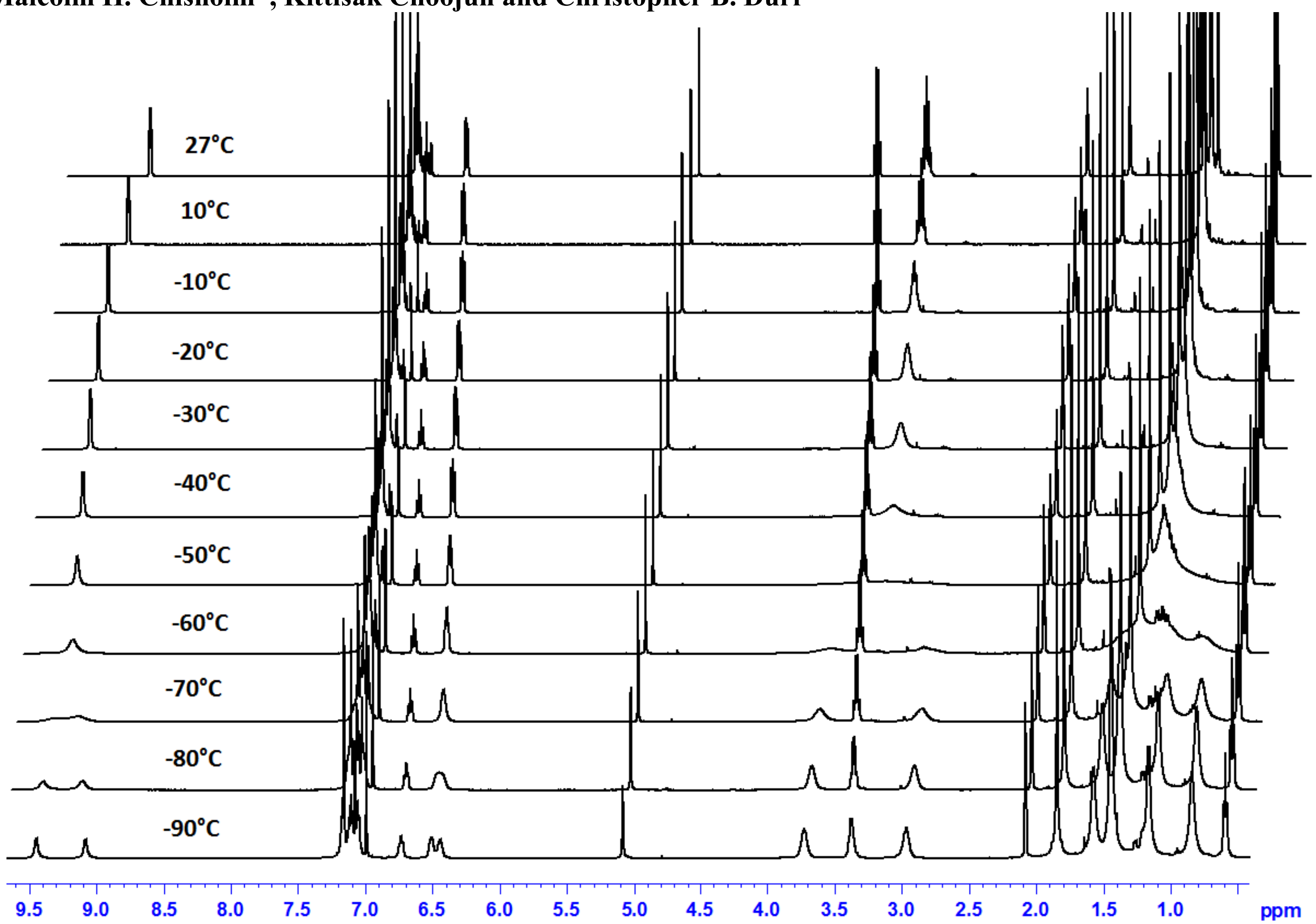
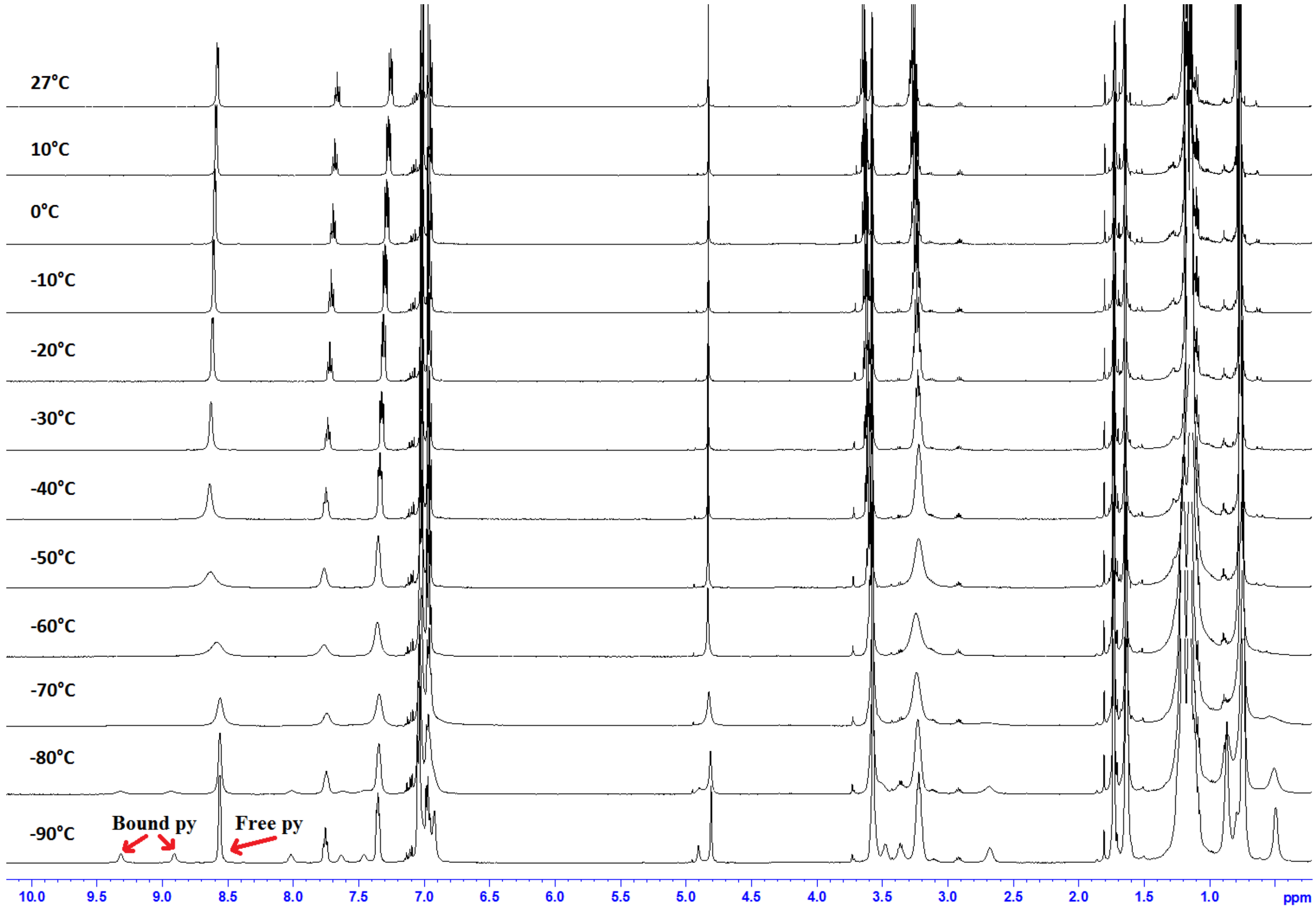
Supporting Information: Ethyl 2-Hydroxy-2-methylpropanoate Derivatives of Magnesium and Zinc. The Effect of Chelation on the Homo- and Copolymerization of Lactide and ε-Caprolactone.

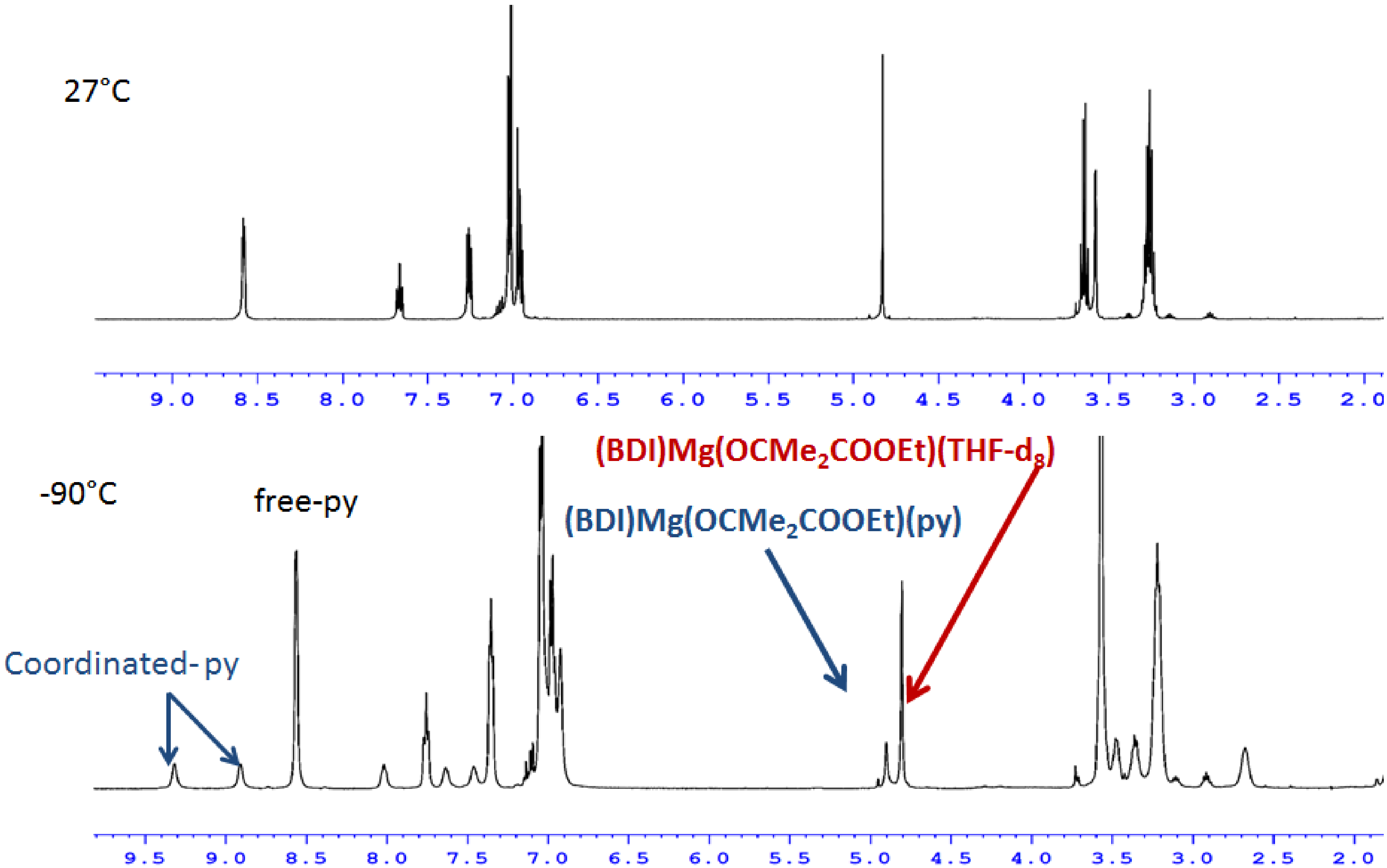
Malcolm H. Chisholm*, Kittisak Choojun and Christopher B. Durr



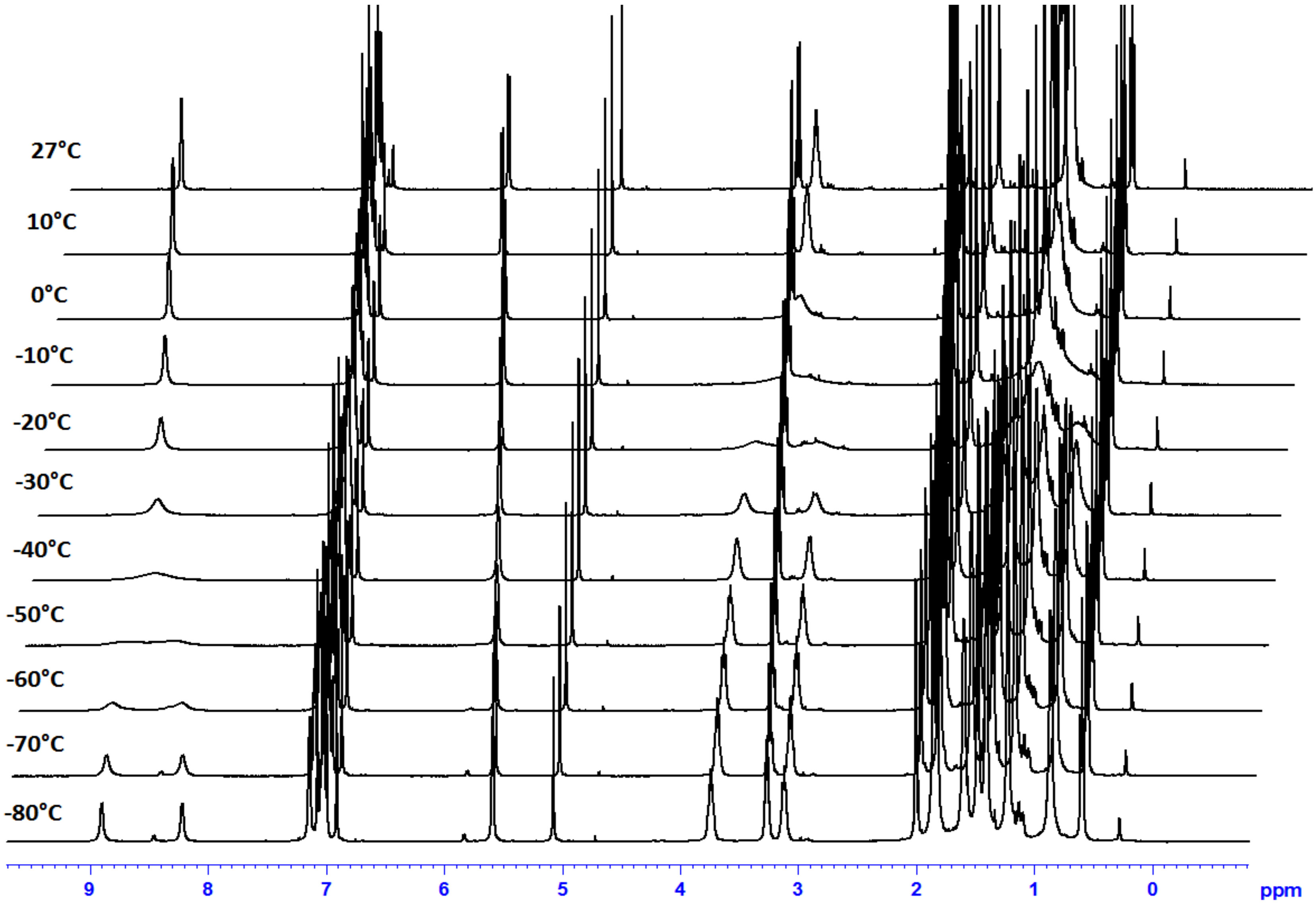
SI. 1. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Mg($OCMe_2COOEt$)(py) in toluene-d_8



SI. 2. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Mg($OCMe_2CEt$)(py) in THF-d_8

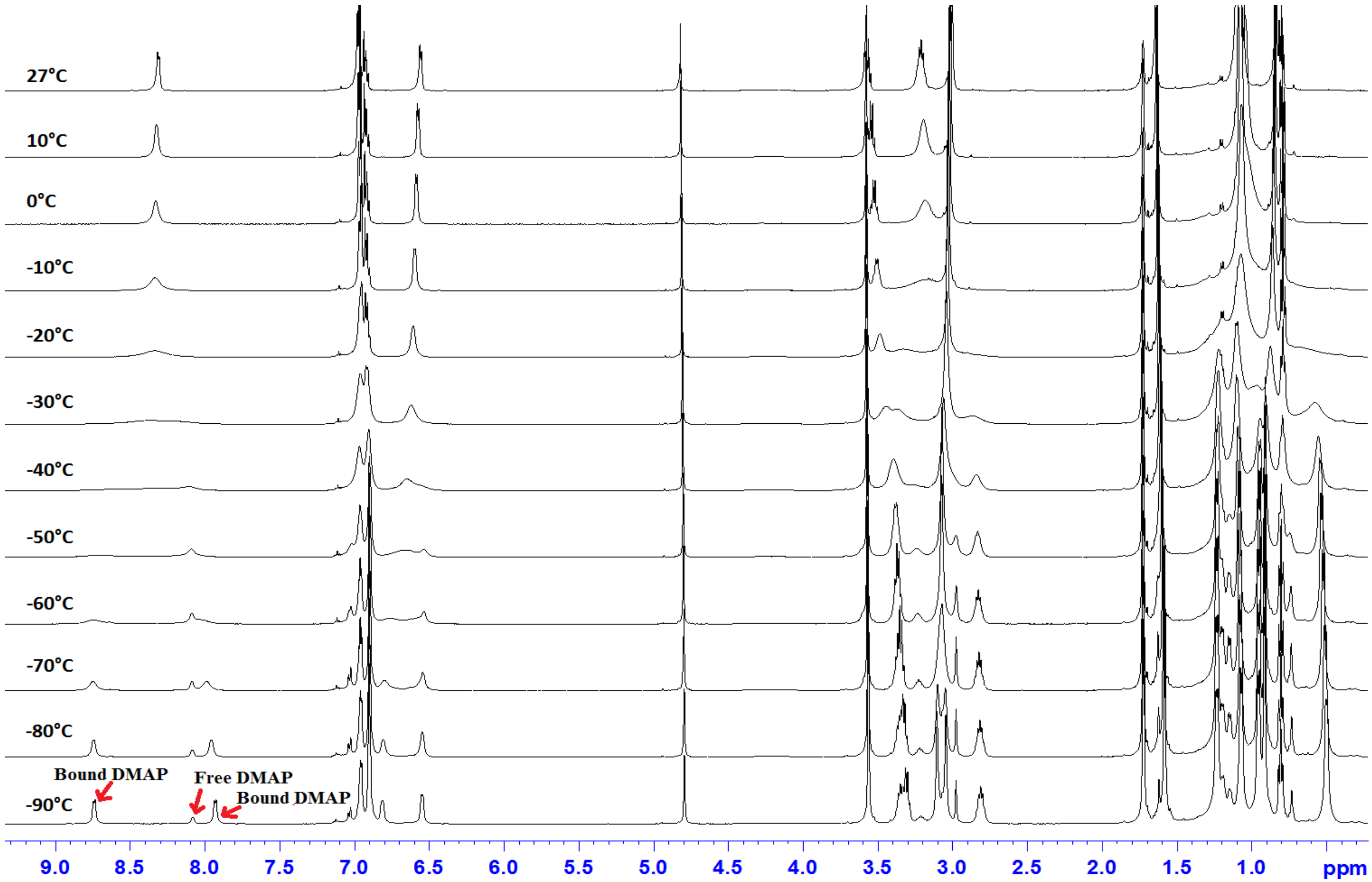


SI. 3. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Mg(OCMe$_2$CEt)(py) in THF-d$_8$ showing the formation of (BDI)Mg(OCMe$_2$COOEt)(THF-d$_8$)

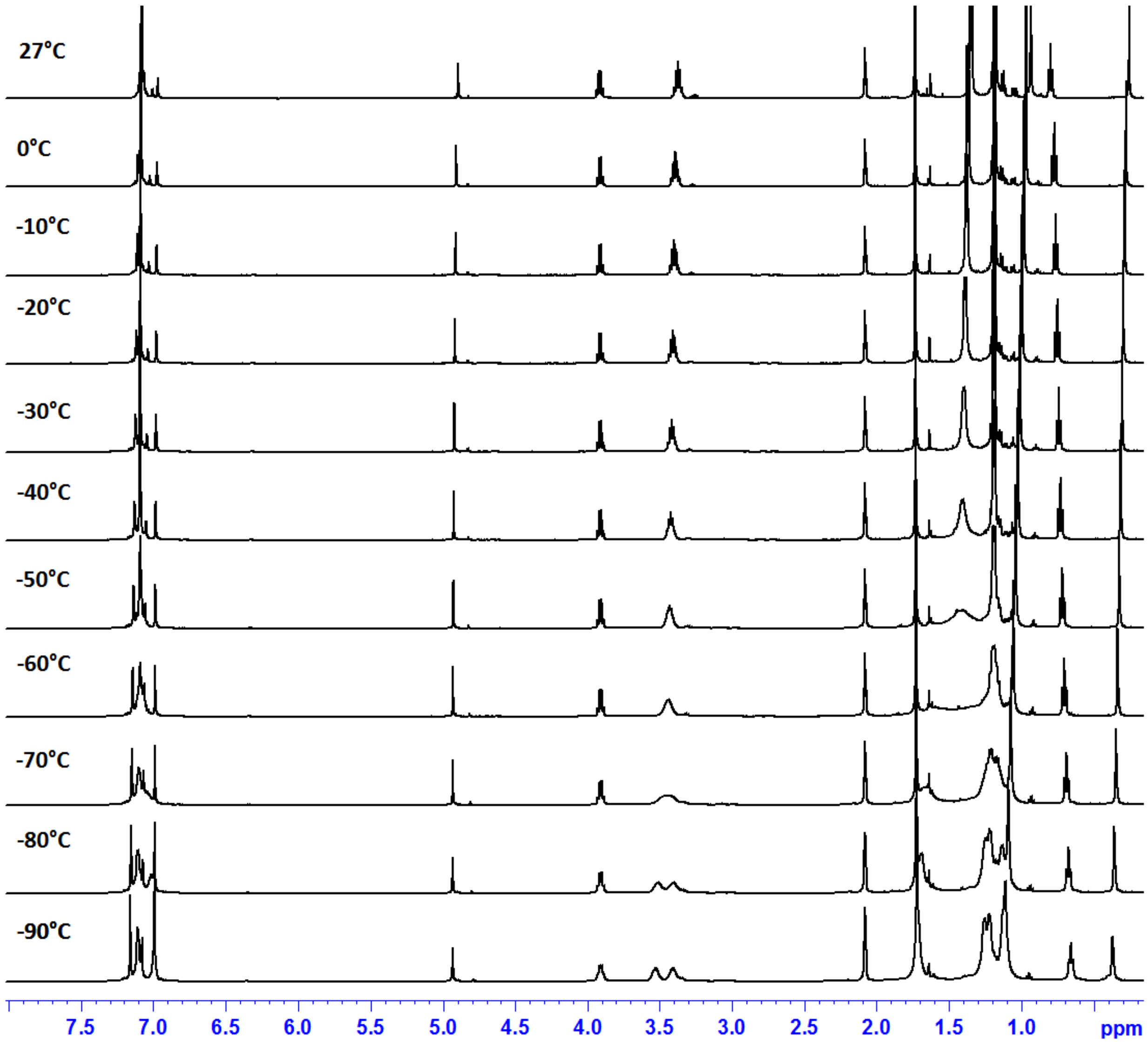


SI. 4. V.T. [1]H 500 MHz NMR of 0.035M (BDI)Mg($OCMe_2COOEt$)(DMAP) in toluene-d_8

Electronic Supplementary Material (ESI) for Dalton Transactions

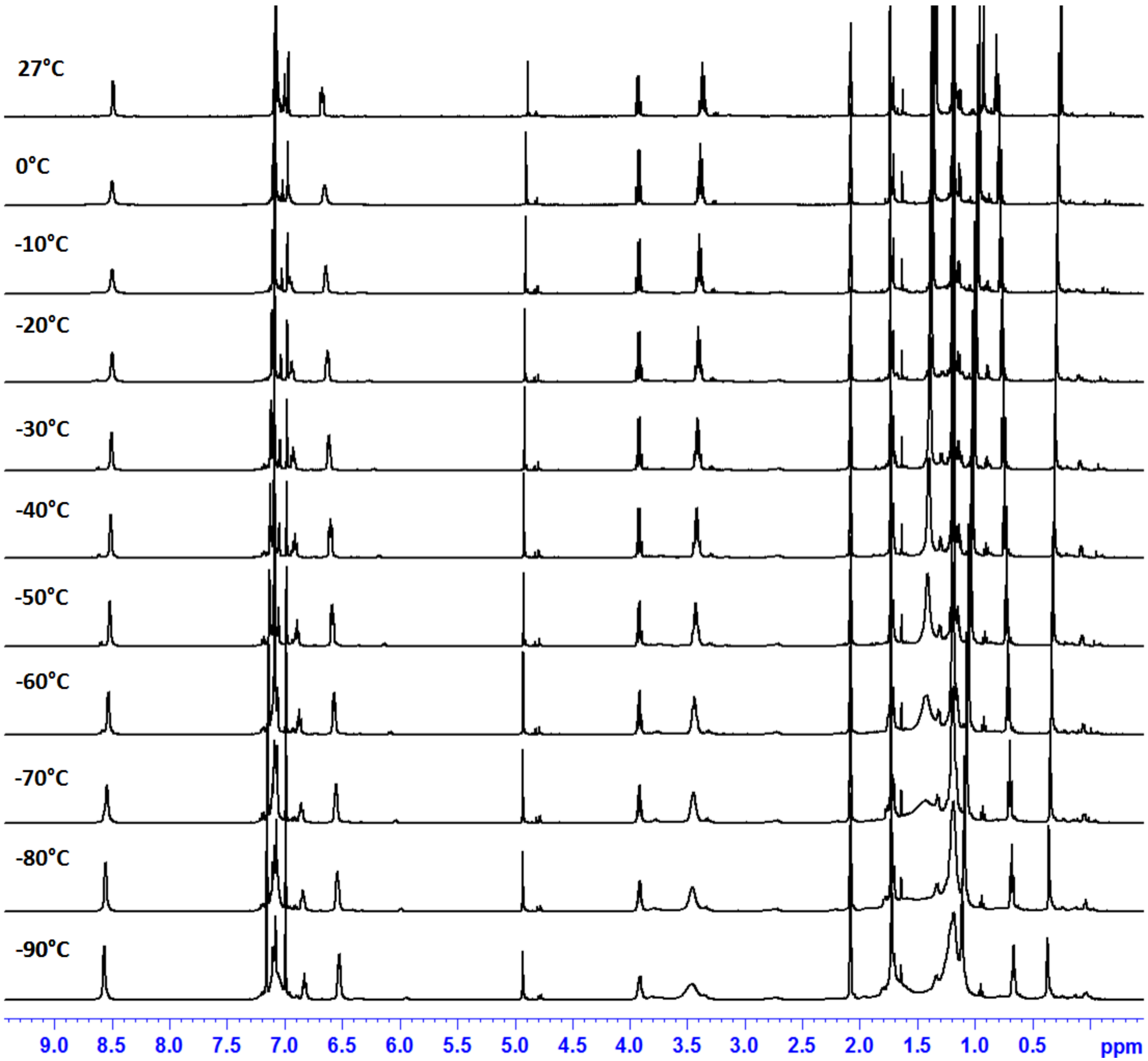


SI. 5. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Mg($OCMe_2COOEt$)(DMAP) in THF-d_8

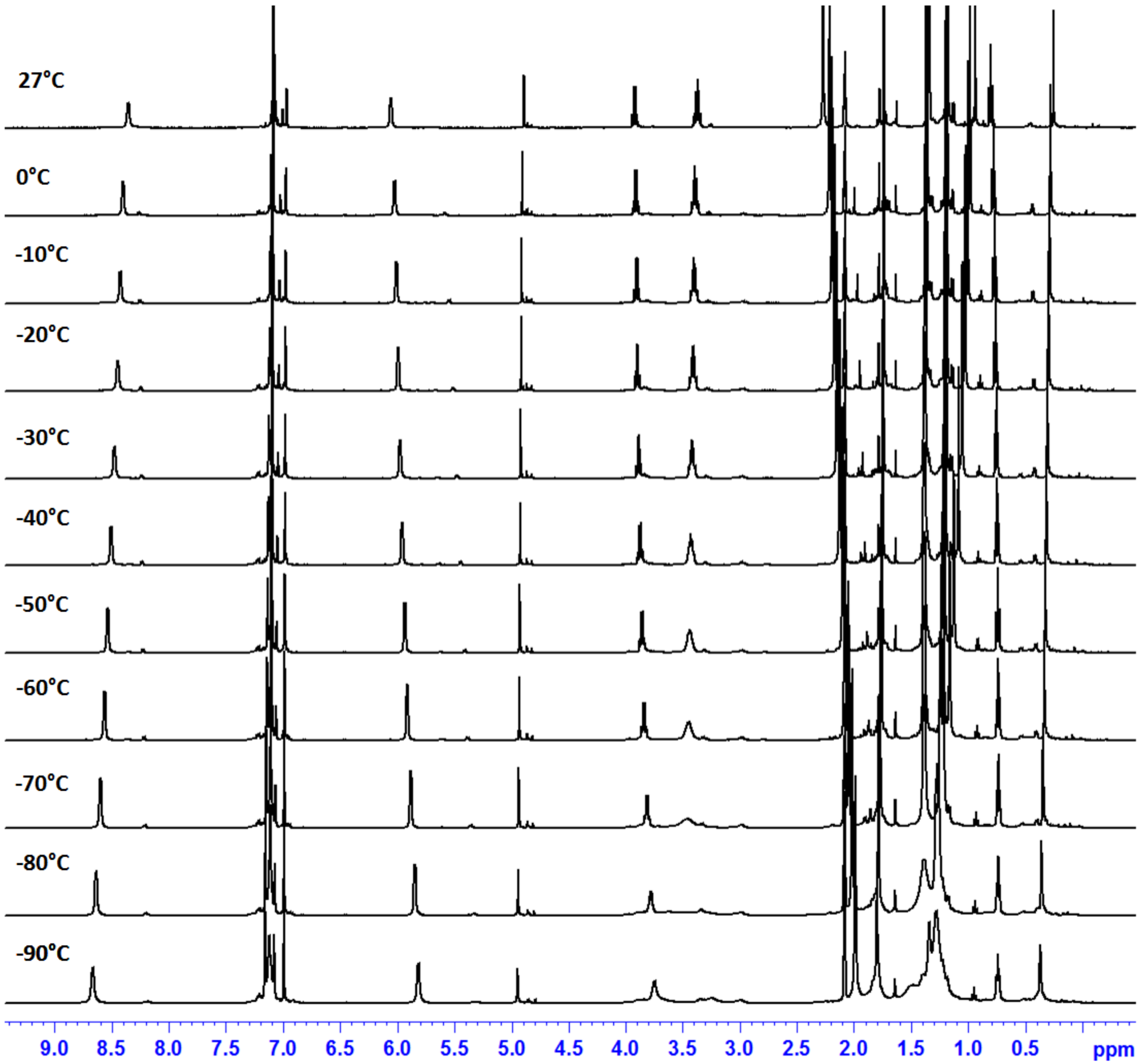


SI. 6. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Zn($OCMe_2COOEt$) in toluene-d_8

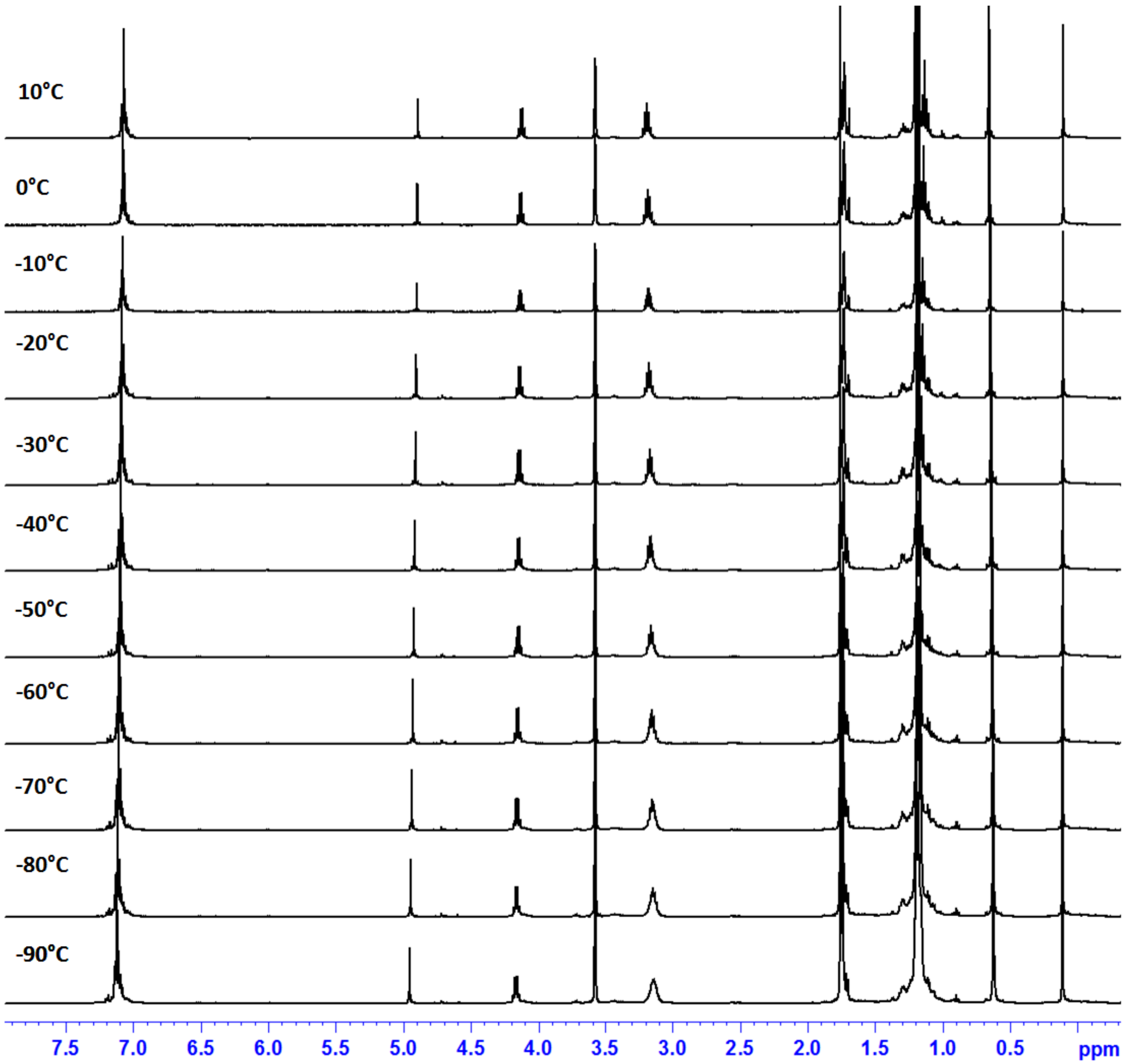
Electronic Supplementary Material (ESI) for Dalton Transactions



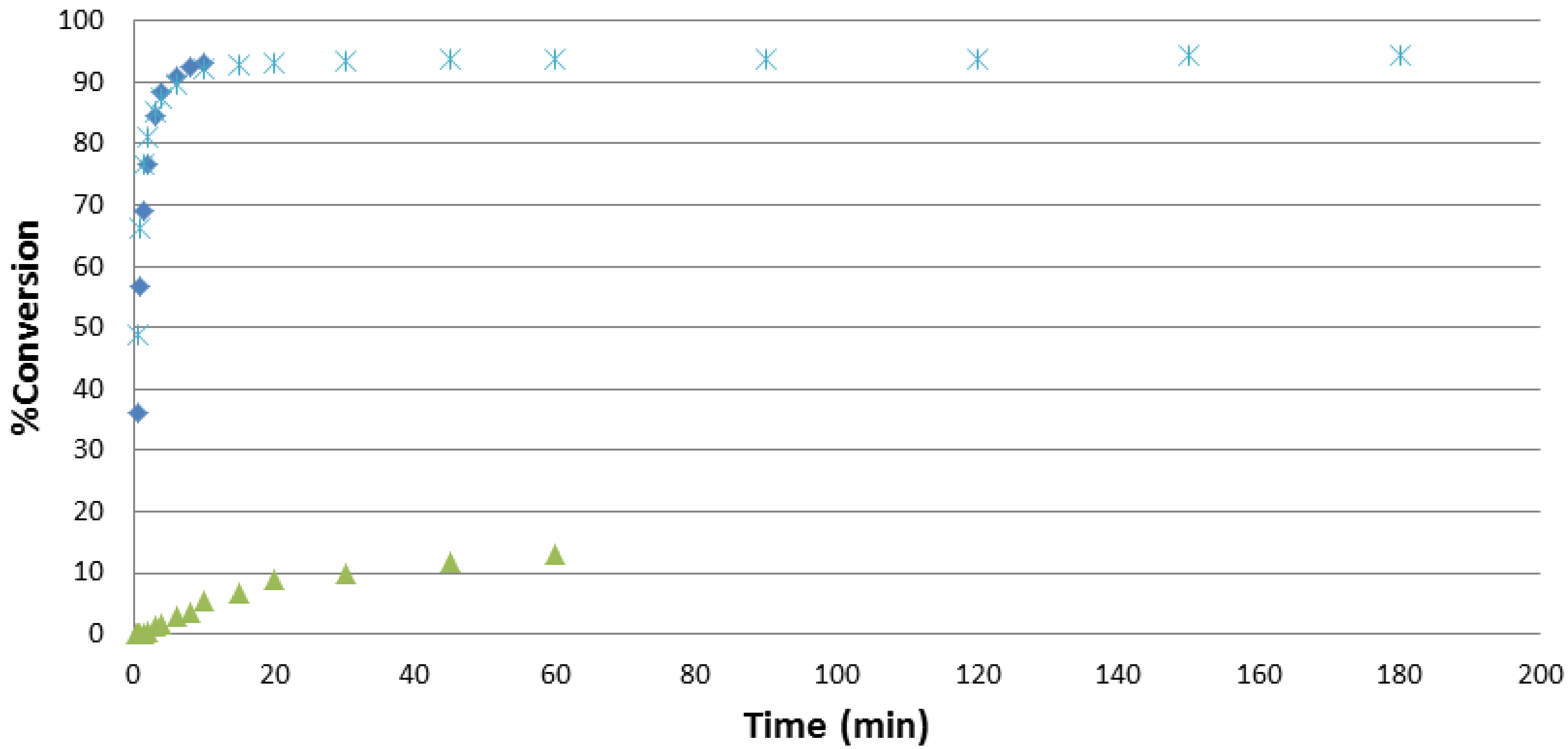
SI. 7. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Zn(OCMe$_2$COOEt) + 0.035M py in toluene-d$_8$



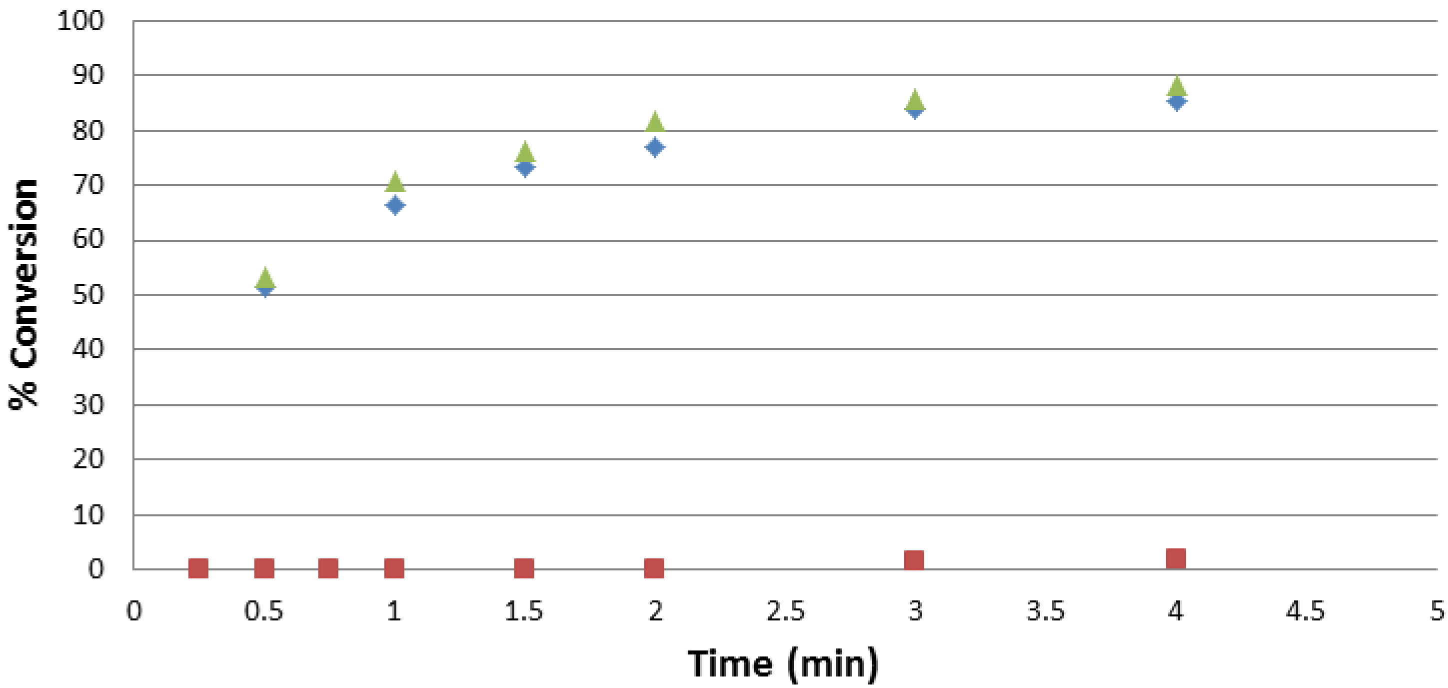
SI. 8. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Zn($OCMe_2COOEt$) + 0.035M DMAP in toluene-d_8



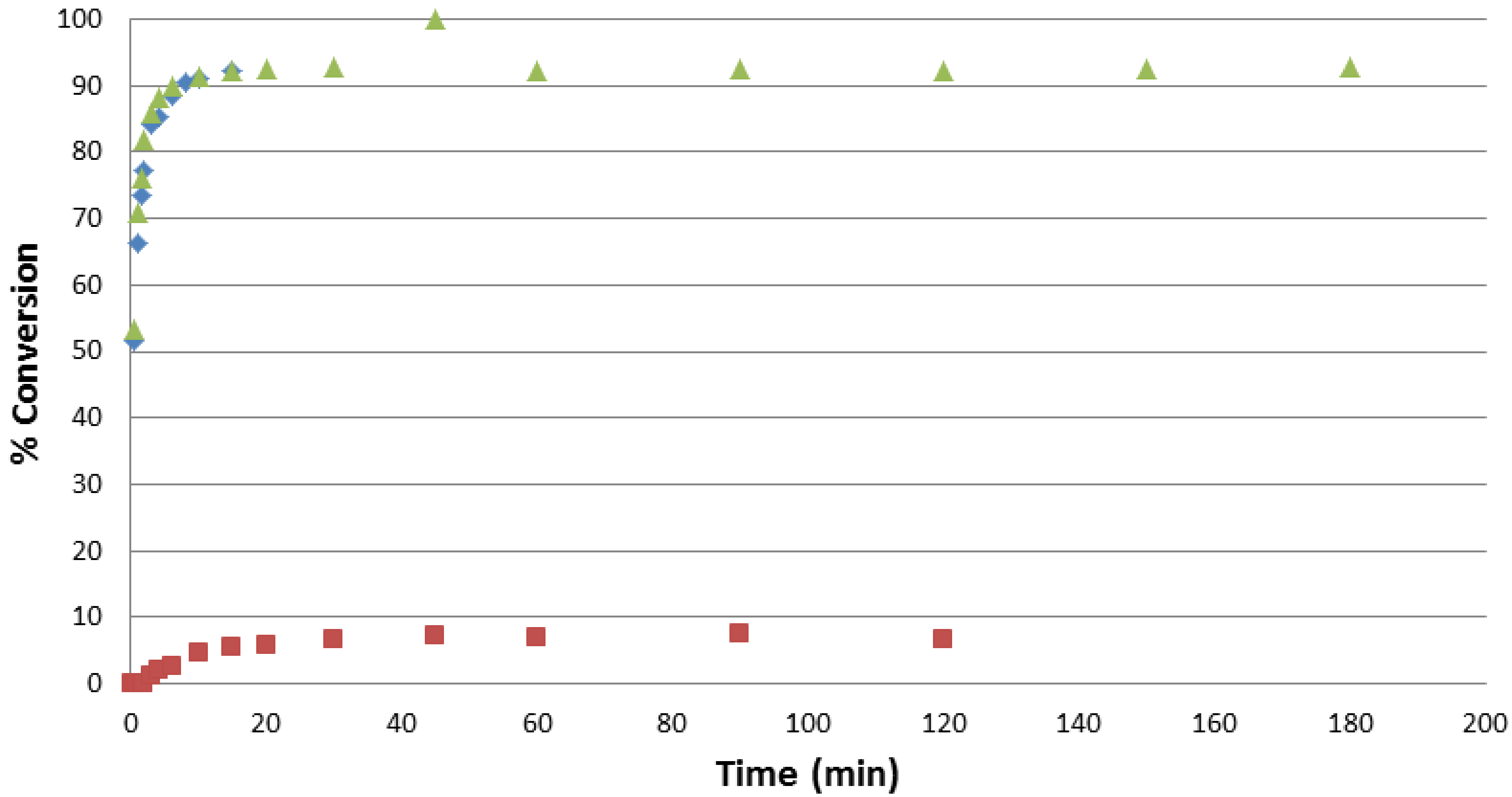
SI. 9. V.T. ^{1}H 500 MHz NMR of 0.035M (BDI)Zn($OCMe_2COOEt$) in THF-d_8



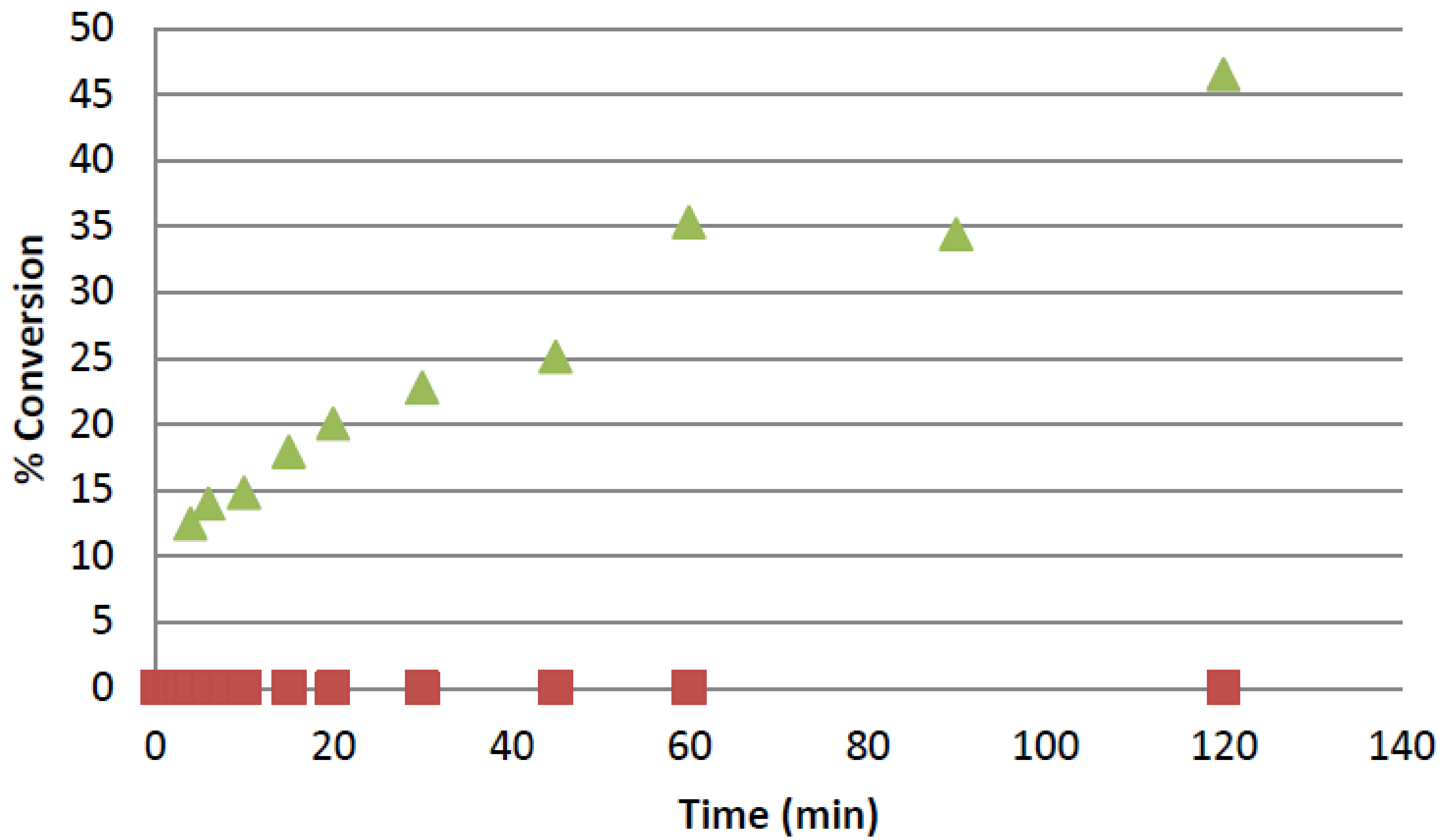
SI. 10 The homo- and copolymerization of ε-CL and *rac*-LA in CH_2Cl_2 at 25°C using (BDI)Mg($OCMe_2COOEt$)(py) as an initiator ([ε-CL]$_o$ and/or ([*rac*-LA]$_o$ = 0.1354 M, [initiator] = 0.035 mM; (◆) the ROP of *rac*-LA ; (▲) the polymerization of ε-CL; (✳) the 1:1 copolymerization of ε-CL and *rac*-LA showing only *rac*-LA conversion



SI. 11 The homo- and copolymerization of ε-CL and *rac*-LA in CH_2Cl_2 at 25°C using (BDI)Mg($OCMe_2COOEt$)(DMAP) as an initiator ([ε-CL]$_o$ and/or ([*rac*-LA]$_o$ = 0.1354 M, [initiator] = 0.035 mM; (◆), the ROP of *rac*-LA; (■),the polymerization of ε-CL; (▲) the 1:1 copolymerization of ε-CL and *rac*-LA showing only *rac*-LA conversion



SI. 12 The homo- and copolymerization of ε-CL and *rac*-LA in CH_2Cl_2 at 25°C using (BDI)Mg($OCMe_2COOEt$)(py) as an initiator ([ε-CL]$_o$ and/or ([*rac*-LA]$_o$ = 0.1354 M, [initiator] = 0.035 mM; (◆) the ROP of *rac*-LA; (▲) the 1:1 copolymerization of ε-CL and *rac*-LA showing only *rac*-LA conversion; (■) the polymerization of ε-CL



SI. 13 The homo- and copolymerization of *ε*-CL and *rac*-LA in CH_2Cl_2 at 25°C using (BDI)Zn($OCMe_2COOEt$) as an initiator ([*ε*-CL] and/or [*rac*-LA] = 0.035mM: (▲) the 1:1 copolymerization of *ε*-CL and *rac*-LA showing only *rac*-LA conversion; (■) the polymerization of *ε*-CL

Table 1. Lactide polymerization

Initiators	Time (min)	%conversion	cal Mn (10^3)	GPC Mn (10^3)	0.58*GPC Mn	PDI
(BDI)Mg(OCMe2COOEt)(py)	3	97	14.0	22.2	12.9	1.21
(BDI)Mg(OCMe2COOEt)(DMAP)	3	97	14.0	23.3	13.5	1.25
(BDI)Zn(OCMe2COOEt)	25	69	12.8	27.8	16.1	1.18

Note: Lactide polymerization conditions a) For [Mg] initiator: ($[LA]_o$ = 0.347 M, $[LA]_o$/[Mg] = 100, at 25°C, b) for [Zn] initiator: $[LA]_o$ = 0.347M, $[LA]_o$/[Zn] =130, at 25°C.