SUPPORTING INFORMATION

ALLYLBORATION AS A VERSATILE TOOL FOR THE *IN-SITU* POST-POLYMERIZATION FUNCTIONALIZATION OF 1,4-*CIS*-POLY(BUTADIENE)

*Hannes Leicht, Steffen Huber, Inigo Göttker-Schnetmann, and Stefan Mecking**

Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78464 Konstanz, Germany. Fax: +49 7531 88-5152; Tel: +49 7531 88-5151

Contents:

Materials and General Considerations

Unless noted otherwise, all manipulations were carried out under an inert atmosphere using standard Schlenk or glove box techniques. Solvents were dried and degassed using standard laboratory techniques.[1]

Allylboronic acid pinacolester (abcr), 4-(1-pyrrolidinyl)benzaldehyde (Sigma Aldrich), *p*-dimethylamino-benzaldehyde (Merck), 1-bromo-4-(bromomethyl)benzene (abcr), and 4-(bromomethyl)benzonitrile (Fluorochem) are commercially available and were used without further purification.

1,4-*cis*-poly(butadiene-co-[(4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane]) (**CoPo-1**) copolymers with different incorporation ratios were synthesized as previously reported.[2] Selected examples are given in the following table:

entry	1	2	3	4
amount of Ni-1 [µmol]	10+10[a)]	10	10+15[a)]	6
temperature [°C]	0	r.t.	r.t.	0
time [h]	1	1	5.5	4
butadiene	9.1 g	10.3 g	9.0 g	1.05 bar
comonomer [mmol]	0.52	2.06	5.18	0.43
yield [g]	5.7	4.9	7.7	13.2
comonomer incorporation [mol%]	0.43	1.85	3.6	0.18
comonomer conversion [%]	87	81	99	99
M_n [10^3 g/mol][b)]	65	37	25	140
M_w/M_n [b)]	2.6	2.4	2.0	1.9
T_g [°C][c)]	-97	-95	-92	-96
1,4-*cis* units [%][d)]	96	96	95	96

a) catalyst was added in two aliquots. b) determined by GPC in THF vs. PS standards. c) determined by DSC. d) determined by ^{13}C NMR.

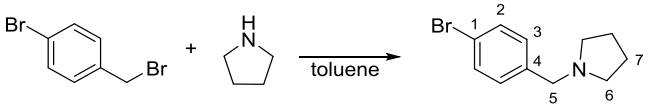
Caution: 1,3-Butadiene (BD) is gaseous at room temperature as well as toxic and carcinogenic. It requires special safety measures to avoid exposure. All operations were performed in a well ventilated fume hood using Viton™ protection gloves and a face-shield in presence of a DRÄGER 1,3-Butadiene Sensor. In order to prevent accidental exposures to BD we recommend to use a trained working protocol.

NMR spectra were recorded on a Varian Unity Inova 400, a Bruker Avance III 400 or a Bruker Avance III 600 spectrometer. ^{1}H chemical shifts were referenced to the residual proton signal of the solvent. ^{13}C chemical shifts were referenced to the carbon signal of the solvent. Multiplicities are given as follows: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, v: virtual multiplet, m: multiplet, br: broad signal or combinations thereof.

A complete assignment of all PBD backbone signals has already been published elsewhere.[2]

1. Syntheses of Aldehydes

1.1. Synthesis of 1-(4-bromobenzyl)pyrrolidine[3]

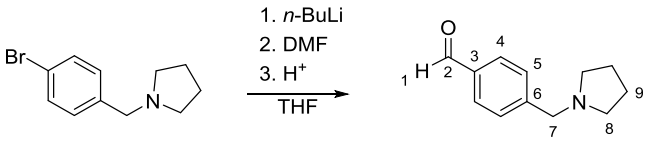


1-bromo-4-(bromomethyl)benzene (20.0 g, 80.0 mmol, 1 equiv.) was dissolved in dry toluene (60 mL). Pyrrolidine (13.1 g, 184 mmol, 2.3 equiv.) was added slowly. The reaction mixture was stirred over night at room temperature. The resulting two-phase mixture was extracted with pentane (50 mL) and Et_2O (50 mL). The combined organic phases were washed with sat. Na_2CO_3 solution, brine, and water. Drying over $MgSO_4$ and

removal of the solvent under reduced pressure gave the desired product 1-(4-bromobenzyl)pyrrolidine (16.6 g, 69.1 mmol, 86%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C) δ = 7.42 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, H2), 7.20 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, H3), 3.55 (s, 2H, H5), 2.78 (m, 4H, H6), 1.77 (m, 4H, H7).

1.2. Synthesis of 4-(pyrrolidine-1-ylmethyl)benzaldehyde

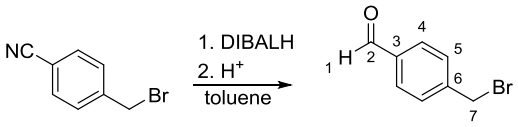


In analogy to Tamborsky *et al.*:[4] 1-(4-bromobenzyl)pyrrolidine (16.6 g, 69.1 mmol, 1 equiv.) was dissolved in THF (60 mL) and cooled to -78 °C. *n*-BuLi (2.5 M in hexane, 29.1 mL, 72.6 mmol, 1.05 eqiv.) was added. The orange reaction mixture was stirred for 10 min at -78 °C. Dry DMF (5.6 mL, 72.6 mmol, 1.05 equiv.) was added. After stirring for 10 min, the reaction mixture was warmed to room temperature. 2.5 M HCl was added until pH = 0-1 was reached, followed by further stirring (15 min) at room temperature. 2 M NaOH was added until pH > 10 was reached. Extraction with Et_2O, drying of the combined organic phases over $MgSO_4$, and removal of the solvent under reduced pressure gave the desired product, 4-(pyrrolidin-1-ylmethyl)benzaldehyde (11.9 g, 63 mmol, 91%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C) δ = 9.98 (s, 1H, H1), 7.82 (d, $^{3}J_{HH}$ = 8.2 Hz 2H, H4), 7.49 (d, $^{3}J_{HH}$ = 8.2 Hz 2H, H5), 3.68 (s, 2H, H7), 2.51 (m, 4H, H8), 1.78 (m, 4H, H9).

^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C) δ =192.1 (C2), 147.0 (C6), 135.4 (C3), 129.9 (C4), 129.3 (C5), 60.5 (C7), 54.4 (C8), 23.65 (C9).

1.3. Synthesis of 4-(Bromomethyl)benzaldehyde[5]

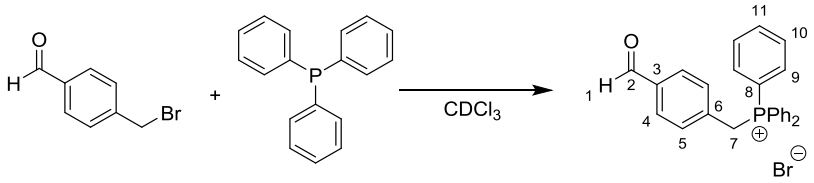


4-(bromomethyl)benzonitrile (5.0 g, 25.2 mmol, 1 equiv.) was dissolved in toluene (50 mL). To this solution was added dropwise at 0 °C DIBALH (5.4 g. 38.3 mmol, 1.5 equiv.) in toluene (50 mL). The reaction mixture was stirred at room temperature for 1 h. 2 M HCl was added until pH < 7 was reached. The reaction mixture was extracted with CH_2Cl_2 and Et_2O (Na-K-tartrate solution was added for improved phase separation). The combined organic phases were washed with brine and H_2O and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product. Purification by extraction in hot hexane gave the desired compound 4-(pyrrolidin-1-ylmethyl)benzaldehyde (3.07 g, 15.4 mmol, 60%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C) δ = 10.02 (s, 1H, H1), 7.87 (d, $^{3}J_{HH}$ = 8.4 Hz 2H, H4), 7.56 (d, $^{3}J_{HH}$ = 8.4 Hz 2H, H5), 4.52 (s, 2H, H7).

^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C) δ =192.1 (C9), 147.0 (C4), 135.4 (C1), 129.9 (C2), 129.3 (C3), 60.5 (C5), 54.4 (C6), 23.65 (C7).

1.4. Synthesis of (4-formylbenzyl)triphenylphosphonium bromide



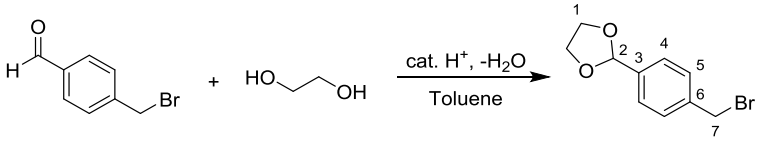
4-(pyrrolidin-1-ylmethyl)benzaldehyde (50 mg, 0.25 mmol, 1 equiv.) was dissolved in 0.6 mL $CDCl_3$. PPh_3 (132 mg, 0.50 mmol, 2 equiv.) was added and the reaction took place over one day at room temperature. The product was precipitated in Et_2O. Centrifugation and purification by subsequent dissolution in CH_2Cl_2 and precipitation in Et_2O (3 times) gave the desired product, (4-formylbenzyl)triphenylphosphonium bromide, in quantitative yield.

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C) δ = 9.84 (s, 1H, H1), 7.84 - 7.66 (m, 9H, H9 and 11), 7.62 - 7.53 (m, 6H, H10), 7.50 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, H4), 7.36 (dd, $^{3}J_{HH}$ = 8.3, $^{4}J_{PH}$ = 2.5 Hz, 2H, H5), 5.76 (d, $^{2}J_{PH}$ = 15.5 Hz, 2H, H7).

^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C) δ = 191.8 (C2), 135.8 (d, $^{5}J_{PC}$ = 3.4 Hz, C3), 135.1 (d, $^{4}J_{PC}$ = 3.2 Hz, C11), 134.8 (d, $^{2}J_{PC}$ = 8.9 Hz, C6), 134.6 (d, $^{2}J_{PC}$ = 9.9 Hz, C9), 132.6 (d, $^{3}J_{PC}$ = 5.5 Hz, C5), 130.2 (d, $^{3}J_{PC}$ = 12.6 Hz, C10), 129.7 (d, $^{4}J_{PC}$ = 3.4 Hz, C4), 117.6 (d, $^{1}J_{PC}$ = 86.0 Hz, C8), 30.3 (d, $^{1}J_{PC}$ = 46.5 Hz, C7).

^{31}P-NMR (162 MHz, $CDCl_3$, 27 °C) δ = 23.9 (s).

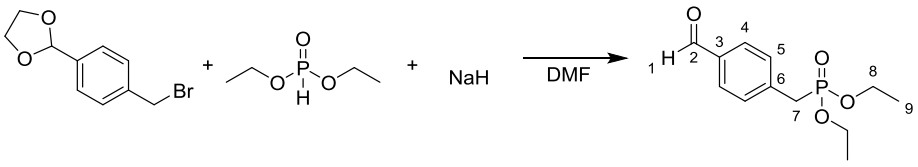
1.5. SYNTHESIS OF 2-(4-(BROMOMETHYL)PHENYL)-1,3-DIOXOLANE



In analogy to Lemcoff *et al.*:[6] 4-(pyrrolidin-1-ylmethyl)benzaldehyde (1.0 g, 5 mmol, 1 equiv.) and ethylene glycol (620 mg, 10 mmol, 2 equiv.) were dissolved in toluene (40 mL). After the addition of *p*-toluenesulfonic acid (small amount, catalytic), the reaction mixture was heated to reflux for 3 h and water was removed using a Dean-Stark apparatus. Extraction with Et_2O/aqueous $NaHCO_3$, drying of the combined organic phases and removal of the solvent gave the desired product, 2-(4-(bromomethyl)phenyl)-1,3-dioxolane (800 mg, 3.3 mmol, 66%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C) δ = 7.46 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, H4), 7.41 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, H5), 5.81 (s, 1H, H2), 4.49 (s, 2H, H7), 4.15 - 3.97 (m, 4H, H1).

1.6. SYNTHESIS OF DIETHYL (4-FORMYLBENZYL)PHOSPHONATE



NaH (17.7 mg, 0.74 mmol, 1 equiv.) and diethyl phosphonate (102.2 mg, 0.74 mmol, 1 equiv.) were stirred in DMF (1.5 mL) for 2 h at room temperature. 2-(4-(bromomethyl)phenyl)-1,3-dioxolane (182 mg, 0.75 mmol, 1.02 equiv.) was added in 1 mL DMF to this mixture which was stirred for another 2 h at room temperature. Aqueous acidic work-up and extraction with CH_2Cl_2/Et_2O gave the title compound, diethyl (4-formylbenzyl)phosphonate (144 mg, 0.56 mmol, 75%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C) δ = 10.02 (s, 1H, H1), 7.86 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, H4), 7.50 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{PH}$ = 2.4 Hz, 2H, H5), 4.06 (dq, $^{3}J_{PH}$ = 9.8, $^{3}J_{HH}$ = 7.1, 4H, H8), 3.25 (d, $^{2}J_{PH}$ = 22.4 Hz, 2H, H7), 1.27 (t, $^{3}J_{HH}$ = 7.1, 6H, H9).

^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C) δ 191.7 (d, $^{6}J_{PC}$ = 1.6 Hz, C2), 138.9 (d, $^{2}J_{PC}$ = 9.3 Hz, C6), 135.0 (d, $^{5}J_{PC}$ = 3.4 Hz, C3), 130.4 (d, $^{3}J_{PC}$ = 6.5 Hz, C5), 129.7 (d, $^{4}J_{PC}$ = 3.1 Hz, C4), 62.2 (d, $^{2}J_{PC}$ = 6.8 Hz, C8), 34.0 (d, $^{1}J_{PC}$ = 137.3 Hz, C7), 16.2 (d, $^{3}J_{PC}$ = 5.9 Hz, C9).

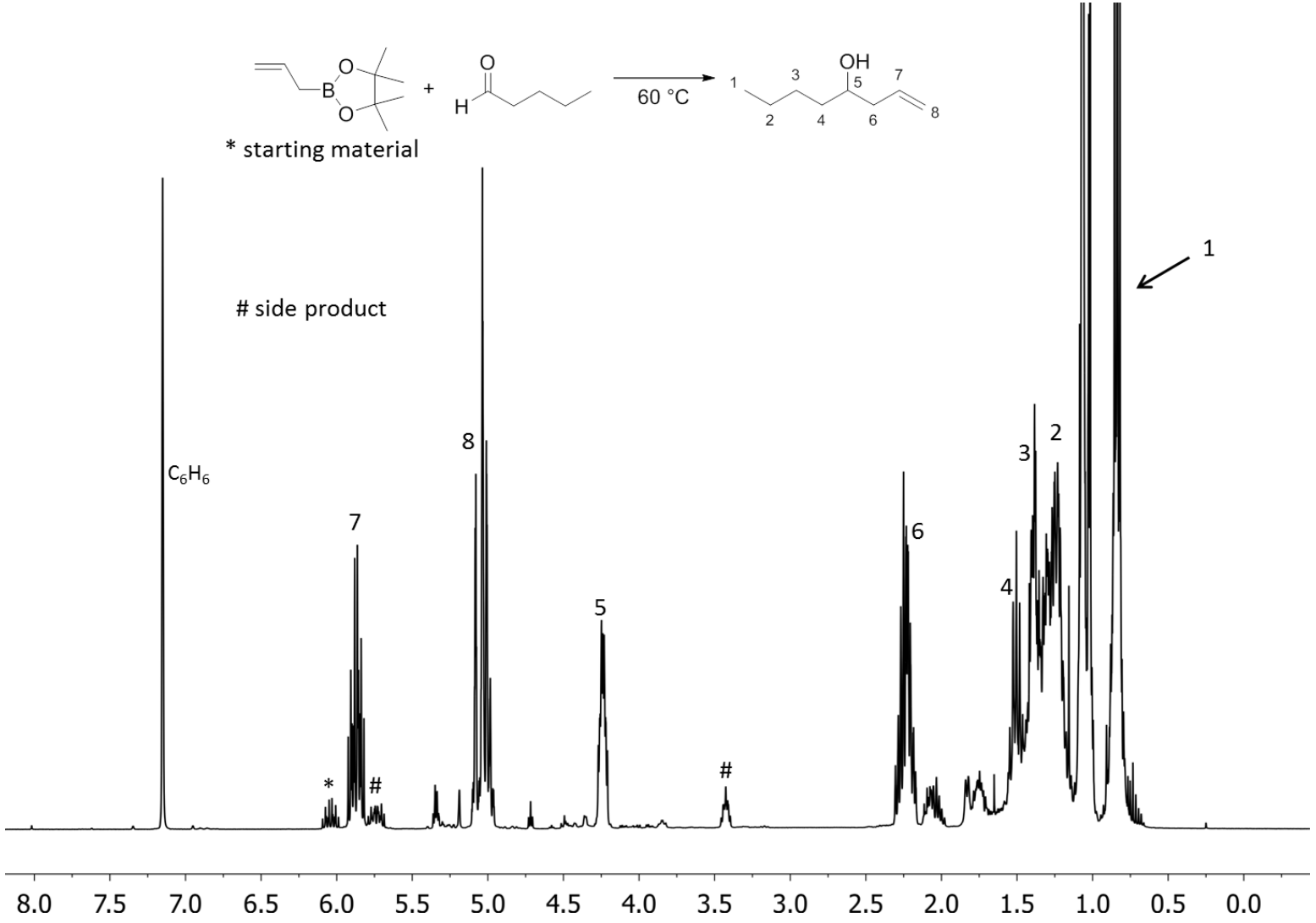
^{31}P-NMR (162 MHz, $CDCl_3$, 27 °C) δ = 24.8 (s).

2. NMR Spectra of Model Reactions of Allylboronic Acid Pinacol Ester with Different Aldehydes

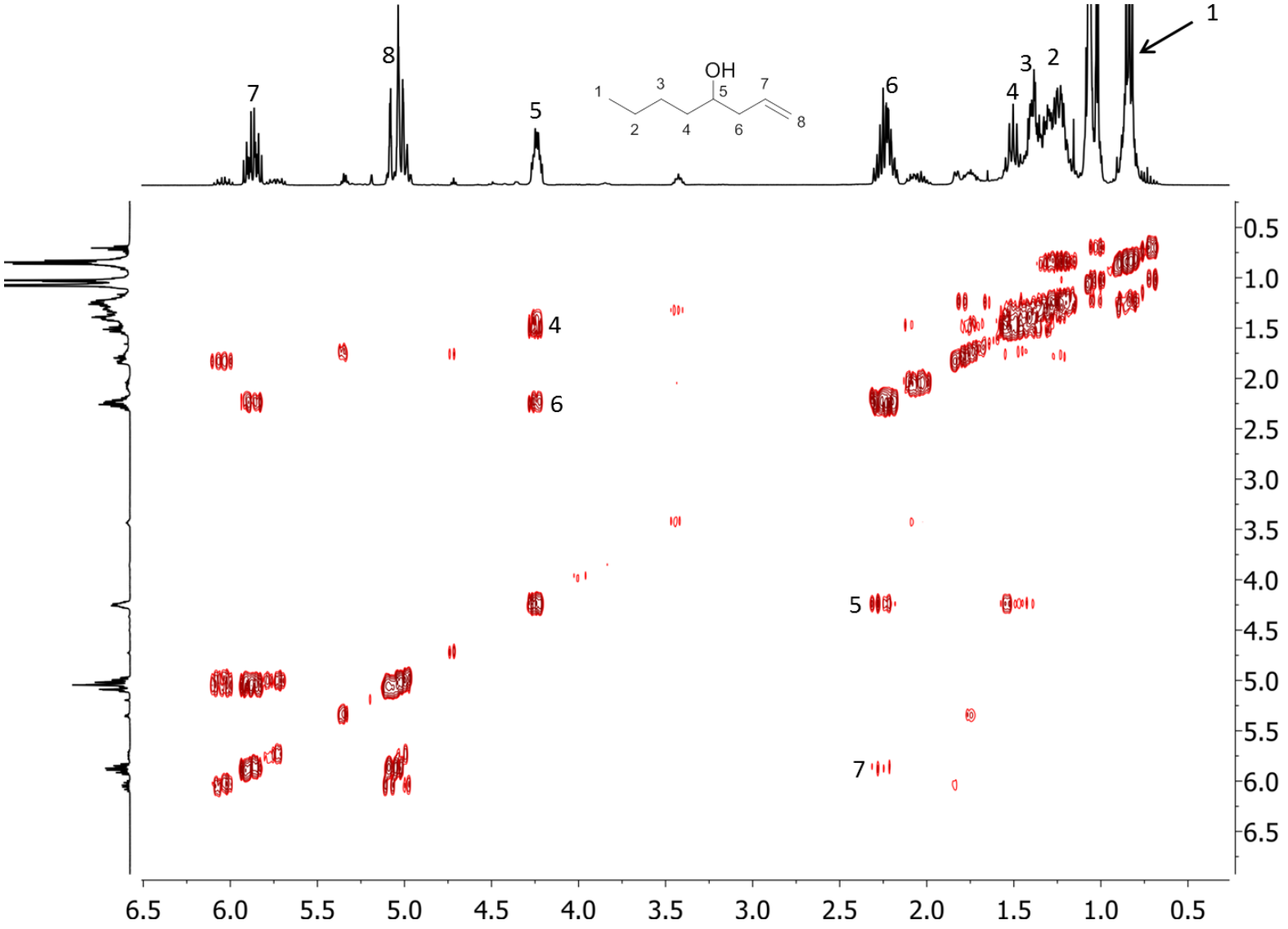
2.1. General Procedure

1 equivalent of allylboronic acid pinacol ester (typically 0.25 mmol) was dissolved in C_6D_6 and 1 to 1.5 equivalents of the aldehyde was added. The reaction mixture was kept at room temperature or heated to 60 °C and followed by NMR-spectroscopy. Spectra were recorded from crude reaction mixtures.

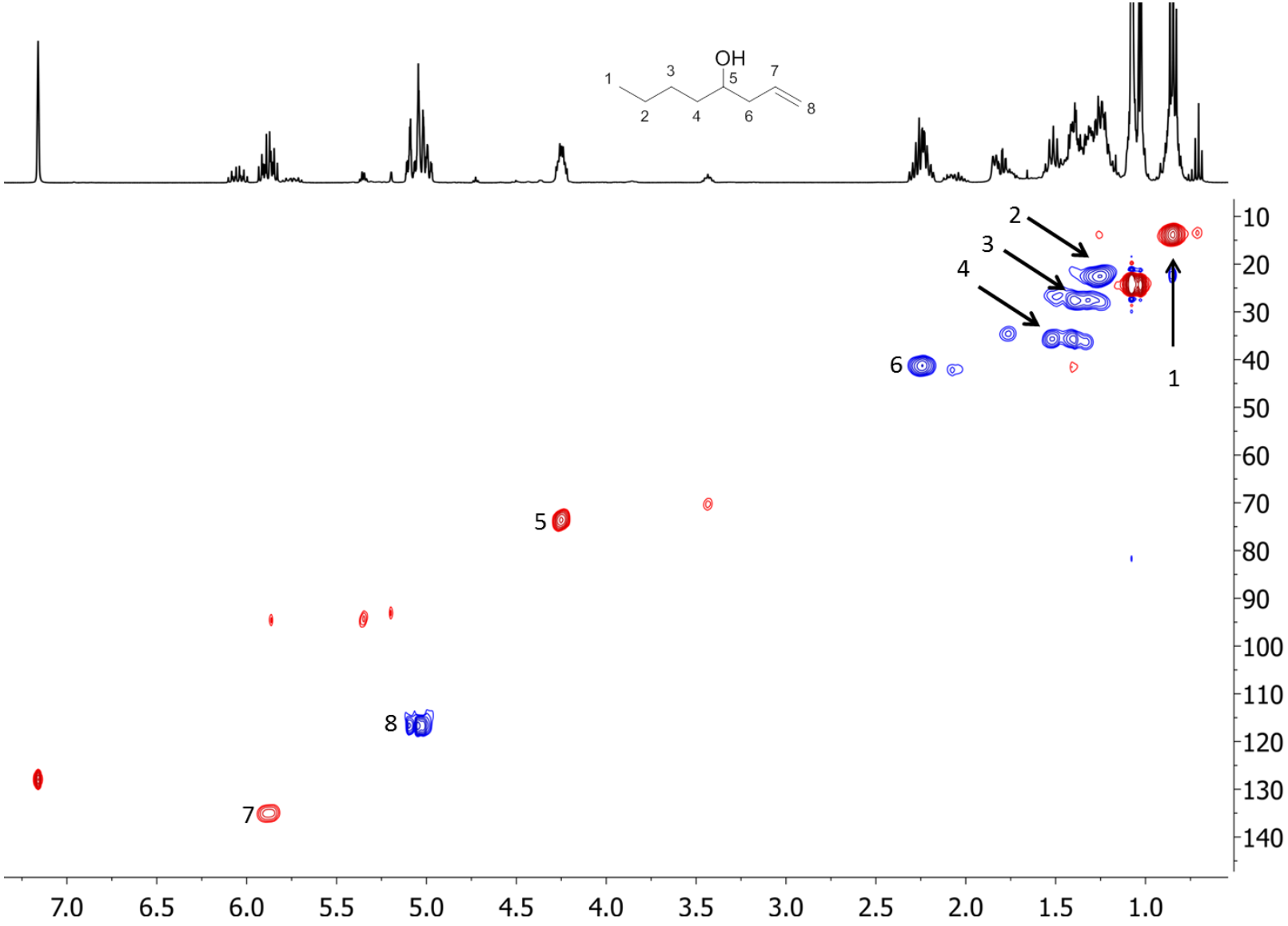
2.2. Reaction of Allylboronic Acid Pinacol Ester with Pentanal



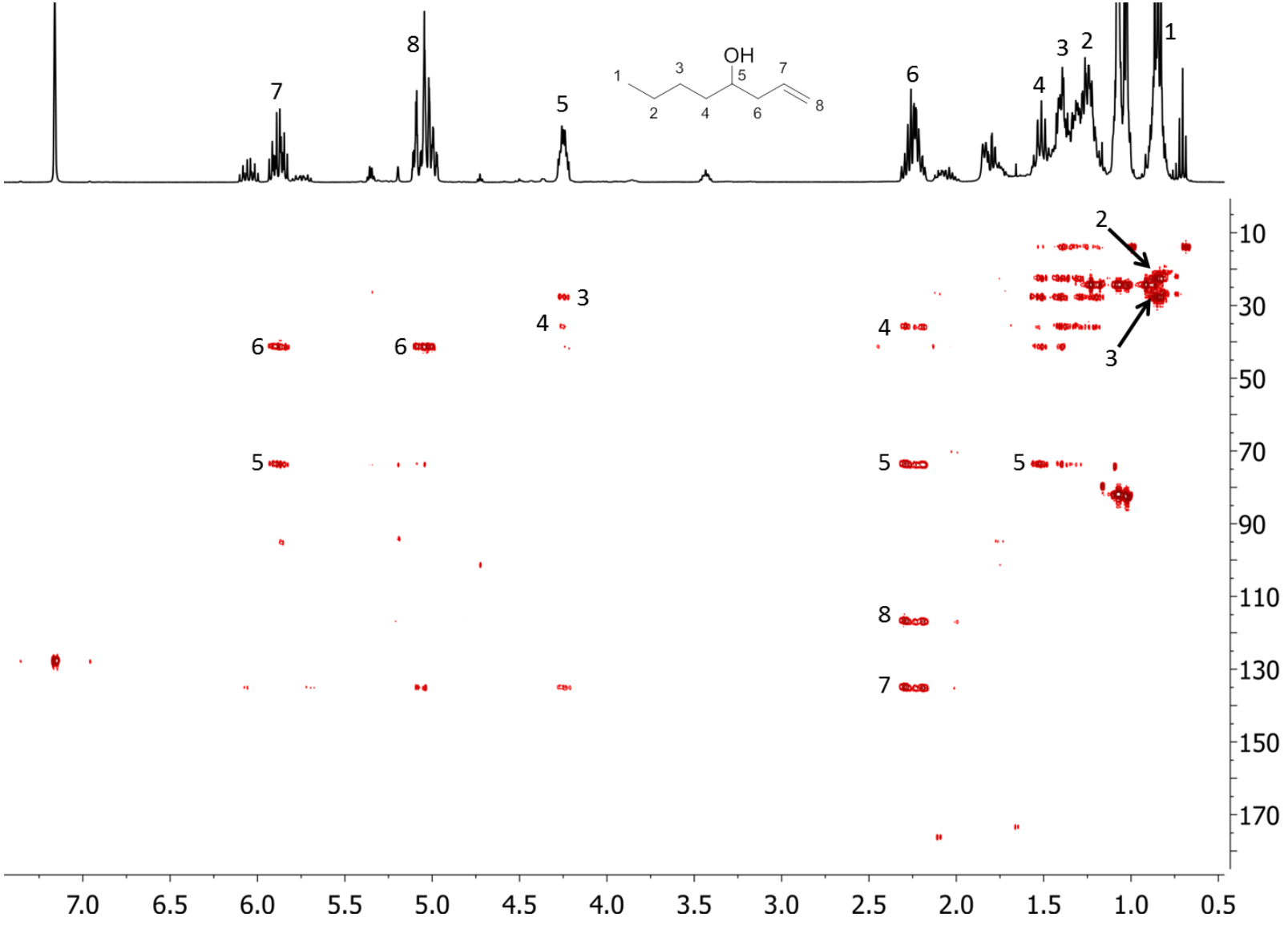
SI 1: ^{1}H NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and pentanal after 24 h at 60 °C (recorded at 27 °C in C_6D_6).



SI 2: COSY NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and pentanal after 5 h at room temperature (recorded at 27 °C in C_6D_6).h

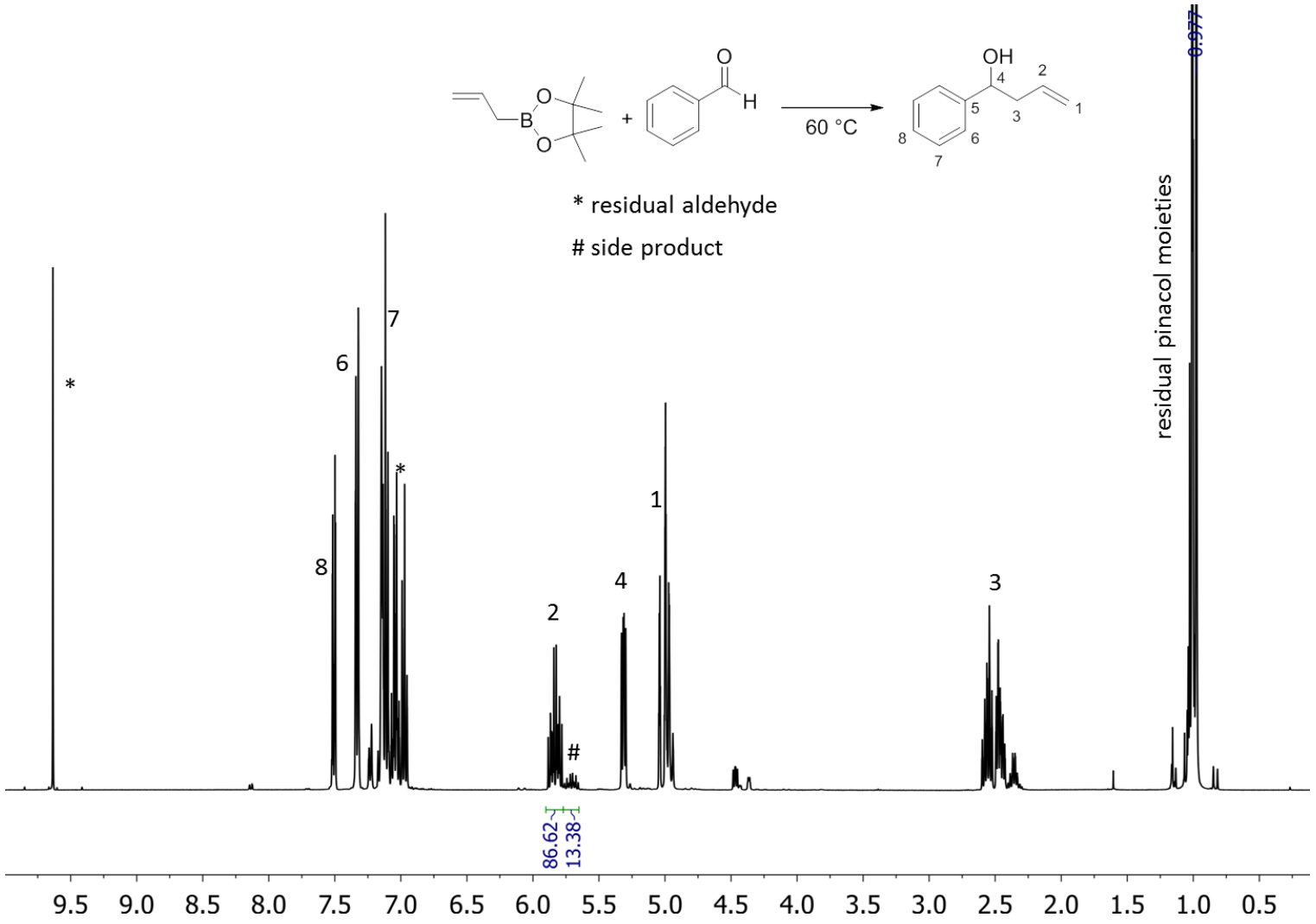


SI 3: HSQC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and pentanal after 5 h at room temperature (recorded at 27 °C in C_6D_6).

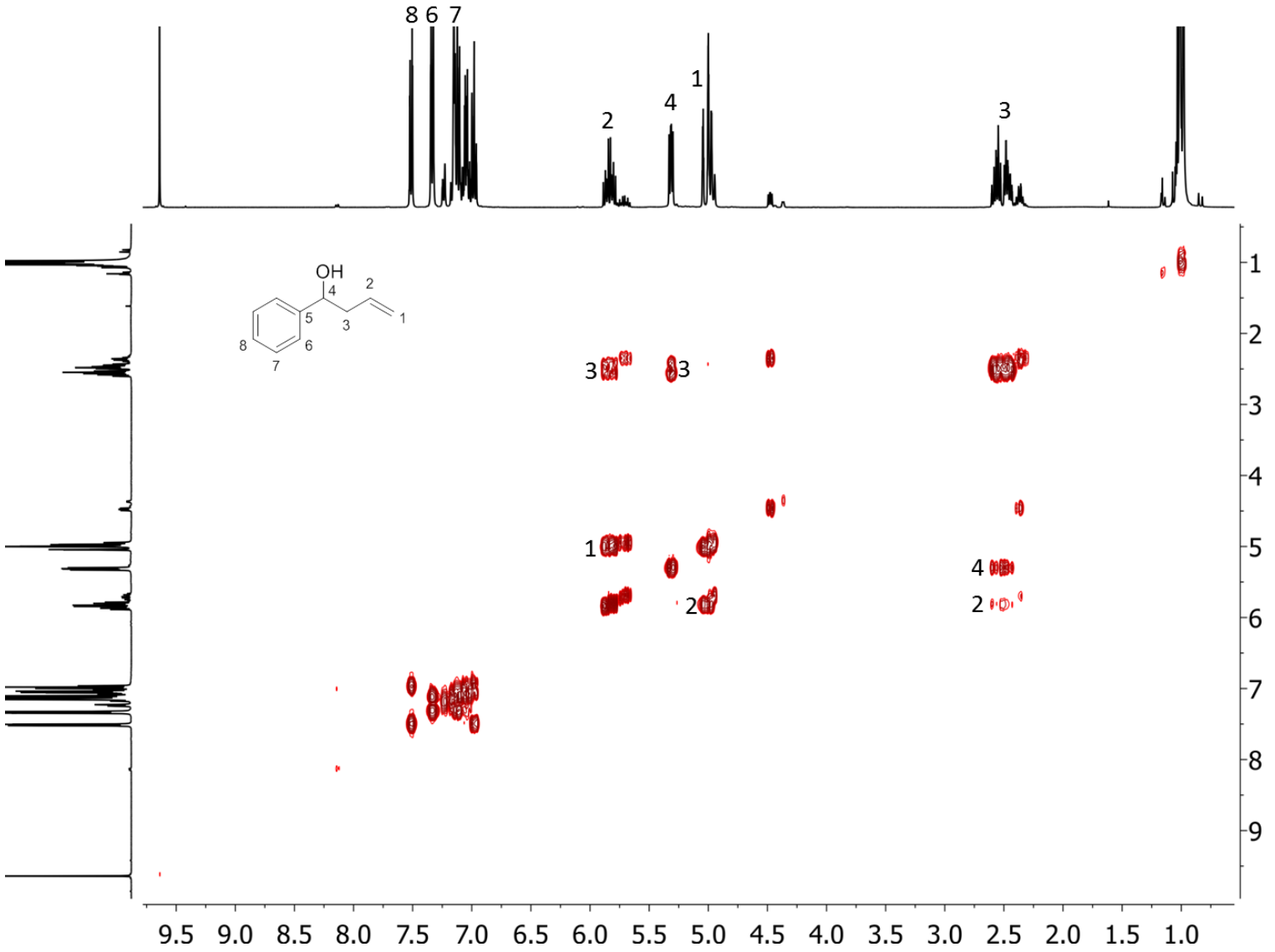


SI 4: HMBC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and pentanal after 5 h at room temperature (recorded at 27 °C in C_6D_6).

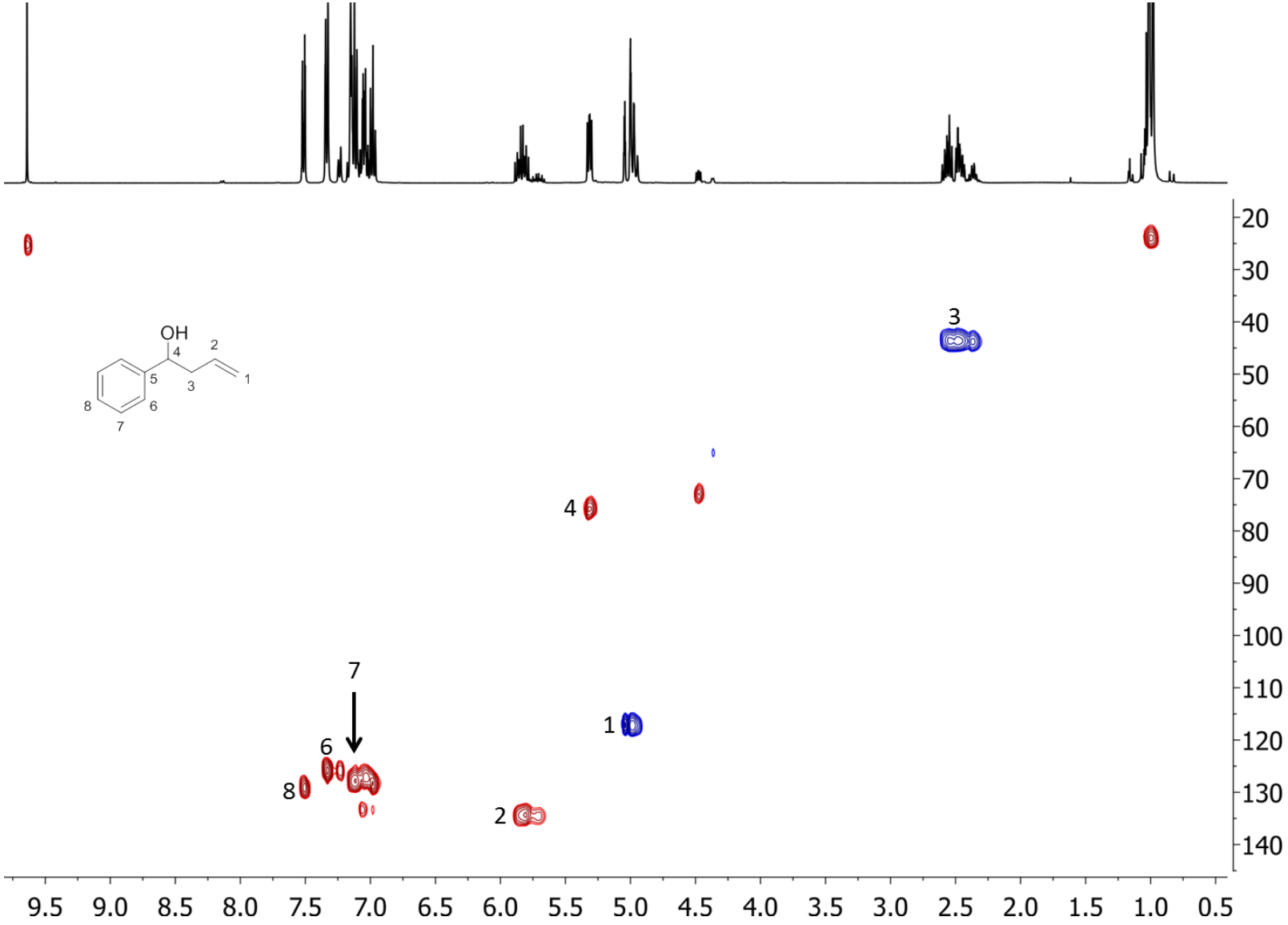
2.3. Reaction of Allylboronic Acid Pinacol Ester with Benzaldehyde



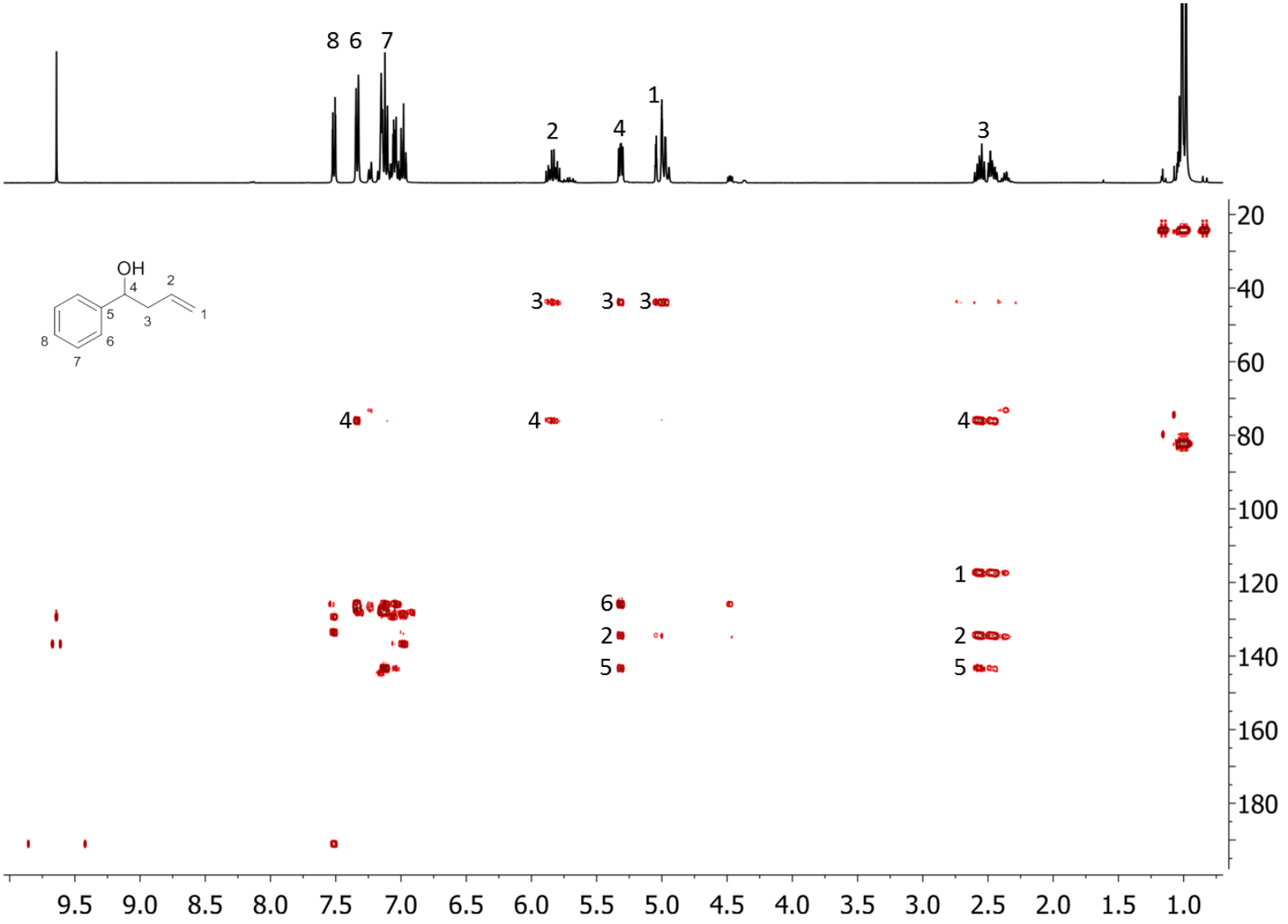
SI 5: ^{1}H NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and benzaldehyde after 12 h at 60 °C (recorded at 27 °C in C_6D_6).



SI 6: COSY NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and benzaldehyde after 12 h at 60 °C (recorded at 27 °C in C_6D_6).

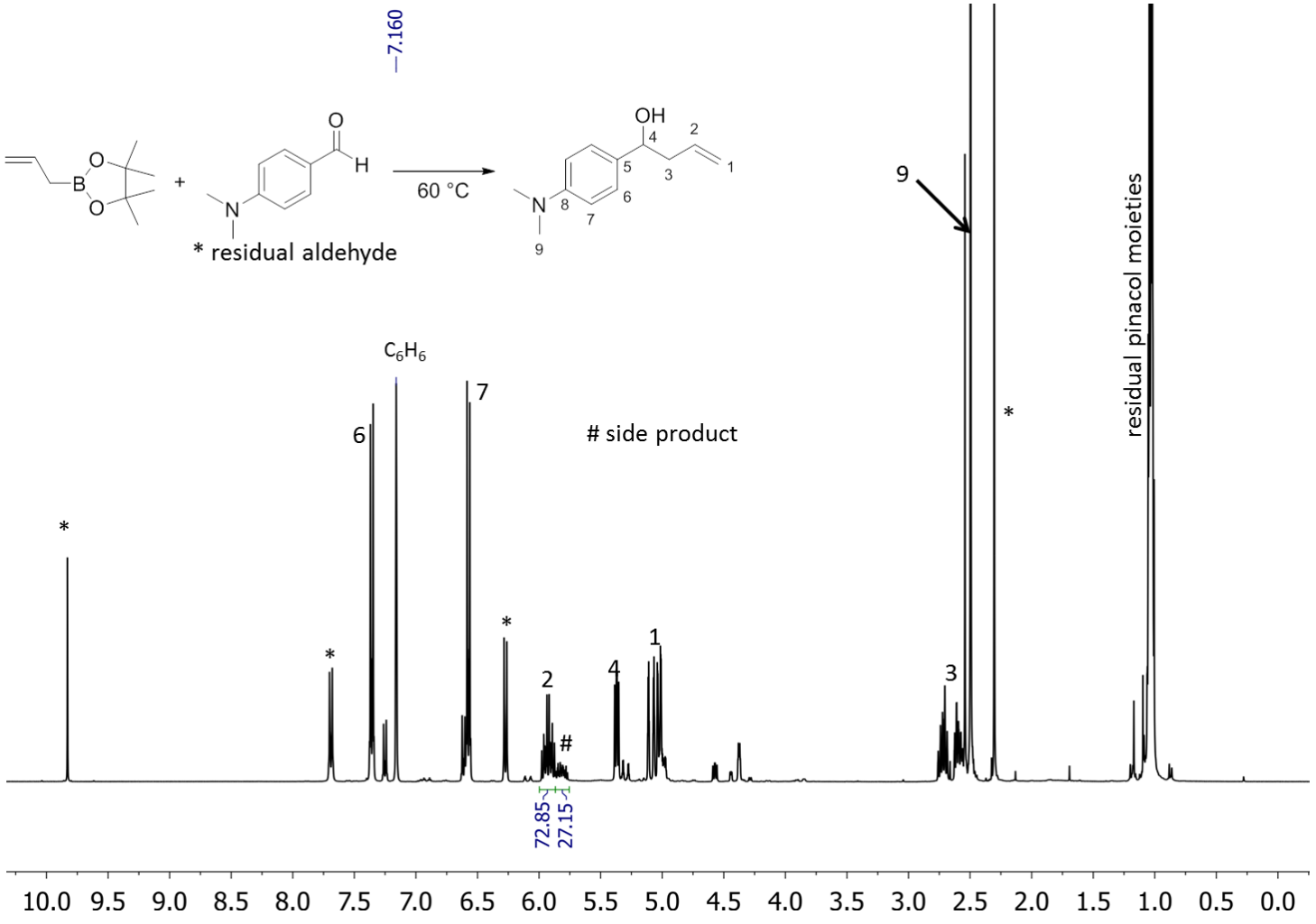


SI 7: HSQC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and benzaldehyde after 12 h at 60 °C (recorded at 27 °C in C_6D_6).

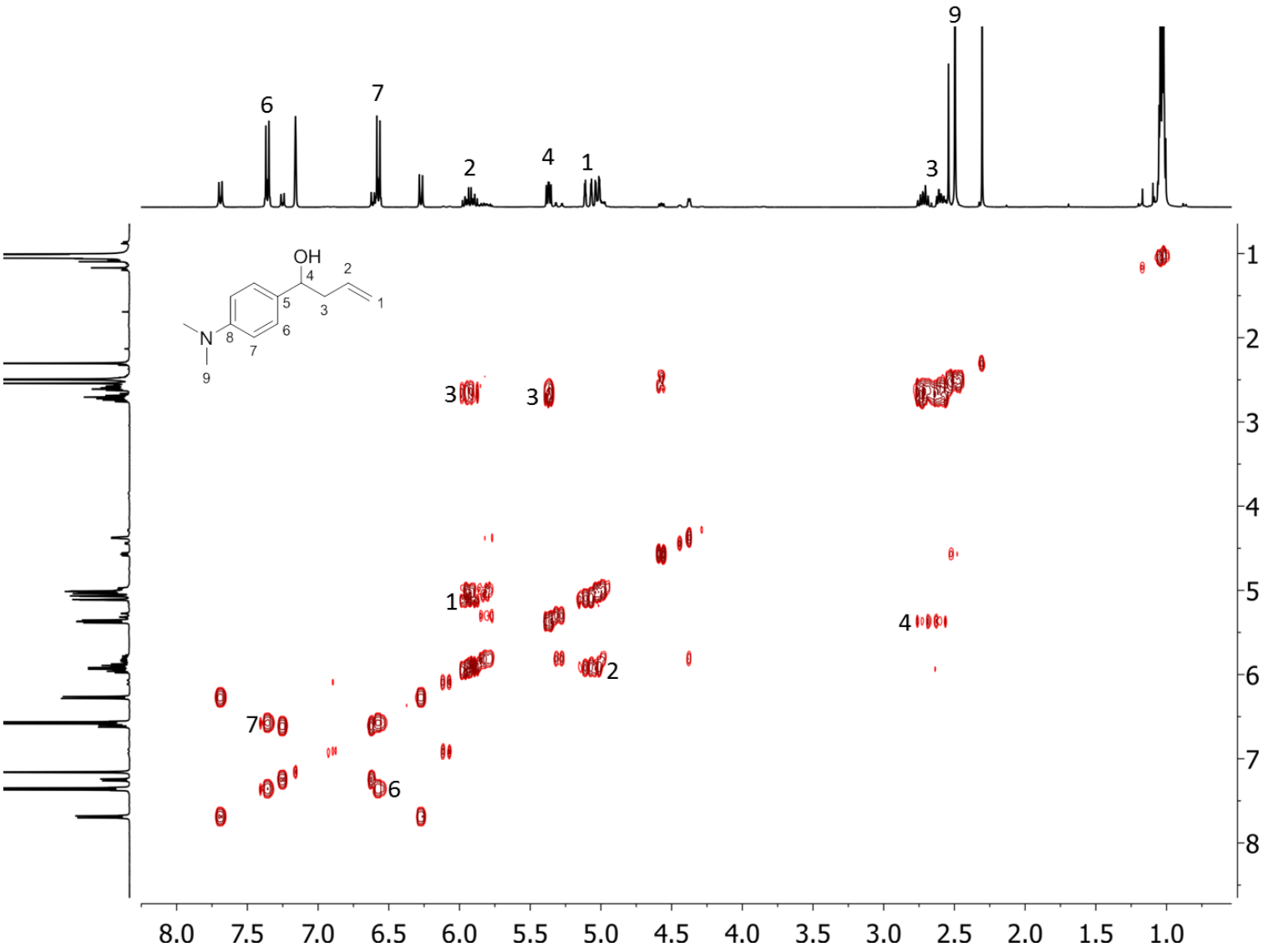


SI 8: HMBC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and benzaldehyde after 12 h at 60 °C (recorded at 27 °C in C_6D_6).

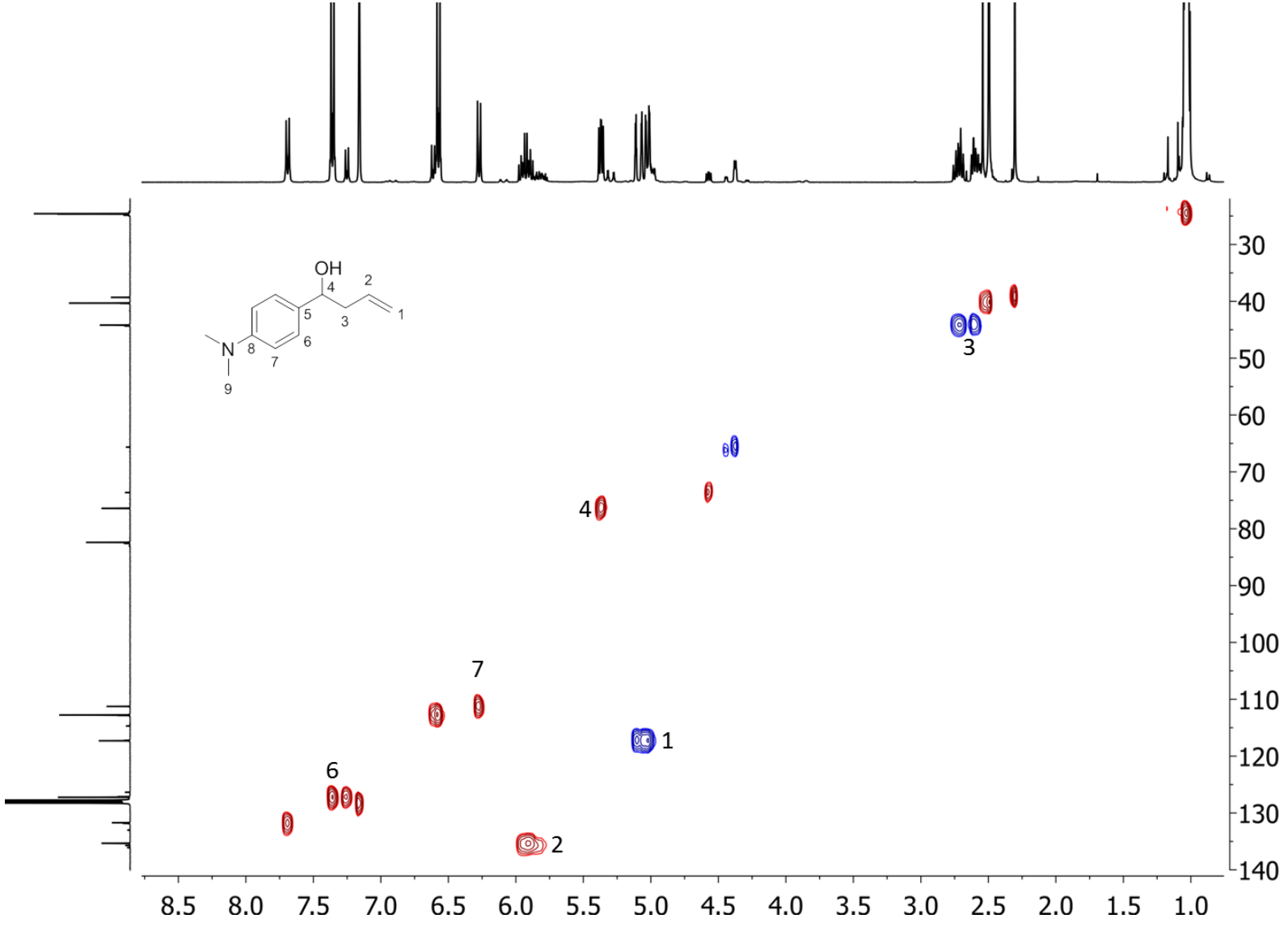
2.4. Reaction of Allylboronic Acid Pinacol Ester with *p*-Dimethylaminobenzaldehyde



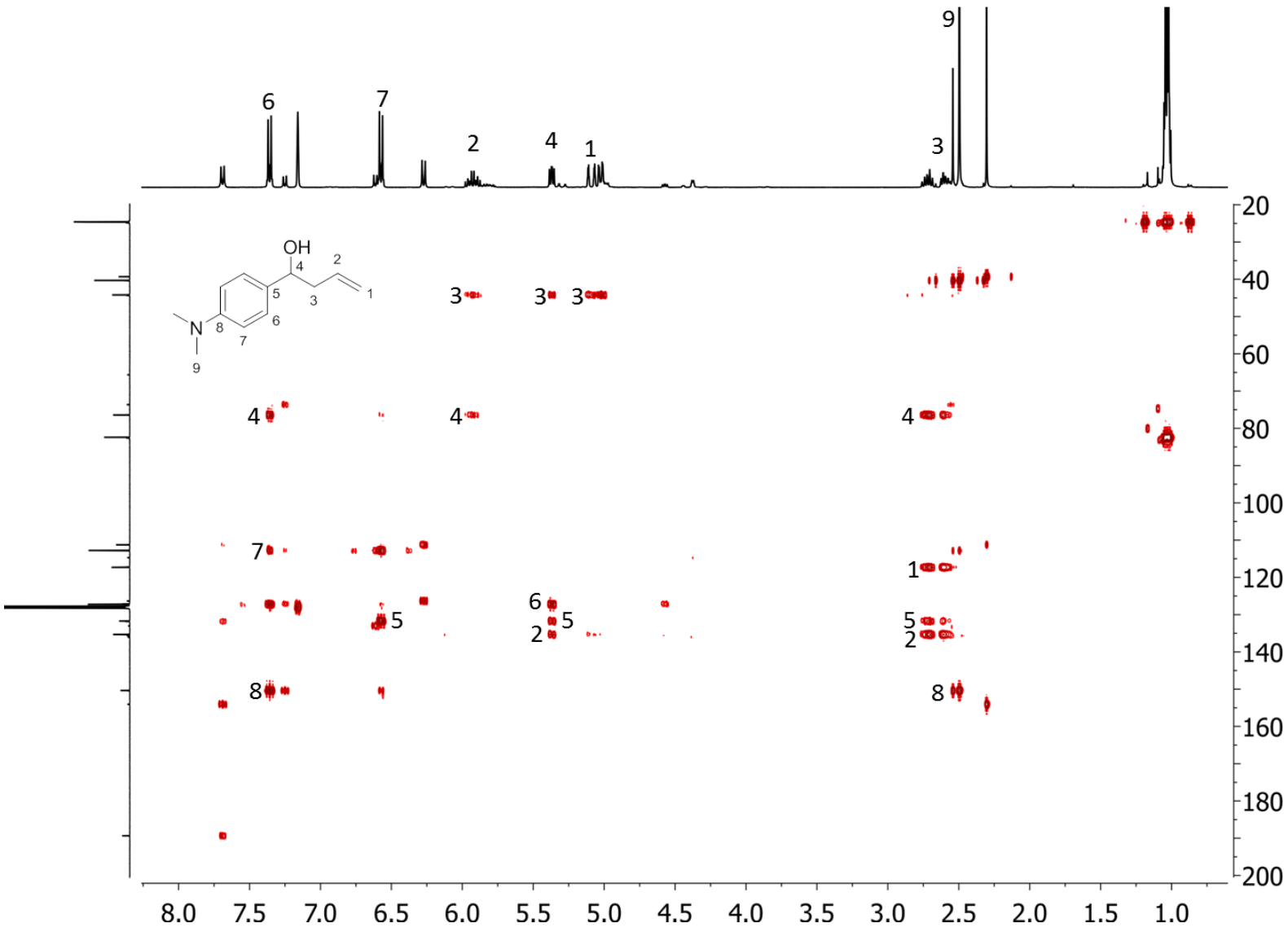
SI 9: ^{1}H NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-dimethylaminobenzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).



SI 10: COSY NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-dimethylaminobenzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

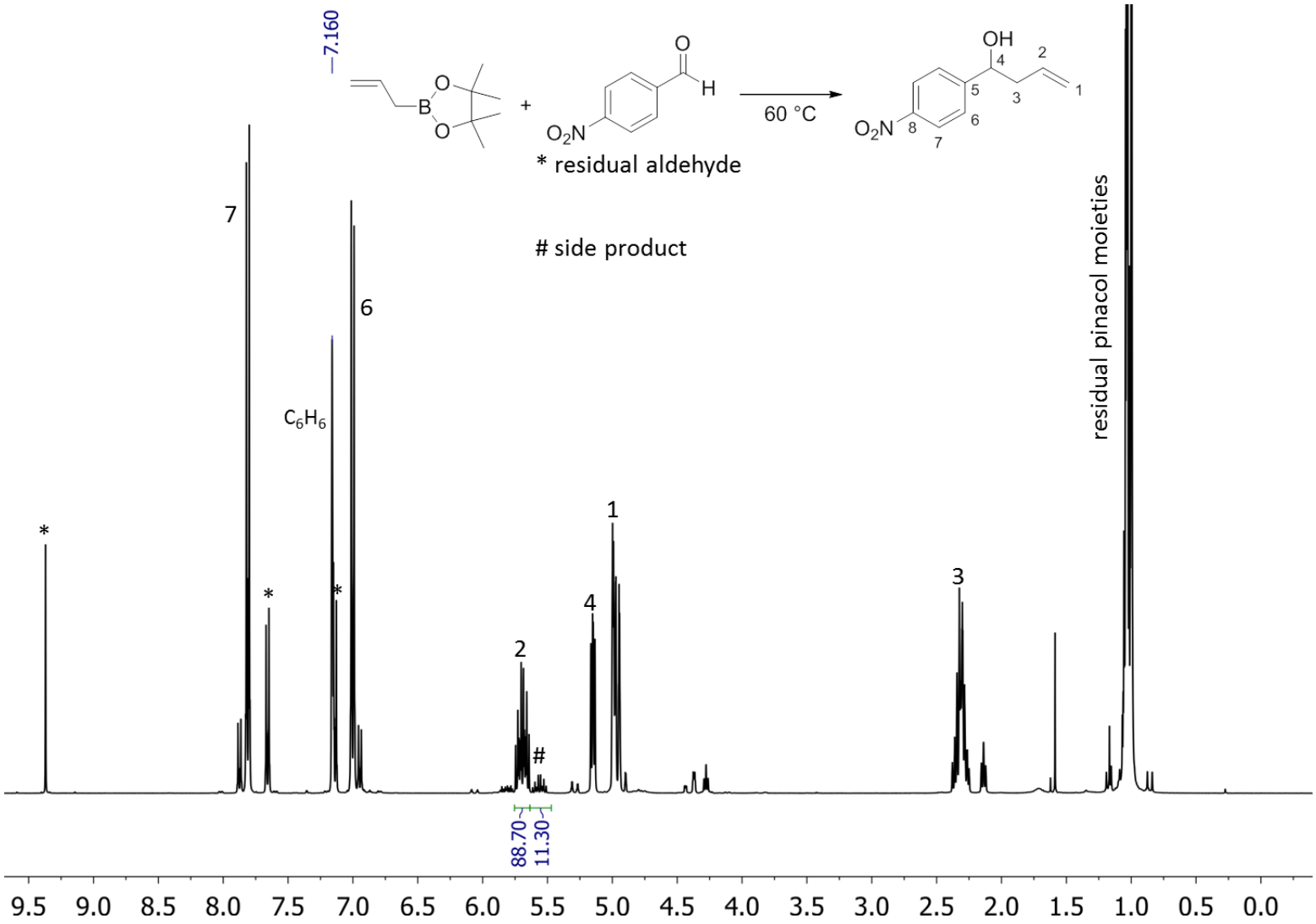


SI 11: HSQC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-dimethylaminobenzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

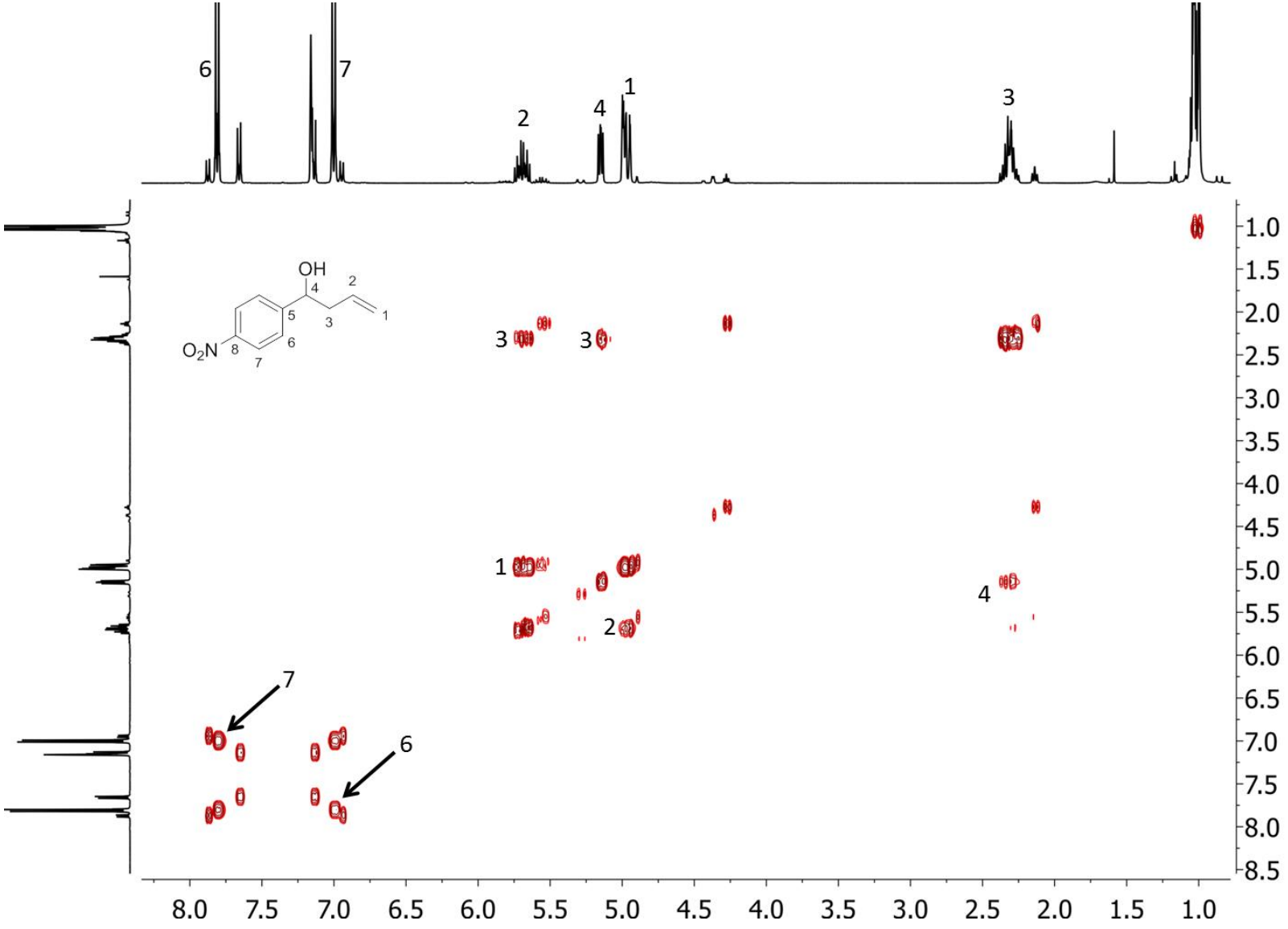


SI 12: HMBC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-dimethylaminobenzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

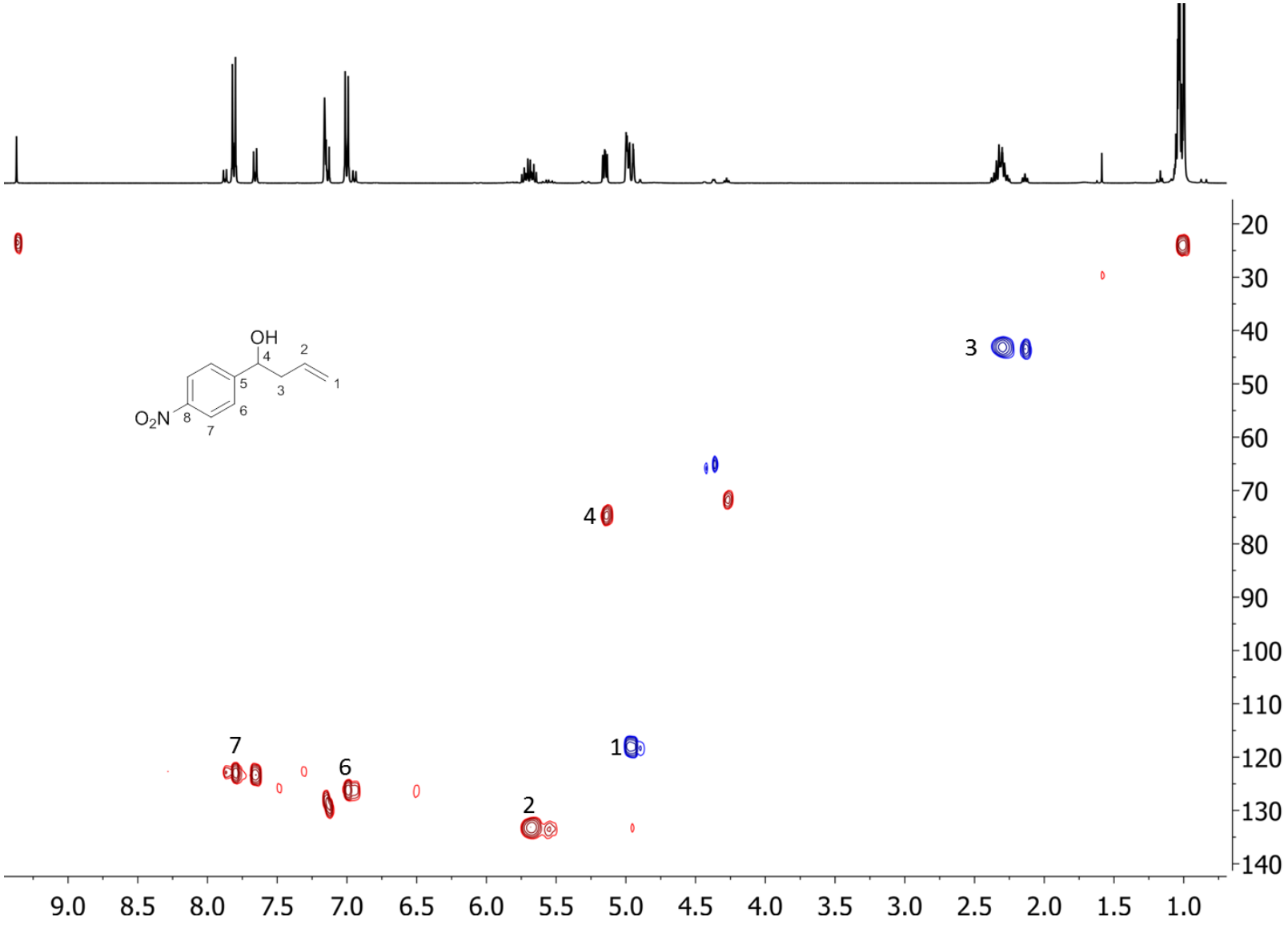
2.5. Reaction of Allylboronic Acid Pinacol Ester with *p*-NO_2-Benzaldehyde



SI 13: ^{1}H NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-NO_2-benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

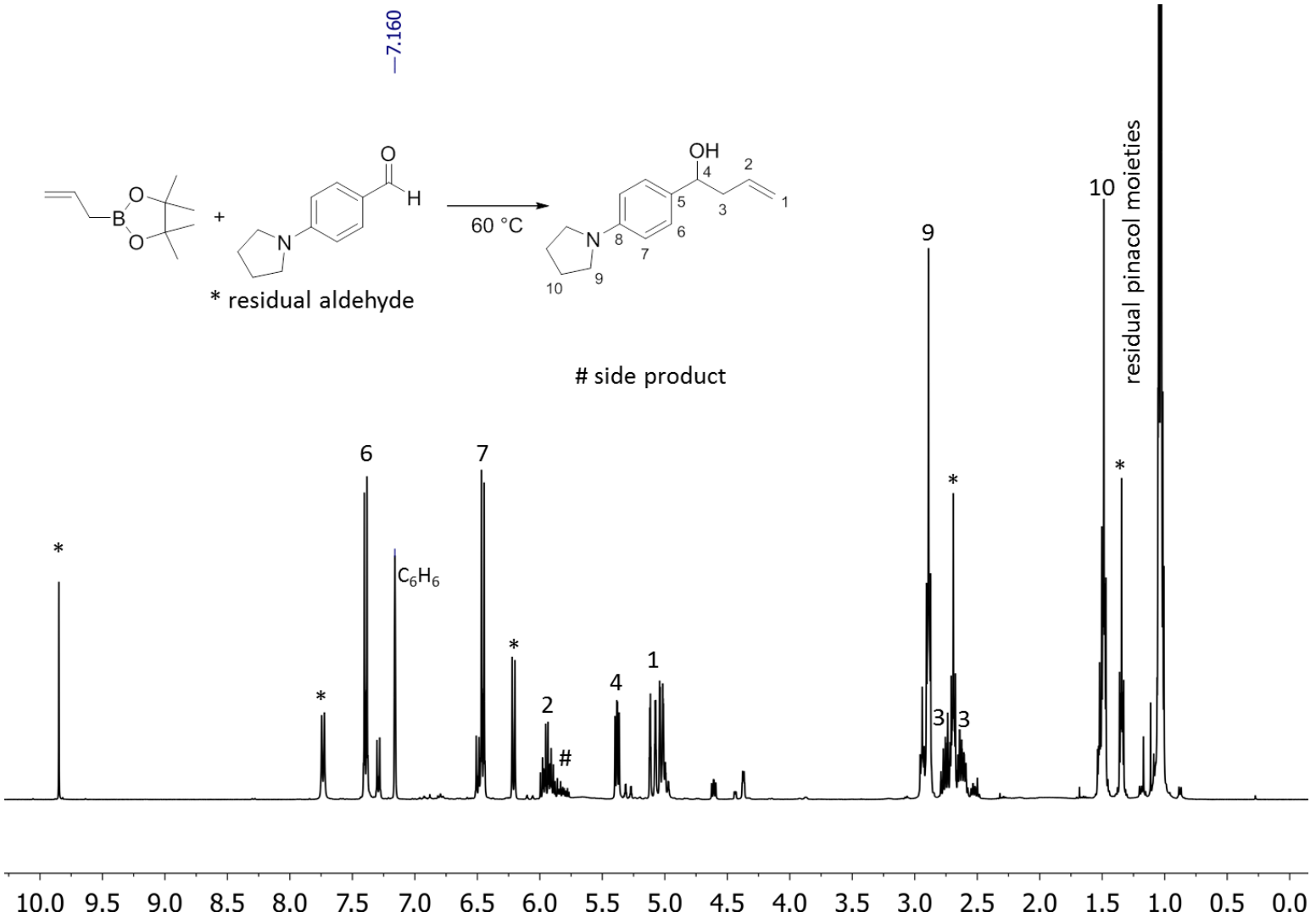


SI 14: COSY NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-NO_2-benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

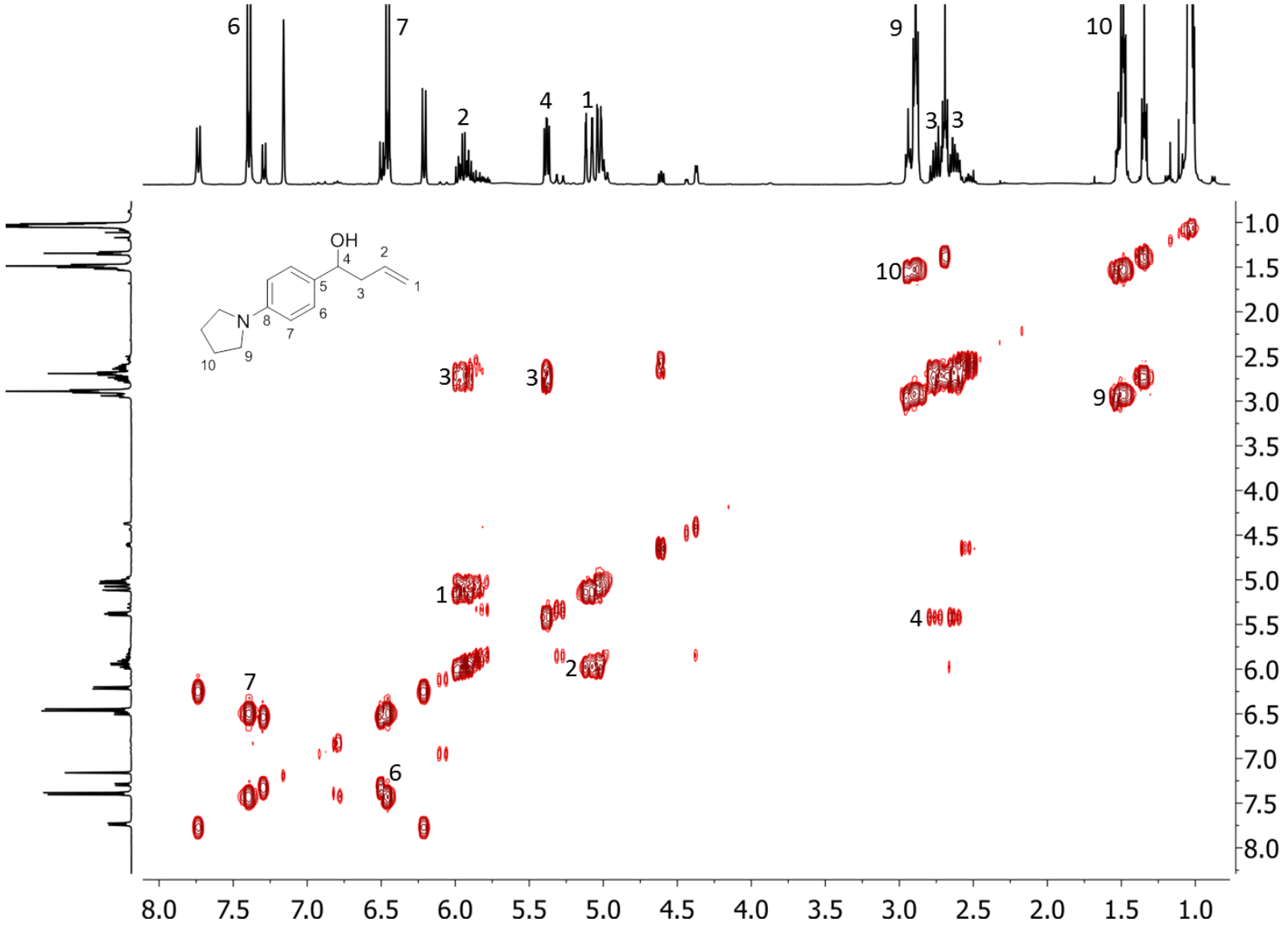


SI 15: HSQC NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and *p*-NO_2-benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

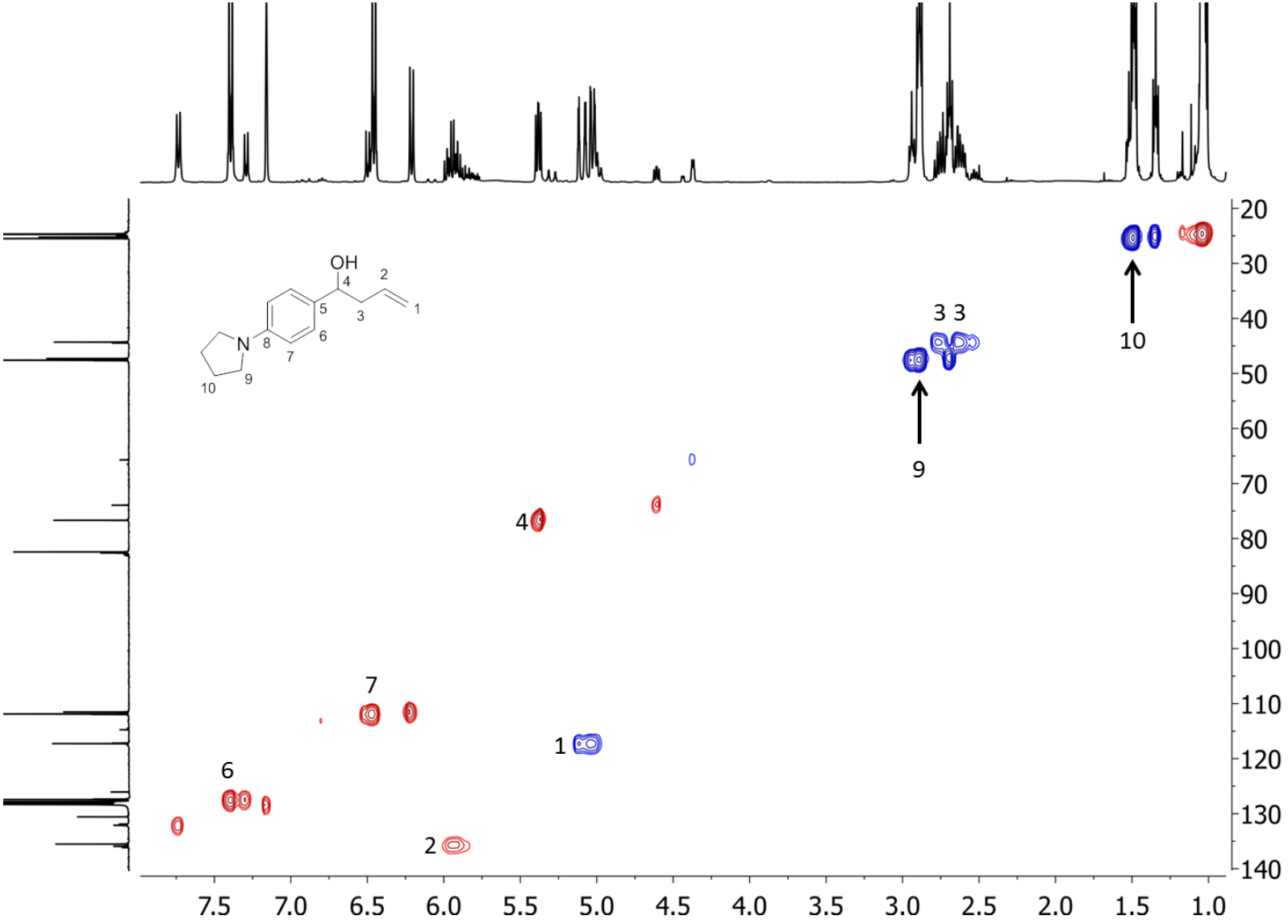
2.6. Reaction of Allylboronic Acid Pinacol Ester with 4-(1-Pyrrolidinyl)benzaldehyde



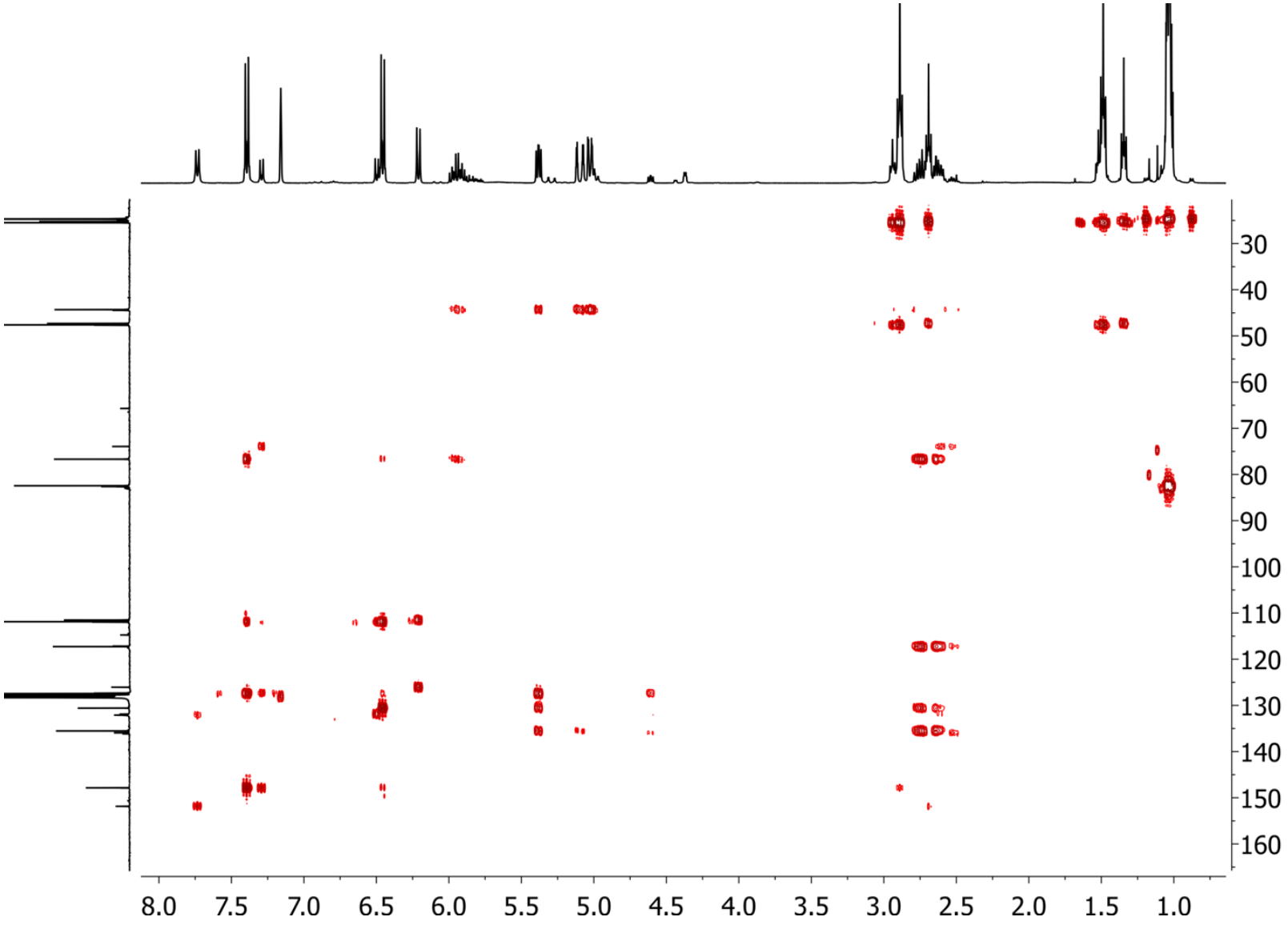
SI 16: ^{1}H NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and 4-(1-pyrrolidinyl)benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).



SI 17: COSY NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and 4-(1-pyrrolidinyl)benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).



SI 18: NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and 4-(1-pyrrolidinyl)benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).



SI 19: NMR-spectrum of the crude reaction mixture of allylboronic acid pinacol ester and 4-(1-pyrrolidinyl)benzaldehyde after 24 h at 60 °C (recorded at 27 °C in C_6D_6).

3. NMR-Spectra of Copolymers Functionalized by Allylboration

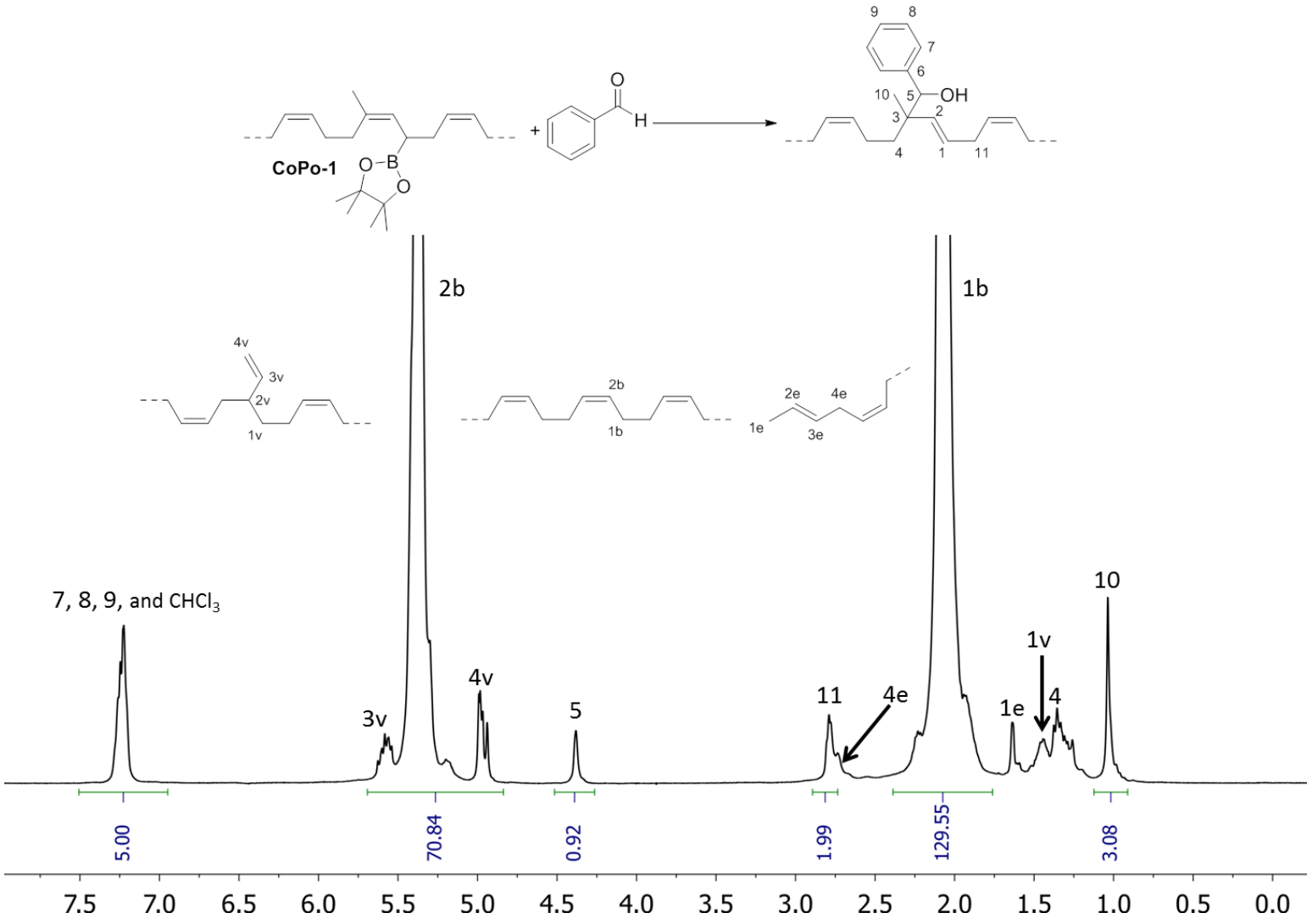
3.1. General Procedure for an Allylboration Reaction with Isolated Copolymer

CoPo-1 (500 mg, 2.5 - 3.5 mol% incorporation of allylboronic acid pinacol ester groups) was dissolved in toluene (5 mL). The used aldehyde (around 10 equiv. compared to the allylboronic acid pinacol ester functionality of the polymer) was added and the mixture was stirred at 60 °C for 2 days. The polymer was purified by precipitation in MeOH. Dissolution in toluene and precipitation in MeOH was repeated two times. The obtained polymer was dried under reduced pressure.

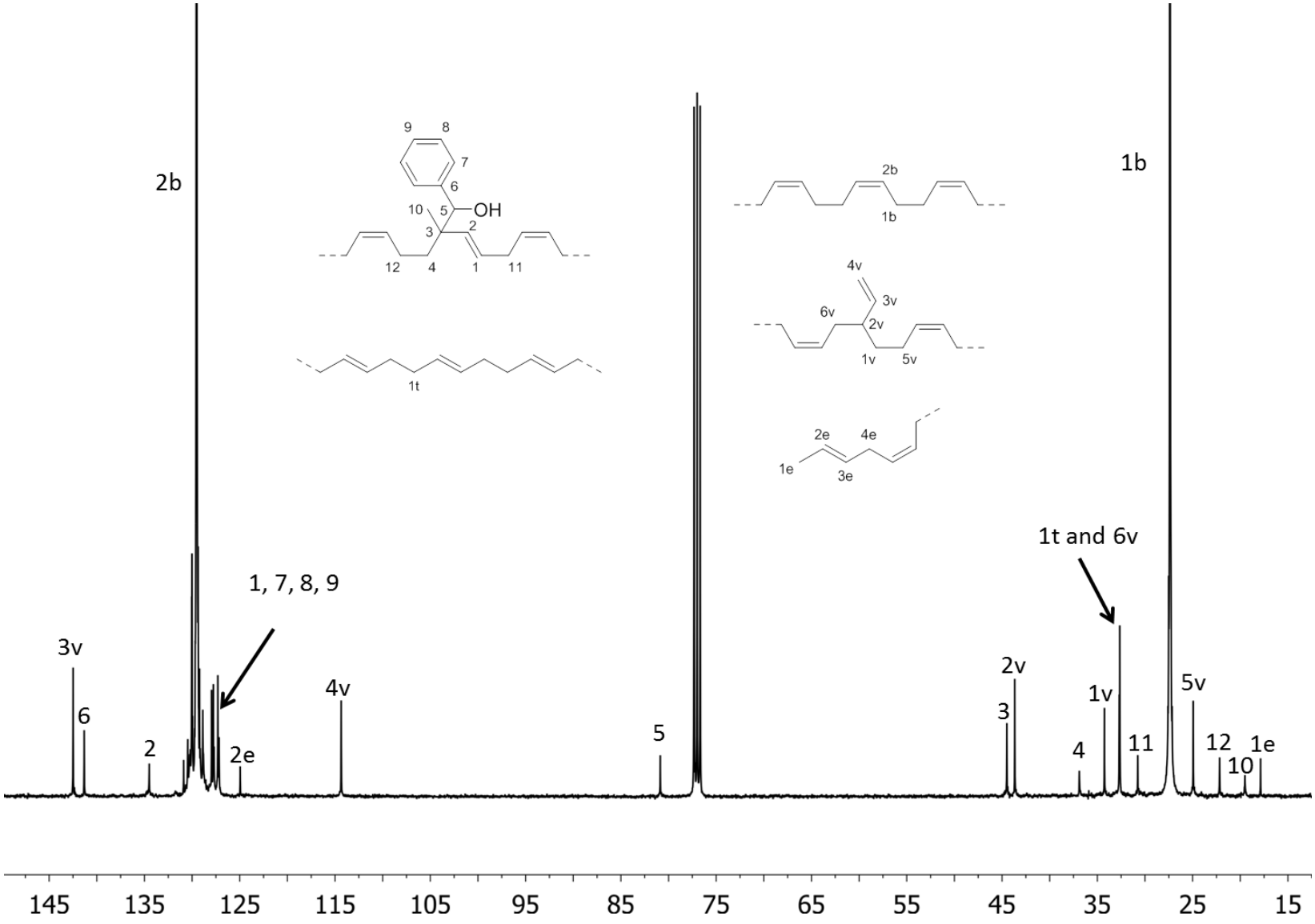
3.2. General Procedure for an Allylboration Reaction with Isolated Copolymer on NMR-scale

CoPo-1 (70 mg, 2.5 -3.5 mol% incorporation of allylboronic acid pinacol ester groups) was dissolved in C_6D_6 (0.6 mL). The used aldehyde (for different applied equivalents cf. Table 1) was added and the mixture was kept at 60 °C until complete conversion was observed by means of ^{1}H-NMR. Characterization of the polymers was performed using the crude reaction mixture or the precipitated polymer.

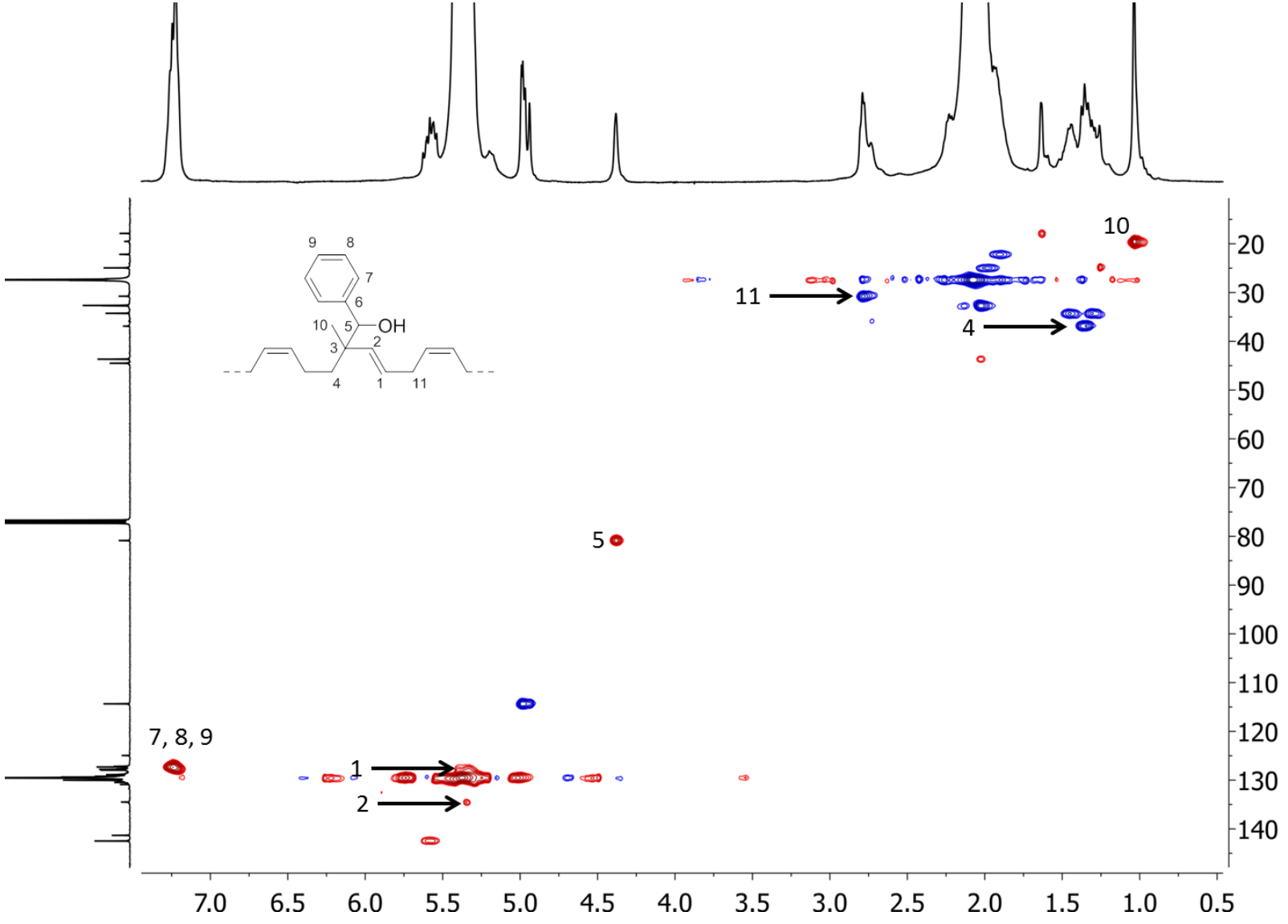
3.3. NMR-Spectra of PBD Functionalized with Benzaldehyde



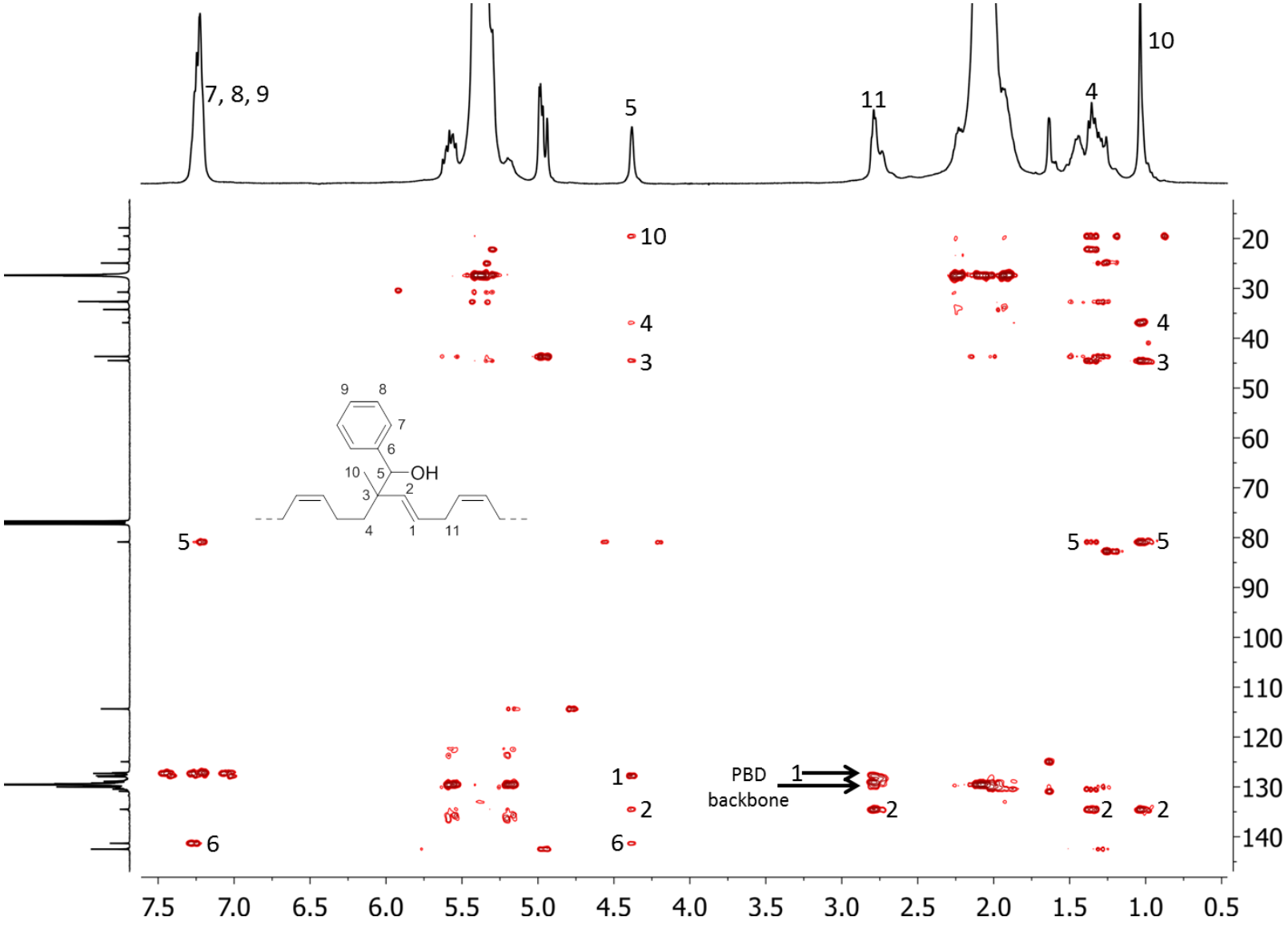
SI 20: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with benzaldehyde (recorded at 27 °C in $CDCl_3$).



SI 21: ^{13}C NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with benzaldehyde (recorded at 27 °C in $CDCl_3$).

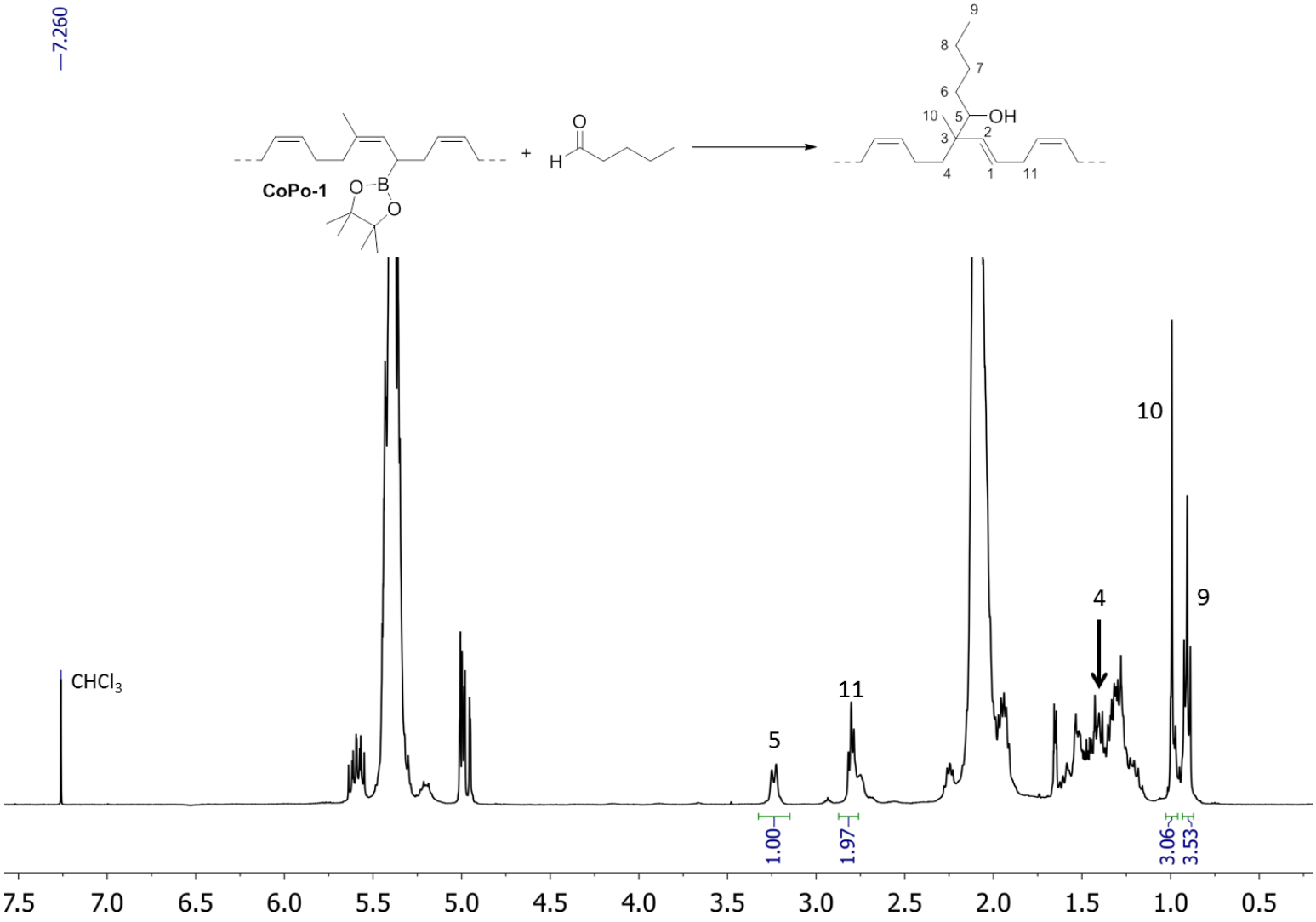


SI 22: HSQC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with benzaldehyde (recorded at 27 °C in $CDCl_3$).

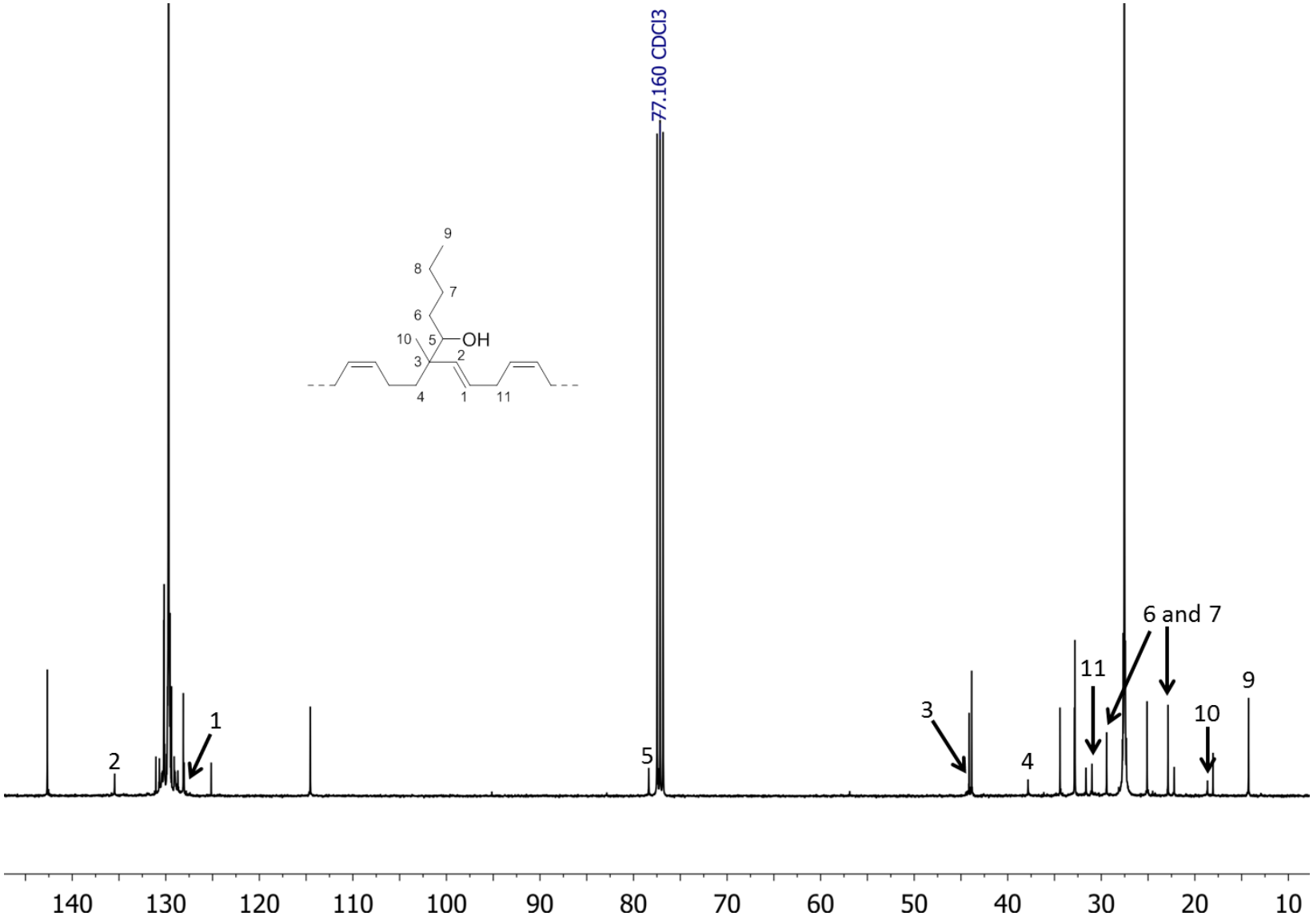


SI 23: HMBC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with benzaldehyde (recorded at 27 °C in $CDCl_3$).

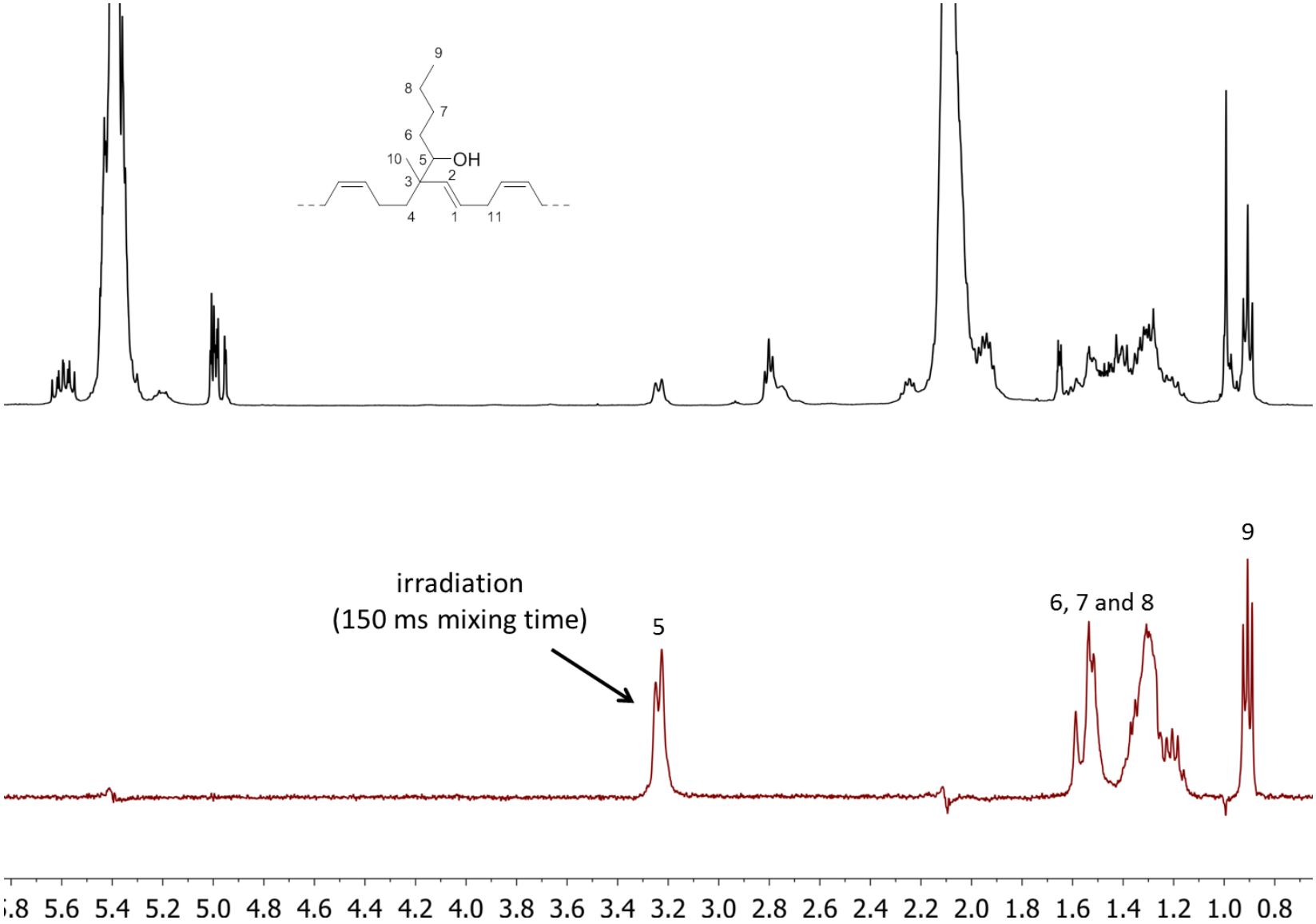
3.4. NMR-Spectra of PBD Functionalized with Pentanal



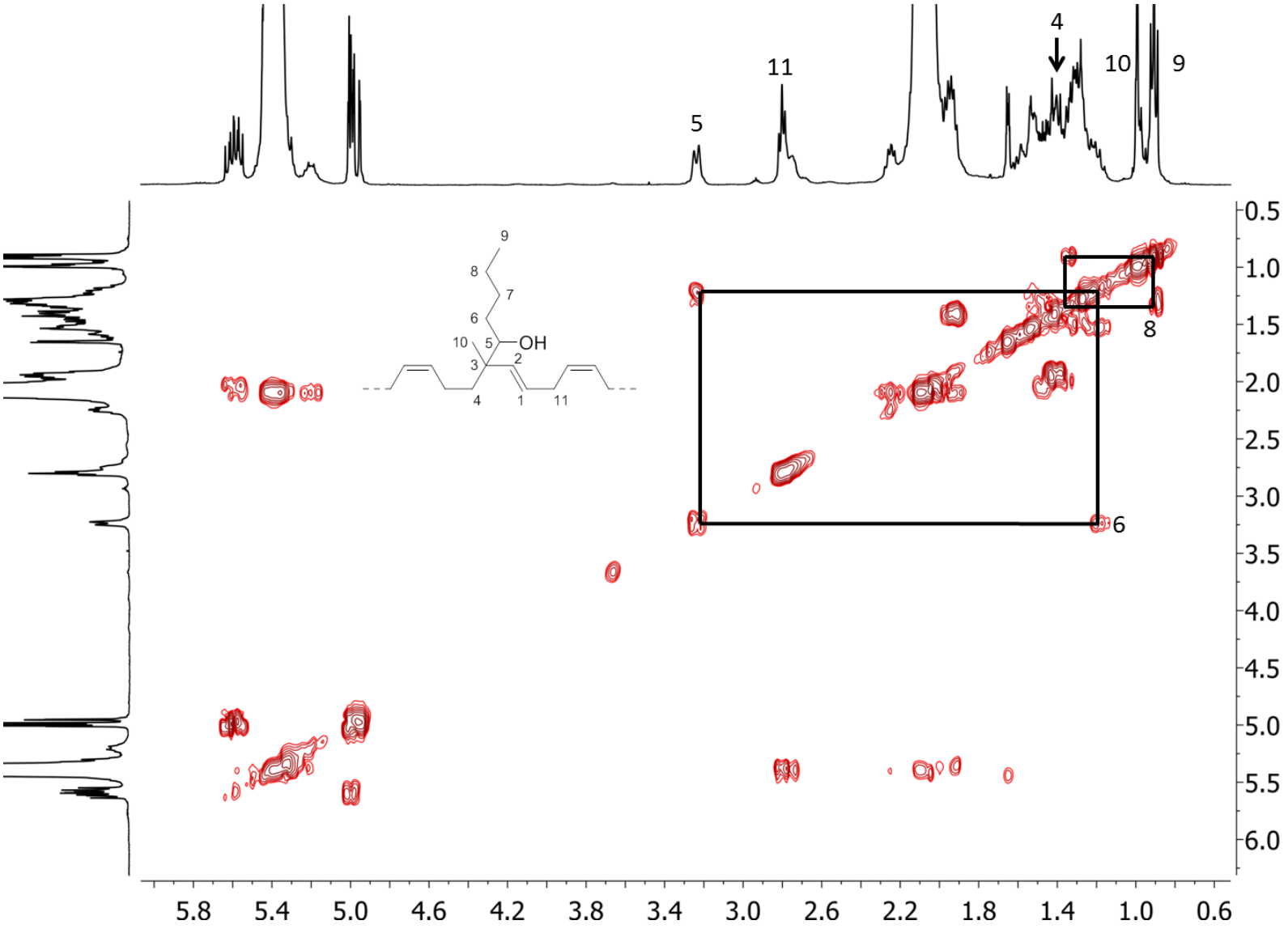
SI 24: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with pentanal (recorded at 27 °C in $CDCl_3$).



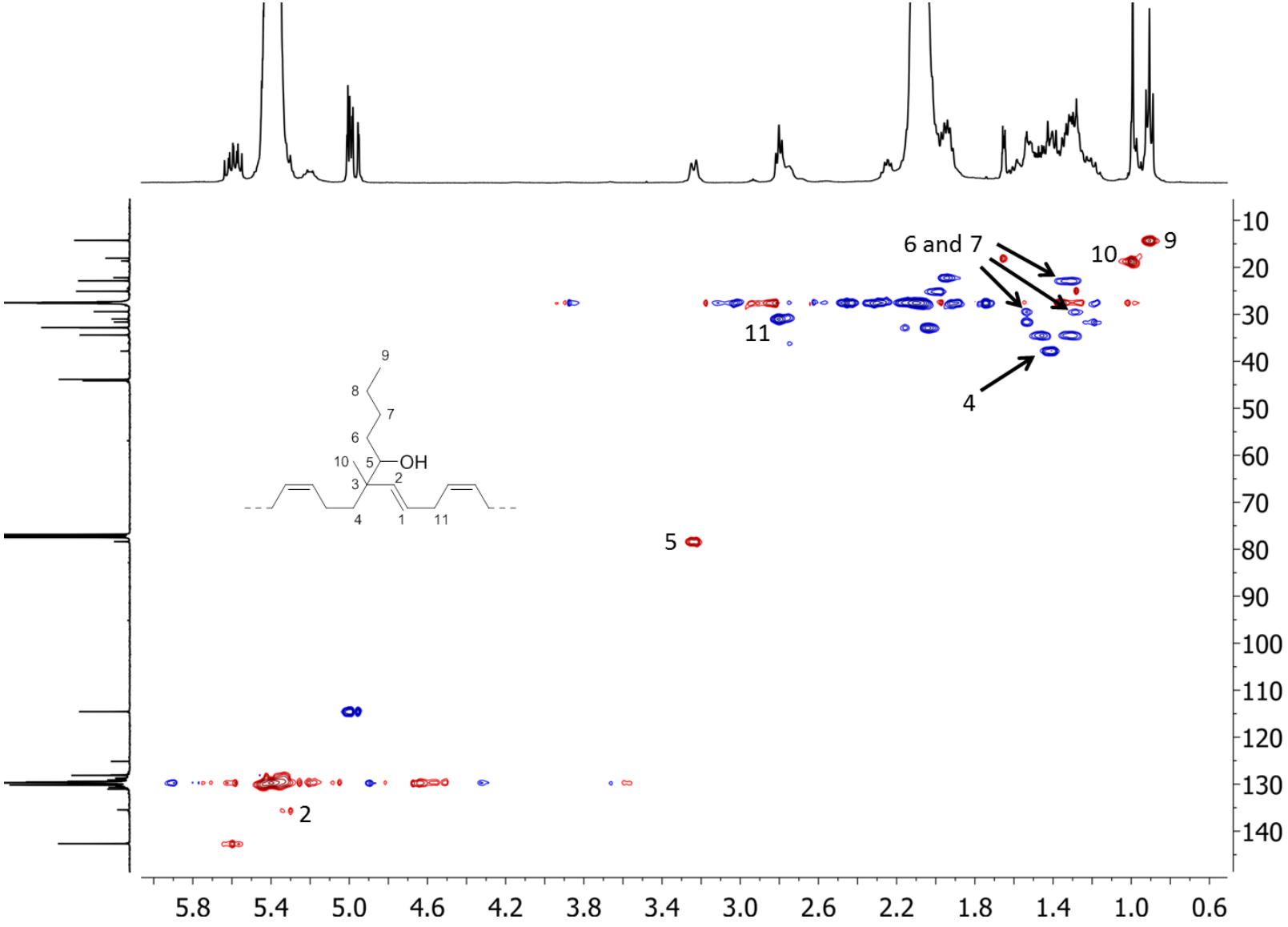
SI 25: ^{13}C NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with pentanal (recorded at 27 °C in $CDCl_3$).



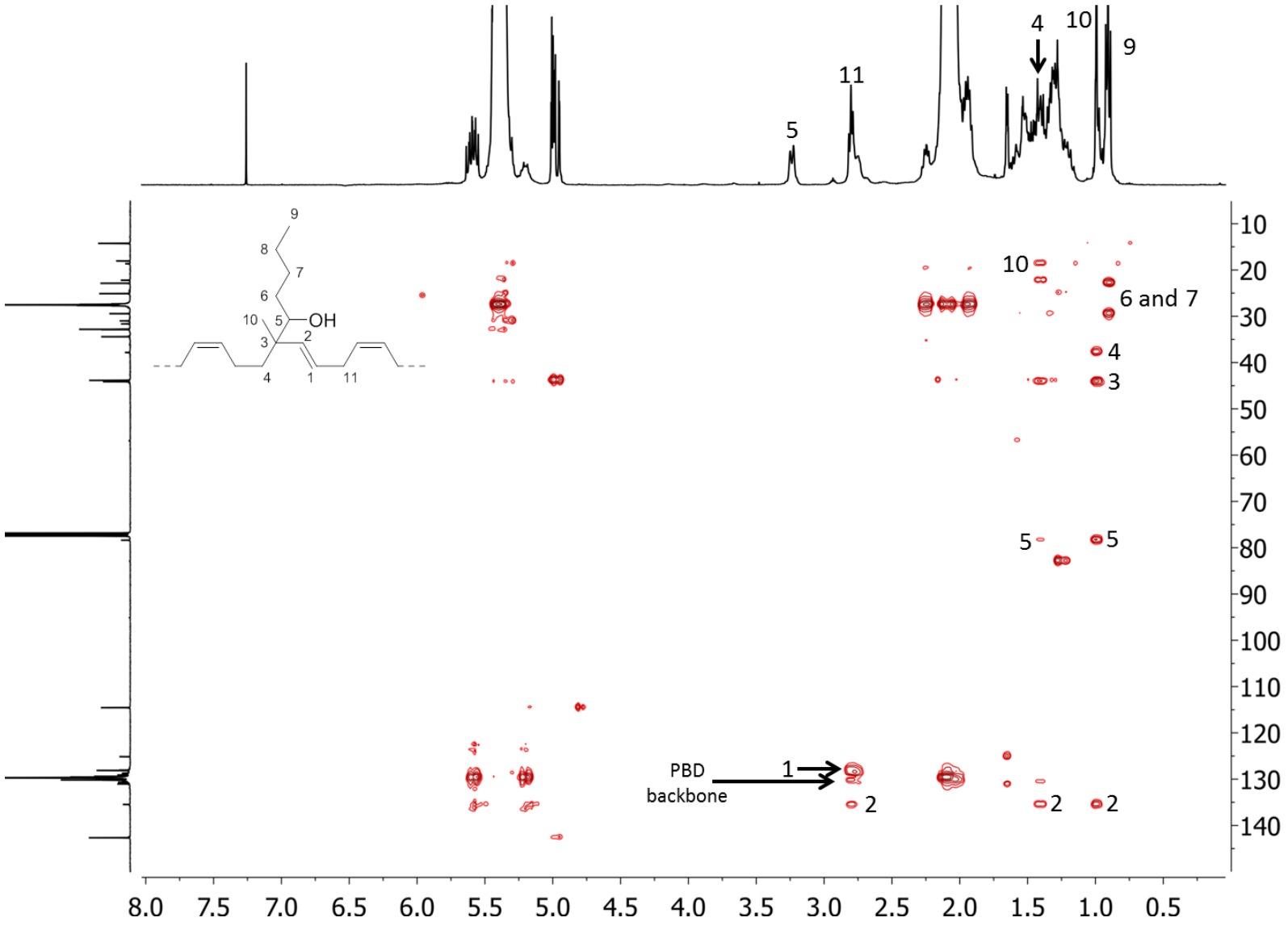
SI 26: ^{1}H NMR-spectrum (black) and 1D-TOCSY spectrum (red) of a copolymer functionalized by allylboration of **CoPo-1** with pentanal (recorded at 27 °C in $CDCl_3$).



SI 27: COSY NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with pentanal (recorded at 27 °C in $CDCl_3$).

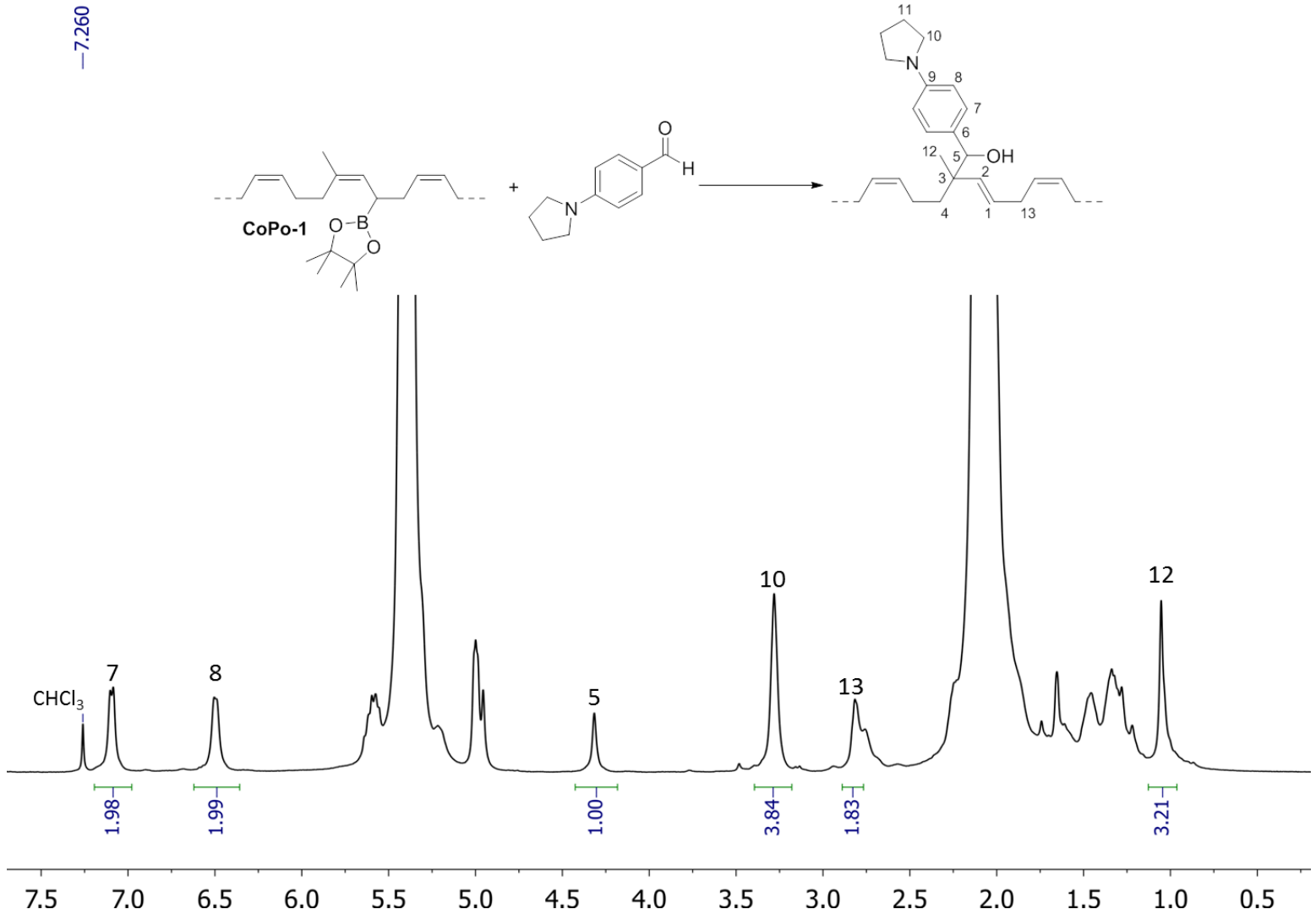


SI 28: HSQC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with pentanal (recorded at 27 °C in $CDCl_3$).

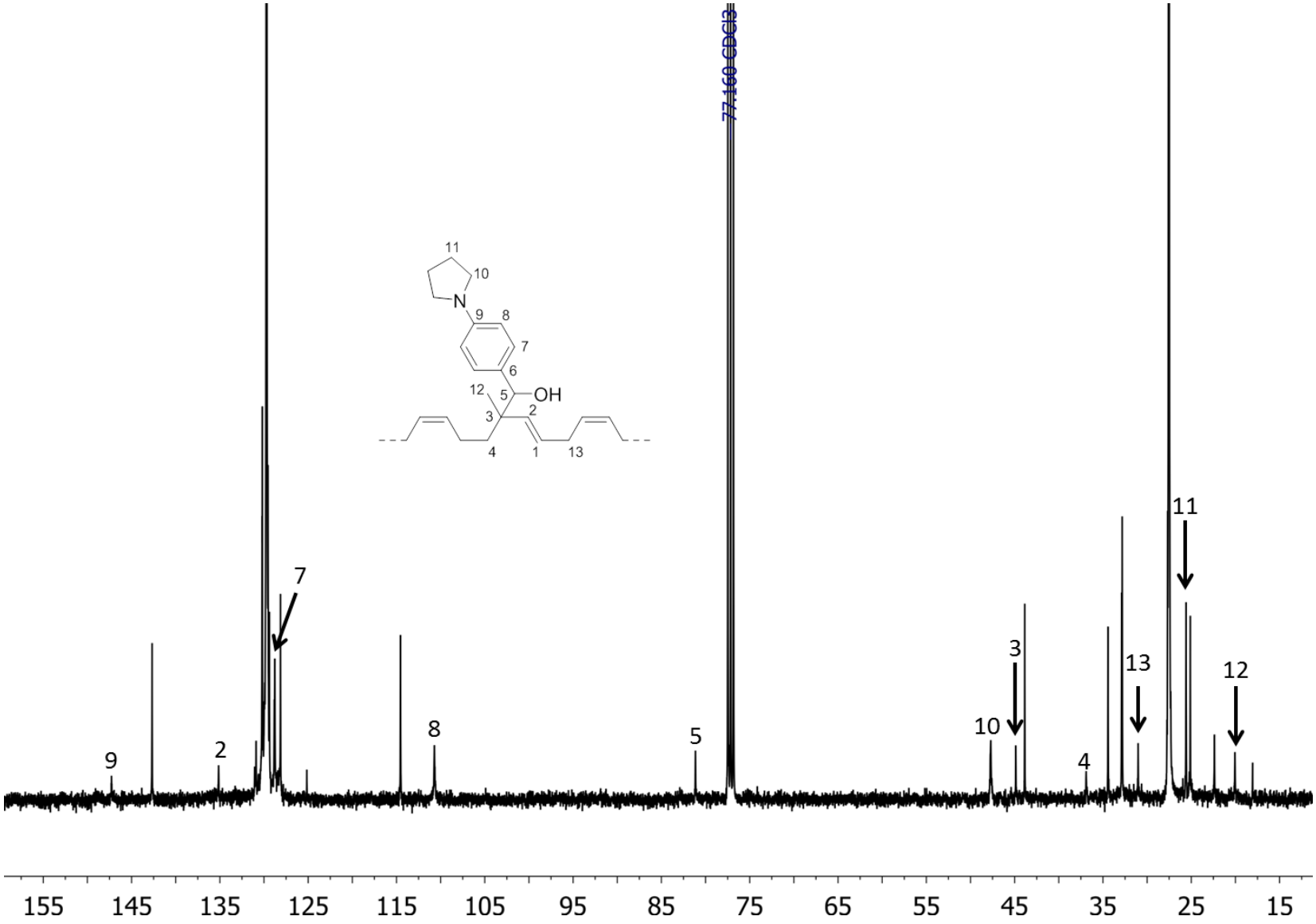


SI 29: HMBC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with pentanal (recorded at 27 °C in $CDCl_3$).

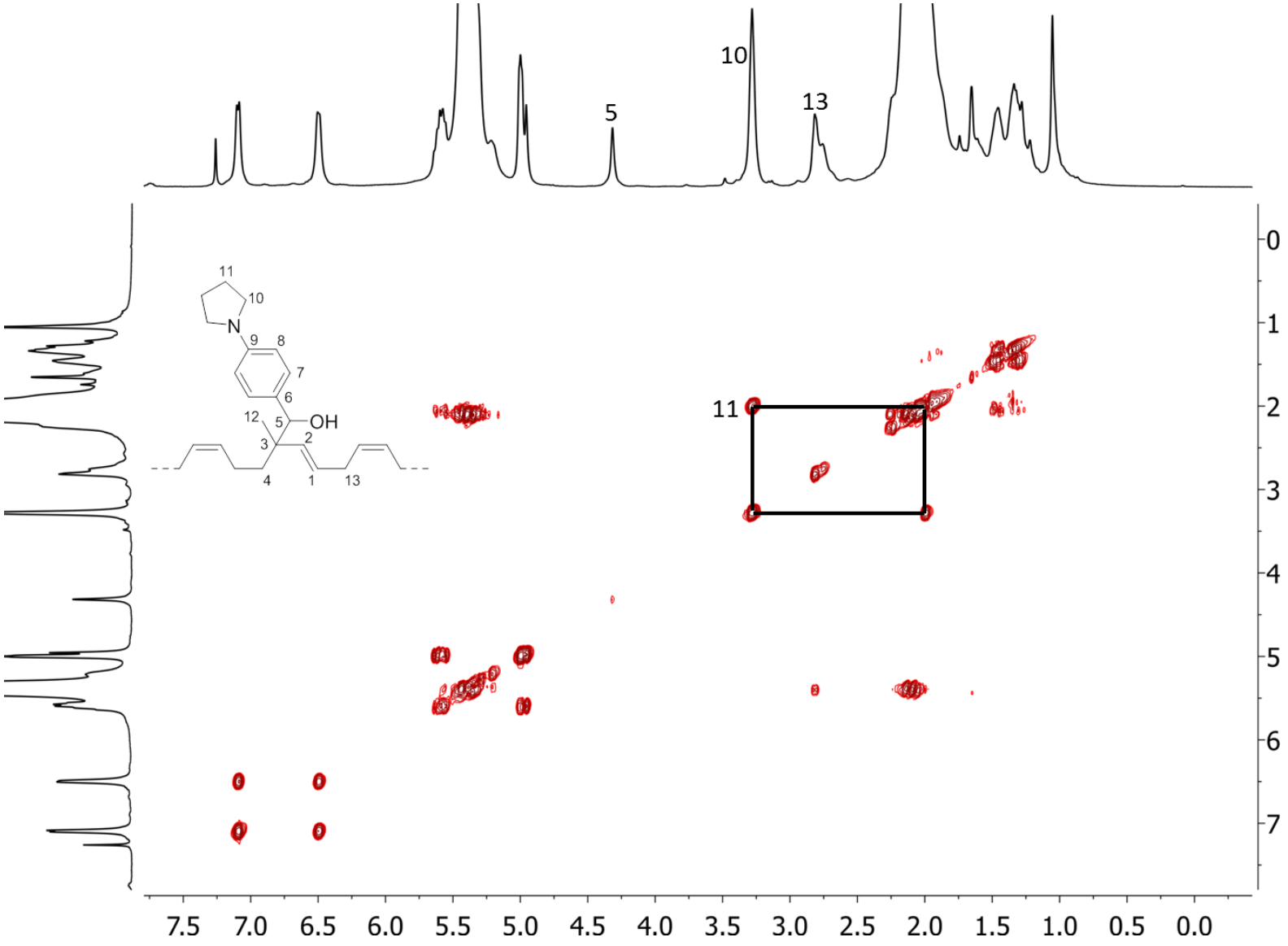
3.5. NMR-Spectra of PBD Functionalized with 4-(1-Pyrrolidinyl)benzaldehyde



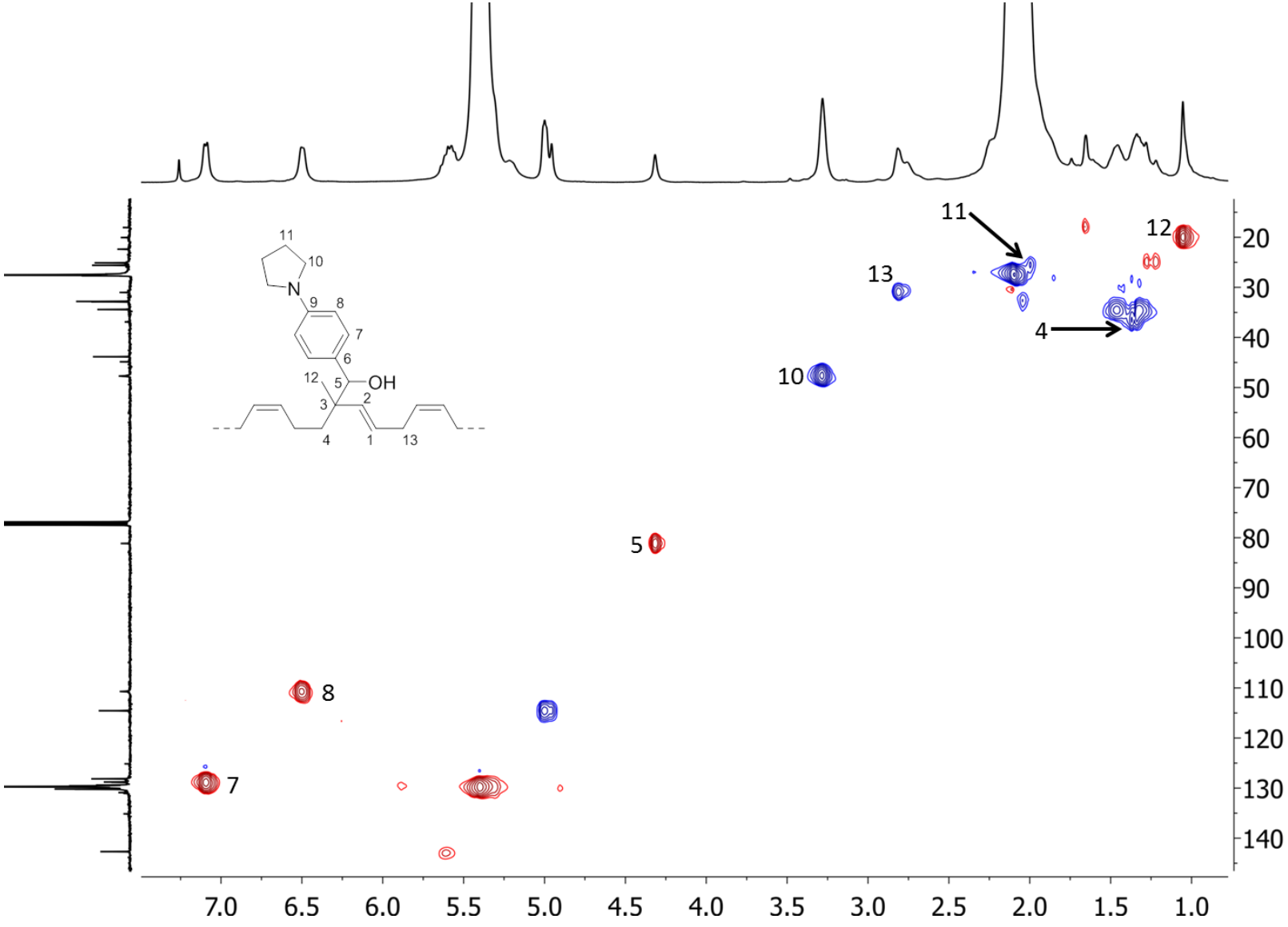
SI 30: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(1-pyrrolidinyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).



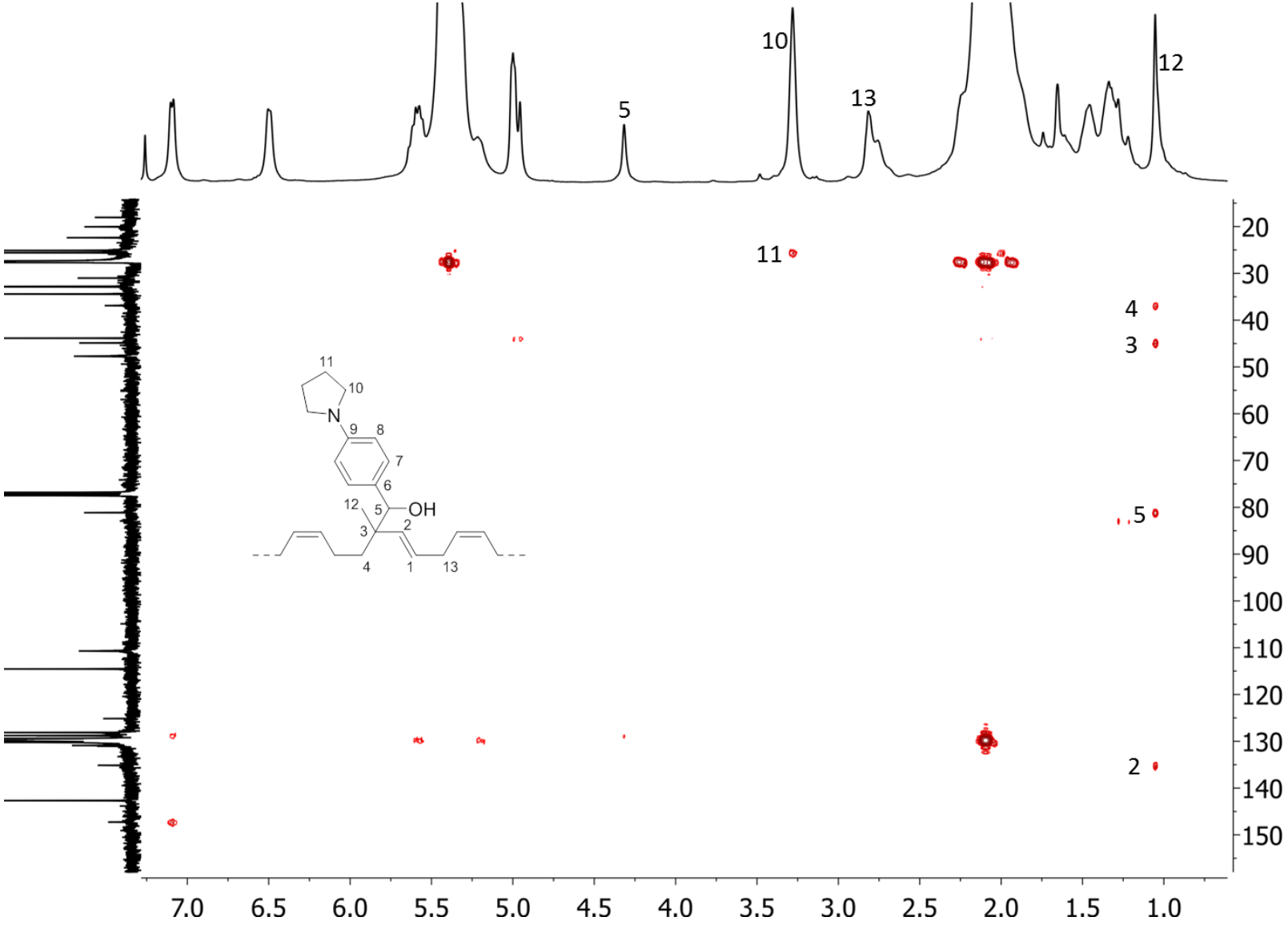
SI 31: ^{13}C NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(1-pyrrolidinyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).



SI 32: COSY NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(1-pyrrolidinyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

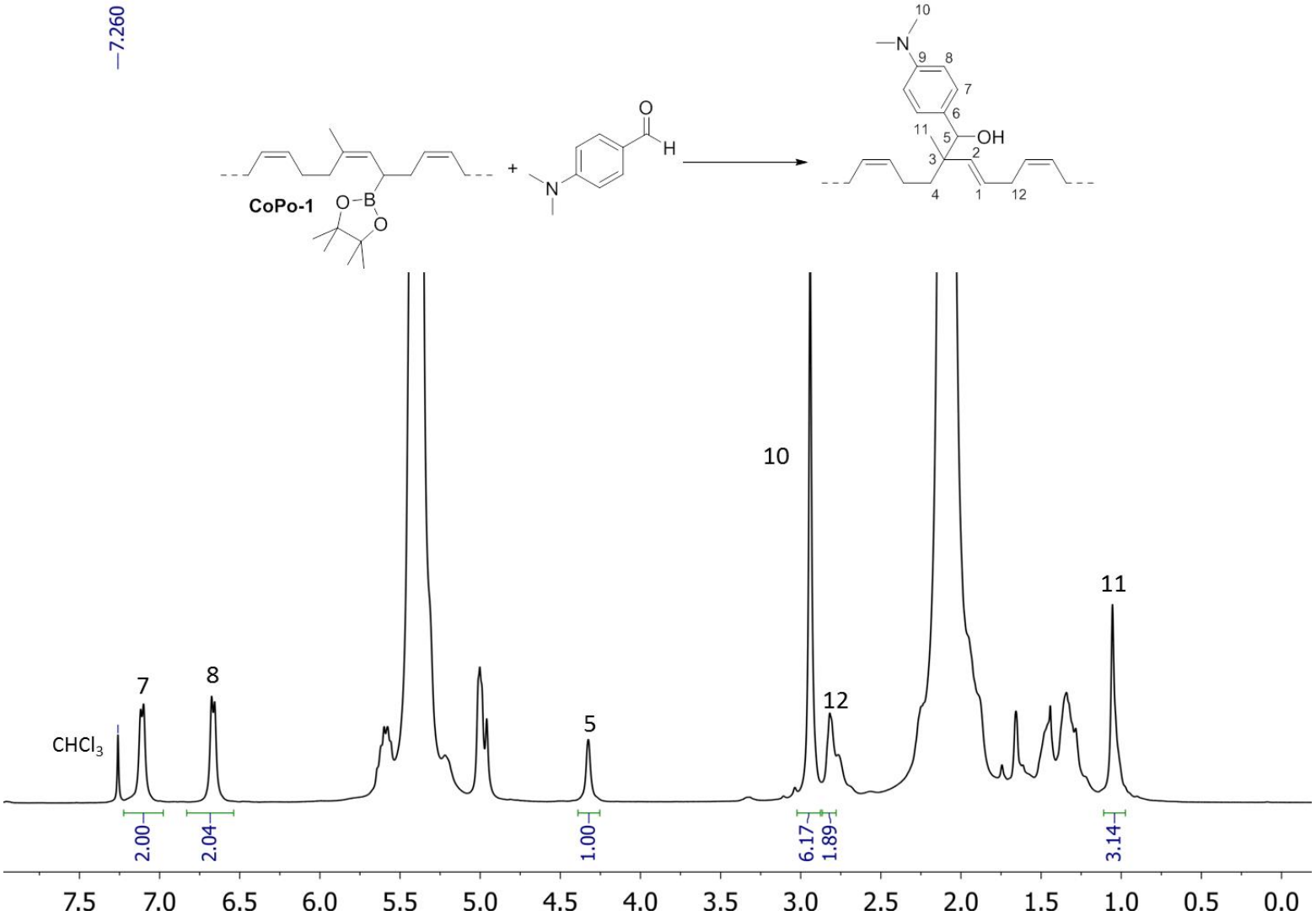


SI 33: HSQC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(1-pyrrolidinyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).



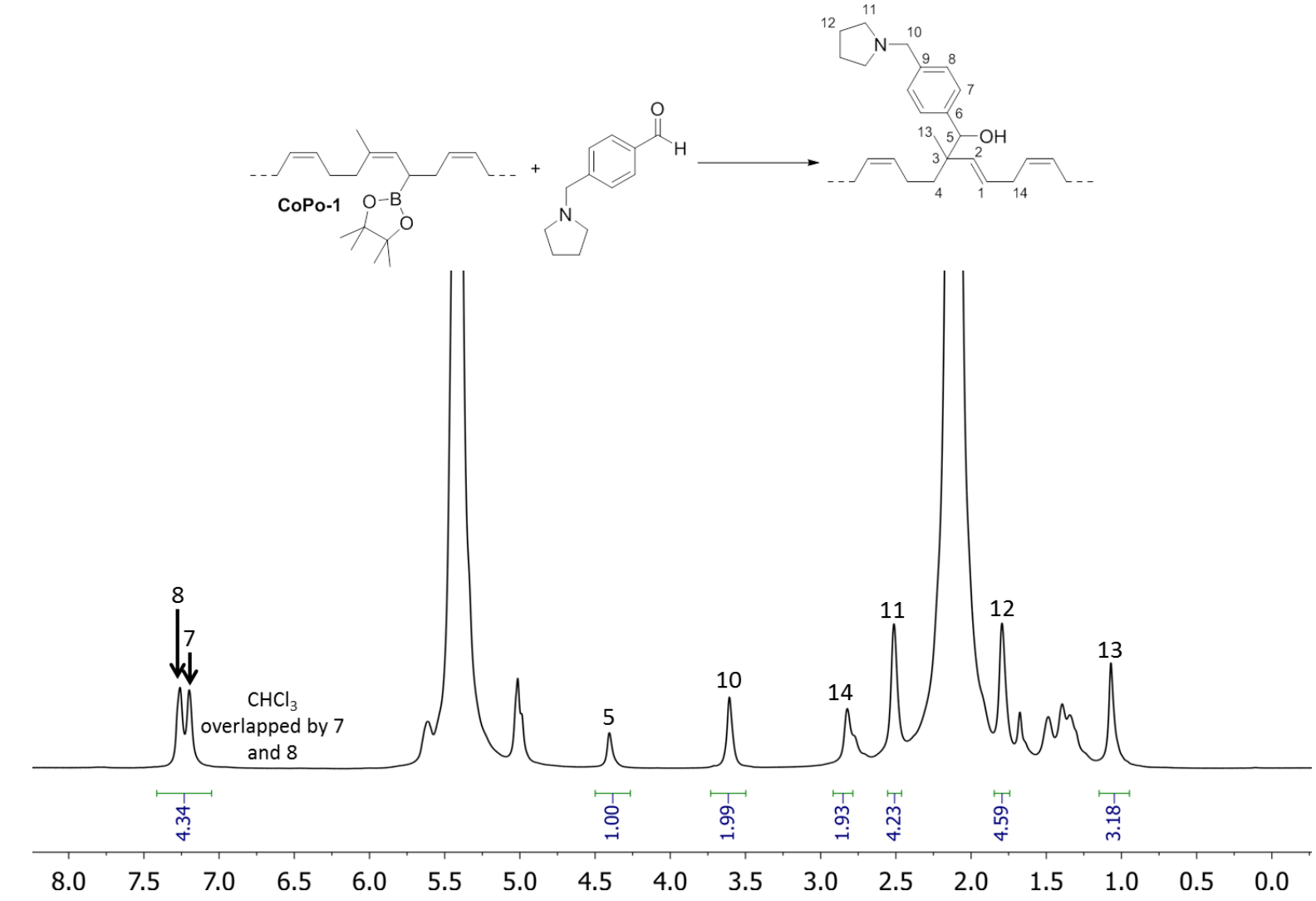
SI 34: HMBC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(1-pyrrolidinyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

3.6. NMR-Spectra of PBD Functionalized with *p*-Dimethylaminobenzaldehyde

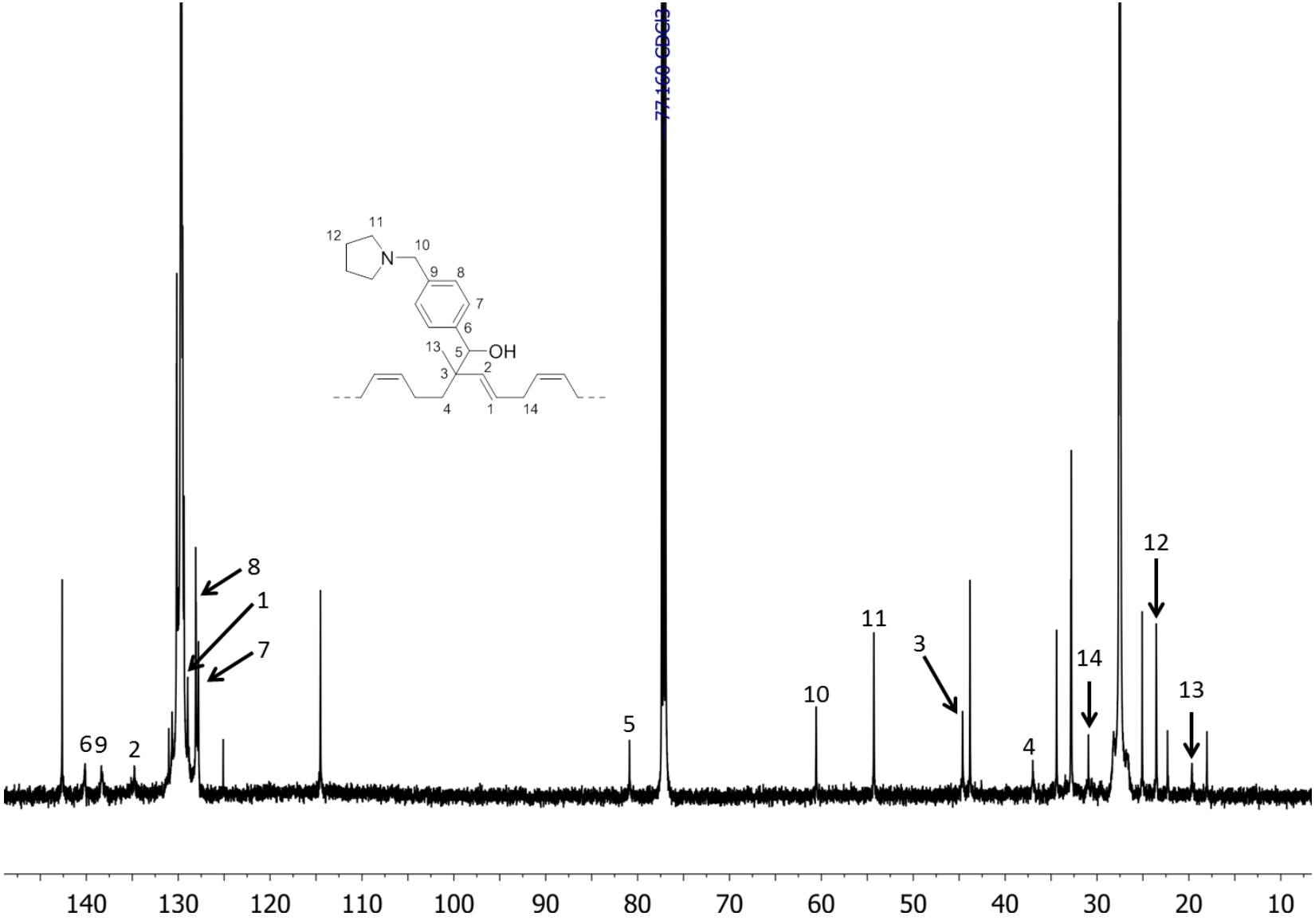


SI 35: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with *p*-dimethylaminobenzaldehyde (recorded at 27 °C in $CDCl_3$).

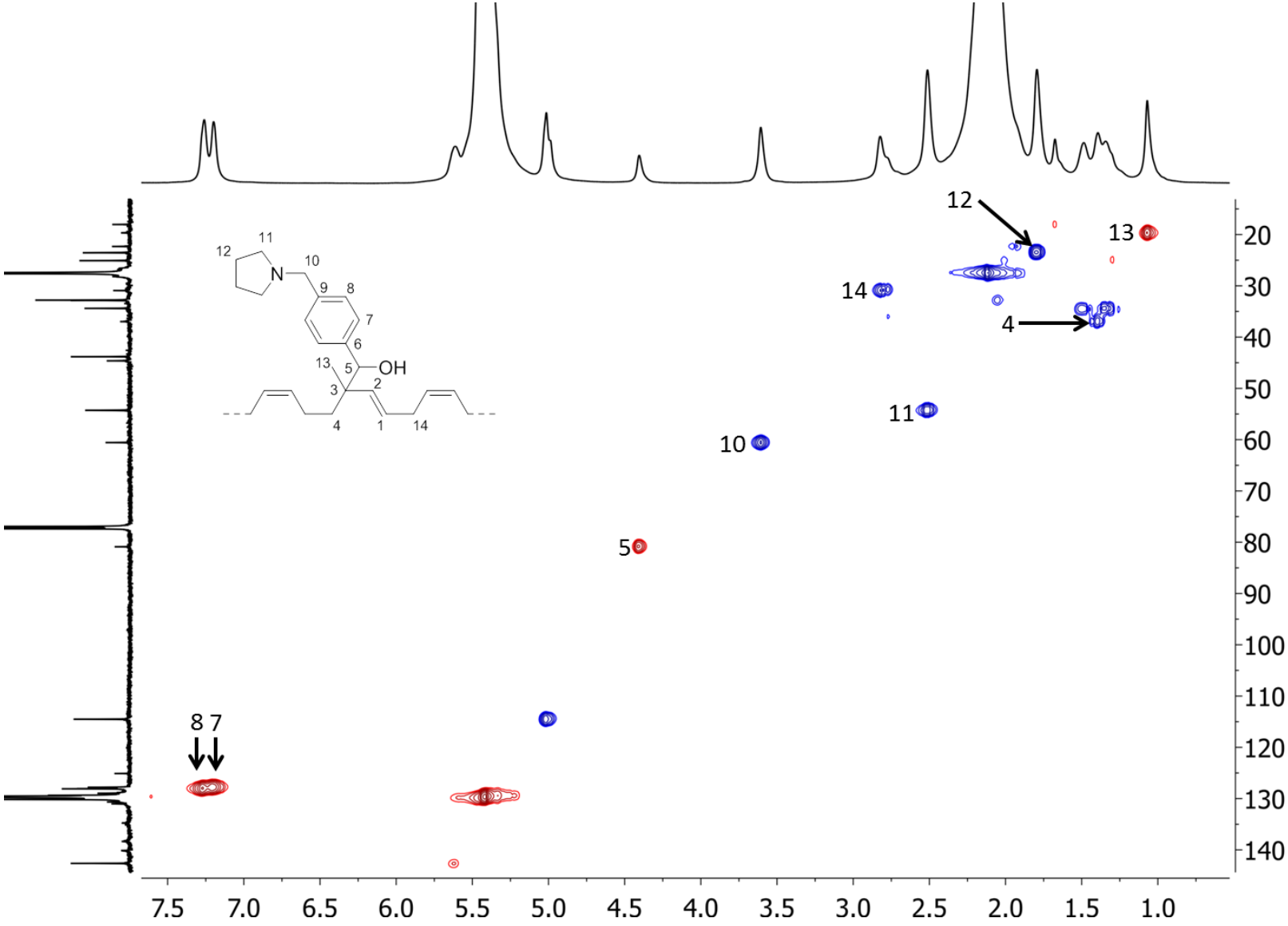
3.7. NMR-Spectra of PBD Functionalized with 4-(Pyrrolidinylmethyl)benzaldehyde



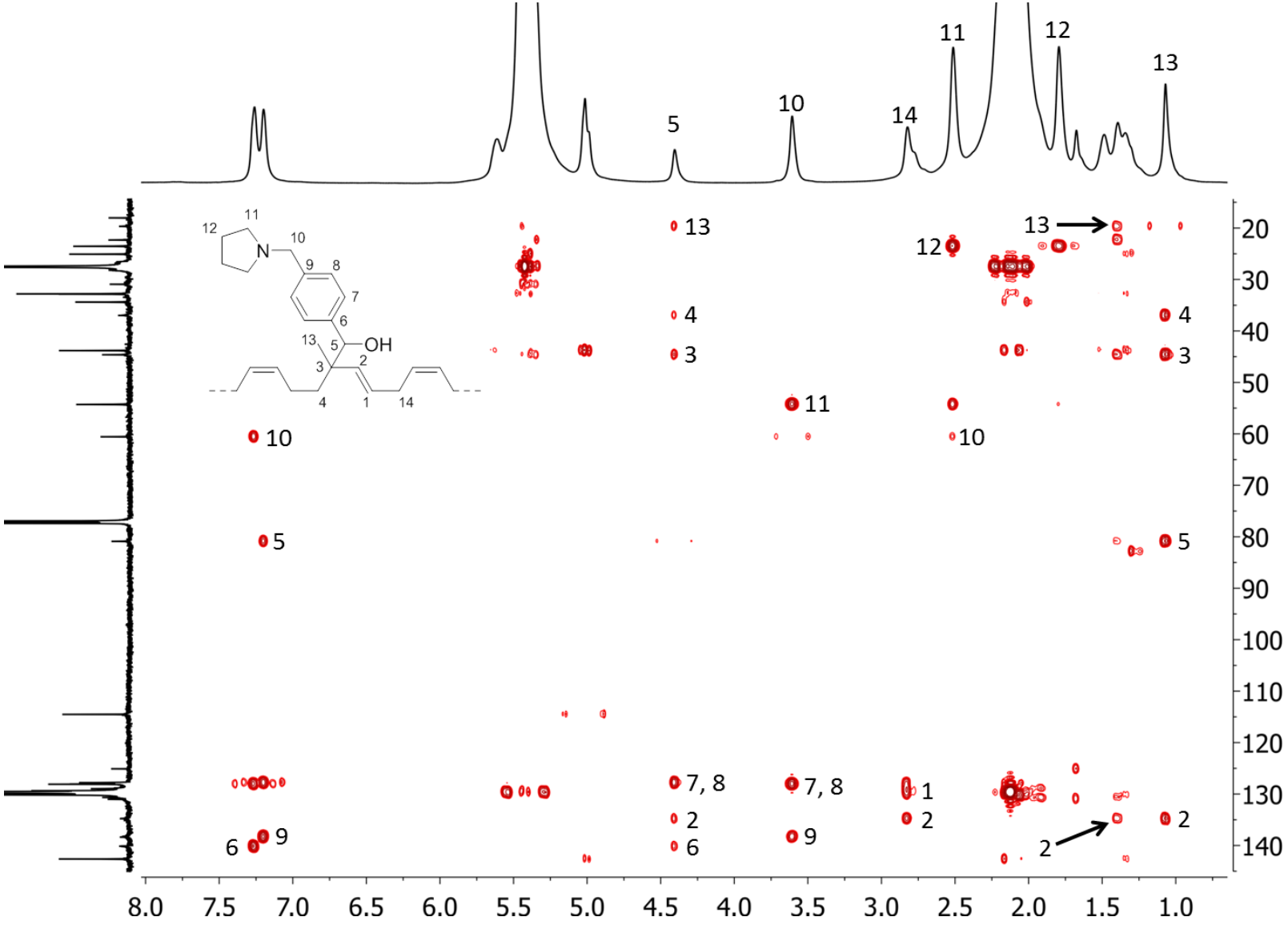
SI 36: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(pyrrolidinylmethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).



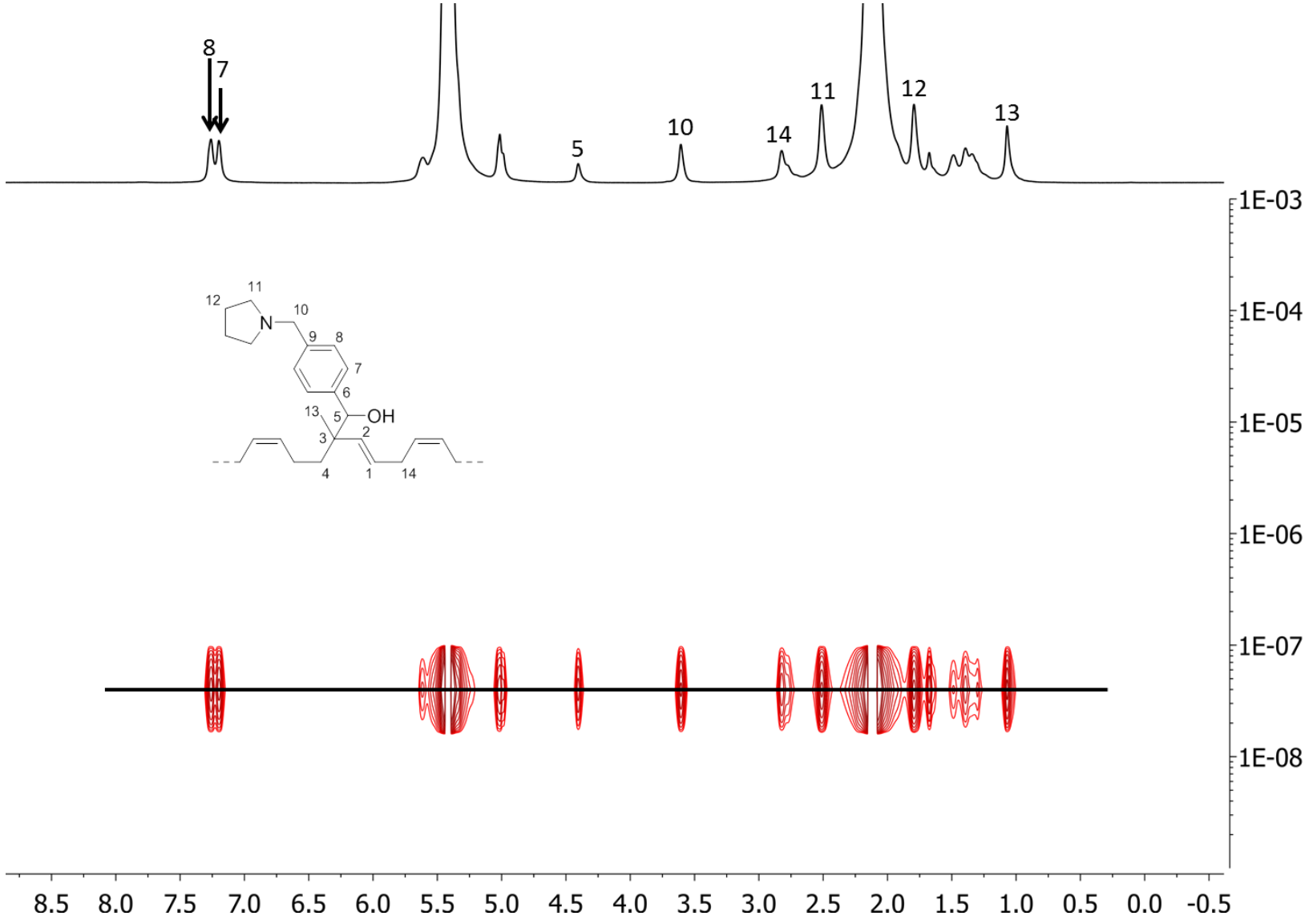
SI 37: ^{13}C NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(pyrrolidinylmethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).



SI 38: HSQC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(pyrrolidinylmethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

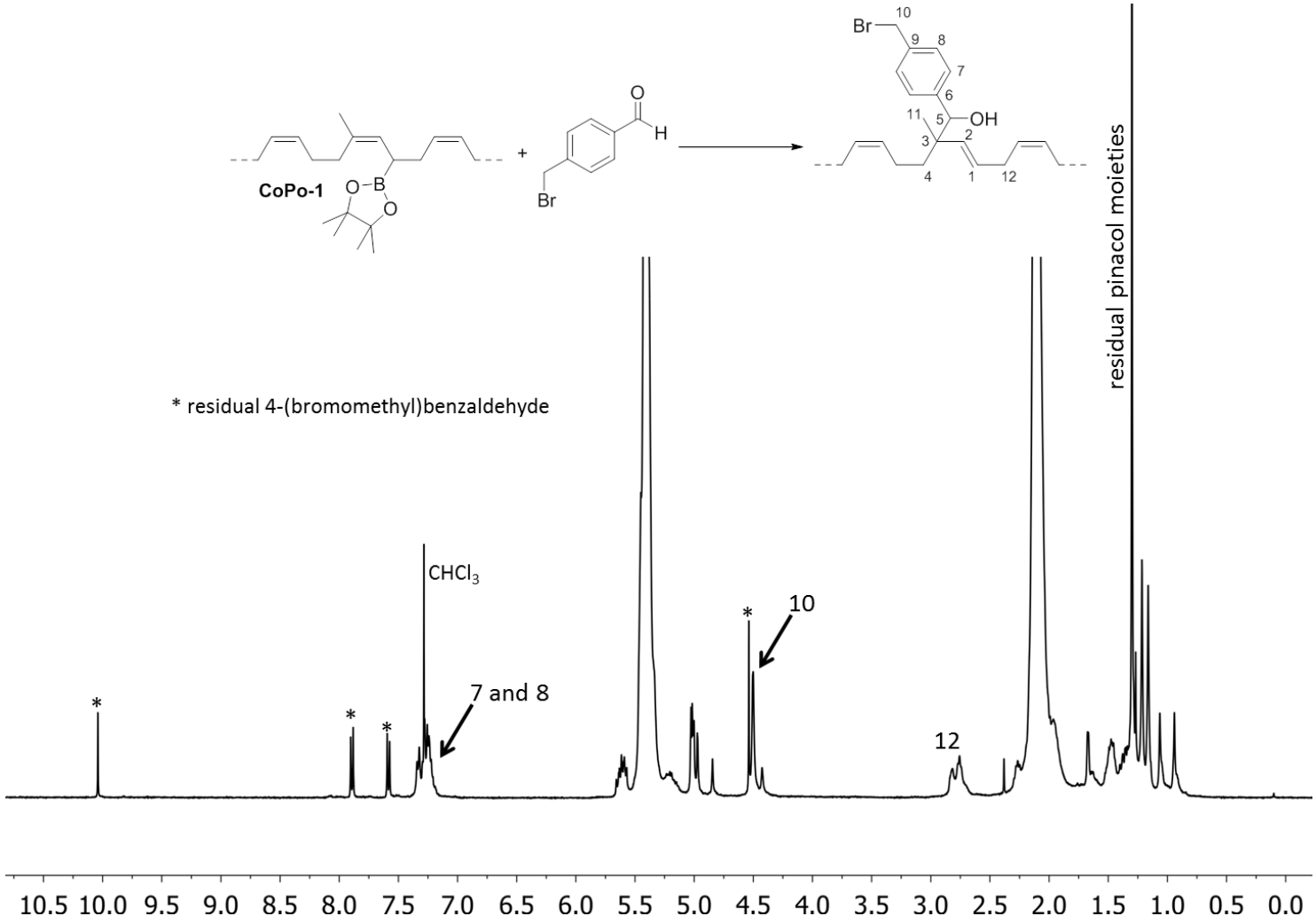


SI 39: HMBC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(pyrrolidinylmethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

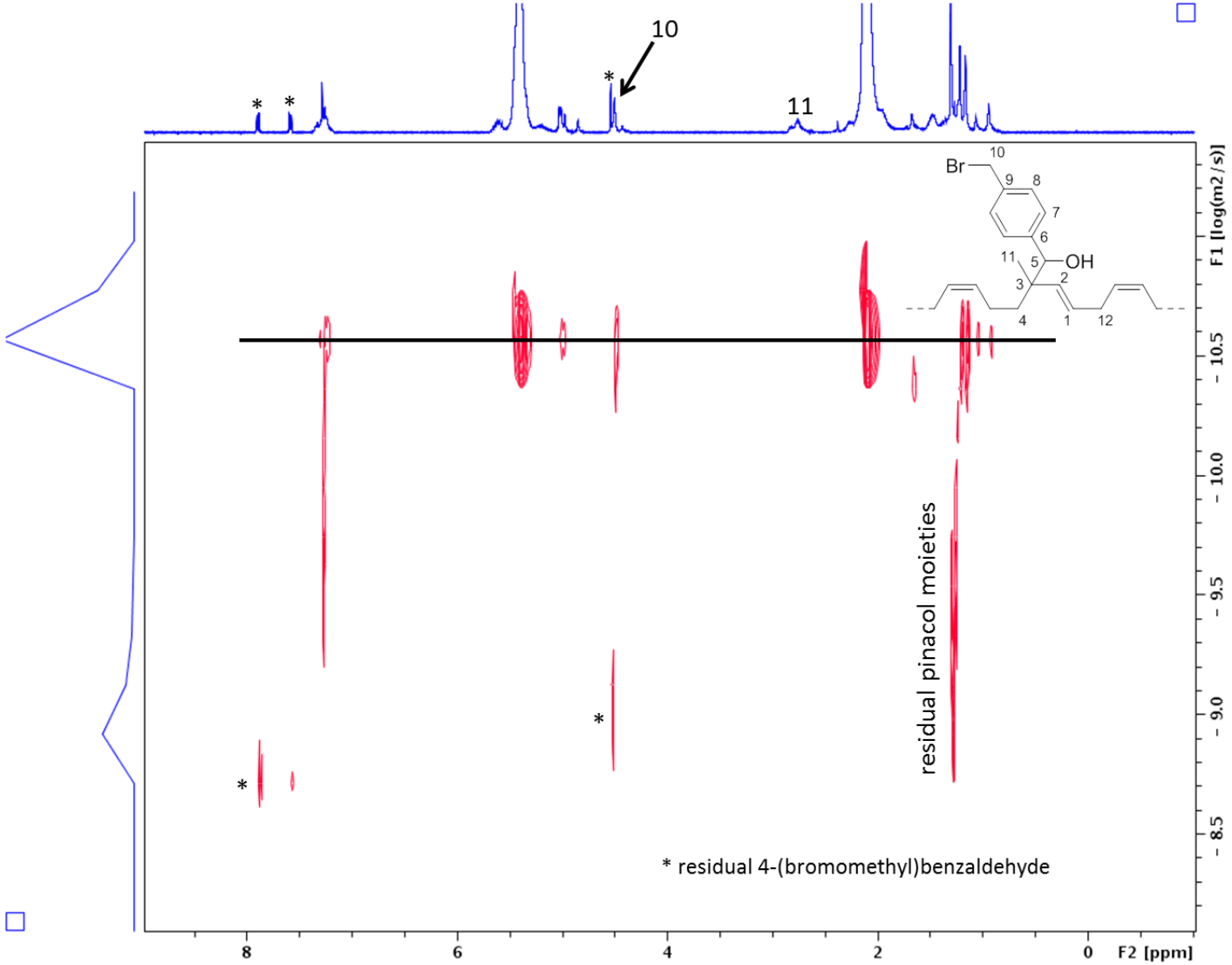


SI 40: DOSY NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with 4-(pyrrolidinylmethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

3.8. NMR-Spectra of PBD Functionalized with 4-(Bromomethyl)benzaldehyde

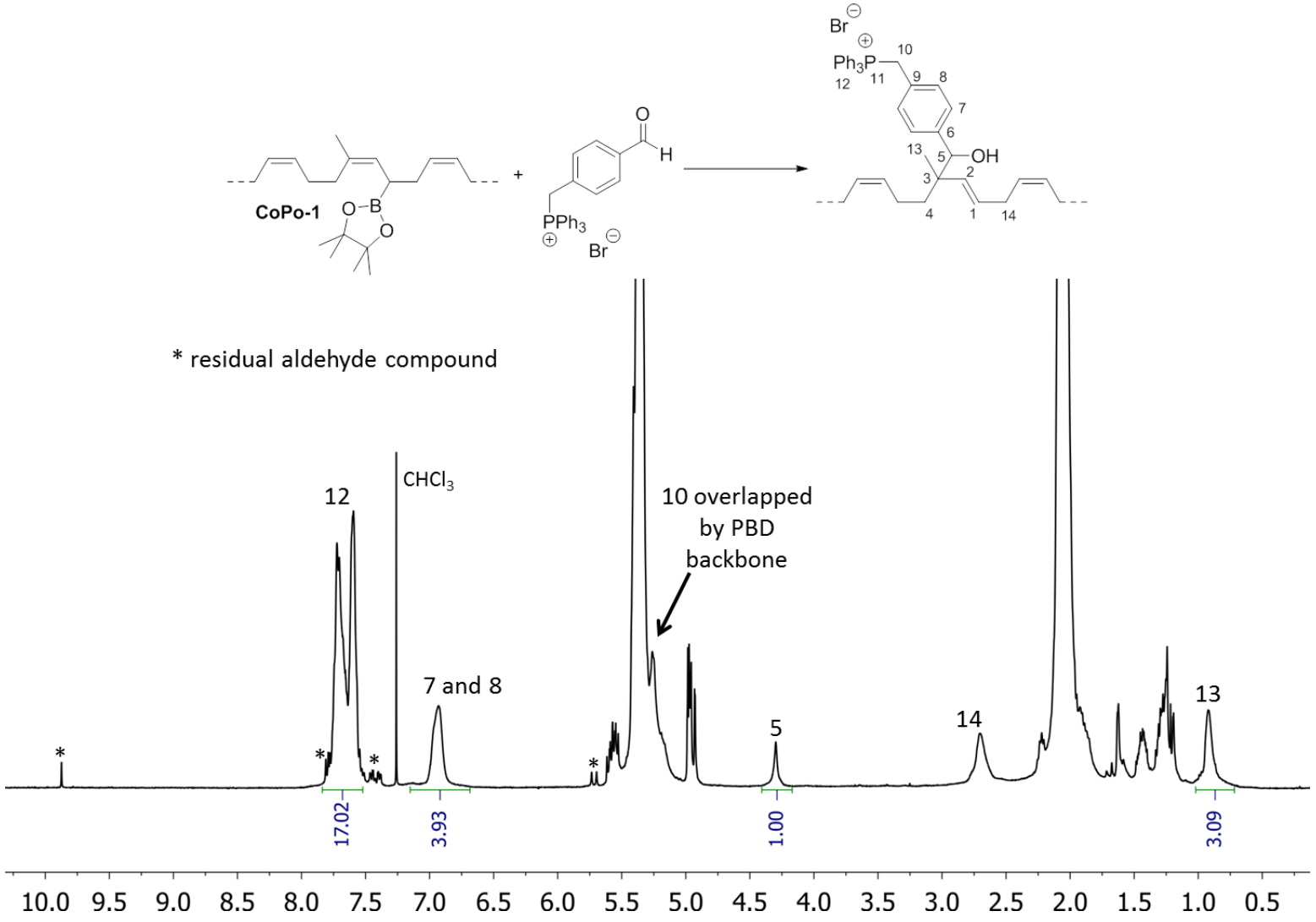


SI 41: ^{1}H NMR-spectrum of the crude reaction mixture of a copolymer functionalized by allylboration of **CoPo-1** with 4-(bromomethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

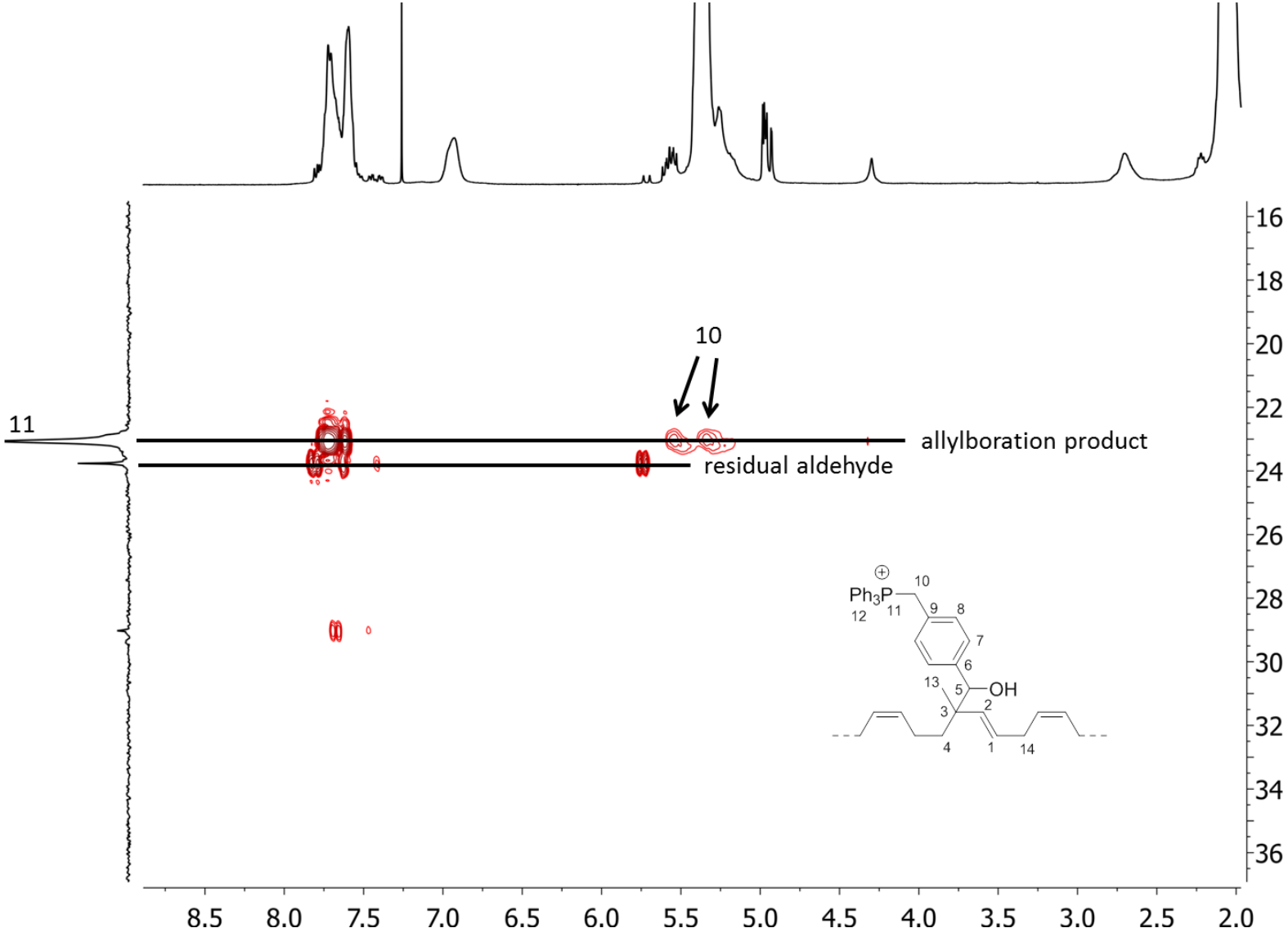


SI 42: DOSY NMR-spectrum of the crude reaction mixture of a copolymer functionalized by allylboration of **CoPo-1** with 4-(bromomethyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

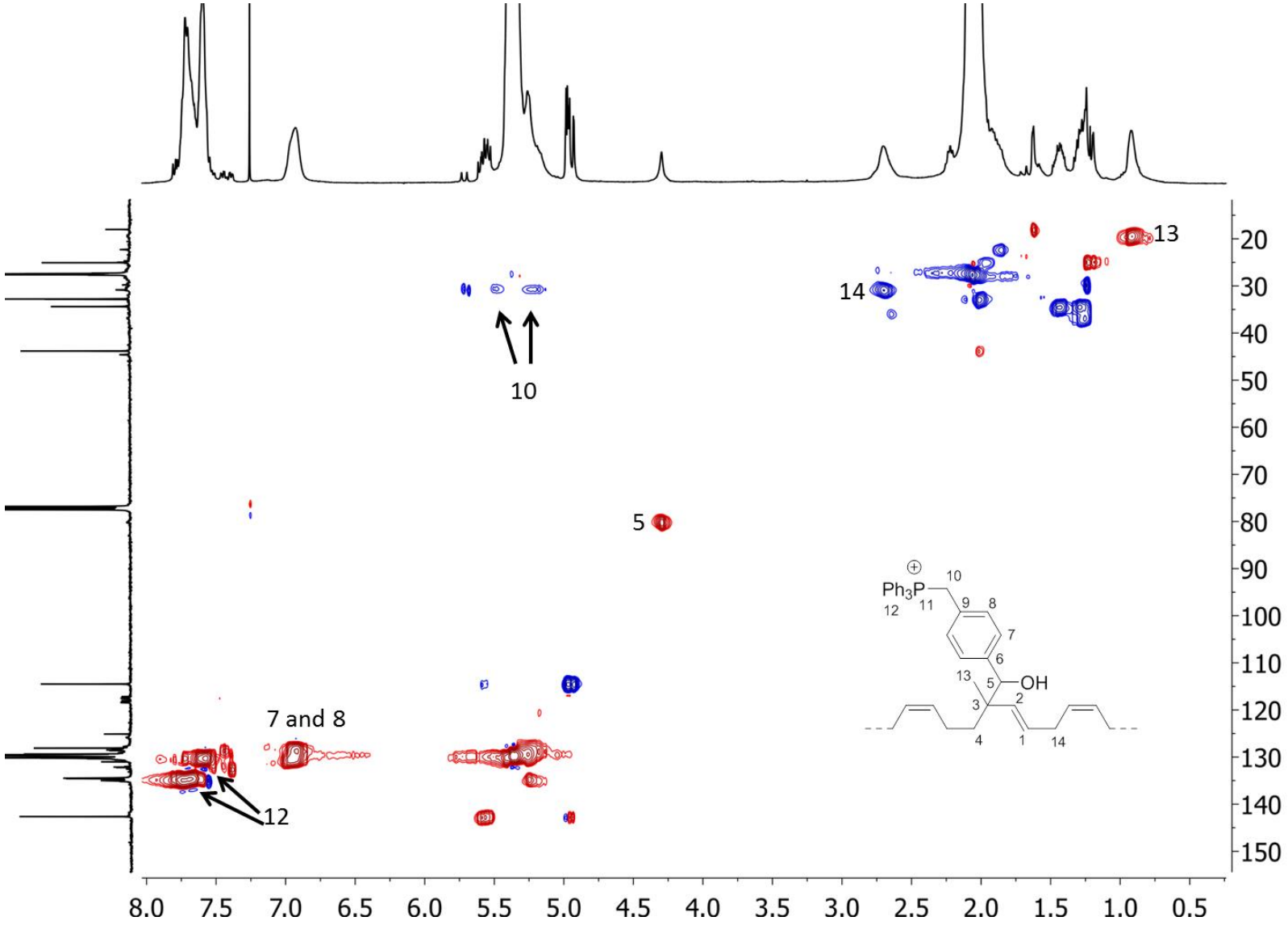
3.9. NMR-Spectra of PBD Functionalized with (4-Formylbenzyl)triphenylphosphonium Bromide



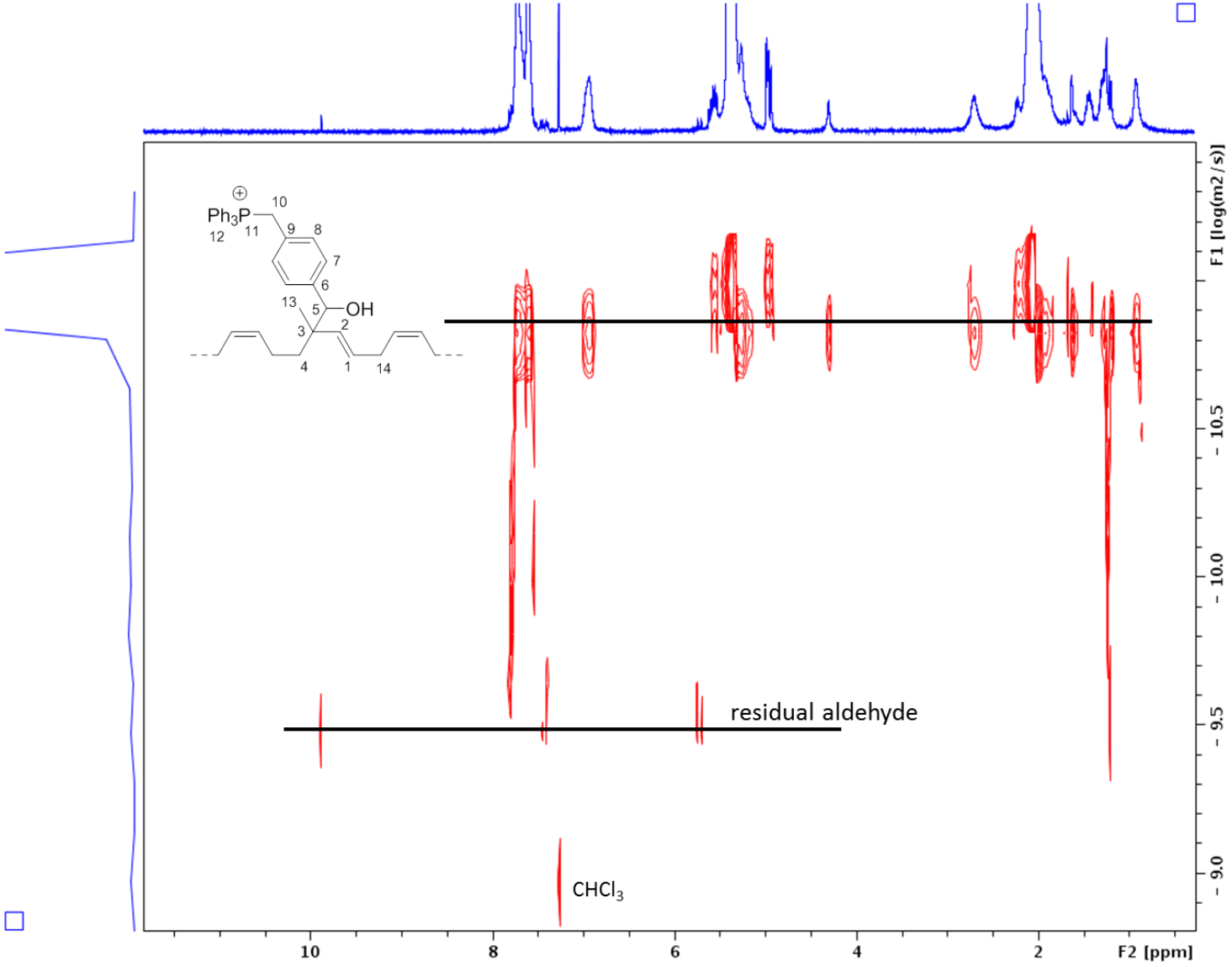
SI 43: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with (4-formylbenzyl)triphenylphosphonium bromide (recorded at 27 °C in $CDCl_3$).



SI 44: ^{31}P-HMBC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with (4-formylbenzyl)triphenylphosphonium bromide (recorded at 27 °C in $CDCl_3$).

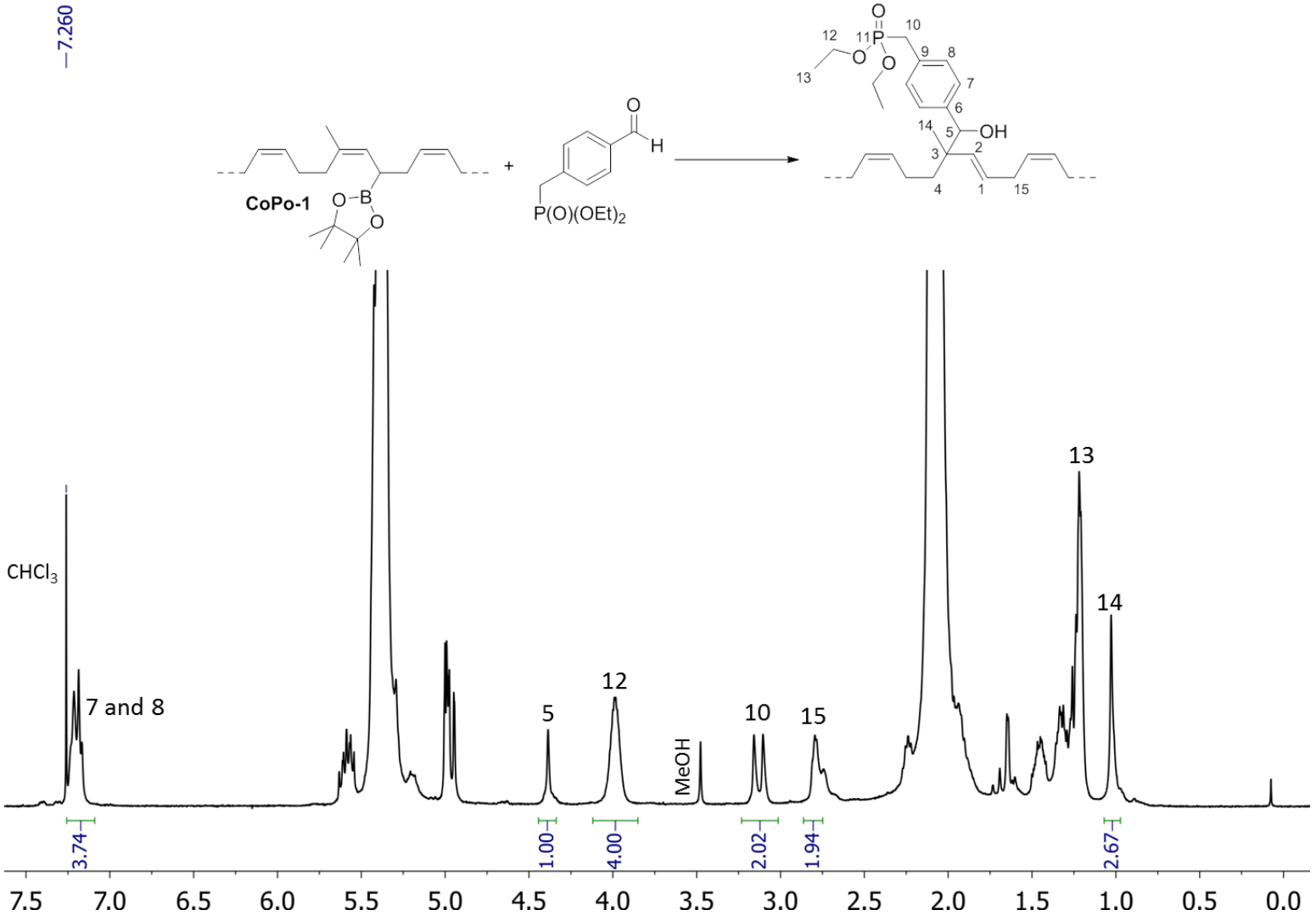


SI 45: HSQC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with (4-formylbenzyl)triphenylphosphonium bromide (recorded at 27 °C in $CDCl_3$).

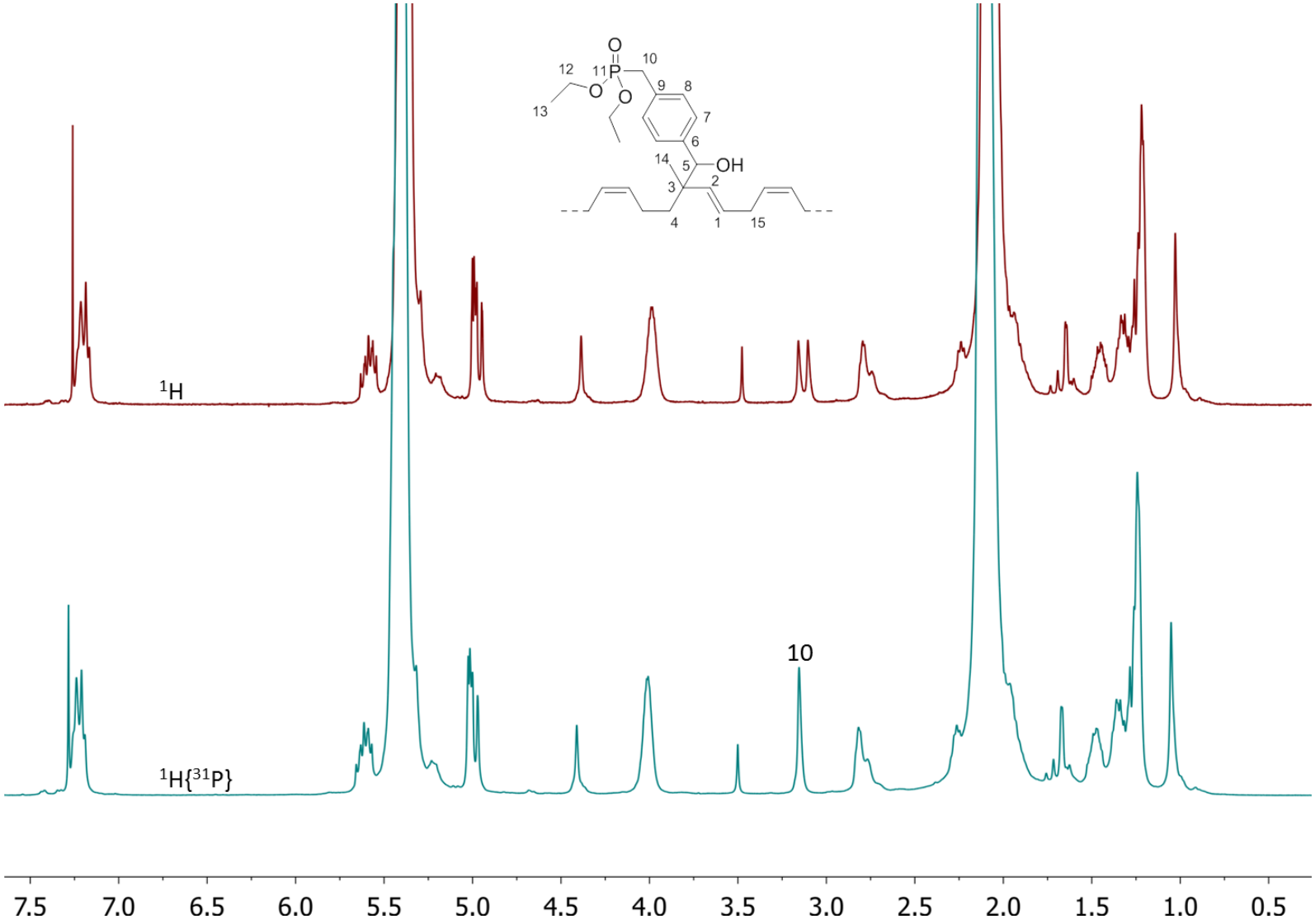


SI 46: DOSY NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with (4-formylbenzyl)triphenylphosphonium bromide (recorded at 27 °C in $CDCl_3$).

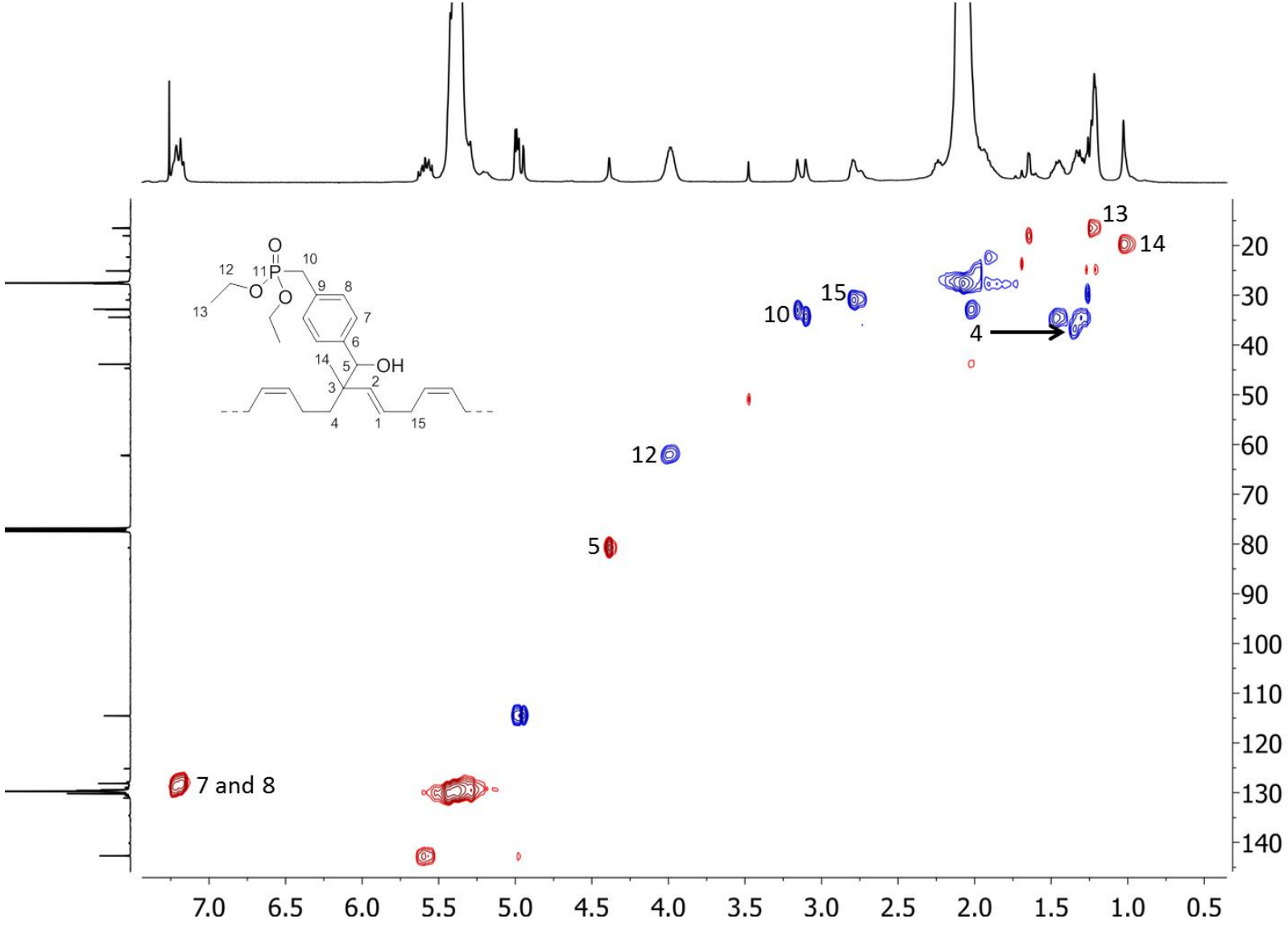
3.10. NMR-Spectra of PBD Functionalized with Diethyl (4-formylbenzyl)phosphonate



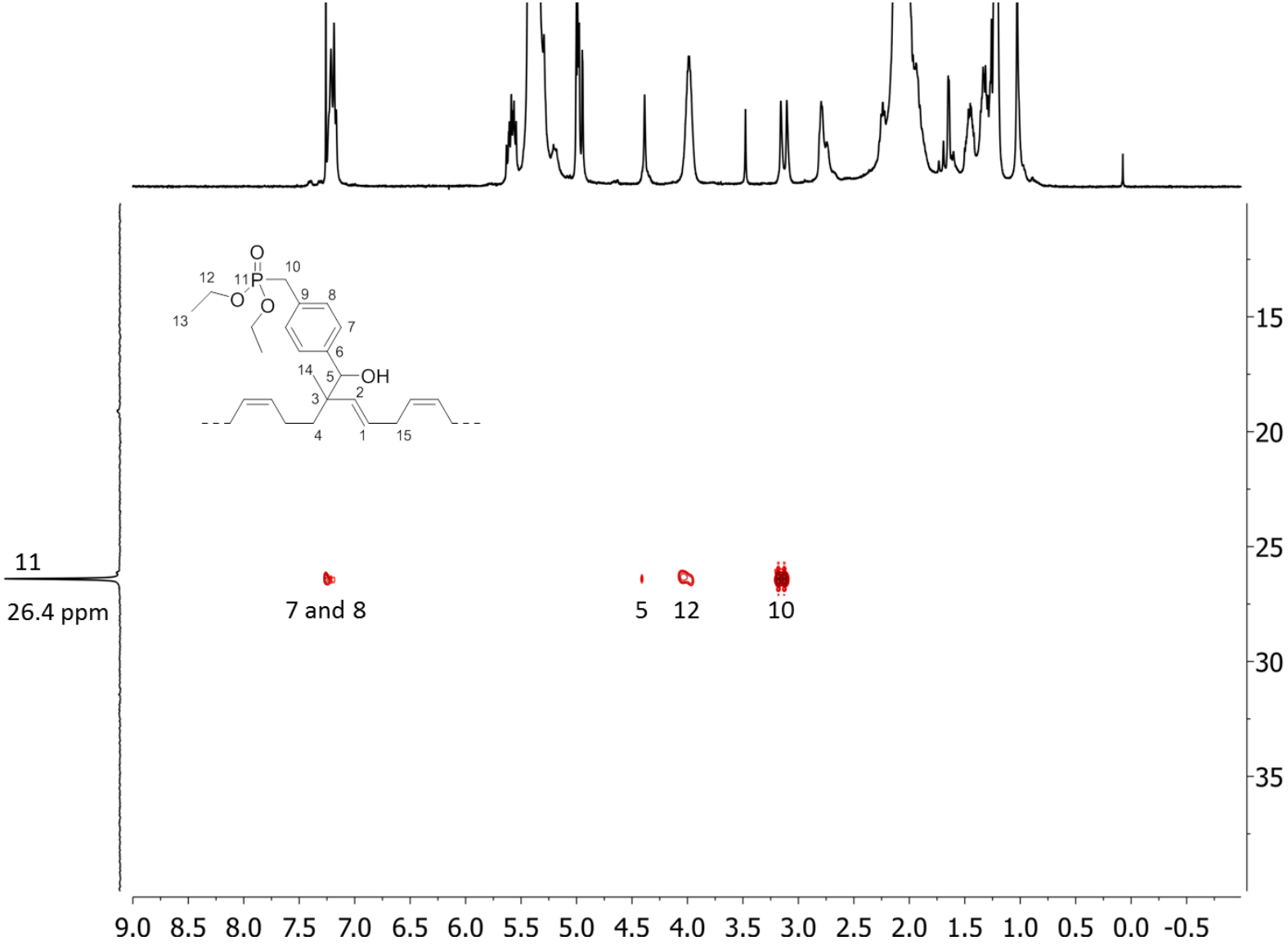
SI 47: ^{1}H NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with diethyl (4-formylbenzyl)phosphonate (recorded at 27 °C in $CDCl_3$).



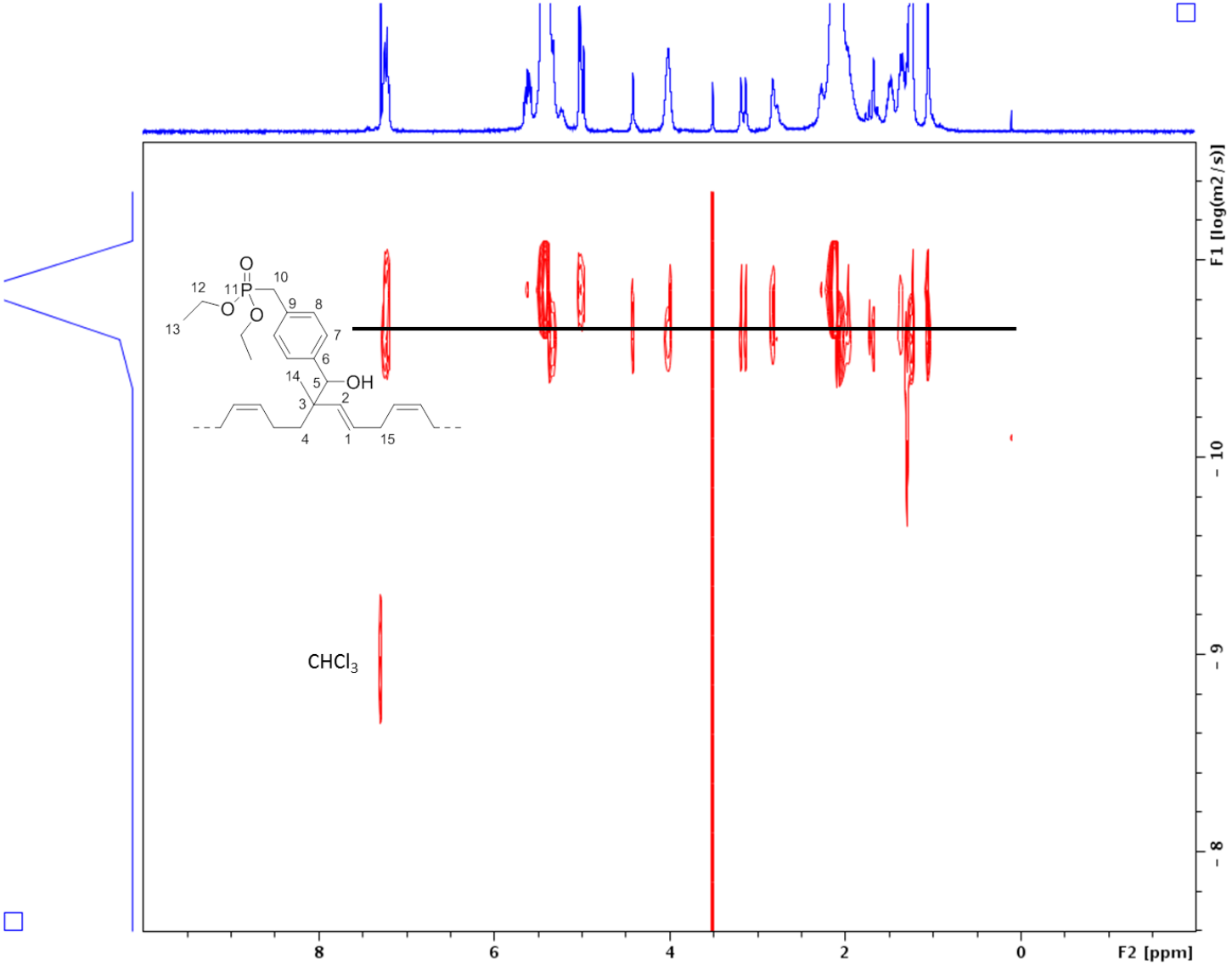
SI 48: ^{1}H NMR-spectrum (top) and ^{1}H{^{31}P} NMR-spectrum (bottom) of a copolymer functionalized by allylboration of **CoPo-1** with diethyl (4-formylbenzyl)phosphonate (recorded at 27 °C in $CDCl_3$).



SI 49: HSQC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with diethyl (4-formylbenzyl)phosphonate (recorded at 27 °C in $CDCl_3$).



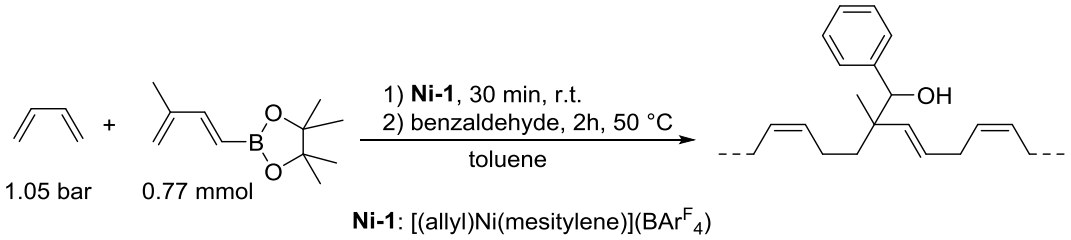
SI 50: ^{31}P-HMBC NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with diethyl (4-formylbenzyl)phosphonate (recorded at 27 °C in $CDCl_3$).



SI 51: DOSY NMR-spectrum of a copolymer functionalized by allylboration of **CoPo-1** with diethyl (4-formylbenzyl)phosphonate (recorded at 27 °C in $CDCl_3$).

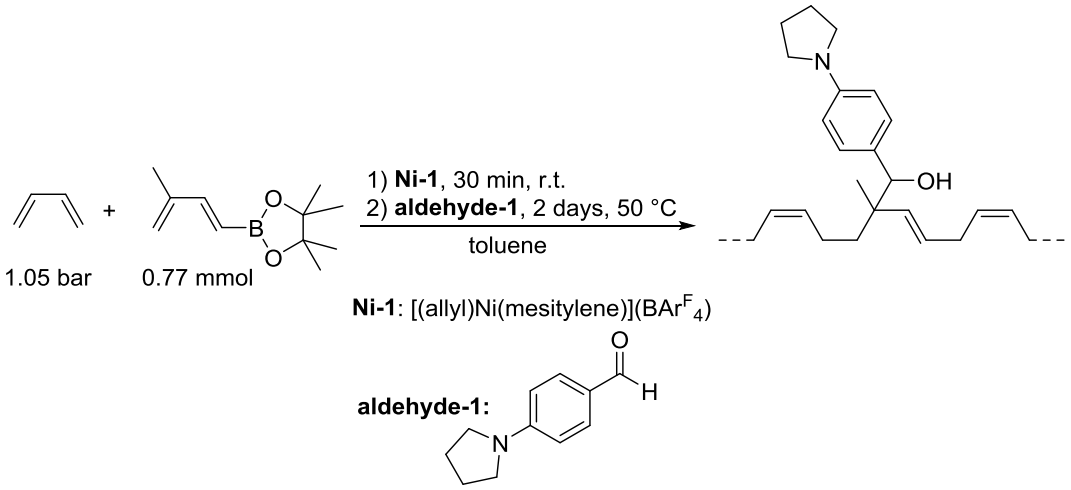
4. Allylboration Reaction *In-situ* Directly after Copolymerization

4.1. *In-situ* Functionalization with Benzaldehyde



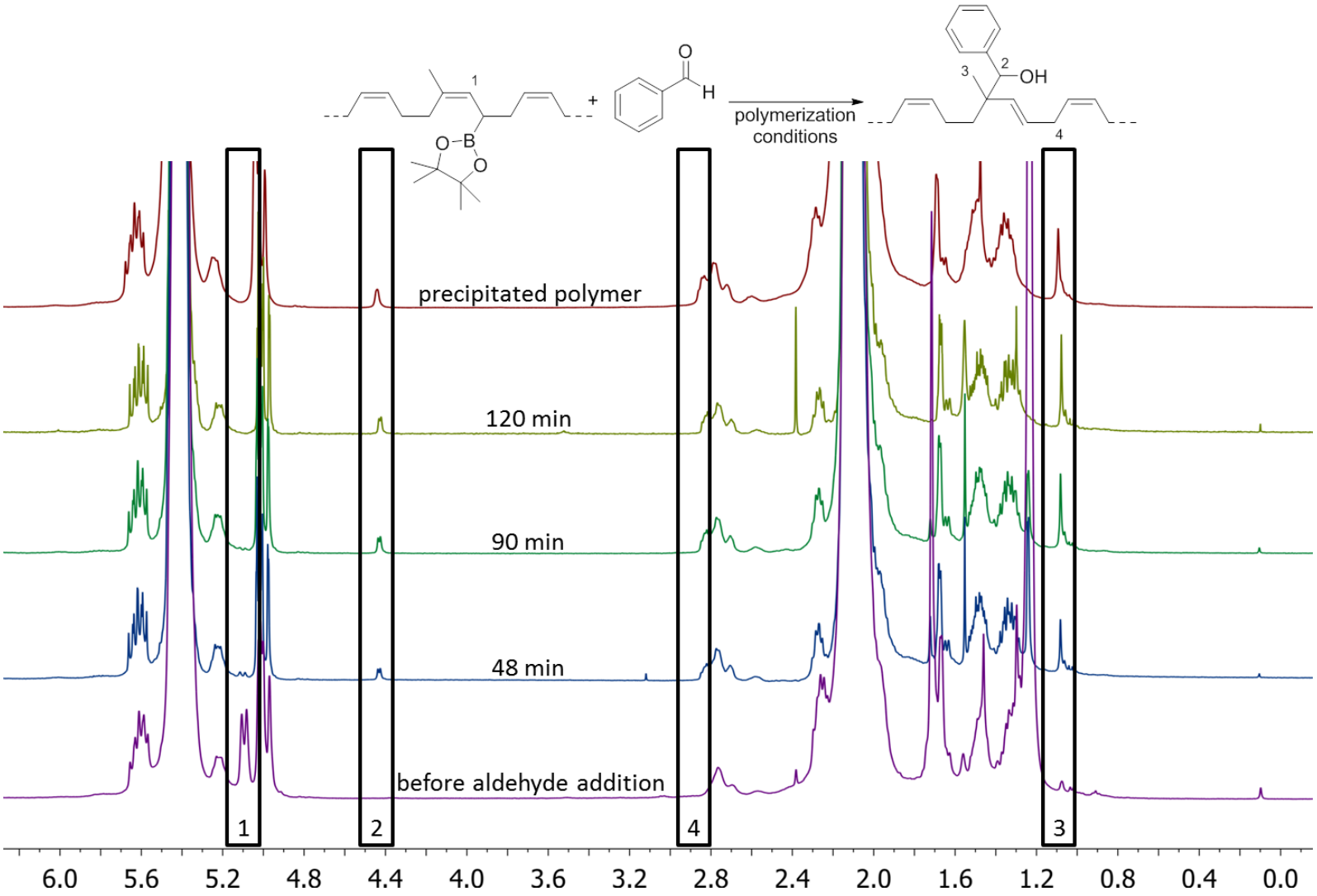
Toluene (19 mL) and 3-methylbuta-1,3-dien-1-ylboronic acid pinacol ester (150 mg, 0.77 mmol, 1 equiv.) were added to a Schlenk flask. The flask was pressurized with 1.05 bar of 1,3-butadiene. **Ni-1** (20 µmol, in 1 mL of toluene) was added to the stirred reaction mixture. The polymerization was conducted at room temperature under a constant butadiene pressure of 1.05 bar for 30 min. The butadiene feed was closed and benzaldehyde (32.5 mmol, 42 equiv.) was added. The mixture was stirred at 50 °C for 2 h and aliquots were taken after 48, 90, and 120 min. Residual butadiene was removed under reduced pressure and the polymer was precipitated in a mixture of 50 mg of BHT and 600 mL of methanol. Drying of the polymer under reduced pressure yielded 7.6 g of functionalized PBD.

4.2. *In-situ* Functionalization with 4-(1-Pyrrolidinyl)benzaldehyde

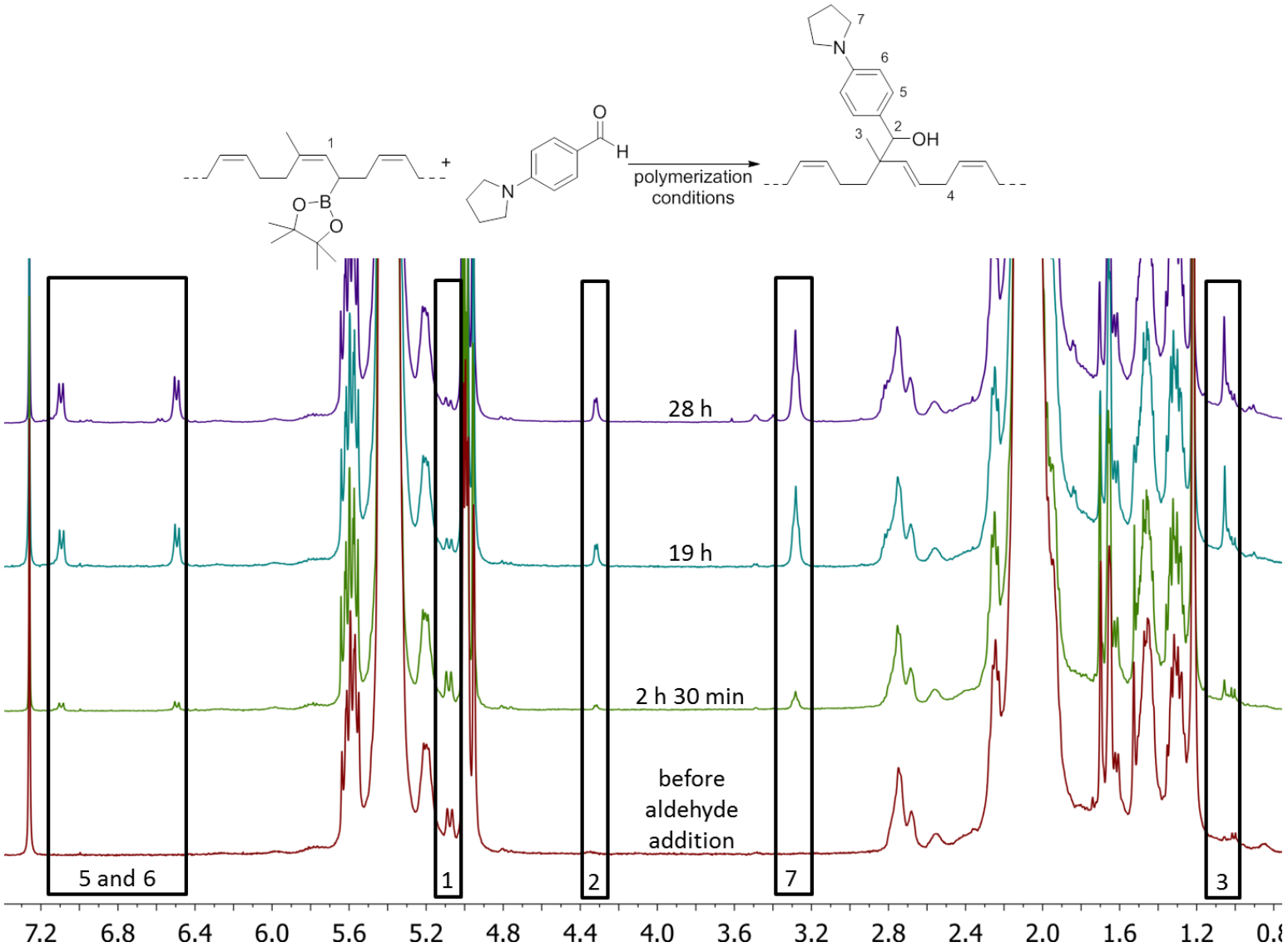


Toluene (19 mL) and 3-methylbuta-1,3-dien-1-ylboronic acid pinacol ester (140 mg, 0.72 mmol, 1 equiv.) were added to a Schlenk flask. The flask was pressurized with 1.05 bar of 1,3-butadiene. **Ni-1** (20 µmol, in 1 mL of toluene) was added to the stirred reaction mixture. The polymerization was conducted at room temperature under a constant butadiene pressure of 1.05 bar for 30 min. The butadiene feed was closed and 4-(1-pyrrolidinyl)benzaldehyde (7 mmol, 10 equiv.) was added. The mixture was stirred at 50 °C for 2 days and aliquots were taken after 2.5, 19, and 28 h. Residual butadiene was removed under reduced pressure and the polymer was precipitated in a mixture of 50 mg of BHT and 600 mL of methanol. Drying of the polymer under reduced pressure yielded 5.8 g of functionalized PBD.

4.3. NMR-Spectra of *In-situ* Functionalization with Benzaldehyde and 4-(1-Pyrrolidinyl)benzaldehyde

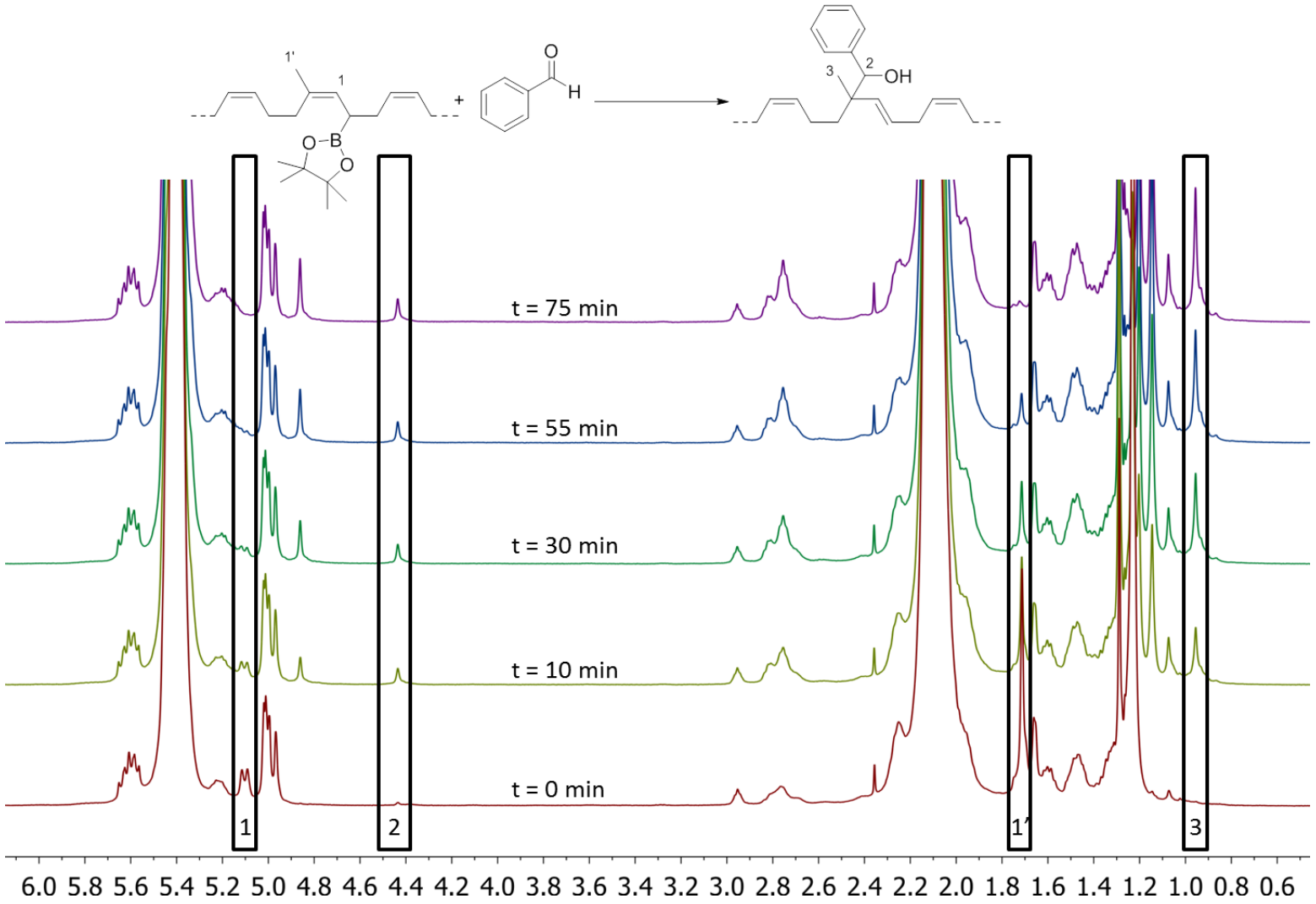


SI 52: ^{1}H NMR-spectra of aliquots taken from *in-situ* functionalization with benzaldehyde (recorded at 27 °C in $CDCl_3$).

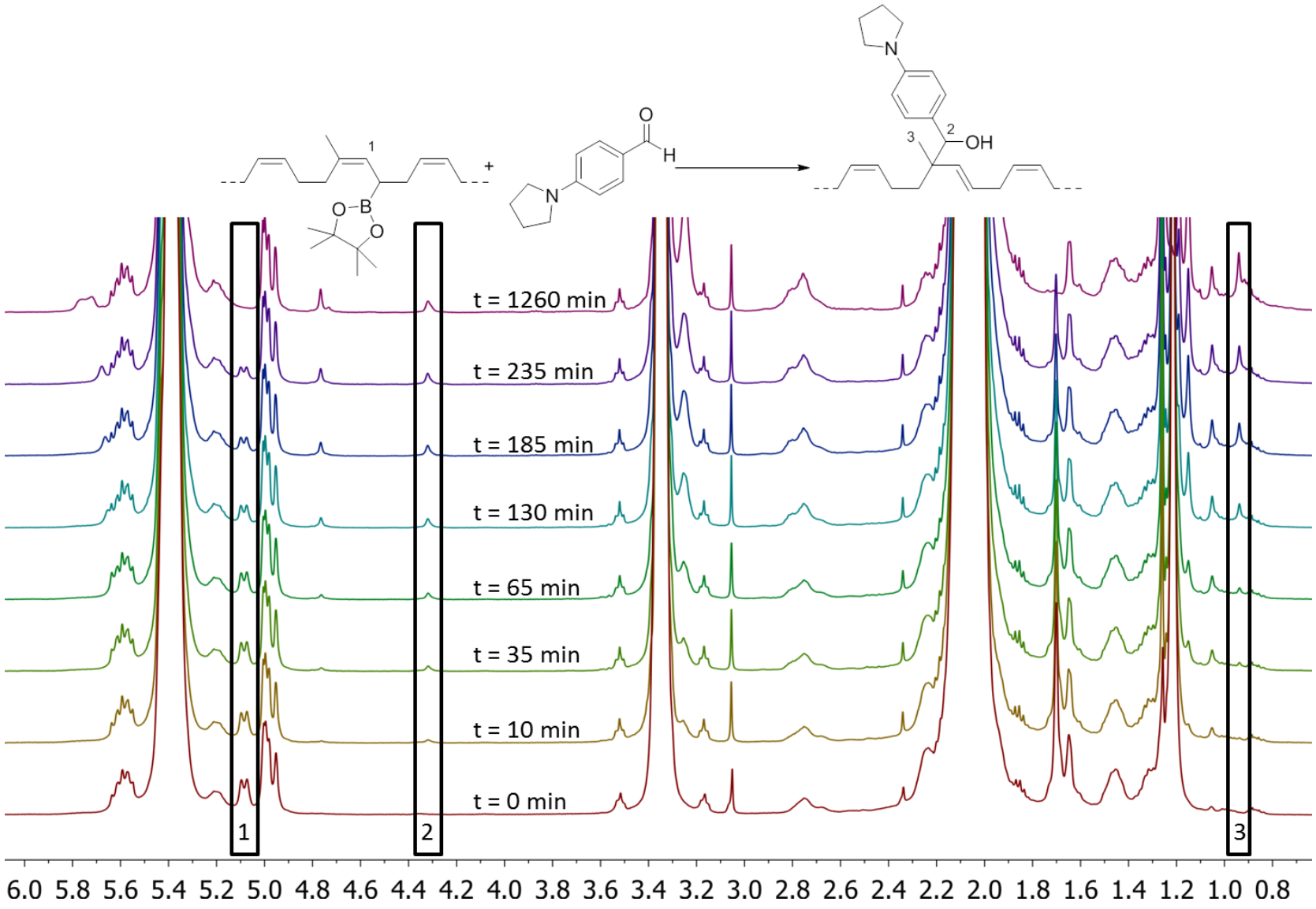


SI 53: ^{1}H NMR-spectra of aliquots taken from *in-situ* functionalization with 4-(1-pyrrolidinyl)benzaldehyde (recorded at 27 °C in $CDCl_3$).

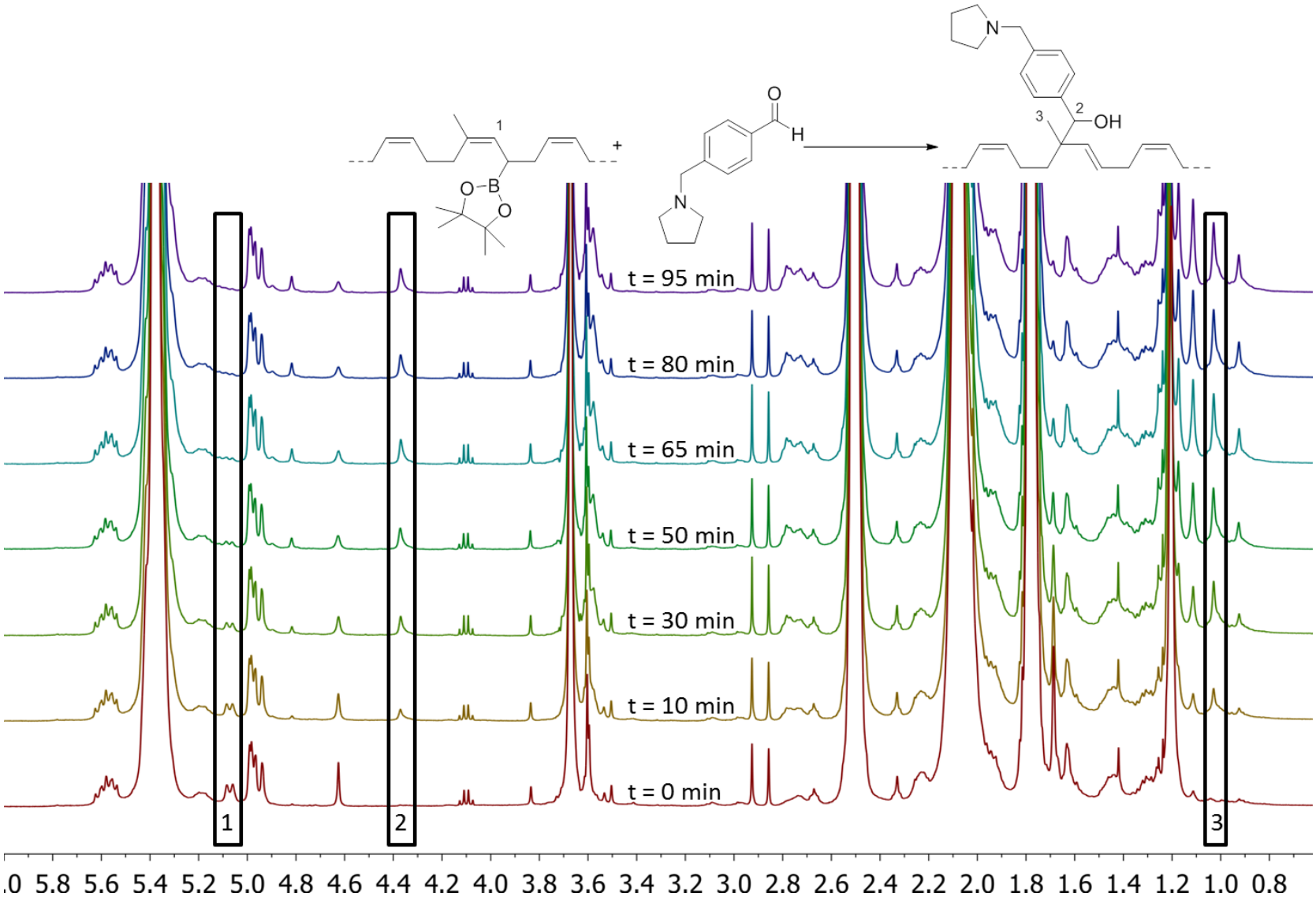
5. Allylboration Reactions with Different Aldehydes Followed over Time



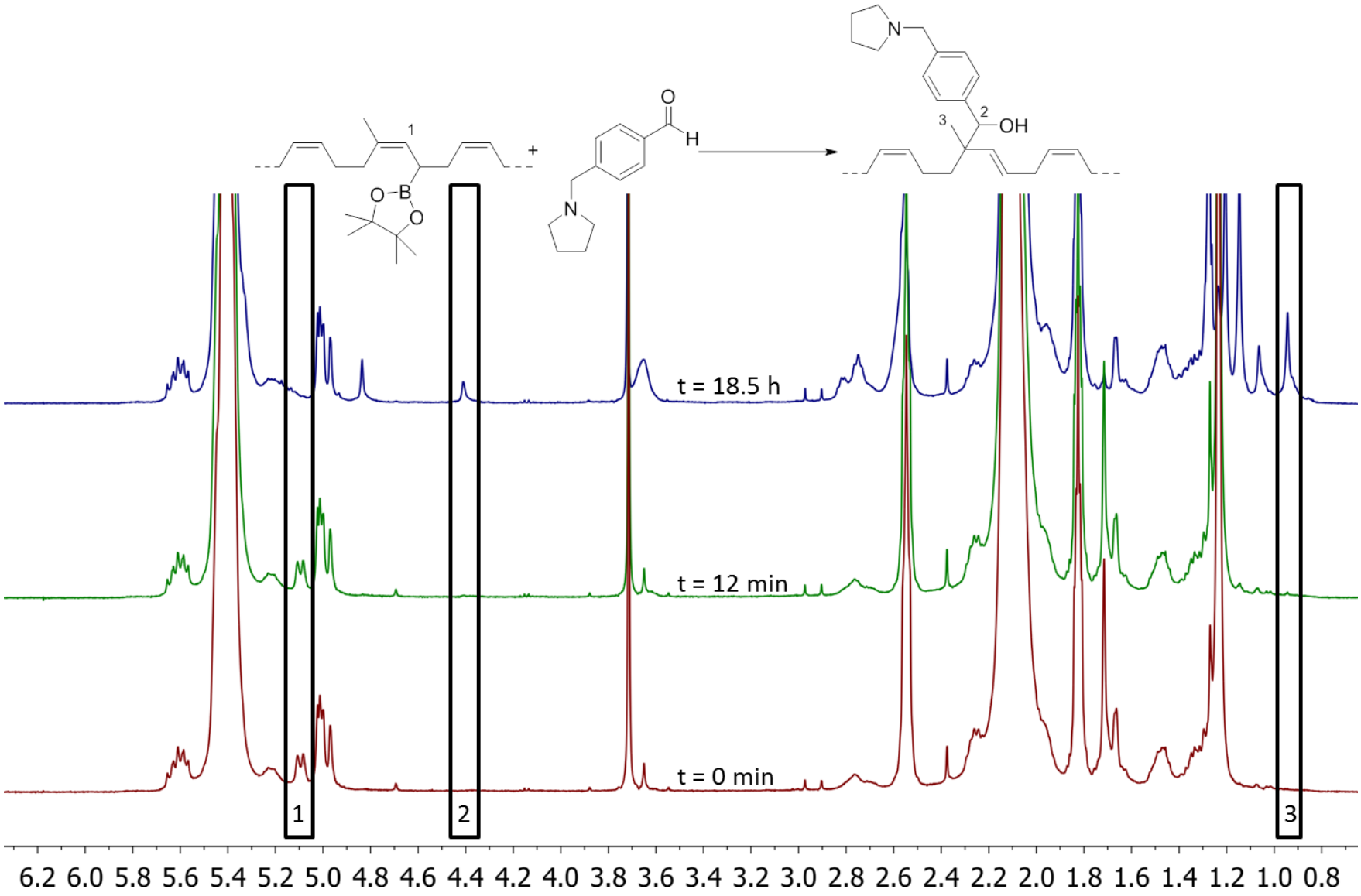
SI 54: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 10 equiv. benzaldehyde at 60 °C (Table 1, entry 1, recorded at 27 °C in $CDCl_3$).



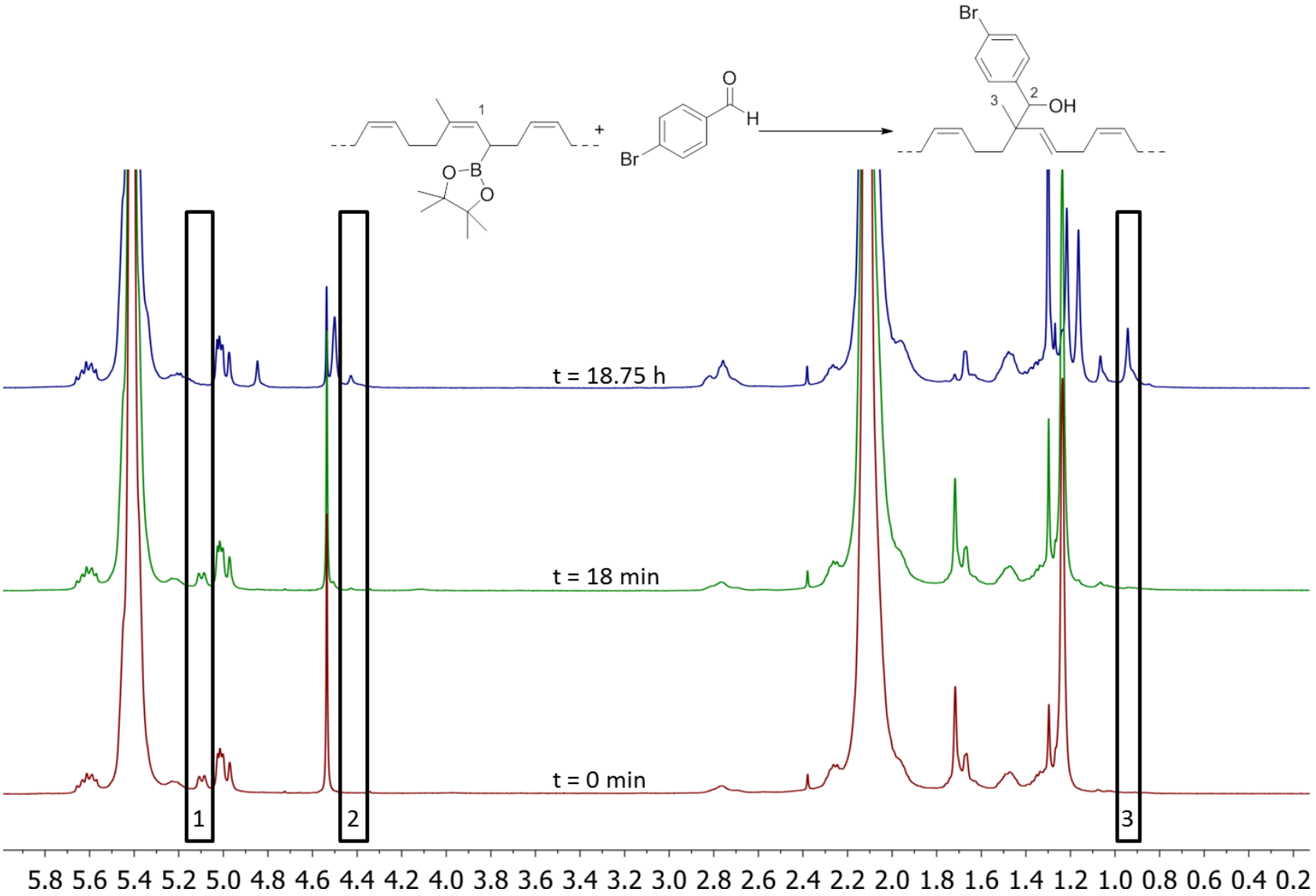
SI 55: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 10 equiv. 4-(1-pyrrolidinyl)benzaldehyde at 60 °C (Table 1, entry 2, recorded at 27 °C in $CDCl_3$).



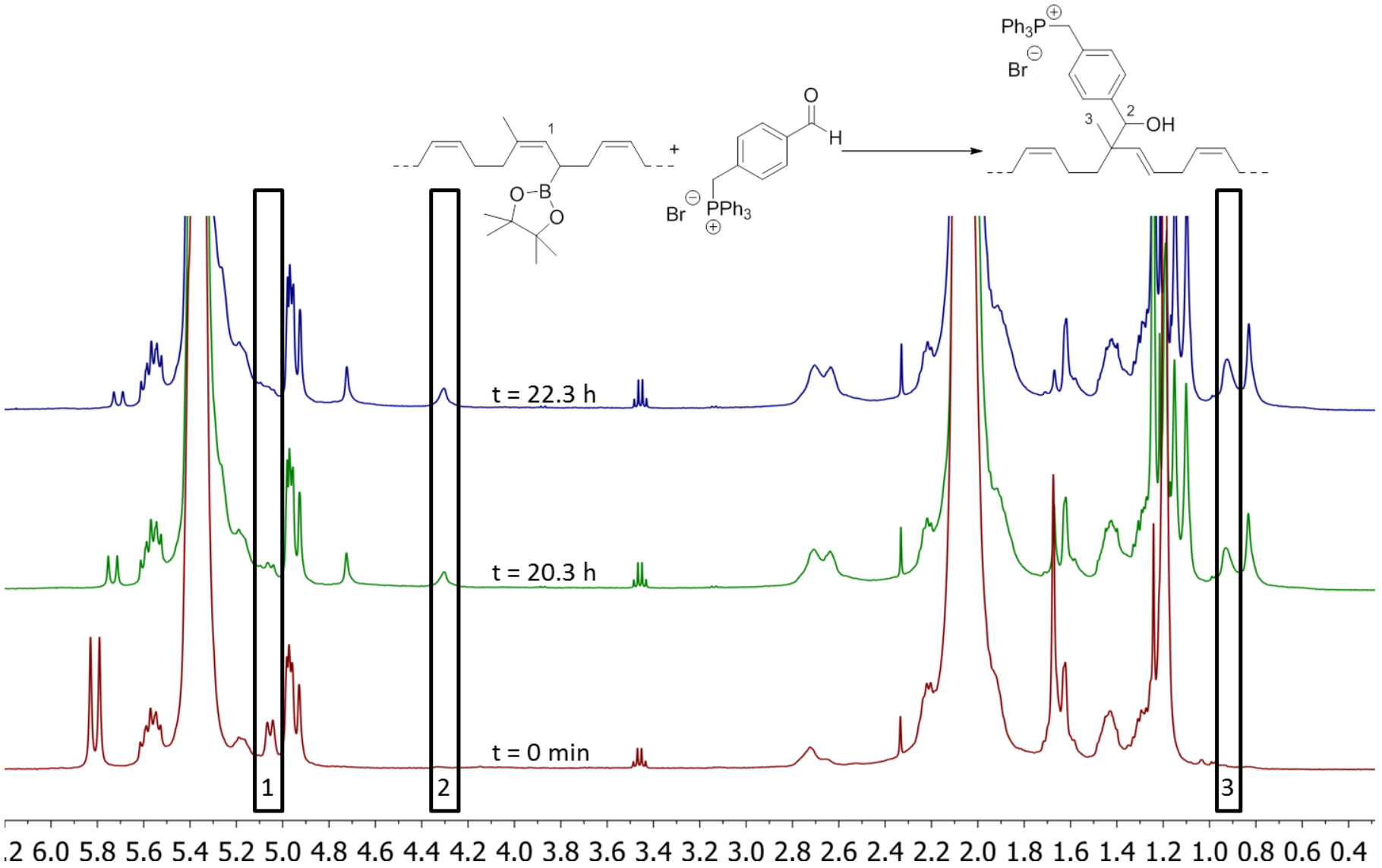
SI 56: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 10 equiv. 4-(pyrrolidinylmethyl)benzaldehyde at 60 °C (Table 1, entry 3, recorded at 27 °C in $CDCl_3$).



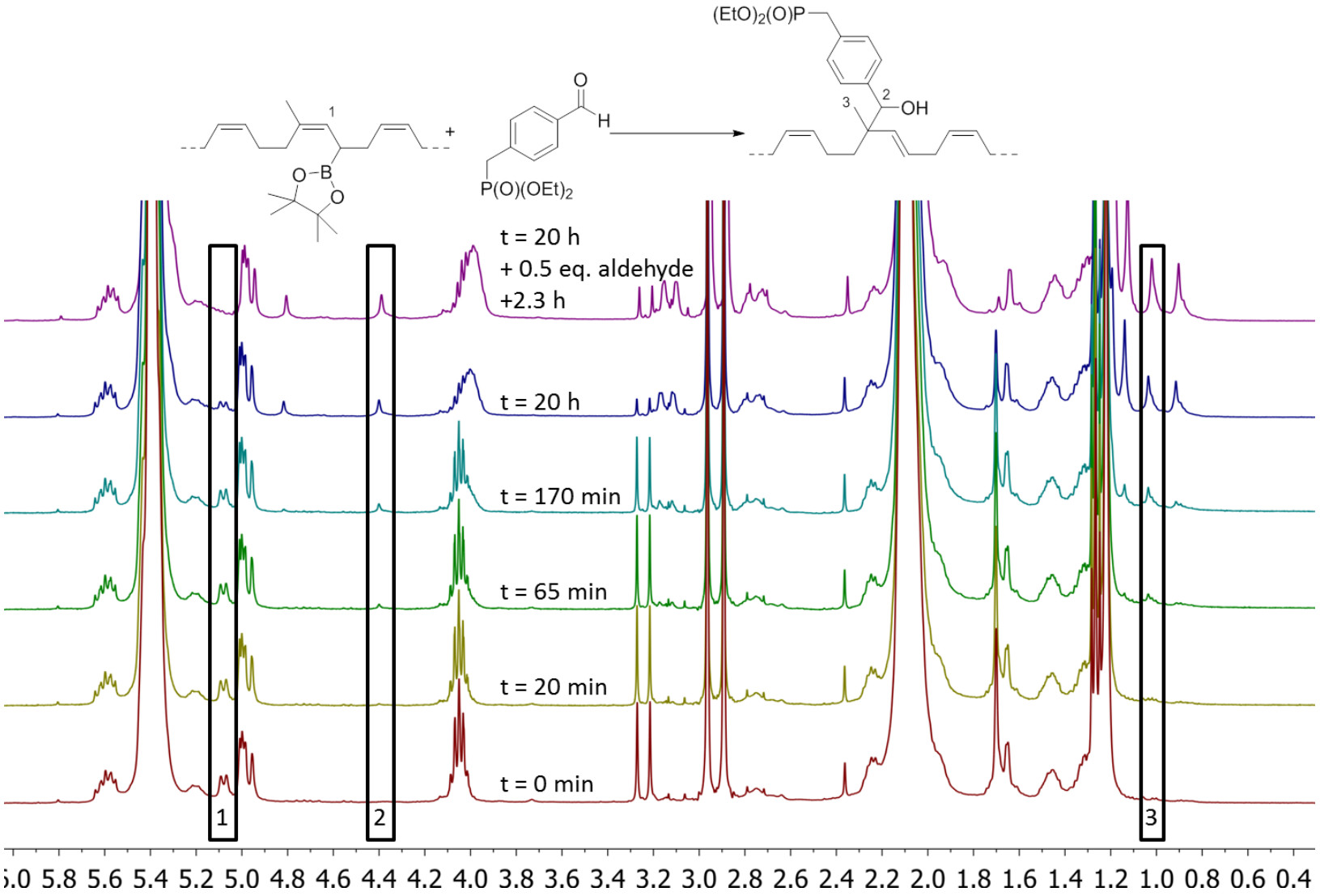
SI 57: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 1 equiv. 4-(pyrrolidinylmethyl)benzaldehyde at 60 °C (Table 1, entry 3, recorded at 27 °C in $CDCl_3$).



SI 58: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 1 equiv. 4-(bromomethyl)benzaldehyde at 60 °C (Table 1, entry 4, recorded at 27 °C in $CDCl_3$).

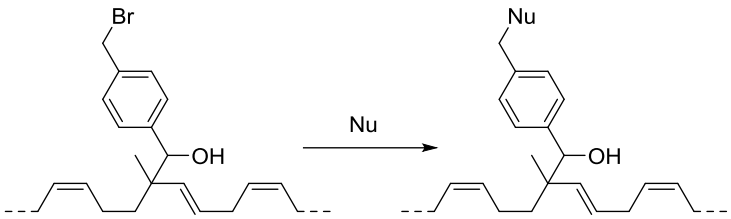


SI 59: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 1 equiv. (4-formylbenzyl)triphenylphosphonium bromide at 60 °C (Table 1, entry 5, recorded at 27 °C in $CDCl_3$).



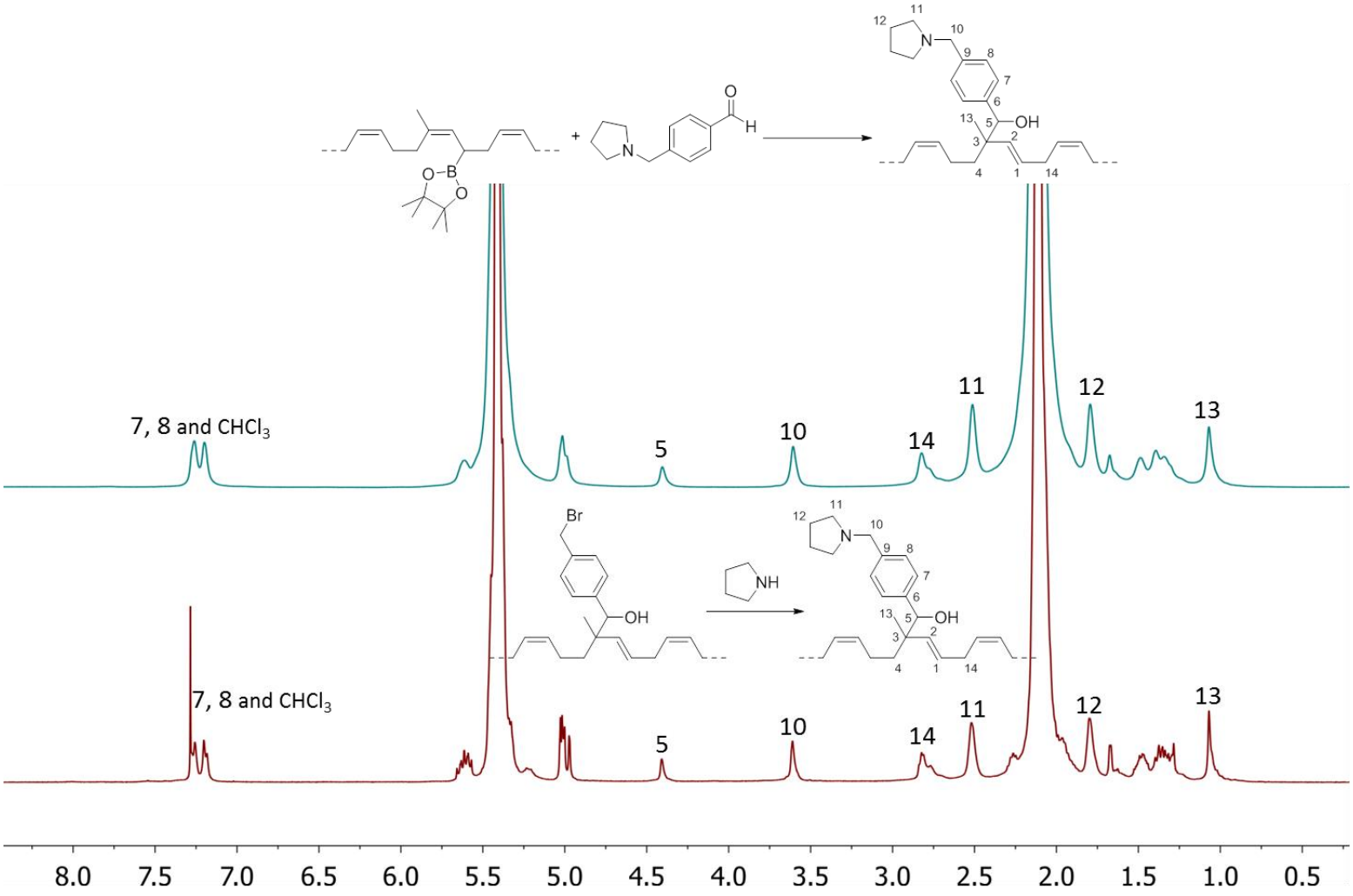
SI 60: ^{1}H NMR-spectra of allylboration reaction of **CoPo-1** with 0.7 equiv. diethyl (4-formylbenzyl)phosphonate at 60 °C. Additional 0.5 equiv. aldehyde were added after 20 h to observe complete conversion after 22.3 h (Table 1, entry 6, recorded at 27 °C in $CDCl_3$).

6. Reactivity of the Bromobenzyl Moiety Introduced by Allyl-boration

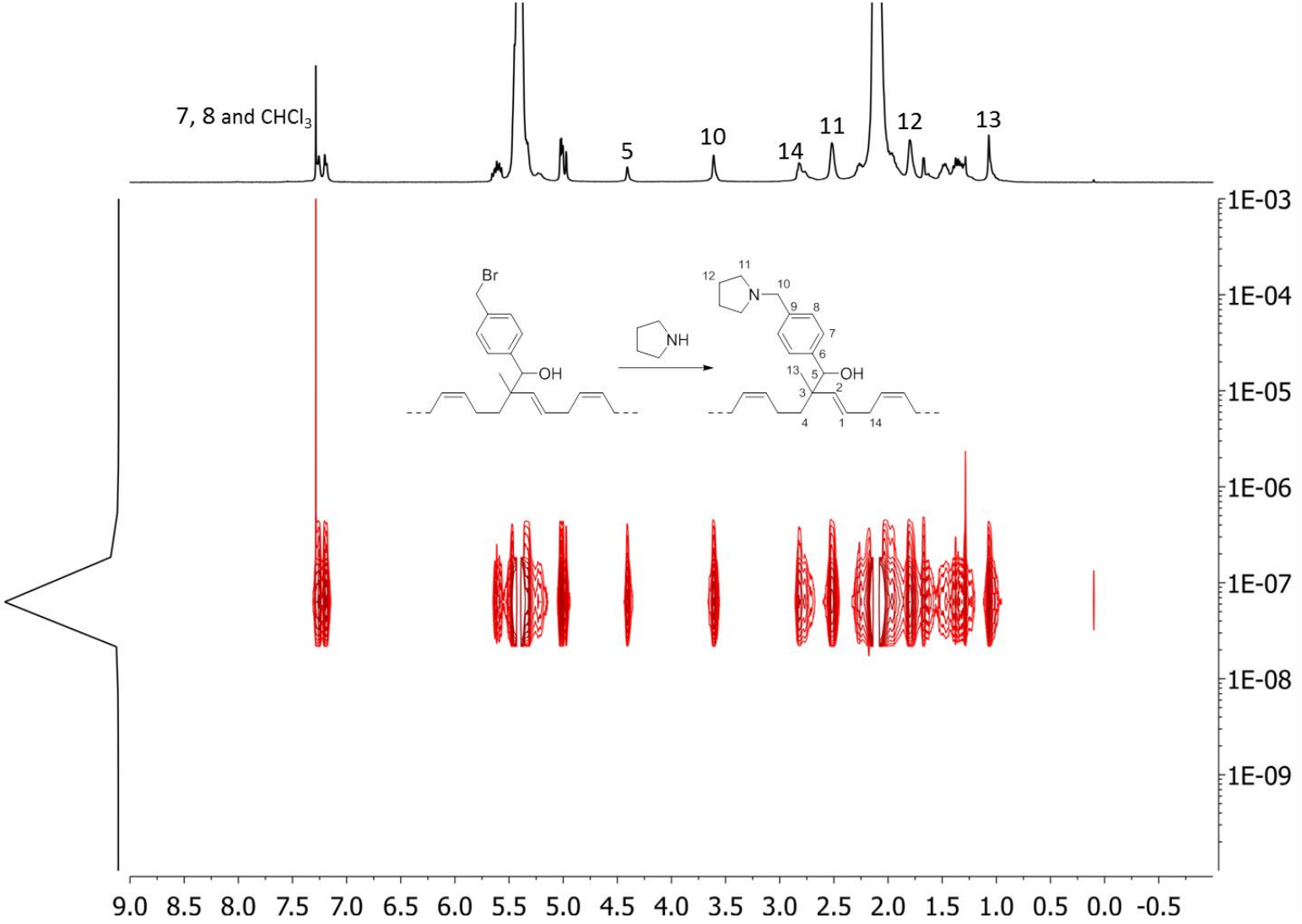


Nu: Pyrrolidine or NH_3

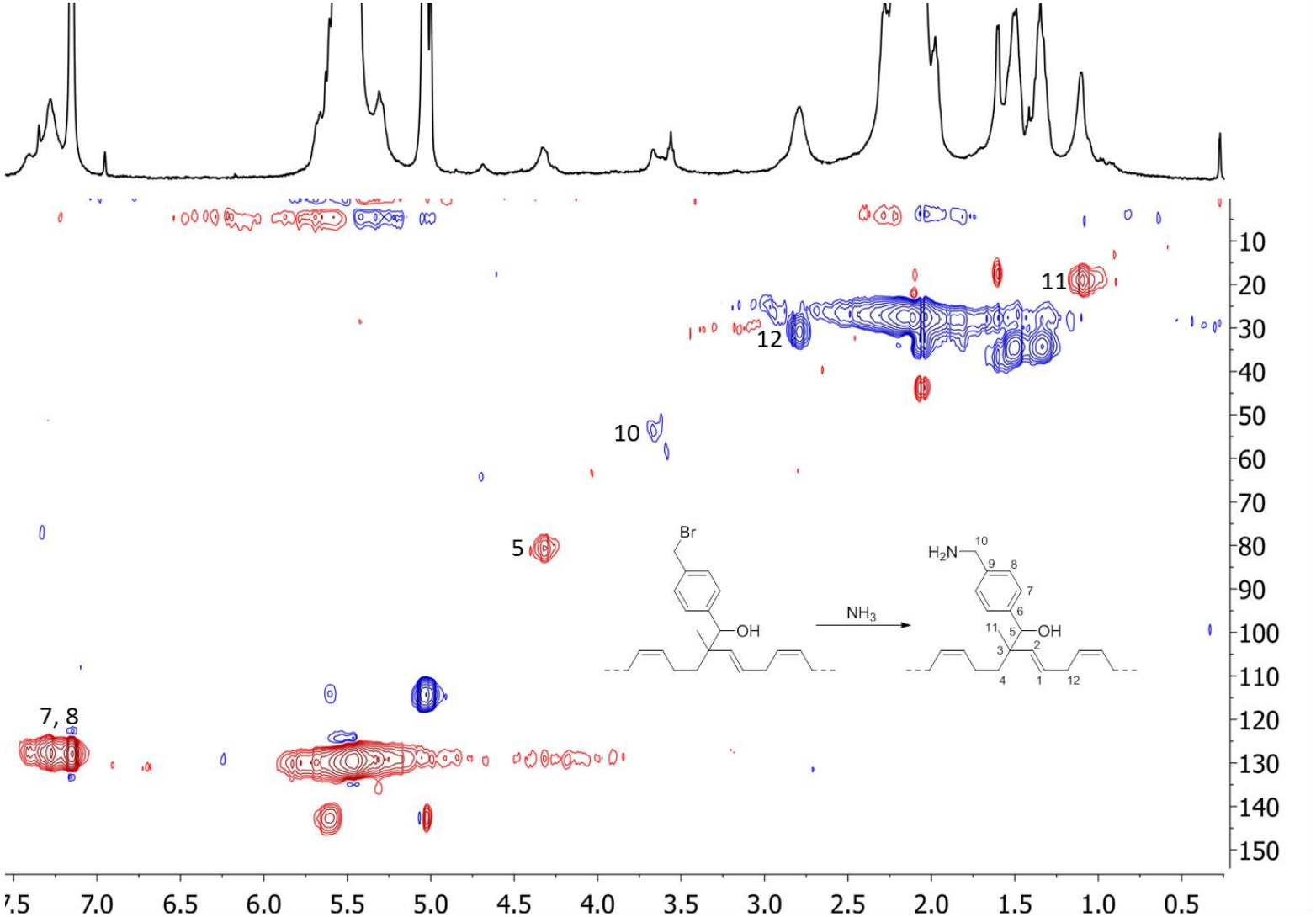
The allyl boration reaction of poly(butadiene-co-[(4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane]) (**CoPo-1**) with 4-(bromomethyl)benzaldehyde yields a copolymer functionalized with a reactive bromobenzyl moiety. Thus, a further, subsequent functionalization by a reaction of the bromobenzyl moiety with a nucleophile was probed: The nucleophile (pyrrolidine or NH_3 in THF, 10 equiv. compared to the bromobenzyl moiety) was added to a solution of the copolymer. Complete nucleophilic substitution occurs after 10 - 30 min at room temperature as observed by means of ^{1}H NMR. Precipitation in MeOH and drying under reduced pressure gives the functionalized copolymer.



SI 61: ^{1}H NMR-spectra of a polymer obtained from allylboration reaction of **CoPo-1** with 4-(pyrrolidinylmethyl)benzaldehyde (top) and a polymer functionalized by the reaction of the bromobenzyl moiety with pyrrolidine (bottom, recorded at 27 °C in $CDCl_3$).



SI 62: DOSY NMR-spectrum of a polymer functionalized by the reaction of the bromobenzyl moiety with pyrrolidine (bottom, recorded at 27 °C in $CDCl_3$).



SI 63: HSQC NMR-spectrum of a polymer functionalized by the reaction of the bromobenzyl moiety with ammonia (bottom, recorded at 27 °C in $CDCl_3$).

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