Supporting Information

Iron^{III} half salen catalysts for atom transfer radical and ring opening polymerizations

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Contents

1. ^{1}H NMR spectra of ligands L2,L4-L6, L8

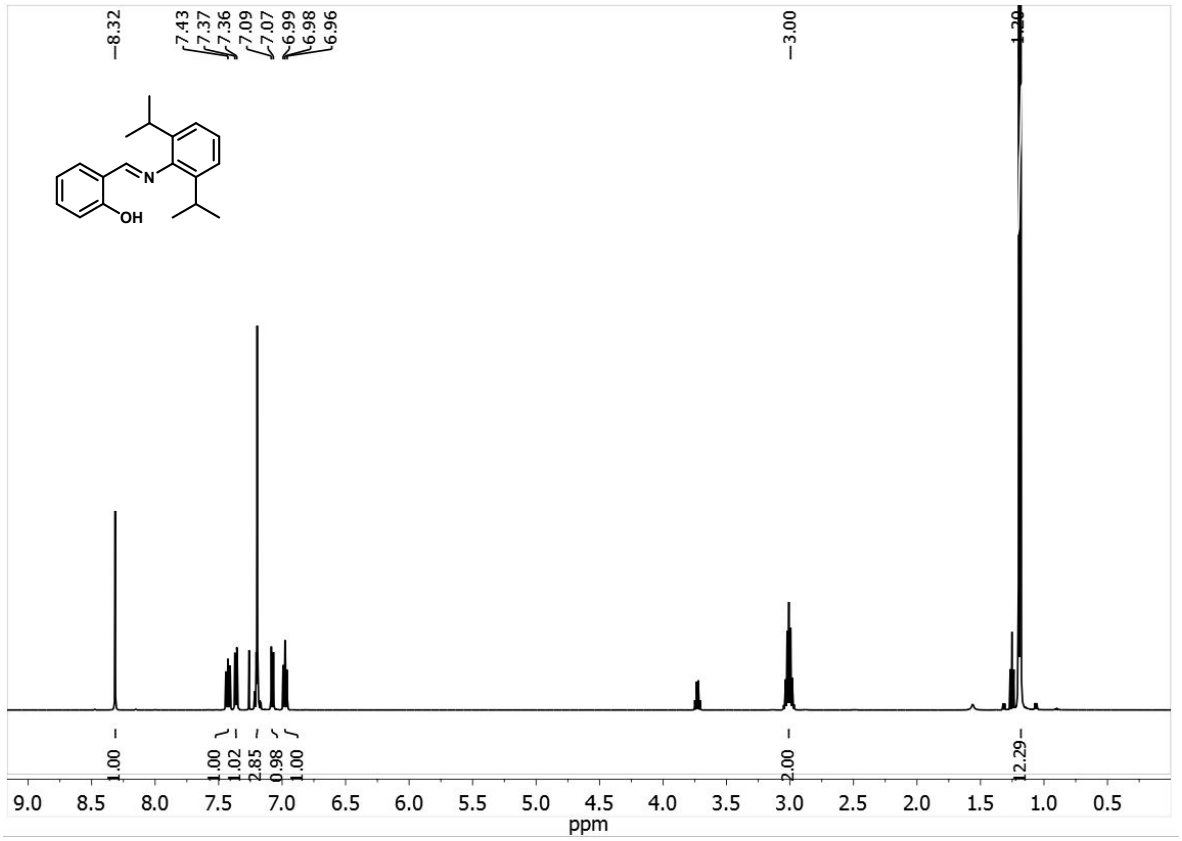


Figure S1 ^{1}H NMR spectrum of **L2** in $CDCl_3$ at 20°C.

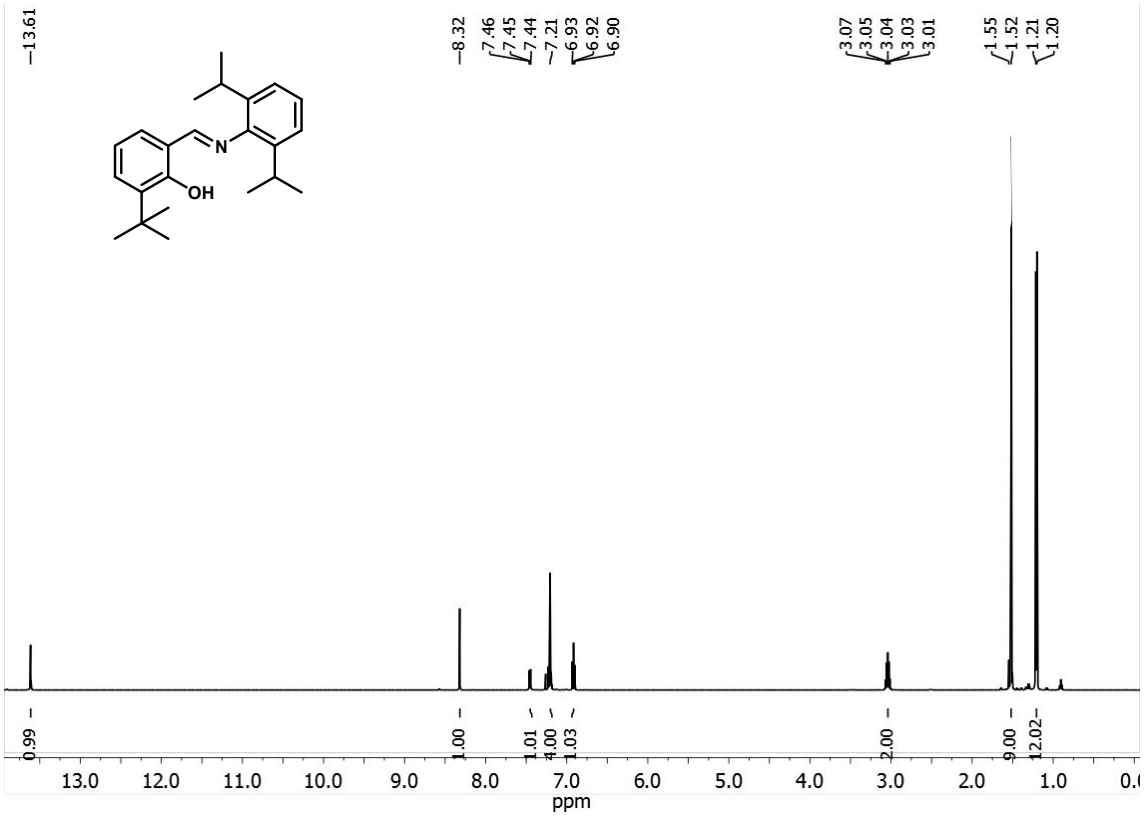


Figure S2 ^{1}H NMR spectrum of **L4** in $CDCl_3$ at 20°C.

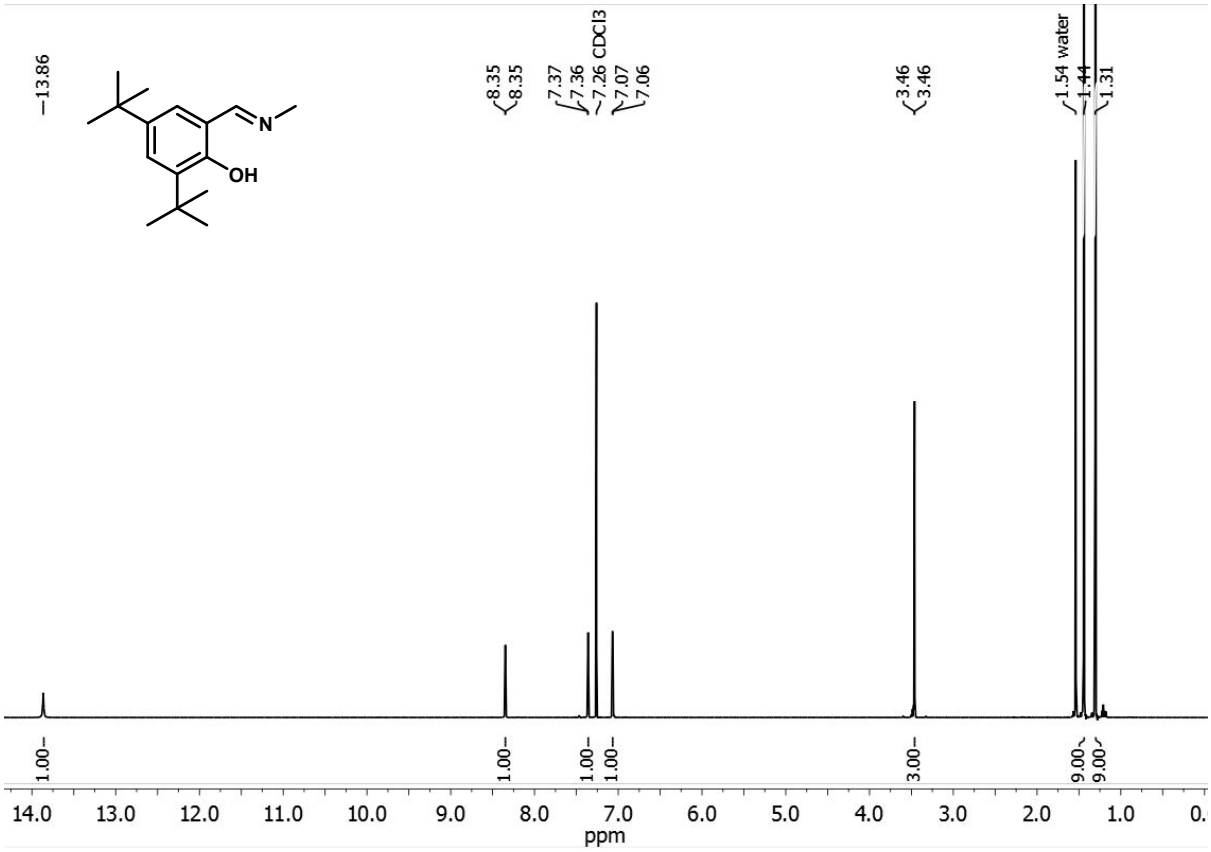


Figure S3 ^{1}H NMR spectrum of **L5** in $CDCl_3$ at 20°C.

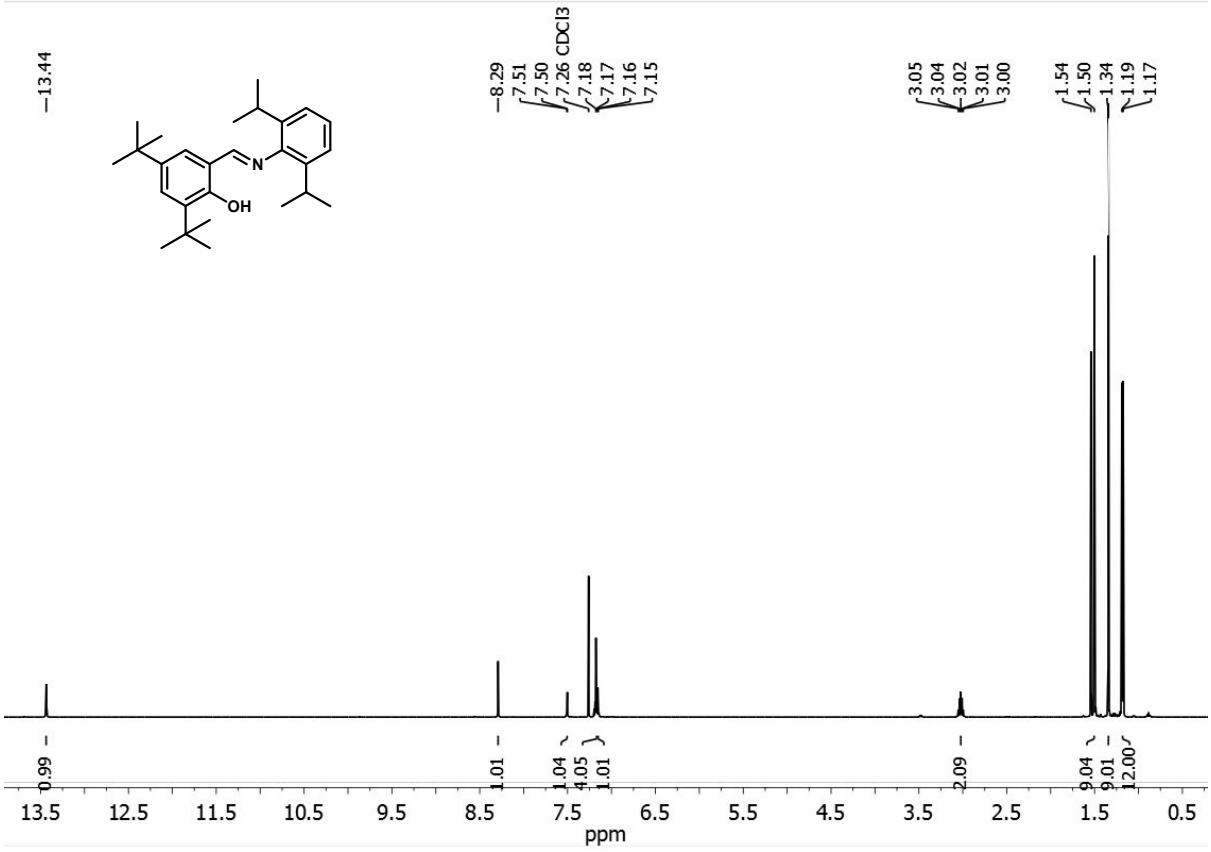


Figure S4 ^{1}H NMR spectrum of **L6** in $CDCl_3$ at 20°C.

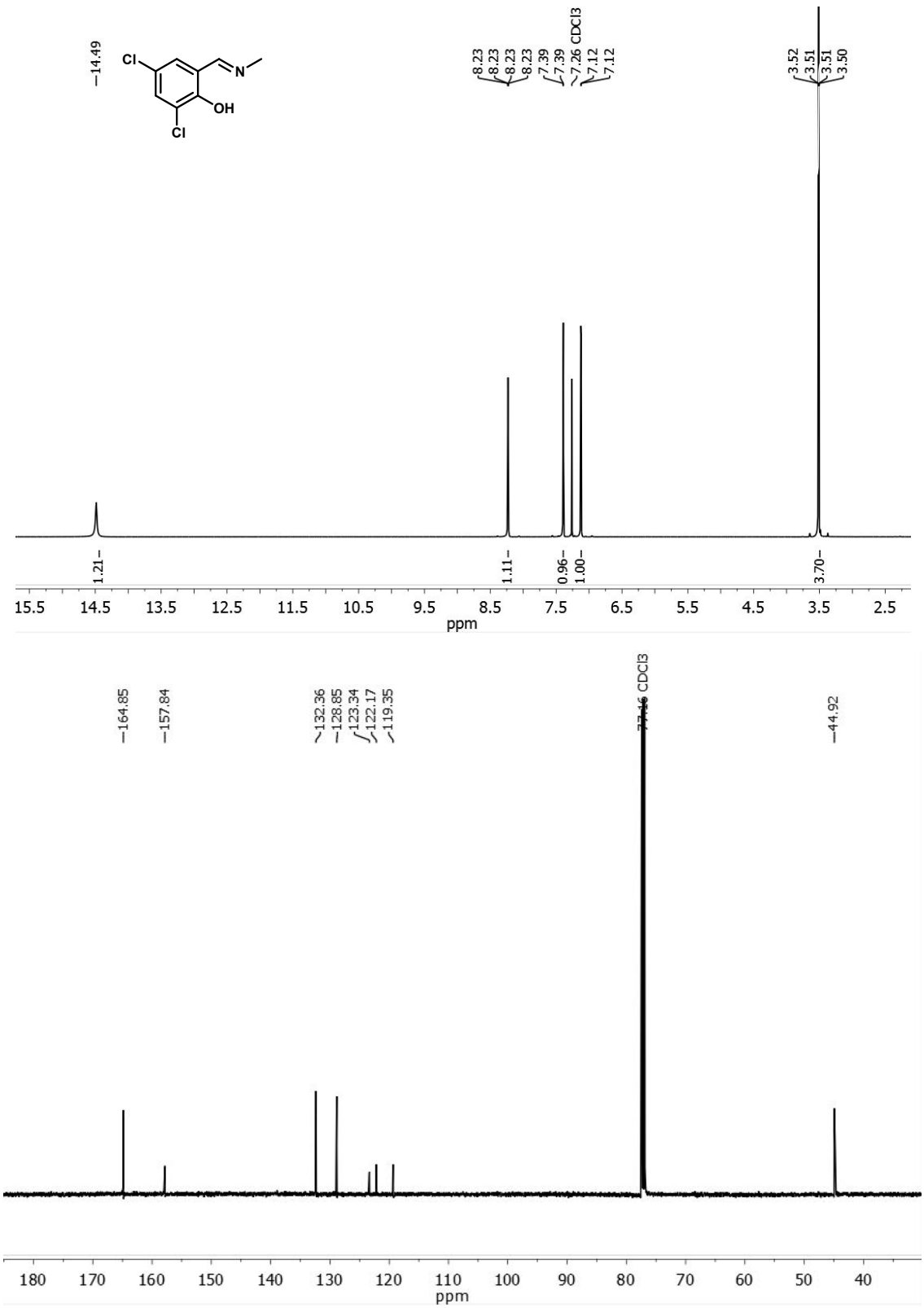


Figure S5 ^{1}H NMR and ^{13}C spectra of **L8** in $CDCl_3$ at 20°C.

2. HRMS spectra of complexes C2, C4-C6, C8

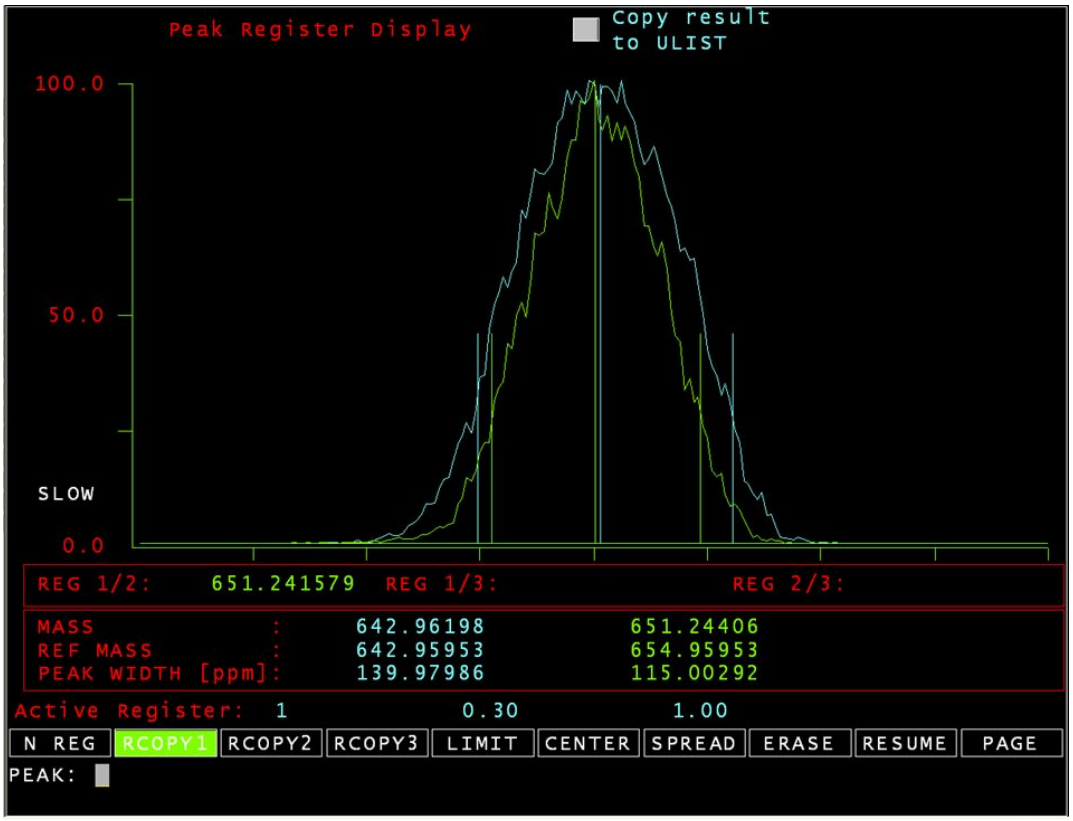


Figure S6 HRMS peak of **C2**.

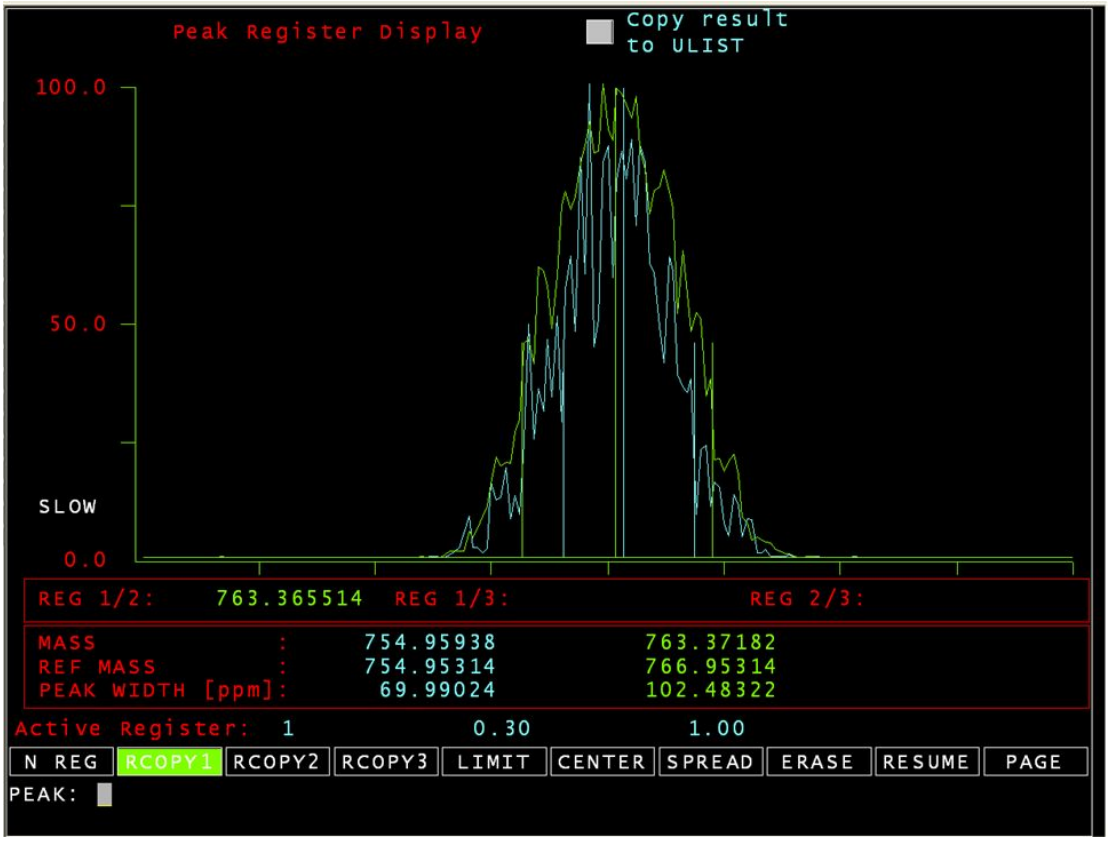


Figure S7 HRMS peak of **C4**.

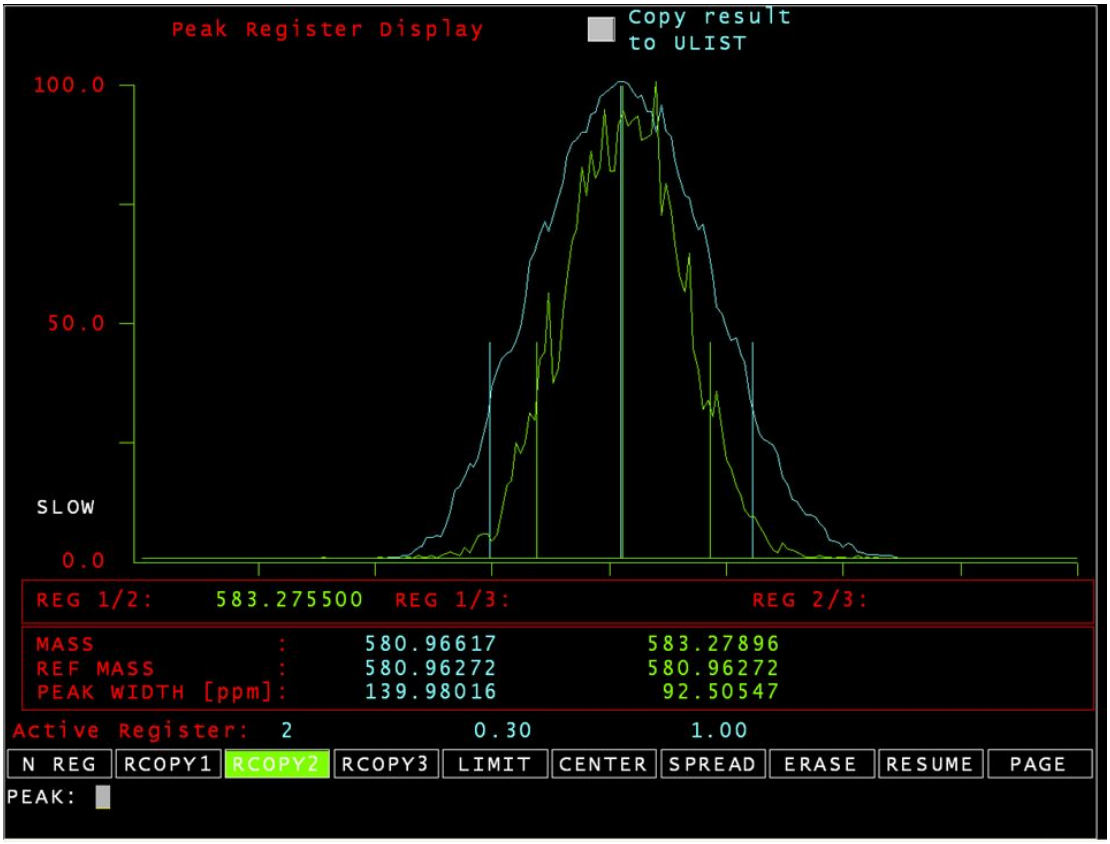


Figure S8 HRMS peak of **C5**.

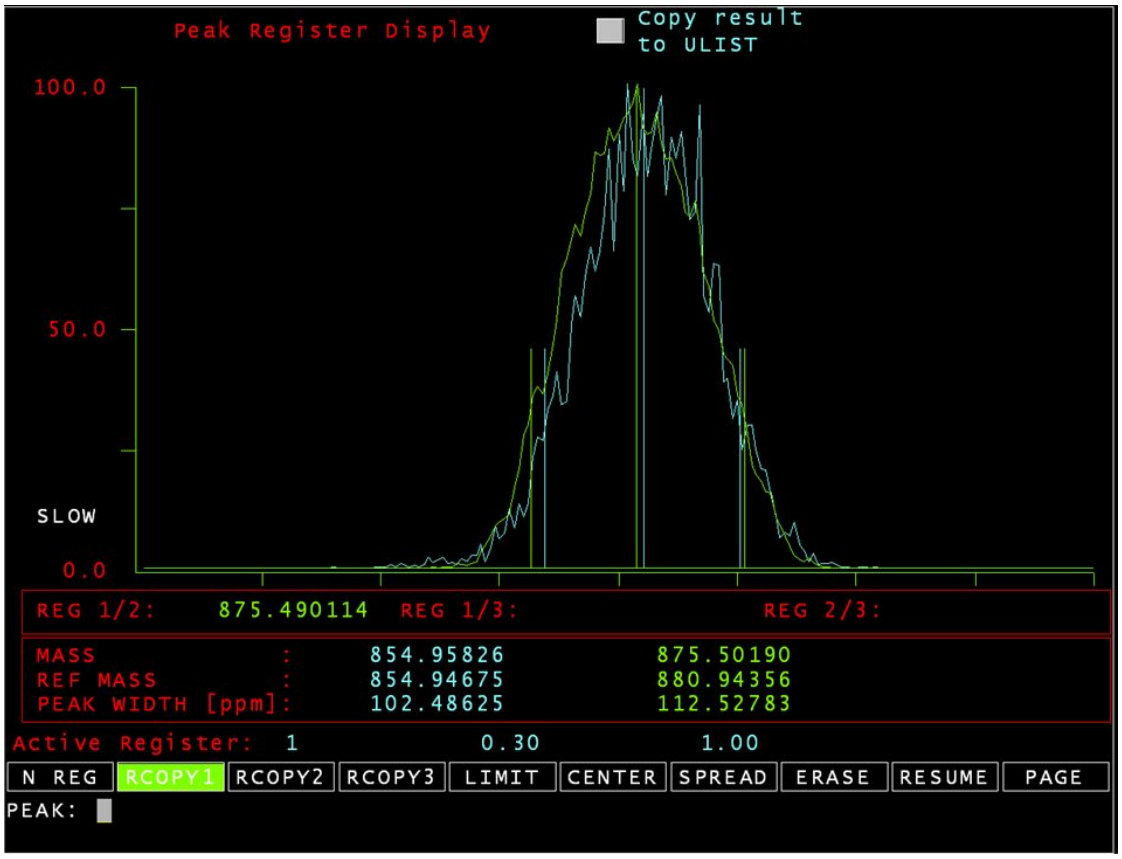


Figure S9 HRMS peak of **C6**.

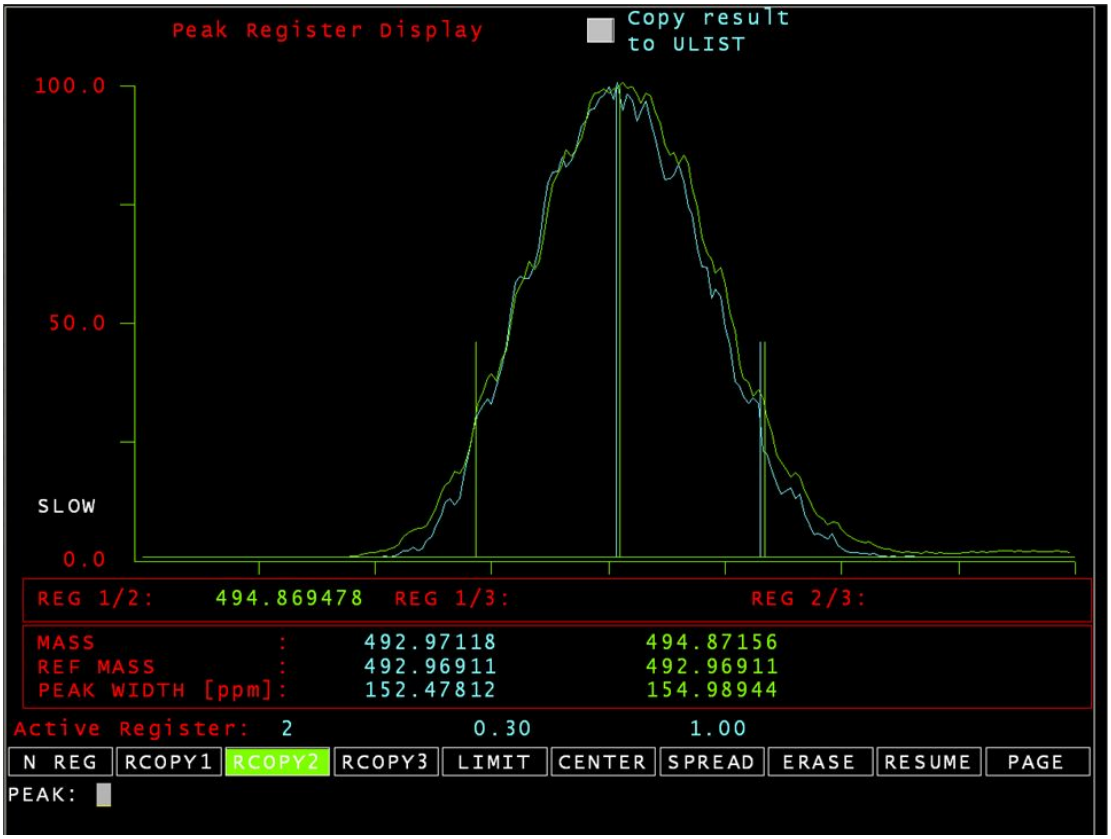


Figure S10 HRMS peak of **C8**.

3. ^{1}H NMR spectra of crude polymerization reaction mixtures

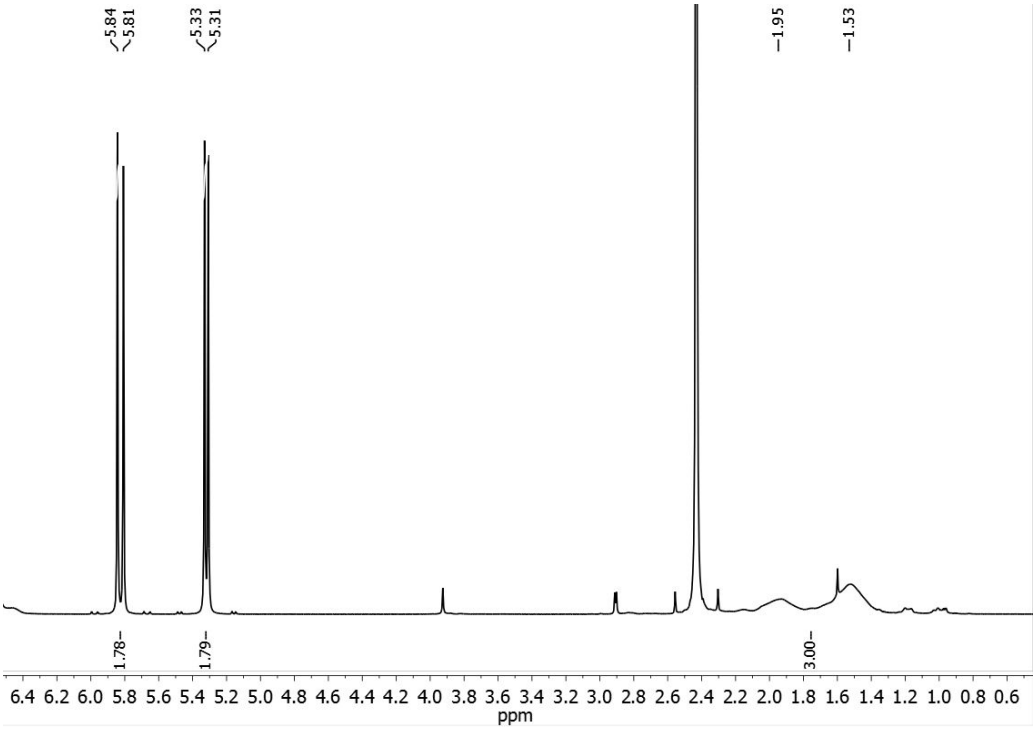


Figure S11 Typical ^{1}H NMR spectrum of a styrene ATRP crude reaction mixture in $CDCl_3$ at 20°C. Conversion was determined via integration of the multiplet polymer peak 2.2-1.2 ppm against the $=CH_2$ styrene (starting material) peak at 5.31 and 5.81 ppm.

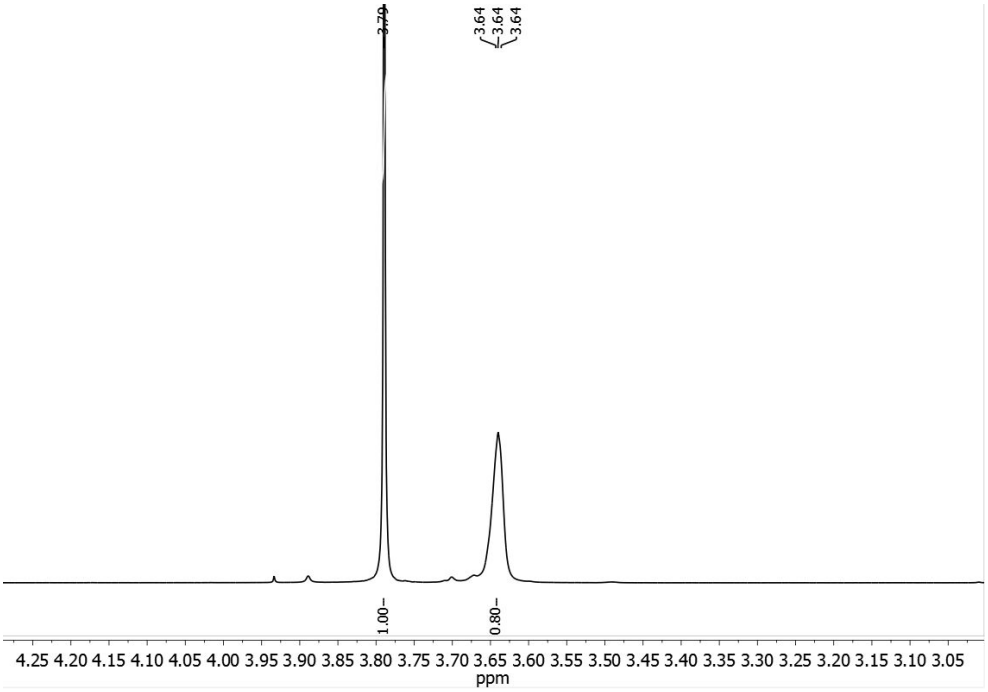


Figure S12 Typical ^{1}H NMR spectrum of a methyl methacrylate ATRP crude reaction mixture in $CDCl_3$ at 20°C. Conversion was determined via integration of the CH_3 polymer (product) peak at 3.64 ppm against the CH_3 methyl methacrylate (starting material) peak at 3.79 ppm.

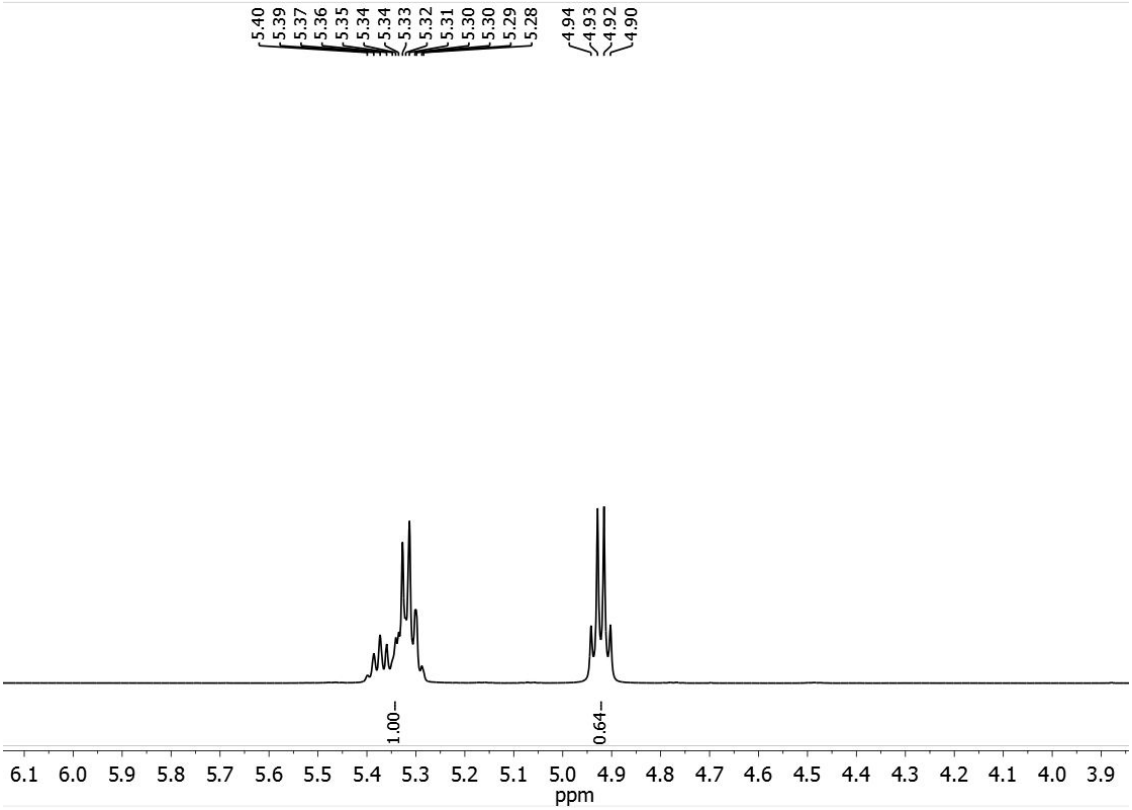


Figure S13 Typical ^{1}H NMR spectrum of a *rac*-lactide ROP crude reaction mixture in $CDCl_3$ at 20°C. Conversion was determined via integration of the C*H*-CH_3 polymer (product) peak 5.28-5.40 ppm against the C*H*-CH_3 lactide (starting material) peak at 4.90-4.92 ppm.

4. ^{1}H NMR spectrum of purified pMMA

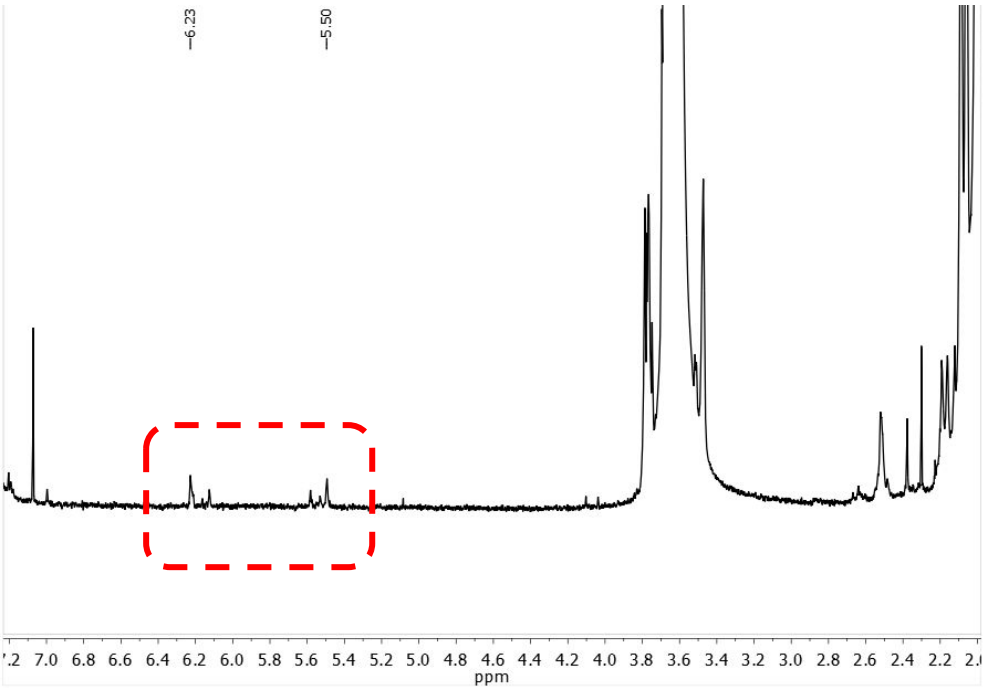


Figure S14 Typical ^{1}H NMR spectrum of a purified pMMA sample, showing olefin terminated polymer chains formed *via* CCT.

5. Tacticity evaluation via ^{1}H NMR spectroscopy

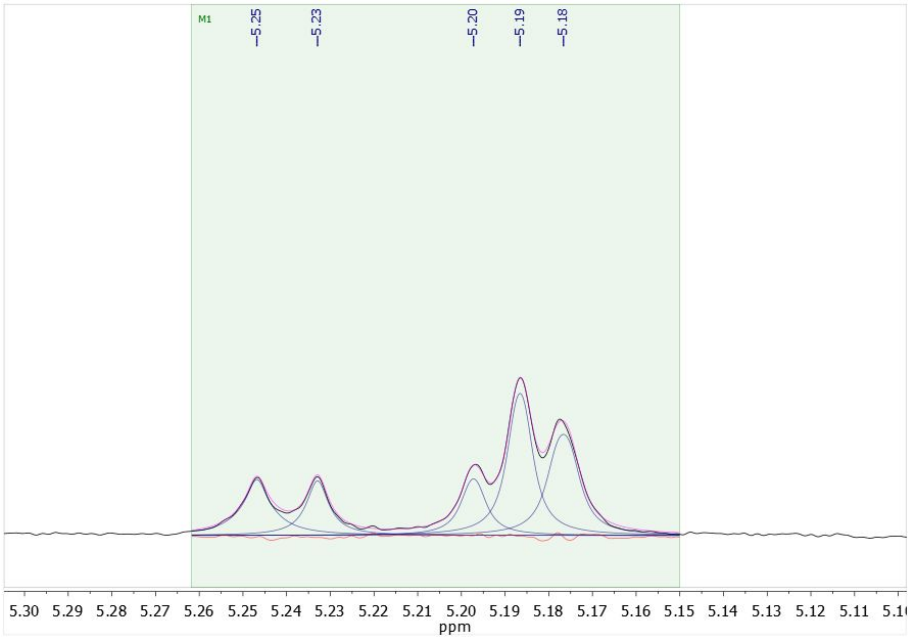


Figure S15 Methine region of a typical homonuclear decoupled ^{1}H NMR spectrum of a purified PLA sample. The tacticity (P_i values) of the polymer samples were evaluated using the method proposed by Coates and Ovitt.[1]

6. Typical GPC chromatograms of purified polymer samples

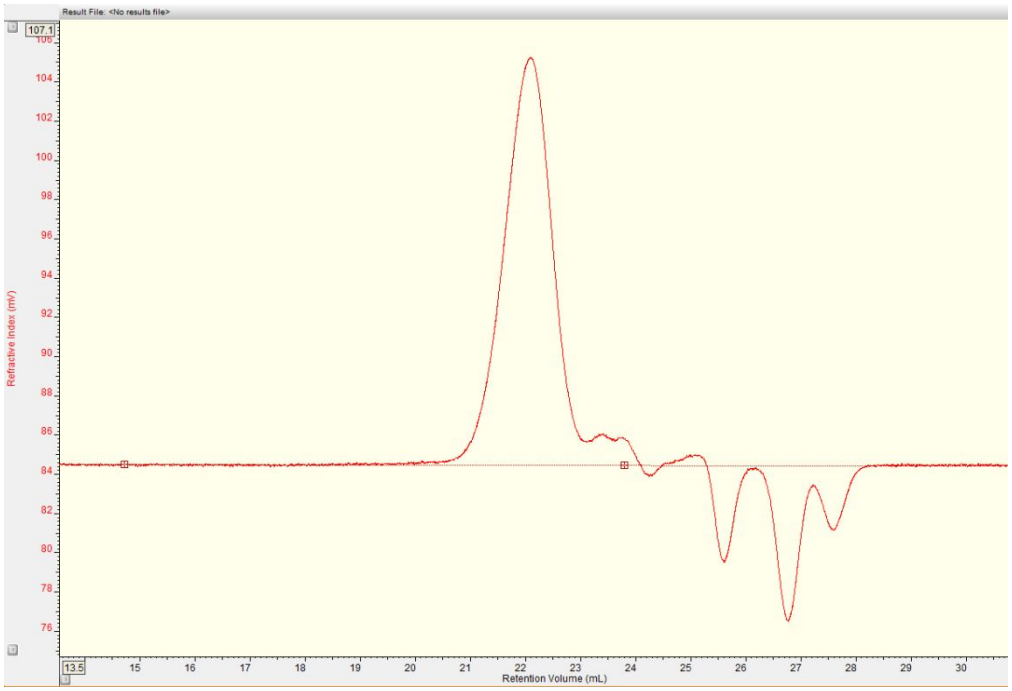


Figure S16 Typical GPC chromatogram of a polystyrene sample formed by catalyst **C7**.

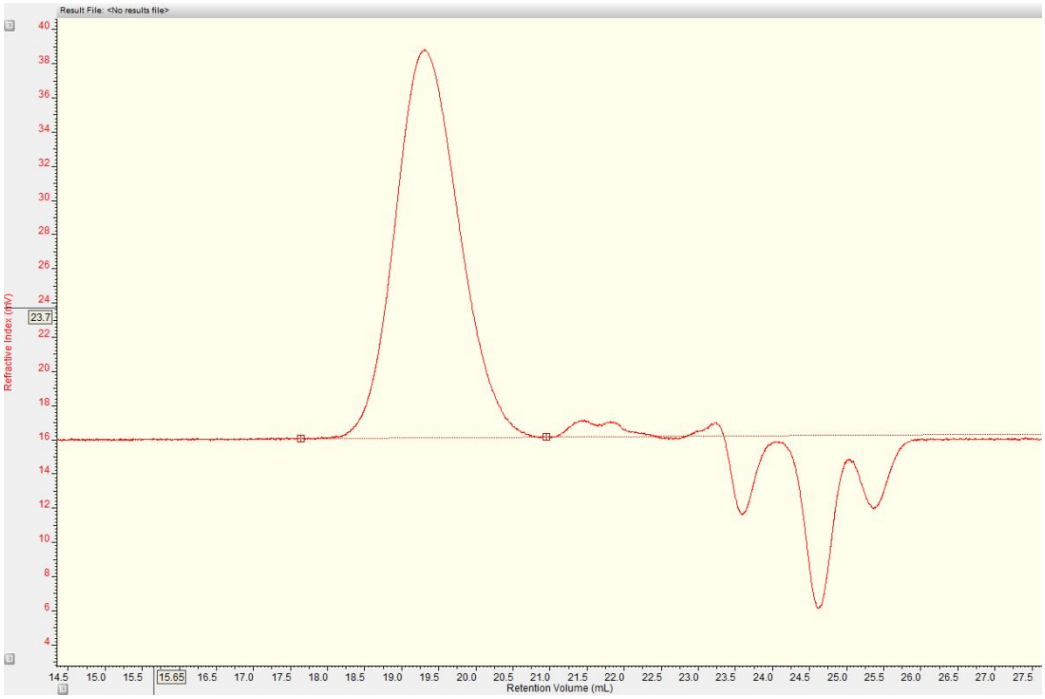


Figure S17 Typical GPC chromatogram of a pMMA sample formed by catalyst **C1**.

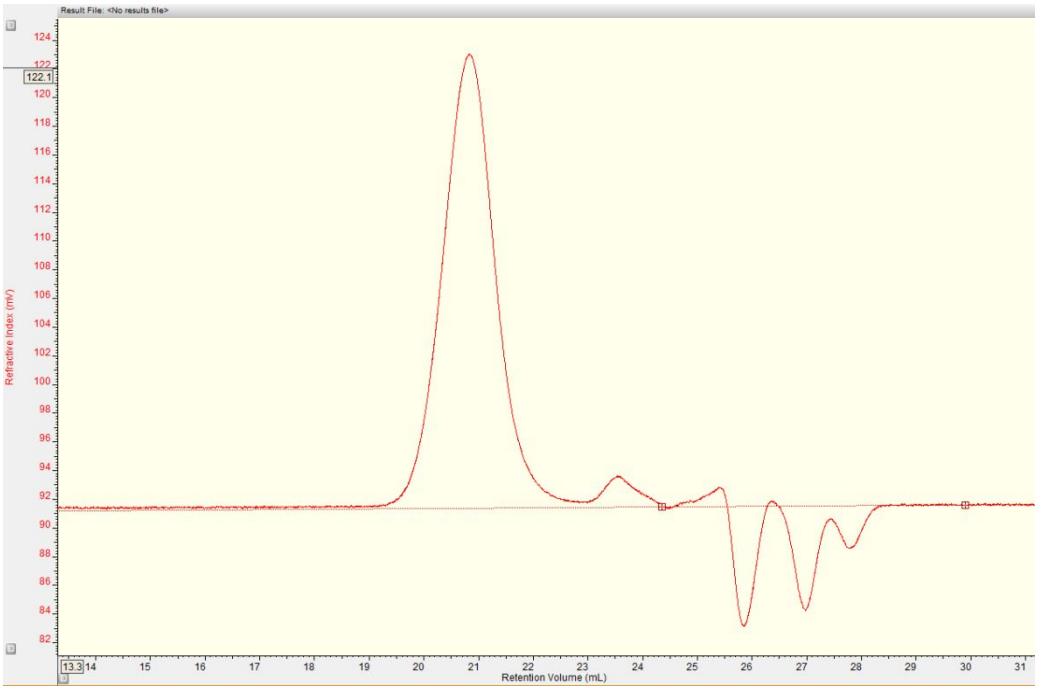
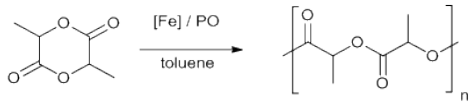


Figure S18 Typical GPC chromatogram of a PLA sample formed by catalyst **C3**.

7. Additional data for lactide polymerization

Table S1 Polymerization of rac-lactide with complexes **C1, C5** and **C8** and additives propylene oxide (PO) or butylene oxide (BO).



Entry	Complex	Additive (PO/Fe)	T (°C)	time (h)	Conv. (%)
1	**C8**	1	120	24	3
2	**C8**	5	120	24	4
3	**C8**	20	120	24	5
4	**C8**	50	120	24	89
5	**C8**	50	85	24	<1
6	**C5**	50	120	2	15
7	**C5**	50	120	2	28
8	**C5**	50	120	2	28
9	**C5**	50	120	2	49
10	**C1**	50 BO	120	2	40
11	**C1**	50 BO	120	2	39
12	**C1**	50 BO	120	2	22

Conditions: [lactide]:[Fe]:[PO] = 100:1:50, lactide concentration in toluene = 1 M, 120°C. Conversion was determined using ^{1}H NMR spectra of crude reaction mixtures. $M_{n,th\ [Fe]}$ = $[lactide]_0$/[Fe] x M(lactide) x conversion.

8. MALDI-ToF spectrum of a typical PLA sample

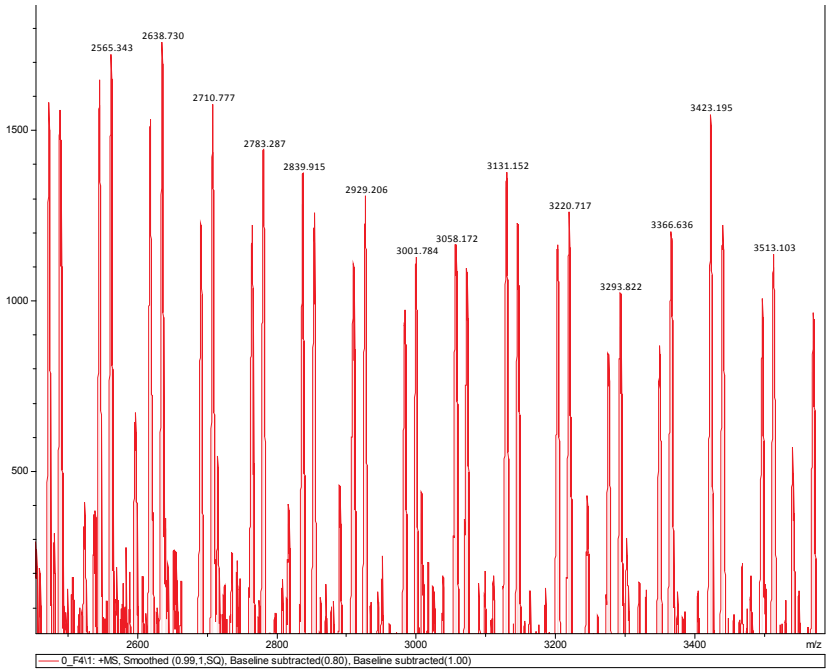


Figure S19 Typical MALDI spectrum of a PLA sample showing the two series peaks with lactide (144.10) and lactic acid (72.05) repeat units.

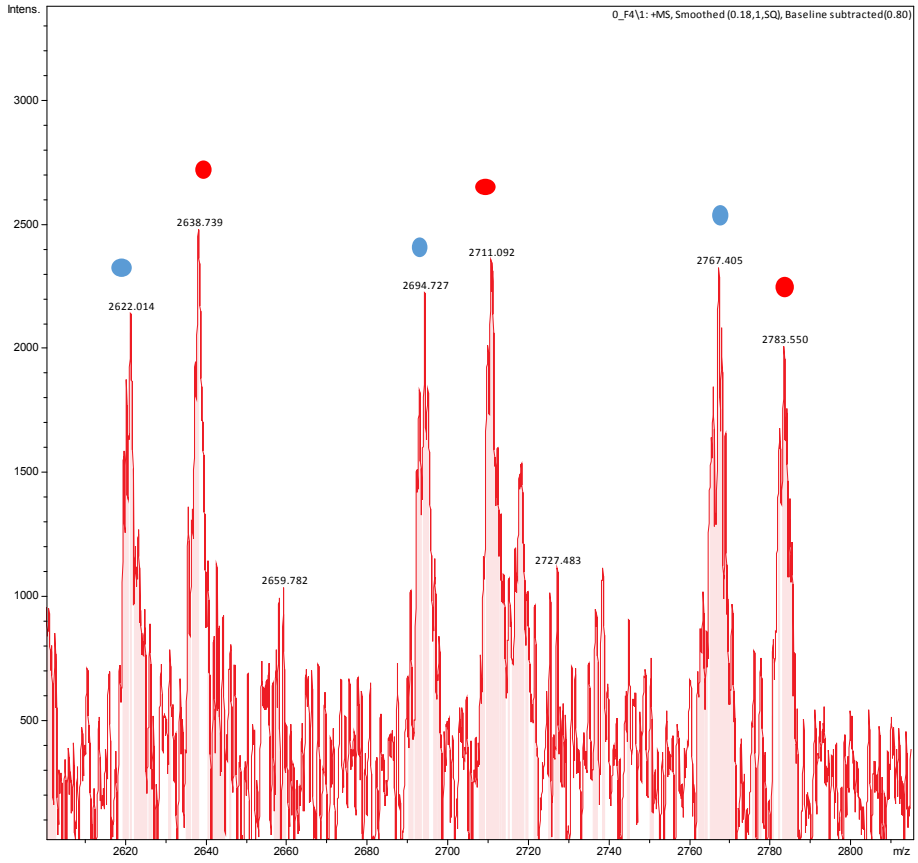


Figure S20 Zoomed in MALDI spectrum of a PLA sample showing the series of peaks corresponding to the α-OCH(Me)CH_2Cl/ω-H end groups (red) and the α-OCH(Me)CH_2OH/ω-H end groups (blue), with Na^+ as the cation.

9. X-ray data for complexes C5, C6 and C8

To establish the degree of trigonal bipyramidal character of the complexes, the τ value by Addison *et al.* was calculated for each complexes (τ = 0 for perfectly square pyramidal and τ = 1 for perfectly trigonal bipyramidal geometries).[2]

C5 CCDC 1868412, τ = (177.44 – 121.00)/60 = 0.94

C6 CCDC 1868413, τ = (173.7 – 121.10)/60 = 0.87

C8 CCDC 1868414, τ = (169.98 – 130.3)/60 = 0.66

Table S2: Crystallographic data and refinement details for **C5**, **C6** and **C8**.

Compound	**C5**	**C6**	**C8**
Formula	$C_{32}H_{48}ClFeN_2O_2$	$C_{54}H_{76}ClFeN_2O_2$	$C_{32}H_{24}Cl_{10}Fe_2N_4O_4$
$D_{calc.}$/ g cm^{-3}	1.184	1.127	1.712
□/mm^{-1}	4.654	3.106	1.488
Formula Weight	584.02	876.46	994.75
Colour	dark red	black	black
Shape	block	plate	block
Size/mm^3	0.21×0.07×0.04	0.14×0.07×0.04	0.38×0.27×0.20
T/K	120.0	120.0	120.0
Crystal System	orthorhombic	orthorhombic	triclinic
Space Group	*Pbca*	*Fdd*2	*P*-1
a/Å	26.4228(3)	32.8617(2)	10.2859(3)
b/Å	14.61318(18)	32.6742(2)	13.7432(4)
c/Å	33.9282(4)	19.24030(10)	15.0395(4)
□/°	90	90	110.704(3)
□/°	90	90	95.752(2)
□/°	90	90	99.856(2)
V/Å^3	13100.4(3)	20658.9(2)	1929.33(10)
Z	16	16	2
Z'	2	1	1
Wavelength/Å	1.54184	1.54184	0.71073
Radiation type	CuK□	CuK□	MoK□
□$_{min}$/°	3.694	3.816	2.716
□$_{max}$/°	76.167	76.086	29.763
Measured Refl.	205663	82834	43240
Independent Refl.	13685	10148	9868
Reflections with I > 2(I)	11358	9510	8584
R_{int}	0.1256	0.0818	0.0359
Parameters	746	563	473
Restraints	3	1	0
Largest Peak	0.704	0.400	0.357
Deepest Hole	-0.675	-1.094	-0.348
GooF	1.027	1.057	1.052
Flack parameter		0.006(4)	
wR_2 (all data)	0.1528	0.1501	0.0648
wR_2	0.1434	0.1473	0.0616
R_1 (all data)	0.0685	0.0598	0.0379
R_1	0.0565	0.0567	0.0301

10. References

(1) Ovitt, T. M.; Coates, G. W., Stereoselective ring-opening polymerization of rac-lactide with a single-site, racemic aluminum alkoxide catalyst: Synthesis of stereoblock poly(lactic acid). *J. Polym. Sci. A* **2000,** *38*, 4686-4692.
(2) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C., Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2[prime or minute]-yl)-2,6-dithiaheptane]copper(II) perchlorate. *Dalton Trans.* **1984**, 1349-1356.