

# Catalyst-Free Formal Conjugate Addition/Aldol or Mannich Multicomponent Reactions of Mixed Aliphatic Organozinc Reagents, $\pi$ -Electrophiles and Michael Acceptors

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## Table of contents

1. General information .....	S2
2. 3CR with carbonyl compounds.....	S2
3. 3CR with sulfonyl imines.....	S16
4. Copies of NMR spectra .....	S20

## 1. General information

All commercially available reagents, including solvents, were used as received.

Room temperature means 18–25 °C.

Melting points (mp) are uncorrected and were measured on a Büchi B-545 apparatus.

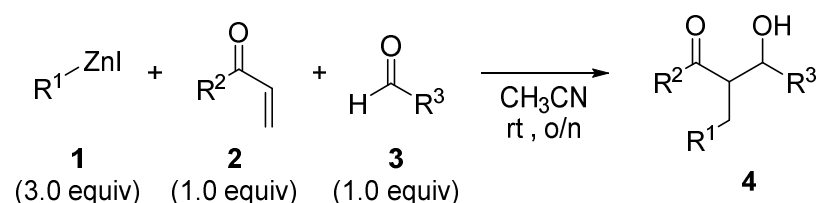
Analytical thin layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Visualization was effected using ultra-violet light ( $\lambda = 254$  nm) and/or a aqueous solution of  $\text{KMnO}_4$ . Flash chromatography (FC) was performed on 40–63  $\mu\text{m}$  silica gel with mixtures of solvents.

High-Resolution Mass Spectra were obtained at the ICOA of the Université of Orléans by electrospray ionization using a Q-TOF analyzer.

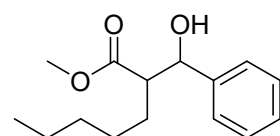
NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer.  $^1\text{H}$  NMR chemical shifts were referenced to the residual solvent signal;  $^{13}\text{C}$  NMR chemical shifts were referenced to the deuterated solvent signal. Multiplicity was defined by DEPT 135 analysis. Data are presented as follows: chemical shift  $\delta$  (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant  $J$  (Hz), integration.

d.r. were determined by GC or  $^1\text{H}$  NMR analysis of the crude reaction mixture.

## 2.3. CR with carbonyl compounds



**General procedure 1 (GP1):** A 10 mL sealable tube equipped with a stir bar and filled with an argon atmosphere was charged with aldehyde **3** (0.5 mmol, 1.0 equiv), acrylate **2** (1.0 equiv) and acetonitrile (2 mL). Under stirring, a solution of organozinc reagent **1** in  $\text{CH}_3\text{CN}$  (3.0 equiv) was added in one portion. The reaction was stirred at room temperature overnight. Then, the reaction mixture was poured into sat aq  $\text{NH}_4\text{Cl}$  (20 mL). The resulting solution was extracted twice with  $\text{EtOAc}$  (15+15 mL) and the combined organic layers were washed brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated. The resulting crude material was purified on silica gel to give product **4**.



d.r. = 74:26

$\text{C}_{15}\text{H}_{22}\text{O}_3$

MW = 250,34

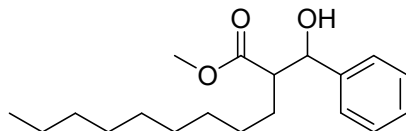
**Compound 4aaa:** Following **GP1** performed with benzaldehyde (47  $\mu\text{L}$ , 0.46 mmol, 1.0 equiv), methyl acrylate (41  $\mu\text{L}$ , 0.46 mmol, 1.0 equiv) and organozinc reagent **1a** (3.0 mL,  $\text{C} = 0.46$  M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [ $\text{V}(\text{SiO}_2) = 20$  mL, Cy/AE: 95:5 (100 mL), 90:10 (100 mL)] as a colorless oil (84 mg, 73%, d.r: 74:26).

$R_f$  (Cy/AE: 95/5, UV+*p*-Anis): 0.37.

**HRMS (ESI<sup>+</sup>):**  $m/z$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> Calcd. for  $\text{C}_{15}\text{H}_{22}\text{NaO}_3$ : 273.1461. Found: 273.1467.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.43–7.22 (m, 10H), 4.96 (d,  $J = 5.5$  Hz, 2H), 3.72 (d,  $J = 1.9$  Hz, 1H), 3.62 (d,  $J = 1.9$  Hz, 3H), 3.60–3.56 (m, 2H), 2.92–2.69 (m, 2H), 2.13 (m, 2H), 1.86–1.53 (m, 4H), 1.52–1.15 (m, 12H), 0.99–0.75 (m, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  175.9 (C), 175.6 (C), 141.6 (2 C), 128.7 (2 CH), 128.3 (2 CH), 127.7 (2 CH), 126.5 (2 CH), 126.1 (2 CH), 75.5 (CH), 74.2 (CH), 53.2 ( $\text{CH}_3$ ), 53.0 ( $\text{CH}_3$ ), 51.7 (CH), 51.6 (CH), 31.7 ( $\text{CH}_2$ ), 31.5 ( $\text{CH}_2$ ), 29.9 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_2$ ), 27.3 ( $\text{CH}_2$ ), 27.0 ( $\text{CH}_2$ ), 22.5 ( $\text{CH}_2$ ), 22.4 ( $\text{CH}_2$ ), 14.0 ( $\text{CH}_3$ ), 14.0 ( $\text{CH}_3$ ).



d.r. = 60:40  
 $\text{C}_{19}\text{H}_{30}\text{O}_3$   
 MW = 306,45

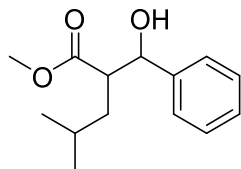
**Compound 4baa:** Following GP1 performed with benzaldehyde (60  $\mu\text{L}$ , 0.59 mmol, 1.0 equiv), methyl acrylate (53  $\mu\text{L}$ , 0.59 mmol, 1.0 equiv) and organozinc reagent **1b** (3.0 mL, C = 0.59 M, 1.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [ $\text{V}(\text{SiO}_2)$  = 20 mL, Cy/AE: 95:5 (100 mL), 90:10 (100 mL), 80:20 (100 mL)] as a colorless oil (149 mg, 82%, d.r: 60:40).

$R_f$  (Cy/AE : 95/5, UV+*p*-Anis): 0.18.

HRMS (ESI $^+$ ): m/z [ $\text{M}+\text{Na}$ ] $^+$  Calcd. for  $\text{C}_{19}\text{H}_{30}\text{NaO}_3$ : 329.2087. Found: 329.2092.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (major dia) 7.38–7.32 (m, 5H), 4.78 (d,  $J$  = 8.7 Hz, 1H), 3.70 (s, 3H), 3.64 (t,  $J$  = 6.6 Hz, 2H), 2.77–2.73 (m, 2H), 1.59–1.55 (m, 4H), 1.28–1.19 (m, 10H), 0.87 (t,  $J$  = 5.4 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (major dia) 176.0 (C), 142.2 (C), 128.7 (2 CH), 128.2 (CH), 126.6 (2 CH), 75.7 (CH), 53.3 ( $\text{CH}_3$ ), 51.9 (CH), 32.0 ( $\text{CH}_2$ ), 29.7 ( $\text{CH}_2$ ), 29.6 ( $\text{CH}_2$ ), 29.5 (2  $\text{CH}_2$ ), 29.4 ( $\text{CH}_2$ ), 27.3 ( $\text{CH}_2$ ), 22.8 ( $\text{CH}_2$ ), 14.2 ( $\text{CH}_3$ ).



d.r. = 90:10  
 $\text{C}_{14}\text{H}_{20}\text{O}_3$   
 MW = 236,31

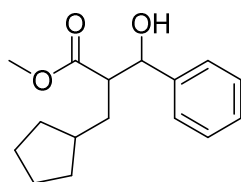
**Compound 4caa:** Following GP1 performed with benzaldehyde (49  $\mu\text{L}$ , 0.48 mmol, 1.0 equiv), ethyl acrylate (43  $\mu\text{L}$ , 0.48 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.36 M, 1.5 mmol, 3.0 equiv), the desired product was obtained after purification by FC [ $\text{V}(\text{SiO}_2)$  = 50 mL, Cy/AE : 95:5 (250 mL), 90:10 (250 mL)] as a yellow oil (112 mg, 99%, d.r : 90:10).

$R_f$  (EP/AE: 95/5 , UV+ $\text{KMnO}_4$ ): 0.34.

HRMS (ESI $^+$ ): m/z [ $\text{M}+\text{Na}$ ] $^+$  Calcd. for  $\text{C}_{14}\text{H}_{20}\text{NaO}_3$ : 259.1305. Found: 259.1310.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47–7.26 (m, 10H), 4.93 (d,  $J$  = 5.2 Hz, 2H), 3.70 (s, 1H), 3.59 (s, 5H), 2.93 (s, 2H), 2.81 (d,  $J$  = 5.4 Hz, 2H), 1.76 (t,  $J$  = 10.2 Hz, 3H), 1.43 (d,  $J$  = 7.6 Hz, 4H), 0.88 (d,  $J$  = 4.6 Hz, 5H), 0.82 (d,  $J$  = 4.5 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  176.1 (C), 175.7 (C), 142.1 (C), 141.6 (C), 128.6 (2 CH), 128.3 (2 CH), 128.1 (CH), 127.7 (CH), 126.5 (2 CH), 126.1 (2 CH), 76.0 (CH), 74.5 (CH), 51.7 (2  $\text{CH}_3$ ), 51.3 (CH), 51.2 (CH), 38.6 ( $\text{CH}_2$ ), 36.1 ( $\text{CH}_2$ ), 26.4 (CH), 26.1 (CH), 23.5 ( $\text{CH}_3$ ), 23.3 ( $\text{CH}_3$ ), 21.5 ( $\text{CH}_3$ ), 21.4 ( $\text{CH}_3$ ).



d.r. = 86:14

 $C_{16}H_{22}O_3$ 

MW = 262,35

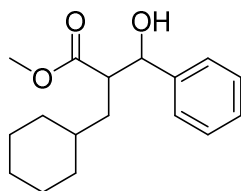
Compound **4daa**: Following **GP1** performed with benzaldehyde (78  $\mu$ L, 0.77 mmol, 1.0 equiv), methyl acrylate (70  $\mu$ L, 0.77 mmol, 1.0 equiv) and organozinc reagent **1d** (8.0 mL, C = 0.29 M, 2.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE : 90:10 (250 mL), 80:20 (125 mL)] as a yellow oil (187 mg, 93%, d.r. 86:14).

$R_f$  (Cy/AE: 95/5, UV+*p*-Anis): 0.18.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for  $C_{16}H_{22}NaO_3$ : 285.1461. Found: 285.1466.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.25 (m, 10H), 4.83 (d, *J* = 4.9 Hz, 2H), 3.50 (s, 6H), 2.84 (t, *J* = 2.2 Hz, 2H), 2.77–2.63 (m, 2H), 1.78 (m, 3H), 1.68–1.49 (m, 8H), 1.49–1.31 (m, 7H), 1.00–0.76 (m, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (major dia) 175.8 (C), 141.6 (C), 128.6 (2 CH), 127.7 (CH), 126.1 (2 CH), 74.4 (CH), 52.5 (CH<sub>3</sub>), 51.7 (CH), 38.3 (CH), 33.4 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 32.0 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>).



d.r. = 88:12

 $C_{17}H_{24}O_3$ 

MW = 276,38

Compound **4eaa**: Following **GP1** performed with benzaldehyde (62  $\mu$ L, 0.61 mmol, 1.0 equiv), methyl acrylate (55  $\mu$ L, 0.61 mmol, 1.0 equiv) and organozinc reagent **1e** (8.0 mL, C = 0.23 M, 1.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE : 90:10 (250 mL), 80:20 (250 mL)] as a colorless solid (126 mg, 75%, d.r. 88:12).

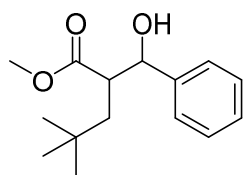
$R_f$  (Cy/AE: 95/5, UV+*p*-Anis): 0.20.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for  $C_{17}H_{24}NaO_3$ : 299.162. Found: 299.1622.

mp: 66 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46–7.22 (m, 10H), 4.90 (d, *J* = 5.7 Hz, 2H), 3.57 (m, 6H), 3.02 (s, 2H), 2.93–2.81 (m, 2H), 1.79–1.53 (m, 12H), 1.53–1.40 (m, 2H), 1.11 (m, 8H), 0.97–0.81 (m, 2H), 0.81–0.58 (m, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (major dia) 175.7 (C), 141.7 (C), 128.3 (2 CH), 127.7 (CH), 126.1 (2 CH), 74.6 (CH), 51.6 (CH<sub>3</sub>), 50.6 (CH), 35.8 (CH), 34.6 (CH<sub>2</sub>), 34.0 (CH<sub>2</sub>), 32.2 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 26.1 (CH<sub>2</sub>).



d.r. = 53:47

 $C_{15}H_{22}O_3$ 

MW = 250,34

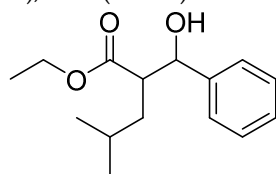
Compound **4faa**: Following **GP1** performed with benzaldehyde (0.17 mL, 1.6 mmol, 1.0 equiv), methyl acrylate (0.14 mL, 1.6 mmol, 1.0 equiv) and organozinc reagent **1f** (8.0 mL, C = 0.61 M, 4.9 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (125 mL)] as a yellow oil (0.317 g, 79%, d.r: 53:47).

**R<sub>f</sub>** (Cy/AE: 95/5, UV+*p*-Anis): 0.20.

**HRMS (ESI<sup>+</sup>)**: m/z [M+H]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>22</sub>NaO<sub>3</sub>: 273.1461. Found: 273.1461.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.33 (m, 10H), 4.81 (d, *J* = 5.7, 1H), 4.64 (d, *J* = 8.3 Hz, 1H), 3.65 (s, 3H), 3.50 (s, 3H), 2.99 (m, 2H), 2.91–2.81 (m, 1H), 2.81–2.72 (m, 1H), 1.89–1.72 (m, 2H), 1.63 (d, *J* = 2.0 Hz, 1H), 1.13 (m, 1H), 0.78 (m, 18H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**: δ 176.8 (C), 176.2 (C), 142.1 (C), 141.6 (C), 128.5 (2 CH), 128.2 (2 CH), 128.1 (CH), 127.7 (CH), 126.7 (2 CH), 126.2 (2 CH), 77.0 (CH), 75.0 (CH), 51.8 (CH<sub>3</sub>), 51.7 (CH<sub>3</sub>), 49.9 (CH), 49.7 (CH), 43.0 (CH<sub>2</sub>), 40.4 (CH<sub>2</sub>), 30.4 (C), 30.2 (C), 29.2 (3 CH<sub>3</sub>), 29.2 (3 CH<sub>3</sub>).



d.r. = 84:16

 $C_{15}H_{22}O_3$ 

MW = 250,34

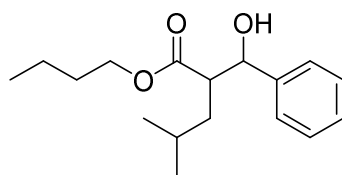
Compound **4cba**: Following **GP1** performed with benzaldehyde (27 μL, 0.27 mmol, 1.0 equiv), ethyl acrylate (29 μL, 0.27 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.20 M, 0.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a colorless oil (67 mg, 99%, d.r: 84:16).

**R<sub>f</sub>** (EP/AE : 95/5, UV+KMnO<sub>4</sub>): 0.30.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>22</sub>NaO<sub>3</sub>: 273.1461. Found: 273.1463.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.42–7.26 (m, 10H), 4.94–4.88 (m, 2H), 4.76 (t, *J* = 11.9, 5.9 Hz, 2H), 4.21–4.11 (m, 2H), 4.04 (m, 2H), 3.05–2.92 (m, 2H), 2.92–2.77 (m, 2H), 1.76 (t, *J* = 11.2 Hz, 2H), 1.53–1.40 (m, 2H), 1.22 (m, 2H), 1.12 (m, 4H), 0.88 (m, 4H), 0.87–0.82 (m, 8H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**: δ 175.6 (C), 175.2 (C), 142.2 (C), 141.6 (C), 128.5 (2 CH), 128.3 (2 CH), 127.9 (CH), 127.7 (CH), 126.4 (2 CH), 126.2 (2 CH), 75.8 (CH), 74.6 (CH), 60.6 (CH<sub>2</sub>), 60.5 (CH<sub>2</sub>), 51.3 (CH), 51.2 (CH), 38.7 (CH<sub>2</sub>), 36.2 (CH<sub>2</sub>), 26.4 (CH), 26.1 (CH), 23.6 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 14.2 (CH<sub>3</sub>), 14.1 (CH<sub>3</sub>).



d.r. = 68:32

 $C_{17}H_{26}O_3$ 

MW = 278,39

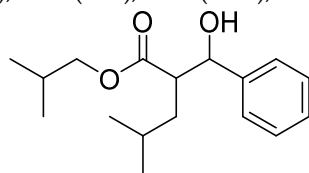
Compound **4cca**: Following **GP1** performed with benzaldehyde (27  $\mu$ L, 0.27 mmol, 1.0 equiv), butyl acrylate (39  $\mu$ L, 0.27 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.20 M, 0.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a yellow oil (75 mg, 99%, d.r.: 68:32).

**R<sub>f</sub>** (EP/AE: 95/5, UV+KMnO<sub>4</sub>): 0.30.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>26</sub>NaO<sub>3</sub>: 301.1774. Found: 301.1775.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.44–7.26 (m, 10H), 4.93 (d, *J* = 5.9 Hz, 1H), 4.84–4.71 (m, 1H), 4.10 (t, *J* = 7.3 Hz, 3H), 4.00 (t, *J* = 6.4 Hz, 1H), 3.05–2.96 (m, 1H), 2.89 (m, 2H), 1.82–1.64 (m, 2H), 1.63–1.40 (m, 7H), 1.39–1.22 (m, 4H), 1.12 (m, 2H), 0.99–0.82 (m, 18H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  175.7 (C), 175.4 (C), 142.3 (C), 141.6 (C), 128.5 (2 CH), 128.3 (2 CH), 127.9 (CH), 127.7 (CH), 126.3 (2 CH), 126.2 (2 CH), 75.8 (CH), 74.6 (CH), 64.5 (CH<sub>2</sub>), 64.4 (CH<sub>2</sub>), 51.3 (CH), 51.2 (CH), 38.8 (CH<sub>2</sub>), 36.2 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 26.4 (CH), 26.1 (CH), 23.6 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 19.0 (2 CH<sub>2</sub>), 13.7 (2 CH<sub>3</sub>).



d.r. = 70:30

 $C_{17}H_{26}O_3$ 

MW = 278,39

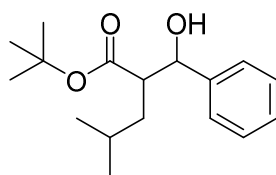
Compound **4cda**: Following **GP1** performed with benzaldehyde (27  $\mu$ L, 0.27 mmol, 1.0 equiv), *iso*-butyl acrylate (39  $\mu$ L, 0.27 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.20 M, 0.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a yellow oil (75 mg, 99%, d.r.: 70:30).

**R<sub>f</sub>** (EP/AE : 95/5, UV+KMnO<sub>4</sub>): 0.32.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>26</sub>NaO<sub>3</sub>: 301.1774. Found: 301.1776.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.43–7.27 (m, 10H), 4.92 (d, *J* = 5.4 Hz, 1H), 4.76 (t, *J* = 6.2 Hz, 1H), 3.91–3.85 (m, 2H), 3.85–3.70 (m, 2H), 3.10–2.94 (m, 2H), 2.83 (m, 2H), 1.94–1.60 (m, 5H), 1.47 (m, 4H), 0.89 (d, *J* = 4.7 Hz, 6H), 0.89–0.83 (m, 17H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  175.7 (C), 175.3 (C), 142.3 (C), 141.7 (C), 128.5 (2 CH), 128.3 (2 CH), 127.9 (CH), 127.7 (CH), 126.4 (2 CH), 126.2 (2 CH), 75.8 (CH), 74.6 (CH), 70.8 (CH<sub>2</sub>), 70.7 (CH<sub>2</sub>), 51.4 (CH), 51.3 (CH), 38.8 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 27.6 (CH), 27.5 (CH), 26.4 (CH), 26.1 (CH), 23.6 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 19.0 (2 CH<sub>3</sub>), 19.0 (2 CH<sub>3</sub>).



d.r. = 53:47

 $C_{17}H_{26}O_3$ 

MW = 278,39

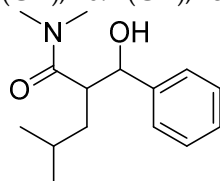
Compound **4cea**: Following **GP1** performed with benzaldehyde (27  $\mu$ L, 0.27 mmol, 1.0 equiv), *tert*-butyl acrylate (39  $\mu$ L, 0.27 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.20 M, 0.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a yellow oil (75 mg, 99%, d.r: 53:47).

**R<sub>f</sub>** (EP/AE: 95/5, UV+KMnO<sub>4</sub>): 0.30.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>26</sub>NaO<sub>3</sub>: 301.1774. Found: 301.1775.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.42–7.26 (m, 10H), 4.87 (m, 1H), 4.74 (m, 1H), 3.19 (d, *J* = 6.9, 1H), 2.83–2.68 (m, 2H), 1.79–1.65 (m, 2H), 1.40 (s, 13H), 1.33 (s, 10H), 0.99–0.83 (m, 12H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  175.1 (C), 174.6 (C), 142.5 (C), 141.7 (C), 128.3 (2 CH), 128.2 (2 CH), 127.7 (CH), 127.6 (CH), 126.5 (2 CH), 126.3 (2 CH), 81.2 (C), 81.0 (C), 75.7 (CH), 74.8 (CH), 51.7 (CH), 51.5 (CH), 39.0 (CH<sub>2</sub>), 36.5 (CH<sub>2</sub>), 28.0 (3 CH<sub>3</sub>), 27.9 (3 CH<sub>3</sub>), 26.4 (CH), 26.1 (CH), 23.7 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>).



d.r. &gt; 95:5

 $C_{15}H_{23}NO_2$ 

MW = 249,35

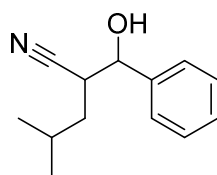
Compound **4cga**: Following **GP1** performed with benzaldehyde (27  $\mu$ L, 0.27 mmol, 1.0 equiv), dimethyl acrylamide (28  $\mu$ L, 0.27 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.20 M, 0.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 90:10 (250 mL), 70:30 (125 mL), 60:40 (125 mL)] as a yellow oil (66 mg, 99%, d.r > 95:5).

**R<sub>f</sub>** (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.10.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>23</sub>NaNO<sub>2</sub>: 272.1621. Found: 272.1630.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.45–7.22 (m, 5H), 4.89 (d, *J* = 3.1 Hz, 1H), 3.05 (d, *J* = 10.9 Hz, 1H), 2.93 (d, *J* = 6.0 Hz, 6H), 2.00 (br s, 1H), 1.84 (t, *J* = 10.5 Hz, 1H), 1.35 (m, 2H), 0.83 (d, *J* = 4.4 Hz, 3H), 0.74 (d, *J* = 4.3 Hz, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  175.9 (C), 142.1 (C), 128.1 (2 CH), 127.3 (CH), 125.9 (2 CH), 74.2 (CH), 46.0 (CH), 37.5 (2 CH<sub>3</sub>), 35.7 (CH<sub>2</sub>), 26.0 (CH), 23.6 (CH<sub>3</sub>), 22.1 (CH<sub>3</sub>).



d.r. = 56:44

 $C_{13}H_{17}NO$ 

MW = 203,29

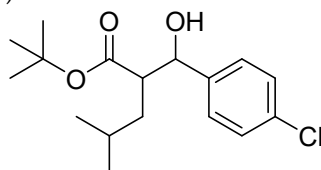
Compound **4cha**: Following **GP1** performed with benzaldehyde (27  $\mu$ L, 0.27 mmol, 1.0 equiv), acrylonitrile (18  $\mu$ L, 0.27 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.20 M, 0.8 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 90:10 (250 mL), 70:30 (125 mL)] as a **pale yellow oil** (55 mg, 99%, d.r: 56:44).

$R_f$  (EP/AE: 95/5, UV+KMnO<sub>4</sub>): 0.31.

HRMS (ESI<sup>+</sup>): m/z [M+H]<sup>+</sup> Calcd. for C<sub>13</sub>H<sub>18</sub>NO: 204.1383. Found: 204.1386.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51–7.34 (m, 10H), 4.86–4.71 (m, 2H), 3.10–2.83 (m, 4H), 1.99–1.80 (m, 2H), 1.68 (m, 1H), 1.51 (m, 1H), 1.45–1.30 (m, 1H), 1.26–1.16 (m, 1H), 0.96 (m, 6H), 0.94–0.82 (m, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.5 (C), 140.0 (C), 128.8 (2 CH), 128.7 (2 CH), 128.7 (2 CH), 126.5 (2 CH), 126.2 (2 CH), 120.3 (2 C), 74.2 (CH), 74.0 (CH), 39.3 (CH), 38.6 (CH), 37.7 (CH<sub>2</sub>), 36.6 (CH<sub>2</sub>), 26.1 (CH), 26.1 (CH), 23.3 (CH<sub>3</sub>), 23.1 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>).



d.r. = 72:28

 $C_{17}H_{25}ClO_3$ 

MW = 312,83

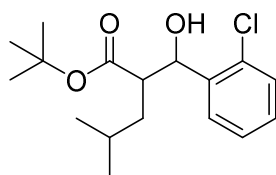
Compound **4ceb**: Following **GP1** performed with 4-chlorobenzaldehyde (51  $\mu$ L, 0.43 mmol, 1.0 equiv), *tert*-butyl acrylate (62  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.32 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a colorless oil (125 mg, 93%, d.r: 72:28).

$R_f$  (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.34.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>25</sub>ClNaO<sub>3</sub>: 335.1384. Found: 335.1384.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33–7.15 (m, 8H), 4.78 (d, *J* = 5.4 Hz, 1H), 4.60 (s, 1H), 3.24 (d, *J* = 6.0 Hz, 1H), 3.03 (s, 1H), 2.67–2.52 (m, 2H), 1.72–1.56 (m, 2H), 1.56–1.33 (m, 4H), 1.28 (m, 18H), 0.88–0.78 (m, 6H), 0.74 (d, *J* = 6.5, 6H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  174.9 (C), 174.6 (C), 141.1 (C), 140.2 (C), 133.3 (C), 133.2 (C), 128.5 (2 CH), 128.3 (2 CH), 127.9 (2 CH), 127.7 (2 CH), 81.5 (C), 81.3 (C), 74.9 (CH), 73.9 (CH), 51.4 (CH), 51.3 (CH), 39.0 (CH<sub>2</sub>), 36.1 (CH<sub>2</sub>), 28.0 (3 CH<sub>3</sub>), 27.9 (3 CH<sub>3</sub>), 26.3 (CH), 26.1 (CH), 23.7 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>).



d.r. = 52:48  
 $C_{17}H_{25}ClO_3$   
 MW = 312,83

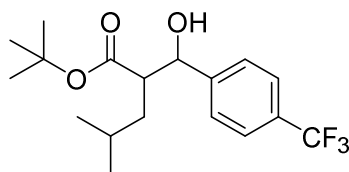
Compound **4cec**: Following **GP1** performed with 2-chlorobenzaldehyde (48  $\mu$ L, 0.43 mmol, 1.0 equiv), *tert*-butyl acrylate (62  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.32 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a pale yellow oil (125 mg, 93%, d.r.: 52:48).

$R_f$  (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.30.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for  $C_{17}H_{25}ClNaO_3$ : 335.1384. Found: 335.1383.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.62 (d, *J* = 7.7 Hz, 1H), 7.48 (m, 1H), 7.46–7.19 (m, 6H), 5.34 (d, *J* = 4.1, 1H), 5.14 (d, *J* = 4.3 Hz, 1H), 2.90 (m, 2H), 1.90–1.53 (m, 2H), 1.44 (m, 11H), 1.33 (m, 13H), 1.03–0.89 (m, 6H), 0.86 (d, *J* = 6.6, 3H), 0.74 (d, *J* = 6.7, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  175.5 (C), 175.3 (C), 140.1 (2 C), 131.9 (2 C), 129.4 (CH), 129.4 (CH), 128.7 (CH), 128.6 (CH), 128.6 (CH), 127.6 (CH), 126.8 (CH), 126.7 (CH), 81.6 (C), 81.3 (C), 72.0 (CH), 71.0 (CH), 48.7 (CH), 47.8 (CH), 39.3 (CH<sub>2</sub>), 35.0 (CH<sub>2</sub>), 28.0 (3 CH<sub>3</sub>), 28.0 (3 CH<sub>3</sub>), 26.4 (CH), 26.1 (CH), 23.5 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>).



d.r. = 58:42  
 $C_{18}H_{25}F_3O_3$   
 MW = 346,39

Compound **4ced**: Following **GP1** performed with 4-trifluoromethylbenzaldehyde (59  $\mu$ L, 0.43 mmol, 1.0 equiv), *tert*-butyl acrylate (62  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.32 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (250 mL)] as a yellow oil (0.149 g, 99%, d.r.: 58:42).

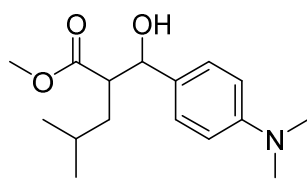
$R_f$  (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.28

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for  $C_{18}H_{25}F_3NaO_3$ : 369.1648. Found: 369.1650.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.56–7.48 (m, 4H), 7.48–7.35 (m, 4H), 4.91–4.83 (m, 1H), 4.69 (m, 1H), 3.45 (d, *J* = 7.4 Hz, 1H), 3.24–3.14 (m, 1H), 2.69–2.53 (m, 2H), 1.73–1.54 (m, 2H), 1.37 (d, *J* = 13.9 Hz, 2H), 1.26 (m, 18H), 1.20–1.09 (m, 3H), 0.82–0.76 (m, 8H), 0.72 (m, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  174.9 (C), 174.8 (C), 146.8 (C), 145.7 (C), 129.9 (q, *J* = 39.1 Hz, C), 129.9 (q, *J* = 25.8 Hz, C), 126.9 (2 CH), 126.6 (2 CH), 125.3 (q, *J* = 3.8 Hz, 2 CH), 125.2 (q, *J* = 3.9 Hz, 2 CH), 124.3 (d, *J* = 271.8 Hz, C), 124.2 (q, *J* = 271.8 Hz, C), 81.8 (C), 81.6 (C), 75.0 (CH), 74.0 (CH), 51.3 (CH), 51.2 (CH), 39.1 (CH<sub>2</sub>), 36.0 (CH<sub>2</sub>), 28.0 (6 CH<sub>3</sub>), 26.3 (CH), 26.2 (CH), 23.7 (CH<sub>3</sub>), 23.3 (CH<sub>3</sub>), 21.8 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>).

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>):  $\delta$  −62.4 (3F), −62.5 (3F).



d.r. = 71:29

 $C_{16}H_{25}NO_3$ 

MW = 279,38

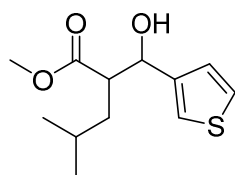
Compound **4cae**: Following **GP1** performed with 4-dimethylaminobenzaldehyde (31 mg, 0.21 mmol, 1.0 equiv), methyl acrylate (19  $\mu$ L, 0.21 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.21 M, 0.63 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 90:10 (125 mL), 70:30 (125 mL), 60:40 (125 mL)] as an orange oil (45 mg, 76%, d.r: 71:29).

$R_f$  (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.20.

HRMS (ESI<sup>+</sup>): m/z [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>26</sub>NO<sub>3</sub>: 280.1907. Found: 280.1909.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.22 (d, *J* = 1.9 Hz, 4H), 6.76–6.67 (m, 4H), 4.80 (d, *J* = 8.6 Hz, 1H), 4.66 (d, *J* = 8.6 Hz, 1H), 3.75 (m, 3H), 3.59–3.54 (m, 3H), 3.02–2.93 (m, 12H), 1.86–1.63 (m, 5H), 1.62–1.38 (m, 5H), 1.00–0.78 (m, 12H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.3 (C), 175.5 (C), 150.4 (C), 150.2 (C), 129.7 (C), 129.6 (C), 127.5 (2 CH), 127.1 (2 CH), 112.4 (2 CH), 112.3 (2 CH), 76.1 (CH), 74.7 (CH), 51.6 (CH<sub>3</sub>), 51.5 (CH<sub>3</sub>), 40.6 (CH), 40.6 (CH), 38.6 (2 CH<sub>3</sub>), 38.3 (2 CH<sub>3</sub>), 37.3 (CH<sub>2</sub>), 36.9 (CH<sub>2</sub>), 26.4 (CH), 26.2 (CH), 23.6 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>).



d.r. = 83:17

 $C_{12}H_{18}O_3S$ 

MW = 242,33

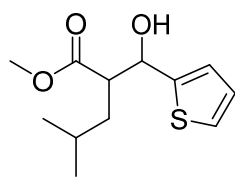
Compound **4caf**: Following **GP1** performed with thiophene 3-carboxyaldehyde (18  $\mu$ L, 0.21 mmol, 1.0 equiv), methyl acrylate (19  $\mu$ L, 0.21 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.21 M, 0.63 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (125 mL), 70:30 (125 mL)] as an orange oil (48 mg, 94%, d.r: 83:7).

$R_f$  (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.10.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for C<sub>12</sub>H<sub>18</sub>NaO<sub>3</sub>S: 265.0869. Found: 265.0872.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.40–7.27 (m, 2H), 7.27–7.18 (m, 2H), 7.08 (m, 2H), 4.84 (t, *J* = 5.8 Hz, 2H), 3.70 (s, 4H), 3.63 (m, 2H), 3.00 (d, *J* = 6.1 Hz, 2H), 2.88 (m, 2H), 1.65 (m, 2H), 1.49 (m, 2H), 1.14 (m, 2H), 0.86 (d, *J* = 6.6, 12H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.0 (C), 175.6 (C), 143.8 (C), 143.1 (C), 126.4 (CH), 126.0 (CH), 125.5 (CH), 125.5 (CH), 121.9 (CH), 121.4 (CH), 71.9 (CH), 71.4 (CH), 51.8 (CH<sub>3</sub>), 51.7 (CH<sub>3</sub>), 50.7 (2 CH), 38.6 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 26.3 (CH), 26.1 (CH), 23.5 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>).



d.r. = 81:19  
 $C_{12}H_{18}O_3S$   
 MW = 242,33

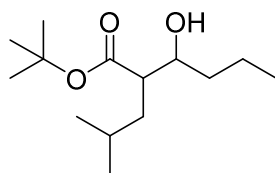
Compound **4cag**: Following **GP1** performed with thiophene 2-carboxyaldehyde (18  $\mu$ L, 0.21 mmol, 1.0 equiv), methyl acrylate (19  $\mu$ L, 0.21 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.21 M, 0.63 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 90:10 (125 mL), 70:30 (125 mL)] as a yellow oil (23 mg, 45%, d.r.: 81:19).

$R_f$  (Cy/AE: 95/5, UV+*p*-Anis): 0.29.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for  $C_{12}H_{18}NaO_3S$ : 265.0869. Found: 265.0870

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34–7.25 (m, 3H), 7.00 (d, *J* = 5.5 Hz, 3H), 5.02 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 5.5 Hz, 4H), 3.11–2.86 (m, 2H), 1.58 (m, 6H), 1.41–1.12 (m, 3H), 0.89 (t, *J* = 6.1 Hz, 11H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  175.9 (2 C), 146.4 (2 C), 126.8 (2 CH), 125.4 (2 CH), 124.9 (2 CH), 71.9 (2 CH), 52.0 (2 CH<sub>3</sub>), 51.5 (2 CH), 38.9 (2 CH<sub>2</sub>), 26.2 (2 CH), 23.3 (2 CH<sub>3</sub>), 21.7 (2 CH<sub>3</sub>).



d.r. = 51:49  
 $C_{14}H_{28}O_3$   
 MW = 244,38

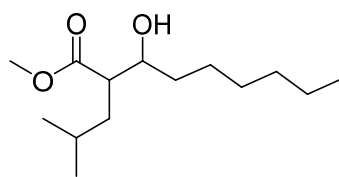
Compound **4ceh**: Following **GP1** performed with butyraldehyde (39  $\mu$ L, 0.43 mmol, 1.0 equiv), *tert*-butyl acrylate (62  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (4.0 mL, C = 0.32 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 80:20 (125 mL)] as a colorless oil (0.104 g, 99%, d.r.: 51:49).

$R_f$  (Cy/AE: 95/5, UV+KMnO<sub>4</sub>): 0.25.

HRMS (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for  $C_{14}H_{28}NaO_3$ : 267.1931. Found: 267.1933.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.75–3.73 (m, 1H), 3.58–3.54 (m, 1H), 2.65–2.57 (m, 2H), 2.39 (dd, *J* = 10.2, 4.6 Hz, 2H), 1.73–1.62 (m, 4H), 1.56–1.43 (m, 22H), 1.36–1.24 (m, 6H), 0.92–0.89 (m, 18H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  175.5 (C), 175.3 (C), 81.1 (C), 81.0 (C), 72.8 (CH), 72.1 (CH), 49.6 (CH), 49.3 (CH), 39.0 (CH<sub>2</sub>), 38.2 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 35.9 (CH<sub>2</sub>), 28.1 (3 CH<sub>3</sub>), 28.1 (3 CH<sub>3</sub>), 26.4 (CH), 26.1 (CH), 23.6 (CH<sub>3</sub>), 23.2 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 19.1 (CH<sub>2</sub>), 19.1 (CH<sub>2</sub>), 14.0 (2 CH<sub>3</sub>).



d.r. = 69:31

$$\text{C}_{14}\text{H}_{28}\text{O}_3$$
$$MW = 244.38$$

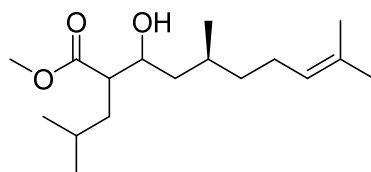
Compound **4cai**: Following **GP1** performed with heptanal (30  $\mu$ L, 0.21 mmol, 1.0 equiv), methyl acrylate (19  $\mu$ L, 0.21 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.21 M, 0.63 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 95:5 (250 mL), 90:10 (125 mL), 80:20 (125 mL)] as a yellow oil (41 mg, 80%, d.r: 69:31).

**R<sub>f</sub> (Cy/AE: 95/5, UV+p-Anis): 0.16.**

**HRMS (ESI<sup>+</sup>):** m/z [M+Na]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>28</sub>NaO<sub>3</sub>; 267.1931. Found: 267.1929.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.74–3.55 (m, 8H), 2.54–2.29 (m, 2H), 2.24 (td, *J* = 8.9, 6.8, 2.9 Hz, 1H), 1.89–1.58 (m, 3H), 1.58–1.28 (m, 8H), 1.21 (m, 16H), 0.83 (d, *J* = 7.0 Hz, 18H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ 176.3 (C), 176.3 (C), 72.8 (CH), 72.4 (CH), 51.6 (CH<sub>3</sub>), 51.5 (CH<sub>3</sub>), 49.0 (CH), 48.9 (CH), 41.5 (CH<sub>2</sub>), 38.8 (CH<sub>2</sub>), 35.9 (CH<sub>2</sub>), 35.9 (CH<sub>2</sub>), 34.2 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 27.6 (CH<sub>2</sub>), 26.4 (CH), 26.2 (CH), 25.9 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 22.8 (CH<sub>3</sub>), 22.6(2 CH<sub>2</sub>), 22.2 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>), 14.1 (2 CH<sub>3</sub>).



d.r. = 27:27:27:19

$$\text{C}_{17}\text{H}_{32}\text{O}_3$$
$$MW = 284,44$$

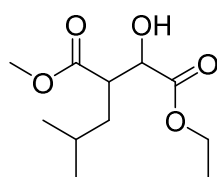
Compound **4caj**: Following **GP1** performed with citronellal (38  $\mu$ L, 0.21 mmol, 1.0 equiv), methyl acrylate (19  $\mu$ L, 0.21 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.21 M, 0.63 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, C<sub>y</sub>/A<sub>E</sub>: 90:10 (250 mL), 80:20 (125 mL), 70:30 (125 mL)] as a yellow oil (54 mg, 90%, d.r. : 27:27:27:19).

**R<sub>f</sub> (C<sub>v</sub>/AE: 95/5, UV+KMnO<sub>4</sub>): 0.28.**

**HRMS (ESI<sup>+</sup>):** m/z [M+H]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>33</sub>O<sub>3</sub>: 285.2424. Found: 285.2423.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.10 (t, *J* = 7.3 Hz, 4H), 3.71 (d, *J* = 2.0 Hz, 13H), 2.53–2.39 (m, 6H), 2.11–1.82 (m, 8H), 1.64 (d, *J* = 31.3 Hz, 31H), 1.44–1.08 (m, 28H), 1.00–0.81 (m, 38H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):** δ 176.3 (C), 176.3 (C), 176.3 (C), 176.1 (C), 131.3 (C), 131.2 (C), 131.2 (2 C), 124.7 (4 CH), 70.9 (CH), 70.6 (CH), 70.3 (CH), 70.0 (CH), 51.6 (CH<sub>3</sub>), 51.6 (CH<sub>3</sub>), 51.5 (2 CH<sub>3</sub>), 49.8 (CH), 49.7 (CH), 49.1 (CH), 48.9 (CH), 43.4 (CH<sub>2</sub>), 43.1 (CH<sub>2</sub>), 41.5 (CH<sub>2</sub>), 41.5 (CH<sub>2</sub>), 38.8 (CH<sub>2</sub>), 38.8 (CH<sub>2</sub>), 37.9 (CH<sub>2</sub>), 37.9 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 36.2 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>), 29.3 (CH), 29.2 (CH), 28.8 (CH), 28.8 (CH), 26.9 (4 CH<sub>2</sub>), 26.4 (CH), 26.4 (CH), 26.2 (CH), 26.2 (CH), 25.7 (4 CH), 25.5 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 23.5 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 23.1 (2 CH<sub>3</sub>), 23.0 (2 CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 20.3 (4 CH<sub>3</sub>), 19.0 (2 CH<sub>3</sub>), 18.9 (2 CH<sub>3</sub>), 17.6 (2 CH<sub>3</sub>).



d.r. = 60:40

 $C_{11}H_{20}O_5$ 

MW = 232,28

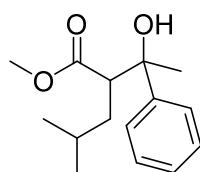
Compound **4cak**: Following **GP1** performed with ethyl glyoxylate (88  $\mu$ L, 0.43 mmol, 1.0 equiv), methyl acrylate (39  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.43 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 80:20 (100 mL), 60:40 (100 mL)] as a colorless oil (149 mg, 69%, d.r: 60:40).

**R<sub>f</sub>** (Cy/AE: 95/5, UV+*p*-Anis): 0.38.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>11</sub>H<sub>20</sub>NaO<sub>5</sub>: 255.1203. Found: 255.1209.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  4.38–4.18 (m, 5H), 3.66 (s, 3H), 3.61 (s, 3H), 3.08 (m, 1H), 2.86–2.76 (m, 1H), 2.11 (d, *J* = 2.0 Hz, 1H), 1.98 (d, *J* = 2.0 Hz, 1H), 1.85–1.56 (m, 3H), 1.63–1.40 (m, 3H), 1.29–1.10 (m, 7H), 0.87–0.80 (m, 12H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  173.8 (C), 173.7 (C), 173.5 (C), 173.4 (C), 71.6 (CH), 71.3 (CH), 62.3 (CH<sub>2</sub>), 62.0 (CH<sub>2</sub>), 52.1 (CH<sub>3</sub>), 52.0 (CH<sub>3</sub>), 47.5 (CH), 46.7 (CH), 36.9 (CH<sub>2</sub>), 36.0 (CH<sub>2</sub>), 26.2 (CH), 25.9 (CH), 23.3 (CH<sub>3</sub>), 22.5 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 21.8 (CH<sub>3</sub>), 14.2 (2 CH<sub>3</sub>).



d.r. = 61:39

 $C_{15}H_{22}O_3$ 

MW = 250,34

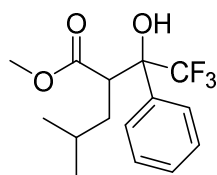
Compound **6caa**: Following **GP1** performed with acetophenone (50  $\mu$ L, 0.43 mmol, 1.0 equiv), methyl acrylate (39  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.43 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 95:5 (100 mL), 90:10 (100 mL)] as a pale yellow oil (108 mg, 74%, d.r: 61:39).

**R<sub>f</sub>** (Cy/AE: 90/10, UV+*p*-Anis): 0.60.

**HRMS (ESI<sup>+</sup>)**: m/z [M+Na]<sup>+</sup> Calcd. for C<sub>15</sub>H<sub>22</sub>NaO<sub>3</sub>: 273.1461. Found: 273.1462.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  7.33 (t, *J* = 8.1 Hz, 3H), 7.31–7.20 (m, 4H), 7.20–7.07 (m, 3H), 3.87–3.55 (m, 4H), 3.27 (d, *J* = 2.0 Hz, 4H), 2.88 (d, *J* = 11.7, 1H), 2.80 (d, *J* = 11.7 Hz, 1H), 1.86–1.76 (m, 1H), 1.76–1.54 (m, 1H), 1.41 (m, 6H), 1.19 (m, 1H), 0.88–0.78 (m, 9H), 0.72–0.66 (m, 3H), 0.66–0.59 (m, 3H).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)**:  $\delta$  177.4 (C), 176.8 (C), 147.4 (C), 145.3 (C), 128.1 (2 CH), 128.0 (2 CH), 126.8 (CH), 126.6 (CH), 124.8 (2 CH), 124.7 (2 CH), 75.1 (C), 74.6 (C), 53.8 (CH<sub>3</sub>), 53.4 (CH<sub>3</sub>), 51.7 (CH), 51.3 (CH), 36.6 (CH<sub>2</sub>), 36.5 (CH<sub>2</sub>), 30.3 (CH<sub>3</sub>), 26.9 (CH<sub>3</sub>), 26.7 (CH), 26.3 (CH), 23.8 (CH<sub>3</sub>), 23.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>).



d.r. = 59:41

 $C_{15}H_{19}F_3O_3$ 

MW = 304,31

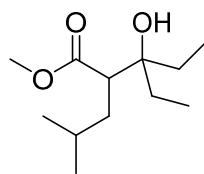
Compound **6cab**: Following **GP1** performed with 2,2,2-trifluoroacetophenone (49  $\mu$ L, 0.36 mmol, 1.0 equiv), methyl acrylate (32  $\mu$ L, 0.36 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.36 M, 1.1 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 95:5 (100 mL), 90:10 (100 mL)] as a colorless oil (110 mg, 99%, d.r: 59:41).

$R_f$  (Cy/AE: 90/10, UV+*p*-Anis): 0.60.

HRMS (ESI<sup>+</sup>): m/z [M+H]<sup>+</sup> Calcd. for  $C_{15}H_{19}F_3O_3$ : 305.1518. Found: 305.1520.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d, *J* = 7.5 Hz, 4H), 7.50–7.31 (m, 6H), 5.11 (s, 1H), 4.53 (s, 1H), 3.85 (s, 3H), 3.79–3.59 (m, 2H), 3.53 (m, 1H), 3.38 (s, 3H), 2.02 (m, 1H), 1.81–1.64 (m, 1H), 1.50–1.20 (m, 3H), 1.02 (d, *J* = 6.5 Hz, 2H), 0.99 (d, *J* = 6.6 Hz, 2H), 0.83 (d, *J* = 6.5 Hz, 4H), 0.79 (d, *J* = 6.6 Hz, 4H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.6 (C), 175.4 (C), 138.1 (C), 135.4 (C), 128.6 (2 CH), 128.6 (2 CH), 128.4 (CH), 128.2 (CH), 126.2 (2 CH), 126.1 (2 CH), 78.0 (q, *J* = 27.5 Hz, 2 C), 52.7 (CH<sub>3</sub>), 51.9 (CH<sub>3</sub>), 48.9 (CH), 45.5 (CH), 36.6 (CH<sub>2</sub>), 35.8 (CH<sub>2</sub>), 26.6 (CH), 25.8 (CH), 23.9 (CH<sub>3</sub>), 23.5 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>). [ $CF_3$  not detected]

 $C_{12}H_{24}O_3$ 

MW = 216,32

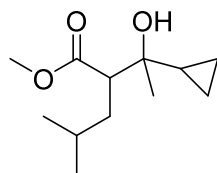
Compound **6cac**: Following **GP1** performed with 3-pentanone (30  $\mu$ L, 0.32 mmol, 1.0 equiv), methyl acrylate (29  $\mu$ L, 0.32 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.32 M, 0.96 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 90:10 (100 mL), 80:20 (50 mL), 70:30 (50 mL)] as a colorless oil (69 mg, 59%).

$R_f$  (Cy/AE: 90/10, UV+*p*-Anis): 0.48.

HRMS (ESI<sup>+</sup>): m/z [M+H]<sup>+</sup> Calcd. for  $C_{12}H_{25}O_3$ : 217.1013. Found: 217.1015.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.69 (s, 3H), 3.66–3.60 (m, 1H), 2.85 (s, 1H), 2.62–2.56 (m, 1H), 1.78 (t, *J* = 12.5 Hz, 1H), 1.59 (m, 1H), 1.51–1.29 (m, 3H), 1.24 (t, *J* = 11.8 Hz, 1H), 0.99–0.80 (m, 9H), 0.80–0.71 (m, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  177.4 (C), 75.0 (C), 51.4 (CH<sub>3</sub>), 49.5 (CH), 35.8 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 26.5 (CH), 26.4 (CH<sub>2</sub>), 23.9 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 7.6 (2 CH<sub>3</sub>).



d.r. = 79:21

 $C_{12}H_{22}O_3$ 

MW = 214,31

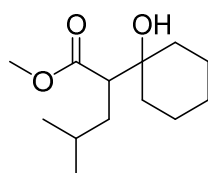
Compound **6cad**: Following **GP1** performed with cyclopropyl methyl ketone (43  $\mu$ L, 0.43 mmol, 1.0 equiv), methyl acrylate (39  $\mu$ L, 0.43 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.43 M, 1.3 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 90:10 (100 mL), 80:20 (100 mL)] as a pale yellow oil (91 mg, 99%, d.r.: 79:21).

**R<sub>f</sub>** (Cy/AE: 90/10, UV+*p*-Anis): 0.60.

**HRMS** (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for C<sub>12</sub>H<sub>22</sub>NaO<sub>3</sub>: 237.1461. Found: 237.1466.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.67 (s, 6H), 2.57–2.50 (m, 4H), 1.79–1.73 (m, 2H), 1.43–1.31 (m, 4H), 1.16 (s, 5H), 1.08 (s, 1H), 0.88–0.80 (m, 15H), 0.31–0.26 (m, 7H).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.9 (C), 176.4 (C), 71.4 (C), 70.8 (C), 54.5 (CH<sub>3</sub>), 53.7 (CH<sub>3</sub>), 51.6 (CH), 51.5 (CH), 36.5 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 26.8 (CH), 26.6 (CH), 25.5 (CH<sub>3</sub>), 25.0 (CH<sub>3</sub>), 23.9 (CH<sub>3</sub>), 23.9 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.1 (2 CH), 1.4 (CH<sub>2</sub>), 1.1 (CH<sub>2</sub>), 0.2 (CH<sub>2</sub>), −0.3 (CH<sub>2</sub>).



C<sub>13</sub>H<sub>24</sub>O<sub>3</sub>  
MW = 228,33

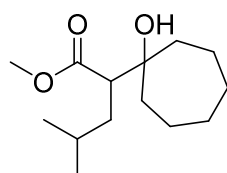
Compound **6cae**: Following **GP1** performed with cyclohexanone (35  $\mu$ L, 0.34 mmol, 1.0 equiv), methyl acrylate (31  $\mu$ L, 0.34 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.34 M, 1.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 95:5 (100 mL), 90:10 (100 mL)] as a colorless oil (78 mg, 99%).

**R<sub>f</sub>** (Cy/AE: 90/10, UV+*p*-Anis): 0.38.

**HRMS** (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for C<sub>13</sub>H<sub>24</sub>NaO<sub>3</sub>: 251.1618. Found: 251.1621.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.67 (s, 3H), 2.68 (br s, 1H), 2.48 (d, *J* = 11.8 Hz, 1H), 1.73–1.70 (m, 2H), 1.62–1.54 (m, 3H), 1.43–1.30 (m, 6H), 1.26–1.16 (m, 2H), 0.88 (s, 6H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  177.1 (C), 71.7 (C), 52.7 (CH<sub>3</sub>), 51.4 (CH), 37.3 (CH<sub>2</sub>), 35.6 (CH<sub>2</sub>), 34.4 (CH<sub>2</sub>), 26.6 (CH), 25.7 (CH<sub>3</sub>), 23.8 (CH<sub>3</sub>), 21.9 (CH<sub>2</sub>), 21.7 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>).



C<sub>14</sub>H<sub>26</sub>O<sub>3</sub>  
MW = 242,36

Compound **6caf**: Following **GP1** performed with cycloheptanone (38  $\mu$ L, 0.34 mmol, 1.0 equiv), methyl acrylate (31  $\mu$ L, 0.34 mmol, 1.0 equiv) and organozinc reagent **1c** (3.0 mL, C = 0.34 M, 1.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 20 mL, Cy/AE: 95:5 (100 mL), 90:10 (100 mL), 70:30 (50 mL)] as a pale yellow oil (40 mg, 48%).

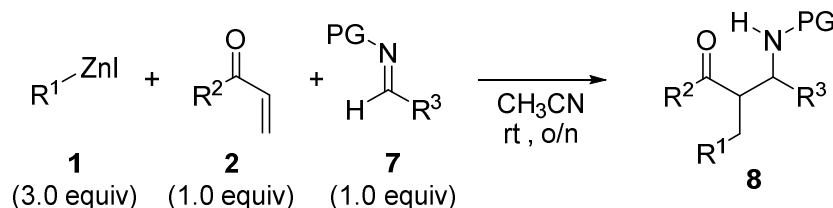
**R<sub>f</sub>** (Cy/AE: 90/10, UV+*p*-Anis): 0.25.

**HRMS** (ESI<sup>+</sup>): m/z [M+Na]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>26</sub>NaO<sub>3</sub>: 265.1774. Found: 265.1780

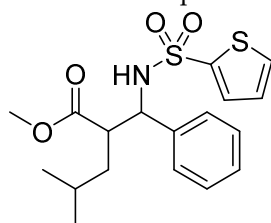
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.62 (s, 3H), 2.73 (s, 1H), 2.47 (d, *J* = 11.7 Hz, 1H), 1.77–1.42 (m, 10H), 1.37–1.24 (m, 5H), 0.83 (s, 6H).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  177.0 (C), 75.7 (C), 52.9 (CH<sub>3</sub>), 51.3 (CH), 40.9 (CH<sub>2</sub>), 37.4 (CH<sub>2</sub>), 36.1 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 26.6 (CH), 23.8 (CH<sub>3</sub>), 22.2 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 21.4 (CH<sub>3</sub>).

### 3.3. CR with sulfonyl imines



**General procedure 2 (GP2):** A 10 mL sealable tube equipped with a stir bar and filled with an argon atmosphere was charged with imine **7** (0.4 mmol, 1.0 equiv), acrylate **2** (2.0 equiv) and acetonitrile (2 mL). Under stirring, a solution of organozinc reagent **1** in CH<sub>3</sub>CN (3.0 equiv) was added in one portion. The reaction was stirred at room temperature overnight. Then, the reaction mixture was poured into sat aq NH<sub>4</sub>Cl (20 mL). The resulting solution was extracted twice with EtOAc (15+15 mL) and the combined organic layers were washed brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The resulting crude material was purified on silica gel to give product **7**.



d.r. = 68:32

C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>S<sub>2</sub>

MW = 381,51

Compound **8caa**: Following **GP2** performed with imine **7a** (251 mg, 1.0 mmol, 1.0 equiv), methyl acrylate (181  $\mu$ L, 2.0 mmol, 2.0 equiv) and organozinc reagent (3.2 mL, C = 0.93 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a white solid (242 mg, 63%, d.r. = 68:32).

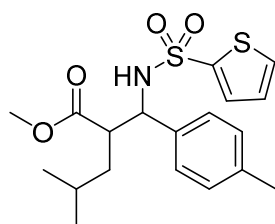
**Melting Point (°C):** 97.0

**R<sub>f</sub> (Cy/AE: 80/20, UV+KMnO<sub>4</sub>):** 0.32, 0.22.

**HRMS (ESI<sup>+</sup>):** m/z [M+H]<sup>+</sup> Calcd. for C<sub>18</sub>H<sub>24</sub>NO<sub>4</sub>S<sub>2</sub>: 382.1147. Found: 382.1145.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.38 (d, *J* = 4.6 Hz, 1H), 7.35–7.31 (m, 2H), 7.26–7.24 (m, 2H), 7.14 (br s, 5H), 7.02–7.01 (m, 4H), 6.84–6.82 (m, 1H), 6.79–6.77 (m, 1H), 6.35 (d, *J* = 9.3 Hz, 1H), 5.86 (d, *J* = 8.9 Hz, 1H), 4.62–4.60 (m, 1H), 4.54–4.50 (m, 1H), 3.53 (s, 3H), 3.39 (s, 3H), 2.83–2.78 (m, 2H), 1.66–1.62 (m, 2H), 1.55–1.44 (m, 3H), 1.30–1.25 (m, 1H), 0.84 (d, *J* = 6.4 Hz, 12H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  175.1 (C), 173.4 (C), 142.1 (C), 141.4 (C), 139.0 (C), 138.2 (C), 132.4 (CH), 132.0 (CH), 131.8 (CH), 131.5 (CH), 128.5 (2 CH), 128.4 (2 CH), 127.9 (CH), 127.7 (CH), 127.2 (CH), 127.0 (CH), 126.8 (2 CH), 126.2 (2 CH), 60.1 (CH), 59.3 (CH), 51.9 (CH<sub>3</sub>), 51.7 (CH<sub>3</sub>), 50.6 (CH), 50.1 (CH), 39.2 (CH<sub>2</sub>), 37.7 (CH<sub>2</sub>), 26.2 (CH), 25.9 (CH), 23.4 (CH<sub>3</sub>), 22.8 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>).



d.r. = 58:42  
 $C_{19}H_{25}NO_4S_2$   
 MW = 395.53

Compound **8cab**: Following **GP2** performed with imine **7b** (265 mg, 1.0 mmol, 1.0 equiv), methyl acrylate (181  $\mu$ L, 2.0 mmol, 2.0 equiv) and organozinc reagent (3.2 mL, C = 0.93 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a white solid (346 mg, 87%, d.r. = 58:42).

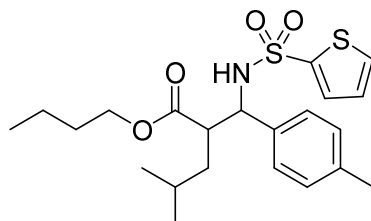
**Melting Point (°C):** 96.5

**R<sub>f</sub>** (Cy/AE: 80/20, UV+KMnO<sub>4</sub>): 0.35, 0.27.

**HRMS (ESI<sup>+</sup>):** m/z [M+H]<sup>+</sup> Calcd. for C<sub>19</sub>H<sub>26</sub>NO<sub>4</sub>S<sub>2</sub>: 396.1297. Found: 396.1298.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.33 (d, *J* = 4.7 Hz, 1H), 7.29 (d, *J* = 4.7 Hz, 1H), 7.26–7.25 (m, 1H), 7.20–7.19 (m, 1H), 6.90–6.84 (m, 8H), 6.78–6.77 (m, 1H), 6.74–6.72 (m, 1H), 6.24 (d, *J* = 9.0 Hz, 1H), 5.80 (d, *J* = 8.9 Hz, 1H), 4.59 (t, *J* = 6.9 Hz, 1H), 4.42 (t, *J* = 8.3 Hz, 1H), 3.48 (s, 3H), 3.34 (s, 3H), 2.75–2.70 (m, 2H), 2.18 (s, 6H), 1.58–1.51 (m, 2H), 1.45–1.38 (m, 3H), 1.20–1.15 (m, 1H), 0.76 (d, *J* = 6.3 Hz, 12H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  174.1 (C), 173.5 (C), 142.1 (C), 141.5 (C), 137.5 (C), 137.3 (C), 136.1 (C), 135.2 (C), 132.4 (CH), 132.0 (CH), 121.7 (CH), 131.4 (CH), 129.2 (2 CH), 129.0 (2 CH), 127.1 (CH), 127.0 (CH), 126.7 (2 CH), 126.1 (2 CH), 59.8 (CH), 59.1 (CH), 51.9 (CH<sub>3</sub>), 51.7 (CH<sub>3</sub>), 50.5 (CH), 50.2 (CH), 39.1 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 26.2 (CH), 25.9 (CH), 23.4 (CH<sub>3</sub>), 22.8 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>).



d.r. = 53:47  
 $C_{22}H_{31}NO_4S_2$   
 MW = 437.61

Compound **8ccb**: Following **GP2** performed with imine **7b** (265 mg, 1.0 mmol, 1.0 equiv), *n*-butyl acrylate (285  $\mu$ L, 2.0 mmol, 2.0 equiv) and organozinc reagent (3.2 mL, C = 0.93 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a white solid (414 mg, 95%, d.r. = 53:47).

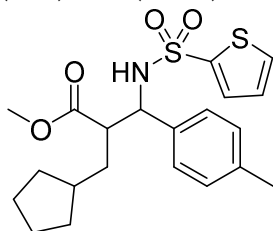
**Melting Point (°C):** 89.5

**R<sub>f</sub>** (Cy/AE: 80/20, UV+KMnO<sub>4</sub>): 0.48.

**HRMS (ESI<sup>+</sup>):** m/z [M+H]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>32</sub>NO<sub>4</sub>S<sub>2</sub>: 438.1773. Found: 438.1776.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.33 (d, *J* = 4.6 Hz, 1H), 7.30 (d, *J* = 4.7 Hz, 1H), 7.24–7.20 (m, 3H), 6.88–6.84 (m, 7H), 6.78–6.74 (m, 2H), 6.27 (d, *J* = 9.1 Hz, 1H), 5.72 (d, *J* = 8.9 Hz, 1H), 4.52–4.49 (m, 1H), 4.38 (t, *J* = 8.4 Hz, 1H), 3.87 (q, *J* = 5.5 Hz, 2H), 3.72 (q, *J* = 5.9 Hz, 2H), 2.72–2.68 (m, 2H), 2.17 (s, 6H), 1.59–1.52 (m, 2H), 1.56–1.33 (m, 4H), 1.27–1.15 (m, 3H), 1.10–1.03 (m, 3H), 0.88–0.83 (m, 2H), 0.78–0.73 (m, 18H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.9 (C), 173.2 (C), 142.3 (C), 141.6 (C), 137.5 (C), 137.2 (C), 136.1 (C), 135.4 (C), 132.4 (CH), 132.0 (CH), 131.7 (CH), 131.3 (CH), 129.1 (2 CH), 129.0 (2 CH), 127.1 (CH), 126.9 (CH), 126.8 (2 CH), 126.1 (2 CH), 64.7 (CH), 64.5 (CH), 60.0 ( $\text{CH}_2$ ), 59.1 ( $\text{CH}_2$ ), 50.7 (CH), 50.1 (CH), 39.3 ( $\text{CH}_2$ ), 38.1 ( $\text{CH}_2$ ), 30.5 ( $\text{CH}_2$ ), 30.4 ( $\text{CH}_2$ ), 26.3 (CH), 25.9 (CH), 23.5 ( $\text{CH}_2$ ), 22.8 ( $\text{CH}_2$ ), 22.0 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_2$ ), 21.1 ( $\text{CH}_3$ ), 21.0 ( $\text{CH}_3$ ), 19.0 ( $\text{CH}_3$ ), 18.9 ( $\text{CH}_3$ ), 13.7 (2  $\text{CH}_3$ ).



d.r. = 52:48

$\text{C}_{21}\text{H}_{27}\text{NO}_4\text{S}_2$

MW = 421.57

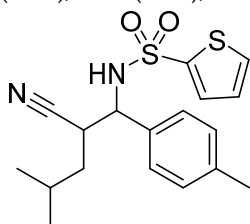
Compound **8dab**: Following **GP2** performed with imine **7b** (265 mg, 1.0 mmol, 1.0 equiv), methyl acrylate (181  $\mu\text{L}$ , 2.0 mmol, 2.0 equiv) and organozinc reagent (3.2 mL, C = 0.95 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [ $\text{V}(\text{SiO}_2)$  = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a colorless oil (153 mg, 36%, d.r. = 52:48).

$R_f$  (Cy/AE: 80/20, UV+ $\text{KMnO}_4$ ): 0.30.

HRMS (ESI $^+$ ): m/z [ $\text{M}+\text{H}$ ] $^+$  Calcd. for  $\text{C}_{21}\text{H}_{28}\text{NO}_4\text{S}_2$ : 422.1460. Found: 422.1462.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.29 (m, 2H), 7.26–7.19 (m, 2H), 6.88–6.82 (m, 8H), 6.80–6.73 (m, 2H), 6.21 (d,  $J$  = 9.2 Hz, 1H), 5.66 (d,  $J$  = 8.6 Hz, 1H), 4.52 (t,  $J$  = 7.3 Hz, 1H), 4.43 (t,  $J$  = 8.4 Hz, 1H), 3.48 (s, 3H), 3.36 (s, 3H), 2.68 (t,  $J$  = 6.7 Hz, 2H), 2.18 (s, 6H), 1.76–1.31 (m, 20H), 1.06–0.91 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2 (C), 173.6 (C), 142.2 (C), 141.5 (C), 137.5 (C), 137.3 (C), 136.2 (C), 135.3 (C), 132.3 (CH), 132.0 (CH), 131.8 (CH), 131.4 (CH), 129.2 (2 CH), 129.1 (2 CH), 127.1 (CH), 127.0 (CH), 126.7 (2 CH), 126.1 (2 CH), 59.7 (CH), 59.1 (CH), 51.9 ( $\text{CH}_3$ ), 51.8 ( $\text{CH}_3$ ), 51.7 (CH), 51.5 (CH), 38.1 ( $\text{CH}_2$ ), 37.8 ( $\text{CH}_2$ ), 36.6 ( $\text{CH}_2$ ), 35.0 ( $\text{CH}_2$ ), 33.1 ( $\text{CH}_2$ ), 32.6 ( $\text{CH}_2$ ), 32.5 ( $\text{CH}_2$ ), 32.1 ( $\text{CH}_2$ ), 25.1 ( $\text{CH}_2$ ), 25.0 ( $\text{CH}_2$ ), 21.2 (CH), 21.1 (CH).



d.r. = 53:47

$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2$

MW = 362.51

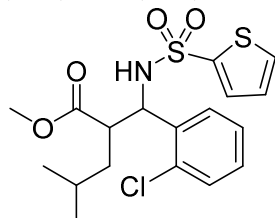
Compound **8cib**: Following **GP2** performed with imine **7b** (265 mg, 1.0 mmol, 1.0 equiv), acrylonitrile (131  $\mu\text{L}$ , 2.0 mmol, 2.0 equiv) and organozinc reagent (3.7 mL, C = 0.80 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [ $\text{V}(\text{SiO}_2)$  = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a colorless oil (269 mg, 74%, d.r. = 53:47).

$R_f$  (Cy/AE: 80/20, UV+ $\text{KMnO}_4$ ): 0.20.

HRMS (ESI $^+$ ): m/z [ $\text{M}+\text{H}$ ] $^+$  Calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_2\text{S}_2$ : 363.1201. Found: 363.1203.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J$  = 4.8 Hz, 1H), 7.41–7.36 (m, 3H), 7.04–7.01 (m, 8H), 6.90–6.82 (m, 2H), 6.14 (br s, 1H), 6.03 (br s, 1H), 4.55 (br s, 1H), 4.40 (br s, 1H), 3.19 (q,  $J$  = 6.6 Hz, 1H), 2.91 (dt,  $J$  = 9.1, 4.1 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.85–1.68 (m, 3H), 1.42–1.28 (m, 3H), 0.93–0.86 (m, 12H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 141.0 (C), 140.9 (C), 138.7 (C), 138.3 (C), 134.1 (C), 132.8 (C), 132.6 (CH), 132.5 (CH), 132.2 (CH), 132.05 (CH), 129.5 (2 CH), 129.4 (2 CH), 127.3 (CH), 127.2 (CH), 127.0 (2 CH), 126.2 (2 CH), 119.7 (C), 119.5 (C), 58.8 (CH), 58.7 (CH), 38.6 (CH), 38.2 (CH<sub>2</sub>), 38.1 (CH<sub>2</sub>), 37.7 (CH), 26.0 (CH<sub>3</sub>), 25.9 (CH<sub>3</sub>), 22.9 (CH), 22.8 (CH), 21.4 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 21.2 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>).



d.r. = 69:31

C<sub>18</sub>H<sub>22</sub>ClNO<sub>4</sub>S<sub>2</sub>

MW = 415,95

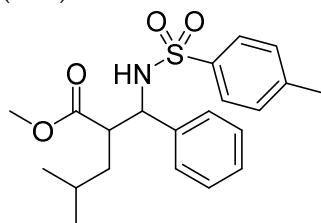
Compound **8cac**: Following **GP2** performed with imine **7c** (286 mg, 1.0 mmol, 1.0 equiv), methyl acrylate (181 μL, 2.0 mmol, 2.0 equiv) and organozinc reagent (3.8 mL, C = 0.79 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a colorless oil (297 mg, 72%, d.r. = 69:31).

**R<sub>f</sub>** (Cy/AE: 80/20, UV+KMnO<sub>4</sub>): 0.23.

**HRMS (ESI<sup>+</sup>)**: m/z [M+H]<sup>+</sup> Calcd. for C<sub>18</sub>H<sub>23</sub>ClNO<sub>4</sub>S<sub>2</sub>: 416.0752. Found: 416.0752.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.33–7.28 (m, 4H), 7.21–7.11 (m, 3H), 7.04–7.01 (m, 4H), 6.97–6.94 (m, 1H), 6.77–6.73 (m, 2H), 6.53 (d, *J* = 9.3 Hz, 1H), 6.00 (d, *J* = 8.6 Hz, 1H), 4.98 (dd, *J* = 9.0, 4.5 Hz, 2H), 3.43 (s, 3H), 3.33 (s, 3H), 2.90–2.85 (m, 2H), 1.64–1.47 (m, 4H), 1.37–1.28 (m, 2H), 0.82–0.75 (m, 12H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 174.9 (C), 173.3 (C), 141.4 (C), 140.7 (C), 136.3 (2 C), 132.5 (C), 132.2 (C), 132.1 (2 CH), 131.7 (2 CH), 129.9 (CH), 129.6 (CH), 129.1 (CH), 128.9 (CH), 127.5 (2 CH), 127.1 (2 CH), 126.9 (CH), 126.8 (CH), 55.6 (2 CH), 51.9 (CH<sub>3</sub>), 51.8 (CH<sub>3</sub>), 48.2 (CH), 47.3 (CH), 39.2 (2 CH<sub>2</sub>), 26.3 (CH), 25.7 (CH), 23.4 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>), 22.2 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>).



d.r. = 56:44

C<sub>21</sub>H<sub>27</sub>NO<sub>4</sub>S

MW = 389,51

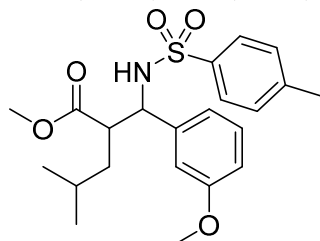
Compound **8cad**: Following **GP2** performed with imine **7d** (259 mg, 1.0 mmol, 1.0 equiv), methyl acrylate (181 μL, 2.0 mmol, 2.0 equiv) and organozinc reagent (3.7 mL, C = 0.80 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE: 90:10 (250 mL), 80:20 (250 mL)] as a colorless oil (289 mg, 74%, d.r. = 56:44).

**R<sub>f</sub>** (Cy/AE: 80/20, UV+KMnO<sub>4</sub>): 0.23.

**HRMS (ESI<sup>+</sup>)**: m/z [M+H]<sup>+</sup> Calcd. for C<sub>21</sub>H<sub>28</sub>NO<sub>4</sub>S: 390.1013. Found: 390.1010.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52–7.46 (m, 4H), 7.09–6.96 (m, 14H), 6.25 (d, *J* = 9.3 Hz, 1H), 6.01 (d, *J* = 9.1 Hz, 1H), 4.52 (t, *J* = 7.7 Hz, 1H), 4.41 (t, *J* = 8.6 Hz, 1H), 3.51 (s, 3H), 3.33 (s, 3H), 2.80–2.73 (m, 2H), 2.29 (s, 3H), 2.28 (s, 3H), 1.61–1.53 (m, 2H), 1.48–1.41 (m, 4H), 0.80–0.74 (m, 12H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.9 (C), 173.5 (C), 143.0 (C), 142.8 (C), 139.2 (C), 138.5 (C), 138.0 (C), 137.4 (C), 129.3 (2 CH), 129.1 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 127.5 (CH), 127.4 (CH), 127.2 (2 CH), 126.9 (4 CH), 126.4 (2 CH), 59.9 (CH), 59.2 (CH), 51.8 (CH<sub>3</sub>), 51.5 (CH<sub>3</sub>), 50.7 (CH), 50.2 (CH), 39.1 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 26.2 (CH<sub>3</sub>), 25.9 (CH<sub>3</sub>), 23.3 (CH), 22.8 (CH), 21.8 (2 CH<sub>3</sub>), 21.4 (2 CH<sub>3</sub>).—



d.r. = 55:45

C<sub>22</sub>H<sub>29</sub>NO<sub>5</sub>S

MW = 419,54

Compound **8cae**: Following **GP2** performed with imine **7e** (289 mg, 1.0 mmol, 1.0 equiv), methyl acrylate (181 μL, 2.0 mmol, 2.0 equiv) and organozinc reagent (3.8 mL, C = 0.79 M, 3.0 mmol, 3.0 equiv), the desired product was obtained after purification by FC [V(SiO<sub>2</sub>) = 50 mL, Cy/AE : 90:10 (250 mL), 80:20 (250 mL)] as a white solid (318 mg, 76%, d.r. = 55:45).

**Melting Point (°C):** 91

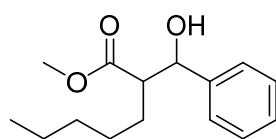
**R<sub>f</sub>** (Cy/AE: 80/20, UV+KMnO<sub>4</sub>): 0.17, 0.10.

**HRMS (ESI<sup>+</sup>):** m/z [M+H]<sup>+</sup> Calcd. for C<sub>22</sub>H<sub>30</sub>NO<sub>5</sub>S: 420.1839. Found: 420.1838.

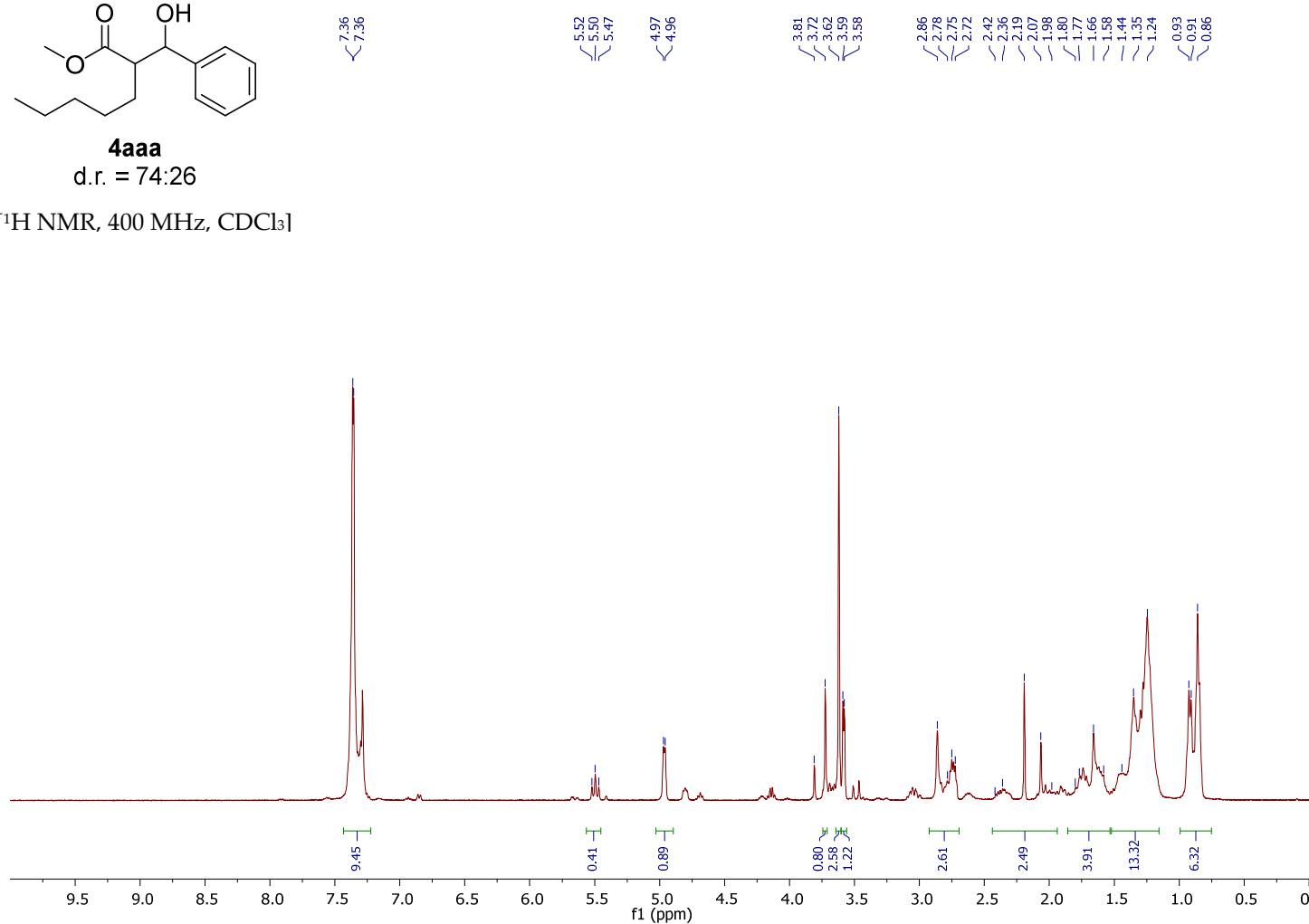
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51–7.46 (m, 4H), 7.07–6.98 (m, 6H), 6.64–6.57 (m, 4H), 6.43–6.40 (m, 2H), 6.19 (d, *J* = 9.3 Hz, 1H), 5.86 (d, *J* = 9.0 Hz, 1H), 4.48 (t, *J* = 7.5 Hz, 1H), 4.38 (t, *J* = 8.5 Hz, 1H), 3.64 (s, 6H), 3.53 (s, 3H), 3.38 (s, 3H), 2.79–2.73 (m, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 1.61–1.54 (m, 2H), 1.48–1.42 (m, 4H), 0.81–0.76 (m, 12H).

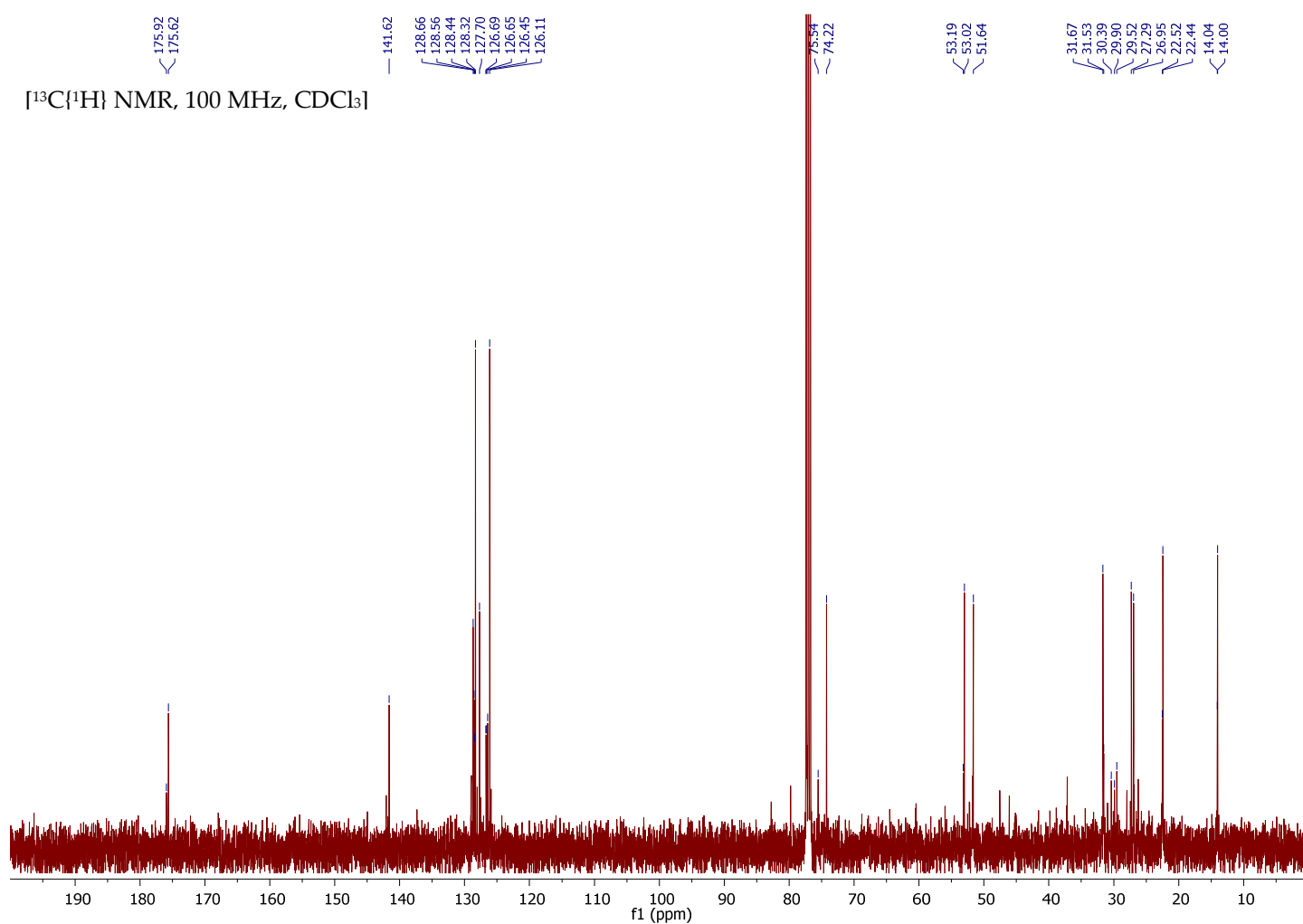
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.0 (C), 173.5 (C), 159.6 (C), 159.3 (C), 143.1 (C), 142.8 (C), 140.8 (C), 140.0 (C), 138.1 (C), 137.5 (C), 129.5 (CH), 129.3 (CH), 129.3 (2 CH), 129.2 (2 CH), 127.2 (2 CH), 127.0 (2 CH), 199.3 (CH), 118.9 (CH), 113.3 (CH), 113.1 (CH), 112.4 (CH), 111.9 (CH), 59.8 (CH), 59.2 (CH), 55.1 (2 CH<sub>3</sub>), 51.9 (CH<sub>3</sub>), 51.7 (CH<sub>3</sub>), 50.5 (CH), 50.1 (CH), 39.2 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 26.2 (CH<sub>3</sub>), 25.9 (CH<sub>3</sub>), 23.4 (CH), 22.8 (CH), 21.9 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>).

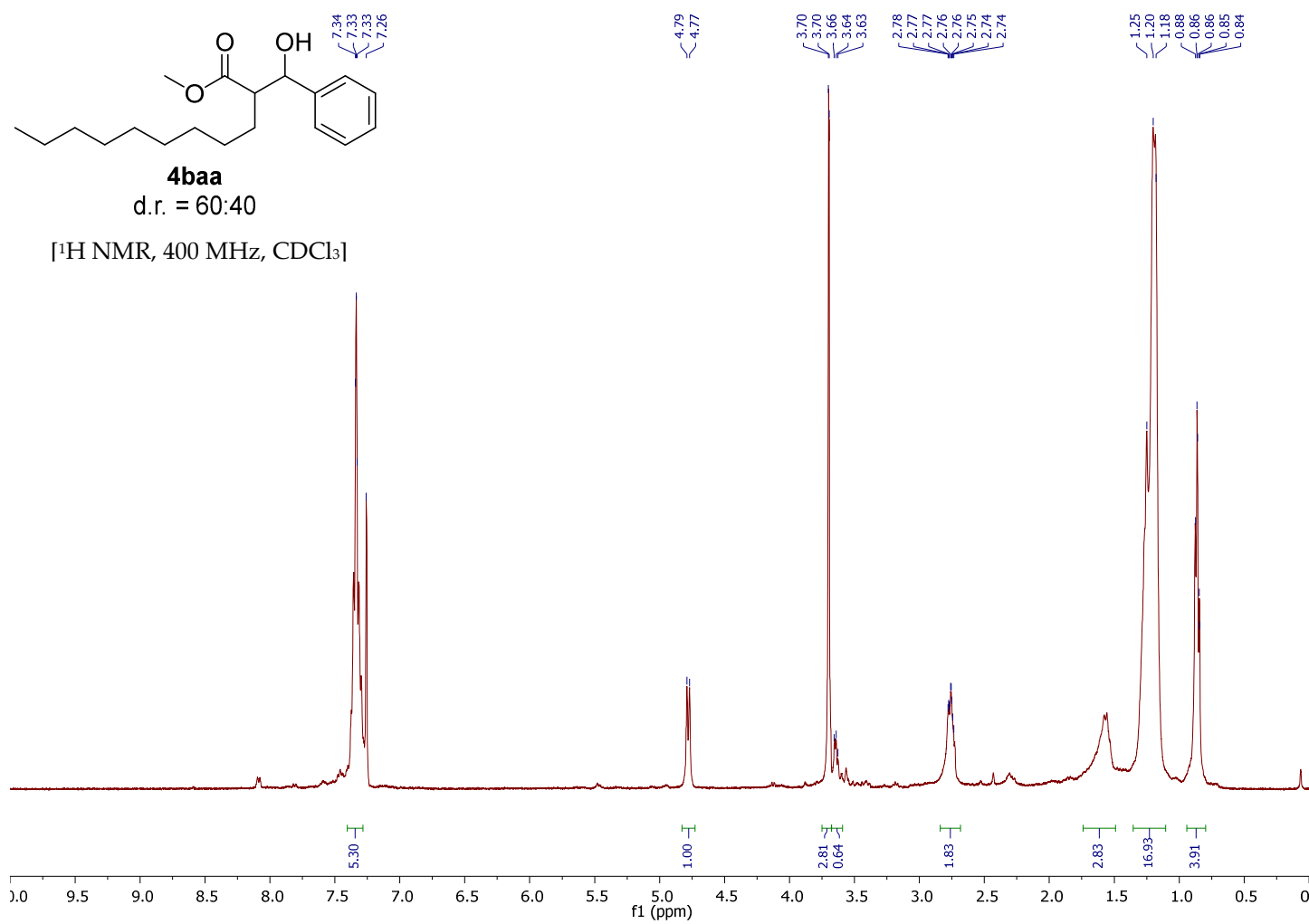
#### 4. Copies of NMR spectra

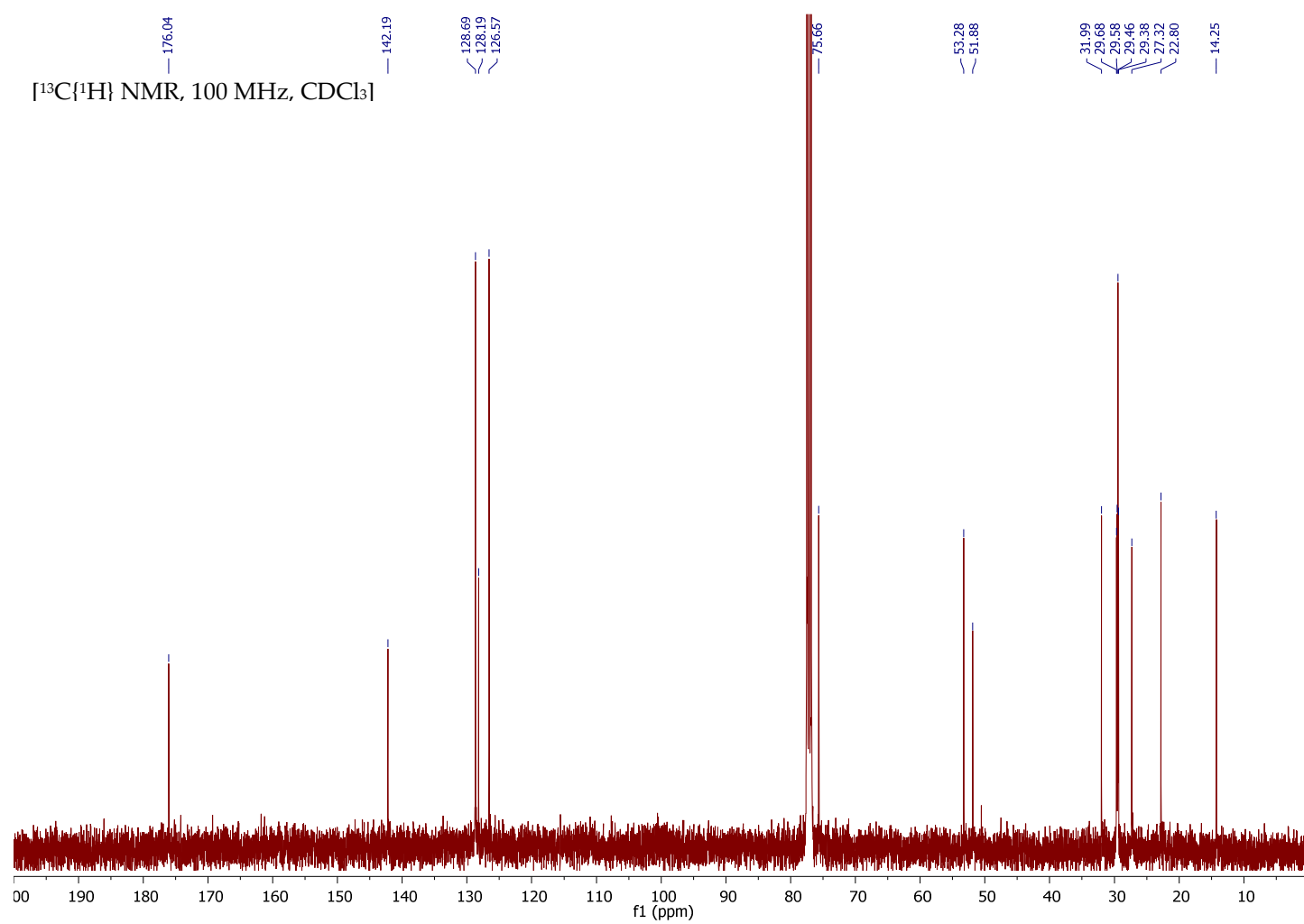
**4aaa**

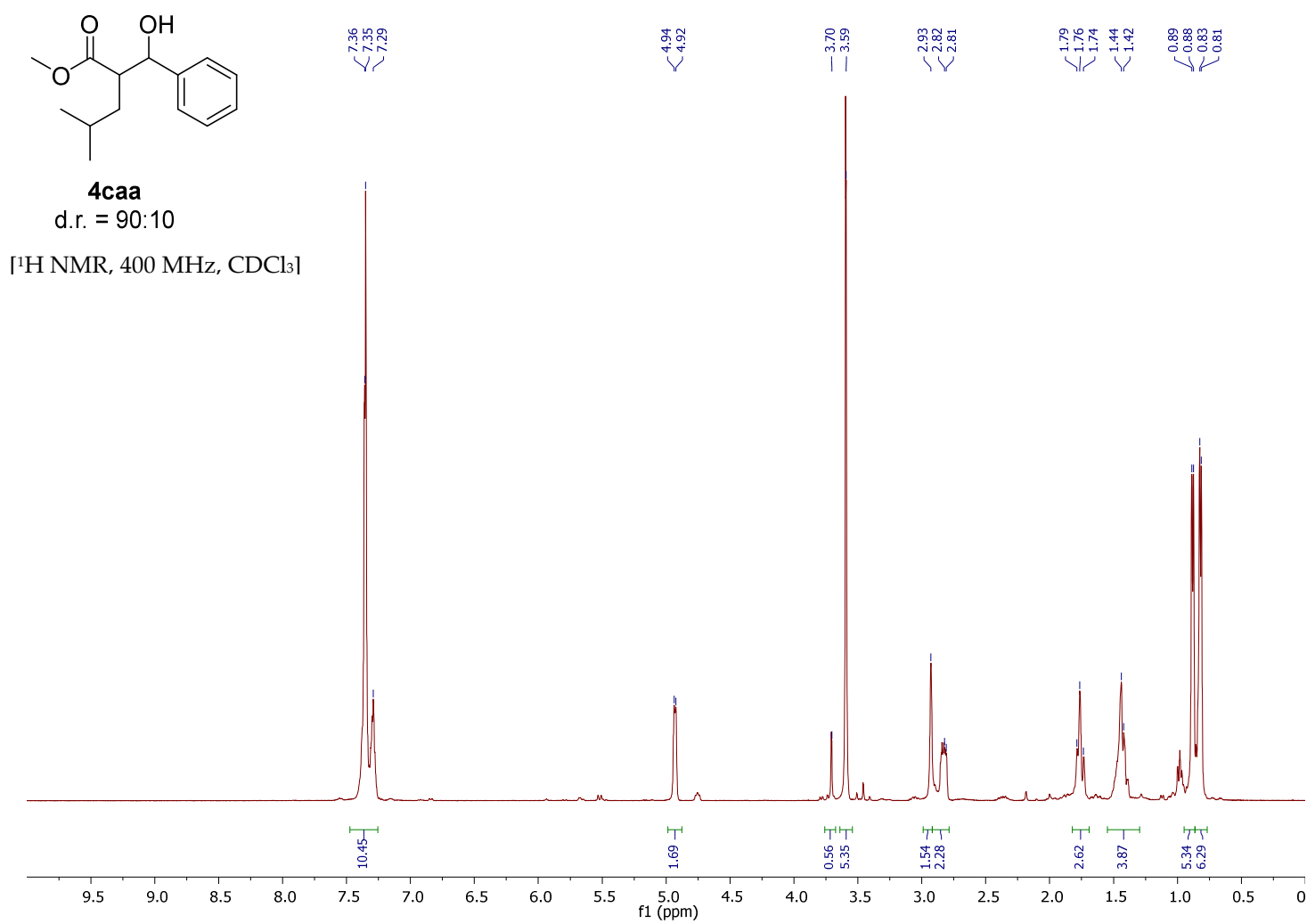
d.r. = 74:26

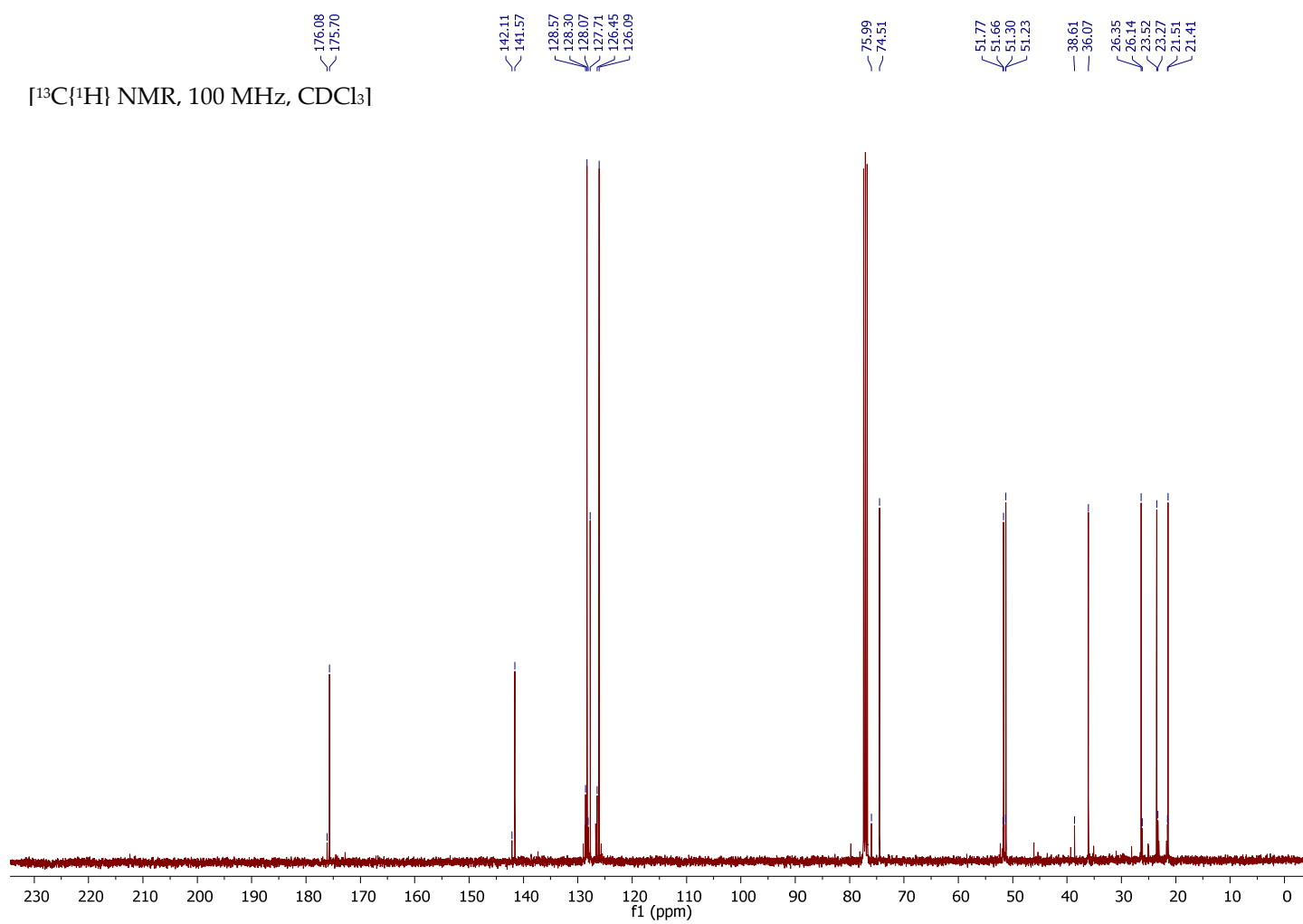
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

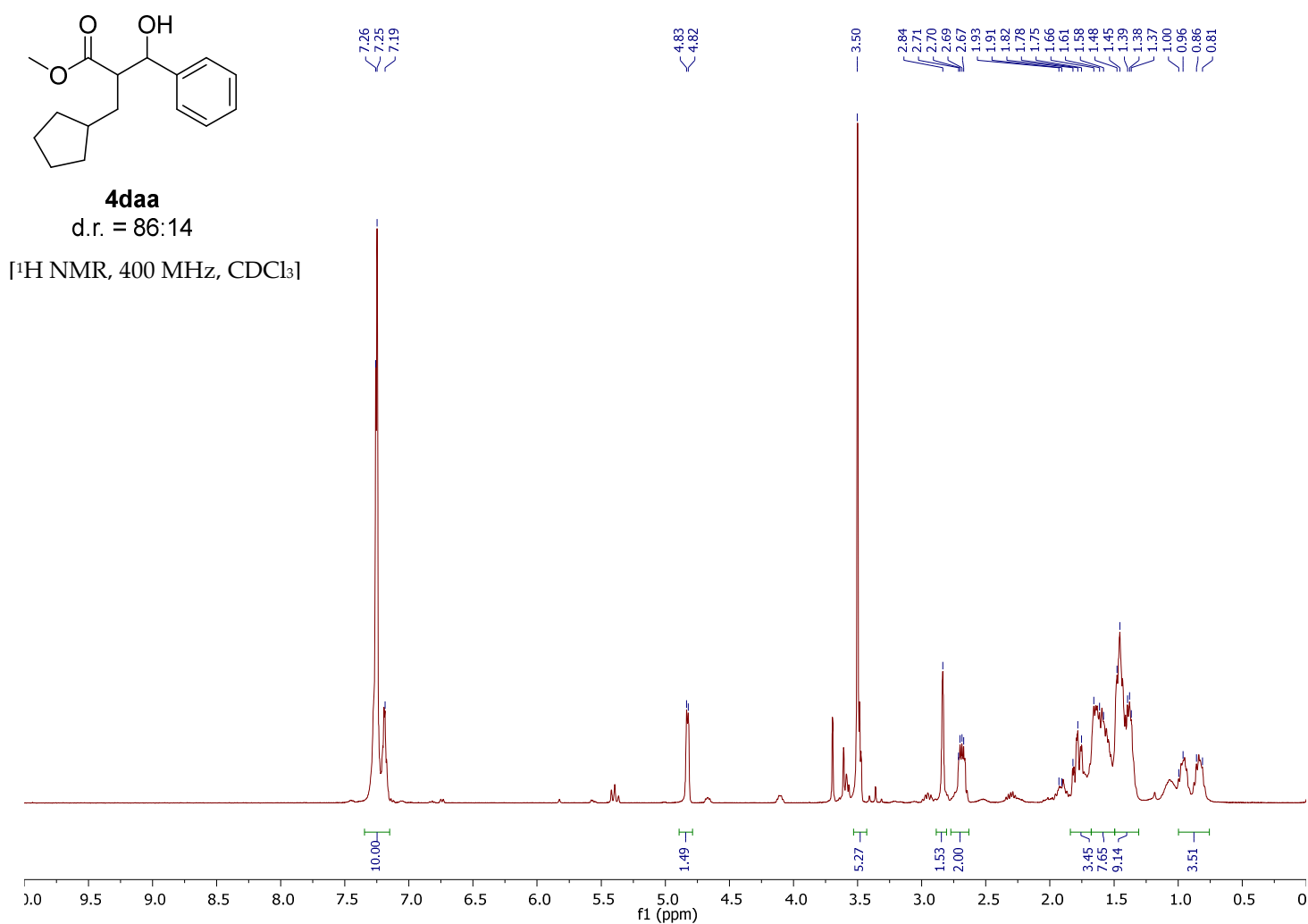


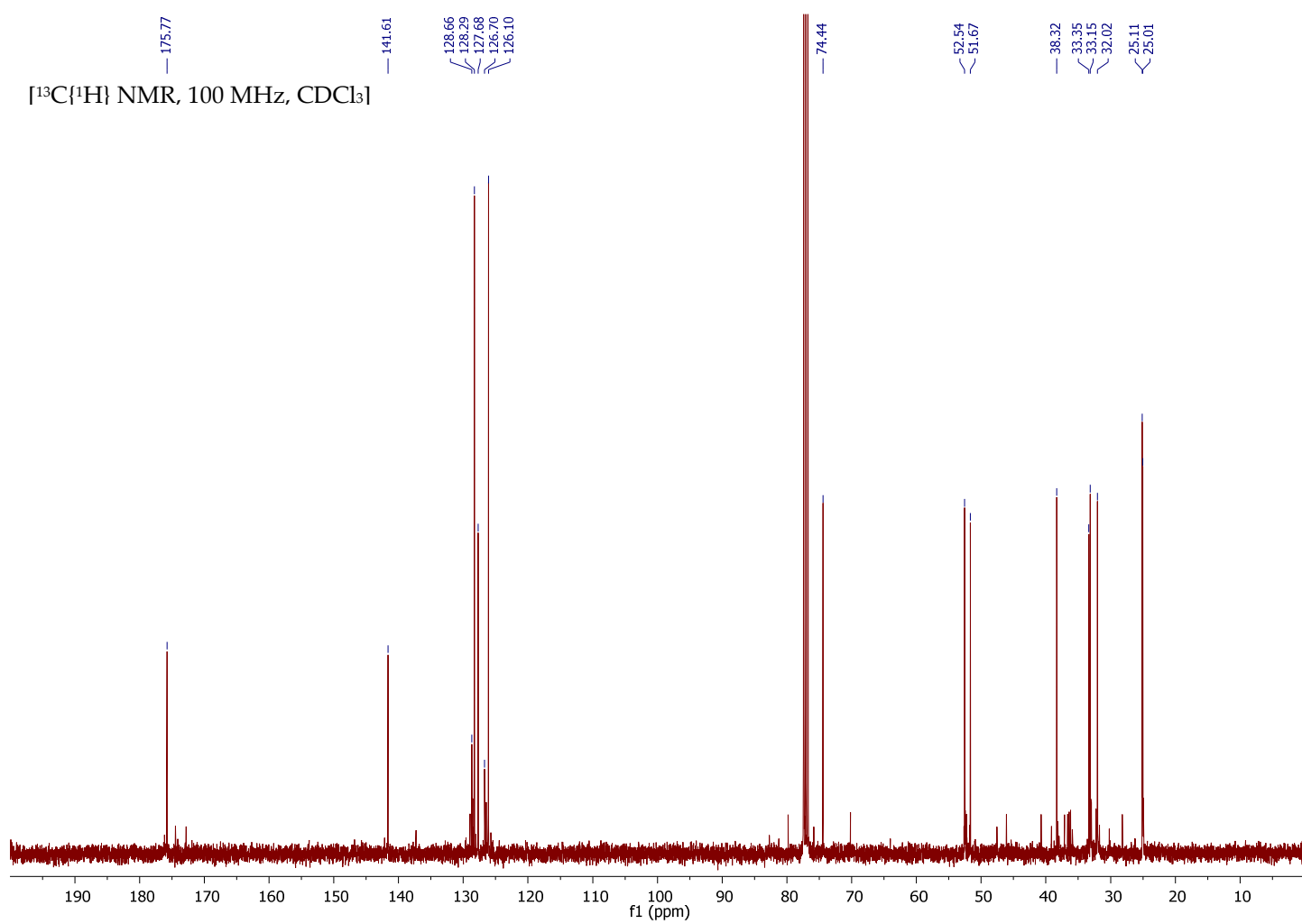


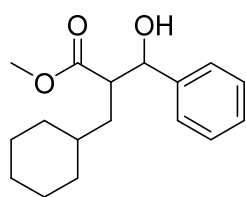




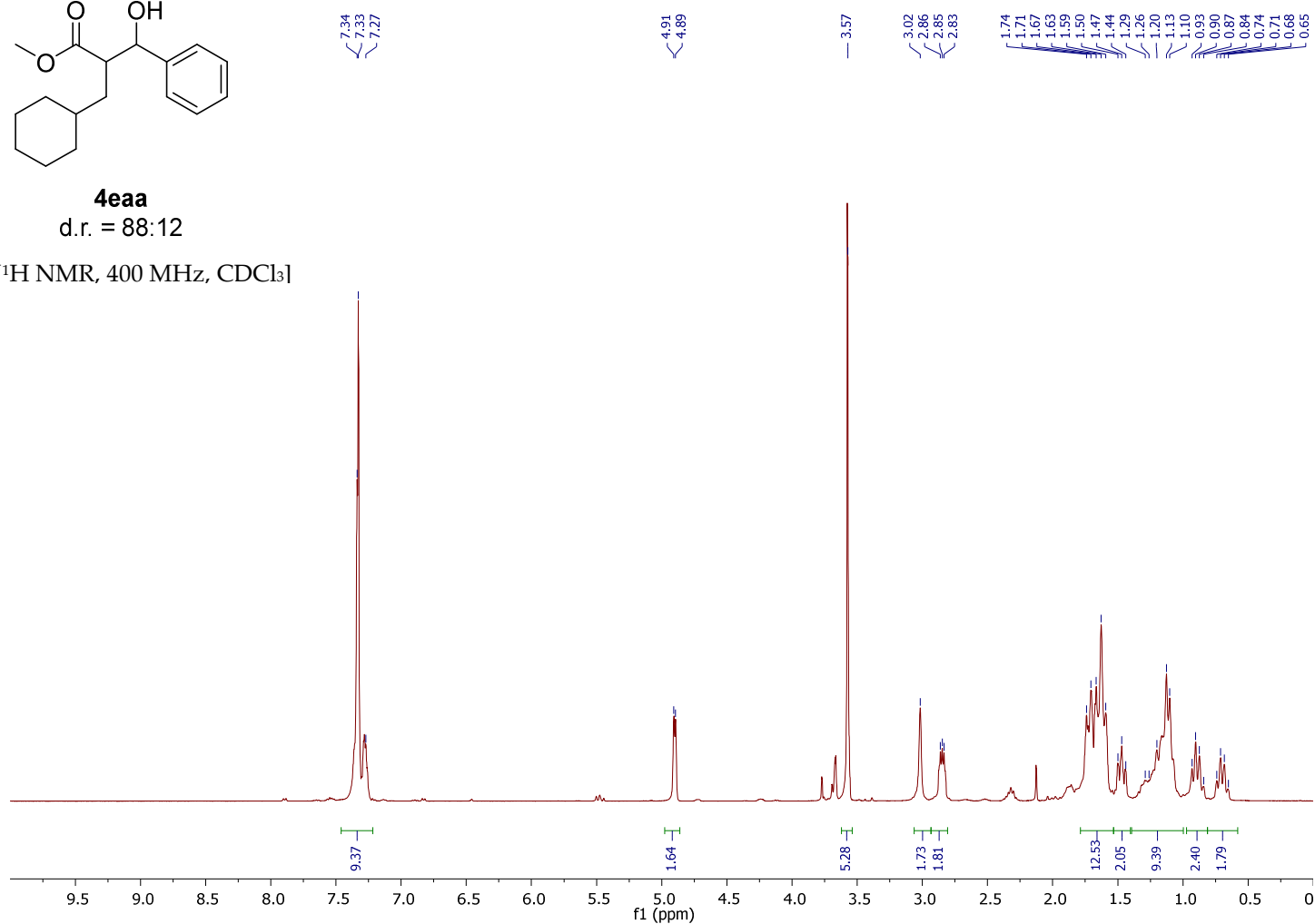


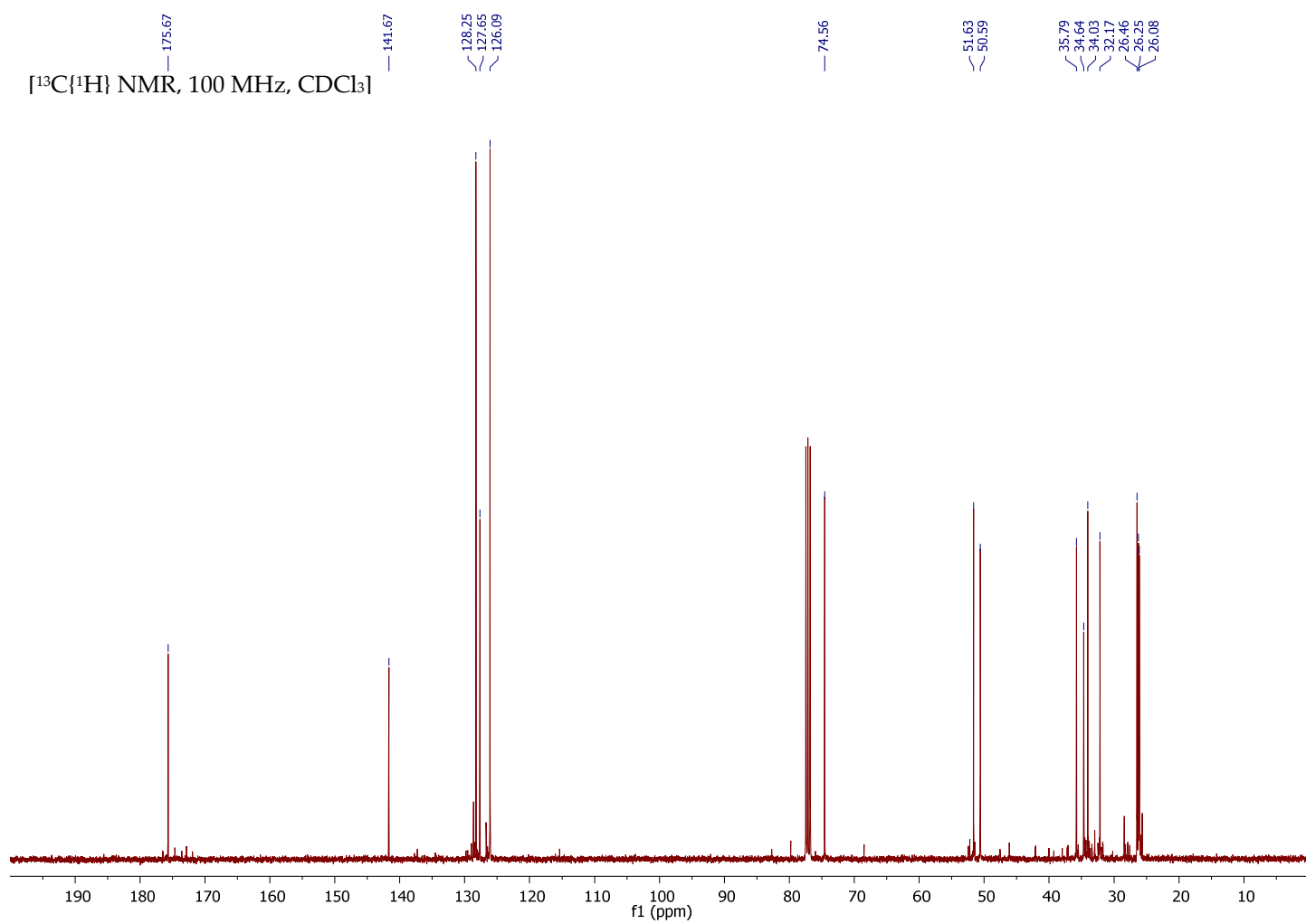


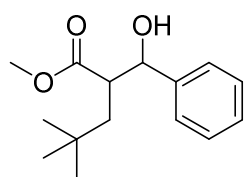


**4eaa**

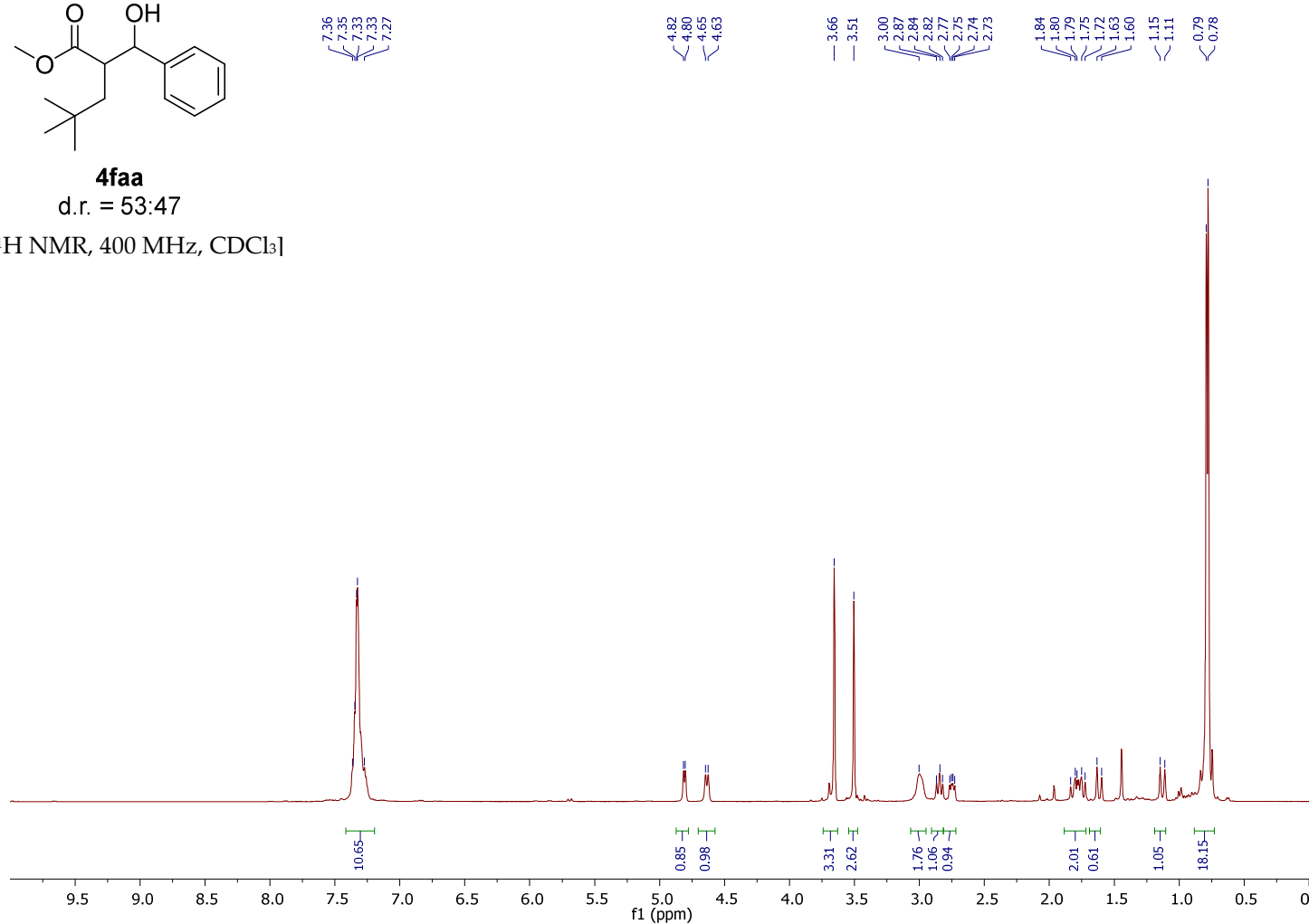
d.r. = 88:12

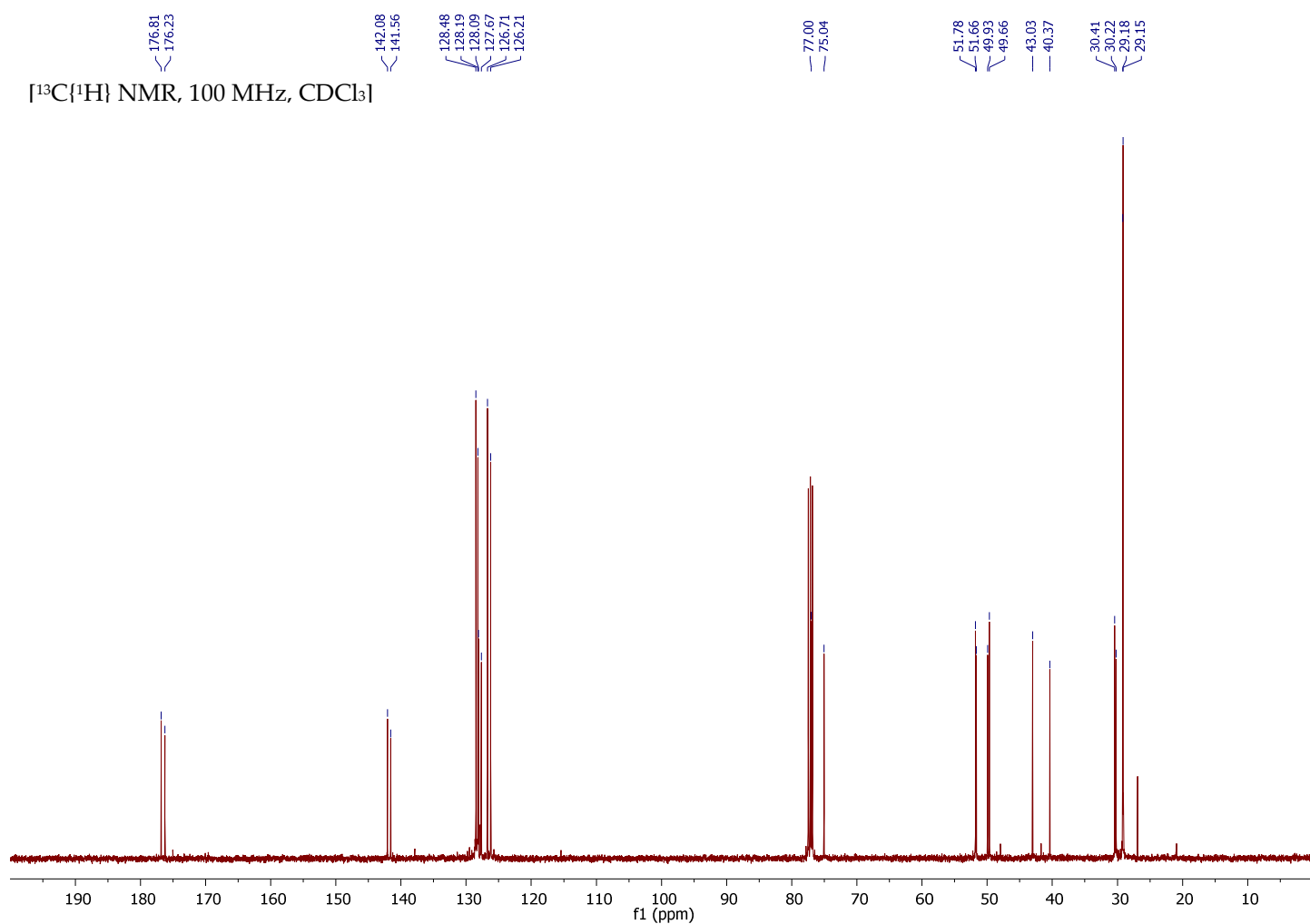
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

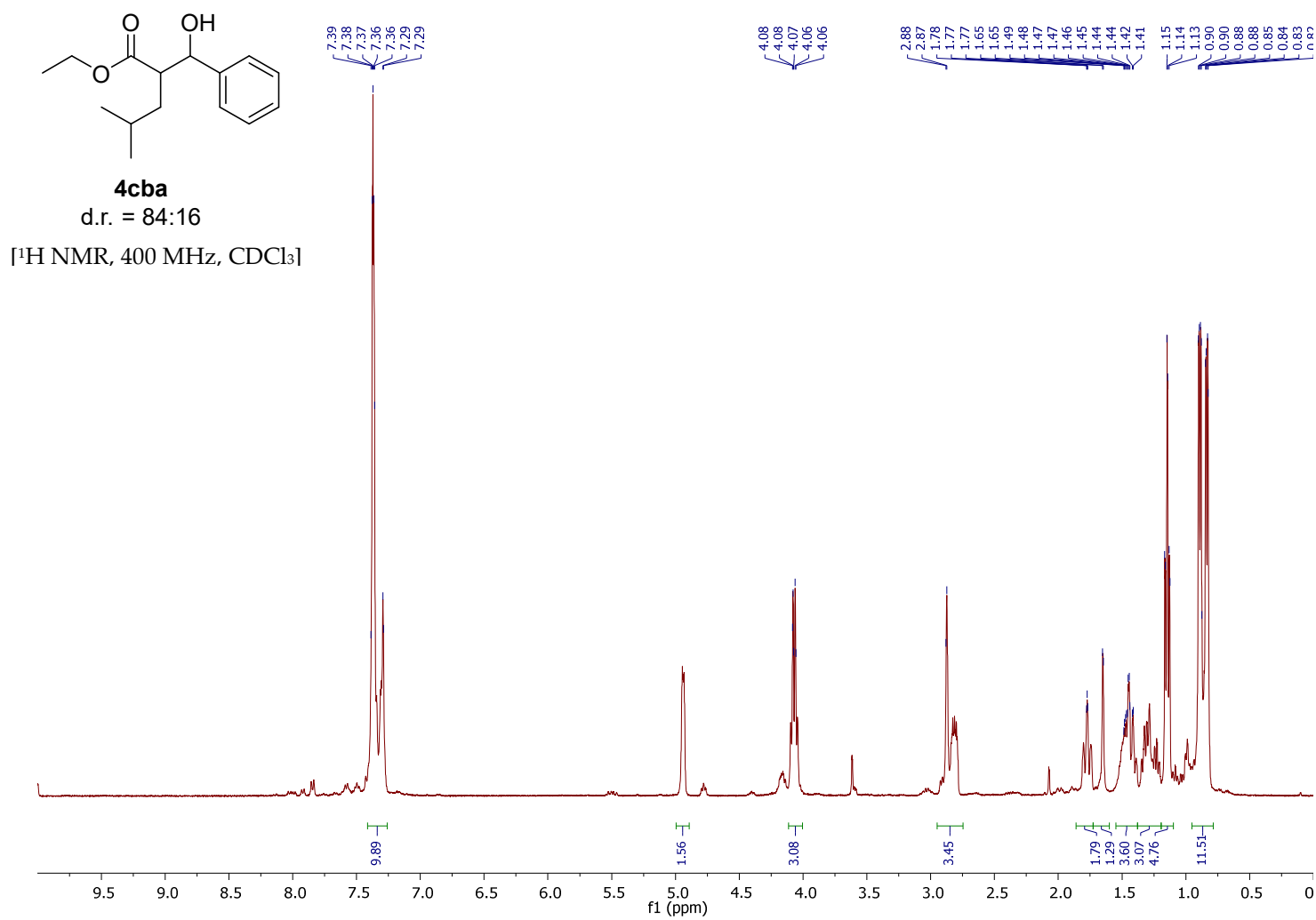


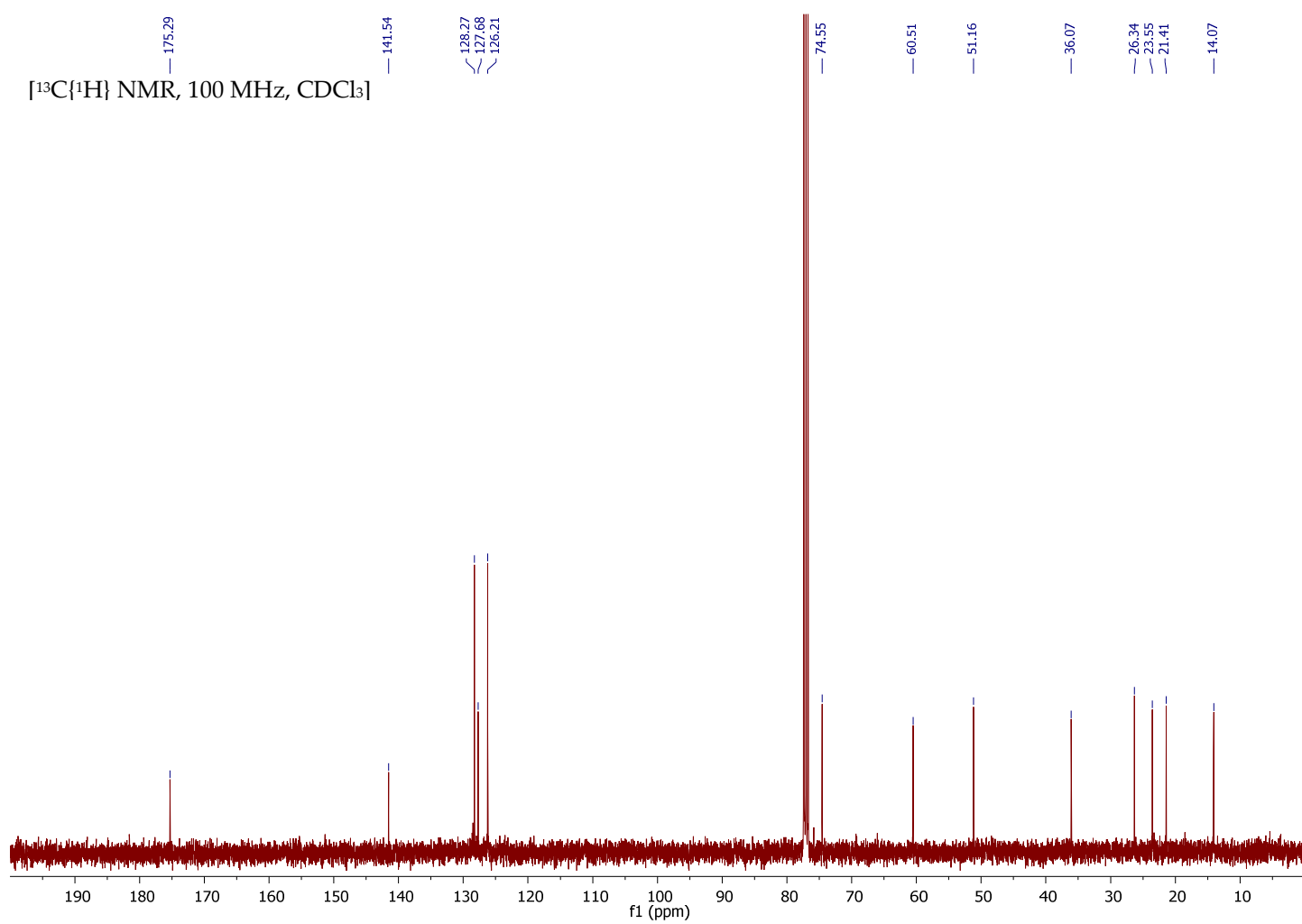
**4faa**

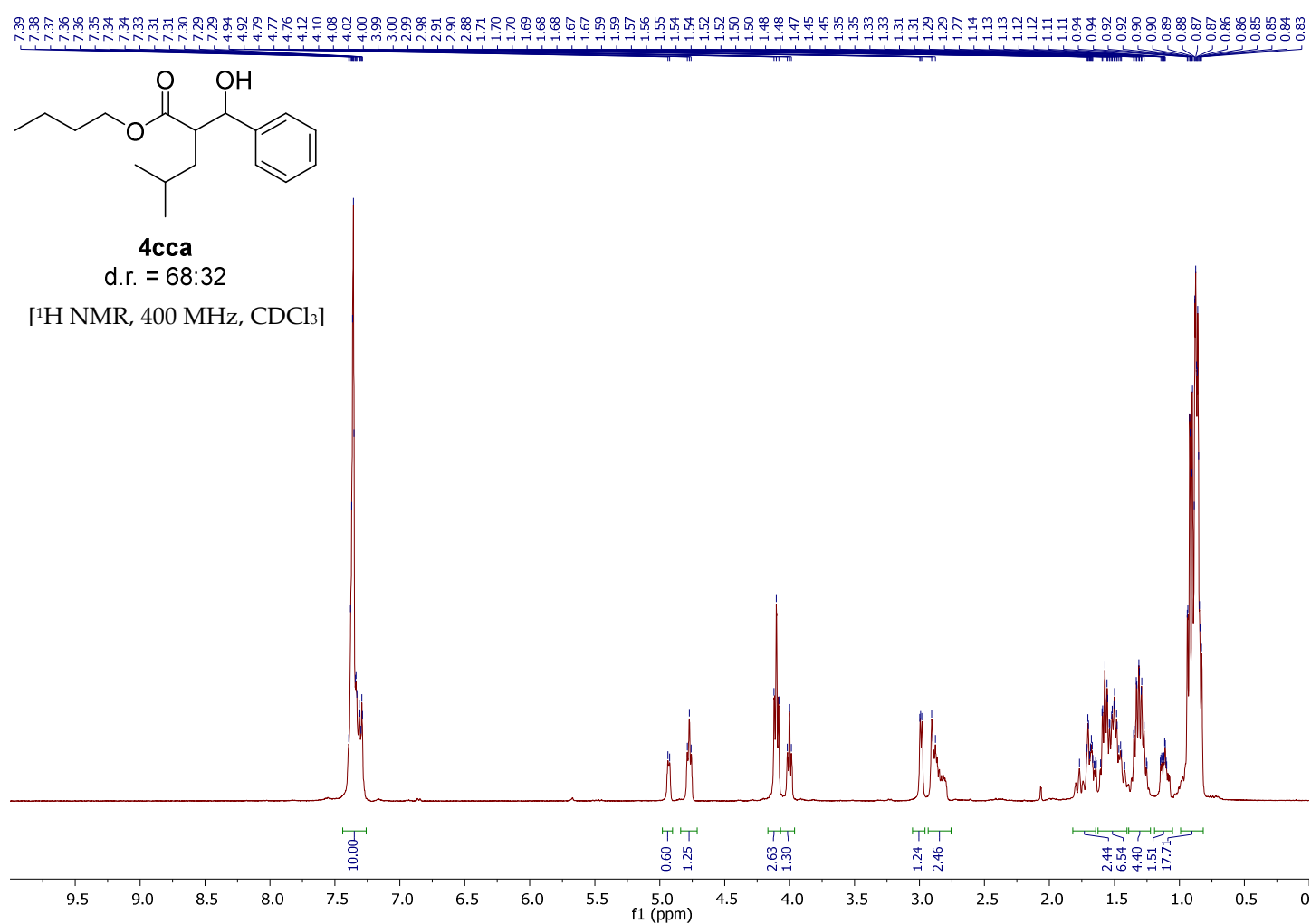
d.r. = 53:47

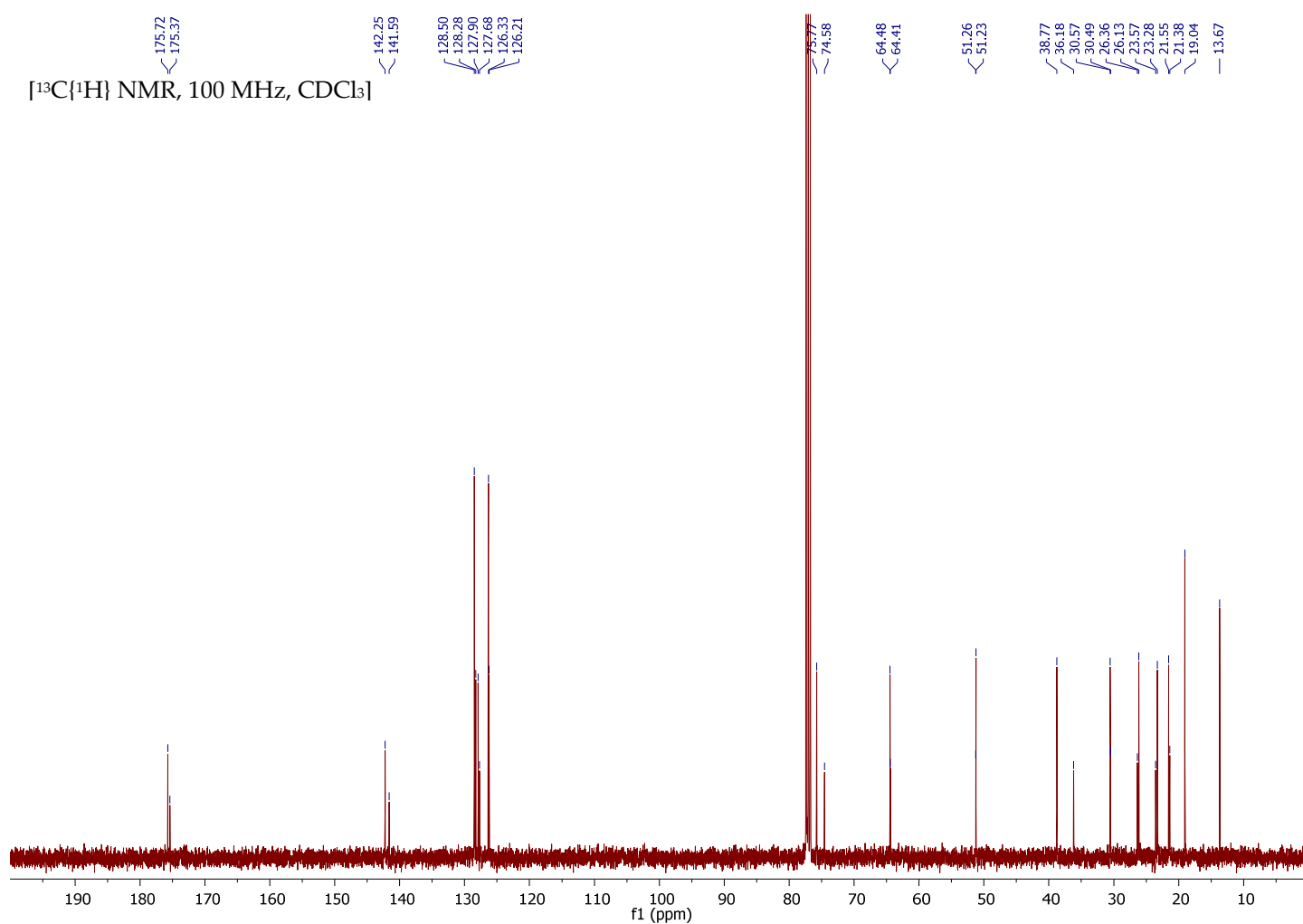
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

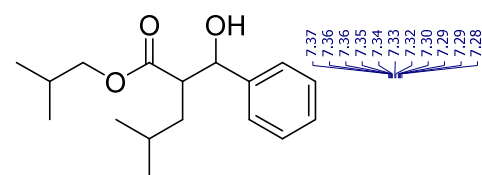




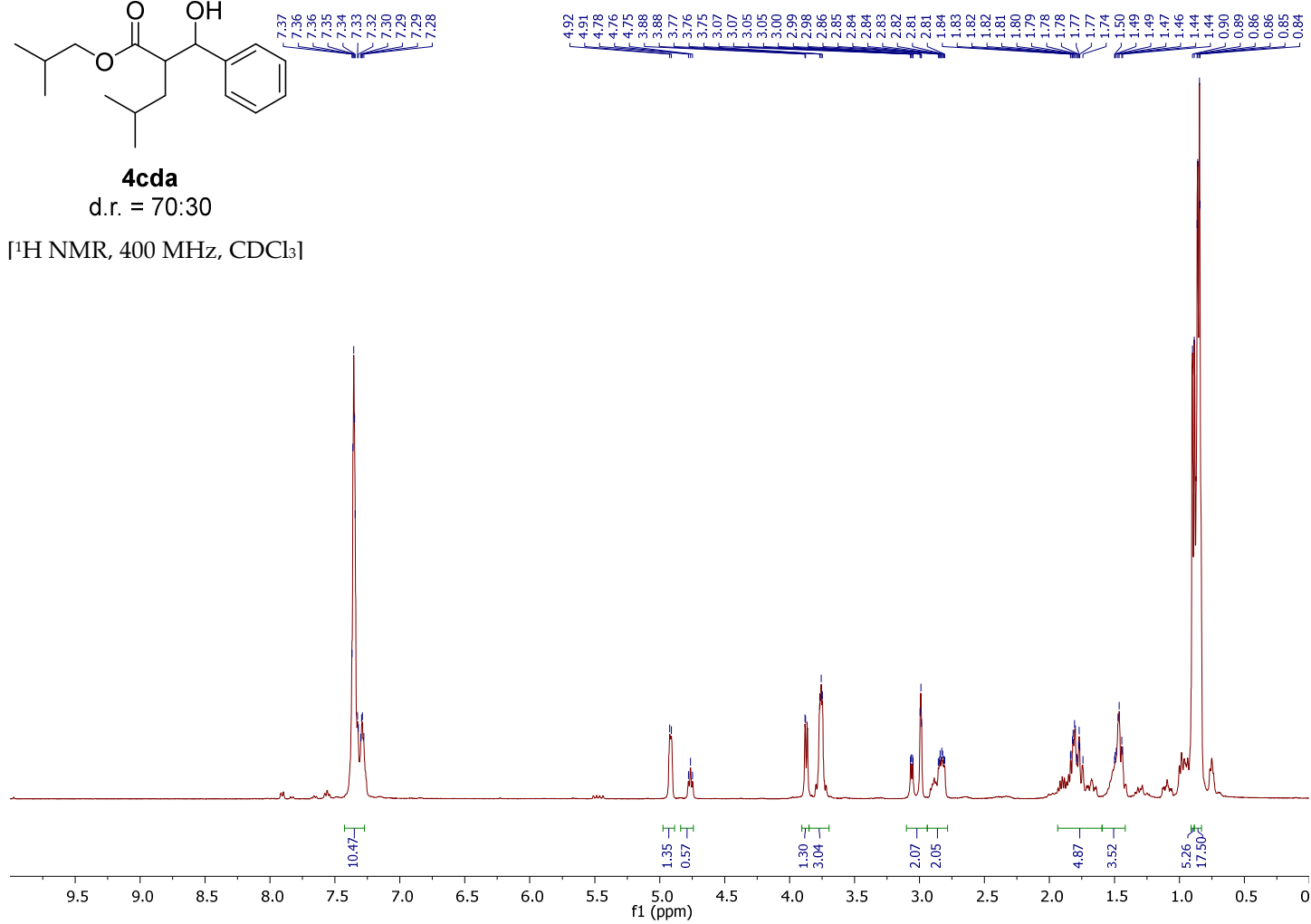


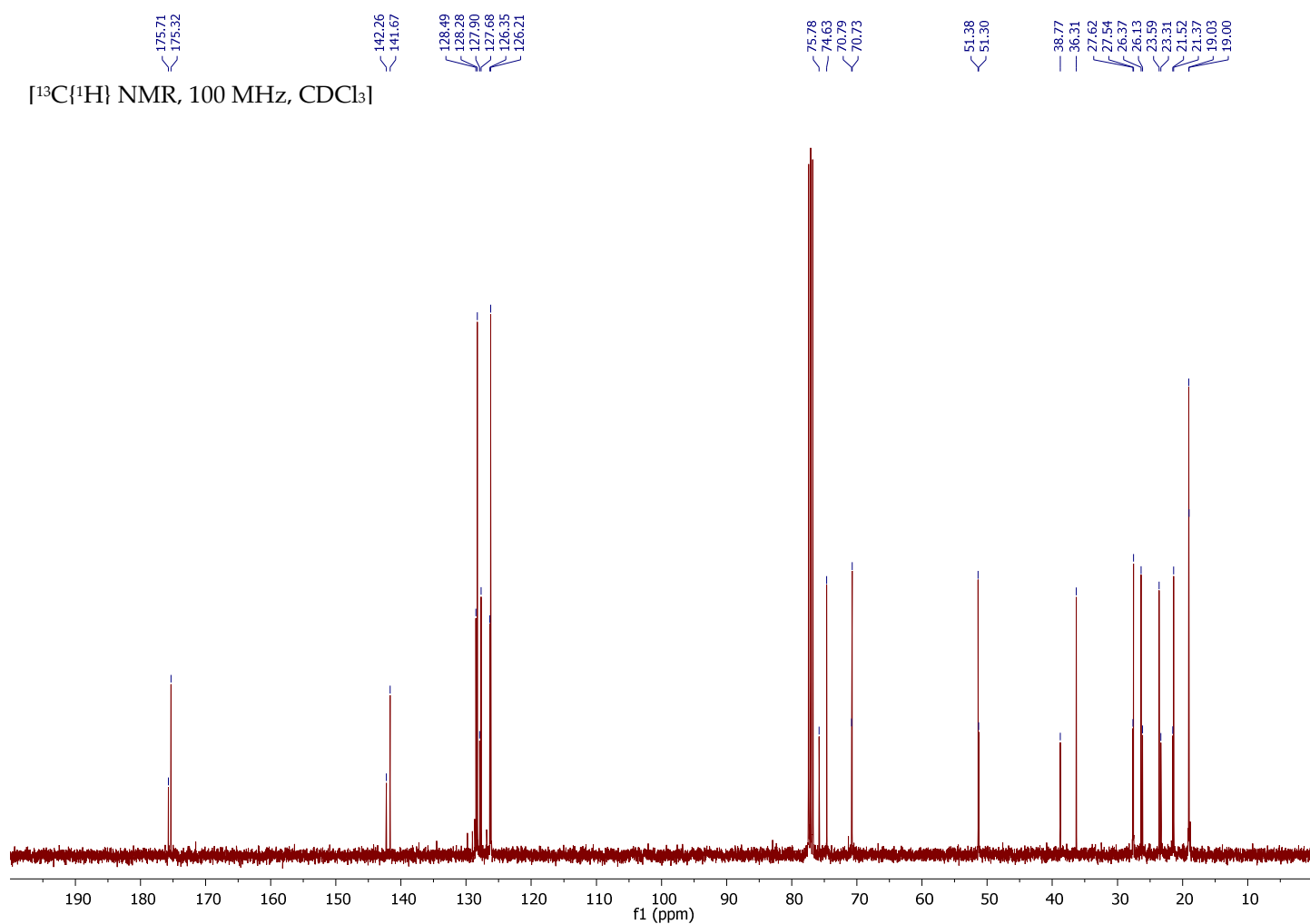


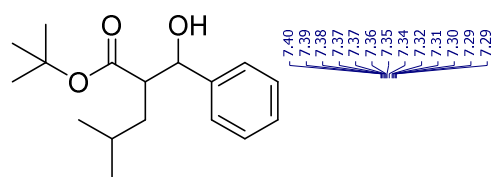


**4cda**

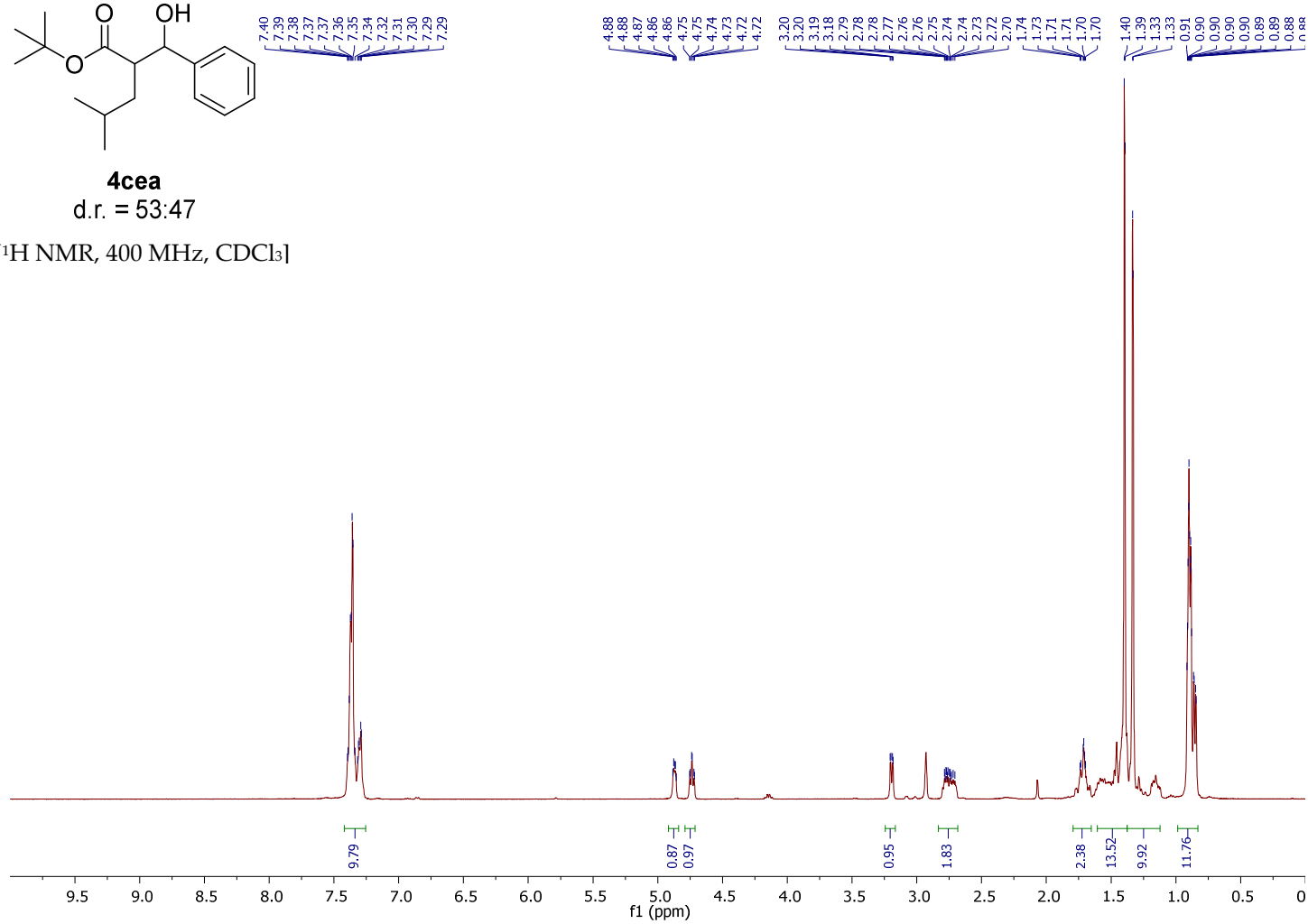
d.r. = 70:30

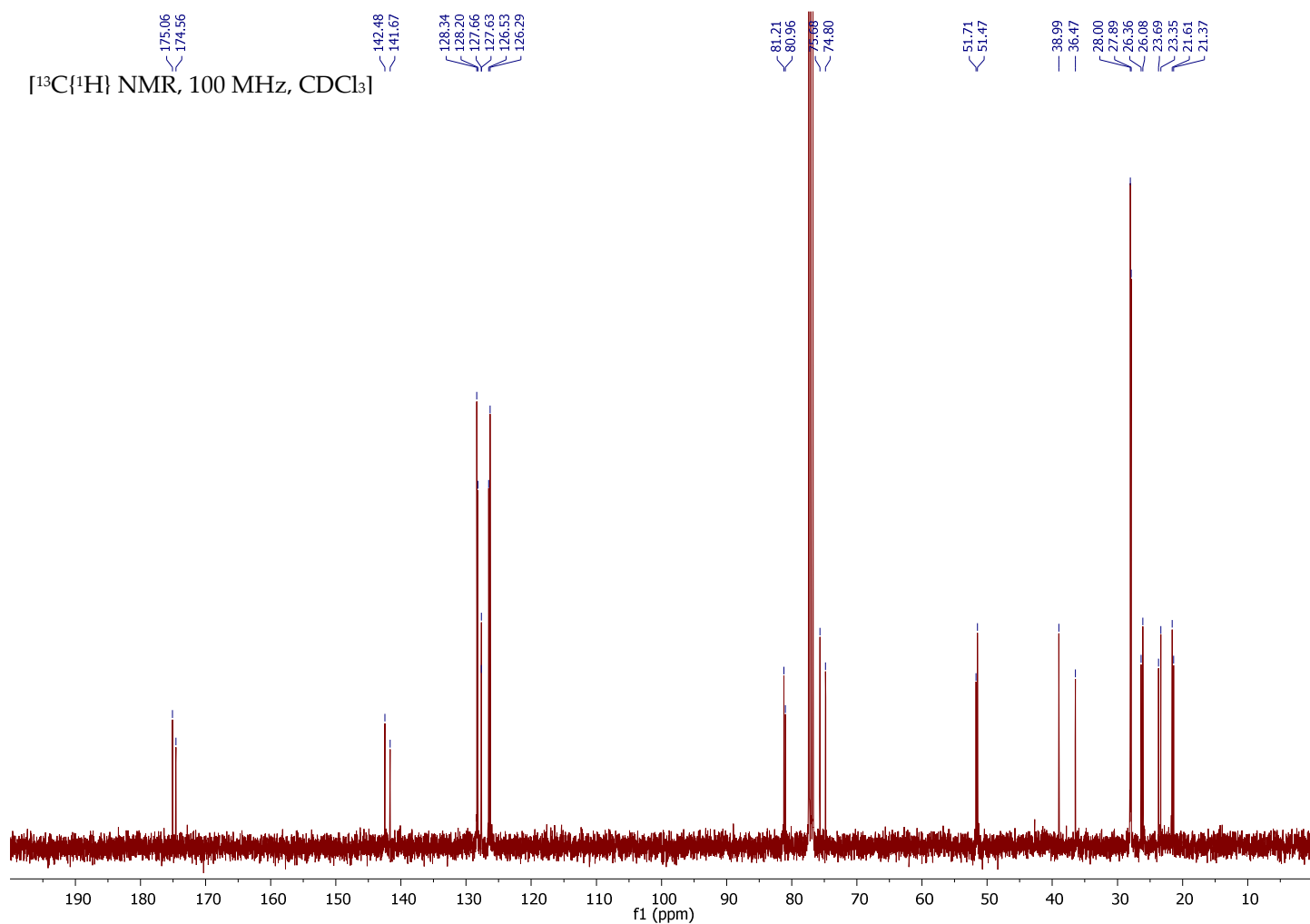
<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>

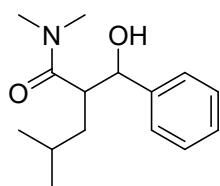


**4cea**

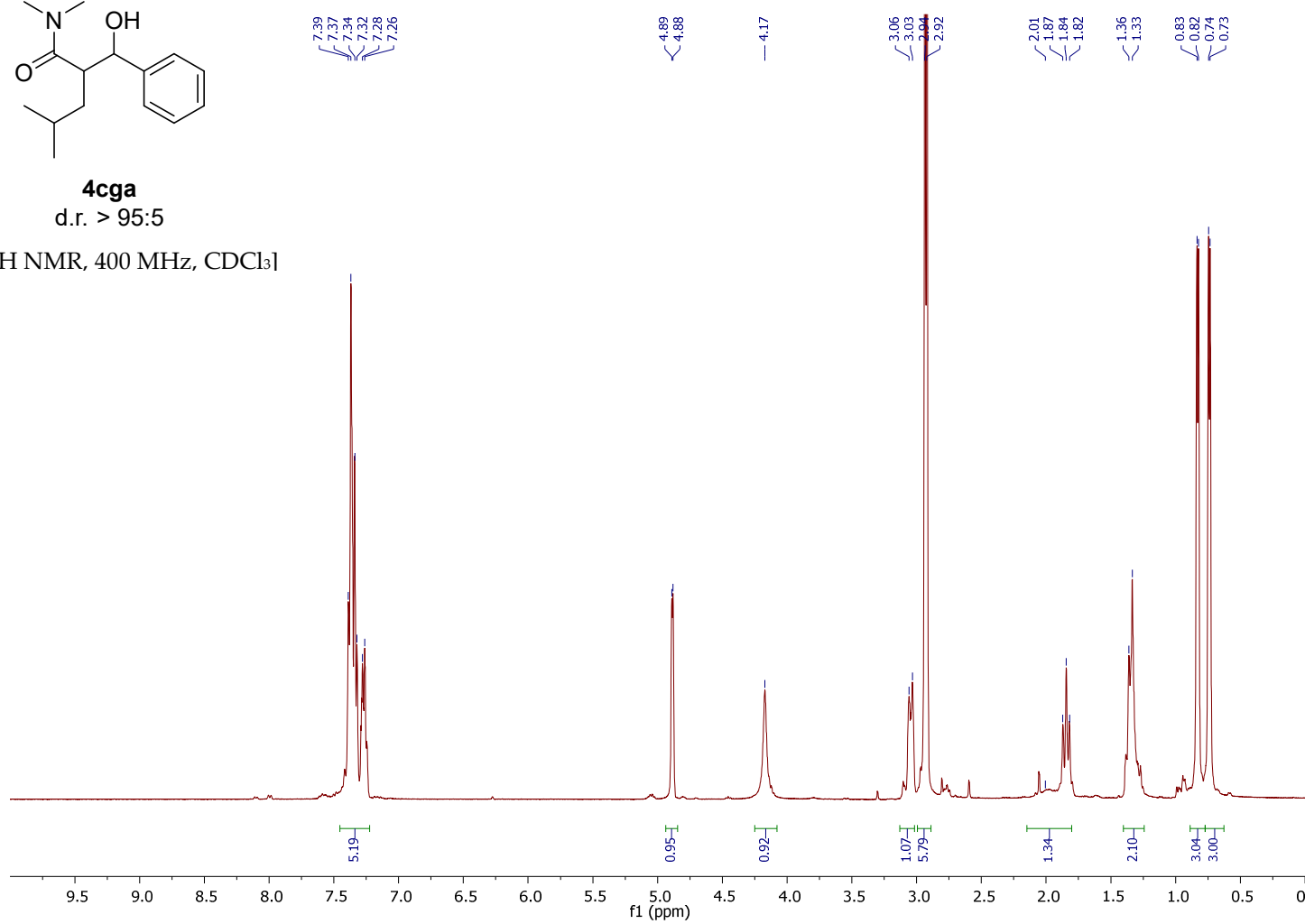
d.r. = 53:47

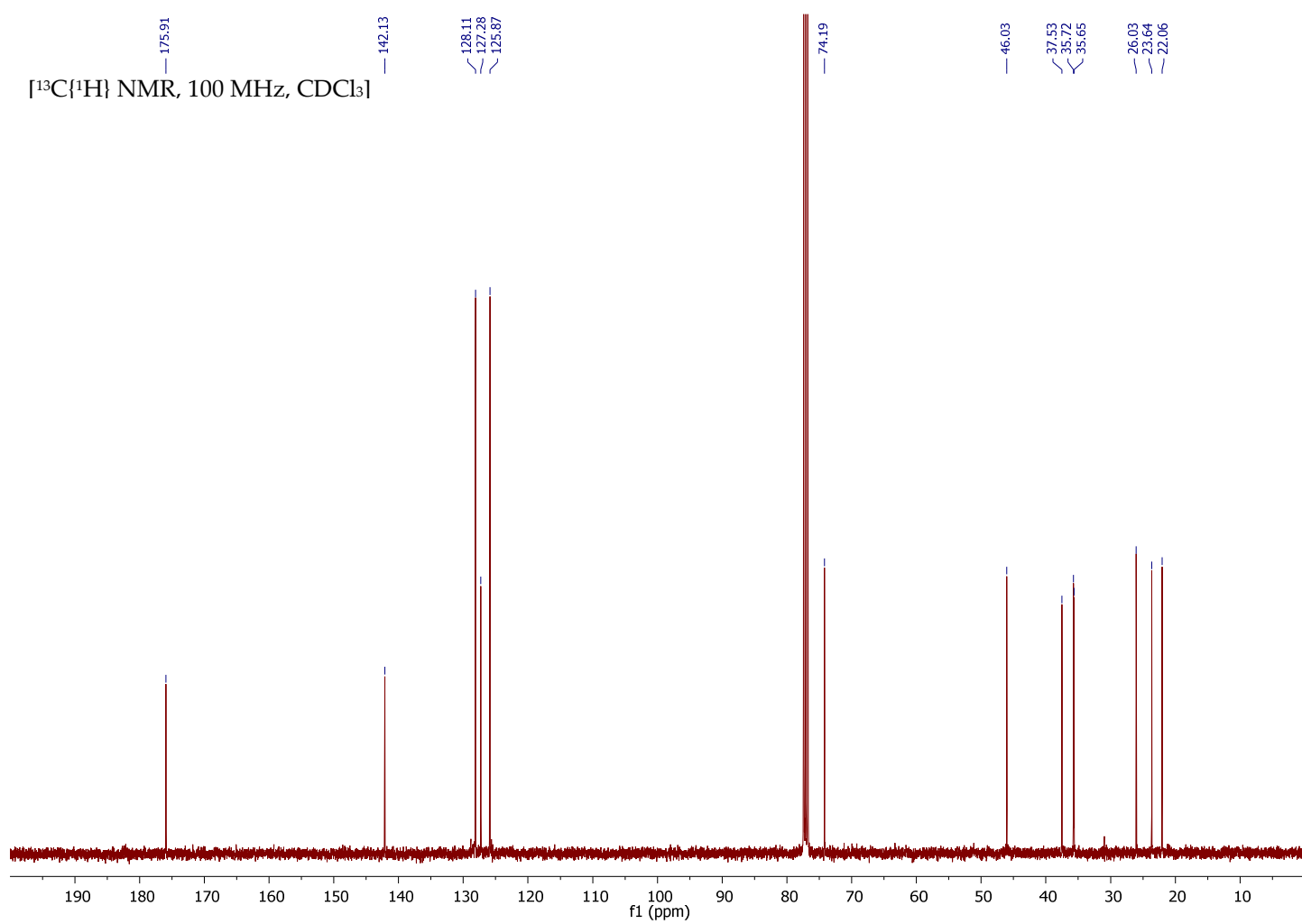
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

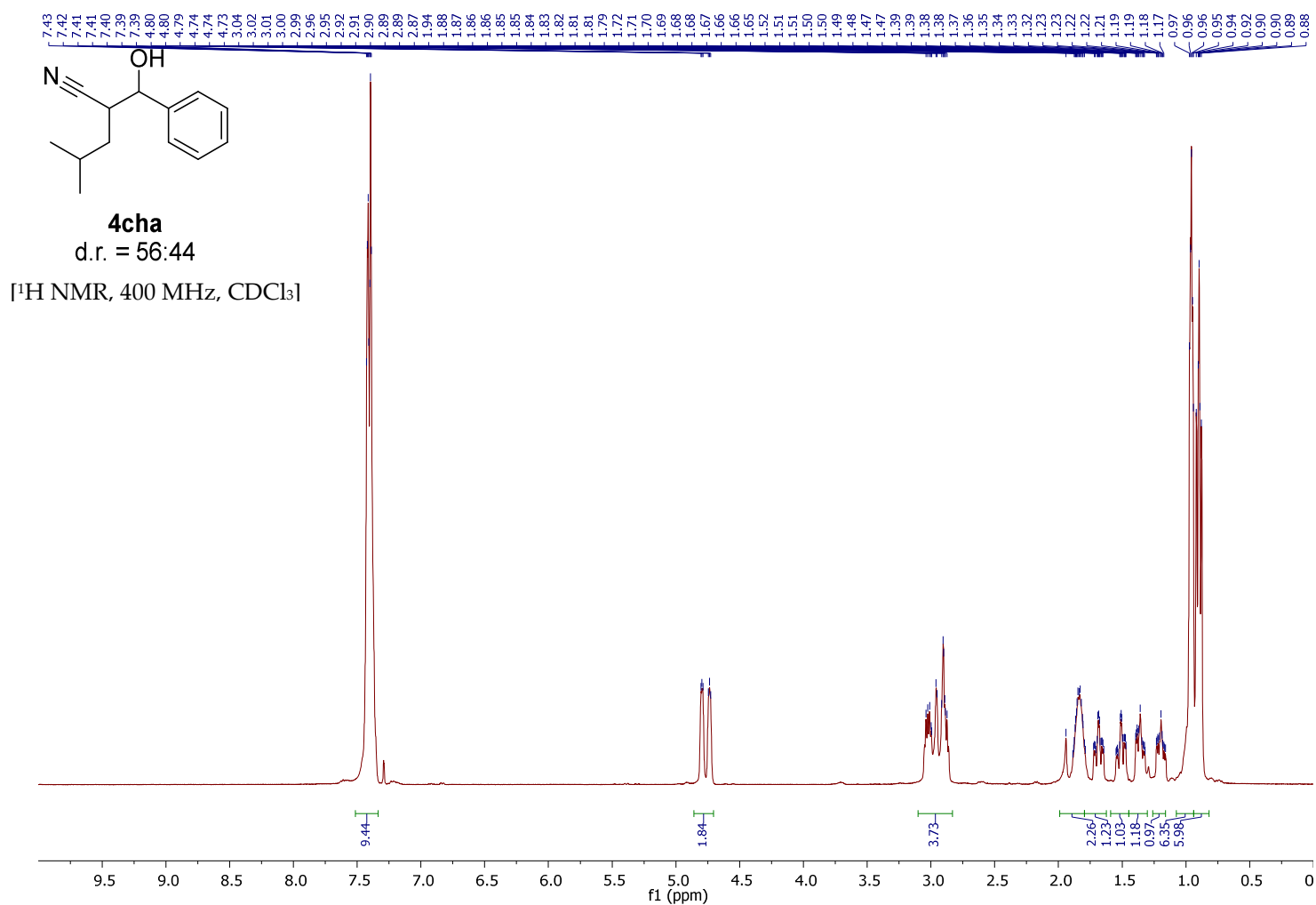


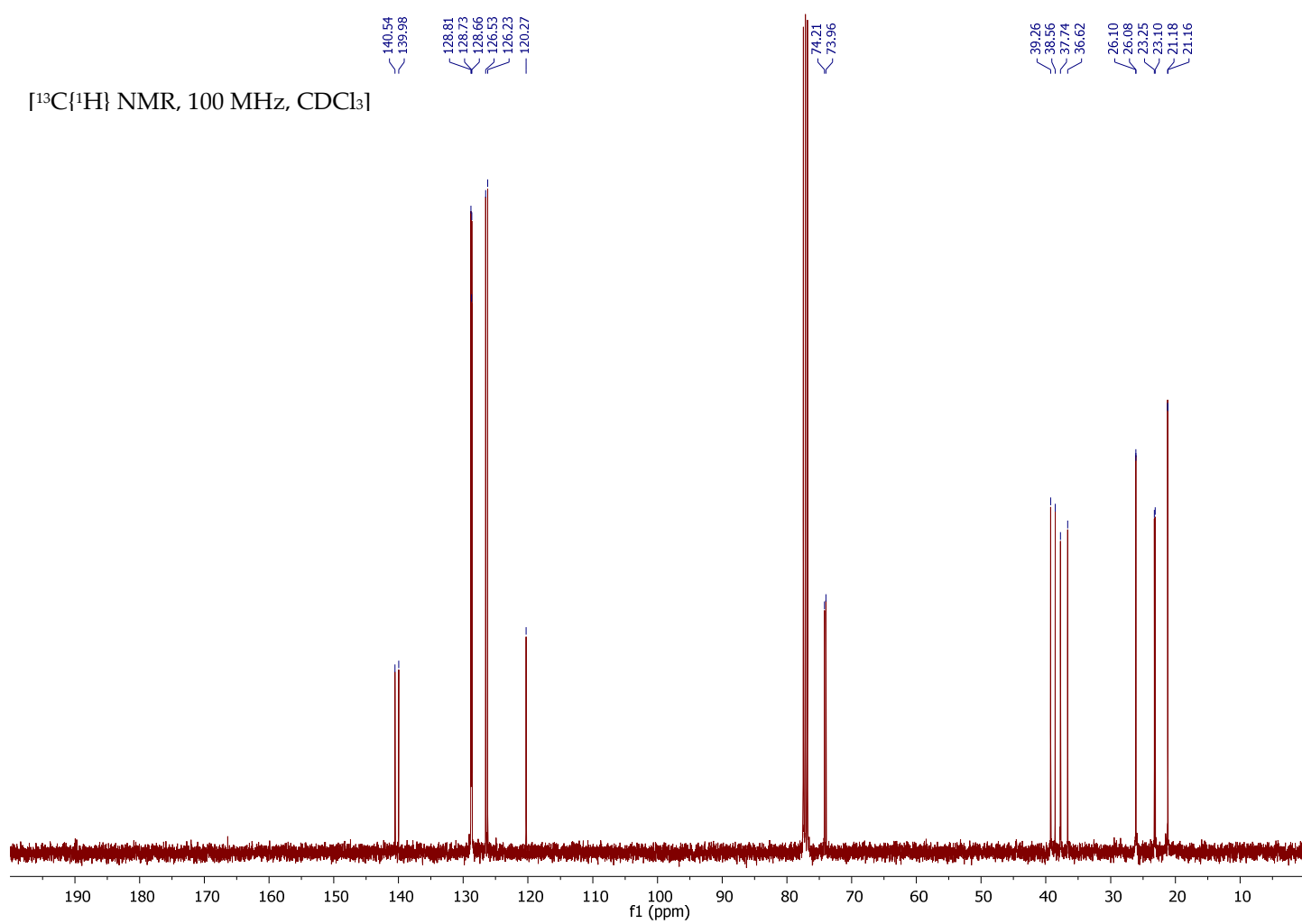
**4cga**

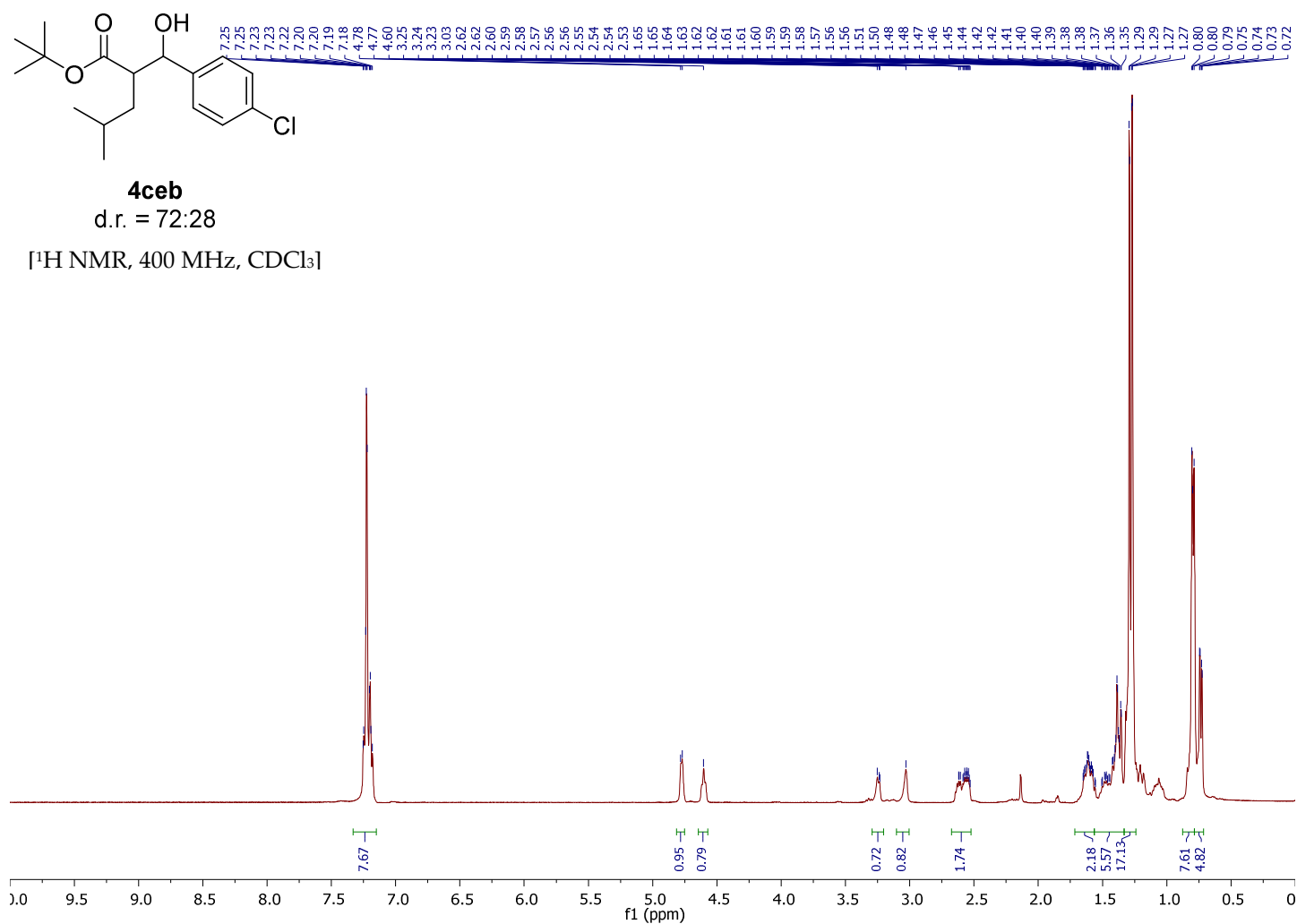
d.r. &gt; 95:5

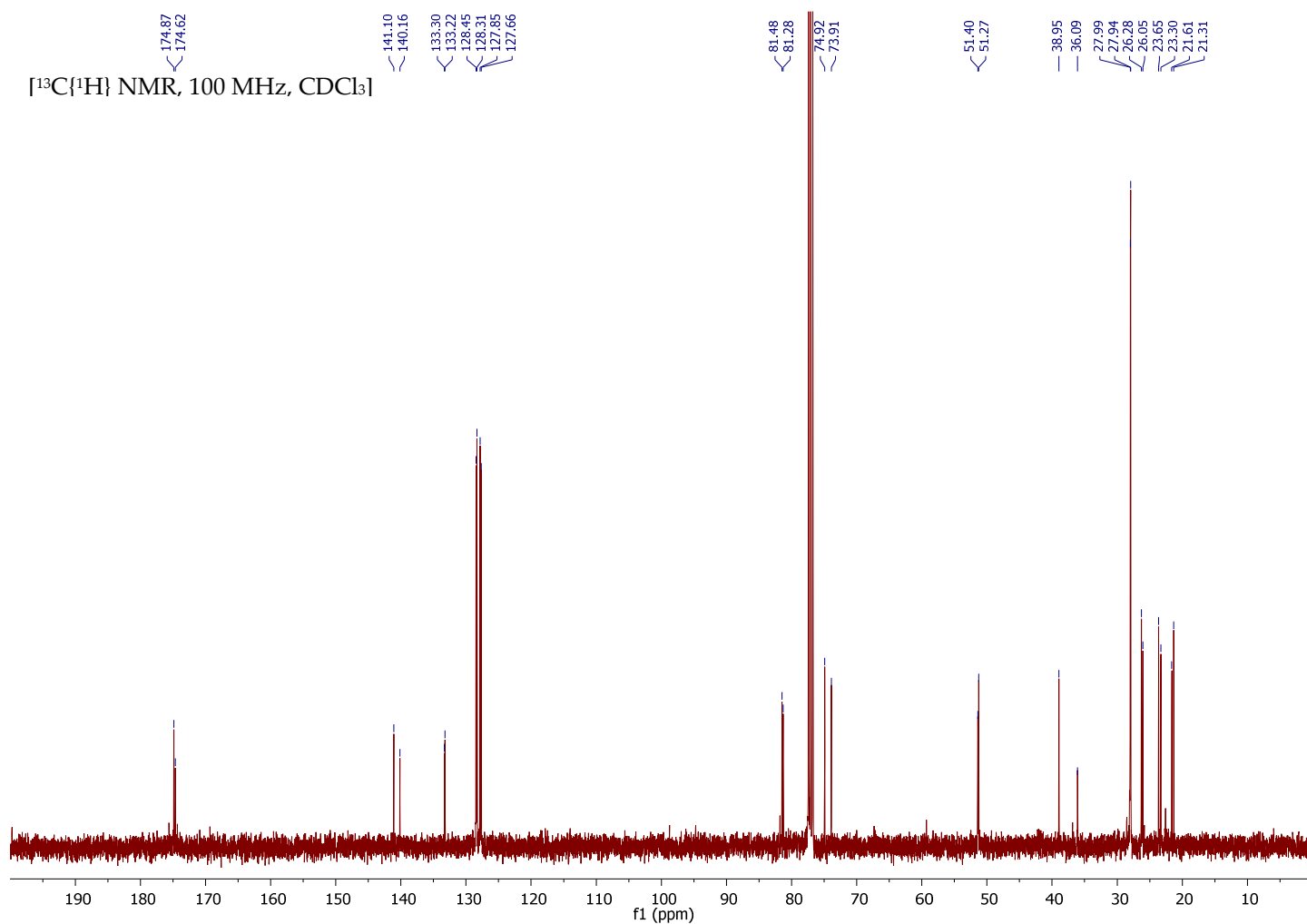
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

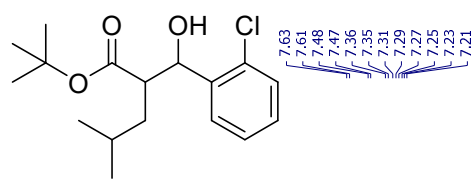




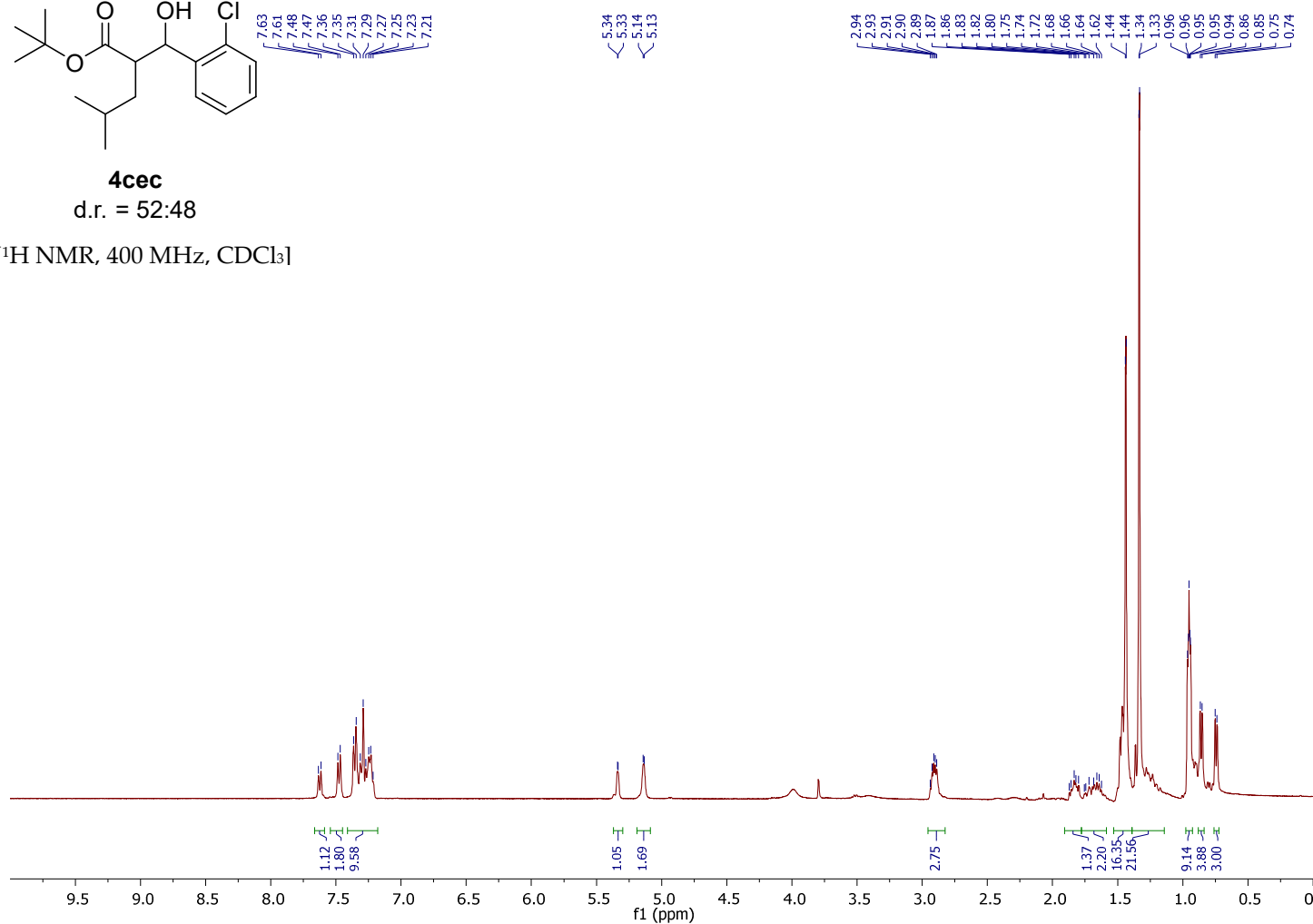


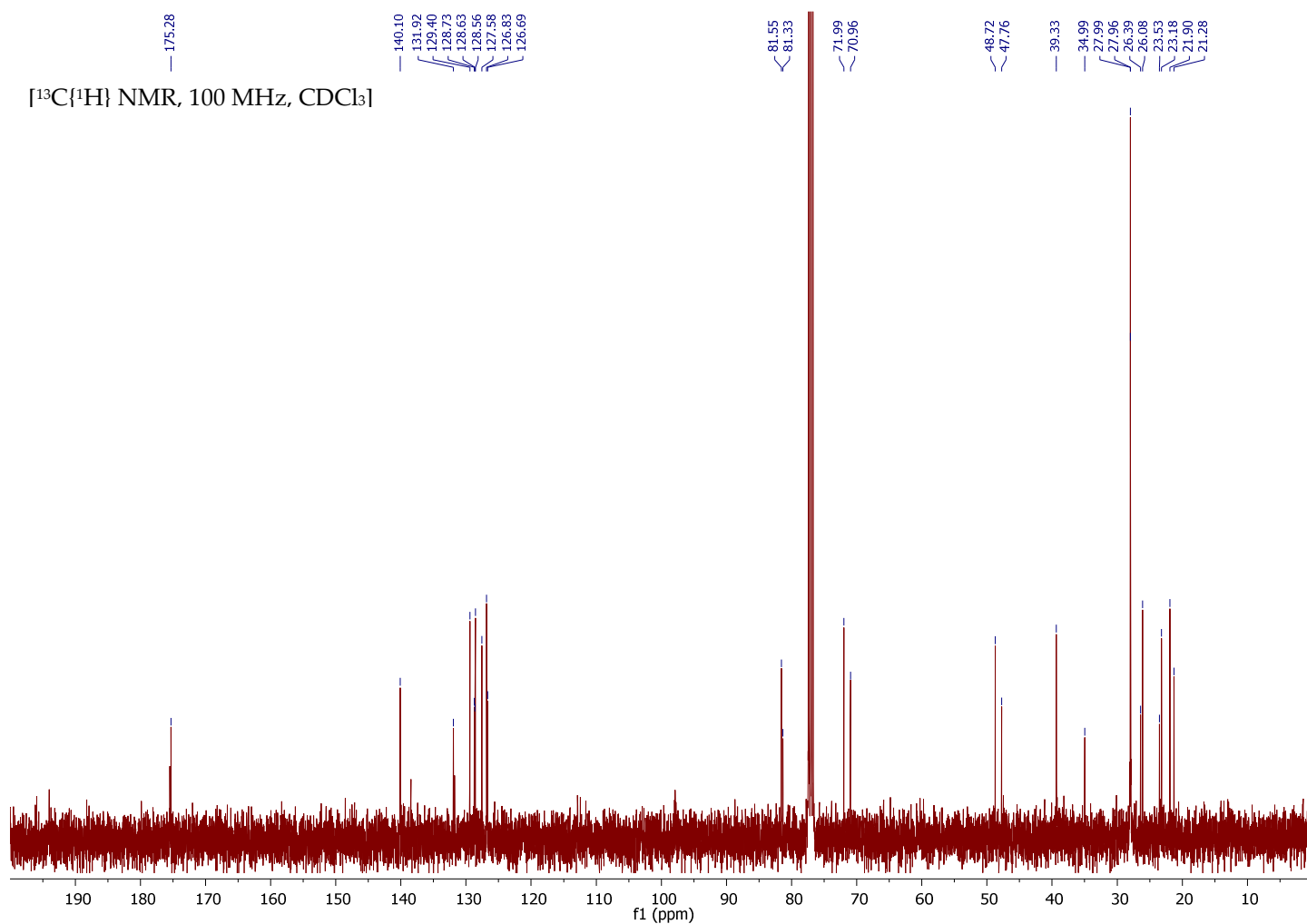


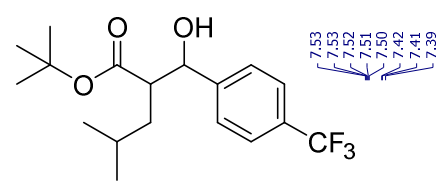


**4cec**

d.r. = 52:48

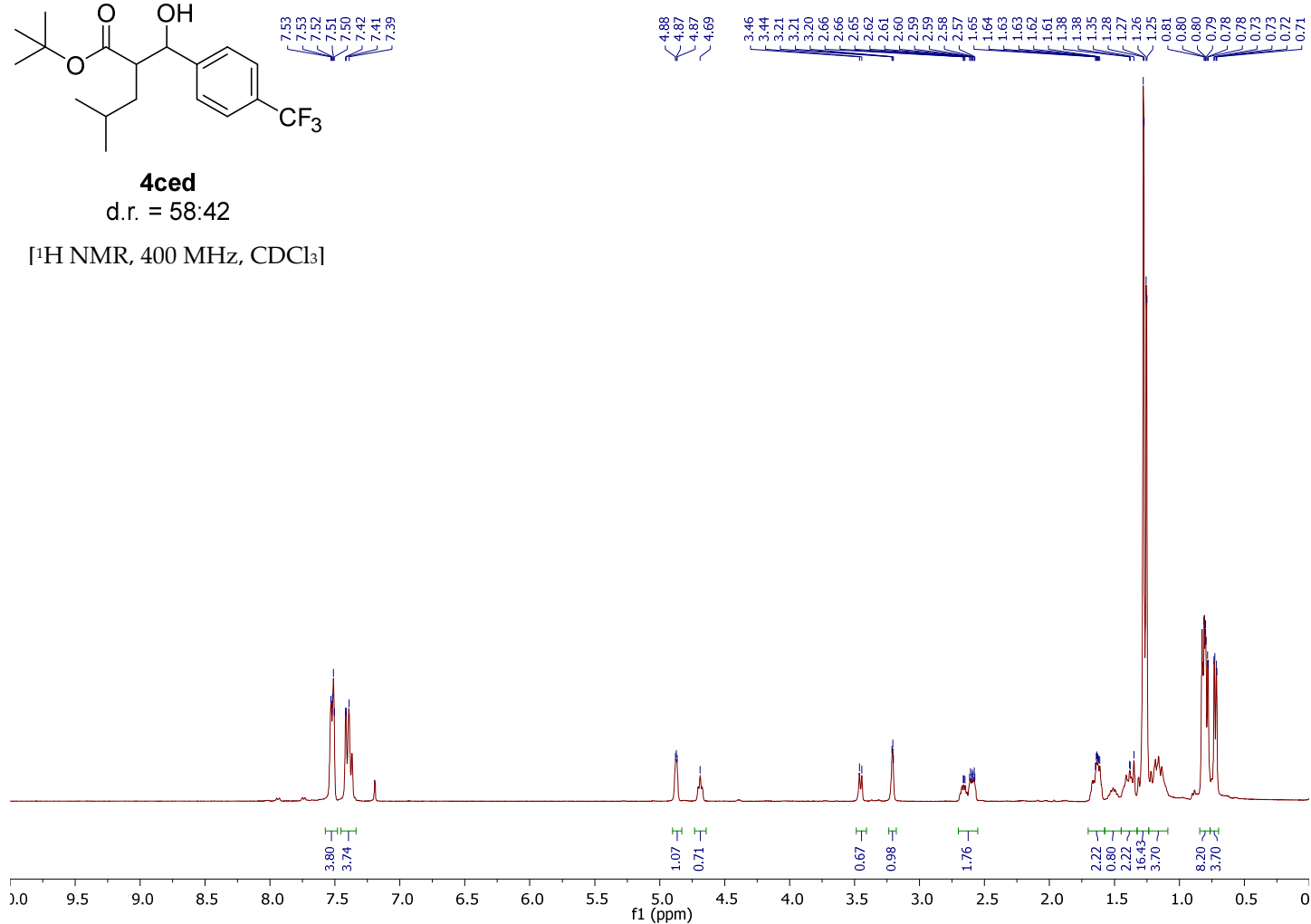
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

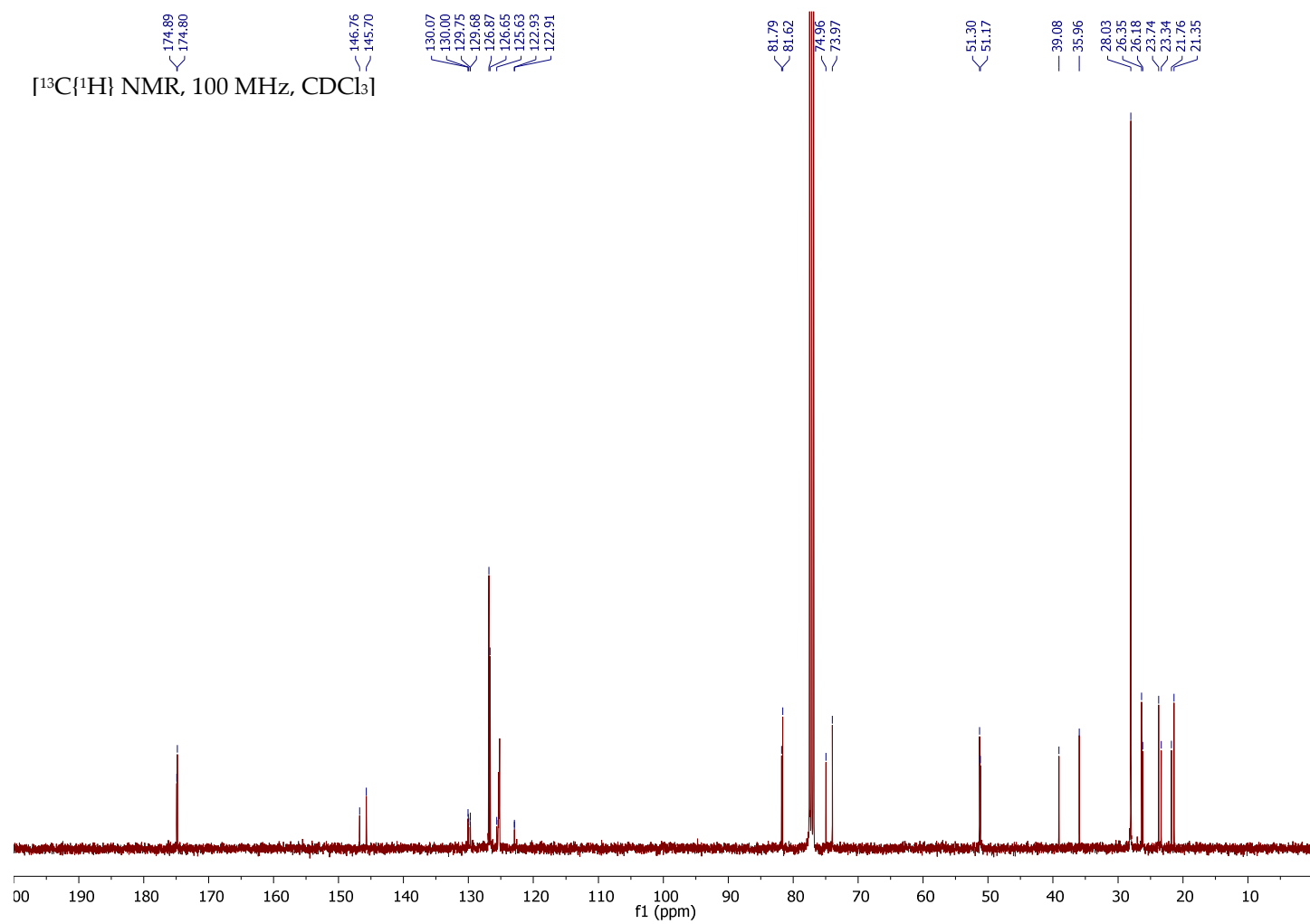


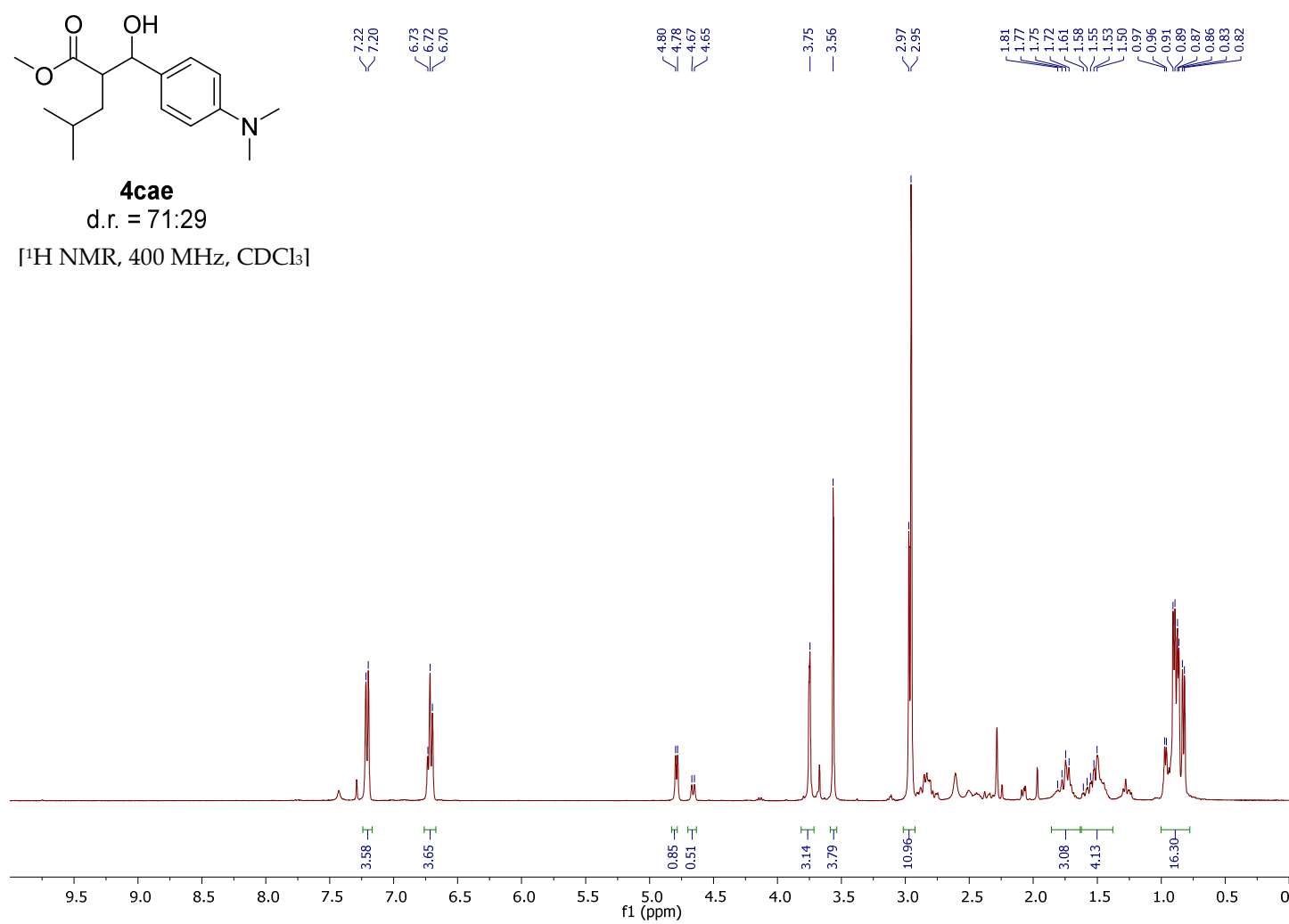


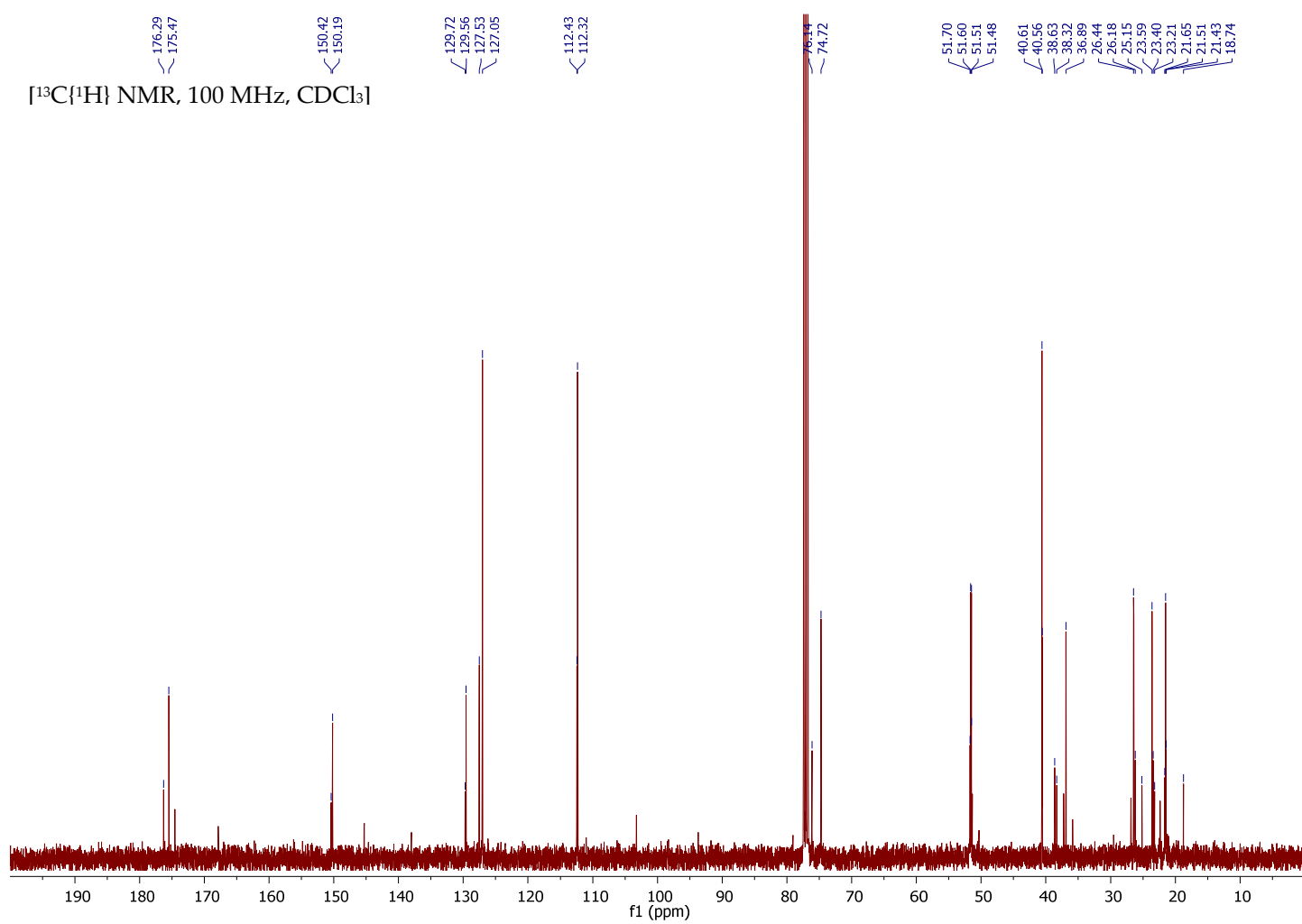
**4ced**  
d.r. = 58:42

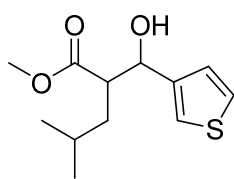
[<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>]



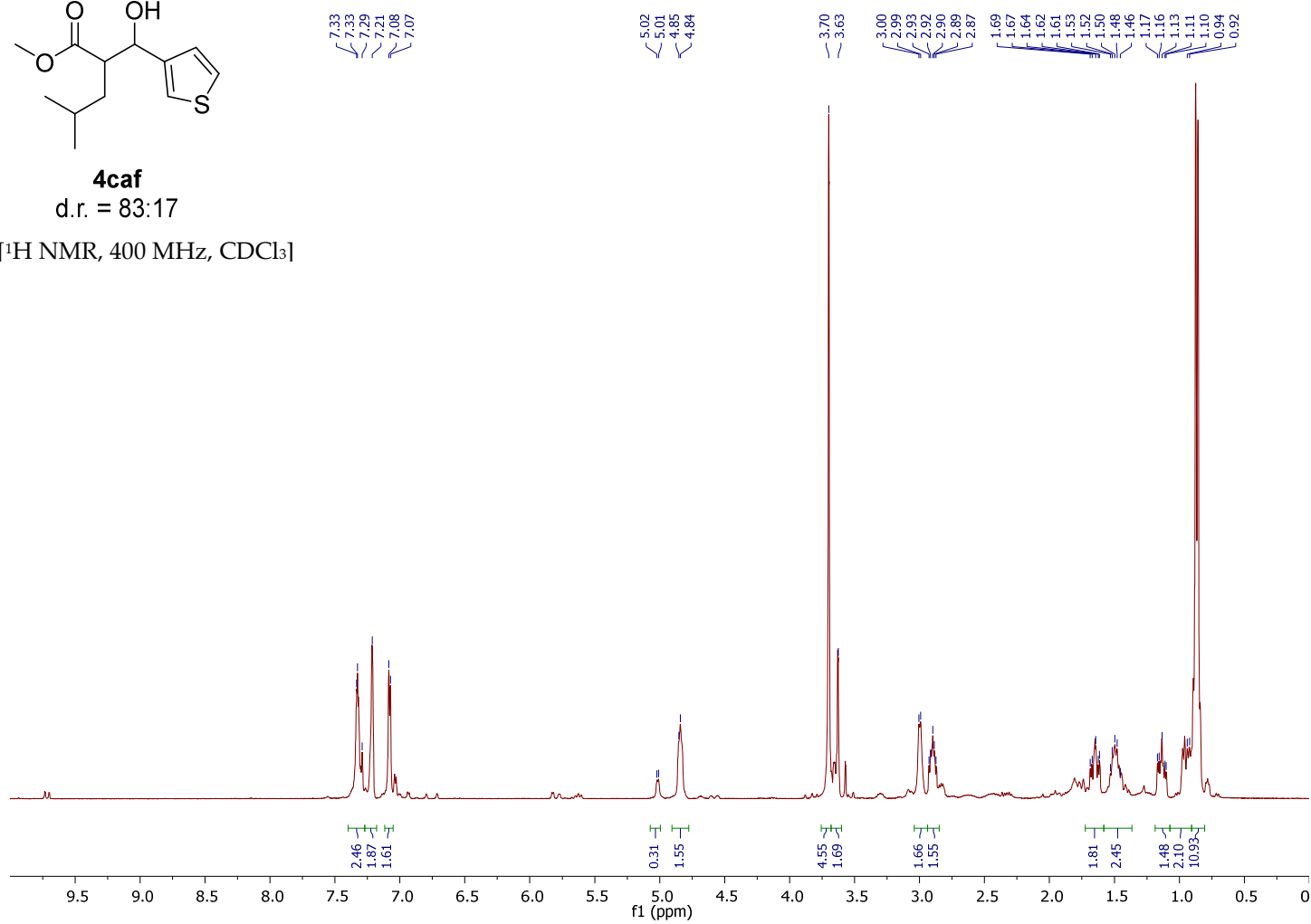


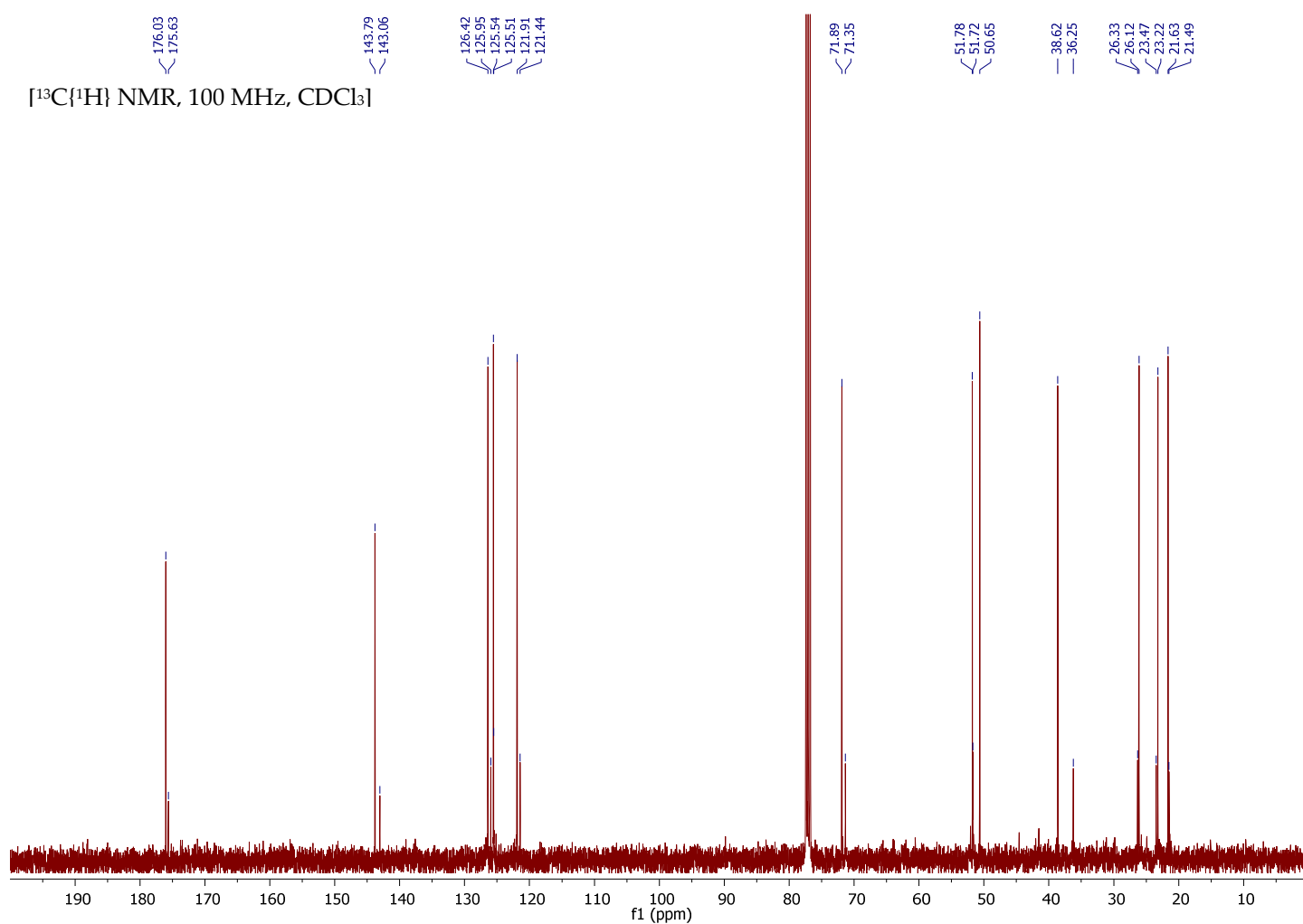


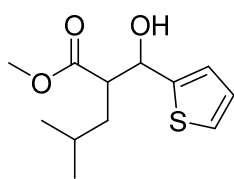


**4caf**

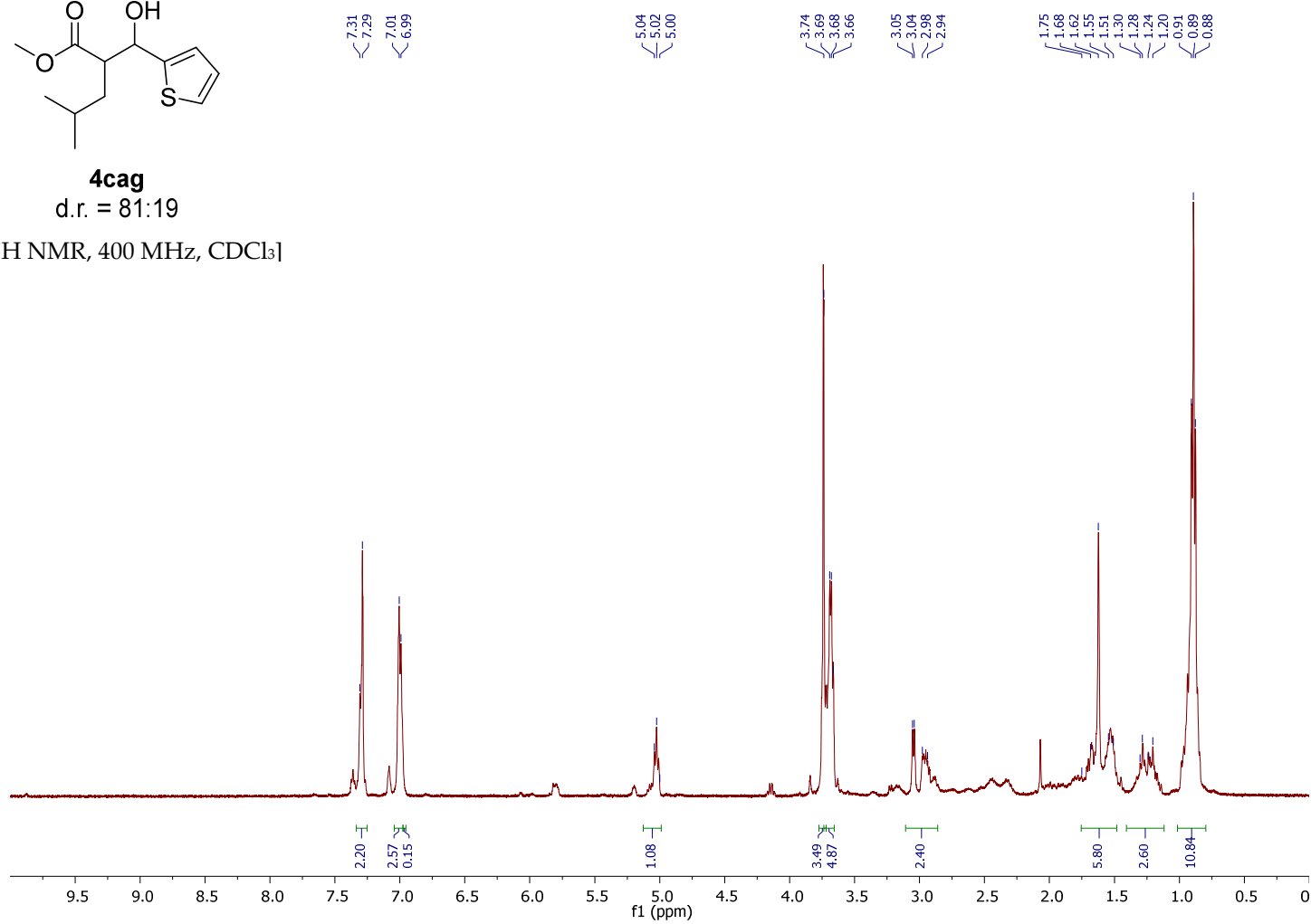
d.r. = 83:17

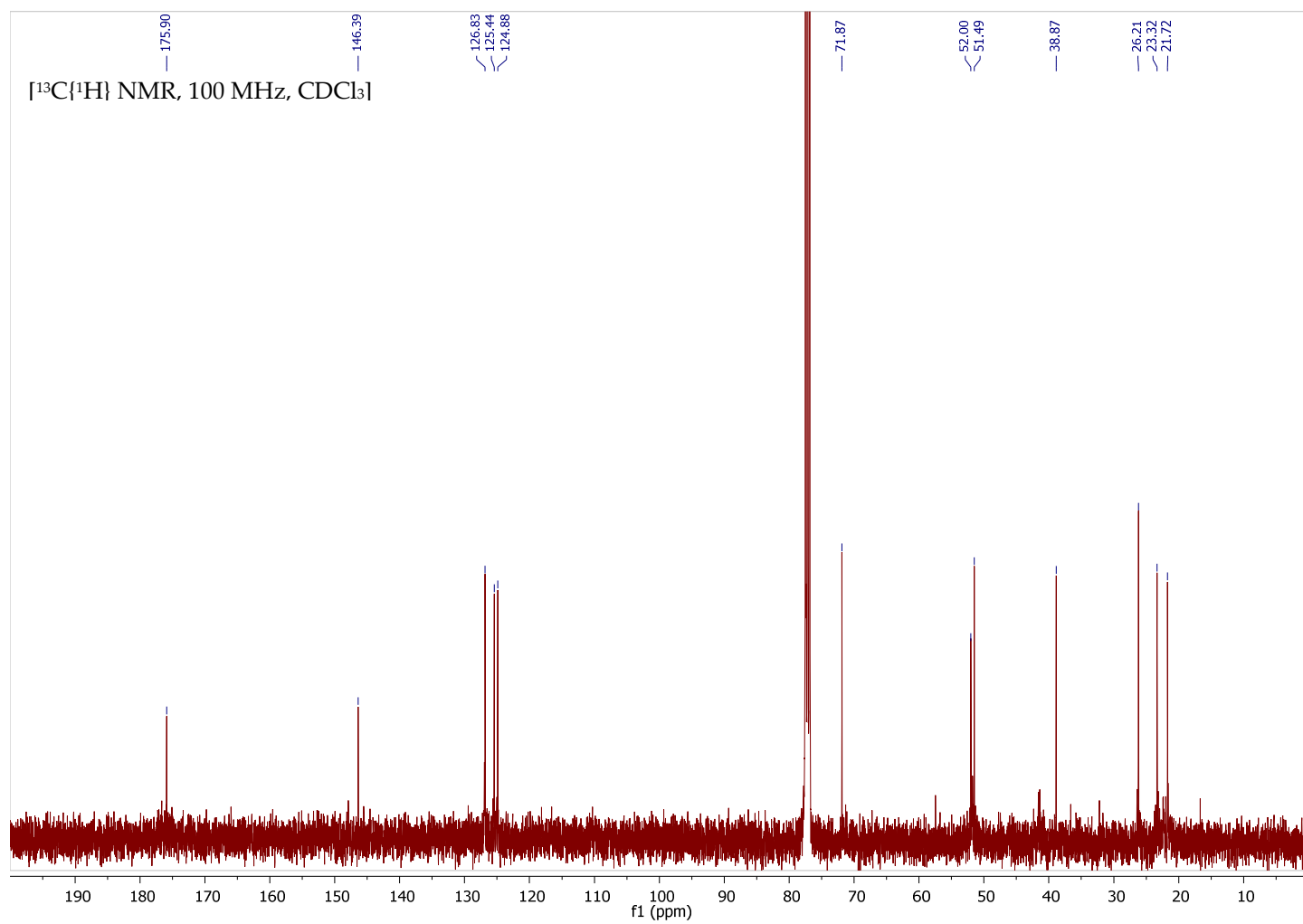
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

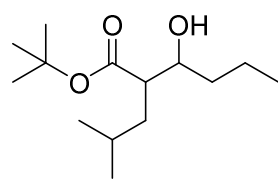


**4cag**

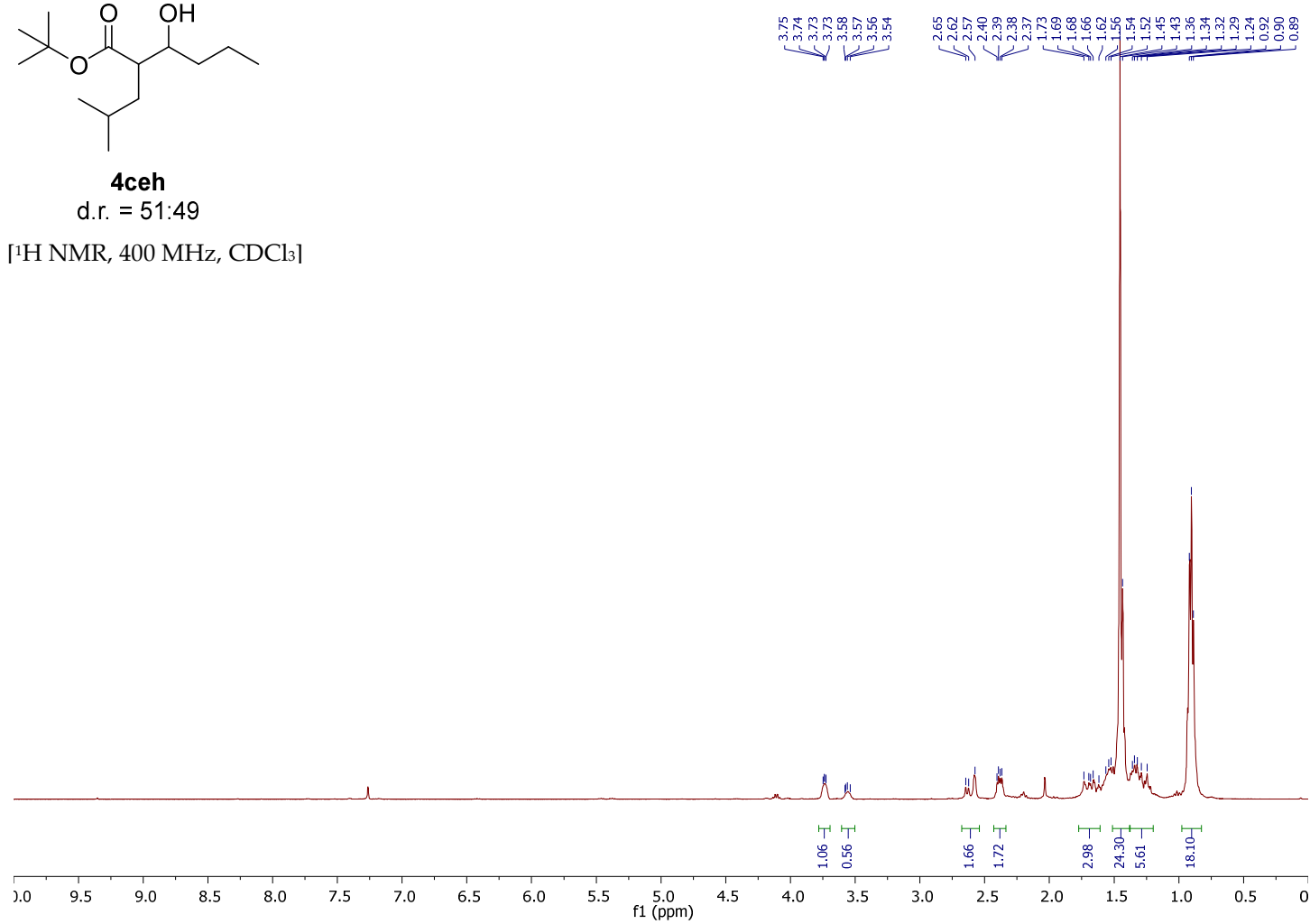
d.r. = 81:19

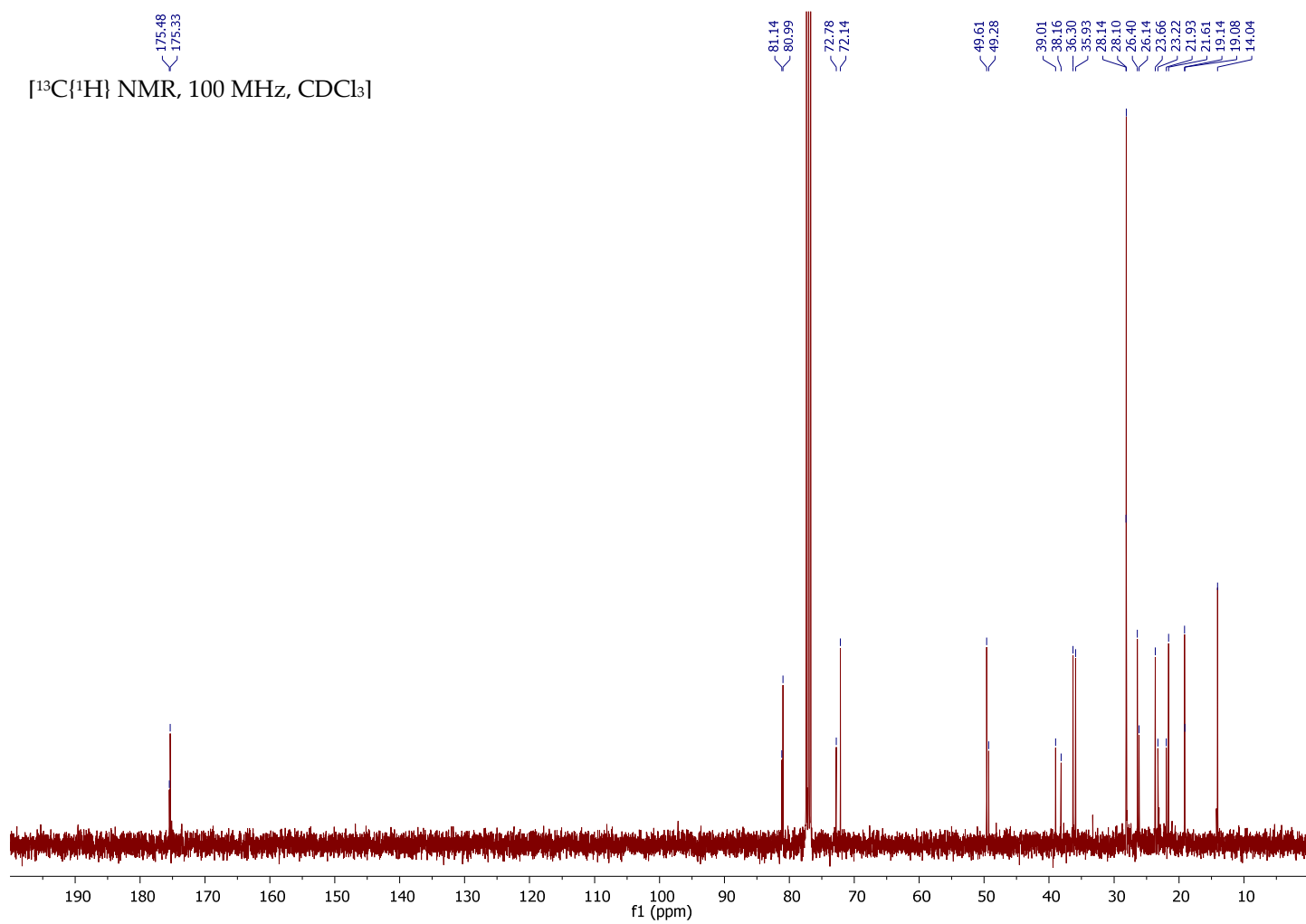
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

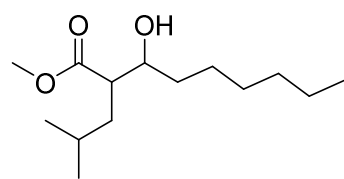


**4ceh**

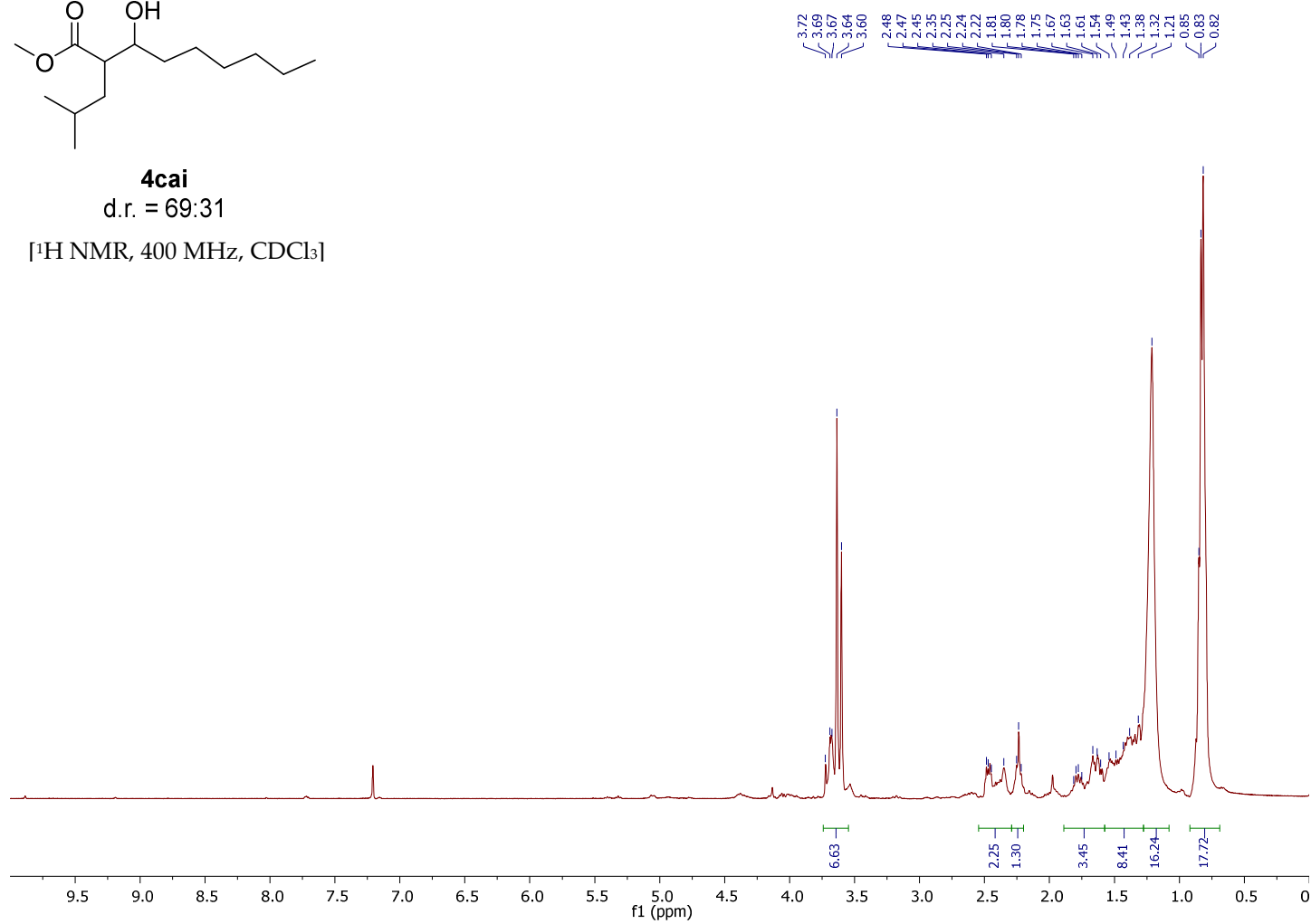
d.r. = 51:49

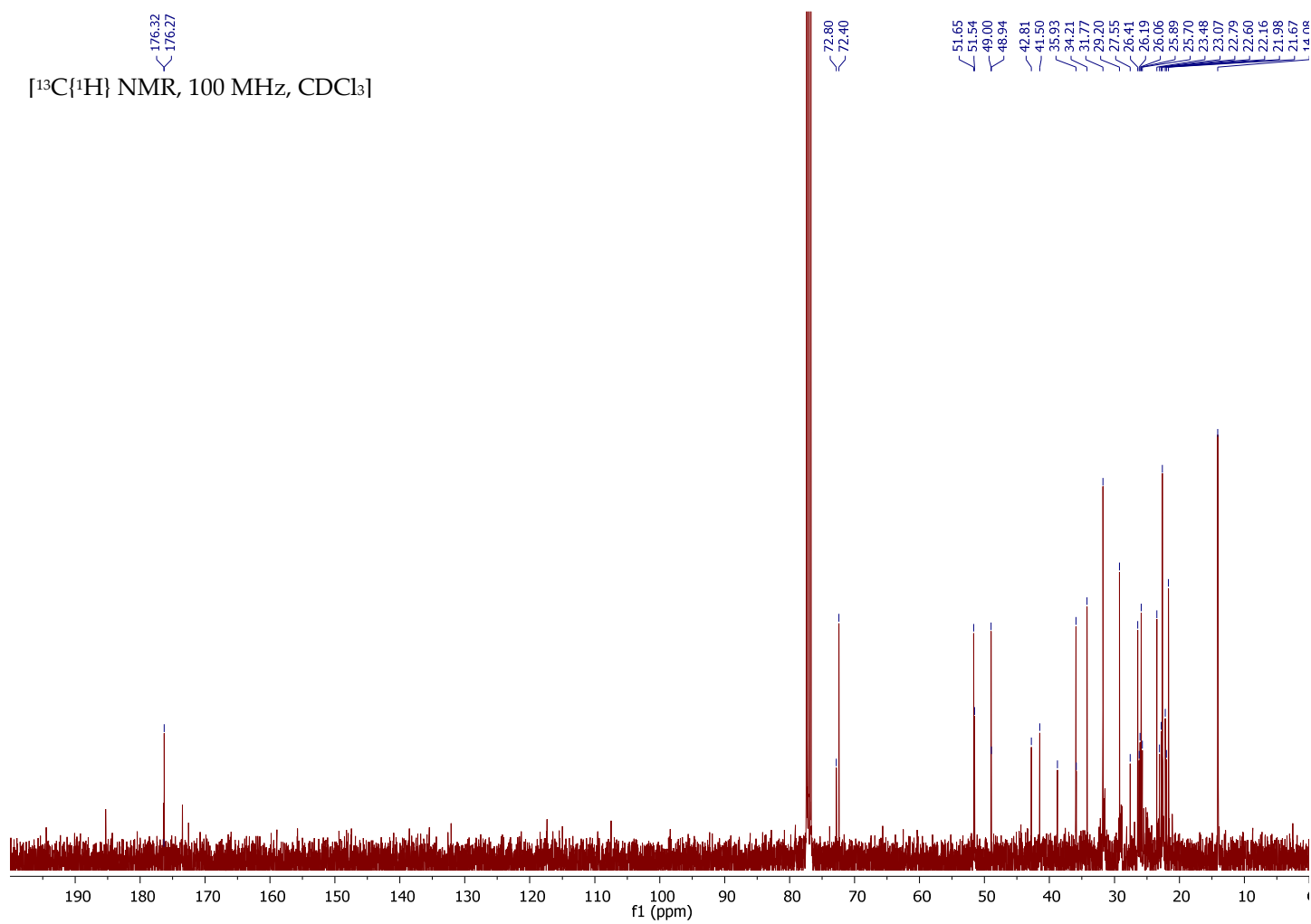
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

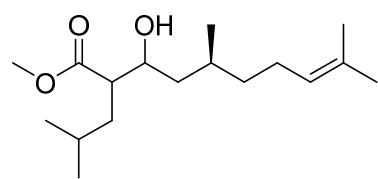


**4ca**

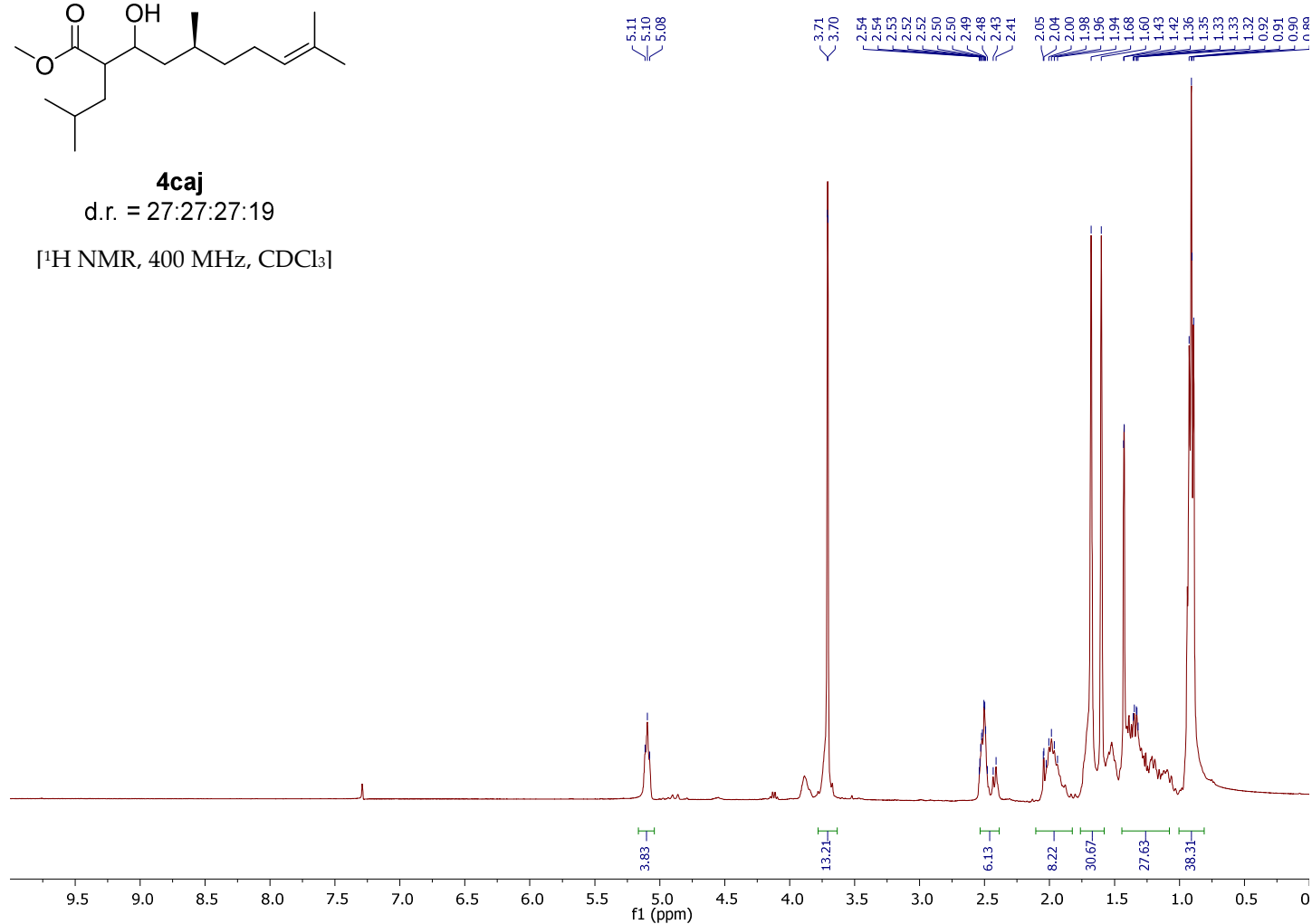
d.r. = 69:31

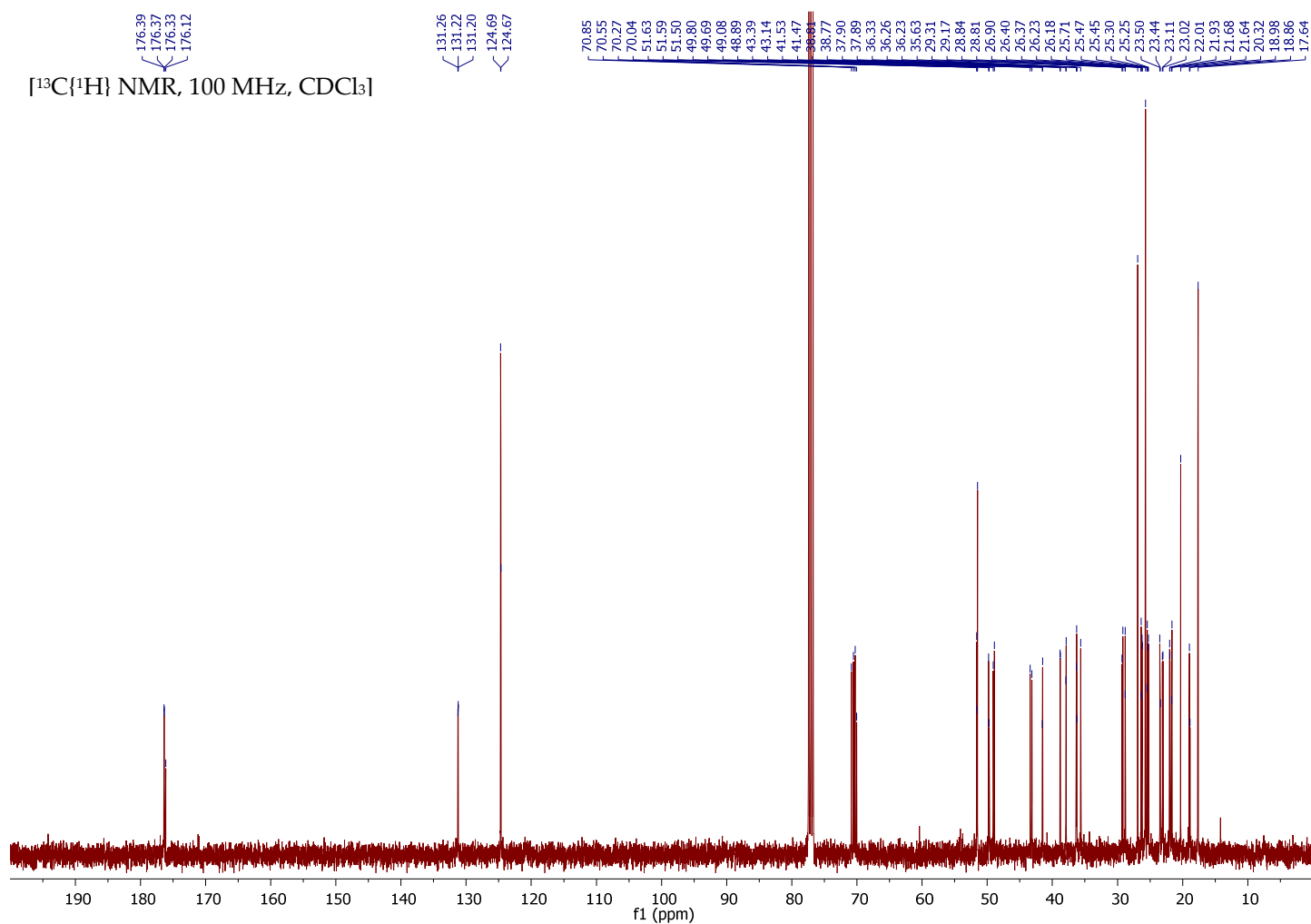
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

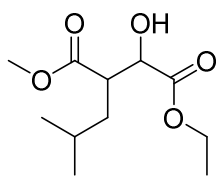


**4caj**

d.r. = 27:27:27:19

 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

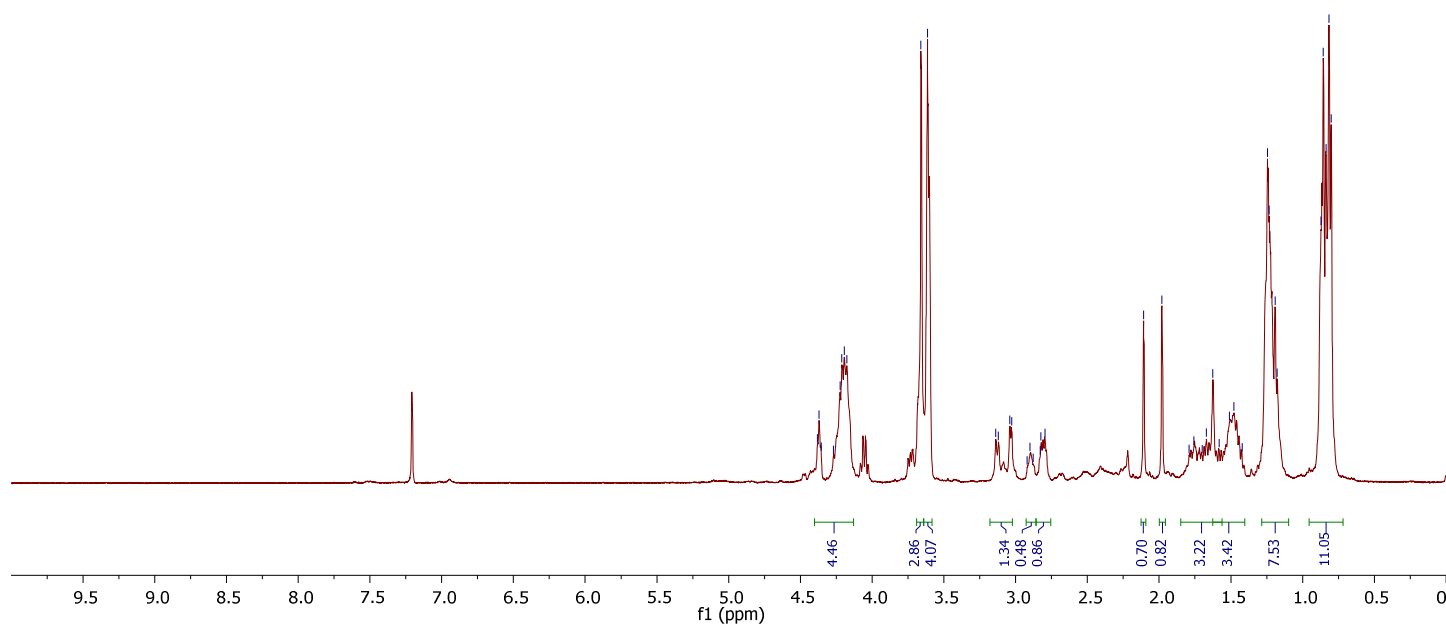


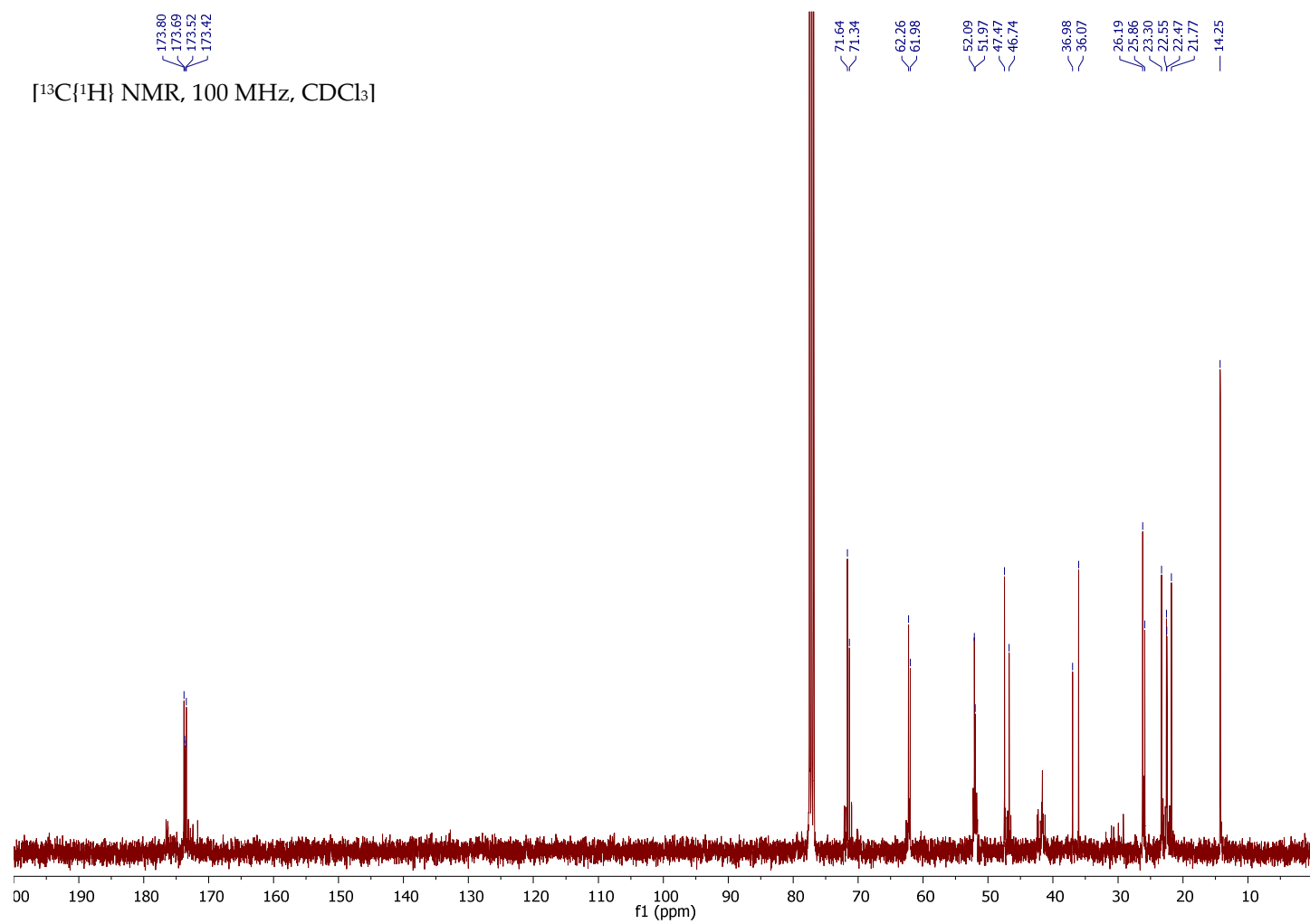
**4cak**

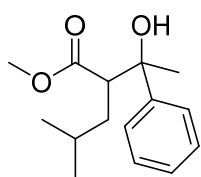
d.r. = 60:40

 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

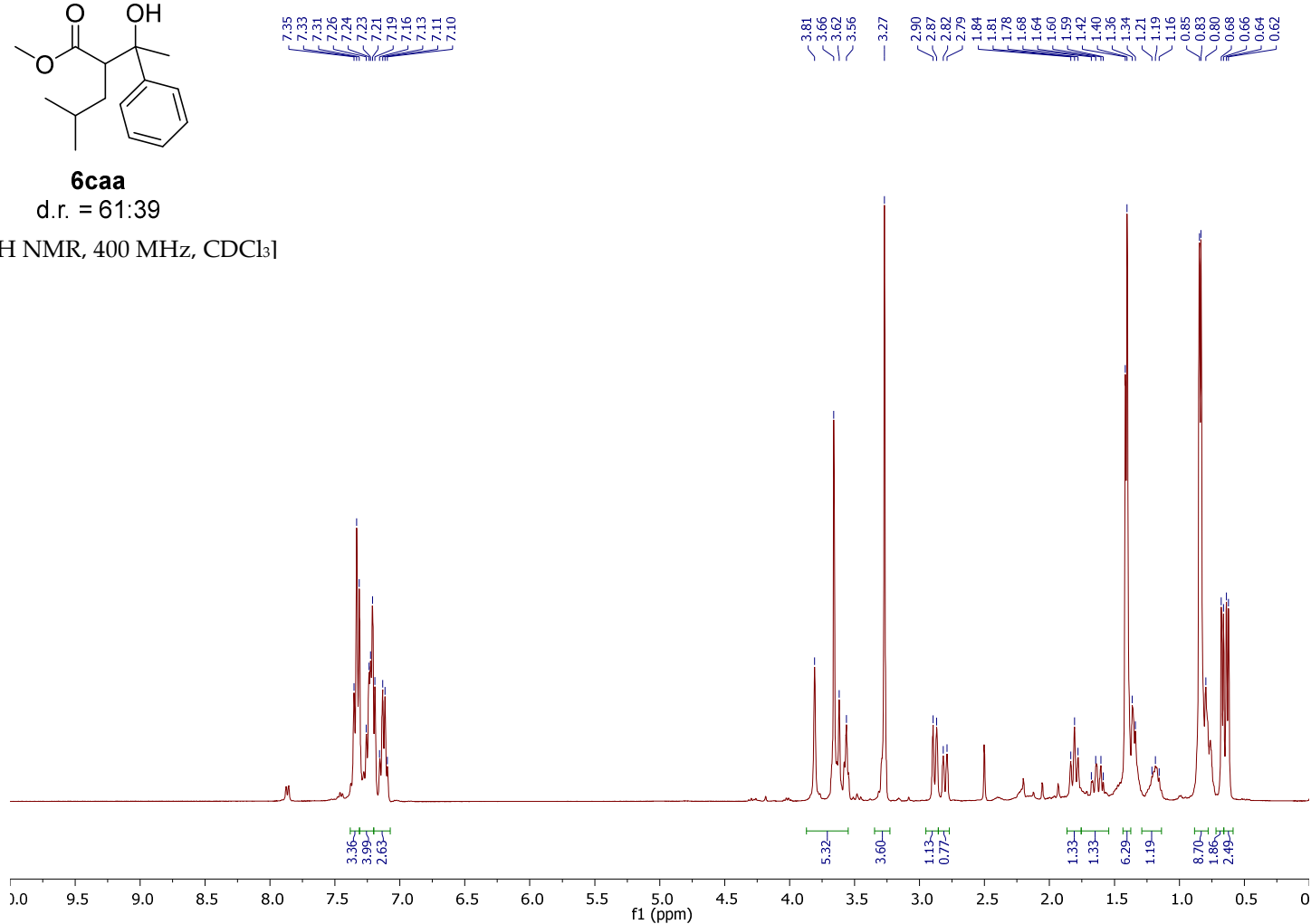
4.38  
4.37  
4.35  
4.27  
4.22  
4.21  
4.19  
4.18  
3.66  
3.64  
3.14  
3.12  
3.04  
3.03  
2.92  
2.90  
2.88  
2.83  
2.82  
2.79  
2.11  
1.98  
1.79  
1.76  
1.70  
1.67  
1.63  
1.58  
1.51  
1.48  
1.42  
1.25  
1.23  
1.19  
1.18  
0.87  
0.86  
0.84  
0.82  
0.80

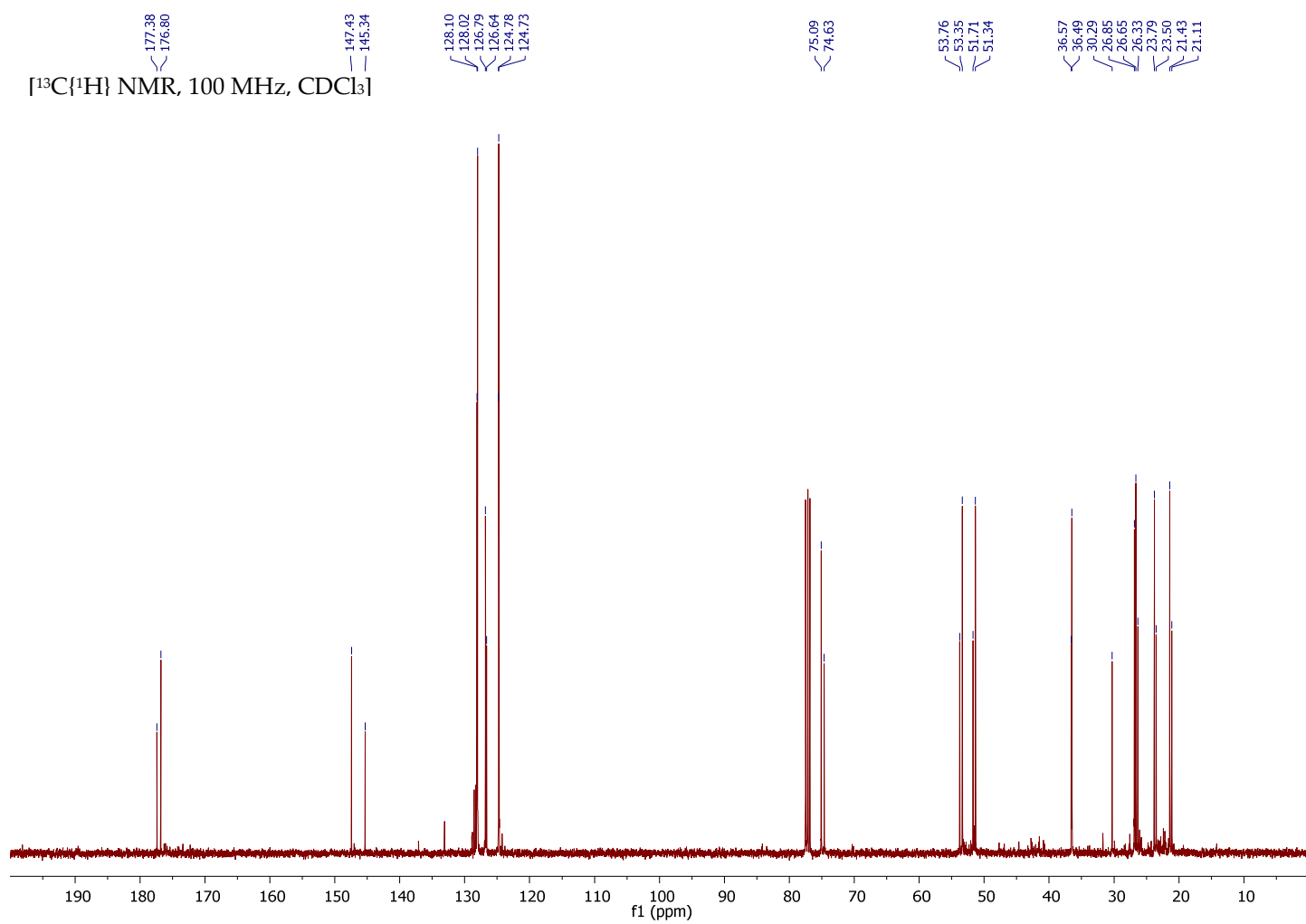


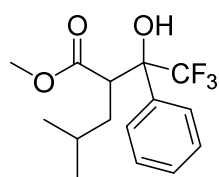


**6caa**

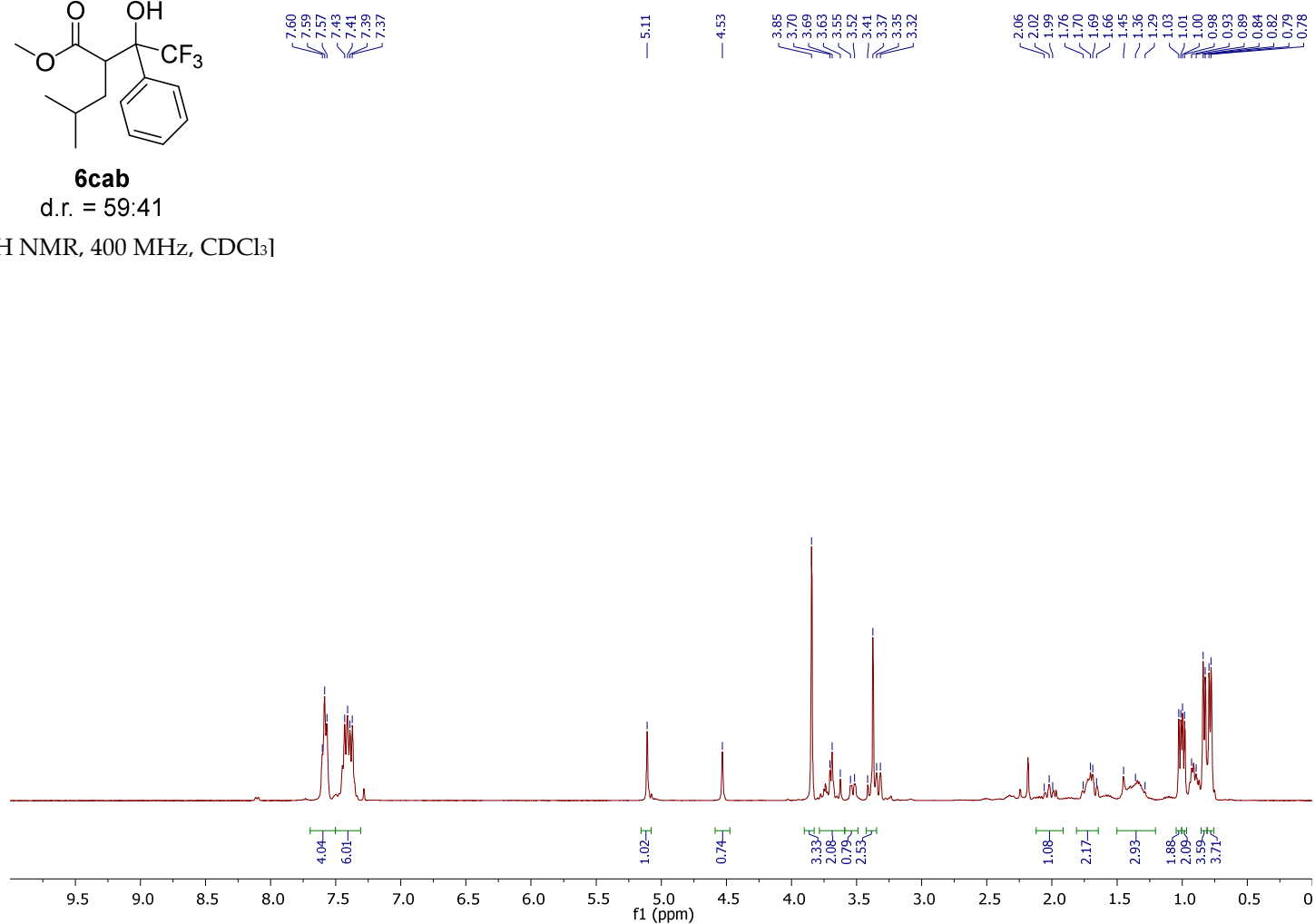
d.r. = 61:39

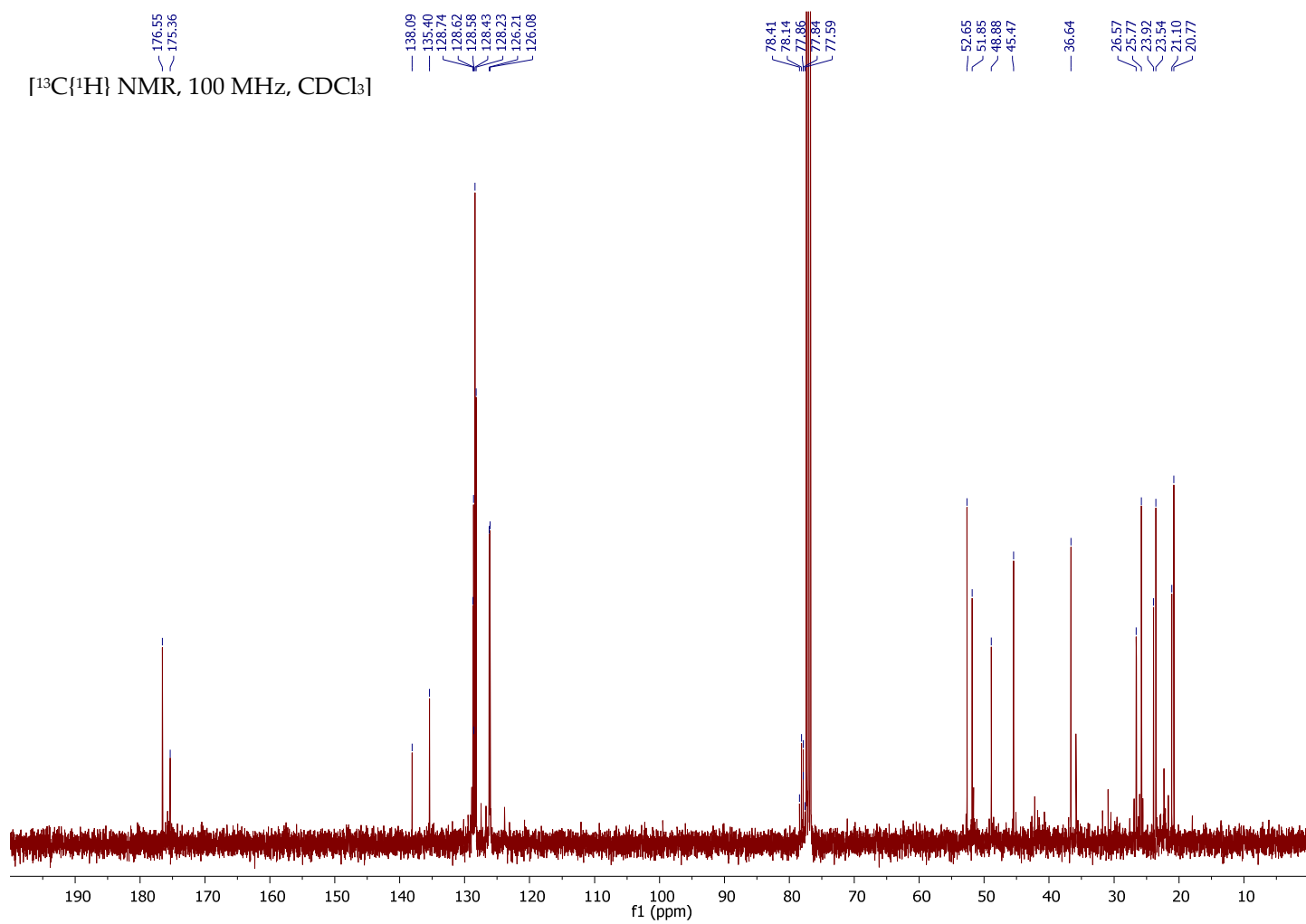
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

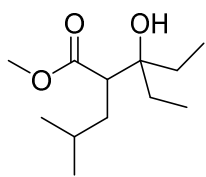


**6cab**

d.r. = 59:41

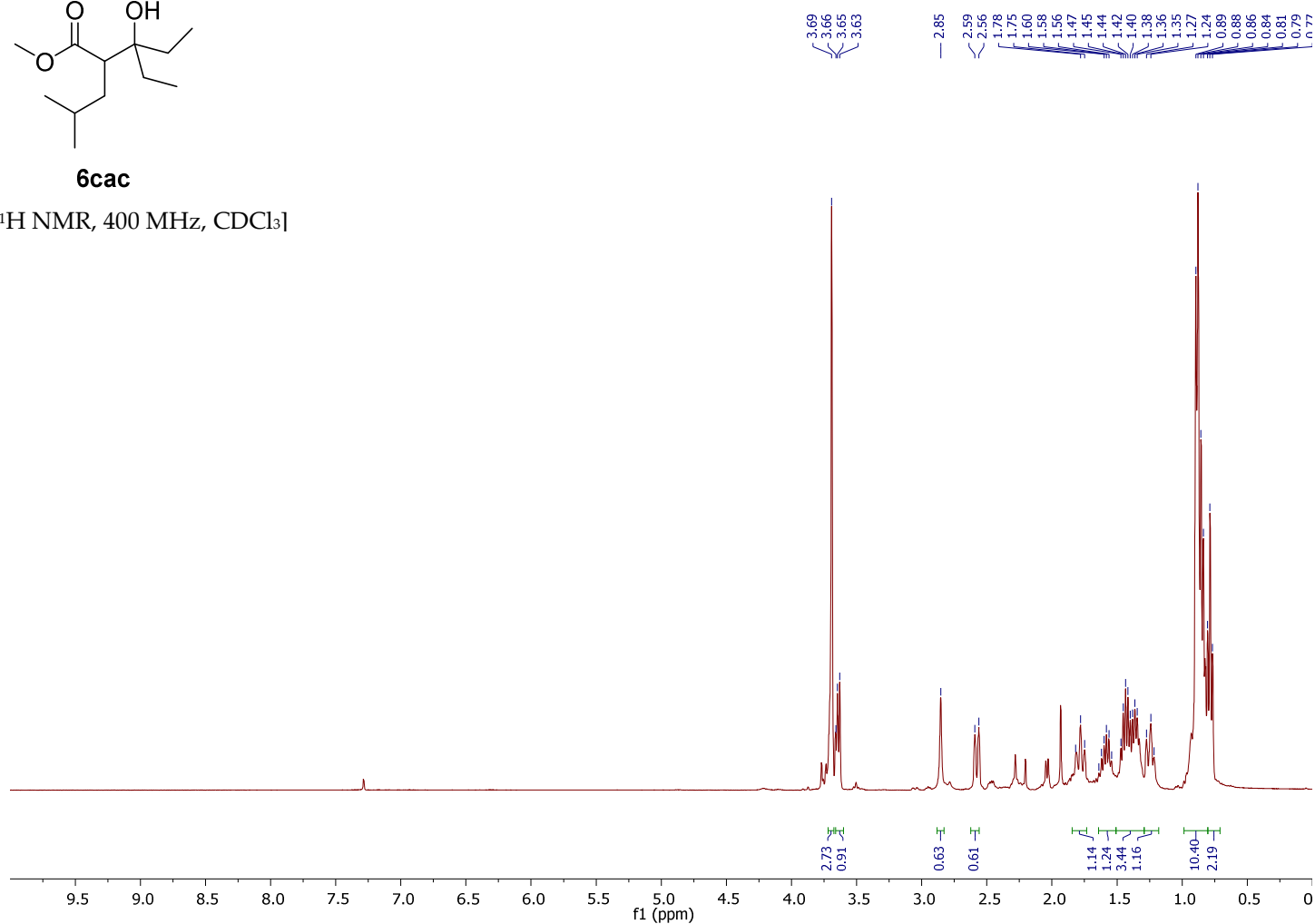
<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>

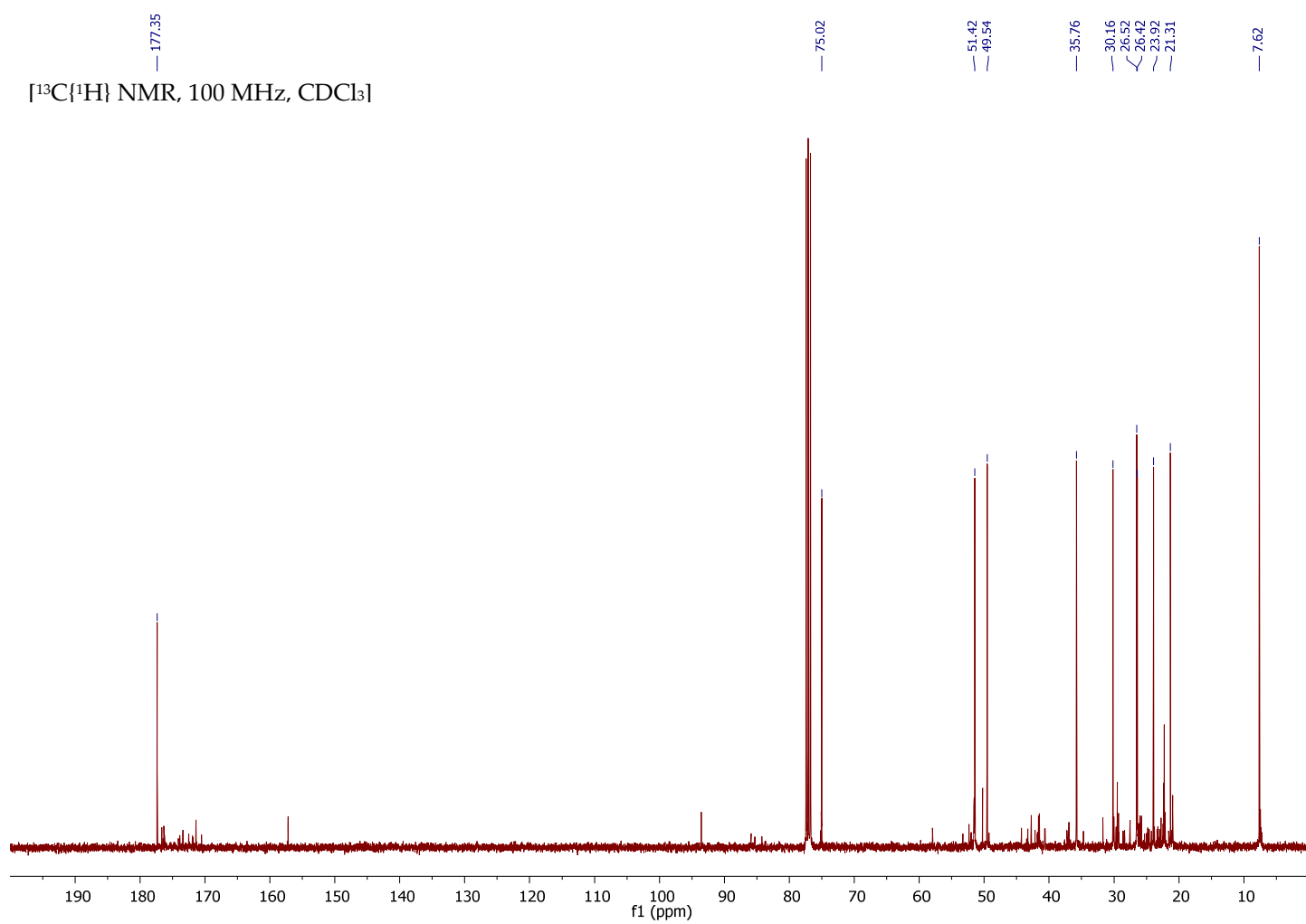


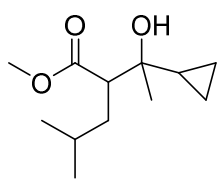


**6cac**

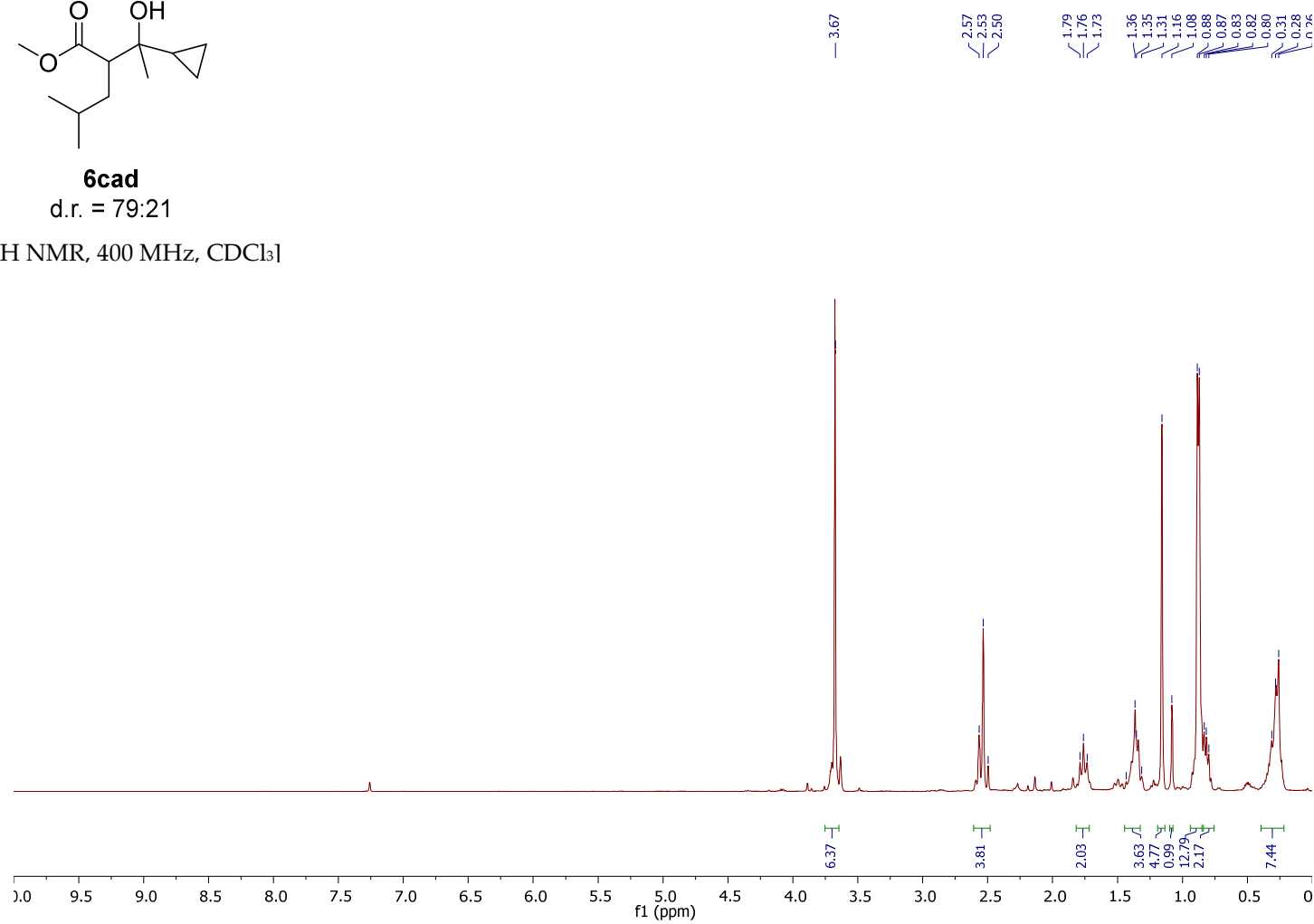
[<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>]

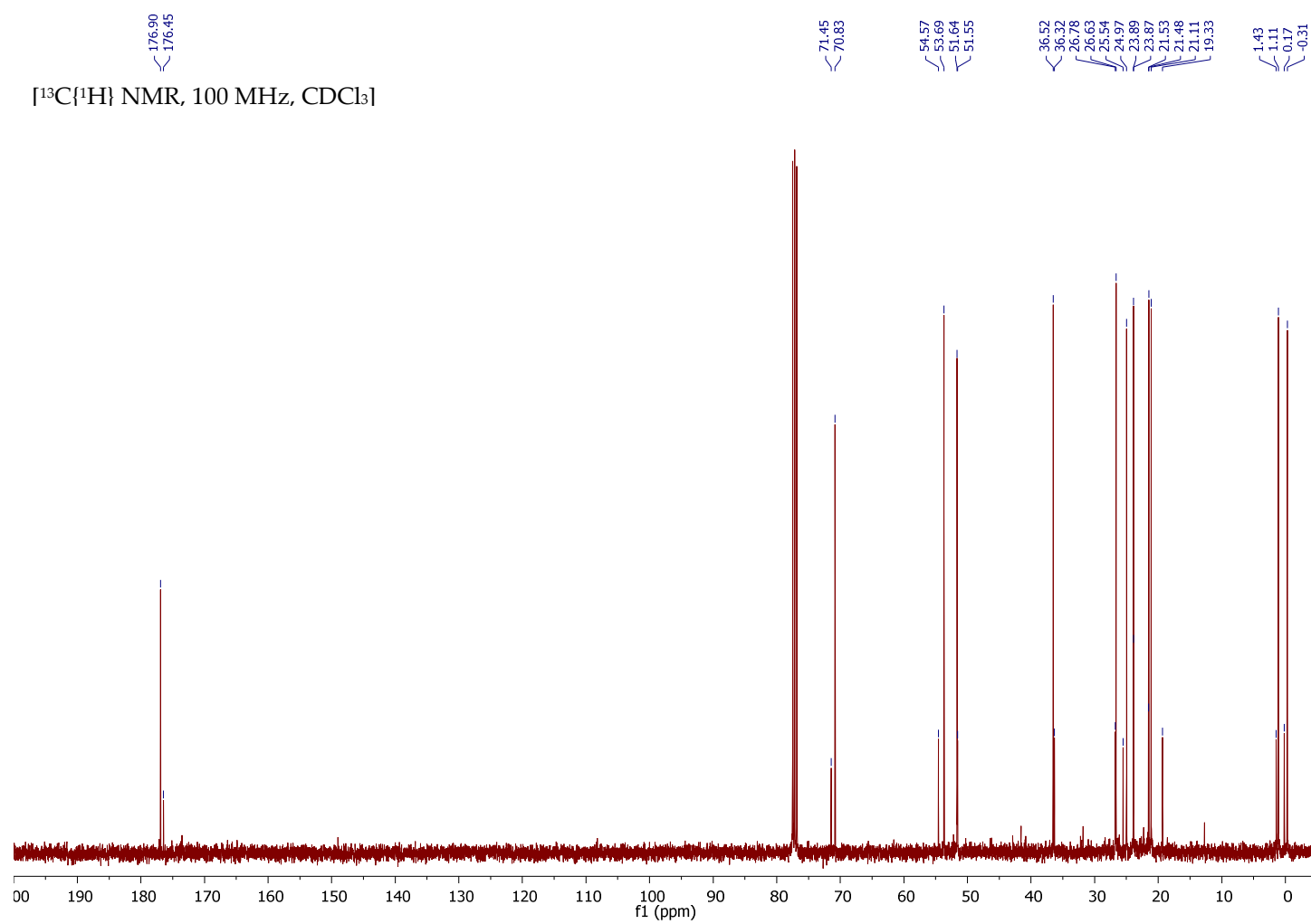


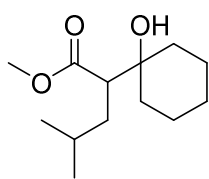
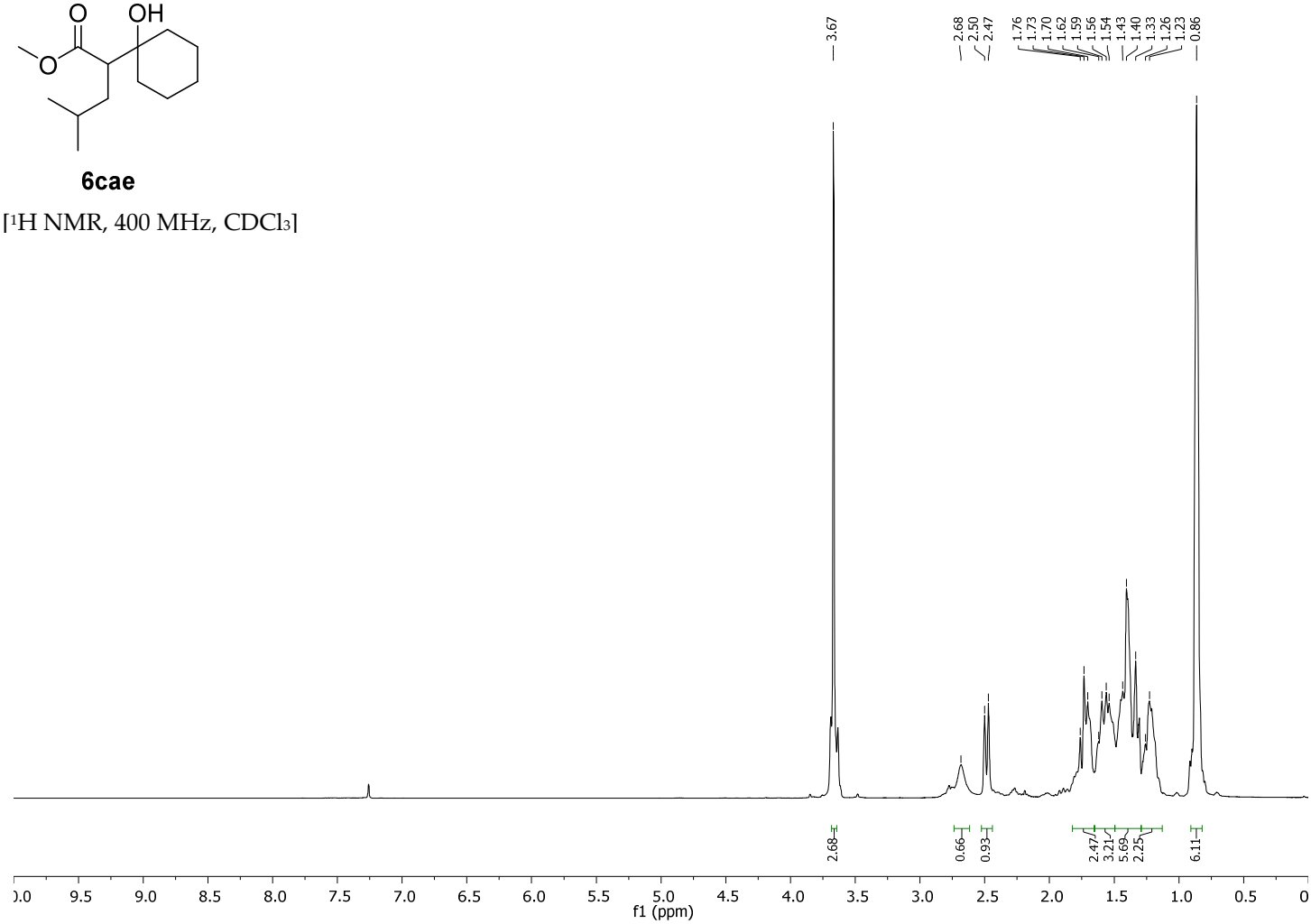


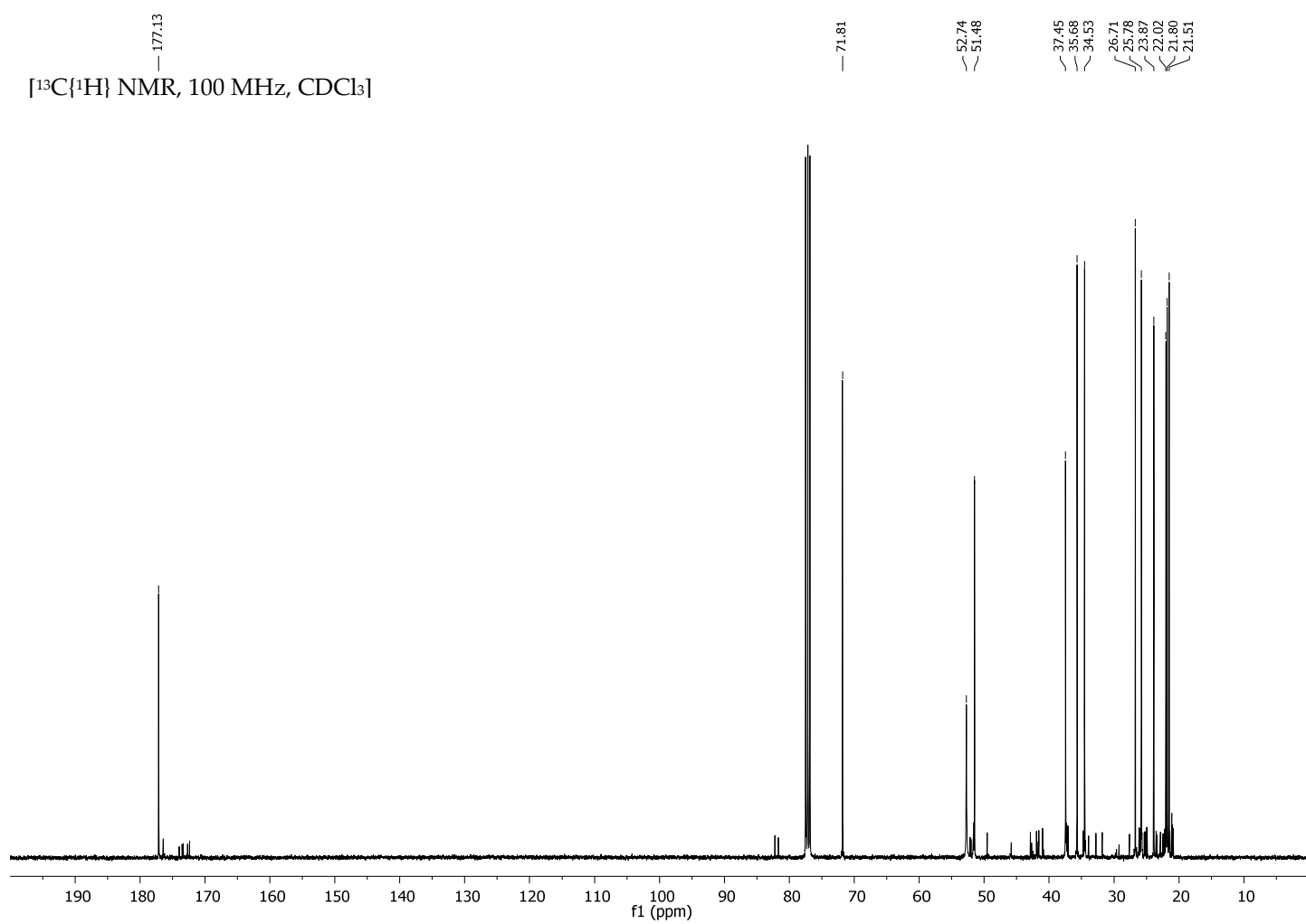
**6cad**

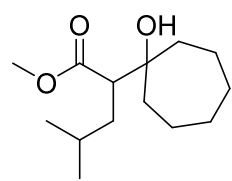
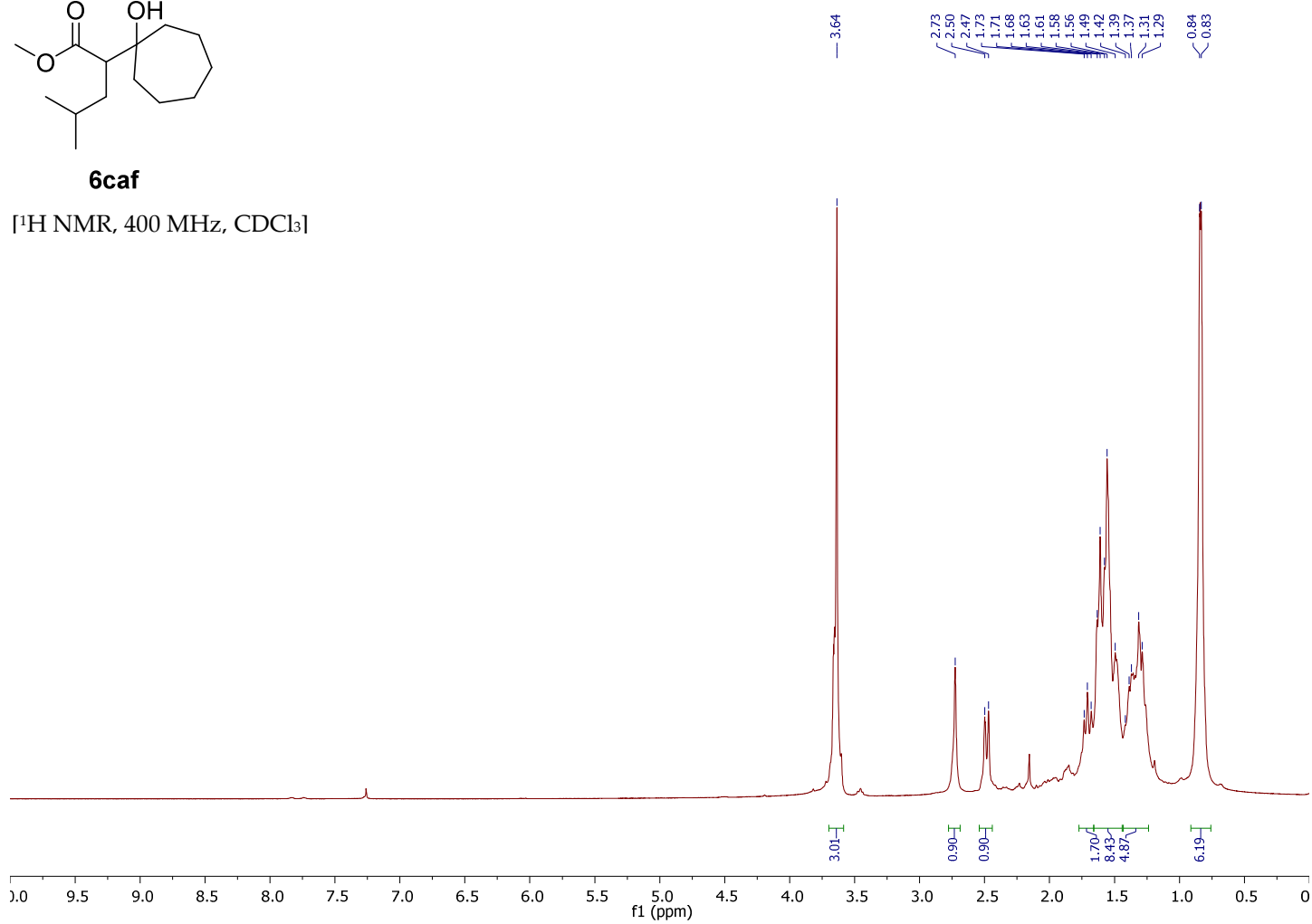
d.r. = 79:21

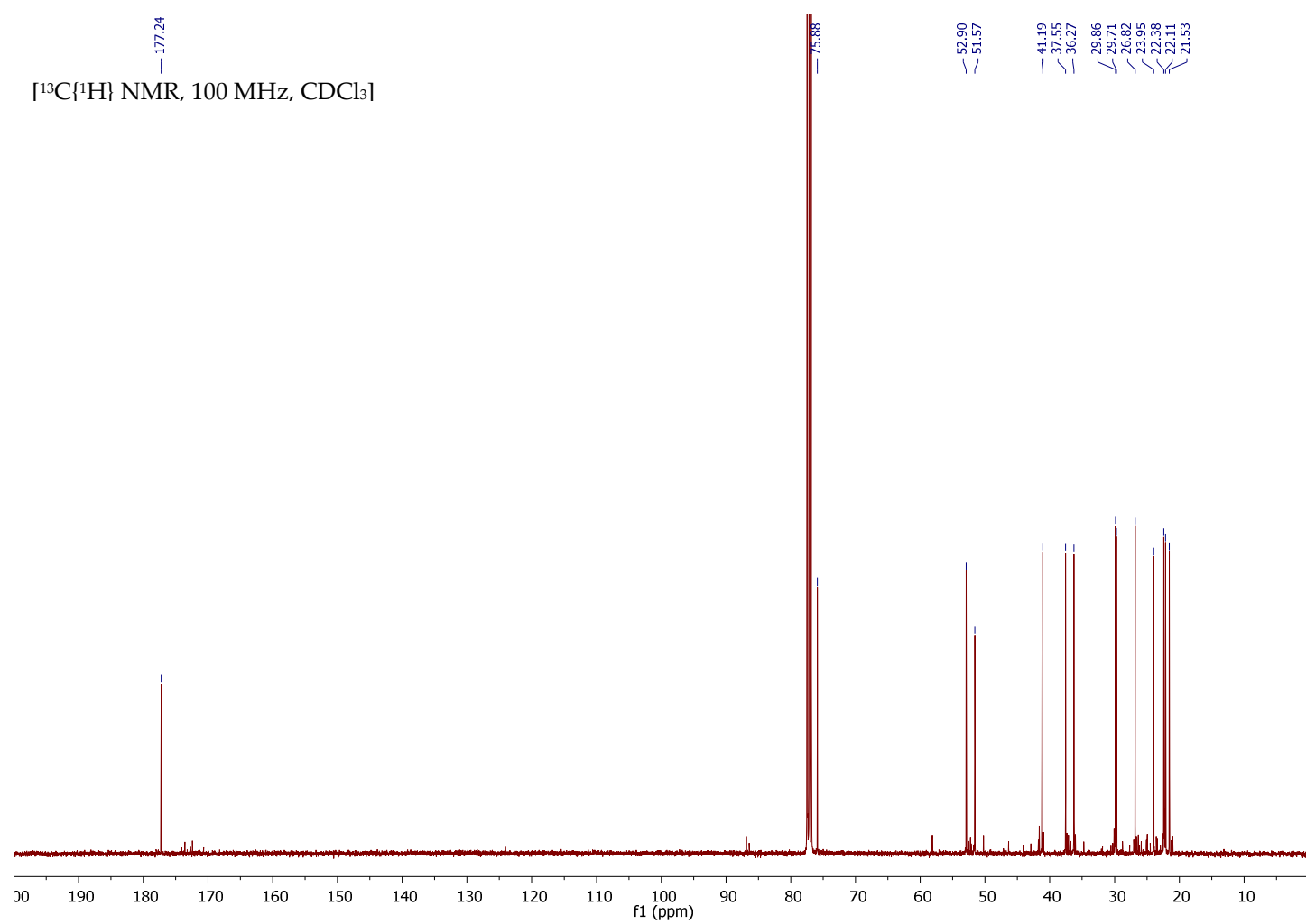
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

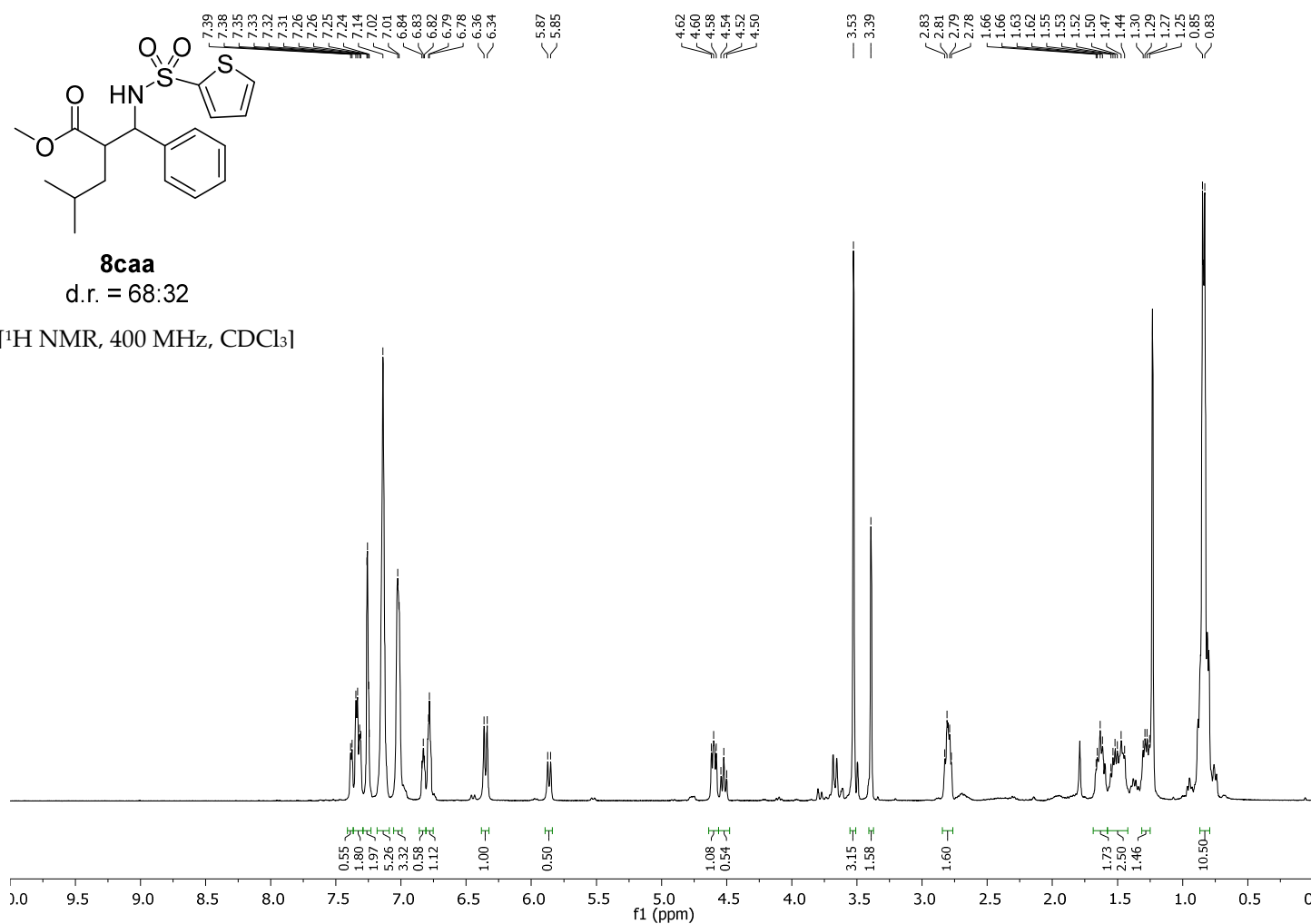


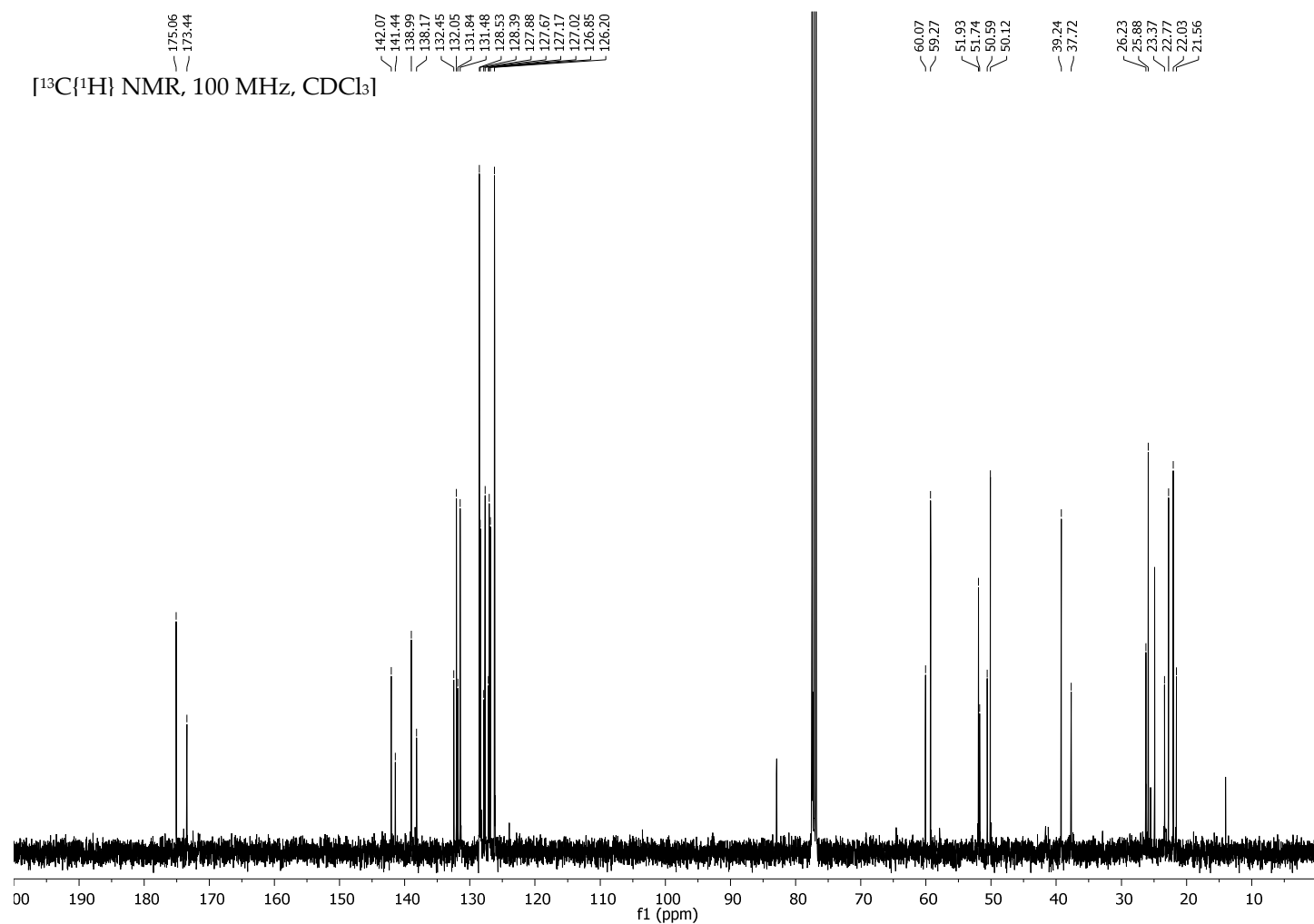
**6cae** $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

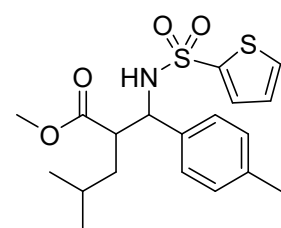


**6caf** $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

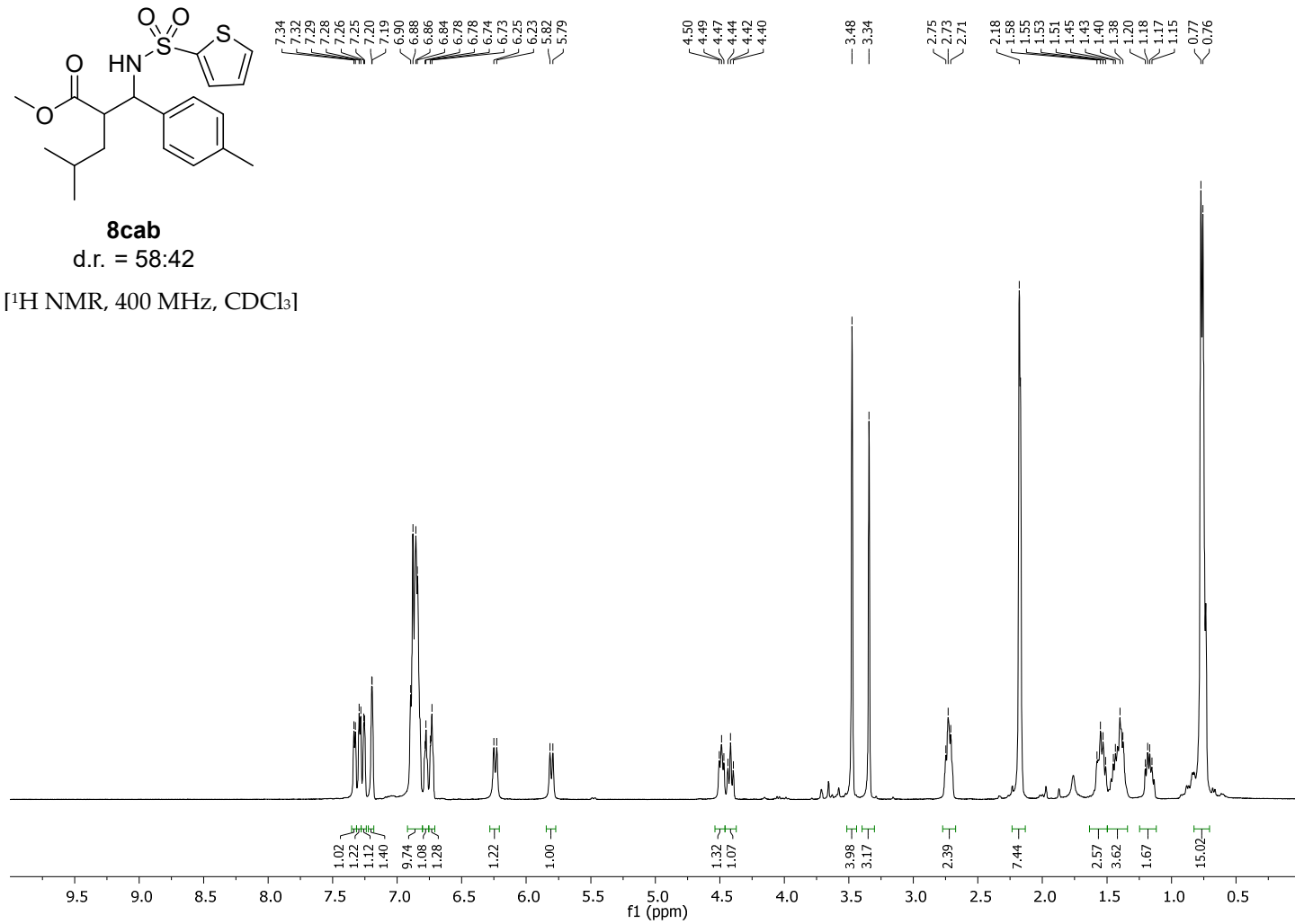


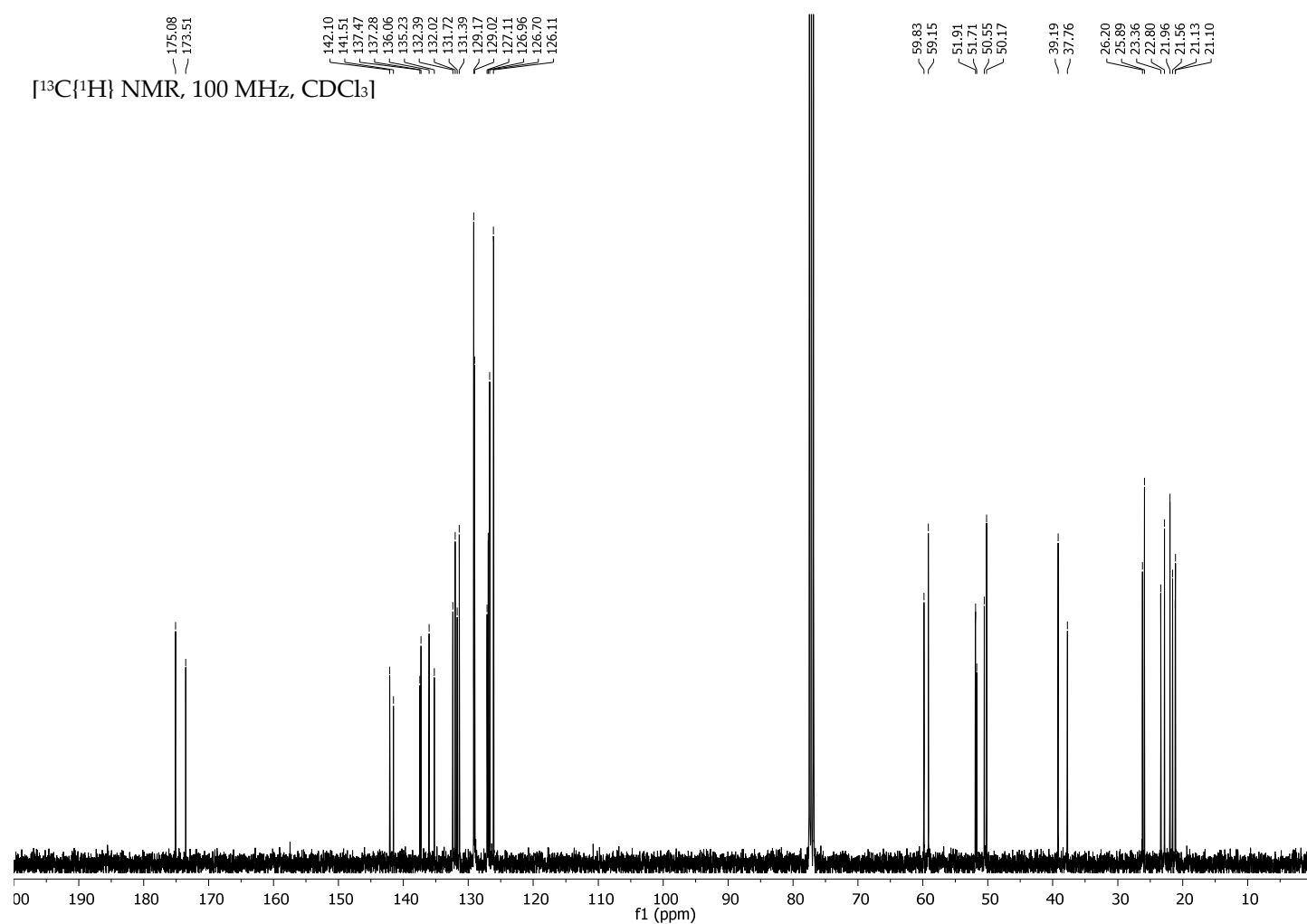


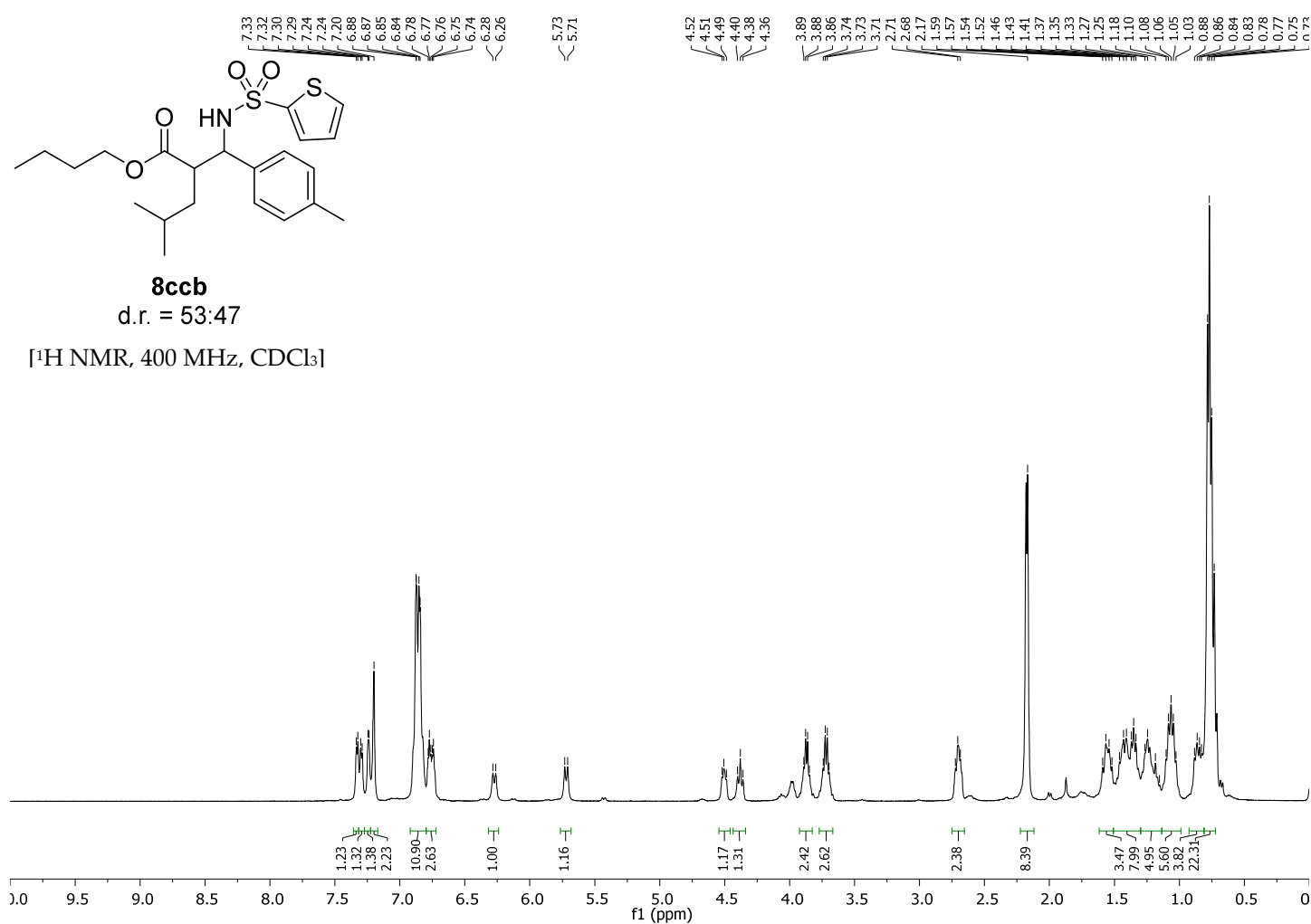


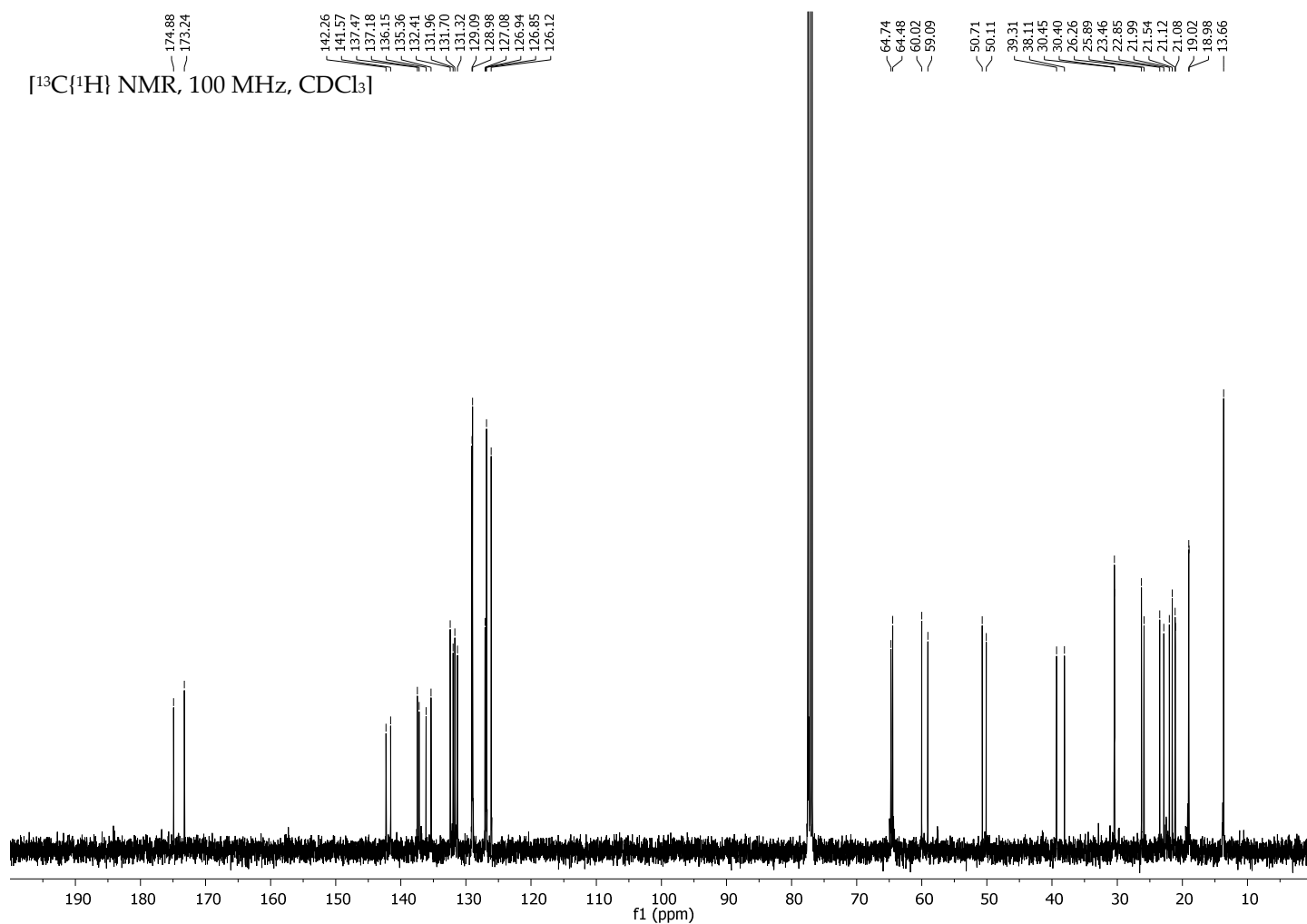
**8cab**

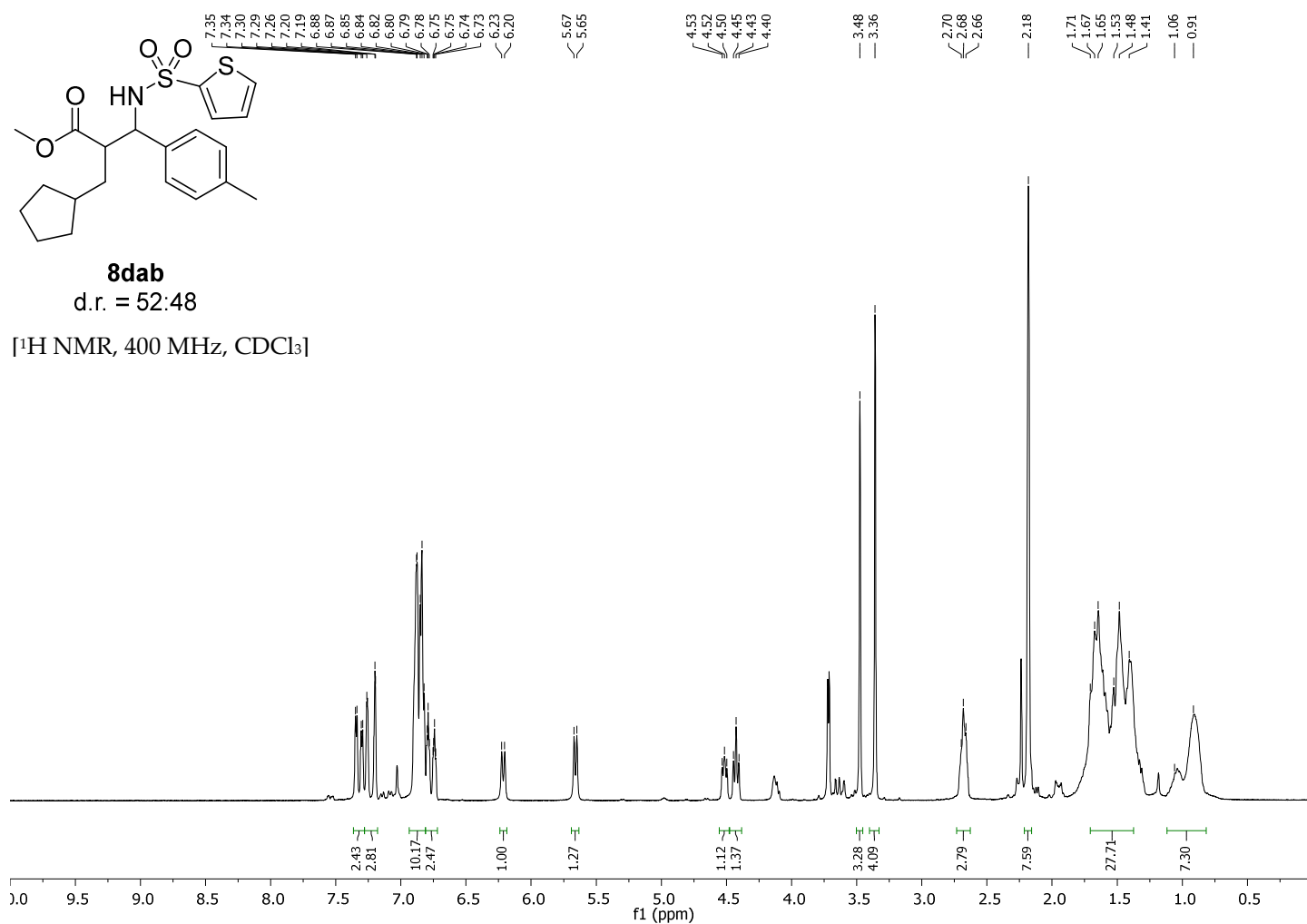
d.r. = 58:42

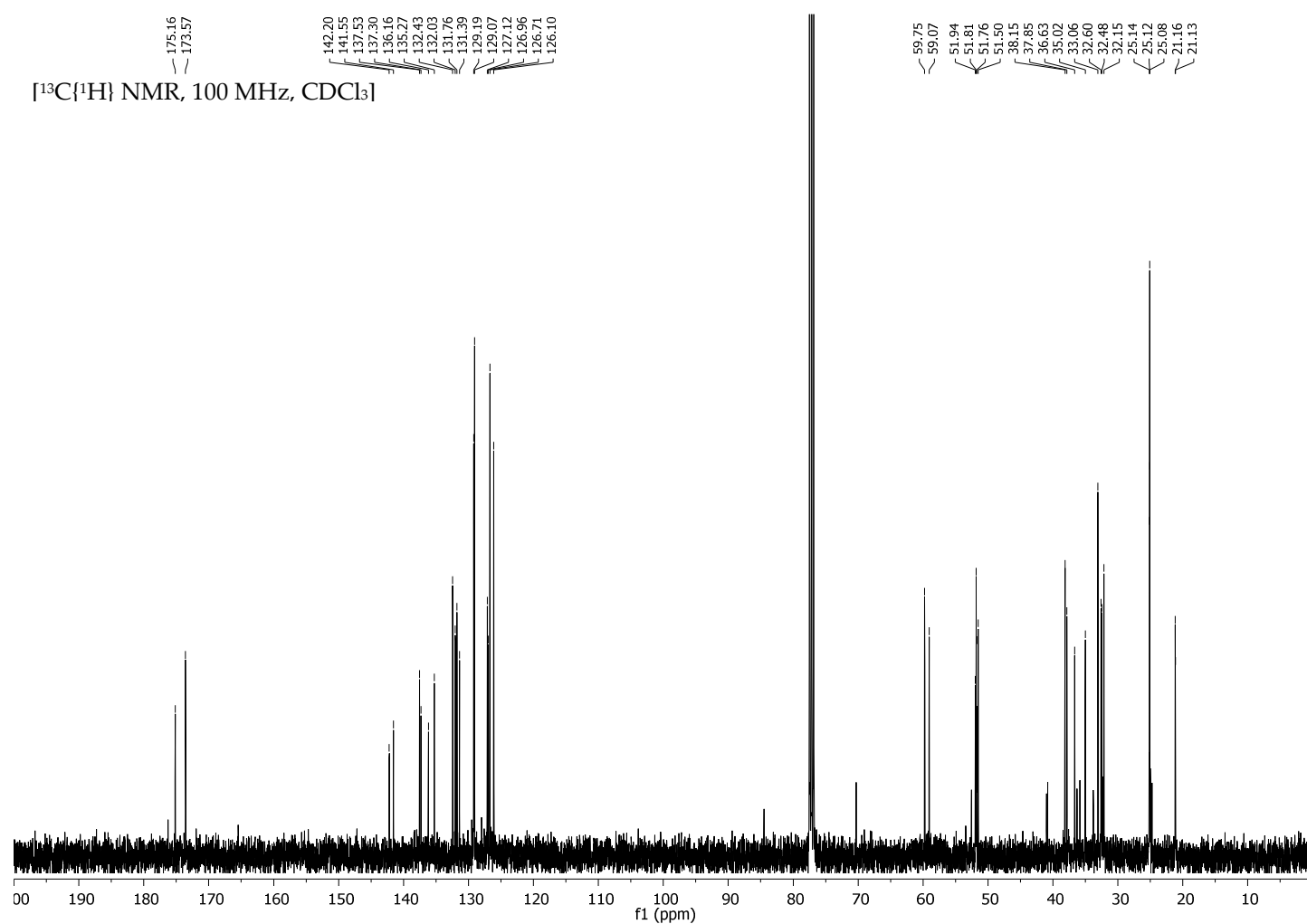
 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 

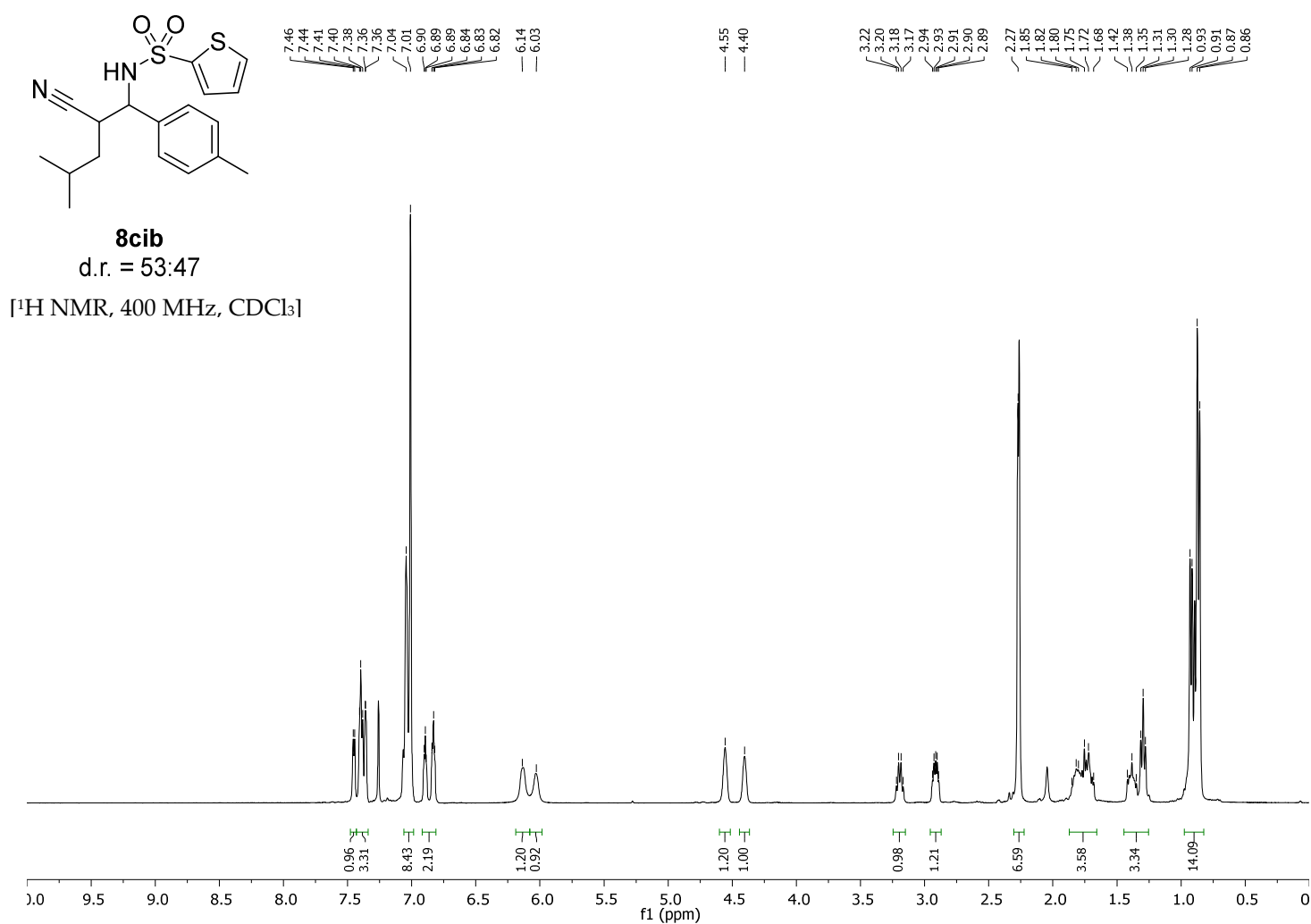


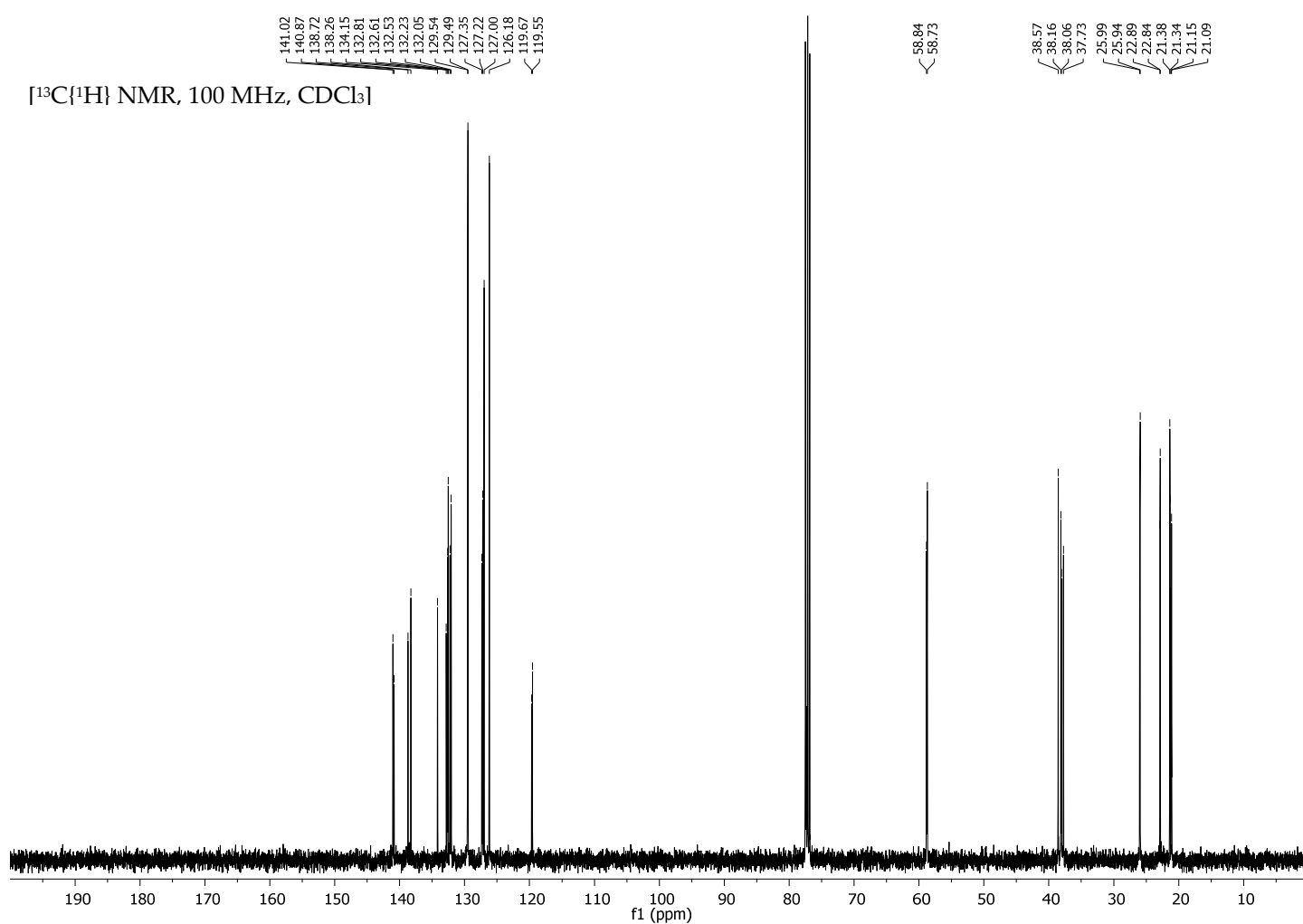


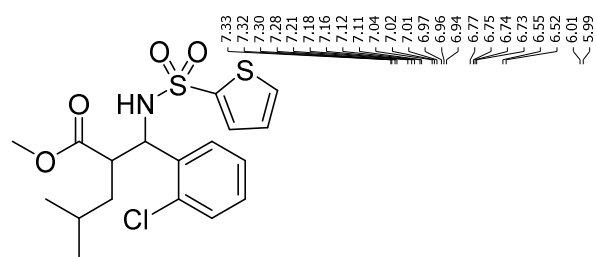




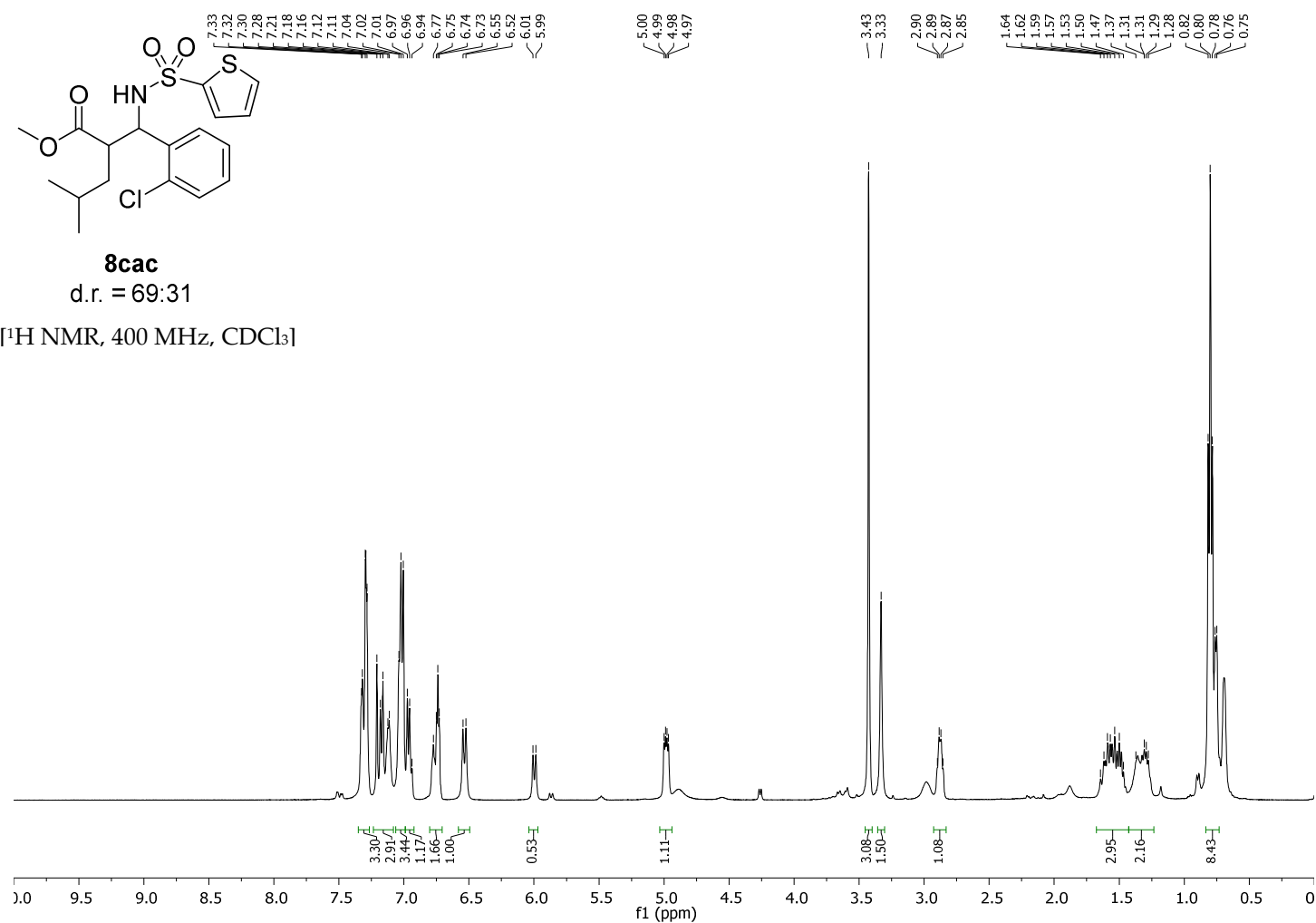


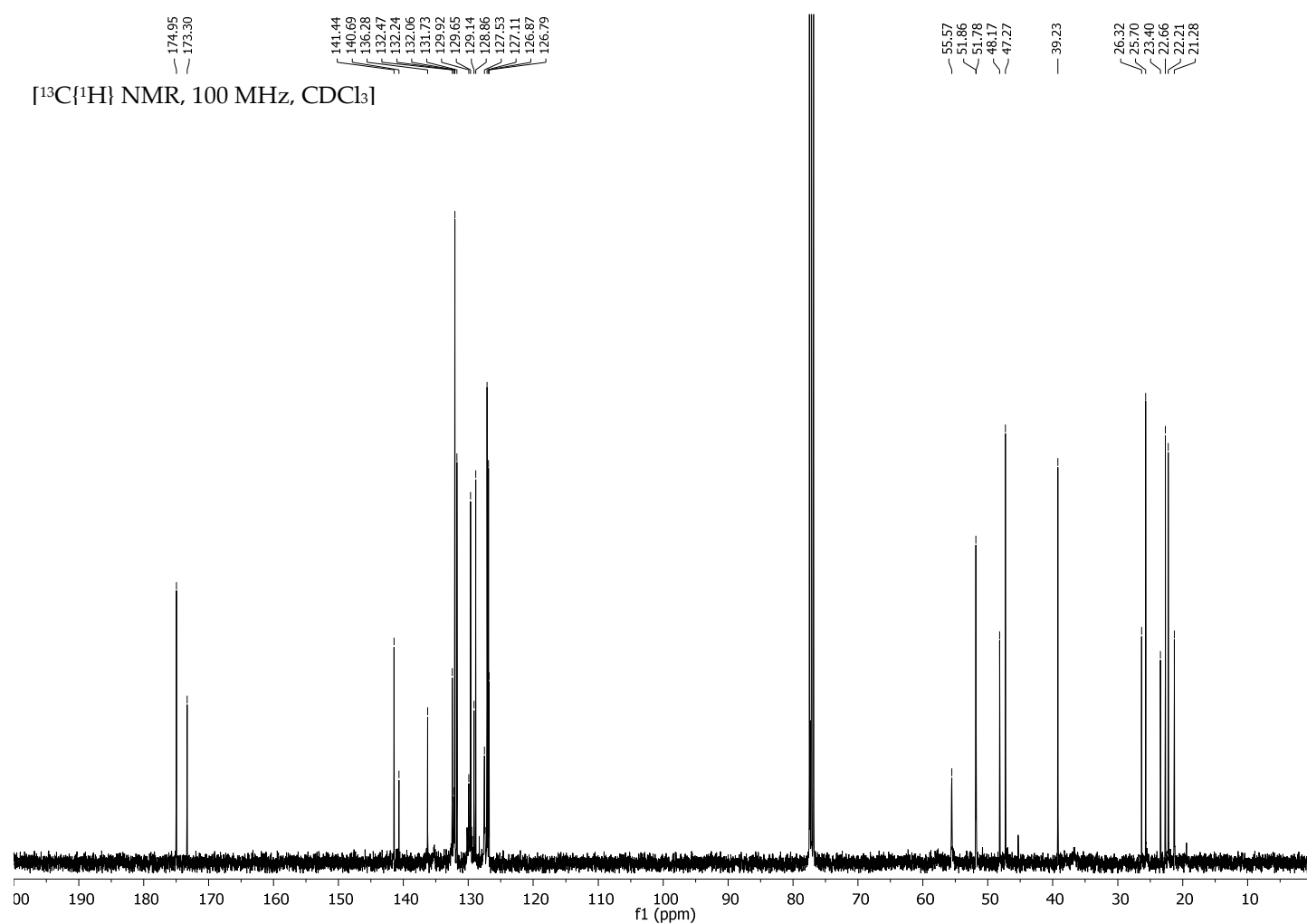


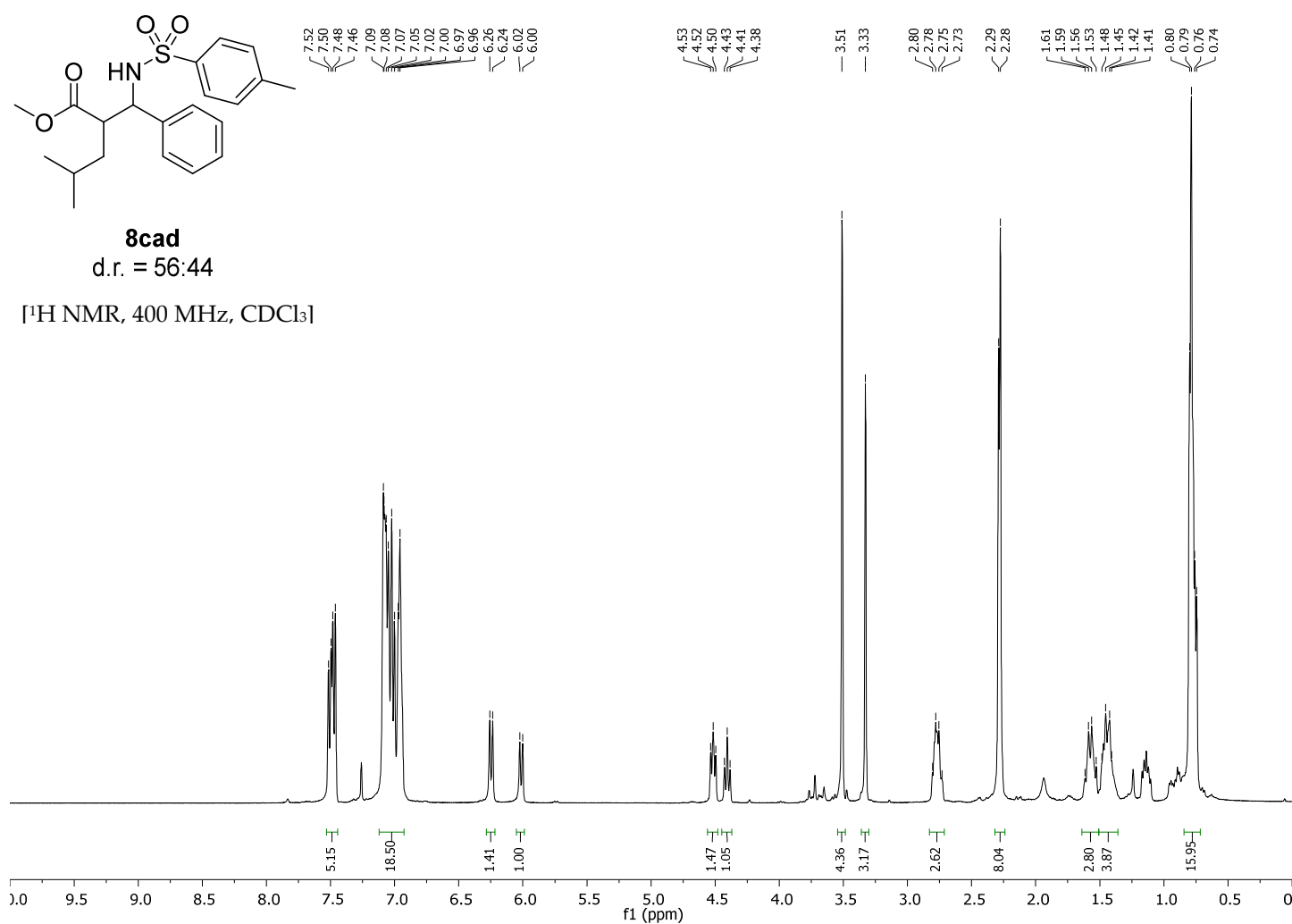


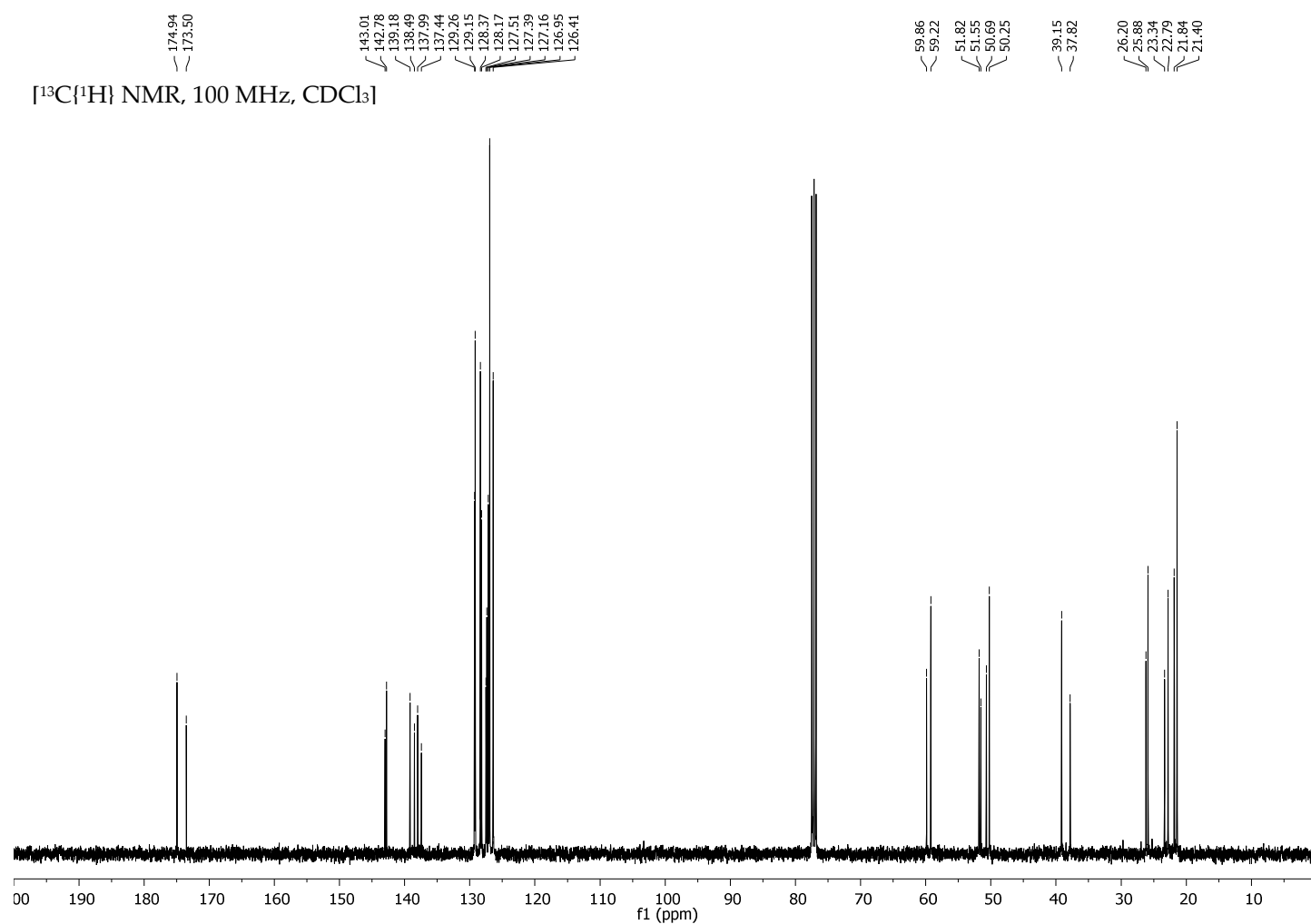
**8cac**

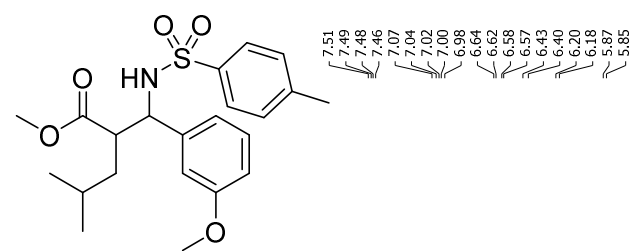
d.r. = 69:31

 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 







**8cae**

d.r. = 55:45

 $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ 