Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Titanium pyridonates and amidates: novel catalysts for the synthesis of random copolymers

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Contents

General experimental conditions. All reactions were performed under an atmosphere of N_2, unless stated otherwise. Amide proligands were synthesised using the method described. 3-Methyl-2-hydroxypyridine and 6-methyl-2-hydroxypyridine are commercially available and sublimed prior to use. 6-Phenyl-2-hydroxypyridine was synthesised following a literature method[1] and further purified by sublimation. Alcohols (reagent grade) were purchased from Fisher Scientific and dried by stirring over powdered, activated 3 Å molecular sieves[2] for 18 h, distilled then degassed using freeze-pump-thaw technique. LA and CL were purchased from commercial sources. LA was sublimed prior to use and CL was stirred over CaH_2 for 2 hours (minimum), filtered through glass paper and then used directly. Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker spectrometer operating at 300 or 400 MHz, and referenced internally according to residual solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (x ppm), multiplicity (s, singlet; br s, broad singlet; d, doublet; br d, broad doublet; t, triplet; q, quartet; quint, quintet; m, multiplet), integration. Molecular weights and polydispersity were estimated by triple detection gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 x 300 mm) HR5E, HR4 and HR2, Waters 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 ml min^{-1} was used and samples were dissolved in THF (~ 4 mg ml^{-1}). The measurements were carried out at laser wavelength of 690 nm, at 25 °C. The data was analysed using the Astra® processing programme provided by Wyatt Technology Corp with a polystyrene standard calibration curve. Theoretical M_n values were calculated based on the assumption that the titanium centre is able to grow two polymer chains from the isopropoxide end-groups. A differential scanning calorimeter (DSC), TA instruments Q2000 calibrated with indium was employed to measure the glass transition temperature (T_g) of the copolymers. Calorimetry was performed in a nitrogen atmosphere with approximately 2.5 - 2.9 mg of copolymer. Samples were heated quickly to 200 °C to remove the thermal history. Then the samples were cooled to -70 °C at a rate of 10 °C min^{-1} and subsequently were heated to 200 °C with the same rate as cooling. The glass transition temperature was traced from the second endothermic sequence.

General procedure for the synthesis of amides. Aniline (13.8 mmol) was dissolved in dichloromethane followed by the addition of NEt_3 (2.5 ml, 18.0 mmol). The solution was cooled to 0 °C and the appropriate acid chloride (18.0 mmol) was added over the course of 5 minutes. The solution was allowed to warm to room temperature and stirred for a further 4 hours. The solution was further diluted with Et_2O and washed with water, 1M HCl and brine. The organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was recrystallised with EtOAc/ hexanes to provide the product, which was further purified by sublimation.

General procedure for the synthesis of bis(pyridonate)-titanium-bis(dimethylamido) or bis(amidate)-titanium-bis(dimethylamido) complexes. In a nitrogen filled glovebox, a Teflon caped vial was charged with 2 mmol (448 mg) of $Ti(NMe_2)_4$ in 2-3 ml of benzene. Two equivalents of proligand were added and a colour change was observed instantly. The solution was stirred at room temperature for 24 h until no further change in colour took place. The solvent was then removed *in vacuo*. The residue was recrystallised using benzene/hexanes. The supernatant was then removed to afford the complex as a red crystalline solid which was used directly in the next stage of synthesis.

General procedure for the synthesis of complexes 1 to 5. Under an atmosphere of nitrogen, a Schlenk tube was charged with 1 mmol of bis(pyridonate)-titanium-bis(dimethylamido) or bis(amidate)-titanium-

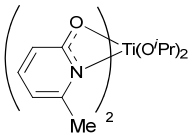
bis(dimethylamido) precursor in 1-2 ml of benzene. Two equivalents of isopropyl alcohol were added using a microsyringe. A colour change was observed instantly. The solution was stirred at room temperature for 1 h, or until no further change in colour took place. The solvent was then removed *in vacuo* and the residue washed with 5 ml cold, dry hexanes and any titanium-oxides removed by filtration. The hexane solution was then concentrated *in vacuo* to afford the analytically pure complex.

The robustness of **1** to **3** was tested by preparing a 0.08 M solution of complex in ethanol. The solution was heated at 200 °C in a small, Teflon-sealed thick-walled reaction tube. After 64 h, the reaction mixture was cooled to RT, the solvent removed *in vacuo* and the residue dissolved in d^6-benzene and analysed by ^{1}H NMR spectroscopy (see page 38). In all cases a yellow solution was obtained. The mixture obtained after heating was compared to pure starting complex and proligand. The proligand is sparingly soluble in d^6-benzene, so one drop DMSO was added to aid solubility.

General procedure for the homopolymerisation of LA or CL. A Young's reaction tube (*i.e.* a Teflon sealed thick-walled reaction vessel of ~30 ml in volume) was charged with a stirrer bar, the appropriate quantity of catalyst followed by CL or LA. PLA synthesis was carried out at 130 °C for 24 h, the reaction was quenched with MeOH, dissolved in dichloromethane and concentrated. The polymer was redissolved in hot dichloromethane, precipitated with MeOH and washed with copious amounts of MeOH. It was then dried under vacuum for 18 h. PCL synthesis was carried out at 100 °C for the stated reaction time, the reaction was then quenched with MeOH, dissolved in dichloromethane and concentrated. The polymer was redissolved in hot dichloromethane, precipitated with MeOH and washed with copious amounts of MeOH. It was then dried under vacuum for 18 h.

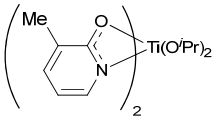
General procedure for the random copolymerisation of LA and CL. A Young's reaction tube was charged with a stirrer bar, the appropriate quantity of catalyst followed by CL and LA. Copolymerisation was carried out at 130 °C for 24 h, the reaction was then quenched with MeOH, dissolved in dichloromethane and concentrated. The polymer was redissolved in hot dichloromethane, precipitated with MeOH and washed with copious amounts of MeOH. It was then dried under vacuum for 18 h.

1.



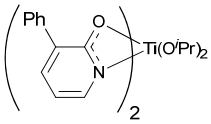
Pale yellow solid, 351 mg (92%). ^{1}H NMR (300 MHz; 298 K; d^6-benzene) δ 6.91 (apparent s, 2H, ArH), 6.26 (d, *J* 6.7 Hz, 2H, ArH), 5.90 (apparent s, 2H, ArH), 4.86 (apparent quintet, *J* 5.9 Hz, 2H, 2 x OCH(CH$_3$)$_2$), 2.15 (s, 6H, 2 x ArCH$_3$), 1.28 (d, *J* 5.9 Hz, 12H, 2 x OCH(CH$_3$)$_2$); ^{13}C NMR (100 MHz; 298 K; d^6-benzene) δ 173.4, 153.4, 141.6, 112.8, 106.2, 80.2, 26.0, 21.5; MS (EI) calcd. for $C_{18}H_{26}N_2O_4Ti$ [M^+] 382.1372, found 382.1374; Anal. calcd. for $C_{18}H_{26}N_2O_4Ti$: C, 56.6; H, 6.9; N, 7.3. Found: C, 56.8; H, 6.9; N, 7.6.

2.



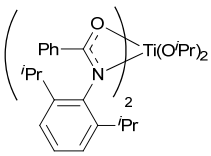
Pale yellow solid, 354 mg (92%). ^{1}H NMR (400 MHz; 298 K; d^6-benzene) δ 7.46 (s, 2H, ArH), 6.88 (d, *J* 6.6 Hz, 2H, ArH), 6.04 (apparent t, *J* 5.6 Hz, 2H, ArH), 4.89 (apparent t, *J* 6.1 Hz, 2H, 2 x OCH(CH$_3$)$_2$), 2.08 (s, 6H, 2 x ArCH$_3$), 1.26 (d, *J* 6.1 Hz, 12H, 2 x OCH(CH$_3$)$_2$); ^{13}C NMR (100 MHz; 298 K; d^6-benzene) δ 171.2, 141.9, 139.7, 121.3, 112.8, 78.9, 26.2, 16.3; MS (EI) calcd. for $C_{18}H_{26}N_2O_4Ti$ [M$^+$] 382.1372, found 382.1372; Anal. calcd. for $C_{18}H_{26}N_2O_4Ti$: C, 56.6; H, 6.9; N, 7.3. Found: C, 56.2; H, 6.6; N, 7.3.

3.



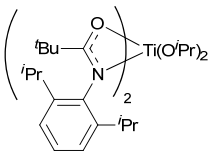
Yellow solid, 415 mg (82%). ^{1}H NMR (400 MHz; 298 K; d^6-benzene) δ 7.94 (apparent d, *J* 7.6 Hz, 4H, ArH), 7.32 (dd, *J* 7.6, 1.4 Hz, 2H, ArH), 7.27 (apparent t, *J* 7.6 Hz, 4H, ArH), 7.14 (m, *J* 7.3 Hz, 4H, ArH), 6.06 (apparent t, *J* 6.2 Hz, 2H, ArH), 4.82 (septet, *J* 6.1 Hz, 2H, 2 x OCH(CH$_3$)$_2$) 1.26 (d, *J* 6.1 Hz, 12H, 2 x OCH(CH$_3$)$_2$); ^{13}C NMR (100 MHz; 298 K; d^6-benzene) δ 171.1, 141.2, 139.7, 136.6, 129.7, 129.04, 128.96, 126.0, 113.7, 80.4, 26.0; MS (ESI) calcd. for $C_{28}H_{30}N_2O_4Ti$ [M$^+$] 506.1683, found 506.1685; Anal. calcd. for $C_{28}H_{30}N_2O_4Ti$: C, 66.7; H, 6.0; N, 5.5. Found: C, 66.7; H, 5.9; N, 5.4.

4.



Off-white solid, 716 mg (99%). ^{1}H NMR (300 MHz; 298 K; d^6-benzene) δ 7.91 (dd, *J* 8.4, 1.4 Hz, 4H, ArH), 7.36 (s, 6H, ArH), 7.05-6.95 (m, 6H, ArH), 4.88 (septet, *J* 6.1 Hz, 2H, 2 x OCH(CH$_3$)$_2$), 4.07 (br. s, 4H, 4 x CH(CH$_3$)$_2$), 1.67 (apparent s, 12H, 2 x OCH(CH$_3$)$_2$) 1.14 (br. s, 24H, 4 x CH(CH$_3$)$_2$); ^{13}C NMR (100 MHz; 298 K; d^6-benzene) δ 178.9, 143.3, 142.6, 132.9, 132.2, 130.3, 128.6, 126.9, 124.6, 79.0, 28.6, 25.7, 24.6; MS (EI) calcd. for $C_{44}H_{58}N_2O_4Ti$ [M$^+$] 726.3876, found 726.3883; Anal. calcd. for $C_{44}H_{58}N_2O_4Ti$: C, 72.7; H, 8.0; N, 3.9. Found: C, 72.9; H, 8.0; N, 4.3.

5.



Yellow solid, 668 mg (97%). ^{1}H NMR (400 MHz; 298 K; d^8-toluene) δ 7.24 (m, 6H, ArH), 4.64 (septet, *J* 6.1 Hz, 2H, 2 x OCH(CH$_3$)$_2$), 4.08-3.58 (apparent br. d, 4H, 4 x CH(CH$_3$)$_2$), 1.80-0.94 (m, 54H, 2 x OCH(CH$_3$)$_2$ & 4 x CH(CH$_3$)$_2$ & 2 x C(CH$_3$)$_3$); ^{13}C NMR (100 MHz; 298 K; d^8-toluene) δ 188.5, 142.1, 137.4, 126.0, 125.6, 77.7, 41.1, 28.1, 27.9, 25.5, 25.2; MS (EI) calcd. for $C_{40}H_{66}N_2O_4Ti$ [M$^+$] 686.4502, found 686.4501; Anal. calcd. for $C_{40}H_{66}N_2O_4Ti$: C, 70.0; H, 9.7; N, 4.1. Found: C, 69.6; H, 9.6; N, 4.7.

X-ray crystallography. The X-ray diffraction experiment on **1** was carried out at 100 K on a Bruker X8 APEX II diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[3] from several series of exposures measuring 0.5° in ω or φ. Absorption corrections were based on equivalent reflections using SADABS.[4] The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms in calculated positions using SHELXL.[5] Crystal structure and refinement data is given in Table S1 and S2. The crystal structure is deposited at the Cambridge Crystallographic Data Centre (CCDC 882572).

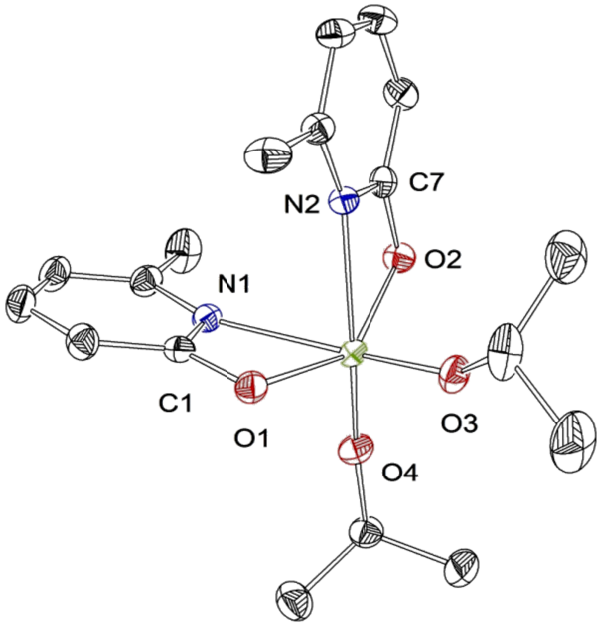


Table S1. Selected bond lengths and angles of **1**.

Bond Length (Å)		**Bond Angle (°)**	
Ti-O1	2.003(1)	N1-Ti-O1	62.72(5)
Ti-O2	1.986(1)	N2-Ti-O2	62.51(5)
Ti-O3	1.785(1)	N1-C1-O1	111.8(2)
Ti-O4	1.766(1)	N2-C7-O2	111.5(2)
Ti-N1	2.219(1)		
Ti-N2	2.250(2)		
C1-O1	1.318(2)		
C7-O2	1.325(2)		
C1-N1	1.344(3)		
C7-N2	1.347(2)		

Table S2. X-Ray crystallography data for **1**.

Colour, habit	colourless plates
Size/mm	0.53x0.45x0.15
Formula	$TiO_4N_2C_{18}H_{26}$
MW	382.13716
Crystal system	monoclinic
Space group	P 2_1/n
R-Factor/ %	3.85
***a*/Å**	11.5499(6)
***b*/Å**	13.1813(6)
***c*/Å**	26.740(1)
***α*/°**	90.00
***β*/°**	102.394(3)
***γ* /°**	90.00
V/Å^3	3976.1(4)
Z	8
***μ* /mm^{-1}**	0.453
T/K	100(2)
$\theta_{min,max}$	2.377, 27.349
Completeness	1.037 to $\theta = 27.349°$
Reflections: total/independent	64731/9484
R_{int}	
Final *R*1 and *wR*2	0.0385, 0.094
Largest peak, hole/eÅ^{-3}	0.295, -0.338
ρ_{calc}/g cm^{-3}	1.277

Homopolymerisation Analysis Data

The discrepancy between the theoretical ($M_n$theo) and observed (experimental) values for number average molecular weight for both LA and CL homopolymers is consistent with transesterification processes that can result in the formation of oligomers, cyclic oligomers (macrocyclisations), and both shorter and longer polymer chains.[6] This discrepancy in theoretical vs. experimental M_n cannot be fully accounted for by assuming only one chain grows from the Ti centre rather than two (*i.e.* $M_n$theo= [M]/[Ti]*%Yield*MW), therefore on-going work is the exploration of the mechanistic details of these novel catalyst systems. This will be reported in due course.

PLA tacticity, where $P_m + P_r = 1$, was calculated using Bernoullian statistics based on the assignments made by Coates and co-workers.[7]

rmr

$$P_r = \sqrt{2(\mathrm{rmr})}$$

rmm

$$P_r^2 - P_r + 2(\mathrm{mmr}) = 0$$

$$P_r^2 - P_r + x = 0$$

$$P_r = \frac{1 \pm \sqrt{1 - 4(1)(x)}}{2} \qquad where\ x = 2(\mathrm{rmm})$$

mmr

$$P_r^2 - P_r + 2(\mathrm{mmr}) = 0$$

$$P_r^2 - P_r + x = 0$$

$$P_r = \frac{1 \pm \sqrt{1 - 4(1)(x)}}{2} \qquad where\ x = 2(\mathrm{mmr})$$

mmm

$$P_r^2 - 3P_r + 2 - 2(\mathrm{mmm}) = 0$$

$$P_r^2 - 3P_r + 2 - 2x = 0$$

$$P_r^2 - 3P_r + y = 0$$

$$P_r = \frac{3 \pm \sqrt{9 - 4(1)(y)}}{2} \qquad where\ x = \mathrm{mmm}$$

$$y = (2 - 2x)$$

mrm

$$P_r = 2\mathrm{mrm}$$

The values of rmr, rmm, mmr, mmm and mrm were determined using the equations above with the integrals obtained from $^1H\{^1H\}$ NMR spectroscopy. Please note that the spectrum can contain artifacts of the raw, non-decoupled spectrum and that these shoulders can be readily removed through a slight shift in the irradiation point and/or increase in the power level.

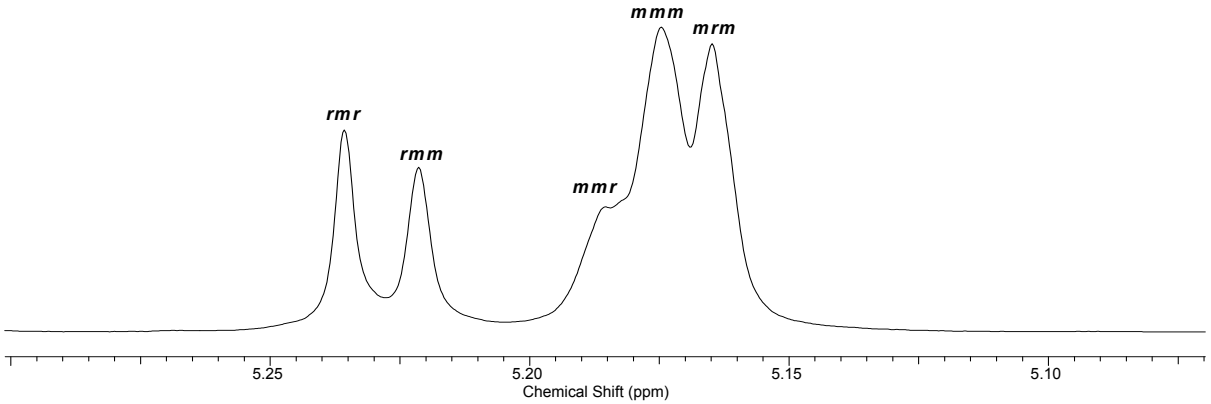
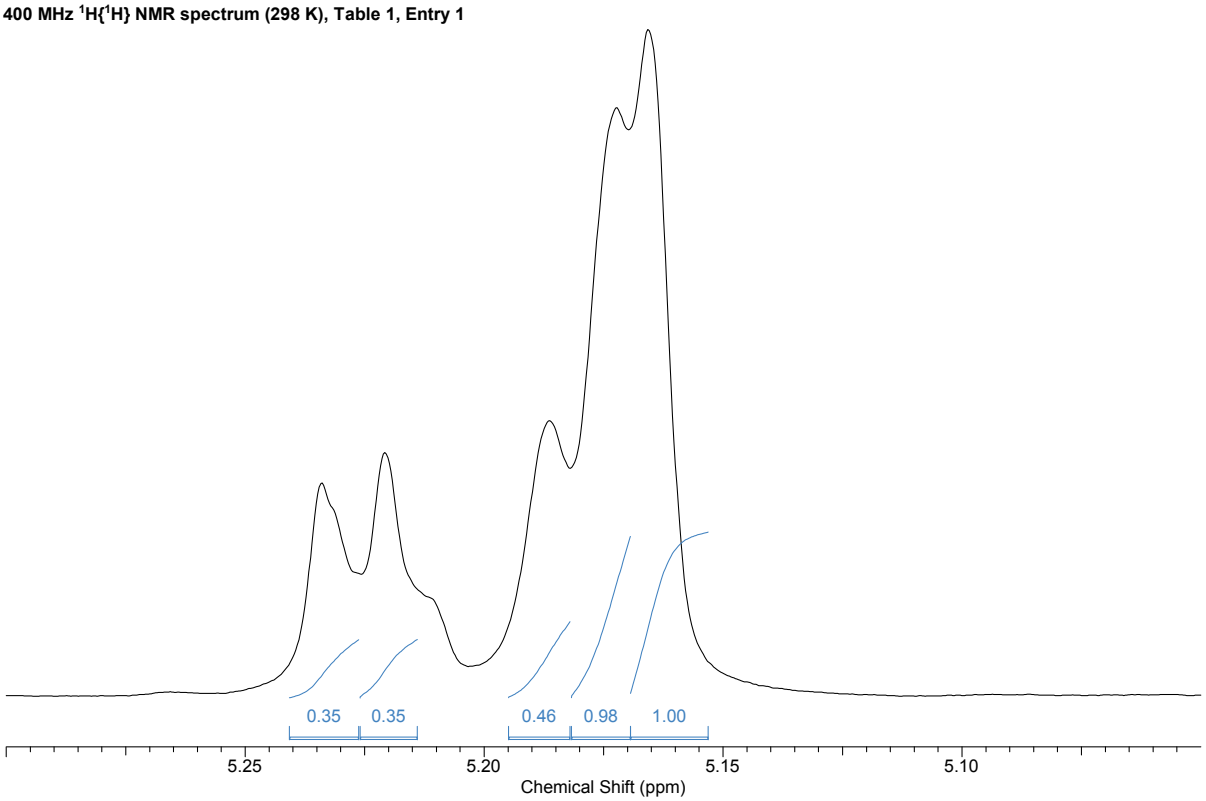


Table 1, Entry 1



GPC trace

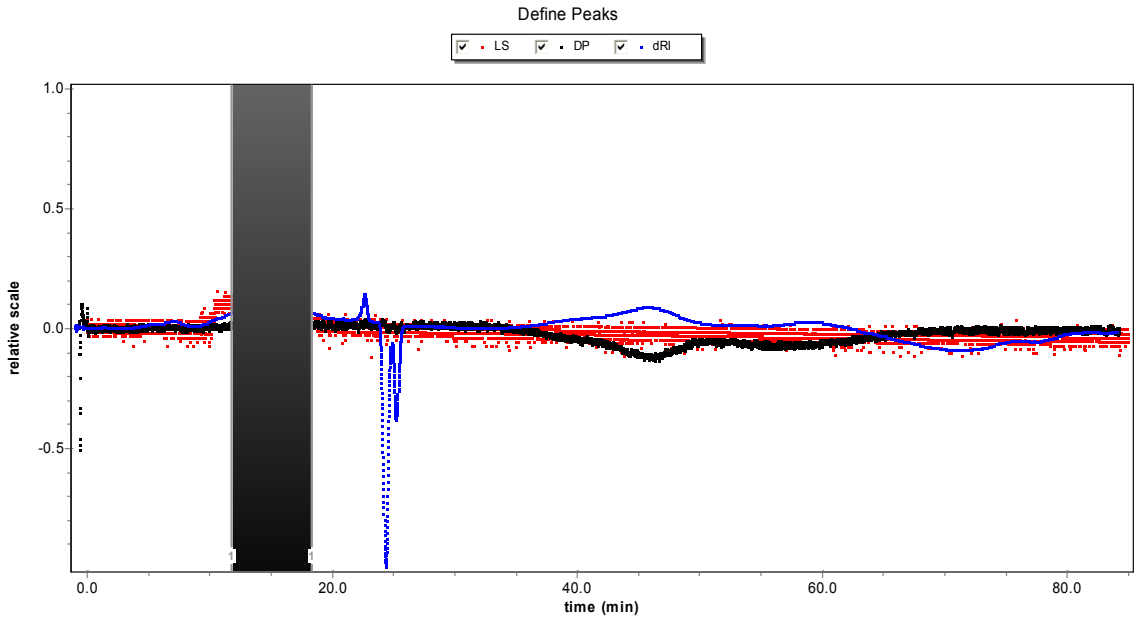
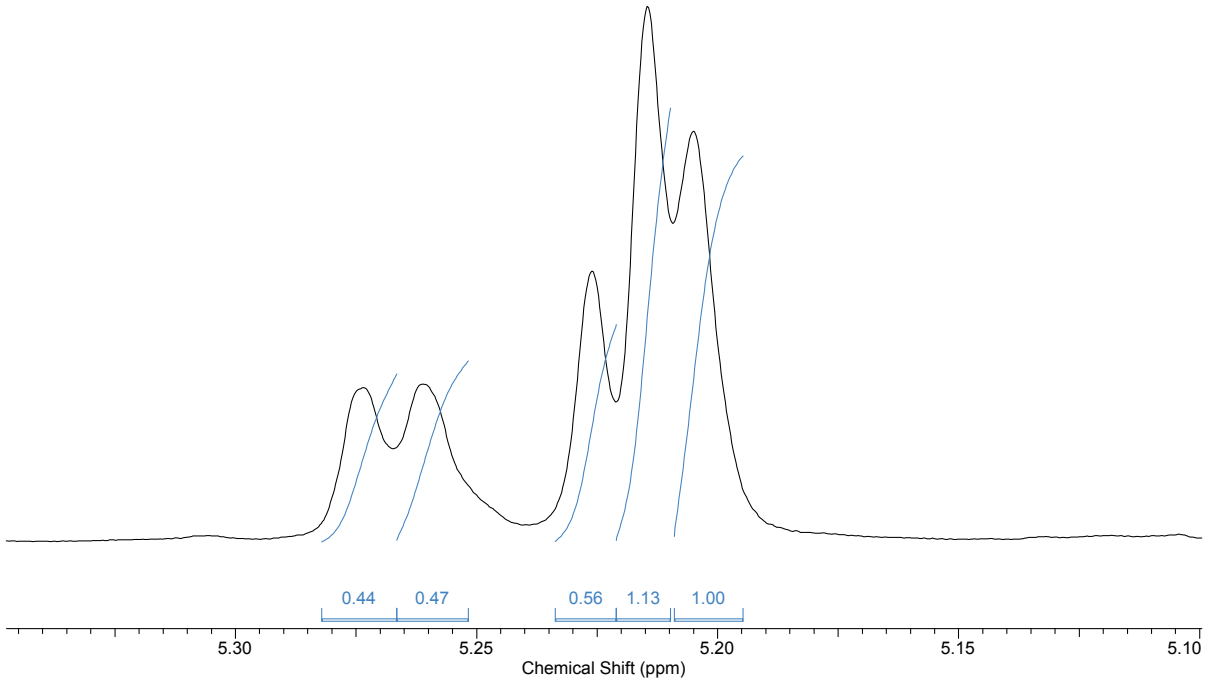


Table 1, Entry 2

400 MHz $^{1}H\{^{1}H\}$ NMR spectrum (298 K), Table 1, Entry 2



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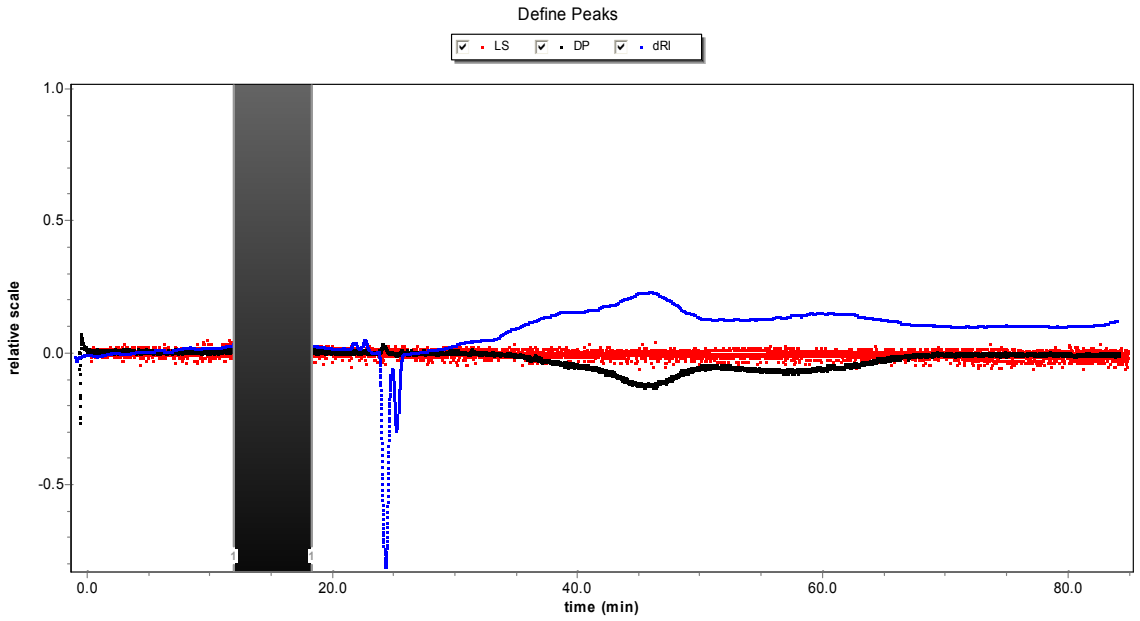

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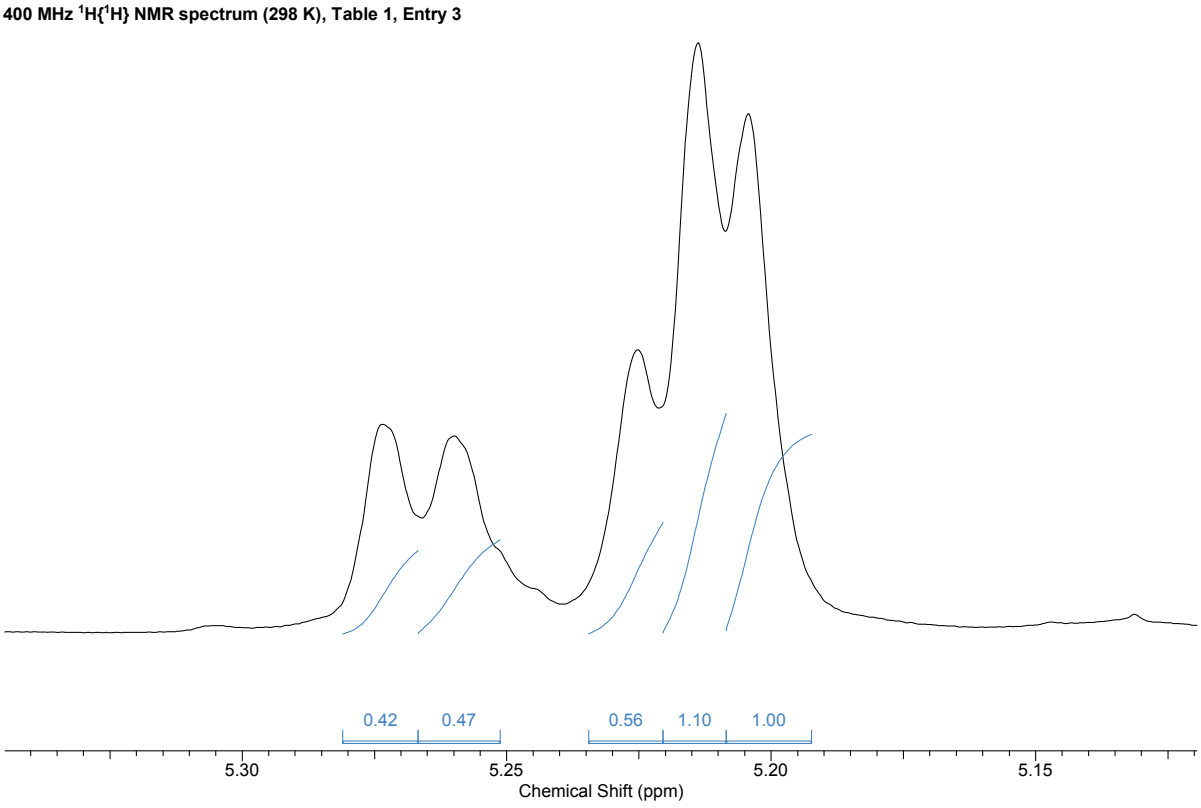

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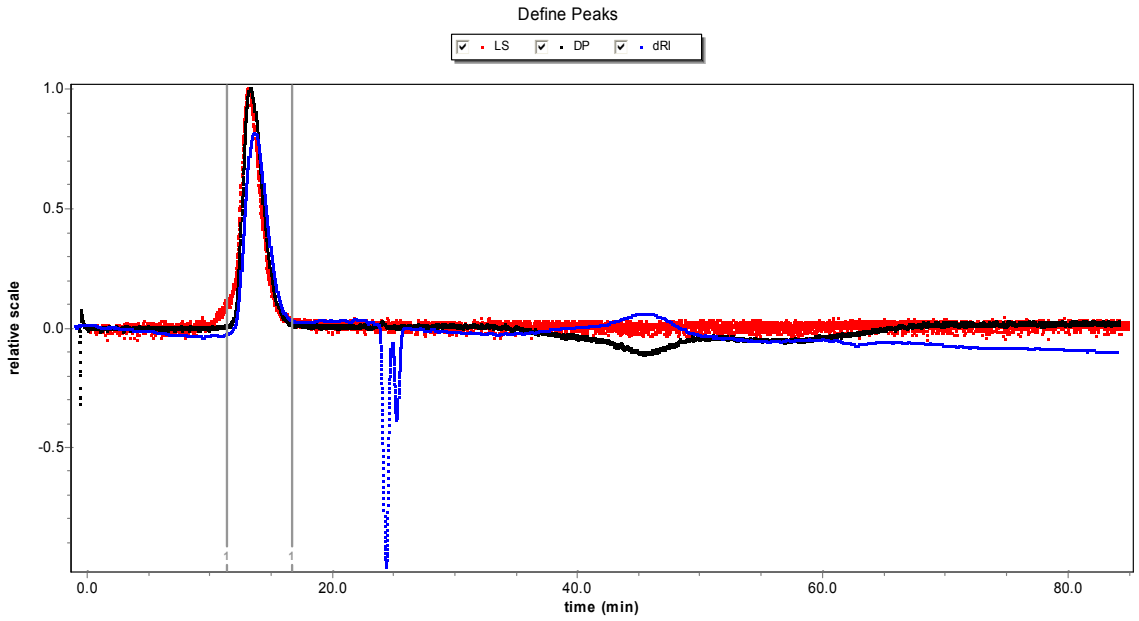
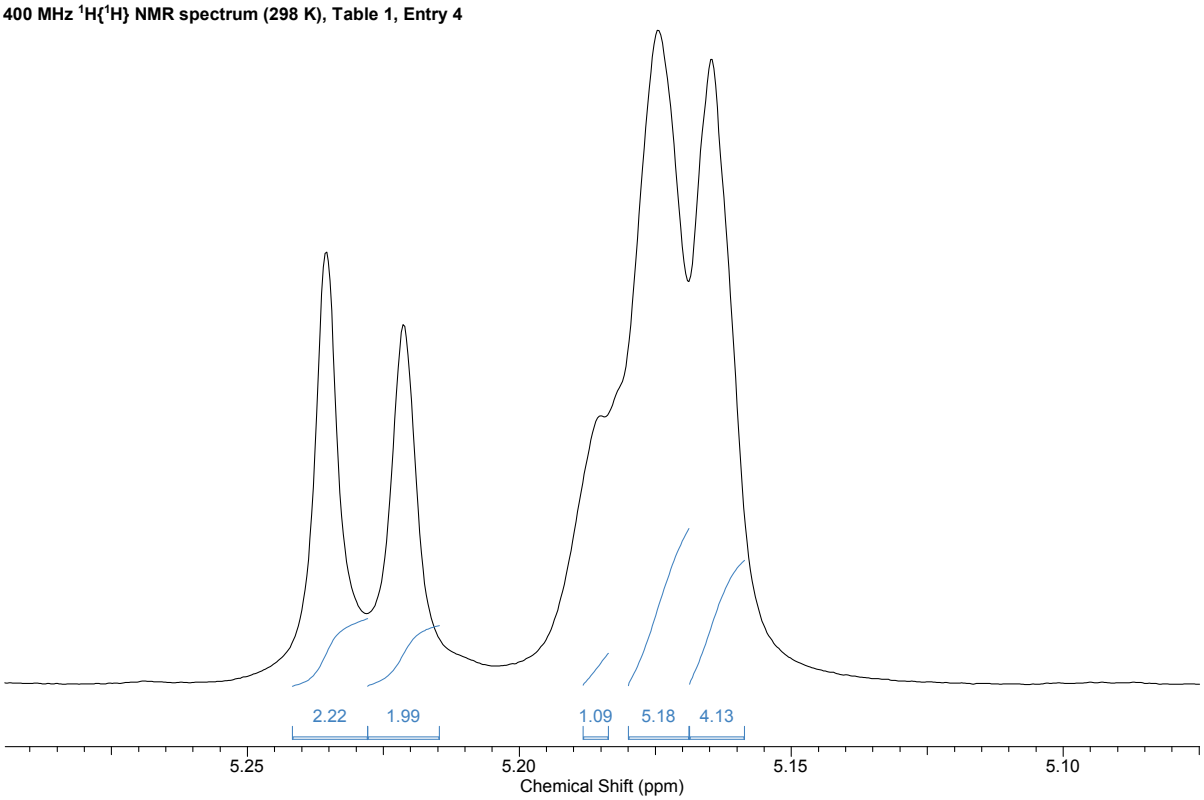


Table 1, Entry 4

400 MHz $^{1}H\{^{1}H\}$ NMR spectrum (298 K), Table 1, Entry 4



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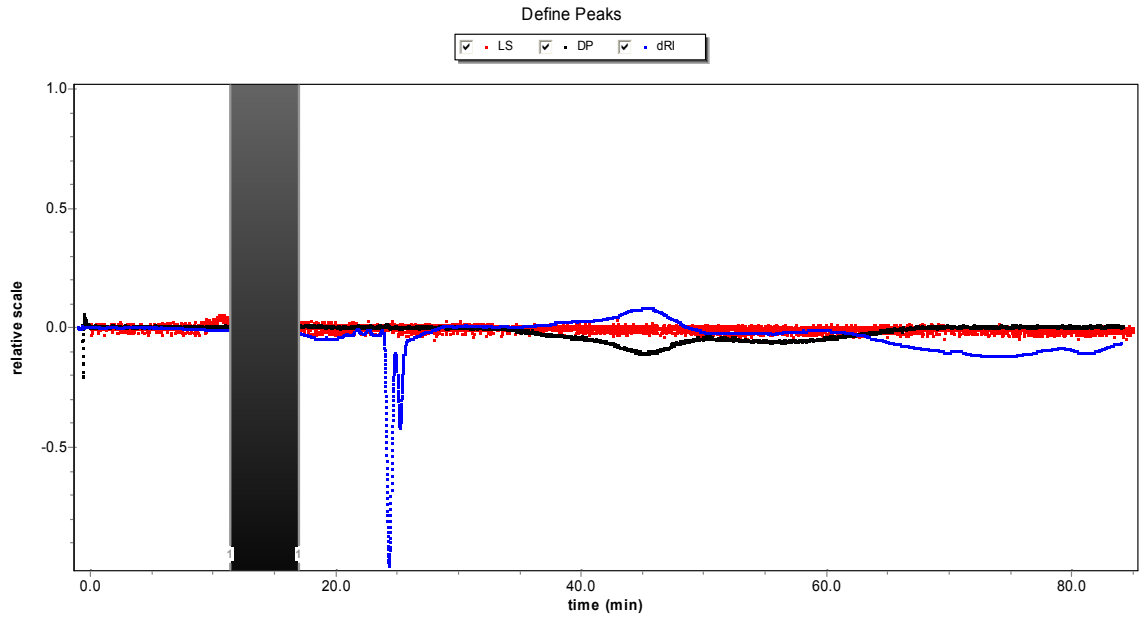

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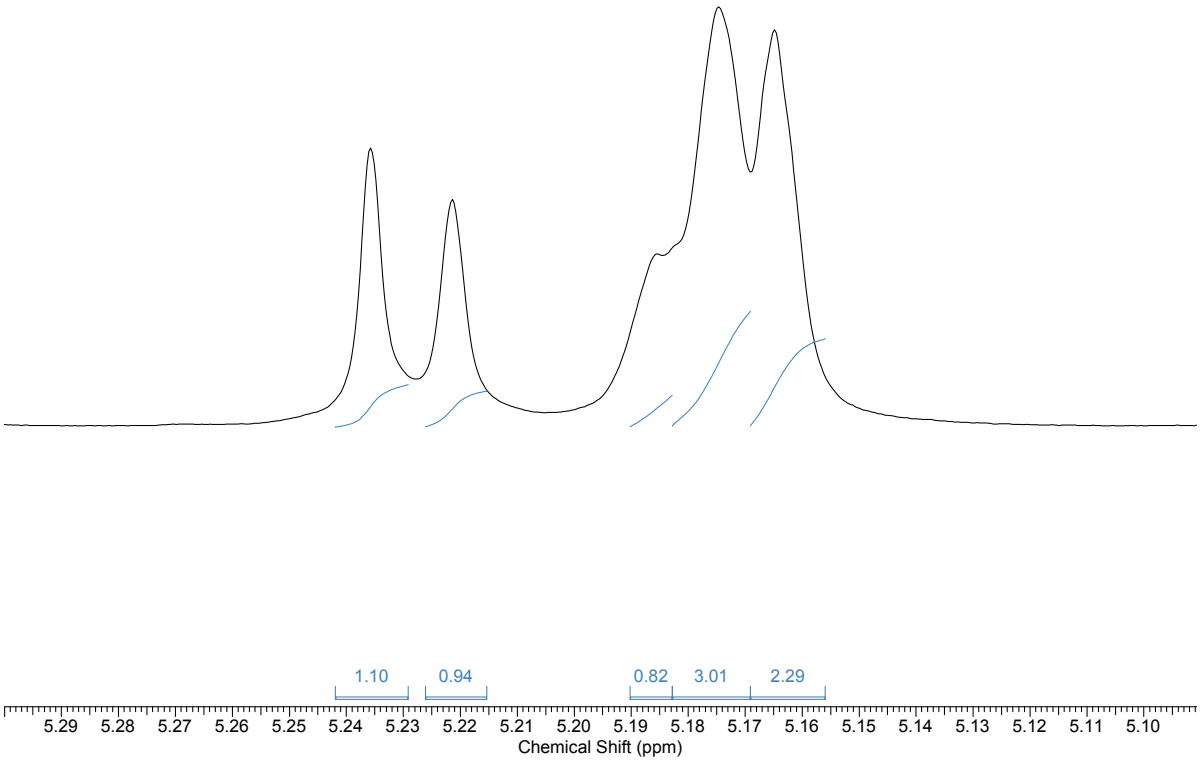
400 MHz $^{1}H\{^{1}H\}$ NMR spectrum (298 K), Table 1, Entry 5



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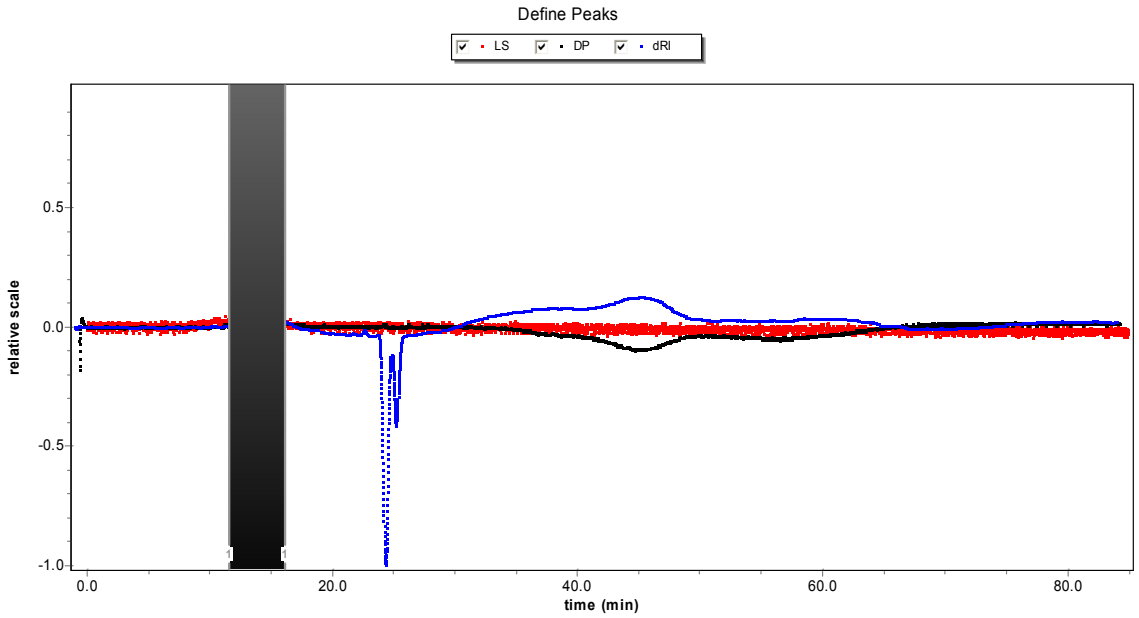

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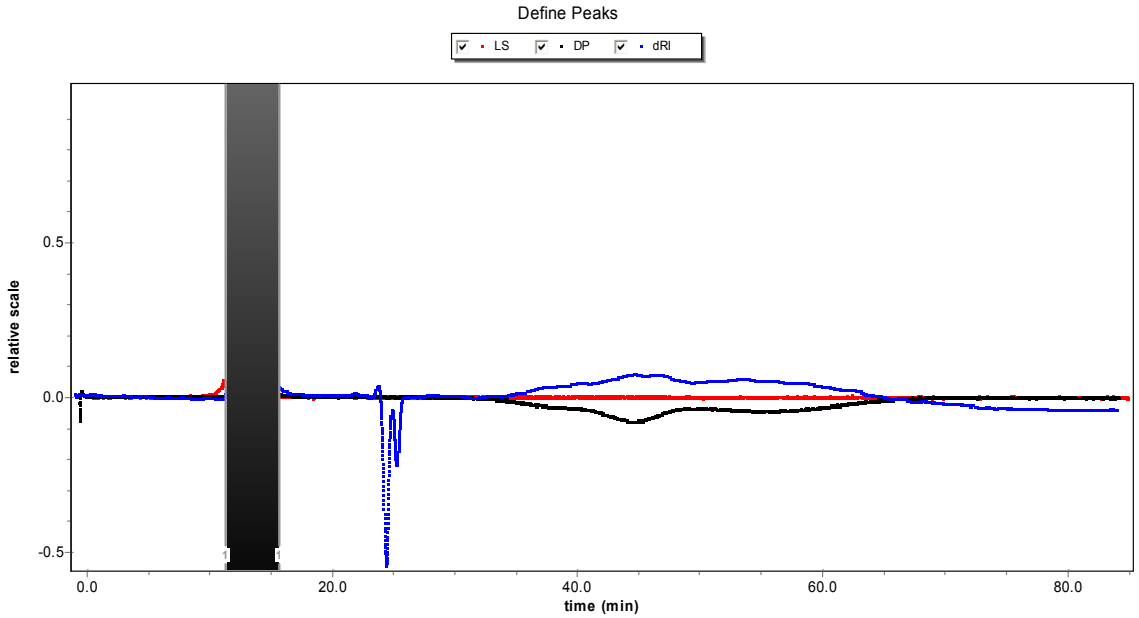

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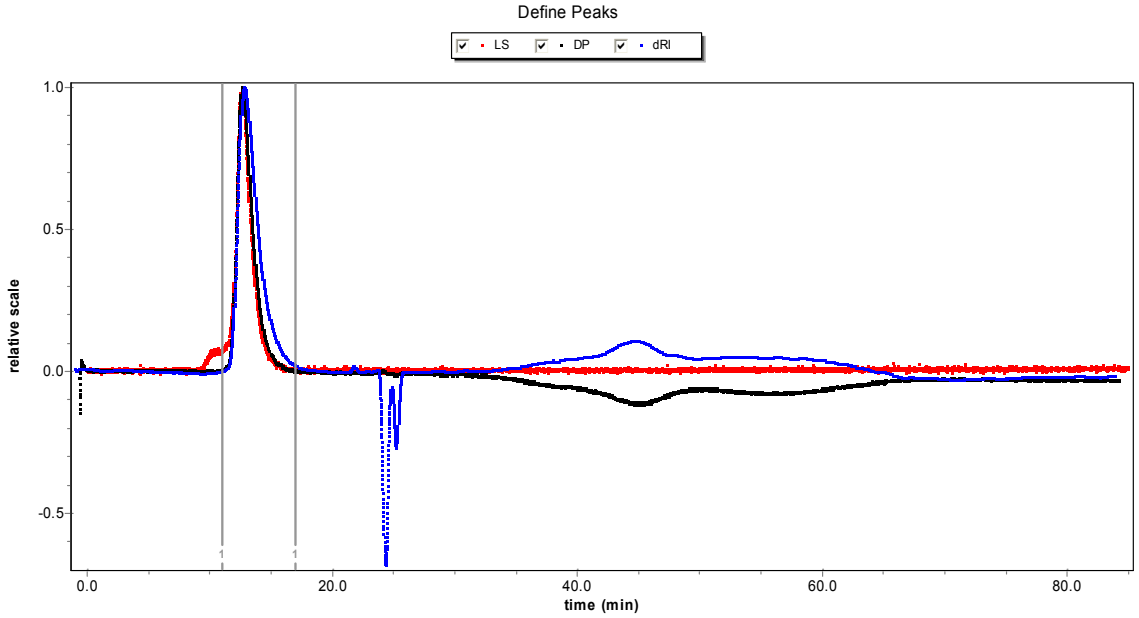

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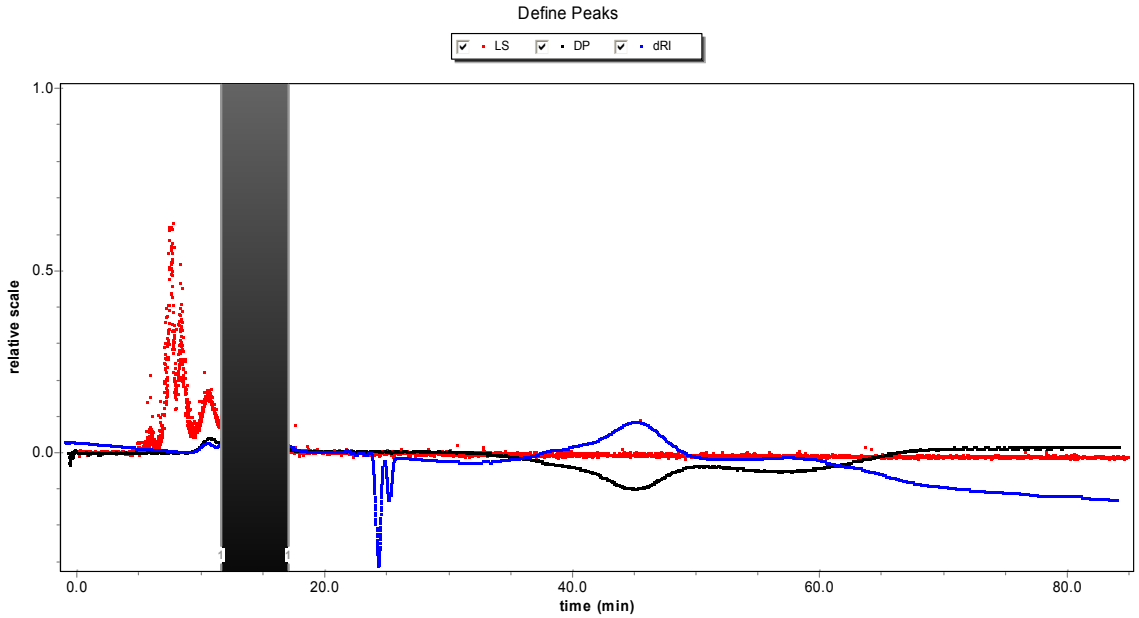

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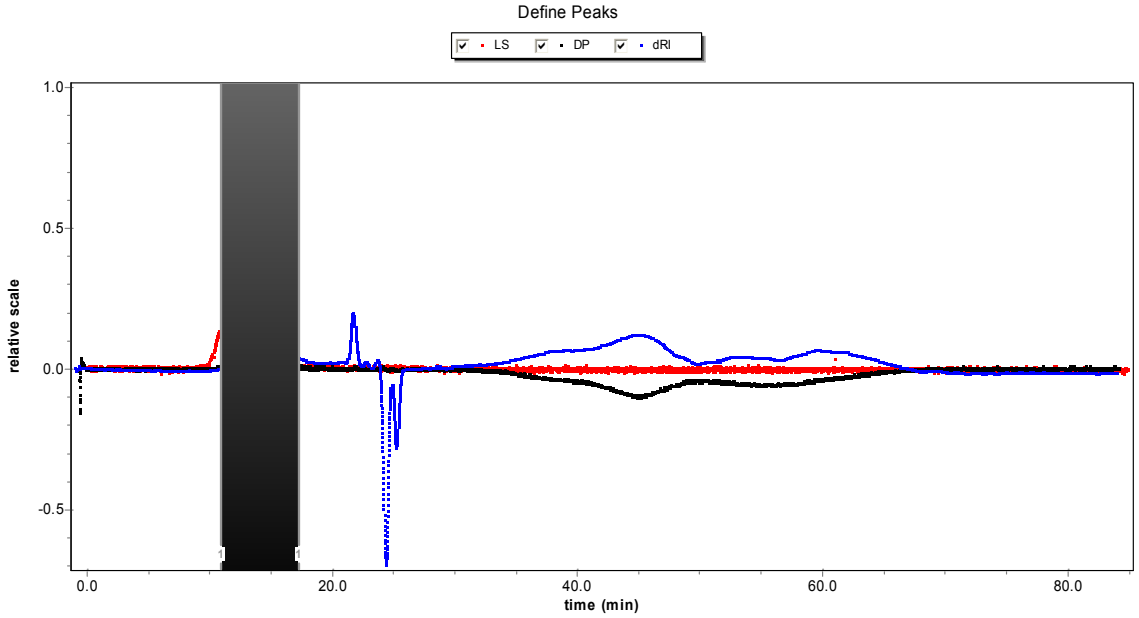

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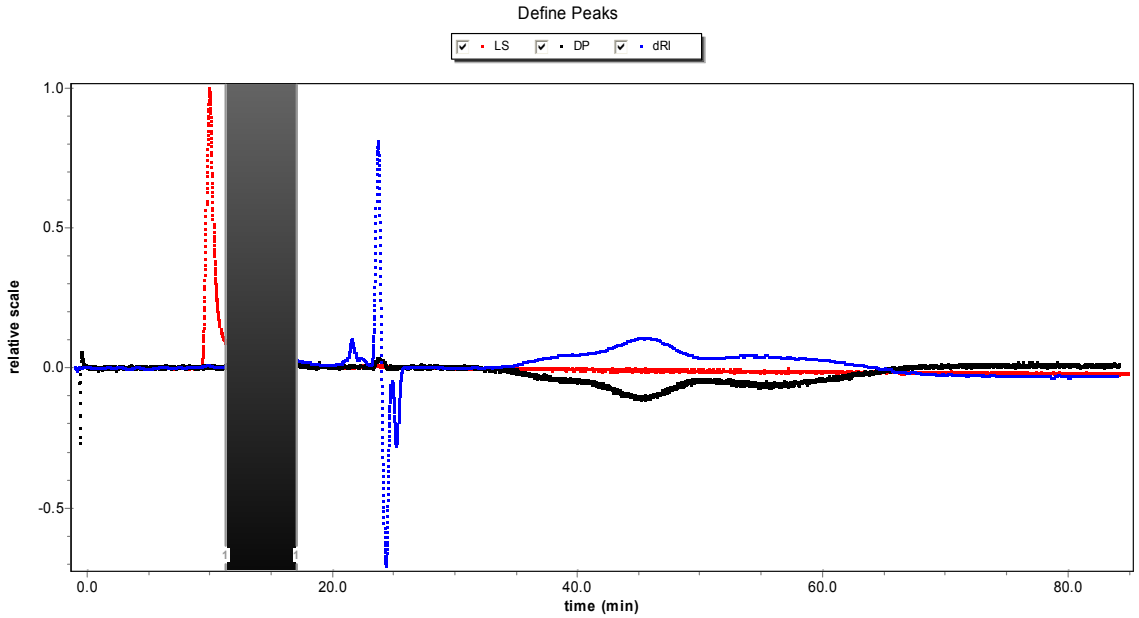


Copolymer Analysis Data

PLA-*co*-PCL

^{1}H NMR (300 MHz; $CDCl_3$) δ 5.24-5.07 (m, C(O)C*H*(CH_3)O), 4.13 (br. s, $CH_2CH_2OC(O)CH(CH_3)$, 4.06 (t, *J* 6.6 Hz, $CH_2CH_2OC(O)CH_2CH_2$), 2.39 (br. s, $CH(CH_3)OC(O)CH_2CH_2$), 2.31 (t, *J* 7.4 Hz, $CH_2CH_2OC(O)CH_2CH_2$), 1.67-1.36 (br. m, $CH(CH_3)$), $C(O)CH_2CH_2CH_2CH_2CH_2O$).

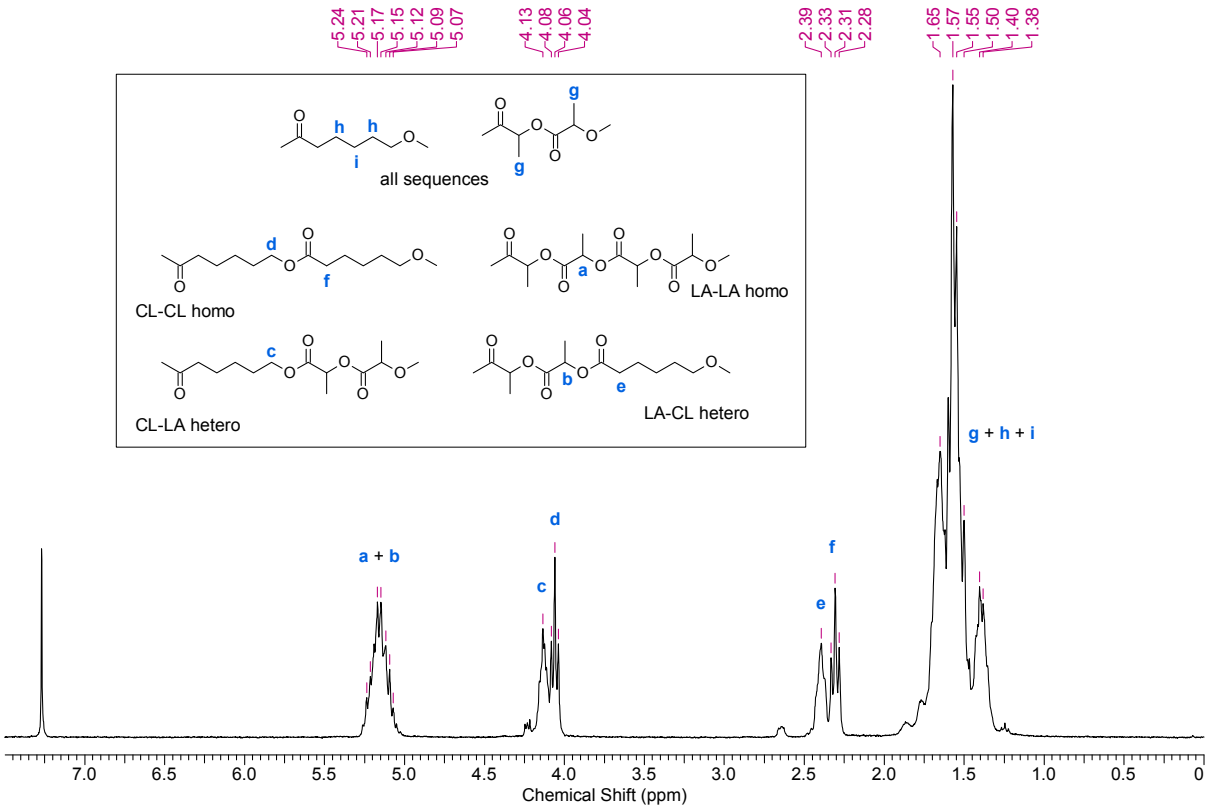
Table S3. Copolymerisation results with dn/dc values.

Entry	Catalyst	Yield (%)[a]	CL/LA (mol%)[b]	L_{CL}/ L_{LL}[c]	dn/dc[d]	M_n ($gmol^{-1}$)[d]	$M_n$theo ($gmol^{-1}$)[e]	PDI[d]
1	**1**	82	28/72	1.8/3.6	0.065	18,750	19,600	1.41
2	**1**	60	12/88	-	0.045	28,780	20,320	1.36
3	**2**	83	36/64	1.9 /2.7	0.060	19,070	19,280	1.29
4	**3**	86	28/72	1.7/3.7	0.057	22,320	19,690	1.38
5	**4**	68	54/46	3.1/4.2	0.064	19,190	18,740	1.37
6	**5**	63	8/92	-	0.051	23,660	21,400	1.38

Random polymerisation 130 °C, 24 h, [monomer]/[Ti] = 600, 0.5 g (3.45 mmol) LA, 0.38 ml (3.45 mmol) CL. dn/dc, M_n and PDI values for all copolymers were determined from the GPC trace using the Astra® programme. Results are an average of three runs. [a]Isolated yield. [b]Ratio of CL/LA determined by ^{1}H NMR. [c]Average CL and LA chain length determined by ^{13}C NMR. [d]Values determined by GPC analysis. [e]$M_n$theo = ([CL]/2[Ti] * $\%_{CL}$ * 114.14) + ([LA]/2[Ti] * $\%_{LA}$ * 144.13): based on two polymer chains growing from the Ti centre.

Ratio of CL/LA

Calculated from the ratio of the methine signal of PLA from 5.24 - 5.07 ppm to the methylene signal of PCL from 4.13 - 4.04 ppm.



Average Sequence Length (L_{CL} and L_{LL})

Calculated from $^{13}C\{^{1}H\}$ NMR spectroscopy at 273 K in $CDCl_3$ and referenced to residual solvent. NMR experiments were run using the *inverse gated* function, with a 1.8 s acquisition time, 9.15 µs pulse width at a resonance frequency of 75 MHz. A minimum of 15,000 scans were required using a ~50 $mgml^{-1}$ solution. Sequence length was determined using adjusted equations from Kasperczyk and Bero to incorporate the effects of transesterification.[8]

$$L_{LL} = \frac{\frac{1}{2}(LLL + LLC + CLL + CLC)}{(CLC + \frac{1}{2}(LLC + CLL)}$$

$$L_{CL} = \frac{(LCL + CCL + LCC + CCC)}{(LCL + \frac{1}{2}(CCL + LCC)}$$

Where:

$$LLL = \tfrac{1}{2}(c+g) + \tfrac{1}{2}d + \tfrac{1}{3}(b+e) + a \qquad LLC = \tfrac{1}{2}d + \tfrac{1}{2}f + \tfrac{1}{3}(b+e)$$

$$CLL = \tfrac{1}{2}(c+g) + \tfrac{1}{2}f + \tfrac{1}{3}(b+e) \qquad CLC = l$$

$$LCL = h + m \qquad CCL = i + o$$

$$LCC = j + o \qquad CCC = k$$

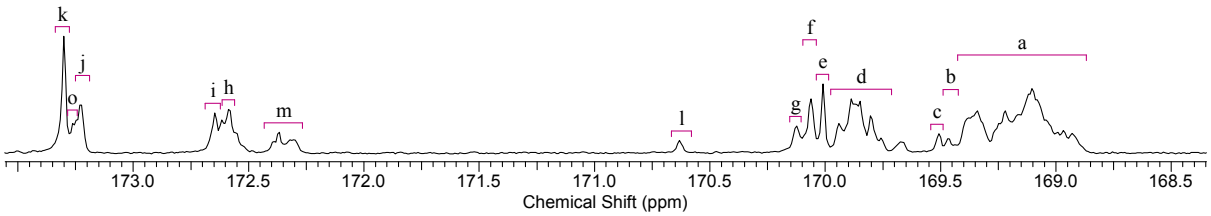
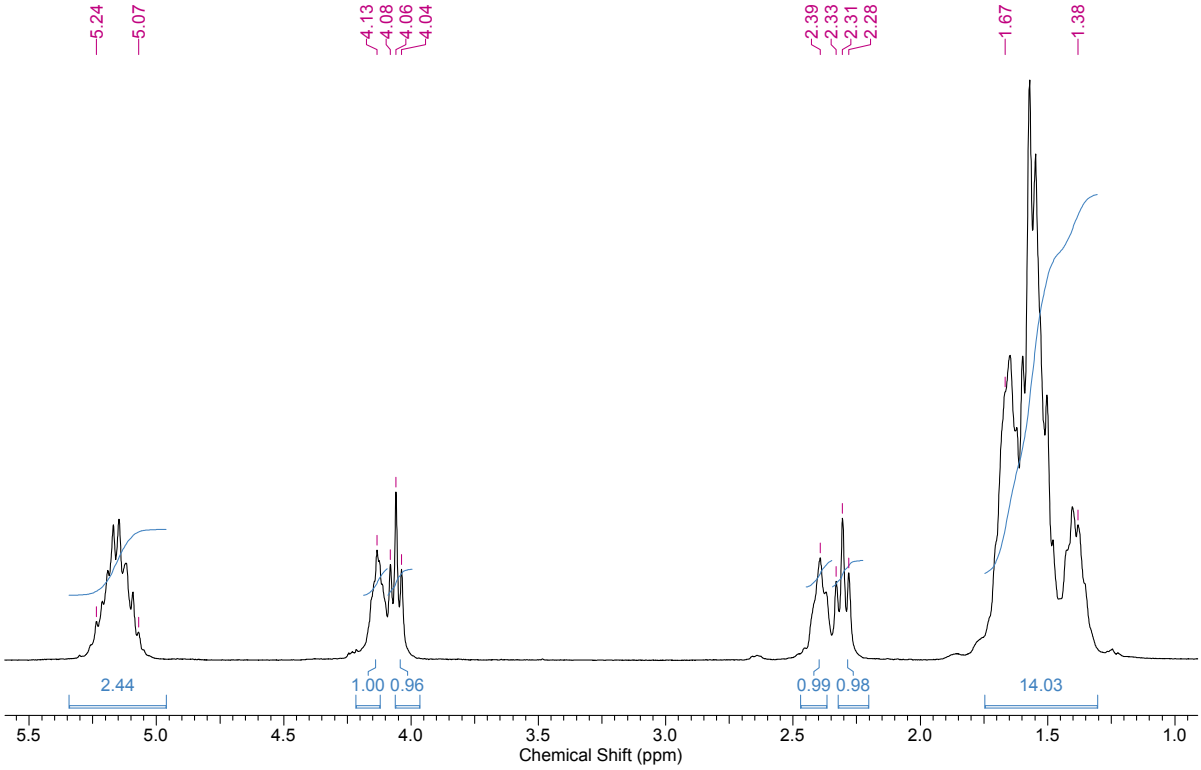
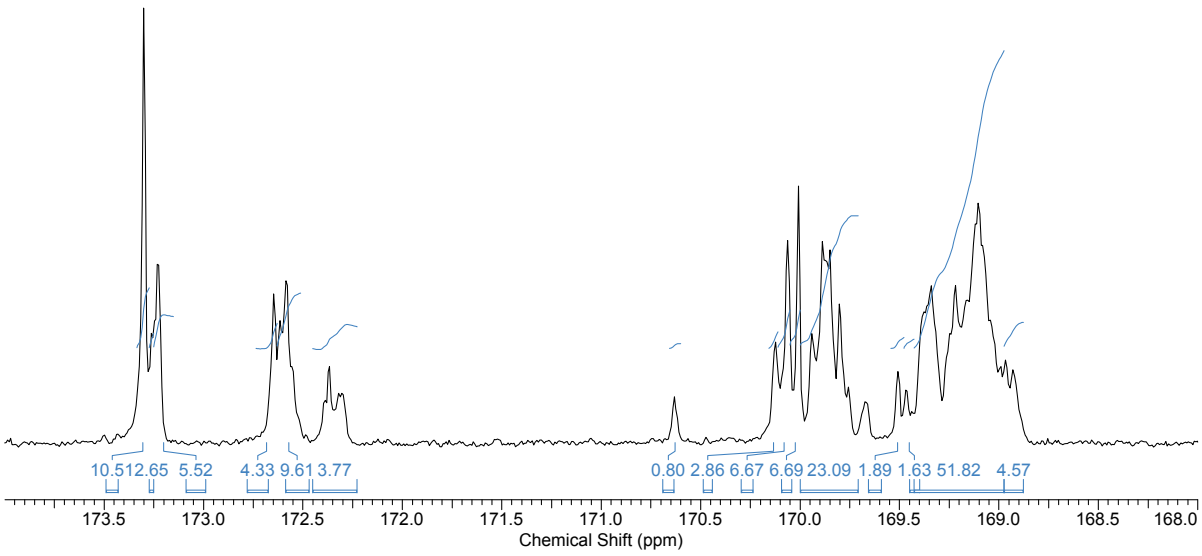


Table S3, Entry 1

300 MHz ^{1}H NMR spectrum (298 K), Table S3, Entry 1



75 MHz ^{13}C{^{1}H} Inv. Gate NMR spectrum (298 K), Table S3, Entry 1



GPC trace

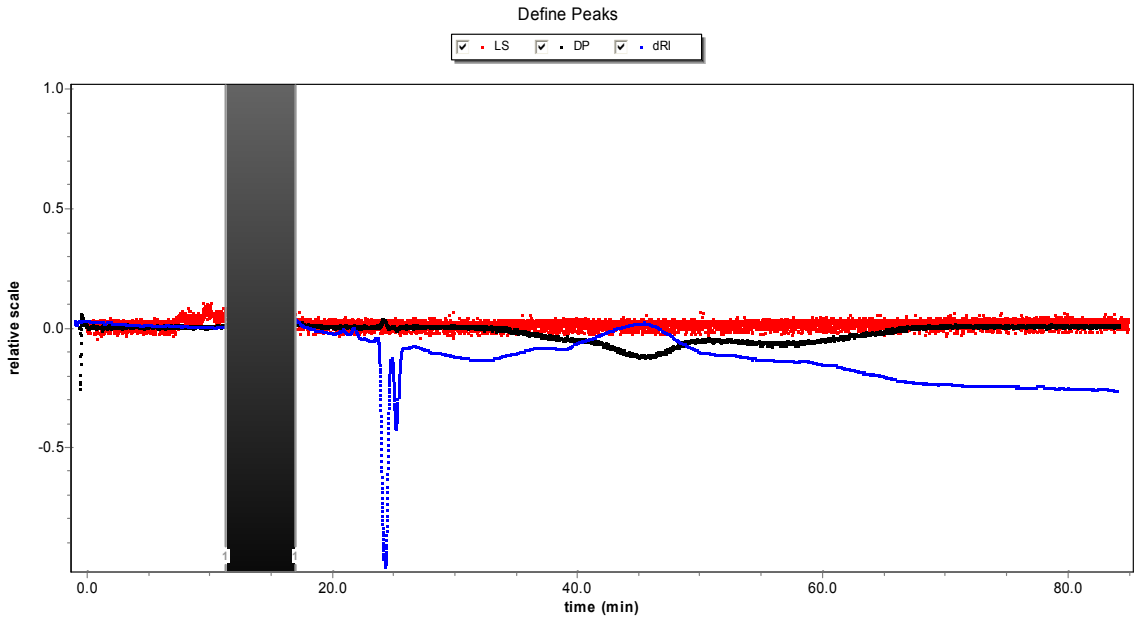
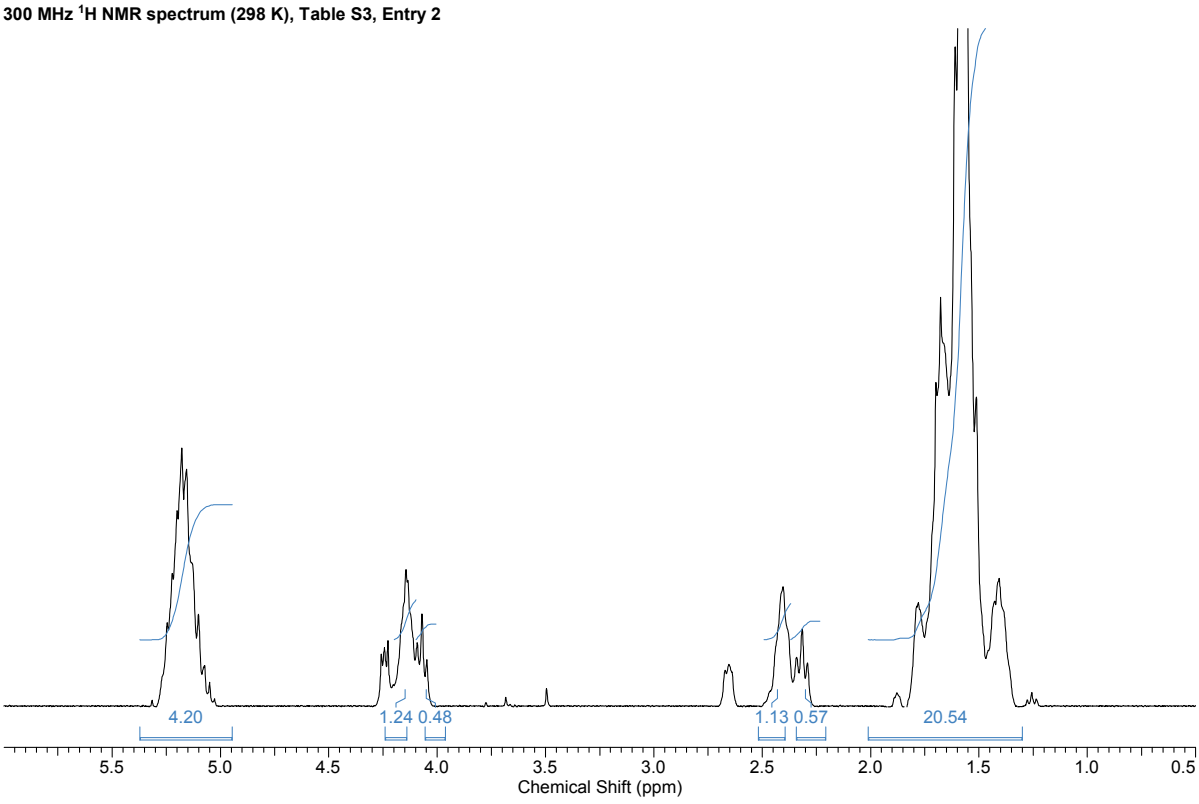


Table S3, Entry 2



GPC trace

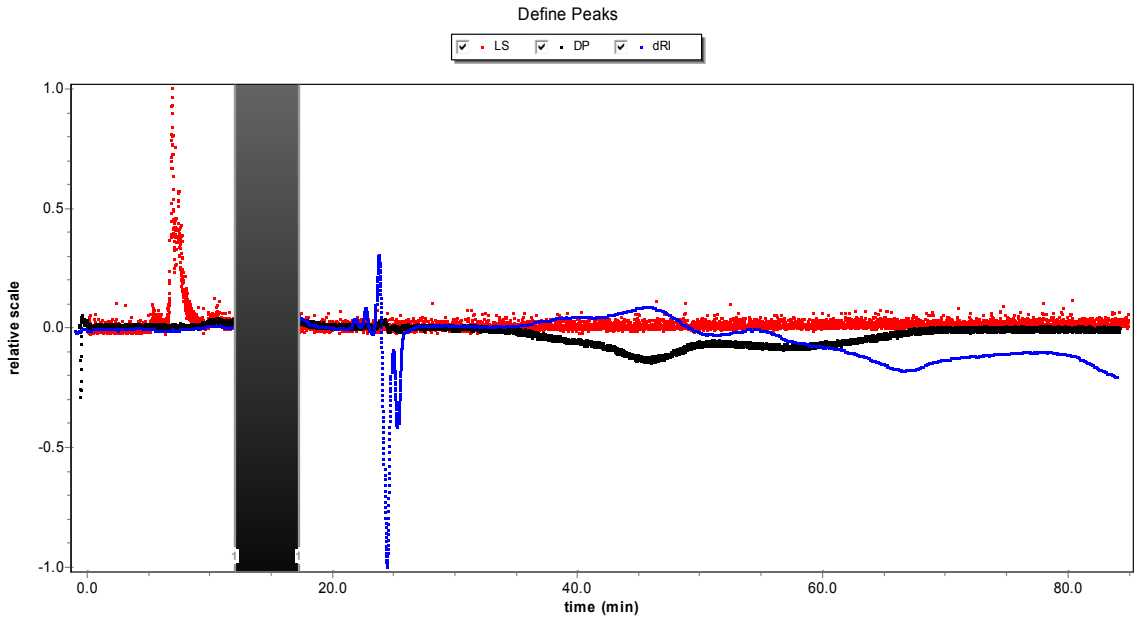
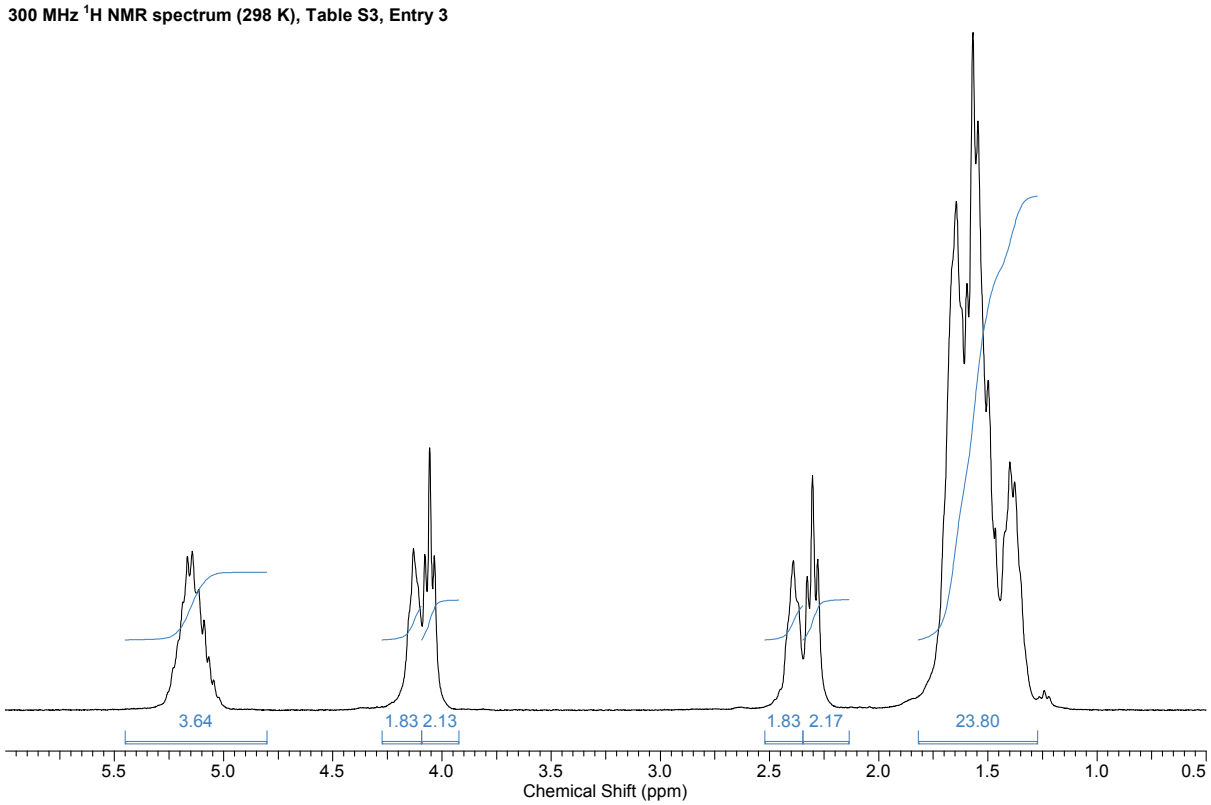
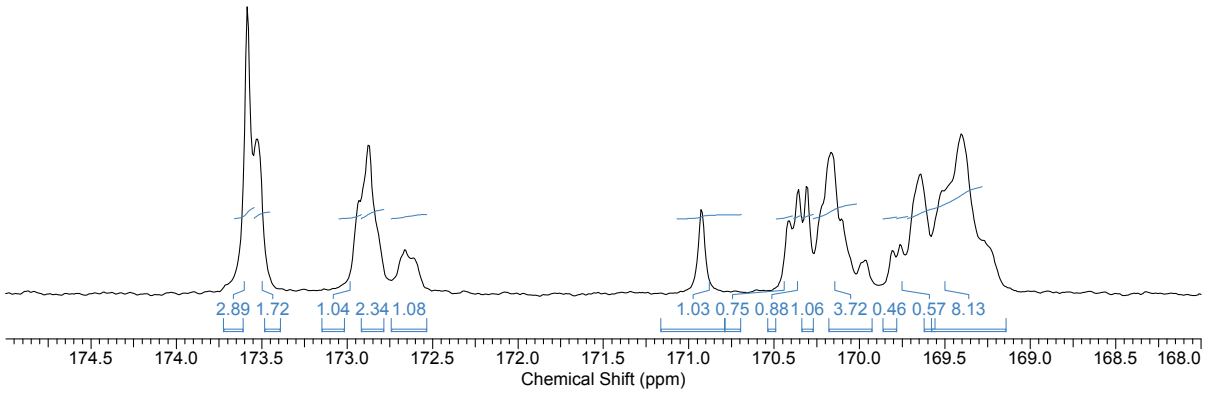


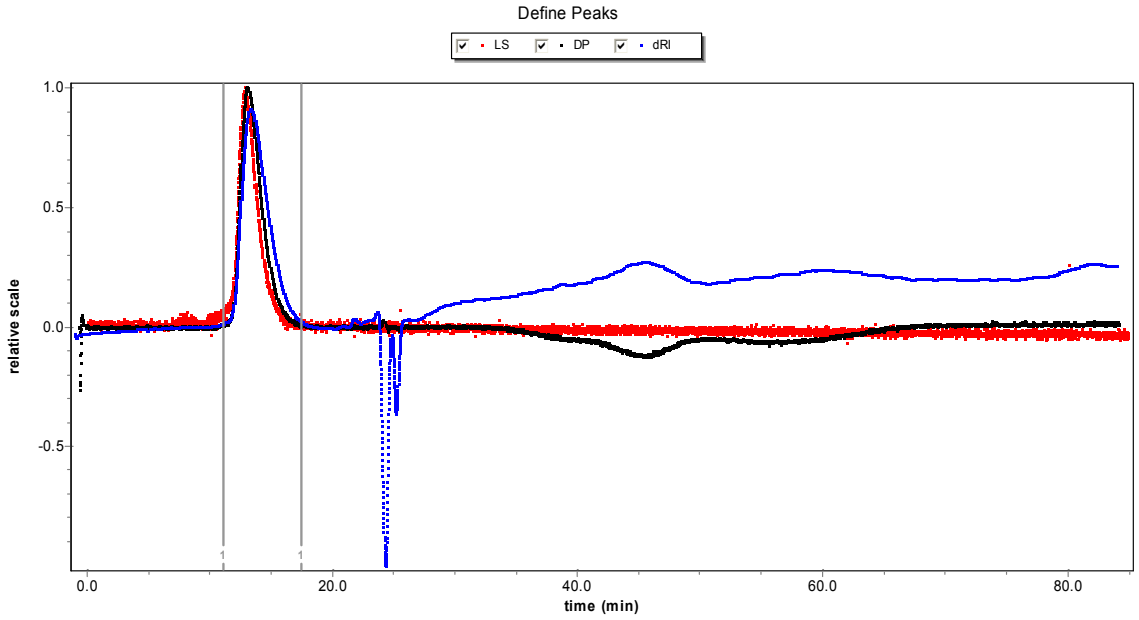
Table S3, Entry 3



75 MHz $^{13}C\{^{1}H\}$ Inv. Gate NMR spectrum (298 K), Table S3, Entry 3



GPC trace



DSC trace

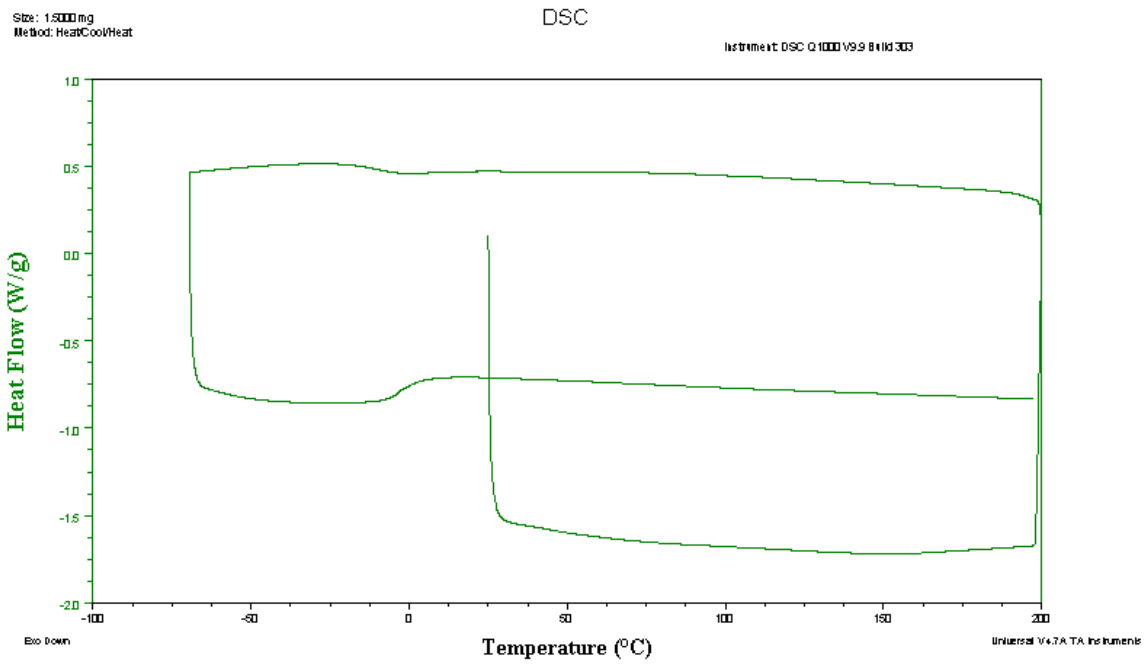


Chart S1: Profile of the consumption of LA and CL during copolymerisation using **2,** measured by integration of the unreacted LA and CL in the ^{1}H NMR spectrum ($CDCl_3$) using 1,3,5-trimethoxybenzene as a standard.

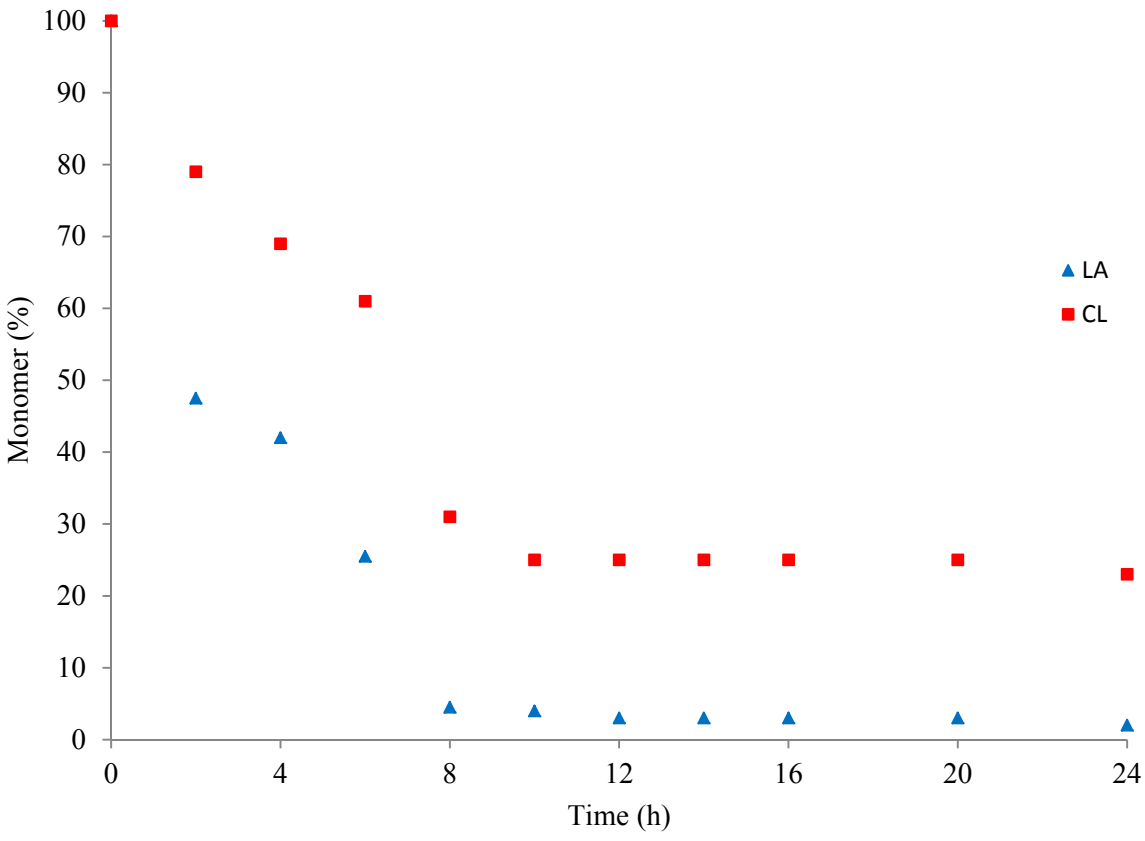


Chart S2: Monitoring the presence of homo- and hetero-diads during copolymerisation with **2**, measured as a ratio by integration of the homo and hetero sequences in the ^{1}H NMR spectrum (d^{6}-DMSO).

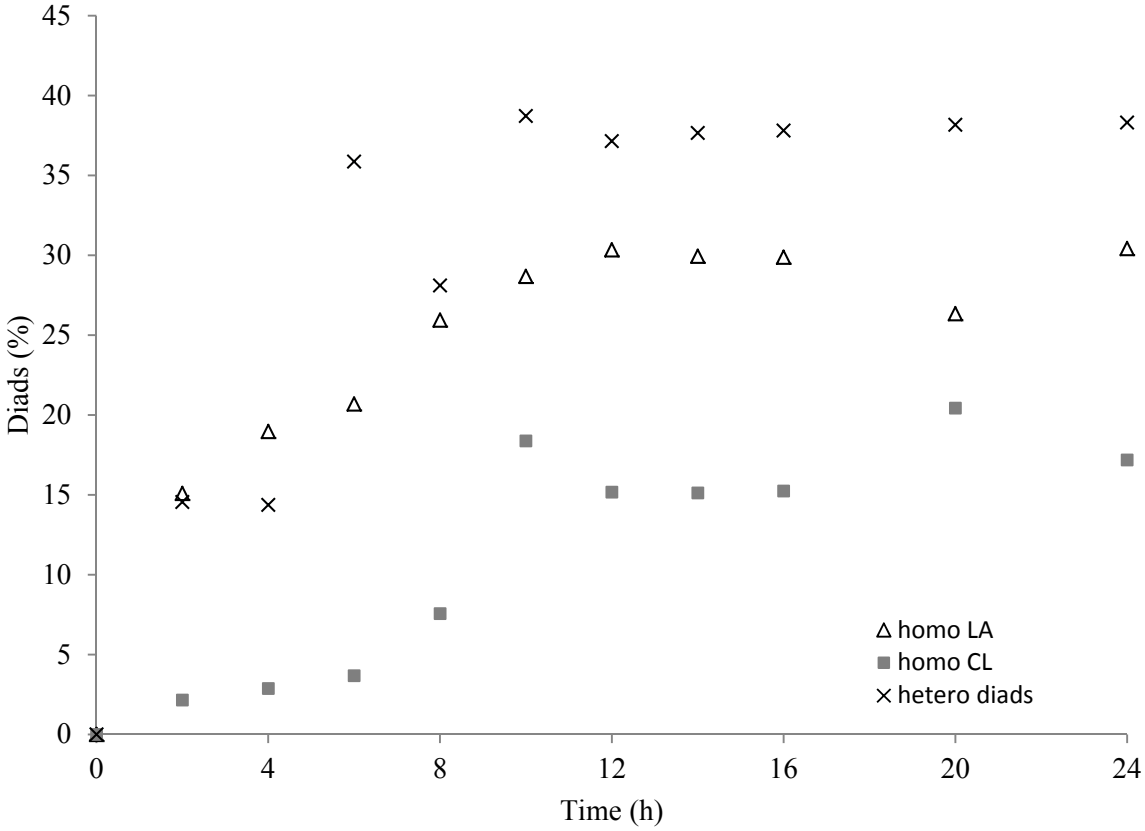
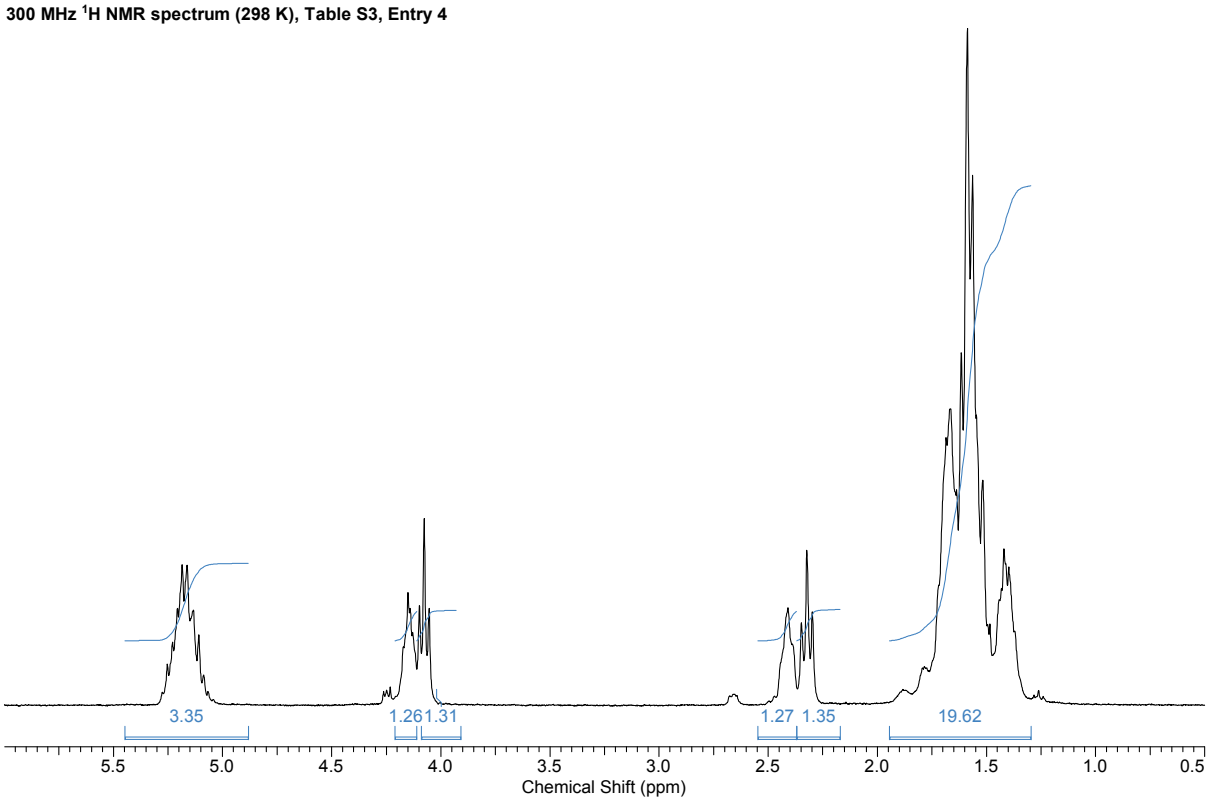
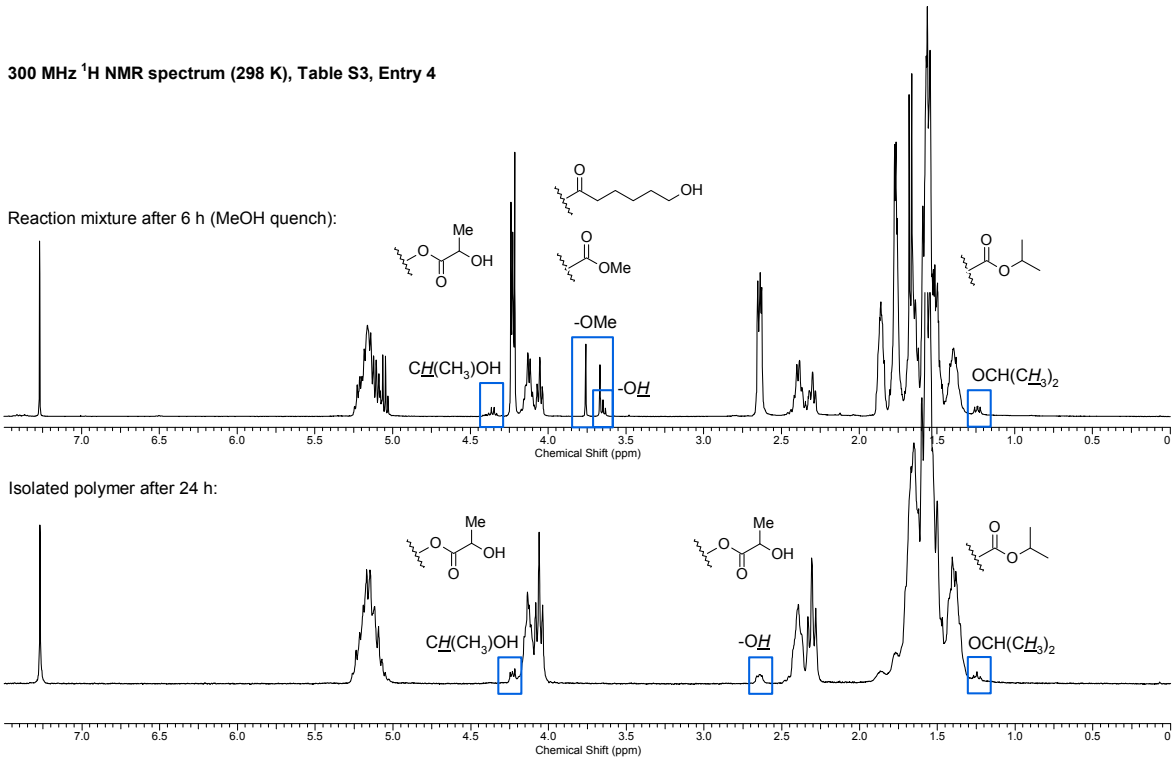


Table S3, Entry 4

300 MHz ^{1}H NMR spectrum (298 K), Table S3, Entry 4

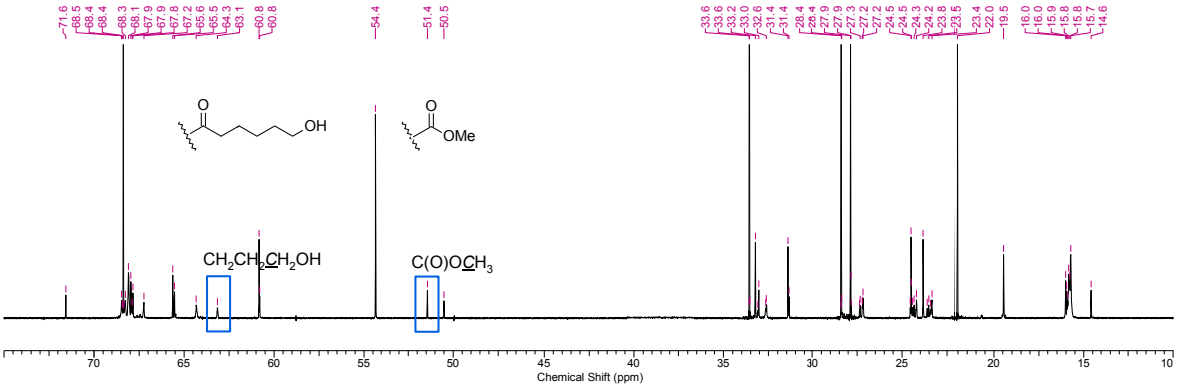


300 MHz ^{1}H NMR spectrum (298 K), Table S3, Entry 4

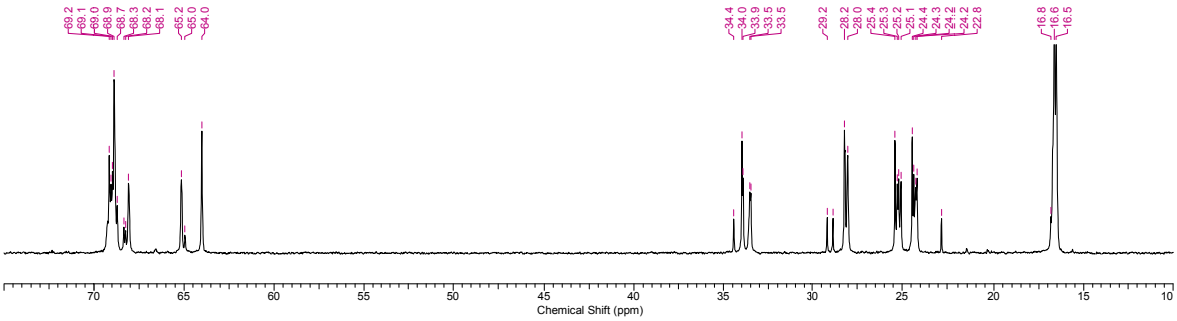


300 MHz ^{13}C NMR spectrum (298 K), Table S3, Entry 4

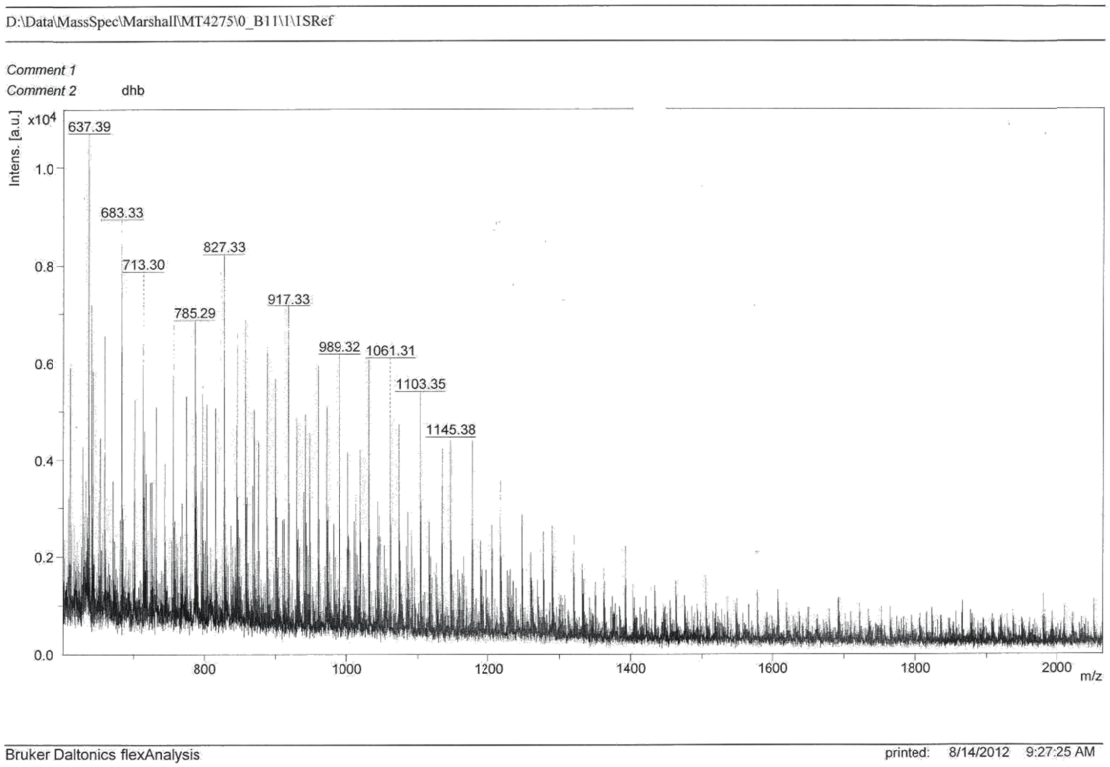
Reaction mixture after 6 h (MeOH quench):

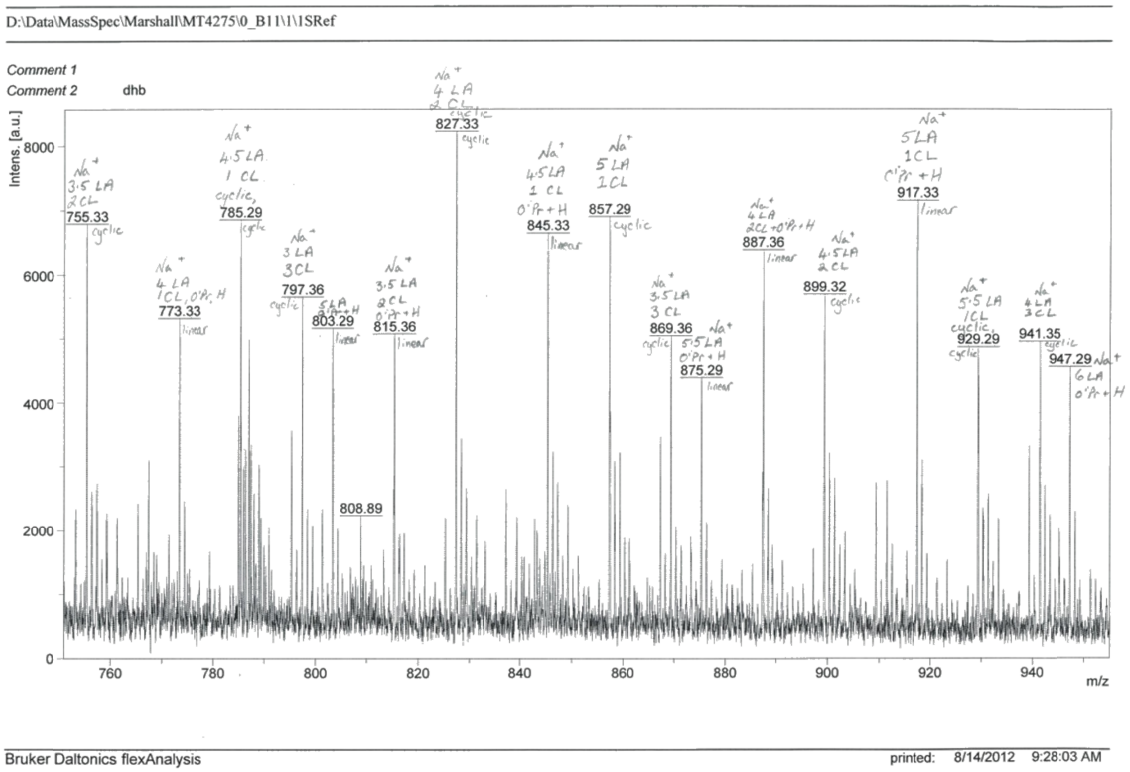


Isolated polymer after 24 h:

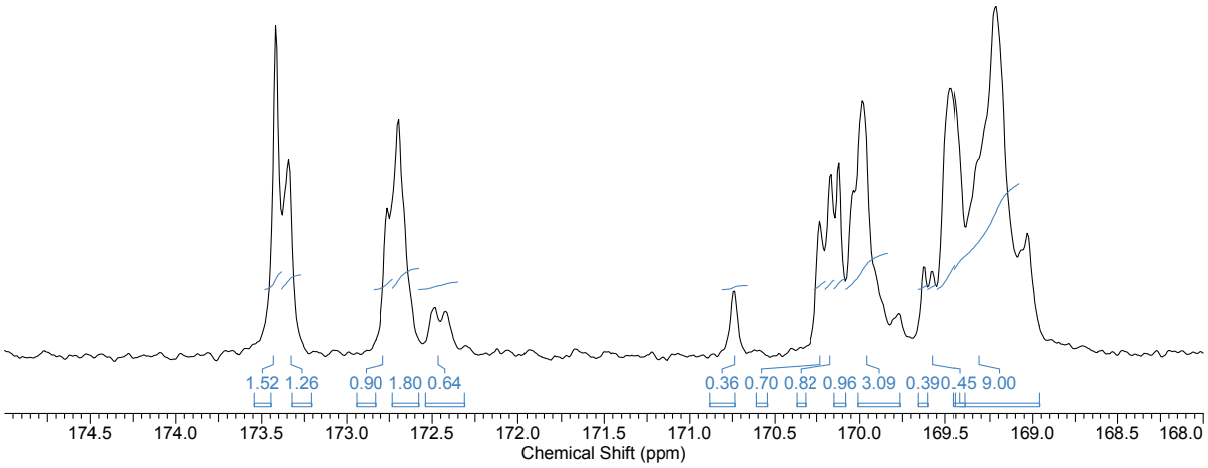


MALDI-TOF spectra





75 MHz $^{13}C\{^{1}H\}$ Inv. Gate NMR spectrum (298 K), Table S3, Entry 4



GPC trace

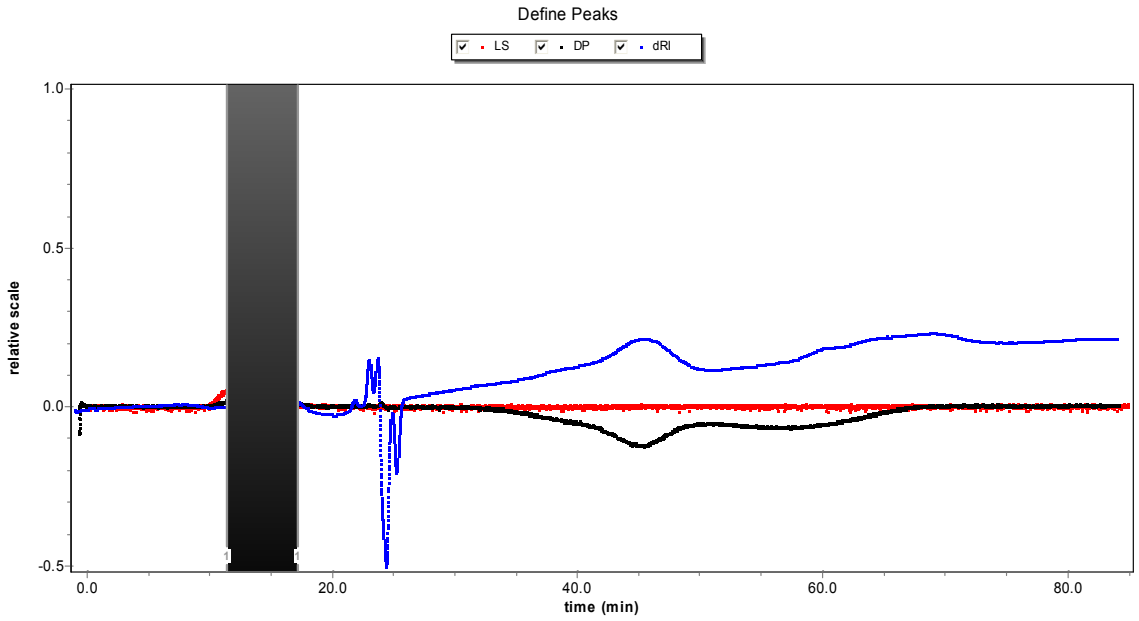
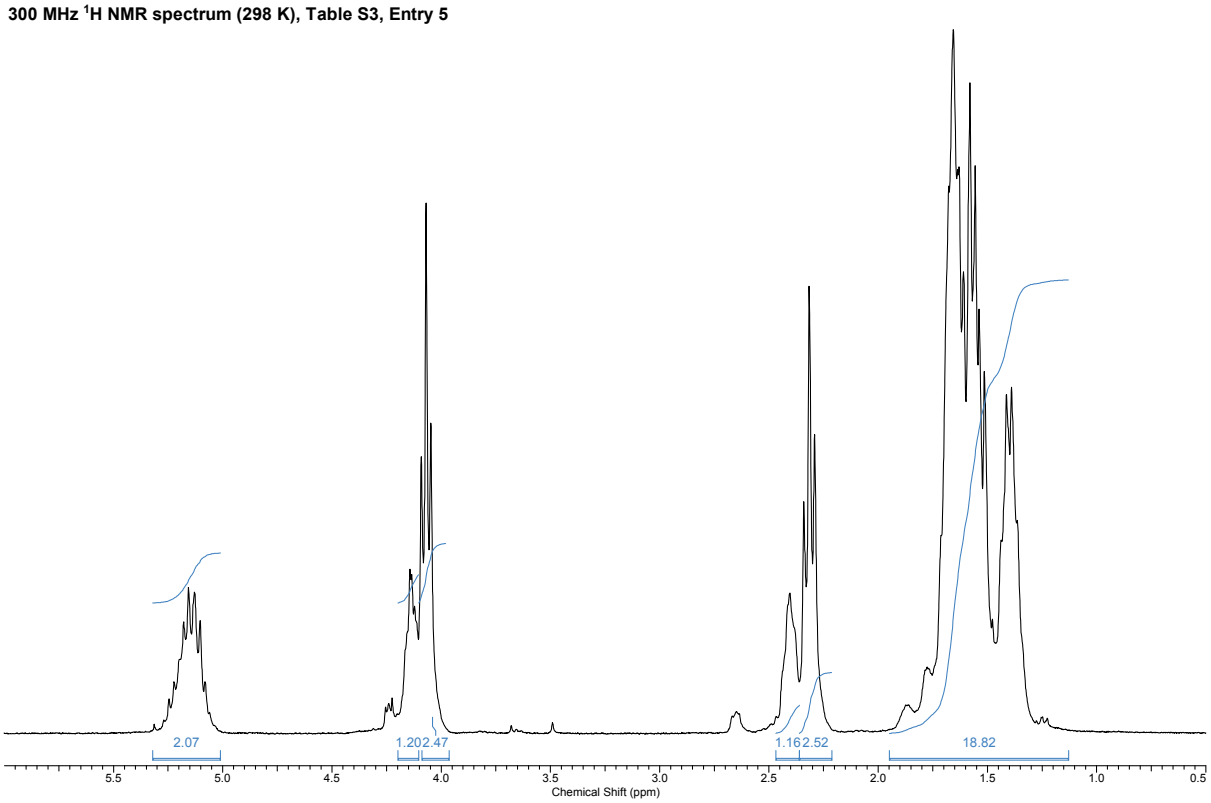
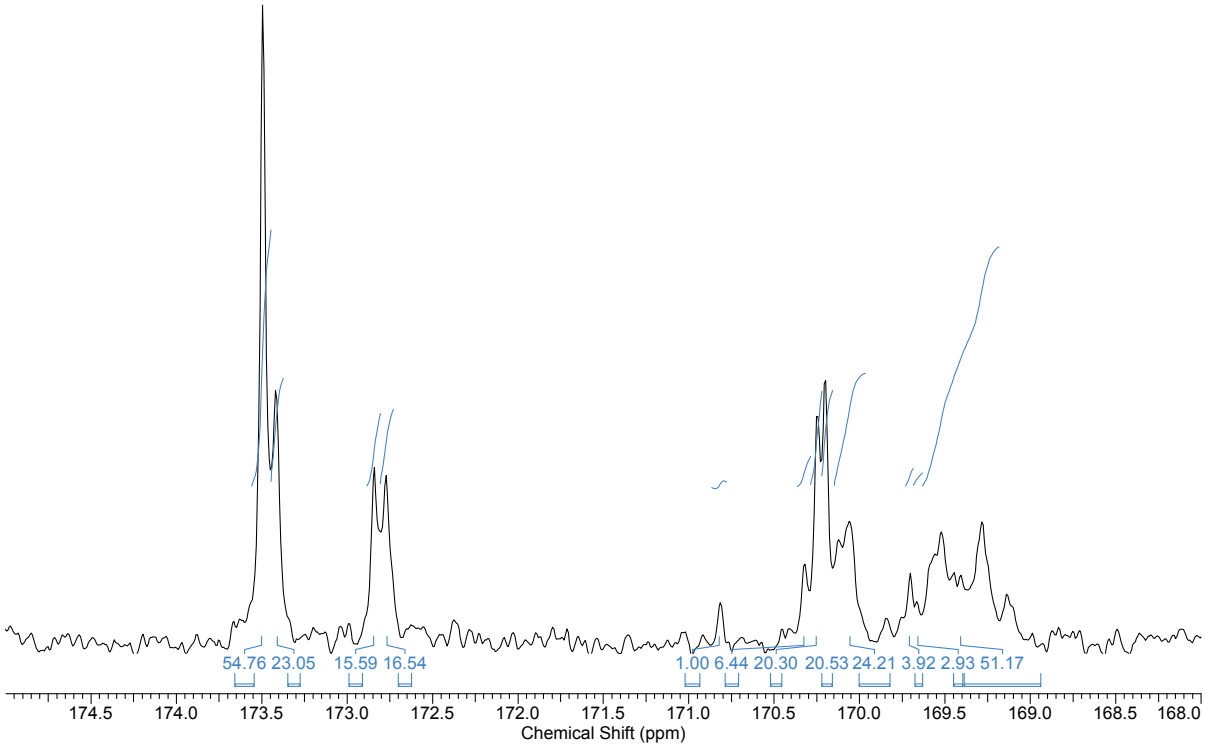

Define Peaks
LS
DP
dRI
1.0
0.5
0.0
-0.5
relative scale
0.0
20.0
40.0
60.0
80.0
time (min)

Table S3, Entry 5

300 MHz ^{1}H NMR spectrum (298 K), Table S3, Entry 5



75 MHz ^{13}C{^{1}H} Inv. Gate NMR spectrum (298 K), Table S3, Entry 5



GPC trace

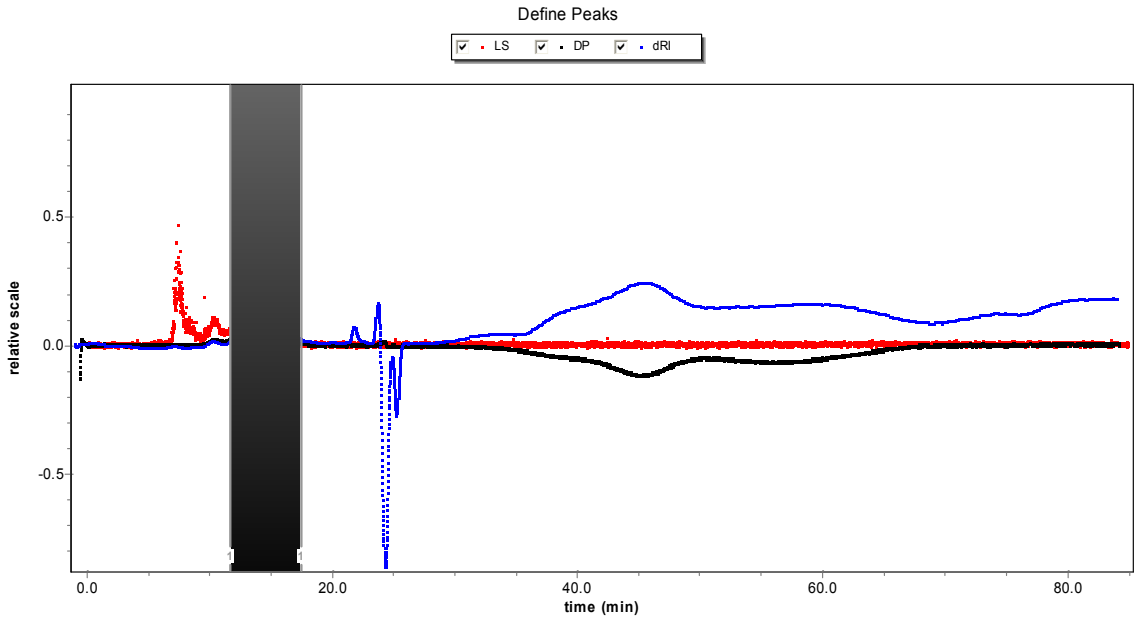
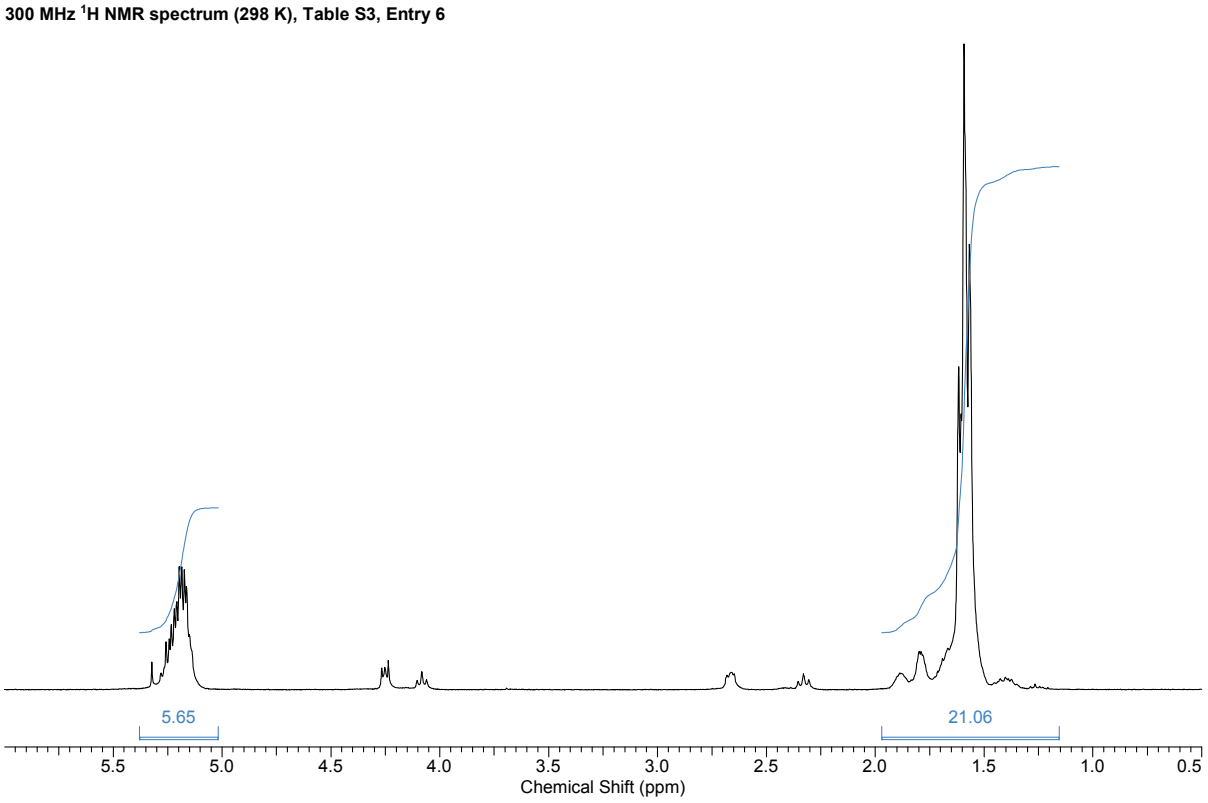
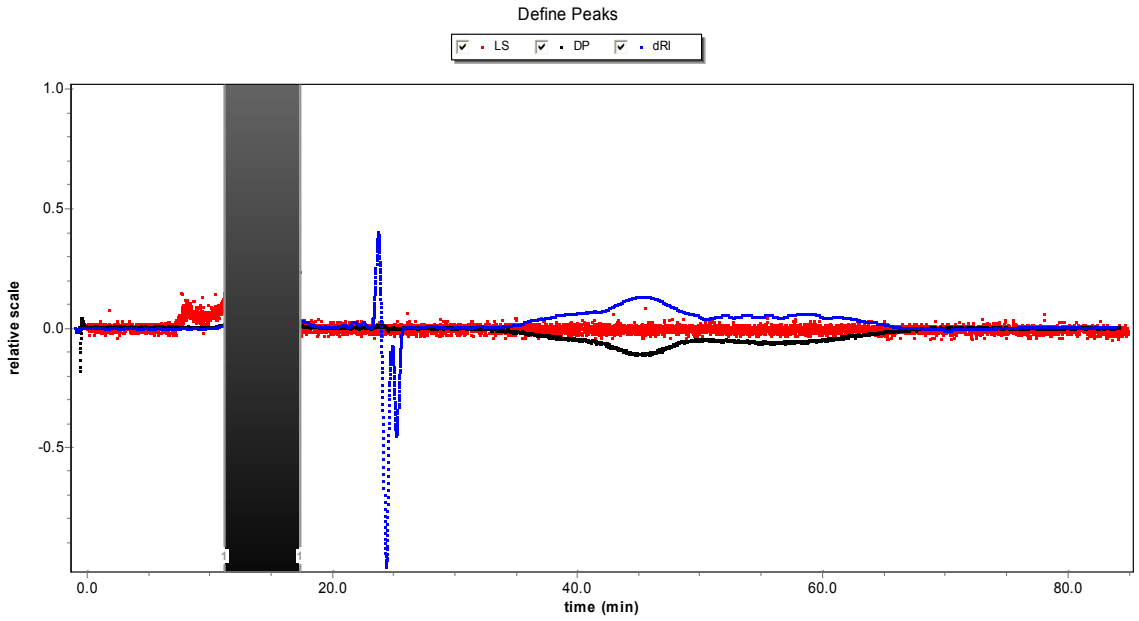


Table S3, Entry 6



GPC trace



References

1) A. Gissot and J. Rebek, *J. Am. Chem. Soc.*, 2004, **126**, 7424.

2) D. R. Burfield and R. H. Smithers, *J. Org. Chem.* 1983, **48**, 2420.

3) Bruker-AXS SAINT, Madison, Wisconsin.

4) G. M. Sheldrick, SADABS V2008/1 or TWINABS V2008/4, University of Göttingen, Germany.

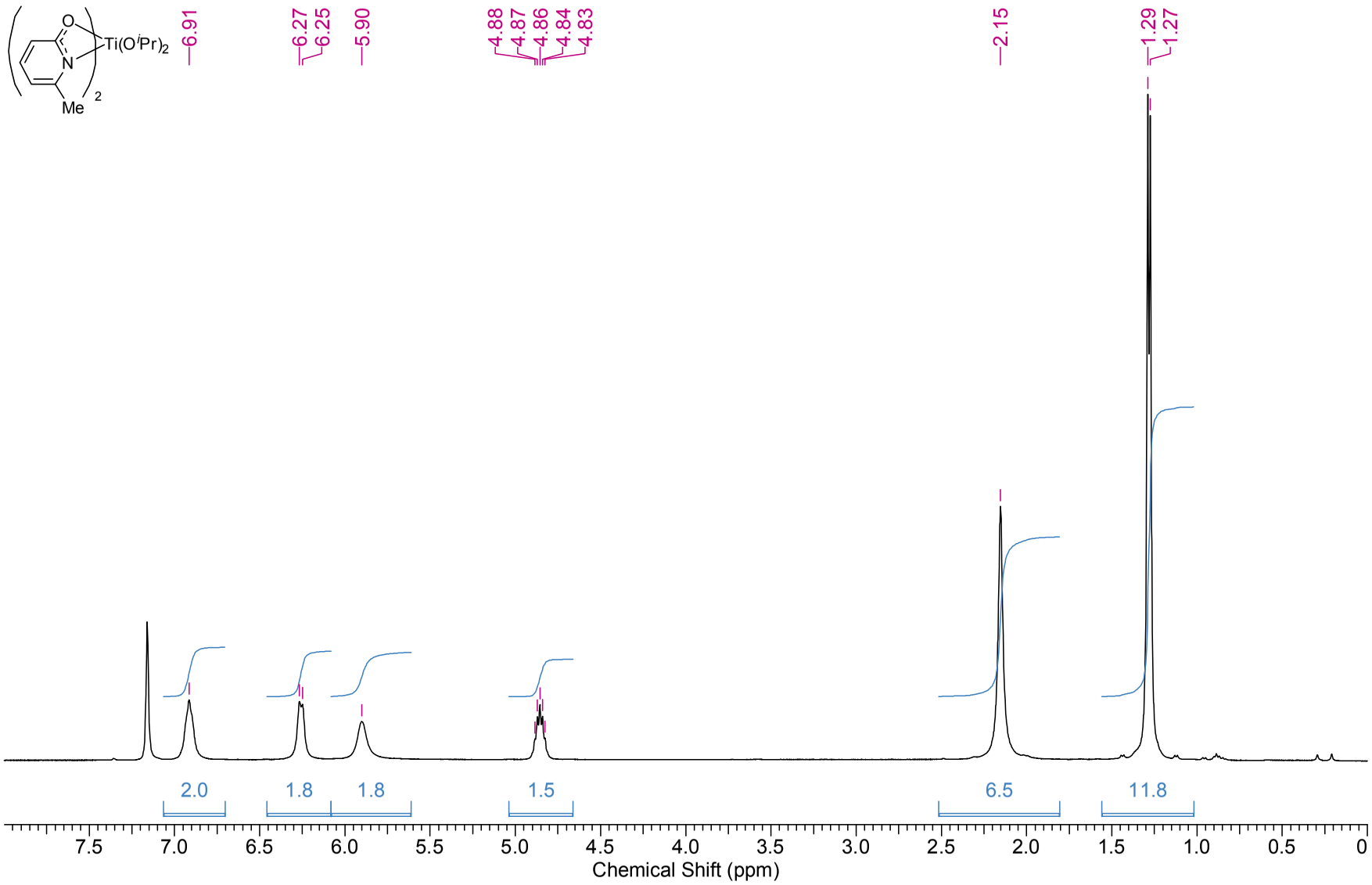
5) G. M. Sheldrick, *Acta Cryst.* **A64**, 2008, 112.

6) a) K. Matyjaszewski and A. H. E. Müller, *Controlled and Living Polymerizations: From Mechanisms to Applications*, Wiley, 2009; b) G. Odian, *Principles of Polymerization,* Wiley, 2004; c) H. Brody, M. Ladacki, R. Milkovitch and M. Szwarc, *J. Polym. Sci.*, 1957, **25**, 221; d) P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.

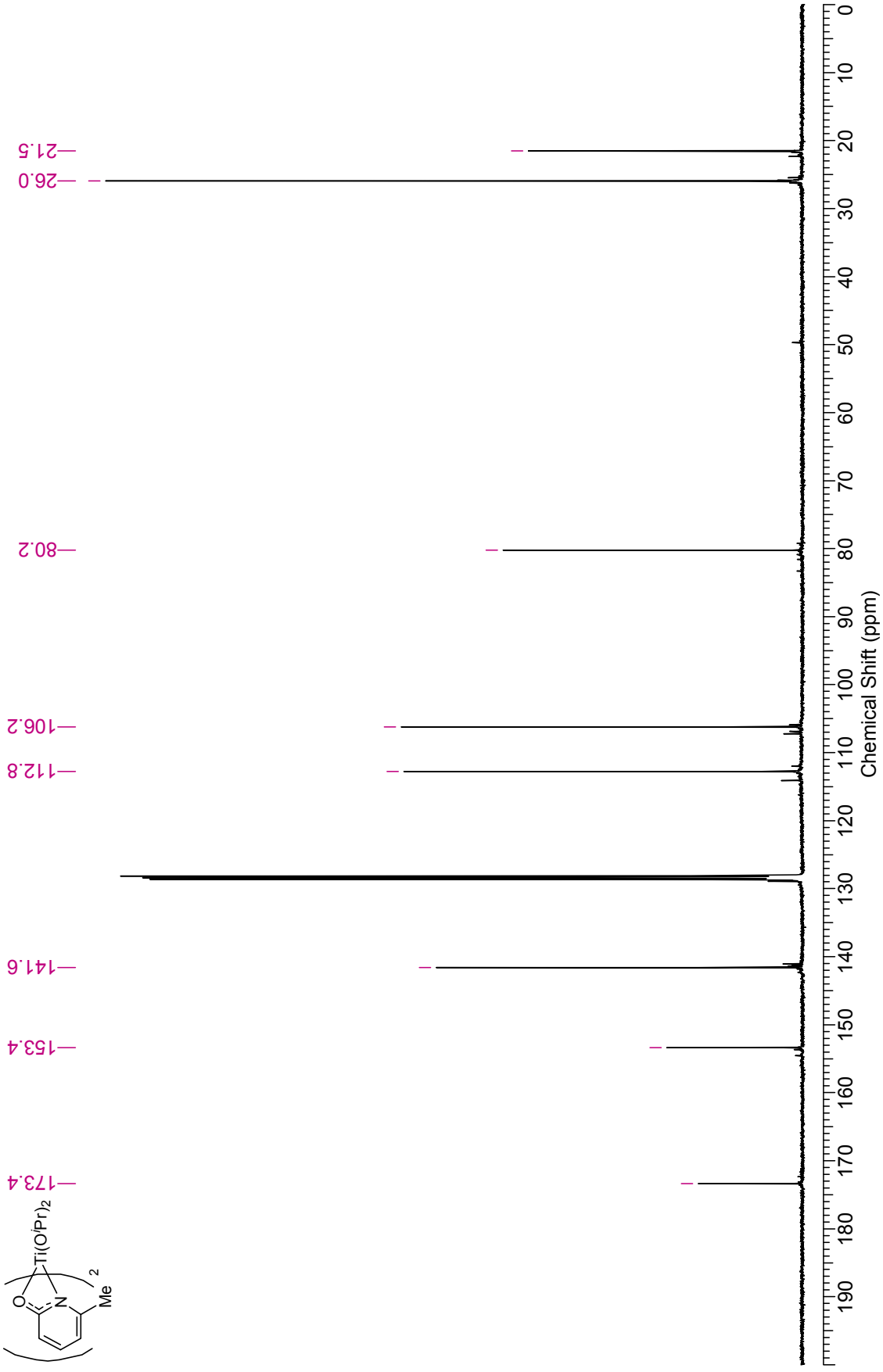
7) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229.

8) J. Kasperczyk and M. Bero, *Makromol. Chem.*, 1993, **194**, 913.

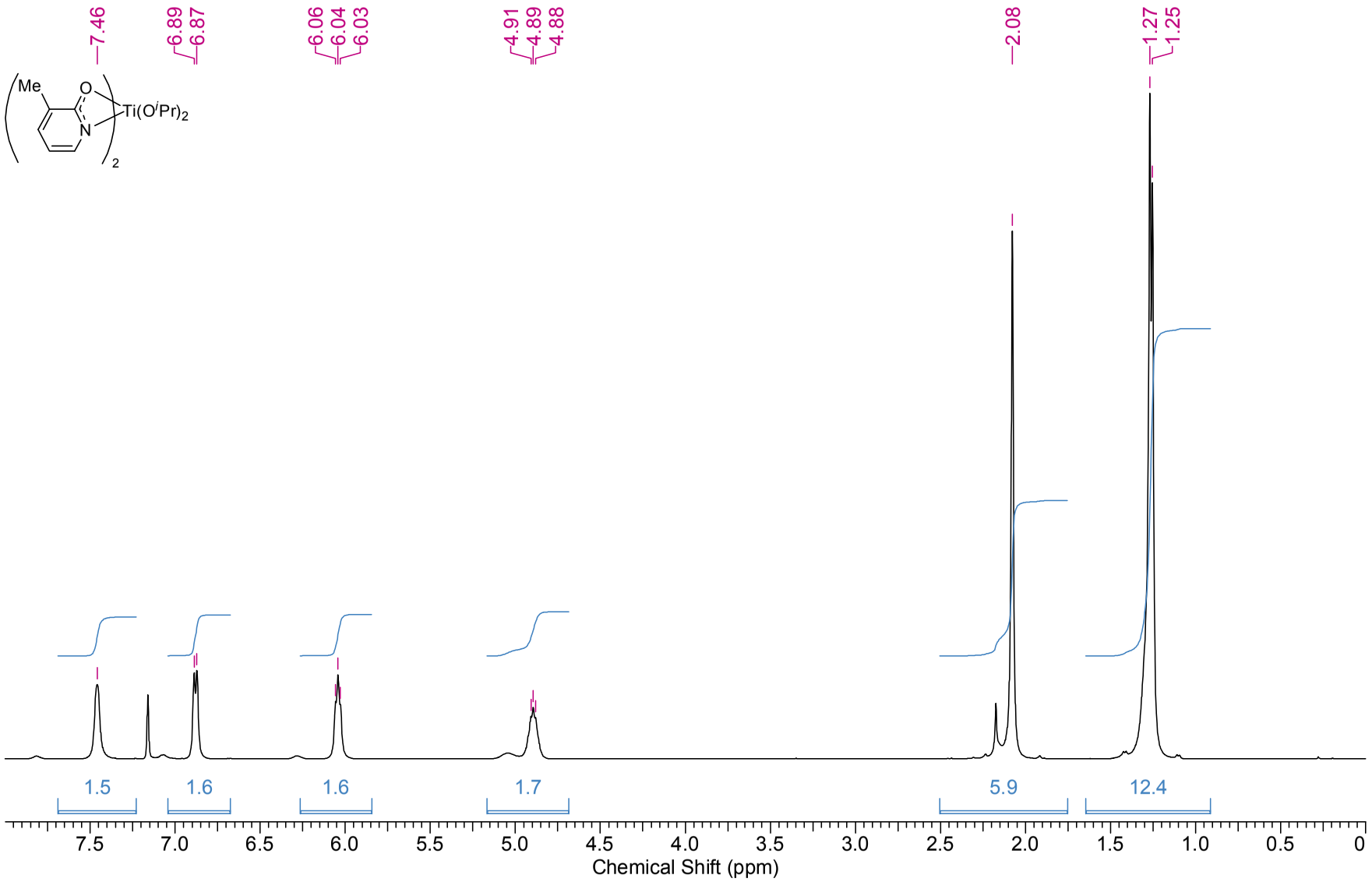
300 MHz ^{1}H NMR spectrum (298 K) for compound 1



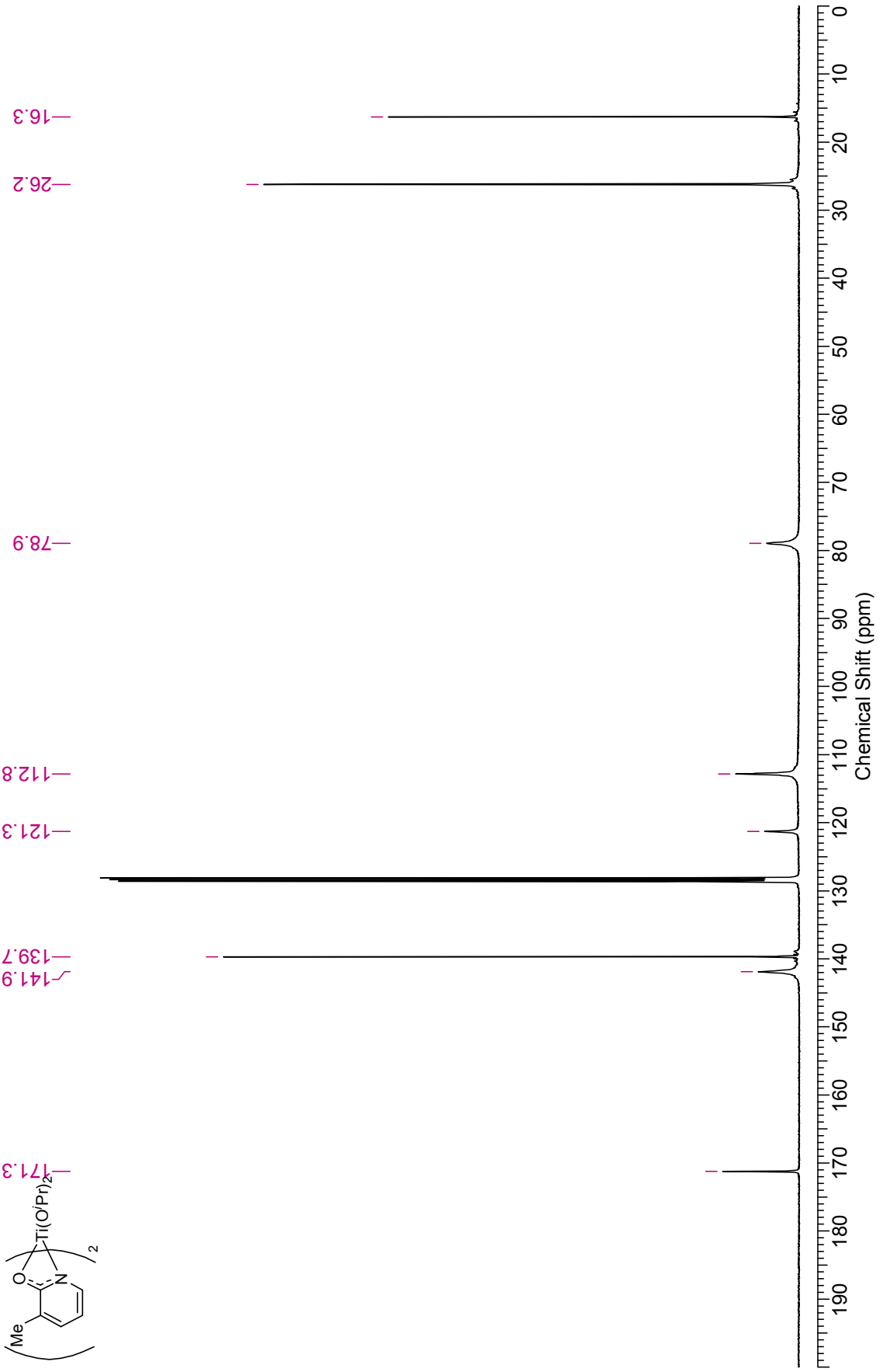
100 MHz $^{13}C\{^{1}H\}$ NMR spectrum (298 K) for compound 1



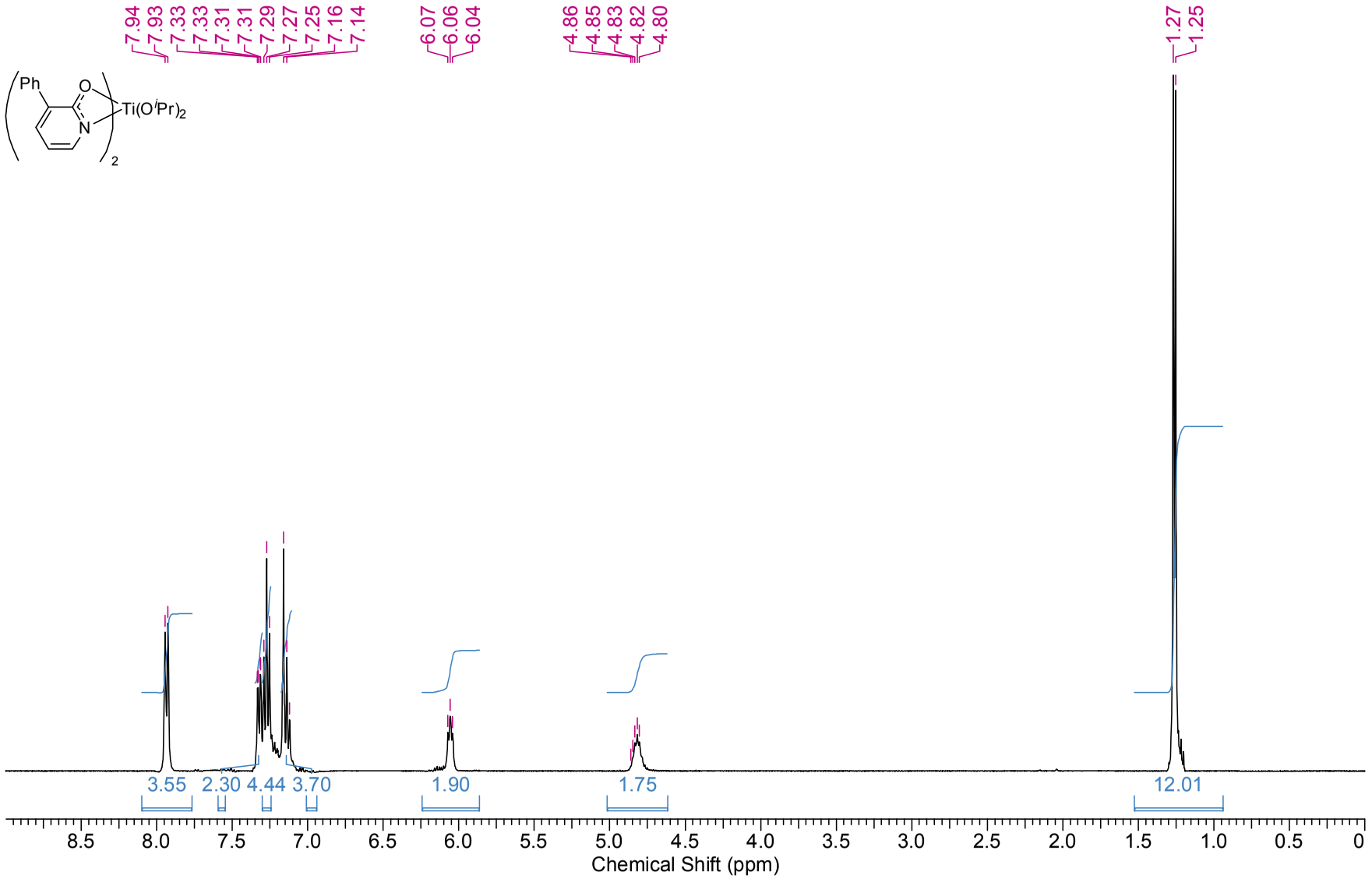
400 MHz ^{1}H NMR spectrum (298 K) for compound 2

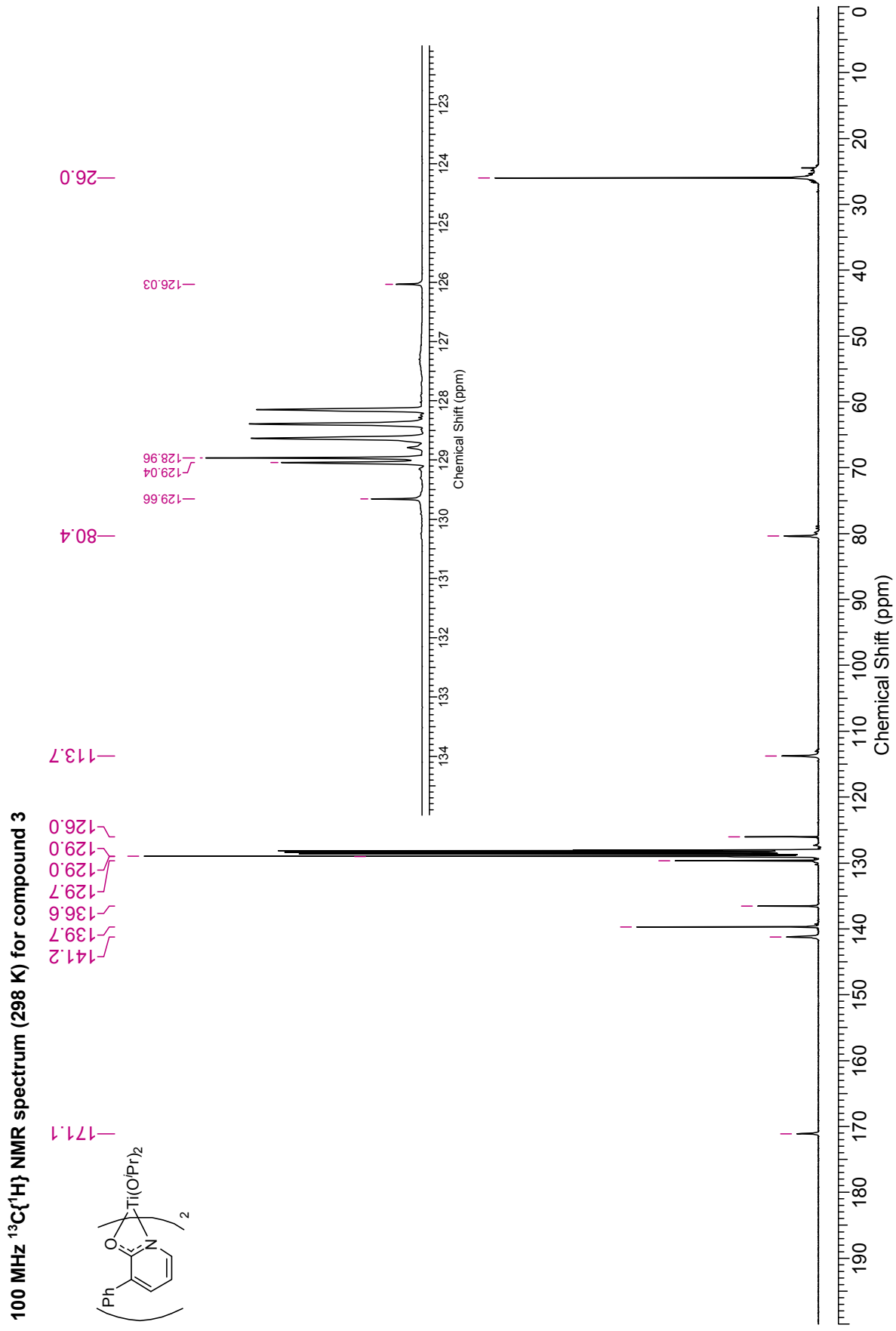


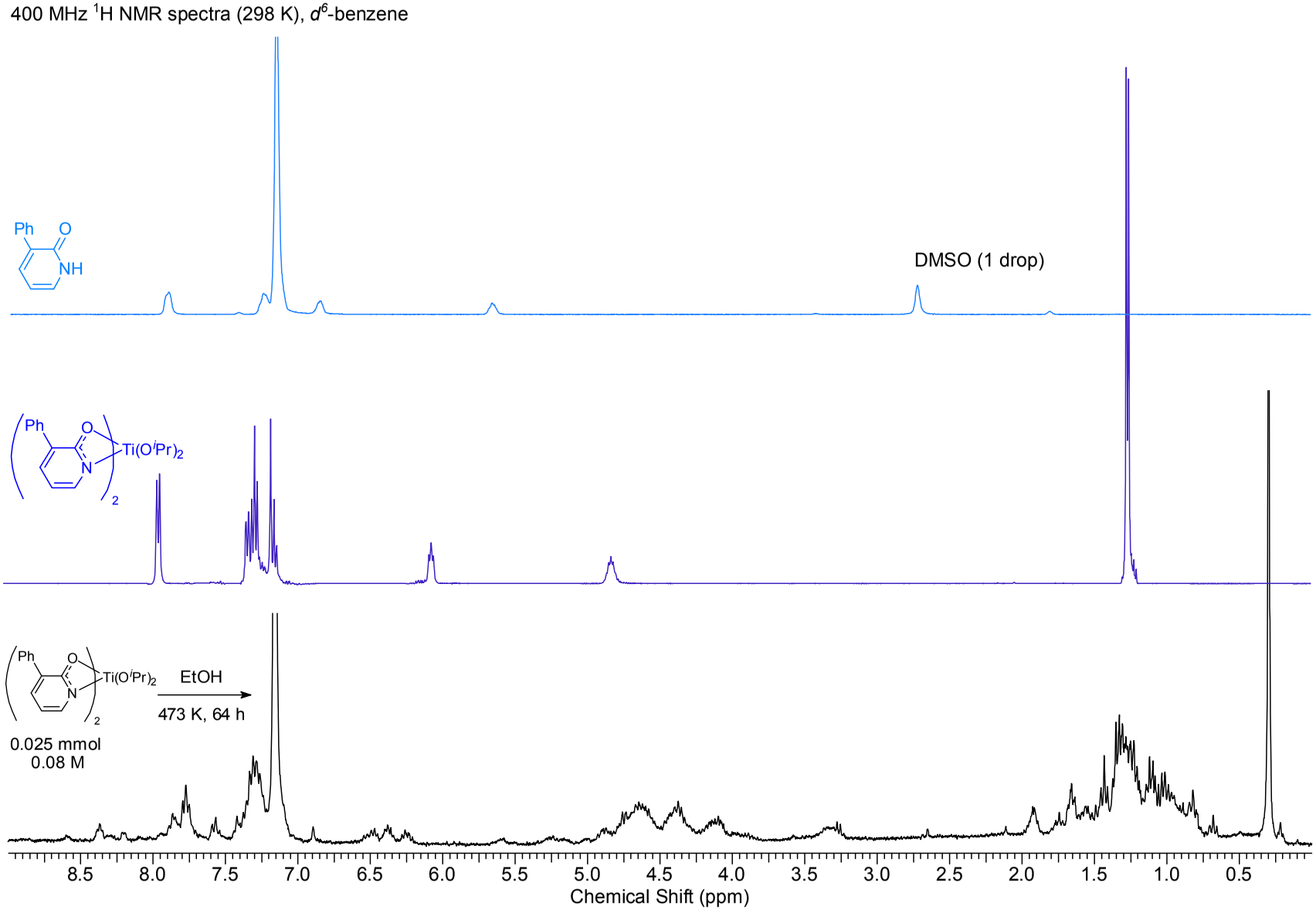
100 MHz $^{13}C\{^1H\}$ NMR spectrum (298 K) for compound 2

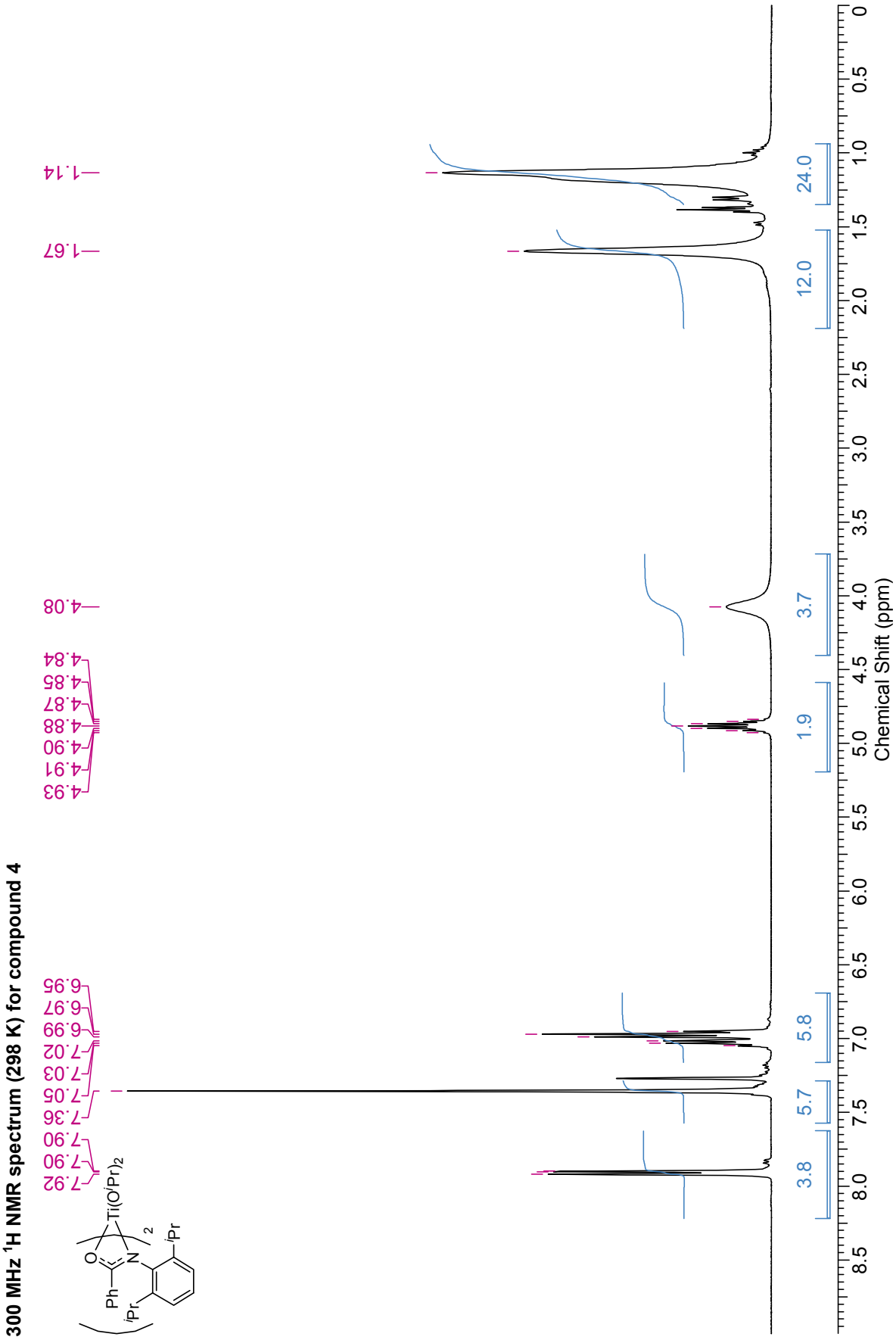


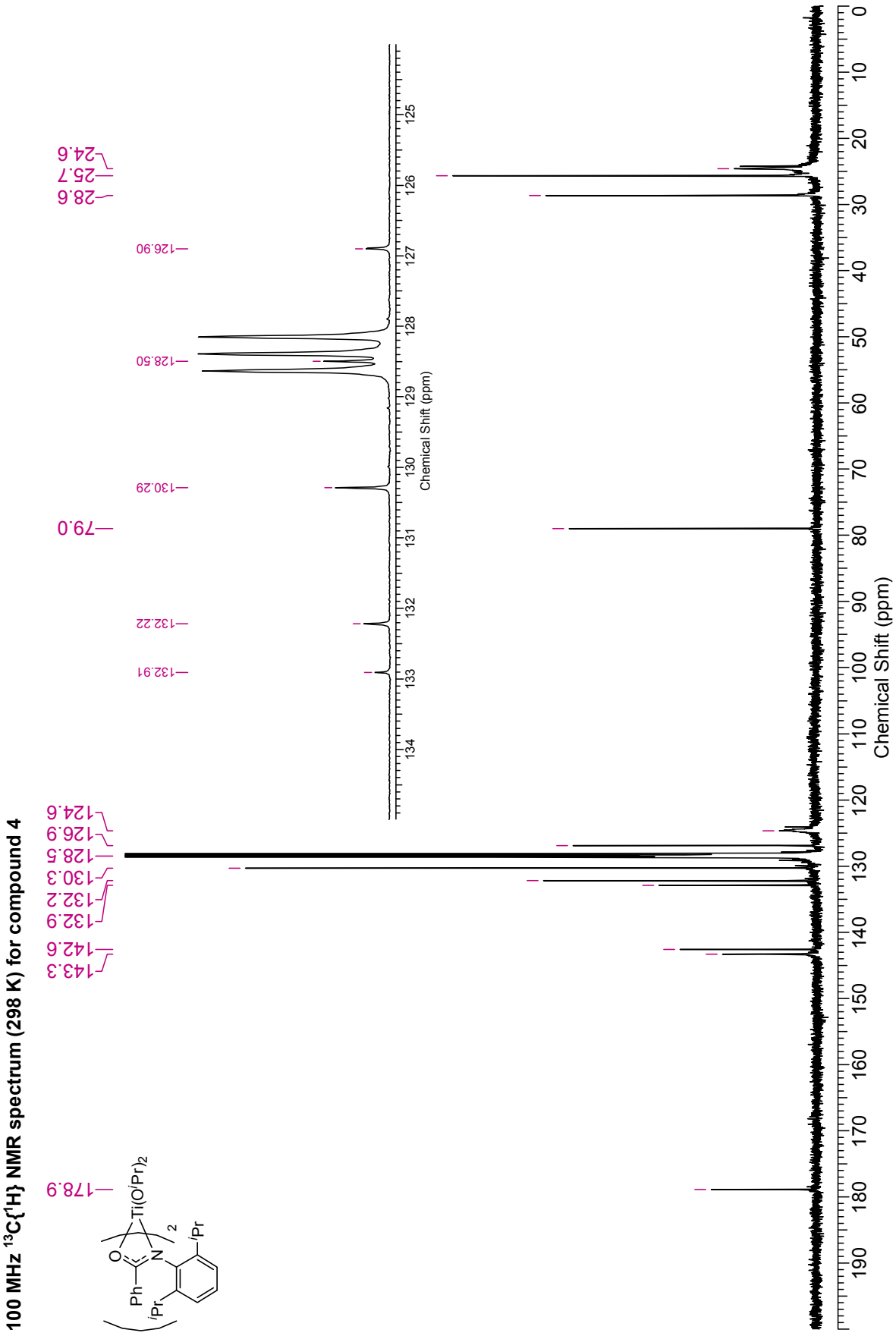
400 MHz ^{1}H NMR spectrum (298 K) for compound 3



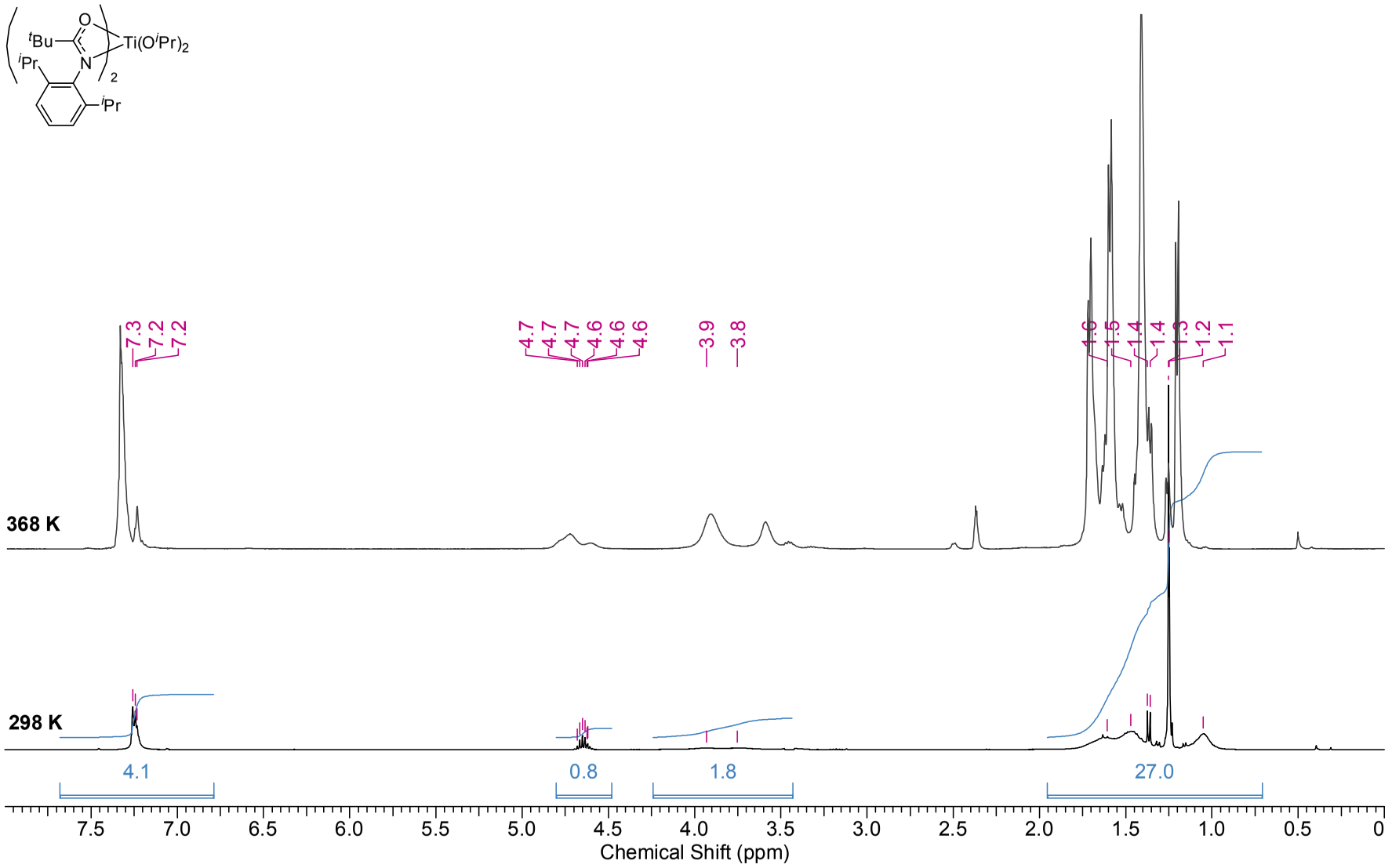

100 MHz $^{13}C\{^{1}H\}$ NMR spectrum (298 K) for compound 3
171.1
141.2
139.7
136.6
129.7
129.0
129.0
129.0
126.0
113.7
80.4
129.66
129.04
128.96
126.03
26.0
Chemical Shift (ppm)
Chemical Shift (ppm)
Ti(O^{i}Pr)$_2$
Ph
O
N
2




300 MHz ¹H NMR spectrum (298 K) for compound 4
Ti(O'Pr)2
Ph
'Pr
'Pr
O
N
2
7.92
7.90
7.90
7.36
7.05
7.03
7.02
6.99
6.97
6.95
4.93
4.91
4.90
4.88
4.87
4.85
4.84
4.08
1.67
1.14
3.8
5.7
5.8
1.9
3.7
12.0
24.0
Chemical Shift (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


100 MHz $^{13}C\{^1H\}$ NMR spectrum (298 K) for compound 4
178.9
143.3
142.6
132.9
132.2
130.3
128.5
126.9
124.6
79.0
28.6
25.7
24.6
126.90
128.50
130.29
132.22
132.91
Ph
^{i}Pr
^{i}Pr
Ti(O^{i}Pr)$_2$
Chemical Shift (ppm)
Chemical Shift (ppm)

400 MHz variable temperature ^{1}H NMR spectra for compound 5



100 MHz $^{13}C\{^{1}H\}$ NMR spectrum (298 K) for compound 5