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Supporting Information

Synthesis and structures of *bis*-ligated zinc complexes supported by tridentate ketoimines that initiate L-lactide polymerization

Kimberly A. Gerling[a], Nomaan M. Rezayee[a], Arnold L. Rheingold[b], David B. Green[a], Joseph M. Fritsch*[a]

[a]Department of Chemistry, Pepperdine University
[b]Department of Chemistry, University of California, San Diego

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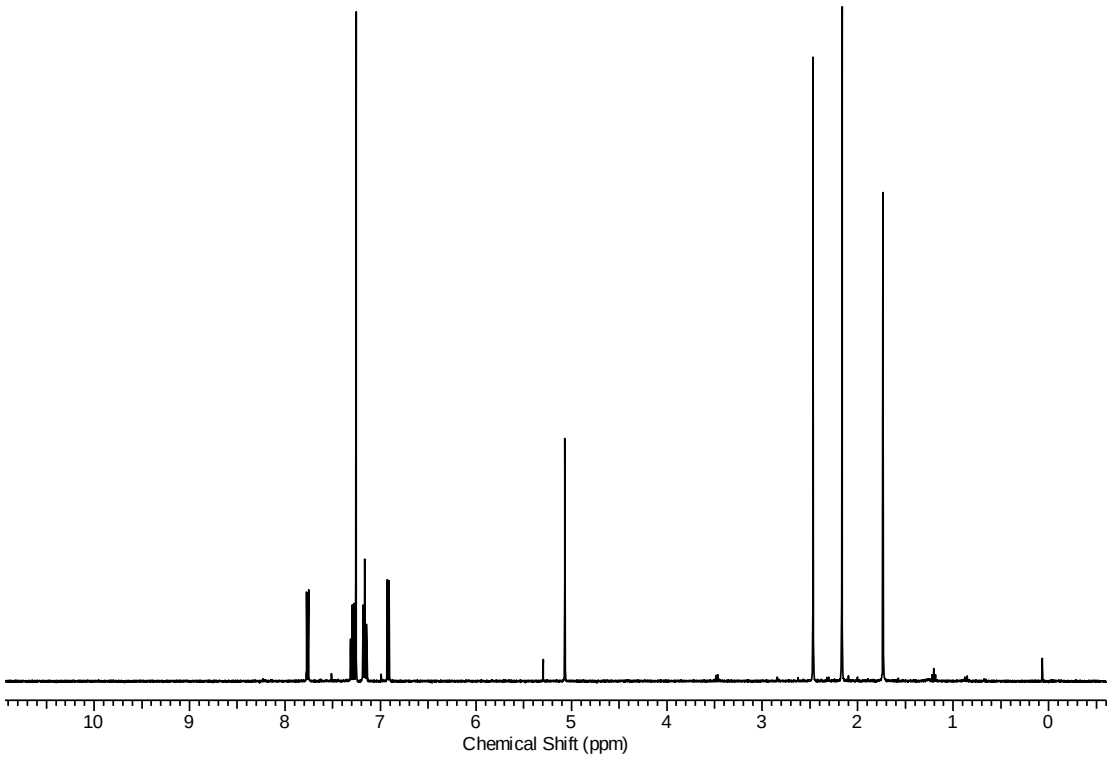
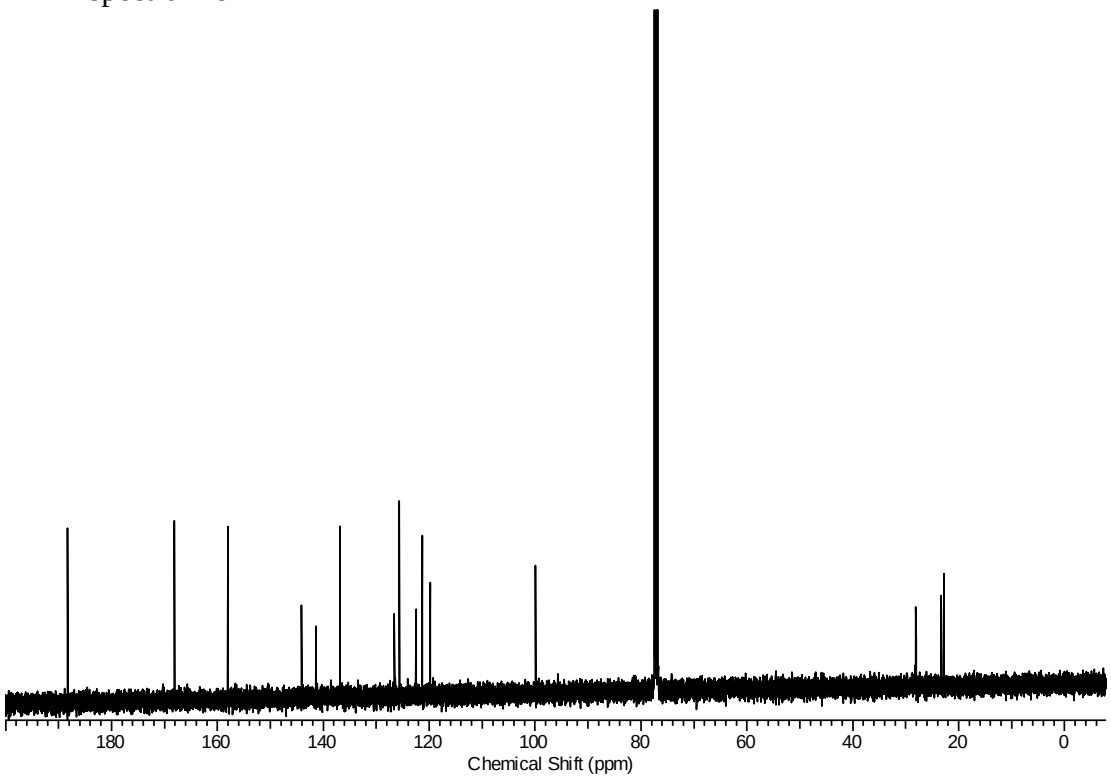
SI Figure 1. NMR spectra of compound **1**.

^{1}H NMR spectrum of **1**

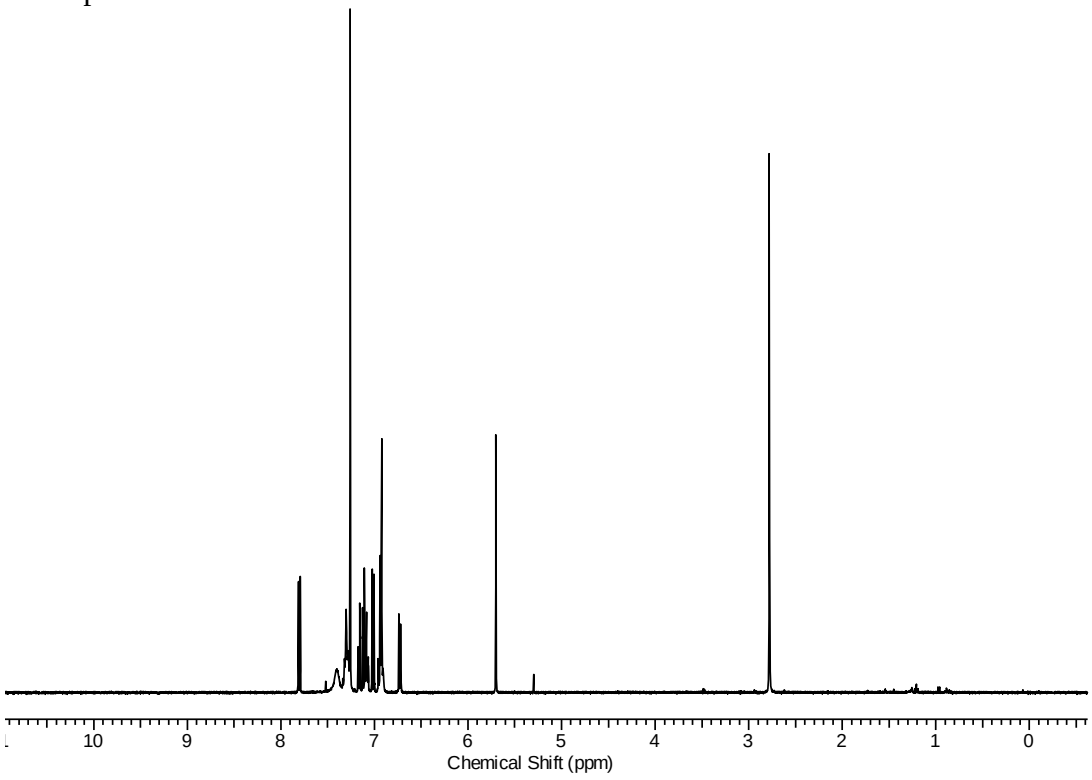


^{13}C NMR spectrum of **1**

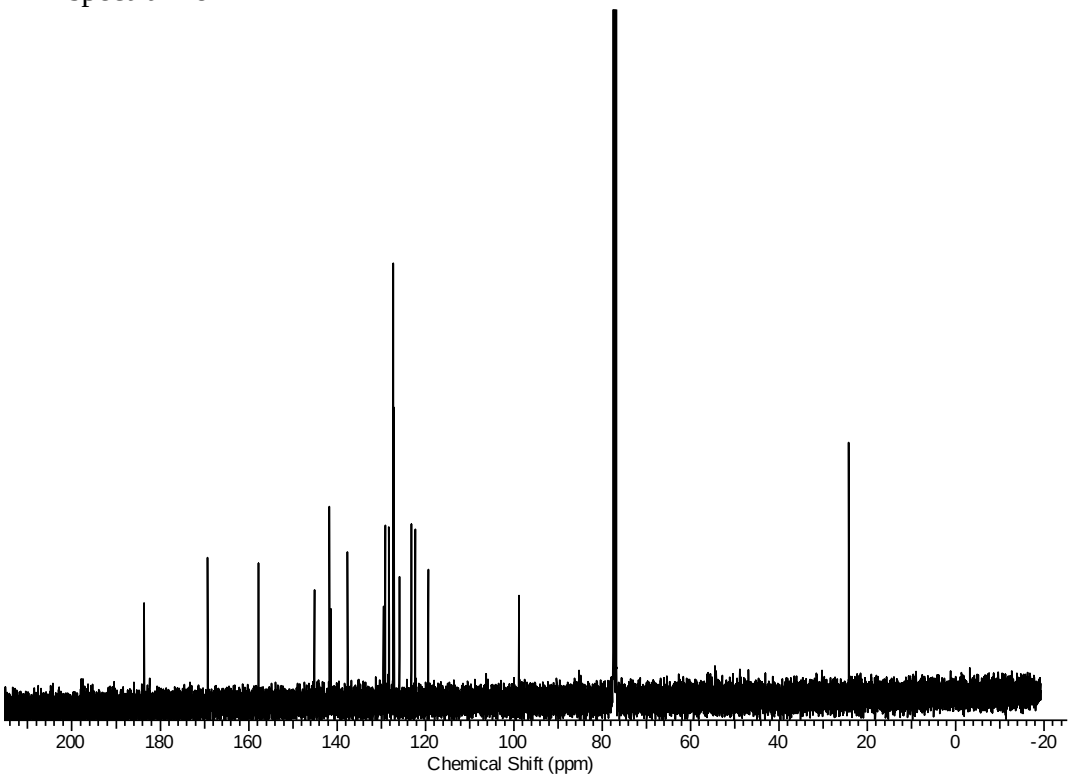


SI Figure 2. NMR spectra of compound **2**.

^{1}H NMR spectrum of **2**

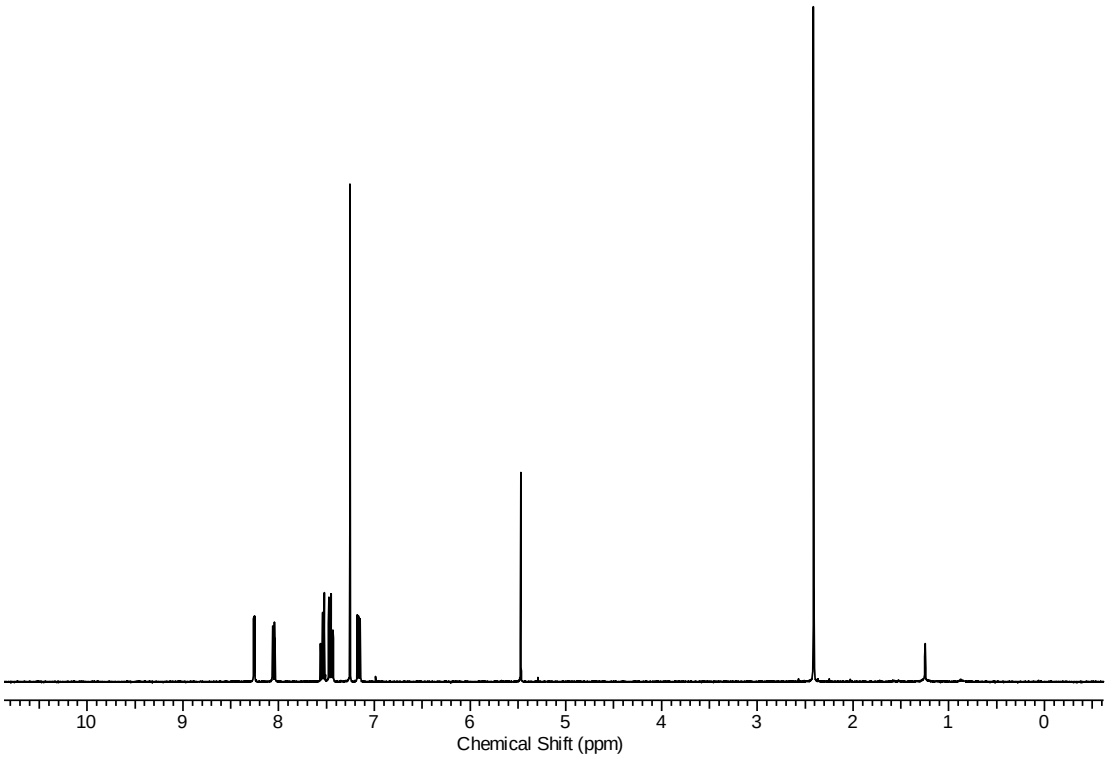


^{13}C NMR spectrum of **2**

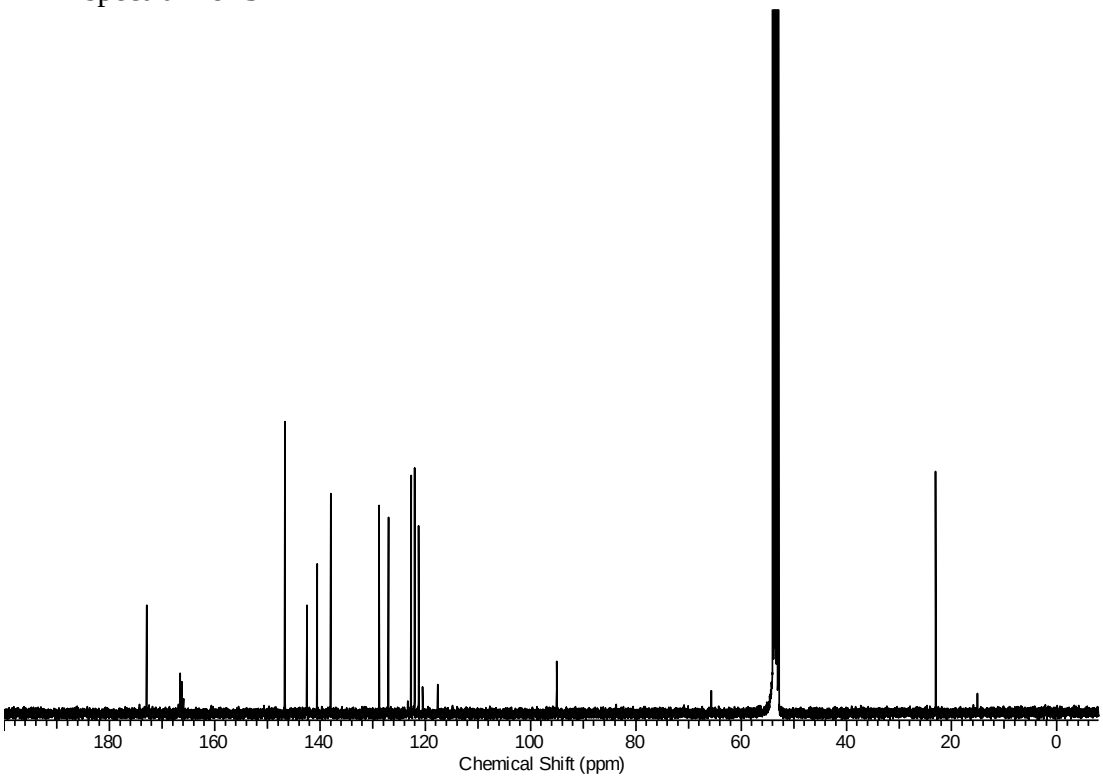


SI Figure 3. NMR spectra of compound **3**.

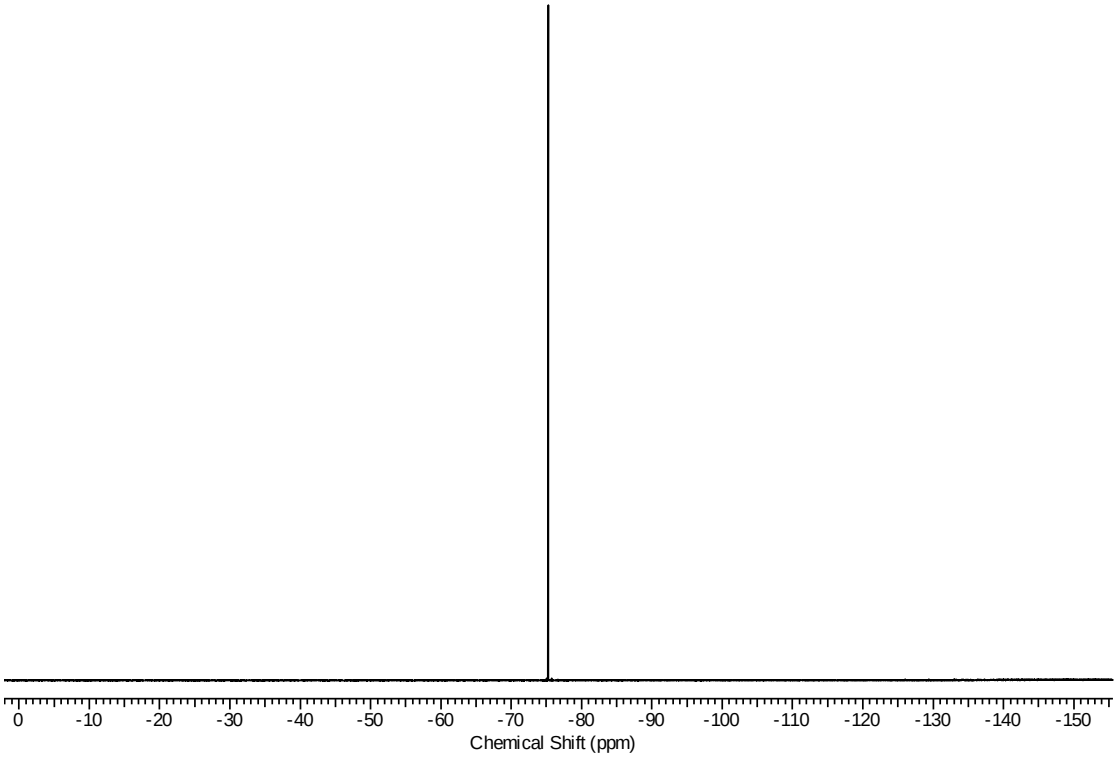
^{1}H NMR spectrum of **3**



^{13}C NMR spectrum of **3**

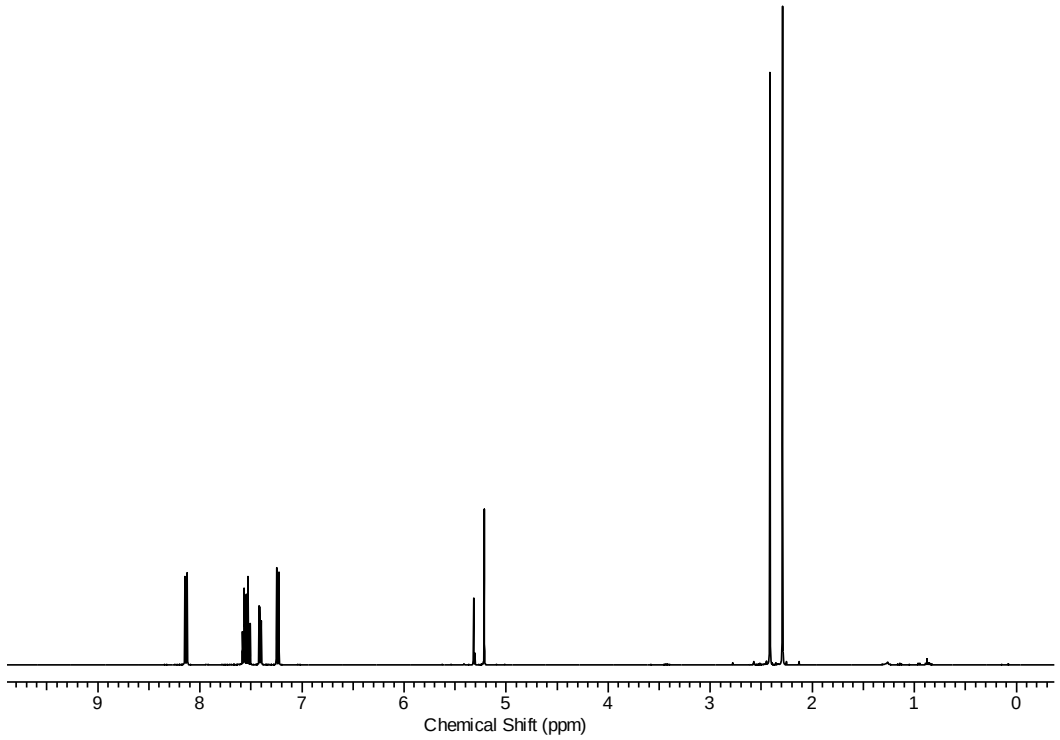


^{19}F NMR spectrum of **3**



SI Figure 4. NMR spectra of compound **4**.

^{1}H NMR spectrum of **4**



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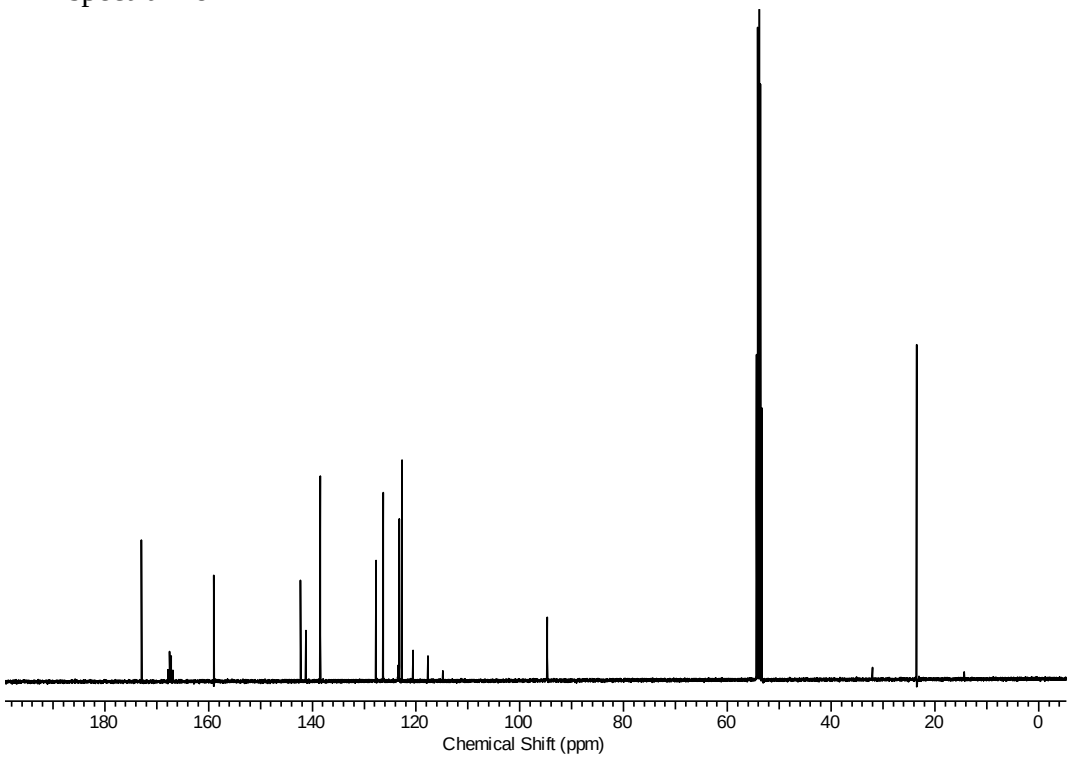

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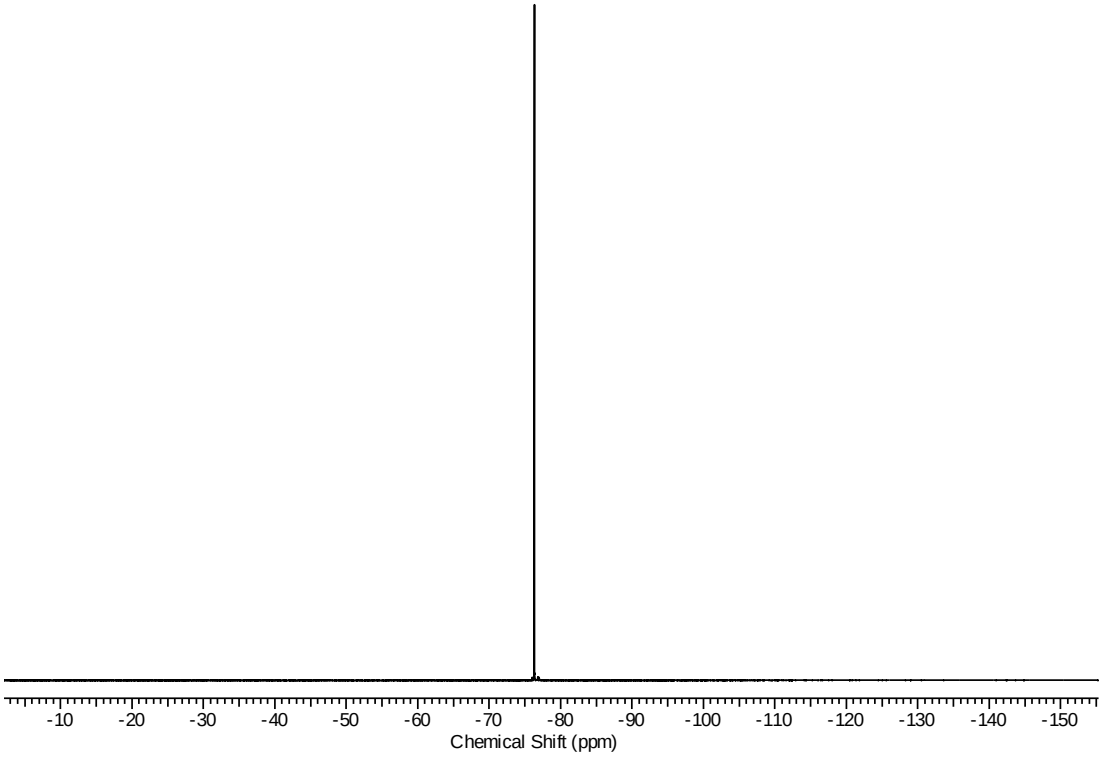

SI Figure 5. NMR spectra of compound **5**.

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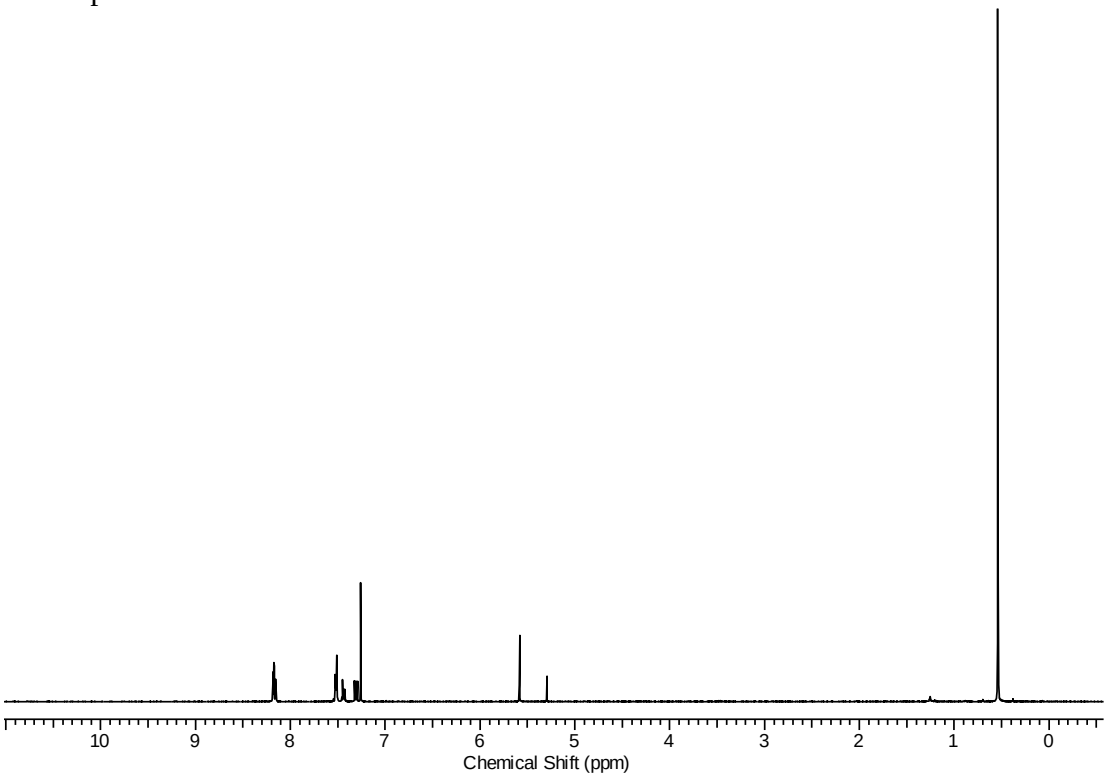

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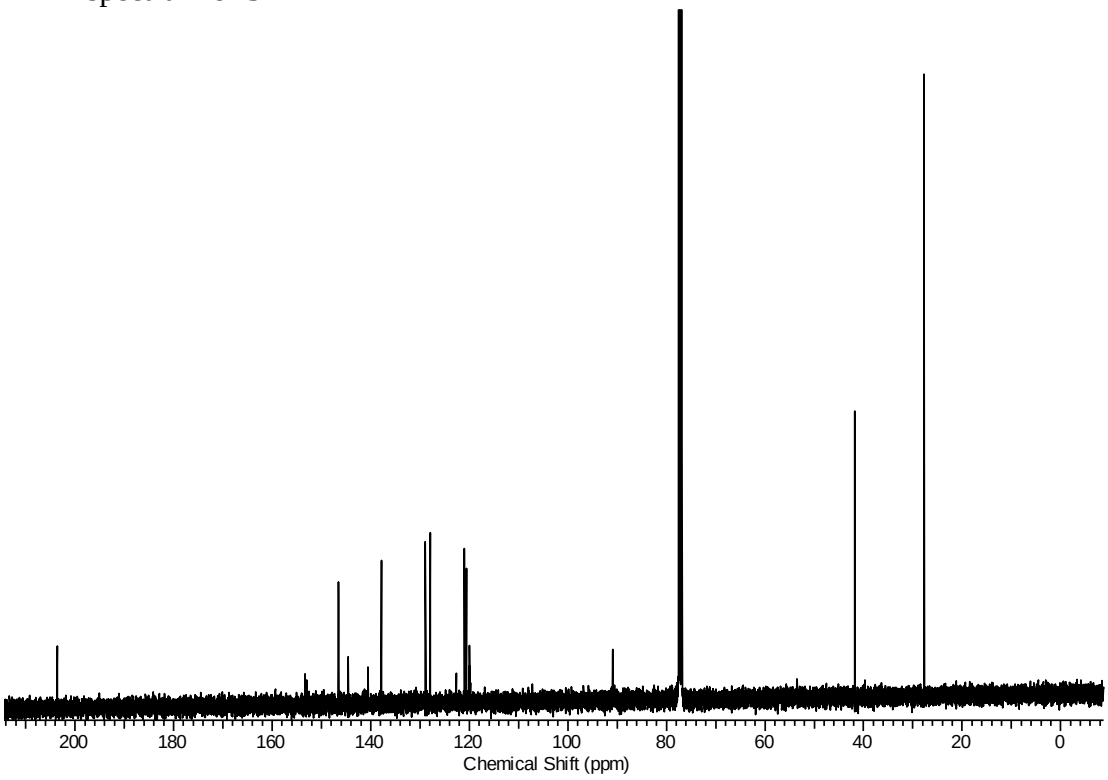

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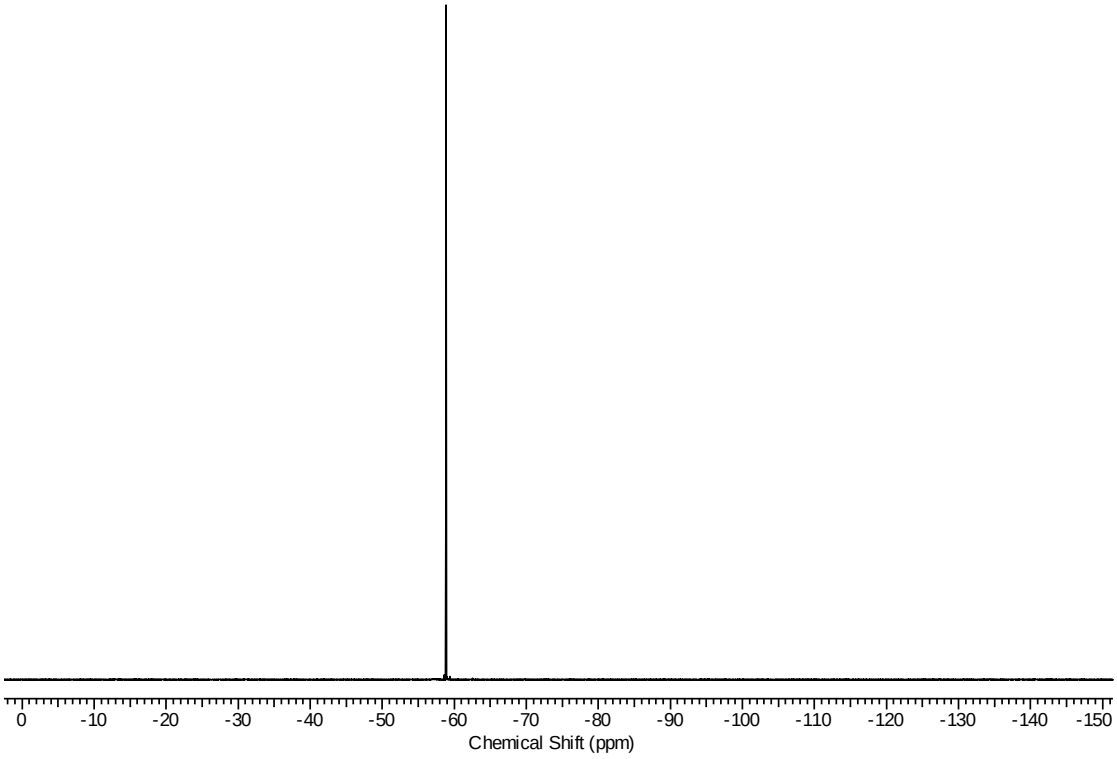
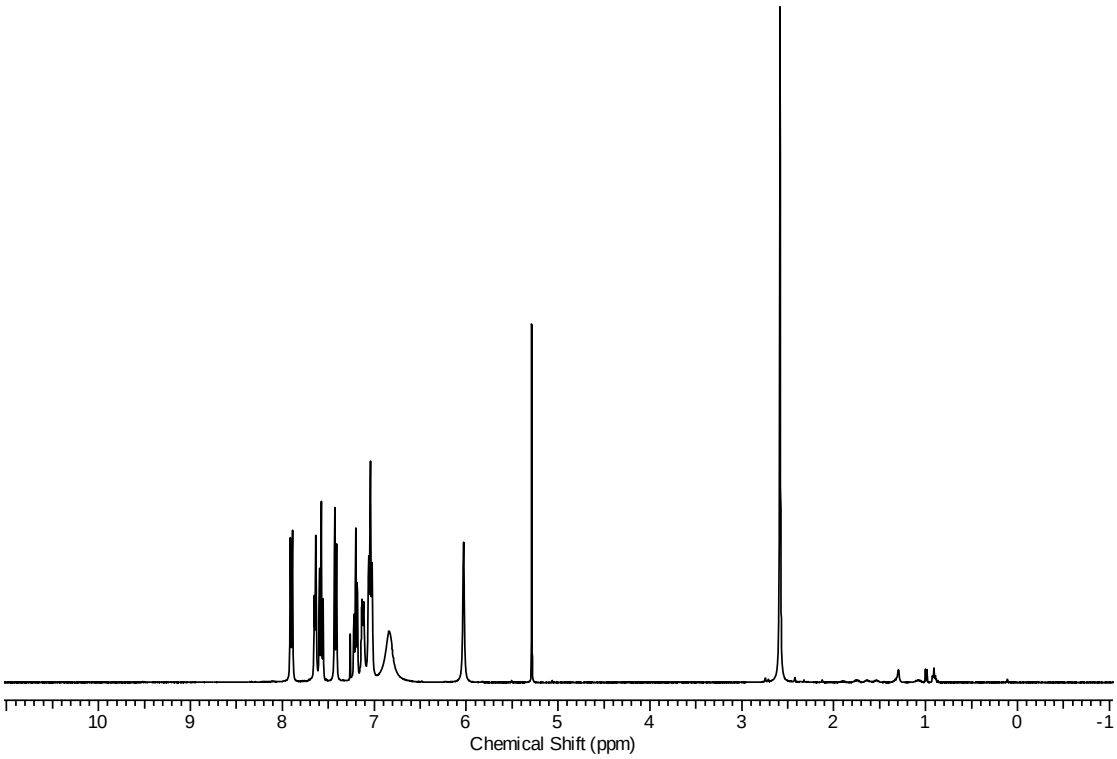


SI Figure 6. NMR spectra of compound **6**.

^{1}H NMR spectrum of **6**



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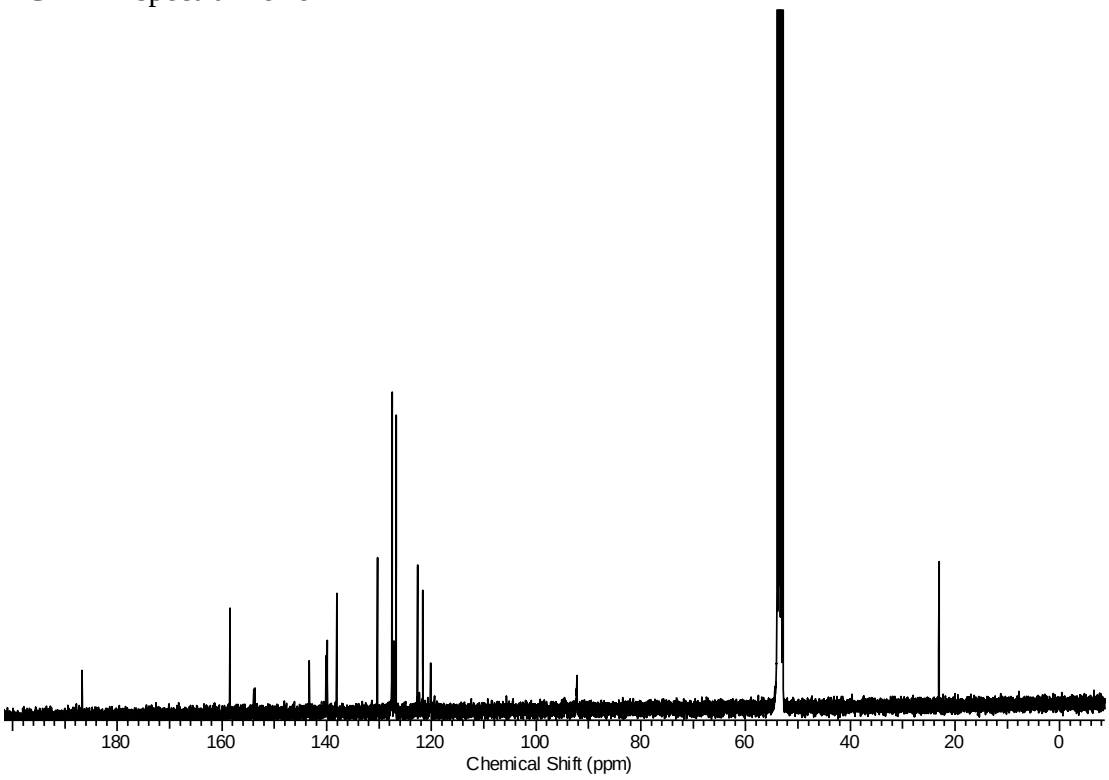
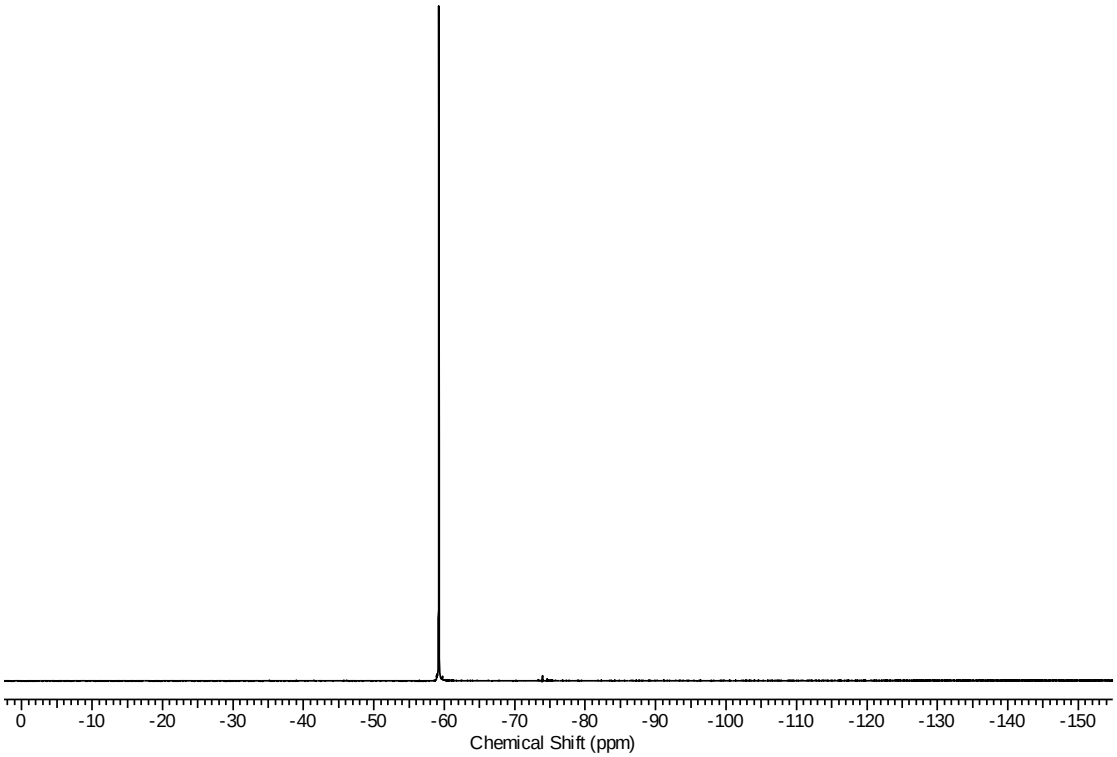
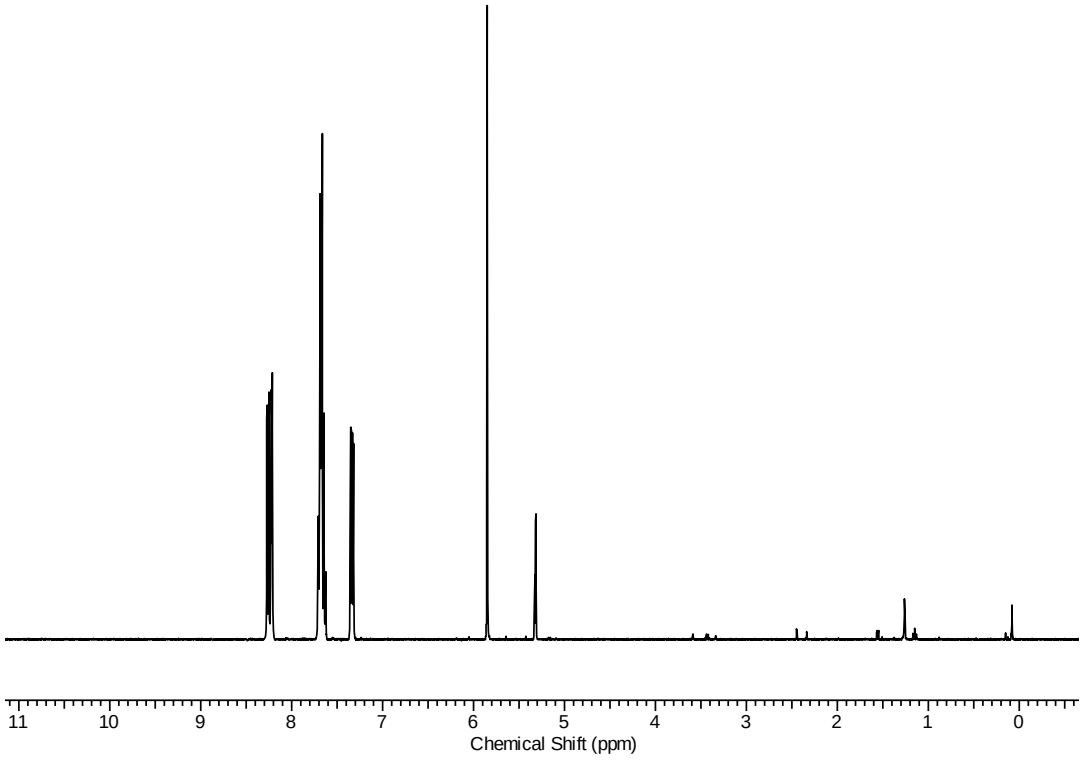


^{19}F NMR spectrum of **6**



SI Figure 7. NMR spectra of compound **7**.

^{1}H NMR spectrum of **7**



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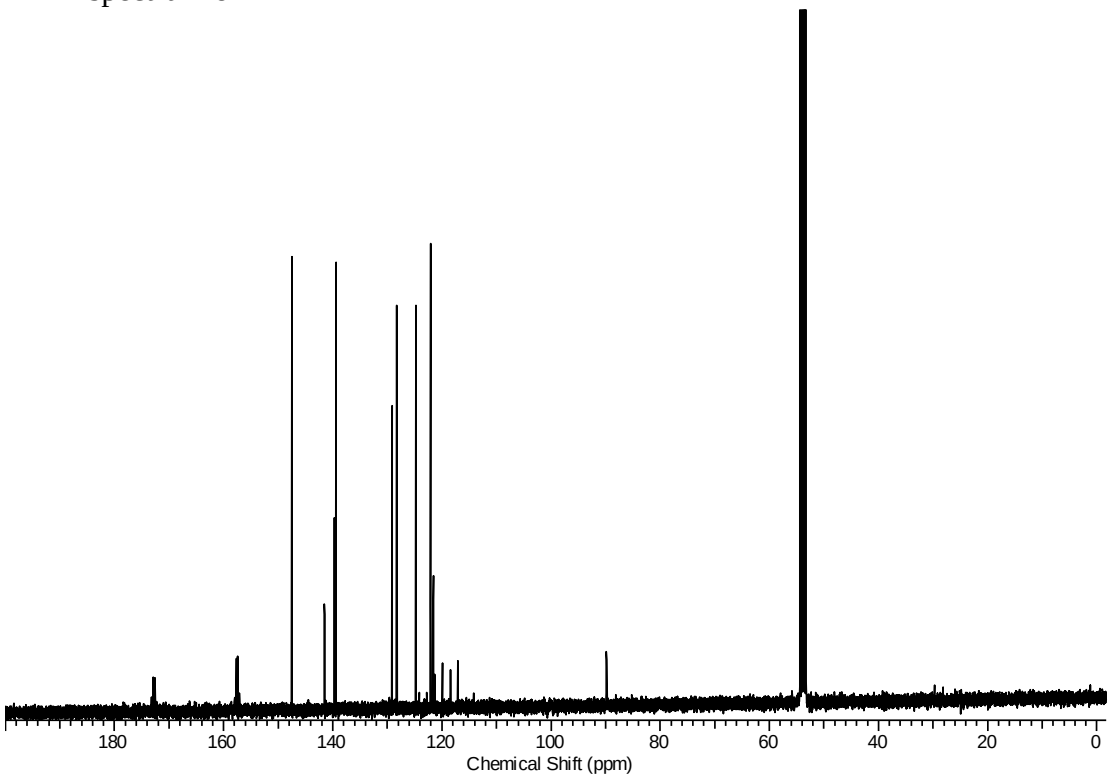

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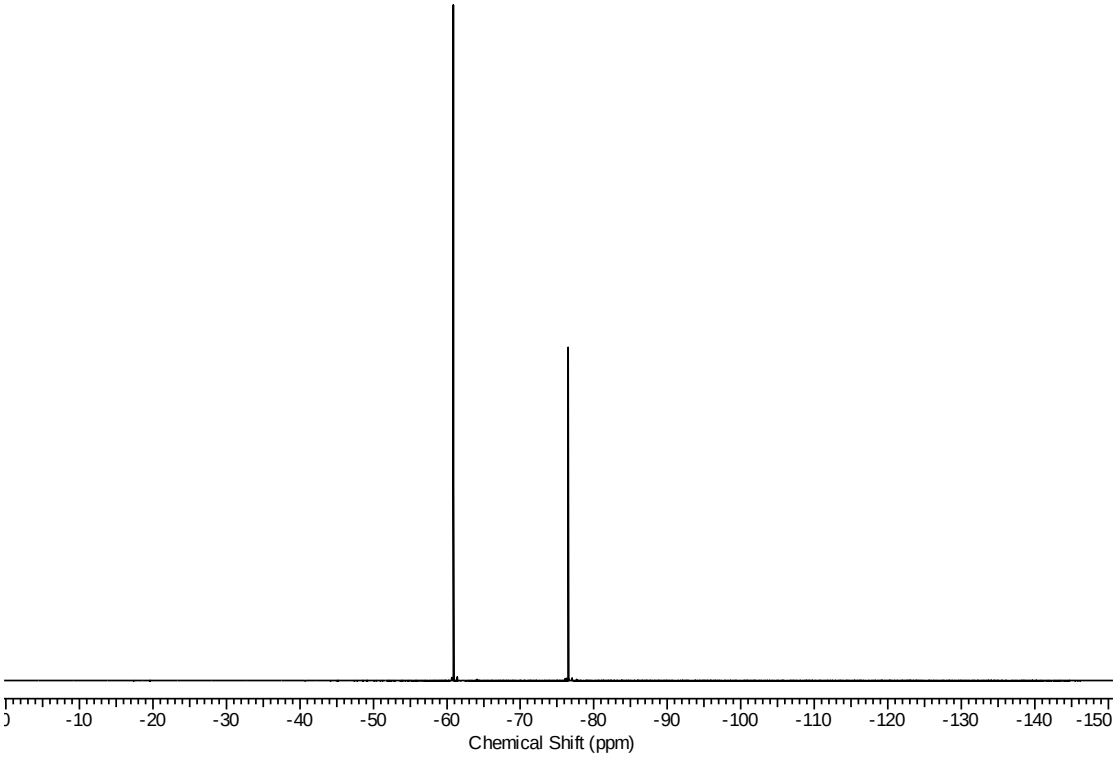
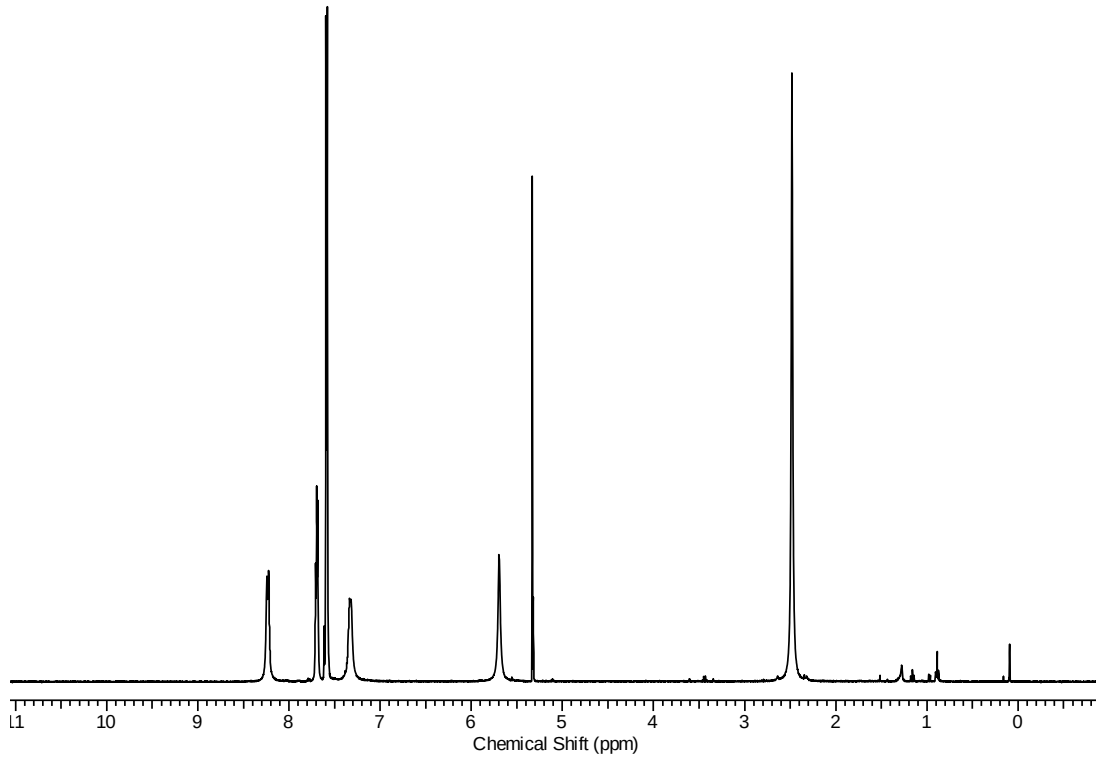


SI Figure 8. NMR spectra of compound **8**.

^{1}H NMR spectrum of **8**



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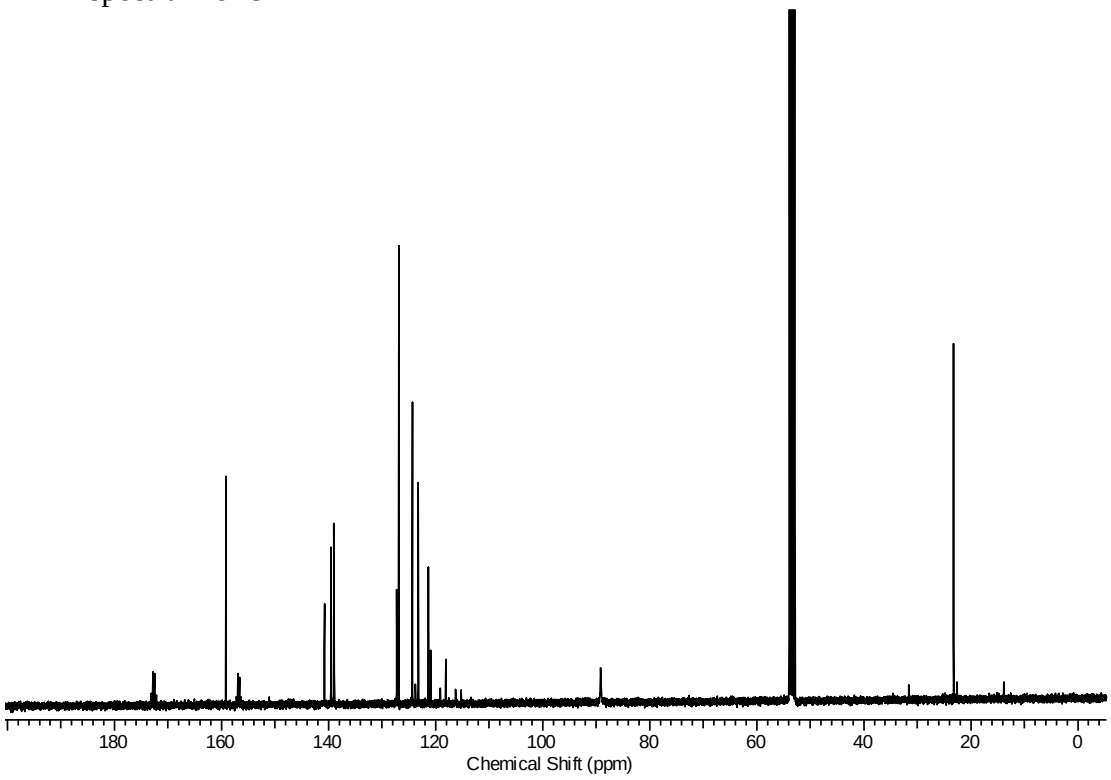
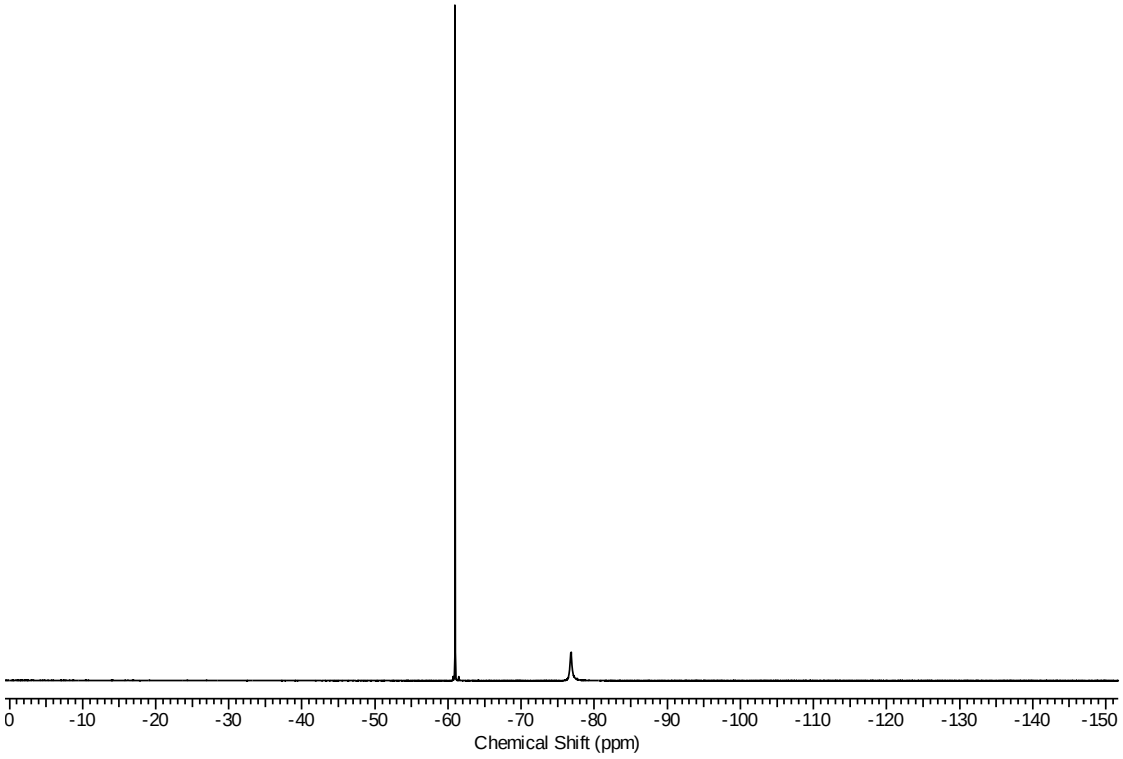
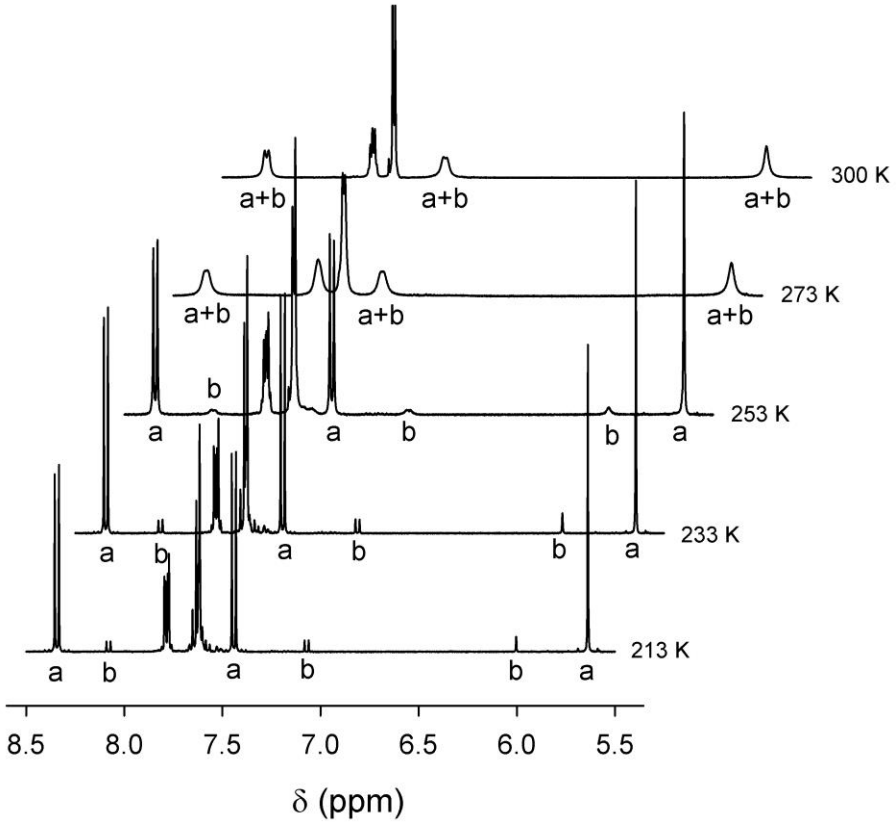


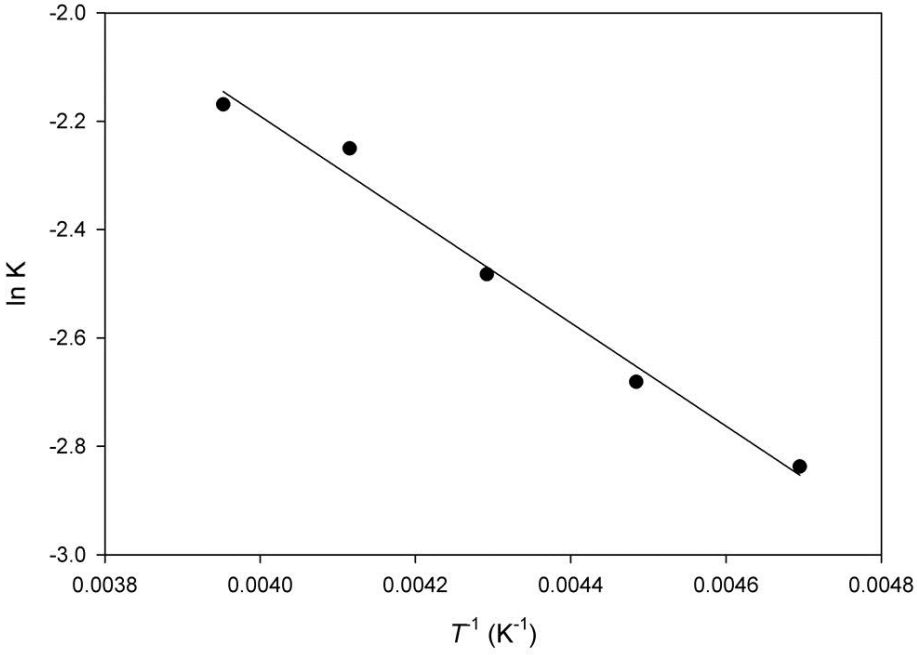
^{19}F NMR spectrum of **8**



SI Fig. 9 VT ^{1}H NMR spectra of **8** in the temperature range of 213 to 300 K in CD_2Cl_2.



SI Fig 10. van't Hoff plot for **8** with varying temperature from 213 to 300K where a = **8** and b = **8'**.



Crystallographic Data and ORTEP Diagrams

SI Table 1. Crystallographic and refinement data for **1**-**3** and **5**.

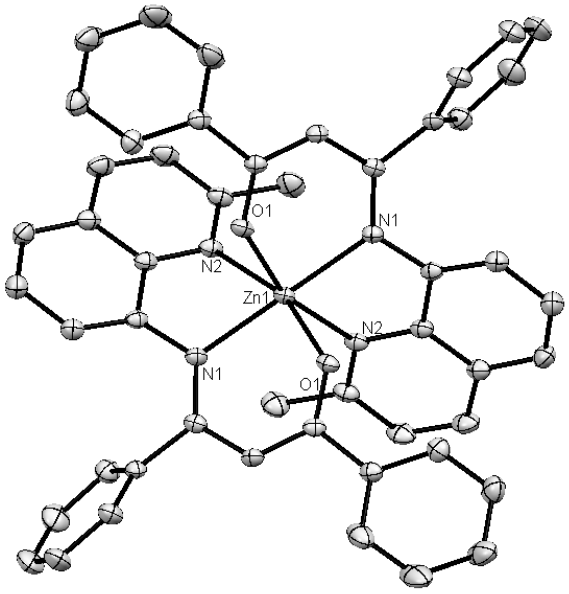
	1	**2•4CH_2Cl_2**[a]	**3**	**5•Et_2O**
Formula	$C_{30}H_{30}N_4O_2$ Zn	$C_{54}H_{46}Cl_8N_4O_2Zn$	$C_{28}H_{20}F_6N_4O_2$ Zn	$C_{34}H_{32}F_6N_4O_2$ Zn
FW	543.95	1131.92	623.85	708.01
T (K)	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c	Cc	$P2_1/n$
a / Å	12.3863(9)	18.4261(19)	10.9999(5)	13.728(2)
b / Å	11.7173(8)	18.3114(19)	21.1507(11)	15.472(2)
c / Å	17.9207(13)	17.7719(19)	12.5158(5)	15.449(2)
α / °	90	90	90	90
β / °	95.189(3)	105.912(1)	112.964(1)	103.124(2)
γ / °	90	90	90	90
V / $Å^3$)	2590.2(3)	5766.6(1)	2681.1(2)	2642.2(3)
Z	4	4	4	4
D_c / g cm^{-3}	1.395	1.304	1.546	1.472
μ / mm^{-1}	0.983	0.838	0.992	0.842
F(000)	1136	2320	1264	1456
Crystal color	yellow	orange	yellow	yellow
Ind. Ref.	7734	8315	4616	5445
Obs. Ref.	19876	38222	16741	22551
R_{int}	0.0457	0.1026	0.0274	0.0716
GOOF on F^2	1.056	1.053	1.071	1.050
R_1 $[I > 2\sigma(I)]$	0.0499	0.0445	0.0273	0.0637
wR_2 $[I > 2\sigma(I)]$	0.1303	0.1246	0.0623	0.1469

[a] One more region of unit cell containing a solvent molecule could not be modeled or identified. This region was squeezed from final refinements.

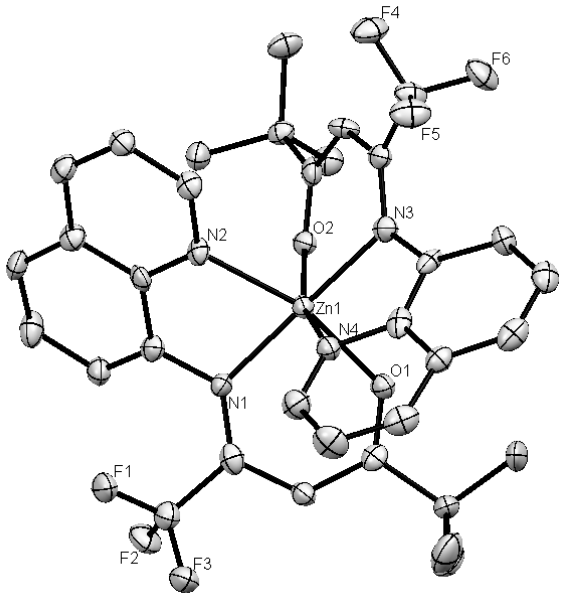
SI Table 2. Crystallographic and refinement data for **6-8**.

	6	**7**	**8**
Formula	$C_{44}H_{38}F_6N_4O_3Zn$	$C_{28}H_{14}F_{12}N_4O_2Zn$	$C_{30}H_{18}F_{12}N_4O_2Zn$
FW	850.15	731.80	759.85
T (K)	150	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a / Å	11.8222(6)	10.944(3)	10.8018(4)
b / Å	14.4520(8)	15.110(4)	16.7358(7)
c / Å	23.0665(13)	17.767(4)	16.7518(7)
α / °	90	90	90
β / °	93.491(1)	104.388(1)	103.113(1)
γ / °	90	90	90
V / Å^3)	3933.7(4)	2846.0(1)	3699(2)
Z	4	4	4
D_c / g cm^{-3}	1.436	1.708	1.711
μ / mm^{-1}	0.699	0.977	0.946
F(000)	1752	1456	1520
Crystal color	yellow	orange	orange
Ind. Ref.	7227	5767	21113
Obs. Ref.	34376	21545	6007
R_{int}	0.0429	0.0347	0.0279
GOOF on F^2	1.005	1.020	1.006
R_1 $[I > 2\sigma(I)]$	0.0396	0.0272	0.0328
wR_2 $[I > 2\sigma(I)]$	0.1052	0.0614	0.0848

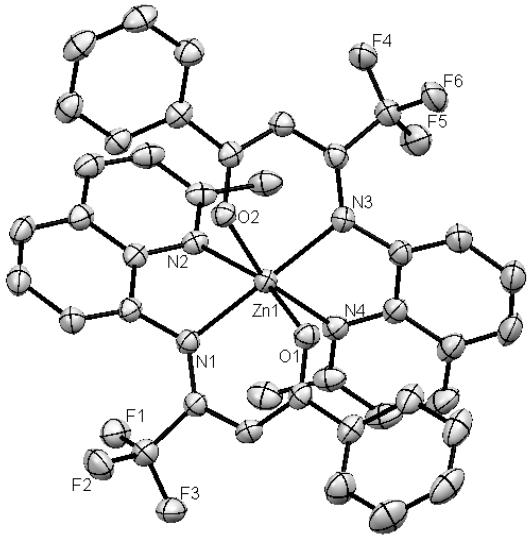
ORTEP Diagrams



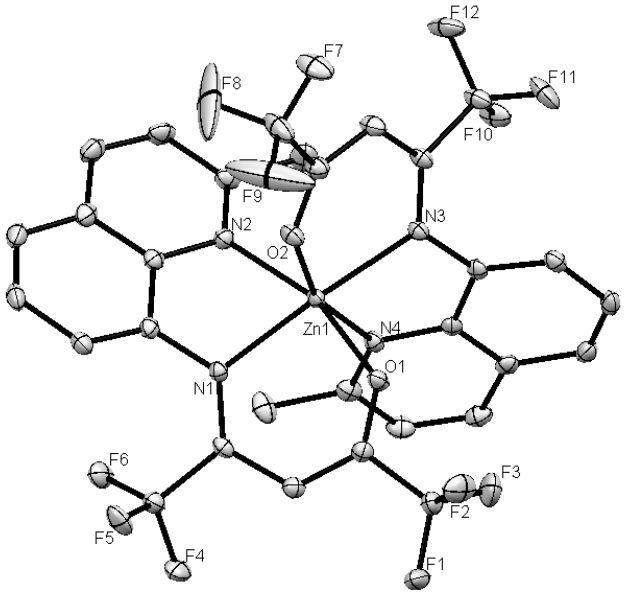
SI Figure 11. ORTEP of the molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms and dichloromethane solvent molecules removed for clarity.



SI Figure 12. ORTEP of the molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.



SI Figure 13. ORTEP of the molecular structure of **6** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms and one molecule of diethyl ether are omitted for clarity.



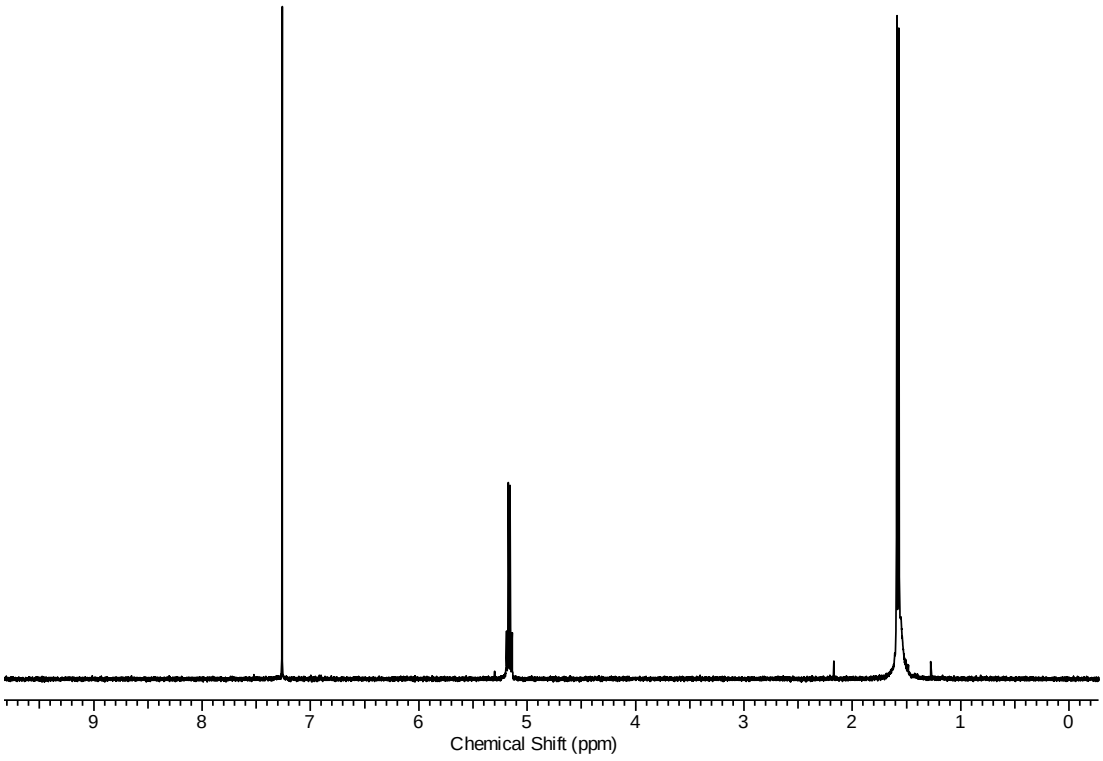
SI Figure 14. ORTEP of the molecular structure of **8** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

SI Table 3. Polylactides isolated from the ROP of L-lactide in bulk melt at 100 °C.

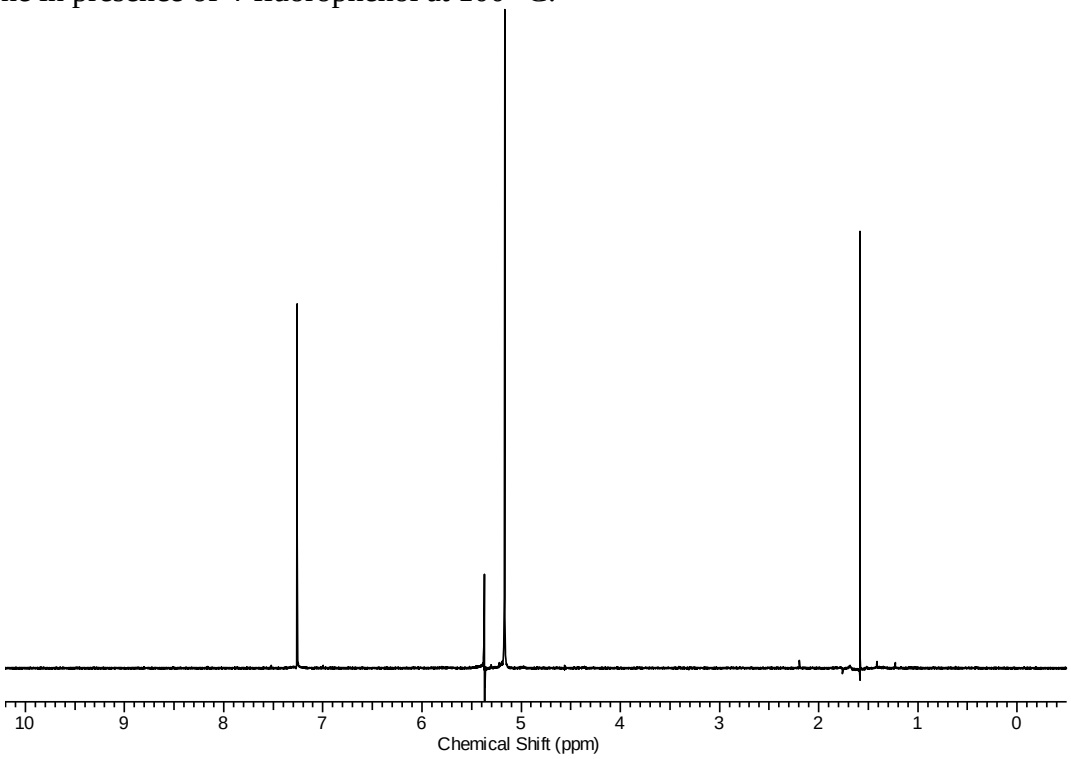
Entry	Cmpd[a]	Phenol / Zn	Time (min)	Conv.[b] (%)	$M_{n,\,calc}$[c] (10^3, g/mol)	$M_{n,\,obs}$[d] (10^3, g/mol)	PDI (M_w/M_n)
1	**1**	0	15	85	6.1	42.1	1.71
2	**1**	1	15	99	7.1	11.4	1.84
3	**3**	0	60	12	0.9	27.6	1.34
4	**3**	1	60	61	4.4	9.0	1.05
5	**5**	0	60	3	0.2	3.01	1.17
6	**5**	1	60	44	3.2	3.7	1.28
7	**6**	0	60	9	0.7	12.4	1.37
8	**6**	1	60	83	6.0	5.6	1.12
9	**8**	0	1440	27	1.9	15.53	1.39
10	**8**	1	1440	67	4.8	8.28	1.35

[a] All reactions were conducted without solvent at 100 °C with L-lac:Zn 50:1. [b] Lactide conversion as determined by ^{1}H NMR. [c] $M_{n,\,calc}$ = (M/I) × (% conv.) × (mol. wt. of lactide). [d] $M_{n,\,obs}$ values were determined by GPC in THF vs polystyrene standards and were corrected with a Mark-Houwink factor = 0.58.

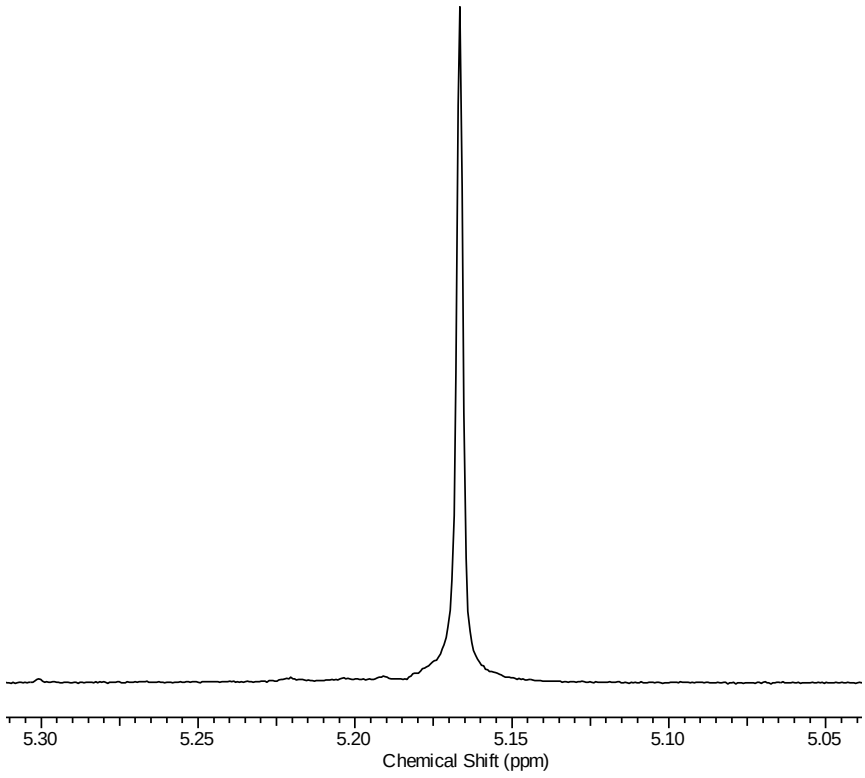
SI Figure 15. ^{1}H NMR spectrum of PLLA isolated from polymerization with **1** in toluene in presence of 4-fluorophenol at 100 °C, Table 2, entry 2.



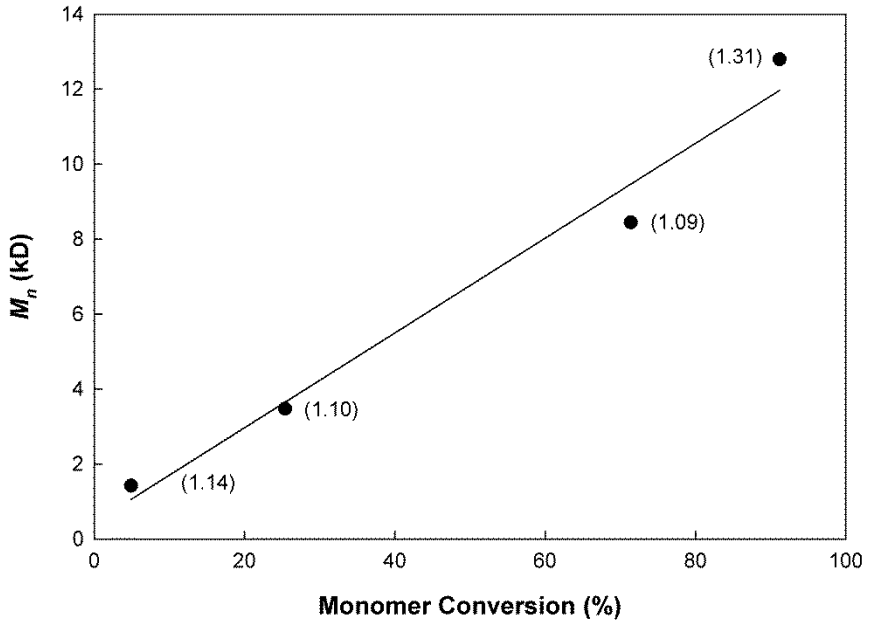
SI Figure 16. $\{^1H\}^1H$ NMR spectrum of isolated PLLA from polymerization with **1** in toluene in presence of 4-fluorophenol at 100 °C.



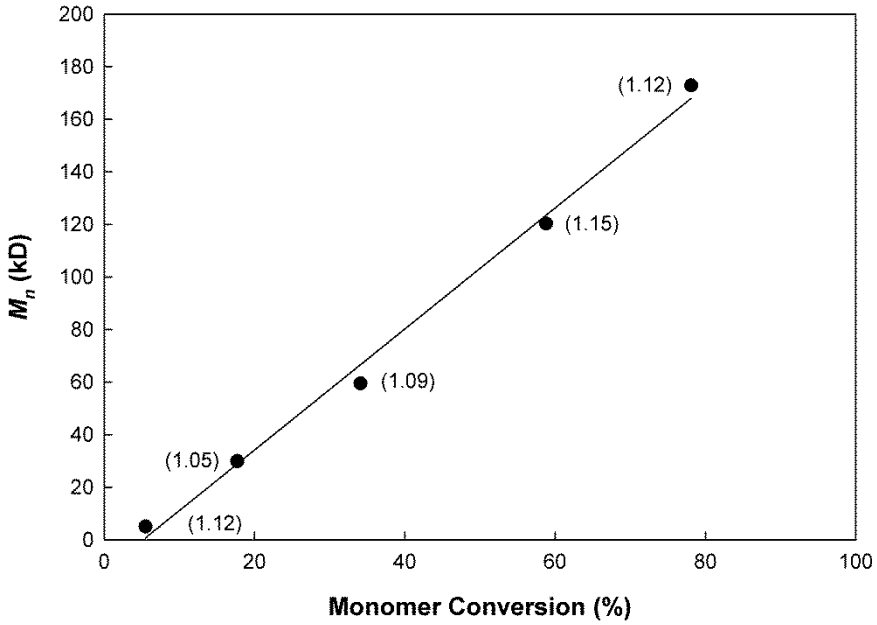
Zoom in of $\{^1H\}^1H$ NMR spectrum



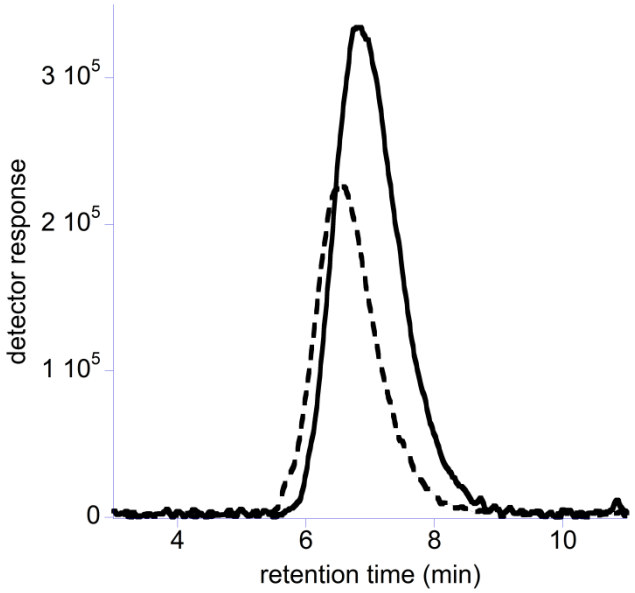
SI Figure 17. M_n versus percentage conversion of PLA produced from the ROP of L-lactide by **1** with 250 mg of L-lactide with 4-fluorophenol ([L-lac]/[**1**]/[co-catalyst] = 100/1/1) and 30 min of reaction time at 100 °C in toluene. PDI values are provided in parentheses.



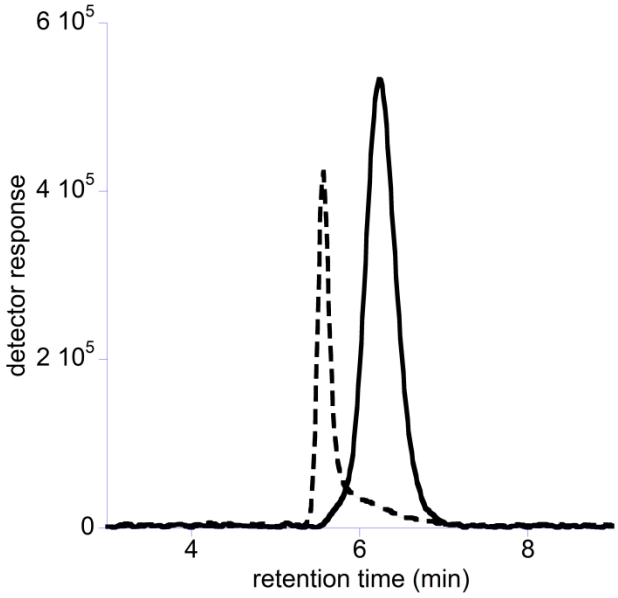
SI Figure 18. M_n versus percentage conversion of PLA produced from the ROP of L-lactide by **1** with 250 mg of L-lactide in absence of 4-fluorophenol ([L-lac]/[**1**]/[co-catalyst] = 100/1/0) and 30 min of reaction time at 100 °C in toluene. PDI values are provided in parentheses.



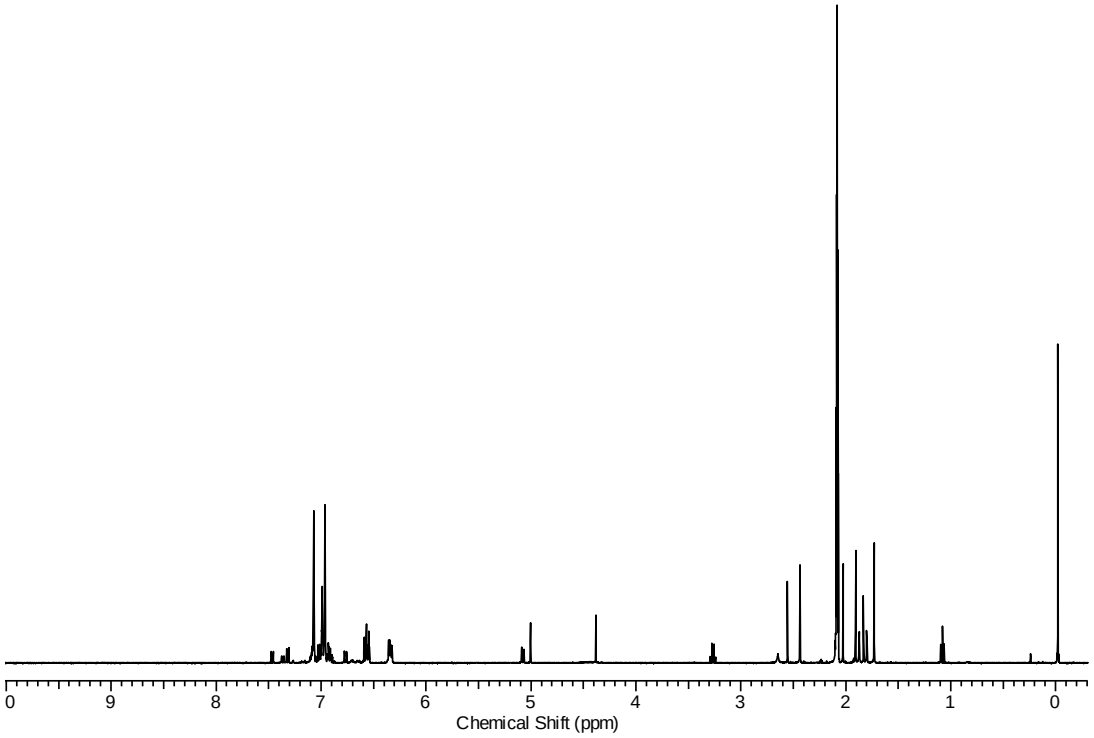
SI Figure 19. Chromatograms of polymeric materials isolated in double feed experiment with **1**. Chromatogram of isolated PLLA after treatment of **1** with 250 mg of L-lactide with 4-fluorophenol ([L-lac]/[**1**]/[co-catalyst] = 100/1/1) and 30 min of reaction time in toluene at 100 °C (solid line, M_n= 16.8 kD, PDI= 1.60) and chromatogram of isolated PLLA after second addition of 250 mg of L-lactide and 30 min of reaction time (dashed line, M_n= 25.7 kD, PDI= 1.56).



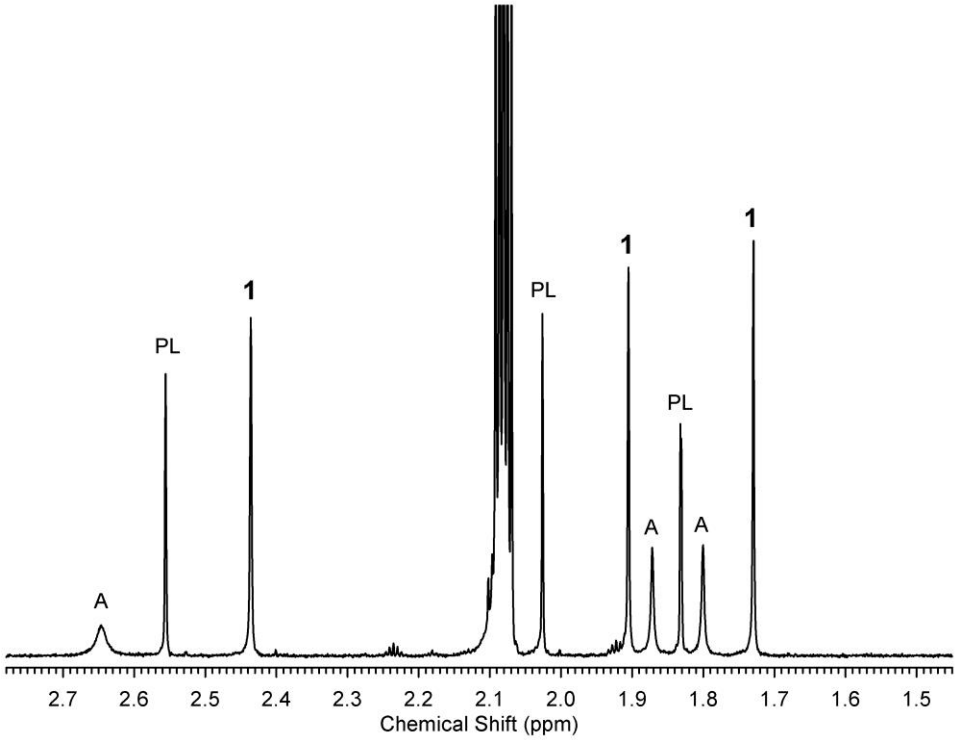
SI Figure 20. Chromatograms of polymeric materials isolated in double feed experiment with **1**. Chromatogram of isolated PLLA after treatment of **1** with 250 mg of L-lactide in absence of 4-fluorophenol ([L-lac]/[**1**]/[co-catalyst] = 100/1/0) and 30 min of reaction time in toluene at 100 °C (solid line, M_n= 68.9 kD, PDI= 1.08) and chromatogram of isolated PLLA after second addition of 250 mg of L-lactide and 30 min of reaction time (dashed line, M_n= 162.4 kD, PDI= 1.17).



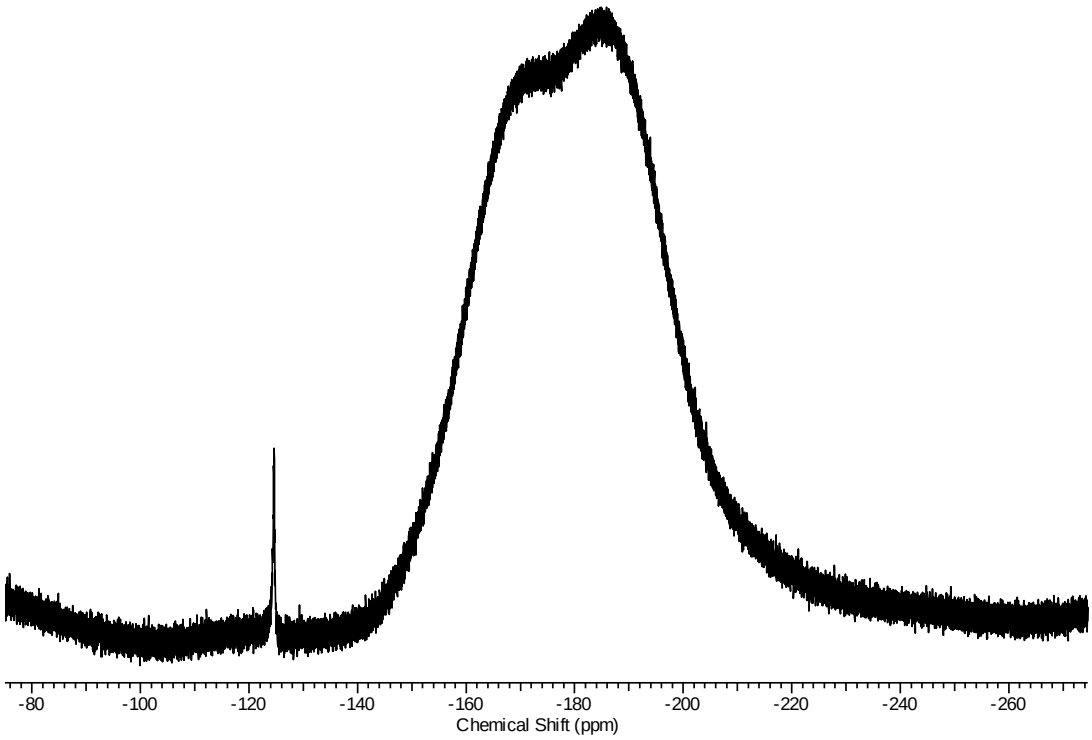
SI Figure 21. ^{1}H NMR spectrum of **1** treated with 4-fluorophenol at 300 K.



Zoom of ^{1}H NMR spectrum from above where compound **1**, pro-ligand (PL) and the in situ alkoxide (A) signals are annotated.



SI Figure 22. ^{19}F NMR spectrum of **1** treated with 4-fluorophenol at 300 K.



SI Figure 23. ^{19}F NMR spectrum of 4-fluorophenol at 300 K.