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Supporting Information

Stannylated Polynorbornenes as New Reagents for a Clean Stille Reaction

Nora Carrera, Enrique Gutiérrez, Rut Benavente, M. Mar Villavieja, Ana C. Albéniz* and Pablo Espinet.*[a]

[a] *IU CINQUIMA/Química Inorgánica.*

Universidad de Valladolid. 47071-Valladolid. Spain.

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1- Preparation and spectroscopic data for the monomer (norbornenyl)-$SnBu_2(C_6H_4OMe)$ (**2**).

2- Spectroscopic data for copolymers **4** and **6**-**8**

3- Spectroscopic data for the coupling products collected in Table 2 (main text)

4- Table with data of a second recycling experiment according to Scheme 3 and entry 5, Table 2 (main text).

5- Figures with NMR spectra of monomer **1**.

6- Figures with NMR spectra of copolymers.

7- Figures with NMR spectra showing the method used for the titration of polymers prior to the Stille reaction.

1- Preparation and spectroscopic data for the monomer (norbornenyl)$SnBu_2(C_6H_4OMe)$ (2).

Dibutyl(p-methoxyphenyl)stannylnorbornene (2). A solution of 4-bromoanisole (2.719 g, 14.536 mmol) in dry THF (30 mL) was added to iodine activated magnesium turnings (0.3862 g, 15.890 mmol) and refluxed for 8 h. The reaction mixture was cooled to 10 ˚C, and **1** (4.000 g, 11.063 mmol) was added to it. The mixture was stirred for 12 h at room temperature and then a 1:1 Et_2O/H_2O mixture (20 mL) was added. The organic layer was separated and the aqueous layer was washed twice with Et_2O (2 x 15 mL). The combined organic solutions were washed with satured aqueous solutions of NH_4Cl (15 mL) and NaCl (2 x 15 mL) and dried over $MgSO_4$. The solvents were evaporated and a yellowish liquid was obtained. Isolated yield: 4.5856 g (95%). The product is a mixture of four isomers: **2a** : **2b** : **2c** : **2d =** 45 : 41 : 7 : 7.

(2-exo) **2a**: ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.47 (m, 2H, H_{ortho}), 6.91 (m, 2H, H_{meta}), 6.11 (m, J = 3.0, 5.6 Hz, 1H, H^6), 5.91 (m, J = 3.0, 5.6 Hz, 1H, H^5), 3.81 (s, 3H, OCH_3), 2.99 (br, 1H, H^4), 2.95 (br, 1H, H^1), 1.87 (m, 1H, H^3), 1.28 (m, 1H, $H^{3'}$), 1.27 (m, 1H, H^7), 1.07 (m, 1H, $H^{7'}$), 0.96 (m, 1H, H^2), 0.95-1.7 (m, 12H, CH_2, Bu), 0.87 (t, 6H, CH_3, Bu). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 159.9 (s, C_{ipso}-OCH_3), 137.2 (s, C_{ortho}), 136.8 (s, $^3J_{Sn-C}$ = 52.0 Hz, C^6), 132.5 (s, C^5), 131.5 (s, C_{ipso}-Sn), 113.4 (s, C_{meta}), 55.0 (s, OCH_3), 48.1 (s, $^3J_{Sn-C}$ = 0 Hz, C^7), 45.0 (s, C^1), 43.0 (s, $^3J_{Sn-C}$ = 11.5 Hz, C^4), 29.1 (s, CH_2), 28.5 (s, C^3), 26.1 (s,

CH_2), 21.2 (s, C^2), 13.3 (s, CH_3), 9.2 (s, CH_2-Sn). $^{119}Sn\{^1H\}$ NMR (11.8 MHz, $CDCl_3$): δ -38.5 (s)

(2-endo) **2b**: ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.47 (m, 2H, H_{ortho}), 6.91 (m, 2H, H_{meta}), 6.00 (m, 1H, H^5), 5.95 (m, 1H, H^6), 3.81 (s, 3H, OCH_3), 3.15 (br, 1H, H^1), 2.96 (br, 1H, H^4), 2.08 (m, 1H, H^3), 1.68 (m, 1H, H^2), 1.5 (m, 1H, H^7), 1.23 (m, 1H, $H^{3'}$), 1.14 (m, 1H, $H^{7'}$), 0.95-1.7 (m, $12H_{Bu}$), 0.87 (t, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 159.8 (s, C_{ipso}-OCH_3), 137.2 (s, C_{ortho}), 135.8 (s, C^5), 135.2 (s, $^3J_{Sn-C}$ = 23.4 Hz, C^6), 131.5 (s, C_{ipso}-Sn), 113.4 (s, C_{meta}), 55.0 (s, OCH_3), 50.4 (s, $^3J_{Sn-C}$ = 48.4 Hz, C^7), 46.0 (s, C^1), 42.0 (s, $^3J_{Sn-C}$ = 19 Hz C^4), 29.1 (s, CH_2), 28 (s, C^3), 26.1 (s, CH_2), 22 (s, C^2), 13.3 (s, CH_3), 10.1 (s, CH_2-Sn). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ -44.2 (s)

2c: ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.47 (m, 2H, H_{ortho}), 6.91 (m, 2H, H_{meta}), 6.02 (m, 2H, H^5, H^6), 3.81 (s, 3H, OCH_3), 3.12 (br, 2H, H^4, H^1), 2.12 (m, 1H, H^7), 0.95-1.7 (m, 16H, $12H_{Bu}$, H^3, $H^{3'}$, H^2, $H^{2'}$) 0.87 (t, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 159.9 (s, C_{ipso}-OCH_3), 137.2 (s, C_{ortho}), 136.5 (s, C^5,C^6), 131.5 (s, C_{ipso}-Sn), 113.4 (s, C_{meta}), 55.0 (s, OCH_3), 46.5 (s, C^1,C^4), 32 (s, C^7), 29.1 (s, CH_2), 26.1 (s, CH_2), 13.3 (s, CH_3), 10.8 (s, CH_2-Sn). $^{119}Sn\{^1H\}$ NMR (11.8MHz, $CDCl_3$): δ -56.3 (s)*.

2d: ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.47 (m, 2H, H_{ortho}), 6.91 (m, 2H, H_{meta}), 3.81 (s, 3H, OCH_3), 0.95-1.7 (m, 16H, $12H_{Bu}$, H^{1-7}), 0.87 (t, 6H, CH_3). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ -55.9 (s)*.

* The assignment of these two signals could be reversed.

2- Spectroscopic data for copolymers 5 and 7-9:

Copol-NB-NB-SnBu$_2$(CH=CH$_2$) (4): ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 6.4 (br, 1H, C*H*=CH$_2$), 6.1 (br, 1H, CH=C*H$_{trans}$*H), 5.6 (br, 1H, CH=CH*H*$_{cis}$), 2.8-0.7 (br, H$_{Bu}$, H$^{1-7}$).

Copol-NB-NB-SnBu$_2$(C$_6$H$_4$F-*p*) (7): ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.4 (br, 2H, H$_{ortho}$), 7.0 (br, 2H, H$_{meta}$), 2.8-0.7 (br, H$_{Bu}$, H$^{1-7}$). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ 163.2 (d, $^1J_{C-F}$ = 244 Hz, *C*$_{para}$-F), 138.0 (s, C$_{ortho}$), 136.0 (s, C$_{ipso}$-Sn), 115.1 (d, $^2J_{C-F}$ = 18.3 Hz, C$_{meta}$), 52.5-49.5 (br, C^{5,6}), 48.0-45.0 (br, C^{1,4}), 41.0-38.0 (br, C^7), 36.5-34.0 (br, C^{1,2}), 29.2 (s, Bu: -CH$_2$-*C*H$_2$-CH$_2$-), 27.5 (s, Bu: -*C*H$_2$-CH$_3$), 13.7 (s, Bu: *C*H$_3$-), 9.3 (br, Bu: -*C*H$_2$-Sn). ^{19}F RMN (282 MHz, $CDCl_3$): δ -113.9 (br).^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): δ -43.1 (br).

Copol-NB-NB-SnBu$_2$(C$_6$H$_4$CF$_3$-*p*) (8): ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.7-7.4 (br, 4H, H$_{arom}$), 2.7-0.7 (br, H$_{Bu}$, H$^{1-7}$). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ 148.0 (br, *C*$_{para}$-CF$_3$), 136.8 (s, C$_{ortho}$), 129.8 (br, C$_{ipso}$-Sn), 124.1 (s, C$_{meta}$), 52.0-49.0 (br, C^{5,6}), 48.0-46.0 (br, C^{1,4}), 42.0-39.0 (br, C^7), 37.0-34.0 (br, C^{1,2}), 29.1 (s, Bu: -CH$_2$-*C*H$_2$-CH$_2$-), 27.5 (s, Bu: -*C*H$_2$-CH$_3$), 13.7 (s, Bu: *C*H$_3$-), 9.3 (br, Bu: -*C*H$_2$-Sn). ^{19}F RMN (282 MHz, $CDCl_3$): δ - 63.21 (br).^{119}Sn{^{1}H} NMR (111 .92 MHz, $CDCl_3$): δ -45.0 (br).

Copol-NB-NB-SnBu$_2$(C$_2$Ph) (9): ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 7.5-7.3 (br, 2H, H$_{ortho}$), 7.3-7.1 (br, 3H, H$_{meta}$, H$_{para}$), 2.7-0.6 (br, H$_{Bu}$, H$^{1-7}$). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ 131.9 (s, *C*$_{ortho}$), 128.1 (s, C$_{meta}$), 127.8 (s, C$_{para}$), 124.0 (s, C$_{ipso}$), 110.5 (s, C≡*C*-Sn), 93 (s, C≡*C*-Ph), 52.0-50.0 (br, C^{5,6}), 48.0-46.0 (br, C^{1,4}), 41.0-38.0 (br, C^7), 36.0-34.0 (br, C^{1,2}),

29.0 (s, Bu, -CH_2-*C*H_2-CH_2-), 27.1 (s, Bu, -*C*H_2-CH_3), 13.6 (s, Bu, *C*H_3-), 11.0 (br, Bu, -*C*H_2-Sn). ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): δ -64.0 (br).

3- Spectroscopic data for the coupling products collected in Table 2 (main text):

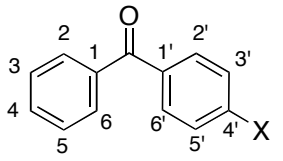
C_6F_5-CH=CH_2 (10): ^{1}H RMN (300.13 MHz, $CDCl_3$): δ 6.60-6.65 (dd, 1H, H^2), 6.10 (d, 1H, H^1), 5.70 (d, 1H, $H^{1'}$). ^{19}F RMN (282 MHz, $CDCl_3$): δ -163.5 (m, $2F_{meta}$), -156.5 (t, $2F_{para}$), -143.9 (m, $2F_{ortho}$).

CH_2=CH-CH_2-(C_6H_4F-*p*) (14): ^{1}H RMN (300.13 MHz, $CDCl_3$): δ 7.15 (m, 2H, $H^{2,6}$), 6.97 (m, 2H, $H^{3,5}$), 5.89 (m, 1H, CH_2=C*H*-CH_2-), 5.09 (d, J = 10.7 Hz, 1H, C*H*H=CH-CH_2-), 5.03 (d, J = 16.1 Hz, 1H, CH*H*=CH-CH_2-), 3.36 (d, J = 5.6 Hz, 2H, CH_2=CH-CH_2-). ^{19}F RMN (282 MHz, $CDCl_3$): δ -116.5 (m).

CH_2=CH-CH_2-(C_6H_4-CF_3-*p*) (15): ^{1}H RMN (300.13 MHz, $CDCl_3$): δ 7.53 (m, 2H, $H^{2,6}$), 7.30 (m, 2H, $H^{3,5}$), 5.89 (m, 1H, CH_2=C*H*-CH_2-), 5.13 (d, J = 11.4 Hz, 1H, C*H*H=CH-CH_2-), 5.09 (d, J = 15.7 Hz, 1H, CH*H*=CH-CH_2-), 3.45 (d, J = 8.5 Hz, 2H, CH_2=CH-CH_2-). ^{19}F RMN (282 MHz, $CDCl_3$): δ -63 (s).

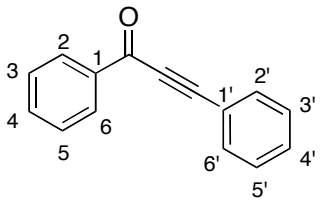
C_6H_5C(O)(C_6H_4-OMe-*p*) (16): ^{1}H RMN (300.13 MHz, $CDCl_3$): δ 7.73 (m, 2H, $H^{2,6}$), 7.64 (m, 2H, $H^{2',6'}$) 7.48 (m, 1H, H^4), 7.39 (m, 2H, $H^{3,5}$), 6.91 (m, 2H, $H^{3',5'}$), 3.89 (s, 3H, OCH_3).

C_6H_5C(O)(C_6H_4F-*p*) (17): ^{1}H RMN (300.13 MHz, $CDCl_3$): δ 7.82 (m, 2H, $H^{2,6}$), 7.78 (m, 2H, $H^{2',6'}$) 7.50 (m, 1H, H^4), 7.39 (m, 2H, $H^{3,5}$), 7.12 (m, 2H, $H^{3',5'}$). ^{19}F RMN (282 MHz, $CDCl_3$): δ -106.4 (s).



X = OMe, F

$C_6H_5C(O)(C_2C_6H_5)$ (18): ^{1}H RMN (300.13 MHz, $CDCl_3$): δ 8.24 (m, 2H, $H^{2,6}$), 7.70 (m, 2H, $H^{3,5}$) 7.62 (m, 1H, H^4), 7.50 (m, 2H, $H^{2',6'}$), 7.40 (m, 2H, $H^{3',5'}$



4- Table with data of a second recycling experiment according to Scheme 3 and entry 5, Table 2 (main text).

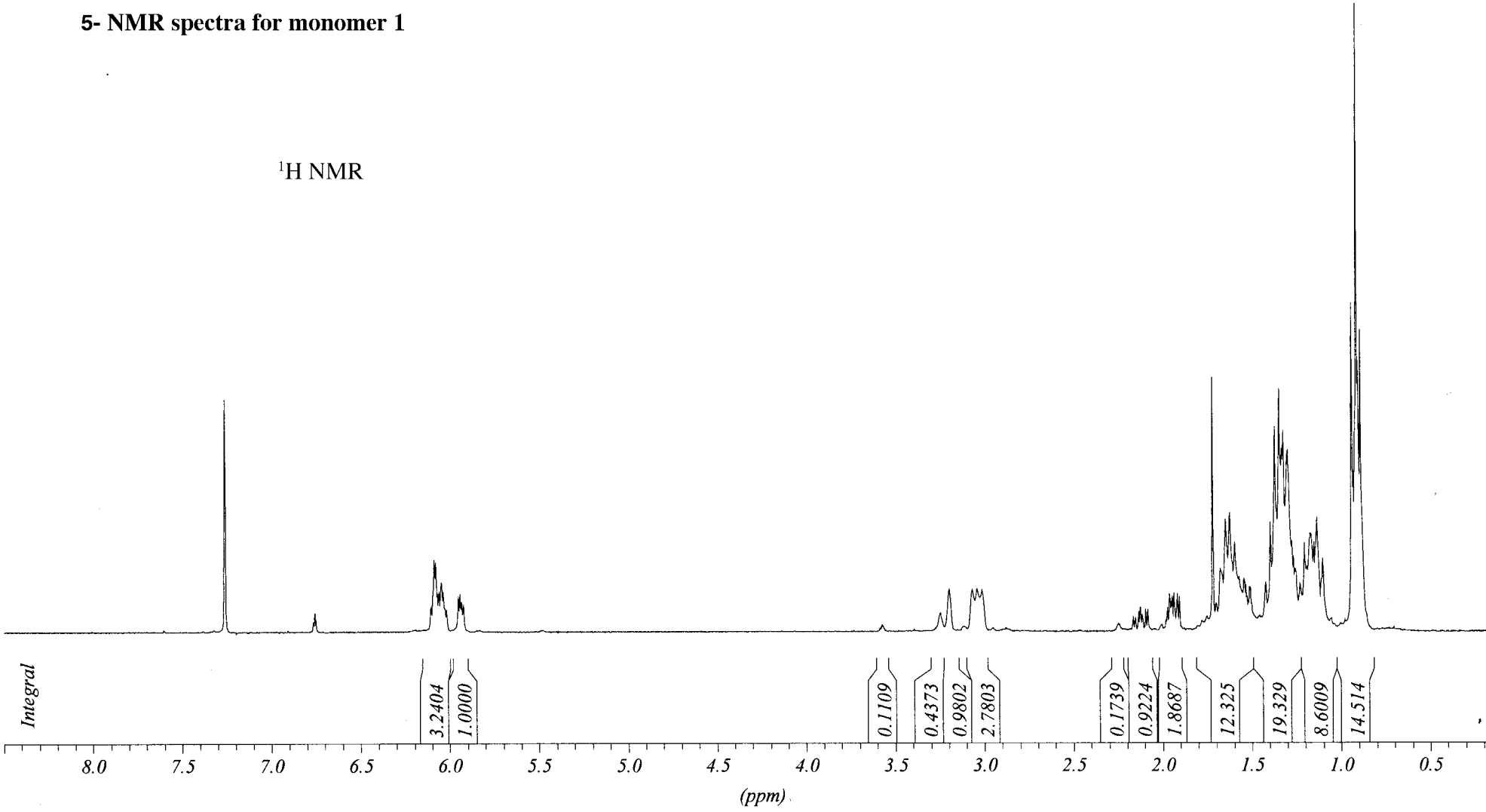
Recycling experiments for copol-NB-NBSnBu$_2$An (**6**) in the Stille reaction (entry 5, Table 2) as shown in Scheme 3.[a]

Cycle no.	Step **A**, yield (%)[b]	Step **B**, **4** yield (%)	Step **C**, **6** yield (%)
1	79	84	96
2	75	98	95
3	79	96	82
4	70	100	100
5	57	100	

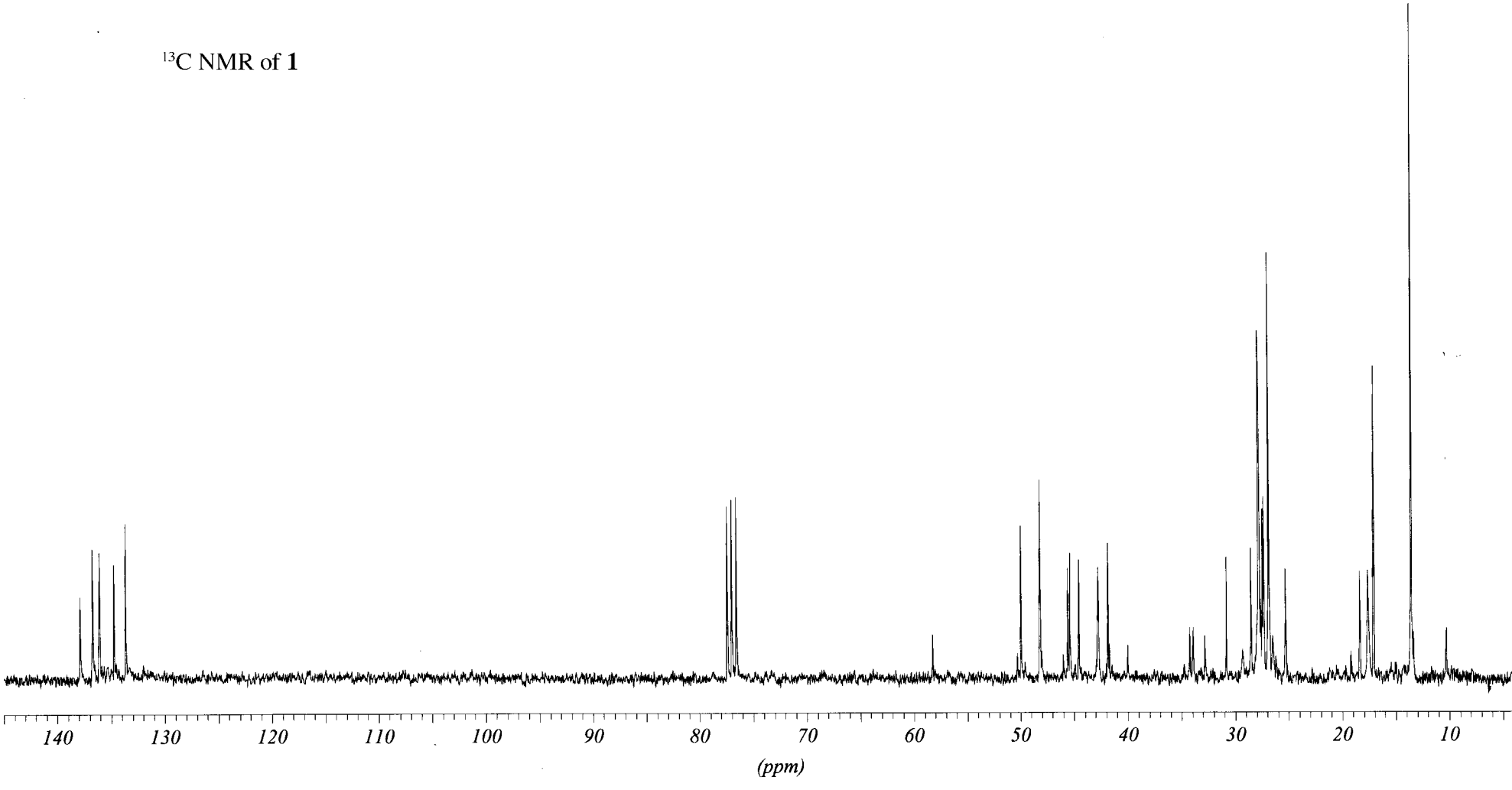
[a] The polymers remain soluble throughout the cycles. [b] Yields were determined by ^{1}H NMR of a sample of the reaction bulk before workup.

5- NMR spectra for monomer 1

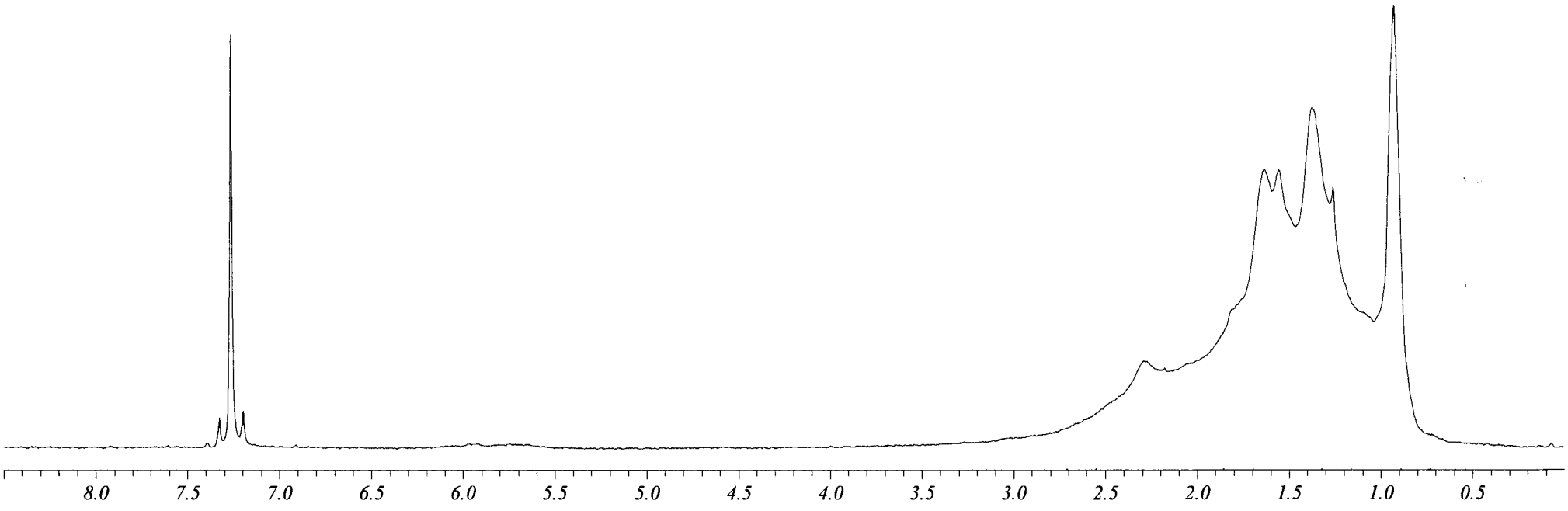
^{1}H NMR



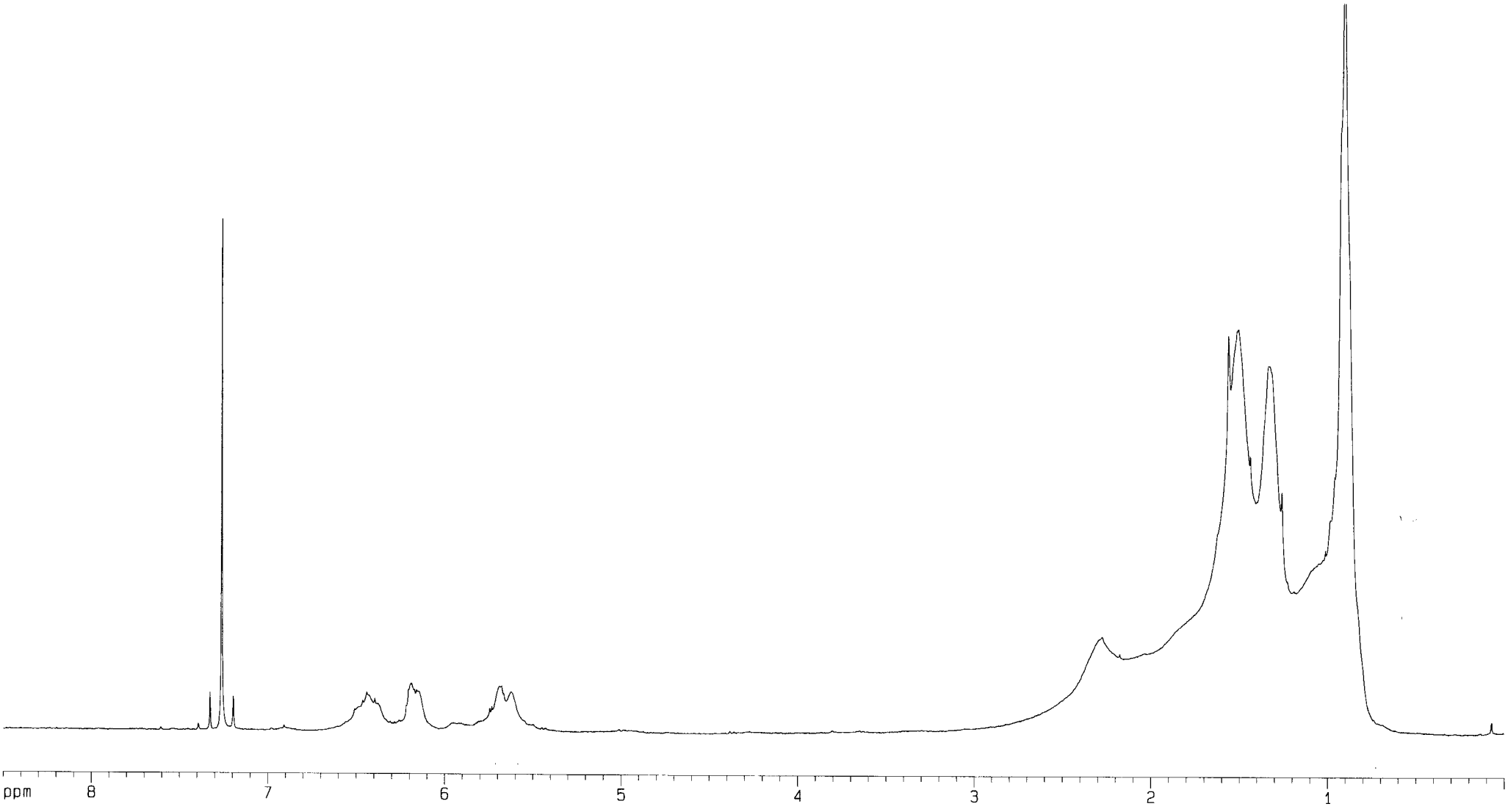
^{13}C NMR of **1**



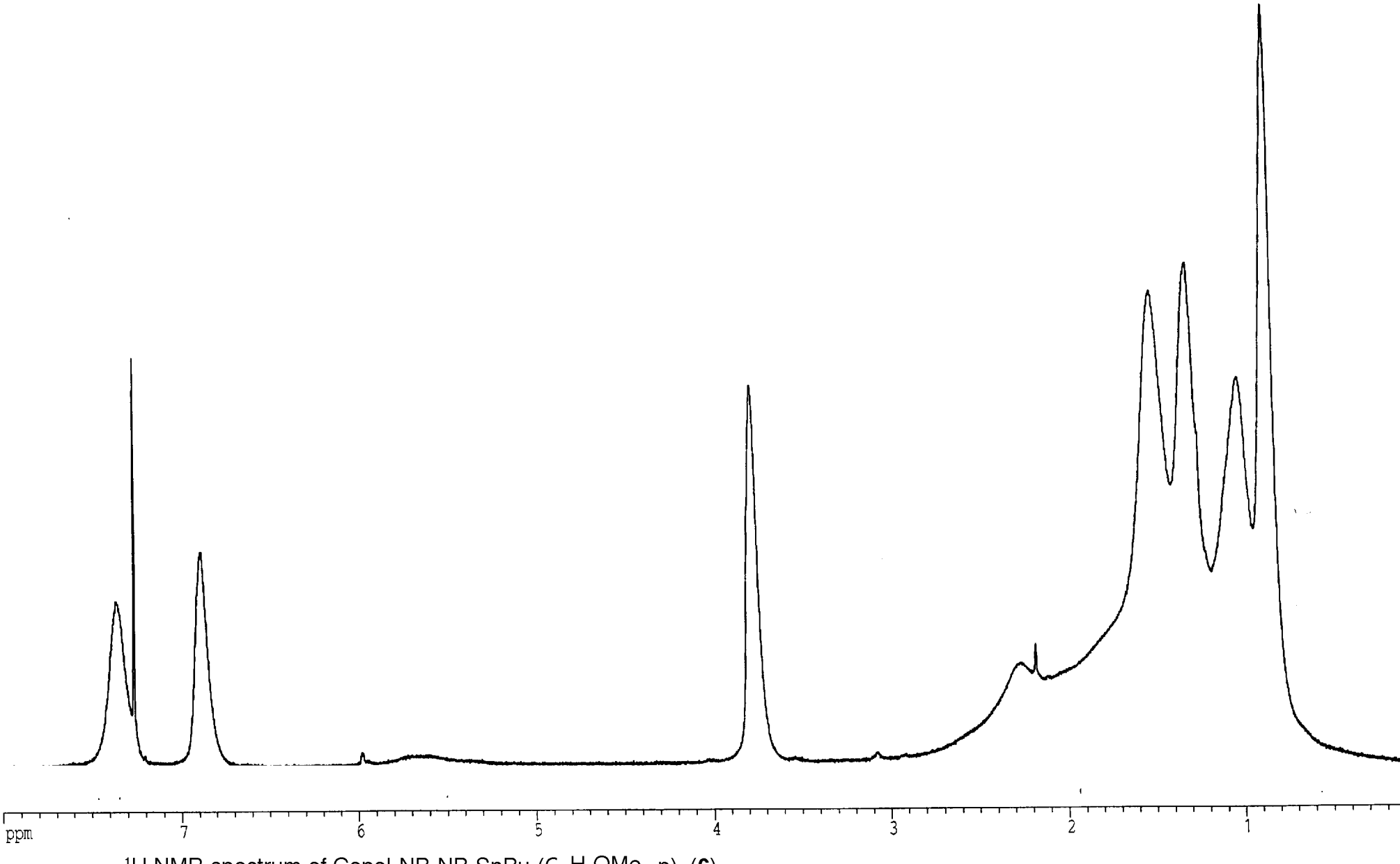
6- ^{1}H NMR spectra of copolymers



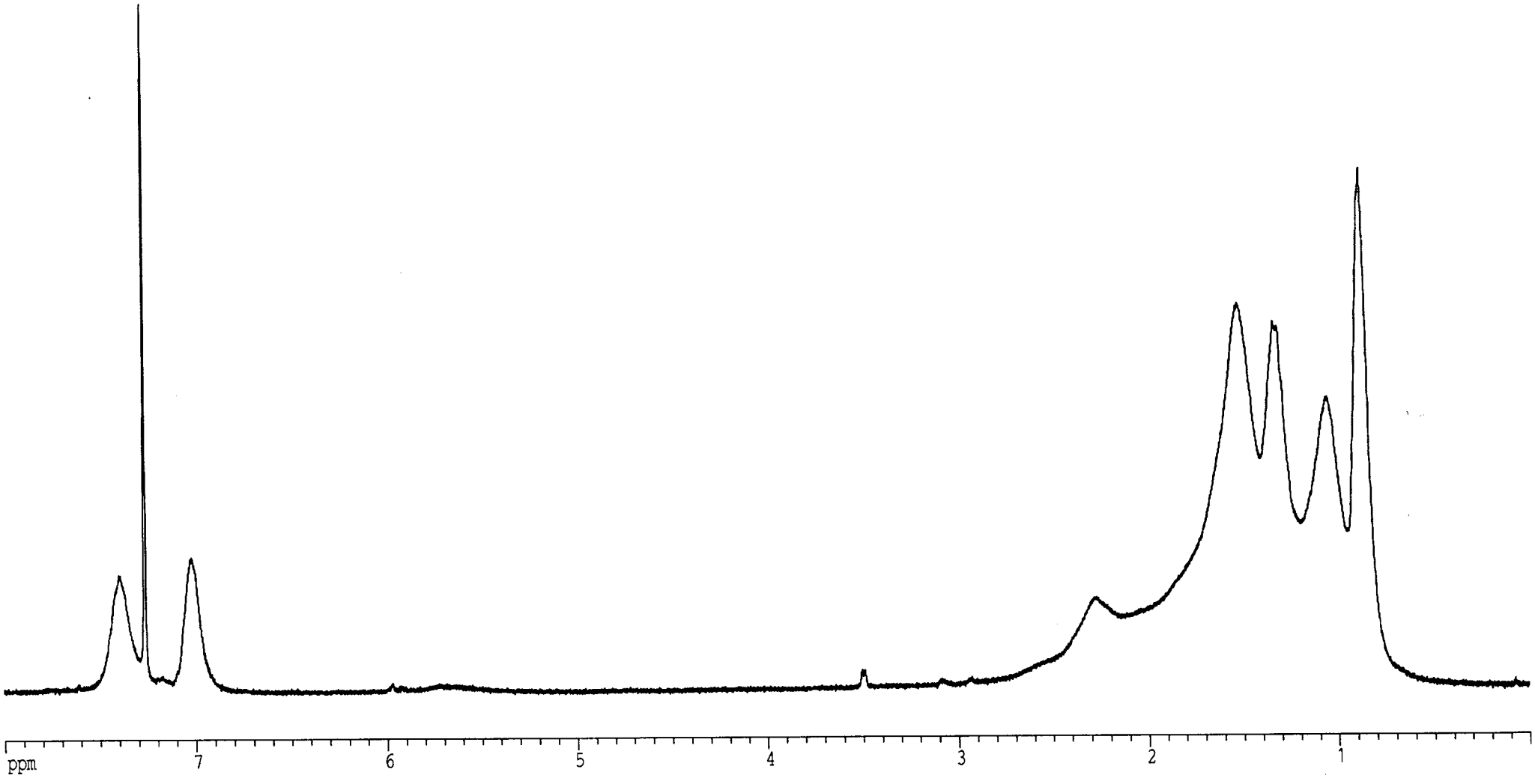
^{1}H NMR spectrum for Cop-NB-NB-$SnBu_2Cl$ (**4**)



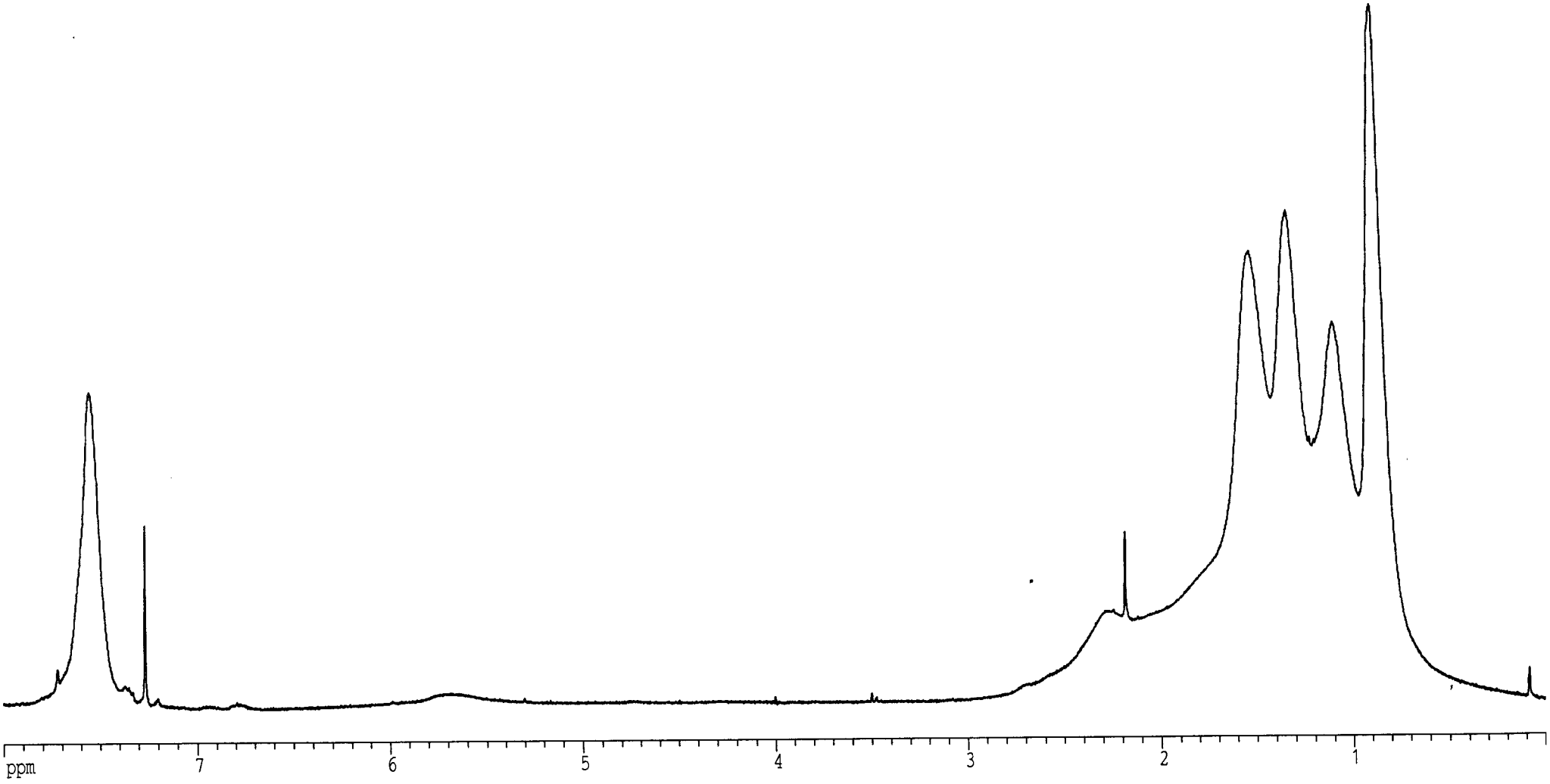
^{1}H NMR spectrum of Copol-NB-NB-SnBu$_2$(CH=CH$_2$) (**5**)



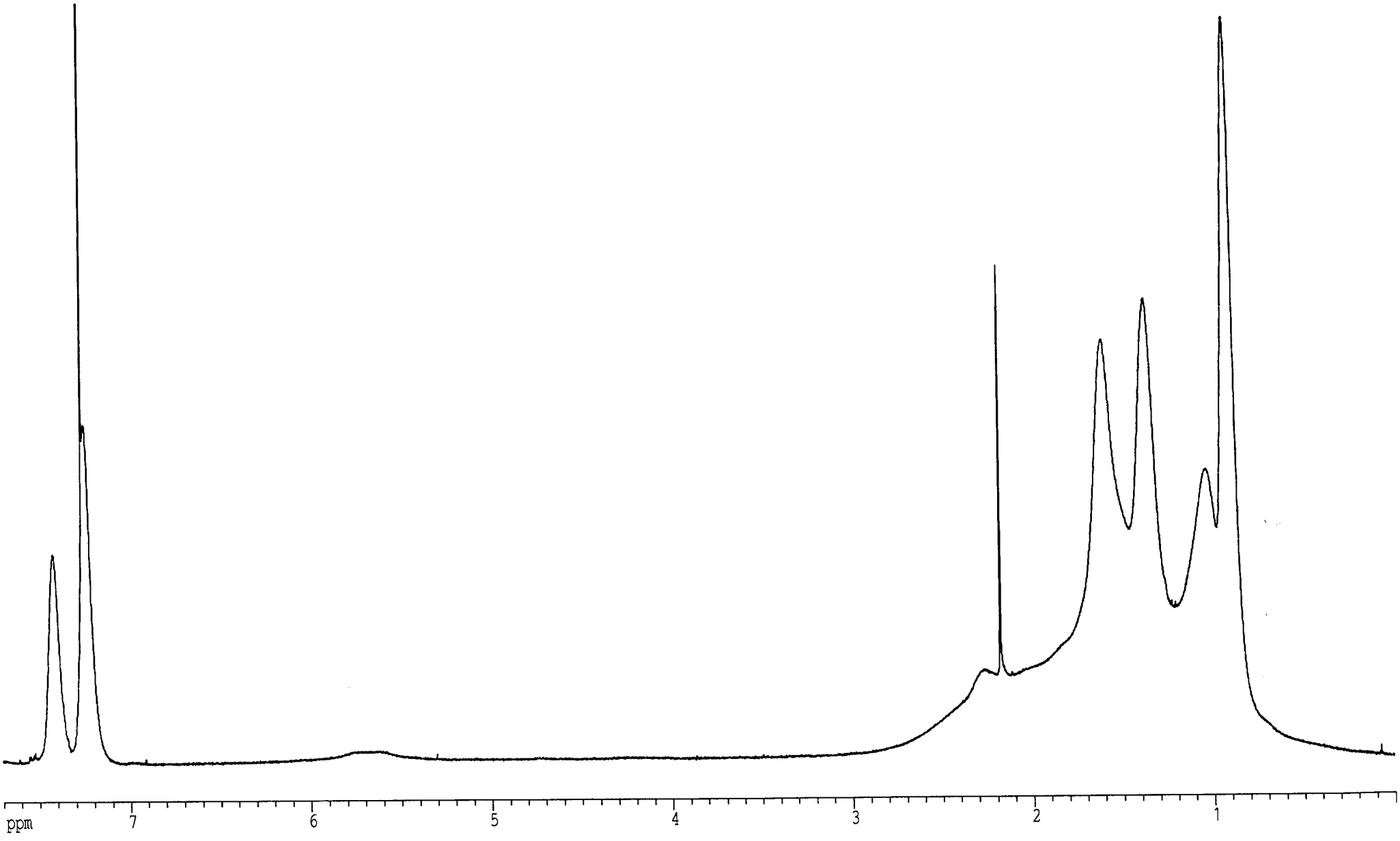
^{1}H NMR spectrum of Copol-NB-NB-$SnBu_2(C_6H_4OMe$ -p) (**6**)



^{1}H NMR spectrum of Copol-NB-NB-$SnBu_2(C_6H_4F\text{-}p)$ (**7**)



^{1}H NMR spectrum of Copol-NB-NB-$SnBu_2(C_6H_4CF_3$-p) (**8**)



^{1}H NMR spectrum of Copol-NB-NB-$SnBu_2$(CCPh) (**9**)

7- ^{1}H NMR spectra showing the the titration of copolymer 6 with ferrocene prior to the Stille reaction