Supporting Information

Bis(phenolate)amine-supported lanthanide borohydride complexes for styrene and *trans*-1,4-isoprene (co-)polymerisations.

Fanny Bonnet,*[a], Hellen E. Dyer,[b] Yassine El Kinani,[a] Carin Dietz,[c] Pascal Roussel,[a] Marc Bria,[d] Marc Visseaux,[a] Philippe Zinck [a] and Philip Mountford.*[b]

[a] Unité de Catalyse et de Chimie du Solide, CNRS, University of Lille 1, Science and Technology, 59655 Villeneuve d'Ascq, France. E-mail : fanny.bonnet@ensc-lille.fr

[b] Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, UK. E-mail: philip.mountford@chem.ox.ac.uk

[c] Laboratory of Polymer Chemistry, Department of Chemical Engineering and Chemistry, University of Technology Eindhoven, Den Dolech 2, Helix, STO 1.37, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[d] Centre Commun de Mesure RMN, University of Lille 1, Science and Technology, 59655 Villeneuve d'Ascq, France.

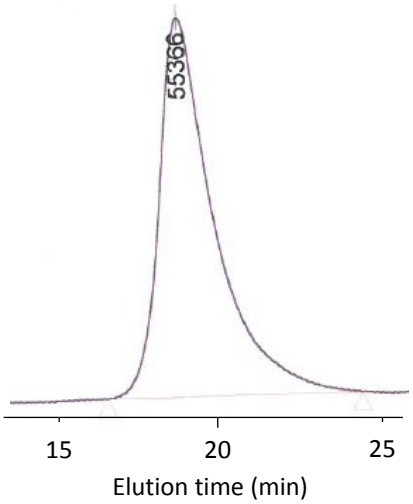


Figure SI1. SEC traces of *trans*-polyisoprene synthesized with catalyst **3-Nd** (run 7, table 1). M_n = 15330 g.mol^{-1} (corrected with coefficient 0.5 [SI1]) and $Đ$ = 1.62.

[SI1] P. Zinck, M. Terrier, A. Mortreux and M. Visseaux, *Polymer Testing*, 2009, **28**, 106.

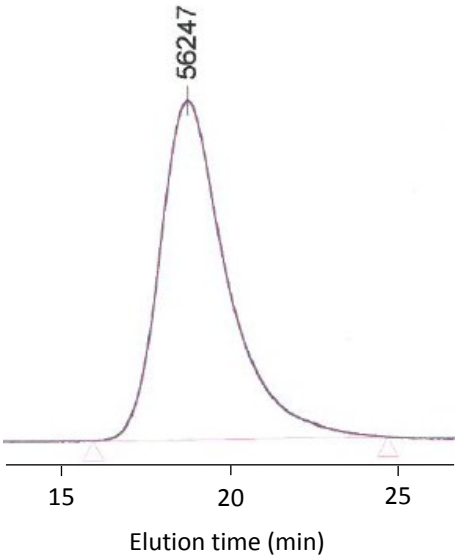


Figure SI2. SEC traces of polystyrene synthesized with catalyst **4-Sm** (run 11, table 2). M_n = 34800 g.mol^{-1} and $Đ$ = 1.58.

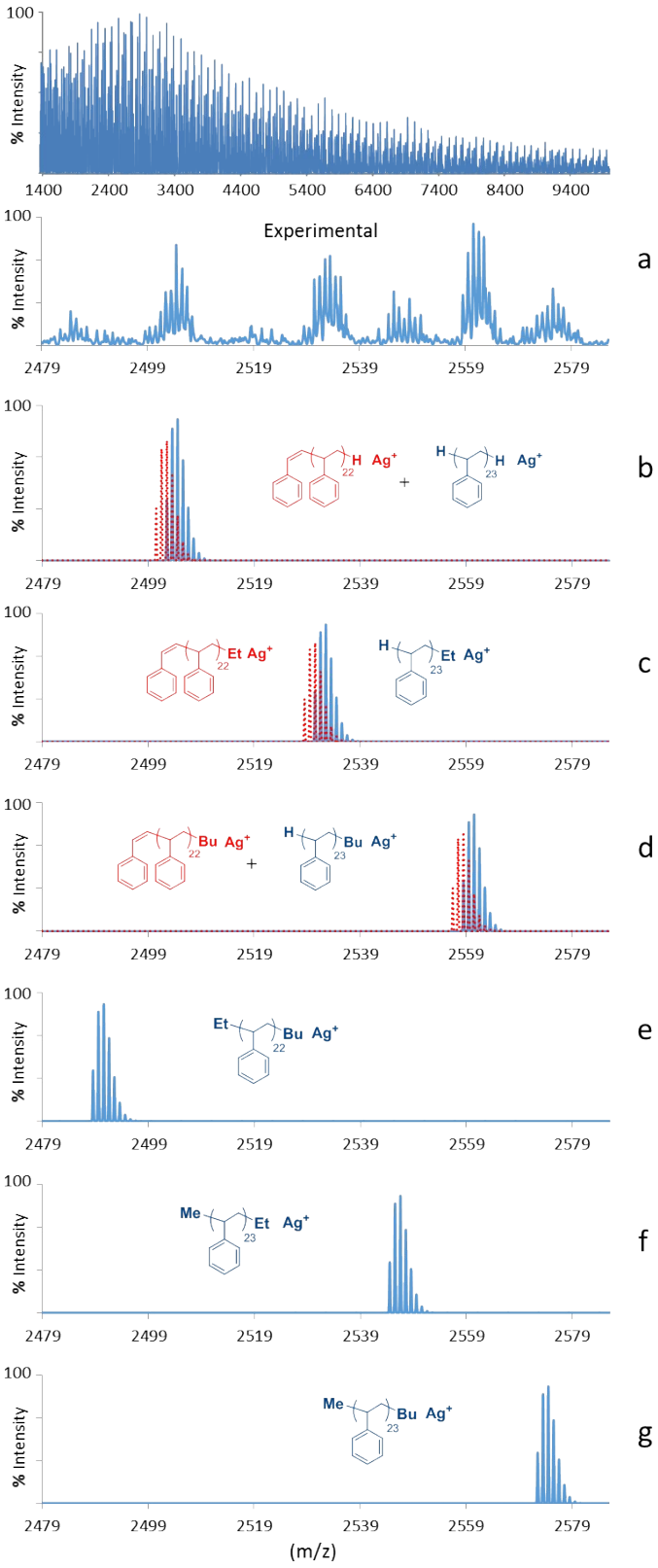


Figure SI3. Experimental and simulated MALDI-ToF mass spectra of the polystyrene (PS) formed with $Sm(O_2N^{py})(BH_4)(THF)$ (**1-Sm**). (a) Expansion of experimental spectrum in the range m/z = 2479-2589 amu. (b) Calculated spectrum for H-terminated PS. (c) Calculated spectrum for Et-terminated PS. (d) Calculated spectrum for Bu-terminated PS. (e) Calculated spectrum for Et and Bu-terminated PS. (f) Calculated spectrum for Me and Et-terminated PS. (g) Calculated spectrum for Me and Bu-terminated PS.

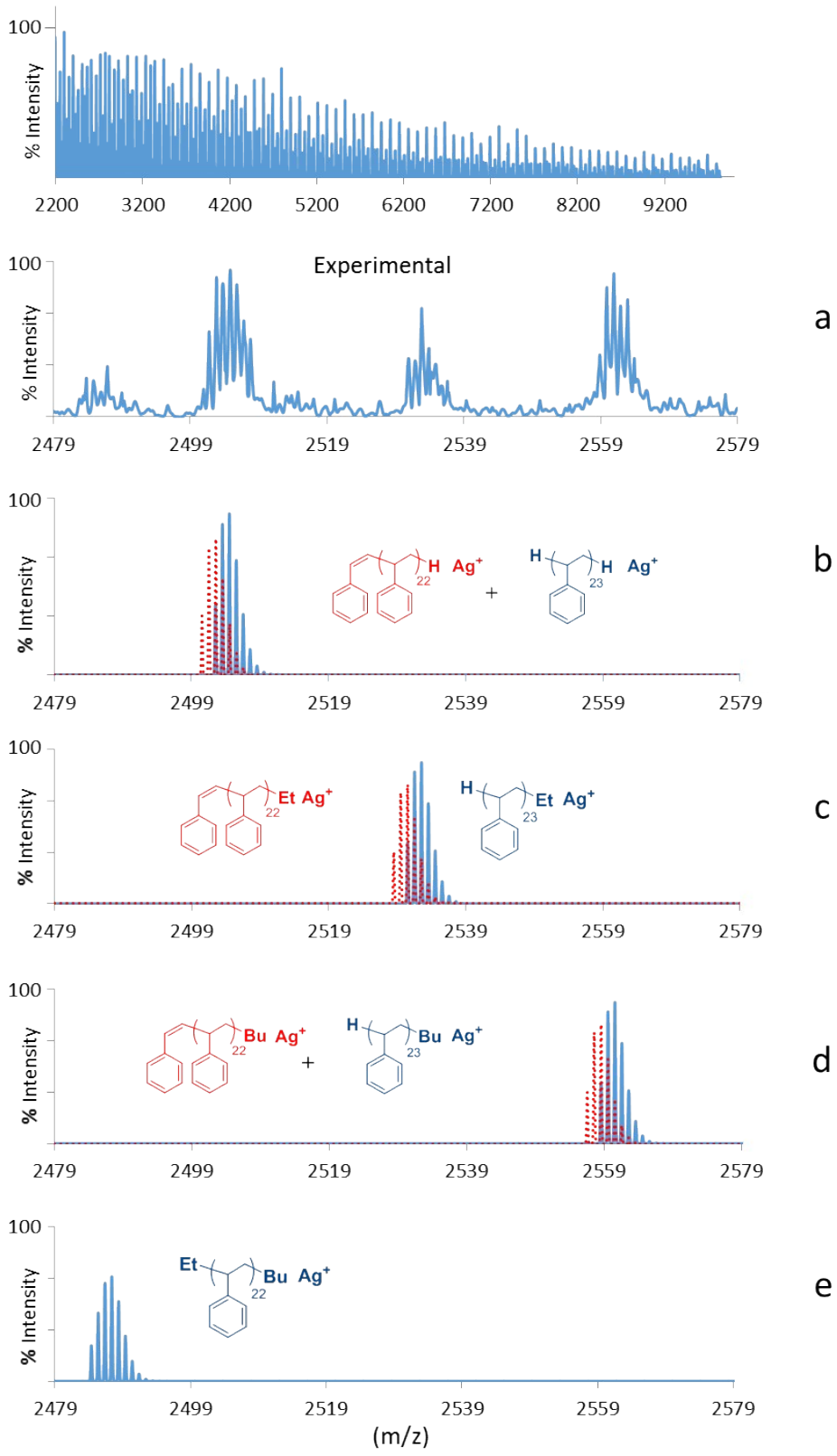


Figure SI4. Experimental and simulated MALDI-ToF mass spectra of the polystyrene (PS) formed with $Sm(O_2N^{OMe})(BH_4)(THF)$ (**2-Sm**). (a) Expansion of experimental spectrum in the range m/z = 2479-2579 amu. (b) Calculated spectrum for H-terminated PS. (c) Calculated spectrum for Et-terminated PS. (d) Calculated spectrum for Bu-terminated PS. (e) Calculated spectrum for Et and Bu-terminated PS.

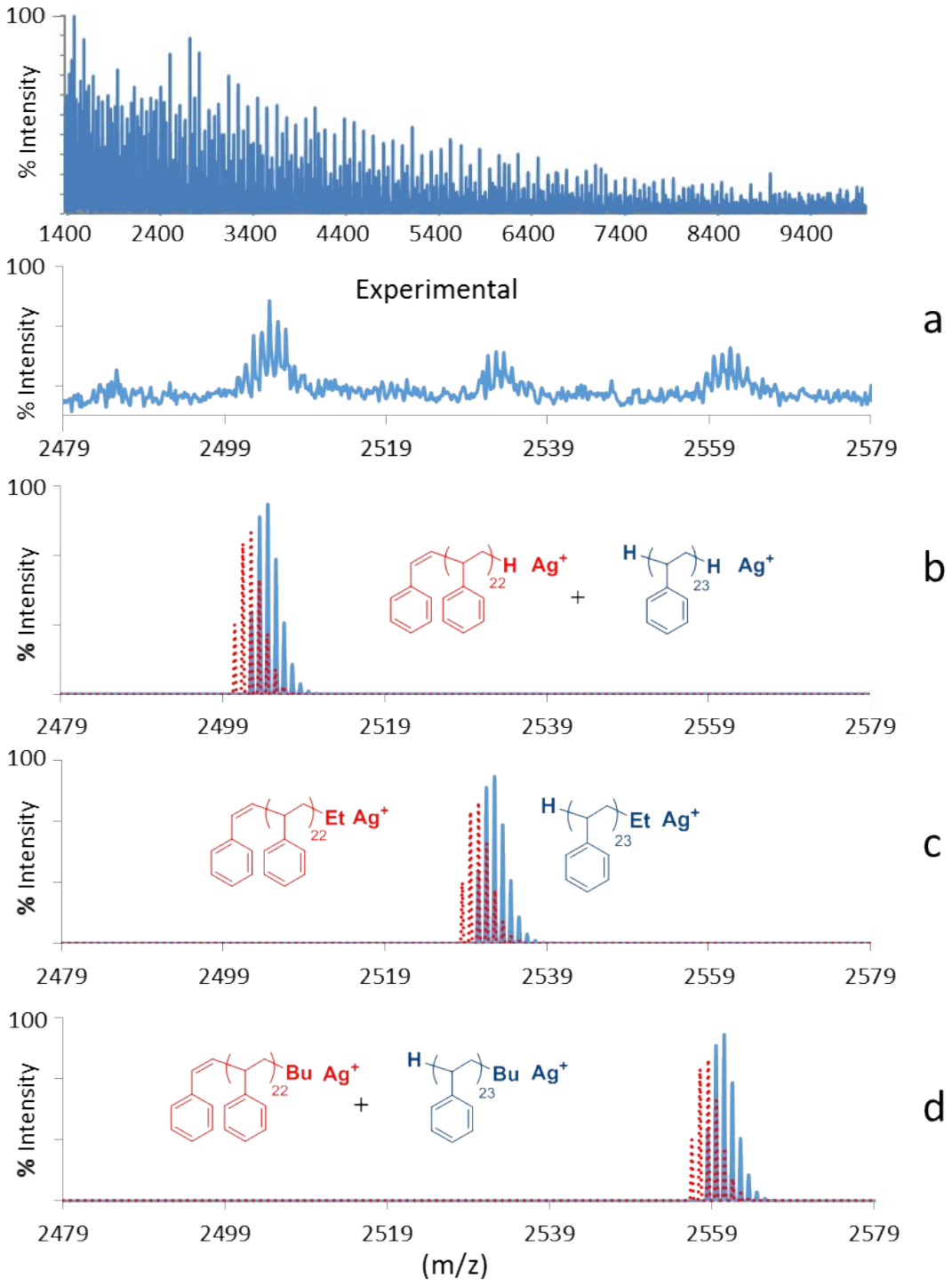


Figure SI5. Experimental and simulated MALDI-ToF mass spectra of the polystyrene (PS) formed with $Sm(O_2N^{pr})(BH_4)(THF)_2$ (**4-Sm**). (a) Expansion of experimental spectrum in the range m/z = 2479-2579 amu. (b) Calculated spectrum for H-terminated PS. (c) Calculated spectrum for Et-terminated PS. (d) Calculated spectrum for Bu-terminated PS.

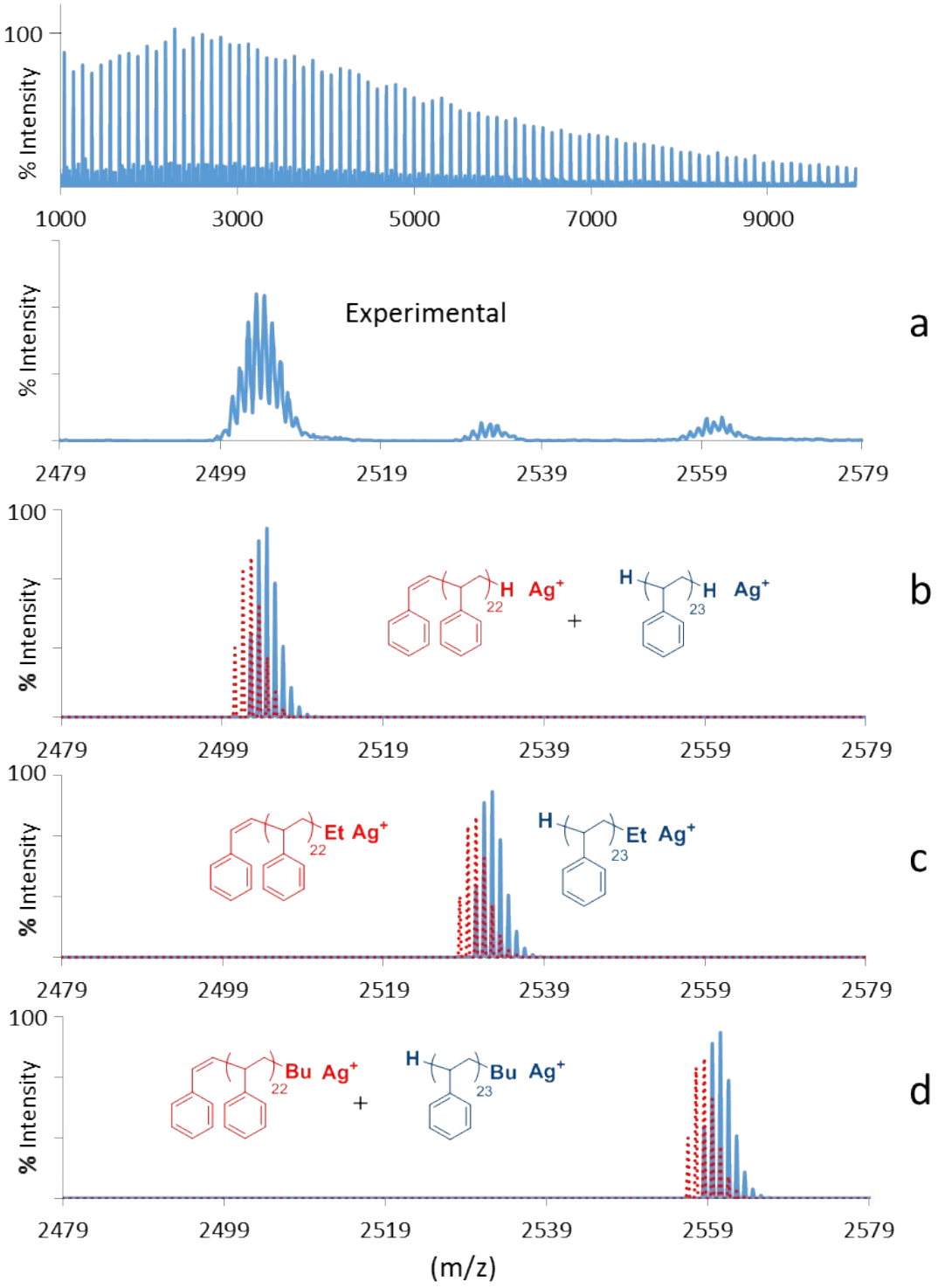


Figure SI6. Experimental and simulated MALDI-ToF mass spectra of the polystyrene (PS) formed with $Nd(O_2N^{NMe2})(BH_4)(THF)$ (**3-Nd**). (a) Expansion of experimental spectrum in the range m/z = 2479-2579 amu. (b) Calculated spectrum for H-terminated PS. (c) Calculated spectrum for Et-terminated PS. (d) Calculated spectrum for Bu-terminated PS.

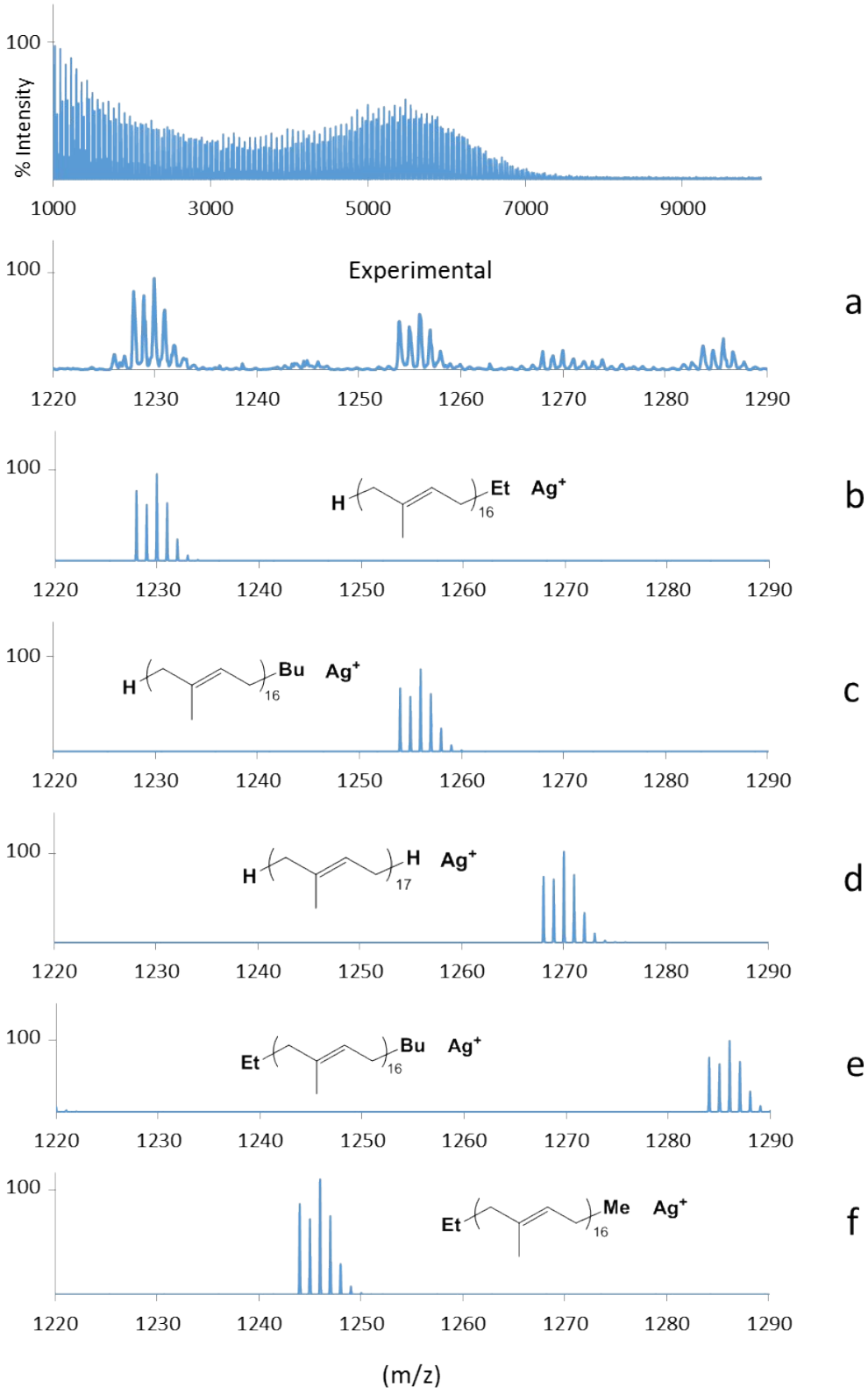
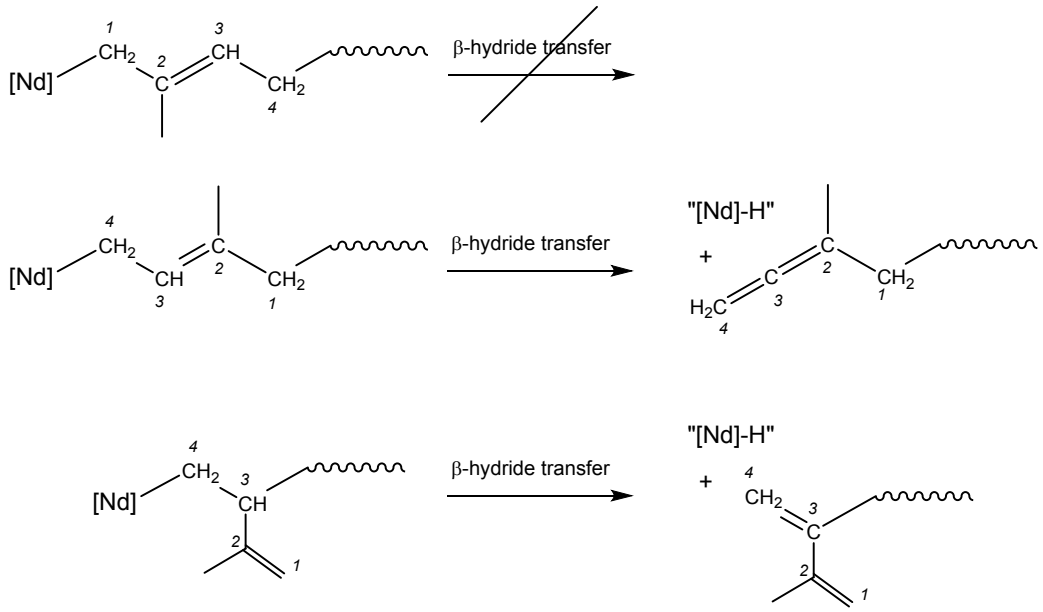


Figure SI7. Experimental and simulated MALDI-ToF mass spectra of the polyisoprene (PI) formed with $Sm(O_2N^{NMe2})(BH_4)(THF)$ (**3-Sm**). (a) Expansion of experimental spectrum in the range m/z = 1220-1290 amu. (b) Calculated spectrum for Et-terminated PI. (b) Calculated spectrum for Bu-terminated PI. (d) Calculated spectrum for H-terminated PI. (e) Calculated for Et- and Bu-terminated PI. (f) Calculated for Et- and Me-terminated PI.



Scheme SI1. Potential occurrence of β-hydride transfer during the propagation according to 1,4- (top), 4,1- (middle), or 3,4- (bottom) mechanisms

Table SI1. CCTP of Isoprene (IP) with complexes **1-** to **4-Sm** and **1-** to **3-Nd** / Mg(^{n}Bu)(Et) or Al(^{i}Bu)$_3$[a]

Run	Complex	[Mg]/[Ln]	[Al]/[Ln]	T (°C)	T (h)	Yield (%)	Microstructure [e]		
							% *trans*-1,4	% *cis*-1,4	% 3,4
1	**1-Sm**	5	-	70	96	29	28.5	2.9	68.6
2	**2-Sm**	5	-	70	96	33	19.3	2.2	78.5
3	**3-Sm**	5	-	70	96	37	17	1	82
4	**4-Sm**	5	-	70	96	28	32.7	2.3	65
5	**1-Nd**	5	-	50	24	12	26	0	74
6	**2-Nd**	5	-	50	24	18	30.8	3	66.2
7	**3-Nd**	5	-	50	24	19	25.6	2.7	71.7
8	**3-Nd**	5	-	70	24	31	17.5	1.5	81
9	**3-Nd**	1	5	50	48	38	82	13.5	4.5
10	**3-Nd**	1	10	50	72	25	82.5	8	9.5

[a] Experimental conditions: [IP]/[Ln] = 800, n Ln = 6.2×10^{-6} mol ; solvent = toluene with V(IP) = V (toluene) [b] Isolated yield. [c] Microstructure of the soluble fraction determined from ^{1}H and ^{13}C NMR spectra in $CDCl_3$.

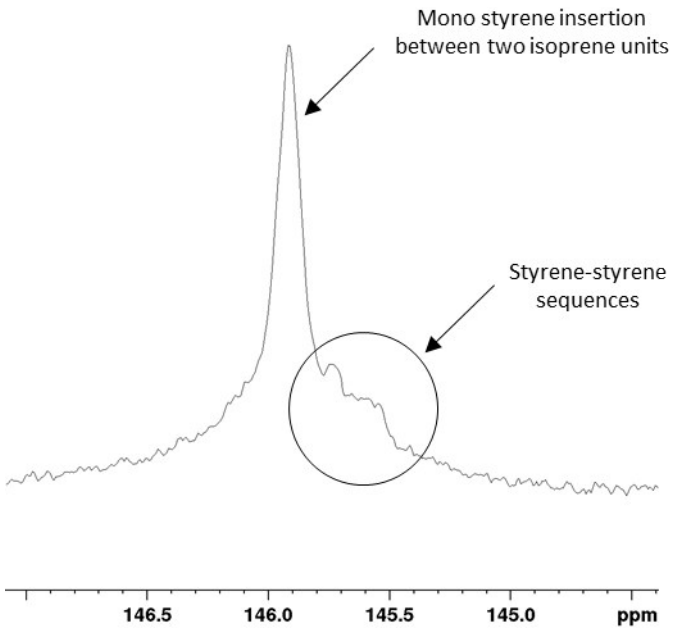


Figure SI8. ^{13}C NMR spectra in the phenyl *ipso* carbon region of the copolymer poly[(1,4-*trans*-isoprene)-co-styrene] synthesized with **2-Nd** in run 24, table 4 ($CDCl_3$, 300K)[1]

[1] P. Zinck, M.Terrier, A. Mortreux, A. Valente, M. Visseaux, *Macromol. Chem. Phys.* 2007, **208**, 973.