Supporting information for

P,*O*-Phosphinophenolate Zinc(II) Species: Synthesis, Structure and Use in the Ring-Opening Polymerization (ROP) of Lactide, ε-Caprolactone and Trimethylene carbonate.

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Table S1. Crystallographic data for compounds **2**·H, **3**, **6'** and **7**.

Compound	**2**·H	**3**	**6'**	**7**
CCDC number	1046464	1046465	1046466	1046467
Chemical formula	$C_{23}H_{25}OP$	$C_{44}H_{46}O_2P_2Zn$	$C_{76}H_{79}O_4P_3Zn_2$	$C_{80}H_{72}O_4P_4Zn_2$
Formula mass	348.40	799.49	1280.04	1351.99
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
a/Å	13.3231(8)	9.528(9)	13.6142(6)	12.2606(9)
b/Å	13.0236(8)	9.803(9)	19.6861(8)	13.4731(9)
c/Å	11.3086(7)	11.432(11)	27.5279(9)	25.2245(18)
α/°	90.00	73.14(2)	90.00	100.950(2)
β/°	95.911(2)	89.54(2)	116.169(2)	91.257(2)
γ/°	90.00	74.29(2)	90.00	114.8770(10)
Unit cell volume/Å^3	1951.8(2)	980.8(16)	6621.5(5)	3687.0(5)
Temperature/K	173(2)	173(2)	173(2)	173(2)
Space group	*Cc*	*P-1*	$P2_1/c$	*P-1*
Z	4	1	4	2
Absorption coef. μ/mm^{-1}	0.148	1.340	0.846	0.784
No. refl. meas.	8582	11885	51511	67283
No. indep. refl.	5080	4650	17480	17771
R_{int}	0.0250	0.1282	0.0295	0.0649
R_1 ($I > 2\sigma(I)$)	0.0401	0.0855	0.0560	0.0427
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0803	0.1796	0.1121	0.0843
R_1 (all data)	0.0581	0.1903	0.0872	0.0810
$wR(F^2)$ (all data)	0.0871	0.2212	0.1288	0.0931
S on F^2	1.028	0.950	1.123	0.948

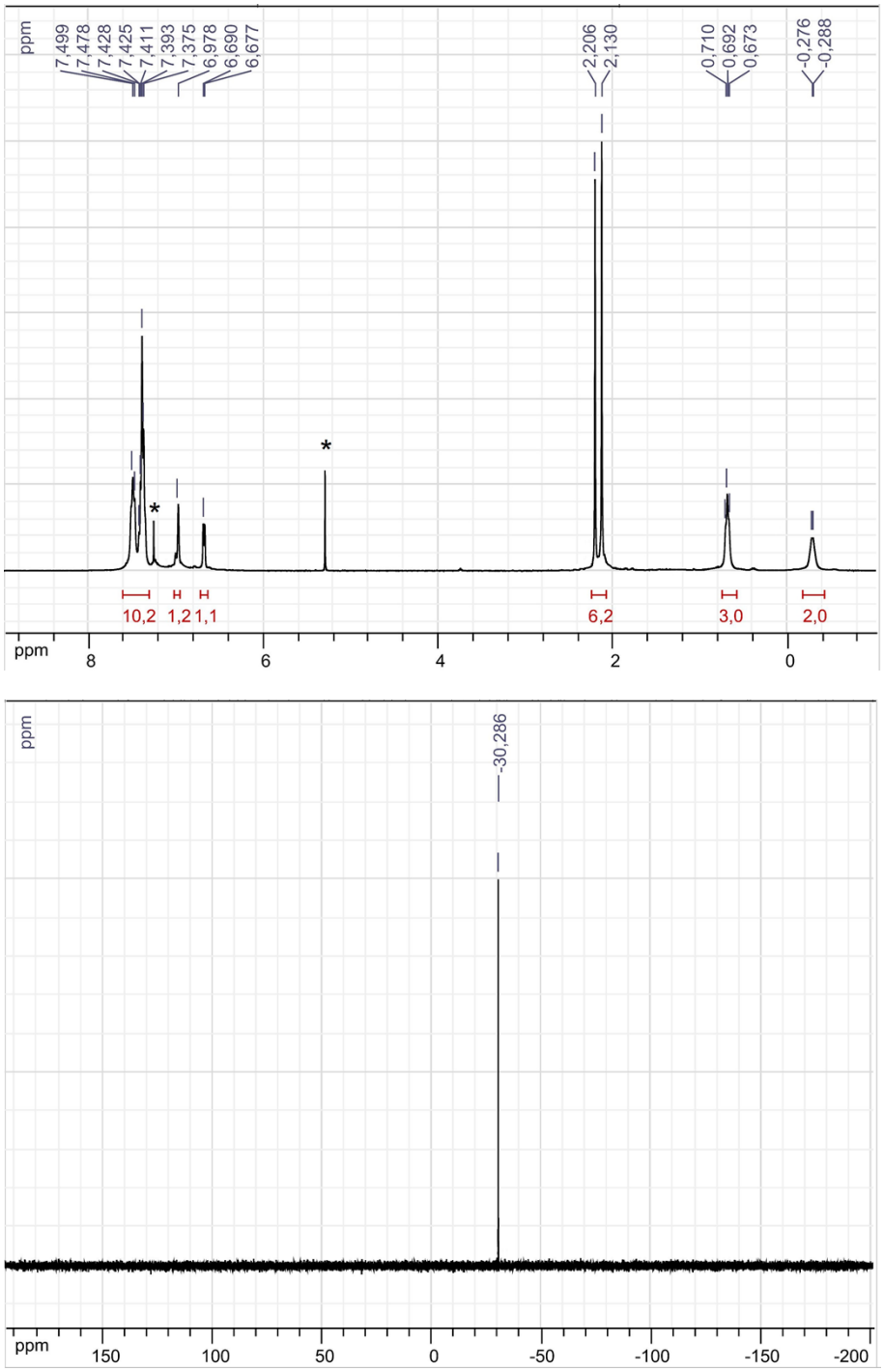


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, RT, top) and $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, RT, bottom) spectra of complex **3**. * Residual CH_2Cl_2.

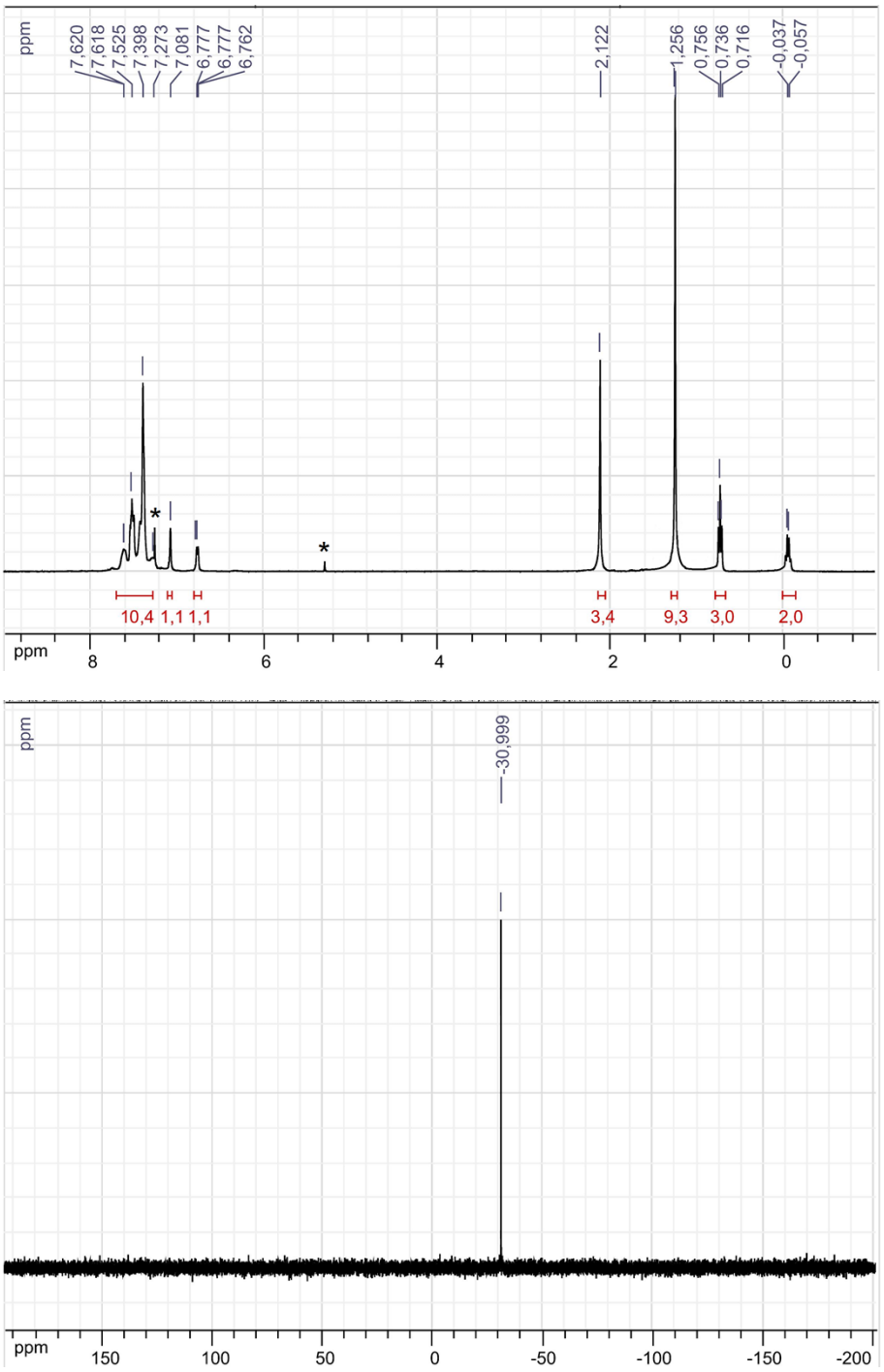


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$, RT, top) and $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, RT, bottom) spectra of complex **4**. * Residual CH_2Cl_2.

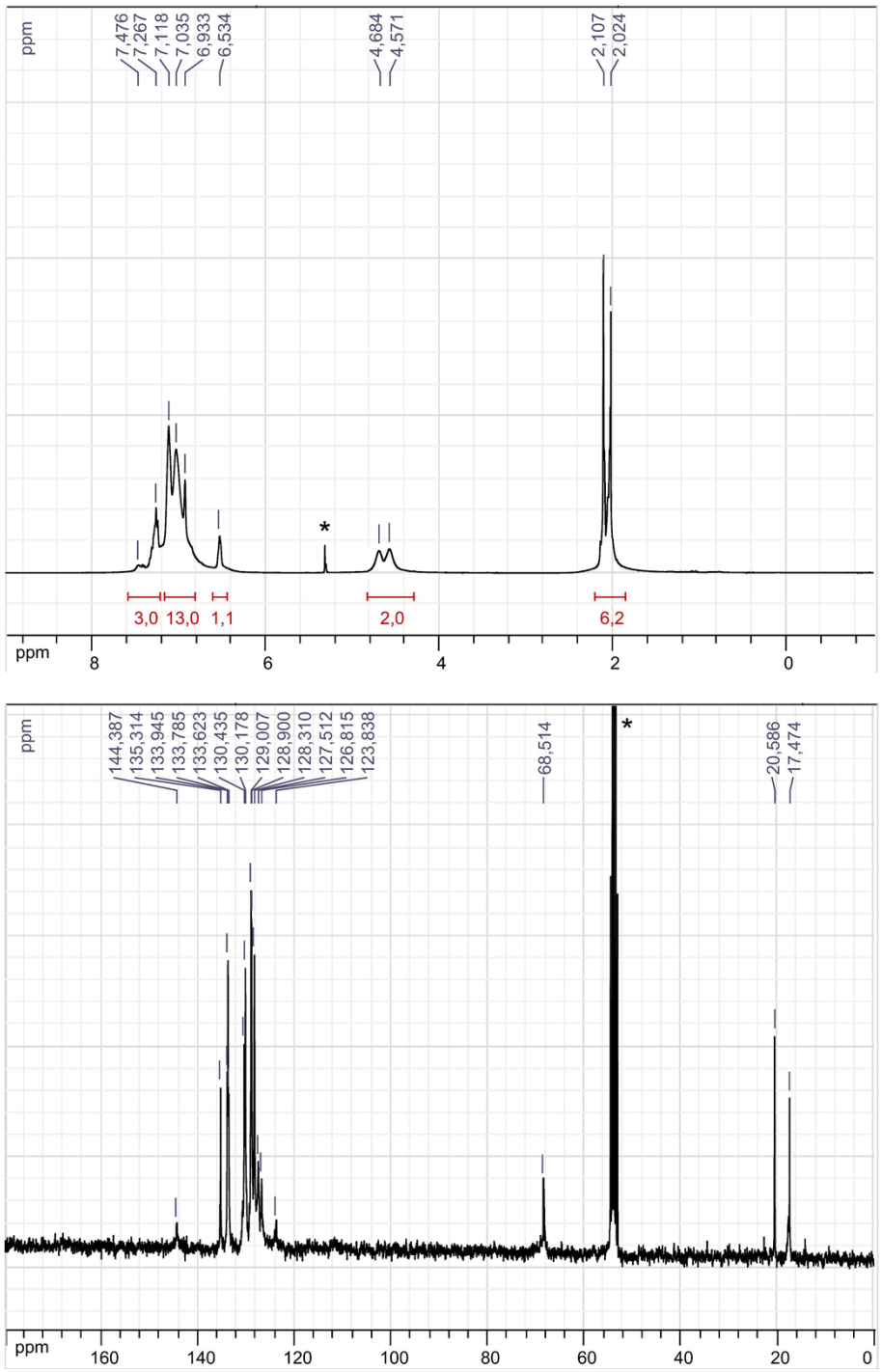


Figure S3A. ^{1}H NMR (400 MHz, CD_2Cl_2, RT, top) and $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2, RT, bottom) spectra of complex **5**. * CD_2Cl_2.

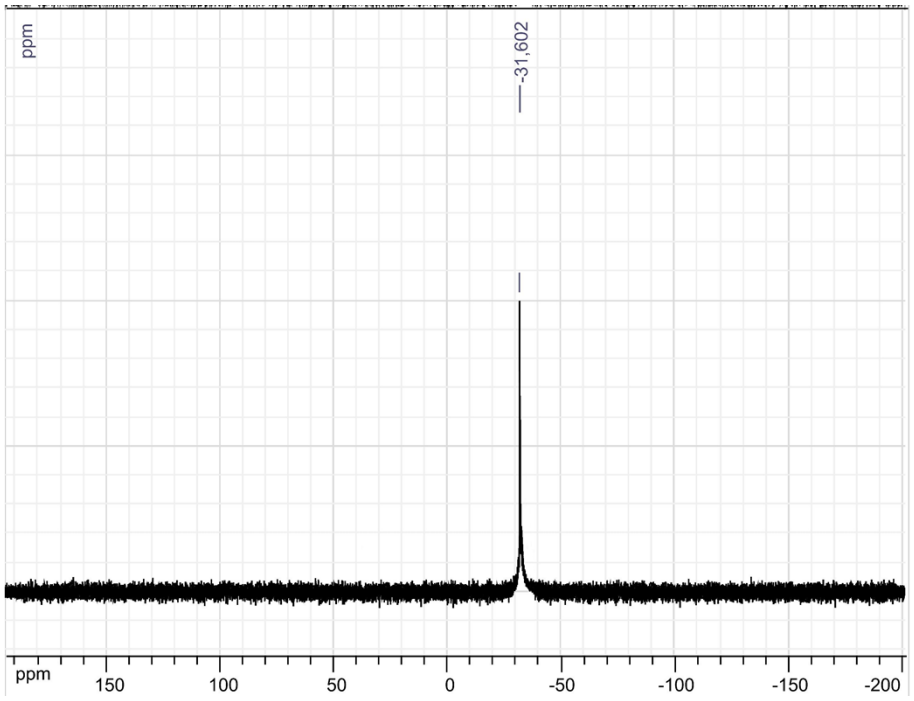


Figure S3B. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, RT) spectrum of complex **5**.

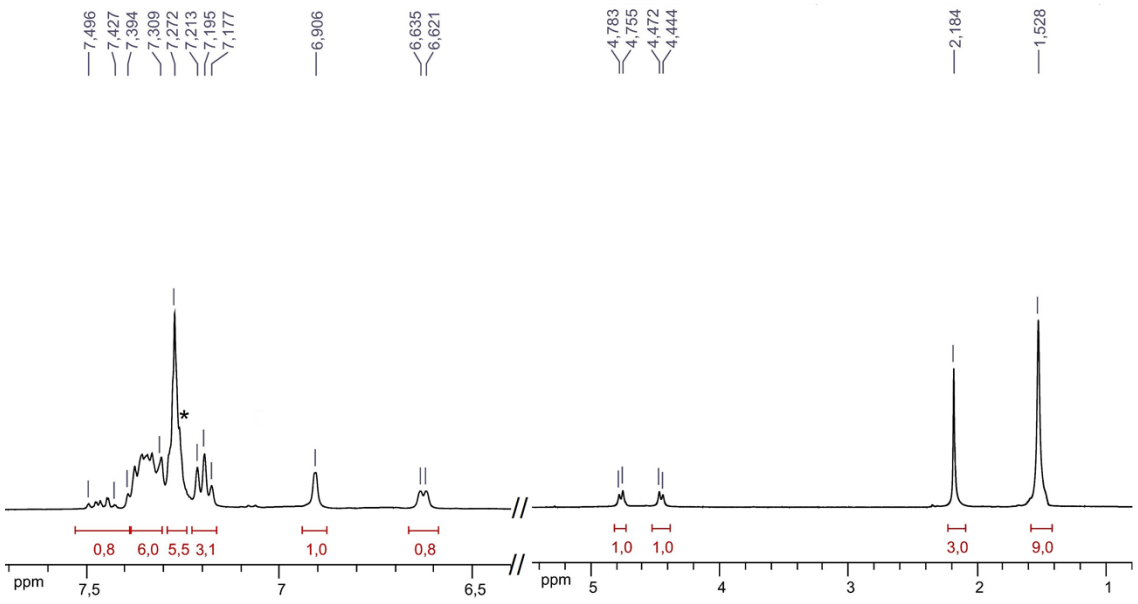


Figure S4A. [7.7-6.5 ppm] and [5.2-1.0 ppm] regions of the ^{1}H NMR (400 MHz, $CDCl_3$, RT) spectrum of complex **6**.

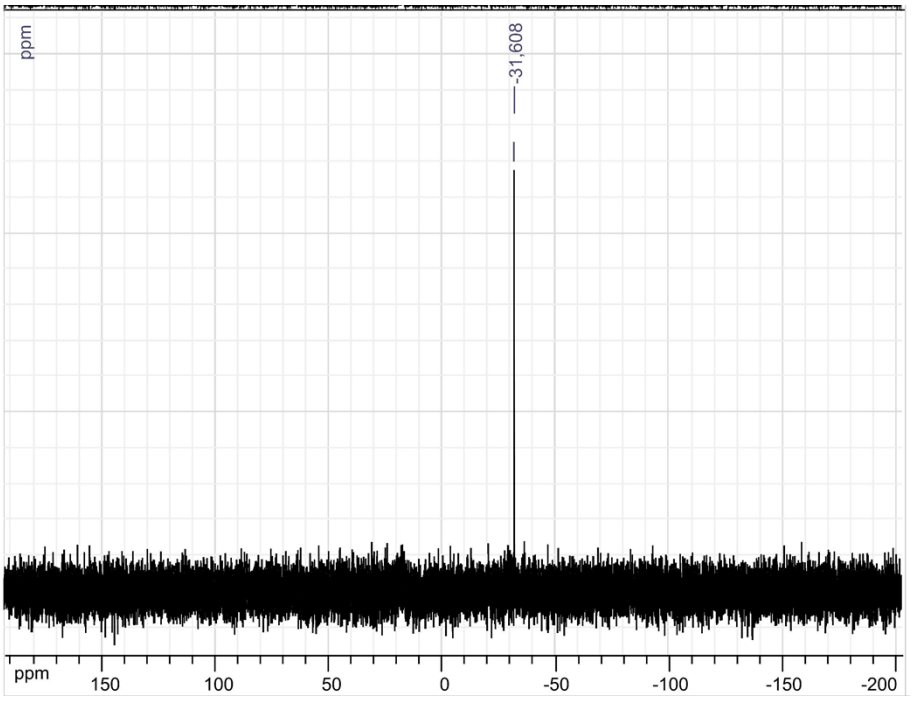


Figure S4B. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, RT, bottom) spectrum of complex **6**.

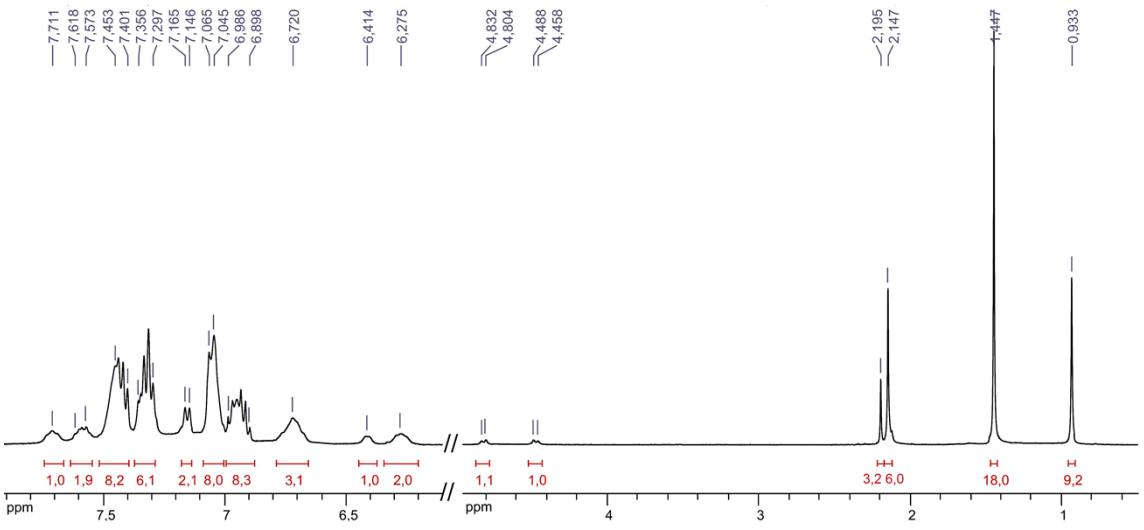


Figure S5A. [8.0-6.0 ppm] and [5.0-0.5 ppm] regions of the ^{1}H NMR (400 MHz, CD_2Cl_2, RT) spectrum of complex **6'**.

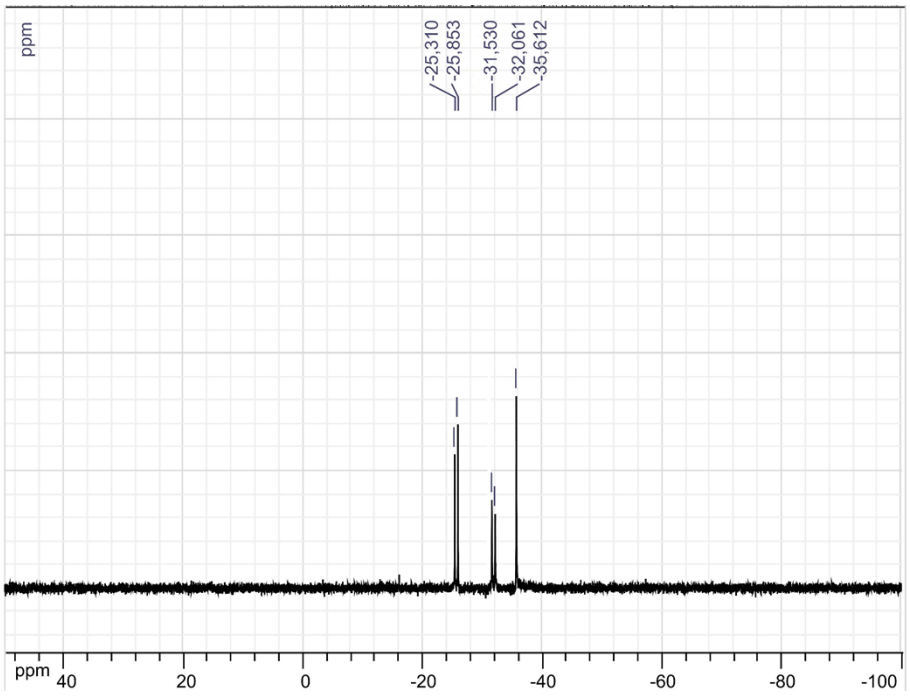


Figure S5B. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, RT) spectrum of complex **6'**.

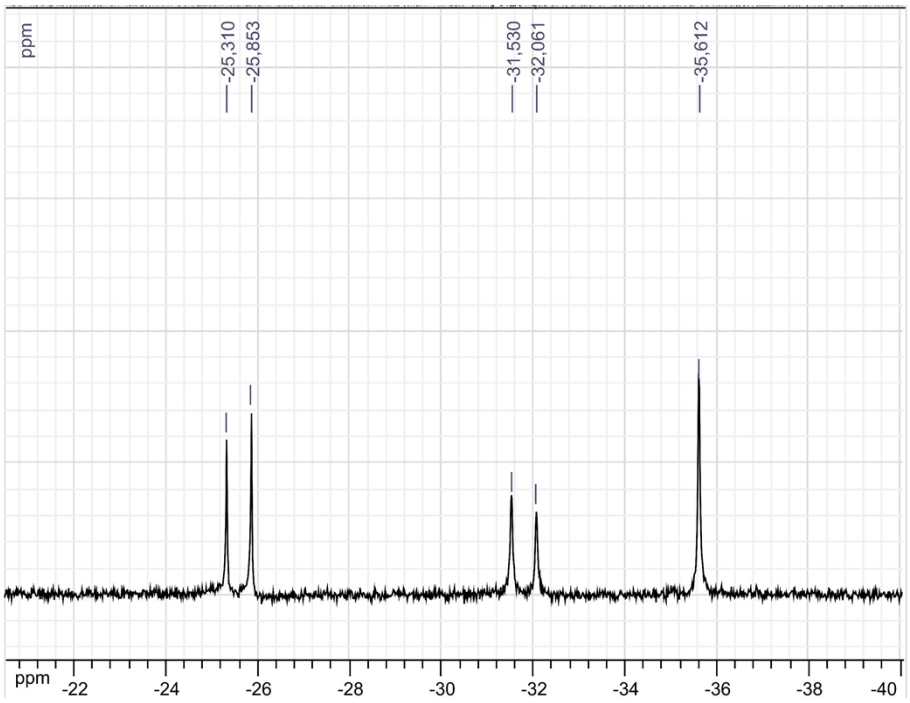
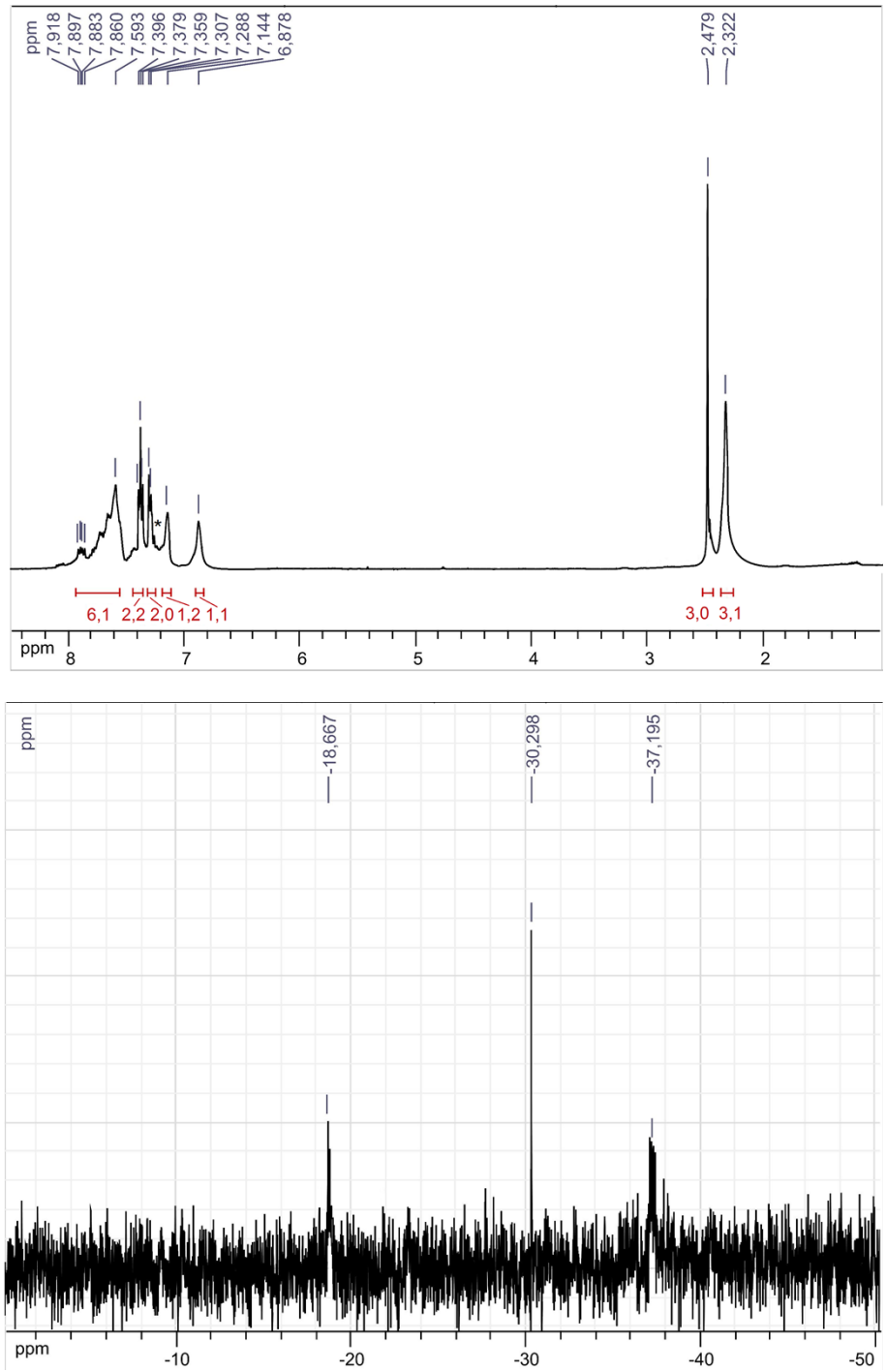
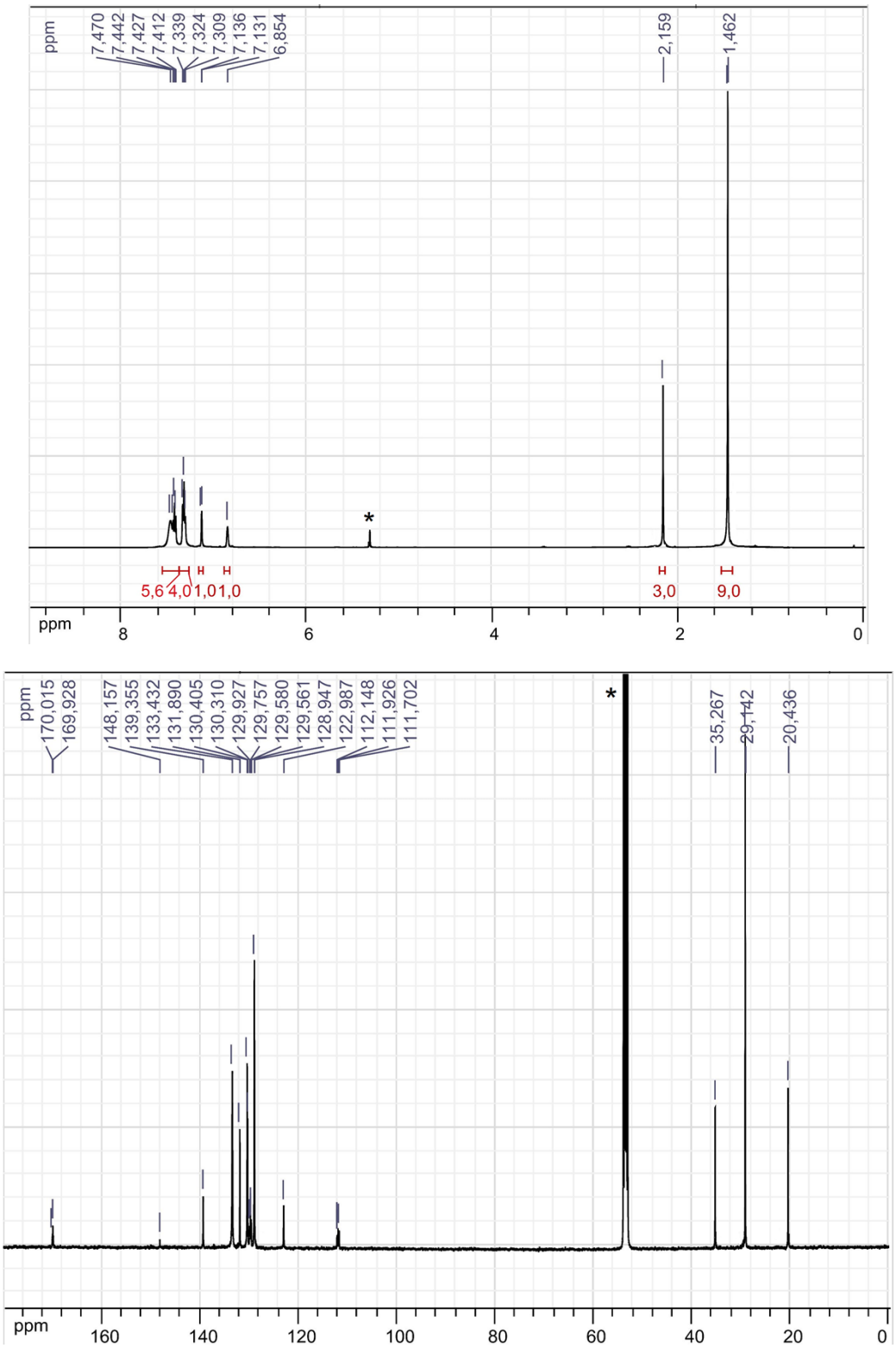


Figure S5C. Zoom-in of the $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, RT) spectrum of complex **6'**.



Figures S6A and S6B. ^{1}H NMR (400 MHz, CD_2Cl_2, RT; top) and $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, RT, bottom) spectra of complex **7**.



Figures S7A and S7B. ^{1}H NMR (500 MHz, CD_2Cl_2, RT; top) and $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_2Cl_2, RT; bottom) spectra of complex **8**. * Residual CH_2Cl_2.

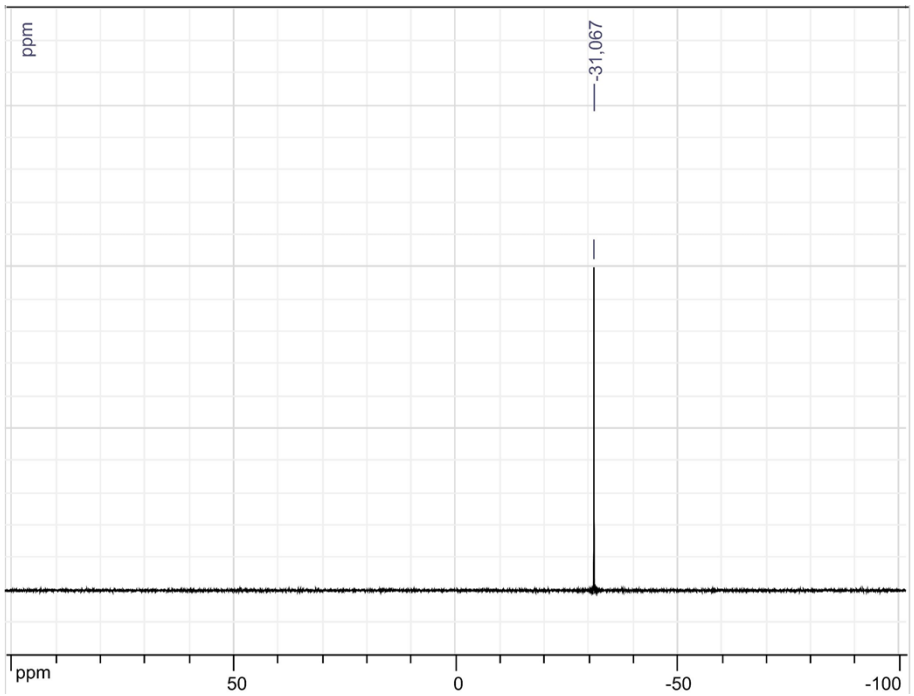


Figure S7C. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, RT) spectrum of complex **8**.

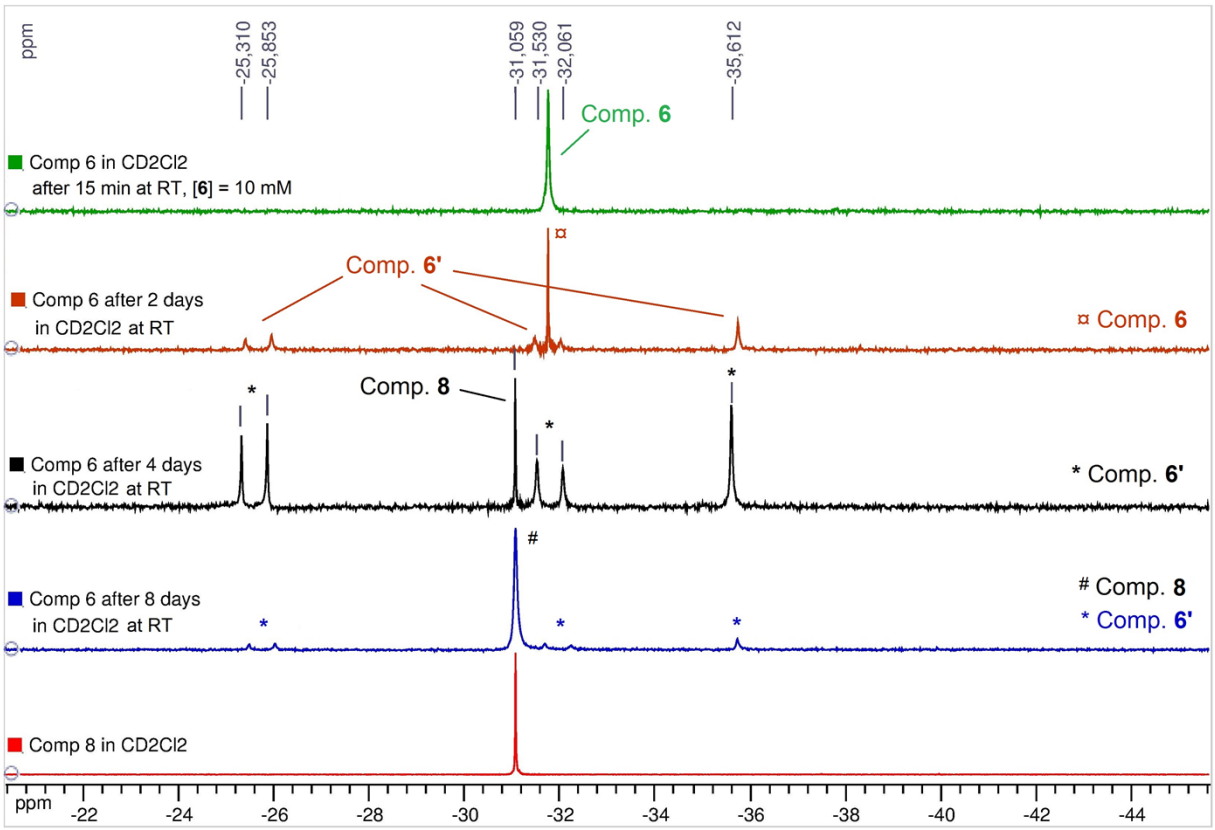


Figure S8A. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, RT) monitoring of the slow decomposition of the heteroleptic species **6** to homoleptic **8** *via* the formation of species **6'**. Conditions: $[\mathbf{6}]_0$ = 10 mM, CD_2Cl_2, RT. For comparison, the $^{31}P\{^{1}H\}$ NMR spectrum of analytically pure **8** (bottom spectrum) as prepared from the reaction of $ZnEt_2$ and 2 equiv. of ligand **2**·H.

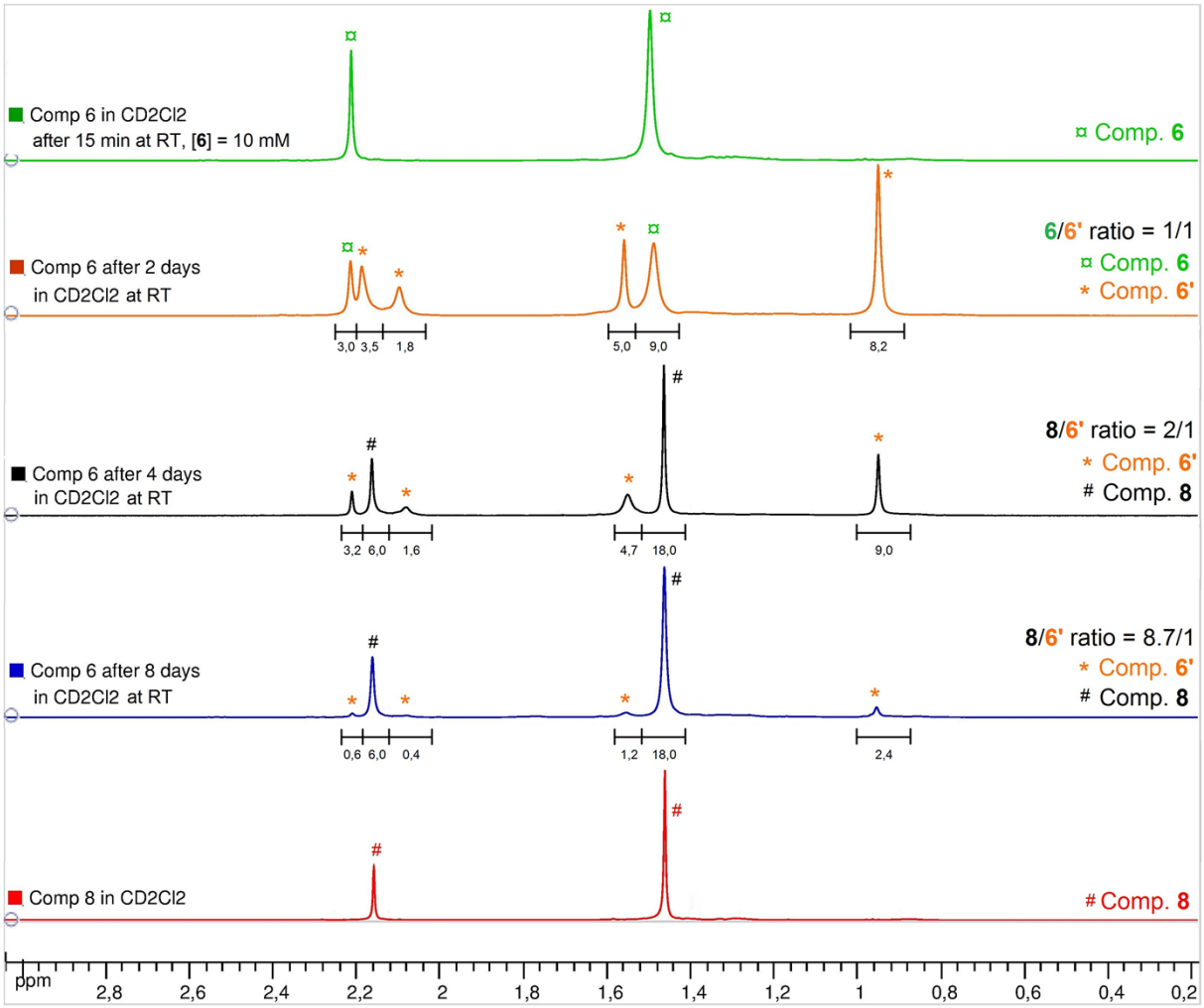
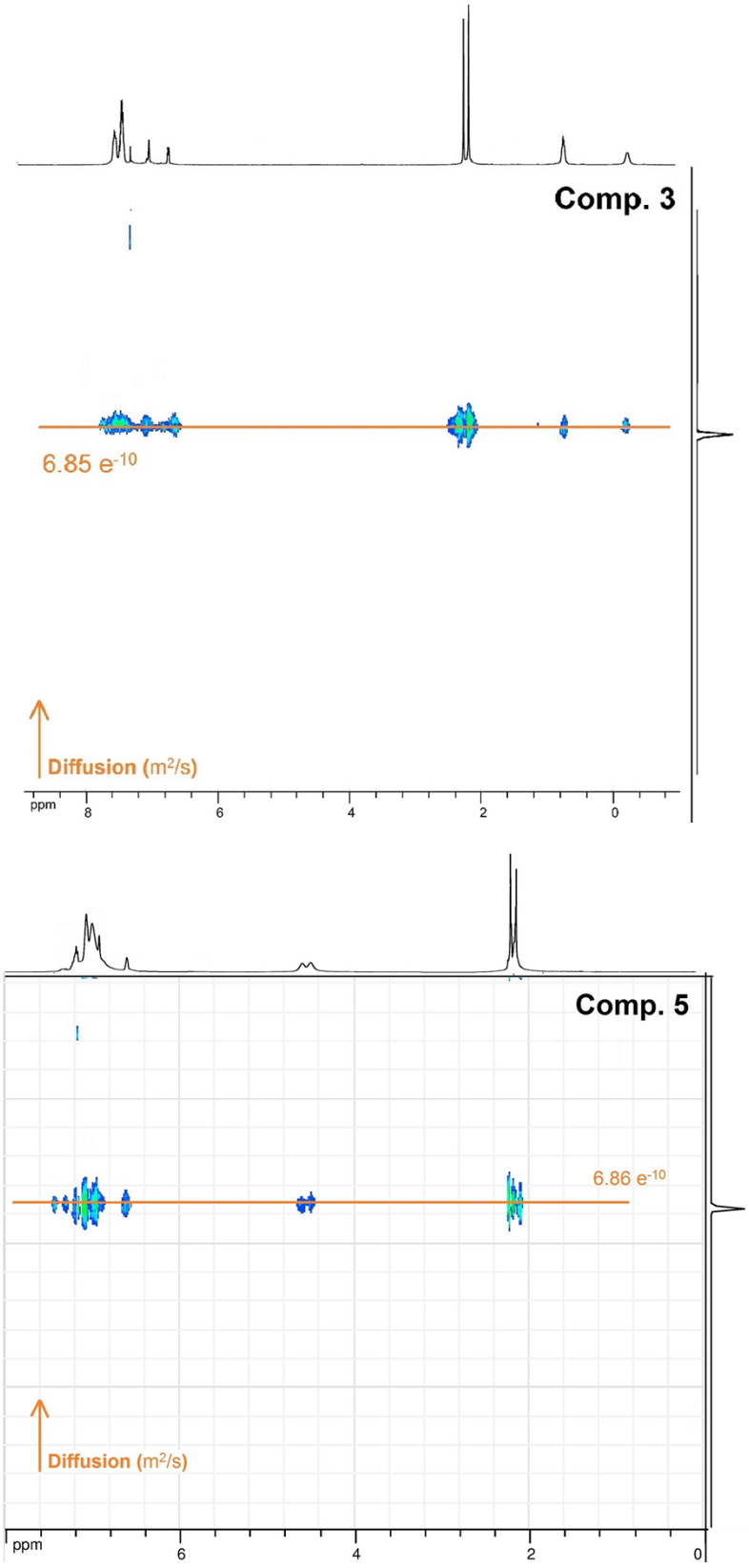
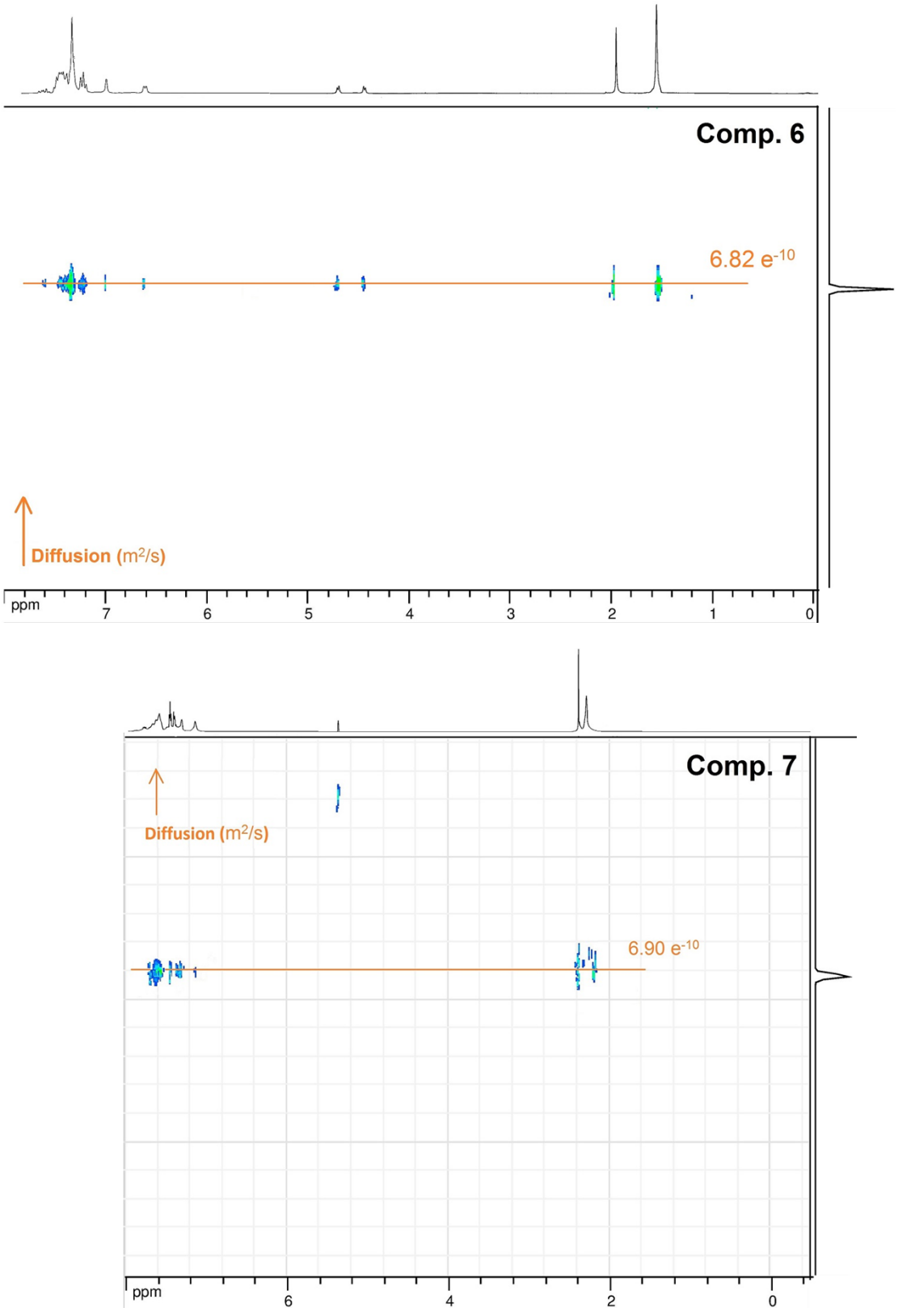


Figure S8B. ^{1}H NMR (162 MHz, CD_2Cl_2, RT) monitoring of the slow decomposition of the heteroleptic species **6** to homoleptic **8** *via* the formation of species **6'**. Conditions: $[\mathbf{6}]_0$ = 10 mM, CD_2Cl_2, RT. For comparison, the $^{31}P\{^{1}H\}$ NMR spectrum of analytically pure **8** (bottom spectrum) as prepared from the reaction of $ZnEt_2$ and 2 equiv. of ligand **2**·H.

Based on the above data, 50% of complex **6** is converted in **6'** after 2 days at RT (orange spectrum above; for the ^{1}H NMR spectrum of pure **6'**, see Fig. S5A). After 4 days, complex **6** is completely consumed with the formation of compounds **6'** and **8** (in a 1/2 **6'**/**8** ratio, black spectrum above). Complex **6'** is thus an intermediate species that progressively converts to homoleptic **8** (blue spectrum above). For comparison, the ^{1}H NMR spectrum of isolated complex **8** in CD_2Cl_2 is also provided (red spectrum).



Figures S9 and S10. Diffusion-ordered NMR (DOSY) spectra of complexes **3** and **5** recorded in $CDCl_3$ at room temperature.



Figures S11 and S12. Diffusion-ordered NMR (DOSY) spectra of complexes **6** and **7** recorded in $CDCl_3$ for **6** and in CD_2Cl_2 for **7**. Both NMR analysis were run at room temperature.

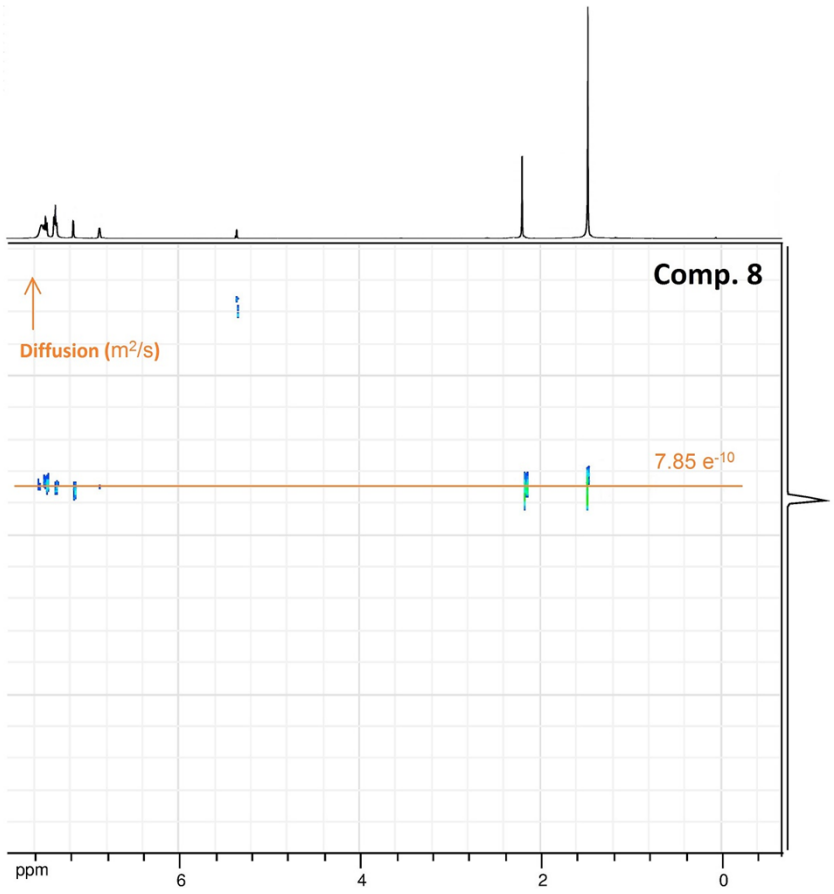


Figure S13. Diffusion-ordered NMR (DOSY) spectra of complex **8** recorded in CD_2Cl_2 at room temperature.

Table S2. Details of the data used for the determination of the hydrodynamic radius (H R in Å) and molecular volume (V_{DOSY} in Å^3).

Comp.	Temp. (K)	Diff. (m^2/s)	Visc.	Gamma[a]	H. R. (Å)[b]	V_{DOSY} (Å^3)[c]
			$CDCl_3$			
3	298	6.85 e^{-10}	5.300 e^{-04}	1.13 e^{-08}	6.01	909
5	298	6.86 e^{-10}	5.300 e^{-04}	1.13 e^{-08}	6.00	905
6	298	6.82 e^{-10}	5.300 e^{-04}	1.14 e^{-08}	6.04	921
			CD_2Cl_2			
7	298	6.90 e^{-10}	4.603 e^{-04}	1.29 e^{-08}	6.87	1358
8	298	7.85 e^{-10}	4.603 e^{-04}	1.14 e^{-08}	6.04	922

Notes: Visc. = Viscosity of the NMR solvent; Diff. = Diffusion; H. R. = hydrodynamic radius; [a] Gamma = (1.38 e^{-23}*Temp.)/(Diff.*Visc.); [b] H. R. = Gamma/(6*π);
[c] $V_{DOSY} = (4/3)\ \pi\ (H.\ R.)^3$

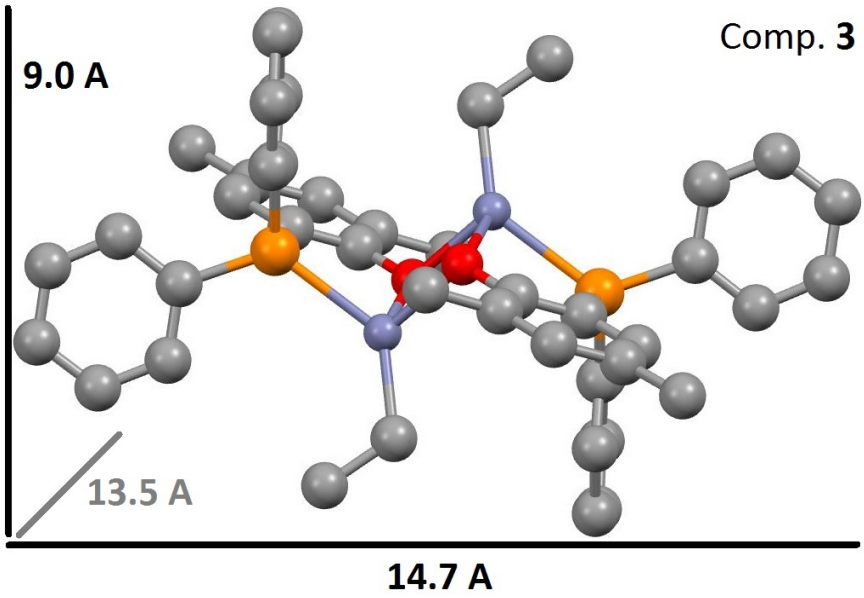


Figure S14. Geometrical parameters (L = 14.7, l = 13.5; H = 9.0 Å) used for the volume estimation of species **3** based on its solid state structure. An ellipsoidal model [V = 4/3 π (L x l x H)] was used. $V_{X\text{-}ray}$ = (4/3) π [(14.7/2) x (13.5/2) x (9.0/2)] = 936 $Å^3$.

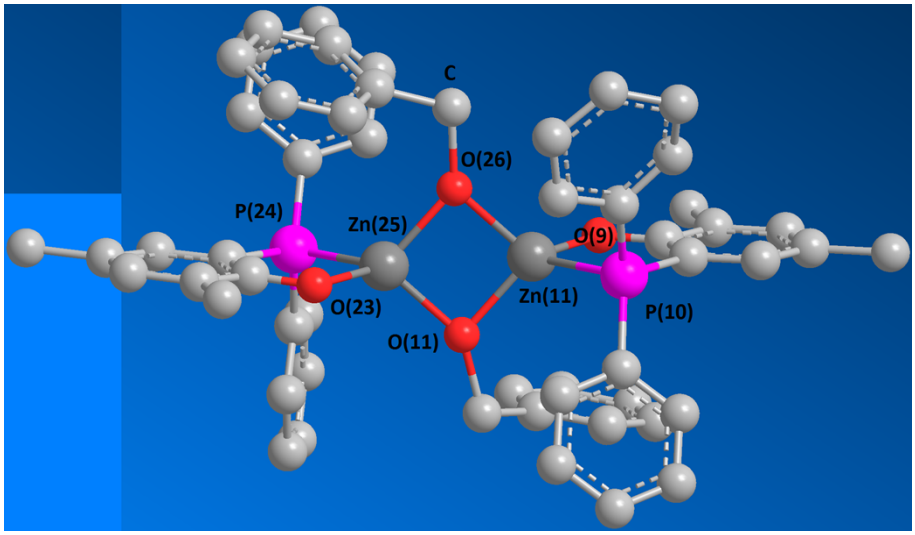


Figure S15. Optimized molecular geometry for complex **5** with Chem3D using the MM2 method. For a listing of MM2 parameters, see page 31.

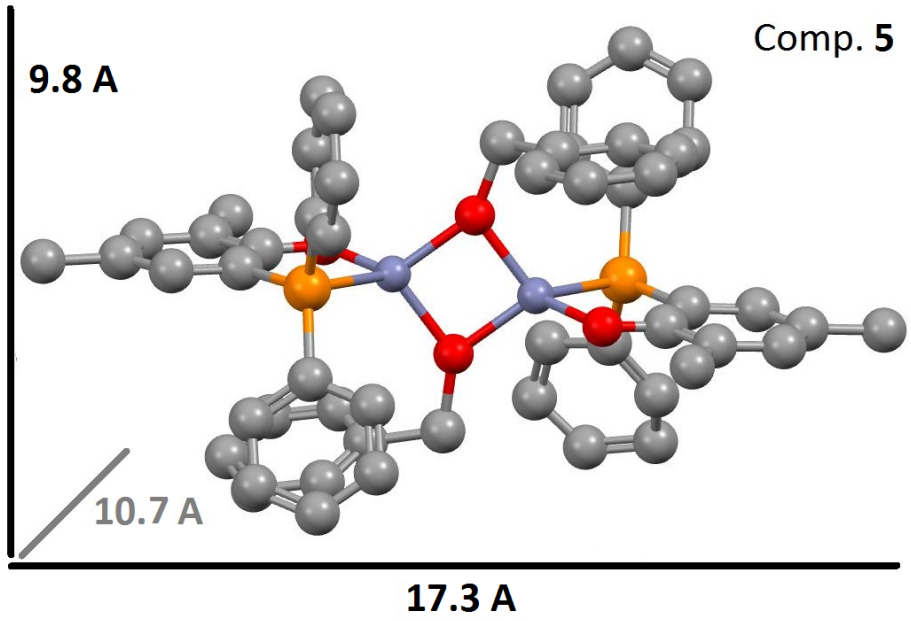


Figure S16. Geometrical parameters (L = 17.3, l = 10.7; H = 9.8 Å) used for the volume estimation of a model compound of species **5** (optimized geometry with Chem3D using the MM2 method, see Fig. S14). An ellipsoidal model [V = (4/3)π(L x l x H)] was used for volume calculation. V = 4/3 π [(17.3/2) x (10.4/2) x (9.8/2)] = 923 $Å^3$.

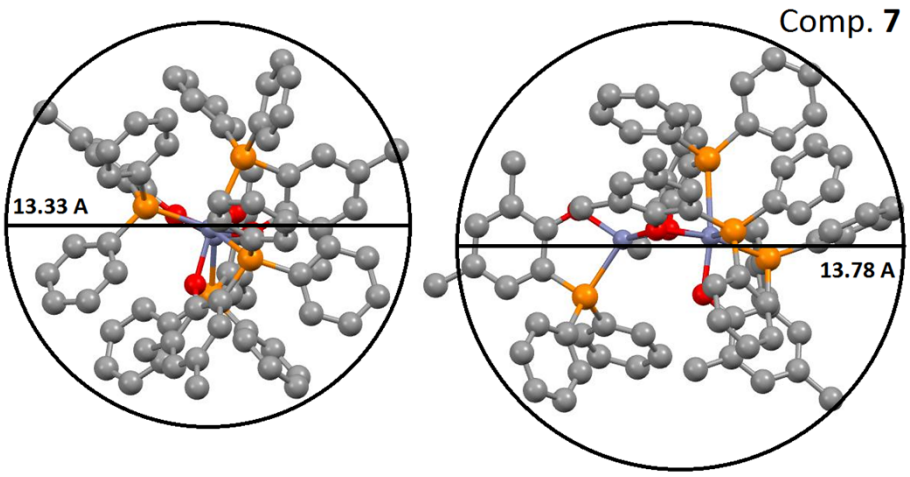


Figure S17. Geometrical parameters used for the estimation used for the volume estimation of species **7** based on its solid state structure. A spherical model was used for volume calculation. Note: an average of the two diameters (along two different axis) was done. $V_{X\text{-ray}}$ = (4/3)π{[(13.33+13.78)/2]/2}^{3} = 1303 $Å^3$.

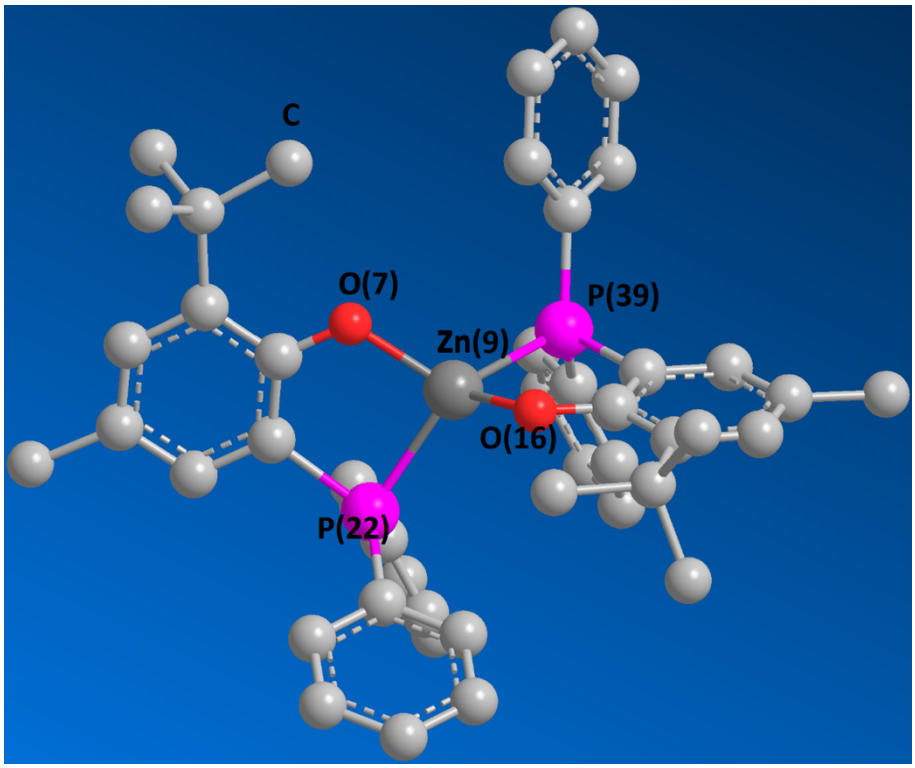


Figure S18. Optimized molecular geometry for complex **8** using Chem3D using the MM2 method. For a listing of MM2 parameters, see page 38.

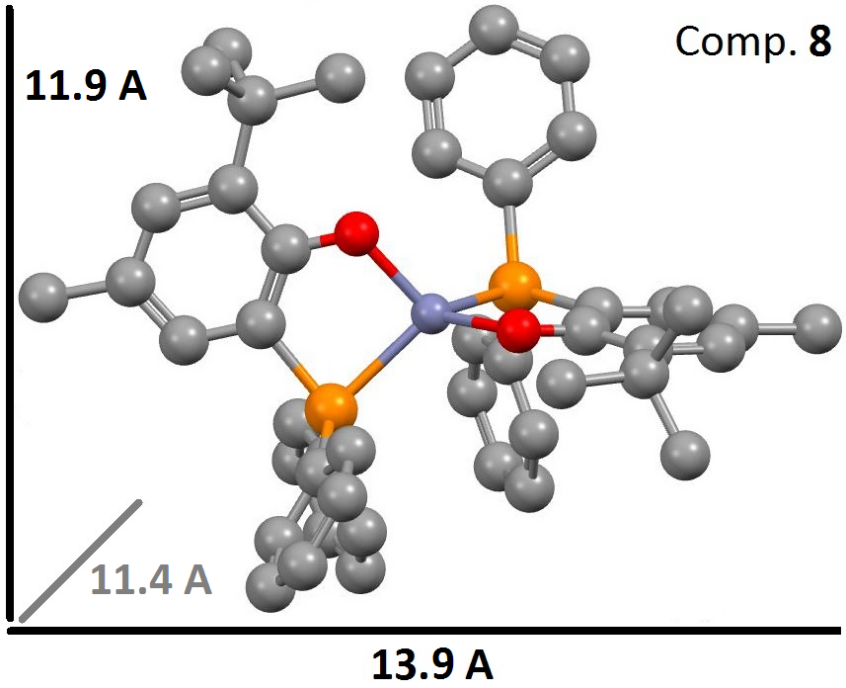
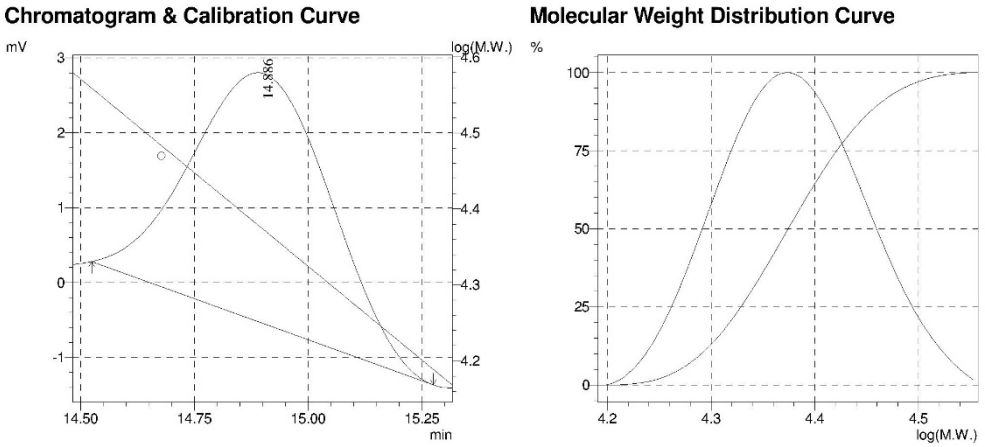


Figure S19. Geometrical parameters (L = 13.9, l = 11.4; H = 11.9 Å) used for the volume estimation of a model compound of species **8** (optimized geometry in the gas phase with Chem3D using the MM2 method, see Fig. S17). An ellipsoidal model [V = (4/3)π(L x l x H)] was used for volume calculation. V = 4/3 π [(13.9/2) x (11.9/2) x (11.4/2)] = 987 $Å^3$.



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	14.525	14.525	36232	279
Top	14.886	14.886	24032	3318
End	15.275	15.275	15443	-1369

Area : 69982
Area% : 100.0000

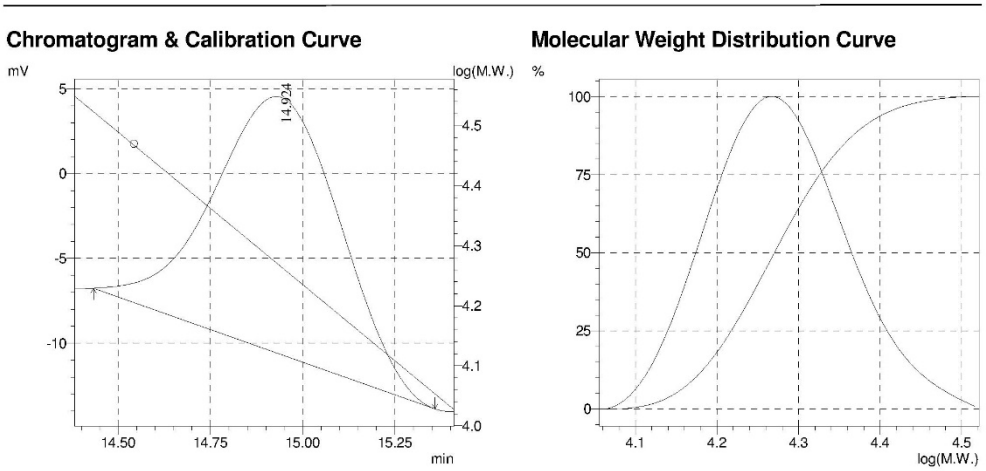
[Average Molecular Weight]

Number Average Molecular Weight(Mn)	23596
Weight Average Molecular Weight(Mw)	24127
Z Average Molecular Weight(Mz)	24674
Z+1 Average Molecular Weight(Mz1)	25230
Mw/Mn	1.02251
Mv/Mn	1.01936
Mz/Mw	1.02266

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	23596
Weight Average Molecular Weight(Mw)	24127
Z Average Molecular Weight(Mz)	24674
Z+1 Average Molecular Weight(Mz1)	25230
Mw/Mn	1.02251
Mv/Mn	1.01936
Mz/Mw	1.02266

Figure S20. SEC traces of isolated PLA prepared *via* ROP of *rac*-lactide with complex **5**. Conditions: 100 equiv. *rac*-LA, room temp., CH_2Cl_2, 97% conversion, 120 min. (Table 1 – Run 1 in the main text)



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	14.433	14.433	33347	-6759
Top	14.924	14.924	18788	15081
End	15.358	15.358	11310	-13881

Area : 359769
Area% : 100.0000

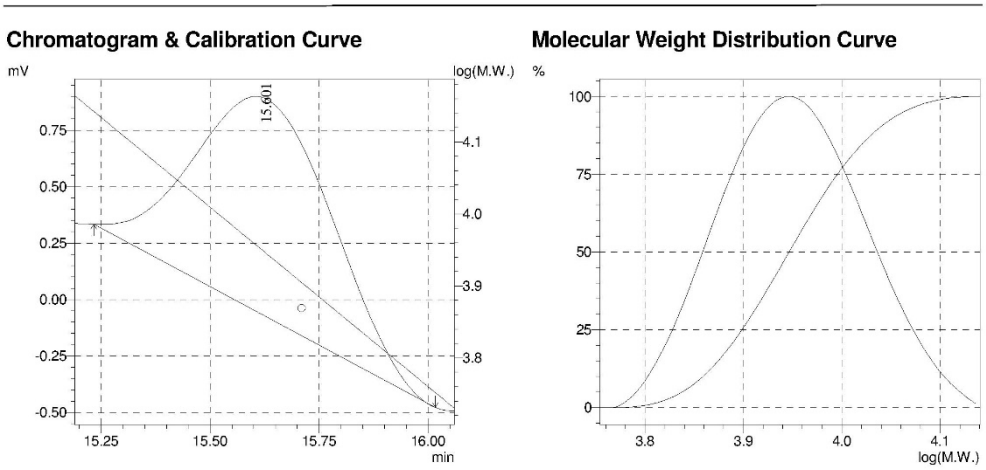
[Average Molecular Weight]

Number Average Molecular Weight(Mn)	18566
Weight Average Molecular Weight(Mw)	19180
Z Average Molecular Weight(Mz)	19836
Z+1 Average Molecular Weight(Mz1)	20530
Mw/Mn	1.03305
Mv/Mn	1.02834
Mz/Mw	1.03421

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	18566
Weight Average Molecular Weight(Mw)	19180
Z Average Molecular Weight(Mz)	19836
Z+1 Average Molecular Weight(Mz1)	20530
Mw/Mn	1.03305
Mv/Mn	1.02834
Mz/Mw	1.03421

Figure S21. SEC traces of isolated PCL prepared *via* ROP of ε-caprolactone with complex **5**. Conditions: 100 equiv. ε-CL, room temp., CH_2Cl_2, 99% conversion, 120 min. (Table 1 – Run 6 in the main text)



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	15.233	15.233	13879	334
Top	15.601	15.601	9098	947
End	16.017	16.017	5647	-478

Area : 21013
Area% : 100.0000

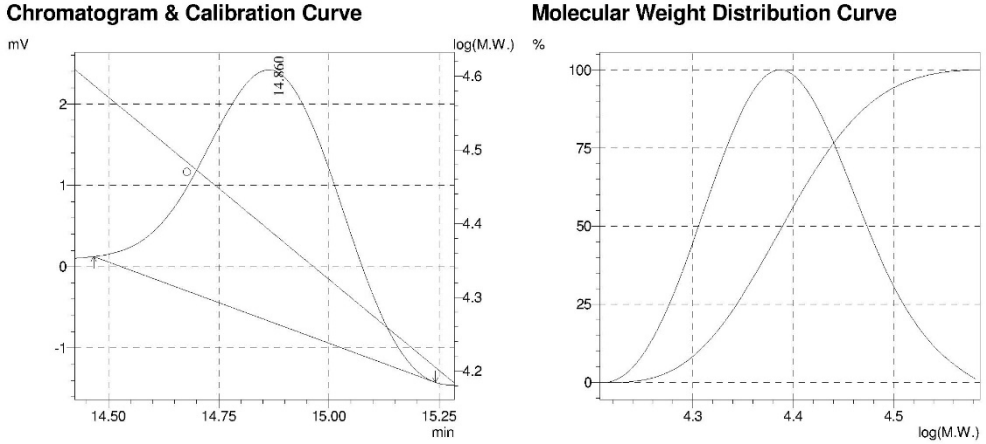
[Average Molecular Weight]

Number Average Molecular Weight(Mn)	10563
Weight Average Molecular Weight(Mw)	11938
Z Average Molecular Weight(Mz)	13810
Z+1 Average Molecular Weight(Mz1)	16062
Mw/Mn	1.13016
Mv/Mn	1.10889
Mz/Mw	1.15684

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	10563
Weight Average Molecular Weight(Mw)	11938
Z Average Molecular Weight(Mz)	13810
Z+1 Average Molecular Weight(Mz1)	16062
Mw/Mn	1.13016
Mv/Mn	1.10889
Mz/Mw	1.15684

Figure S22. SEC traces of isolated PTMC prepared *via* ROP of trimethylene carbonate with complex **5**. Conditions: 100 equiv. TMC, room temp., CH_2Cl_2, 87% conversion, 120 min. (Table 1 – Run 9 in the main text)



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	14.467	14.467	38717	125
Top	14.860	14.860	24762	3082
End	15.242	15.242	16039	-1424

Area : 65327
Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	24458
Weight Average Molecular Weight(Mw)	25029
Z Average Molecular Weight(Mz)	25623
Z+1 Average Molecular Weight(Mz1)	26235
Mw/Mn	1.02332
Mv/Mn	1.02004
Mz/Mw	1.02373

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	24458
Weight Average Molecular Weight(Mw)	25029
Z Average Molecular Weight(Mz)	25623
Z+1 Average Molecular Weight(Mz1)	26235
Mw/Mn	1.02332
Mv/Mn	1.02004
Mz/Mw	1.02373

Figure S23. SEC traces of isolated PLA prepared *via* ROP of *rac*-lactide with complex **5**. Conditions: 500 equiv. *rac*-LA, 4 equiv. BnOH, room temp., CH_2Cl_2, 99% conversion, 450 min. (Table 1 – Run 3 in the main text).

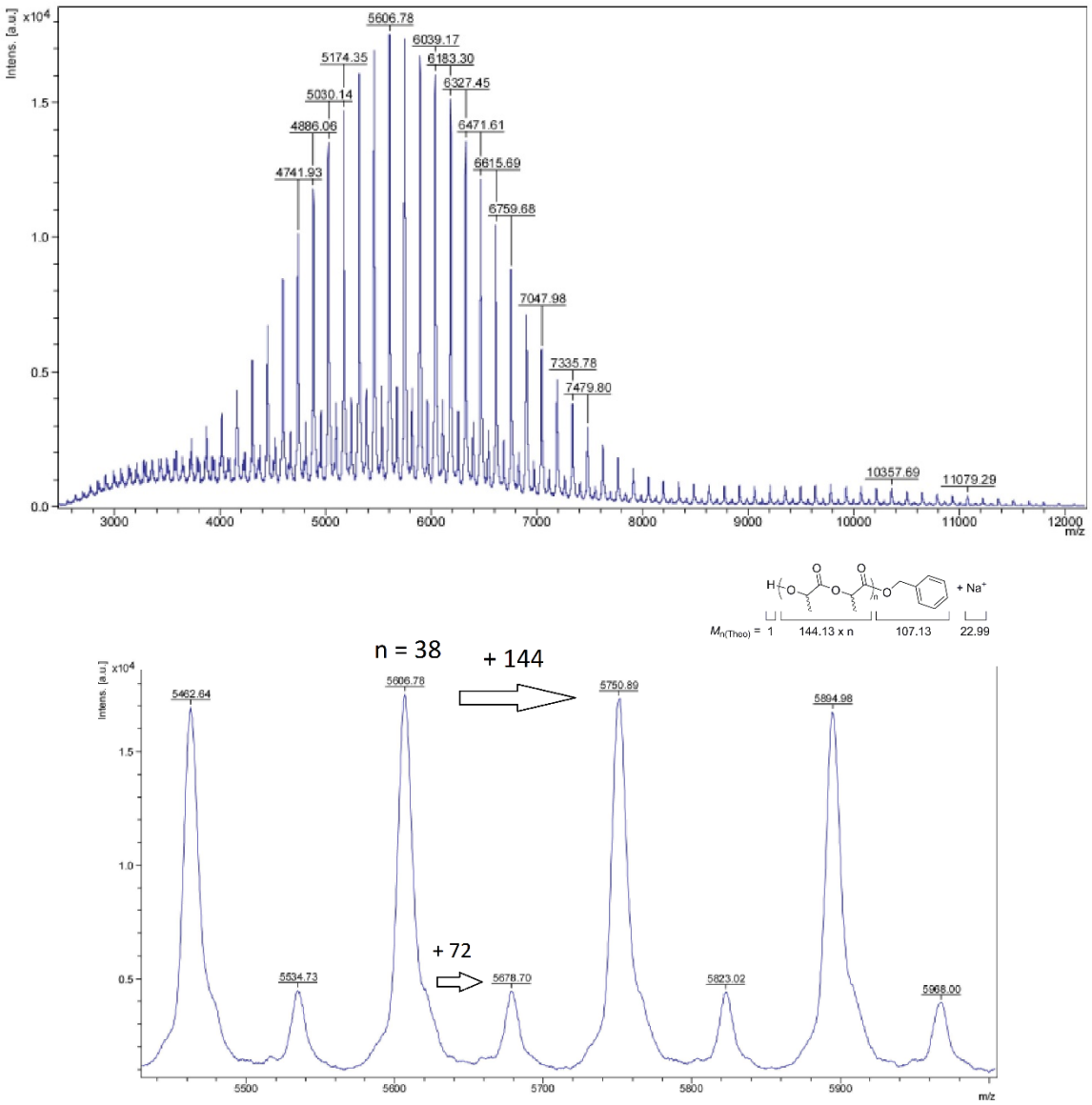


Figure S24. MALDI-TOF spectrum of a PLA sample prepared by ROP of *rac*-LA initiated by complex **5** (top), and zoom in the region of the most intense peaks (bottom). Conditions: 100 equiv. *rac*-LA, $[LA]_0$ = 1 M, CH_2Cl_2, room temp., polymer isolated at 42% conversion.

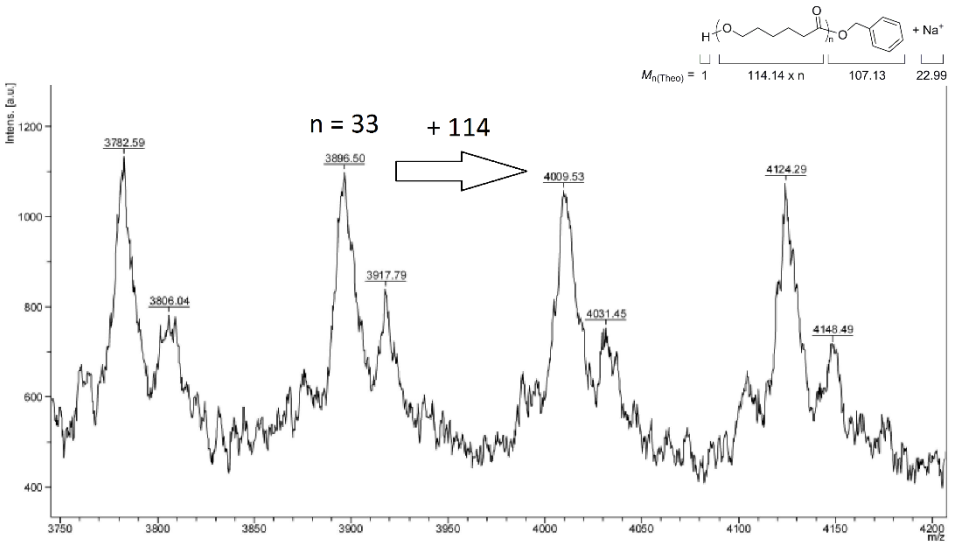


Figure S25. Zoom of the MALDI-TOF spectrum, in the region of the most intense peaks, of a PCL sample prepared by ROP of ε-CL initiated by complex **5**. Conditions: 100 equiv. ε-CL, $[CL]_0$ = 1 M, CH_2Cl_2, room temp., polymer isolated at 39% conversion. Note: the small peaks correspond to the K^+ ion instead of the Na^+ one.

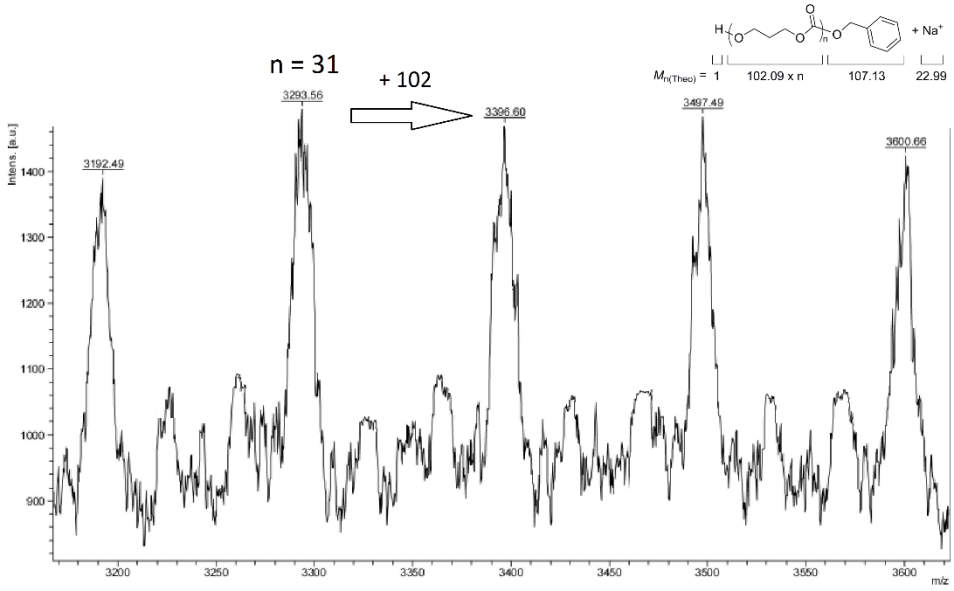


Figure S26. Zoom of the MALDI-TOF spectrum, in the region of the most intense peaks, of a PTMC sample prepared by ROP of TMC initiated by complex **5**. Conditions: 100 equiv. TMC, $[TMC]_0$ = 1 M, CH_2Cl_2, room temp., polymer isolated at 36% conversion.

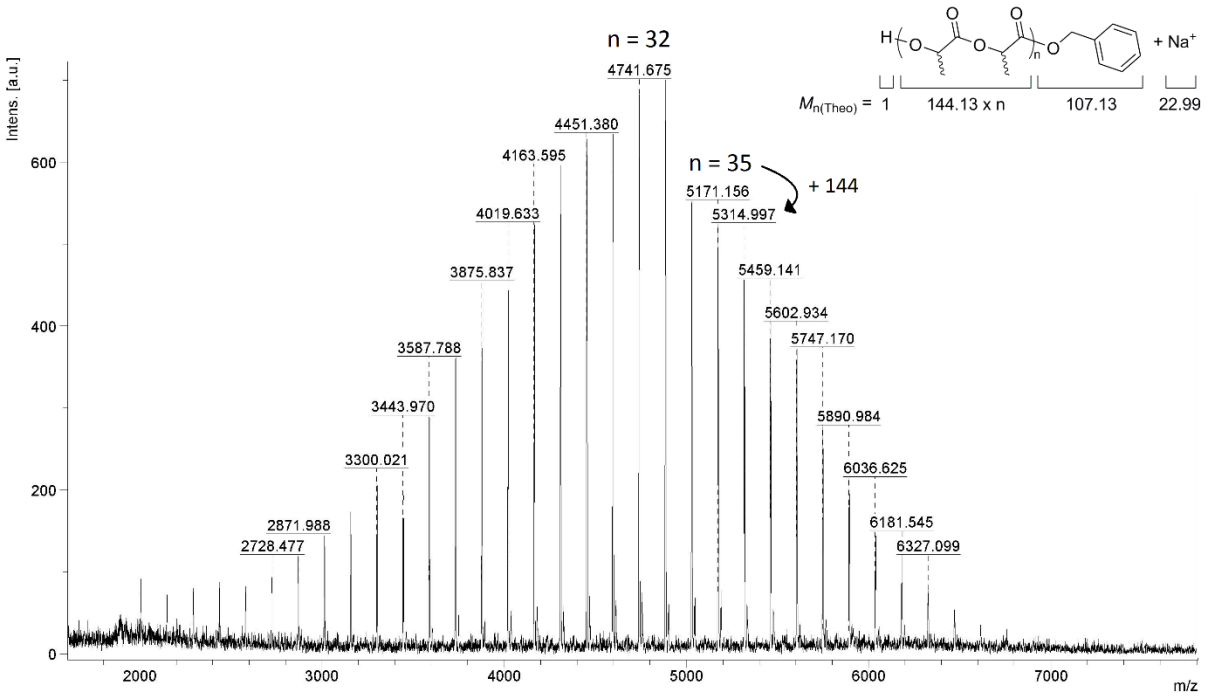


Figure S27. Zoom of the MALDI-TOF spectrum, in the region of the most intense peaks, of a PLA sample prepared by ROP of *rac*-LA initiated by complex **7** in the presence of BnOH. Conditions: 100 equiv. *rac*-LA, 1 equiv. BnOH, $[LA]_0$ = 1 M, CH_2Cl_2, room temp., polymer isolated at 51% conversion.

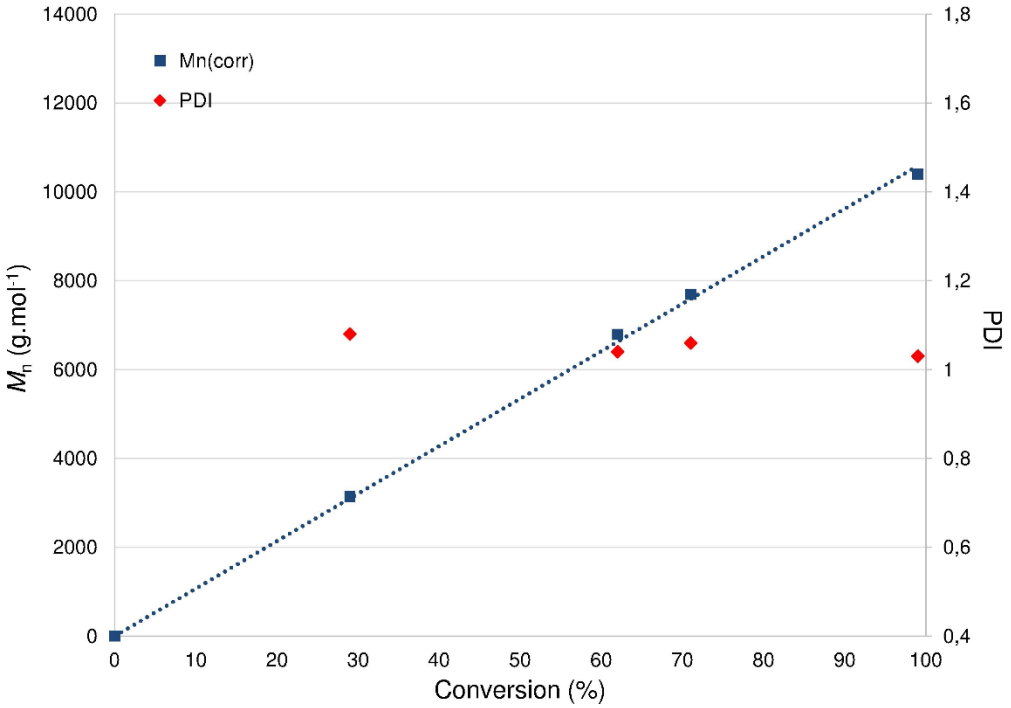


Figure S28. Linear dependence of M_n and PDI [M_w/M_n] values of PCL versus monomer (ε-CL) conversion with **5** as a catalyst. Reaction conditions: $[Zn]/[CL]_0$ = 100, $[CL]_0$ = 1 M, CH_2Cl_2, room temp.

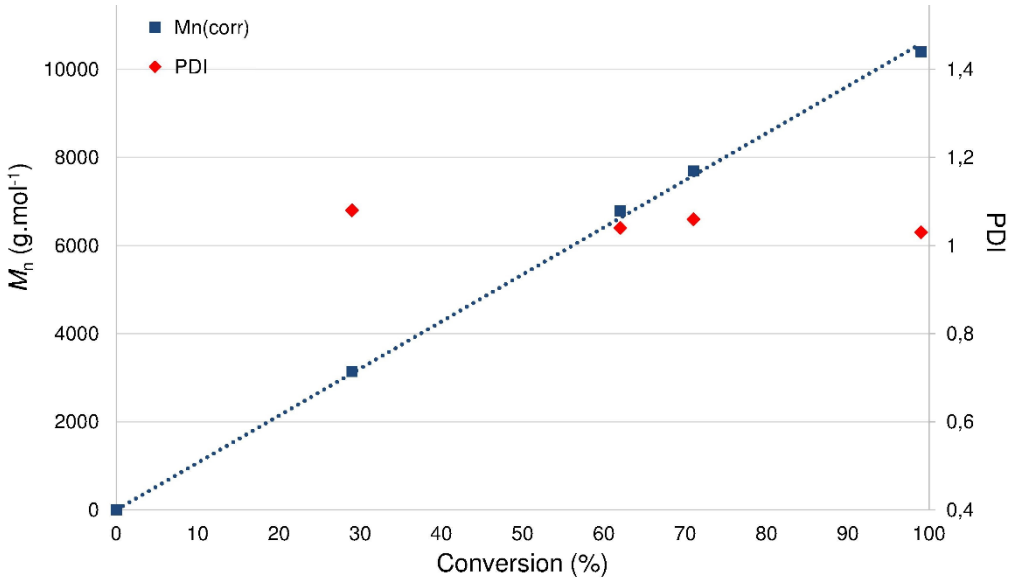


Figure S29. Linear dependence of M_n and nearly constant PDI [M_w/M_n] of PTMC versus monomer (TMC) conversion with **5** as a catalyst. Reaction conditions: $[Zn]/[TMC]_0 = 100$, $[TMC]_0 = 1$ M, CH_2Cl_2, room temp.

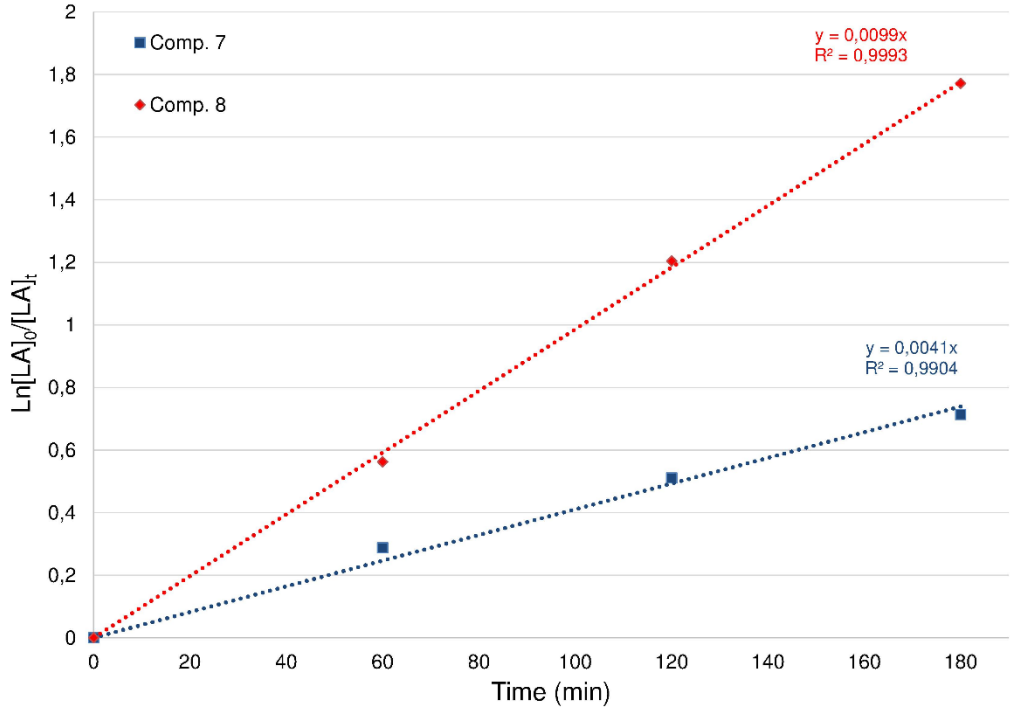
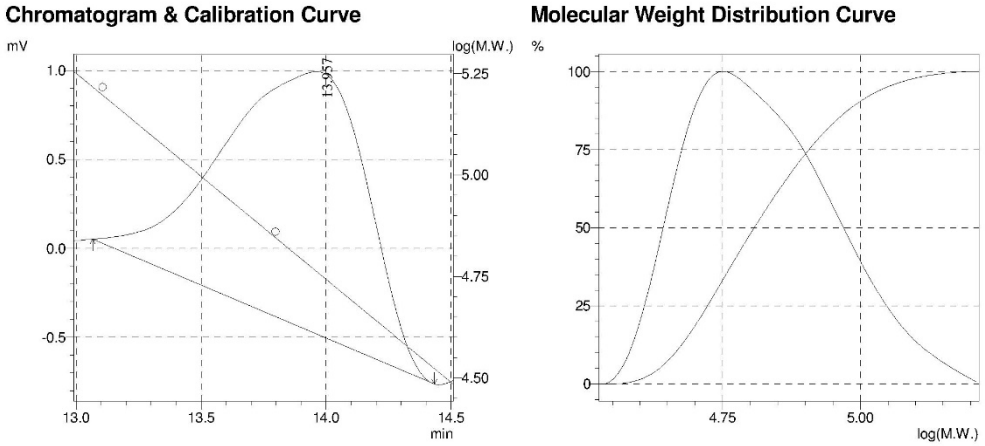


Figure S30. Semilogarithmic plots of *rac*-LA conversion versus time for complexes **7** (blue) and **8** (red) in the presence of BnOH. Reaction conditions: Zn/*rac*-LA/BnOH = 1/100/1, [*rac*-$LA]_0 = 1$ M, CH_2Cl_2, room temp.



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	13.067	13.067	164775	51
Top	13.957	13.957	58189	1472
End	14.433	14.433	33347	-762

Area : 58090
Area% : 100.0000

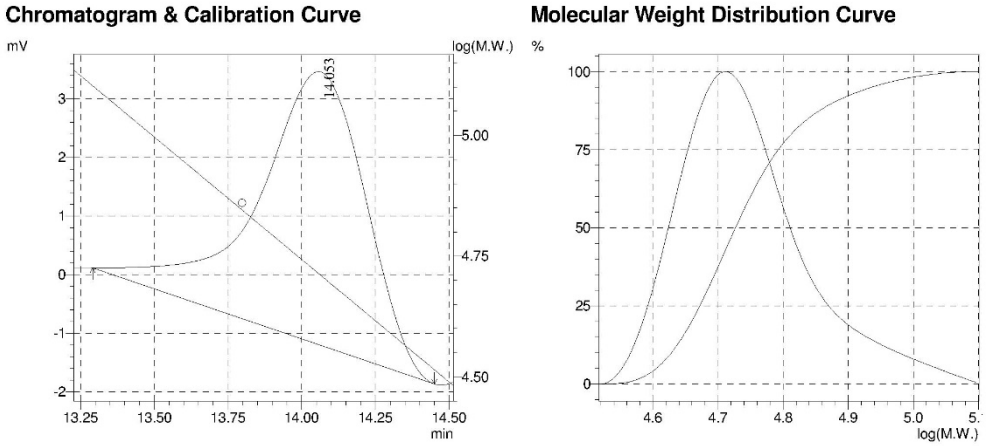
[Average Molecular Weight]

Number Average Molecular Weight(Mn)	63771
Weight Average Molecular Weight(Mw)	69399
Z Average Molecular Weight(Mz)	76134
Z+1 Average Molecular Weight(Mz1)	83770
Mw/Mn	1.08825
Mv/Mn	1.07487
Mz/Mw	1.09705

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	63771
Weight Average Molecular Weight(Mw)	69399
Z Average Molecular Weight(Mz)	76134
Z+1 Average Molecular Weight(Mz1)	83770
Mw/Mn	1.08825
Mv/Mn	1.07487
Mz/Mw	1.09705

Figure S31. SEC traces of isolated PTMC/PLLA block-copolymer prepared *via* sequential ROP of trimethylene carbonate and L-lactide by the complex **5**. Conditions: 100 equiv. TMC, 100 equiv. L-LA, room temp., CH_2Cl_2, 91% and 97% conversion, respectively, 6 h. (Table 2 – Run 1 in the main text).



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	13.292	13.292	126666	111
Top	14.053	14.053	51997	4652
End	14.450	14.450	32704	-1866

Area : 117442
Area% : 100.0000

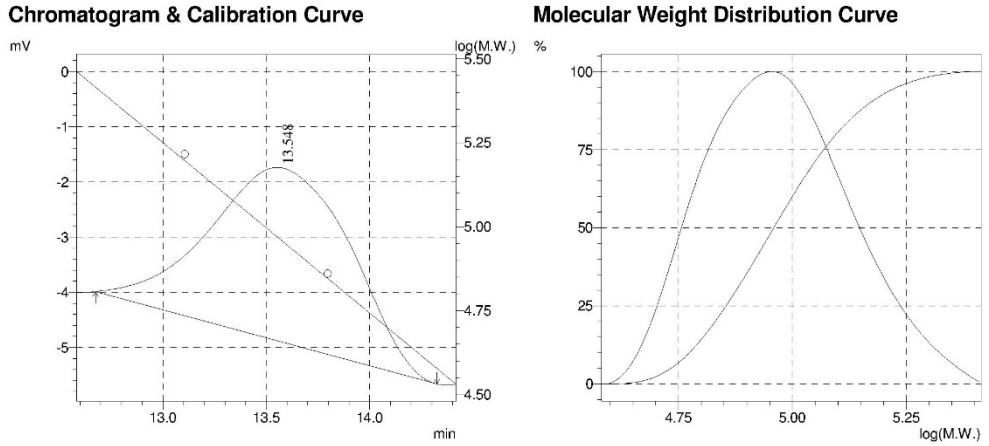
[Average Molecular Weight]

Number Average Molecular Weight(Mn)	54046
Weight Average Molecular Weight(Mw)	56873
Z Average Molecular Weight(Mz)	60421
Z+1 Average Molecular Weight(Mz1)	64802
Mw/Mn	1.05231
Mv/Mn	1.04419
Mz/Mw	1.06238

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	54046
Weight Average Molecular Weight(Mw)	56873
Z Average Molecular Weight(Mz)	60421
Z+1 Average Molecular Weight(Mz1)	64802
Mw/Mn	1.05231
Mv/Mn	1.04419
Mz/Mw	1.06238

Figure S32. SEC traces of isolated PCL/PLLA block-copolymer prepared *via* sequential ROP of ε-caprolactone and L-lactide by the complex **5**. Conditions: 100 equiv. ε-CL, 100 equiv. L-LA, room temp., CH_2Cl_2, 75% and 99% conversion, respectively, 6h30. (Table 2 – Run 2 in the main text).



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	12.675	12.675	260455	-3988
Top	13.548	13.548	93919	3135
End	14.325	14.325	37849	-5663

Area : 149402
Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	87789
Weight Average Molecular Weight(Mw)	98888
Z Average Molecular Weight(Mz)	112104
Z+1 Average Molecular Weight(Mz1)	126838
Mw/Mn	1.12643
Mv/Mn	1.10737
Mz/Mw	1.13364

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	87789
Weight Average Molecular Weight(Mw)	98888
Z Average Molecular Weight(Mz)	112104
Z+1 Average Molecular Weight(Mz1)	126838
Mw/Mn	1.12643
Mv/Mn	1.10737
Mz/Mw	1.13364

Figure S33. SEC traces of isolated PTMC/PCL/PLLA block-terpolymer prepared *via* sequential ROP of trimethylene carbonate, ε-caprolactone and L-lactide by the complex **5**. Conditions: 100 equiv. TMC, 100 equiv. ε-CL, 100 equiv. L-LA, room temp., CH_2Cl_2, 99%, 95% and 98% conversion, respectively, 9h30. (Table 2 – Run 5 in the main text).

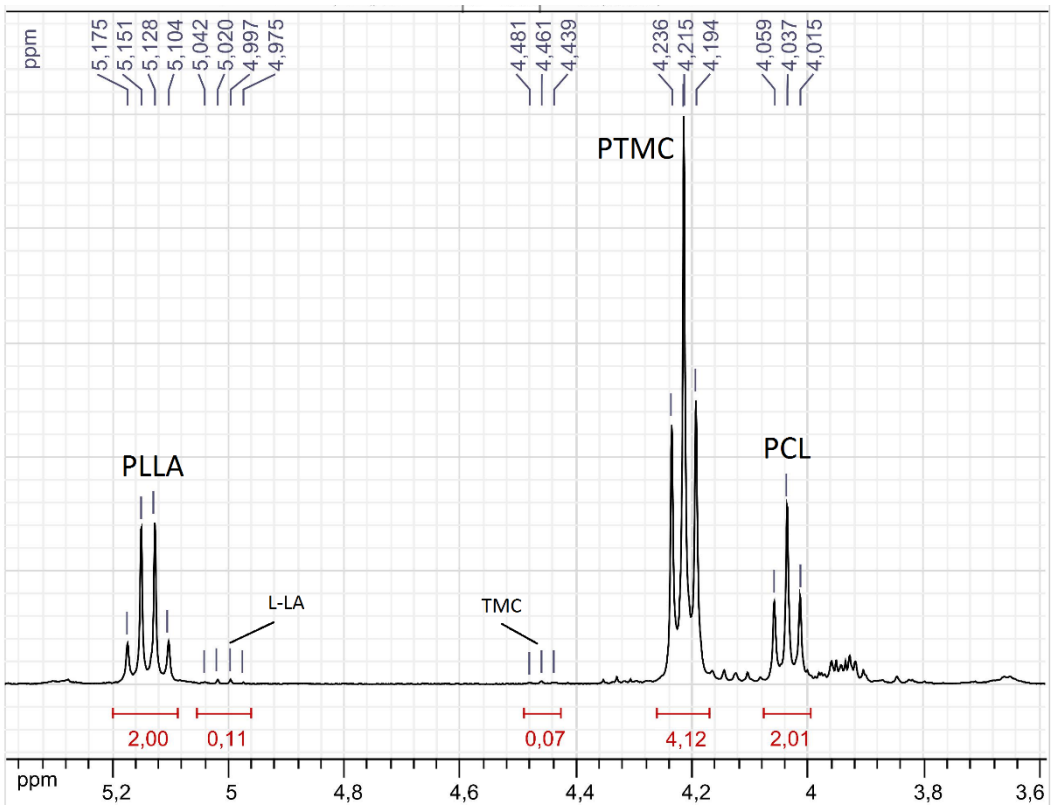


Figure S34. ^{1}H NMR spectrum of a TMC/*ε*-CL/L-LA block *ter*-polymerisation run *via* sequential ROP of trimethylene carbonate, *ε*-caprolactone and L-lactide by the complex **5** after 9 hours. Conditions: 100 equiv. TMC, 100 equiv. *ε*-CL, 100 equiv. L-LA, room temp., CH_2Cl_2, 99%, 95% and 95% conversion, respectively, 9 h.

Notes: 1) the conversions of TMC and *ε*-CL were precisely determined before addition of the next monomer, *i.e.* *ε*-CL and L-LA, respectively; 2) 3% L-LA were consumed between the acquisition of this spectrum and the stopping of the run and the analysis of the isolated polymer. (Table 2 – Run 7 in the main text).

MM2 parameters used for Complex 5

MM2 Constant Value Quality

Cubic stretch constant-2.000 4

Quartic stretch constant2.333 4

X-B,C,N,O-Y Stretch-Bend interaction force constant0.120 4

X-B,C,N,O-H Stretch-Bend interaction force constant0.090 4

X-Si,P-Y Stretch-Bend force constant0.200 4

X-Ga,Ge,As,Se,Br-Y Stretch-Bend force constant0.250 3

Sextic bending constant (10**8)7.000 4*

Dielectric constant for dipoles1.500 4

Cutoff distance for charge/charge interactions35.000 4

Cutoff distance for charge/dipole interactions25.000 4

Cutoff distance for dipole/dipole interactions18.000 4

Cutoff distance for van der Waals interactions10.000 4

MM2 c3dAtomRadius Eps Weight Reduct Lone Pairs Quality

2 1.940 0.044 12.000 0.000 0 4

1 1.900 0.044 12.000 0.000 0 4

41 1.740 0.050 15.995 0.000 1 3

25 2.180 0.168 30.974 0.000 0 4

303 2.268 0.200 63.929 0.000 0 1

6 1.740 0.050 15.995 0.000 2 4

5 1.500 0.047 1.008 0.915 0 4

Bond KS Bond Length Dipole Quality

2-2 9.600 1.337 0.000 4

2-5 4.600 1.100 0.000 4

2-25 2.910 1.828 1.040 4

2-41 10.000 1.225 0.950 3

1-2 4.400 1.497 0.300 4

1-5 4.600 1.113 0.000 4

20-41 4.600 0.600 -0.750 3

1-6 5.360 1.402 0.440 4

6-20 4.600 0.600 0.900 4

Angle KB XR2 XRH XH2 Quality

2-2-5 0.360 120.0 120.5 0.0 4

2-2-2 0.430 120.0 0.0 0.0 4

2-2-25 0.380 120.0 0.0 0.0 4

2-2-41 0.600 120.0 118.1 0.0 3

1-2-2 0.550 121.4 122.0 120.0 4

5-1-5 0.320 109.4 109.0 109.5 4

2-1-5 0.360 109.4 109.4 110.0 4

2-41-20 0.350 122.2 0.0 0.0 3

2-25-2 0.480 93.2 0.0 0.0 4

5-1-6 0.540 106.7 106.7 106.7 4

2-1-6 0.700 109.5 0.0 0.0 4

Atoms Force Constant Quality

2-2 0.050 4

2-5 0.050 4

2-25 0.500 3

2-41 0.050 3

1-2 0.050 4

0-0 0.050 1

20-41 0.050 3

Torsional V1 V2 V3 Quality

5-2-2-25 0.000 16.250 0.000 4

2-2-2-5 0.000 9.000 -1.060 4

2-2-2-25 0.000 16.250 0.000 4

2-2-2-2 -0.930 8.000 0.000 4

1-2-2-5 0.000 12.500 0.000 4

1-2-2-2 -0.270 10.000 0.000 4

0-0-0-0 0.000 10.000 0.000 1

2-2-2-41 0.000 15.000 0.000 3

2-2-25-2 0.000 0.000 0.330 4

1-2-2-41 0.000 15.000 0.000 2

2-2-41-20 0.000 0.000 0.250 3

2-2-1-5 0.000 0.000 -0.240 4

5-1-6-20 0.000 0.000 0.000 4

2-1-6-20 0.000 0.000 0.000 3

2-2-1-6 0.000 0.000 0.000 3

5-2-2-5 0.000 15.000 0.000 4

Torsional V1 V2 V3 Quality

0-0-0-0 0.000 0.000 0.000 1

PiAtom Electron Ionization Repulsion Quality

2 1 -11.160 11.134 4

41 2 -17.600 19.342 4

PiBond DForce DLength Quality

2-2 4.600 0.166 4

2-41 5.440 0.196 3

VDW Interaction Radius Eps Quality

1-5 3.340 0.046 4

Atoms DLength Quality

5-1-6 -0.002 4

Bond lengths and angles

Atom	Bond atom	Bond length (Å)	Angle atom	Angle (°)
C(2)	*C(1)*	*1.337*		
C(3)	*C(2)*	*1.337*	*C(1)*	*120.000*
C(4)	*C(3)*	*1.337*	*C(2)*	*119.999*
C(6)	*C(1)*	*1.337*	*C(2)*	*120.000*
O(9)	*C(3)*	*2.492*	*C(2)*	*126.851*
Zn(11)	*O(9)*	*1.830*	*C(3)*	*120.187*
P(10)	*C(2)*	*1.828*	*C(1)*	*128.998*
C(5)	*C(4)*	*1.337*	*C(3)*	*120.001*
O(12)	*Zn(11)*	*1.890*	*O(9)*	*120.000*
Zn(25)	*O(12)*	*1.949*	*Zn(11)*	*85.604*
O(26)	*Zn(11)*	*1.890*	*O(9)*	*120.000*
O(23)	*Zn(25)*	*1.890*	*O(12)*	*120.000*
C(17)	*O(23)*	*1.225*	*Zn(25)*	*104.000*
C(16)	*C(17)*	*1.388*	*O(23)*	*120.529*
C(18)	*C(17)*	*1.337*	*C(16)*	*119.998*
C(15)	*C(16)*	*1.343*	*C(17)*	*115.026*
P(24)	*Zn(25)*	*2.344*	*O(12)*	*120.000*
C(19)	*C(18)*	*1.337*	*C(17)*	*120.000*
C(20)	*C(15)*	*1.337*	*C(16)*	*120.000*
C(29)	*P(10)*	*2.022*	*C(2)*	*98.742*
C(39)	*P(10)*	*1.856*	*C(2)*	*109.500*
C(51)	*P(24)*	*1.828*	*C(16)*	*148.747*
C(52)	*P(24)*	*1.856*	*C(16)*	*109.500*
C(31)	*C(29)*	*1.395*	*P(10)*	*119.999*
C(35)	*C(29)*	*1.395*	*P(10)*	*119.999*
C(32)	*C(31)*	*1.395*	*C(29)*	*119.997*
C(33)	*C(32)*	*1.395*	*C(31)*	*120.000*

C(34)	*C(35)*	*1.395*	*C(29)*	*120.000*
C(53)	*C(51)*	*1.395*	*P(24)*	*119.999*
C(57)	*C(51)*	*1.395*	*P(24)*	*119.999*
C(54)	*C(53)*	*1.395*	*C(51)*	*119.997*
C(55)	*C(54)*	*1.395*	*C(53)*	*120.000*
C(56)	*C(57)*	*1.395*	*C(51)*	*120.000*
C(60)	*C(52)*	*1.337*	*P(24)*	*120.000*
C(112)	*C(52)*	*2.083*	*P(24)*	*122.574*
C(61)	*C(60)*	*1.497*	*C(52)*	*122.000*
C(88)	*C(61)*	*1.337*	*C(60)*	*120.000*
C(110)	*C(112)*	*1.337*	*C(52)*	*107.911*
C(89)	*C(39)*	*1.337*	*P(10)*	*120.000*
C(116)	*C(39)*	*5.333*	*P(10)*	*78.401*
C(91)	*C(89)*	*1.497*	*C(39)*	*122.000*
C(92)	*C(91)*	*1.337*	*C(89)*	*120.000*
C(114)	*C(116)*	*1.337*	*C(39)*	*66.710*
C(7)	*C(6)*	*1.497*	*C(1)*	*120.000*
C(8)	*C(4)*	*1.497*	*C(3)*	*120.000*
C(21)	*C(20)*	*1.497*	*C(15)*	*121.782*
C(22)	*C(18)*	*1.497*	*C(17)*	*120.000*
C(13)	*O(12)*	*1.637*	*Zn(11)*	*140.016*
C(14)	*C(13)*	*1.497*	*O(12)*	*109.500*
C(41)	*C(14)*	*1.395*	*C(13)*	*119.998*
C(45)	*C(14)*	*1.395*	*C(13)*	*119.998*
C(42)	*C(41)*	*1.395*	*C(14)*	*119.997*
C(43)	*C(42)*	*1.395*	*C(41)*	*120.001*
C(44)	*C(45)*	*1.395*	*C(14)*	*119.999*
C(27)	*O(26)*	*1.402*	*Zn(11)*	*131.266*
C(28)	*C(27)*	*1.497*	*O(26)*	*109.500*
C(46)	*C(28)*	*1.395*	*C(27)*	*119.998*

C(50)	*C(28)*	*1.395*	*C(27)*	*119.999*
C(47)	*C(46)*	*1.395*	*C(28)*	*119.997*
C(48)	*C(47)*	*1.395*	*C(46)*	*120.000*
C(49)	*C(50)*	*1.395*	*C(28)*	*120.000*
Lp(59)	*O(9)*	*0.600*	*C(3)*	*114.698*
Lp(108)	*O(12)*	*0.600*	*Zn(11)*	*135.000*
Lp(119)	*O(12)*	*0.600*	*Zn(11)*	*100.810*
Lp(120)	*O(23)*	*0.600*	*C(17)*	*110.797*
Lp(121)	*O(26)*	*0.684*	*Zn(11)*	*84.603*
Lp(122)	*O(26)*	*0.706*	*Zn(11)*	*96.778*
H(40)	*C(91)*	*1.127*	*C(89)*	*118.805*
H(58)	*C(61)*	*1.087*	*C(60)*	*112.712*
H(62)	*C(60)*	*1.100*	*C(52)*	*119.949*
H(64)	*C(5)*	*1.100*	*C(4)*	*120.000*
H(73)	*C(15)*	*1.100*	*C(16)*	*120.000*
H(74)	*C(19)*	*1.100*	*C(18)*	*121.782*
H(83)	*C(31)*	*1.100*	*C(29)*	*120.001*
H(84)	*C(32)*	*1.100*	*C(31)*	*120.000*
H(85)	*C(33)*	*1.100*	*C(32)*	*119.998*
H(86)	*C(34)*	*1.100*	*C(33)*	*120.001*
H(87)	*C(35)*	*1.100*	*C(29)*	*120.000*
H(90)	*C(89)*	*1.123*	*C(39)*	*119.348*
H(93)	*C(41)*	*1.100*	*C(14)*	*120.002*
H(94)	*C(42)*	*1.100*	*C(41)*	*120.000*
H(95)	*C(43)*	*1.100*	*C(42)*	*119.999*
H(96)	*C(44)*	*1.100*	*C(43)*	*120.001*
H(97)	*C(45)*	*1.100*	*C(14)*	*120.000*
H(98)	*C(46)*	*1.100*	*C(28)*	*120.002*
H(99)	*C(47)*	*1.100*	*C(46)*	*120.000*
H(100)	*C(48)*	*1.100*	*C(47)*	*119.998*

H(101)	*C(49)*	*1.100*	*C(48)*	*120.002*
H(102)	*C(50)*	*1.100*	*C(28)*	*120.000*
H(103)	*C(53)*	*1.100*	*C(51)*	*120.002*
H(104)	*C(54)*	*1.100*	*C(53)*	*120.000*
H(105)	*C(55)*	*1.100*	*C(54)*	*119.998*
H(106)	*C(56)*	*1.100*	*C(55)*	*120.002*
H(107)	*C(57)*	*1.100*	*C(51)*	*120.000*
H(109)	*C(88)*	*1.106*	*C(61)*	*121.248*
H(111)	*C(110)*	*1.113*	*C(88)*	*119.999*
H(113)	*C(114)*	*1.113*	*C(92)*	*119.999*
H(115)	*C(92)*	*1.100*	*C(91)*	*119.899*
H(117)	*C(112)*	*1.100*	*C(52)*	*126.043*
H(118)	*C(116)*	*1.100*	*C(39)*	*146.642*
H(63)	*C(1)*	*1.100*	*C(2)*	*120.000*
H(71)	*C(13)*	*1.113*	*O(12)*	*109.442*
H(72)	*C(13)*	*1.113*	*O(12)*	*109.461*
H(81)	*C(27)*	*1.113*	*O(26)*	*109.442*
H(82)	*C(27)*	*1.113*	*O(26)*	*109.462*
H(65)	*C(7)*	*1.113*	*C(6)*	*109.500*
H(66)	*C(7)*	*1.111*	*C(6)*	*111.973*
H(67)	*C(7)*	*1.111*	*C(6)*	*112.318*
H(68)	*C(8)*	*1.113*	*C(4)*	*109.500*
H(69)	*C(8)*	*1.121*	*C(4)*	*109.159*
H(70)	*C(8)*	*1.116*	*C(4)*	*111.294*
H(75)	*C(21)*	*1.113*	*C(20)*	*109.500*
H(76)	*C(21)*	*1.105*	*C(20)*	*110.429*
H(77)	*C(21)*	*1.115*	*C(20)*	*99.851*
H(78)	*C(22)*	*1.113*	*C(18)*	*109.500*
H(79)	*C(22)*	*1.078*	*C(18)*	*129.277*
H(80)	*C(22)*	*1.131*	*C(18)*	*125.000*

MM2 parameters used for complex 7

MM2 Constant Value Quality

Cubic stretch constant-2.000 4

Quartic stretch constant2.333 4

X-B,C,N,O-Y Stretch-Bend interaction force constant0.120 4

X-B,C,N,O-H Stretch-Bend interaction force constant0.090 4

X-Si,P-Y Stretch-Bend force constant0.200 4

X-Ga,Ge,As,Se,Br-Y Stretch-Bend force constant0.250 3

Sextic bending constant (* 10**8)7.000 4

Dielectric constant for dipoles1.500 4

Cutoff distance for charge/charge interactions35.000 4

Cutoff distance for charge/dipole interactions25.000 4

Cutoff distance for dipole/dipole interactions18.000 4

Cutoff distance for van der Waals interactions10.000 4

MM2 c3d	AtomRadius	Eps	Weight	Reduct	Lone Pairs	Quality
2	1.940	0.044	12.000	0.000	0	4
41	1.740	0.050	15.995	0.000	1	3
1	1.900	0.044	12.000	0.000	0	4
303	2.268	0.200	63.929	0.000	0	1
25	2.180	0.168	30.974	0.000	0	4
5	1.500	0.047	1.008	0.915	0	4

Bond	KS	Bond Length	Dipole	Quality
2-2	9.600	1.337	0.000	4
1-2	4.400	1.497	0.300	4
2-5	4.600	1.100	0.000	4
2-25	2.910	1.828	1.040	4

2-41 10.000 1.225 0.950 3

20-41 4.600 0.600 -0.750 3

1-5 4.600 1.113 0.000 4

1-1 4.400 1.523 0.000 4

Angle KB XR2 XRH XH2 Quality

1-2-2 0.550 121.4 122.0 120.0 4

2-2-2 0.430 120.0 0.0 0.0 4

2-2-5 0.360 120.0 120.5 0.0 4

2-2-25 0.380 120.0 0.0 0.0 4

2-2-41 0.600 120.0 118.1 0.0 3

2-41-20 0.350 122.2 0.0 0.0 3

5-1-5 0.320 109.4 109.0 109.5 4

2-1-5 0.360 109.4 109.4 110.0 4

1-1-1 0.450 109.5 109.5 109.5 4

1-1-2 0.450 109.5 109.5 109.5 4

1-1-5 0.360 109.4 109.4 110.0 4

2-25-2 0.480 93.2 0.0 0.0 4

Atoms Force Constant Quality

2-2 0.050 4

1-2 0.050 4

2-5 0.050 4

2-25 0.500 3

2-41 0.050 3

0-0 0.050 1

20-41 0.050 3

Torsional	V1	V2	V3	Quality
1-2-2-5	0.000	12.500	0.000	4
1-2-2-2	-0.270	10.000	0.000	4
2-2-2-5	0.000	9.000	-1.060	4
2-2-2-2	-0.930	8.000	0.000	4
1-2-2-41	0.000	15.000	0.000	2
2-2-2-41	0.000	15.000	0.000	3
1-1-2-2	-0.440	0.240	0.060	4
2-2-1-5	0.000	0.000	-0.240	4
5-2-2-25	0.000	16.250	0.000	4
2-2-2-25	0.000	16.250	0.000	4
0-0-0-0	0.000	10.000	0.000	1
2-2-25-2	0.000	0.000	0.330	4
2-2-41-20	0.000	0.000	0.250	3
1-1-1-5	0.000	0.000	0.267	4
2-1-1-5	0.000	0.000	0.500	4
5-2-2-5	0.000	15.000	0.000	4

PiAtom	Electron	Ionization	Repulsion	Quality
2	1	-11.160	11.134	4
41	2	-17.600	19.342	4

PiBond	DForce	DLength	Quality
2-2	4.600	0.166	4
2-41	5.440	0.196	3

VDW Interaction	Radius	Eps	Quality
1-5	3.340	0.046	4

Bond lengths and angles

Atom	Bond atom	Bond length (Å)	Angle atom	Angle (°)
C(2)	C(1)	1.349		
C(3)	C(2)	1.341	C(1)	124.249
H(52)	C(2)	1.101	C(1)	120.303
C(4)	C(3)	1.339	C(2)	117.704
C(8)	C(3)	1.510	C(2)	120.652
C(5)	C(4)	1.341	C(3)	120.112
H(53)	C(4)	1.102	C(3)	119.255
C(6)	C(1)	1.356	C(2)	117.150
O(7)	C(6)	1.237	C(1)	118.641
C(18)	C(1)	1.548	C(2)	116.985
P(22)	C(5)	1.873	C(4)	116.123
C(23)	P(22)	1.824	C(5)	111.780
Zn(9)	O(7)	1.895	C(6)	117.503
O(16)	Zn(9)	1.896	O(7)	118.837
C(29)	P(22)	1.827	C(5)	114.955
P(39)	Zn(9)	2.345	O(7)	119.682
C(14)	P(39)	1.874	Zn(9)	85.539
C(40)	P(39)	1.827	C(14)	109.911
C(46)	P(39)	1.825	C(14)	113.217
C(13)	C(14)	1.341	P(39)	116.500
C(15)	C(14)	1.359	C(13)	121.694
C(10)	C(15)	1.355	C(14)	119.258

C(11)	C(10)	1.349	C(15)	117.094
C(35)	C(10)	1.547	C(11)	117.326
C(12)	C(13)	1.339	C(14)	119.918
C(17)	C(12)	1.510	C(11)	120.637
H(57)	C(11)	1.101	C(10)	120.182
H(58)	C(13)	1.102	C(12)	119.555
C(24)	C(23)	1.344	P(22)	120.800
C(28)	C(23)	1.344	P(22)	119.984
C(25)	C(24)	1.342	C(23)	120.425
H(71)	C(24)	1.102	C(23)	120.879
C(26)	C(25)	1.342	C(24)	120.090
H(72)	C(25)	1.103	C(24)	120.023
C(27)	C(28)	1.342	C(23)	120.443
H(73)	C(26)	1.103	C(25)	120.133
H(74)	C(27)	1.103	C(26)	119.918
H(75)	C(28)	1.103	C(23)	120.837
C(30)	C(29)	1.344	P(22)	121.470
C(34)	C(29)	1.345	P(22)	119.316
C(31)	C(30)	1.342	C(29)	120.403
H(76)	C(30)	1.102	C(29)	120.923
C(32)	C(31)	1.342	C(30)	120.123
H(77)	C(31)	1.103	C(30)	119.996
C(33)	C(34)	1.342	C(29)	120.465
H(78)	C(32)	1.103	C(31)	120.140
H(79)	C(33)	1.103	C(32)	119.884
H(80)	C(34)	1.103	C(29)	120.732
C(41)	C(40)	1.344	P(39)	120.708

C(45)	C(40)	1.344	P(39)	120.242
C(42)	C(41)	1.342	C(40)	120.612
H(90)	C(41)	1.102	C(40)	120.907
C(43)	C(42)	1.342	C(41)	120.019
H(91)	C(42)	1.103	C(41)	119.985
C(44)	C(45)	1.342	C(40)	120.512
H(92)	C(43)	1.103	C(42)	120.126
H(93)	C(44)	1.103	C(43)	119.893
H(94)	C(45)	1.103	C(40)	120.752
C(47)	C(46)	1.344	P(39)	120.260
C(51)	C(46)	1.344	P(39)	120.512
C(48)	C(47)	1.342	C(46)	120.435
H(95)	C(47)	1.103	C(46)	120.725
C(49)	C(48)	1.342	C(47)	120.064
H(96)	C(48)	1.103	C(47)	120.023
C(50)	C(51)	1.342	C(46)	120.429
H(97)	C(49)	1.103	C(48)	120.116
H(98)	C(50)	1.103	C(49)	119.909
H(99)	C(51)	1.102	C(46)	120.891
C(19)	C(18)	1.546	C(1)	108.651
C(20)	C(18)	1.550	C(1)	109.267
C(21)	C(18)	1.548	C(1)	117.756
C(36)	C(35)	1.549	C(10)	108.493
C(37)	C(35)	1.548	C(10)	117.679
C(38)	C(35)	1.547	C(10)	109.230
H(54)	C(8)	1.114	C(3)	110.374
H(55)	C(8)	1.113	C(3)	112.698

H(56)	C(8)	1.114	C(3)	110.209
H(59)	C(17)	1.114	C(12)	110.522
H(60)	C(17)	1.114	C(12)	110.094
H(61)	C(17)	1.113	C(12)	112.659
H(62)	C(19)	1.114	C(18)	111.518
H(63)	C(19)	1.112	C(18)	113.027
H(64)	C(19)	1.114	C(18)	110.711
H(65)	C(20)	1.111	C(18)	113.869
H(66)	C(20)	1.113	C(18)	111.750
H(67)	C(20)	1.114	C(18)	110.674
H(68)	C(21)	1.113	C(18)	111.604
H(69)	C(21)	1.113	C(18)	112.736
H(70)	C(21)	1.113	C(18)	111.644
H(81)	C(36)	1.111	C(35)	113.419
H(82)	C(36)	1.113	C(35)	111.756
H(83)	C(36)	1.114	C(35)	110.633
H(84)	C(37)	1.113	C(35)	112.332
H(85)	C(37)	1.113	C(35)	112.328
H(86)	C(37)	1.114	C(35)	111.437
H(87)	C(38)	1.111	C(35)	113.403
H(88)	C(38)	1.114	C(35)	110.689
H(89)	C(38)	1.113	C(35)	111.541
Lp(100)	O(7)	0.594	C(6)	127.634
Lp(101)	O(16)	0.596	Zn(9)	111.744