Electronic Supplementary Information

Titanium Complexes of Pyrrolylaldiminate Ligands and Their Exploitation for the Ring-Opening Polymerization of Cyclic Esters

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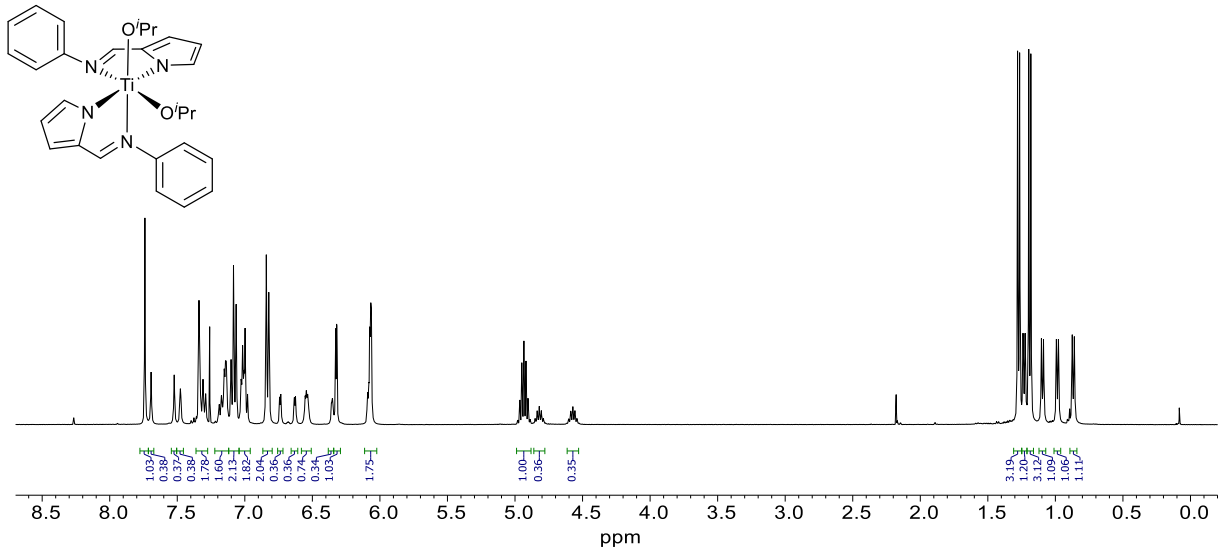


Fig. S1 ^{1}H NMR spectrum of **1** in $CDCl_3$ at 298 K.

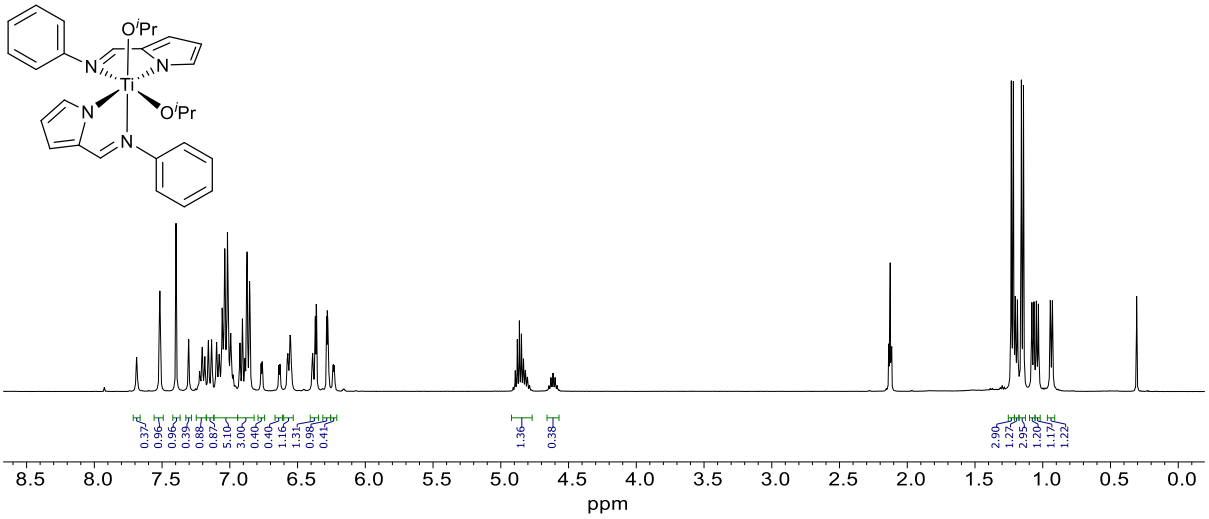


Fig. S2 ^{1}H NMR spectrum of **1** in toluene-d_8 at 298 K.

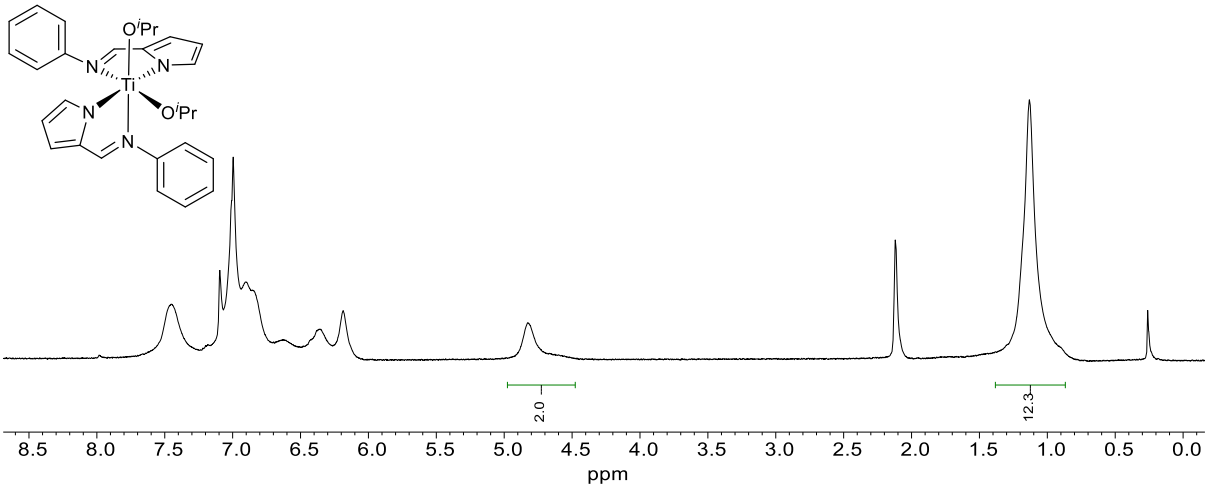
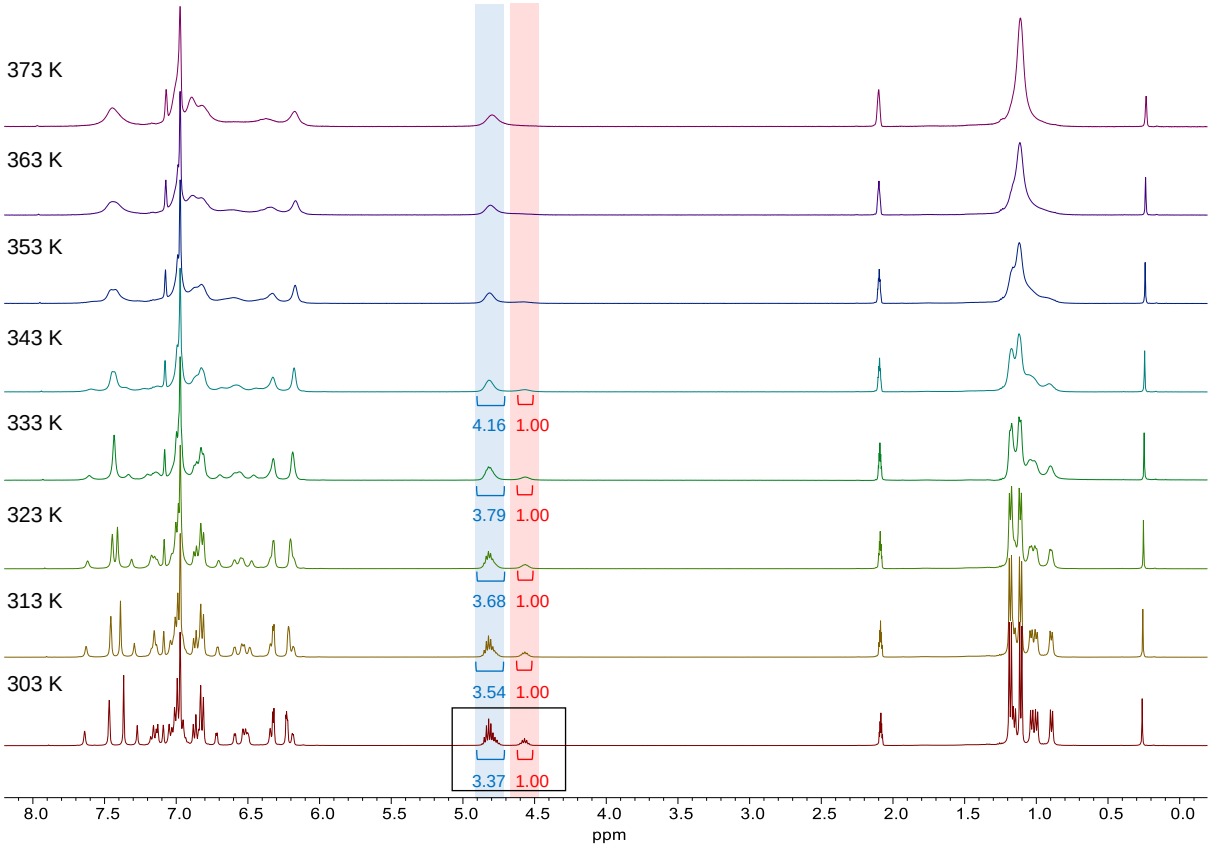


Fig. S3 ^{1}H NMR spectrum of **1** in toluene-d_8 at 363 K.



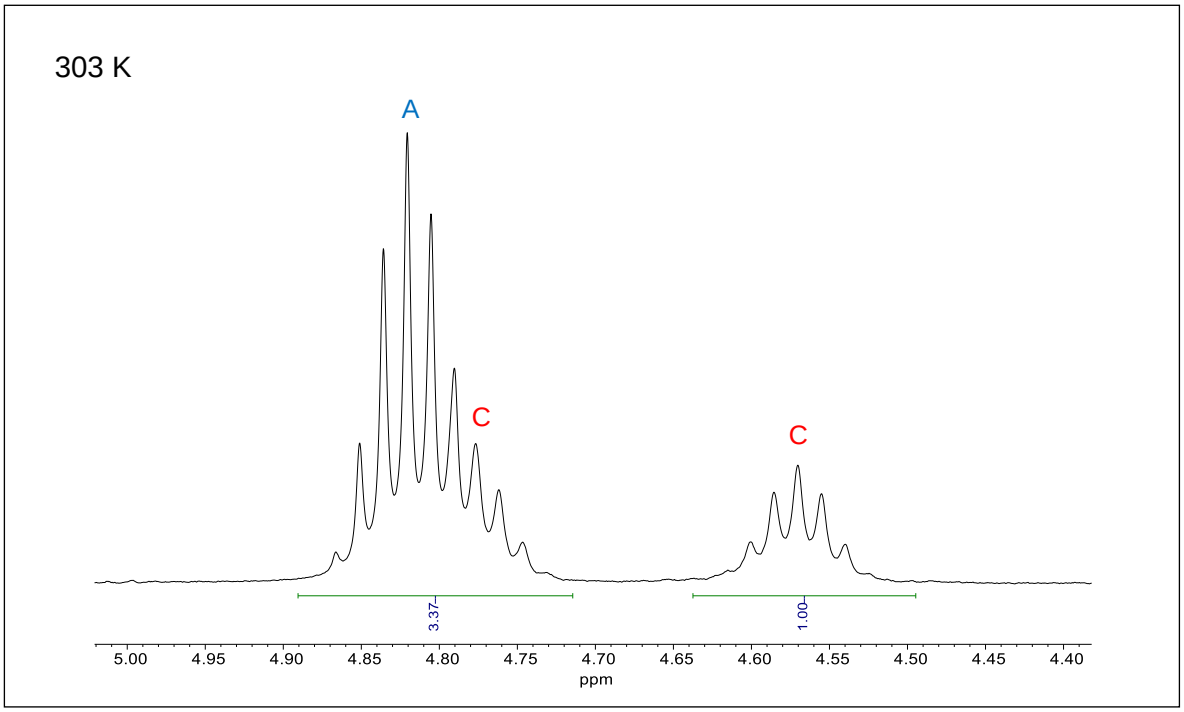
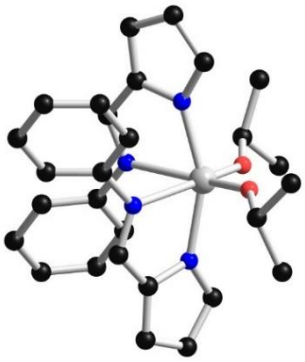
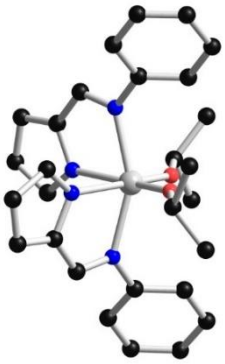


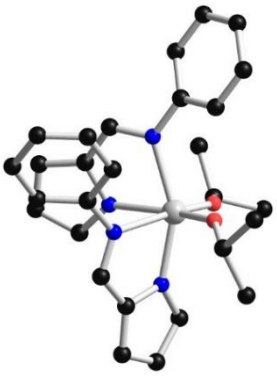
Fig. S4 ^{1}H NMR spectra of **1** in toluene-d_8 at different temperatures.



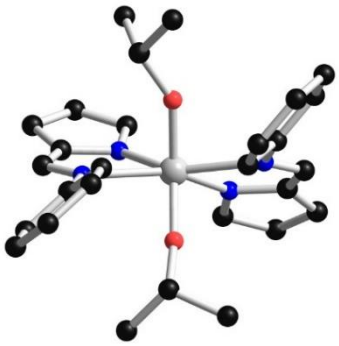
A
trans-N
cis-NR
cis-O^{i}Pr
Δ*G* = 0.0 kcal/mol



B
cis-N
trans-NR
cis-O^{i}Pr
Δ*G* = +3.3 kcal/mol



C
cis-N
cis-NR
cis-O^{i}Pr
Δ*G* = +3.3 kcal/mol



D
cis-N
cis-NR
trans-O^{i}Pr
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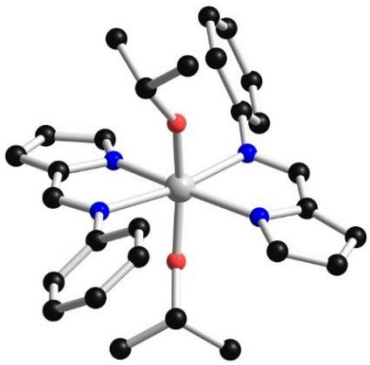

E
trans-N
trans-NR
trans-O^{i}Pr
Δ*G* = +21.1 kcal/mol

Fig. S5 Relative free energies of five possible stereoisomers of complex **1** calculated using the SMD(toluene)/M062X method with the 6-311+G(d,p) basis set for nonmetal atoms and the def2-tzvpp for Ti.

Cartesian coordinates of five possible stereoisomers of complex **1**

A

Ti	-0.3211	-0.6790	-1.2592
N	-2.3716	-0.3447	-1.0908
C	-2.8582	0.0982	0.1175
C	-3.4298	-0.4858	-1.9125
C	-4.2454	0.2444	0.0496
C	-4.6105	-0.1332	-1.2519
H	-3.2984	-0.8304	-2.9290
H	-4.8933	0.5786	0.8466
H	-5.6047	-0.1517	-1.6717
N	1.6995	-0.3207	-0.9101
C	2.1261	0.9853	-0.8450
C	2.7900	-1.0987	-0.7688
C	3.5086	1.0269	-0.6515
C	3.9329	-0.3103	-0.6053
H	2.7055	-2.1766	-0.7909
H	4.1151	1.9162	-0.5615
H	4.9413	-0.6711	-0.4709
C	-1.9045	0.2815	1.1560
H	-2.2204	0.6538	2.1313
C	1.1306	1.9860	-1.0181
H	1.3962	3.0418	-0.9550
C	-1.1083	2.5830	-1.3697
C	-2.0697	2.4495	-2.3745
C	-1.1963	3.6472	-0.4683
C	-3.0947	3.3783	-2.4848
H	-2.0016	1.6123	-3.0589
C	-2.2263	4.5753	-0.5860
H	-0.4698	3.7333	0.3328
C	-3.1777	4.4446	-1.5921
H	-3.8365	3.2648	-3.2669
H	-2.2910	5.3951	0.1203
H	-3.9833	5.1642	-1.6763
C	0.3148	0.2250	1.9084
C	1.3063	-0.7346	2.1262
C	0.3335	1.4144	2.6418
C	2.2950	-0.5120	3.0740
H	1.2904	-1.6472	1.5424
C	1.3262	1.6292	3.5934
H	-0.4168	2.1746	2.4514
C	2.3099	0.6703	3.8109
H	3.0611	-1.2623	3.2322
H	1.3368	2.5559	4.1556
H	3.0874	0.8440	4.5454
N	-0.0848	1.6107	-1.2718
N	-0.6661	-0.0229	0.9187
O	-0.2324	-0.7021	-3.0359
O	-0.3342	-2.3906	-0.7726
C	0.2335	0.0293	-4.1569
C	1.6870	-0.3363	-4.4200
C	-0.6667	-0.2719	-5.3445
H	0.1723	1.0991	-3.9161
H	2.3062	-0.1043	-3.5500
H	2.0683	0.2223	-5.2787
H	1.7712	-1.4055	-4.6323
H	-1.7027	-0.0051	-5.1217
H	-0.6286	-1.3383	-5.5825
H	-0.3458	0.2949	-6.2220
C	-0.7956	-3.2718	0.2370
C	-2.1873	-3.7640	-0.1322
C	0.2009	-4.4103	0.3870
H	-0.8525	-2.7112	1.1796
H	-2.8806	-2.9251	-0.2285
H	-2.5661	-4.4424	0.6366
H	-2.1534	-4.2990	-1.0849
H	1.1904	-4.0289	0.6506
H	0.2826	-4.9623	-0.5530
H	-0.1224	-5.0995	1.1711

B

Ti	-0.609668	-0.740380	0.417992
N	-0.624811	-1.085510	-1.726669
C	-0.421916	-2.407275	-2.059597
C	-0.838709	-0.429868	-2.869203
C	-0.512607	-2.573579	-3.453904
C	-0.779312	-1.308450	-3.971667
H	-1.031664	0.635159	-2.870038
H	-0.396720	-3.500898	-3.995852
H	-0.914641	-1.039440	-5.008195
N	1.523914	-0.584347	0.024734
C	1.914424	0.685142	-0.341978
C	2.634565	-1.321408	0.096614
C	3.311014	0.734001	-0.504604
C	3.771663	-0.550201	-0.224579
H	2.592499	-2.366038	0.376935
H	3.892653	1.599362	-0.787871
H	4.792693	-0.899960	-0.245204
C	-0.231068	-3.310541	-0.994741
H	-0.072249	-4.370806	-1.191645
C	0.903299	1.663508	-0.422924
H	1.148516	2.689729	-0.696864
C	-1.352527	2.311205	-0.211212
C	-2.295114	2.390319	0.816253
C	-1.444757	3.174470	-1.305736
C	-3.306661	3.339548	0.754813
H	-2.224768	1.700545	1.650294
C	-2.465280	4.117595	-1.362095
H	-0.730822	3.089285	-2.118099
C	-3.396655	4.206053	-0.332340
H	-4.032208	3.400239	1.557998
H	-2.534779	4.778939	-2.218116
H	-4.192236	4.940136	-0.380479
C	-0.062154	-3.757537	1.316030
C	-0.902707	-3.687729	2.429258
C	0.988658	-4.677660	1.297261
C	-0.705844	-4.550179	3.499660
H	-1.700557	-2.953170	2.443215
C	1.182650	-5.532919	2.376679
H	1.662477	-4.706960	0.447651
C	0.336535	-5.474077	3.479292
H	-1.365840	-4.496163	4.357941
H	2.004889	-6.238928	2.357399
H	0.492708	-6.139389	4.320027
N	-0.327339	1.336148	-0.127944
N	-0.277267	-2.866955	0.234337
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O	-2.393213	-0.822888	0.402755
C	0.752071	-0.131294	3.065668
C	1.020458	-1.268448	4.038851
C	0.305861	1.145854	3.761247
H	1.666473	0.070687	2.493174
H	1.342112	-2.165419	3.503790
H	1.807509	-0.981972	4.741399
H	0.115813	-1.508442	4.604469
H	0.126902	1.934851	3.026371
H	-0.618946	0.970346	4.317937
H	1.073699	1.491623	4.457984
C	-3.506269	-1.187704	-0.394163
C	-4.380575	0.034005	-0.629109
C	-4.254890	-2.311771	0.306809
H	-3.130285	-1.550165	-1.359440
H	-3.817400	0.823408	-1.132924
H	-5.238175	-0.232550	-1.252525
H	-4.749134	0.425686	0.323057
H	-3.599695	-3.173426	0.455612
H	-4.615453	-1.973695	1.282333
H	-5.112575	-2.630319	-0.291192

C

Ti	-0.2013	-0.8132	-1.2476
N	-2.1922	-0.2427	-1.0874
C	-2.6230	0.2207	0.1355
C	-3.2448	-0.1936	-1.9249
C	-3.9755	0.5642	0.0612
C	-4.3729	0.2984	-1.2579
H	-3.1493	-0.5167	-2.9521
H	-4.5802	0.9572	0.8653
H	-5.3540	0.4383	-1.6860
N	0.0987	1.3305	-1.3410
C	1.3605	1.7266	-0.9497
C	-0.6503	2.4355	-1.4019
C	1.3974	3.1209	-0.7752
C	0.1119	3.5745	-1.0676
H	-1.6974	2.3829	-1.6732
H	2.2559	3.7059	-0.4781
H	-0.2418	4.5944	-1.0562
C	-1.6538	0.2849	1.1775
H	-1.9268	0.6775	2.1581
C	2.3226	0.7107	-0.8060
H	3.3485	0.9676	-0.5460
C	2.9905	-1.5218	-1.0954
C	2.7202	-2.8436	-0.7335
C	4.2586	-1.2074	-1.6019
C	3.7084	-3.8157	-0.8255
H	1.7259	-3.1014	-0.3982
C	5.2434	-2.1840	-1.6856
H	4.4670	-0.2092	-1.9684
C	4.9791	-3.4914	-1.2901
H	3.4774	-4.8352	-0.5370
H	6.2178	-1.9217	-2.0819
H	5.7471	-4.2518	-1.3662
C	0.5598	0.0059	1.9043
C	1.4231	-1.0666	2.1375
C	0.7540	1.2123	2.5797
C	2.4551	-0.9410	3.0580
H	1.2742	-1.9895	1.5877
C	1.7892	1.3308	3.5014
H	0.1199	2.0613	2.3467
C	2.6403	0.2573	3.7450
H	3.1199	-1.7786	3.2356
H	1.9398	2.2724	4.0169
H	3.4496	0.3563	4.4586
N	1.9723	-0.5386	-0.9945
N	-0.4545	-0.1339	0.9296
O	-0.1941	-1.0275	-3.0070
O	-0.4397	-2.4762	-0.6194
C	-0.1338	-0.3074	-4.2275
C	1.2973	0.1466	-4.4718
C	-0.6569	-1.1985	-5.3428
H	-0.7788	0.5751	-4.1265
H	1.6280	0.8087	-3.6687
H	1.3671	0.6894	-5.4179
H	1.9628	-0.7203	-4.5155
H	-1.6719	-1.5360	-5.1228
H	-0.0173	-2.0783	-5.4505
H	-0.6692	-0.6551	-6.2908
C	-1.1299	-3.2540	0.3420
C	-2.5379	-3.5407	-0.1619
C	-0.3547	-4.5376	0.6076
H	-1.1921	-2.6713	1.2710
H	-3.0791	-2.6113	-0.3508
H	-3.0927	-4.1216	0.5792
H	-2.4929	-4.1124	-1.0929
H	0.6227	-4.3345	1.0524
H	-0.2078	-5.0857	-0.3272
H	-0.9105	-5.1743	1.3003

D

Ti	0.057797	-0.219898	-0.021294
N	-2.017062	-0.404372	0.313339
C	-2.872993	-0.099810	-0.726580
C	-2.763666	-1.036475	1.246049
C	-4.168780	-0.520527	-0.427056
C	-4.095973	-1.124268	0.837355
H	-2.319683	-1.404393	2.158968
H	-5.037293	-0.413118	-1.060443
H	-4.902095	-1.575596	1.395485
N	0.064825	-0.107695	2.084910
C	1.219290	-0.471456	2.746953
C	-0.725781	0.492913	3.002037
C	1.136254	-0.123917	4.094287
C	-0.111413	0.498603	4.255677
H	-1.693728	0.886751	2.729598
H	1.895926	-0.288843	4.844537
H	-0.527081	0.906770	5.164434
C	-2.272581	0.372683	-1.924709
H	-2.881721	0.659188	-2.783036
C	2.284377	-0.951037	1.937240
H	3.214274	-1.306954	2.382539
C	3.080794	-1.437199	-0.223848
C	3.393407	-0.713782	-1.377456
C	3.689718	-2.673744	-0.000047
C	4.320244	-1.211999	-2.284110
H	2.908527	0.242129	-1.545611
C	4.615457	-3.167968	-0.913360
H	3.410888	-3.258201	0.870001
C	4.935054	-2.441458	-2.056280
H	4.567450	-0.636025	-3.168975
H	5.078693	-4.132140	-0.736971
H	5.653773	-2.832203	-2.766937
C	-0.288740	0.859173	-3.103823
C	0.860094	0.168320	-3.499889
C	-0.681862	2.000774	-3.808122
C	1.598879	0.606429	-4.590630
H	1.161792	-0.714802	-2.948078
C	0.065186	2.434581	-4.898981
H	-1.551251	2.562150	-3.483414
C	1.206678	1.742894	-5.293826
H	2.481971	0.054682	-4.892839
H	-0.240550	3.325637	-5.435225
H	1.787353	2.087796	-6.141038
N	2.114206	-0.911189	0.658591
N	-0.981553	0.391588	-1.966317
O	0.789272	1.384822	-0.268734
O	0.205891	-1.820644	-0.832559
C	1.426667	2.527181	-0.786621
C	2.672710	2.816037	0.039467
C	0.444334	3.689345	-0.764315
H	1.712745	2.320011	-1.827854
H	3.353119	1.961666	0.029524
H	3.200241	3.687184	-0.357732
H	2.390767	3.017642	1.076402
H	-0.465493	3.427704	-1.308228
H	0.174516	3.927899	0.268136
H	0.886107	4.575469	-1.227100
C	-0.292869	-2.698382	-1.817872
C	-1.479480	-3.472756	-1.261609
C	0.842135	-3.612740	-2.259196
H	-0.631978	-2.101425	-2.675767
H	-2.285194	-2.795047	-0.968907
H	-1.865605	-4.166453	-2.013591
H	-1.173070	-4.047206	-0.382862
H	1.704085	-3.025967	-2.591333
H	1.161674	-4.238634	-1.421532
H	0.521159	-4.260809	-3.079105

E

Ti	-0.159192	-0.527454	0.156698
N	-2.222323	-0.035860	0.423591
C	-2.796037	0.395263	-0.764435
C	-3.178313	0.086396	1.361464
C	-4.129077	0.767671	-0.551100
C	-4.371454	0.573639	0.809036
H	-2.995004	-0.167061	2.394359
H	-4.810384	1.141251	-1.302027
H	-5.287884	0.759074	1.347951
N	1.967416	-0.906803	0.377884
C	2.302863	-1.126235	1.696964
C	3.120230	-0.752135	-0.285576
C	3.698989	-1.123947	1.850793
C	4.221748	-0.880936	0.582651
H	3.137210	-0.552736	-1.348058
H	4.238539	-1.283304	2.772992
H	5.261839	-0.814233	0.301823
C	-2.003044	0.467945	-1.933735
H	-2.456427	0.804794	-2.866735
C	1.246739	-1.324790	2.611070
H	1.458192	-1.613900	3.640935
C	-1.034981	-1.610838	3.076164
C	-1.920265	-2.597352	2.643477
C	-1.203749	-1.011436	4.322862
C	-2.969935	-2.989062	3.463592
H	-1.777679	-3.027091	1.658185
C	-2.261667	-1.406778	5.137058
H	-0.527584	-0.222609	4.633543
C	-3.145777	-2.393297	4.711014
H	-3.657715	-3.754787	3.123818
H	-2.399958	-0.932881	6.102155
H	-3.971587	-2.693172	5.345215
C	0.099133	0.253868	-2.996523
C	1.129017	-0.679683	-3.146415
C	-0.026132	1.293713	-3.924577
C	2.004115	-0.590476	-4.221829
H	1.226489	-1.478304	-2.417871
C	0.851750	1.372992	-4.998824
H	-0.790210	2.051273	-3.791898
C	1.867385	0.433336	-5.154887
H	2.793400	-1.325696	-4.330807
H	0.749732	2.183508	-5.711212
H	2.552272	0.504742	-5.991152
N	0.013419	-1.221981	2.199314
N	-0.750993	0.131929	-1.878531
O	0.337244	1.196414	0.351565
O	-0.450697	-2.180209	-0.529434
C	1.203945	2.148359	-0.223227
C	2.254543	2.542788	0.805198
C	0.388523	3.337319	-0.710090
H	1.708458	1.686052	-1.084830
H	2.813661	1.663727	1.135635
H	2.958899	3.263168	0.380147
H	1.770910	2.998060	1.674000
H	-0.374504	3.008163	-1.419196
H	-0.113485	3.818447	0.133748
H	1.030891	4.071493	-1.203516
C	-0.940989	-2.995925	-1.563269
C	-2.347293	-3.466193	-1.211021
C	0.012650	-4.162416	-1.781883
H	-0.992935	-2.395792	-2.483099
H	-2.982956	-2.613203	-0.959237
H	-2.795616	-4.000743	-2.052772
H	-2.316279	-4.144809	-0.353559
H	1.017081	-3.805273	-2.021473
H	0.075397	-4.765637	-0.872114
H	-0.333913	-4.798184	-2.600887

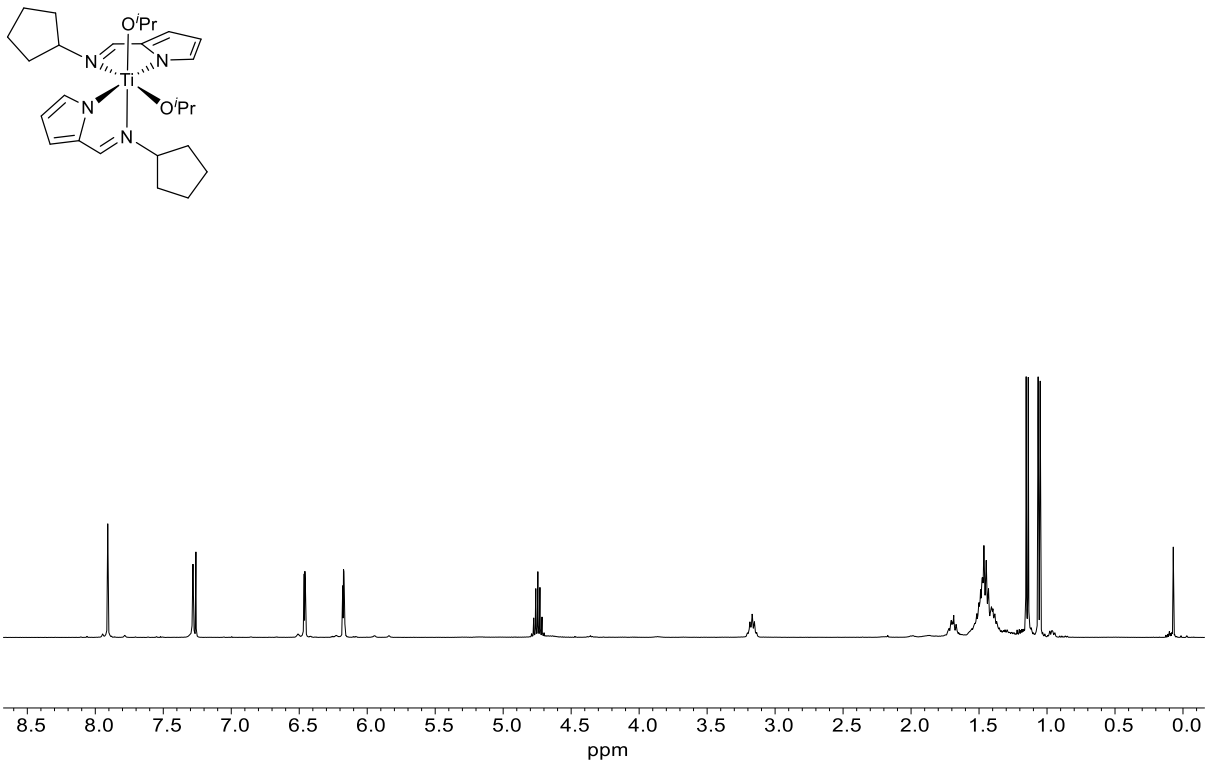

Fig. S6 ^{1}H NMR spectrum of **2** in $CDCl_3$ at 298 K.

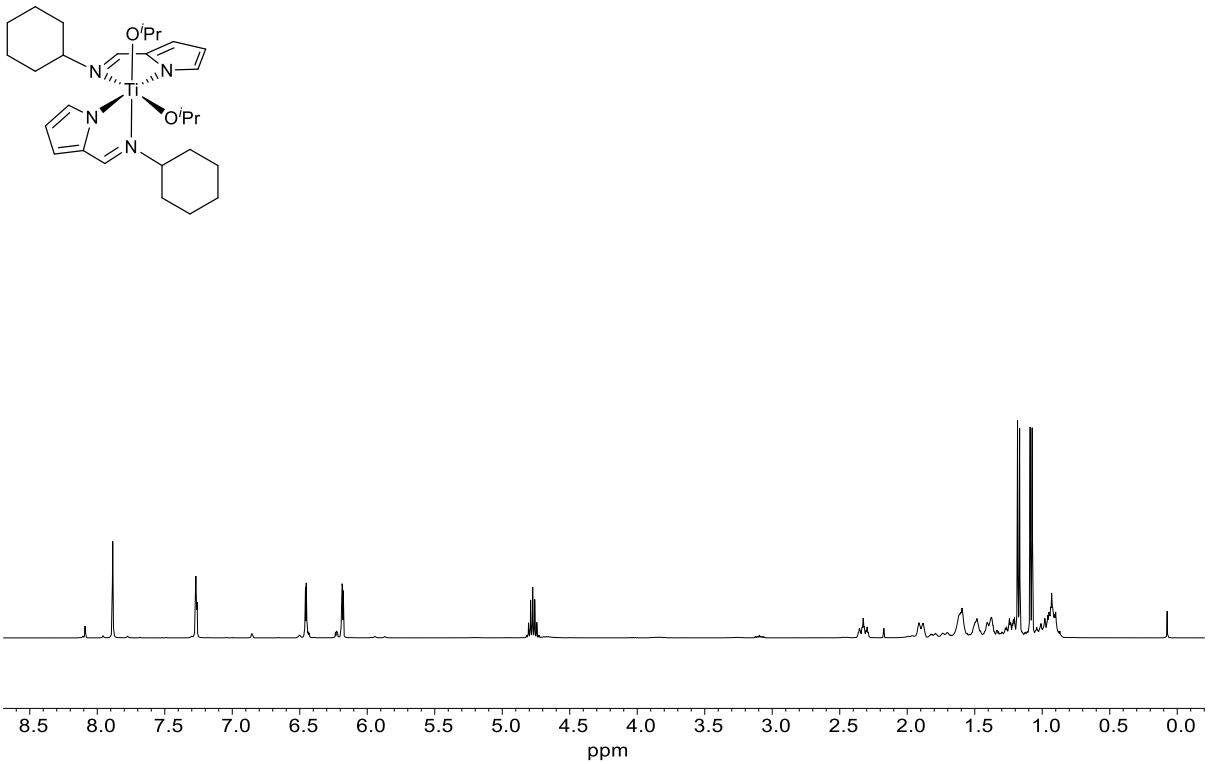

Fig. S7 ^{1}H NMR spectrum of **3** in $CDCl_3$ at 298 K.

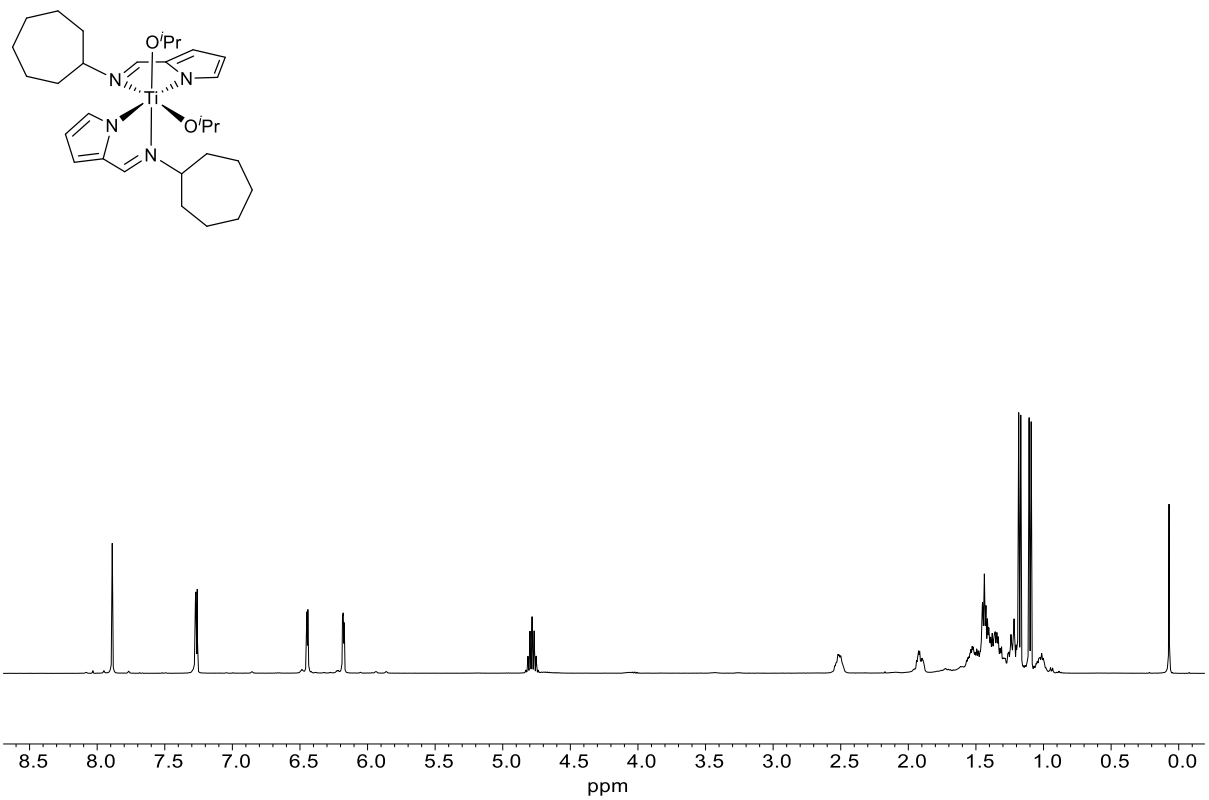

Fig. S8 ^{1}H NMR spectrum of **4** in $CDCl_3$ at 298 K.

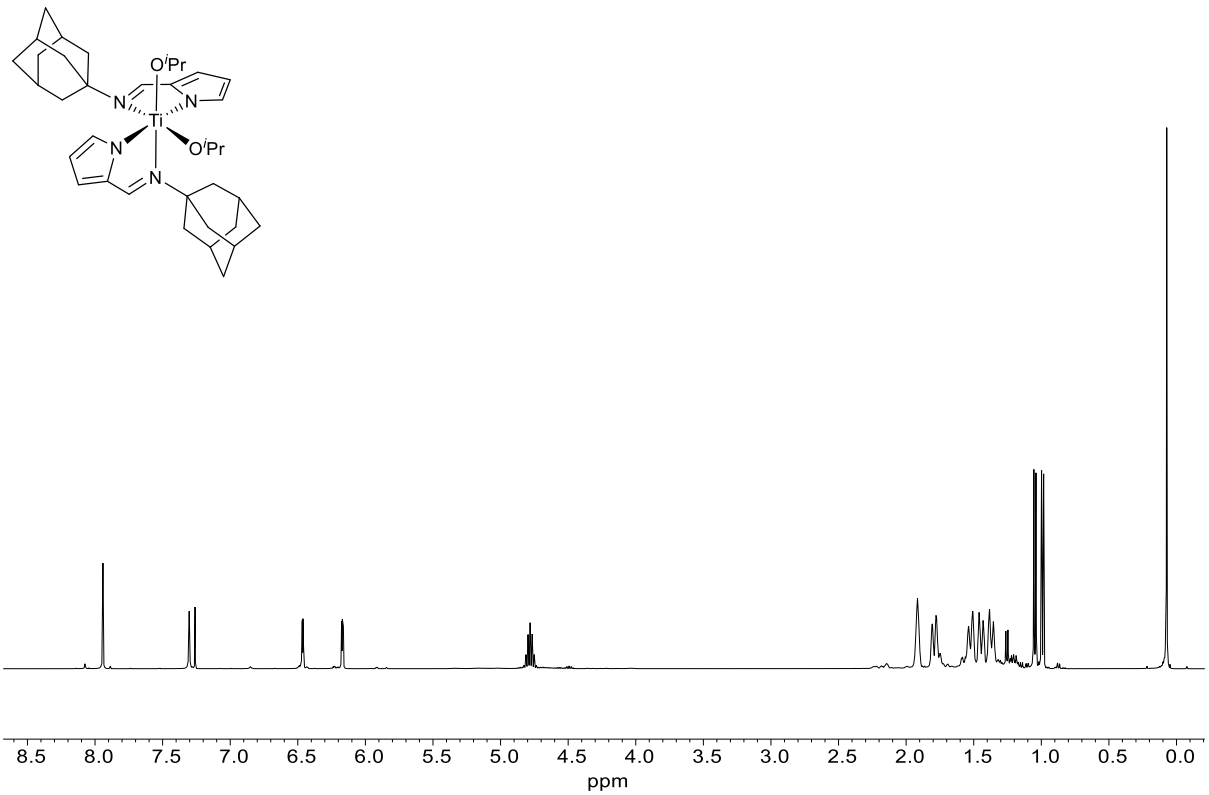

Fig. S9 ^{1}H NMR spectrum of **5** in $CDCl_3$ at 298 K.

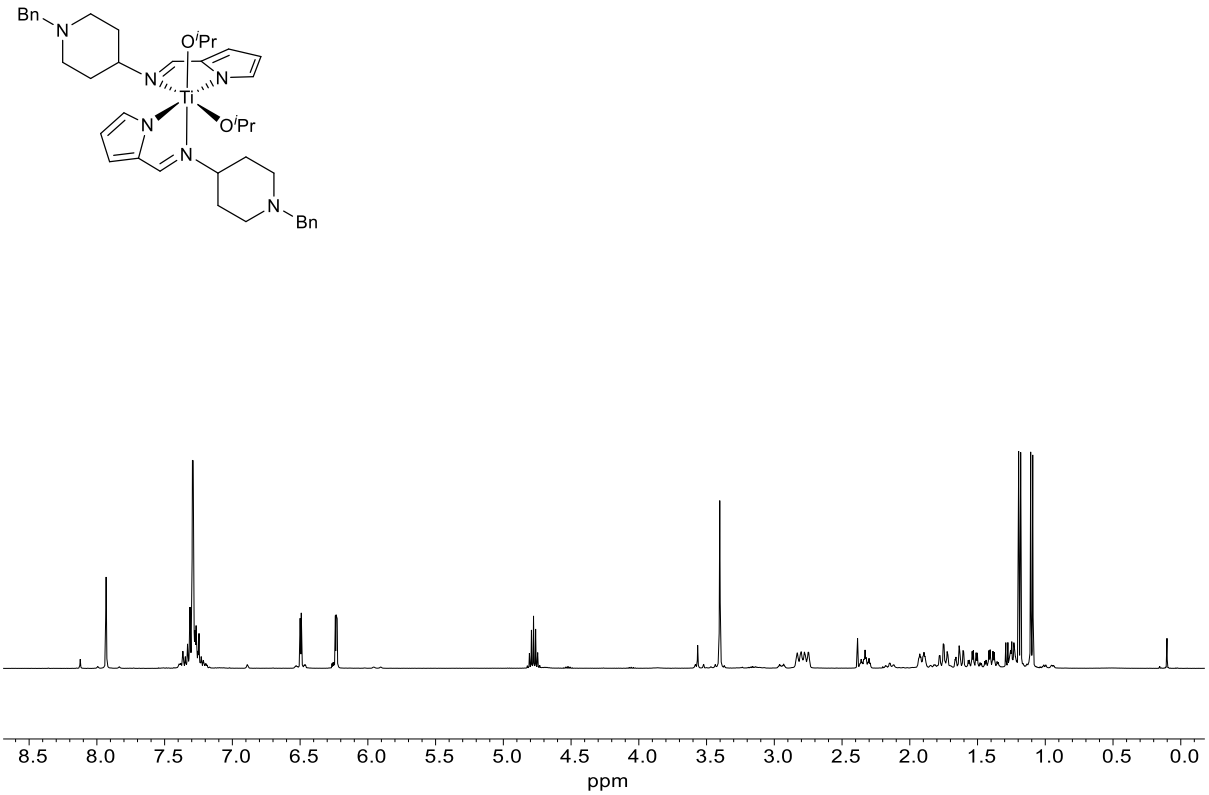

Fig. S10 ^{1}H NMR spectrum of **6** in $CDCl_3$ at 298 K.

Table S1 Crystal data and structure refinement for the complex **2.**

Empirical formula	$C_{26}H_{40}N_4O_2Ti$
Formula weight	488.52
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.9560(9)
b/Å	16.7630(17)
c/Å	18.1781(19)
α/°	90
β/°	75.196(3)
γ/°	90
Volume/Å^3	2638.5(5)
Z	4
ρ_{calc}g/cm^3	1.230
μ/mm^{-1}	2.966
F(000)	1048.0
Crystal size/mm^3	0.04 × 0.02 × 0.02
Radiation	CuK*α* (λ = 1.54178)
2*Θ* range for data collection/°	7.288 to 137.29
Index ranges	$-10 \le h \le 10$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	42047
Independent reflections	4688 [R_{int} = 0.0705, R_{sigma} = 0.0426]
Data/restraints/parameters	4688/144/357
Goodness-of-fit on F^2	1.219
Final *R* indexes [$I >= 2\sigma(I)$]	R_1 = 0.1454, wR_2 = 0.3409
Final *R* indexes [all data]	R_1 = 0.1465, wR_2 = 0.3410
Largest diff. peak/hole / e Å^{-3}	0.73/–0.58

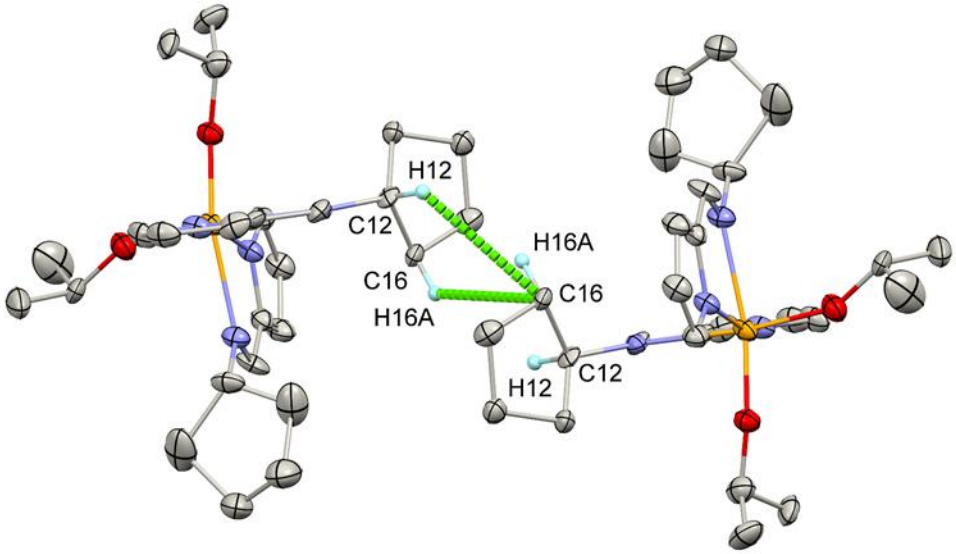

Fig. S11 A view of the C–H···C interactions (C16–H16A···C16 and C12–H12···C16) forming between two cyclopentyl moieties representing weak Van der Waals forces between molecules of **2**.

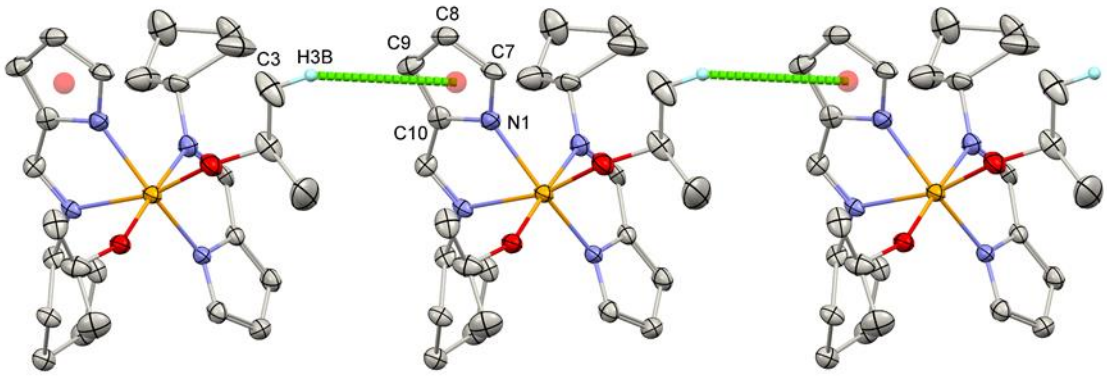

Fig. S12 A view of the chain of the molecules of **2** related by a translational symmetry illustrating the C–H···C_g interactions (C3–H3B···C_g). Note that, C_g is the centroid of the pyrrole ring (N1 and C7 to C10).

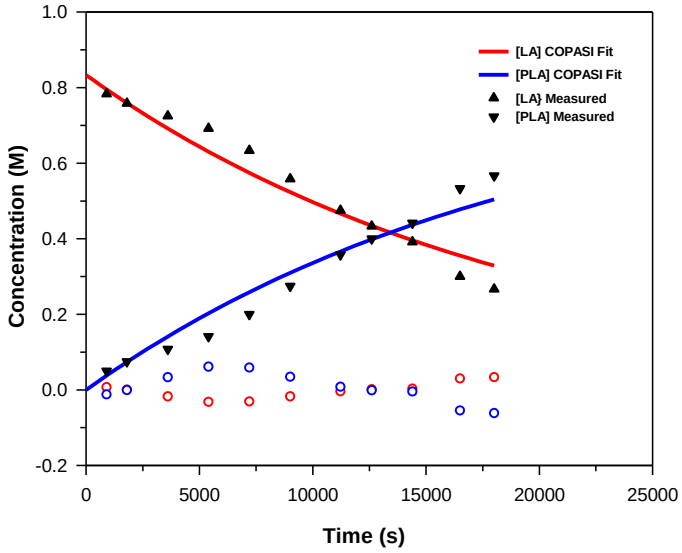

Fig. S13 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **2** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

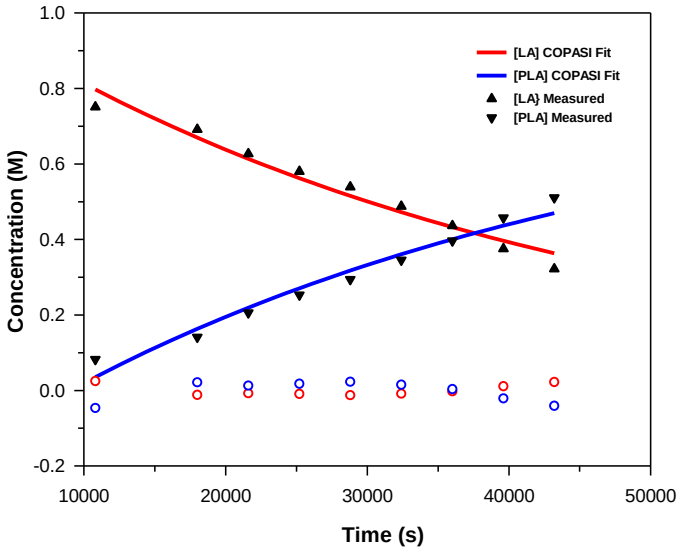

Fig. S14 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **3** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

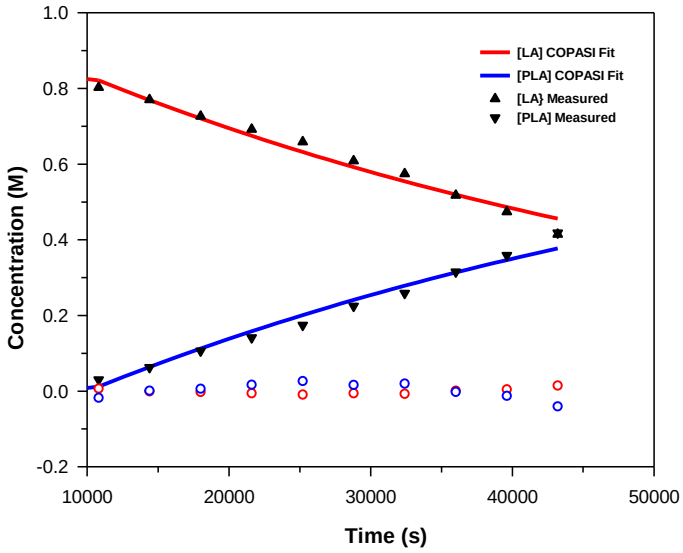

Fig. S15 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **4** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

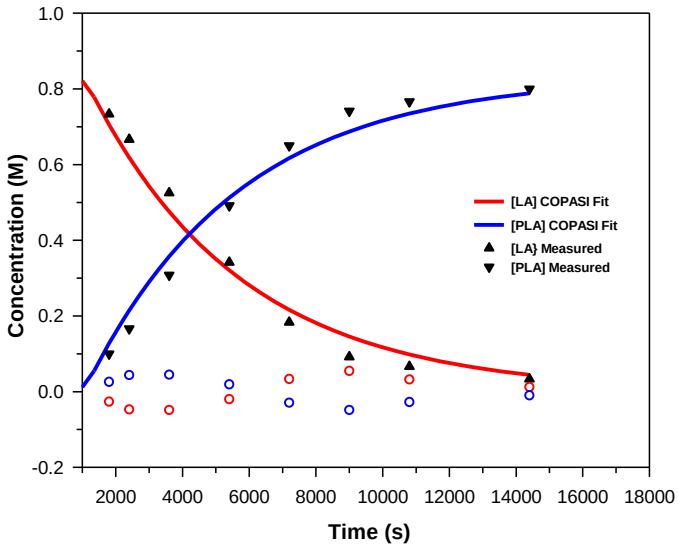

Fig. S16 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **5** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

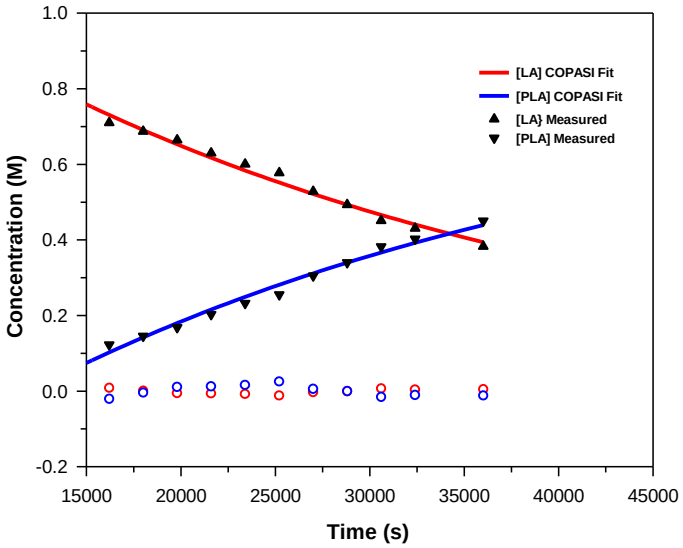

Fig. S17 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **6** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

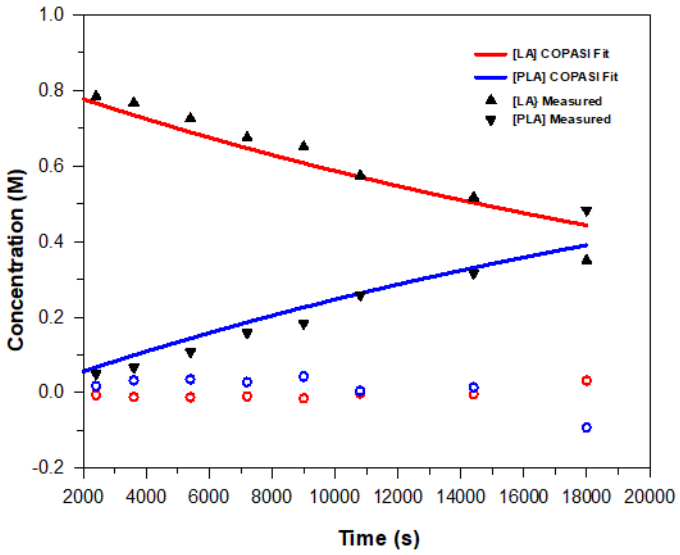

Fig. S18 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **1** at 100 °C along with the fits (blue and red lines) and errors determined by COPASI.

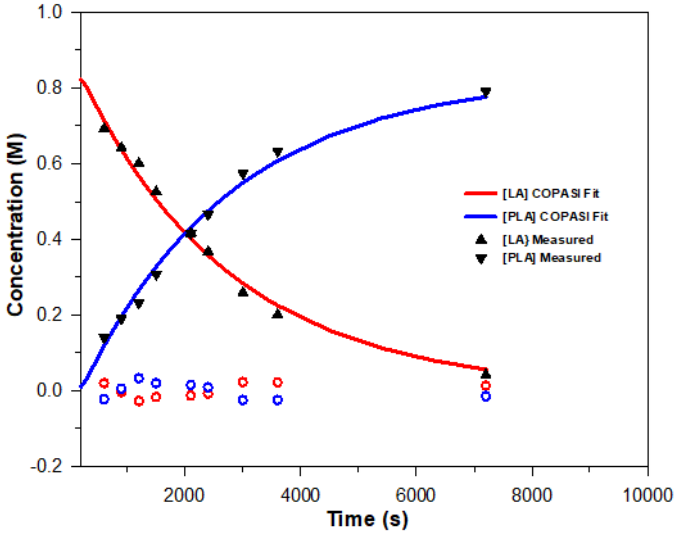

Fig. S19 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **2** at 100 °C along with the fits (blue and red lines) and errors determined by COPASI.

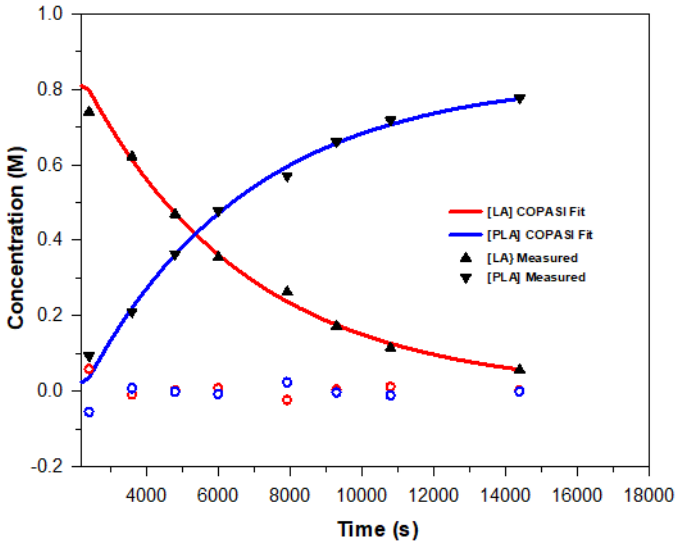

Fig. S20 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **3** at 100 °C along with the fits (blue and red lines) and errors determined by COPASI.

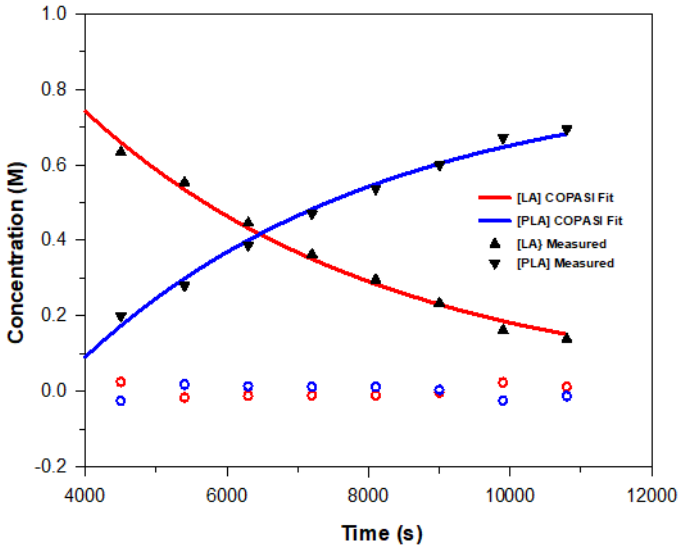

Fig. S21 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **4** at 100 °C along with the fits (blue and red lines) and errors determined by COPASI.

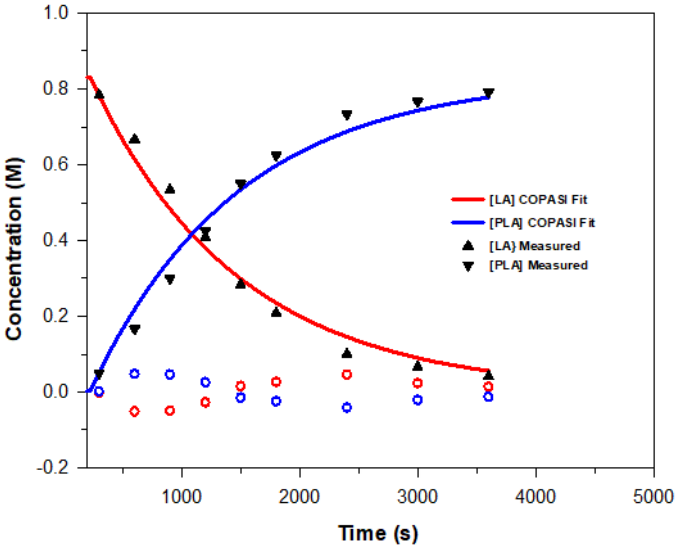

Fig. S22 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **5** at 100 °C along with the fits (blue and red lines) and errors determined by COPASI.

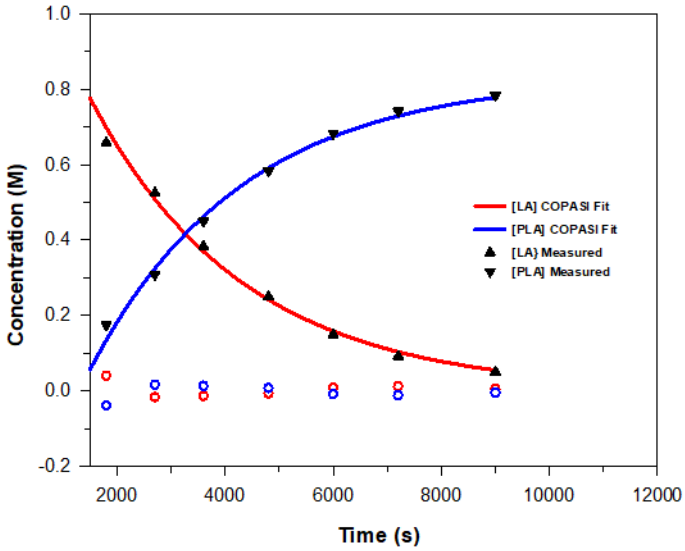

Fig. S23 Concentration versus time profile for the ^{1}H NMR resonance decay of *rac*-LA (▲) and the growth of PLA (▼) for the ROP of *rac*-LA by complex **6** at 100 °C along with the fits (blue and red lines) and errors determined by COPASI.

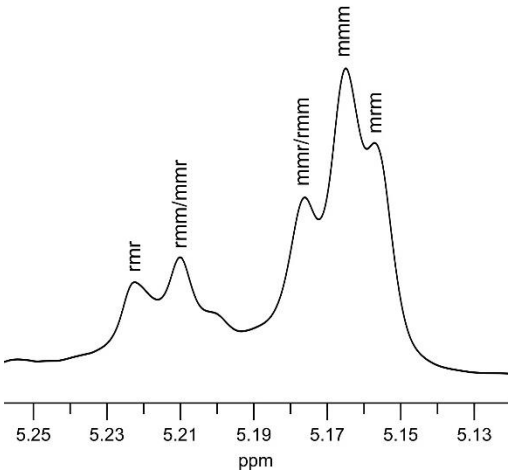

Fig. S24 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 70 ºC in toluene (400 MHz, $CDCl_3$) using complex **1**.

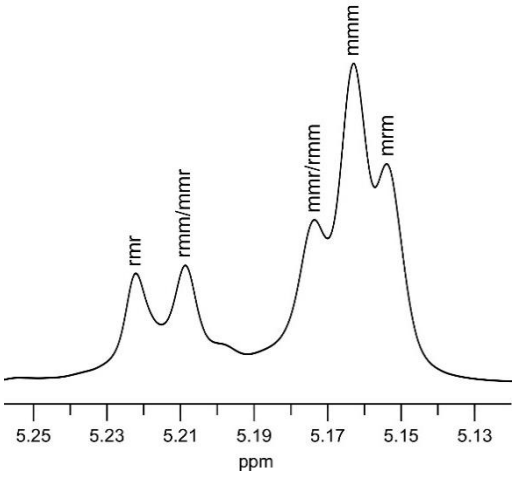

Fig. S25 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 70 ºC in toluene (400 MHz, $CDCl_3$) using complex **2**.

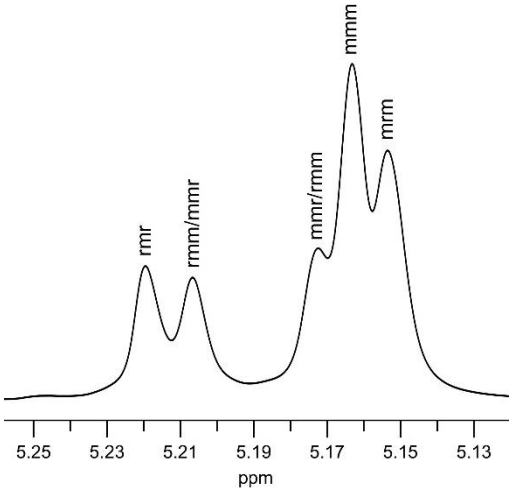

Fig. S26 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 70 ºC in toluene (400 MHz, $CDCl_3$) using complex **3**.

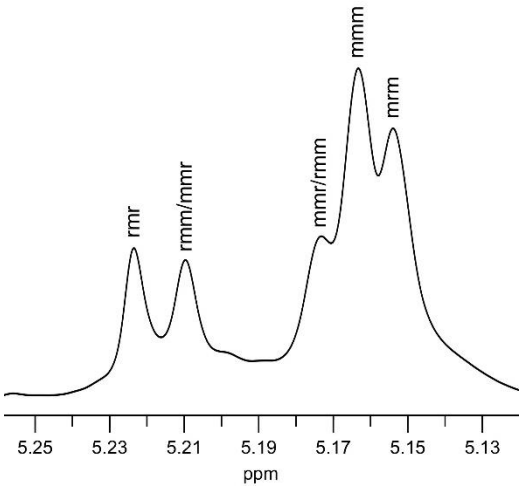

Fig. S27 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 70 ºC in toluene (400 MHz, $CDCl_3$) using complex **4**.

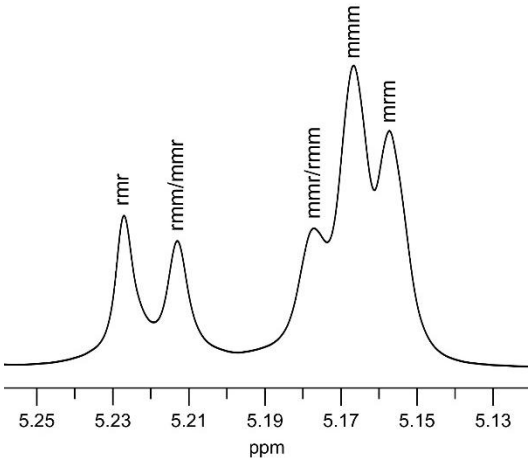

Fig. S28 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 70 ºC in toluene (400 MHz, $CDCl_3$) using complex **5**.

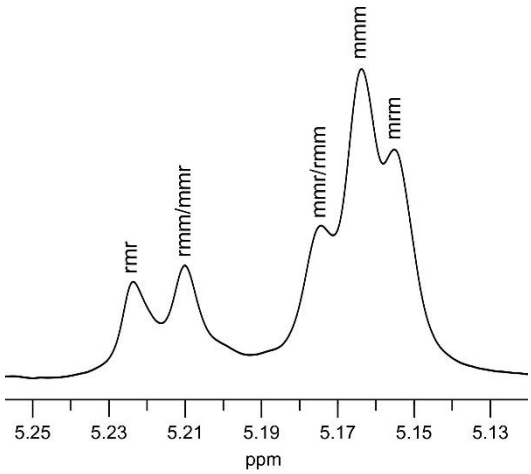

Fig. S29 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 70 ºC in toluene (400 MHz, $CDCl_3$) using complex **6**.

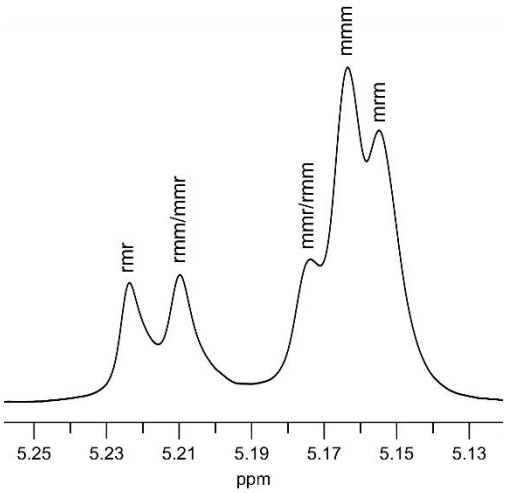

Fig. S30 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 100 ºC in toluene (400 MHz, $CDCl_3$) using complex **1**.

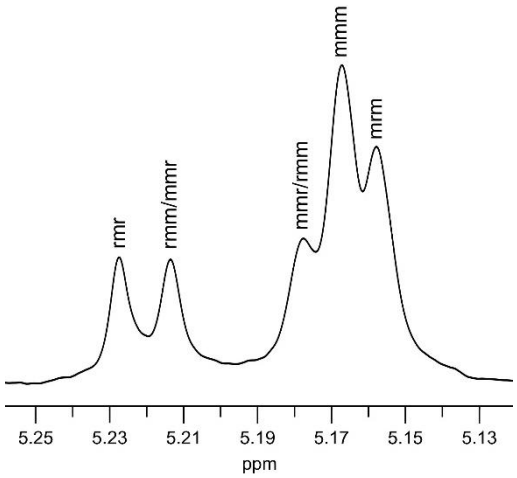

Fig. S31 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 100 ºC in toluene (400 MHz, $CDCl_3$) using complex **2**.

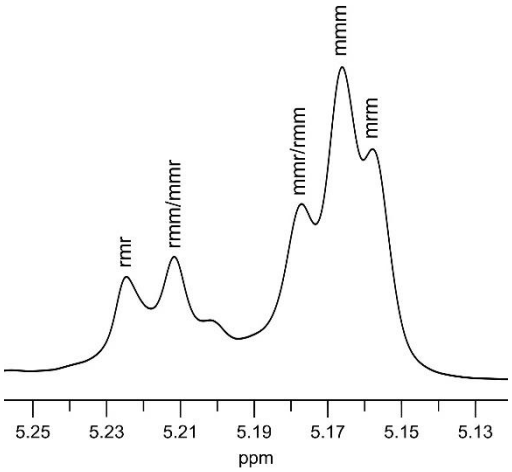

Fig. S32 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 100 ºC in toluene (400 MHz, $CDCl_3$) using complex **3**.

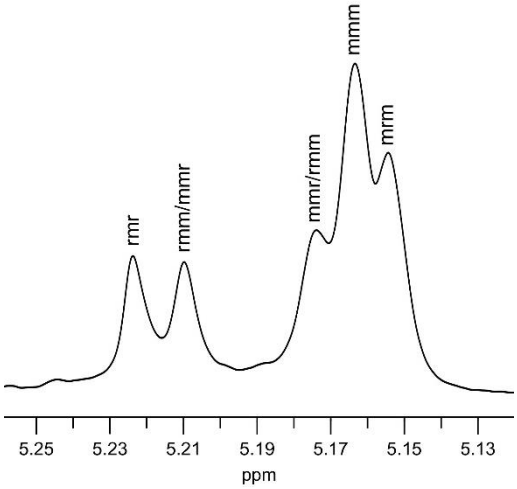

Fig. S33 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 100 ºC in toluene (400 MHz, $CDCl_3$) using complex **4**.

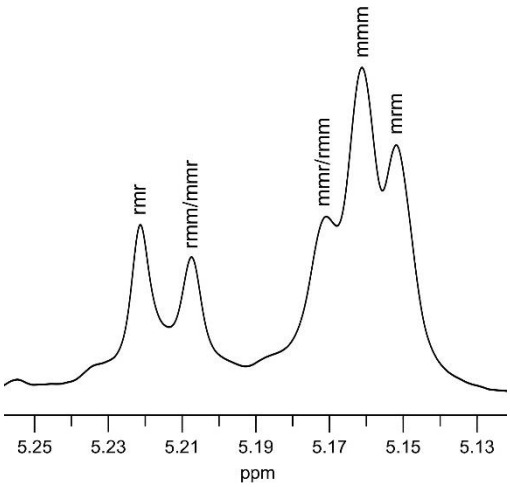

Fig. S34 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 100 ºC in toluene (400 MHz, $CDCl_3$) using complex **5**.

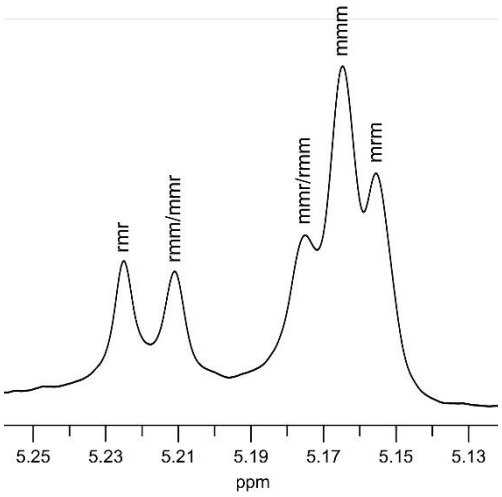

Fig. S35 Homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA prepared from *rac*-LA at 100 ºC in toluene (400 MHz, $CDCl_3$) using complex **6**.

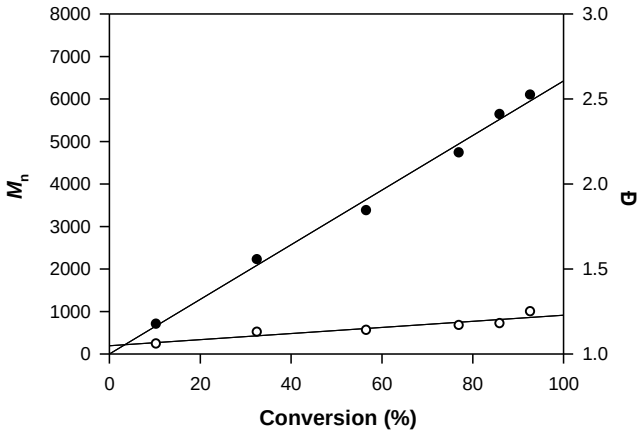

Fig. S36 Plot of PCL M_n (●) (versus polystyrene standards) and PDI (○) as a function of monomer conversion for a ε-CL polymerisation using **5** ([ε-CL]$_0$/[Ti] = 100, toluene, 70 ºC).

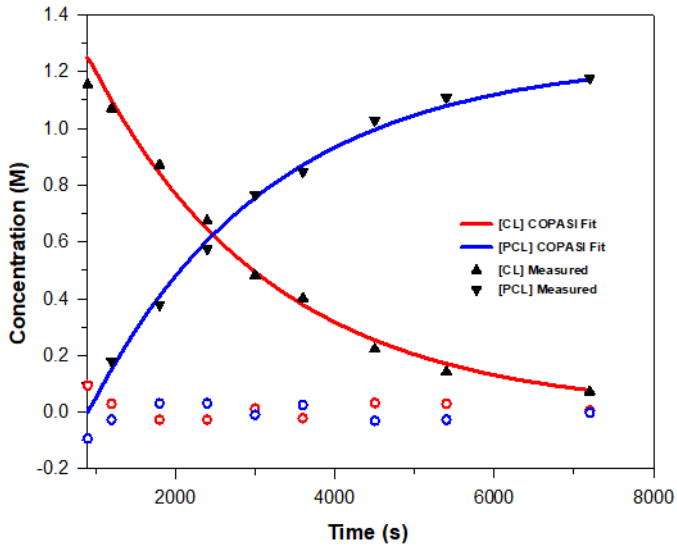

Fig. S37 Concentration versus time profile for the ^{1}H NMR resonance decay of ε-CL (▲) and the growth of PCL (▼) for the ROP of ε-CL by complex **1** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

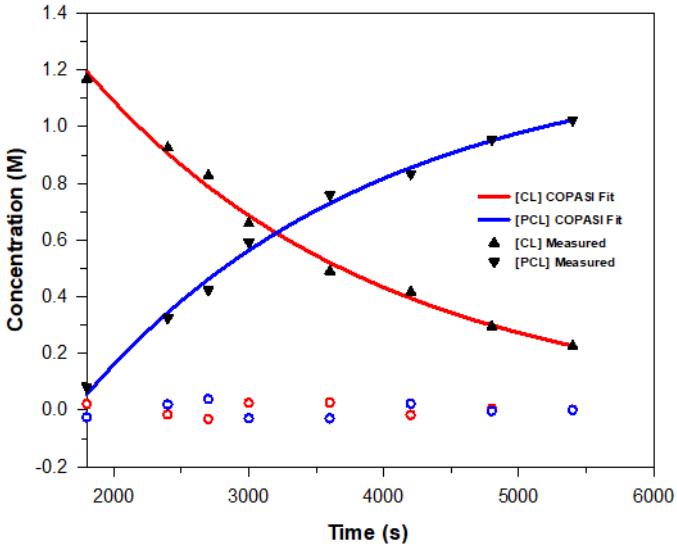

Fig. S38 Concentration versus time profile for the ^{1}H NMR resonance decay of ε-CL (▲) and the growth of PCL (▼) for the ROP of ε-CL by complex **2** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

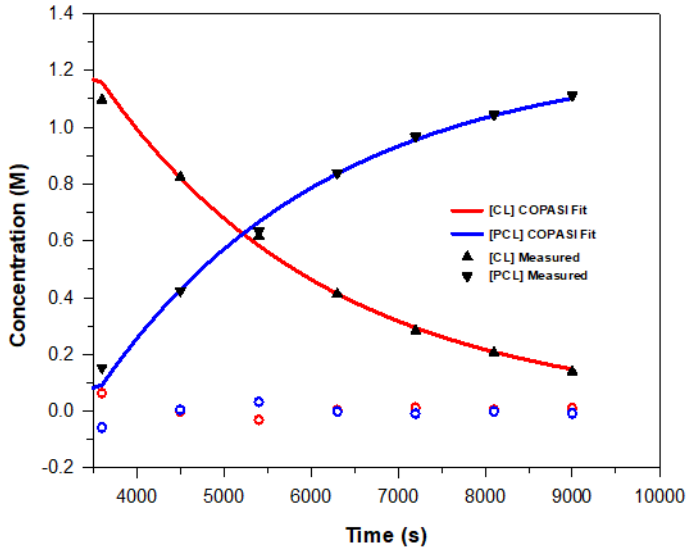

Fig. S39 Concentration versus time profile for the ^{1}H NMR resonance decay of ε-CL (▲) and the growth of PCL (▼) for the ROP of ε-CL by complex **3** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

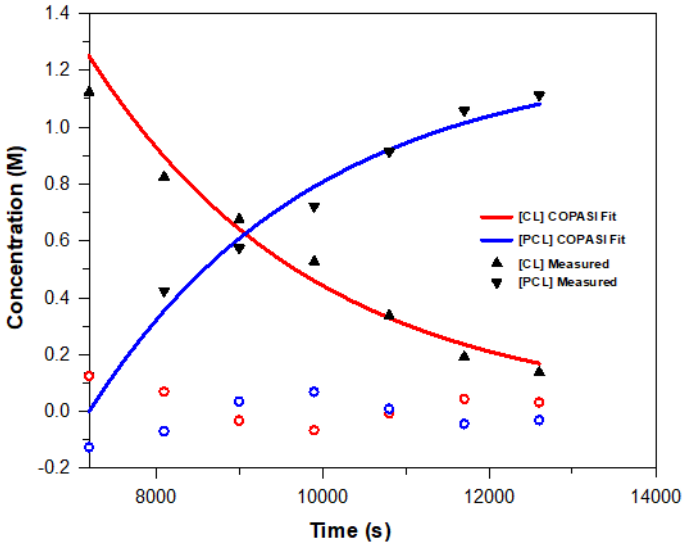

Fig. S40 Concentration versus time profile for the ^{1}H NMR resonance decay of ε-CL (▲) and the growth of PCL (▼) for the ROP of ε-CL by complex **4** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

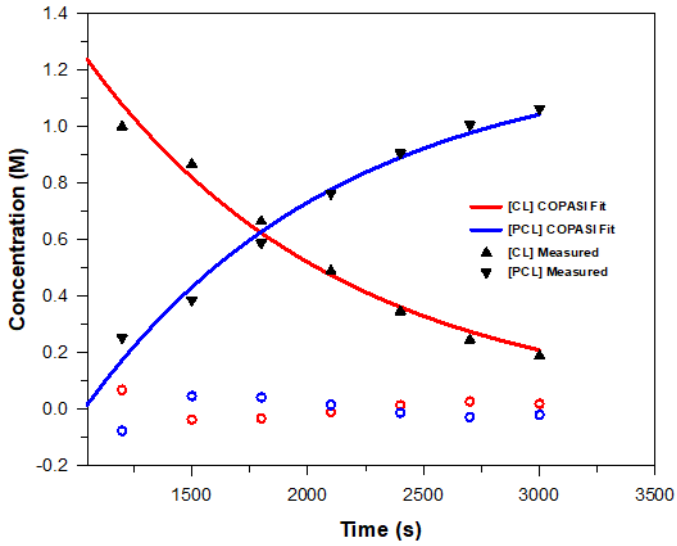

Fig. S41 Concentration versus time profile for the ^{1}H NMR resonance decay of ε-CL (▲) and the growth of PCL (▼) for the ROP of ε-CL by complex **5** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

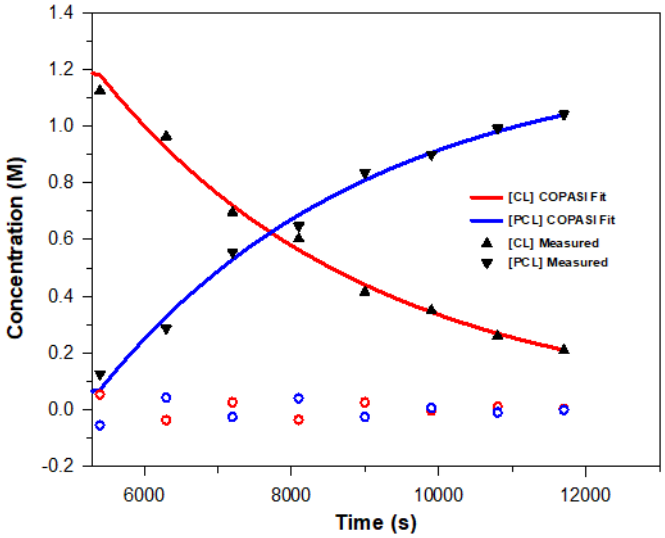

Fig. S42 Concentration versus time profile for the ^{1}H NMR resonance decay of ε-CL (▲) and the growth of PCL (▼) for the ROP of ε-CL by complex **6** at 70 °C along with the fits (blue and red lines) and errors determined by COPASI.

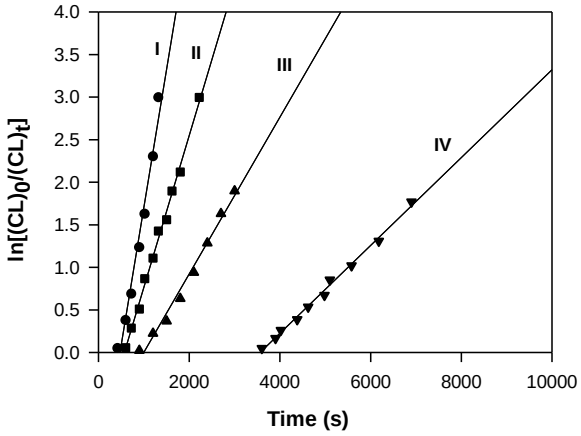

Fig. S43 Semilogarithmic plots of $\ln[CL]_0/[CL]_t$ versus time for ε-CL polymerization using complex **5** as an initiator at different temperatures in toluene ($[\varepsilon\text{-CL}]_0/[Ti] = 100$, $[\varepsilon\text{-CL}]_0 = 1.25$ M. **I**: T = 90 °C, $k_{app} = (32.32 \pm 0.26) \times 10^{-4}$ s^{-1}; **II**: T = 80 °C, $k_{app} = (18.71 \pm 0.13) \times 10^{-4}$ s^{-1}; **III**: T = 70 °C, $k_{app} = (9.12 \pm 0.68) \times 10^{-4}$ s^{-1}; **IV**: T = 60 °C, $k_{app} = (32.32 \pm 0.26) \times 10^{-4}$ s^{-1}).

Table S2 Kinetic data for the ε-CL polymerizations using complex **5**.

T (°C)	T (K)	1/T (K^{-1})	k_{app} (10^4 s^{-1})	k_p	ln(k_p/T)
60	333	0.003003	5.04 ± 0.22	0.040316	–9.01915
70	343	0.002915	9.12 ± 0.68	0.073680	–8.44575
80	353	0.002833	18.71 ± 0.13	0.149675	–7.76576
90	363	0.002755	32.32 ± 0.26	0.258578	–7.24696