

Supporting Information for

A Bicyclo[4.2.0]octene-Derived Monomer Provides Completely Linear Alternating Copolymers via Alternating Ring-Opening Metathesis Polymerization (AROMP)

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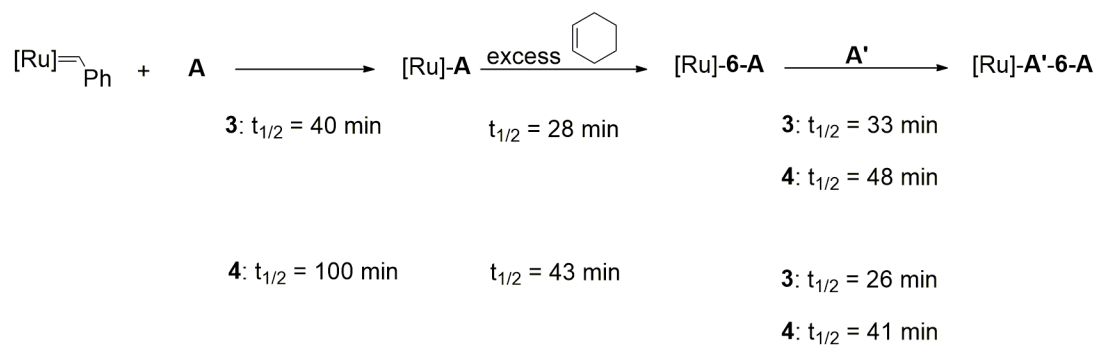
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Table S1. Molecular weight and D_M determined by GPC using polystyrene standards.

Polymer	Temp	Cald. M_n	M_n	M_w	D_M
poly(4- <i>alt</i> -6) ₁₆	25 °C	5064	10005	22682	2.0
poly(4- <i>alt</i> -6) ₁₆	35 °C	5064	10005	18855	1.8
poly(4- <i>alt</i> -6- <i>d</i> ₁₀) ₁₅	35 °C	5064	12716	21298	1.7
poly(4- <i>alt</i> -6) ₃₄	35 °C	12504	14552	26512	1.8
poly(4- <i>alt</i> -6) ₃₆	60 °C	12504	11420	24936	2.1
poly(3- <i>alt</i> -6- <i>d</i> ₁₀) ₆	25 °C	1556	2046	7677	3.75

GPC determined M_n is larger than calculated M_n due to the Benoit effect.¹

Scheme S1. $t_{1/2}$ for each AROM-2 reaction step.



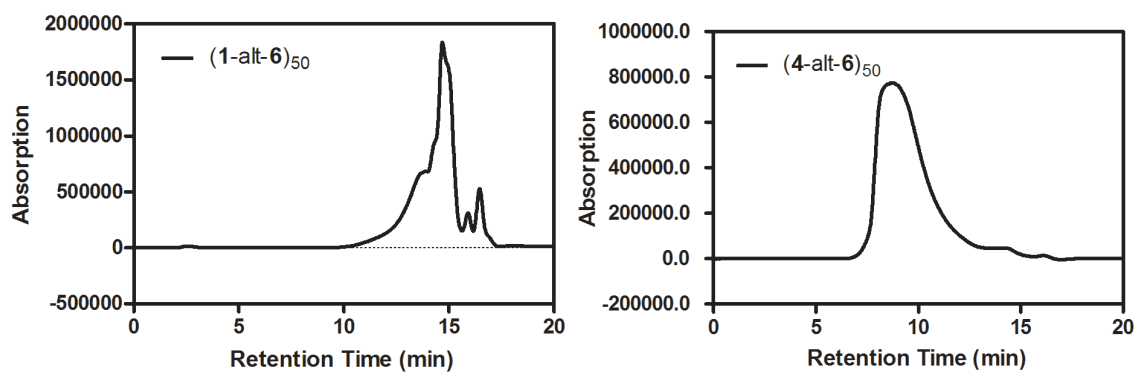
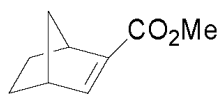


Figure S1. GPC traces of alternating copolymer poly(4-*alt*-6)₅₀ and the corresponding traces of poly(1-*alt*-6)₅₀.



Compound 2

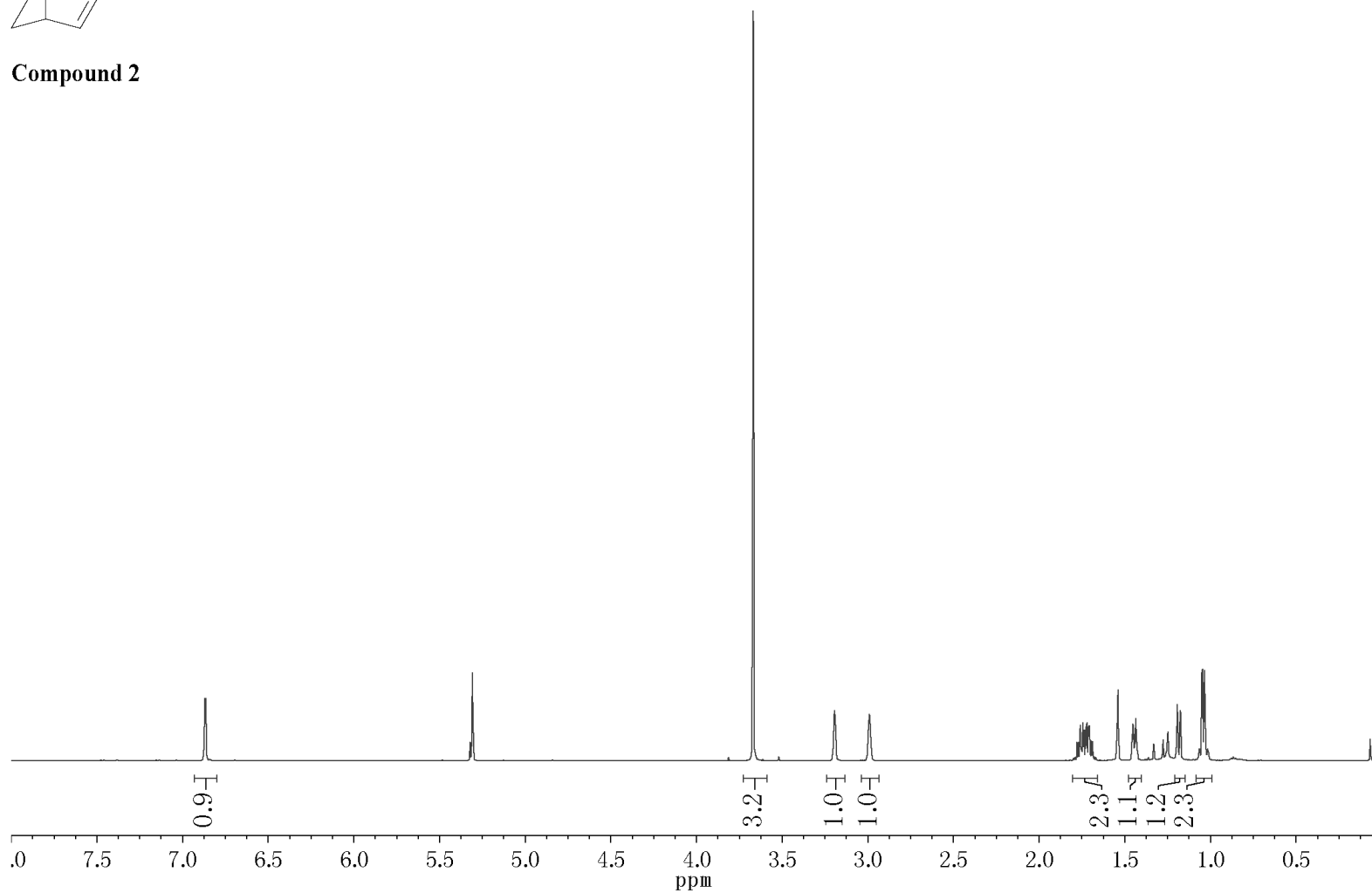
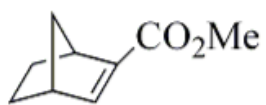


Figure S2. ^1H NMR spectrum of **2** in CD_2Cl_2 .



Compound 2

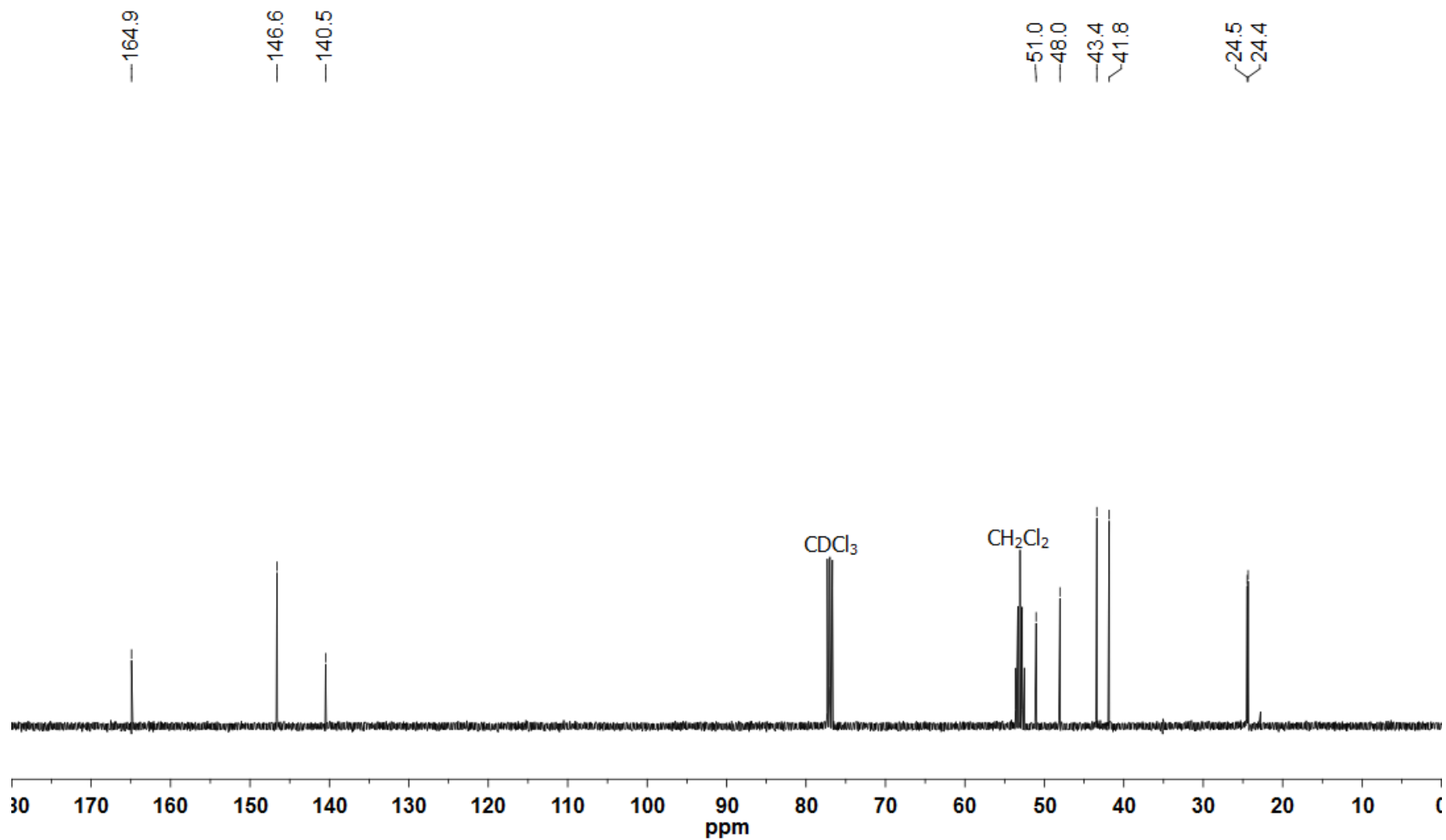
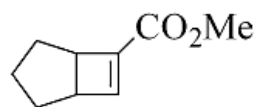


Figure S3. ^{13}C NMR spectrum of **2** in CDCl_3 .



Compound 3

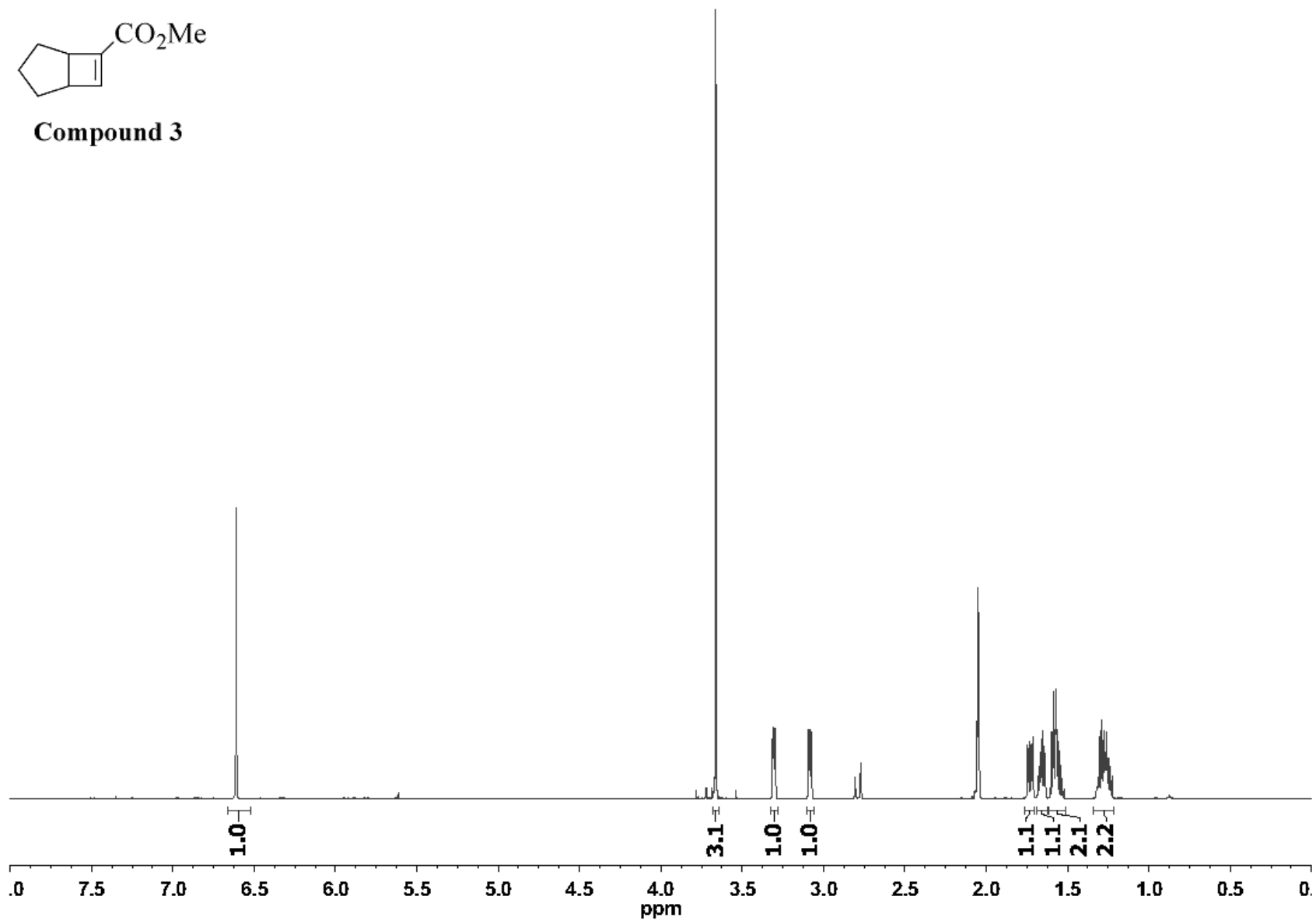
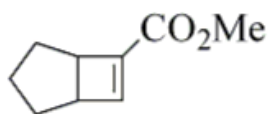


Figure S4. ^1H NMR spectrum of **3** in acetone- d_6 .



Compound 3

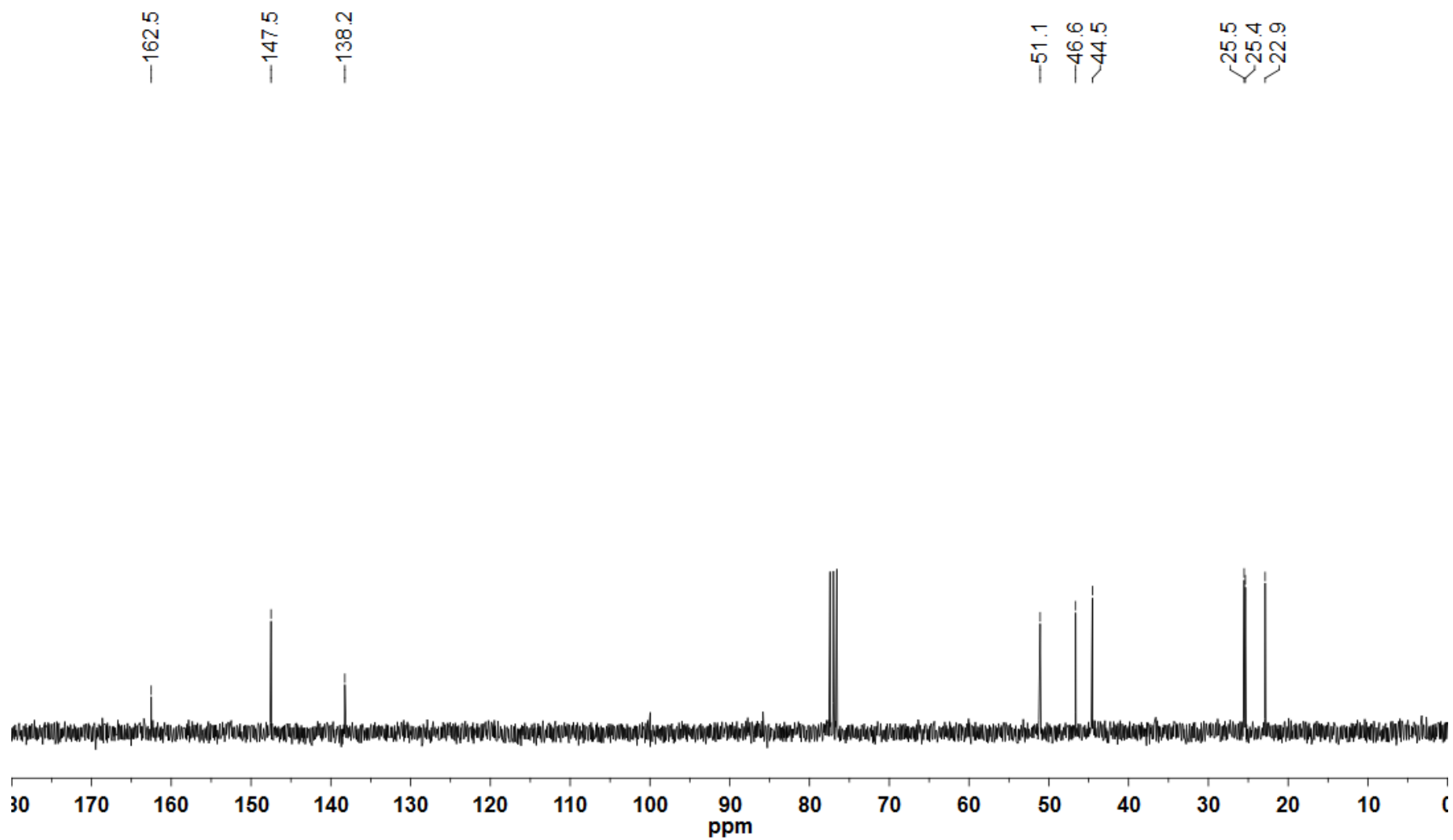
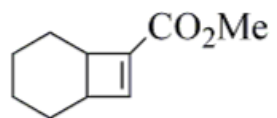


Figure S5. ^{13}C NMR spectrum of **3** in CDCl_3 .



Compound 4

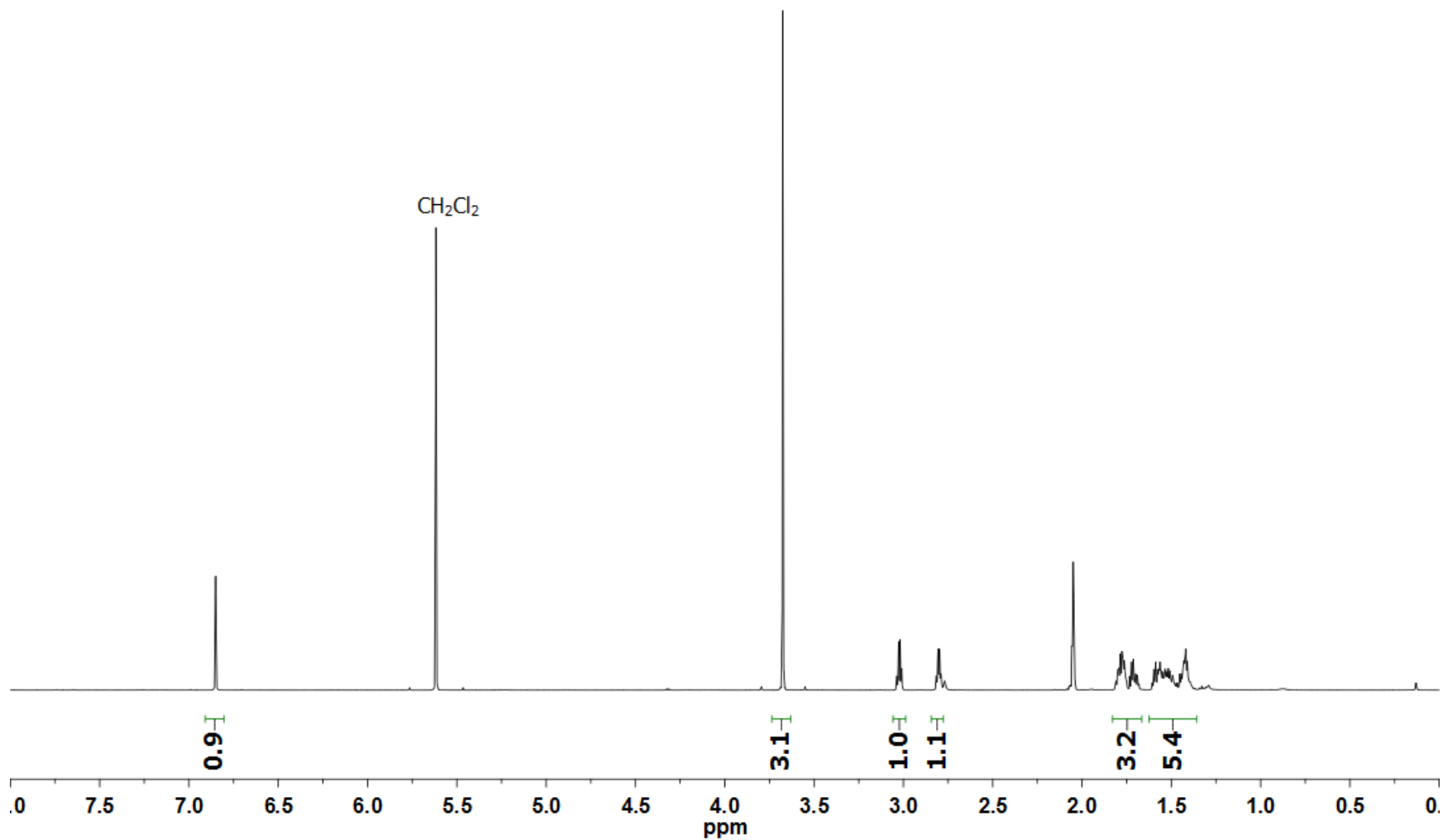
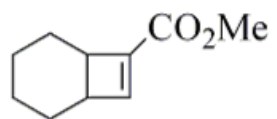


Figure S6. ^1H NMR spectrum of **4** in acetone- d_6 .



Compound 4

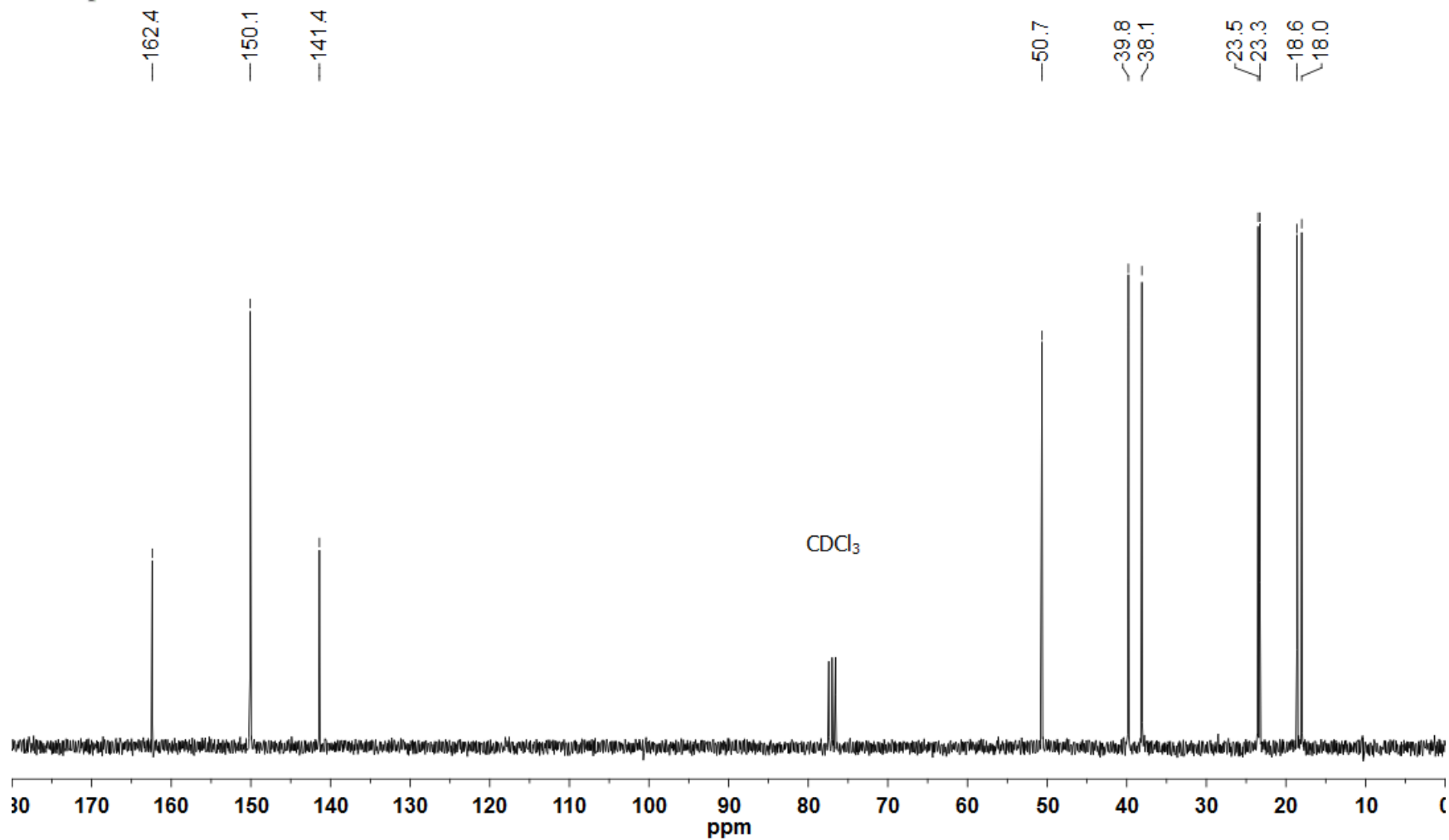
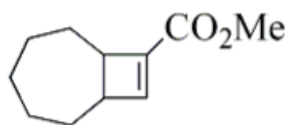


Figure S7. ¹³C NMR spectrum of **4** in CDCl₃.



Compound 5

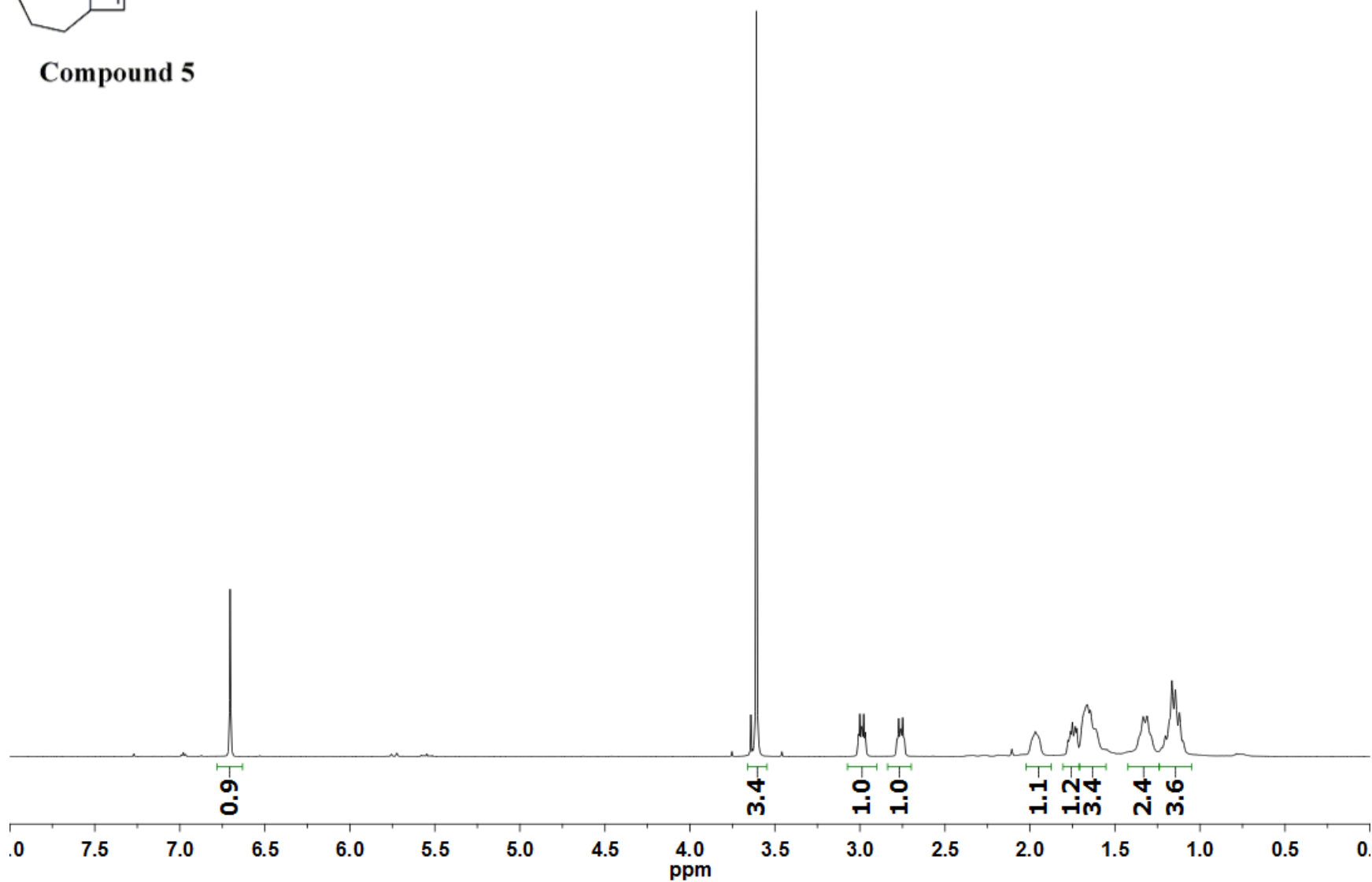
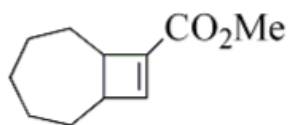


Figure S8. ¹H NMR spectrum of **5** in CDCl₃.



Compound 5

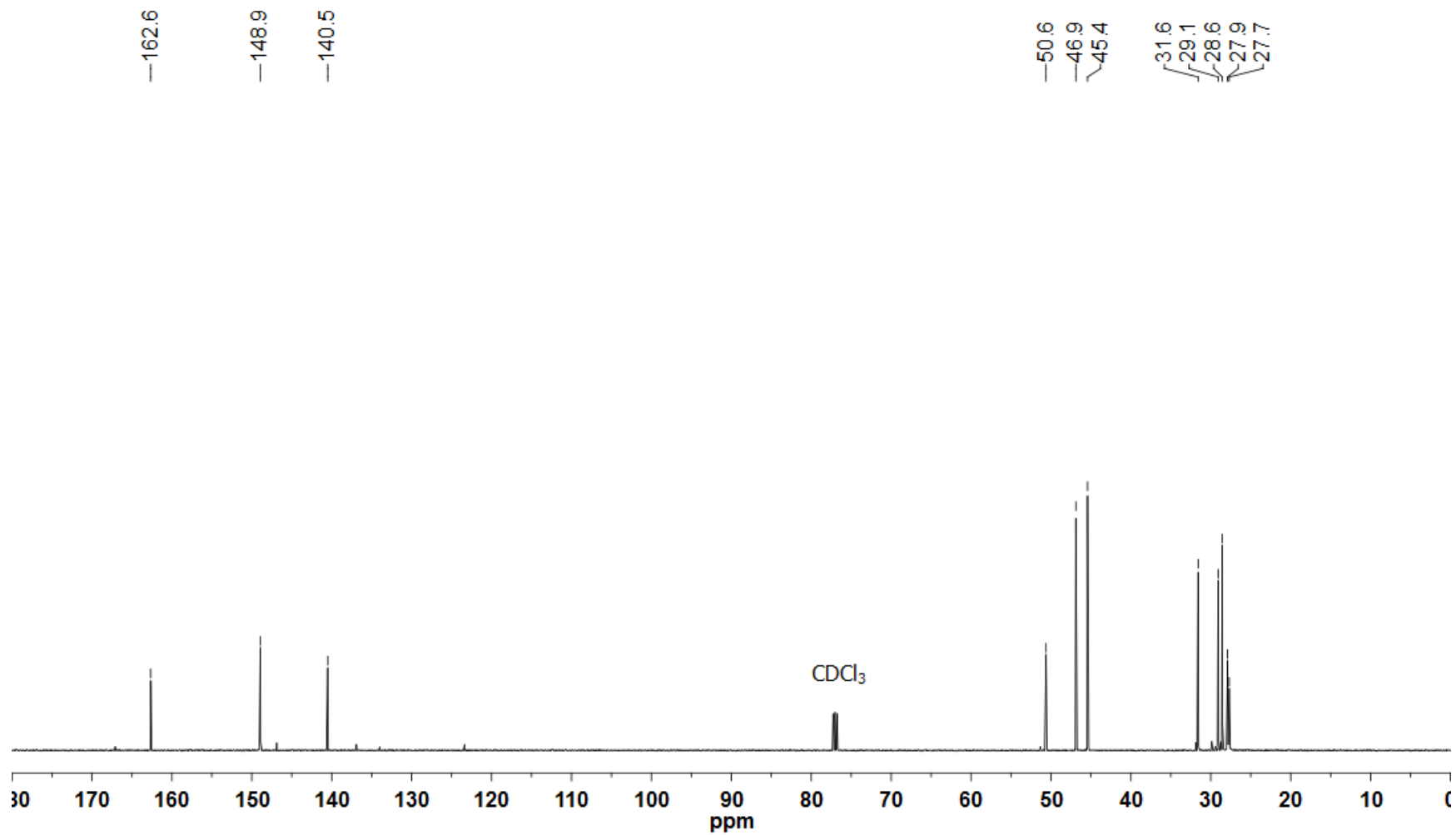


Figure S9. ¹³C NMR spectrum of **5** in CDCl₃.

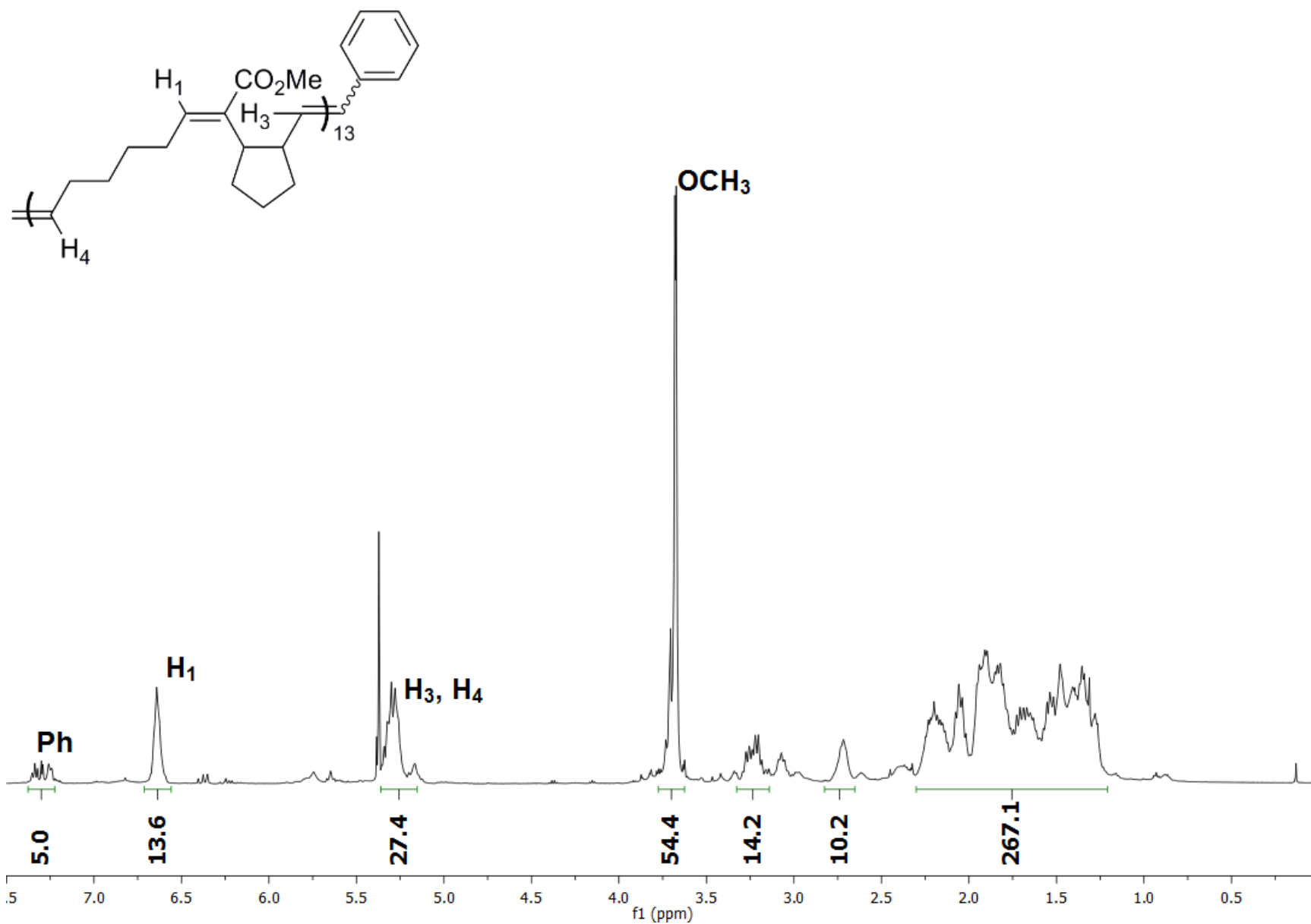


Figure S10. ¹H NMR spectrum of poly(3-*alt*-6)₁₃ in CD₂Cl₂.

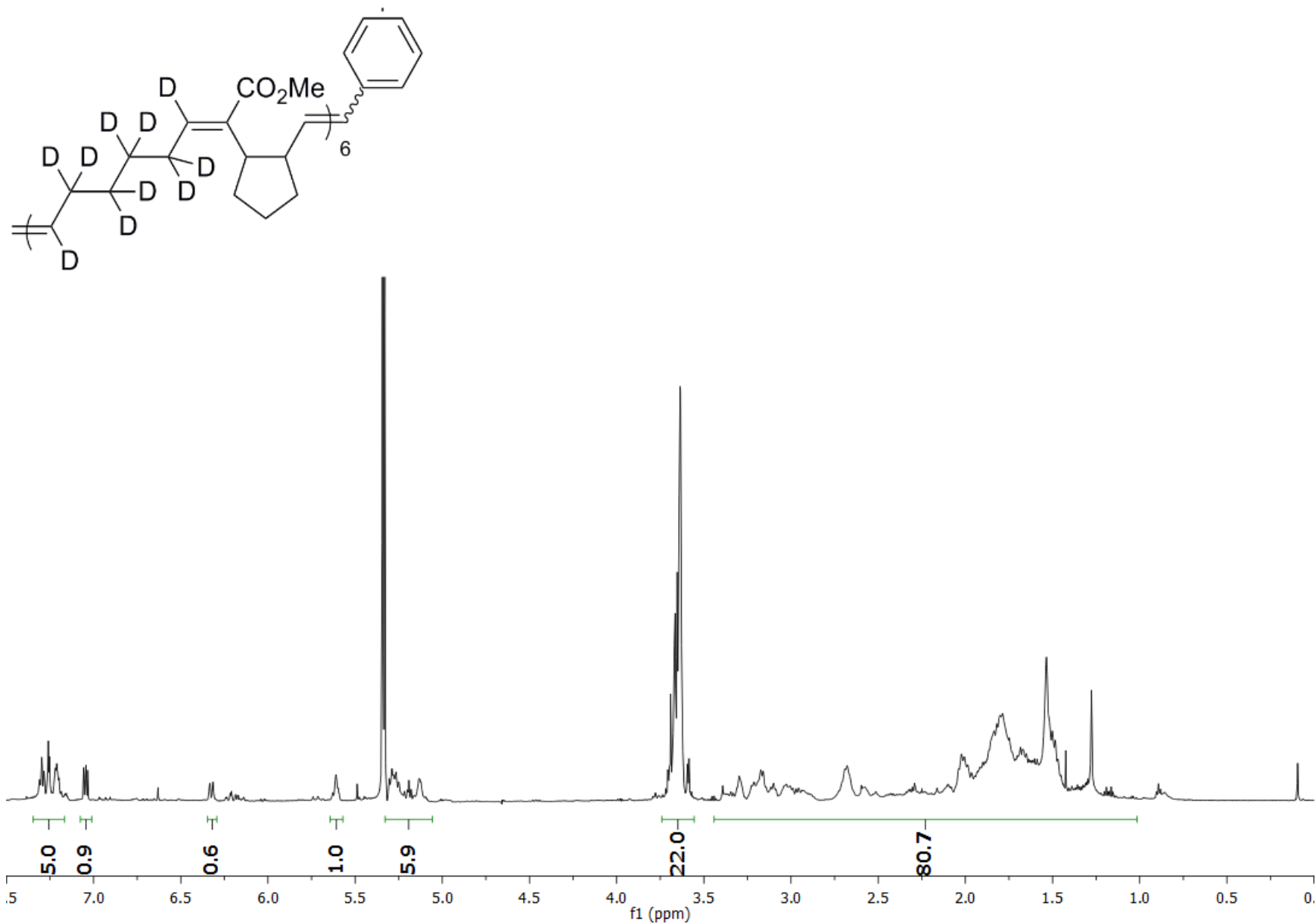


Figure S11. ¹H NMR spectrum of poly(3-*alt*-6-**d**₁₀)₆ in CD₂Cl₂.

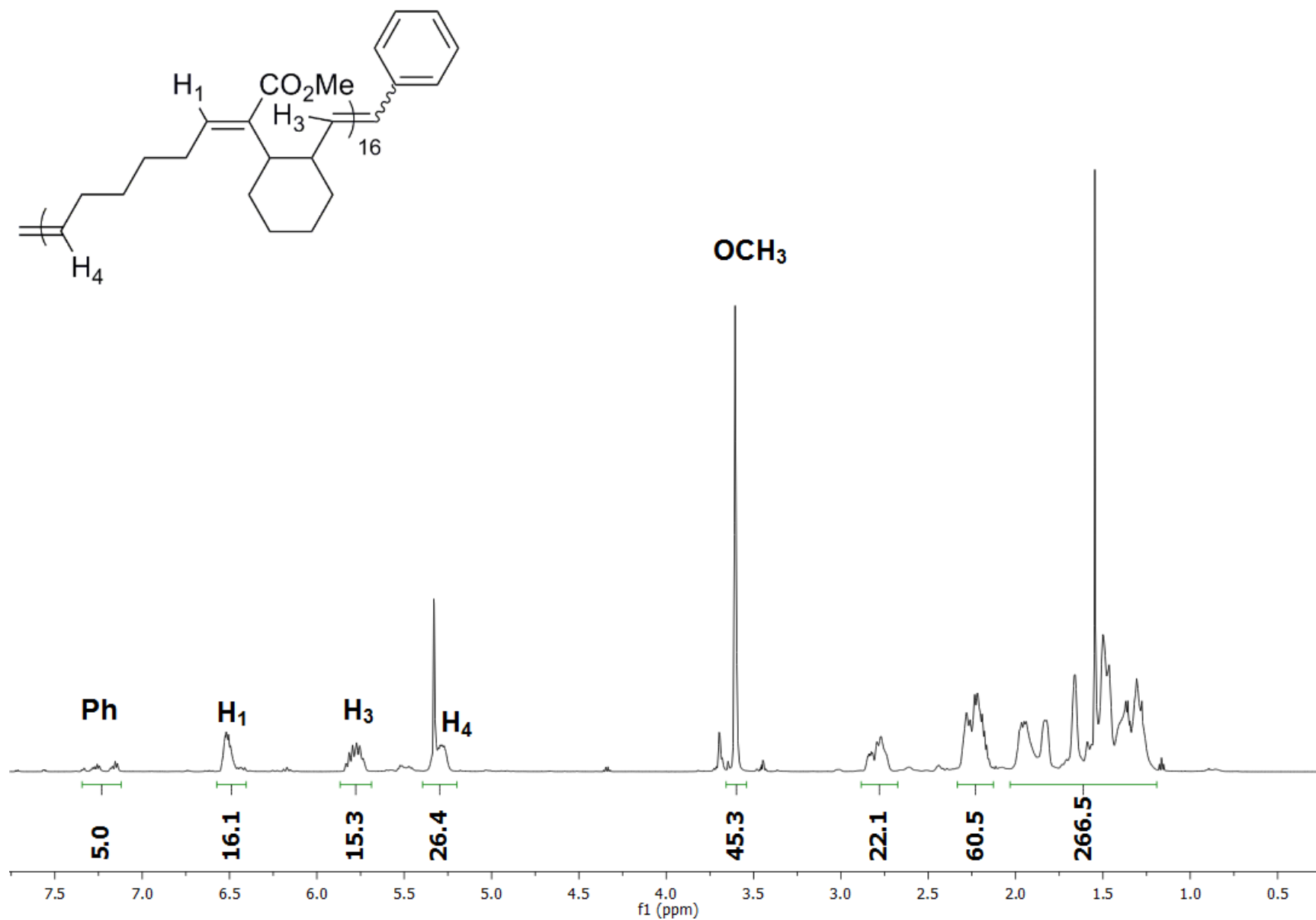


Figure S12. ¹H NMR spectrum of poly(4-alt-6)₁₆ obtained at 25 °C in CD₂Cl₂.

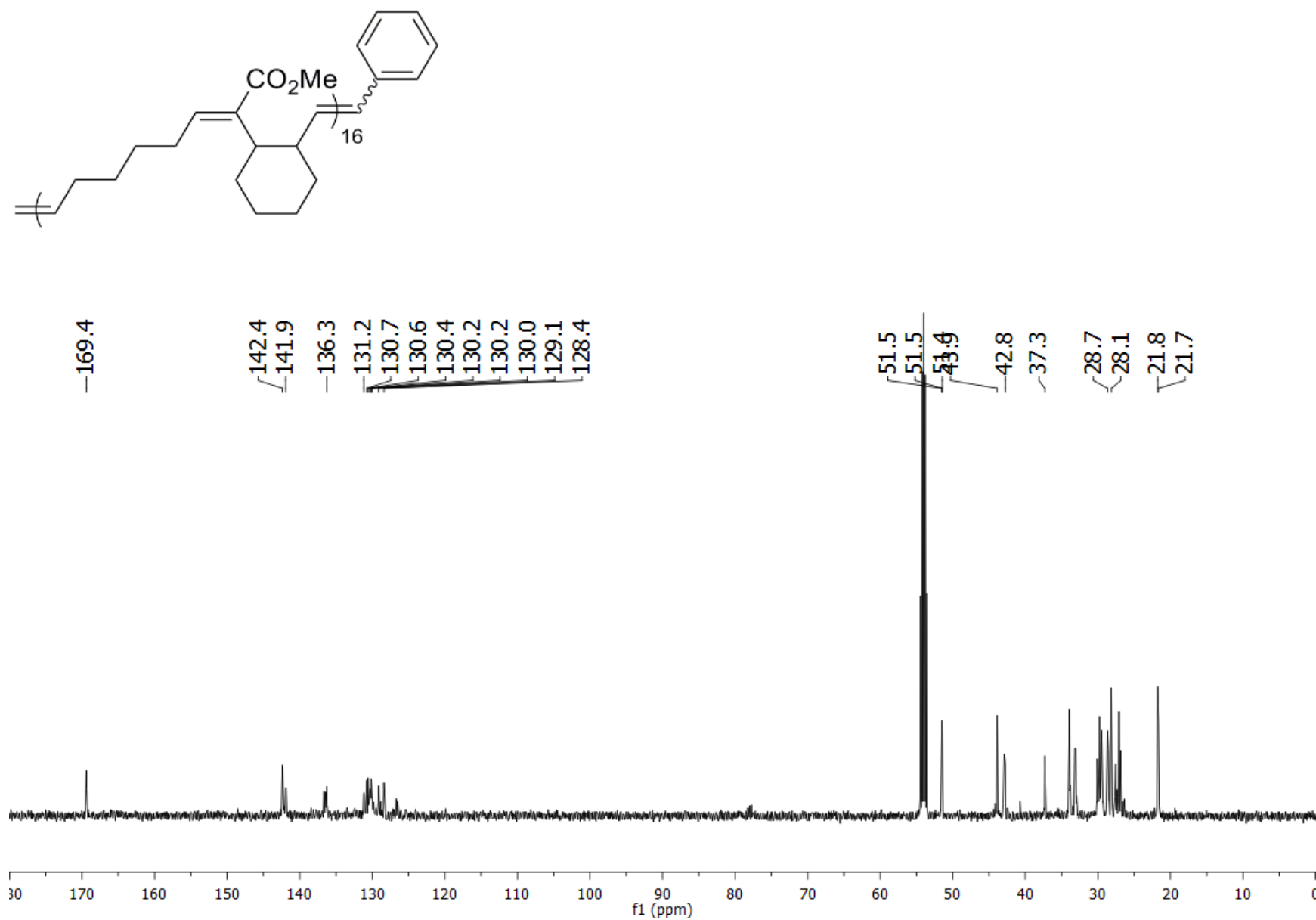


Figure S13. ^{13}C NMR spectrum of poly(4-*alt*-6)₁₆ obtained at 25 °C in CD₂Cl₂.

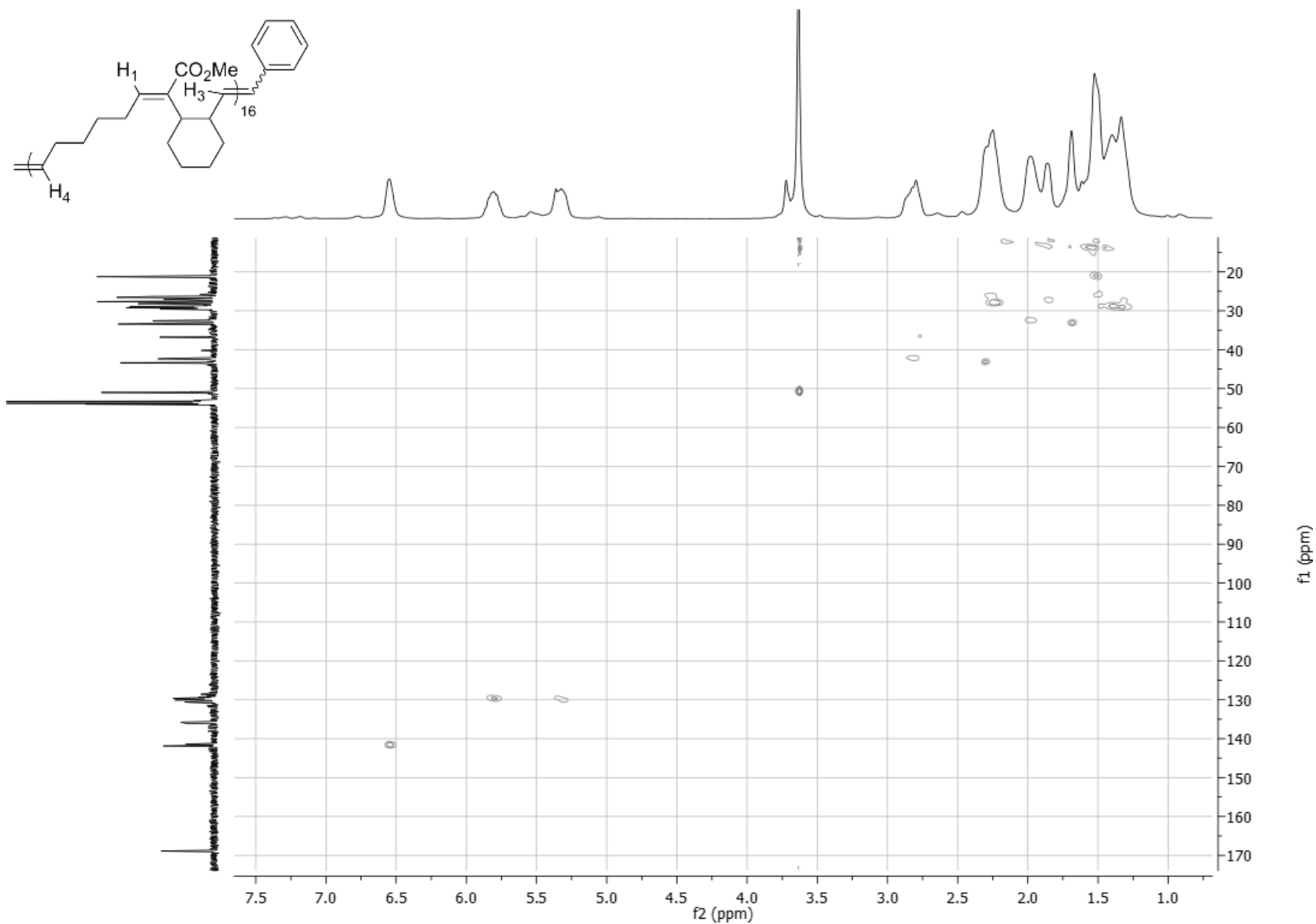


Figure S14. HSQC spectrum of poly(4-*alt*-6)₁₆ obtained at 25 °C in CD₂Cl₂.

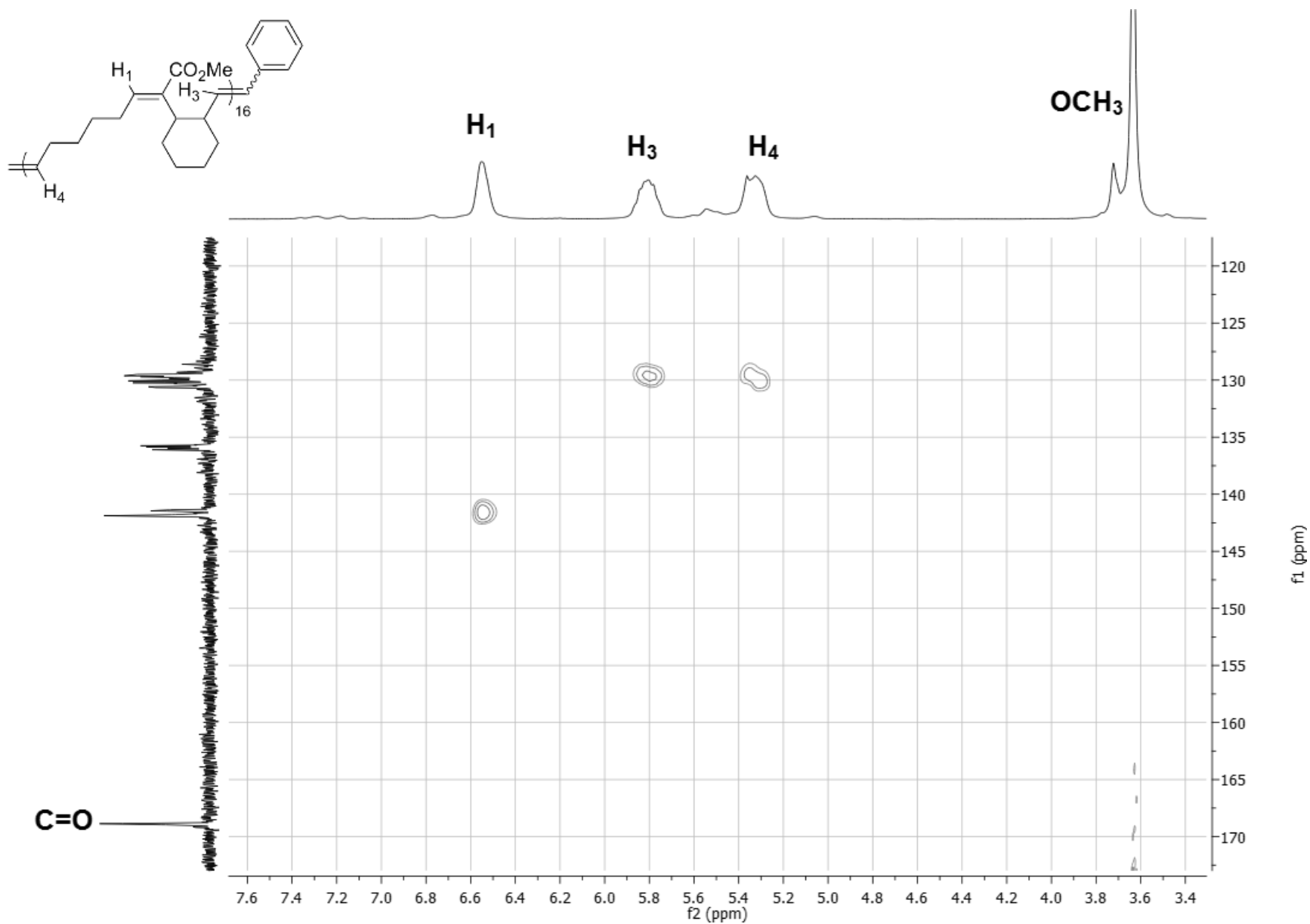


Figure S15. Alkene region of HSQC spectrum of poly(4-*alt*-6)₁₆ obtained at 25 °C in CD₂Cl₂.

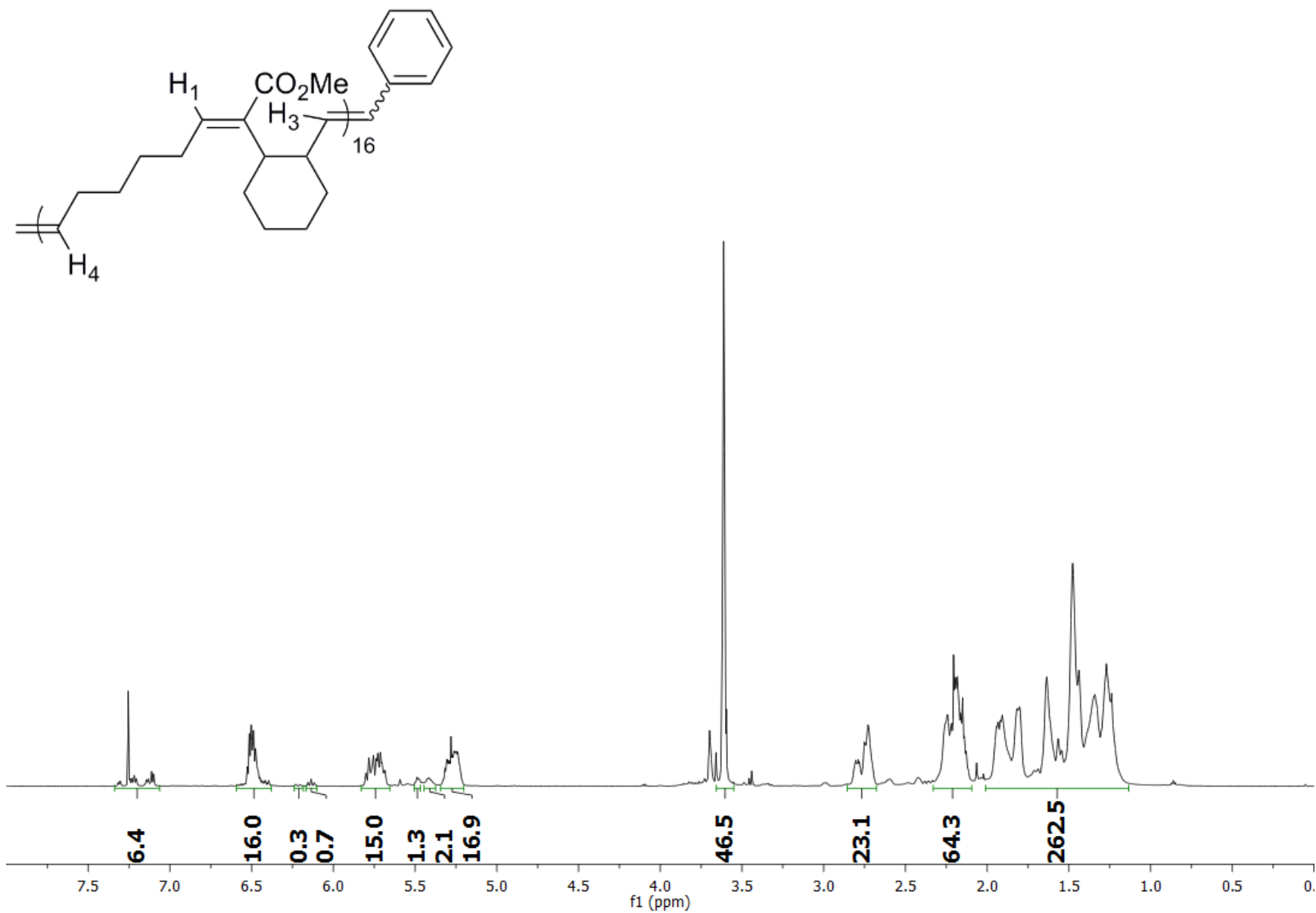


Figure S16. ¹H NMR spectrum of poly(4-*alt*-6)₁₆ obtained at 35 °C in CDCl₃.

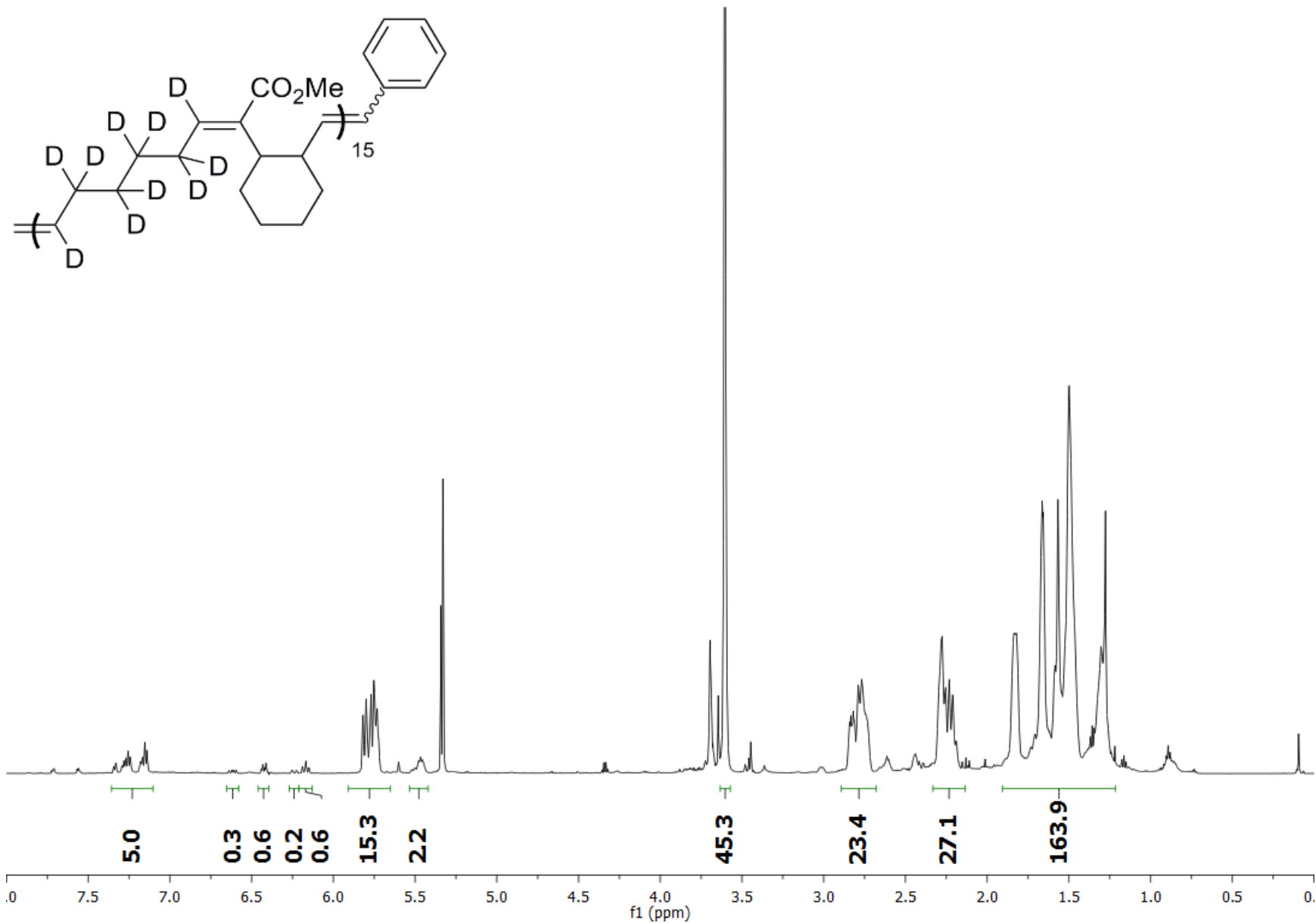


Figure S17. ^1H NMR spectrum of $\text{poly}(4\text{-alt-6-}d_{10})_{15}$ in CD_2Cl_2 .

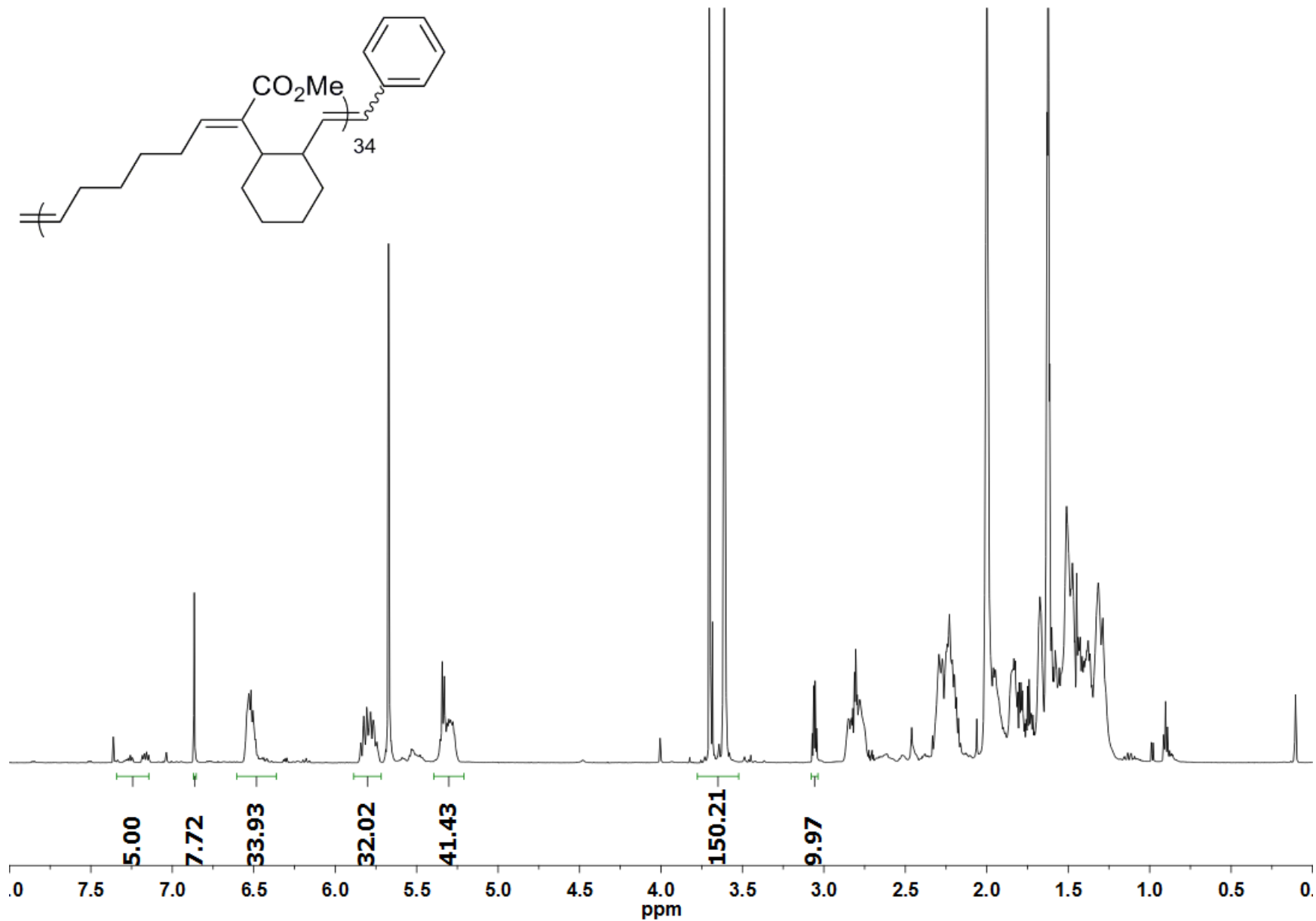


Figure S18. ¹H NMR spectrum of crude poly(4-*alt*-6)₃₄ obtained at 35 °C in CD₂Cl₂.

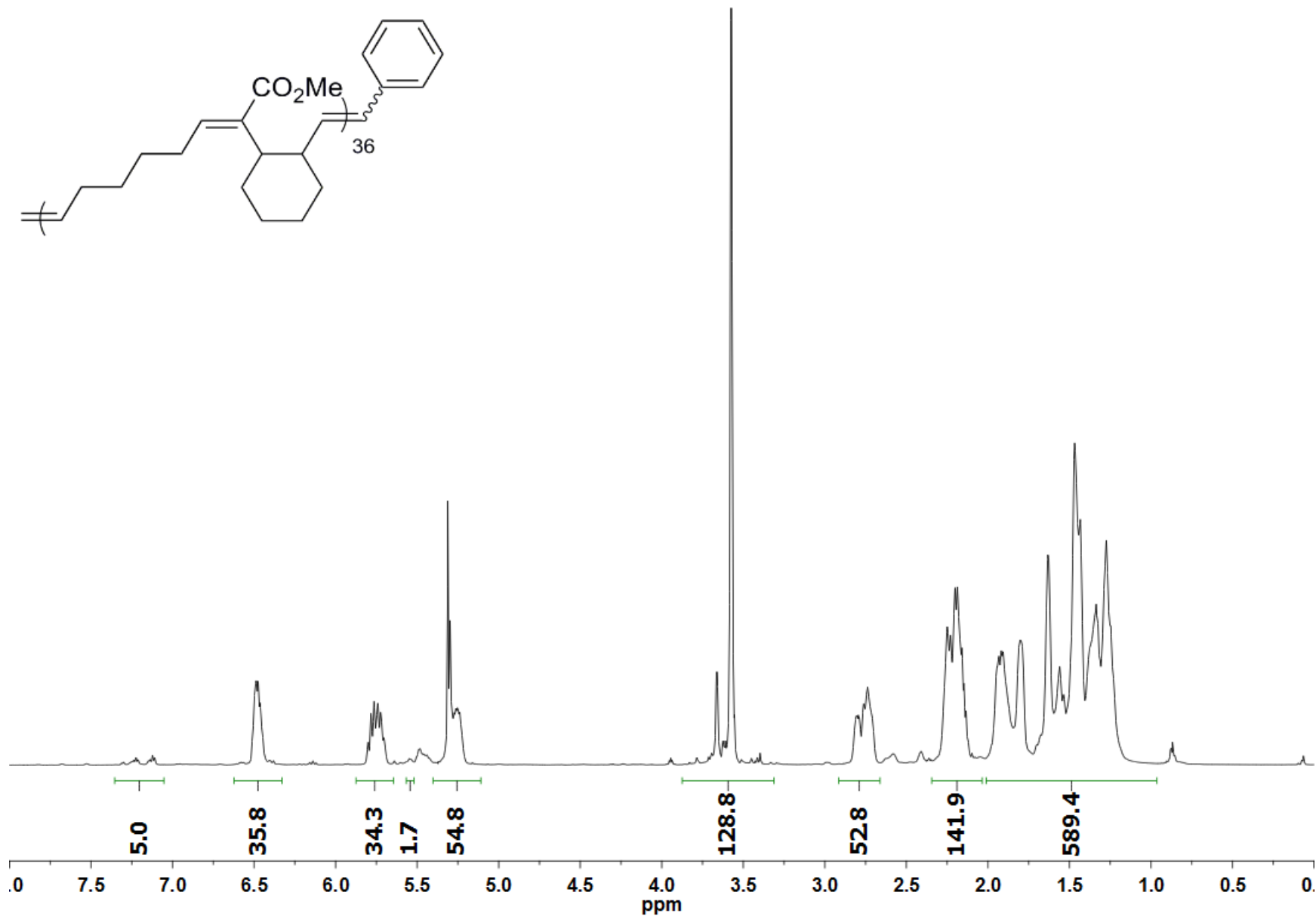


Figure S19. ¹H NMR spectrum of poly(4-*alt*-6)₃₆ obtained at 60 °C in CD₂Cl₂.

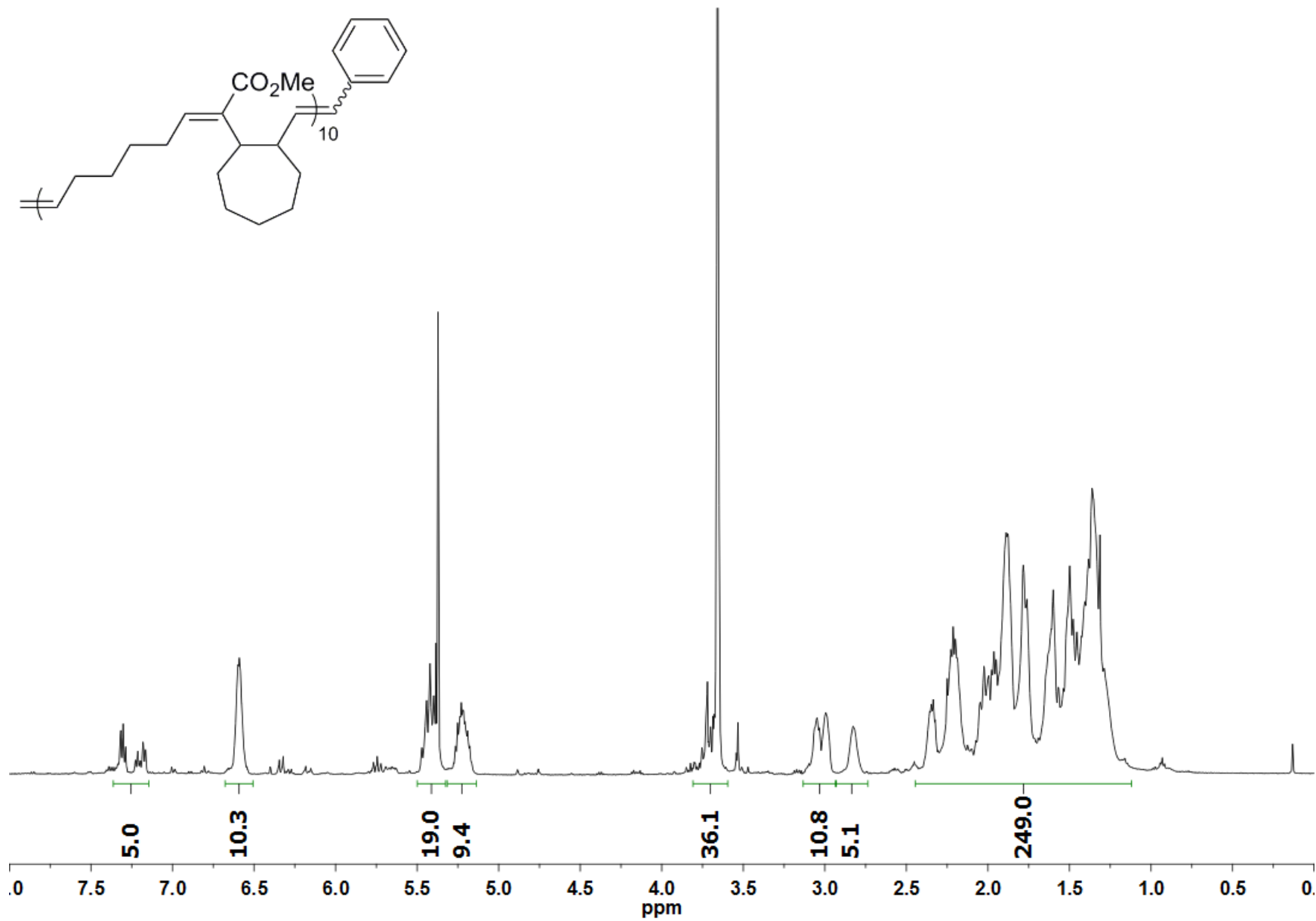


Figure S20. ¹H NMR spectrum of poly(5-*alt*-6)₁₀ in CD₂Cl₂.

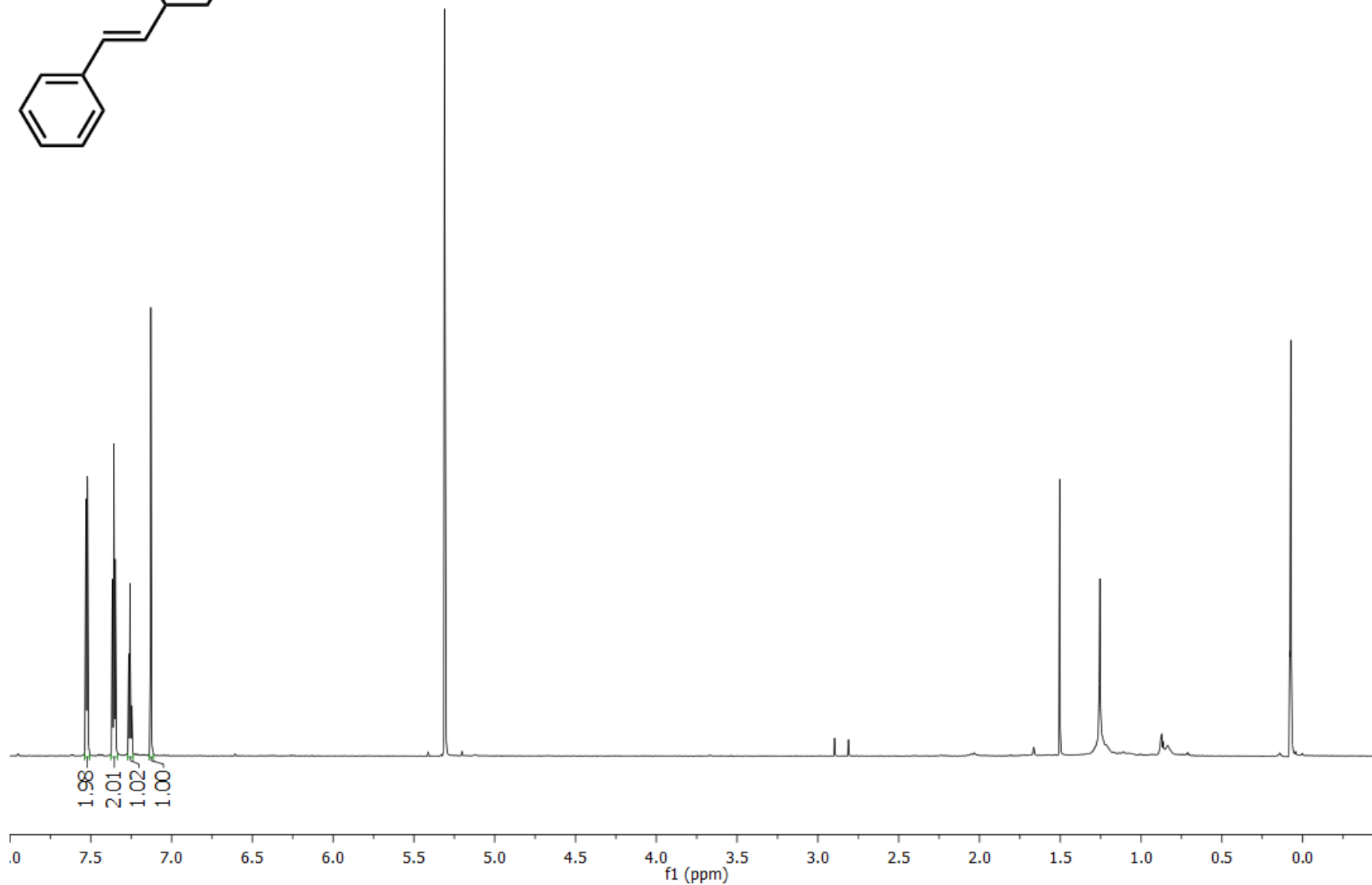
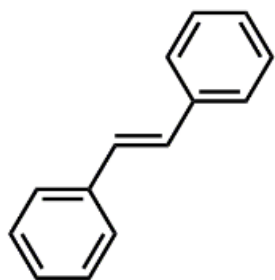


Figure S21. ^1H NMR spectrum of *E*-stilbene in CD_2Cl_2 .

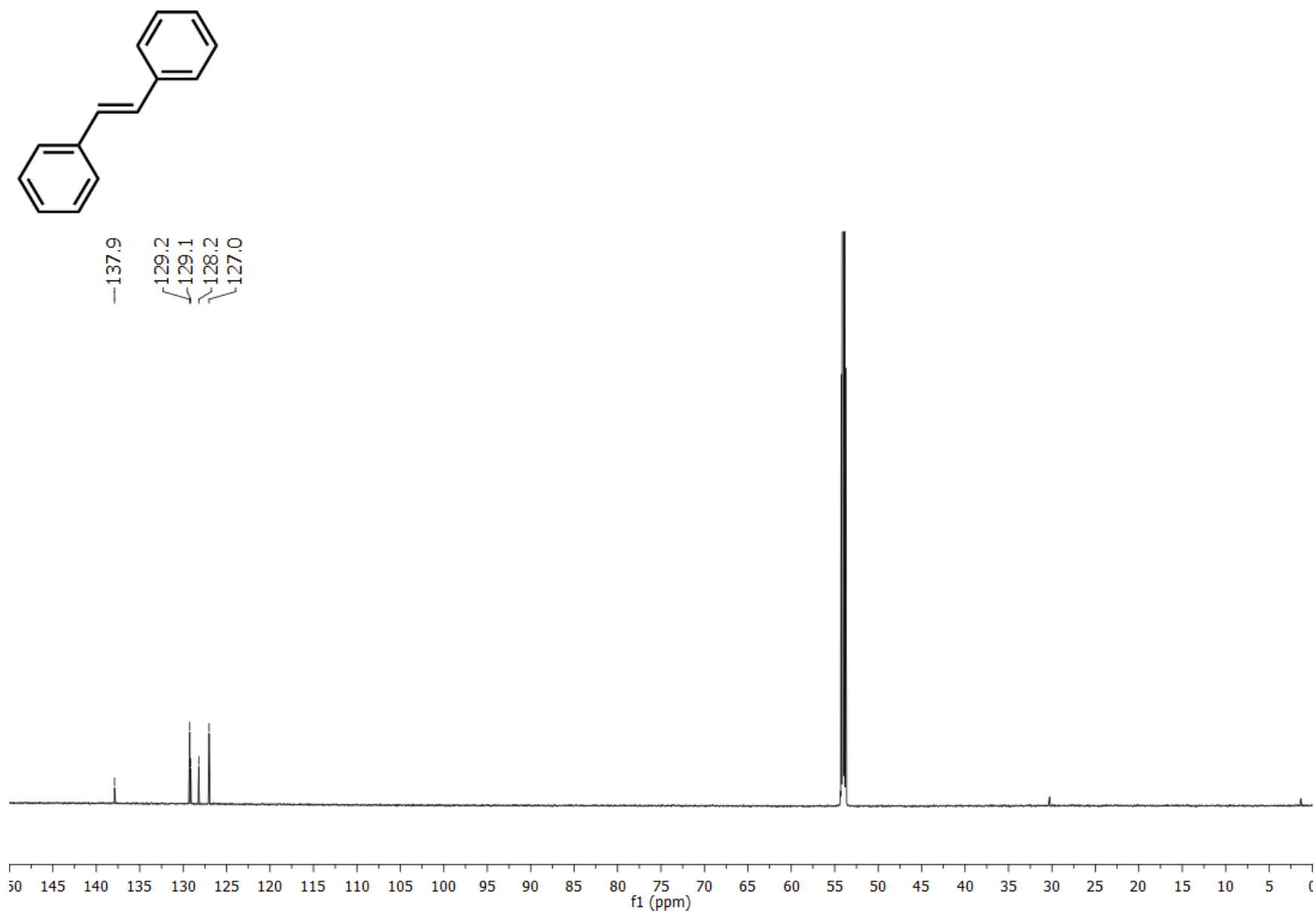


Figure S22. ¹³C NMR spectrum of *E*-stilbene in CD₂Cl₂ (fraction I).

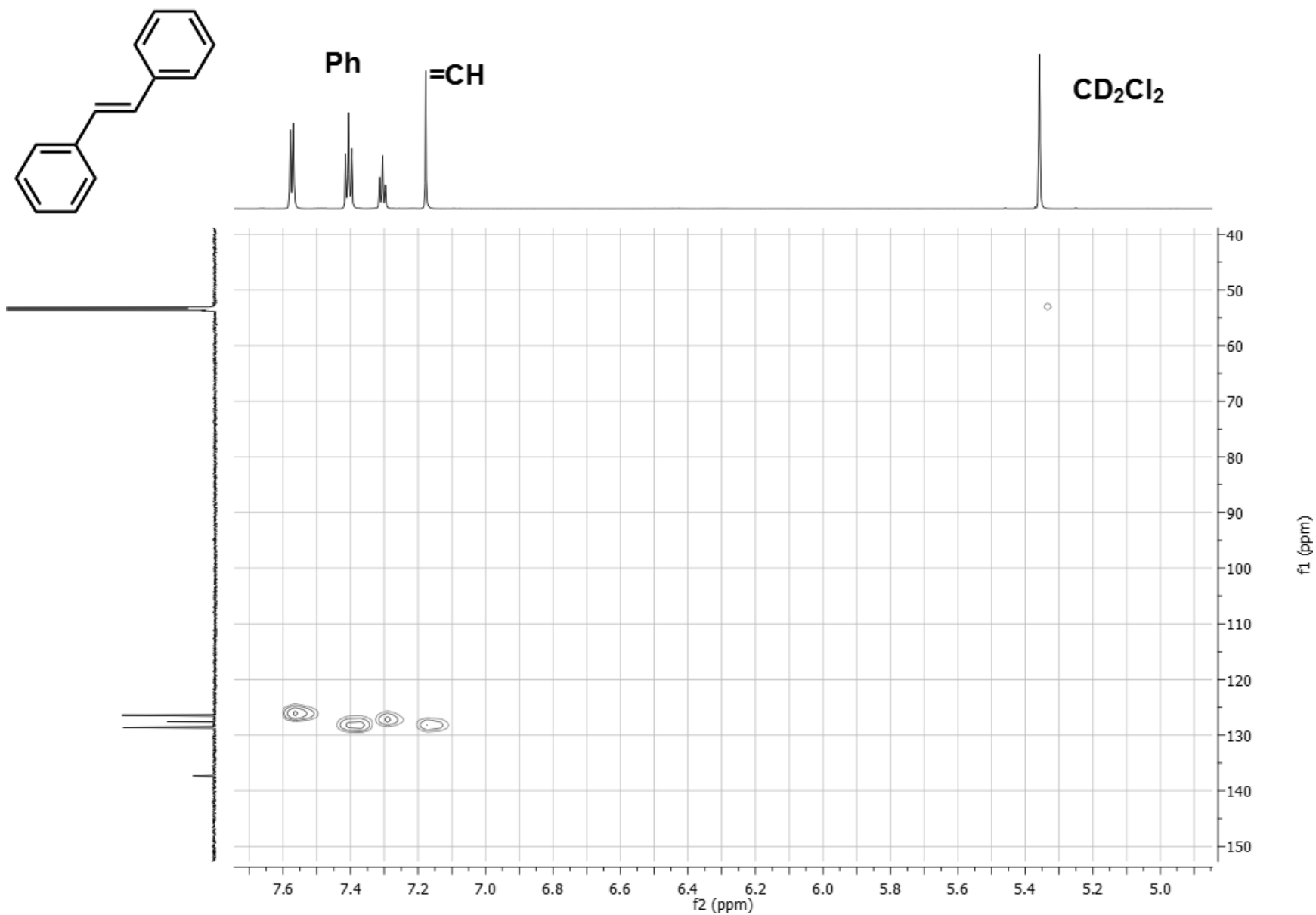


Figure S23. HSQC spectrum of *E*-stilbene in CD₂Cl₂ (fraction I).

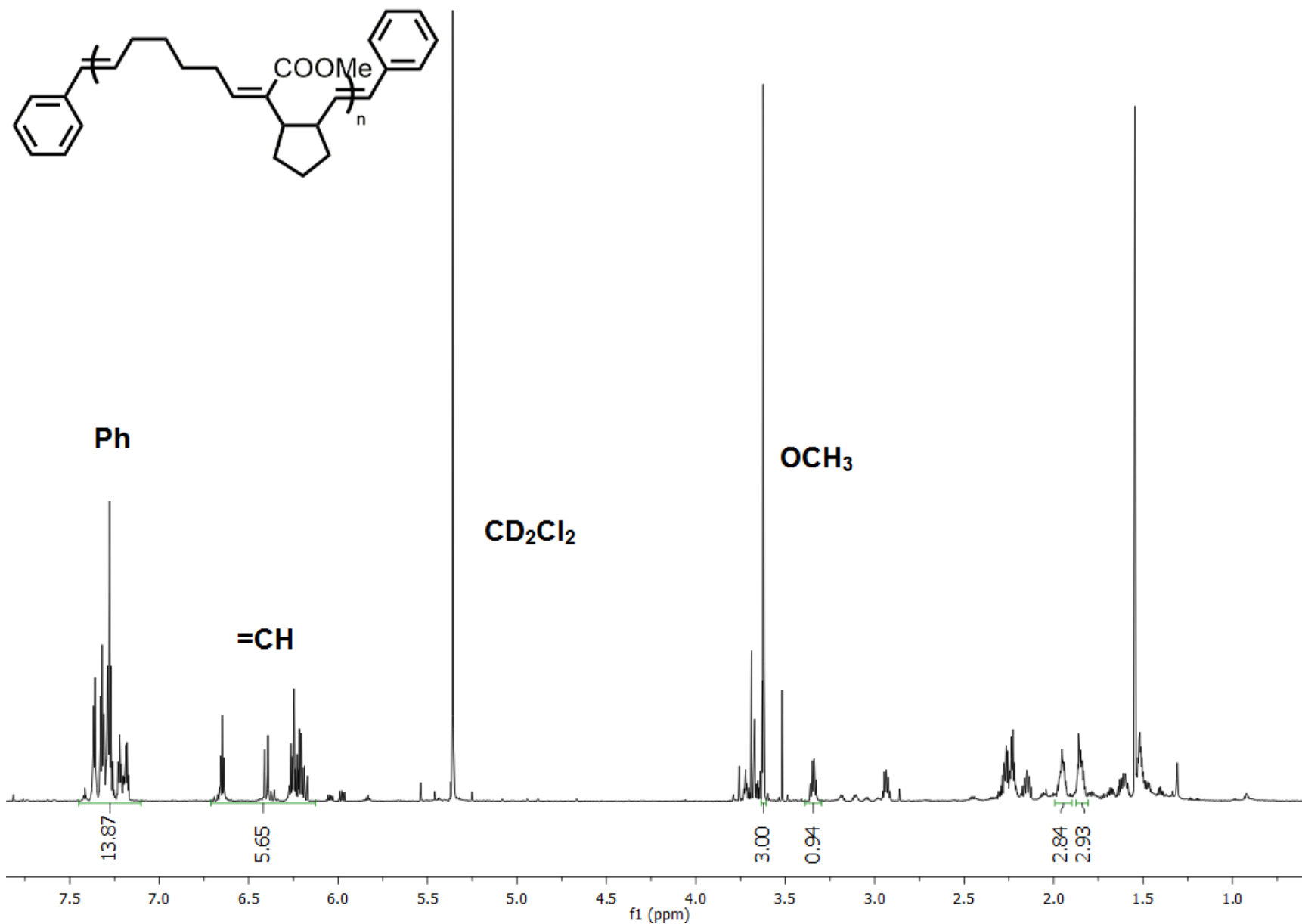


Figure S24. ¹H NMR spectrum of partially purified Ph-(3-*alt*-6)-Ph in CD₂Cl₂ (fraction II).

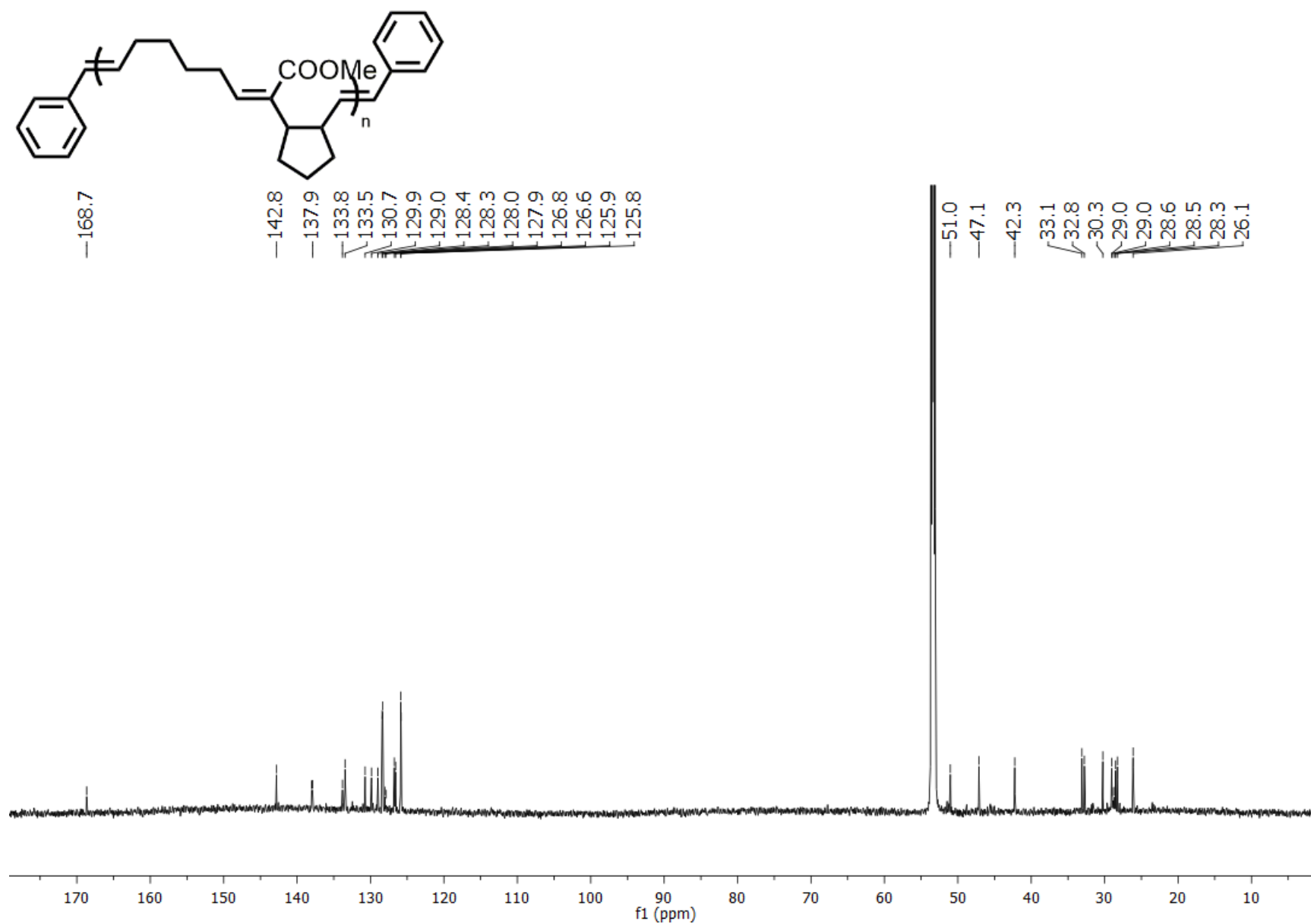


Figure S25. ¹³C NMR spectrum of partially purified Ph-(3-*alt*-6)-Ph in CD₂Cl₂ (fraction II).

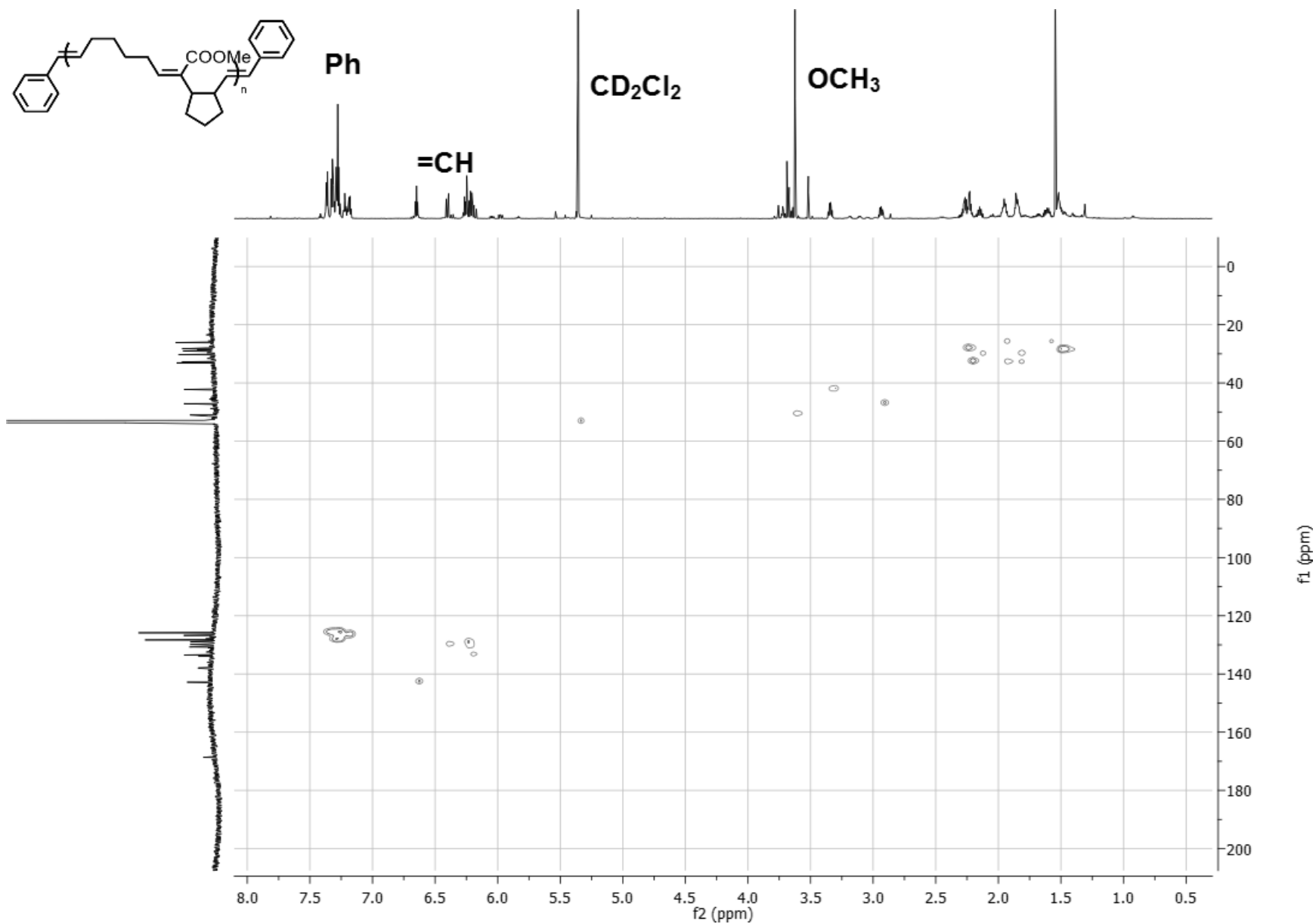


Figure S26. ^1H NMR spectrum of partially purified Ph-(3-*alt*-6)-Ph in CD_2Cl_2 (fraction II).

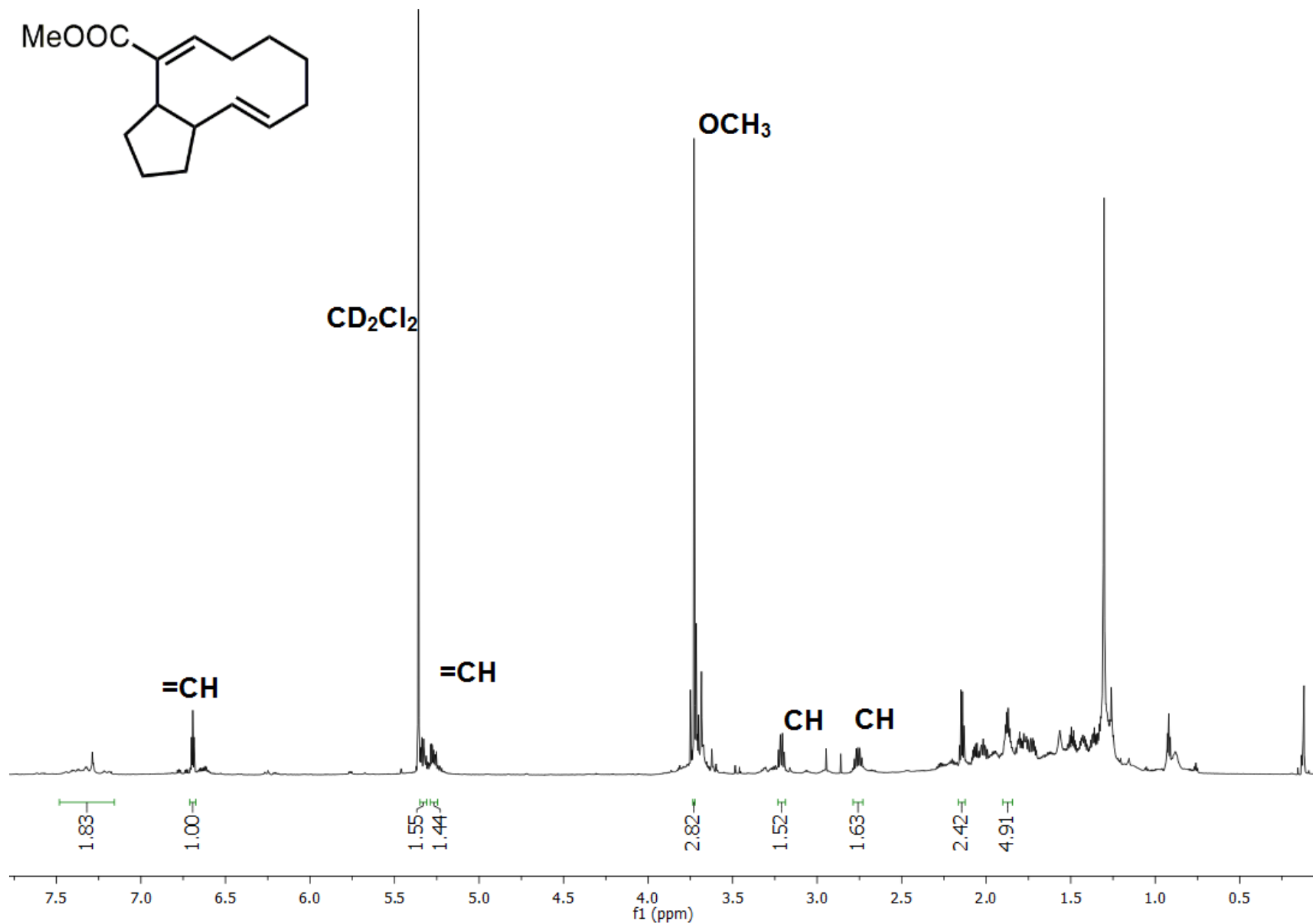


Figure S27. ^1H NMR spectrum of partially purified *cyc*-(3-*alt*-6)₁ in CD_2Cl_2 (fraction III).

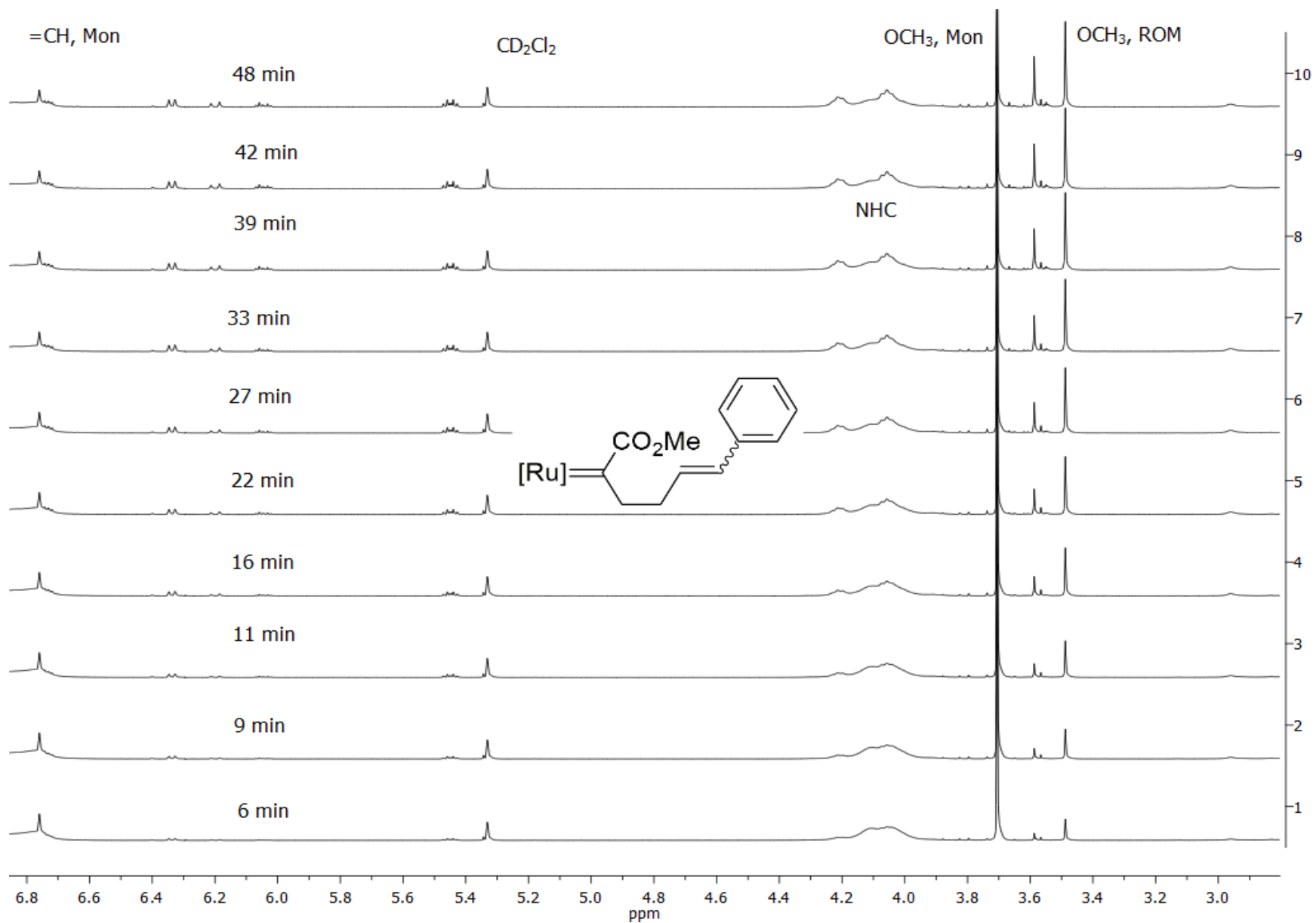


Figure S28. ROM of monomer **1** in CD₂Cl₂ monitored by ¹H NMR spectroscopy as a function of time.

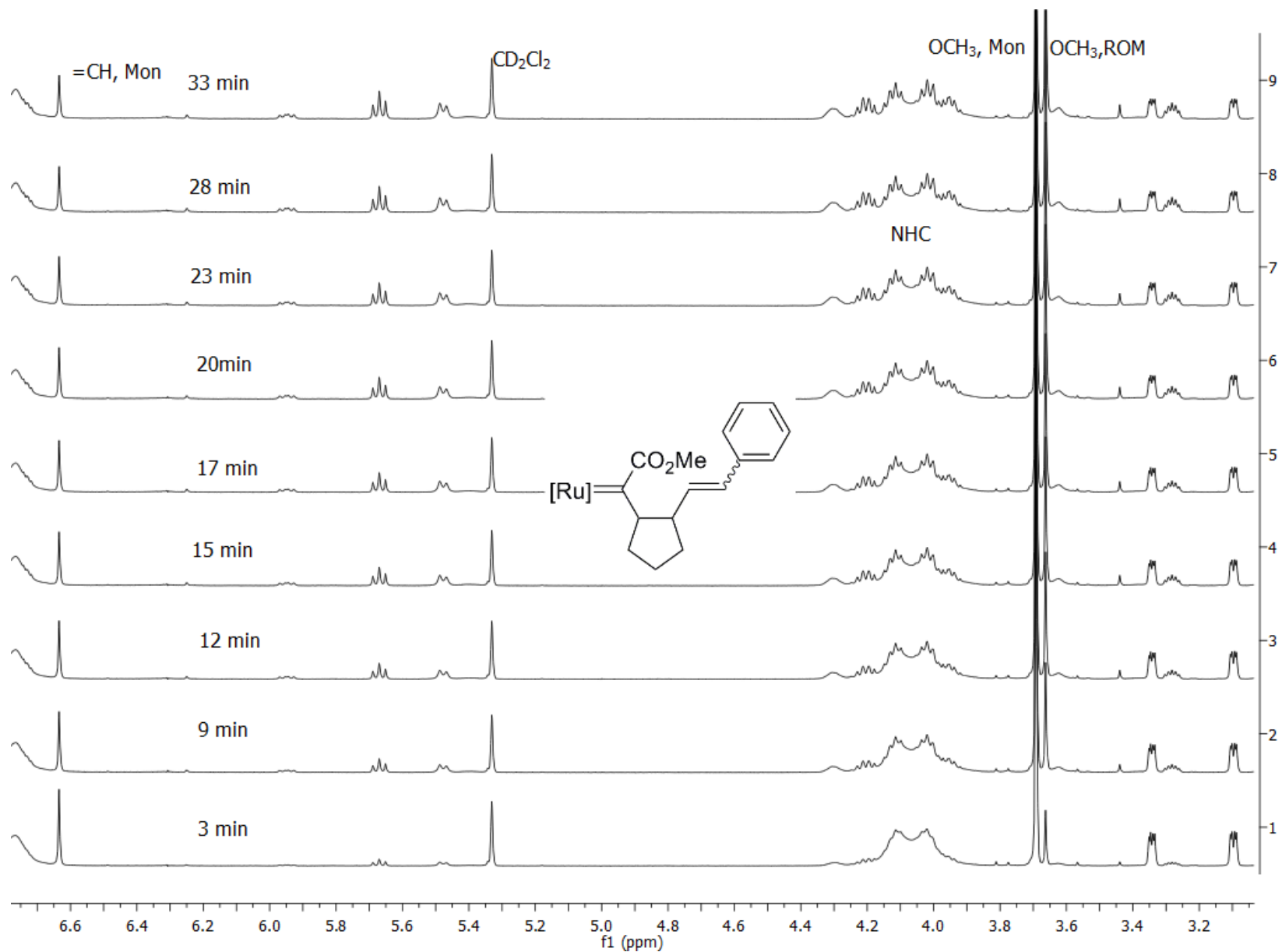


Figure S29. ROM of monomer **3** in CD_2Cl_2 monitored by ^1H NMR spectroscopy as a function of time.

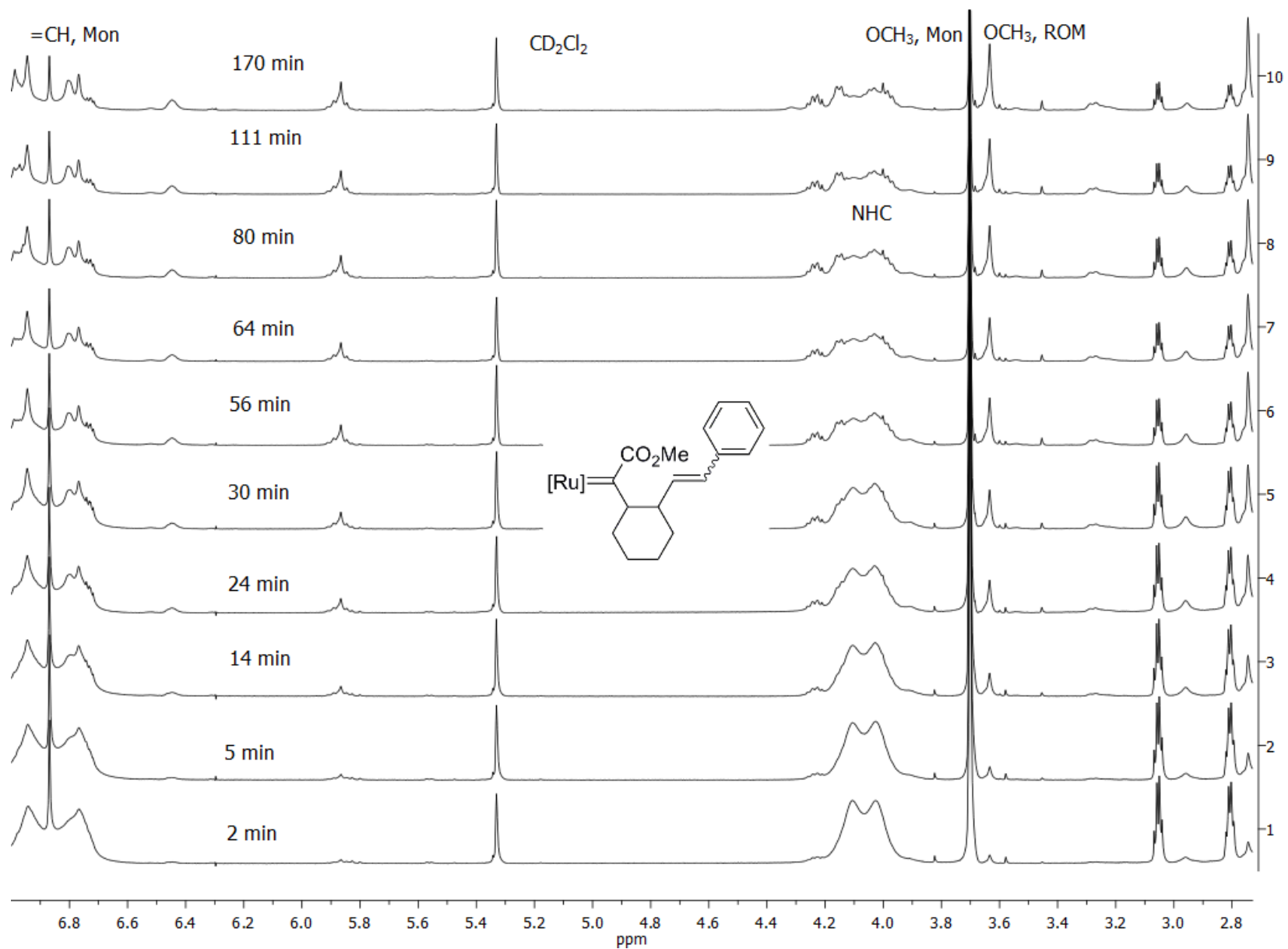


Figure S30. ROM of monomer **4** in CD_2Cl_2 monitored by ^1H NMR spectroscopy as a function of time.

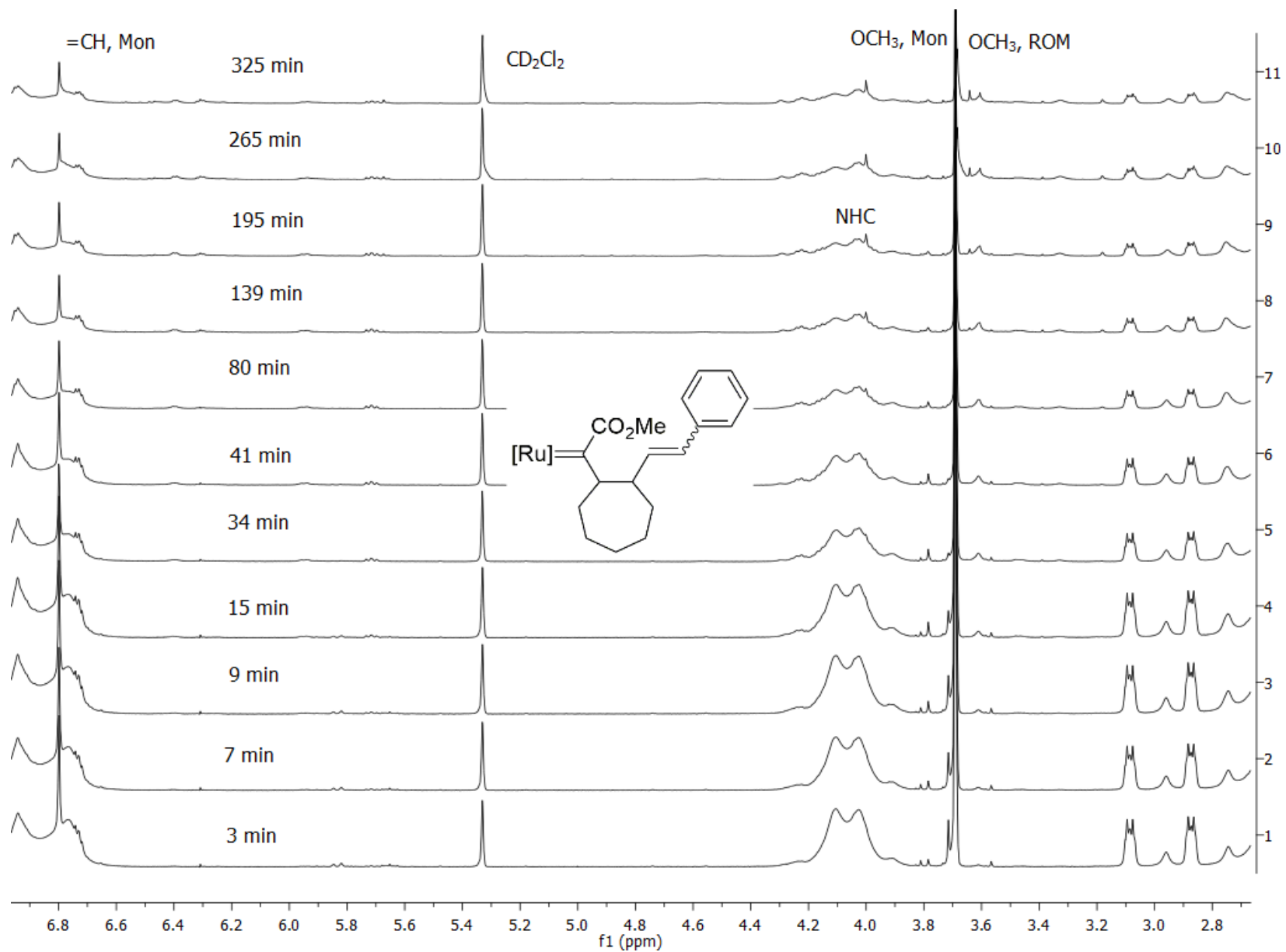


Figure S31. ROM of monomer **5** in CD₂Cl₂ monitored by ¹H NMR spectroscopy as a function of time.

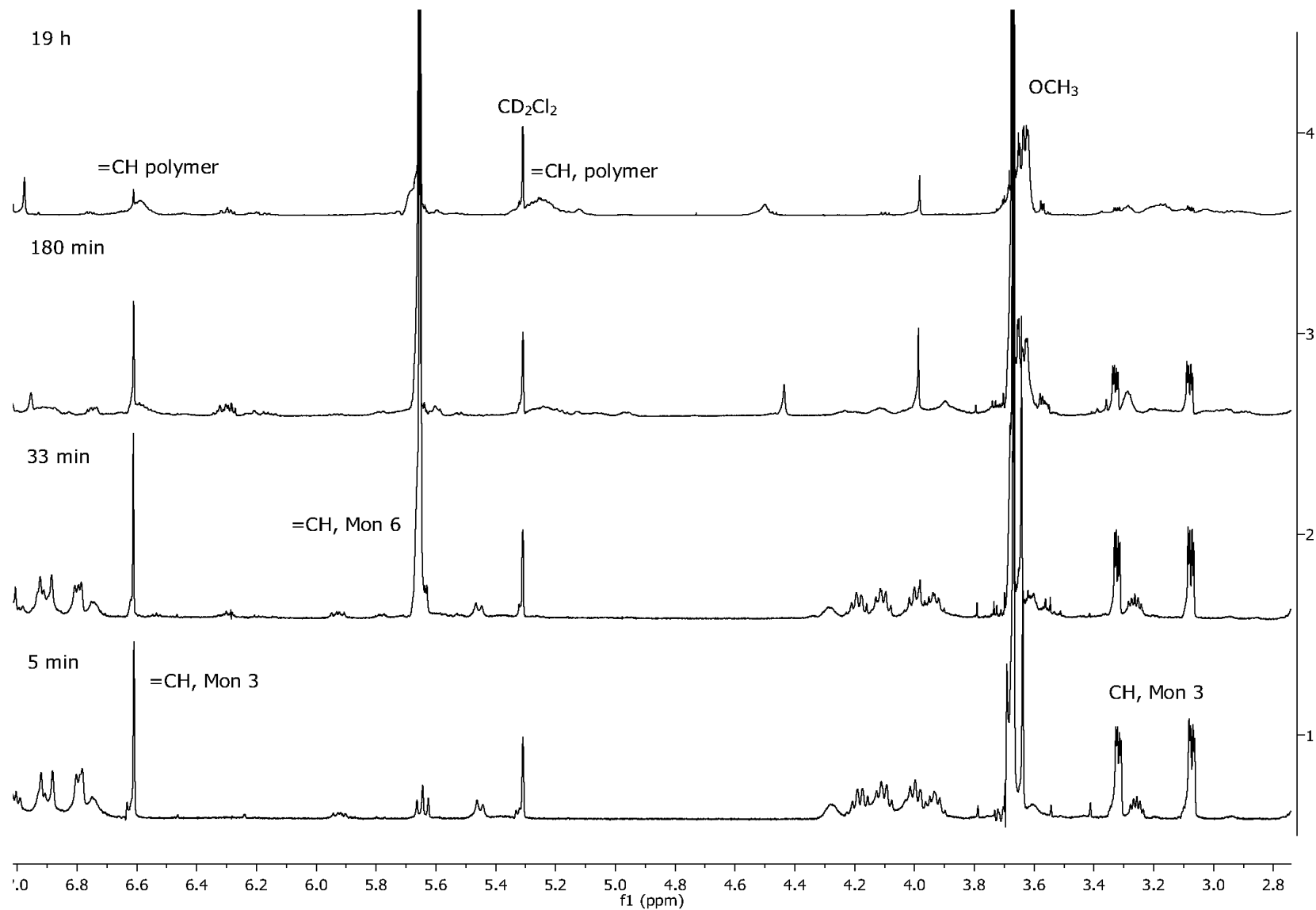


Figure S32. AROMP of monomer **3** and cyclohexene **6** ([Ru]:**3**:**6**=1:25:50) in CD₂Cl₂ monitored by ¹H NMR spectroscopy as a function of time.

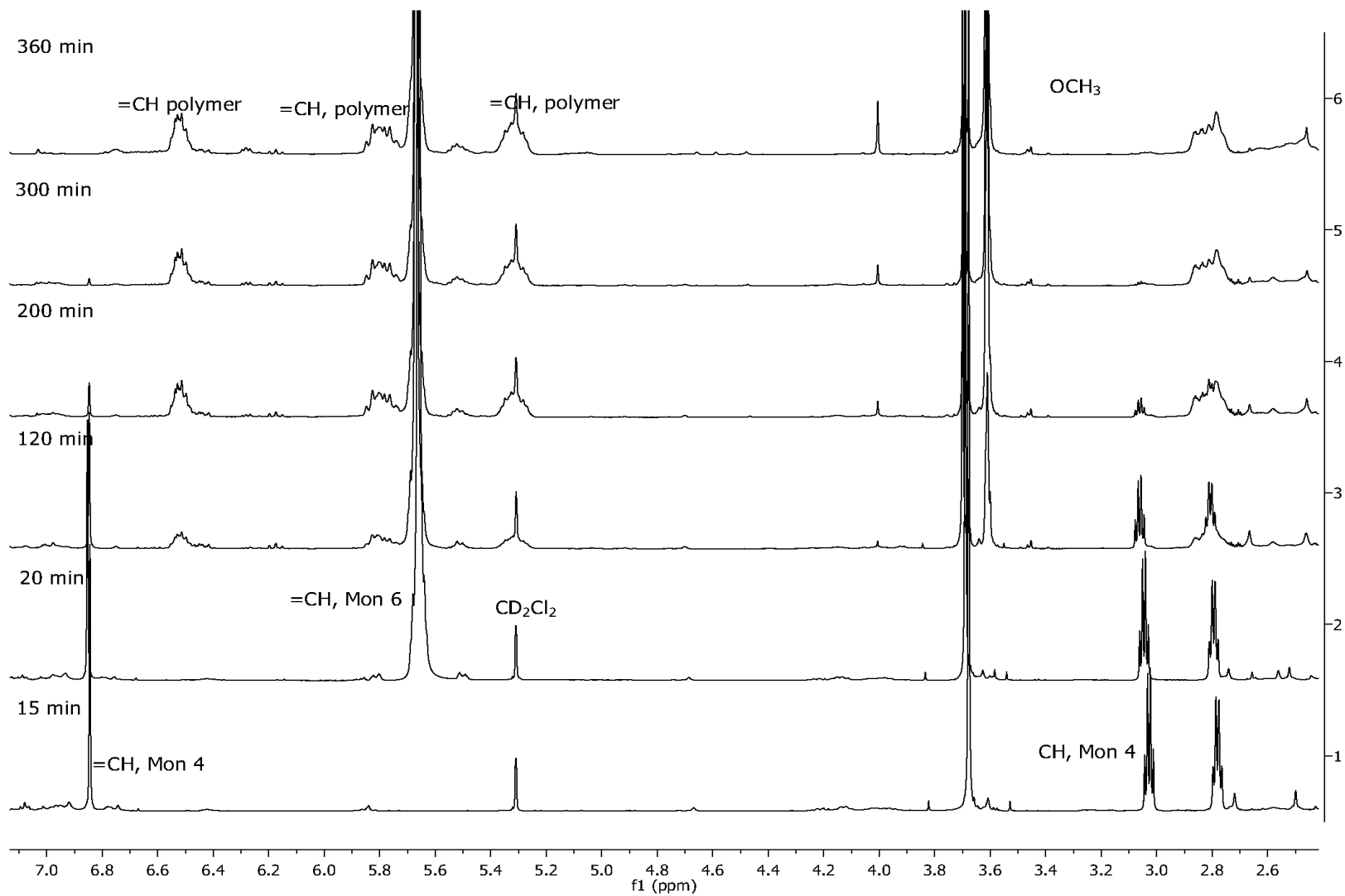


Figure S33. AROMP of monomer **4** and cyclohexene **6** ([Ru]:**4**:**6**=1:20:40) in CD₂Cl₂ monitored by ^1H NMR spectroscopy as a function of time.

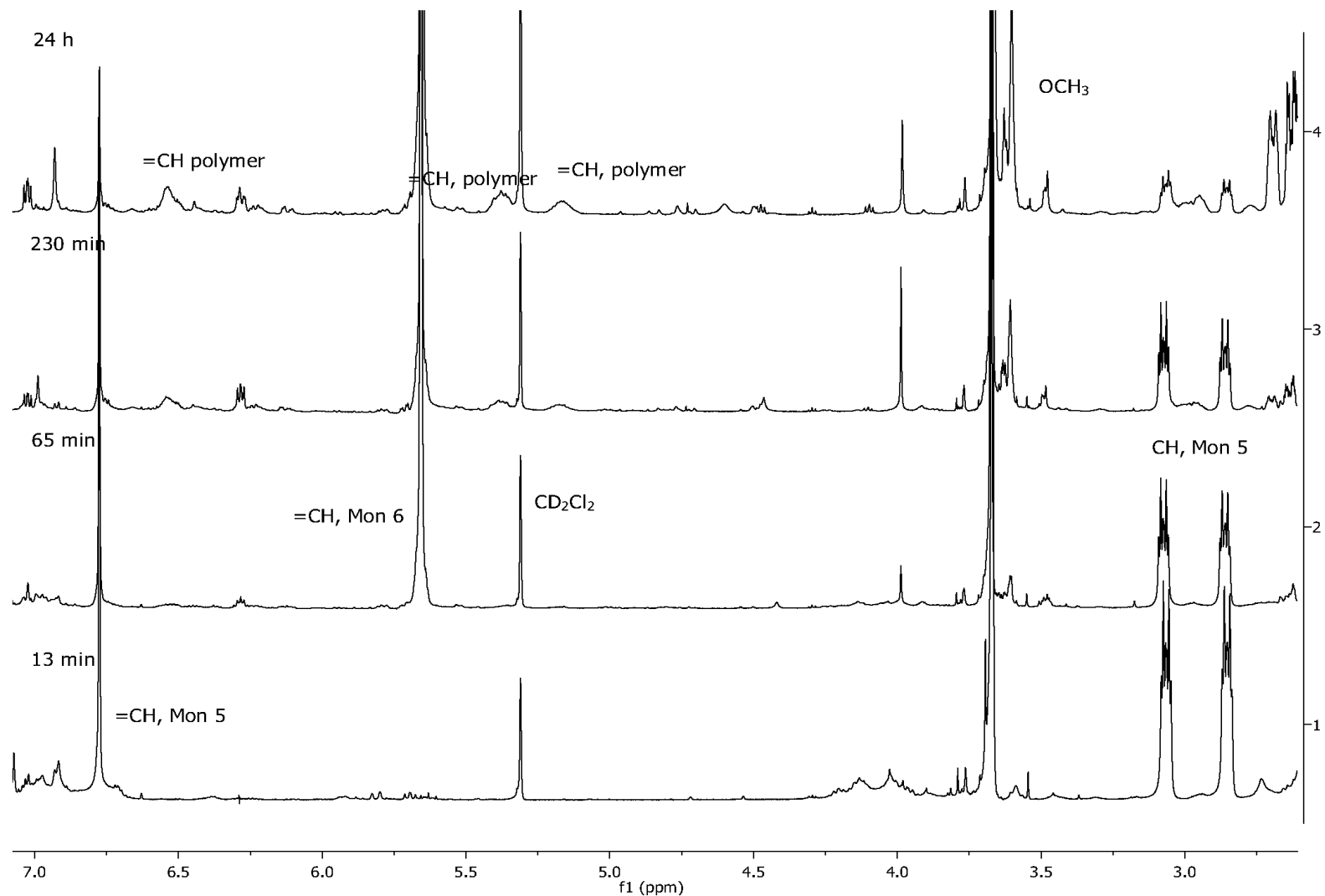


Figure S34. AROMP of monomer **5** and cyclohexene **6** ([Ru]:**5**:**6**=1:50:100) in CD₂Cl₂ monitored by ^1H NMR spectroscopy as a function of time.

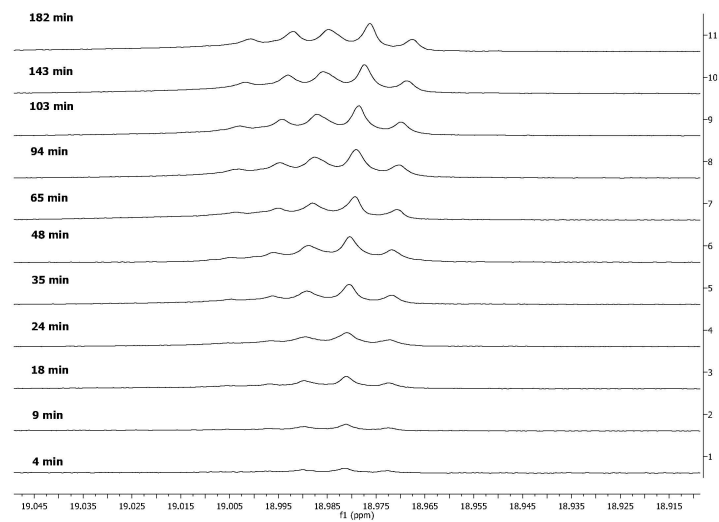


Figure S35. The AROM conversion of [Ru]-**4** enic carbene to [Ru]-**6-4** alkylidene with excess cyclohexene **6** in CD₂Cl₂.

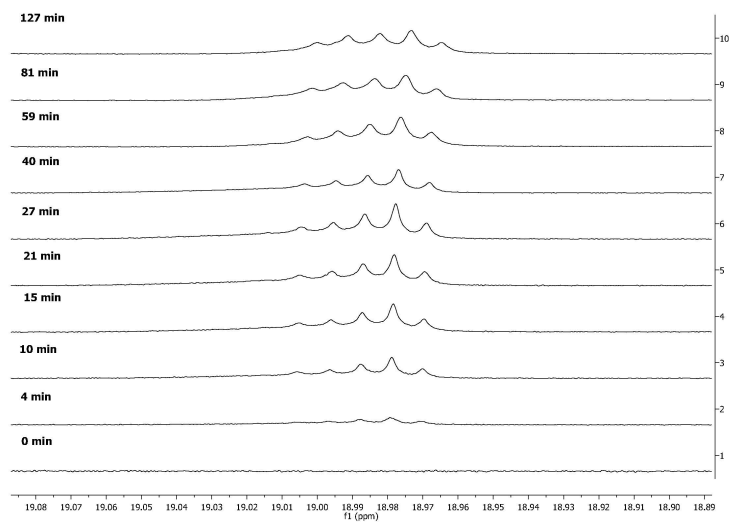


Figure S36. The AROM conversion of [Ru]-**3** enoic carbene to [Ru]-**6-3** alkylidene with excess cyclohexene **6** in CD₂Cl₂.

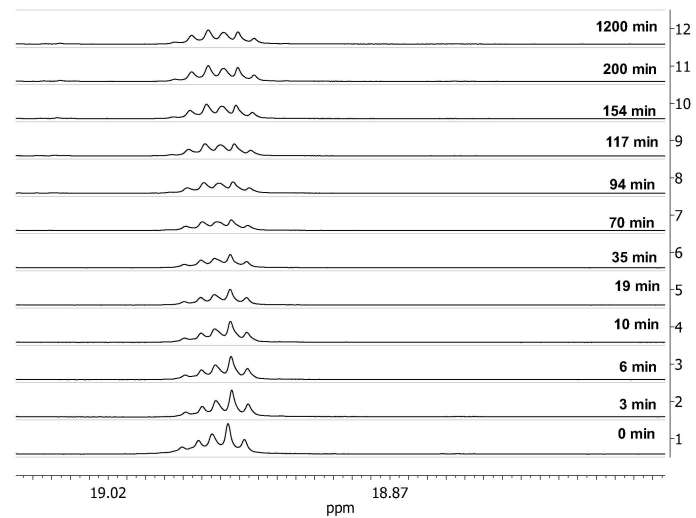


Figure S37. Conversion of [Ru]-**6-4** alkylidene (1 eq) to [Ru]-**6-4-6-4** alkylidene in double AROM (AROM-2) with monomer **4** (1 eq) in the presence of excess cyclohexene **6** in CD₂Cl₂.

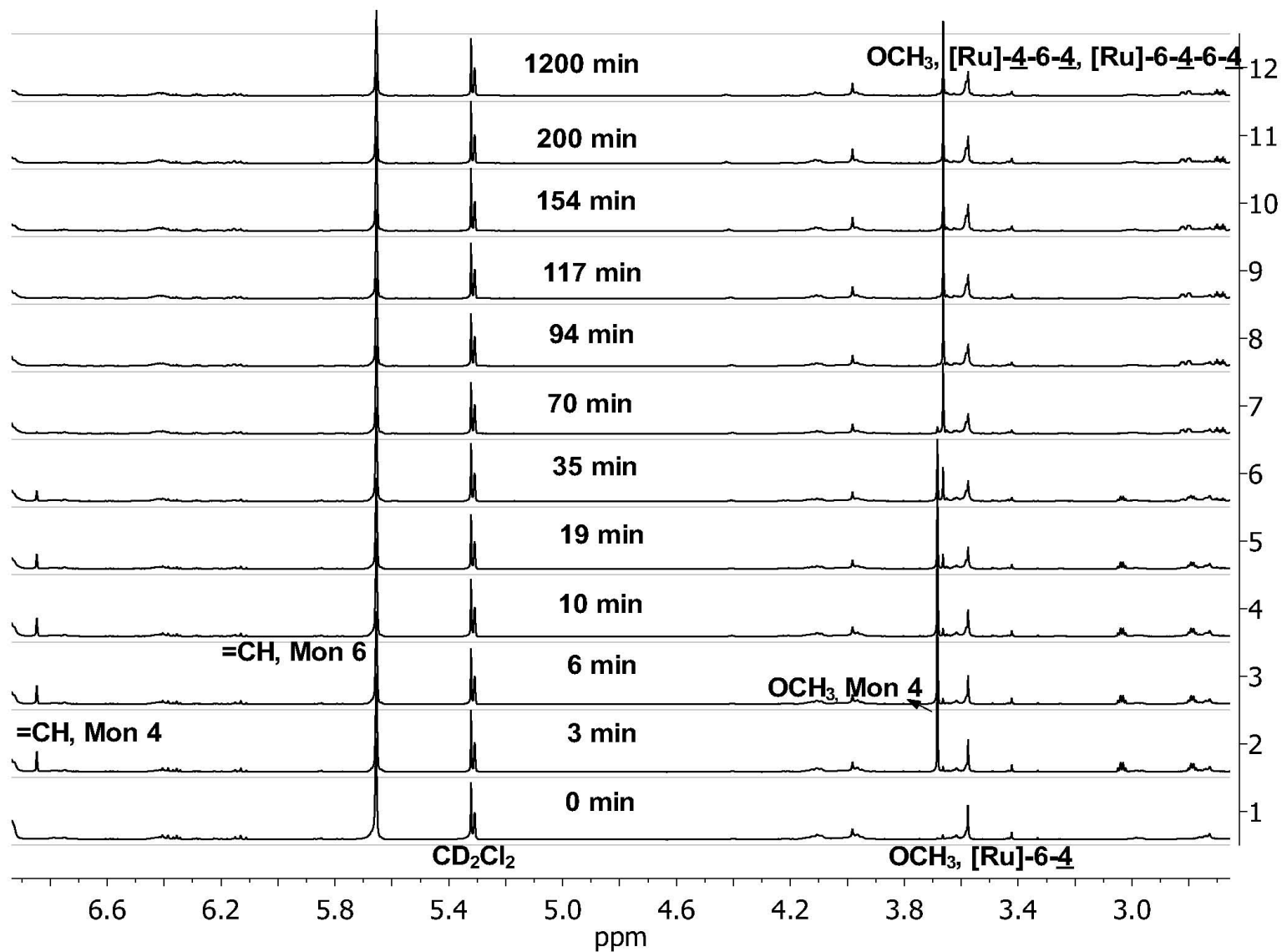


Figure S38. Conversion of monomer **4** (1 eq) in double AROM (AROM-2) with [Ru]-**6-4** (1 eq) and excess cyclohexene **6** in CD₂Cl₂.

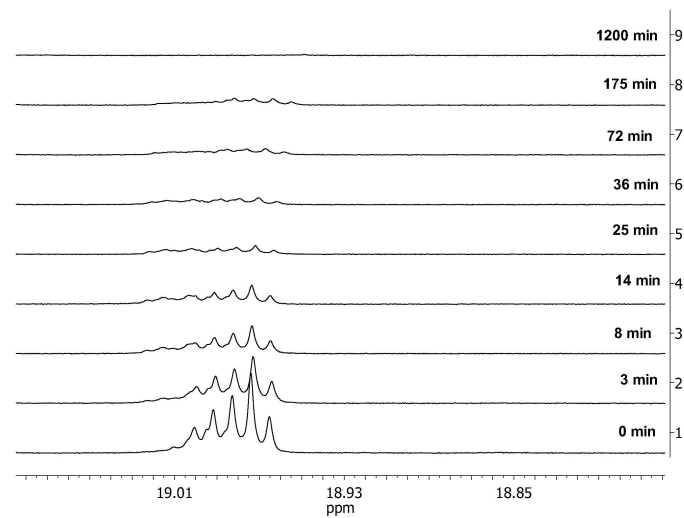


Figure S39. Conversion of [Ru]-**6-3** alkylidene (1 eq) to [Ru]-**6-3-6-3** alkylidene in double AROM (AROM-2) with monomer **3** (1eq) in the presence of excess cyclohexene **6** in CD₂Cl₂.

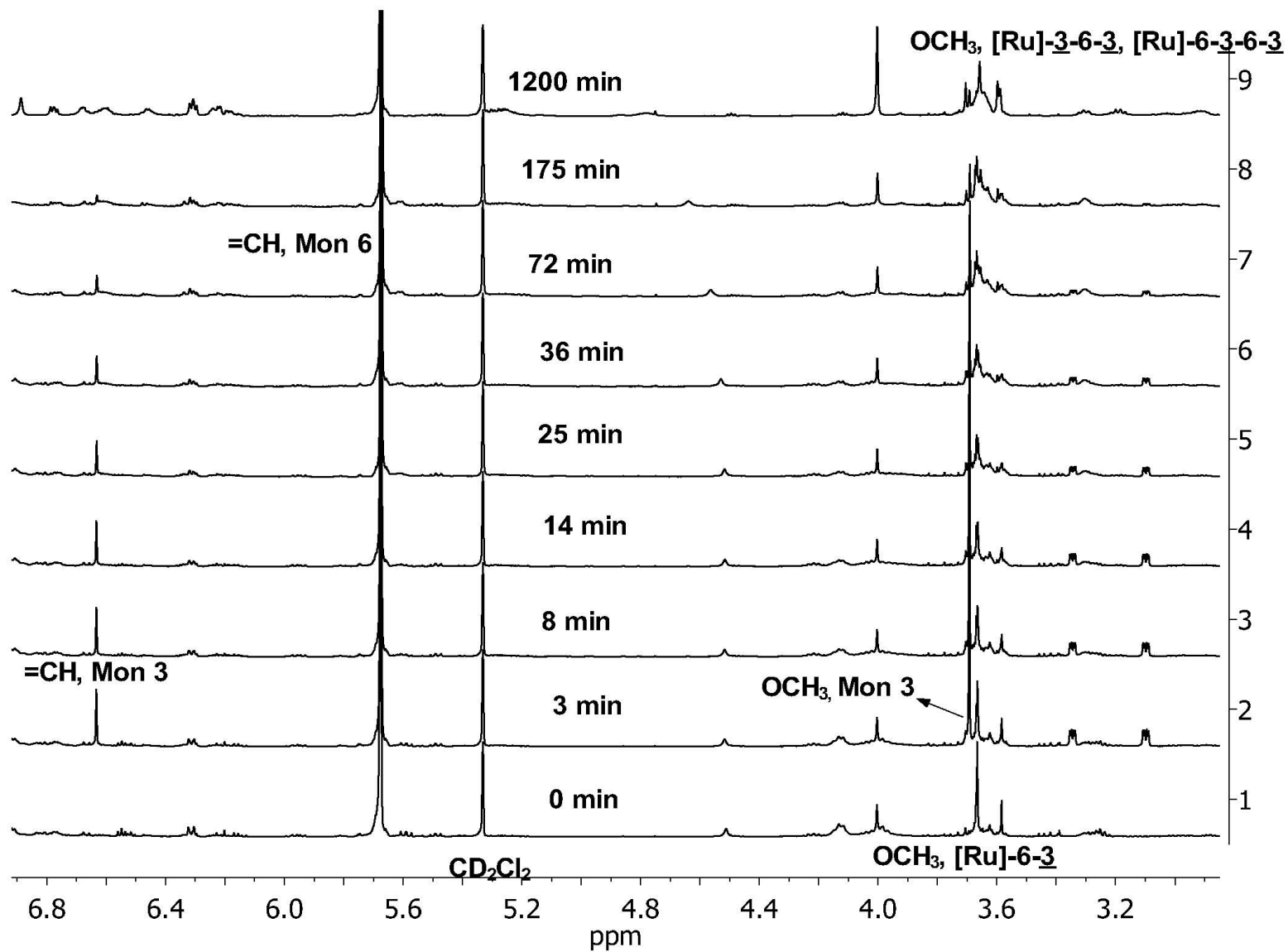


Figure S40. Conversion of monomer **3** (1 eq) in double AROM (AROM-2) with [Ru]-**6-3** (1 eq) and excess cyclohexene **6** in CD₂Cl₂.

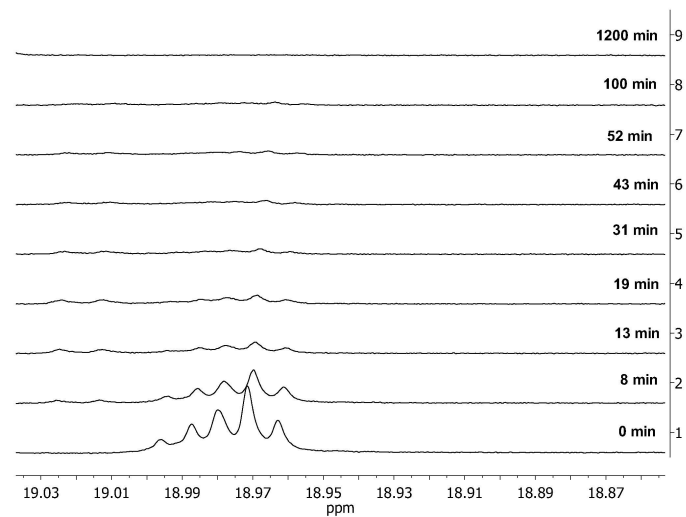


Figure S41. Conversion of [Ru]-**6-4** alkylidene (1 eq) to [Ru]-**6-3-6-4** alkylidene in double AROM (AROM-2) with monomer **3** (1 eq) in the presence of excess cyclohexene **6** in CD₂Cl₂.

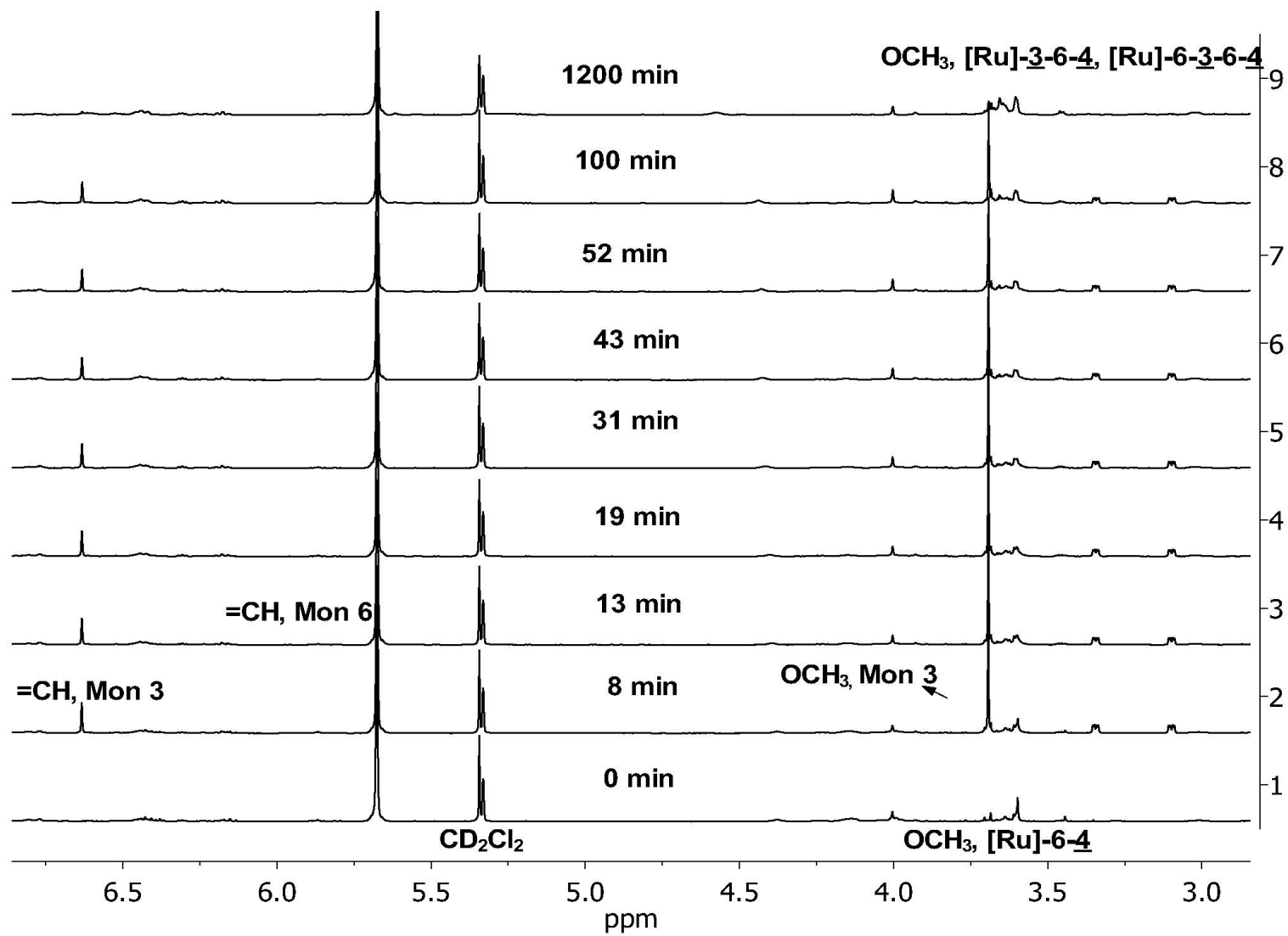


Figure S42. Conversion of monomer **3** (1 eq) in double AROM (AROM-2) with [Ru]-**6-4** (1 eq) and excess cyclohexene **6** in CD₂Cl₂.

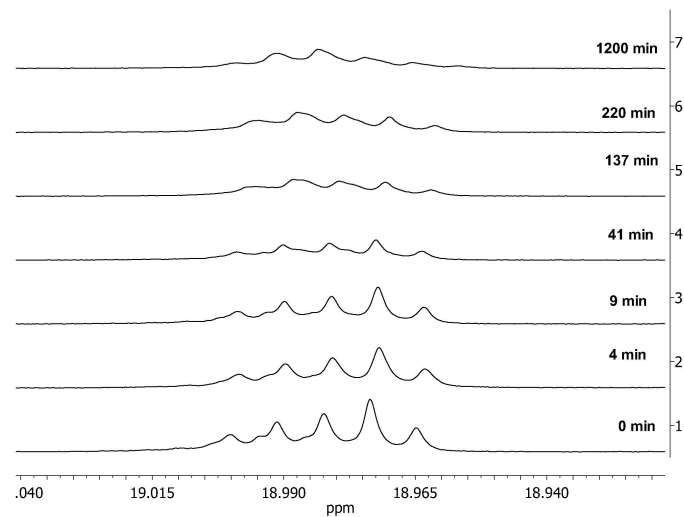


Figure S43. Conversion of [Ru]-**6-3** alkylidene (1 eq) to [Ru]-**6-4-6-3** alkylidene in double AROM (AROM-2) with monomer **4** (1 eq) in the presence of excess cyclohexene **6** in CD₂Cl₂.

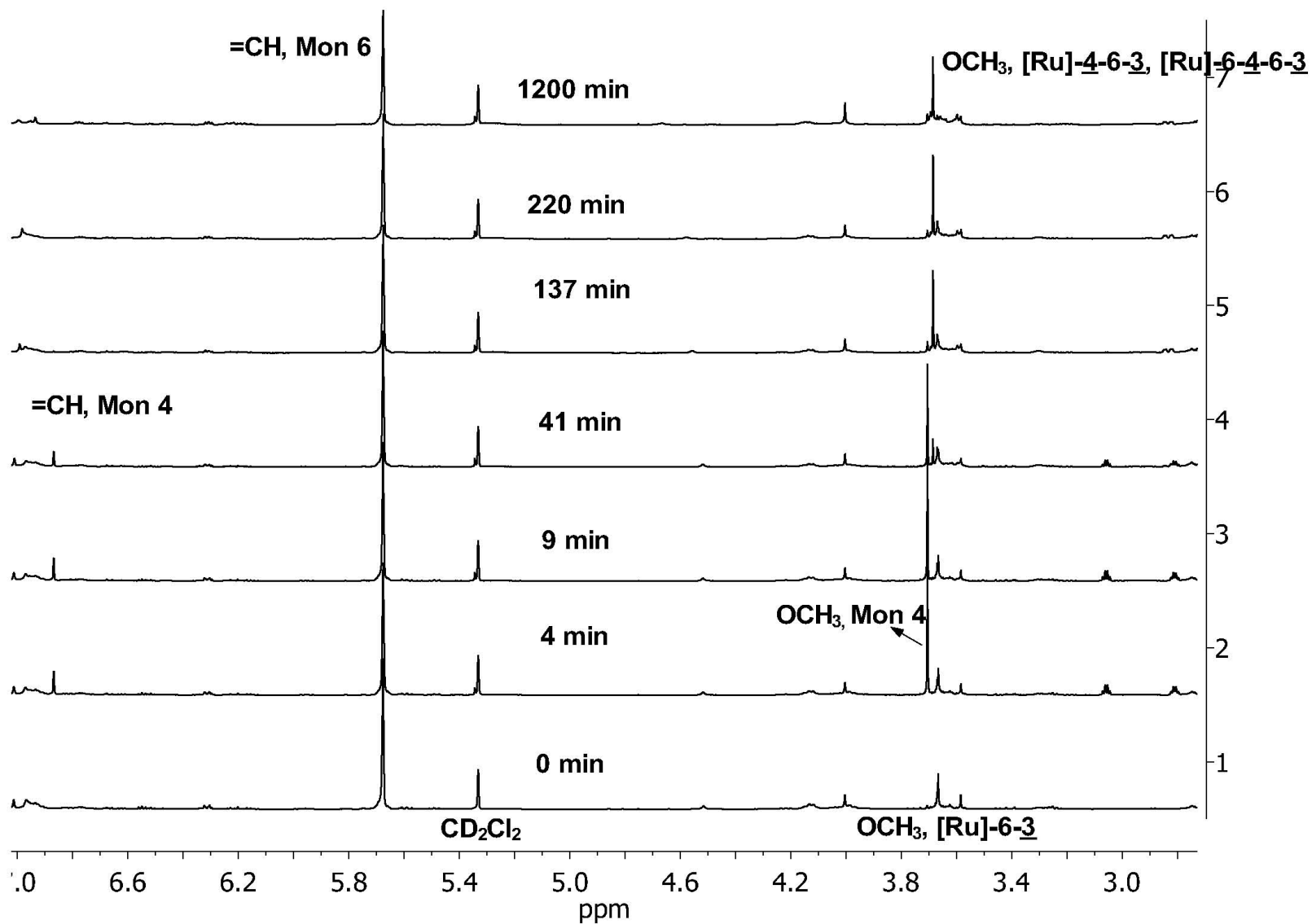


Figure S44. Conversion of monomer 4 (1 eq) in double AROM (AROM-2) with [Ru]-6-3 (1 eq) and excess cyclohexene 6 in CD₂Cl₂.

References

- (1) Lapinte, V.; de Frémont, P.; Montembault, V.; Fontaine, L. *Macromol. Chem. Phys.* **2004**, "Ring opening metathesis polymerization (ROMP) of cis- and trans-3,4-bis(acetyloxymethyl)cyclobut-1-enes and synthesis of block copolymers," *205*, 1238-1245.
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