10 H), 4.35 (br. m, 4 H). ^{13}C NMR (126 MHz, THF-d_8) δ 146.05, 128.40, 126.74, 126.47, 65.55.

Synthesis and characterisation of Ca(OBn)$_2$

BnOH (20.6 µL, 0.20 mmol) was dissolved in dry THF (2.5 mL) in a Schlenk flask. Ca(HMDS)$_2$(THF)$_2$ (50 mg, 0.10 mmol) was slowly added into the BnOH solution. The resulting mixture was stirred for 16 h at ambient temperature under an argon atmosphere in the glove box with the Schlenk tap open to allow H_2 gas evolution. THF was subsequently removed *in vacuo* resulting in an off-white sticky solid, which was used directly in preparation of a stock solution for polymerisation studies.

^{1}H NMR (500 MHz, THF-d_8) δ 7.35 (br. d, 4 H), 7.14 (br. t, 4 H), 7.04 (br. t, 2 H), 4.92 (br. d, 2 H), 4.85 (br. d, 2 H). ^{13}C NMR (126 MHz, THF-d_8) δ 128.32, 126.91, 126.41. The quaternary *ipso*-C and Ca-OCH_2Ph were not observed by ^{13}C NMR spectroscopy (as was the case with previously reported complex **9**, **[LCa$_2$OBn]**).[3]

Synthesis and characterisation of Zn(OBn)$_2$

BnOH (82.4 µL, 0.79 mmol) was dissolved in dry THF (3 mL) in a Schlenk flask. $ZnEt_2$ (48.9 mg, 0.40 mmol) was slowly added into the BnOH solution. The resulting mixture was stirred for 16 h at ambient temperature under an argon atmosphere in the glove box with the Schlenk tap open to allow ethane gas evolution. THF was subsequently removed *in vacuo* resulting in a white powder, which was used directly in polymerisation studies; the characterisation was hindered by low solubility of **Zn(OBn)$_2$** in common NMR solvents.

General experimental procedure for the ring-opening polymerisation of *rac*-LA with complexes 3-5

In the glove box, in two separate air-tight vials with magnetic stirrer bars, *rac*-LA (100 eq., 100 mg, 0.70 mmol) was dissolved in dry THF (0.5 mL), and complex **3**, **4** or **5** (7 µmol) and BnOH (0.72 µL, 7 µmol) were dissolved in dry THF (0.2 mL). To ensure *rac*-LA dissolution, both solutions were stirred for 1 min at ambient temperature using DrySyn heating blocks before the catalyst and BnOH solution was added to the LA solution. The reaction was subsequently stirred for the required time. Upon completion, the reaction was quenched in excess hexane, so that the polymer precipitated from solution which terminates the reaction. The quenched reaction mixture was immediately capped and shaken to ensure that all of the polymer precipitated. The volatiles were subsequently removed under compressed air and an aliquot was dissolved in $CDCl_3$ for NMR spectroscopic analysis. Reactions were performed in duplicate to ensure data reproducibility.

General experimental procedure for the ring-opening polymerisation of *rac*-LA with complexes 1-2 and M(OBn)$_2$ (where M = Mg, Ca or Zn)

In the glove box, in two separate air-tight vials with magnetic stirrer bars, *rac*-LA (100 eq., 100 mg, 0.70 mmol) was dissolved in dry THF (0.5 mL), and complex **1-2** (7 µmol) and **M(OBn)$_2$** (7 µmol, M = Mg, Ca or Zn) were dissolved in dry THF (0.2 mL). To ensure *rac*-LA dissolution, both solutions were stirred for 1 min at ambient temperature using DrySyn heating blocks before the catalyst solution was added to the LA solution. The reaction was subsequently stirred for the required time. Upon completion, the reaction was quenched in excess hexane, so that the polymer precipitated from solution which terminates the reaction. The quenched reaction mixture was immediately capped and shaken to ensure that all of the polymer precipitated. The volatiles were subsequently removed under compressed air and an aliquot was dissolved in $CDCl_3$ for NMR spectroscopic analysis. Reactions were performed in duplicate to ensure data reproducibility.

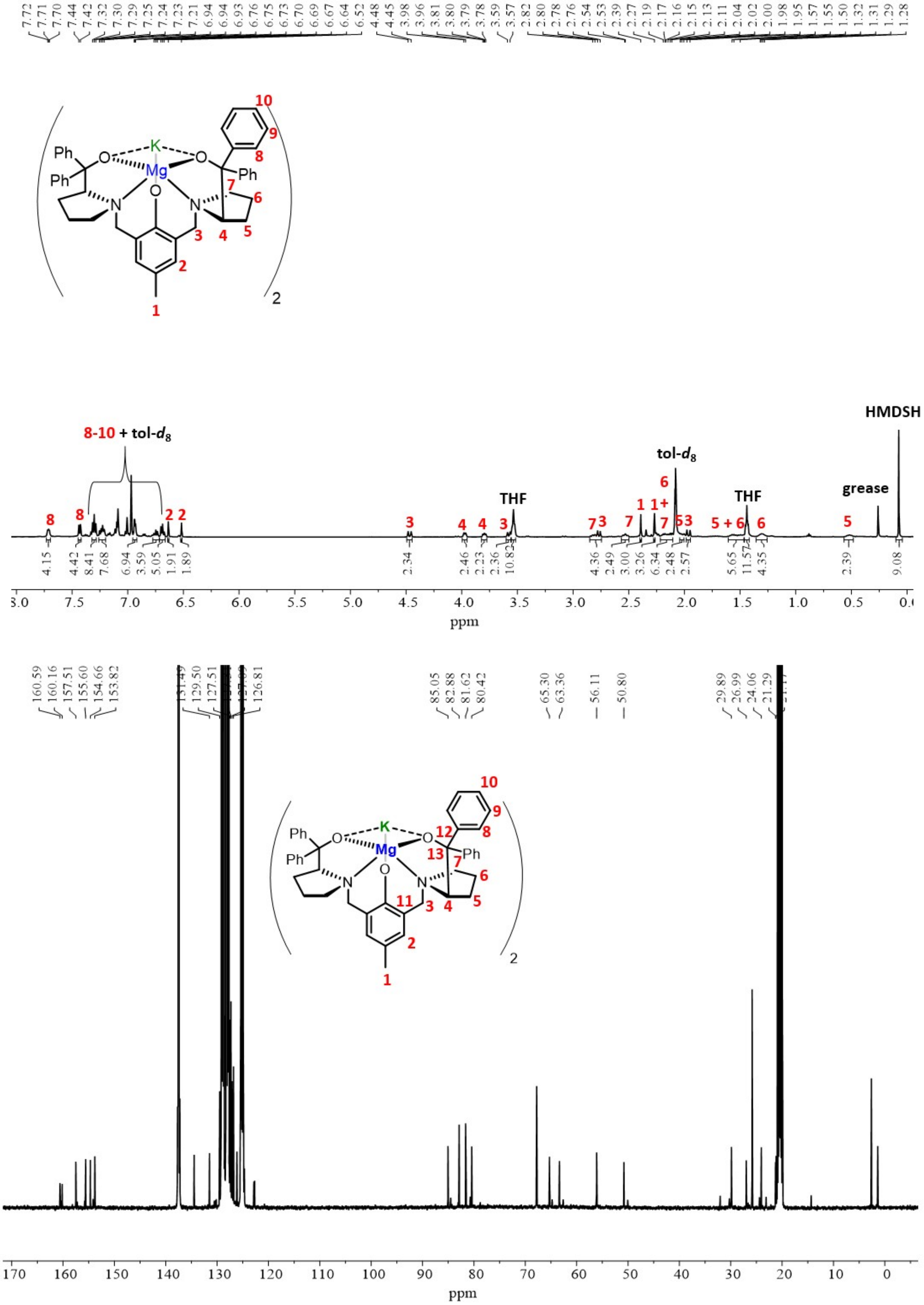


Figure S1. ^{1}H and ^{13}C NMR spectra of complex **3** in toluene-d_8 (298 K). Two sets of complex ^{1}H and ^{13}C NMR signals suggest an asymmetric nature of **3** in toluene-d_8.[3,5]

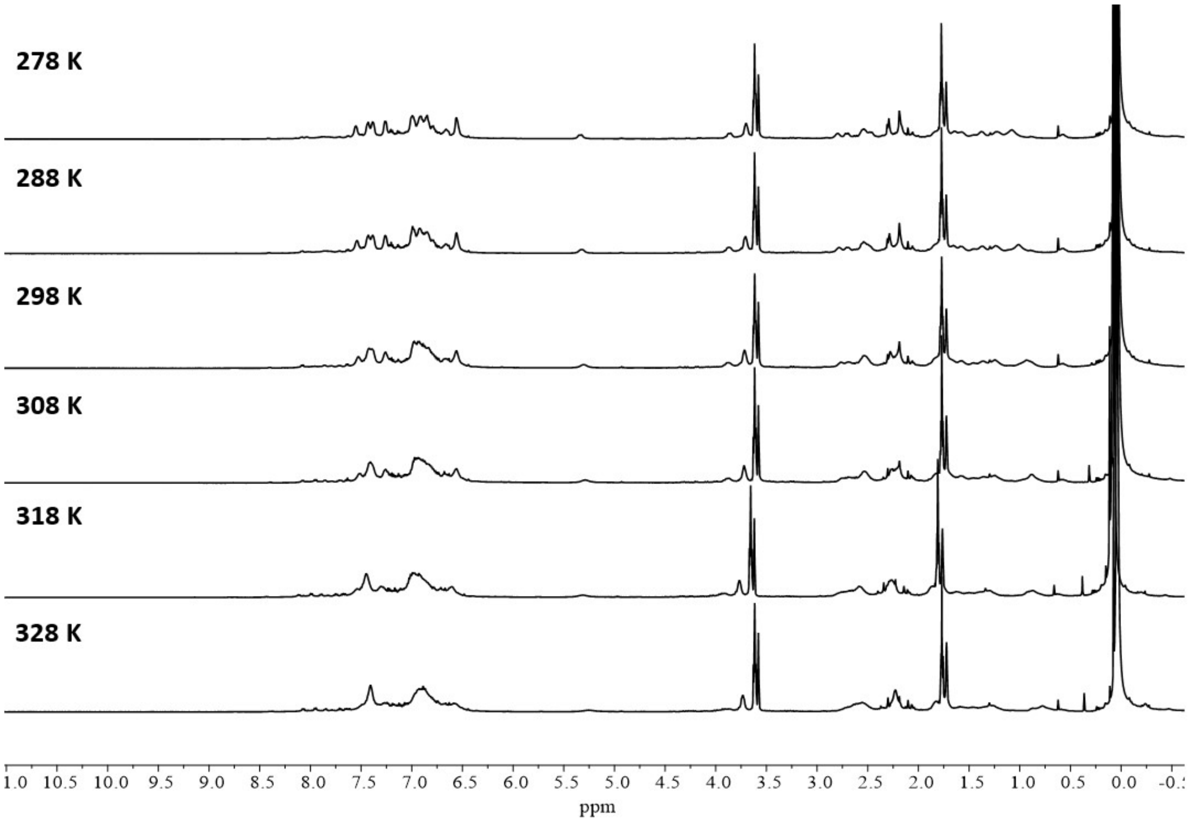


Figure S2. Variable temperature (VT) ^{1}H NMR spectra of complex **3** in THF-d_8. This figure shows that all of complex **2** reacted with $Mg(HMDS)_2$ in THF-d_8 at R.T., as evidenced by the disappearance of the diagnostic signal for the two benzylic O*H* moieties of **2** at 10.5 ppm.[2] VT ^{1}H NMR spectra were recorded between 5-55 °C to see whether the broad and complex signals for **3** could be resolved at lower or higher temperatures. As complicated spectra were also observed at 5-55 °C, **3** was instead characterised by NMR spectroscopy in toluene-d_8 (Fig. S1).

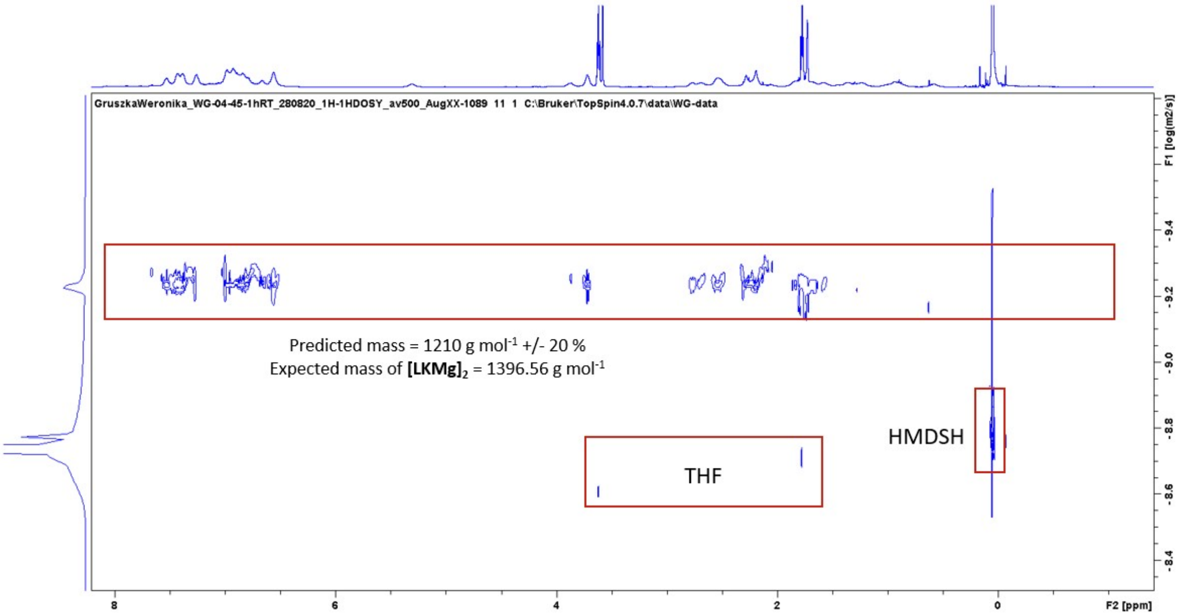


Figure S3. DOSY NMR spectrum of complex **3** in THF-d_8 (298 K).

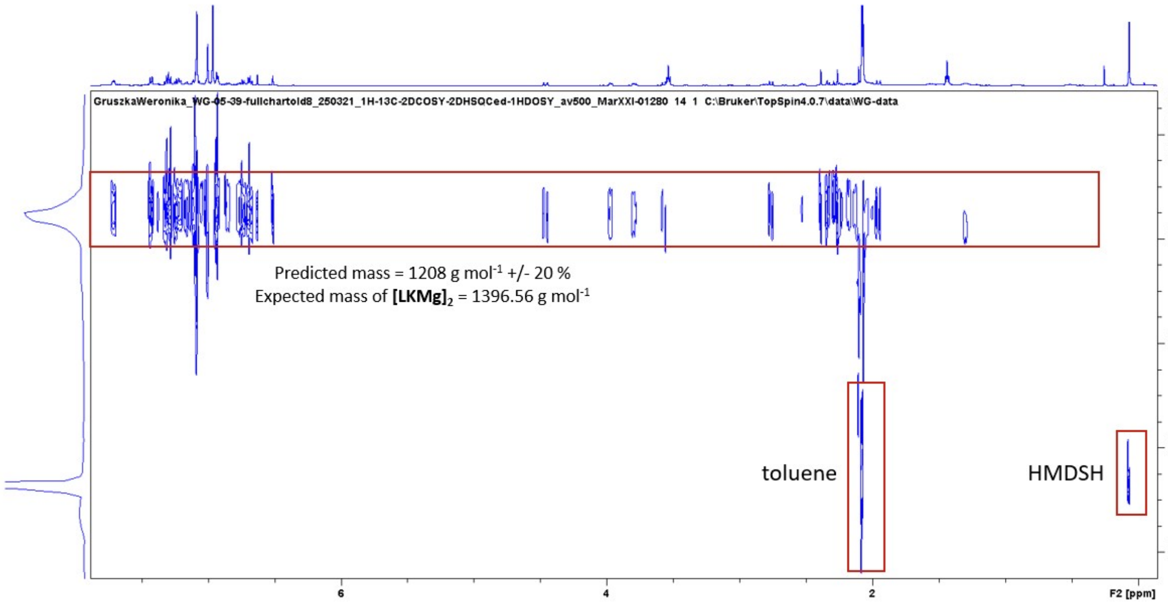


Figure S4. DOSY NMR spectrum of complex **3** in toluene-d_8 (298 K).

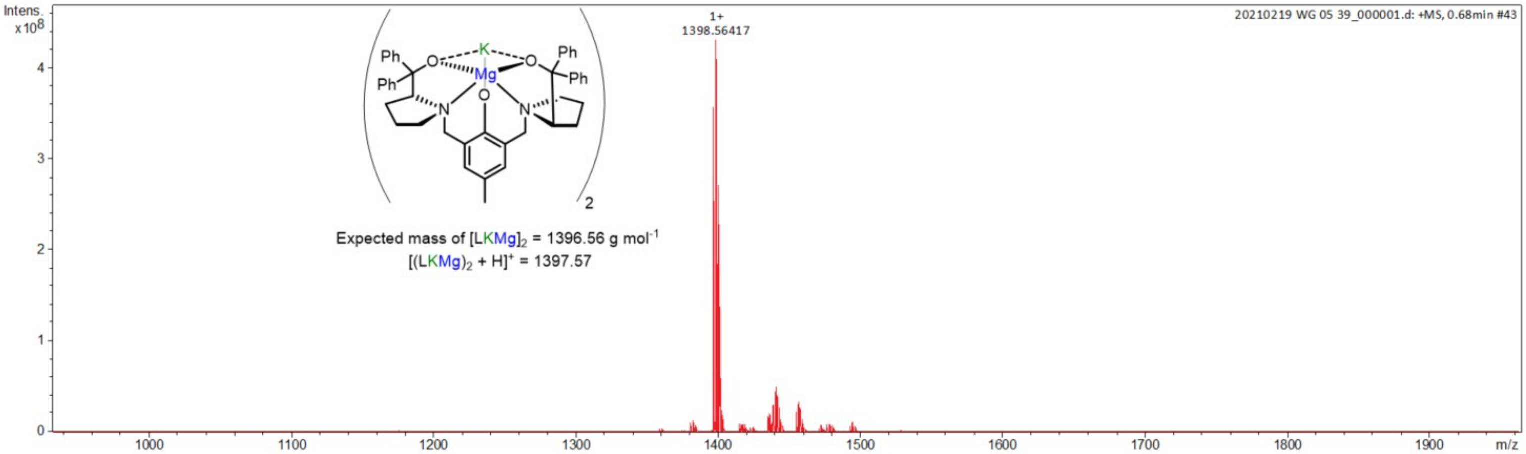


Figure S5. APPI-MS spectrum of complex **3**.

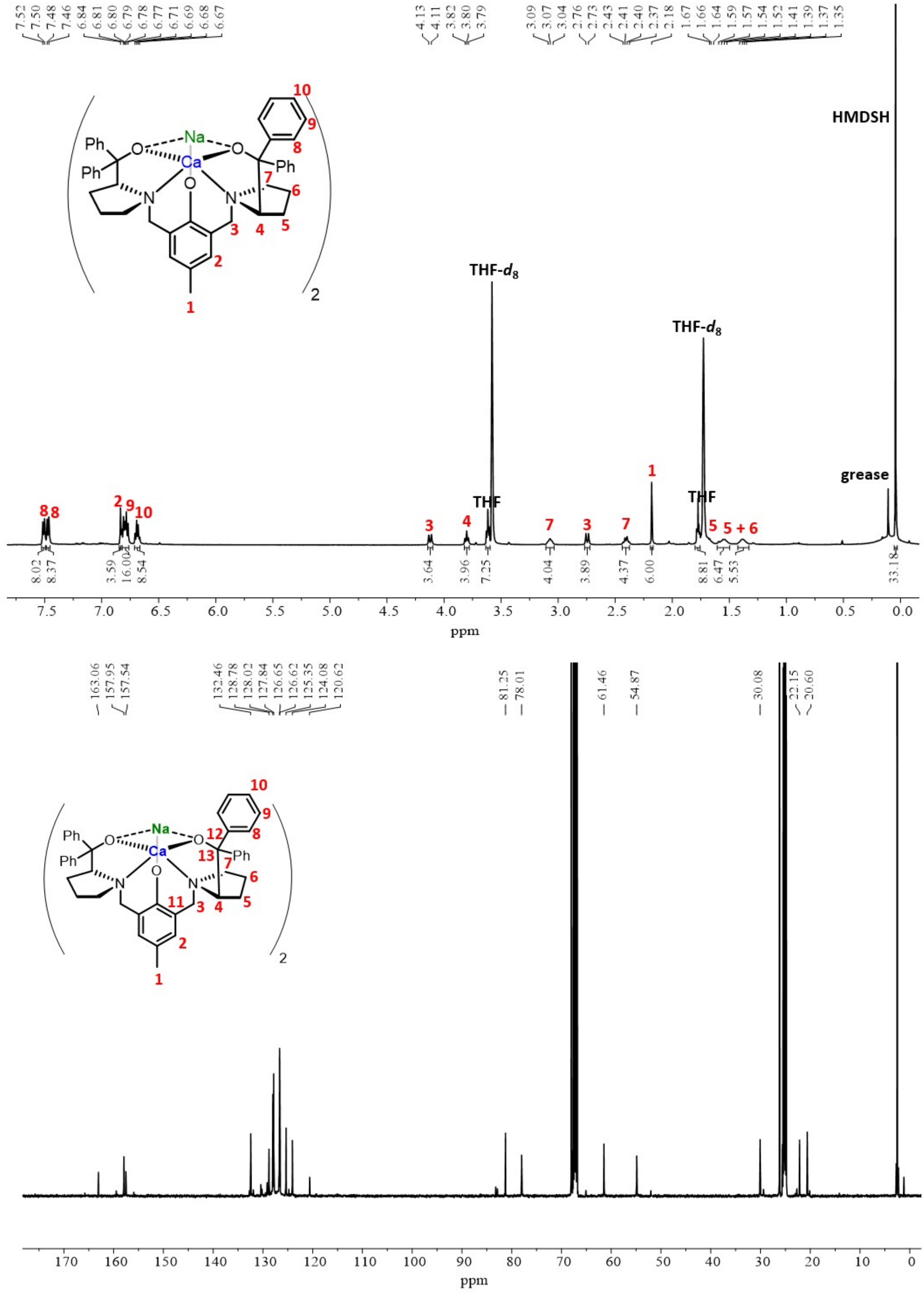


Figure S6. ^1H and ^{13}C NMR spectra of complex **4** in THF-d_8 (298 K).

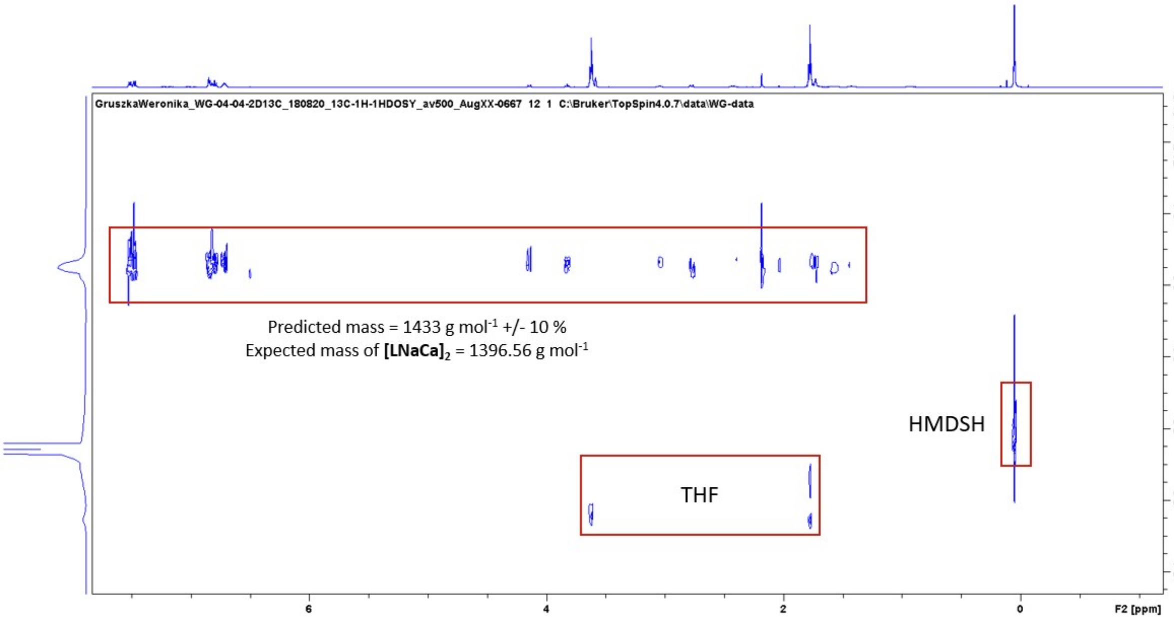


Figure S7. DOSY NMR spectrum of complex **4** in THF-d_8 (298 K).

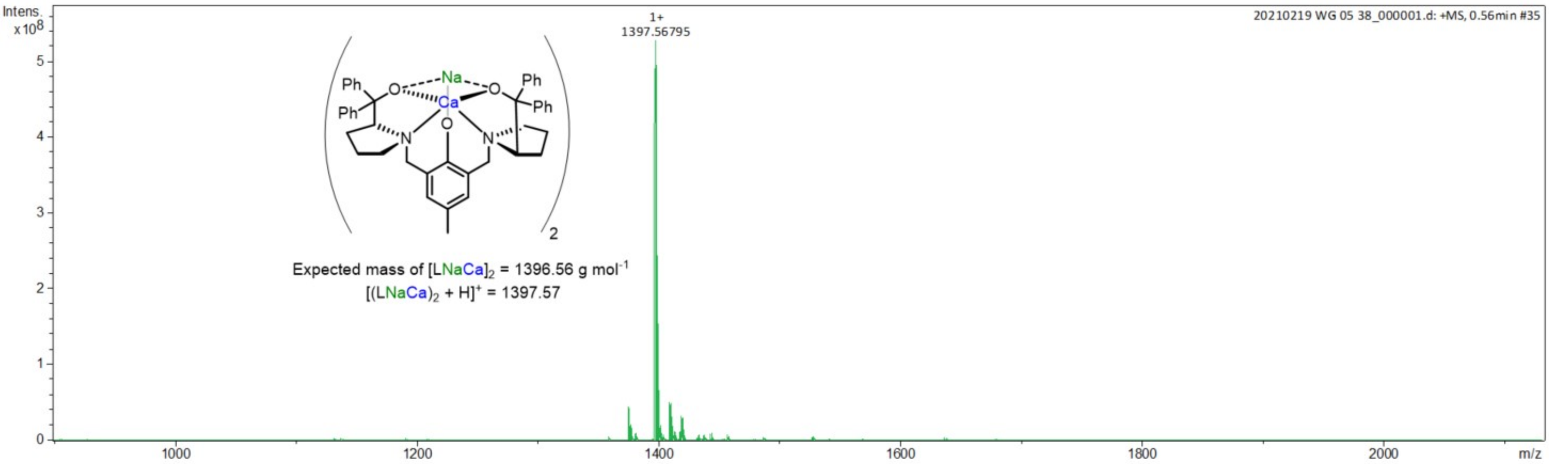
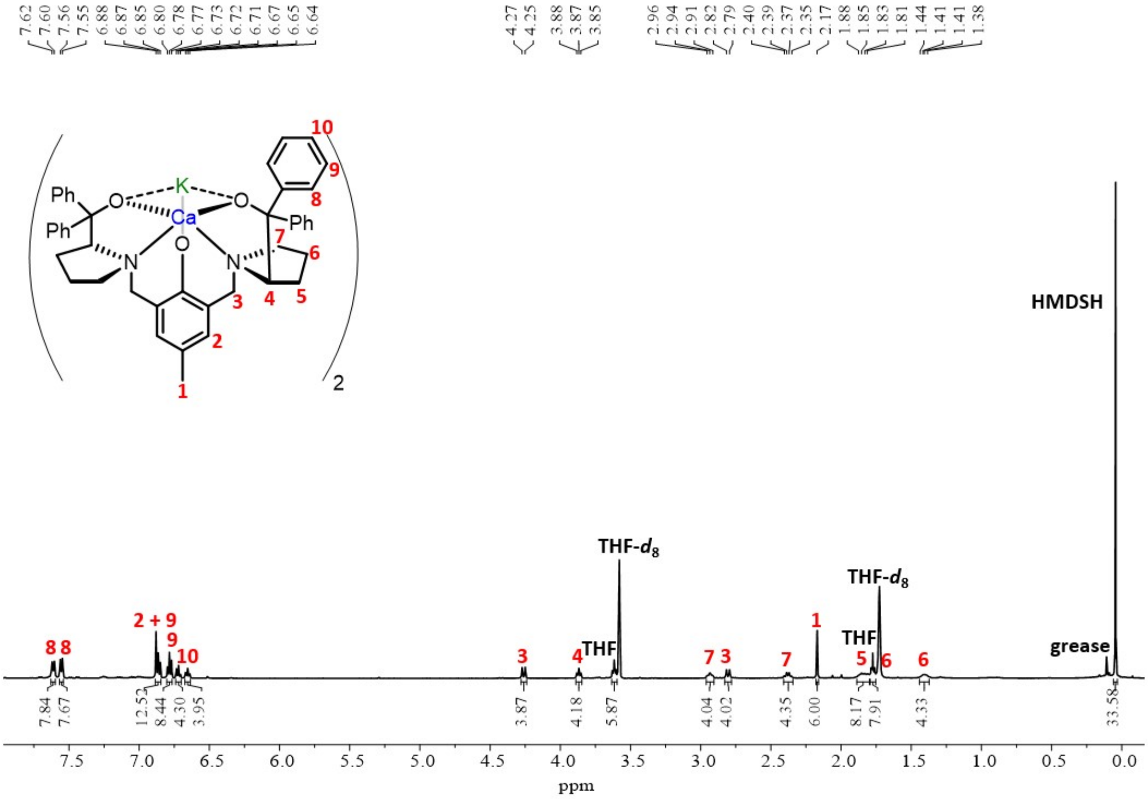


Figure S8. APPI-MS spectrum of complex **4**.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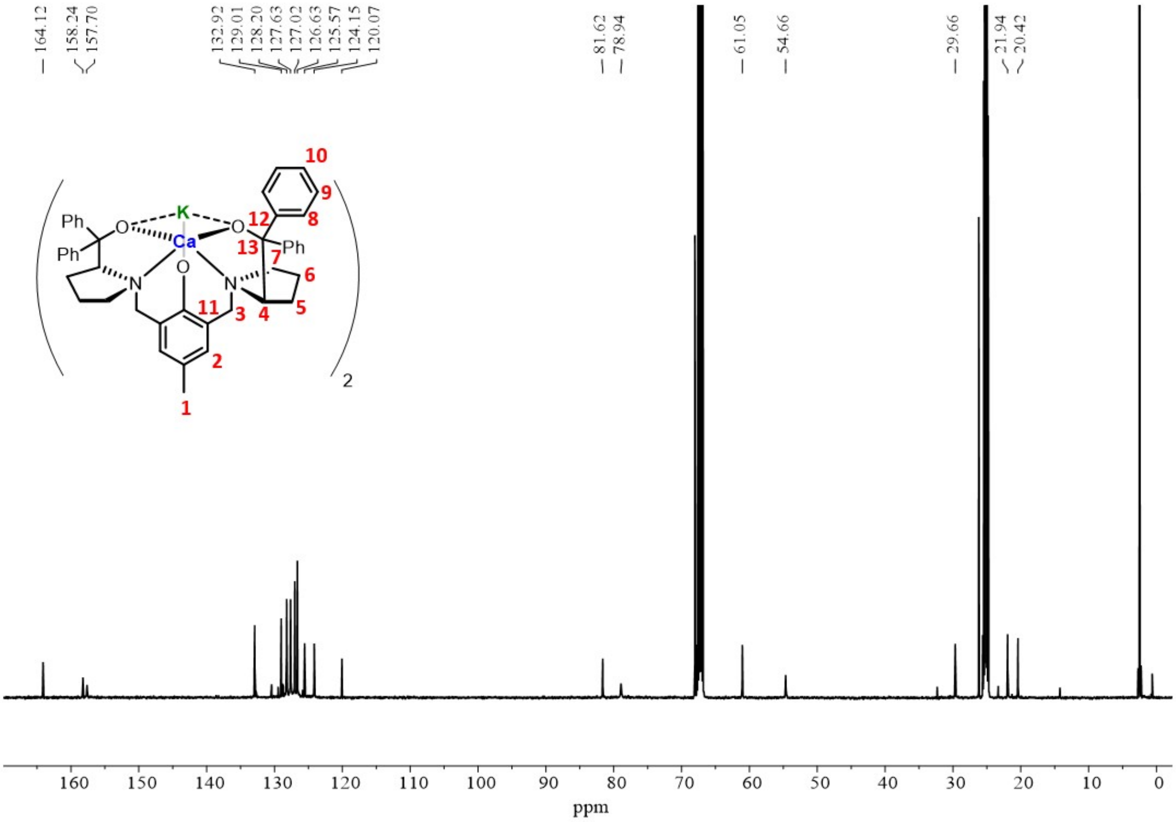
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Figure S9. ^{1}H and ^{13}C NMR spectra of complex **5** in THF-d_8 (298 K).

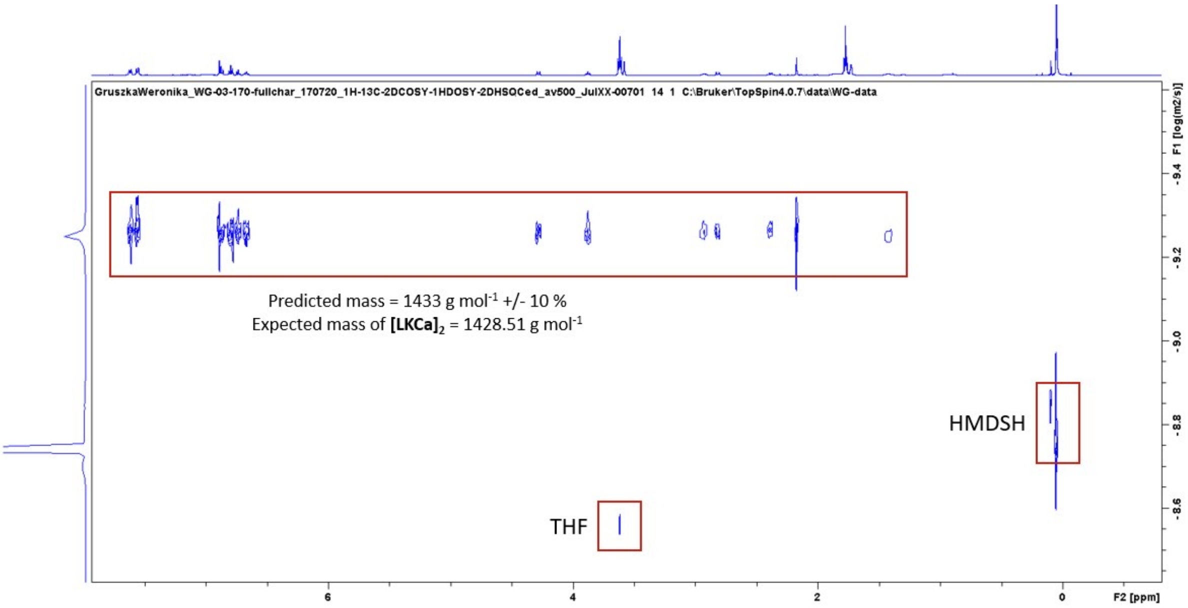

Figure S10. DOSY NMR spectrum of complex **5** in THF-d_8 (298 K).

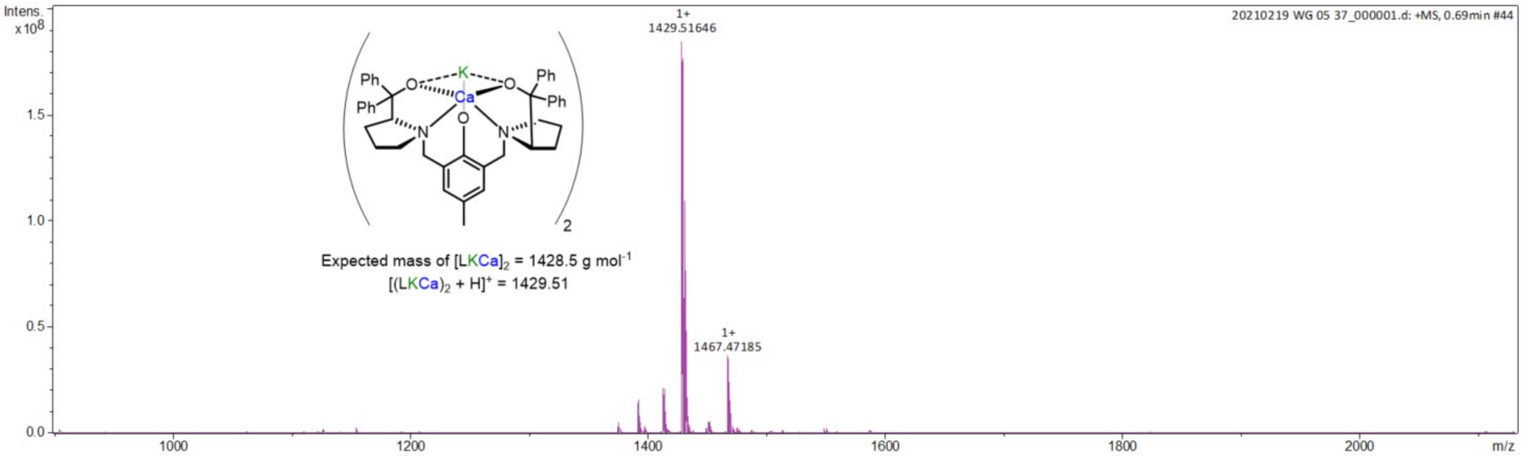

Figure S11. APPI-MS spectrum of complex **5**.

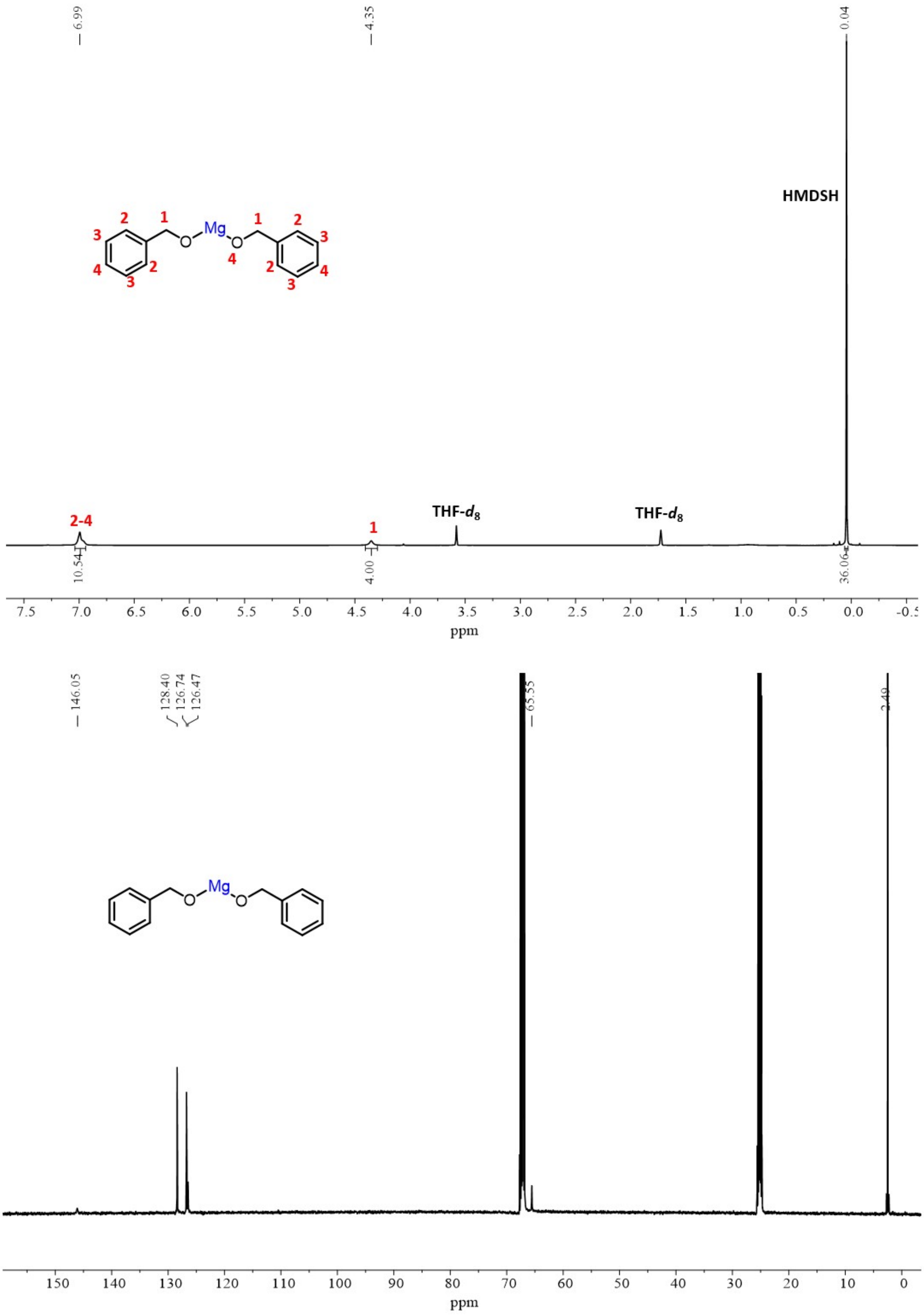

Figure S12. ^{1}H and ^{13}C NMR spectra of **$Mg(OBn)_2$** in THF-d_8 (298 K). Residual HMDSH was identified by comparison to reference ^{1}H and ^{13}C NMR spectra of HMDSH in THF-d_8.

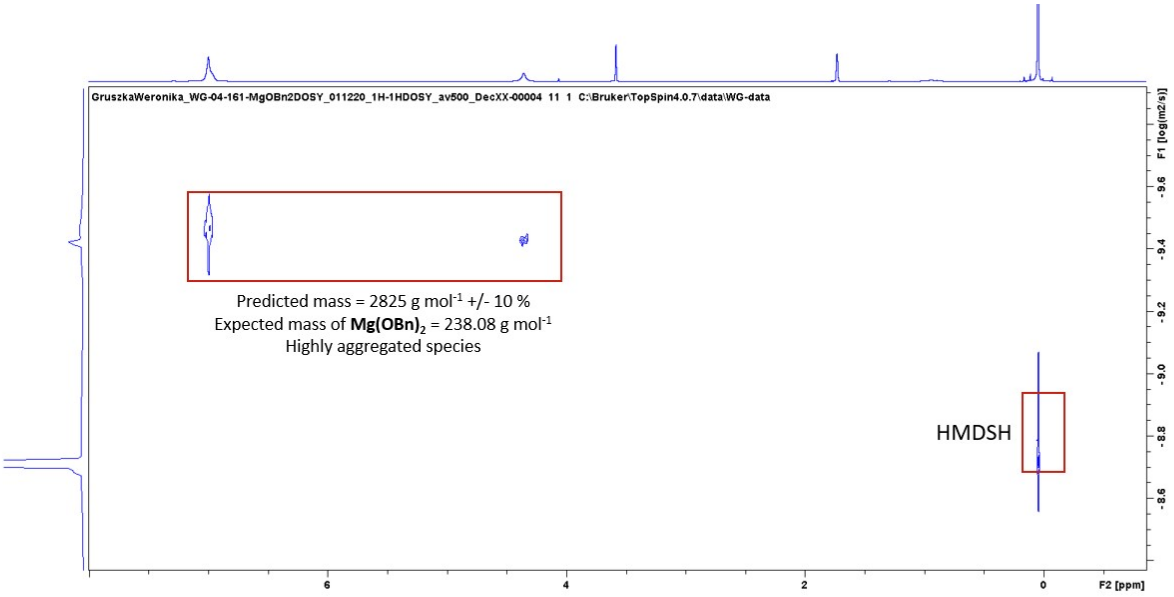

Figure S13. DOSY NMR spectrum of **Mg(OBn)$_2$** in THF-d_8 (298 K). *N.B.* Predicted mass of HMDSH = 139 g mol^{-1} (which lies close to the expected mass of HMDSH = 161.39 g mol^{-1}).

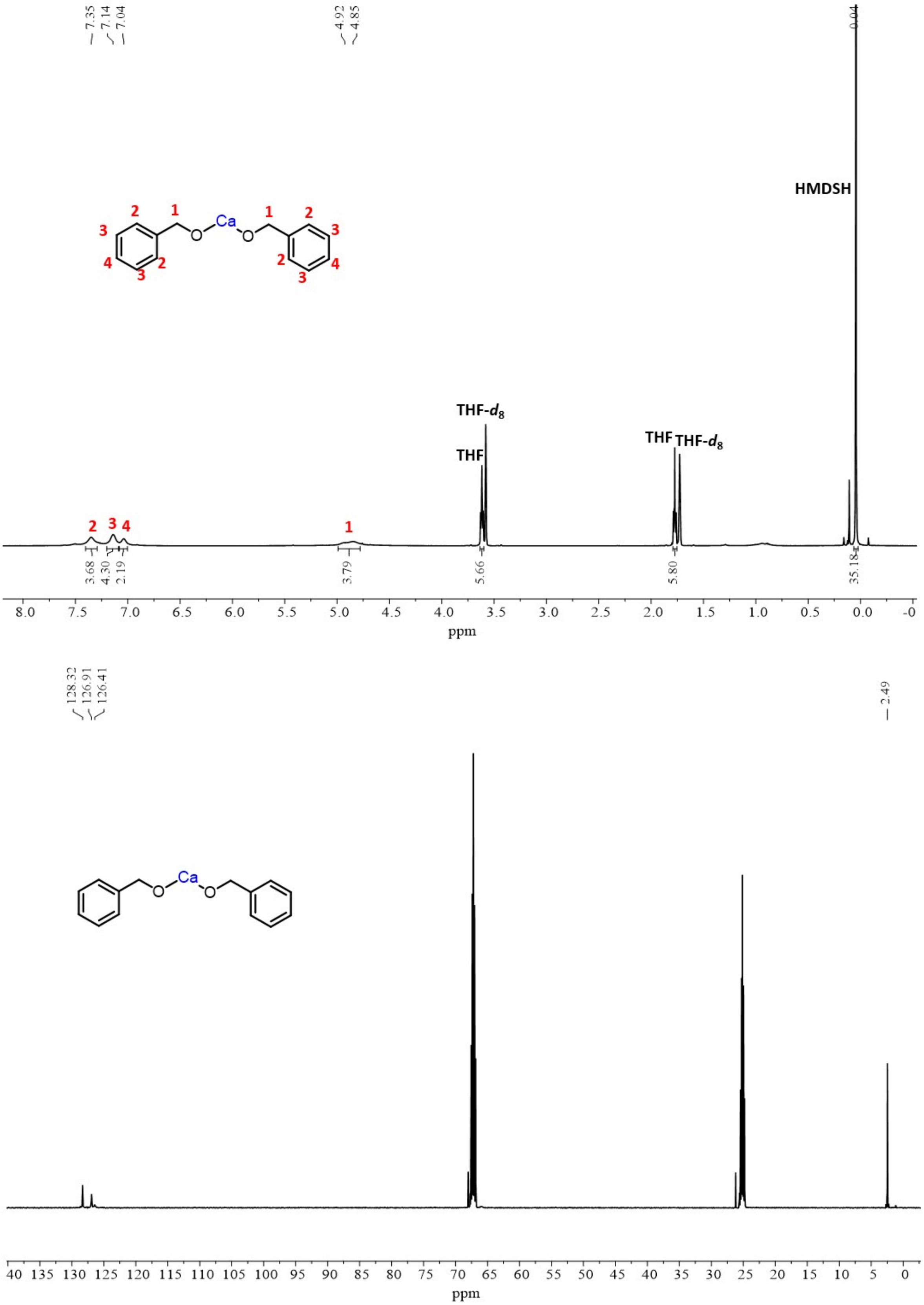

Figure S14. ^{1}H and ^{13}C NMR spectra of **Ca(OBn)$_2$** in THF-d_8 (298 K). Residual HMDSH was identified by comparison to reference ^{1}H and ^{13}C NMR spectra of HMDSH in THF-d_8.

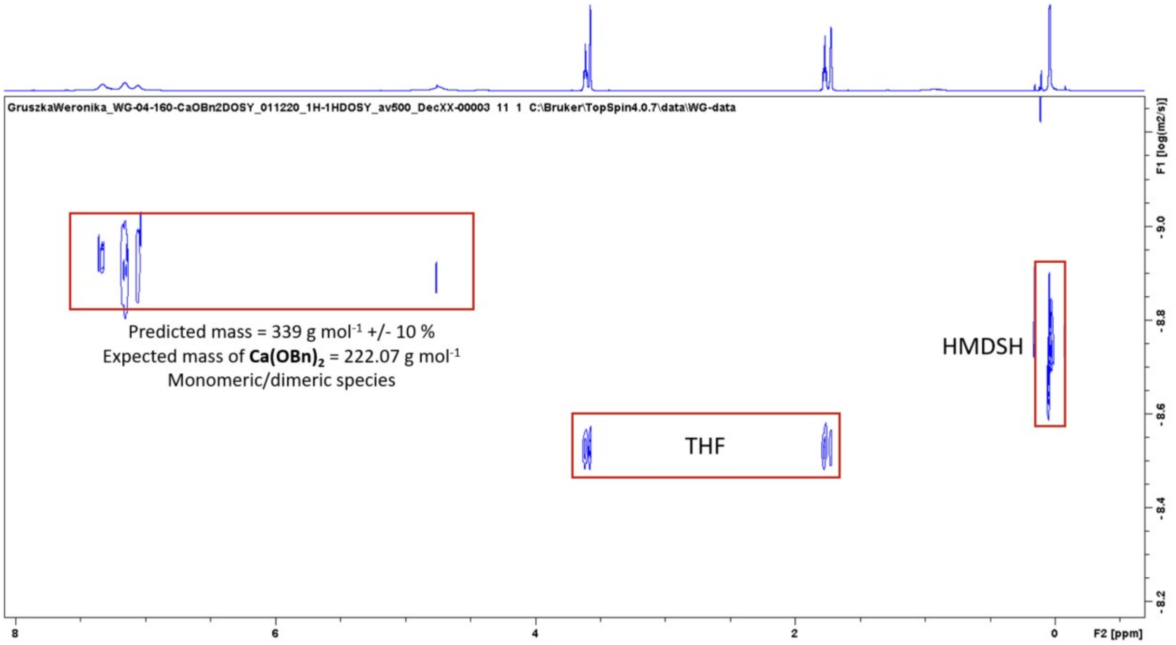

Figure S15. DOSY NMR spectrum of **Ca(OBn)$_2$** in THF-d_8 (298 K). *N.B.* Predicted mass of HMDSH = 139 g mol^{-1} (which lies close to the expected mass of HMDSH = 161.39 g mol^{-1}).

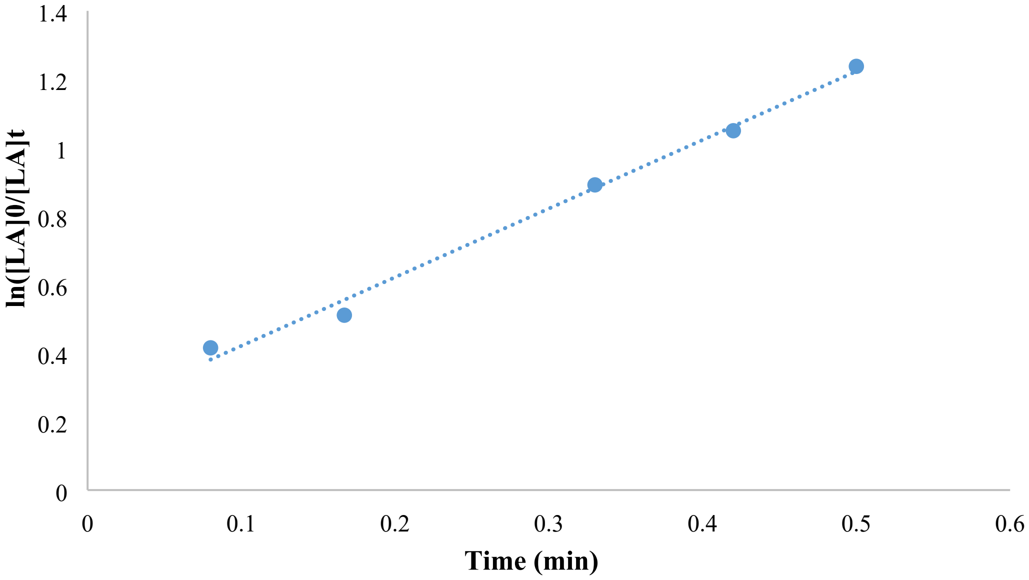

Figure S16. Plot of ln([LA]$_0$/[LA]$_t$) *vs*. time (min) for ROP of *rac*-LA with complex **4** ([LA] = 1 M in THF, R.T., 1 eq. BnOH used).

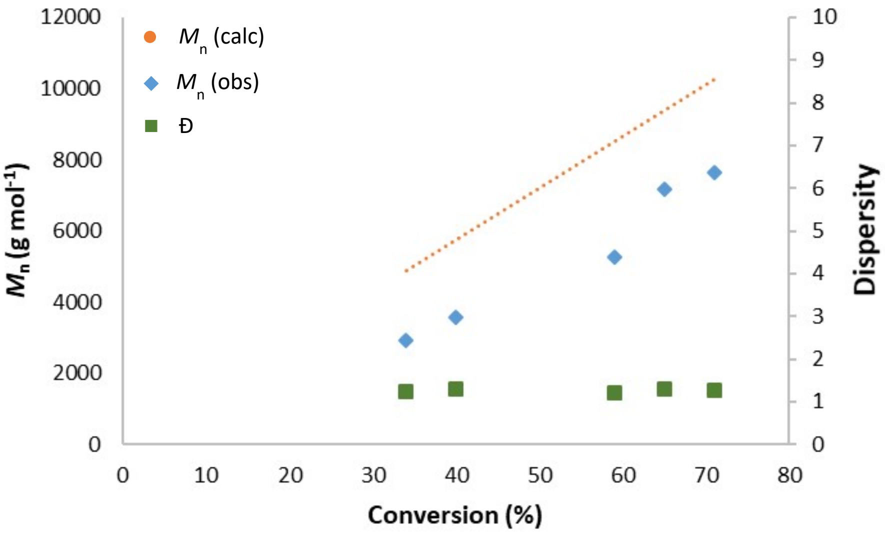

Figure S17. Comparison between experimental and calculated M_n values and dispersity values at increasing conversions of *rac*-LA in the presence of complex **4** and 1 eq. BnOH in THF at R.T.

Table S1. Results for the ROP of *rac*-LA in THF at R.T. catalysed by complexes **3**-**5** and 1 eq. BnOH at various catalyst loadings.

Entry	**Cat.**	**LA:cat:BnOH**	**Time (s)**	**Conv.^{a} (%)**	**$M_{n,obs}$^{b} (Da)**	**$M_{n,calc}$^{c} (Da)**	**$Đ^b$**
1	**3**	200:1:1	5	53	13800	15300	1.56
2	**3**	300:1:1	5	38	19700	16400	1.53
3	**3**	300:1:1	40	78	20600	33700	1.75
4	**3**	500:1:1	60	49	23200	35300	1.67
5	**3**	500:1:1	240	60	24300	43200	1.80
6	**4**	200:1:1	5	50	7700	14400	1.36
7	**4**	300:1:1	5	15	3000	6500	1.28
8	**4**	300:1:1	40	77	23000	33300	1.99
9	**4**	500:1:1	180	50	16000	36000	1.55
10	**4**	500:1:1	360	51	20500	36800	1.79
11	**5**	200:1:1	5	76	11800	21900	1.64
12	**5**	300:1:1	5	53	21500	22900	1.64
13	**5**	300:1:1	40	67	18600	29000	1.79
14	**5**	500:1:1	60	49	22400	35300	1.51
15	**5**	500:1:1	240	47	24500	33900	1.44

[LA] = 1 M in THF. Cat. + BnOH and LA pre-stirred separately for 1 min in THF at R.T. before mixing. ^{a} Conversion calculated using ^{1}H NMR spectroscopy. ^{b} $M_{n,obs}$ and $Đ$ determined by SEC using polystyrene standards in THF. Values corrected by Mark-Houwink factor (0.58).[6] ^{c} $M_{n,calc}$ of polymers calculated from the monomer conversion $M_{n,calc}$ = M_0 x ([M]/[I]) x conversion assuming 1 chain per catalyst.

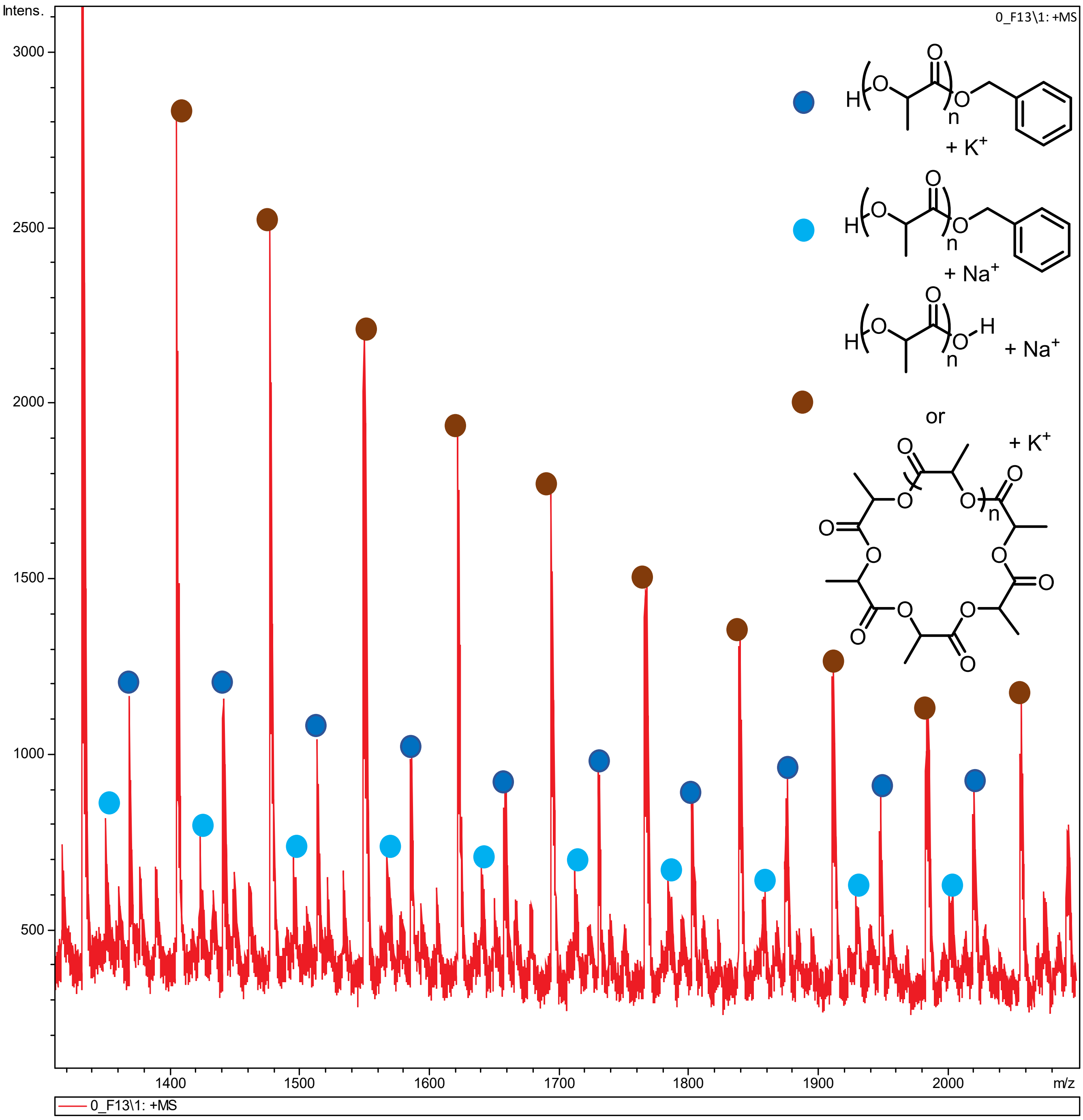

Figure S18. MALDI-ToF spectrum of PLA resulting from 98% conversion of *rac*-LA in the presence of complex **3** + 1 eq. BnOH (THF, R.T.).

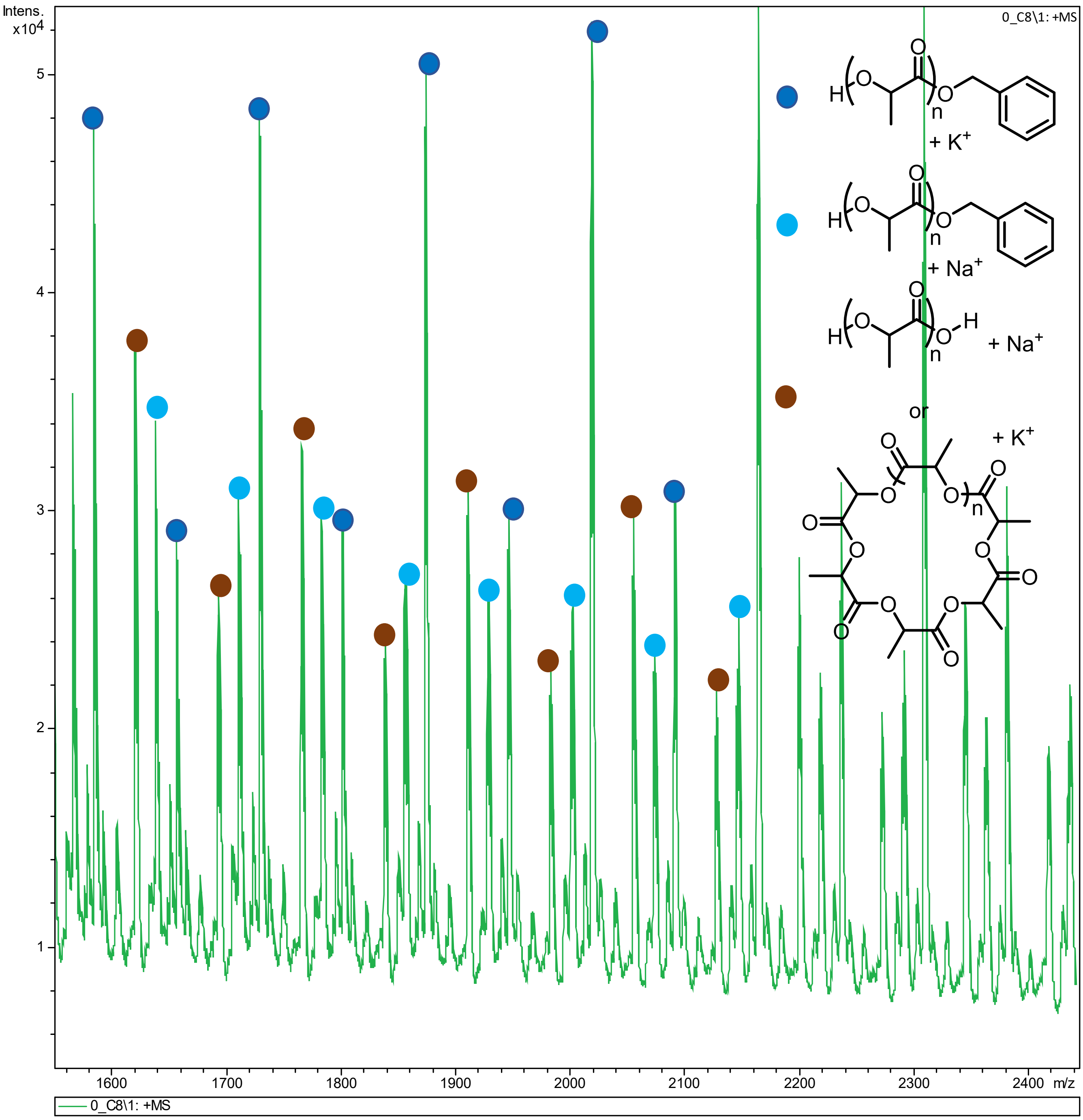

Figure S19. MALDI-ToF spectrum of PLA resulting from 34% conversion of *rac*-LA in the presence of complex **4** + 1 eq. BnOH (THF, R.T.)

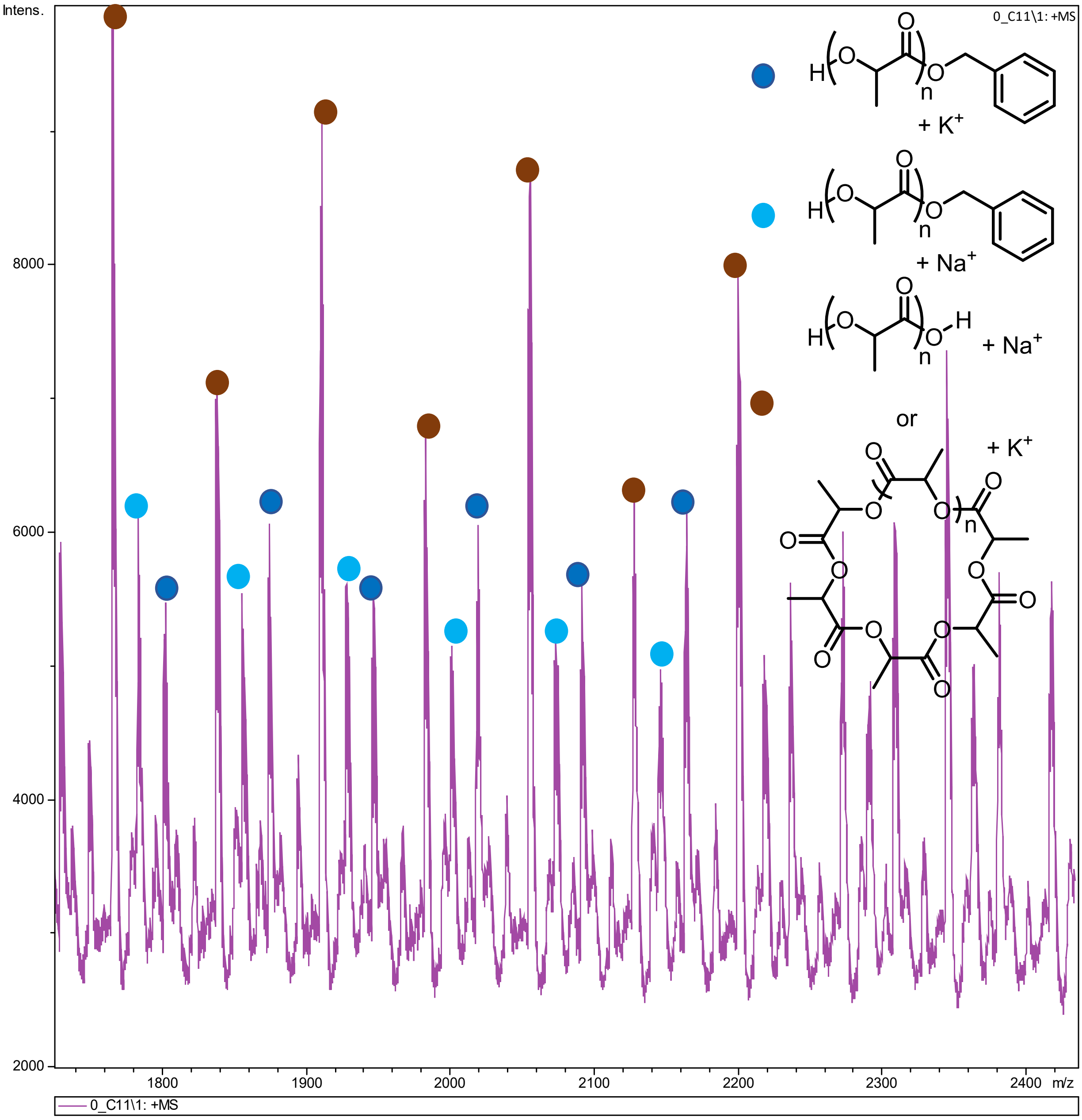

Figure S20. MALDI-ToF spectrum of PLA resulting from 59% conversion of *rac*-LA in the presence of complex **4** + 1 eq. BnOH (THF, R.T.)

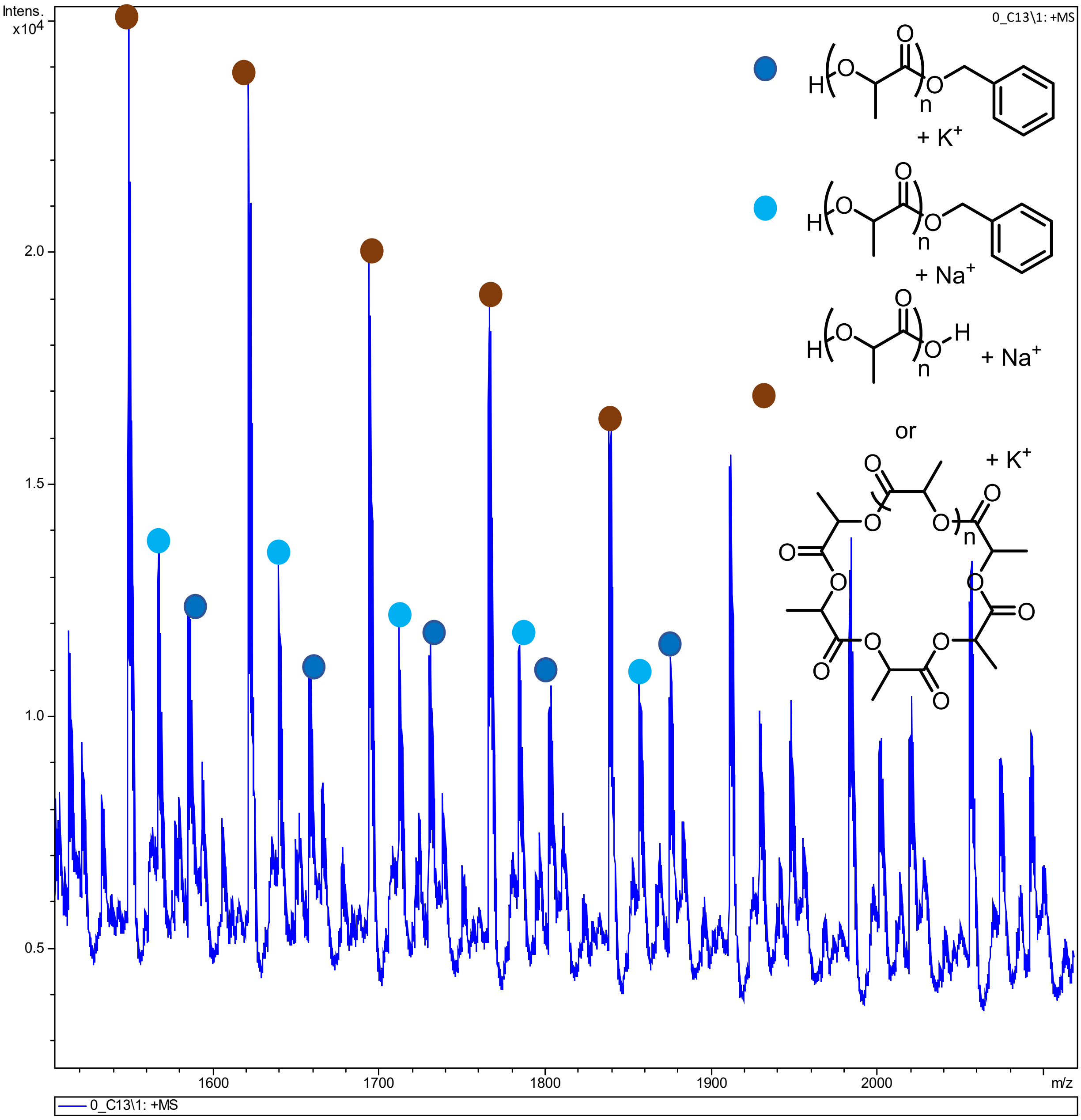

Figure S21. MALDI-ToF spectrum of PLA resulting from 85% conversion of *rac*-LA in the presence of complex **4** + 1 eq. BnOH (THF, R.T.)

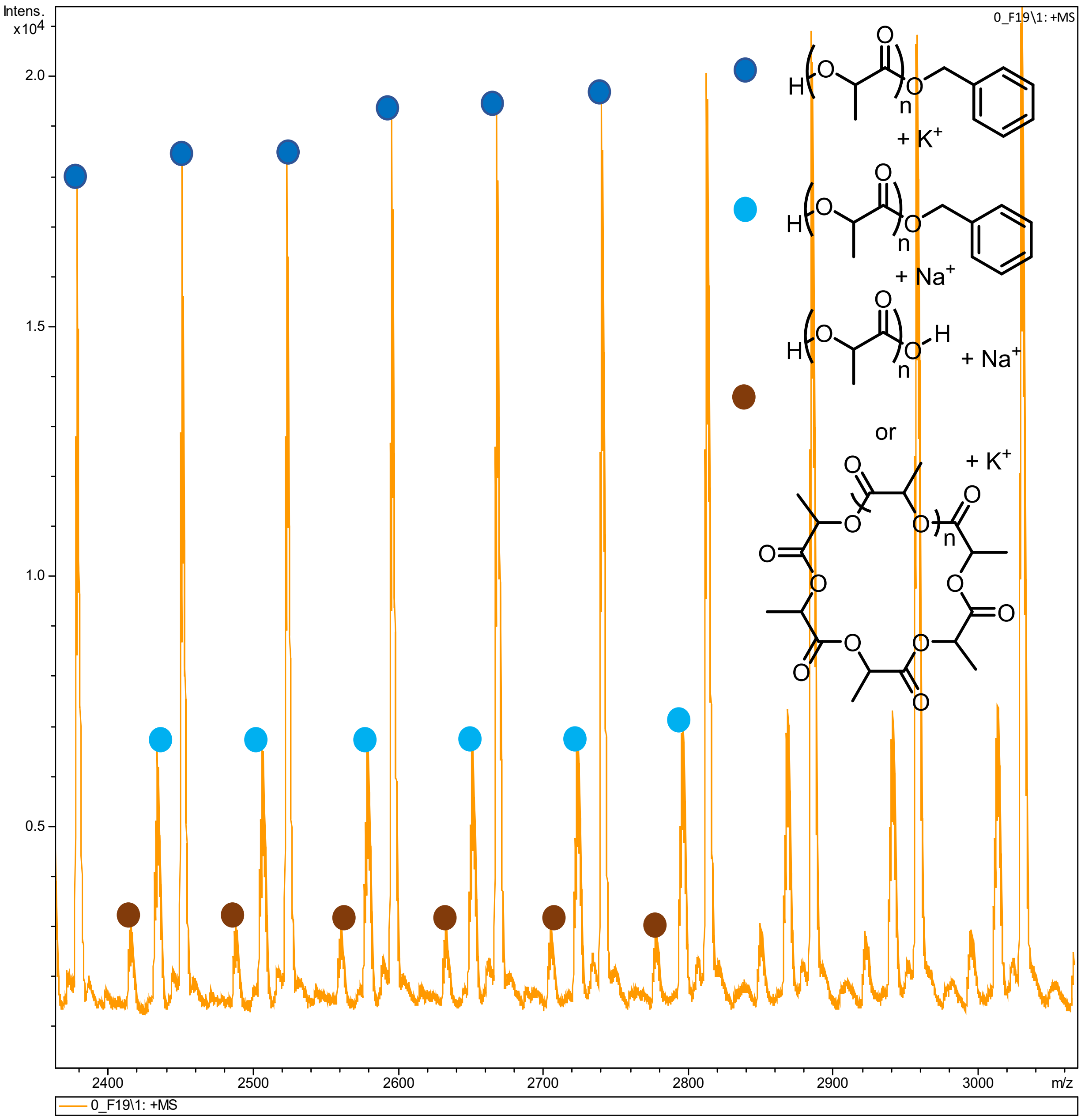

Figure S22. MALDI-ToF spectrum of PLA resulting from 87% conversion of *rac*-LA in the presence of complex **5** + 1 eq. BnOH (THF, R.T.)

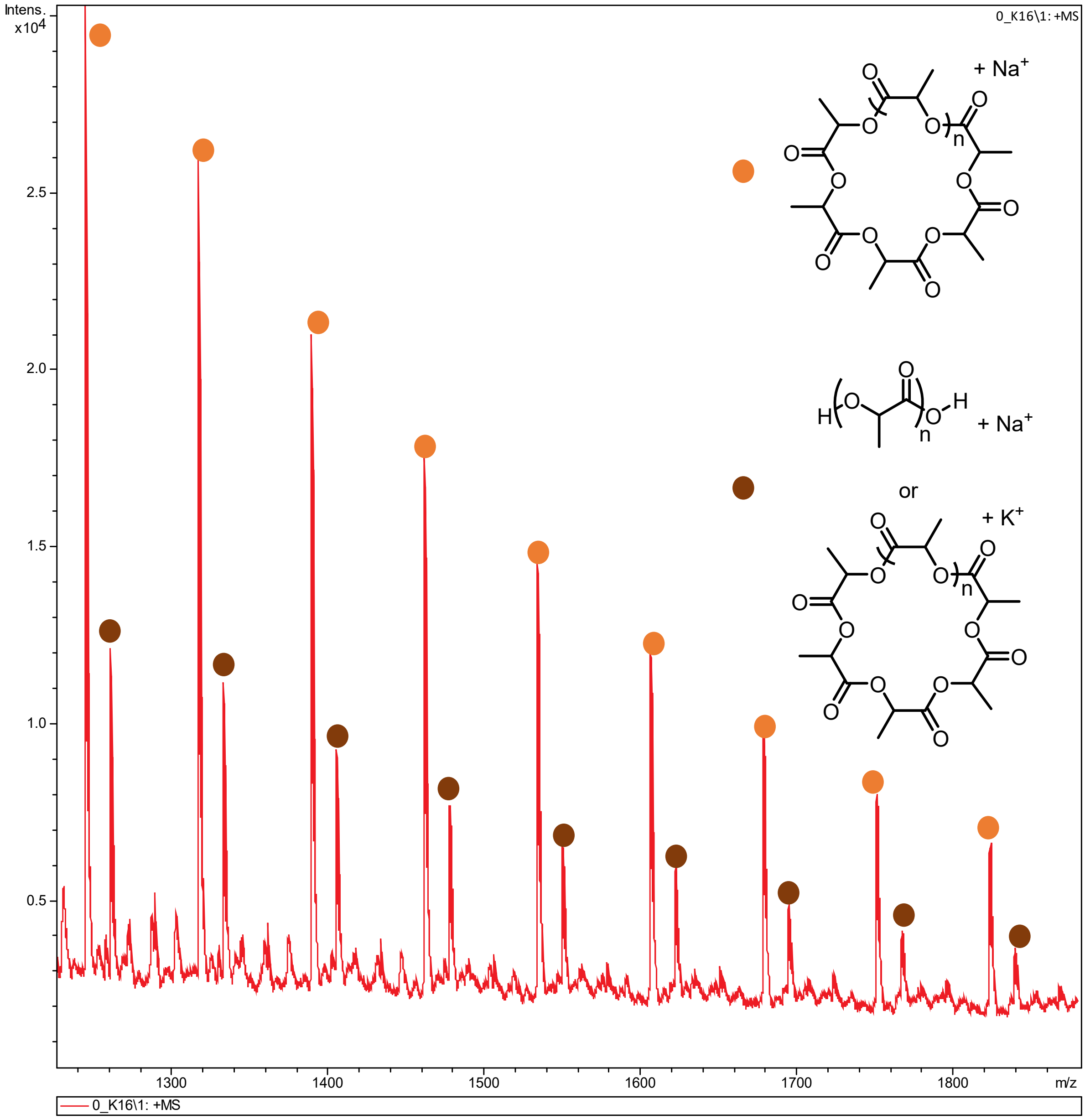

Figure S23. MALDI-ToF spectrum of PLA resulting from 87% conversion of *rac*-LA in the presence of complex **1** (THF, R.T.).

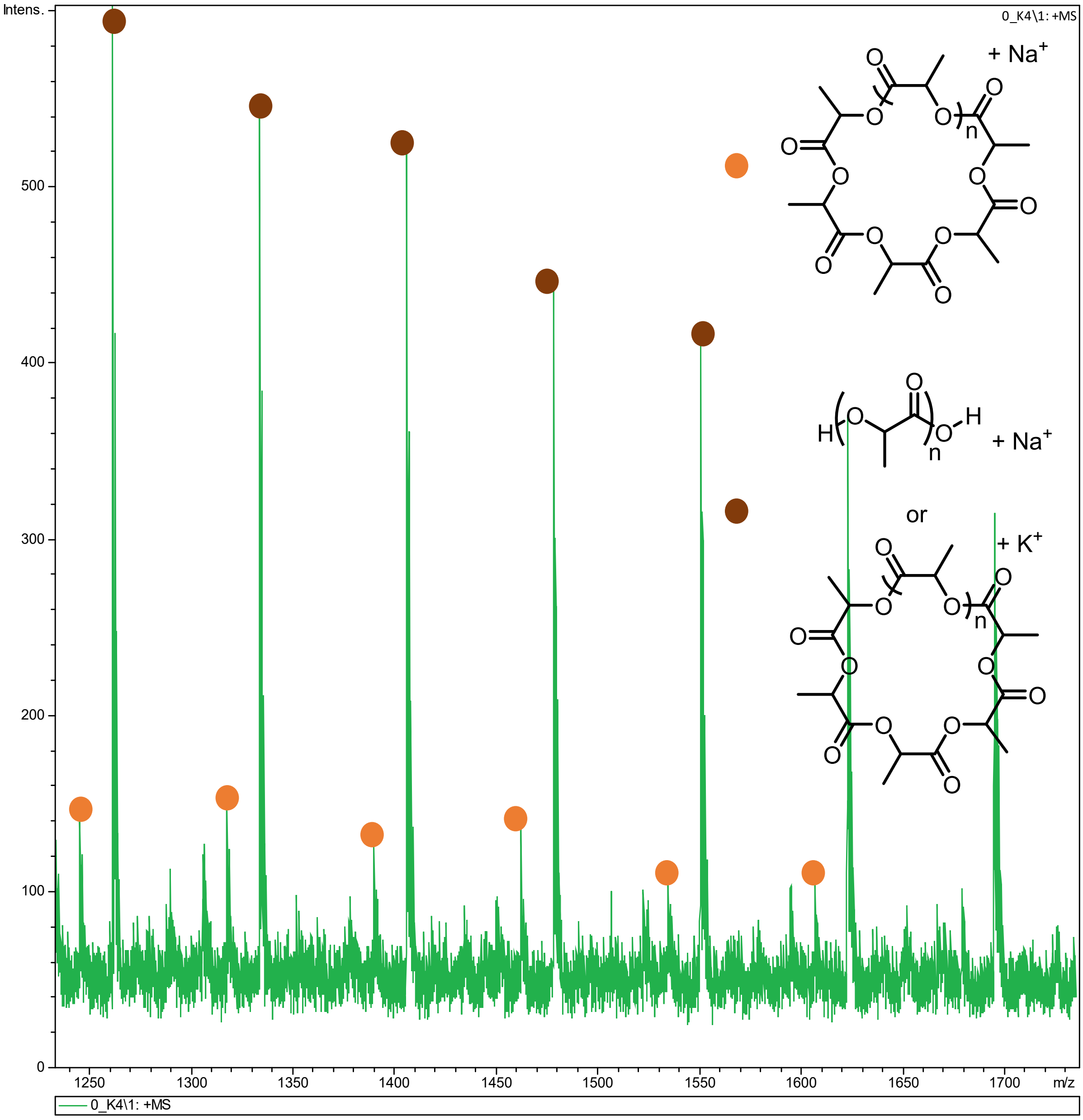

Figure S24. MALDI-ToF spectrum of PLA resulting from 33% conversion of *rac*-LA in the presence of complex **2** (0.5 mol% catalyst loading, THF, R.T.).

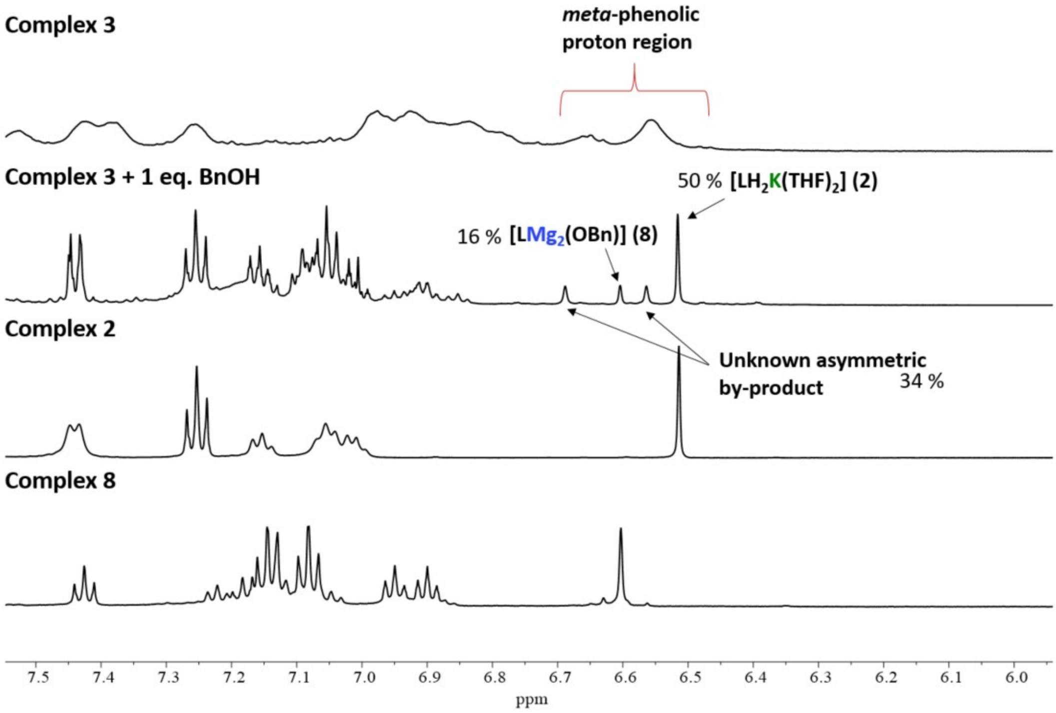

Figure S25. ^{1}H NMR spectrum of the alcoholysis reaction of **3** with 1 eq. BnOH in THF-d_8 at R.T.

Figure S26. Overlaid aromatic region of the ^{1}H NMR spectra of the alcoholysis reaction of **3** with 1 eq. BnOH, and complexes **3** (**[LKMg]$_2$**), **2** (**[LH$_2$K(THF)$_2$]**) and **8** (**[LMg$_2$OBn]**) in THF-d_8 at R.T.

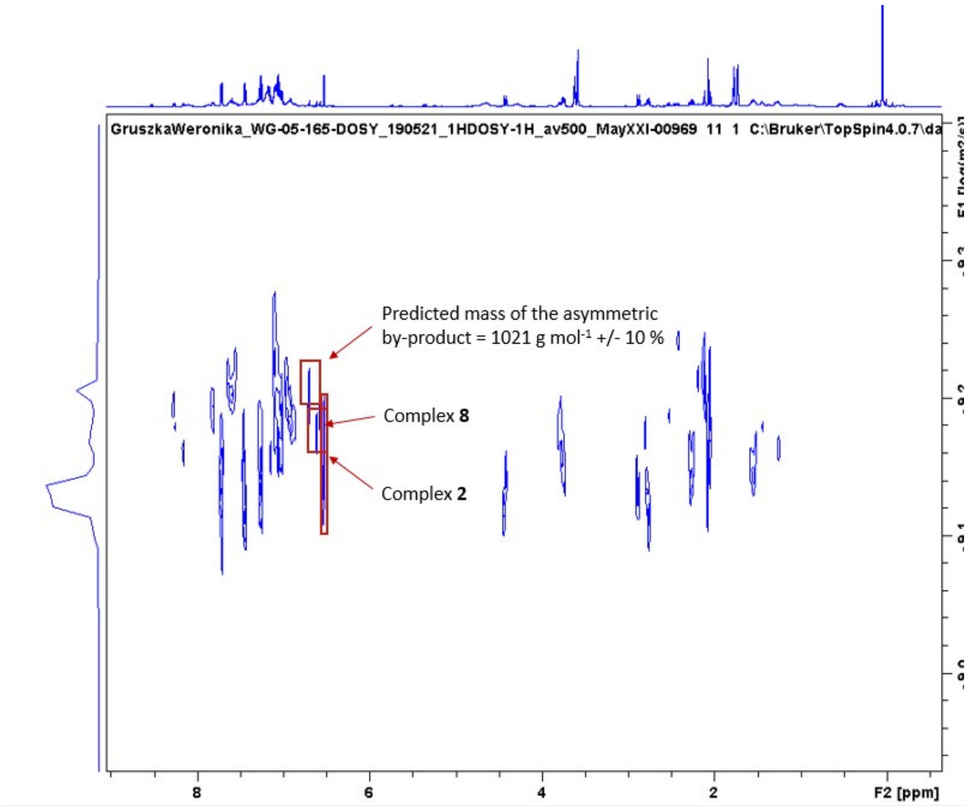

Figure S27. DOSY NMR spectrum of the alcoholysis reaction of **3** with 1 eq. BnOH in THF-d_8 at R.T.

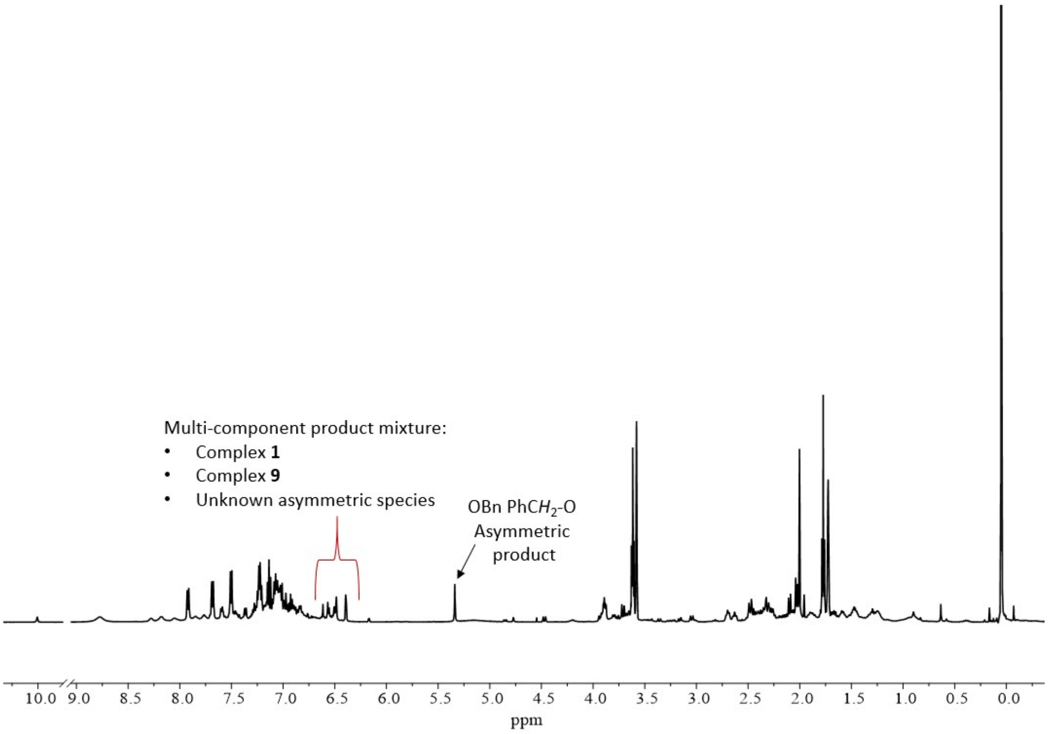

Figure S28. ^{1}H NMR spectrum of the alcoholysis reaction of **4** with 1 eq. BnOH in THF-d_8 at R.T.

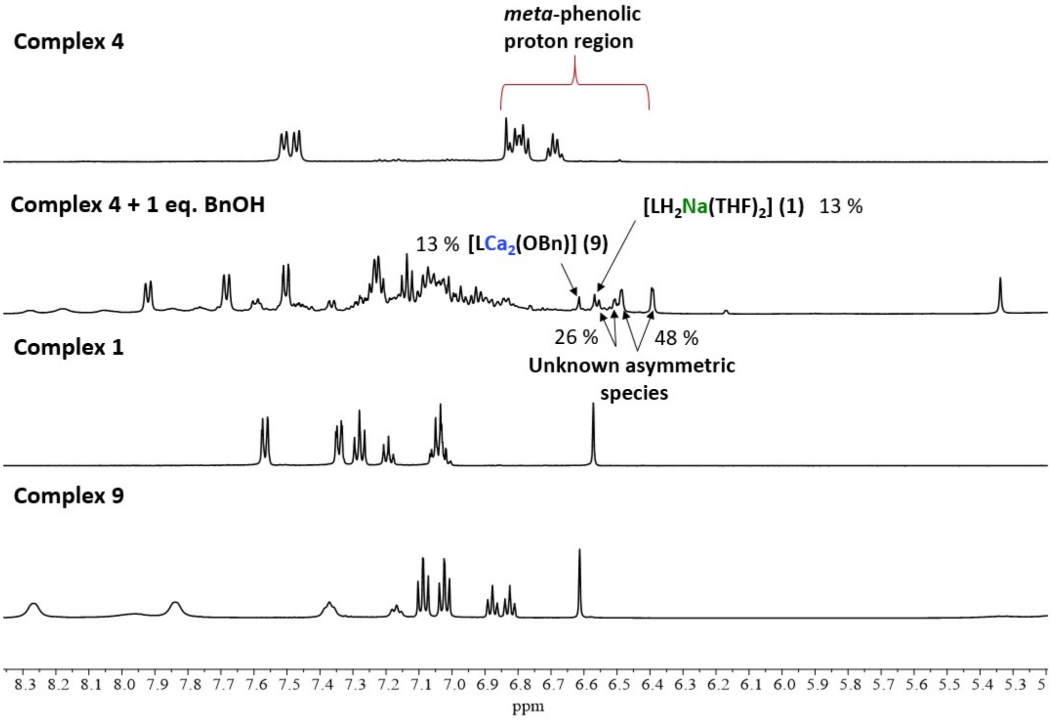

Figure S29. Overlaid aromatic region of the ^{1}H NMR spectra of the alcoholysis reaction of **4** with 1 eq. BnOH, and complexes **4** (**[LNaCa]$_2$**), **1** (**[LH$_2$Na(THF)$_2$]**) and **9** (**[LCa$_2$OBn]**) in THF-d_8 at R.T.

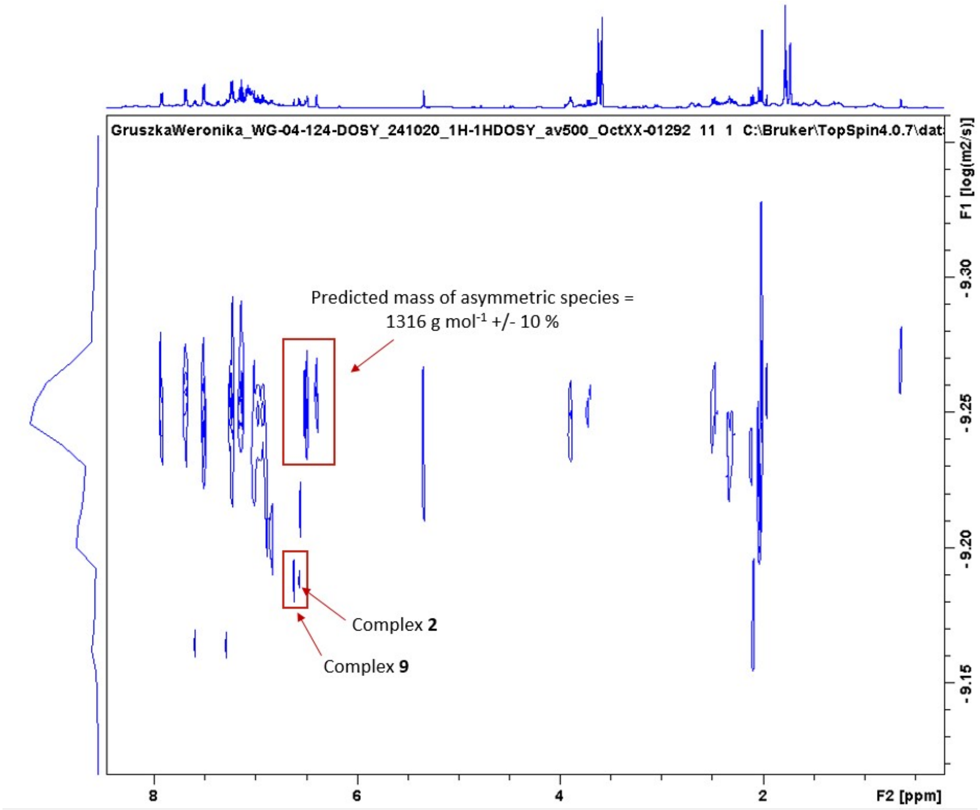

Figure S30. DOSY NMR spectrum of the alcoholysis reaction of **4** with 1 eq. BnOH in THF-d_8 at R.T.

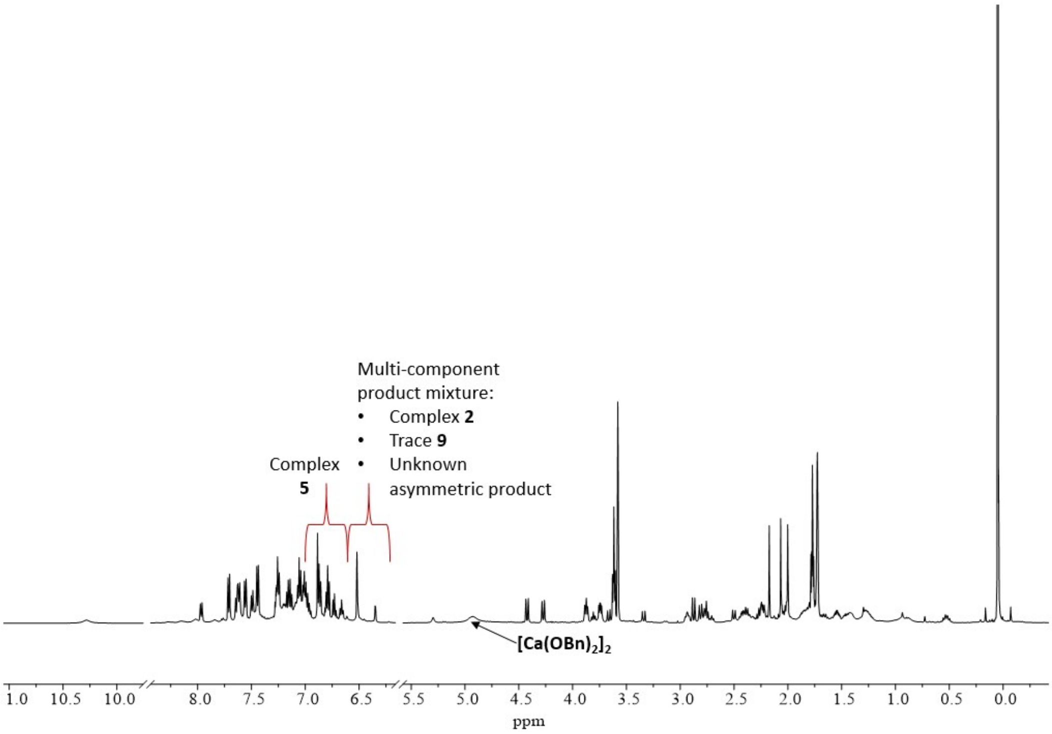

Figure S31. ^{1}H NMR spectrum of the alcoholysis reaction of **5** with 1 eq. BnOH in THF-d_8 at R.T.

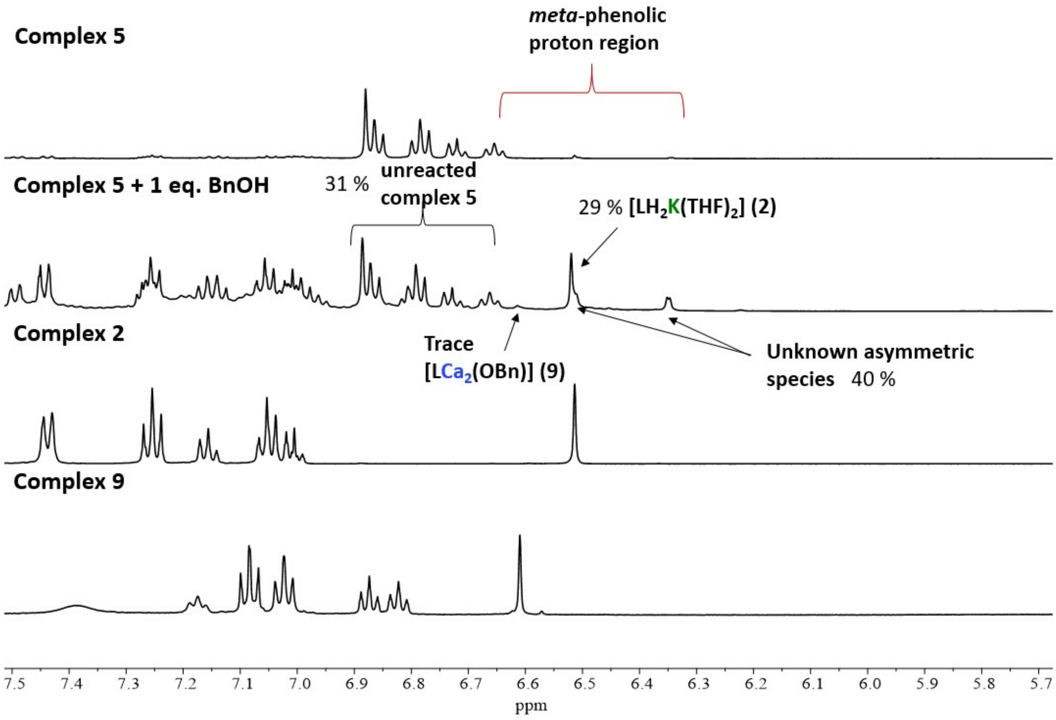

Figure S32. Overlaid aromatic region of the ^{1}H NMR spectra of the alcoholysis reaction of **5** with 1 eq. BnOH, and complexes **5** (**[LKCa]$_2$**), **2** (**[LH$_2$K(THF)$_2$]**) and **9** (**[LCa$_2$OBn]**) in THF-d_8 at R.T.

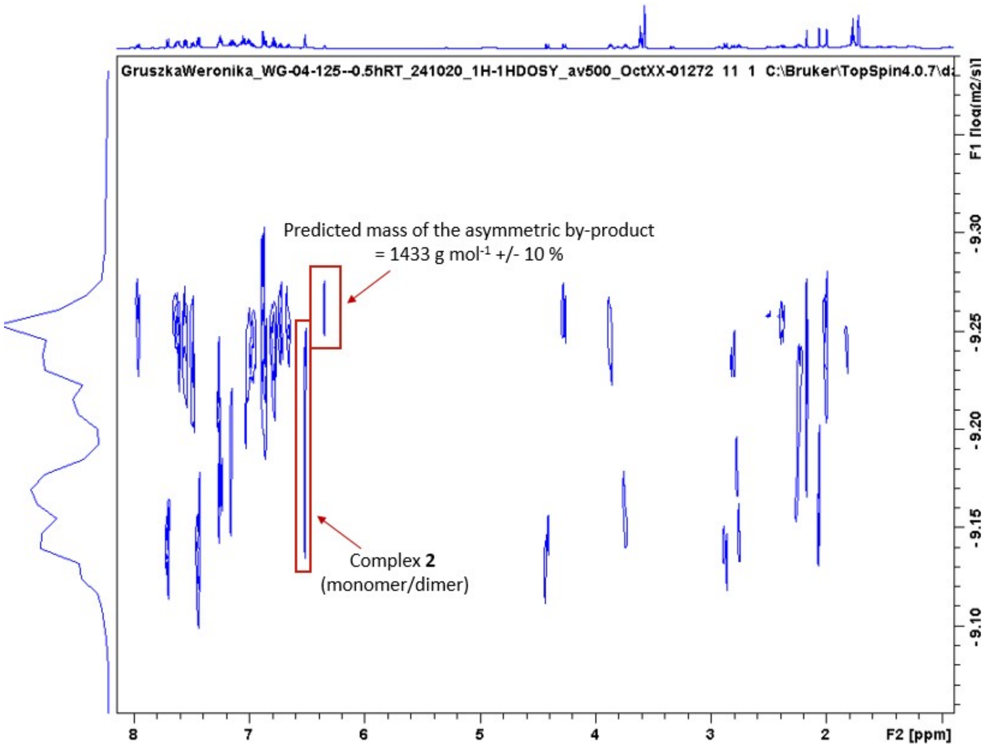

Figure S33. DOSY NMR spectrum of the alcoholysis reaction of **5** with 1 eq. BnOH in THF-d_8 at R.T.

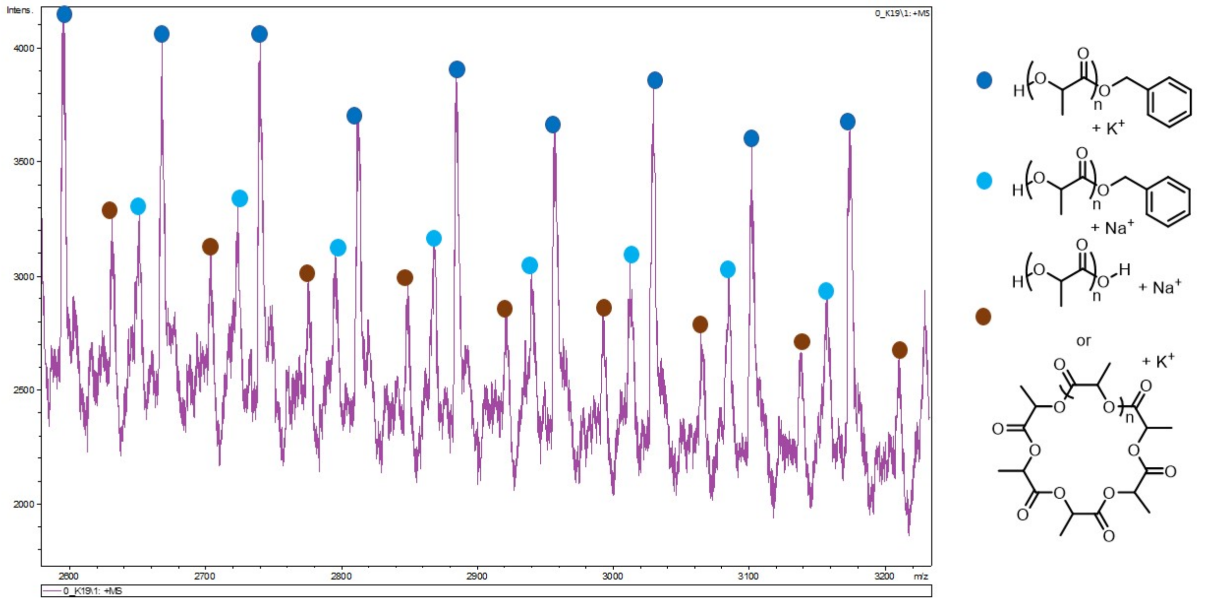

Figure S34. MALDI-ToF spectrum of PLA resulting from 87% conversion of *rac*-LA in the presence of a 1:1 mixture of complex **1** and **Ca(OBn)$_2$** (THF, R.T.).

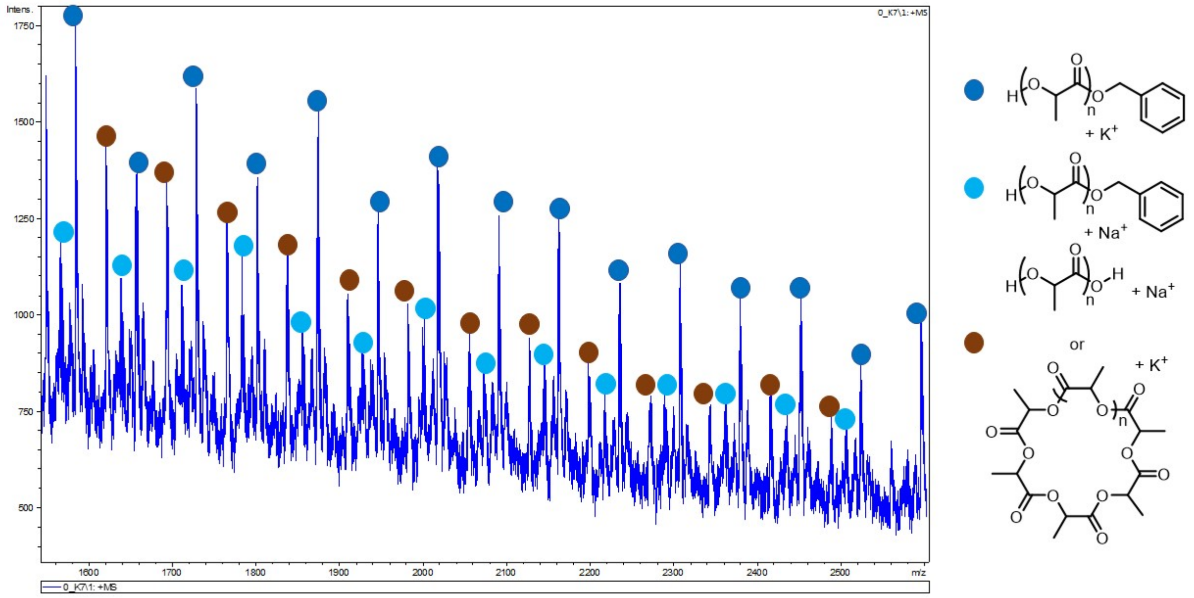

Figure S35. MALDI-ToF spectrum of PLA resulting from 88% conversion of *rac*-LA in the presence of a 1:1 mixture of complex **2** and **Ca(OBn)$_2$** (THF, R.T.).

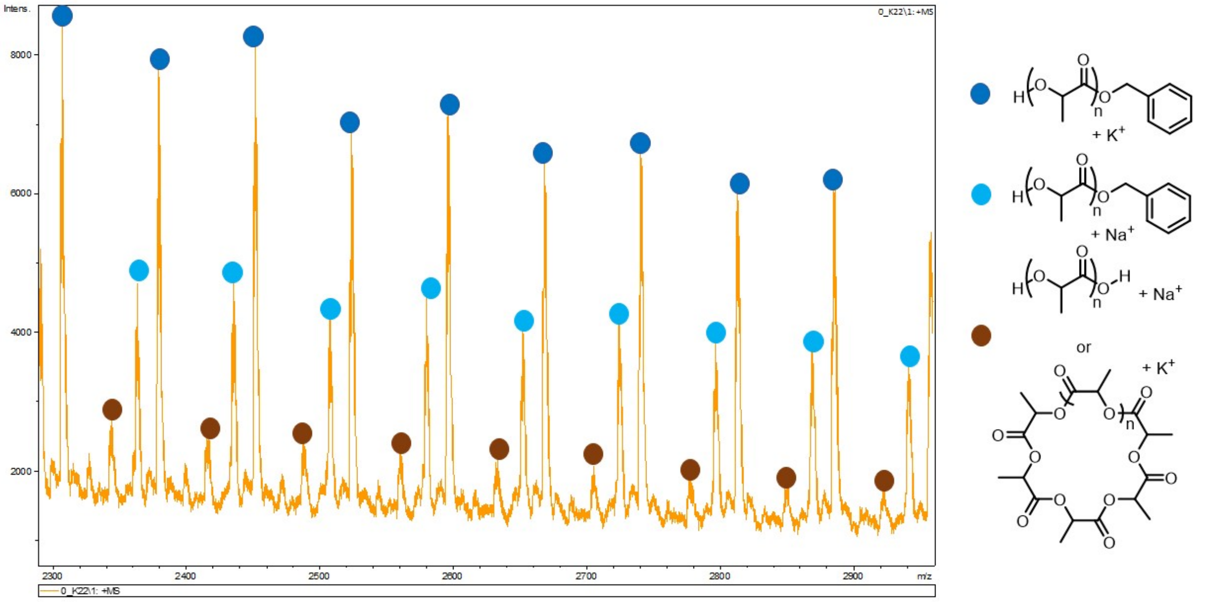

Figure S36. MALDI-ToF spectrum of PLA resulting from 76% conversion of *rac*-LA in the presence of a 1:1 mixture of complex **1** and **$Mg(OBn)_2$** (THF, R.T.).

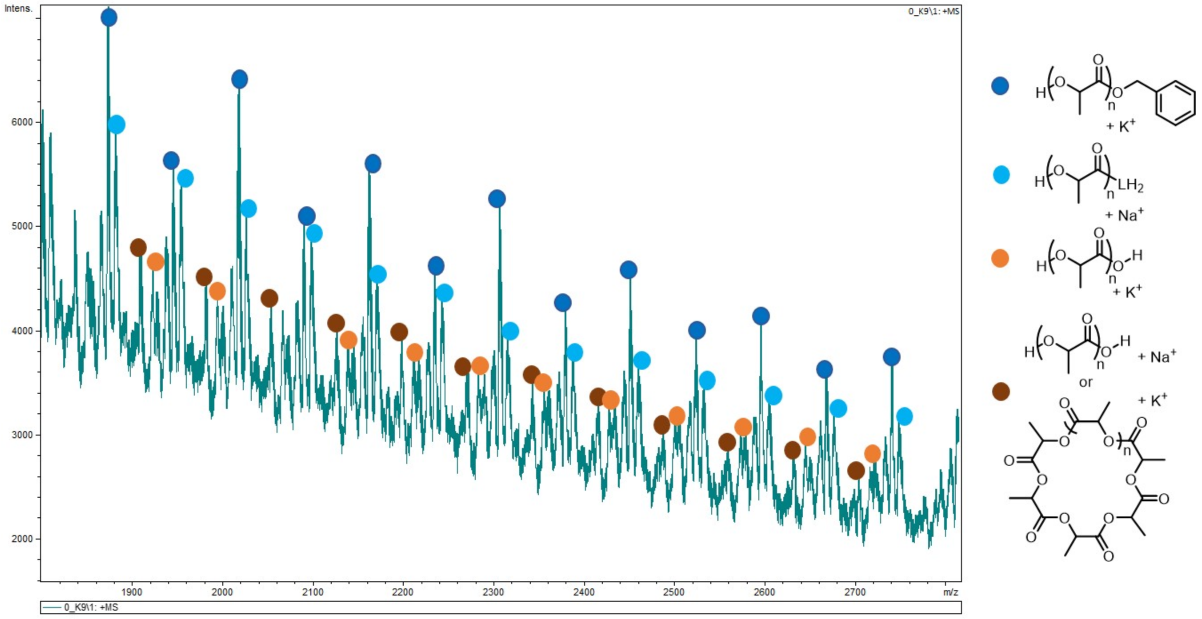

Figure S37. MALDI-ToF spectrum of PLA resulting from 83% conversion of *rac*-LA in the presence of a 1:1 mixture of complex **2** and **$Mg(OBn)_2$** (THF, R.T.).

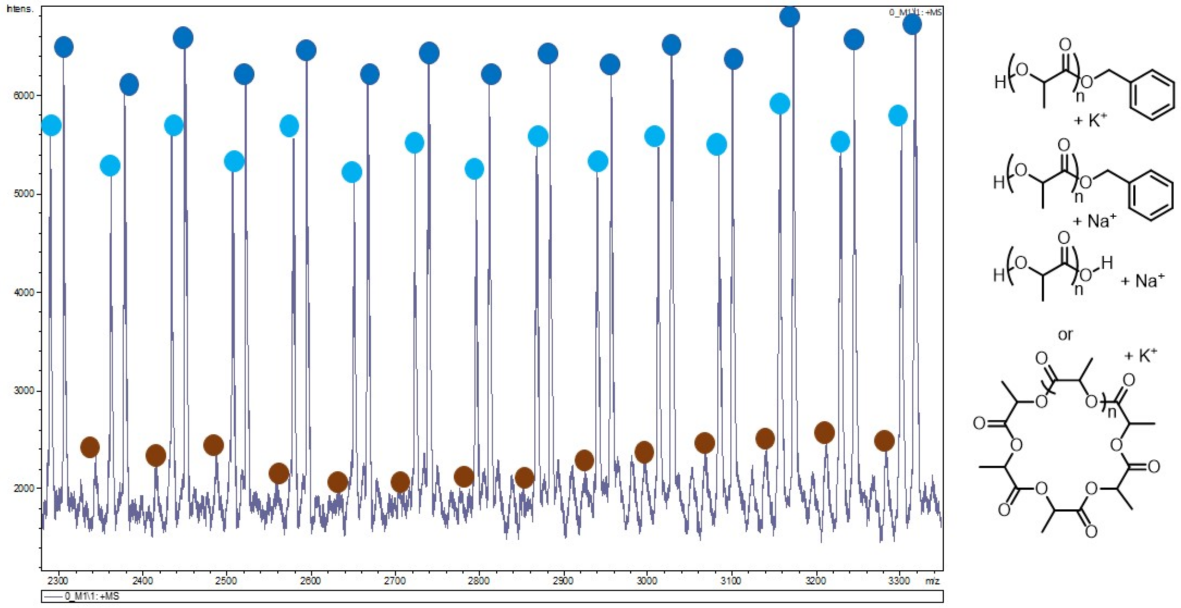

Figure S38. MALDI-ToF spectrum of PLA resulting from 50% conversion of *rac*-LA in the presence of a 1:1 mixture of complex **1** and **Zn(OBn)$_2$** (THF, R.T.).

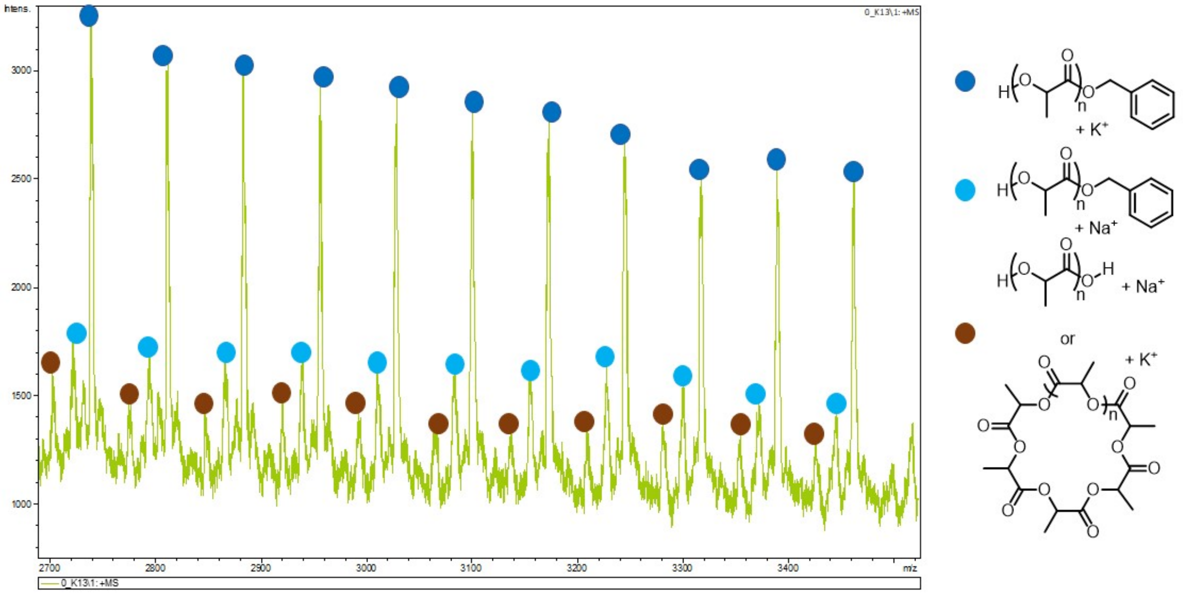

Figure S39. MALDI-ToF spectrum of PLA resulting from 89% conversion of *rac*-LA in the presence of a 1:1 mixture of complex **2** and **Zn(OBn)$_2$** (THF, R.T.).

Table S2. Results for the ROP of *rac*-LA in THF at R.T catalysed by 1:1 mixtures of **1** or **2** and **M(OBn)$_2$** (where M = Mg, Ca or Zn) at lower catalyst loadings.

Entry	**Cat.**	**No. of eq. of LA**	**Time (s)**	**Conv.**[a] **(%)**	$M_{n,obs}$[b] **(Da)**	$M_{n,calc}$[c] **(Da)**	**Đ**[b]
1[d]	**1**	100	5	94	16300	13500	1.68
2[d]	**2**	100	5	94	16500	13500	1.82
3	**1**	200	5	36	-	-	-
4	**2**	200	5	33	-	-	-
5	**Ca(OBn)$_2$**	200	5	19	5200	2700	1.30
6	**Mg(OBn)$_2$**	200	5	9	-	-	-
7	**Zn(OBn)**$_2$	200	5	17	-	-	-
8	**1** + **Ca(OBn)$_2$**	200	5	74	20200	10700	1.88
9	**2** + **Ca(OBn)$_2$**	200	5	86	18300	12400	2.22
10	**1** + **Mg(OBn)$_2$**	200	5	44	13900	6300	1.58
11	**2** + **Mg(OBn)$_2$**	200	5	86	18300	12400	1.87
12	**1** + **Zn(OBn)$_2$**	200	5	34	6800	4900	1.39
13	**2** + **Zn(OBn)$_2$**	200	5	71	14100	10200	1.67
14	**1**	300	5	27	-	-	-
15	**Zn(OBn)$_2$**	300	5	5	-	-	-
16	**1** + **Zn(OBn)$_2$**	300	5	45	13400	9700	1.65
17	**1** + **Ca(OBn)$_2$**	300	5	65	24700	14100	1.69
18	**1** + **Ca(OBn)$_2$**	500	60	57	29500	20500	1.74
19	**1** + **Ca(OBn)$_2$**	1000	60	33	24900	23800	1.51
20	**2** + **Ca(OBn)$_2$**	300	5	66	28100	14300	1.75
21	**2** + **Ca(OBn)$_2$**	500	60	73	28900	26300	1.66
22	**2** + **Ca(OBn)$_2$**	1000	60	35	31400	25200	1.65
23	**1** + **Mg(OBn)$_2$**	300	5	42	20800	9100	1.56
24	**1** + **Mg(OBn)$_2$**	500	60	23	11300	8300	1.46
25	**1** + **Mg(OBn)$_2$**	1000	60	14	-	-	-
26	**2** + **Mg(OBn)$_2$**	300	5	69	31200	14900	1.49
27	**2** + **Mg(OBn)$_2$**	500	60	39	23700	14100	1.60
28	**2** + **Mg(OBn)$_2$**	1000	60	17	-	-	-

[LA] = 1 M in THF. Catalyst(s) and LA pre-stirred separately for 1 min in THF at R.T. before mixing. [a] Conversion calculated using ^{1}H NMR spectroscopy. [b] $M_{n,obs}$ and Đ determined by SEC using polystyrene standards in THF. Values corrected by Mark-Houwink factor (0.58).[6] [c] $M_{n,calc}$ of polymers calculated from the monomer conversion $M_{n,calc}$ = M_0 x ([M]/[I]) x conversion assuming 2 chains per catalyst. [d] 1 eq. BnOH used. $M_{n,calc}$ of polymers calculated assuming 1 chain per catalyst.

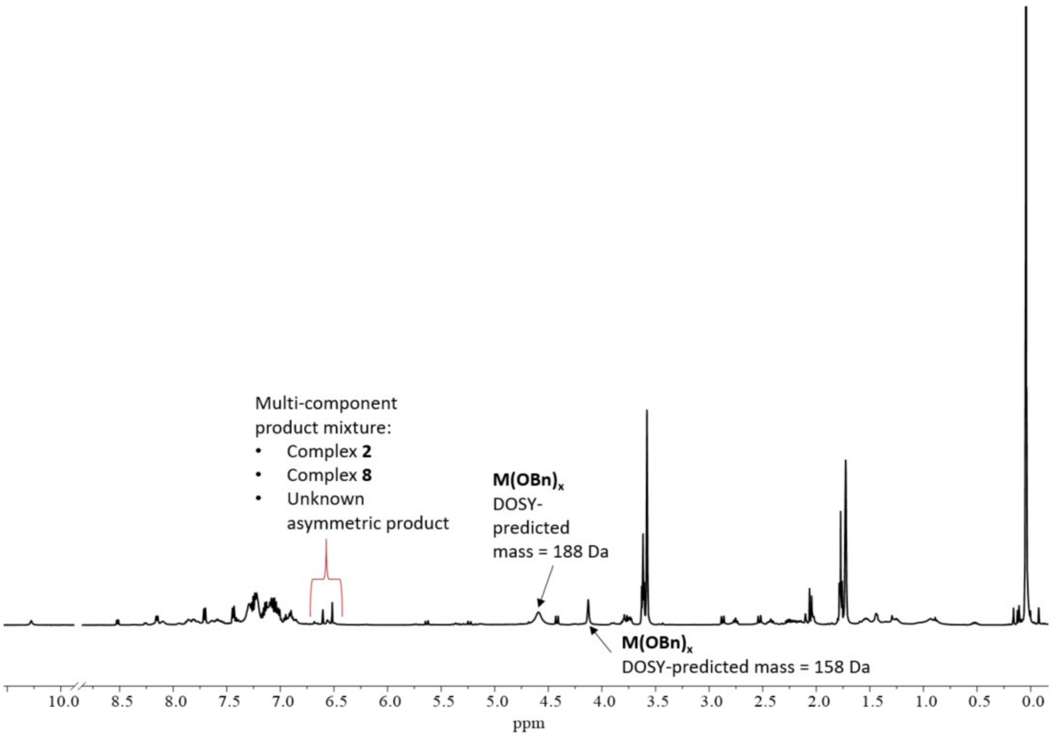

Figure S40. ^{1}H NMR spectrum of a 1:1 mixture of complex **2**:**Mg(OBn)$_2$** in THF-d_8 at R.T.

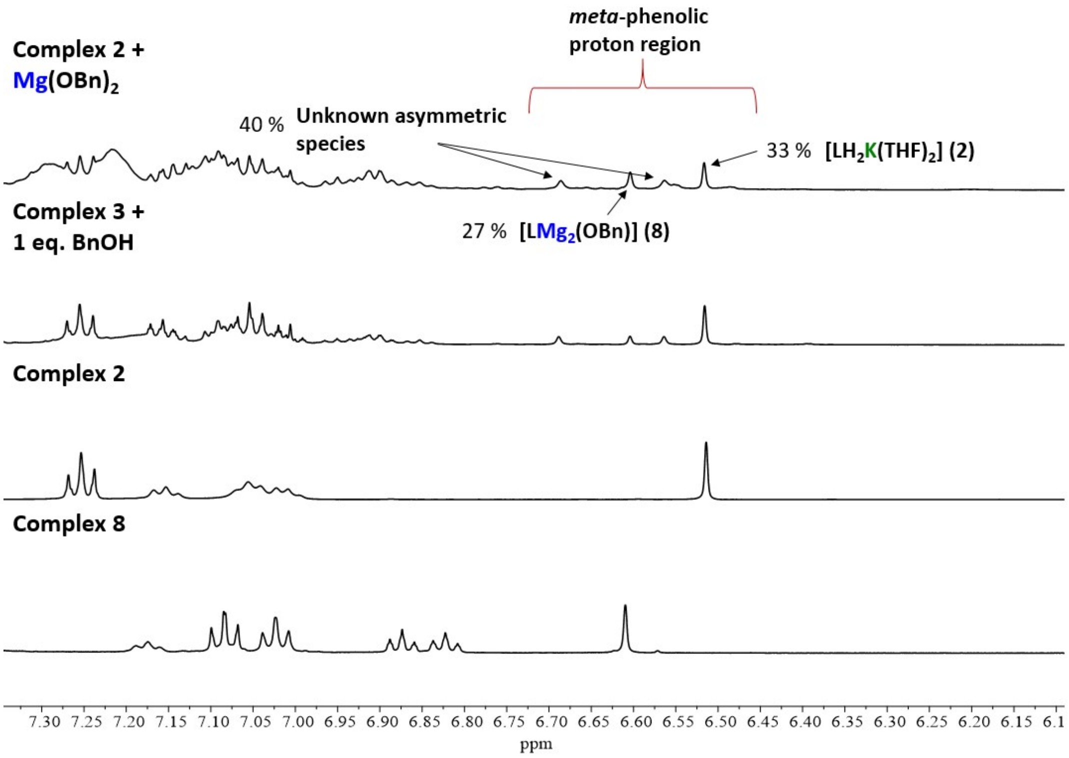

Figure S41. Overlaid aromatic region of the ^{1}H NMR spectra of a 1:1 mixture of complex **2**:**Mg(OBn)$_2$**, alcoholysis products from reaction of complex **3** with 1 eq. BnOH, and complexes **2** (**[LH$_2$K(THF)$_2$]**) and **8** (**[LMg$_2$OBn]**) in THF-d_8 at R.T.

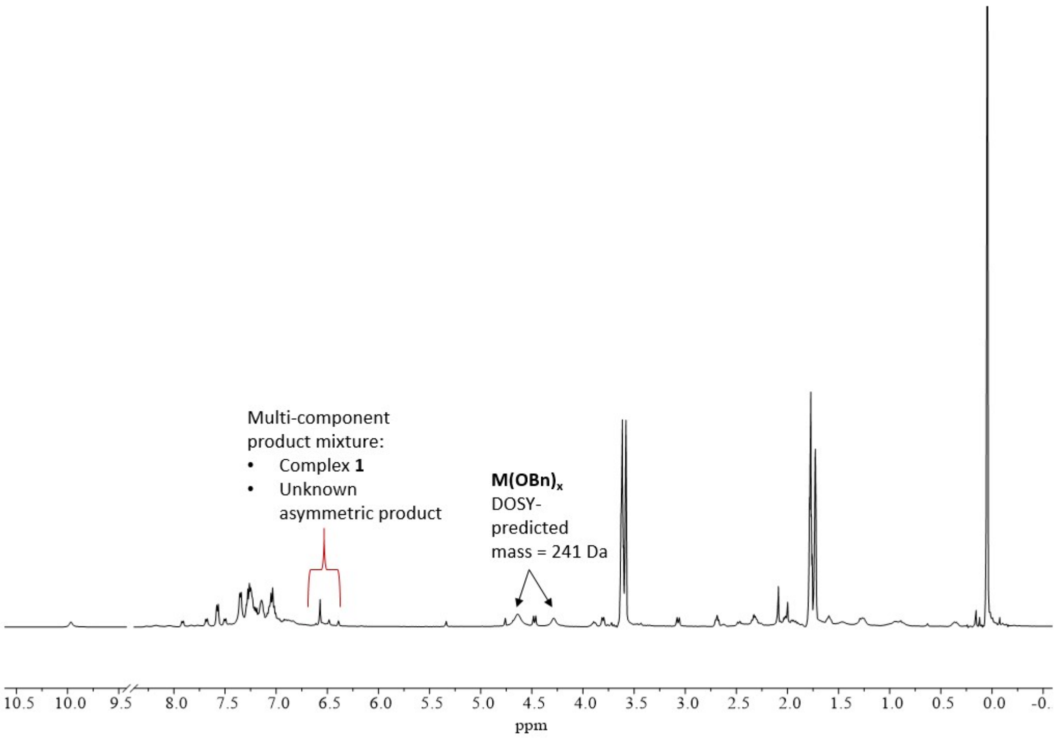

Figure S42. ^{1}H NMR spectrum of a 1:1 mixture of complex **1**:**Ca(OBn)$_2$** in THF-d_8 at R.T.

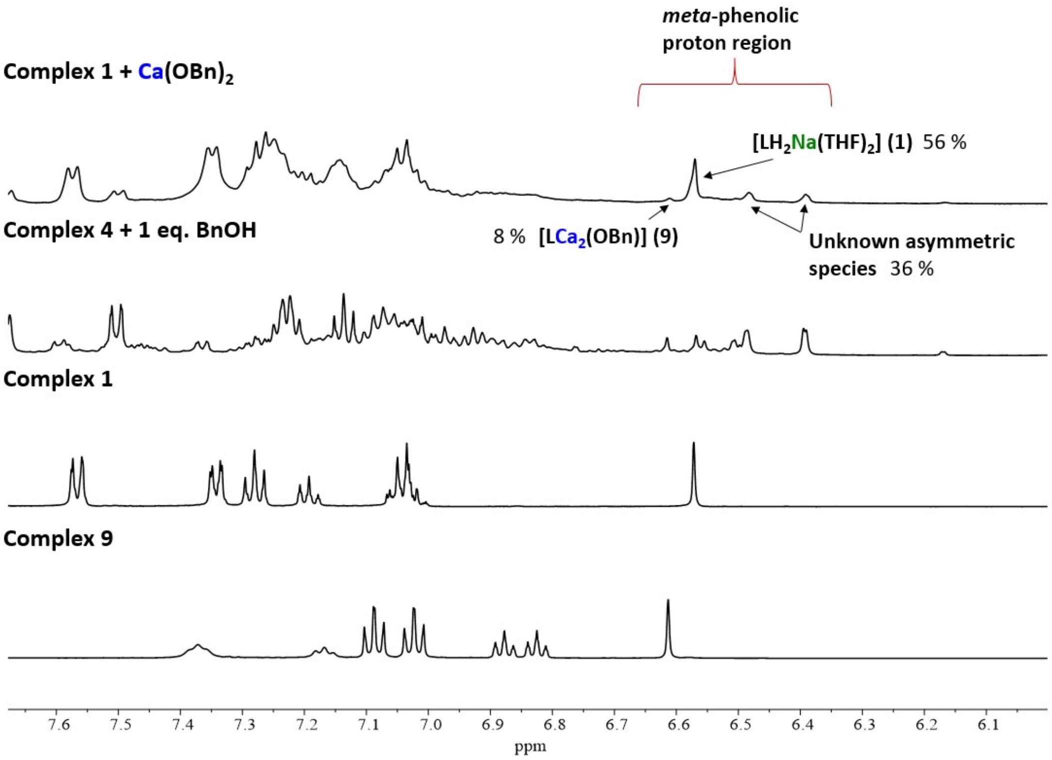

Figure S43. Overlaid aromatic region of the ^{1}H NMR spectra of a 1:1 mixture of complex **1**:**Ca(OBn)$_2$**, alcoholysis products from reaction of complex **4** with 1 eq. BnOH, and complexes **1** (**[LH$_2$Na(THF)$_2$]**) and **9** (**[LCa$_2$OBn]**) in THF-d_8 at R.T.

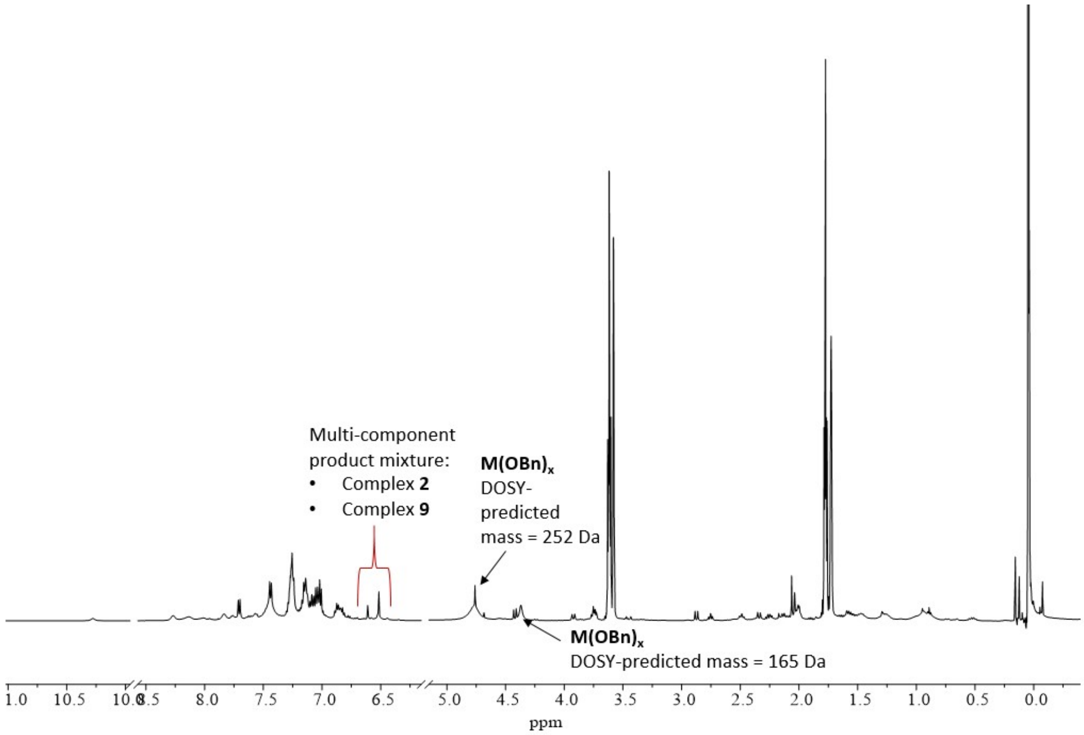

Figure S44. ^{1}H NMR spectrum of a 1:1 mixture of complex **2**:**Ca(OBn)$_2$** in THF-d_8 at R.T.

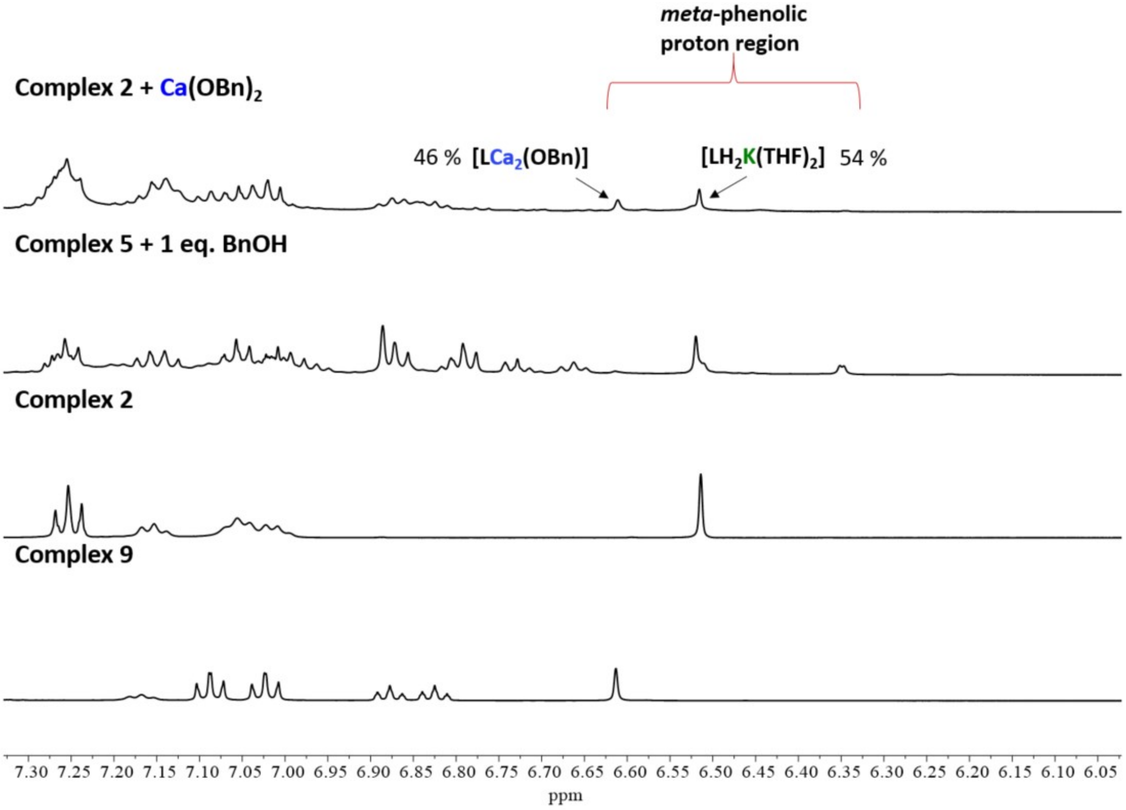

Figure S45. Overlaid aromatic region of the ^{1}H NMR spectra of a 1:1 mixture of complex **2**:**Ca(OBn)$_2$**, alcoholysis products from reaction of complex **5** with 1 eq. BnOH, and complexes **2** (**[LH$_2$K(THF)$_2$]**) and **9** (**[LCa$_2$OBn]**) in THF-d_8 at R.T.

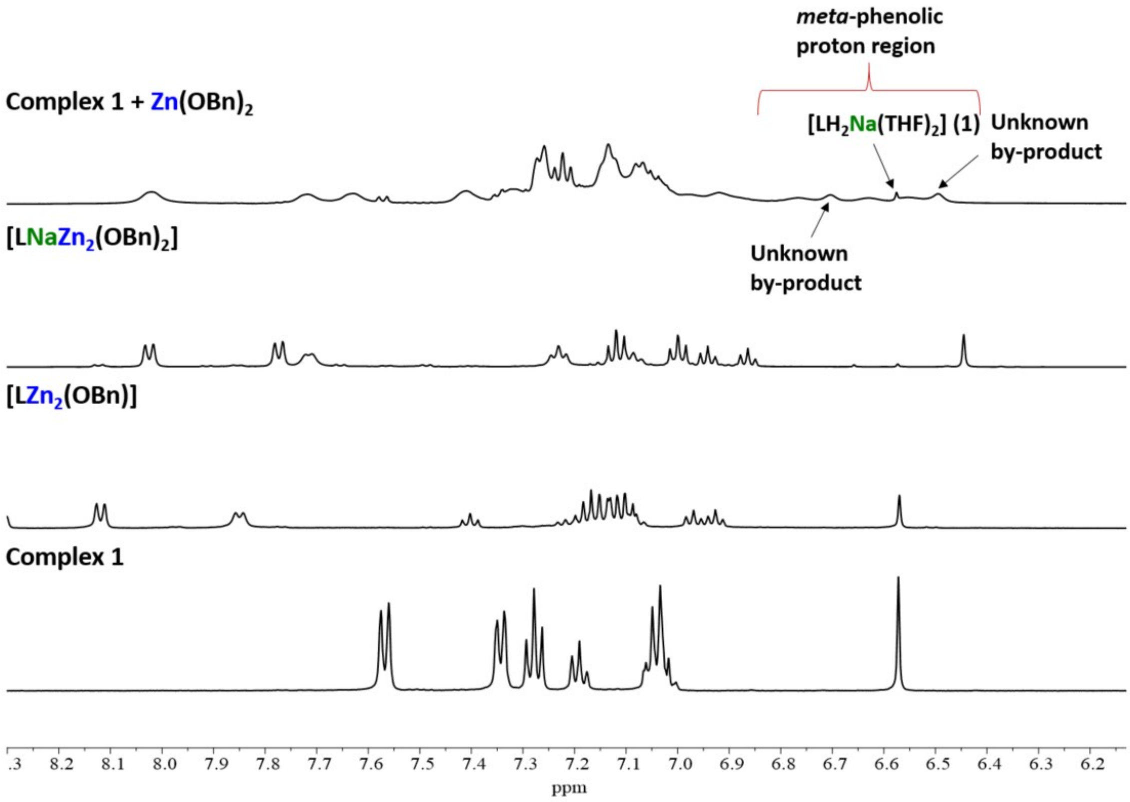

Figure S46. Overlaid aromatic region of the ^{1}H NMR spectra of a 1:1 mixture of complex **1**:**Zn(OBn)$_2$** (as used in polymerisation studies (Tables 1 and S2)) and complexes **[LNaZn$_2$(OBn)$_2$]**, **[LZn$_2$(OBn)]** and **1** (**[LH$_2$Na(THF)$_2$]**) in THF-d_8 at R.T. Interestingly, the 1:1 mixture of **1**:**Zn(OBn)$_2$** gave no ^{1}H NMR resonances for **[LNaZn$_2$(OBn)$_2$]**[2] or **[LZn$_2$OBn]**,[5] which contrasts with the *in situ* formation of **8-9** from **1-2** and **Mg(OBn)$_2$** or **Ca(OBn)$_2$**.

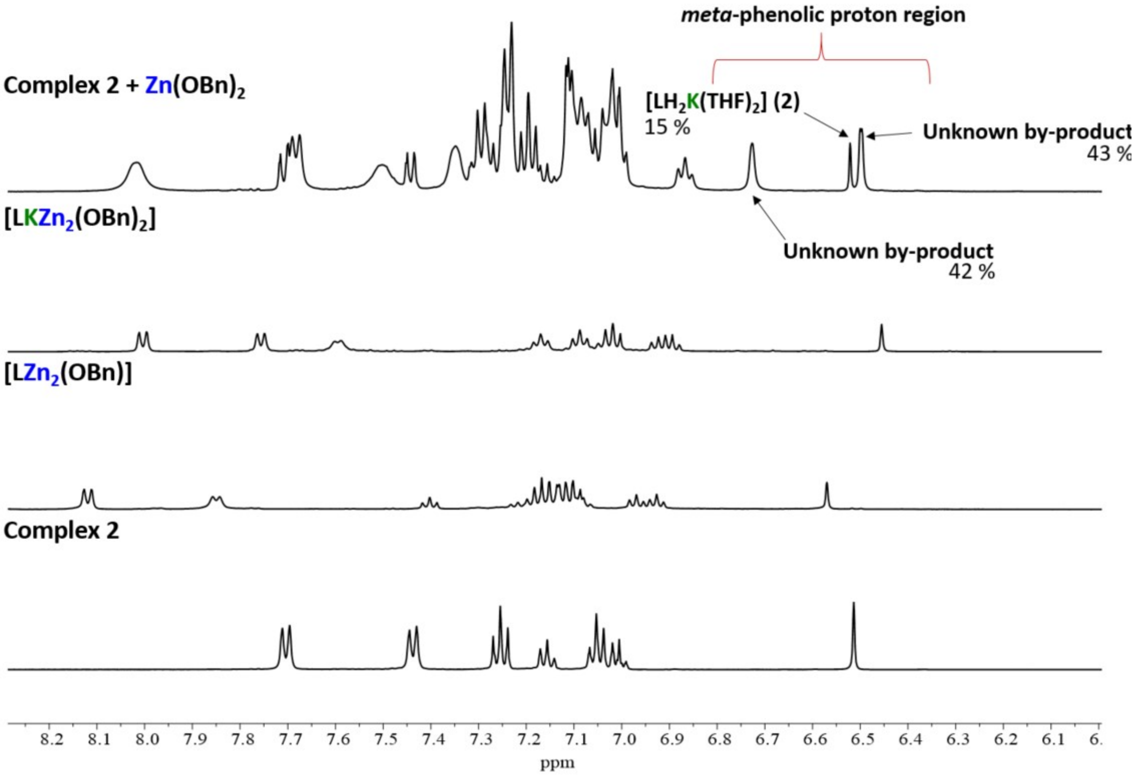

Figure S47. Overlaid aromatic region of the ^{1}H NMR spectra of a 1:1 mixture of complex **2**:**Zn(OBn)$_2$** (as used in polymerisation studies (Tables 1 and S2)), and complexes **[LKZn$_2$(OBn)$_2$]**, **[LZn$_2$(OBn)]** and **2** (**[LH$_2$K(THF)$_2$]**) in THF-d_8 at R.T. Interestingly, the 1:1 mixture of **2**:**Zn(OBn)$_2$** gave no ^{1}H NMR resonances for **[LKZn$_2$(OBn)$_2$]**[2] or **[LZn$_2$OBn]**,[5] which contrasts with the *in situ* formation of **8-9** from **1-2** and **Mg(OBn)$_2$** or **Ca(OBn)$_2$**.

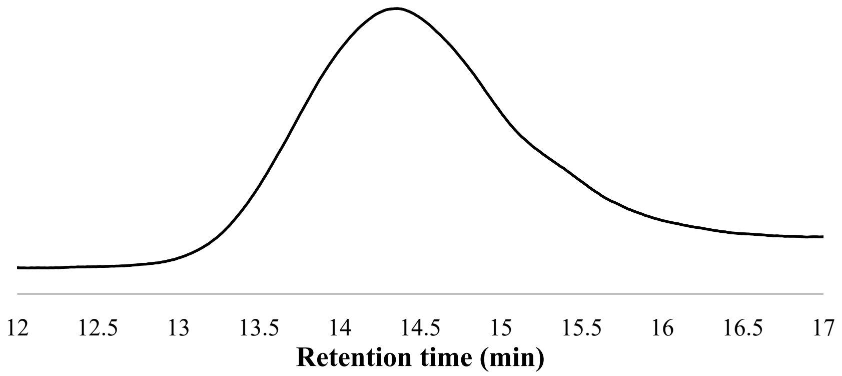

Figure S48. Example SEC trace of PLA generated in the presence of complex **3** + 1 eq. BnOH in THF at R.T. (Entry 2, Table 1).

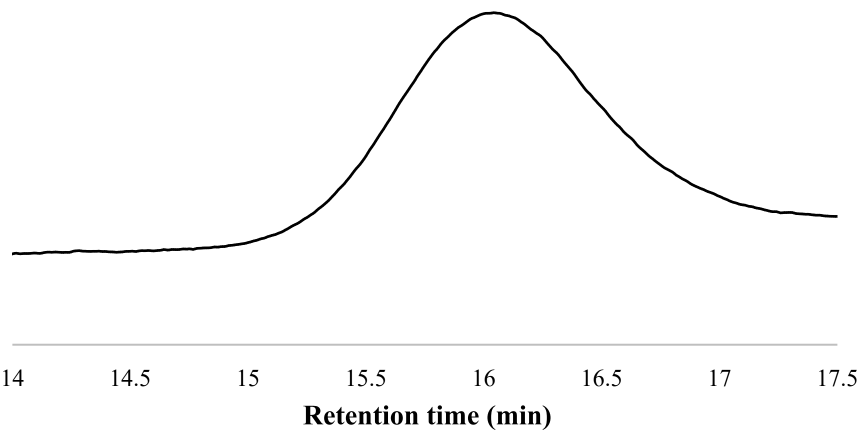

Figure S49. Example SEC trace of PLA generated in the presence of complex **4** + 1 eq. BnOH in THF at R.T. (Entry 4, Table 1).

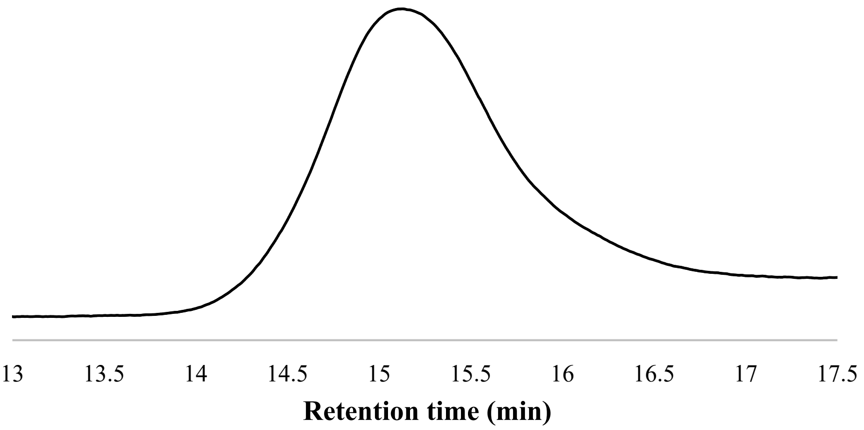

Figure S50. Example SEC trace of PLA generated in the presence of complex **5** + 1 eq. BnOH in THF at R.T. (Entry 7, Table 1).

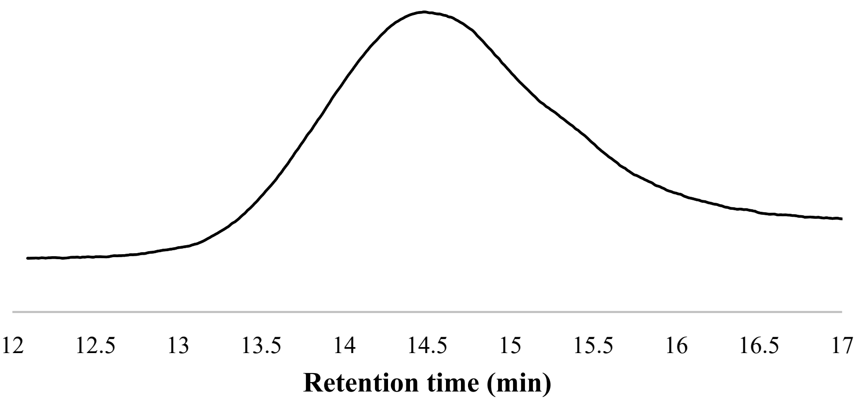

Figure S51. Example SEC trace of PLA generated in the presence of a 1:1 complex **1**:**Ca(OBn)$_2$** mixture in THF at R.T. (Entry 14, Table 1).

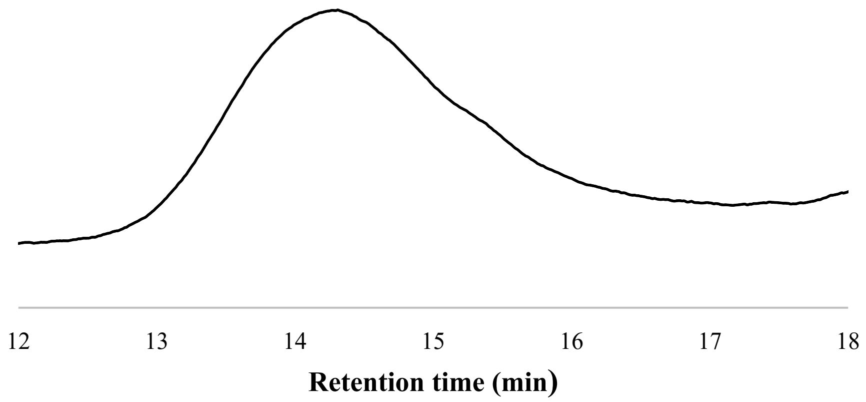

Figure S52. Example SEC trace of PLA generated in the presence of a 1:1 complex **2**:**Ca(OBn)$_2$** mixture in THF at R.T. (Entry 15, Table 1).

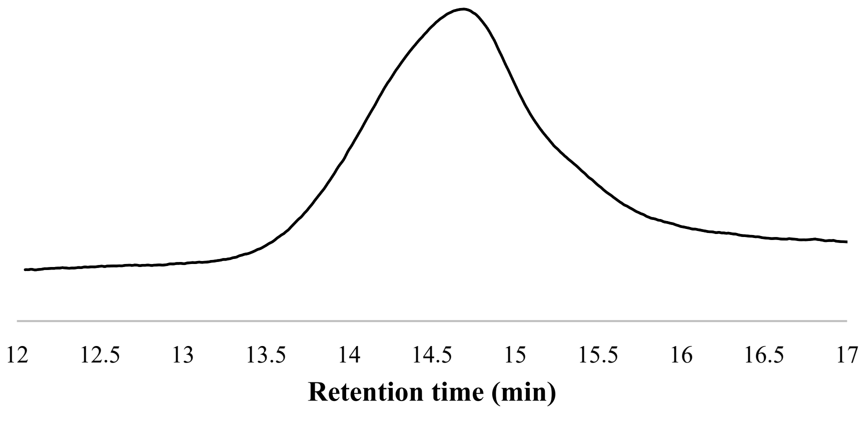

Figure S53. Example SEC trace of PLA generated in the presence of a 1:1 complex **2**:**Mg(OBn)$_2$** mixture in THF at R.T. (Entry 17, Table 1).

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