

Sustainable production of biofuel precursors by aldol condensation with biomass-derived 5-methylfurfural

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Experimental details and characteristics of compounds

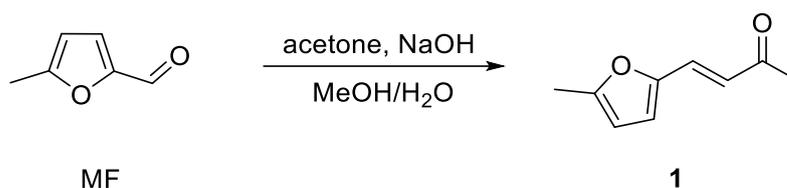
General information.

Commercially available reagents and solvents were of analytical grade or were purified prior to use by standard methods. NMR spectra were recorded using a Bruker Fourier 300 HD, Bruker Avance III 400 and Bruker DRX-500 spectrometers at the following frequencies: 300.1/400.1/500.1 MHz (^1H), 75.5/100.6/125.8 MHz (^{13}C). The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, o = octet, n = nonet, m = multiplet, br = broad. NMR chemical shifts were measured relative to residual protio solvent peaks. Processing was carried out using the MestReNova software.

General method for aldol condensation reaction.

To aqueous NaOH (0.25 M, 1 ml), the appropriate ketone (0.5 mmol for the synthesis of compounds **7-10**; 2 mmol for the synthesis of compounds **2,3**; 10 mmol for the synthesis of compounds **1,4-6**) was added followed by solution of 5-methylfurfural (100 μL , 1 mmol) in MeOH (1 ml), and the reaction mixture was stirred at ~ 24 $^\circ\text{C}$ for 12 h. The products were isolated by extraction with Et₂O (mono-aldol products **1-5** and di-aldol **9**), by filtration (di-aldol products **7,8,10**) or by column chromatography (mono-aldol **6**).

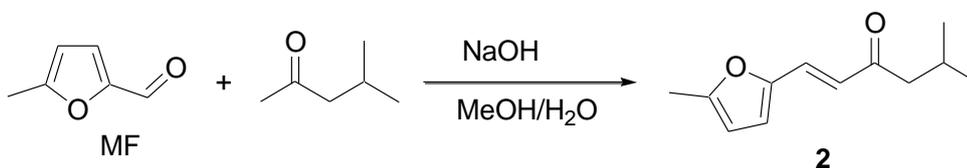
(E)-4-(5-Methylfuran-2-yl)but-3-en-2-one (1).



Compound **1** was obtained as a light-yellow oil with a yield of 91%.

^1H NMR (300 MHz, acetone- d_6): δ 7.30 (d, $J = 16.0$ Hz, 1H), 6.74 (d, $J = 3.3$ Hz, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.22 (dd, $J = 3.3, 0.7$ Hz, 1H), 2.34 (s, 3H), 2.26 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetone- d_6): δ 197.2, 156.6, 150.6, 130.0, 123.6, 118.2, 110.0, 27.5, 13.8. The NMR data were in accordance with the literature.^[S1]

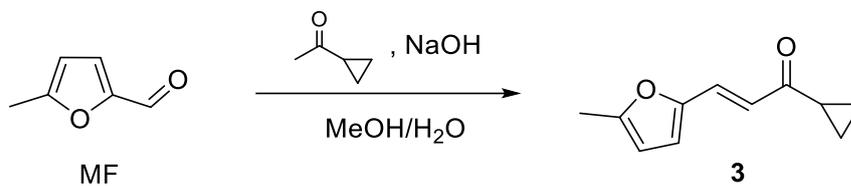
(E)-5-Methyl-1-(5-methylfuran-2-yl)hex-1-en-3-one (2).



Compound **2** was obtained as a brownish oil with an yield of 98%.

^1H NMR (300 MHz, acetone- d_6): δ 7.31 (d, $J = 15.9$ Hz, 1H), 6.74 (d, $J = 3.3$ Hz, 1H), 6.51 (d, $J = 15.9$ Hz, 1H), 6.22 (dd, $J = 3.2, 0.8$ Hz, 1H), 2.49 (d, $J = 7.0$ Hz, 2H), 2.35 (s, 3H), 2.15 (dp, $J = 13.5, 6.7$ Hz, 1H), 0.93 (d, $J = 6.7$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetone- d_6): δ 199.2, 156.5, 150.8, 129.1, 123.2, 118.3, 110.0, 50.3, 25.8, 22.9, 13.8. The NMR data were in accordance with the literature.^[S2]

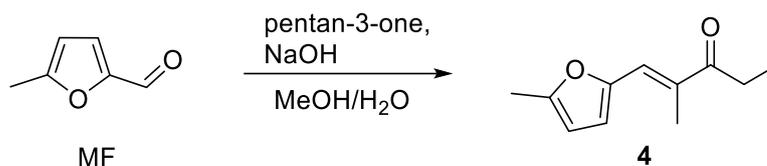
(E)-1-Cyclopropyl-3-(5-methylfuran-2-yl)prop-2-en-1-one (3).



Compound **3** was obtained as a yellowish oil with a yield of 91%.

^1H NMR (300 MHz, CDCl_3): δ (d, $J = 15.9$ Hz, 1H), 6.69 (d, $J = 15.7$ Hz, 1H), 6.55 (d, $J = 3.2$ Hz, 1H), 6.08 (d, $J = 2.6$ Hz, 1H), 2.35 (s, 3H), 2.12 (m, 1H), 1.12 (m, 2H), 0.92 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 199.7, 155.7, 150.0, 128.4, 121.9, 117.6, 109.2, 20.2, 14.1, 11.1.

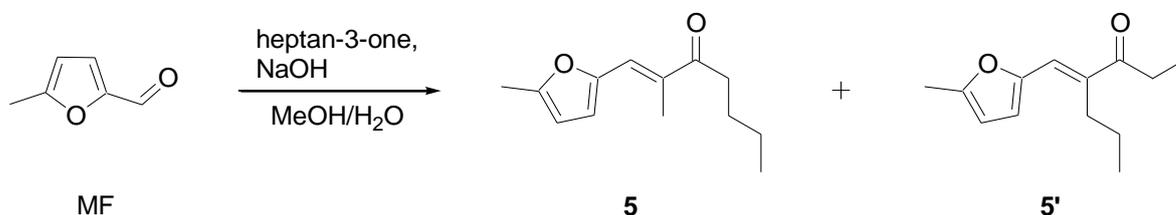
(E)-2-Methyl-1-(5-methylfuran-2-yl)pent-1-en-3-one (4).



Compound **4** was obtained as an orange oil with a yield of 94% and ~90% purity (by NMR).

¹H NMR (300 MHz, CDCl₃): δ 7.24 (br. s, 1H), 6.57 (d, *J* = 3.3 Hz, 2H), 6.13 (d, *J* = 3.2 Hz, 2H), 2.76 (q, *J* = 7.3 Hz, 4H), 2.36 (s, 6H), 2.12 (s, 6H), 1.14 (t, *J* = 7.3 Hz, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 202.1, 154.9, 150.6, 132.1, 125.8, 116.8, 109.0, 30.6, 14.0, 13.2, 9.2.

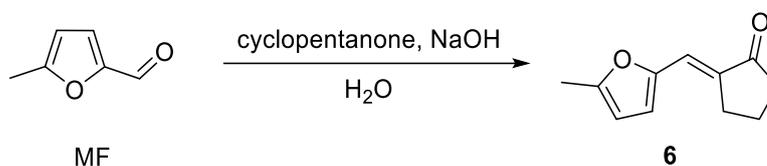
(E)-2-Methyl-1-(5-methylfuran-2-yl)hept-1-en-3-one (5).



Mixture of compounds **5** and **5'** (94%, ~10:1 ratio) was obtained as the yellowish oil.

¹H NMR (300 MHz, CDCl₃): δ 7.24 (br. s, 0.9H), 7.16 (br. s, 0.1H), 6.58 (d, *J* = 3.3 Hz, 0.9H), 6.54 (d, *J* = 3.3 Hz, 0.1H), 6.13 (d, *J* = 3.3 Hz, 0.9H), 6.11 (br. s, 0.1H), 2.77 – 2.69 (m, 1.8H), 2.65 – 2.60 (m, 0.2H), 2.36 (s, 3H), 2.11 (s, 2.4H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.36 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 0.3H), 0.93 (t, *J* = 7.3 Hz, 2.7H). ¹³C NMR (75 MHz, CDCl₃, signals of the compound **5'** are in parentheses) δ 201.9, 154.9, 150.6, 132.4, 125.9, (125.4), 116.8, (116.5), 109.0, (108.9), 37.2, (30.6), (28.9), 27.5, 22.7, (22.13), (14.54), 14.1, 14.0, 13.2, (9.21).

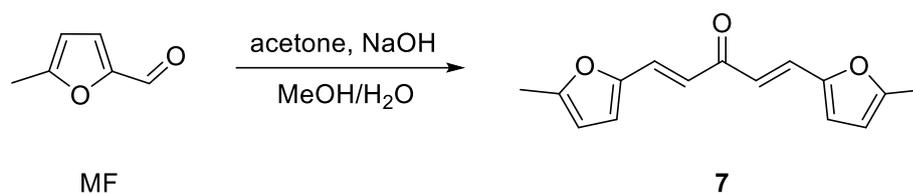
(E)-2-[(5-Methylfuran-2-yl)methylene]cyclopentan-1-one (6).



Compound **6** was obtained as light-yellow amorphous solid with an yield of 86%.

¹H NMR (300 MHz, acetone-*d*₆): δ 6.98 (t, *J* = 2.7 Hz, 1H), 6.72 (d, *J* = 3.3 Hz, 1H), 6.25 (d, *J* = 3.3 Hz, 1H), 2.93 (td, *J* = 7.3, 2.5 Hz, 2H), 2.36 (s, 3H), 2.29 (t, *J* = 7.8 Hz, 2H), 2.04 – 1.94 (m, 2H). ¹³C{¹H} NMR (75 MHz, acetone-*d*₆): δ 206.5, 156.3, 151.7, 133.4, 118.3, 118.1, 110.0, 38.2, 29.7, 20.4, 13.8. NMR data were in accordance with the literature.^[S2]

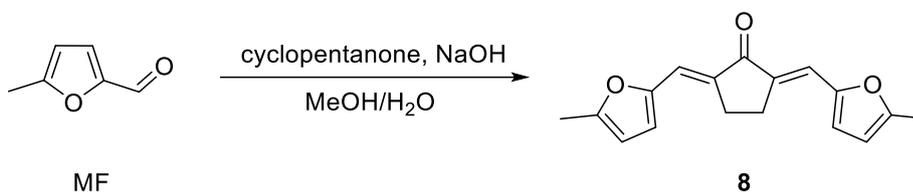
(1E,4E)-1,5-Bis(5-methylfuran-2-yl)penta-1,4-dien-3-one (7).



Compound **7** was obtained as reddish powder with a yield of 91%, m.p. 94-95 °C.

^1H NMR (300 MHz, acetone- d_6): δ 7.43 (d, $J = 15.6$ Hz, 2H), 6.86 (d, $J = 15.6$ Hz, 2H), 6.79 (d, $J = 3.3$ Hz, 2H), 6.24 (d, $J = 3.3$ Hz, 2H), 2.37 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, acetone- d_6): δ 187.7, 156.6, 151.2, 129.4, 122.5, 118.5, 110.2, 13.8. NMR data were in accordance with the literature.^[S3]

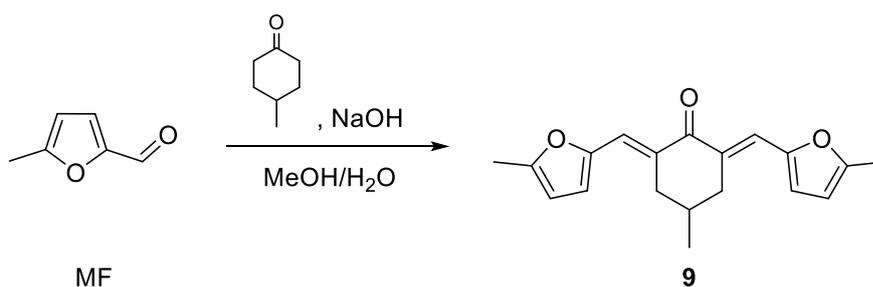
(2E,5E)-2,5-Bis[(5-methylfuran-2-yl)methylene]cyclopentan-1-one (8).



Compound **8**, an orange powder, yield 97%, m.p. 102-104 °C (lit.^[S4] 106 °C).

^1H NMR (300 MHz, DMSO- d_6): δ 7.11 (s, 2H), 6.85 (d, $J = 3.3$ Hz, 2H), 6.35 (d, $J = 3.3$ Hz, 2H), 2.96 (s, 4H), 2.37 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO- d_6): δ 193.7, 155.7, 150.6, 134.4, 118.6, 118.1, 109.8, 25.4, 13.7. NMR data were in accordance with the literature.^[S4]

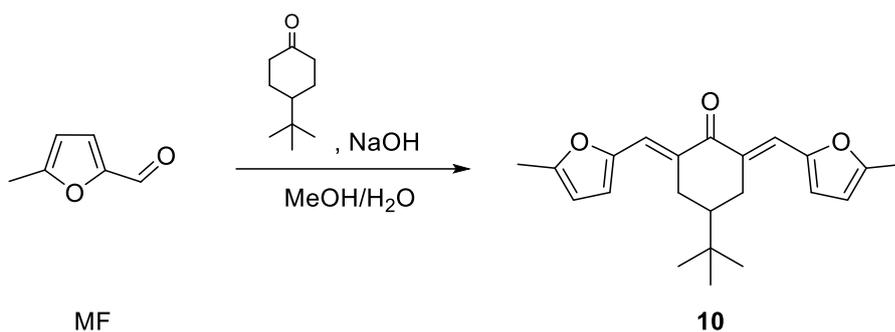
(2E,6E)-4-Methyl-2,6-bis[(5-methylfuran-2-yl)methylene]cyclohexan-1-one (9).



Compound **9** was obtained as yellow oil with a yield of 92%.

^1H NMR (300 MHz, CDCl_3): δ 7.49 (s, 2H), 6.57 (d, $J = 3.3$ Hz, 2H), 6.12 (d, $J = 3.0$ Hz, 2H), 3.20 (dd, $J = 16.7, 3.8$ Hz, 2H), 2.46 (m, 2H), 2.37 (s, 6H), 2.18 – 1.90 (m, 1H), 1.16 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 188.9, 155.2, 151.6, 131.1, 123.7, 117.8, 109.0, 36.2, 28.2, 22.0, 14.2.

(2E,6E)-4-(tert-Butyl)-2,6-bis[(5-methylfuran-2-yl)methylene]cyclohexan-1-one (10)



Compound **9** was obtained as yellow powder with a yield of 95%, m.p. 110-112 °C.

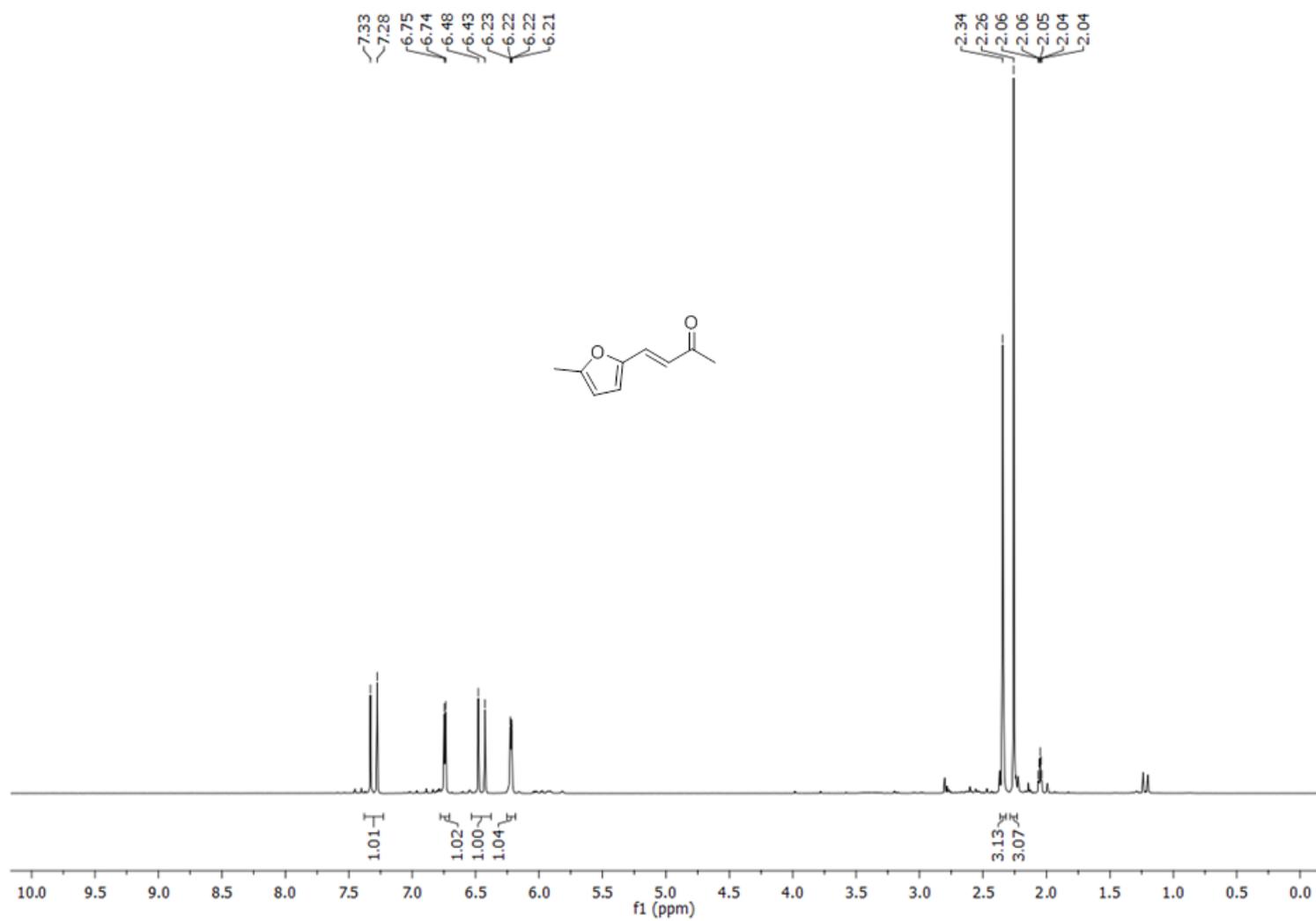
^1H NMR (300 MHz, CDCl_3): δ 7.46 (d, $J = 2.2$ Hz, 2H), 6.56 (d, $J = 3.3$ Hz, 2H), 6.12 (d, $J = 3.1$ Hz, 2H), 3.36 (dd, $J = 16.3, 3.1$ Hz, 2H), 2.45 – 2.25 (m, 8H), 1.57 (tt, $J = 13.0, 3.6$ Hz, 1H), 1.04 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 189.4, 155.1, 151.6, 132.0, 123.3, 117.7, 109.0, 43.4, 32.6, 29.3, 27.5, 14.1.

References

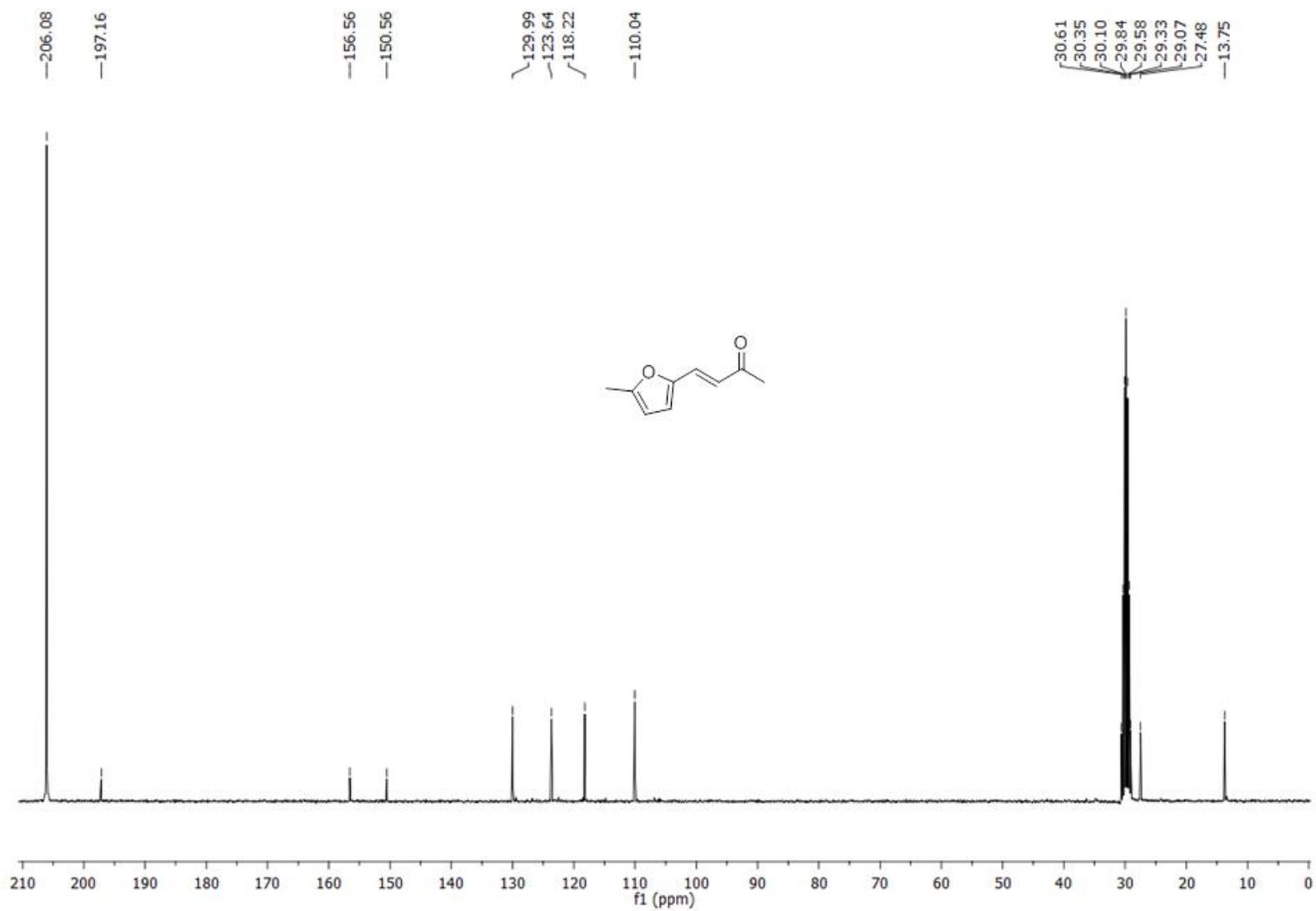
- S1 B. J. Gorsline, L. Wang, P. Ren and B. P. Carrow, *J. Am. Chem. Soc.*, 2017, **139**, 9605.
- S2 K. I. Galkin and V. P. Ananikov, *ChemSusChem*, 2019, **12**, 185.
- S3 K. Gupta and S. K. Singh, *ACS Sustainable Chem. Eng.*, 2018, **6**, 4793.
- S4 S. Z. Vatsadze, M. A. Manaenkova, N. V. Sviridenkova, N. V. Zyk, D. P. Krut'ko, A. V. Churakov, M. Yu. Antipin, J. A. K. Howard and H. Lang, *Russ. Chem. Bull.*, 2006, **55**, 1184.

Spectral Data

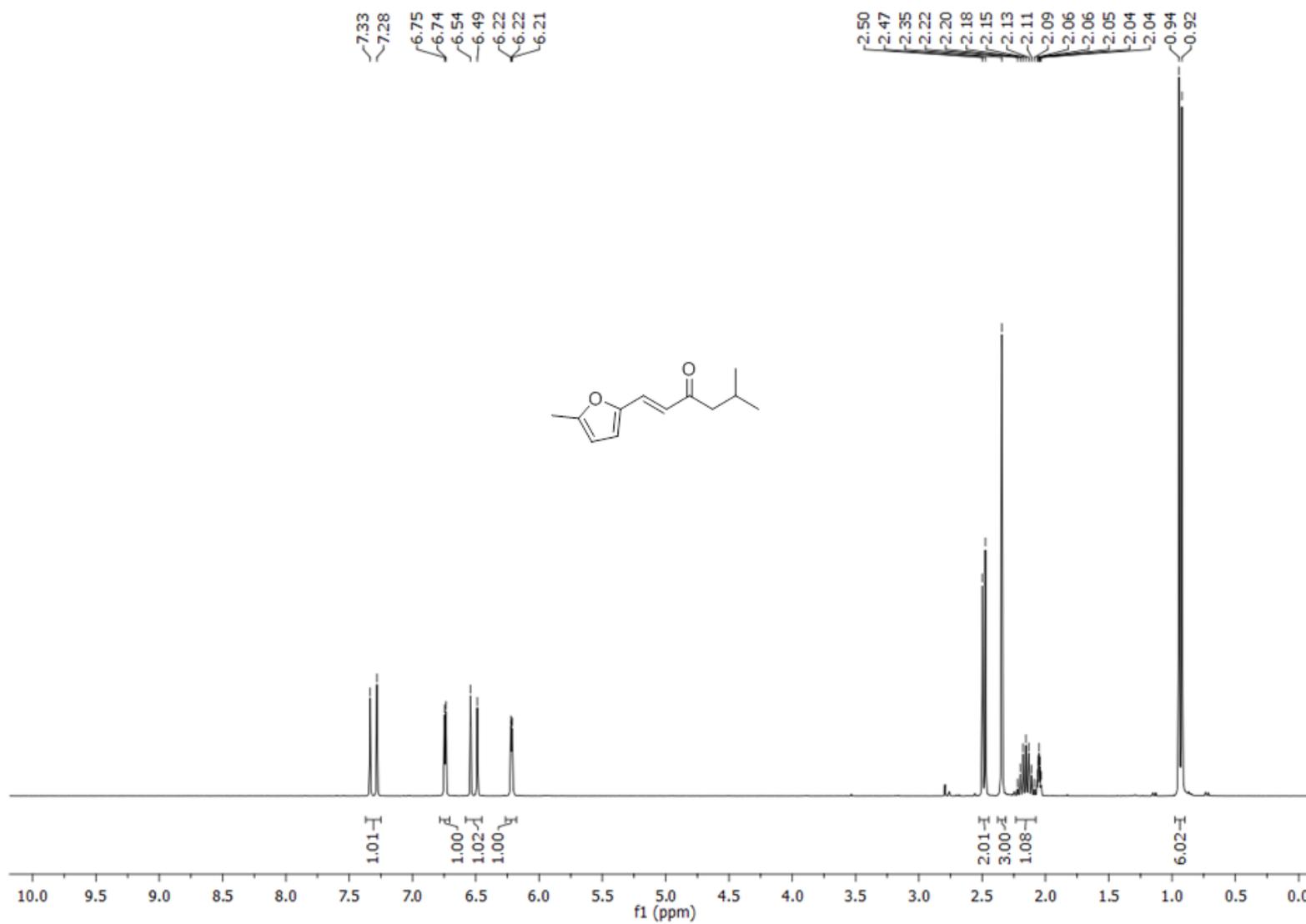
^1H NMR spectrum of compound **1**.



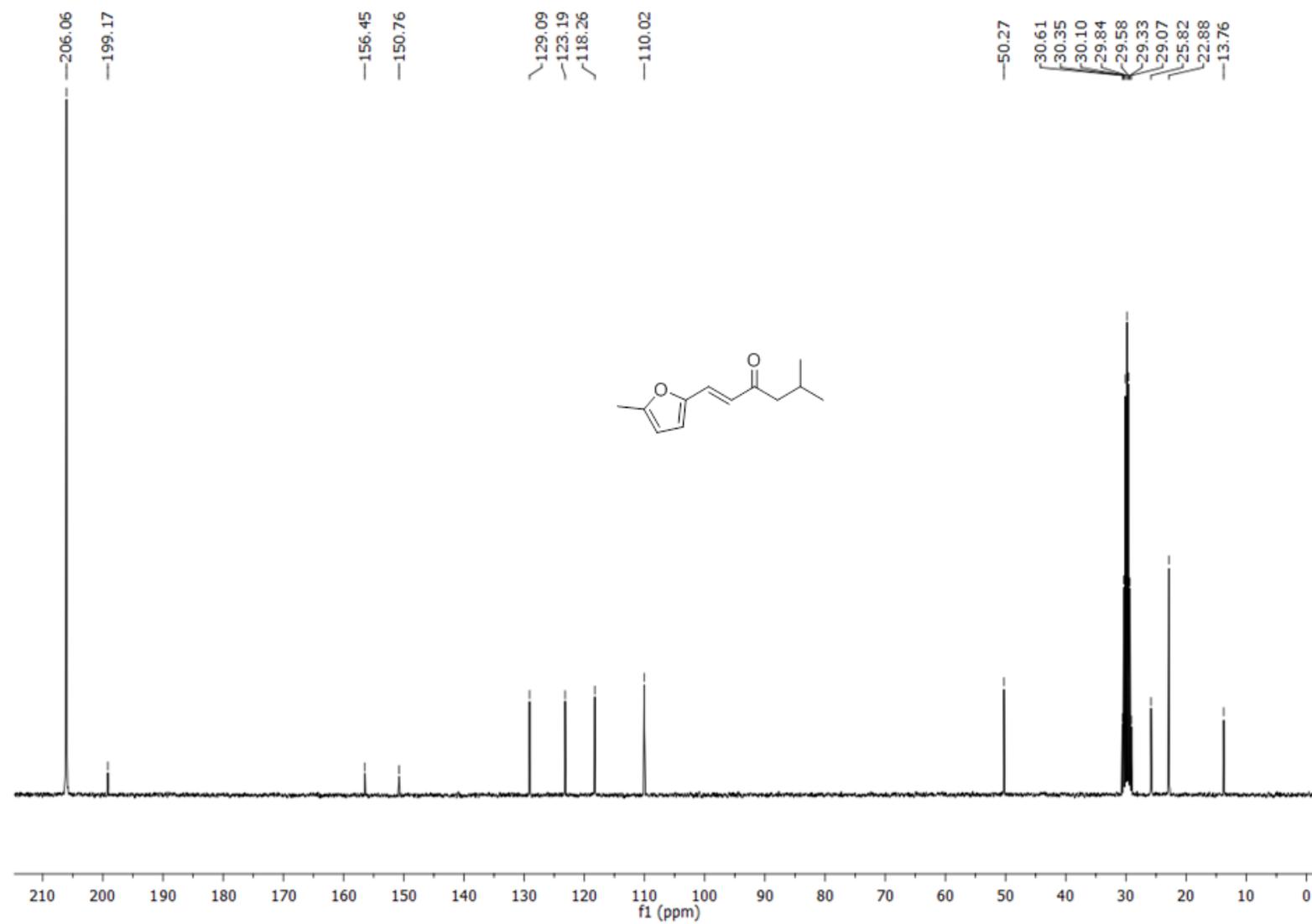
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1**.



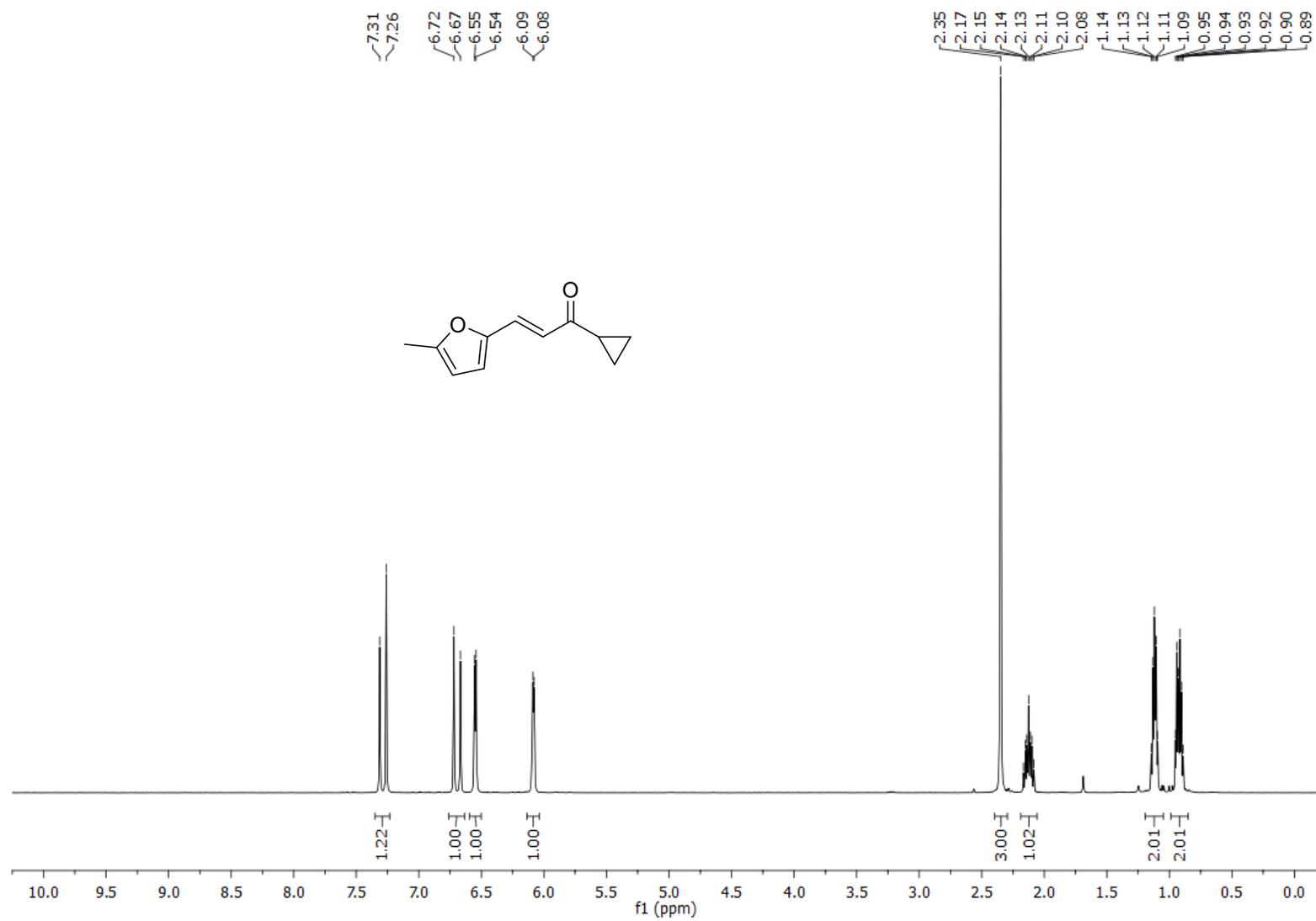
¹H NMR spectrum of compound **2**.



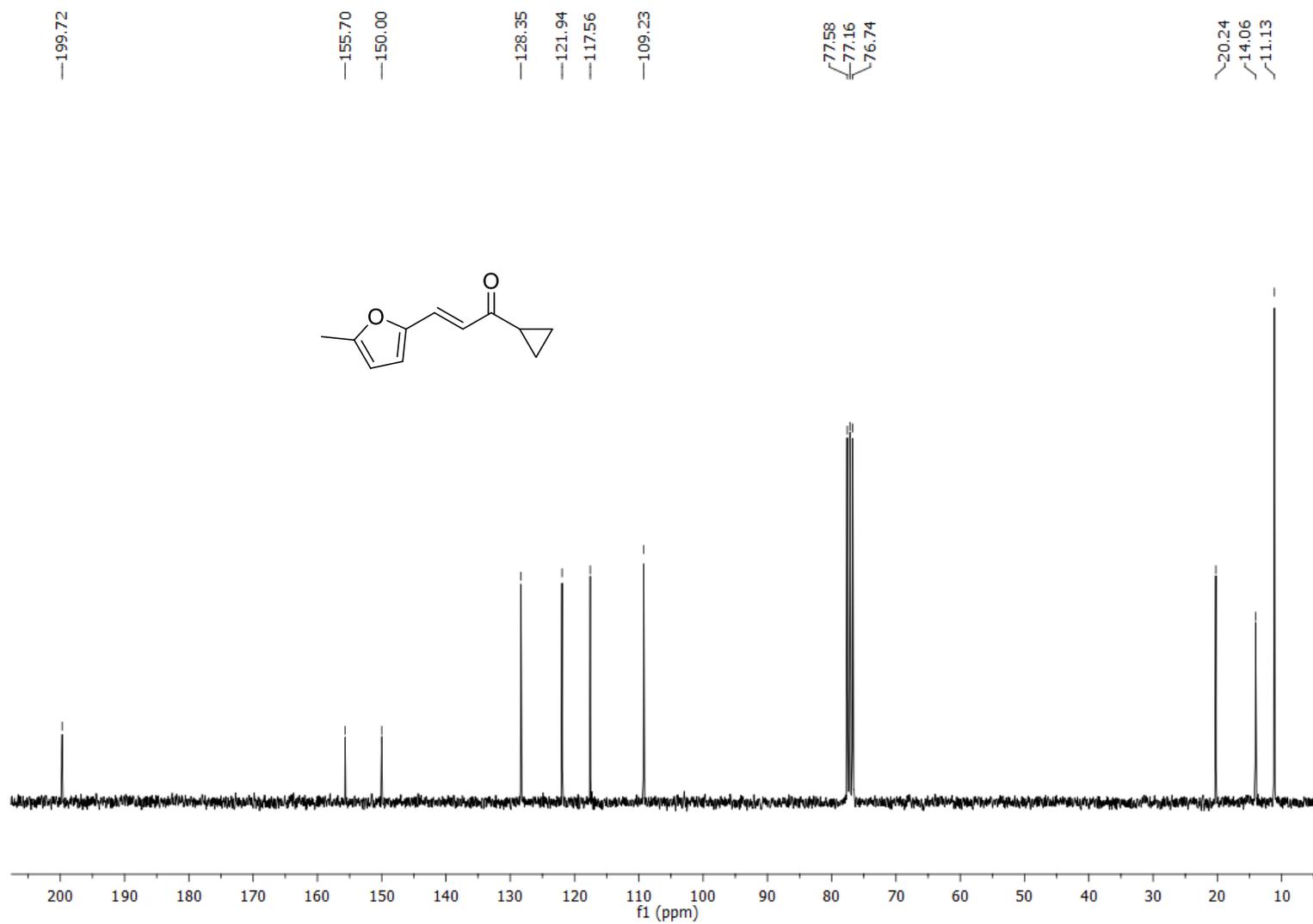
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **2**.



¹H NMR spectrum of compound **3**.



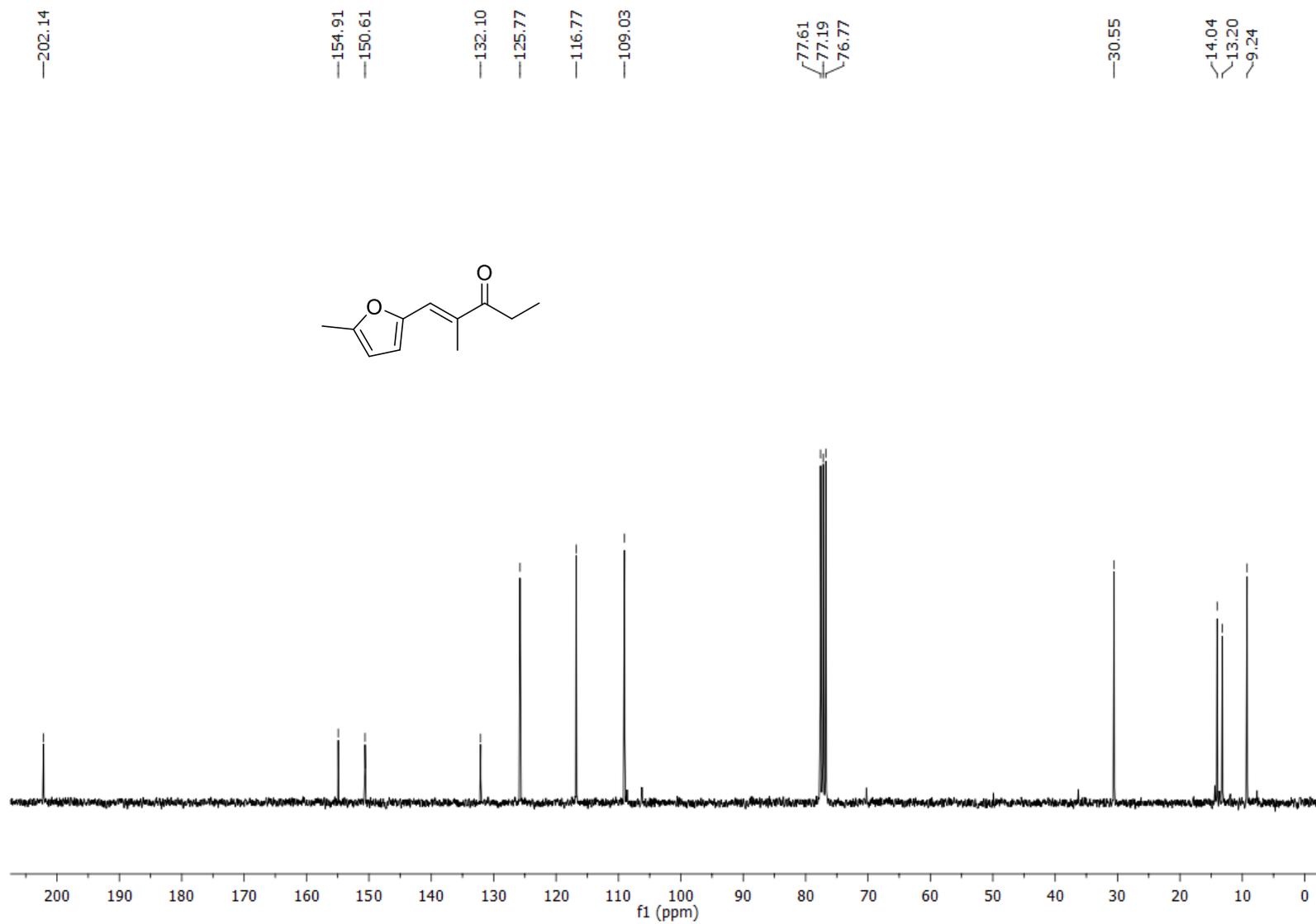
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3**.



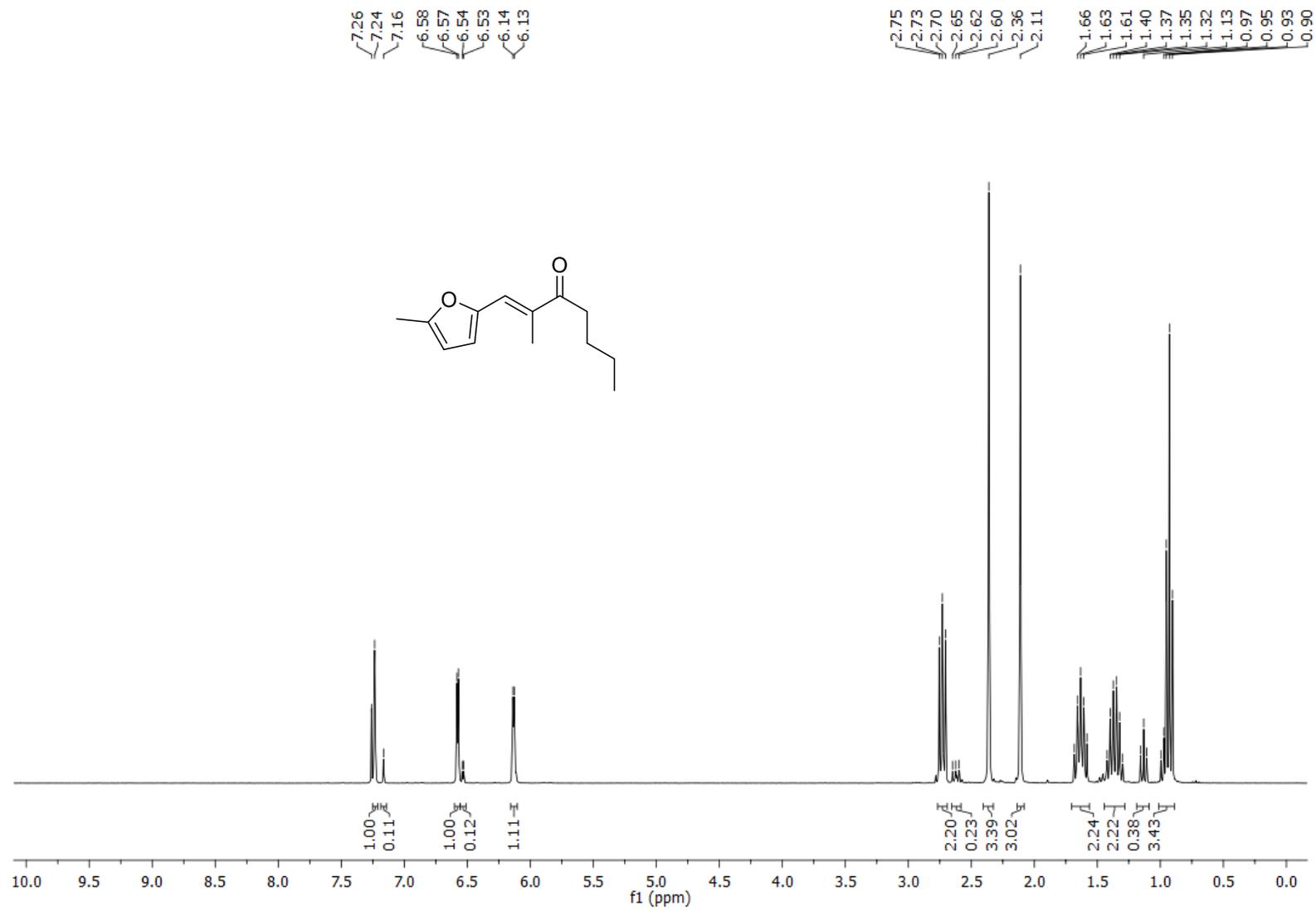
¹H NMR spectrum of compound **4**.



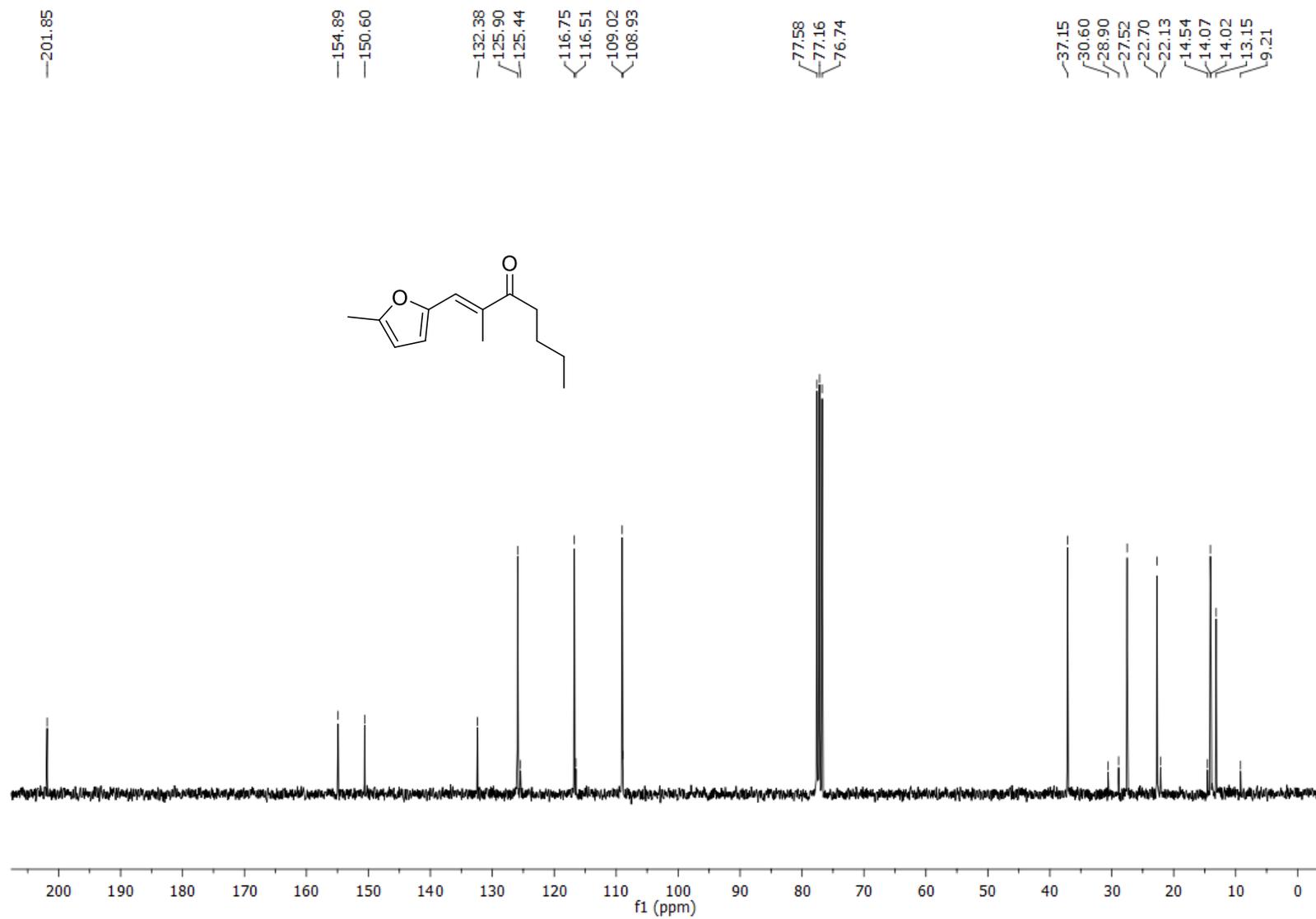
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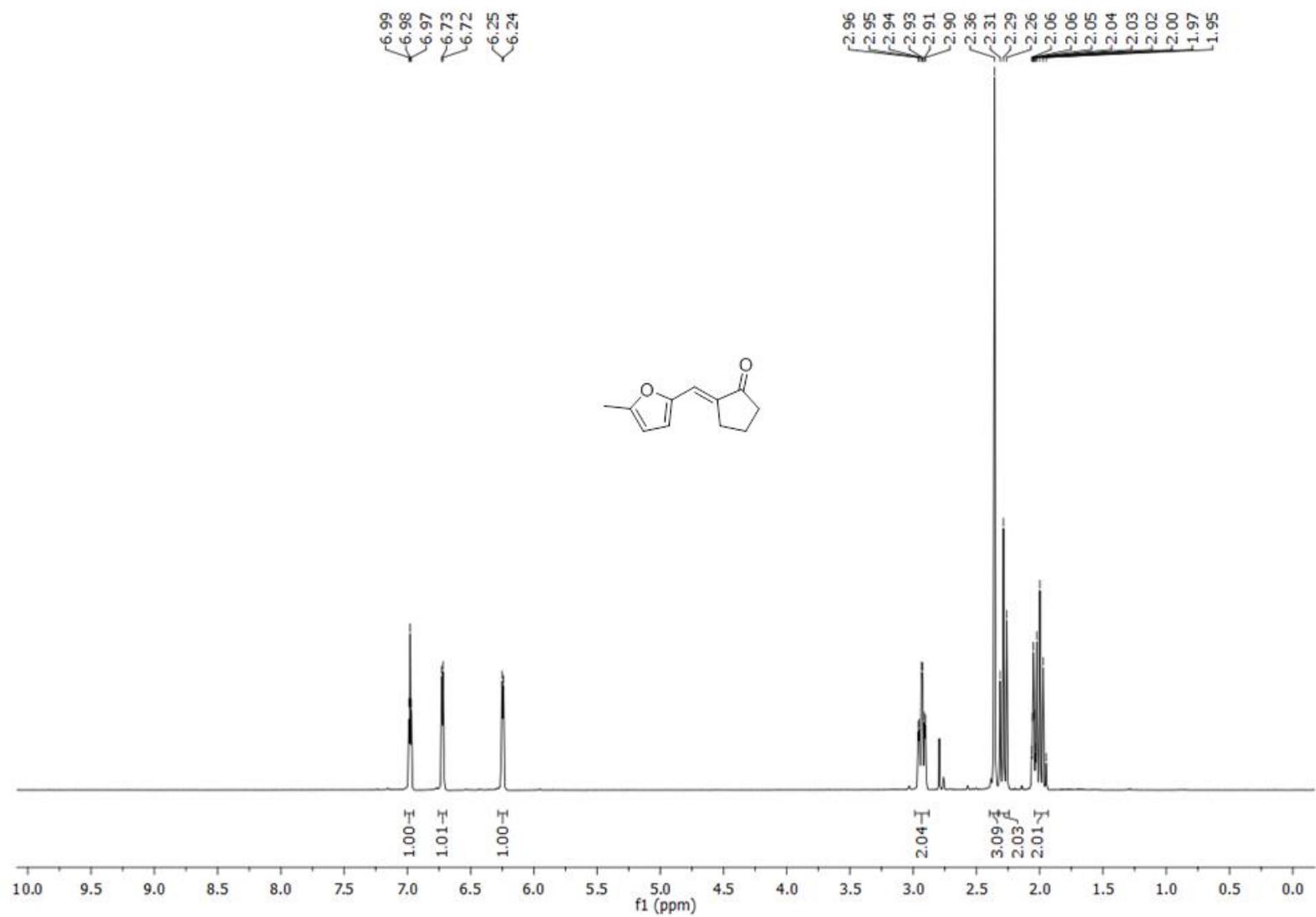
¹H NMR spectrum of compound **5**.



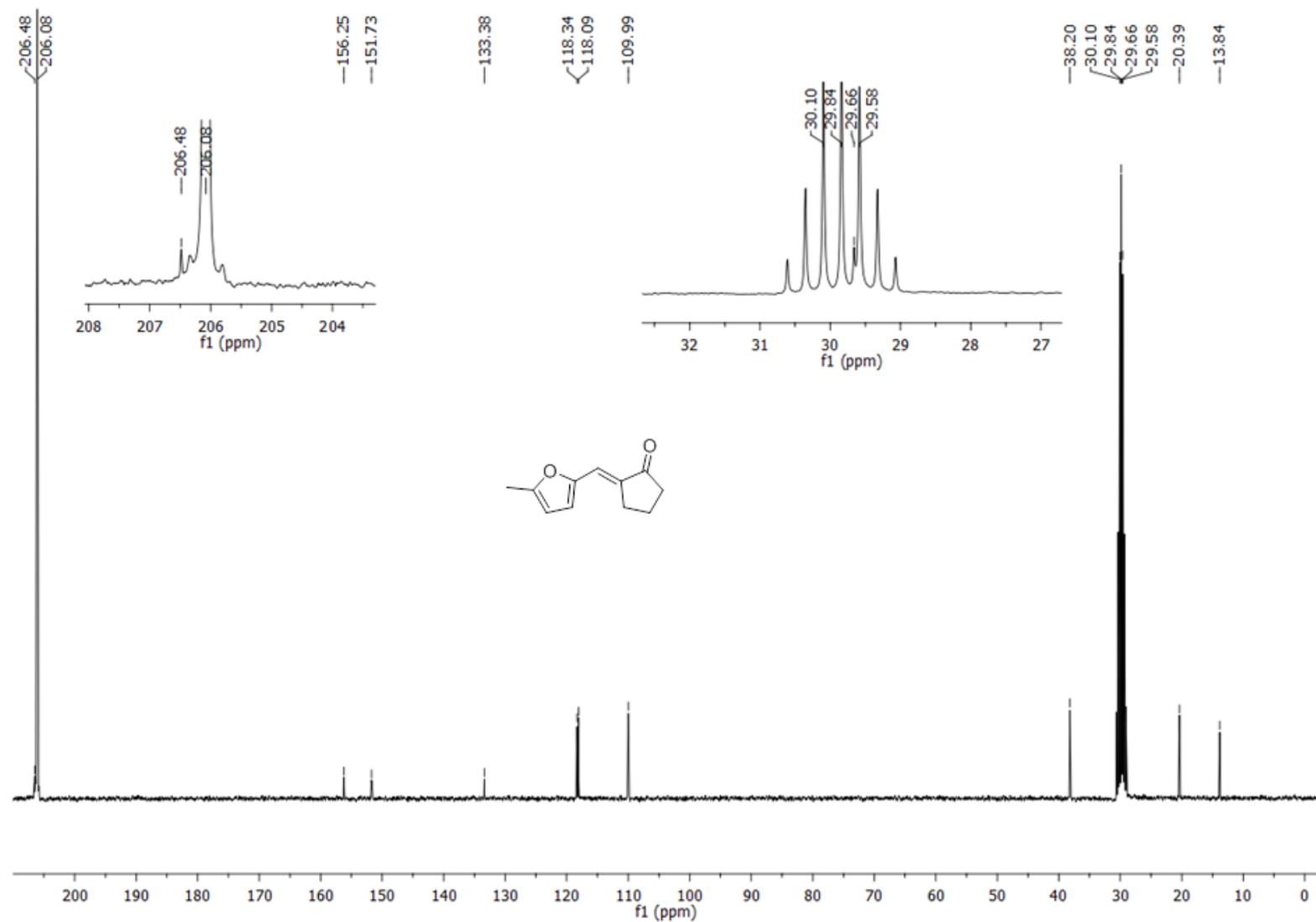
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **5**.



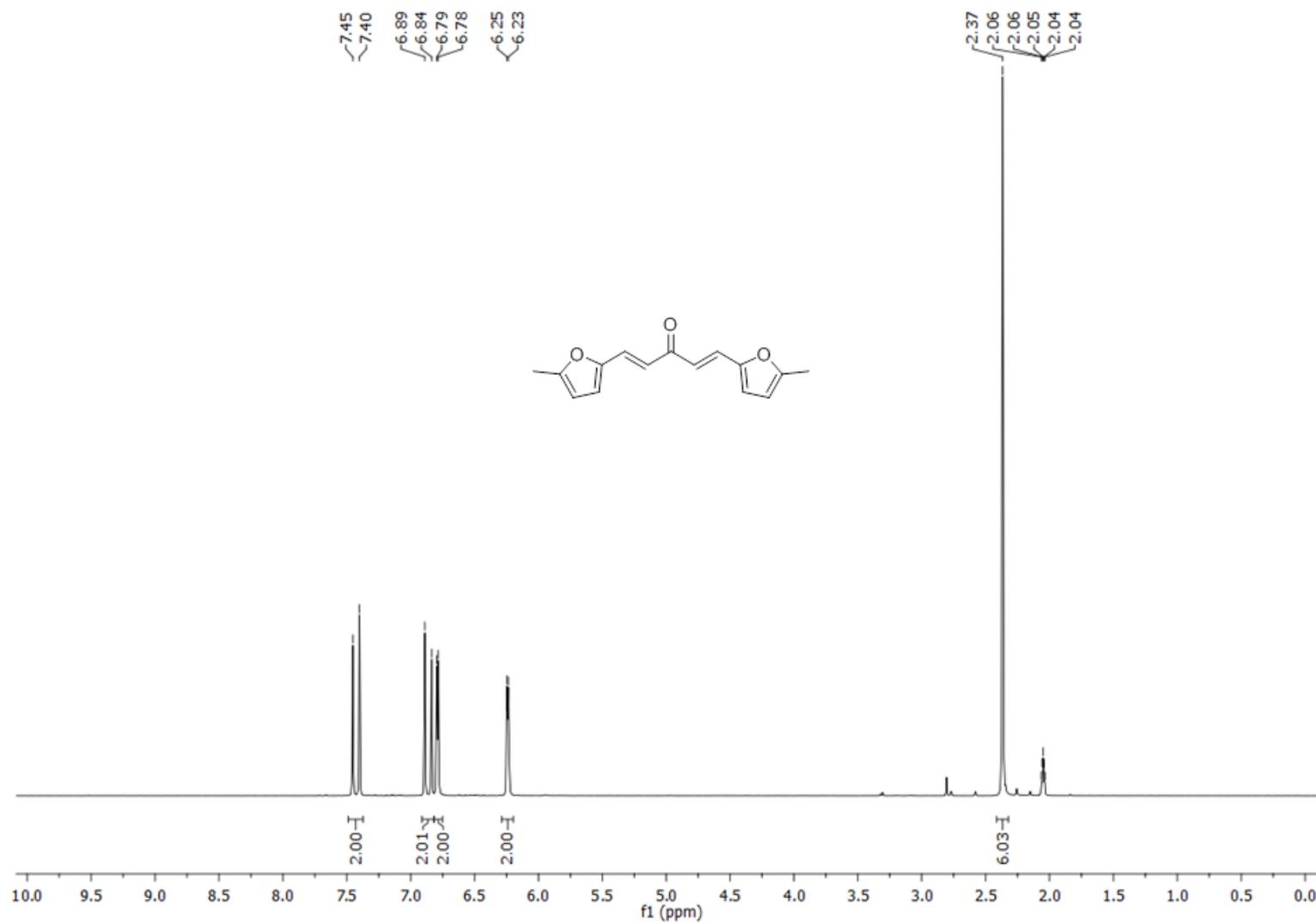
¹H NMR spectrum of compound **6**.



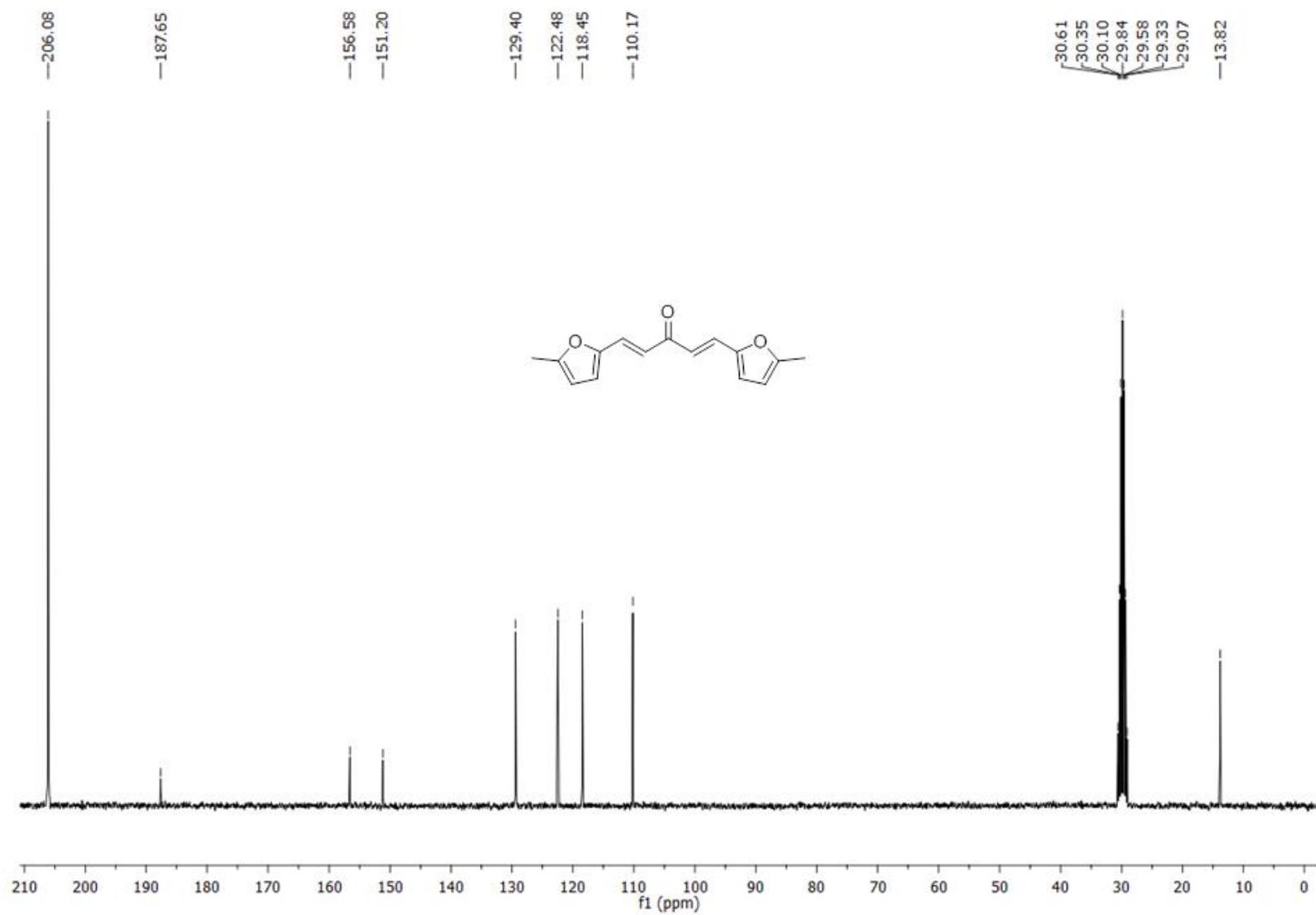
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **6**.



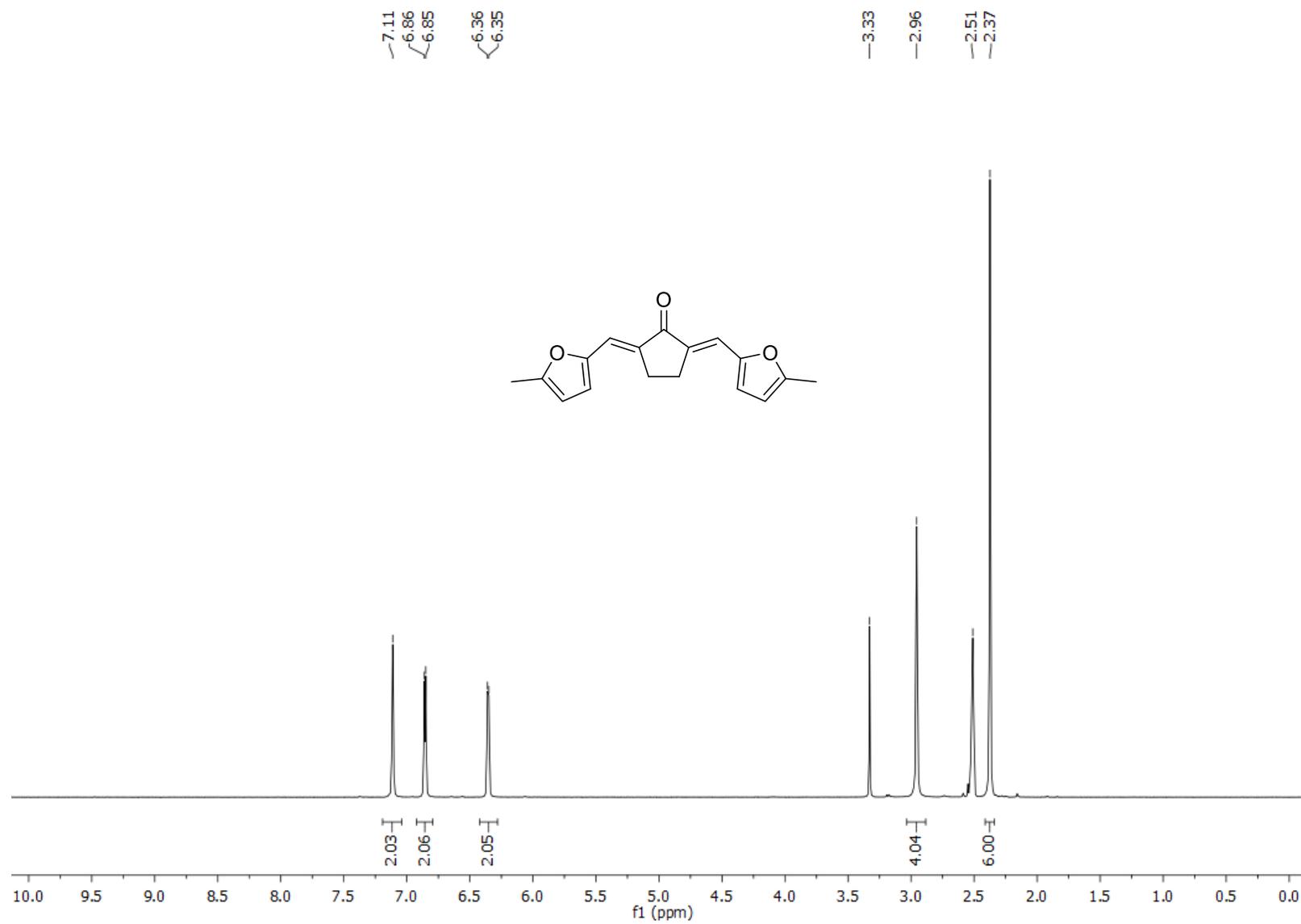
¹H NMR spectrum of compound 7.



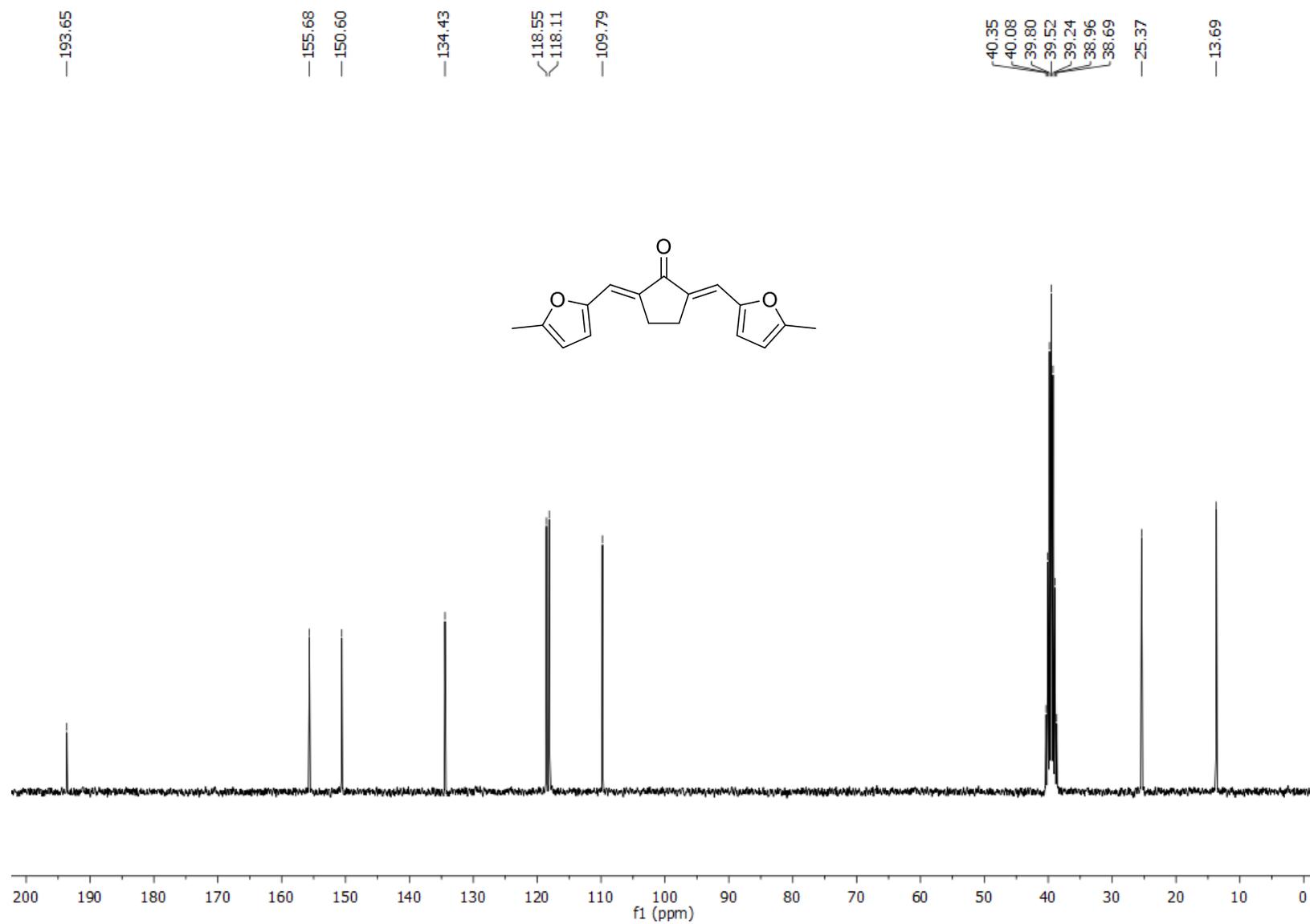
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 7.



¹H NMR spectrum of compound **8**.



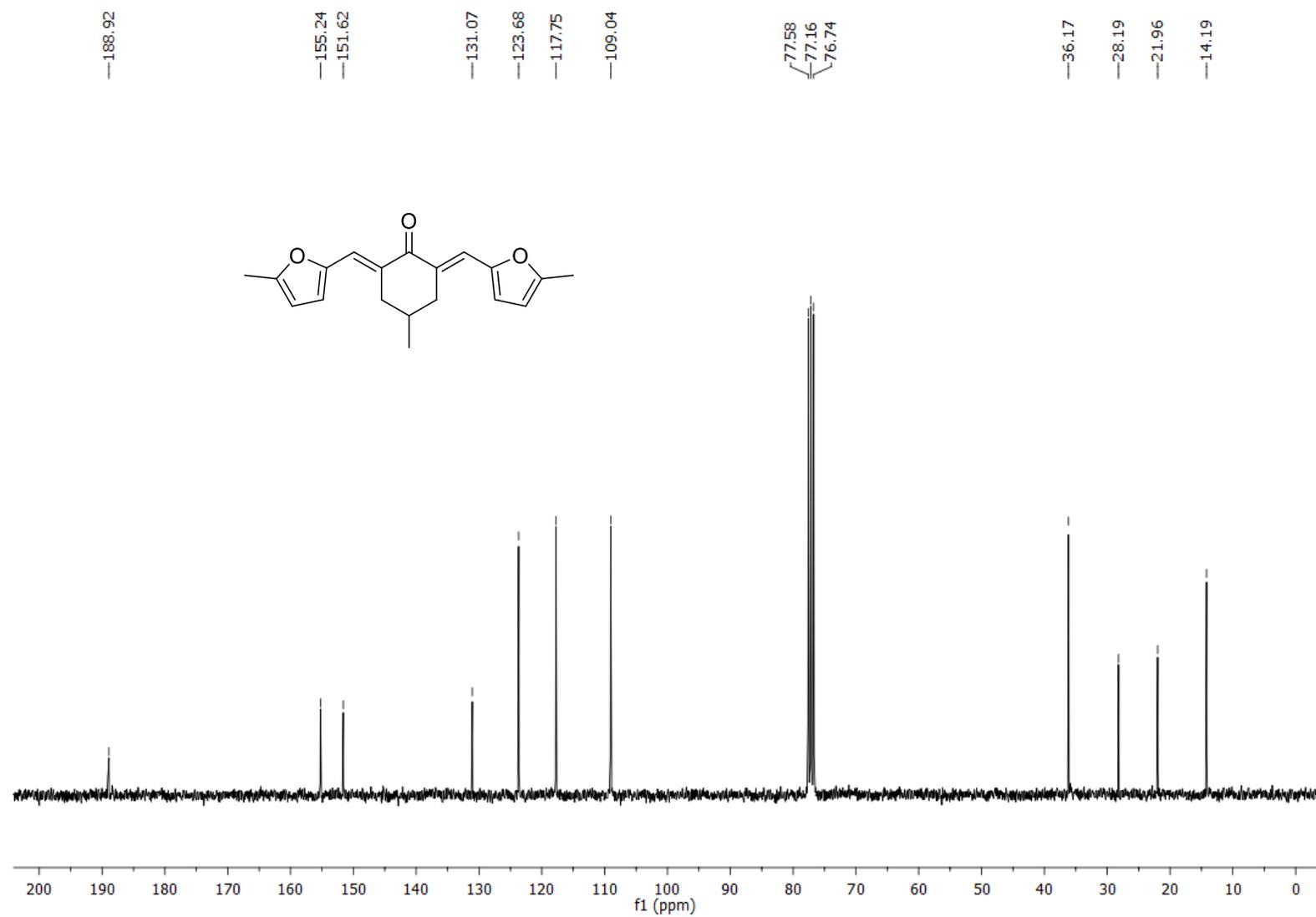
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **8**.



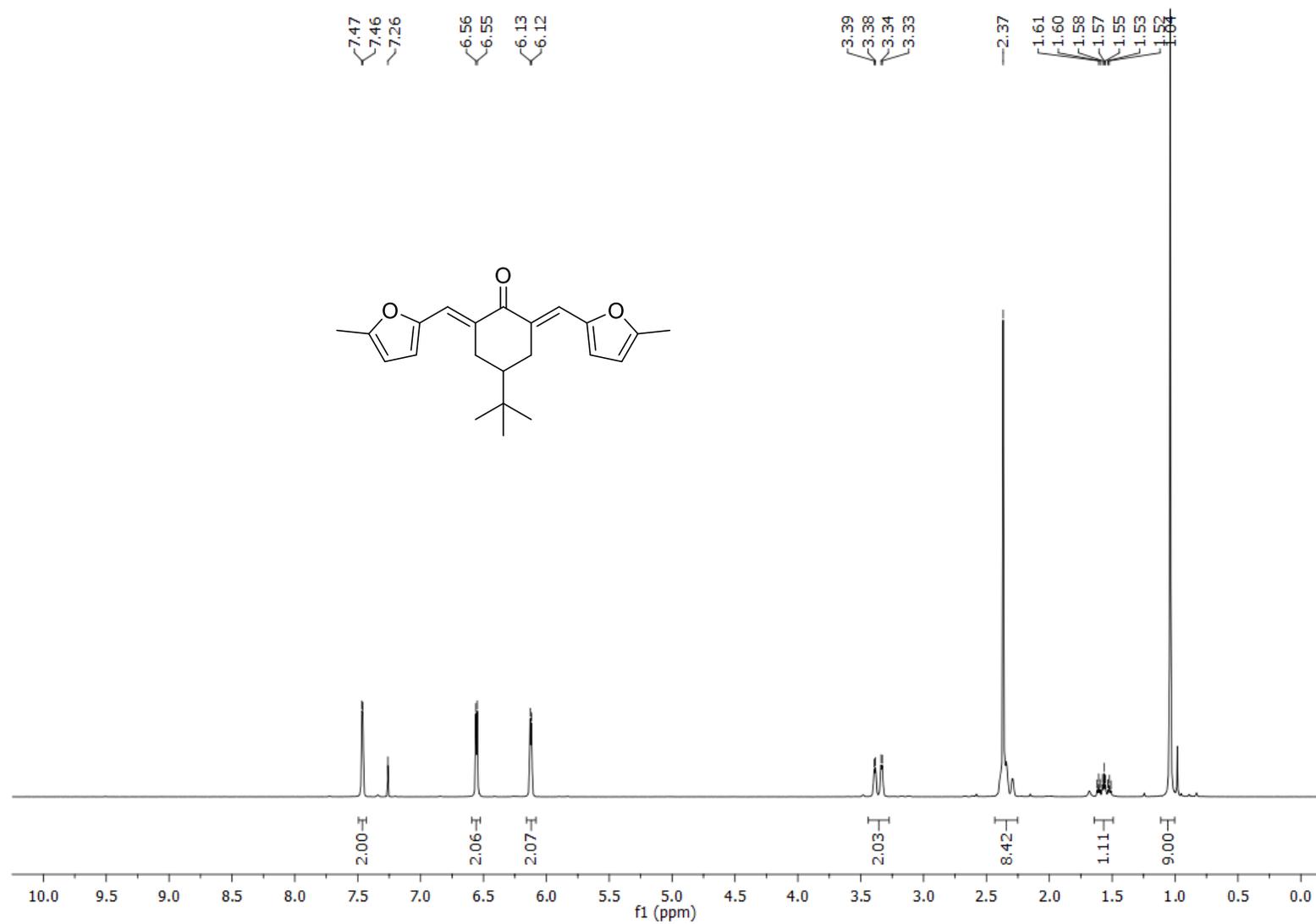
¹H NMR spectrum of compound **9**.



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **9**.



¹H NMR spectrum of compound **10**.



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **10**.

