Photocatalyzed anti-Markovnikov addition of carboxylic acids to alkenes: ionic mechanism under radical conditions

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Table of Contents

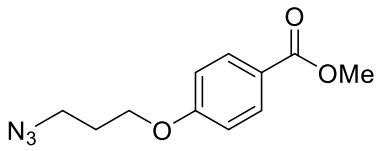
General Methods

Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. For irradiation, 60W 400 nm LED chip was used. Reactions were performed in a glass tube (outer diameter 12 mm, inner diameter 9 mm), which was placed in a glass jacket cooling with water (water temperature ca. 20 °C). The distance between the reaction vessel and diodes was about 1 cm.

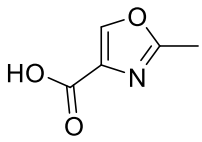
Starting materials

Acetonitrile, ethylacetate, 1,2-dichloroetahe, toluene and dichloromethane were purified by distillation over CaH_2 under argon.

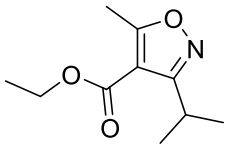
Following compounds were prepared according to literature procedures:



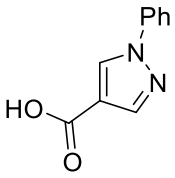
SI-1 [1]



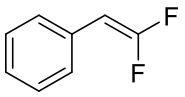
SI-2 [2]



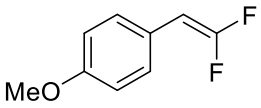
SI-3 [3]



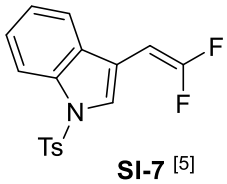
SI-4 [4]



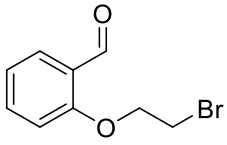
SI-5 [5]



SI-6 [5]

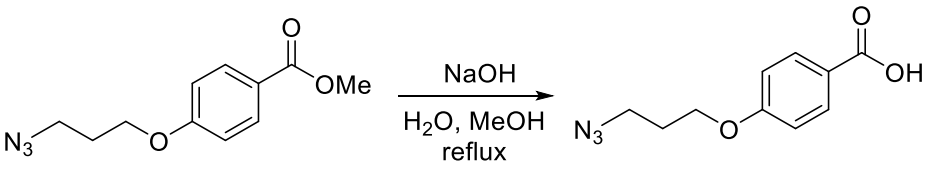


SI-7 [5]



SI-8 [6]

4-(3-Azidopropoxy)benzoic acid (2l)



Methyl 4-(3-azidopropoxy)benzoate (1 equiv, 21.2 mmol, 5 g) was added into a 100 mL flask containing a solution of NaOH (3 equiv, 63 mmol, 2.5 g) in water (50 mL) and MeOH (5 ml) at room temperature, and the mixture was stirred under reflux for 45 min. The mixture was cooled to room temperature and washed with MeO*t*-Bu (2×10 mL). Organics were discarded and the aqueous layer was acidified by diluted HCl to pH = 3. The formed precipitate was filtered off, washed with cold water (2×5 mL) and recrystallised from aq. ethanol (4% water).

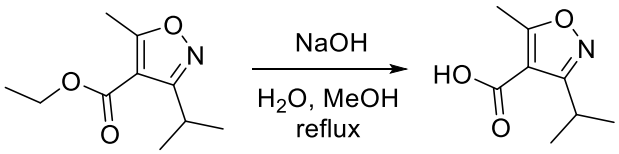
Yield 4.12 g, 88%. Colorless solid. Mp 116-118 °C.

^{1}H NMR (300 MHz, DMSO-d_6), δ: 7.89 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 4.11 (t, J = 6.2 Hz, 2H), 3.51 (t, J = 6.7 Hz, 2H). 2.00 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6), δ: 167.5, 162.4, 131.8, 123.7, 114.7, 65.4, 48.1, 28.5.

HRMS (ESI): calcd for $C_{10}H_{12}N_3O_3$ (M+H) 222.0873, found 222.0879, calcd for $C_{10}H_{11}N_3O_3Na$ (M+Na) 244.0693, found 244.0702.

3-Isopropyl-5-methylisoxazole-4-carboxylic acid (2p)



Ethyl 3-isopropyl-5-methylisoxazole-4-carboxylate (1 equiv, 16.2 mmol, 3.2 g) was added into a 100 mL flask containing a solution of NaOH (3 equiv, 50 mmol, 1.95 g) in water (32 mL) and MeOH (3 ml) at room temperature, and the mixture was stirred under reflux for 45 min. The mixture was cooled to room temperature and washed with MeO*t*-Bu (2×10 mL). Organics were discarded and the aqueous layer was acidified by diluted HCl to pH = 3. Formed precipitate was filtered off, washed with cold water (2×5 mL) and recrystallised from aq. ethanol (4% water).

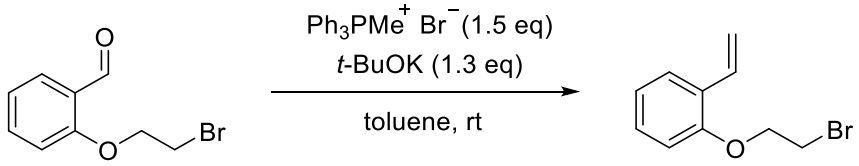
Yield 2.52 g, 93%. Colorless solid. Mp 108-110 °C.

^{1}H NMR (300 MHz, DMSO-d_6), δ: 2.38 (hept, J = 6.8 Hz, 1H), 2.59 (s, 3H), 1.22 (d, J = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6), δ: 175.3, 168.2, 163.6, 108.2, 26.4, 21.2, 13.4.

HRMS (ESI): calcd for $C_8H_{12}NO_3$ (M+H) 170.0812, found 170.0813.

1-(2-Bromoethoxy)-2-vinylbenzene (SI-9) [7]



SI-8 **SI-9**

Potassium *tert*-butoxide (1.3 equiv, 10.4 mmol, 1.16 g) was added into a 100 mL flask containing a solution of methyltriphenylphosphonium bromide (1.5 equiv, 12.0 mmol, 4.28 g) in toluene (30 mL) at room temperature, and the mixture was heated at 80 °C for 40 min with stirring. The mixture was cooled to 0 °C and **SI-8** (1.0 equiv, 8.0 mmol, 1.83 g) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3×30 mL). The combined organic layers were filtered through Na_2SO_4 and concentrated under reduced pressure. The resulting slurry was filtered and washed with hexane. The filtrate was concentrated and purified by column chromatography on silica gel.

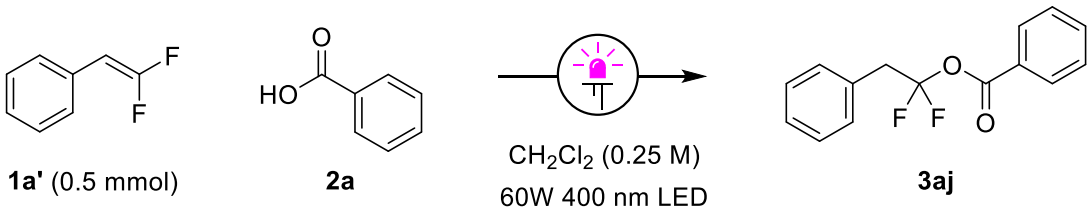
Yield 1.55 g, 85%. Colorless oil.

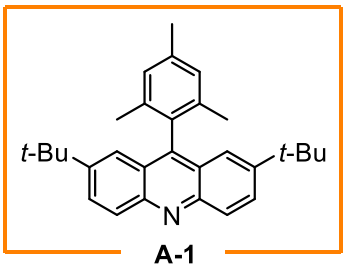
Chromatography: hexane/EtOAc, 20/1. R_f 0.5.

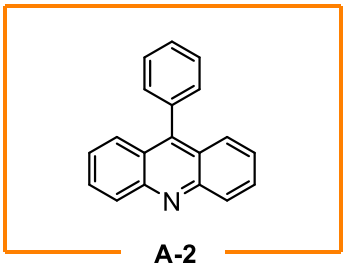
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.52 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.24 (ddd, *J* = 8.2, 7.3, 1.7 Hz, 1H), 7.12 (dd, *J* = 17.8, 11.2 Hz, 1H), 7.00 (td, *J* = 7.4, 1.1 Hz, 1H), 6.85 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.80 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.31 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.32 (t, *J* = 6.2 Hz, 2H), 3.68 (t, *J* = 6.2 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 155.1, 131.3, 128.8, 127.0, 126.6, 121.4, 114.8, 112.2, 68.1, 29.5.

Optimization studies







Time	$PhCO_2H$	Cat	Additive	Conversion of **1a'**, %	Yield of **3aj**, % [a]
2 h	1.5 eq	5% **A-2**	–	20	14
8 h	2.5 eq	7.5% **A-2**	2,4,6-collidine (1 eq)	34	33
24 h	2.5 eq	10% **A-2**	2,4,6-collidine (1 eq)	69	66
4 h	2.5 eq	10% **A-2**	2,4,6-collidine (0.5 eq)	35	33
4 h	2.5 eq	10% **A-2**	2,4,6-collidine (0.25 eq)	49	46
4 h	2.5 eq	10% **A-2**	2,4,6-collidine (0.1 eq)	49	40
4 h	1.5 eq	10% **A-2**	2,4,6-collidine (0.25 eq)	39	37
24 h	2.5 eq	15% **A-2**	2,4,6-collidine (0.25 eq)	78	72 (54[b])
24 h	2.5 eq	10% **A-1**	2,4,6-collidine (0.5 eq)	100	93 (88[b])
8 h	2.5 eq	10% **A-1**	2,4,6-collidine (0.5 eq)	100	92 (88[b])

[a] ^{19}F NMR yields with $PhCF_3$ as an internal standard. [b] Isolated yields.

General procedures

Synthesis of phenethyl ethers (General procedure A)

A screw capped tube containing a stirring bar was charged with alkene **1** (2.0 equiv, 1 mmol), acid **2** (1.0 equiv, 0.5 mmol), 2,7-di-*tert*-butyl-9-mesitylacridine **A-1** (10 mol%, 14.4 mg) and CH_2Cl_2 (2 mL). The tube was flushed with argon during one minute, closed with a puncturable screw cap, and an empty syringe with a plunger was introduced with a needle as a pressure compensator. Then, the reaction mixture was irradiated using 60W 400 nm LEDs for 8 hours (16 h for **3b, 3e, 3g, 3m, 3n, 3s, 3t**). After completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography.

Synthesis of phenethyl ethers (General procedure B)

A screw capped tube containing a stirring bar was charged with alkene **1** (1 equiv, 0.5 mmol), acid **2** (2.5 equiv, 1.25 mmol), 2,7-di-*tert*-butyl-9-mesitylacridine **A-1** (10 mol%, 14.4 mg) and 2 mL of CH_2Cl_2 (MeOH for **5**). The tube was flushed with argon during one minute, closed with a puncturable screw cap, and an empty syringe with a plunger was introduced with a needle as a pressure compensator. Then, the reaction mixture was irradiated using 60W 400 nm LEDs for 8 hours. After completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography.

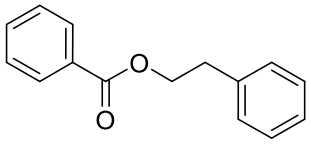
Synthesis of 1,1-difluoro-2-phenethyl ethers (General procedure C)

A screw capped tube containing a stirring bar was charged with alkene **1** (1 equiv, 0.5 mmol), acid **2** (2.5 equiv, 1.25 mmol), 2,4,6-collidine (0.5 equiv, 0.25 mmol, 30 mg), 2,7-di-*tert*-butyl-9-mesitylacridine **A-1** (10 mol%, 14.4 mg) and CH_2Cl_2 (2 mL). The tube was flushed with argon during one minute, closed with a puncturable screw cap, and an empty syringe with a plunger was introduced with a needle as a pressure compensator. Then, the reaction mixture was irradiated using 60W 400 nm LEDs for 8 hours. After completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography.

Synthesis of 1,1-difluoro-2-phenethyl ethers (General procedure D)

A screw capped tube containing a stirring bar was charged with alkene **1** (2.0 equiv, 1 mmol), acid **2** (1.0 equiv, 0.5 mmol), 2,4,6-collidine (0.1 equiv, 0.05 mmol, 6 mg), 2,7-di-*tert*-butyl-9-mesitylacridine **A-1** (10 mol%, 14.4 mg) and CH_2Cl_2 (2 mL). The tube was flushed with argon during one minute, closed with a puncturable screw cap, and an empty syringe with a plunger was introduced with a needle as a pressure compensator. Then, the reaction mixture was irradiated using 60W 400 nm LEDs for 8 hours. After completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography.

2-Phenylethyl benzoate (3a) [8]



Yield 86 mg (76%, General procedure A), 97 mg (86%, General procedure B). Colorless oil.

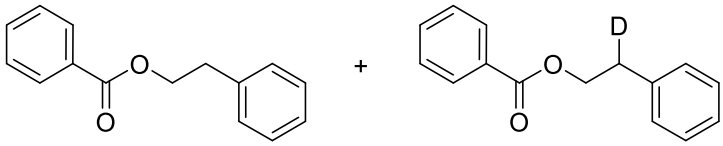
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.12 – 8.04 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 7.42 – 7.26 (m, 5H), 4.60 (t, J = 6.9 Hz, 2H), 3.14 (t. J = 6.9 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.5, 138.0, 132.9, 130.4, 129.6, 129.0, 128.6, 128.4, 126.6, 65.5, 35.3.

HRMS (ESI): calcd for $C_{15}H_{15}O_2$ (M+H) 227.1067, found 227.1061, calcd for $C_{15}H_{14}O_2Na$ (M+Na) 249.0886, found 249.0891, calcd for $C_{15}H_{14}O_2K$ (M+K) 265.0625, found 265.0623.

Mixture of 2-phenylethyl benzoate (3a) and 2-phenylethyl-2-d benzoate (*d*$_1$-3a)

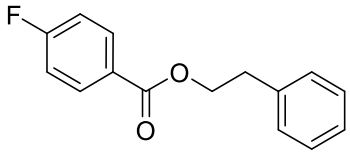


Yield 98 mg (87%, General procedure B). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.12 – 8.04 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 7.42 – 7.26 (m, 5H), 4.60 (m, 2H), 3.14 (m, 1.4 H).

2-Phenylethyl 4-fluorobenzoate (3b) [9]



Yield 87 mg (78%, General procedure A). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.75.

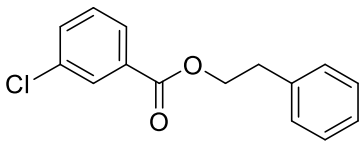
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.09 (dd, J = 9.1 Hz, J = 5.4 Hz, 2H), 7.43 – 7.25 (m, 5H), 7.19 – 7.08 (m, 2H), 4.59 (t, J = 7.0 Hz, 2H), 3.13 (t, J = 7.0 Hz, 2H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -106.5.

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.8 (d, J = 254 Hz), 165.5, 137.9, 132.1 (d, J = 9.3 Hz), 129.0, 128.6, 126.7, 115.6 (d, J = 22 Hz), 65.6, 35.3.

HRMS (ESI): calcd for $C_{15}H_{14}FO_2$ (M+Na) 245.0972, found 245.0977, calcd for $C_{15}H_{13}FO_2Na$ (M+Na) 267.0792, found 267.0803.

2-Phenylethyl 3-chlorobenzoate (3c)



Yield 119 mg (91%, General procedure A). Colorless oil.

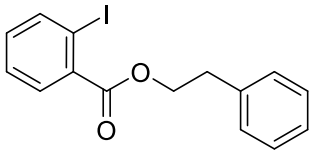
Chromatography: CH_2Cl_2. R_f 0.75.

^1H NMR (300 MHz, $CDCl_3$), δ: 8.08 – 8.04 (m, 1H), 7.98 – 7.93 (m, 1H), 7.58 – 7.52 (m, 1H), 7.43 – 7.28 (m, 6H), 4.60 (t, *J* = 7.0 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 165.3, 137.7, 134.6, 133.0, 132.1, 129.8, 129.7, 129.0, 128.7, 127.7, 126.8, 65.9, 35.2.

HRMS (ESI): calcd for $C_{15}H_{17}Cl^{35}NO_2$ (M+NH_4) 278.0942, found 278.0933, calcd for $C_{15}H_{17}Cl^{37}NO_2$ (M+NH_4) 280.0914, found 280.0905, calcd for $C_{15}H_{13}Cl^{35}O_2Na$ (M+Na) 283.0496, found 283.0496, calcd for $C_{15}H_{13}Cl^{37}O_2Na$ (M+Na) 285.0468, found 285.0463, calcd for $C_{15}H_{13}Cl^{35}O_2K$ (M+K) 299.0236, found 299.0230, calcd for $C_{15}H_{13}Cl^{37}O_2K$ (M+K) 301.0207, found 301.0233.

2-Phenylethyl 2-iodobenzoate (3d) [10]



Yield 76 mg (43%, General procedure A). Colorless oil.

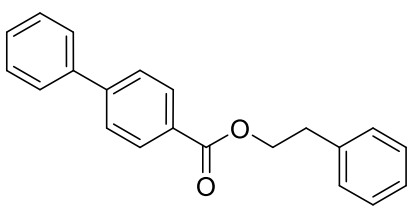
Chromatography: CH_2Cl_2. R_f 0.7.

^1H NMR (300 MHz, $CDCl_3$), δ: 8.01 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.25 (m, 6H), 7.19 – 7.11 (m, 1H), 4.62 (t, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.1 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 166.4, 141.4, 137.7, 135.2, 132.7, 131.0, 129.1, 128.7, 128.0, 126.8, 94.2, 66.1, 35.1.

HRMS (ESI): calcd for $C_{15}H_{14}IO_2$ (M+H) 353.0033, found 353.0027, calcd for $C_{15}H_{17}INO_2$ (M+NH_4^+) 370.0298, found 370.0294, calcd for $C_{15}H_{13}IO_2Na$ (M+Na) 374.9852, found 374.9846, calcd for $C_{15}H_{13}IO_2K$ (M+K) 390.9592, found 390.9585.

2-Phenylethyl biphenyl-4-carboxylate (3e) [11]



Yield 142 mg (94%, General procedure A). Colorless oil.

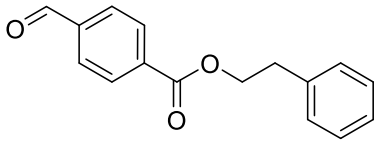
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.24 – 8.16 (m, 2H), 7.78 – 7.65 (m, 4H), 7.60 – 7.32 (m, 8H), 4.66 (t, *J* = 7.0 Hz, 2H), 3.19 (t, *J* = 7.0 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.4, 145.7, 140.1, 138.0, 130.2, 129.2, 129.1, 129.0, 128.9, 128.2, 127.4, 127.1, 126.7, 65.6, 35.4.

HRMS (ESI): calcd for $C_{21}H_{19}O_2$ (M+H) 303.1380, found 303.1386, calcd for $C_{21}H_{22}NO_2$ (M+NH_4) 320.1645, found 320.1646, calcd for $C_{21}H_{18}O_2Na$ (M+Na) 325.1199, found 325.1198, calcd for $C_{21}H_{18}O_2K$ (M+K) 341.0938, found 341.0936.

2-Phenylethyl 4-formylbenzoate (3f) [12]



Yield 109 mg (76%, General procedure A). Colorless oil.

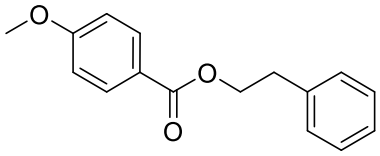
Chromatography: CH_2Cl_2. R_f 0.5.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 10.8 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.22 (m, 5H), 4.59 (t, *J* = 7.0 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 191.6, 165.4, 139.2, 137.7, 135.2, 130.2, 129.5, 129.0, 128.7, 126.7, 66.0, 35.2.

HRMS (ESI): calcd for $C_{16}H_{14}O_3Na$ (M+Na) 277.0835, found 277.0838.

2-Phenylethyl 4-methoxybenzoate (3g) [13]



Yield 104 mg (81%, General procedure A). Colorless oil.

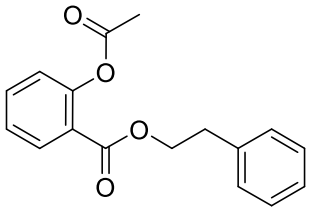
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.02 (d, *J* = 9.1 Hz, 2H), 7.40 – 7.22 (m, 5H), 6.94 (d, *J* = 9.1 Hz, 2H), 4.54 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 3.10 (t, *J* = 7.0 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.3, 163.4, 138.1, 131.6, 129.0, 128.6, 126.6, 122.8, 113.9, 65.2, 55.4, 35.4.

HRMS (ESI): calcd for $C_{16}H_{17}O_3$ (M+H) 257.1172, found 257.1177, calcd for $C_{16}H_{20}NO_3$ (M+NH_4) 274.1438, found 274.1444, calcd for $C_{16}H_{16}O_3Na$ (M+Na) 279.0992, found 279.0998, calcd for $C_{16}H_{16}O_3K$ (M+K) 295.0731, found 295.0731.

2-Phenylethyl 2-(acetyloxy)benzoate (3h)



Yield 107 mg (75%, General procedure A). Colorless oil.

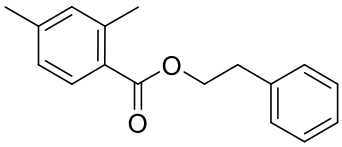
Chromatography: CH_2Cl_2. R_f 0.7.

^1H NMR (300 MHz, $CDCl_3$), δ: 8.01 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.41 – 7.25 (m, 6H), 7.14 (dd, *J* = 8.1 Hz, *J* = 1.1 Hz, 1H), 4.54 (t, *J* = 7.8 Hz, 2H), 3.09 (t, *J* = 7.8 Hz, 2H), 2.33 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 169.7, 164.4, 150.8, 137.7, 133.9, 131.7, 129.0, 128.6, 126.7, 126.0, 123.8, 123.4, 65.6, 35.1, 21.0.

HRMS (ESI): calcd for $C_{17}H_{17}O_4$ (M+H) 285.1121, found 285.1116, calcd for $C_{17}H_{20}NO_4$ ($M+NH_4$) 302.1387, found 302.1385, calcd for $C_{17}H_{16}O_4Na$ (M+Na) 307.0941, found 307.0933, calcd for $C_{17}H_{16}O_4K$ (M+K) 323.0680, found 323.0689.

2-Phenylethyl 2,4-dimethylbenzoate (3i)



Yield 105 mg (83%, General procedure A). Colorless oil.

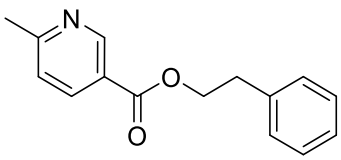
Chromatography: CH_2Cl_2. R_f 0.75.

^1H NMR (300 MHz, $CDCl_3$), δ: 7.90 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.29 (m, 5H), 7.15 – 7.08 (m, 2H), 4.60 (t, *J* = 7.0 Hz, 2H), 3.16 (t, *J* = 7.0 Hz, 2H), 2.64 (s, 3H), 2.41 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ:167.5, 142.5, 140.5, 138.2, 132.7, 130.0, 129.0, 128.6, 126.8, 126.6, 126.5, 65.1, 35.4, 21.9, 21.4.

HRMS (ESI): calcd for $C_{17}H_{19}O_2$ (M+H) 255.1380, found 255.1383, calcd for $C_{17}H_{22}NO_2$ ($M+NH_4^+$) 272.1645, found 272.1649, calcd for $C_{17}H_{18}O_2Na$ (M+Na) 277.1199, found 277.1202, calcd for $C_{17}H_{18}O_2Na$ (M+K) 293.0938, found 293.1749.

2-Phenylethyl 6-methylpyridine-3-carboxylate (3j)



Yield 99 mg (82%, General procedure A). Colorless oil.

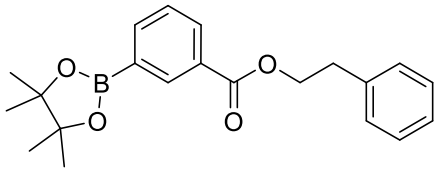
Chromatography: CH_2Cl_2. R_f 0.45.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 9.06 (d, *J* = 1.7 Hz, 1H), 8.09 (dd, *J* = 8.0 Hz, *J* = 1.7 Hz, 1H), 7.33 – 7.12 (m, 6H), 4.52 (t, *J* = 6.9 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H), 2.57 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.3, 163.0, 150.4, 137.7, 137.2, 128.9, 128.6, 126.6, 123.4, 122.9, 65.6, 35.2, 24.7.

HRMS (ESI): calcd for $C_{15}H_{16}NO_2$ (M+H) 242.1176, found 242.1169, calcd for $C_{15}H_{15}NO_2Na$ (M+Na) 264.0995, found 264.0987.

3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzoic acid phenethyl ester (3k)



Yield 125 mg (71%, General procedure A). Colorless oil.

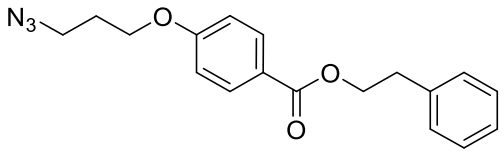
Chromatography: CH_2Cl_2. R_f 0.35.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.38 (s, 1H), 8.03 – 7.98 (m, 1H), 7.92 – 7.86 (m, 1H), 7.38 – 7.10 (m, 6H), 4.43 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.6, 139.2, 137.9, 136.0, 132.3, 129.8, 129.1, 128.6, 127.8, 126.6, 84.1, 65.1, 35.3, 24.9.

HRMS (ESI): calcd for $C_{21}H_{26}BO_4$ (M+H) 353.1922, found 353.9134.

2-Phenylethyl 4-(3-azidopropoxy)benzoate (3l)



Yield 86 mg (53%, General procedure A). Colorless oil.

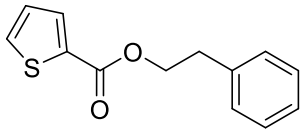
Chromatography: CH_2Cl_2. R_f 0.65.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.00 (d, *J* = 9 Hz, 2H), 7.39 – 7.24 (m, 5H), 6.94 (d, *J* = 9 Hz, 2H), 4.54 (t, *J* = 6.9 Hz, 2H), 4.13 (t, *J* = 6.9 Hz, 2H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.16 – 2.04 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.2, 162.4, 138.0, 131.6, 129.0, 128.5, 126.6, 123.0, 114.0, 65.2, 64.7, 48.1, 35.3, 28.7.

HRMS (ESI): calcd for $C_{18}H_{20}N_3O_3$ (M+H) 326.1499, found 326.1505, calcd for $C_{18}H_{23}N_4O_3$ (M+NH_4) 343.1765, found 343.1770, calcd for $C_{18}H_{19}N_3O_3Na$ (M+Na) 348.1319, found 348.1324, calcd for $C_{18}H_{19}N_3O_3K$ (M+K) 364.1058, found 364.1061.

2-Phenylethyl thiophene-2-carboxylate (3m) [14]



Yield 82 mg (71%, General procedure A). Colorless oil.

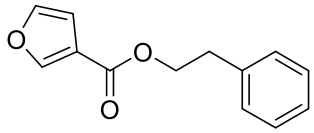
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.85 (dd, *J* = 3.2 Hz, *J* = 1.3 Hz, 1H), 7.57 (dd, *J* = 5.0 Hz, *J* = 1.3 Hz, 1H), 7.42 – 7.26 (m, 5H), 7.13 (dd, *J* = 5.0 Hz, *J* = 3.2 Hz, 1H), 4.57 (t, *J* = 7.1 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 162.1, 137.8, 133.9, 133.5, 132.4, 129.1, 128.6, 127.8, 126.7, 65.7, 35.3.

HRMS (ESI): calcd for $C_{13}H_{12}O_2Na$ (M+Na) 255.0450, found 255.0445, calcd for $C_{13}H_{12}O_2K$ (M+K) 271.0190, found 271.0179.

2-Phenylethyl furan-3-carboxylate (3n)



Yield 70 mg (65%, General procedure A). Colorless oil.

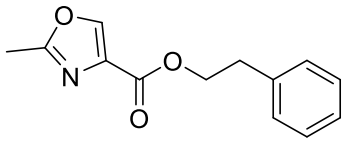
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.03 (dd, *J* = 1.6 Hz, *J* = 0.6 Hz, 1H), 7.44 (t, *J* = 1.6 Hz, 1H), 7.40 – 7.26 (m, 5H), 6.78 (dd, *J* = 1.6 Hz, *J* = 0.6 Hz, 1H), 4.51 (t, *J* = 6.9 Hz, 2H), 3.08 (t, *J* = 6.9 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 163.0, 147.8, 143.8, 137.9, 129.0, 128.6, 126.6, 119.5, 109.9, 65.0, 35.2.

HRMS (ESI): calcd for $C_{13}H_{12}O_3Na$ (M+Na) 239.0679, found 239.0678.

2-Phenylethyl 2-methyl-1,3-oxazole-4-carboxylate (3o)



Yield 96 mg (83%, General procedure A), 83 mg (72%, General procedure B). Colorless oil.

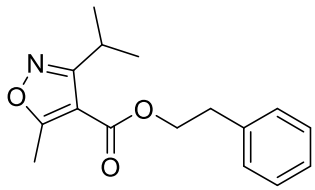
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.05 (s, 1H), 7.32 – 7.16 (m, 5H), 4.50 (t, *J* = 7.3 Hz, 2H), 3.04 (t. *J* = 7.3 Hz, 2H), 2.47 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 162.4, 161.1, 143.8, 137.4, 133.3, 128.9, 128.5, 126.6, 65.4, 35.1, 13.8.

HRMS (ESI): calcd for $C_{13}H_{14}NO_3$ (M+H) 232.0968, found 232.0975, calcd for $C_{13}H_{13}NO_3Na$ (M+Na) 254.0788, found 254.0798, calcd for $C_{13}H_{13}NO_3K$ (M+K) 270.0527, found 270.0535.

2-Phenylethyl 5-methyl-3-(1-methylethyl)isoxazole-4-carboxylate (3p)



Yield 117 mg (86%, General procedure A). Colorless oil.

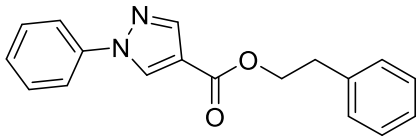
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.39 – 7.23 (m, 5H), 4.55 (t, *J* = 6.9 Hz, 2H), 3.37 (hept, *J* = 6.9 Hz, 1H), 3.08 (t, *J* = 6.9 Hz, 2H), 2.54 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 175.3, 168.2, 162.3, 137.6, 128.8, 128.6, 126.7, 107.6, 64.9, 35.0, 26.6, 20.9, 13.4.

HRMS (ESI): calcd for $C_{16}H_{20}NO_3$ (M+H) 274.1438, found 274.1443, calcd for $C_{16}H_{19}NO_3Na$ (M+Na) 296.1257, found 296.1258.

2-Phenylethyl 1-phenyl-1H-pyrazole-4-carboxylate (3q)



Yield 133 mg (91%, General procedure A). Colorless solid. Mp 93 - 95 °C (hexane).

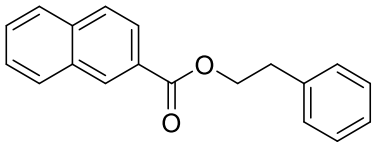
Chromatography: CH_2Cl_2. R_f 0.45.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.40 (d, *J* = 0.5 Hz, 1H), 8.10 (d, *J* = 0.5 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.54 – 7.47 (m, 2H), 7.42 – 7.28 (m, 6H), 4.52 (t, *J* = 7.1 Hz, 2H), 3.09 (t, *J* = 7.1 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ:162.7, 142.2, 139.4, 137.9, 130.1, 129.8, 129.0, 128.6, 127.6, 126.7, 119.6, 116.8, 64.9, 35.5.

HRMS (ESI): calcd for $C_{18}H_{17}N_2O_2$ (M+H) 293.1285, found 293.1289, calcd for $C_{18}H_{16}N_2O_2Na$ (M+Na) 315.1104, found 315.1106.

2-Phenylethyl naphthalene-2-carboxylate (3r) [15]



Yield 126 mg (91%, General procedure A). Colorless oil.

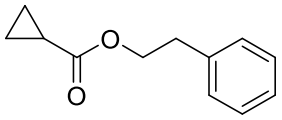
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.70 (s, 1H), 8.17 (dd, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.68 – 7.56 (m, 2H), 7.48 – 7.32 (m, 5H), 4.70 (t, *J* = 7.1 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.7, 138.1, 135.6, 132.6, 131.1, 129.5, 129.1, 128.7, 128.3, 128.2, 127.9, 127.7, 126.8, 126.7, 125.3, 65.7, 35.4.

HRMS (ESI): calcd for $C_{19}H_{17}O_2$ (M+H) 277.1223, found 277.1226, calcd for $C_{19}H_{16}O_2Na$ (M+Na) 299.1043, found 299.1046.

2-Phenylethyl cyclopropanecarboxylate (3s)



Yield 58 mg (61%, General procedure A), 65 mg (68%, General procedure B). Colorless oil.

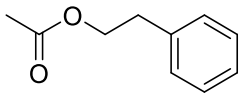
Chromatography: CH_2Cl_2. R_f 0.8.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.40 – 7.22 (m, 5H), 4.33 (t, *J* = 7.2 Hz, 2H), 2.98 (t. *J* = 7.2 Hz, 2H), 1.69 – 1.58 (m, 1H), 1.05 – 0.95 (m, 2H), 0.91 – 0.82 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 174.8, 137.9, 129.0, 128.5, 126.5, 64.9, 35.2, 12.8, 8.3.

HRMS (ESI): calcd for $C_{12}H_{15}O_2$ (M+H) 191.1067, found 191.1068, calcd for $C_{12}H_{18}NO_2$ (M+NH_4) 208.1332, found 208.1335, calcd for $C_{12}H_{14}O_2Na$ (M+Na) 213.0886, found 213.0893.

2-Phenylethyl acetate (3t) [16]



Yield 53 mg (65%, General procedure A), 52 mg (63%, General procedure B). Colorless oil.

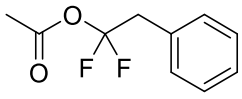
Chromatography: CH_2Cl_2. R_f 0.8.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.39 – 7.22 (m, 5H), 4.33 (t, *J* = 6.9 Hz, 2H), 2.98 (t. *J* = 6.9 Hz, 2H), 2.07 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 171.0, 137.9, 129.0, 128.6, 126.6, 64.9, 35.1, 21.0.

HRMS (ESI): calcd for $C_{10}H_{13}O_2$ (M+H) 165.0910, found 165.0906, calcd for $C_{10}H_{12}O_2Na$ (M+Na) 187.0730, found 187.0724.

1,1-Difluoro-2-phenylethyl acetate (3u)



Yield 75 mg (75%, General procedure C), 48 mg (48%, General procedure D). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.8.

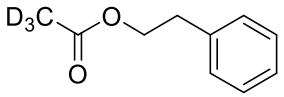
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.42 – 7.29 (m, 5H), 3.58 (t, *J* = 12.7 Hz, 2H), 2.11 (s, 3H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -71.0 (t, *J* = 12.7 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.8 (t, *J* = 2.8 Hz), 131.4 (t, *J* = 3.3 Hz), 130.3, 128.6, 127.8, 123.3 (t, *J* = 269 Hz), 40.9 (t, *J* = 28.0 Hz), 21.3 (t, *J* = 1.1 Hz).

HRMS (ESI): calcd for $C_{10}H_{10}F_2O_2Na$ (M+Na) 223.0541, found 223.0541.

2-phenylethyl d$_3$-acetate (3v)



Yield 67 mg (71%, General procedure A). Colorless oil.

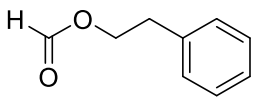
Chromatography: CH_2Cl_2. R_f 0.85.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.39 – 7.22 (m, 5H), 4.33 (t, *J* = 6.9 Hz, 2H), 2.98 (t. *J* = 6.9 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 171.0, 137.9, 129.0, 128.5, 126.6, 64.9, 35.1, 20.3 (hept., *J* = 19.8 Hz).

HRMS (ESI): calcd for $C_{10}H_{10}D_3O_2$ (M+H) 190.0918, found 190.0924.

2-Phenylethyl formate (3w) [15]



Yield 28 mg (37%, General procedure A), 40 mg (53%, General procedure B). Colorless oil.

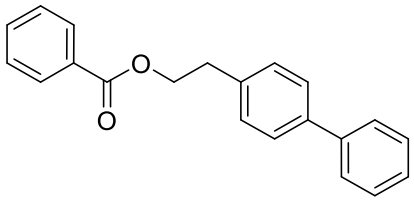
Chromatography: CH_2Cl_2. R_f 0.85.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 (s, 1H), 7.42 – 7.24 (m, 5H), 4.44 (t, *J* = 7.0 Hz, 2H), 3.03 (t. *J* = 7.0 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 161.0, 137.5, 128.9, 128.6, 126.8, 64.4, 35.0.

HRMS (ESI): calcd for $C_9H_{10}O_2Na$ (M+Na) 173.0573, found 173.0579.

2-Biphenyl-4-ylethyl benzoate (3x) [18]



Yield 122 mg (81%, General procedure B). Colorless oil.

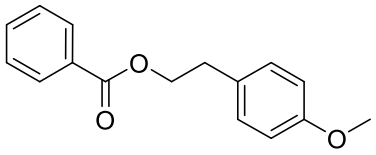
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.11 – 8.04 (m, 2H), 7.67 – 7.55 (m, 5H), 7.52 – 7.35 (m, 7H), 4.63 (t, *J* = 6.9 Hz, 2H), 3.16 (t, *J* = 6.9 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 166.6, 140.9, 139.6, 137.0, 132.9, 130.4, 129.6, 129.4, 128.8, 128.4, 127.3, 127.2, 127.1, 65.4, 34.9.

HRMS (ESI): calcd for $C_{21}H_{22}NO_2$ (M+NH_4) 320.1645, found 320.1656, calcd for $C_{21}H_{18}O_2Na$ (M+Na) 325.1199, found 325.1209.

2-(4-Methoxyphenyl)ethyl benzoate (3y) [19]



Yield 101 mg (79%, General procedure B). Colorless oil.

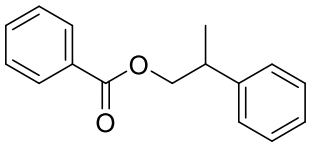
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 (d, *J* = 8.5 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 7.29 – 7.21 (m, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.54 (t, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 3.06 (t, *J* = 6.9 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.5, 158.4, 132.9, 130.4, 130.0, 129.8, 129.6, 128.4, 114.0, 65.8, 55.3, 34.4.

HRMS (ESI): calcd for $C_{16}H_{17}O_3$ (M+H) 257.1172, found 257.1164, calcd for $C_{16}H_{20}NO_3$ (M+NH_4) 274.1438, found 274.1441, calcd for $C_{16}H_{16}O_3Na$ (M+Na) 279.0992, found 279.0995, calcd for $C_{16}H_{16}O_3K$ (M+K) 295.0731, found 295.0719.

2-Phenylpropyl benzoate (3z) [20]



Yield 86 mg (72%, General procedure B). Colorless oil.

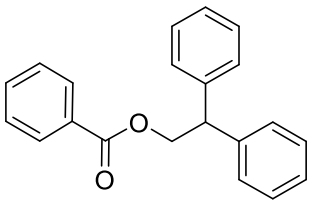
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.09 – 8.01 (m, 2H), 7.62 – 7.54 (m, 1H), 7.50 – 7.43 (m, 2H), 7.42 – 7.25 (m, 5H), 4.55 – 4.39 (m, 2H), 3.37 – 3.24 (m, 1H), 1.46 (d, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.5, 143.2, 132.9, 130.4, 129.6, 128.6, 128.4, 127.4, 126.8, 69.9, 39.1, 18.1.

HRMS (ESI): calcd for $C_{16}H_{17}O_2$ (M+H) 241.1223, found 241.1231, calcd for $C_{16}H_{20}NO_2$ (M+NH_4) 258.1489, found 258.1496, calcd for $C_{16}H_{16}O_2Na$ (M+Na) 263.1043, found 263.1052.

2,2-Diphenylethyl benzoate (3aa) [21]



Yield 148 mg (98%, General procedure B). Colorless oil.

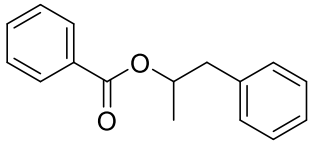
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 – 7.99 (m, 2H), 7.62 – 7.54 (m, 1H), 7.49 – 7.29 (m, 12H), 4.99 (d, *J* = 7.5 Hz, 2H), 4.63 (t, *J* = 7.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.5, 141.3, 133.0, 130.3, 129.9, 129.7, 128.6, 128.4, 126.9, 67.3, 50.1.

HRMS (ESI): calcd for $C_{21}H_{22}NO_2$ (M+NH_4) 320.1645, found 320.1642, calcd for $C_{21}H_{18}O_2Na$ (M+Na) 325.1199, found 325.1195, calcd for $C_{21}H_{18}O_2K$ (M+K) 341.0938, found 341.0950.

1-Methyl-2-phenylethyl benzoate (3ab) [22]



Yield 73 mg (61%, General procedure B). Colorless oil.

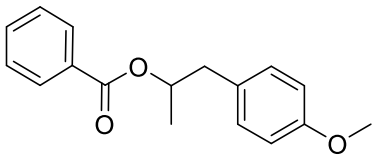
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.10 – 8.03 (m, 2H), 7.62 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 7.37 – 7.21 (m, 5H), 5.48 – 5.35 (m, 1H), 3.13 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.95 (dd, *J* = 13.7, 6.5 Hz, 1H), 1.39 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.1, 137.6, 132.8, 130.8, 129.5, 129.4, 128.4, 128.3, 126.5, 72.2, 42.4, 19.5.

HRMS (ESI): calcd for $C_{16}H_{17}O_2$ (M+H) 241.1223, found 241.1233, calcd for $C_{16}H_{20}NO_2$ (M+NH_4) 258.1489, found 258.1497, calcd for $C_{16}H_{16}O_2Na$ (M+Na) 263.1043, found 263.1052.

2-(4-Methoxyphenyl)-1-methylethyl benzoate (3ac) [23]



Yield 100 mg (74%, General procedure B). Colorless oil.

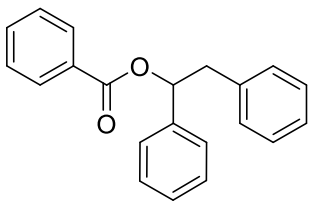
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.06 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.50 – 7.42 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.43 – 5.30 (m, 1H), 3.88 (s, 3H), 3.06 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.88 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.0, 158.3, 132.8, 130.8, 130.5, 129.6, 129.5, 128.3, 113.8, 72.3, 55.2, 41.4, 19.4.

HRMS (ESI): calcd for $C_{17}H_{22}NO_3$ (M+NH_4) 288.1594, found 288.1596, calcd for $C_{17}H_{18}O_3Na$ (M+Na) 293.1148, found 293.1155, calcd for $C_{17}H_{18}O_3K$ (M+K) 309.0888, found 309.0889.

1,2-Diphenylethyl benzoate (3ad) [24]



Yield 119 mg (79%, General procedure B). Colorless oil.

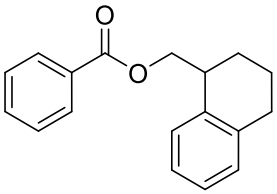
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.15 – 8.09 (m, 2H), 7.64 – 7.57 (m, 1H), 7.53 – 7.19 (m, 12H), 6.27 (dd, *J* = 7.5 Hz, *J* = 6.1 Hz, 1H), 3.43 (dd, *J* = 13.8, 7.5 Hz, 1H), 3.27 (dd, *J* = 13.8, 6.1 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.5, 140.2, 137.0, 133.0, 130.4, 129.7, 129.6, 128.5, 128.4, 128.3, 128.0, 126.7, 126.6, 77.3, 43.3.

HRMS (ESI): calcd for $C_{21}H_{22}NO_2$ (M+NH_4) 320.1645, found 320.1639, calcd for $C_{21}H_{18}O_2Na$ (M+Na) 325.1199, found 325.1198, calcd for $C_{21}H_{18}O_2K$ (M+K) 341.0938, found 341.0923.

1,2,3,4-Tetrahydronaphthalen-1-ylmethyl benzoate (3ae)



Yield 102 mg (77%, General procedure B). Colorless oil.

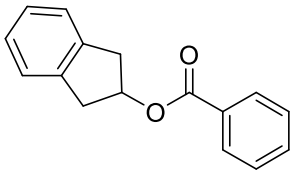
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.14 – 8.08 (m, 2H), 7.64 – 7.56 (m, 1H), 7.53 – 7.45 (m, 2H), 7.37 – 7.32 (m, 1H), 7.23 – 7.14 (m, 3H), 4.61 (dd, *J* = 11.0, 5.1 Hz, 1H), 4.44 (dd, *J* = 11.0, 9.1 Hz, 1H), 3.40 – 3.29 (m, 1H), 2.92 – 2.73 (m, 2H), 2.08 – 1.74 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.6, 137.9, 136.0, 132.9, 130.4, 129.6, 129.4, 128.1, 128.0, 126.4, 125.8, 68.6, 37.2, 29.6, 25.5, 19.4.

HRMS (ESI): calcd for $C_{18}H_{22}NO_2$ (M+NH_4) 284.1645, found 284.1647, calcd for $C_{18}H_{18}O_2Na$ (M+Na) 289.1199, found 289.1206, calcd for $C_{18}H_{18}O_2K$ (M+K) 305.0938, found 305.0951.

2,3-Dihydro-1H-inden-2-yl benzoate (3af) [25]



Yield 115 mg (97%, General procedure B). Colorless oil.

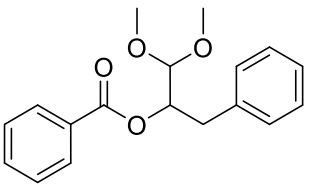
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.09 – 8.02 (m, 2H), 7.61 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 7.34 – 7.21 (m, 4H), 5.83 (hept, *J* = 3.3 Hz, 1H), 3.49 (dd, *J* = 16.9 Hz, *J* = 6.6 Hz, 2H), 3.22 (dd, *J* = 16.9 Hz, *J* = 3.3 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ:168.5, 140.5, 132.9, 130.4, 129.7, 128.3, 126.8, 124.7, 75.9, 39.7.

HRMS (ESI): calcd for $C_{16}H_{15}O_2$ (M+H) 239.1067, found 239.1075, calcd for $C_{16}H_{14}O_2Na$ (M+Na) 261.0886, found 291.0898.

1-Benzyl-2,2-dimethoxyethyl benzoate (3ag)



Yield 62 mg (41%, General procedure B). Colorless oil.

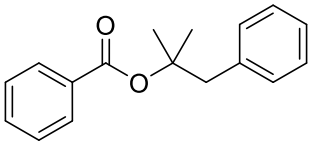
Chromatography: CH_2Cl_2. R_f 0.65.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.06 – 8.00 (m, 2H), 7.61 – 7.53 (m, 1H), 7.49 – 7.41 (m, 2H), 7.31 – 7.14 (m, 5H), 5.51 – 5.43 (m, 1H), 4.45 (d, *J* = 5.2 Hz, 1H), 3.49 (s, 3H), 3.46 (s, 3H), 3.18 (dd, *J* = 14.3, 4.1 Hz, 1H), 3.07 (dd, *J* = 14.3, 8.1 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 165.7, 137.2, 133.0, 129.7, 129.6, 129.3, 128.4, 128.3, 126.5, 103.9, 73.5, 55.1, 54.6, 35.5.

HRMS (ESI): calcd for $C_{18}H_{24}NO_4$ (M+NH_4) 318.1700, found 318.1698, calcd for $C_{18}H_{20}O_4Na$ (M+Na) 323.1254, found 323.1262, calcd for $C_{18}H_{20}O_4K$ (M+K) 339.0993, found 339.0993.

1,1-Dimethyl-2-phenylethyl benzoate (3ah) [22]



Yield 74 mg (58%, General procedure B). Colorless oil.

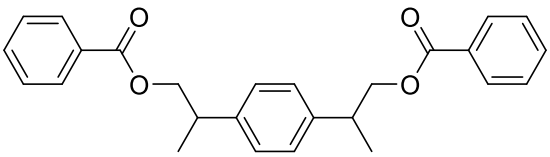
Chromatography: CH_2Cl_2. R_f 0.75.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.04 – 7.97 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.34 – 7.23 (m, 5H), 3.26 (s, 2H), 1.63 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.0, 137.3, 132.5, 132.0, 130.7, 129.4, 128.2, 128.0, 126.5, 83.0, 46.7, 26.2.

HRMS (ESI): calcd for $C_{17}H_{22}NO_2$ (M+NH_4) 272.1645, found 272.1666, calcd for $C_{17}H_{18}O_2Na$ (M+Na) 227.1199, found 227.1202.

Benzene-1,4-diyldipropane-2,1-diyl dibenzoate (3ai)



Yield 177 mg (88%, General procedure A, 4 equiv $PhCO_2H$ were used). Colorless oil.

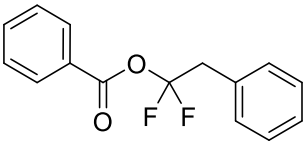
Chromatography: CH_2Cl_2. R_f 0.8.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 – 7.91 (m, 4H), 7.61 – 7.52 (m, 2H), 7.48 – 7.37 (m, 4H), 7.31 – 7.27 (m, 4H), 4.49 – 4.35 (m, 4H), 3.34 – 3.21 (m, 2H), 1.42 (d, *J* = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ:166.5, 141.5, 132.9, 130.3, 129.5, 128.3, 127.5, 69.9, 38.7, 18.0.

HRMS (ESI): calcd for $C_{26}H_{27}O_4$ (M+H) 403.1904, found 403.1901, calcd for $C_{26}H_{30}NO_4$ (M+NH_4^+) 420.2169, found 420.2166, calcd for $C_{26}H_{26}O_4Na$ (M+Na) 425.1723, found 425.1720.

1,1-Difluoro-2-phenylethyl benzoate (3aj) [26]



Yield 115 mg (88%, General procedure C), 124 mg (95%, General procedure D). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.7.

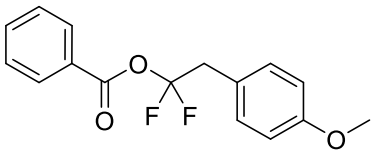
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.00 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.52 – 7.44 (m, 2H), 7.41 – 7.32 (m, 5H), 3.74 (t, *J* = 12.6 Hz, 2H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -70.6 (t, *J* = 12.6 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 161.6 (t, *J* = 2.7 Hz), 134.2, 131.4 (t, *J* = 2.7 Hz), 130.6, 130.3, 130.2, 128.8, 128.6, 127.8, 124.0 (t, *J* = 270 Hz), 41.2 (t, *J* = 28.6 Hz).

HRMS (ESI): calcd for $C_{15}H_{16}F_2NO_2$ (M+NH_4) 280.1144, found 280.1147, calcd for $C_{15}H_{15}F_2O_2Na$ (M+Na) 285.0698, found 285.0709.

1,1-Difluoro-2-(4-methoxyphenyl)ethyl benzoate (3ak)



Yield 133mg (91%, General procedure C), 137 mg (94%, General procedure D). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.7.

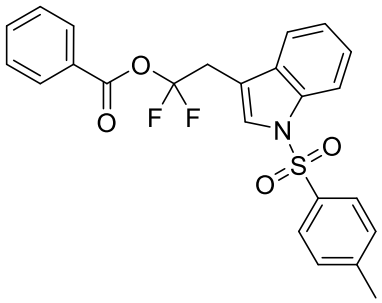
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.01 (d, *J* = 8.6 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.52 – 7.43 (m, 2H), 7.32 – 7.25 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.67 (t, *J* = 12.6 Hz, 2H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -71.0 ((t, *J* = 12.6 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 161.7 (t, *J* = 2.8 Hz), 159.3, 134.2, 131.4, 130.1, 128.7, 124.1 (t, *J* = 269 Hz), 123.4 (t, *J* = 4.7 Hz), 114.0, 55.2, 40.4 (t, *J* = 28.6 Hz).

HRMS (ESI): calcd for $C_{16}H_{18}F_2NO_3$ (M+NH_4) 310.1249, found 310.1241, calcd for $C_{16}H_{14}F_2O_3Na$ (M+Na) 315.0803, found 315.0800.

1,1-Difluoro-2-[1-(4-tolylsulfonyl)-1*H*-indol-3-yl]ethyl benzoate (3al)



Yield 175 mg (77%, General procedure C), 223 mg (98%, General procedure D). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.3.

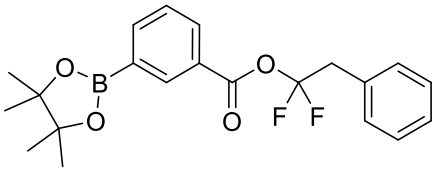
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.05 – 7.91 (m, 3H), 7.72 – 7.57 (m, 5H), 7.50 – 7.41 (m, 2H), 7.40 – 7.23 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 13.2 Hz, 2H), 2.28 (s, 3H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -69.7 (t, *J* = 12.7 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 161.6 (t, *J* = 2.9 Hz), 145.0, 135.0, 134.3, 130.6, 130.2, 129.8, 128.7, 128.2, 126.9, 126.7, 126.0, 125.0, 123.9, 123.6 (t, *J* = 272 Hz), 123.5, 119.7, 113.8, 112.7 (t, *J* = 3.8 Hz), 31.4 (t, *J* = 30.1 Hz), 21.5.

HRMS (ESI): calcd for $C_{24}H_{20}F_2NO_4S$ (M+H) 456.1076, found 456.1074, calcd for $C_{24}H_{23}F_2N_2O_4S$ (M+NH_4) 473.1341, found 473.1343, calcd for $C_{24}H_{19}F_2NO_4SNa$ (M+Na) 478.0895, found 478.0894, calcd for $C_{24}H_{19}F_2NO_4SK$ (M+K) 494.0634, found 494.0628.

3-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzoic acid 1,1-difluoro-2-phenyl-ethyl ester (3am)



Yield 180 mg (93%, General procedure D). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.4.

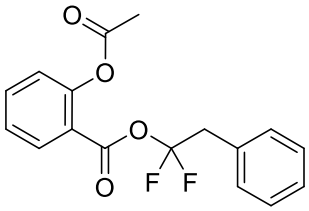
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.45 (s, 1H), 8.11 – 8.04 (m, 2H), 7.48 (t, *J* = 8.3 Hz, 1H), 7.42 – 7.30 (m, 5H), 3.73 (t, *J* = 12.6 Hz, 2H), 1.39 (s, 12H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: -70.6 (t, *J* = 12.6 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 161.7 (t, *J* = 2.2 Hz), 140.4, 136.4, 132.7, 131.3 (t, *J* = 3.3 Hz), 130.4, 128.6, 128.1, 128.0, 127.8, 127.5, 124.0 (t, *J* = 270 Hz), 84.3, 41.3 (t, *J* = 28.6 Hz), 24.3.

HRMS (ESI): calcd for $C_{21}H_{27}BF_2NO_4Na$ (M+NH_4) 406.1999, found 406.1989, calcd for $C_{21}H_{23}BF_2O_4Na$ (M+Na) 411.1553, found 411.1543.

1,1-Difluoro-2-phenylethyl 2-(acetyloxy)benzoate (3an)



Yield 157 mg (98%, General procedure D). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.65.

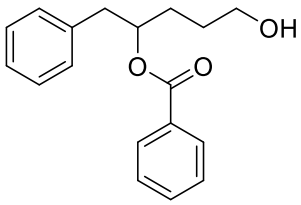
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.88 (dd, *J* = 8.0 Hz, *J* = 1.7 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.41 – 7.26 (m, 6H), 7.15 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 1H), 3.71 (t, *J* = 12.6 Hz, 2H), 2.32 (s, 3H).

^{19}F NMR (282 MHz, $CDCl_3$), δ: - 70.3 (t, *J* = 12.6 Hz).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 169.4, 159.4, 151.4, 135.1, 132.0, 131.2 (t, *J* = 3.3 Hz), 130.4, 128.7, 127.9, 127.6 126.2, 124.3, 124.0 (t, *J* = 281 Hz), 41.0 (t, *J* = 28 Hz), 20.8.

HRMS (ESI): calcd for $C_{17}H_{18}F_2NO_4$ (M+NH_4) 338.1198, found 338.1192, calcd for $C_{17}H_{14}F_2O_4Na$ (M+Na) 343.0752, found 343.0750, calcd for $C_{17}H_{14}F_2O_4K$ (M+K) 359.0492, found 359.0483.

1-benzyl-4-hydroxybutyl benzoate (3ao)



Yield 68 mg (48%, General procedure B). Colorless oil.

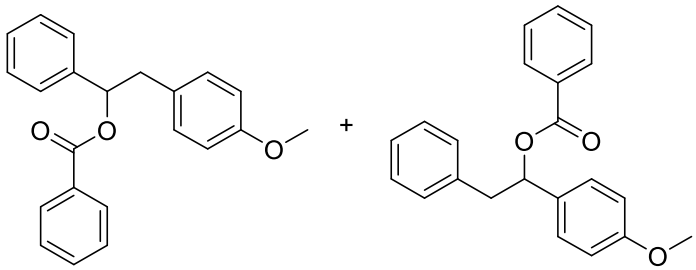
Chromatography: CH_2Cl_2. R_f 0.35.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.08 – 8.01 (m, 2H), 7.62 – 7.54 (m, 1H), 7.50 – 7.41 (m, 2H), 7. 34 – 7.18 (m, 5H), 5.44 – 5.34 (m, 1H), 3.76 (t, *J* = 6.2 Hz, 2H), 3.15 – 2.93 (m, 2H), 1.86 – 1.57 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.3, 137.4, 132.9, 130.5, 129.6, 129.5, 128.4, 128.3, 126.6, 75.2, 62.5, 41.7, 29.9, 28.6.

HRMS (ESI): calcd for $C_{18}H_{21}O_3$ (M+H) 285.1485, found 285.1490, calcd for $C_{18}H_{24}NO_3$ (M+NH_4) 302.1751, found 302.1750, calcd for $C_{18}H_{20}O_3Na$ (M+Na) 307.1305, found 307.1309.

Mixture of 2-(4-methoxyphenyl)-1-phenylethyl benzoate and 1-(4-methoxyphenyl)-2-phenylethyl benzoate (3ap)



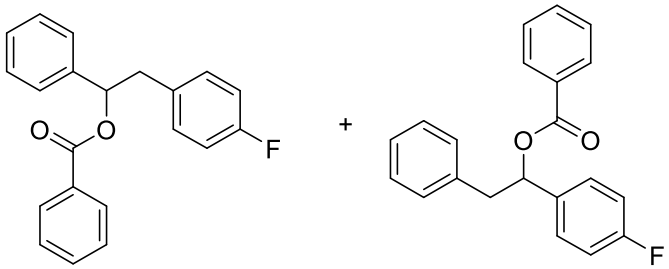
Yield 141 mg (85%, General procedure B). Colorless oil. Ratio of regioisomers: 2.4:1.

Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.16 – 8.07 (m, 2H), 7.64 – 7.07 (m, 12H), 6.27 – 6.18 (m, 1H), 3.83 (s, 0.9H), 3.80 (s, 2.1H), 3.47 – 3.14 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 167.4, 160.2, 158.1, 139.8, 130.1, 129.8, 129.5, 128.4, 128.3, 128.1, 127.8, 127.4, 126.8, 114.3, 114.0, 76.4, 75.8, 55.6, 55.5, 44.0.

Mixture of 1-(4-fluorophenyl)-2-phenylethyl benzoate and 2-(4-fluorophenyl)-1-phenylethyl benzoate (3aq)



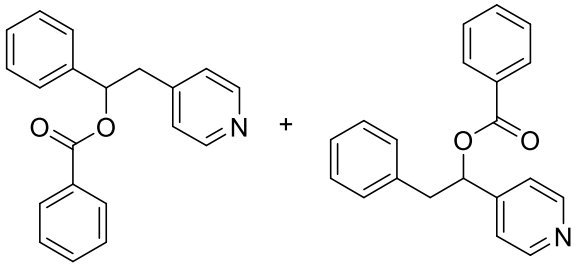
Yield 155 mg (97%, General procedure B). Colorless oil. Ratio of regioisomers: 1:1.4.

Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.15 – 8.07 (m, 2H), 7.6 – 7.55 (m, 2H), 7.54 – 7.44 (m, 2H). 7.43 – 6.88 (m, 8H), 6.26 – 6.18 (m, 1H), 3.47 – 3.18 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.5, 165.3 (d, J = 256 Hz), 158.3 (d, J = 255 Hz), 132.9, 130.4, 130.1, 130.0, 129.64, 129.62, 129.60, 129.42, 129.40, 128.7, 128.4, 127.3, 127.08, 127.06, 127.04126.0, 115.7, 115.4, 76.01, 75.96, 43.5, 43.3.

Mixture of 1-phenyl-2-pyridin-4-ylethyl benzoate and 2-phenyl-1-pyridin-4-ylethyl benzoate (3ar)



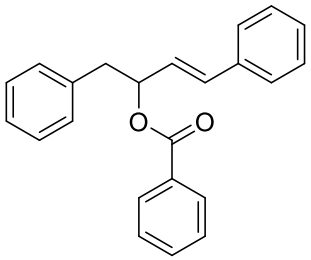
Yield 95 mg (63%, General procedure B). Colorless oil. Ratio of regioisomers: 1:16.

Chromatography: CH_2Cl_2. R_f 0.6.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.63 – 8.48 (m, 2H), 8.11 – 8.02 (m, 2H), 7.78 – 7.42 (m, 4H). 7.31 – 7.07 (m, 6H), 6.28 – 6.22 (m, 0.07H), 6.21 – 6.12 (m, 0.93H), 3.41 – 3.15 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ:166.5, 148.5, 146.6, 137.5, 132.9, 129.6, 128.4, 128.3, 127.5, 126.5, 124.0, 76.2, 43.2, 41.8.

(2*E*)-1-benzyl-3-phenylprop-2-en-1-yl benzoate (3as)



Yield 103 mg (62%, General procedure B). Colorless oil.

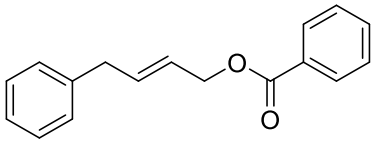
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.02 – 8.00 (m, 2H), 7.45 – 7.14 (m, 13H), 6.63 (d, J = 6.7 Hz, 1H), 6.11 – 6.06 (m, 1H), 5.85 (q, J = 6.7 Hz, 1H), 3.18 (ddd, J = 13.3, 6.5, 0.8 Hz, 1H), 2.93 (ddd, J = 13.3, 6.7, 0.8 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 167.2, 137.5, 135.7, 133.0, 131.7, 130.0, 129.3, 128.7, 128.5, 128.1, 127.9, 127.4, 127.3, 127.1, 125.3, 72.9, 41.5.

HRMS (ESI): calcd for $C_{23}H_{21}O_2$ (M+H) 329.4111, found 329.4105, calcd for $C_{23}H_{20}O_2Na$ (M+Na) 351.3929, found 351.3936.

(2*E*)-4-phenylbut-2-en-1-yl benzoate (3at)



Yield 81 mg (64%, General procedure B). Colorless oil.

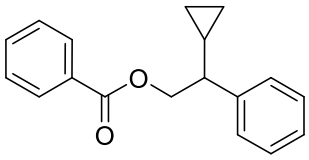
Chromatography: CH_2Cl_2. R_f 0.75.

^1H NMR (300 MHz, $CDCl_3$), δ: 8.11 – 8.06 (m, 2H), 7.62 – 7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 7.37 – 7.21 (m, 5H), 6.12 – 5.72 (m, 2H), 4.84 (dd, *J* = 6.2, 1.0 Hz, 1H), 3.46 (d, *J* = 6.7 Hz, 2H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 166.6, 138.9, 136.0, 133.4, 131.0, 129.2, 129.0, 128.6, 128.2, 126.2, 125.4, 61.9, 34.5

HRMS (ESI): calcd for $C_{17}H_{17}O_2$ (M+H) 253.3151, found 253.3146, calcd for $C_{17}H_{16}O_2Na$ (M+Na) 275.2970, found 275.2972.

2-Cyclopropyl-2-phenylethyl benzoate (3au)



Yield 92 mg (69%, General procedure B). Colorless oil.

Chromatography: CH_2Cl_2. R_f 0.75.

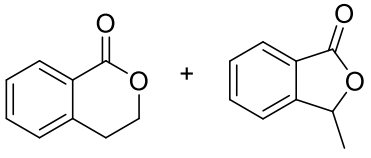
^1H NMR (300 MHz, $CDCl_3$), δ: 7.99 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.25 (m, 7H), 4.68 (dd, *J* = 10.9, 6.5 Hz, 1H), 4.57 (dd, *J* = 10.9, 7.2 Hz, 1H), 2.36 (dt, *J* = 9.8, 6.8 Hz, 1H), 1.24 – 1.08 (m, 1H), 0.75 – 0.64 (m, 1H), 0.58 – 0.46 (m, 1H), 0.45 – 0.36 (m, 1H), 0.25 – 0.11 (m, 1H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 166.5, 142.1, 132.8, 130.4, 129.6, 128.4, 128.3, 127.9, 126.7, 69.0, 50.0, 13.8, 5.3, 3.5.

HRMS (ESI): calcd for $C_{18}H_{19}O_2$ (M+H) 267.1380, found 267.1373, calcd for $C_{18}H_{22}NO_2$ ($M+NH_4$) 284.1645, found 284.1635, calcd for $C_{18}H_{18}O_2Na$ (M+Na) 289.1199, found 289.1196, calcd for $C_{18}H_{18}O_2K$ (M+K) 305.0938, found 305.0935.

Mixture of 3,4-dihydro-1*H*-isochromen-1-one and 3-methyl-2-benzofuran-1(3*H*)-one (3aw)

A screw capped tube with a pressure compensator containing a stirring bar, 2-vinylbenzoic acid (148 mg, 1 mmol), 2,7-di-*tert*-butyl-9-mesitylacridine (10 mol%, 14.4 mg) and 2 mL of CH_2Cl_2 was irradiated using 60W 400 nm LEDs for 8 hours. Then, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography.



Yield 50 mg (54%). Colorless oil. Ratio of isomers: 1.6:1.

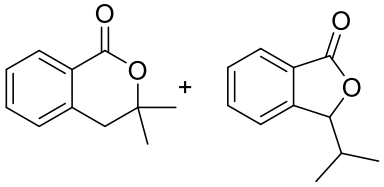
Chromatography: CH_2Cl_2. R_f 0.8.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.14 – 7.85 (m, 5.2H), 7.73 – 7.24 (m, 7.8H), 5.59 – 5.46 (m, 1H). 4.56 (t, *J* = 6.1 Hz, 3.2H), 3.08 (t, *J* = 6.1 Hz, 3.2H), 1.66 (d, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 168.8, 166.8, 149.6, 137.6, 134.2, 133.9, 129.6, 129.1, 129.0, 128.5, 127.9, 127.1, 126.4, 125.6, 123.9, 78.3, 65.2, 26.6, 20.9.

Mixture of 3,3-dimethyl-3,4-dihydro-1*H*-isochromen-1-one and 3-(1-methylethyl)-2-benzofuran-1(3*H*)-one (3ax)

A screw capped tube with a pressure compensator containing a stirring bar, 2-(2-methylprop-1-en-1-yl)benzoic acid (176 mg, 1 mmol), 2,7-di-*tert*-butyl-9-mesitylacridine (10 mol%, 14.4 mg) and 2 mL of CH_2Cl_2 was irradiated using 60W 400 nm LEDs for 8 hours. Then, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography.



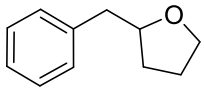
Yield 116 mg (66%). Colorless oil. Ratio of isomers: 1:1.5.

Chromatography: CH_2Cl_2. R_f 0.8.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.62 – 7.46 (m, 1.5H), 7.44 – 7.33 (m, 1.5H), 7.31 – 7.24 (m, 3H), 5.11 (d, *J* = 2.4 Hz, 1H). 2.80 (s, 2H), 1.21 (s, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.56 (d, *J* = 6.1 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 170.8, 148.9, 148.3, 140.7, 134.2, 133.9, 129.4, 129.0, 126.7, 125.6, 122.3, 122.1, 116.8, 85.6, 85.0, 33.4, 18.7, 16.0, 15.6.

2-Benzyltetrahydrofuran (4) [27]



Yield 67 mg (83%, General procedure B). Colorless oil.

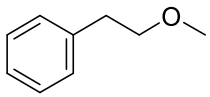
Chromatography: CH_2Cl_2. R_f 0.9.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.27 – 7.07 (m, 5H), 4.05 – 3.94 (m, 1H), 3.86 – 3.76 (m, 1H), 3.71 – 3.60 (m, 1H), 2.85 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.67 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.93 – 1.65 (m, 3H), 1.55 – 1.41 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 139.0, 129.3, 128.4, 126.2, 80.1, 67.9, 42.0, 31.0, 25.6.

HRMS (ESI): calcd for $C_{11}H_{15}O$ (M+H) 163.1117, found 163.1115, calcd for $C_{11}H_{18}NO$ (M+NH_4^+) 180.1383, found 180.1386, calcd for $C_{11}H_{14}ONa$ (M+Na) 185.0937, found 185.1039.

(2-Methoxyethyl)benzene (6) [26]



Yield 51 mg (65%, General procedure B). Colorless oil.

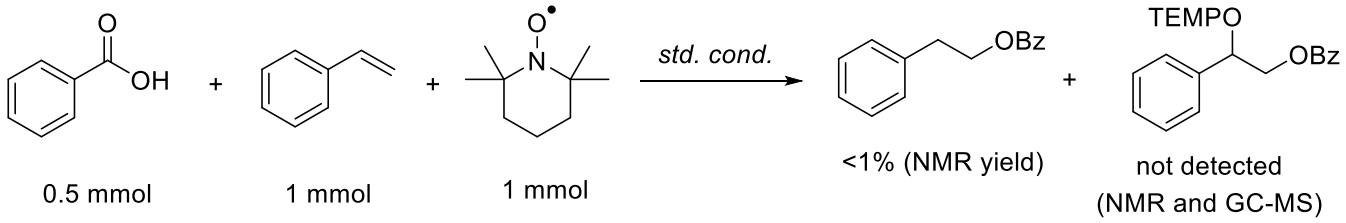
Chromatography: CH_2Cl_2. R_f 0.9.

^1H NMR (300 MHz, $CDCl_3$), δ: 7.40 – 7.21 (m, 5H), 3.65 (t, J = 7.1 Hz, 2H), 3.40 (s, 3H), 2.94 (t. J = 7.1 Hz, 2H).

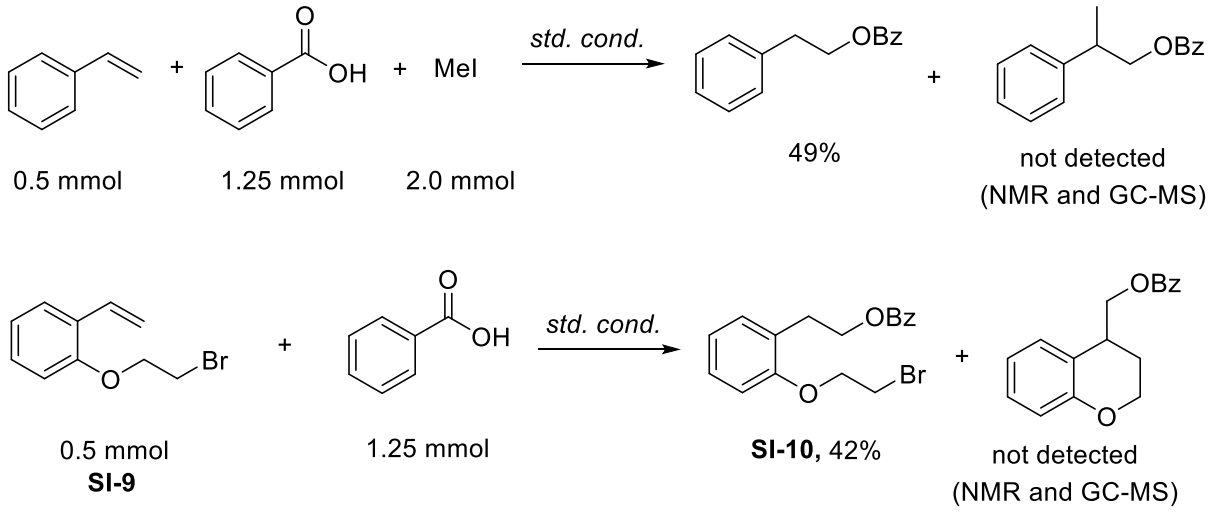
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 139.0, 128.9, 128.4, 126.2, 73.7, 58.7, 36.3.

HRMS (ESI): calcd for $C_9H_{12}ONa$ (M+Na) 159.0780, found 159.0780.

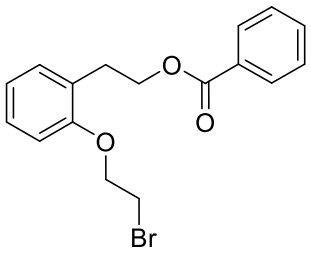
Radical trapping experiment



Carbanion trapping experiment



2-(2-Bromoethoxy)phenethyl benzoate (SI-10)



Yield 72 mg (42%, General procedure B). Colorless oil.

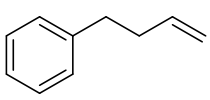
Chromatography: CH_2Cl_2. R_f 0.7.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.07 – 7.94 (m, 2H), 7.53 (m, 1H), 7.42 (m, 2H), 7.23 (m, 2H), 6.95 (m, 1H), 6.83 (m, 1H), 4.56 (t, J = 6.9 Hz, 2H), 4.31 (t, J = 6.1 Hz, 2H), 3.66 (t, J = 6.1 Hz, 2H), 3.14 (t, J = 6.9 Hz, 2H).

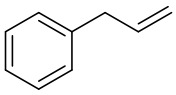
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 166.7, 156.3, 132.9, 131.2, 130.6, 129.7, 128.4, 128.1, 126.8, 121.4, 111.5, 67.9, 64.5, 30.2, 29.5.

HRMS (ESI): calcd for $C_{17}H_{18}Br^{79}O_3$ (M+H) 349.0434, found 349.0426, calcd for $C_{17}H_{18}Br^{81}O_3$ (M+H) 351.0414, found 351.0407, calcd for $C_{17}H_{17}Br^{79}O_3Na$ (M+Na) 371.0253, found 371.0248, calcd for $C_{17}H_{17}Br^{81}O_3Na$ (M+Na) 373.0234, found 373.0234.

Unsuccessful substrates



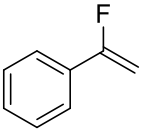
<5 %
alkene conversion



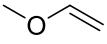
<5 %
alkene conversion

<5 %
alkene conversion

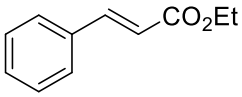
<5 %
alkene conversion



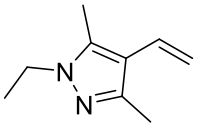
<10 %
alkene conversion



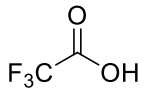
<5 %
acid conversion



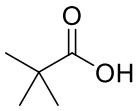
<10 %
alkene conversion



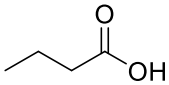
<20 % yield



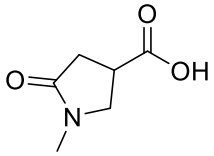
<5 % yield



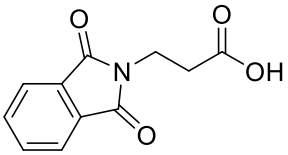
product was
not detected



<5 % yield



<5 % yield



<5 % yield

DFT calculations

All calculations were carried out using the Gaussian16 package.[29] Geometries of stationary points were optimized using the (u)ωB97XD functional with the def2-TZVP basis set and verified by vibrational analysis. Solvation effects were evaluated using the PCM model (acetonitrile as solvent). Oxidation potentials of the discussed species were predicted according to the literature protocol.[30] Energies of structures are given in Hartrees.

Benzyl radical

SCF Energy = -270.628417878
Zero-point correction = 0.115463
Thermal correction to Energy = 0.121075
Thermal correction to Enthalpy = 0.122019
Thermal correction to Gibbs Free Energy = 0.085826
Sum of electronic and zero-point Energies = -270.512955
Sum of electronic and thermal Energies = -270.507343
Sum of electronic and thermal Enthalpies = -270.506399
Sum of electronic and thermal Free Energies = -270.542591

C	-0.993575000	0.000003000	0.000086000
C	-0.252591000	-1.217659000	-0.000008000
C	-0.252606000	1.217629000	0.000004000
C	1.134023000	-1.211268000	-0.000007000
C	1.134066000	1.211249000	-0.000012000
C	1.838930000	0.000017000	0.000005000
H	-0.795312000	-2.166524000	-0.000042000
H	-0.795231000	2.166546000	-0.000002000
H	1.679857000	-2.157667000	-0.000015000
H	1.679837000	2.157687000	-0.000036000
H	2.930909000	-0.000021000	-0.000025000
C	-2.403632000	0.000020000	-0.000046000
H	-2.963864000	0.937571000	-0.000054000
H	-2.963878000	-0.937537000	0.000041000

Benzyl carbanion

SCF Energy = -270.727769551
Zero-point correction = 0.113545
Thermal correction to Energy = 0.119386
Thermal correction to Enthalpy = 0.120330
Thermal correction to Gibbs Free Energy = 0.084363
Sum of electronic and zero-point Energies = -270.614225
Sum of electronic and thermal Energies = -270.608384
Sum of electronic and thermal Enthalpies = -270.607439
Sum of electronic and thermal Free Energies = -270.643406

C	-1.040587000	-0.000043000	0.000040000
C	-0.244176000	-1.212626000	0.000203000
C	-0.244230000	1.212580000	0.000193000
C	1.140678000	-1.198259000	0.000005000
C	1.140617000	1.198293000	-0.000030000
C	1.877316000	0.000035000	-0.000177000
H	-0.768007000	-2.175757000	0.000408000
H	-0.768153000	2.175662000	0.000382000

H	1.673982000	-2.156564000	0.000046000
H	1.673887000	2.156619000	-0.000003000
H	2.969628000	0.000075000	-0.000478000
C	-2.428552000	-0.000016000	-0.000089000
H	-2.993715000	0.937807000	-0.000351000
H	-2.994027000	-0.937630000	-0.000869000

Phenethyl radical

SCF Energy = -309.883946182
Zero-point correction = 0.142416
Thermal correction to Energy = 0.150072
Thermal correction to Enthalpy = 0.151016
Thermal correction to Gibbs Free Energy = 0.108999
Sum of electronic and zero-point Energies = -309.741530
Sum of electronic and thermal Energies = -309.733874
Sum of electronic and thermal Enthalpies = -309.732930
Sum of electronic and thermal Free Energies = -309.774947

C	0.479224000	0.211664000	0.193687000
C	-0.404993000	1.278279000	-0.001752000
C	-0.042913000	-1.089099000	0.220390000
C	-1.773778000	1.055622000	-0.163704000
C	-1.408529000	-1.316427000	0.059013000
C	-2.280477000	-0.242949000	-0.133718000
H	-0.016716000	2.300229000	-0.029720000
H	0.634446000	-1.934768000	0.369508000
H	-2.446396000	1.902844000	-0.316908000
H	-1.795540000	-2.337886000	0.084397000
H	-3.350833000	-0.419577000	-0.261403000
C	1.962961000	0.445932000	0.383937000
H	2.232731000	0.240714000	1.436166000
H	2.172214000	1.526601000	0.248988000
C	2.834676000	-0.360314000	-0.516742000
H	3.884535000	-0.526733000	-0.264258000
H	2.488528000	-0.647667000	-1.513437000

Phenethyl carbanion

SCF Energy = -309.960909483
Zero-point correction = 0.141477
Thermal correction to Energy = 0.148649
Thermal correction to Enthalpy = 0.149593
Thermal correction to Gibbs Free Energy = 0.109820
Sum of electronic and zero-point Energies = -309.819432
Sum of electronic and thermal Energies = -309.812260
Sum of electronic and thermal Enthalpies = -309.811316
Sum of electronic and thermal Free Energies = -309.851090

C	0.490883000	0.127836000	0.259349000
C	-0.328412000	1.247849000	0.072408000
C	-0.118422000	-1.136910000	0.205995000
C	-1.704178000	1.119607000	-0.148227000
C	-1.488766000	-1.274411000	-0.002030000
C	-2.292102000	-0.143064000	-0.182406000
H	0.122394000	2.245039000	0.103758000
H	0.513252000	-2.021984000	0.316993000

H	-2.317155000	2.013372000	-0.293052000
H	-1.938532000	-2.270935000	-0.025805000
H	-3.366957000	-0.249186000	-0.349070000
C	1.982328000	0.260237000	0.477552000
H	2.221600000	-0.269362000	1.423089000
H	2.162893000	1.339784000	0.716434000
C	2.805440000	-0.352134000	-0.668045000
H	3.881902000	-0.180131000	-0.415570000
H	2.639974000	0.299347000	-1.564353000

9-Phenylacridinium cation

SCF Energy = -786.256111778
Zero-point correction = 0.280394
Thermal correction to Energy = 0.294458
Thermal correction to Enthalpy = 0.295403
Thermal correction to Gibbs Free Energy = 0.238737
Sum of electronic and zero-point Energies = -785.975718
Sum of electronic and thermal Energies = -785.961653
Sum of electronic and thermal Enthalpies = -785.960709
Sum of electronic and thermal Free Energies = -786.017375

C	2.065722000	-3.598217000	0.090941000
C	2.731395000	-2.399828000	0.047518000
C	1.986309000	-1.196862000	0.023390000
C	0.560362000	-1.222458000	0.031454000
C	-0.086701000	-2.495779000	0.093021000
C	0.646827000	-3.650118000	0.119752000
C	-0.147870000	0.000000000	0.000000000
C	0.560363000	1.222458000	-0.031454000
C	1.986310000	1.196861000	-0.023390000
C	2.731396000	2.399826000	-0.047518000
H	3.821644000	2.360324000	-0.034229000
C	2.065724000	3.598216000	-0.090941000
C	0.646829000	3.650118000	-0.119752000
C	-0.086700000	2.495779000	-0.093021000
H	2.637347000	-4.527701000	0.110870000
H	3.821643000	-2.360326000	0.034229000
H	-1.175547000	-2.531536000	0.123951000
H	0.144781000	-4.617038000	0.168618000
H	2.637350000	4.527700000	-0.110870000
H	0.144784000	4.617038000	-0.168618000
H	-1.175546000	2.531537000	-0.123951000
C	-1.633977000	0.000000000	0.000000000
C	-2.335818000	-0.423379000	-1.135092000
C	-2.335818000	0.423380000	1.135092000
C	-3.729143000	-0.416670000	-1.133780000
H	-1.788896000	-0.751746000	-2.021690000
C	-3.729143000	0.416671000	1.133780000
H	-1.788896000	0.751746000	2.021690000
C	-4.426793000	0.000001000	0.000000000
H	-4.271457000	-0.740700000	-2.024038000
H	-4.271457000	0.740702000	2.024038000
H	-5.518599000	0.000001000	0.000000000
N	2.618633000	-0.000001000	0.000000000
H	3.636771000	-0.000001000	0.000000000

9-Phenylacridinyl radical

SCF Energy = -786.398877452
Zero-point correction = 0.276770
Thermal correction to Energy = 0.291209
Thermal correction to Enthalpy = 0.292154
Thermal correction to Gibbs Free Energy = 0.233710
Sum of electronic and zero-point Energies = -786.122107
Sum of electronic and thermal Energies = -786.107668
Sum of electronic and thermal Enthalpies = -786.106724
Sum of electronic and thermal Free Energies = -786.165167

C	2.070961000	-3.637698000	0.094137000
C	2.725209000	-2.409636000	0.053640000
C	1.991300000	-1.218232000	0.025634000
C	0.566113000	-1.240049000	0.029428000
C	-0.062964000	-2.507731000	0.082877000
C	0.672024000	-3.684276000	0.112421000
C	-0.154865000	0.000000000	0.000000000
C	0.566113000	1.240049000	-0.029428000
C	1.991300000	1.218232000	-0.025634000
C	2.725209000	2.409636000	-0.053640000
H	3.816954000	2.364447000	-0.046079000
C	2.070961000	3.637698000	-0.094137000
C	0.672024000	3.684276000	-0.112421000
C	-0.062964000	2.507731000	-0.082877000
H	2.654817000	-4.560054000	0.115925000
H	3.816954000	-2.364447000	0.046079000
H	-1.153138000	-2.550661000	0.103150000
H	0.155711000	-4.645512000	0.152715000
H	2.654817000	4.560054000	-0.115925000
H	0.155711000	4.645512000	-0.152715000
H	-1.153138000	2.550661000	-0.103150000
C	-1.641510000	0.000000000	0.000000000
C	-2.358425000	-0.411733000	-1.132776000
C	-2.358425000	0.411733000	1.132776000
C	-3.752823000	-0.412714000	-1.133382000
H	-1.811851000	-0.734070000	-2.022632000
C	-3.752823000	0.412714000	1.133382000
H	-1.811851000	0.734070000	2.022632000
C	-4.454164000	0.000000000	0.000000000
H	-4.294552000	-0.735135000	-2.025491000
H	-4.294552000	0.735135000	2.025491000
H	-5.546401000	0.000000000	0.000000000
N	2.635538000	0.000000000	0.000000000
H	3.648246000	0.000000000	0.000000000

9-(2-Chlorophenyl)acridinium cation

SCF Energy = -1245.70802405
Zero-point correction = 0.270360
Thermal correction to Energy = 0.285757
Thermal correction to Enthalpy = 0.286701
Thermal correction to Gibbs Free Energy = 0.226135
Sum of electronic and zero-point Energies = -1245.437664

Sum of electronic and thermal Energies = -1245.422267
Sum of electronic and thermal Enthalpies = -1245.421323
Sum of electronic and thermal Free Energies = -1245.481889

C	2.170665000	3.619676000	-0.156396000
C	2.860542000	2.437264000	-0.075538000
C	2.143806000	1.217597000	-0.119842000
C	0.723470000	1.214241000	-0.247322000
C	0.049044000	2.471053000	-0.330653000
C	0.755314000	3.641082000	-0.285658000
C	0.045757000	-0.020992000	-0.280504000
C	0.766318000	-1.228883000	-0.190819000
C	2.186544000	-1.176067000	-0.070007000
C	2.946844000	-2.366429000	0.021408000
H	4.032537000	-2.308581000	0.110720000
C	2.299810000	-3.575198000	-0.000263000
C	0.885159000	-3.652675000	-0.112370000
C	0.136860000	-2.511849000	-0.205198000
H	2.718714000	4.562789000	-0.121624000
H	3.947090000	2.422898000	0.023472000
H	-1.036677000	2.479173000	-0.433255000
H	0.236774000	4.598208000	-0.350557000
H	2.881918000	-4.495537000	0.071631000
H	0.399689000	-4.629055000	-0.123538000
H	-0.948711000	-2.565238000	-0.292439000
C	-1.435791000	-0.052477000	-0.423429000
C	-2.271595000	0.030913000	0.696010000
C	-2.015693000	-0.173092000	-1.690759000
C	-3.657517000	-0.005400000	0.562181000
C	-3.400119000	-0.208935000	-1.833386000
H	-1.368178000	-0.238659000	-2.567506000
C	-4.218254000	-0.126293000	-0.707059000
H	-4.286721000	0.059293000	1.450592000
H	-3.840524000	-0.304201000	-2.827015000
H	-5.304033000	-0.156512000	-0.813495000
N	2.794269000	0.033032000	-0.041728000
H	3.808641000	0.053258000	0.045611000
Cl	-1.566317000	0.181748000	2.283360000

9-(2-Chlorophenyl)acridinyl radical

SCF Energy = -1245.85326004
Zero-point correction = 0.267086
Thermal correction to Energy = 0.282770
Thermal correction to Enthalpy = 0.283714
Thermal correction to Gibbs Free Energy = 0.221816
Sum of electronic and zero-point Energies = -1245.586174
Sum of electronic and thermal Energies = -1245.570490
Sum of electronic and thermal Enthalpies = -1245.569546
Sum of electronic and thermal Free Energies = -1245.631444

C	2.160310000	3.666151000	-0.163850000
C	2.844674000	2.456965000	-0.079449000
C	2.145090000	1.245638000	-0.123197000
C	0.726736000	1.232040000	-0.255160000
C	0.064671000	2.479824000	-0.338690000

C	0.765984000	3.675963000	-0.294223000
C	0.042349000	-0.024730000	-0.291771000
C	0.781352000	-1.246632000	-0.191951000
C	2.199279000	-1.190601000	-0.064175000
C	2.952169000	-2.366107000	0.036077000
H	4.038379000	-2.297936000	0.132346000
C	2.322342000	-3.607284000	0.016925000
C	0.929246000	-3.685510000	-0.101552000
C	0.174921000	-2.525436000	-0.202465000
H	2.716646000	4.604915000	-0.127886000
H	3.932478000	2.442505000	0.023429000
H	-1.022242000	2.489973000	-0.442579000
H	0.229116000	4.624208000	-0.361927000
H	2.920292000	-4.517367000	0.096203000
H	0.433856000	-4.658308000	-0.114026000
H	-0.911027000	-2.589844000	-0.295074000
C	-1.436700000	-0.063179000	-0.426950000
C	-2.284958000	0.030837000	0.685543000
C	-2.037152000	-0.202323000	-1.685726000
C	-3.672718000	-0.009866000	0.560061000
C	-3.422007000	-0.245931000	-1.829633000
H	-1.391846000	-0.277411000	-2.564029000
C	-4.240201000	-0.149785000	-0.704283000
H	-4.298561000	0.065753000	1.450374000
H	-3.863817000	-0.356044000	-2.821772000
H	-5.326597000	-0.184059000	-0.806846000
N	2.813951000	0.043026000	-0.039701000
H	3.821983000	0.067982000	0.054395000
Cl	-1.592273000	0.203780000	2.281300000

2,7-Di-*tert*-butyl-9-mesitylacridinium cation

SCF Energy = -1218.31457562
Zero-point correction = 0.587731
Thermal correction to Energy = 0.618444
Thermal correction to Enthalpy = 0.619388
Thermal correction to Gibbs Free Energy = 0.524877
Sum of electronic and zero-point Energies = -1217.726845
Sum of electronic and thermal Energies = -1217.696132
Sum of electronic and thermal Enthalpies = -1217.695187
Sum of electronic and thermal Free Energies = -1217.789698

C	0.001674000	-0.272717000	-0.000002000
C	1.222319000	-0.978917000	0.000017000
C	1.199769000	-2.400344000	0.000092000
N	0.006200000	-3.038427000	0.000094000
C	-1.189641000	-2.404385000	0.000042000
C	-1.216907000	-0.983185000	0.000013000
C	2.416106000	-3.123058000	0.000171000
H	2.399137000	-4.214127000	0.000264000
C	3.601665000	-2.438099000	0.000136000
C	2.486513000	-0.315425000	-0.000030000
H	2.470995000	0.773482000	-0.000116000
C	3.670522000	-1.007840000	0.000011000
C	-2.483271000	-0.324018000	-0.000019000
H	-2.471519000	0.764843000	-0.000037000

C	-3.665057000	-1.020312000	-0.000037000
C	-2.403550000	-3.131151000	0.000012000
H	-2.382882000	-4.222130000	0.000023000
C	-3.591496000	-2.450246000	-0.000037000
H	4.527182000	-3.017358000	0.000206000
H	-4.515047000	-3.032641000	-0.000076000
C	-0.001933000	1.216425000	0.000013000
C	-0.002150000	1.905396000	-1.225012000
C	-0.002353000	1.905322000	1.225080000
C	-0.005989000	3.301714000	-1.200163000
C	-0.006198000	3.301643000	1.200310000
C	-0.010803000	4.018078000	0.000094000
H	-0.004106000	3.845172000	-2.149159000
H	-0.004492000	3.845046000	2.149337000
C	0.011377000	1.152620000	2.529986000
H	-0.043166000	1.840308000	3.383790000
H	-0.836482000	0.453836000	2.599043000
H	0.931158000	0.555651000	2.633646000
C	0.011866000	1.152758000	-2.529954000
H	-0.835682000	0.453602000	-2.599023000
H	-0.042996000	1.840459000	-3.383728000
H	0.931913000	0.556206000	-2.633666000
C	-0.050812000	5.523357000	0.000129000
H	0.439142000	5.938373000	-0.891712000
H	-1.092882000	5.881810000	-0.000036000
H	0.438820000	5.938329000	0.892169000
C	5.038773000	-0.322506000	-0.000063000
C	4.908639000	1.205017000	-0.000288000
H	4.378833000	1.570696000	-0.893058000
H	4.378865000	1.570972000	0.892388000
H	5.910096000	1.659639000	-0.000374000
C	5.813785000	-0.750598000	-1.260250000
H	5.978937000	-1.837712000	-1.296347000
H	5.272290000	-0.457255000	-2.172618000
H	6.801102000	-0.264529000	-1.276856000
C	5.813728000	-0.750243000	1.260280000
H	6.801060000	-0.264200000	1.276776000
H	5.272205000	-0.456602000	2.172535000
H	5.978833000	-1.837353000	1.296719000
C	-5.035408000	-0.339129000	-0.000104000
C	-5.809149000	-0.769221000	1.260177000
H	-6.797733000	-0.285731000	1.276844000
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H	-5.268368000	-0.474371000	2.172481000
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2,7-Di-*tert*-butyl-9-mesitylacridinyl radical

SCF Energy = -1218.45191085
Zero-point correction = 0.584604
Thermal correction to Energy = 0.614464
Thermal correction to Enthalpy = 0.615408
Thermal correction to Gibbs Free Energy = 0.524112
Sum of electronic and zero-point Energies = -1217.867307
Sum of electronic and thermal Energie s= -1217.837447
Sum of electronic and thermal Enthalpies = -1217.836503
Sum of electronic and thermal Free Energies = -1217.927799

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References

1. C. N. Kona, R. Oku, S. Nakamura, M. Miura, K. Hirano and Y. Nishii, Aromatic halogenation using carborane catalyst, *Chem*, 2024, **10**, 402-413.
2. L. J. Street, F. Sternfeld, R. A. Jelley, A. J. Reeve, R. W. Carling, K. W. Moore, R. M. McKernan, B. Sohal, S. Cook, A. Pike, G. R. Dawson, F. A. Bromidge, K. A. Wafford, G. R. Seabrook, S. A. Thompson, G. Marshall, G. V. Pillai, J. L. Castro, J. R. Atack and A. M. MacLeod, Synthesis and Biological Evaluation of 3-Heterocyclyl-7,8,9,10-tetrahydro-(7,10-ethano)-1,2,4-triazolo[3,4-a]phthalazines and Analogues as Subtype-Selective Inverse Agonists for the GABAAα5 Benzodiazepine Binding Site, *J. Med. Chem.*, 2004, **47**, 3642-3657.
3. F. Benfatti, G. Cardillo, S. Contaldi, L. Gentilucci, E. Mosconi, A. Tolomelli, E. Juaristi and G. Reyes-Rangel, A convenient synthesis of functionalized isoxazolines and related 5-hydroxyisoxazolidine-4-carboxylates, *Tetrahedron*, 2009, **65**, 2478-2483.
4. R. C. Silva, A. De Freitas, B. Vicente, V. Midlej and M. S. dos Santos, Exploring novel pyrazole-nitroimidazole hybrids: Synthesis and antiprotozoal activity against the human pathogen trichomonas vaginalis, *Biorg. Med. Chem.*, 2024, **102**, 117679.
5. M. O. Zubkov, M. D. Kosobokov, Vitalij V. Levin, V. A. Kokorekin, A. A. Korlyukov, J. Hu and A. D. Dilman, A novel photoredox-active group for the generation of fluorinated radicals from difluorostyrenes, *Chem. Sci.*, 2020, **11**, 737-741.
6. M. Ashram, Synthesis of calix[4]crowns containing soft donor atoms and a study of their metal–cation binding properties: highly selective receptors for Cu^{2+}, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1662-1668.
7. R. R. III Cesati, J. de Armas, A. H. Hoveyda, Olefins Turned Alkylating Agents: Diastereoselective Intramolecular Zr-Catalyzed Olefin Alkylations, *Org. Lett.* 2002, **4**, 395–398.
8. C.-T. Chen and Y. S. Munot, Direct Atom-Efficient Esterification between Carboxylic Acids and Alcohols Catalyzed by Amphoteric, Water-Tolerant $TiO(acac)_2$, *J. Org. Chem.*, 2005, **70**, 8625-8627.
9. G. Pathak, D. Das and S. L. Rokhum, A microwave-assisted highly practical chemoselective esterification and amidation of carboxylic acids, *RSC Adv.*, 2016, **6**, 93729-93740.
10. K. Umetsu and N. Asao, Gold-catalyzed transesterification of ortho-alkynylbenzoic acid esters: a novel protecting group for alcohols and phenols, *Tetrahedron Lett.*, 2008, **49**, 7046-7049.
11. X. Huang, X. Li, M. Zou, S. Song, C. Tang, Y. Yuan and N. Jiao, From Ketones to Esters by a Cu-Catalyzed Highly Selective C(CO)–C(alkyl) Bond Cleavage: Aerobic Oxidation and Oxygenation with Air, *J. Am. Chem. Soc.*, 2014, **136**, 14858-14865.
12. P. Villo, O. Dalla-Santa, Z. Szabó and H. Lundberg, Kinetic Analysis as an Optimization Tool for Catalytic Esterification with a Moisture-Tolerant Zirconium Complex, *J. Org. Chem.*, 2020, **85**, 6959-6969.
13. N. Iranpoor, H. Firouzabadi, E. Etemadi-Davan, A. Nematollahi and H. R. Firouzi, A novel nickel-catalyzed synthesis of thioesters, esters and amides from aryl iodides in the presence of chromium hexacarbonyl, *New J. Chem.*, 2015, **39**, 6445-6452.
14. M. Dinesh, R. Ranganathan, S. Archana, M. Sathishkumar, M. S. Roshan Banu and A. Ponnuswamy, Staudinger's phosphazene as an efficient esterifying reagent, *Synth. Commun.*, 2016, **46**, 1454-1460.

15. S. Mayr, M. Marin-Luna and H. Zipse, Size-Driven Inversion of Selectivity in Esterification Reactions: Secondary Beat Primary Alcohols, *J. Org. Chem.*, 2021, **86**, 3456-3489.
16. M. Yadegari, M. Moghadam, S. Tangestaninejad, V. Mirkhani and I. Mohammadpoor-Baltork, Electron-deficient [TiIV(salophen)$(OTf)_2$]: A new and highly efficient catalyst for the acetylation of alcohols and phenols with acetic anhydride, *Polyhedron*, 2011, **30**, 2237-2243.
17. L. De Luca, G. Giacomelli and A. Porcheddu, Mild and Highly Selective Formyl Protection of Primary Hydroxyl Groups, *J. Org. Chem.*, 2002, **67**, 5152-5155.
18. V. Do Cao, S. Lee and S. Joung, In-situ Utilization of Non-Stabilized Diazoalkanes from (3+2) Cycloaddition of Linear N,N-Disilyl Enamines and Azides, *Adv. Synth. Catal.*, 2024, **366**, 114-120.
19. J. S. Quesnel, A. Fabrikant and B. A. Arndtsen, A flexible approach to Pd-catalyzed carbonylations via aroyl dimethylaminopyridinium salts, *Chem. Sci.*, 2016, **7**, 295-300.
20. S. Mayr and H. Zipse, Size-Induced Inversion of Selectivity in the Acylation of 1,2-Diols, *Chem. Eur. J.*, 2021, **27**, 18084-18092.
21. S. Lim, M. Ji, X. Wang, C. Lee and H.-Y. Jang, Copper-Catalyzed Cross-Coupling of Thiols, Alcohols, and Oxygen for the Synthesis of Esters, *Eur. J. Org. Chem.*, 2015, **2015**, 591-595.
22. O. P. Williams, A. F. Chmiel, M. Mikhael, D. M. Bates, C. S. Yeung and Z. K. Wickens, Practical and General Alcohol Deoxygenation Protocol, *Angew. Chem. Int. Ed.*, 2023, **62**, e202300178.
23. J. Perkowski and D. A. Nicewicz, Direct Catalytic Anti-Markovnikov Addition of Carboxylic Acids to Alkenes, *J. Am. Chem. Soc.*, 2013, **135**, 10334-10337.
24. S. C. Mallojjala, V. O. Nyagilo, S. A. Corio, A. Adili, A. Dagar, K. A. Loyer, D. Seidel and J. S. Hirschi, Probing the Free Energy Landscape of Organophotoredox-Catalyzed Anti-Markovnikov Hydrofunctionalization of Alkenes, *J. Am. Chem. Soc.*, 2022, **144**, 17692-17699.
25. S.-M. Wang, N. S. Alharbi and H.-L. Qin, Construction of Esters through Sulfuryl Fluoride (SO_2F_2) Mediated Dehydrative Coupling of Carboxylic Acids with Alcohols at Room Temperature, *Synthesis*, 2019, **51**, 3901-3907.
26. Z. Song and W. Yi, One-Pot Synthesis of Fluorovinyl Acetates and β,β-Difluoro Carboxylates from a Hypervalent Iodine and Hydrogen Fluoride-Based Fluorination Reagent, *Adv. Synth. Catal.*, 2016, **358**, 2727-2732.
27. D. Crich, X. Huang and M. Newcomb, Inter- and Intramolecular Pathways for the Formation of Tetrahydrofurans from β-(Phosphatoxy)alkyl Radicals. Evidence for a Dissociative Mechanism, *J. Org. Chem.*, 2000, **65**, 523-529.
28. X.-K. Fu and S.-Y. Wen, Preparation of Zirconium (Benzyldiethylammonio-Methylphosphonate Chloride) and Ptc Reactions, *Synth. Commun.*, 1995, **25**, 2435-2442.
29. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N.

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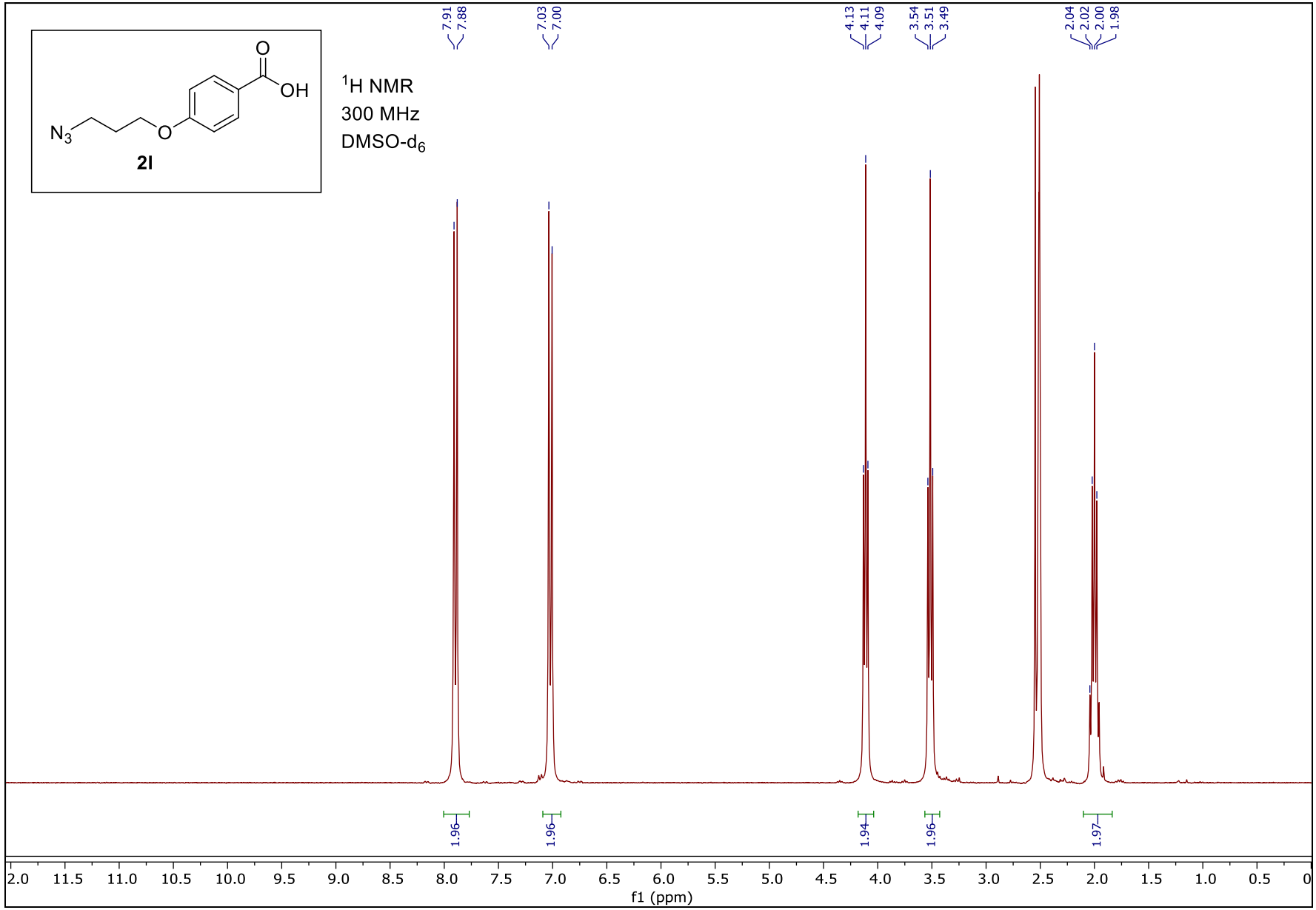
30. H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* 2016, **27**, 714-723.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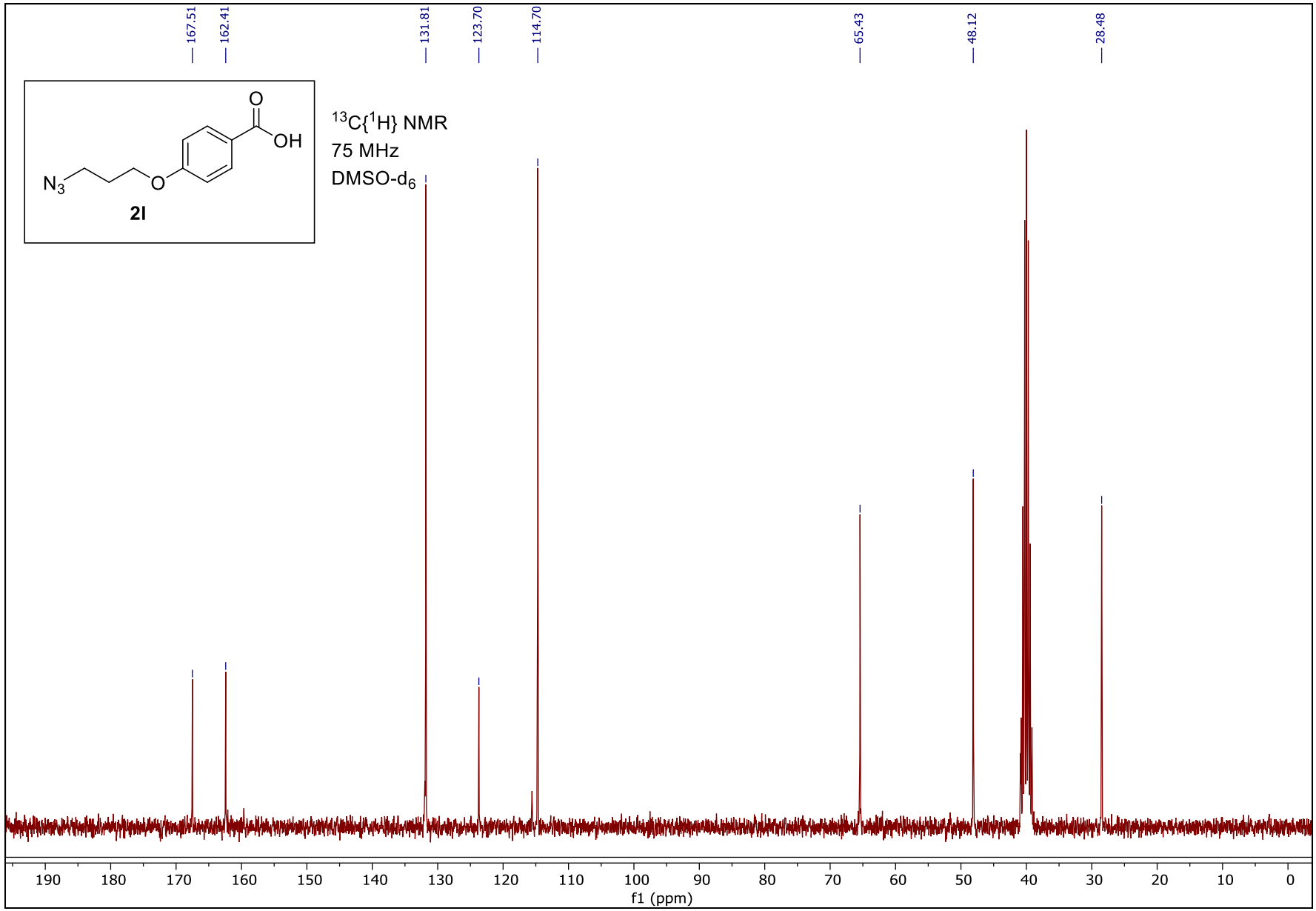
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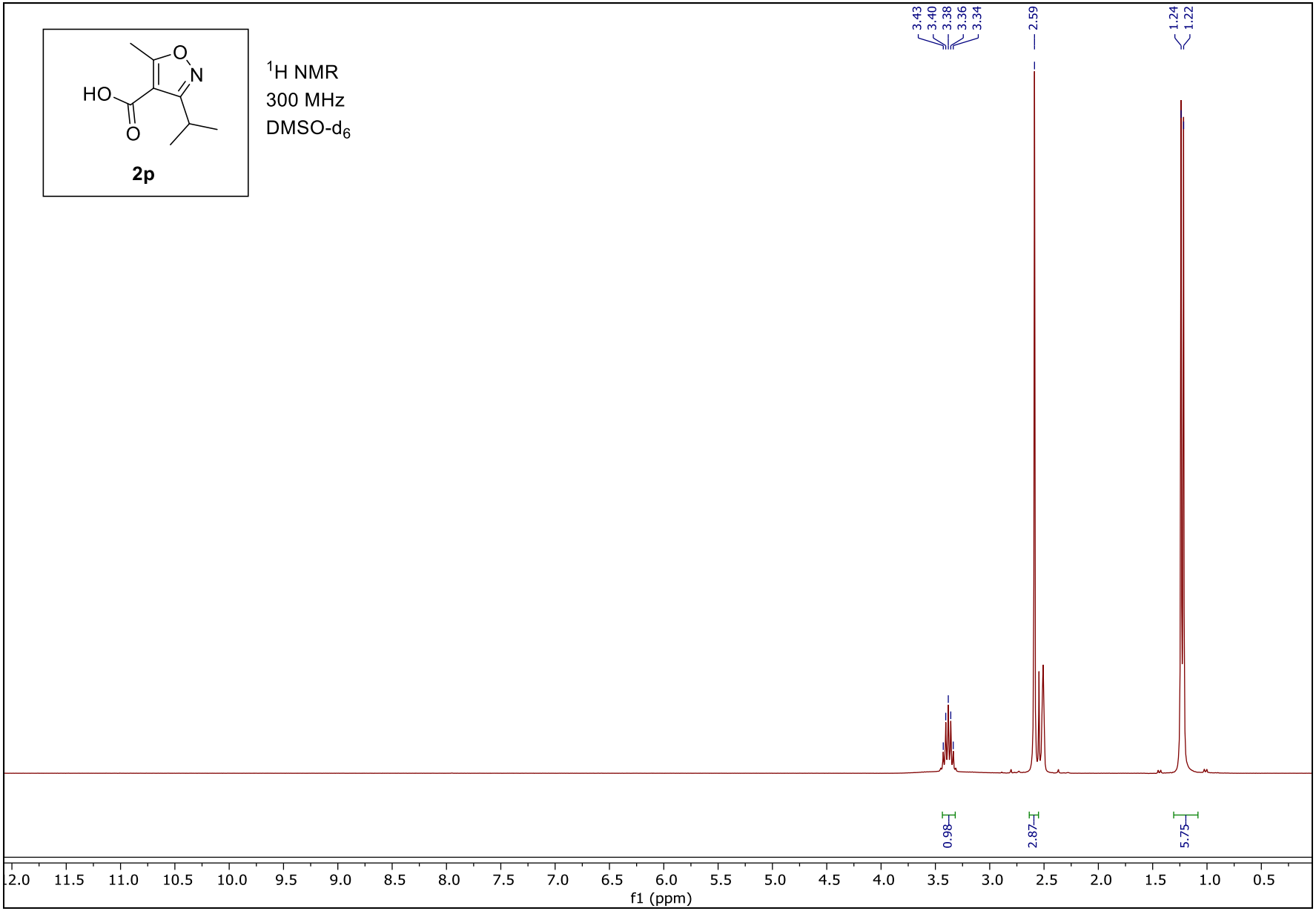
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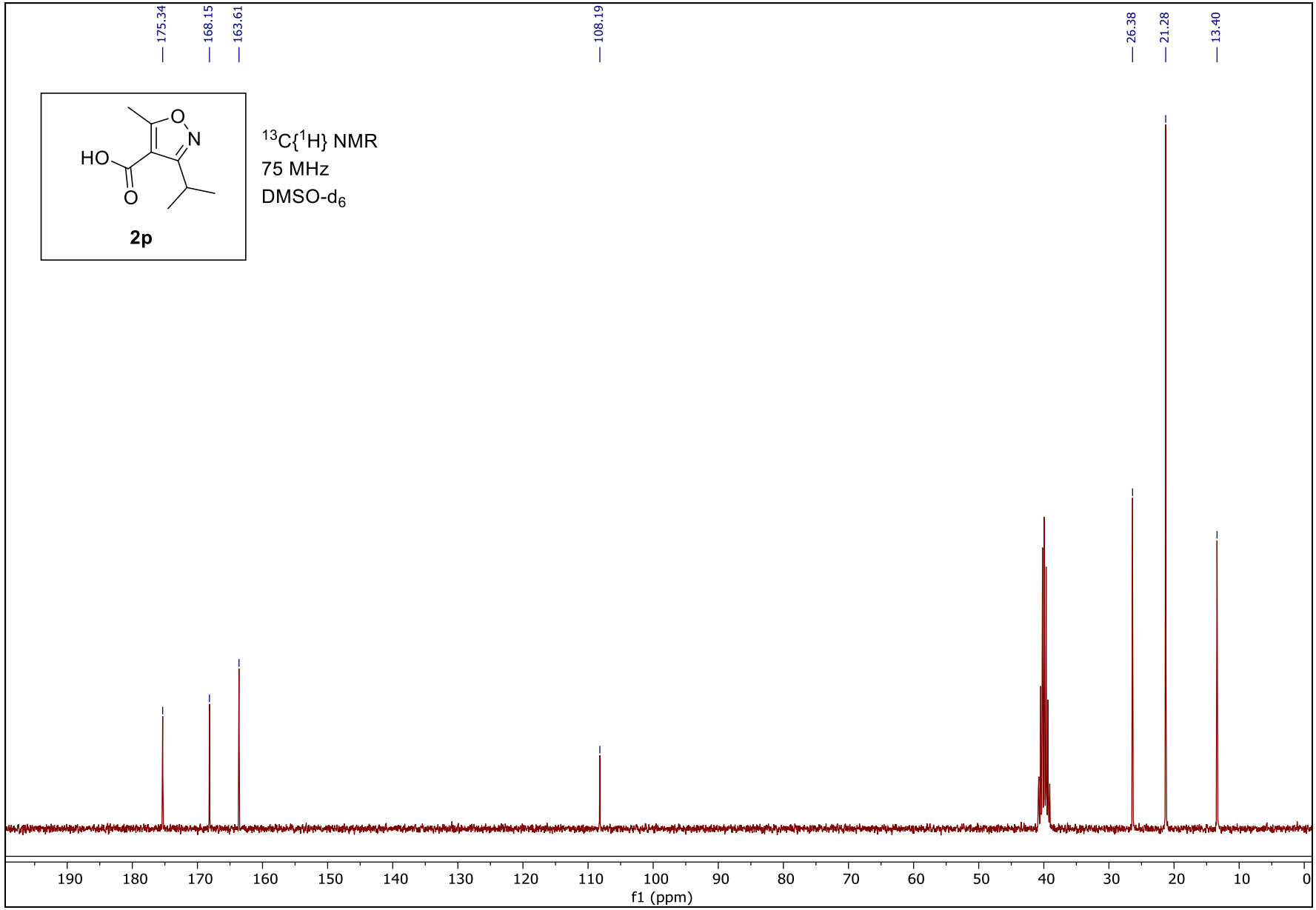
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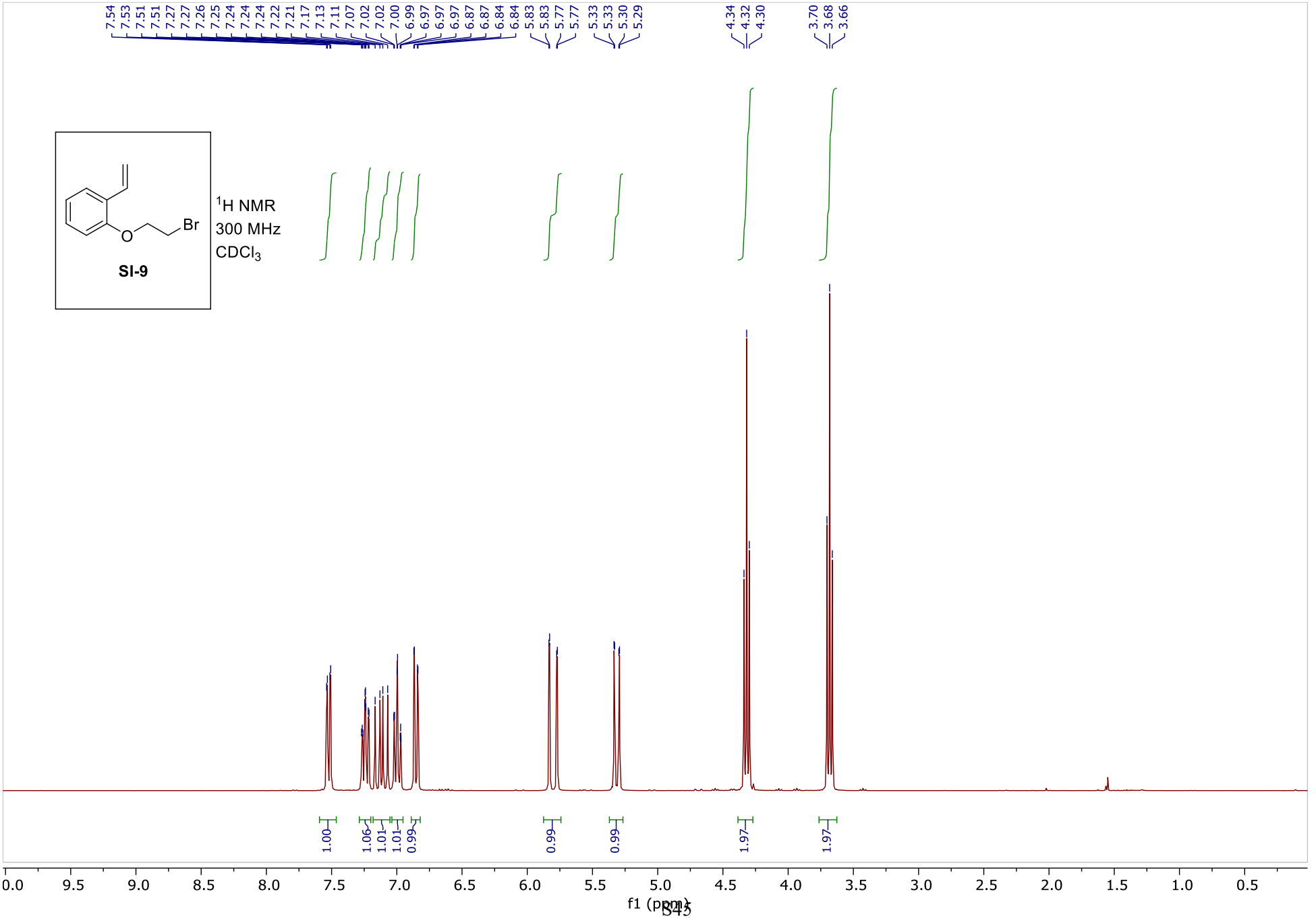
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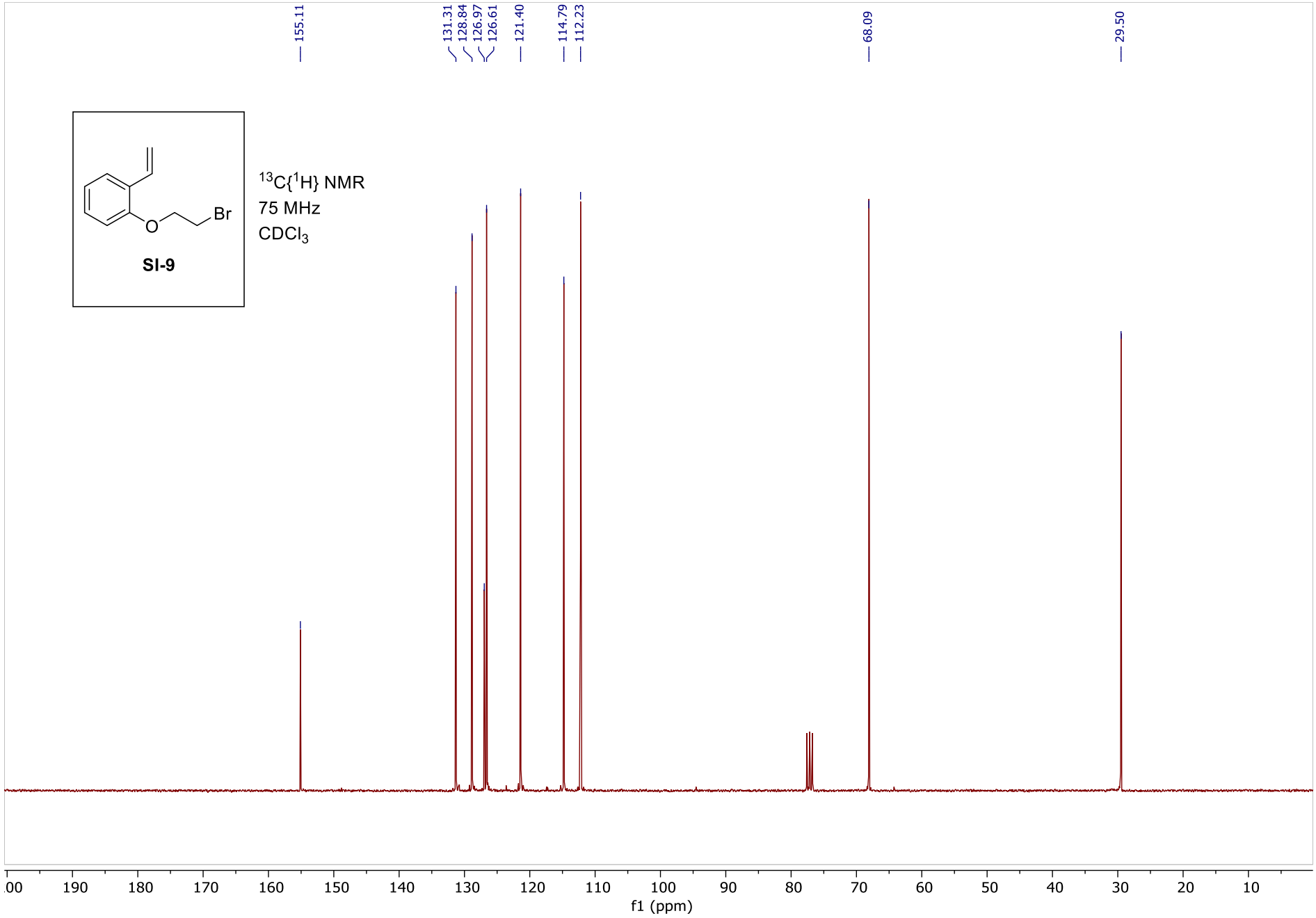
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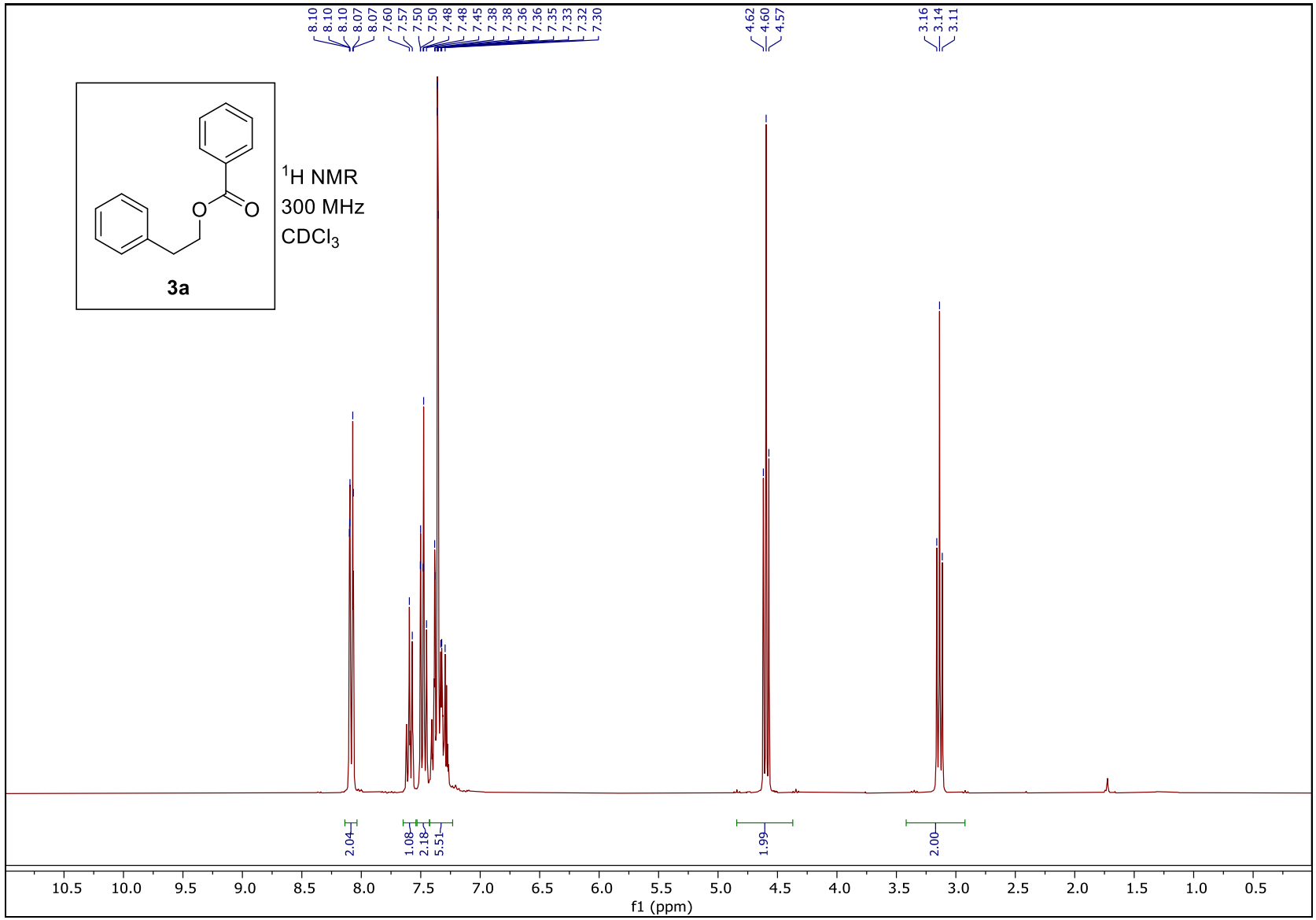
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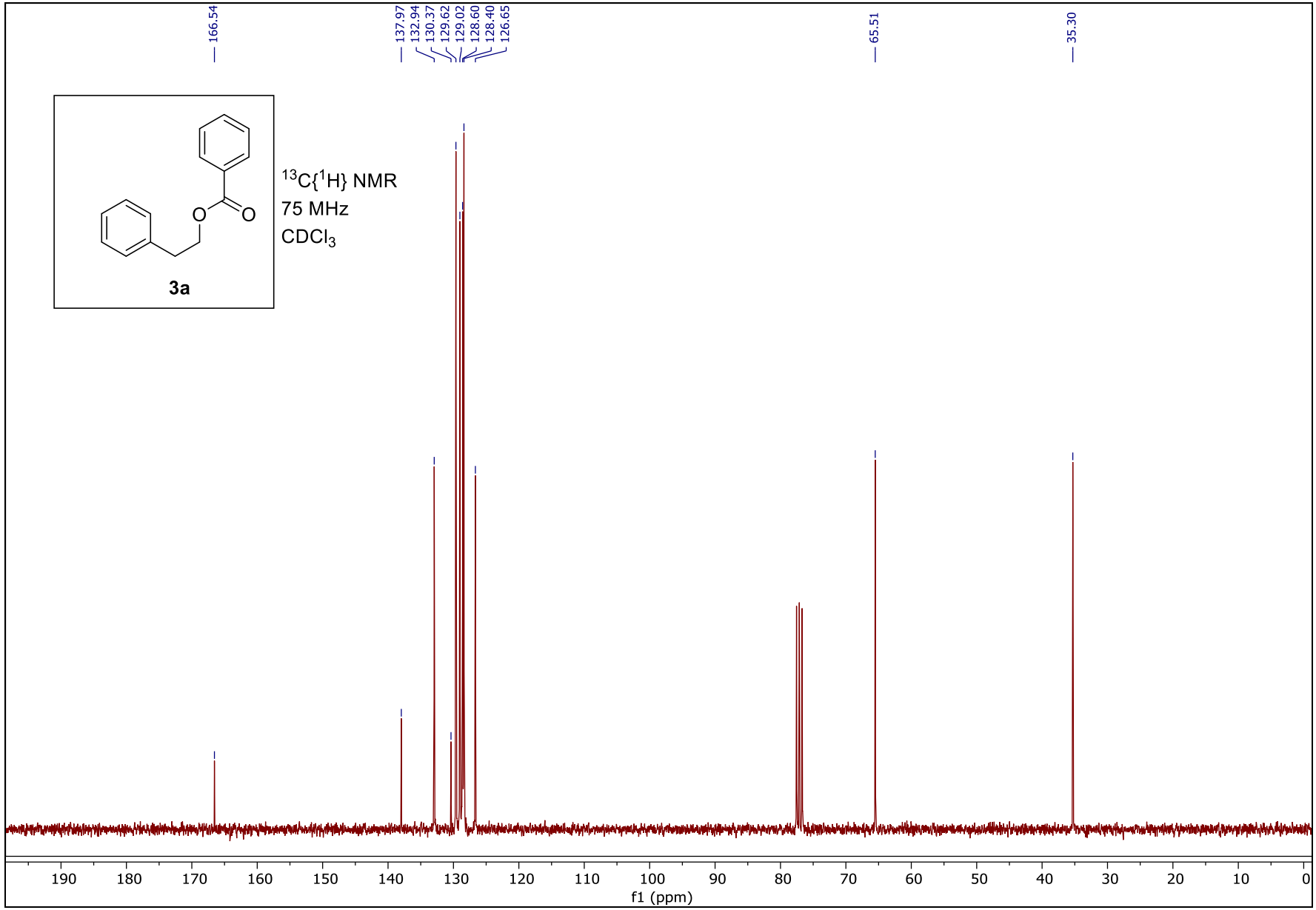
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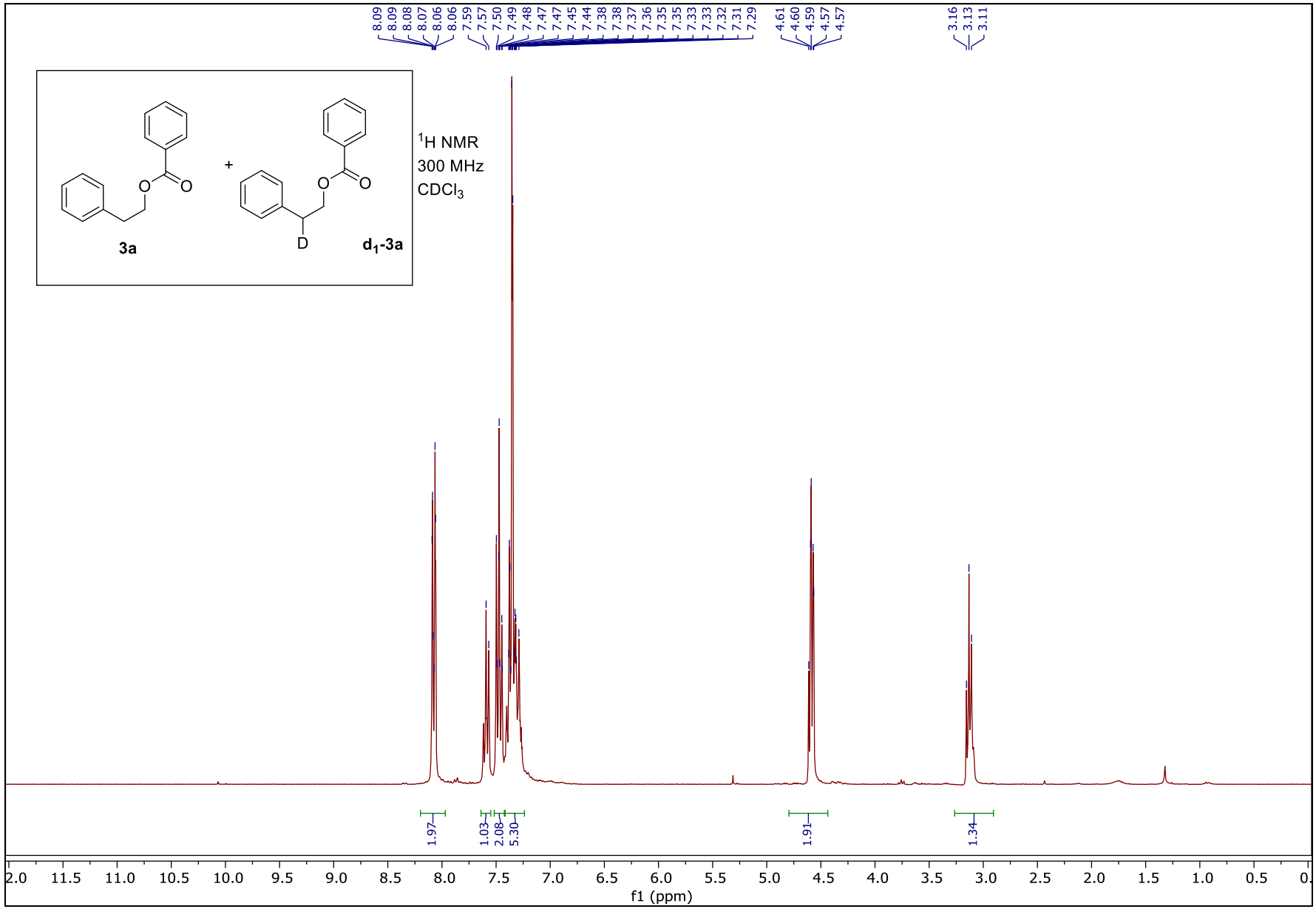
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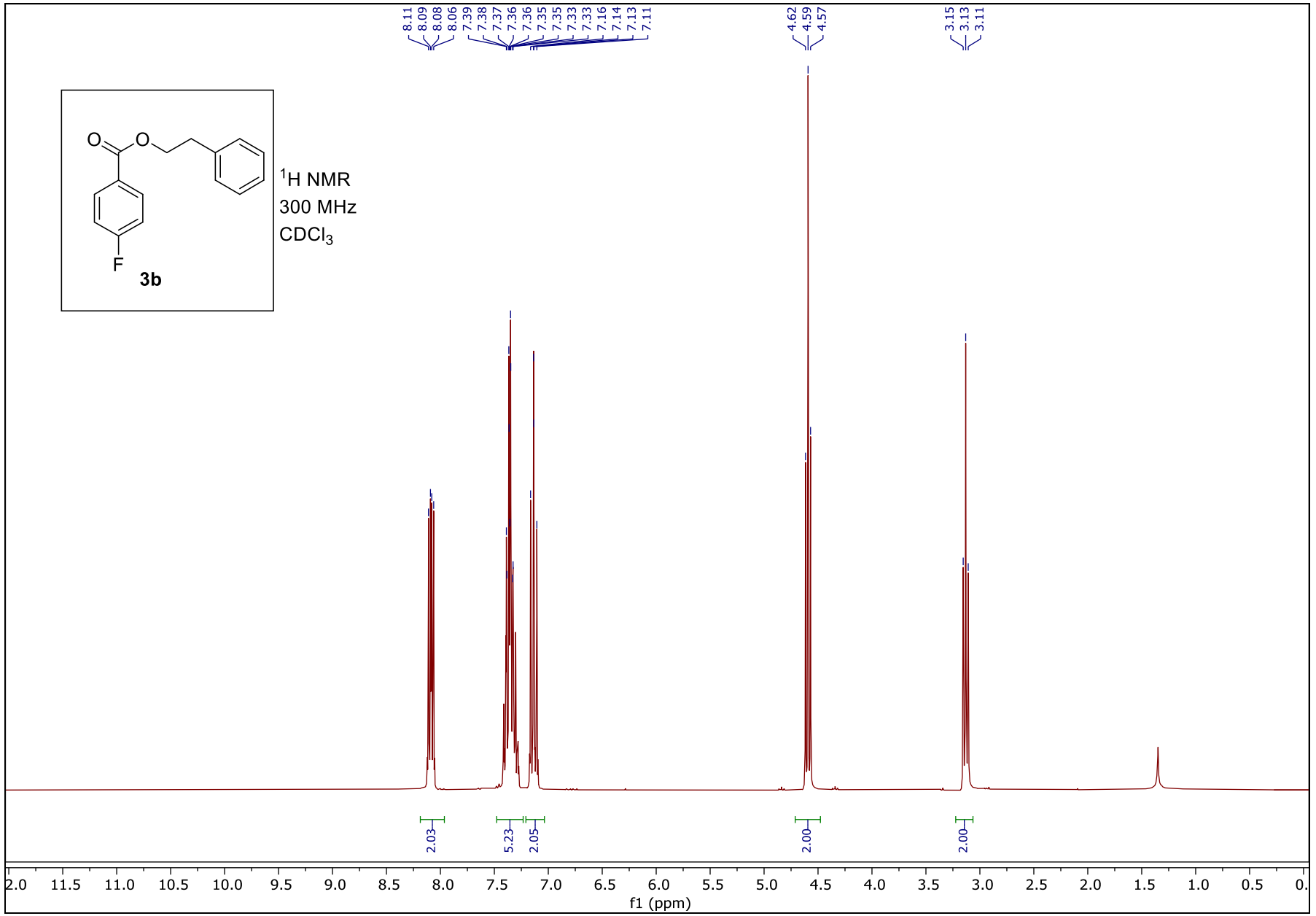
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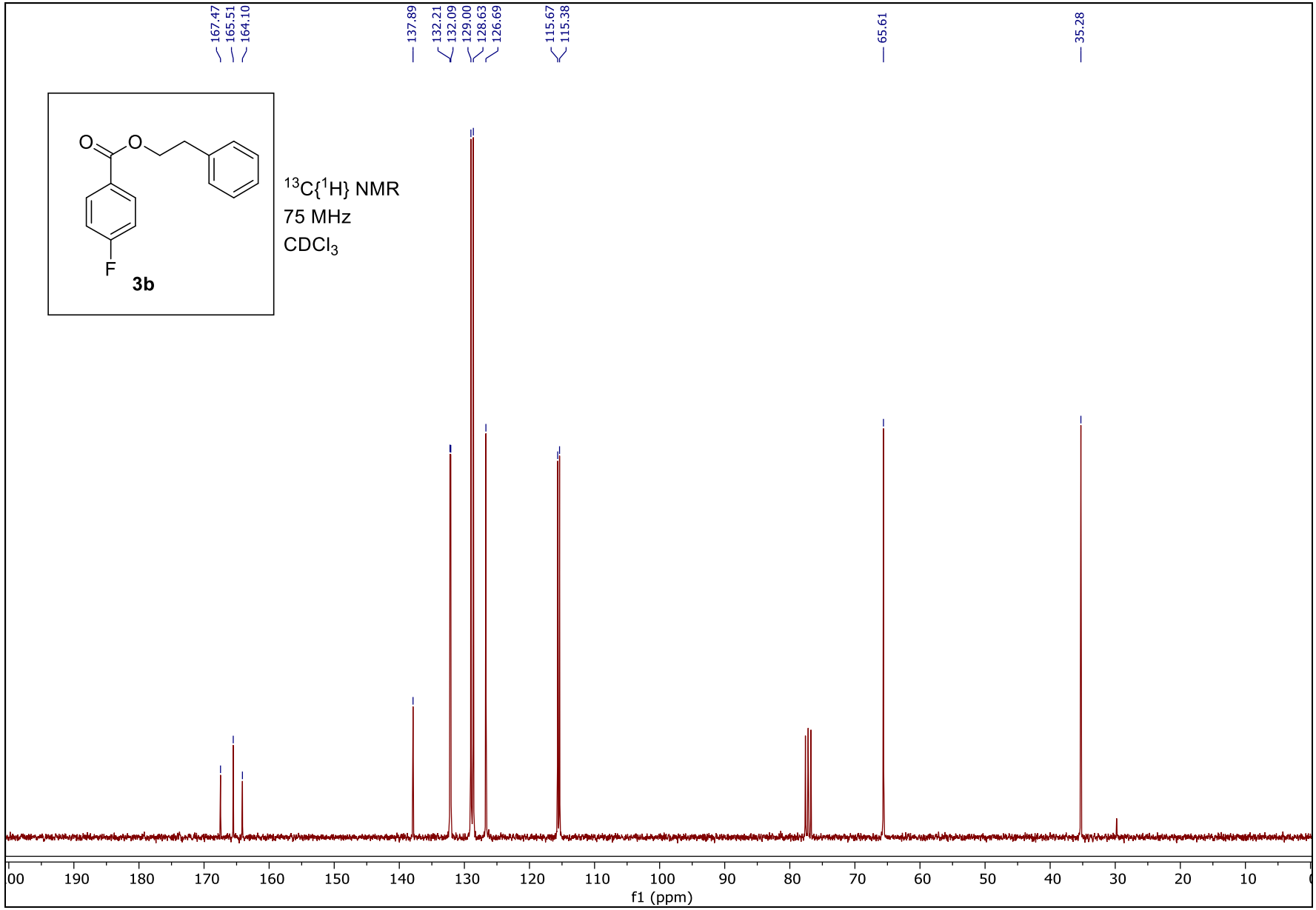
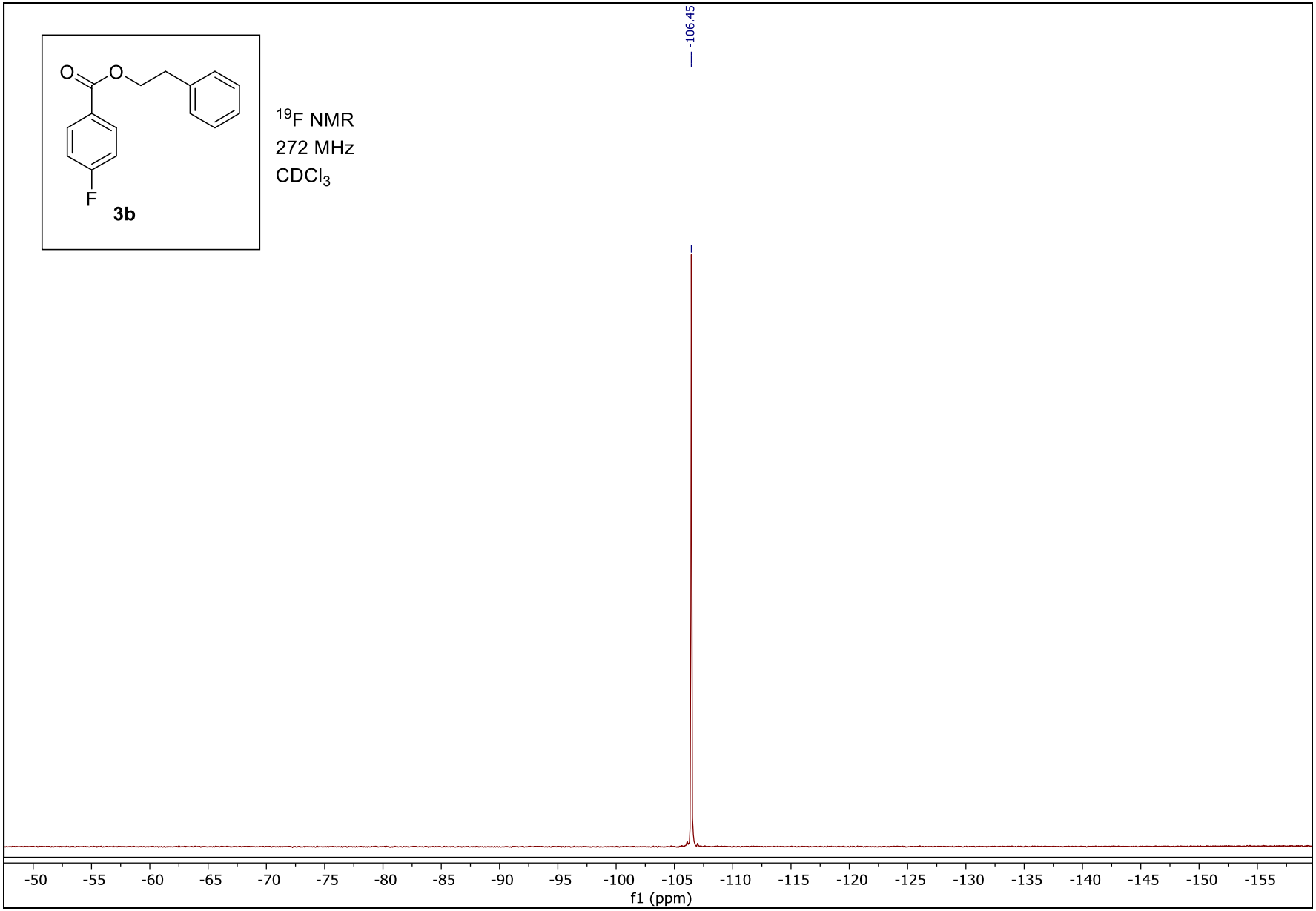
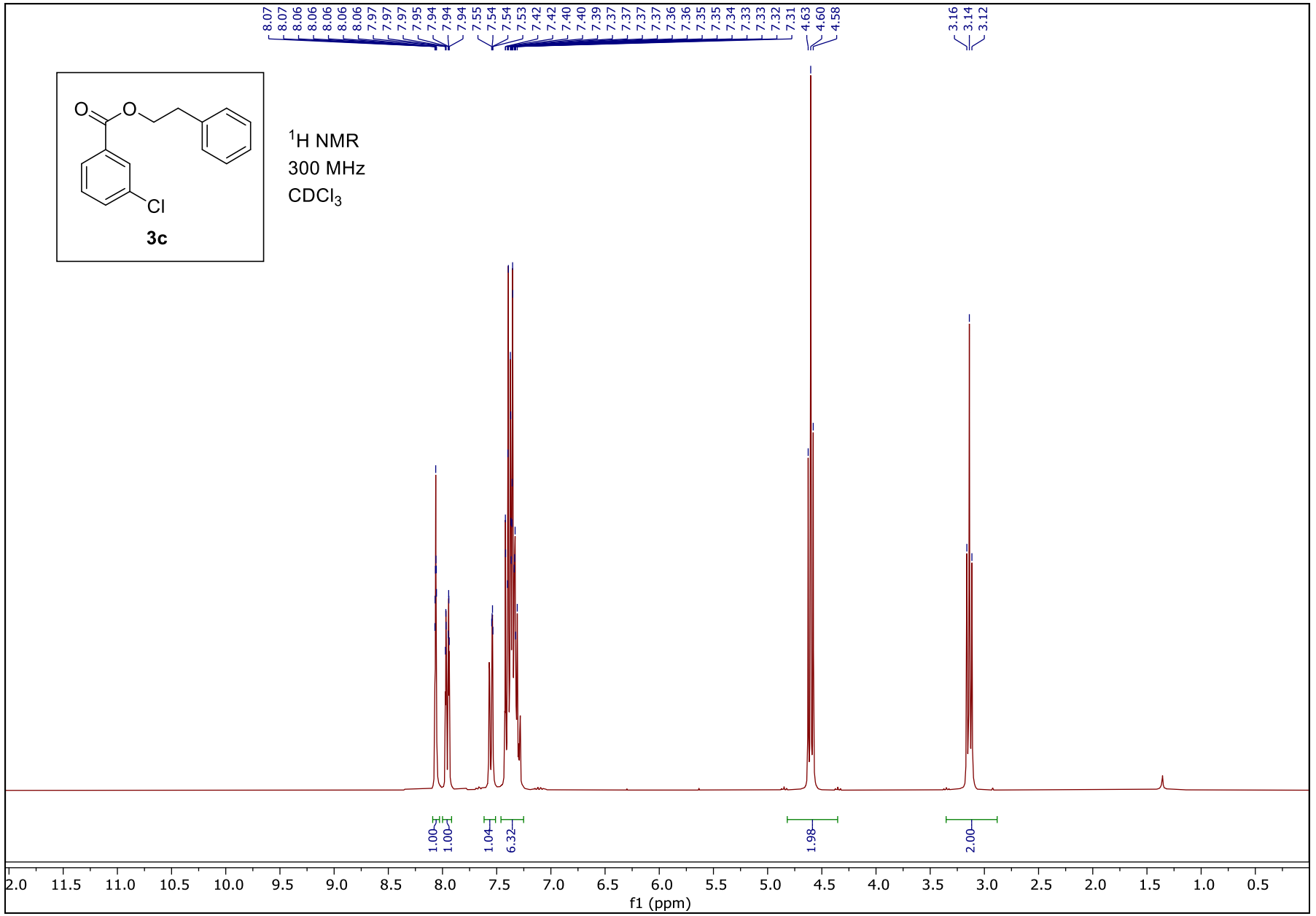
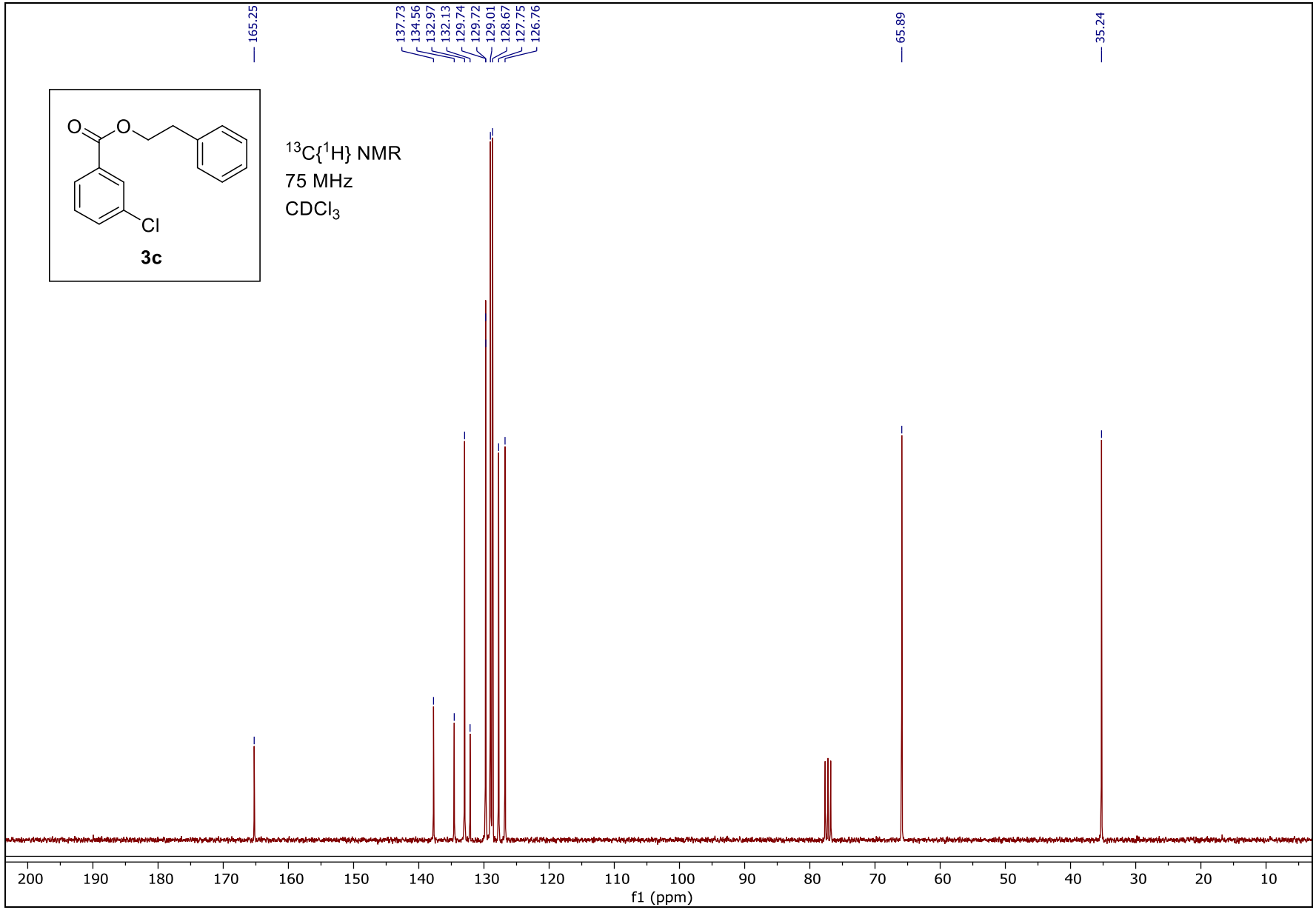
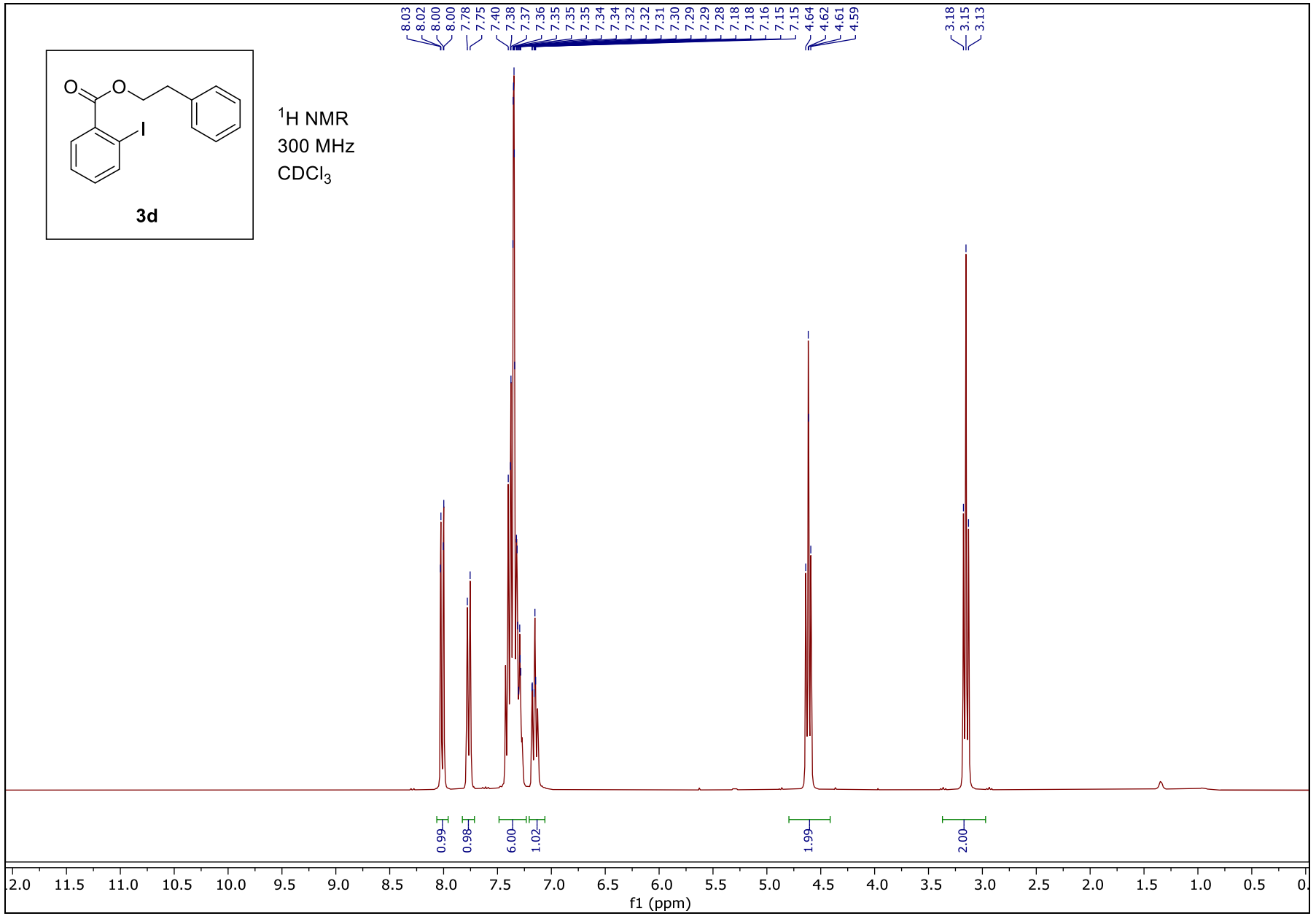
2.00
f1 (ppm)

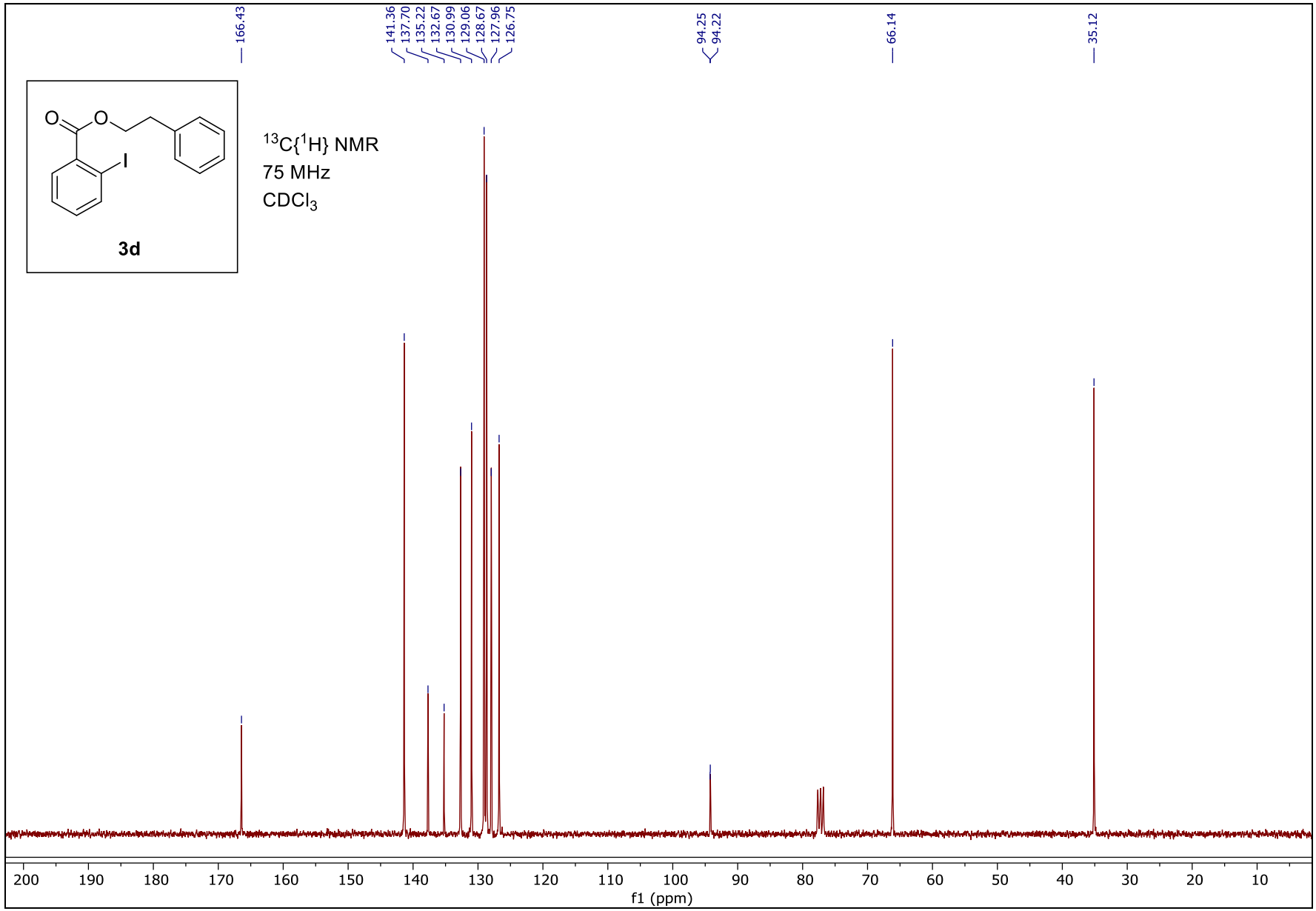

167.47
165.51
164.10
137.89
132.21
132.09
129.00
128.63
126.69
115.67
115.38
65.61
35.28
O
O
F
3b
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
f1 (ppm)

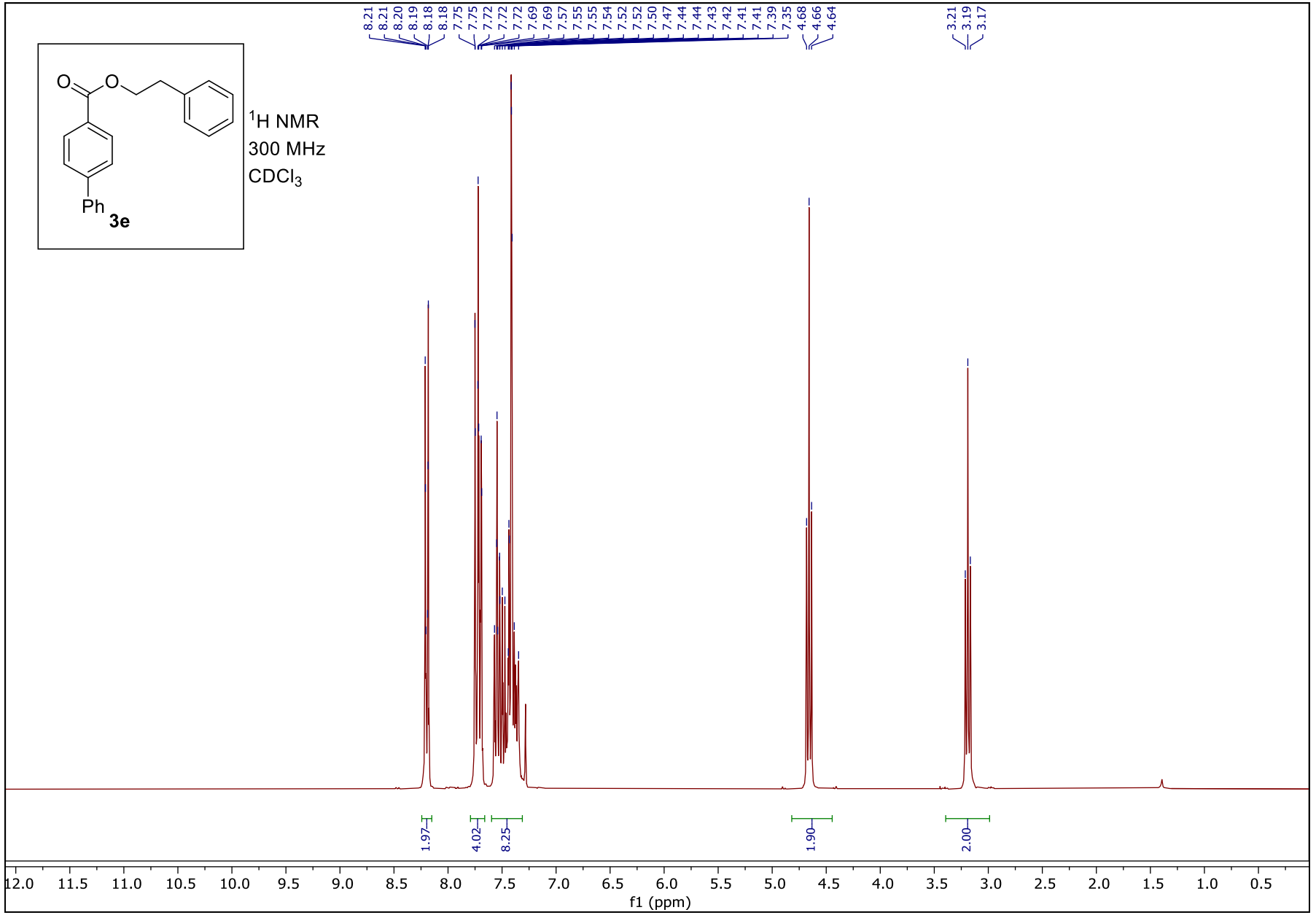

-106.45
3b
^{19}F NMR
272 MHz
$CDCl_3$
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)

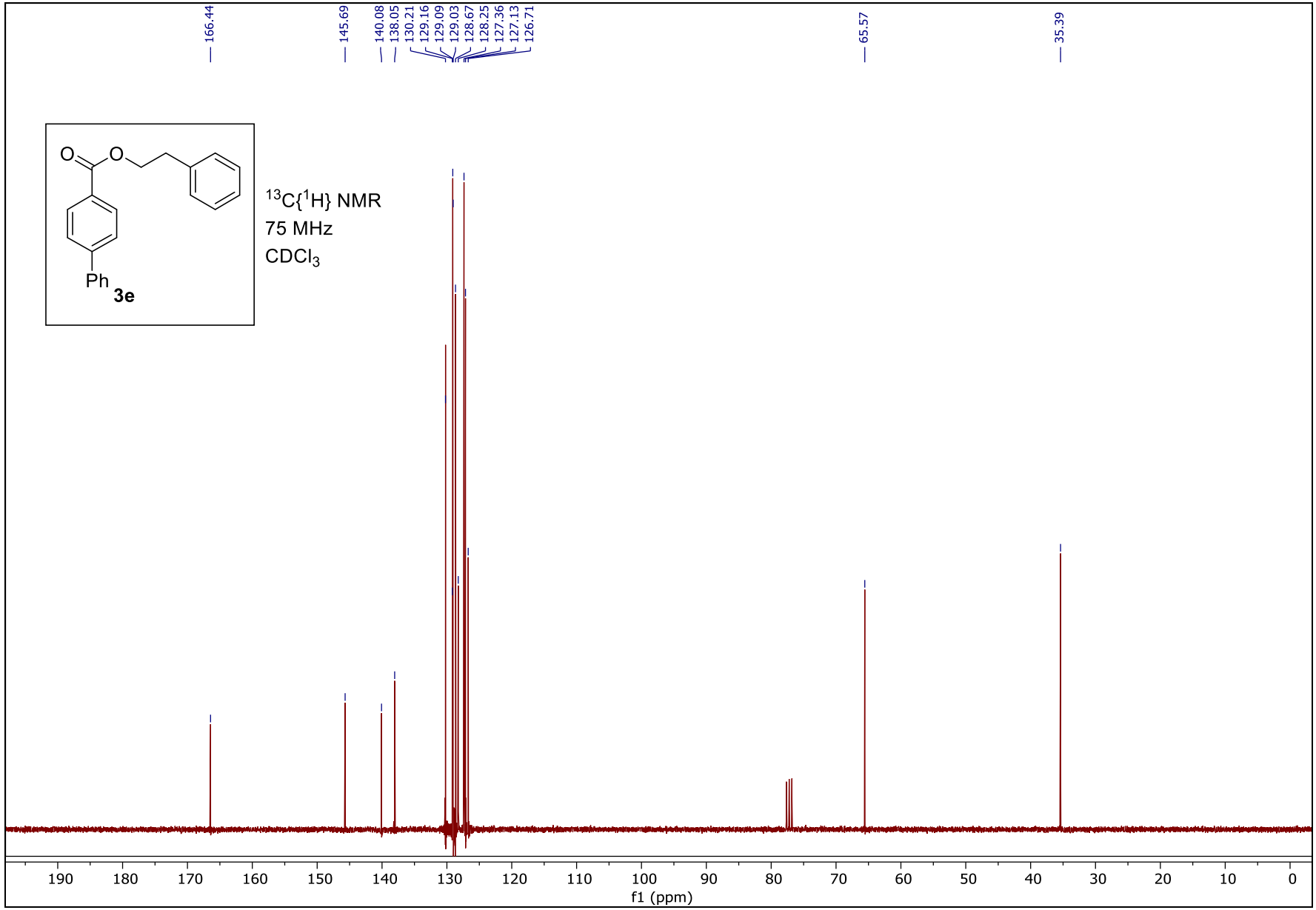

8.07 8.07 8.06 8.06 8.06 8.06 8.06 8.06 7.97 7.97 7.97 7.95 7.94 7.94 7.94 7.55 7.54 7.54 7.53 7.42 7.42 7.40 7.40 7.39 7.37 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 4.63 4.60 4.58 3.16 3.14 3.12
O
O
Cl
3c
1H NMR
300 MHz
CDCl3
1.00 1.00 1.04 6.32 1.98 2.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

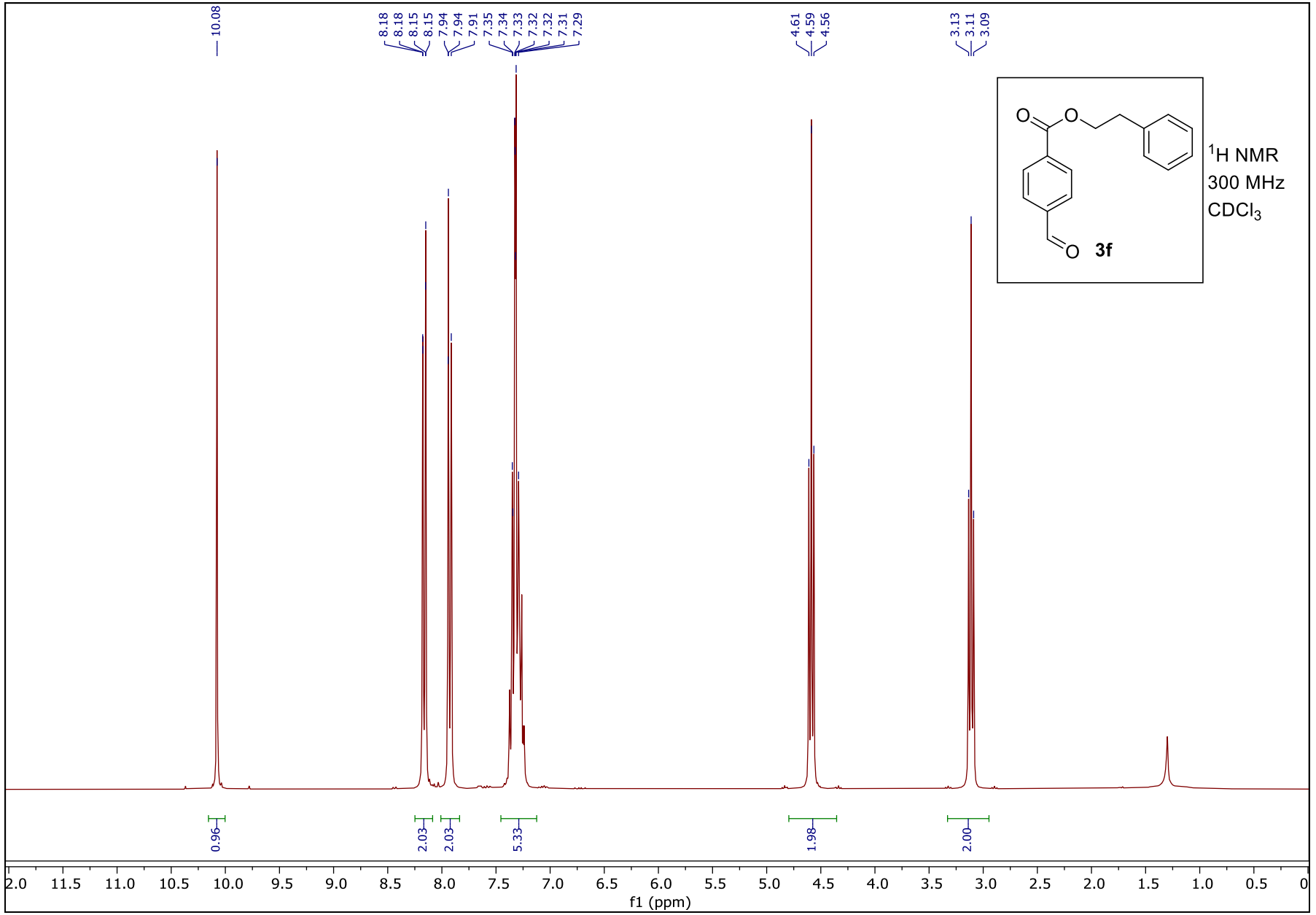

165.25
137.73
134.56
132.97
132.13
129.74
129.72
129.01
128.67
127.75
126.76
65.89
35.24
O
O
Cl
3c
13C{1H} NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

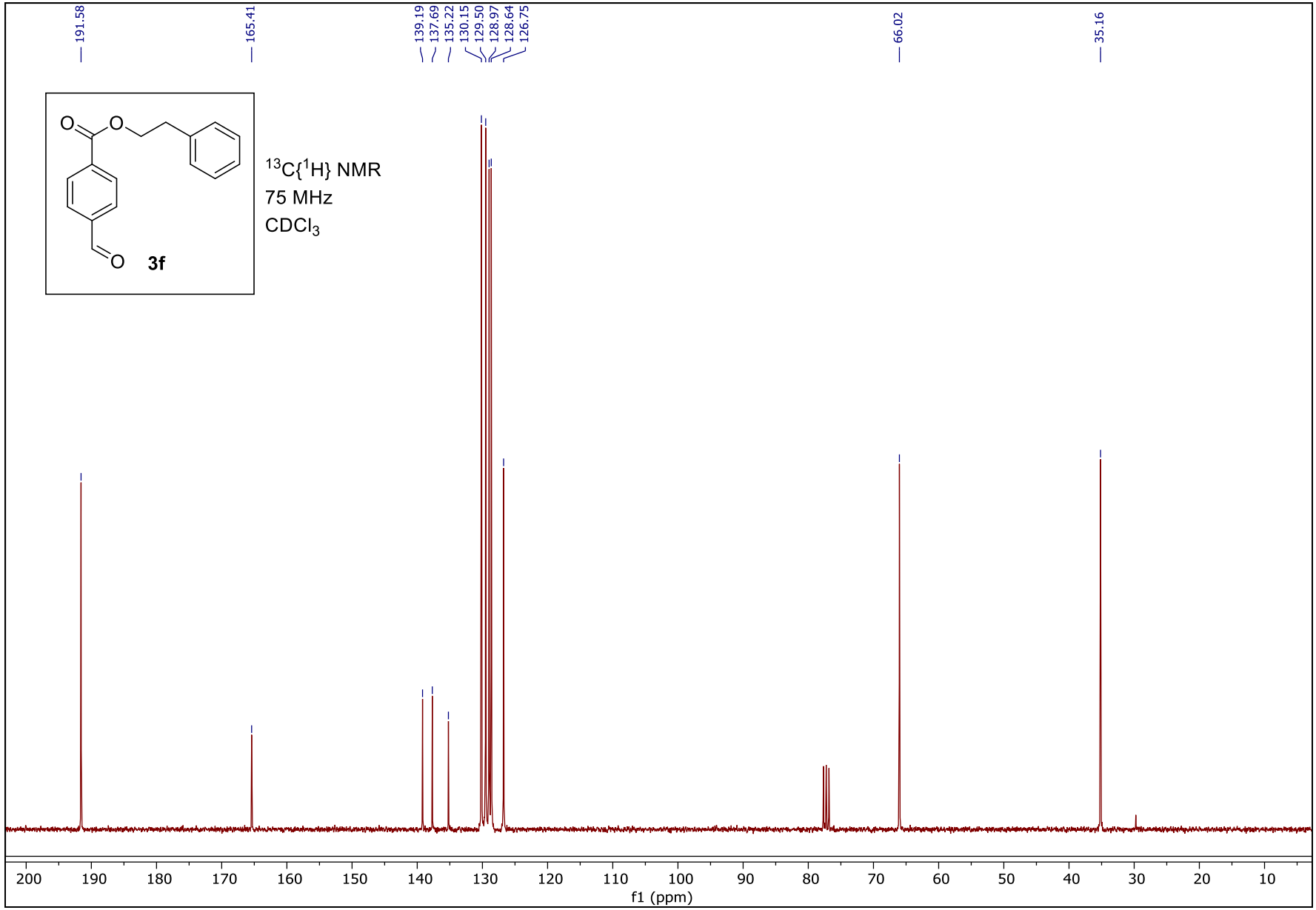

3d
^{1}H NMR
300 MHz
$CDCl_3$
8.03 8.02 8.00 8.00 7.78 7.75 7.40 7.38 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.18 7.18 7.16 7.15 7.15 4.64 4.62 4.61 4.59 3.18 3.15 3.13
0.99 0.98 6.00 1.02 1.99 2.00
f1 (ppm)

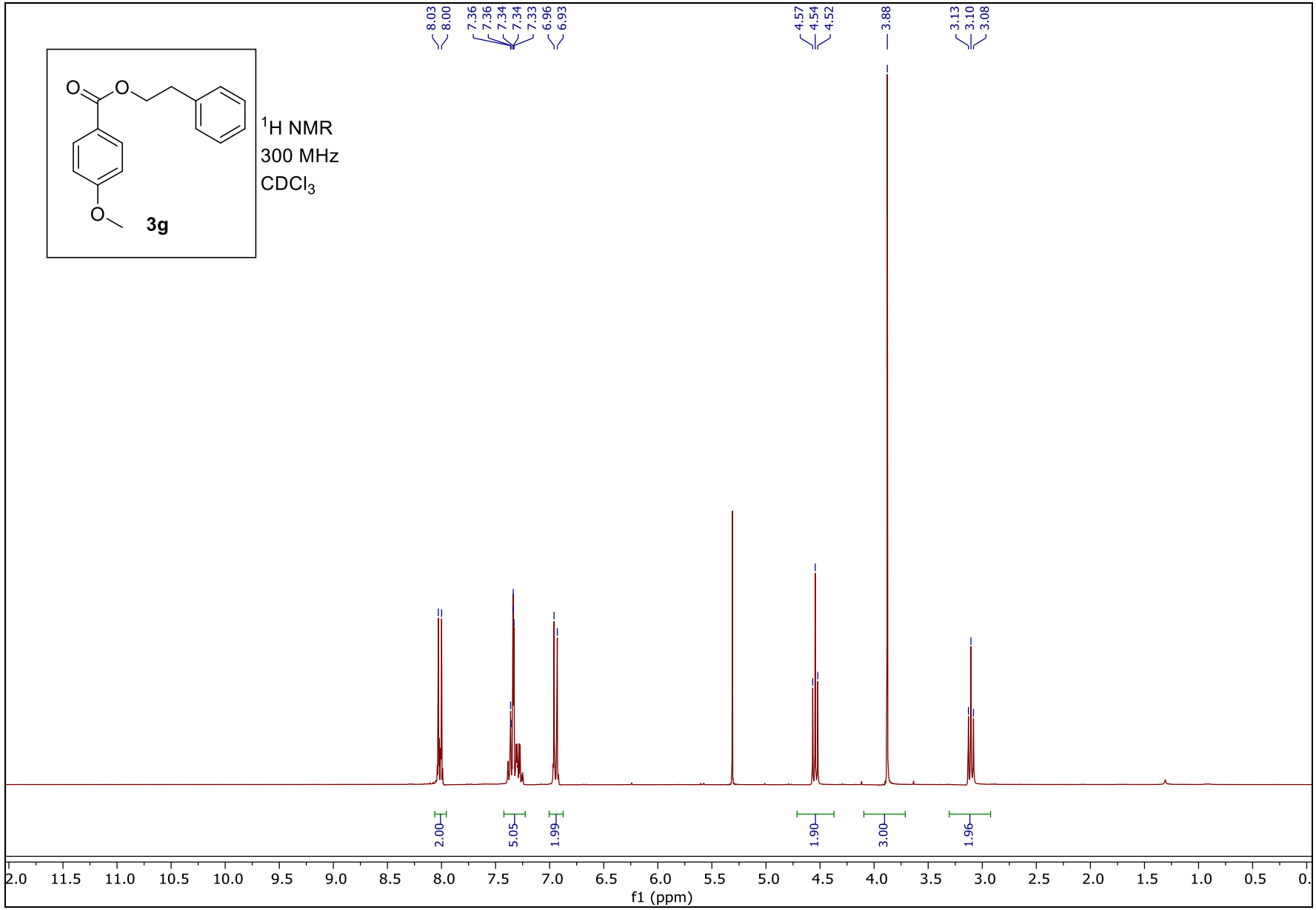

166.43
141.36
137.70
135.22
132.67
130.99
129.06
128.67
127.96
126.75
94.25
94.22
66.14
35.12
O
O
I
3d
13C{1H} NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

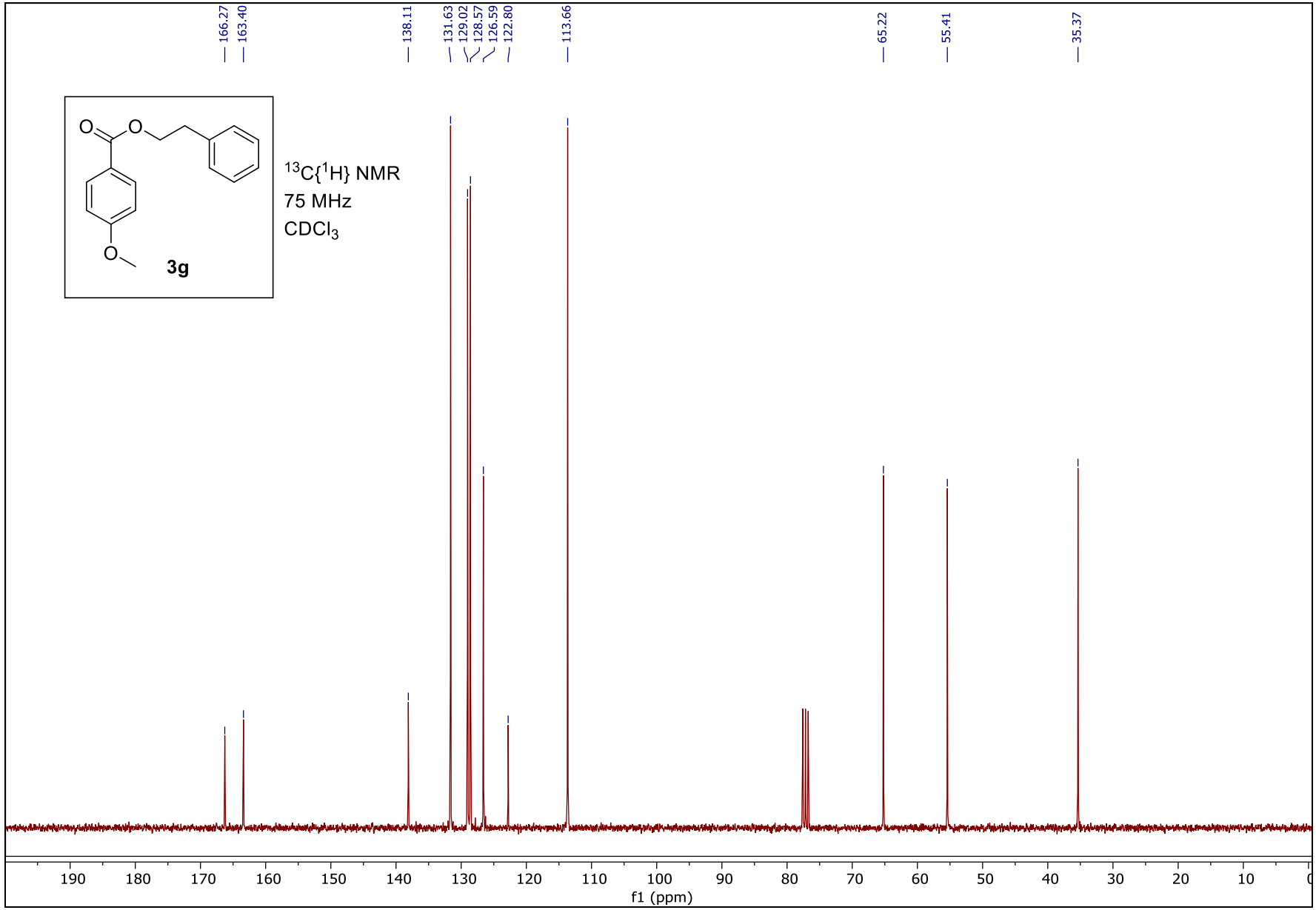

8.21
8.21
8.20
8.19
8.18
8.18
7.75
7.75
7.72
7.72
7.72
7.69
7.69
7.57
7.55
7.55
7.54
7.52
7.52
7.50
7.47
7.44
7.44
7.43
7.42
7.41
7.41
7.39
7.35
4.68
4.66
4.64
3.21
3.19
3.17
O
O
Ph
3e
1H NMR
300 MHz
CDCl3
1.97
4.02
8.25
1.90
2.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

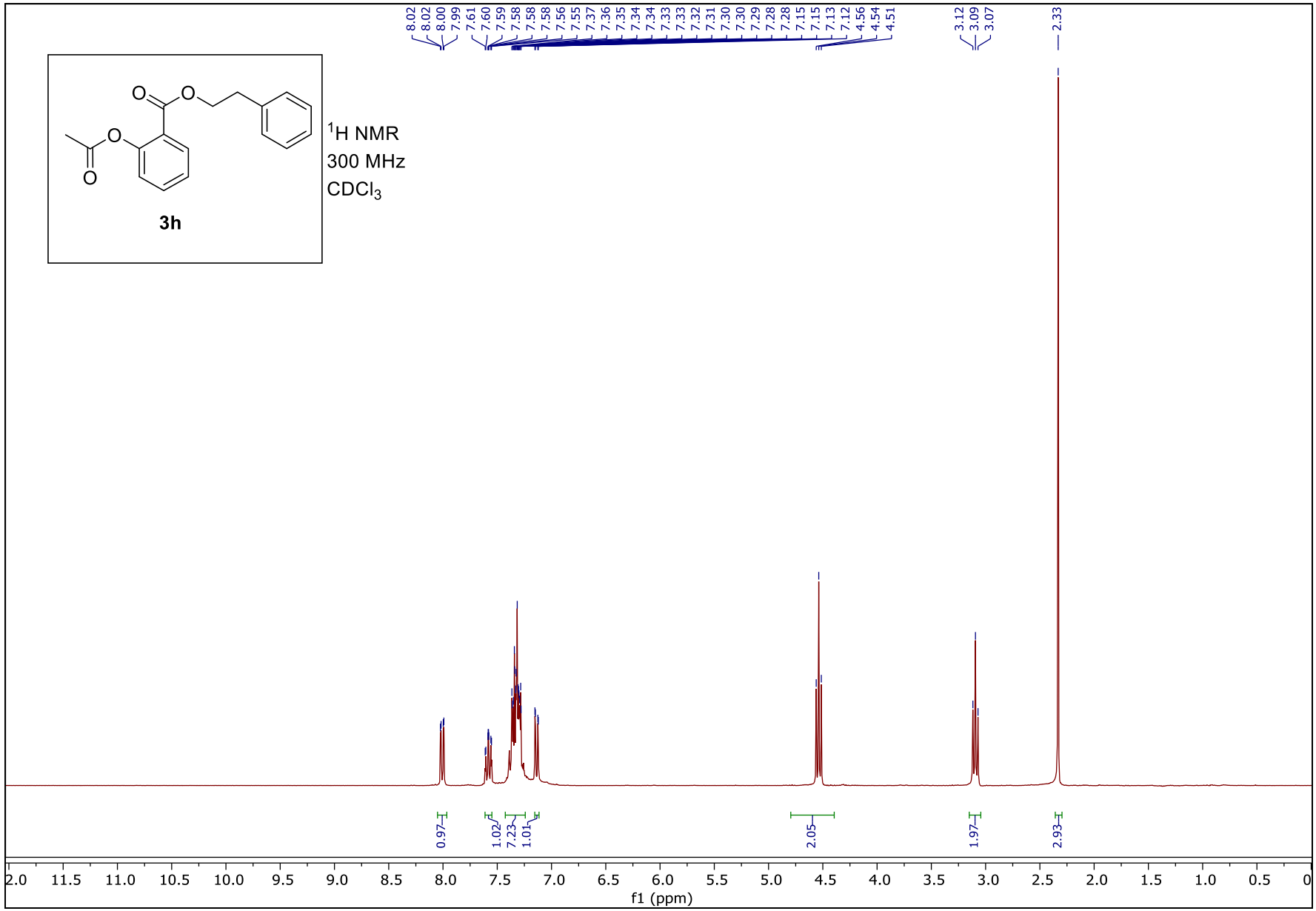

166.44
145.69
140.08
138.05
130.21
129.16
129.09
129.03
128.67
128.25
127.36
127.13
126.71
65.57
35.39
O
O
Ph
3e
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

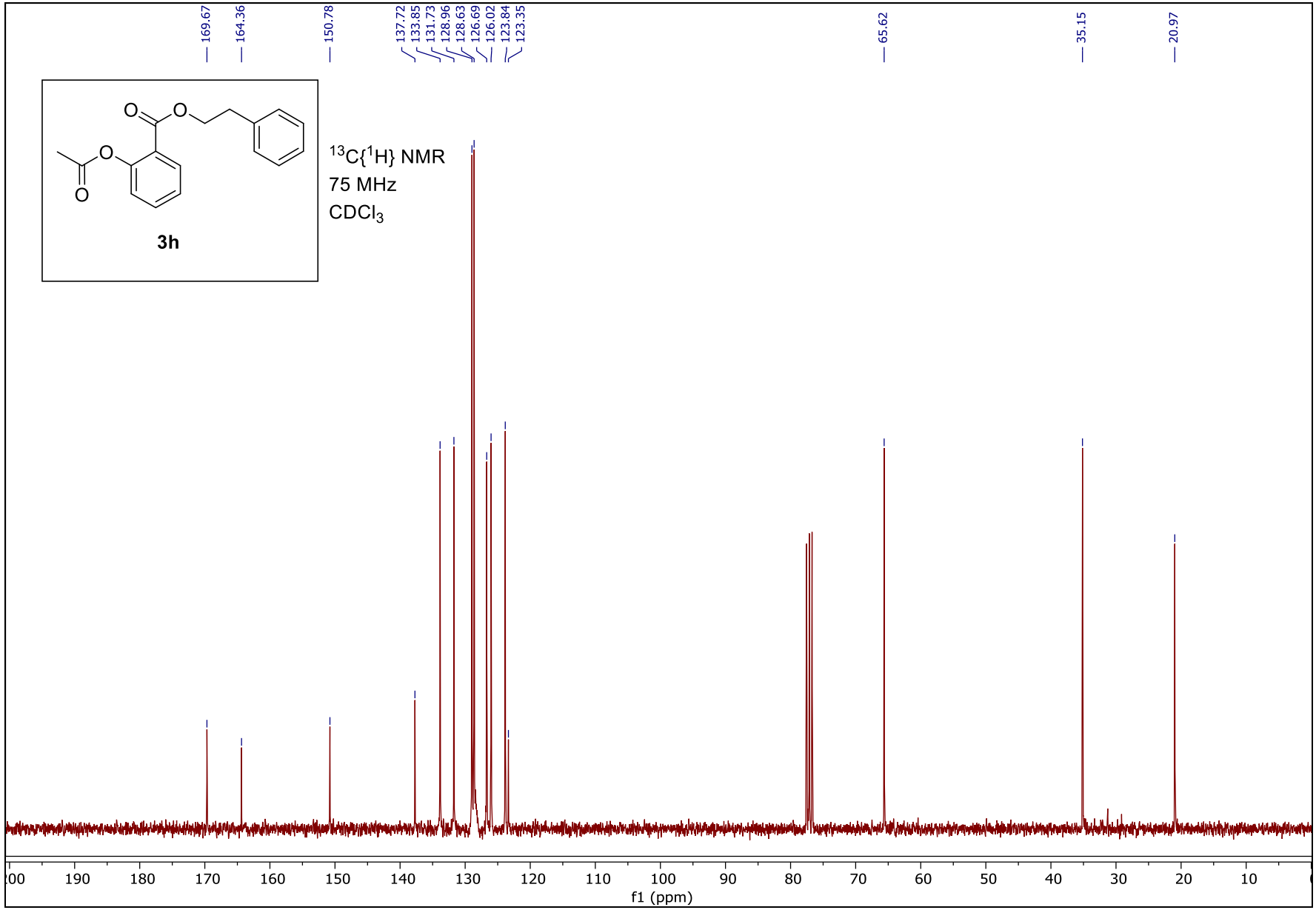

10.08
8.18
8.18
8.15
8.15
7.94
7.94
7.91
7.35
7.34
7.33
7.32
7.32
7.31
7.29
4.61
4.59
4.56
3.13
3.11
3.09
O
O
O
3f
1H NMR
300 MHz
CDCl3
0.96
2.03
2.03
5.33
1.98
2.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

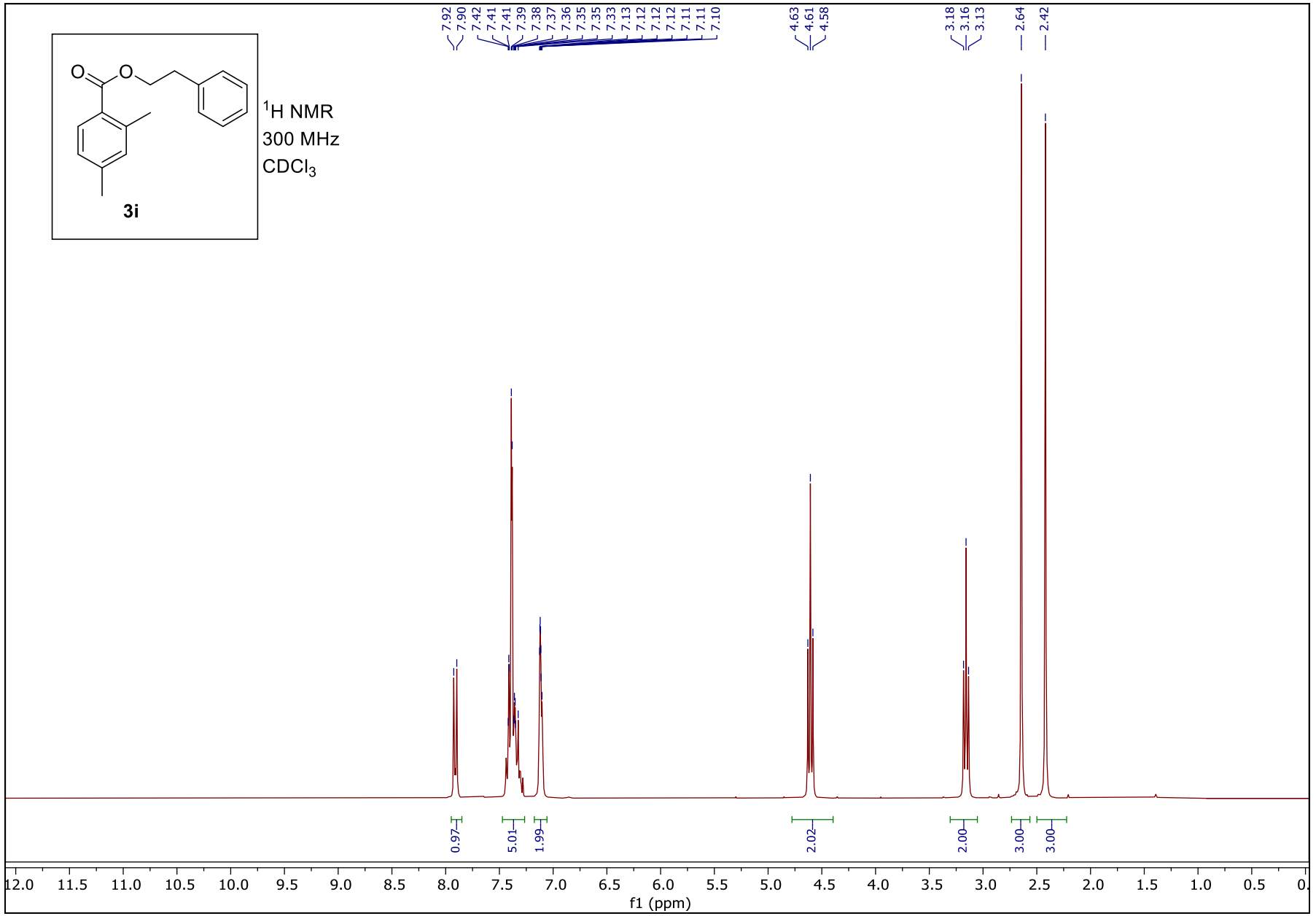

191.58
165.41
139.19
137.69
135.22
130.15
129.50
128.97
128.64
126.75
66.02
35.16
O
O
O
3f
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

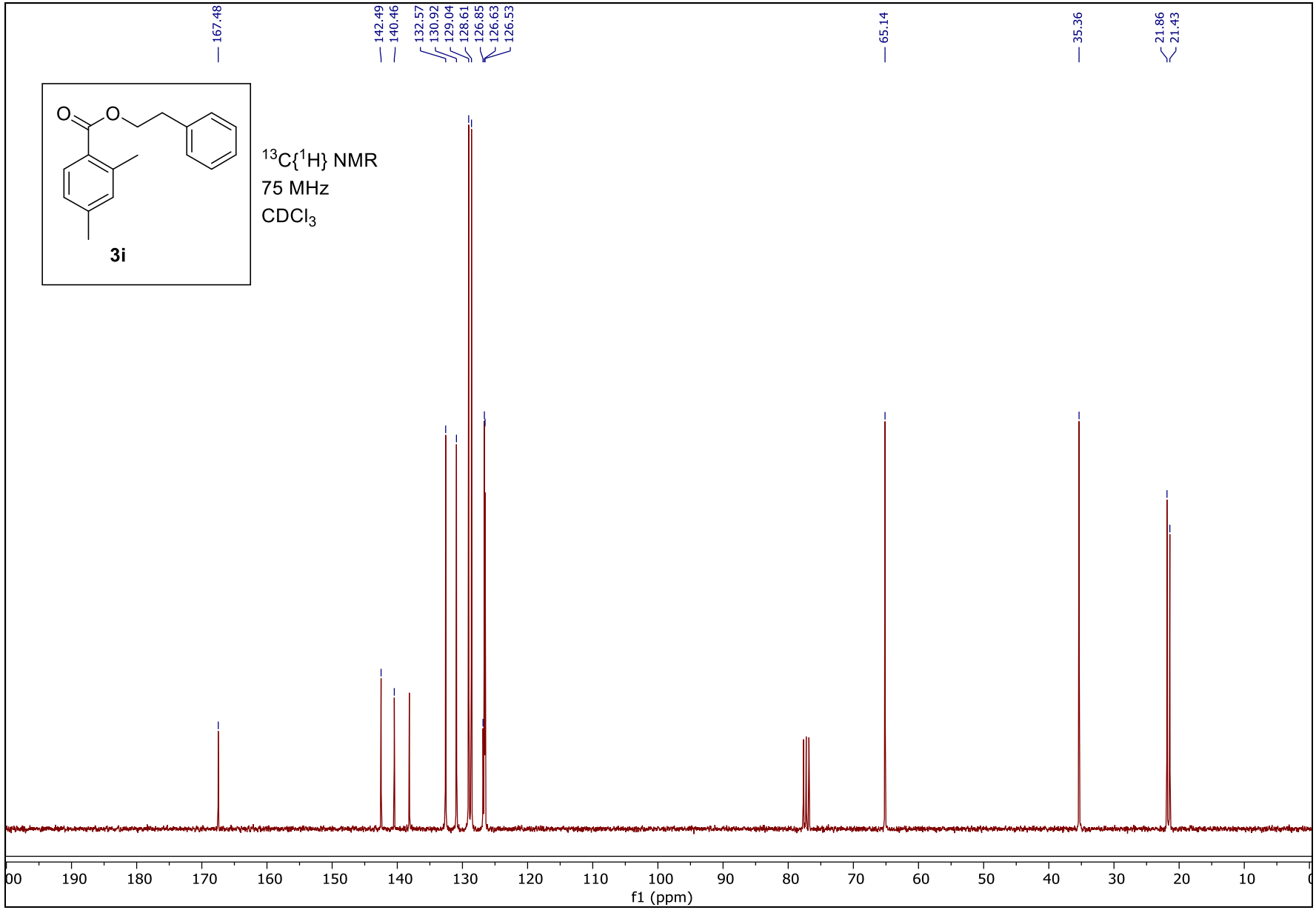

3g
1H NMR
300 MHz
CDCl3
8.03
8.00
7.36
7.36
7.34
7.34
7.33
6.96
6.93
4.57
4.54
4.52
3.88
3.13
3.10
3.08
2.00
5.05
1.99
1.90
3.00
1.96
f1 (ppm)

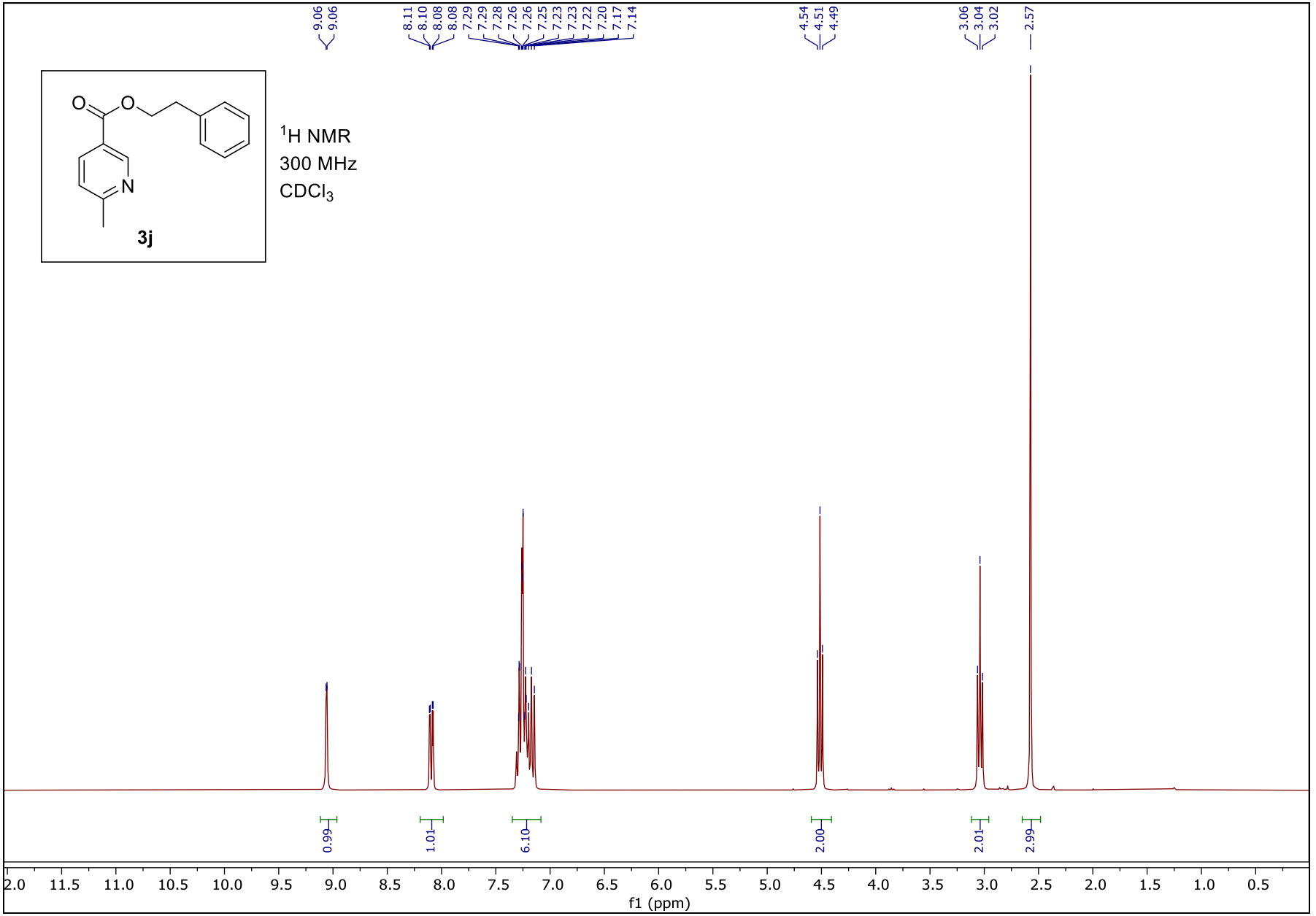

166.27
163.40
138.11
131.63
129.02
128.57
126.59
122.80
113.66
65.22
55.41
35.37
3g
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

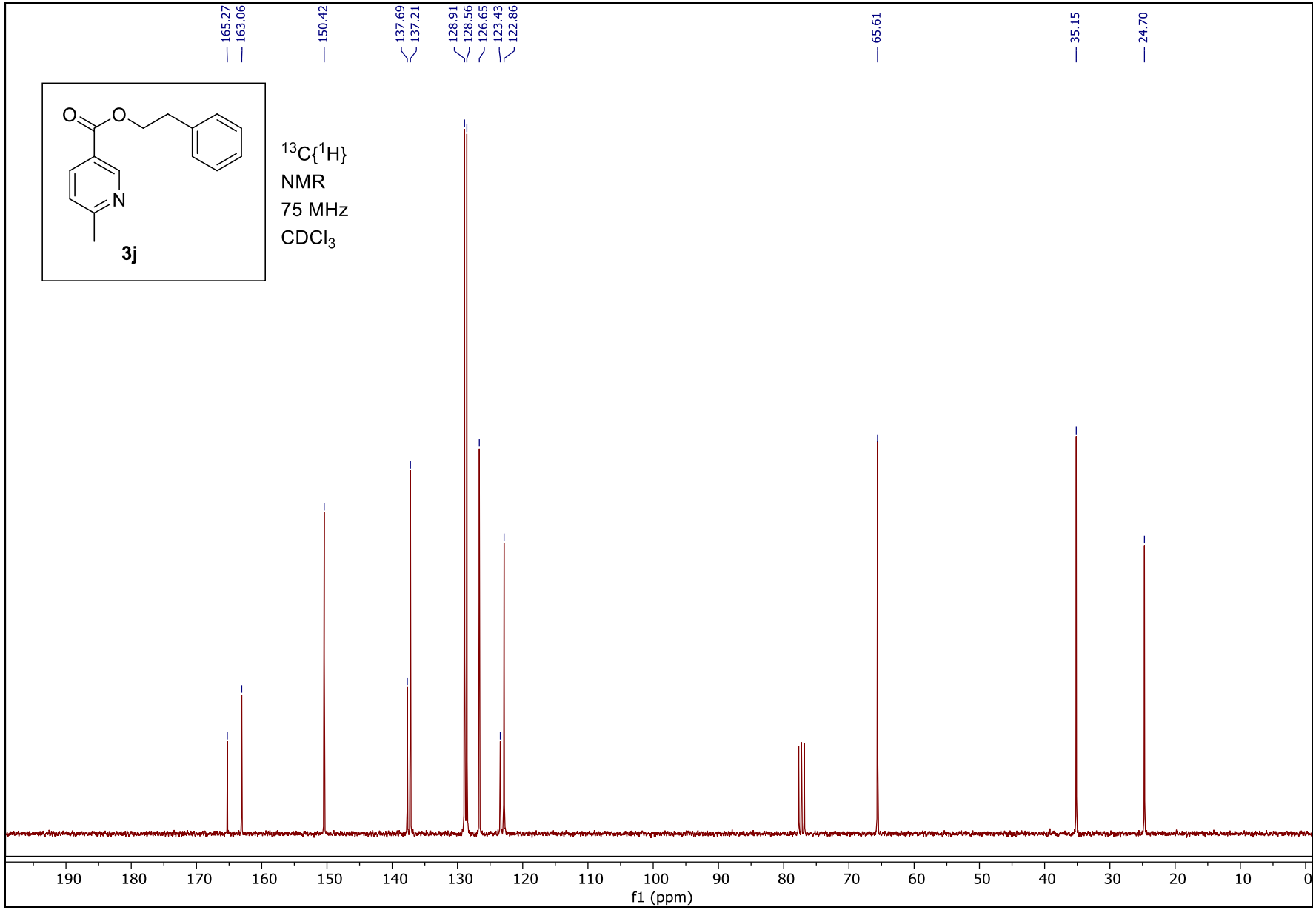

3h
1H NMR
300 MHz
CDCl3
f1 (ppm)

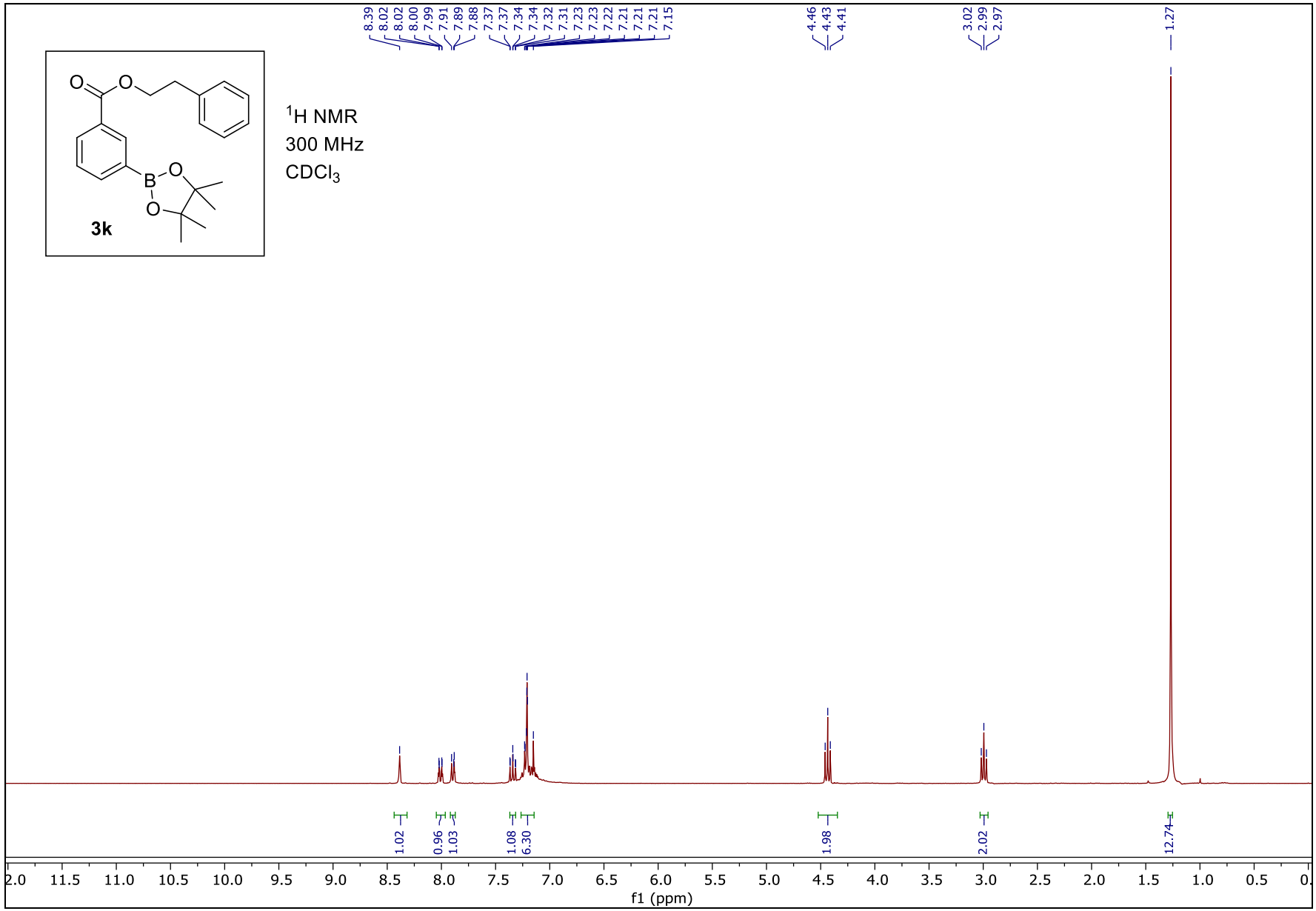

169.67
164.36
150.78
137.72
133.85
131.73
128.96
128.63
126.69
126.02
123.84
123.35
65.62
35.15
20.97
3h
13C{1H} NMR
75 MHz
CDCl3
f1 (ppm)

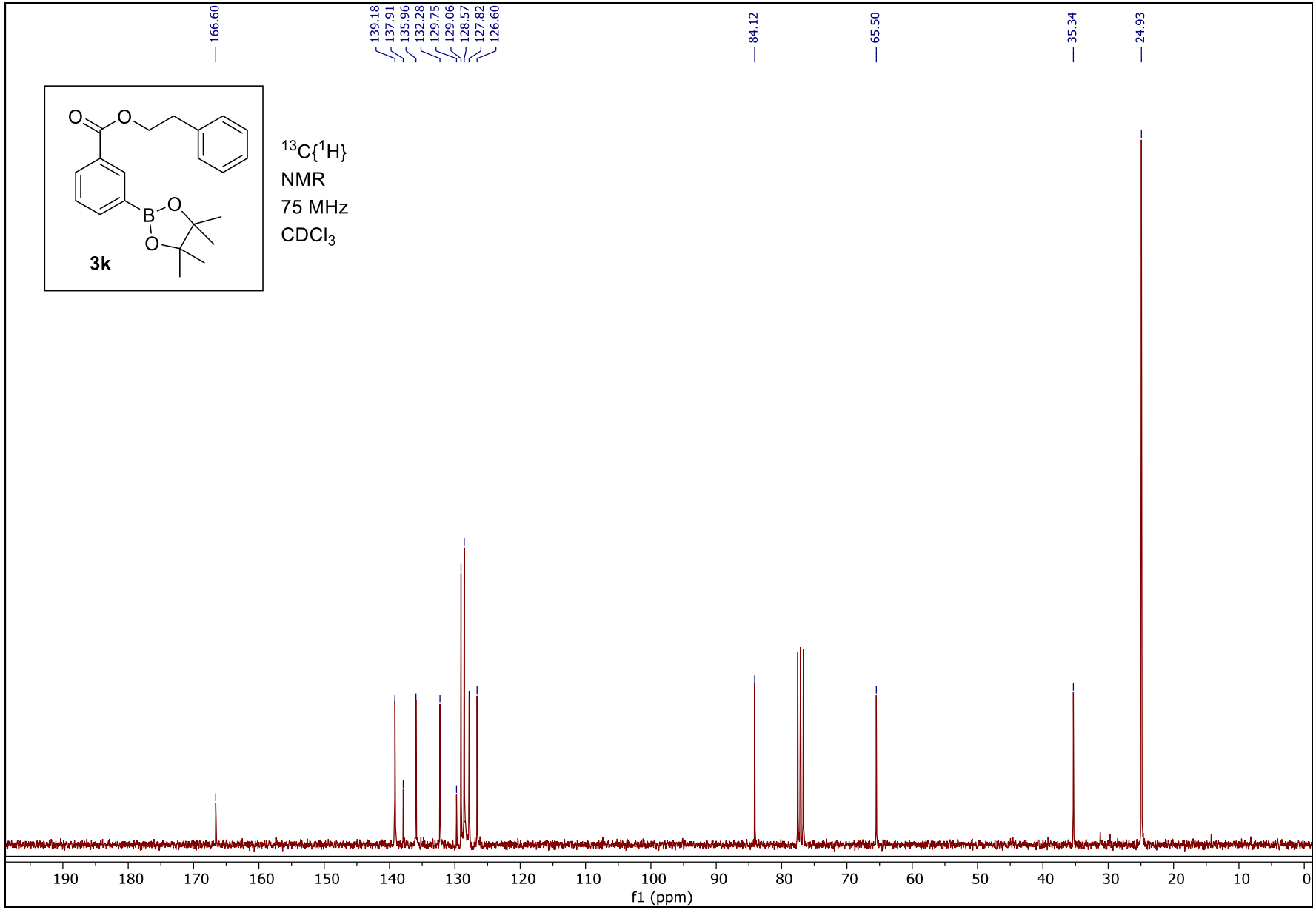

3i
^{1}H NMR
300 MHz
$CDCl_3$
7.92
7.90
7.42
7.41
7.41
7.39
7.38
7.37
7.36
7.35
7.35
7.33
7.13
7.12
7.12
7.12
7.11
7.11
7.10
4.63
4.61
4.58
3.18
3.16
3.13
2.64
2.42
0.97
5.01
1.99
2.02
2.00
3.00
3.00
f1 (ppm)

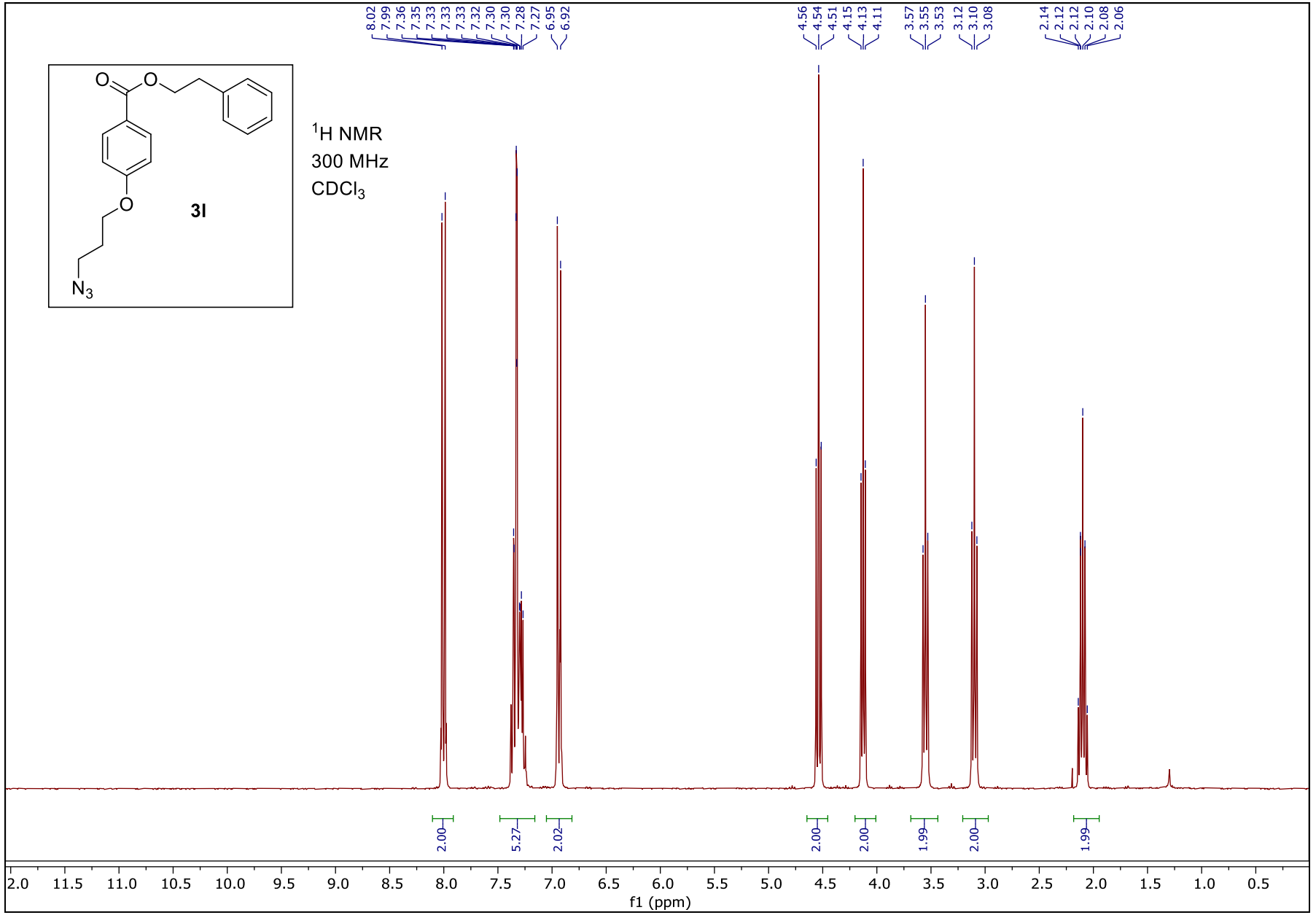

167.48
142.49
140.46
132.57
130.92
129.04
128.61
126.85
126.63
126.53
65.14
35.36
21.86
21.43
3i
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
f1 (ppm)

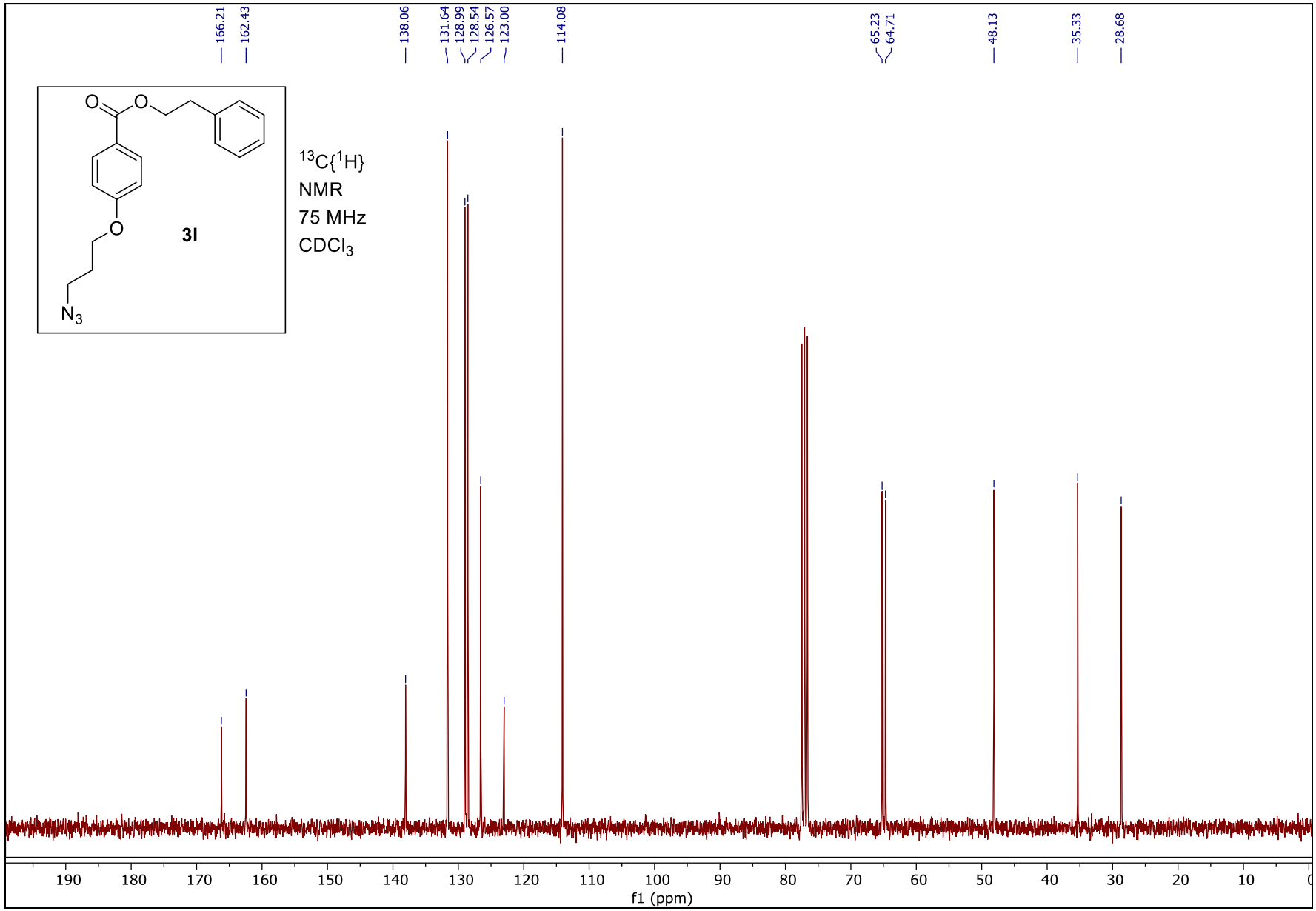

9.06
9.06
8.11
8.10
8.08
8.08
7.29
7.29
7.28
7.26
7.26
7.25
7.23
7.23
7.22
7.20
7.17
7.14
4.54
4.51
4.49
3.06
3.04
3.02
2.57
O
O
N
3j
1H NMR
300 MHz
CDCl3
0.99
1.01
6.10
2.00
2.01
2.99
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

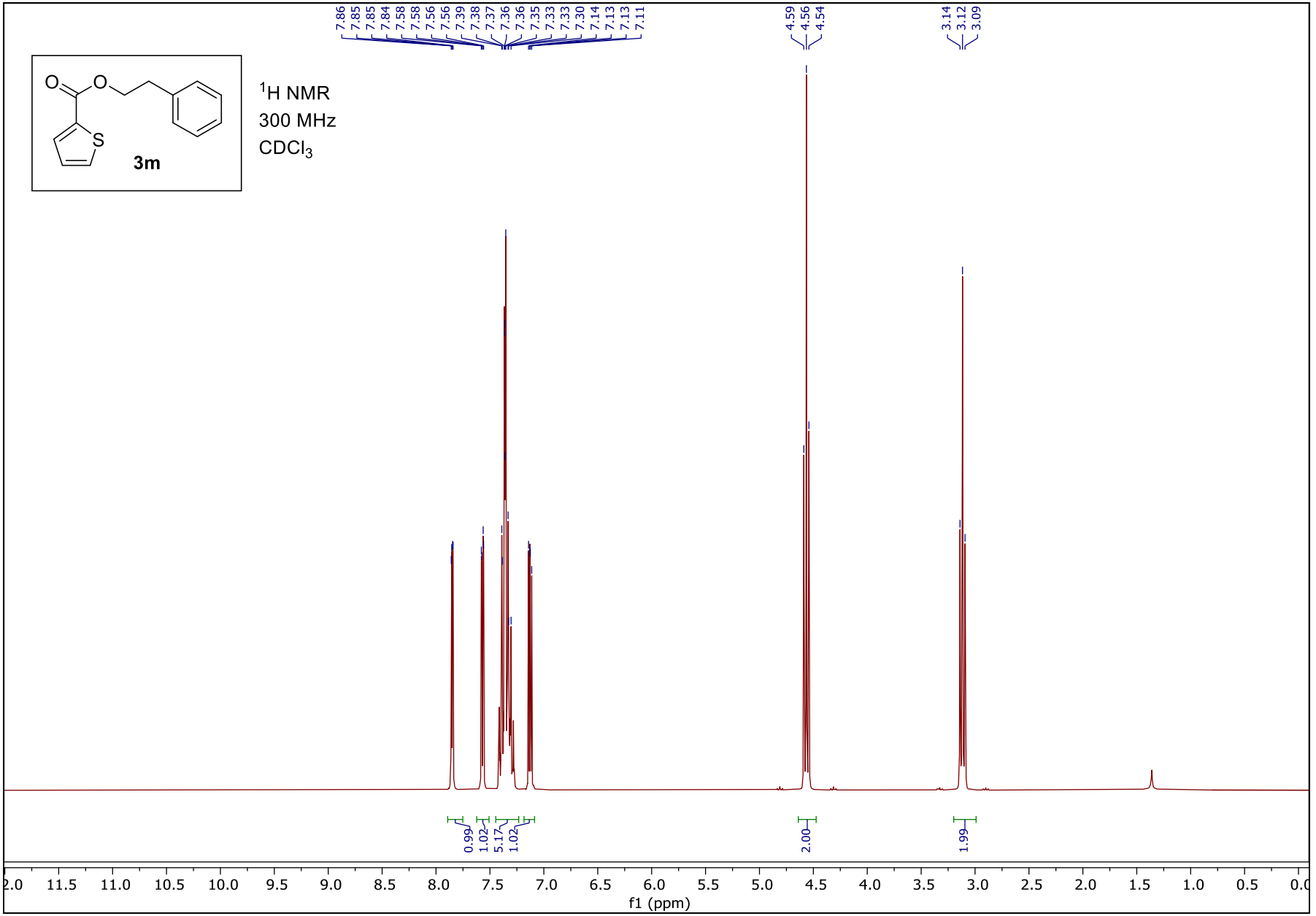

165.27
163.06
150.42
137.69
137.21
128.91
128.56
126.65
123.43
122.86
65.61
35.15
24.70
3j
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

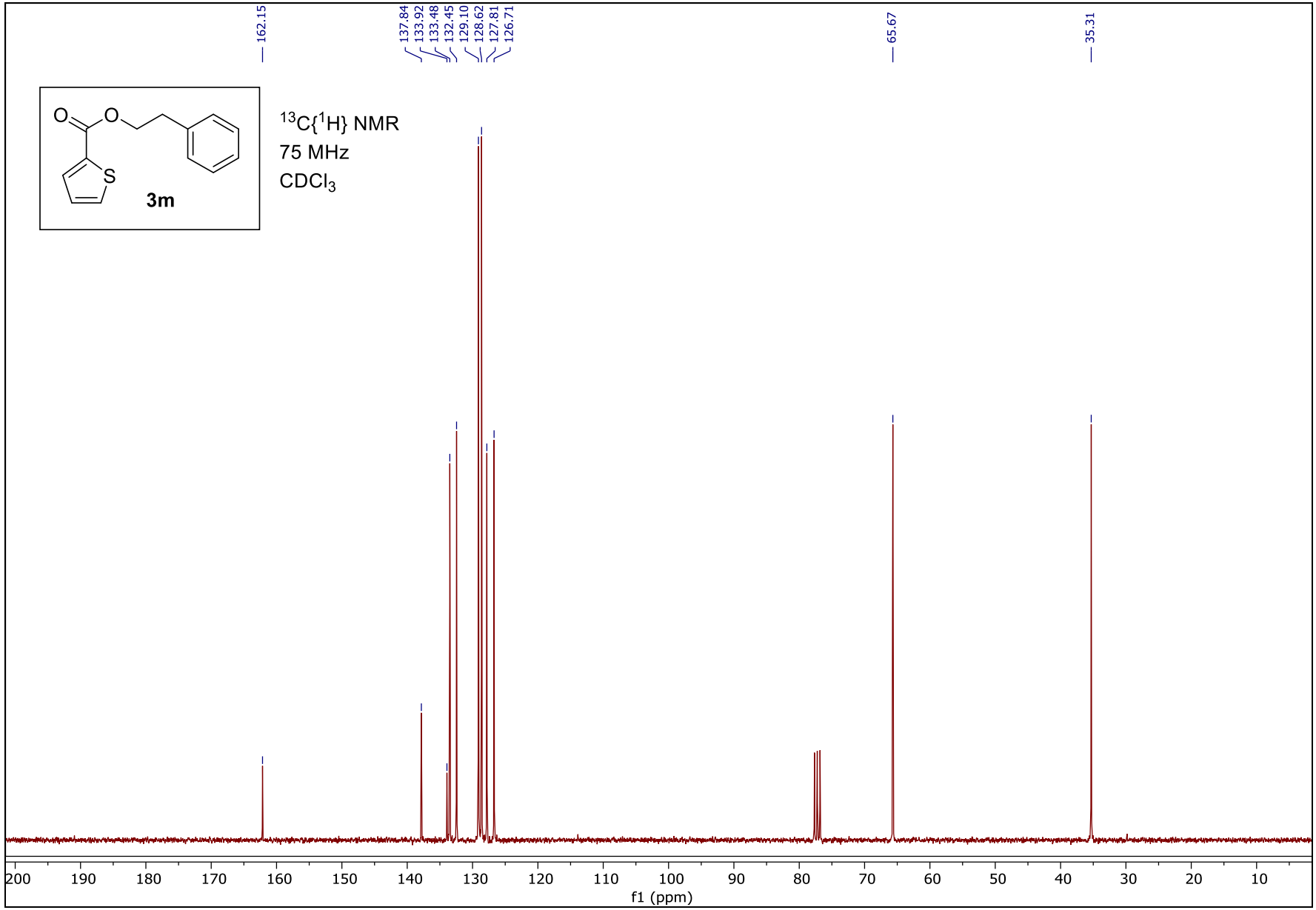

3k
1H NMR
300 MHz
CDCl3
8.39
8.02
8.02
8.00
7.99
7.91
7.89
7.88
7.37
7.37
7.34
7.34
7.32
7.31
7.23
7.23
7.22
7.21
7.21
7.21
7.15
4.46
4.43
4.41
3.02
2.99
2.97
1.27
1.02
0.96
1.03
1.08
6.30
1.98
2.02
12.74
f1 (ppm)

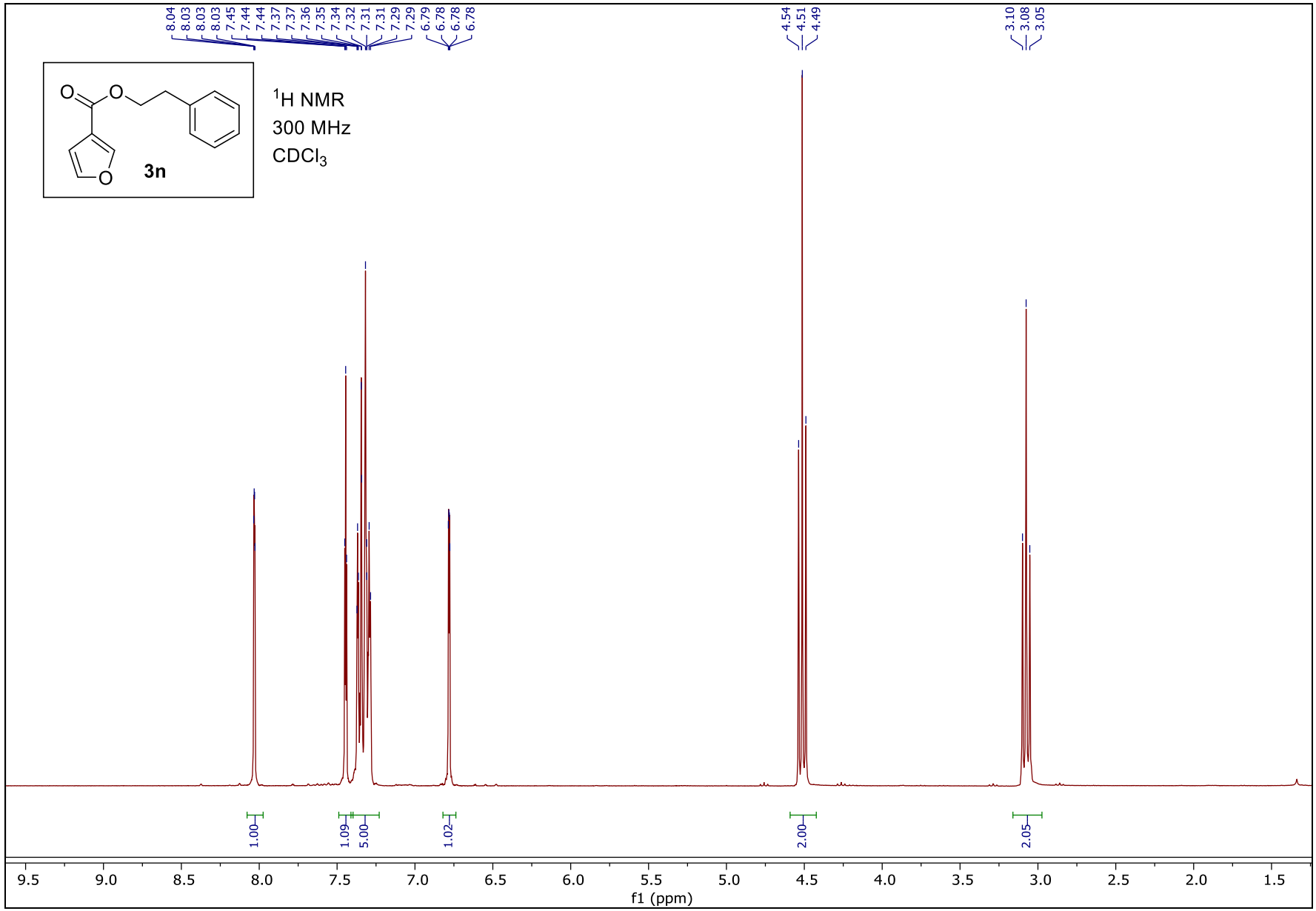

166.60
139.18
137.91
135.96
132.28
129.75
129.06
128.57
127.82
126.60
84.12
65.50
35.34
24.93
3k
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

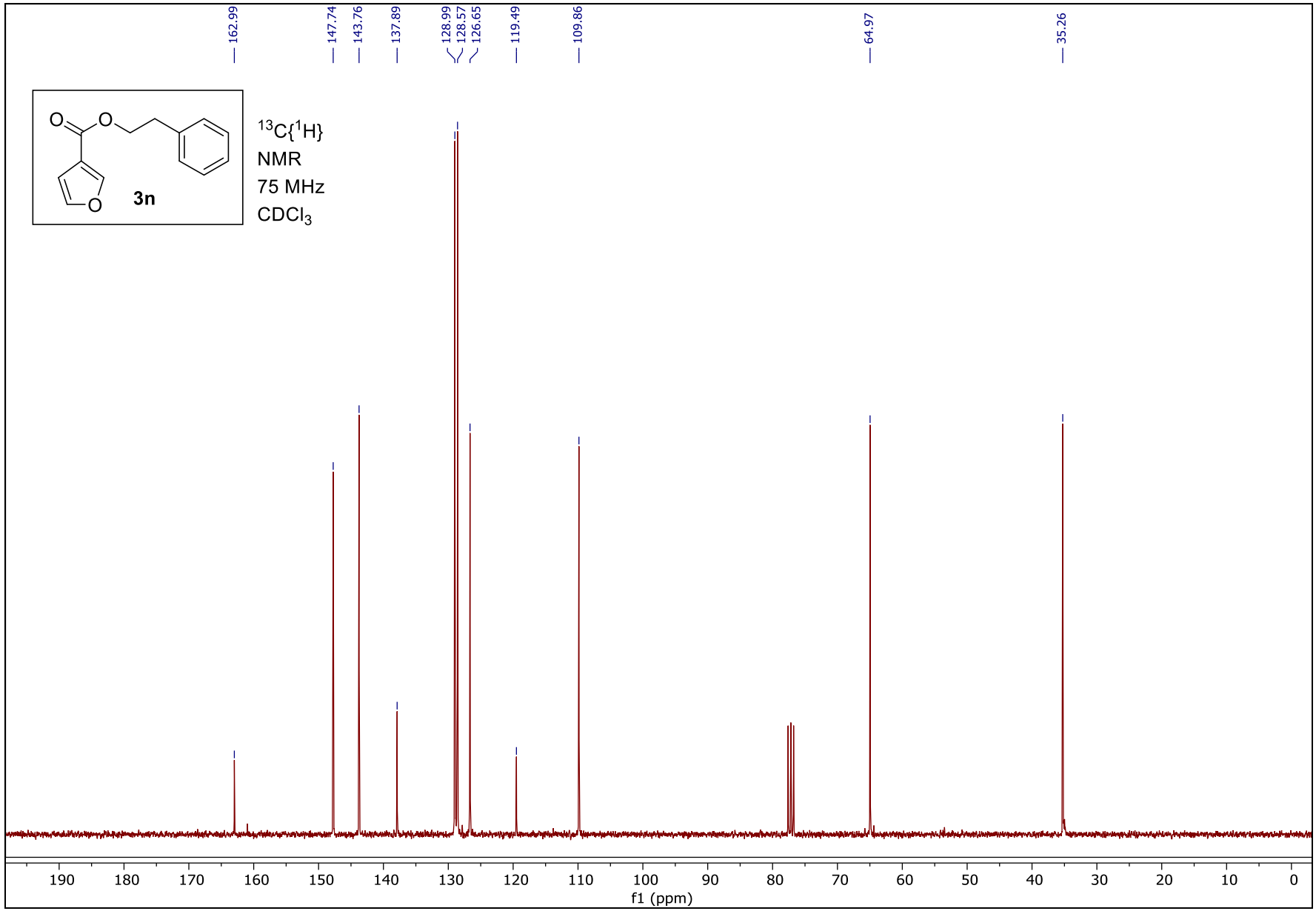

8.02
7.99
7.36
7.35
7.33
7.33
7.33
7.32
7.30
7.30
7.28
7.27
6.95
6.92
4.56
4.54
4.51
4.15
4.13
4.11
3.57
3.55
3.53
3.12
3.10
3.08
2.14
2.12
2.12
2.10
2.08
2.06
O
O
O
N3
3l
1H NMR
300 MHz
CDCl3
2.00
5.27
2.02
2.00
2.00
1.99
2.00
1.99
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

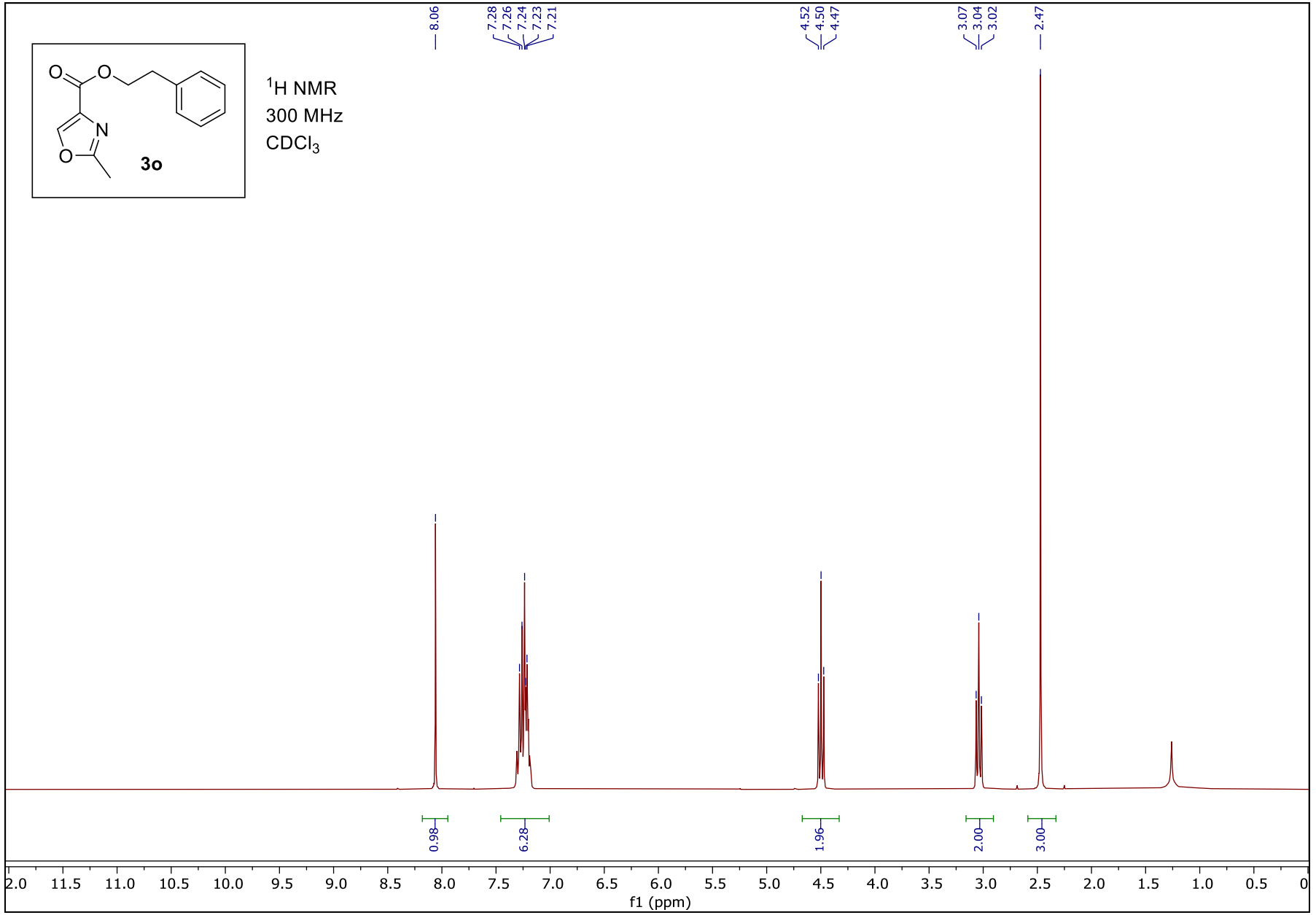

166.21
162.43
138.06
131.64
128.99
128.54
126.57
123.00
114.08
65.23
64.71
48.13
35.33
28.68
O
O
O
N3
3l
13C{1H}
NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

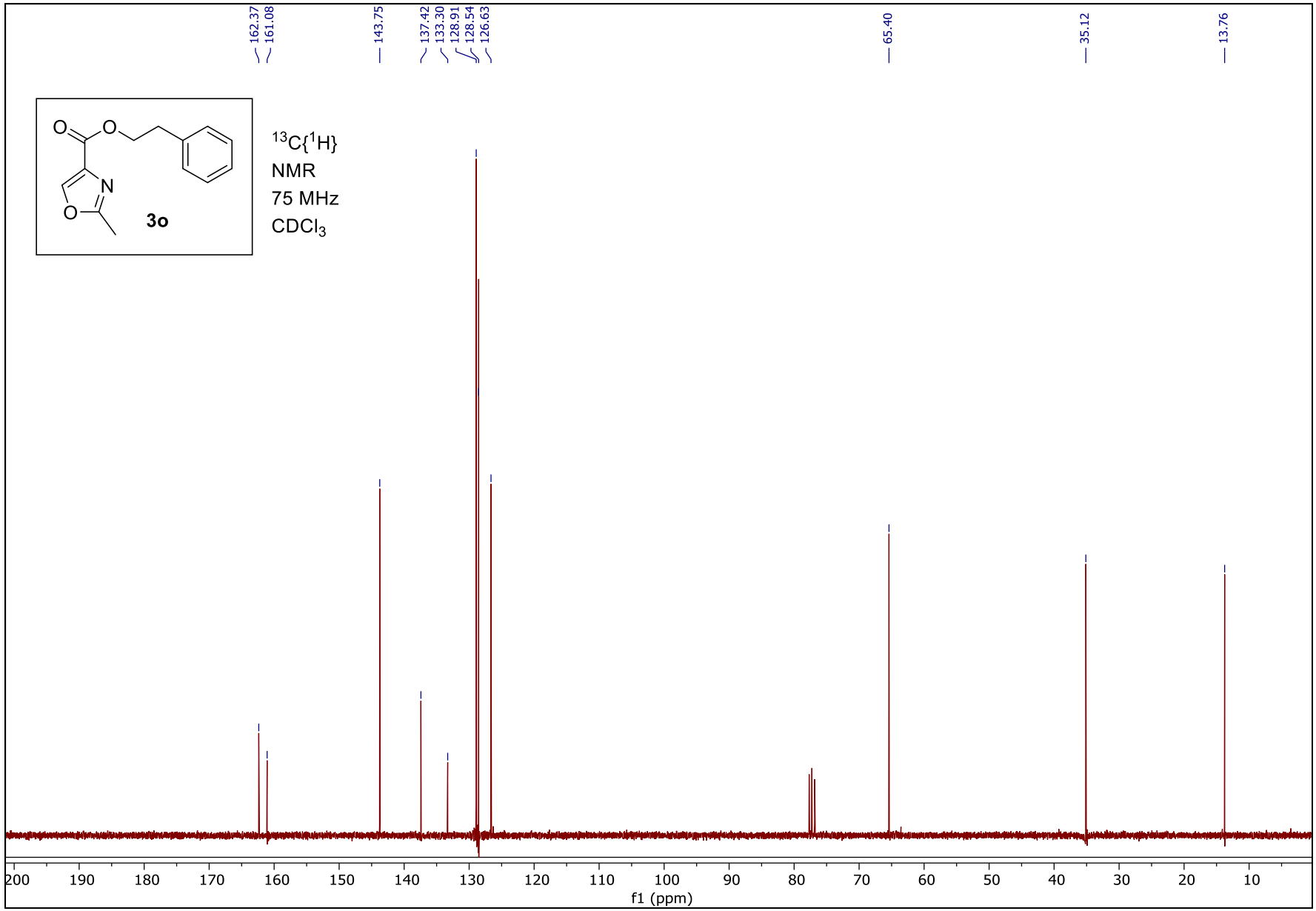

7.86
7.85
7.85
7.84
7.58
7.58
7.56
7.56
7.39
7.38
7.37
7.36
7.36
7.35
7.33
7.33
7.30
7.14
7.13
7.13
7.11
4.59
4.56
4.54
3.14
3.12
3.09
O
O
S
3m
1H NMR
300 MHz
CDCl3
0.99
1.02
5.17
1.02
2.00
1.99
f1 (ppm)

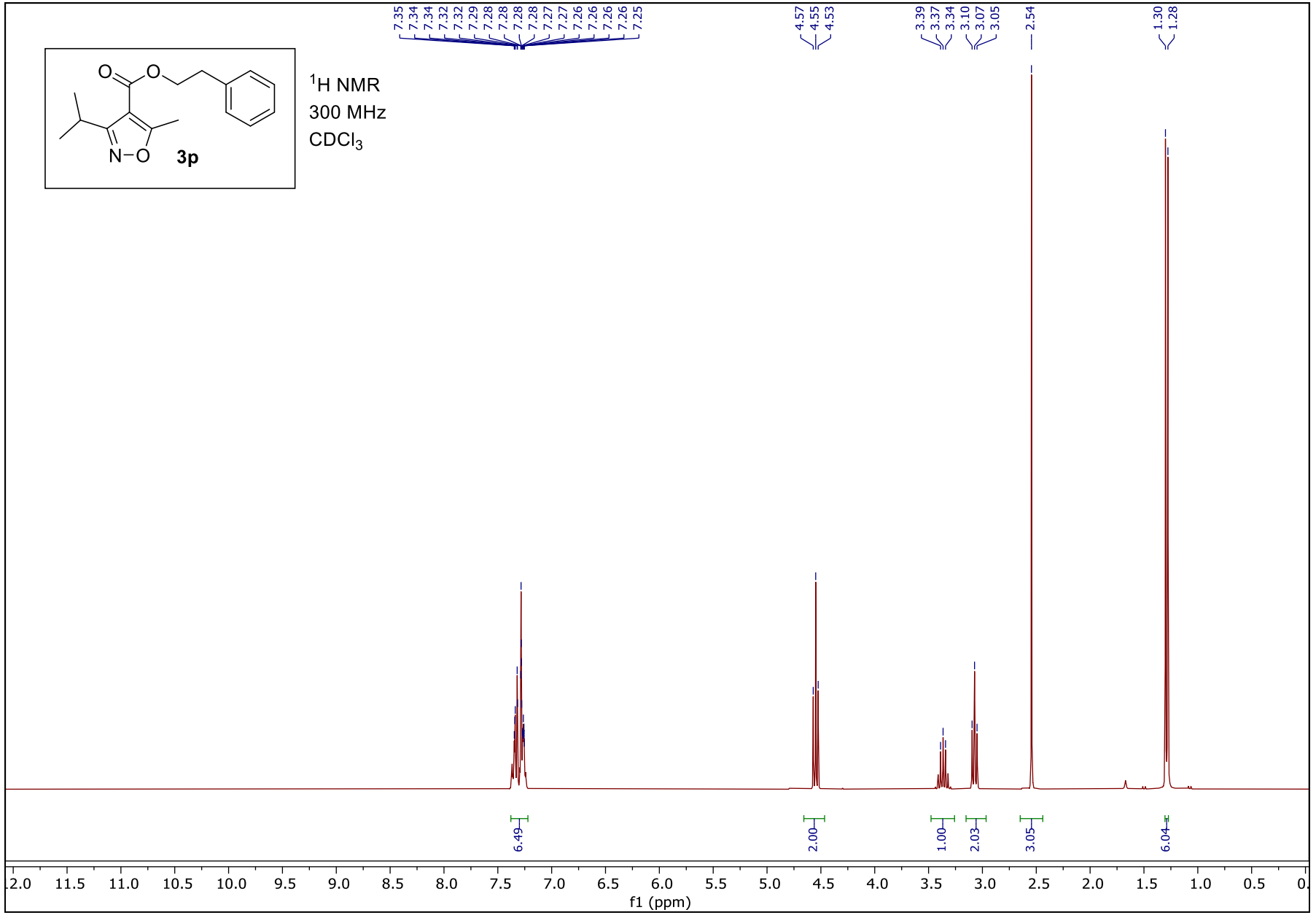

162.15
137.84
133.92
133.48
132.45
129.10
128.62
127.81
126.71
65.67
35.31
3m
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

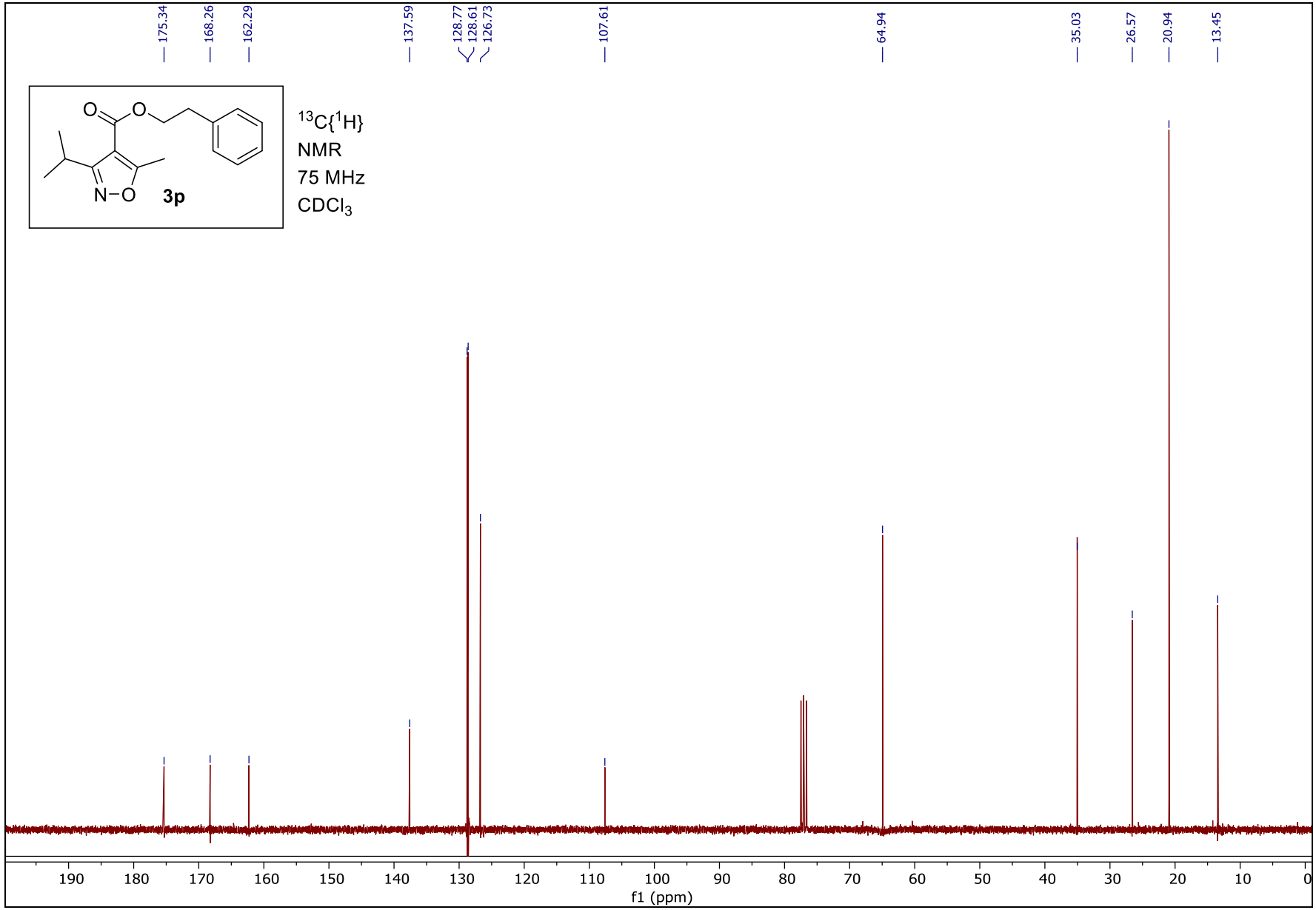

8.04
8.03
8.03
8.03
7.45
7.44
7.44
7.37
7.37
7.36
7.35
7.34
7.32
7.31
7.31
7.29
7.29
6.79
6.78
6.78
6.78
4.54
4.51
4.49
3.10
3.08
3.05
O
O
O
3n
1H NMR
300 MHz
CDCl3
1.00
1.09
5.00
1.02
2.00
2.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

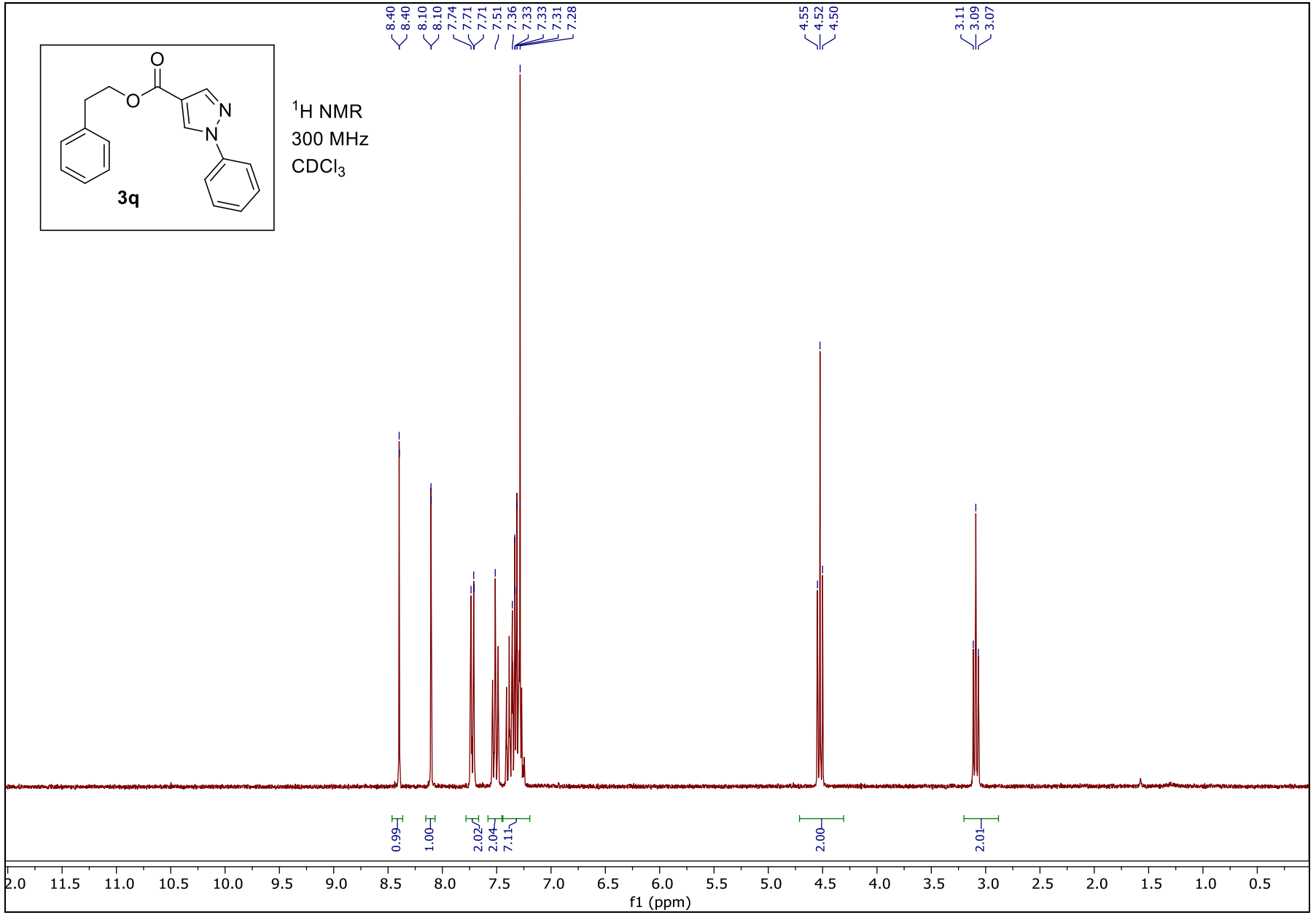

162.99
147.74
143.76
137.89
128.99
128.57
126.65
119.49
109.86
64.97
35.26
3n
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

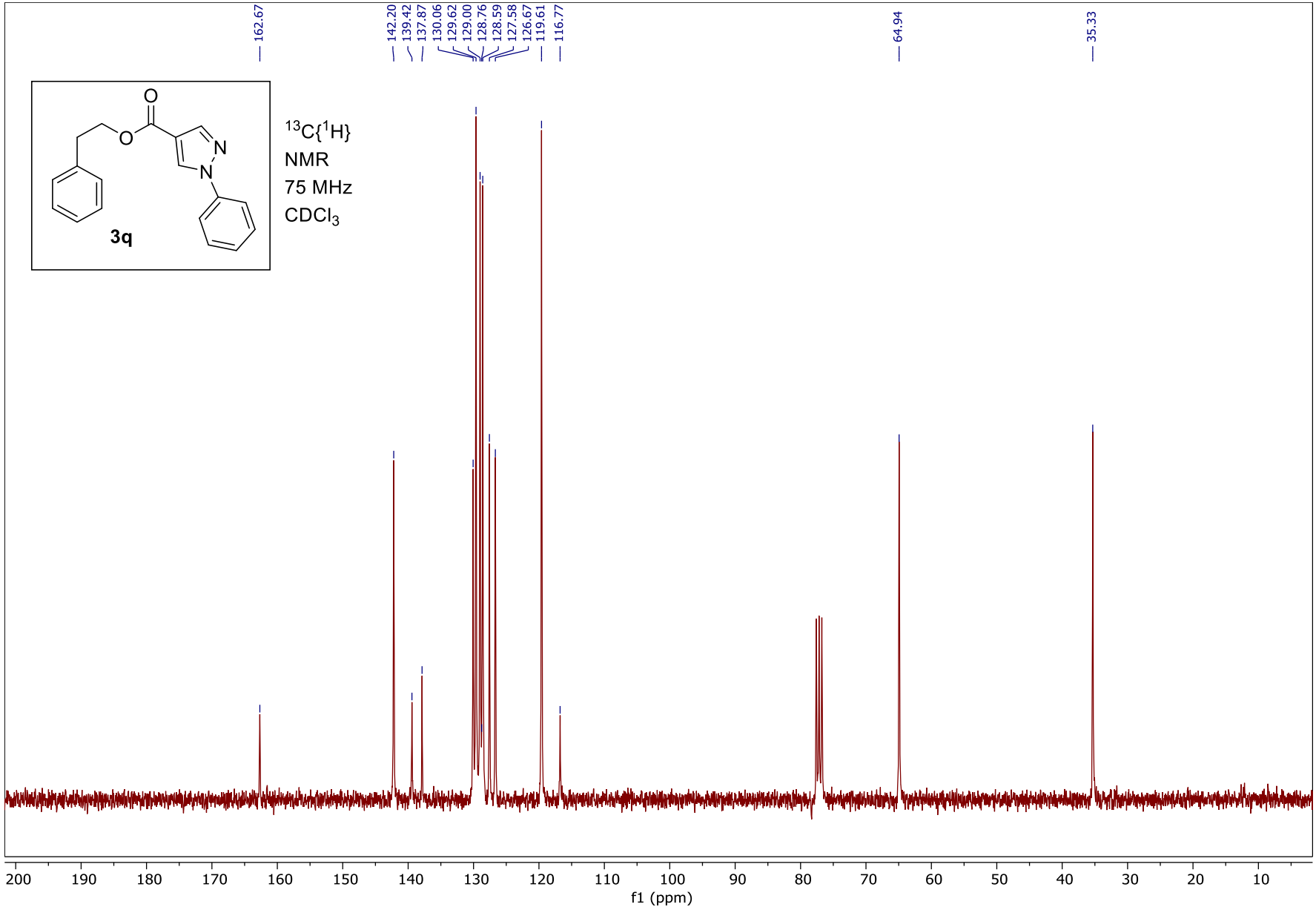

8.06
7.28
7.26
7.24
7.23
7.21
4.52
4.50
4.47
3.07
3.04
3.02
2.47
3o
1H NMR
300 MHz
CDCl3
0.98
6.28
1.96
2.00
3.00
f1 (ppm)

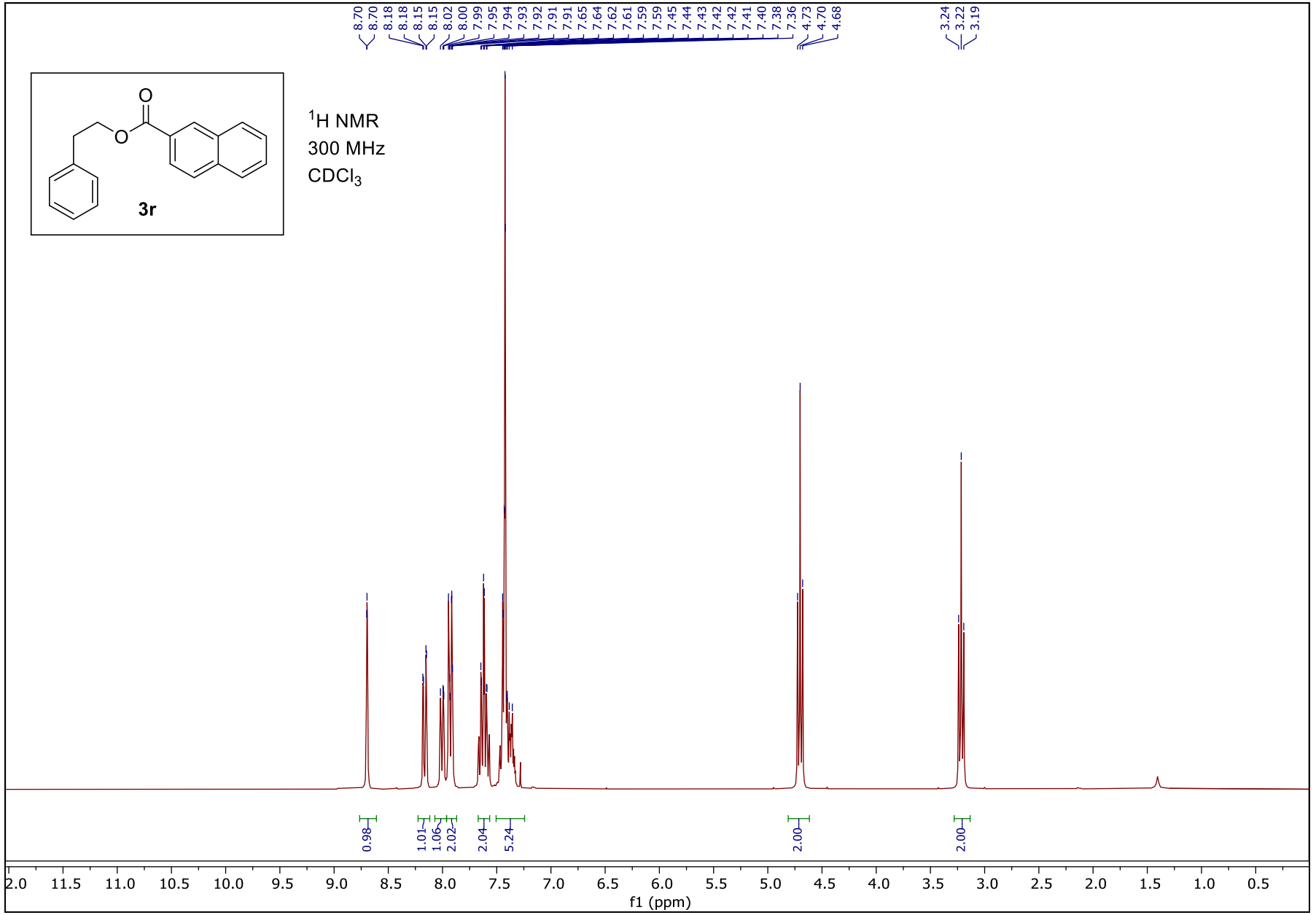

162.37
161.08
143.75
137.42
133.30
128.91
128.54
126.63
65.40
35.12
13.76
O
O
N
O
3o
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

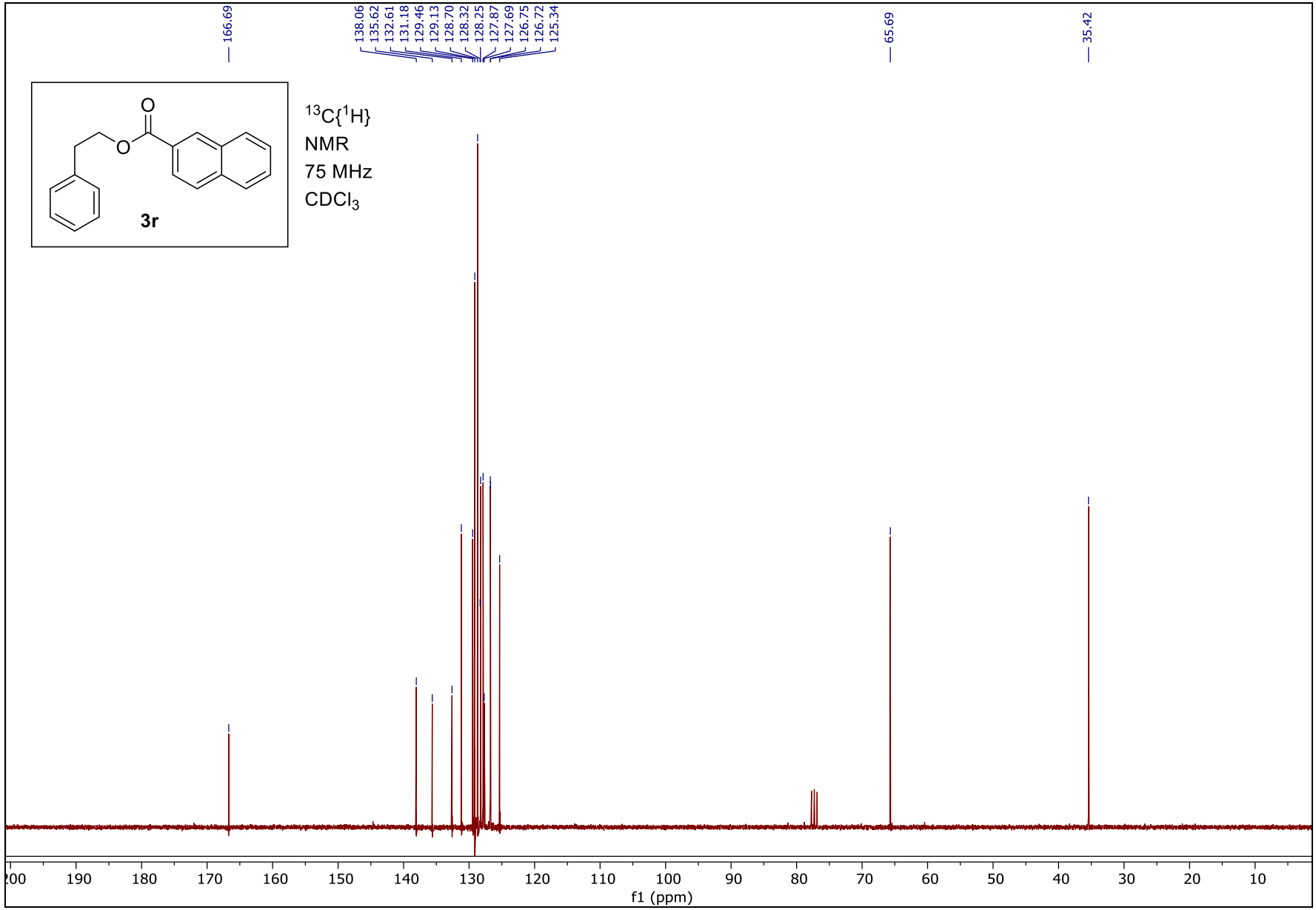

7.35
7.34
7.34
7.32
7.32
7.29
7.28
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
4.57
4.55
4.53
3.39
3.37
3.34
3.10
3.07
3.05
2.54
1.30
1.28
O
O
N–O
3p
^{1}H NMR
300 MHz
$CDCl_3$
6.49
2.00
1.00
2.03
3.05
6.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

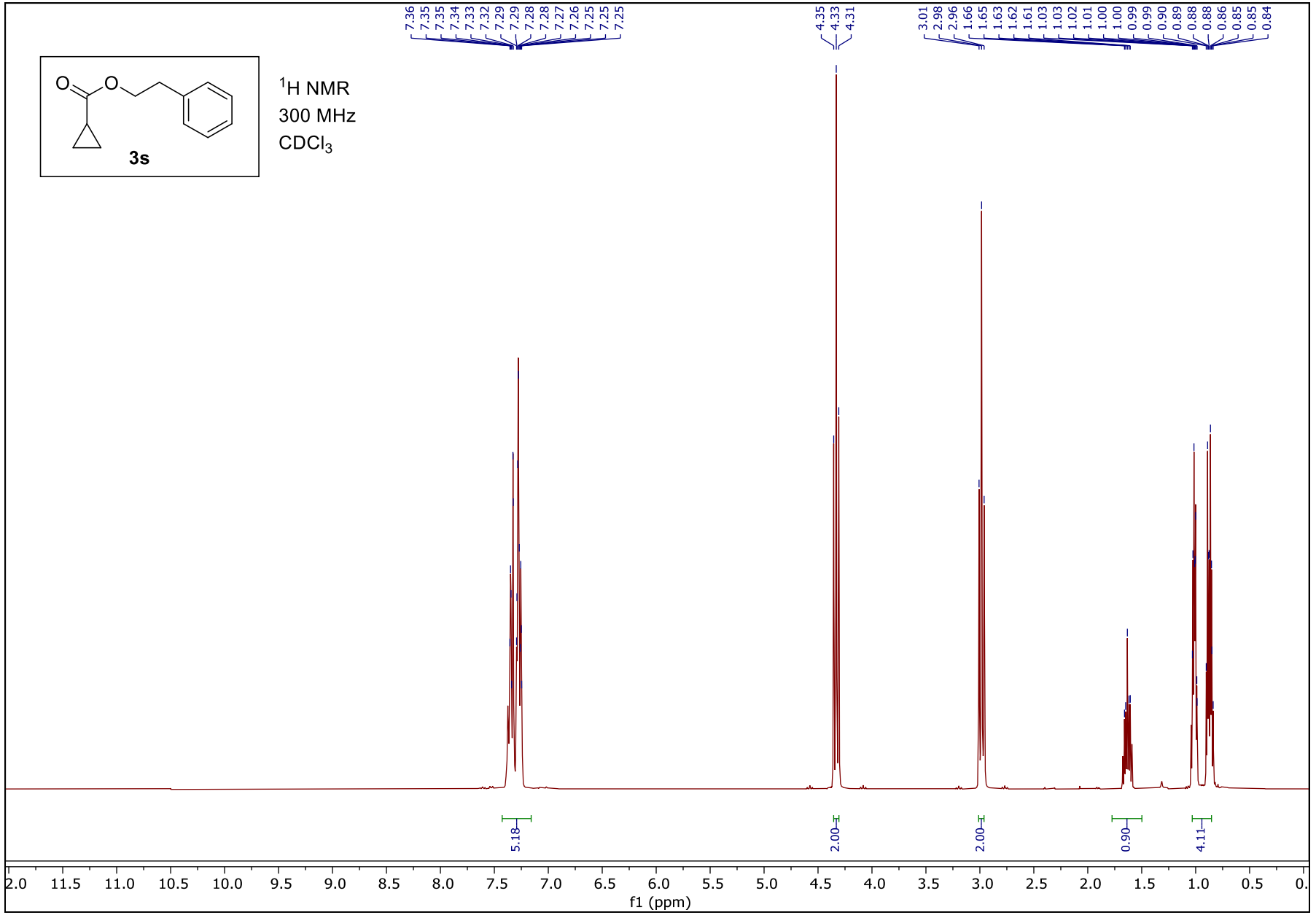

175.34
168.26
162.29
137.59
128.77
128.61
126.73
107.61
64.94
35.03
26.57
20.94
13.45
O
O
N–O
3p
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

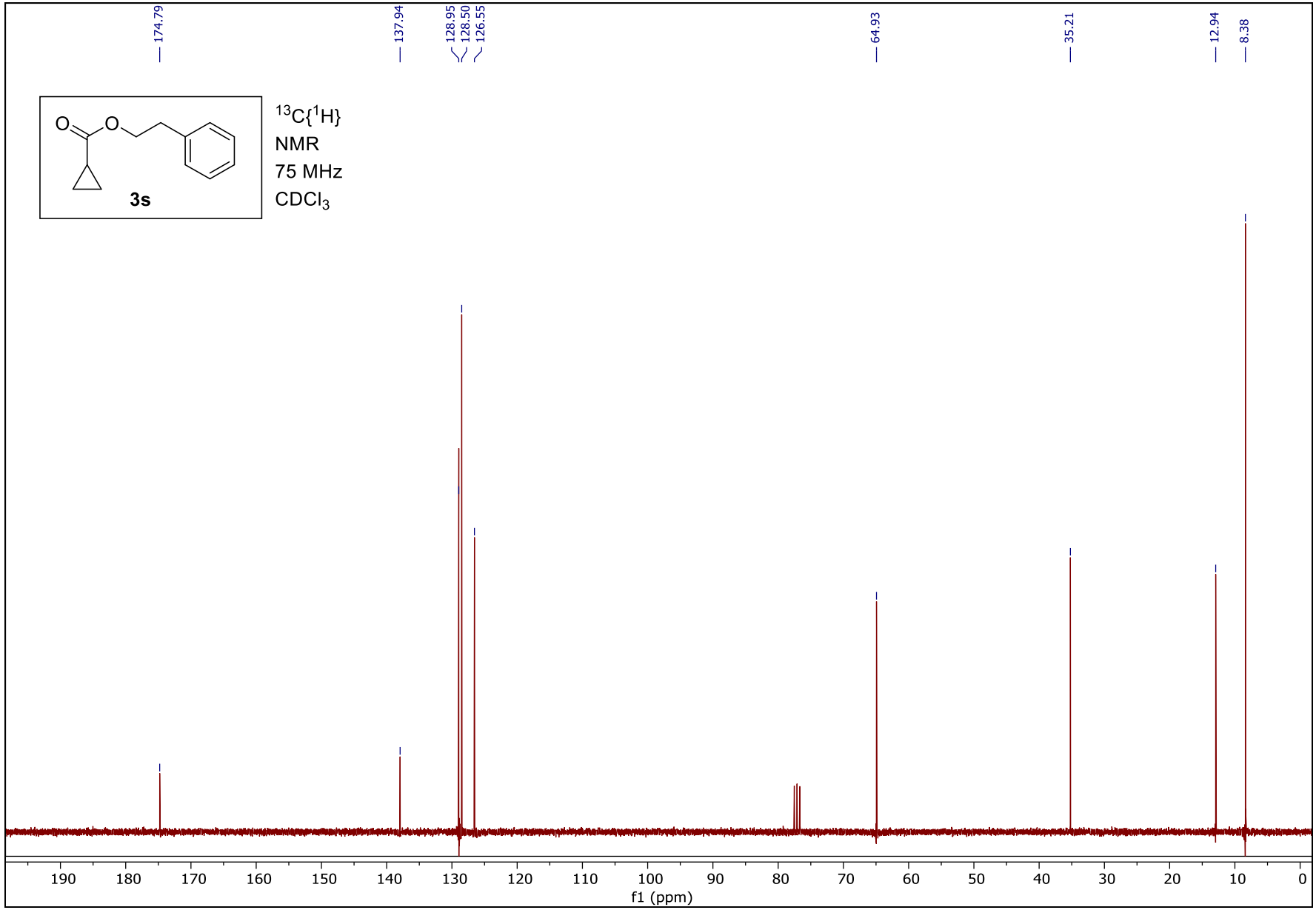

3q
^{1}H NMR
300 MHz
$CDCl_3$
8.40
8.40
8.10
8.10
7.74
7.71
7.71
7.51
7.36
7.33
7.33
7.31
7.28
4.55
4.52
4.50
3.11
3.09
3.07
0.99
1.00
2.02
2.04
7.11
2.00
2.01
f1 (ppm)

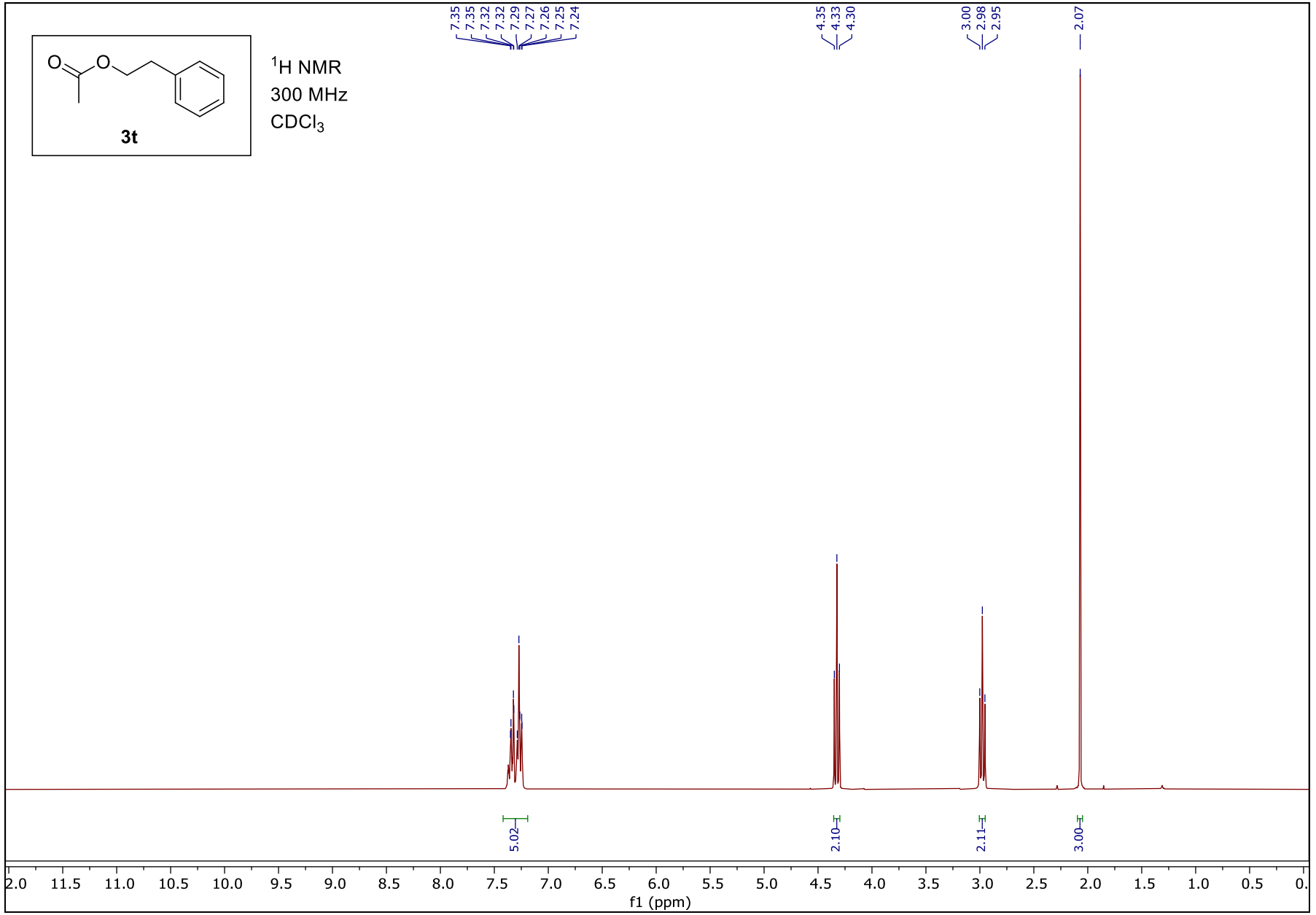

162.67
142.20
139.42
137.87
130.06
129.62
129.00
128.76
128.59
127.58
126.67
119.61
116.77
64.94
35.33
O
O
N
N
3q
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

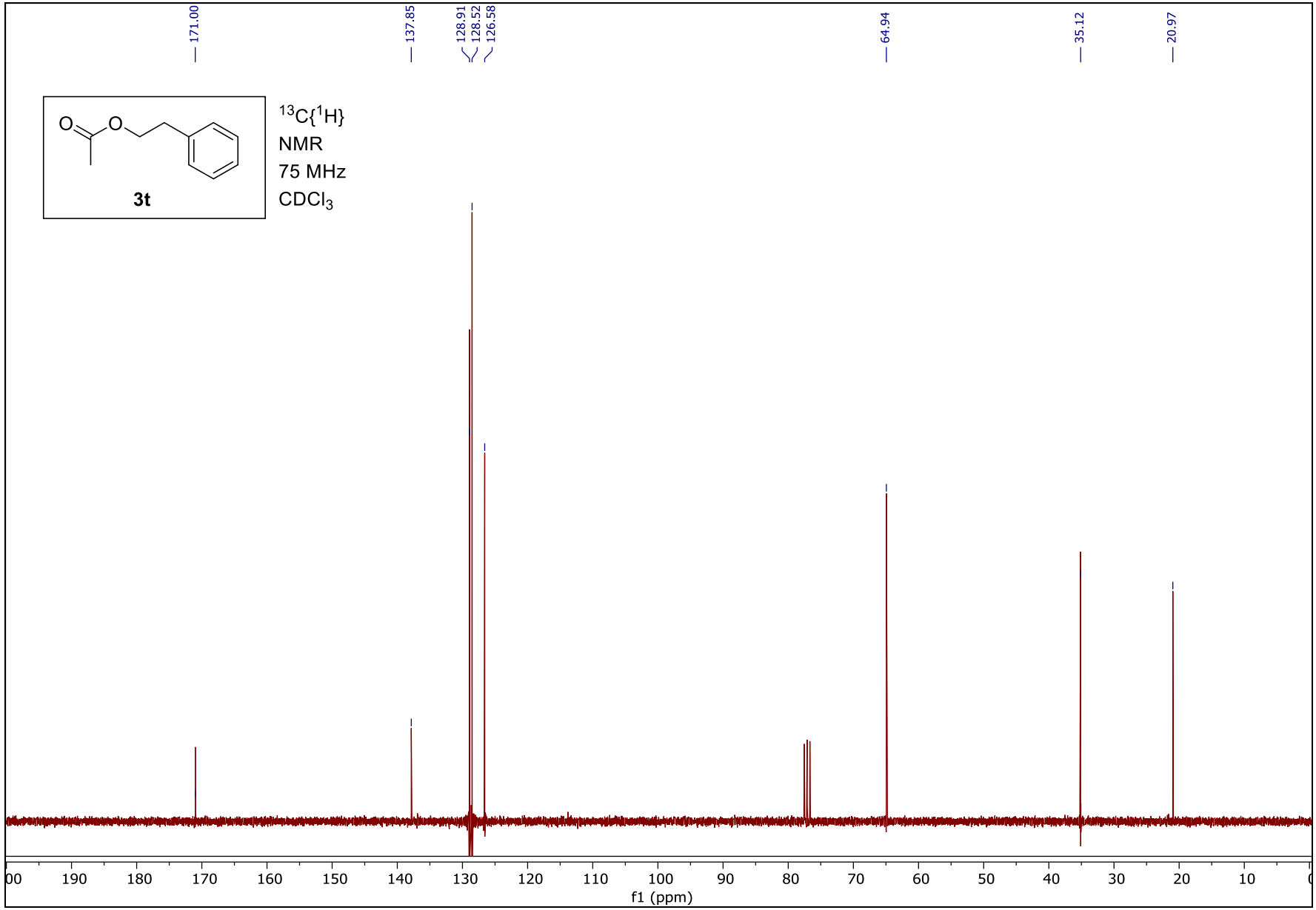

8.70
8.70
8.18
8.15
8.15
8.02
8.00
7.99
7.95
7.94
7.93
7.92
7.91
7.91
7.65
7.64
7.62
7.61
7.59
7.59
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.38
7.36
4.73
4.70
4.68
3.24
3.22
3.19
O
O
3r
1H NMR
300 MHz
CDCl3
0.98
1.01
1.06
2.02
2.04
5.24
2.00
2.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

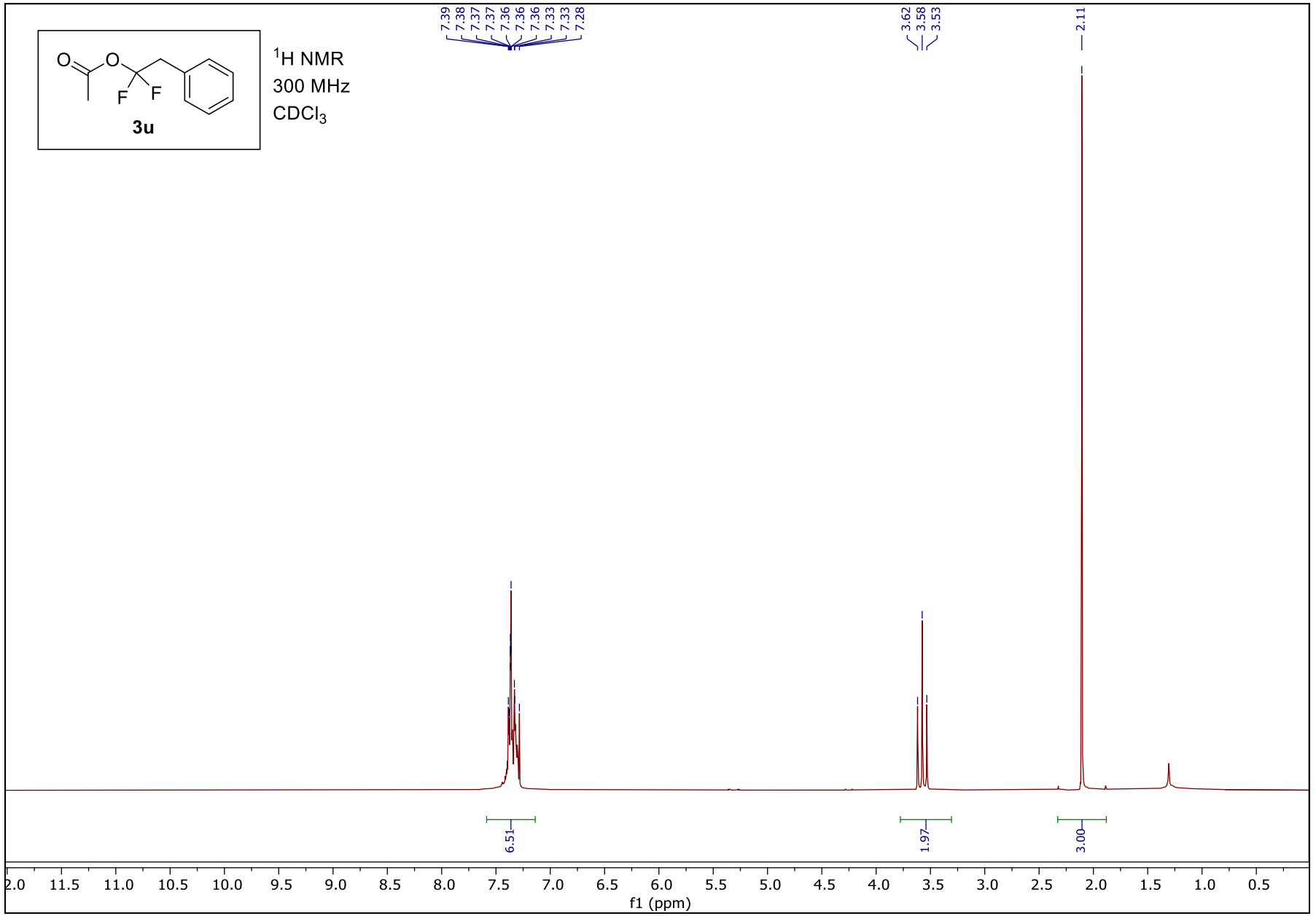

166.69
138.06
135.62
132.61
131.18
129.46
129.13
128.70
128.32
128.25
127.87
127.69
126.75
126.72
125.34
65.69
35.42
O
O
3r
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

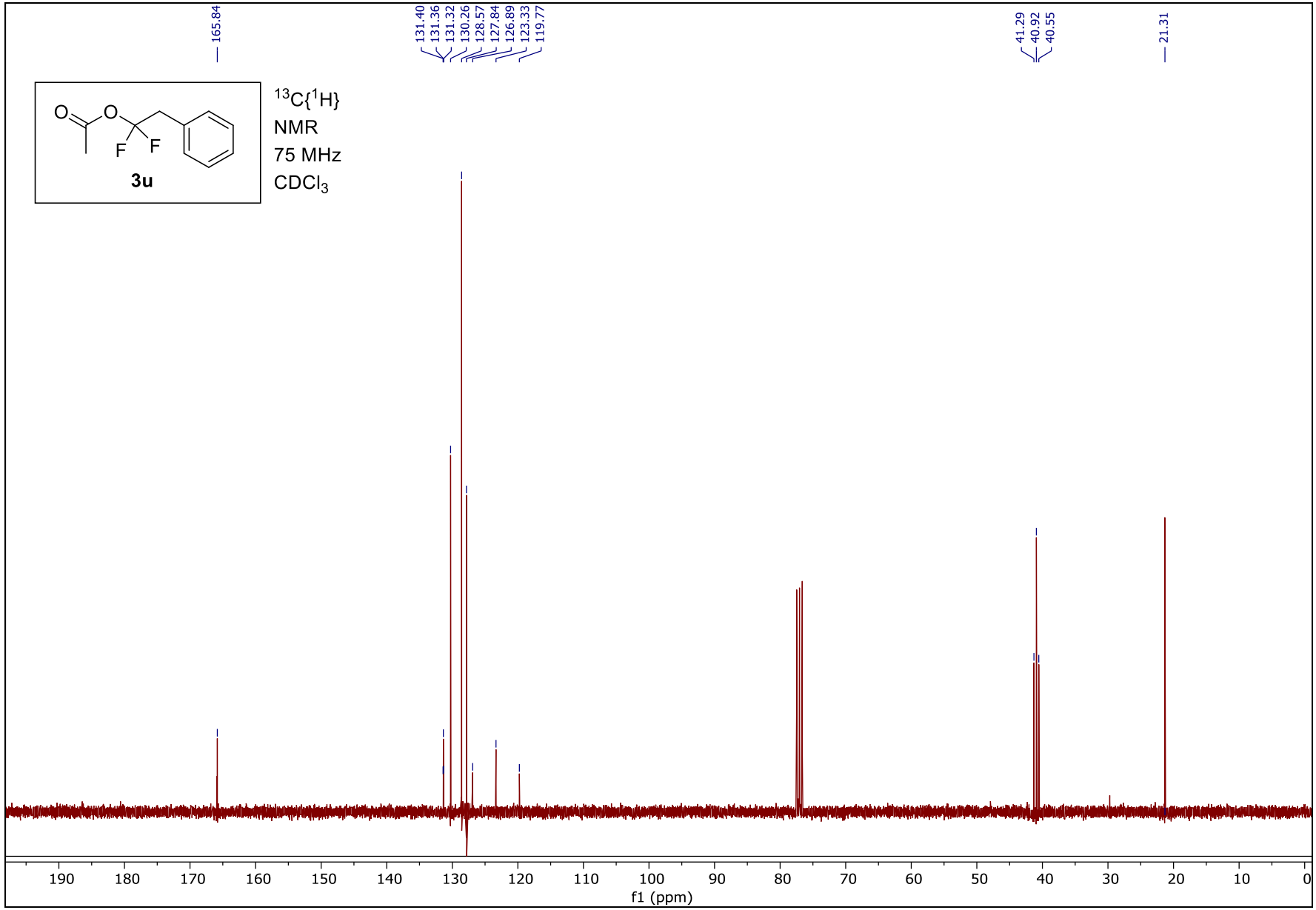

3s
1H NMR
300 MHz
CDCl3
7.36 7.35 7.35 7.34 7.33 7.32 7.29 7.29 7.28 7.28 7.27 7.26 7.25 7.25 7.25
4.35 4.33 4.31
3.01 2.98 2.96 1.66 1.65 1.63 1.62 1.61 1.03 1.03 1.02 1.01 1.00 1.00 0.99 0.99 0.90 0.89 0.88 0.88 0.86 0.85 0.85 0.84
5.18
2.00
2.00
0.90
4.11
f1 (ppm)

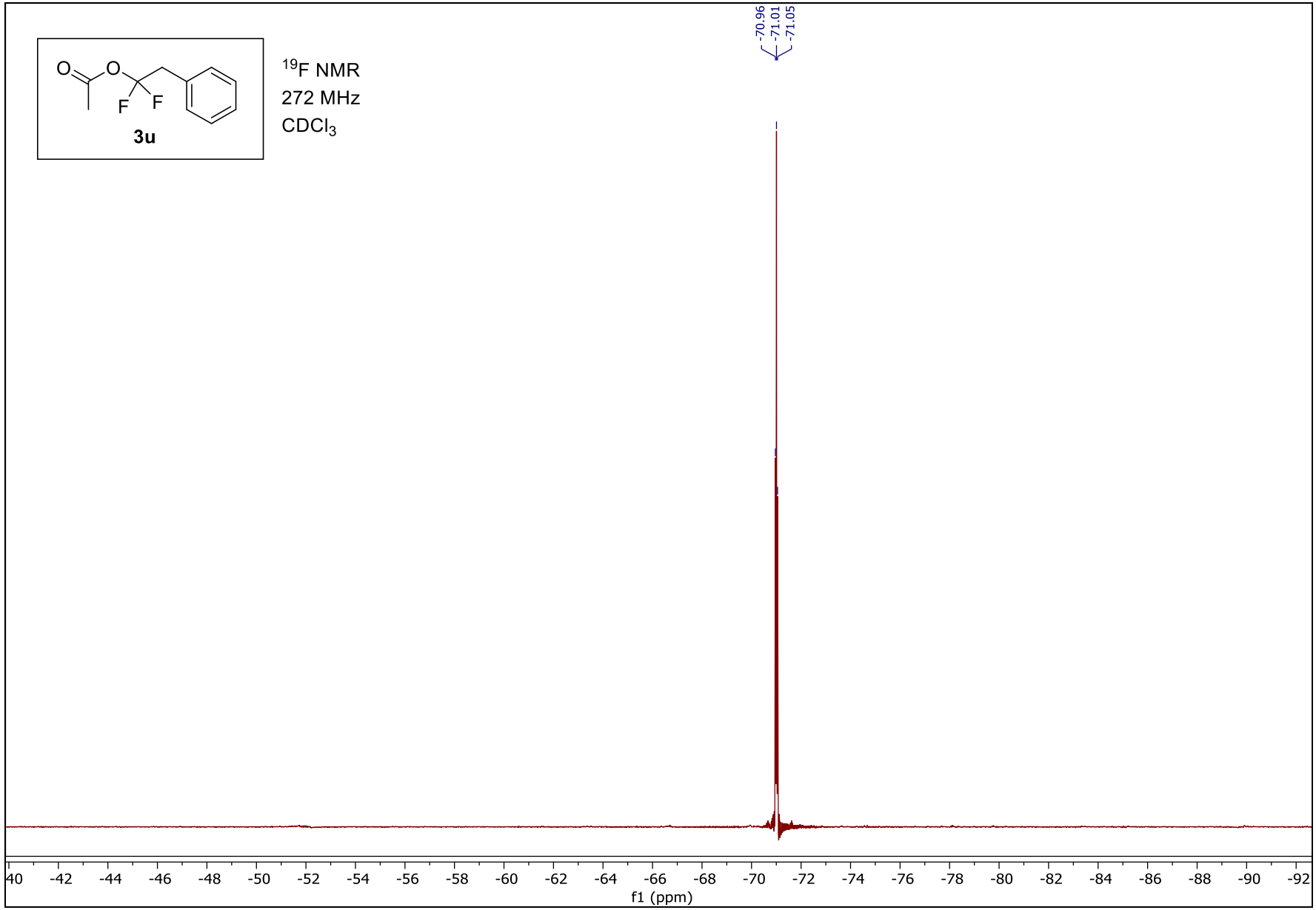

174.79
137.94
128.95
128.50
126.55
64.93
35.21
12.94
8.38
3s
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

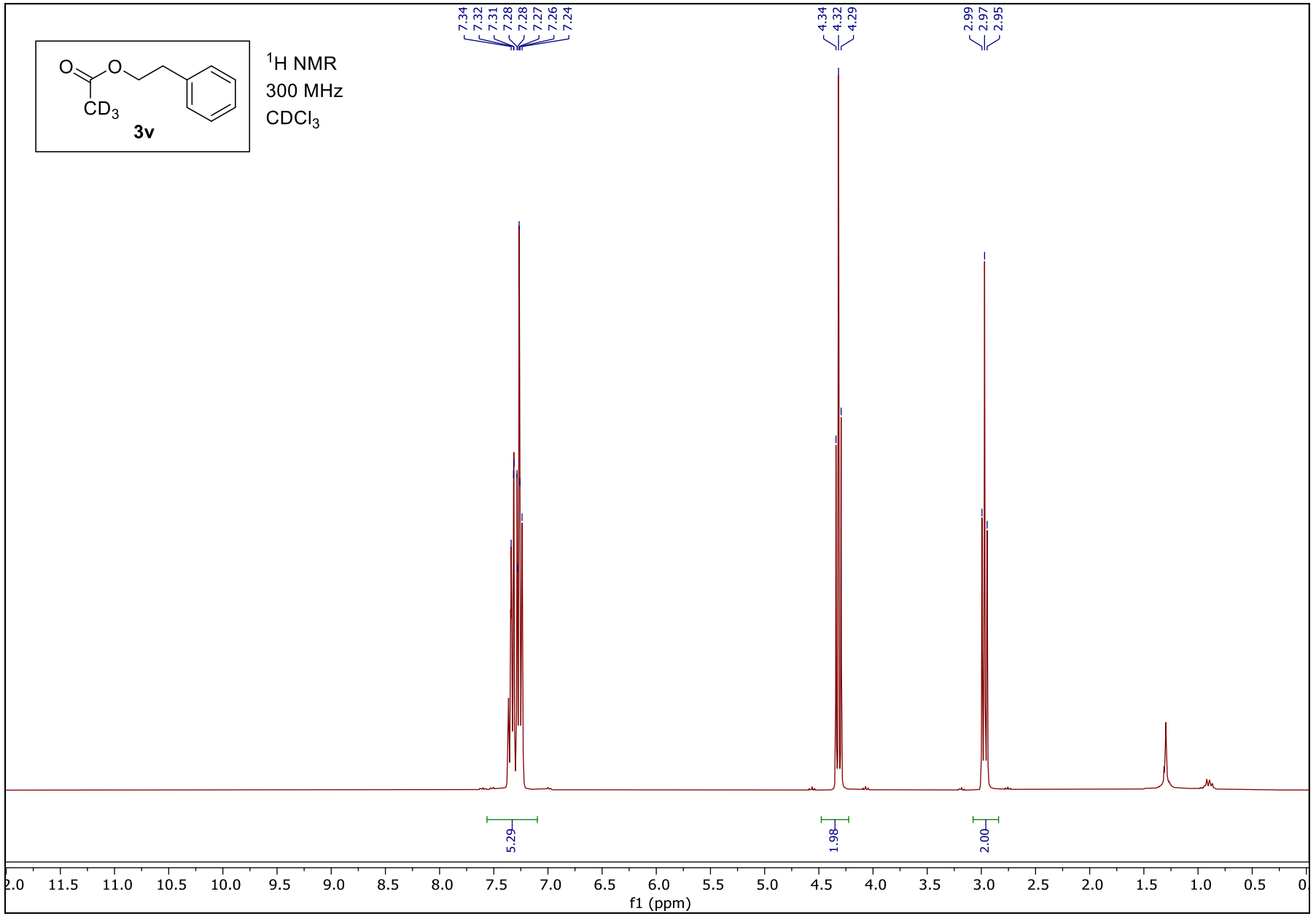

3t
^{1}H NMR
300 MHz
$CDCl_3$
7.35
7.35
7.32
7.32
7.29
7.27
7.26
7.25
7.24
4.35
4.33
4.30
3.00
2.98
2.95
2.07
5.02
2.10
2.11
3.00
f1 (ppm)

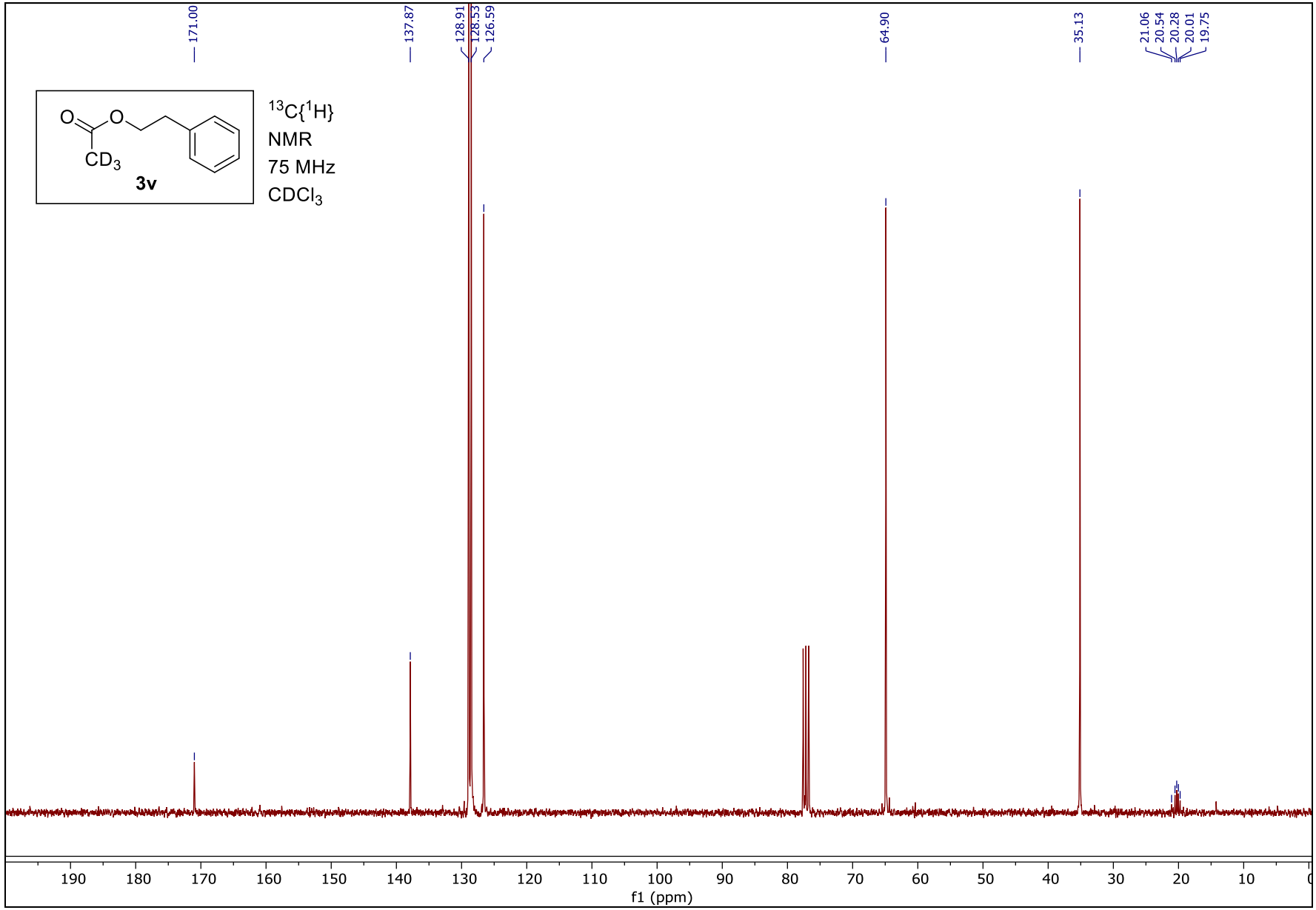

171.00
137.85
128.91
128.52
126.58
64.94
35.12
20.97
3t
13C{1H}
NMR
75 MHz
CDCl3
f1 (ppm)

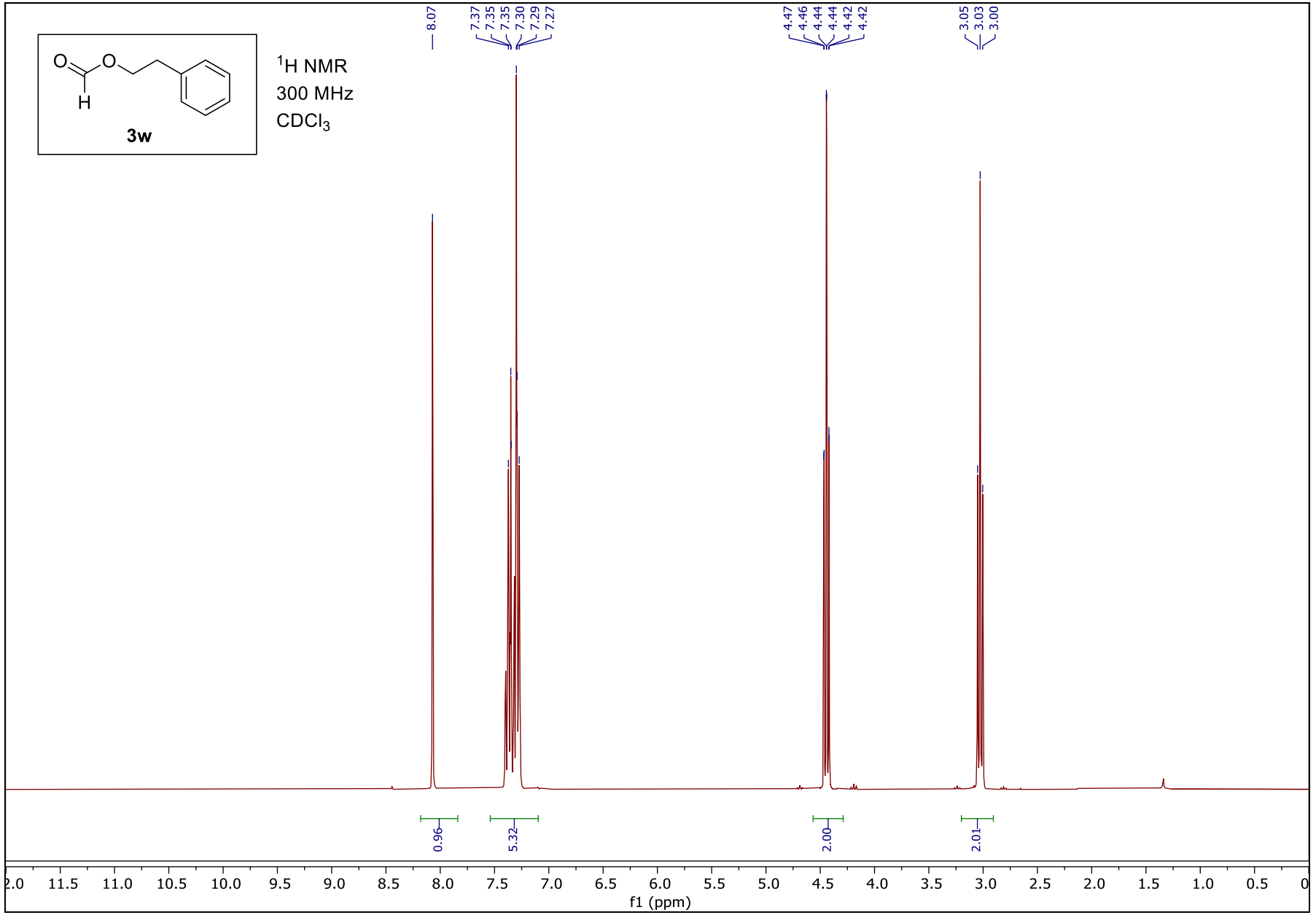

3u
1H NMR
300 MHz
CDCl3
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.33
7.33
7.28
3.62
3.58
3.53
2.11
6.51
1.97
3.00
f1 (ppm)

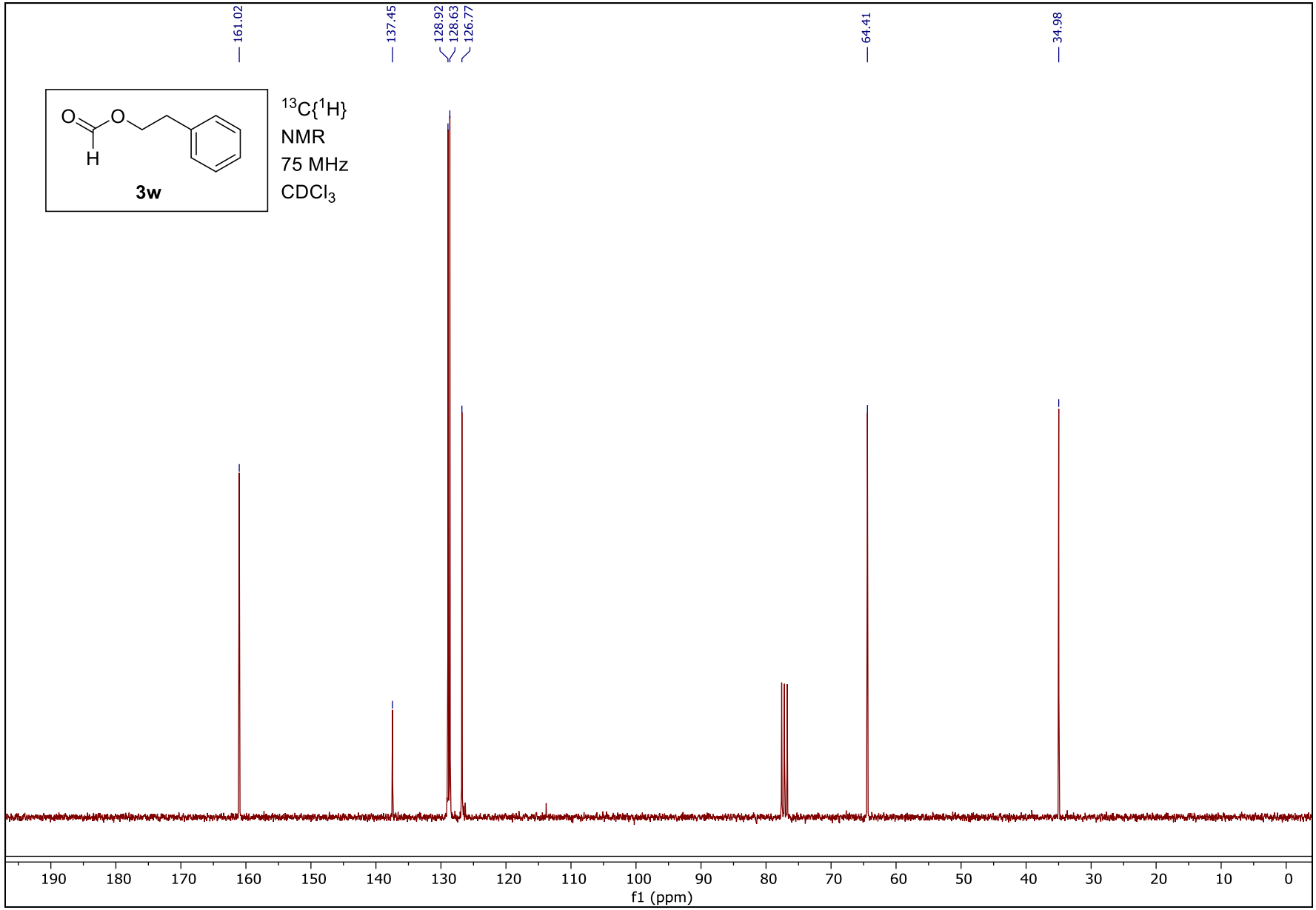

165.84
131.40
131.36
131.32
130.26
128.57
127.84
126.89
123.33
119.77
41.29
40.92
40.55
21.31
O
O
F
F
3u
13C{1H}
NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

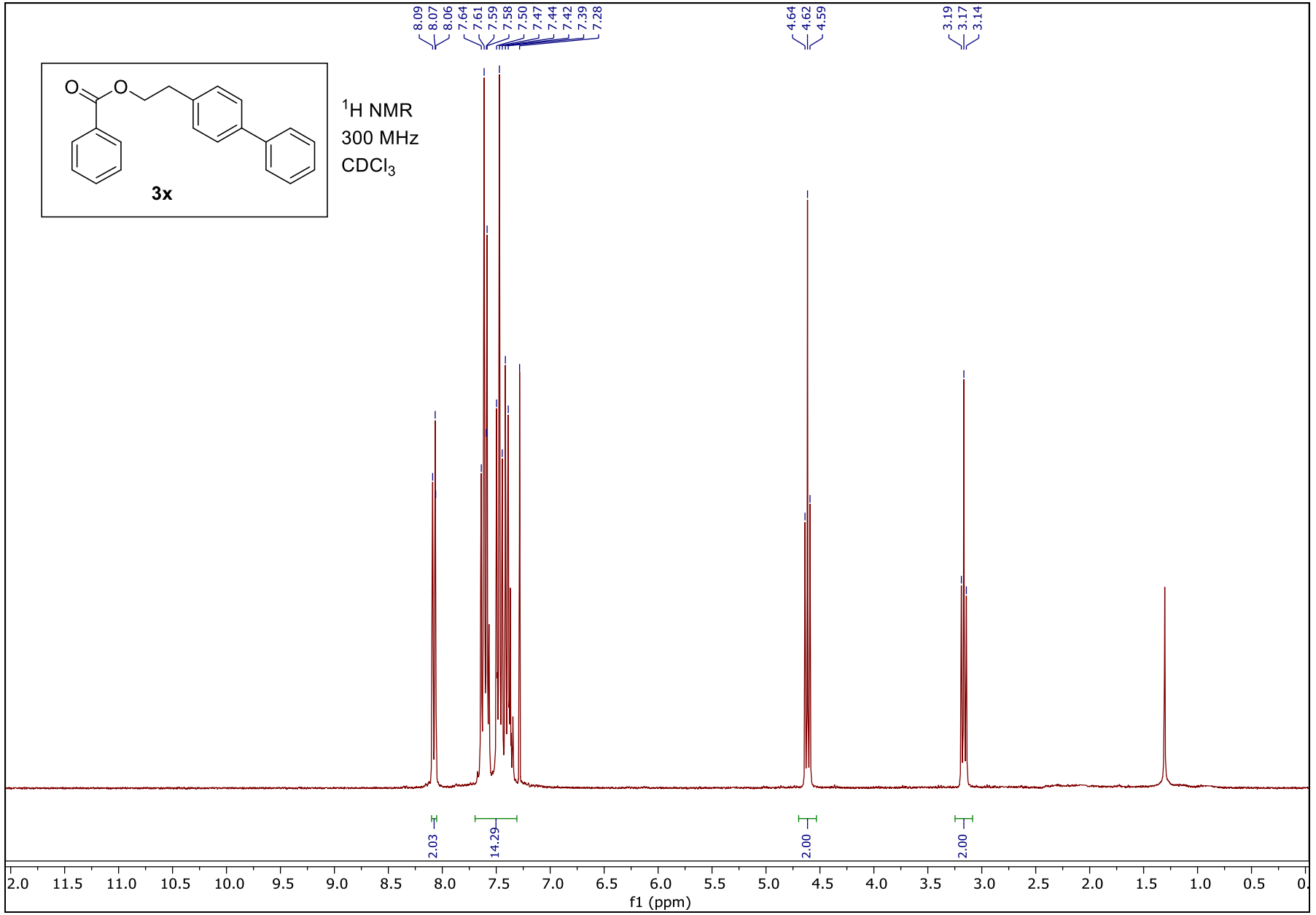

3u
19F NMR
272 MHz
CDCl3
-70.96
-71.01
-71.05
40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92
f1 (ppm)

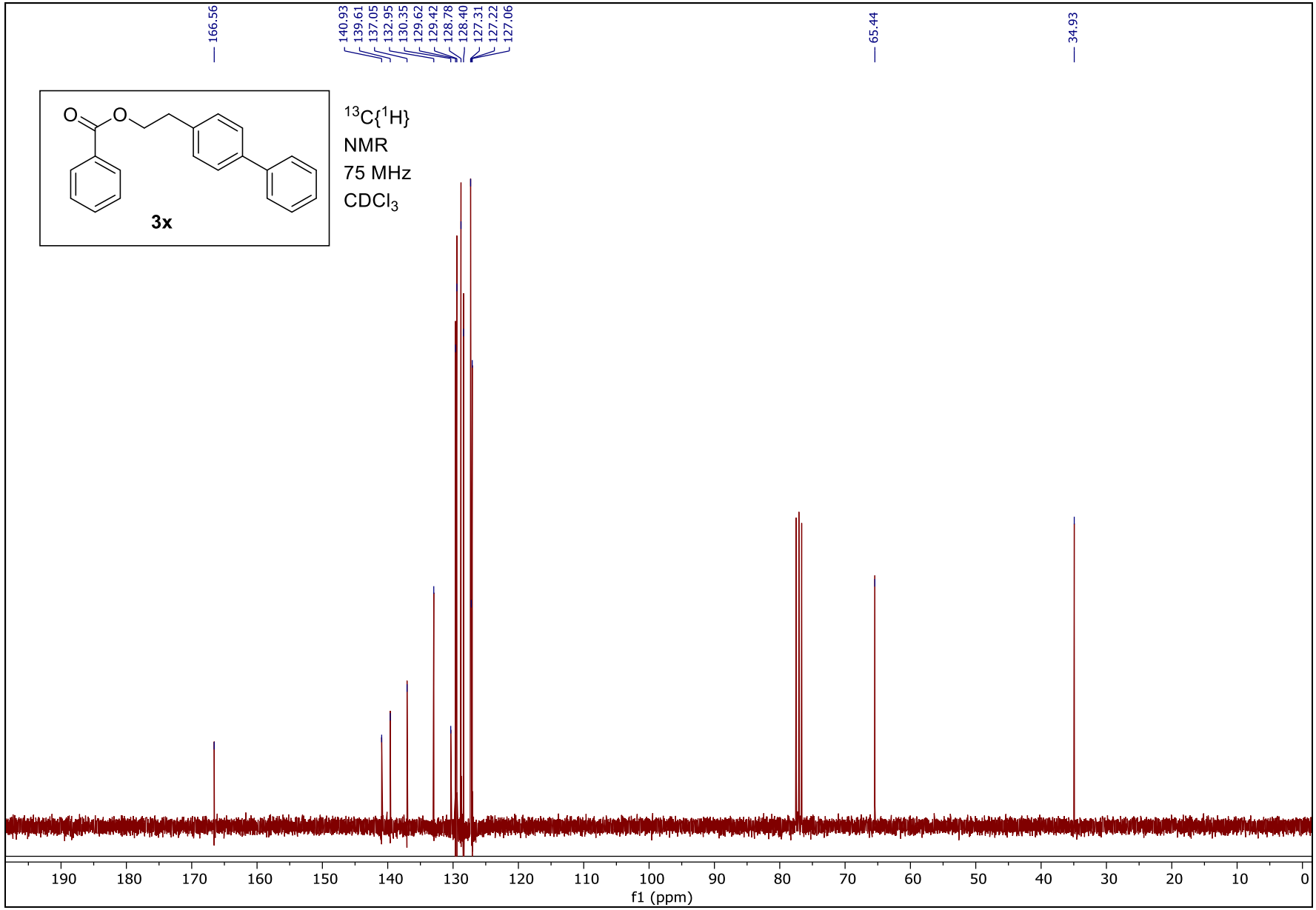

7.34
7.32
7.31
7.28
7.28
7.27
7.26
7.24
4.34
4.32
4.29
2.99
2.97
2.95
O
O
CD3
3v
1H NMR
300 MHz
CDCl3
5.29
1.98
2.00
f1 (ppm)

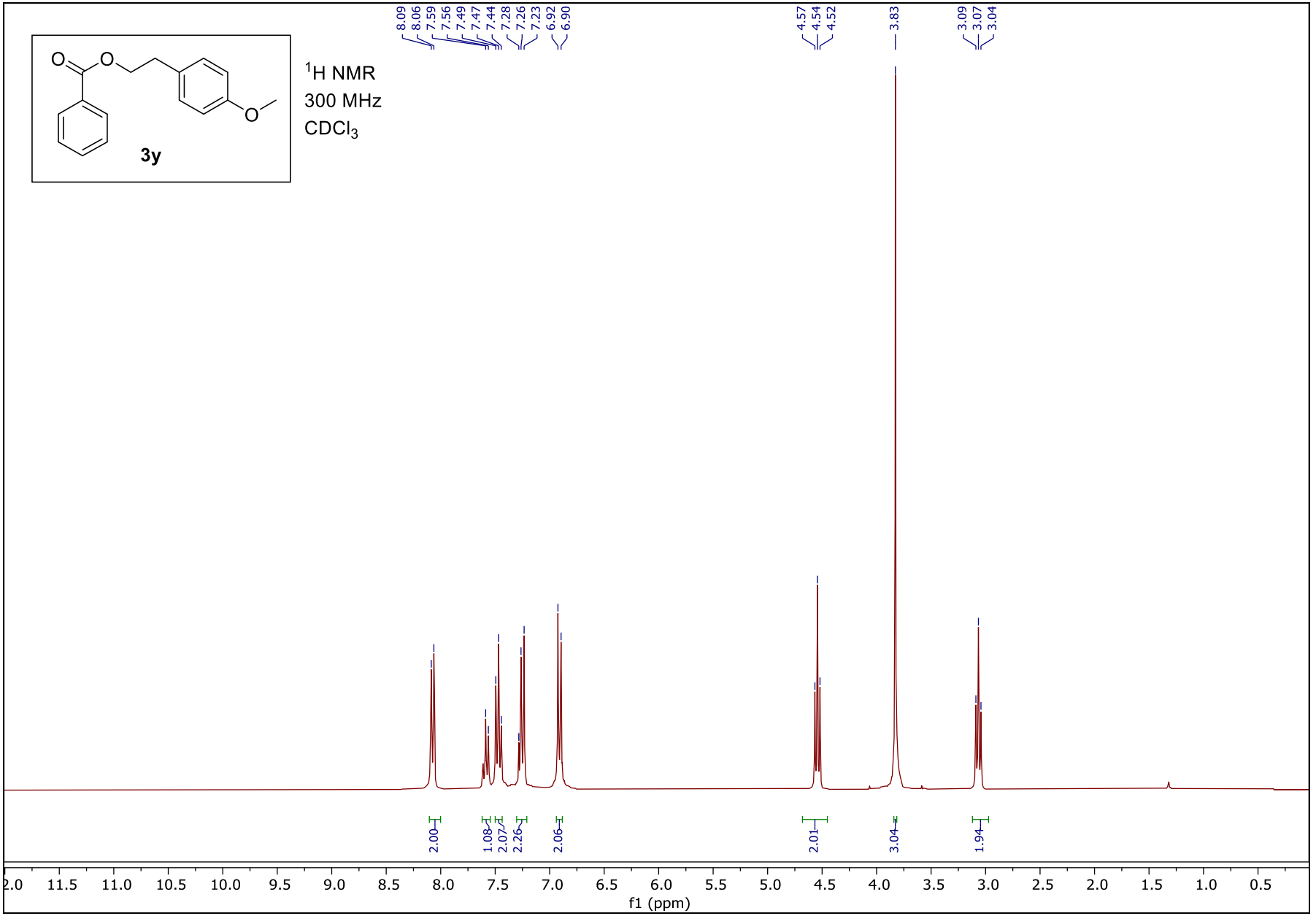

171.00
137.87
128.91
128.53
126.59
64.90
35.13
21.06
20.54
20.28
20.01
19.75
O
O
CD3
3v
13C{1H}
NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

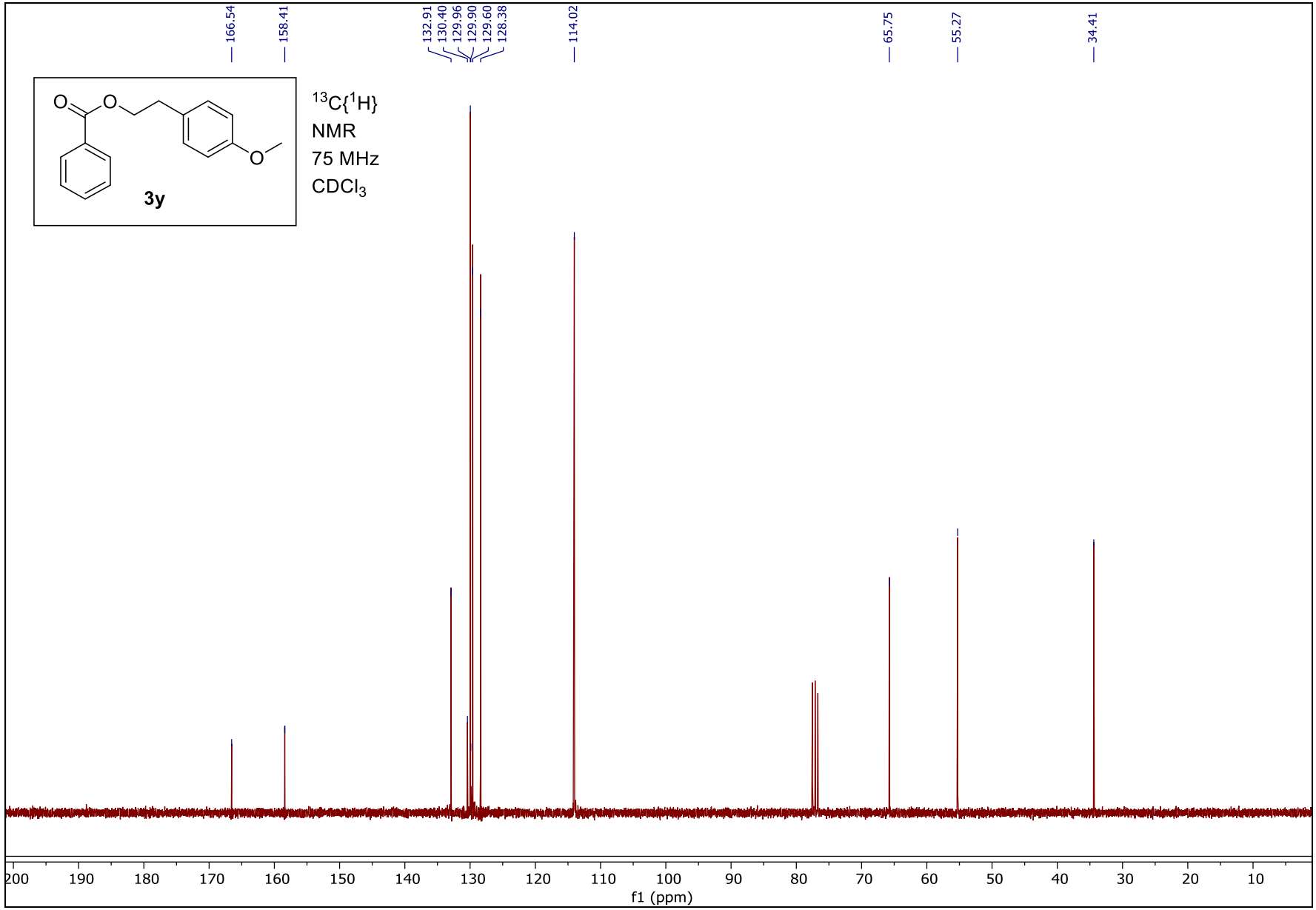

3w
1H NMR
300 MHz
CDCl3
8.07
7.37
7.35
7.35
7.30
7.29
7.27
4.47
4.46
4.44
4.44
4.42
4.42
3.05
3.03
3.00
0.96
5.32
2.00
2.01
f1 (ppm)

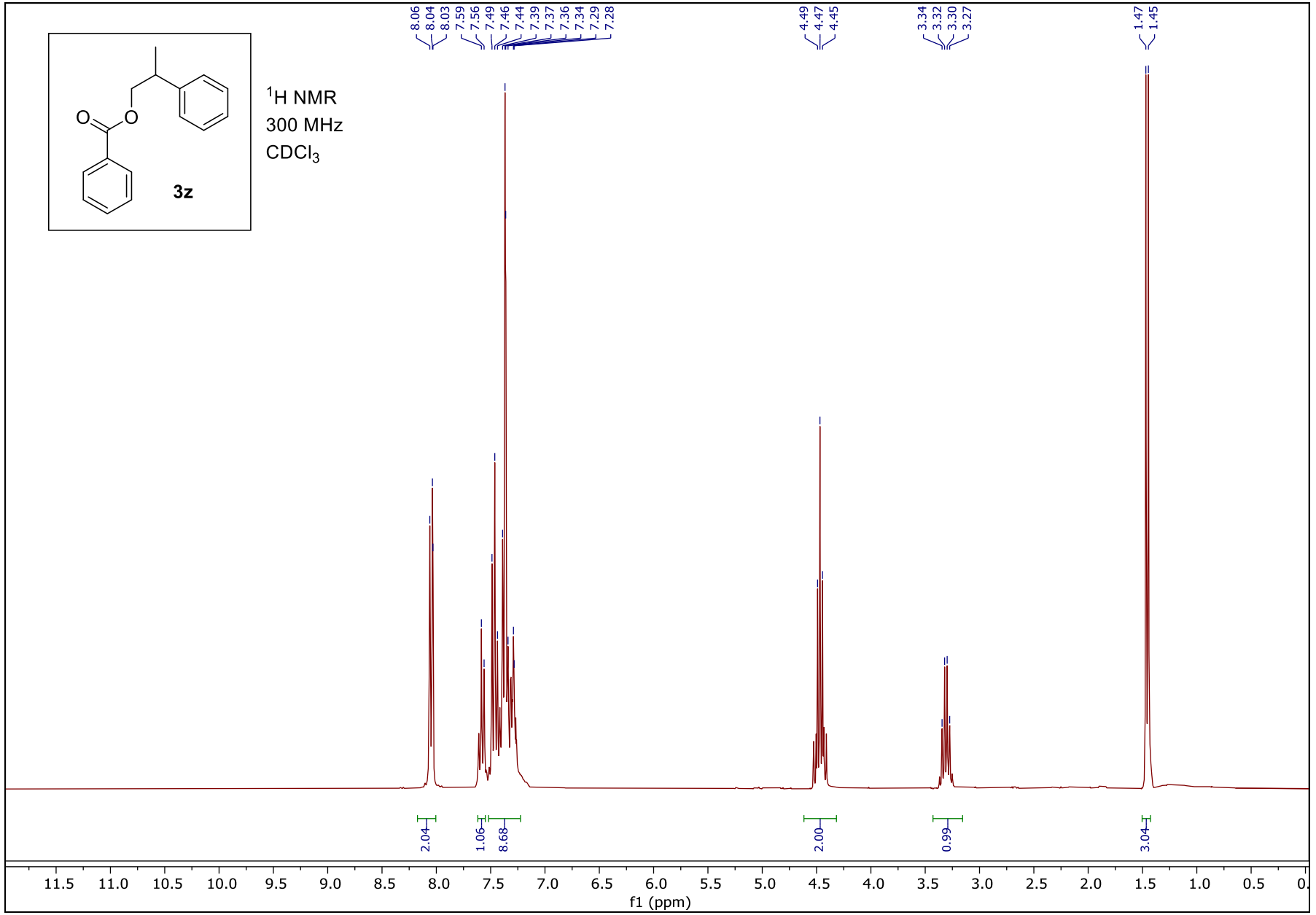

161.02
137.45
128.92
128.63
126.77
64.41
34.98
O
O
H
3w
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

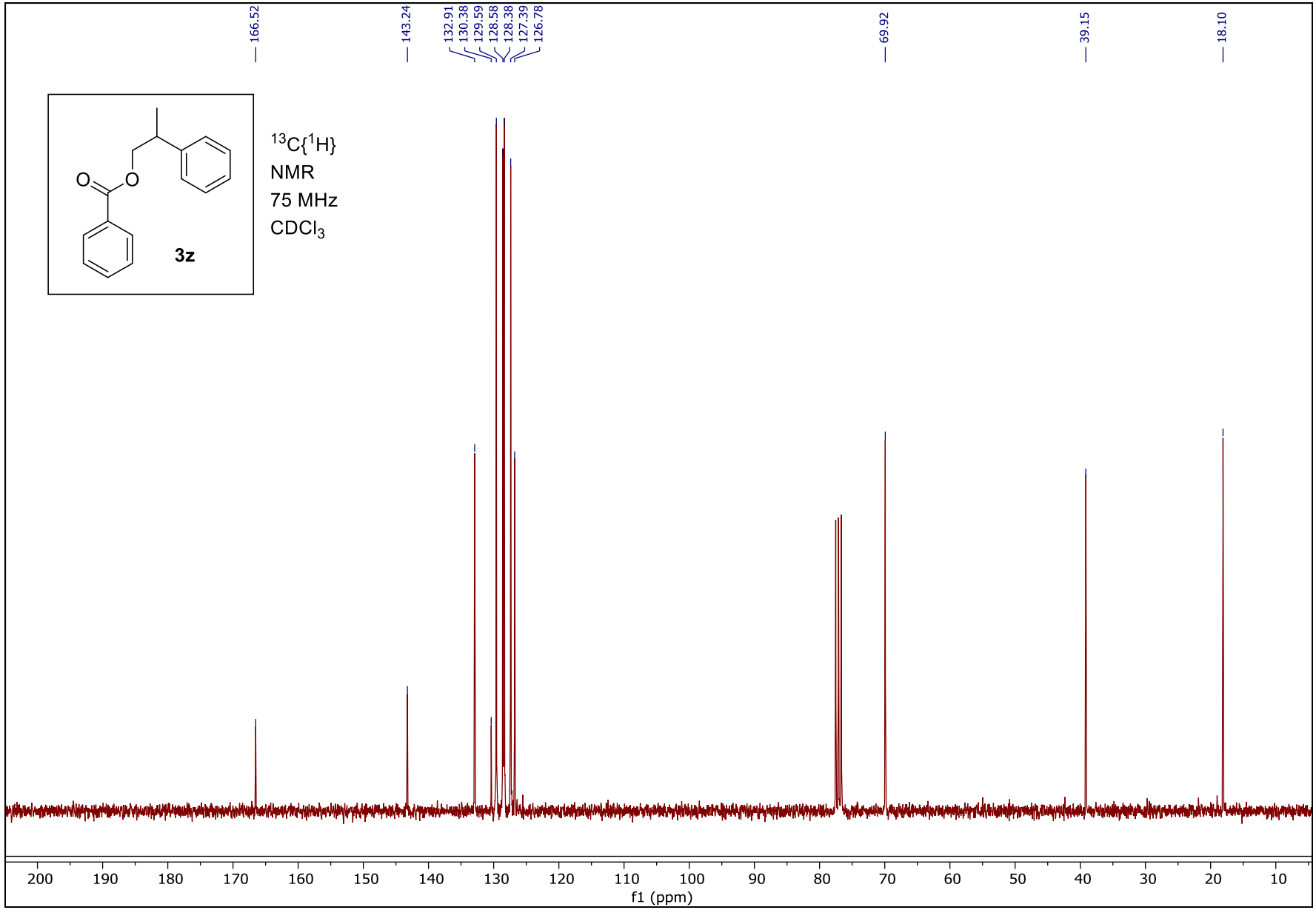

8.09
8.07
8.06
7.64
7.61
7.59
7.58
7.50
7.47
7.44
7.42
7.39
7.28
4.64
4.62
4.59
3.19
3.17
3.14
3x
1H NMR
300 MHz
CDCl3
2.03
14.29
2.00
2.00
f1 (ppm)

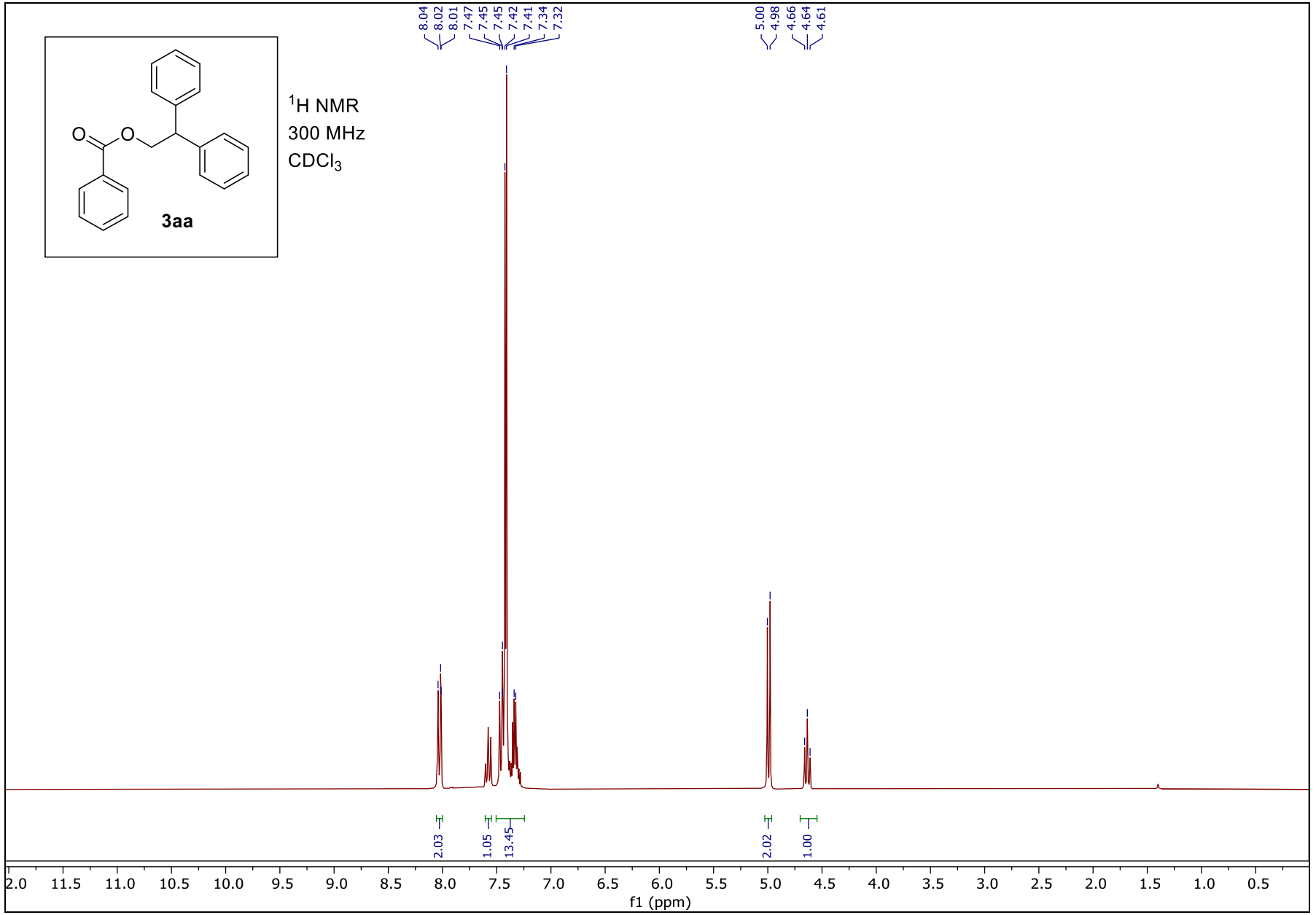

166.56
140.93
139.61
137.05
132.95
130.35
129.62
129.42
128.78
128.40
127.31
127.22
127.06
65.44
34.93
O
O
3x
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

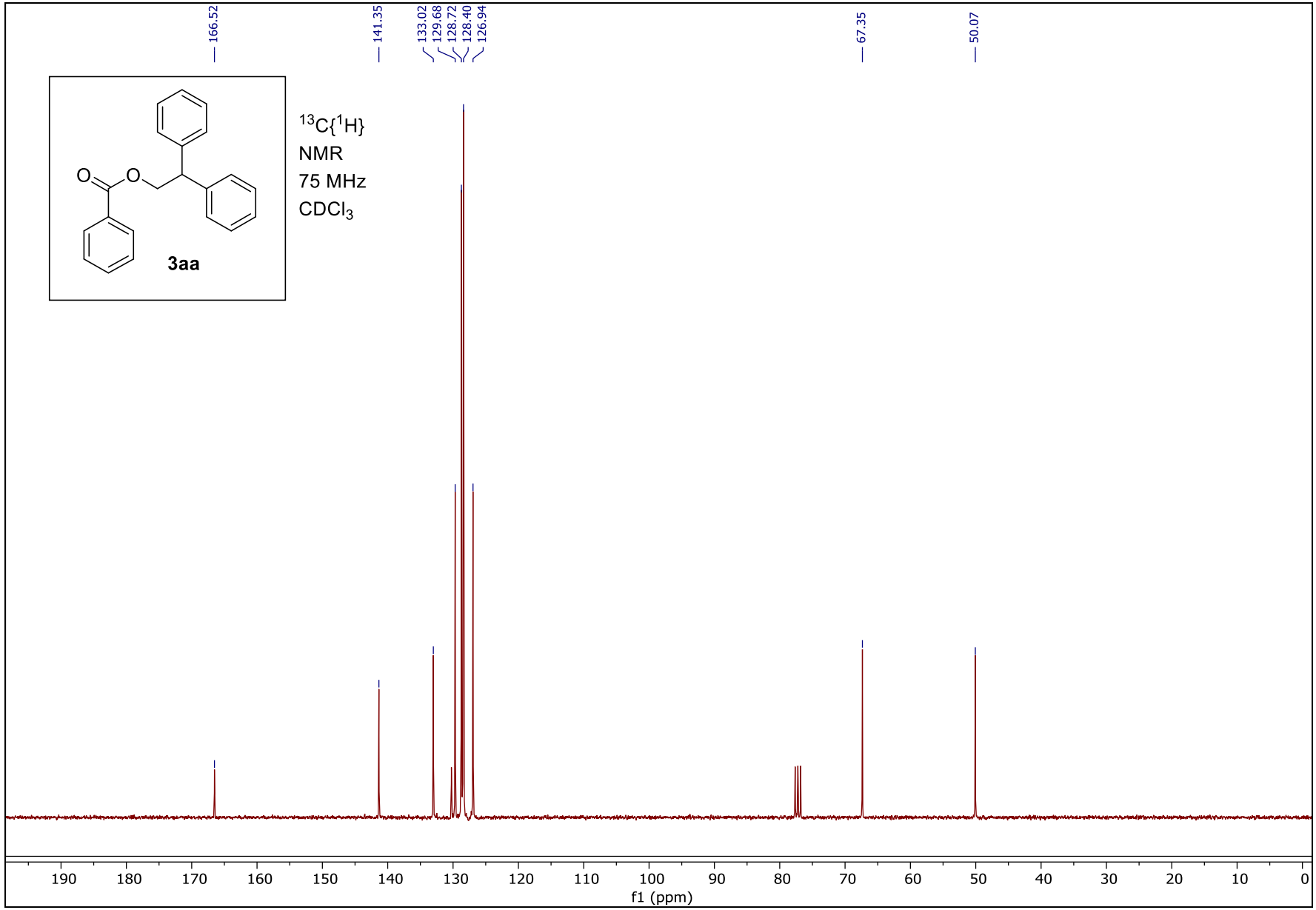

3y
1H NMR
300 MHz
CDCl3
8.09
8.06
7.59
7.56
7.49
7.47
7.44
7.28
7.26
7.23
6.92
6.90
4.57
4.54
4.52
3.83
3.09
3.07
3.04
2.00
1.08
2.07
2.26
2.06
2.01
3.04
1.94
f1 (ppm)

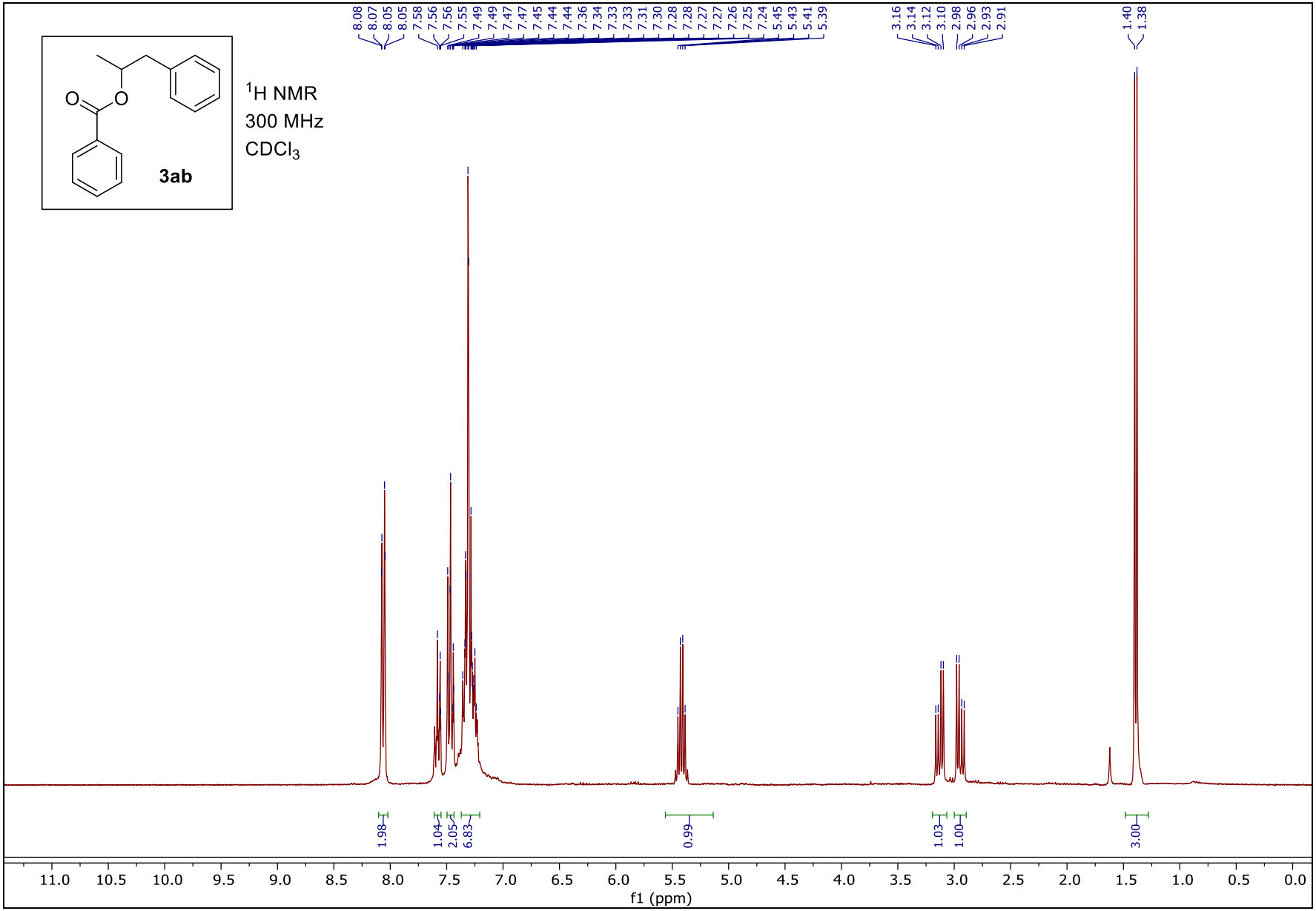

166.54
158.41
132.91
130.40
129.96
129.90
129.60
128.38
114.02
65.75
55.27
34.41
O
O
O
3y
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

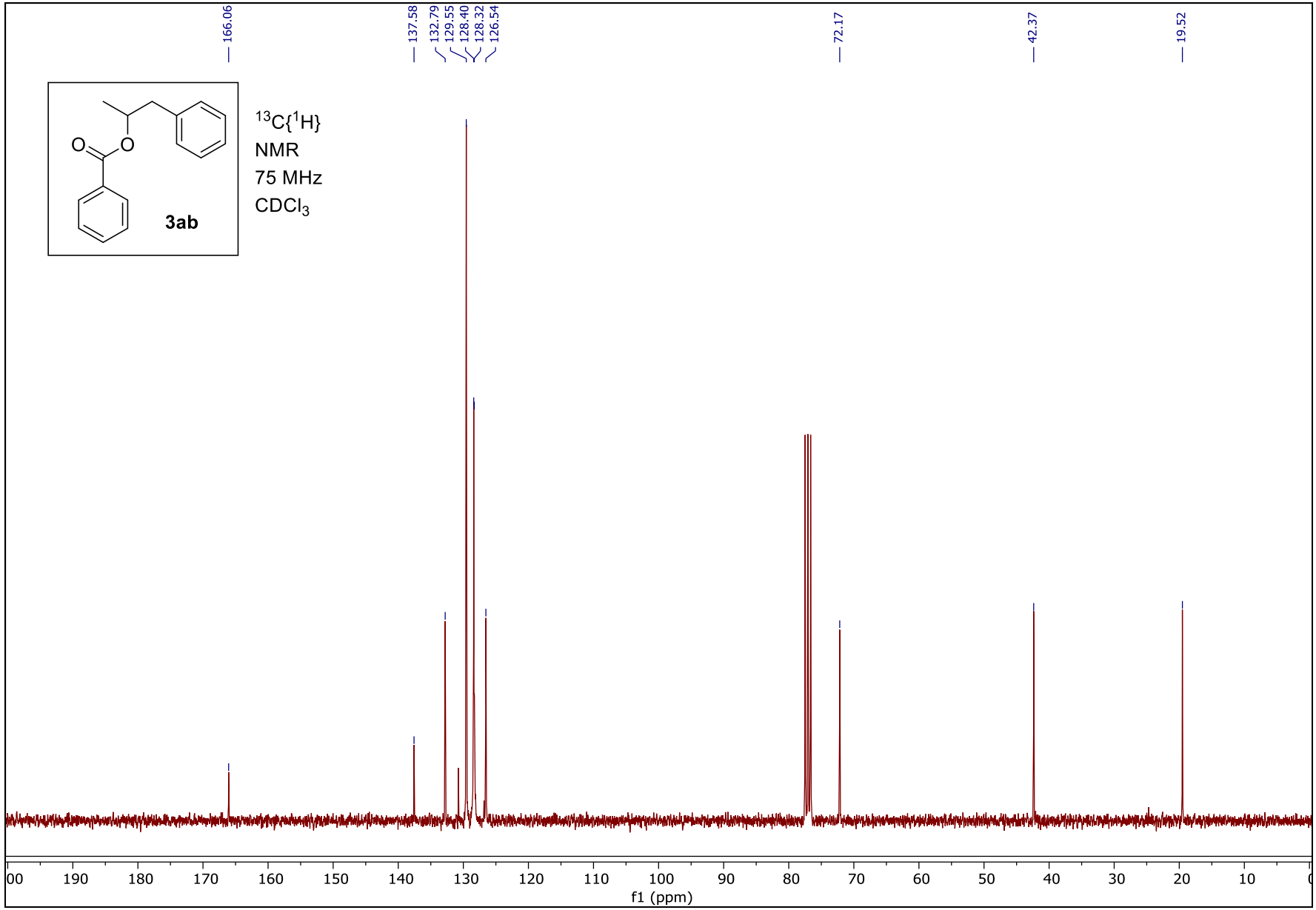

3z
^{1}H NMR
300 MHz
$CDCl_3$
8.06
8.04
8.03
7.59
7.56
7.49
7.46
7.44
7.39
7.37
7.36
7.34
7.29
7.28
4.49
4.47
4.45
3.34
3.32
3.30
3.27
1.47
1.45
2.04
1.06
8.68
2.00
0.99
3.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

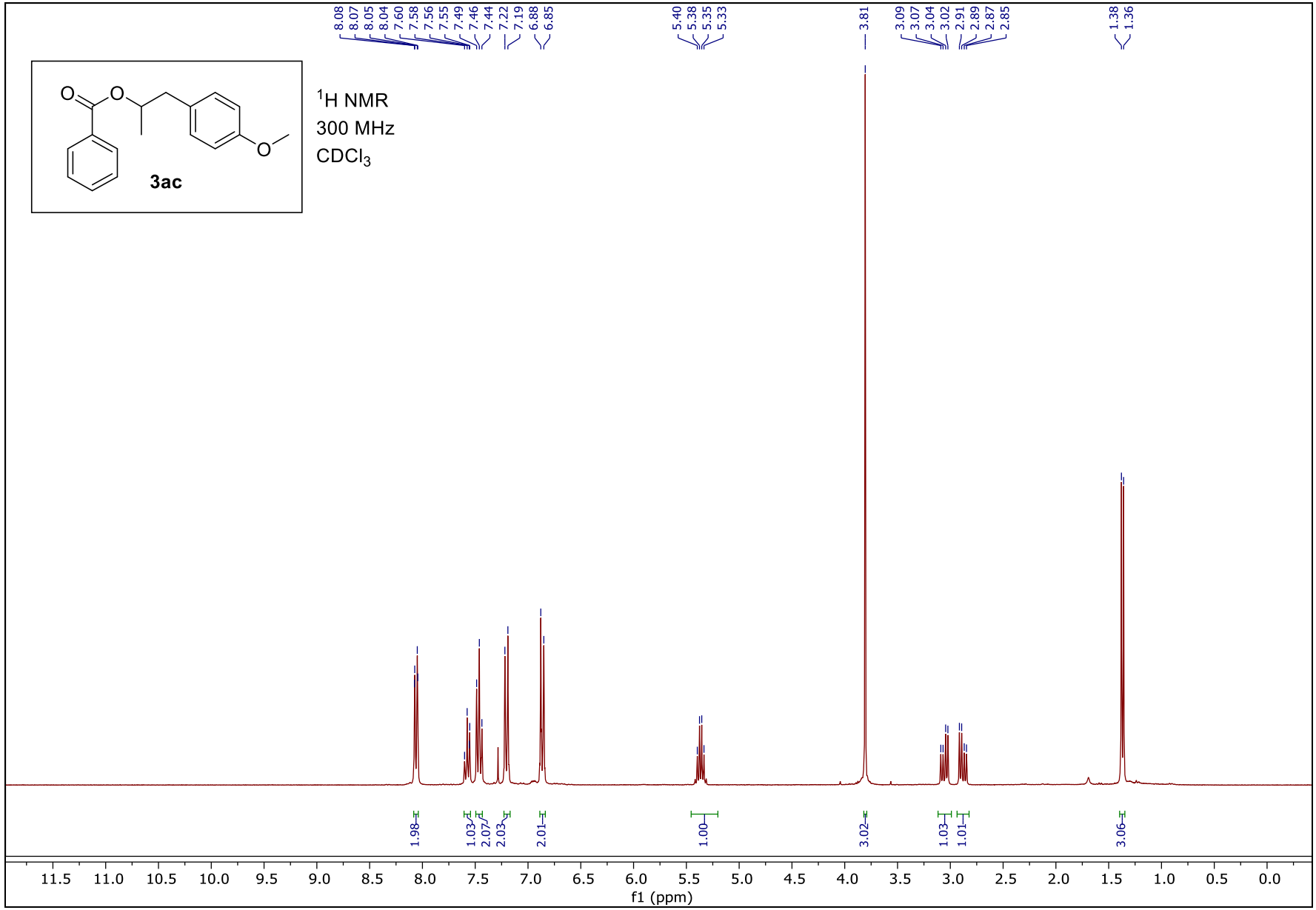

166.52
143.24
132.91
130.38
129.59
128.58
128.38
127.39
126.78
69.92
39.15
18.10
O
O
3z
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

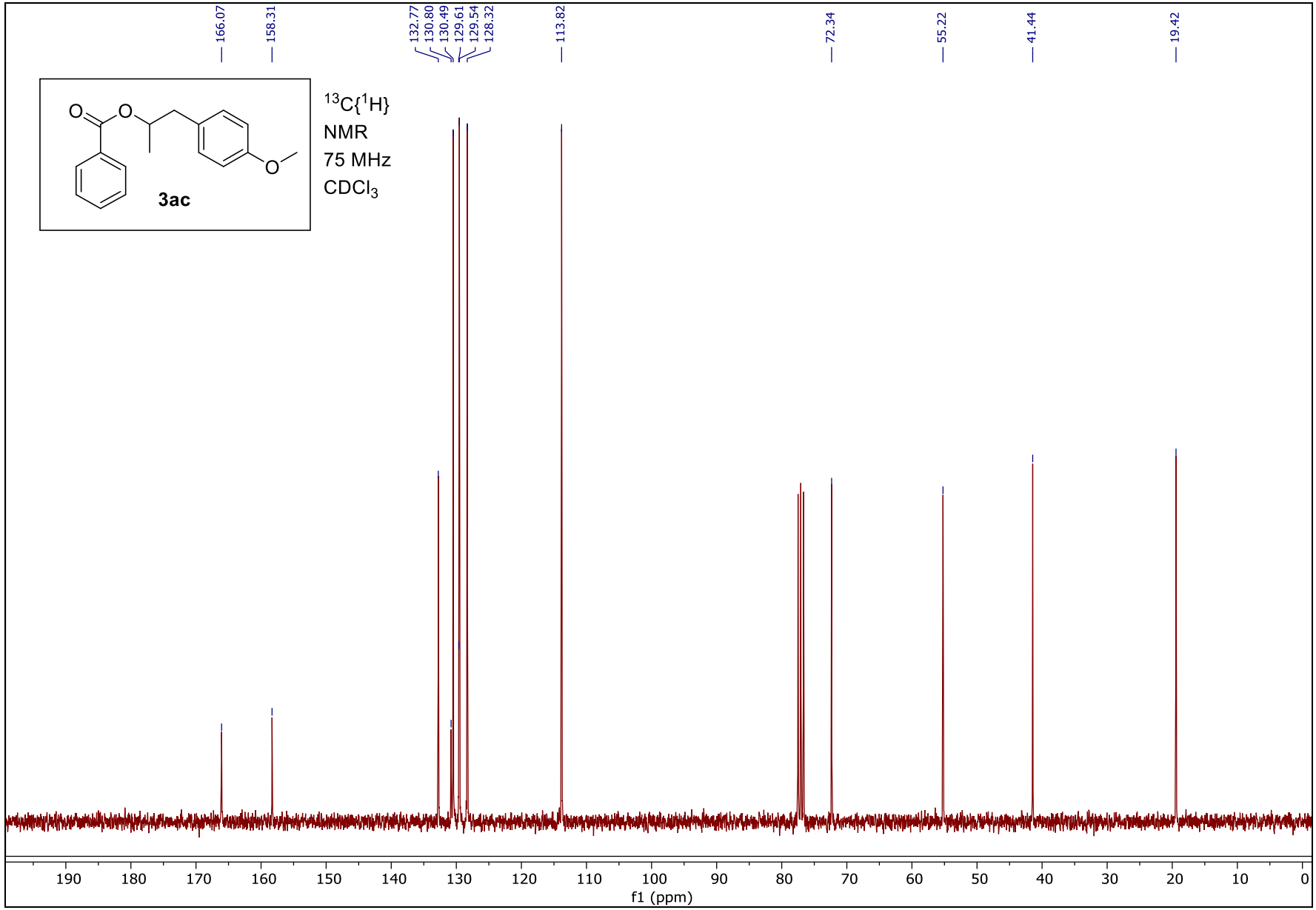

8.04
8.02
8.01
7.47
7.45
7.45
7.42
7.41
7.34
7.32
5.00
4.98
4.66
4.64
4.61
O
O
3aa
^{1}H NMR
300 MHz
$CDCl_3$
2.03
1.05
13.45
2.02
1.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

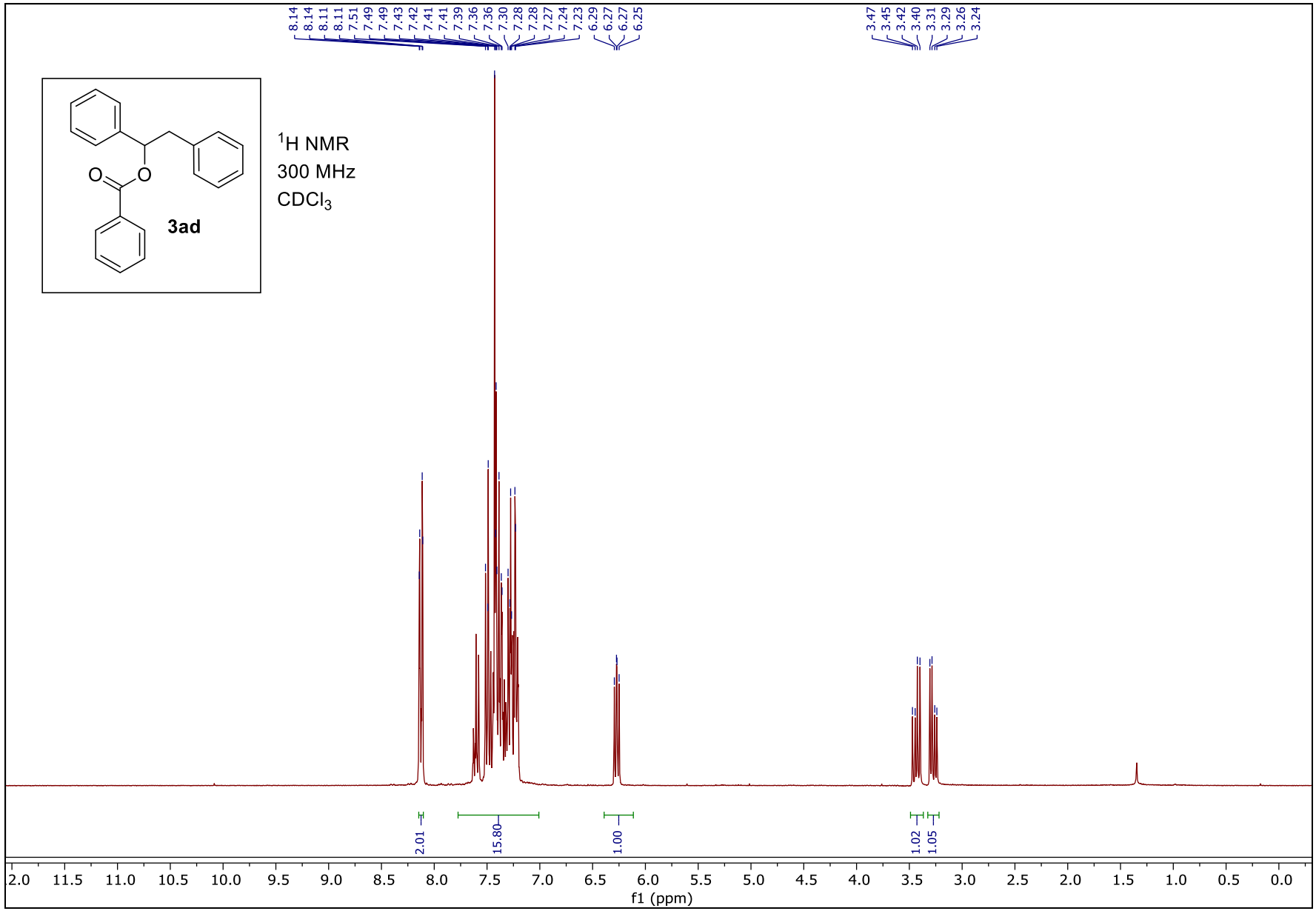

166.52
141.35
133.02
129.68
128.72
128.40
126.94
67.35
50.07
O
O
3aa
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

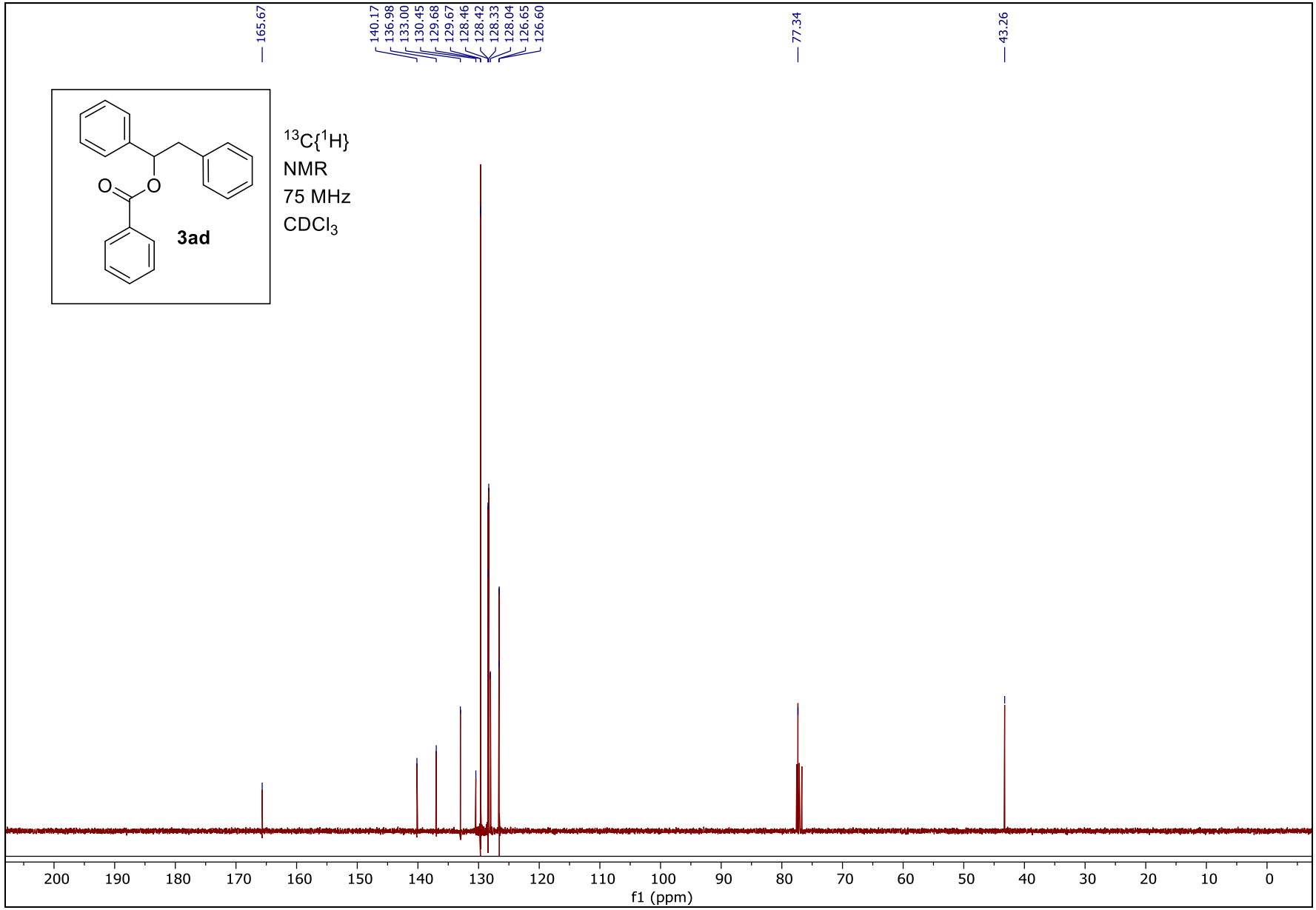

3ab
^{1}H NMR
300 MHz
$CDCl_3$
8.08 8.07 8.05 8.05 7.58 7.56 7.56 7.55 7.49 7.49 7.47 7.47 7.45 7.44 7.44 7.36 7.34 7.33 7.33 7.31 7.30 7.28 7.28 7.27 7.27 7.26 7.25 7.24 5.45 5.43 5.41 5.39
3.16 3.14 3.12 3.10 2.98 2.96 2.93 2.91
1.40 1.38
1.98 1.04 2.05 6.83 0.99 1.03 1.00 3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

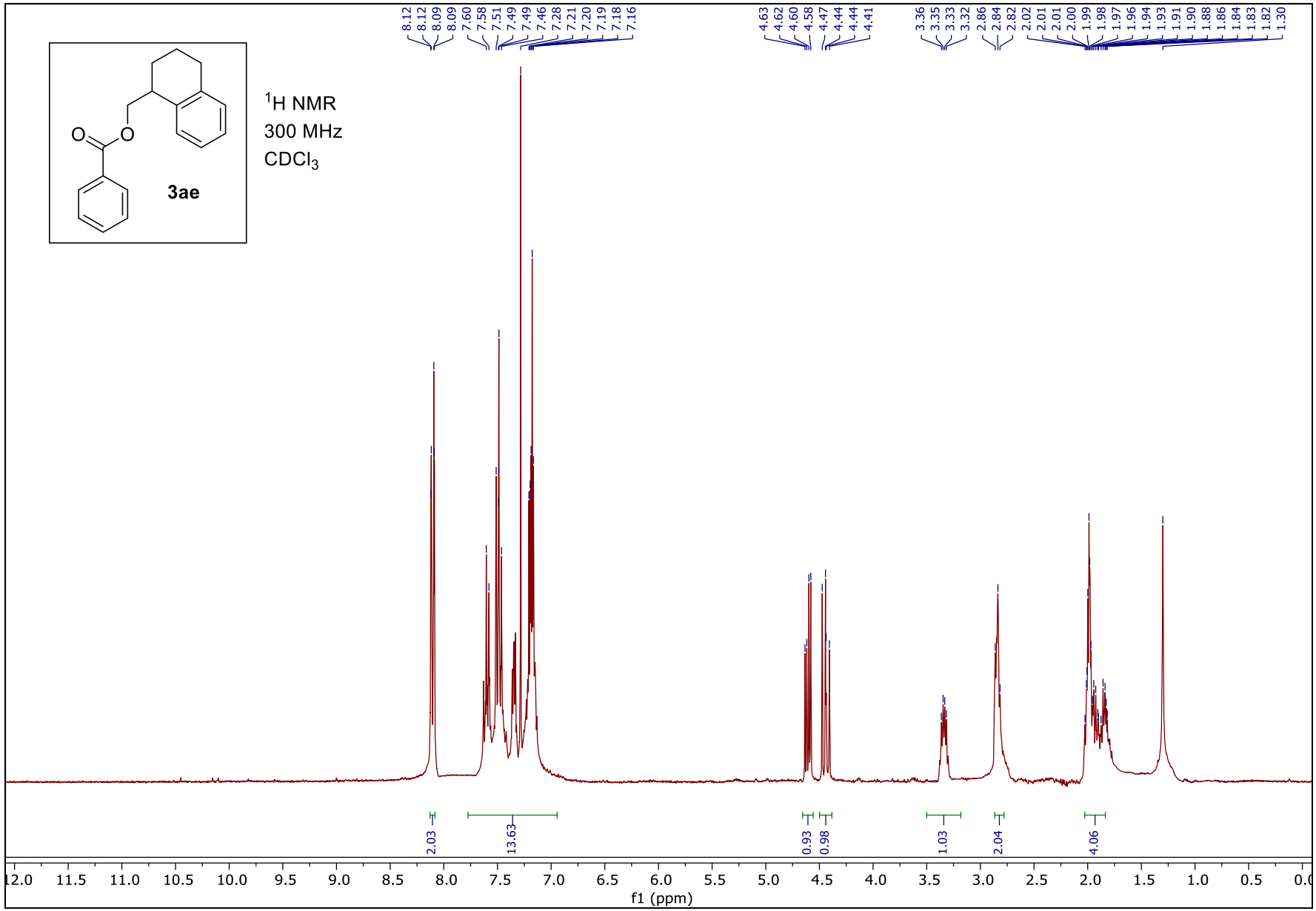

166.06
137.58
132.79
129.55
128.40
128.32
126.54
72.17
42.37
19.52
O
O
3ab
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
f1 (ppm)

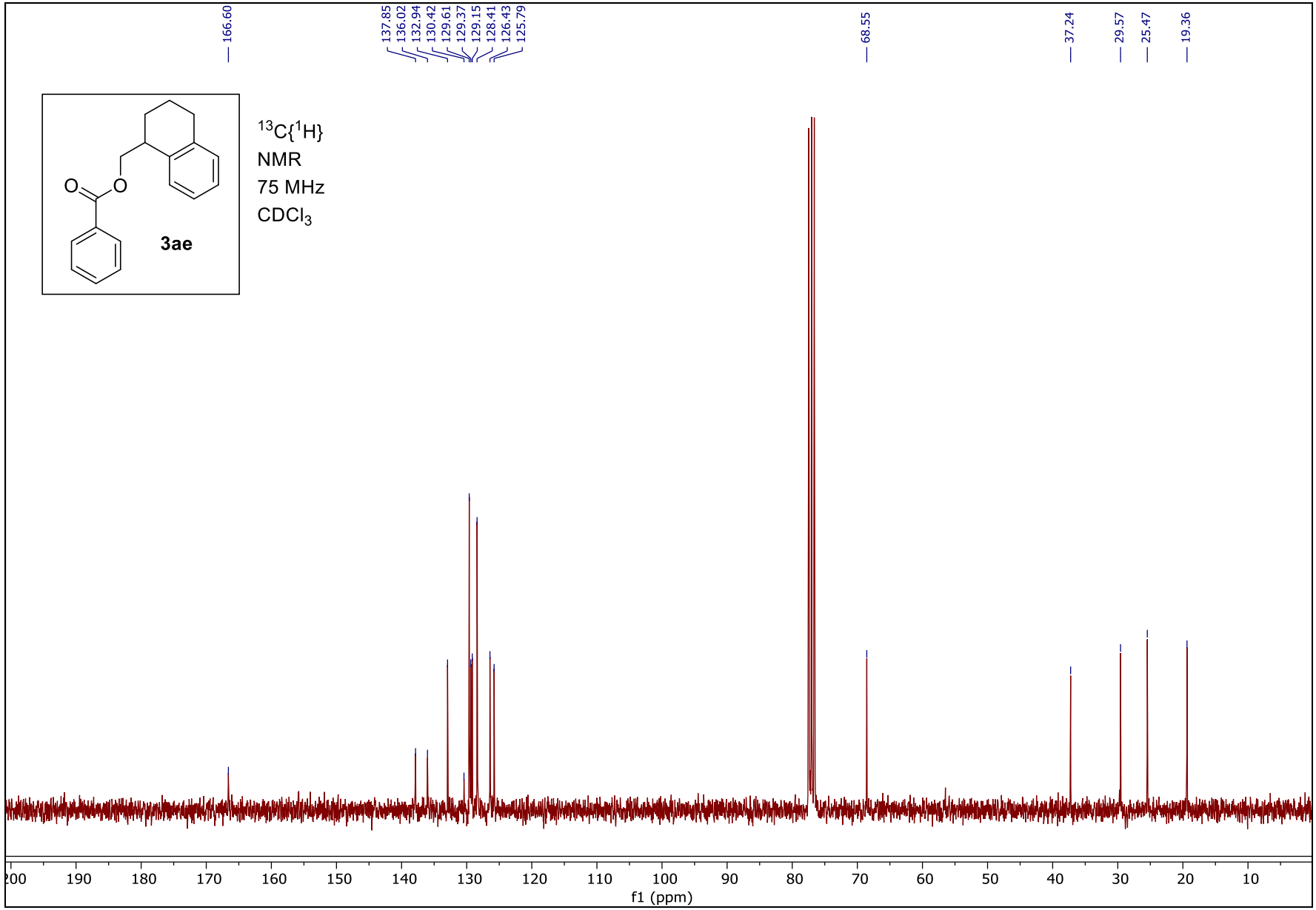

3ac
1H NMR
300 MHz
CDCl3
8.08
8.07
8.05
8.04
7.60
7.58
7.56
7.55
7.49
7.46
7.44
7.22
7.19
6.88
6.85
5.40
5.38
5.35
5.33
3.81
3.09
3.07
3.04
3.02
2.91
2.89
2.87
2.85
1.38
1.36
1.98
1.03
2.07
2.03
2.01
1.00
3.02
1.03
1.01
3.06
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

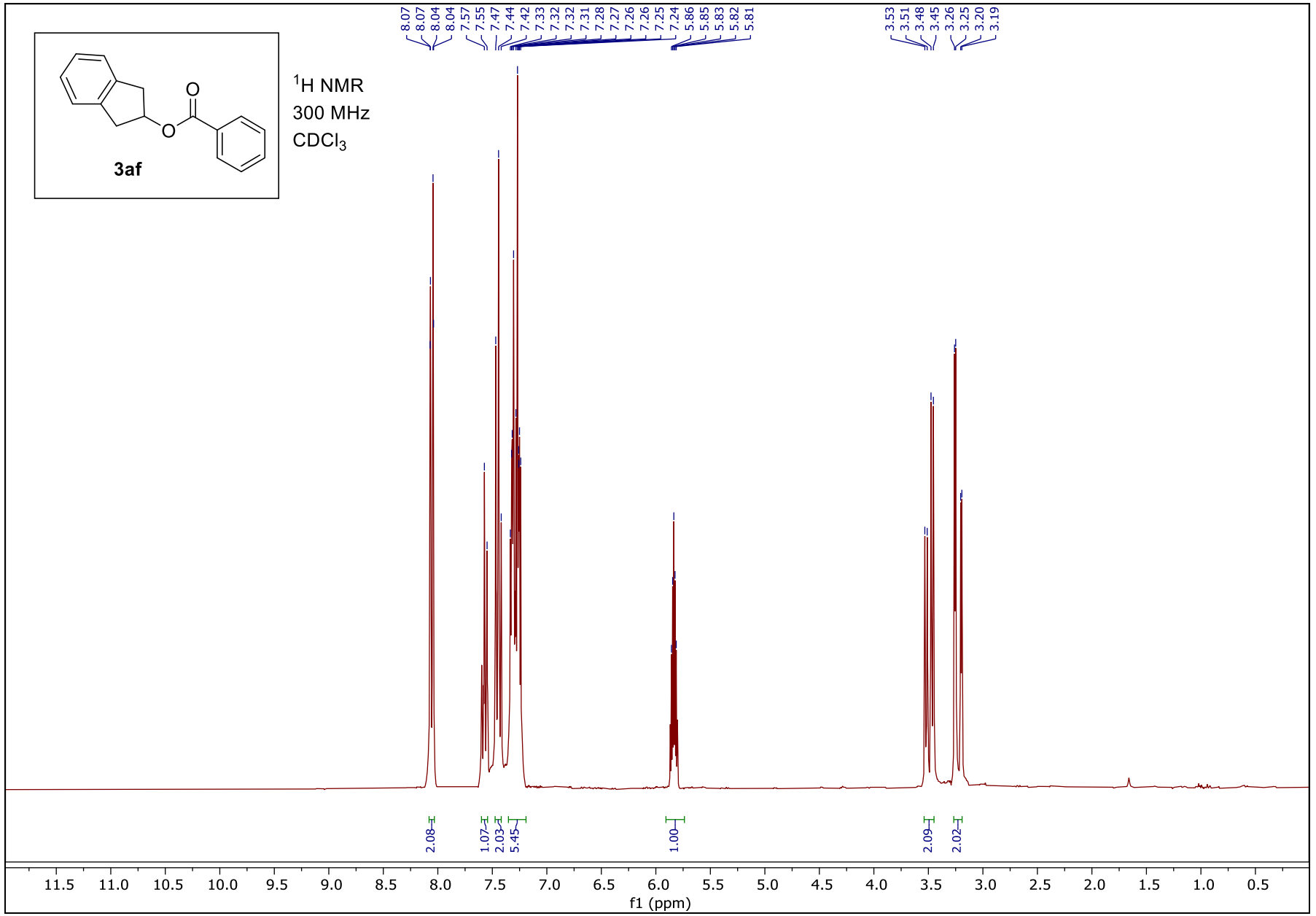

166.07
158.31
132.77
130.80
130.49
129.61
129.54
128.32
113.82
72.34
55.22
41.44
19.42
3ac
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

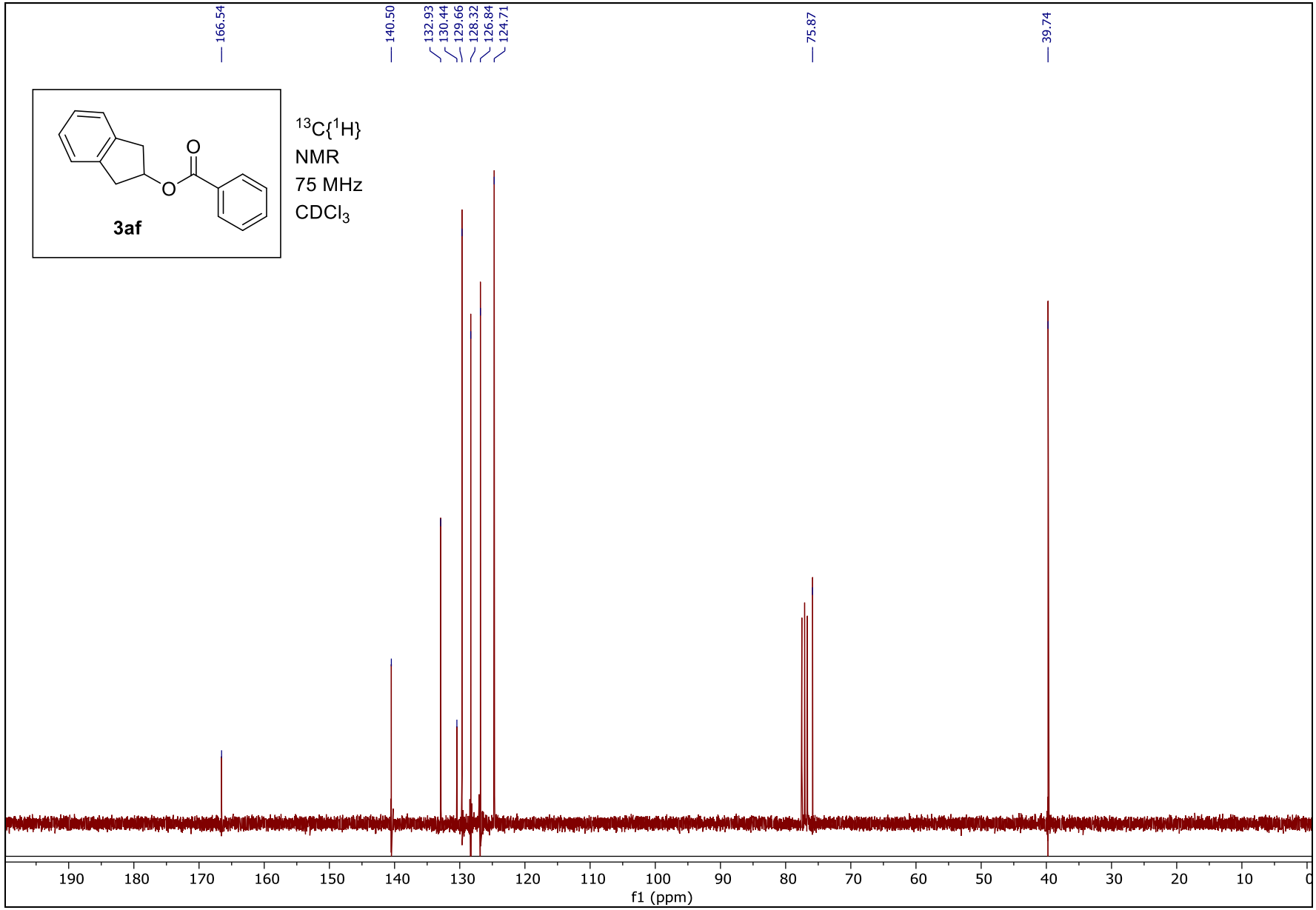

8.14
8.14
8.11
8.11
7.51
7.49
7.49
7.43
7.42
7.41
7.41
7.39
7.36
7.36
7.30
7.28
7.28
7.27
7.24
7.23
6.29
6.27
6.27
6.25
3.47
3.45
3.42
3.40
3.31
3.29
3.26
3.24
O
O
3ad
1H NMR
300 MHz
CDCl3
2.01
15.80
1.00
1.02
1.05
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

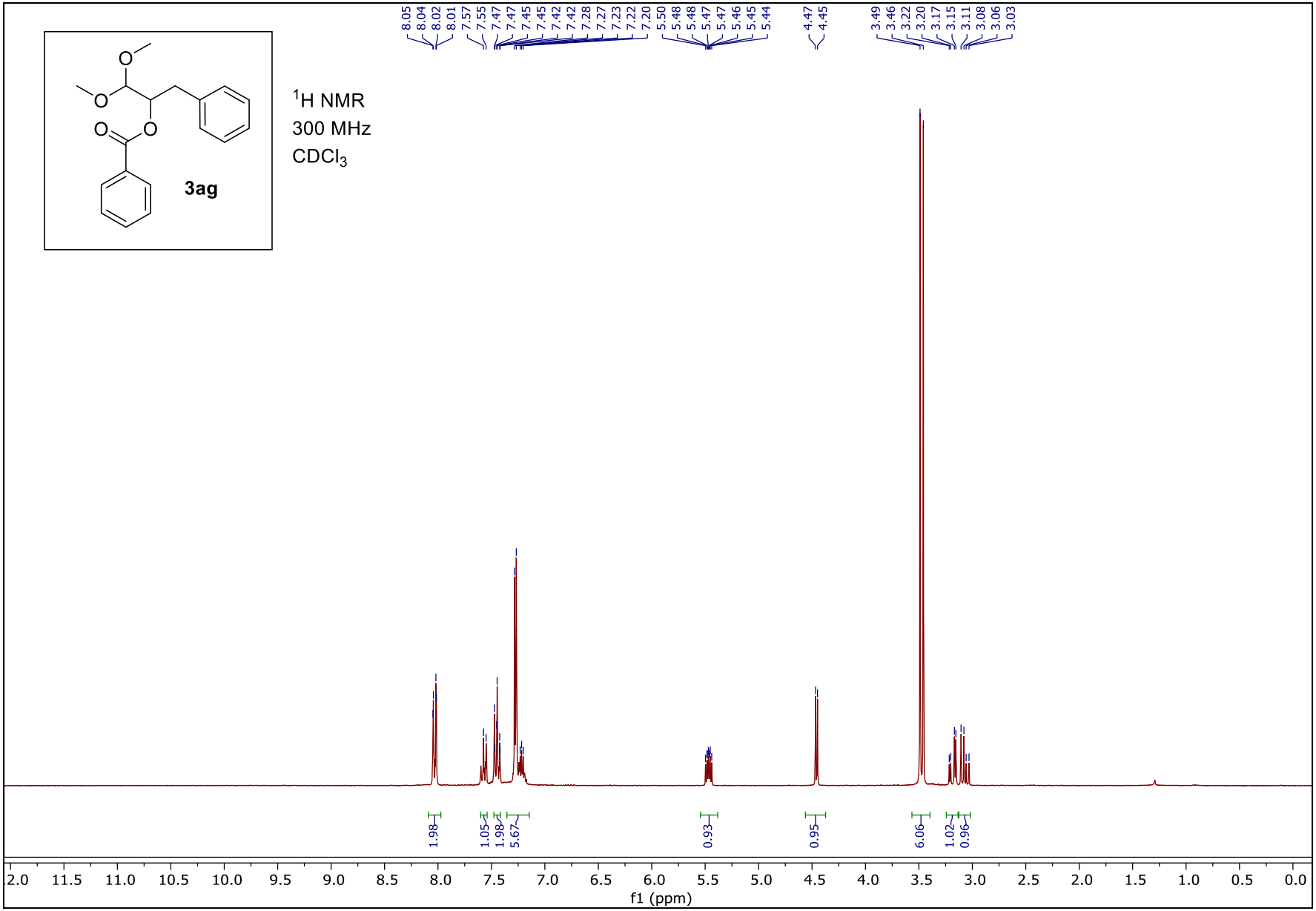

165.67
140.17
136.98
133.00
130.45
129.68
129.67
128.46
128.42
128.33
128.04
126.65
126.60
77.34
43.26
O
O
3ad
13C{1H}
NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

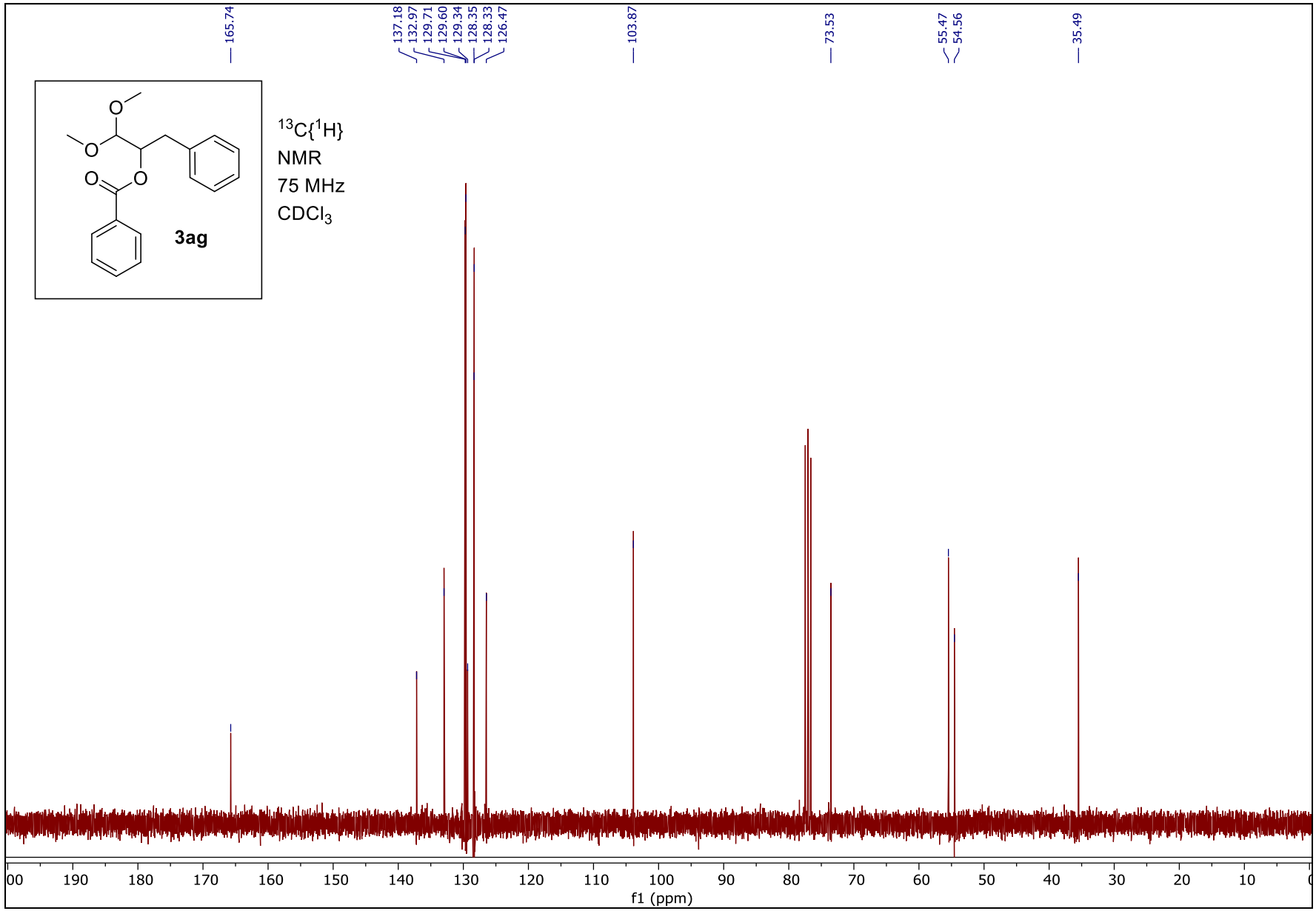

3ae
^{1}H NMR
300 MHz
$CDCl_3$
f1 (ppm)

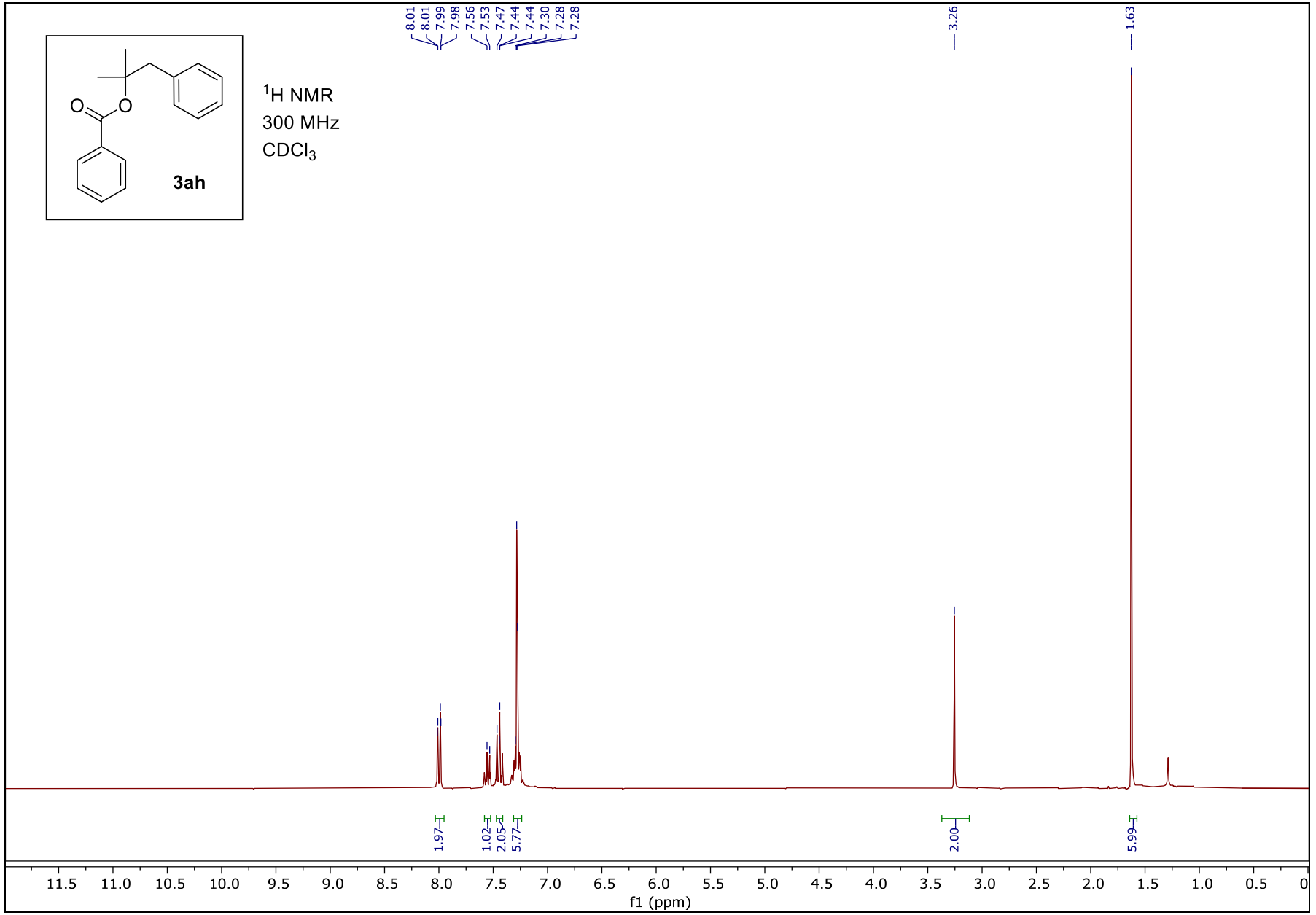

166.60
137.85
136.02
132.94
130.42
129.61
129.37
129.15
128.41
126.43
125.79
68.55
37.24
29.57
25.47
19.36
O
O
3ae
13C{1H}
NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

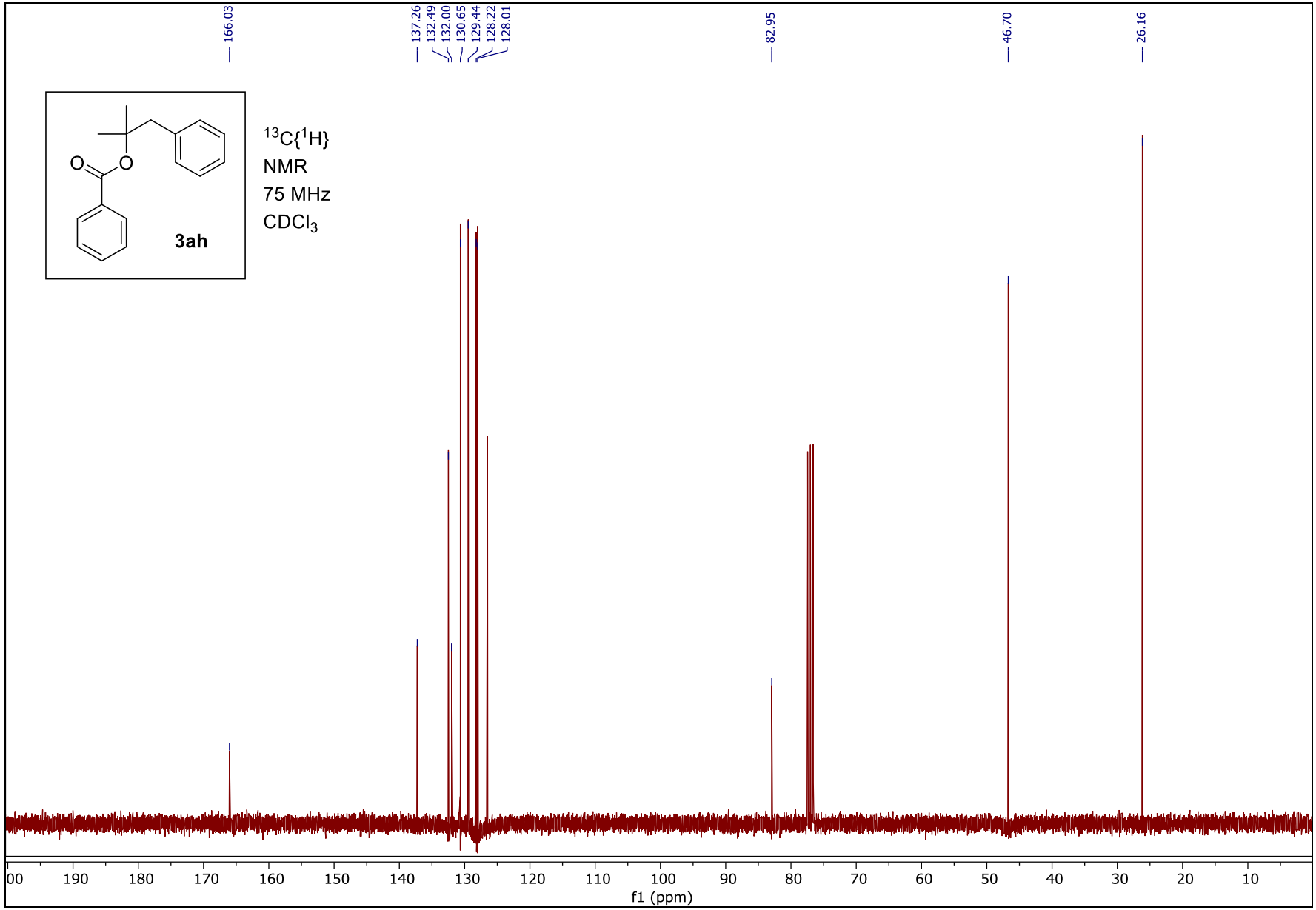

3af
^{1}H NMR
300 MHz
$CDCl_3$
8.07
8.07
8.04
8.04
7.57
7.55
7.47
7.44
7.42
7.33
7.32
7.32
7.31
7.28
7.27
7.26
7.26
7.25
7.24
5.86
5.85
5.83
5.82
5.81
3.53
3.51
3.48
3.45
3.26
3.25
3.20
3.19
2.08
1.07
2.03
5.45
1.00
2.09
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

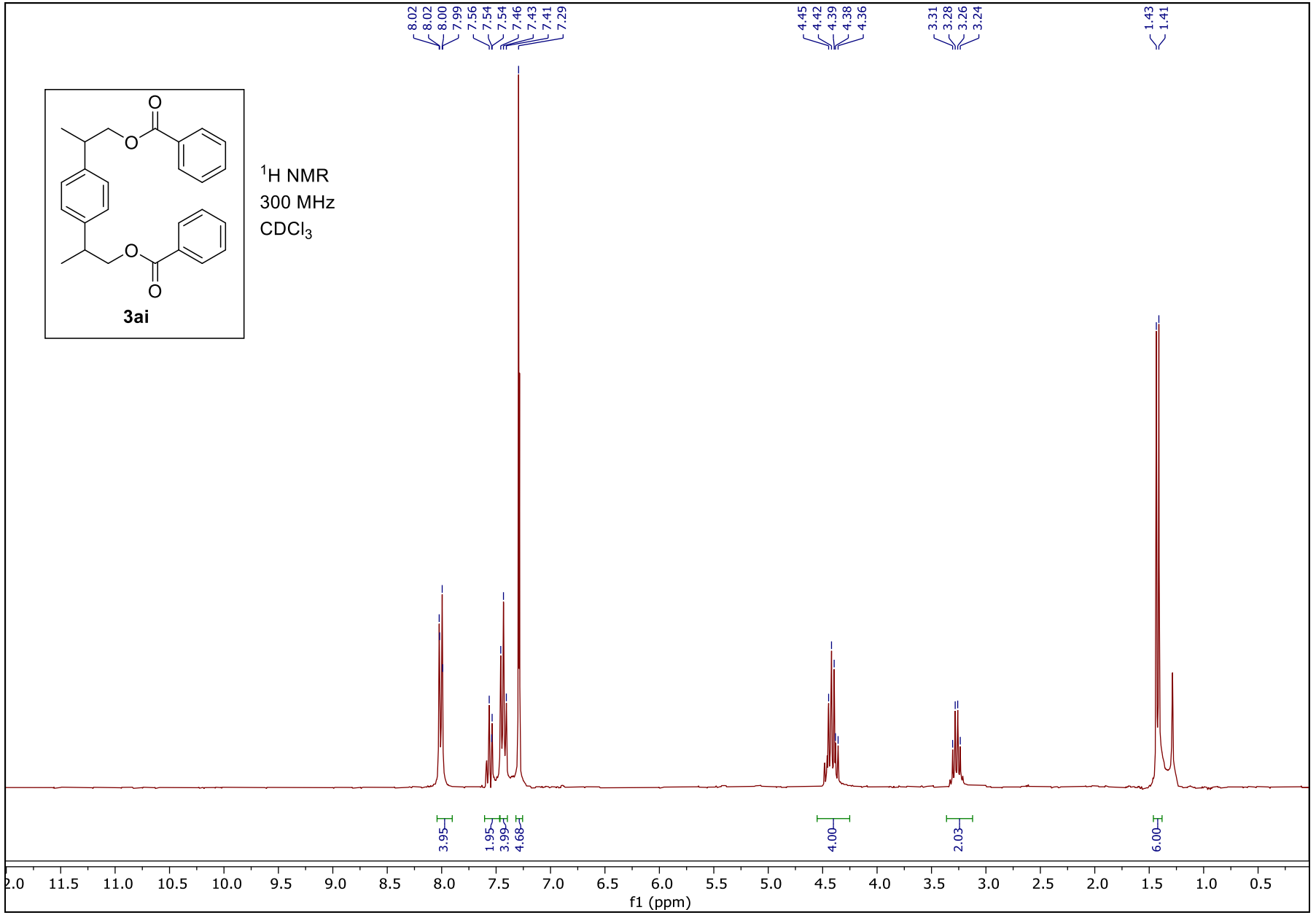

166.54
140.50
132.93
130.44
129.66
128.32
126.84
124.71
75.87
39.74
O
O
3af
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

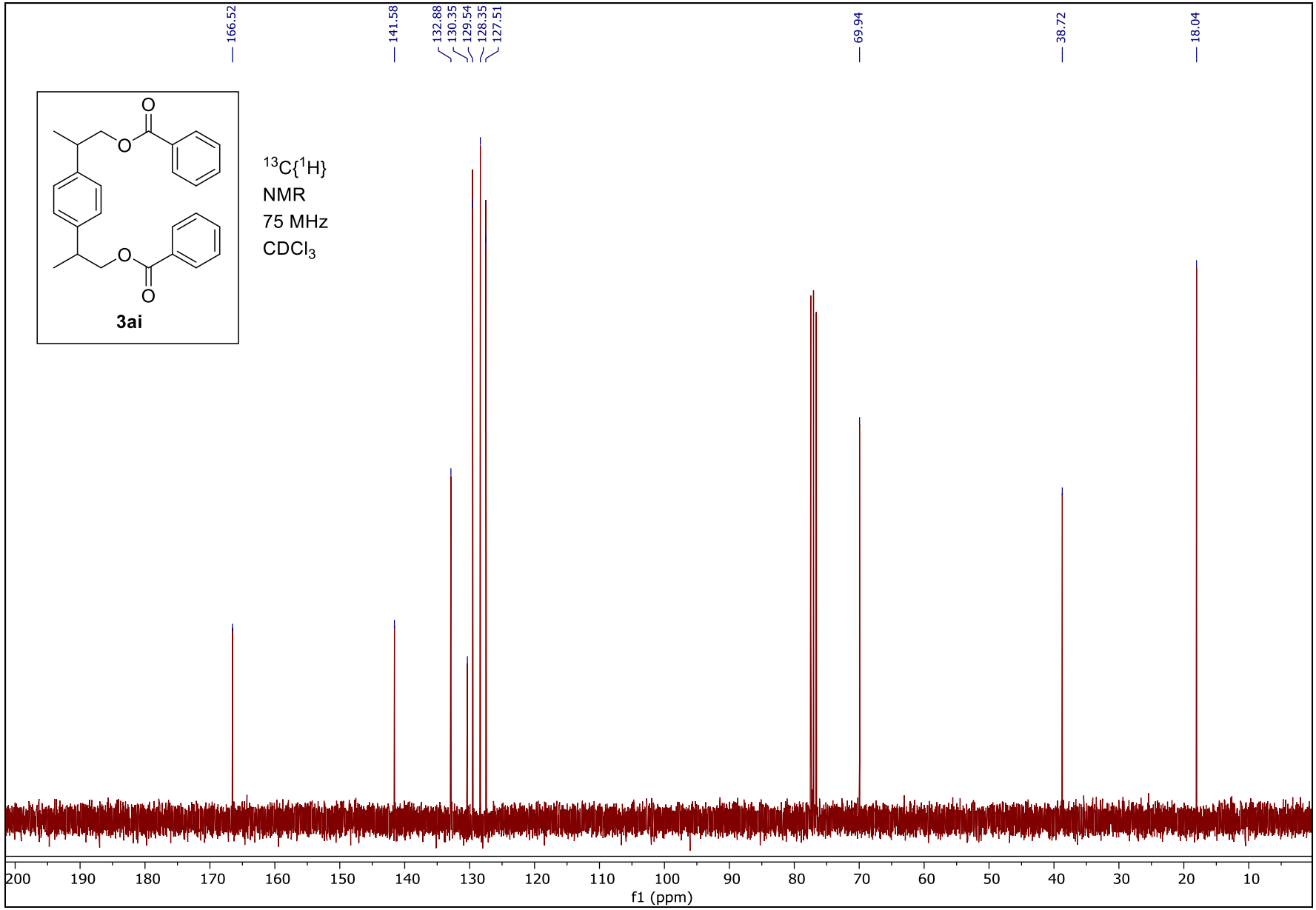

3ag
^{1}H NMR
300 MHz
$CDCl_3$
8.05 8.04 8.02 8.01 7.57 7.55 7.47 7.47 7.45 7.45 7.42 7.42 7.28 7.27 7.23 7.22 7.20 5.50 5.48 5.48 5.47 5.47 5.46 5.45 5.44 4.47 4.45 3.49 3.46 3.22 3.20 3.17 3.15 3.11 3.08 3.06 3.03
1.98 1.05 1.98 5.67 0.93 0.95 6.06 1.02 0.96
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

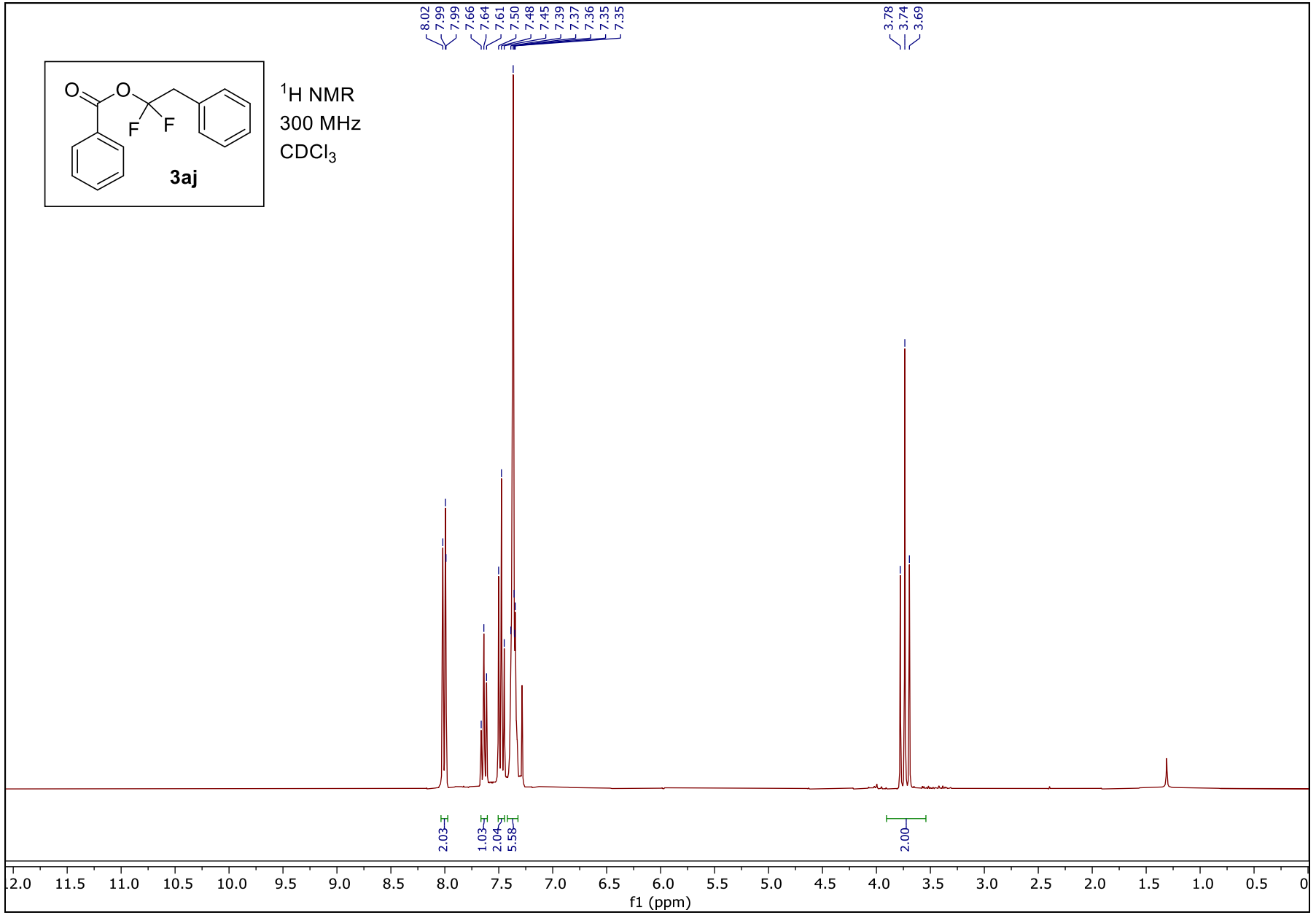

165.74
137.18
132.97
129.71
129.60
129.34
128.35
128.33
126.47
103.87
73.53
55.47
54.56
35.49
3ag
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
f1 (ppm)

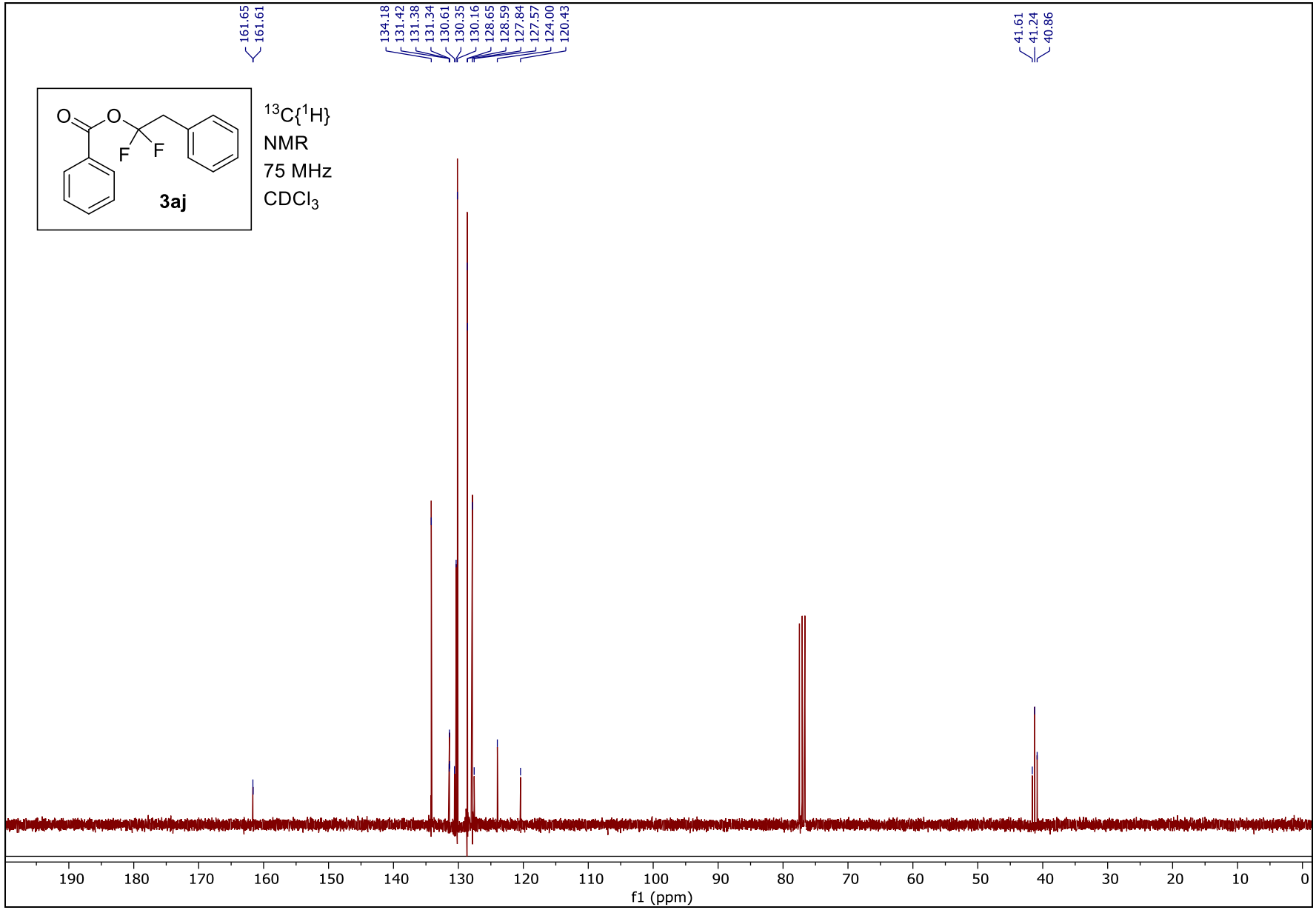

3ah
^{1}H NMR
300 MHz
$CDCl_3$
8.01
8.01
7.99
7.98
7.56
7.53
7.47
7.44
7.44
7.30
7.28
7.28
3.26
1.63
1.97
1.02
2.05
5.77
2.00
5.99
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

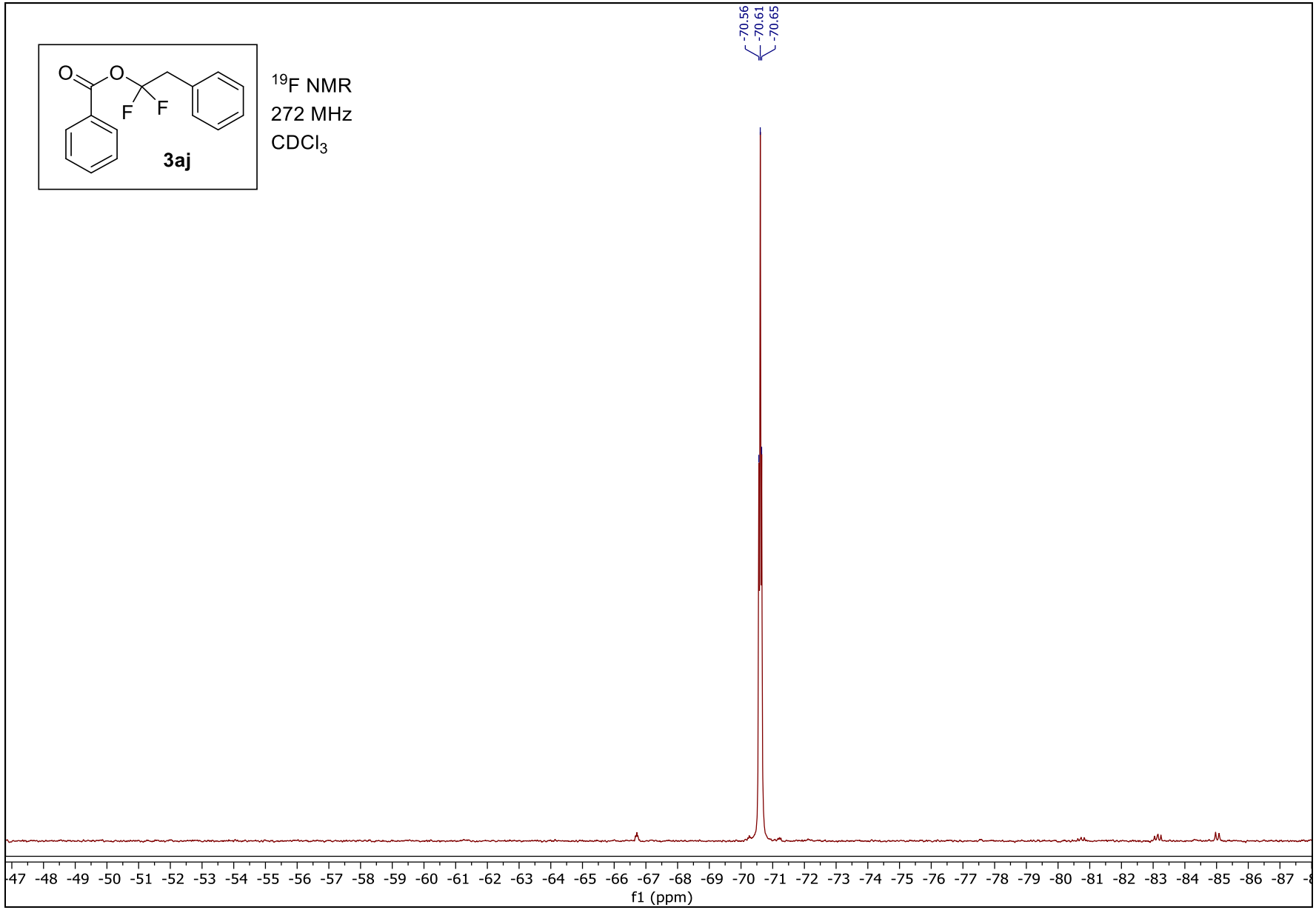

166.03
137.26
132.49
132.00
130.65
129.44
128.22
128.01
82.95
46.70
26.16
O
O
3ah
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

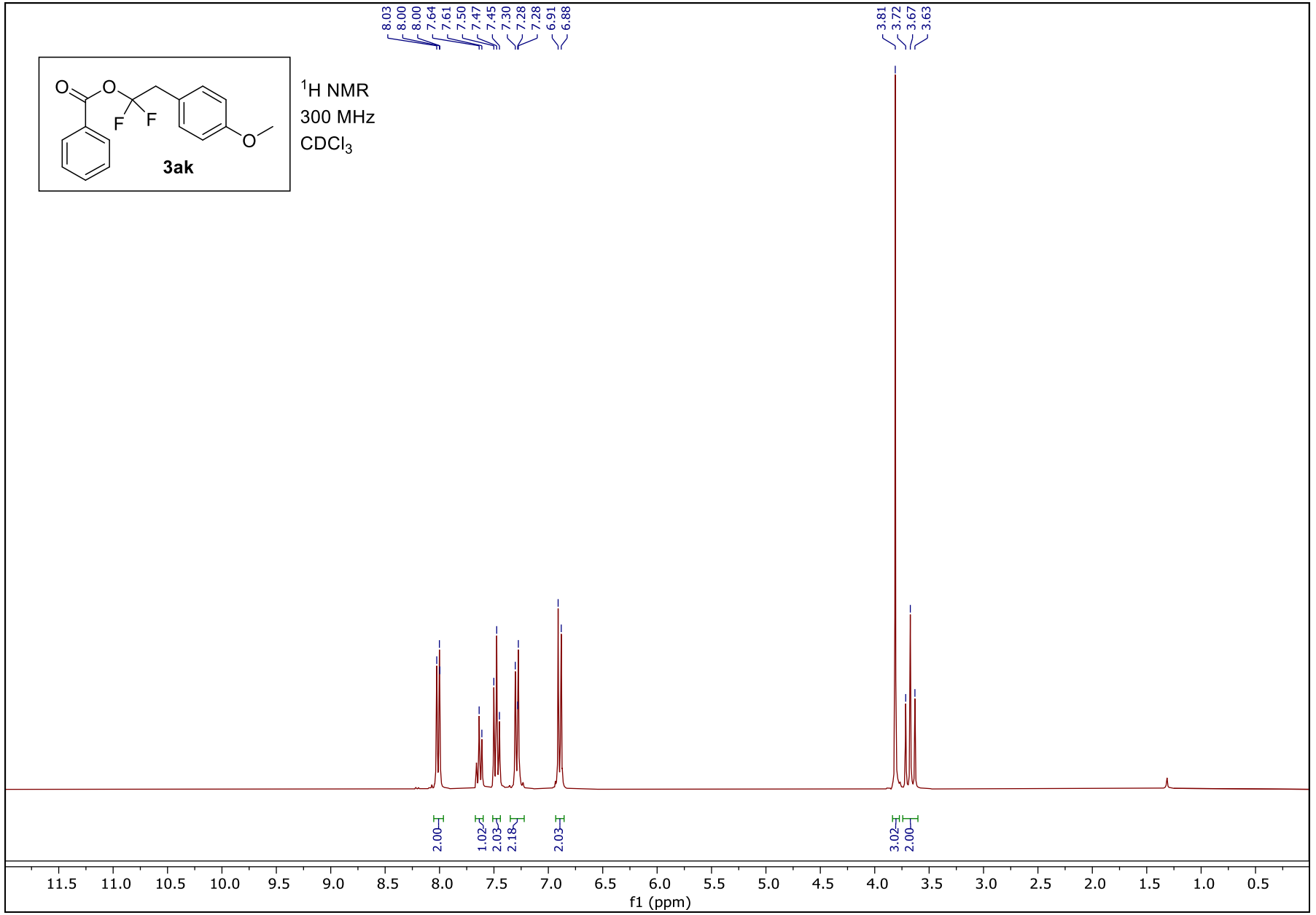

8.02
8.02
8.00
7.99
7.56
7.54
7.54
7.46
7.43
7.41
7.29
4.45
4.42
4.39
4.38
4.36
3.31
3.28
3.26
3.24
1.43
1.41
O
O
O
O
3ai
1H NMR
300 MHz
CDCl3
3.95
1.95
3.99
4.68
4.00
2.03
6.00
f1 (ppm)

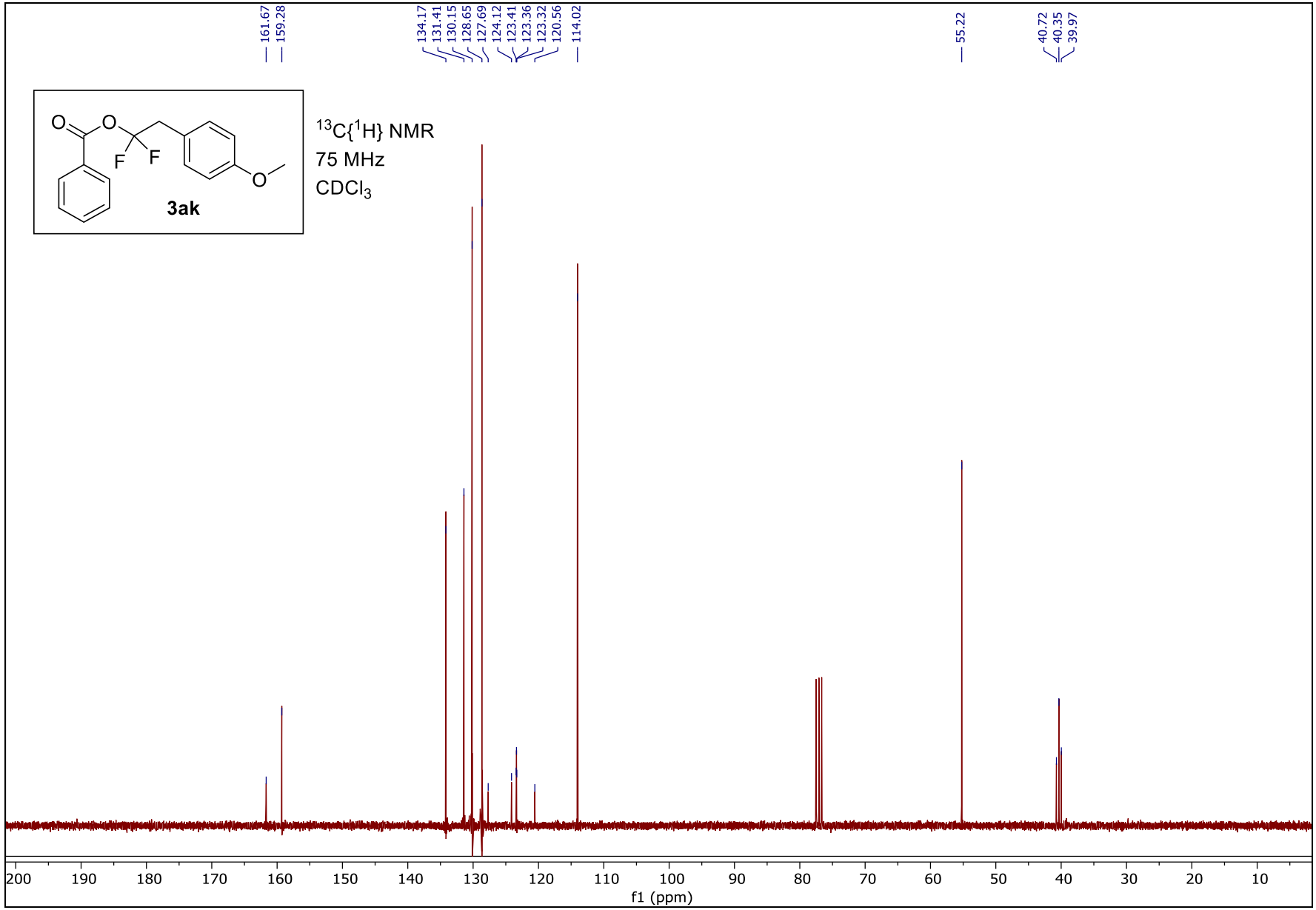

166.52
141.58
132.88
130.35
129.54
128.35
127.51
69.94
38.72
18.04
O
O
O
O
3ai
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

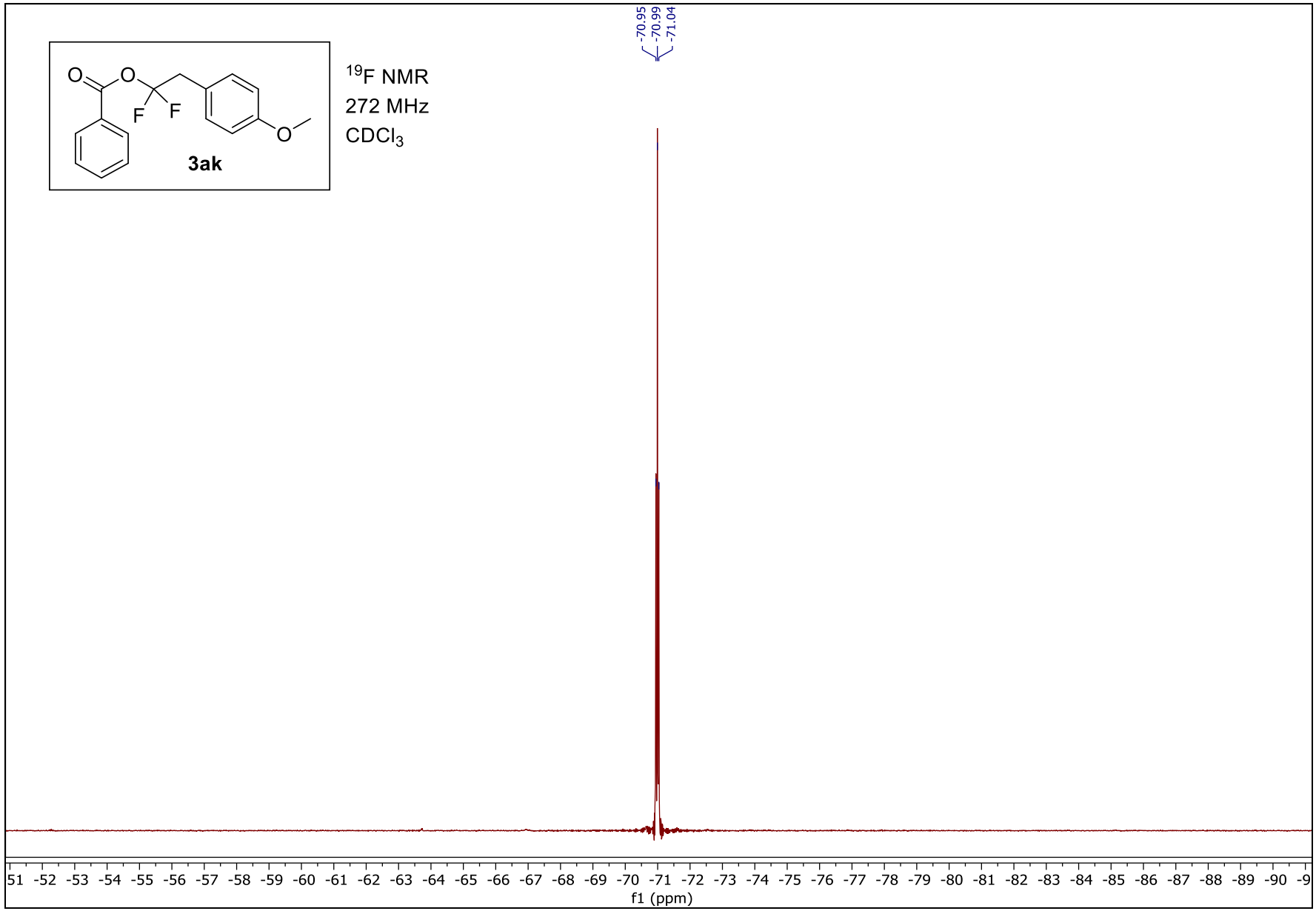

8.02
7.99
7.99
7.66
7.64
7.61
7.50
7.48
7.45
7.39
7.37
7.36
7.35
7.35
3.78
3.74
3.69
O
O
F
F
3aj
^{1}H NMR
300 MHz
$CDCl_3$
2.03
1.03
2.04
5.58
2.00
f1 (ppm)

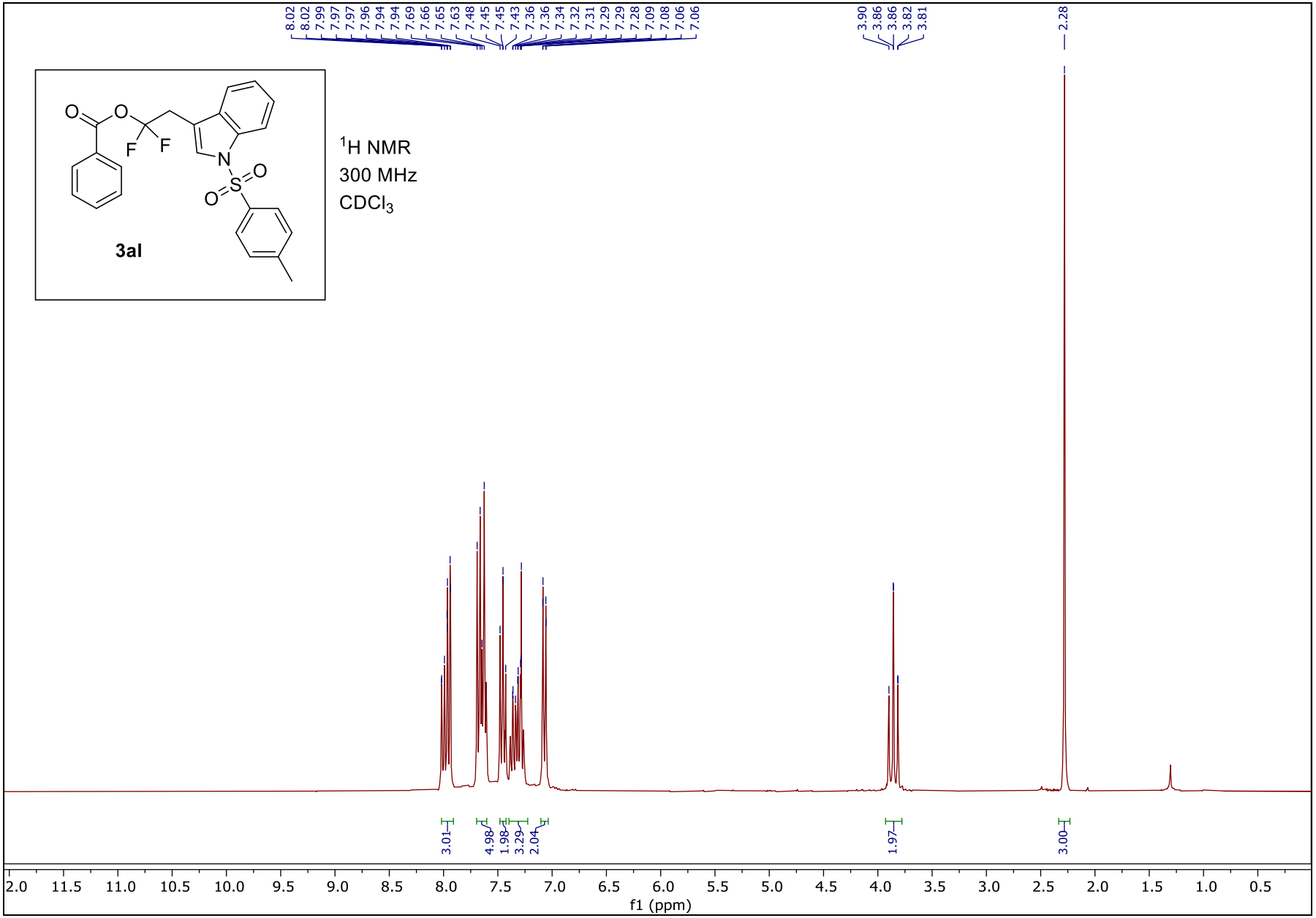

161.65
161.61
134.18
131.42
131.38
131.34
130.61
130.35
130.16
128.65
128.59
127.84
127.57
124.00
120.43
41.61
41.24
40.86
O
O
F
F
3aj
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

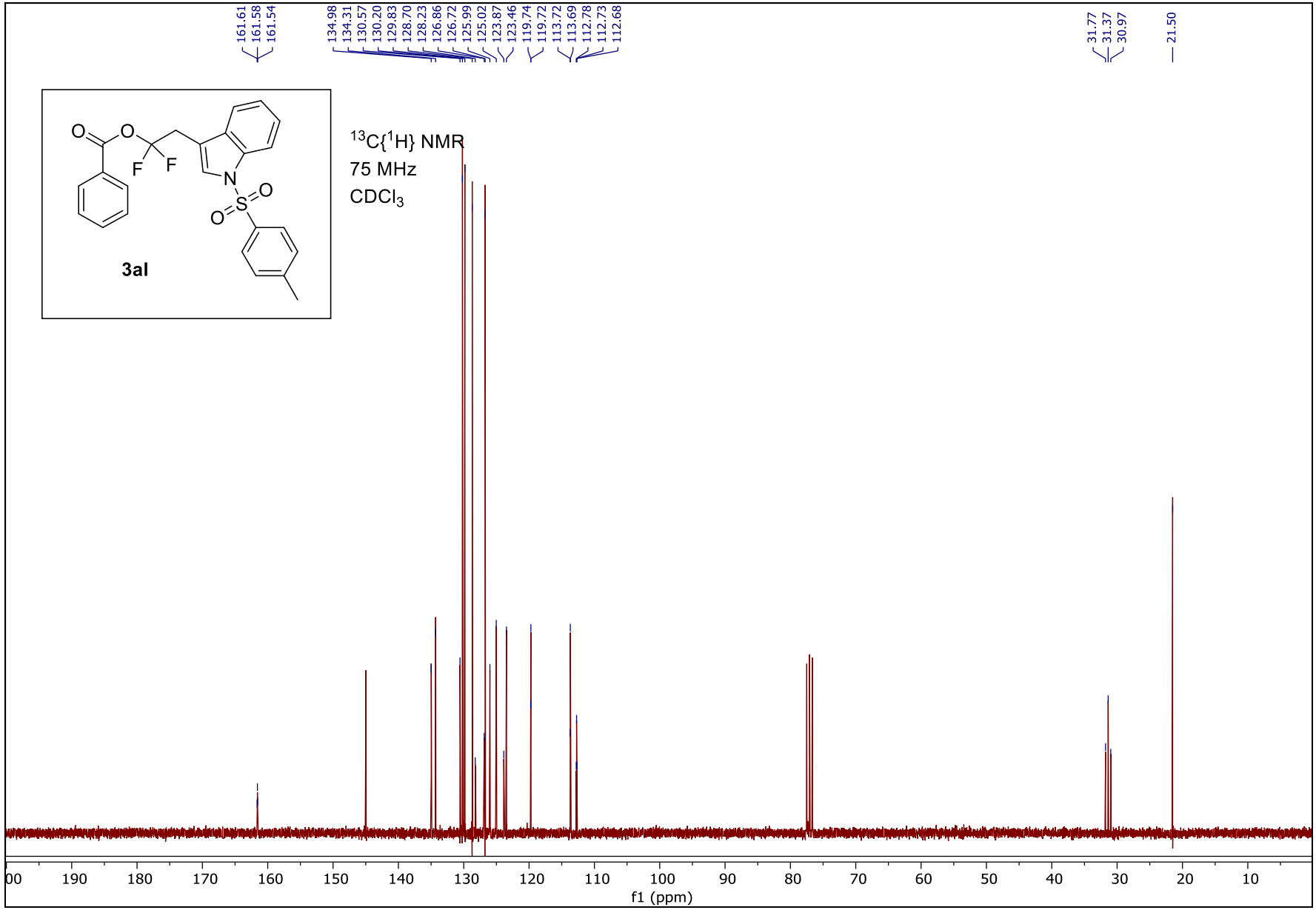

-70.56
-70.61
-70.65
3aj
19F NMR
272 MHz
CDCl3
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87
f1 (ppm)

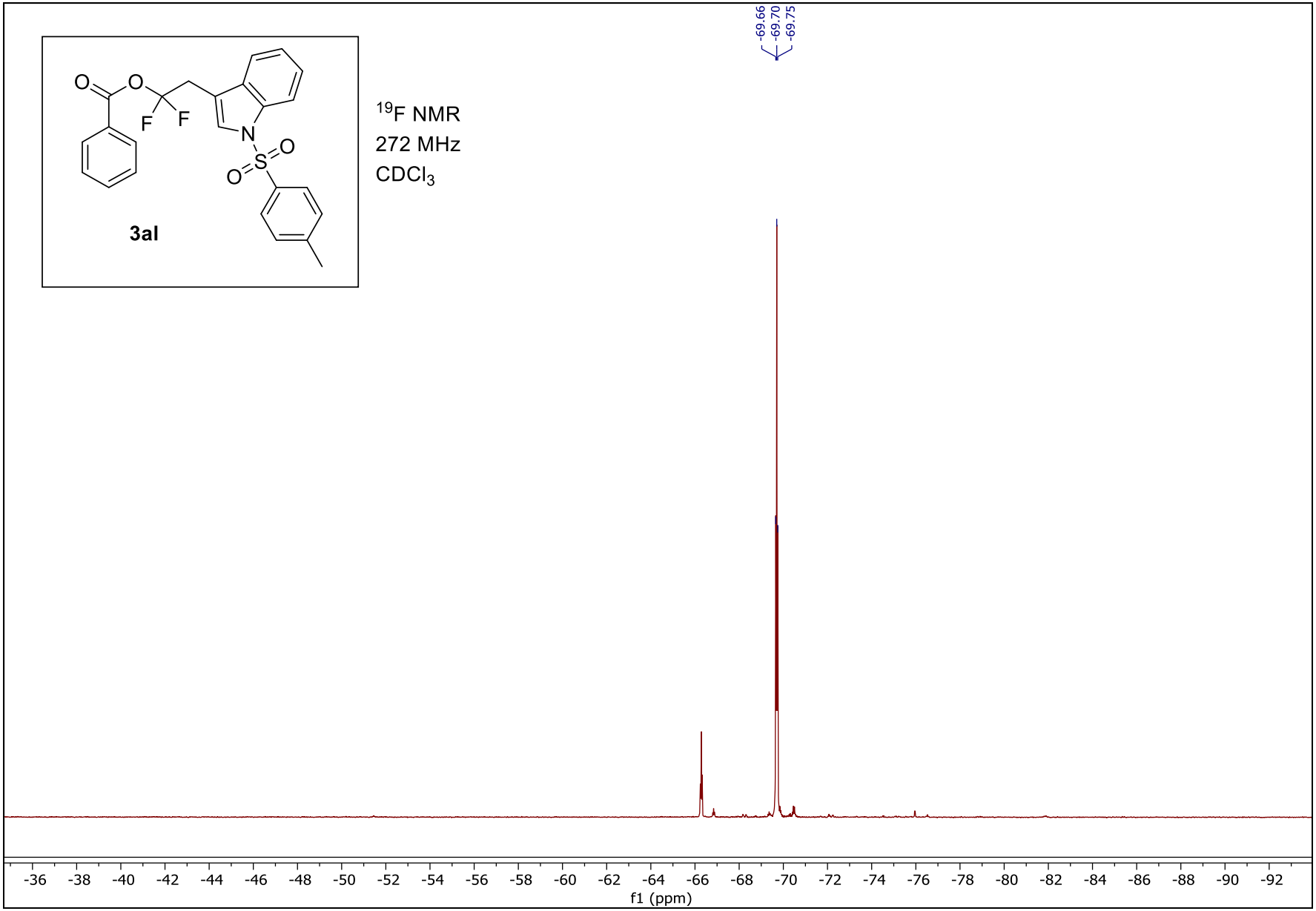

8.03
8.00
8.00
7.64
7.61
7.50
7.47
7.45
7.30
7.28
7.28
6.91
6.88
3.81
3.72
3.67
3.63
O
O
F
F
O
3ak
1H NMR
300 MHz
CDCl3
2.00
1.02
2.03
2.18
2.03
3.02
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

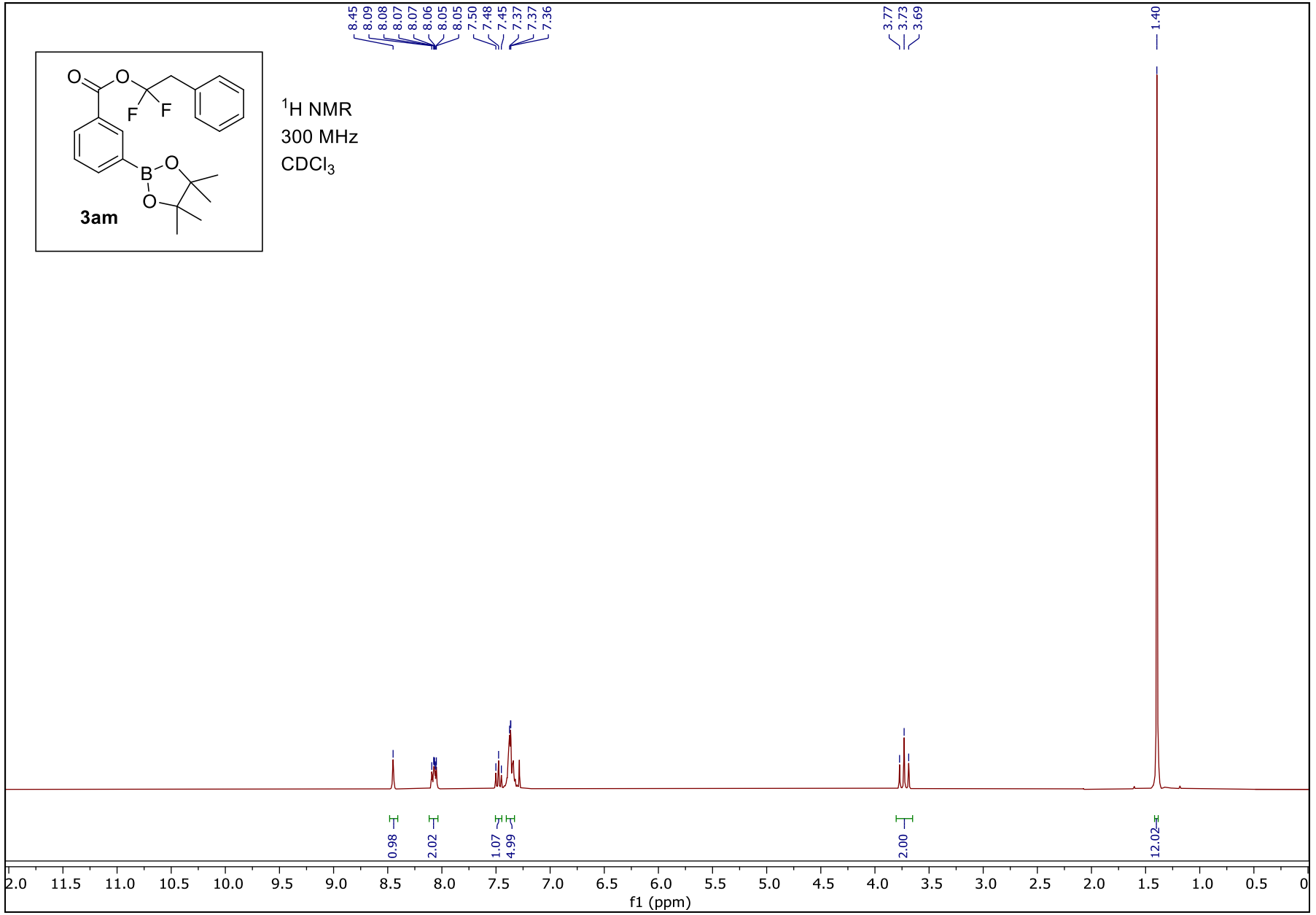

161.67
159.28
134.17
131.41
130.15
128.65
127.69
124.12
123.41
123.36
123.32
120.56
114.02
55.22
40.72
40.35
39.97
3ak
13C{1H} NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

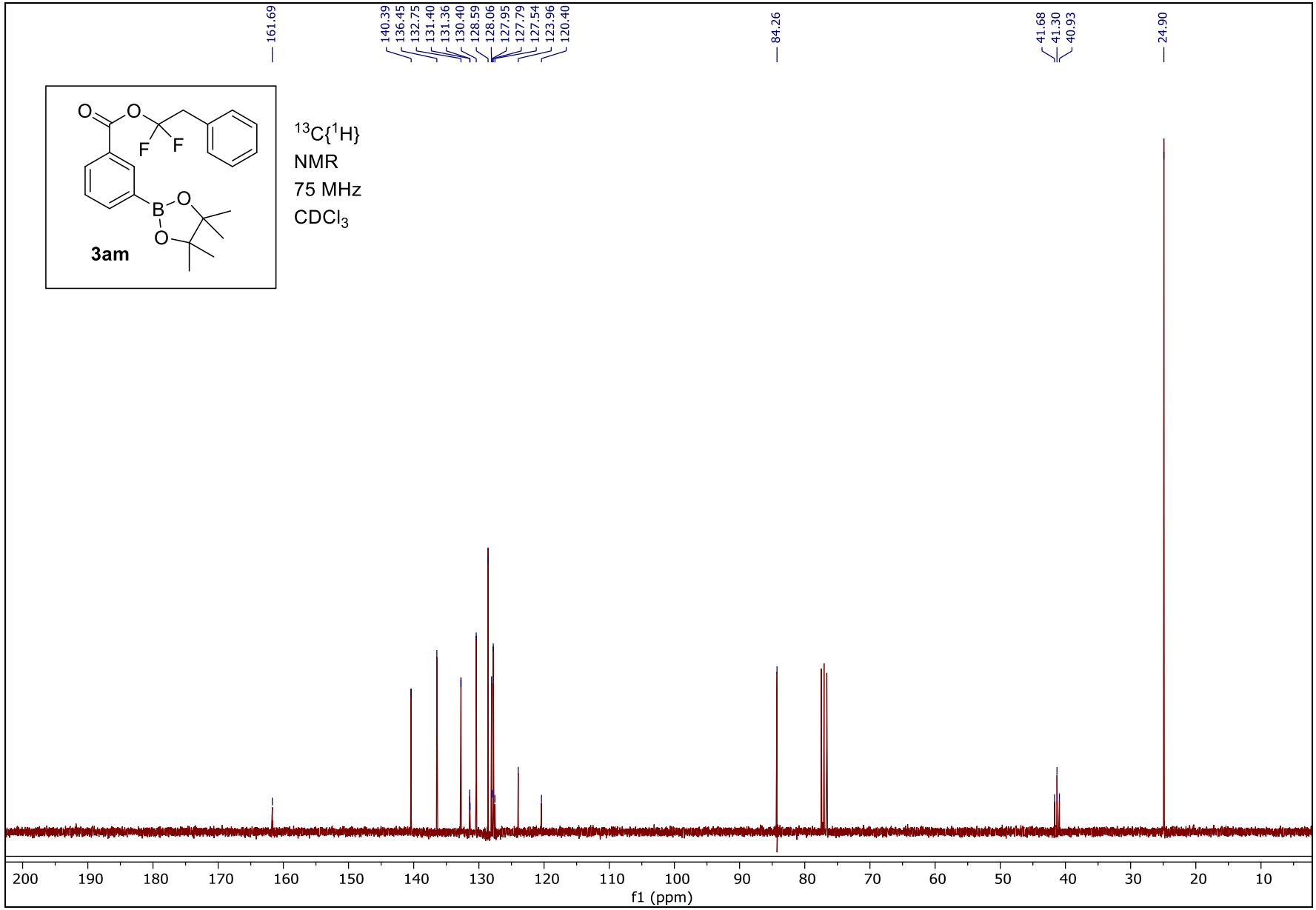

-70.95
-70.99
-71.04
O
O
F
F
O
3ak
19F NMR
272 MHz
CDCl3
51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87 -88 -89 -90 -9
f1 (ppm)

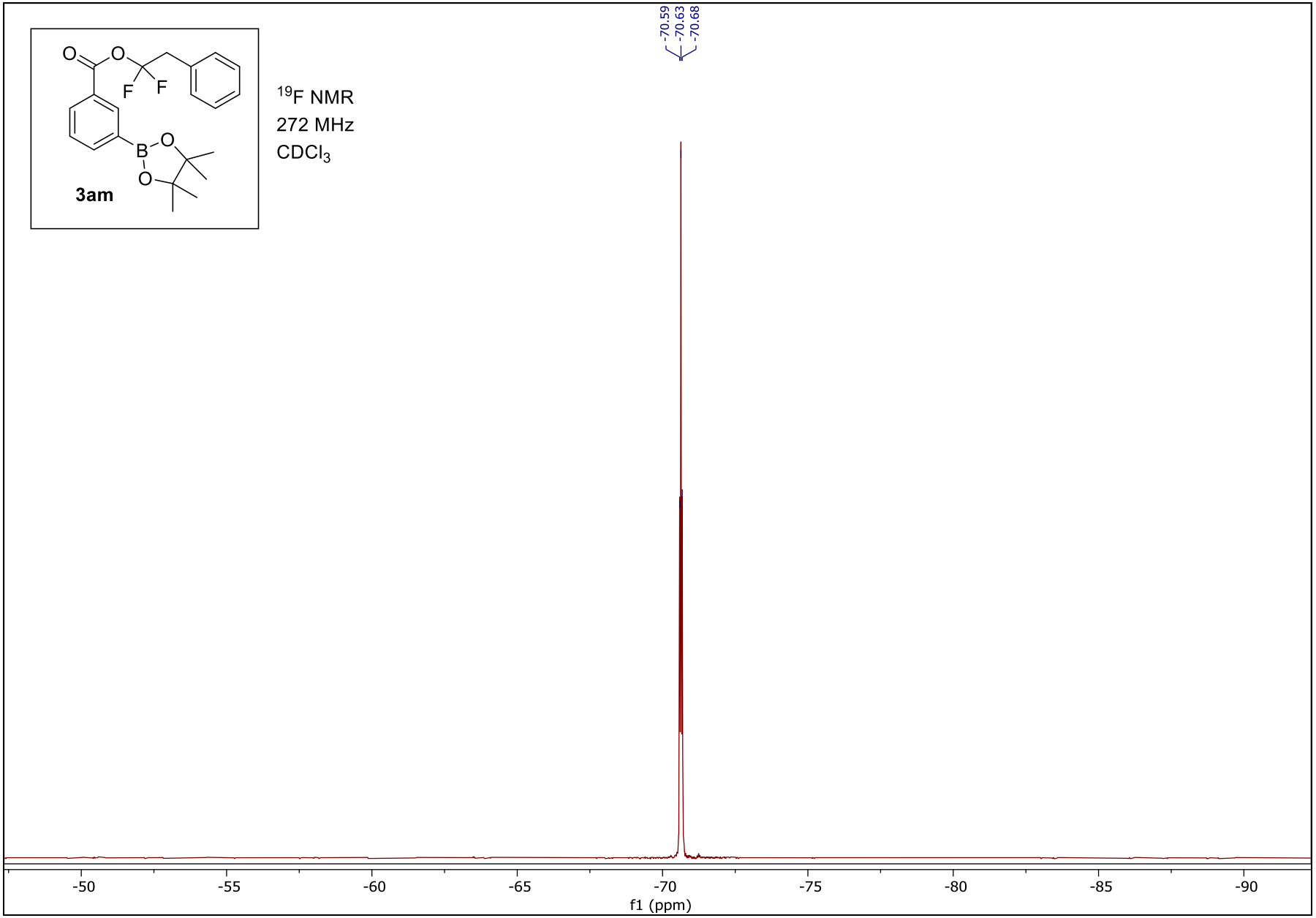

8.02
8.02
7.99
7.97
7.97
7.96
7.94
7.94
7.69
7.66
7.65
7.63
7.48
7.45
7.45
7.43
7.36
7.36
7.34
7.32
7.31
7.29
7.29
7.28
7.09
7.08
7.06
7.06
3.90
3.86
3.86
3.82
3.81
2.28
O
O
F
F
N
O
S
O
3al
1H NMR
300 MHz
CDCl3
3.01
4.98
1.98
3.29
2.04
1.97
3.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

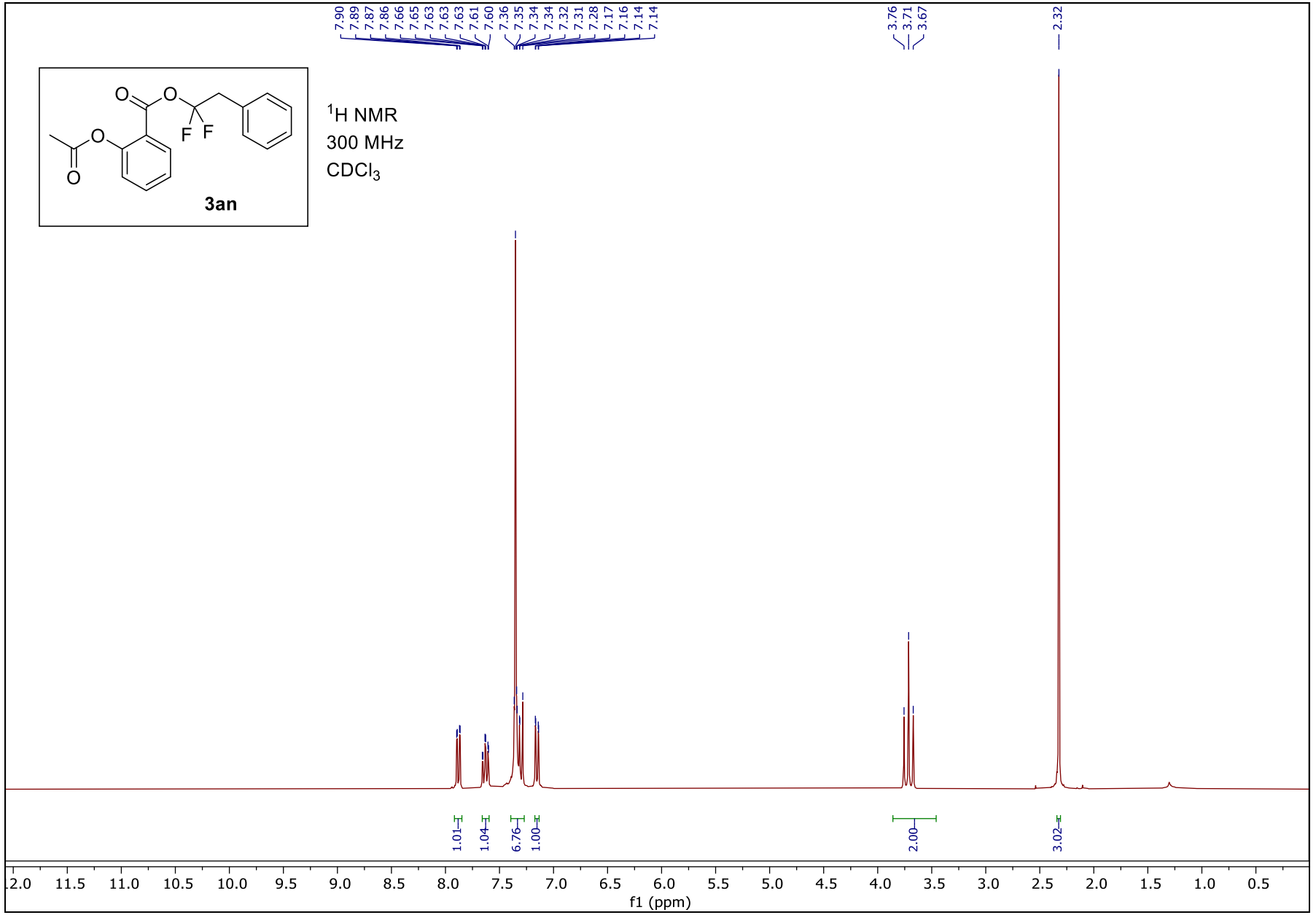

161.61
161.58
161.54
134.98
134.31
130.57
130.20
129.83
128.70
128.23
126.86
126.72
125.99
125.02
123.87
123.46
119.74
119.72
113.72
113.69
112.78
112.73
112.68
31.77
31.37
30.97
21.50
O
O
F
F
N
S
O
O
3al
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

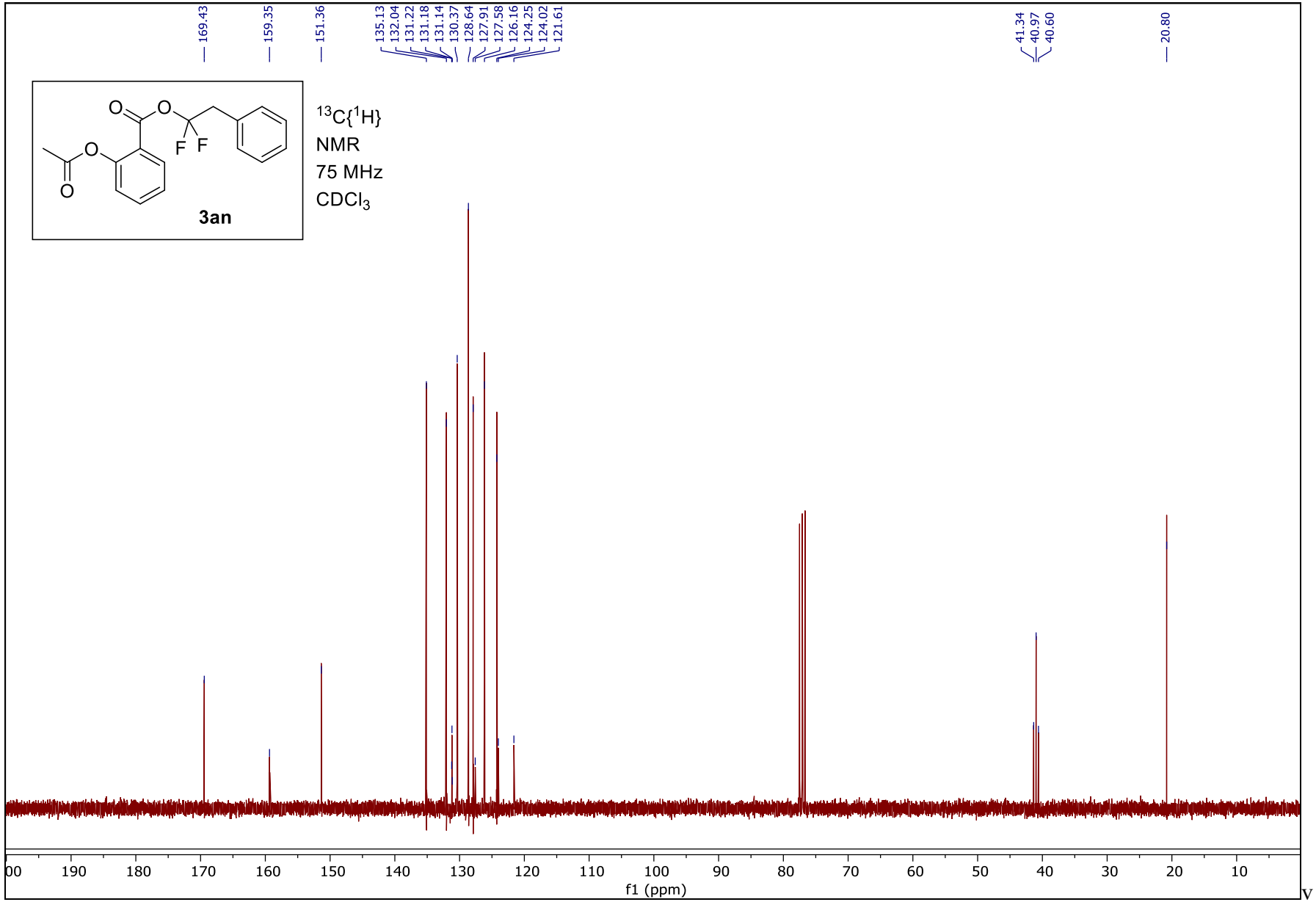

-69.66
-69.70
-69.75
3aI
^{19}F NMR
272 MHz
$CDCl_3$
-36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92
f1 (ppm)

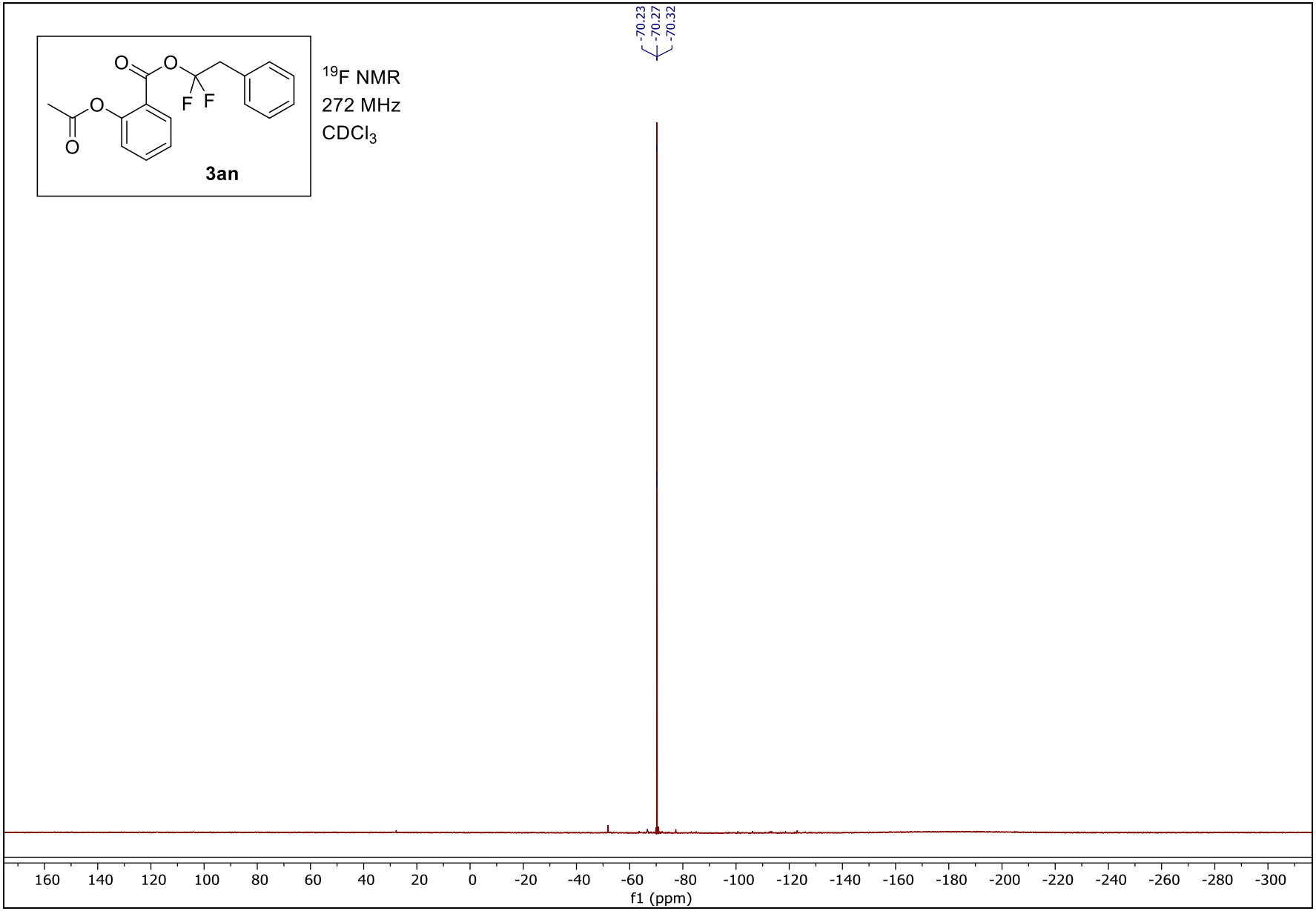

8.45
8.09
8.08
8.07
8.07
8.06
8.05
8.05
7.50
7.48
7.45
7.37
7.37
7.36
3.77
3.73
3.69
1.40
O
O
F
F
B
O
O
3am
1H NMR
300 MHz
CDCl3
0.98
2.02
1.07
4.99
2.00
12.02
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

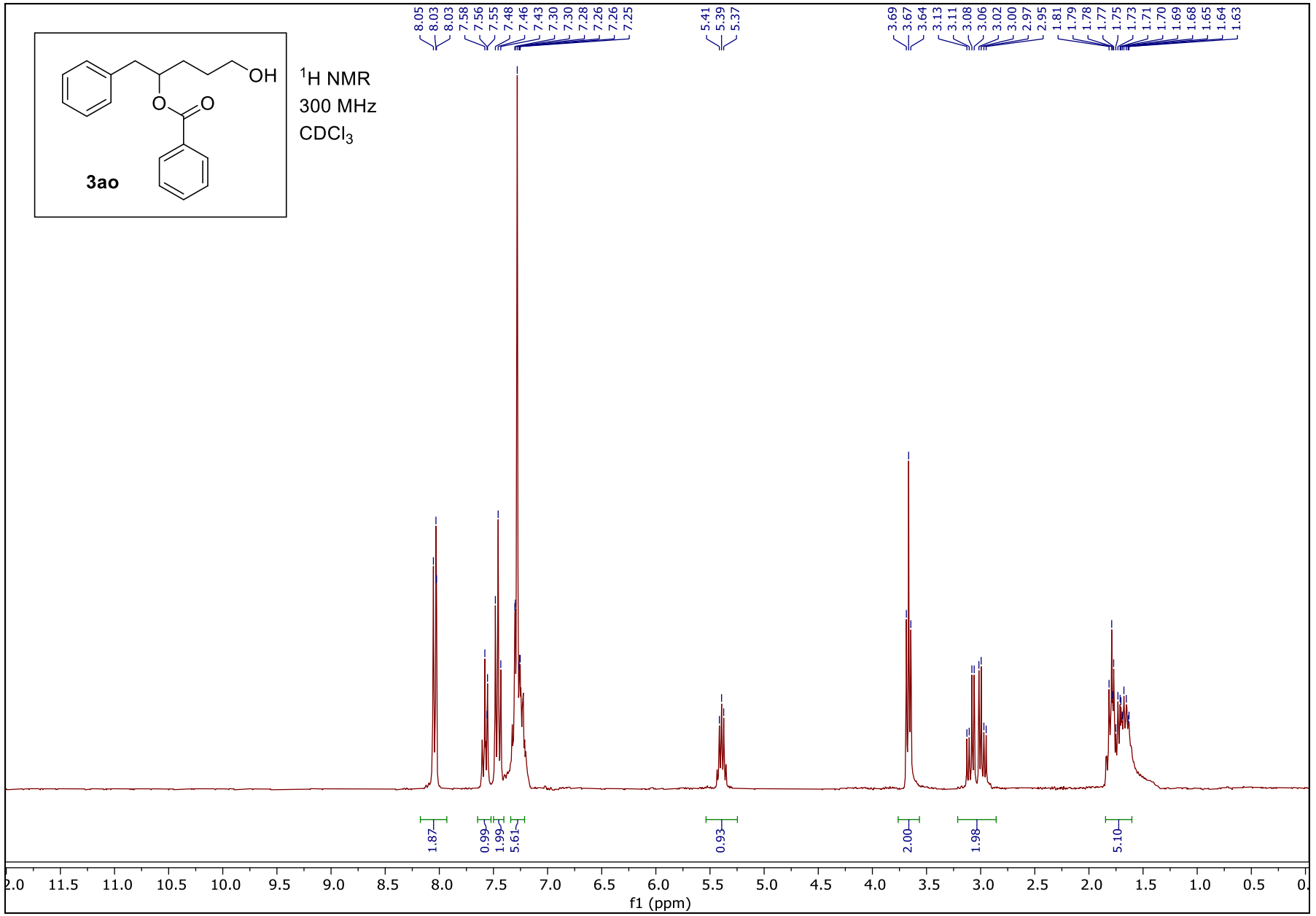

161.69
140.39
136.45
132.75
131.40
131.36
130.40
128.59
128.06
127.95
127.79
127.54
123.96
120.40
84.26
41.68
41.30
40.93
24.90
3am
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

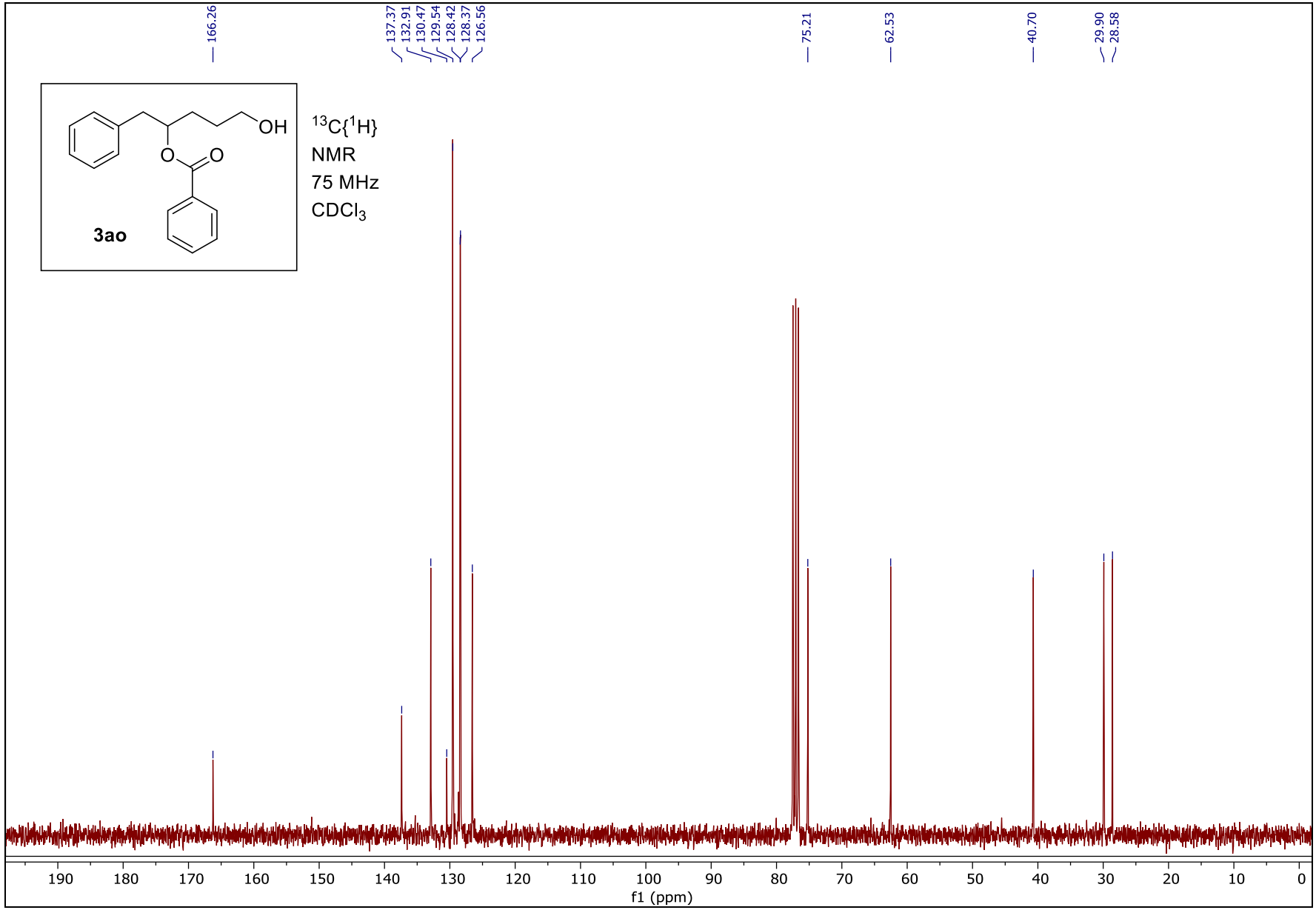

-70.59
-70.63
-70.68
3am
^{19}F NMR
272 MHz
$CDCl_3$
-50
-55
-60
-65
-70
-75
-80
-85
-90
f1 (ppm)

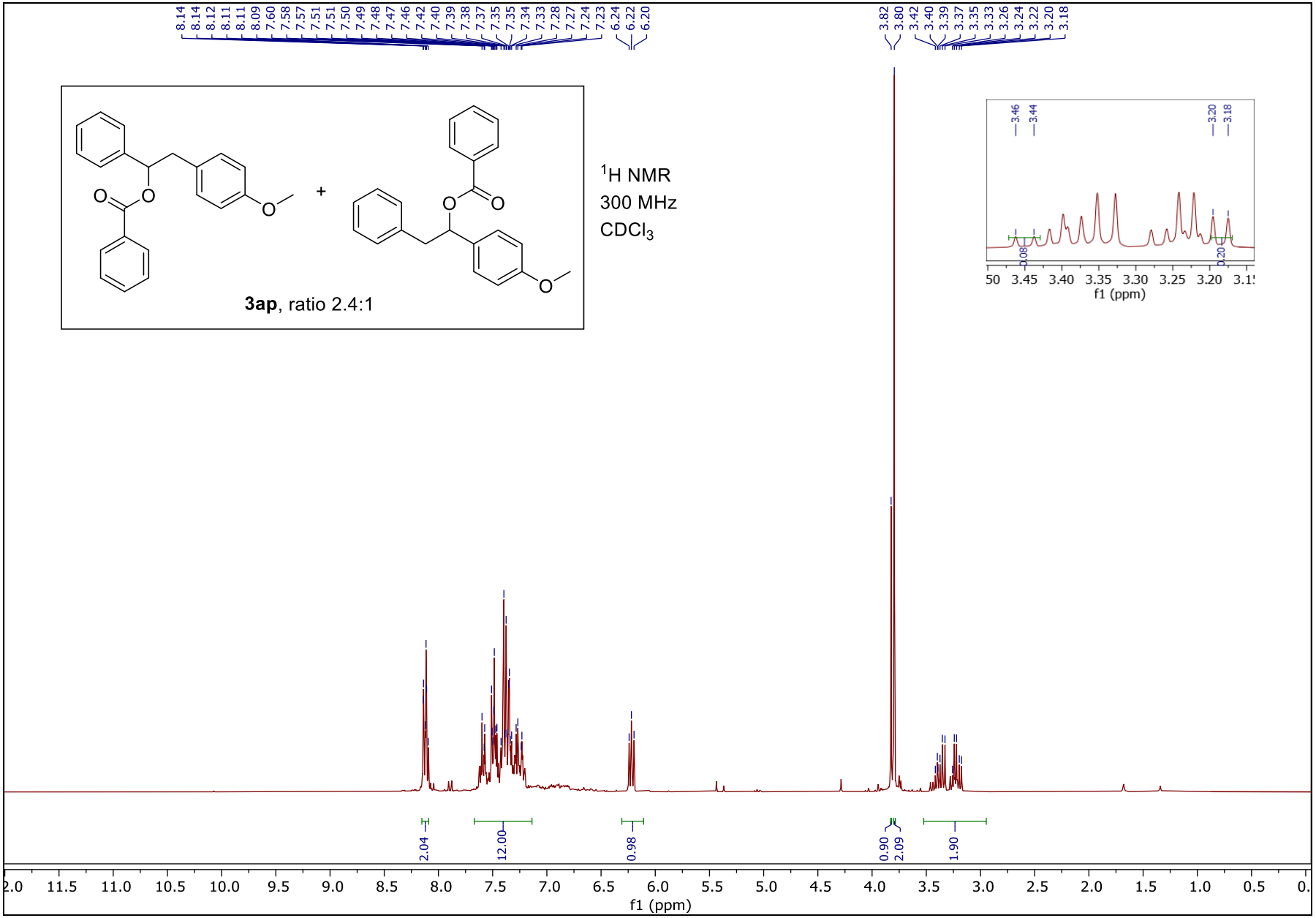

7.90
7.89
7.87
7.86
7.66
7.65
7.63
7.63
7.63
7.61
7.60
7.36
7.35
7.34
7.34
7.32
7.31
7.28
7.17
7.16
7.14
7.14
3.76
3.71
3.67
2.32
O
O
O
O
F F
3an
1H NMR
300 MHz
CDCl3
1.01
1.04
6.76
1.00
2.00
3.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

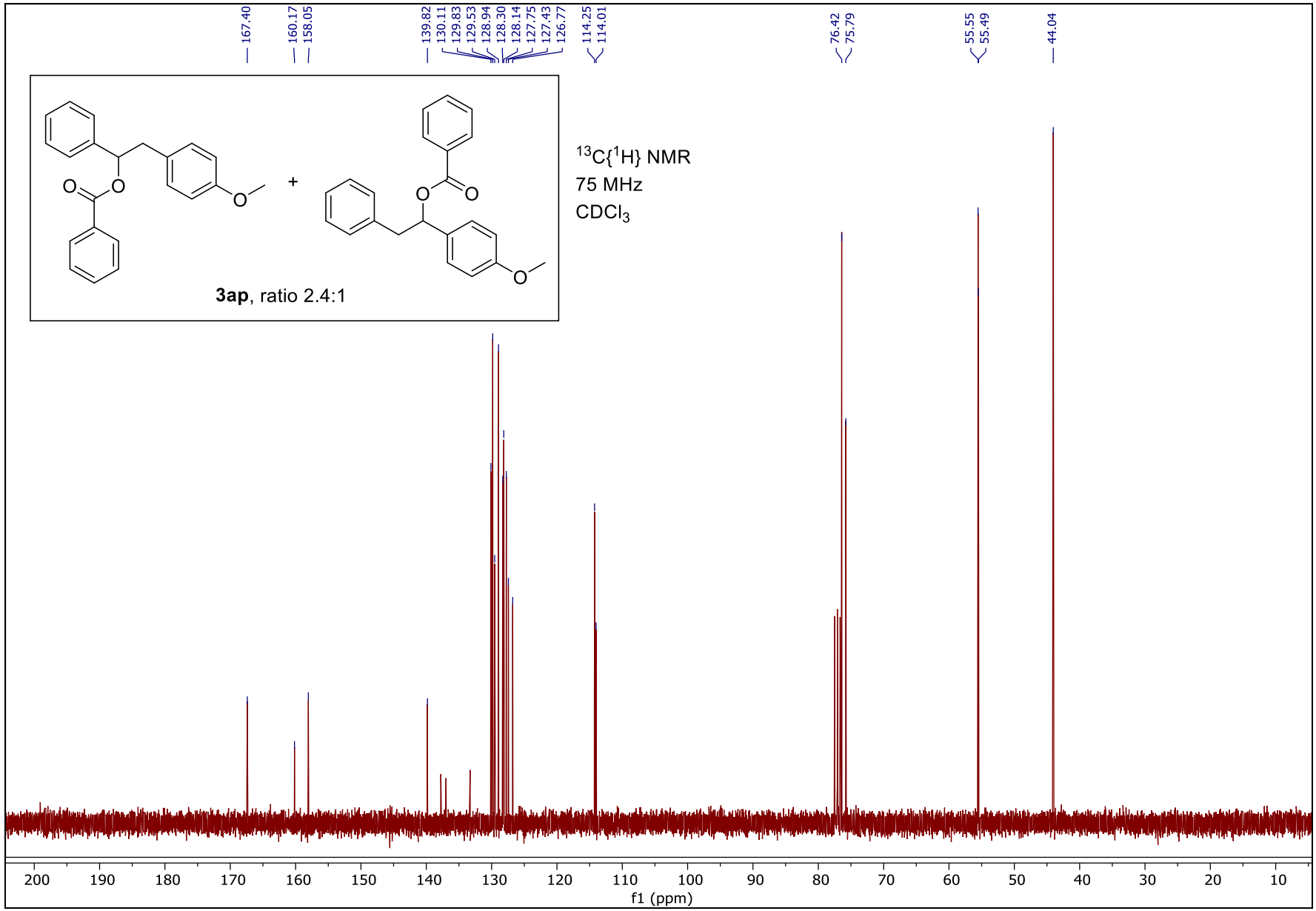

169.43
159.35
151.36
135.13
132.04
131.22
131.18
131.14
130.37
128.64
127.91
127.58
126.16
124.25
124.02
121.61
41.34
40.97
40.60
20.80
3an
13C{1H}
NMR
75 MHz
CDCl3
f1 (ppm)

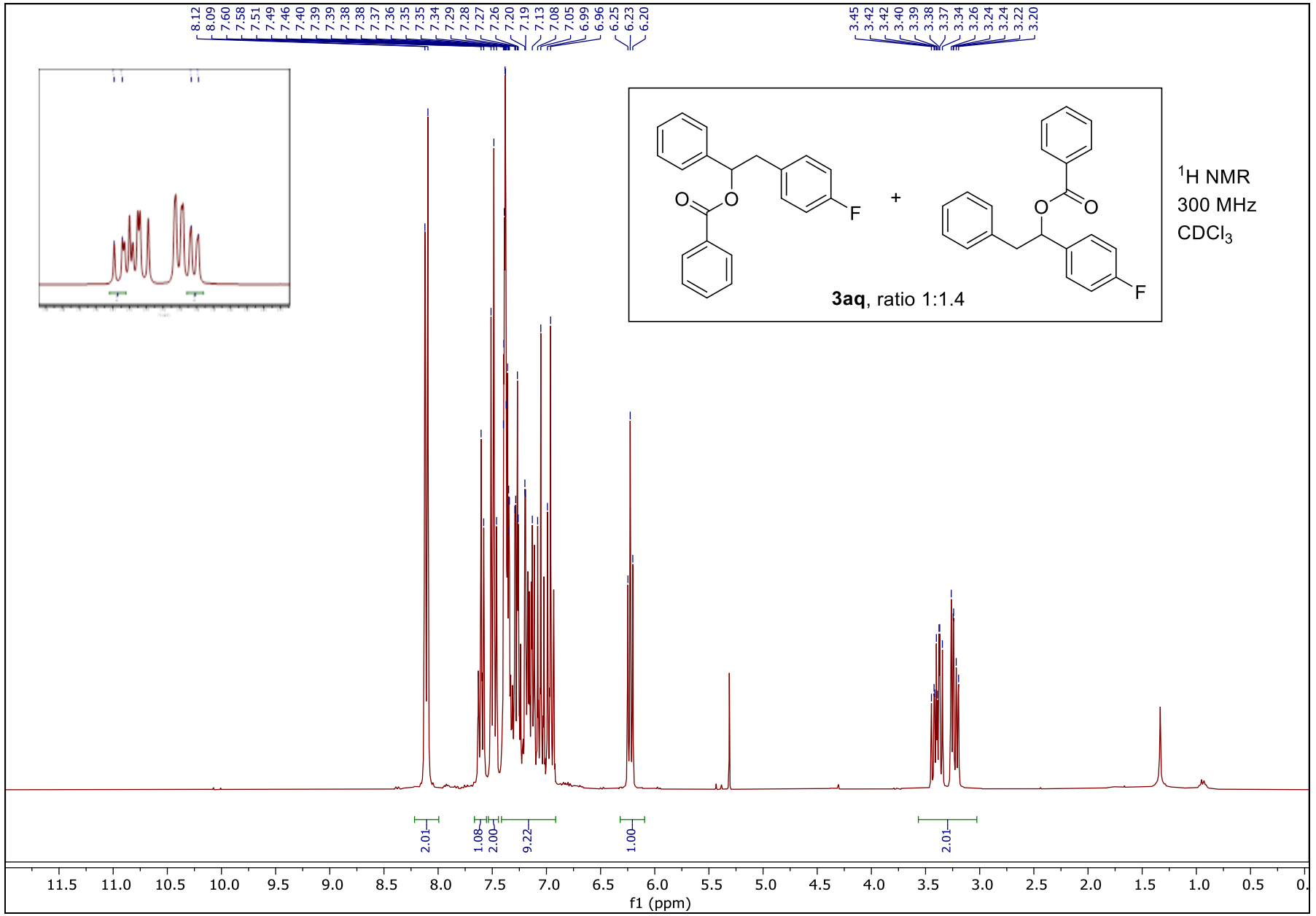

-70.23
-70.27
-70.32
O
O
O
F F
O
O
3an
19F NMR
272 MHz
CDCl3
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

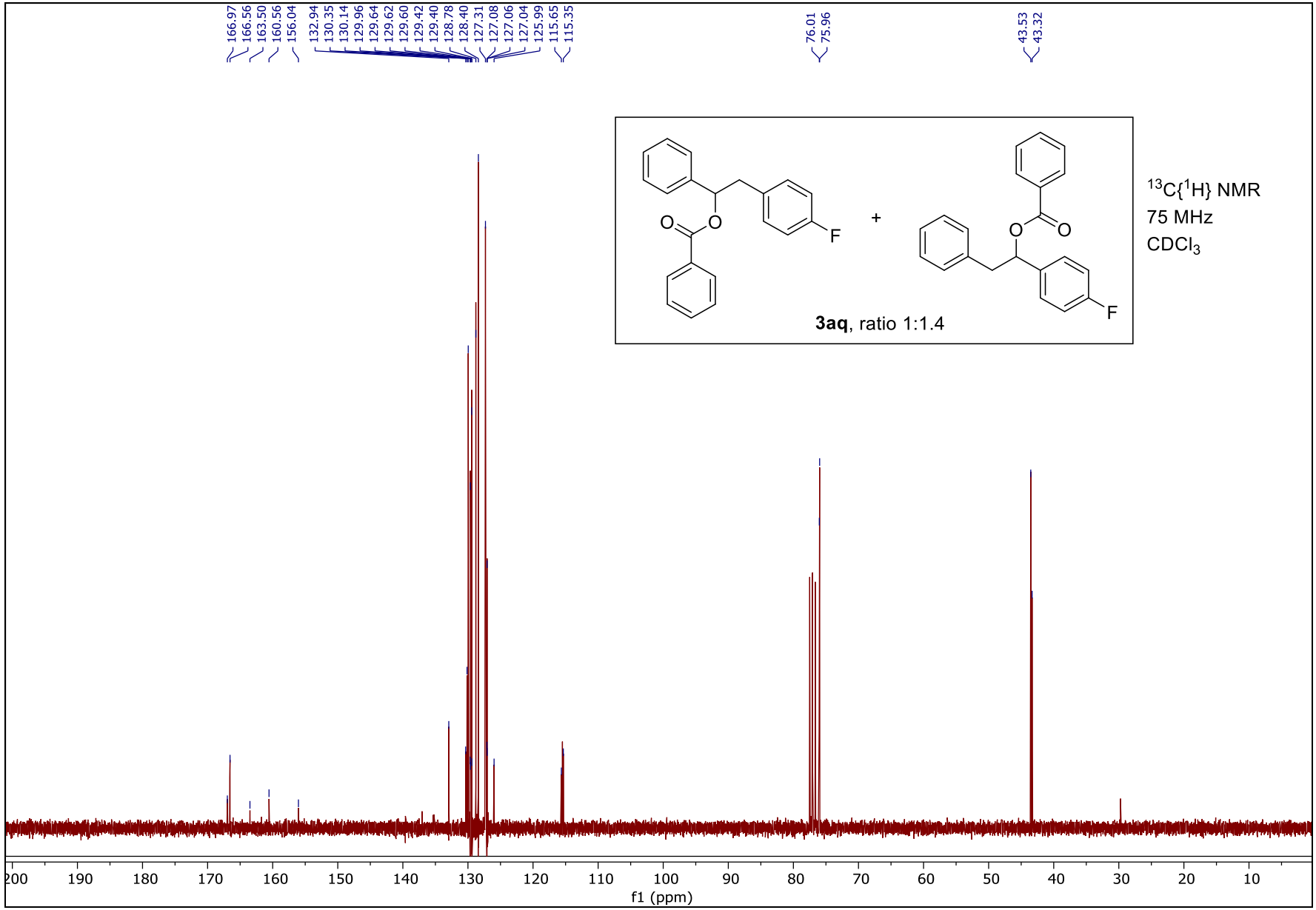

3ao
^{1}H NMR
300 MHz
$CDCl_3$
8.05
8.03
8.03
7.58
7.56
7.55
7.48
7.46
7.43
7.30
7.30
7.28
7.26
7.26
7.25
5.41
5.39
5.37
3.69
3.67
3.64
3.13
3.11
3.08
3.06
3.02
3.00
2.97
2.95
1.81
1.79
1.78
1.77
1.75
1.73
1.71
1.70
1.69
1.68
1.65
1.64
1.63
1.87
0.99
1.99
5.61
0.93
2.00
1.98
5.10
f1 (ppm)

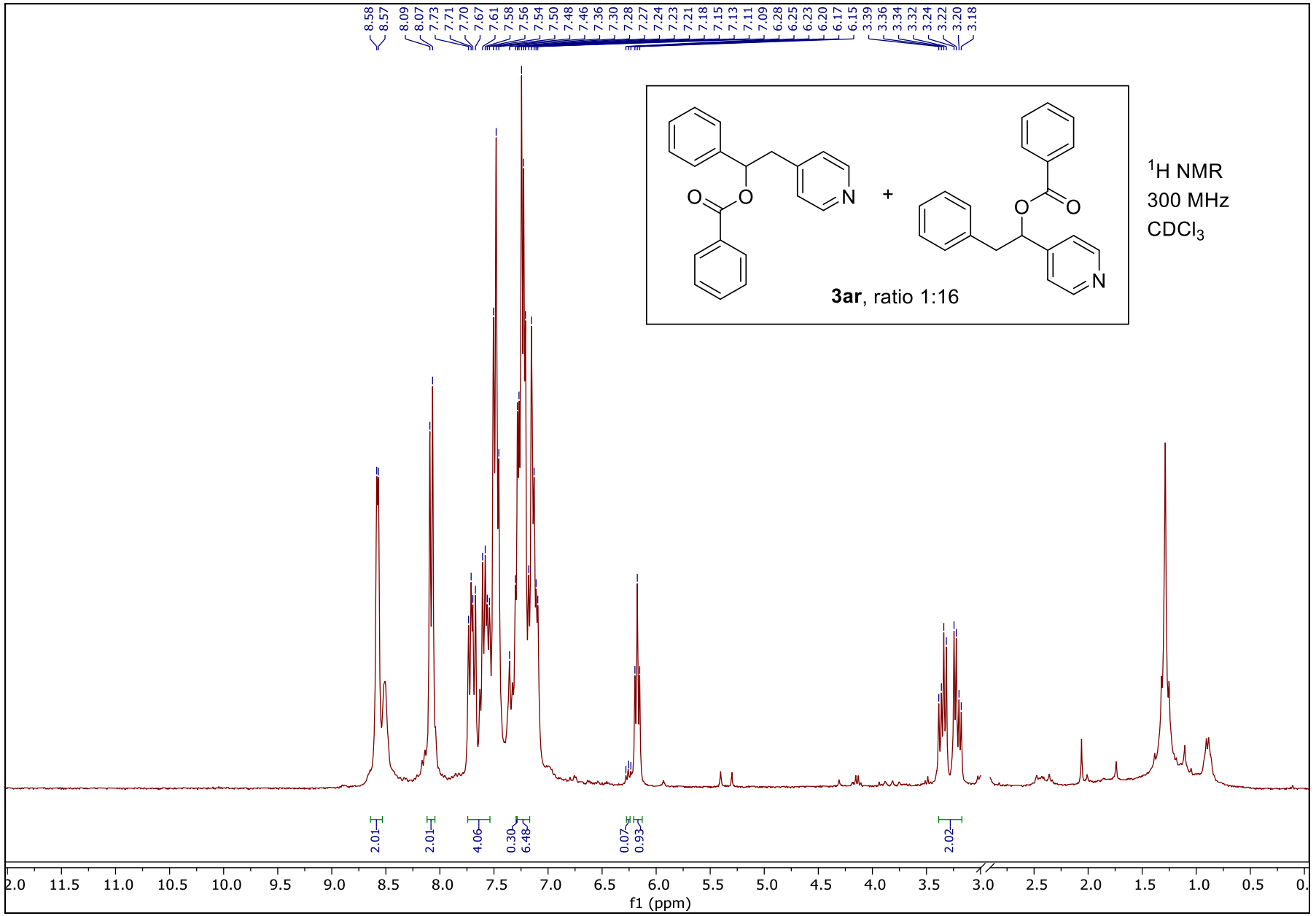

166.26
137.37
132.91
130.47
129.54
128.42
128.37
126.56
75.21
62.53
40.70
29.90
28.58
OH
O
O
3ao
13C{1H}
NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

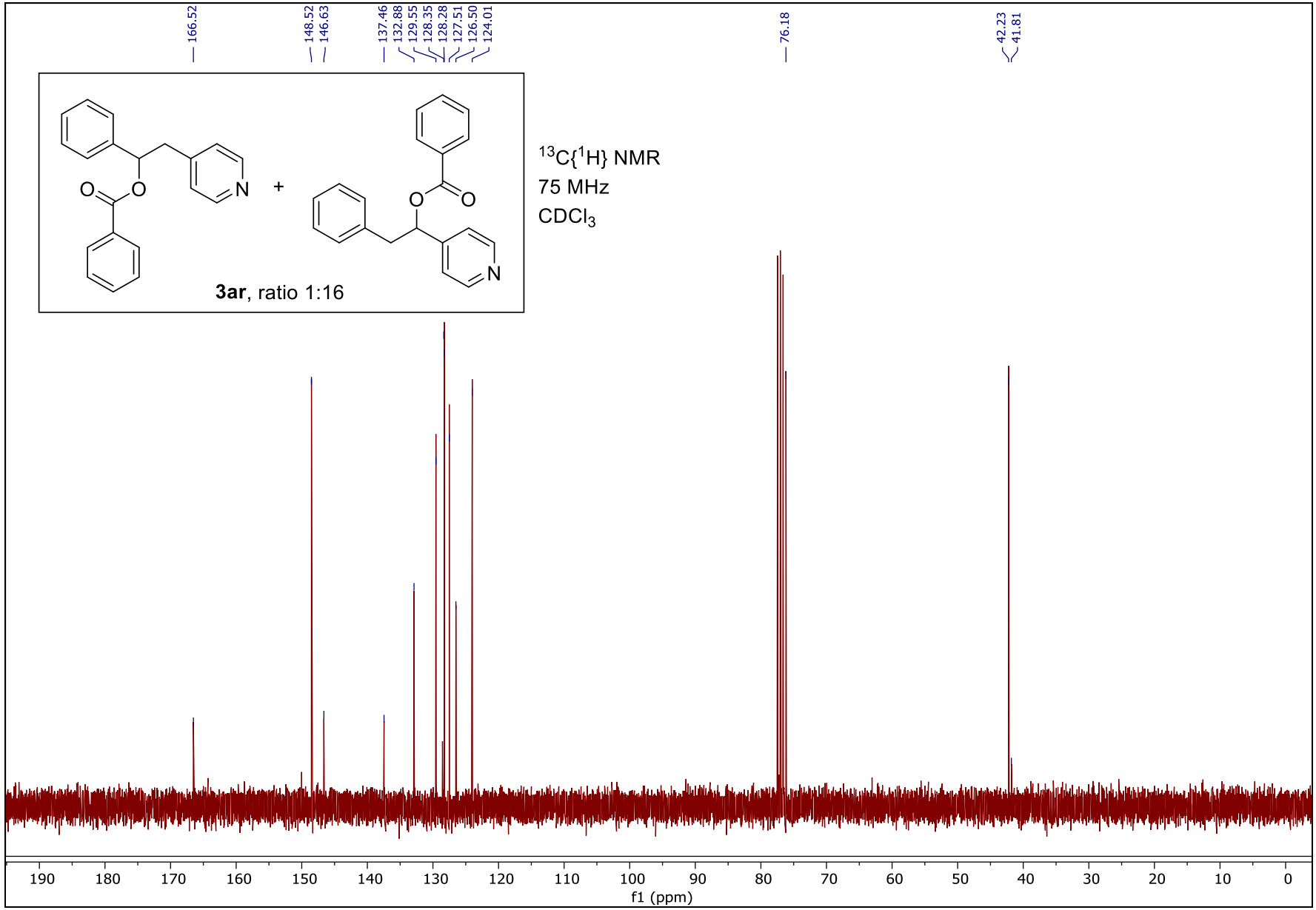

3ap, ratio 2.4:1
1H NMR
300 MHz
CDCl3
f1 (ppm)

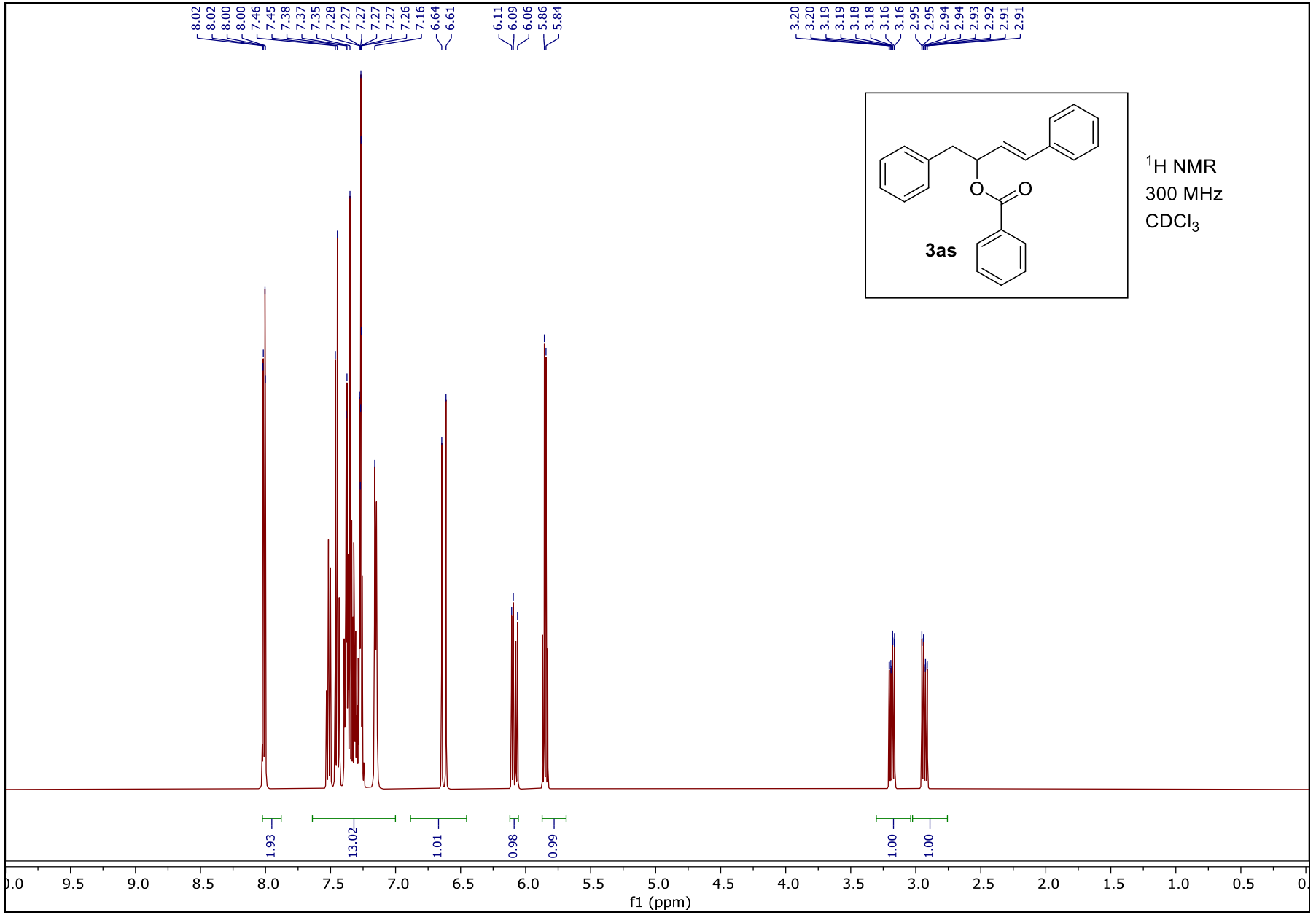

167.40
160.17
158.05
139.82
130.11
129.83
129.53
128.94
128.30
128.14
127.75
127.43
126.77
114.25
114.01
76.42
75.79
55.55
55.49
44.04
3ap, ratio 2.4:1
13C{1H} NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

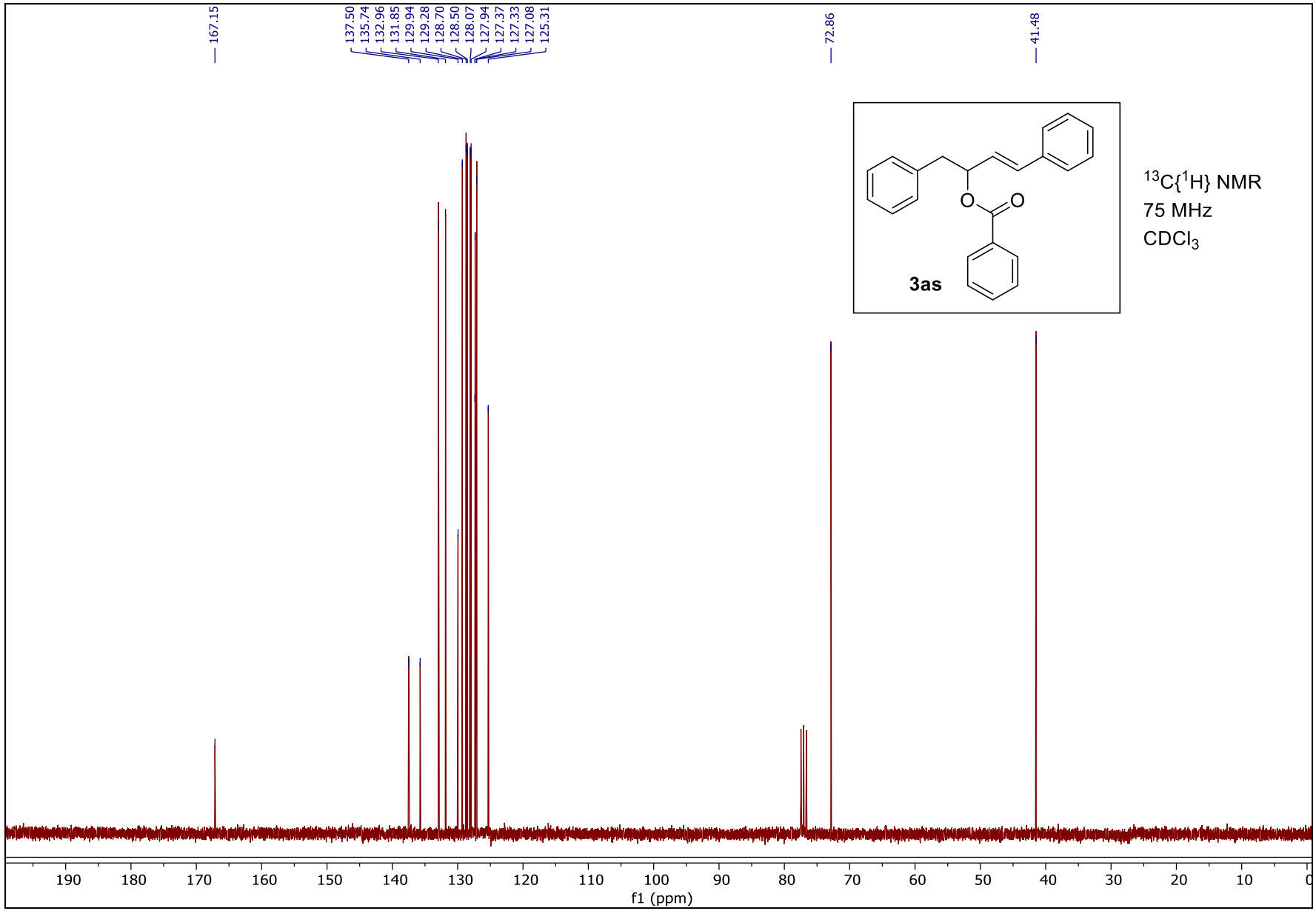

8.12 8.09 7.60 7.58 7.51 7.49 7.46 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.34 7.29 7.28 7.27 7.26 7.20 7.19 7.13 7.08 7.05 6.99 6.96 6.25 6.23 6.20
3.45 3.42 3.42 3.40 3.39 3.38 3.37 3.34 3.26 3.24 3.24 3.22 3.20
O O F + O O F
3aq, ratio 1:1.4
1H NMR
300 MHz
CDCl3
2.01 1.08 2.00 9.22 1.00 2.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

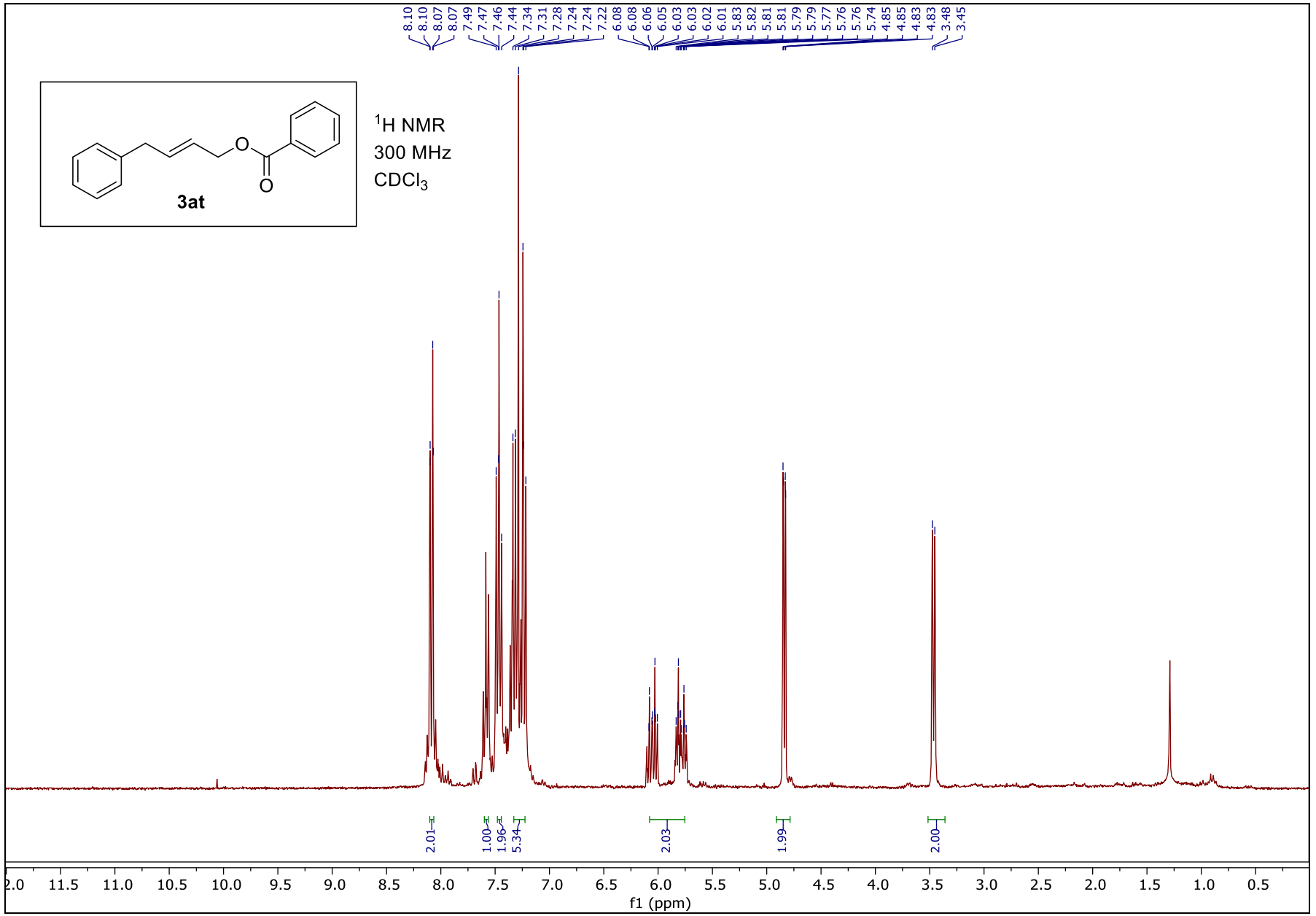

166.97
166.56
163.50
160.56
156.04
132.94
130.35
130.14
129.96
129.64
129.62
129.60
129.42
129.40
128.78
128.40
127.31
127.08
127.06
127.04
125.99
115.65
115.35
76.01
75.96
43.53
43.32
O
O
F
+
O
O
F
3aq, ratio 1:1.4
13C{1H} NMR
75 MHz
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

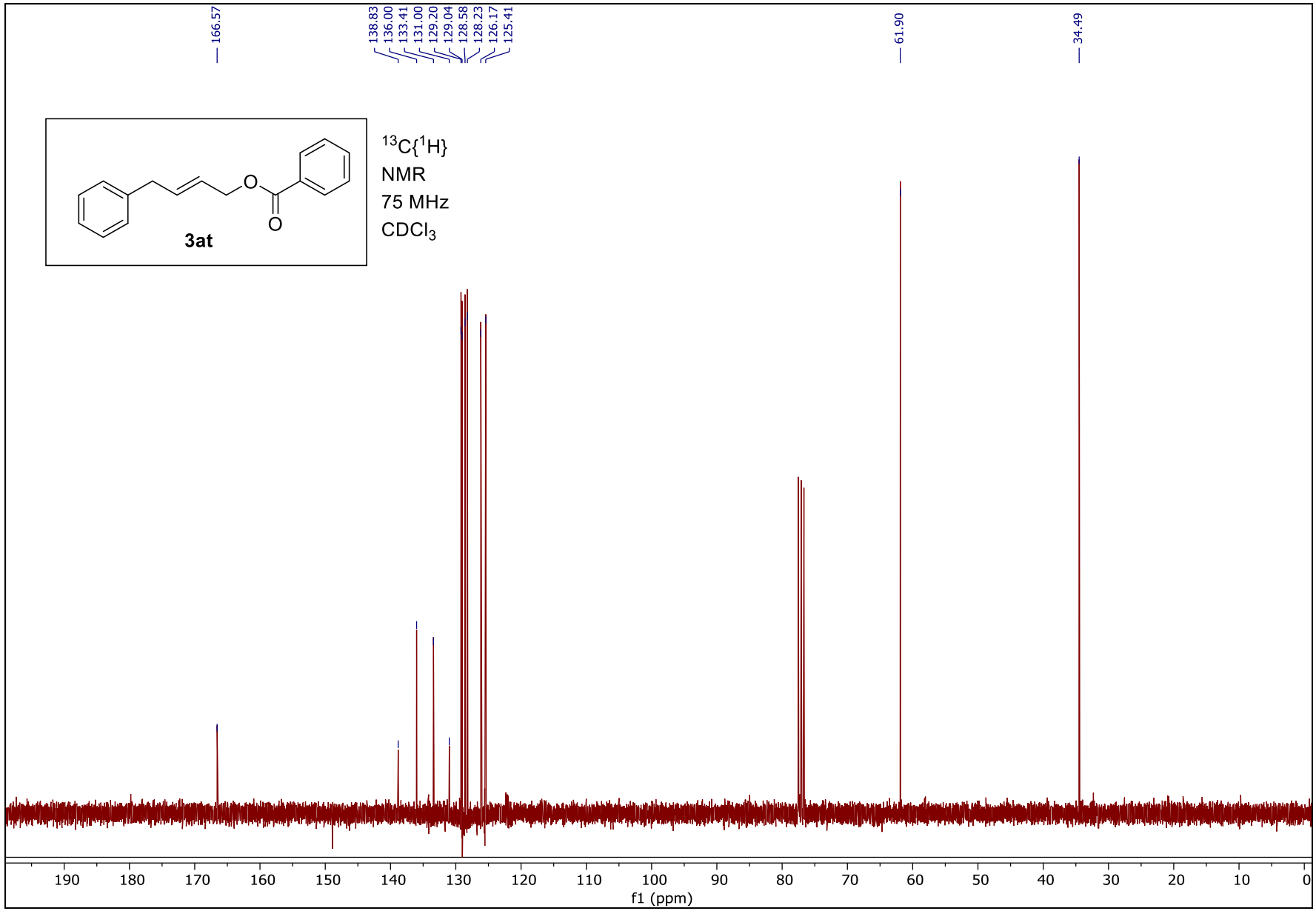

8.58 8.57 8.09 8.07 7.73 7.71 7.70 7.67 7.61 7.58 7.56 7.54 7.50 7.48 7.46 7.36 7.30 7.28 7.27 7.24 7.23 7.21 7.18 7.15 7.13 7.11 7.09 6.28 6.25 6.23 6.20 6.17 6.15 3.39 3.36 3.34 3.32 3.24 3.22 3.20 3.18
O
O
N
+
O
O
N
3ar, ratio 1:16
1H NMR
300 MHz
CDCl3
2.01 2.01 4.06 0.30 6.48 0.07 0.93 2.02
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

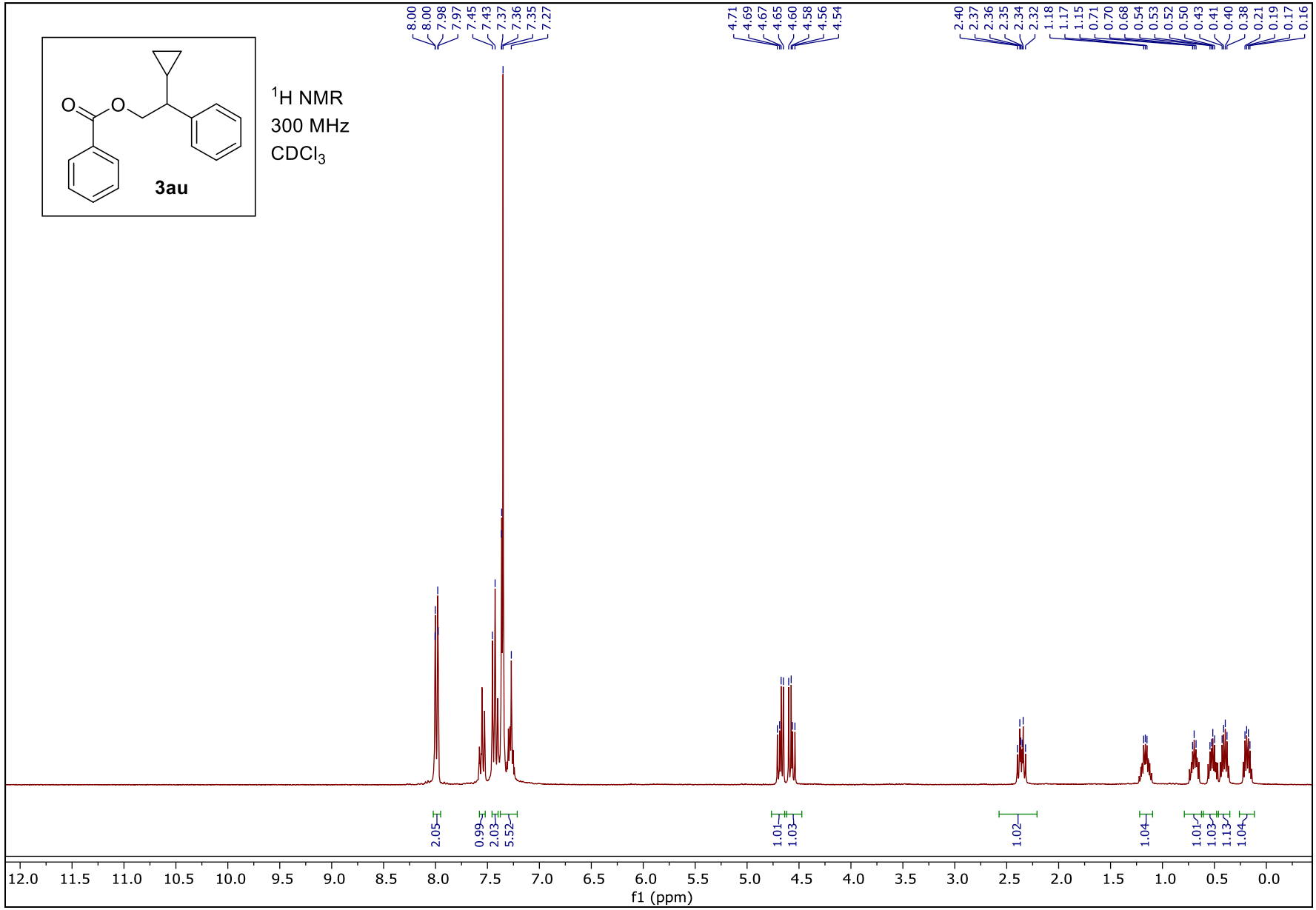

166.52
148.52
146.63
137.46
132.88
129.55
128.35
128.28
127.51
126.50
124.01
76.18
42.23
41.81
O
O
N
+
O
O
N
3ar, ratio 1:16
13C{1H} NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

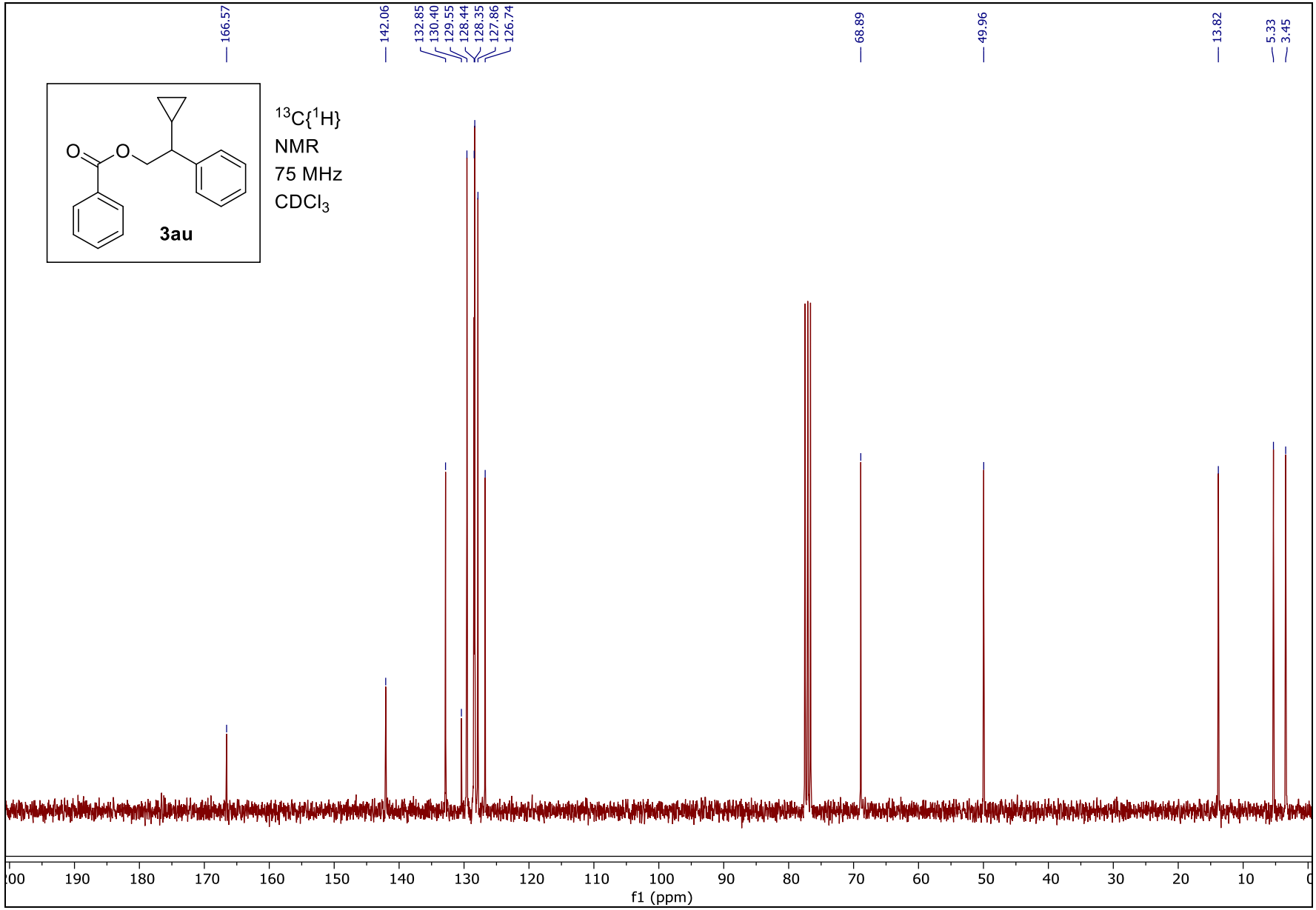

8.02
8.02
8.00
8.00
7.46
7.45
7.38
7.37
7.35
7.28
7.27
7.27
7.27
7.27
7.26
7.16
6.64
6.61
6.11
6.09
6.06
5.86
5.84
3.20
3.20
3.19
3.19
3.18
3.18
3.16
3.16
2.95
2.95
2.94
2.94
2.93
2.92
2.91
2.91
O
O
3as
1H NMR
300 MHz
CDCl3
1.93
13.02
1.01
0.98
0.99
1.00
1.00
f1 (ppm)

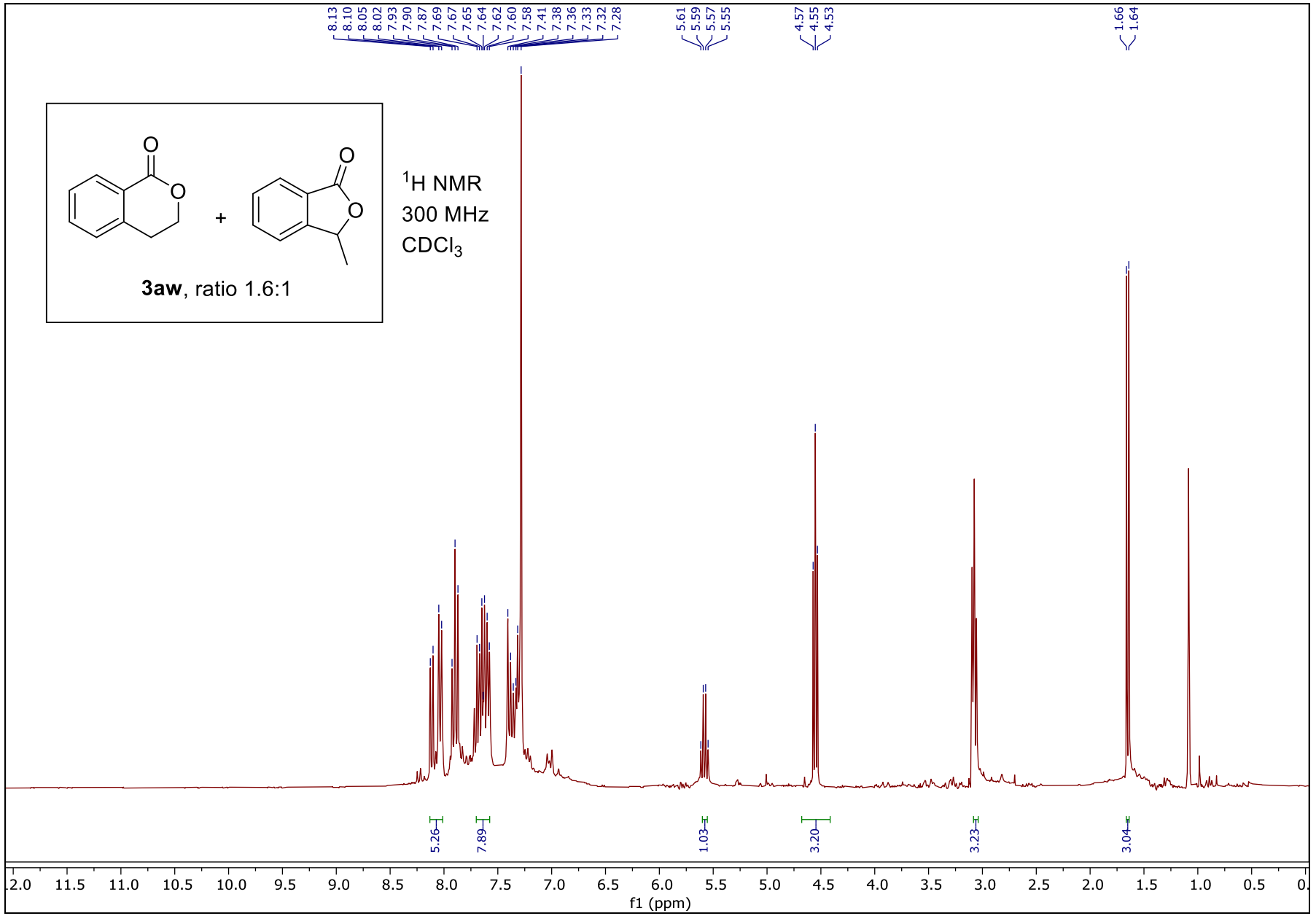

167.15
137.50
135.74
132.96
131.85
129.94
129.28
128.70
128.50
128.07
127.94
127.37
127.33
127.08
125.31
72.86
41.48
O
O
3as
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

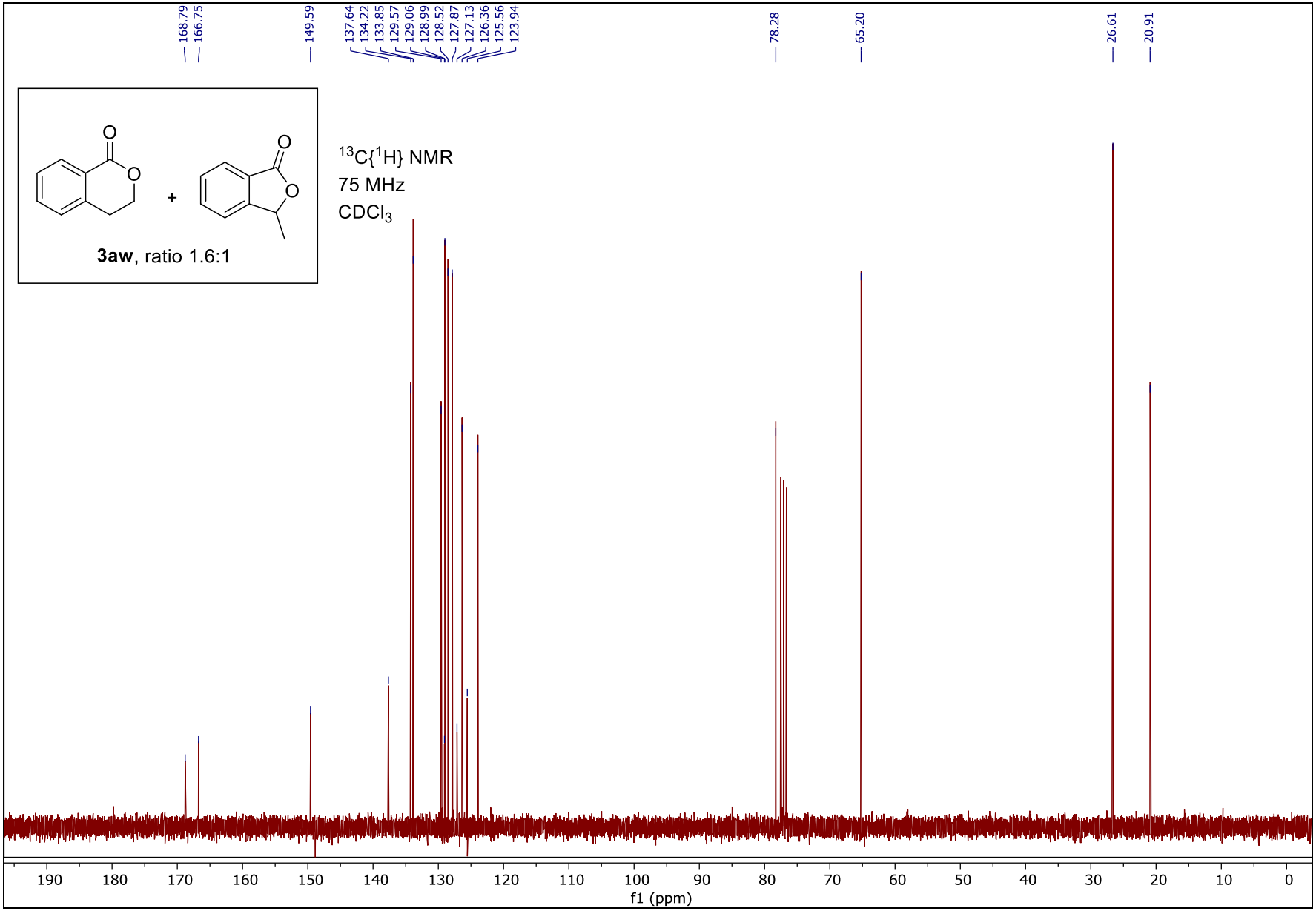

8.10
8.10
8.07
8.07
7.49
7.47
7.46
7.44
7.34
7.31
7.28
7.24
7.24
7.22
6.08
6.08
6.06
6.05
6.03
6.03
6.02
6.01
5.83
5.82
5.81
5.81
5.79
5.79
5.77
5.76
5.76
5.74
4.85
4.85
4.83
4.83
3.48
3.45
O
O
3at
1H NMR
300 MHz
CDCl3
2.01
1.00
1.96
5.34
2.03
1.99
2.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

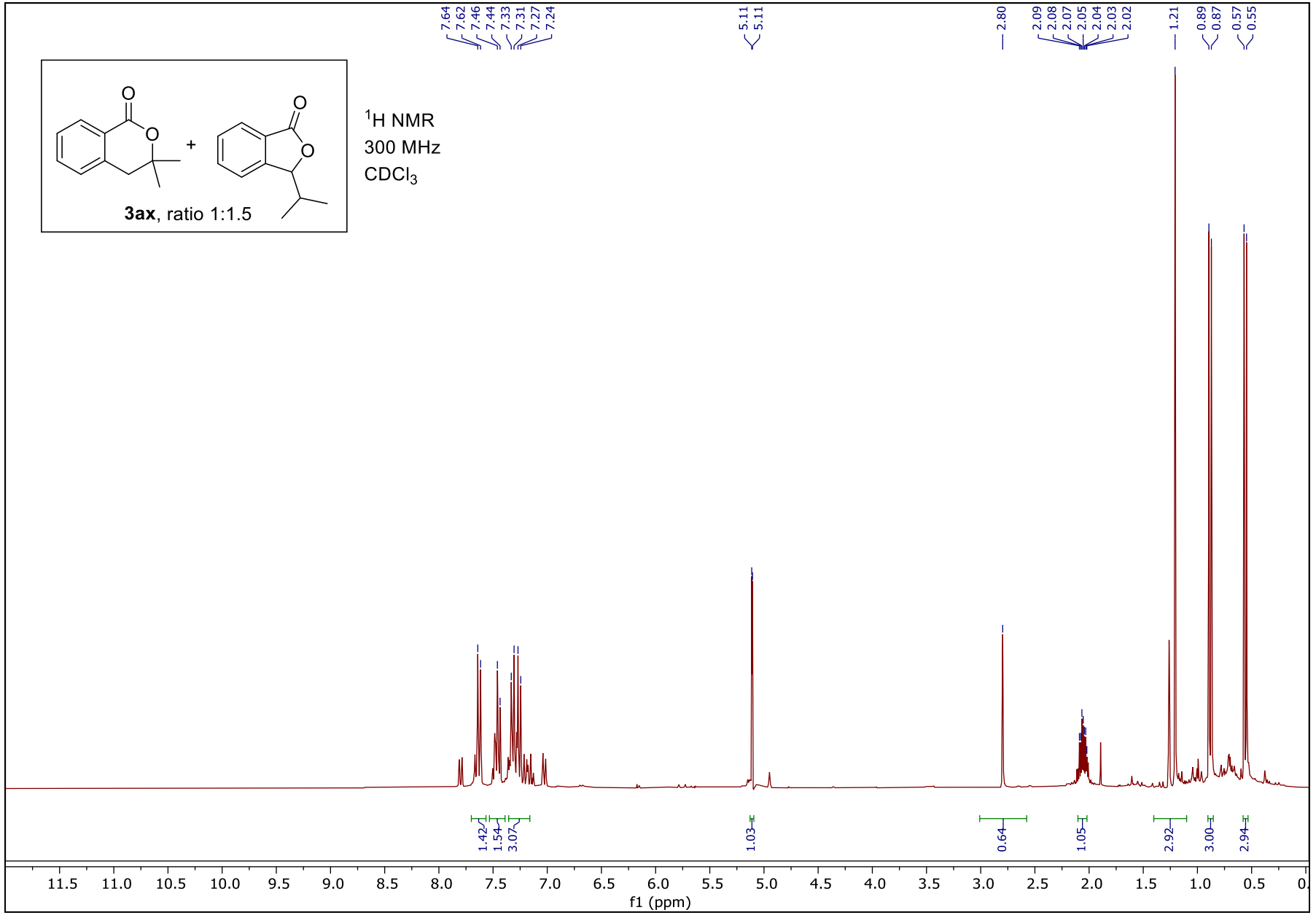

166.57
138.83
136.00
133.41
131.00
129.20
129.04
128.58
128.23
126.17
125.41
61.90
34.49
3at
13C{1H}
NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

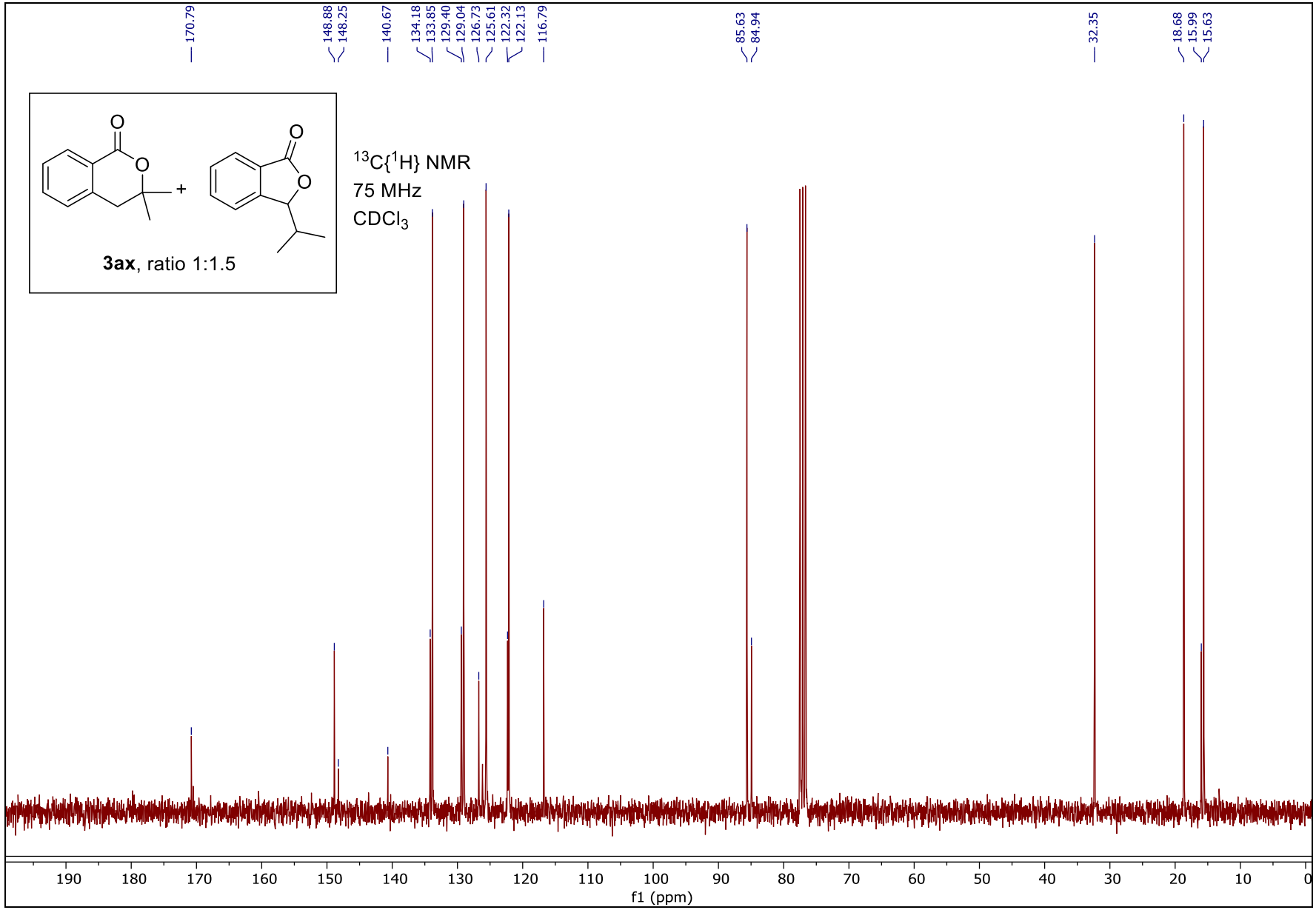

3au
1H NMR
300 MHz
CDCl3
8.00
8.00
7.98
7.97
7.45
7.43
7.37
7.36
7.35
7.27
4.71
4.69
4.67
4.65
4.60
4.58
4.56
4.54
2.40
2.37
2.36
2.35
2.34
2.32
1.18
1.17
1.15
0.71
0.70
0.68
0.54
0.53
0.52
0.50
0.43
0.41
0.40
0.38
0.21
0.19
0.17
0.16
2.05
0.99
2.03
5.52
1.01
1.03
1.02
1.04
1.01
1.03
1.13
1.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

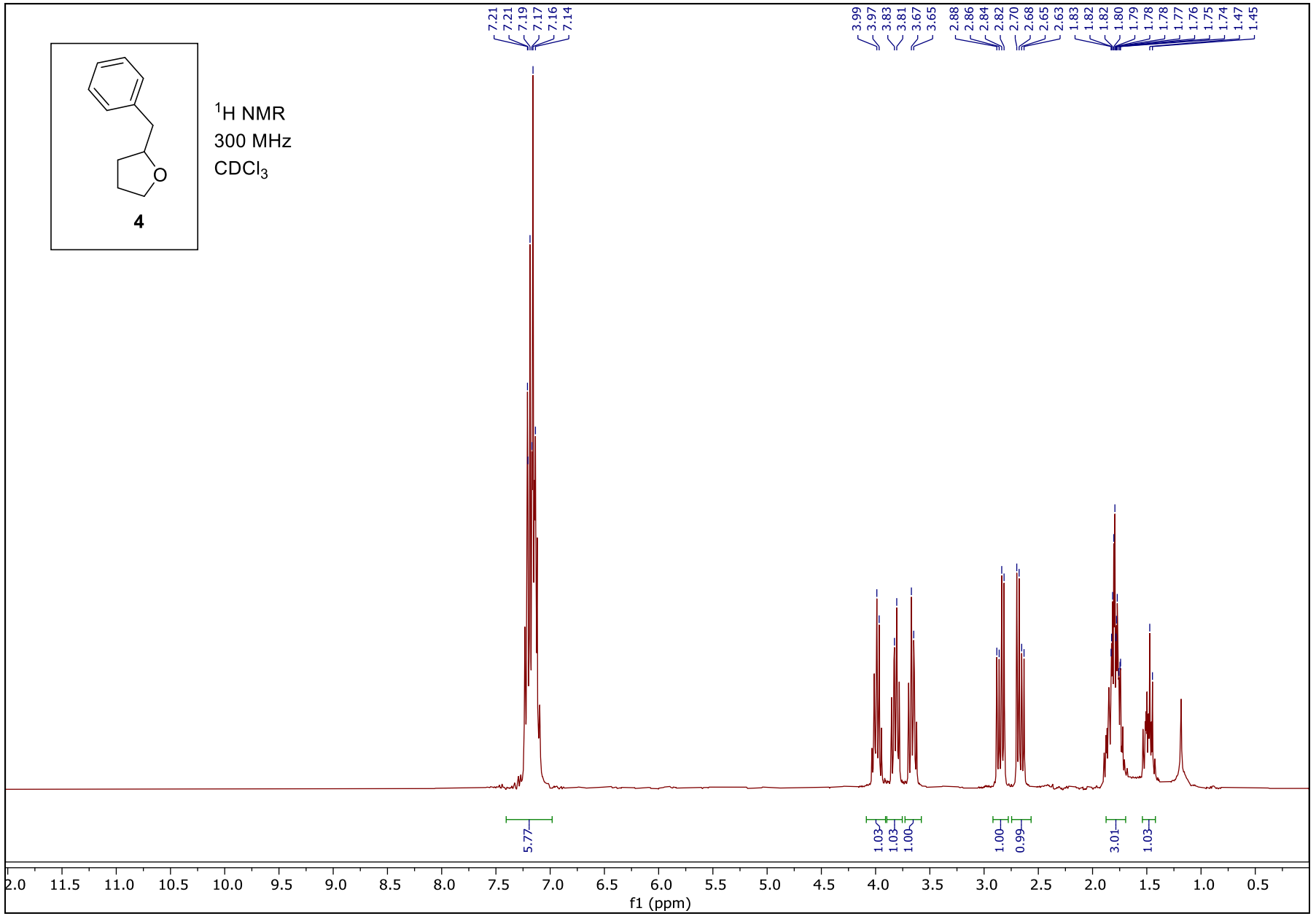

166.57
142.06
132.85
130.40
129.55
128.44
128.35
127.86
126.74
68.89
49.96
13.82
5.33
3.45
O
O
3au
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

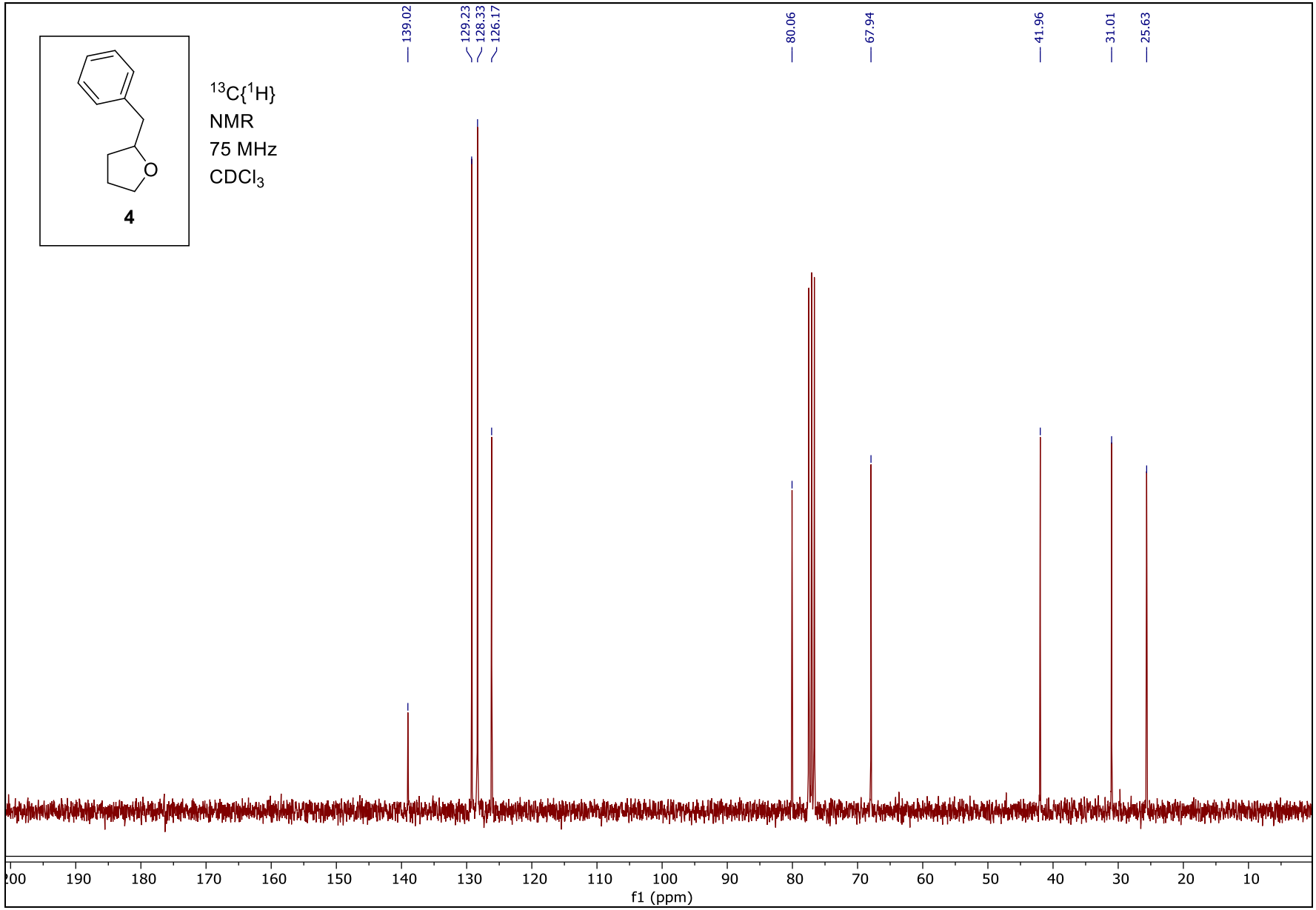

8.13
8.10
8.05
8.02
7.93
7.90
7.87
7.69
7.67
7.65
7.64
7.62
7.60
7.58
7.41
7.38
7.36
7.33
7.32
7.28
5.61
5.59
5.57
5.55
4.57
4.55
4.53
1.66
1.64
+
3aw, ratio 1.6:1
1H NMR
300 MHz
CDCl3
5.26
7.89
1.03
3.20
3.23
3.04
f1 (ppm)

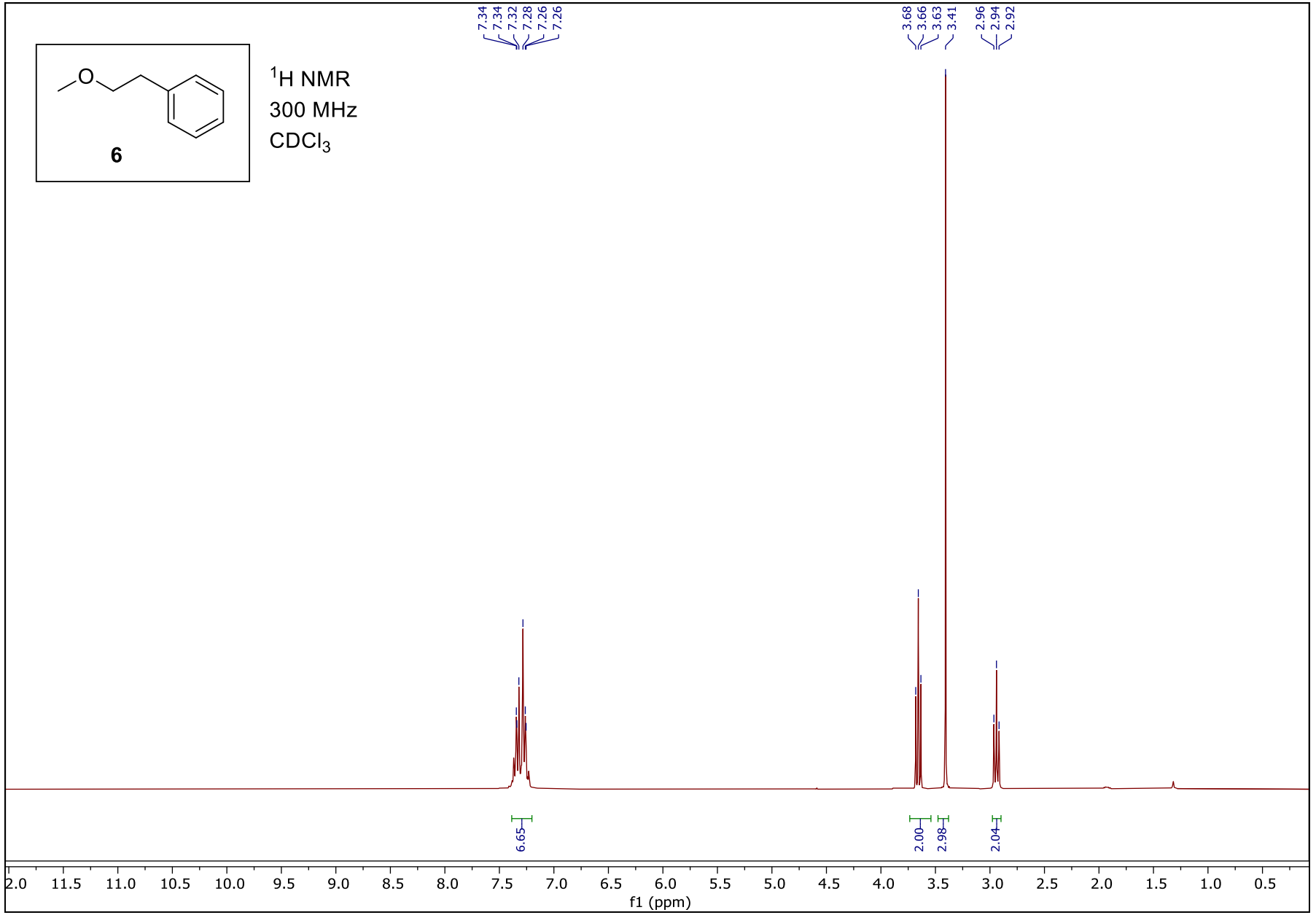

168.79
166.75
149.59
137.64
134.22
133.85
129.57
129.06
128.99
128.52
127.87
127.13
126.36
125.56
123.94
78.28
65.20
26.61
20.91
3aw, ratio 1.6:1
13C{1H} NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

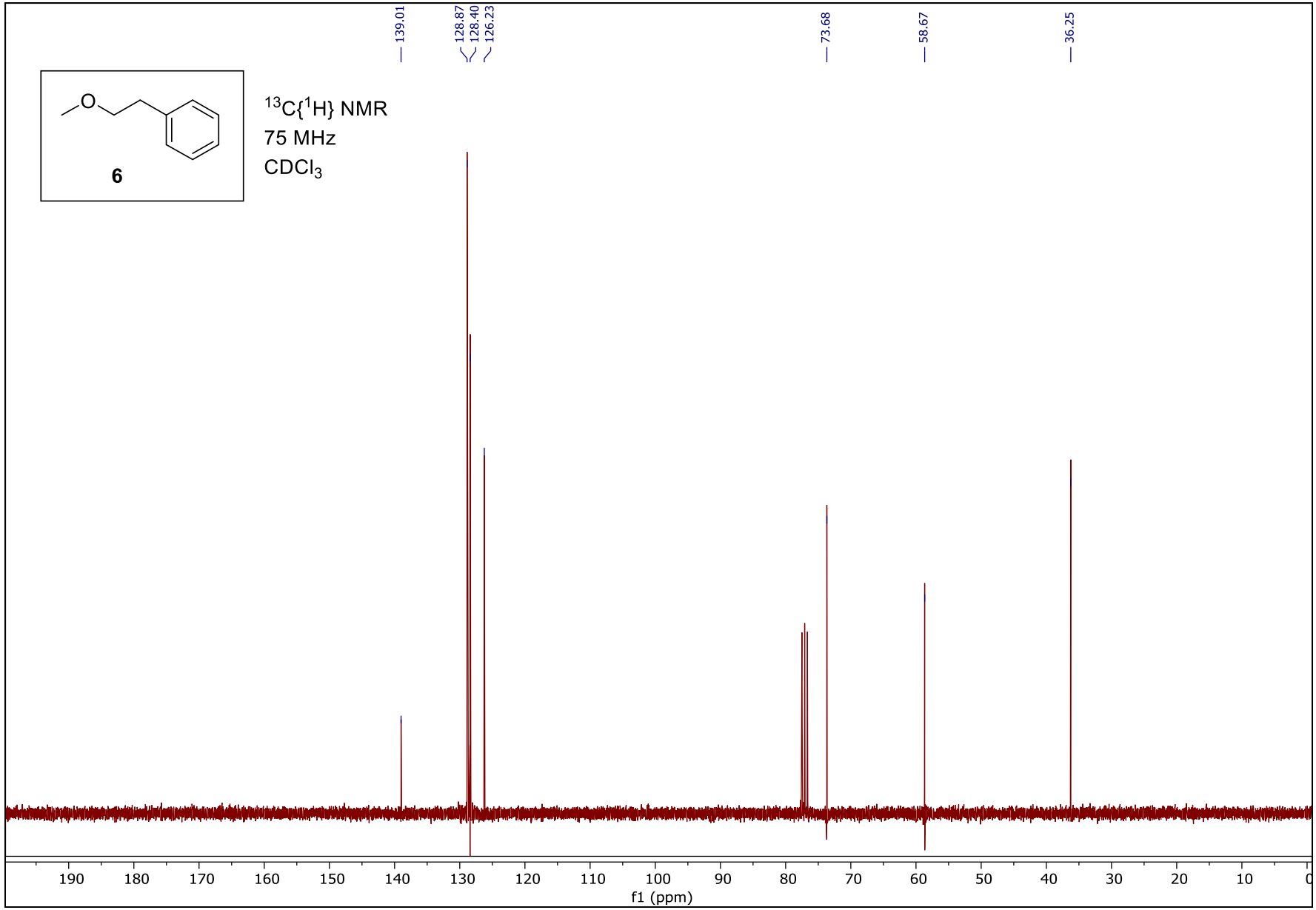

7.64
7.62
7.46
7.44
7.33
7.31
7.27
7.24
5.11
5.11
2.80
2.09
2.08
2.07
2.05
2.04
2.03
2.02
1.21
0.89
0.87
0.57
0.55
3ax, ratio 1:1.5
1H NMR
300 MHz
CDCl3
1.42
1.54
3.07
1.03
0.64
1.05
2.92
3.00
2.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

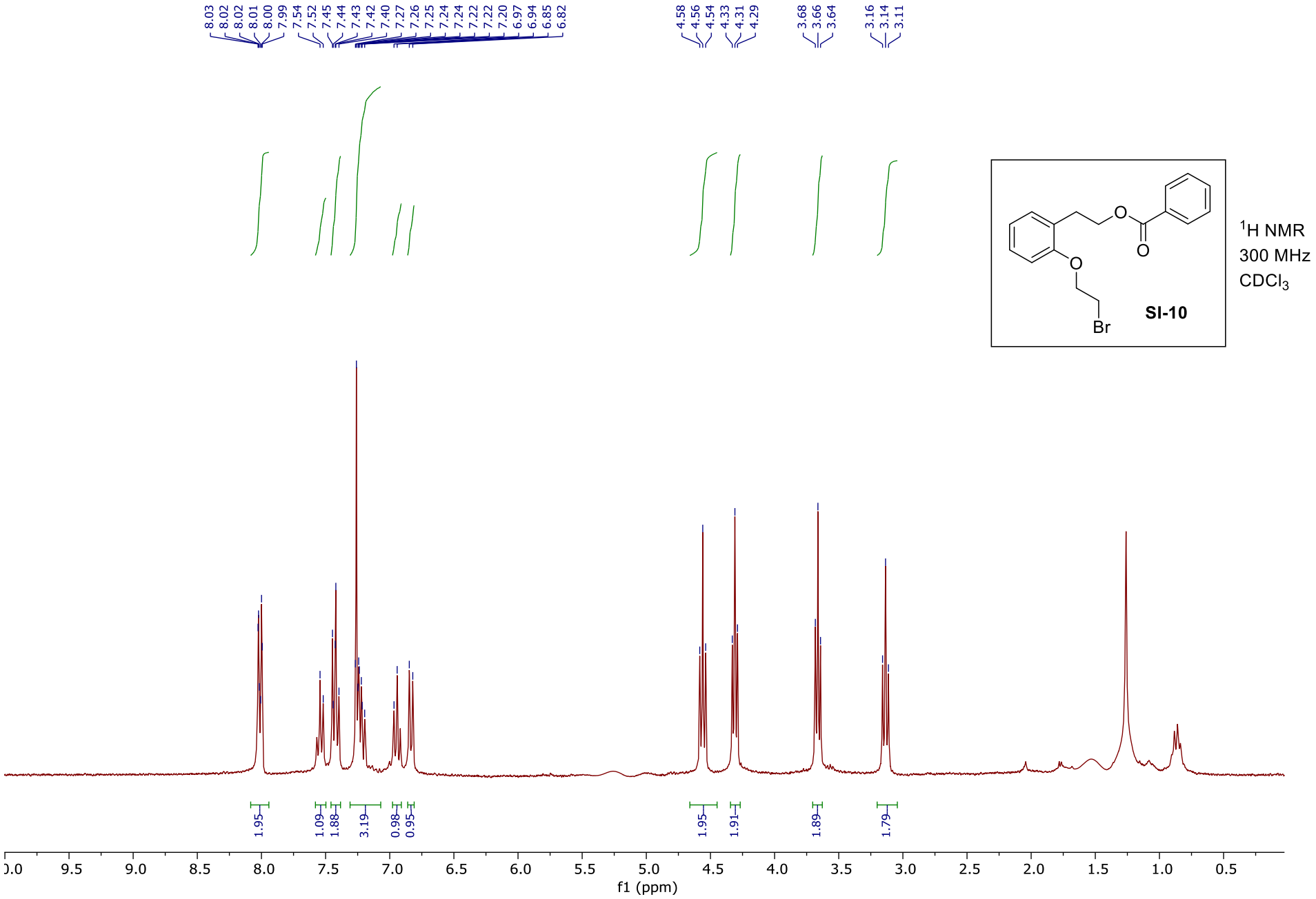

170.79
148.88
148.25
140.67
134.18
133.85
129.40
129.04
126.73
125.61
122.32
122.13
116.79
85.63
84.94
32.35
18.68
15.99
15.63
3ax, ratio 1:1.5
13C{1H} NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

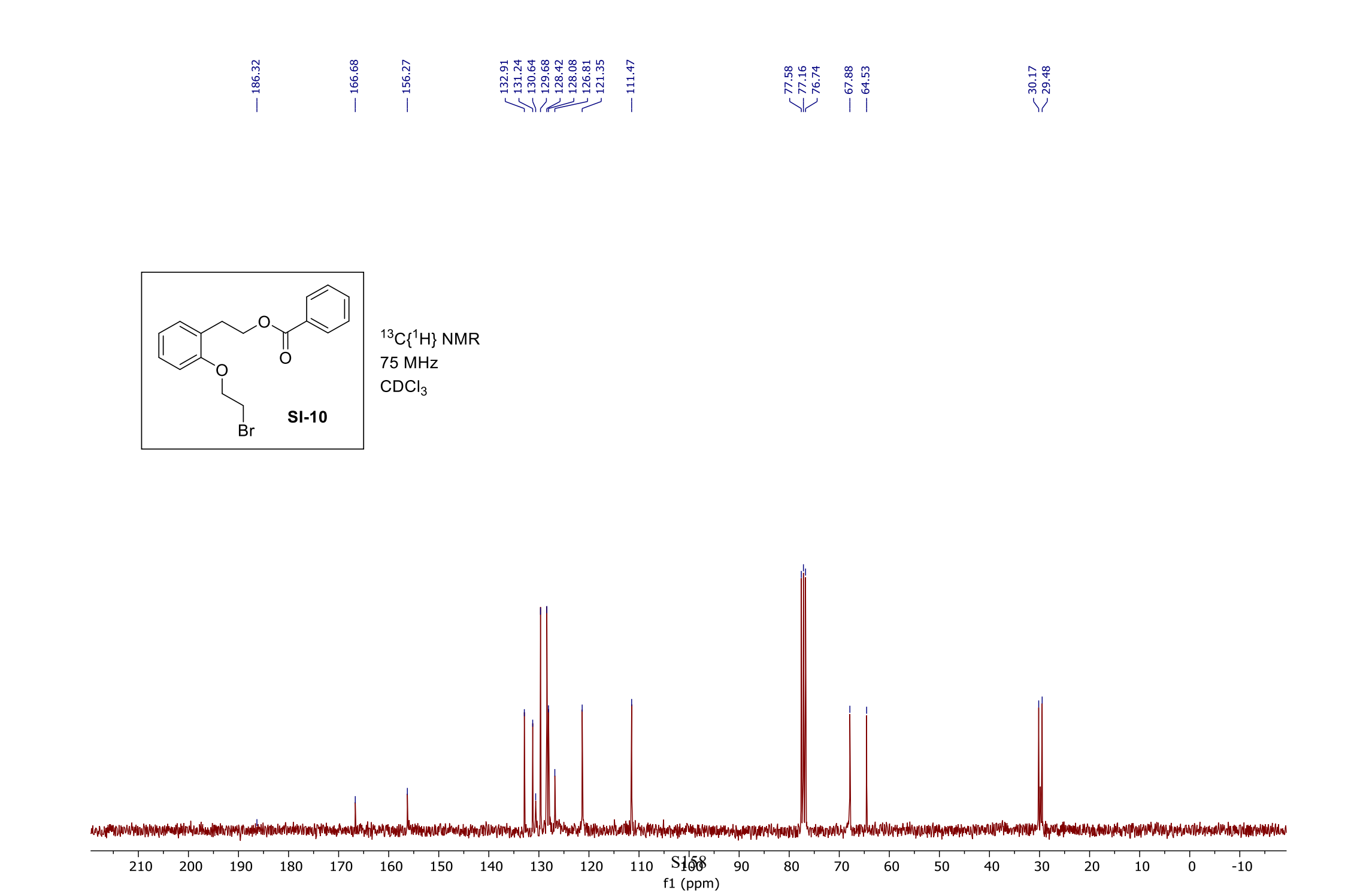

4
1H NMR
300 MHz
CDCl3
7.21
7.21
7.19
7.17
7.16
7.14
3.99
3.97
3.83
3.81
3.67
3.65
2.88
2.86
2.84
2.82
2.70
2.68
2.65
2.63
1.83
1.82
1.82
1.80
1.79
1.78
1.78
1.77
1.76
1.75
1.74
1.47
1.45
5.77
1.03
1.03
1.00
1.00
0.99
3.01
1.03
f1 (ppm)


139.02
129.23
128.33
126.17
80.06
67.94
41.96
31.01
25.63
O
4
$^{13}C\{^{1}H\}$
NMR
75 MHz
$CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.34
7.34
7.32
7.28
7.26
7.26
3.68
3.66
3.63
3.41
2.96
2.94
2.92
O
6
1H NMR
300 MHz
CDCl3
6.65
2.00
2.98
2.04
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


139.01
128.87
128.40
126.23
73.68
58.67
36.25
O
6
13C{1H} NMR
75 MHz
CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.03
8.02
8.02
8.01
8.00
7.99
7.54
7.52
7.45
7.44
7.43
7.42
7.40
7.27
7.26
7.25
7.24
7.24
7.22
7.22
7.20
6.97
6.94
6.85
6.82
4.58
4.56
4.54
4.33
4.31
4.29
3.68
3.66
3.64
3.16
3.14
3.11
O
O
O
Br
SI-10
1H NMR
300 MHz
CDCl3
1.95
1.09
1.88
3.19
0.98
0.95
1.95
1.91
1.89
1.79
f1 (ppm)


186.32
166.68
156.27
132.91
131.24
130.64
129.68
128.42
128.08
126.81
121.35
111.47
77.58
77.16
76.74
67.88
64.53
30.17
29.48
O
O
O
Br
SI-10
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)