SUPPORTING INFORMATION

SYNERGETIC EFFECT OF MONOMER FUNCTIONAL GROUP COORDINATION IN CATALYTIC INSERTION POLYMERIZATION

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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]

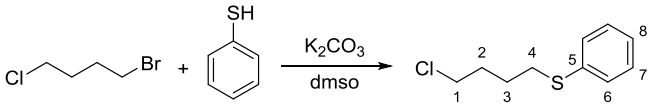
Chloroprene was commercially available (abcr) or synthesized by HCl elimination from 3,4,-dichlorobut-1-ene with KOH in DMSO at 75 °C. 1,3-Butadien was commercially available (Air Liquide) and passed through a commercial drying column (Air Liquide) prior to use. All other commercially available reagents were used without further purification. (5-Methylenehept-6-enyl)-phenylaniline (**Ph_2N-4-BD**), (4-methylenehex-5-enyl)aniline (**PhNH-3-BD**), and [(mesitylene)Ni(allyl)][BAr^F_4] (**Ni-1**) were synthesized as previously reported.[2] For a complete characterization of a Ph_2N-functionalized copolymer see Leicht, H.; Göttker-Schnetmann, I.; Mecking, S. *ACS Macro Lett.* **2016,** 5, (6), 777-780.

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 or in a glove box. In order to prevent accidental exposures to BD we recommend using 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 combination thereof.

1. Syntheses of Comonomers and Model Compounds

1.1. Synthesis of (4-chlorobutyl)(phenyl)sulfide

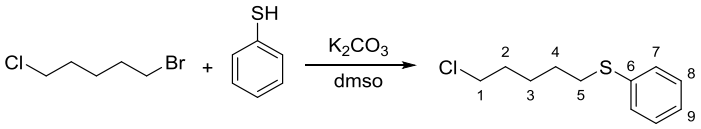


Thiophenol (8.19 g, 74.3 mmol, 0.98 equiv.) was dissolved in dmso (100 mL). K_2CO_3 (15.8 g, 113.7 mmol, 1.5 equiv.) and 1-bromo-4-chlorobutane (13.0 g, 75.8 mmol, 1.0 equiv.) were added. After 10 min at room temperature, the reaction mixture was heated to 50 °C and kept at that temperature for 2 h. Et_2O was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product, (4-chlorobutyl)(phenyl)sulfide (14 g, 70 mmol, 94 %) as colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C): δ = 7.41 – 7.35 (m, 2H, H6), 7.35 – 7.29 (m, 2H, H7), 7.24 – 7.19 (m, 1H, H8), 3.57 (t, $^3J_{HH}$ = 6.5 Hz, 2H, H1), 2.98 (t, $^3J_{HH}$ = 7.1 Hz, 2H, H4), 1.99 – 1.91 (m, 2H, H2), 1.89 – 1.78 (m, 2H, H3).

^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C): δ = 136.4 (C5), 129.4 (C6), 129.0 (C7), 126.1 (C8), 44.5 (C1), 33.1 (C4), 31.5 (C2), 26.4 (C3).

1.2. SYNTHESIS OF (5-CHLOROPENTYL)(PHENYL)SULFIDE

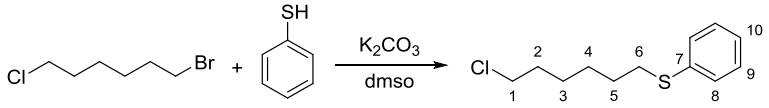


Thiophenol (7.7 g, 70.1 mmol, 1 equiv.) was dissolved in dmso (100 mL). K_2CO_3 (14.5 g, 105.1 mmol, 1.5 equiv.) and 1-bromo-5-chloropentane (13.0 g, 70.1 mmol, 1.0 equiv.) were added. After 10 min at room temperature, the reaction mixture was heated to 50 °C and kept at that temperature for 1.5 h. Et_2O was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product, (5-chloropentyl)(phenyl)sulfide (14.5 g, 68 mmol, 96 %) as colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C): δ = 7.40 – 7.29 (m, 4H, H7 and H8), 7.25 – 7.17 (m, 1H, H9), 3.55 (t, $^3J_{HH}$ = 6.6 Hz, 2H, H1), 3.07 – 2.82 (t, $^3J_{HH}$ = 7.1 Hz, 2H, H5), 1.86 – 1.77 (m, 2H, H2), 1.76 – 1.67 (m, 2H, H4), 1.66 – 1.56 (m, 2H, H3).

^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C): δ = 136.7 (C6), 129.1 (C7), 128.9 (C8), 125.9 (C9), 44.8 (C1), 33.5 (C5), 32.2 (C2), 28.5 (C4), 26.1 (C3).

1.3. SYNTHESIS OF (6-CHLOROHEXYL)(PHENYL)SULFIDE

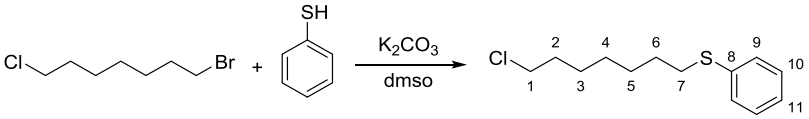


Thiophenol (7.7 g, 70.1 mmol, 1 equiv.) was dissolved in dmso (100 mL). K_2CO_3 (14.5 g, 105.1 mmol, 1.5 equiv.) and 1-bromo-6-chlorohexane (14.0 g, 70.1 mmol, 1.0 equiv.) were added. After 10 min at room temperature, the reaction mixture was heated to 50 °C and kept at that temperature for 2 h. Et_2O was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product, (6-chlorohexyl)(phenyl)sulfide (15.2 g, 66.5 mmol, 95 %) as colorless oil.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.30 – 7.25 (m, 2H, H8), 7.08 – 7.01 (m, 2H, H9), 6.97 – 6.91 (m, 1H, H10), 3.06 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H1), 2.61 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H6), 1.47 – 1.23 (m, 4H, H5 and H2), 1.14 – 0.93 (m, 4H, H3 and H4).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 137.4 (C7), 128.9 (C8), 128.8 (C9), 125.5 (C10), 44.4 (C1), 33.1 (C6), 32.2 (C2), 28.8 (C5), 27.7 (C3 or C4), 26.2 (C3 or C4).

1.4. SYNTHESIS OF (7-CHLOROHEPTYL)(PHENYL)SULFIDE



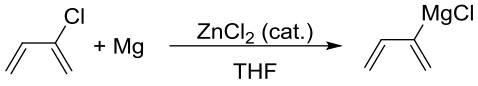
Thiophenol (1.5 g, 14.05 mmol, 1 equiv.) was dissolved in dmso (45 mL). K_2CO_3 (2.9 g, 21.1 mmol, 1.5 equiv.) and 1-bromo-7-chloroheptane (3.0 g, 14.2 mmol, 1.01 equiv.) were added. After 30 min at room temperature, the reaction mixture was heated to 50 °C and kept at that temperature for 1.5 h. Et_2O was added and the

organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product, (7-chloroheptyl)(phenyl)sulfide (3.0 g, 12.4 mmol, 88 %) as light yellow oil.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.33 – 7.24 (m, 2H, H9), 7.10 – 7.01 (m, 2H, H10), 6.98 – 6.89 (m, 1H, H11), 3.16 – 3.03 (m, 2H, H1), 2.65 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H7), 1.55 – 1.27 (m, 4H, H2 and H6), 1.20 – 1.00 (m, 4H, H3 and H5), 0.99 – 0.84 (m, 2H, H4).

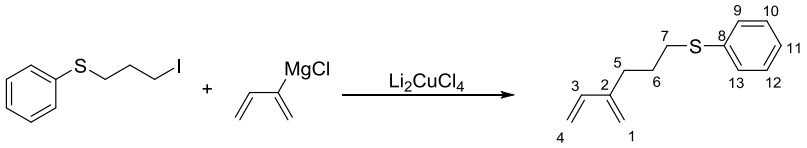
^{13}C-NMR (101 MHz, $CDCl_3$, 27 °C): δ = 137.0 (C8), 128.9 (C9), 128.9 (C10), 125.7 (C11), 45.1 (C1), 33.6 (C7), 32.6 (C2), 29.1 (C6), 28.6 (C3 or C5), 28.5 (C4), 26.8 (C3 or C5).

1.5. SYNTHESIS OF BUTA-1,3-DIEN-2-YLMAGNESIUM CHLORIDE[3]



A flame dried three-neck flask was charged with magnesium turnings (8.3 g, 338.90 mmol, 3.75 equiv.). These were layered with THF (20 mL). Subsequently, 1,2-dibromoethane (0.1 mL) and a solution of zinc(II) chloride were added. The zinc(II) chloride solution was prepared by dissolving dry zinc(II) chloride (0.93 g, 6.80 mmol, cat.) in THF (8 mL) under vigorous stirring. Additional 12 mL of THF were added. A 50 wt% solution of chloroprene in xylene (40 g, 225.90 mmol, 2.50 equiv.) was diluted with THF (40 mL). Upon addition of a few mL of the premixed chloroprene solution, a slight boiling of the reaction mixture was visible. Thereafter, the residual chloroprene solution was added drop-wise. Subsequently, the mixture was heated to 50 °C for 4 h and a green solution, which contained the desired product, buta-1,3-dien-2-ylmagnesiumchloride, was obtained. The solution was directly used in the following step without further purification.

1.6. SYNTHESIS OF (4-METHYLENEHEX-5-ENYL)(PHENYL)SULFIDE (**PHS-3-BD**)



((3-iodopropyl)thio)-benzene (0.7 g, 2.5 mmol, may be synthesized according to Lete et al.[4]) was cooled to -20 °C, Li_2CuCl_4 (0.01 equiv, 21.2 mg LiCl + 33.6 mg $CuCl_2$) in 5 mL THF was added. Chloroprene-Grignard solution (2.75 mmol, 1.1 equiv in 2 mL THF) was added dropwise. The solvent was removed under reduced pressure after stirring for 30 min and warming to room temperature. Column chromatography (PE/EtOAc 20:1) gave 342.3 mg (1.68 mmol, 67%) of the desired compound as yellowish oil.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.28 – 7.25 (m, 2H, H9 and 13), 7.02 – 6.99 (m, 2H, H10 and 12), 6.93 – 6.90 (m, 1H, H11), 6.25 (dd, $^3J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 17.6 Hz, 1H, H3), 5.08 (d, $^3J_{HH}$ = 17.6 Hz, 1H, H4), 4.91 (d, $^3J_{HH}$ = 10.8 Hz, 1H, H4), 4.89 (s, 1H, H1), 4.83 (s, 1H, H1), 2.67 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H7), 2.27 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H5), 1.80 (quint, $^3J_{HH}$ = 7.2 Hz, 2H, H6).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 145.6 (C2), 138.9 (C3), 137.5 (C8), 129.3 (C9 and C13), 129.1 (C10 and C12), 125.8 (C11), 116.4 (C1), 113.5 (C4), 33.3 (C7), 30.5 (C5), 27.8 (C6).

1.7. SYNTHESIS OF (5-METHYLENEHEPT-6-ENYL)(PHENYL)SULFIDE (**PHS-4-BD**)

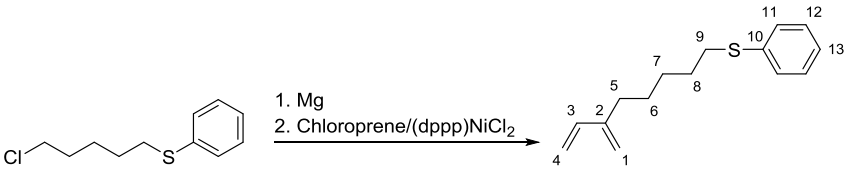
Mg turnings (0.29 g, 12 mmol, 1.2 equiv.) were layered with THF and activated with 1,2-dibromoethane. The reaction was started by addition of (4-chlorobutyl)(phenyl)sulfide (2.0 g, 10 mmol, 1 equiv.) in THF (total amount ca. 15 mL) and followed by heating to 45 °C for 3.5 h. The formed Grignard reagent was used in the next step without further purification.

Chloroprene (1.06 g, 12 mmol, 1.2 equiv, in 15 mL THF) and (dppp)$NiCl_2$ (0.05 g, 0.1 mmol, 0.01 equiv.) were mixed in another flask. The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 1.5 h. THF was removed under reduced pressure and Et_2O was added. The organic phase was washed with an NH_4Cl solution and water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (pentane:ethyl acetate = 100:3 v/v) to yield the desired product, (5-methylenehept-6-en-1-yl)(phenyl)sulfide (930 mg, 4.3 mmol, 43%).

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.28 – 7.24 (m, 2H, H10), 7.04 (vt, $^3J_{HH}$ = 7.9 Hz, 2H, H11), 6.93 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H12), 6.31 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, H3), 5.11 (d, $^3J_{HH}$ = 17.6 Hz, 1H, H4), 4.96 (d, $^3J_{HH}$ = 10.8 Hz, 1H, H4), 4.93 (s, 1H, H1), 4.86 (s, 1H, H1), 2.63 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H8), 2.01 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H5), 1.47 (m, 4H, H6 and H7).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 146.3 (C2), 139.2 (C3), 137.8 (C9), 129.3 (C10), 129.1 (C11), 125.8 (C12), 116.0 (C1), 113.3 (C4), 33.5 (C8), 31.1 (C5), 29.3 (C7), 27.5 (C6).

1.8. SYNTHESIS OF (6-METHYLENEOCT-7-ENYL)(PHENYL)SULFIDE (**PHS-5-BD**)



Mg turnings (0.29 g, 12 mmol, 1.2 equiv.) were layered with THF and activated with 1,2-dibromoethane. The reaction was started by addition of (5-chloropentyl)(phenyl)sulfide (2.15 g, 10 mmol, 1 equiv.) in THF (total amount ca. 15 mL) and followed by heating to 50 °C for 2.5 h. The formed Grignard reagent was used in the next step without further purification.

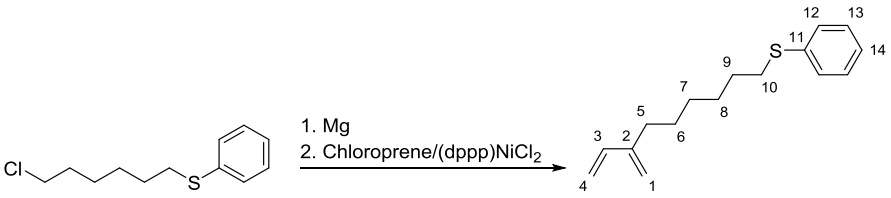
Chloroprene (1.06 g, 12 mmol, 1.2 equiv, in 15 mL THF) and (dppp)$NiCl_2$ (0.1 g, 0.2 mmol, 0.02 equiv.) were mixed in another flask. The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 1.5 h. THF was removed under reduced pressure and Et_2O was added. The organic phase was washed with an NH_4Cl solution and water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (pentane:ethyl acetate = 100:2 v/v) to yield the desired product, (6-methyleneoct-7-enyl)(phenyl)sulfide (784 mg, 3.4 mmol, 34%).

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.27 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H11), 7.03 (vt, $^3J_{HH}$ = 7.9 Hz, 2H, H12), 6.94 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H13), 6.34 (dd, $^3J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 10.9 Hz, 1H, H3), 5.14 (d, $^3J_{HH}$ = 17.9, 1H, H4),

4.99 – 4.94 (m, 2H, H1 and H4), 4.90 (s, 1H, H1), 2.64 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H9), 2.06 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H5), 1.48 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, H8), 1.32 (m, 2H, H6), 1.23 (m, 2H, H7).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 146.6 (C2), 139.4 (C3), 137.9 (C10), 129.3 (C11), 129.1 (C12), 125.8 (C13), 115.9 (C1), 113.2 (C4), 33.6 (C9), 31.5 (C5), 29.3 (C8), 28.9 (C7), 27.9 (C6).

1.9. SYNTHESIS OF (7-METHYLENENON-8-ENYL)(PHENYL)SULFIDE (**PHS-6-BD**)



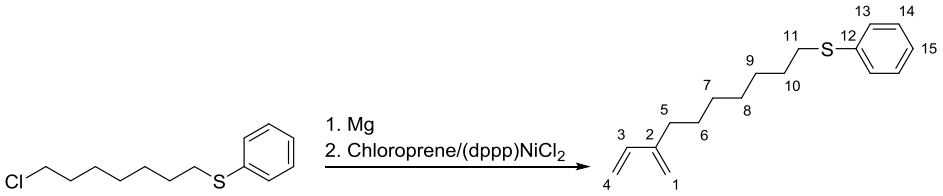
Mg turnings (0.29 g, 12 mmol, 1.2 equiv.) were layered with THF and activated with 1,2-dibromoethane. The reaction was started by addition of (6-chlorohexyl)(phenyl)sulfide (2.29 g, 10 mmol, 1 equiv.) in THF (total amount ca. 15 mL) and followed by heating to 50 °C for 2.5 h. The formed Grignard reagent was used in the next step without further purification.

Chloroprene (1.06 g, 12 mmol, 1.2 equiv, in 15 mL THF) and (dppp)$NiCl_2$ (0.1 g, 0.2 mmol, 0.02 equiv.) were mixed in another flask. The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 1.5 h. THF was removed under reduced pressure and Et_2O was added. The organic phase was washed with an NH_4Cl solution and water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (pentane:ethyl acetate = 100:2 v/v) to yield the desired product, (7-methylenenon-8-en-1-yl)(phenyl)sulfide (985 mg, 4.0 mmol, 40%).

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.29 – 7.20 (m, 2H, H12), 7.10 – 7.00 (m, 2H, H13), 7.00 – 6.90 (m, 1H, H14), 6.34 (dd, $^3J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 10.9 Hz, 1H, H3), 5.16 (d, $^3J_{HH}$ = 17.5 Hz, 1H, H4), 4.99 – 4.91 (m, 3H, H1 and H4), 2.67 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H10), 2.09 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H5), 1.48 (quint, $^3J_{HH}$ = 7.6 Hz, 2H, H9), 1.36 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, H6), 1.27 – 1.18 (m, 2H, H8), 1.16 – 1.07 (m, 2H, H7).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 146.7 (C2), 139.4 (C3), 137.9 (C11), 129.1 (C12), 129.1 (C13), 125.8 (C14), 115.9 (C1), 113.2 (C4), 33.7 (C10), 31.6 (C5), 29.5 (C9), 29.4 (C7), 29.0 (C8), 28.4 (C6).

1.10. SYNTHESIS OF (8-METHYLENEDEC-9-ENYL)(PHENYL)SULFIDE (**PHS-7-BD**)



Mg turnings (0.20 g, 8.4 mmol, 1.2 equiv.) were layered with THF and activated with 1,2-dibromoethane. The reaction was started by addition of (7-chloroheptyl)(phenyl)sulfide (1.7 g, 7 mmol, 1 equiv.) in THF (total amount ca. 10 mL) and followed by heating to 50 °C for 3 h. The formed Grignard reagent was used in the next step without further purification.

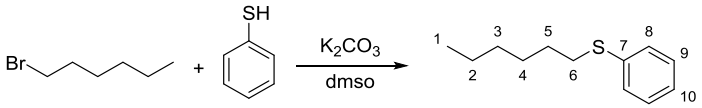
Chloroprene (0.74 g, 8.4 mmol, 1.2 equiv, in 10 mL THF) and (dppp)$NiCl_2$ (0.08 g, 0.14 mmol, 0.02 equiv.) were mixed in another flask. The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 1.5 h. THF was removed under reduced pressure and Et_2O was added. The organic phase was washed with an NH_4Cl solution and water, dried over $MgSO_4$ and the solvent was removed under reduced

pressure. The crude product was purified by column chromatography (pentane:ethyl acetate = 100:2 v/v) to yield the desired product, (8-methylenedec-9-en-1-yl)(phenyl)sulfide (767 mg, 2.9 mmol, 42%).

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.29 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H13), 7.04 (vt, $^3J_{HH}$ = 7.8 Hz, 2H, H14), 6.94 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H15), 6.37 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, H3), 5.20 (d, $^3J_{HH}$ = 17.6, 1.2 Hz, 1H, H4), 5.03 – 4.91 (m, 3H, H1 and H4), 2.68 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H11), 2.13 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H5), 1.50 (quint, $^3J_{HH}$ = 7.3 Hz, 2 H, H10), 1.41 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, H6), 1.16 (m, 6H, H7, H8, and H9).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 146.9 (C2), 139.5 (C3), 137.9 (C12), 129.2 (C13 or C14), 129.1 (C13 or C14), 125.8 (C15), 115.8 (C1), 113.2 (C4), 33.7 (C11), 31.7 (C5), 29.8 – 29.4 (3C, C7, C8, and C9), 29.1 (C10), 28.4 (C6).

1.11. SYNTHESIS OF HEXYL(PHENYL)SULFIDE (**PHS-6**)

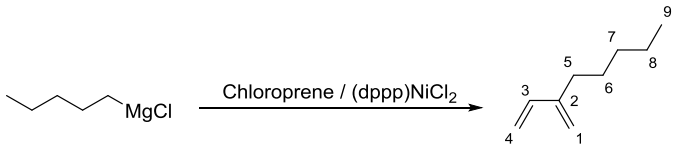


Thiophenol (5.5 g, 50 mmol, 1 equiv.) was dissolved in dmso (75 mL). K_2CO_3 (10.4 g, 75 mmol, 1.5 equiv.) and 1-bromohexane (9.6 g, 58.5 mmol, 1.17 equiv.) were added. After 10 min at room temperature, the reaction mixture was heated to 50 °C and kept at that temperature for 2 h. Et_2O was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product hexyl(phenyl)sulfide in quantitative yield as colorless oil.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.32 – 7.25 (m, 2H, H8), 7.07 – 7.00 (m, 2H, H9), 6.93 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, H10), 2.67 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H6), 1.49 (quint, $^3J_{HH}$ = 7.4 Hz, 1H, H5), 1.29 – 1.01 (m, 6H, H2, H3, and H4), 0.82 (t, $^3J_{HH}$ = 7.2 Hz, 3H, H1).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 138.0 (C7), 129.2 (C8), 129.1 (C9), 125.7 (C10), 33.7 (C6), 31.7 (C3), 29.5 (C5), 28.8 (C4), 22.9 (C2), 14.3 (C1).

1.12. SYNTHESIS OF 3-METHYLENEOCTENE (**5-BD**)

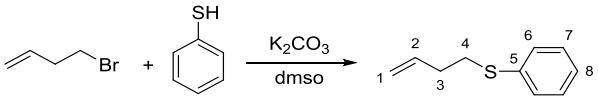


(dppp)$NiCl_2$ (0.1 g, 0.2 mmol, 0.02 equiv.) and chloroprene (0.94, 10.5 mmol, 1.05 equiv.) were dissolved in THF (5 mL). The reaction mixture was cooled to 0 °C and a pentylmagnesium chloride solution (2.0 M in THF, 5 mL, 1.0 equiv.) was added dropwise. The mixture was stirred for 40 minutes at room temperature. The solvent was removed and pentane (5 mL) was added. The resulting suspension was filtered over celite and the product was used as pentane stock solution without further purification.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 6.37 (dd, $^3J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, H3), 5.19 (d, $^3J_{HH}$ = 17.7 Hz, 1H, H4), 5.01 – 4.93 (m, 3H, H1 and H4), 2.15 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H5), 1.46 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, H6), 1.27 – 1.19 (m, 4H, H7 and H8), 0.87 (t, $^3J_{HH}$ = 6.8 Hz, 3H, H9).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 146.9 (C2), 139.5 (C3), 115.7 (C1), 113.1 (C4), 32.2 (C8), 31.8 (C5), 28.3 (C6), 23.0 (C7), 14.3 (C9).

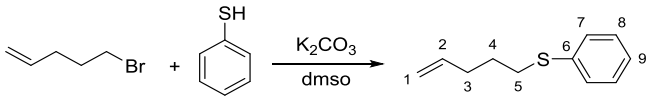
1.13. SYNTHESIS OF BUT-3-ENYL(PHENYL)SULFIDE (**PHS-4-ENE**)



Thiophenol (777 mg, 7.05 mmol, 1 equiv.) was dissolved in dmso (10 mL). K_2CO_3 (947 mg, 10.6 mmol, 1.5 equiv.) and 4-bromobutene (1.0 g, 7.4 mmol, 1.05 equiv.) were added. The reaction mixture was stirred at 65 °C for 30 min and subsequently at 50 °C for 1 h. Pentane was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product but-3-enyl(phenyl)sulfide (711 mg, 4.3 mmol, 61%) as colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.26 – 7.21 (m, 2H, H6), 7.04 – 6.97 (m, 2H, H7), 6.94 – 6.89 (m, 1H, H8), 5.63 (ddt, $^3J_{HH}$ = 16.3 Hz, $^3J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, H2), 4.94 – 4.86 (m, 2H, H1), 2.65 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H4), 2.22 – 2.12 (m, 2H, H3).

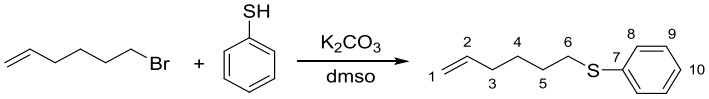
1.14. SYNTHESIS OF PENT-4-ENYL(PHENYL)SULFIDE (**PHS-5-ENE**)



Thiophenol (777 mg, 7.05 mmol, 1 equiv.) was dissolved in dmso (10 mL). K_2CO_3 (947 mg, 10.6 mmol, 1.5 equiv.) and 5-bromopentene (1.1 g, 7.4 mmol, 1.05 equiv.) were added. The reaction mixture was stirred at 65 °C for 30 min and subsequently at 50 °C for 1 h. Pentane was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product pent-4-enyl(phenyl)sulfide (740 mg, 4.2 mmol, 59%) as colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.29 – 7.23 (m, 2H, H7), 7.06 – 6.98 (m, 2H, H8), 6.95 – 6.88 (m, 1H, H9), 5.57 (ddt, $^3J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, 1H, H2), 4.97 – 4.88 (m, 2H, H1), 2.63 (t, $^3J_{HH}$ = = 7.3 Hz, 2H, H5), 1.99 – 1.89 (m, 2H, H3), 1.54 (tt, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, H4).

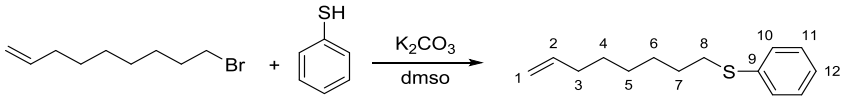
1.15. SYNTHESIS OF HEX-5-ENYL(PHENYL)SULFIDE (**PHS-6-ENE**)



Thiophenol (777 mg, 7.05 mmol, 1 equiv.) was dissolved in dmso (10 mL). K_2CO_3 (947 mg, 10.6 mmol, 1.5 equiv.) and 6-bromohexene (1.2 g, 7.4 mmol, 1.05 equiv.) were added. The reaction mixture was stirred at 65 °C for 30 min and subsequently at 50 °C for 1 h. Pentane was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product hex-5-enyl(phenyl)sulfide (690 mg, 3.6 mmol, 48%) as colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.30 – 7.24 (m, 2H, H8), 7.06 – 6.99 (m, 2H, H9), 6.96 – 6.90 (m, 1H, H10), 5.65 (ddt, $^3J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 6.7 Hz, 1H, H2), 4.98 – 4.91 (m, 2H, H1), 2.62 (t, $^3J_{HH}$ = = 7.3 Hz, 2H, H6), 1.87 – 1.78 (m, 2H, ^{H3}), 1.47 (vquint, $^3J_{HH}$ = 7.8 Hz, 2H, H5), 1.29 (vquint, $^3J_{HH}$ = 7.1 Hz, 2H, H4).

1.16. SYNTHESIS OF OCT-7-ENYL(PHENYL)SULFIDE (**PHS-8-ENE**)

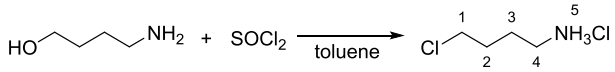


Thiophenol (6.6 g, 59.6 mmol, 1 equiv.) was dissolved in dmso (250 mL). K_2CO_3 (12.4 g, 89.4 mmol, 1.5 equiv.) and 8-bromooctene (11.5 g, 60.2 mmol, 1.01 equiv.) were added. The reaction mixture was stirred at 50 °C for 2 h. Et_2O was added and the organic phase was washed with water. Drying of the organic phase over $MgSO_4$ and removal of the solvent under reduced pressure yielded the desired product oct-7-enyl(phenyl)sulfide (12.5 mg, 56.7 mmol, 95%) as light yellow liquid. Parts of the crude product were purified by column chromatography (pentane:ethyl acetate = 50:1 v/v) prior to the use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.28 (m, 2H, H10), 7.04 (m, 2H, H11), 6.94 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H12), 5.74 (ddt, $^3J_{HH}$ = 17.2 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, H2), 5.05 – 4.95 (m, 2H, H1), 2.66 (t, $^3J_{HH}$ = 7.3 Hz, 2H, H8), 1.92 (vt, $^3J_{HH}$ = 6.9 Hz, 2H, H3), 1.48 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, H7), 1.21 (m, 4H, H4 and H6), 1.09 (m, 2H, H5).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C): δ = 139.1 (C2), 137.9 (C9), 129.2 (C10), 129.1 (C11), 125.8 (C12), 114.6 (C1), 34.1 (C3), 33.7 (C8), 29.4 (C7), 29.1 (C5), 28.9 (C4 and C6).

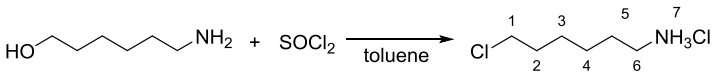
1.17. SYNTHESIS OF 4-CHLOROBUTANAMINE HYDROCHLORIDE



4-Aminobutanol (5.0 g, 56 mmol, 1 equiv.) was dissolved in toluene (100 mL) and thionyl chloride (5.3 mL, 72.8 mmol, 1.3 equiv.) was added. The reaction mixture was heated to 80 °C for 17 h. The formed precipitate was filtered off and washed with toluene and pentane. Drying under reduced pressure gave the desired product, 4-chlorobutanamine hydrochloride (7.5 g, 52 mmol, 93%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C): δ = 8.30 (s, 3H, H5), 3.59 (t, $^3J_{HH}$ = 5.9 Hz, 2H, H1), 3.16 – 3.01 (sbr, 2H, H4), 2.09 – 1.82 (m, 4H, H2 and H3).

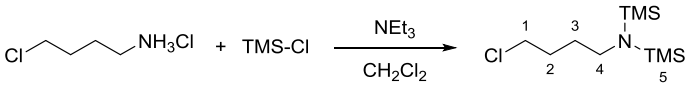
1.18. SYNTHESIS OF 6-CHLOROHEXANAMINE HYDROCHLORIDE



6-Aminohexanol (5.0 g, 42.7 mmol, 1 equiv.) was dissolved in toluene (100 mL) and thionyl chloride (4 mL, 55.6 mmol, 1.3 equiv.) was added. The reaction mixture was heated to 80 °C for 17 h. Et_2O (100 mL) was added, the formed precipitate was filtered off and washed with toluene and pentane. Drying under reduced pressure gave the desired product, 6-chlorohexanamine hydrochloride (6.9 g, 40.2 mmol, 94%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C): δ = 8.25 (s, 3H, H7), 3.53 (t, $^3J_{HH}$ = 6.6 Hz, 2H, H1), 3.08 – 2.94 (m, 2H, H6), 1.88 – 1.71 (m, 4H, H2 and H5), 1.56 – 1.35 (m, 4H, H3 and H4).

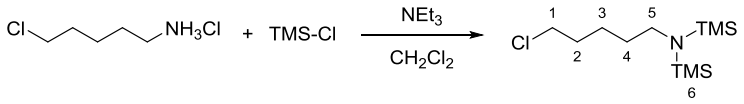
1.19. SYNTHESIS OF (4-CHLOROBUTYL)-BIS(TRIMETHYLSILYL)AMINE[5]



4-Chlorobutanamine hydrochloride (3.0 g, 20.8 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (25 mL). Trimethylsilyl chloride (6.1 mL, 47.9 mmol, 2.3 equiv.) and NEt_3 (10.5 g, 104.1 mmol, 5 equiv.) were added. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the residue was extracted with pentane (ca. 50 mL). Removal of the solvent gave the desired product, (4-chlorobutyl)bis(trimethylsilyl)amine (3.9 g, 15.6 mmol, 75%) as colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 3.06 (t, $^3J_{HH}$ = 6.2 Hz, 2H, H1), 2.66 – 2.55 (m, 2H, H4), 1.42 – 1.27 (m, 4H, H2 and H3), 0.14 (s, 18H, H5).

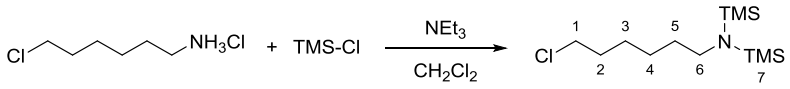
1.20. SYNTHESIS OF (5-CHLOROPENTYL)-BIS(TRIMETHYLSILYL)AMINE[5]



5-Chloropentanamine hydrochloride (5.0 g, 32 mmol, 1 equiv., synthesized in analogy to 4-chlorobutanamine hydrochloride) was dissolved in CH_2Cl_2 (35 mL). Trimethylsilyl chloride (9.3 mL, 73.6 mmol, 2.3 equiv.) and NEt_3 (16.2 g, 160 mmol, 5 equiv.) were added. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the residue was extracted with pentane (ca. 50 mL). Removal of the solvent gave the desired product, (5-chlorpentyl)bis(trimethylsilyl)amine (6.7 g, 25.3 mmol, 79%) as colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 3.09 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H1), 2.70 – 2.59 (m, 2H, H5), 1.46 – 1.33 (m, 2H, H2), 1.33 – 1.20 (m, 2H, H4), 1.15 – 1.01 (m, 2H, H3), 0.15 (s, 18H, H6).

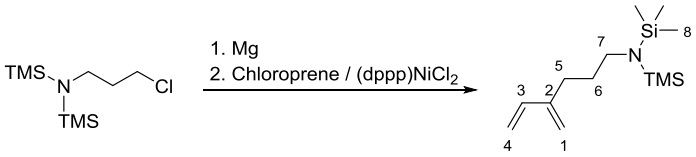
1.21. SYNTHESIS OF (6-CHLOROHEXYL)-BIS(TRIMETHYLSILYL)AMINE[5]



6-Chlorohexanamine hydrochloride (4.3 g, 25 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (35 mL). Trimethylsilyl chloride (7.3 mL, 57.5 mmol, 2.3 equiv.) and NEt_3 (12.6 g, 125 mmol, 5 equiv.) were added. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and the residue was extracted with pentane (ca. 50 mL). Removal of the solvent gave the desired product, (6-chlorohexyl)bis(trimethylsilyl)amine (5.7 g, 20.3 mmol, 81%) as colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 3.11 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H1), 2.78 – 2.64 (m, 2H, H6), 1.42 (quint, $^3J_{HH}$ = 6.7 Hz, 2H, H2), 1.38 – 1.28 (m, 2H, H3), 1.21 – 1.11 (m, 2H, H5), 1.03 – 0.92 (m, 2H, H4), 0.17 (s, 18H, H7).

1.22. SYNTHESIS OF (4-METHYLENE-5-HEXENYL)-BIS(TRIMETHYLSILYL)AMINE (**TMS_2N-3-BD**)



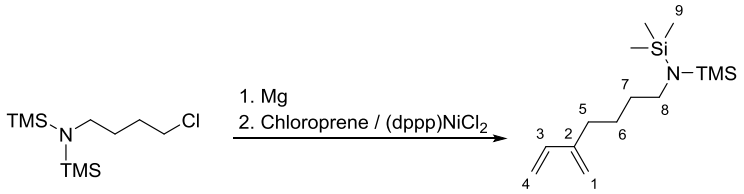
Magnesium turnings (2.25 g, 92.5 mmol, 1.5 equiv.) were layered with THF and activated with dibromoethane (0.36 mL, 0.79 g, 4.2 mmol). A mixture of (3-chloropropyl)-bis(trimethylsilyl)amine (15.0 g, 63.1 mmol, 1 equiv., synthesized according to Davis et al.[5]) and dibromoethane (0.36 mL, 0.79 g, 4.2 mmol) in THF (63 mL) was added dropwise and the reaction mixture was stirred for 2 h at 60 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

(dppp)$NiCl_2$ (0.252 g, 0.50 mmol) and chloroprene (5.9 g, 66.2 mmol, 1.05 equiv.) were dissolved in THF (21 mL). The reaction mixture was cooled to 0 °C and after the dropwise addition of the (3-(bis(trimethylsilyl)-amino)propyl)magnesium chloride solution, the mixture was stirred for 10 minutes at 0 °C and afterwards for 40 minutes at room temperature. Heptane (100 mL) was added to the reaction mixture and THF was removed under reduced pressure. The resulting brown suspension was filtered over celite and the solvent was removed under reduced pressure. The crude product was purified by distillation (73 °C / $3.3 \cdot 10^{-1}$ mbar) to yield (4-methylene-5-hexenyl)-bis(trimethylsilyl)-amine (12.27 g , 48 mmol, 76%) as a colorless liquid.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C) δ = 6.31 (dd, $^3J_{HH}$= 17.6 and 11.2 Hz, 1H, H3), 5.17 (d, $^3J_{HH}$= 17.6 Hz, 1H, H4), 4.97 (d, $^3J_{HH}$= 11.2 Hz, 1H, H4), 4.93 (s, 2H, H1), 2.78 (m, 2H, H7), 2.06 (t, $^3J_{HH}$= 7.6 Hz, 2H, H5), 1.59 (m, 2H, H6), 0.13 (s, 18H, H8).

^{13}C-NMR (100 MHz, C_6D_6, 27 °C) δ = 146.3 (C2), 139.2 (C3), 116.1 (C1), 113.4 (C4), 45.9 (C7), 34.1 (C5), 29.4 (C6), 2.3 (C8).

1.23. SYNTHESIS OF (5-METHYLENEHEPT-6-ENYL)-BIS(TRIMETHYLSILYL)AMINE (**TMS_2N-4-BD**)



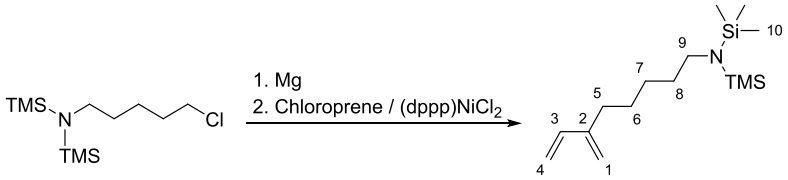
Magnesium turnings (137 mg, 5.6 mmol, 1.2 equiv.) were layered with THF (4 mL) and activated with dibromoethane. (4-chlorobutyl)-bis(trimethylsilyl)amine (1.2 g, 4.7 mmol, 1 equiv.) in THF (4 mL) was added dropwise and the reaction mixture was stirred for 3 h at 50 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

(dppp)$NiCl_2$ (50 mg, 0.094 mmol, 0.02 equiv.) and chloroprene (5.6 mmol, 1.2 equiv.) were mixed in THF (7 mL). The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 2 h. THF was removed and pentane (20 mL) was added. The formed precipitate was filtered off and the solvent was removed under reduced pressure to give (5-methylenehept-6-enyl)-bis(trimethylsilyl)amine as a light orange liquid (1.1 g, 4.0 mmol, 85%). Parts of the crude product were separated from (dppp)$NiCl_2$ residues by vacuum transfer (80 °C / $2.2 \cdot 10^{-1}$ mbar) prior to use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 6.35 (dd, $^3J_{HH}$ = 17.8, 10.9, 1H, H3), 5.17 (d, $^3J_{HH}$ = 17.8, 1H, H4), 5.04 – 4.89 (m, 3H, H4 and H1), 2.74 (m, 2H, H8), 2.24 – 1.99 (t, $^3J_{HH}$ = 7.4, 2H, H5), 1.57 – 1.00 (m, 4H, H6 and H7), 0.16 (s, 18H, H9).

^{13}C-NMR (400 MHz, C_6D_6, 27 °C): δ = 146.7 (C2), 139.4 (C3), 115.7 (C1), 113.2 (C4), 45.9 (C8), 35.9 (C6), 31.6 (C5), 25.9 (C7), 2.4 (C9).

1.24. SYNTHESIS OF (6-METHYLENEOCT-7-ENYL)-BIS(TRIMETHYLSILYL)AMINE (**TMS_2N-5-BD**)



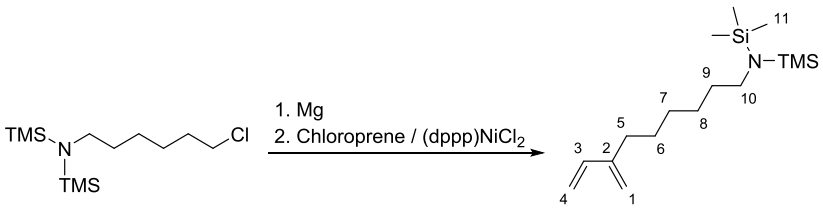
Magnesium turnings (291 mg, 12 mmol, 1.2 equiv.) were layered with THF (5 mL) and activated with dibromoethane. (5-chloropentyl)-bis(trimethylsilyl)amine (2.65 g, 10 mmol, 1 equiv.) in THF (5 mL) was added dropwise and the reaction mixture was stirred for 3.5 h at 50 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

(dppp)$NiCl_2$ (100 mg, 0.2 mmol, 0.02 equiv.) and chloroprene (12 mmol, 1.2 equiv.) were mixed in THF (10 mL). The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 2 h. THF was removed and pentane (30 mL) was added. The formed precipitate was filtered off and the solvent was removed under reduced pressure to give (6-methyleneoct-7-enyl)-bis(trimethylsilyl)amine as a light orange liquid (2.5 g, 8.8 mmol, 88%). Parts of the crude product were separated from (dppp)$NiCl_2$ residues by vacuum transfer (85 °C / $2.3 \cdot 10^{-1}$ mbar) prior to use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 6.34 (dd, $^3J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 10.9 Hz, 1H, H3), 5.19 (d, $^3J_{HH}$ = 17.6 Hz, 1H, H4), 4.97 (vd, $^3J_{HH}$ = 10.3 Hz, 3H, H1 and H4), 2.79 – 2.70 (m, 2H, H9), 2.15 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H5), 1.53 – 1.34 (m, 4H, H6 and H8), 1.15 (quint, $^3J_{HH}$ = 8.0 Hz, 2H, H5), 0.16 (s, 18H, H10).

^{13}C-NMR (400 MHz, C_6D_6, 27 °C): δ = 146.7 (C2), 139.4 (C3), 115.9 (C1), 113.2 (C4), 46.0 (C9), 35.9 (C8), 31.9 (C5), 28.4 (C6), 27.4 (C7), 2.4 (C10).

1.25. SYNTHESIS OF (7-METHYLENENON-8-ENYL)-BIS(TRIMETHYLSILYL)AMINE (**TMS_2N-6-BD**)



Magnesium turnings (291 mg, 12 mmol, 1.2 equiv.) were layered with THF (5 mL) and activated with dibromoethane. (6-chlorohexyl)-bis(trimethylsilyl)amine (2.80 g, 10 mmol, 1 equiv.) in THF (5 mL) was added

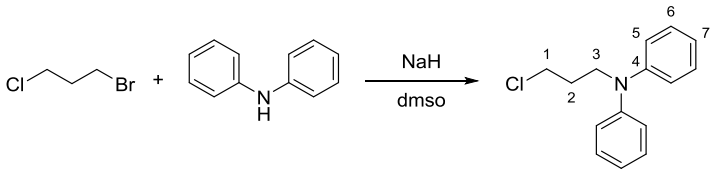
dropwise and the reaction mixture was stirred for 4 h at 50 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

(dppp)$NiCl_2$ (100 mg, 0.2 mmol, 0.02 equiv.) and chloroprene (12 mmol, 1.2 equiv.) were mixed in THF (10 mL). The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 2 h. THF was removed and pentane (30 mL) was added. The formed precipitate was filtered off and the solvent was removed under reduced pressure to give (7-methylenenon-8-enyl)-bis(trimethylsilyl)amine as a light orange liquid (2.8 g, 9.3 mmol, 93%). Parts of the crude product were separated from (dppp)$NiCl_2$ residues by vacuum transfer (98 °C / $2.1 \cdot 10^{-1}$ mbar) prior to use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 6.36 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 10.7 Hz, 1H, H3), 5.20 (d, $^3J_{HH}$ = 17.7 Hz, 1H, H4), 5.04 – 4.91 (m, 3H, H1 and H4), 2.83 – 2.69 (m, 2H, H10), 2.21 – 2.11 (m, 2H, H5), 1.55 – 1.34 (m, 4H, H6 and H9), 1.33 – 1.19 (m, 2H, H7), 1.19 – 1.07 (m, 2H, H8), 0.17 (s, 18H, H11).

^{13}C-NMR (400 MHz, C_6D_6, 27 °C): δ = 146.9 (C2), 139.5 (C3), 115.8 (C1), 113.2 (C4), 46.1 (C10), 36.0 (C9), 31.8 (C5), 29.8 (C7), 28.7 (C6), 27.5 (C8), 2.4 (C11).

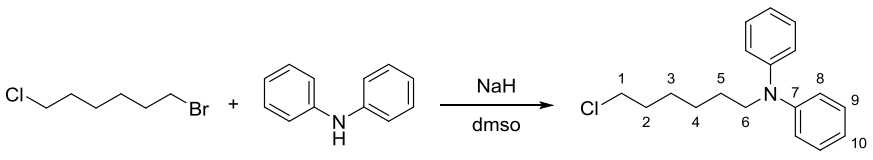
1.26. SYNTHESIS OF (3-CHLOROPROPYL)-PHENYLANILINE



NaH (0.96 g, 40 mmol, 1 equiv.) was suspended in dmso (20 mL). Phenylaniline (6.77 g, 40 mmol, 1 equiv.) in dmso (20 mL) was added dropwise to the suspension. After complete addition, the reaction mixture was heated to 50 °C for 1.5 h. 1-Bromo-3-chloropropane (6.30 g, 40 mmol, 1 eqiuv.) was added and the mixture was stirred for further 35 min at room temperature. Et_2O was added and the organic phase was washed with water. The organic phase was dried over $MgSO_4$ and removal of the solvent under reduced pressure gave the desired product, crude (3-chloropropyl)-phenylaniline (2.76 g, 11.2 mmol, 28%). Parts of the crude product were purified by column chromatography (pentane:ethyl acetate = 18:1 v/v) prior to the use in the next step.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.13 – 7.06 (m, 4H, H6), 6.95 – 6.88 (m, 4H, H5), 6.87 – 6.81 (m, 2H, H7), 3.55 (t, $^3J_{HH}$ = 6.9 Hz, 2H, H1), 3.06 (t, $^3J_{HH}$ = 6.2 Hz, 2H, H3), 1.69 (quint, $^3J_{HH}$ = 6.5 Hz, 2H, H2).

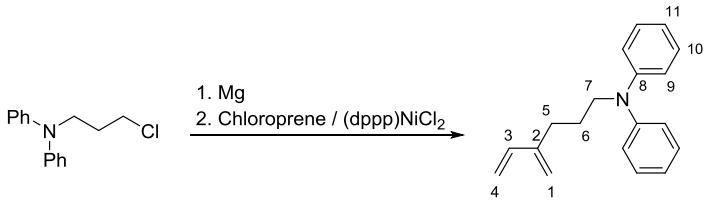
1.27. SYNTHESIS OF (6-CHLOROHEXYL)-PHENYLANILINE



NaH (1.20 g, 50 mmol, 1 equiv.) was suspended in dmso (30 mL). Phenylaniline (8.46 g, 50 mmol, 1 equiv.) in dmso (35 mL) was added dropwise to the suspension. After complete addition, the reaction mixture was heated to 50 °C for 0.5 h. 1-Bromo-6-chlorohexane (10.1 g, 50.5 mmol, 1.01 eqiuv.) was added and the mixture was stirred for further 30 min at room temperature. Pentane was added and the organic phase was washed with water. The organic phase was dried over $MgSO_4$ and removal of the solvent under reduced pressure gave the desired product, (6-chlorohexyl)-phenylaniline (13.8 g, 47.8 mmol, 96%).

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.17 – 7.09 (m, 4H, H9), 6.99 – 6.92 (m, 4H, H8), 6.87 – 6.81 (m, 2H, H10), 3.44 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H1), 3.10 – 3.00 (m, 2H, H6), 1.53 – 1.24 (m, 4H, H2 and H5), 1.08 – 0.90 (m, 4H, H3 and H4).

1.28. SYNTHESIS OF (4-METHYLENEHEX-5-ENYL)-PHENYLANILINE (**PH$_2$N-3-BD**)



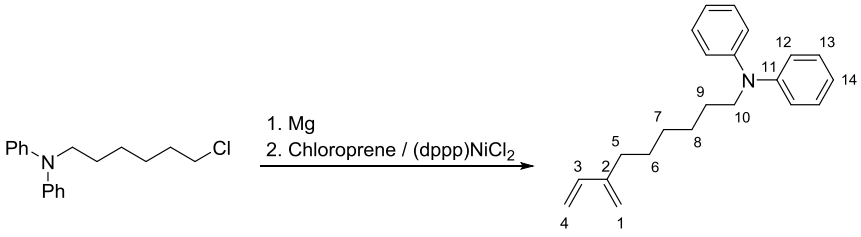
Magnesium turnings (136 mg, 5.7 mmol, 1.2 equiv.) were layered with THF (5 mL) and activated with dibromoethane. (3-chloropropyl)-phenylaniline (1.16 g, 4.7 mmol, 1 equiv.) in THF (5 mL) was added and the reaction mixture was stirred for 3 h at 50 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

(dppp)$NiCl_2$ (50 mg, 0.09 mmol, 0.02 equiv.) and chloroprene (5.7 mmol, 1.2 equiv.) were mixed in THF (7 mL). The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 2 h. Et_2O (30 mL) was added and the formed precipitate was filtered off. The organic phase was washed with brine and water, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give (4-methylenehex-5-enyl)-phenylaniline (981 mg, 3.7 mmol, 79%). Parts of the product were subjected to column chromatography (pentane:ethyl acetate = 25:1 v/v) prior to use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.12 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H10), 6.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H9), 6.84 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H11), 6.29 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 10.7 Hz, 1H, H4), 5.08 (d, $^3J_{HH}$ = 17.6 Hz, 1H, H4), 4.95 – 4.89 (m, 2H, H1 and H4), 4.82 (s, 1H, H1), 3.52 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H7), 2.07 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H5), 1.78 (vquint, $^3J_{HH}$ = 6.6 Hz, 2H, H6).

^{13}C-NMR (400 MHz, C_6D_6, 27 °C): δ = 148.7 (C8), 146.0 (C2), 139.1 (C3), 129.6 (C10), 121.6 (C11), 121.5 (C9), 116.1 (C1), 113.4 (C4), 52.2 (C7), 29.0 (C5), 26.1 (C6).

1.29. SYNTHESIS OF (7-METHYLENENON-8-ENYL)-PHENYLANILINE (**PH$_2$N-6-BD**)



Magnesium turnings (0.88 g, 36 mmol, 1.2 equiv.) were layered with THF (15 mL) and activated with dibromoethane. (6-chlorohexyl)-phenylaniline (8.64 g, 30 mmol, 1 equiv.) in THF (15 mL) was added and the reaction mixture was stirred for 3 h at 50 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

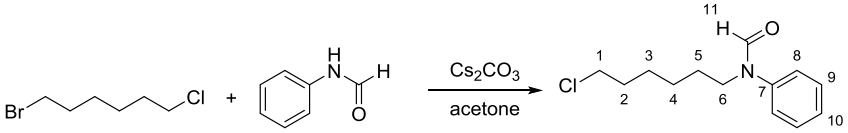
(dppp)$NiCl_2$ (325 mg, 0.6 mmol, 0.02 equiv.) and chloroprene (36 mmol, 1.2 equiv.) were mixed in THF (20 mL). The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 2 h.

Et_2O (30 mL) was added and the formed precipitate was filtered off. The organic phase was washed with brine and water, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give (7-methylenenon-8-enyl)-phenylaniline (6.44 g, 21 mmol, 70%). Parts of the product were subjected to column chromatography (pentane:ethyl acetate = 15:1 v/v) prior to use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.17 – 7.10 (m, 4H, H13), 7.02 – 6.96 (m, 4H, H12), 6.89 – 6.82 (m, 2H, H14), 6.36 (dd, $^3J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, H3), 5.18 (d, $^3J_{HH}$ = 17.6 Hz, 1H, H4), 5.02 – 4.89 (m, 3H, H1 and H4), 3.50 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H10), 2.10 (t, $^3J_{HH}$ = 7.5 Hz, 2H, H5), 1.61 – 1.48 (m, 2H, H9), 1.44 – 1.33 (m, 2H, H6), 1.15 – 1.08 (m, 4H, H7 and H8).

^{13}C-NMR (400 MHz, C_6D_6, 27 °C): δ = 148.8 (C11), 146.8 (C2), 139.4 (C3), 129.6 (C13), 121.5 (C14), 121.5 (C12), 115.8 (C1), 113.2 (C4), 52.5 (C10), 31.7 (C5), 29.6 (C7), 28.5 (C6), 27.9 (C9), 27.2 (C8).

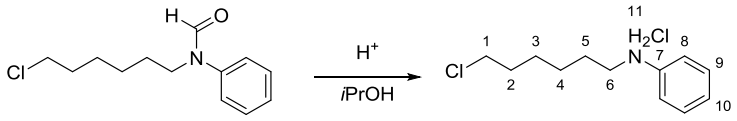
1.30. SYNTHESIS OF (6-CHLOROHEXYL)-PHENYLFORMAMIDE



According to Imamura et al.:[6] 1-Bromo-6-chlorohexane (4.79 g, 24 mmol, 1.2 equiv.) and *N*-phenylformamide (2.42 g, 20 mmol, 1 equiv.) were dissolved in acetone (20 mL). Cs_2CO_3 (7.82 g, 24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at 50 °C for 24 h. The solid phase of the suspension was separated by centrifugation and washed with acetone. The organic phases were combined and acetone was removed under reduced pressure to yield the desired product (6-chlorohexyl)-phenylformamide in quantitative yield. The crude product contains ca. 20% of the starting material 1-bromo-6-chlorohexane and was used without further purification in the next step.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 8.29 (s, 1H, H11), 7.03 – 6.95 (m, 2H, H9), 6.94 – 6.87 (m, 1H, H10), 6.71 – 6.62 (m, 2H, H8), 3.61 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H1), 3.04 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H6), 1.38 – 1.22 (m, 4H, H2 and H5), 1.09 – 0.86 (m, 4H, H3 and H4).

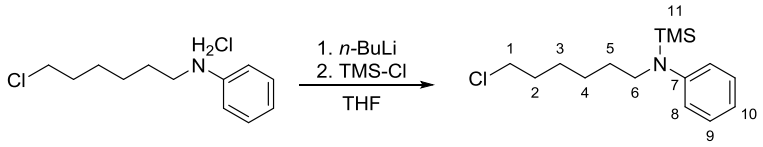
1.31. SYNTHESIS OF (6-CHLOROHEXYL)ANILINE HYDROCHLORIDE



(6-Chlorohexyl)-phenylformamide (20 mmol) was dissolved in *i*PrOH (19 mL) and concentrated HCl was added (4.4 mL). The reaction mixture was heated to 53 °C for 5 h. The product was then precipitated by the addition of CH_3Cl/Et_2O and collected by filtration. Recrystallization from CH_3Cl/Et_2O gave the desired product (6-chlorohexyl)aniline hydrochloride (3.63 g, 14.6 mmol, 73%).

^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C): 11.43 (br s, 2H, H11), 7.69 – 7.61 (m, 2H, H9), 7.51 – 7.40 (m, 3H, H8 and H10), 3.48 (t, $^3J_{HH}$ = 6.5 Hz, 2H, H1), 3.27 (t, $^3J_{HH}$ = 7.8 Hz, 2H, H6), 1.94 – 1.82 (m, 2H, H2), 1.76 – 1.64 (m, 2H, H5), 1.43 – 1.29 (m, 4H, H3 and H4).

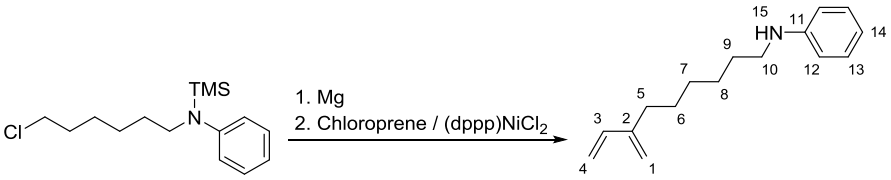
1.32. SYNTHESIS OF (6-CHLOROHEXYL)-(PHENYL)-TRIMETHYLSILYLAMINE



(6-Chlorohexyl)aniline hydrochloride (1.54 g, 7.0 mmol, 1 equiv.) was suspended in THF (10 mL) and cooled to -78 °C. *n*-BuLi (9.6 mL 1.6 M in hexanes, 15.4 mmol, 2.2 equiv.) was added dropwise followed by the addition of TMS-Cl (1.2 mL, 9.1 mmol, 1.3 equiv.). The reaction mixture was stirred for further 15 min at -78 °C, warmed to room temperature, and then stirred at that temperature for 1 h. THF was removed under reduced pressure and the residue was extracted with pentane, insoluble parts were removed by filtration. Removal of the solvent under reduced pressure gave the desired product (6-chlorohexyl)-(phenyl)-trimethylsilylamine (1.44 g, 5.1 mmol, 72%).

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): 7.21 – 7.16 (m, 2H, H9), 7.01 – 6.96 (m, 2H, H8), 6.88 (t, $^3J_{HH}$ = 7.2 Hz, 1H, H10), 3.15 (t, $^3J_{HH}$ = 7.1 Hz, 2H, H1), 3.06 (t, $^3J_{HH}$ = 6.7 Hz, 2H, H6), 1.34 (vhept, $^3J_{HH}$ = 6.8 Hz, 4H, H2 and H5), 1.15 – 0.93 (m, 4H, H3 and H4), 0.19 (s, 9H, H11).

1.33. SYNTHESIS OF (7-METHYLENENON-8-ENYL)ANILINE (**PHNH-6-BD**)



Magnesium turnings (161 mg, 6.63 mmol, 1. equiv.) were layered with THF (2 mL) and activated with dibromoethane. (6-Chlorohexyl)-(phenyl)-trimethylsilylamine (1.44 g, 5.1 mmol, 1 equiv.) in THF (6 mL) was added and the reaction mixture was stirred for 2 h at 50 °C. Residual magnesium was filtered off, and the clear solution was used in the next step.

(dppp)$NiCl_2$ (55 mg, 0.1 mmol, 0.02 equiv.) and chloroprene (6.12 mmol, 1.2 equiv.) were mixed in THF (10 mL). The THF solution containing the Grignard reagent was slowly added to this mixture and heated to 50 °C for 1 h. An NH_4Cl solution was added and the mixture was extracted with Et_2O. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give (7-methylenenon-8-enyl)aniline (1.09 g, 4.75 mmol, 93%). Parts of the product were subjected to column chromatography (pentane:ethyl acetate = 100:1.5 v/v) prior to use in polymerizations.

^{1}H-NMR (400 MHz, C_6D_6, 27 °C): δ = 7.23 – 7.17 (m, 2H, H13), 6.77 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H14), 6.51 – 6.46 (m, 2H, H12), 6.39 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, H3), 5.21 (d, $^3J_{HH}$ = 17.6 Hz, 1H, H4), 5.04 – 4.96 (m, 3H, H1 and H4), 3.06 (br s, 1H, H15), 2.83 – 2.74 (m, 2H, H10), 2.16 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H5), 1.48 – 1.37 (m, 2H, H6), 1.31 – 1.20 (m, 2H, H9), 1.20 – 1.08 (m, 4H, H7 and H8).

^{13}C-NMR (101 MHz, C_6D_6, 27 °C) δ = 149.0 (C11), 146.8 (C2), 139.5 (C3), 129.5 (C13), 117.4 (C14), 115.9 (C1), 113.2 (C4), 113.0 (C12), 44.0 (C10), 31.7 (C5), 29.8 (C9), 29.7 (C7 or C8), 28.5 (C6), 27.3 (C7 or C8).

2. Polymerization Procedures

2.1. Copolymerizations in NMR tubes catalyzed by **Ni-1**

Ni-1 was weighted into an NMR tube. The used comonomer was mixed with a certain amount of a BD stock solution (2.1 mmol BD per gram solution in C_6D_6). C_6D_6 was added to this mixture, if necessary, to reach a total volume of 0.6 mL. To start the polymerization, the BD/comonomer solution was transferred to the NMR tube containing the catalyst immediately before starting the NMR measurements. The NMR tube containing the catalyst was cooled to -78 °C before addition of the diene solution for polymerizations at temperatures below room temperature.

3. Kinetic Data

3.1. Additional Kinetic Data and Measurement Details

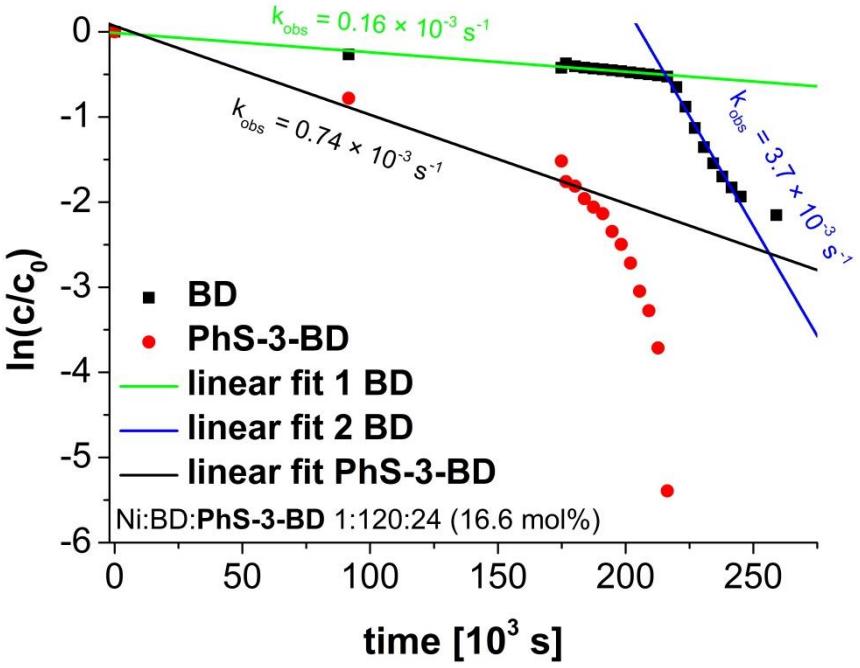
^{1}H NMR Spectra were recorded with a relaxation delay time of D1 = 5 s and an acquisition time of 10 s. The recorded spectra were processed in MestReNova™ (v 8.1) and the consumption of BD and the comonomer was determined. For this purpose, the olefinic monomer signals were integrated using the Data Analysis Tool of MestReNova™. When a proper integration of the olefinic signal of the comonomer was not possible, a characteristic signal of a -CH_2- group of the side chain was used. The obtained time-intensity data were transferred to Origin™ and plotted. In cases where spectra of one sample were recorded in different runs, a standardization of the intensity values was applied prior to plotting the data by using the intensity of the solvent signal as reference. Because polymerizations undergo a significant change of the BD:comonomer ratio throughout the whole reaction, linear fitting using 1st order conditions was applied only to initial data points of the reaction when necessary. This ensures to obtain rate constants and monomer reactivity ratios from the initial stage of the copolymerization and hence comparability of the data. Rate constants k were calculated by dividing the value of the linear fits' slopes by the catalyst concentration.

Table S 1: Overview of (additional) rate constants obtained from kinetic NMR experiments for (co)polymerizations of BD with different comonomers and model compounds catalyzed by **Ni-1**. Parts of the data have been presented already in the manuscript as part of Table 1.

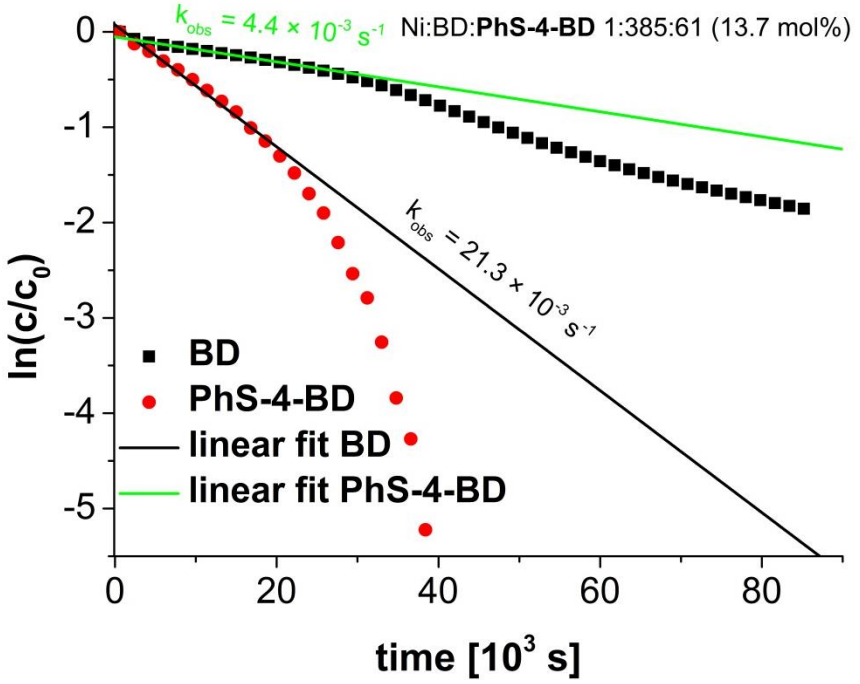
entry	CoMo or additive	k_{BD} [10^{-3} s^{-1}]	k_{CoMo} [10^{-3} s^{-1}]	r_{CoMo} [a]
S1-1[b]	**PhS-3-BD**	0.16	0.74	4.6
S1-2[c]	**PhS-4-BD**	4.4	21	4.9
S1-3[c]	**PhS-5-BD**	5.6	9.1	1.6
S1-4[c]	**PhS-6-BD**	9.0	15	1.7
S1-5[c]	**PhS-7-BD**	4.7	7.6	1.6
S1-6[d]	**PhNH-3-BD**	0.086	0.683	7.90
S1-7[d]	**PhNH-6-BD**	32.6	40.6	1.3
S1-8[e]	**Ph_2N-3-BD**	57.5	51.7	0.9
S1-9[e]	**Ph_2N-4-BD**	80.5	104.4	1.3
S1-10[e]	**Ph_2N-6-BD**	66.4	94.9	1.4
S1-11[f]	**TMS_2N-3-BD**	31.2	26.0	0.8
S1-12[f]	**TMS_2N-4-BD**	123.7	150.8	1.2
S1-13[f]	**TMS_2N-5-BD**	61.2	79.5	1.3
S1-14[f]	**TMS_2N-6-BD**	82.2	126.5	1.5
S1-15[g]	**5-BD**	n.a.[k]	n.a.[k]	2.2
S1-16[g]	**IP**	n.a.[k]	n.a.[k]	1.2
S1-17[h]	**PhS-6**	49		
S1-18[i]	**PhNH-3**	40		
S1-19[j]	**PhS-4-Ene**	28		
S1-20[j]	**PhS-6-Ene**	83		
S1-21[j]	**PhS-8-Ene**	78		

a) monomer reactivity ratio $r_{CoMo} = k_{CoMo}/k_{BD}$ b) Ni:BD:CoMo = 1:120:24, T = 40 °C c) Ni:BD:CoMo = ca. 1:400:60, T = 40 °C d) Ni:BD:CoMo = ca. 1:400:75, T = 40 °C e) Ni:BD:CoMo = ca. 1:500:100, T = 40 °C f) Ni:BD:CoMo = ca. 1:450:90, T = 40 °C g) Ni:BD:CoMo = ca. 1:200:30, T = -15 °C h) Ni:BD:additive = ca. 1:400:60, T = 40 °C i) Ni:BD:additive = 1:120:28, T = 40 °C j) Ni:BD:additive = ca. 1:400:75, T = 40 °C k) not applicable, as reactions were conducted at a different temperature.

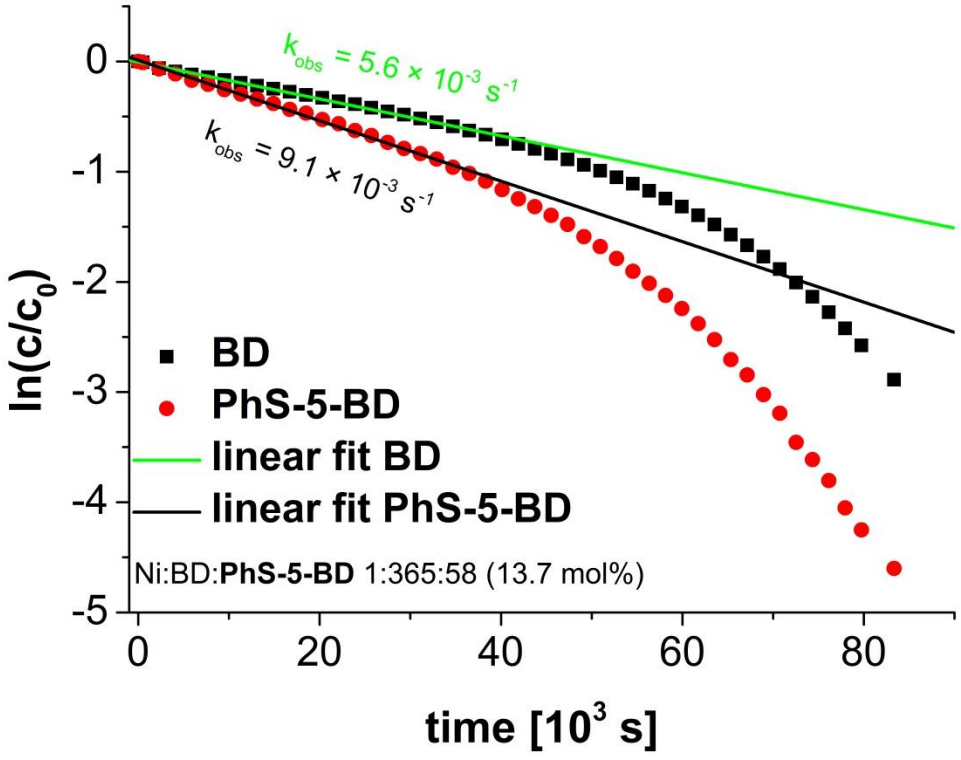
3.2. KINETIC PLOTS



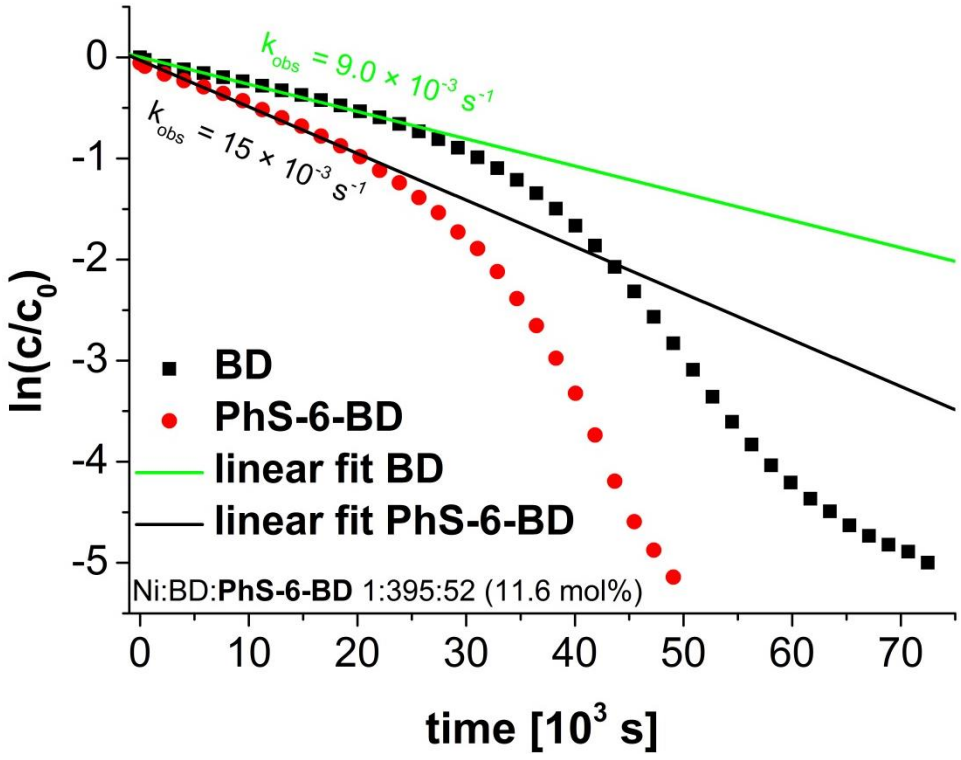
SI 1: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhS-3-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 14 × 10^{-3} mol L^{-1}. This plot has been presented already in the manuscript as part of Figure 1.



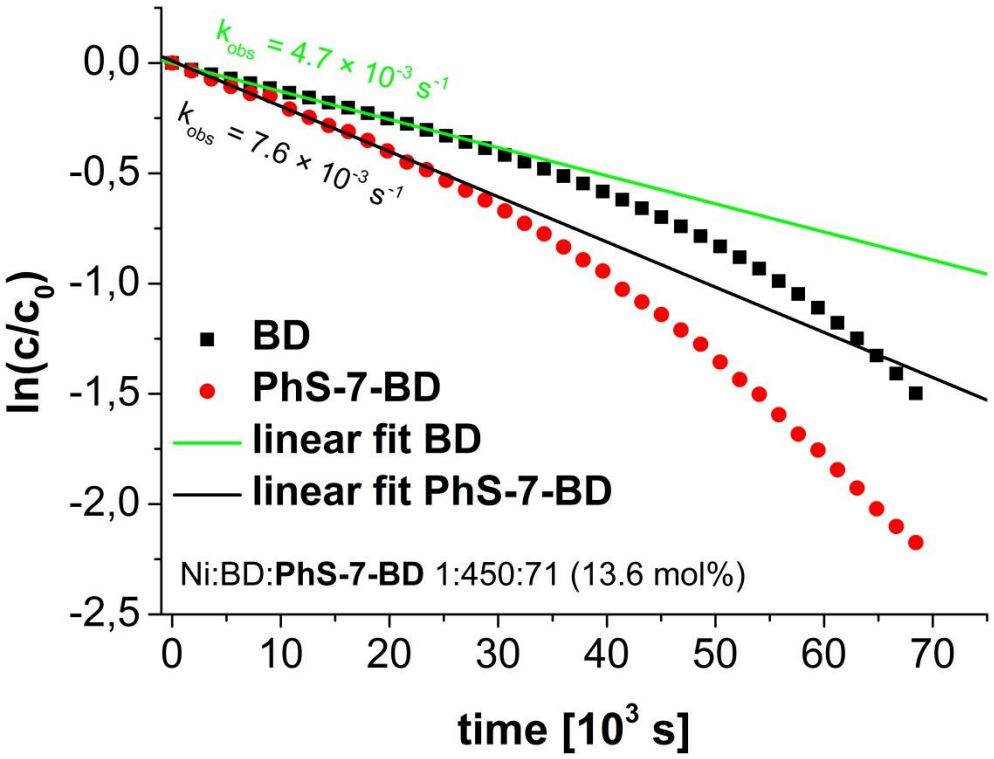
SI 2: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhS-4-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 3 × 10^{-3} mol L^{-1}.



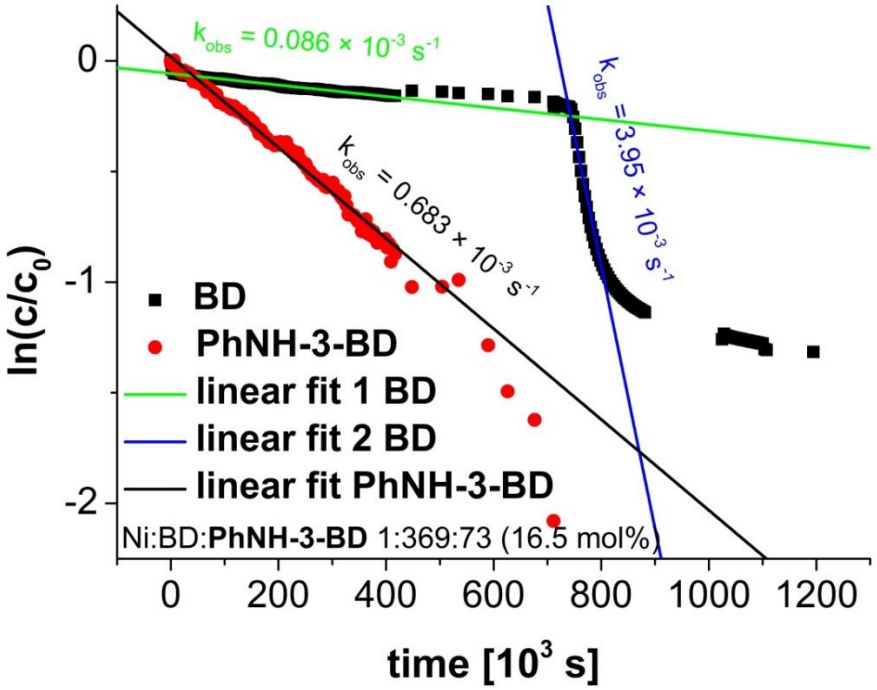
SI 3: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhS-5-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 3 × 10^{-3} mol L^{-1}.



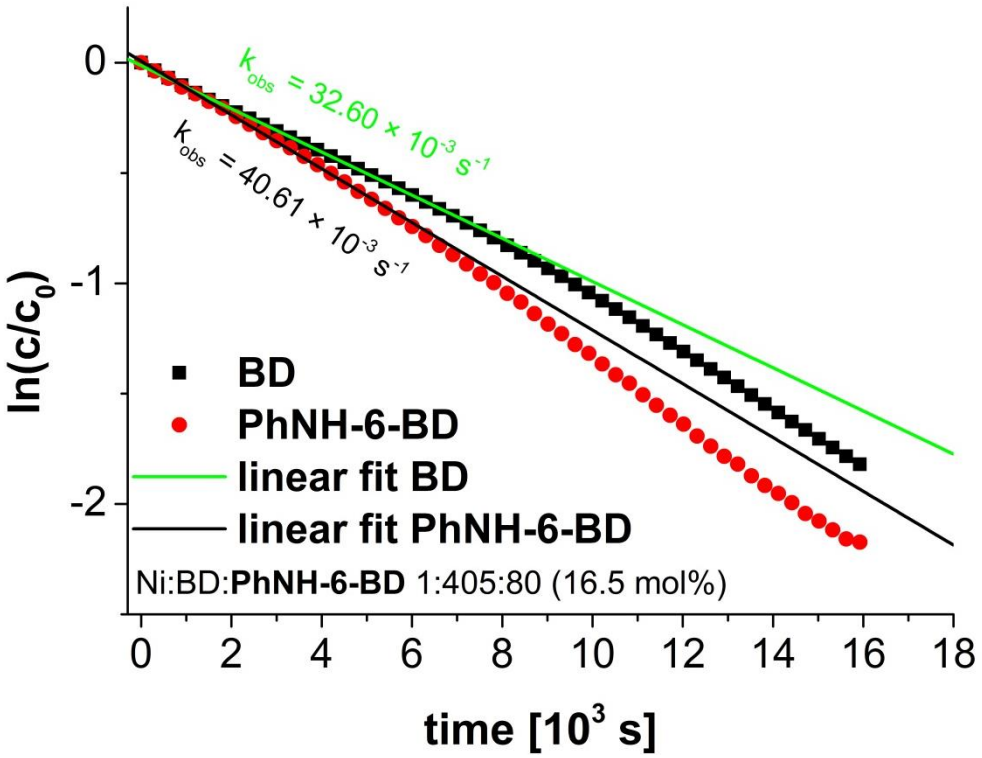
SI 4: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhS-6-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 3 × 10^{-3} mol L^{-1}.



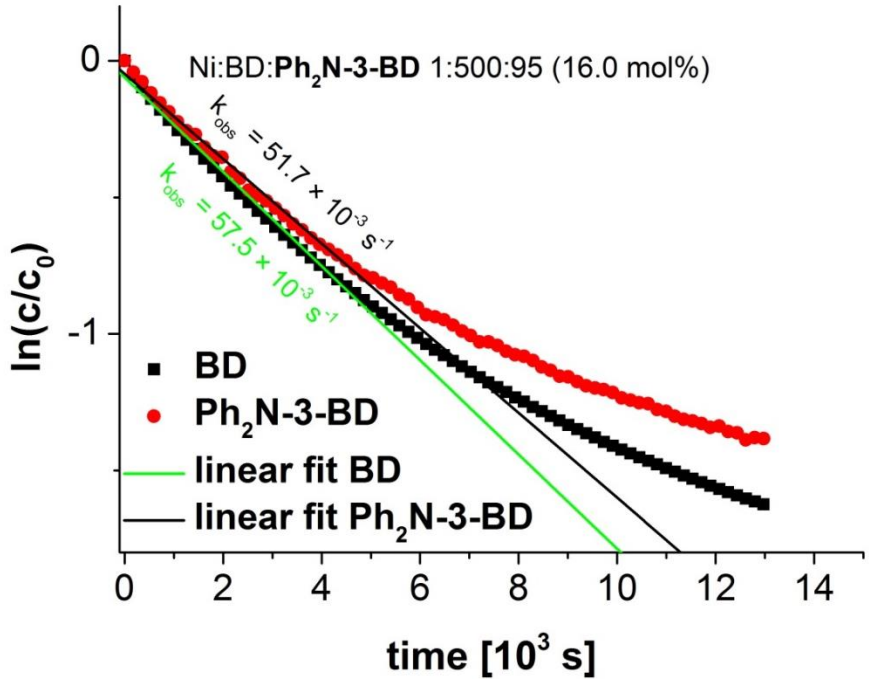
SI 5: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhS-7-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 2.7 × 10^{-3} mol L^{-1}.



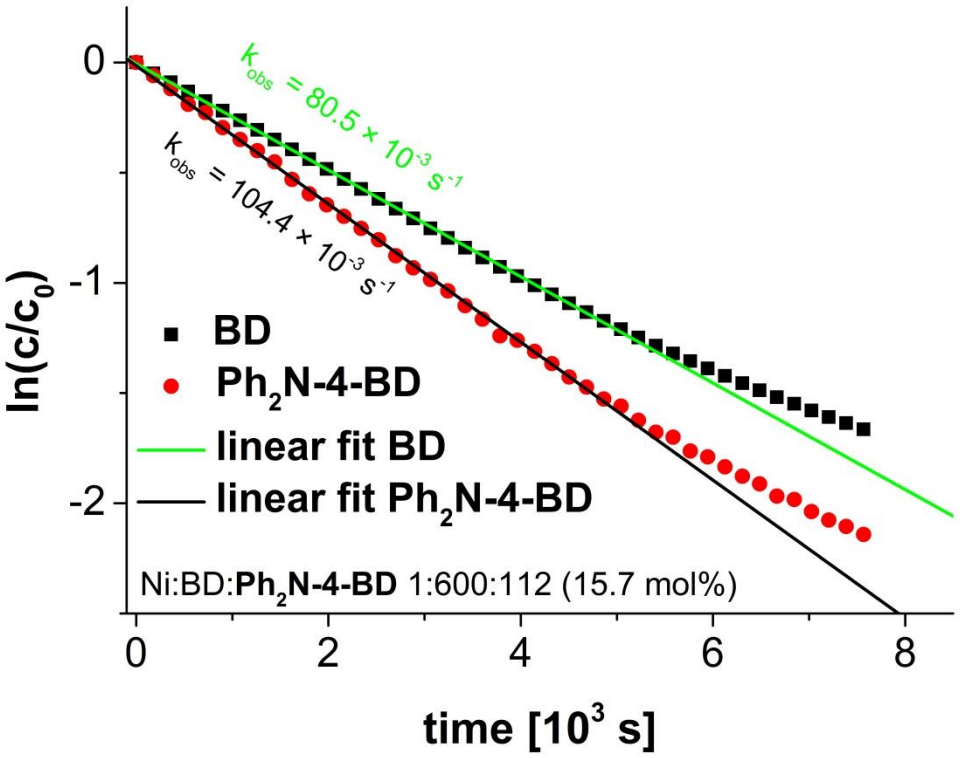
SI 6: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhNH-3-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3 × 10^{-3} mol L^{-1}. This plot has been presented already in the manuscript as part of Figure 1.



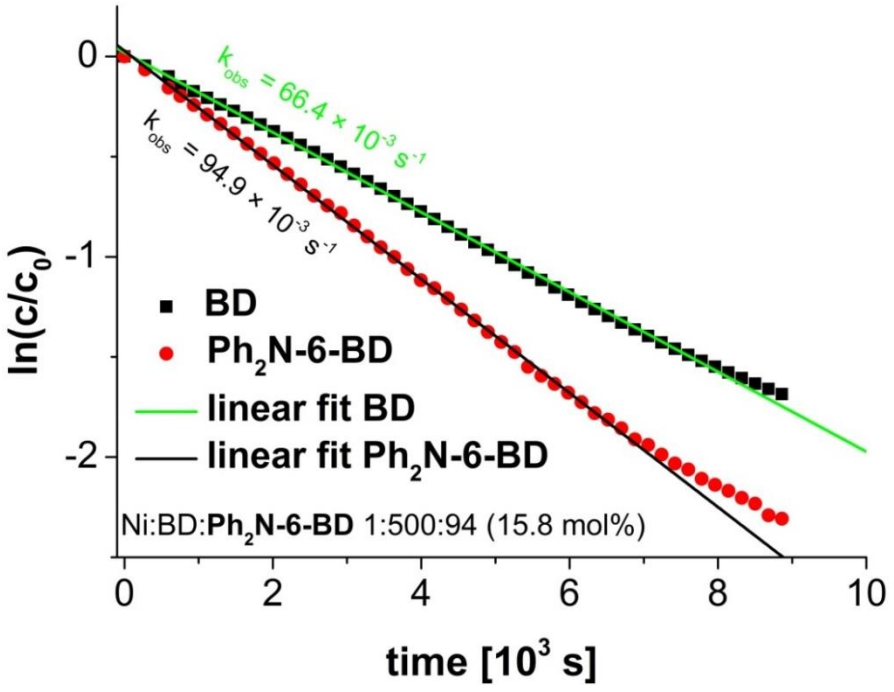
SI 7: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **PhNH-6-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3×10^{-3} mol L^{-1}.



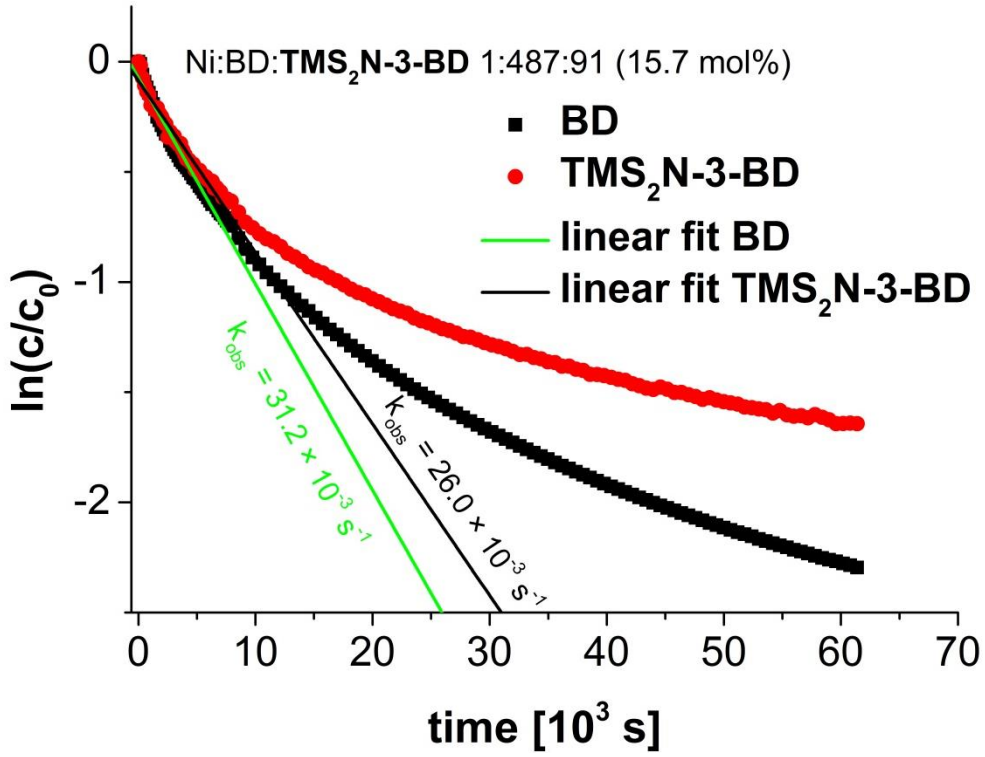
SI 8: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **Ph_2N-3-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 3×10^{-3} mol L^{-1}.



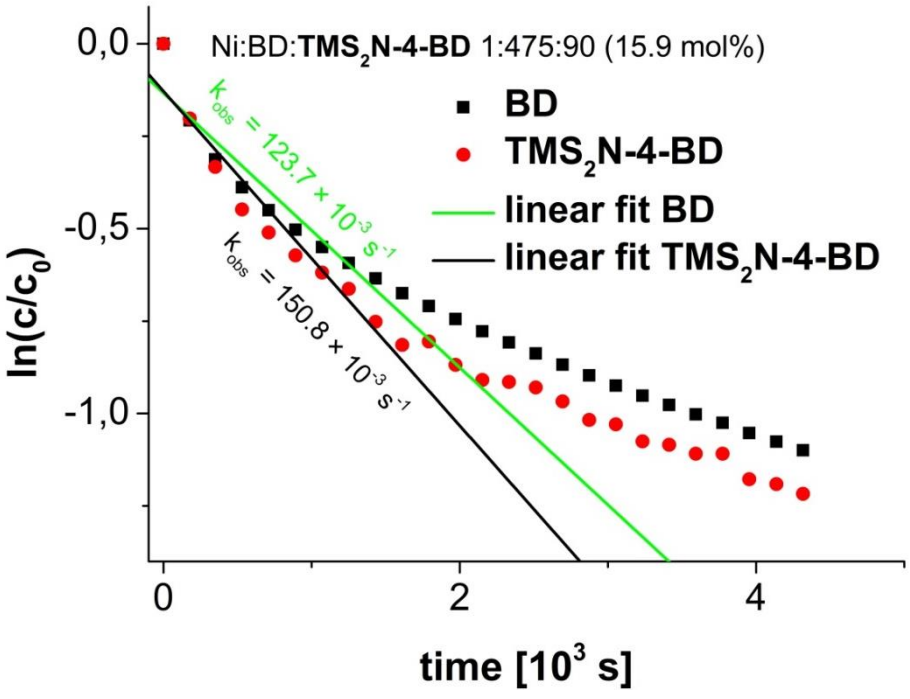
SI 9: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **Ph_2N-4-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**] = 3×10^{-3} mol L^{-1}.



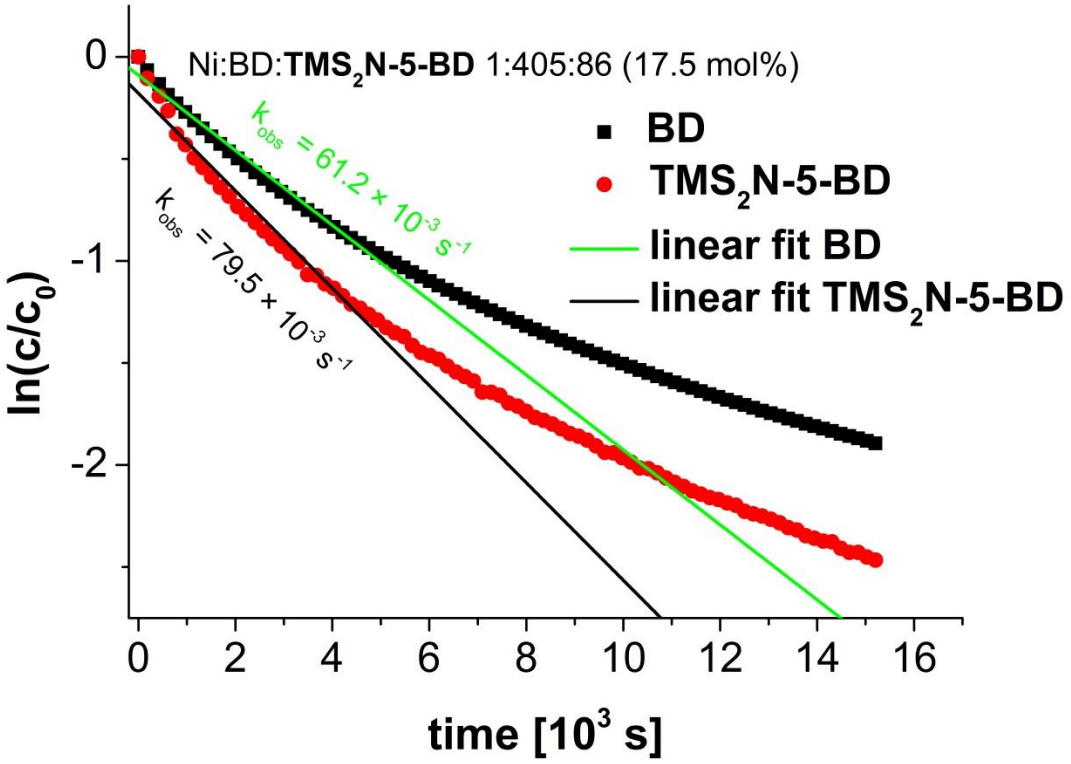
SI 10: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **Ph_2N-6-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3×10^{-3} mol L^{-1}.



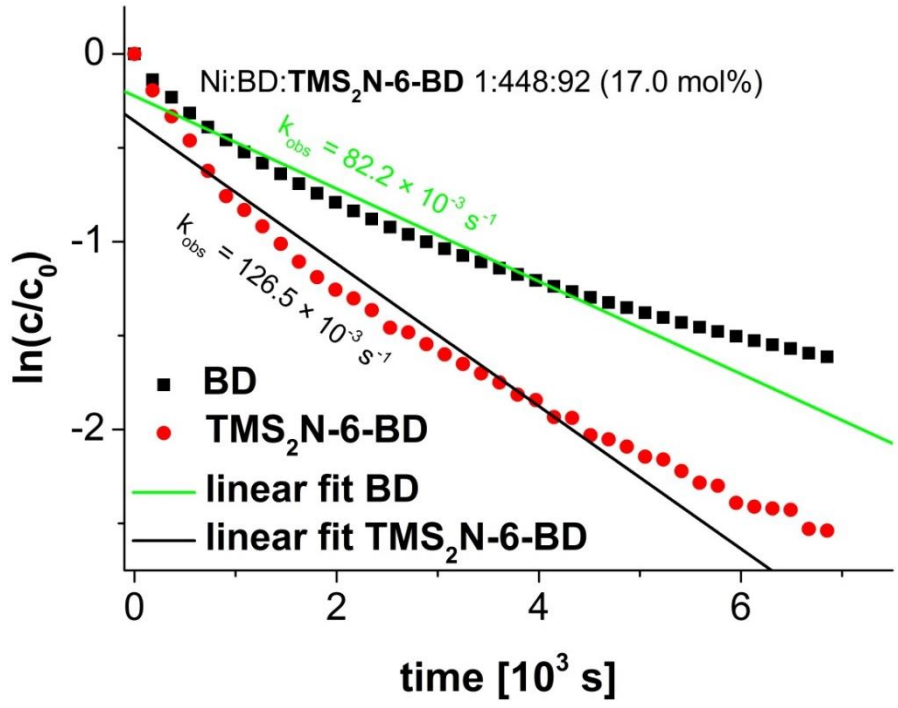
SI 11: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **TMS_2N-3-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3×10^{-3} mol L^{-1}.



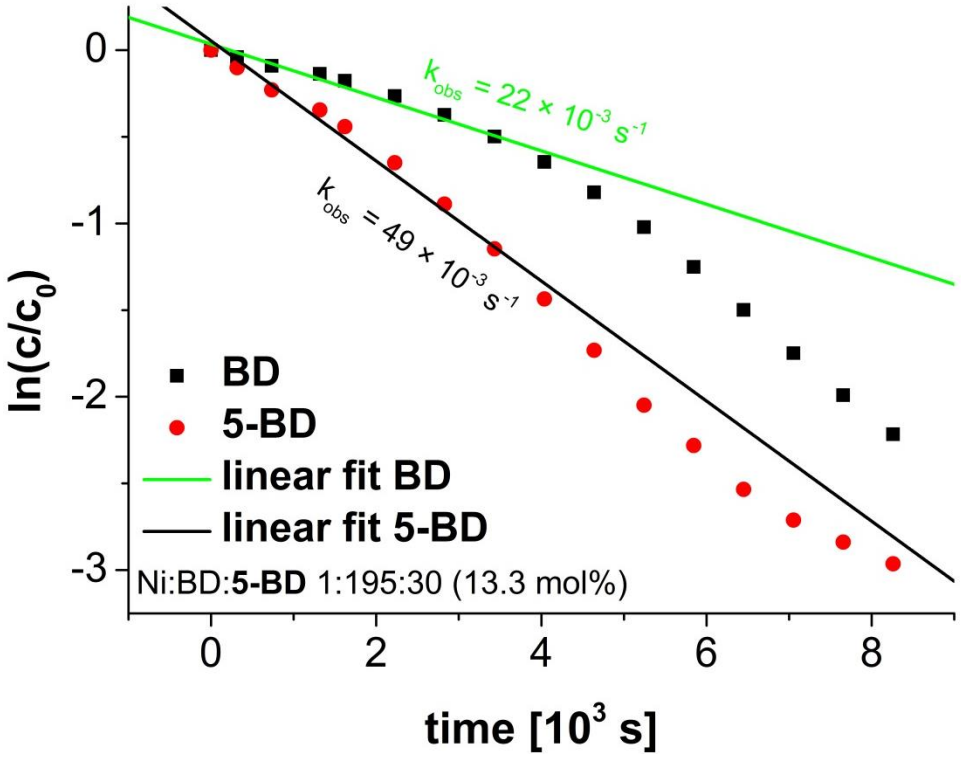
SI 12: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **TMS_2N-4-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3×10^{-3} mol L^{-1}.



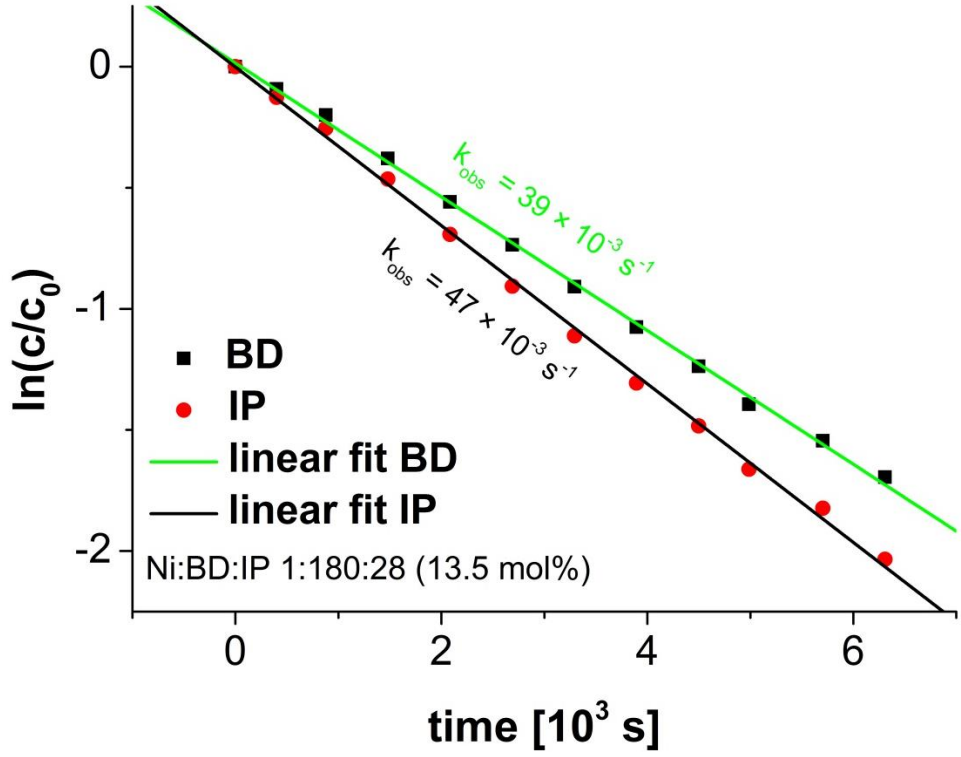
SI 13: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **TMS_2N-5-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3×10^{-3} mol L^{-1}.



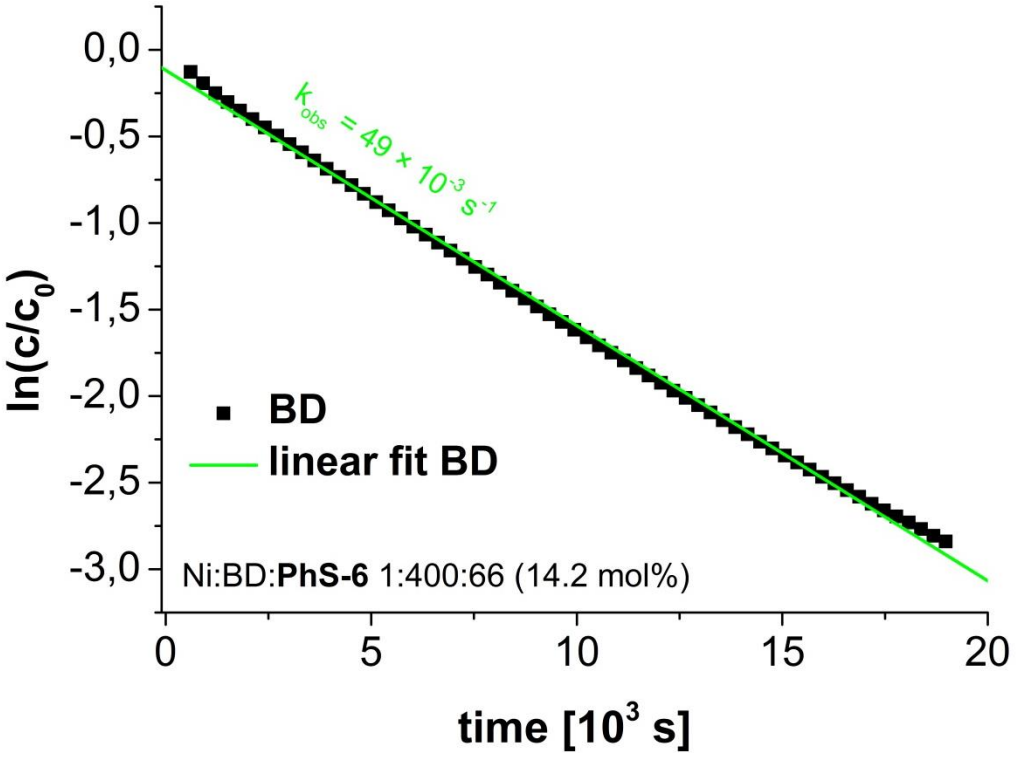
SI 14: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **TMS_2N-6-BD** at 40 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 3×10^{-3} mol L^{-1}.



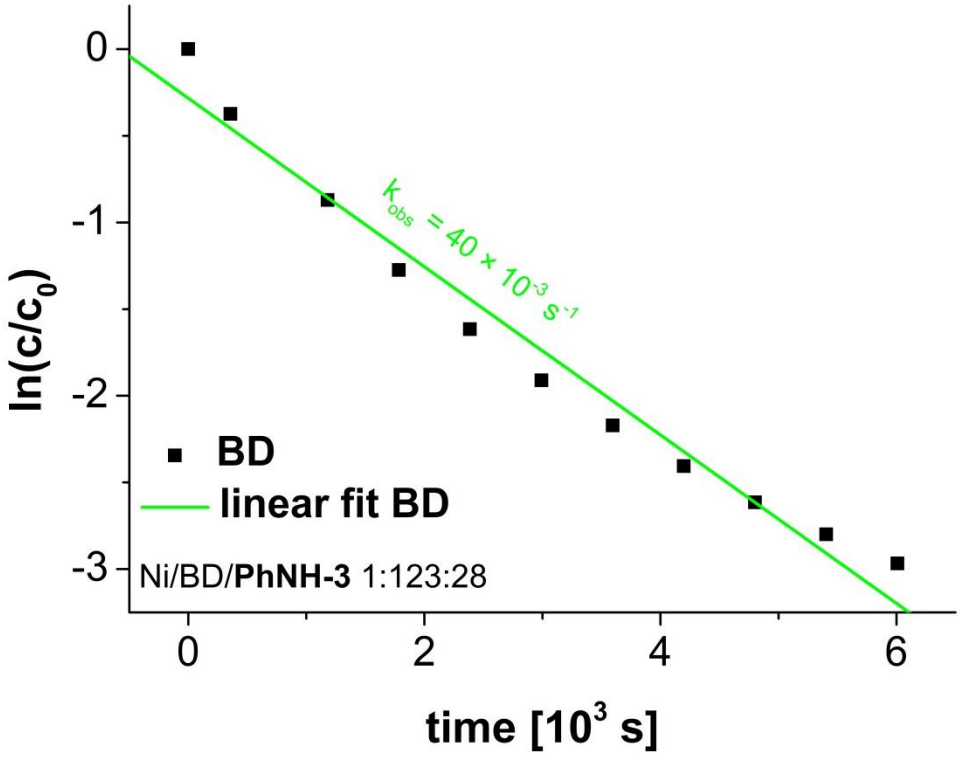
SI 15: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **5-BD** at -15 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 7 × 10^{-3} mol L^{-1}.



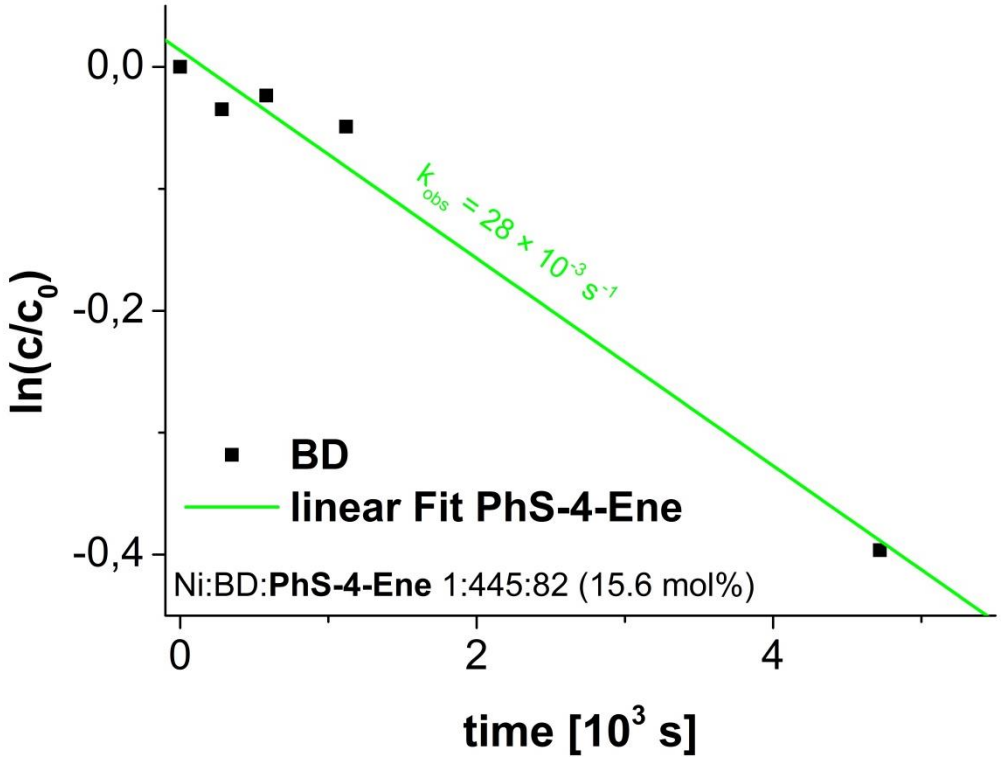
SI 16: Plots and linear fits of kinetic data obtained from a copolymerization of BD and **IP** at -15 °C. The shown k_{obs} values were calculated using the slopes of the linear fits and a **Ni-1** concentration of [**Ni-1**]= 7 × 10^{-3} mol L^{-1}.



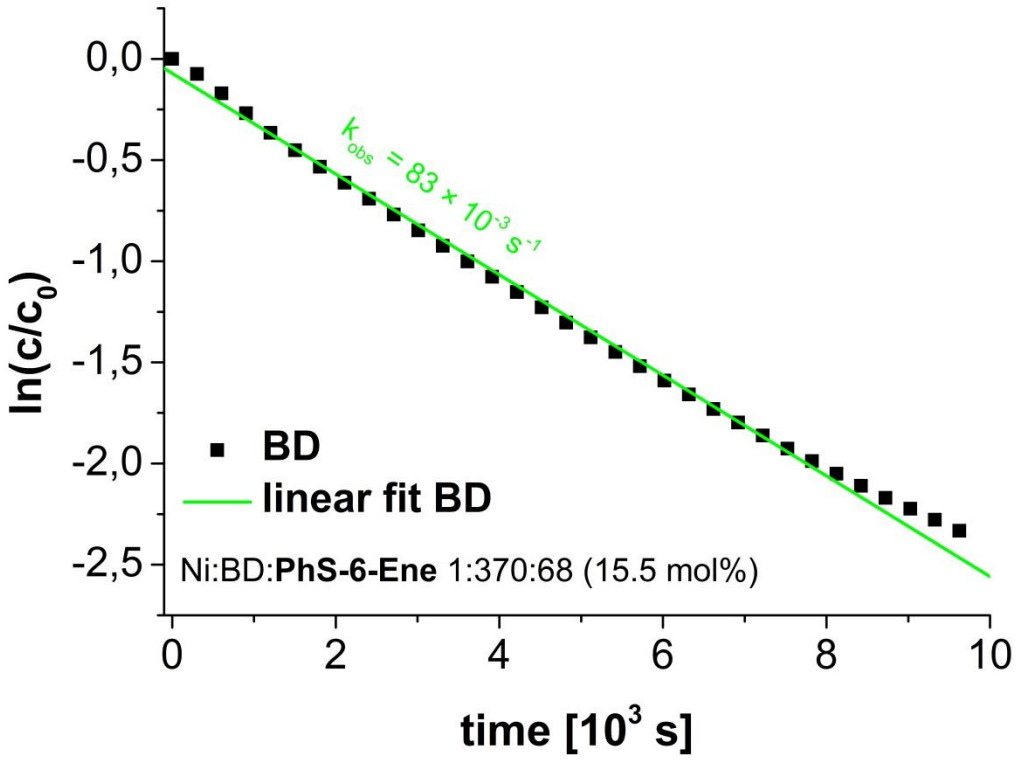
SI 17: Plot and linear fit of kinetic data obtained from a homopolymerization of BD in the presence of **PhS-6** at 40 °C. The shown k_{obs} value was calculated using the slopes of the linear fit and a **Ni-1** concentration of [**Ni-1**] = 3×10^{-3} mol L^{-1}.



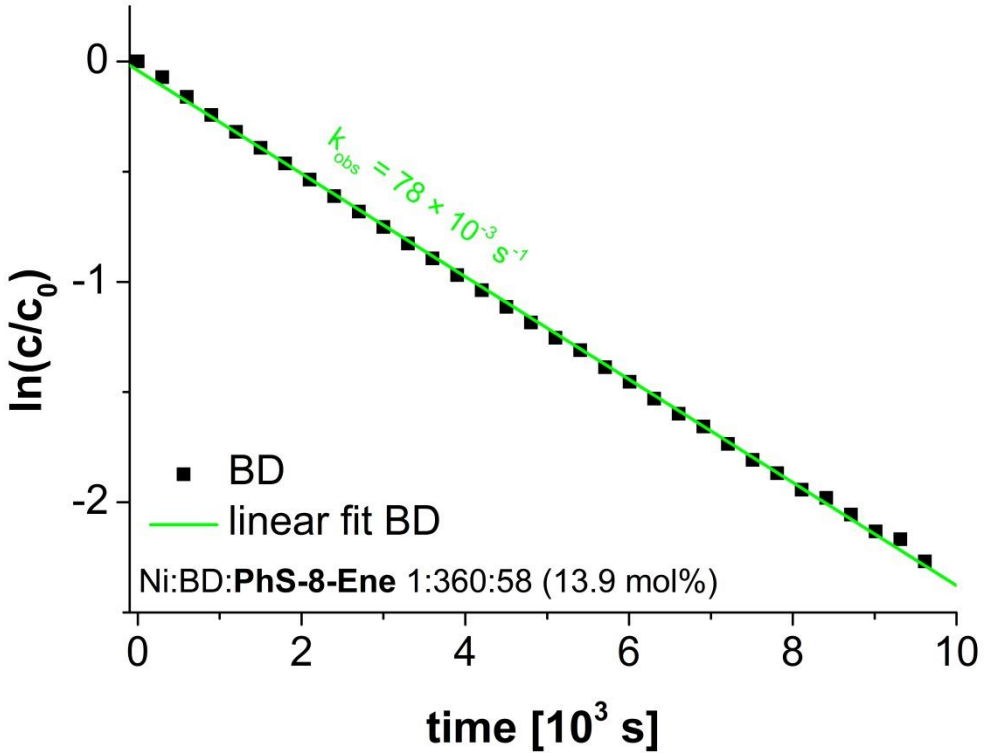
SI 18: Plot and linear fit of kinetic data obtained from a homopolymerization of BD in the presence of **PhNH-3** at 40 °C. The shown k_{obs} value was calculated using the slopes of the linear fit and a **Ni-1** concentration of [**Ni-1**] = 12×10^{-3} mol L^{-1}.



SI 19: Plot and linear fit of kinetic data obtained from a homopolymerization of BD in the presence of **PhS-4-Ene** at 40 °C. The shown k_{obs} value was calculated using the slopes of the linear fit and a **Ni-1** concentration of [**Ni-1**] = 3 × 10^{-3} mol L^{-1}.



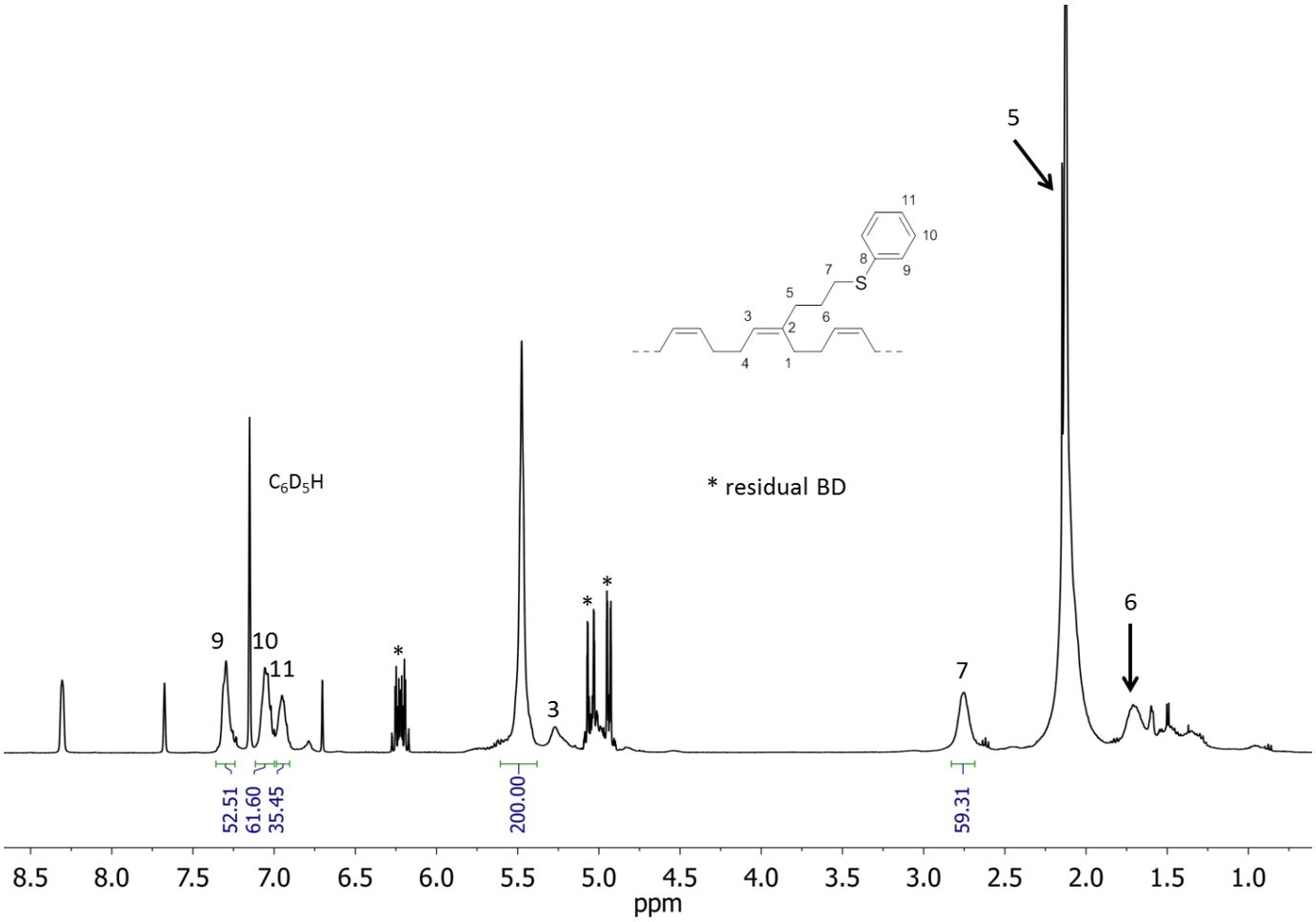
SI 20: Plot and linear fit of kinetic data obtained from a homopolymerization of BD in the presence of **PhS-6-Ene** at 40 °C. The shown k_{obs} value was calculated using the slopes of the linear fit and a **Ni-1** concentration of [**Ni-1**] = 3 × 10^{-3} mol L^{-1}.



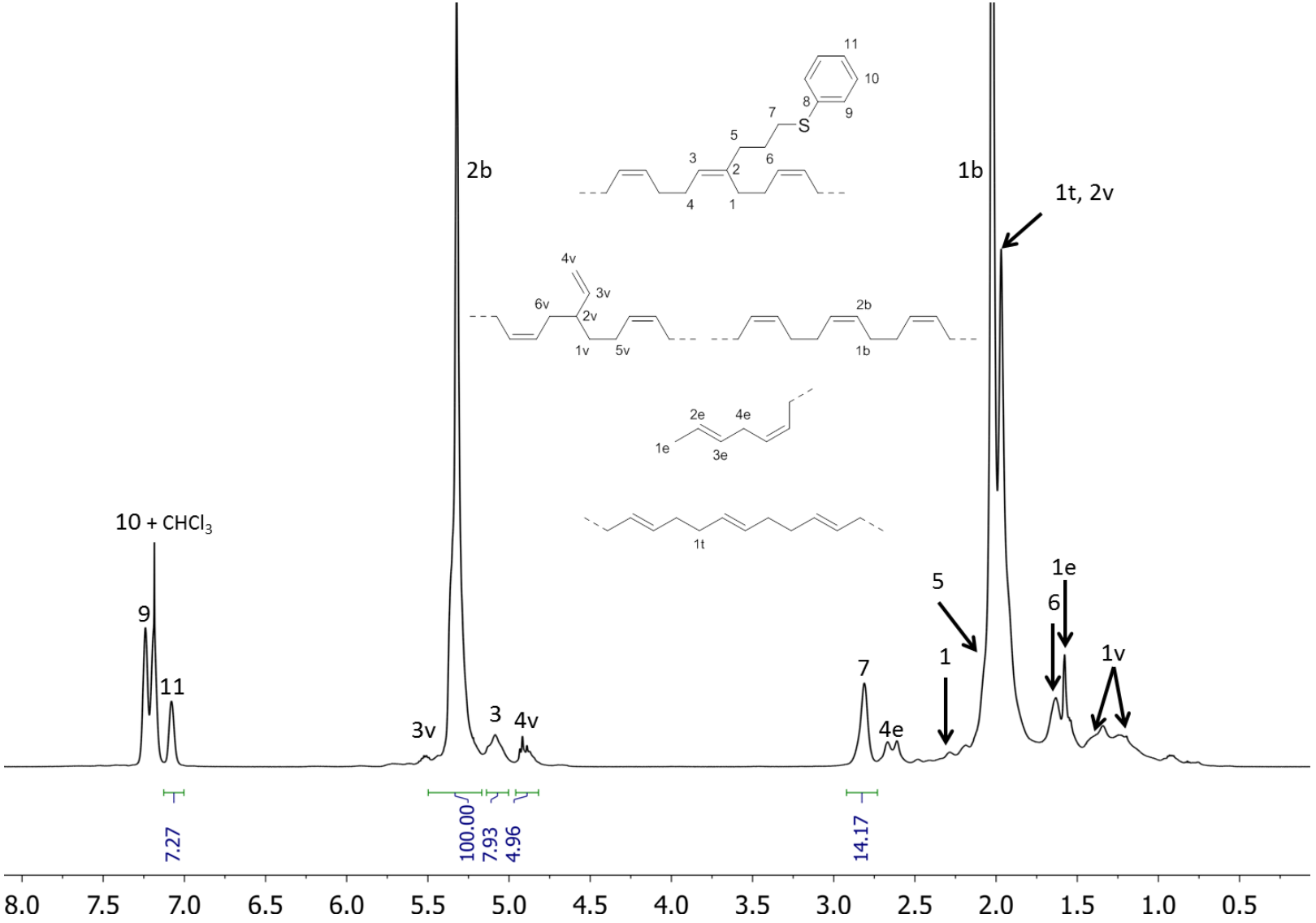
SI 21: Plot and linear fit of kinetic data obtained from a homopolymerization of BD in the presence of **PhS-8-Ene** at 40 °C. The shown k_{obs} value was calculated using the slopes of the linear fit and a **Ni-1** concentration of [**Ni-1**] = 3×10^{-3} mol L^{-1}.

4. Selected NMR-Spectra of Ni-catalyzed Copolymerizations

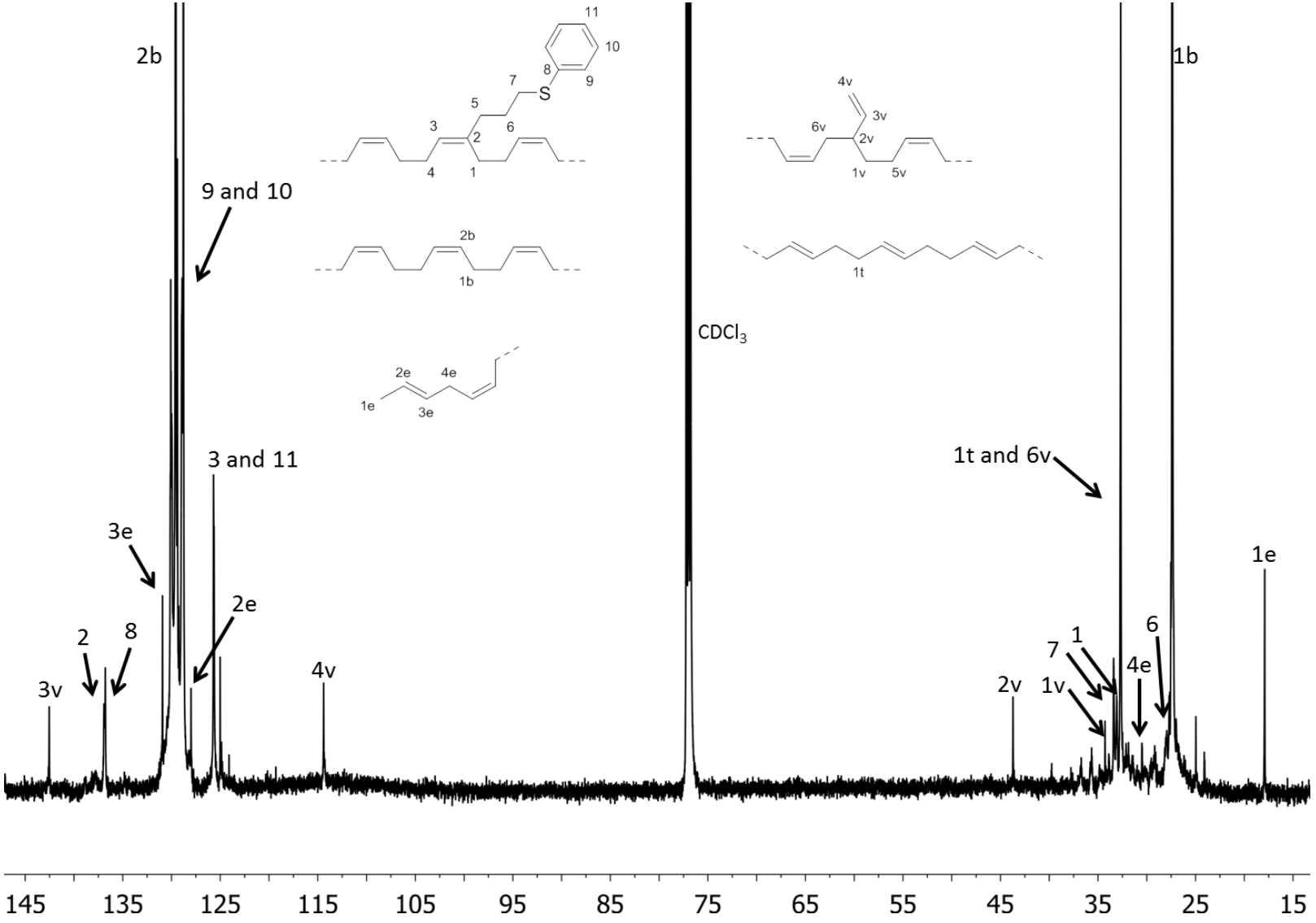
4.1. Copolymerizations with **PhS-3-BD**



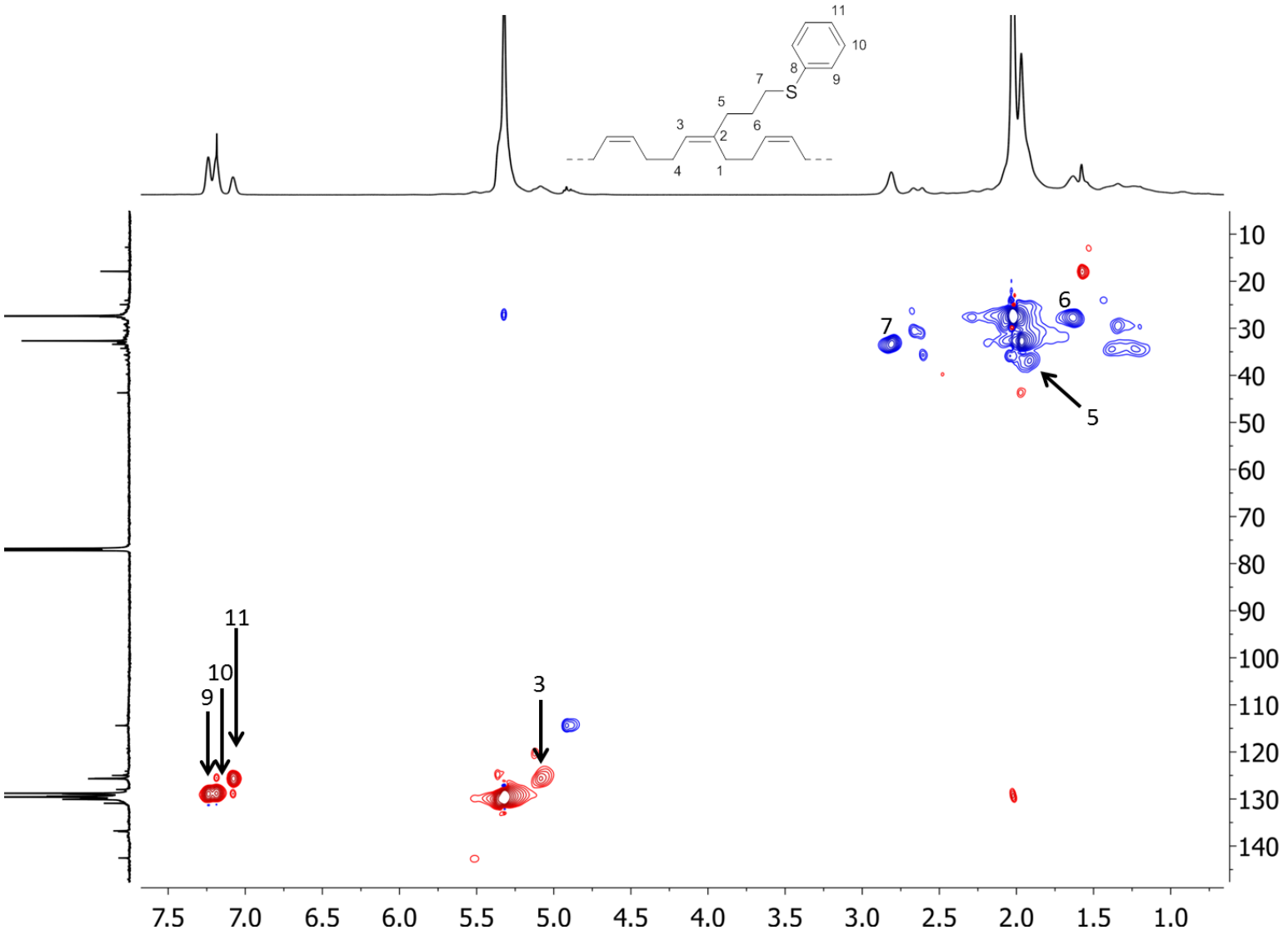
SI 22: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhS-3-BD** (entry 1-1, recorded at 40 °C in C_6D_6).



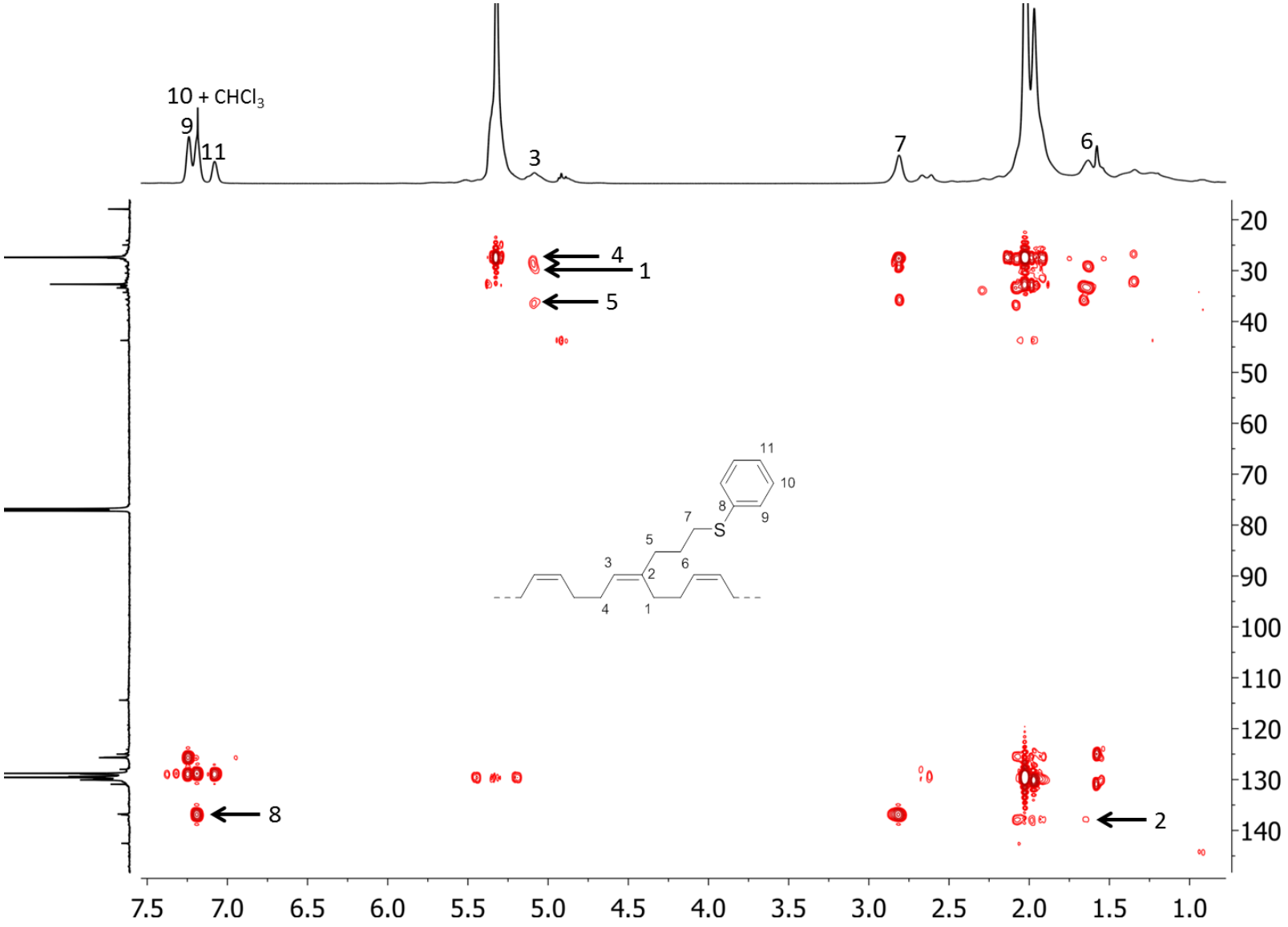
SI 23: ^{1}H NMR spectrum of a copolymer synthesized from BD and **PhS-3-BD** (7 mol% **PhS-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).



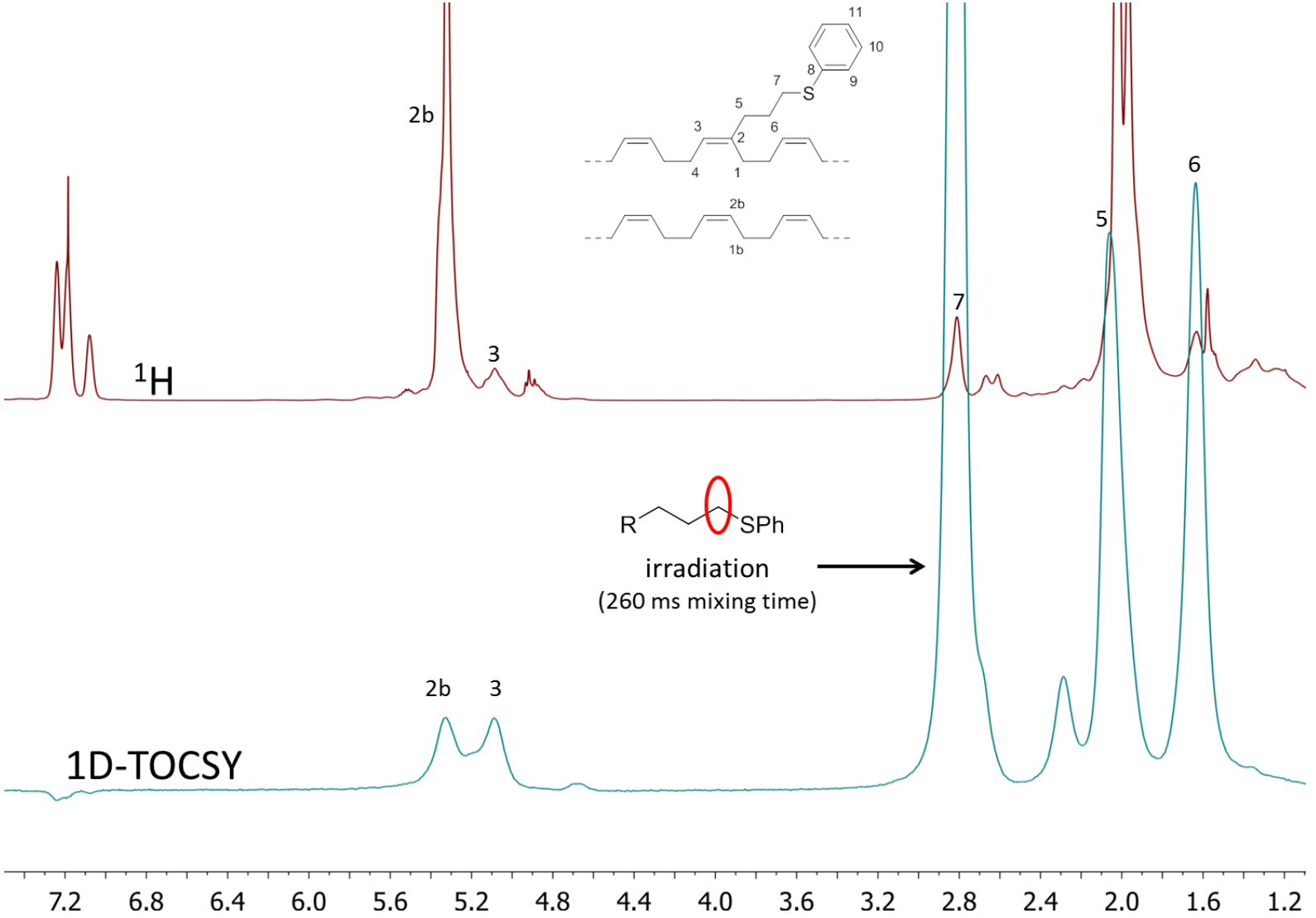
SI 24: ^{13}C NMR spectrum of a copolymer synthesized from BD and **PhS-3-BD** (7 mol% **PhS-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).



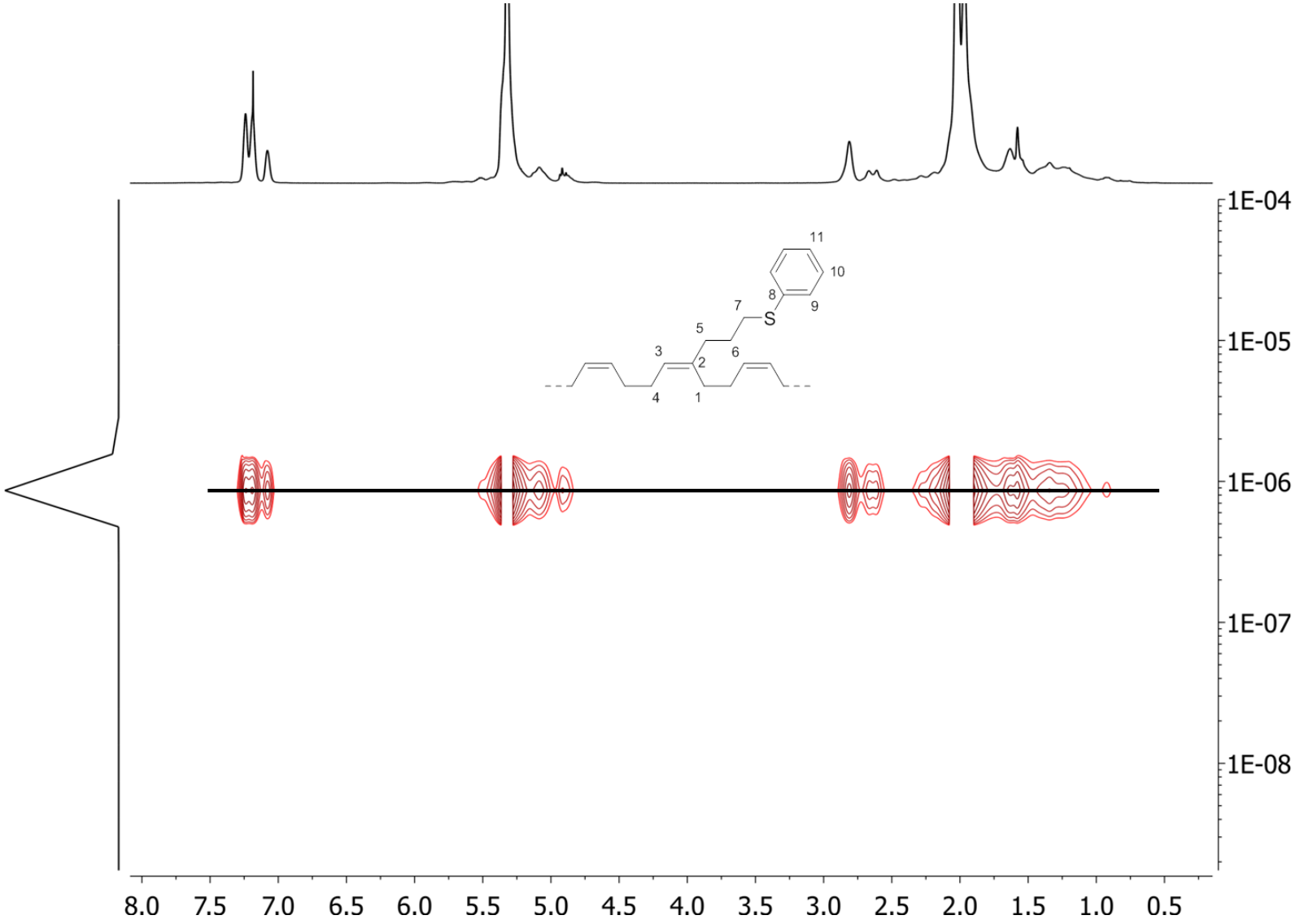
SI 25: HSQC NMR spectrum of a copolymer synthesized from BD and **PhS-3-BD** (7 mol% **PhS-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).



SI 26: HMBC NMR spectrum of a copolymer synthesized from BD and **PhS-3-BD** (7 mol% **PhS-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).

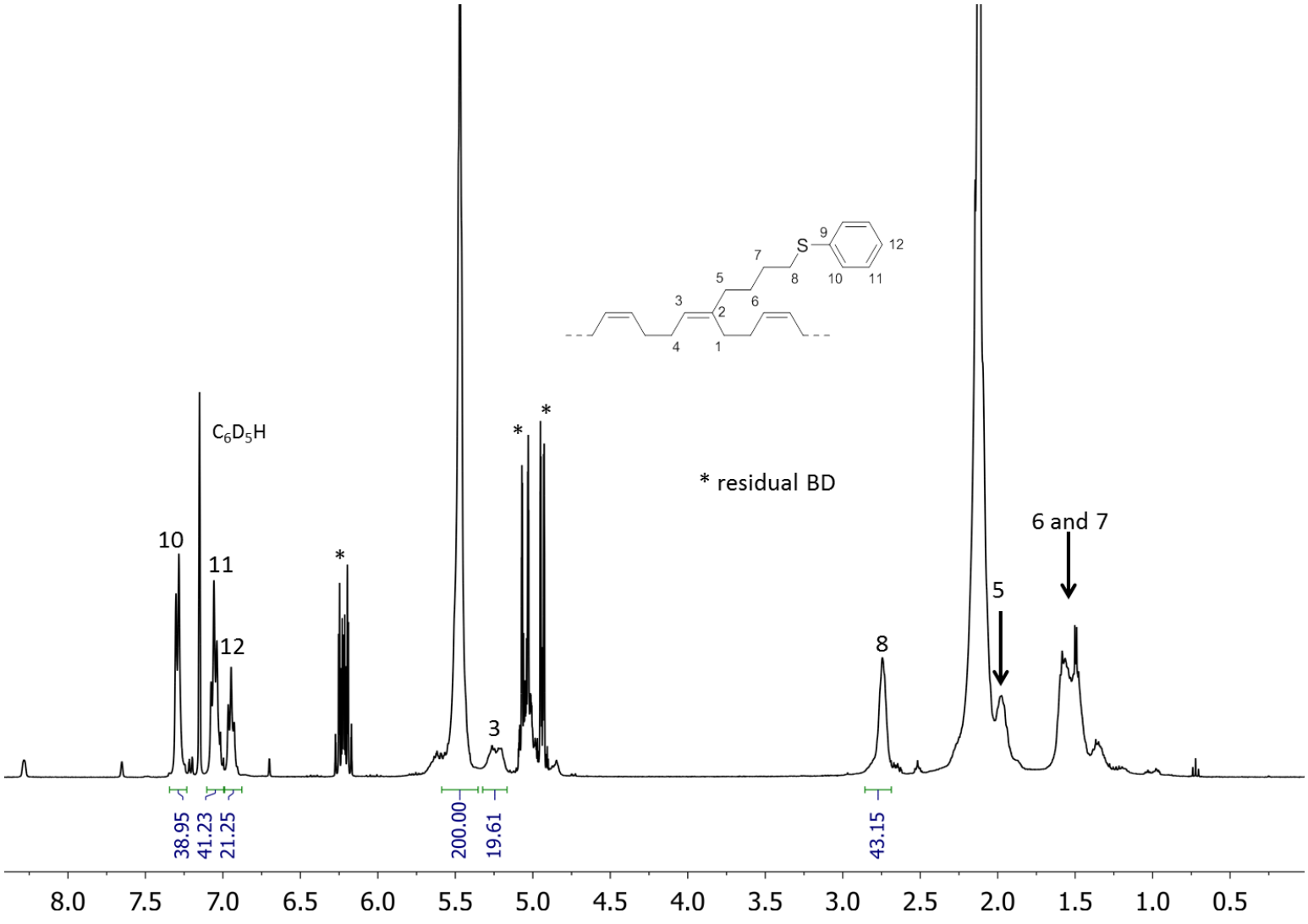


SI 27: 1D-TOCSY and ^{1}H-spectrum of a copolymer synthesized from BD and **PhS-3-BD** (7 mol% **PhS-3-BD** incorporation, recorded at 27 °C in $CDCl_3$). Mixing time in TOCSY experiment was 260 ms.



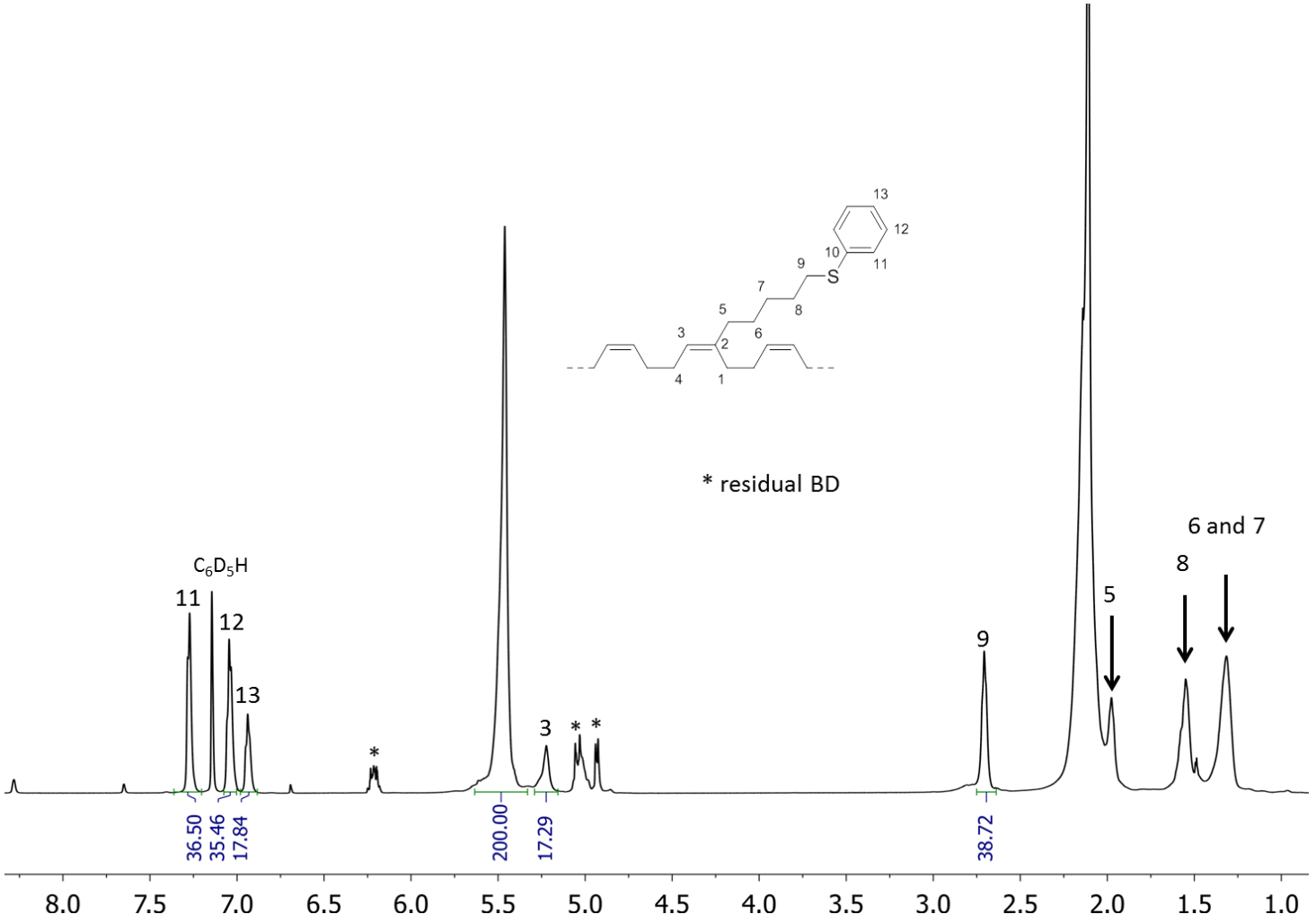
SI 28: DOSY NMR spectrum of a copolymer synthesized from BD and **PhS-3-BD** (7 mol% **PhS-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).

4.2. COPOLYMERIZATIONS WITH **PHS-4-BD**



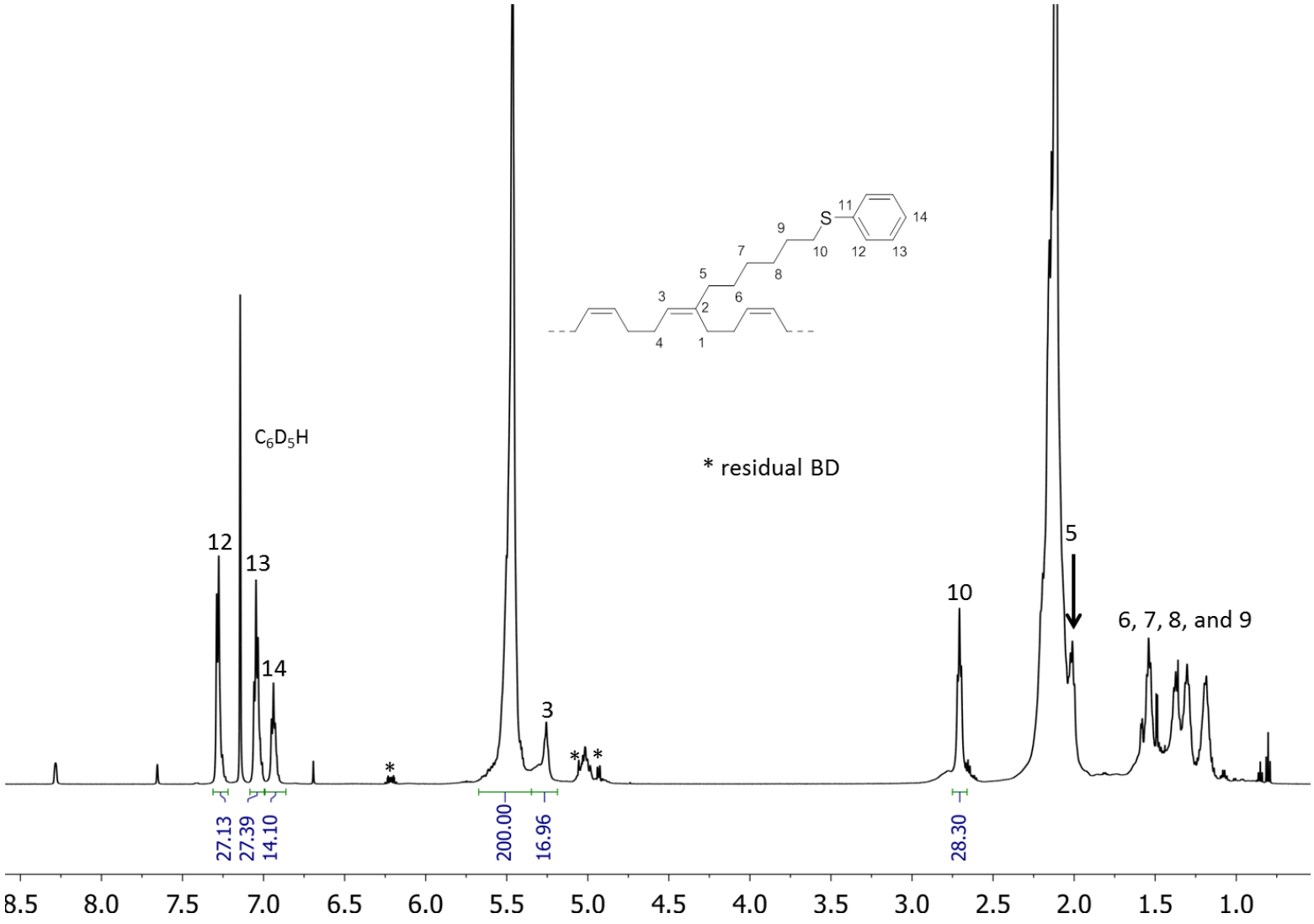
SI 29: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhS-4-BD** (entry 1-2, recorded at 40 °C in C_6D_6).

4.3. COPOLYMERIZATIONS WITH **PHS-5-BD**



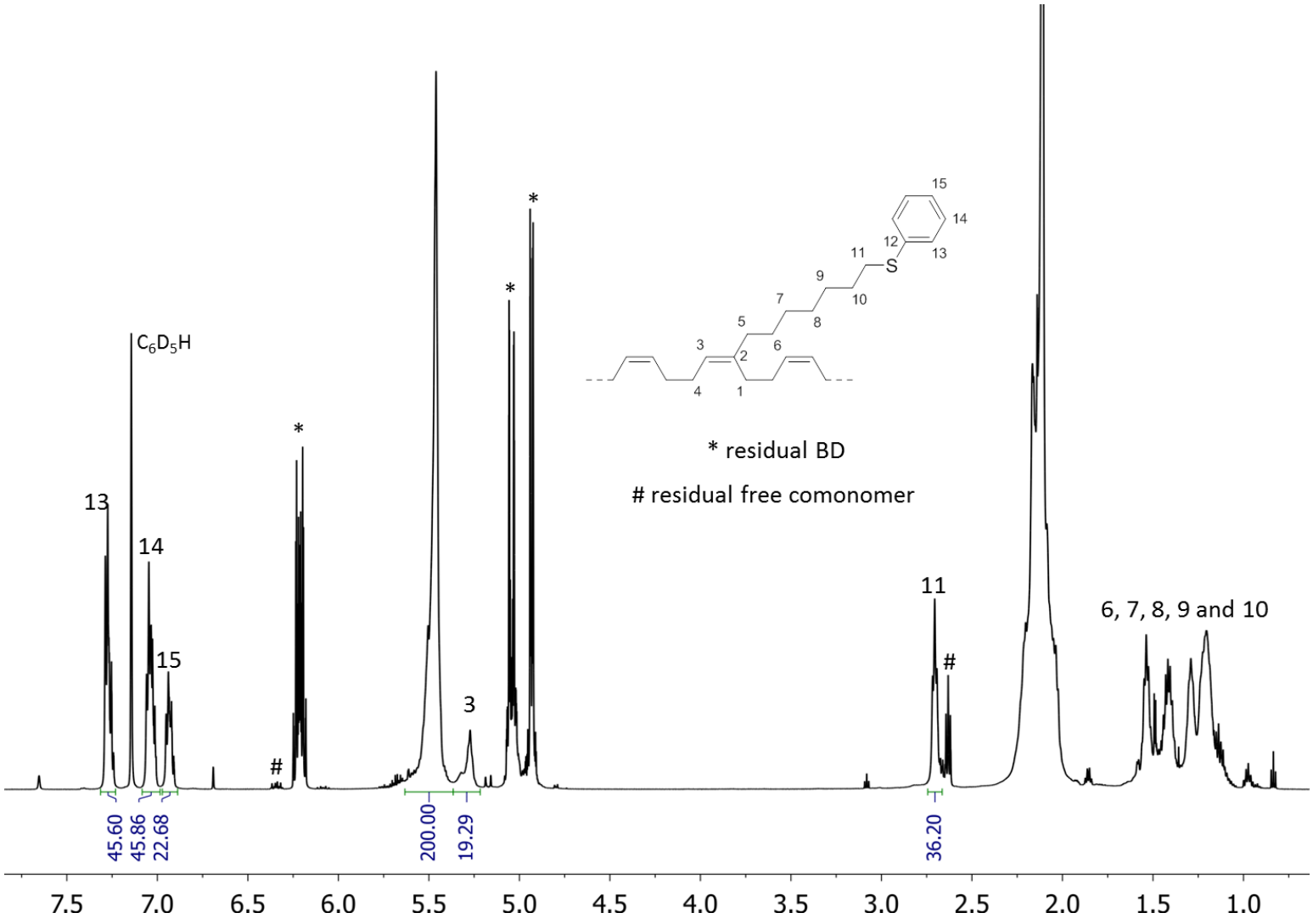
SI 30: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhS-5-BD** (entry 1-3, recorded at 40 °C in C_6D_6).

4.4. COPOLYMERIZATIONS WITH **PHS-6-BD**



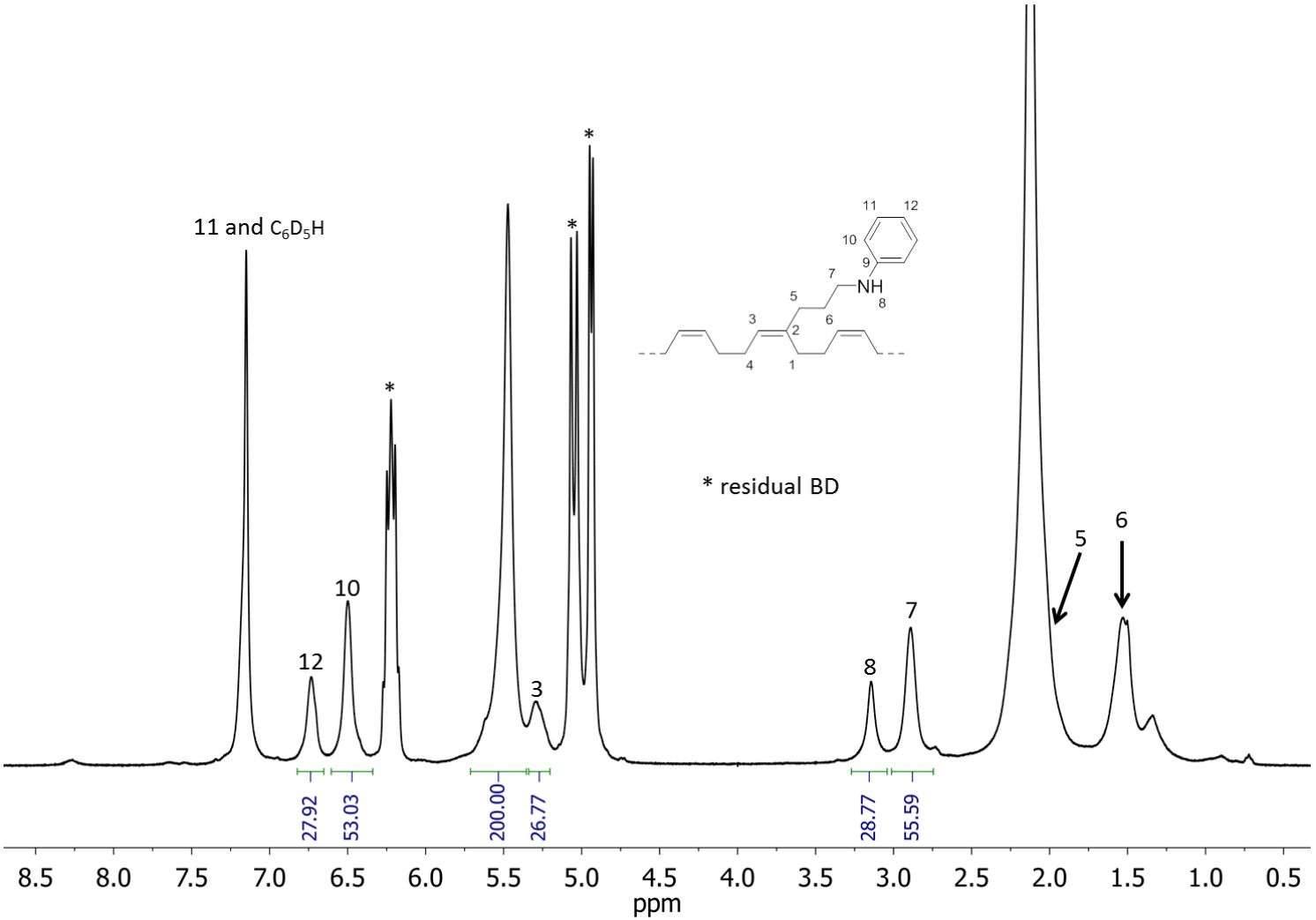
SI 31: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhS-6-BD** (entry 1-4, recorded at 40 °C in C_6D_6).

4.5. COPOLYMERIZATIONS WITH **PHS-7-BD**



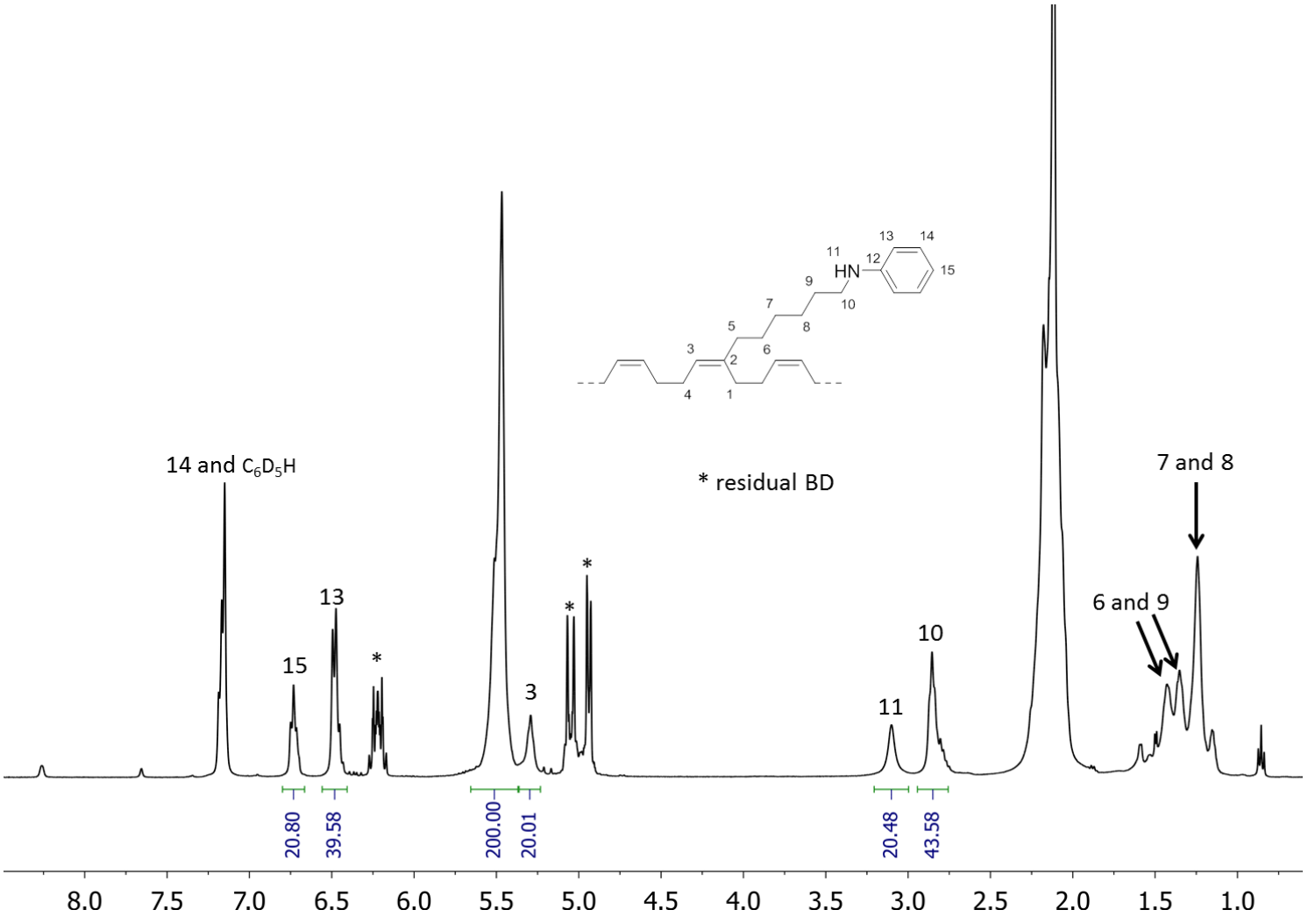
SI 32: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhS-7-BD** (entry 1-5, recorded at 40 °C in C_6D_6).

4.6. COPOLYMERIZATIONS WITH **PHNH-3-BD**

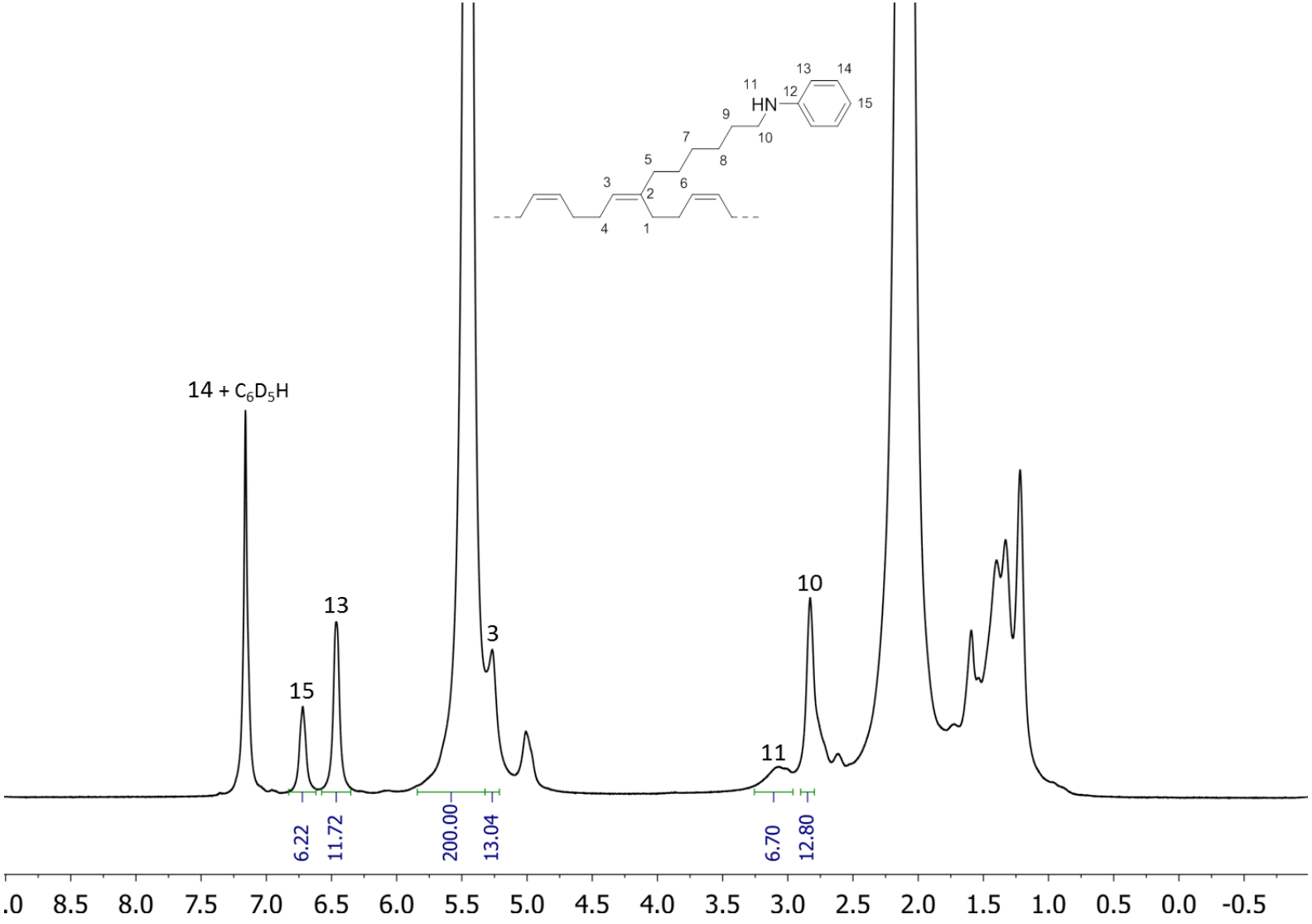


SI 33: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhNH-3-BD** (entry 1-6, recorded at 40 °C in C_6D_6).

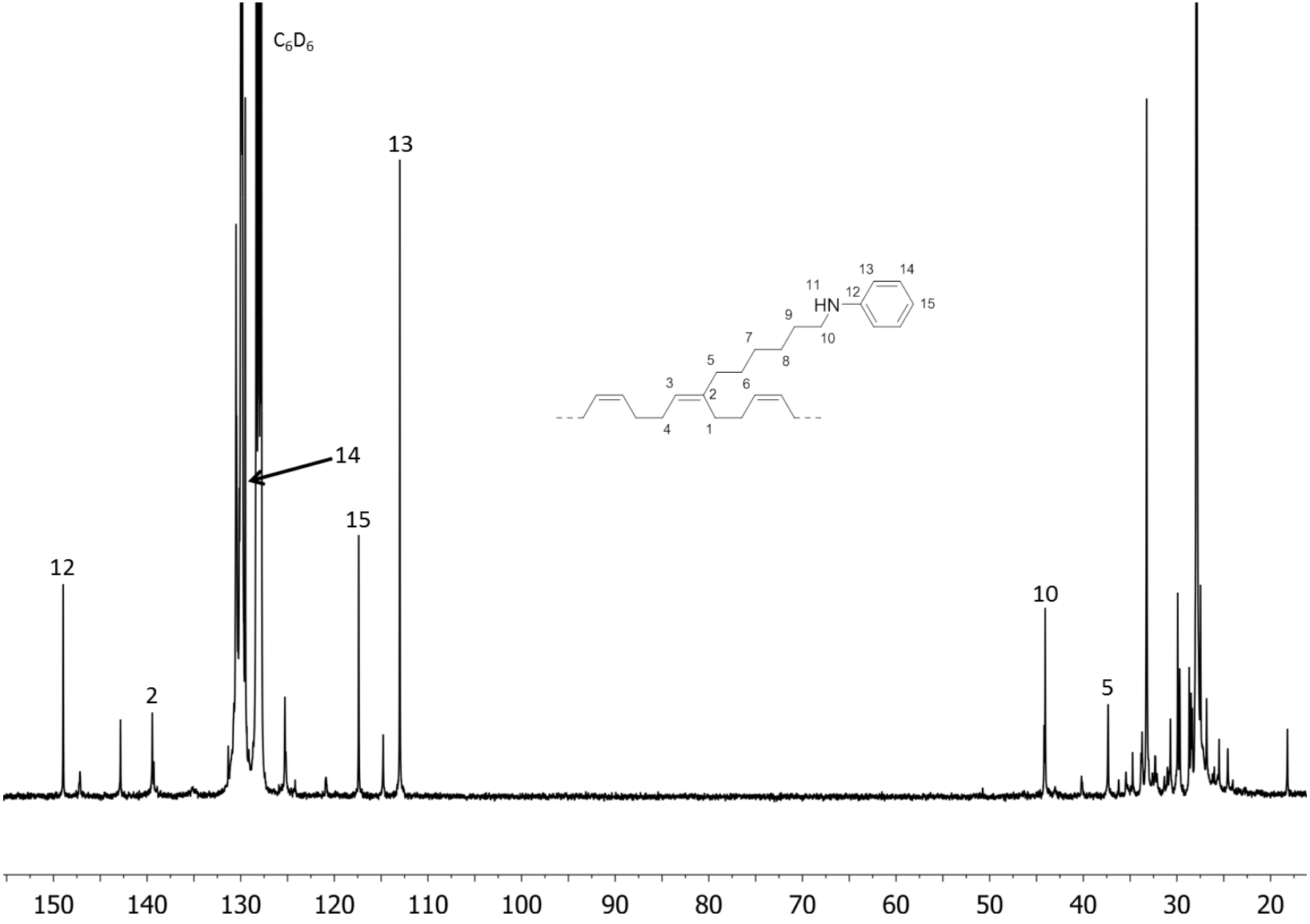
4.7. COPOLYMERIZATIONS WITH **PHNH-6-BD**



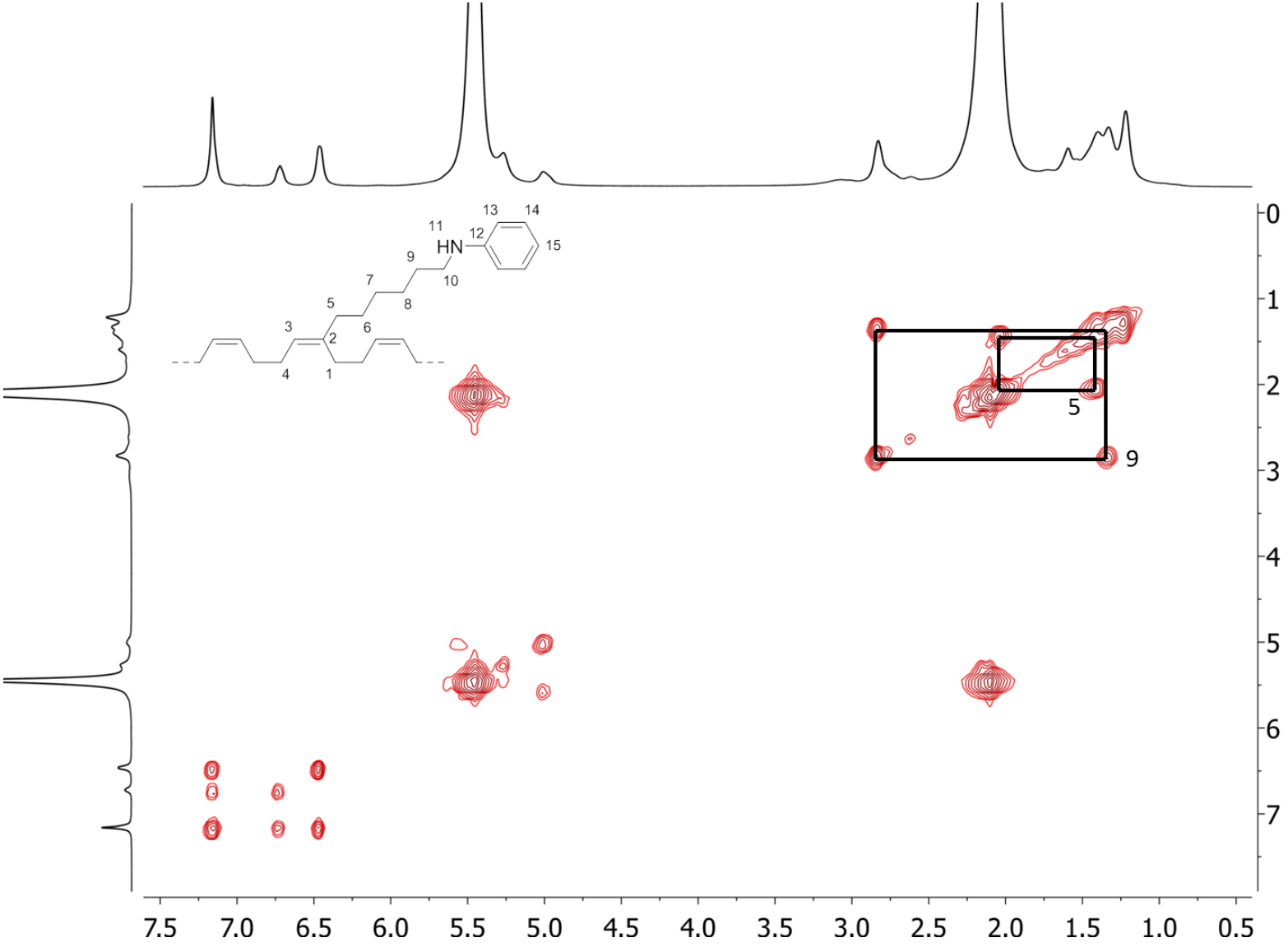
SI 34: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **PhNH-6-BD** (entry 1-7, recorded at 40 °C in C_6D_6).



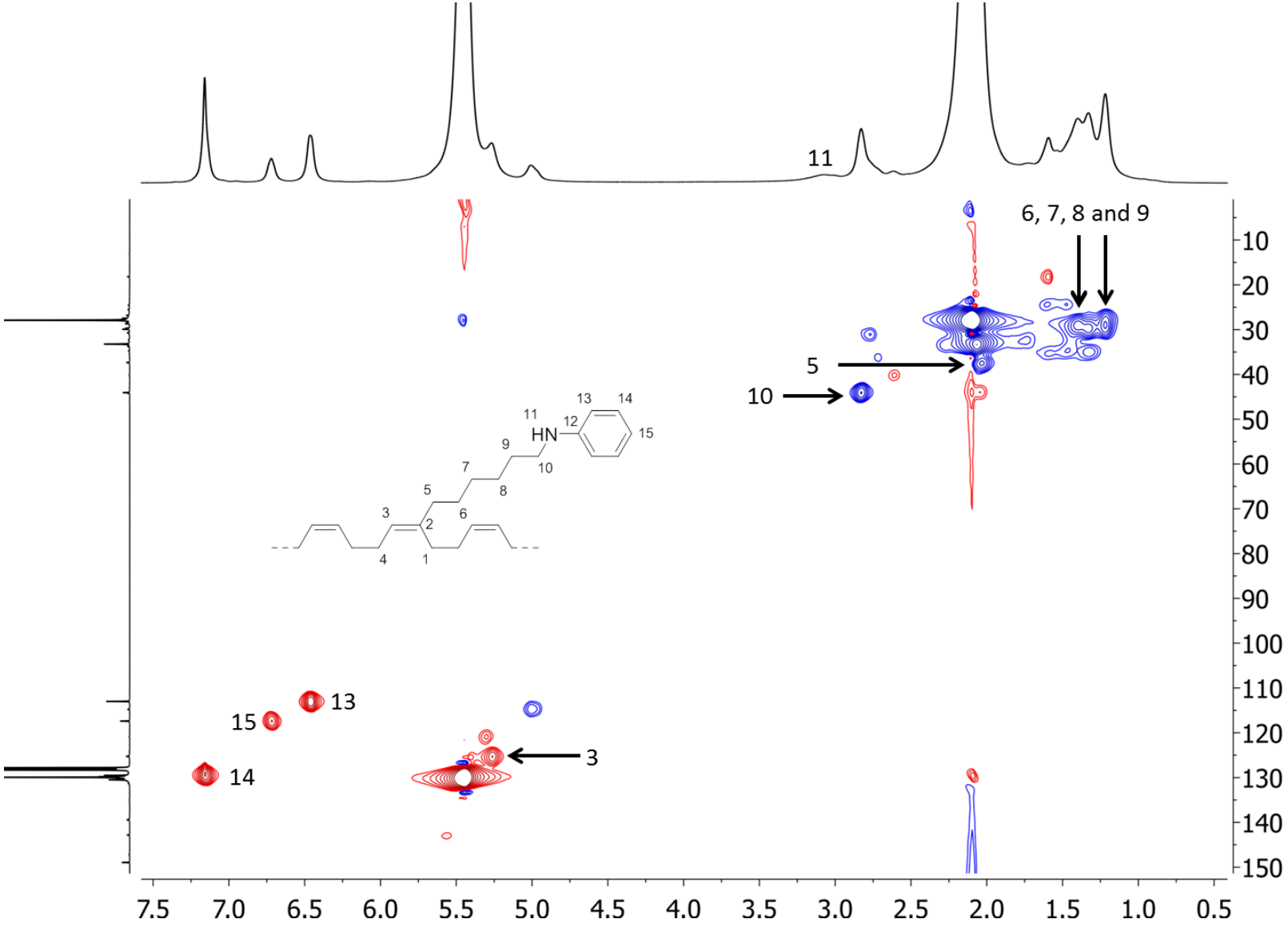
SI 35: ^{1}H NMR spectrum of a copolymer synthesized from BD and **PhNH-6-BD** (6 mol% **PhNH-6-BD** incorporation, recorded at 27 °C in C_6D_6).



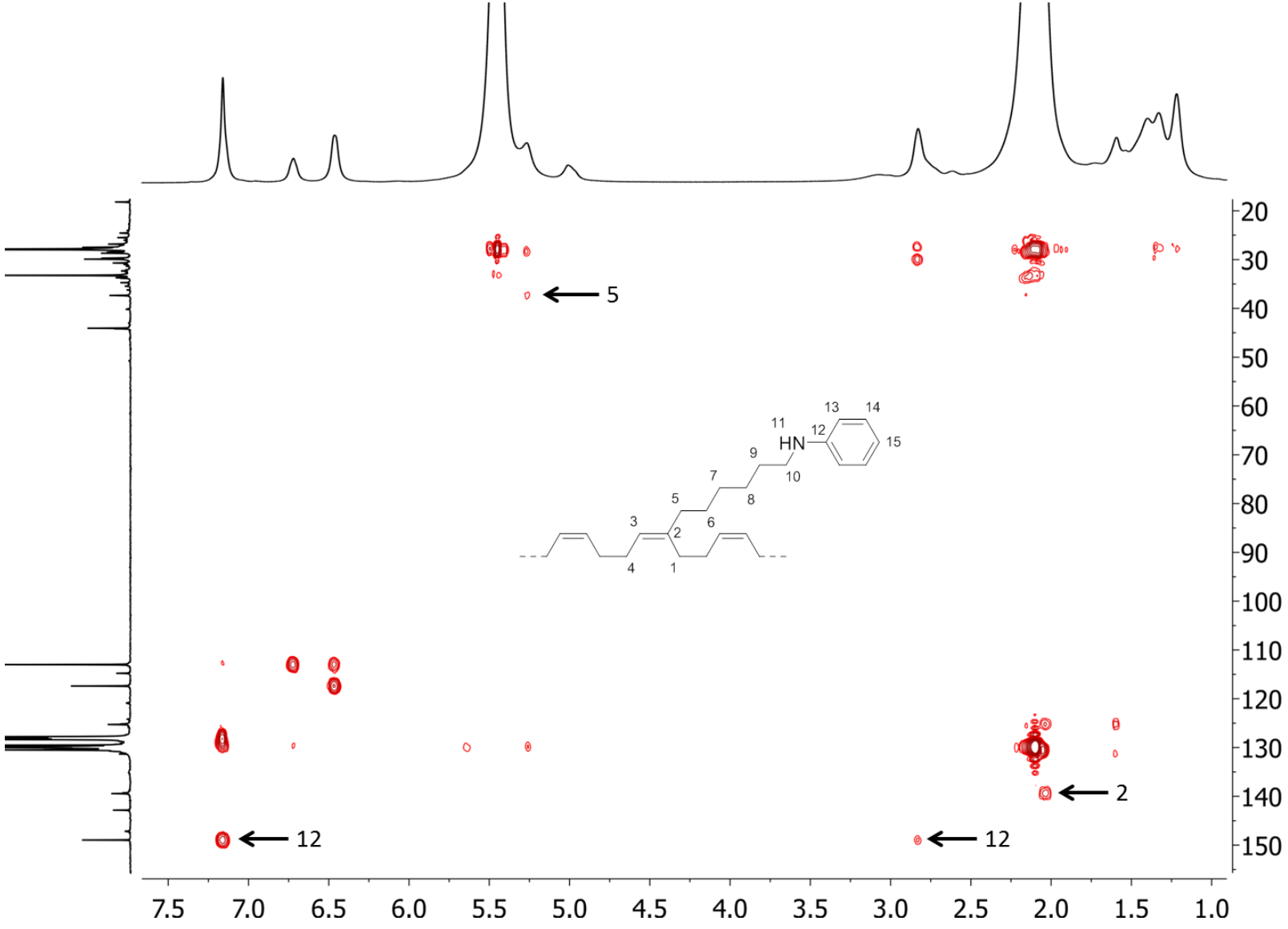
SI 36: ^{13}C NMR spectrum of a copolymer synthesized from BD and **PhNH-6-BD** (6 mol% **PhNH-6-BD** incorporation, recorded at 27 °C in C_6D_6).



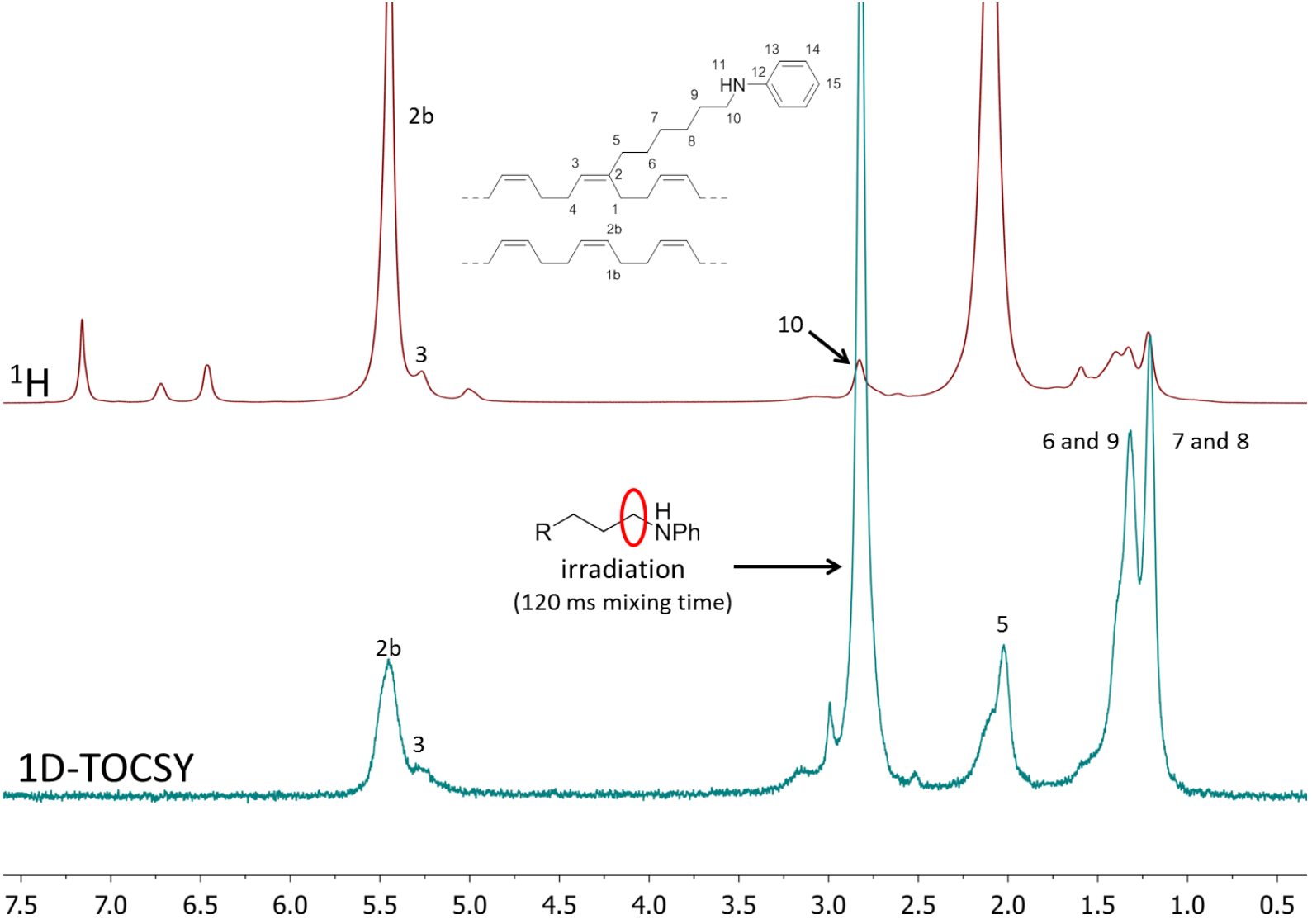
SI 37: COSY NMR spectrum of a copolymer synthesized from BD and **PhNH-6-BD** (6 mol% **PhNH-6-BD** incorporation, recorded at 27 °C in C_6D_6).



SI 38: HSQC NMR spectrum of a copolymer synthesized from BD and **PhNH-6-BD** (6 mol% **PhNH-6-BD** incorporation, recorded at 27 °C in C_6D_6).

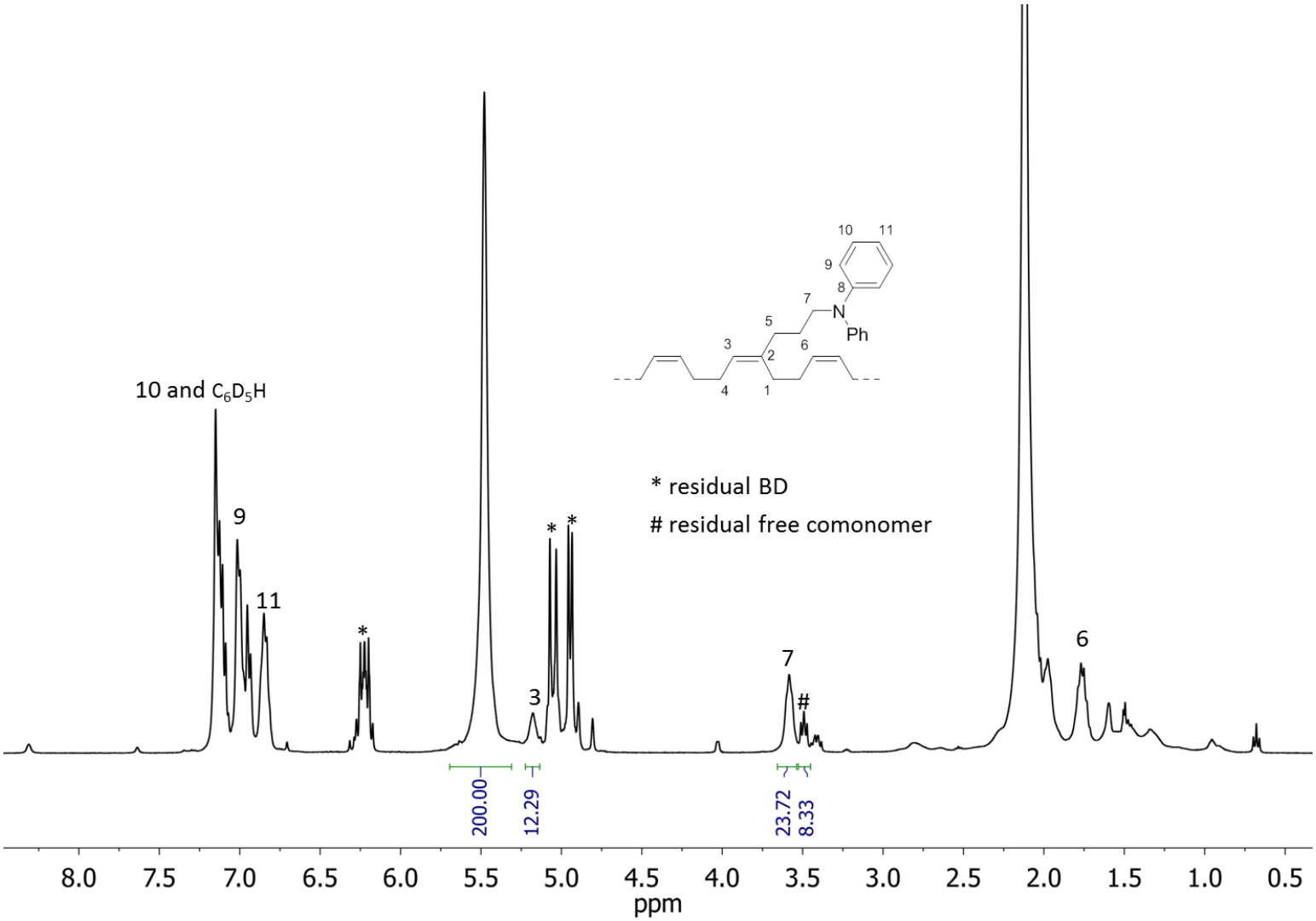


SI 39: HMBC NMR spectrum of a copolymer synthesized from BD and **PhNH-6-BD** (6 mol% **PhNH-6-BD** incorporation, recorded at 27 °C in C_6D_6).



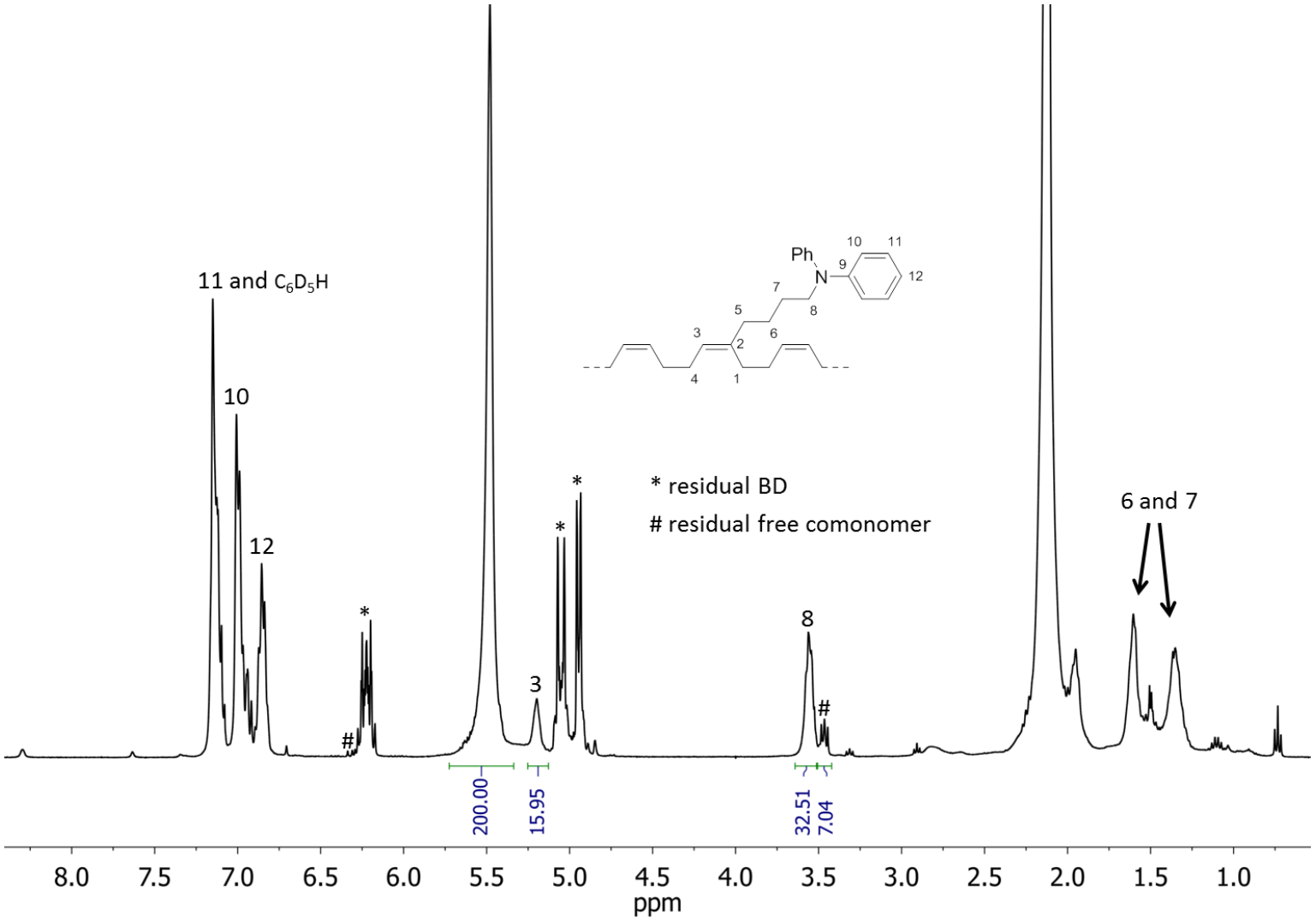
SI 40: 1D-TOCSY and ^{1}H-spectrum of a copolymer synthesized from BD and **PhNH-6-BD** (6 mol% **PhNH-6-BD** incorporation, recorded at 27 °C in C_6D_6). Mixing time in TOCSY experiment was 120 ms.

4.8. COPOLYMERIZATIONS WITH **PH_2N-3-BD**



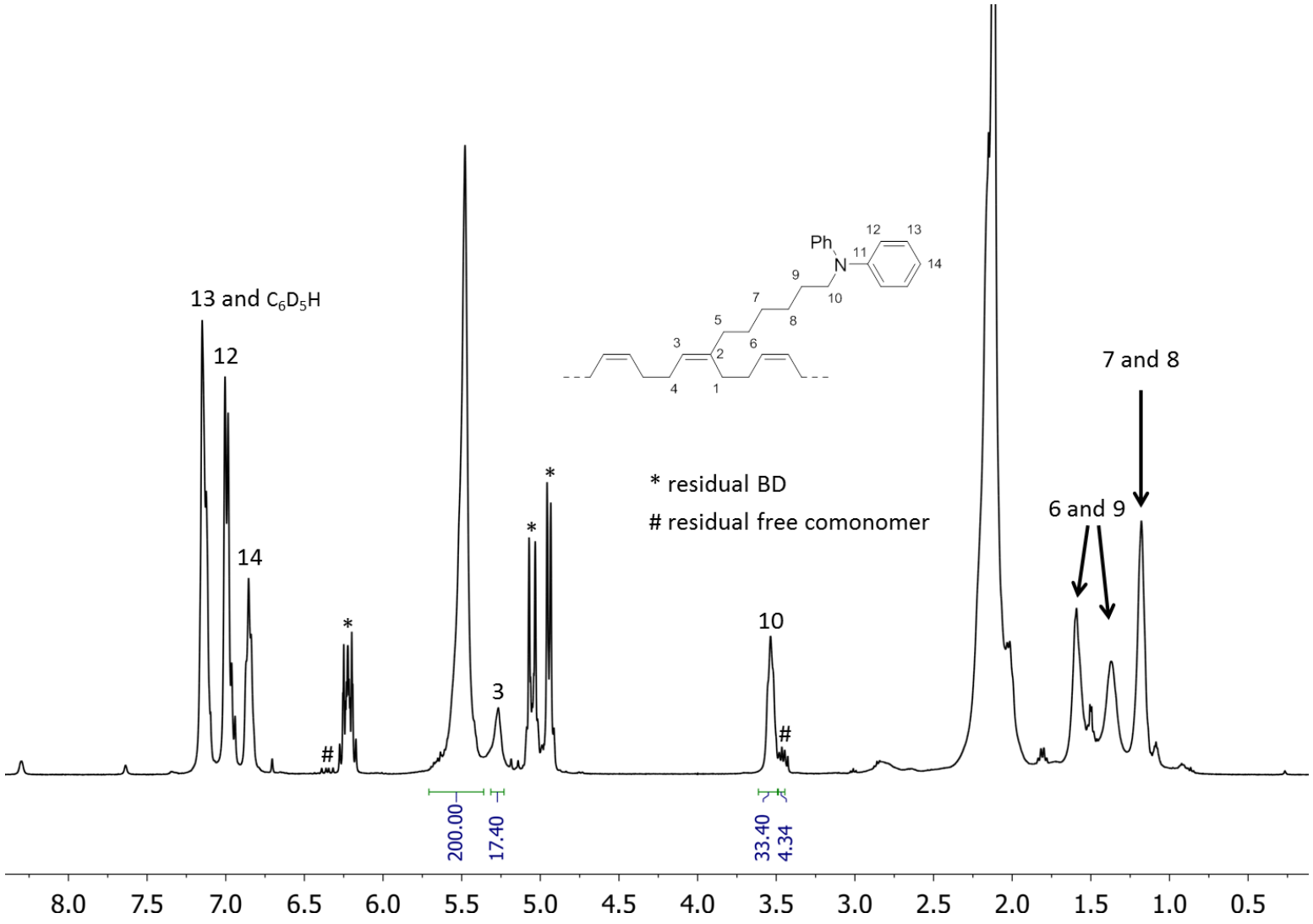
SI 41: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **Ph_2N-3-BD** (entry S1-8, recorded at 40 °C in C_6D_6).

4.9. COPOLYMERIZATIONS WITH **PH_2N-4-BD**



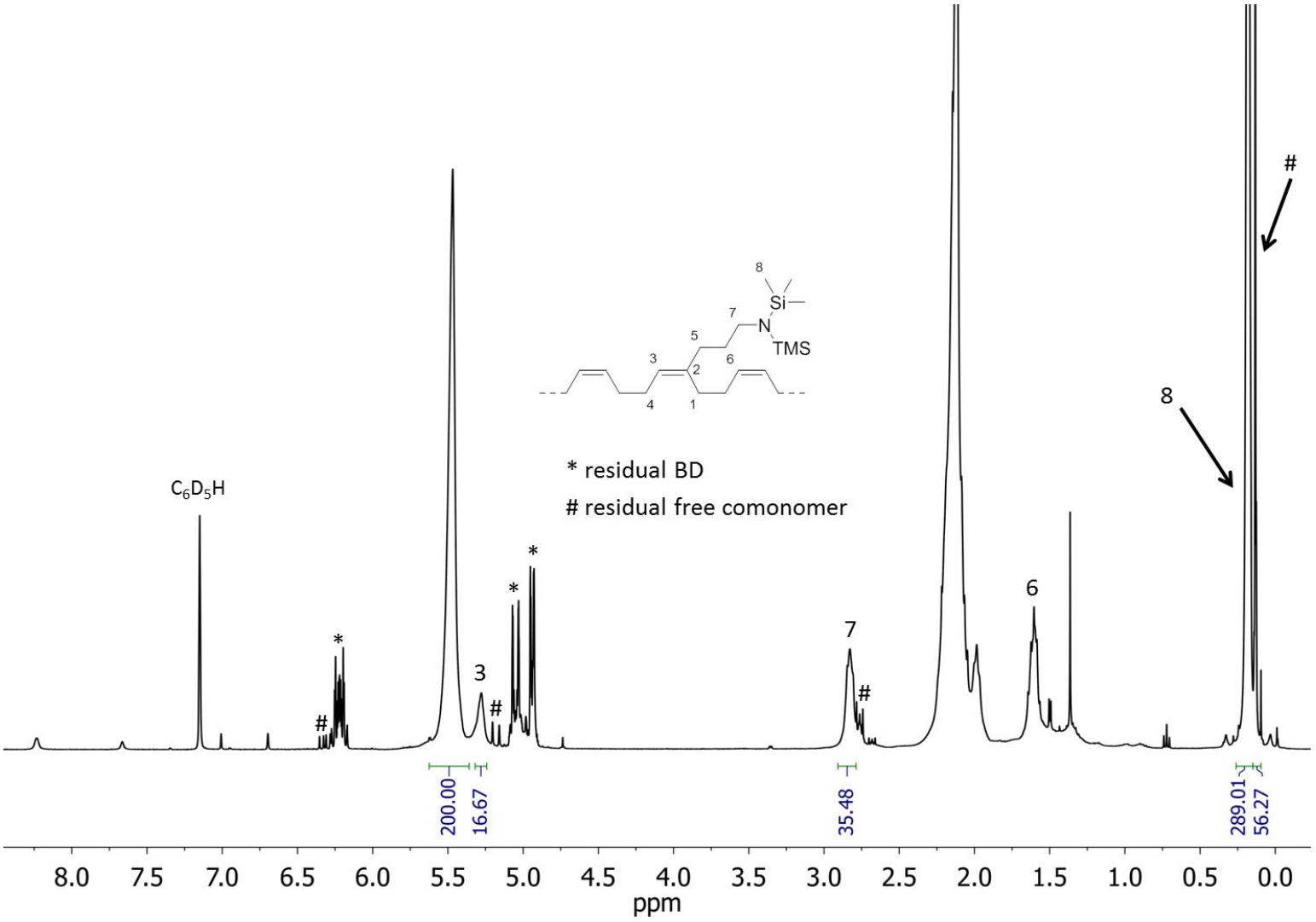
SI 42: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **Ph_2N-4-BD** (entry S1-9, recorded at 40 °C in C_6D_6).

4.10. COPOLYMERIZATIONS WITH **PH_2N-6-BD**

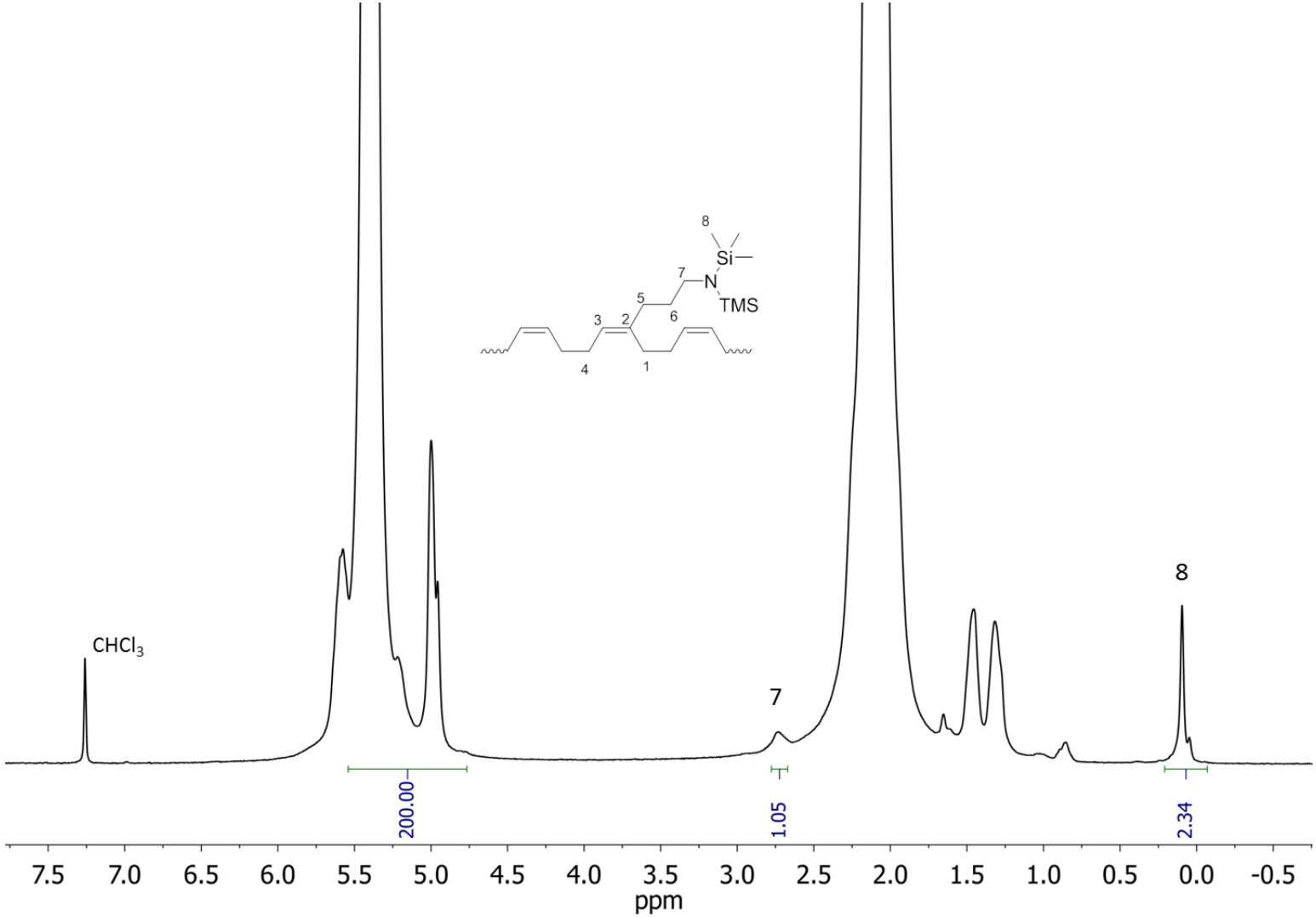


SI 43: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **Ph_2N-6-BD** (entry S1-10, recorded at 40 °C in C_6D_6).

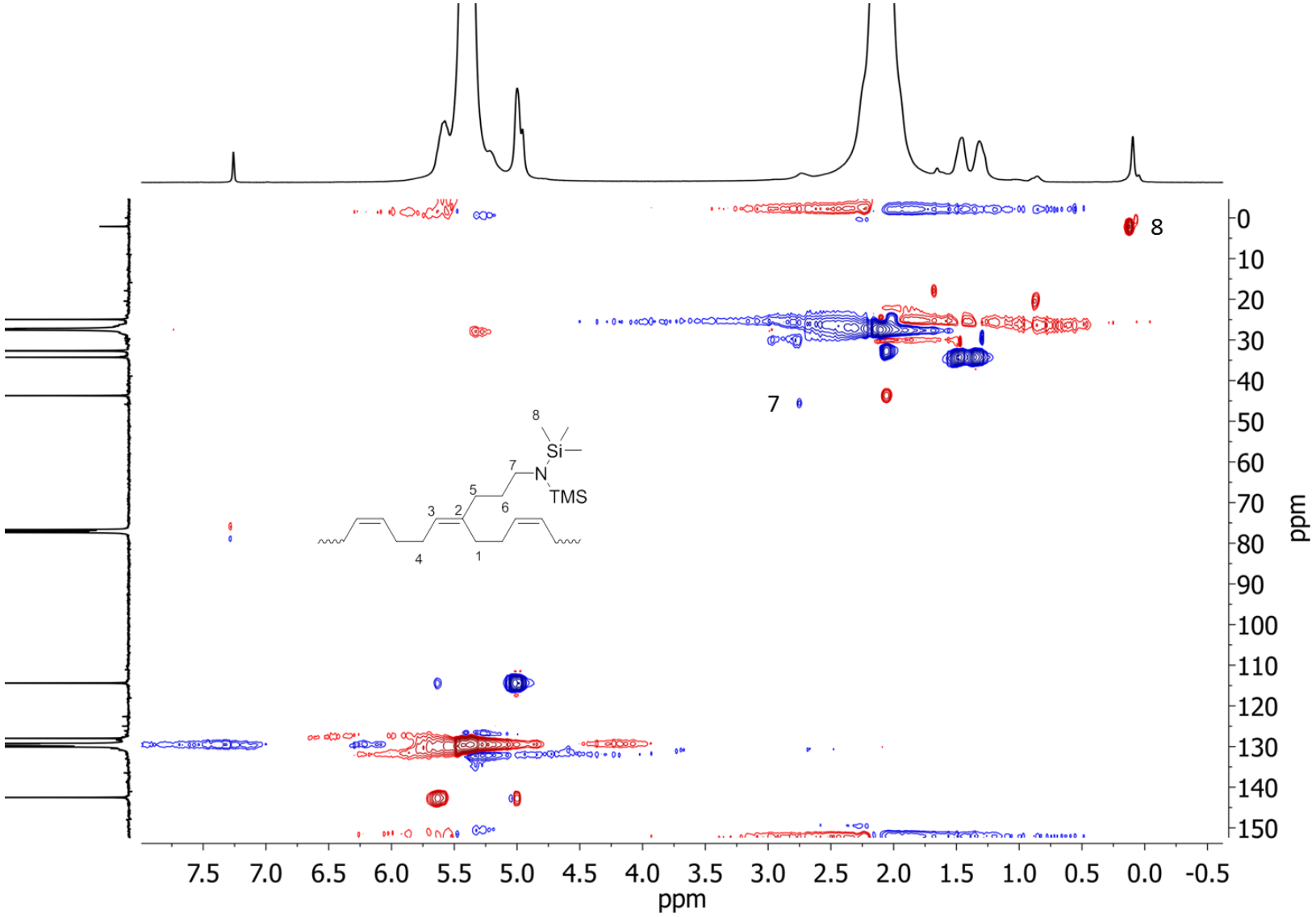
4.11. COPOLYMERIZATIONS WITH **TMS_2N-3-BD**



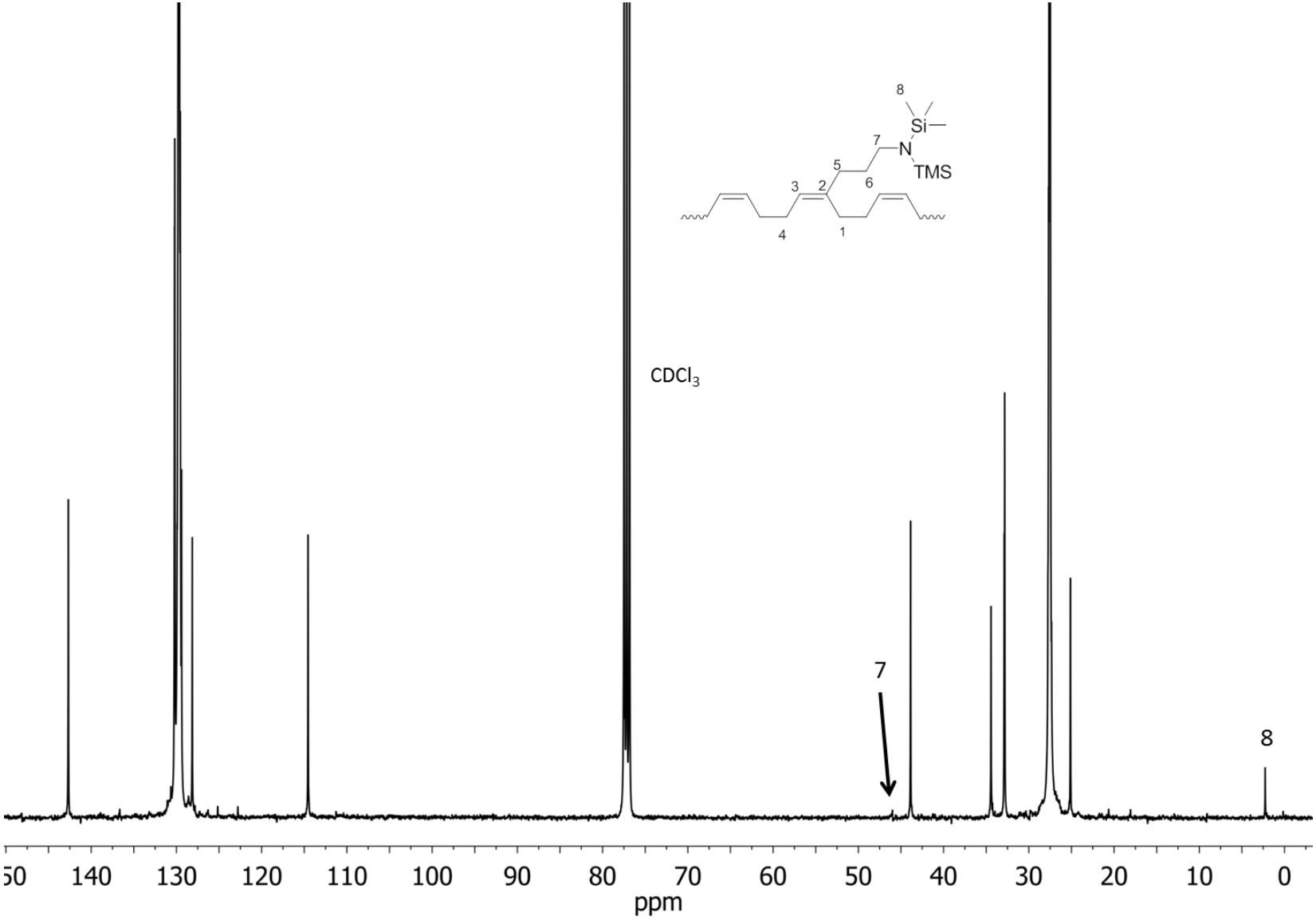
SI 44: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **TMS_2N-3-BD** (entry S1-11, recorded at 40 °C in C_6D_6).



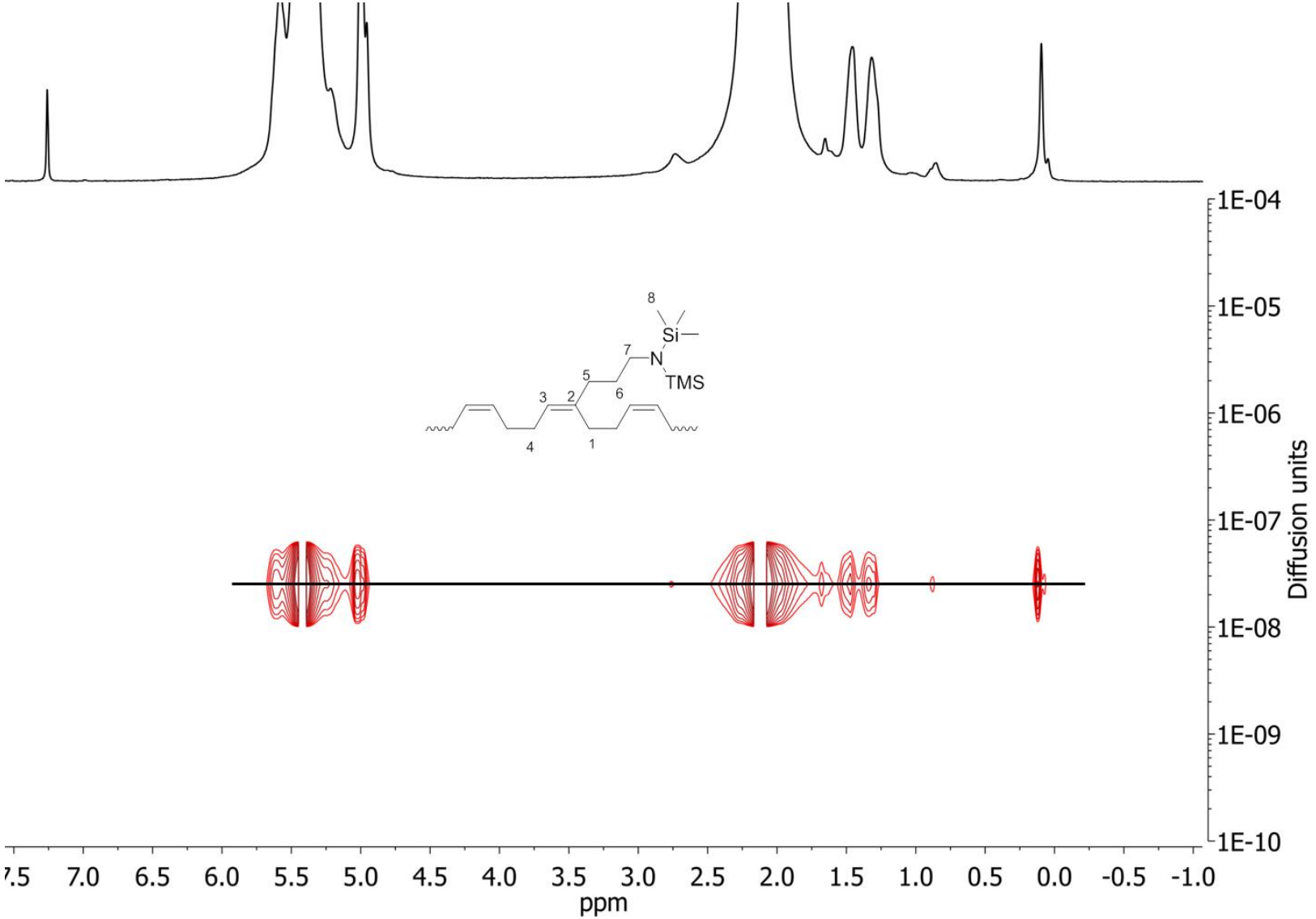
SI 45: ^{1}H NMR-spectrum of a copolymer synthesized from BD and **TMS_2N-3-BD** (0.1 mol% **TMS_2N-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).



SI 46: HSQC NMR-spectrum of a copolymer synthesized from BD and **TMS_2N-3-BD** (0.1 mol% **TMS_2N-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).

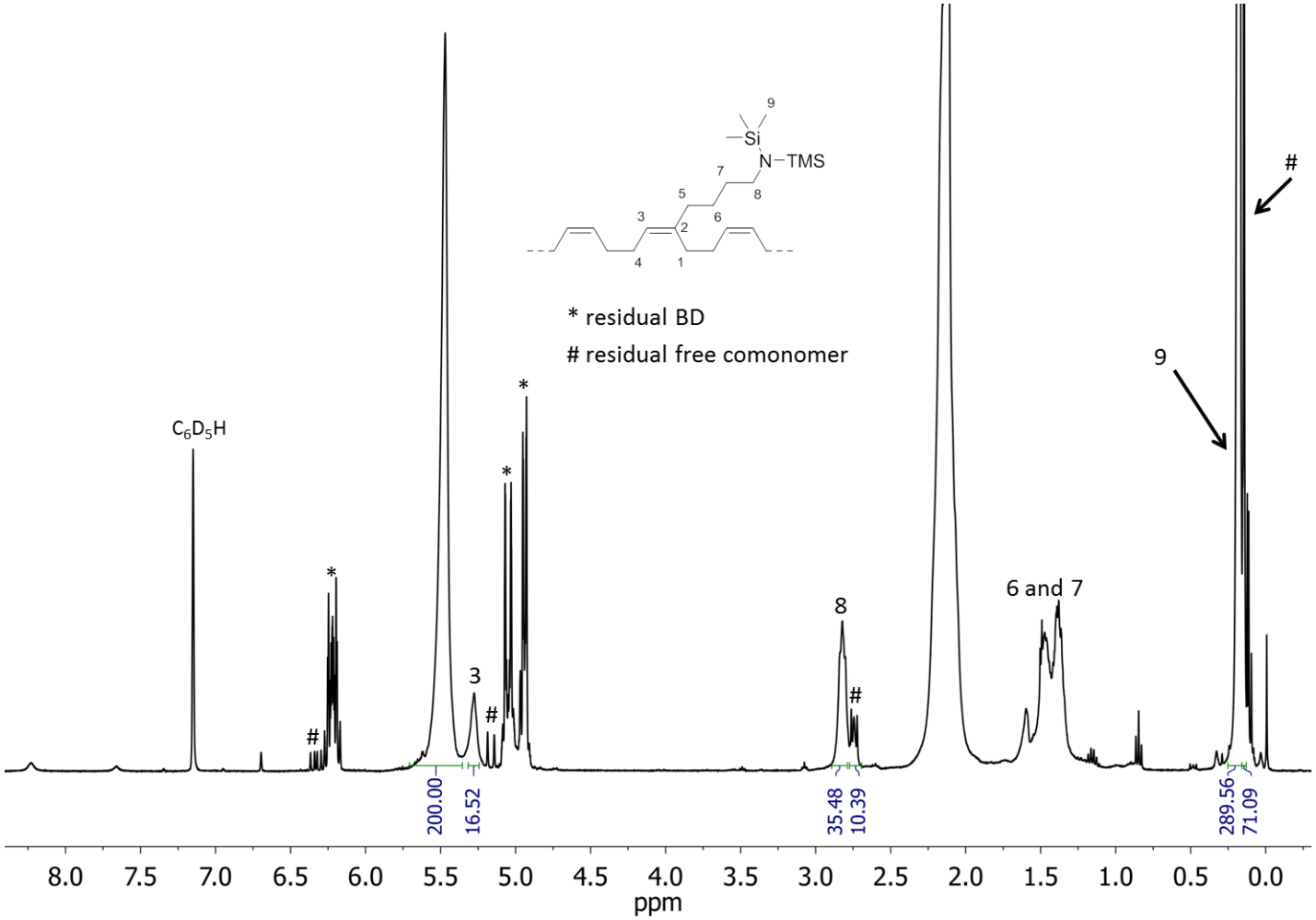


SI 47: ^{13}C NMR-spectrum of a copolymer synthesized from BD and **TMS_2N-3-BD** (0.1 mol% **TMS_2N-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).



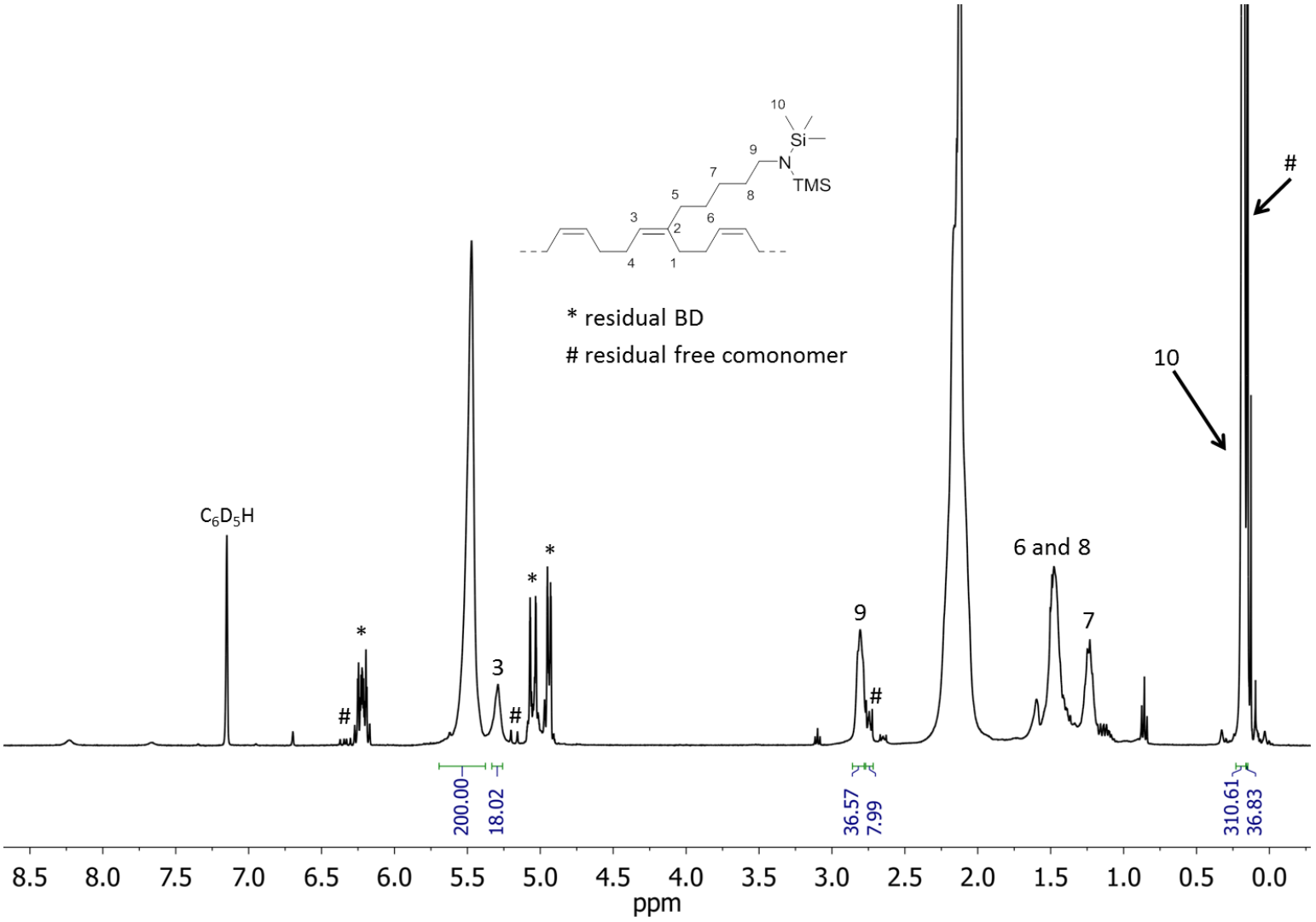
SI 48: DOSY NMR-spectrum of a copolymer synthesized from BD and **TMS_2N-3-BD** (0.1 mol% **TMS_2N-3-BD** incorporation, recorded at 27 °C in $CDCl_3$).

4.12. COPOLYMERIZATIONS WITH **TMS_2N-4-BD**



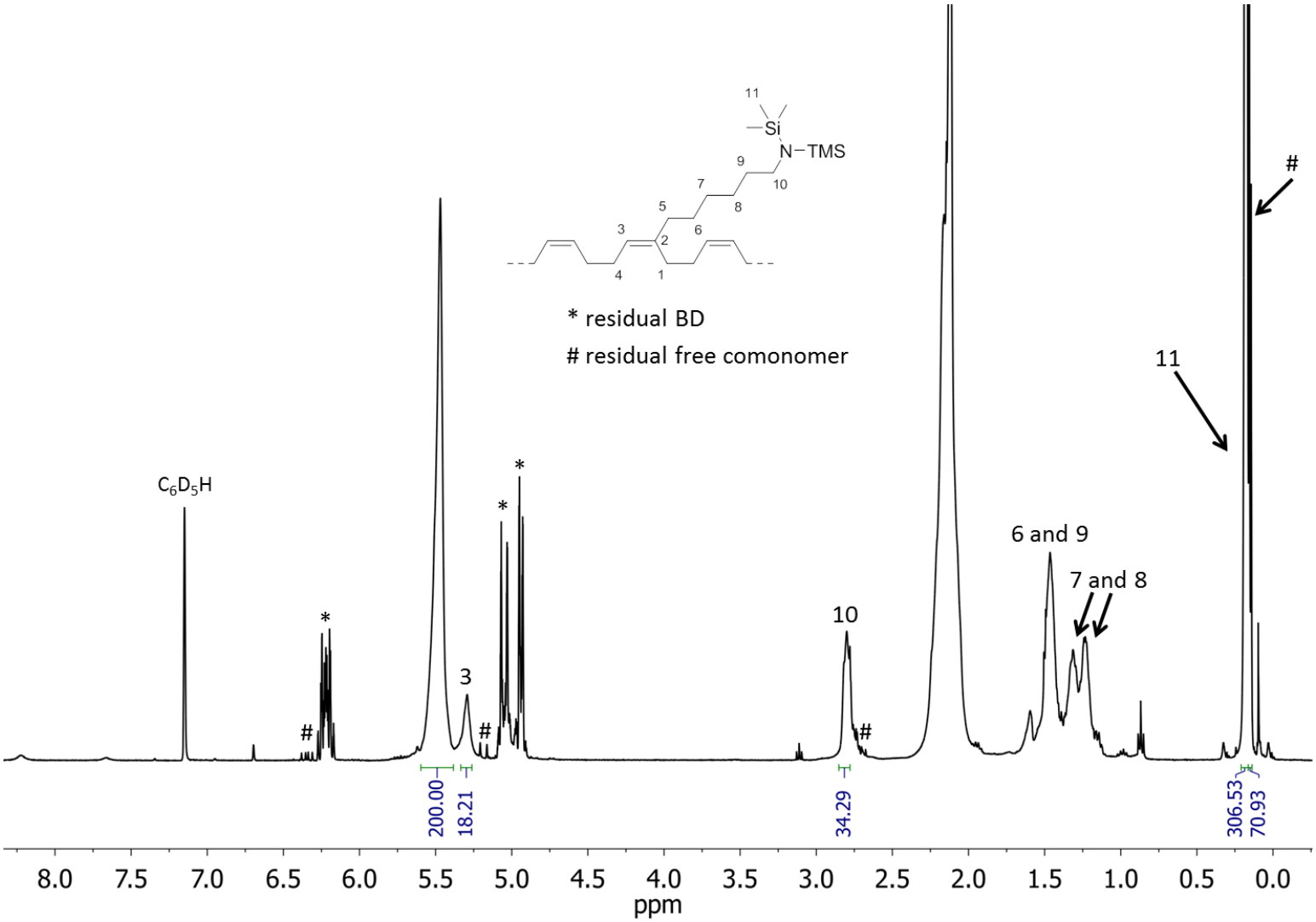
SI 49: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **TMS_2N-4-BD** (entry S1-12, recorded at 40 °C in C_6D_6).

4.13. COPOLYMERIZATIONS WITH **TMS_2N-5-BD**



SI 50: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **TMS_2N-5-BD** (entry S1-13, recorded at 40 °C in C_6D_6).

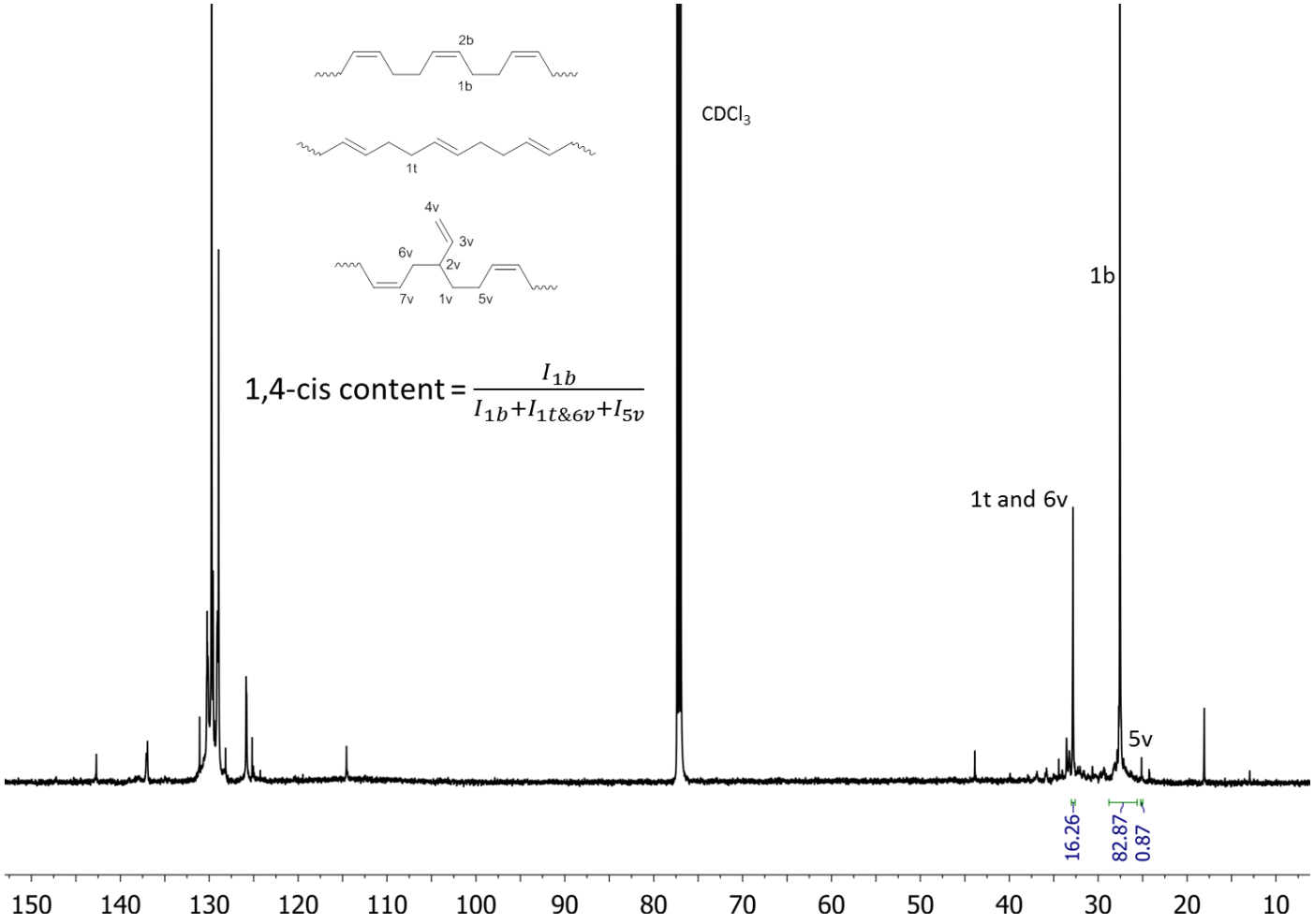
4.14. COPOLYMERIZATIONS WITH **TMS_2N-6-BD**



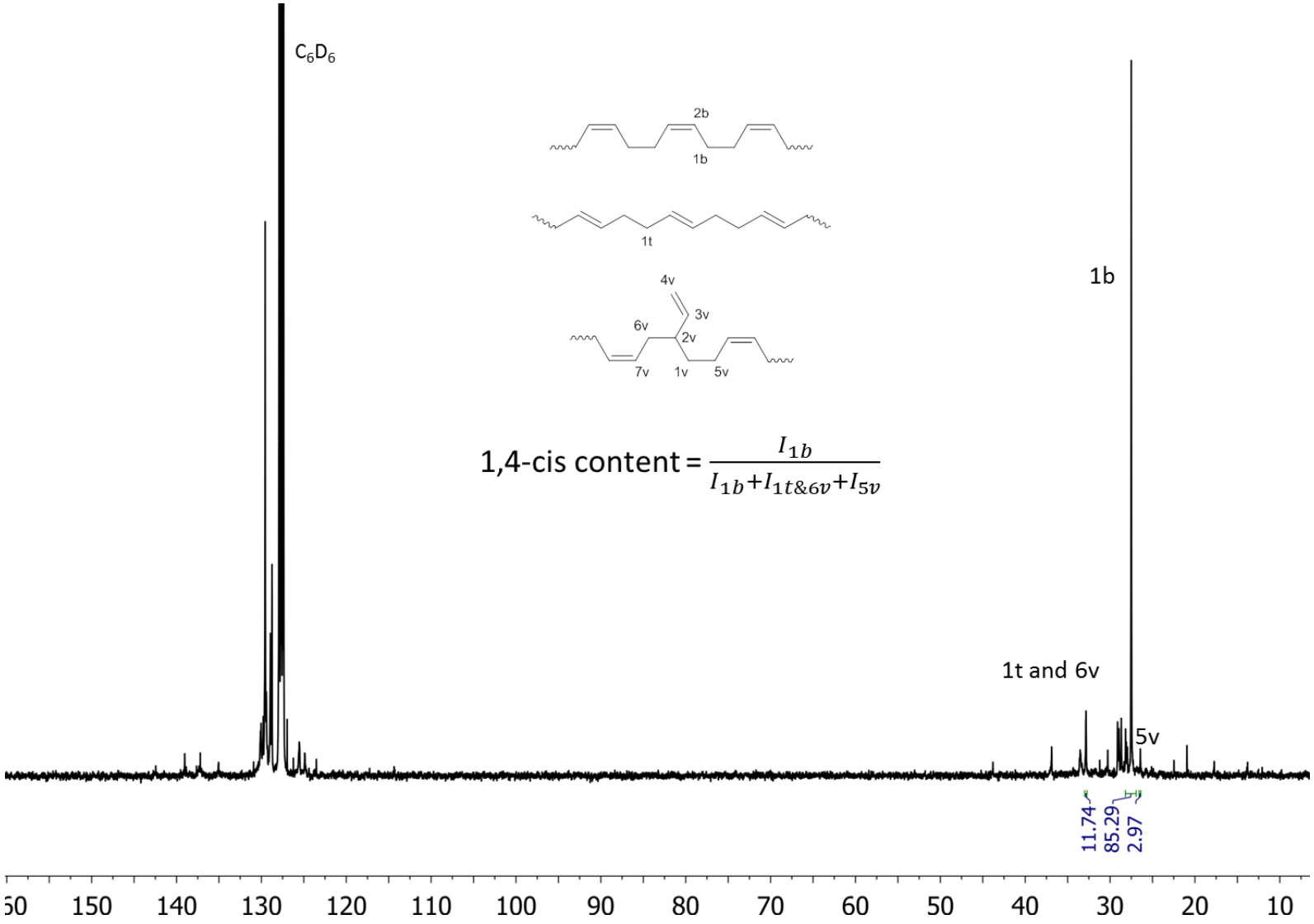
SI 51: ^{1}H NMR *in-situ* spectrum of a copolymerization of BD and **TMS_2N-6-BD** (entry S1-14, recorded at 40 °C in C_6D_6).

5. Selected ^{13}C NMR Spectra for Microstructure Determination

The microstructures of the copolymers were determined by ^{13}C inverse gated decoupled NMR spectroscopy

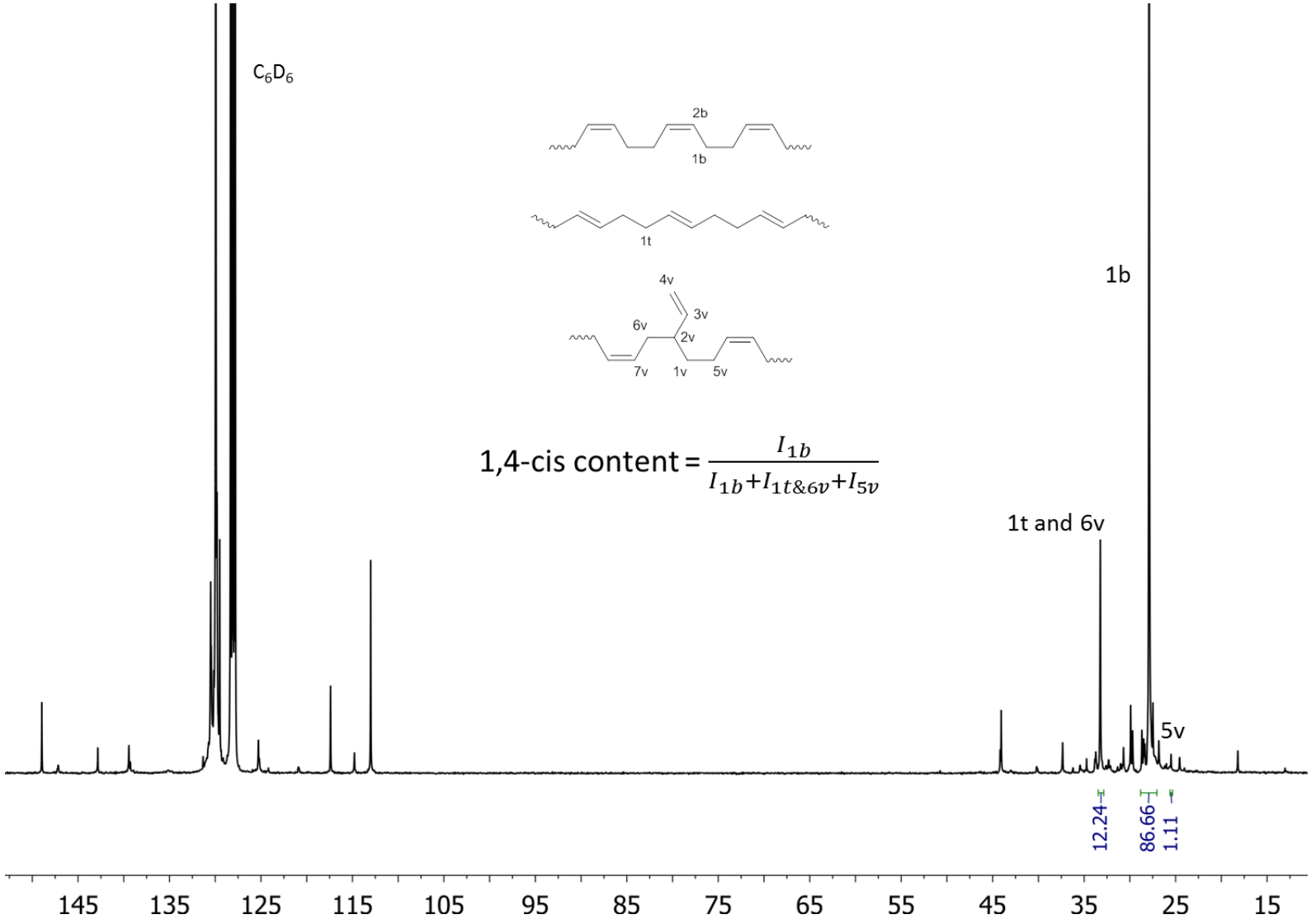


SI 52: Microstructure determination using ^{13}C inverse gated decoupled NMR spectroscopy of copolymer synthesized from **PhS-3-BD** and BD (entry 1-1, recorded at 27 °C in $CDCl_3$).

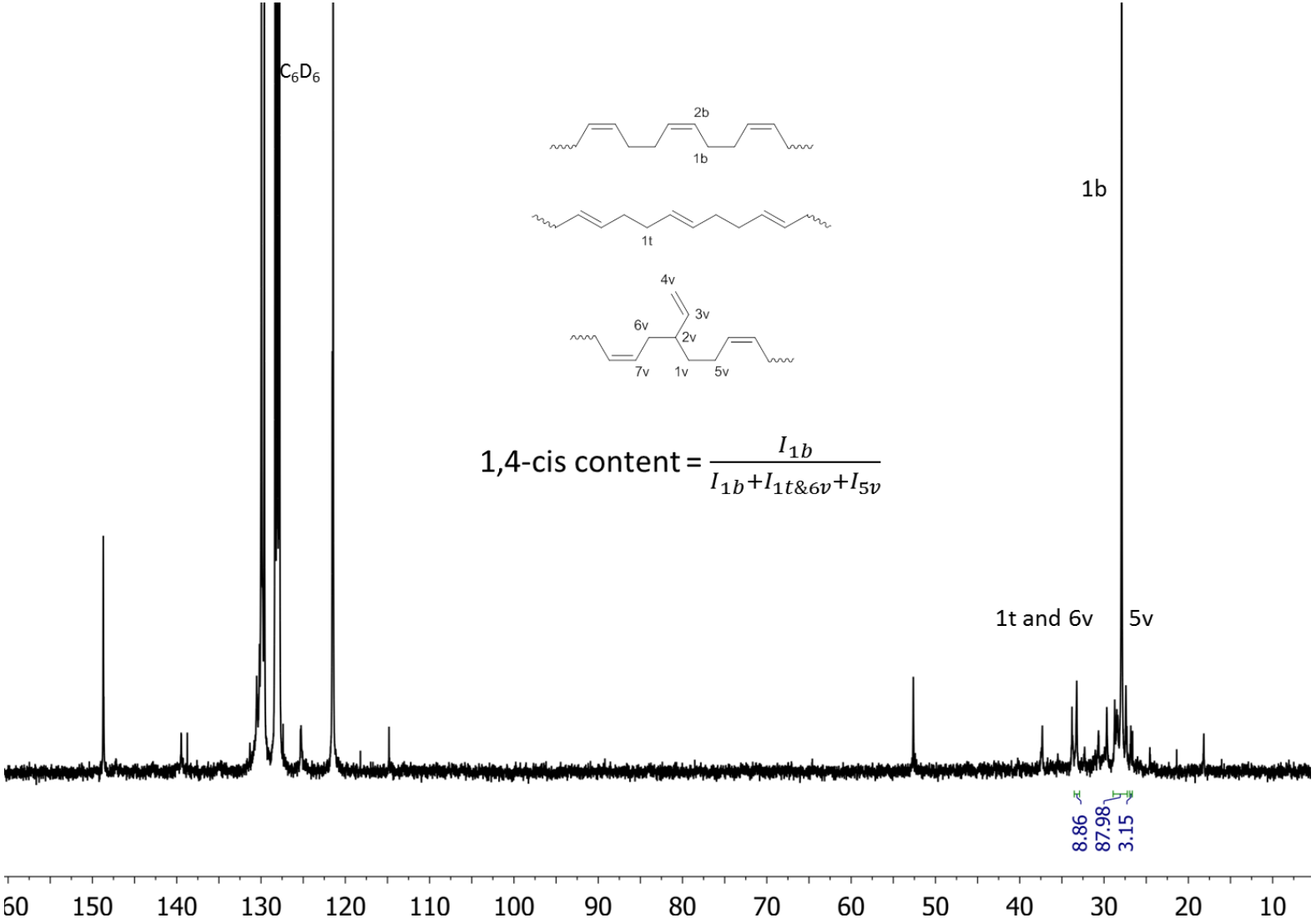


$$\text{1,4-cis content} = \frac{I_{1b}}{I_{1b}+I_{1t\&6v}+I_{5v}}$$

SI 53: Microstructure determination using ^{13}C inverse gated decoupled NMR spectroscopy of copolymer synthesized from **PhS-6-BD** and BD (entry 1-4, recorded at 27 °C in C_6D_6).



SI 54: Microstructure determination using ^{13}C inverse gated decoupled NMR spectroscopy of copolymer synthesized from **PhNH-6-BD** and BD (entry 1-7, recorded at 27 °C in C_6D_6).



SI 55: Microstructure determination using ^{13}C inverse gated decoupled NMR spectroscopy of copolymer synthesized from **Ph_2N-6-BD** and BD (entry S1-10, recorded at 27 °C in C_6D_6).

6. REFERENCES

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