Electronic Supplementary Information

Scandium-catalyzed stereoselective block and alternating copolymerization of diphenylphosphinostyrenes and isoprene

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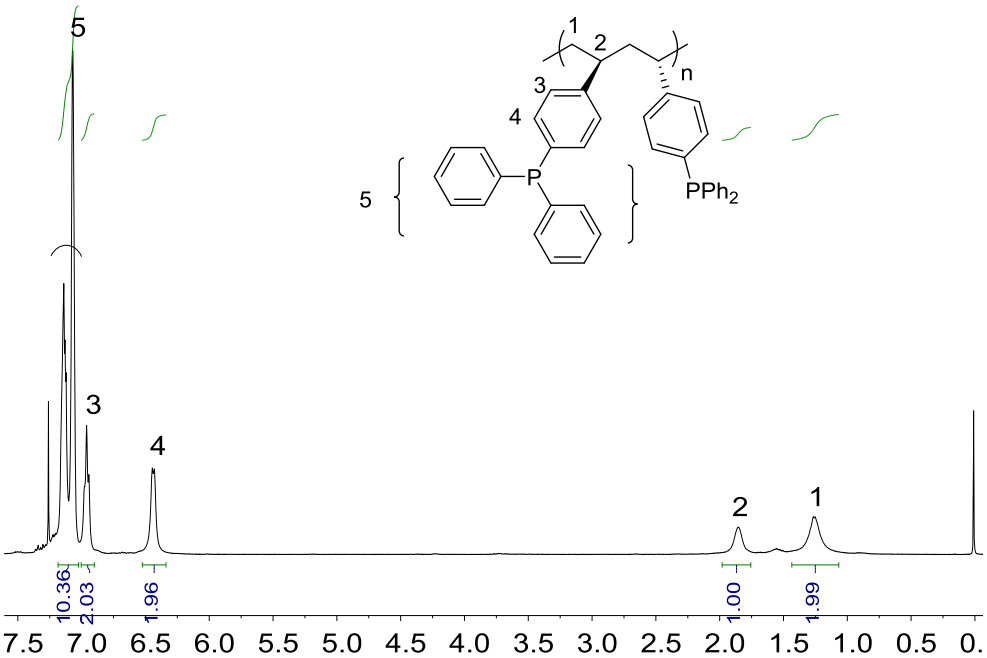


Fig. S1 ^{1}H-NMR spectrum of a *p*-StPPh_2 homopolymer prepared by$(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2$-*o*$)_2$ (Table 1, Run 1).

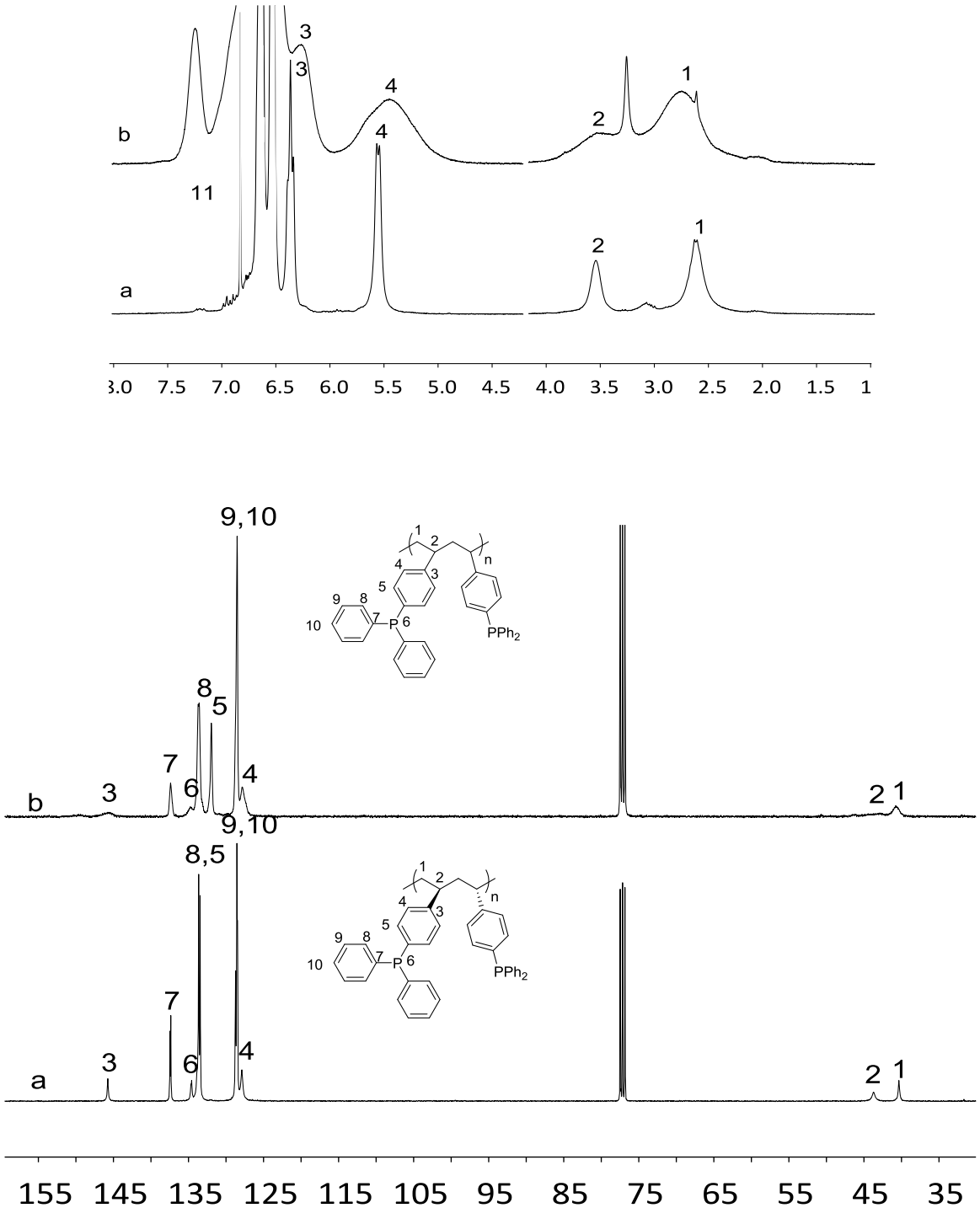


Fig. S2 ^{1}H, ^{13}C-NMR spectrum of a *p*-$StPPh_2$ homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (a) (Table 1, Run 1) and AIBN (b) (A procedure for the polymerize of *p*-$StPPh_2$ by AIBN: AIBN (1.6 mg 10 μmol) in toluene (2 mL) was added under stirring to a mixture of *p*-$StPPh_2$ (0.58 g, 2.0 mmol) in toluene (2 mL). The polymerization was carried out at 80 °C for 24 h. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol, and dried under vacuum at 40 °C to a constant weight.)

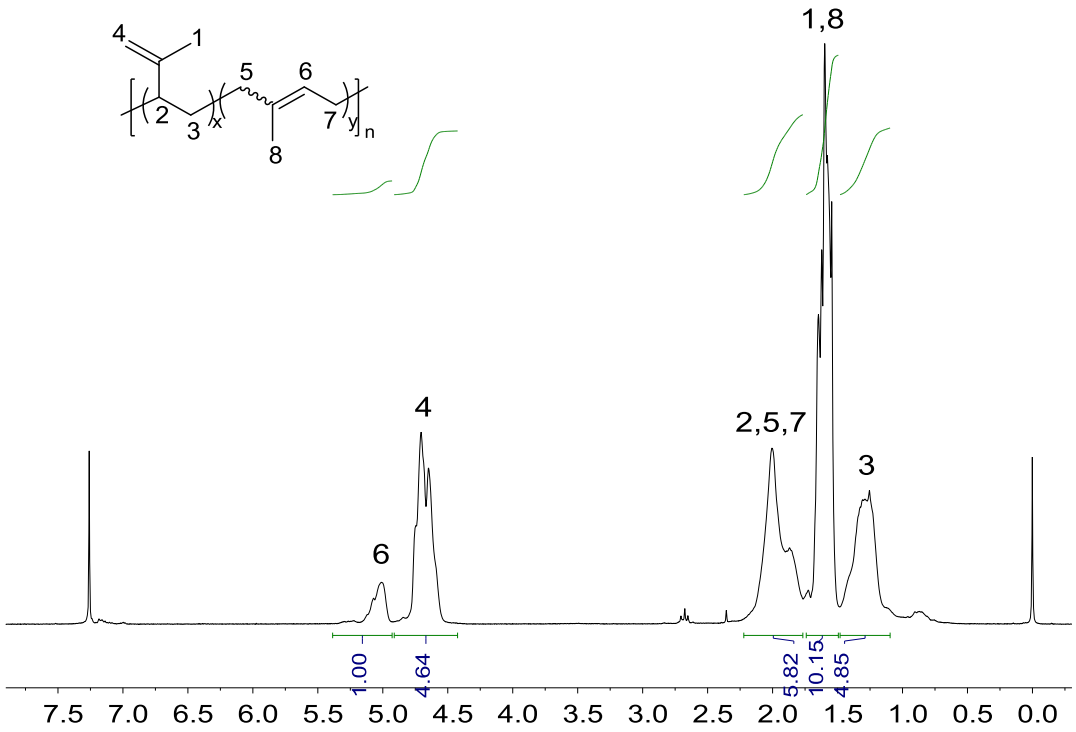


Fig. S3 ^{1}H-NMR spectrum of an IP homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (Table 1, Run 2).

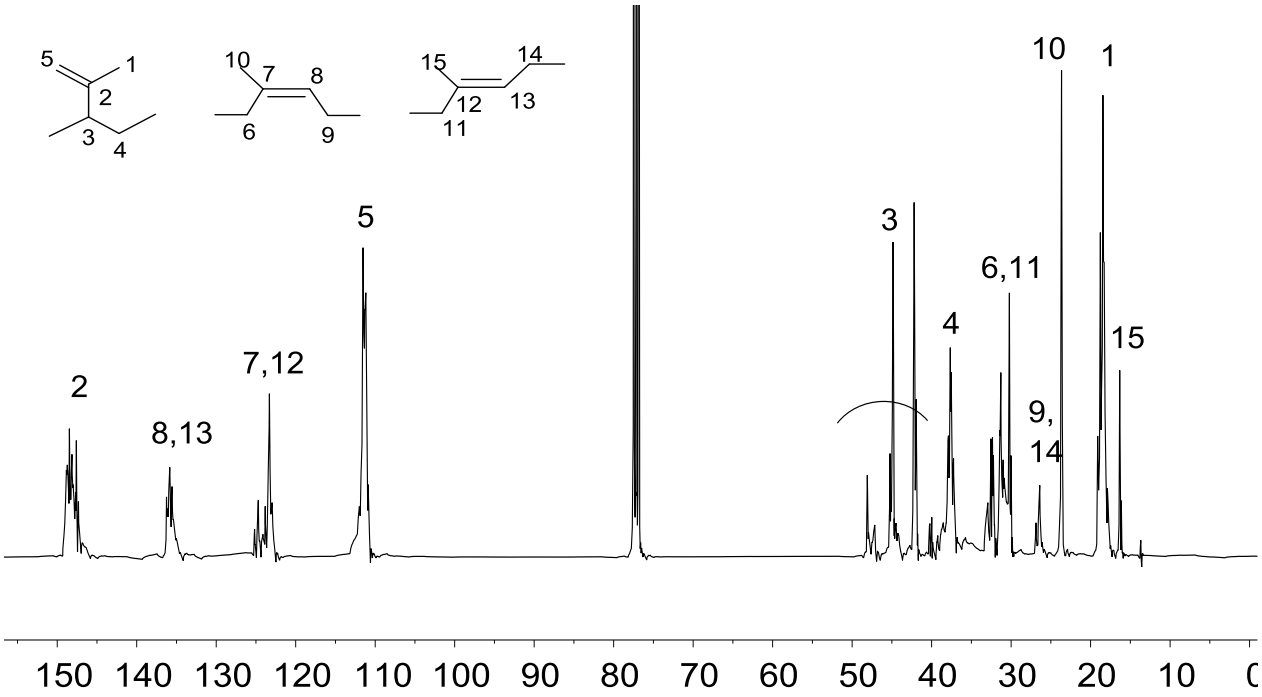


Fig. S4 ^{13}C-NMR spectrum of an IP homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (Table 1, Run 2).

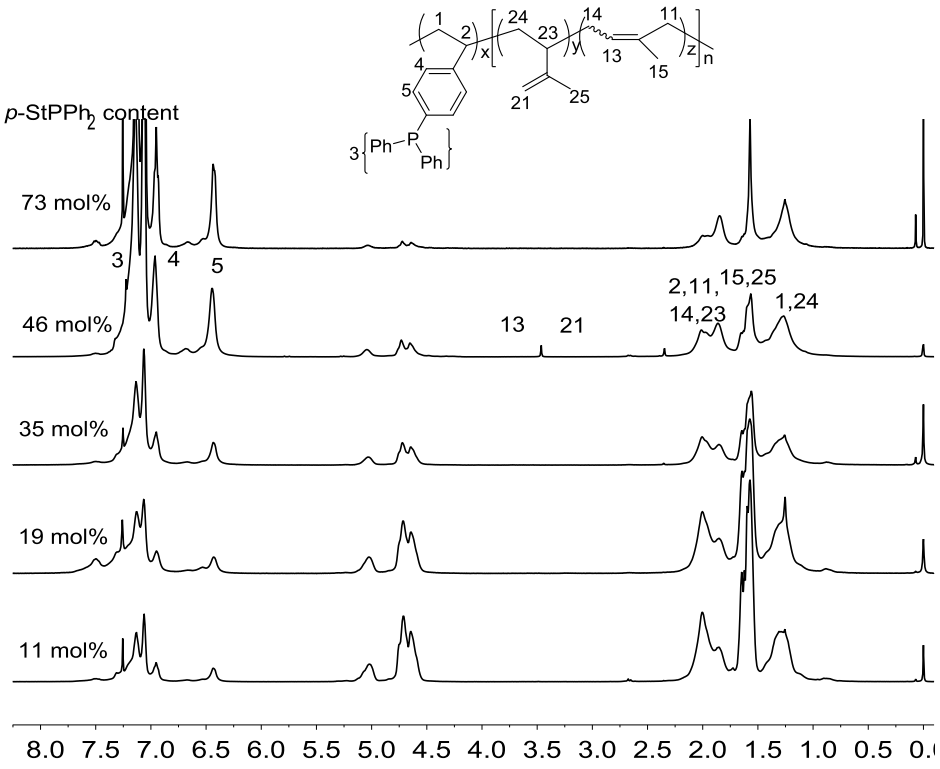


Fig. S5 ^{1}H-NMR spectra of *p*-StPPh$_2$–IP copolymers with different *p*-StPPh$_2$ content prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$.

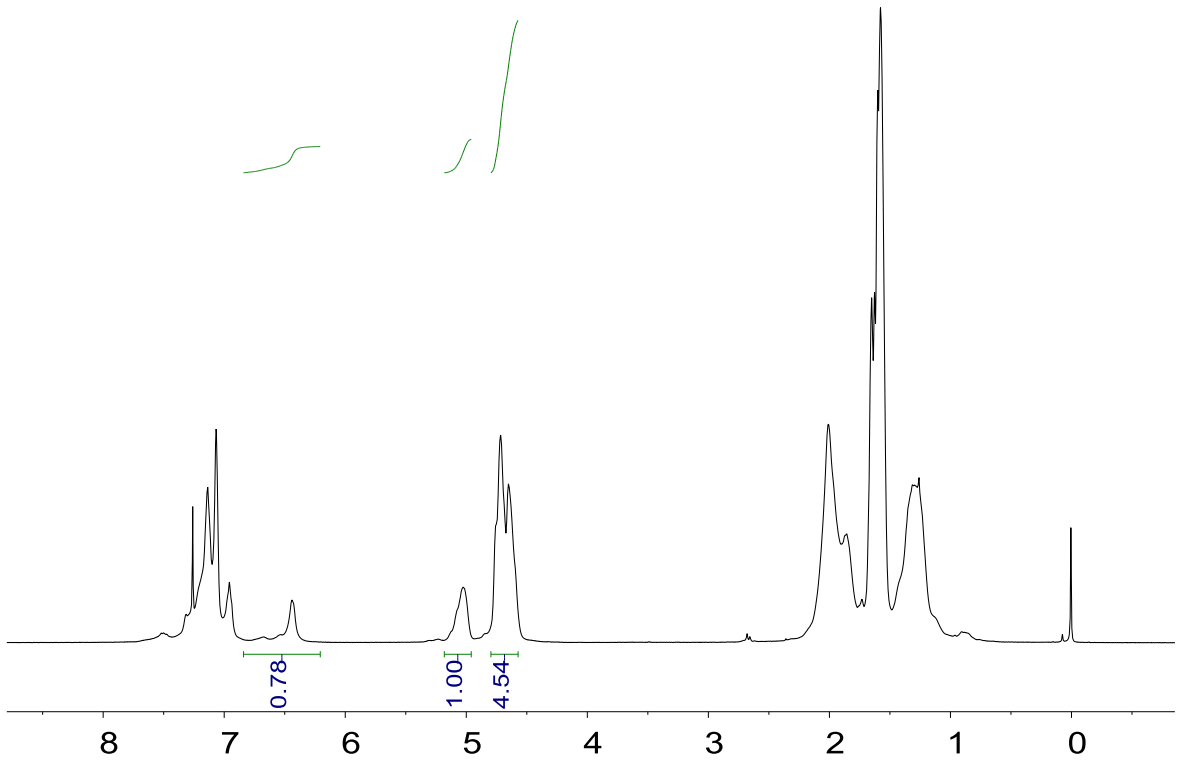


Fig. S6 ^{1}H-NMR spectrum of a *p*-StPPh$_2$–IP copolymer (Table 1, Run 3).

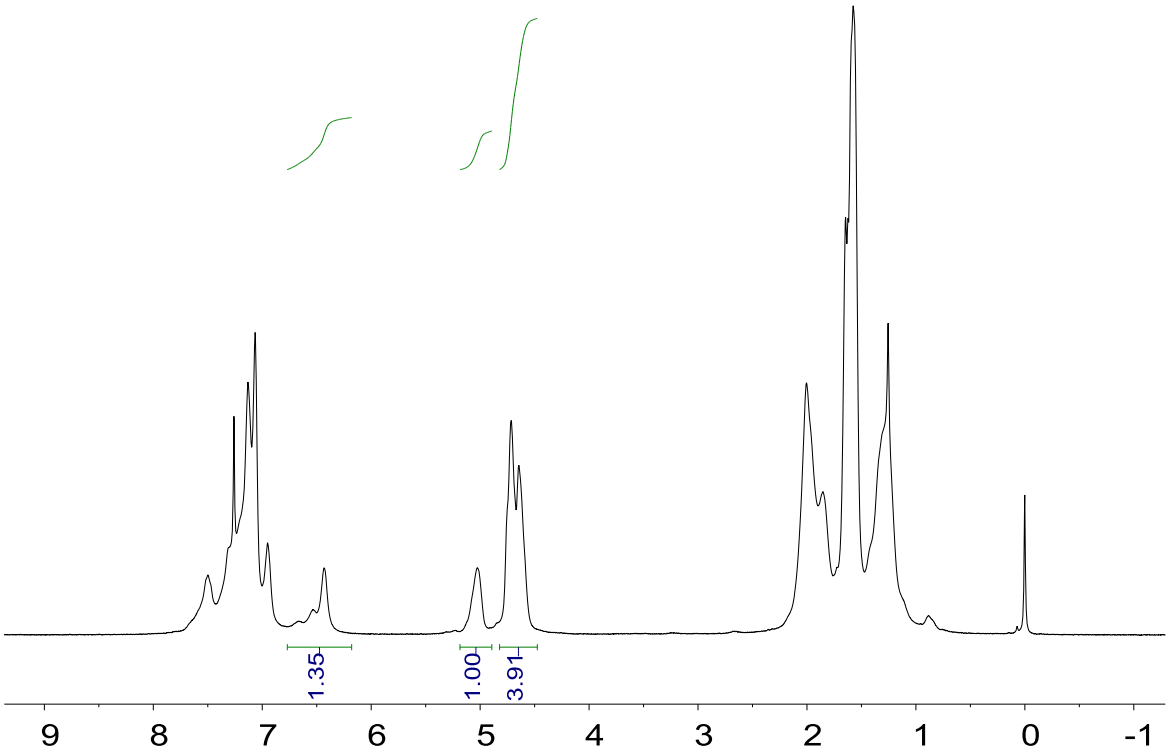


Fig. S7 ^{1}H-NMR spectrum of a *p*-StPPh$_2$–IP copolymer (Table 1, Run 4).

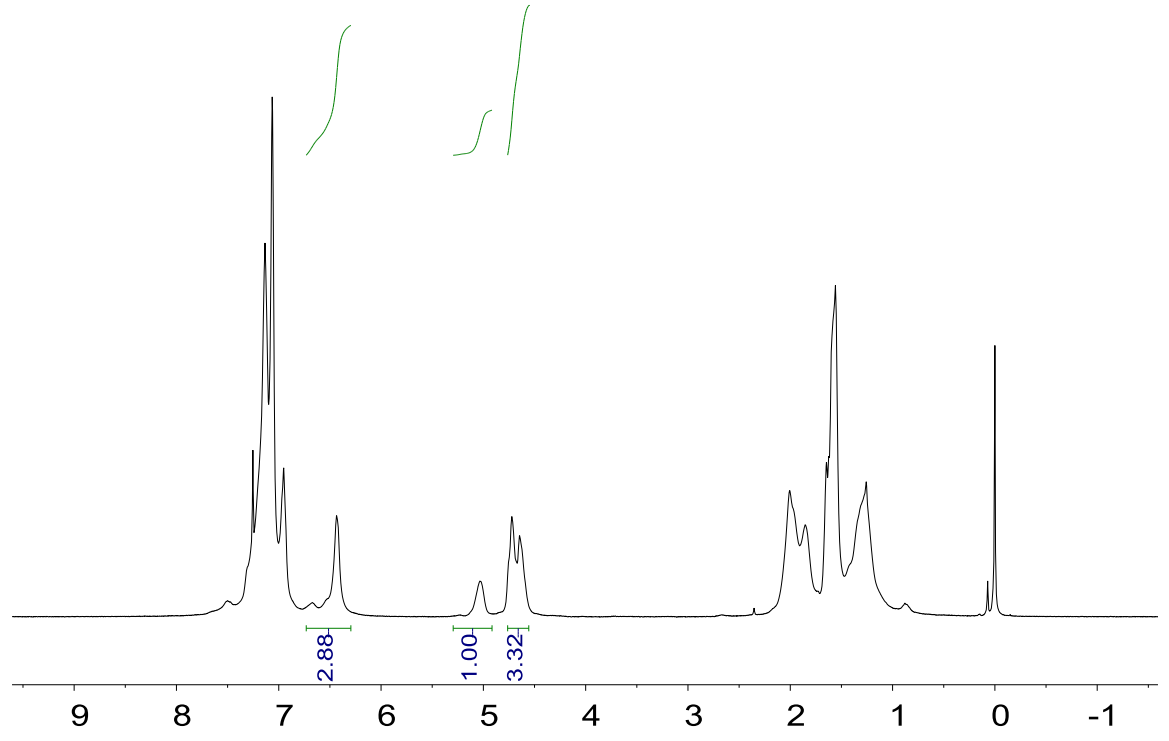


Fig. S8 ^{1}H-NMR spectrum of a *p*-StPPh$_2$–IP copolymer (Table 1, Run 5).

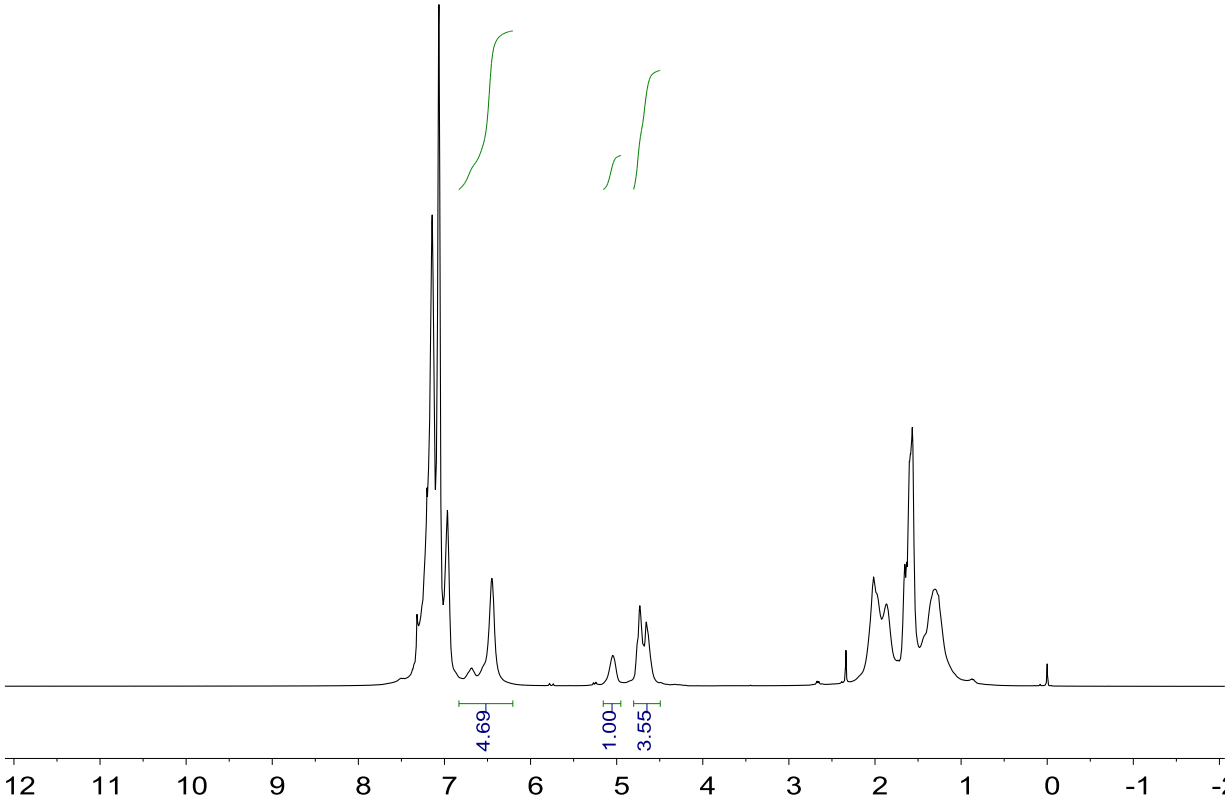


Fig. S9 ^{1}H-NMR spectrum of a *p*-StPPh$_2$–IP copolymer (Table 1, Run 6).

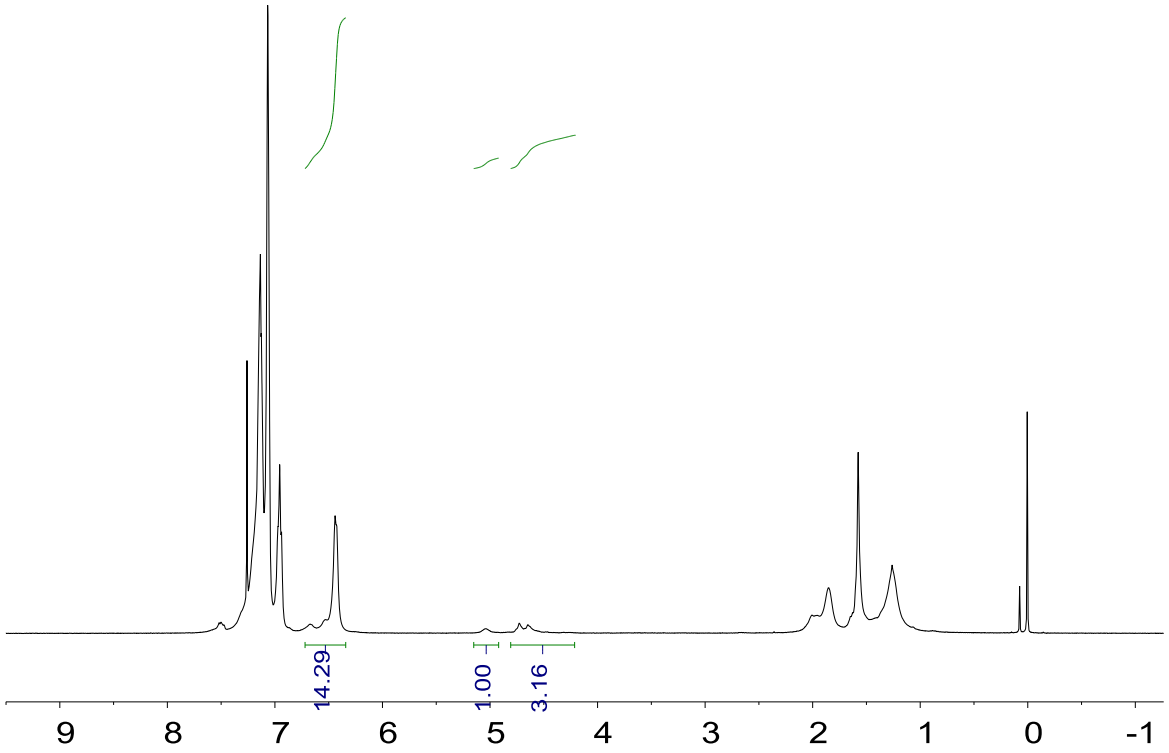


Fig. S10 ^{1}H-NMR spectrum of a *p*-StPPh$_2$–IP copolymer (Table 1, Run 7).

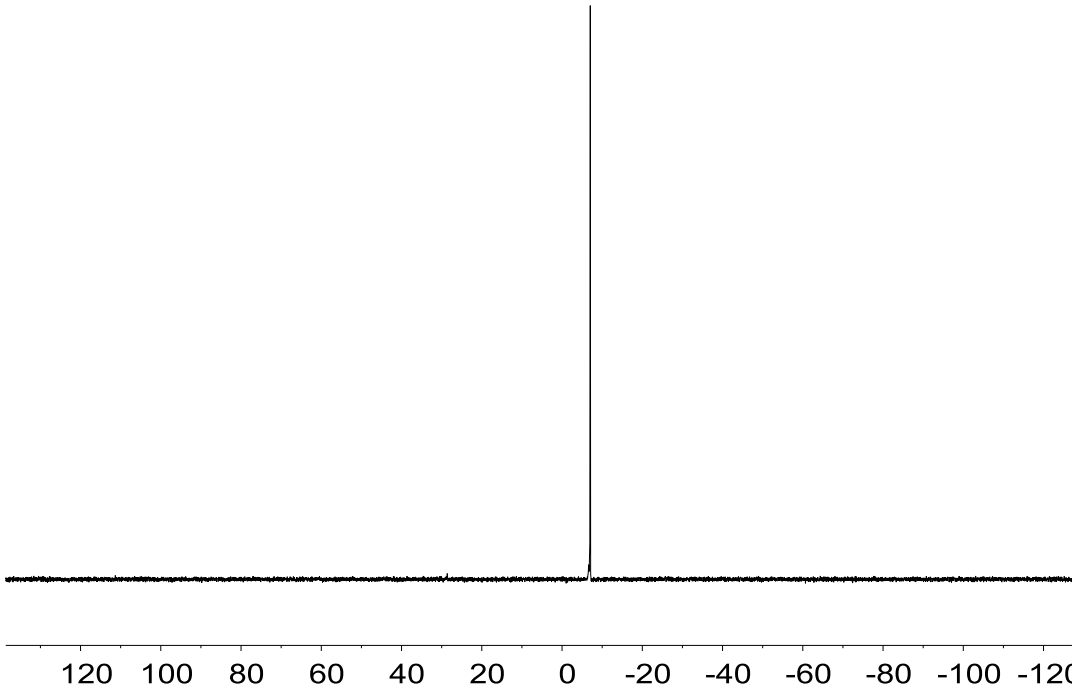


Fig. S11 ^{31}P-NMR spectrum of a *p*-StPPh$_2$–IP copolymer (Table 1, Run 7).

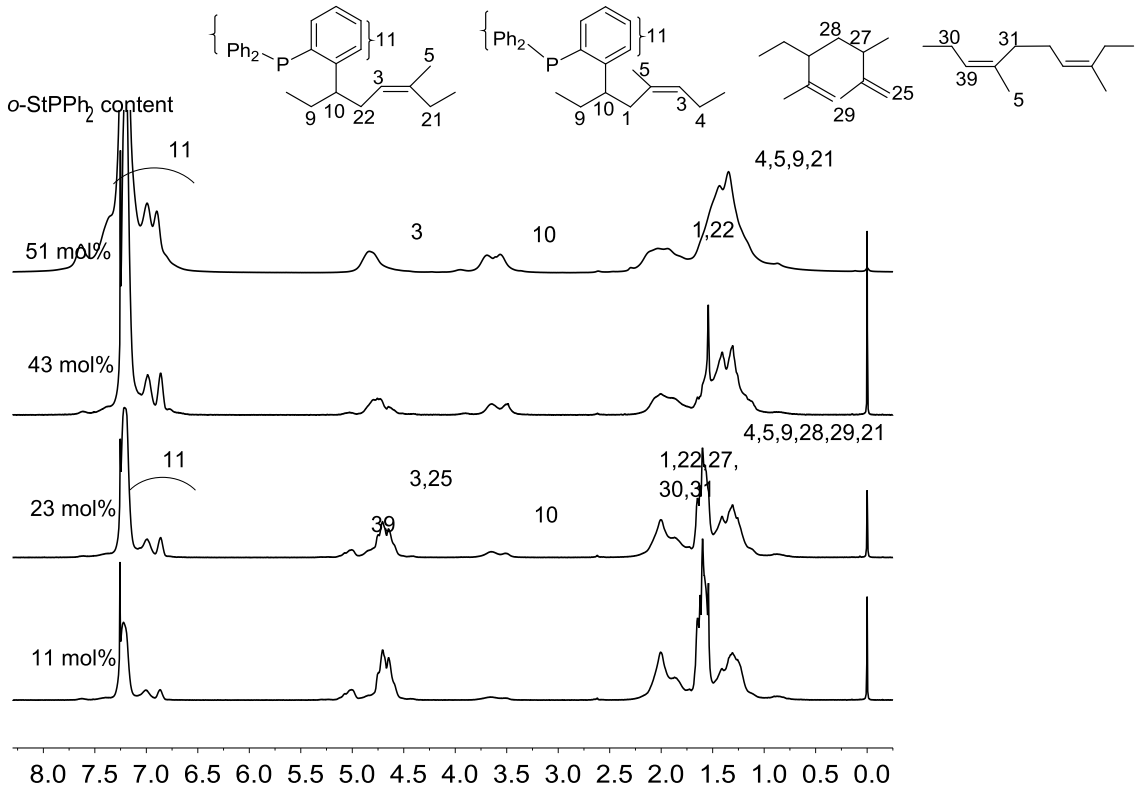


Fig. S12 ^{1}H-NMR spectra of *o*-StPPh$_2$–IP copolymers with different *o*-StPPh$_2$ content prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$.

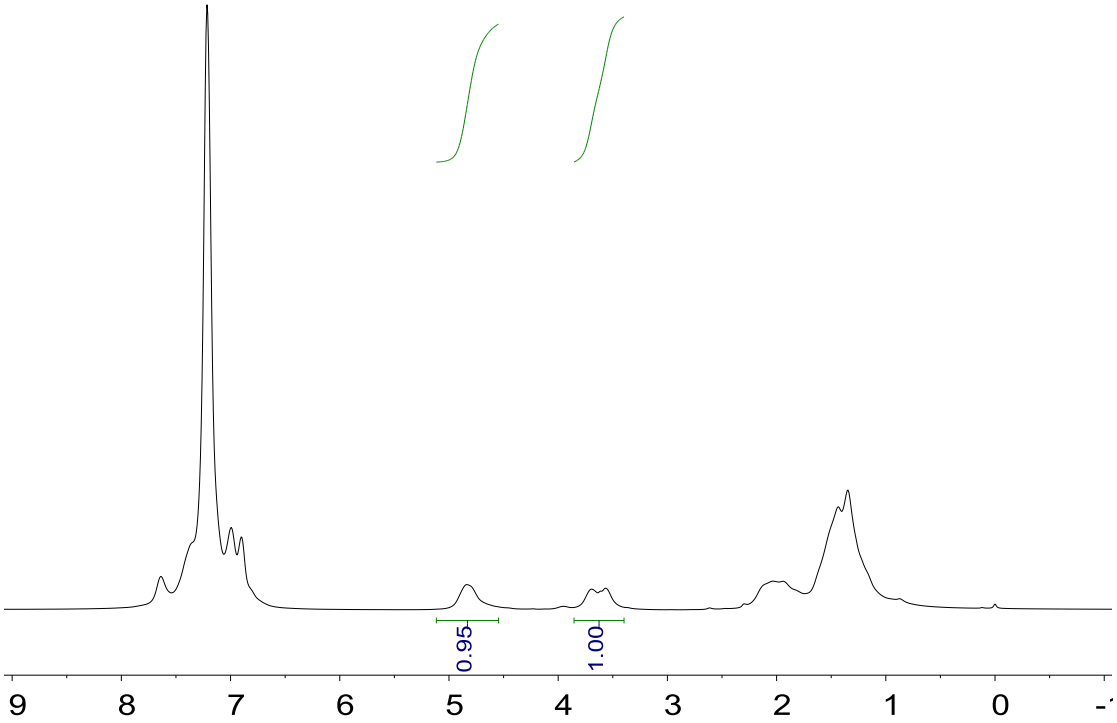


Fig. S13 ^{1}H-NMR spectrum of an *o*-StPPh$_2$–IP copolymer (Table 2, Run 2).

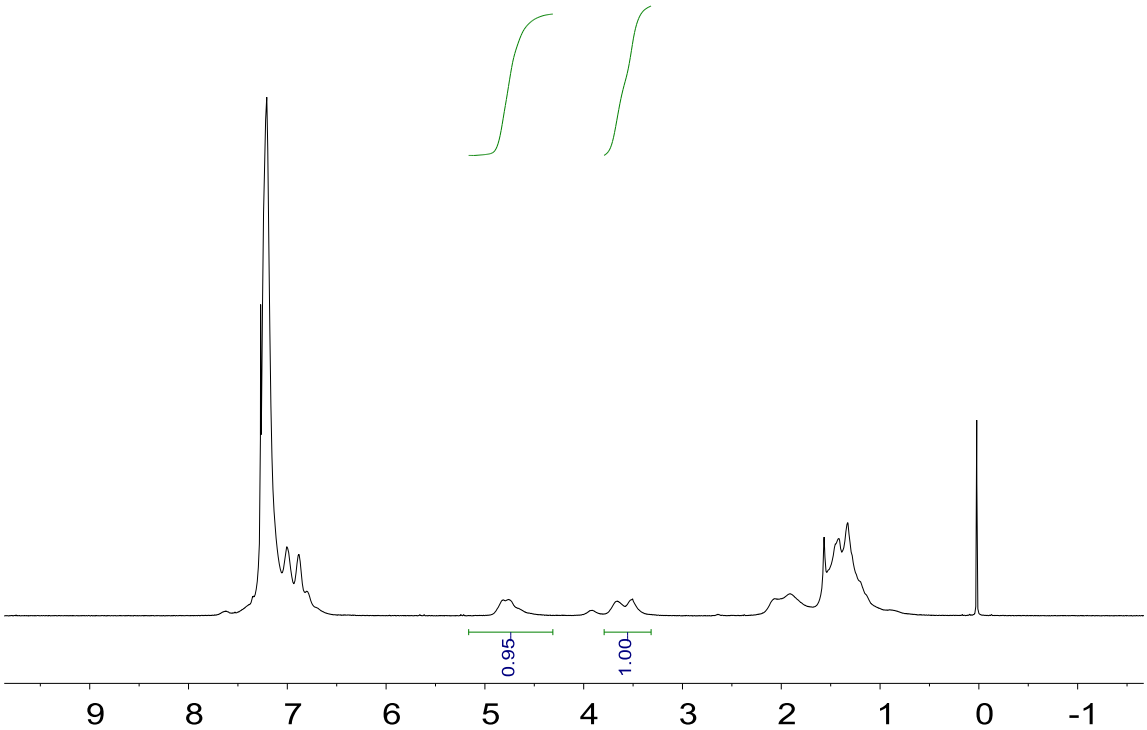


Fig. S14 ^{1}H-NMR spectrum of an *o*-StPPh$_2$–IP copolymer (Table 2, Run 3).

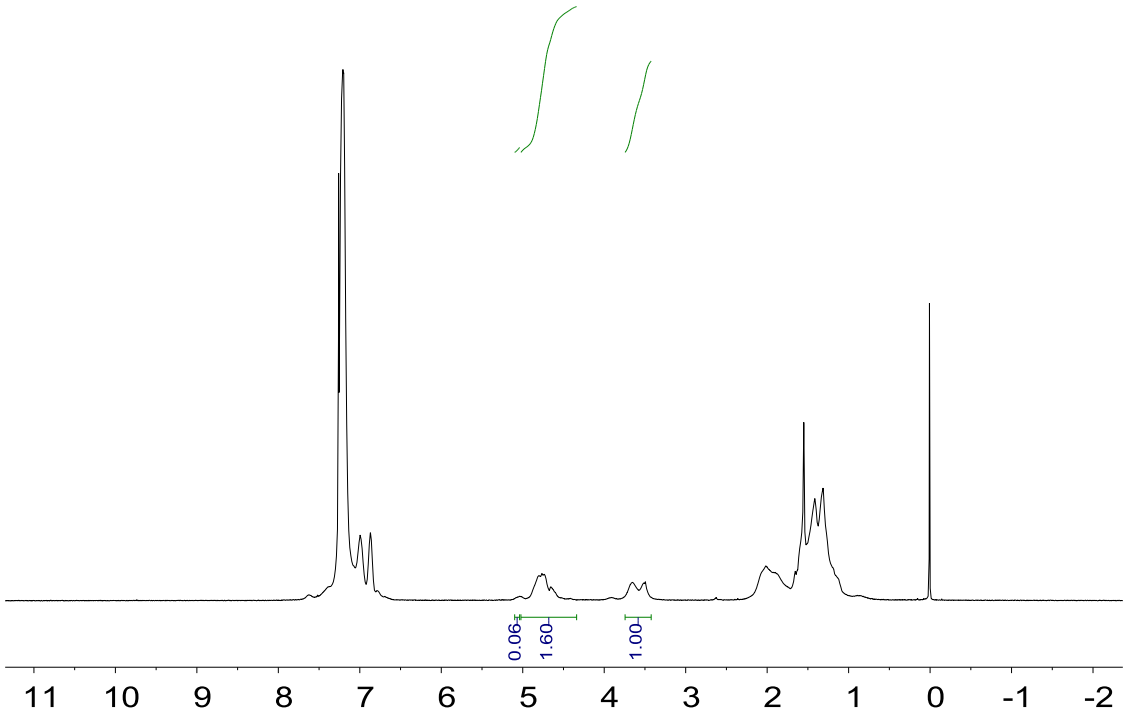


Fig. S15 ^{1}H-NMR spectrum of an *o*-StPPh$_2$–IP copolymer (Table 2, Run 4).

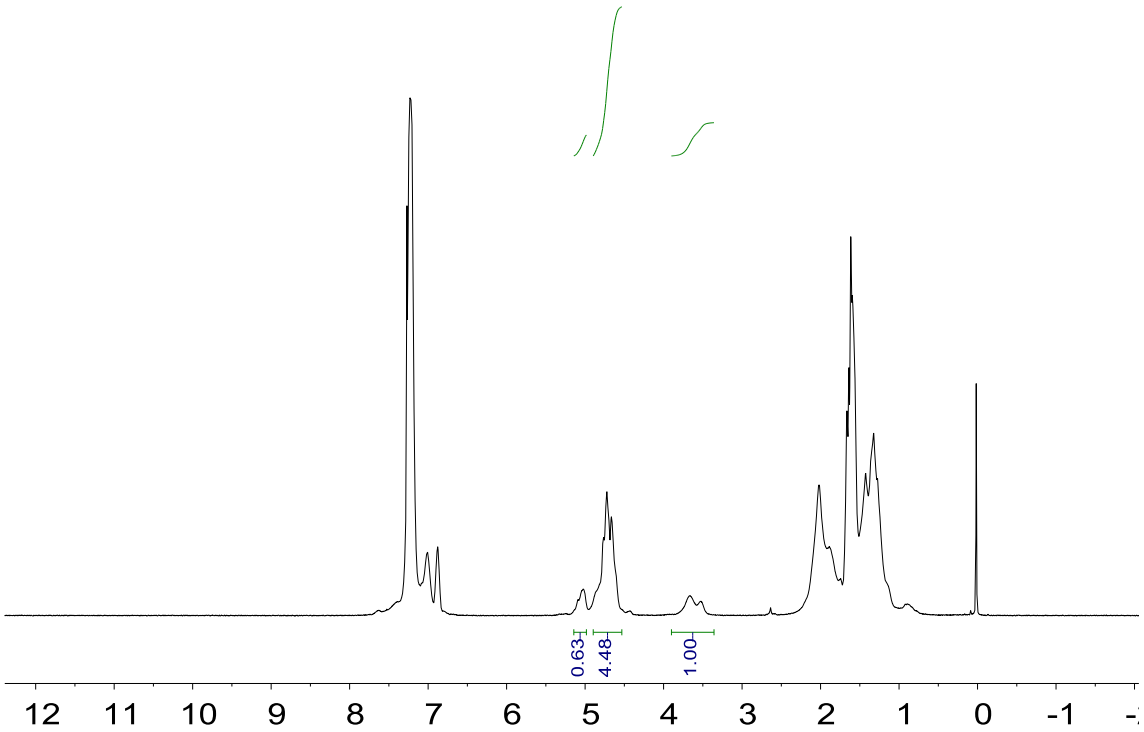


Fig. S16 ^{1}H-NMR spectrum of an *o*-StPPh$_2$–IP copolymer (Table 2, Run 5).

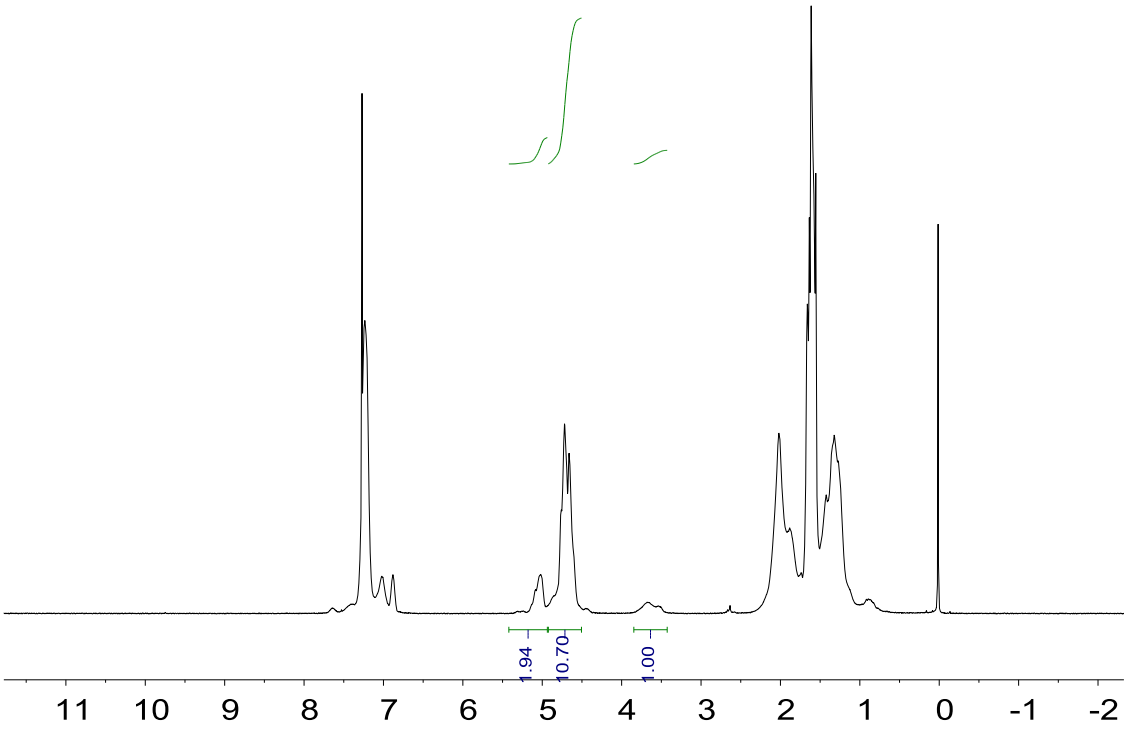


Fig. S17 ^{1}H -NMR spectrum of an *o*-StPPh$_2$–IP copolymer (Table 2, Run 6).

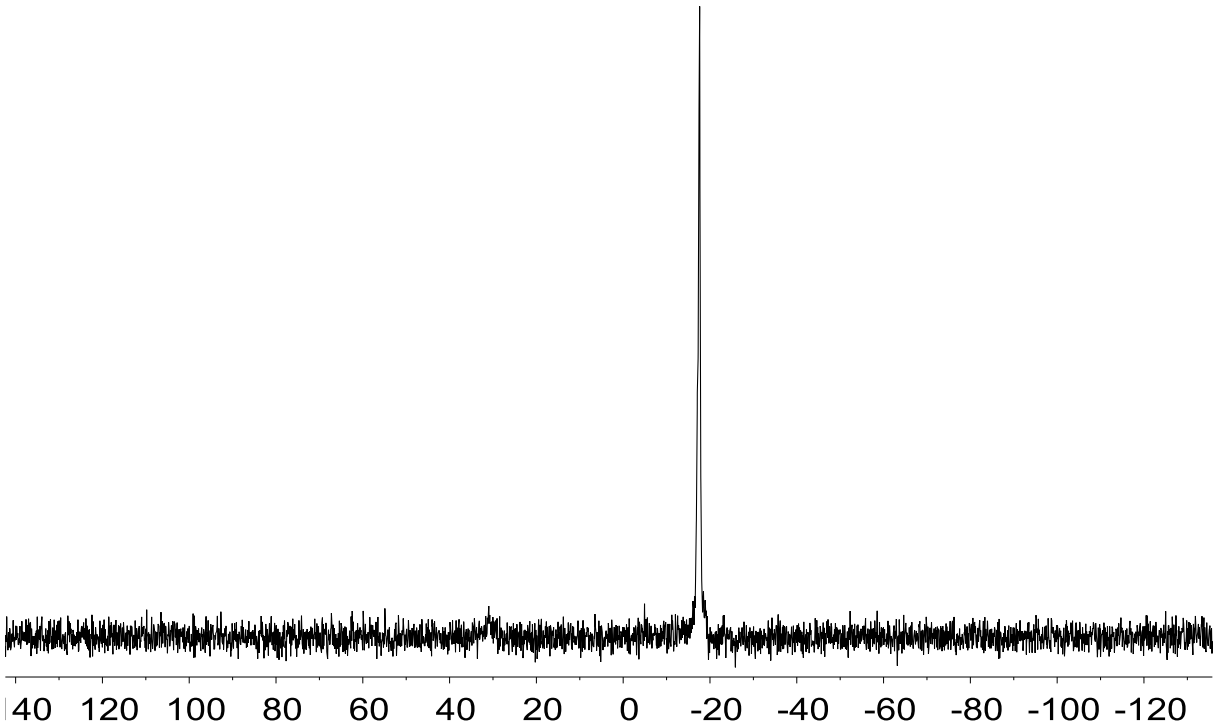


Fig. S18 ^{13}P-NMR spectrum of an *o*-StPPh$_2$–IP copolymer (Table 2, Run 2).

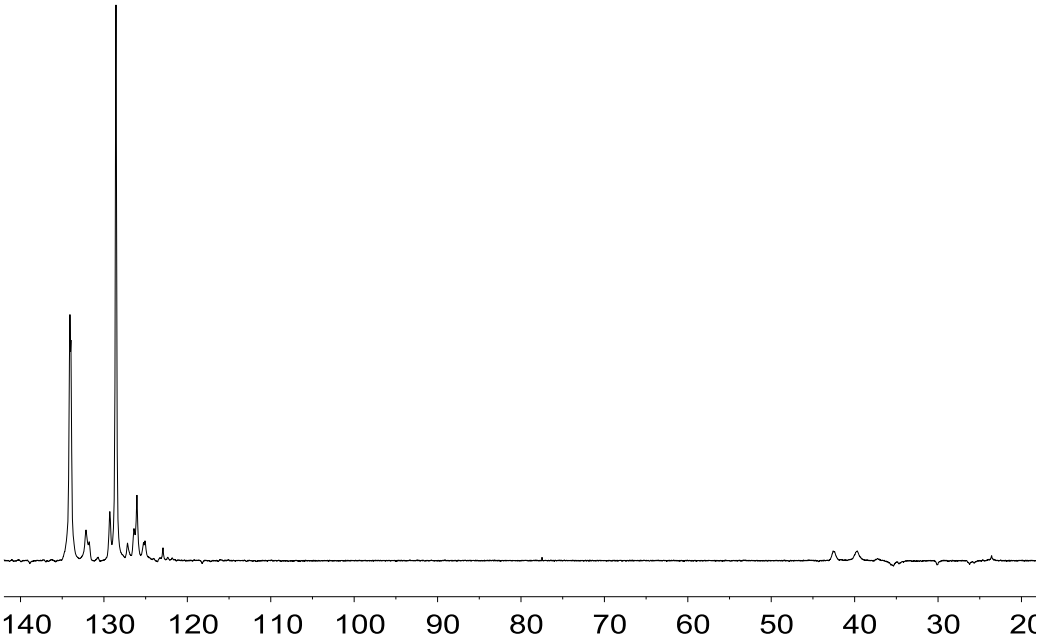


Fig. S19 DEPT135-^{13}C NMR spectrum of a poly(*o*-StPPh$_2$-*alt*-IP) prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$.

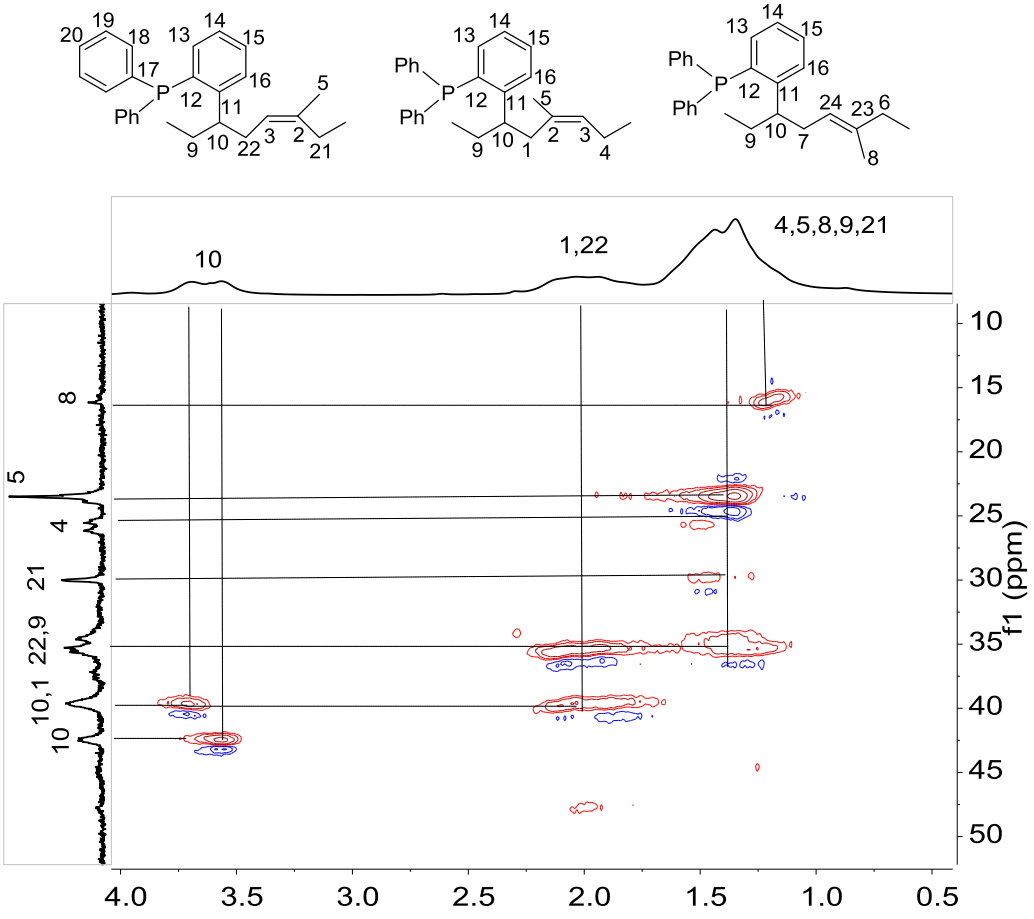


Fig. S20 HSQC NMR spectrum of a poly(*o*-StPPh$_2$-*alt*-IP) prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$.

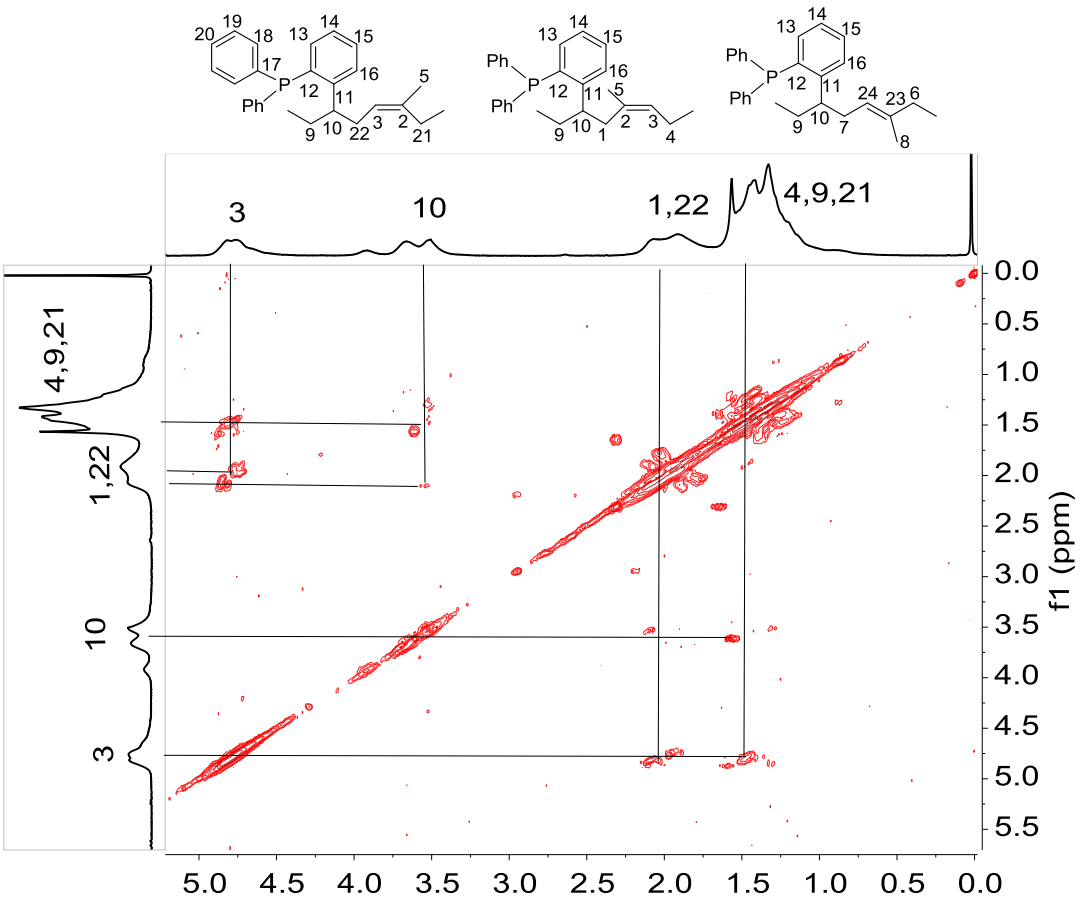


Fig. S21 gCOSY ^{1}H-^{1}H NMR spectrum of a poly(*o*-StPPh$_2$-*alt*-IP) prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$.

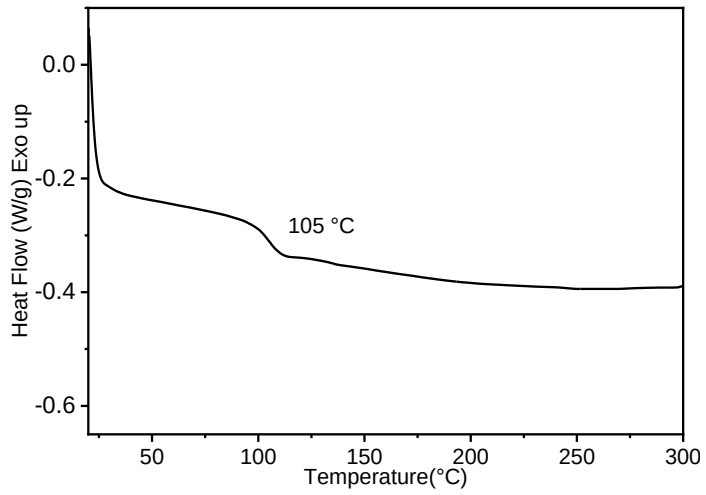


Fig. S22 DSC curve of a *p*-StPPh$_2$ homopolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$.

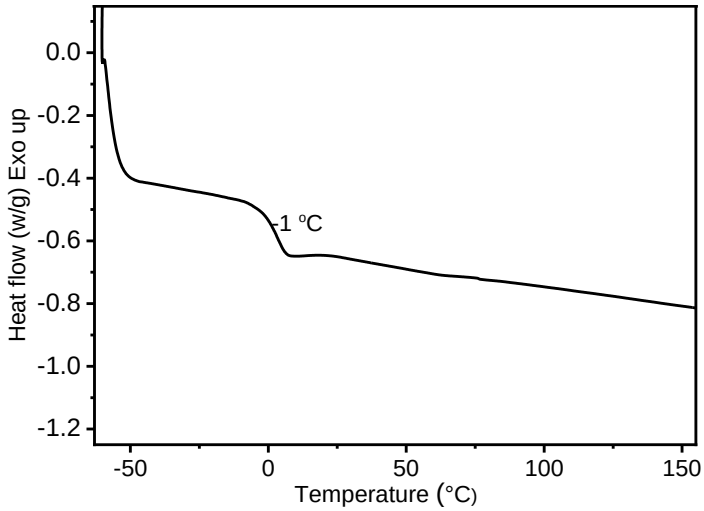


Fig. S23 DSC curve of an IP homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$.

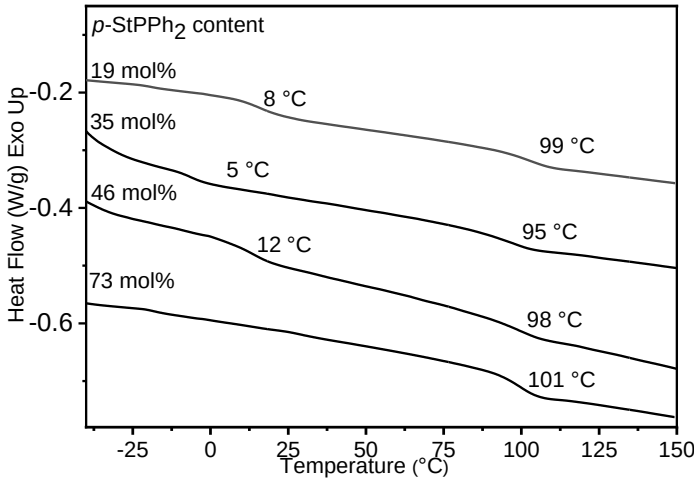


Fig. S24 DSC curves of *p*-$StPPh_2$-IP block copolymers with different composition.

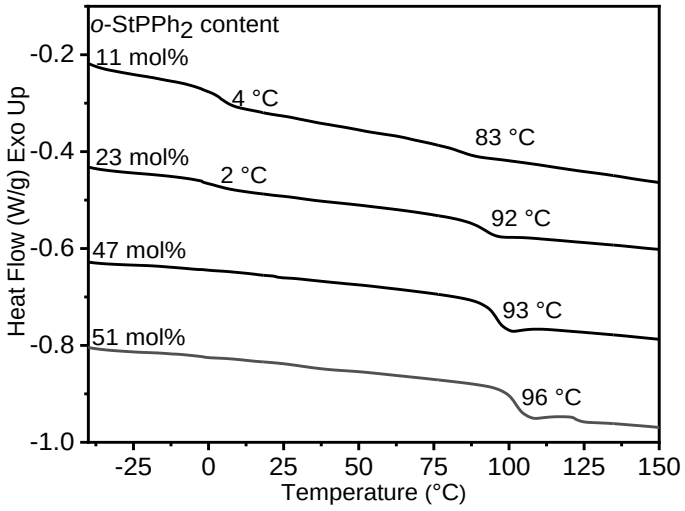


Fig. S25 DSC curves of *o*-$StPPh_2$-IP copolymers with different composition.

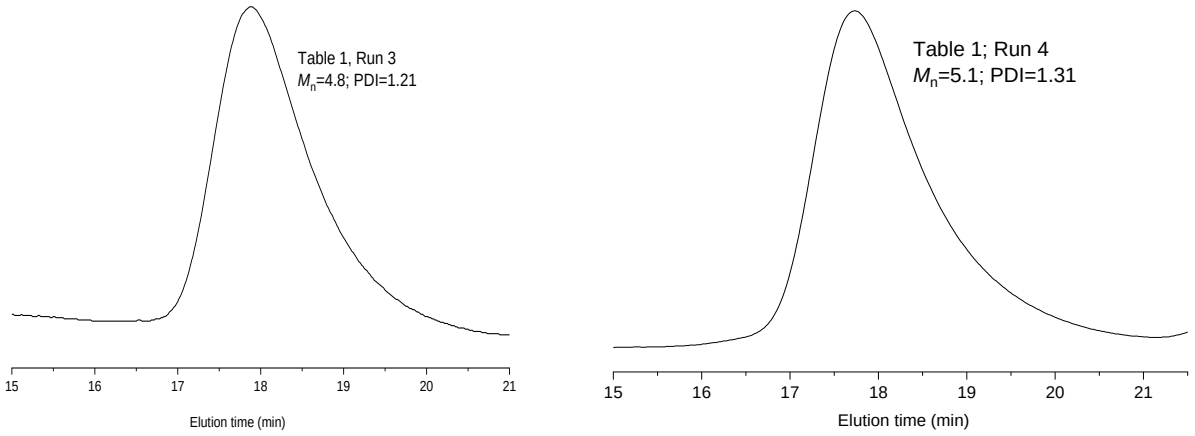


Fig. S26 GPC curves of *p*-StPPh$_2$-IP copolymers with RI detection mode using THF as eluent..

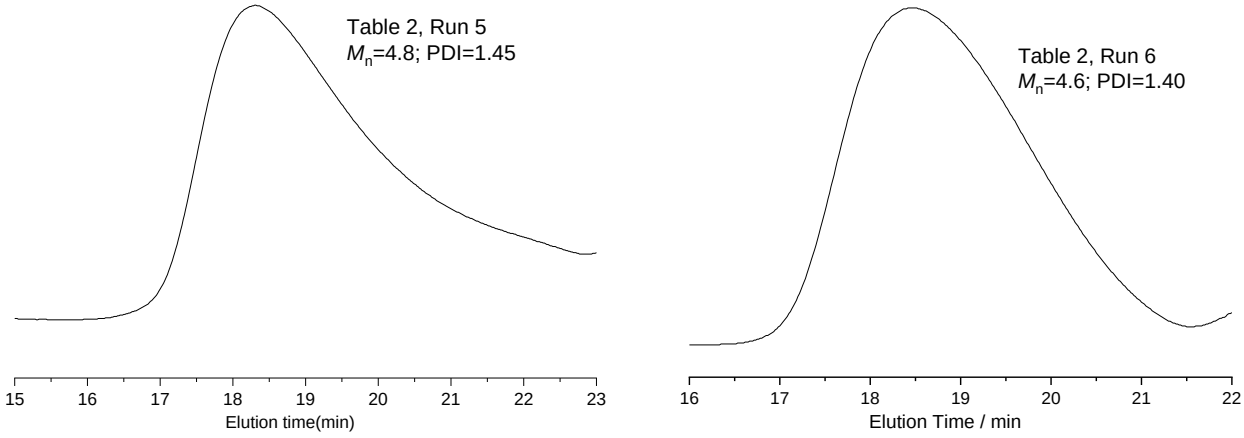


Fig. S27 GPC curves of *o*-StPPh$_2$-IP copolymers with RI detection mode using THF as eluent.

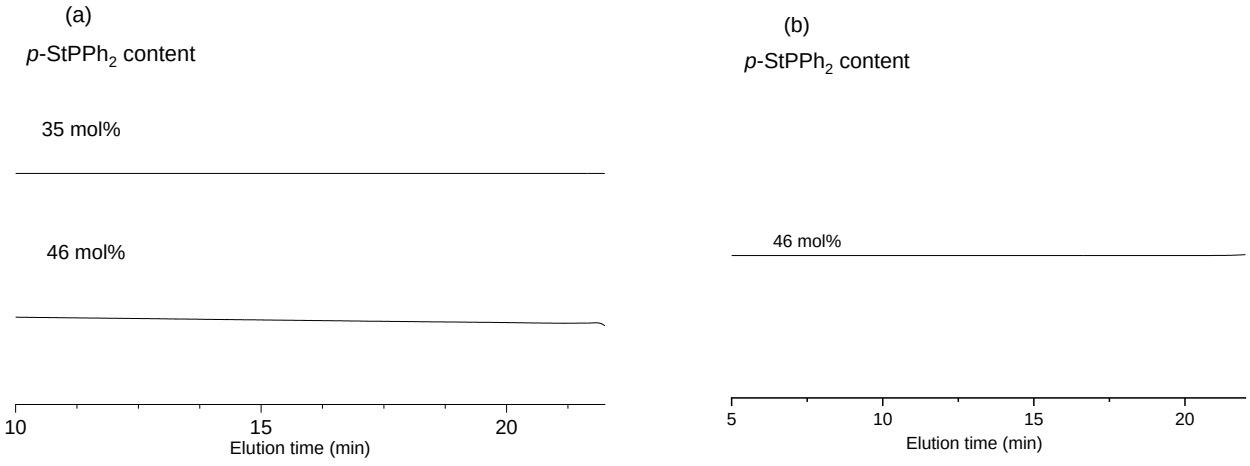


Fig. S28 GPC curves of *p*-StPPh$_2$-IP copolymers with RI detection mode using THF (a) and chloroform (b) as eluent.

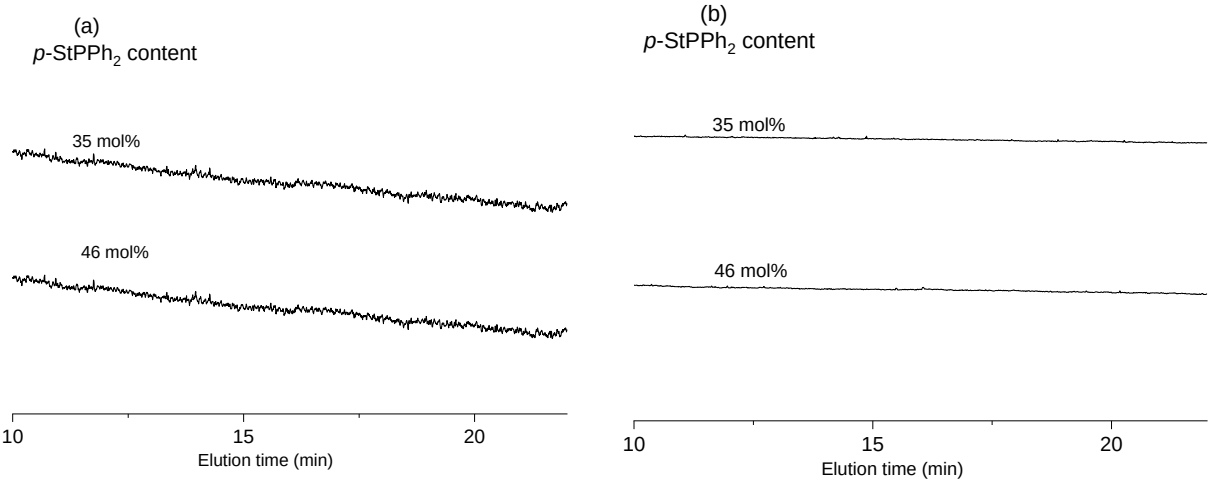


Fig. S29 GPC curves of *p*-$StPPh_2$-IP copolymers with RALS (a) and LALS (b) detection mode using THF as eluent.

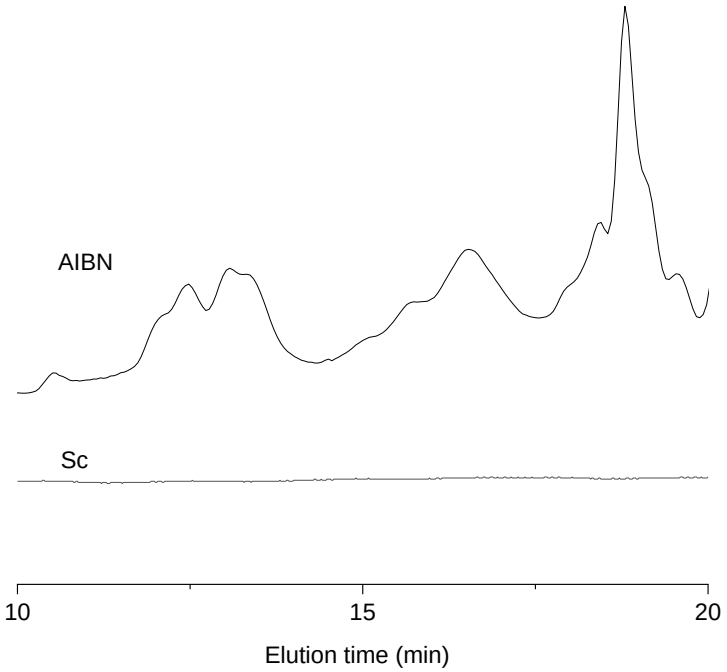


Fig. S30 GPC curves of *p*-$StPPh_2$ homopolymers prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ and AIBN with RI detection mode using THF as eluent.

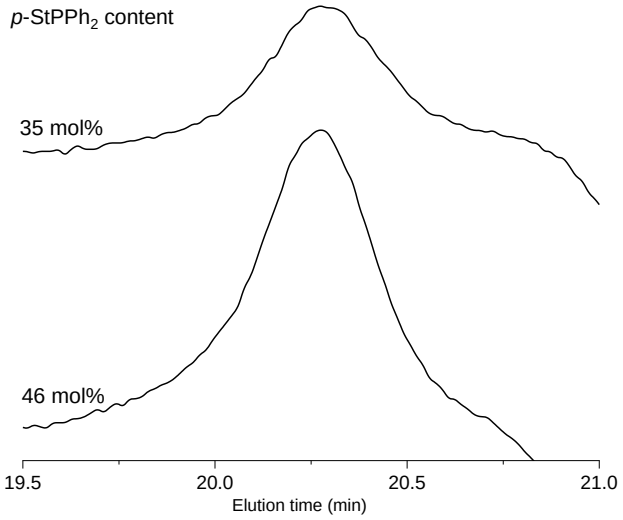


Fig. S31 GPC curves of *p*-StPPh$_2$-IP copolymers with UV detection mode using THF as eluent.

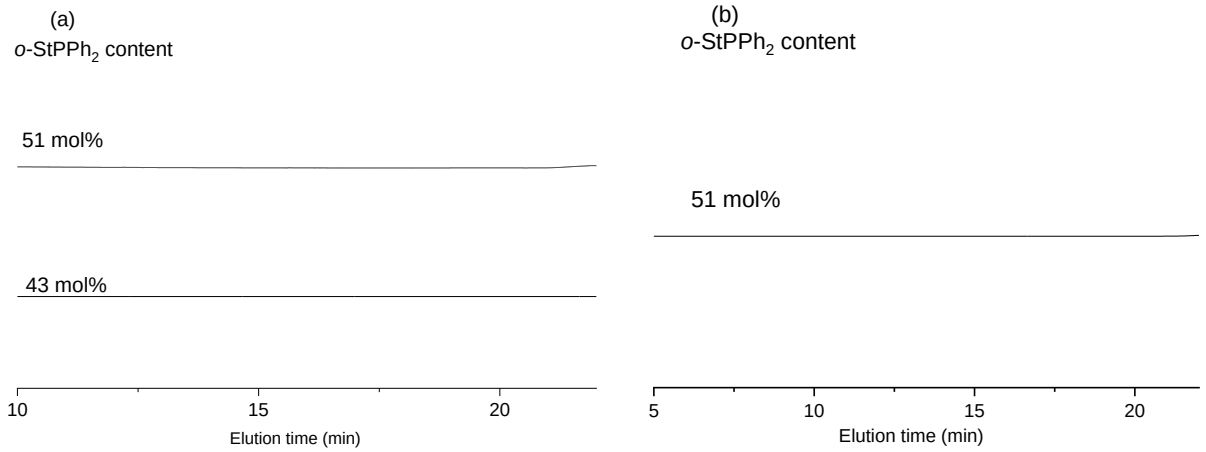


Fig. S32 GPC curves of *o*-StPPh$_2$-IP copolymers with RI detection mode THF (a) and chloroform (b) as eluent.

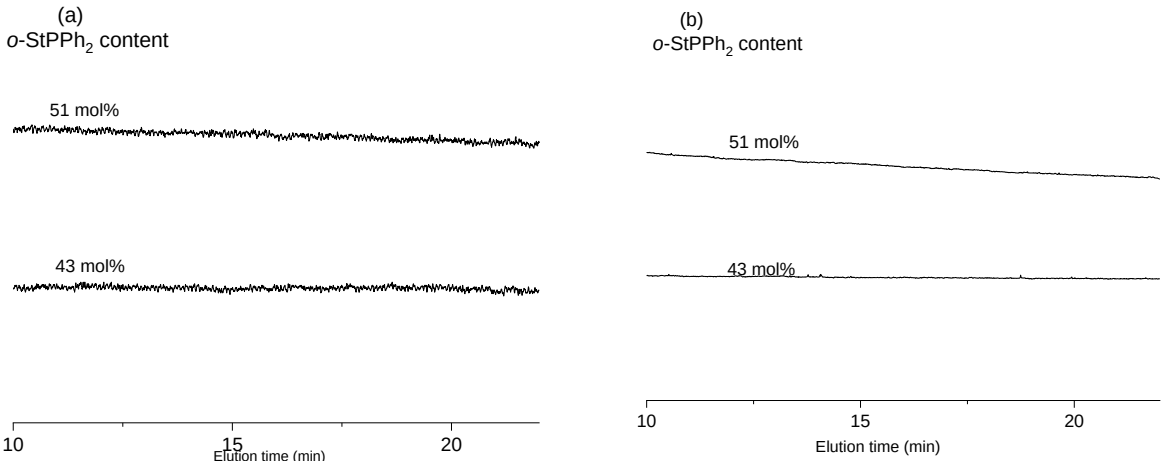


Fig. S33 GPC curves of *o*-StPPh$_2$-IP copolymers with RALS (a) and LALS (b) detection mode using THF as eluent.

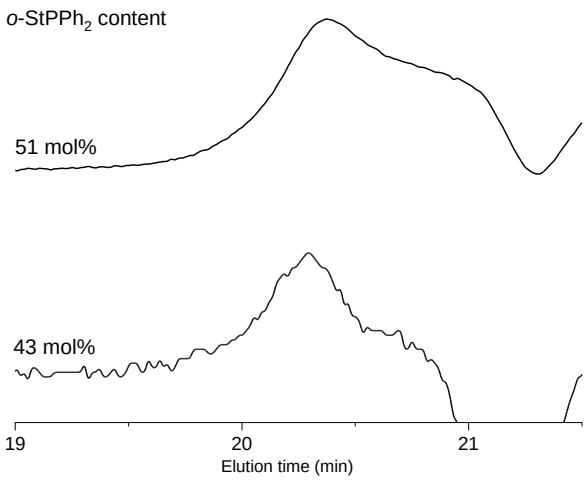


Fig. S34 GPC curves of *o*-$StPPh_2$-IP copolymers with UV detection mode using THF as eluent.

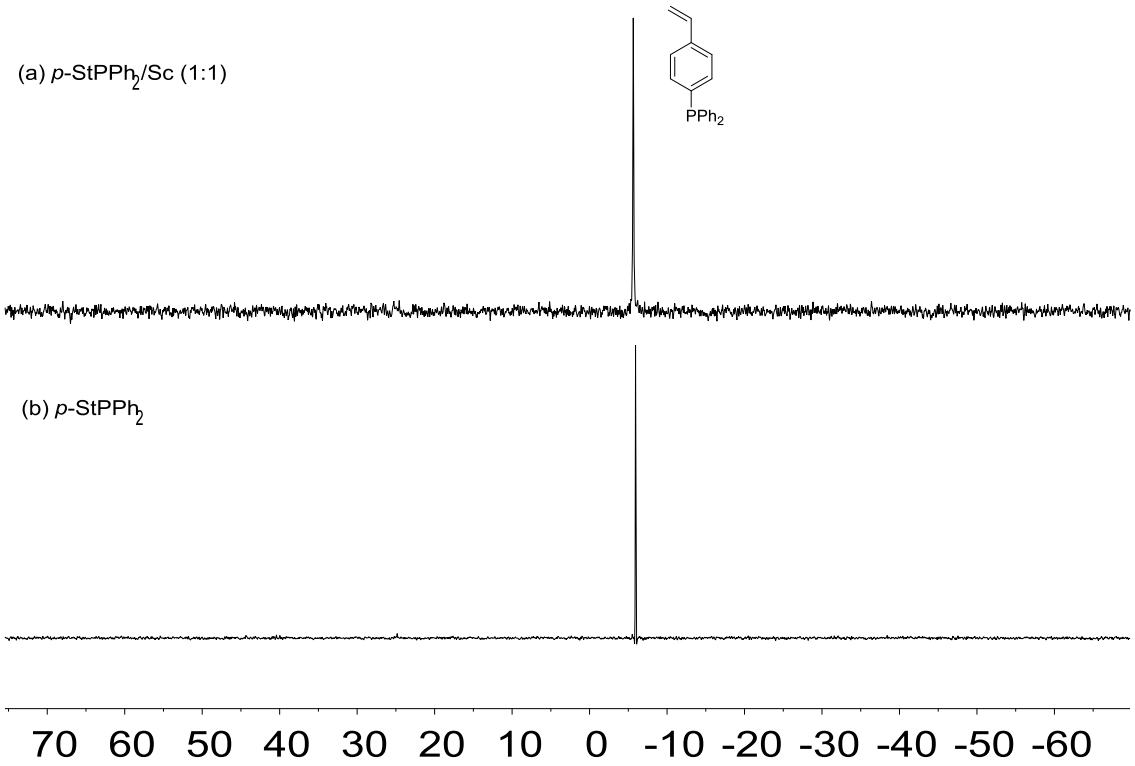


Fig. S35 ^{31}P-NMR spectra of (a) *p*-$StPPh_2$ monomer with $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2/[Ph_3C][B(C_6F_5)_4]$ (molar ratio 1/1) and (b) *p*-$StPPh_2$ monomer only.

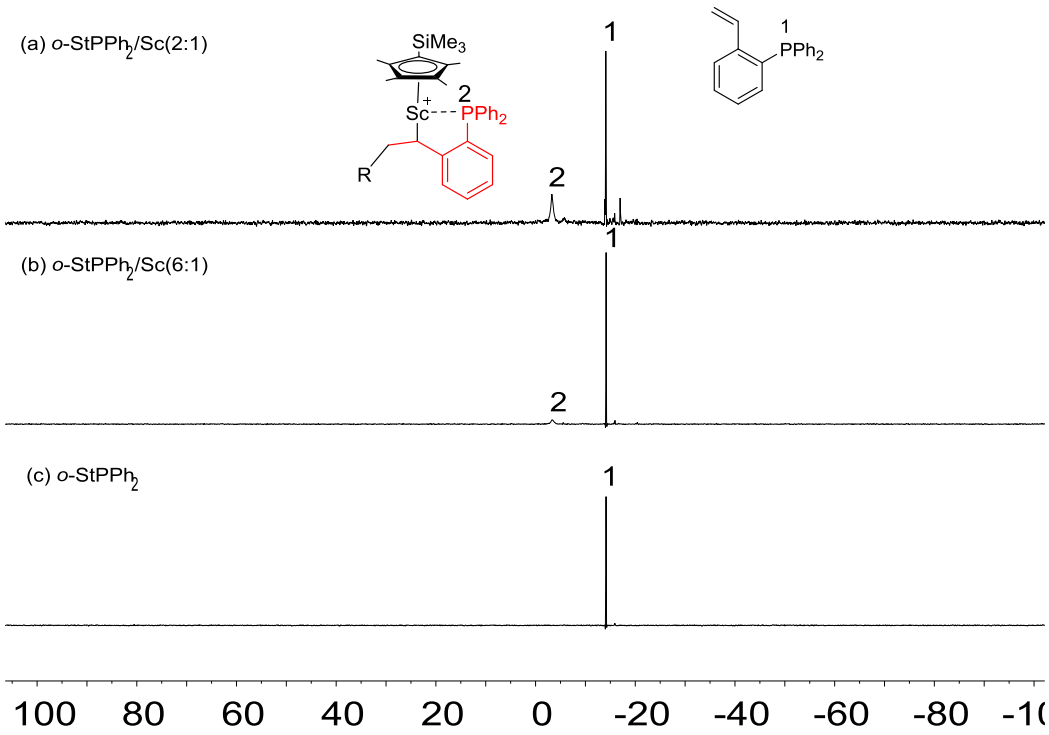
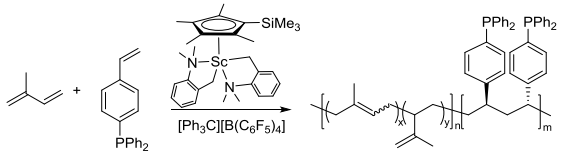


Fig. S36 ^{31}P-NMR spectra of (a) *o*-StPPh$_2$ monomer with ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$/[Ph_3C][$B(C_6F_5)_4$] (molar ratio 2/1), (b) *o*-StPPh$_2$ monomer with ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$/[Ph_3C][$B(C_6F_5)_4$] (molar ratio 6/1) and (c) *o*-StPPh$_2$ monomer only.

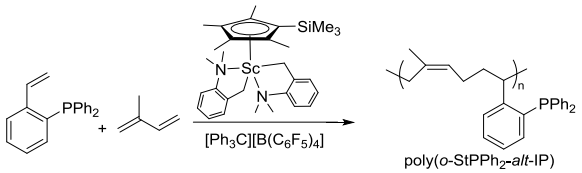
Table S1 A kinetics investigation of *p*-StPPh$_2$/IP (feed ratio 250/250) copolymerization[a]



Run	Time (min)	Yield (%)	Composition (mol%)[b]		Conversions (mol%)	
			p-StPPh$_2$	IP(1,4/3,4)	*p*-StPPh$_2$	IP
1	5	15	0	100(30/70)	0	82
2	10	17	0	100(32/68)	0	92
3	15	19	0	100(34/66)	0	99
4	20	21	3	97(34/66)	3	99
5	25	28	10	90(34/66)	11	99
6	35	48	27	73(34/66)	36	99
7	50	78	42	58(34/66)	74	99
8	60	91	47	53(34/66)	91	99

[a] Conditions: [Sc] (5 μmol), [Ph_3C][$B(C_6F_5)_4$] (5 μmol), toluene (3 mL), 25 °C. [b] Determined by ^{1}H-NMR.

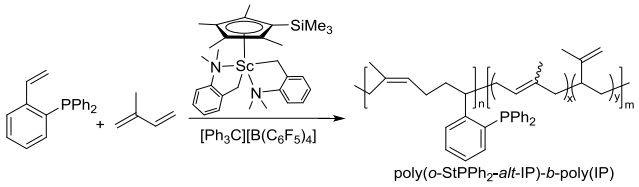
Table S2 A kinetics investigation of *o*-StPPh$_2$/IP (feed ratio 250/250) copolymerization[a]



Run	Time (min)	Yield (%)	Composition (mol%)[b]		Conversions (mol%)	
			o-StPPh$_2$	IP(1,4/3,4)	*o*-StPPh$_2$	IP
1	60	42	51	49(100/0)	42	40
2	120	66	51	49(100/0)	66	64
3	240	97	51	49(100/0)	97	94

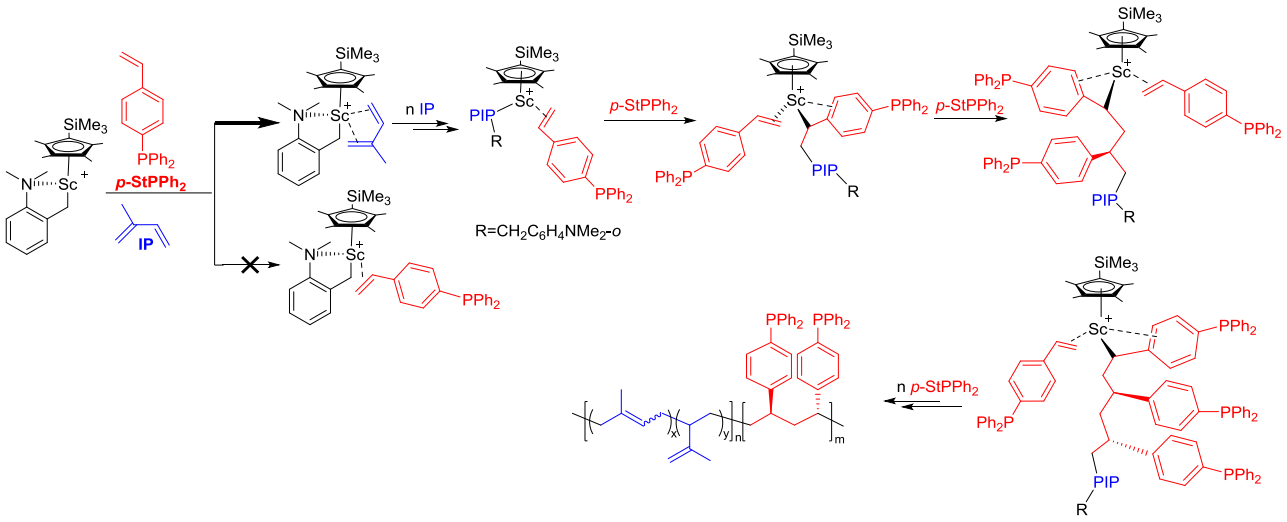
[a] Conditions: [Sc] (5 μmol), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (5 μmol), toluene (3 mL), 25 °C. [b] Determined by ^{1}H-NMR.

Table S3 A kinetics investigation of *o*-StPPh$_2$/IP (feed ratio 250/375) copolymerization[a]

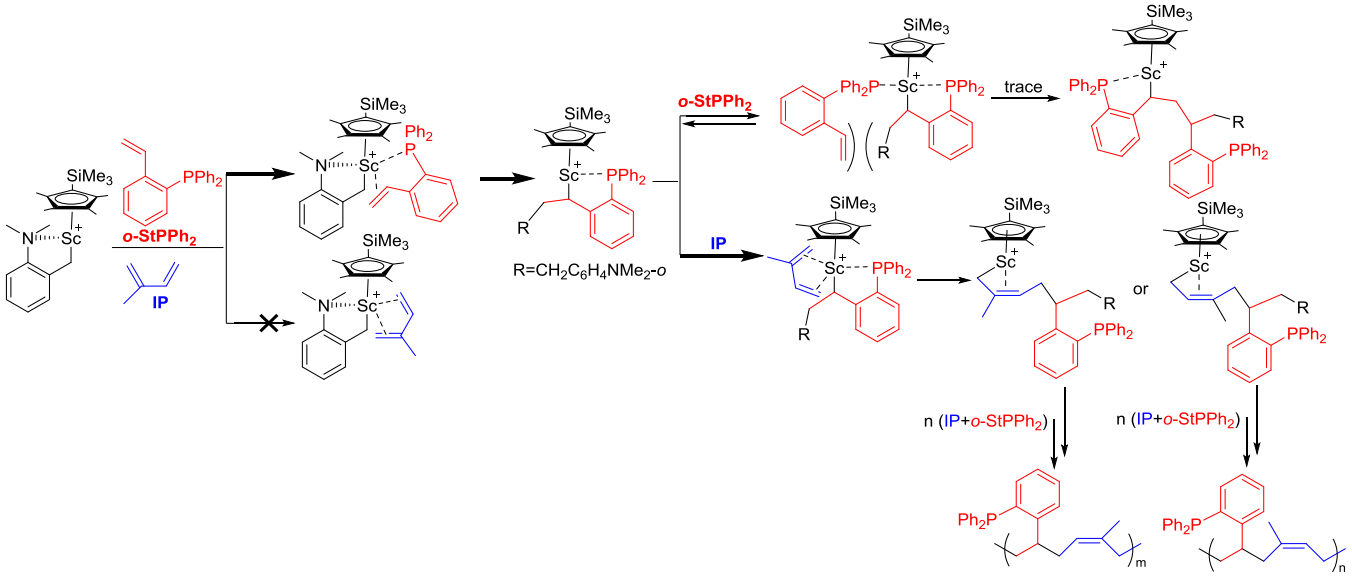


Run	Time (min)	Yield (%)	Composition (mol%)[b]		Conversions (mol%)	
			o-StPPh$_2$	IP(1,4/3,4)	*o*-StPPh$_2$	IP
1	0.2	90	51	49(100/0)	99	65
2	0.5	94	44	56(81/19)	99	83
3	1	96	42	58(77/23)	99	93
4	8	98	38	62(71/29)	99	96
5	10	98	38	62(71/29)	99	96

[a] Conditions: [Sc] (5 μmol), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (5 μmol), toluene (3 mL), 25 °C. [b] Determined by ^{1}H-NMR.



Scheme S1 Possible mechanism of the copolymerization of *p*-StPPh$_2$ and IP by (C$_5$Me$_4$SiMe$_3$)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$.



Scheme S2 Possible mechanism of the alternating copolymerization of *o*-StPPh$_2$ and IP by (C$_5$Me$_4$SiMe$_3$)Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$.