Supporting Information

Ru-catalyzed Isomerization Provides Access to Alternating Copolymers via Ring-Opening Metathesis Polymerization

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This material consists of experimental methods to prepare amides **1** and 52 figures (Figure S1~S56), to present more experimental data.

Materials and Methods

Solvents, e.g. CH_2Cl_2 and THF were purified with Pure Process Technology (PPT). Poly(styrene) standards were purchased from Sigma-Aldrich Co. LLC. without further purification. Mallinckrodt silica gel 60 (230-400 mesh) was used for column chromatography. Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates ($60F_{254}$), flash chromatography on silica gel-60 (230-400 mesh), and Combi-Flash chromatography on RediSep normal phase silica columns (silica gel-60, 230-400 mesh). Bruker Nanobay 400 and Avance III 500 MHz NMR instruments were used for analysis. Chemical shifts were calibrated from residual undeuterated solvents; they are denoted in ppm (δ).

General Procedures for the Synthesis of Bicyclo[n.2.0]acids.

The methyl bicyclic cyclobutenecarboxylate, [n.2.0] ester was obtained according to the literature (1, 2). Then [n.2.0] ester in THF was cooled in an ice bath, 2N KOH was added, and the solution was stirred for 30 min. The ice bath was removed and the reaction mixture was allowed to warm to 25 °C and stirred for another 4 h. THF was evaporated and the aqueous solution was acidified with 2N HCl to pH 2. The solution was extracted with CH_2Cl_2 (3 × 20 mL) and the combined CH_2Cl_2 solution was dried over anhydrous $MgSO_4$. The solvent was removed after filtration and the product was used without further purification.

[4.2.0] Acid 5. The methyl bicyclo[4.2.0]oct-7-ene-7-carboxylate (2.00 g, 12.0 mmol) in THF (5 mL) was hydrolyzed in the presence of 2N KOH (20 mL), and the product bicyclo[4.2.0]oct-7-ene-7-carboxylic acid **5** (1.74 g, 95%) was used without further purification.

[3.2.0] Acid 6. The methyl bicyclo[3.2.0]hepta-6-ene-6-carboxylate (500 mg, 3.29 mmol) was hydrolyzed by the procedure described above to yield acid **6** (350 mg, 80%). It was converted to the desired amide without further purification.

General Procedure for the Synthesis of Bicyclo[n.2.0]alkene Amides.

Bicyclo[n.2.0]alkene carboxylic acid (n = 3 or 4), ethyl, dimethylaminopropyl carbodiimide hydrochloride (EDC•HCl), and the desired amine were dissolved in dry CH_2Cl_2 in a 50-mL flask. The solution was cooled in an ice bath and DIPEA was added.

The mixture was stirred for 8 h at 25 °C until the acid was consumed. The reaction mixture was washed sequentially with 5% $NaHCO_3$ (3×), 1N HCl (3×) and brine (2×) and dried over anhydrous $MgSO_4$. The solvent was filtered and removed by evaporation. The crude product was subjected to silica flash chromatography.

[4.2.0] Amide 1a. Acid **5** (100 mg, 0.66 mmol), L-Ala-OMe•HCl (104 mg, 0.72 mmol), EDC•HCl (139 mg, 0.72 mmol) and DIPEA (370 μL, 2.1 mmol) were allowed to react in 20 mL CH_2Cl_2 and subjected to work up as described. Chromatography (97:3/CH_2Cl_2:MeOH) yielded amide **1a** as a mixture of diastereomers (146 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.70 (d, *J* = 6.7 Hz, 1H, =CH), 6.19 (d, *J* = 5.6 Hz, 1H, CONH), 4.61 (qd, *J* = 7.2, 2.6 Hz, 1H, side chain CH), 3.71 (s, 3H, OCH_3), 3.05 (m, 1H, CH), 2.74 (m, 1H, CH), 1.79 (m, 1H, CH_2), 1.69 (m, 2H, CH_2), 1.52 (m, 3H, CH_2), 1.39 (m, 5H, CH_2 and CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5 (COOR), 162.1 (CONH), 145.2 (=CH), 144.1 (=CH), 52.4 (OCH_3), 47.5 (side chain CH), 39.3 (CH), 37.6 (CH), 23.8 (CH_2), 23.6 (CH_2), 18.7 (CH_2), 18.5 (CH_2), 18.2 (CH_3). Apparent peak doublets that arise from the presence of two diastereomers were reported as a single chemical shift. HRMS (ESI) calcd. for $C_{13}H_{19}NO_3$ $[M+H]^+$ 238.1438, found 238.1429.

[4.2.0] Amide 1b. Acid **5** (100 mg, 0.66 mmol), Gly-OMe•HCl (87 mg, 0.69 mmol), EDC•HCl (139 mg, 0.72 mmol) and DIPEA (570 µL, 3.3 mmol) were allowed to react in 20 mL CH_2Cl_2 and subjected to work up as described. Chromatography (97:3/CH_2Cl_2:MeOH) yielded amide **1b,** (146 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H, =CH), 6.36 (s, 1H, CONH), 4.03 (m, 2H, side chain CH_2), 3.70 (s, 3H, OCH_3), 3.02 (dd, *J* = 10.4, 5.3 Hz, 1H, CH), 2.74 (dd, *J* = 9.7, 4.8 Hz, 1H, CH), 1.77 (m, 1H, CH_2), 1.67 (m, 2H, CH_2), 1.52 (m, 3H, CH_2), 1.37 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3 (COOR), 162.6 (CONH), 145.1 (=CH), 143.9 (=CH), 52.1 (OCH_3), 40.5 (side chain CH_2), 39.3 (CH), 37.6 (CH), 23.6 (CH_2), 23.5 (CH_2), 18.5 (CH_2), 18.1 (CH_2). HRMS (ESI) calcd. for $C_{12}H_{17}NO_3$ $[M+H]^+$ 224.1281, found 224.1273.

[4.2.0] Amide 1c. Acid **5** (300 mg, 2.0 mmol), propyl amine (130 mg, 2.2 mmol), EDC•HCl (421 mg, 2.2 mmol) and DIPEA (767 µL, 4.4 mmol) were allowed to react in 60 mL CH_2Cl_2 and subjected to work up as described. Chromatography (97:3/CH_2Cl_2:MeOH) yielded amide **1c,** (307 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ

6.69 (d, J = 0.9 Hz, 1H, =CH), 5.77 (s, 1H, CONH), 3.25 (qd, J = 13.3, 6.3 Hz, 2H, CH_2), 3.02 (dd, J = 10.4, 5.6 Hz, 1H, CH), 2.76 (q, J = 4.9 Hz, 1H, CH), 1.82 (m, 1H, CH_2), 1.70 (m, 2H, CH_2), 1.54 (m, 5H, side chain CH_2 and ring CH_2), 1.42 (m, 2H, CH_2), 0.91 (t, J = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9 (CONH), 144.6 (=CH), 144.0 (=CH), 40.6 (side chain CH_2), 39.3 (CH), 37.4 (CH), 23.9 (CH_2), 23.7 (CH_2), 22.8 (side chain CH_2), 18.7 (CH_2), 18.2 (CH_2), 11.2(CH_3). HRMS (ESI) calcd. for $C_{12}H_{19}NO$ $[M+H]^+$ 194.1539, found 194.1532.

[4.2.0] Amide 1d. Acid **5** (300 mg, 2.0 mmol), aniline (204 mg, 2.2 mmol), EDC•HCl (421 mg, 2.2 mmol) and DIPEA (767 µL, 4.4 mmol) were allowed to react in 60 mL CH_2Cl_2 and subjected to work up as described. Chromatography (98:2/CH_2Cl_2:MeOH) yielded amide **1d**, (170 mg, 40%) free of the major impurity *N*-phenyl-8-(phenylamino)bicyclo[4.2.0]octane-7-carboxamide. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 7.8 Hz, 2H, Ph), 7.36 (s, 1H, CONH), 7.31 (t, J = 7.9 Hz, 2H, Ph), 7.10 (t, J = 7.4 Hz, 1H, Ph), 6.83 (s, 1H, =CH), 3.15 (dd, J = 10.5, 5.5 Hz, 1H, CH), 2.82 (q, J = 5.1 Hz, 1H, CH), 1.89 (m, 1H), 1.78 (m, 2H), 1.60 (m, 3H), 1.46 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.6 (CONH), 145.4 (=CH), 145.0 (=CH), 137.6 (Ph), 129.0 (Ph), 129.0 (Ph), 124.2 (Ph), 124.2 (Ph), 119.6 (Ph), 39.6 (CH), 37.6 (CH), 24.0 (CH_2), 23.7 (CH_2), 18.8 (CH_2), 18.3 (CH_2). HRMS (ESI) calcd. for $C_{15}H_{17}NO$ $[M+H]^+$ 228.1383, found 228.1382.

[4.2.0] Amide 1e. Acid **5** (97 mg, 0.64 mmol), 3-*p*-tolyl-propan-1-amine (100 mg, 0.67 mmol), EDC•HCl (129 mg, 0.67 mmol) and DIPEA (226 μL, 1.3 mmol) were allowed to react in 20 mL CH_2Cl_2 and subjected to work up as described. Chromatography (97:3/CH_2Cl_2:MeOH) yielded amide **1e**, (147 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 – 6.97 (m, 4H, Ph), 6.65 (s, 1H, =CH), 5.66 (m, 1H, CONH), 3.35 (m, 2H, side chain CH_2), 2.97 (dd, J = 10.5, 5.6 Hz, 1H, CH), 2.75 (q, J = 5.1 Hz, 1H, CH), 2.62 (t, J = 7.6 Hz, 2H, side chain CH_2), 2.30 (s, 3H, CH_3), 1.84 (m, 2H, side chain CH_2), 1.78 (m, 2H, CH_2), 1.65 (m, 1H, CH_2), 1.55 (m, 3H, CH_2), 1.42 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.7 (CONH), 144.7 (=CH), 143.7 (=CH), 138.3 (Ph), 135.3 (Ph), 129.0 (Ph), 129.0 (Ph), 128.1 (Ph), 128.1 (Ph), 39.2 (side chain CH_2), 38.6 (CH), 37.4 (CH), 32.9 (side chain CH_2), 31.2 (side chain CH_2), 23.9 (CH_2), 23.7 (CH_2),

20.8 (side chain CH_3), 18.6 (CH_2), 18.2 (CH_2). HRMS (ESI) calcd. for $C_{19}H_{25}NO$ $[M+H]^+$ 284.2009, found 284.2005.

[4.2.0] Amide 1f. Acid **5** (200 mg, 2.0 mmol), *(S)*-2-phenylglycinol (400 mg, 2.2 mmol), EDC•HCl (281 mg, 2.2 mmol) and DIPEA (767 μL, 4.4 mmol) were allowed to react in 40 mL CH_2Cl_2 and subjected to work up as described. The crude product was developed on silica TLC plates with 20:1/CH_2Cl_2:MeOH and two partially separated spots were observed with R_f values = 0.32 and 0.25. Chromatography (97:3/CH_2Cl_2:MeOH) yielded two diastereomers: **A** (60 mg, 11%) and **A*** (50 mg, 9%). Each diastereomer (50 mg, 0.18 mmol) was mixed with acetic anhydride (20.7 mg, 0.203 mmol) and TEA (20.5 mg, 0.203 mmol) in anhydrous CH_2Cl_2, and the mixture was stirred for 16 h. After concentrating *in vacuo*, the reaction mixture was subjected to flash chromatography (97:3/CH_2Cl_2:MeOH) to yield amide **1f** (41 mg, 62%) from the higher R_f alcohol **A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.23 (m, 5H, Ph), 6.75 (s, 1H, =CH), 6.20 (d, *J* = 7.8 Hz, 1H, CONH), 5.35 (td, *J* = 7.8, 5.0 Hz, 1H, CH), 4.50 (dd, *J* = 11.5, 7.7 Hz, 1H, CH_2O), 4.26 (dd, *J* = 11.5, 4.6 Hz, 1H, OCH_2), 3.06 (q, *J* = 5.5 Hz, 1H, CH), 2.78 (q, *J* = 4.9 Hz, 1H, CH), 2.04 (s, 3H, CH_3), 1.83 (m, 1H, CH_2), 1.76 – 1.68 (m, 2H, CH_2), 1.58 (m, 3H, CH_2), 1.44 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2 (COOR), 162.2 (CONH), 145.1 (=CH), 144.3 (=CH), 138.2 (Ph), 128.7 (Ph), 128.7 (Ph), 127.9 (Ph), 126.6 (Ph), 126.6 (Ph), 65.8 (OCH_2), 52.1 (side chain CH), 39.4 (CH), 37.6 (CH), 23.8 (CH_2), 23.7 (CH_2), 20.7 (CH_3), 18.7 (CH_2), 18.3 (CH_2). HRMS (ESI) calcd. for $C_{20}H_{25}NO_3$ $[M+H]^+$ 314.1751, found 314.1749. Amide **1f*** (45 mg, 66%) was obtained from the lower R_f alcohol **A***. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.23 (m, 5H, Ph), 6.76 (s, 1H, =CH), 6.27 (d, *J* = 7.2 Hz, 1H, CONH), 5.35 (td, *J* = 7.8, 4.6 Hz, 1H, CH), 4.54 (dd, *J* = 11.5, 7.7 Hz, 1H, CH_2O), 4.27 (dd, *J* = 11.5, 4.5 Hz, 1H, OCH_2), 3.07 (dd, *J* = 10.5, 5.6 Hz, 1H, CH), 2.81 (dd, *J* = 9.9, 4.9 Hz, 1H, CH), 2.03 (s, 3H, CH_3), 1.87 (m, 1H, CH_2), 1.75 (m, 2H, CH_2), 1.59 (m, 3H, CH_2), 1.46 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5 (COOR), 162.2 (CONH), 144.8 (=CH), 144.4 (=CH), 138.3 (Ph), 128.8 (Ph), 128.8 (Ph), 127.9 (Ph), 126.5 (Ph), 126.5 (Ph), 66.1 (OCH_2), 52.3 (side chain CH), 39.4 (CH), 37.7 (CH), 24.0 (CH_2), 23.7 (CH_2), 20.8 (CH_3), 18.7 (CH_2), 18.3 (CH_2). HRMS (ESI) calcd. for $C_{20}H_{25}NO_3$ $[M+H]^+$ 314.1751, found 314.1742.

[3.2.0] Amide 4. Acid **6** (138 mg, 1 mmol), L-Ala-OMe•HCl (157 mg, 1.1 mmol), EDC•HCl (210 mg, 1.1 mmol) and DIPEA (570 μL, 3.3 mmol) were allowed to react in 25 mL CH_2Cl_2 and subjected to work up as described. Chromatography (97:3/CH_2Cl_2:MeOH) yielded amide **4** as a mixture of diastereomers (157 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.49 (d, J = 5.0 Hz, 1H, =CH), 6.21 (s, 1H, CONH), 4.64 (m, 1H, CH), 3.75 (s, 3H, OCH_3), 3.32 (s, 1H, CH), 3.02 (d, J = 7.2 Hz, 1H, CH), 1.78-1.70 (m, 1H), 1.68-1.60 (m, 2H, CH_2), 1.57-1.54 (m, 1H, CH_2), 1.40 (d, J = 7.1 Hz, 3H, CH_3), 1.30-1.23 (m, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.5 (COOR), 161.6 (CONH), 142.1 (=CH), 140.6 (=CH), 52.4 (OCH_3), 47.4 (side chain CH), 45.8 (CH), 43.9 (CH), 25.6 (CH_2), 25.4 (CH_3), 23.0 (CH_2), 23.1 (CH_2), 18.6 (CH_2), 18.6 (CH_2). Apparent peak doublets that arise from the presence of two diastereomers were reported as a single chemical shift. HRMS (ESI) calcd. for $C_{12}H_{17}NO_3$ $[M+H]^+$ 224.1281, found 224.1278.

1e isomerization monitored by ^{13}C NMR spectroscopy. Amide **1e** (19.2 mg, 67 μmol, 1 equiv) and catalyst 2 (60 mg, 67 μmol, 1 equiv) were mixed in CD_2Cl_2 in an NMR tube and the reaction was monitored with ^{13}C NMR spectroscopy at 35 °C (Figure S4).

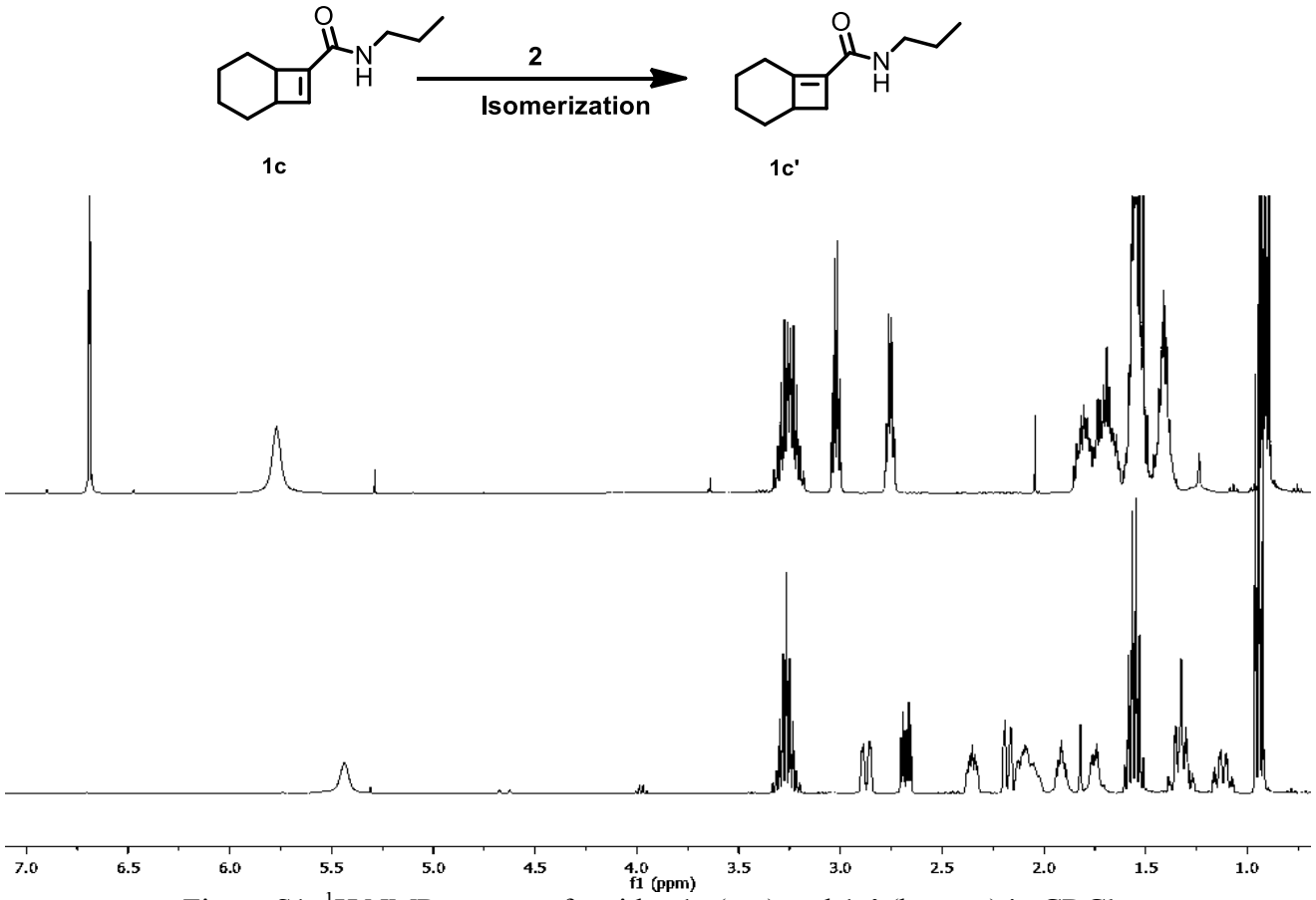


Figure S1. ^{1}H NMR spectra of amides **1c** (top) and **1c'** (bottom) in $CDCl_3$.

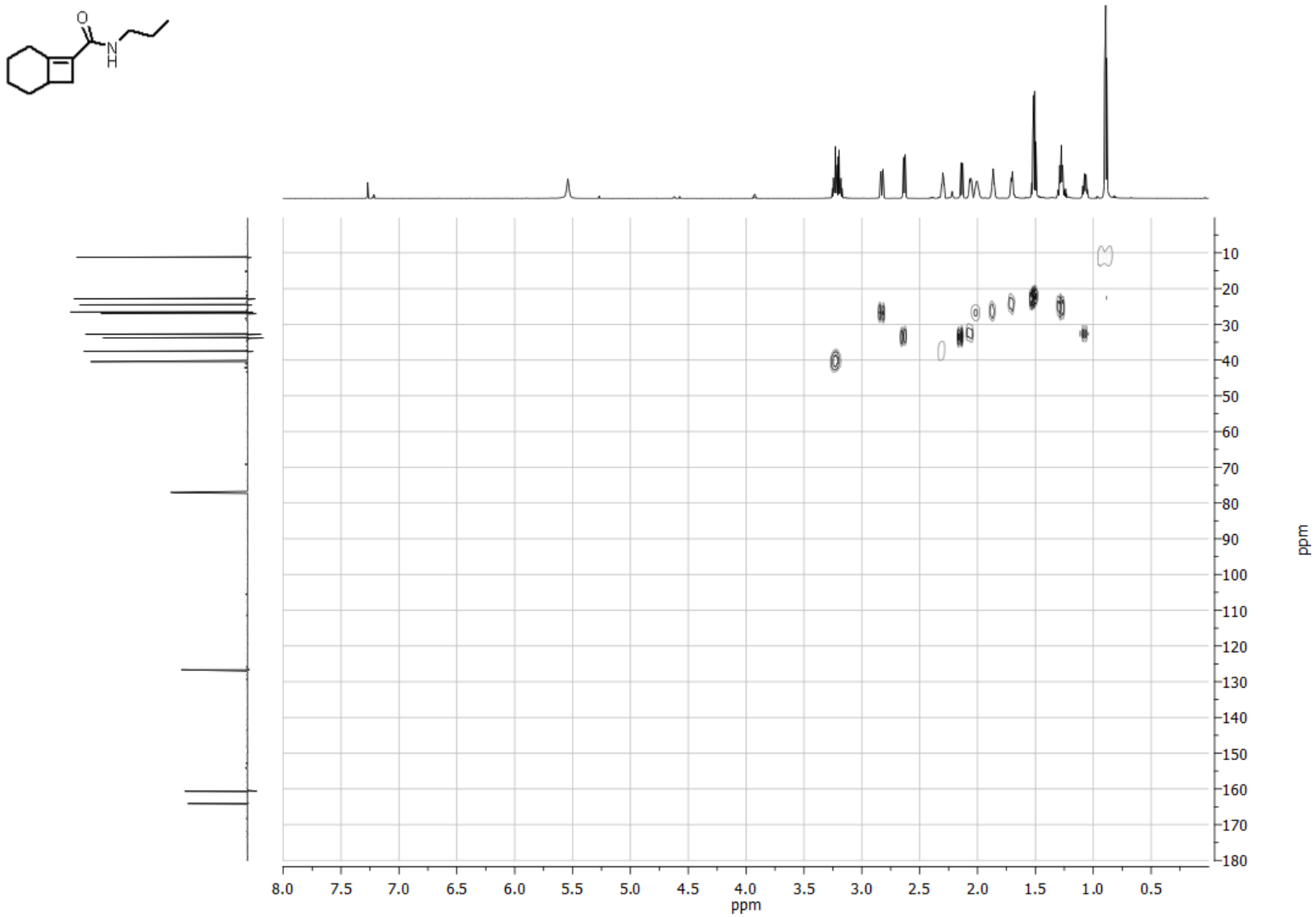


Figure S2. HSQC spectrum of amide **1c'** in $CDCl_3$.

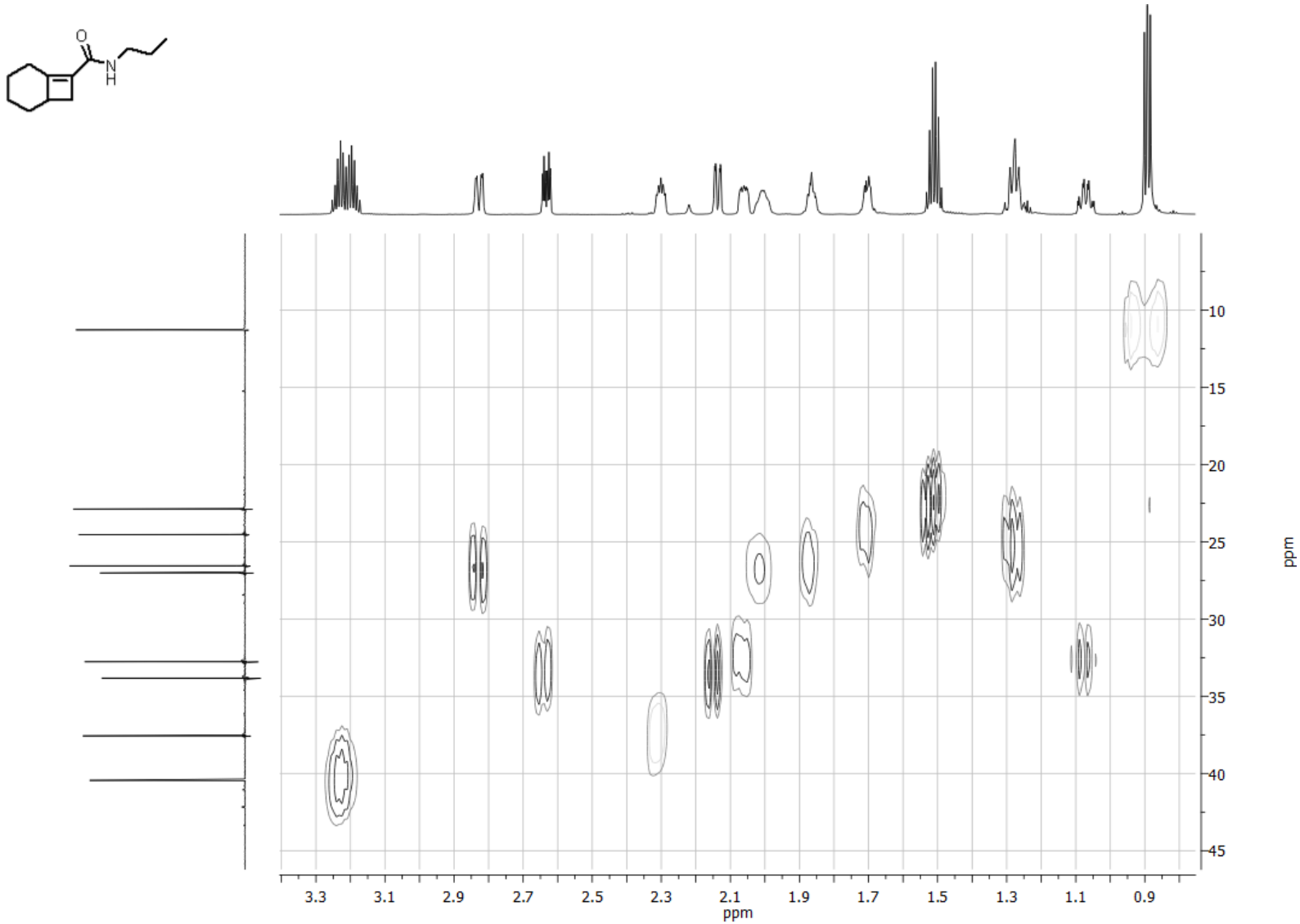
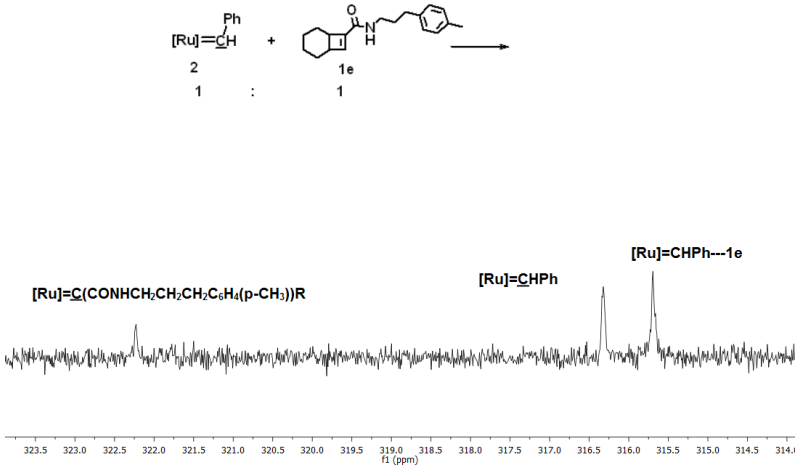


Figure S3. HSQC spectrum (upfield) of amide **1c'** in $CDCl_3$.

a



b

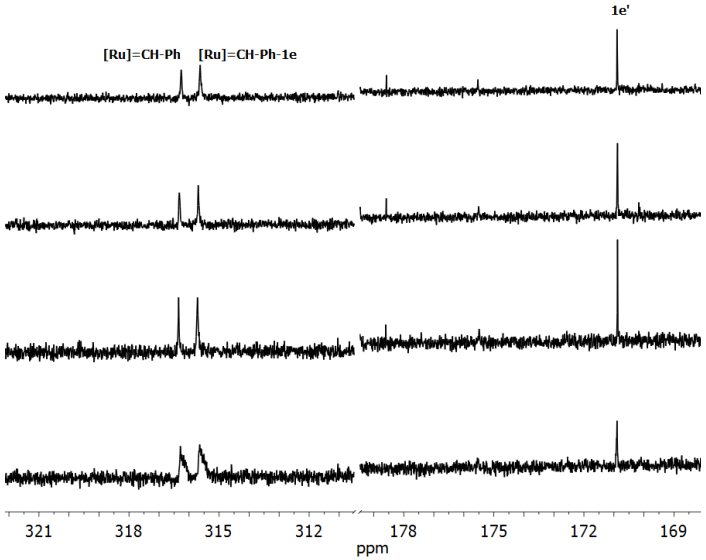


Figure S4. Kinetic ^{13}C NMR spectra of **1e** isomerization in the presence of catalyst **2** (1:1 ratio) in CD_2Cl_2.
(a) 70-90 min after mixing. (b) From bottom to top, spectra were obtained at 0-20 min, 40-55 min, 70-90 min, and 110-130 min.

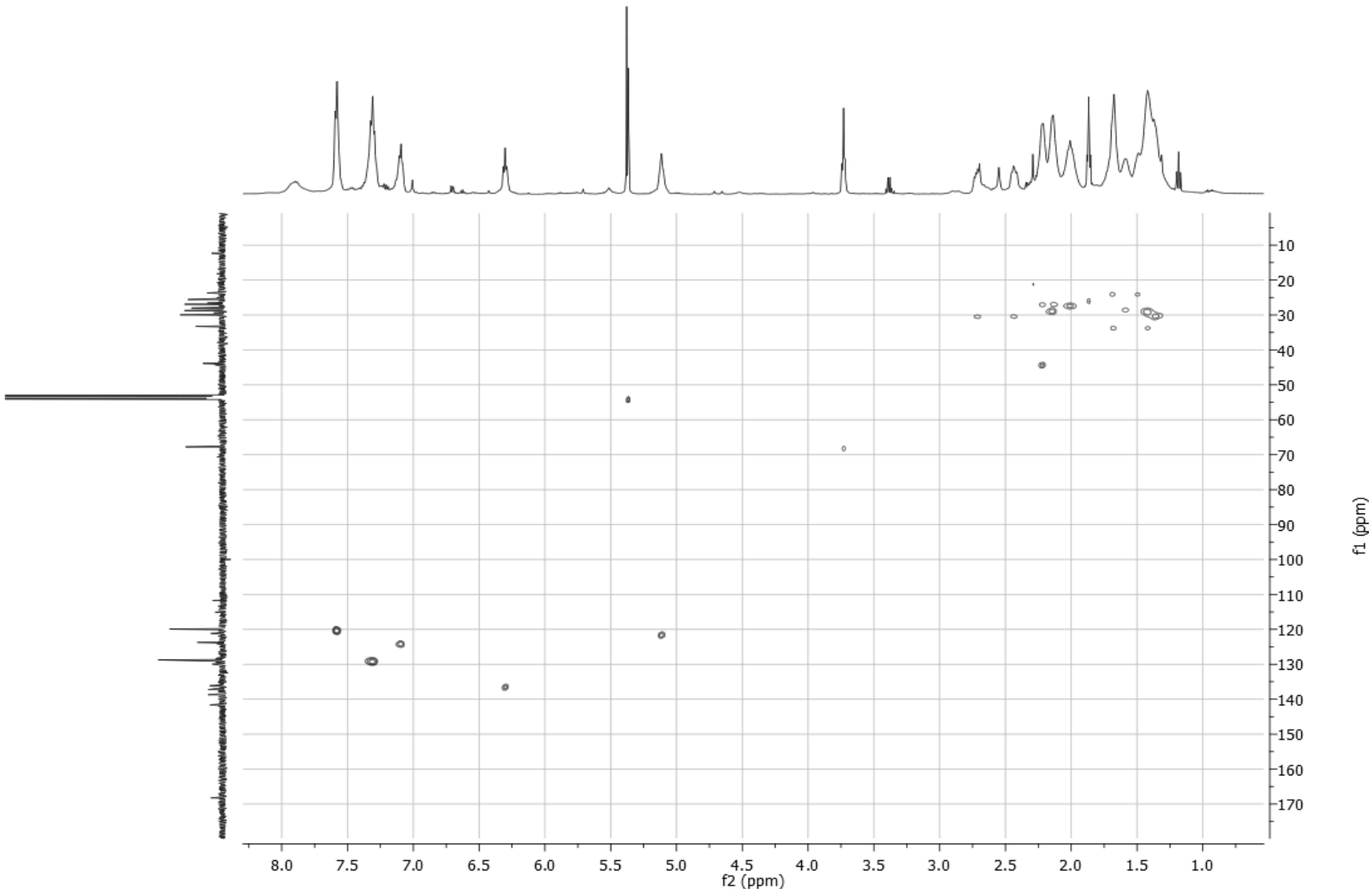


Figure S5. HSQC spectrum of poly(**1d'**-*alt*-**3**)$_{50}$ in CD_2Cl_2.

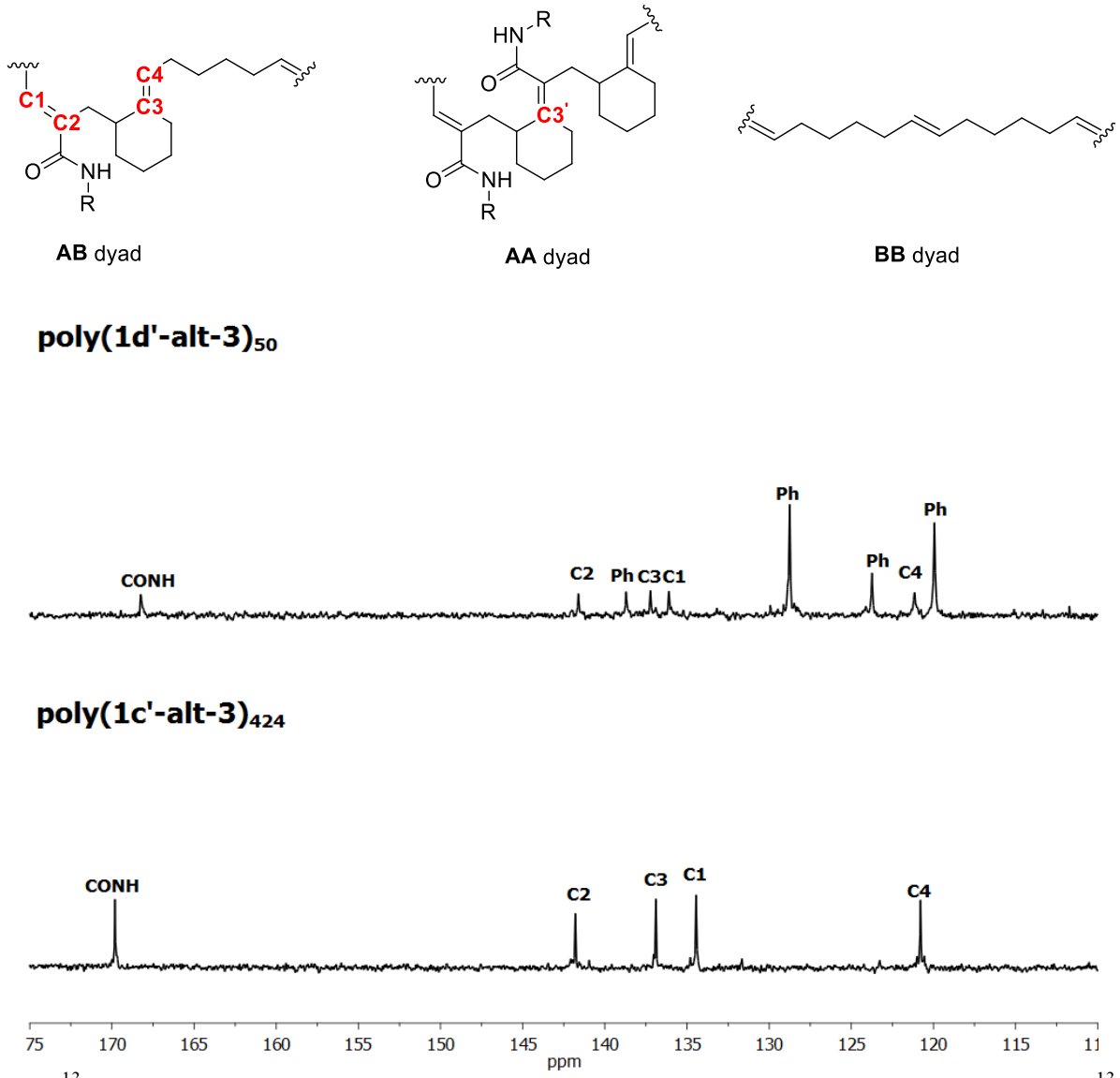


Figure S6. Partial ^{13}C NMR spectra of AROMP polymers illustrate the absence of **AA** dyad or **BB** dyad ^{13}C resonances.

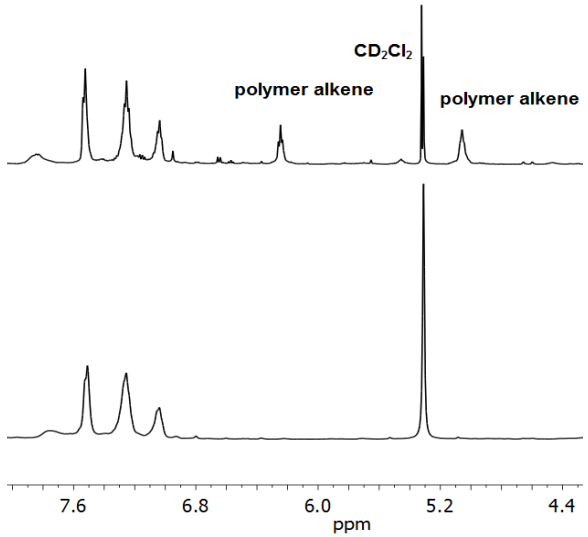


Figure S7. ^{1}H NMR spectra of poly(**1d'**-*alt*-**3**)$_n$ with (bottom) and without (top) deuterium labeling in CD_2Cl_2.

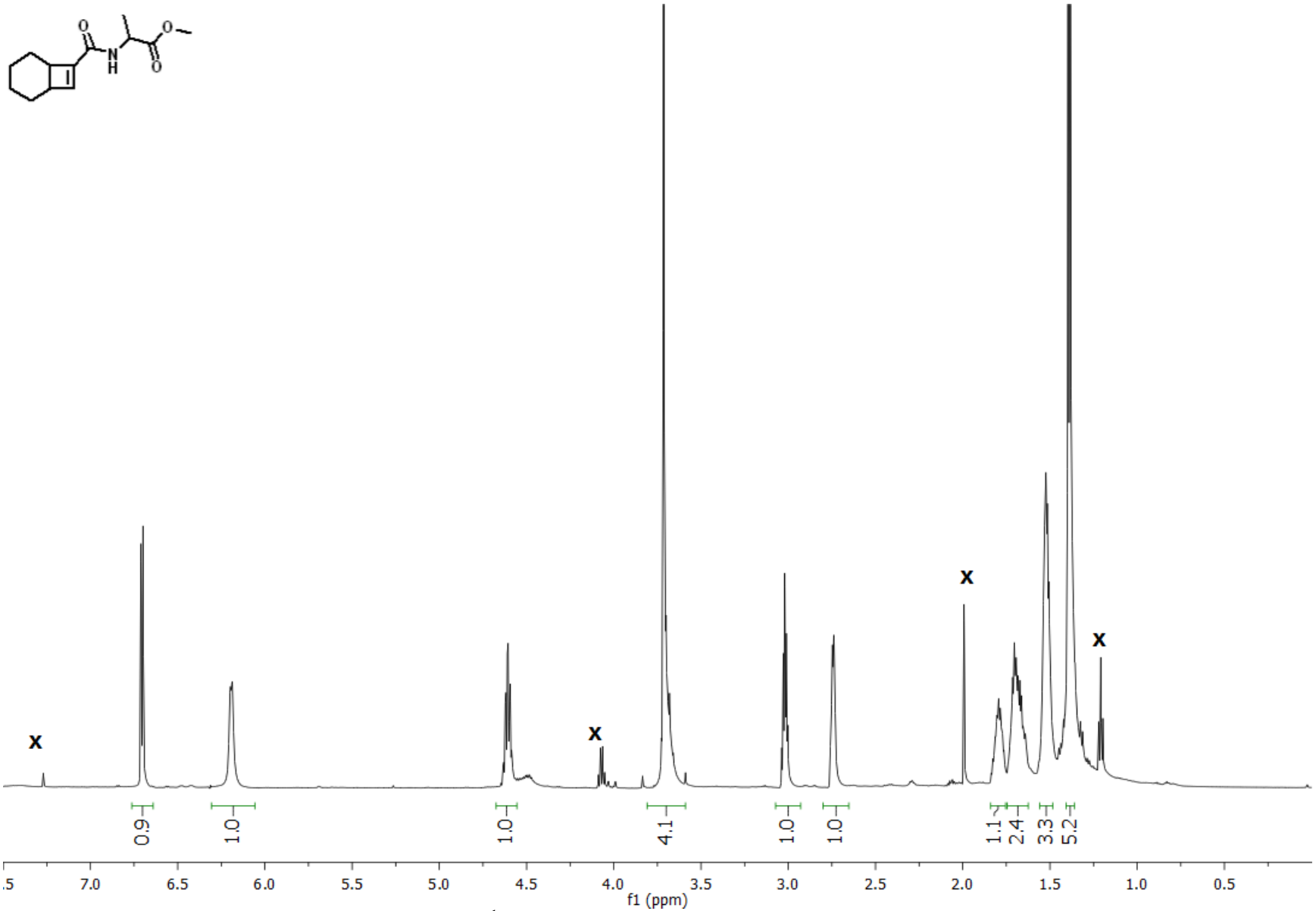


Figure S8. ^{1}H NMR spectrum of amide **1a** in $CDCl_3$.

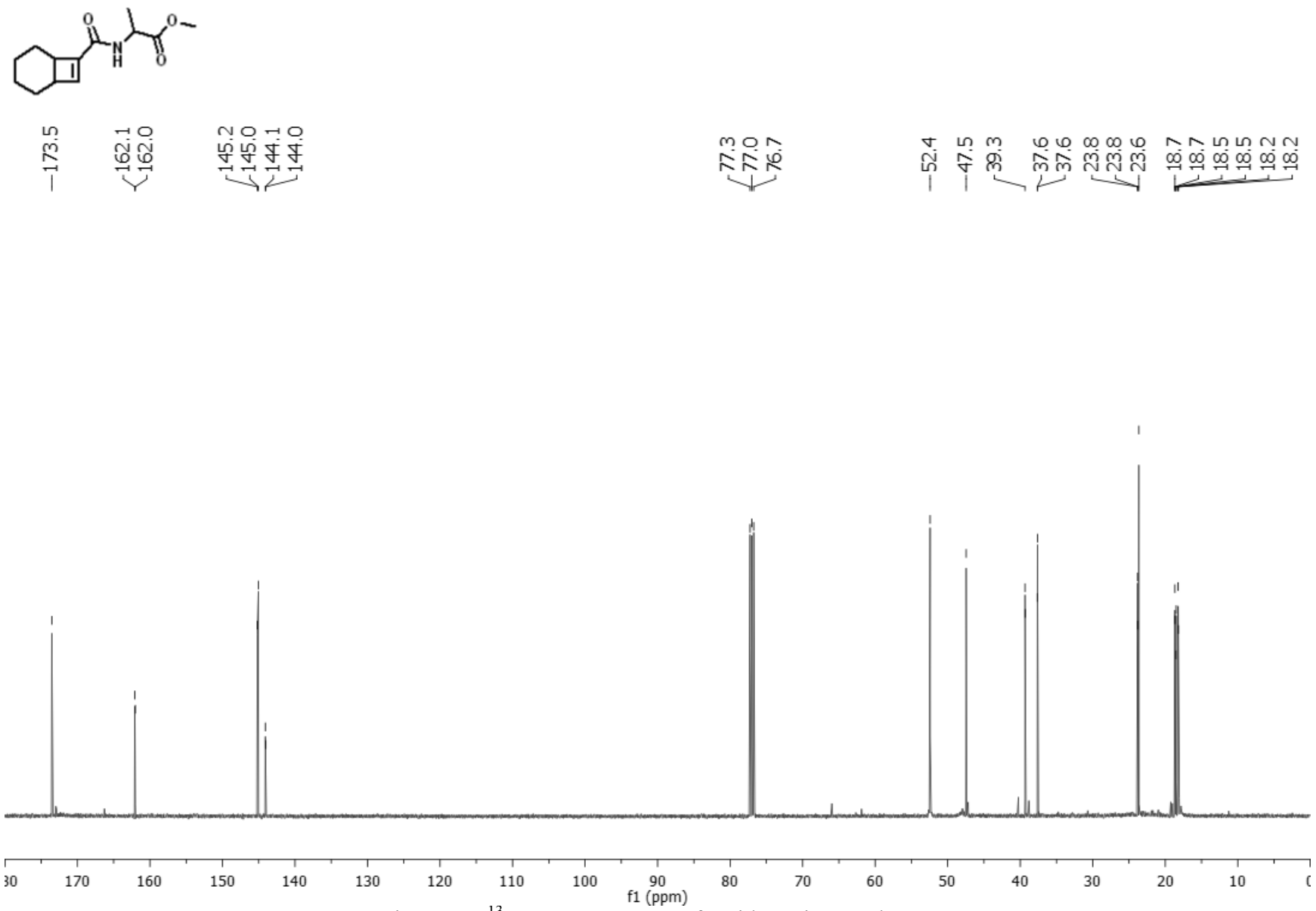


Figure S9. ^{13}C NMR spectrum of amide **1a** in $CDCl_3$.

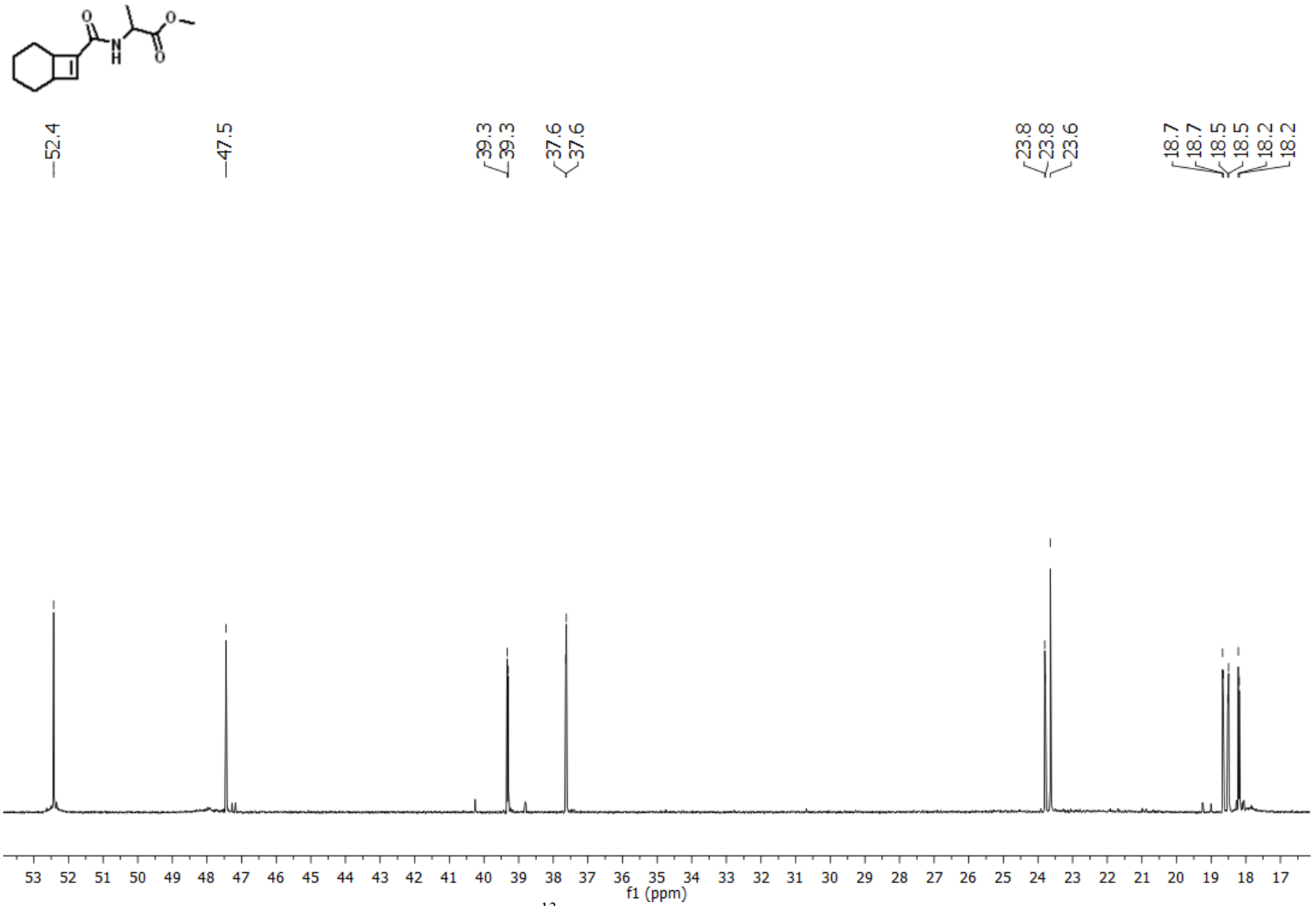


Figure S10. Partial ^{13}C NMR spectrum of amide **1a** in $CDCl_3$.

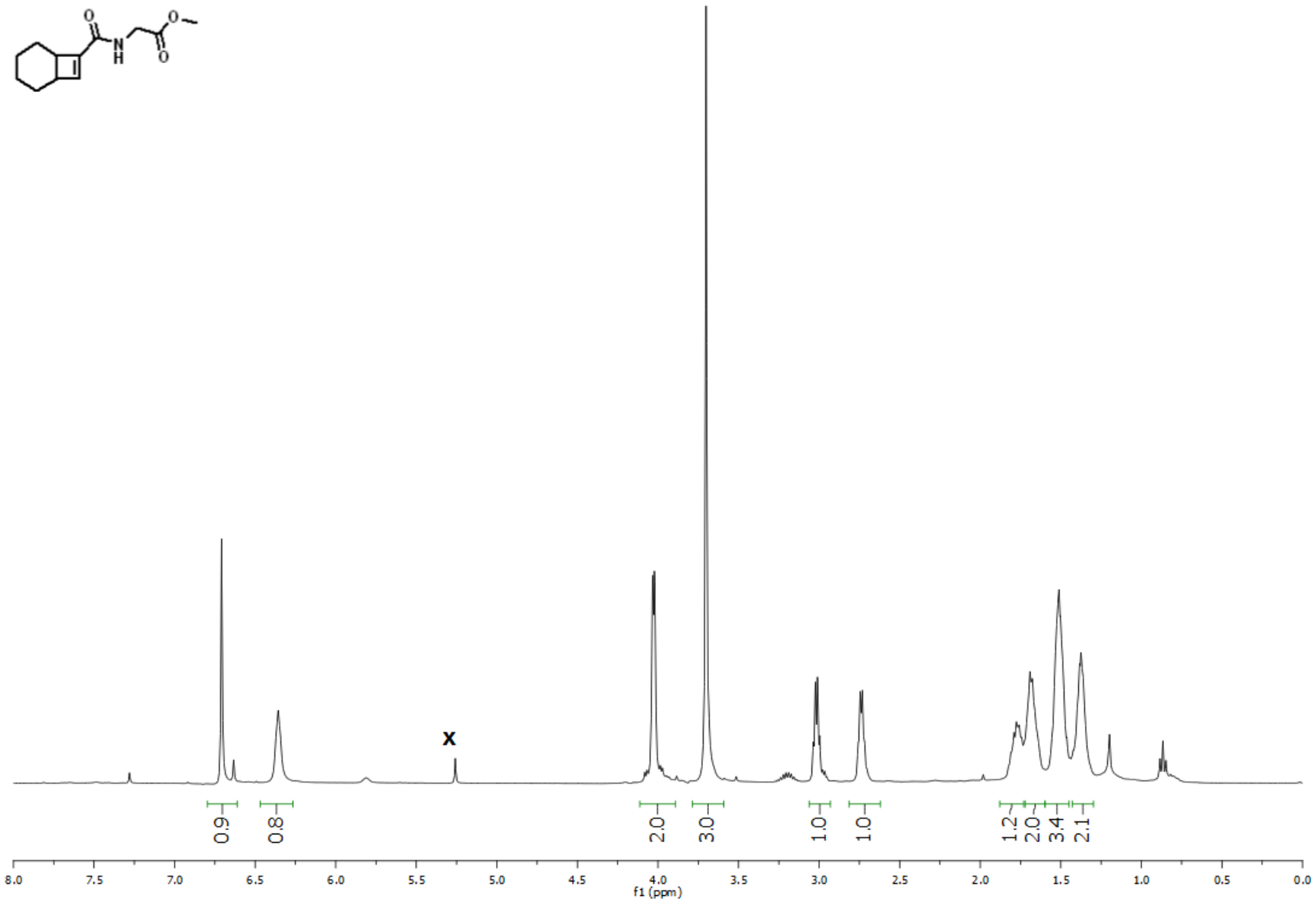


Figure S11. ^{1}H NMR spectrum of amide **1b** in $CDCl_3$.

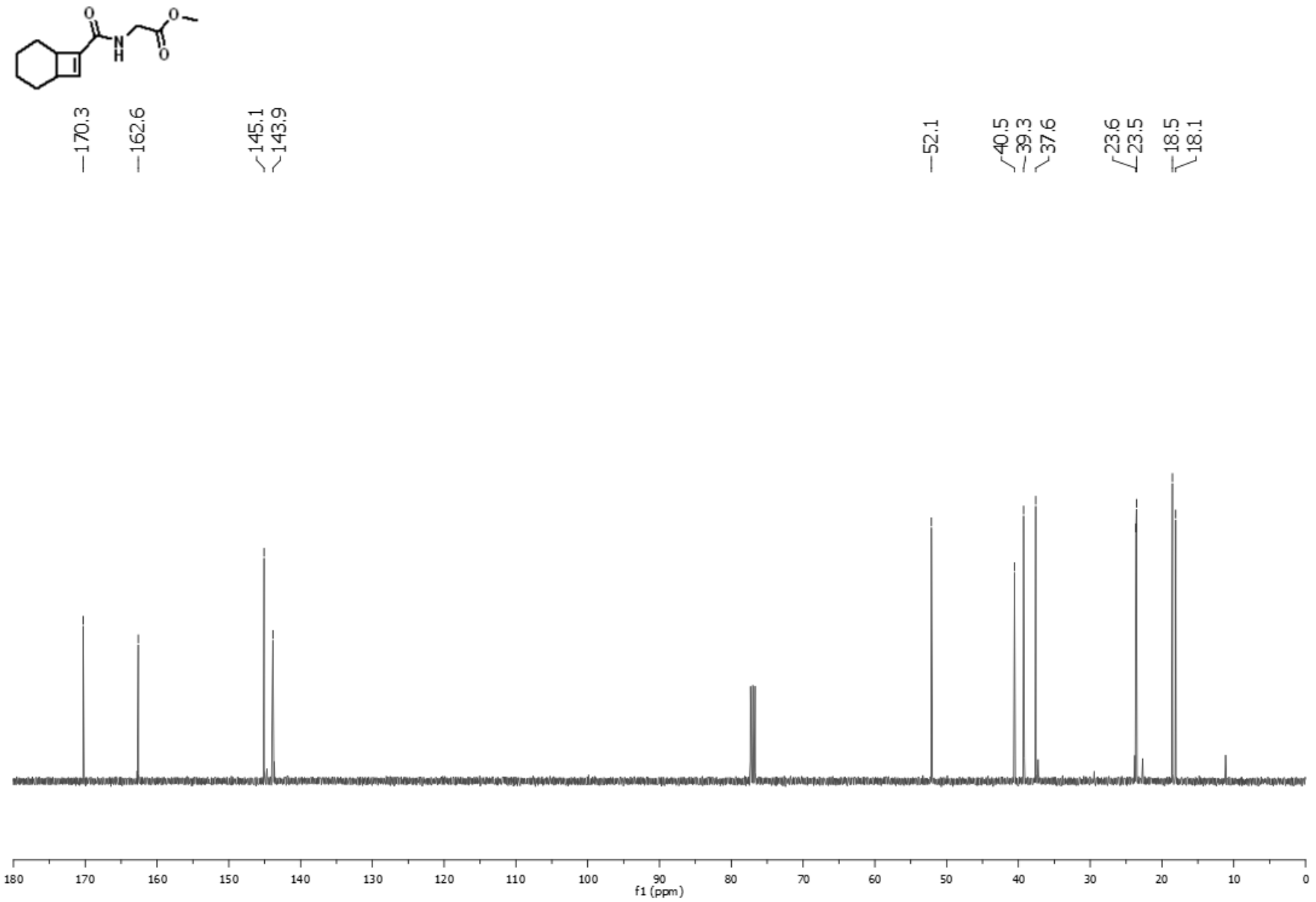


Figure S12. ^{13}C NMR spectrum of amide **1b** in $CDCl_3$.

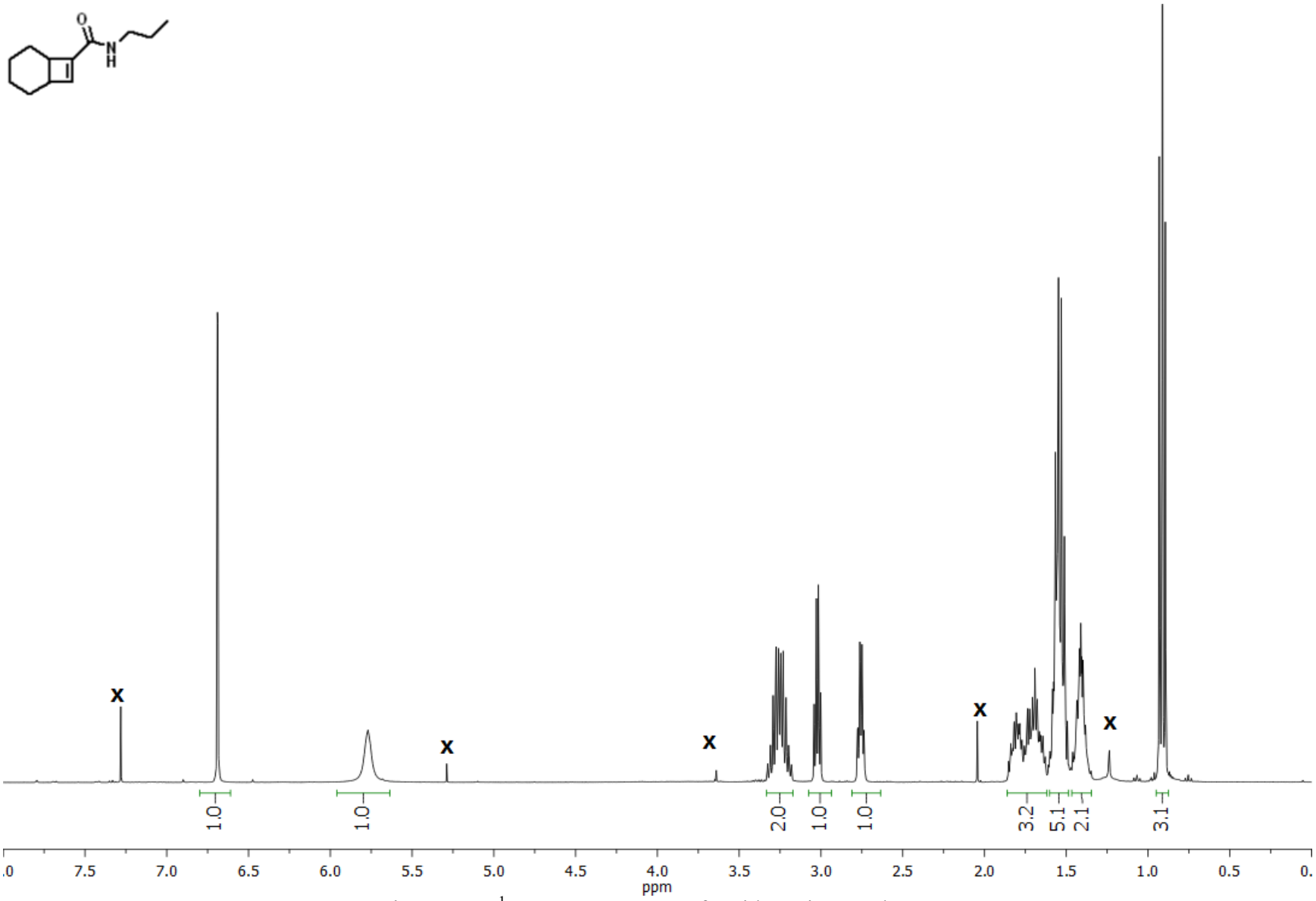


Figure S13. ^{1}H NMR spectrum of amide **1c** in $CDCl_3$.

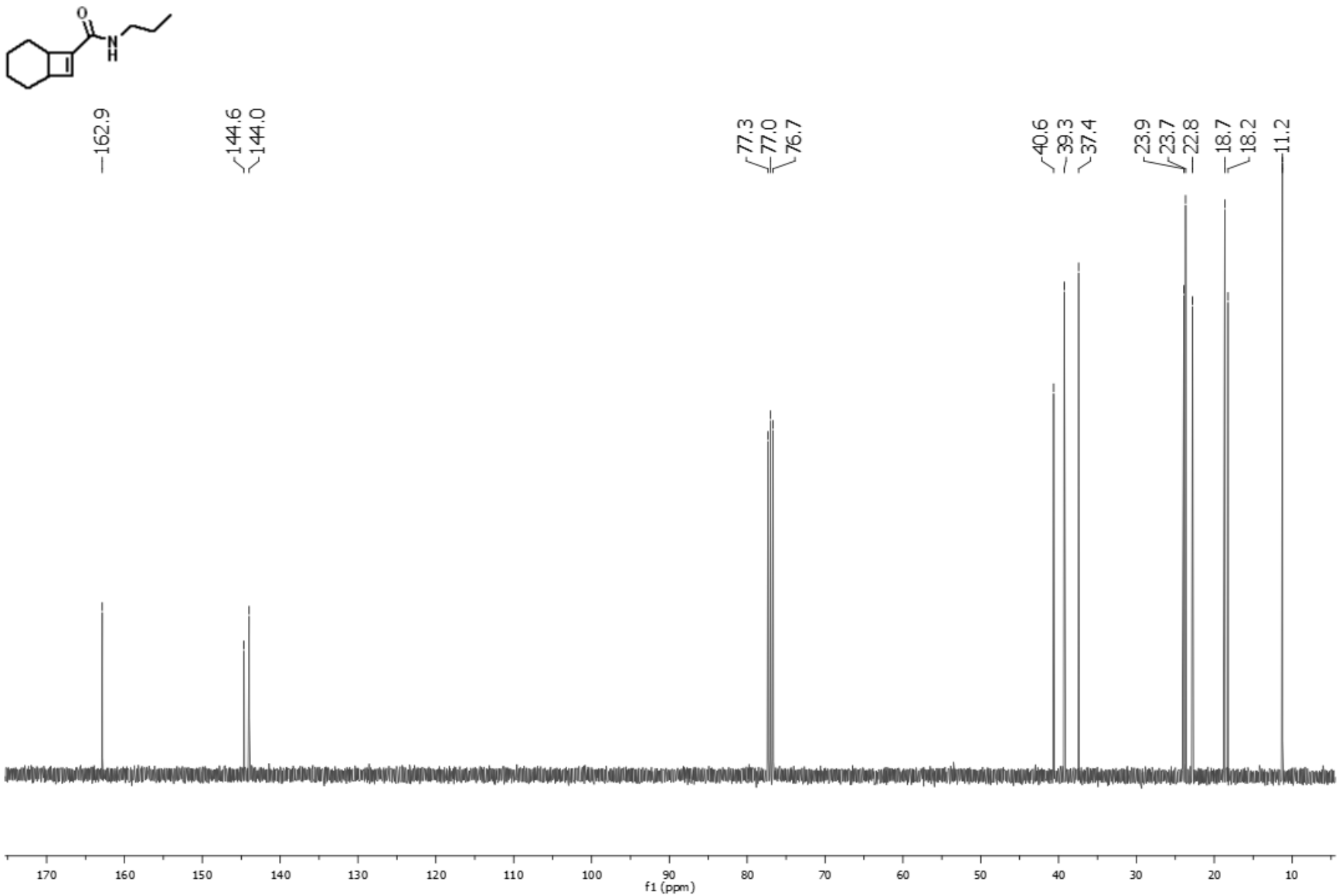


Figure S14. ^{13}C NMR spectrum of amide **1c** in $CDCl_3$.

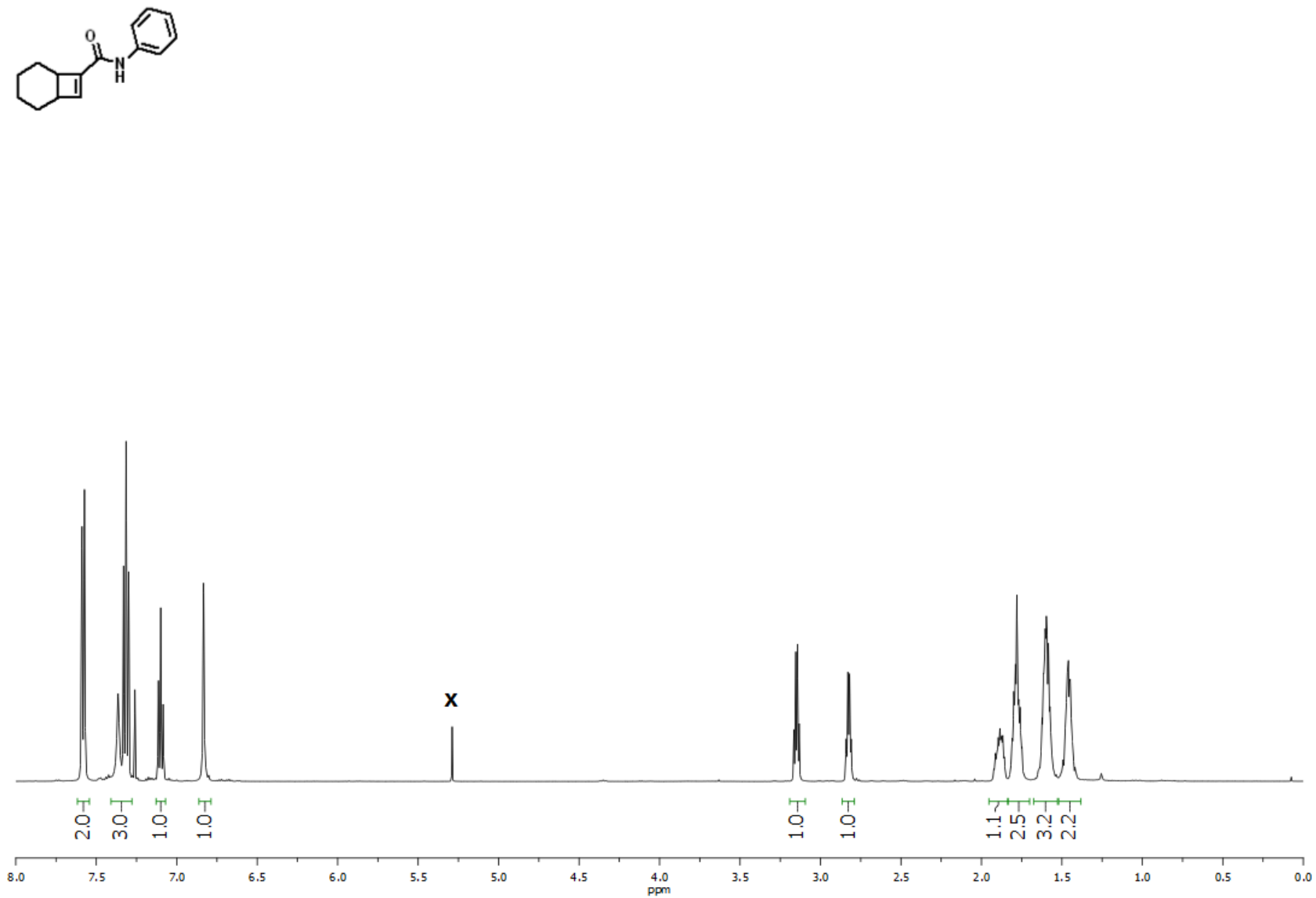


Figure S15. ^{1}H NMR spectrum of amide **1d** in CD_2Cl_2.

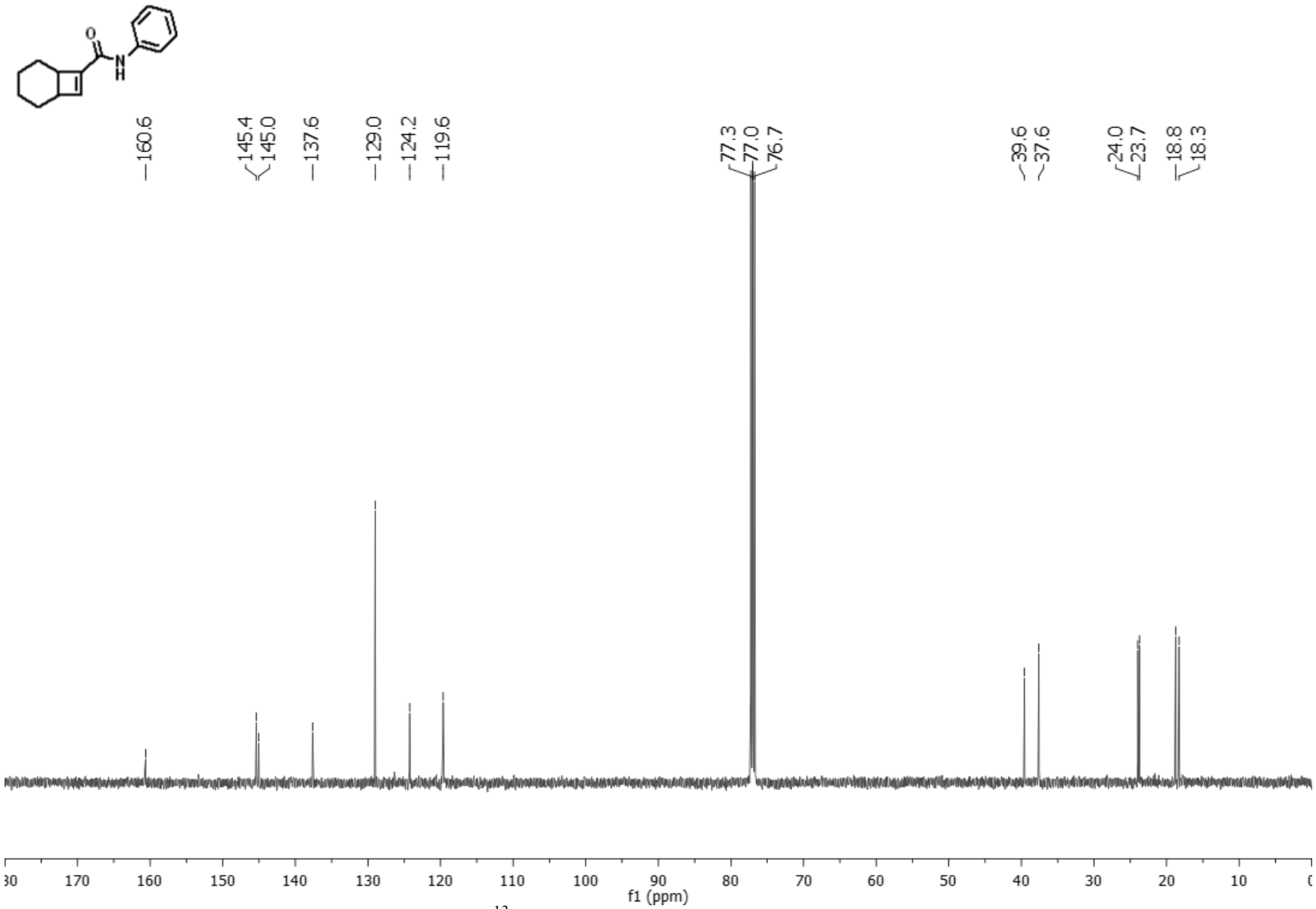


Figure S16. ^{13}C NMR spectrum of amide **1d** in $CDCl_3$.

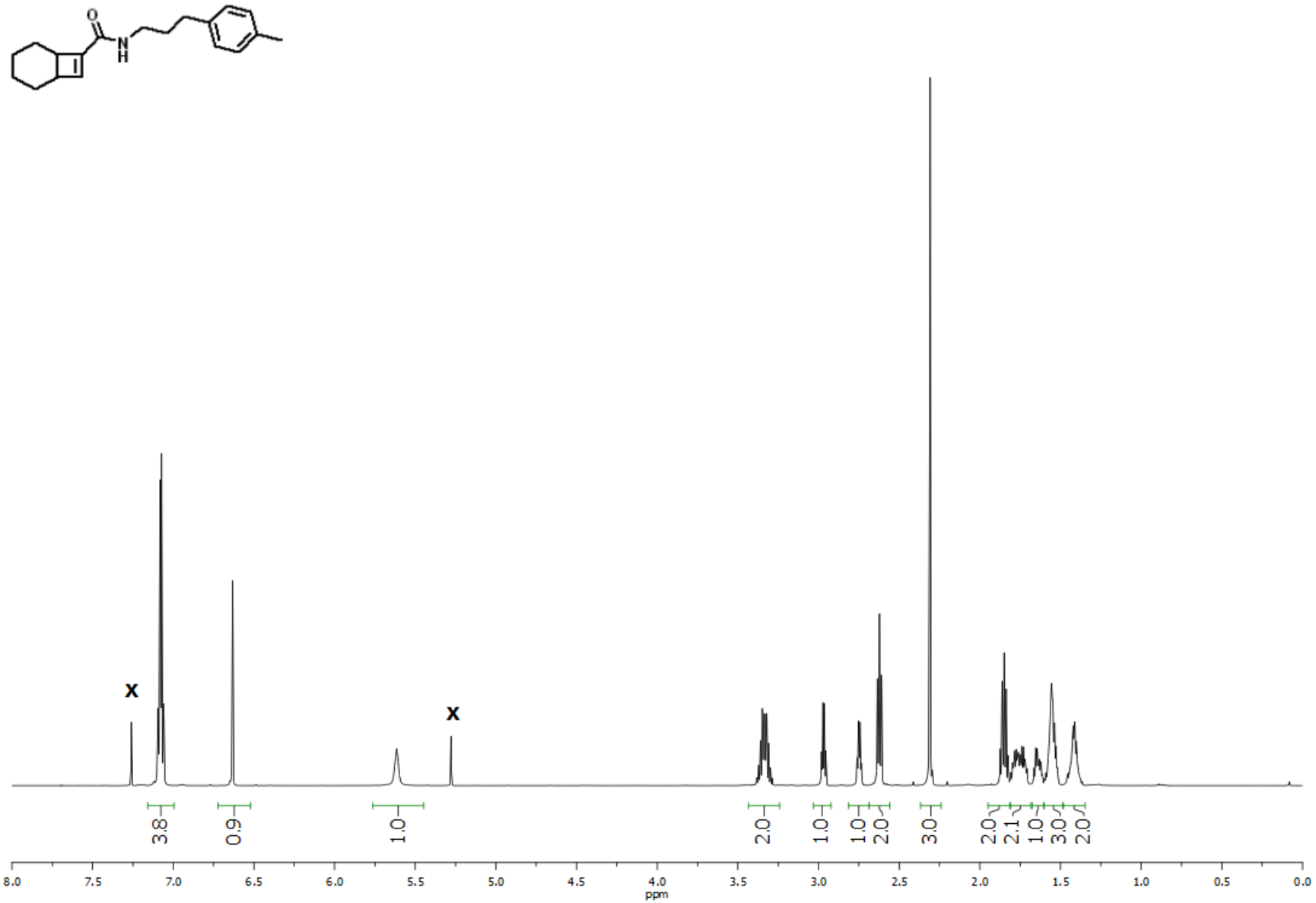


Figure S17. ^{1}H NMR spectrum of amide **1e** in $CDCl_3$.

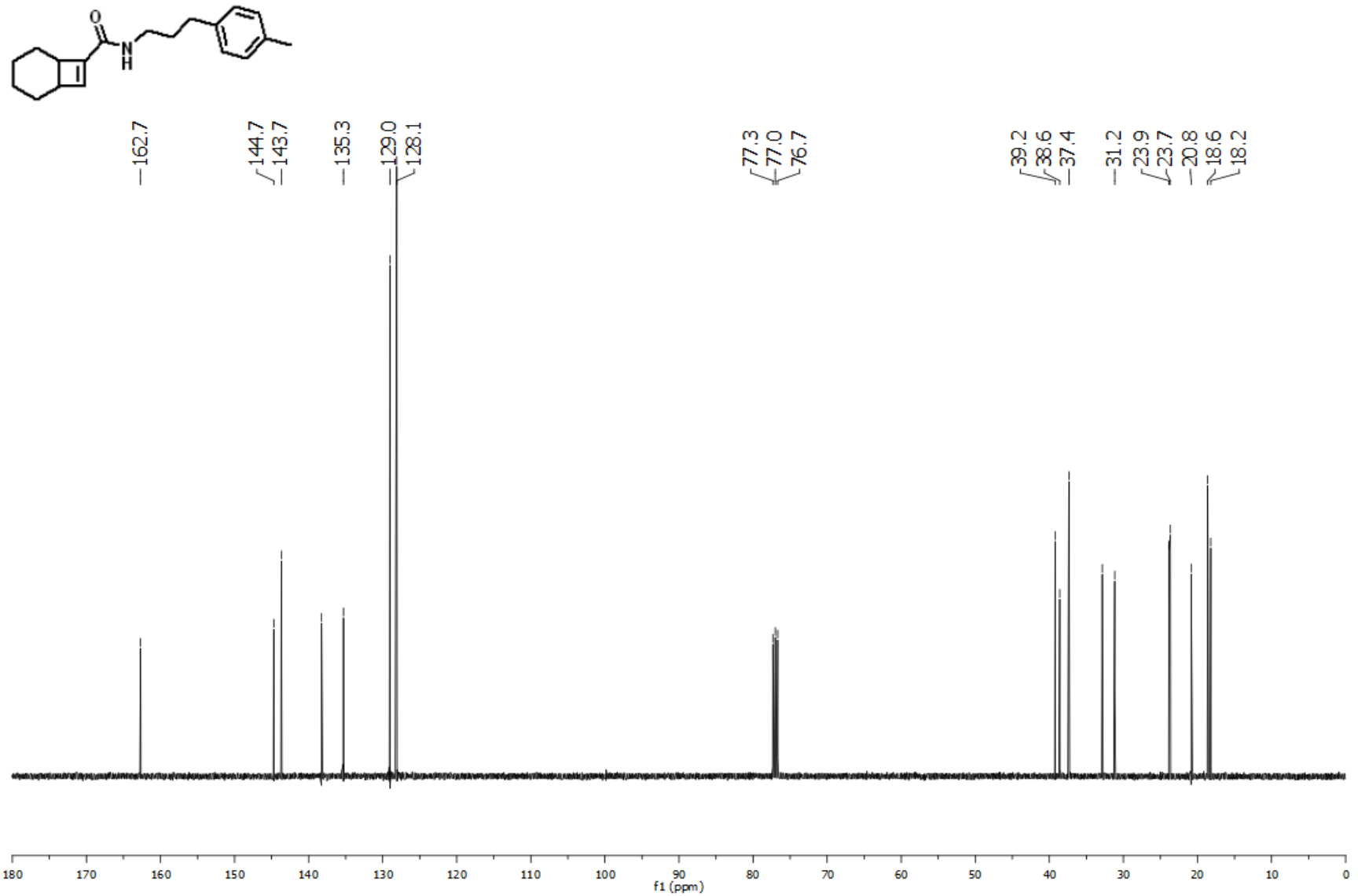


Figure S18. ^{13}C NMR spectrum of amide **1e** in $CDCl_3$.

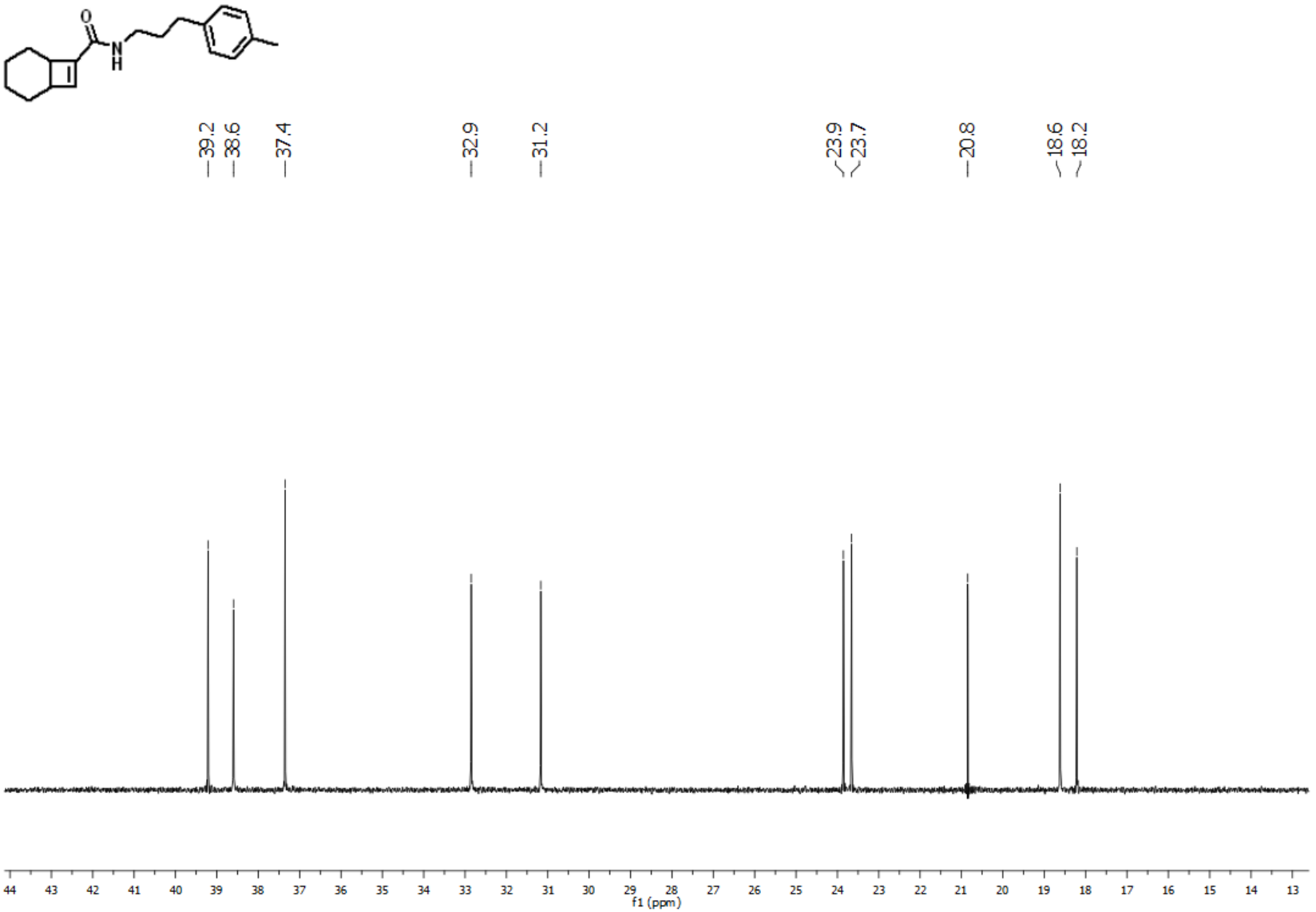


Figure S19. Partial ^{13}C NMR spectrum of amide **1e** in $CDCl_3$.

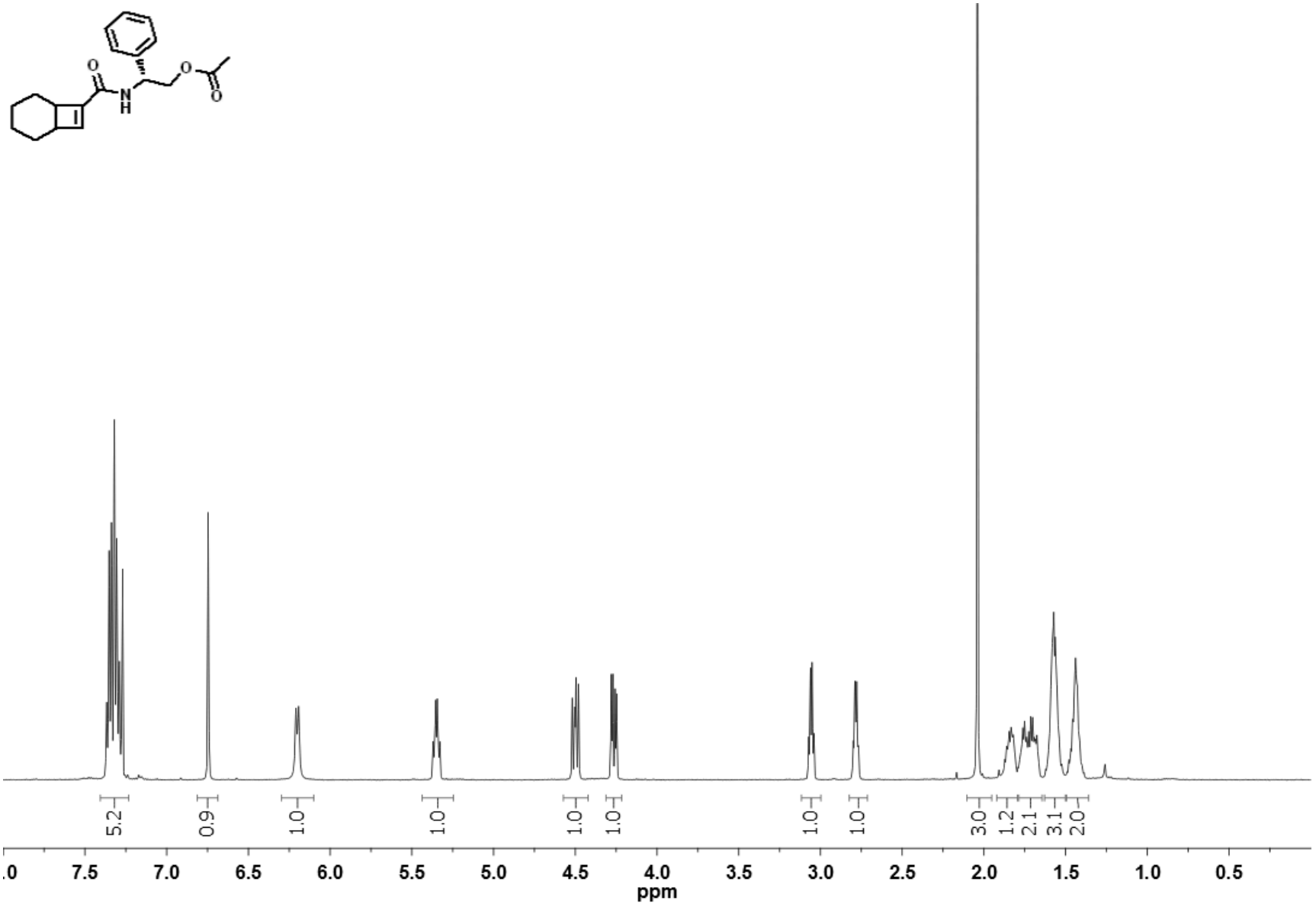


Figure S20. ^{1}H NMR spectrum of amide **1f** in $CDCl_3$.

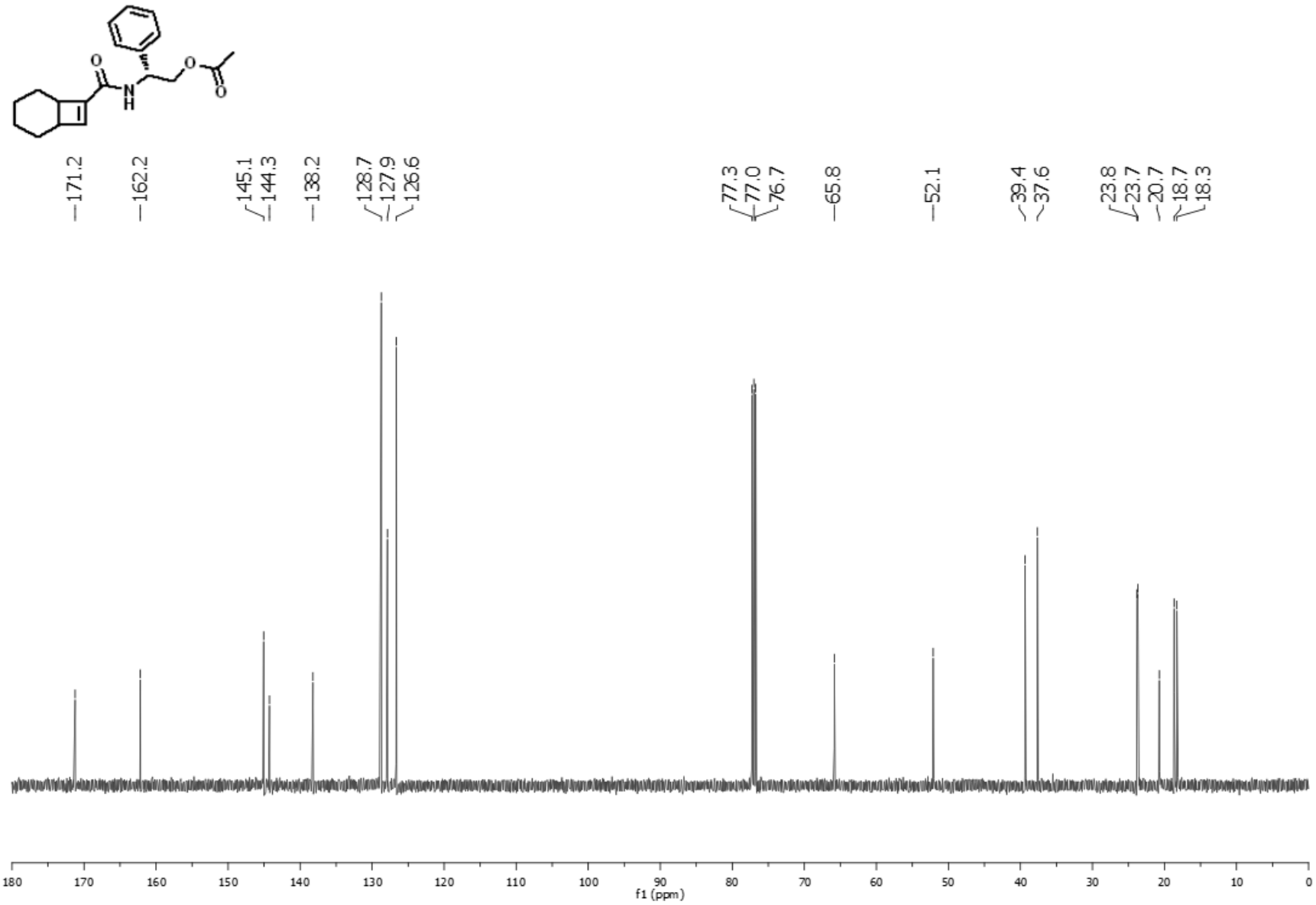


Figure S21. ^{13}C NMR spectrum of amide **1f** in $CDCl_3$.

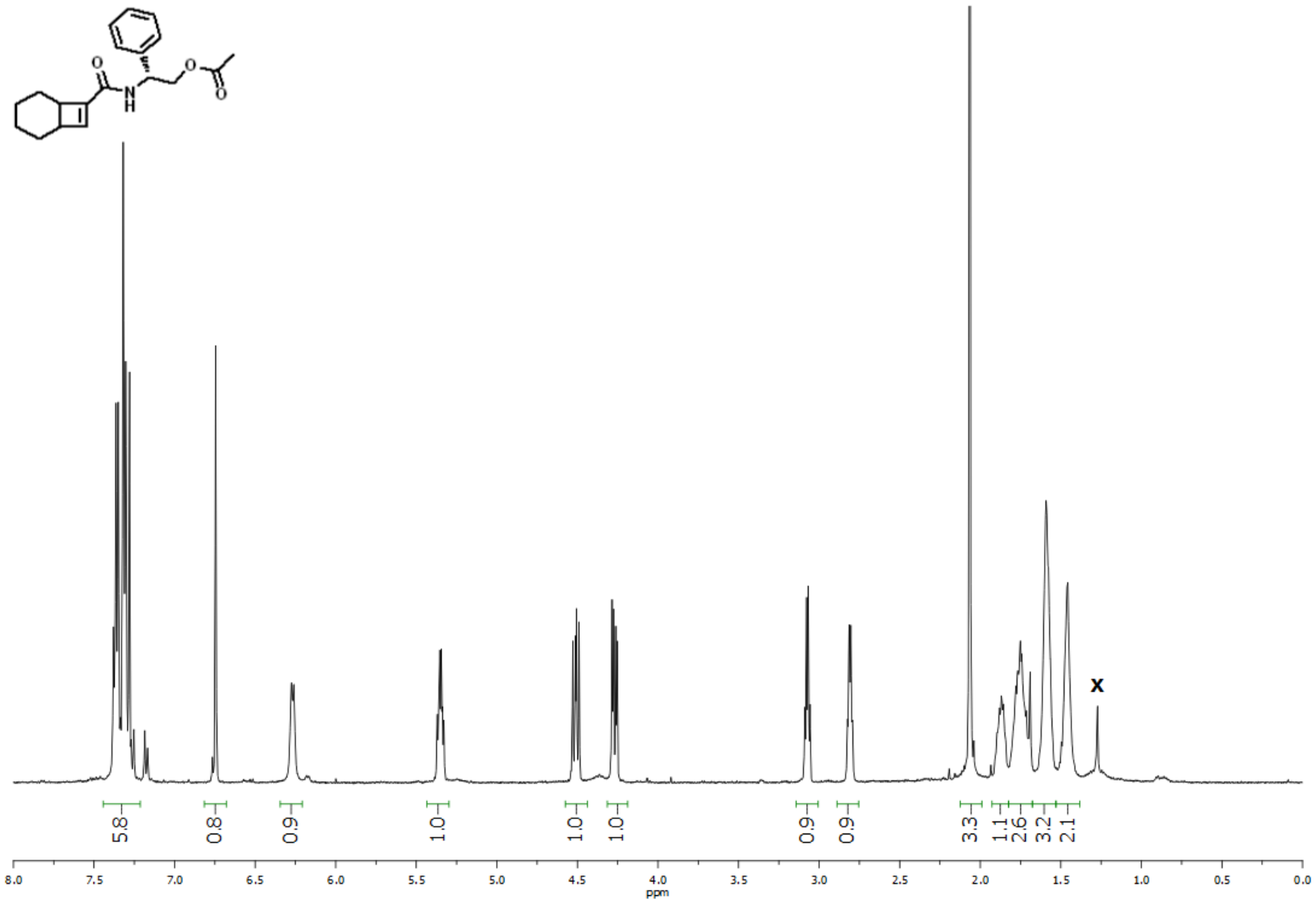


Figure S22. ^{1}H NMR spectrum of amide **1f*** in $CDCl_3$.

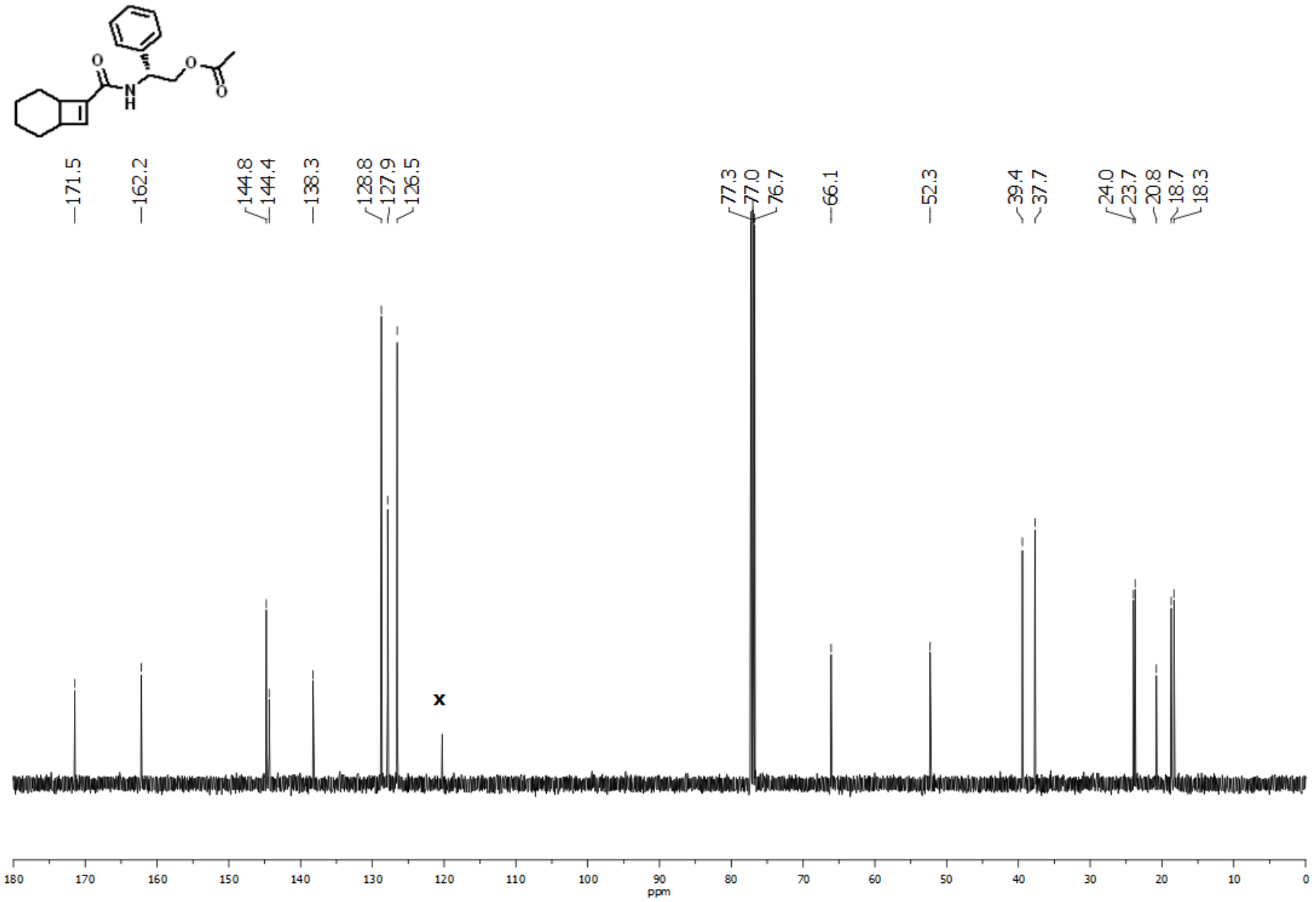


Figure S23. ^{13}C NMR spectrum of amide **1f*** in $CDCl_3$.

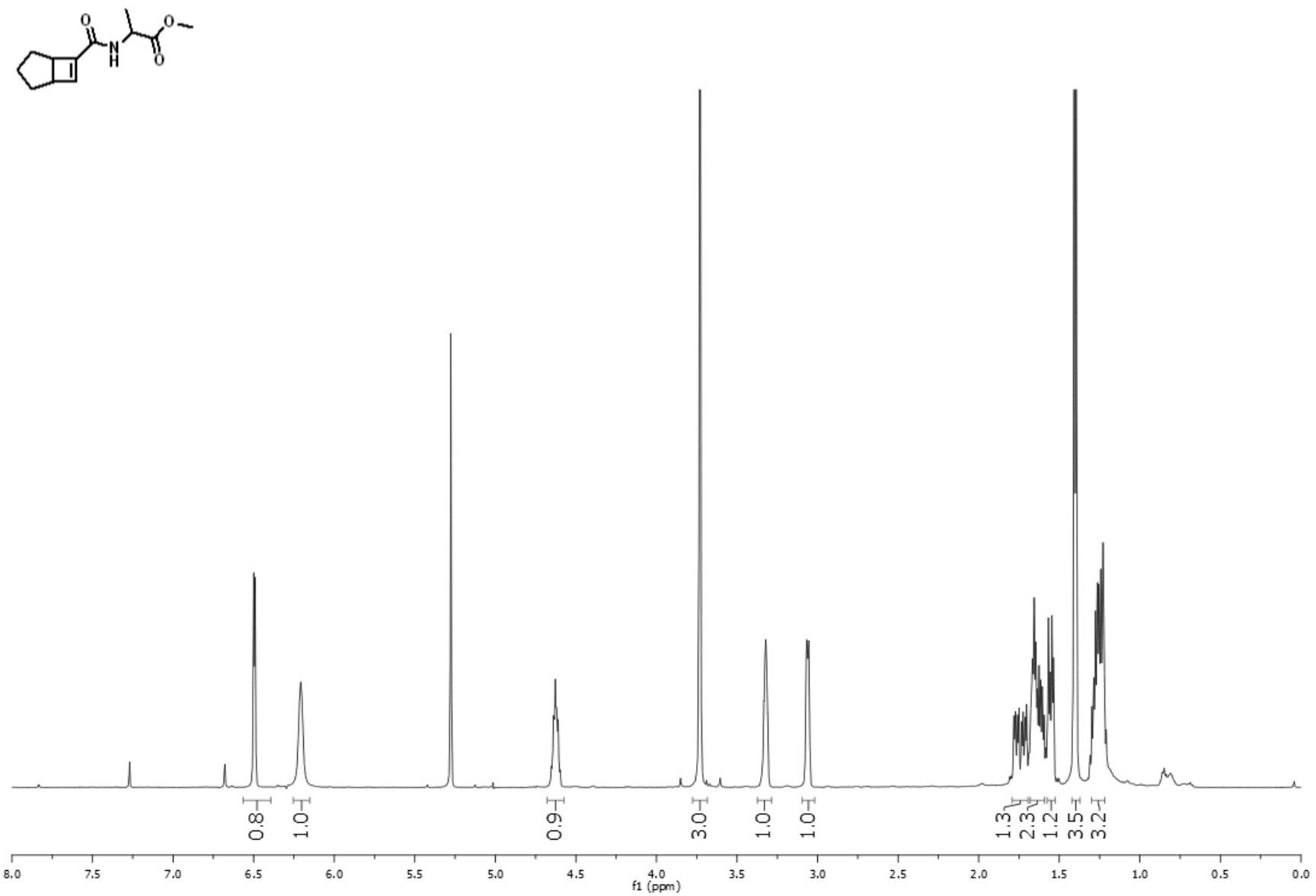


Figure S24. ^{1}H NMR spectrum of amide **4** in CD_2Cl_2.

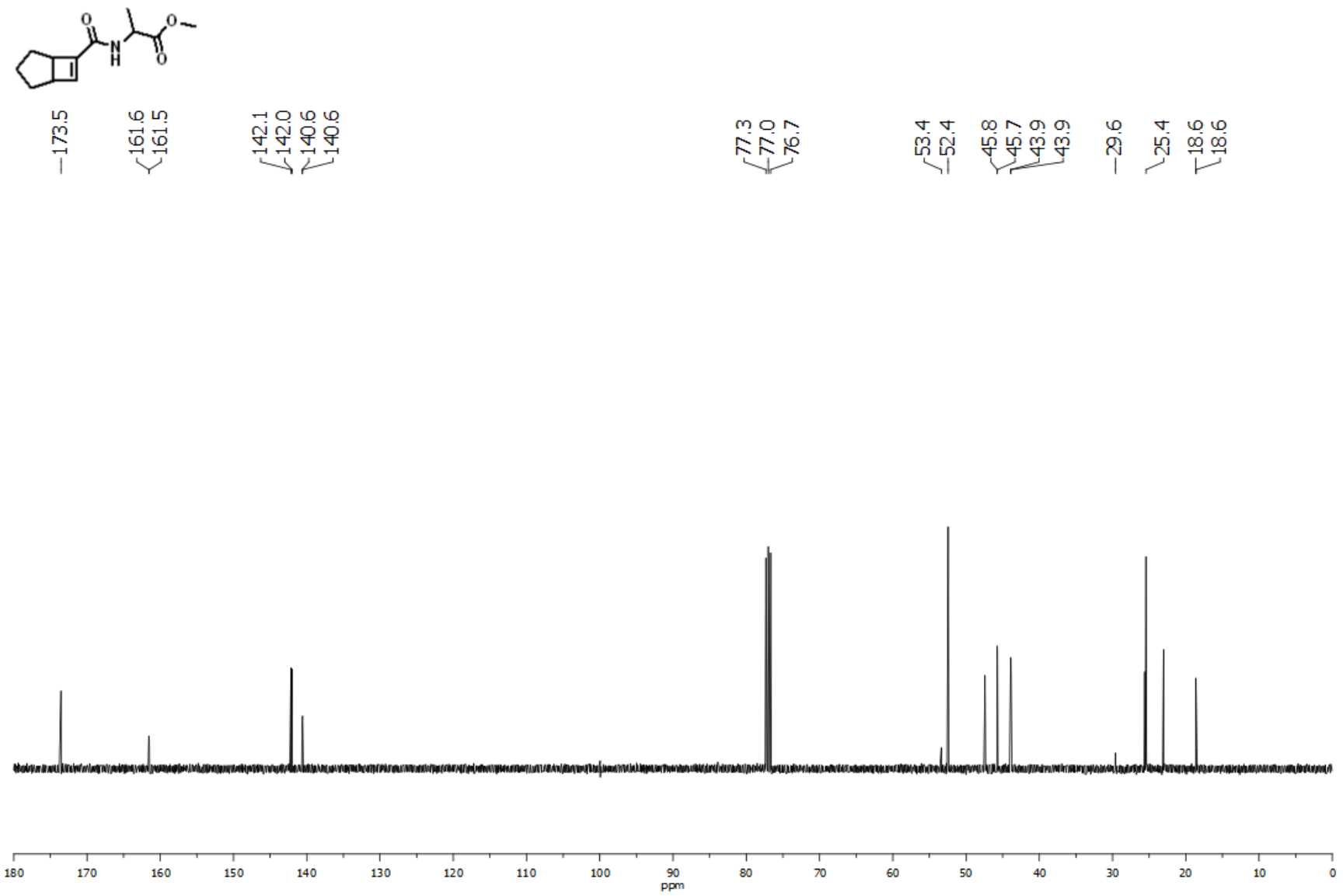


Figure S25. ^{13}C NMR spectrum of amide **4** in $CDCl_3$.

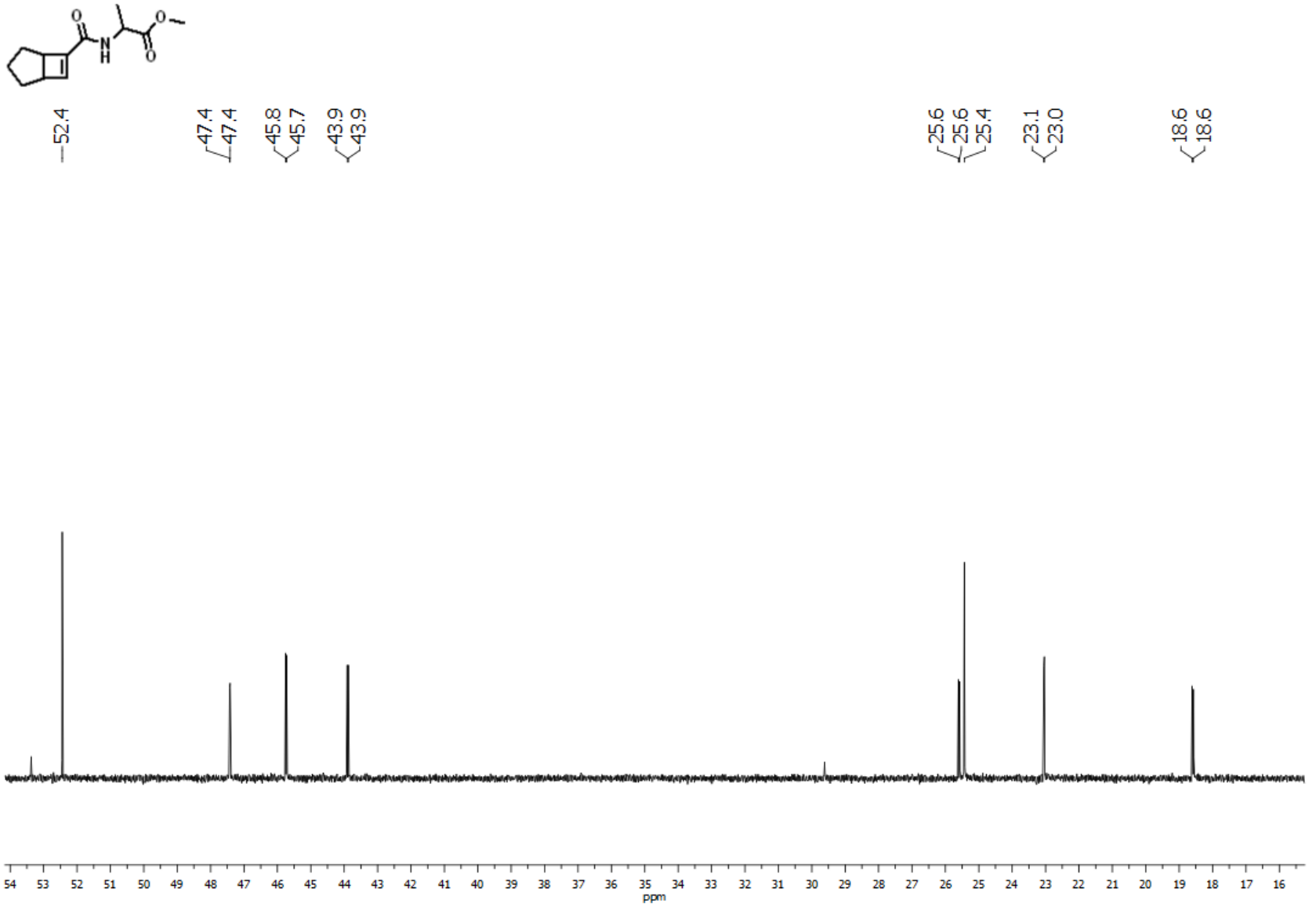


Figure S26. Partial ^{13}C NMR spectrum of amide **4** in $CDCl_3$.

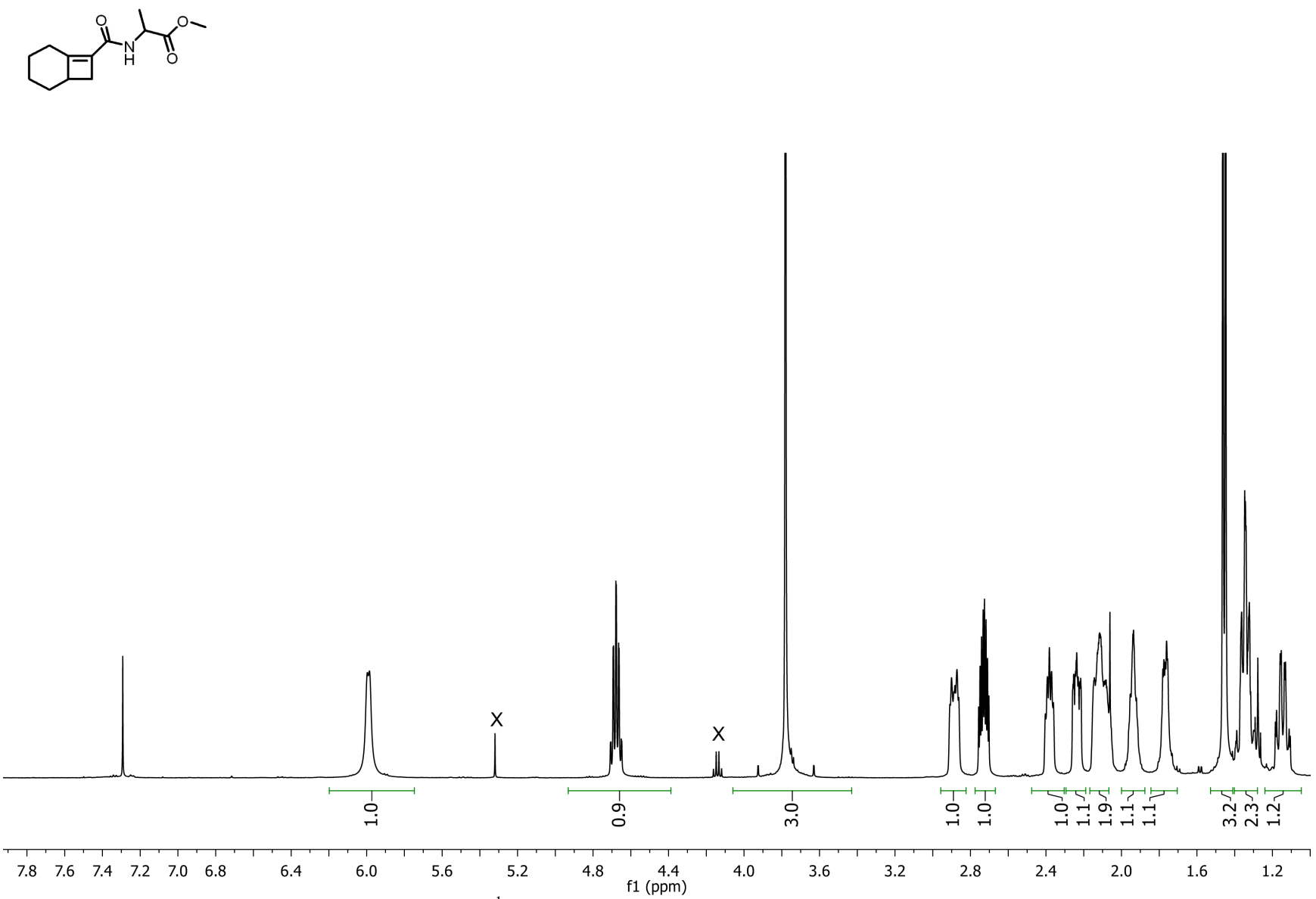


Figure S27. ^{1}H NMR spectrum of amide **1a'** in $CDCl_3$

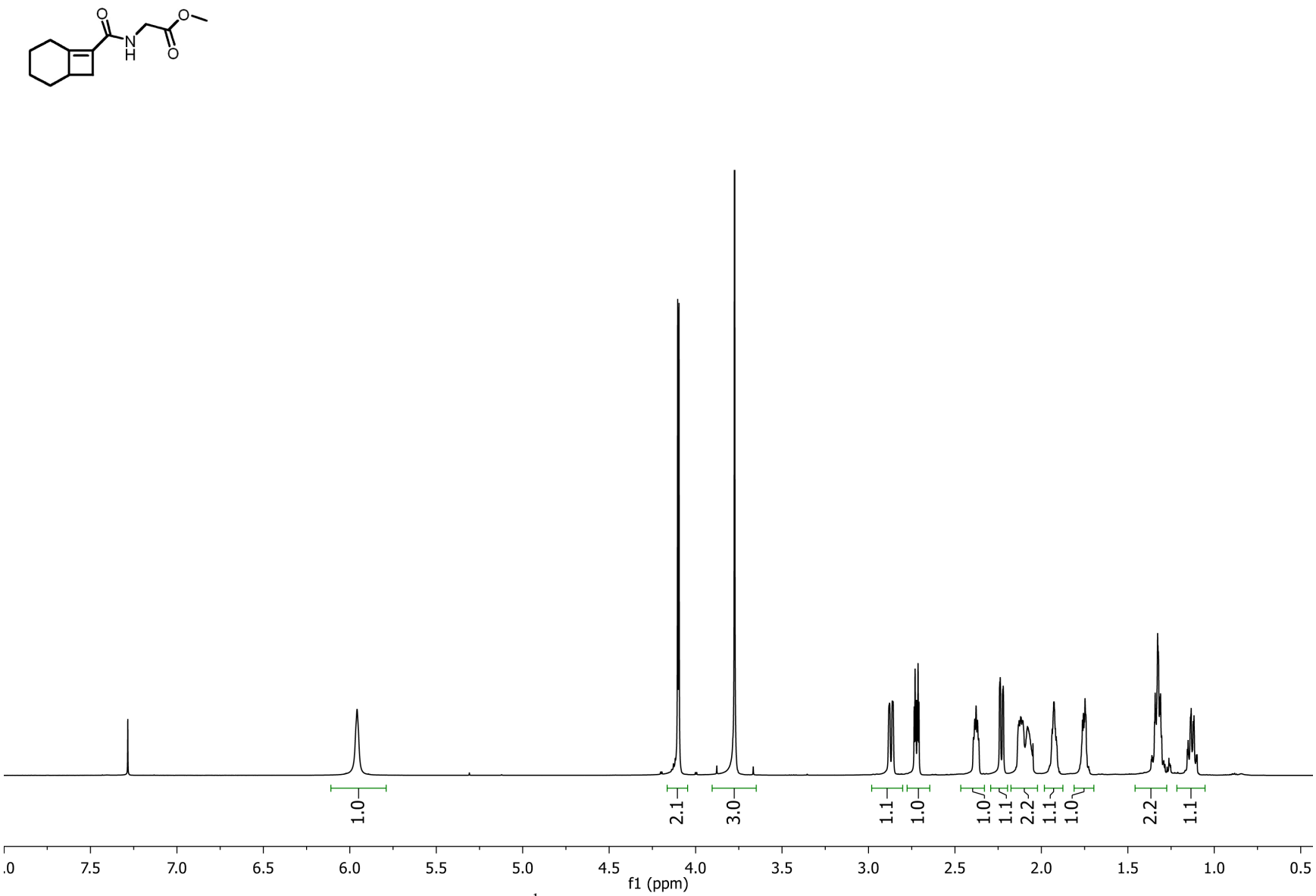


Figure S28. ^{1}H NMR spectrum of amide **1b'** in $CDCl_3$

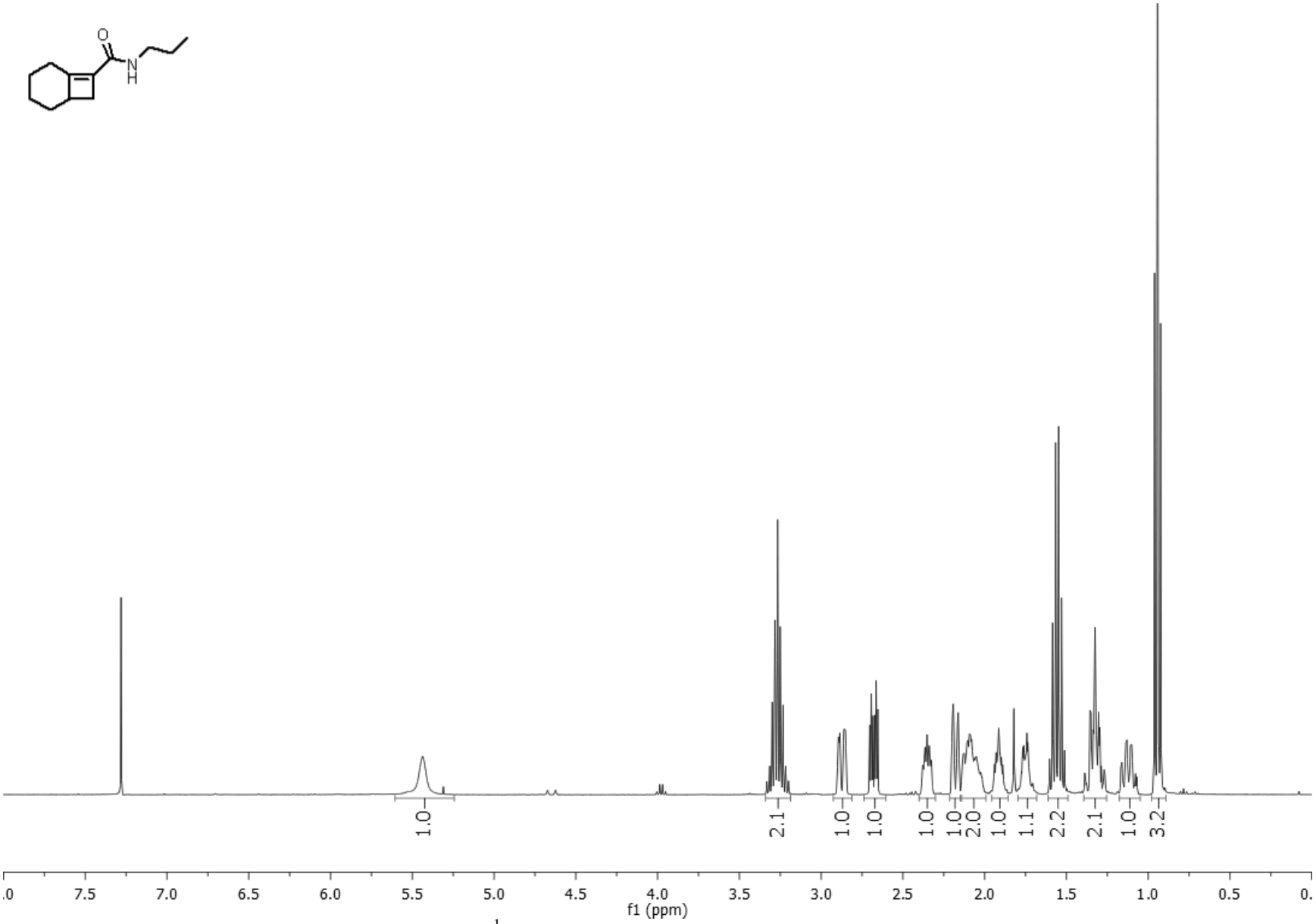


Figure S29. ^{1}H NMR spectrum of amide **1c'** in $CDCl_3$.

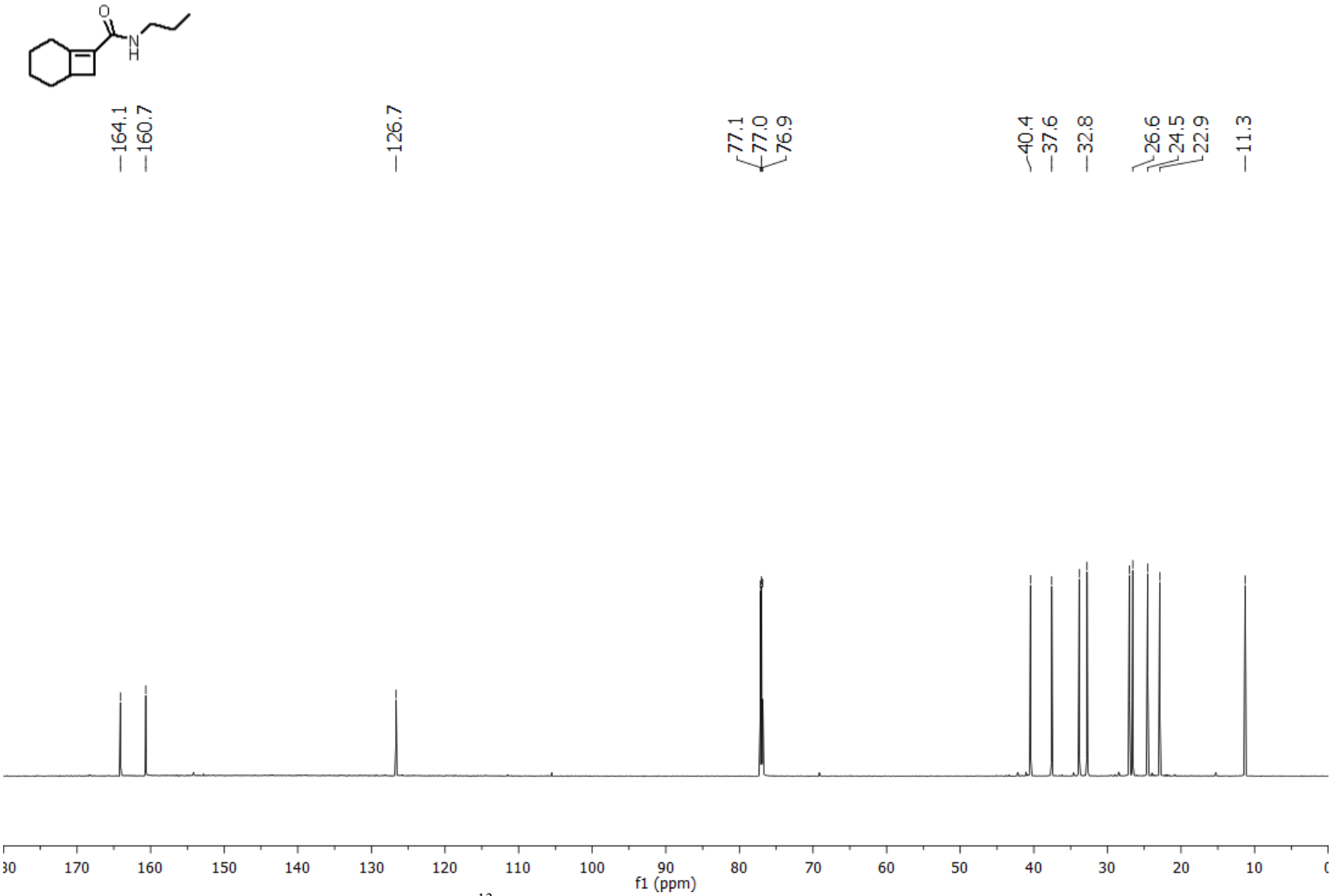


Figure S30. ^{13}C NMR spectrum of amide **1c'** in $CDCl_3$.

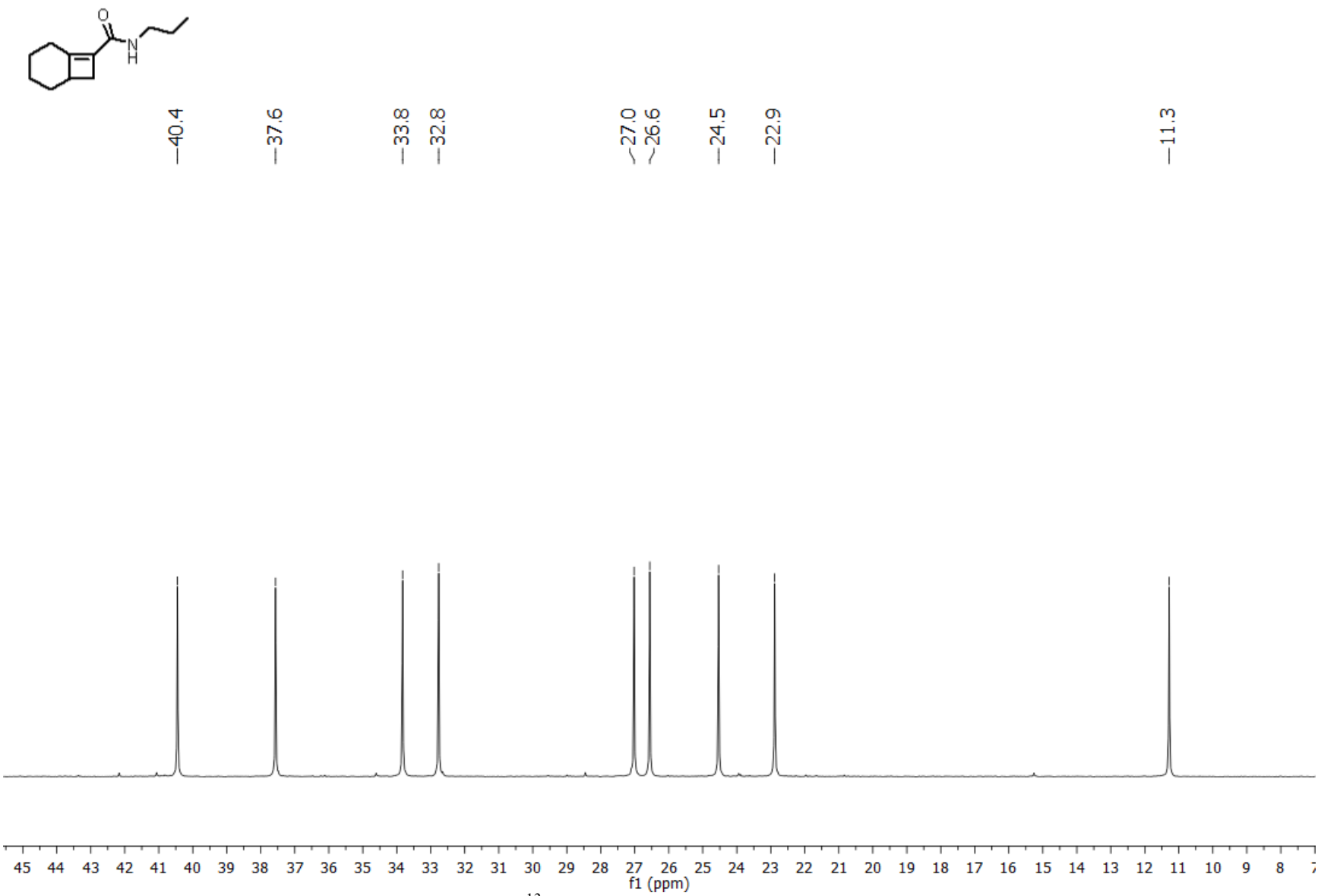


Figure S31. Partial ^{13}C NMR spectrum of amide **1c'** in $CDCl_3$.

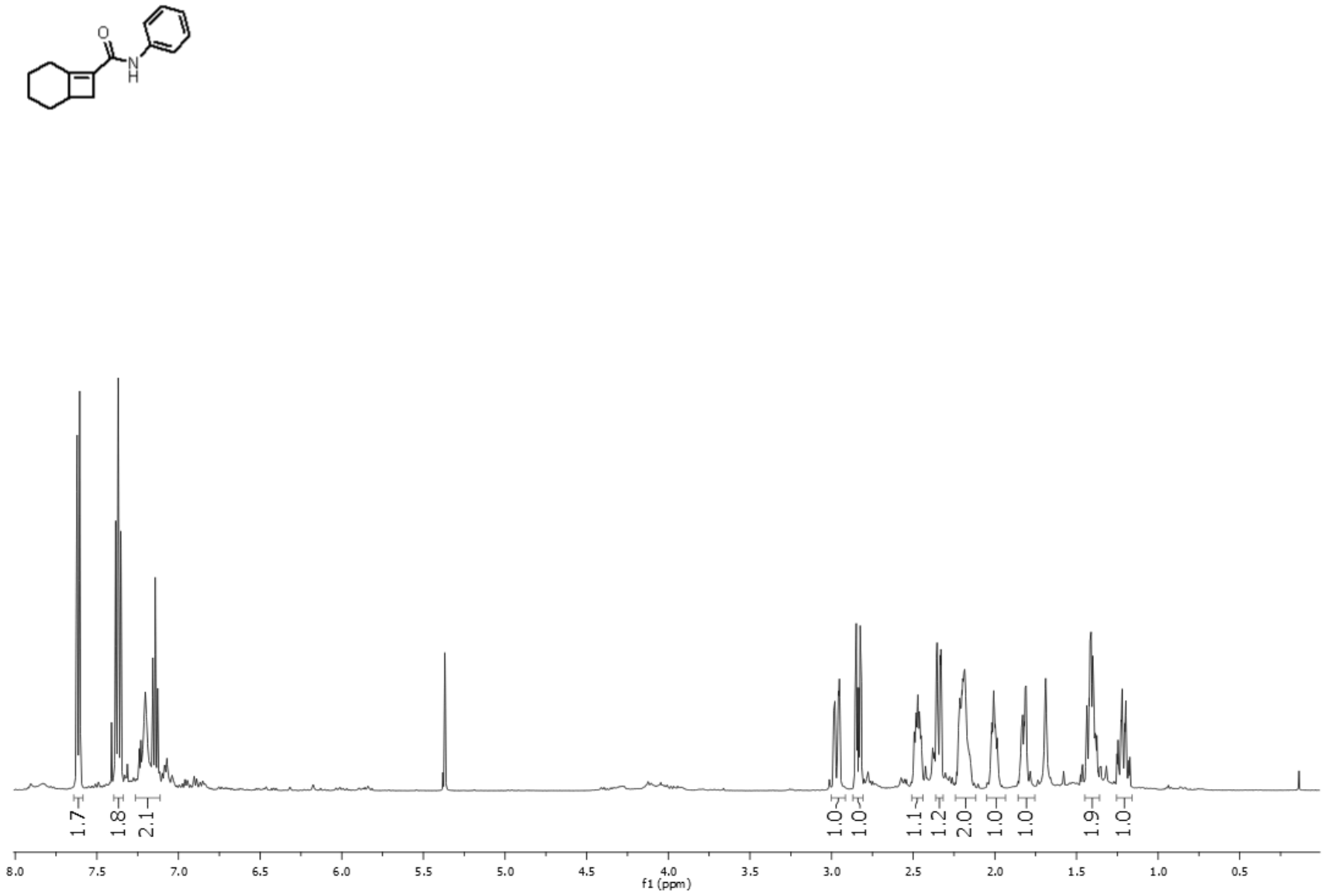


Figure S32. ^{1}H NMR spectrum of crude amide **1d** and alkylidene **2** in CD_2Cl_2 with 100% **1d** isomerized to **1d'**.

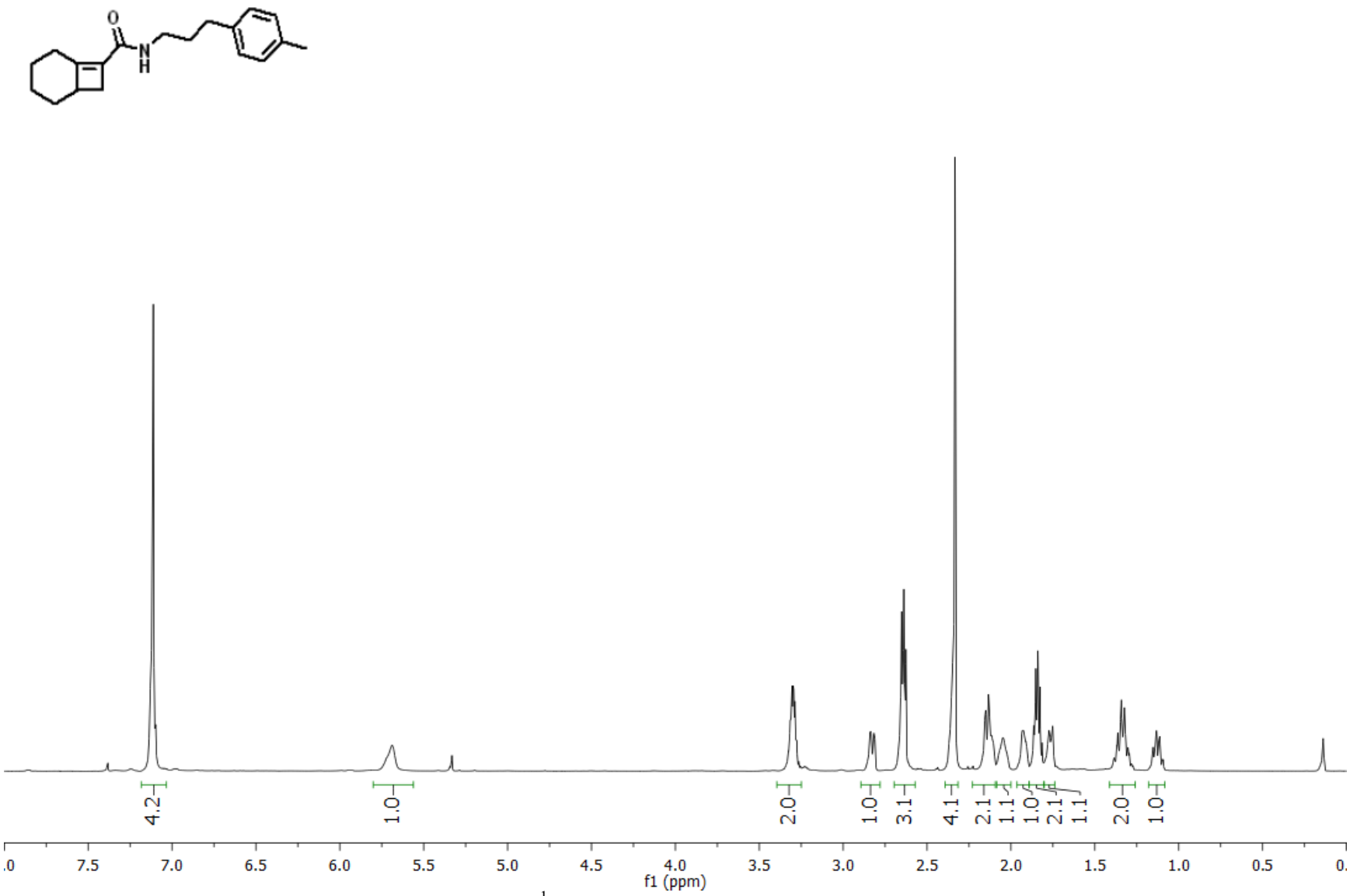


Figure S33. ^{1}H NMR spectrum of amide **1e'** in CD_2Cl_2.

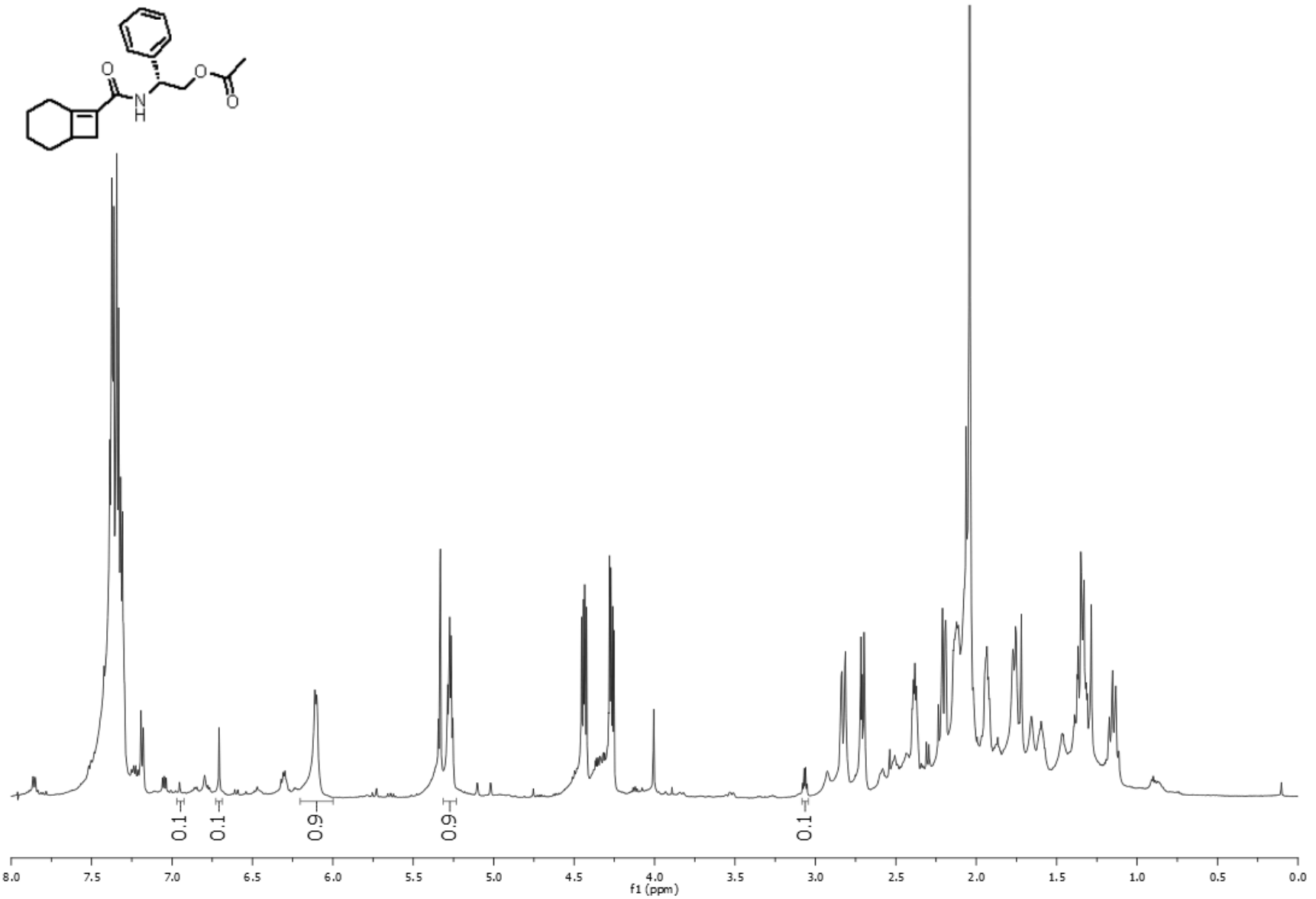


Figure S34. ^{1}H NMR spectrum of amide **1f** and alkylidene **2** in CD_2Cl_2 with 90% **1f** isomerized to **1f'**.

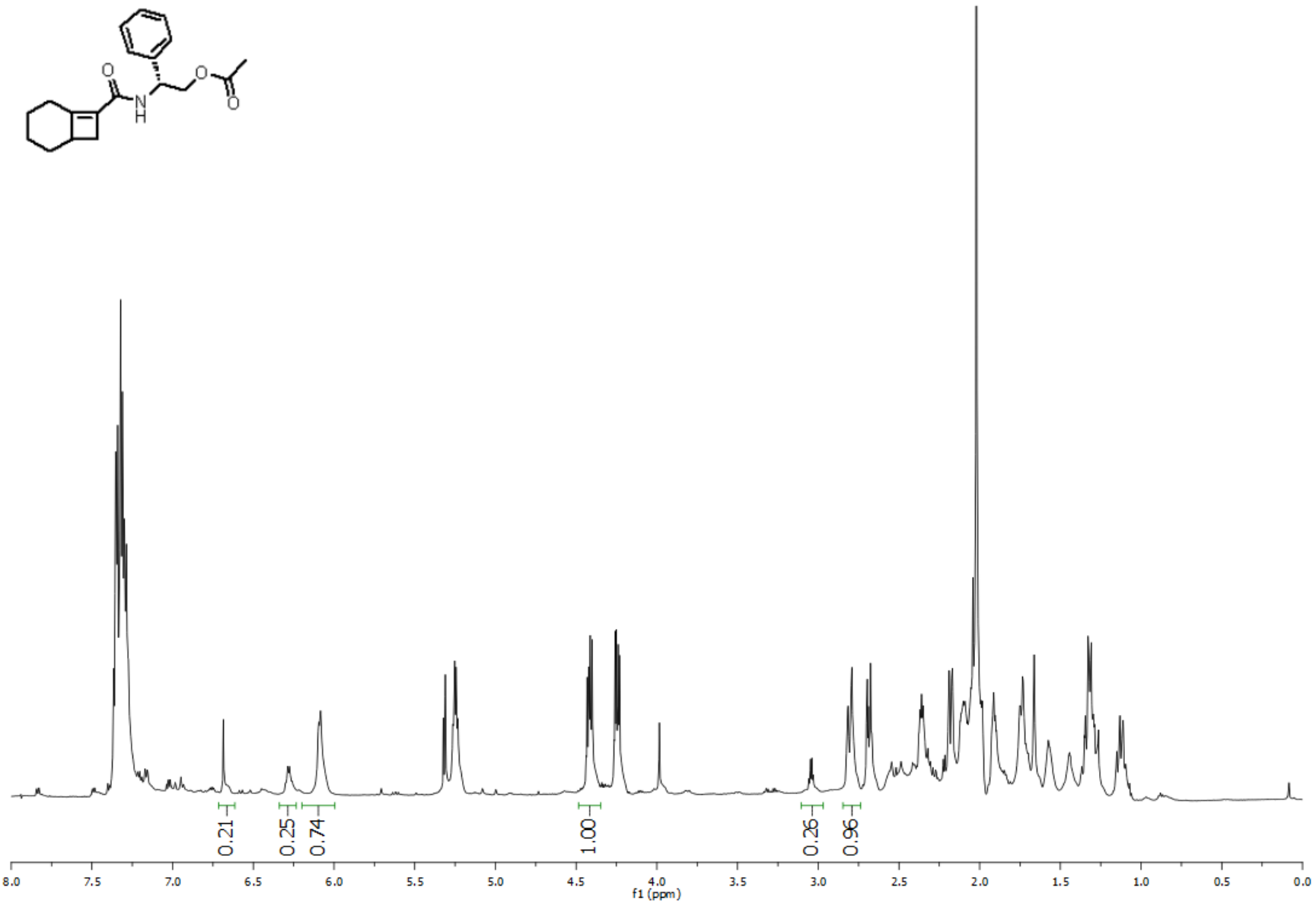


Figure S35. ^{1}H NMR spectrum of amide **1f*** and **2** in CD_2Cl_2 with 79% **1f*** isomerized to **1f*'**.

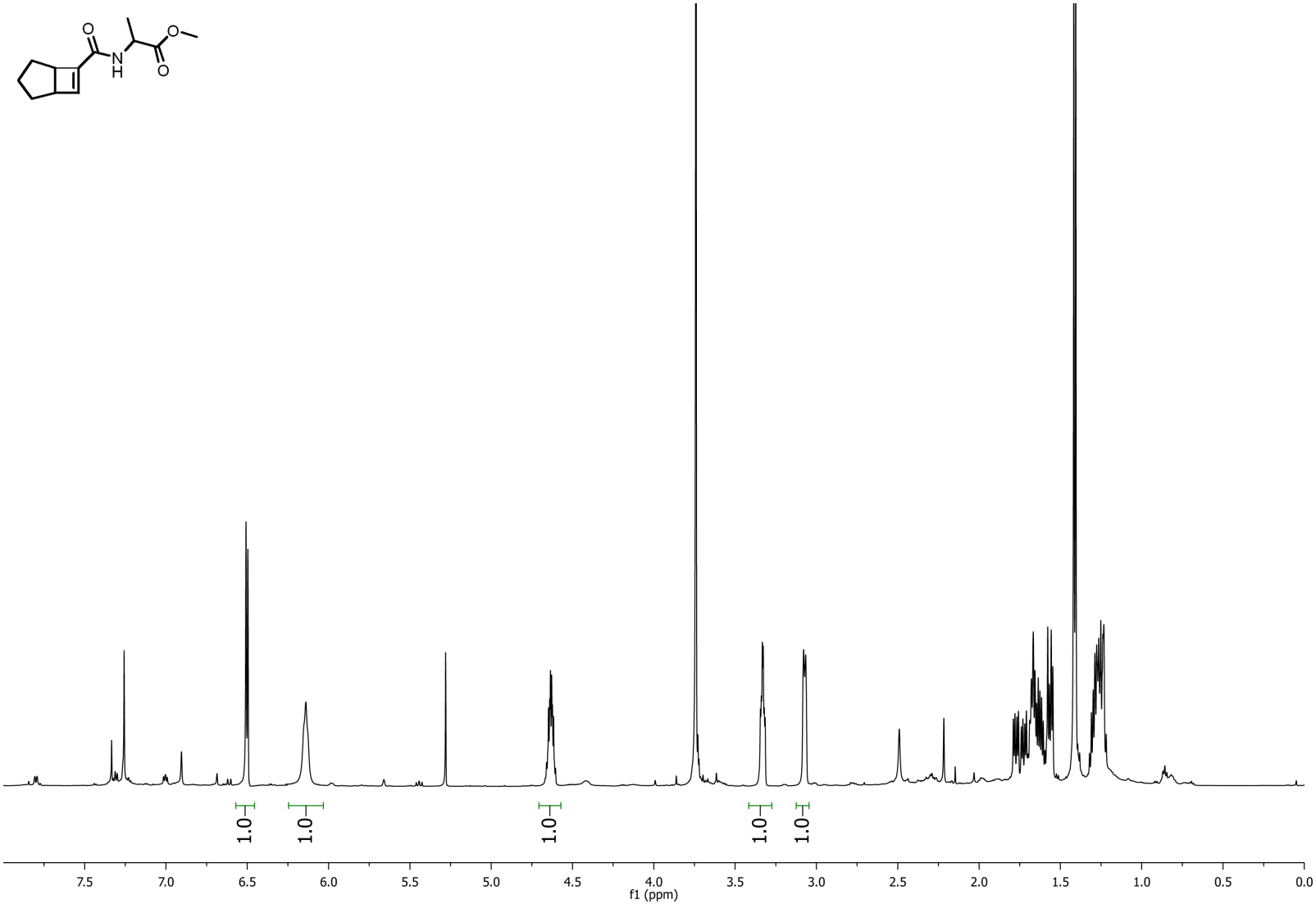


Figure S36. ^{1}H NMR spectrum of amide **4** and alkylidene **2** in CD_2Cl_2. No isomerization is observed.

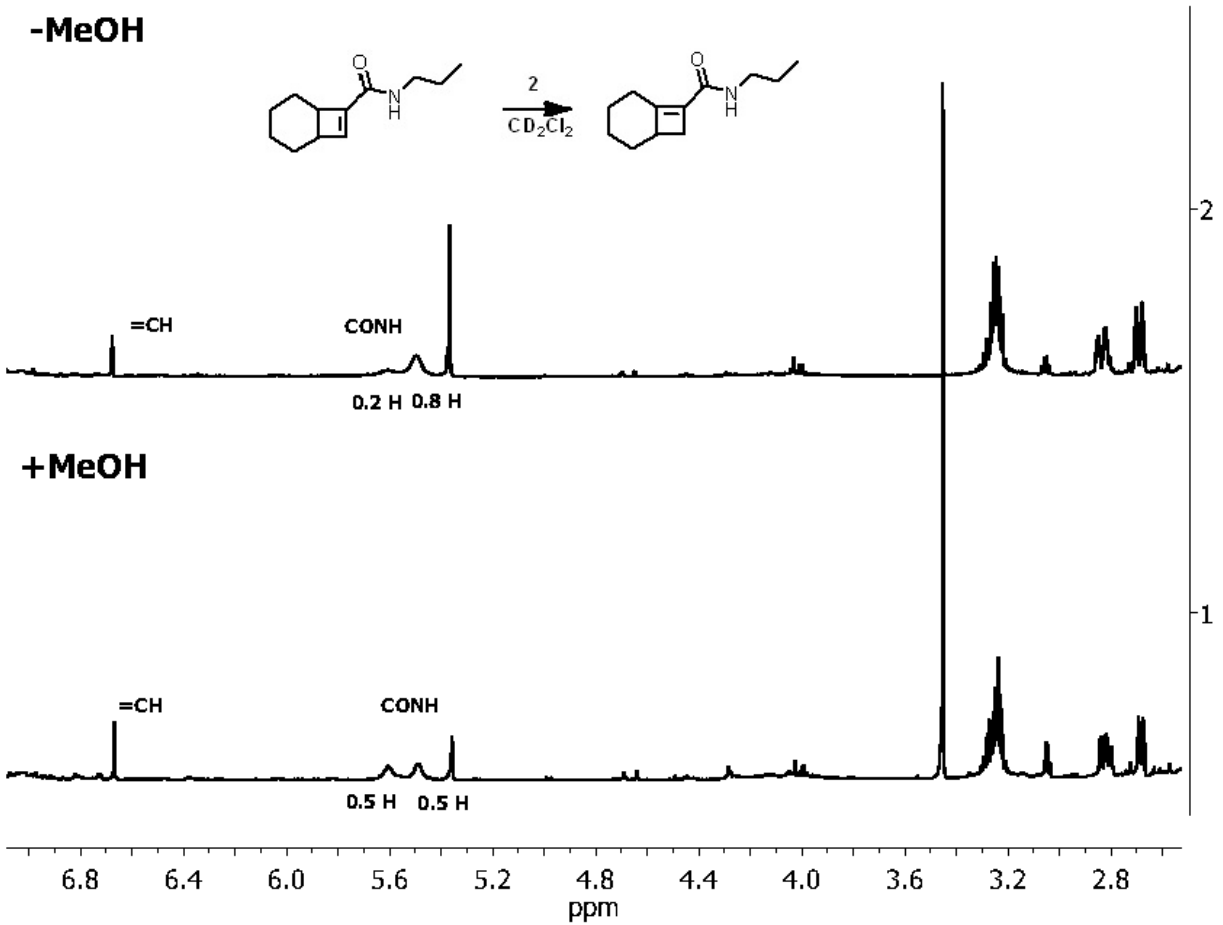


Figure S37. Isomerization of **1c** with and without 50 μL of MeOH in the presence of **2** in CD_2Cl_2. Spectra were obtained 1 hour after mixing monomer with catalyst.

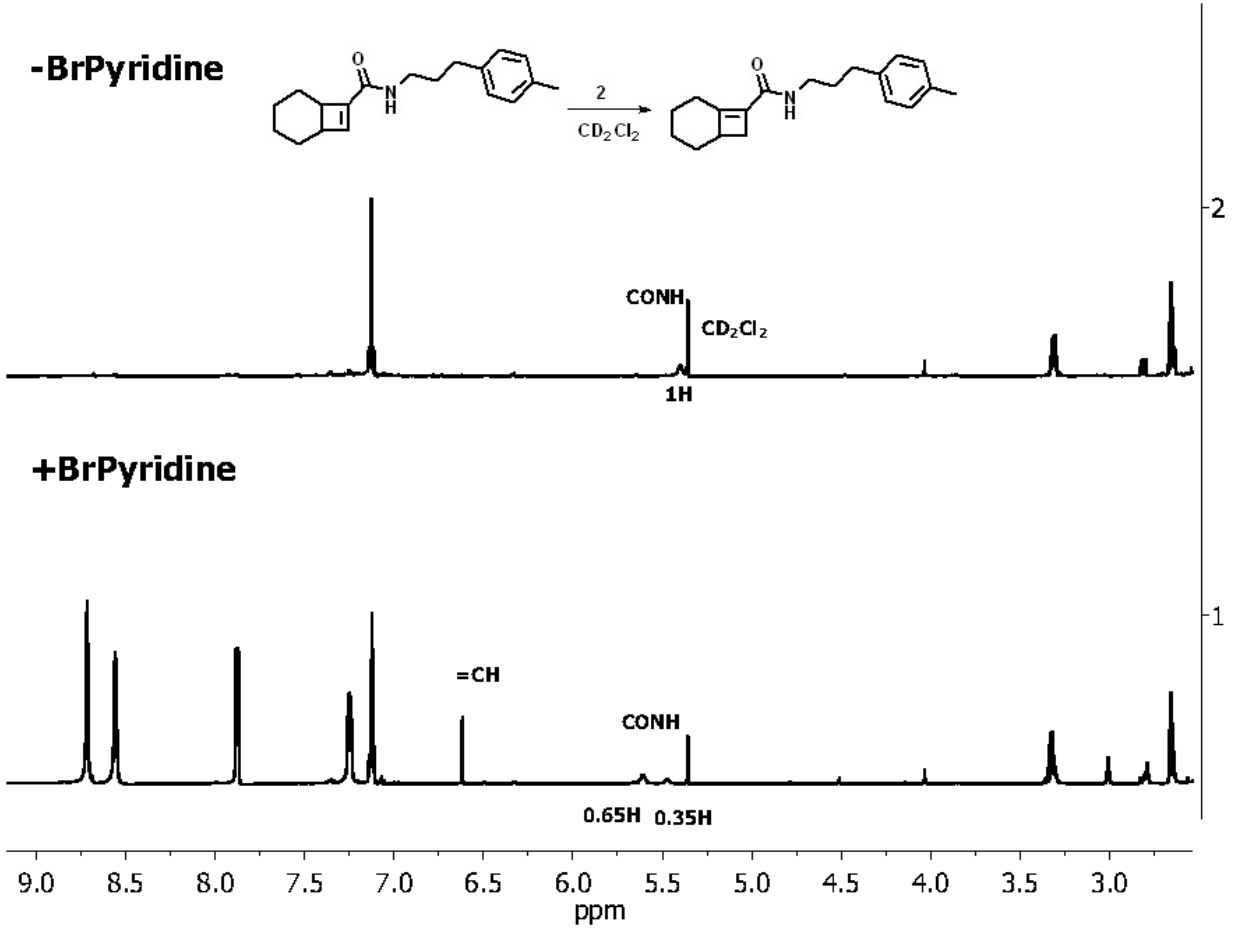


Figure S38. Isomerization of **1e** with and without 50 equiv of 3-bromopyridine in the presence of **2** in CD_2Cl_2. Spectra were obtained 16 hours after mixing monomer and catalyst.

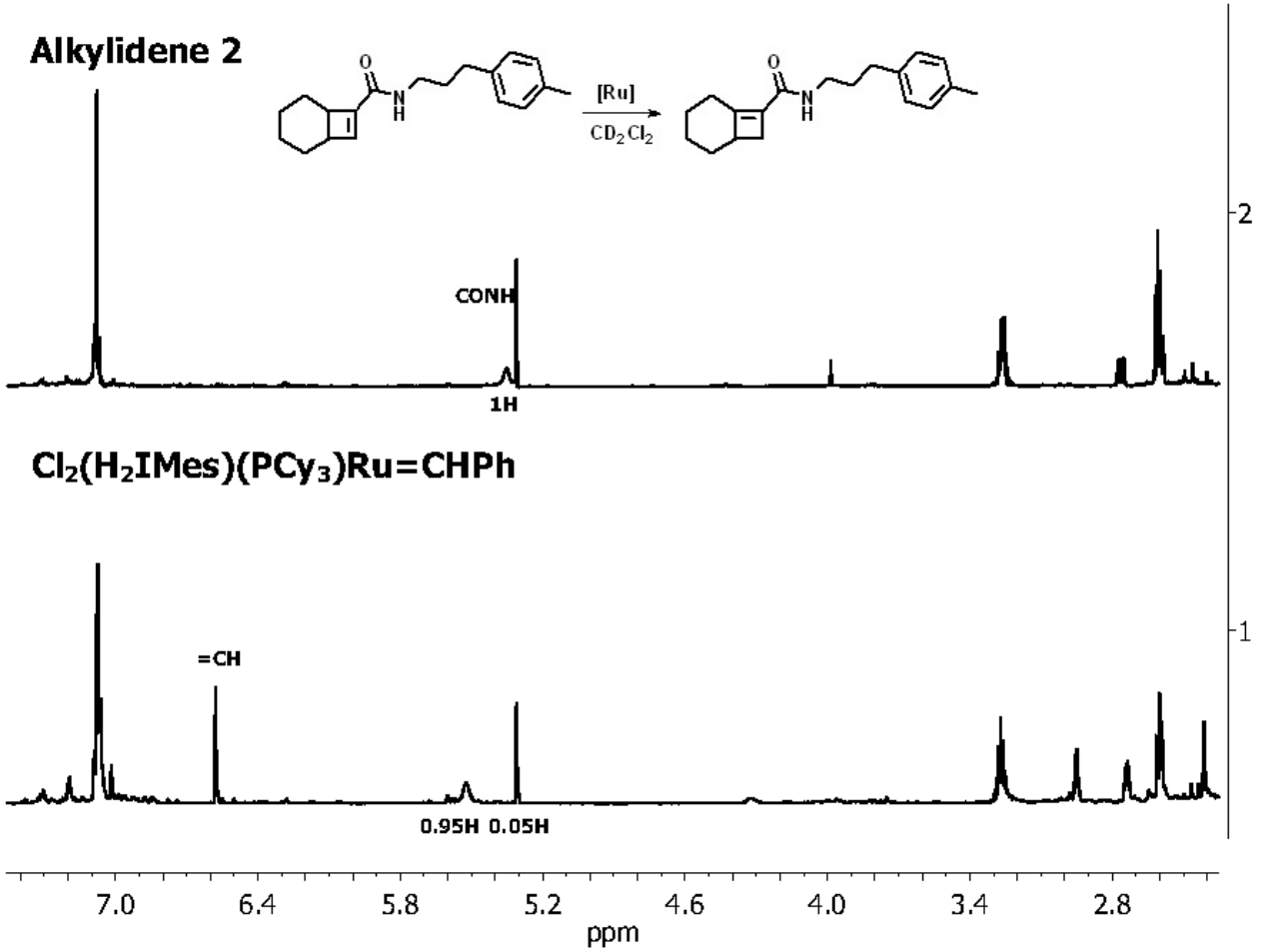


Figure S39. Isomerization of **1e** in the presence of $Cl_2(H_2IMes)(PCy_3)Ru=CHPh$ (10 mol%) or alkylidene **2** (10 mol%) in CD_2Cl_2. Spectra were obtained 14 hours after mixing monomer and catalyst.

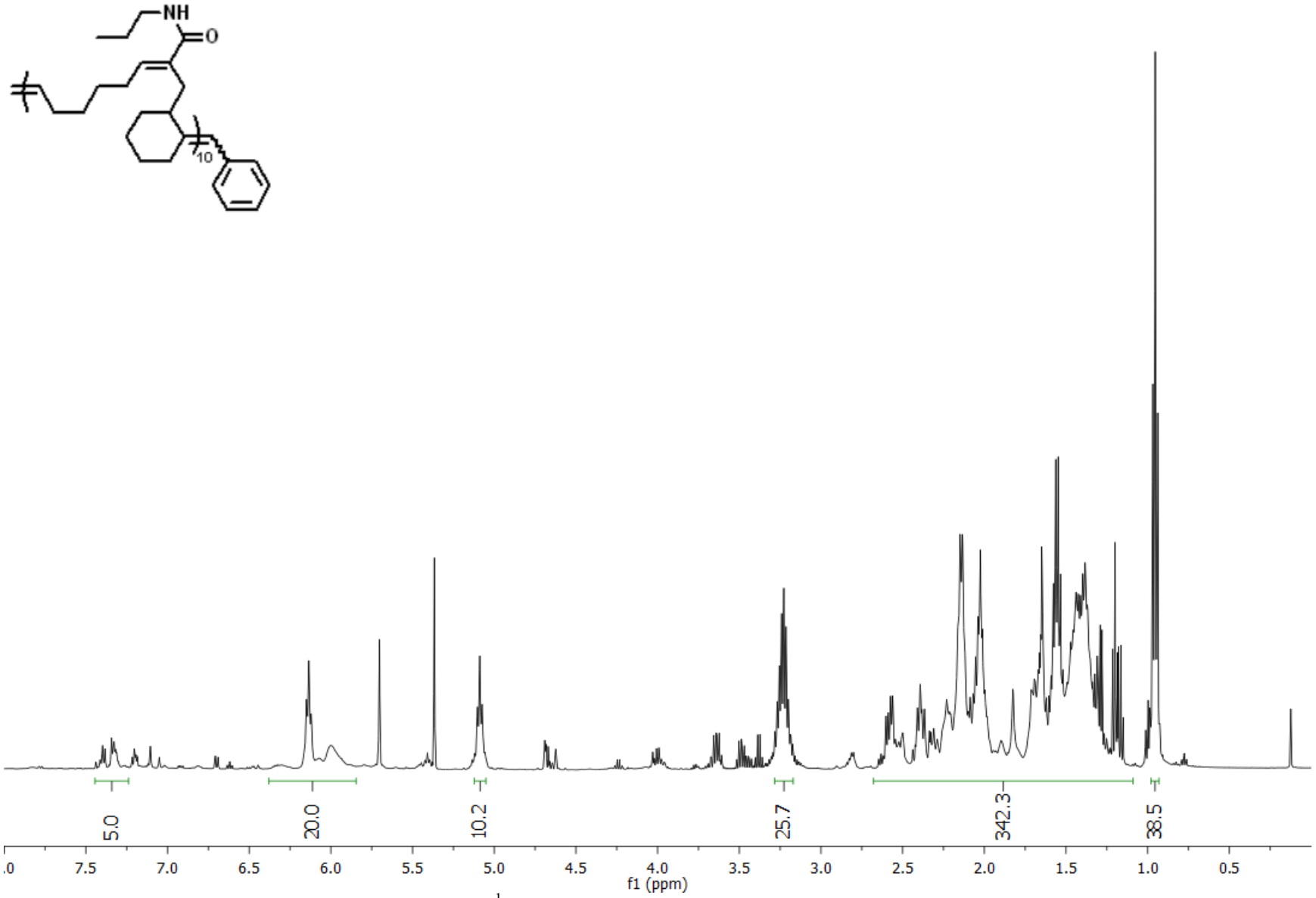


Figure S40. ^{1}H NMR spectrum of poly(**1c'**-*alt*-**3**)$_{10}$ in CD_2Cl_2.

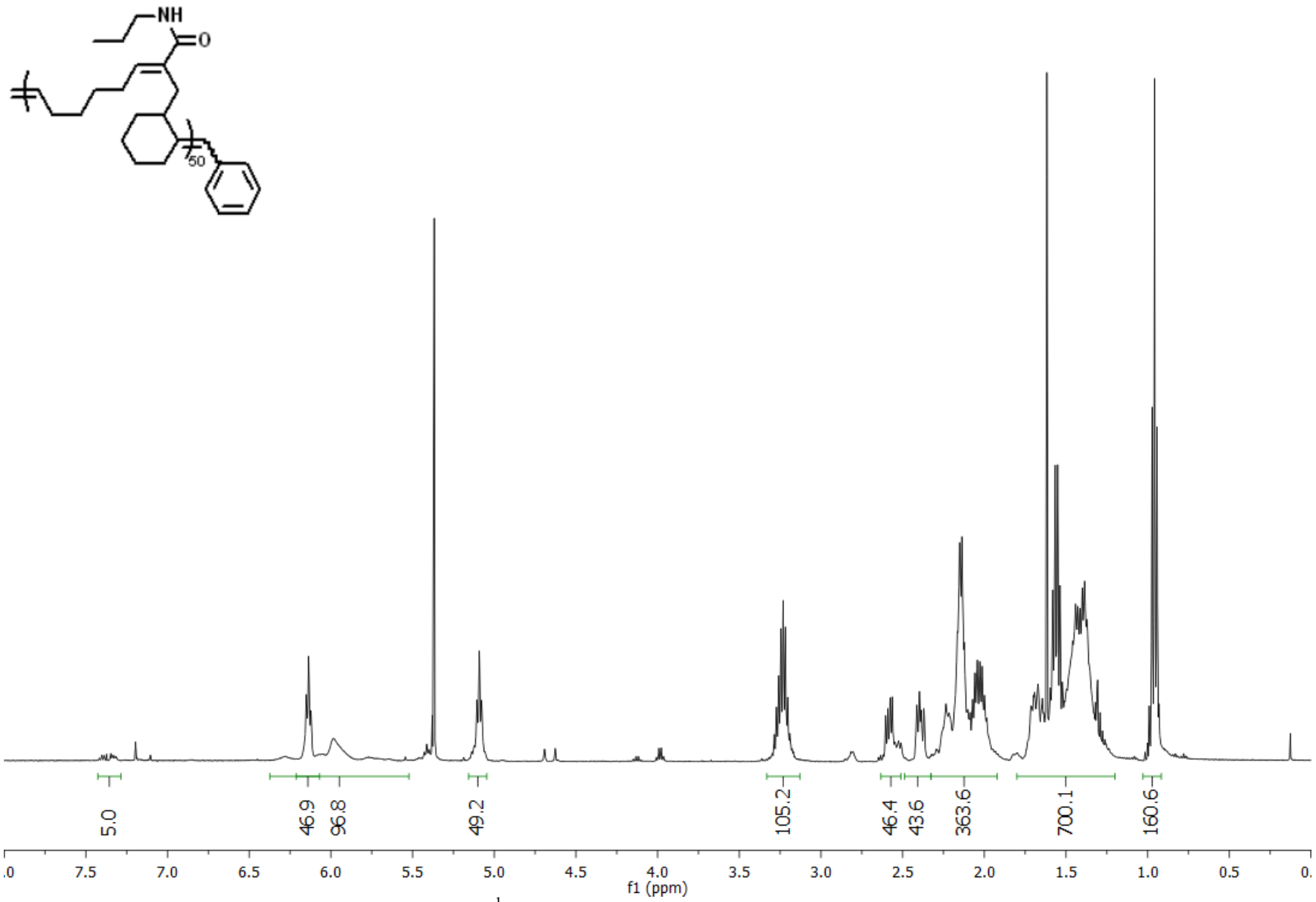


Figure S41. ^{1}H NMR spectrum of poly(**1c'**-*alt*-**3**)$_{50}$ in CD_2Cl_2.

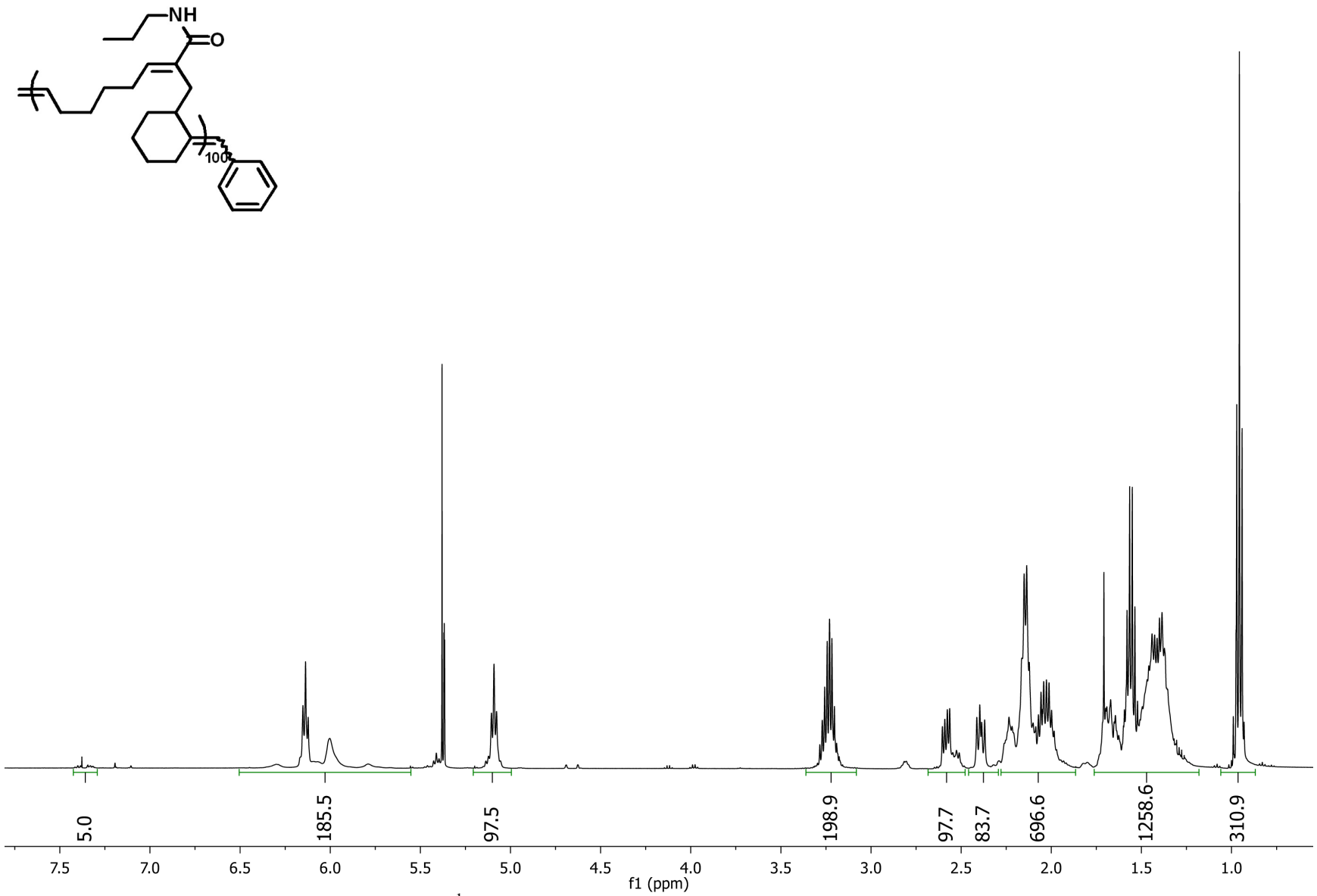


Figure S42. ^{1}H NMR spectrum of poly(**1c'**-*alt*-**3**)$_{100}$ in CD_2Cl_2.

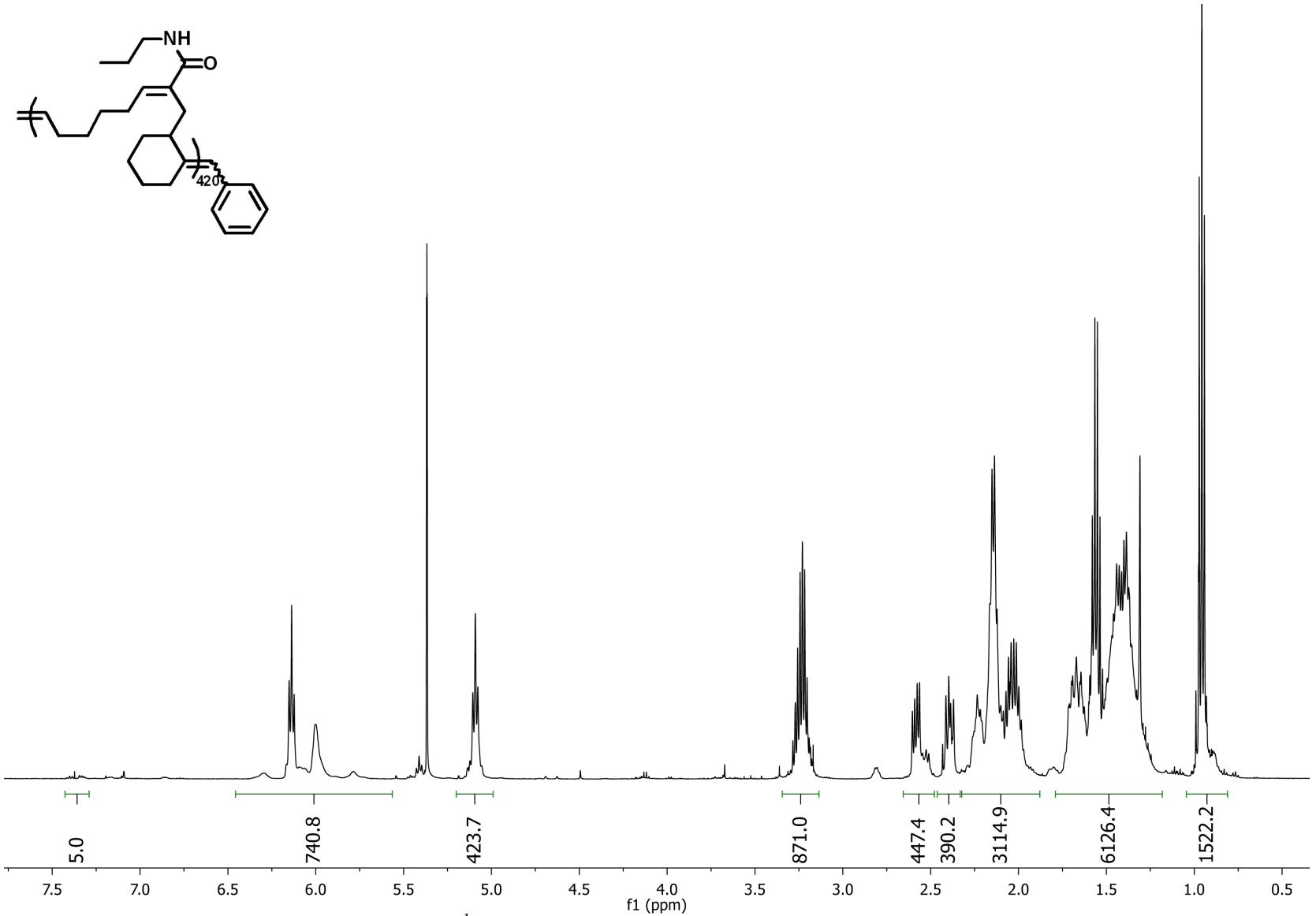


Figure S43. ^{1}H NMR spectrum of poly(**1c'**-*alt*-**3**)$_{420}$ in CD_2Cl_2.

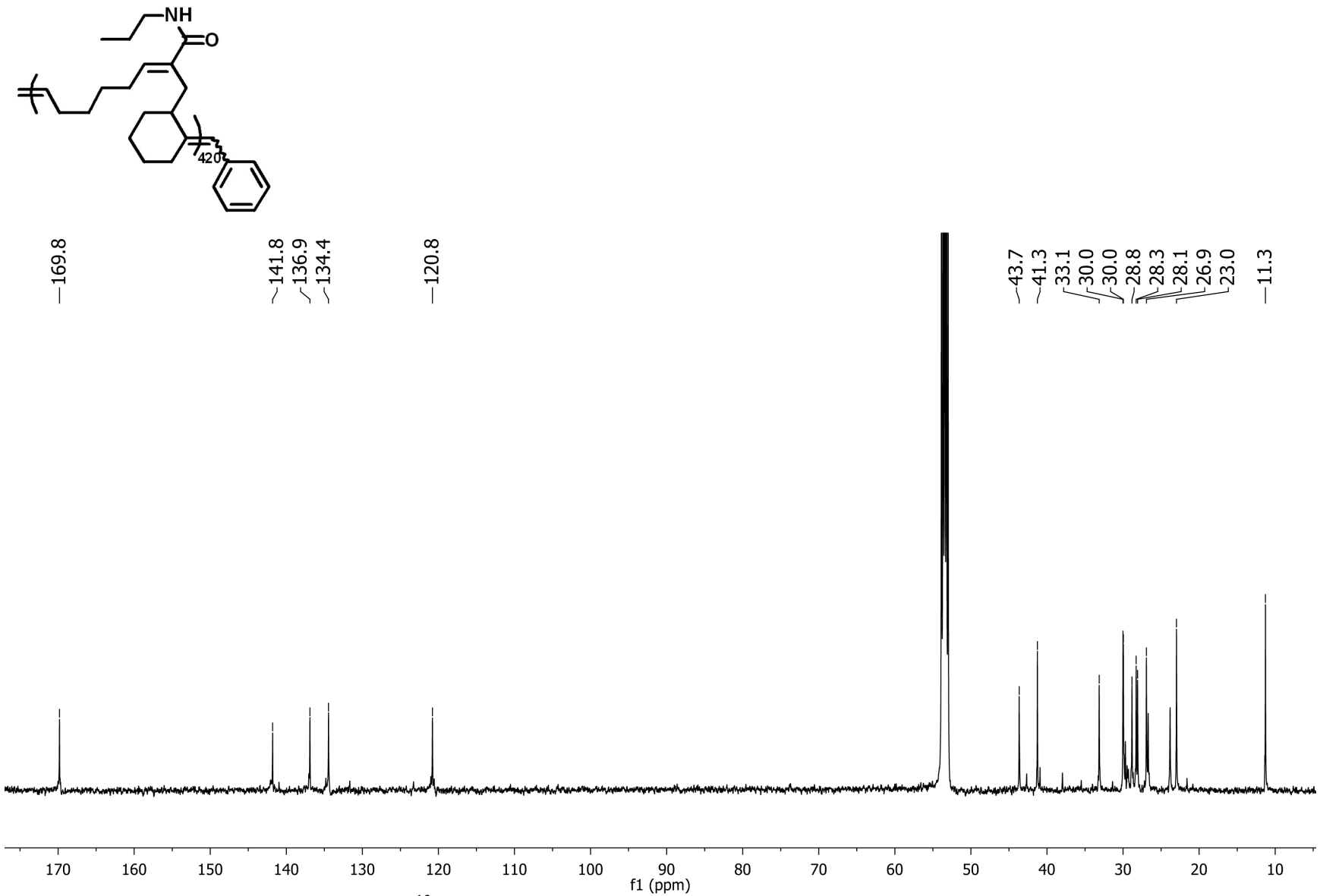


Figure S44. ^{13}C NMR spectrum of poly(**1c'**-*alt*-**3**)$_{420}$ in CD_2Cl_2.

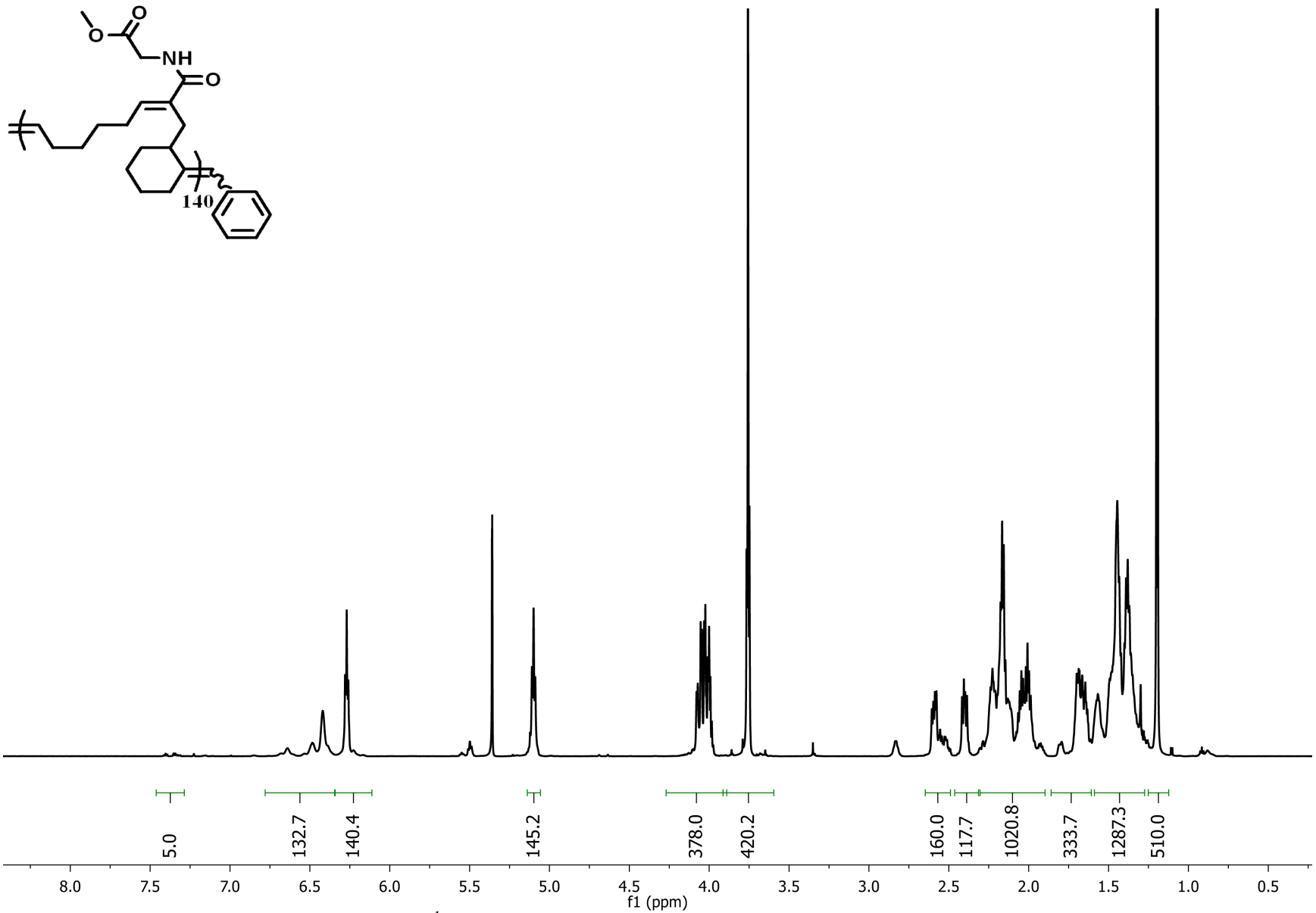


Figure S45. ^{1}H NMR spectrum of poly(**1b'**-*alt*-**3**)$_{140}$ in CD_2Cl_2.

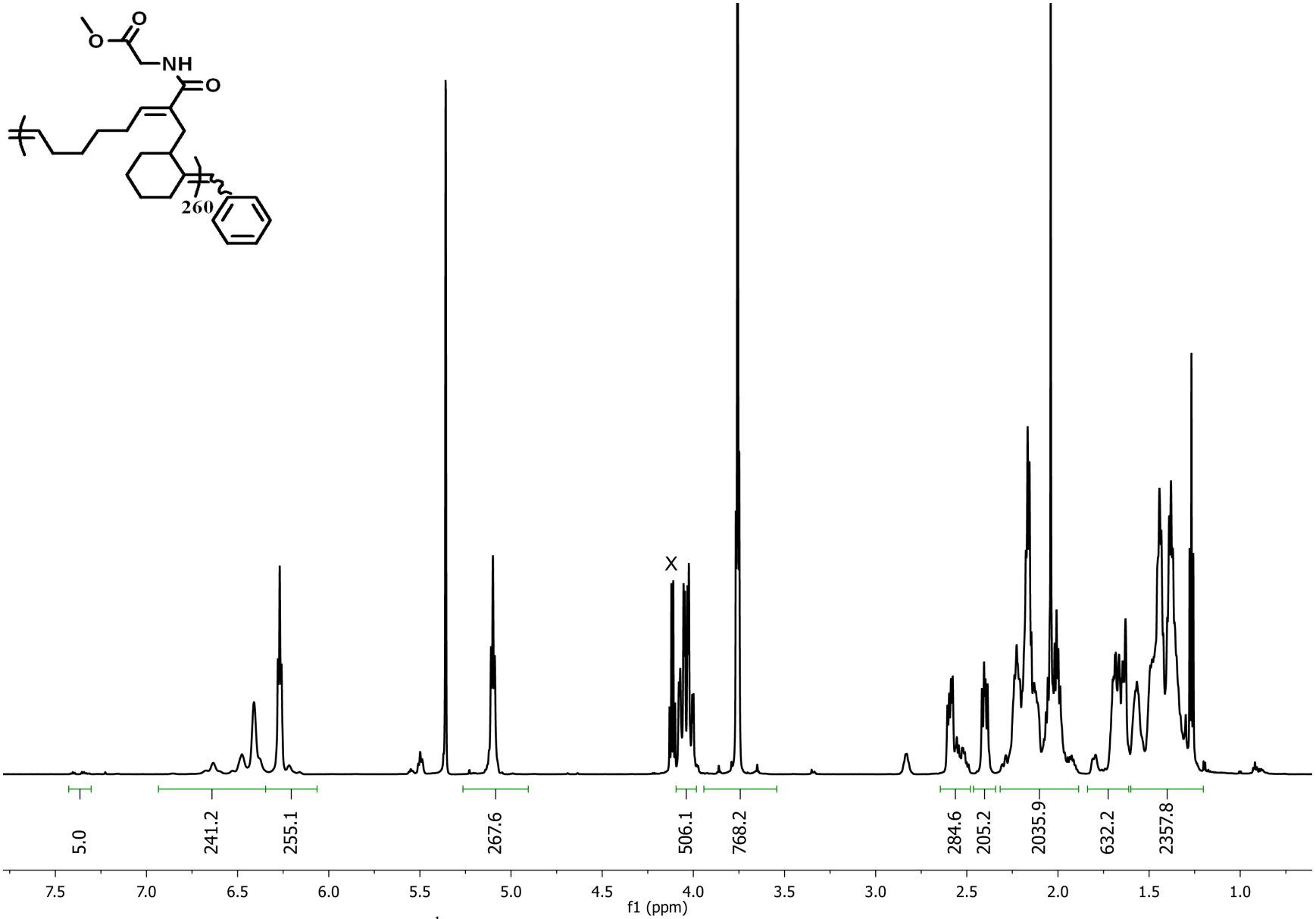


Figure S46. ^{1}H NMR spectrum of poly(**1b'**-*alt*-**3**)$_{260}$ in CD_2Cl_2.

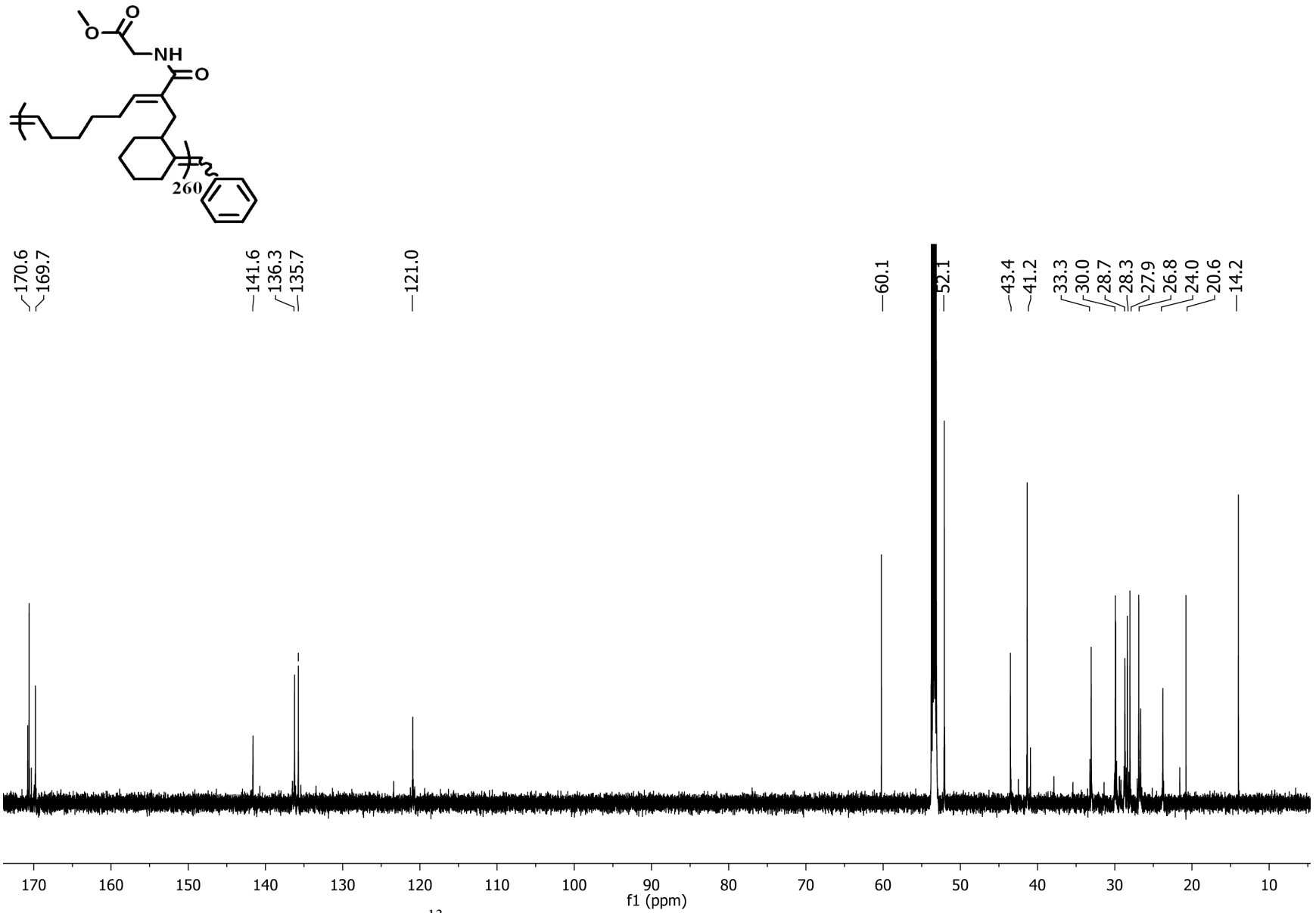


Figure S47. ^{13}C NMR spectrum of poly(**1b'**-*alt*-3)$_{260}$ in CD_2Cl_2.

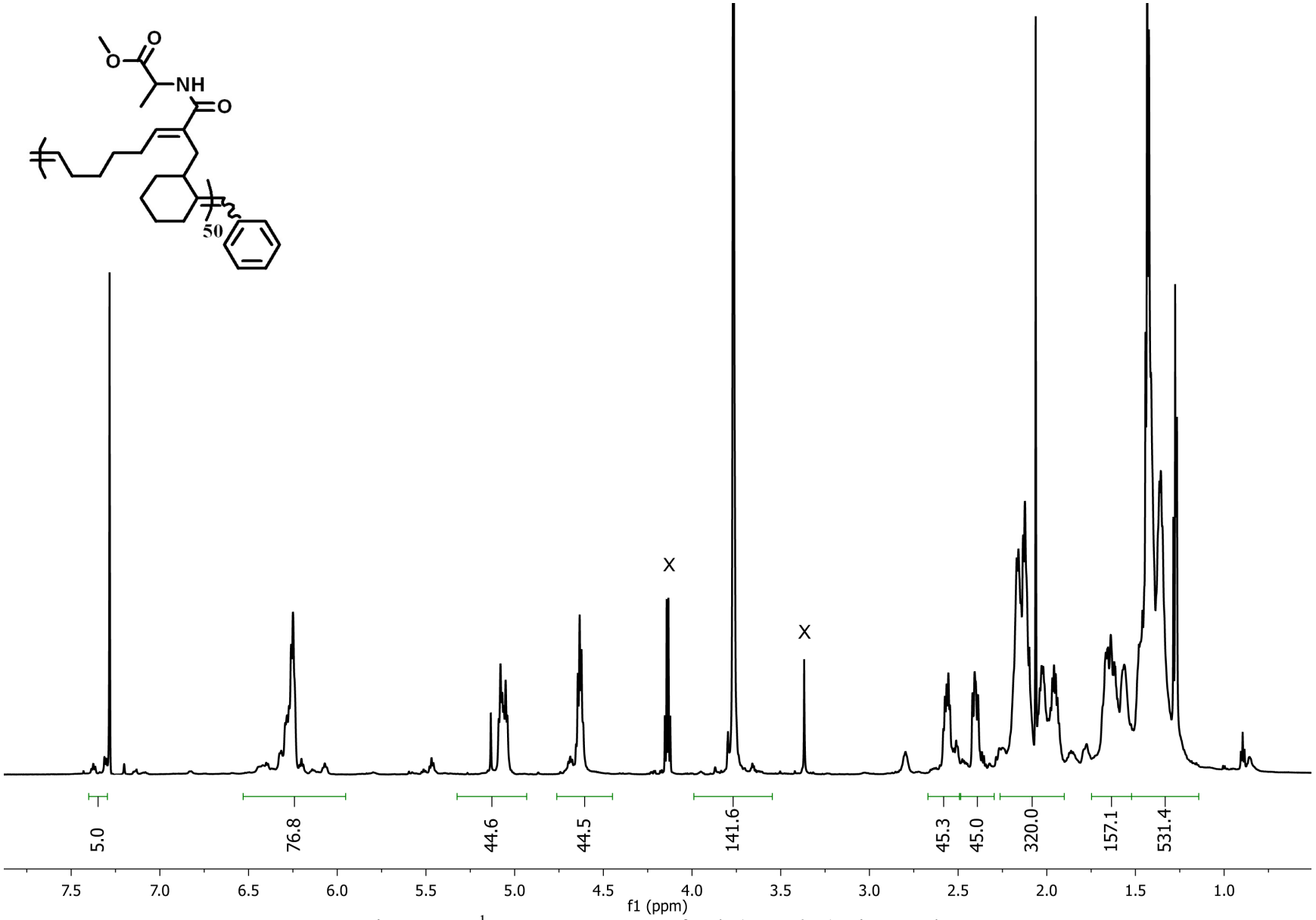


Figure S48. ^{1}H NMR spectrum of poly(**1a'**-*alt*-**3**)$_{50}$ in $CDCl_3$.

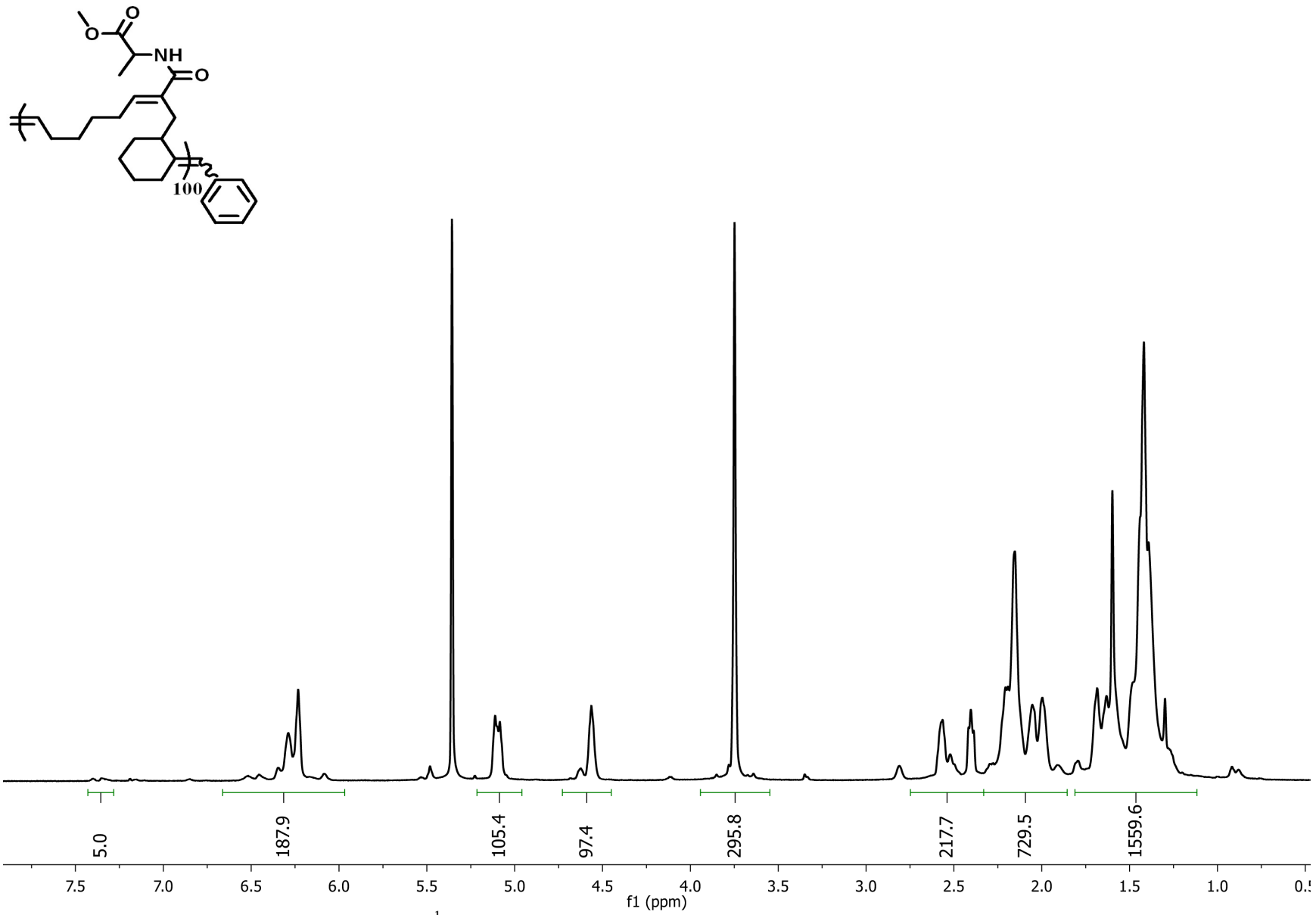


Figure S49. ^{1}H NMR spectrum of poly(**1a'**-*alt*-**3**)$_{100}$ in CD_2Cl_2.

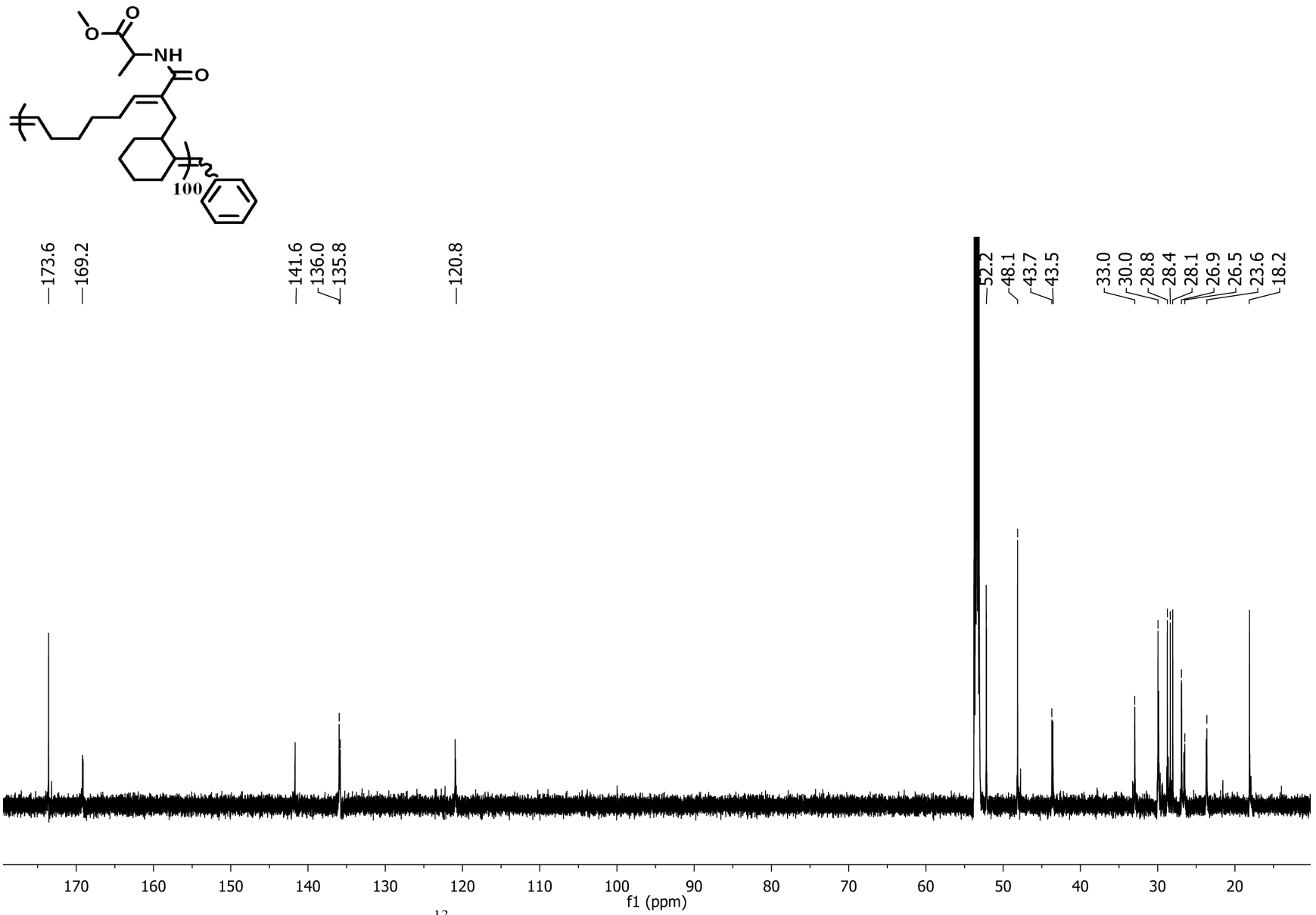


Figure S50. ^{13}C NMR spectrum of poly(**1a'**-*alt*-**3**)$_{100}$ in CD_2Cl_2

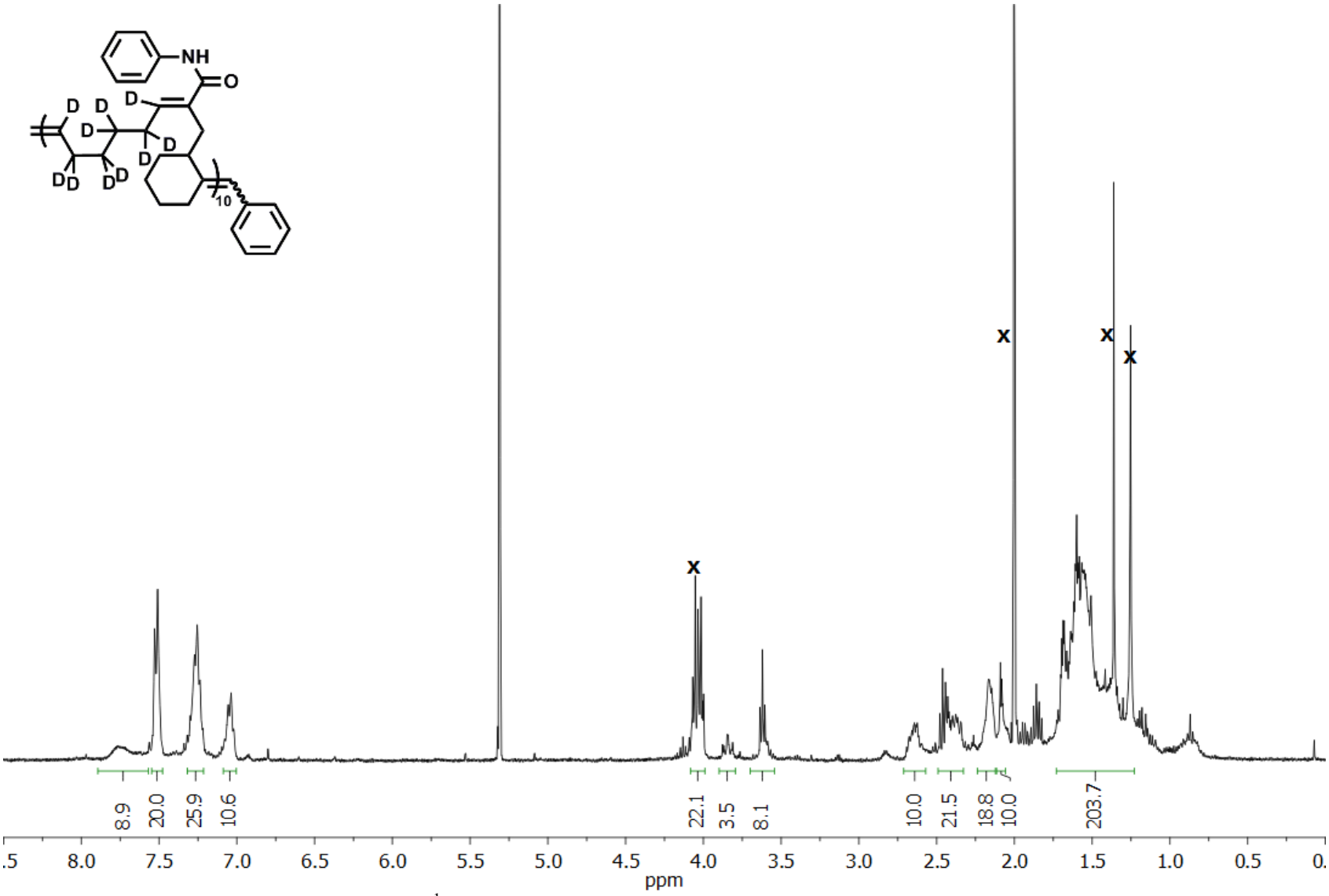


Figure S51. ^{1}H NMR spectrum of poly(**1d'**-*alt*-**3-D$_{10}$**)$_{10}$ in CD_2Cl_2.

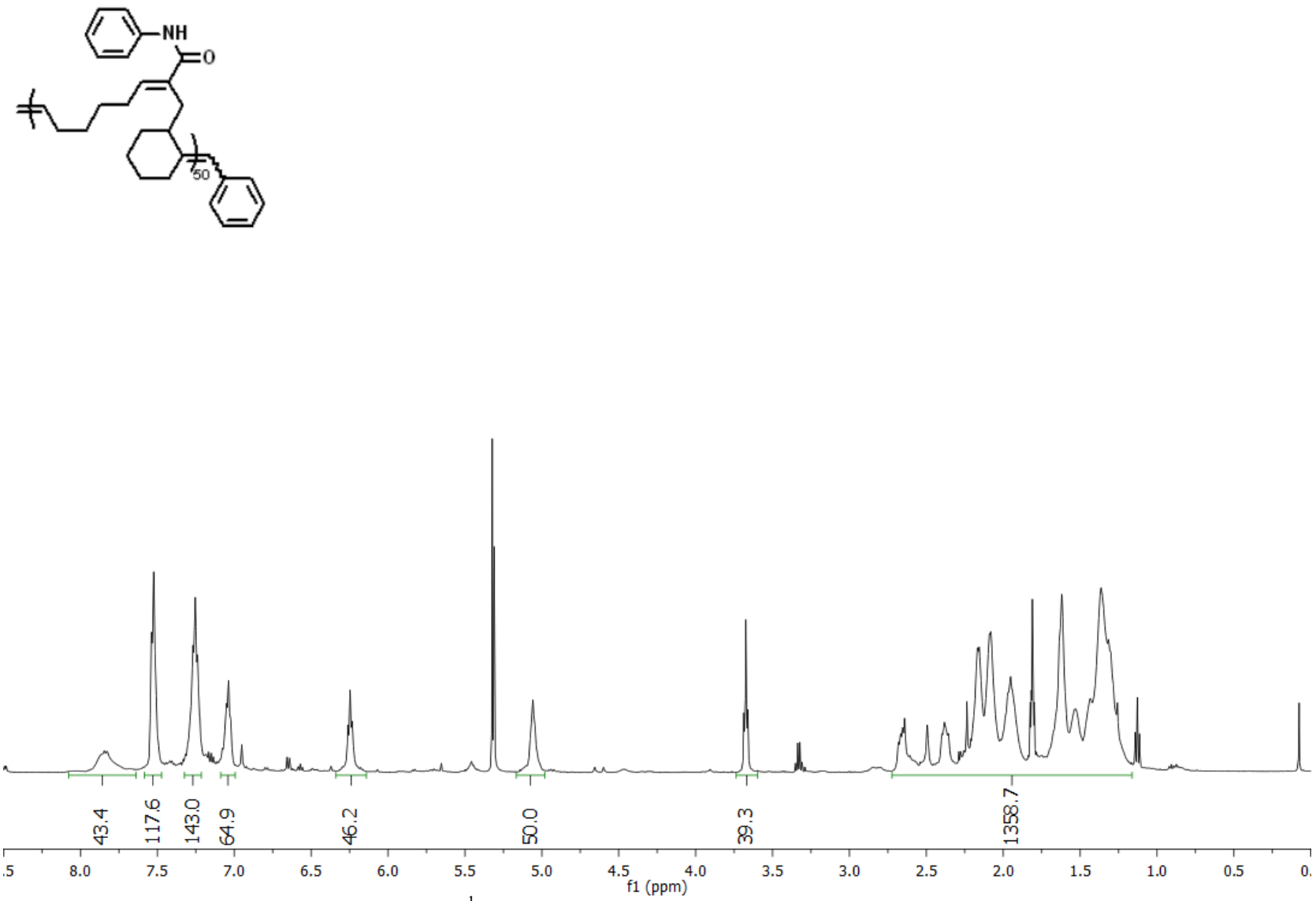


Figure S52. ^{1}H NMR spectrum of poly(**1d'**-*alt*-**3**)$_{50}$ in CD_2Cl_2.

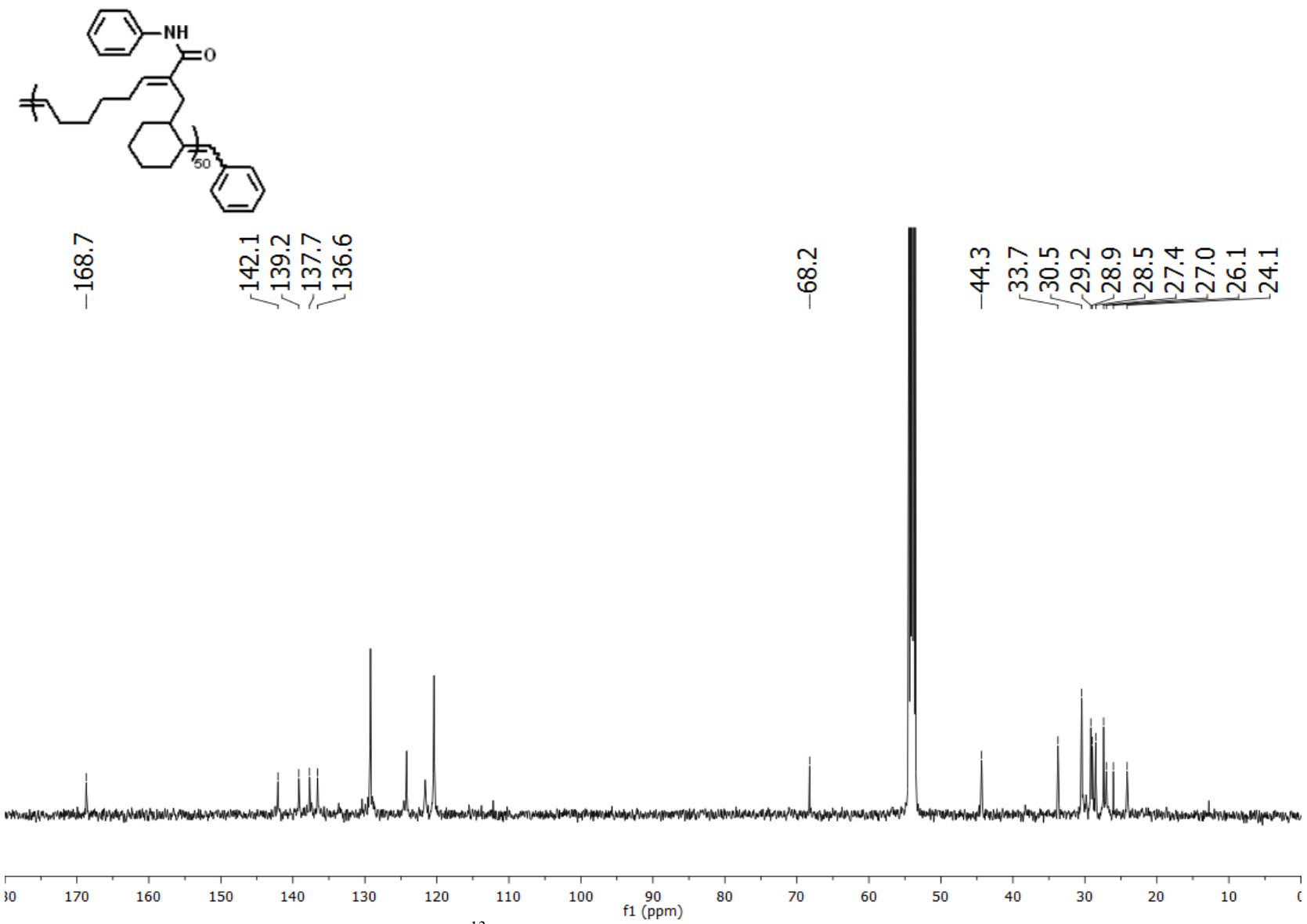


Figure S53. ^{13}C NMR spectrum of poly(**1d'**-*alt*-**3**)$_{50}$ in CD_2Cl_2.

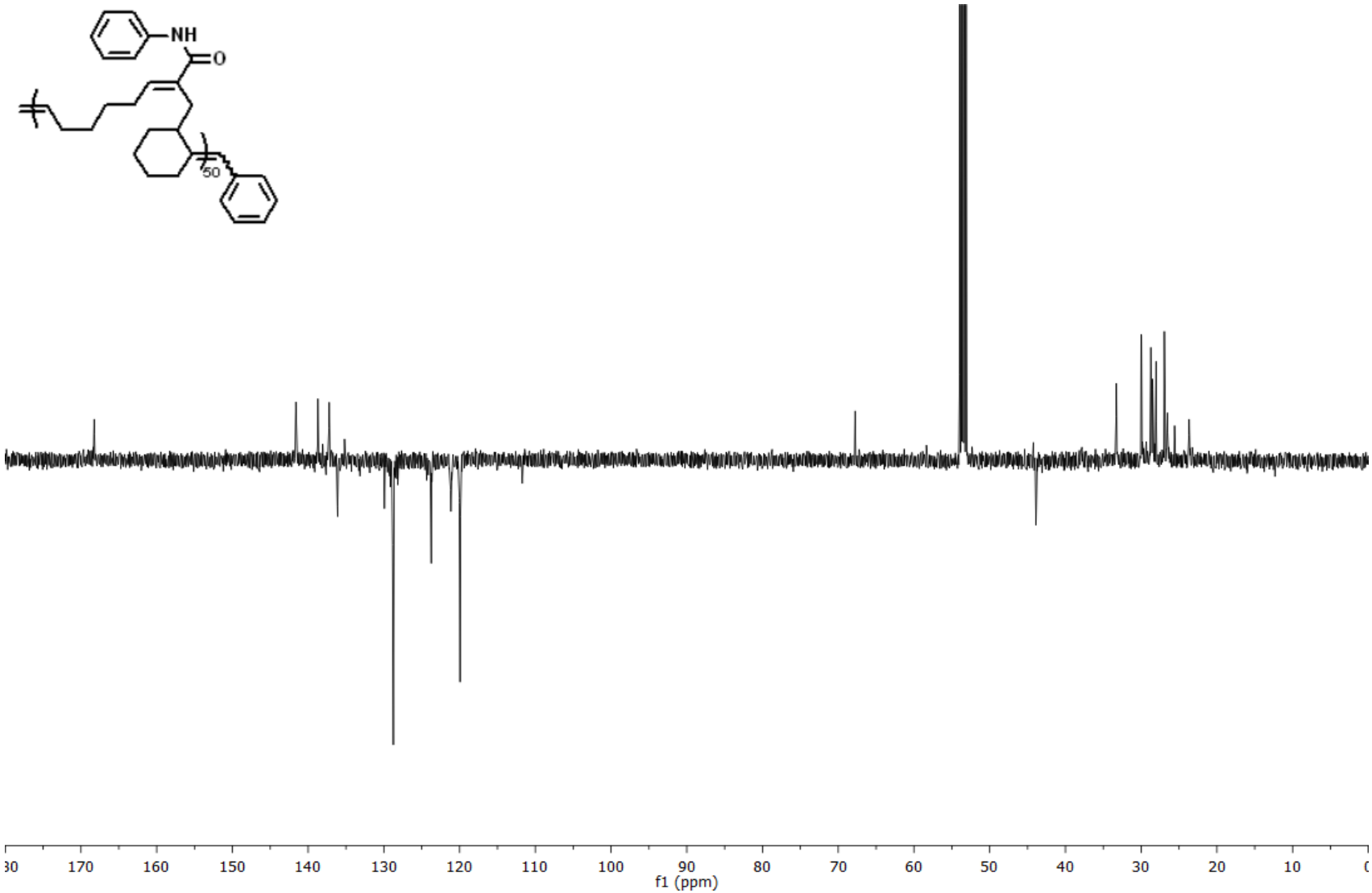


Figure S54. APT spectrum of poly(**1d'**-*alt*-**3**)$_{50}$ in CD_2Cl_2.

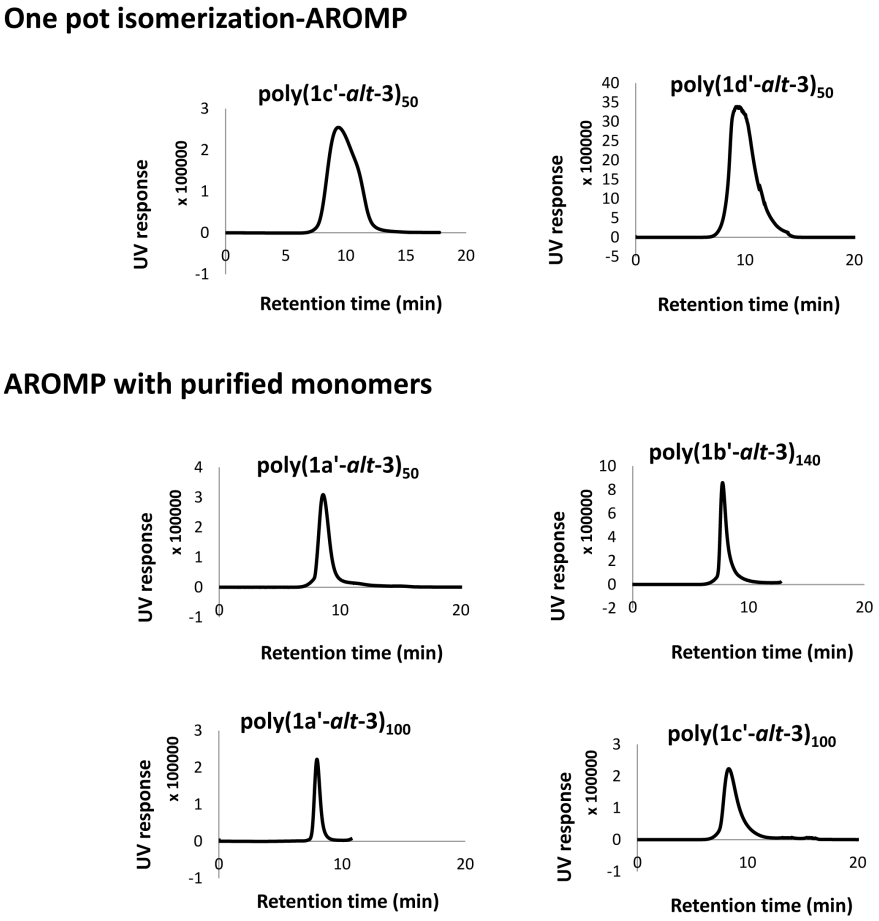


Figure S55. Molar mass dispersity ($Đ_M$) traces of isomerized amide AROMP polymers.

Phenogel 5µm MXL LC column (300x7.8mm, 100KDa exclusion limit), Phenomenex, was used with a flow rate of 0.7 mL/min in methylene chloride at 30°C. 50-mers of **1c'** and **1d'** were prepared in a one-pot procedure from **1c** or **1d**. All others were prepared with isomerized and purified amides.

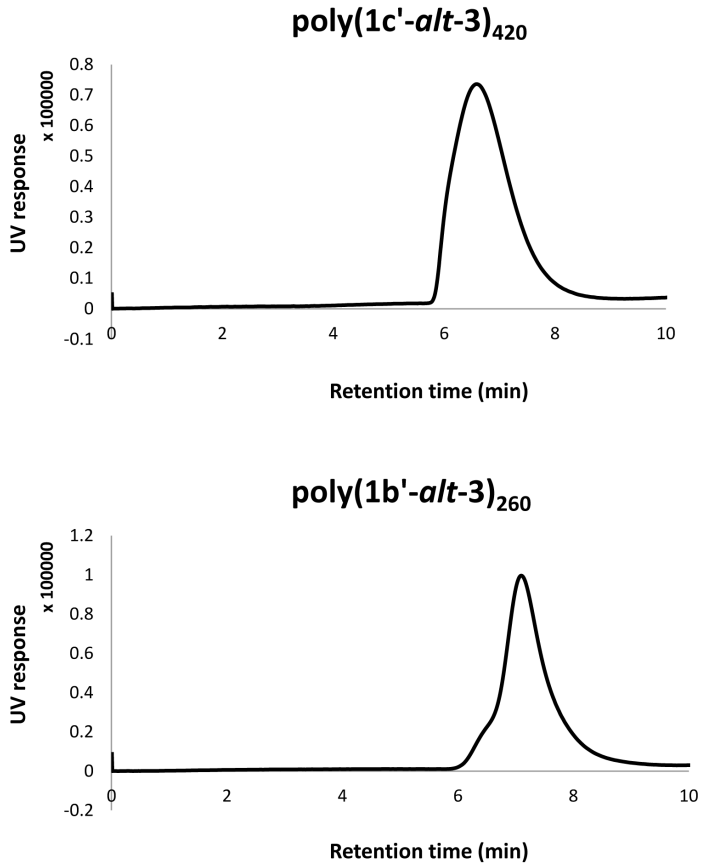


Figure S56. Molar mass dispersity ($Đ_M$) trace of long linear isomerized amide AROMP polymers Phenogel 5µm 10E4A, LC column (300x7.8mm, 500KDa exclusion limit), Phenomenex, was used with a flow rate of 1.00 mL/min in THF at 30°C. Both polymers were prepared with isomerized and purified amides.

References

1. Snider BB, Rodini DJ, Cionn RSE, & Sealfon S (1979) Lewis acid catalyzed reactions of methyl propiolate with unactivated alkenes. *J. Am. Chem. Soc.* 101:5283-5493.
2. Tan L, Parker KA, & Sampson NS (2014) A bicyclo[4.2.0]octene-derived monomer provides completely linear alternating copolymers via alternating ring-opening metathesis polymerization (AROMP). *Macromolecules* 47:6572–6579.