Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Salan Group 13 complexes – structural study and lactide polymerisation

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General synthetic conditions for the synthesis of M(1)X complexes (M = Ga, In)

Ligand (**1**H_2 or **2**H_2) (2.6 mmol) dissolved in THF (10 mL) was added dropwise to a stirred suspension of potassium hydride (5.2 mmol) in THF (10 mL) and stirred for 16 hours. The solution was then cooled to -78 °C and a solution of $GaCl_3$/$InCl_3$ (2.6 mmol) in anhydrous THF (10 mL) was added dropwise and after complete addition, the solution was left to stir for 2 hours more. After this time, the solvent was removed and the white powder which was solubilised in chloroform and filtered through a pad of celite. The supernatant was collected and removal of solvent yielding the crude product which was then purified. Washing with hexane yielded a white solid which was recrystallised in a toluene/hexane mixture

General synthetic conditions for the synthesis of Al(1)Cl complexes

To a stirred solution of Ligand (**1**H_2 or **2**H_2) (2.6 mmol) in toluene (10 mL) at -78 °C, diethylaluminium chloride 1.0M in hexanes (1.742 mL, 1.73 mmol) was added dropwise. The solution was then warmed up to 25 °C and stirred for 1 hour. *In vacuo* removal of the solvent, washing with hexanes and recrystallization in a hexane/toluene mixture yielded a white crystalline solid.

Al(**1**)Cl

(0.6 g, 0.94 mmol, 55%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ_H, ppm); 7.23 (s, 2H; ArH), 6.73 (s, 2H; ArH), 4.45 (m, 2H,; NC*H*HC), 3.32 (m, 6H; NC*H*), 2.84 (m, 2H; NCH*H*C) 2.17 (m, 2H; CH_2N), 1.98 (m, 2H; CH_2N), 1.86 (m, 2H; C*H*H), 1.42 (s, 18H; C(CH_3)$_3$)) 1.24 (s, 18H; C(CH_3)$_3$)); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ_C, ppm); 156.2 (*C*-O), 138.4 (Ar), 138.1 (Ar), 124.4 (*C*-H, Ar), 123.2 (*C*-H, Ar), 120.4 (Ar), 67.8 (N*C*H), 62.3 (N*C*H$_2$), 54.5 (N*C*H$_2$), 35.3 (*C*(CH_3)$_3$), 34.3 (*C*(CH_3)$_3$), 32.1 (C(*C*H_3)$_3$), 30.1 (C(*C*H_3)$_3$, 27.0 (*C*H_2), 21.8 (*C*H_2). Elemental Analysis (CHN), (Calculated) C: 71.61%, H: 9.17%, N: 4.39% (Experimental) C: 69.17 %, H: 9.12%, N: 4.31%.

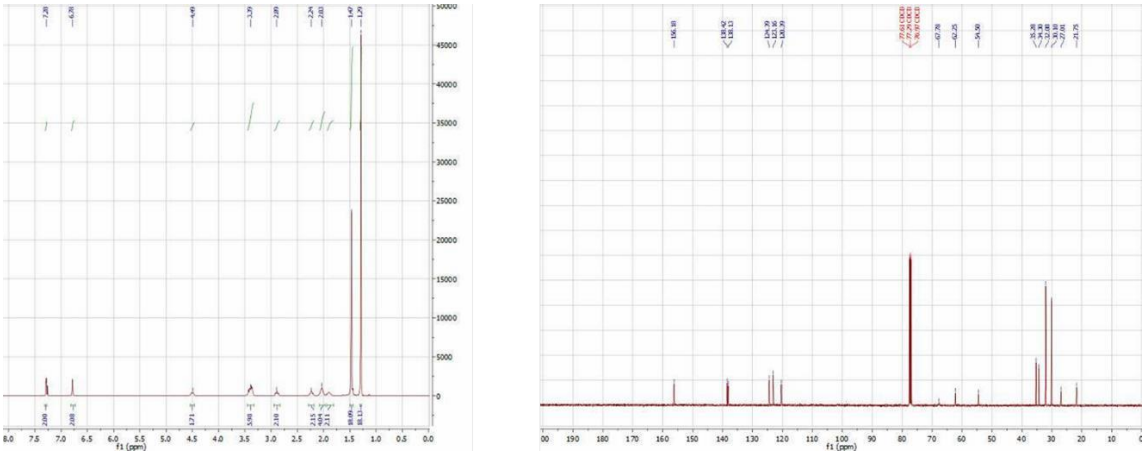


Figure SI 1: NMR spectra ($CDCl_3$) for Al(**1**)Cl

Ga(**1**)Cl

(0.93g, 1.37 mmol, 53%). ^{1}H-NMR (400MHz, $CDCl_3$, δ_H, ppm); 7.28 (s, 2H, Ar), 6.77 (s, 2H, Ar), 4.66 (d, 2H, 12.2 Hz, NC*H*HC), 3.75 (d, 2H, 2.5 Hz, NC*H*), 3.36 (d, 2H, 12.2 Hz, NCH*H*C) 2.92 (4H, m, CH_2N), 2.27 (m, 2H, C*H*H), 2.03 (m, 4H, CH_2), 1.90 (m, 2H, CH*H*), 1.48 (s, 18H, ^{t}Bu) 1.28 (s, 18H, ^{t}Bu); ^{13}C{^{1}H} (100MHz, $CDCl_3$, δ_C, ppm); 158.5 (*C*-O), 139.2 (Ar), 137.9 (Ar), 124.7 (*C*-H, Ar), 123.8 (*C*-H, Ar), 119.9 (Ar), 68.3 (N*C*H), 67.2 (N*C*H), 62.6 (N*C*H$_2$), 54.2 (N*C*H$_2$), 35.5 (*C*(CH_3)$_3$), 34.4 (*C*(CH_3)$_3$), 32.2 (C(*C*H_3)$_3$), 30.2 (C(*C*H_3)$_3$, 26.9 (*C*H_2), 26.0 (*C*H_2), 21.5 (*C*H_2). Elemental Analysis (CHN), (Calculated) C: 67.11%, H: 8.60%, N: 4.12% (Experimental) C: 66.82%, H: 8.56%, N: 4.64%.

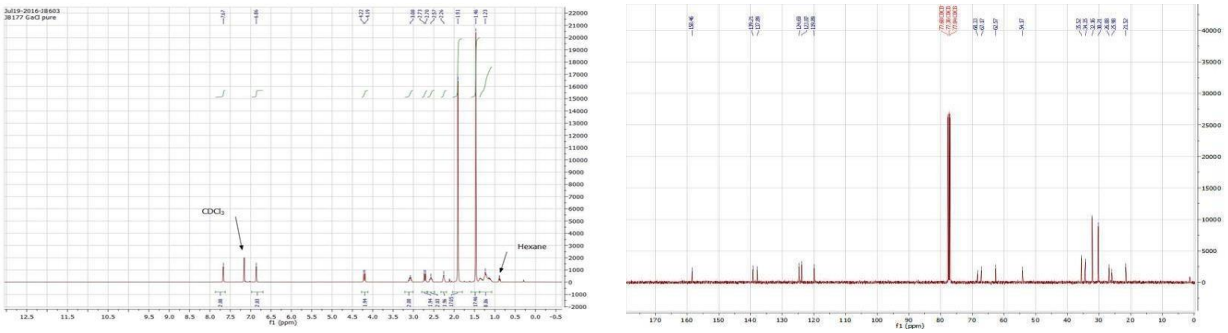


Figure SI 2: NMR spectra ($CDCl_3$) for Ga(**1**)Cl

In(**1**)Cl

(1.61 g, 2.22 mmol, 85%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ_H, ppm); 7.30 (s, 2H; ArH), 6.76 (s, 2H; ArH), 4.73 (d, 12.7 Hz, 2H,; NC*H*HC), 3.41 (d, 2H, 2.5 Hz; NC*H*), 3.34 (d, 2H, 12.7 Hz; NCH*H*C) 3.10 (m, 2H; CH_2N), 3.00 (m, 2H; CH_2N), 2.31 (m, 2H; C*H*H), 2.03 (m, 4H; CH_2), 1.90 (m, 2H; CH*H*), 1.50 (s, 18H; C$(CH_3)_3$)) 1.28 (s, 18H; C$(CH_3)_3$)); ^{13}C-NMR (100 MHz, $CDCl_3$, δ_C, ppm); 159.5 (*C*-O), 138.5 (Ar), 136.2 (Ar), 123.9 (*C*-H, Ar), 123.8 (*C*-H, Ar), 118.8 (Ar), 66.1 (N*C*H), 61.6 (N*C*H_2), 52.4 (N*C*H_2), 34.2 (*C*$(CH_3)_3$), 32.9 (*C*$(CH_3)_3$), 30.8 (C(*C*$H_3)_3$), 28.7 (C(*C*$H_3)_3$, 25.3 (*C*H_2), 20.1 (*C*H_2). Elemental Analysis (CHN), (Calculated) C: 62.94%, H: 8.06%, N: 3.86% (Experimental) C: 63.01 %, H: 8.08%, N: 3.86%.

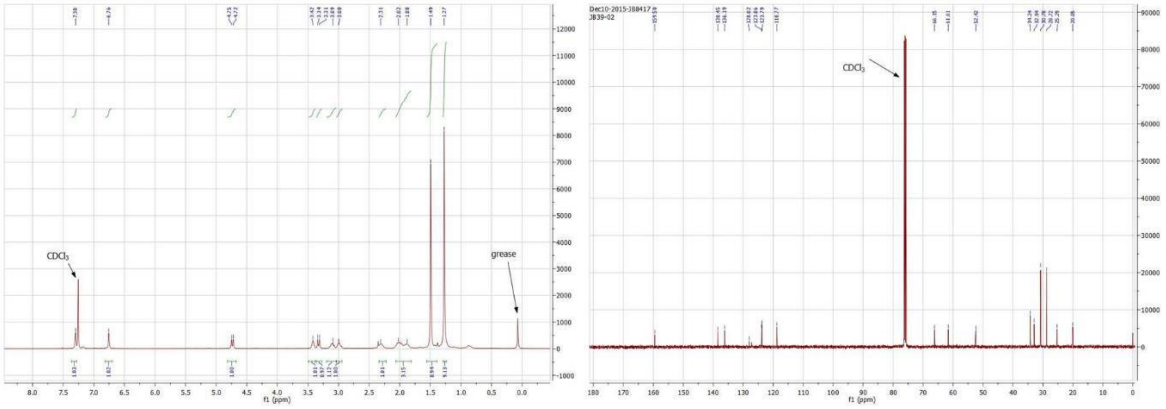


Figure SI 3: NMR spectra ($CDCl_3$) for In(**1**)Cl

In(**1**)I

(345 mg, 0.42 mmol, 42%).^{1}H-NMR (400 MHz, $CDCl_3$, 253 K, δ_H, ppm); 7.29 (s, 2H; ArH), 6.76 (s, 2H; ArH), 4.76 (d, 12.7 Hz, 2H; NC*H*HC), 3.53 (d, 2.5 Hz 2H; NC*H*), 3.34 (d, 12.7 Hz, 2H; NCH*H*C) 3.10 (m, 2H; CH_2N), 2.97 (m, 2H; CH_2N), 2.31 (m, 2H; C*H*H), 1.99 (m, 4H; CH_2), 1.90 (m, 2H; CH*H*), 1.50 (s, 18H, (C(*C*$H_3)_3$), 1.28 (s, 18H, (C(*C*$H_3)_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, 298 K, δ_C, ppm); 139.49 (Ar), 125.2 (Ar), 67.5 (N*C*H), 54.16 (N*C*H_2), 52.4 (N*C*H_2), 35.3 (*C*$(CH_3)_3$), 34.3 (*C*$(CH_3)_3$), 32.1 (C(*C*$H_3)_3$), 30.4 (C(*C*$H_3)_3$, 27.0 (*C*H_2), 20.9 (*C*H_2). Elemental Analysis (CHN), (Calculated) C: 55.89%, H: 7.16%, N: 3.43% (Experimental) C: 56.05 %, H: 7.19%, N: 3.42%.

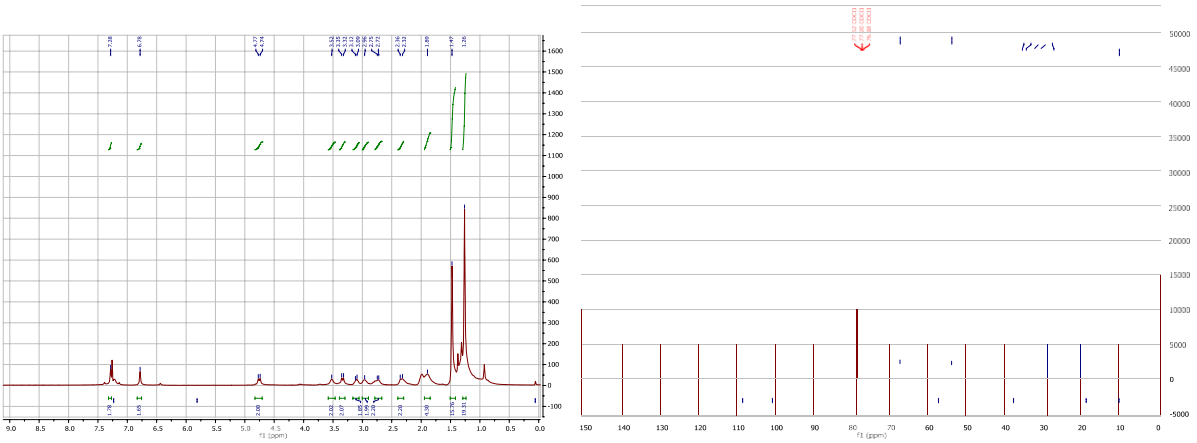


Figure SI 4: NMR spectra ($CDCl_3$) for In(**1**)I

General synthetic conditions for the synthesis of In_2(1)OEt/OH complex

NaOEt (2.4 mmol) in toluene (10 mL) was added dropwise to a stirred solution of In(**1**)Cl (0.44 mmol) in toluene (20 mL), the solution was then stirred for 16 hours. Filtration of the supernatant and *in vacuuo* removal of the solvent yielded an orange precipitate which was recrystallised in hexane (2 mL).

In(1)OEt/OH (155 mg, 0.21 mmol, 8%). ^{1}H-NMR (400 MHz, toluene-d_8, 238 K, δ_H, ppm);

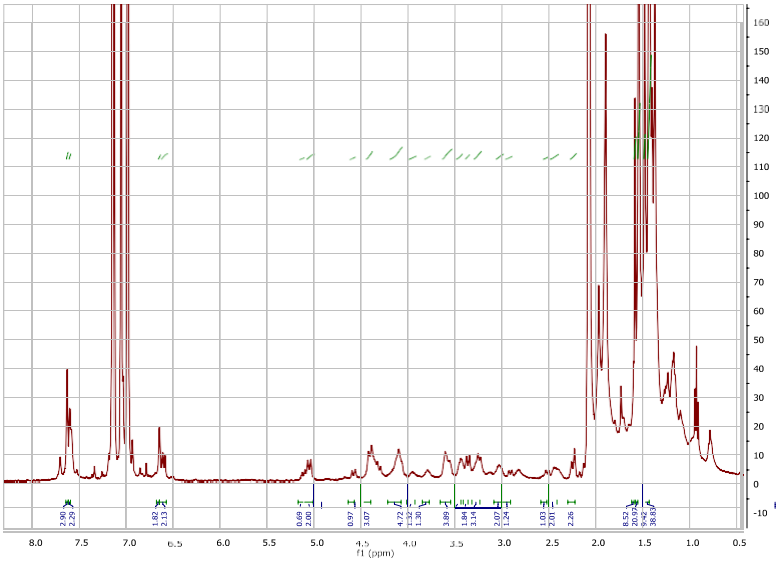


Figure SI 5: ^{1}H NMR spectra ($CDCl_3$) for In_2(**1**)$_2$(OH(OEt)

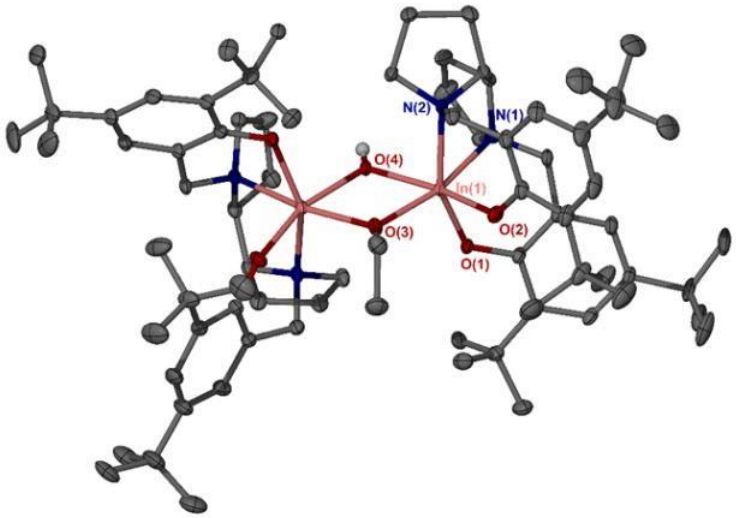


Figure SI6 : Solid-state structure for In2(1)2(OH)(OEt) ellipsoids are shown at the 30% probability level and all hydrogen atoms have been removed for clarity, selected bond lengths (Å) and angles (□) are: In(1)-O(2) 2.100(2), In(1)-O(1) 2.103(2), In(1)-O(3) 2.1338(17), In(1)-O(4) 2.1755(17), In(1)-N(2) 2.321(2), In(1)-N(1) 2.353(3). O(2)-In(1)-O(1) 91.96(8), O(2)-In(1)-O(3) 91.86(9), O(1)-In(1)-O(3) 105.49(6), O(2)-In(1)-O(4) 163.04(9), O(1)-In(1)-O(4) 97.74(6).

Al(**2**)Cl

(680 mg, 1.16 mmol, 61%). ^{1}H-NMR (400MHz, $CDCl_3$, δ_H, ppm): (*Major Series*) 7.30 (s, 2H, Ar), 6.81 (s, 2H, Ar), 4.52-4.49 (d, 12.4 Hz, 2H, CH*H*N), 3.20 (d, 12.4 Hz, 2H, C*H*HN), 2.98 (m, 4H, NCH_2), 2.44 (s, 6H, NCH_3), 1.47 (s, 18H, ^{t}Bu), 1.29 (s, 18H, ^{t}Bu), Due to significant overlap in tBu, Ar region full assignment of minor series is not possible. But it is clear from the NMR below. ^{13}C-NMR (100MHz, $CDCl_3$, δ_C, ppm): 155.7 (*C*-O), 138.6 (Ar), 138.4 (Ar), 124.5 (Ar), 123.3 (Ar), 119.7 (Ar), 63.0 (CH_2N), 55.2 (CH_2N), 45.6 (NCH_3), 35.5 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 30.1 ($C(CH_3)_3$). Elemental Analysis (CHN): (Calculated) C: 69.77%, H: 9.30%, N: 4.79% (Experimental) C: 67.57%, H: 9.50%, N: 4.75%.

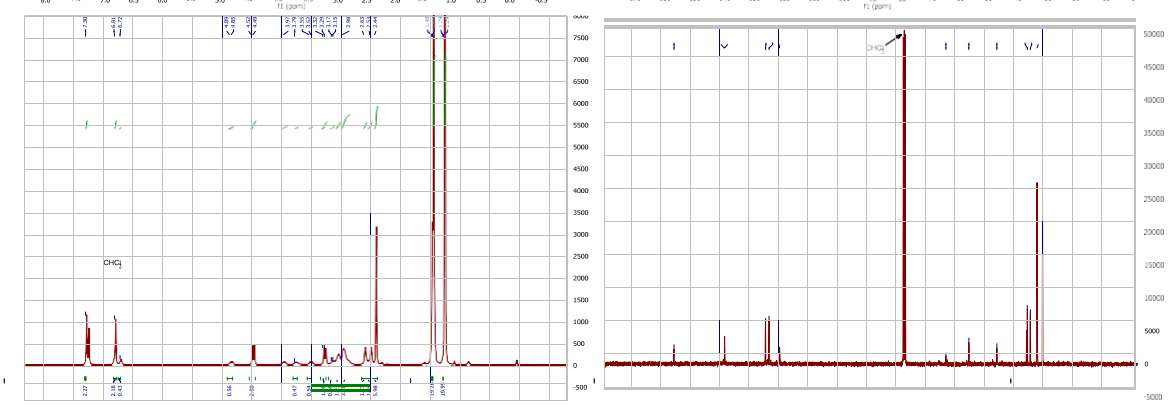


Figure SI 7: NMR spectra ($CDCl_3$) for Al(**2**)Cl

Ga(**2**)Cl

(565 mg, 0.9 mmol, 48%). ^{1}H-NMR (400MHz, $CDCl_3$, δ_H, ppm): 7.31 (s, 2H, Ar), 6.80 (s, 2H, Ar), 4.71-4.68 (d, 12.1 Hz, 2H, C*H*HN), 3.25-3.22 (d, 12.1 Hz, 2H, CH*H*N), 3.16 (m, 2H, CH_2N), 2.95 (m, 2H, CH_2N), 2.42 (s, 6H, CH_3), 1.51 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu); ^{13}C-NMR (100MHz, $CDCl_3$, δ_C, ppm): 158.0 (*C*-O), 139.3 (Ar), 138.6 (Ar), 124.8 (Ar), 124.1 (Ar), 199.8 (Ar), 63.4 (*C*H_2N), 55.1 (*C*H_2N), 45.0 (N*C*H_3), 35.5 (*C*$(CH_3)_3$), 34.2 (*C*$(CH_3)_3$), 32.0 (C(*C*$H_3)_3$), 30.2 (C(*C*$H_3)_3$). Elemental Analysis (CHN): (Calculated) C: 65.03%, H: 8.67%, N: 4.46% (Experimental) C: 64.92%, H: 8.80%, N: 4.57%.

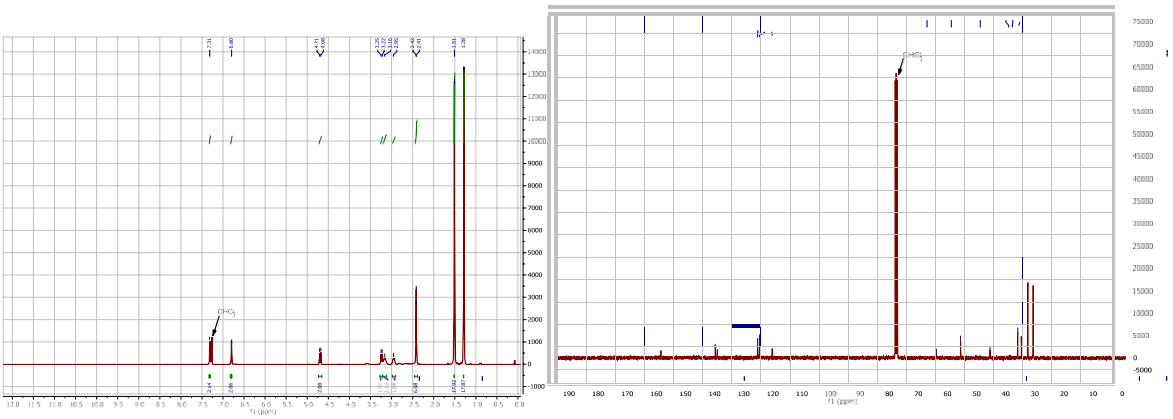


Figure SI 8: NMR spectra ($CDCl_3$) for Ga(**2**)Cl

In(**2**)Cl

(790 mg, 1.18 mmol, 42%). ^{1}H-NMR (400MHz, $CDCl_3$, δ_H, ppm): 7.31 (d, 2.5 Hz, 2H, Ar), 6.78 (d, 2.5 Hz, 2H, Ar), 4.81 (d, 11.8 Hz, 2H, CH*H*N), 3.20 (d, 11.83 Hz, 4H, C*H*HN), 2.93 (m, 2H, NCH*H*C), 2.40 (s, 6H, NC*H*$_3$), 1.53 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu); ^{13}C-NMR (100MHz, $CDCl_3$, δ_C, ppm): 160.5 (*C*-O), 139.8 (Ar), 138.3 (Ar), 129.3 (Ar), 128.4 (Ar), 64.3 (*C*H_2N), 55.4 (*C*H_2N), 43.8 (N*C*H_3), 35.2 (*C*$(CH_3)_3$), 33.9 (*C*$(CH_3)_3$), 31.7 (C(*C*$H_3)_3$), 29.9 (C(*C*$H_3)_3$). Elemental Analysis (CHN), (Calculated) C: 60.67 %, H: 8.09%, N: 4.16%, (Experimental) C: 60.71 %, H: 8.14%, N: 4.16%

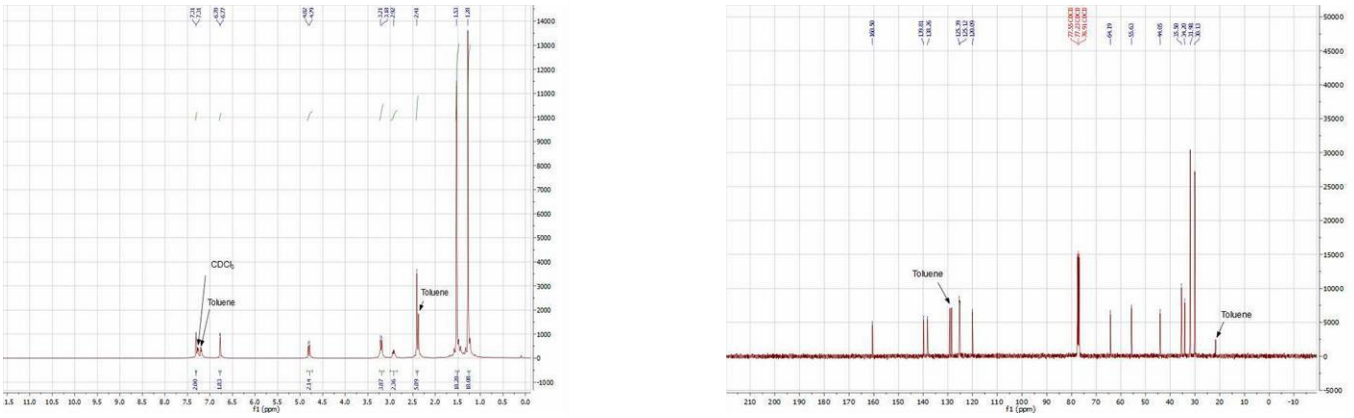


Figure SI 9: NMR spectra ($CDCl_3$) for In(**2**)Cl

Representative Polymer Characterisation

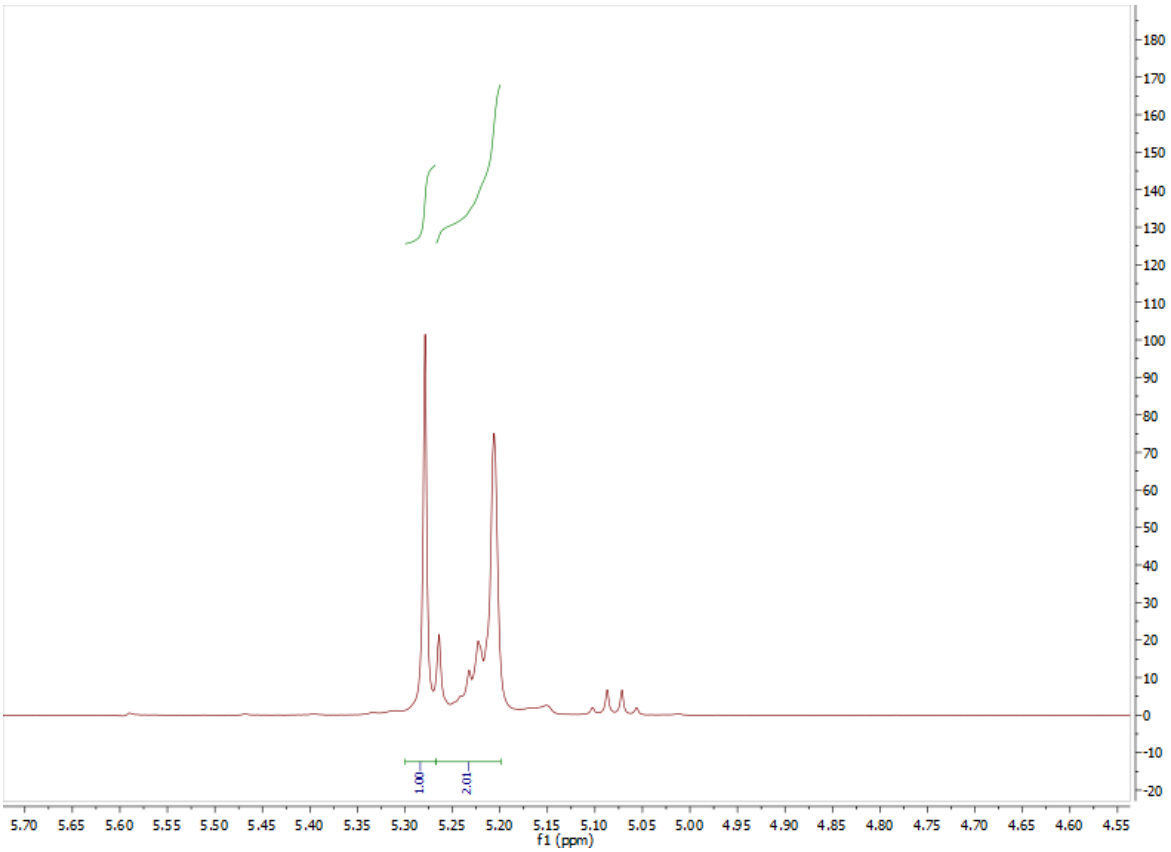


Figure SI 10. Methine region of the $^{1}H\{^{1}H\}$NMR ($CDCl_3$, 400 MHz) spectrum of PLA, synthesised polymerisation of rac-lactide 100:1:1:1 with In(**1**)Cl – Table 2 Entry 1.

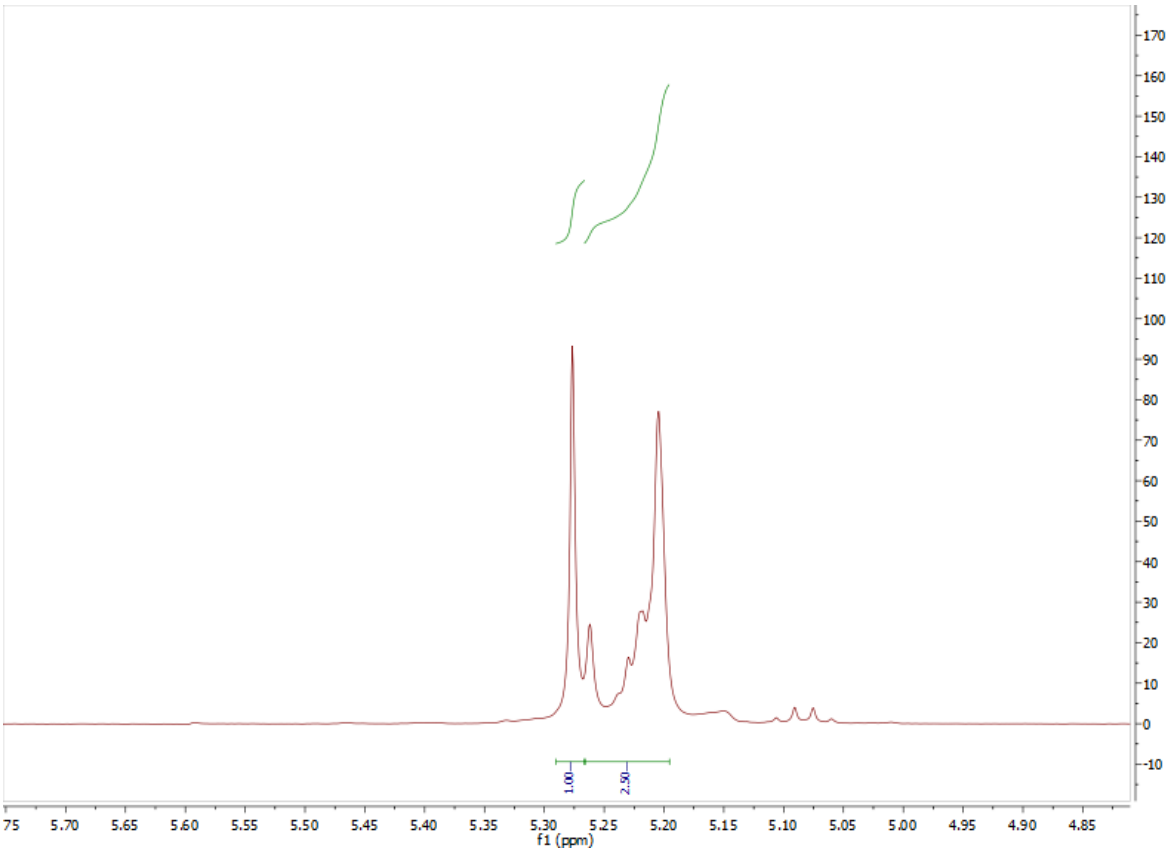
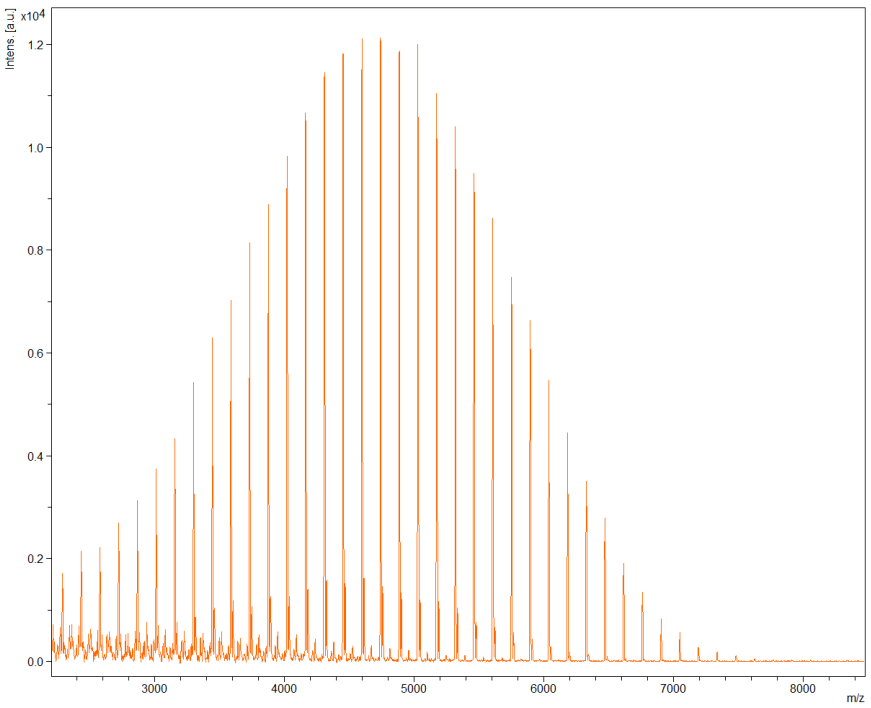


Figure SI 11. Methine region of the $^{1}H\{^{1}H\}$ NMR ($CDCl_3$, 400 MHz) spectrum of PLA, synthesised polymerisation of rac-lactide 300:1:1:0 with In(**1**)Cl, table 1 entry 2



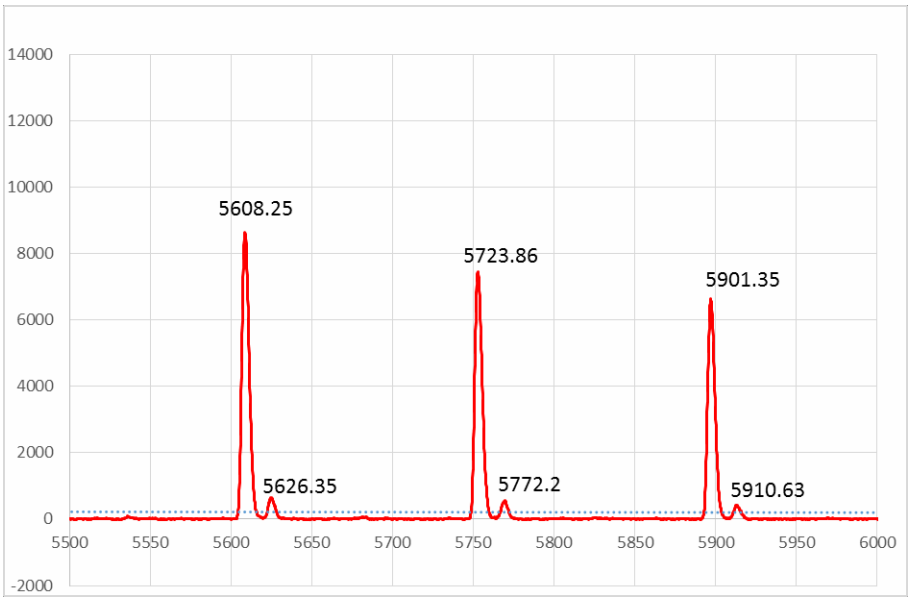


Figure SI 12: MALDI-ToF MS for the isolated PLA samples form Table 1 entry 1. Peak at 5608.25 = $H(C_6H_8O_4)nOCH_2Ph+Na$ where n = 38

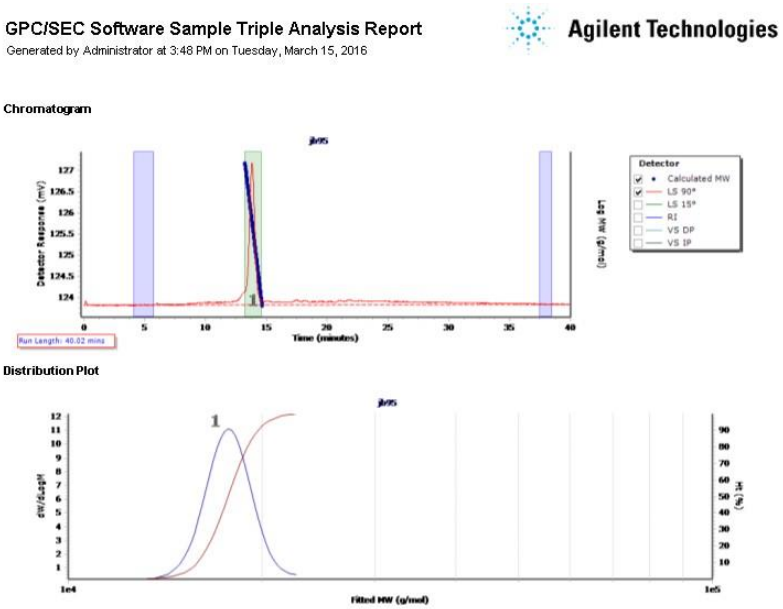


Figure SI13 GPC trace of PLA catalysed by In(1)Cl**I** 100:1:1:1 ([LA]:[I]:[BnOH]:[NEt_3] – Entry 1 Table 1.

Table SI 1 Crystallographic Parameters

Compound reference	Al(**1**)Cl	Ga(**1**)Cl	In(**1**)Cl	Al(**2**)Cl	Ga(**2**)Cl	In(**2**)Cl	In(**1**)I	In_2(**1**)$_2$OHOEt
Chemical formula	$C_{38}H_{58}AlClN_2O_2$	$C_{38}H_{58}ClGaN_2O_2$	$C_{38}H_{58}ClInN_2O_2$	$C_{38\text{-}50}H_{64\text{-}50}AlClN_2O_2$	$C_{40}H_{68}ClGaN_2O_2$	$C_{48}H_{70}ClInN_2O_2$	$C_{38}H_{58}IInN_2O_2$	$C_{93}H_{157}In_2N_4O_6$
Formula Mass	637.29	680.03	725.13	649.85	714.13	857.33	816.58	1656.86
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
a/Å	22.54430(10)	22.41840(10)	12.3467(3)	33.7559(5)	32.9563(6)	21.6467(9)	12.01000(10)	17.9334(3)
b/Å	12.93050(10)	12.91110(10)	15.8230(4)	13.9577(2)	14.0324(2)	13.1050(7)	16.7440(2)	16.6462(2)
c/Å	25.52250(10)	25.80380(10)	19.2186(5)	17.7422(3)	17.9476(2)	32.3338(9)	18.8821(2)	32.2729(3)
α/°	90	90	90	90	90	90	90	90
β/°	93.527(3)	93.3540(10)	94.865(3)	102.820(2)	101.3759(15)	90	92.9080(10)	99.1720(10)
γ/°	90	90	90	90	90	90	90	90
Unit cell volume/Å^3	7425.95(7)	7456.02(7)	3741.05(16)	8150.9(2)	8136.9(2)	9172.5(7)	3792.21(7)	9511.0(2)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150.01(10)	150(2)	150(2)	150(2)
Space group	*I*2/*a*	*I*2/*a*	*P*2$_1$/*c*	*C*2/*c*	*C*12/*c*1	*Pbca*	*P*2$_1$/*c*	*I*2/*a*
No. of formula units per unit cell, *Z*	8	8	4	8	8	8	4	4
No. of reflections measured	62374	82162	51666	82822	46467	63191	29570	68760
No. of independent reflections	6820	7485	7472	8175	8157	9393	7205	8390
R_{int}	0.0257	0.0222	0.0280	0.0413	0.0267	0.0408	0.0297	0.0485
Final R_1 values ($I > 2\sigma(I)$)	0.0377	0.0290	0.0202	0.0746	0.0426	0.0311	0.0230	0.0383
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0967	0.0773	0.0497	0.2122	0.1126	0.0774	0.0574	0.1091
Final R_1 values (all data)	0.0385	0.0297	0.0214	0.0768	0.0458	0.0346	0.0251	0.0435
Final $wR(F^2)$ values (all data)	0.0974	0.0779	0.0503	0.2142	0.1154	0.0793	0.0586	0.1140