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Supplementary Materials

Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Octahedral Nickel Carboxylate Complexes

Alexey Nikiforov [1], Natalia Panina [2], Daniil Blinou [3], Vladislav Gurzhiy [4], Juliya Nashchekina [5], Evgenia Korzhikova-Vlakh [1,4,*], Alexey Eremin [1] and Mariia Stepanova [1,*]

1 Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg 199004, Russia
2 Department of Inorganic Chemistry, Saint-Petersburg State Institute of Technology (Technical University), St. Petersburg, 190013, Russia
3 Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991, Russia
4 Saint-Petersburg State University, St. Petersburg, 199034, Russia
5 Institute of Cytology, Russian Academy of Sciences, St. Petersburg 194064, Russia
* Correspondence: vlakh@hq.macro.ru (E.K.-V.); maristepanova@hq.macro.ru (M.S.)

Table S1. Geometric parameters of intramolecular hydrogen bonds in compounds *trans*-[Ni(DBED)$_2$(O$_2$CCF$_3$)$_2$]·C$_6$H$_6$ - **1** and *trans*-[Ni(DBED)$_2$(O$_2$CC(CH$_3$)$_3$)$_2$]·(CH$_3$)$_3$CCO$_2$H – **2** (DBED – *N*,*N*′-dibenzylethylenediamine).

Compound	Donor (D)	Acceptor (A)	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
1	N2-H2	O2	0.98	2.003	2.893	150.0
2	N2-H2	O5	0.98	2.252	3.001	132.5
2	N1-H1	O5	0.98	2.195	2.988	137.2
2	N1-H1	O5A	0.98	2.195	2.862	144.9

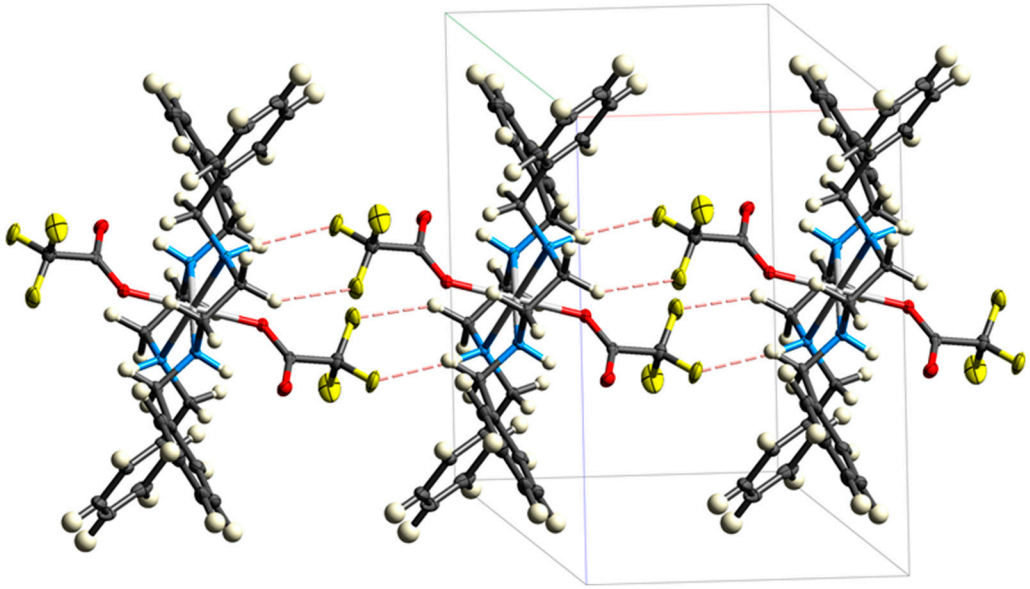


Figure S1. C-H···F and N-H···F close contacts in crystal structure of **1**.

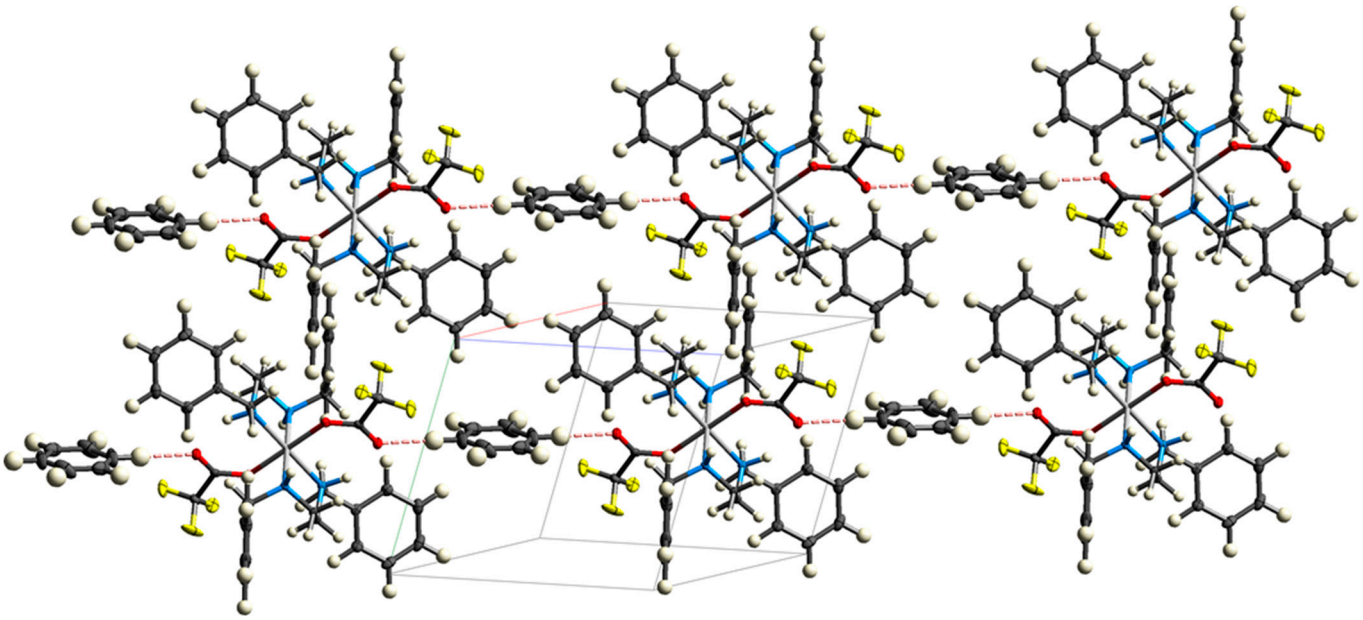


Figure S2. Network system C-H···O hydrogen bonds of complex units with solvate molecules of benzene in the crystal structure of compound **1**.

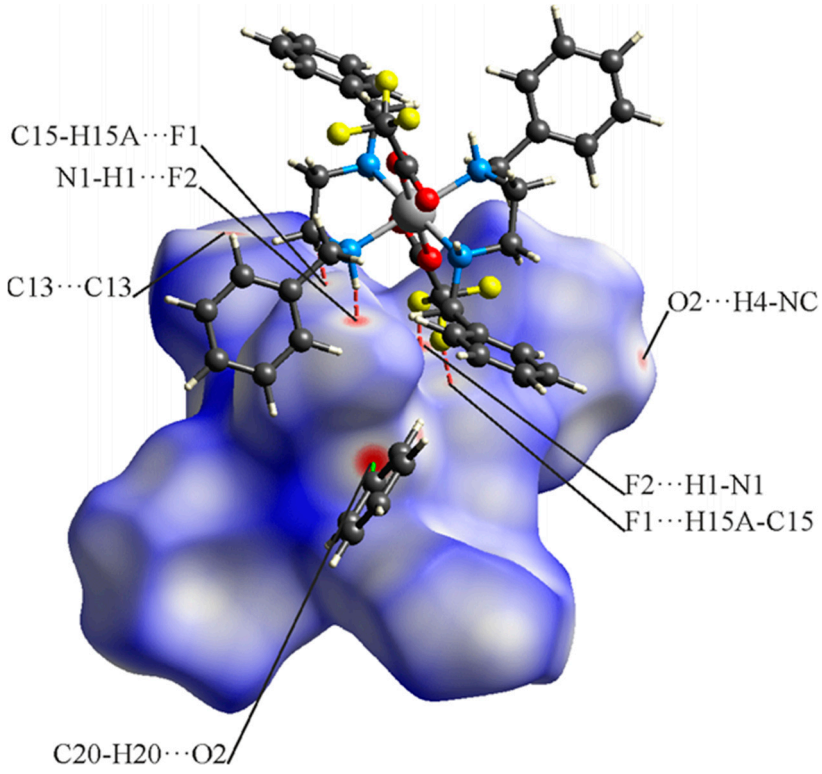


Figure S3. Hirshfeld surfaces (HS) of complex **1** over the d_{norm} map in the range −0.2399–1.5851 a.u.

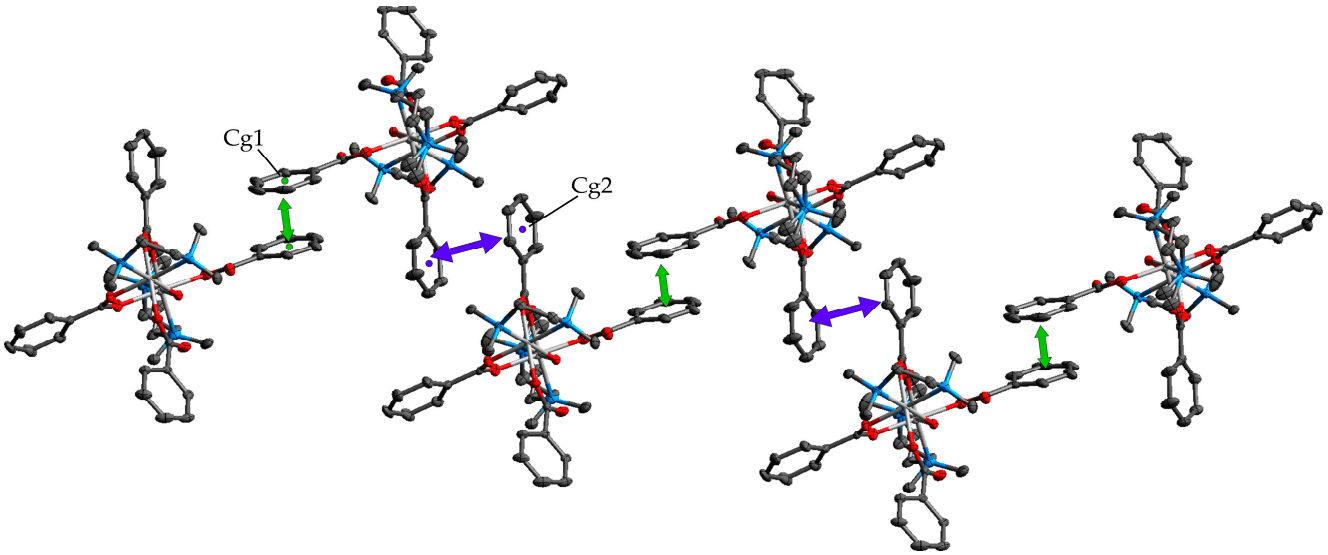


Figure S4. Fragment of the crystal structure of [$Ni_2(\mu\text{-}OH_2)(\mu\text{-}O_2CC_6H_5)_2(O_2CC_6H_5)_2(TEMED)_2$] (TEMED—*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) - **4**: offset-face-to-face π···π stacking interactions of phenyl substituents of benzoate ligands.

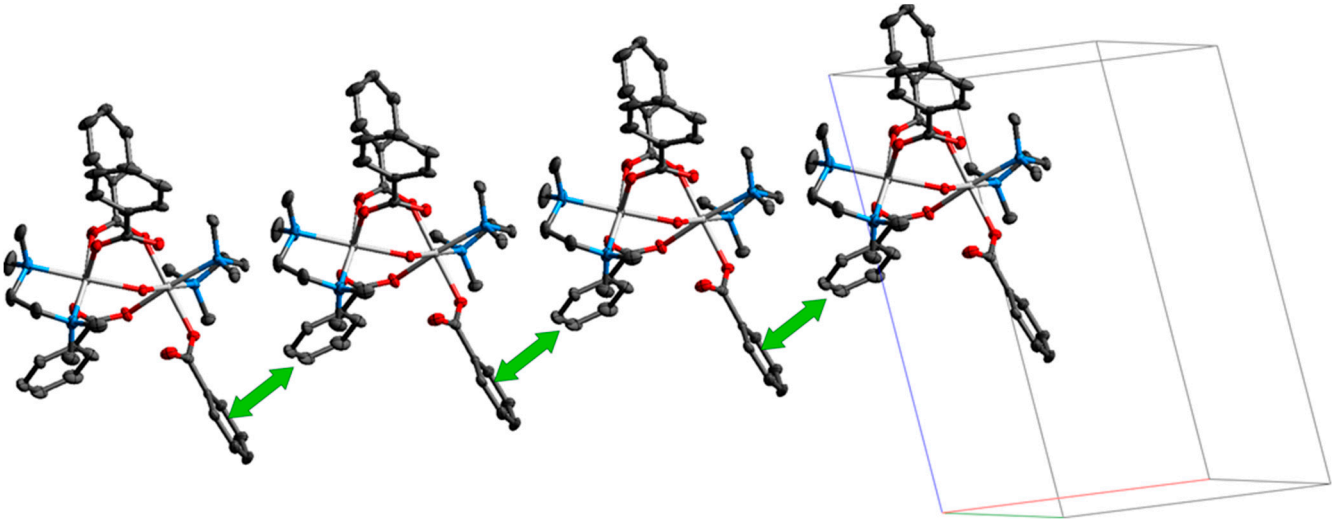
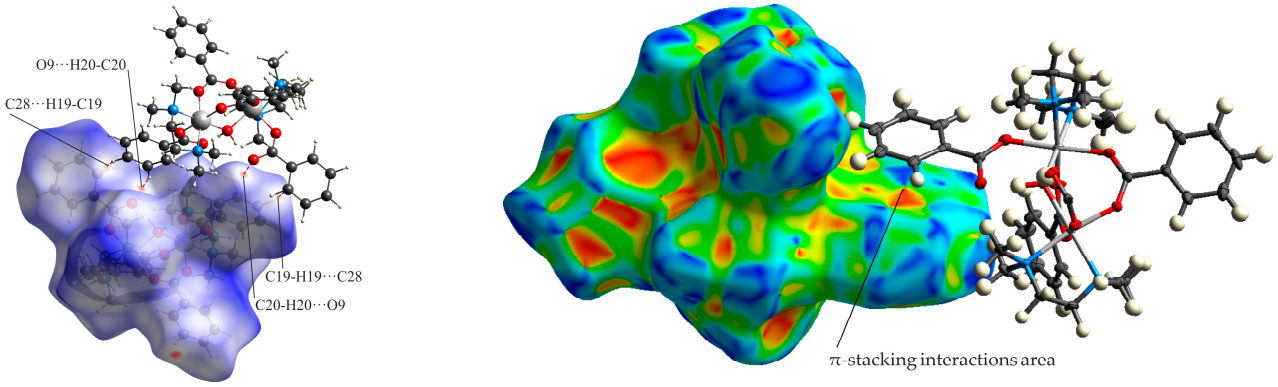


Figure S5. Fragment of the crystal structure of complex **4**: C-H···π face-to-plane interactions of phenyl substituents of benzoate ligands (the compound unit cell is shown).



(**a**) (**b**)

Figure S6. HS of **4**: (**a**) over the d_{norm} map in the range −0.1278 – 1.5984 a.u, (**b**) over the shape index map.

Table S2. Some values of average Ni-N and Ni-O bond lengths for complexes **1–4**.

	Bond length (average) (Å)			
	1	**2**	**3** [S1]	**4**
L	DBED	DBED	TEMED	TEMED
R	CF_3	$C(CH_3)_3$	CF_3	C_6H_5
Ni – (L-k²*N,N`*)	2.120	2.157	2.162	2.172
Ni – (O_2CR-k*O*)	2.094	2.066	2.104	2.093
Ni – (O_2CR-k²*O,O`*)	–	–	2.064	2.029
Ni – (μ-OH_2)	–	–	2.154	2.084

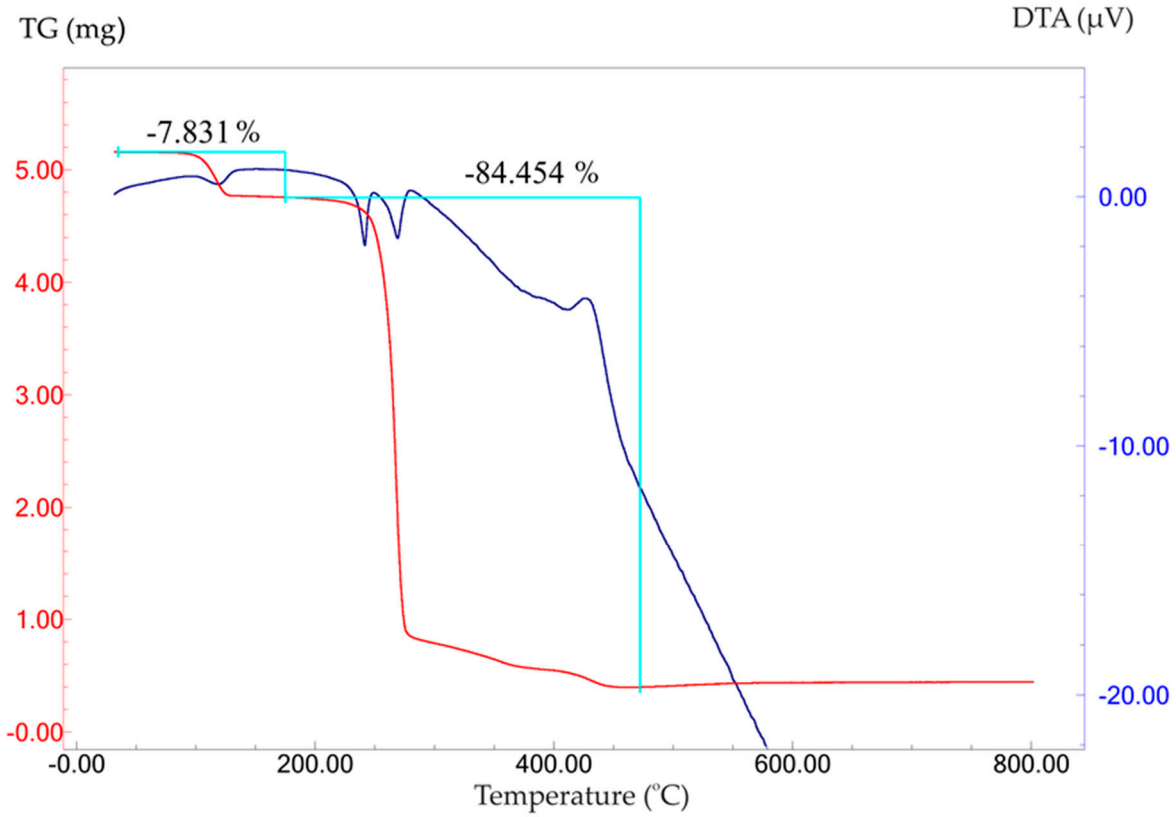


Figure S7. Thermogravimetric analysis (TGA) of complex **1**.

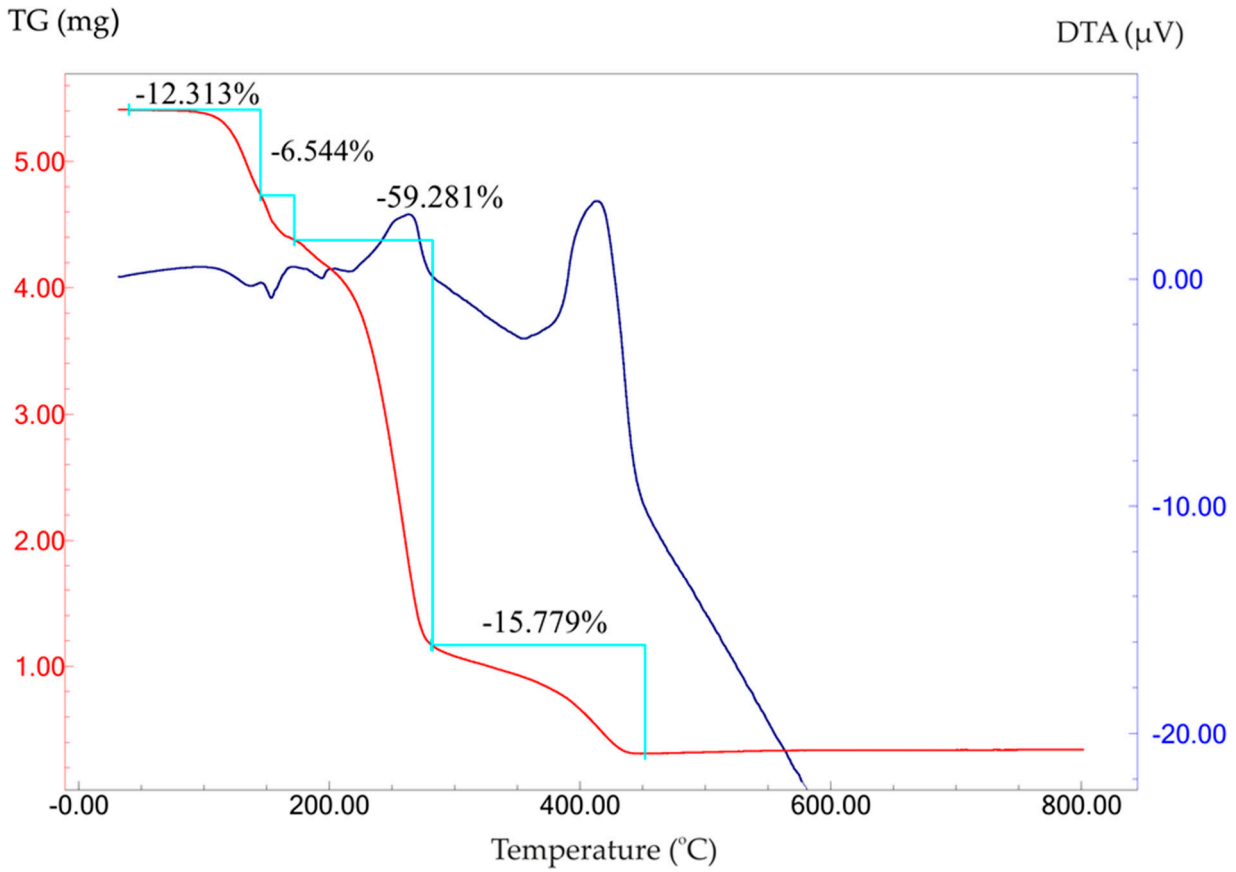


Figure S8. TGA of complex **2**.

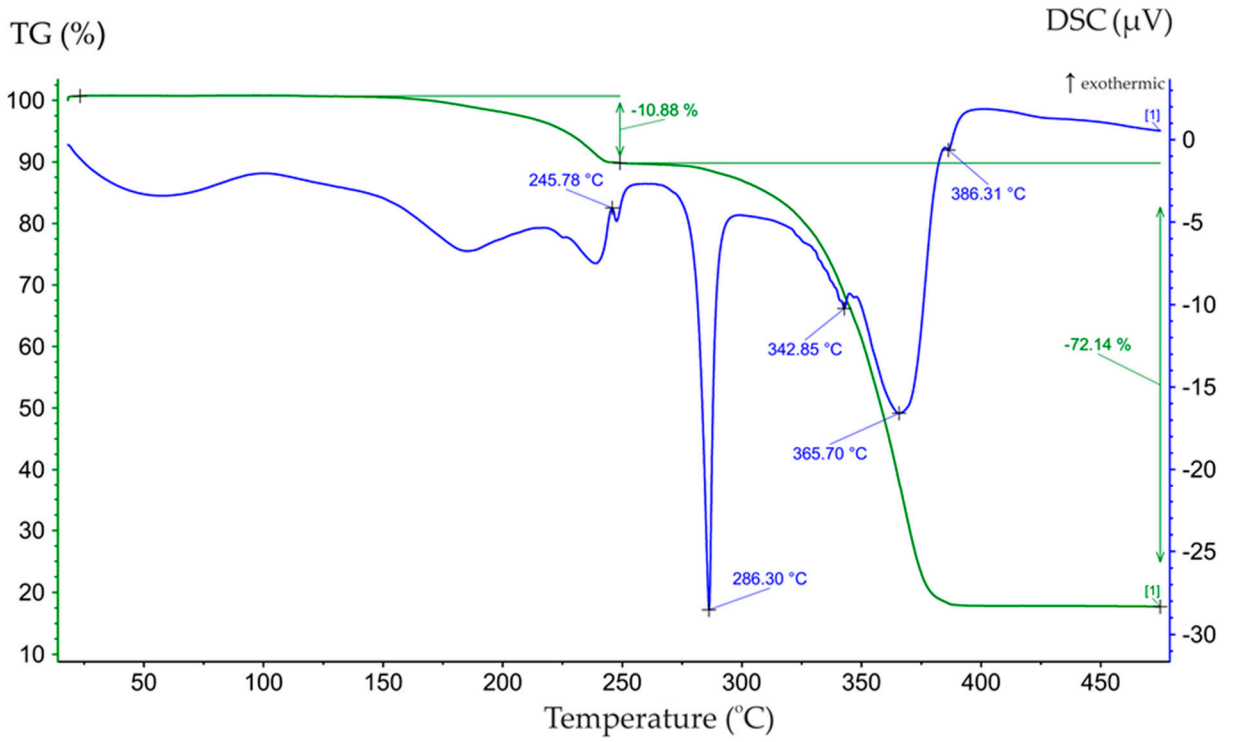


Figure S9. Simultaneous thermal analysis of complex **4**.

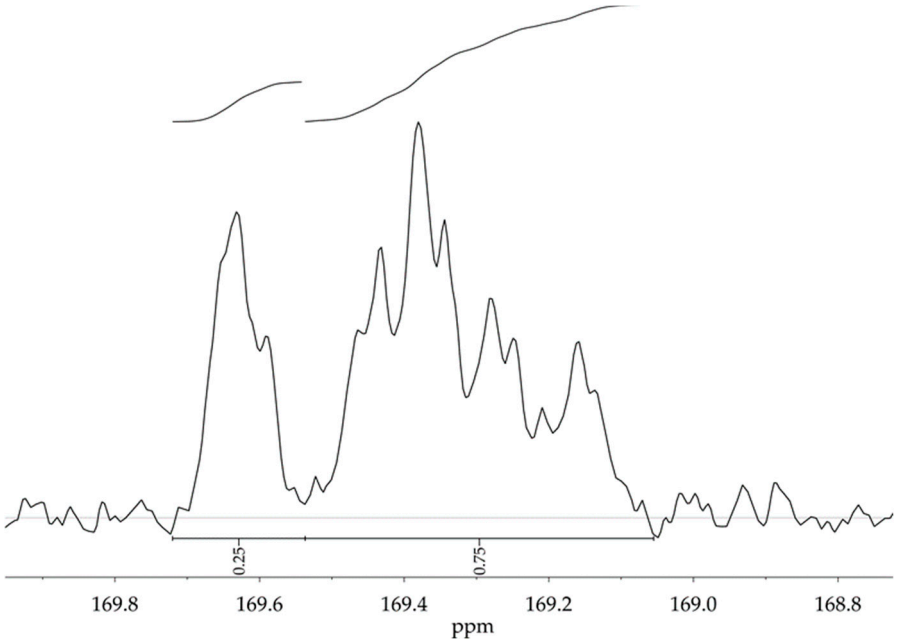


Figure S10. Fragment of carbonyl region of ^{13}C NMR spectrum in $CDCl_3$ of precipitated poly-D,L-lactide, obtained with compound **2**. Reaction conditions: [*rac*-lactide]/[Ni] 250/1, toluene, 72 h, 140 °C, argon atmosphere.

Table S3. Calculated molecular formulas and masses of dialkyl lactamide species in electrospray ionization (ESI) mass-spectra of model reaction mixture ([*rac*-lactide]/[Ni] –3/1, toluene, 72 h, 140 °C, argon atmosphere).

n	**((DBED)(Lac)$_n$(CO))+Na$^+$**		**((DBED)(Lac)$_n$(CO)+C$_2$H$_4$−O)+Na$^+$**	
	m/z$_{(experimental)}$	**m/z$_{(theoretical)}$**	**m/z$_{(experimental)}$**	**m/z$_{(theoretical)}$**
1	363.1689	363.1685	not detected	375.2048
2	435.1902	435.1896	not detected	447.2260
3	507.2115	507.2107	519.2479	519.2471
4	579.2333	579.2318	591.2692	591.2682
5	651.2553	651.2530	663.2904	663.2894
6	723.2791	723.2741	735.3123	735.3105
7	795.3015	795.2952	807.3340	807.3316
8	not detected	867.3164	879.3560	879.3527
9	939.3479	939.3375	951.3783	951.3738

Lac - lactoyl OCH_3CHCO group.

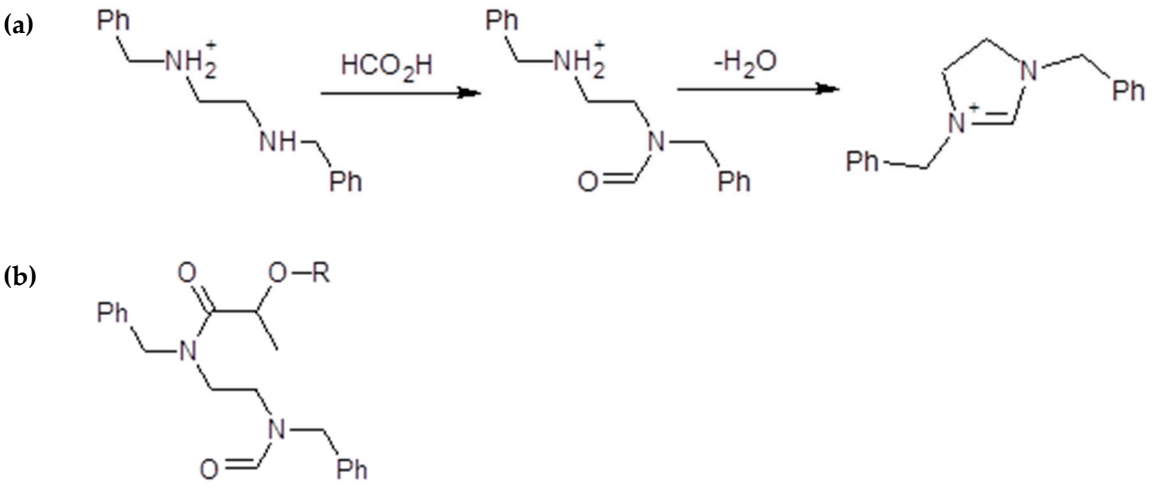
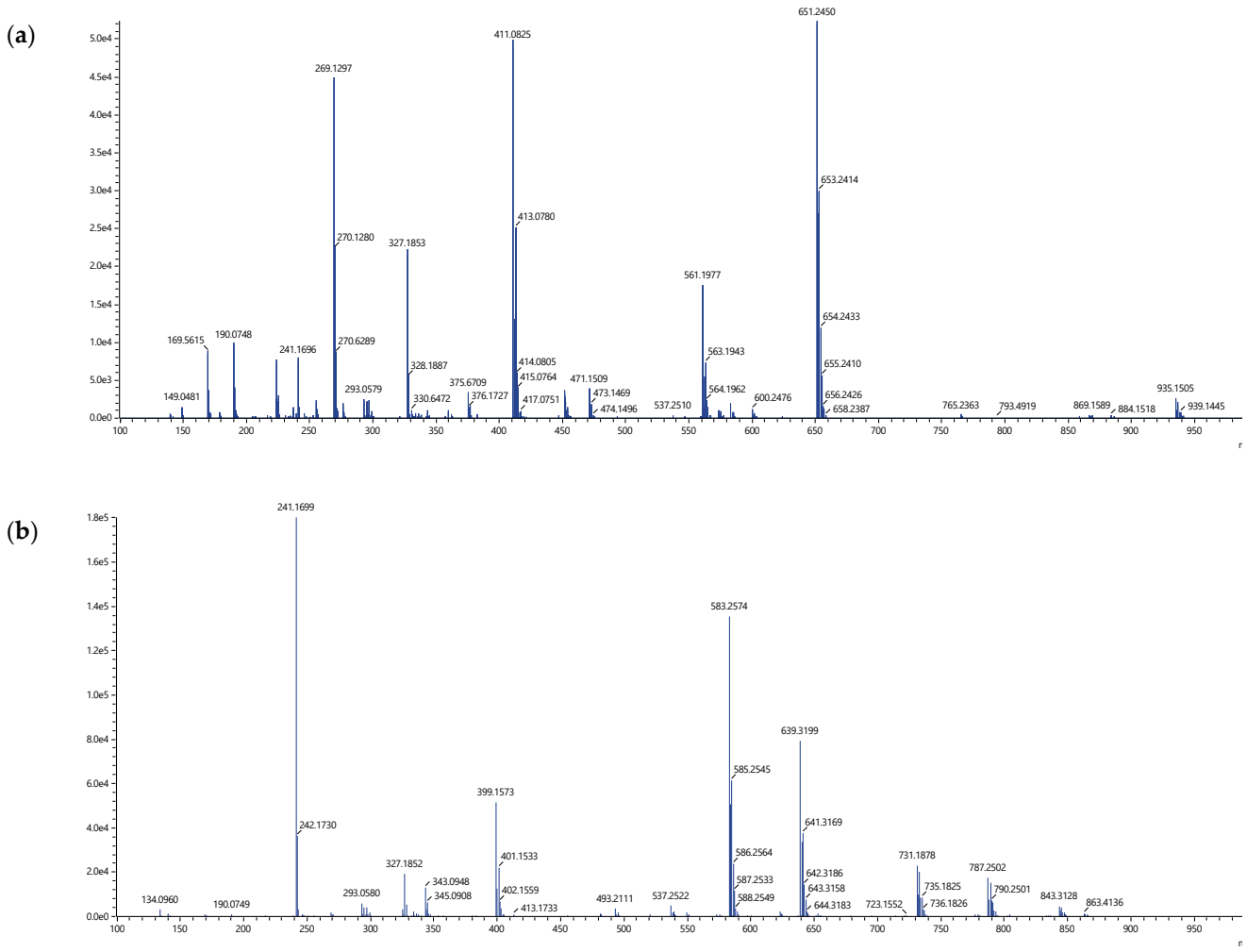
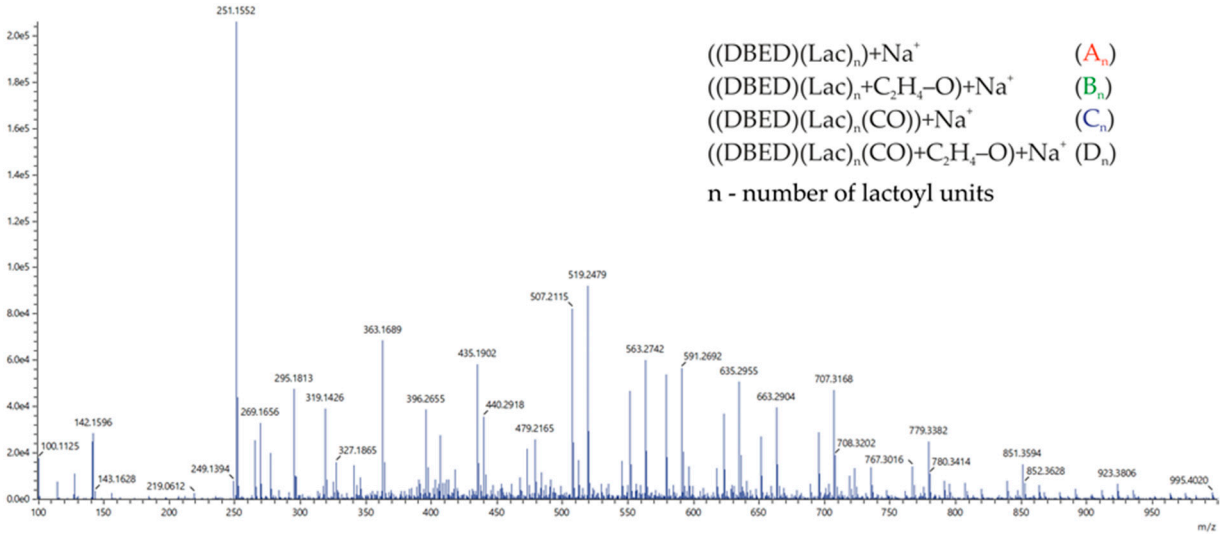


Figure S11. Proposed transformation pathway of DBED ligand (**a**) and structure of [(DBED)(Lac)$_n$(CO)] formylated dialkyl lactamide species (**b**) in ESI mass spectrometry experiment.

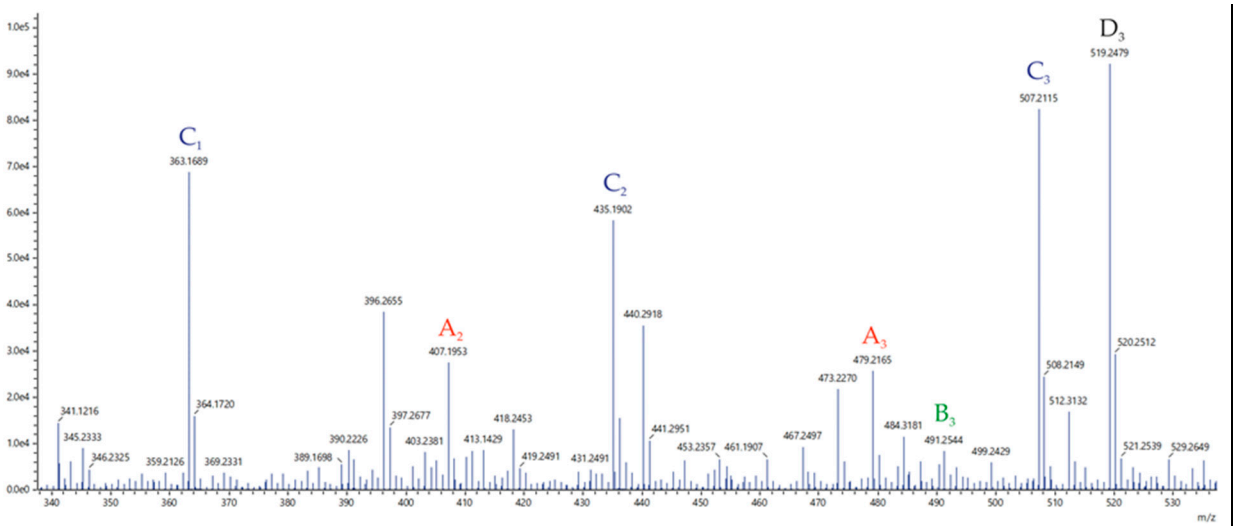


Figures S12. ESI mass-spectra of **1** (**a**) and **2** (**b**).

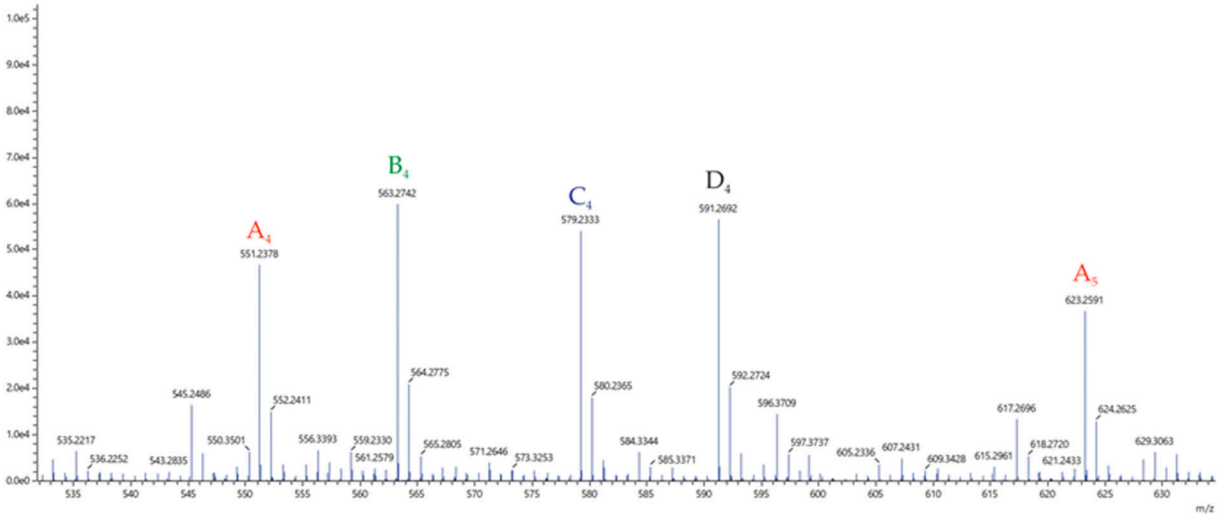
(**a**)


((DBED)(Lac)n)+Na+ (An)
((DBED)(Lac)n+C2H4–O)+Na+ (Bn)
((DBED)(Lac)n(CO))+Na+ (Cn)
((DBED)(Lac)n(CO)+C2H4–O)+Na+ (Dn)
n - number of lactoyl units
m/z

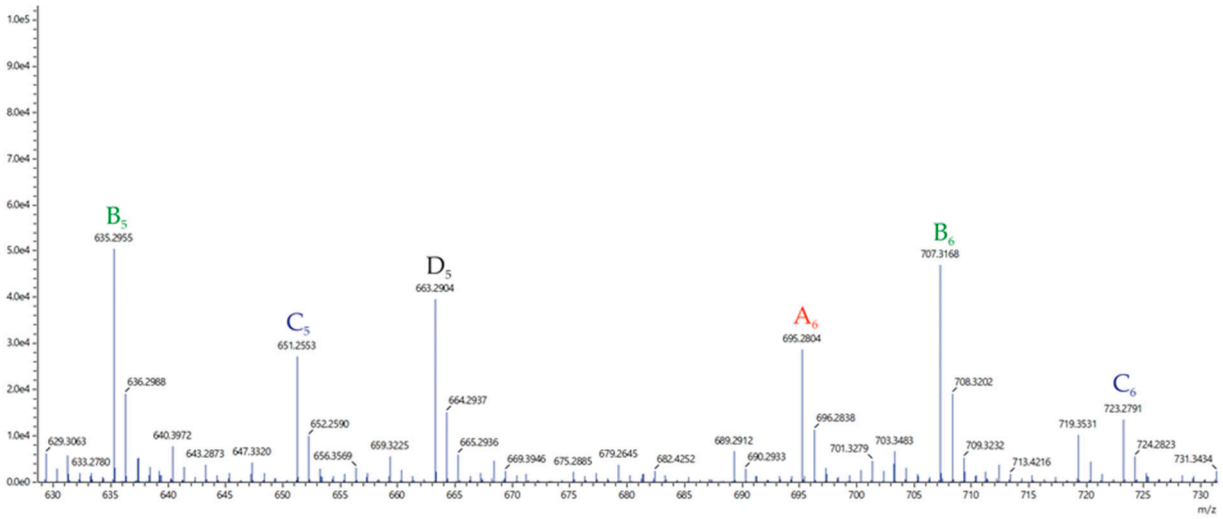
(**b**)


C1
C2
C3
D3
A2
A3
B3
m/z

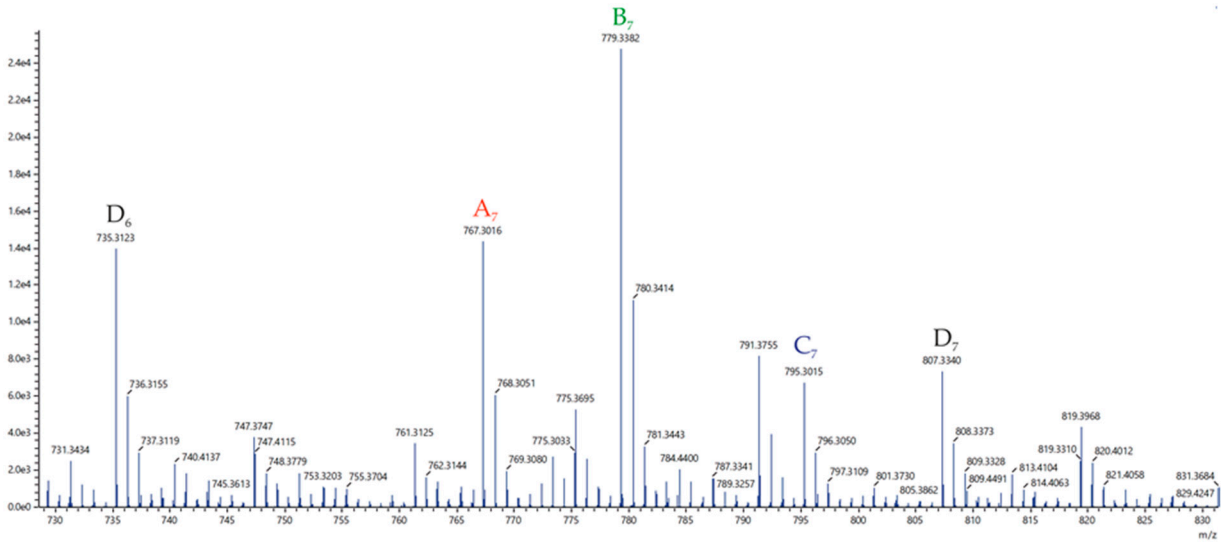
(**c**)


A4
B4
C4
D4
A5
m/z

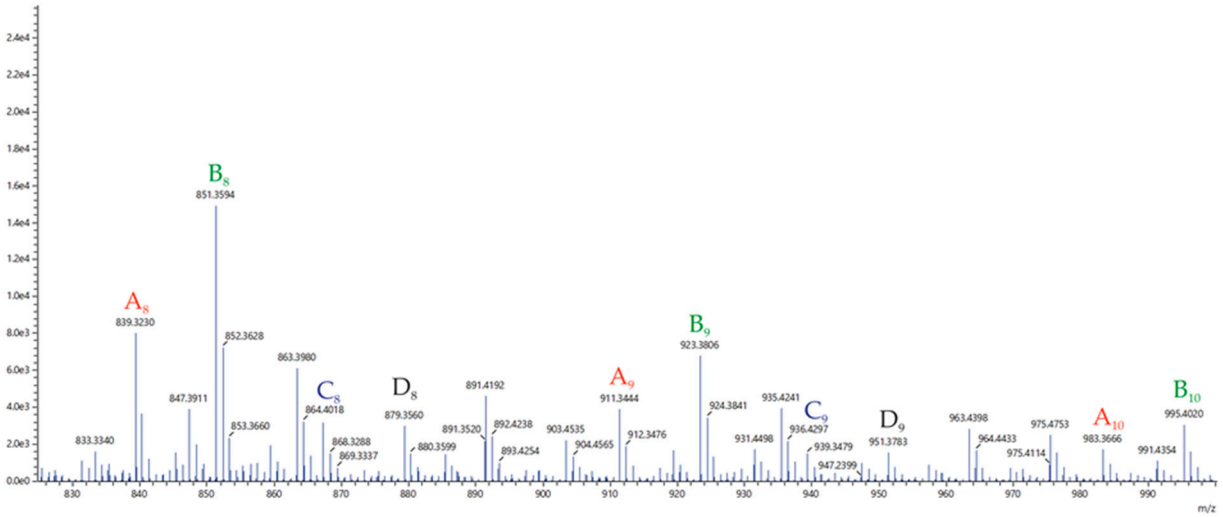
(**d**)



(**e**)



(**f**)



Figures S13. Electrospray ionization mass-spectra of model polymerization mixtures ([*rac*-lactide]/[Ni] –3/1, toluene, 72h, 140°C, argon atmosphere): (**a**) general view (100-1000 *m*/*z*), (**b**) part of the spectrum (338-538 *m*/*z*), (**c**) part of the spectrum (532-635 *m*/*z*), (**d**) part of the spectrum (628-731 *m*/*z*), (**e**) part of the spectrum (728-831 *m*/*z*), (**f**) (824-1000 *m*/*z*).

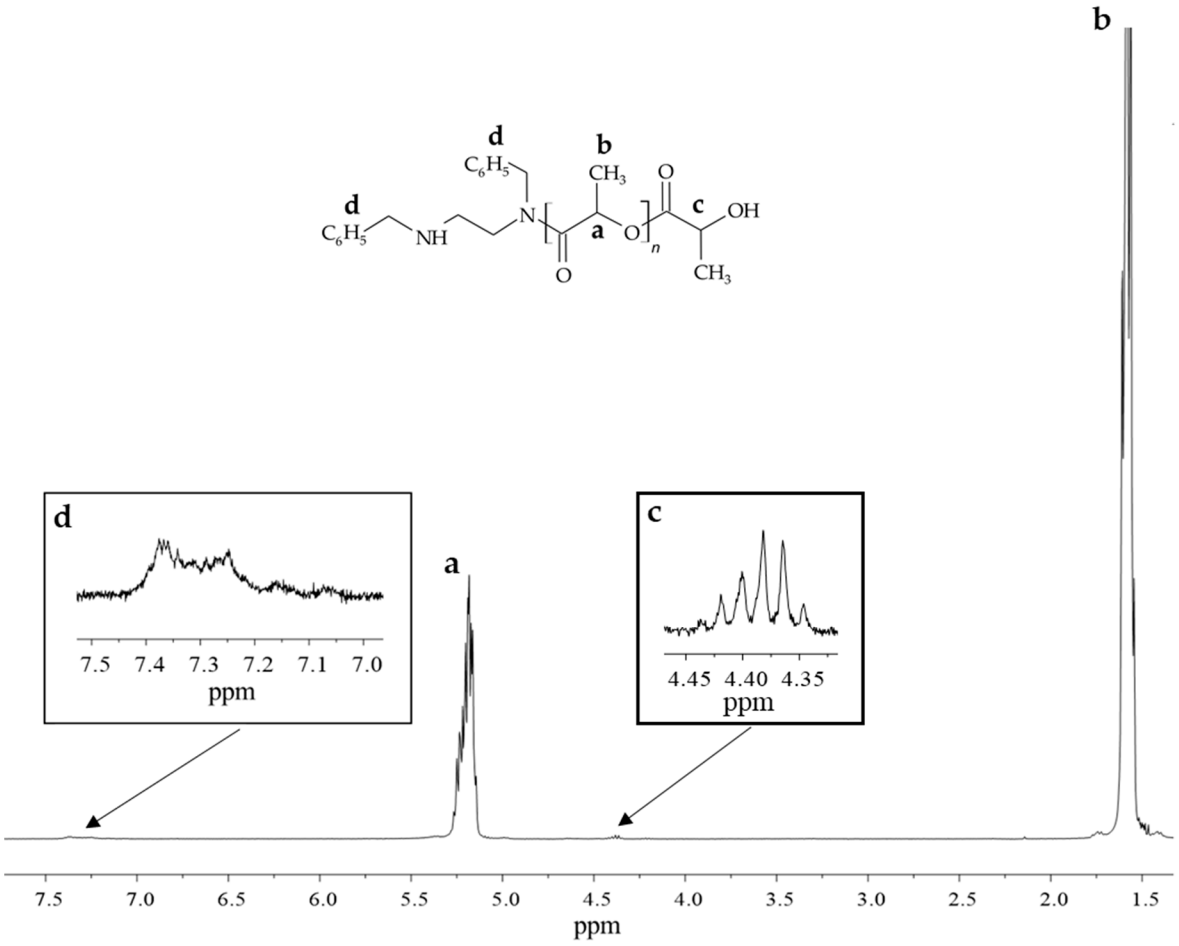


Figure S14. ^{1}H 1D DOSY NMR spectrum in $CDCl_3$ of precipitated poly-D,L-lactide, obtained with compound **2** (gradient intensity 90%). Reaction conditions: [*rac*-lactide]/[Ni] 250/1, toluene, 72 h, 140 °C, argon atmosphere.

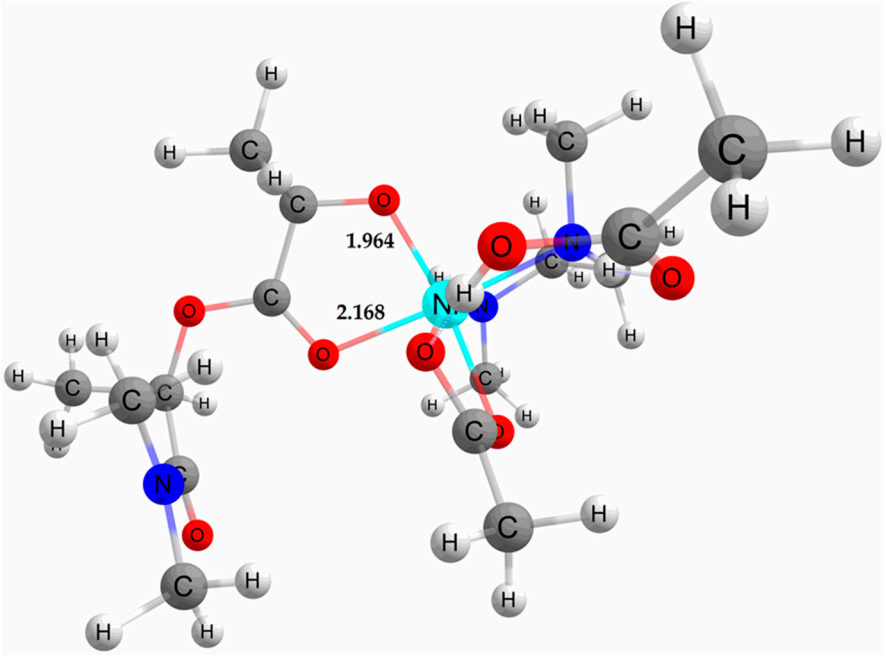


Figure S15. Optimized structure of the **X** compound. Bond lengths are given in Å.

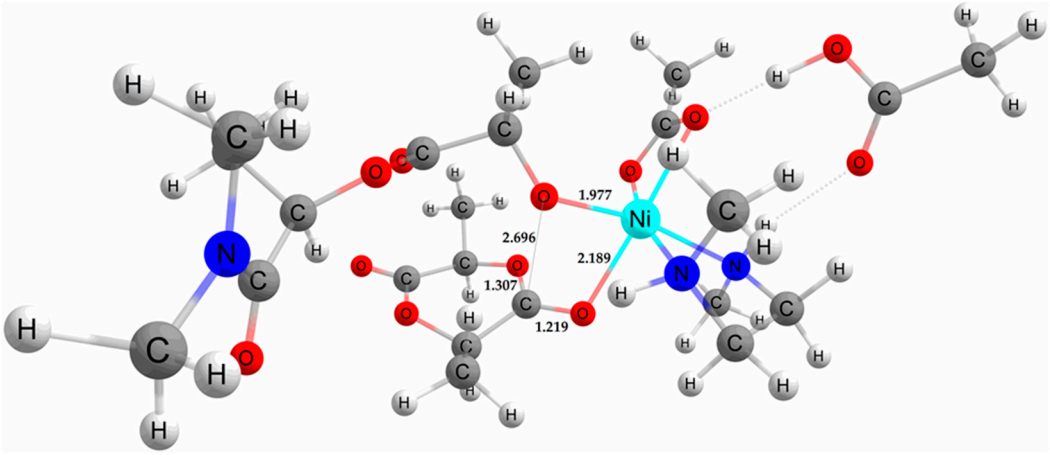


Figure S16. Optimized structure of the **XI** compound. Bond lengths are given in Å.

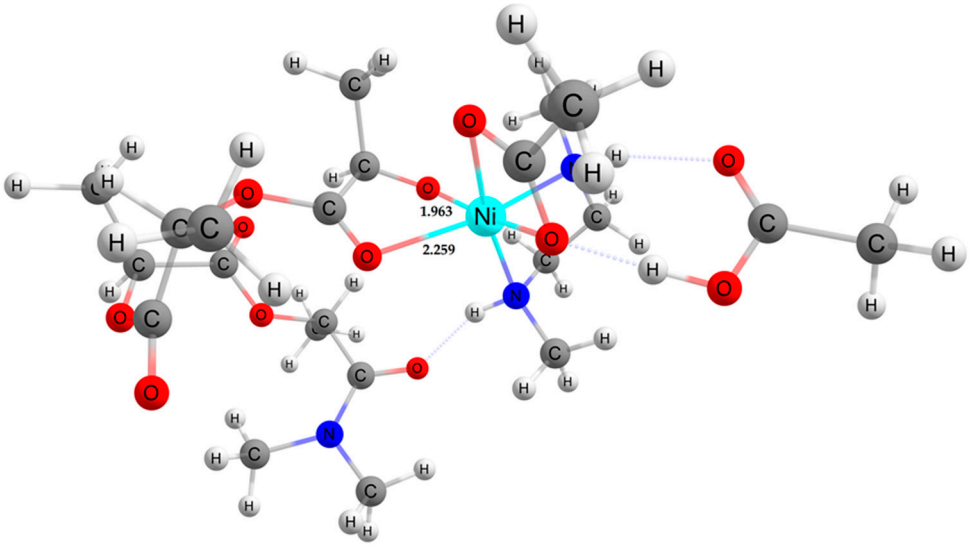


Figure S17. Optimized structure of the **XIII** compound. Bond lengths are given in Å.

References

S1. Ahlgrén, M.; Turpeinen, U. The Structure of μ-Aqua-Bis(μ-Trifluoroacetato-O,O')-Bis[(*N*,*N*,*N'*,*N'*-Tetramethylethylenediamine)(Trifluoroacetato)Nickel(II)]. *Acta Crystallogr B* **1982**, *38*, 276-279, doi:10.1107/s0567740882002611.