



Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

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Supporting Information

Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

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Materials and Methods

All reactions were carried out under an inert atmosphere (nitrogen) using standard techniques for manipulating air-sensitive compounds unless otherwise stated.¹ All glassware was stored in an oven or was flame-dried prior to use under an inert atmosphere of nitrogen or argon as stated. Anhydrous solvents were obtained either by filtration through drying columns² (CH₂Cl₂) on an mBraun system or by distillation over sodium/benzophenone (Et₂O, toluene, pentane, heptane, methylcyclohexane). Analytical thin-layer chromatography (TLC) was performed on EMD TLC plates pre-coated with 250 μ m thickness silica gel 60 F254 plates visualized by fluorescence quenching under UV light and stained using potassium permanganate stain. Flash chromatography was performed on Silicycle silica gel 60 (40–63 μ m) using a forced flow of eluent at 0.3–0.5 bar pressure.³ Yields refer to purified and spectroscopically pure compounds (all polymers are spectroscopically pure with the exception of polyfarnesenes where traces of monomers, precipitated with the bulk, remain). ¹H NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer operating at 500 MHz. ¹³C NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer operating at 125 MHz. 10 seconds and 5 seconds were used as relaxation times for ¹H NMR and ¹³C NMR, respectively, for the determination of selectivities in polymerization reactions. Prior to use, CDCl₃ was passed through a plug of basic alumina and CD₂Cl₂ was degassed by the freeze-pump-thaw method⁴ and dried over 4 Å molecular sieves. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard. For ¹H NMR: CDCl₃ = δ 7.26 ppm, CD₂Cl₂: δ 5.32 ppm. For ¹³C NMR: CDCl₃ = δ 77.16 ppm, CD₂Cl₂ = δ 53.80 ppm. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant in Hz, and integration. For paramagnetic molecules, the ¹H NMR and ¹³C NMR data are reported with the chemical shift followed by the peak width at half-height in Hz. Magnetic susceptibility measurements for all iron complexes were obtained using the Evans method⁵ and are reported as follows: (field strength, solvent): μ_{eff} (concentration in mg/mL). ⁵⁷Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN). Isomer shifts are quoted relative to Fe metal at room temperature. Data was analyzed and simulated with WMOSS software (Web Research Corp., Edina, MN). Elemental analysis was performed by Robertson Microlit Laboratories (Madison, NJ). Mass spectra were

¹ Shriver, D. F.; Drezdon, M. A. Inert-Atmosphere Glove Boxes. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley & Sons: New York, 1986; pp. 45–67.

² Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

³ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

⁴ Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Amsterdam, 2003; pp. 29–30.

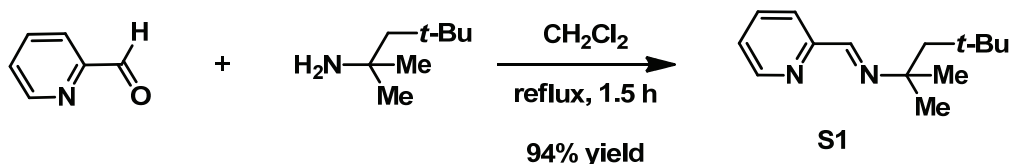
⁵ Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

obtained at the Harvard University Mass Spectrometry Facilities. High resolution mass spectra were obtained on an Agilent 6210 Time-of-Flight LC/MS or an Agilent 1100 ESI attached to a Bruker Daltonics MicrOTOF-Q II. Bulb-to-bulb distillation was carried out using a Büchi B-585 Kugelrohr. Molar masses of polyisoprenes were determined using size exclusion chromatography with a Varian GPC, fitted with a 3-column set and a RI detector, using THF as the eluent and polystyrenes as standards (Grinstaff group, Boston University). SEC chromatography data are reported as average polar mass in weight (M_w) in g/mol and polydispersity (D). Gas chromatography was performed on a Shimadzu GC-2014 equipped with an AOC-20i auto-injector and a set of hydrophobic columns (Restec Rtx-200MS, Crossbond trifluoropropylmethyl polysiloxane, 30 meter 0.25 mmID, 1 μ m df). Temperature ramps were realized between 170°C and 250°C to separate the different isomers of farnesene.

Reagents: All reagents were purchased from standard commercial sources (Aldrich, Strem, Alfa Aesar or TCI) and used as received unless otherwise noted. 2-pyridinecarboxaldehyde (Aldrich, 98%) was distilled prior to use. 2,2,4-pentane-2-amine (Aldrich, 97%) was distilled prior to use. Supermesitylamine (Aldrich, 98%) was used as received. Iron(II) chloride (98% Aldrich or 99.99% Strem) was used as received. Trityl tetrakis(pentafluorophenyl)borate (bright yellow powder, 98%, Strem) was used as received. Isoprene (99%, Alfa Aesar or TCI) was distilled over (*n*-Bu)₂Mg or Al(*i*-Bu)₃ and degassed by the freeze-pump-thaw method⁴ prior to use. Myrcene was distilled over Al(*i*-Bu)₃ and degassed by the freeze-pump-thaw method⁴ prior to use. Farnesene was used as received as the isomer mixture (*Z*- and *E*- β -farnesene as well as *Z*- and *E*- α -farnesene). Trimethylaluminum, triethylaluminum and tri-*isobutyl*aluminum were purchased neat in metallic canisters from Aldrich (97%, 93%, and 95% purity, respectively). Trialkylaluminum alkylating reagents were either *cannula*-transferred from storage tanks and used as is or redistilled prior to use (no major difference was observed).

Experimental Data

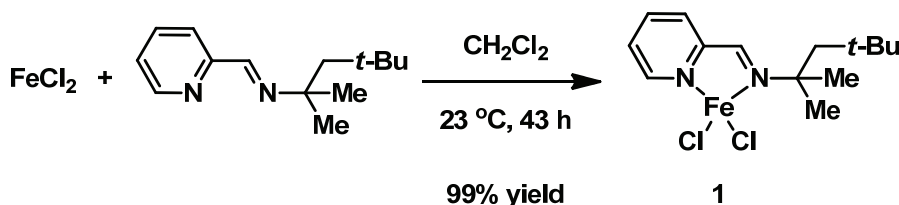
Experimental Procedures and Compound Characterization



(*E*)-2,4,4-Trimethyl-*N*-(pyridin-2-ylmethylene)pentan-2-amine (**S1**)

In air, to a solution of 2-pyridinecarboxaldehyde (0.338 g, 0.300 mL, 3.15 mmol, 1.01 equiv) in CH_2Cl_2 (10 mL) was added 2,4,4-trimethylpentan-2-amine (0.402 g, 0.500 mL, 3.11 mmol, 1.00 equiv). After heating at reflux for 1.5 h with azeotropic removal of water using a Dean-Stark trap, the reaction mixture was concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation (250 mTorr, 140 °C) to give the title compound as colorless oil (0.639 g, 94% yield).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 25 °C, δ): 8.61 (dt, $J = 4.9, 1.0$ Hz, 1H), 8.33 (s, 1H), 8.03 (dt, $J = 7.8, 1.0$ Hz, 1H), 7.71 (m, 1H), 7.26 (ddd, $J = 7.8, 4.9, 1.0$ Hz, 1H), 1.70 (s, 2H), 1.33 (s, 6H), 0.94 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): 156.0, 155.9, 149.3, 136.6, 124.4, 120.8, 61.6, 56.6, 32.2, 31.9, 29.7. HRMS-ESI (m/z): Calcd for $[\text{C}_{14}\text{H}_{22}\text{N}_2+\text{H}]$, 219.1856. Found, 219.1854.

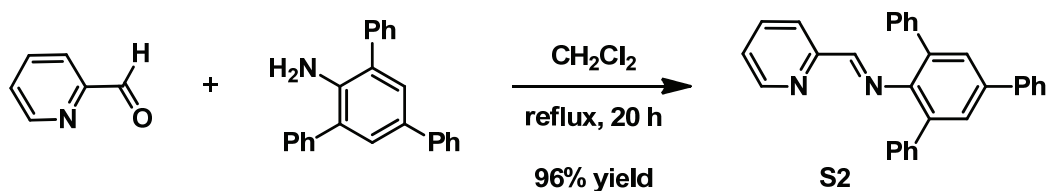


(*E*)-2,4,4-Trimethyl-*N*-(pyridin-2-ylmethylene)pentan-2-amine iron(II) chloride (**1**)

A solution of (*E*)-2,4,4-trimethyl-*N*-(pyridin-2-ylmethylene)propan-2-amine (**S1**), (0.300 g, 1.37 mmol, 1.00 equiv) in CH_2Cl_2 (8 mL) was added to iron(II) chloride (174 mg, 1.37 mmol, 1.00 equiv). The reaction mixture was stirred at 23 °C for 43 h. The reaction mixture was filtered over a celite pad, eluting with CH_2Cl_2 , and the filtrate was concentrated under reduced pressure. The residue was washed with Et_2O (2×5 mL) and dried under reduced pressure to afford the title compound as an orange solid (0.471 g, 99% yield). X-Ray quality crystals were grown from vapor diffusion of pentane (3 mL) into a solution (1 mL, 10 mg) of the title compound in CH_2Cl_2 at 23 °C (use a 4-mL straight-walled vial in a 20-mL capped vial).

Magnetic susceptibility (500 MHz, CD_2Cl_2): $\mu_{\text{eff}} = 5.45 \mu_{\text{B}}$ (8.43 mg/mL). NMR Spectroscopy: ^1H NMR (500 MHz, CD_2Cl_2 , 25 °C, δ): 82.92 ($\Delta\nu_{1/2} = 258$ Hz), 64.16 ($\Delta\nu_{1/2} = 702$ Hz), 57.30 ($\Delta\nu_{1/2} = 77$ Hz), 52.50 ($\Delta\nu_{1/2} = 61$ Hz), -3.23 ($\Delta\nu_{1/2} = 82$ Hz), -15.99 ($\Delta\nu_{1/2} = 334$ Hz), -17.94

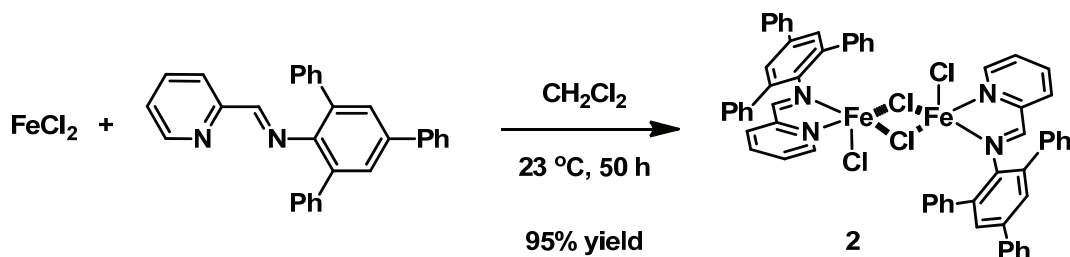
($\Delta\nu_{1/2} = 39$ Hz), -24.21 ($\Delta\nu_{1/2} = 550$ Hz). ^{13}C NMR (125 MHz, CD_2Cl_2 , 25 °C, δ): 298.8 ($\Delta\nu_{1/2} = 296$ Hz), 246.7 ($\Delta\nu_{1/2} = 89$ Hz), 245.4 ($\Delta\nu_{1/2} = 84$ Hz), 142.6 ($\Delta\nu_{1/2} = 97$ Hz), 111.7 ($\Delta\nu_{1/2} = 252$ Hz), 107.5 ($\Delta\nu_{1/2} = 208$ Hz), 78.5 ($\Delta\nu_{1/2} = 153$ Hz), 36.6 ($\Delta\nu_{1/2} = 143$ Hz), 29.6 ($\Delta\nu_{1/2} = 187$ Hz), 27.4 ($\Delta\nu_{1/2} = 78$ Hz), 17.5 ($\Delta\nu_{1/2} = 29$ Hz). Mössbauer Spectroscopy (95 K): $\delta = 0.9$ mm/s, $\Delta E_Q = 2.8$ mm/s. Anal Calcd for $\text{C}_{14}\text{H}_{22}\text{Cl}_2\text{FeN}_2$: C, 48.73; H, 6.43; N, 8.12. Found: C, 48.81; H, 6.15; N: 8.00. X-Ray data included in X-Ray Crystallographic Analysis section.



Iminopyridine **S2**

In air, to a solution of 2,4,6-triphenylaniline (0.964 g, 3.00 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) was added 2-pyridinecarboxaldehyde (0.326 g, 0.290 mL, 3.05 mmol, 1.02 equiv). After heating at reflux for 20 h with azeotropic removal of water using a Dean-Stark trap, the reaction mixture was concentrated under reduced pressure. The residue was purified by trituration with hexanes and dried in vacuo to give the title compound as a yellow solid (1.18 g, 96% yield).

Melting Point: 141–144 °C. NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 25 °C, δ): 8.52 (d, $J = 4.6$ Hz, 1H), 8.08 (s, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.67–7.70 (m, 3H), 7.66 (s, 2H), 7.44–7.48 (m, 7H), 7.30–7.37 (m, 5H), 7.22–7.27 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): 165.4, 154.3, 149.4, 147.1, 140.6, 139.8, 137.9, 136.5, 134.0, 130.2, 128.9, 128.8, 128.2, 127.4, 127.1, 126.9, 125.1, 121.2. HRMS-ESI (m/z): Calcd for $[\text{C}_{30}\text{H}_{22}\text{N}_2+\text{Na}]$, 433.1675. Found, 433.1657.



Iron(II) chloride complex **2**

A solution of iminopyridine **S2** (0.150 g, 0.365 mmol, 1.00 equiv) in CH_2Cl_2 (5 mL) was added to iron(II) chloride (46.3 mg, 0.365 mmol, 1.00 equiv). The reaction mixture was stirred at 23 °C for 72 h. The reaction mixture was filtered over a celite pad. The residue on the filter cake was eluted with about 5 mL CH_2Cl_2 and the combined filtrates were concentrated under reduced pressure. The residue was washed with pentane (2×7 mL) and dried under reduced pressure to afford the title compound as a green solid (0.187 g, 95% yield). The title compound was insufficiently soluble in a deuterated solvent, such as CD_2Cl_2 , to obtain a ^{13}C NMR. X-Ray

quality crystals were grown from vapor diffusion of diethyl ether into a solution of the title compound in CH₂Cl₂ (3 to 5 mg dissolved in 1 mL, then filtered over a pad of celite) at –35 °C over 48 h.

Magnetic susceptibility (500 MHz, CD₂Cl₂): $\mu_{\text{eff}} = 5.28 \mu_{\text{B}}$ (7.4 mg/mL).⁵ NMR Spectroscopy: ¹H NMR (500 MHz, CD₂Cl₂, 25 °C, δ): 80.28 ($\Delta\nu_{1/2} = 187$ Hz), 67.24 ($\Delta\nu_{1/2} = 741$ Hz), 57.84 ($\Delta\nu_{1/2} = 73$ Hz), 54.71 ($\Delta\nu_{1/2} = 68$ Hz), 7.35 ($\Delta\nu_{1/2} = 19$ Hz), 6.62 ($\Delta\nu_{1/2} = 42$ Hz), 6.51 ($\Delta\nu_{1/2} = 28$ Hz), 4.65 ($\Delta\nu_{1/2} = 54$ Hz), 3.72 ($\Delta\nu_{1/2} = 29$ Hz), 1.84 ($\Delta\nu_{1/2} = 22$ Hz), 1.28 ($\Delta\nu_{1/2} = 50$ Hz), 0.88 ($\Delta\nu_{1/2} = 24$ Hz), –13.62 ($\Delta\nu_{1/2} = 58$ Hz). Mössbauer Spectroscopy (95 K): $\delta = 1.07$ mm/s, $\Delta E_{\text{Q}} = 3.35$ mm/s. Anal Calcd for C₆₀H₄₄Cl₄Fe₂N₄: C, 67.07; H, 4.13; N, 5.21. Found: C, 66.23; H, 4.22; N: 4.87. X-Ray data included in X-Ray Crystallographic Analysis section.

⁵ Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

Experimental Procedures for Polymerization

All polymerization reactions were conducted using inert atmosphere (nitrogen) using a glovebox or conventional Schlenk techniques (for the 10g scales).

Example 1: *trans*-1,4-Polyisoprene (in toluene)

To a 20 mL scintillation vial was added iron(II) chloride complex **1** (3.2 mg, 9.3 μ mol, 1.0 equiv) and 2 mL of toluene, followed by triisobutylaluminum (5.5 mg, 28 μ mol, 3.0 equiv) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μ mol, 1.0 equiv) was added as a solution in 2 mL toluene at 23°C. The reaction mixture was stirred for 2 min and isoprene (0.681 g, 1.00 mL, 10.0 mmol, 1.08×10^3 equiv) was added. The reaction mixture was stirred for 2 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 700mg).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ , relaxation time 10s): olefinic H atoms for 1,4-motif: 5.12 (s, $\Delta\nu_{1/2}$ = 35 Hz, 1H); 3,4-motif: 4.73 (d, *br*, $J \sim 20$ Hz, 1H), 4.66 (d, *br*, $J \sim 20$ Hz, 1H); aliphatic H atoms for 1,4-motif: 2.07 (s, *b*, 2H), 1.99 (d, *b*, $J \sim 5$ Hz, 2H), 1.60 (s, 3H),); 3,4-motif : 2.20 (s, *br*, 2H), 1.86 (m, *br*, 2H), 1.68 (s, *b*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ , relaxation time 5s): olefinic C atoms for *trans*-1,4-motif: 135.1, 124.4; 3,4-motif: 147.8, 111.4, aliphatic C atoms for *trans*-1,4-motif: 39.9, 26.9, 16.2 (CH_3 -methyl); for *cis*-1,4-motif: 23.7 (CH_3 -methyl); 3,4-motif: 45.0 (m), 37.6 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 125,000 g/mol, D = 2.0. Selectivity: 1,4 / 3,4 = 12:1 and *trans*-1,4 / *cis*-1,4 > 99:1 (92% of *trans*-1,4-polyisoprene in the bulk).

Example 2: *trans*-1,4-Polyisoprene (higher molar mass in Me-cyclohexane/toluene 5:1)

To a 20 mL scintillation vial was added iron(II) chloride complex **1** (3.2 mg, 9.3 μ mol, 1.0 equiv) and 5 mL of Me-cyclohexane, followed by triisobutylaluminum (5.5 mg, 28 μ mol, 3.0 equiv) in 1 mL of Me-cyclohexane at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μ mol, 1.0 equiv) was added as a solution in 3 mL of a 1:1 mixture of Me-cyclohexane and toluene at 23°C. The reaction mixture was stirred for 2 min and isoprene (1.362 g, 2.00 mL, 20.0 mmol, 2.15×10^3 equiv) was added. The reaction mixture was stirred for 4 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried under vacuo overnight (yield >99% 1.4 g).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ , relaxation time 10s): olefinic H atoms for 1,4-motif: 5.12 (s, $\Delta\nu_{1/2}$ = 50 Hz, 1H); 3,4-motif: 4.73 (d, *br*, 1H), 4.66 (d, *br*, 1H); aliphatic H atoms for 1,4-motif: 2.07 (s, *br*, 2H), 1.99 (d, *br*, $J \sim 5$ Hz, 2H), 1.60 (s, 3H),); 3,4-motif : 2.20

(s, *br*, 2H), 1.86 (m, *br*, 2H), 1.68 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ , relaxation time 5s): olefinic C atoms for *trans*-1,4-motif: 135.1, 124.4; 3,4-motif: 147.8, 111.4, aliphatic C atoms for *trans*-1,4-motif: 39.9, 26.9, 16.2 (CH_3 -methyl); for *cis*-1,4-motif: 23.7 (CH_3 -methyl); 3,4-motif: 45.0 (m), 37.6 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): $M_w = 600,000$ g/mol, $D = 2.5$. Selectivity: 1,4 / 3,4 > 12:1 and *trans*-1,4 / *cis*-1,4 > 99:1 (93% of *trans*-1,4-polyisoprene in the bulk).

Example 3: *trans*-1,4-Polyisoprene (in heptane/toluene 5:1)

To a 20 mL scintillation vial was iron(II) chloride complex **1** (3.2 mg, 9.3 μmol , 1.0 equiv) and 5 mL of heptane, followed by triisobutylaluminum (5.5 mg, 28 μmol , 3.0 equiv) in 1 mL of heptane at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a solution in 3 mL of a 1:1 mixture of heptane and toluene at 23°C. The reaction mixture was stirred for 2 min and isoprene (1.362 g, 2.00 mL, 20.0 mmol, 2.15×10^3 equiv) was added. The reaction mixture was stirred for 4 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 1.4 g).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ , relaxation time 10s): olefinic H atoms for 1,4-motif: 5.12 (s, $\Delta\nu_{1/2} = 45$ Hz, 1H); 3,4-motif: 4.73 (d, *br*, 1H), 4.66 (d, *br*, 1H); aliphatic H atoms for 1,4-motif: 2.07 (s, *br*, 2H), 1.99 (d, *br*, $J \sim 5$ Hz, 2H), 1.60 (s, 3H),); 3,4-motif : 2.20 (s, *br*, 2H), 1.86 (m, *br*, 2H), 1.68 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ , relaxation time 5s): olefinic C atoms for *trans*-1,4-motif: 135.1, 124.4; 3,4-motif: 147.8, 111.4, aliphatic C atoms for *trans*-1,4-motif: 39.9, 26.9, 16.2 (CH_3 -methyl); for *cis*-1,4-motif: 23.7 (CH_3 -methyl); 3,4-motif: 45.0 (m), 37.6 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): $M_w = 500,000$ g/mol, $D = 2.6$. Selectivity: 1,4 / 3,4 > 12:1 and *trans*-1,4 / *cis*-1,4 > 99:1 (92.5% of *trans*-1,4-polyisoprene in the bulk).

Example 4: *trans*-1,4-Polyisoprene (10g scale)

To a 500 mL round-bottom flask was added iron(II) chloride complex **1** (9.6 mg, 28 μmol , 1.0 equiv) and 10 mL of toluene, followed by triisobutylaluminum (16.5 mg, 84 μmol , 3.0 equiv) in 5 mL toluene at 23°C. The reaction mixture was stirred for 3 min and trityl tetrakis(pentafluorophenyl)borate (25.8 mg, 28 μmol , 1.0 equiv) was added as a solution in 5 mL toluene at 23°C. The reaction mixture was stirred for 2 min and 50 mL of *Me*-cyclohexane was added to bring the total volume to 70 mL, and then isoprene (10.0 g, 14.7 mL, 147 mmol, 5.25×10^3 equiv) was added. The reaction mixture was stirred for 5 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (50 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 10.1 g after drying overnight under vacuum).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ , relaxation time 10s): olefinic protons

for 1,4-motif: 5.12 (s, $\Delta\nu_{1/2}$ = 45 Hz, 1H); 3,4-motif: 4.73 (d, *br*, 1H), 4.66 (d, *b*, 1H); aliphatic protons for 1,4-motif: 2.07 (s, *br*, 2H), 1.99 (d, *br*, $J \sim 5$ Hz, 2H), 1.60 (s, 3H),); 3,4-motif : 2.20 (s, *br*, 2H), 1.86 (m, *br*, 2H), 1.68 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ , relaxation time 5s): olefinic carbons for *trans*-1,4-motif: 135.1, 124.4; 3,4-motif: 147.8, 111.4, aliphatic carbons for *trans*-1,4-motif: 39.9, 26.9, 16.2; for *cis*-1,4-motif: 23.7 (CH_3 -methyl); 3,4-motif: 45.0 (m), 37.6 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 650,000 g/mol, D = 3.9. Selectivity 1,4 / 3,4 = 12:1 and *trans*-1,4 / *cis*-1,4 > 99:1 (92.5% of *trans*-1,4-polyisoprene in the bulk).

Example 5: *cis*-1,4-Polyisoprene (in toluene)

To a 20 mL scintillation vial was iron(II) chloride complex **2** (5.0 mg, 9.3 μmol , 1.0 equiv) and 2 mL of toluene, followed by triethylaluminum (3.2 mg, 28 μmol , 3.0 equiv) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a solution in 2 mL toluene at 23°C. The reaction mixture was stirred for 5 min at -78°C and cold isoprene (0.681 g, 1.00 mL, 10.0 mmol, 1.08×10^3 equiv) was added. The reaction mixture was stirred for 4 hours at -78 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 700mg).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): olefinic H atoms for 1,4-motif: 5.12 (s, $\Delta\nu_{1/2}$ = 50 Hz, 1H); 3,4-motif: 4.72 (*br*, 1H), 4.68 (*br*, 1H); aliphatic H atoms for 1,4-motif: 2.03 (*br*, 4H), 1.70 (s, 3H); 3,4-motif : 2.22 (*br*, 1H), 1.80 (m, *br*, 2H), 1.32 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): olefinic C atoms for *cis*-1,4-motif: 135.6 (m), 134.0 (m), 126.5 (m), 125.3 (m); 3,4-motif: 147.7, 111.5, aliphatic C atoms for *cis*-1,4-motif: 33.2 (m), 30.8, 28.5(m), 26.1(m), 23.7; 3,4-motif: 45.4 (m), 36.8 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 140,000 g/mol, D = 1.7. Selectivity 1,4 / 3,4 = 6:1 and *cis*-1,4 / *trans*-1,4 > 99:1 (85% of *cis*-1,4-polyisoprene in the bulk).

Example 6: *cis*-1,4-Polyisoprene (in Me-cyclohexane at room temperature)

To a 20 mL scintillation vial was added iron(II) chloride complex **2** (5.0 mg, 9.3 μmol , 1.0 equiv) and 2 mL of Me-cyclohexane, followed by triethylaluminum (3.2 mg, 28 μmol , 3.0 equiv) in 1 mL Me-cyclohexane at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a dispersion in 2 mL Me-cyclohexane at 23°C. The reaction mixture was stirred for 2 min and isoprene (0.681 g, 1.00 mL, 10.0 mmol, 1.08×10^3 equiv) was added. The reaction mixture was stirred for 2 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 700mg).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): olefinic H atoms for 1,4-motif: 5.12

(s, $\Delta\nu_{1/2}$ = 40 Hz, 1H); 3,4-motif: 4.72 (d, 1H, *br*), 4.68 (d, 1H, *br*); aliphatic H atoms for 1,4-motif: 2.03 (4H, *br*), 1.70 (3H, *br*); 3,4-motif : 2.22 (1H, *br*), 1.80 (m, *br*, 2H), 1.32 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): olefinic C atoms for *cis*-1,4-motif: 135.6 (m), 134.0 (m), 126.5 (m), 125.3 (m); 3,4-motif: 147.7, 111.5, aliphatic C atoms for *cis*-1,4-motif: 33.2 (m), 30.8, 28.5(m), 26.1(m), 23.7; 3,4-motif: 45.4 (m), 36.8 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 100,000 g/mol, D = 2.3. Selectivity 1,4 / 3,4 = 3:1 and *cis*-1,4 / *trans*-1,4 > 99:1 (75% of *cis*-1,4-polyisoprene in the bulk).

Example 7: *cis*-1,4-Polyisoprene (in toluene at room temperature)

To a 20 mL scintillation vial was iron(II) chloride complex **2** (5.0 mg, 9.3 μmol , 1.0 equiv) and 2 mL of toluene, followed by triethylaluminum (3.2 mg, 28 μmol , 3.0 equiv) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a solution in 2 mL toluene at 23°C. The reaction mixture was stirred for 2 min and isoprene (0.681 g, 1.00 mL, 10.0 mmol, 1.08×10^3 equiv) was added. The reaction mixture was stirred for 1 hour at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 700mg).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): olefinic H atoms for 1,4-motif: 5.12 (s, $\Delta\nu_{1/2}$ = 40 Hz, 1H); 3,4-motif: 4.72 (*br*, 1H), 4.68 (*br*, 1H); aliphatic H atoms for 1,4-motif: 2.03 (*br*, 4H), 1.70 (s, *br* 3H); 3,4-motif : 2.22 (*br*, 1H), 1.80 (m, *br*, 2H), 1.32 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): olefinic C atoms for *cis*-1,4-motif: 135.6 (m), 134.0 (m), 126.5 (m), 125.3 (m); 3,4-motif: 147.7, 111.5, aliphatic C atoms for *cis*-1,4-motif: 33.2 (m), 30.8, 28.5(m), 26.1(m), 23.7; 3,4-motif: 45.4 (m), 36.8 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 150,000 g/mol, D = 1.9. Selectivity 1,4 / 3,4 = 2:1 and *cis*-1,4 / *trans*-1,4 > 99:1 (66% of *cis*-1,4-polyisoprene in the bulk).

Example 8: *cis*-1,4-Polyisoprene (10g scale)

To a 500 mL round-bottom flask was added iron(II) chloride **2** (15.0 mg, 28 μmol , 1.0 equiv) and 10 mL of toluene, followed by triethylaluminum (9.6 mg, 84 μmol , 3.0 equiv) in 5 mL toluene at 23°C. The reaction mixture was stirred for 5 min and trityl tetrakis(pentafluorophenyl)borate (25.8 mg, 28 μmol , 1.0 equiv) was added as a solution in 5 mL toluene at 23°C. The reaction mixture was mixed for 5 min at -78°C and 50 mL of *Me*-cyclohexane was added to bring the total volume to 70 mL, and then isoprene (10.0 g, 14.7 mL, 147 mmol, 5.25×10^3 equiv) was added at -78°C. The reaction mixture was stirred for 5 hours at -78 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (50 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 10.1 g after drying overnight under vacuum).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): olefinic H atoms for 1,4-motif: 5.12

(s, $\Delta\nu_{1/2}$ = 50 Hz, 1H); 3,4-motif: 4.72 (*br*, 1H), 4.68 (*br*, 1H); aliphatic H atoms for 1,4-motif: 2.03 (*br*, 4H), 1.70 (s, 3H); 3,4-motif: 2.22 (*br*, 1H), 1.80 (m, *br*, 2H), 1.32 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): olefinic C atoms for *cis*-1,4-motif: 135.6 (m), 134.0 (m), 126.5 (m), 125.3 (m); 3,4-motif: 147.7, 111.5, aliphatic C atoms for *cis*-1,4-motif: 33.2 (m), 30.8, 28.5(m), 26.1(m), 23.7; 3,4-motif: 45.4 (m), 36.8 (m), 18.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 800,000 g/mol, D = 3.5. Selectivity 1,4 / 3,4 = 5:1 and *cis*-1,4 / *trans*-1,4 > 99:1 (83% of *cis*-1,4-polyisoprene in the bulk).

Example 9: *trans*-1,4-Poly- β -myrcene

To a 20 mL scintillation vial was added iron(II) chloride complex **1** (3.2 mg, 9.3 μmol , 1.0 equiv) and 2 mL of toluene, followed by triisobutylaluminum (9.2 mg, 46 μmol , 5.0 equiv) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a solution in 2 mL toluene at 23°C. The reaction mixture was stirred for 2 min and β -myrcene (2.384 g, 3.00 mL, 17.5 mmol, 1.89×10^3 equiv) was added. The reaction mixture was stirred for 2 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield 91% 2.17 g).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ , relaxation time 10s): olefinic H atoms for 1,4-motif: 5.13 (s, $\Delta\nu_{1/2}$ = 35 Hz, 2H); 3,4-motif: 4.76 (d, *br*, $J \sim 20$ Hz, 1H), 4.72 (d, *br*, $J \sim 20$ Hz, 1H); aliphatic H atoms for 1,4-motif: 2.03 (t, *br*, 2H, $J \sim 16$ Hz), 2.08 (s, *br*, 2H), 1.99 (s, *b*, 2H), 1.68 (s, 3H), 1.60 (s, 3H); 3,4-motif: non-detectable. ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ , relaxation time 5s): olefinic C atoms for *trans*-1,4-motif: 139.2, 131.6, 125.0, 124.6; 3,4-motif: non-detectable, aliphatic C atoms for *trans*-1,4-motif: 37.5, 30.6, 27.3, 27.1, 25.9, 17.8 (CH_3 -methyl); for *cis*-1,4-motif: non-detectable; 3,4-motif: non-detectable. SEC chromatography (eluent: THF, Polystyrene standards): M_w = 250,000 g/mol, D = 2.1. Selectivity: 1,4 / 3,4 = 12:1 and *trans*-1,4 / *cis*-1,4 > 20:1.

Example 10: *cis*-1,4-Poly- β -myrcene

To a 20 mL scintillation vial was added iron(II) chloride complex **2** (5.0 mg, 9.3 μmol , 1.0 equiv) and 2 mL of toluene, followed by triethylaluminum (5.3 mg, 46 μmol , 5.0 equiv) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a dispersion in 2 mL toluene at 23°C. The reaction mixture was stirred for 2 min and β -myrcene (2.384 g, 3.00 mL, 17.5 mmol, 1.89×10^3 equiv) was added. The reaction mixture was stirred for 2 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a colorless gum that was dried in vacuo overnight (yield >99% 2.07 g).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): olefinic H atoms for 1,4-motif: 5.11

(s, $\Delta\nu_{1/2}$ = 40 Hz, 2H); 3,4-motif: 4.76 (m, *br*, 2H); aliphatic H atoms for 1,4-motif: 2.04 (t, *br*, 2H, $J \sim 15$ Hz), 2.06 (s, *br*, 2H), 2.00 (s, *b*, 2H), 1.67 (s, 3H), 1.59 (s, 3H); 3,4-motif : 2.17 (*br*, 1H), 1.85 (m, *br*, 2H), 1.37 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): olefinic C atoms for *cis*-1,4-motif: 139.5 (m), 131.4 (m), 124.7 (m); 3,4-motif: 152.2, 109.1, aliphatic C atoms for *cis*-1,4-motif: 37.3, 37.0, 29.7(6), 28.5(m), 27.2, 25.8, 17.8; 3,4-motif: 44.8, 33.4 (m), 26.6. SEC chromatography (eluent: THF, Polystyrene standards): M_w = 230,000 g/mol, D = 2.2. Selectivity 1,4 / 3,4 = 4:1 and *cis*-1,4 / *trans*-1,4 > 20:1.

Example 11: *trans*-1,4-Poly- β -farnesene

To a 20 mL scintillation vial was added iron(II) chloride complex **1** (3.2 mg, 9.3 μmol , 1.0 equiv) and 2 mL of toluene, followed by triisobutylaluminum (28 mg, 140 μmol , 15 equiv, to activate and dry the commercially available mixture of farnesene isomers) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a solution in 2 mL toluene at 23°C. The reaction mixture was stirred for 2 min and a mixture of farnesene isomers (3.58 g, 4.50 mL, 17.5 mmol, 1.89×10^3 equiv) containing an extra quantity of triisobutylaluminum (28 mg, 140 μmol , 15 equiv, to dry the commercially available mixture of farnesene isomers), was added. The reaction mixture was stirred for 2 hours at 23 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a white gum (yield 61%, 2.2 g after drying overnight under vacuum, residues of α -farnesene are still present in the bulk, the yield is slightly overestimated).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ , relaxation time 10s): olefinic H atoms for 1,4-motif: 5.14 (s, $\Delta\nu_{1/2}$ = 45 Hz, 3H); 3,4-motif: 4.78 (d, *br*, $J \sim 10$ Hz, 1H), 4.66 (d, *br*, $J \sim 10$ Hz, 1H); aliphatic H atoms for 1,4-motif: 2.03 (m, *b*, 2H), 1.99 (m, *b*, 2H), 1.67 and 1.60 (s, *br*, 9H); 3,4-motif : non-detectable. ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ , relaxation time 5s): olefinic C atoms for *trans*-1,4-motif: 139.2, 135.3, 131.5, 125.3, 124.9, 124.5; 3,4-motif: 109.9, aliphatic C atoms for *trans*-1,4-motif: 39.9, 37.6, 32.1, 30.9, 30.6, 27 (m), 25.8, 23.6, 22.6, 17.6, 16.2 (CH_3 -methyl); for *cis*-1,4-motif: 22.6 (CH_3 -methyl); 3,4-motif: 22.5 (m). SEC chromatography (eluent: THF, Polystyrene standards): M_w = 110,000 g/mol, D = 1.5. Selectivity: 1,4 / 3,4 = 11:1 and *trans*-1,4 / *cis*-1,4 > 20:1.

Example 12: *cis*-1,4-Poly- β -farnesene

To a 20 mL scintillation vial was iron(II) chloride complex **2** (5.0 mg, 9.3 μmol , 1.0 equiv) and 2 mL of toluene, followed by triethylaluminum (16 mg, 140 μmol , 15 equiv, to activate and dry the commercially available mixture of farnesene isomers) in 1 mL toluene at 23°C. The reaction mixture was stirred for 2 min and trityl tetrakis(pentafluorophenyl)borate (8.6 mg, 9.3 μmol , 1.0 equiv) was added as a dispersion in 2 mL toluene at 23°C. The reaction mixture was mixed for 2 min and a mixture of farnesene isomers (3.58 g, 4.50 mL, 17.5 mmol, 1.89×10^3 equiv) containing an extra quantity of triethylaluminum (16 mg, 140 μmol , 15 equiv, to dry the

commercially available mixture of farnesene isomers), was added at 23°C. The reaction mixture was stirred for 5 hours at -78 °C. The reaction mixture was quenched by opening to air and diluting with DCM from the squirt bottle (10 mL). The title compound was isolated by precipitation in cold methanol to yield a white gum (yield 53%, 1.9 g after drying overnight under vacuum, residues of α -farnesene are still present in the bulk, the yield is slightly overestimated).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): olefinic H atoms for 1,4-motif: 5.14 (s, $\Delta\nu_{1/2} = 40$ Hz, 3H); 3,4-motif: 4.78 (d, *br*, $J \sim 10$ Hz, 1H), 4.66 (d, *br*, $J \sim 10$ Hz, 1H); aliphatic H atoms for 1,4-motif: 2.03 (m, *b*, 2H), 1.99 (m, *b*, 2H), 1.67 and 1.60 (s, *br*, 9H); 3,4-motif: 2.15 (*br*, 1H), ~ 1.9 (m, *br*, 2H), 1.36 (s, *br*, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 25 °C, δ): olefinic C atoms for *cis*-1,4-motif: 139.5, 135.0, 131.3, 125.1, 124.4; 3,4-motif: 152.2, 146.1, 109.9, 109.1, 107.2, aliphatic C atoms for *cis*-1,4-motif: 37.3, 32.5, 29.7, 27 (m), 23.6, 22.6, 17.8, 16.2; 3,4-motif: 22.5. SEC chromatography (eluent: THF, Polystyrene standards): $M_w = 100,000$ g/mol, $D = 1.4$. Selectivity 1,4 / 3,4 = 4:1 and *cis*-1,4 / *trans*-1,4 > 20:1.

Control Experiments

Control experiments have been run and no noticeable polymerization was obtained when either of the components was left out. Trialkylaluminum derivatives alone or in combination with either of the two other ingredients provided less than 5% conversion of the isoprene into various isomers and cyclization products which is characteristic of cationic processes that are usually difficult to control especially at ambient temperature with isoprene (or other dienes) as monomers. $[\text{Ph}_3\text{C}^+][\text{BArF}_{20}]^-$ alone or in combination with either of the two other ingredients did not yield polydiene. Without iron chloride, no polymer was generated either.

References and Notes

The determination of NMR chemical shifts was accomplished using the following references, matching with values displayed in their Supplementary Information respective sections:⁶⁻¹¹

W. Gao, D. Cui *J. Am. Chem. Soc.* **2008**, *130*, 4984-4991

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A review concerning polyisoprenoids has been published:¹²

Peruch et al. *Polym. Int.* **2012**, *61*, 149-156

The use of AlEt₃ in the octyl-iminopyridine ferrous chloride catalyzed polymerization of isoprene, stereoselective for *trans*-1,4-polyisoprene, resulted in a slightly less selective polymerization (91-92% *trans*-1,4-polyisoprene at 23°C).

The use of Al*i*Bu₃ in the supermesityl-iminopyridine ferrous chloride catalyzed polymerization of isoprene, stereoselective for *cis*-1,4-polyisoprene, resulted in a slightly less selective polymerization (55-60% *cis*-1,4-polyisoprene at 23°C).

The ferrous chloride complexes are relatively bench-stable, they slowly oxidize to Fe(III), after several days spent on the bench: their bright color (orange for **1** or green for **2**) turns to rust.

Warning, the manipulation of trialkylaluminum reagents is hazardous. They are extremely pyrophoric reagents that should be handled with care. If a fire is ignited, two ways to extinguish it are reliable: a thick fire-proof safety blanket and either a powder or CO₂ extinguisher.

Equations used to determine selectivities

Polyisoprene

$$[\%1,4 - \text{motif}] = \frac{A(\sim CH = CMe - 1,4 - \text{motif})}{A(\sim CH = CMe - 1,4 - \text{motif}) + \frac{A(CH_2 = CMe - 3,4 - \text{motif})}{2}}$$

$$[\%1,4 - \text{motif}] = \frac{A(5.12\text{ppm})}{A(5.12\text{ppm}) + \frac{A(4.5 - 4.9\text{ppm})}{2}}$$

$$[\%trans - 1,4 - \text{motif}] = \frac{A(CH_3 - trans - 1,4 - \text{motif})}{A(CH_3 - trans - 1,4 - \text{motif}) + A(CH_3 - cis - 1,4 - \text{motif})}$$

$$[\%trans - 1,4 - \text{motif}] = \frac{A(16.2\text{ppm})}{A(16.2\text{ppm}) + A(23.7\text{ppm})}$$

$$[\%cis - 1,4 - \text{motif}] = \frac{A(CH_3 - cis - 1,4 - \text{motif})}{A(CH_3 - cis - 1,4 - \text{motif}) + A(CH_3 - trans - 1,4 - \text{motif})}$$

$$[\%cis - 1,4 - \text{motif}] = \frac{A(23.7\text{ppm})}{A(23.7\text{ppm}) + A(16.2\text{ppm})}$$

Polymyrcene

$$[\%1,4 - \text{motif}] = \frac{\frac{A(\sim CH = CMe)}{2}}{\frac{A(\sim CH = CMe)}{2} + \frac{A(CH_2 = CMe - 3,4 - \text{motif})}{2}}$$

$$[\%1,4 - \text{motif}] = \frac{A(5.12\text{ppm})}{A(5.12\text{ppm}) + A(4.76\text{ppm})}$$

$$[\%trans - 1,4 - \text{motif}] = \frac{A(\sim CH_2 - trans - 1,4 - \text{motif})}{A(\sim CH_2 - trans - 1,4 - \text{motif}) + A(\sim CH_2 - cis - 1,4 - \text{motif})}$$

$$[\%trans - 1,4 - \text{motif}] = \frac{A(30.6\text{ppm})}{A(30.6\text{ppm}) + A(29.6\text{ppm})}$$

$$[\%cis - 1,4 - \text{motif}] = \frac{A(\sim CH_2 - cis - 1,4 - \text{motif})}{A(\sim CH_2 - cis - 1,4 - \text{motif}) + A(\sim CH_2 - trans - 1,4 - \text{motif})}$$

$$[\%cis - 1,4 - \text{motif}] = \frac{A(29.6\text{ppm})}{A(29.6\text{ppm}) + A(30.6\text{ppm})}$$

Polyfarnesene

$$[\%1,4 - \text{motif}] = \frac{\frac{A(\sim CH = CMe)}{3}}{\frac{A(\sim CH = CMe)}{3} + \frac{A(CH_2 = CMe - 3,4 - \text{motif})}{2}}$$

$$[\%1,4 - \text{motif}] = \frac{\frac{A(5.13\text{ppm})}{3}}{\frac{A(5.13\text{ppm})}{3} + \frac{A(4.6 - 4.8\text{ppm})}{2}}$$

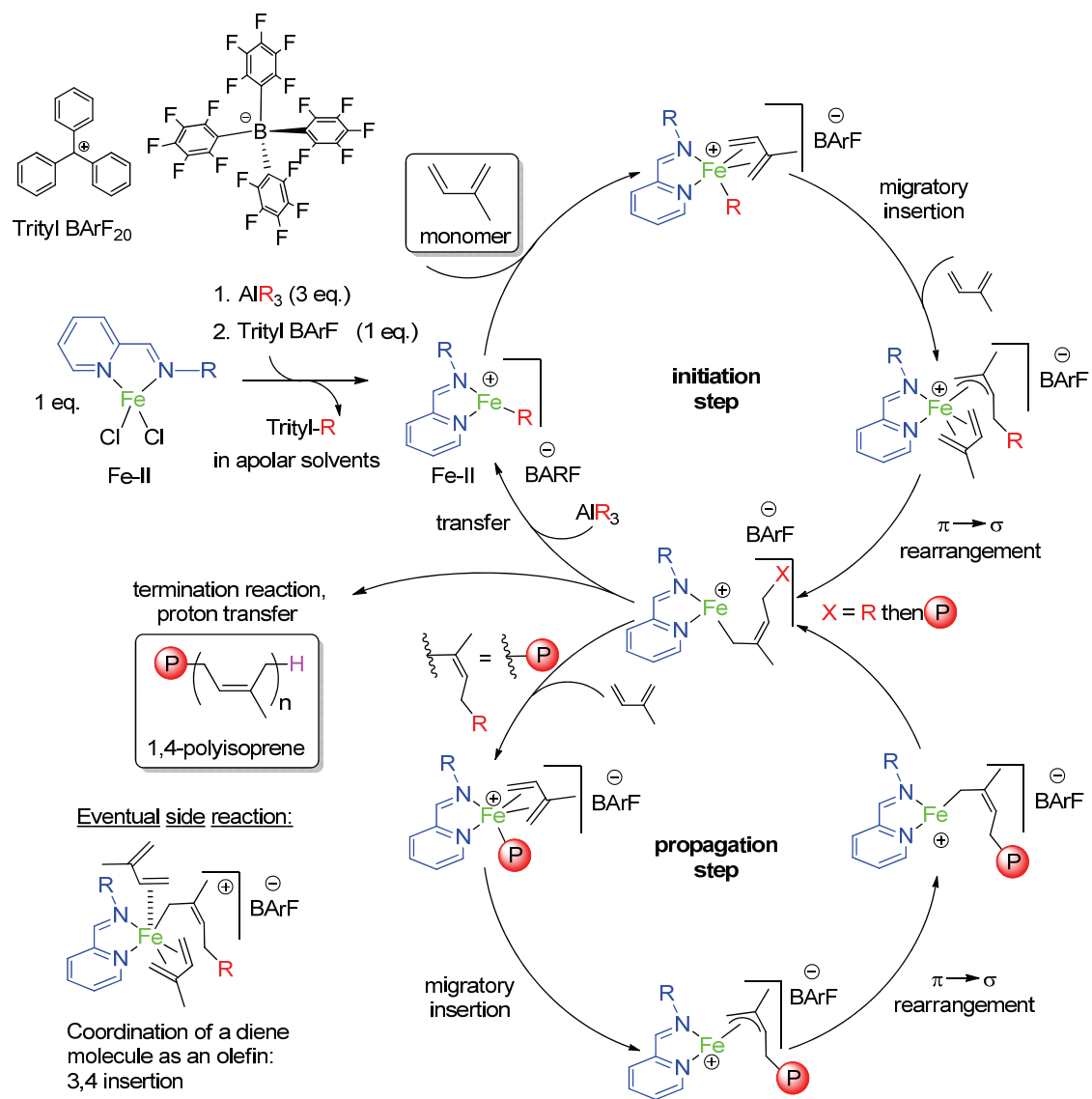
$$[\%trans - 1,4 - \text{motif}] = \frac{A(\sim CH_2 - trans - 1,4 - \text{motif})}{A(\sim CH_2 - trans - 1,4 - \text{motif}) + A(\sim CH_2 - cis - 1,4 - \text{motif})}$$

$$[\%trans - 1,4 - \text{motif}] = \frac{A(32.1\text{ppm})}{A(32.1\text{ppm}) + A(29.7\text{ppm})}$$

$$[\%cis - 1,4 - \text{motif}] = \frac{A(\sim CH_2 - cis - 1,4 - \text{motif})}{A(\sim CH_2 - cis - 1,4 - \text{motif}) + A(\sim CH_2 - trans - 1,4 - \text{motif})}$$

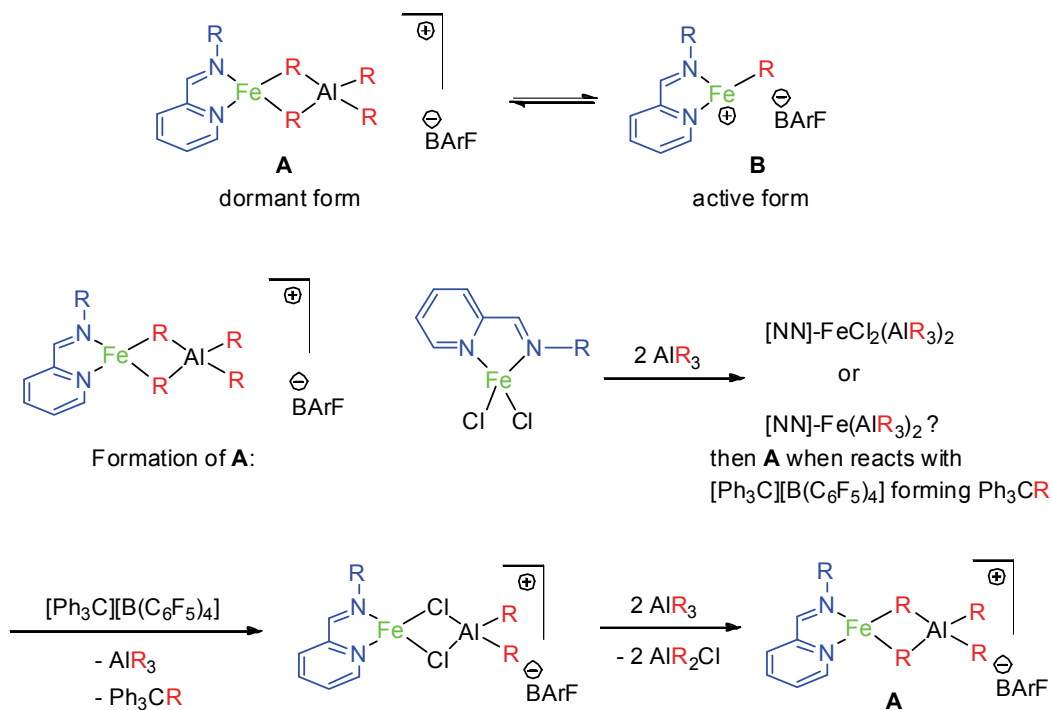
$$[\%cis - 1,4 - \text{motif}] = \frac{A(29.7\text{ppm})}{A(29.7\text{ppm}) + A(32.1\text{ppm})}$$

Putative polymerization reaction pathways

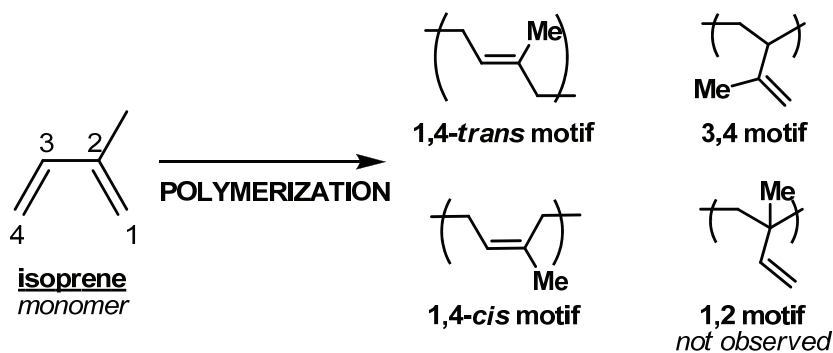


Putative alkylation/de-alkylation pathways

A molecule of AlR_3 can form a bimetallic onium complex together with the iron center:



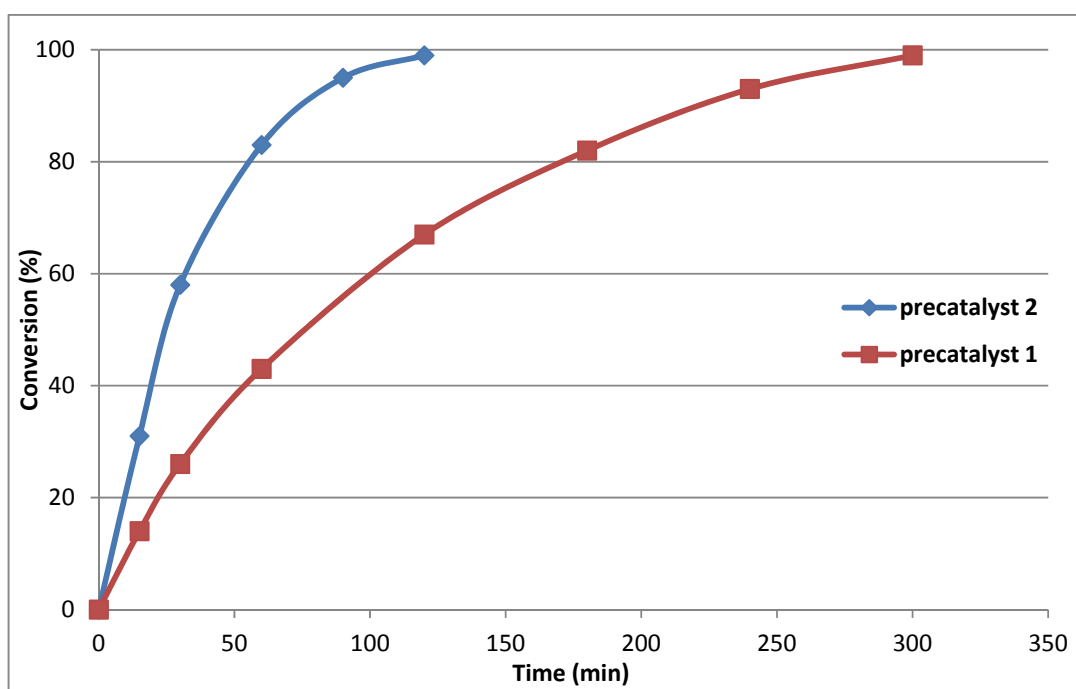
Different isomeric motifs obtained during isoprene polymerization



Photos depicting the aspect of the synthesized polyisoprenes

Kinetic Profile of Polymerization

Kinetic experiments were conducted according polymerization procedures depicted in examples 1 and 5 of the SI. Different aliquots were taken during the course of the reaction to determine conversion *vs.* time. Conversions were determined *via* ^1H NMR, using the characteristic chemical shifts of the olefinic protons of polyisoprene (5.12 and 4.6–4.8 ppm) and those of isoprene [6.45 (dd, $J = 17.5$ Hz, $J = 10.5$ Hz, 1H), 5.18 (d, $J = 17.5$ Hz, 1H), 5.08 (d, $J = 10.5$ Hz, 1H), 4.9 ppm (m, 2H) and 1.85 (t, $^4J = 1.2$ Hz).



The formula used to determine conversion is the following:

$$\text{Conv.}(\%) = \frac{\text{Area normalized for polymer}}{\text{Area normalized for polymer} + \text{Area normalized for monomer}}$$

$$\text{Conv.}(\%) = \frac{(A(5.05\text{to}5.25) - 2 \times A(6.4\text{to}6.5))}{(A(5.05\text{to}5.25) - 2 \times A(6.4\text{to}6.5)) + A(6.4\text{to}6.5)}$$

The experiment with precatalyst **2** yields an activity of $1 \text{ kg polyisoprene} \cdot \text{g Fe}^{-1} \cdot \text{h}^{-1}$

The experiment with precatalyst **1** yields an activity of $0.33 \text{ kg polyisoprene} \cdot \text{g Fe}^{-1} \cdot \text{h}^{-1}$

These numbers were derived using pseudo-linear portions of the curves between 20 and 80% conversion (jump in conversion achieved in 50 min for precatalyst **2** and 150 min for precatalyst **1**).

SEC Analysis

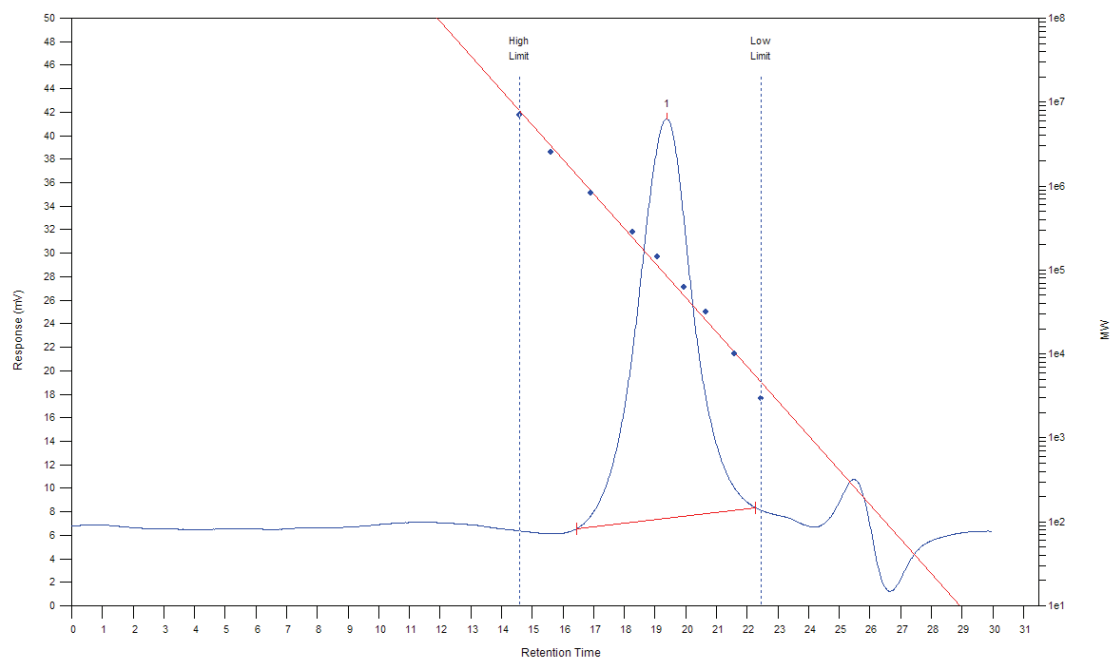


Figure S1. Size-exclusion chromatogram of *trans*-1,4-polyisoprene $M_w = 125,000$ g/mol, $D = 2.0$. Baselines automatically generated by the software, polydispersity values might be slightly higher than shown (same comment for Figure S2).

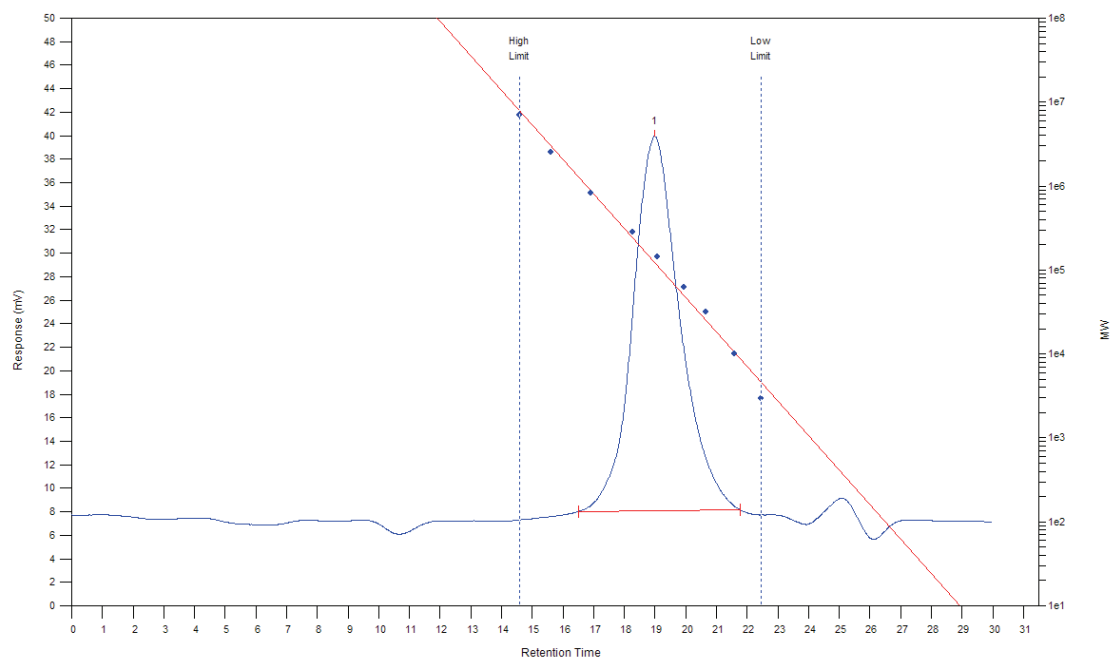


Figure S2. Size-exclusion chromatogram of *cis*-1,4-polyisoprene $M_w = 140,000$ g/mol, $D = 1.7$.

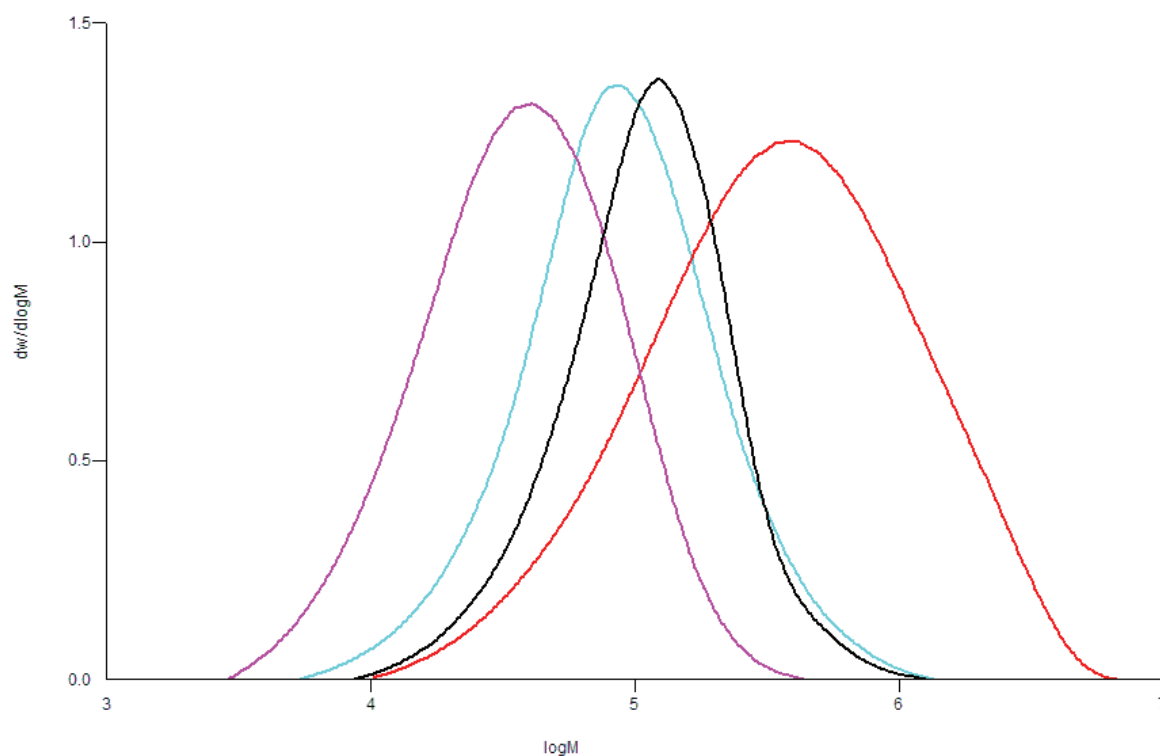


Figure S3. Molar mass distributions: living character of the Iron catalyzed polymerization of isoprene. The blue curve represents the SEC- M_n trace of chain extension of a pre-existing polymer of lower molar masses represented by the pink curve. Similarly, the red curve represents the chain extension to higher molar masses of a pre-existing polymer of medium molar masses represented by the black curve.

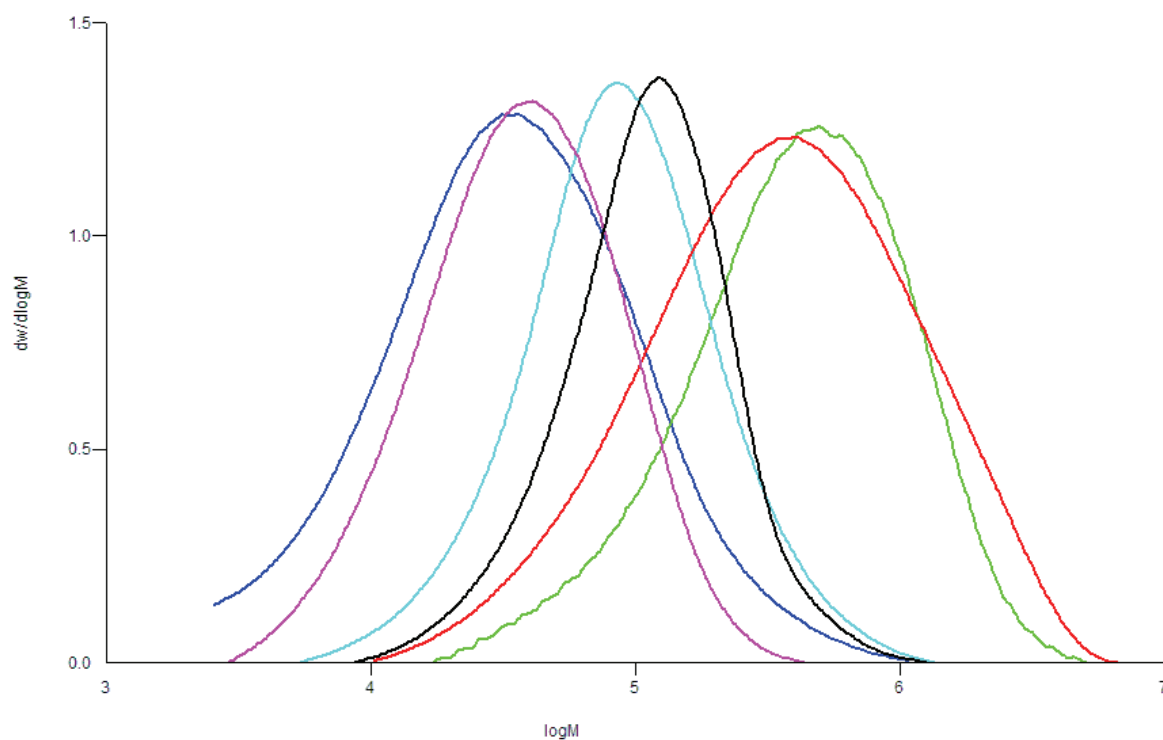


Figure S4. Accessible molar masses, obtained from the various polymerization reactions reported above varying the ratio [isoprene]/[Fe]. Green (example 8) and red (example 4) curves are obtained with a ratio of 5000. The black curve represents an aliquot of example 4, after 1h of polymerization. The light blue (example 2) curve is obtained with a ratio of 2000. The blue curve (example 1) is obtained with a ratio of 1000. The pink curve is obtained represents an aliquot of example 2.

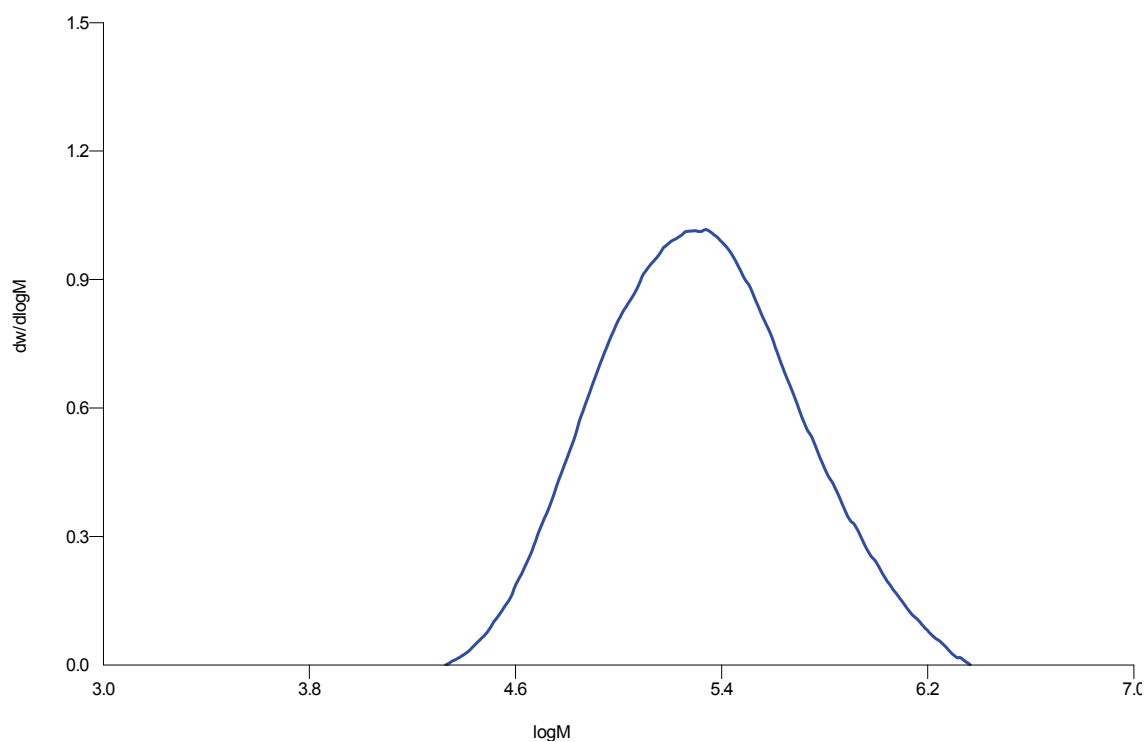


Figure S5. Size-exclusion chromatogram of *trans*-1,4-poly- β -myrcene $M_w = 250,000$ g/mol, $D = 2.1$.

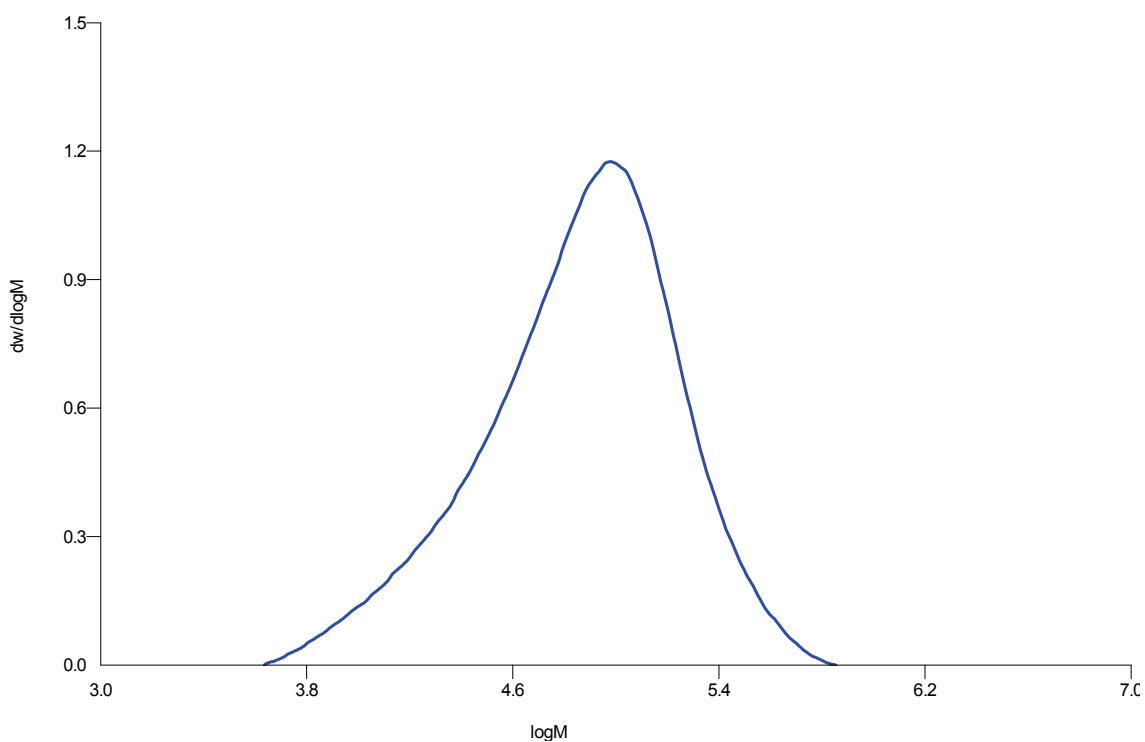


Figure S6. Size-exclusion chromatogram of *trans*-1,4-poly- β -farnesene $M_w = 110,000$ g/mol, $D = 1.5$.

GC Analysis

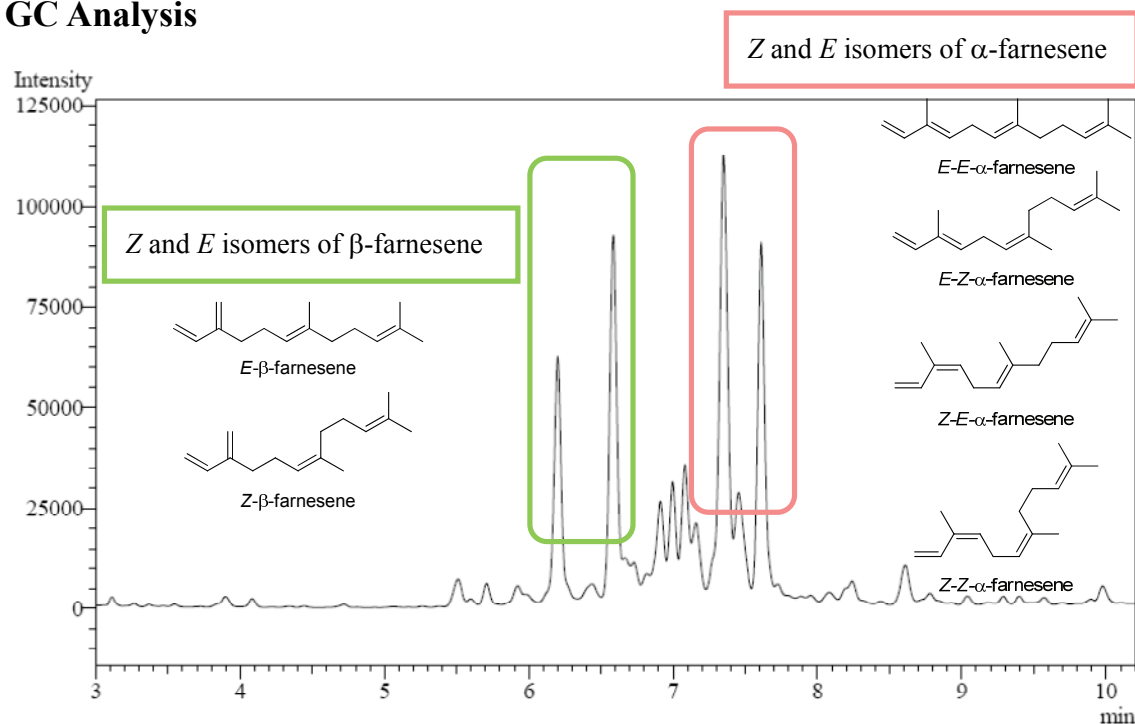


Figure S7. Gas chromatogram of the commercially available mixture of farnesene isomers (in green β -farnesene isomers, in pink two major isomers among the four possible isomers of α -farnesene. β -farnesene isomers have lower bp° than α -farnesene counterparts.⁷

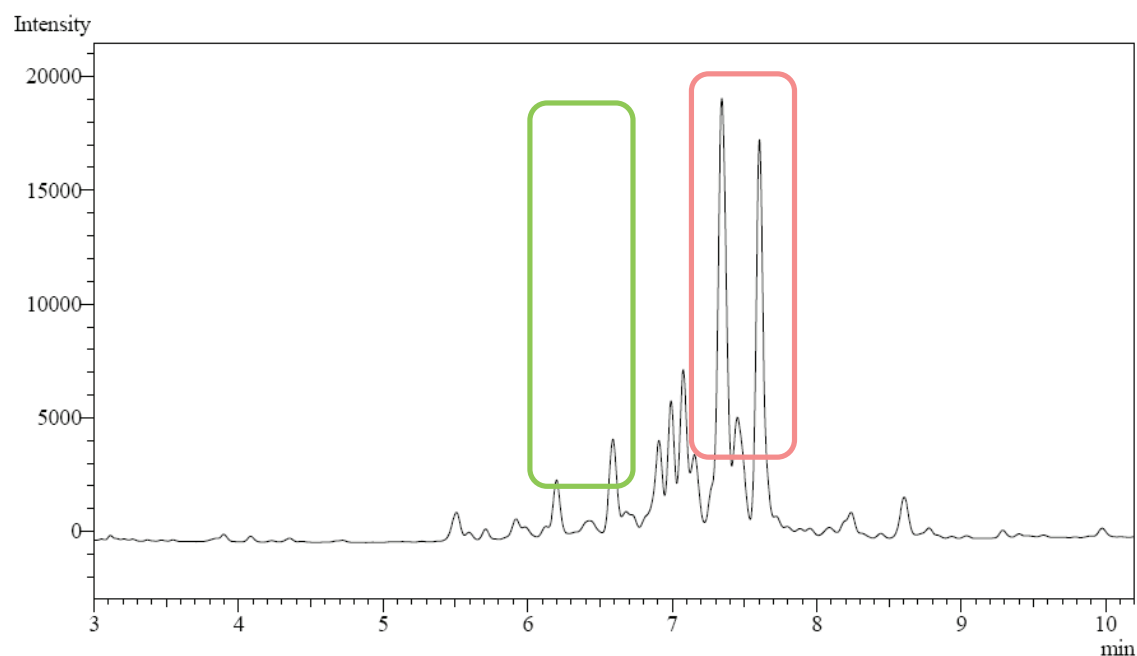


Figure S8. Gas chromatogram of the solution obtained after precipitation of the *trans*-1,4-poly- β -farnesene (ex. 11): the two peaks corresponding to the β -isomers have almost disappeared.

⁷ Wang, S. C.; Tseng, T. Y.; Huang, C. M.; Tsai, T. H. *Journal of Chromatography B* **2004**, 812, 193-202

X-Ray Crystallographic Analysis

iron(II) chloride complex 1 (CCDC 853130)

Experimental

The title compound crystallized as orange plates from a vapor diffusion of pentane into a CH₂Cl₂ solution at 23 °C. A crystal 0.001 mm x 0.050 mm x 0.100 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX II DUO CCD diffractometer equipped with an Oxford Cryosystems nitrogen flow apparatus and Cu K α radiation (λ = 1.54178 Å). The data collection method involved 1.0° scans in ω at 30°, 55°, 90°, and 115° in 2 θ . Data integration down to 0.84 Å resolution was carried out using SAINT V7.46 (Bruker diffractometer, 2009) with reflection spot size optimization. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by direct methods and refined by least-squares methods against F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on their respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1 and geometric parameters are shown in Table 2. Ortep plots were produced with SHELXL-97 (Sheldrick, 2008).

References

- Bruker AXS (2009). *APEX2 v2009.3.0*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Bruker AXS (2009). *SADABS*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Bruker AXS (2009). *SAINT V7.46A*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. *Acta Cryst.* (2008). A64, 112–122.
- Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 206-222. Dordrecht, The Netherlands: Kluwer.
- Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 476-516. Dordrecht, The Netherlands: Kluwer.

$R(F) = R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR(F^2) = wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$, and $S =$ Goodness-of-fit on $F^2 = [\Sigma w (F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

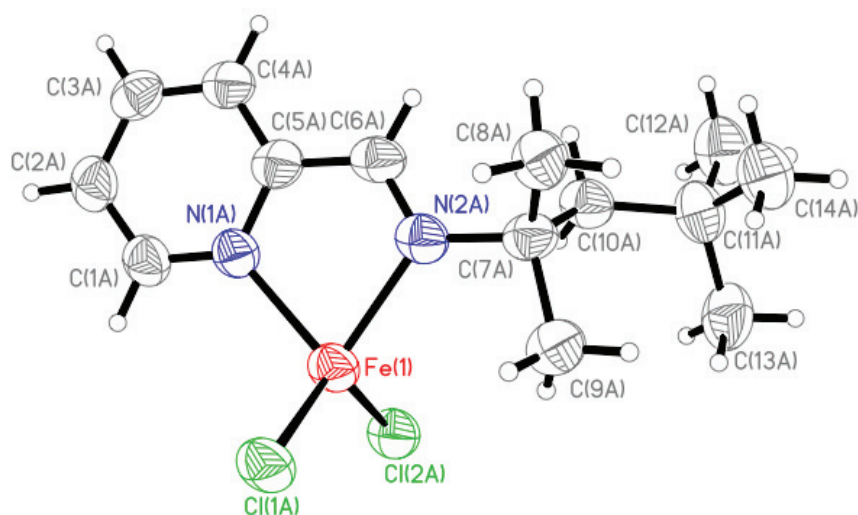


Figure S9. The X-ray structure of (*E*)-2,4,4-trimethyl-*N*-(pyridin-2-ylmethylene)pentan-2-amine iron(II) chloride **1** with hydrogens and with the atom labeling scheme employed. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S1. Crystal data and structure refinement for (*E*)-2,4,4-trimethyl-*N*-(pyridin-2-ylmethylene)pentan-2-amine iron(II) chloride.

Identification code	CCDC 853130
Chemical formula	C ₁₄ H ₂₂ Cl ₂ FeN ₂
Molecular weight	345.09
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.0412 (4), 12.8066 (7), 16.8314 (10)
α , β , γ (°)	99.106 (3), 97.796 (3), 97.609 (4)
<i>V</i> (Å ³)	1674.53 (16)

<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	10.06
Crystal size (mm)	0.10 × 0.05 × 0.01
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan, <i>SADABS</i> (Sheldrick,2008)
<i>T</i> _{min} , <i>T</i> _{max}	0.036, 0.633
No. of measured, 26716, 5572, 3897 independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	
<i>R</i> _{int}	0.085
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.079, 0.204, 1.07
No. of reflections	5572
No. of parameters	353
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.12, -0.62

Iron(II) chloride complex 2 (CCDC 853131)

Experimental

The title compound crystallized as green needles from a vapor diffusion of diethyl ether into a CH₂Cl₂ solution at −35 °C. A crystal 0.01 mm x 0.01 mm x 0.05 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX II DUO CCD diffractometer equipped with an Oxford Cryosystems nitrogen flow apparatus and Cu *K*α radiation (λ = 1.54178 Å). The data collection method involved 1.0° scans in *ω* at 30°, 55°, 90°, and 115° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V7.46 (Bruker diffractometer, 2009) with reflection spot size optimization. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The crystal diffracted weakly, resulting in the high *R*_{int}. Two partial solvent molecules, dichloromethane and diethyl ether, were

removed using Platon Squeeze, because they were difficult to locate on the difference map. The structure was solved by direct methods and refined by least-squares methods against F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on their respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1 and geometric parameters are shown in Table 2. Ortep plots were produced with SHELXL-97 (Sheldrick, 2008).

References

Bruker AXS (2009). *APEX2 v2009.3.0*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2009). *SADABS*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2009). *SAINT V7.46A*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. *Acta Cryst.* (2008). A64, 112–122.

Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 206-222. Dordrecht, The Netherlands: Kluwer.

Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 476-516. Dordrecht, The Netherlands: Kluwer.

$R(F) = R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR(F^2) = wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$, and $S = \text{Goodness-of-fit on } F^2 = [\Sigma w (F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

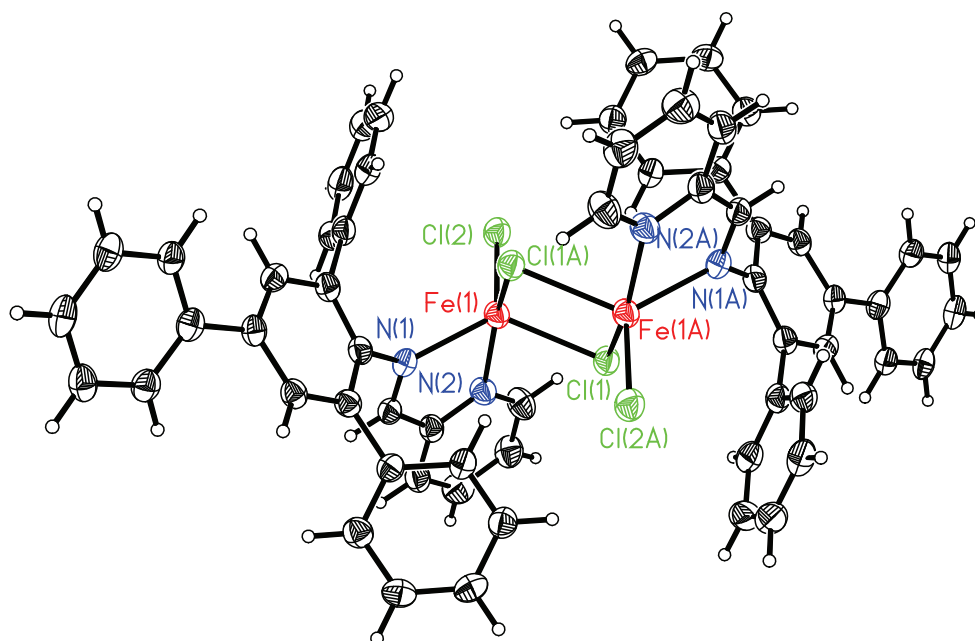


Figure S10. The X-ray structure of (*E*)-3,5-diphenyl-*N*-(pyridin-2-ylmethylene)biphenyl-2-amine iron(II) chloride **2** with hydrogens and with the atom labeling scheme employed for heteroatoms. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

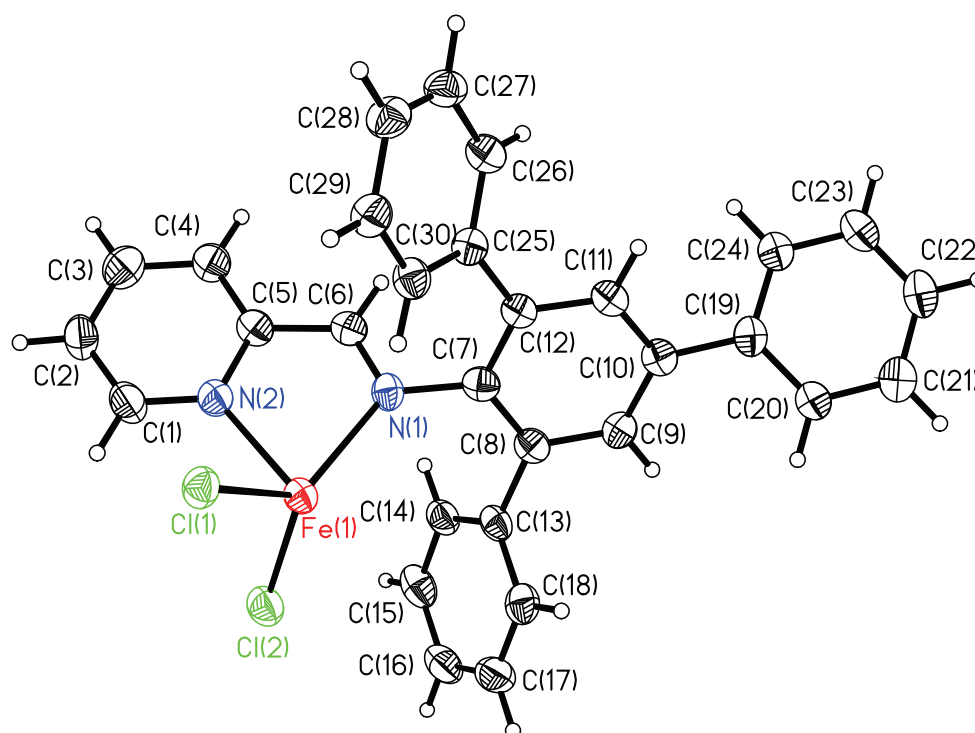


Figure S11. The X-ray structure of one half of the dimeric unit of (*E*)-3,5-diphenyl-*N*-(pyridin-2-ylmethylene)biphenyl-2-amine iron(II) chloride **2** with hydrogens and with the atom labeling scheme employed. The nonhydrogen atoms are depicted with 50% probability ellipsoids.

Table S2. Crystal data and structure refinement for (*E*)-2,4,4-trimethyl-*N*-(pyridin-2-ylmethylene)pentan-2-amine iron(II) chloride.

Identification code	CCDC 853131
Chemical formula	C ₆₀ H ₄₄ Cl ₄ Fe ₂ N ₄
<i>M</i> _r	1074.49
Crystal system, space group	Orthorhombic, <i>Pccn</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.6880 (16), 28.115 (2), 10.4622 (9)
<i>V</i> (Å ³)	5791.2 (8)
<i>Z</i>	4

Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	6.01
Crystal size (mm)	0.05 × 0.01 × 0.01
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan, <i>SADABS</i> (Sheldrick, 2008)
$T_{\min}$, $T_{\max}$	0.753, 0.942
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	69244, 5053, 3940
R_{int}	0.131
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.151, 1.10
No. of reflections	5053
No. of parameters	316
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.92, -0.50

Spectroscopic Data (Mössbauer analysis)

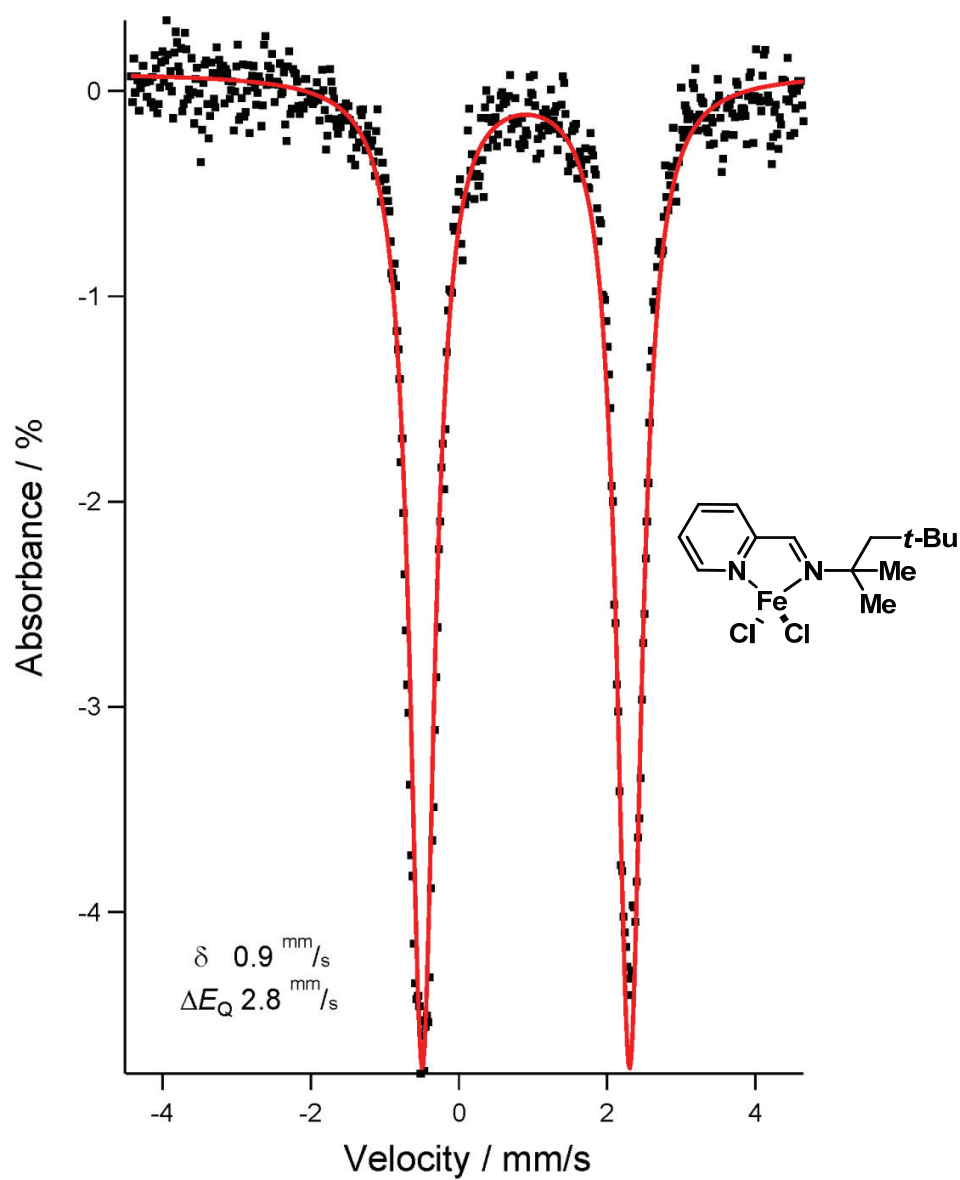


Figure S12. Mössbauer spectrum of (*E*)-2,4,4-trimethyl-*N*-(pyridin-2-ylmethylene)pentan-2-amine iron(II) chloride (**1**) at 90 K.

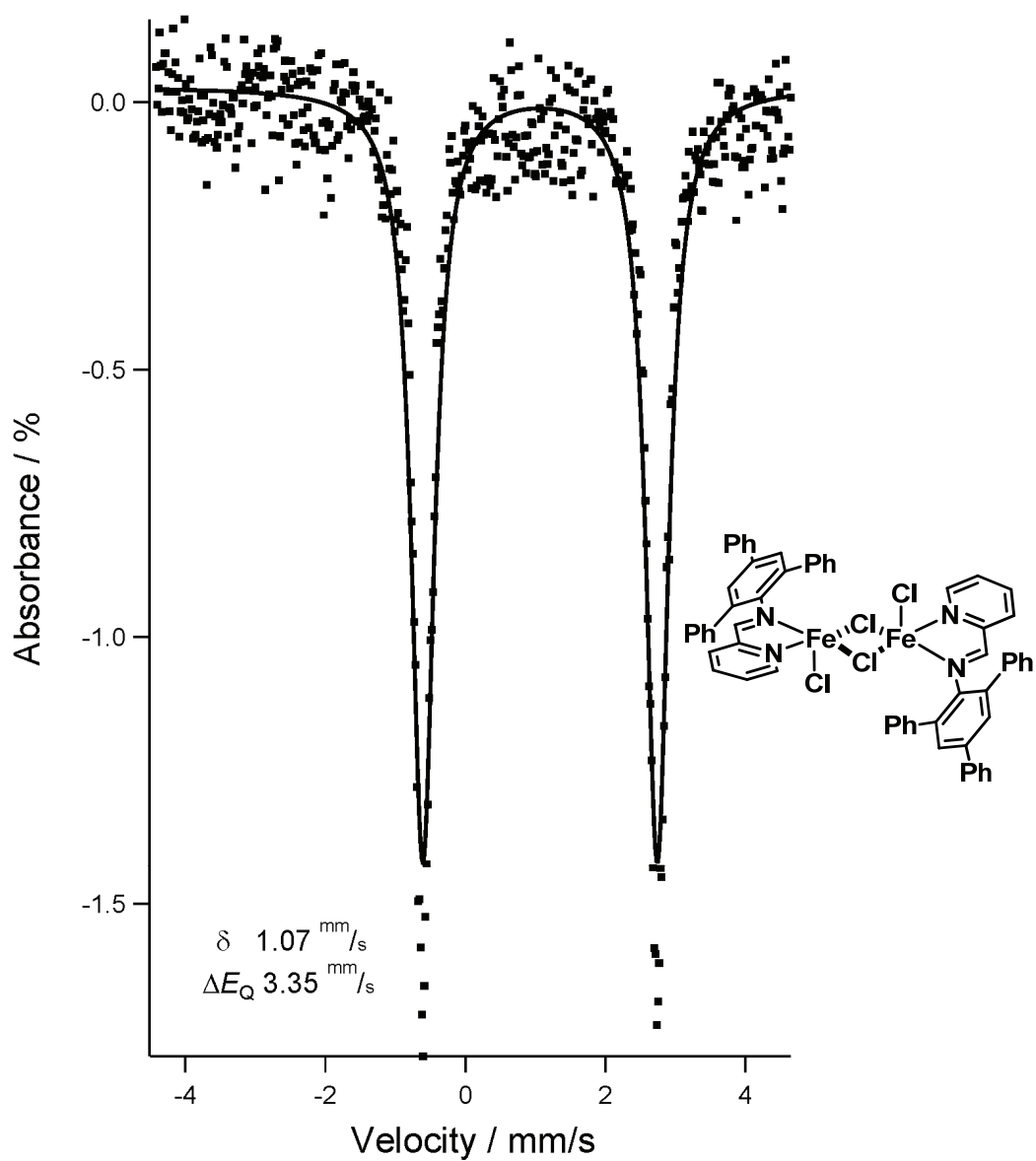
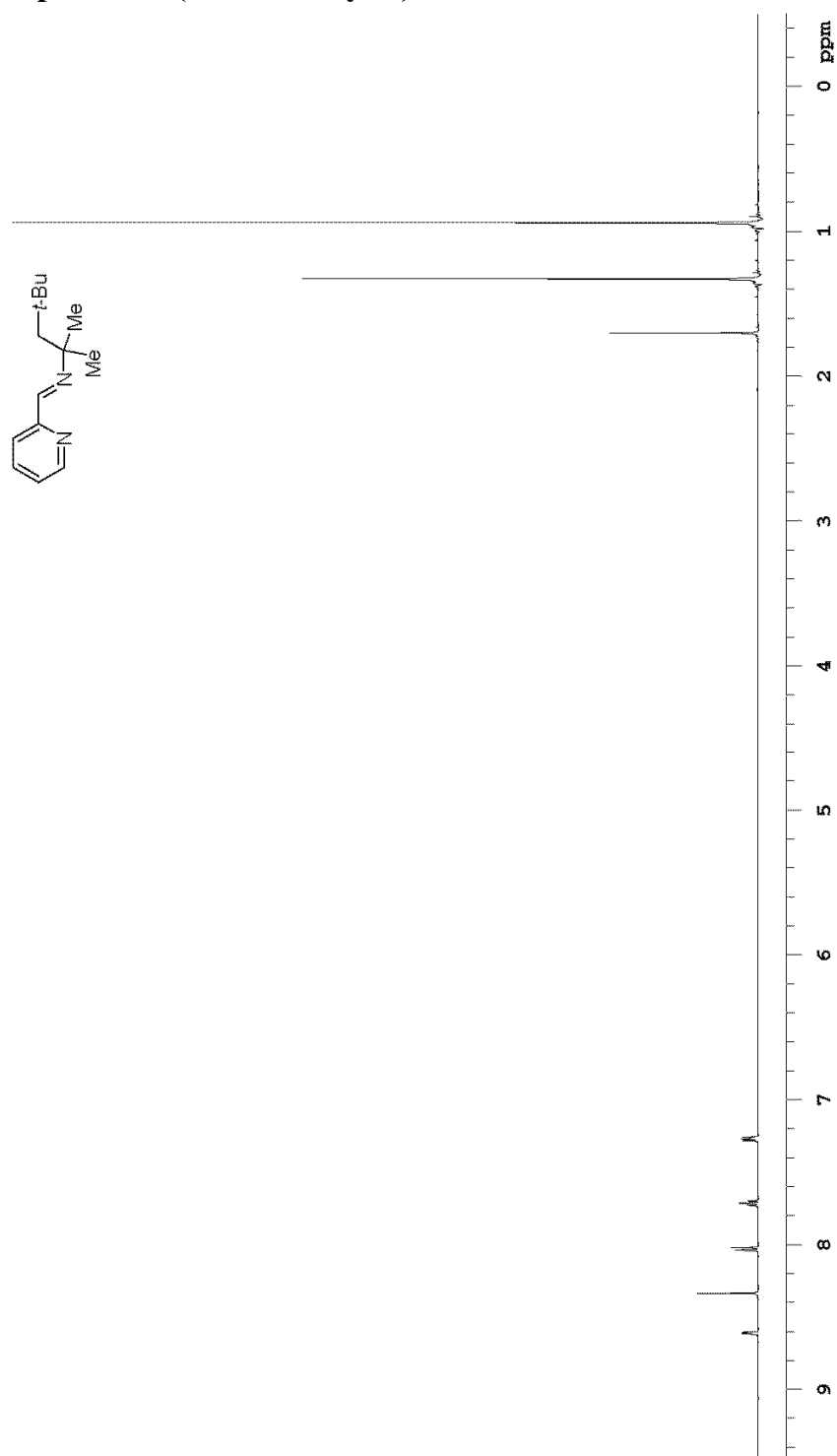
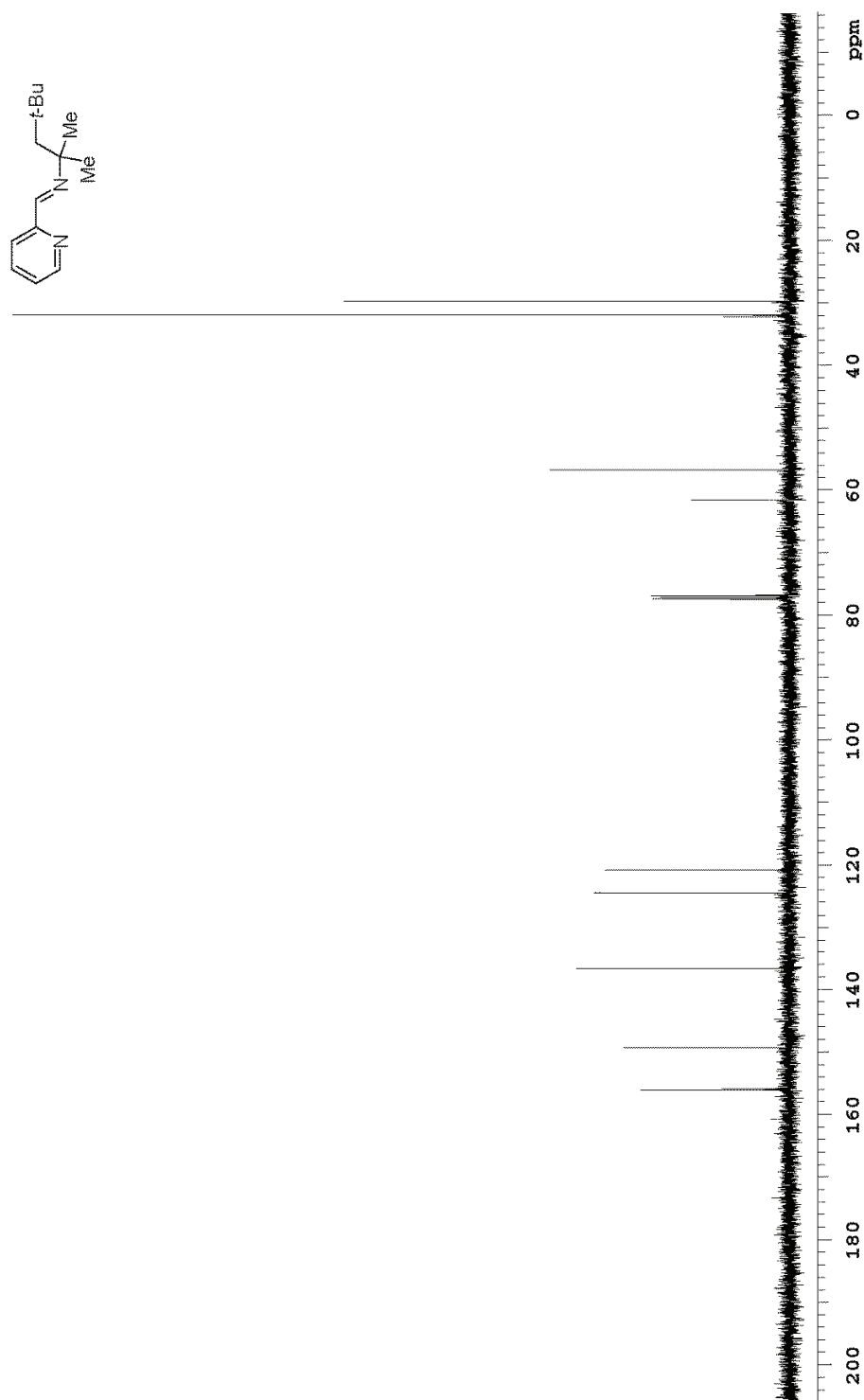


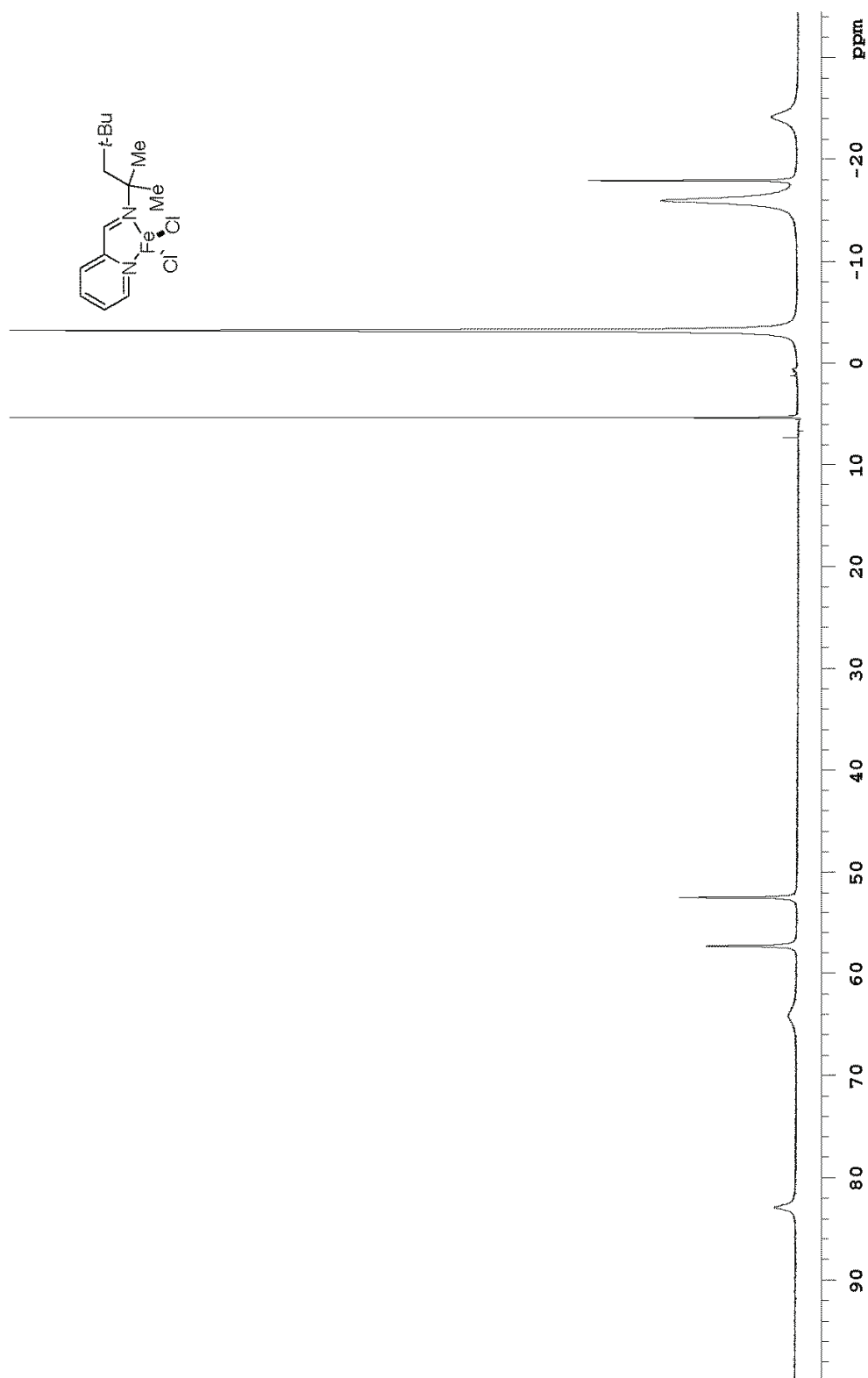
Figure S13. Mössbauer spectrum of (*E*)-3,5-diphenyl-*N*-(pyridin-2-ylmethylene)biphenyl-2-amine iron(II) chloride (**2**) at 90 K.

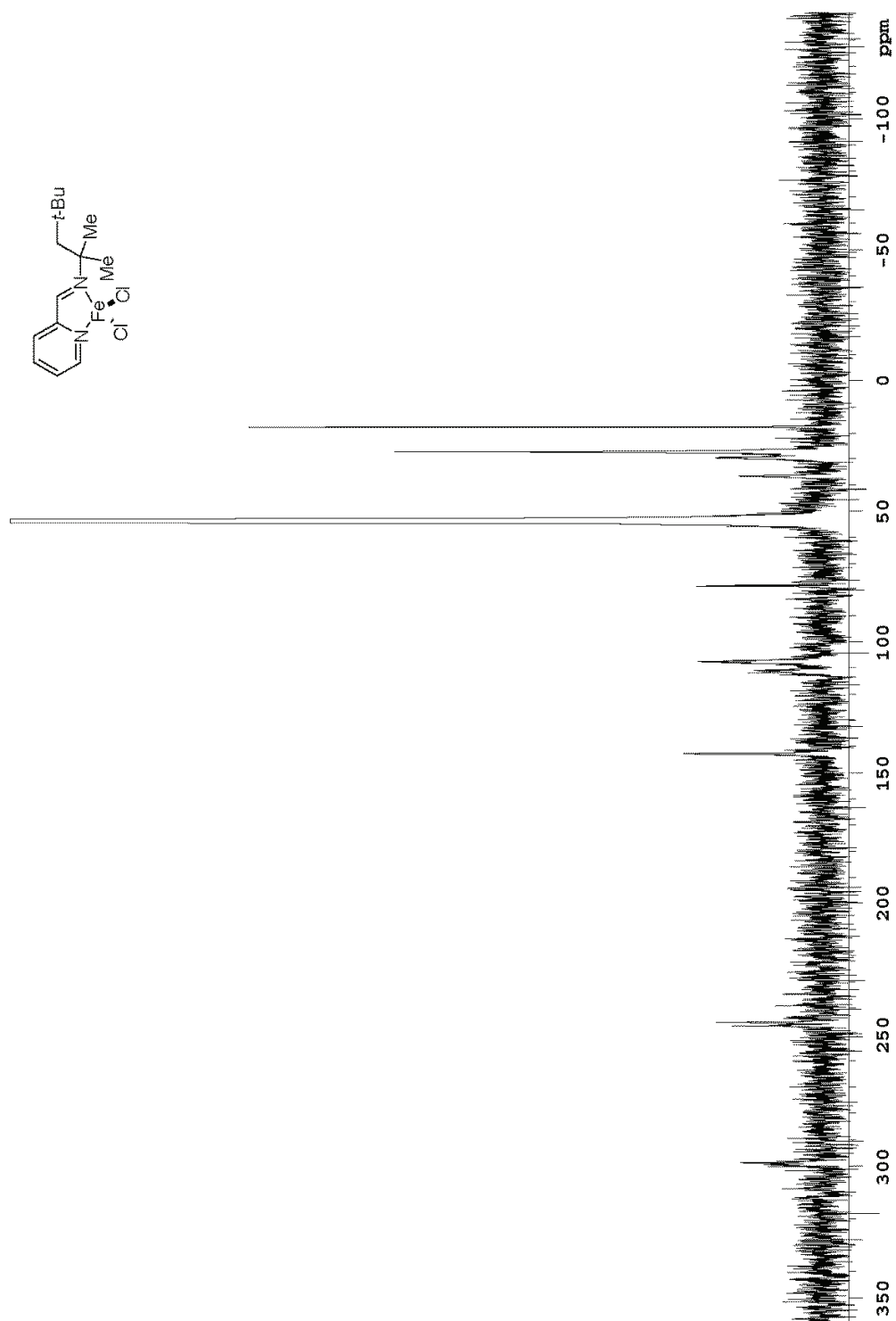
Spectroscopic Data (NMR analysis)

NMR 1: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of **S1**

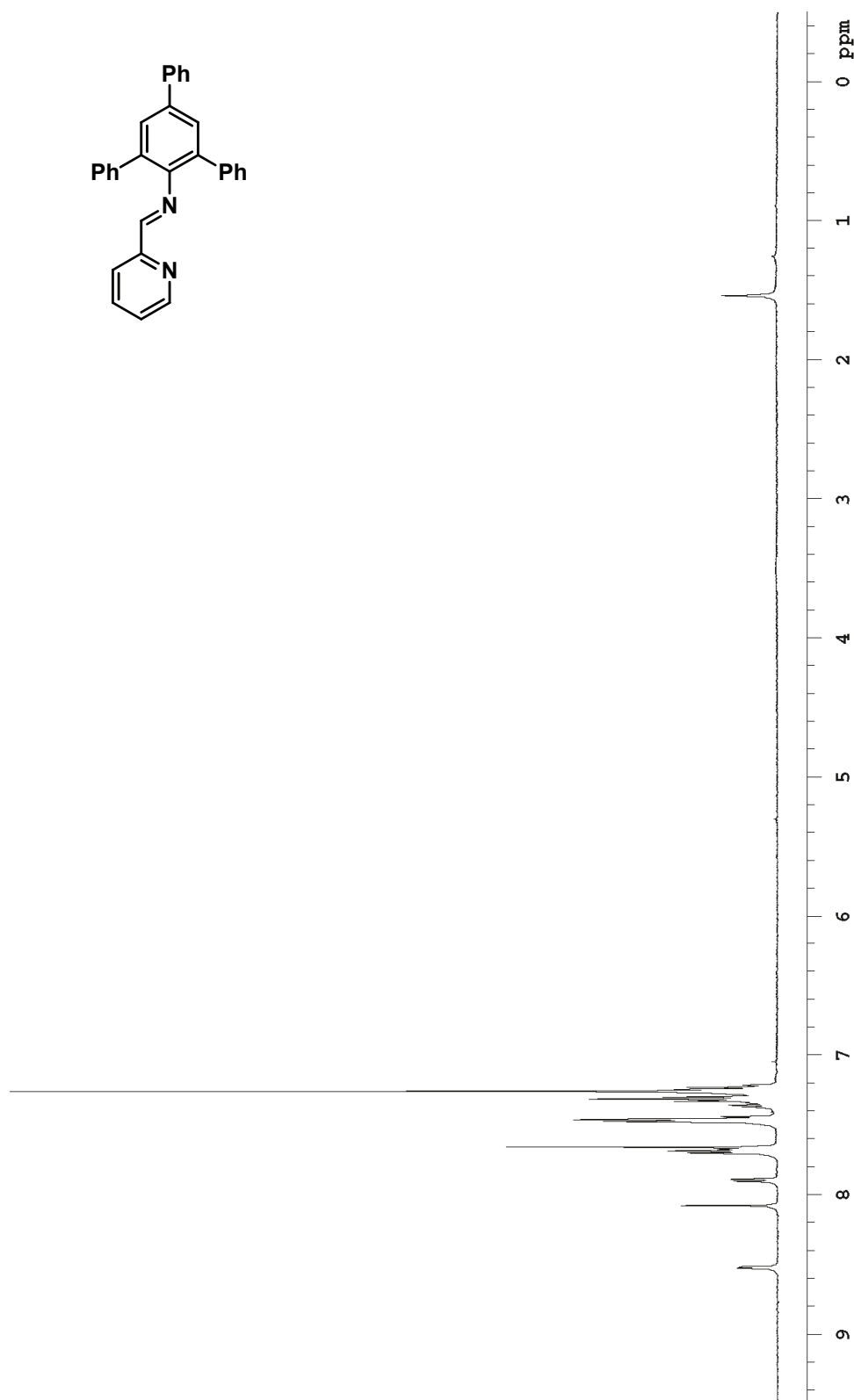


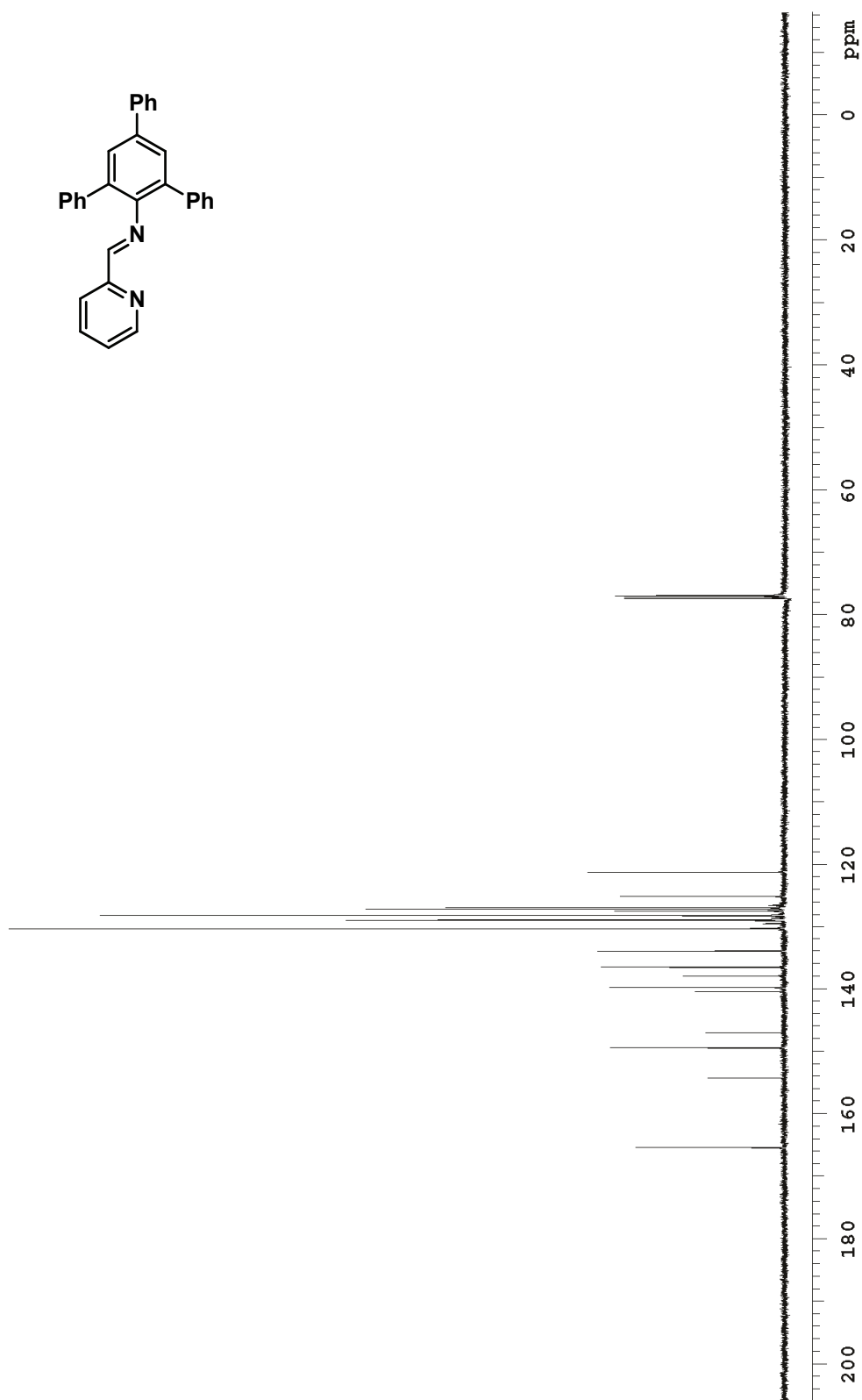
NMR 2: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of **S1**

NMR 3: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of **1**

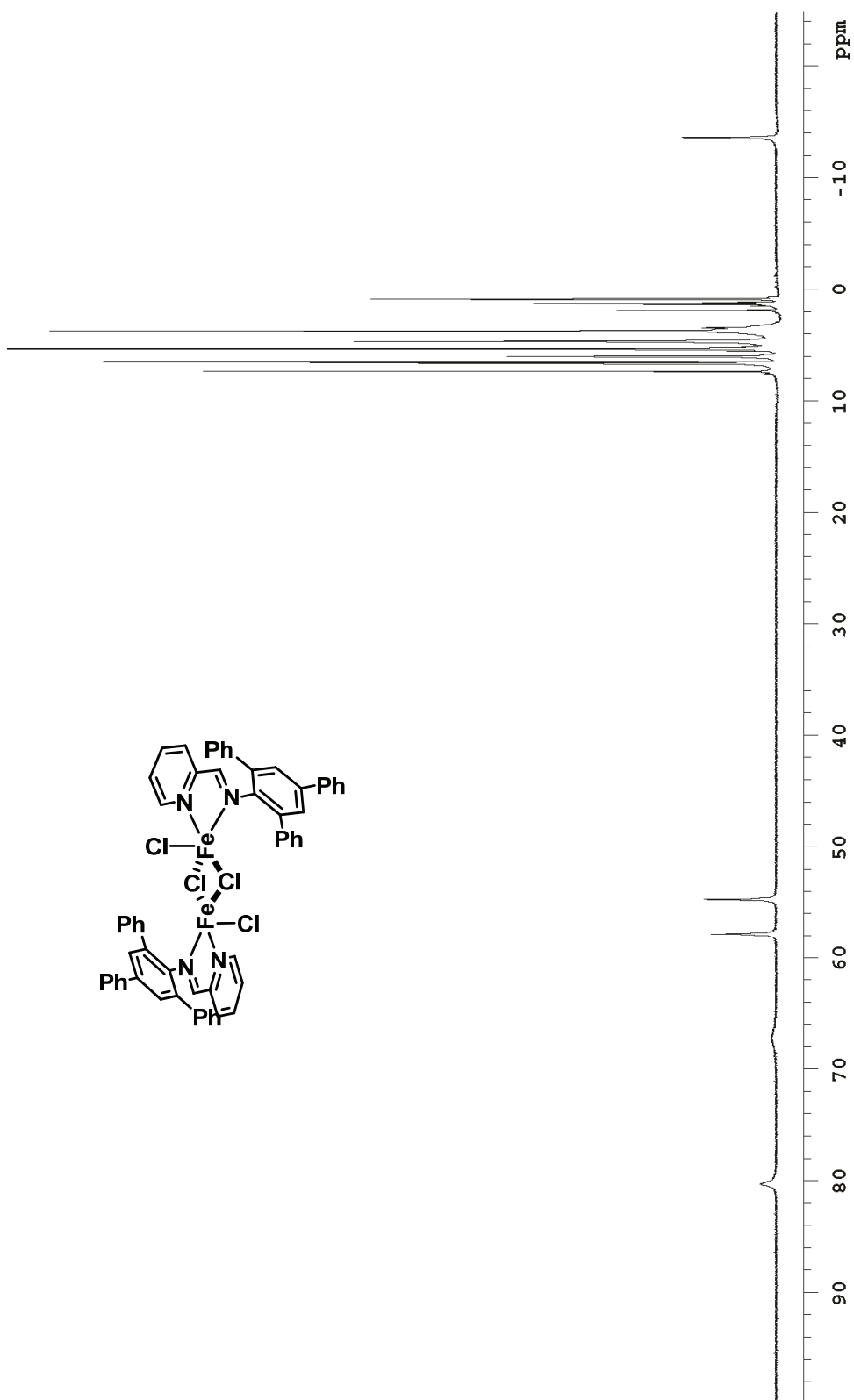


NMR 4: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **1**

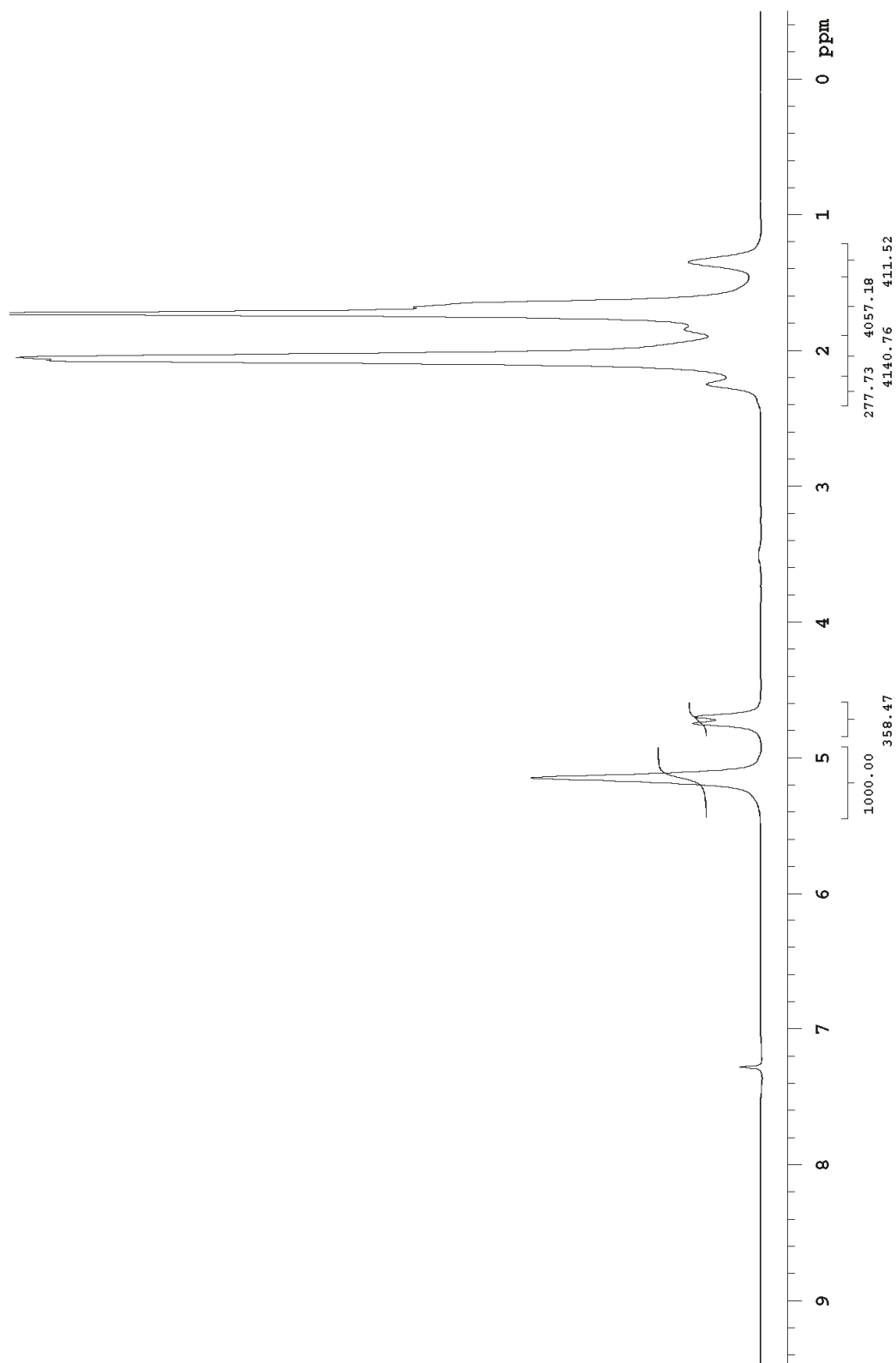
NMR 5: ¹H NMR spectrum (500 MHz, CDCl₃, 25 °C) of **S2**



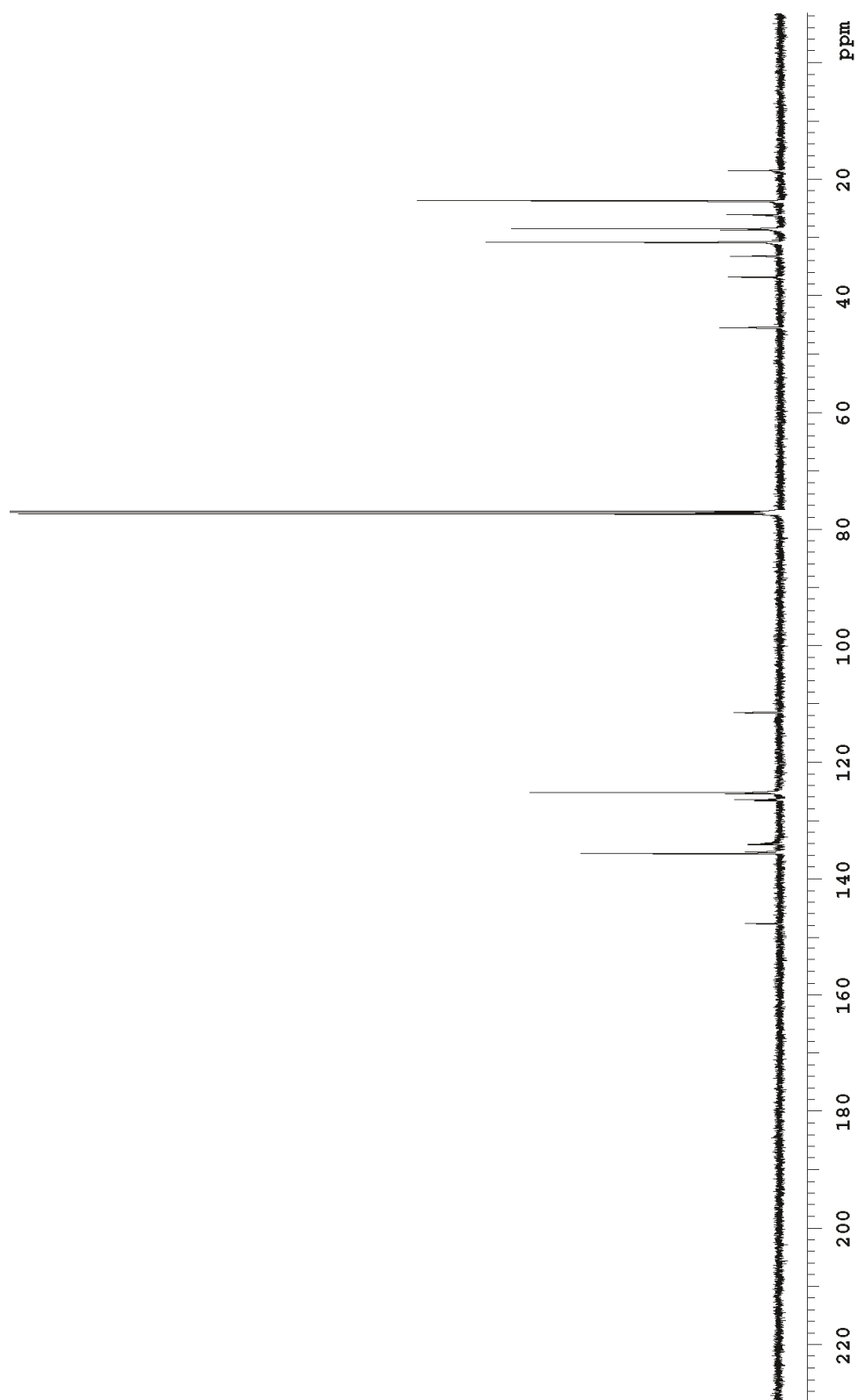
NMR 6: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of **S2**



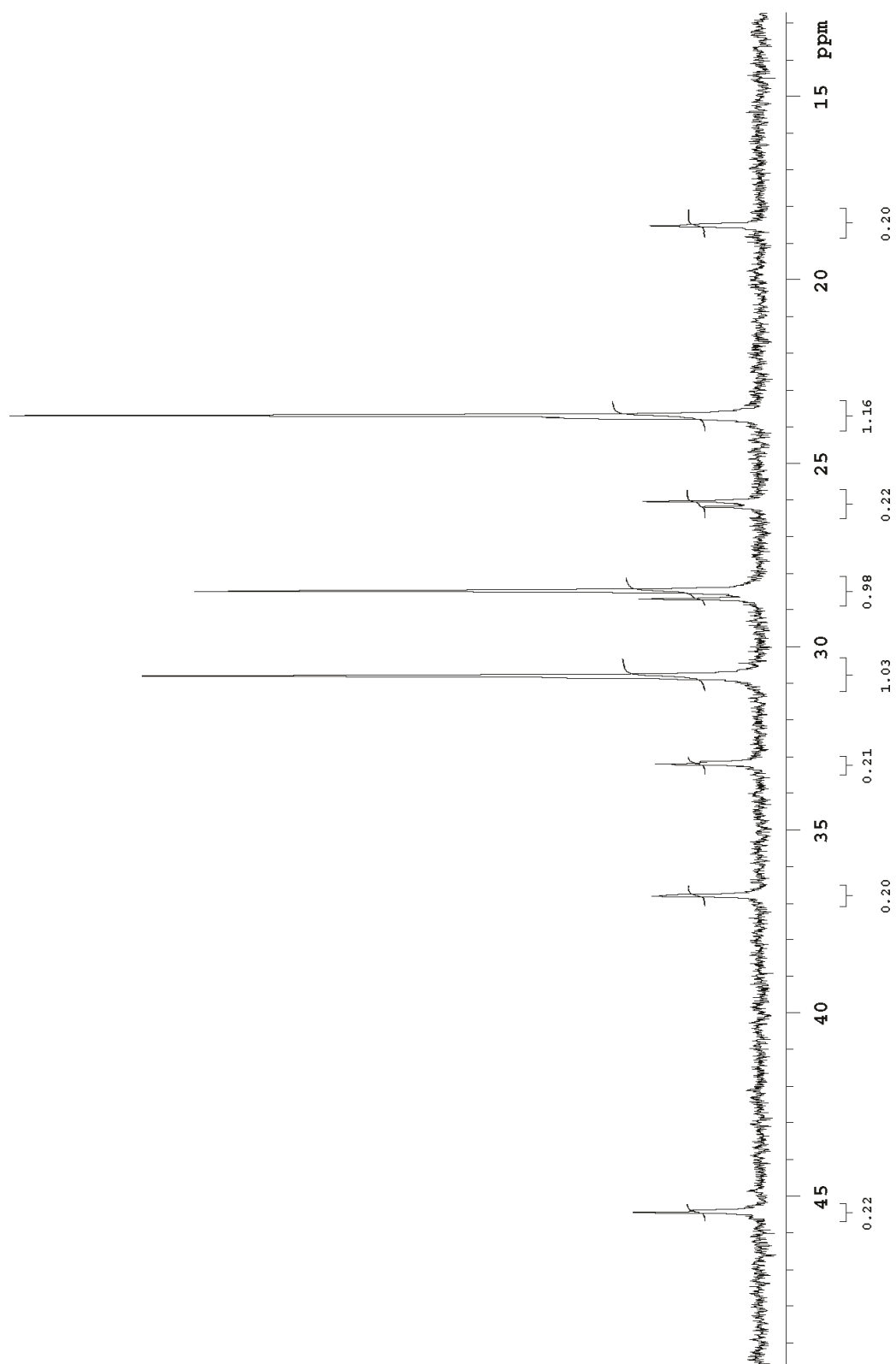
NMR 7: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of **2**



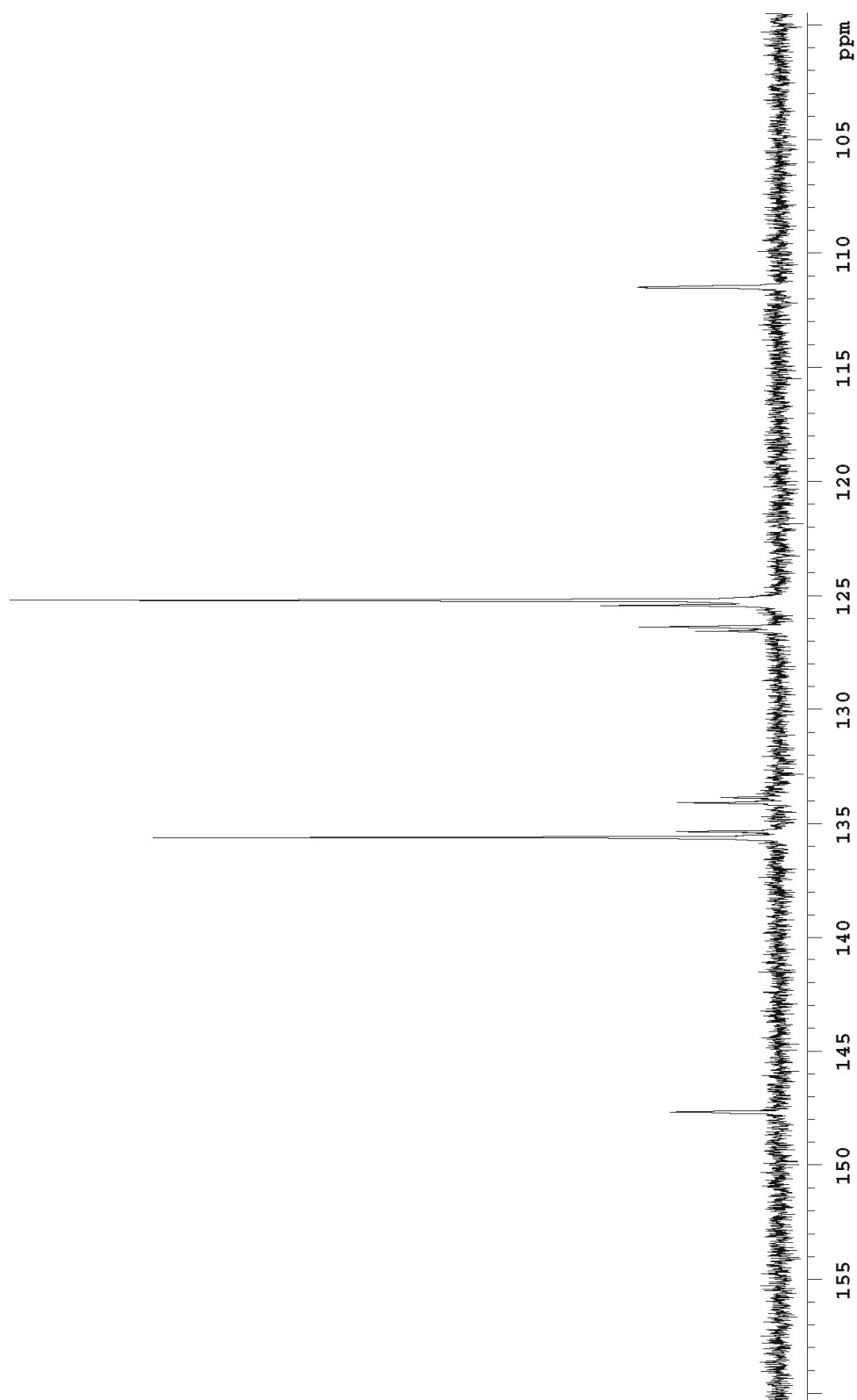
NMR 8: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *cis*-1,4-polyisoprene (ex. 5)



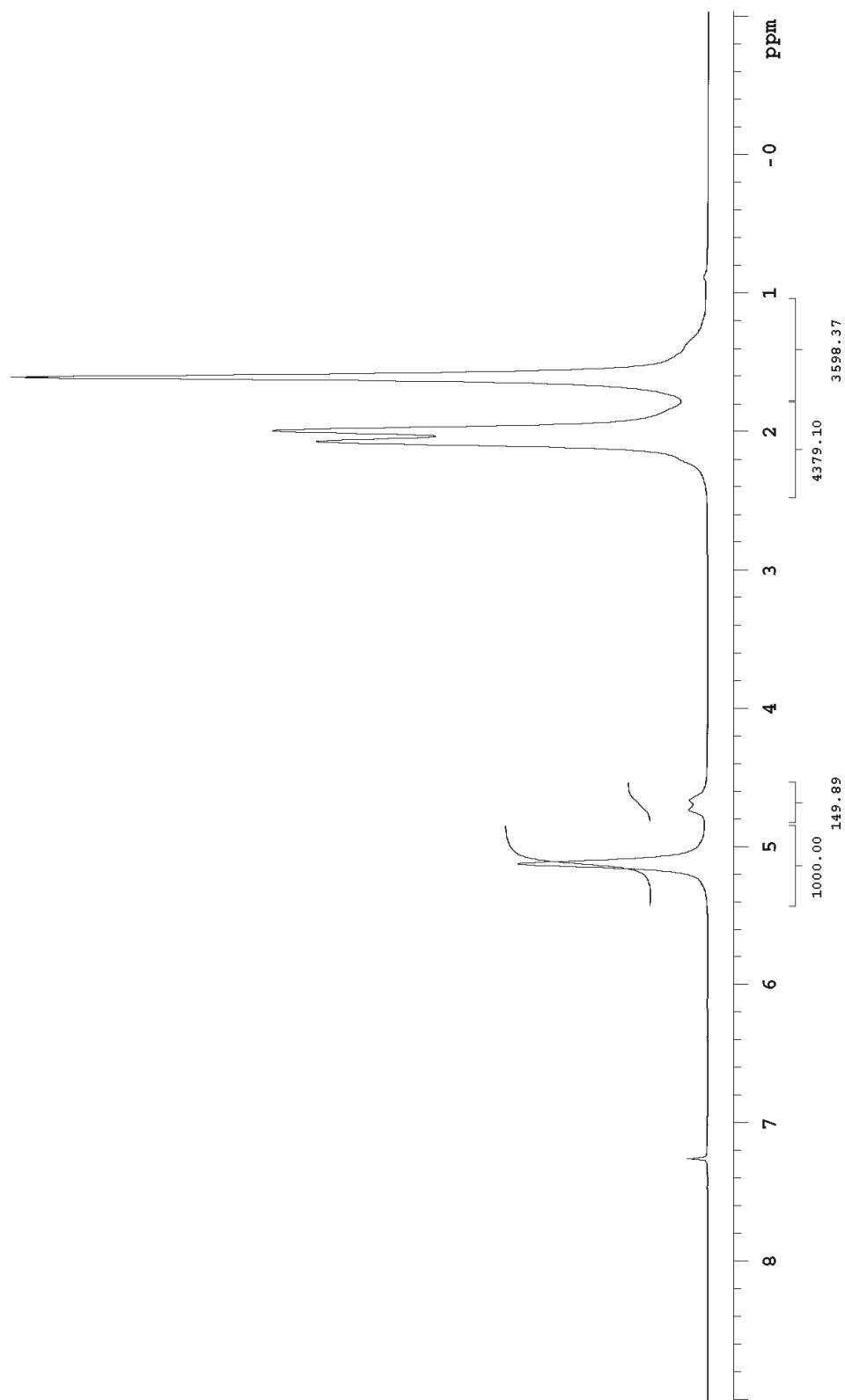
NMR 9: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *cis*-1,4-polyisoprene (ex. 5)



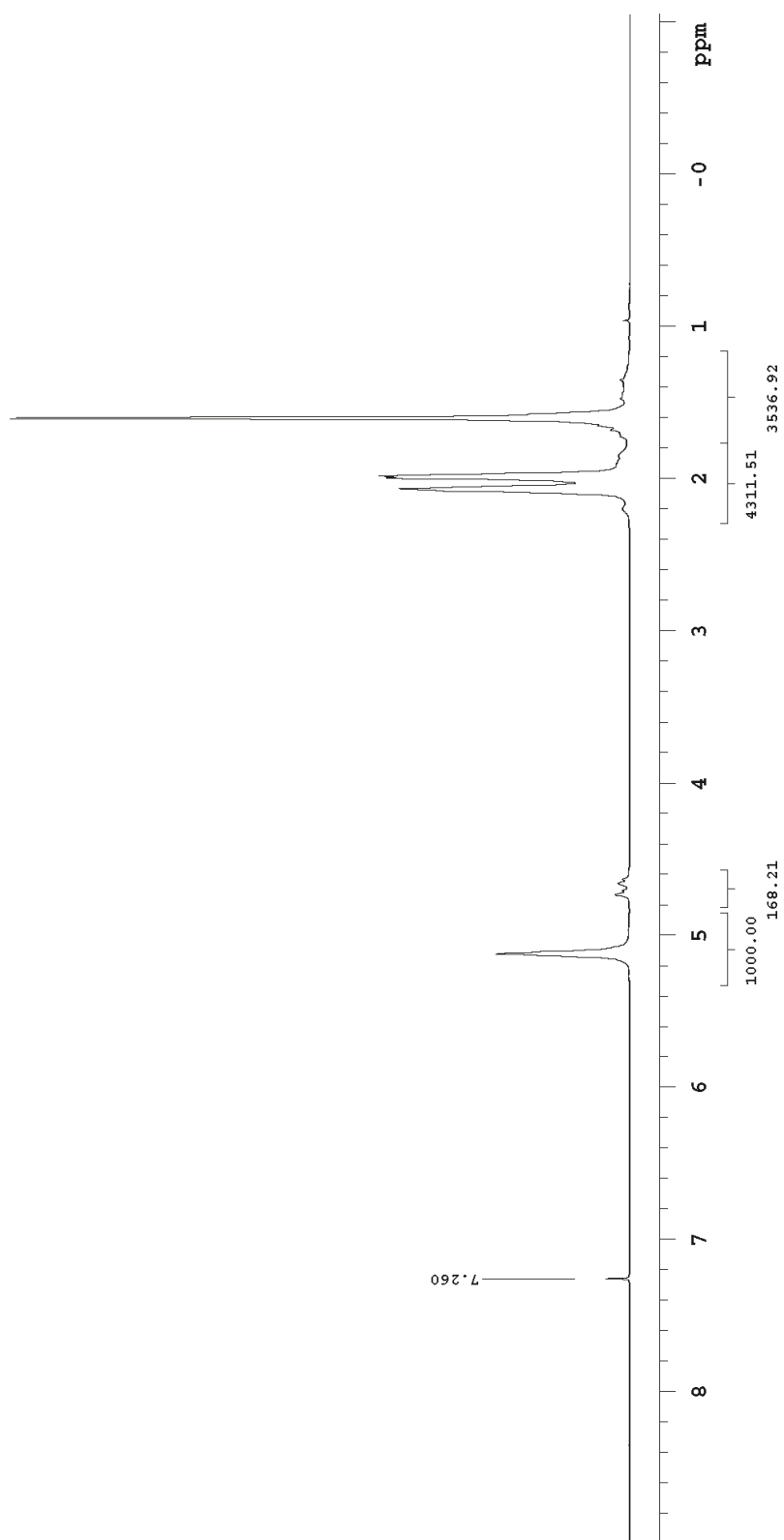
NMR 10: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of *cis*-1,4-polyisoprene (aliphatic region)



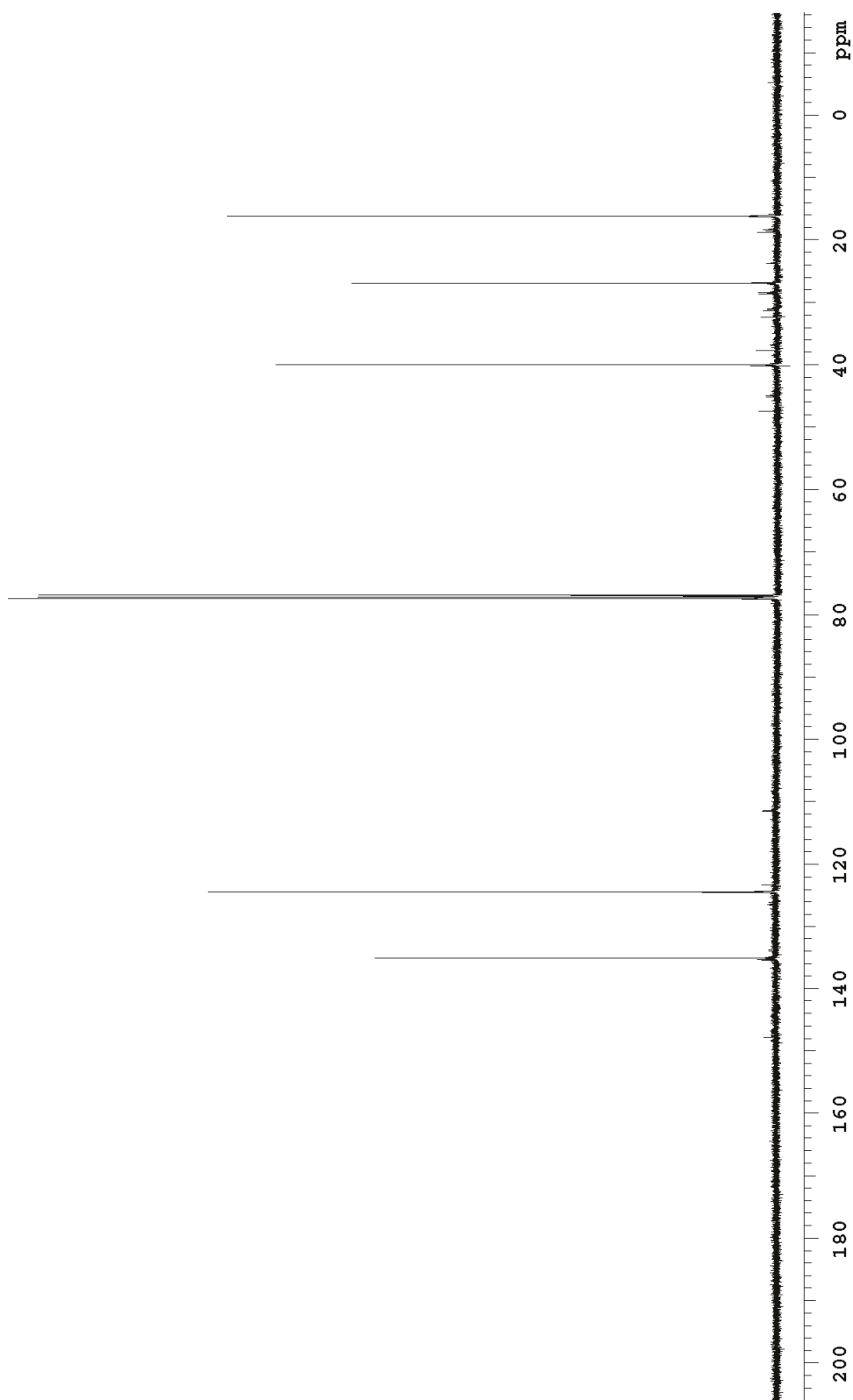
NMR 11: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *cis*-1,4-polyisoprene (olefinic region)



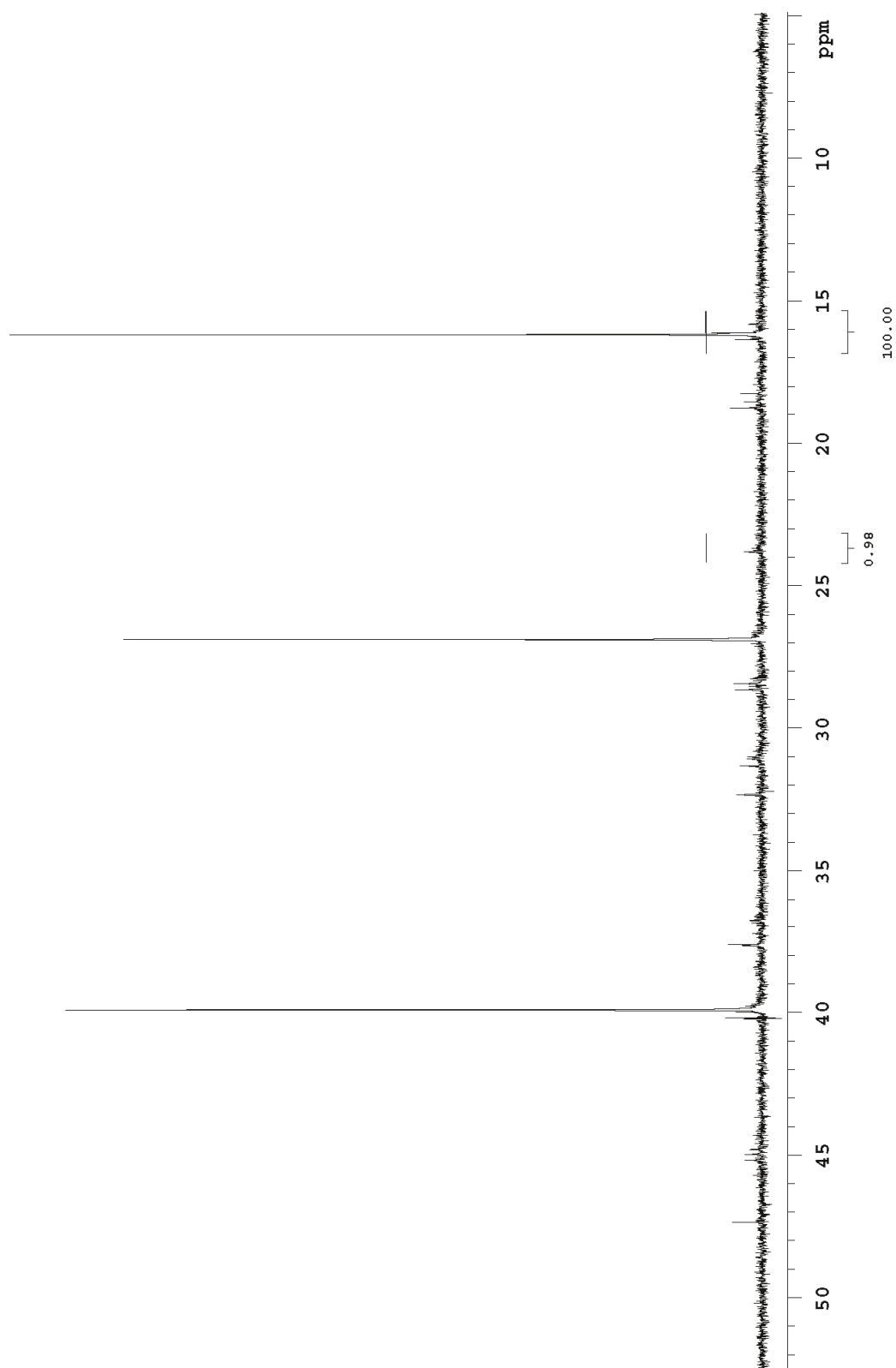
NMR 12: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of *trans*-1,4-polyisoprene (ex. 2)



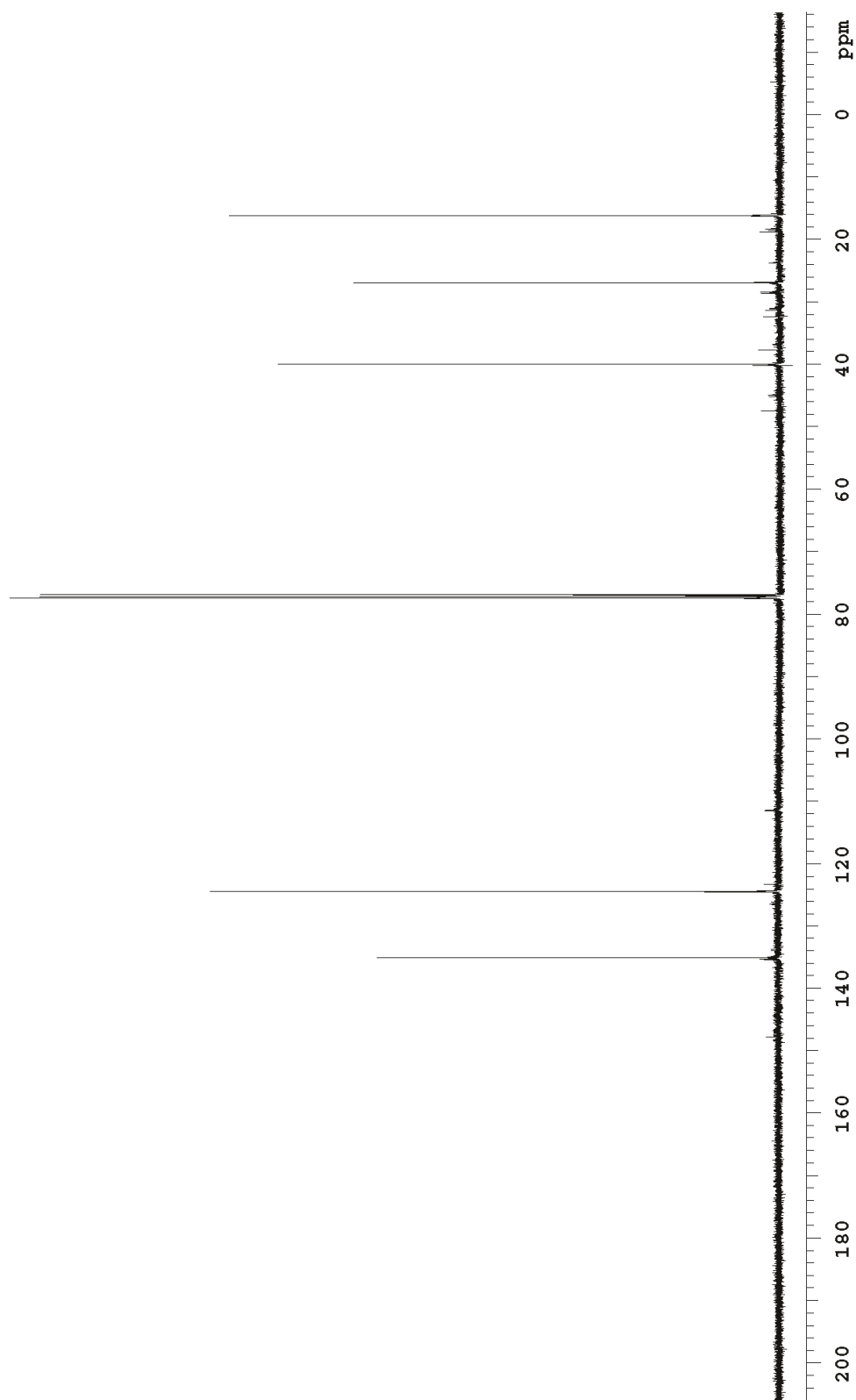
NMR 13: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of *trans*-1,4-polyisoprene (ex. 1)



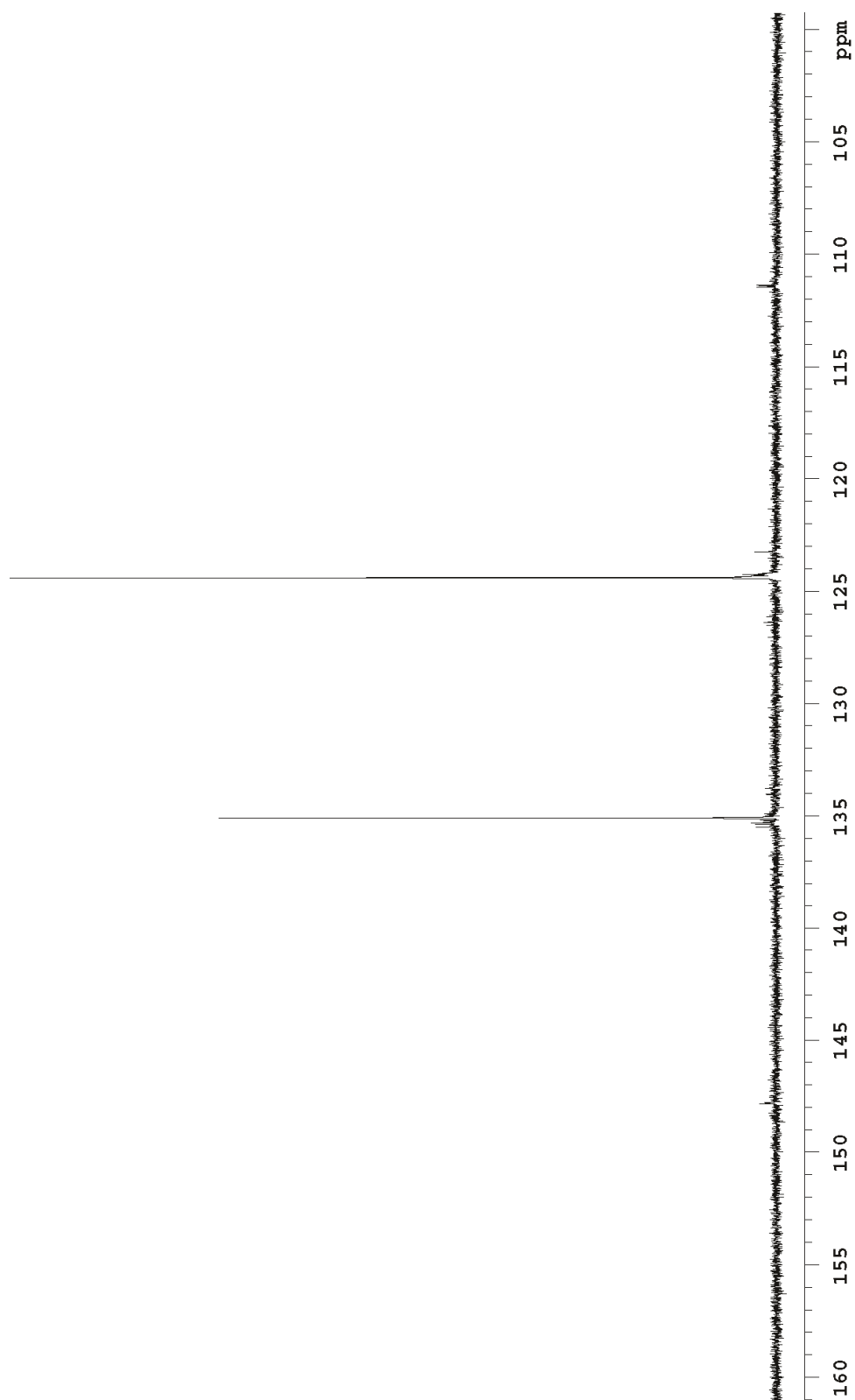
NMR 14: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-polyisoprene (ex. 2)



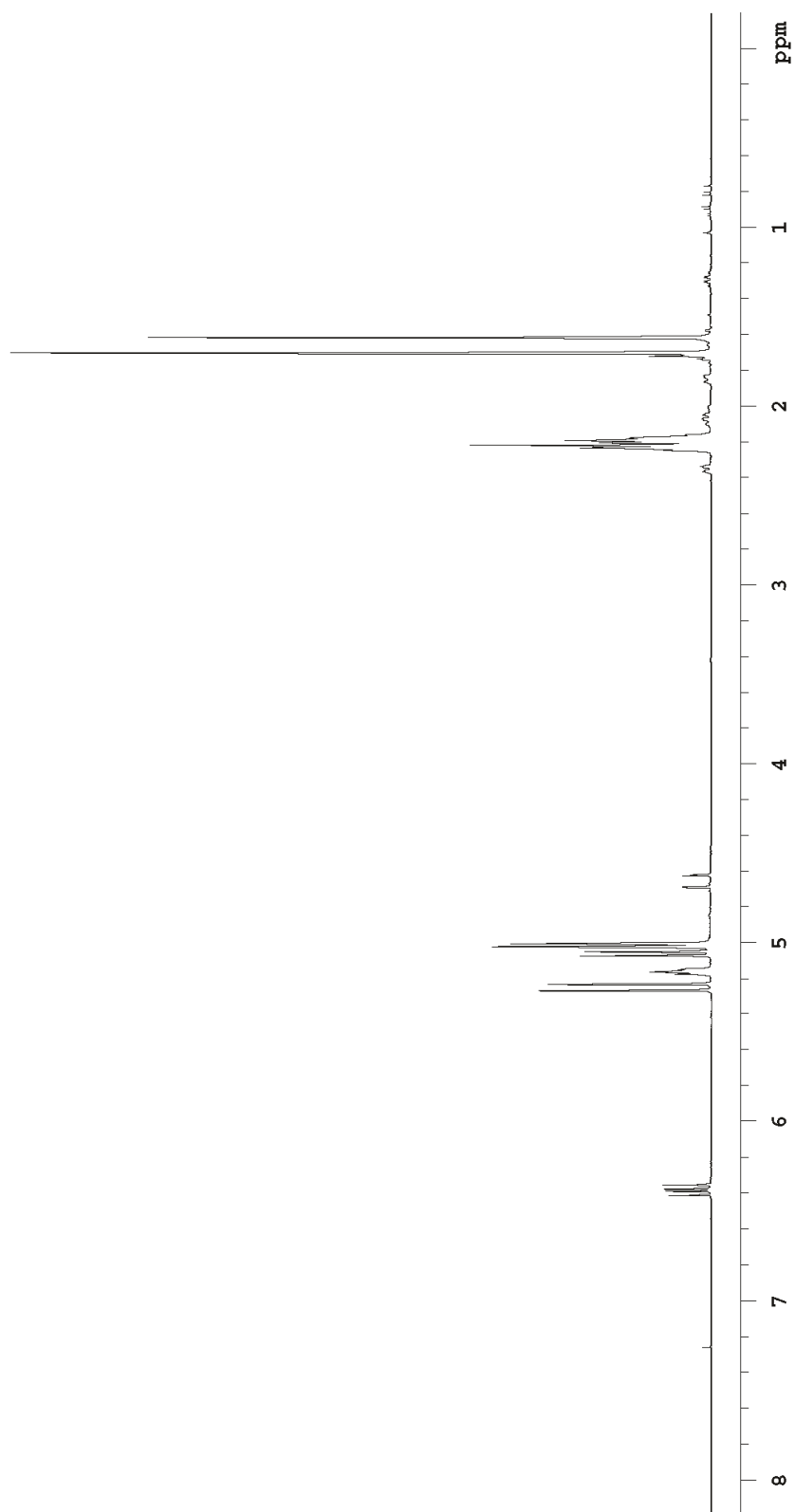
NMR 15: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-polyisoprene (aliphatic region)



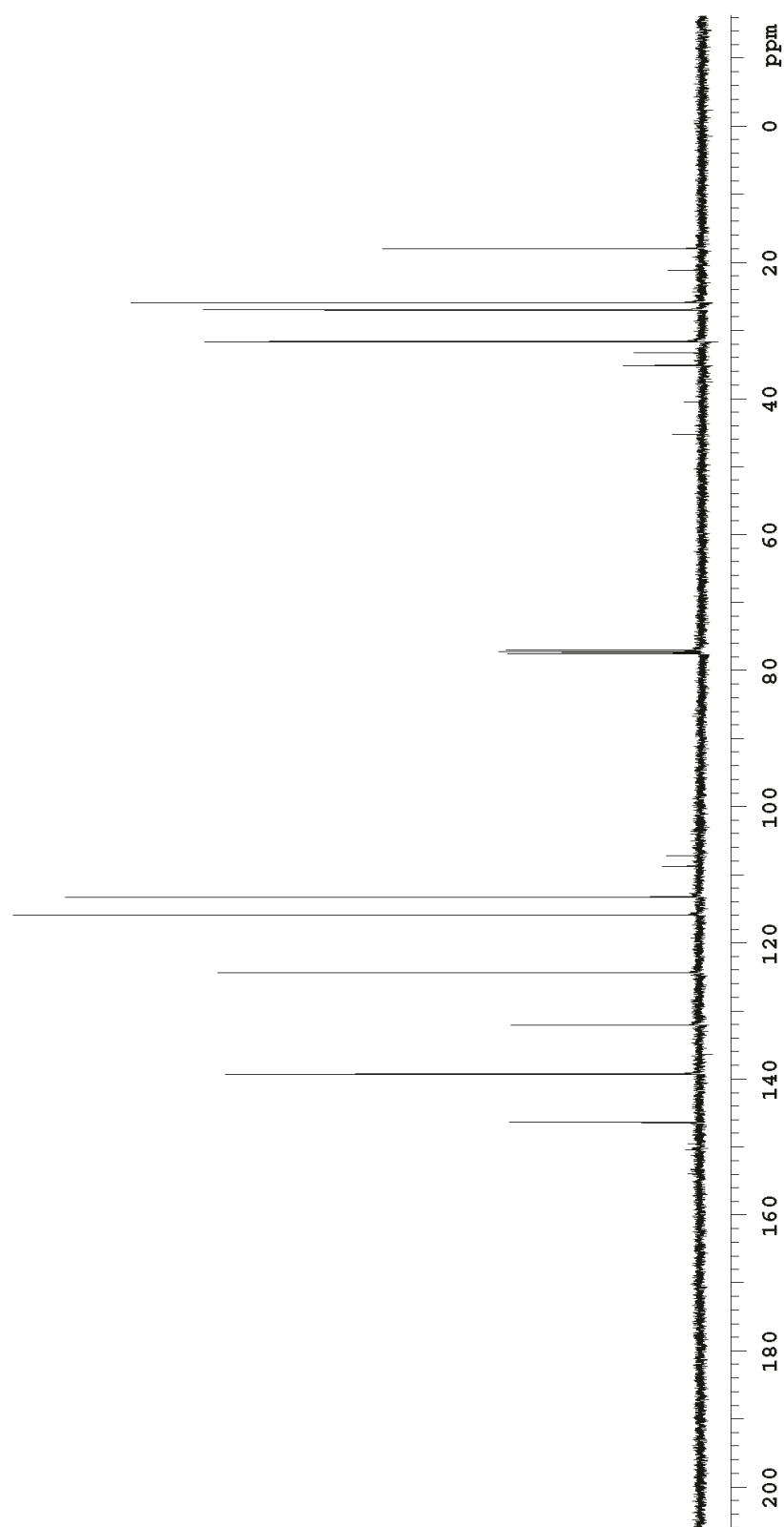
NMR 16: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^{\circ}\text{C}$) of *trans*-1,4-polyisoprene (full)



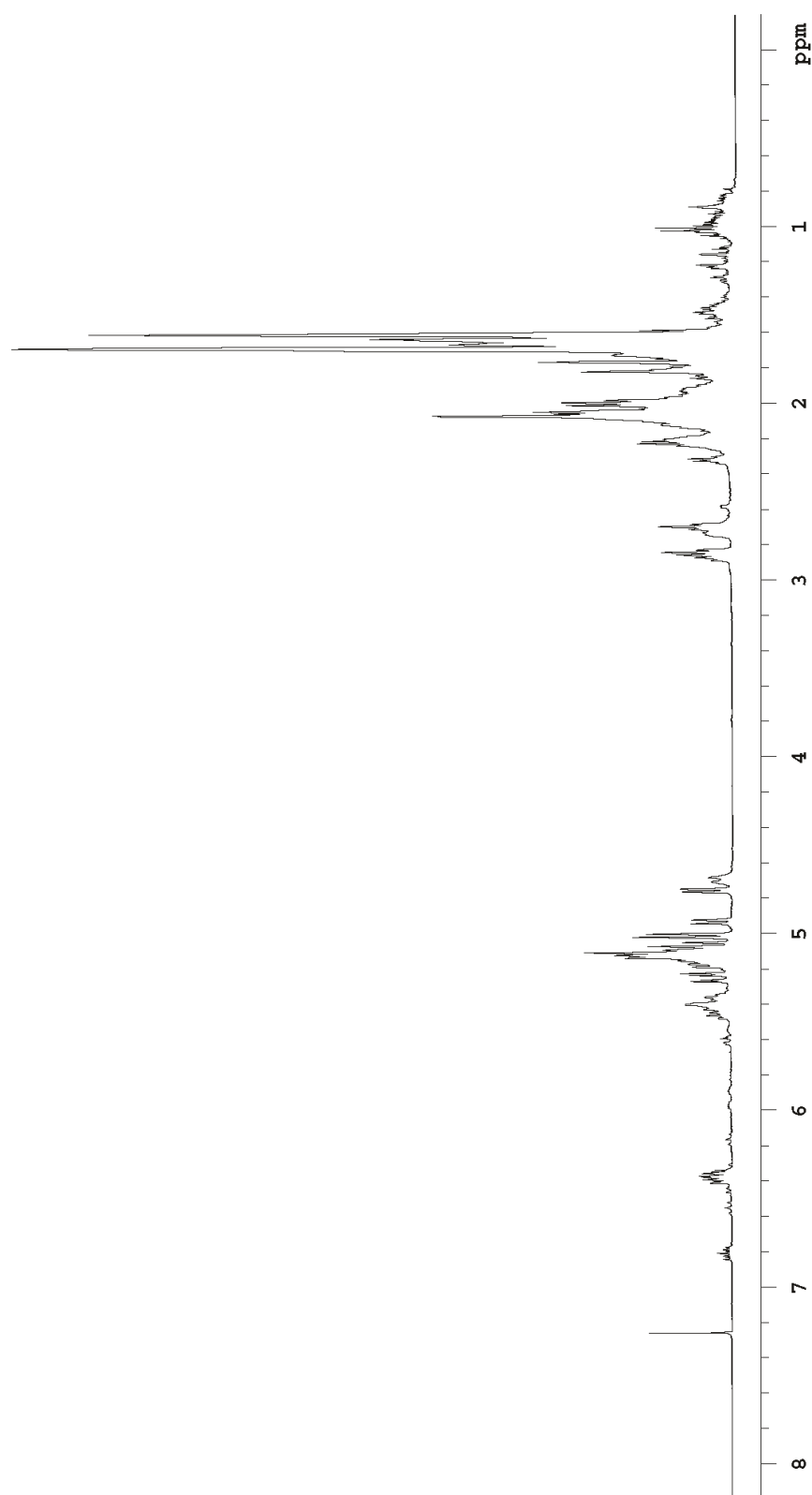
NMR 17: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-polyisoprene (olefinic region)



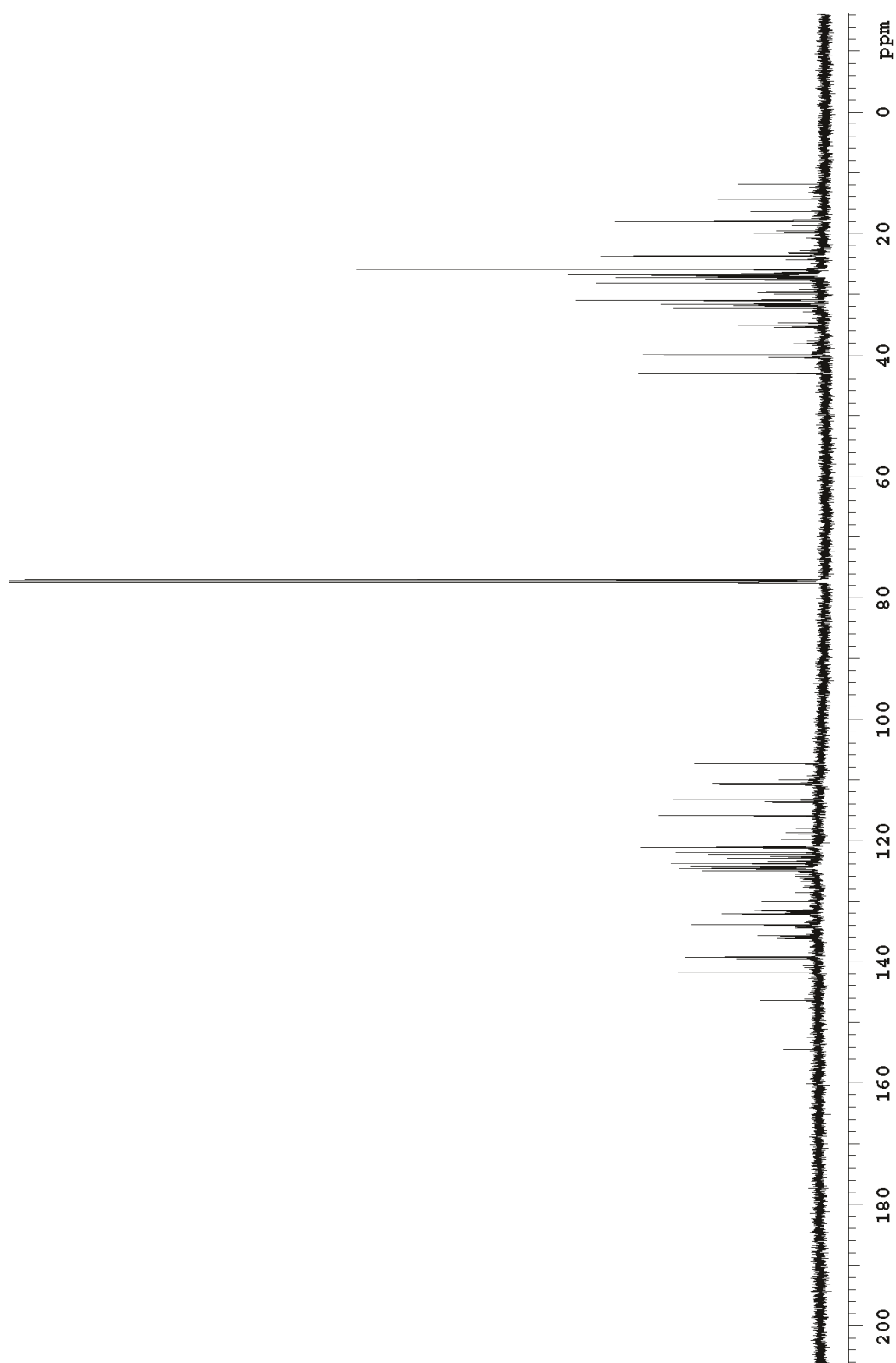
NMR 18: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of β -myrcene



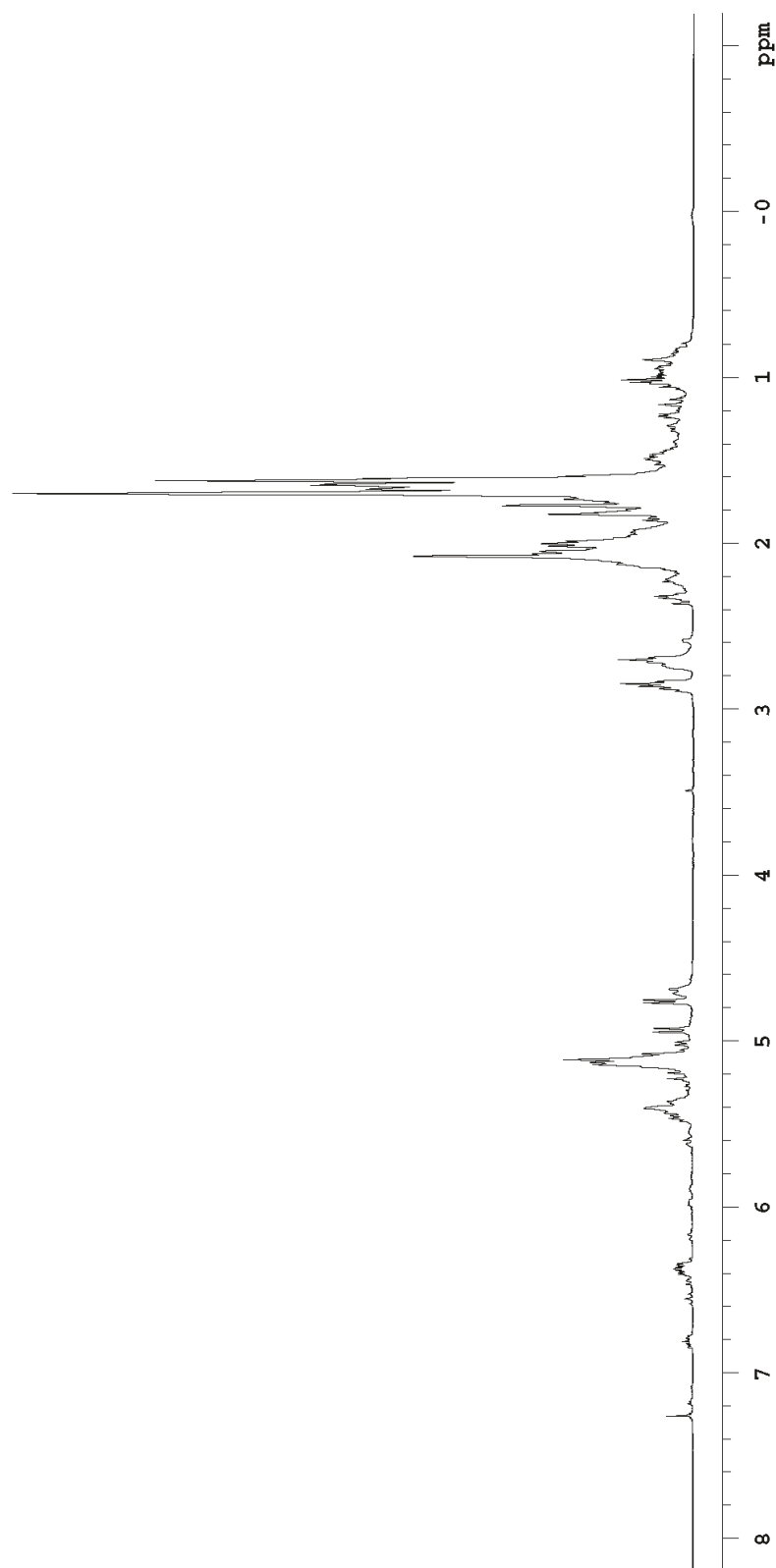
NMR 19: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of β -myrcene



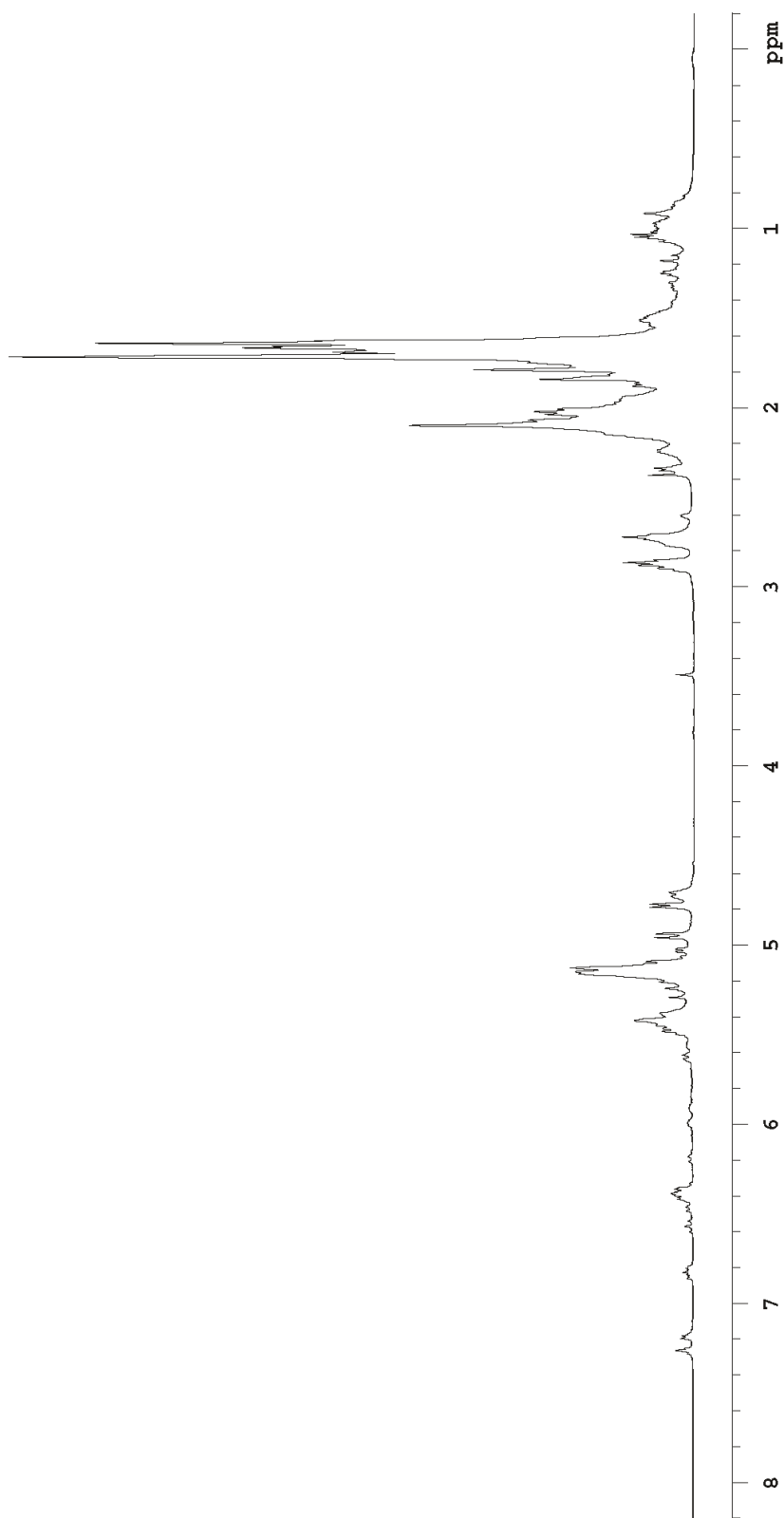
NMR 20: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of *farnesene* (mixture)



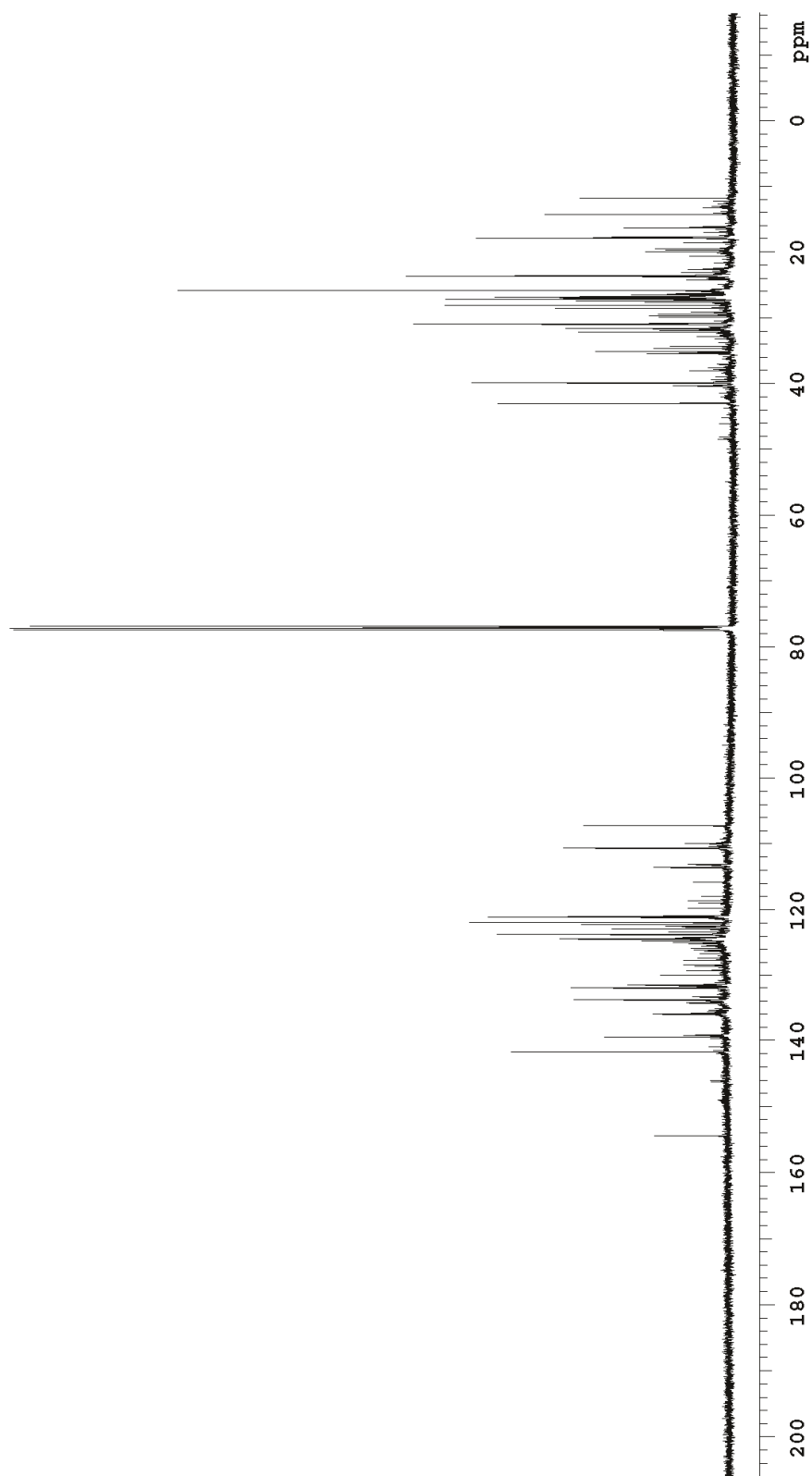
NMR 21: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of *farnesene* (mixture)



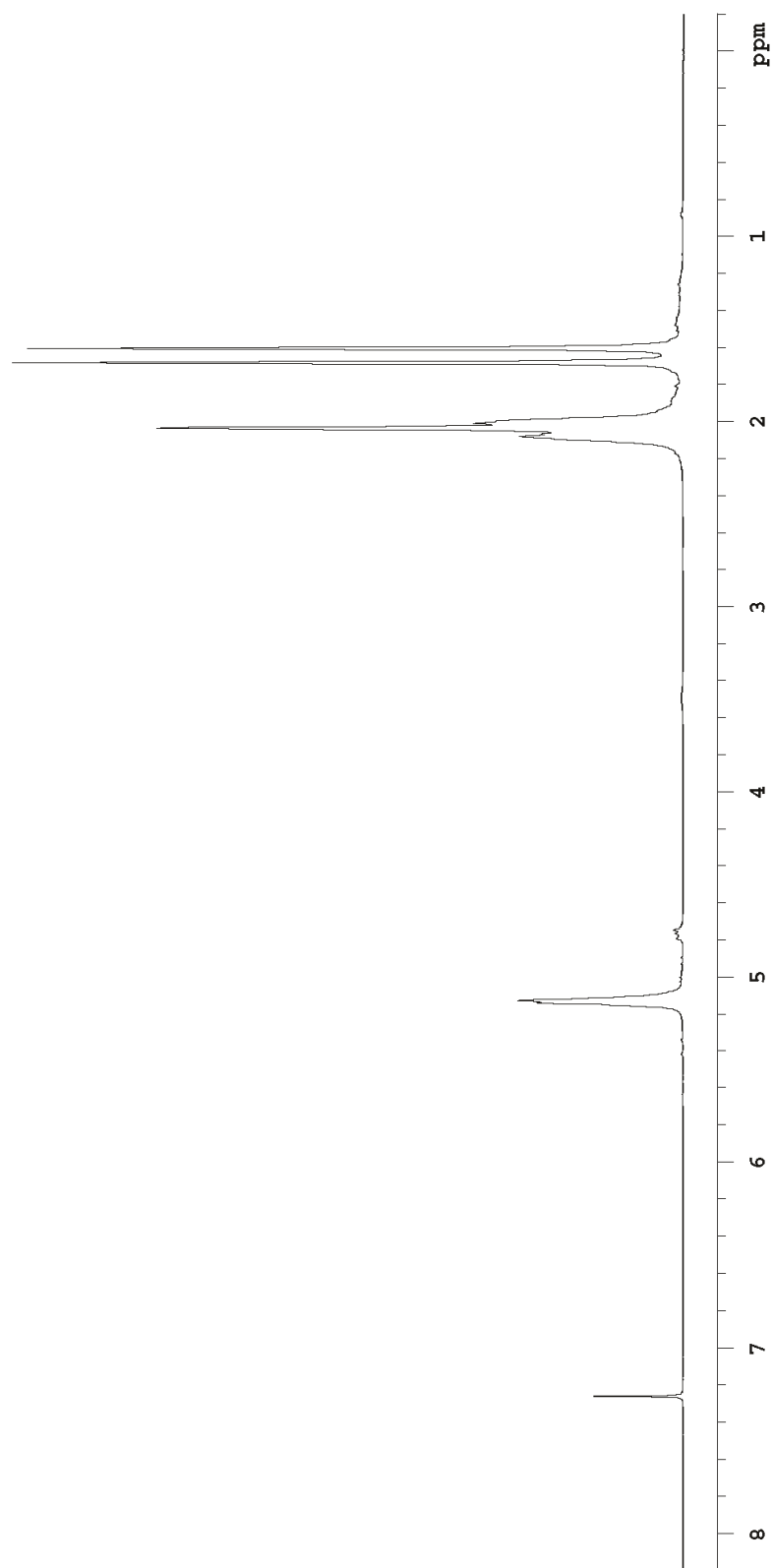
NMR 22: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of *farnesene* (α -isomer) (ex. 10)



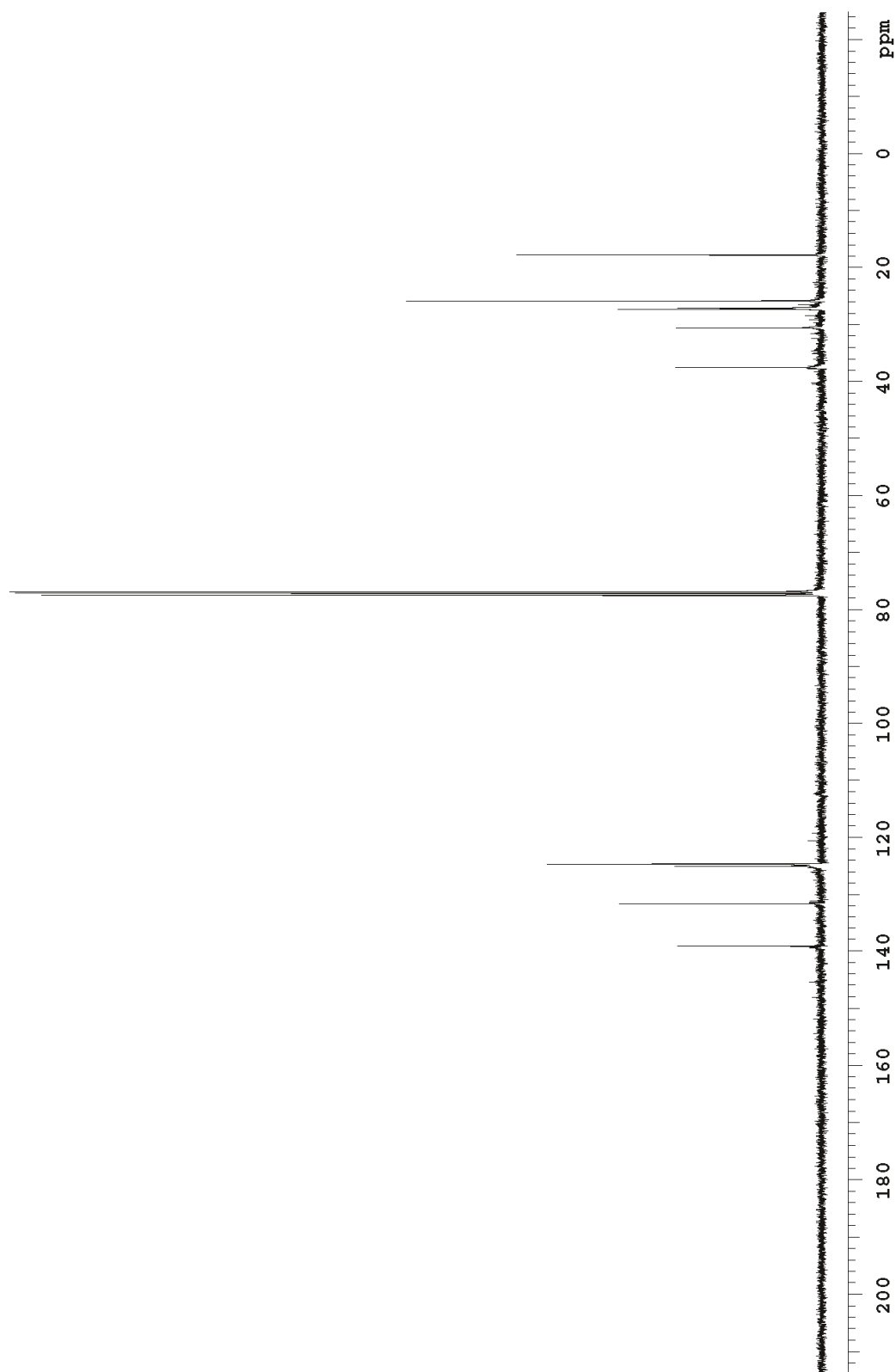
NMR 23: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 °C) of *farnesene* (α -isomer) (ex. 9)



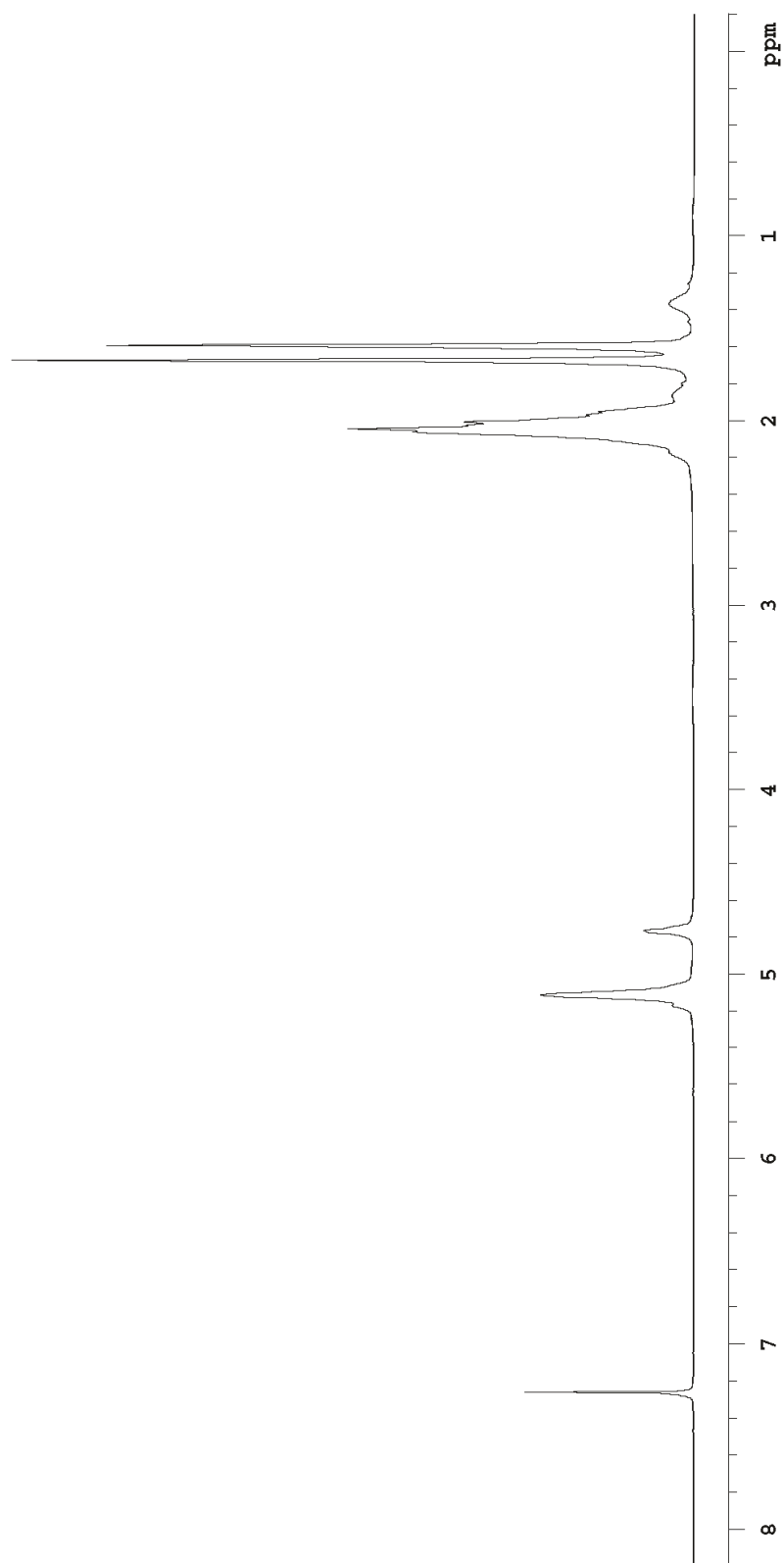
NMR 24: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *farnesene* (α -isomer)



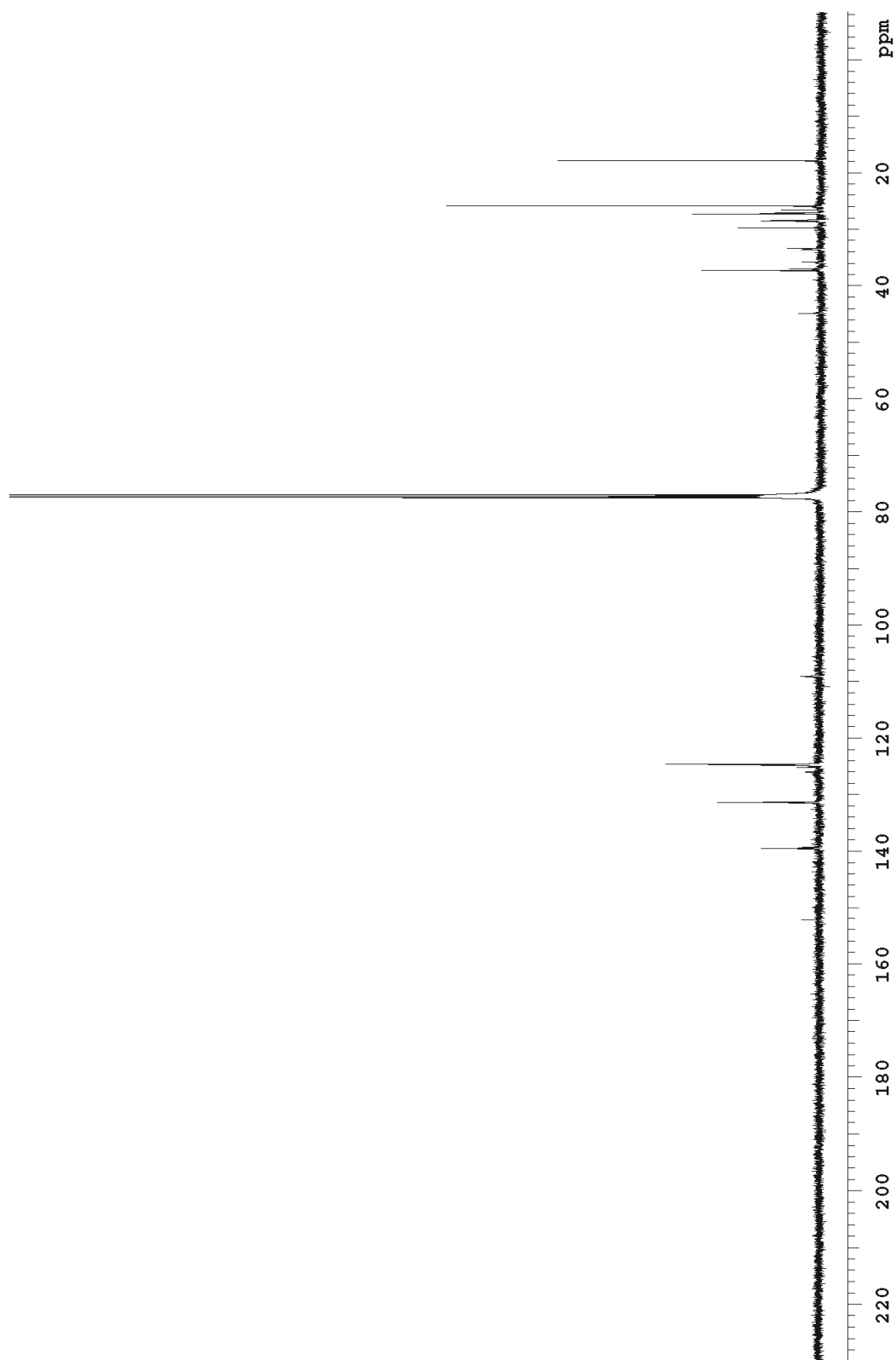
NMR 25: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-poly- β -myrcene (ex. 9)



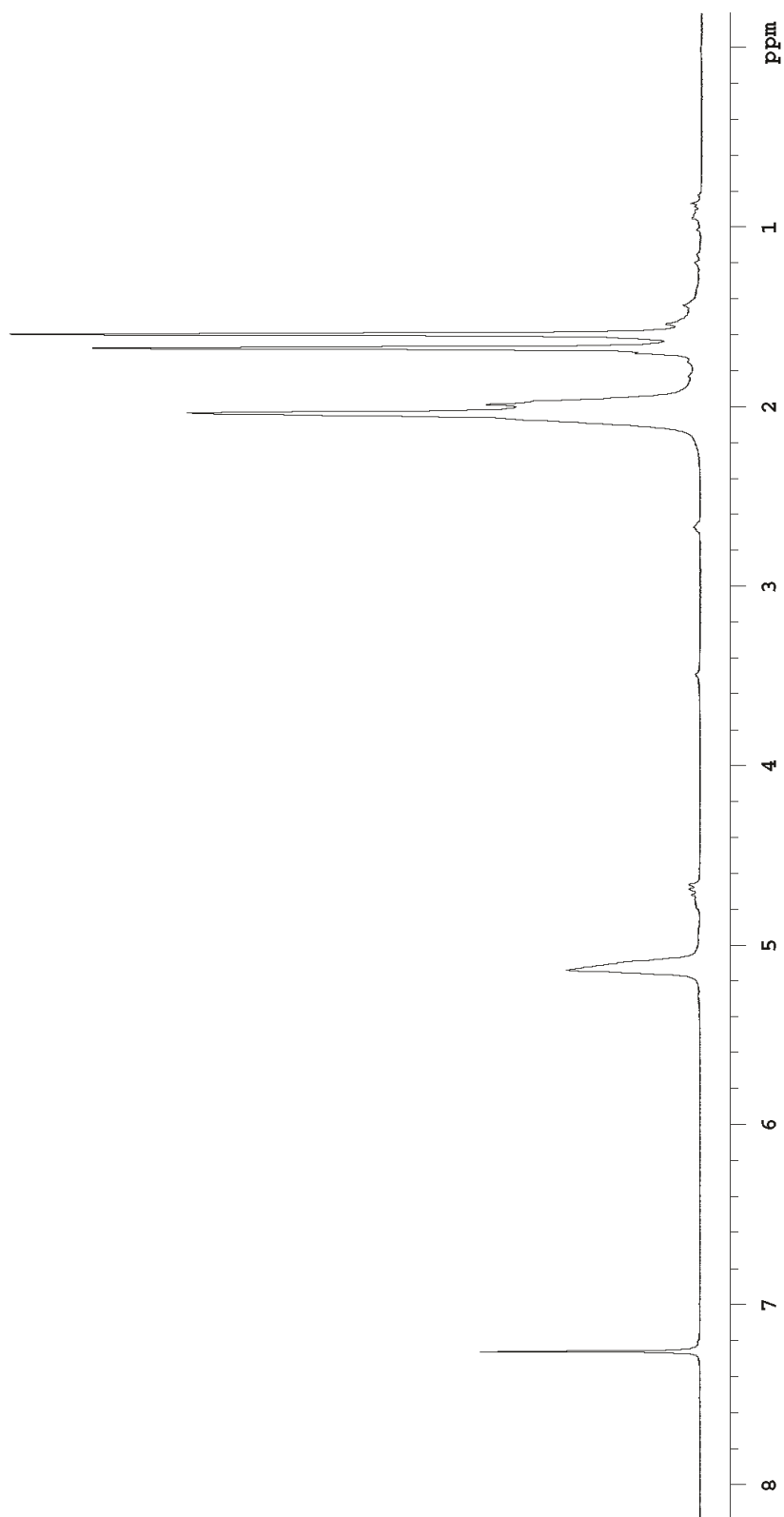
NMR 26: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-poly- β -myrcene (ex. 9)



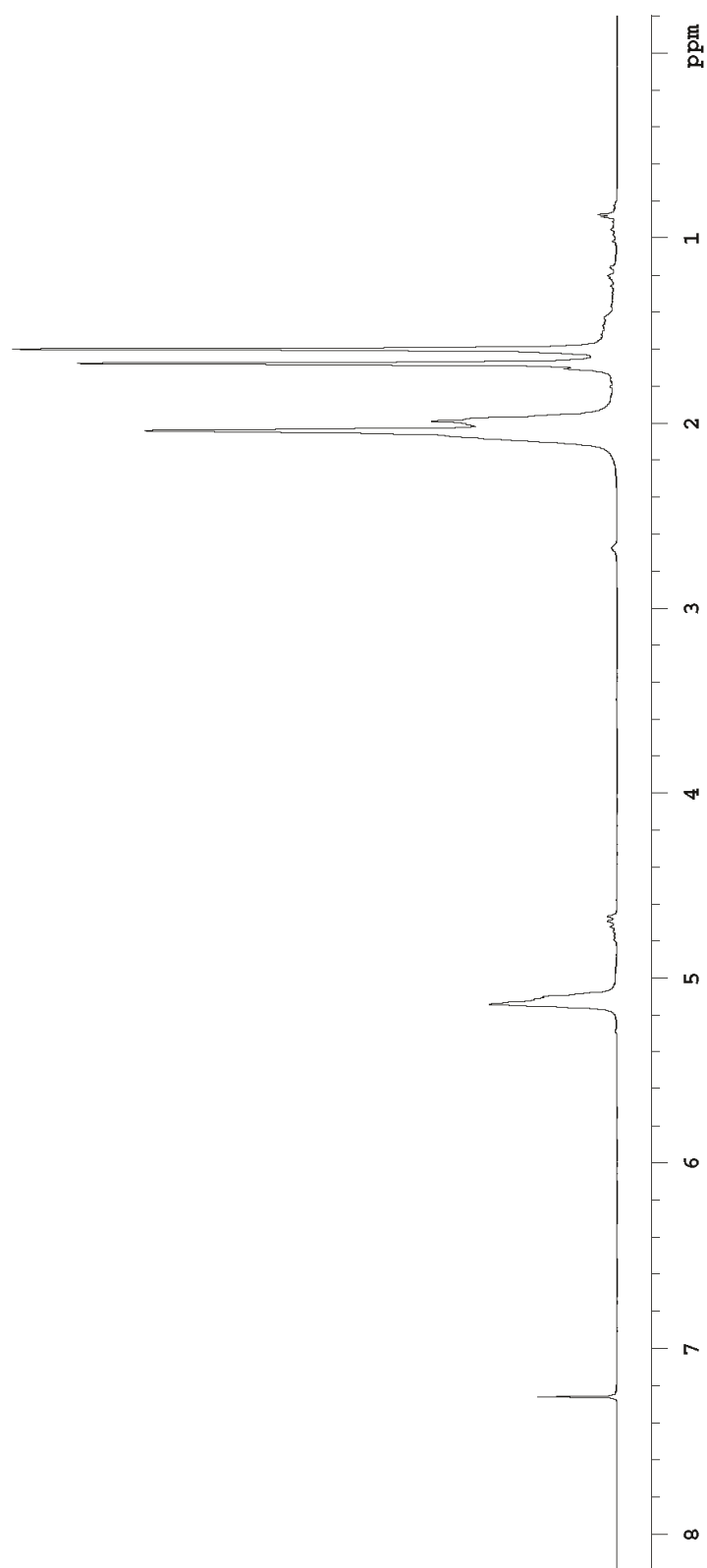
NMR 27: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *cis*-1,4-poly- β -myrcene (ex. 10)



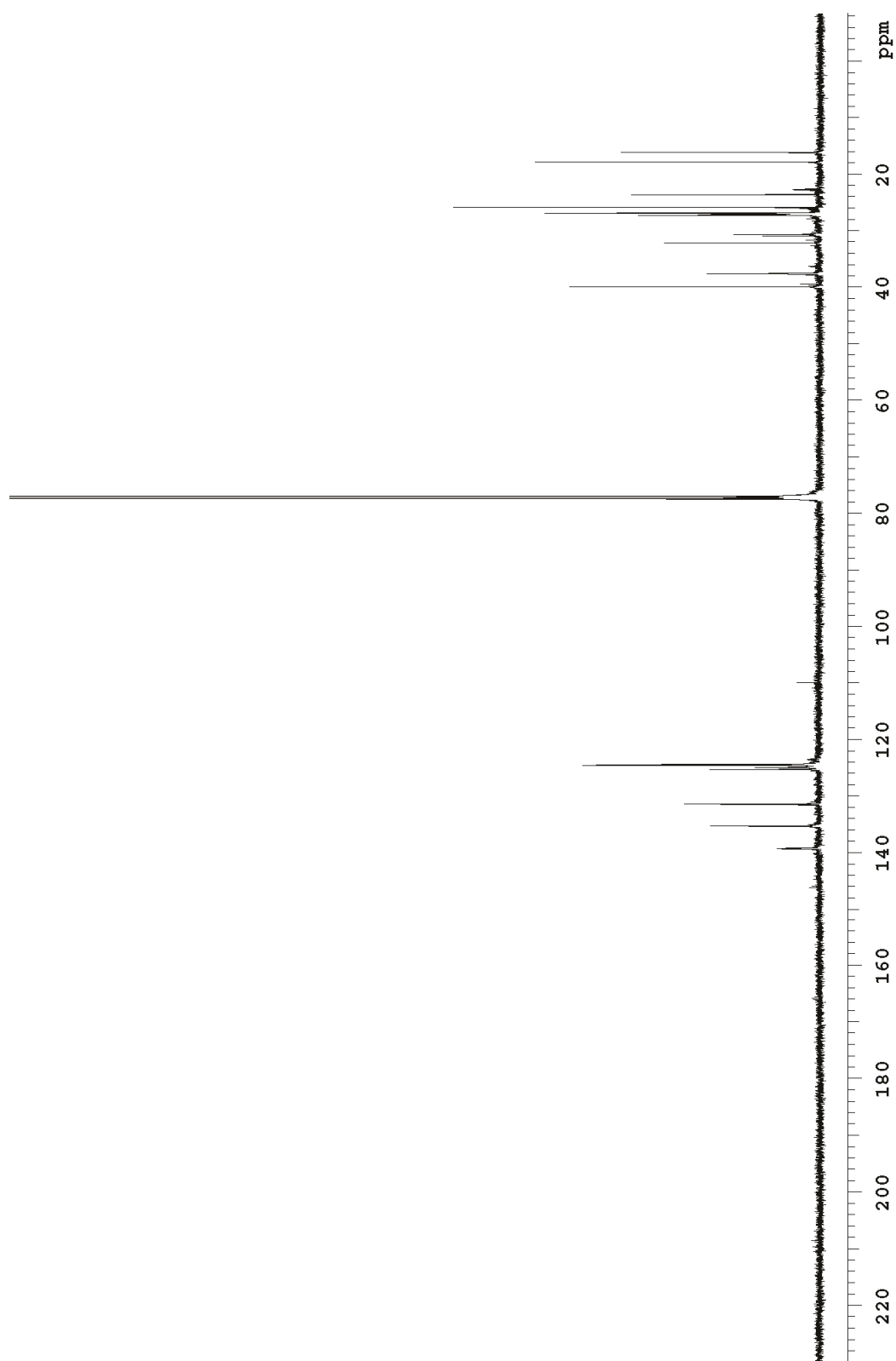
NMR 28: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of *cis*-1,4-poly- β -myrcene (ex. 10)



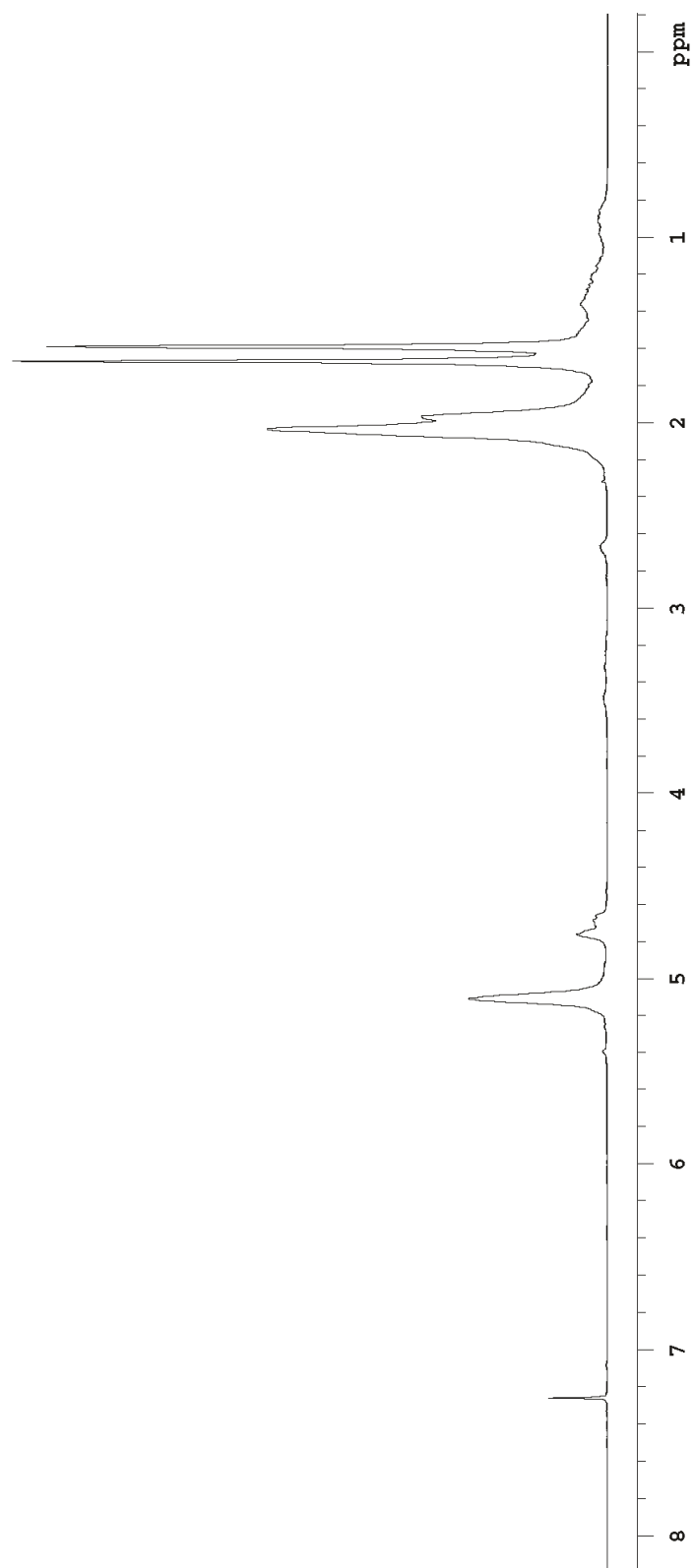
NMR 29: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-poly- β -farnesene (ex. 11)



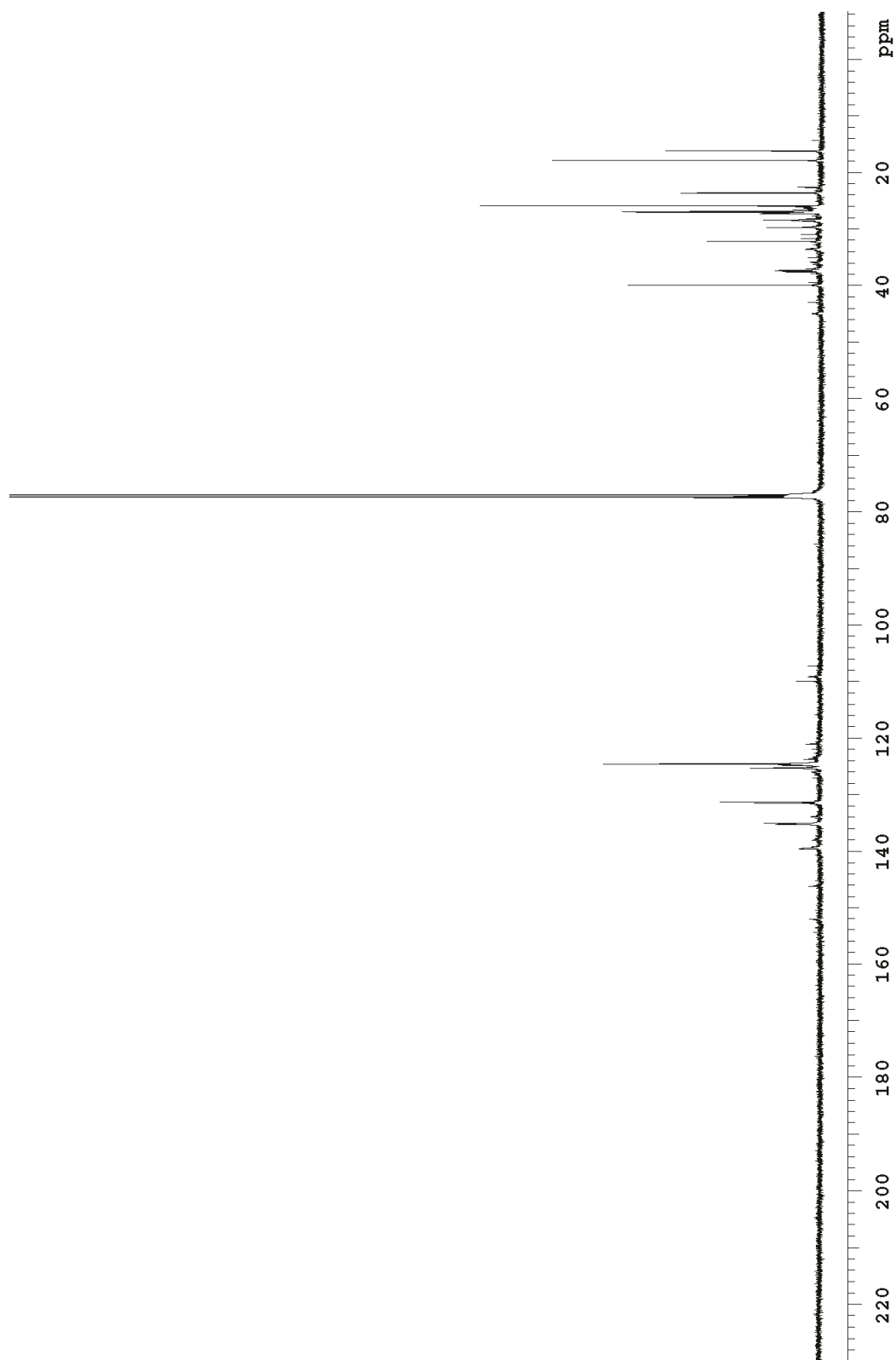
NMR 30: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *trans*-1,4-poly- β -farnesene (ex. 11)



NMR 31: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 °C) of *trans*-1,4-poly- β -farnesene (ex. 11)



NMR 32: ^1H NMR spectrum (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *cis*-1,4-poly- β -farnesene (ex. 12)



NMR 33: ^{13}C NMR spectrum (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) of *cis*-1,4-poly- β -farnesene (ex. 12)

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