

Evidence of Coordinative Chain Transfer Polymerization of Isoprene using Iron Iminopyridine/ ZnEt_2 Catalytic Systems

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1. General Information

All manipulations were performed under an inert atmosphere by using Schlenk techniques or in a dry glovebox ($O_2 < 1$ ppm, $H_2O < 1$ ppm, Jacomex, France). Toluene was purified through an alumina column (Mbraun SPS), followed by trap-to-trap distillation over sodium/benzophenone and stored on 4 Å molecular sieves in a glove box. Isoprene (Aldrich) was dried over calcium hydride, distilled once over 4 Å molecular sieves, and stored at -20°C in a glove box. Triisobutylaluminum [$Al(i\text{Bu})_3$, Aldrich], diethyl zinc solution [$ZnEt_2$, [C] = 1 M in toluene, Aldrich] and trityl tetrakis(pentafluorophenyl)borate $\{[B(C_6F_5)_4][CPh_3]\}$ (TCI Europe) were used as received. The ligands and the corresponding iron complexes **1-4** were prepared using a modified procedure described in the literature.¹ ^1H NMR spectra were recorded on a Bruker Avance 300 instrument at 300 K. All ^1H chemical shifts (reported in [ppm]) were determined by using residual signals of the deuterated solvents. In the case of polymers analyses, the conversion as well as the composition of the polymers and the microstructural magnitudes were determined as reported by mean of ^1H and ^{13}C NMR spectroscopy by using the Topspin or MestreNova softwares. Differential Scanning Calorimetry (DSC) experiments were carried out on a DSC 25TA (Thermal Analysis) instrument which was calibrated with a high purity indium sample according to standard procedures. The samples (≈ 4 mg) were put in sealed pans and analyzed in the temperature range from -90 to $+140^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The T_g values corresponding to the second heating were calculated and reported. Size exclusion chromatography (SEC) analyses of the samples were performed in THF (+ 0.2 % toluene) as an eluent at 40°C (1 mL/min) with a Waters SIS HPLC pump, a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards.

1. (a) T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola and M. Leskelä, *J. Organomet. Chem.*, 2000, **606**, 112; (b) C. Bianchini, L.H. Man, G. Mantovani, A. Meli and W. Oberhauser, *New J. Chem.*, 2002, **26**, 387; (c) Y. Cao, Y. Zhang, L. Zhang, D. Zhang, X. Leng and Z. Huang, *Org. Chem. Front.*, 2014, **1**, 1101; (d) T.V. Laine, M. Klinga and M. Leskelä, *Eur. J. Inorg. Chem.*, 1999, 959; (e) O.H. Hashmi, Y. Champouret and M. Visseaux, *Molecules*, 2019, **24**, 3024.

2. General Experimental Procedures

2.1 General Procedure for the Synthesis of Ligands

A solution of the corresponding substituted aniline (1.3 eq.) and 2-pyridinecarboxaldehyde/2-acetyl pyridine (1 eq.) in methanol with catalytic amounts of formic acid was prepared in a round-bottomed flask equipped with a magnetic stirrer. The resulting mixture was refluxed overnight at 90 °C before concentrating it under reduced pressure. The yellow mixture obtained was further dissolved in pentane, dried over sodium sulfate and filtered. The filtrate was further concentrated to obtain a crude product, which was further recrystallized in methanol at -20 °C to obtain yellow crystals.

2.2 General Procedure for the Synthesis of Complexes

A solution of the corresponding ligand (1 eq.) and anhydrous FeCl₂ (1 eq.) in dry THF was prepared in a Schlenk inside the glove box. The mixture was stirred overnight under argon, concentrated under reduced pressure and washed with dry pentane (3 times). The solid was further dried under vacuum to obtain the desired complexes as purple powders.

2.3 General Procedure for Isoprene Polymerization

A Schlenk frit (100 mL) was heated, dried in a vacuum and purged with argon three times before introducing it to the glove box. Iron (II) chloride complex (10 μmol, 1 eq.) and toluene (17 mL) were added to the reactor followed by the addition of triisobutylaluminum (30 μmol, 3 eq.) at 23 °C. The reaction mixture was stirred for 2-3 mins and a solution of trityltetrakis(pentafluorophenyl)borate (10 μmol, 1 eq.) in toluene (3 mL) was added to the reaction mixture at 23 °C. The mixture was stirred for 2 min and ZnEt₂ (50-1000 μmol) was added under stirring conditions before adding isoprene (1.362 g, 2 mL, 2000 eq.). The reaction mixture was stirred for 6 hours before opening it to air and quenching it by 2-3 drops of diluted HCl (1 M) followed by its dilution with toluene. The polymer was precipitated in ethanol (150 mL) containing the stabilizing agent BHT (tert-butyl hydroxytoluene), isolated and dried in vacuum for 4 h to yield a gummy solid.

The aliquots were taken to determine the conversion by using the chemical shifts of the olefinic protons of polyisoprene (5.11 and 4-4.6 ppm) and isoprene (6.5-6.42 ppm). These aliquots were quenched with dry isopropanol present inside the NMR tubes containing a benzene capillary.

The percentage conversion was calculated according to the equation:

$$[\% \text{ Conversion}] = \frac{\text{Area normalised for polymer}}{\text{Area normalised for polymer} + \text{Area normalised for monomer} *}$$

$$= \frac{I(5.14 - 5.10 \text{ ppm}) + \frac{I(4.72 - 4.67 \text{ ppm})}{2}}{I(5.14 - 5.10 \text{ ppm}) + \frac{I(4.72 - 4.67 \text{ ppm})}{2} + (I(6.5 - 6.42 \text{ ppm}) \text{ or } I(5.22 - 5 \text{ ppm}))}$$

*Can be chosen between the two olefinic regions of isoprene depending on the better resolution of peaks

2.4. Calculation of Microstructure Contents

The characteristic signals of polyisoprene in a ¹H NMR spectrum were found at 5.14-5.10 ppm and 4.72-4.67 ppm corresponding to 1,4 and 3,4 units respectively, as previously reported in the literature.² The percentage content of 1,4 and 3,4 units was determined according to the equations:

$$[\%1,4 \text{ content}] = \frac{I(5.14 - 5.10 \text{ ppm})}{I(5.14 - 5.10 \text{ ppm}) + \frac{I(4.72 - 4.67 \text{ ppm})}{2}}$$

$$[\%3,4 \text{ content}] = \frac{\frac{I(4.72 - 4.67 \text{ ppm})}{2}}{I(5.14 - 5.10 \text{ ppm}) + \frac{I(4.72 - 4.67 \text{ ppm})}{2}}$$

The characteristic signals at 16.2 and 23.8 ppm in the ¹³C NMR spectra correspond to the methyl carbon of *cis*-1,4 and *trans*-1,4 polyisoprene motifs respectively.³ Therefore, the percentage of *cis*-1,4 and *trans*-1,4 content is given by the equations:

$$[\%trans - 1,4 \text{ content}] = \frac{I(16.2 \text{ ppm})}{I(16.2 \text{ ppm}) + I(23.8 \text{ ppm})}$$

$$[\%cis - 1,4 \text{ content}] = \frac{I(23.8 \text{ ppm})}{I(16.2 \text{ ppm}) + I(23.8 \text{ ppm})}$$

² D. H. Beebe, *Polymer*, 1978, **19**, 231–233.

³ Y. Tanaka, H. Sato and T. Seimiya, *Polym. J.*, 1975, **7**, 264–266.

3. Supplementary Data

3.1 SEC chromatograms of polyisoprene according to the data presented in Table 1

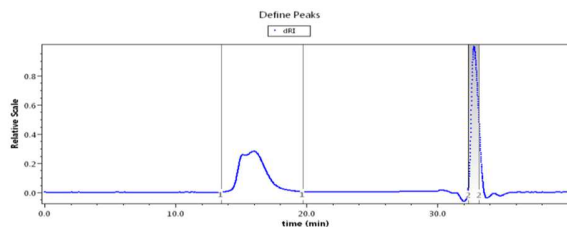


Fig S1. Entry 1, Table 1 ($M_n = 487\,500$ g/mol, $\mathcal{D} = 1.6$)

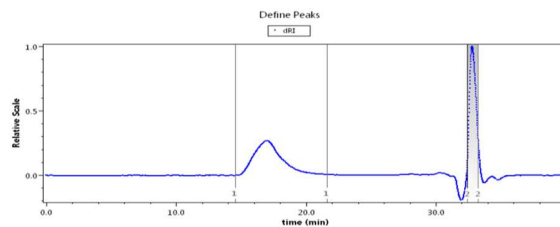


Fig S2. Entry 2, Table 1 ($M_n = 180\,000$ g/mol, $\mathcal{D} = 1.7$)

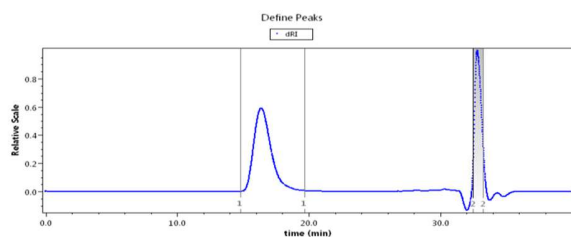


Fig S3. Entry 3, Table 1 ($M_n = 250\,000$ g/mol, $\mathcal{D} = 1.3$)

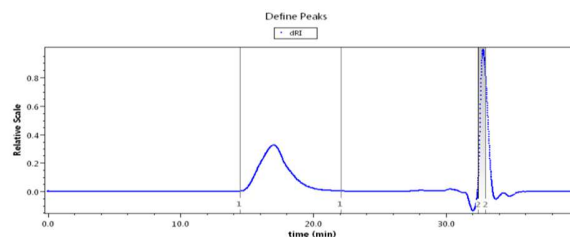


Fig S4. Entry 4, Table 1 ($M_n = 195\,000$ g/mol, $\mathcal{D} = 1.8$)

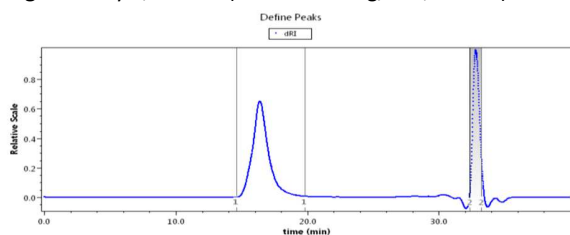


Fig S5. Entry 5, Table 1 ($M_n = 261\,000$ g/mol, $\mathcal{D} = 1.3$)

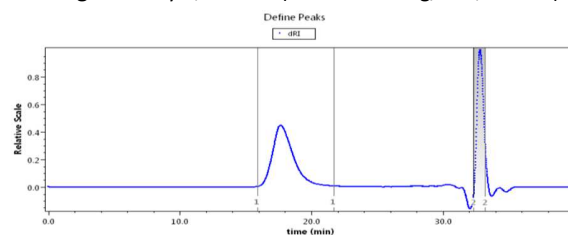


Fig S6. Entry 6, Table 1 ($M_n = 86\,000$ g/mol, $\mathcal{D} = 1.3$)

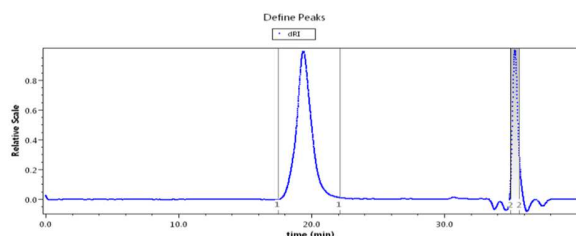


Fig S7. Entry 7, Table 1 ($M_n = 155\,000$ g/mol, $\mathcal{D} = 1.3$)

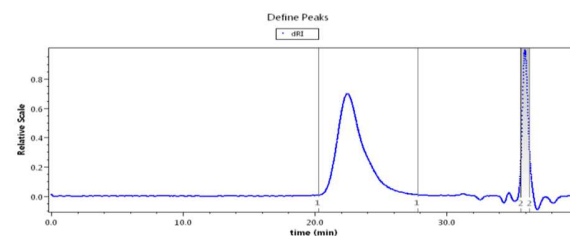


Fig S8. Entry 8, Table 1 ($M_n = 20\,500$ g/mol, $\mathcal{D} = 1.3$)

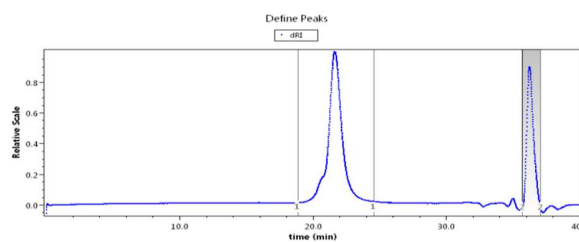


Fig S9. Entry 9, Table 1 ($M_n = 41\,000$ g/mol, $\mathcal{D} = 1.2$)

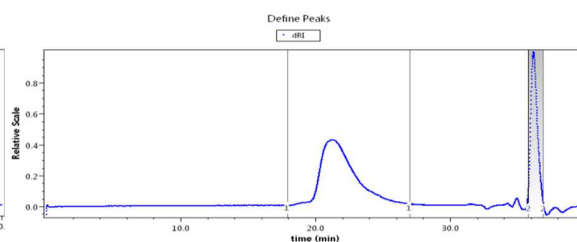


Fig S10. Entry 10, Table 1 ($M_n = 40\,000$ g/mol, $\mathcal{D} = 1.6$)

3.2 NMR spectra of polyisoprene according to the data presented in Table 1

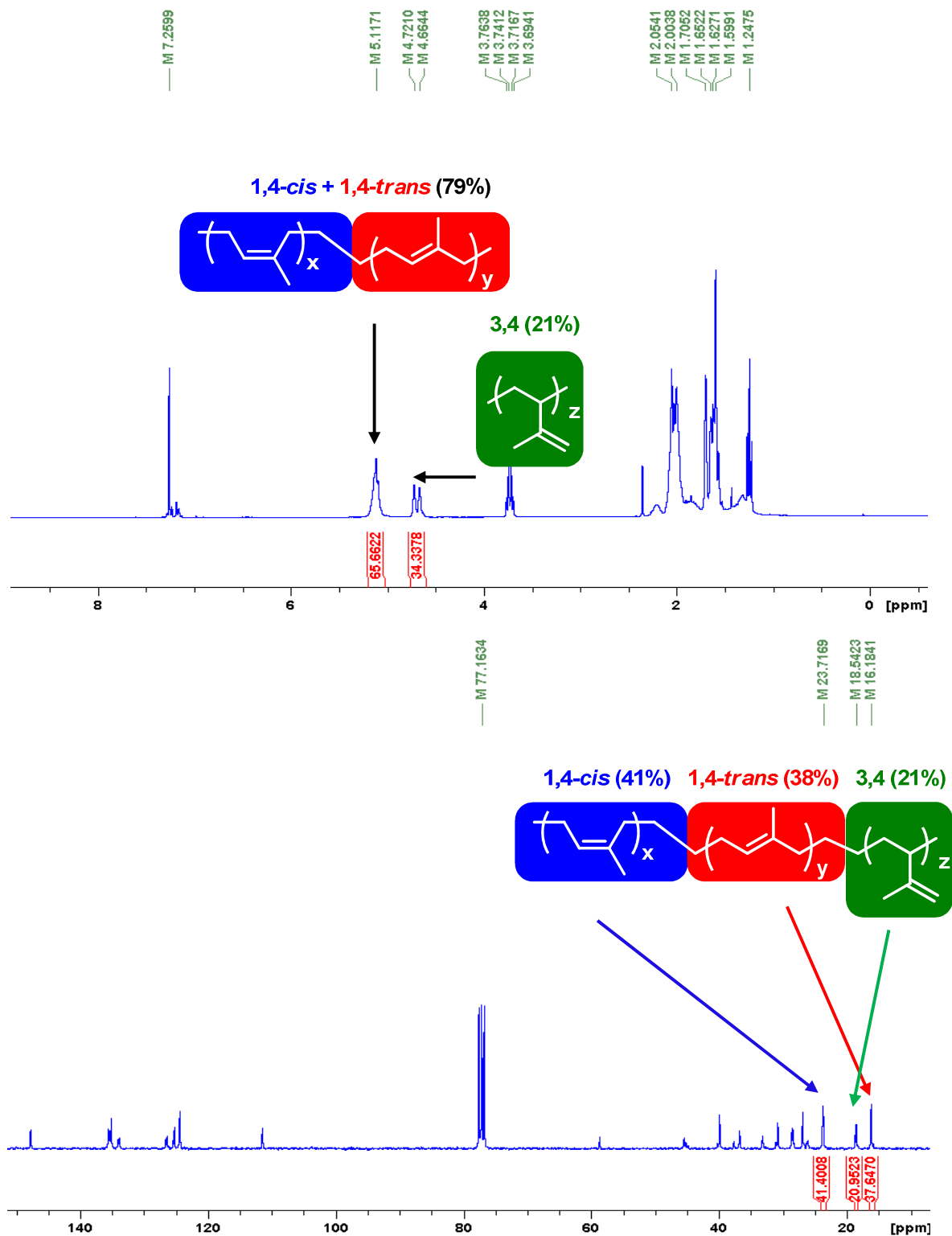


Fig. S11 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 1** in **Table 1** (300 MHz, CDCl₃, 25 °C)

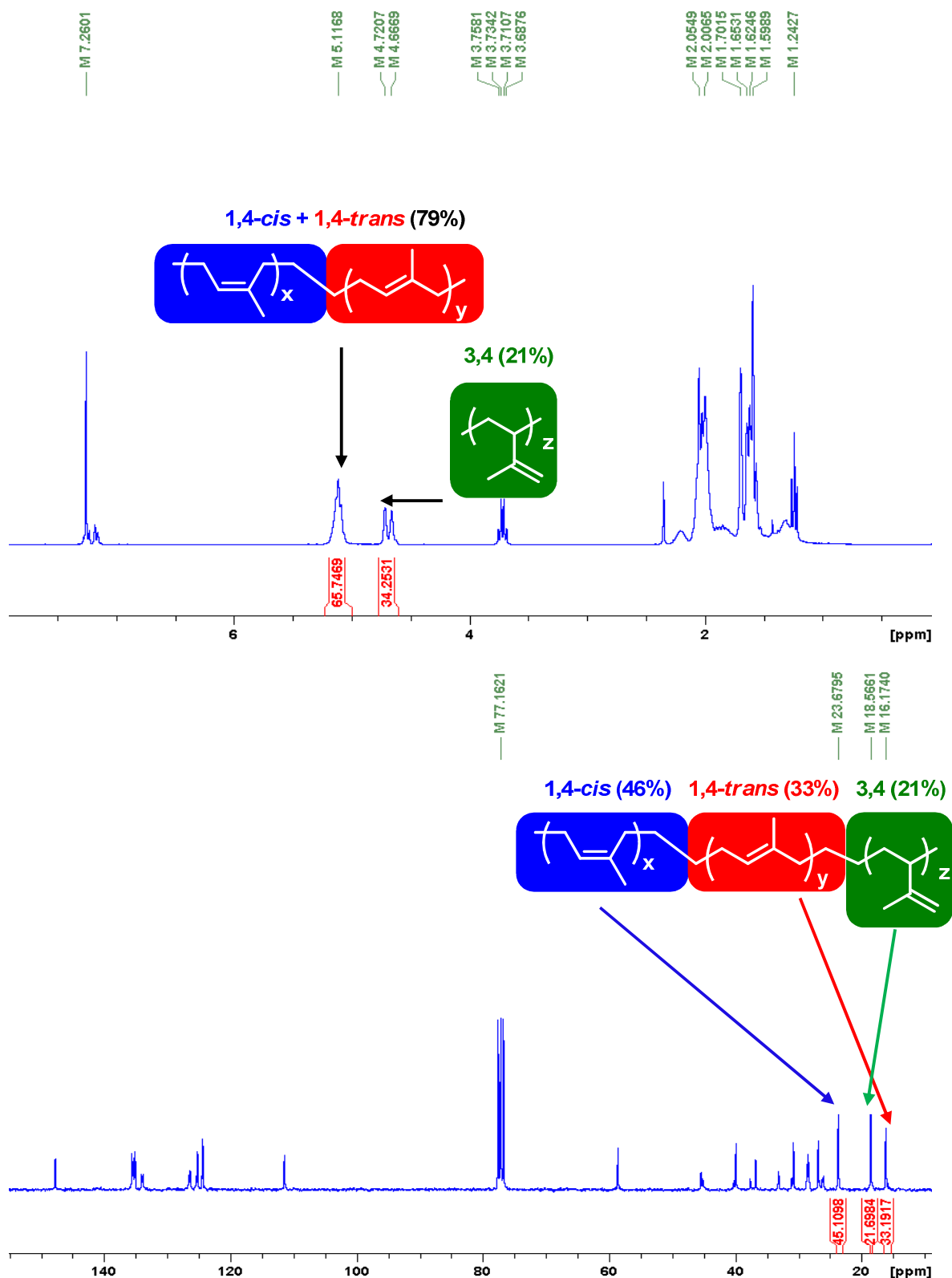


Fig. S12 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 2** in **Table 1** (300 MHz, CDCl₃, 25 °C)

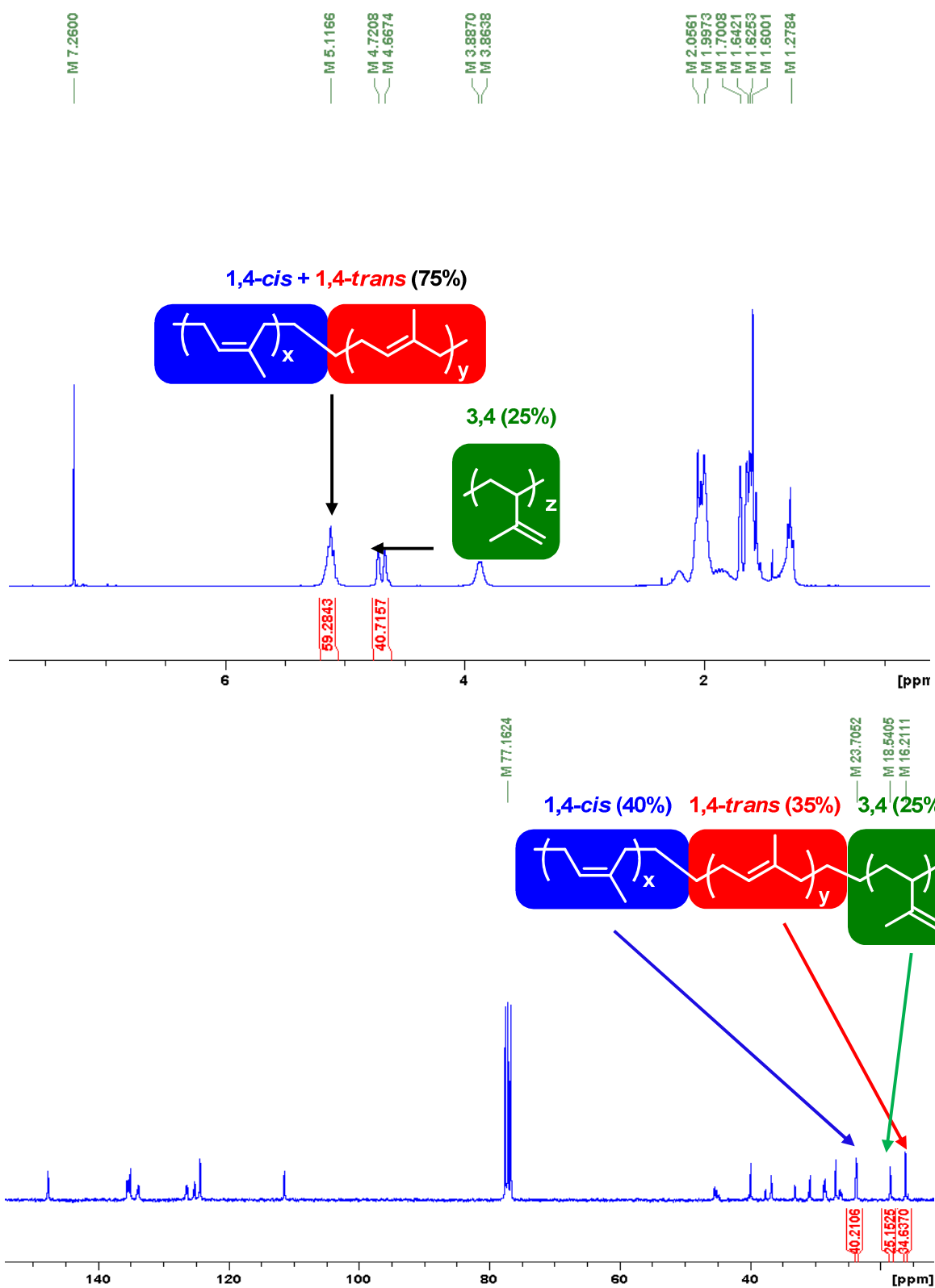


Fig. S13 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 3** in **Table 1** (300 MHz, CDCl₃, 25 °C)

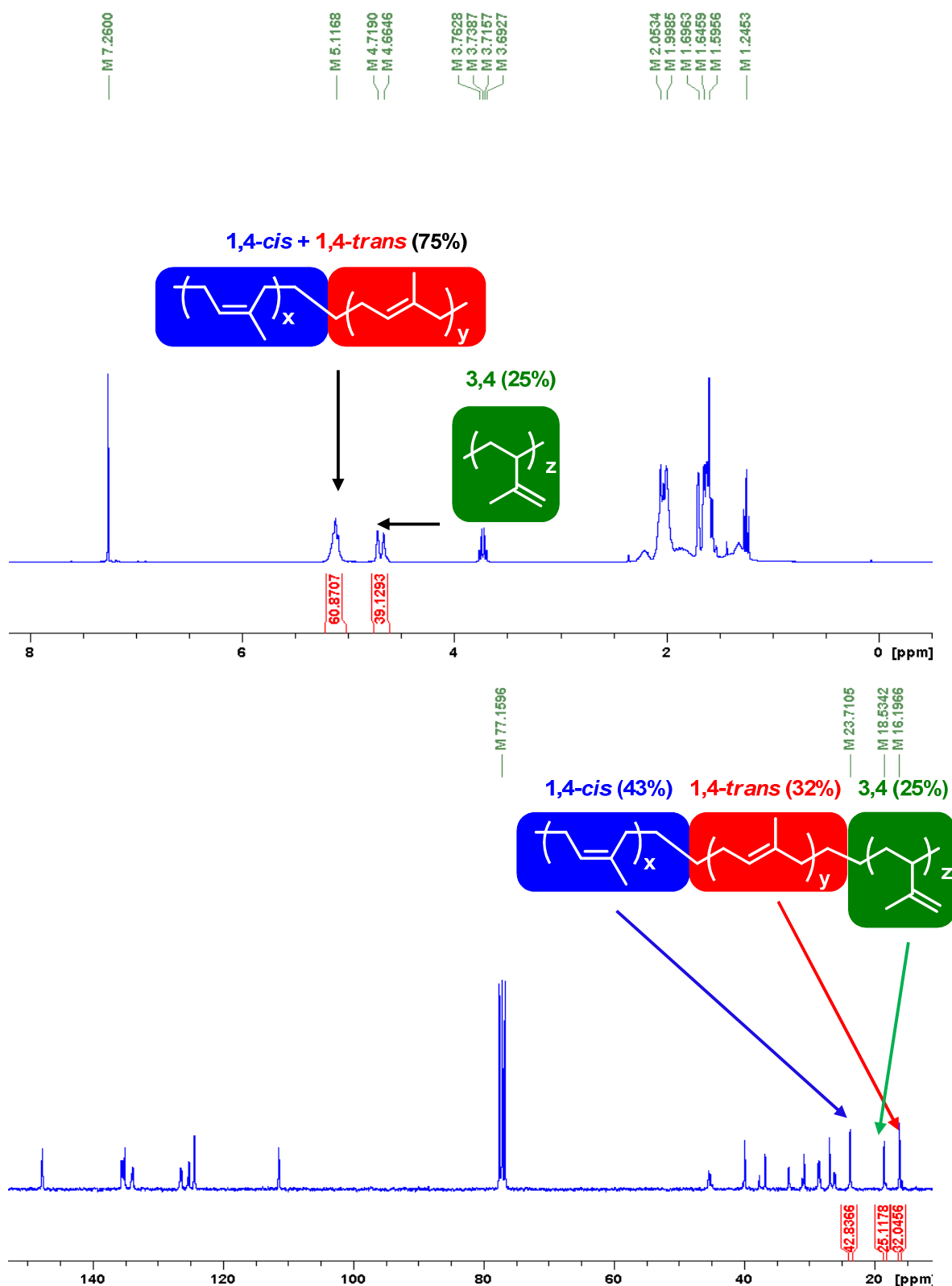


Fig. S14 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 4** in **Table 1** (300 MHz, CDCl₃, 25 °C)

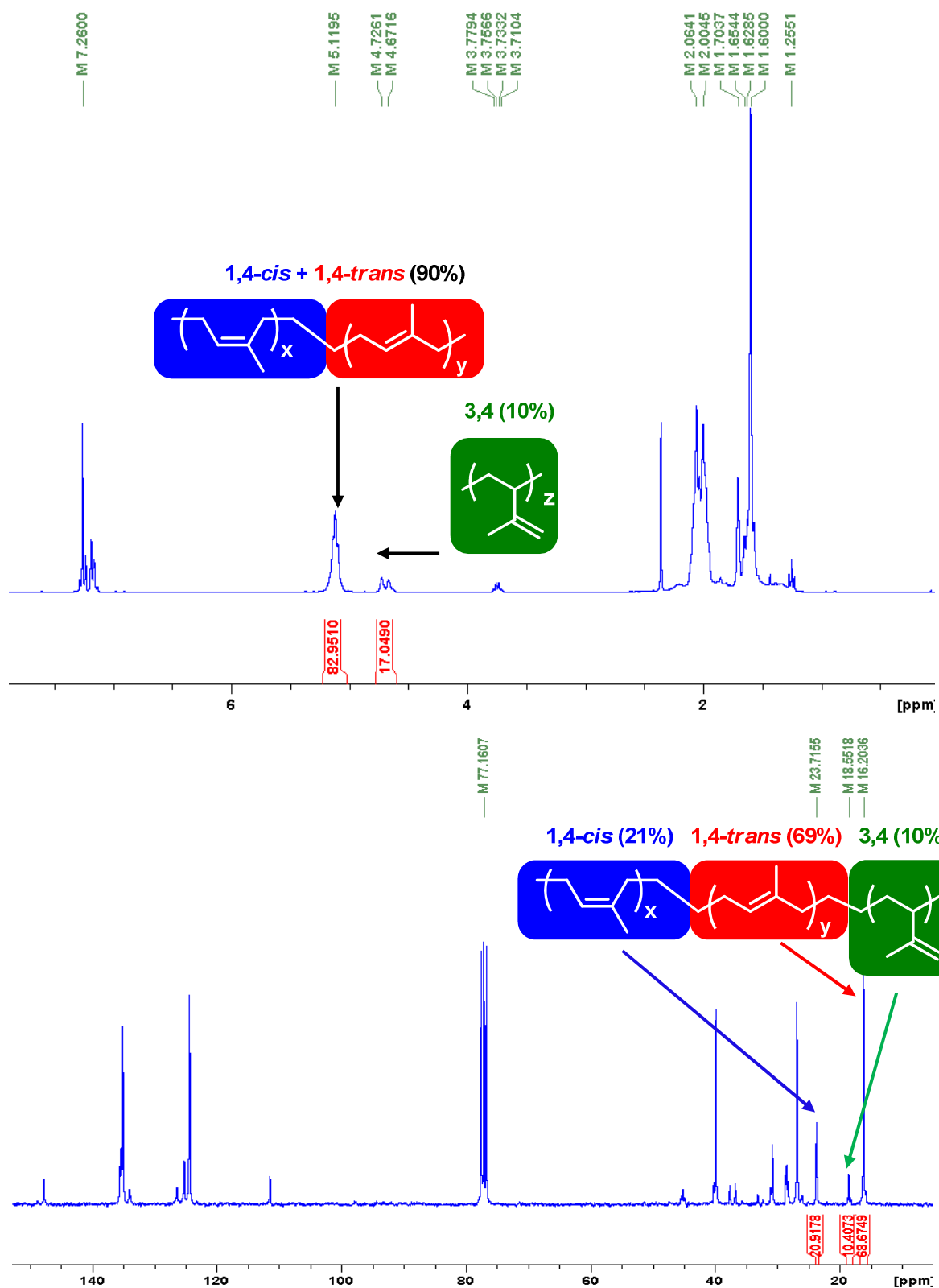


Fig. S15 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 5** in **Table 1** (300 MHz, CDCl₃, 25 °C)

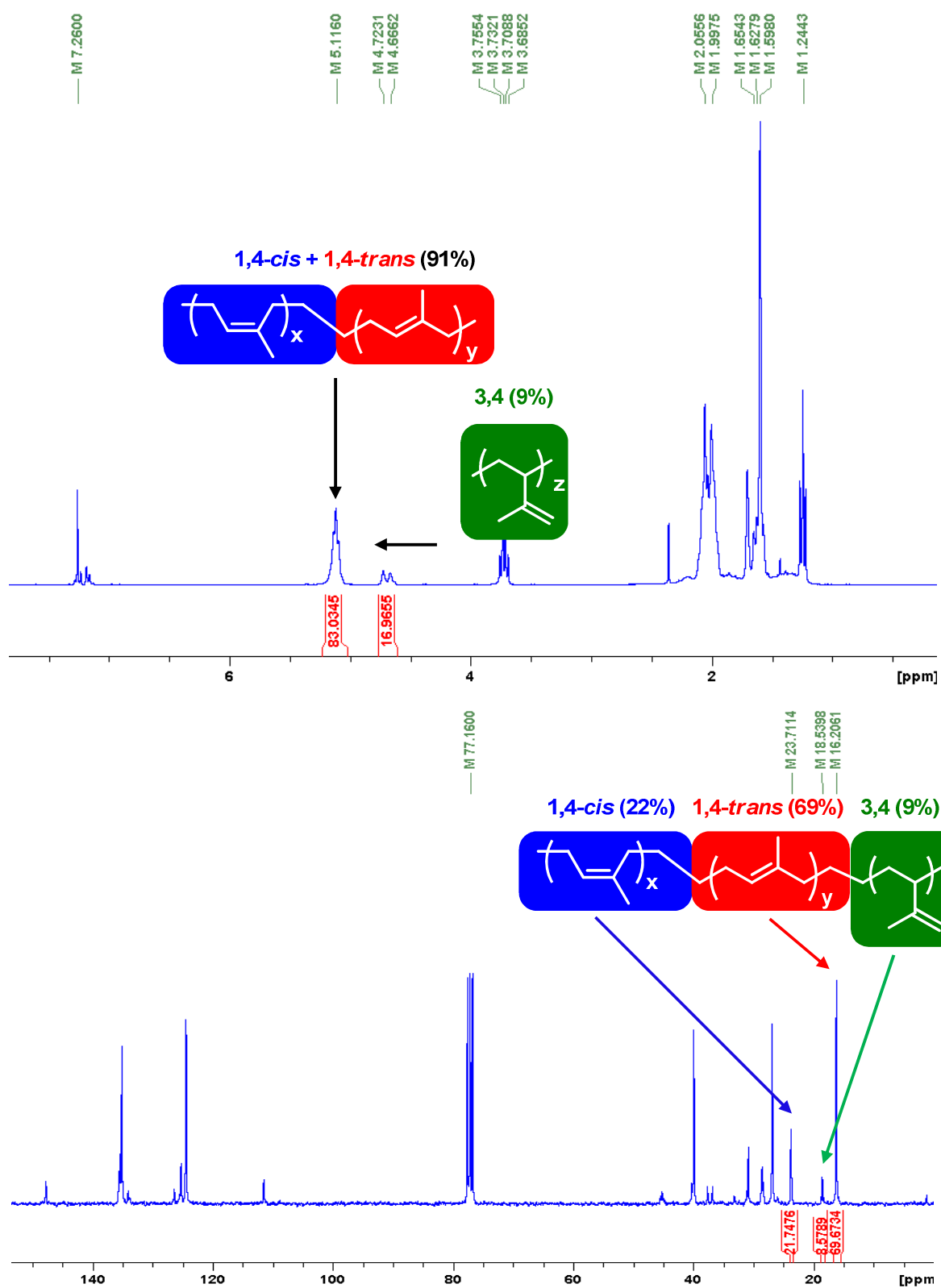


Fig. S16 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 6** in **Table 1** (300 MHz, CDCl₃, 25 °C)

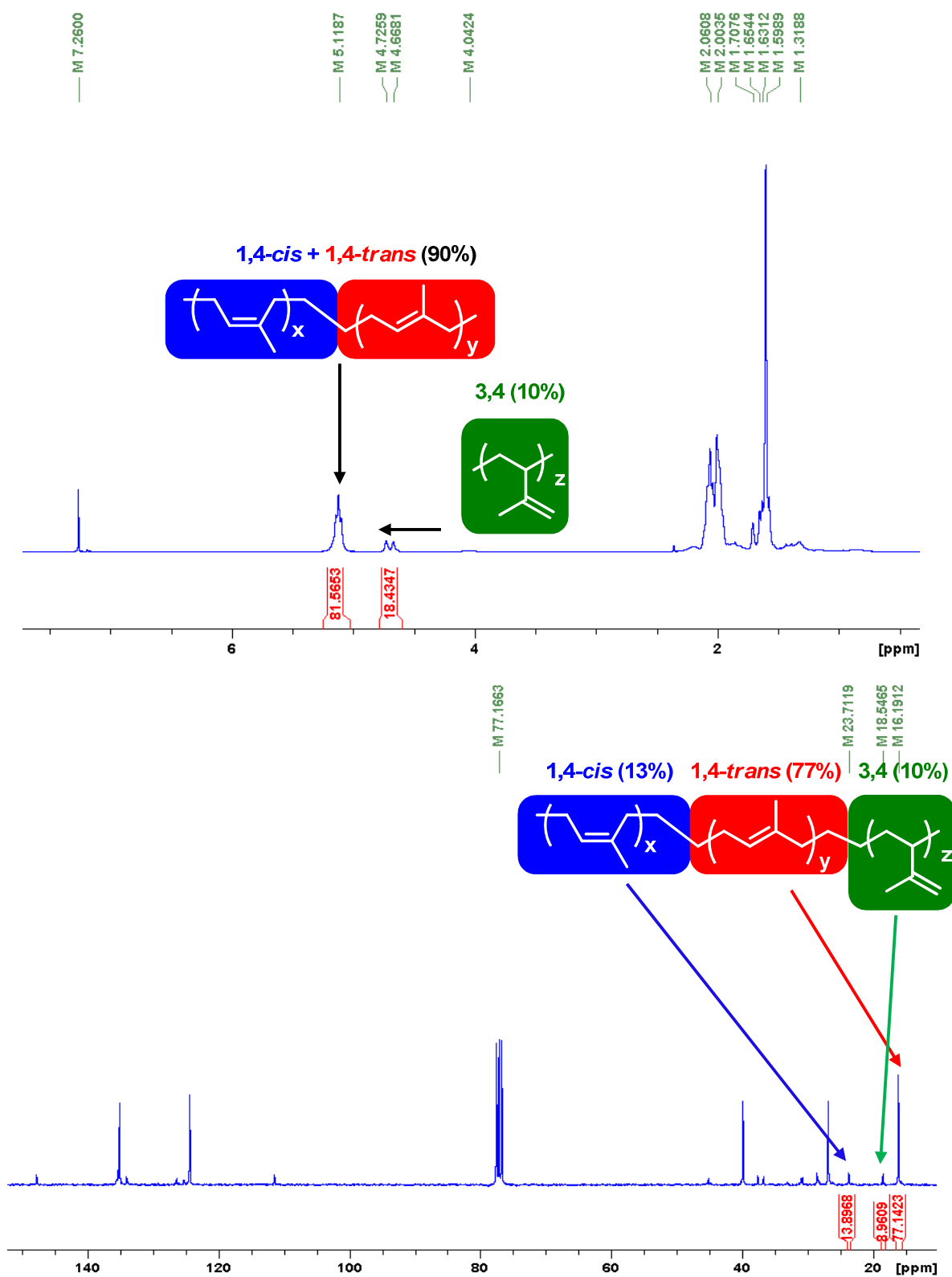


Fig. S17 ^1H (top) & ^{13}C (bottom) NMR spectra of the polymer obtained from **Entry 7** in **Table 1** (300 MHz, CDCl_3 , 25 $^\circ\text{C}$)

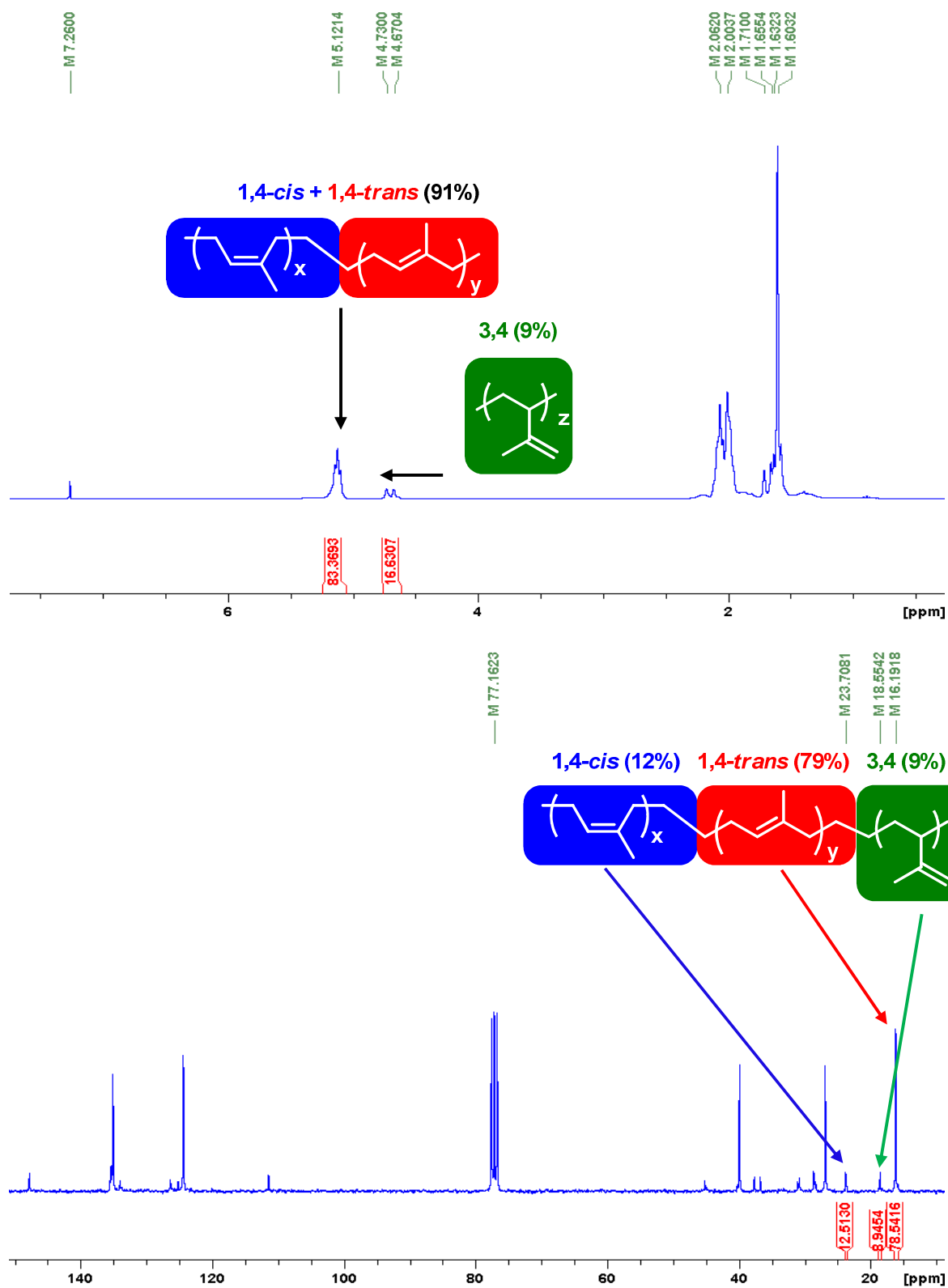


Fig. S18 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 8** in **Table 1** (300 MHz, CDCl₃, 25 °C)

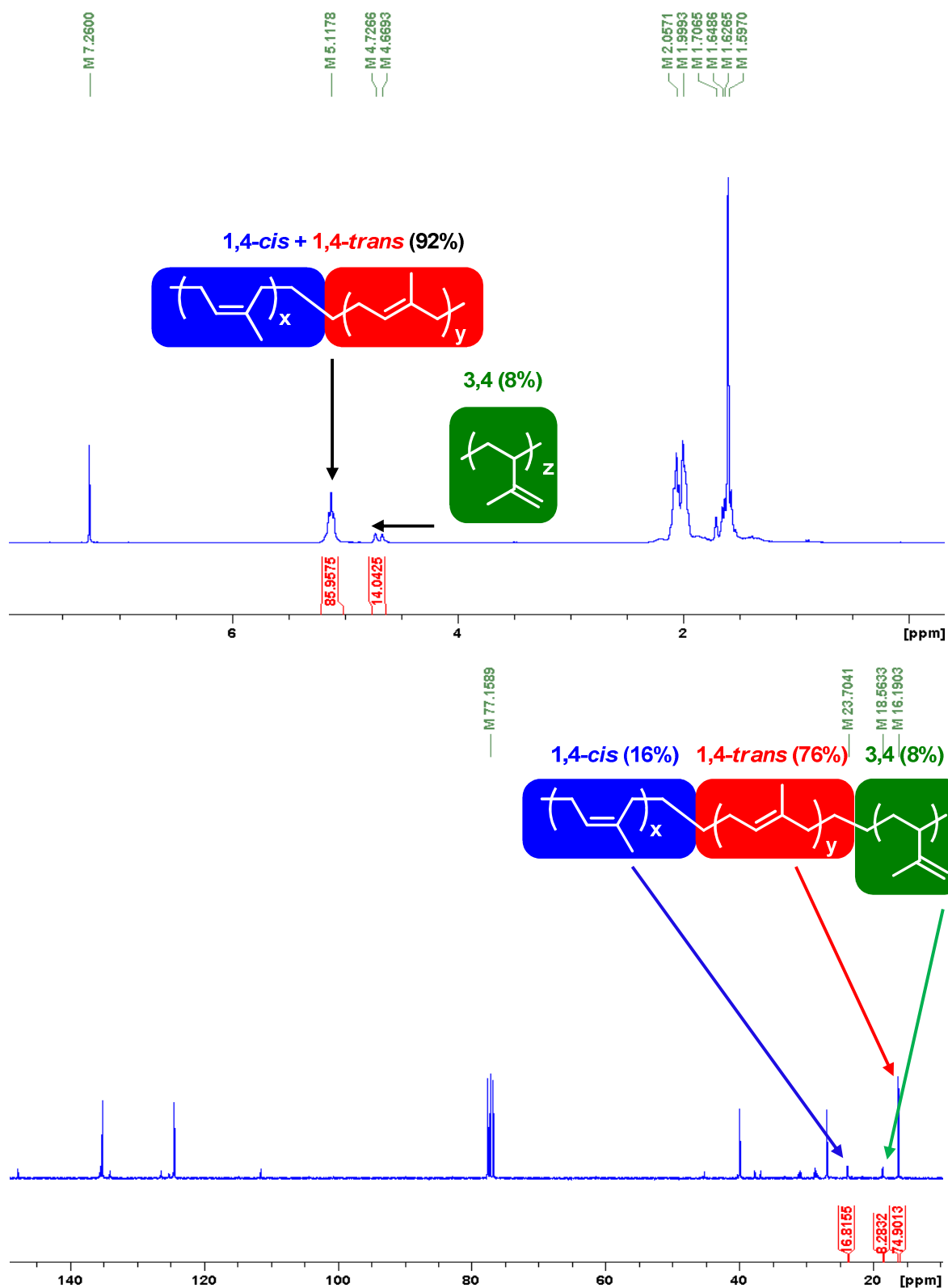


Fig. S19 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from Entry 9 in Table 1 (300 MHz, CDCl₃, 25 °C)

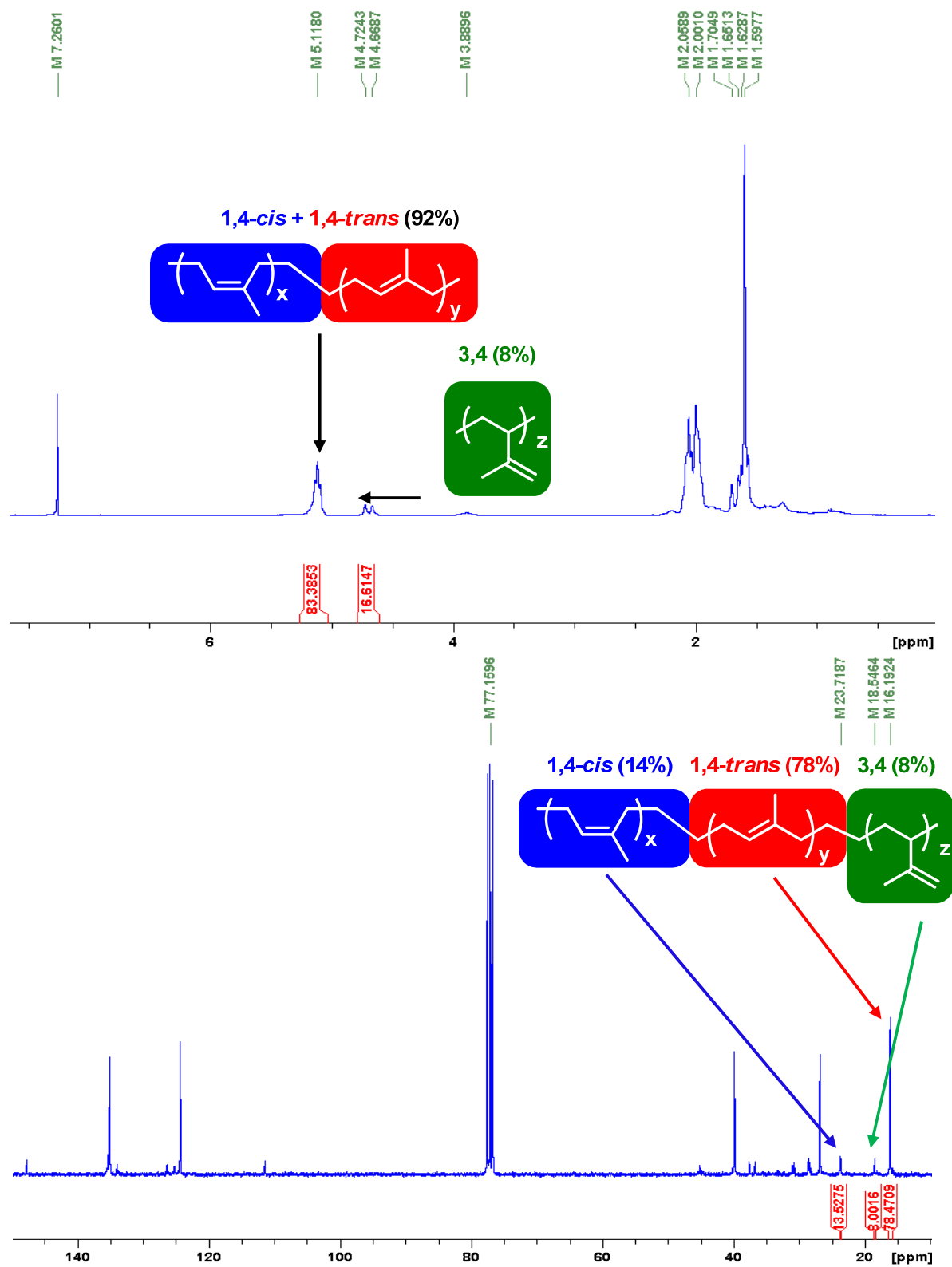


Fig. S20 ^1H (top) & ^{13}C (bottom) NMR spectra of the polymer obtained from **Entry 10** in **Table 1** (300 MHz, CDCl_3 , 25°C)

3.3 CCTP of isoprene using 4/MAO in presence of different amount of ZnEt₂

Table S1 CCTP of isoprene using 4/MAO catalytic system with different quantities of ZnEt₂^a

Entry ^a	[ZnEt ₂]/[4]	Conv. (%)	$M_{n(\text{exp})}$ ^b (g/mol)	\mathcal{D} ^b	N chains ^c
1	0	>99	94 000	1.4	-
2	10	>99	34 600	1.4	2.7
3	50	>99	18 000	1.4	5.2

^a Polymerization conditions: 10 μmol of Fe complex, isoprene/4/MAO = 2000/1/100, toluene = 20 mL, [C]isoprene = 1 mol/L, temperature = 25 °C, time = 6h. ^b Determined by size exclusion chromatography (SEC) analysis in THF using polystyrene standards. ^c N chains = $M_{n(\text{exp})}$ without CTA/ $M_{n(\text{exp})}$ with CTA

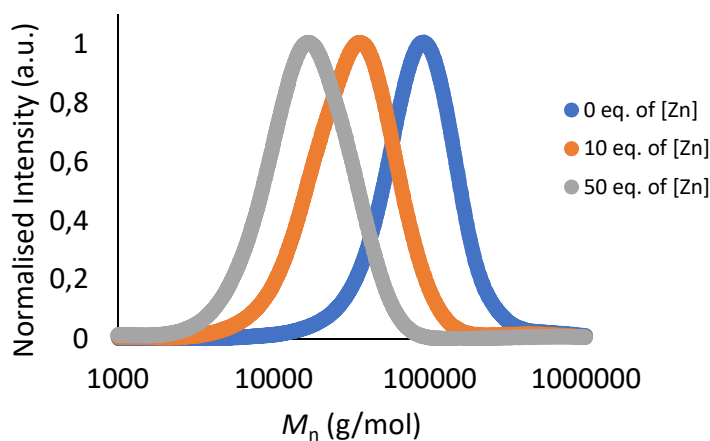


Fig. S21 Effect of quantity of ZnEt₂ on the M_n using 4/MAO catalytic system (according to data in Table S1)

Original SEC chromatograms of polyisoprene according to the data presented in Table S1

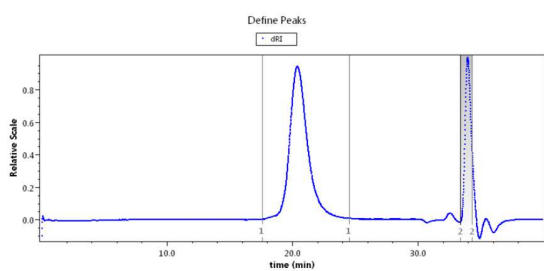


Fig. S22 Entry 1, Table S1 ($M_n = 94\ 000$ g/mol, $\mathcal{D} = 1.4$)

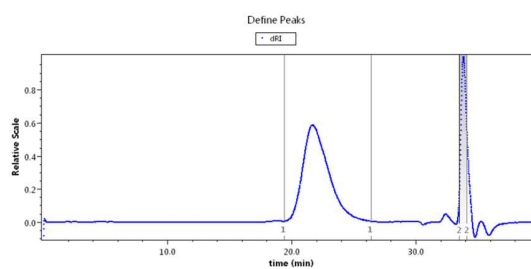


Fig. S23 Entry 2, Table S1 ($M_n = 34\ 600$ g/mol, $\mathcal{D} = 1.4$)

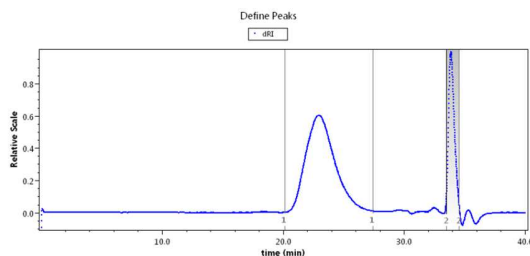


Fig. S24 Entry 3, Table S1 ($M_n = 18\ 000$ g/mol, $\mathcal{D} = 1.4$)

3.4 Kinetic profile of isoprene polymerization using **4** in absence and in presence of ZnEt₂

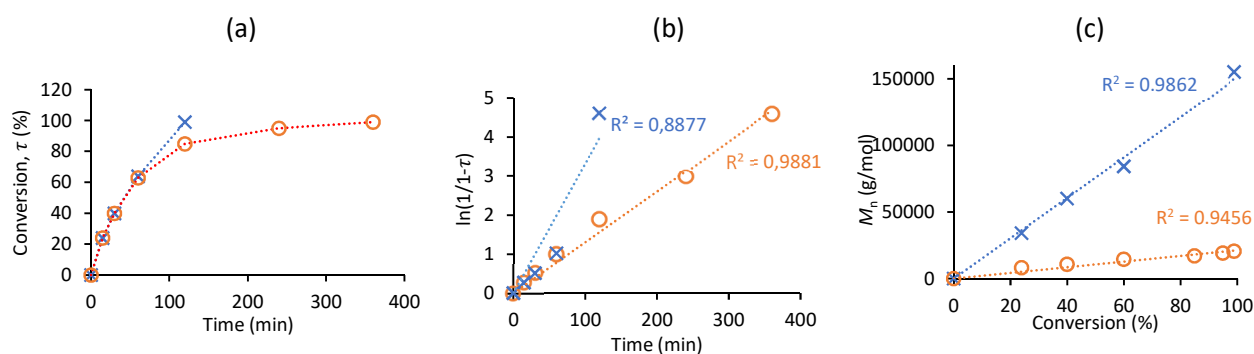
Table S2 Isoprene polymerization using **4**/AlⁱBu₃/[B(C₆F₅)₄][CPh₃] in absence and presence of ZnEt₂^a

Entry ^a	ZnEt ₂ (eq/Fe)	Time (min)	Conv. (%)	<i>M_n</i> (exp) ^b (g/mol)	<i>D</i> ^b
1	0	15	24	34 000	1.5
2		30	40	60 000	1.8
3		60	64	84 000	2.0
4		120	99	155 000	1.3
5	10	15	24	8 000	1.3
6		30	40	10 600	1.3
7		60	63	14 500	1.3
8		120	85	17 000	1.3
9		240	95	19 000	1.3
10		360	99	20 500	1.3

^a Polymerization conditions: 10 μmol of Fe complex, isoprene/**4**/AlⁱBu₃/[B(C₆F₅)₄][CPh₃] = 2000/1/3/1, toluene = 20 mL, [C]isoprene = 1 mol/L, T = 25 °C. ^b Determined by SEC analysis in THF using polystyrene standards.

Results and Discussion: The chain transfer between the catalyst originating from **4** and ZnEt₂ was also examined through the kinetic profile of isoprene polymerization at 25 °C, without and with 10 eq. of ZnEt₂/Fe (Table S2). These studies were conducted with 2 000 eq. of isoprene during which various aliquots were taken at different times of the polymerization to determine the conversions *via* ¹H NMR. The molar mass of each sample of PI for each run was determined through SEC analysis. From the kinetic plots (Fig. S25a), it is clearly evident that the addition of 10 eq. ZnEt₂ prolonged the polymerization time substantially, indicating the occurrence of transfer of the growing polymeric chain between **4** and Zn. This was confirmed through a significant drop in the molecular weights of the obtained polymer at each aliquot and mostly visible in the end where *M_n* drops from 155 000 g/mol in the absence of CTA (conv. > 99% at 120 min) to 20 500 g/mol *via* CCTP of isoprene with 10 eq. of ZnEt₂ (conv. > 99% at 240 min). It also appears that the polymerization nearly follows a first order kinetic profile with and without CTA (the process being even better controlled under transfer regime, R² = 0.9881 with ZnEt₂ vs R² = 0.8877 without ZnEt₂, respectively, Fig. S25b), indicating minimal loss of active species during the polymerization. In addition, the plot of *M_n* vs. conversion presented in Fig. S25c is clearly consistent with a controlled polymerization process in absence and in the presence of CTA, as assessed by the linear relationship observed.

Fig. S25 Monomer conversion (τ) in function of time (left, a), first order kinetics plot (middle, b), dependence of *M_n* vs conversion (right, c) for isoprene/**4**/AlⁱBu₃/[B(C₆F₅)₄][CPh₃] (2000/1/3/1) catalytic



system in the absence (×) and the presence of 10 eq. ZnEt₂/Fe (○) (according to data in Table S2)

Original SEC chromatograms of polyisoprene according to the data presented in Table S2

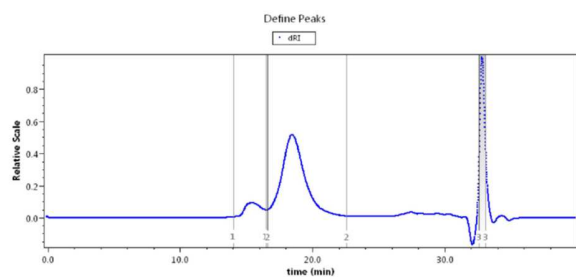


Fig. S26 Entry 1, Table S2 ($M_n = 34\,000$ g/mol, $D = 1.5$)

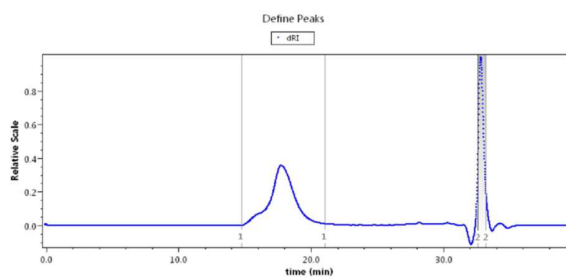


Fig. S27 Entry 2, Table S2 ($M_n = 60\,000$ g/mol, $D = 1.8$)

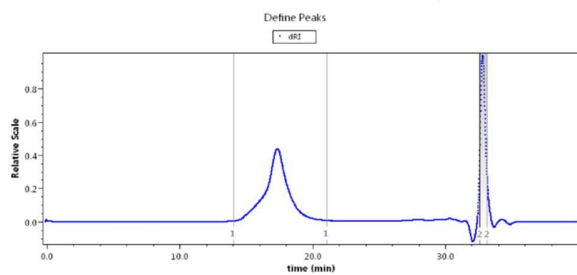


Fig. S28 Entry 3, Table S2 ($M_n = 84\,000$ g/mol, $D = 2.0$)

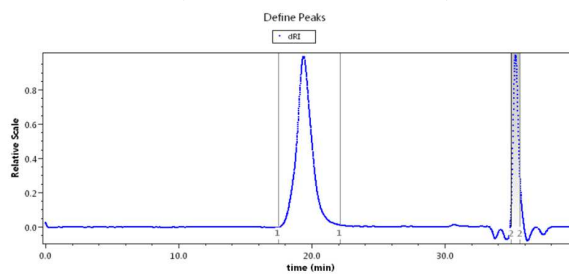


Fig. S29 Entry 4, Table S2 ($M_n = 155\,000$ g/mol, $D = 1.3$)

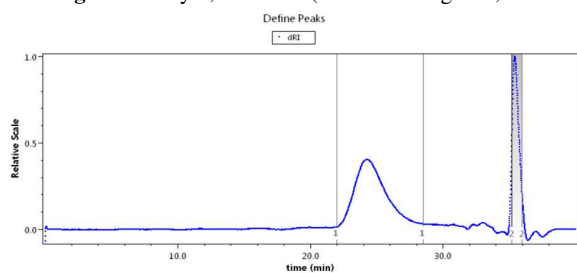


Fig. S30 Entry 5, Table S2 ($M_n = 8\,000$ g/mol, $D = 1.3$)

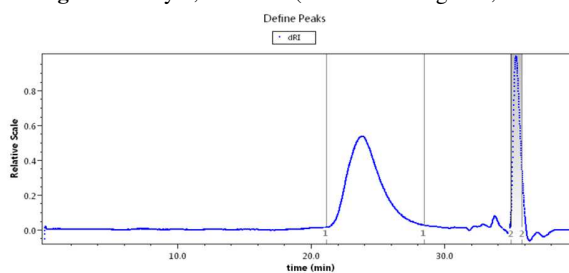


Fig. S31 Entry 6, Table S2 ($M_n = 10\,600$ g/mol, $D = 1.3$)

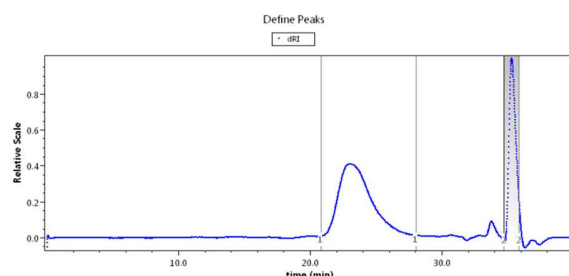


Fig. S32 Entry 7, Table S2 ($M_n = 14\,500$ g/mol, $D = 1.3$)

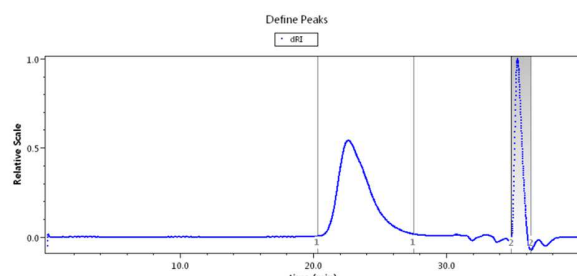


Fig. S33 Entry 8, Table S2 ($M_n = 17\,000$ g/mol, $D = 1.3$)

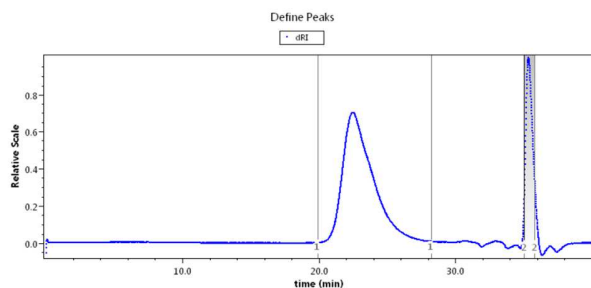


Fig. S34 Entry 9, Table S2 ($M_n = 19\,000$ g/mol, $D = 1.3$)

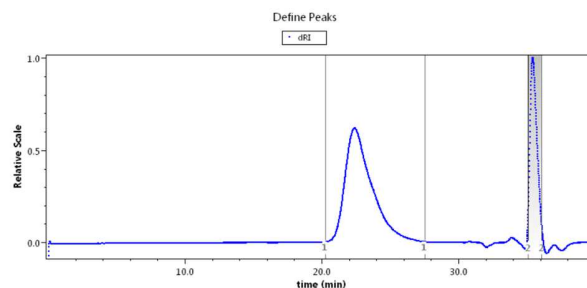


Fig. S35 Entry 10, Table S2 ($M_n = 20\,500$ g/mol, $D = 1.3$)

3.5 SEC chromatograms of polyisoprene according to the data presented in Table 2

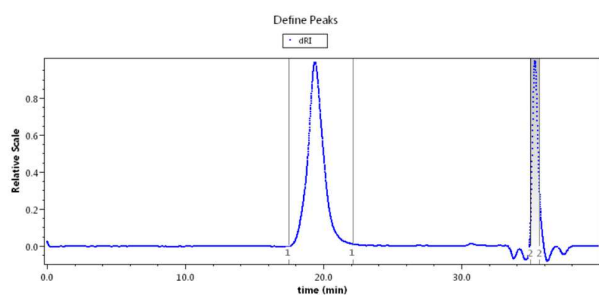


Fig. S36 Entry 1, Table 2 ($M_n = 155\,000$ g/mol, $D = 1.3$)

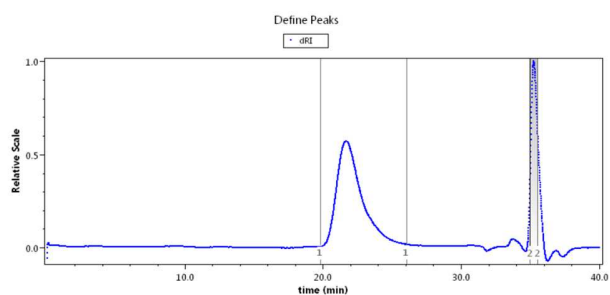


Fig. S37 Entry 2, Table 2 ($M_n = 33\,000$ g/mol, $D = 1.5$)

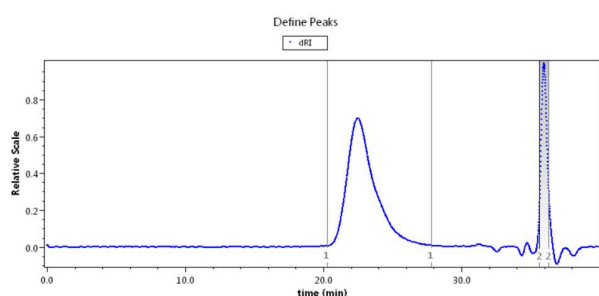


Fig. S38 Entry 3, Table 2 ($M_n = 20\,500$ g/mol, $D = 1.3$)

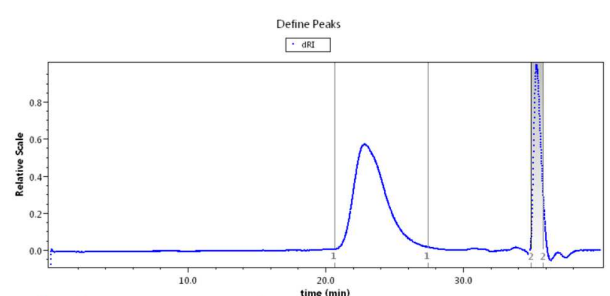


Fig. S39 Entry 4, Table 2 ($M_n = 15\,000$ g/mol, $D = 1.2$)

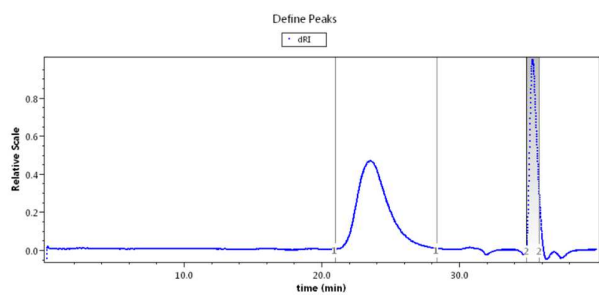


Fig. S40 Entry 5, Table 2 ($M_n = 12\,000$ g/mol, $D = 1.3$)

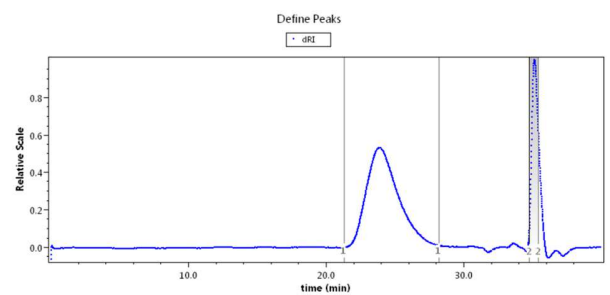


Fig. S41 Entry 6, Table 2 ($M_n = 10\,000$ g/mol, $D = 1.3$)

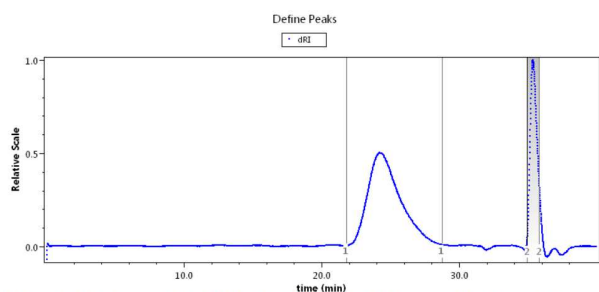


Fig. S42 Entry 7, Table 2 ($M_n = 8\,000$ g/mol, $D = 1.3$)

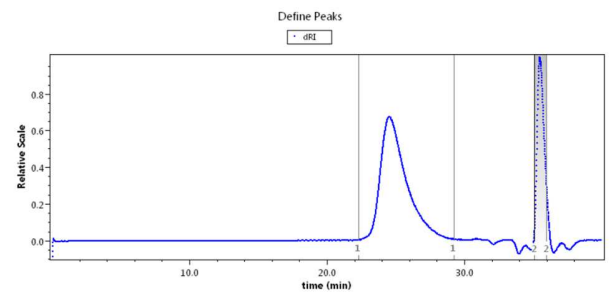


Fig. S43 Entry 8, Table 2 ($M_n = 6\,600$ g/mol, $D = 1.2$)

3.6 NMR spectra of polyisoprene according to the data presented in Table 2

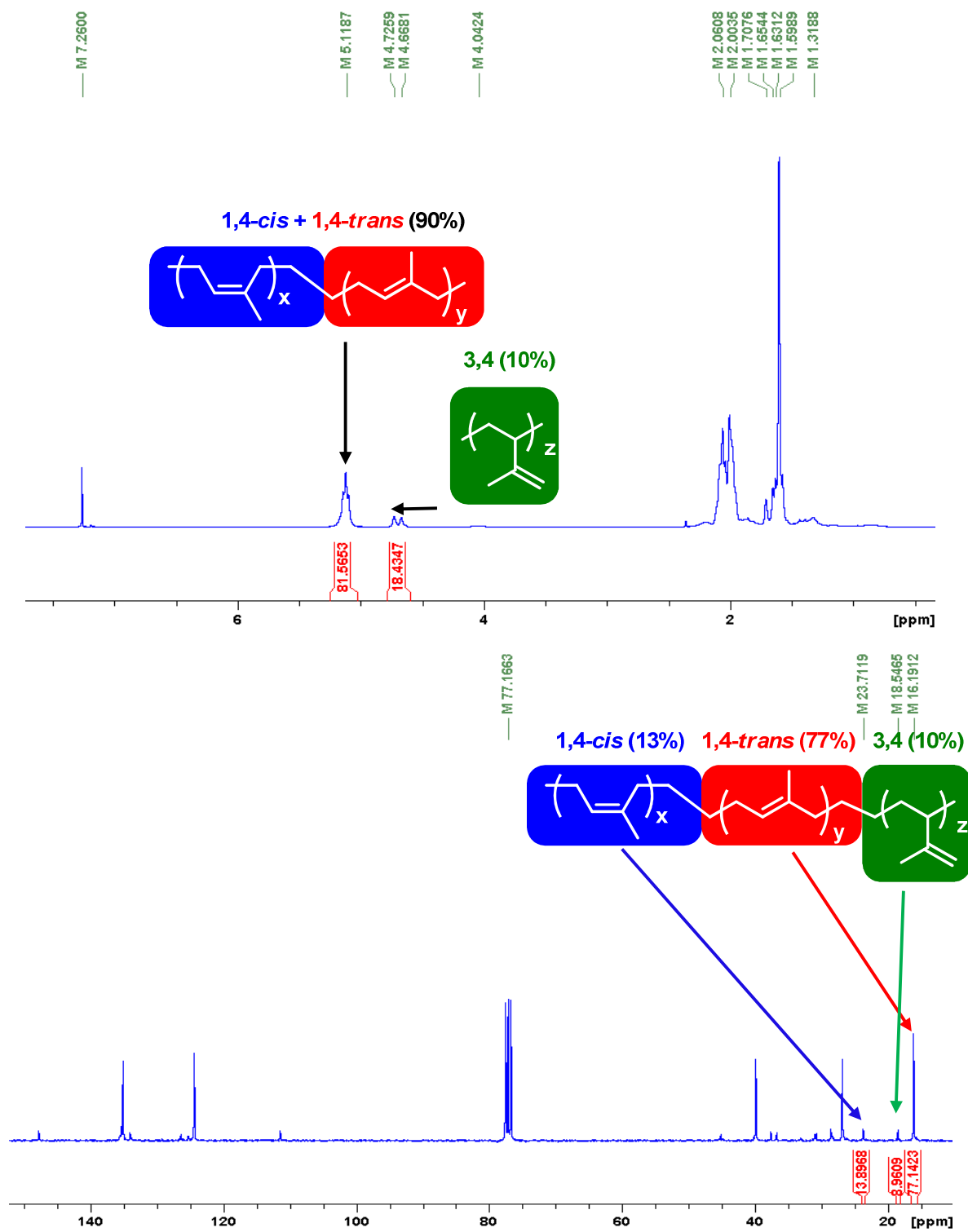


Fig. S44 Microstructure content of the polymer obtained from **Entry 1** (0 eq. of ZnEt_2) in **Table 2** with ^1H (top) & ^{13}C (bottom) NMR (300 MHz, CDCl_3 , 25 °C)

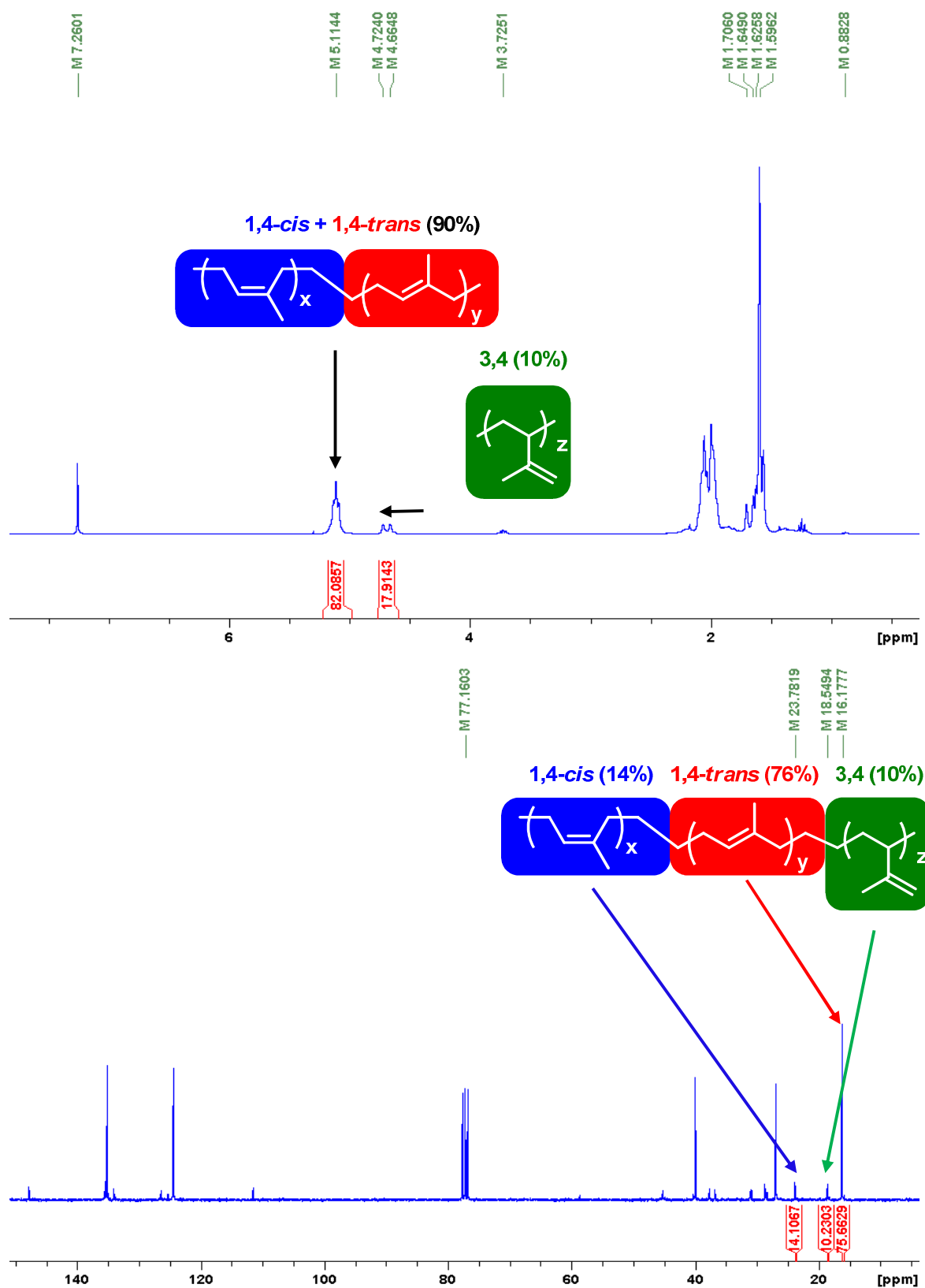


Fig. S45 Microstructure content of the polymer obtained from **Entry 2** (5 eq. of ZnEt₂) in **Table 2** with ¹H (top) & ¹³C (bottom) NMR (300 MHz, CDCl₃, 25 °C)

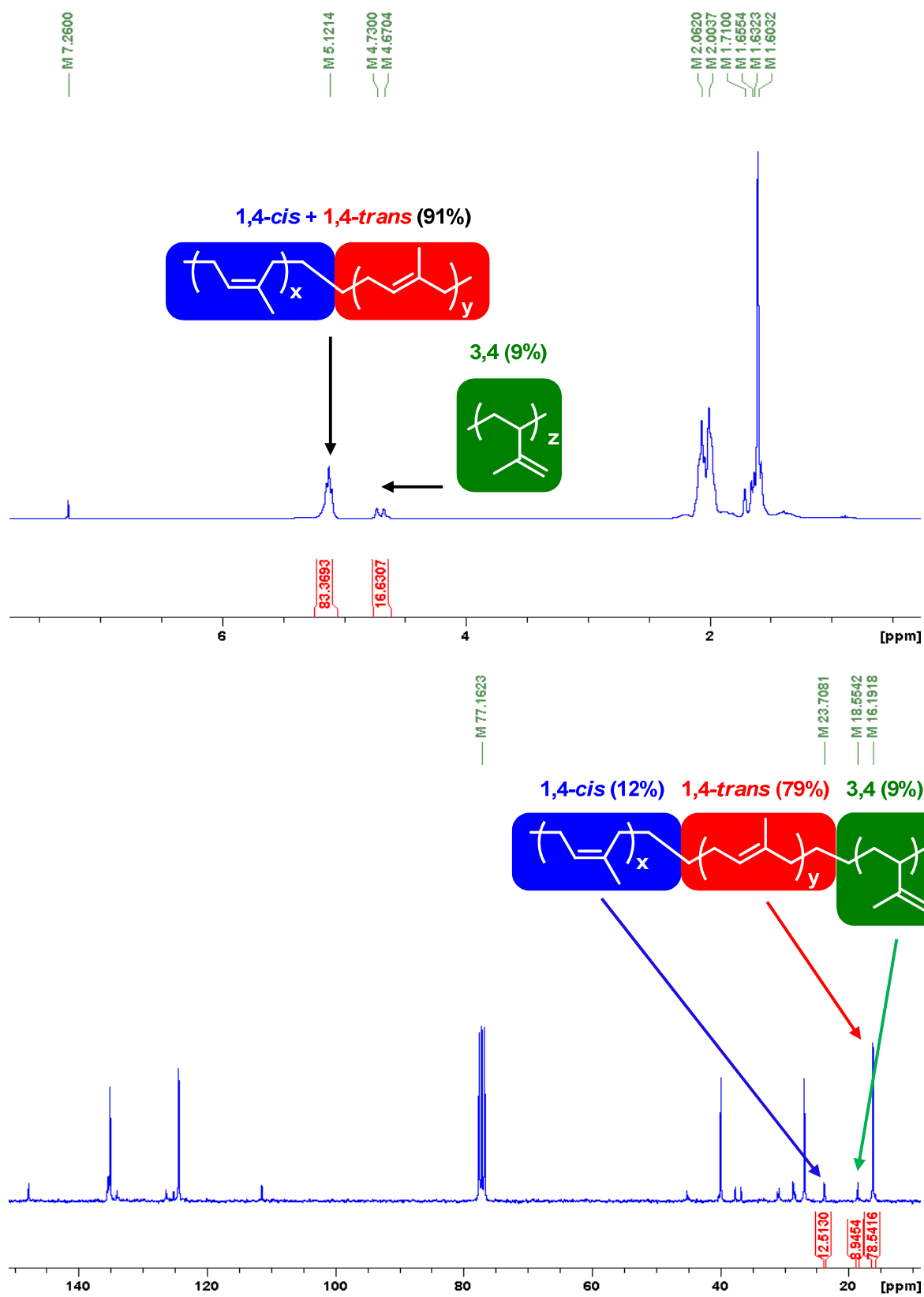


Fig. S46. Microstructure content of the polymer obtained from **Entry 3** (10 eq. of ZnEt₂) in **Table 2** with ¹H (top) & ¹³C (bottom) NMR (300 MHz, CDCl₃, 25 °C)

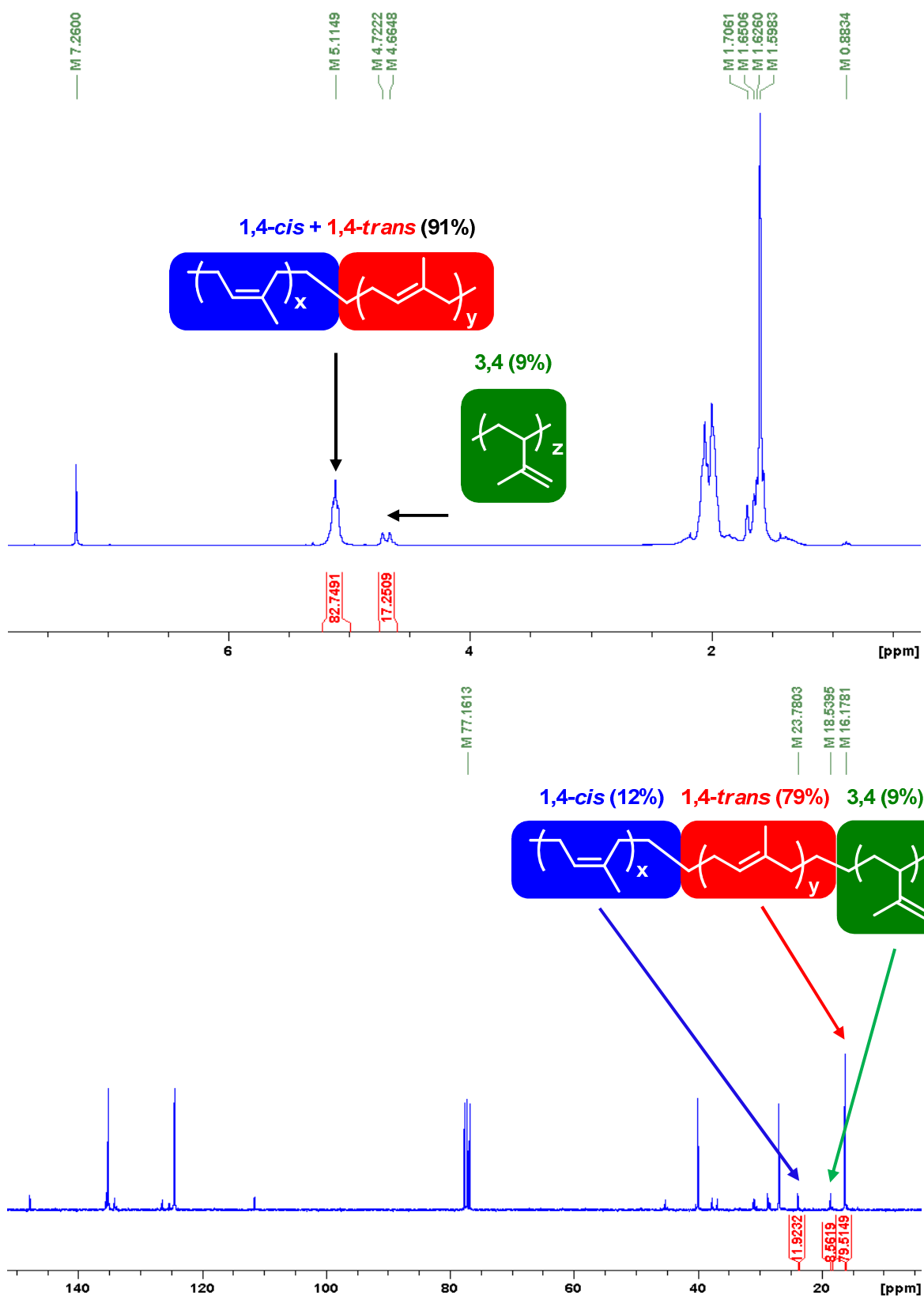


Fig. S47 Microstructure content of the polymer obtained from **Entry 4** (20 eq. of ZnEt₂) in **Table 2** with ¹H (top) & ¹³C (bottom) NMR (300 MHz, CDCl₃, 25 °C)

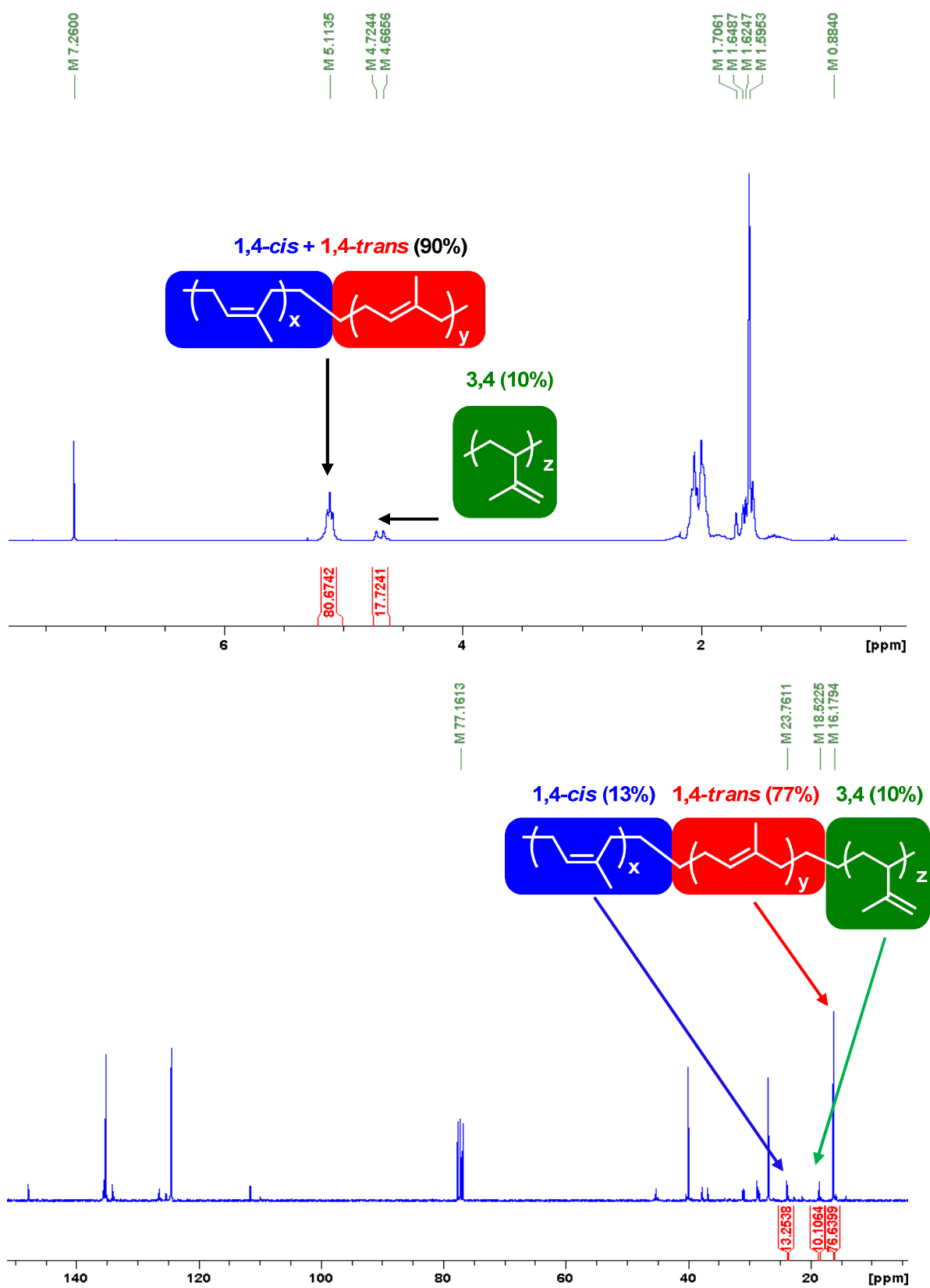


Fig. S48 Microstructure content of the polymer obtained from **Entry 5** (30 eq. of ZnEt₂) in **Table 2** with ¹H (top) & ¹³C (bottom) NMR (300 MHz, CDCl₃, 25 °C)

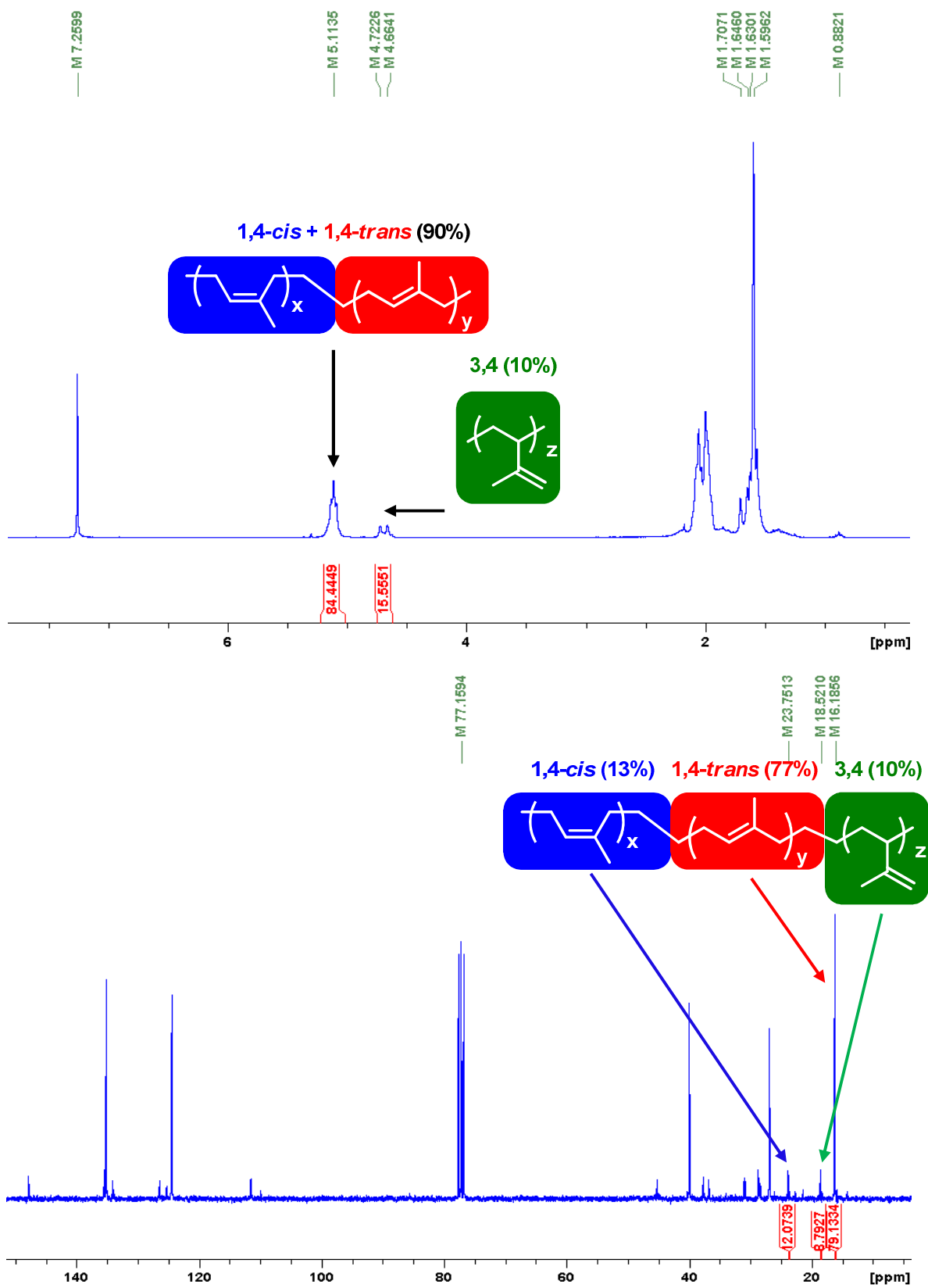


Fig. S49 Microstructure content of the polymer obtained from **Entry 6** (40 eq. of ZnEt_2) in **Table 2** with ^1H (top) & ^{13}C (bottom) NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$)

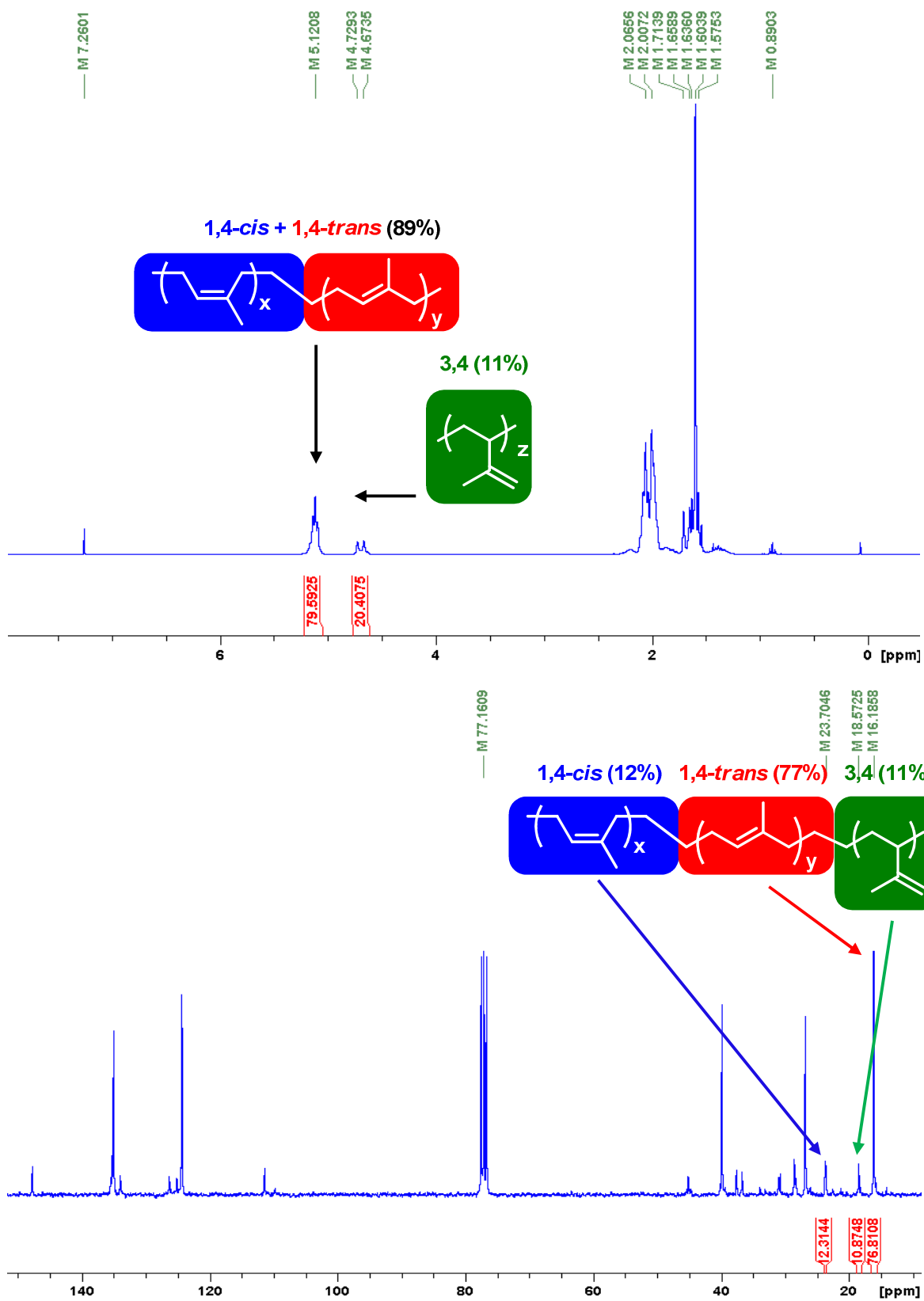


Fig. S50 Microstructure content of the polymer obtained from **Entry 7** (50 eq. of ZnEt₂) in **Table 2** with ¹H (top) & ¹³C (bottom) NMR (300 MHz, CDCl₃, 25 °C)

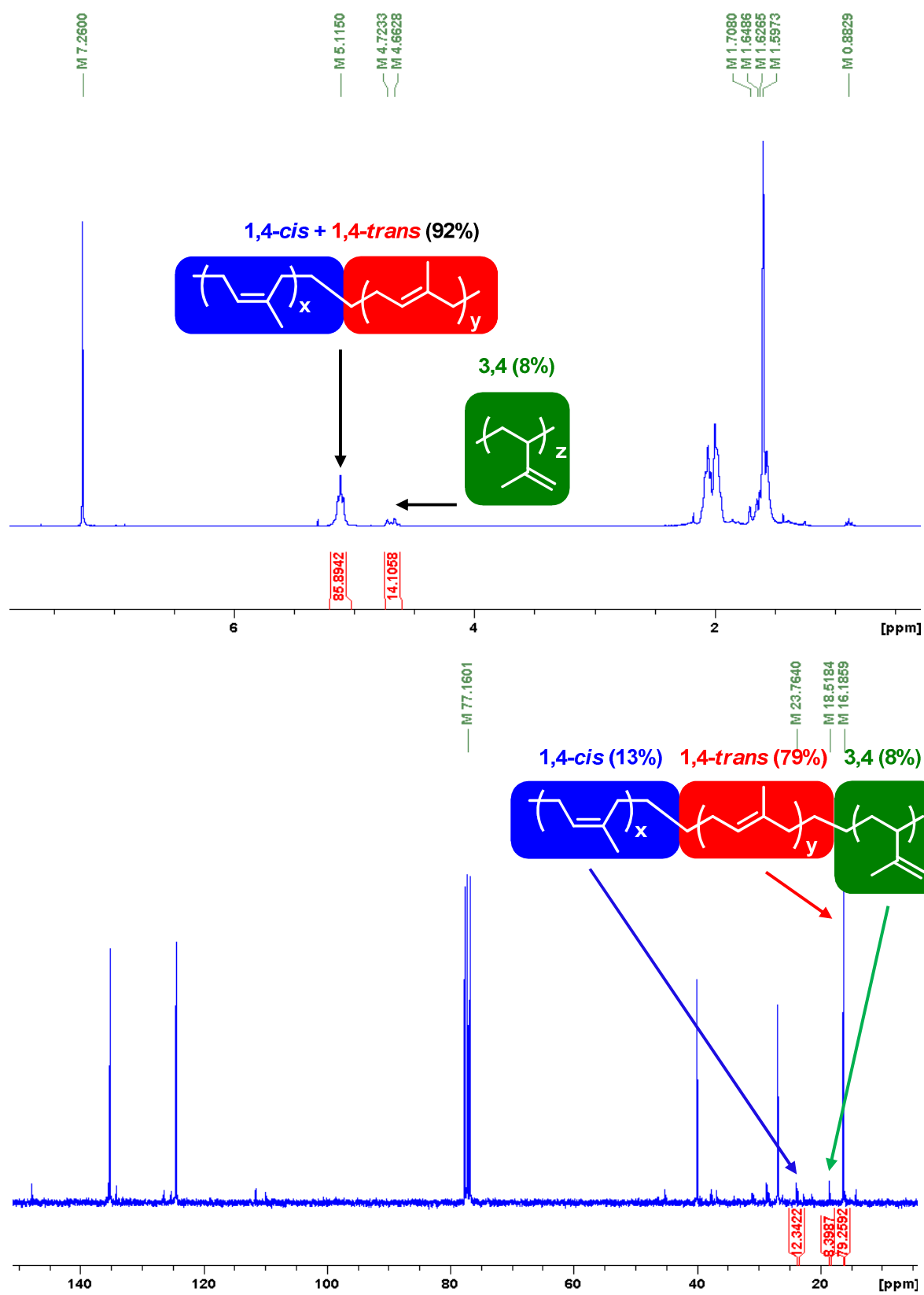
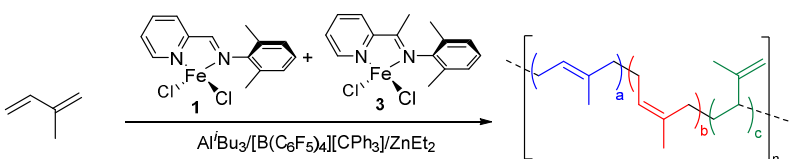


Fig. S51 Microstructure content of the polymer obtained from **Entry 8** (100 eq. of ZnEt₂) in **Table 2** with ¹H (top) & ¹³C (bottom) NMR (300 MHz, CDCl₃, 25 °C)

3.7 Results of the Chain Shuttling Polymerization (CSP) of isoprene using **1** and **3**

Table S3 Screening **1+3**/AlⁱBu₃/[B(C₆F₅)₄][CPh₃]/ZnEt₂ catalytic systems for the CSP of isoprene^a



Entry ^a	Complex 3/1	Time (min)	Conv. (%)	$M_n(\text{exp})^b$ (g/mol)	\bar{D}^b	Microstructure ^c (%)		T_g (°C) ^d
						1,4 (<i>trans/cis</i>)	3,4	
1*	10/0	360	> 99	86 000	1.3	91 (69/22)	9	-61.7
2	9/1	360	> 99	97 000	1.5	89 (66/23)	11	-60.3
3**	5/5	360	> 99	120 000	1.5	85 (40/45)	15	-56.8
4	1/9	360	> 99	150 000	1.5	79 (38/41)	21	-51.2
5*	0/10	360	> 99	180 000	1.7	79 (33/46)	21	-51.6
6 ^{e,**}	5/5	360	> 99	380 000	1.6	84 (43/41)	16	-55.5

^a Polymerization conditions: 10 μmol of complex **1+3**, isoprene/**1+3**/AlⁱBu₃/[B(C₆F₅)₄][CPh₃]/ZnEt₂ = 2 000/1/3/1/10, toluene = 20 mL, [C]isoprene = 1 mol/L, temperature = 25 °C. ^b Determined by SEC analysis in THF using polystyrene standards. ^c Determined by ¹H NMR and ¹³C NMR. ^d Determined by DSC. ^e Without ZnEt₂. * Data extracted from Table 1. ** Data extracted from Table 3

Results and Discussion: The CSP of isoprene was carried out at room temperature for 6 hours using different ratios of a mixture of complexes **1** and **3** combined with AlⁱBu₃/[B(C₆F₅)₄][CPh₃] in the presence of 10 eq. of ZnEt₂/**1+3** (Table S3). The SEC chromatograms, NMR spectra and DSC thermograms of all samples are presented in Figs S52-S57, S58-S63, S64-S69, respectively. Firstly, the catalytic system **3**/AlⁱBu₃/[B(C₆F₅)₄][CPh₃]/ZnEt₂ (2 000/1/3/1/10) produced polyisoprene (M_n = 86 000 g/mol, \bar{D} = 1.3) whose microstructure contains *trans*-1,4/*cis*-1,4/3,4 units = 69/22/9 with a T_g value of -61.7 °C (Entry 1, Table S3). By adding a small amount of complex **1** (**3/1** ratio = 9/1), a minor decrease in the *trans*-1,4 selectivity was observed with a modest increase of 3,4 units in the resulting polyisoprene (*trans*-1,4/3,4 = 66/11, Entry 2, Table S3), which also exhibits slightly higher values of T_g and M_n (T_g = -60.3 vs -61.7 °C and M_n = 97 000 vs 86 000 g/mol for **3/1** = 9/1 and **3** alone, respectively). Most interestingly, when a 1/1 ratio of complexes **3/1** was used in presence of 10 eq. of ZnEt₂, the resulting polyisoprene exhibits average values of microstructure contents, M_n and T_g values (*trans*-1,4/*cis*-1,4/3,4 = 40/45/15, M_n = 120 000 g/mol, T_g = -56.8 °C, Entry 3, Table S3) of both individual catalytic systems under CCTP. The same polymerization was also carried out in the absence of ZnEt₂ and resulted in a polyisoprene presenting a stereo-, regio-regularity along with a T_g value *quasi* similar to that obtained in the presence of CTA (Entry 3 vs 6, Table S3, Figs S71 and S72, respectively). The unique glass transition found at -55.5 °C was expected given that the physical mixture of the two homopolymers, produced independently by CCTP, displays a single T_g of -57.1 °C (Fig. S70) due to the miscibility of the blend. However, the resulting M_n of the polymer produced under CSP was found to be 3 times lower than that achieved without ZnEt₂ (M_n = 180 000 vs 380 000 g/mol, respectively, Fig S73), which is similar to the number of chains generated for each independent complexes under CCTP ($N = 2.7 - 3$). An increase ratio of complex **1** to **3** (**3/1** = 1/9, Entry 4, Table S3) has led to the polyisoprene displaying a microstructure content along with M_n and T_g values that tend to be closer to the polymer produced by complex **1** alone (Entry 5, Table S3). In summary, despite the similarity of the DSC chromatograms and NMR spectra of the polymers resulting from a 1/1 ratio of complexes **1** and **3** in the absence and the presence of ZnEt₂, these results prevent us from stating unequivocally that the cross-transfer process has actually taken place, however, the 3-fold reduction in the M_n of the polymer produced in the presence of ZnEt₂ compared to that without ZnEt₂ strongly suggests the occurrence of a CSP process. Alternatively, it is also possible that the growing chains on each iron catalyst are not transferred from one to the other through the Zn CTA, thus producing a mixture of two homopolymers that incorporate the signature of each catalytic system rather than a single copolymer chain with a multiblock structure.

SEC chromatograms of polyisoprene according to the data presented in Table S3

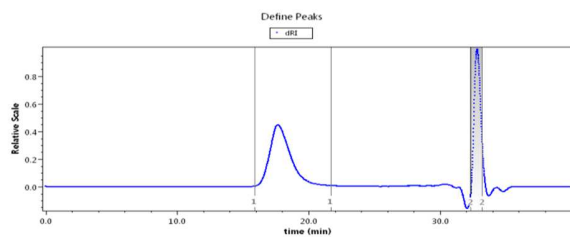


Fig. S52 (= Fig. S6) Entry 1, Table S3 ($M_n = 86\,000$ g/mol, $D = 1.3$)

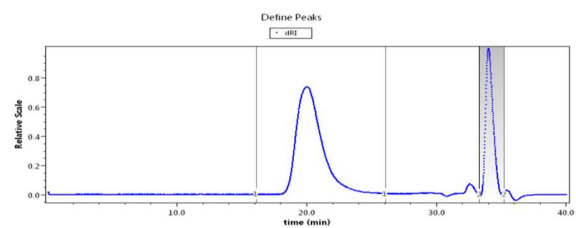


Fig. S53 Entry 2, Table S3 ($M_n = 97\,000$ g/mol, $D = 1.5$)

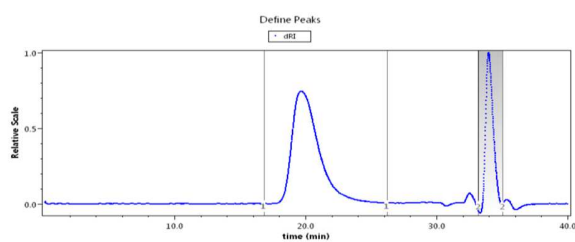


Fig. S54 Entry 3, Table S3 ($M_n = 120\,000$ g/mol, $D = 1.3$)

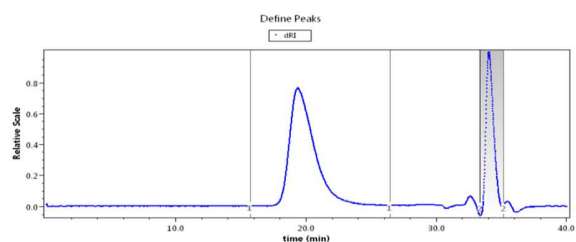


Fig. S55 Entry 4, Table S3 ($M_n = 150\,000$ g/mol, $D = 1.5$)

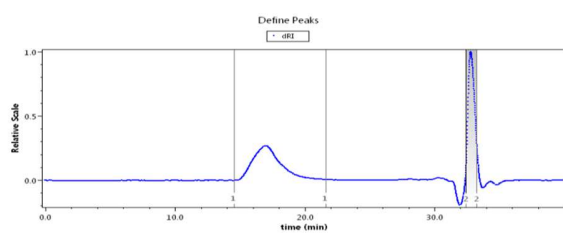


Fig. S56 (= Fig. S2) Entry 5, Table S3 ($M_n = 180\,000$ g/mol, $D = 1.3$)

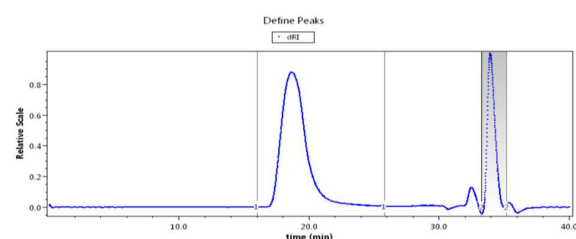


Fig. S57 Entry 6, Table S3 ($M_n = 380\,000$ g/mol, $D = 1.6$)

NMR spectra of polyisoprene according to the data presented in Table S3

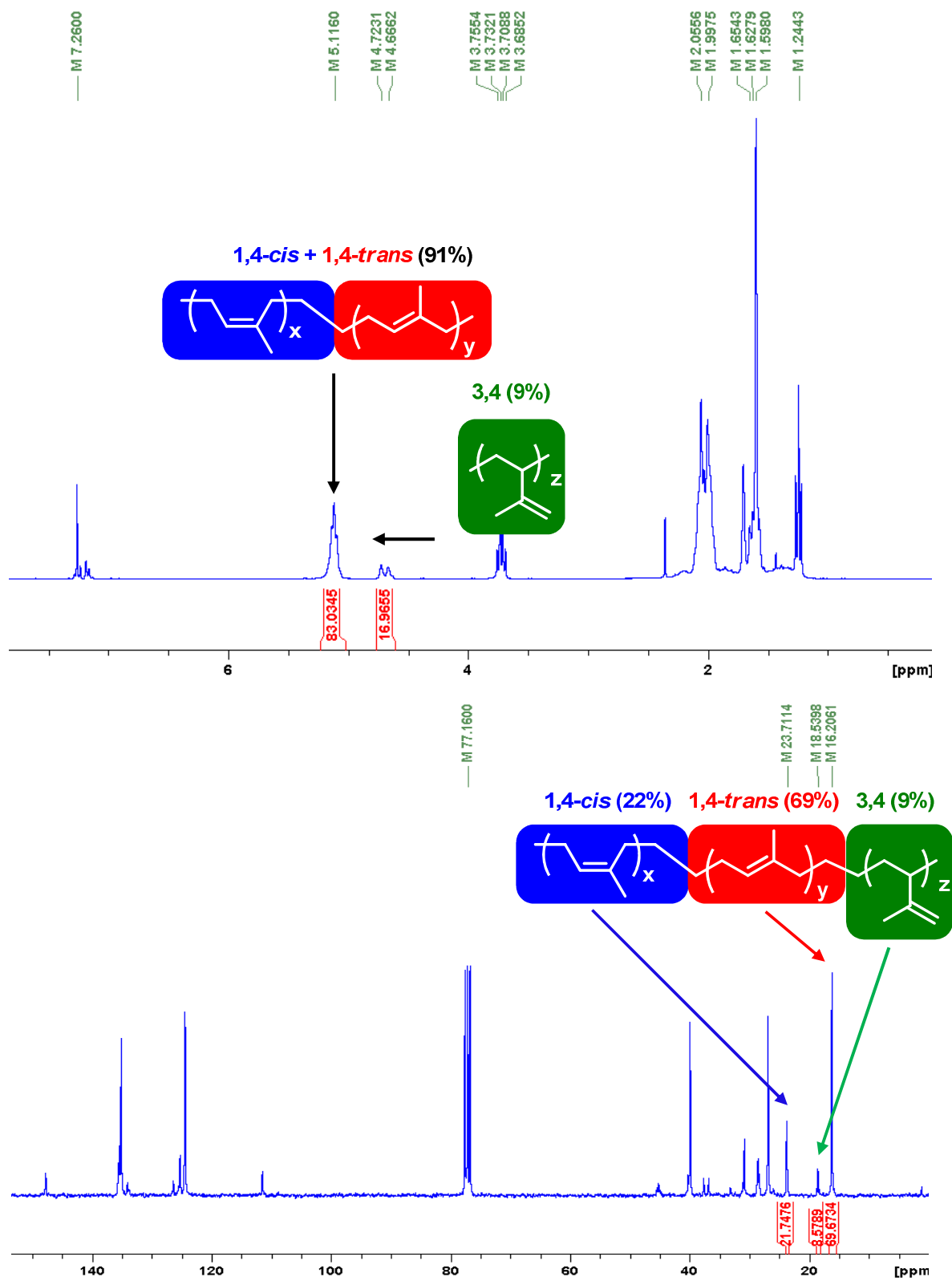


Fig. S58 (= Fig. S16) ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from Entry 1 in Table S3 (300 MHz, CDCl₃, 25 °C)

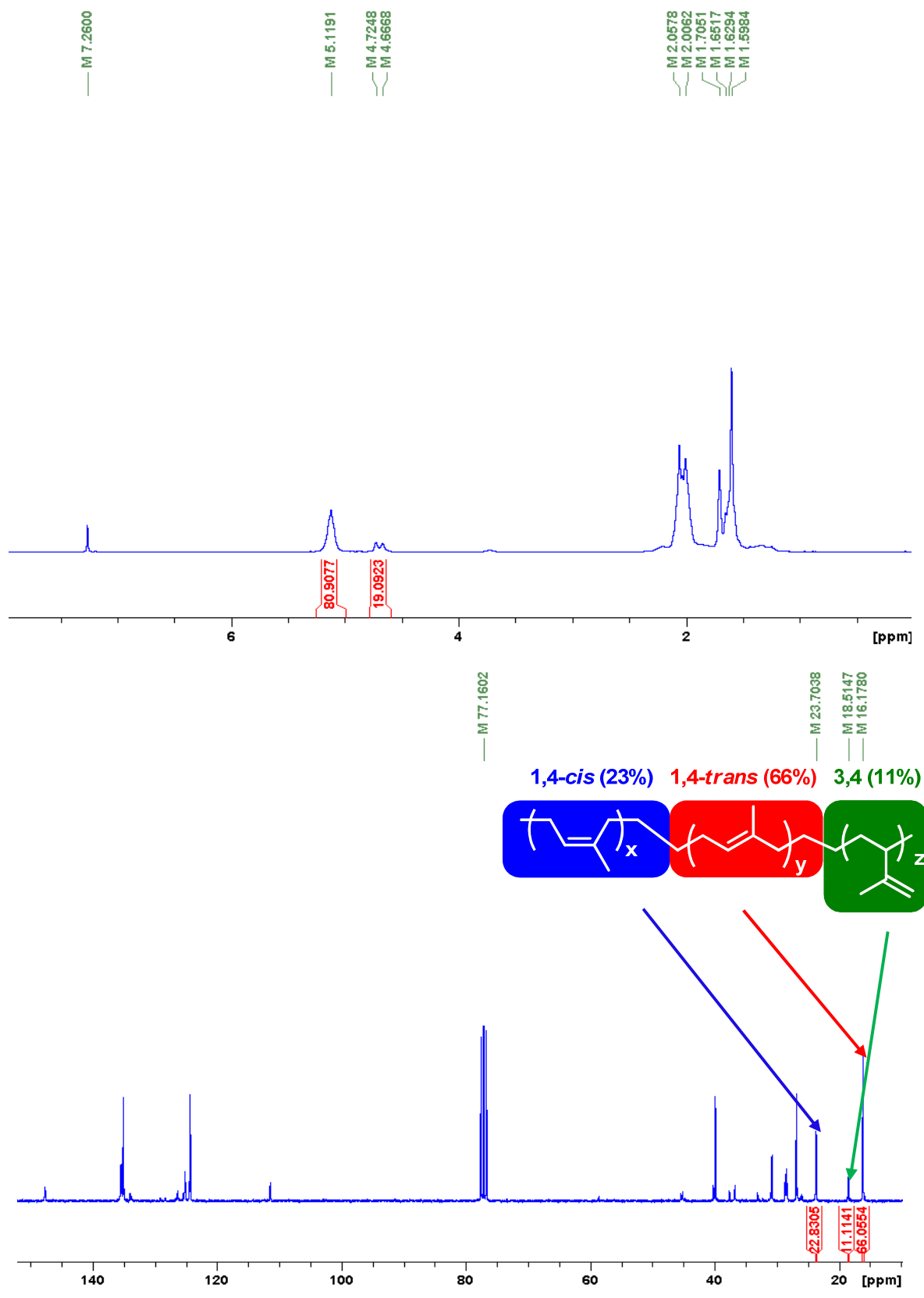


Fig. S59 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 2** in **Table S3** (300 MHz, CDCl₃, 25 °C)

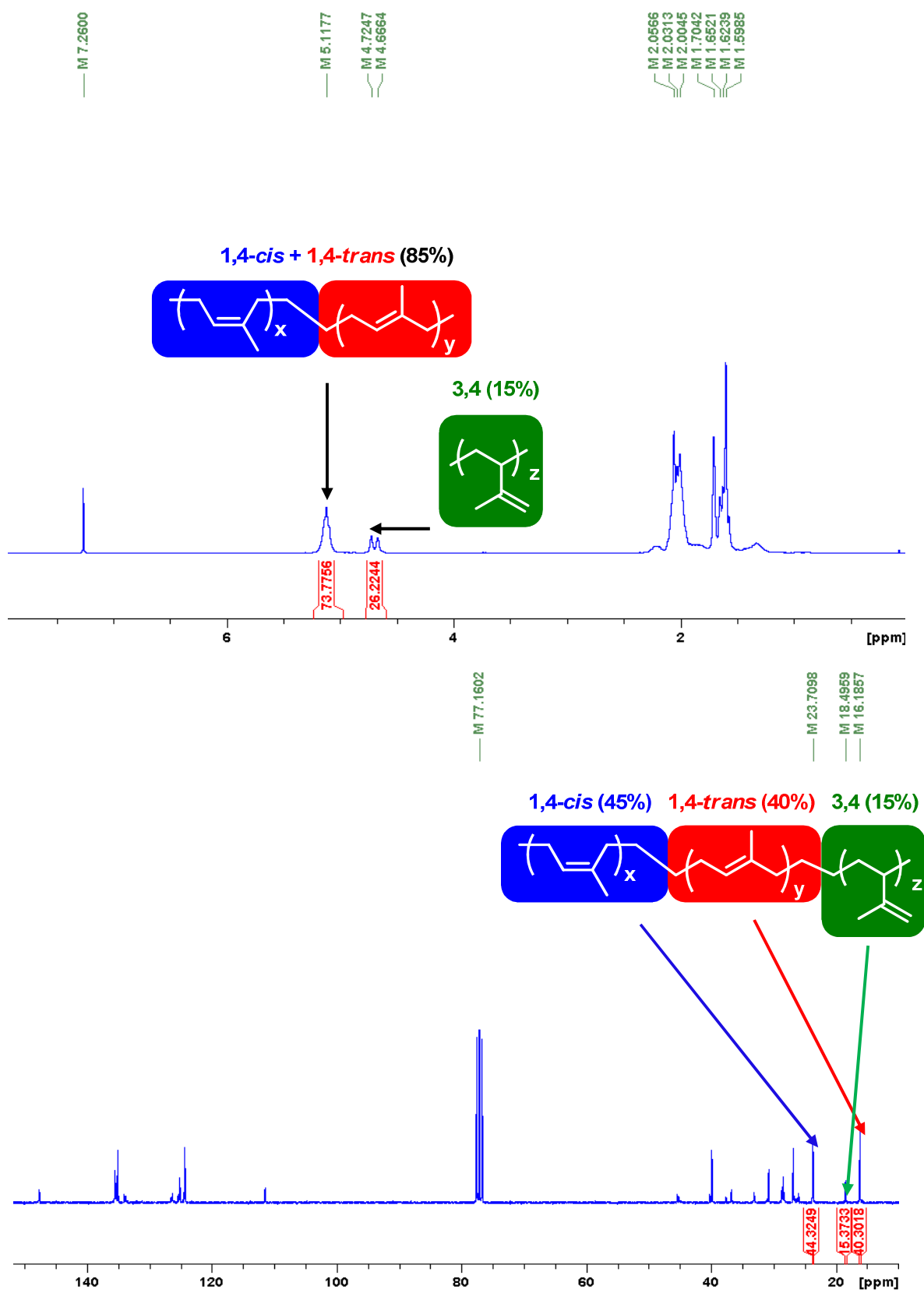


Fig. S60 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 3** in **Table S3** (300 MHz, CDCl₃, 25 °C)

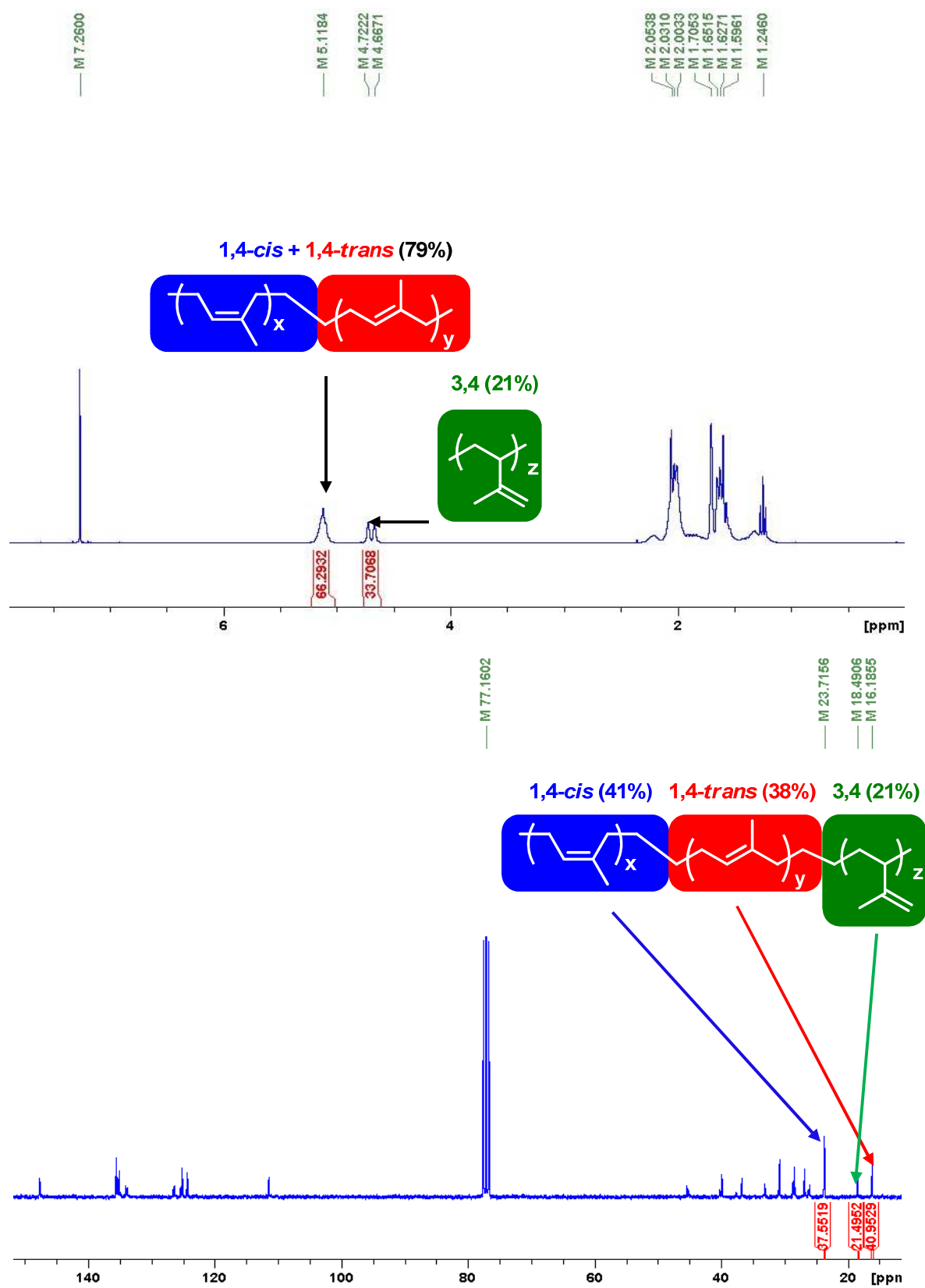


Fig. S61 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from Entry 4 in Table S3 (300 MHz, CDCl₃, 25 °C)

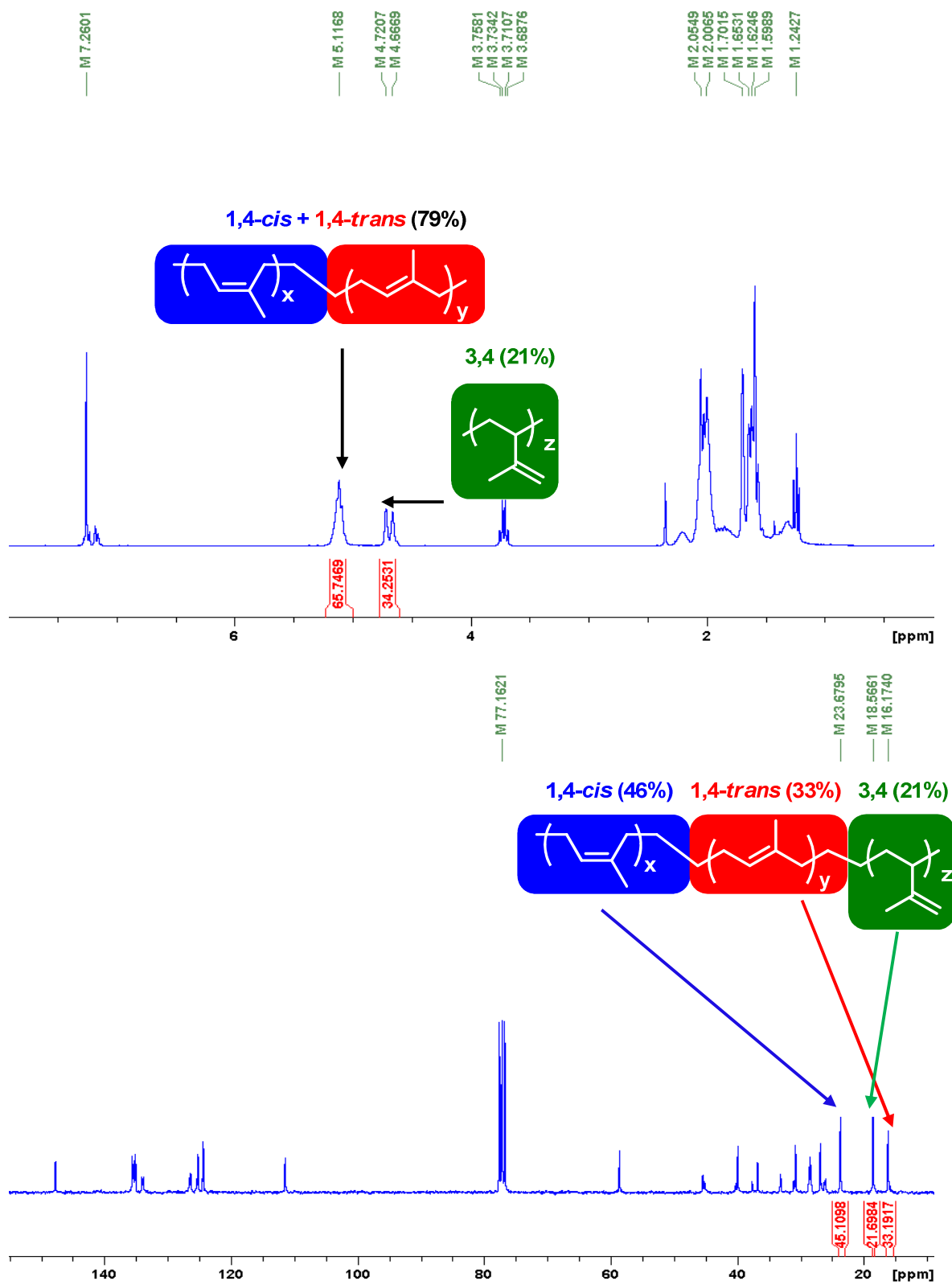


Fig. S62 (= Fig. S12) ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 5** in **Table S3** (300 MHz, CDCl₃, 25 °C)

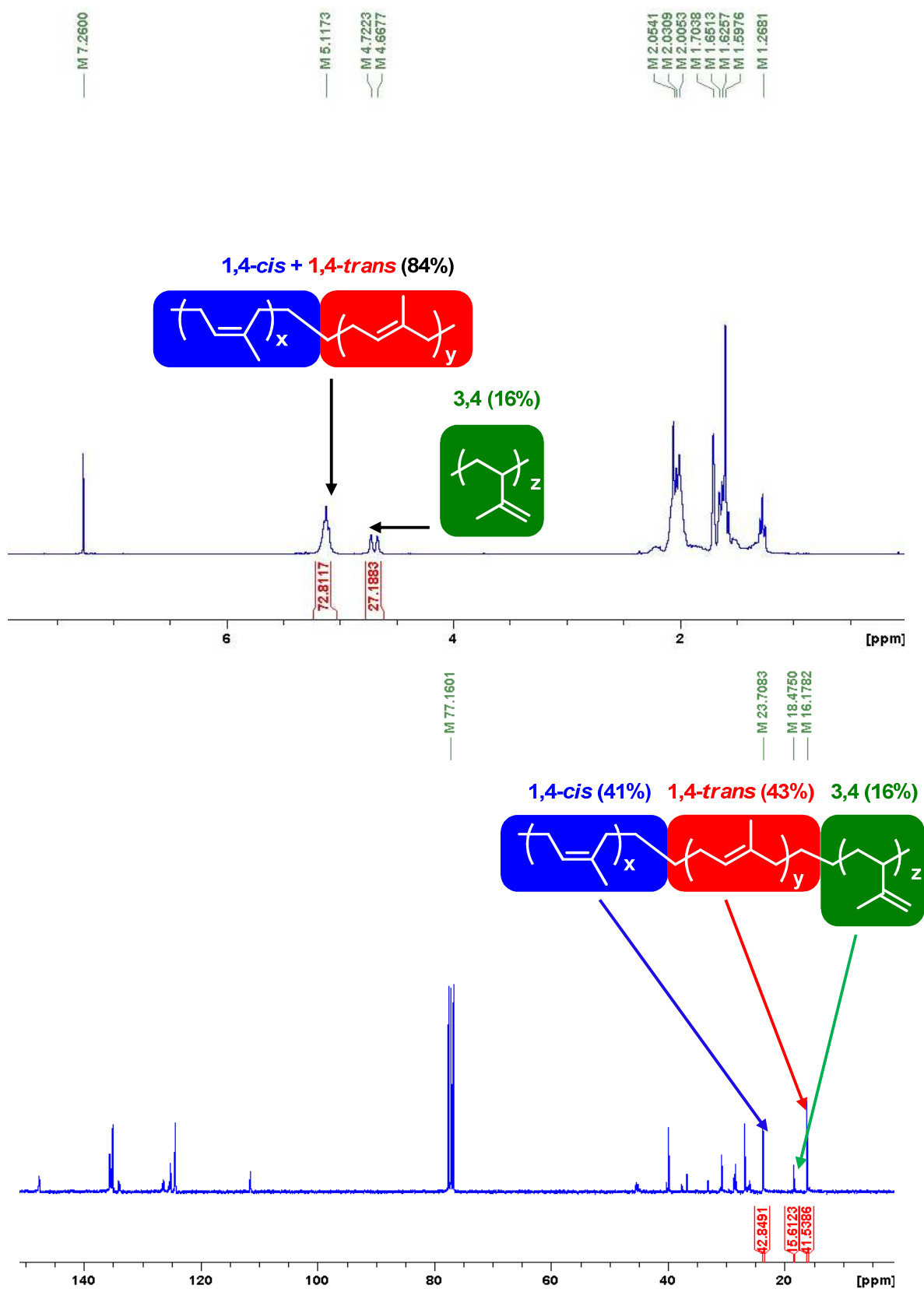


Fig. S63 ¹H (top) & ¹³C (bottom) NMR spectra of the polymer obtained from **Entry 6** in **Table S3** (300 MHz, CDCl₃, 25 °C)

DSC thermograms (2nd Heating) of polyisoprene according to the data presented in Table S3

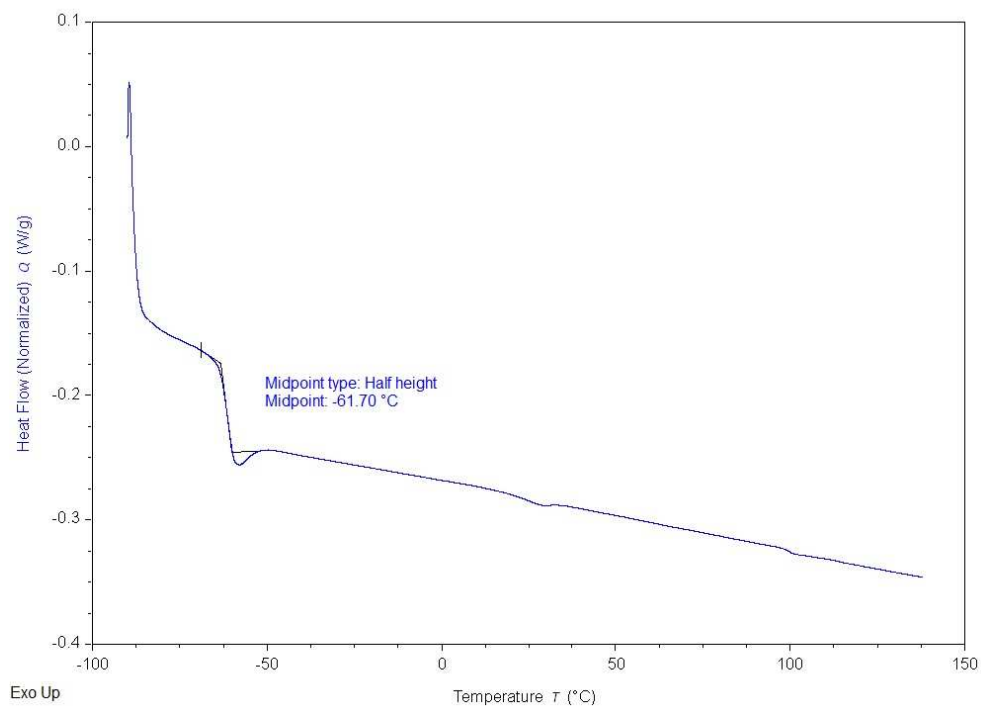


Fig. S64 Entry 1, Table S3 ($T_g = -61.7$ °C)

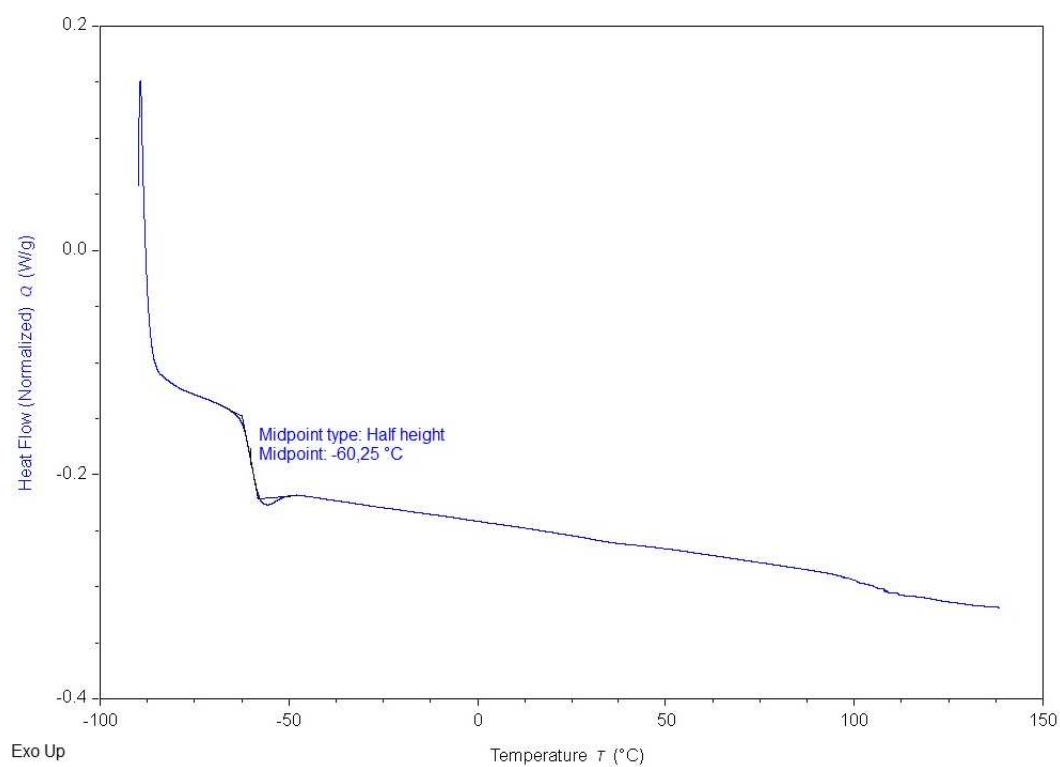


Fig. S65 Entry 2, Table S3 ($T_g = -60.3$ °C)

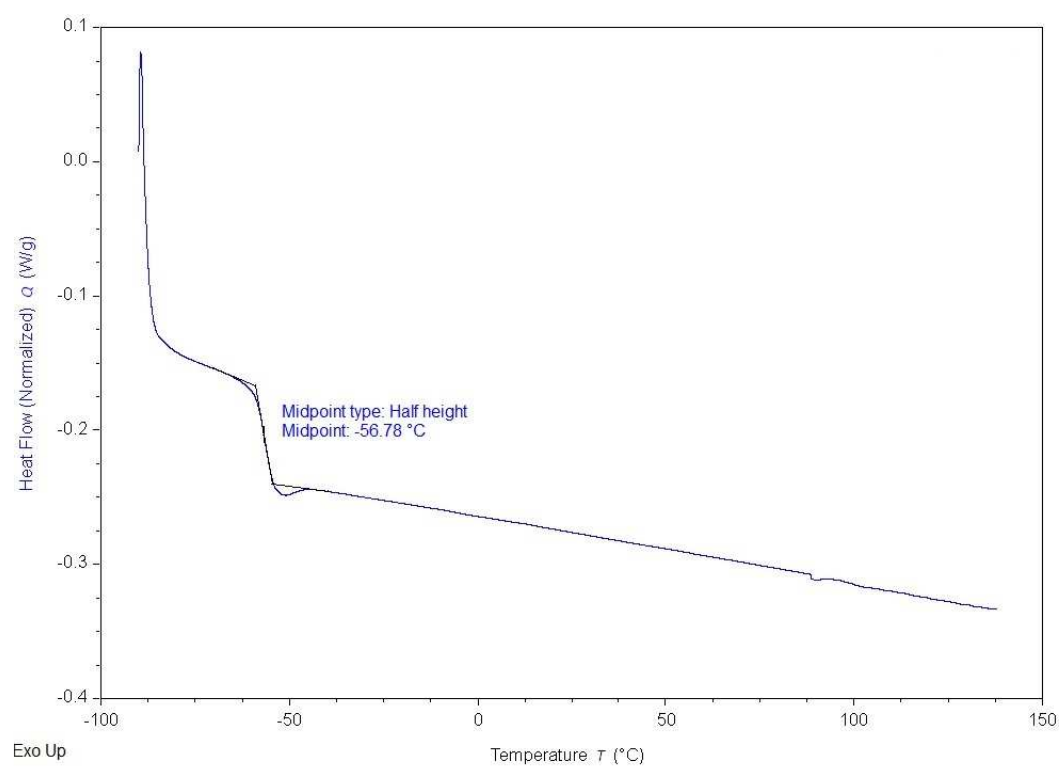


Fig. S66 Entry 3, Table S3 ($T_g = -56.8$ $^{\circ}\text{C}$)

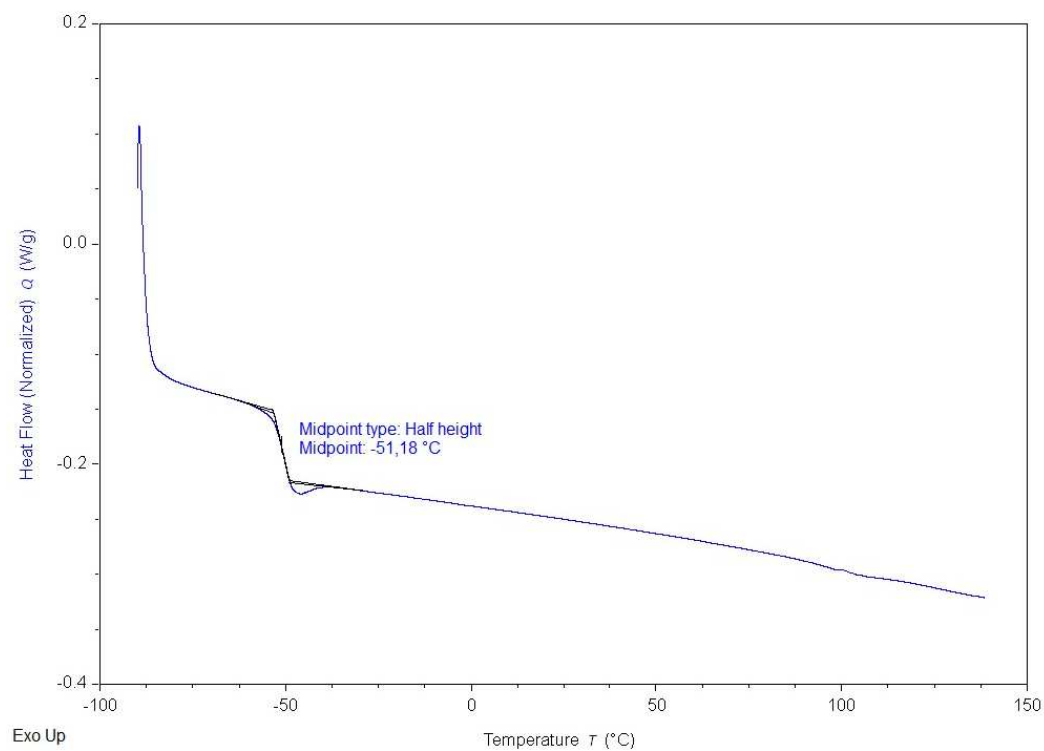


Fig. S67 Entry 4, Table S3 ($T_g = -51.2$ $^{\circ}\text{C}$)

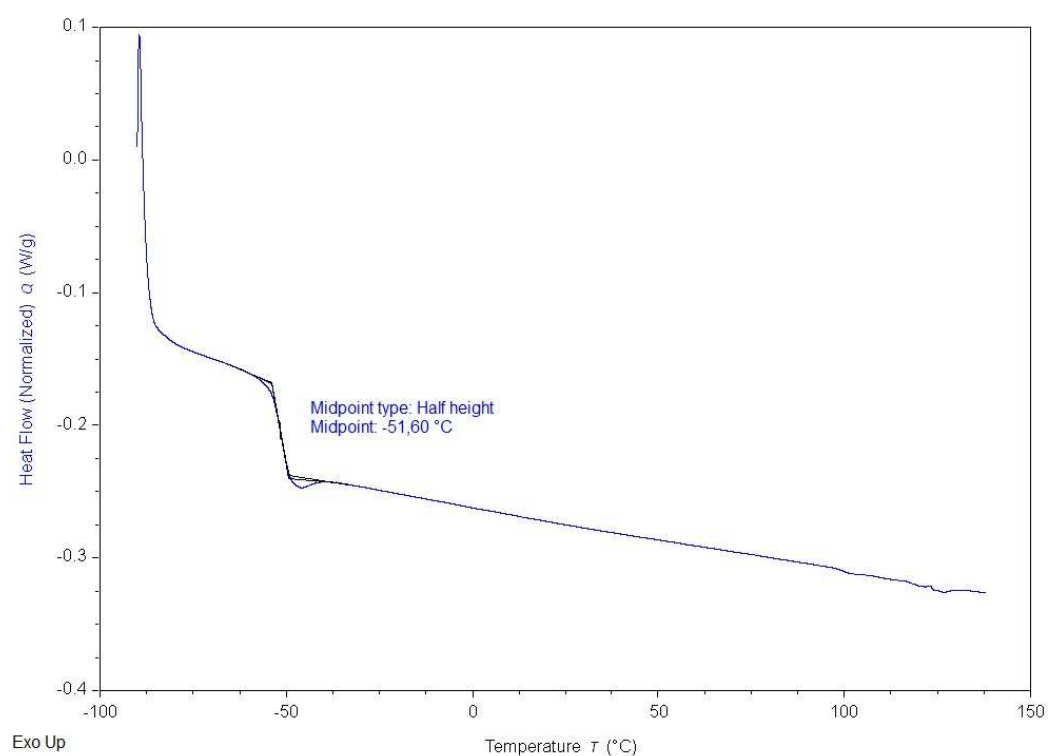


Fig. S68 Entry 5, Table S3 ($T_g = - 51.6$ °C)

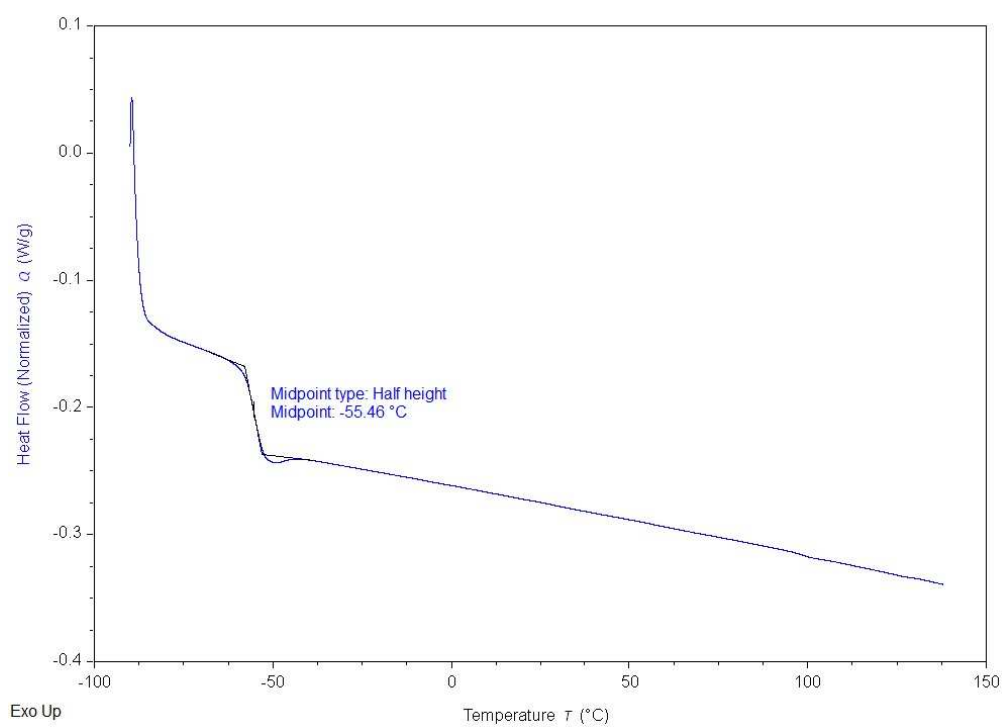


Fig. S69 Entry 6, Table S3 ($T_g = - 55.5$ °C)

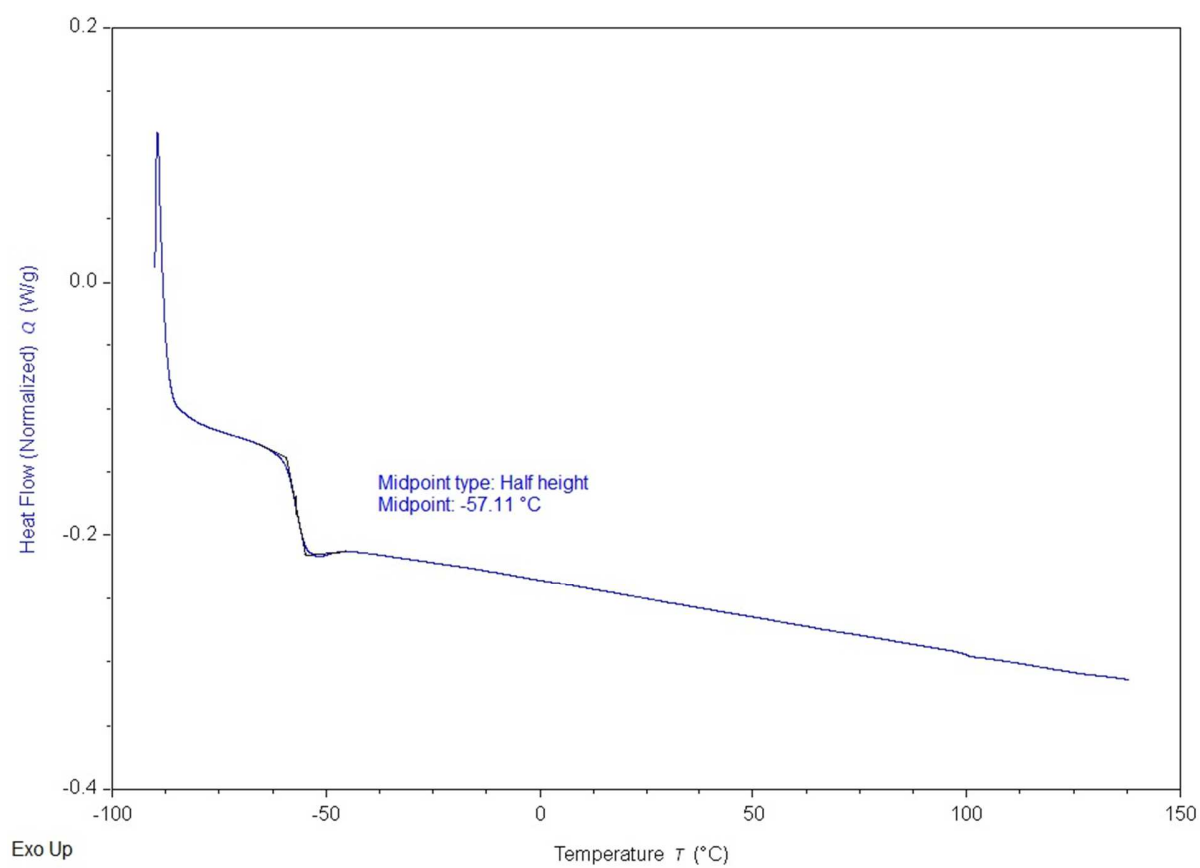


Fig. S70 Thermogram of the physical mixture of homopolymers (ratio 1/1 in mass) produced independently by CCTP with complexes **1** (isoprene/1/AlⁱBu₃/[B(C₆F₅)₄][CPh₃]/ZnEt₂ = 2 000/1/3/1/10, Entry 5, Table S3) and **3** (isoprene/3/AlⁱBu₃/[B(C₆F₅)₄][CPh₃]/ZnEt₂ = 2 000/1/3/1/10, Entry 1, Table S3) ($T_g = -57.1$ °C)

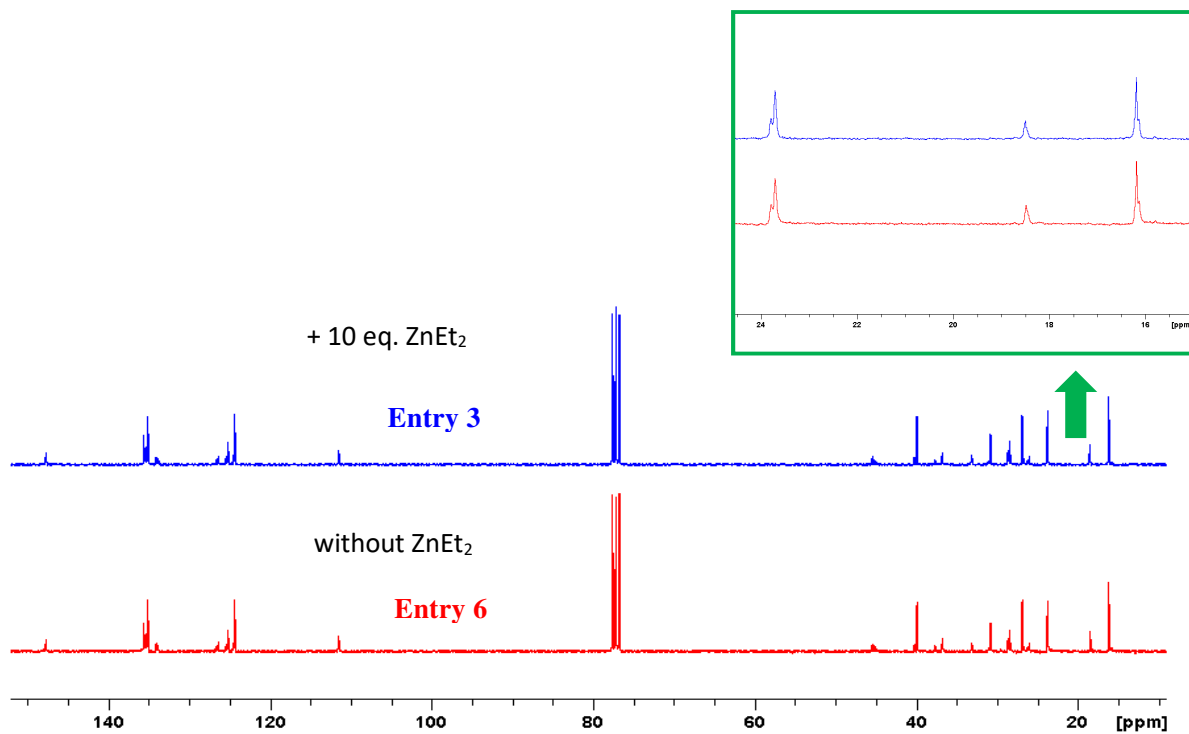
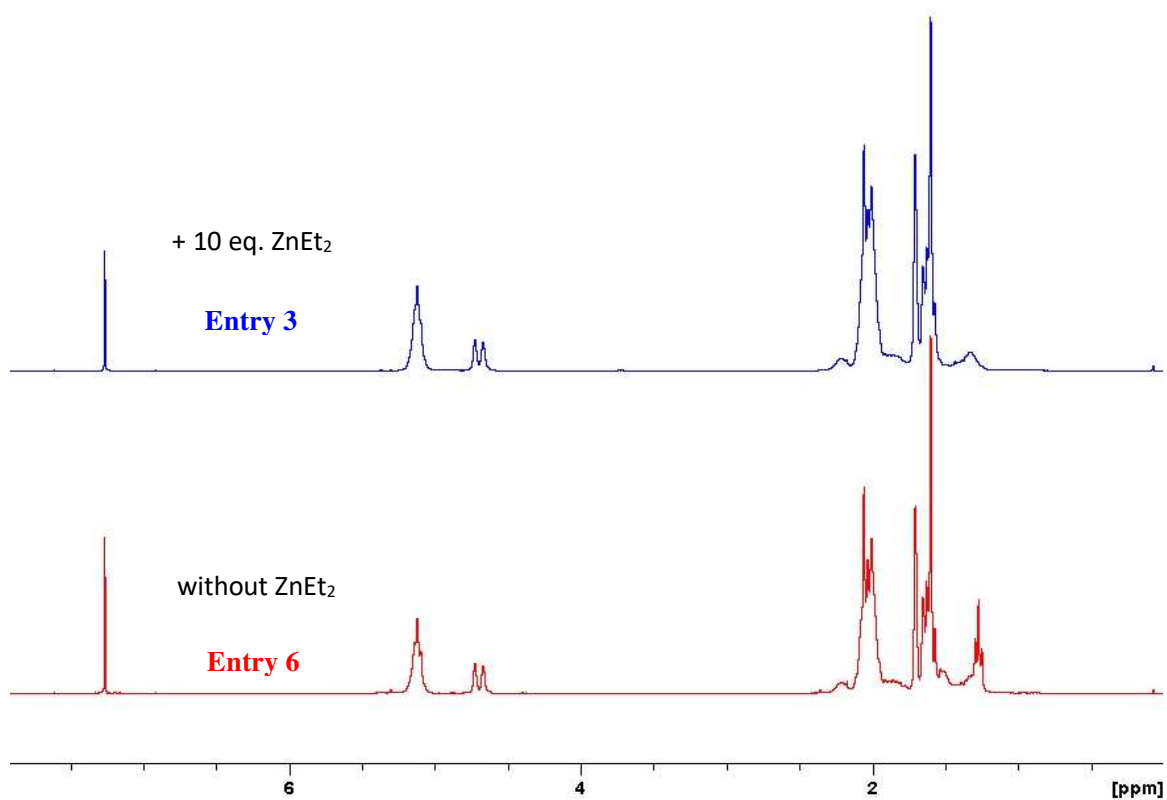


Fig. S71 Stacked NMR spectra (¹H top and ¹³C bottom) of polyisoprene according to the data presented in Table S3 (Entry 3 vs Entry 6)

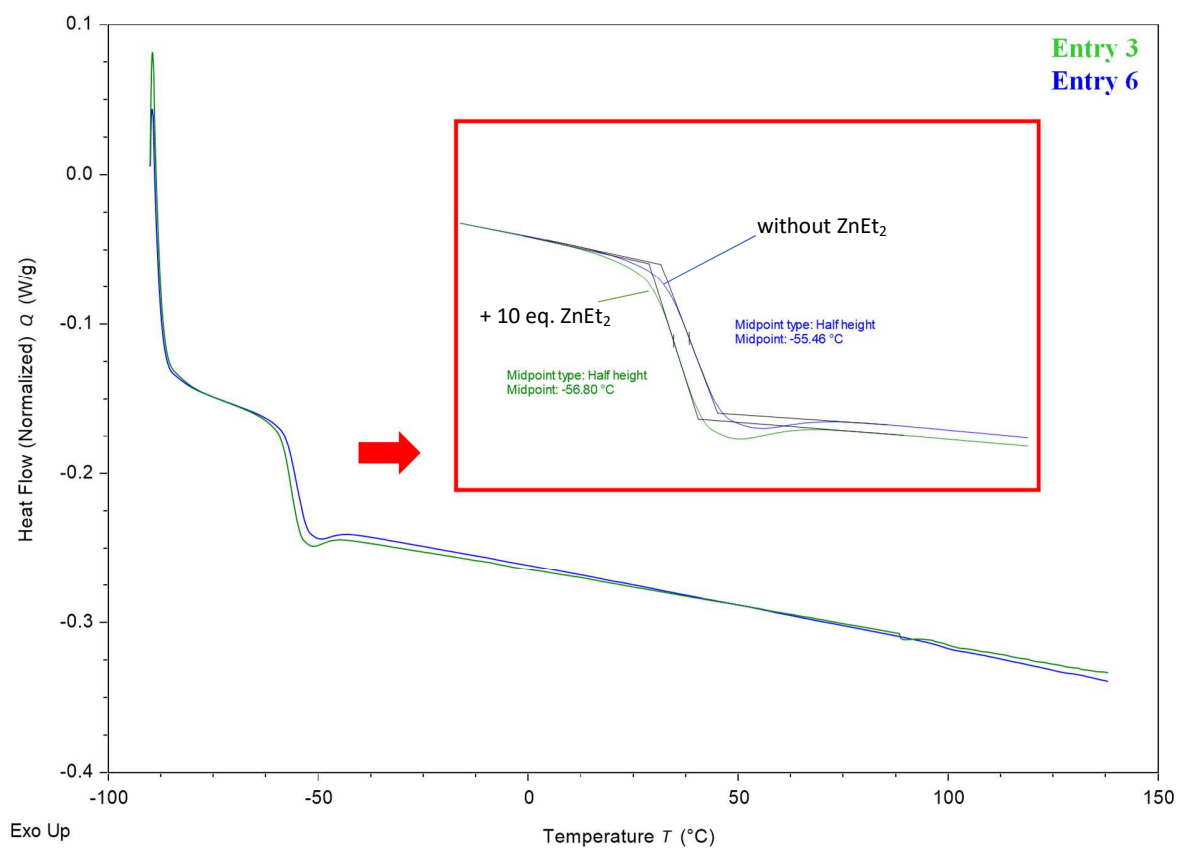


Fig. S72 Stacked DSC thermograms (2nd Heating) of polyisoprene according to the data presented in Table S3 (Entry 3 vs Entry 6)

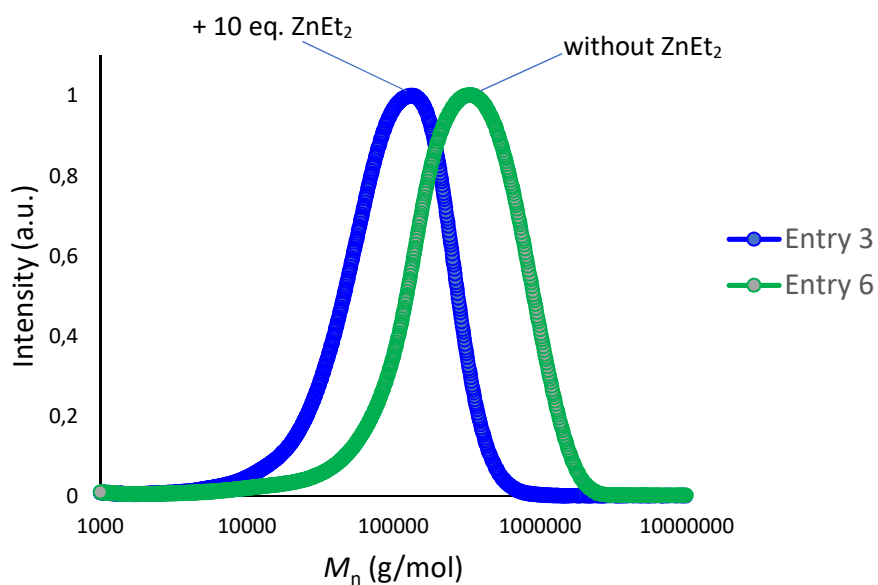


Fig. S73 Stacked SEC chromatograms of polyisoprene according to the data presented in Table S3 (Entry 3 vs Entry 6)