catalysts

MDPI

Supporting information

Polymetallic Group 4 Complexes: Catalysts for the Ring Opening Polymerisation of *rac*-Lactide

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Contents

1. ^{1}H NMR and ^{13}C NMR spectra
2. ESI High Resolution Mass Spectrometry data
3. SCXRD Data complexes 5-8
4. ^{1}H NMR spectra of the PLA produced in the ROP *rac*-lactide
5. Supplementary polymerisation data

1. ^{1}H NMR and ^{13}C NMR spectra

4

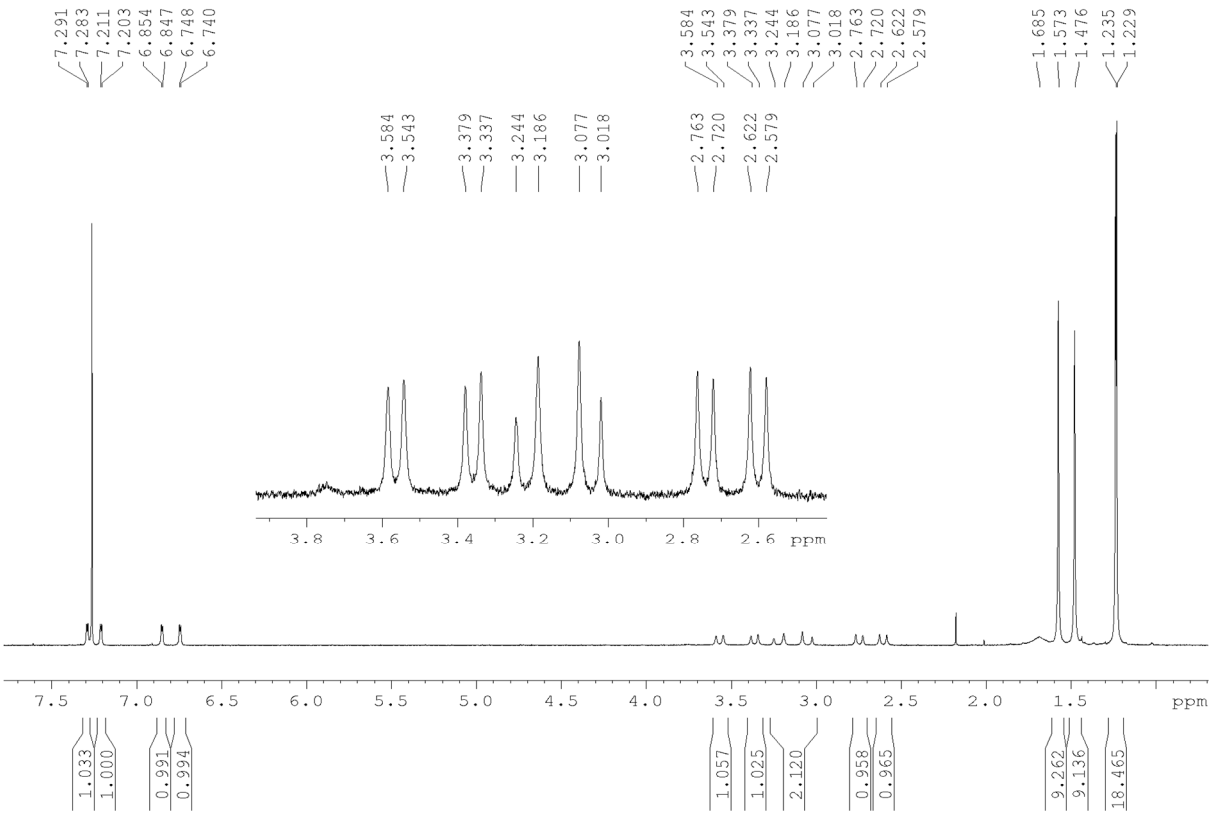

Figure S1. ^{1}H NMR spectrum of complex **4** (300 MHz, $CDCl_3$, 25 °C).

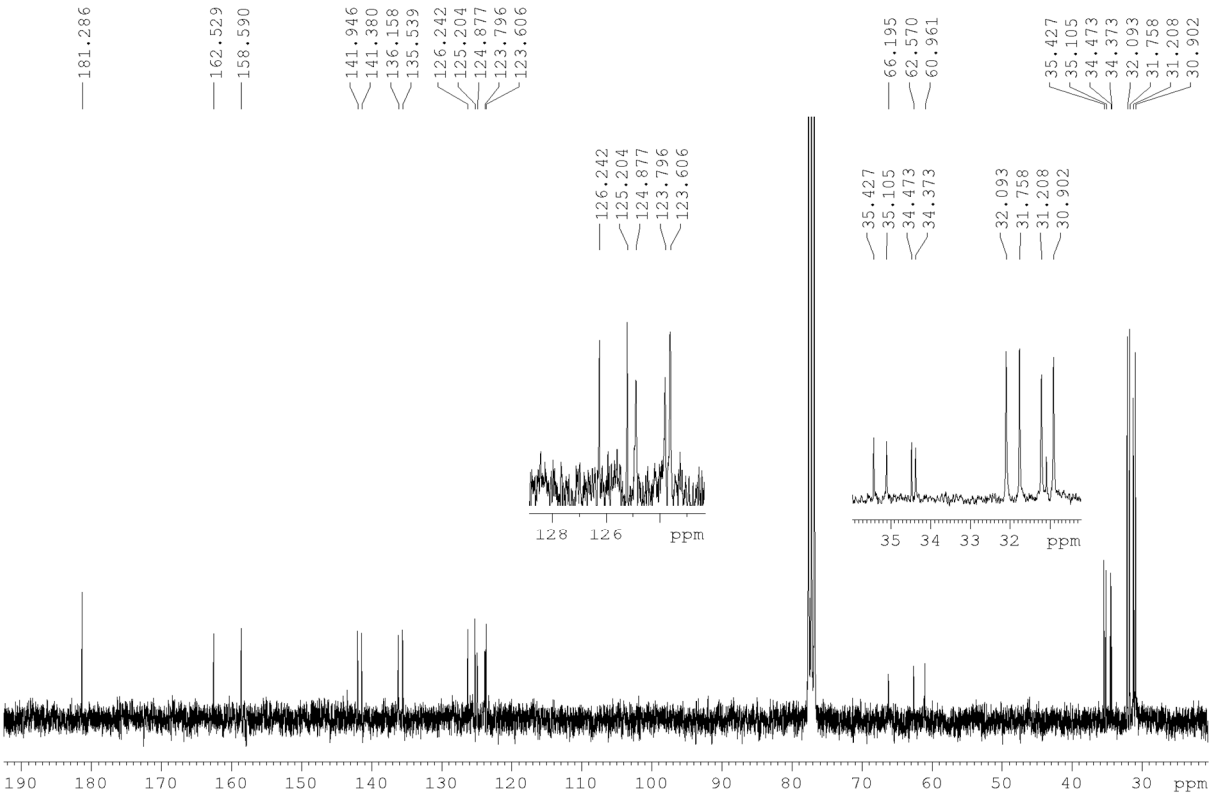

Figure S2. ^{13}C NMR spectrum of complex 4 (75.5 MHz, $CDCl_3$, at 25 °C).

5

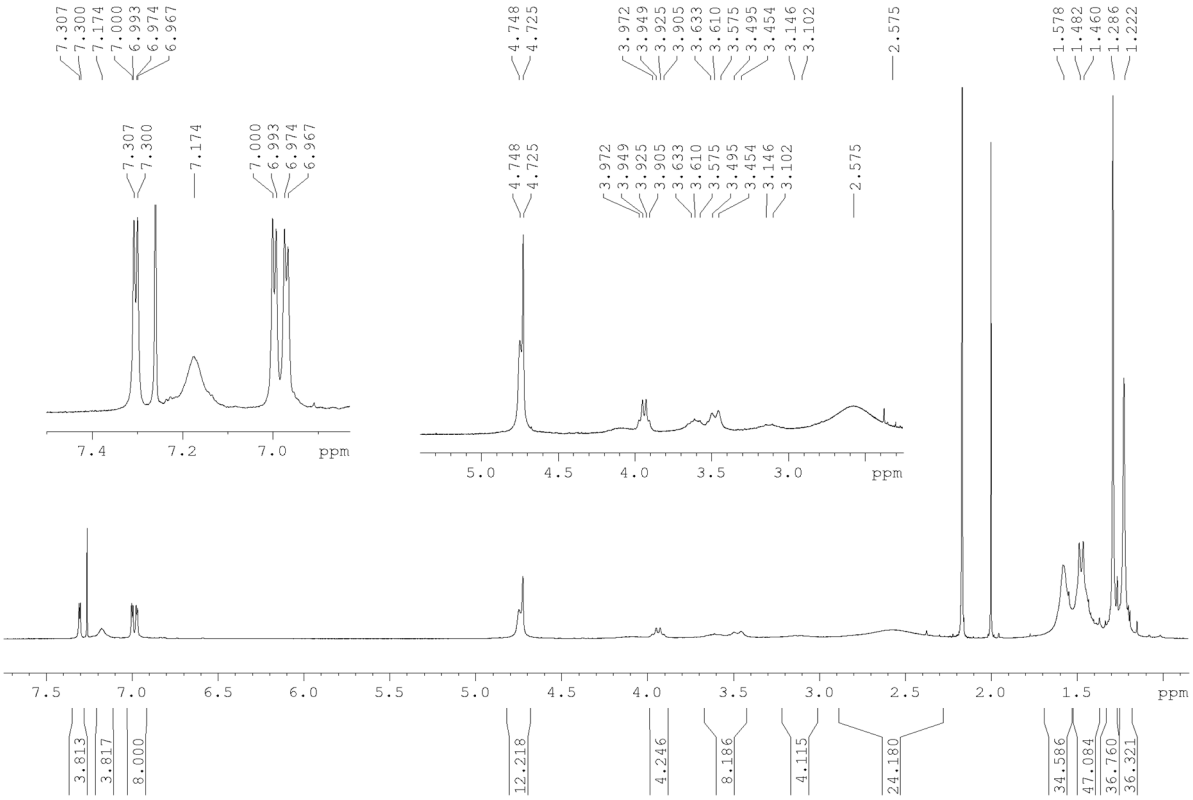

Figure S3. ^{1}H NMR spectrum of complex 5 (300 MHz, $CDCl_3$, 25 °C).

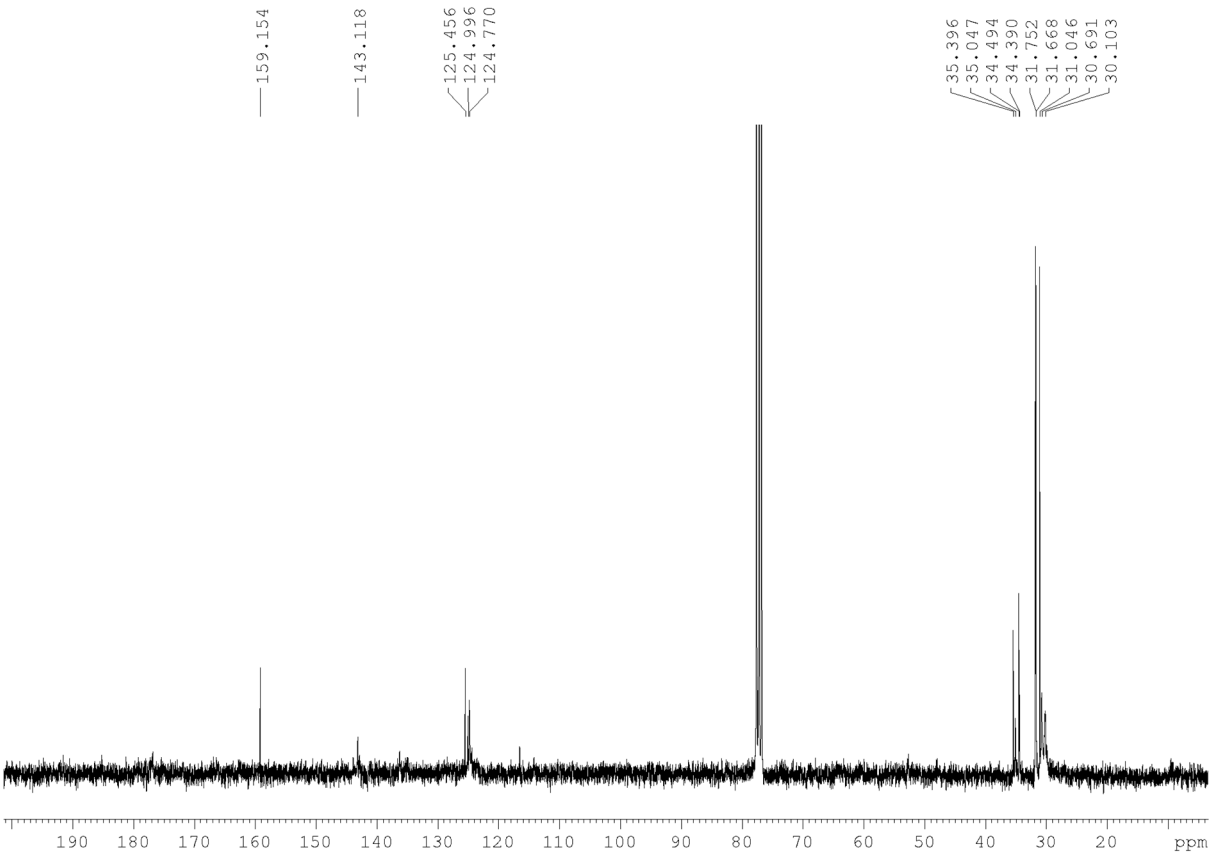

Figure S4. ^{13}C NMR spectrum of complex 5 (75.5 MHz, $CDCl_3$, at 25 °C).

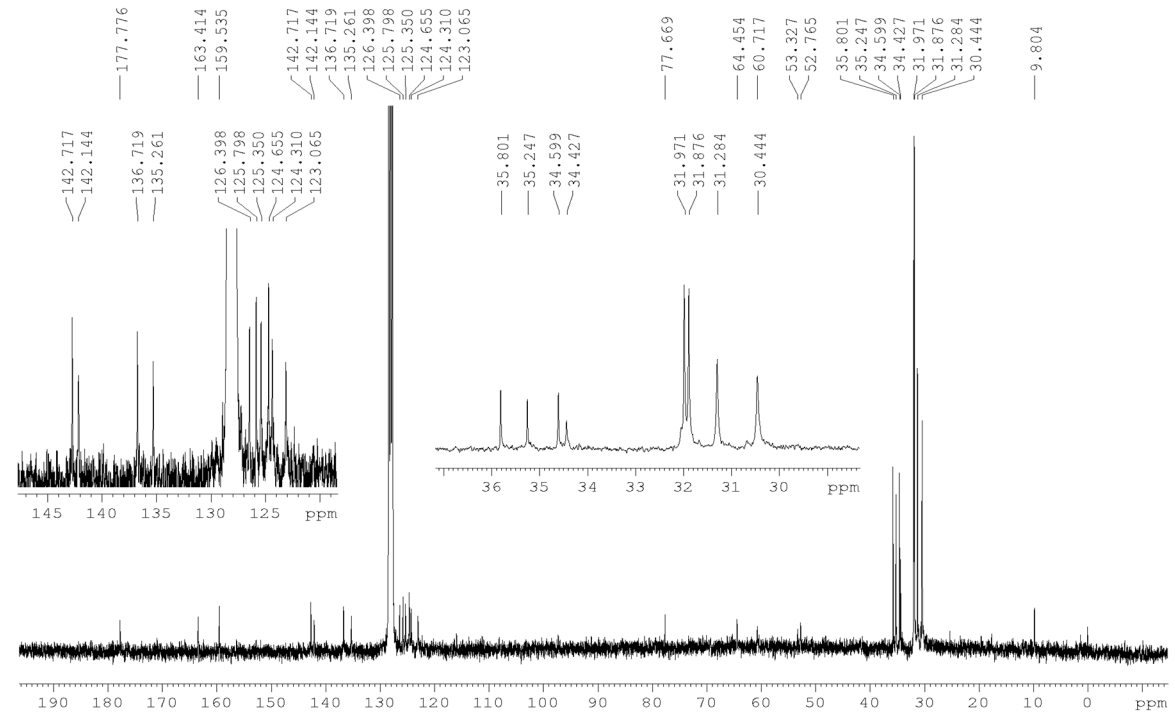

Figure S5. ^{13}C NMR spectrum of complex 5 (75.5 MHz, C_6D_6, at 25 °C).

6

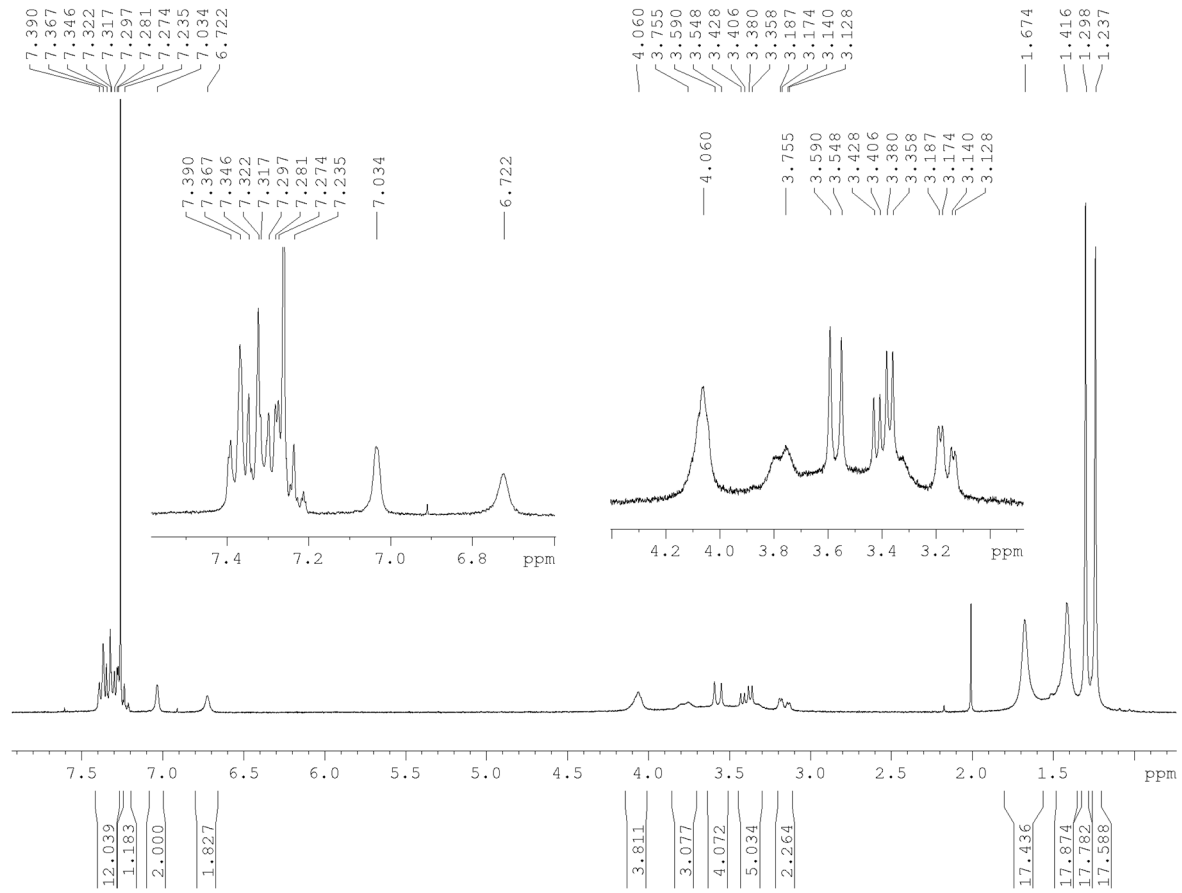

Figure S6. ^{1}H NMR spectrum of complex 6 (300 MHz, $CDCl_3$, 25 °C).

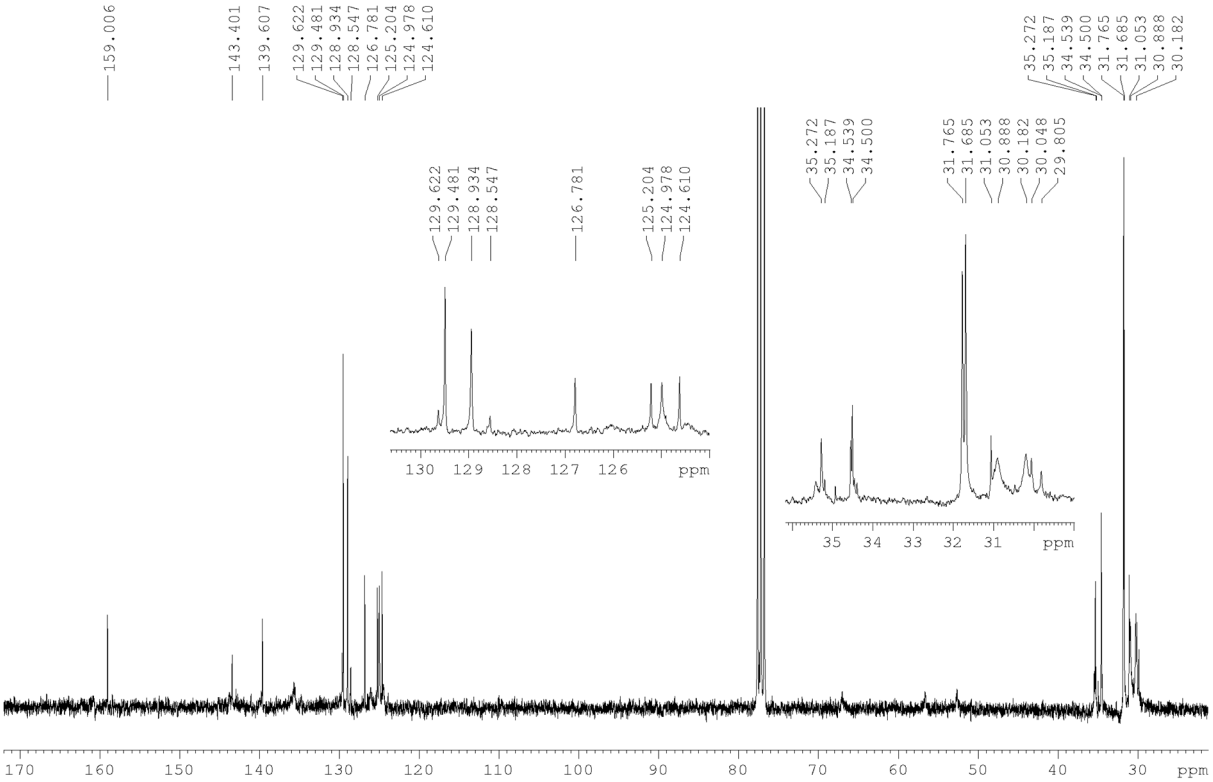

Figure S7. ^{13}C NMR spectrum of complex 6 (75.5 MHz, $CDCl_3$, at 25 °C).

7

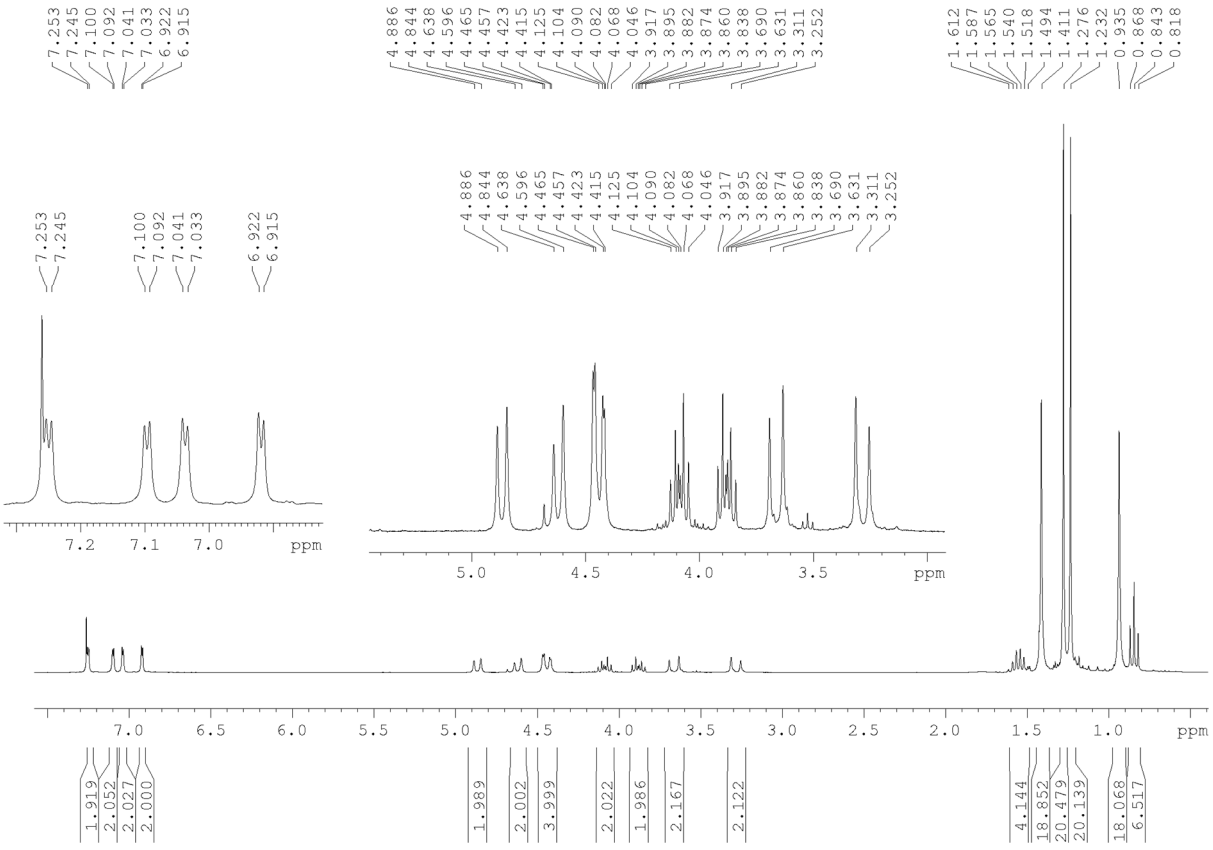

Figure S8. ^{1}H NMR spectrum of complex 7 (300 MHz, $CDCl_3$, 25 °C).

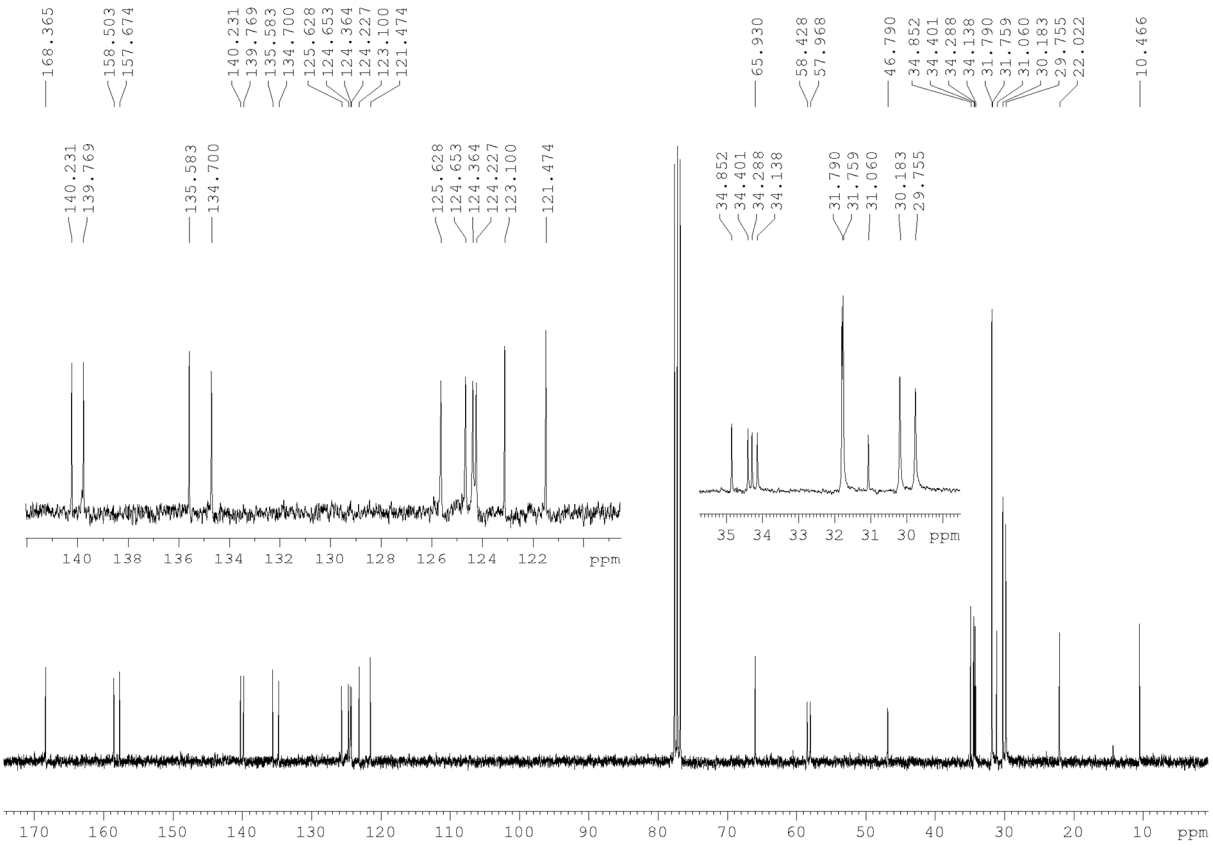

Figure S9. ^{13}C NMR spectrum of complex 7 (75.5 MHz, $CDCl_3$, at 25 °C).

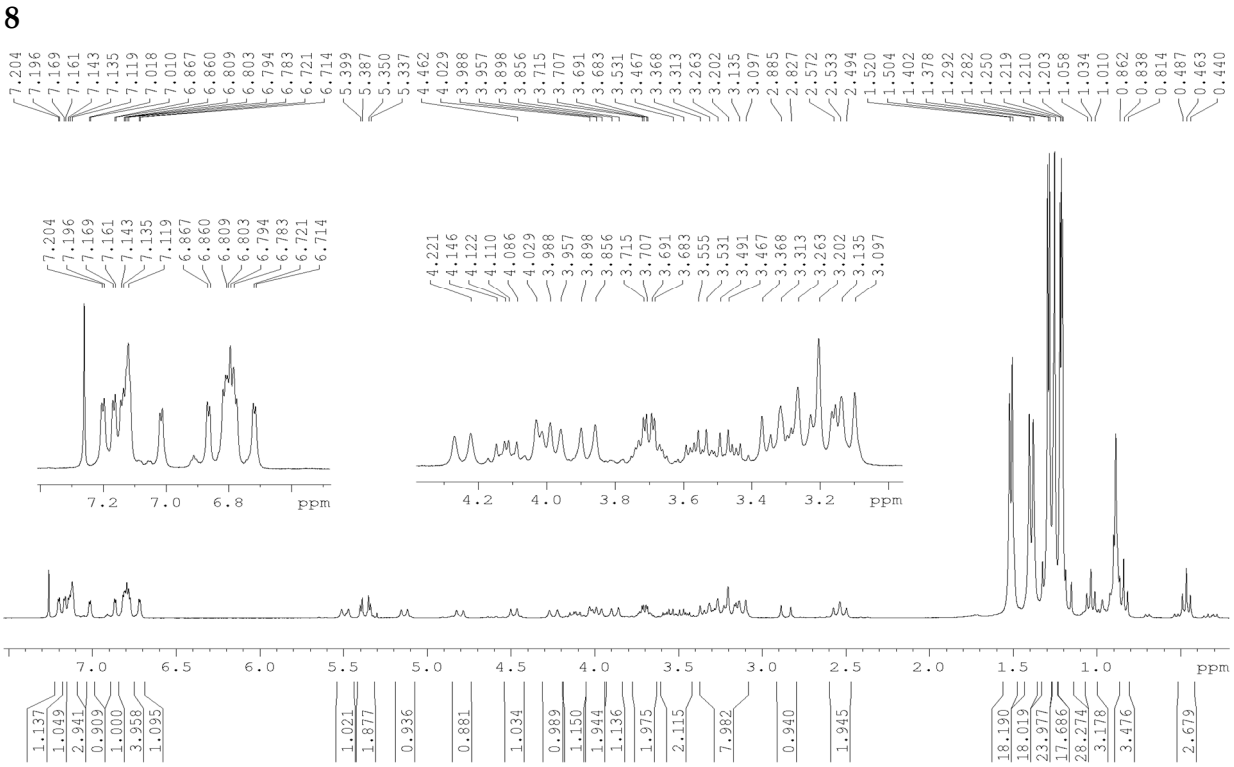

Figure S10. ^{1}H NMR spectrum of complex 8 (300 MHz, $CDCl_3$, 25 °C).

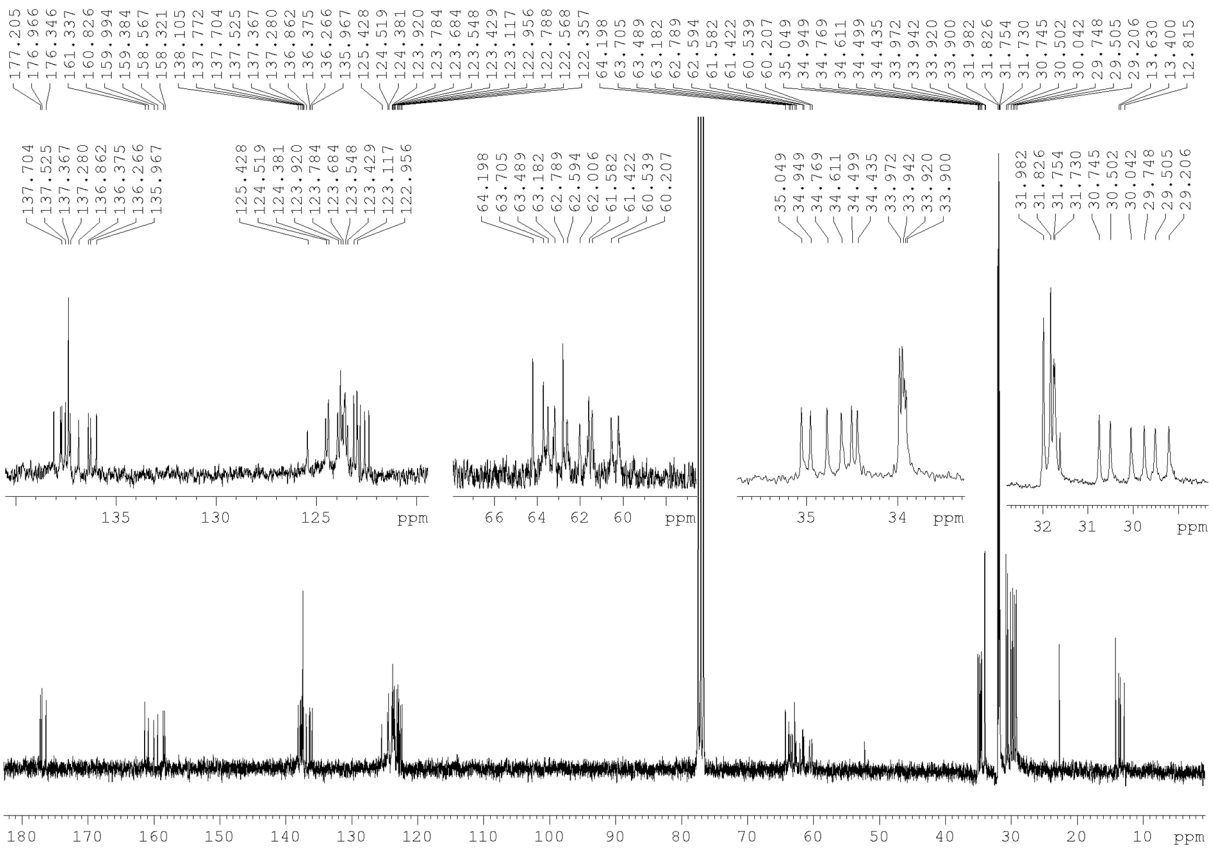

Figure S11. ^{13}C NMR spectrum of complex 8 (75.5 MHz, $CDCl_3$, at 25 °C).

2. ESI High Resolution Mass Spectrometry data

4

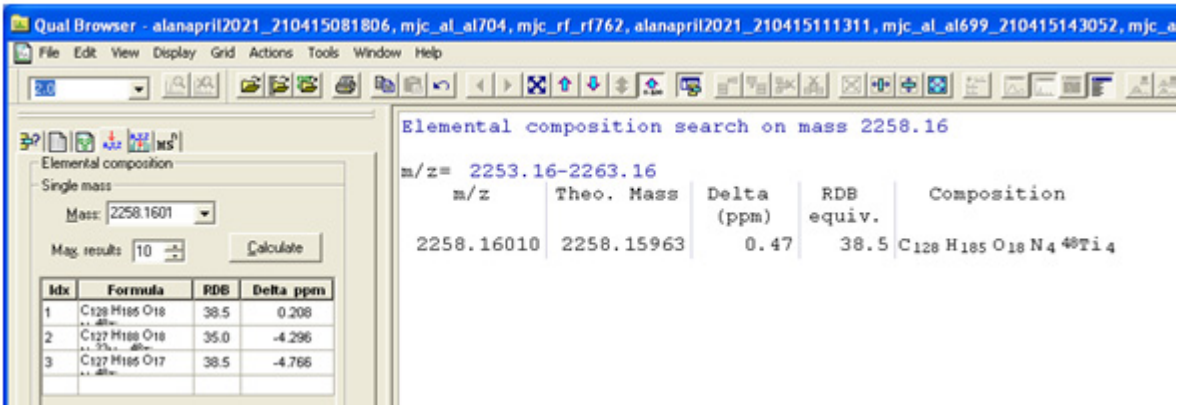

Figure S12. HRMS data for complex 4.

5

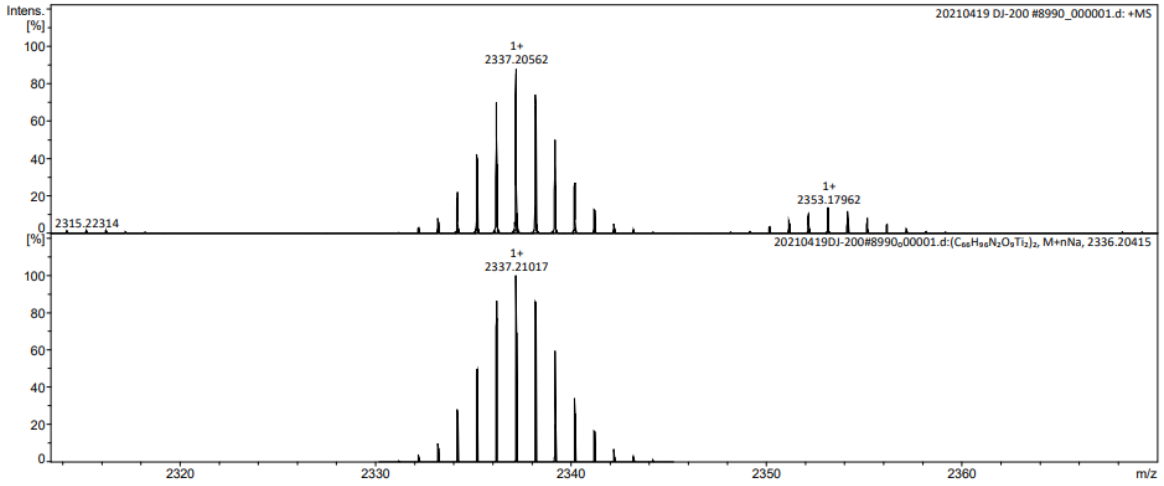

Figure S13. HRMS data for complex 5.

6

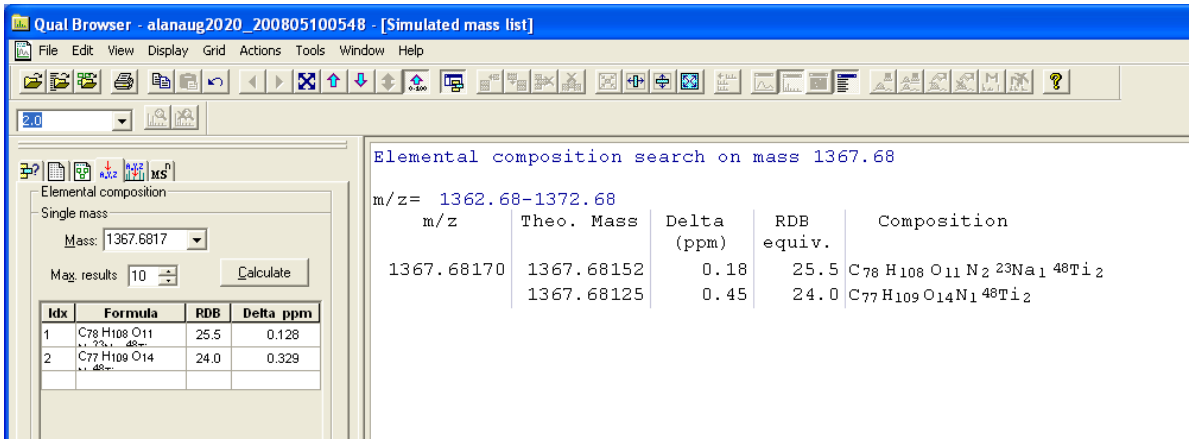

Figure S14. HRMS data for complex 6.

7

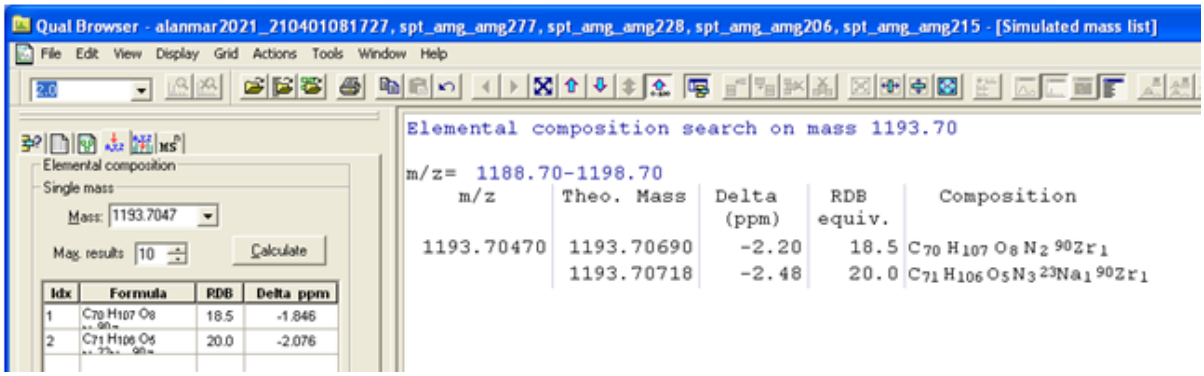

Figure S15. HRMS data for complex 7.

8

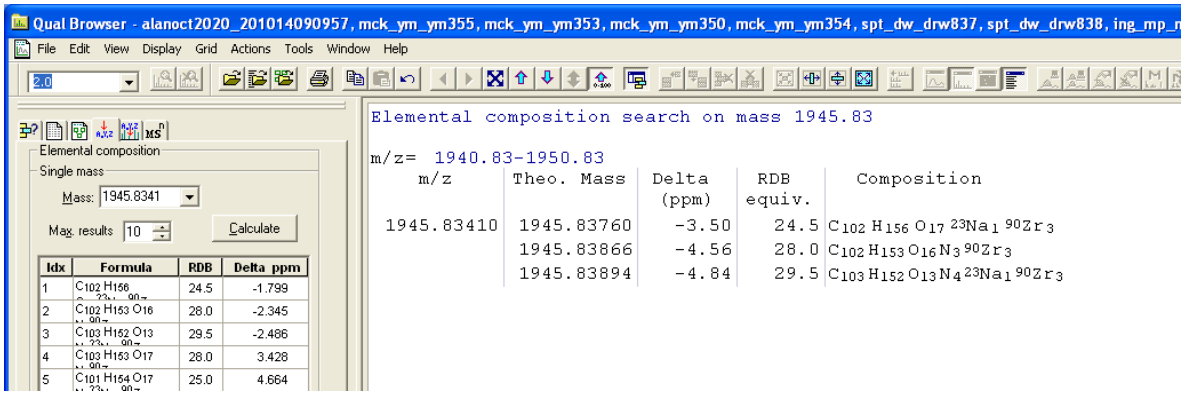

Figure S16. HRMS data for complex 8.

3. SCXRD Data complexes 5-8

Table S1. Crystallographic and refinement details for complexes 5-8.

Complex	**5**	**6**	**7**	**8**
Empirical formula	$C_{132}H_{200}N_4O_{22}Ti_4$	$C_{78}H_{113}N_2O_{14}Ti_2$	$C_{79}H_{127}N_2O_8Zr$	$C_{108}H_{164}Cl_8N_4O_{16}Zr_3$
Formula weight	2386.55	1398.50	1324.04	2331.68
Temperature/K	100.0	101.0	100	100.0
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	P1	C2/c	P-1	$P2_1/c$
a/Å	15.0160(3)	53.205(3)	11.765(12)	27.937(4)
b/Å	16.6810(3)	11.0906(6)	17.677(16)	16.546(3)
c/Å	16.7181(3)	29.7233(15)	19.150(18)	28.529(5)
α/°	85.4102(10)	90	84.00(3)	90
β/°	68.5703(9)	105.349(4)	75.13(4)	112.709(3)
γ/°	63.9006(9)	90	87.11(5)	90
Volume/Å^3	3484.25(12)	16913.3(16)	3827(6)	12165(4)
Z	1	8	2	4
ϱ_{calc}g/cm^3	1.137	1.098	1.149	1.273
μ/mm^{-1}	2.382	2.057	1.582	0.486
F(000)	1284.0	6008.0	1438.0	4896.0
Crystal size/mm^3	0.2 × 0.08 × 0.04	0.18 × 0.02 × 0.02	0.4 × 0.28 × 0.14	0.36 × 0.34 × 0.28
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.706 to 133.406	6.166 to 142.308	4.796 to 153	4.946 to 55.348
Index ranges	-17 ≤ h ≤ 17 -19 ≤ k ≤ 19 -19 ≤ l ≤ 19	-64 ≤ h ≤ 64 -13 ≤ k ≤ 13 -36 ≤ l ≤ 33	-14 ≤ h ≤ 14 -21 ≤ k ≤ 22 0 ≤ l ≤ 24	-36 ≤ h ≤ 36 -21 ≤ k ≤ 21 -35 ≤ l ≤ 34
Reflections collected	48607	173688	15318	190137
Independent reflections	22005 [R_{int} = 0.0762, R_{sigma} = 0.0948]	15996 [R_{int} = 0.4729, R_{sigma} = 0.2027]	15318 [R_{int} = 0.0340 R_{sigma} = 0.0521]	26560 [R_{int} = 0.0661, R_{sigma} = 0.0422]
Data/restraints/parameters	22005/16/1696	15996/57/943	15318/72/878	26560/6/1363
Goodness-of-fit on F^2	1.054	1.030	1.055	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1100	R_1 = 0.1365, wR_2 = 0.3464	R_1 = 0.0533, wR_2 = 0.1251	R_1 = 0.0864, wR_2 = 0.2234
Final R indexes [all data]	R_1 = 0.0781, wR_2 = 0.1243	R_1 = 0.2263, wR_2 = 0.4147	R_1 = 0.0636, wR_2 = 0.1335	R_1 = 0.1081, wR_2 = 0.2391
Largest diff. peak/hole / e Å^{-3}	0.31/-0.52	0.94/-0.95	0.69/-0.55	2.20/-2.01
Flack parameter	-0.017(4)			

Disorder existed in all four structures and distances and displacement parameters were restrained to achieve a converged refinement and chemically sensible model.

In **6** four molecules of $CDCl_3$ and one molecule of CH_3CN solvent was squeezed using the procedure implemented in OLEX2. The data were weak and not single which caused the very high Rint values. Many attempts were made to improve the model by changing scaling and integration parameters. However, the overall structure is clear.

In **7**, the structure was refined with hklf 5 data as a two component twin

List of restraints and constraints applied to the crystal data

for 5

distance restraints

DFIX 1.5 C44A C37 C45A C44A C46 C44A C47A C44A

SADI C28 C26 C27A C26 C27 C26 C29A C26 C29 C26

SADI Ti4 H20a Ti4 H20b

for 6

distance restraints

DFIX 1.5 C85 C37 C38 C37 C40 C37

SADI Ti1 H5a Ti1 H5b

SADI Ti2 H11a Ti2 H11b

FLAT C44 C45 C46 C47 C48 C49

DFIX -2.2 H3 H5a (must be more than 2.2 A apart)

displacement parameter restraints

EADP C85 C40

EADP C39 C38

EADP C87 C86

RIGU C37 C44 > C49 C85 C86 C87

for 7

twinned structure refined wth hklf 5 data as two components

distance restraints

DFIX 1.5 C4T C3S C4T C5S

DFIX 1.5 C68 C69 C70 C69

DFIX 1.5 C68 C69A C69A C70 C70 C69 C68 C69

DFIX 1.4 O4 C33 O4 C33A O4 C32 O8 C68

DFIX 1.5 C34 C33 C34 C35

DFIX 1.5 C5S C6S C5S C4T C4T C3S C3S C2S C1S C2S

DFIX 1.5 C34 C35 C34 C33

DFIX 1.5 C5S C4S C4S C3S

DFIX 1.5 C34A C33A C34 C33 C34 C35 C34A C35A

displacement parameter restraints

EADP C4S C4T

EADP C33 C33A

ISOR 0.01 0.02 C33A C33

RIGU C6S C5S C4S C4T C3S C2S

for 8

distance restraints

DFIX 1.5 C68A C65 C66 C65 C66A C65 C67 C65 C68 C65

DFIX 2.1 C68A C66A
displacement parameter restraints
EADP O16A O16

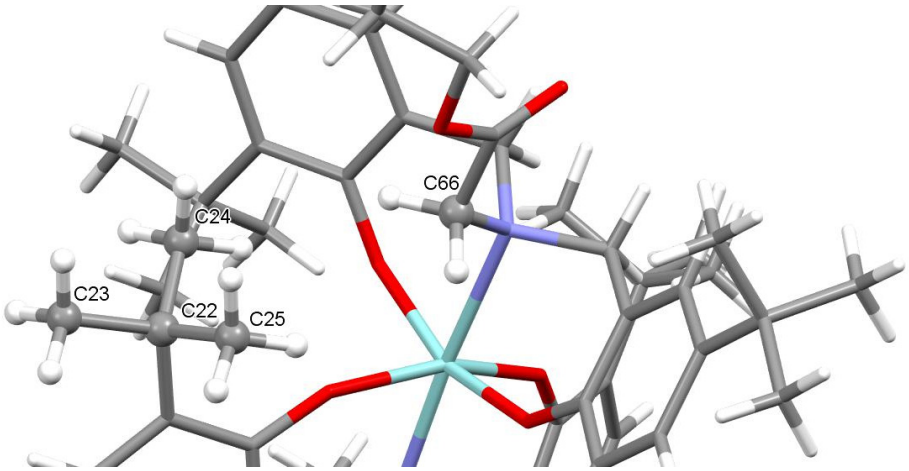

Figure S17. Crystal structure of 7, structure represented by capped stick, CH_2 of pendant arm and ^{t}Bu group in close contact represented by ball and stick. Solvent omitted for clarity. Colour key: light blue is Zr, grey is carbon, red is oxygen and purple is nitrogen.

4. ^{1}H NMR spectra of the PLA produced in the ROP *rac*-lactide

Typical ^{1}H NMR of PLA

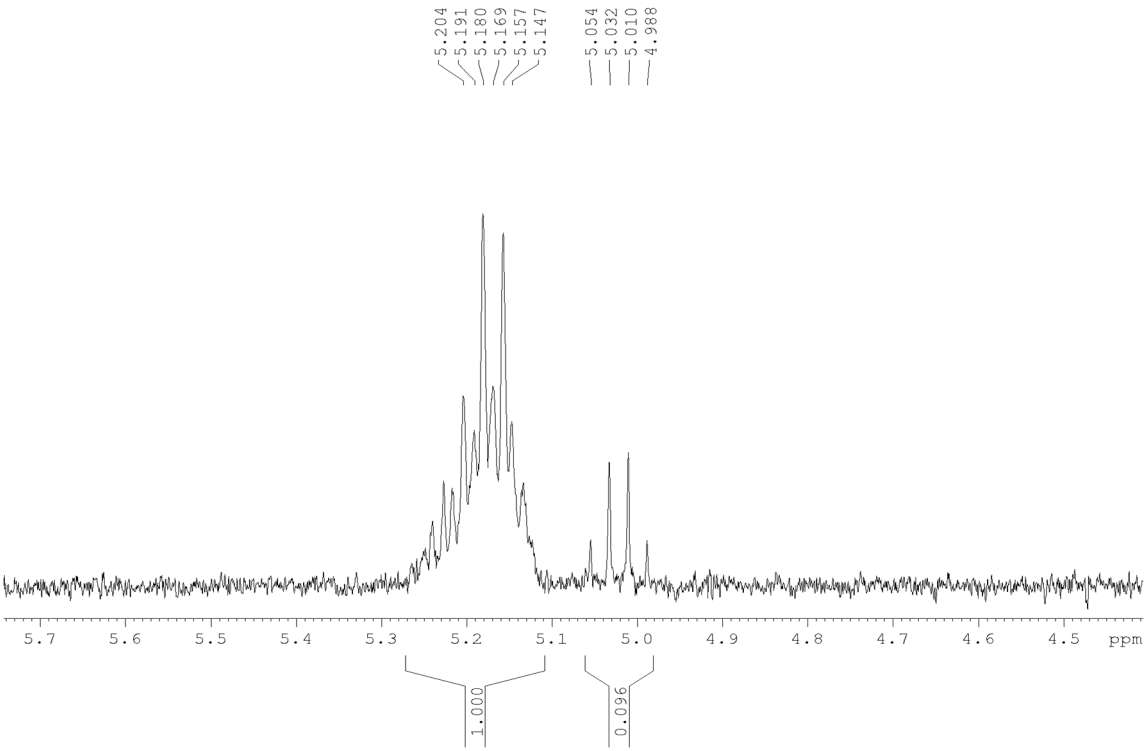

Figure S18. ^{1}H NMR spectra of crude ROP reaction mixture (300 MHz, $CDCl_3$, at 25 °C). Conversion determine by integration of La (CH-CH_3) peak δ 4.99–5.05 versus PLA (CH-CH_3) peak δ 5.12–5.27.

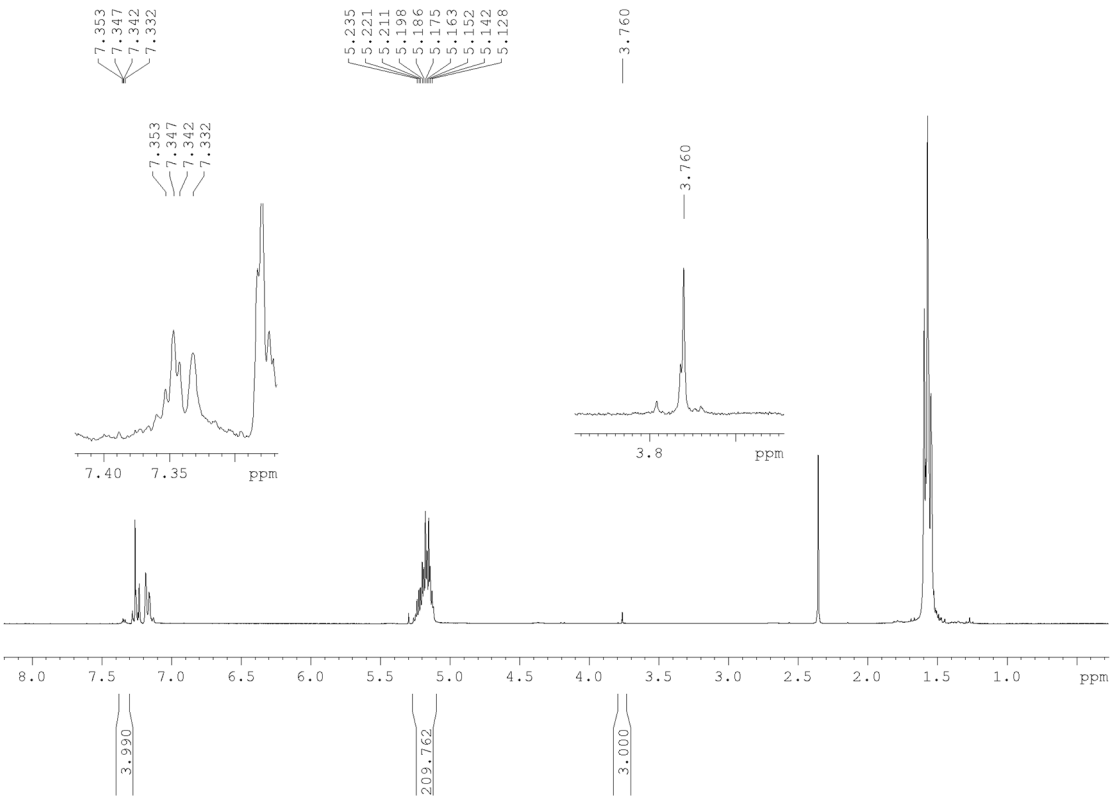

Figure S19. ^{1}H NMR spectra of purified PLA sample (300 MHz, $CDCl_3$, at 25 °C). Peaks at δ 7.36–7.31 ppm correspond to the benzyl end group. The peak at δ corresponds to the methoxy end group.

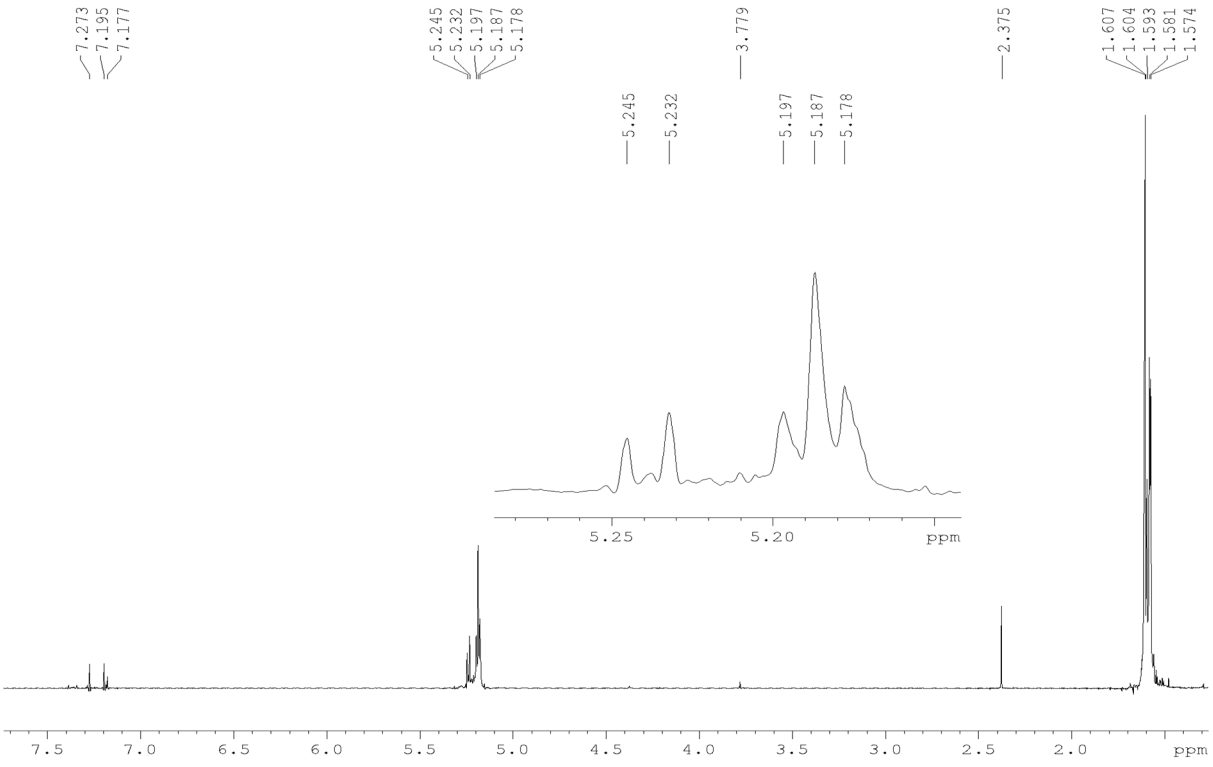

Figure S20. Example homonuclear decoupled ^{1}H NMR spectra of purified PLA sample produced during the ROP of *rac*-Lactide. (800 MHz, $CDCl_3$, 25 °C)**.**

5. Supplementary polymerisation data

Table S2. Supplementary polymerisation data.

Entry	Cat.	[M]:[La]	T (°C)	Time (h)	Conversion (%)[c]	P_i[d]	$M_{n(cal)}$[e]	$M_{n(obs)}$	$Đ$
1[a]	**4**	"1:100"	100	24	0	-	0	-	-
2[ab]	**4**	"1:200"	130	48	45	-	13100	-	-
3[a]	**5**	"1:100"	100	24	0	-	0	-	-
4b[a]	**5**	"1:200"	130	48	73	-	21200	-	-
5[a]	**6**	"1:100"	100	24	0	-	0	-	-
6[ab]	**6**	"1:100"	100	48	40	-	5900	-	-
7[a]	**7**	"1:100"	100	24	0	-	0	-	-
8[a]	**7**	"1:100"	100	24	68	-	9900	-	-
9[a]	**8**	"1:100"	100	24	91	-	13200	-	-
10[b]	**8**	"1:200"	130	48	96	1.6	27800	10600	0.55

Conditions [M]= 0.01 M, toluene. [a] Recovery of polymer samples unsuccessful, likely due to the formation of short polymer chains. [b] [M]:[BnOH]=1:2. [c] Calculated from ^{1}H NMR analysis of the integration of the lactide and poly(lactic acid) resonances in the methylene region. [c] Determined using homonuclear decoupled NMR spectroscopy and the method proposed by Coates and Ovitt.[11] [d] Calculated as $M_{n(calc)}$ = (([La]/[M])×conversion×MW_{La})+($MW_{End\ groups}$).

References

1. T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316-1326.
2. C. J. Ph. Dubois, R. Jéróme, and Ph. Teyssié, *Macromolecules*, 1991, **24**, 2266-2270.