**Supporting Information**

# Decarboxylative arylation with diaryliodonium(III) salts: Alternative approach for catalyst-free difluoroenolate coupling to aryldifluoromethyl ketones

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**Table of Contents**

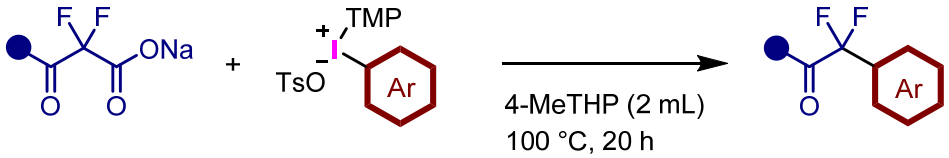
## 1. General Information

**Experiment and materials:** All commercially available reagents were used as received unless otherwise noted. The substrates, α,α-difluoro-β-ketoacid sodium salts and diaryliodonium salts, were synthesized according to the procedures described below. Reaction solvents were dried over MS 4A prior to use. All reactions that required heating were performed using an oil bath or a metal block as a heating source. Flash column chromatography was carried out on Merck Silica gel 60 (230-400 mesh) or aluminium oxide. Preparative thin-layer chromatography was carried out using Merck Millipore PLC Silica gel 60 $F_{254}$ (2 mm, 20×20 cm).

**Analysis:** Melting points were measured using a Büchi B 545 apparatus and are uncorrected. $^{1}H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-AL400 spectrometer ($^{1}H$ NMR: 400 MH, $^{19}F$ NMR: 376 MHz, and $^{13}C$ NMR: 100 MHz), a JEOL JNM-ECZR500 ($^{1}H$ NMR: 500 MHz, $^{19}F$ NMR: 471 MHz, and $^{13}C$ NMR: 126 MHz), or a Bruker Avance IV NEO-500 ($^{1}H$ NMR: 500 MHz, $^{19}F$ NMR: 471 MHz, and $^{13}C$ NMR: 126 MHz) at 25 °C. The chemical shifts in $^{1}H$ NMR spectra were recorded relative to residual solvent peaks ($CDCl_3$: δ 7.26, DMSO-$d_6$: δ 2.50). The chemical shifts in $^{19}F$ NMR spectrum were recorded relative to residual solvent peaks ($PhCF_3$: δ −63.0, 4-fluorotoluene: δ −121.0). The chemical shifts in $^{13}C$ NMR spectrum were recorded relative to residual solvent peaks ($CDCl_3$: δ 77.0, DMSO-$d_6$: δ 39.5). The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimetres ($cm^{-1}$) for strong and structurally important peaks. Analytical TLC was carried out on Merck Silica gel $F_{254}$ plates (0.25 mm). The spots and bands were detected by UV irradiation (254 or 365 nm) or by staining with 3% *p*-anisaldehyde followed by heating. High-resolution mass spectra (HRMS) were obtained using a Thermo Scientific Exactive Plus Orbitrap (Thermo Fisher Scientific, Inc., Waltham, MA, USA).

## 2. Decarboxylative Arylation

### 2-1. General Procedure




**1-Na** 0.3 mmol

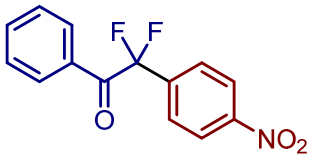
**2-OTs-TMP** 0.20 mmol

**3**

A screw-capped test tube was charged with α,α-difluoro-β-ketoacid sodium salt **1-Na** (0.30 mmol, 1.5 eq) and diaryliodonium salt **2-OTs-TMP** (0.20 mmol), and then 4-MeTHP (2.0 mL) was added to the tube. The mixture was stirred at 100 °C for 20 h using a metal block. Insoluble materials were removed through a silica gel plug eluting with dichloromethane. After concentration of the filtrate under reduced pressure, the residue was purified by column chromatography to afford the corresponding α-aryl-α,α-difluoromethylketone **3**.

### 2-2. Substrate Scope for Decarboxylative Arylation

**2,2-Difluoro-2-(4-nitrophenyl)-1-phenylethan-1-one (3aa)**




The title compound (**3aa**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.7 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.0 mg, 0.20 mmol). $^{19}$F NMR analysis of the crude mixture revealed that **3aa** was afforded in 89% yield. Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 1:20) afforded **3aa** in 85% yield (47.3 mg, 0.171 mmol) as a yellow solid.

**Melting Point:** 85.3–86.1 °C

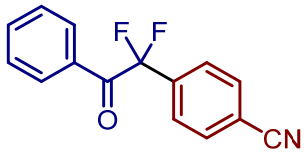
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.50 (dd, *J* = 8.8, 7.6 Hz, 2H) ppm.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ −98.15 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 187.85 (t, *J* = 31.3 Hz), 149.35, 139.11 (t, *J* = 25.1 Hz), 134.80, 131.44, 130.23 (t, *J* = 2.9 Hz), 128.88, 127.25 (t, *J* = 6.2 Hz), 123.84, 116.24 (t, *J* = 255 Hz) ppm.

Spectrum data of **3aa** were matched with the product reported in literature.[S1]

**4-(1,1-Difluoro-2-oxo-2-phenylethyl)benzonitrile (3ab)**




The title compound (**3ab**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.2 mg, 0.30 mmol) and (4-cyanophenyl)(TMP)iodonium tosylate (**2b-OTs-TMP**, 113.7 mg, 0.20 mmol). Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 1:20) afforded **3ab** in 82% yield (42.2 mg, 0.164 mmol) as a colorless oil.

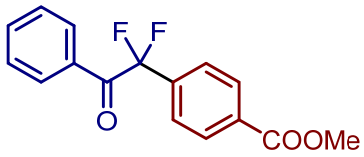
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.58 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 187.92 (t, *J* = 31.7 Hz), 137.43 (t, *J* = 25.1 Hz), 134.74, 132.46, 131.46 (t, *J* = 2.0 Hz), 130.21 (t, *J* = 2.9 Hz), 128.83, 126.70 (t, *J* = 6.2 Hz), 117.75, 116.20 (t, *J* = 254 Hz), 114.90 (t, *J* = 2.1 Hz) ppm.

Spectrum data of **3ab** were matched with the product reported in literature.[S1]

**Methyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)benzoate (3ac)**




The title compound (**3ac**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.6 mg, 0.30 mmol) and (4-methoxycarbonylphenyl)(TMP)iodonium tosylate (**2c-OTs-TMP**, 120.4 mg, 0.20 mmol). Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 1:50) afforded **3ac** in 61% yield (35.3 mg, 0.123 mmol) as a colorless solid.

**Melting Point:** 62.6–63.3 °C

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 3.93 (s, 3H) ppm.

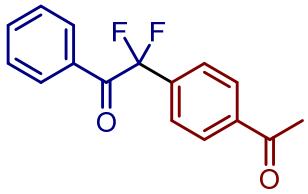
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.40 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 188.37 (t, *J* = 31.4 Hz), 166.07, 137.26 (t, *J* = 24.8 Hz), 134.46, 132.43, 131.76, 130.23 (t, *J* = 3.0 Hz), 129.96, 128.73, 125.86 (t, *J* = 6.0 Hz), 116.53 (t, *J* = 255 Hz), 52.43 ppm.

**IR (KBr):** 3155, 3072, 2953, 2851, 2255, 1939, 1717, 1598, 1580, 1450 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_{16}H_{13}O_3F_2^+$, 291.0827; found, 291.0825.

**2-(4-Acetylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ad)**




The title compound (**3ad**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.9 mg, 0.30 mmol) and (4-acetylphenyl)(TMP)iodonium tosylate (**2d-OTs-TMP**, 114.8 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$,

AcOEt/hexane = 1:20) afforded **3ad** in 70% yield (38.6 mg, 0.141 mmol) as a colorless oil.

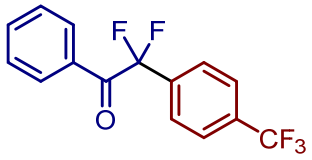
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.04 (d, *J* = 8.0 Hz, 4H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 2.62 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.42 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 197.20, 188.33 (t, *J* = 31.4 Hz), 138.84, 137.30 (t, *J* = 24.8 Hz), 134.50, 131.73, 130.22 (t, *J* = 3.0 Hz), 128.75, 128.61, 126.11 (t, *J* = 5.4 Hz), 116.53 (t, *J* = 255 Hz), 26.74 ppm.

Spectrum data of **3ad** were matched with the product reported in literature.[S1,2]

**2,2-Difluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (3ae)**




The title compound (**3ae**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 67.2 mg, 0.30 mmol) and (4-trifluoromethylphenyl)(TMP)iodonium tosylate (**2e-OTs-TMP**, 122.8 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:30) afforded **3ae** in 67% yield (40.5 mg, 0.135 mmol) as a colorless oil.

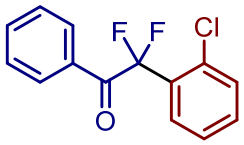
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.75 (s, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −63.34 (s, 3F), −98.21 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 188.28 (t, *J* = 30.8 Hz), 136.66 (t, *J* = 23.1 Hz), 134.59, 132.94 (q, *J* = 33.1 Hz), 131.69, 130.25 (t, *J* = 3.0 Hz), 128.80, 126.39 (t, *J* = 6.0 Hz), 125.79 (q, *J* = 3.5 Hz), 123.51 (q, *J* = 273 Hz), 116.42 (t, *J* = 255 Hz) ppm.

Spectrum data of **3ae** were matched with the product reported in literature.[S3]

**2-(2-Chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (3ad)**




The title compound (**3af**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.9 mg, 0.30 mmol) and (2-chlorophenyl)(TMP)iodonium tosylate (**2f-OTs-TMP**, 115.2 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:99) and then preparative thin layer chromatography ($SiO_2$, AcOEt/hexane = 1:99) afforded **3af** in 36% yield (19.1 mg, 0.0719 mmol) as a colorless oil.

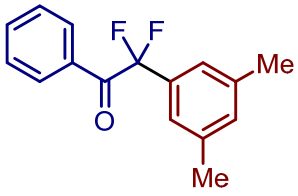
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.08 (d, *J* = 7.4 Hz, 2H), 7.83.781 (m, 1H), 7.62 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.4, 0.9 Hz, 2H), 7.467.41 (m, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −97.76 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 187.81 (t, *J* = 31.3 Hz), 134.09, 132.37, 132.16, 132.00, 131.78, 130.79, 130.03 (t, *J* = 2.8 Hz), 128.61, 127.45 (t, *J* = 8.7 Hz), 126.88, 115.86 (t, *J* = 255.8 Hz) ppm.

Spectrum data of **3af** were matched with the product reported in literature.[S2]

**2-(3,5-Dimethylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ag)**




The title compound (**3ag**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 67.2 mg, 0.30 mmol) and (3,5-dimethylphenyl)(TMP)iodonium tosylate (**2g-OTs-TMP**, 114.1 mg, 0.20 mmol) in toluene at 130 °C. Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:99) and then preparative thin layer chromatography ($SiO_2$, AcOEt/hexane = 1:99) afforded **3ag** in 53% yield

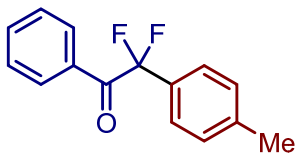
(27.4 mg, 0.105 mmol) as a colorless oil.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.58 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.22 (s, 2H), 7.10 (s, 1H) 2.34 (s, 6H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −97.58 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 189.15 (t, *J* = 31.1 Hz), 138.67, 134.10, 132.98 (t, *J* = 24.8 Hz), 132.59 (t, *J* = 2.1 Hz), 132.24, 130.29 (t, *J* = 2.9 Hz), 128.58, 123.16 (t, *J* = 5.9 Hz), 116.97 (t, *J* = 253.3 Hz), 21.31 ppm.

**2,2-Difluoro-2-(4-methylphenyl)-1-phenylethan-1-one (3ah)**




The title compound (**3ah**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 67.2 mg, 0.30 mmol) and (3,5-dimethylphenyl)(TMP)iodonium tosylate (**2h-OTs-TMP**, 111.3 mg, 0.20 mmol) in toluene at 130 °C. Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:99) and then preparative thin layer chromatography ($SiO_2$, AcOEt/hexane = 1:99) afforded **3ah** in 61% yield (29.9 mg, 0.121 mmol) as a colorless oil.

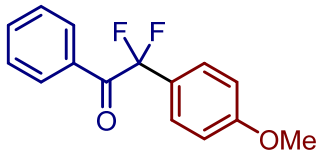
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.58 (tt, *J* = 7.4, 1.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 8.0, 2H), 2.38 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −97.42 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 189.09 (t, *J* = 31.1 Hz), 141.18 (t, *J* = 2.0 Hz), 134.10, 132.21 130.45, 130.26 (t, *J* = 2.8 Hz), 130.05, 129.51, 128.58, 125.53 (t, *J* = 5.9 Hz), 117.04 (t, *J* = 253.3 Hz), 21.34 ppm.

Spectrum data of **3ah** were matched with the product reported in literature.[S1]

**2,2-Difluoro-2-(4-methoxylphenyl)-1-phenylethan-1-one (3ai)**




The title compound (**3xx**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 67.2 mg, 0.30 mmol) and (3,5-dimethylphenyl)(TMP)iodonium tosylate (**2i-OTs-TMP**, 114.5 mg, 0.20 mmol) in toluene at 130 °C. Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:99) and then preparative thin layer chromatography ($SiO_2$, AcOEt/hexane = 1:9) afforded **3ai** in 46% yield (24.3 mg, 0.0927 mmol) as a colorless oil.

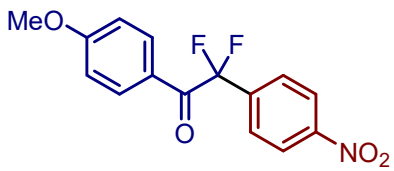
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.58 (tt, *J* = 7.5, 1.6 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.8, 2H), 3.82 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −96.49 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 189.17 (t, *J* = 31.5 Hz), 161.47, 134.08, 132.25, 130.26 (t, *J* = 3.0 Hz), 128.59, 127.23 (t, *J* = 5.9 Hz), 125.17 (t, *J* = 25.6 Hz), 117.04 (t, *J* = 253.0 Hz), 55.35 ppm.

Spectrum data of **3ai** were matched with the product reported in literature.[S1,2,3]

**2,2-Difluoro-1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (3ba)**




The title compound (**3ba**) was synthesized by the general procedure using sodium 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (**1b-Na**, 76.7 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 116.1 mg, 0.20 mmol). Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 3:97) afforded **3ba** in 78% yield (48.1 mg,

0.157 mmol) as a yellow solid.

**Melting Point:** 86.4–87.0 °C

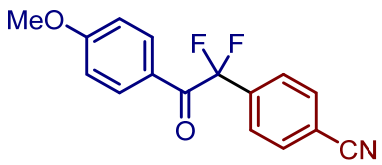
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H) ppm.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ −97.71 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 186.13 (t, *J* = 30.9 Hz), 164.81, 149.30, 139.55 (t, *J* = 25.1 Hz), 132.83 (t, *J* = 3.3 Hz), 127.20 (t, *J* = 6.2 Hz), 124.30 (t, *J* = 2.1 Hz), 123.75, 116.40 (t, *J* = 254 Hz), 114.20, 55.57 ppm.

Spectrum data of **3ba** were matched with the product reported in literature.[S1]

**4-(1,1-Difluoro-2-(4-methoxyphenyl)-2-oxoethyl)benzonitrile (3bb)**




The title compound (**3bb**) was synthesized by the general procedure using sodium 3-(4-(*tert*-butyl)phenyl)-2,2-difluoro-3-oxopropanoate (**1b-Na**, 76.5 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2b-OTs-TMP**, 113.0 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:10) afforded **3bb** in 69% yield (39.2 mg, 0.138 mmol) as a colorless oil.

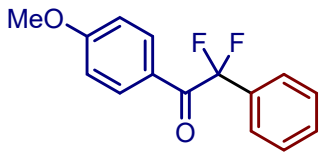
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.05 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.13 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** 186.22 (t, *J* = 30.9 Hz), 164.72, 137.86 (t, *J* = 25.1 Hz), 132.83 (t, *J* = 3.3 Hz), 132.40, 126.67 (t, *J* = 6.2 Hz), 124.26 (t, *J* = 2.1 Hz), 117.81, 116.35 (t, *J* = 254 Hz), 114.74 (t, *J* = 2.1 Hz), 114.15, 55.59 ppm.

Spectrum data of **3bb** were matched with the product reported in literature.[S1]

**2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylethan-1-one (3bj)**




The title compound (**3bf**) was synthesized by the general procedure using sodium 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (**1b-Na**, 75.65 mg, 0.30 mmol) and phenyl(TMP)iodonium tosylate (**2j-OTs-TMP**, 124.6 mg, 0.20 mmol). $^{19}$F NMR analysis of the crude mixture revealed that **3bj** was afforded in 70% yield. After the reaction mixture was concentrated under reduced pressure, hexane was added to the residue. Insoluble material was filtered to partially remove TMP-I. Further purification by preparative thin-layer chromatography ($SiO_2$, AcOEt/hexane = 1:25) afforded **3bj** in 57% yield (29.8 mg, 0.114 mmol) as a colorless oil. The isolated yield was dropped due to the unisolable contamination with decarboxylative protonation product of the starting material.

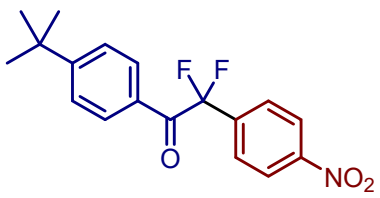
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.95 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.40–7.34 (m, 3H), 6.83 (dd, *J* = 8.8, 2.8 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −97.35 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 187.28 (t, *J* = 30.2 Hz), 164.29, 133.46 (t, *J* = 25.4 Hz), 132.85 (t, *J* = 3.0 Hz), 130.77, 128.75, 125.53 (t, *J* = 6.0 Hz), 124.86, 116.97 (t, *J* = 253 Hz), 113.92, 55.52 ppm.

Spectrum data of **3bj** were matched with the product reported in literature.[S1,2]

**1-(4-(*tert*-Butyl)phenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ca)**



The title compound (**3ca**) was synthesized by the general procedure using sodium 3-(4-(*tert*-butyl)phenyl)-2,2-difluoro-3-oxopropanoate (**1c-Na**, 83.5 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.8 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:30) afforded **3ca** in 77% yield (51.5 mg, 0.154 mmol) as a yellow oil.

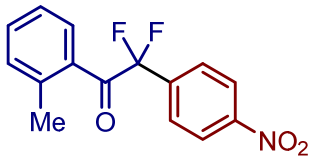
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.33 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 1.33 (s, 9H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.14 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 187.34 (t, *J* = 30.9 Hz), 158.96, 149.30, 139.36 (t, *J* = 25.4 Hz), 130.29 (t, *J* = 2.4 Hz), 128.77, 127.21 (t, *J* = 6.0 Hz), 125.91, 123.84, 116.24 (t, *J* = 257 Hz), 35.31, 30.86 ppm.

Spectrum data of **3ca** were matched with the product reported in literature.[S4]

**2,2-Difluoro-1-(4-methylphenyl)-2-(4-nitrophenyl)ethan-1-one (3da)**




The title compound (**3da**) was synthesized by the general procedure using sodium 2,2-difluoro-3-(2-methylphenyl)-3-oxopropanoate (**1d-Na**, 70.4 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.2 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 3:97, and then $SiO_2$, toluene/hexane = 2:3) afforded **3da** in 72% yield (42.2 mg, 0.145 mmol) as a colorless oil.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.32 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.30 (d, *J* =7.5 Hz, 1H), 7.28 (dd, *J* = 7.5, 7.5 Hz, 1H), 2.38 (s, 3H) ppm.

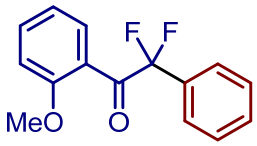
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −99.63 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 191.40 (t, *J* = 30.9 Hz), 149.35, 140.11, 139.21 (t, *J* = 26.6 Hz), 132.77, 132.09, 131.99, 129.23 (t, *J* = 4.9 Hz), 127.28 (t, *J* = 6.0 Hz), 125.55, 123.84, 115.77 (t, *J* = 257 Hz), 20.98 ppm.

**IR (KBr):** 2936, 2864, 1735, 1602, 1530, 1410, 899 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_{15}H_{12}O_3NF_2^+$, 292.0780; found, 292.077

**2,2-Difluoro-1-(2-methoxyphenyl)-2-phenylethan-1-one (3ef)**




The title compound (**3ef**) was synthesized by the general procedure using sodium 2,2-difluoro-3-(2-methoxyphenyl)-3-oxopropanoate (**1e-Na**, 76.0 mg, 0.30 mmol) and phenyl(TMP)iodonium tosylate (**2j-OTs-TMP**, 108.1 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:20) afforded **3ej** in 42% yield (22.0mg, 0.0839 mmol) as a colorless oil.

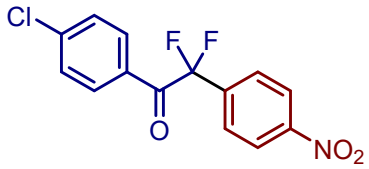
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.49–7.45 (m, 5H), 6.99 (dd, *J* = 7.5, 7.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.66 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −100.59 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 193.42 (t, *J* = 33.2 Hz), 158.14, 133.79, 133.24 (t, *J* = 25.4 Hz), 130.47, 130.00, 128.34, 125.82 (t, *J* = 6.0 Hz), 124.79, 120.38, 116.05 (t, *J* = 254 Hz), 111.47, 55.28 ppm.

Spectrum data of **3ej** were matched with the product reported in literature.[S5]

**1-(4-Chlorophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3fa)**




The title compound (**3fa**) was synthesized by the general procedure using sodium 3-(4-chlorophenyl)-2,2-difluoro-3-oxopropanoate (**1f-Na**, 77.9 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 116.5 mg, 0.20 mmol). Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 1:9) afforded **3fa** in 76% yield (47.1 mg, 0.151 mmol) as a yellow solid.

**Melting Point:** 56.8–57.2 °C

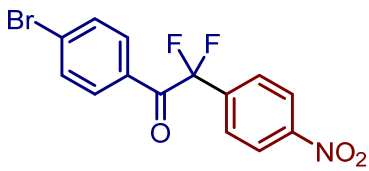
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.33 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.16 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 186.76 (t, *J* = 32.7 Hz), 149.41, 141.64, 138.71 (t, *J* = 24.8 Hz), 131.63 (t, *J* = 3.0 Hz), 129.69, 129.32, 127.27 (t, *J* = 6.0 Hz), 123.88, 116.23 (t, *J* = 257 Hz) ppm.

Spectrum data of **3fa** were matched with the product reported in literature.[S2]

**1-(4-Bromophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ga)**




The title compound (**3ga**) was synthesized by the general procedure using sodium 3-(4-bromophenyl)-2,2-difluoro-3-oxopropanoate (**1g-Na**, 90.6 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.1 mg, 0.20 mmol). Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 1:9) afforded **3ga** in 78% yield (55.9 mg,

0.157 mmol) as a yellow solid.

**Melting Point:** 98.7–99.0 °C

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.33 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H) ppm.

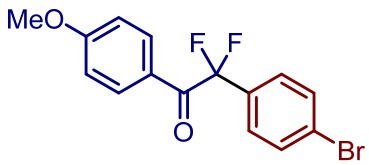
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.21 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 187.00 (t, *J* = 32.1 Hz), 149.42, 138.67 (t, *J* = 24.8 Hz), 132.33, 131.62 (t, *J* = 3.0 Hz), 130.5, 130.09, 127.27 (t, *J* = 6.0 Hz), 123.88, 116.21 (t, *J* = 256 Hz) ppm.

**IR (KBr):** 3086, 2870, 1929, 1794, 1698, 1584, 1346, 1254, 1009 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_{14}H_9O_3BrF_2^+$, 355.9728; found, 355.9729.

**2-(4-Bromophenyl)-2,2-difluoro-1-(4-methoxyphenyl)ethan-1-one (3bk)**




The title compound (**3bk**) was synthesized by the general procedure using sodium 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (**1b-Na**, 552.0 mg, 2.19 mmol) and (4-bromophenyl)(TMP)iodonium tosylate (**2k-OTs-TMP**, 933.7 mg, 1.50 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:30) afforded **3bk** in 70% yield (358.5 mg, 1.05 mmol) as a colorless oil.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H) ppm.

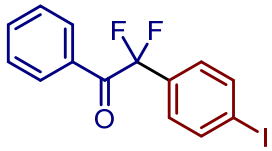
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −97.41 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 186.80 (t, *J* = 30.9 Hz), 164.47, 132.85 (t, *J* = 3.0 Hz), 132.45 (t, *J* = 25.4 Hz), 132.00, 127.35 (t, *J* = 6.0 Hz), 125.41, 124.59, 116.73 (t, *J* = 255 Hz), 114.02, 55.57 ppm.

**IR (KBr):** 2936, 2843, 1698, 1599, 1509, 1269, 1179, 1133, 912, 827 $cm^{-1}$.

**HRMS-DART (m/z):** ([M+H]$^+$) calcd for $C_{15}H_{12}O_2BrF_2^+$, 340.9983; found, 340.9984.

**2,2-difluoro-2-(4-iodophenyl)-1-phenylethan-1-one (3al)**




The title compound (**3al**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.4 mg, 0.30 mmol) and (4-iodophenyl)(TMP)iodonium tosylate (**2l-OTs-TMP**, 134.1 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:30) afforded **3al** in 71% yield (51.2 mg, 0.143 mmol) as a colorless solid.

**Melting Point:** 67.4–68.5 °C

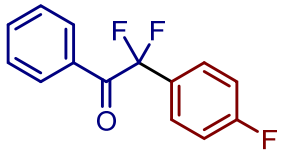
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.03 (d, $J$ = 8.0 Hz, 2H), 7.82 (d, $J$ = 8.0 Hz, 2H), 7.61 (t, $J$ = 7.5 Hz, 1H), 7.46 (t, $J$ = 7.8 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −98.23 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 188.40 (t, $J$ = 31.4 Hz), 137.97, 134.40, 132.64 (t, $J$ = 25.4 Hz), 131.78, 130.21, 128.70, 127.35 (t, $J$ = 6.0 Hz), 116.69 (t, $J$ = 254.5 Hz), 97.69 ppm.

Spectrum data of **3al** were matched with the product reported in literature.[S2]

**2,2-Difluoro-2-(4-fluorophenyl)-1-phenylethan-1-one (3am)**




The title compound (**3am**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 67.2 mg, 0.30 mmol) and (4-fluorophenyl)(TMP)iodonium tosylate (**2m-OTs-TMP**, 112.0 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:99) and then preparative thin layer chromatography ($SiO_2$, AcOEt/hexane =

1:99) afforded **3am** in 72% yield (36.1 mg, 0.144 mmol) as a yellow oil.

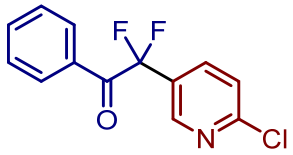
**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 7.15 Hz, 2H), 7.637.59 (m, 3H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H) ppm.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ −96.82 (s, 2F), −109.29 (s, 1F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 188.75 (t, *J* = 31.4 Hz), 164.13 (d, *J* = 251.7 Hz), 134.34, 131.98, 130.28 (t, *J* = 3.1 Hz), 129.11 (dt, *J* = 26.3, 3.2 Hz), 128.71, 128.01 (dt, *J* = 8.9, 6.0 Hz), 116.65 (t, *J* = 254.3 Hz), 116.0 (d, *J* = 22.3 Hz) ppm.

Spectrum data of **3am** were matched with the product reported in literature.[S3]

**2-(6-Chloropyridin-3-yl)-2,2-difluoro-1-phenylethan-1-one (3an)**




The title compound (**3an**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 68.1 mg, 0.31 mmol) and (6-chloropyridin-3-yl)(TMP)iodonium tosylate (**2n-OTs-TMP**, 116.0 mg, 0.20 mmol). Purification by column chromatography ($Al_2O_3$, AcOEt/hexane = 1:10) afforded **3an** in 67% yield (35.2 mg, 0.133 mmol) as a colorless oil.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.62 (d, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 7.83 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H) ppm.

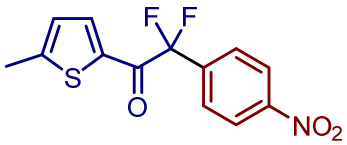
**$^{19}$F NMR (376 MHz, $CDCl_3$):** δ −97.98 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 187.74 (t, *J* = 31.7 Hz), 154.08, 147.40 (t, *J* = 7.0 Hz), 136.65 (t, *J* = 5.8 Hz), 134.84, 131.30 (t, *J* = 2.5 Hz), 130.26 (t, *J* = 3.3 Hz), 128.88, 127.96 (t, *J* = 25.6 Hz), 124.23, 116.19 (t, *J* = 255 Hz) ppm.

**IR (KBr):** 3584, 3156, 3070, 1595, 1466, 1377, 1249, 1099, 907 $cm^{-1}$.

**HRMS-DART (m/z):** ([M+H]$^+$) calcd for $C_{13}H_9ONClF_2^+$, 268.0335; found, 268.0335.

**2,2-Difluoro-1-(5-methylthiophen-2-yl)-2-(4-nitrophenyl)ethan-1-one (3ha)**




The title compound (**3ha**) was synthesized by the general procedure using sodium 2,2-difluoro-3-(5-methylthiophen-2-yl)-3-oxopropanoate (**1h-Na**, 73.6 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.2 mg, 0.20 mmol). Purification by column chromatography ($SiO_2$, AcOEt/hexane = 3:97, and then $SiO_2$, $Et_2O$/hexane = 1:5) afforded **3ha** in 61% yield (36.4 mg, 0.122 mmol) as a yellow oil.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 4.3 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 4.3 Hz, 1H), 2.57 (s, 3H) ppm.

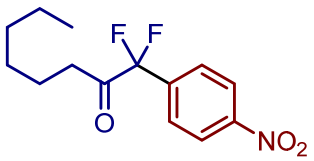
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −99.79 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 180.44 (t, *J* = 32.1 Hz), 154.17, 149.33, 139.12 (t, *J* = 26.0 Hz), 137.03 (t, *J* = 4.9 Hz), 135.26 (t, *J* = 2.4 Hz), 127.93, 127.22 (t, *J* = 5.9 Hz), 123.81, 115.77 (t, *J* = 256 Hz), 16.12 ppm.

**IR (KBr):** 3119, 2923, 1667, 1530, 1441, 1353, 1255, 1066 cm$^{-1}$.

**HRMS-DART (m/z):** ([M+H]$^+$) calcd for $C_{13}H_{10}O_3NF_2S^+$, 298.0344; found, 298.0343.

**1,1-Difluoro-1-(4-nitrophenyl)octan-2-one (3ia)**




The title compound (**3ia**) was synthesized by the general procedure using sodium 2,2-difluoro-3-oxononanoate (**1i-Na**, 69.0 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-**

**OTs-TMP**, 117.5 mg, 0.20 mmol). $^{19}$F NMR analysis of the crude mixture revealed that **3ia** was afforded in 40% yield. Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:10, $Al_2O_3$, AcOEt/hexane = 1:20) afforded **3ia** in 23% yield (13.0 mg, 0.046 mmol) as a yellow oil. The isolated yield was dropped due to the unisolable contamination with iodotrimethoxybenzene.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 1.63–1.56 (m, 2H), 1.30–1.19 (m, 6H), 0.89–0.81 (m, 3H) ppm.

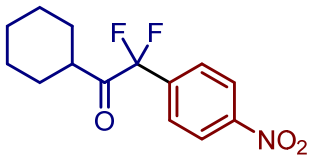
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −106.43 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 199.27 (t, *J* = 31.4 Hz), 149.44, 138.26 (t, *J* = 25.4 Hz), 127.13 (t, *J* = 6.7 Hz), 123.84, 114.81 (t, *J* = 256 Hz), 36.47, 31.35, 28.46, 22.59, 22.36, 13.94 ppm.

**IR (KBr):** 2926, 1742, 1530, 1351, 1265, 913, 747 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_{14}H_{18}O_3NF_2^+$, 286.1249; found, 286.1247.

**1-Cyclohexyl-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ja)**




The title compound (**3ja**) was synthesized by the general procedure using sodium 3-cyclohexyl-2,2-difluoro-3-oxopropanoate (**1j-Na**, 67.7 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.6 mg, 0.20 mmol). $^{19}$F NMR analysis of the crude mixture revealed that **3ja** was afforded in 36% yield. Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:50) afforded **3ja** in 28% yield (15.6 mg, 0.056 mmol) as a colorless oil. The isolated yield was dropped due to the unisolable contamination with iodotrimethoxybenzene.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.31 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 2.98–2.92 (m, 1H), 1.82–1.75 (m, 4H), 1.71–1.67 (m, 1H), 1.43–1.19 (m, 5H) ppm.

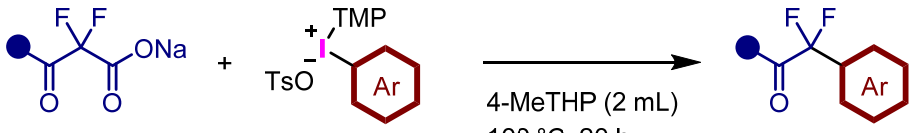
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −106.43 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 202.02 (t, $J$ = 30.2 Hz), 149.37, 138.58 (t, $J$ = 25.4 Hz), 127.16 (t, $J$ = 6.0 Hz), 123.80, 115.04 (t, $J$ = 257 Hz), 45.22, 28.46, 25.37, 25.25 ppm.

**IR (KBr):** 2923, 1734, 1532, 1351, 1273, 1124, 1076, 856 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_{14}H_{16}O_3NF_2^+$, 284.1093; found, 284.1090.

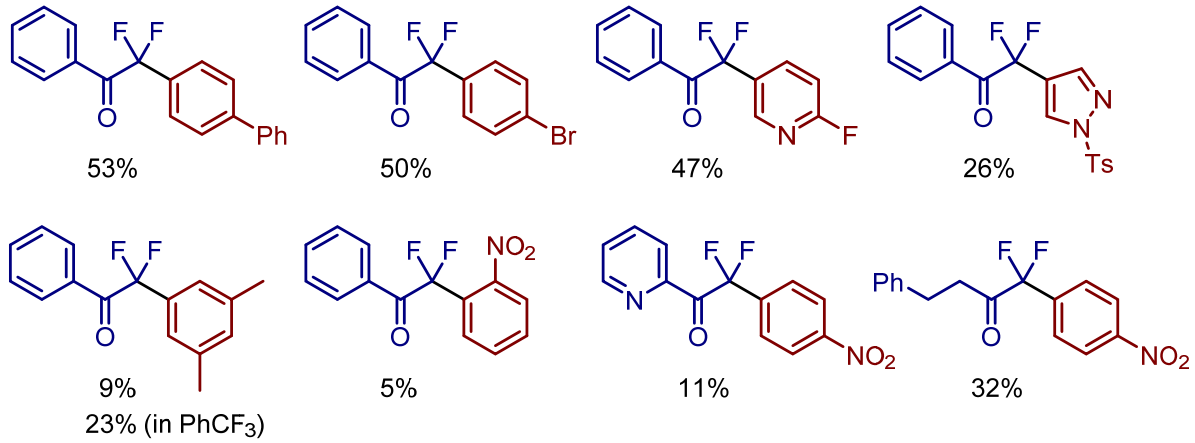
## 2-3. Additional Examples for Decarboxylative Arylation Products




**1-Na**
0.3 mmol

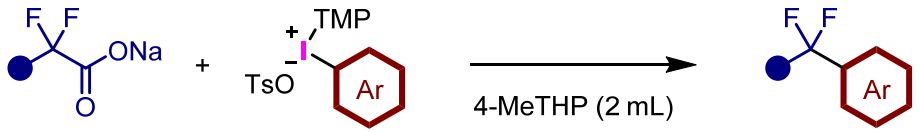
**2-OTs-TMP**
0.20 mmol

**3**



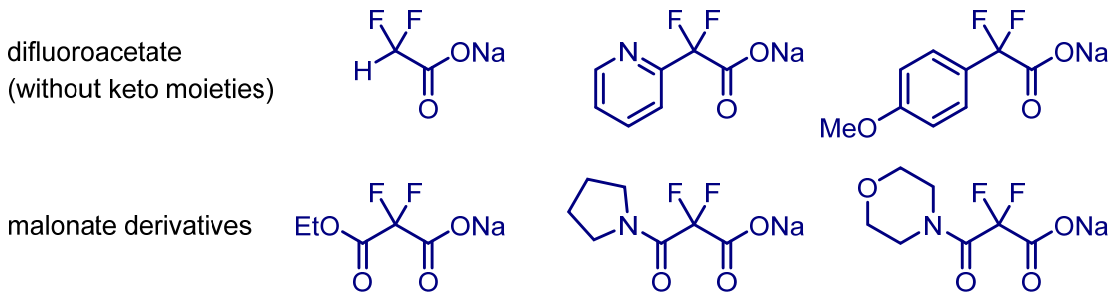

## 2-4. Examination with Other Difluoroacetate Derivatives

In addition to the α,α-difluoro-β-ketoacid sodium salts, we have examined the other types of difluoroacetate derivatives, such as difluoroacetate, aryldifluoroacetates, and malonate derivatives without β-keto moieties, as shown in below. The corresponding decarboxylative arylation compounds could not be afforded.




**2-OTs-TMP**
0.20 mmol

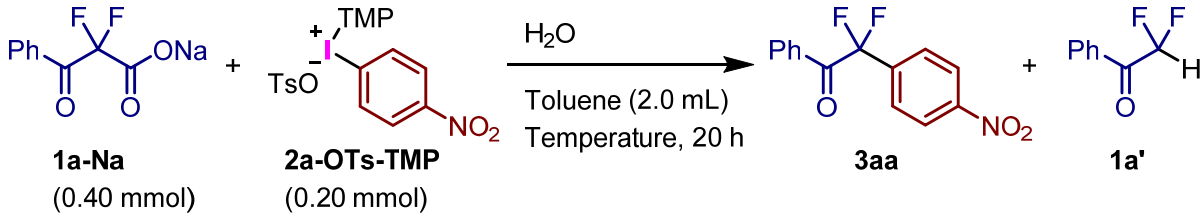
not detected



## 3. Mechanistic Studies for Decarboxylative Arylation with 2a-OTs-TMP

### 3-1. Investigation for Decarboxylative Protonation of 1a-Na (Fig. S1)

We investigated the decarboxylative arylation using **1a-Na** with **2a-OTs-TMP** in the presence of various amounts of water at 70 or 100 °C. The yields of decarboxylative protonation product (**1a′**) were increased with the addition of water at elevated reaction temperature.




| Temperature | Amount of $H_2O$ | Yield of **3aa** [a] | Ammoun of **1a'** | Yield of **1a'** [b] |
|---|---|---|---|---|
| 70 °C | 0 eq | 34% | 0.012 mmol | 3% |
| | 1 eq | 40% | 0.052 mmol | 13% |
| | 10 eq | 34% | 0.148 mmol | 37% |
| 100 °C | 0 eq | 77% | 0.154 mmol | 39% |
| | 1 eq | 47% | 0.171 mmol | 43% |
| | 10 eq | 22% | 0.179 mmol | 45% |

[a] $^{19}F$ NMR yield based on **2a-OTs-TMP** (0.20 mmol).
[b] $^{19}F$ NMR yield based on **1a-Na** (0.40 mmol).

**Fig. S1.** Investigation for decarboxylative protonation of **1a-Na**.

### 3-2. Preparation of Plausible Intermediate 1a2a-TMP (Fig. S2)

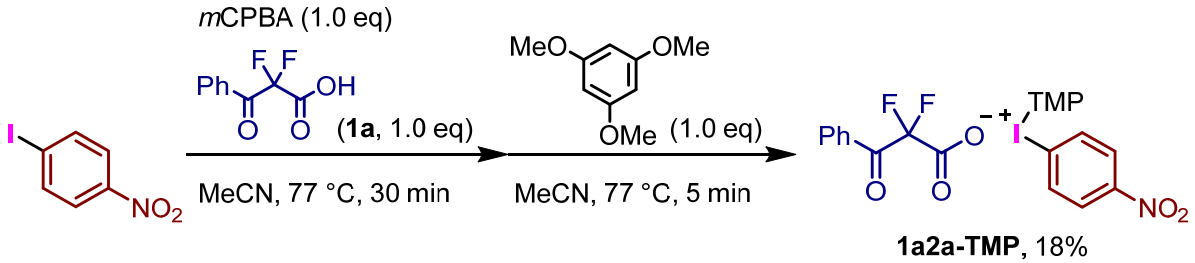
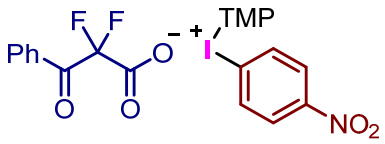



**Fig. S2.** Preparation of Plausible Intermediate **1a2a-TMP**.

**1a2a-TMP** was prepared according to the modified procedure previously described.[S6] 1-Iodo-4-nitrobenzene (496.8 mg, 2.00 mmol) was dissolved in MeCN (10 mL), and 2,2-difluoro-3-oxo-3-phenylpropanoic acid (348.5 mg, 2.02 mmol) and *m*CPBA (497.3 mg, 2.02 mmol) were added in this order. After attaching a reflux condenser, the reaction mixture was stirred at 77 °C for 30 min using an oil bath. 1,3,5-Trimethoxybenzene (340.4 mg, 2.02 mmol) was added to the reaction mixture, which was stirred at 77 °C for additional 5 min using an oil bath. After cooling to room temperature, the volatiles were removed under reduced pressure. Addition of a mix solvent of diethyl ether and MeOH (20:1) and stirring at room temperature generated a precipitant, which was collected by vacuum filtration and was washed with diethyl ether. Drying under vacuum afforded the corresponding TMP-iodonium salt **1a2a-TMP** in 18% yield (222.9 mg, 0.36 mmol) as a yellow solid.

**(4-Nitrophenyl)(TMP)iodonium 2,2-difluoro-3-oxo-3-phenylpropanoate (1a2a-TMP)**




**Melting Point:** 113.1–114.9 °C

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 8.20 (d, $J$ = 7.8 Hz, 2H), 8.12 (d, $J$ = 7.8 Hz, 2H), 7.97 (d, $J$ = 7.2 Hz, 2H), 7.65 (t, $J$ = 7.0 Hz, 1H), 7.51 (t, $J$ = 7.2 Hz, 2H), 6.48 (s, 2H), 3.94 (s, 6H), 3.83 (s, 3H) ppm.

**$^{19}$F NMR (376 MHz, DMSO-$d_6$):** δ −107.19 (s, 2F) ppm.

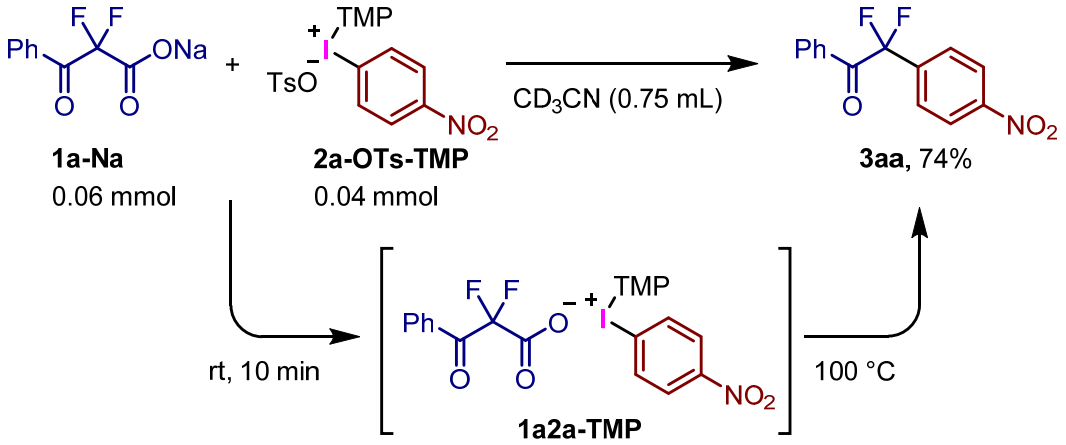
**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 189.29 (t, $J$ = 27.2 Hz), 166.33, 162.74 (t, $J$ = 24.3 Hz), 159.46, 148.90, 135.29, 133.82, 132.42, 129.11, 128.54, 125.85, 123.17, 111.07 (t, $J$ = 262 Hz), 92.10, 88.10, 57.33, 56.15 ppm.

**IR (KBr):** 3100, 2948, 1655, 1579, 1342, 1117, 847 cm$^{-1}$.

**HRMS-DART (m/z):** ([M−carboxylate]$^+$) calcd for $C_{15}H_{15}O_5NI^+$, 415.9989; found, 415.9986:

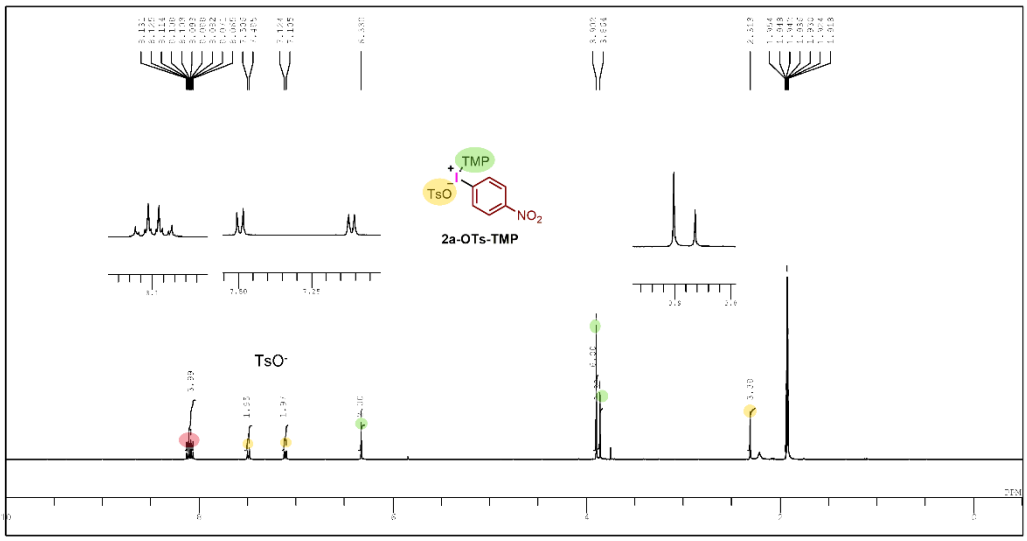
([M−diaryliodonium]$^{-}$) calcd for $C_{14}H_9O_3NF_2^{+}$, 199.0201; found, 199.0215.

### 3-3. NMR Experiment for Decarboxylative Arylation with 2a-OTs-TMP (Figure 3b)

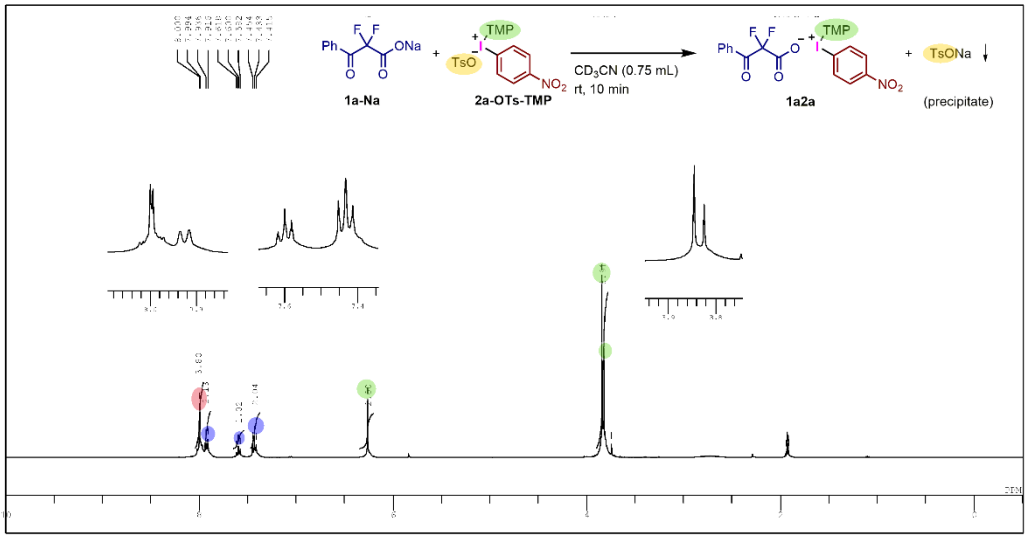



A well-dried NMR tube with a J. Young valve was charged with sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 14.4 mg, 0.06 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 24.8 mg, 0.04 mmol), and $CD_3CN$ (0.75 mL) and $PhCF_3$ (internal standard for $^{19}F$ NMR, 6.20 mg, 0.04 mmol) were added. After stored at room temperature for 10 minutes, $^{1}H$ NMR analysis of the reaction mixture indicated the consumption of **2a-OTs-TMP** and the generation of **1a2a-TMP** (Figure S1). The reaction mixture was stored at 100 °C using an oil bath and was monitored by $^{19}F$ NMR. The yield achieved to 74% in 3 h and did not change even after 20 h (Fig. S3). The reaction of **1a-Na** with **2a-OTs-TMP** in MeCN according to the general procedure afforded **3aa** in 67% yield as shown in Table 1 (entry 10), whereas the NMR monitoring using $CD_3CN$ resulted in 74% yield. The NMR experiments were carried out on a small scale (0.04 mmol of TMP-iodonium salt) under the diluted conditions (in 0.75 mL of solvent, 0.053 M), and the yield was directly measured by $^{19}F$ NMR spectroscopy. On the other hand, the reaction described in Table 1 was according to the general procedure (0.20 mmol of TMP-iodonium salt in 2.0 mL solvent, 0.10 M, using a screw-capped test tube) and the reaction mixture was filtered through a silica gel plug prior to analysis by $^{19}F$ NMR spectroscopy. These changings presumably caused the difference in these yields.

a)




b)




c)

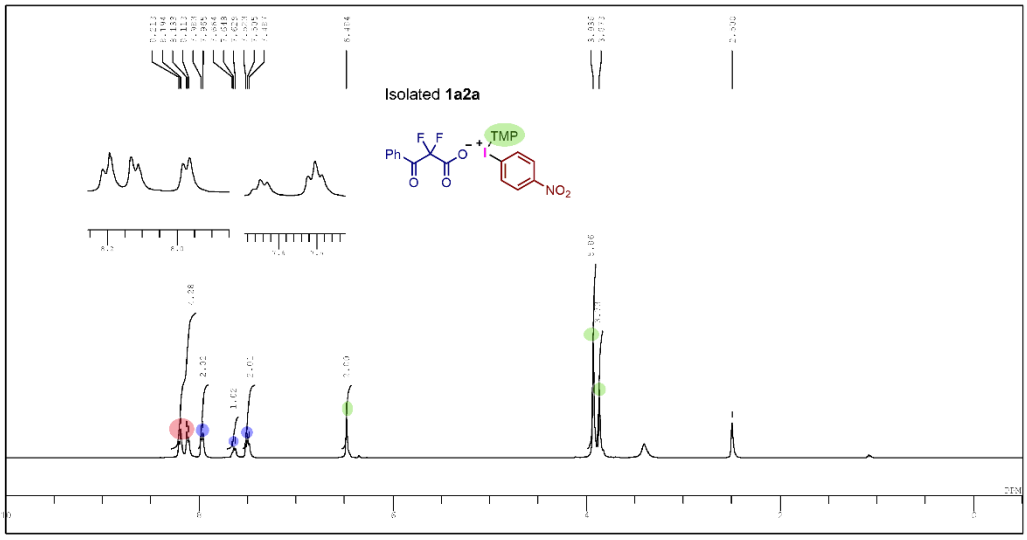
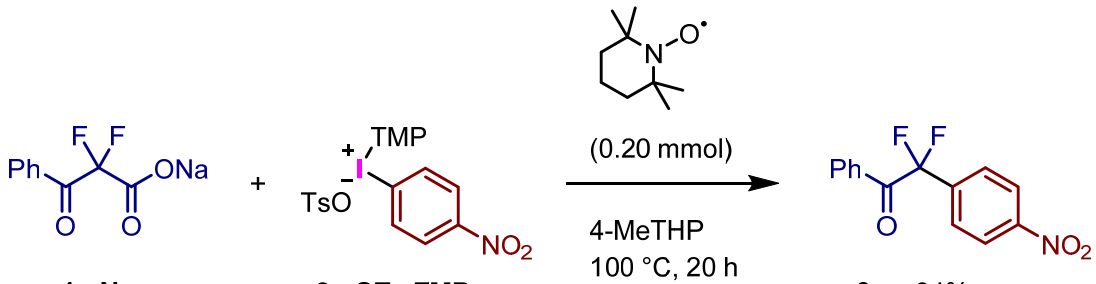



**Fig. S3.** a) $^{1}$H NMR spectrum of **2a-OTs-TMP** in $CD_3CN$. b) $^{1}$H NMR spectrum of in situ generated **1a2a-TMP** in $CD_3CN$. c) $^{1}$H NMR spectrum of isolated **1a2a-TMP** in DMSO-$d_6$.

| Time (h) | Yield of **3aa** |
|---|---|
| 0 | 0% |
| 0.25 | 63% |
| 0.5 | 68% |
| 1 | 72% |
| 3 | 74% |
| 5 | 74% |
| 10 | 73% |
| 20 | 74% |


**Fig. S4.** Reaction profile of **1a-Na** with **2a-OTs-TMP** for generation of **3aa**

### 3-3. Decarboxylative Arylation in the Presence of TEMPO (Fig. 3c)




**1a-Na**
0.30 mmol

**2a-OTs-TMP**
0.20 mmol

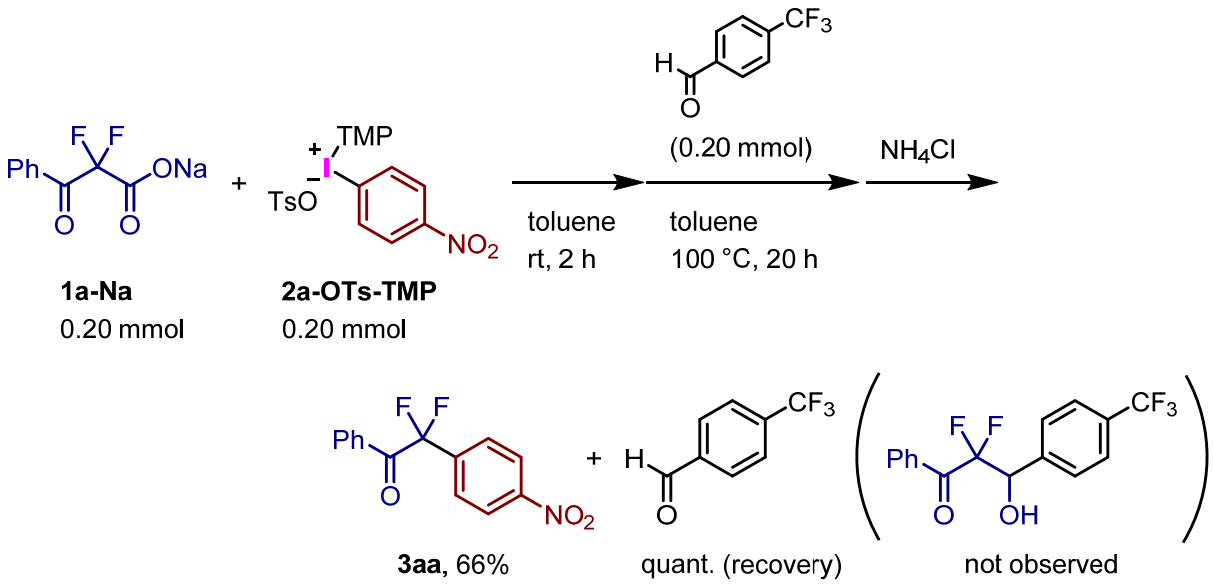
**3aa**, 84%

The reaction of **1a-Na** and **2a-OTs-TMP** in the presence of TEMPO produced **3aa** in 84% yield, which was comparable yield to that without TEMPO (89%). These results indicate that the present reaction does not involve radical species generated by Hunsdiecker-type decarboxylation and/or single-electron-transfer (SET) process.

**Procedure.** A screw-capped test tube was charged with sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 66.7 mg, 0.30 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.0 mg, 0.20 mmol), and then 4-MeTHP (2.0 mL) was added to the tube. After the addition of TEMPO (31.2 mg, 0.20 mmol), the mixture was stirred at 100 °C for 20 h using a metal block. Insoluble materials were removed through silica gel plug eluting with

dichloromethane, and then the filtrate was concentrated under reduced pressure. $^{19}F$ NMR analysis of the crude mixture revealed that **3aa** was afforded in 84% yield.

### 3-4. Decarboxylative Arylation in the Presence of Aldehyde (Fig. 3d)

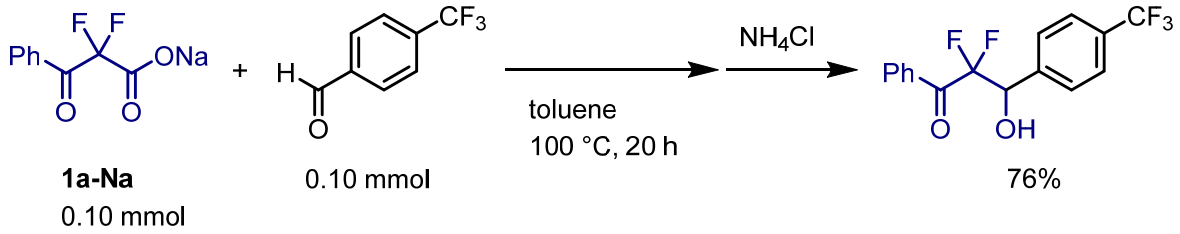



The reaction of **1a-Na** and **2a-OTs-TMP** in the presence of 4-(trifluoromethyl)benzaldehyde produced **3aa** in 66% yield, wherein β-hydroxy ketone via decarboxylative aldol reaction of **1a-Na** with 4-(trifluoromethyl)benzaldehyde was not observed. These results suggest that the present reaction proceeds intramolecularly via ligand coupling of iodonium difluoroenolate salts rather than the intermolecular reaction of free-difluoroenolate, such as sodium difluoroenolate, with diaryliodonium salts.

**Procedure.** A screw-capped test tube was charged with sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 44.4 mg, 0.20 mmol) and (4-nitrophenyl)(TMP)iodonium tosylate (**2a-OTs-TMP**, 118.0 mg, 0.20 mmol), and then toluene (2.0 mL) was added to the tube. After stirring at room temperature for 2 h, 4-(trifluoromethyl)benzaldehyde (34.8 mg, 0.20 mmol) dissolved in toluene (0.50 mL) was added to the tube. The mixture was stirred at 100 °C for 20 h using an oil bath. After cooling to room temperature, the reaction was quenched with a saturated $NH_4Cl$ aqueous solution (1.0 mL). The organic layer was separated, and the aqueous

layer was extracted with diethyl ether (2 × 1 mL). The combined organic solution was washed with brine (2 mL) and was dried over $MgSO_4$. After filtration, PhF (19 μL, 0.20 mmol) was added to the filtrate. $^{19}F$ NMR analysis of the crude mixture revealed that **3aa** was afforded in 66% yield and 4-(trifluoromethyl)benzaldehyde was quantitatively recovered.

### 3-5. Decarboxylative Aldol Reaction of 1a-Na with Aldehyde (Fig. 3d)




**1a-Na**
0.10 mmol

0.10 mmol

76%

**1a-Na** underwent decarboxylative aldol reaction with 4-(trifluoromethyl)benzaldehyde even in the absence of additive to afford the corresponding β-hydroxy ketone in 76% yield.

**Procedure.** In a screw-capped test tube, sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 22.2 mg, 0.10 mmol) was dissolved in toluene (1.0 mL), and then 4-(trifluoromethyl)benzaldehyde (17.4 mg, 0.10 mmol) dissolved in toluene (0.25 mL) was added to the tube. The mixture was stirred at 100 °C for 20 h using an oil bath. After cooling to room temperature, the reaction was quenched with a saturated $NH_4Cl$ aqueous solution (1.0 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 1 mL). The combined organic solution was washed with brine (2 mL) and was dried over $MgSO_4$. After filtration, PhF (19 μL, 0.20 mmol) was added to the filtrate. $^{19}F$ NMR analysis of the crude mixture revealed that β-hydroxy ketone was afforded in 76% yield.

## 4. Introduction of Electron-Rich Aryl Group

### 4-1. NMR Experiment for Decarboxylative Arylation with 2x-OTs-TMP (Fig. S5)

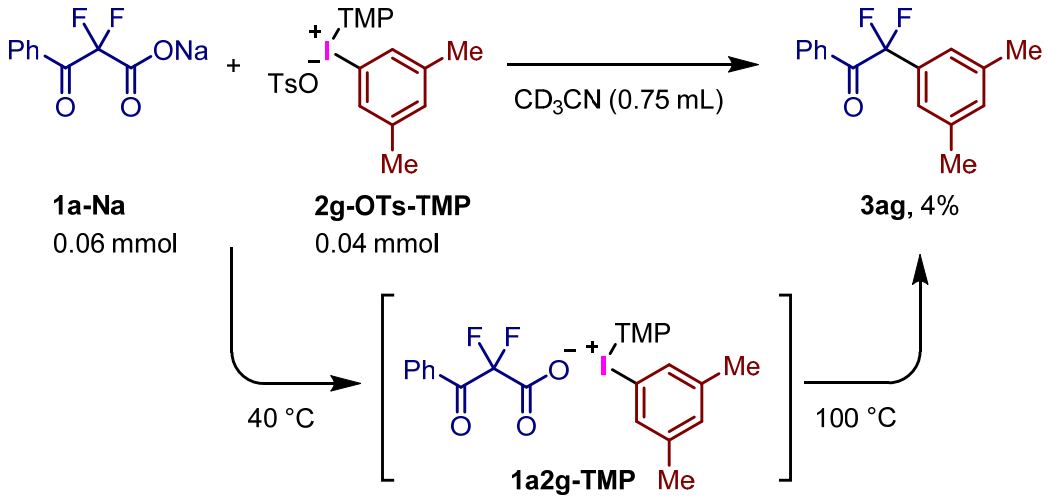
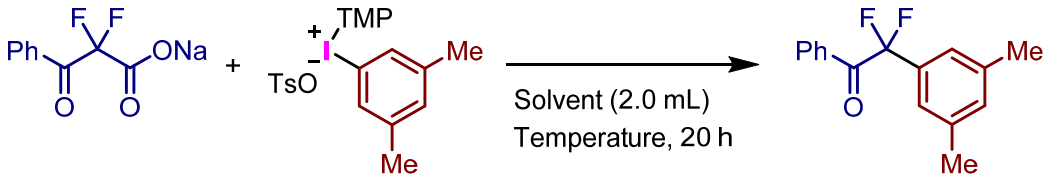



**Fig. S5.** NMR Experiment for Decarboxylative Arylation with **2a-OTs-TMP**.

The reaction of **1a-Na** with **2g-OTs-TMP** in $CD_3CN$ at room temperature was monitored by NMR spectroscopy in the similar manner as **2a-OTs-TMP**. In this case, the ligand exchange requires slight heating at 40 °C, and the following decarboxylative ligand coupling mostly did not proceed at 100 °C presumably due to the low electrophilicity of xylyl group.

### 4-2. Optimization of Reaction Conditions Using 2g-OTs-TMP (Fig. S6)

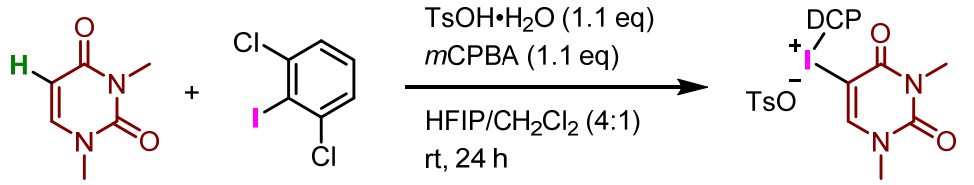



| Solvent | Temperature | NMR Yield |
|---|---|---|
| 4-MeTHP | 100 °C | 11% |
| Octafluorotoluene | 100 °C | 12% |
| $PhCF_3$ | 100 °C | 37% |
| Toluene | 130 °C | 53% (isol.) |

**Fig. S6.** Optimization for Decarboxylative Arylation with **2g-OTs-TMP**.

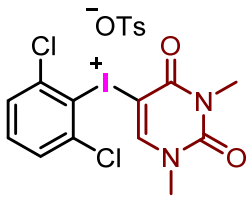
## 5. Functionalization of Dimethyluracil

### 5-1. Preparation of Dimethyluracil-Iodonium Salts




The uracil-iodonium salts were prepared according to the modified procedure previously described.[S7] *N*,*N*-Dimethyluracil (364.4 mg, 2.61 mmol) and 2,6-dichloroiodobenzene (802.9 mg, 2.94 mmol) were dissolved in a mix solvent of HFIP (8.0 mL) and dichloromethane (2.0 mL), and *p*-toluenesulfonic acid (551.6 mg, 2.90 mmol) and *m*-CPBA (714.9 mg, 2.90 mmol) were added in this order. The mixture was stirred at room temperature for 24 h, and then the volatiles were removed under reduced pressure. Addition of a mix solvent of diethyl ether and MeOH (20:1) and stirring at room temperature generated a precipitant, which was collected by vacuum filtration and was washed with diethyl ether. Drying under vacuum afforded the corresponding uracil(DCP)iodonium tosylate **2o-OTs-DCP** in 72% yield (1.096 g, 1.88 mmol) as a colorless solid.

**(*N*,*N*-Dimethyluracil-5-yl)(DCP)iodonium tosylate (2o-OTs-DCP)**

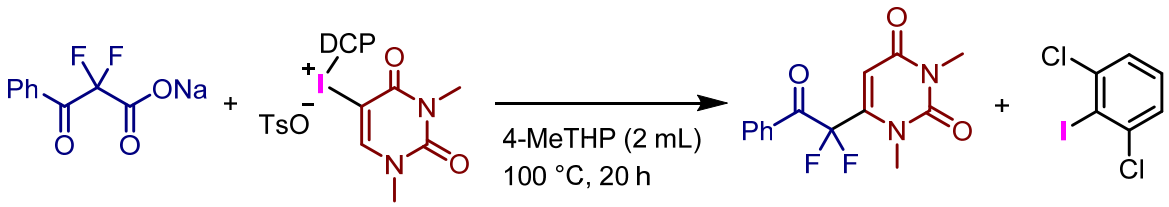



**$^1$H NMR (400 MHz, $CD_3OD$):** δ 9.01 (s, 1H), 7.72–7.63 (m, 5H), 7.24 (d, *J* = 7.8 Hz, 2H), 3.50 (s, 3H), 3.30 (s, 3H), 2.39 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, $CD_3OD$):** δ 160.39, 156.77, 152.21, 143.49, 141.73, 141.23, 136.51, 130.02, 129.83, 126.91, 122.46, 90.02, 38.31, 29.74, 21.30 ppm.

Spectrum data of **2o-OTs-DCP** were matched with the product reported in literature.[S7]

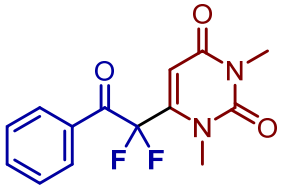
### 5-2. Decarboxylative Arylation Using Dimethyluracil-Iodonium Salts




| **1a-Na** | **2o-OTs-DCP** | **3ao** | recovery |
|---|---|---|---|
| 0.30 mmol | 0.20 mmol | 65% | 64% |

A screw-capped test tube was charged with sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a-Na**, 67.2 mg, 0.30 mmol) and dimethyluracil(DCP)iodonium tosylate (**2o-OTs-DCP**, 117.6 mg, 0.20 mmol), and then 4-MeTHP (2.0 mL) was added to the tube. The mixture was stirred at 100 °C for 20 h using a metal block. Insoluble materials were removed through silica gel plug eluting with dichloromethane. After concentration of the filtrate, the residue was purified by column chromatography ($SiO_2$, AcOEt/hexane = 1:2) to afford the corresponding difluoromethylketone **3ao** in 65% yield (38.3 mg, 0.130 mmol) as a colorless oil along with 2,6-dichloroiodobenzene (DCP-I) in 64% yield (35.1 mg, 0.129 mmol).

### 6-(1,1-Difluoro-2-oxo-2-phenylethyl)-*N*,*N*-dimethyluracil (3ao)




**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, $J$ = 7.6 Hz, 2H), 7.74 (t, $J$ = 7.6 Hz, 1H), 7.57 (t, $J$ = 8.0 Hz, 2H), 6.23 (s, 1H), 3.38 (s, 3H), 3.29 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −99.39 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 186.00 (t, *J* = 30.1 Hz), 161.58, 151.98, 144.85 (t, *J* = 26.0 Hz), 135.69, 130.45, 130.37 (t, *J* = 2.9 Hz), 129.19, 113.48 (t, *J* = 259 Hz), 102.55 (t, *J* = 9.1 Hz), 33.48 (t, *J* = 3.7 Hz), 28.31 ppm.

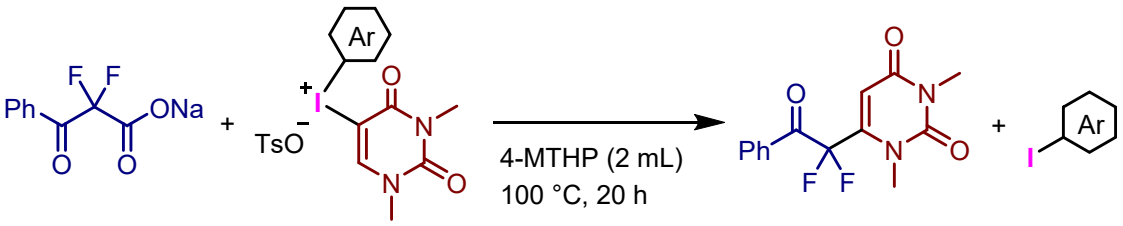
**IR (KBr):** 2965, 1713, 1677, 1448, 1370, 1276, 1215, 1093, 759 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_{14}H_{13}O_3N_2F_2^+$, 295.0889; found, 295.0887.

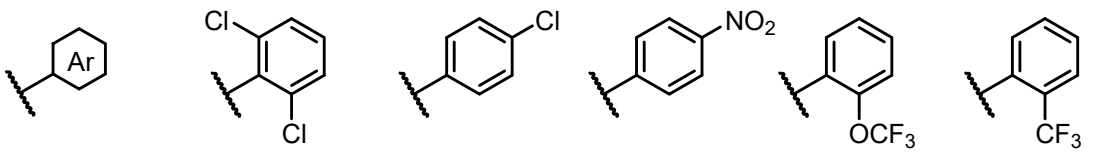
The identification of **3ao** was referred to the similar compound reported in literature.[S8]

### 5-3. Reaction of Dimethyluracil-Iodonium Salts with Various Dummy Ligands

We examined the decarboxylative arylation using dimethyluracil-iodonium tosylates bearing various dummy aryl ligands as shown in below. In all cases, the bond formation proceeded selectively with the dimethyluracil group to afford **3ao**. Electron-deficient aryl groups provided the promising results. Among these iodonium salts, the use of dimethyluracil(DCP)iodonium tosylates resulted in 65% yield of the desired products along with 64% yield of 2,6-dichloroiodobenzene. In the case of 4-chlorophenyl and 2-trifluoromethoxyphenyl groups, the corresponding iodoarenes were recovered in low yields due to their high volatilities.



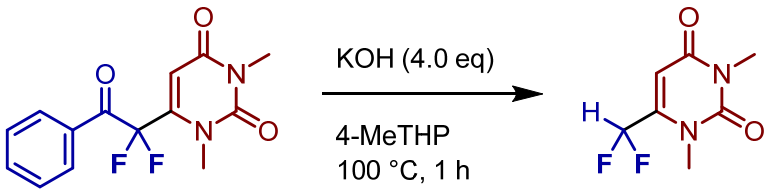

**1a-Na** 0.30 mmol | **2o-OTs-Ar** 0.20 mmol | **3ao** | recovery




| | | | | | |
|---|---|---|---|---|---|
| yield of **3ai** | 65% | 65% | 54% | 54% | 34% |
| recovery of I-Ar | 64% | 32% | 86% | not detected | not detected |

## 6. Further Transformation of α-Aryl-α,α-difluoromethyl Ketone

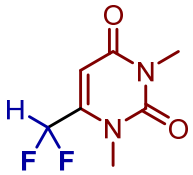
### 6-1. Difluoromethylation




**3ao** **4o**, 64%

Uracil derivative **3ao** (82.4 mg, 0.28 mmol) was dissolved in 4-MeTHP (5.0 mL), and ground powder KOH (61.7 mg, 1.1 mmol) was added. The mixture was stirred at 100 °C for 1 h using an oil bath. The volatiles were removed under reduced pressure and then AcOEt was added to the residue. Insoluble materials were removed by filtration through $SiO_2$ plug eluting with AcOEt. The filtrate was concentrated in vacuo to afford difluoromethyl uracil derivative **4o** in 64% yield (32.4 mg, 0.180 mmol) as a colorless oil.

**6-Difluoromethyl-*N*,*N*-dimethyluracil (4o)**



**$^1$H NMR (500 MHz, $CDCl_3$):** δ 6.39 (t, *J* = 52.8 Hz, 1H), 6.00 (s, 1H), 3.49 (s, 3H), 3.36 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −118.76 (d, *J* = 55.1 Hz, 2F) ppm.

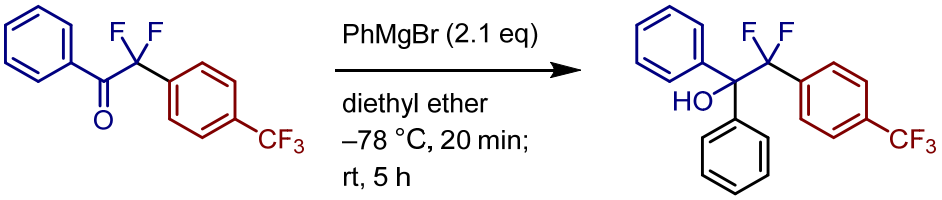
**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 161.67, 151.93, 143.90 (t, *J* = 23.5 Hz), 110.72 (t, *J* = 242 Hz), 102.69 (t, *J* = 8.3 Hz), 31.75 (t, *J* = 3.7 Hz), 28.27 ppm.

**IR (KBr):** 3699, 2962, 2904, 1683, 1635, 1092, 911, 748 $cm^{-1}$.

**HRMS-DART (m/z):** ($[M+H]^+$) calcd for $C_7H_9O_2N_2F_2^+$, 191.0627; found, 191.0624.

The identification of **4o** was referred to the corresponding trifluoromethyluracil derivative reported in literature.[S9]

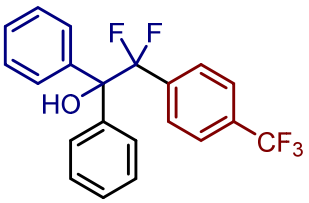
### 6-2. Reaction with Phenylmagnesium Bromide




**3ae**, 0.11 mmol **5aeb**, 61%

The title reaction was carried out according to the modified procedures previously described.[S3] Difluoromethyl ketone derivative **3ae** (25.3 mg, 0.11 mmol) was dissolved in $Et_2O$ (1.0 mL), and PhMgBr (0.06 mL, 3.9 M in $Et_2O$, 0.23 mmol) was added to the solution at −78 °C. The mixture was stirred at −78 °C for 20 min, and then at room temperature for 5 h. The reaction was quenched with a 1 M HCl aqueous solution (1.0 mL) and was transferred to a separation funnel with $Et_2O$ (2.0 mL). The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (2 × 10 mL). The combined organic solution was washed with sat. $NaHCO_3$ aqueous solution (10 mL) and was dried over $Na_2SO_4$. After filtration, the volatiles were removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$, AcOEt/hexane = 1:5) to afford the corresponding alcohol **5aeb** in 61% yield (25.3 mg, 0.0669 mmol) as a colorless oil.

**2,2-Difluoro-1,1-diphenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (5aeb)**




**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.45–7.43 (m, 4H), 7.30–7.27 (m, 6H), 7.19 (d, *J* = 8.3 Hz, 2H), 2.84 (s, 1H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −62.89 (s, 3F), −102.33 (s, 2F) ppm.

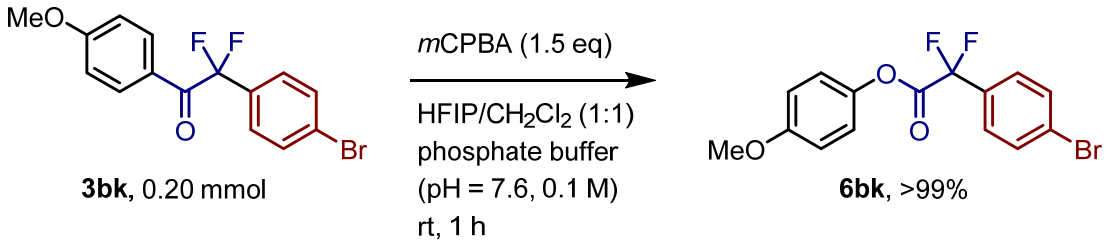
**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 141.11, 137.98 (t, *J* = 26.0 Hz), 131.54 (q, *J* = 32.6 Hz), 128.04,

127.95 (t, $J$ = 6.3Hz), 127.93, 127.89, 123.95 (q, $J$ = 3.6 Hz), 123.78 (q, $J$ = 274 Hz), 122.71 (t, $J$ = 257 Hz), 80.72 (t, $J$ = 28.4 Hz) ppm.

**IR (KBr):** 3538, 3059, 2923, 1496, 1449, 1411, 899, 874 $cm^{-1}$.

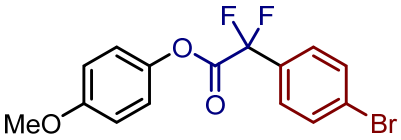
**HRMS-DART (m/z):** ($[M-OH]^+$) calcd for $C_{21}H_{14}F_5^+$, 361.1010; found, 361.1013: ($[M-H]^-$) calcd for $C_{21}H_{14}OF_5^+$, 377.0959; found, 377.0969

### 6-3. Baeyer–Villiger Oxidation




Baeyer–Villiger oxidation was carried out according to the procedures previously described.[S10] Difluoromethyl ketone derivative **3bk** (68.8 mg, 0.20 mmol) was dissolved in a mix solvent of HFIP (1.0 mL) and $CH_2Cl_2$ (1.0 mL), and phosphate buffer (pH = 7.6, 0.1 M, 0.2 mL) and *m*CPBA (62.6 mg, 0.25 mmol) were added in this order. The mixture was stirred at room temperature for 1 h. After volatiles are removed under reduced pressure, the residue was transferred to a separatory funnel with a mix solvent of AcOEt and $Et_2O$ (10:1, 15 mL). The solution was washed with sat. $Na_2SO_3$ aqueous solution (2 × 15 mL), sat. $NaHCO_3$ aqueous solution (2 × 15 mL), and brine (15 mL). After dried over $Na_2SO_4$ and filtration, the filtrate was concentrated under reduced pressure. $^{19}F$ NMR analysis of the residual mixture indicated that the corresponding difluoroester **6bk** was obtained in quantitative yield. Purification by column chromatography ($SiO_2$, AcOEt/hexane = 1:5) to afford **6bk** in 87% yield (62.7 mg, 0.176 mmol) as a colorless oil. The isolated yield was dropped presumably due to the decomposition of the product during the silica gel column chromatography.

**4-Methoxyphenyl 2-(4-bromophenyl)-2,2-difluoroacetate (6bk)**




**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 9.2 Hz, 2H), 3.79 (s, 3H) ppm.

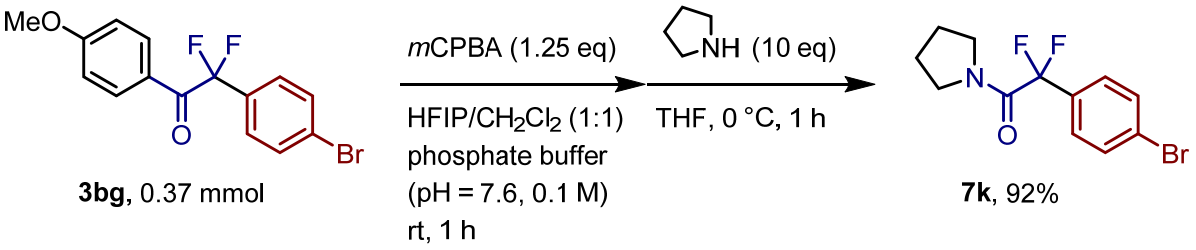
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −106.41 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 162.49 (t, *J* = 35.7 Hz), 157.88, 143.17, 132.14, 131.39 (t, *J* = 26.6 Hz), 127.27 (t, *J* = 6.0 Hz), 126.02, 121.49, 114.57, 113.06 (t, *J* = 253 Hz), 55.60 ppm.

**IR (KBr):** 3308, 1751, 1596, 1509, 1232, 1104, 990, 830 $cm^{-1}$.

**HRMS-DART (m/z):** ([M+H]$^+$) calcd for $C_{15}H_{12}O_3BrF_2^+$, 356.9932; found, 356.9930.

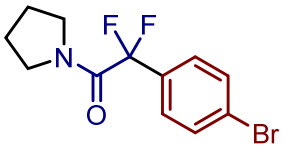
**6-4. Amidation**




Difluoromethyl ketone derivative **3bk** (126.1 mg, 0.37 mmol) was dissolved in a mix solvent of HFIP (2.0 mL) and $CH_2Cl_2$ (2.0 mL), and phosphate buffer (pH = 7.6, 0.1 M, 0.37 mL) and *m*CPBA (114.5 mg, 0.46 mmol) were added in this order. The mixture was stirred at room temperature for 1 h. After volatiles are removed under reduced pressure, the residue was transferred to a separatory funnel with a mix solvent of AcOEt and $Et_2O$ (10:1, 15 mL). The solution was washed with sat. $Na_2SO_3$ aqueous solution (2 × 15 mL), sat. $NaHCO_3$ aqueous solution (2 × 15 mL), and brine (15 mL). After dried over $Na_2SO_4$ and filtration, the filtrate was concentrated under reduced pressure. The residual mixture was dissolved in THF (5.0 mL) and pyrrolidine (263.11 mg, 3.7 mmol) was added dropwise at 0 °C. The mixture was stirred at this

temperature before addition of phosphate buffer (pH = 7.6, 0.1 M, 20 mL) to quench the reaction. The resulting mixture was transferred to separatory funnel with AcOEt (20 mL). The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 × 20 mL). The combined organic solution was washed with brine (20 mL) and was dried over $Na_2SO_4$. After filtration, the filtrate was concentrated. The residue was purified by column chromatography ($SiO_2$, AcOEt/hexane = 1:3) to afford difluoroamide **7k** in 92% yield (103.0 mg, 0.339 mmol) as a colorless oil.

**2-(4-Bromophenyl)-2,2-difluoro-1-(pyrrolidin-1-yl)ethan-1-one (7k)**



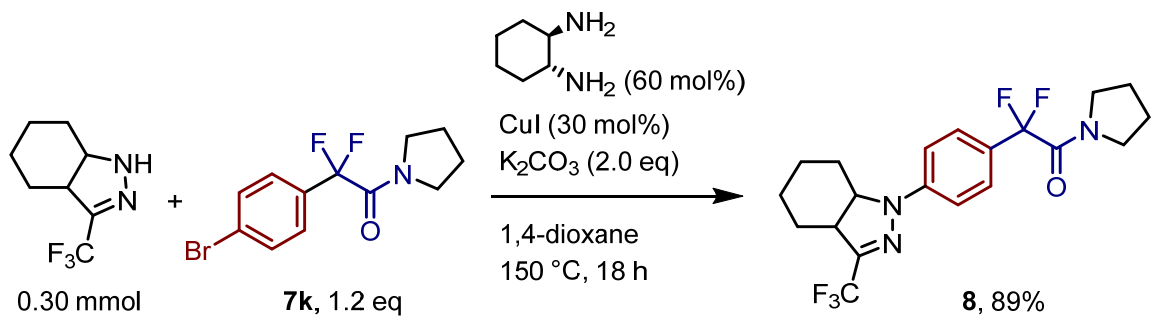

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 1.88 (tt, *J* = 6.8, 6.8 Hz, 2H), 1.83 (tt, *J* = 6.8, 6.8 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −99.04 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 161.66 (t, *J* = 30.8 Hz), 132.39 (t, *J* = 26.0 Hz), 131.84, 127.22 (t, *J* = 5.4 Hz), 125.26, 115.15 (t, *J* = 253 Hz), 47.57, 46.70 (t, *J* = 5.4 Hz), 26.38, 23.24 ppm.

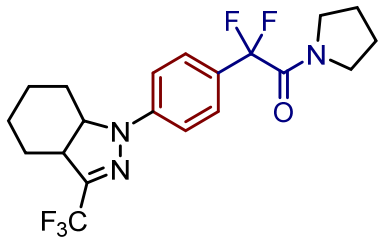
**IR (KBr):** 2973, 2881, 1668, 1444, 1275, 1258, 1074, 999, 836 $cm^{-1}$.

**6-5. Synthesis of 8**



The title compound **8** was synthesized according to the modified procedures previously described.[S11]

3-Trifluoromethyl-4,5,6,7-tetrahydro-1*H*-indazole (56.8 mg, 0.30 mmol) and difluoroamide **7k** (109.49 mg, 0.36 mmol) were dissolved in 1,4-dioxane (1.5 mL), and copper iodide (16.4 mg, 0.09 mmol), *trans*-1,2-diaminocyclohexane (20 μL mg, 0.18 mmol), and $K_2CO_3$ (82.7 mg, 0.60 mmol) were added. The reaction mixture was stirred at 150 °C for 18 h. After cooling to room temperature, the reaction was quenched with a saturated $NH_4Cl$ aqueous solution (3.0 mL) and was transferred to a separation funnel with AcOEt (5 mL). The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 × 5 mL). The combined organic solution was washed with brine (5 mL) and was dried over $Na_2SO_4$. After filtration, the filtrate was concentrated. The residue was purified by column chromatography ($SiO_2$, AcOEt/hexane = 1:4 to 1:3) to afford **8** in 89% yield (110.6 mg, 0.268 mmol) as a colorless solid.




**Melting Point:** 114.4–115.9 °C

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 2.74 (brs, 2H), 2.67 (brs, 2H), 1.89-1.80 (m, 8H) ppm.

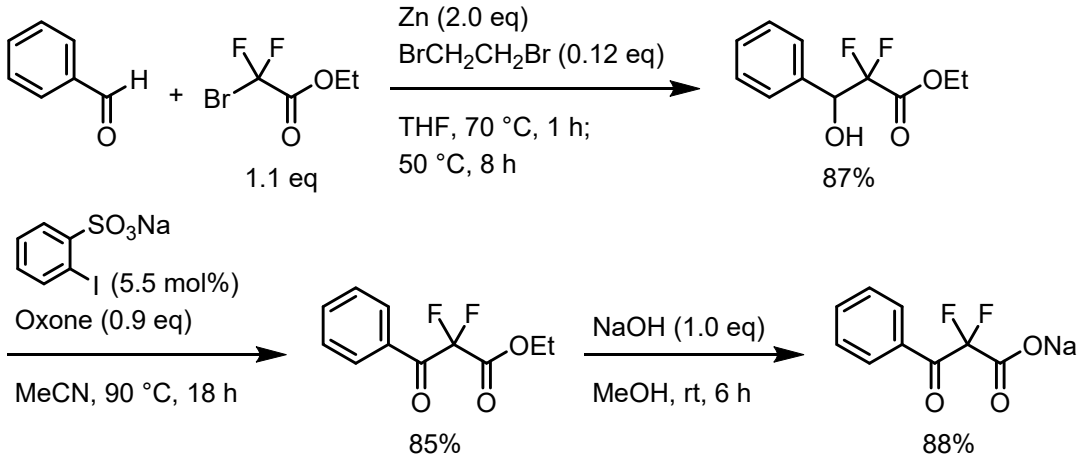
**$^{19}$F NMR (471 MHz, $CDCl_3$):** δ −62.20 (s, 3F), −98.95 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, $CDCl_3$):** δ 161.70 (t, *J* = 30.8 Hz), 140.91, 140.83, 140.58, 132.65 (t, *J* = 26.0 Hz), 126.69 (t, *J* = 6.0 Hz), 123.49, 121.83 (q, *J* = 270 Hz), 116.79, 115.01 (t, *J* = 252 Hz), 47.57, 46.72 (t, *J* = 4.9 Hz), 26.37, 23.56, 23.25, 22.40, 22.02, 19.94 ppm.

Spectrum data of **8** were matched with the product reported in literature.[S12]

## 7. Preparation of Substrates

### 7-1. Preparation of α,α-Difluoro-β-ketoacid Sodium Salt 1



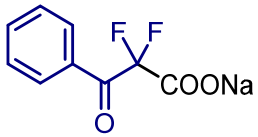

α,α-Difluoro-β-ketoacid sodium salts were prepared according to the procedures previously described.[S13,14]

**Step 1**: An oven-dried three-necked flask equipped with reflux condenser was charged with zinc powder (3.99 g, 60 mmol), dried THF (30 mL), and 1,2-dibromoethane (0.30 mL, 3.6 mmol) under nitrogen atmosphere. To activate zinc, the mixture was heated with a flame burner until THF boiled, and then cooled to rt. Heating/cooling sequence was repeated five times. A mixture of benzaldehyde (3.18 g, 30 mmol) and ethyl bromodifluoroacetate (6.70 g, 33 mmol) was added dropwise to the activated zinc in THF at 70 °C using an oil bath. The reaction mixture was stirred at 70 °C for 1 h, and then stirred at 50 °C for 8 h using an oil bath. After cooling to room temperature, the reaction was quenched with 1 N HCl (30 mL) and was transferred to a separation funnel with AcOEt (50 mL). The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 × 50 mL). The combined organic solution was washed with brine (50 mL) and was dried over $Na_2SO_4$. After filtration, the filtrate was concentrated. The residue was purified by column chromatography ($SiO_2$, AcOEt/hexane = 1:10) to afford ethyl 2,2-difluoro-3-hydroxy-3-phenylpropanoate in 87% yield (6.00 g, 26.1 mmol) as a yellow oil. [S13]

**Step 2**: Ethyl 2,2-difluoro-3-hydroxy-3-phenylpropanoate (3.75 g, 16.3 mmol) was dissolved in MeCN (80 mL), and subsequently sodium 2-iodobenzenesulfonate (281 mg, 0.90 mmol) and Oxone (9.07 g, 14.7 mmol) were added. The mixture was stirred at 90 °C for 18 h using an oil bath. After cooling to room temperature, insoluble materials were removed by filtration through Celite plug, eluting with AcOEt. The filtrate was washed with water (3 × 60 mL) followed by brine (50 mL), and then the solution was dried over $Na_2SO_4$. After filtration, the filtrate was concentrated. The residue was purified by column chromatography ($SiO_2$, AcOEt/hexane = 1:20) to afford ethyl 2,2-difluoro-3-oxo-3-phenylpropanoate in 85% yield (3.16 g, 13.8 mmol) as a yellow oil.[S14]

**Step 3**: Ethyl 2,2-difluoro-3-oxo-3-phenylpropanoate (1.99 g, 8.7 mmol) was dissolved in MeOH (10.0 mL). A solution of NaOH (348.2 mg, 8.7 mmol) dissolved in MeOH (10.0 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 6 h. The volatiles were removed under reduced pressure. Addition of AcOEt (30 mL) and diethyl ether (30 mL) generated a white precipitant, which was collected by vacuum filtration and was washed with diethyl ether. Drying under vacuum afforded sodium 2,2-difluoro-3-oxo-3-phenylpropanoate **1a-Na** in 88% yield (1.83 g, 8.25 mmol) as a colorless solid.

**Sodium 2,2-difluoro-3-oxo-3-phenylpropanoate (1a-Na)**




Colorless solid

**Melting Point:** 162.6–163.5 °C (decomp.)

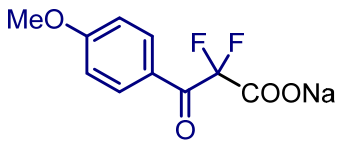
**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 7.98 (d, $J$ = 8.3 Hz, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.51 (t, $J$ = 7.1 Hz, 2H) ppm.

**$^{19}$F NMR (376 MHz, DMSO-$d_6$):** δ −107.26 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 189.44 (t, $J$ = 27.5 Hz), 162.96 (t, $J$ = 25.0 Hz), 134.00, 132.51, 129.24 (t, $J$ = 2.5 Hz), 128.67, 111.27 (t, $J$ = 265 Hz) ppm.

The identification of **1a-Na** was referred to the corresponding potassium salt reported in literature.[S13]

**Sodium 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (1b-Na)**




Red solid

**Melting Point:** 177.0–179.2 °C (decomp.)

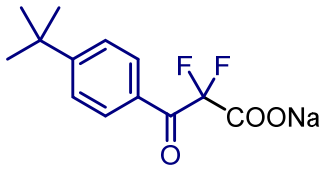
**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 8.00 (d, $J$ = 8.6 Hz, 2H), 7.05 (d, $J$ = 8.6 Hz, 2H), 3.84 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** δ −106.95 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 187.80 (t, $J$ = 27.1 Hz), 163.67, 163.18 (t, $J$ = 42.8 Hz), 131.72, 125.37, 113.92, 111.39 (t, $J$ = 263.0 Hz), 55.67 ppm.

The identification of **1b-Na** was referred to the corresponding potassium salt reported in literature.[S13]

**Sodium 3-(4-(tert-butyl)phenyl)-2,2-difluoro-3-oxopropanoate (1c-Na)**




Colorless solid.

**Melting Point:** 171.2–172.0 °C (decomp.)

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 7.96 (d, $J$ = 8.3 Hz, 2H), 7.54 (d, $J$ = 8.3 Hz, 2H), 1.29 (s,

9H) ppm.

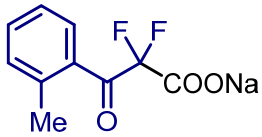
**$^{19}$F NMR (376 MHz, DMSO-$d_6$):** −107.30 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 188.86 (t, $J$ = 27.5 Hz), 163.08 (t, $J$ = 24.5 Hz), 157.05, 129.98, 129.21, 125.43, 111.23 (t, $J$ = 261 Hz), 34.93, 30.73 ppm.

**IR (KBr):** 3068, 2962, 1703, 1607, 1399, 1279, 1164, 1105, 924 cm$^{-1}$.

**HRMS-DART (m/z):** ([M−Na]$^-$) calcd for $C_{13}H_{13}O_3F_2^+$, 255.0827; found, 255.0840.

**Sodium 2,2-difluoro-3-(2-methylphenyl)-3-oxopropanoate (1d-Na)**




Colorless solid.

**Melting Point:** 167.3–168.4 °C (decomp.)

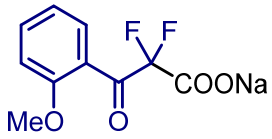
**$^1$H NMR (500 MHz, DMSO-$d_6$):** δ 7.91 (d, $J$ = 7.4 Hz, 1H), 7.45 (t, $J$ = 7.4 Hz, 1H), 7.32-7.26 (m, 2H), 2.41 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** −106.86 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 193.22 (t, $J$ = 29.0 Hz), 163.02 (t, $J$ = 25.2 Hz), 138.83, 133.03, 131.96, 131.67, 129.87 (t, $J$ = 3.1 Hz), 125.45, 111.08 (t, $J$ = 265 Hz), 20.91 ppm.

**IR (KBr):** 3074, 2978, 1693, 1387, 1295, 1259, 1180, 1112, 916 cm$^{-1}$.

**Sodium 2,2-difluoro-3-(2-methoxyphenyl)-3-oxopropanoate (1e-Na)**




Colorless solid.

**Melting Point:** 144.5–144.9 °C

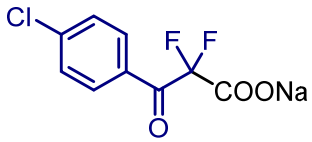
**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 7.75 (d, $J$ = 7.3 Hz, 1H), 7.53 (t, $J$ = 8.0 Hz, 1H), 7.12 (d, $J$ = 8.3 Hz, 1H), 7.01 (t, $J$ = 7.6 Hz, 1H), 3.77 (s, 3H) ppm.

**$^{19}$F NMR (376 MHz, DMSO-$d_6$):** −108.56 (s, 2F) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ191.77 (t, $J$ = 29.0 Hz), 163.28 (t, $J$ = 25.0 Hz), 158.47, 133.95, 130.40, 124.14, 120.01, 112.48, 111.31 (t, $J$ = 262 Hz), 55.59 ppm.

**IR (KBr):** 3072, 2948, 2842, 1701, 1599, 1488, 1306, 1269, 1156, 1021 cm$^{-1}$.

**Sodium 3-(4-chlorophenyl)-2,2-difluoro-3-oxopropanoate (1f-Na)**




Colorless solid

**Melting Point:** 164.5–165.1 °C (decomp.)

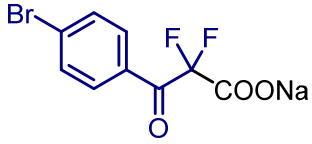
**$^1$H NMR (500 MHz, DMSO-$d_6$):** δ 8.01 (d, $J$ = 8.6 Hz, 2H), 7.62 (d, $J$ = 8.6 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** δ −107.50 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 188.68 (t, $J$ = 27.7 Hz), 162.58 (t, $J$ = 25.8 Hz), 138.94 (s), 131.24 (s), 131.07 (s), 128.88 (s), 111.16 (t, $J$ = 268 Hz) ppm.

The identification of **1f-Na** was referred to the corresponding potassium salt reported in literature.[S15]

**Sodium 3-(4-bromophenyl)-2,2-difluoro-3-oxopropanoate (1g-Na)**




Colorless solid

**Melting Point:** 171.6–172.3 °C (decomp.)

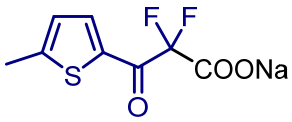
**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 7.93 (d, $J$ = 8.6 Hz, 2H), 7.77 (d, $J$ = 8.6 Hz, 2H) ppm.

**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** δ −107.55 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 188.88 (t, $J$ = 28.3 Hz), 162.74 (t, $J$ = 24.6 Hz), 131.87, 131.54, 131.15 (t, $J$ = 2.5 Hz), 128.31, 111.15 (t, $J$ = 264 Hz) ppm.

**IR (KBr):** 3279, 2815, 1677, 1635, 1405, 1175, 1097, 838 cm$^{-1}$.

**Sodium 2,2-difluoro-3-(5-methylthiophen-2-yl)-3-oxopropanoate (1h-Na)**




Colorless solid

**Melting Point:** 170.9–171.5 °C

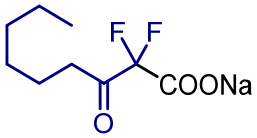
**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 7.80 (d, $J$ = 4.0 Hz, 1H), 6.98 (d, $J$ = 3.4 Hz, 1H), 2.52 (s, 3H) ppm.

**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** δ −107.34 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 182.33 (t, $J$ = 29.0 Hz), 162.68 (t, $J$ = 24.6 Hz), 151.17 (s), 136.64 (s), 136.34 (t, $J$ = 3.2 Hz), 127.90 (s), 111.18 (t, $J$ = 264 Hz), 15.64 ppm.

The identification of **1h-Na** was referred to the corresponding potassium salt reported in literature.[S13]

**Sodium 2,2-difluoro-3-oxononanoate (1i-Na)**




Colorless solid

**Melting Point:** 138.9–139.8 °C (decomp.)

**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 2.59 (t, $J$ = 7.4 Hz, 2H), 1.49-1.44 (m, 2H), 1.26–1.23 (m,

6H), 0.85 (t, $J$ = 6.9 Hz, 3H) ppm.

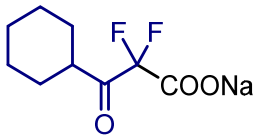
**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** δ −113.47 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 201.38 (t, $J$ = 27.7 Hz), 162.60 (t, $J$ = 25.2 Hz), 110.90 (t, $J$ = 265 Hz), 36.57, 31.09, 28.05, 22.46, 22.00, 13.94 ppm.

**IR (KBr):** 2931, 1746, 1686, 1405, 1208, 1130, 1028, 817 cm$^{-1}$.

**HRMS-DART (m/z):** ([M−Na]$^-$) calcd for $C_9H_{13}O_3F_2^+$, 207.0827; found, 207.0840.

**Sodium 3-cyclohexyl-2,2-difluoro-3-oxopropanoate (1j-Na)**




Colorless solid

**Melting Point:** 180.2–181.8 °C (decomp.)

**$^1$H NMR (500 MHz, DMSO-$d_6$):** δ 2.70 (s, 1H), 1.88–1.60 (m, 5H), 1.28–1.11 (m, 5H) ppm.

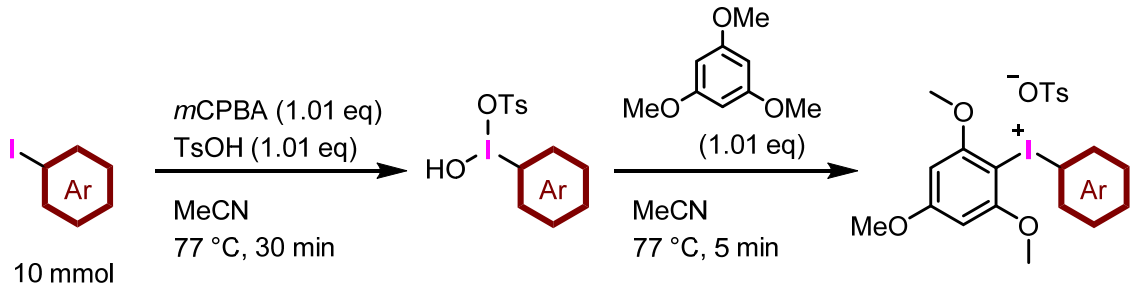
**$^{19}$F NMR (471 MHz, DMSO-$d_6$):** δ −113.09 (s, 2F) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 203.80 (t, $J$ = 26.5 Hz), 162.55 (t, $J$ = 23.9 Hz), 111.13 (t, $J$ = 266 Hz), 44.86, 28.29, 25.34, 25.02 ppm.

The identification of **1j-Na** was referred to the corresponding potassium salt reported in literature.[S13]

### 7-2. Preparation of Diaryliodonium Salt 2

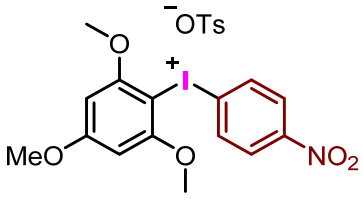
#### 7-2-1. Preparation of Diaryliodonium Salt 2-OTs-TMP




Diaryliodonium salts were prepared according to the procedures previously described.[S6]

Aryl iodide (10 mmol) was dissolved in MeCN (30 mL), and *p*-toluenesulfonic acid (1.92 g, 10.1 mmol) and *m*CPBA (1.74 g, 10.1 mmol) were added in this order. After attaching a reflux condenser, the reaction mixture was stirred at 77 °C for 30 min using an oil bath. 1,3,5-Trimethoxybenzene (1.69 g, 10.1 mmol) was added to the reaction mixture, which was stirred at 77 °C for additional 5 min. After cooling to room temperature, the volatiles were removed under reduced pressure. Addition of a mix solvent of diethyl ether and MeOH (20:1) and stirring at room temperature generated a precipitant, which was collected by vacuum filtration and was washed with diethyl ether. Drying under vacuum afforded the corresponding TMP-iodonium tosylate.

**(4-Nitrophenyl)(TMP)iodonium tosylate (2a-OTs-TMP)**




52% yield (over two-steps). Yellow solid.

**Melting Point:** 161.4–162.5 °C

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 8.21 (d, $J$ = 9.3 Hz, 2H), 8.15 (d, $J$ = 8.8 Hz, 2H), 7.46 (d,

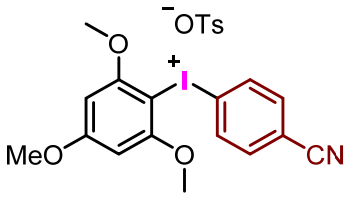
$J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 6.49 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 2.27 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.5, 159.5, 149.1, 145.5, 137.8, 135.5, 128.1, 126.1, 125.5, 122.5, 92.2, 87.2, 57.5, 56.3, 20.8 ppm.

**IR (KBr):** 2978, 1583, 1525, 1456, 1342, 1191, 1131, 1044, 816, 749 cm$^{-1}$.

Spectrum data of **2a-OTs-TMP** were matched with the product reported in literature.[S6]

**(4-Cyanophenyl)(TMP)iodonium tosylate (2b-OTs-TMP)**




83% yield (over two-steps). Colorless solid.

**Melting Point:** 186.8–187.9 °C

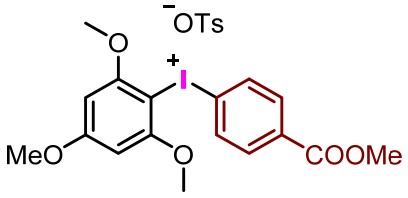
**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 8.07 (d, $J$ = 7.8 Hz, 2H), 7.90 (d, $J$ = 8.3 Hz, 2H), 7.47 (d, $J$ = 7.3 Hz, 2H), 7.10 (d, $J$ = 7.3 Hz, 2H), 6.48 (s, 2H), 3.93 (s, 6H), 3.87 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.5, 159.5, 145.5, 137.9, 134.91, 134.87, 128.2, 125.5, 121.1, 117.7, 114.1, 92.2, 87.1, 57.5, 56.3, 20.9 ppm.

**IR (KBr):** 3022, 2949, 2230, 1581, 1468, 1413, 1342, 1191, 1129, 1044, 1014, 816, 750 cm$^{-1}$.

**HRMS-DART (m/z):** ([M−OTs]$^{+}$) calcd for $C_{16}H_{15}INO_3^{+}$, 396.0091; found, 396.0089.

**(4-Methoxycarbonylphenyl)(TMP)iodonium tosylate (2c-OTs-TMP)**



69% yield (over two-steps). Colorless solid.

**Melting Point:** 168.6–170.1 °C

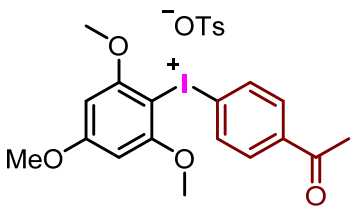
**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.95 (d, $J$ = 8.8 Hz, 2H), 7.47 (d, $J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 3.84 (s, 3H), 2.27 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.4, 165.2, 159.5, 145.5, 137.8, 134.6, 132.1, 131.8, 128.1, 125.5, 121.1, 92.2, 87.1, 57.4, 56.2, 52.7, 20.8 ppm.

**IR (KBr):** 2949, 1726, 1582, 1464, 1412, 1342, 1277, 1191, 1126, 1044, 1014, 818, 752 cm$^{-1}$.

Spectrum data of **2c-OTs-TMP** were matched with the product reported in literature.[S6,16]

**(4-Acetylphenyl)(TMP)iodonium tosylate (2d-OTs-TMP)**




51% yield (over two-steps), Colorless solid.

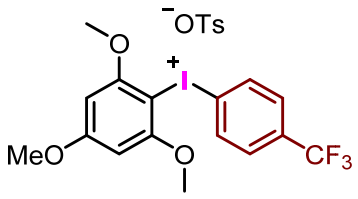
**Melting Point:** 202.5–203.7 °C

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 8.04 (d, $J$ = 8.8 Hz, 2H), 7.95 (d, $J$ = 8.3 Hz, 2H), 7.47 (d, $J$ = 8.3 Hz, 2H), 7.10 (d, $J$ = 8.3 Hz, 2H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 2.56 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 197.25, 166.29, 159.36, 145.67, 138.57, 137.59, 134.42, 130.79, 128.03, 125.46, 120.82, 92.10, 87.04, 57.39, 56.21, 26.90, 20.81 ppm.

Spectrum data of **2d-OTs-TMP** were matched with the product reported in literature.[S16]

**(4-Trifluoromethylphenyl)(TMP)iodonium tosylate (2e-OTs-TMP)**




62% yield (over two-steps). Colorless solid.

**Melting Point:** 165.1–166.3 °C

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 8.12 (d, $J$ = 8.3 Hz, 2H), 7.81 (d, $J$ = 8.8 Hz, 2H), 7.47 (d, $J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 3.94 (s, 6H), 3.87 (s, 3H), 2.27 (s, 3H) ppm.

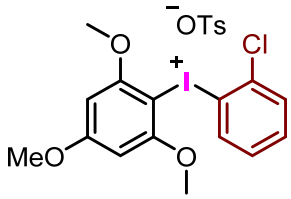
**$^{19}$F NMR (376 MHz, DMSO-$d_6$):** δ −64.4 (s, 3F) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.5, 159.5, 145.5, 137.8, 135.1, 131.4 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 128.1, 125.5, 123.5 (q, $^{1}J_{C\text{-}F}$ = 271.7 Hz), 120.4, 92.2, 87.1, 57.5, 56.3, 20.8 ppm.

**IR (KBr):** 2977, 2945, 1584, 1457, 1395, 1342, 1324, 1190, 1129, 1066, 1045, 817, 749 cm$^{-1}$.

Spectrum data of **2e-OTs-TMP** were matched with the product reported in literature.[S6]

**(2-Chlorophenyl)(TMP)iodonium tosylate (2f-OTs-TMP)**




78% yield (over two-steps). Colorless solid

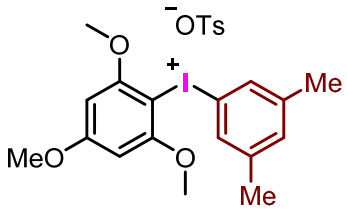
**Melting Point:** 145.3–148.5 °C

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 8.18 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.63 (t, $J$ = 7.7 Hz, 1H), 7.46 (d, $J$ = 8.0 Hz, 2H), 7.39 (dt, $J$ = 7.7, 1.5 Hz, 1H), 7.11 (d, $J$ = 8.0 Hz, 2H), 6.43 (s, 2H), 3.93 (s, 6H), 3.85 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.2, 159.5, 145.8, 138.8, 137.6, 135.7, 134.0, 130.1, 129.7, 128.0, 125.5, 118.9, 92.0, 87.3, 64.9, 56.1, 20.8 ppm.

Spectrum data of **2f-OTs-TMP** were matched with the product reported in literature.[S17]

**(3,5-Dimethylphenyl)(TMP)iodonium tosylate (2g-OTs-TMP)**




83% yield (over two-steps). Colorless Solid

**Melting Point:** 132.3–133.9 °C

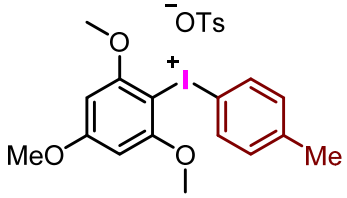
**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 7.55 (s, 2H), 7.47 (d, $J$ = 7.8 Hz, 2H), 7.24 (s, 1H), 7.11 (d, $J$ = 7.8 Hz, 2H), 6.46 (s, 2H), 3.95 (s, 6H), 3.86 (s, 3H), 2.28 (s, 3H), 2.27 (s, 6H) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 166.1, 159.4, 145.6, 141.0, 137.7, 133.0, 131.7, 128.0, 125.5, 115.7, 92.1, 86.8, 57.3, 56.2, 20.7, 20.6 ppm.

**IR (KBr):** 2950, 1583, 1456, 1412, 1339, 1206, 1124, 1045, 1014, 815, 750 cm$^{-1}$.

Spectrum data of **2g-OTs-TMP** were matched with the product reported in literature.[S6]

**(4-Methylphenyl)(TMP)iodonium tosylate (2h-OTs-TMP)**




82% yield (over two-steps). Colorless Solid

**Melting Point:** 177.8–179.0 °C

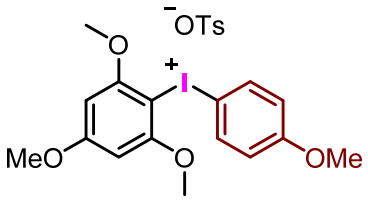
**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 7.80 (d, $J$ = 7.8 Hz, 2H), 7.47 (d, $J$ = 7.8 Hz, 2H), 7.26 (d, $J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 6.45 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 166.1, 159.3, 145.7, 141.9, 137.6, 134.4, 132.1, 128.1, 125.5, 112.5, 92.0, 87.2, 57.3, 56.2, 20.8, 20.8 ppm.

**IR (KBr):** 2977, 2944, 1583, 1456, 1413, 1341, 1256, 1192, 1129, 1044, 1014, 815, 750 $cm^{-1}$.

Spectrum data of **2h-OTs-TMP** were matched with the product reported in literature.[S6,16]

**(4-Methoxylphenyl)(TMP)iodonium tosylate (2i-OTs-TMP)**




The title compound was prepared according to the modified procedure. The reaction was carried out in $CH_2Cl_2$ at room temperature in each step.[S16]

66% yield (over two-steps). Colorless Solid

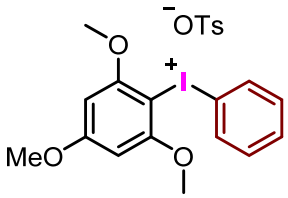
**Melting Point:** 183.5–185.6 °C

**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 7.84 (d, $J$ = 9.0 Hz, 2H), 7.47 (d, $J$ = 7.9 Hz, 2H), 7.11 (d, $J$ = 7.9 Hz, 2H), 7.00 (d, $J$ = 9.0 Hz, 2H), 6.44 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 3.77 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 166.0, 161.6, 159.2, 145.8, 137.6, 136.5, 128.0, 125.5, 117.2, 105.1, 92.0, 87.6, 57.3, 56.1, 55.6, 20.8 ppm.

Spectrum data of **2i-OTs-TMP** were matched with the product reported in literature.[S16]

**Phenyl(TMP)iodonium tosylate (2j-OTs-TMP)**




68% yield (over two-steps). Purple Solid

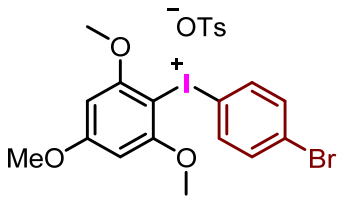
**Melting Point:** 202.5–203.7 °C

**$^1$H NMR (500 MHz, DMSO-$d_6$):** δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.60 (t, $J$ = 6.9 Hz, 1H), 7.49-7.44 (m, 4H), 7.11 (d, $J$ = 7.4 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 166.16, 159.40, 145.64, 137.69, 134.35, 131.58, 131.54, 128.11, 125.51, 116.16, 92.05, 87.06, 57.35, 56.19, 20.81 ppm.

Spectrum data of **2j-OTs-TMP** were matched with the product reported in literature.[S6]

**(4-Bromophenyl)(TMP)iodonium tosylate (2k-OTs-TMP)**




96% yield (over two-steps). Colorless solid

**Melting Point:** 197.2–198.5 °C

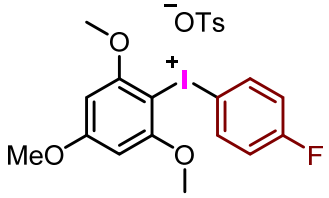
**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 7.83 (d, $J$ = 8.8 Hz, 2H), 7.65 (d, $J$ = 8.3 Hz, 2H), 7.47 (d, $J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.3, 159.4, 145.6, 137.7, 136.3, 134.4, 128.1, 125.5, 125.4, 114.7, 92.1, 87.2, 57.4, 56.2, 20.8 ppm.

**IR (KBr):** 2938, 1581, 1468, 1413, 1341, 1191, 1128, 1045, 1014, 815, 750 cm$^{-1}$.

**HRMS-DART (m/z):** ([M−OTs]$^+$) calcd for $C_{15}H_{15}BrIO_3^+$, 448.9244; found, 448.9243.

**(4-Fluorophenyl)(TMP)iodonium tosylate (2l-OTs-TMP)**



78% yield (over two-steps). Colorless solid

**Melting Point:** 192.4–193.8 °C

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 7.99–7.95 (m, 2H), 7.47 (d, $J$ = 8.1 Hz, 2H), 7.35–7.30 (m, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.28 (s, 3H) ppm.

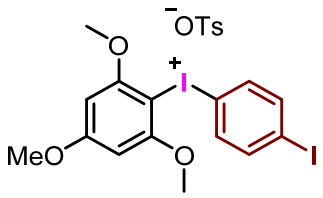
**$^{19}$F NMR (376 MHz, DMSO-$d_6$):** δ −131.7 (s, 1H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.2, 163.6 (d, $J$ = 248.6 Hz), 159.4, 145.6, 137.7, 137.2 (d, $J$ = 8.2 Hz), 128.1, 125.5, 118.9 (d, $J$ = 23.1 Hz), 110.4 (d, $J$ = 3.3 Hz), 92.1, 87.5, 57.4, 56.2, 20.8 ppm.

**IR (KBr):** 2943, 1582, 1479, 1412, 1341, 1227, 1191, 1126, 1044, 1014, 820, 750 cm$^{-1}$.

**HRMS-DART (m/z):** ([M−OTs]$^{+}$) calcd for $C_{15}H_{15}FIO_3^{+}$, 389.0044; found, 389.0047.

**(4-Iodophenyl)(TMP)iodonium tosylate (2m-OTs-TMP)**




70% yield (over two-steps). Colorless solid

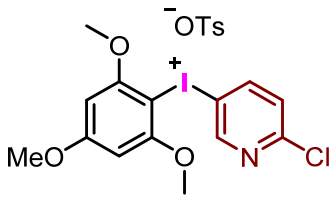
**Melting Point:** 213.3–214.7 °C

**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 7.81 (d, $J$ = 8.8 Hz, 2H), 7.66 (d, $J$ = 8.8 Hz, 2H), 7.46 (d, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 6.46 (s, 2H), 3.93 (s, 6H), 3.87 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (126 MHz, DMSO-$d_6$):** δ 166.24, 159.34, 145.72, 140.18, 137.61, 136.00, 128.07, 125.49, 115.48, 99.45, 92.07, 87.06, 57.36, 56.20, 20.82 ppm.

**IR (KBr):** 3092, 2940, 1584, 1340, 1230, 1210, 1162, 1010, 909, 798 cm$^{-1}$.

**(6-Chloropyridin-3-yl)(TMP)iodonium tosylate (2n-OTs-TMP)**




52% yield (over two-steps). Colorless solid.

**Melting Point:** 171.9–172.8 °C

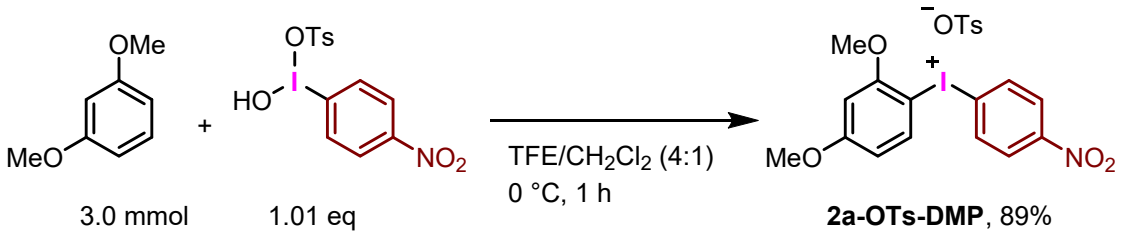
**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 8.85 (d, $J$ = 2.0 Hz, 1H), 8.36 (dd, $J$ = 8.5, 2.0 Hz, 1H), 7.62 (d, $J$ = 8.3 Hz, 1H), 7.46 (d, $J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 166.4, 159.3, 153.6, 152.7, 145.5, 145.2, 137.8, 128.1, 127.5, 125.5, 113.9, 92.1, 87.2, 57.4, 56.2, 20.8 ppm.

**IR (KBr):** 3024, 2950, 1582, 1457, 1413, 1342, 1191, 1129, 1044, 1014, 816, 749 cm$^{-1}$.

Spectrum data of **2n-OTs-TMP** were matched with the product reported in literature.[S6]

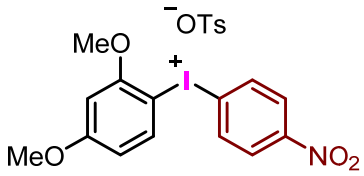
### 7-2-2. Preparation of Diaryliodonium Salt 2a-OTs-Ar




Hydroxy(4-nitrophenyl)iodonium tosylate (1.33 g, 3.03 mmol) was dissolved in 2,2,2-trifluoroethanol (40 mL). A solution of 1,3-dimethoxybenzene (0.40 mL, 3.0 mmol) dissolved in $CH_2Cl_2$ (10 mL) was added at 0 °C. The mixture was stirred at 0 °C for 1 h, and then the volatiles were removed under reduced pressure. Addition of a mix solvent of diethyl ether and MeOH (20:1) and stirring at room temperature generated a precipitant, which was collected by vacuum filtration and washed with diethyl ether. Drying under vacuum afforded **2a-OTs-DMP**

in 90% yield (1.50 g, 2.70 mmol) as a colorless solid.

**(4-Nitrophenyl)(DMP)iodonium tosylate (2a-OTs-DMP)**



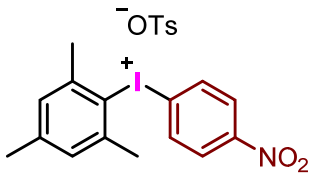

**Melting Point:** 206.3–207.4 °C

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 8.28-8.23 (m, 5H), 7.45 (d, $J$ = 7.8 Hz, 2H), 7.09 (d, $J$ = 7.8 Hz, 2H), 6.80 (d, $J$ = 2.4 Hz, 1H), 6.69 (dd, $J$ = 9.0, 2.7 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 2.27 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 165.0, 158.3, 149.2, 145.5, 138.6, 137.7, 135.9, 128.1, 126.0, 125.5, 122.6, 109.1, 99.9, 96.1, 57.3, 56.1, 20.8 ppm.

**IR (KBr):** 3095, 2945, 1573, 1526, 1355, 1231, 1159, 1008, 850 cm$^{-1}$.

**(4-Nitrophenyl)(Mes)iodonium tosylate (2a-OTs-Mes)**




The title compound (**2a-OTs-Mes**) was prepared according to the above method using hydroxy(4-nitrophenyl)iodonium tosylate (1.33 g, 3.03 mmol) and mesitylene (0. 42 mL, 3.0 mmol) for 3 h. **2a-OTs-Mes** was afforded in 84% yield (1.36 g, 2.52 mmol) as a colorless solid.

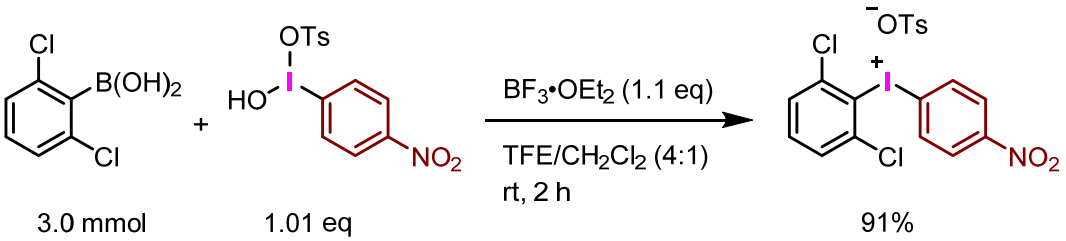
**Melting Point:** 207.2–207.8 °C

**$^1$H NMR (400 MHz, DMSO-$d_6$):** δ 8.24 (d, $J$ = 8.8 Hz, 2H), 8.18 (d, $J$ = 8.8 Hz, 2H), 7.44 (d, $J$ = 8.3 Hz, 2H), 7.23 (s, 2H), 7.09 (d, $J$ = 7.8 Hz, 2H), 2.58 (s, 6H), 2.30 (s, 3H), 2.28 (s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 149.2, 145.4, 143.5, 141.8, 137.8, 135.6, 129.9, 128.1, 126.2, 125.5, 123.0, 120.9, 26.3, 20.8, 20.6 ppm.

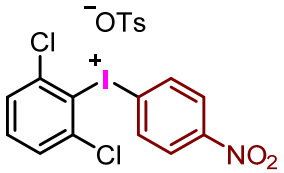
**IR (KBr):** 3109, 2983, 2922, 1531, 1356, 1223, 1174, 850, 813 $cm^{-1}$.

### 7-2-3. Preparation of Diaryliodonium Salt 2a-OTs-DCP




2,6-Dichlorophenylboronic acid (574 mg, 3.0 mmol) was dissolved in TFE (40 mL). After cooled to 0 °C, boron trifluoride etherate (0.42 mL, 3.3 mmol) was added dropwise, and then the mixture was stirred at 0 °C for 10 min. A solution of hydroxy(4-nitrophenyl)iodonium tosylate (1.33 g, 3.03 mmol) dissolved in $CH_2Cl_2$ (10 mL) was added. The mixture was stirred at rt for 2 h, and then the volatiles were removed under reduced pressure. Addition of a mix solvent of diethyl ether and MeOH (20:1) and stirring at room temperature generated a precipitant, which was collected by vacuum filtration and washed with diethyl ether. Drying under vacuum afforded **2a-OTs-DCP** in 91% yield (1.54 g, 2.72 mmol) as a colorless solid.

**(4-Nitrophenyl)(DCP)iodonium tosylate (2a-OTs-DCP)**




**Melting Point:** 204.0–204.1 °C

**$^{1}$H NMR (400 MHz, DMSO-$d_6$):** δ 8.39 (d, $J$ = 8.8 Hz, 2H), 8.28 (d, $J$ = 8.8 Hz, 2H), 7.83 (d, $J$ = 8.3 Hz, 2H), 7.71 (t, $J$ = 8.0 Hz, 1H), 7.44 (d, $J$ = 7.8 Hz, 2H), 7.10 (d, $J$ = 7.8 Hz, 2H), 2.27

(s, 3H) ppm.

**$^{13}$C NMR (100 MHz, DMSO-$d_6$):** δ 149.6, 145.4, 138.3, 137.8, 136.3, 136.0, 129.2, 128.1, 126.6, 125.5, 125.1, 123.4, 20.8 ppm.

**IR (KBr):** 3095, 3048, 1529, 1426, 1348, 1214, 1162, 1003, 849, 787 $cm^{-1}$.

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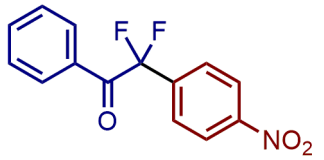
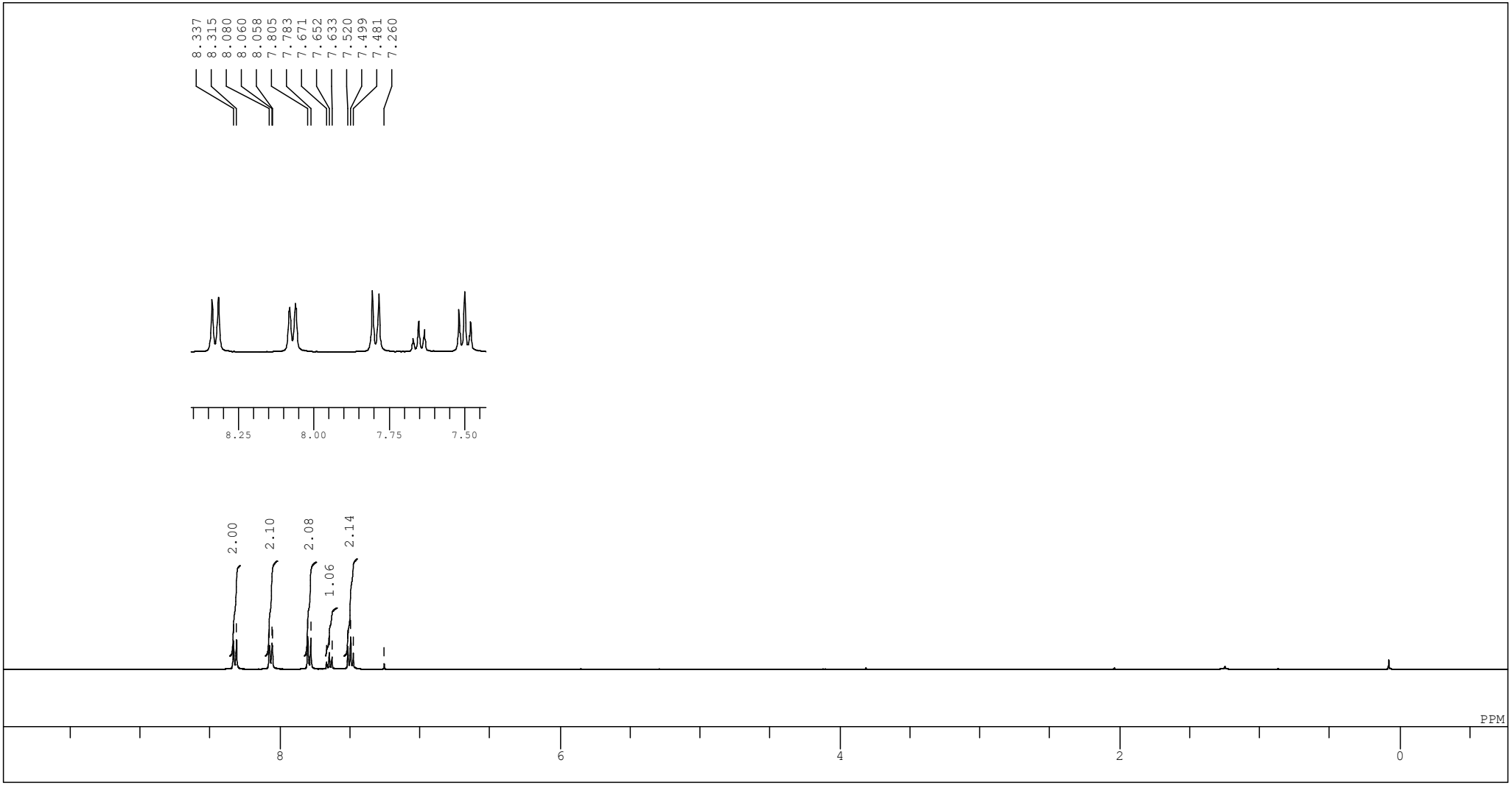
**9. NMR Spect**

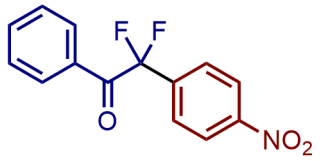
2,2-Difluoro-2-(4-nitrophenyl)-1-phenylethan-1-one (3aa)



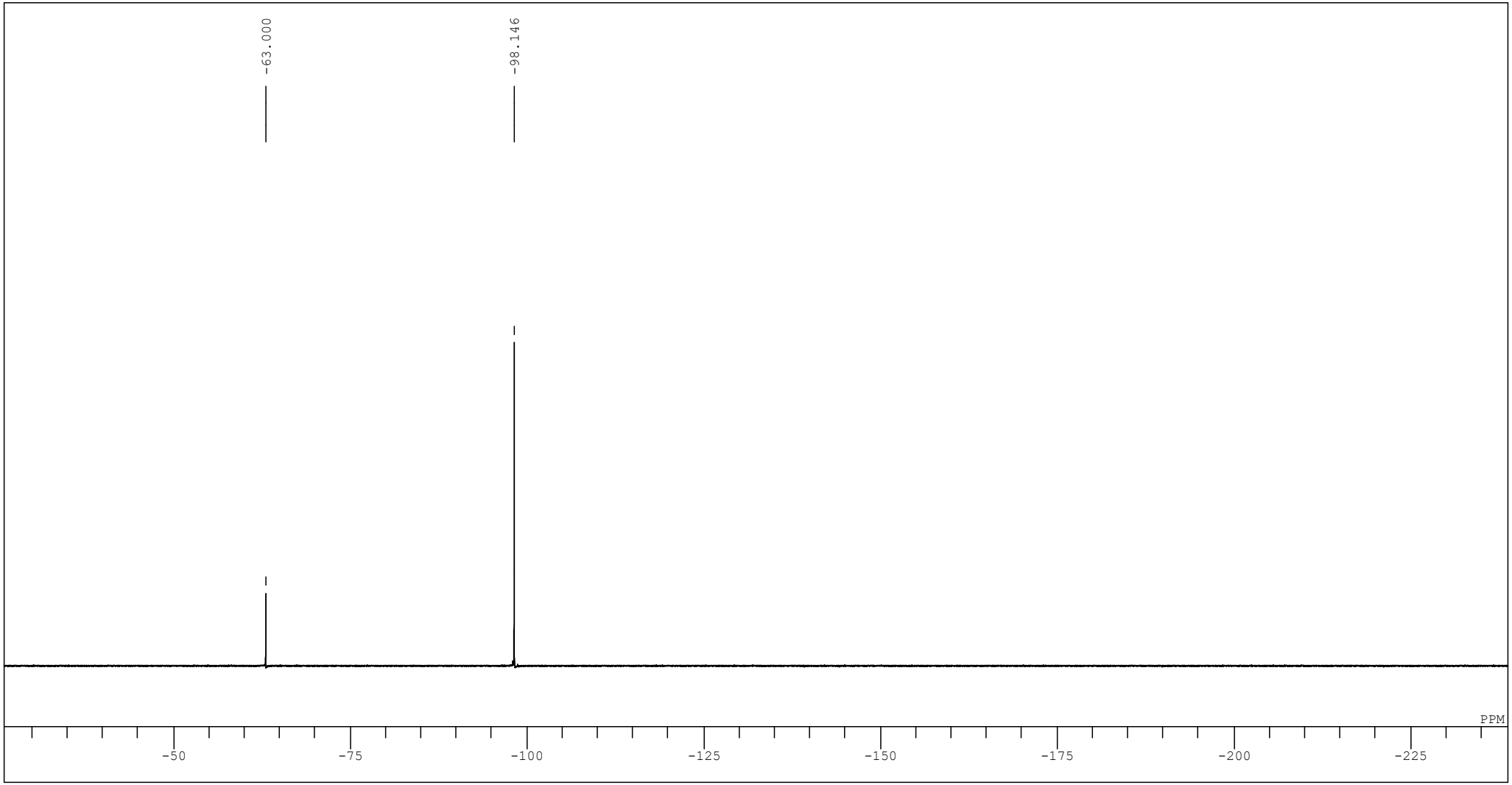

$^1$H NMR (400 MHz, $CDCl_3$)



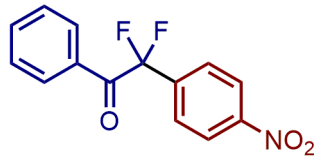
2,2-Difluoro-2-(4-nitrophenyl)-1-phenylethan-1-one (3aa)



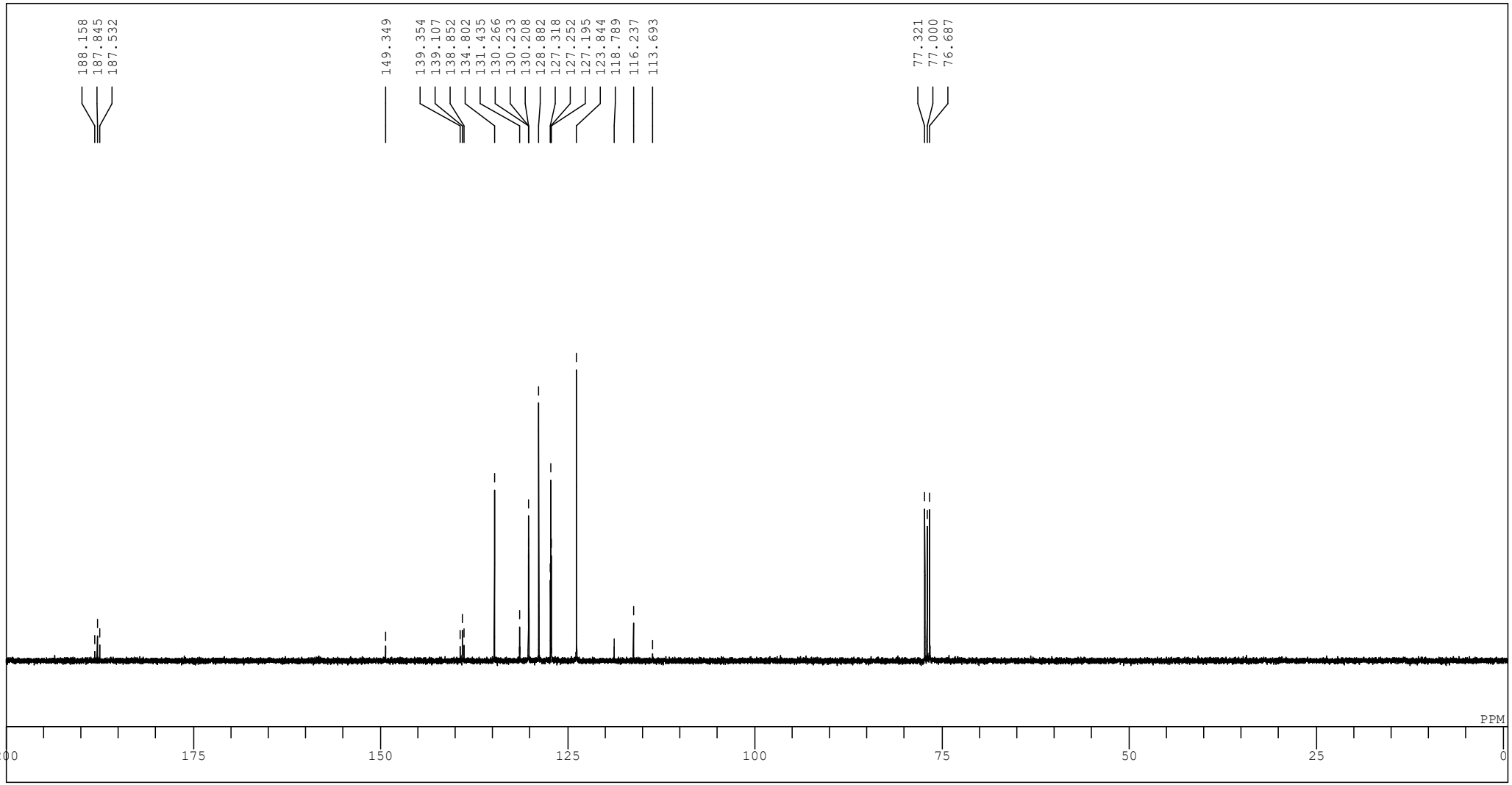

$^{19}F$ NMR (376 MHz, $CDCl_3$)



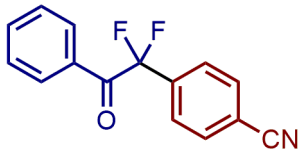
2,2-Difluoro-2-(4-nitrophenyl)-1-phenylethan-1-one (3aa)



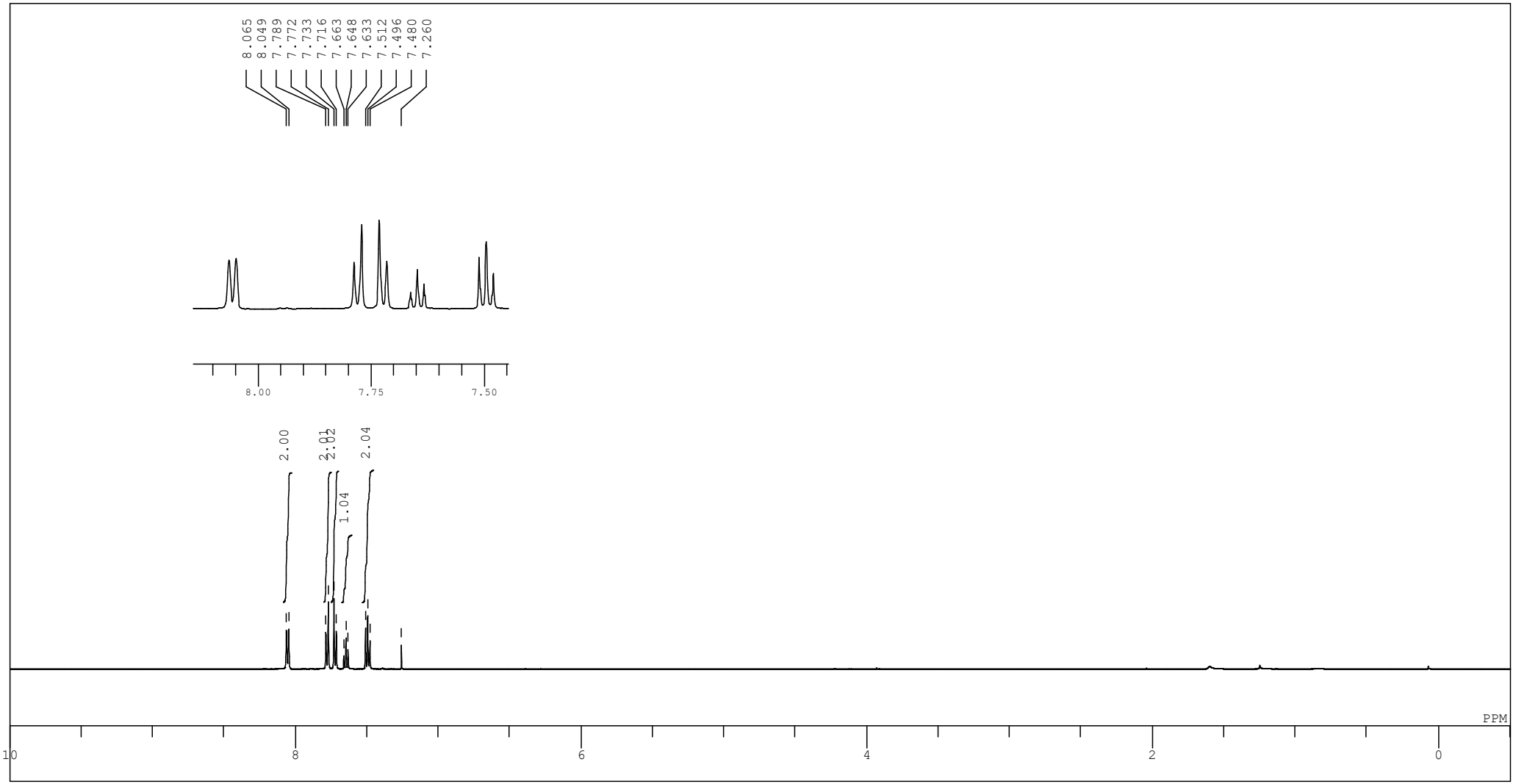

$^{13}C$ NMR (100 MHz, $CDCl_3$)



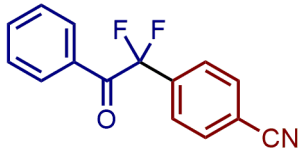
4-(1,1-Difluoro-2-oxo-2-phenylethyl)benzonitrile (3ab)



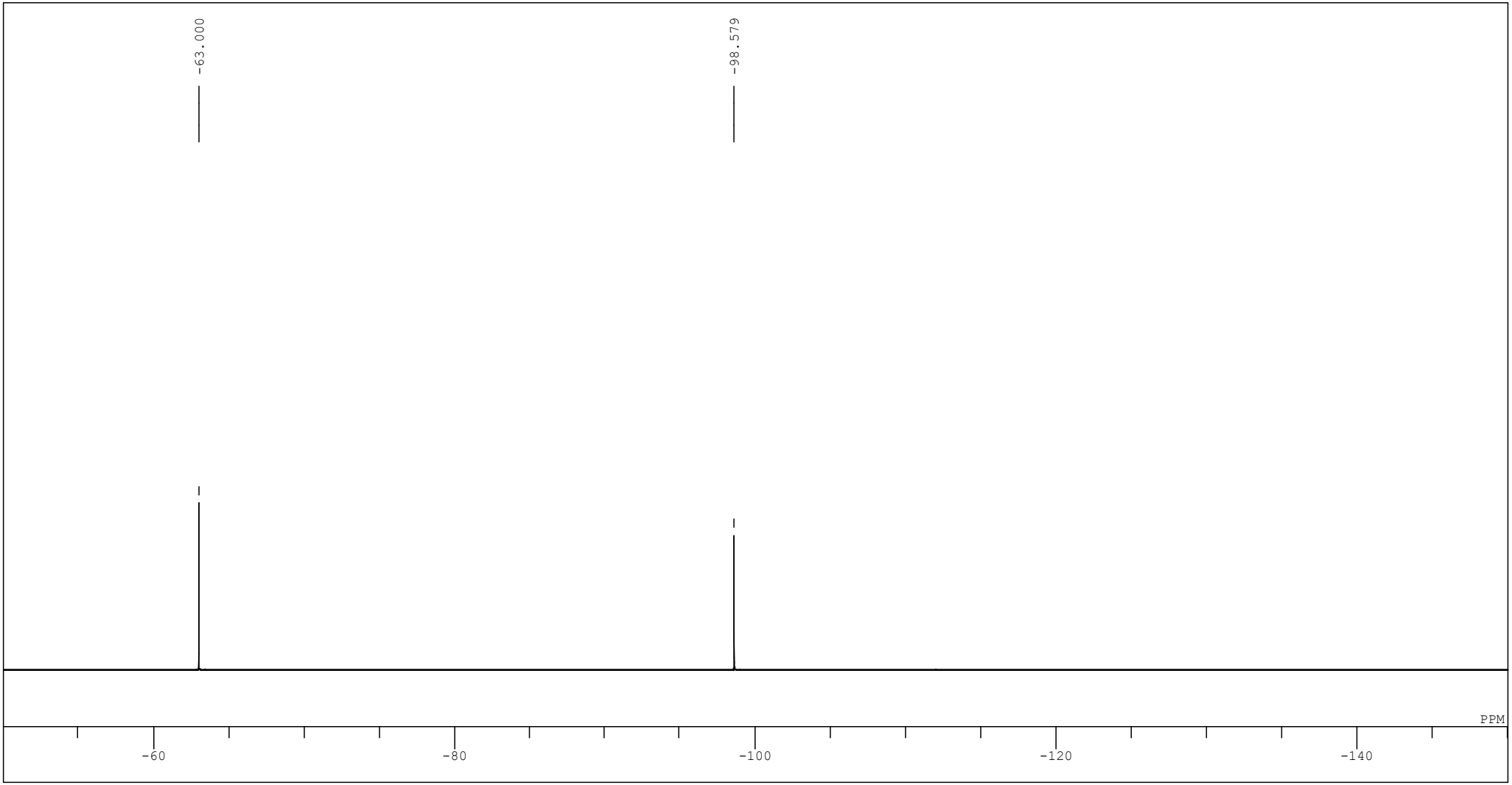

$^1$H NMR (500 MHz, $CDCl_3$)



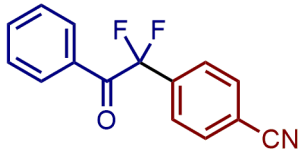
4-(1,1-Difluoro-2-oxo-2-phenylethyl)benzonitrile (3ab)



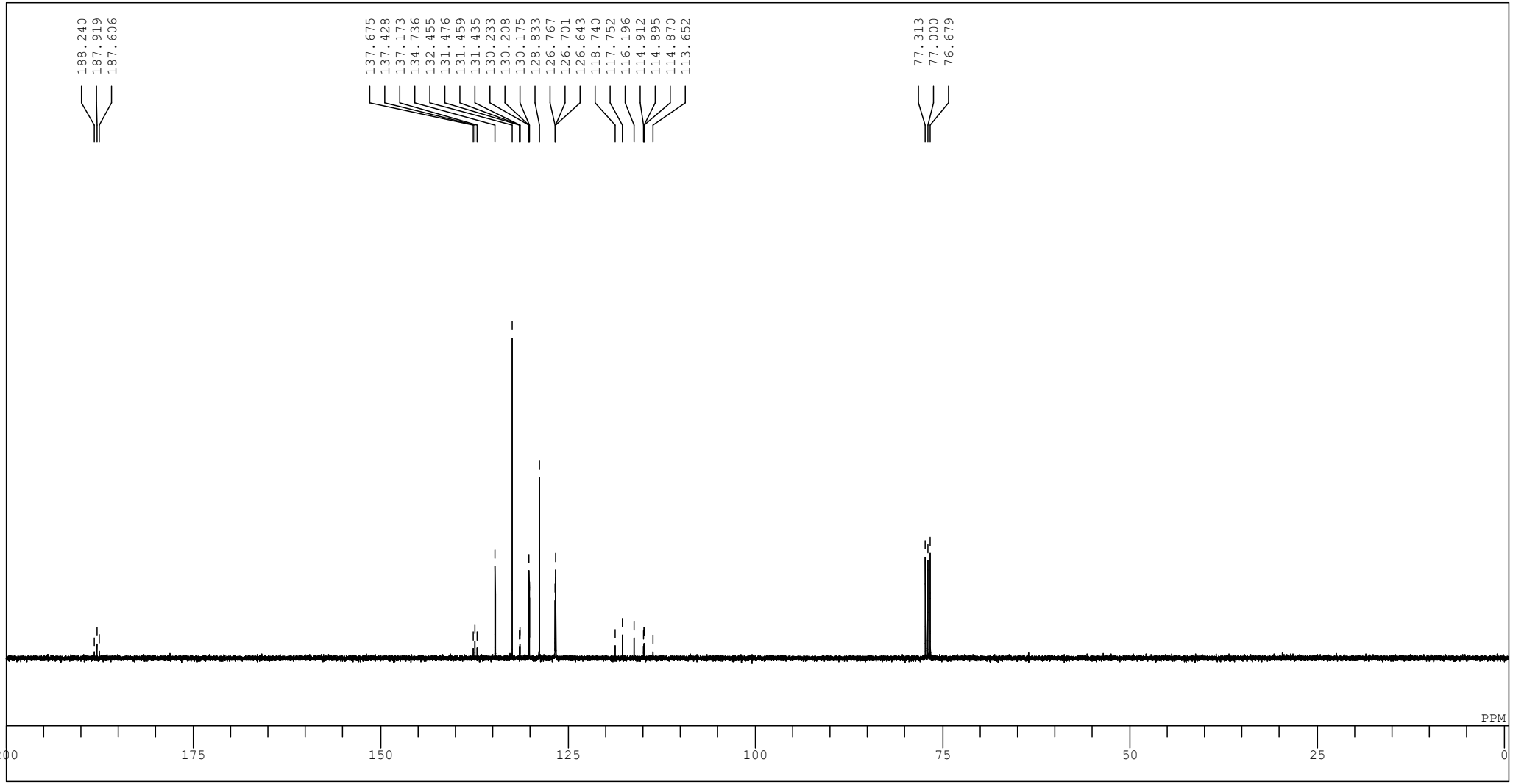

$^{19}F$ NMR (471 MHz, $CDCl_3$)



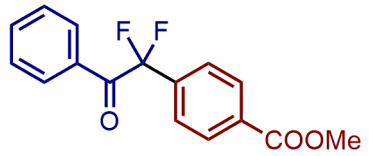
4-(1,1-Difluoro-2-oxo-2-phenylethyl)benzonitrile (3ab)



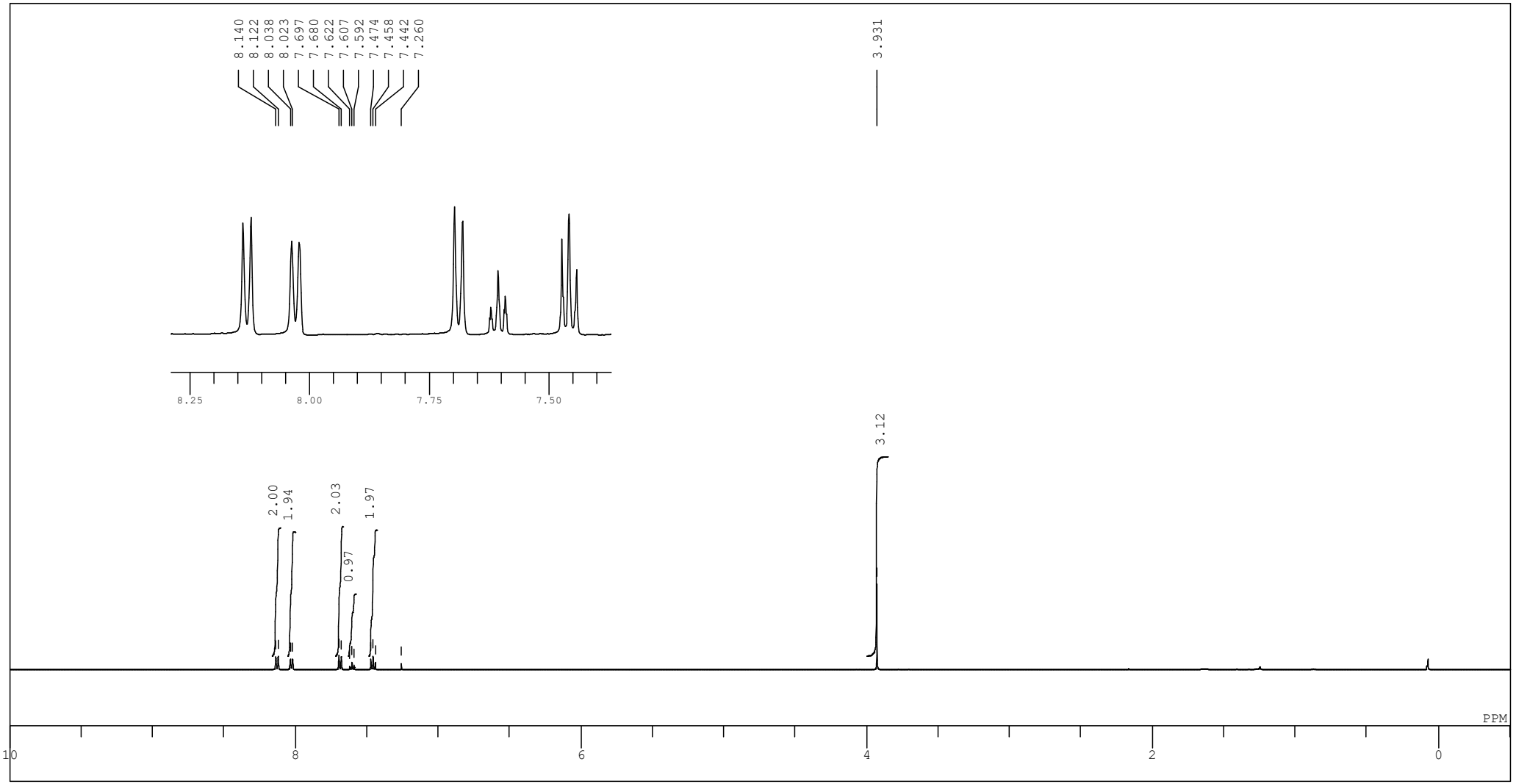

$^{13}C$ NMR (100 MHz, $CDCl_3$)



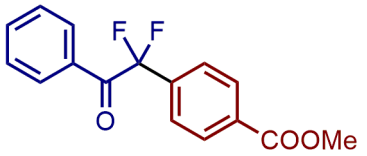
Methyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)benzoate (3ac)



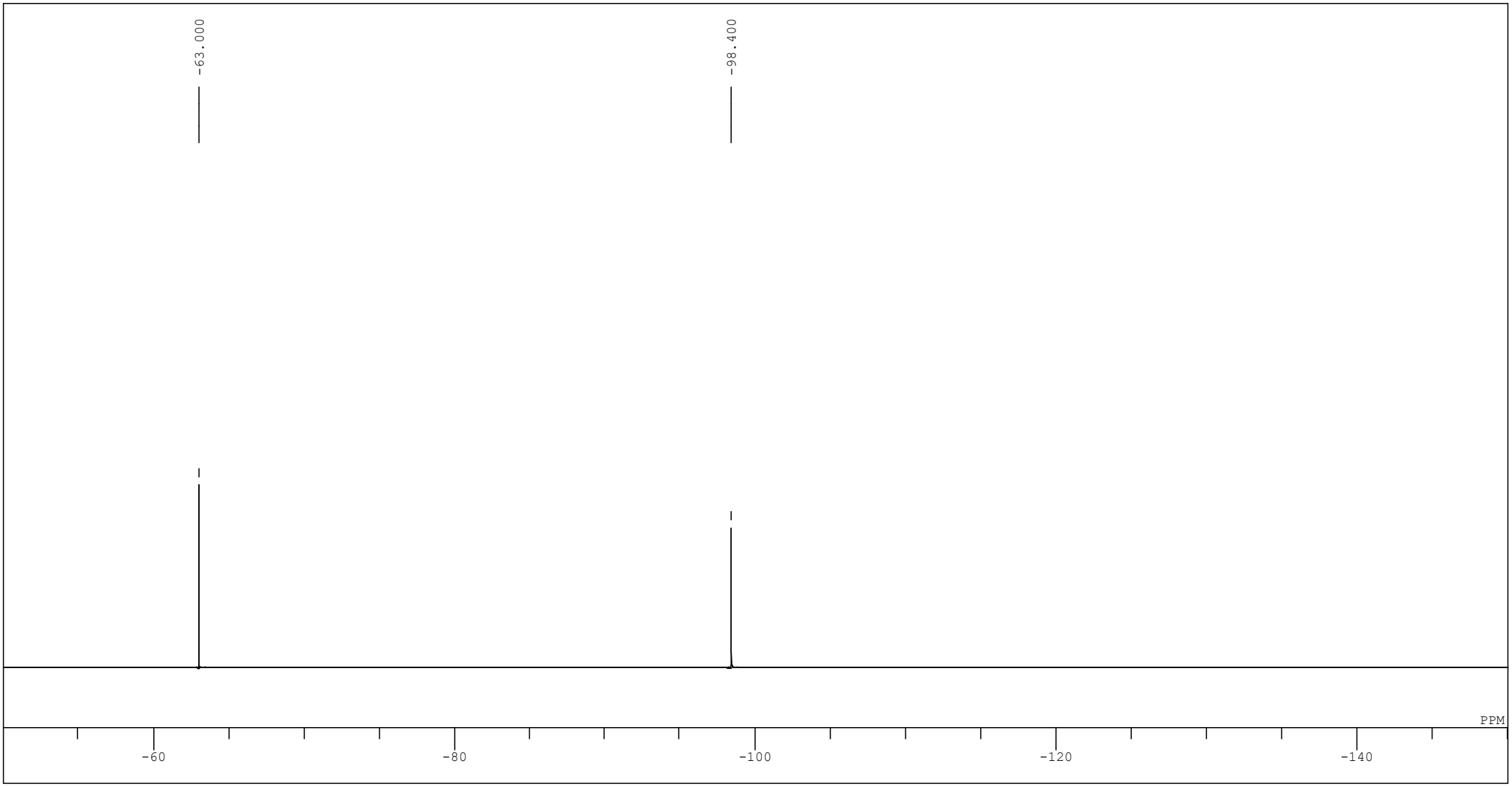

$^1$H NMR (500 MHz, $CDCl_3$)



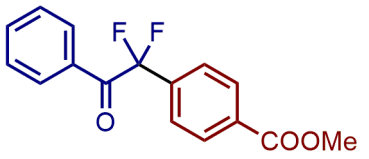
Methyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)benzoate (3ac)



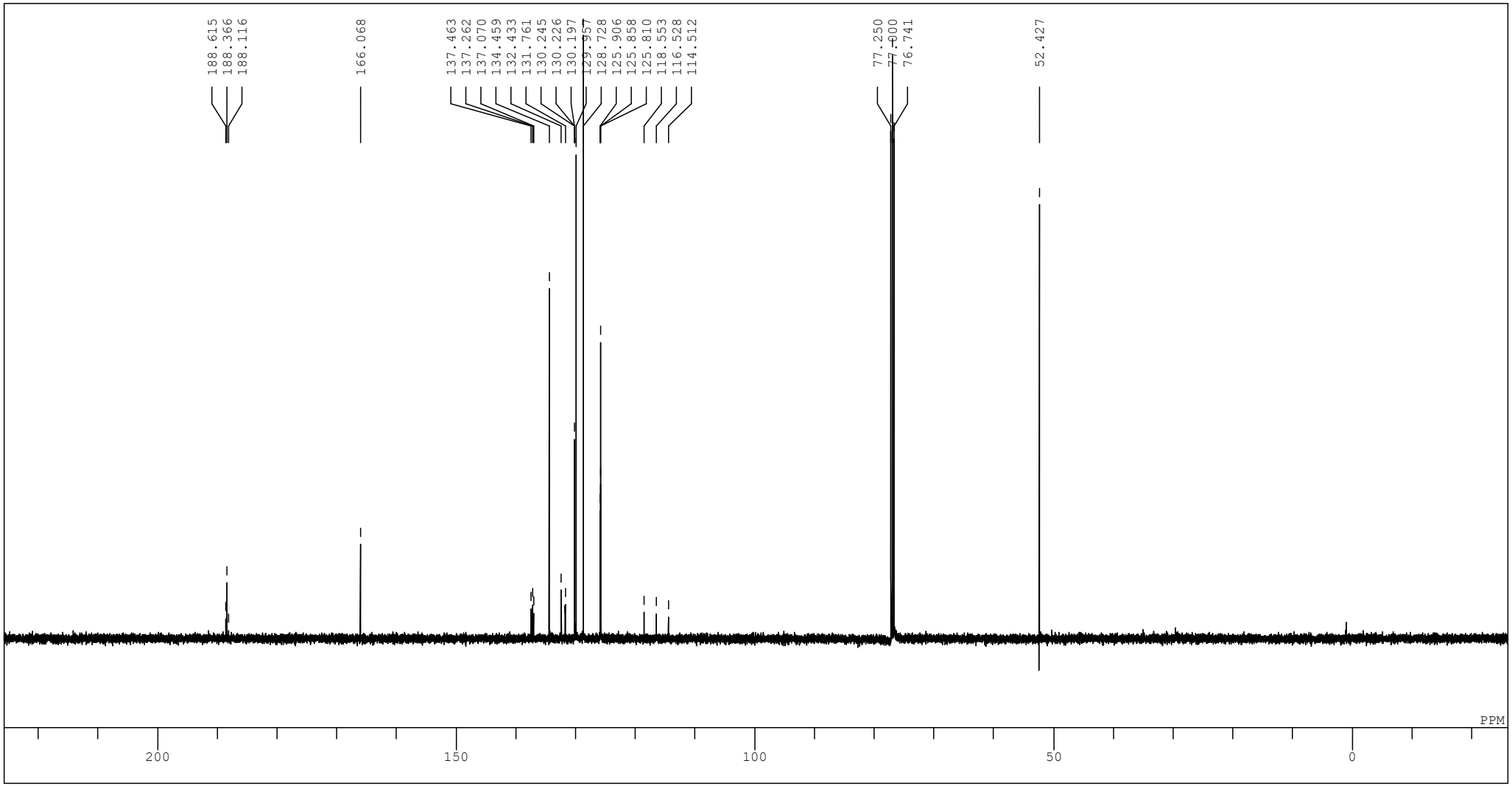

$^{19}F$ NMR (471 MHz, $CDCl_3$)



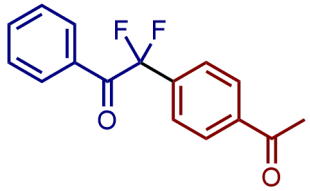
Methyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)benzoate (3ac)



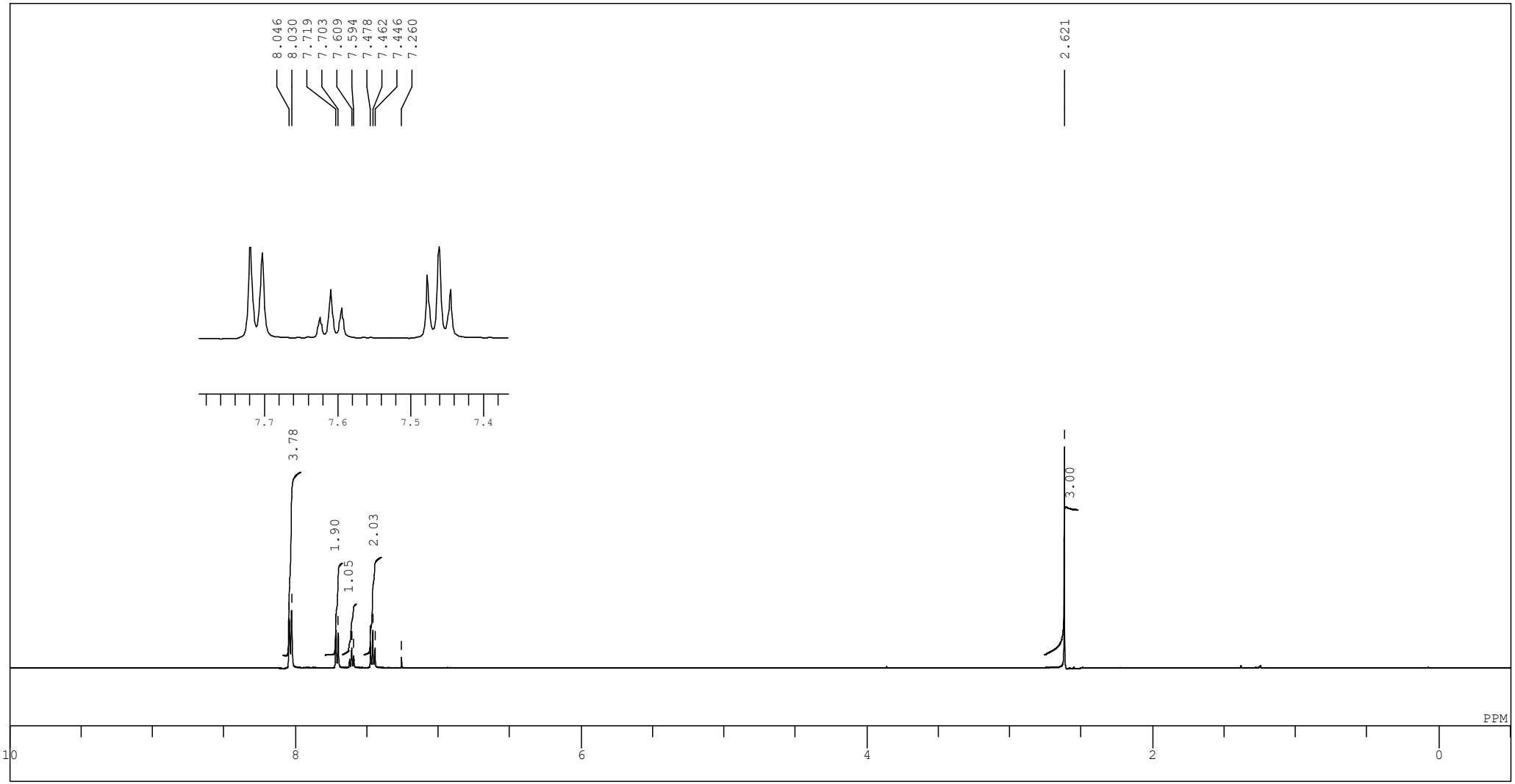

$^{13}C$ NMR (126 MHz, $CDCl_3$)



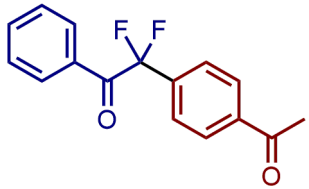
2-(4-Acetylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ad)



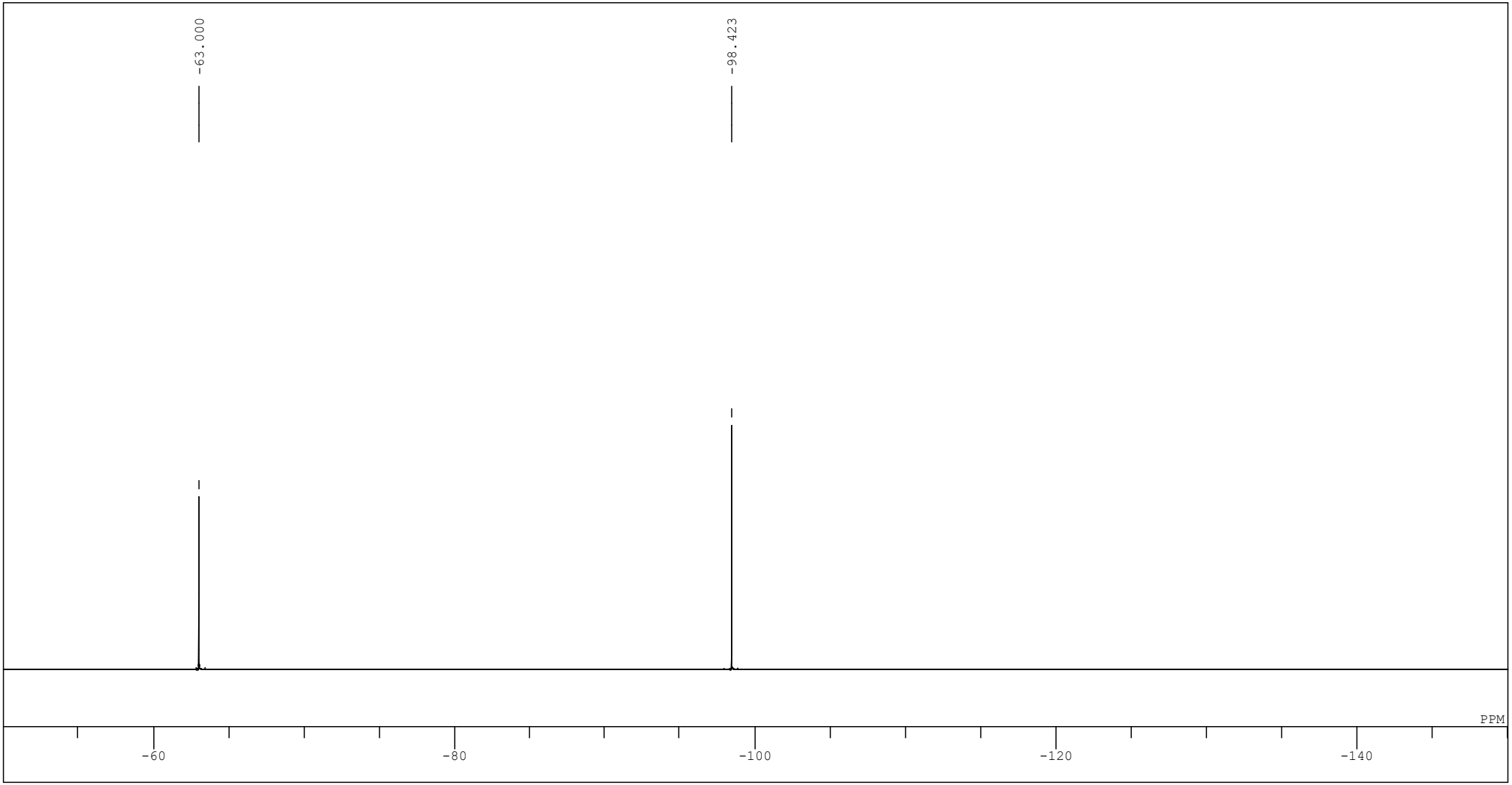

$^1$H NMR (500 MHz, $CDCl_3$)



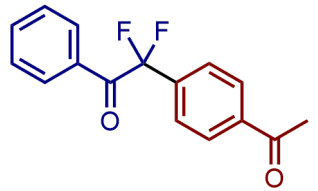
2-(4-Acetylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ad)



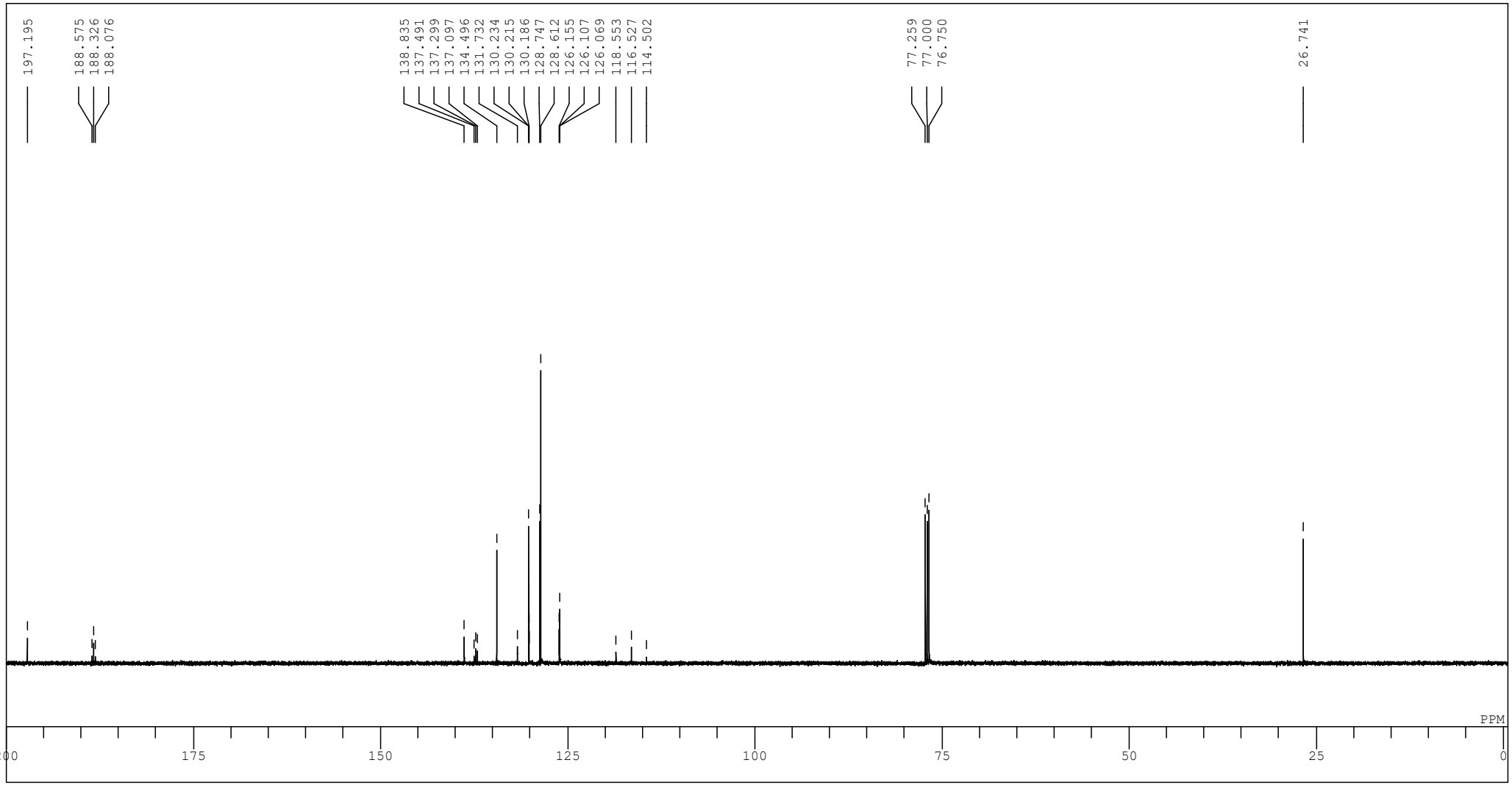

$^{19}F$ NMR (471 MHz, $CDCl_3$)



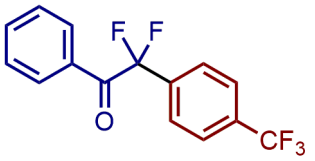
2-(4-Acetylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ad)



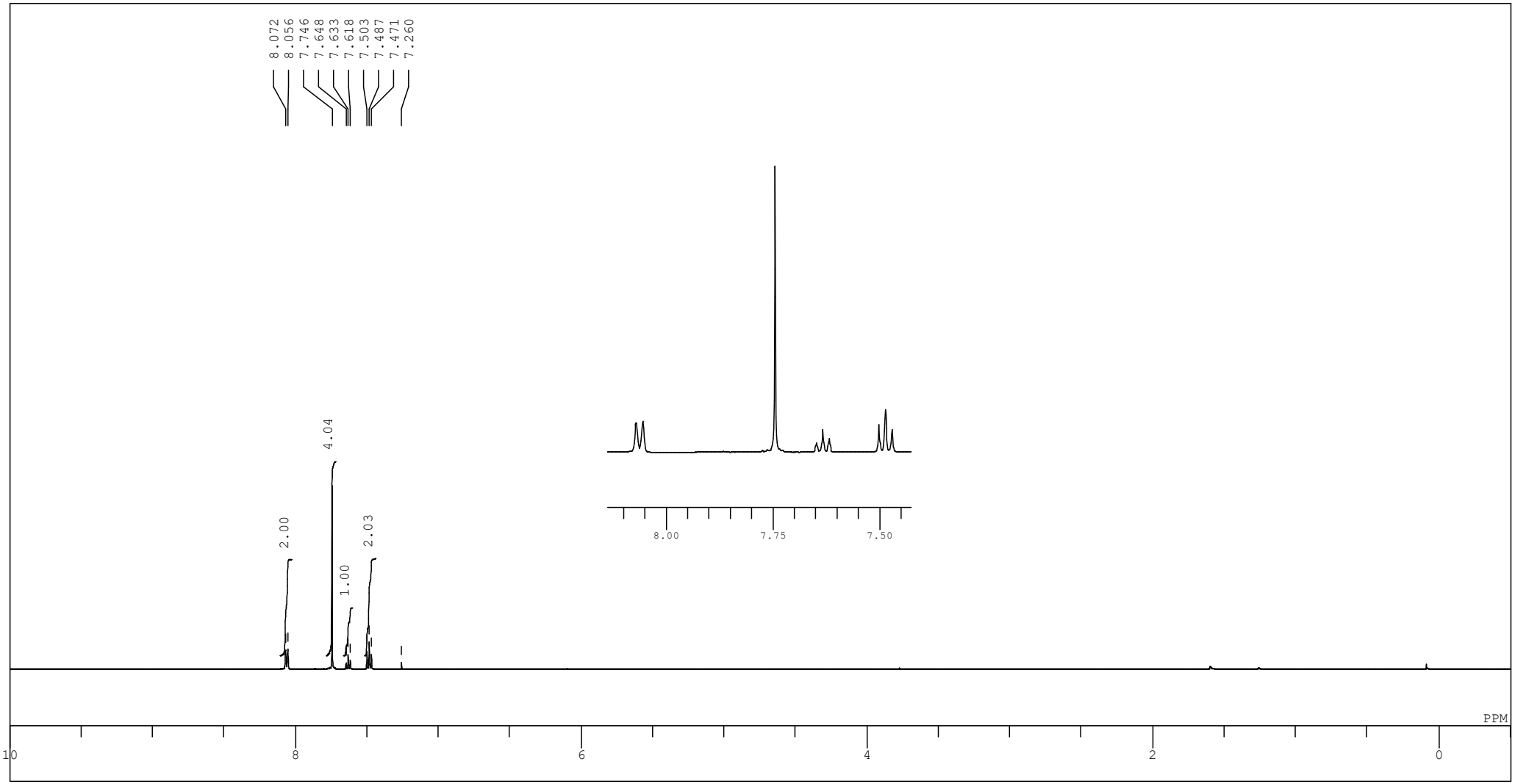

$^{13}C$ NMR (126 MHz, $CDCl_3$)



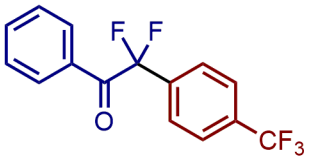
2,2-Difluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (3ae)



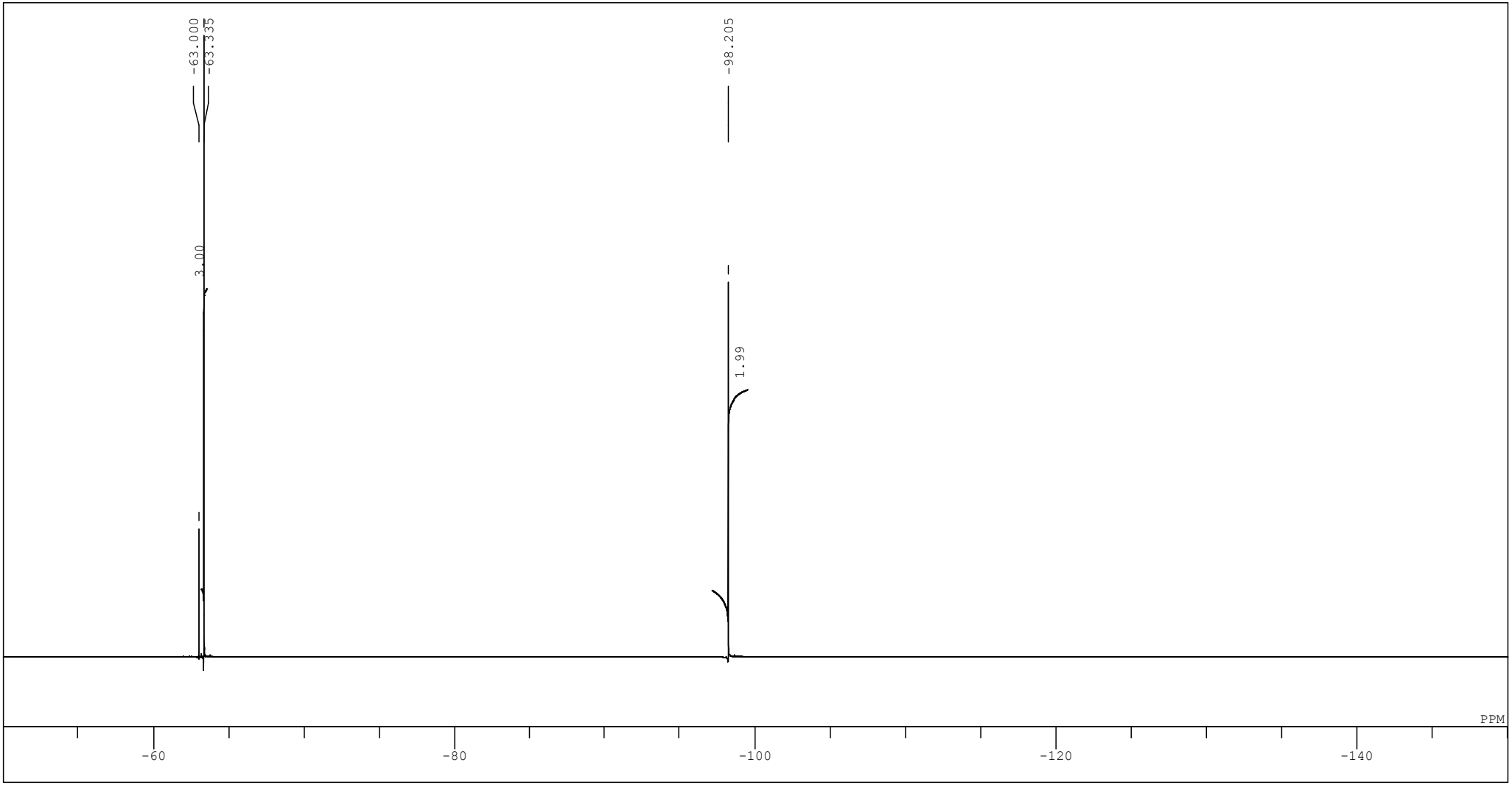

$^1$H NMR (500 MHz, $CDCl_3$)



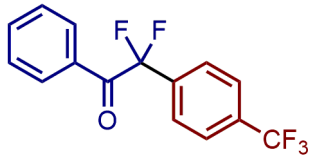
2,2-Difluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (3ae)



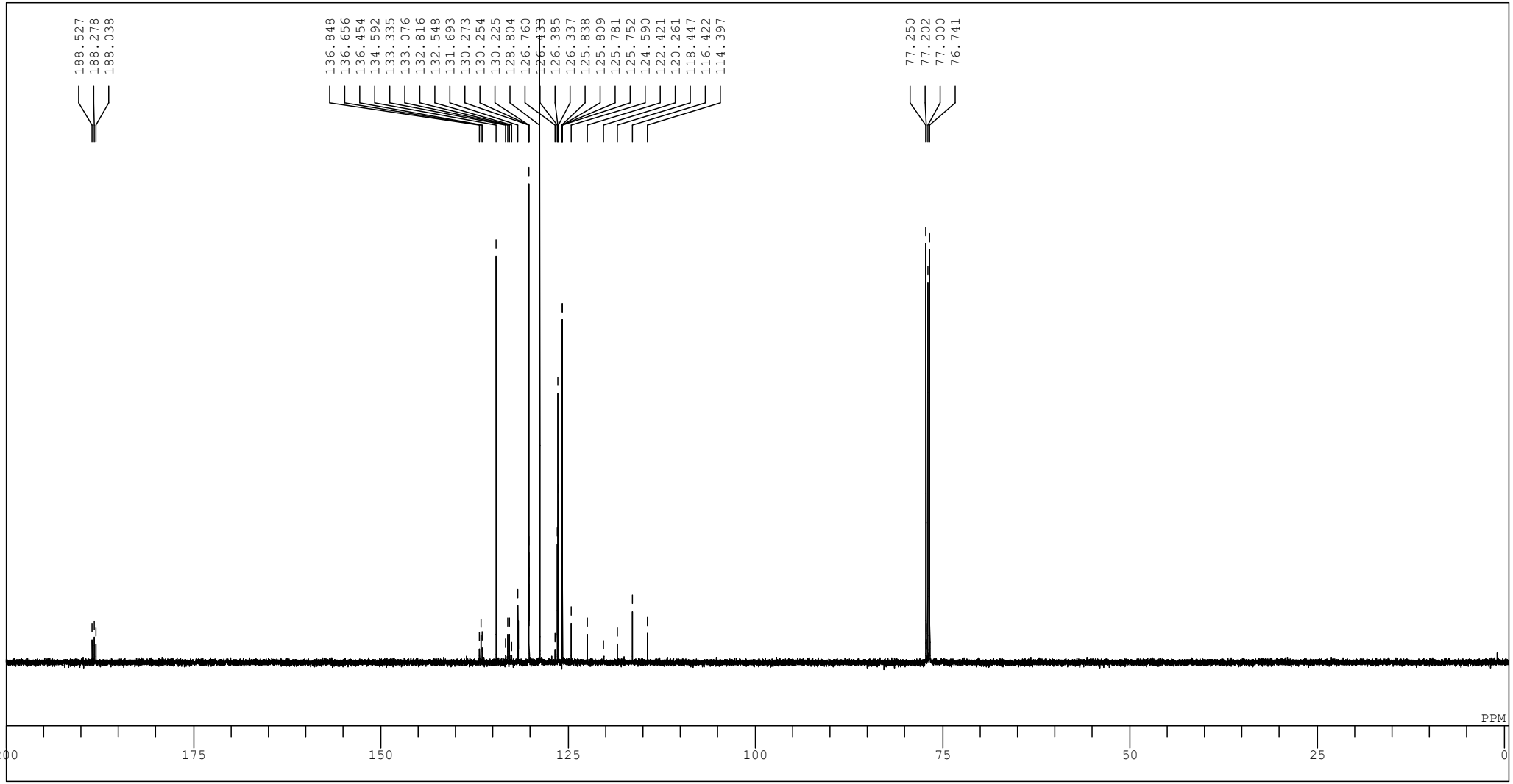

$^{19}F$ NMR (471 MHz, $CDCl_3$)



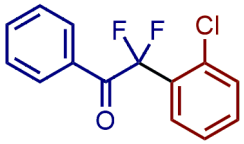
2,2-Difluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (3ae)



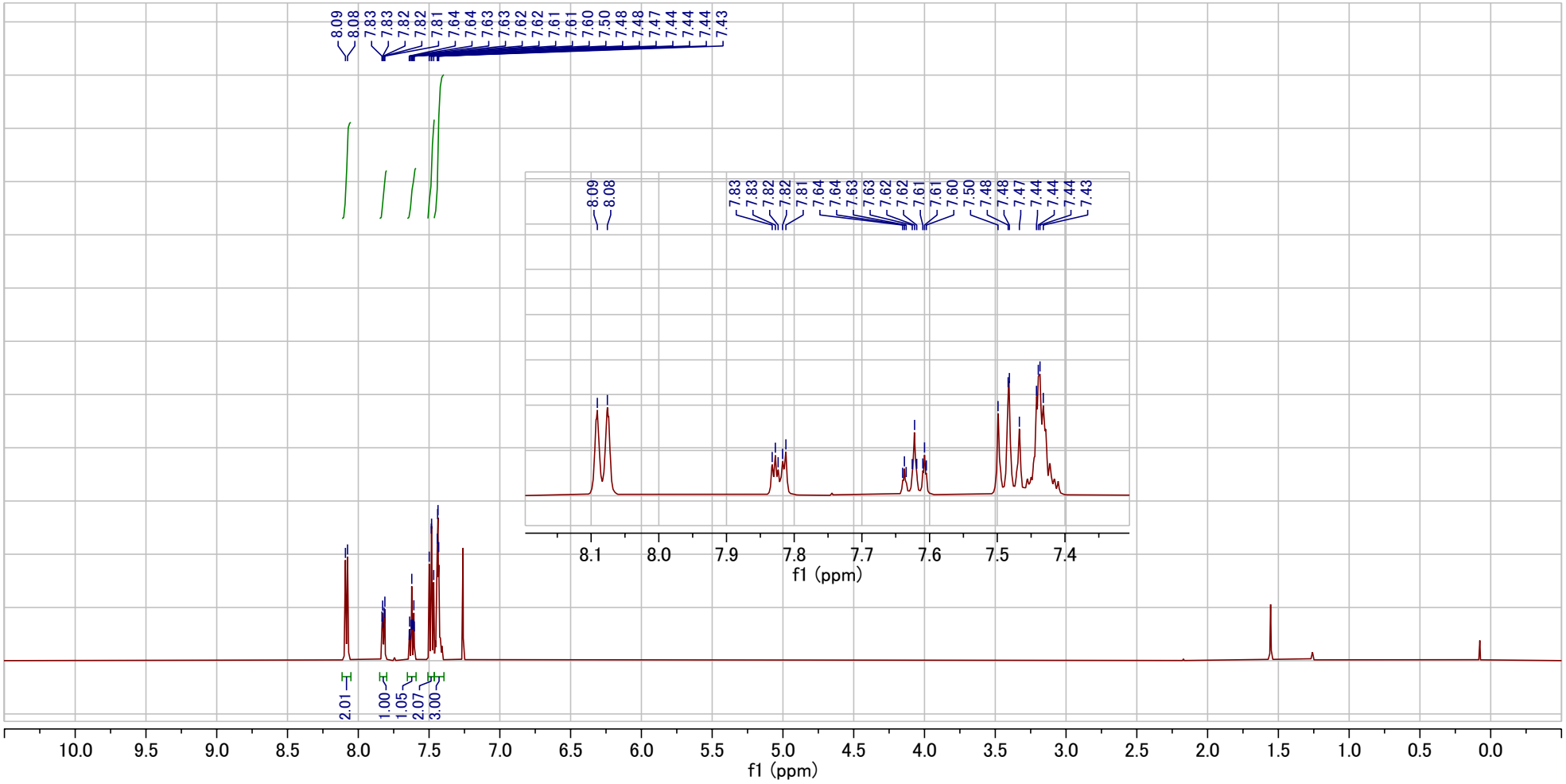

$^{13}C$ NMR (126 MHz, $CDCl_3$)



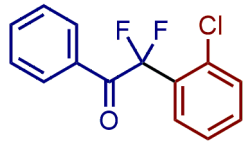
2-(2-Chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (3af)



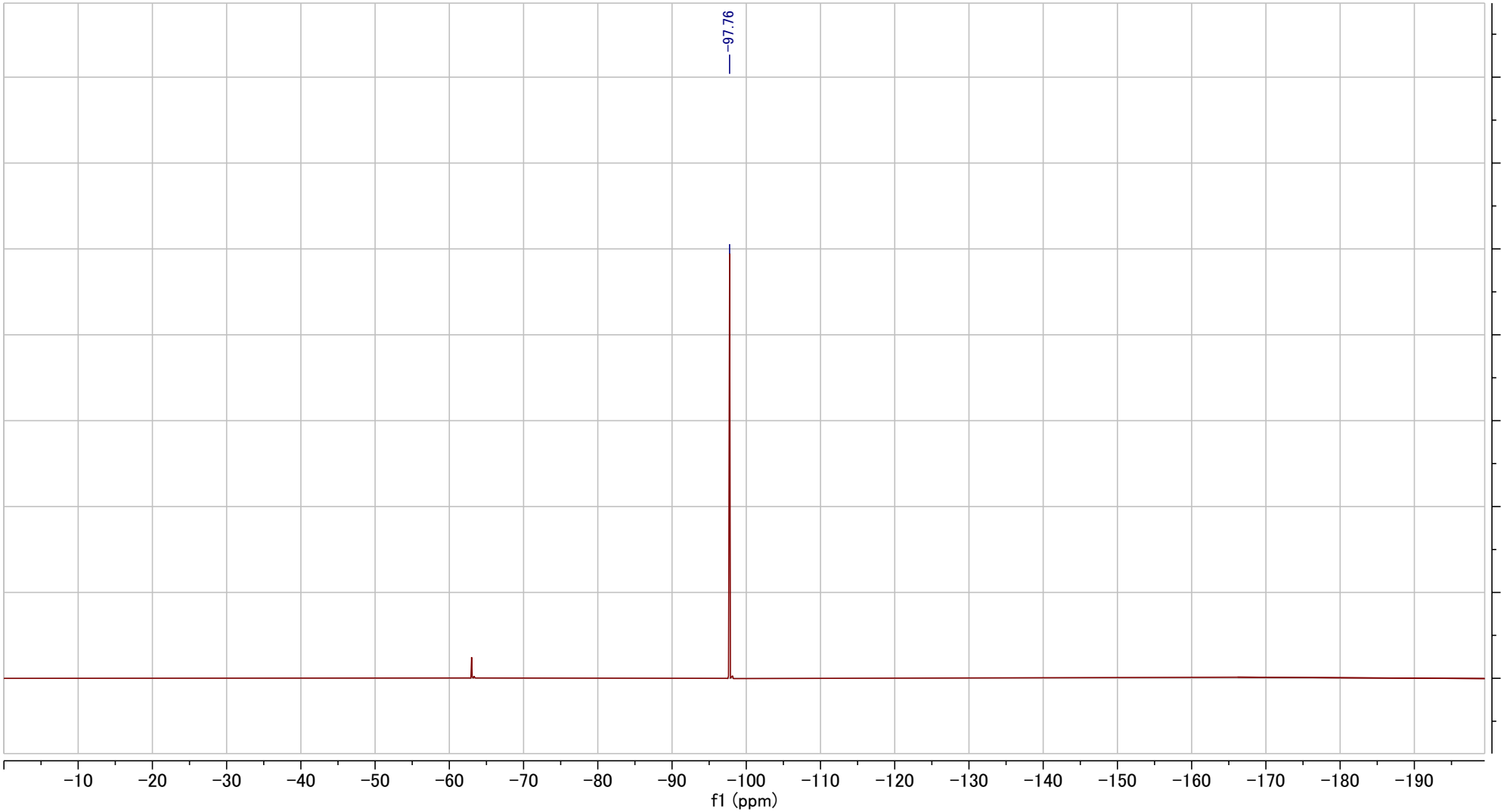

$^1$H NMR (500 MHz, $CDCl_3$)



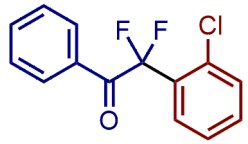
2-(2-Chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (3af)



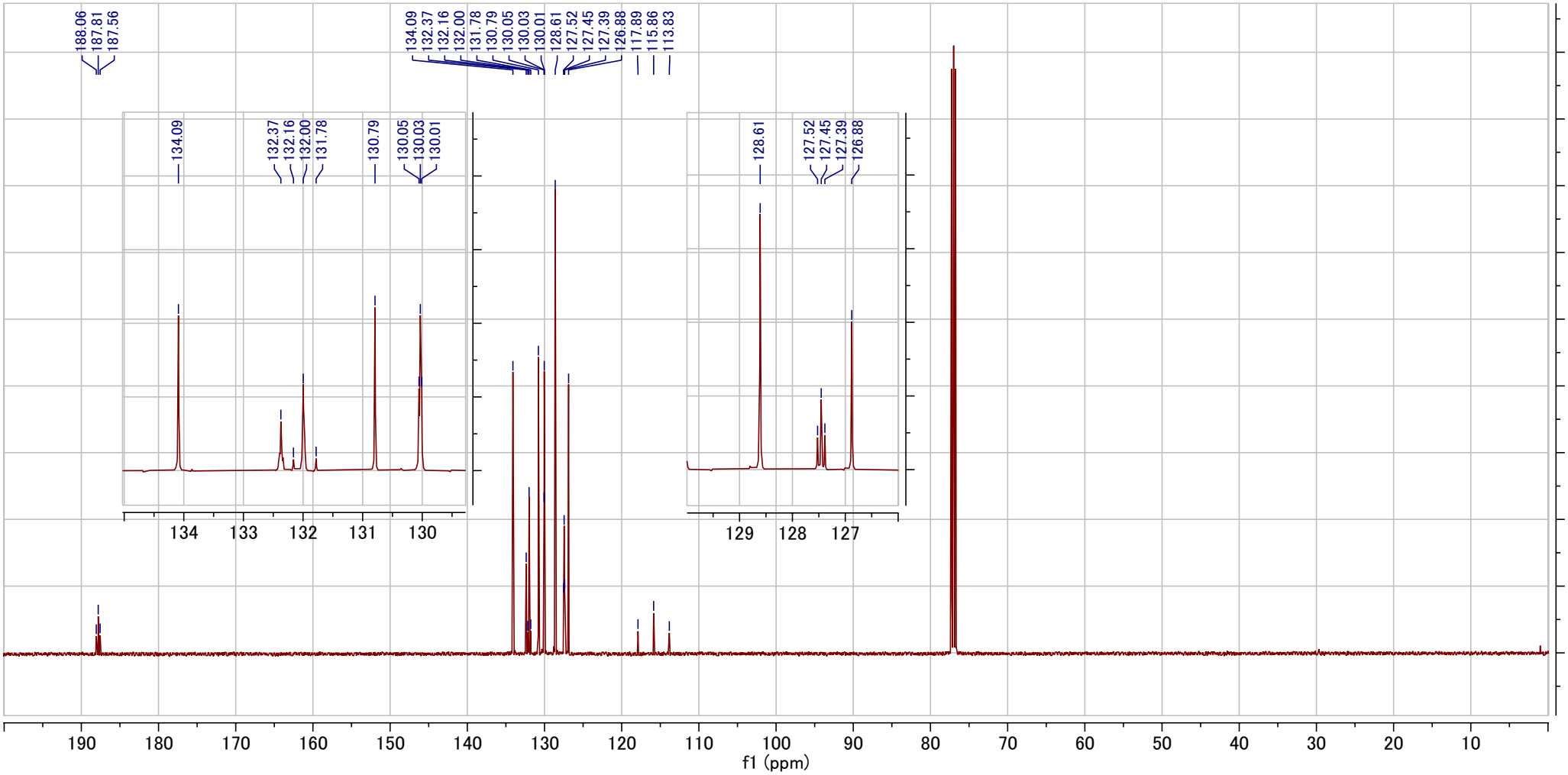

$^{19}F$ NMR (471 MHz, $CDCl_3$)



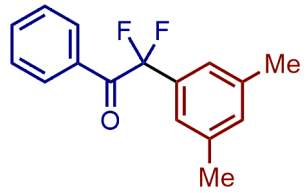
2-(2-Chlorophenyl)-2,2-difluoro-1-phenylethan-1-one (3af)



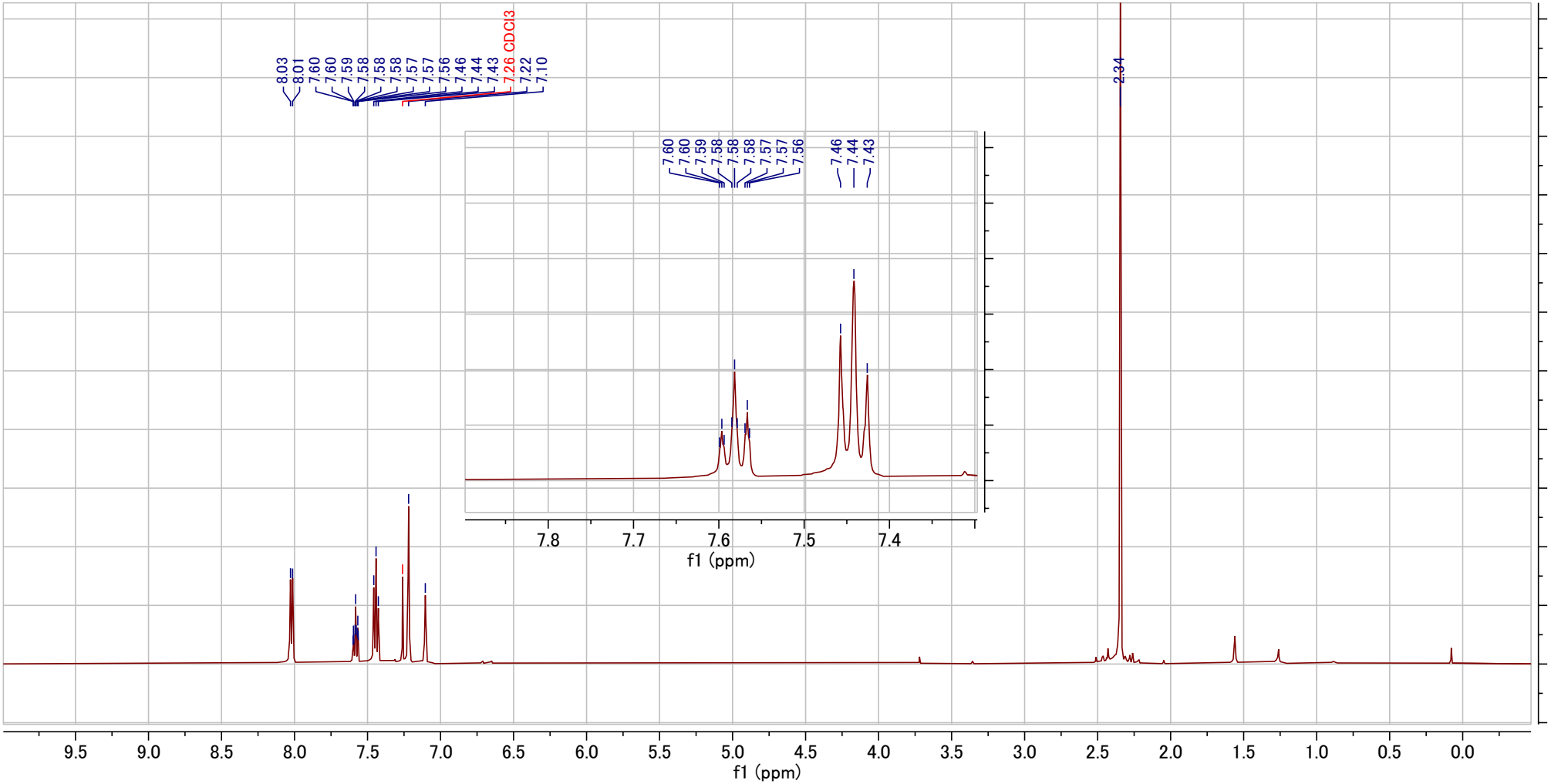

$^{13}C$ NMR (126 MHz, $CDCl_3$)



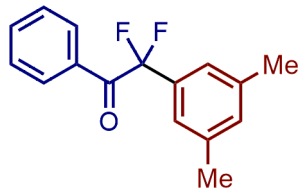
2-(3,5-Dimethylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ag)



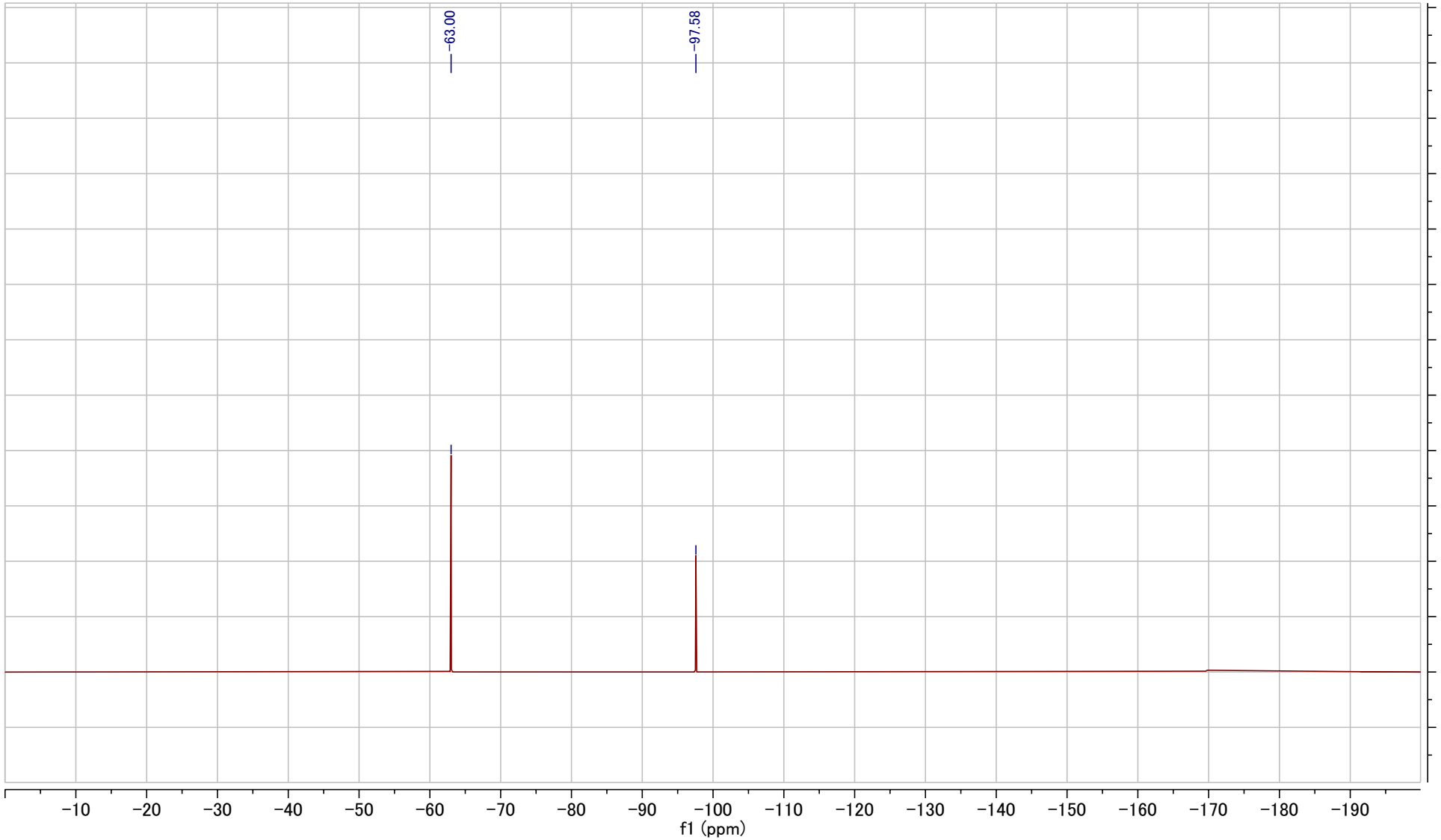

$^1$H NMR (500 MHz, $CDCl_3$)



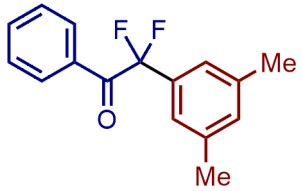
2-(3,5-Dimethylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ag)



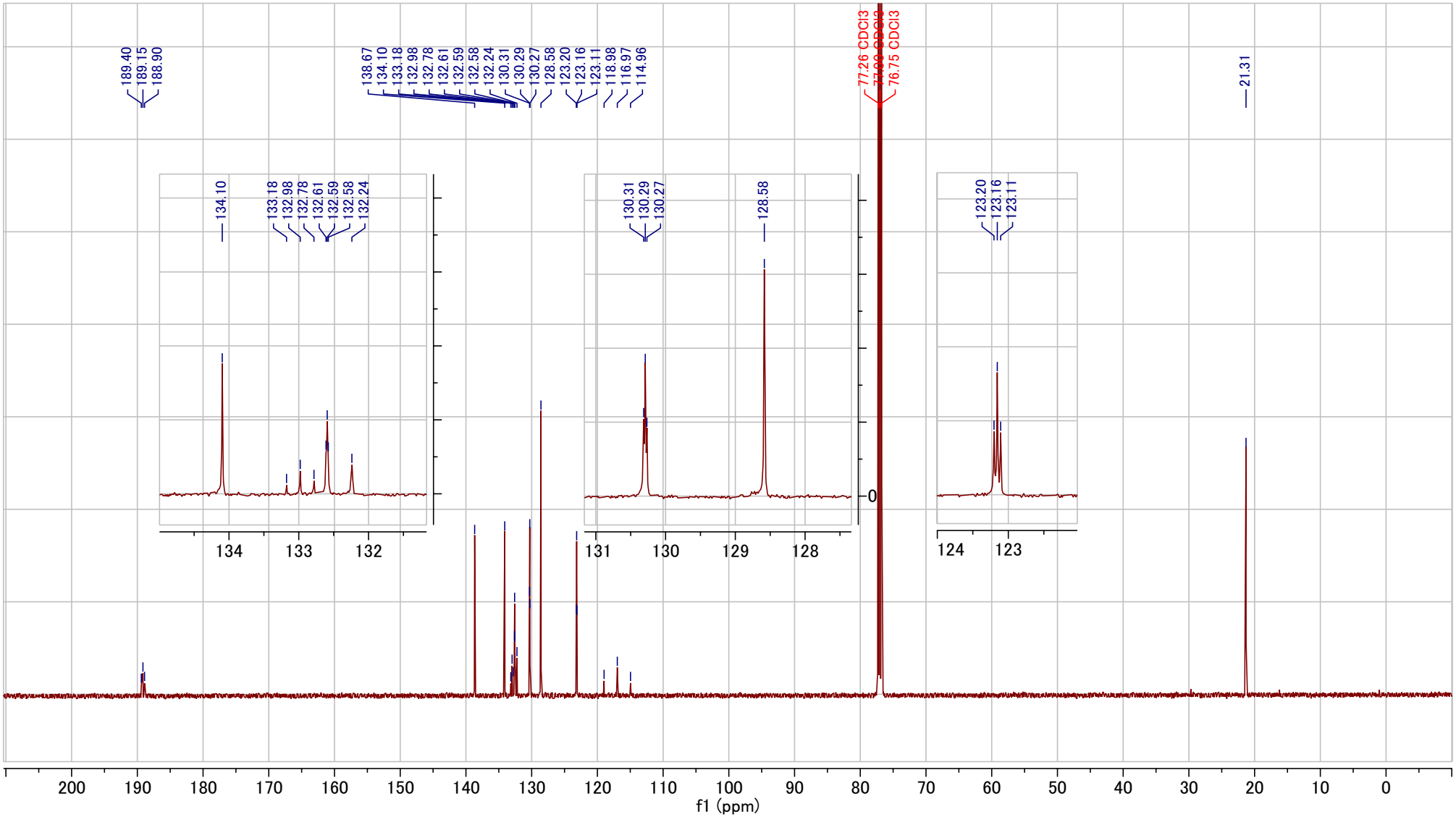

$^{19}F$ NMR (471 MHz, $CDCl_3$)



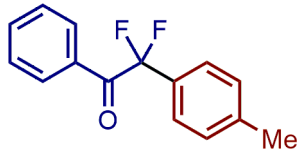
2-(3,5-Dimethylphenyl)-2,2-difluoro-1-phenylethan-1-one (3ag)



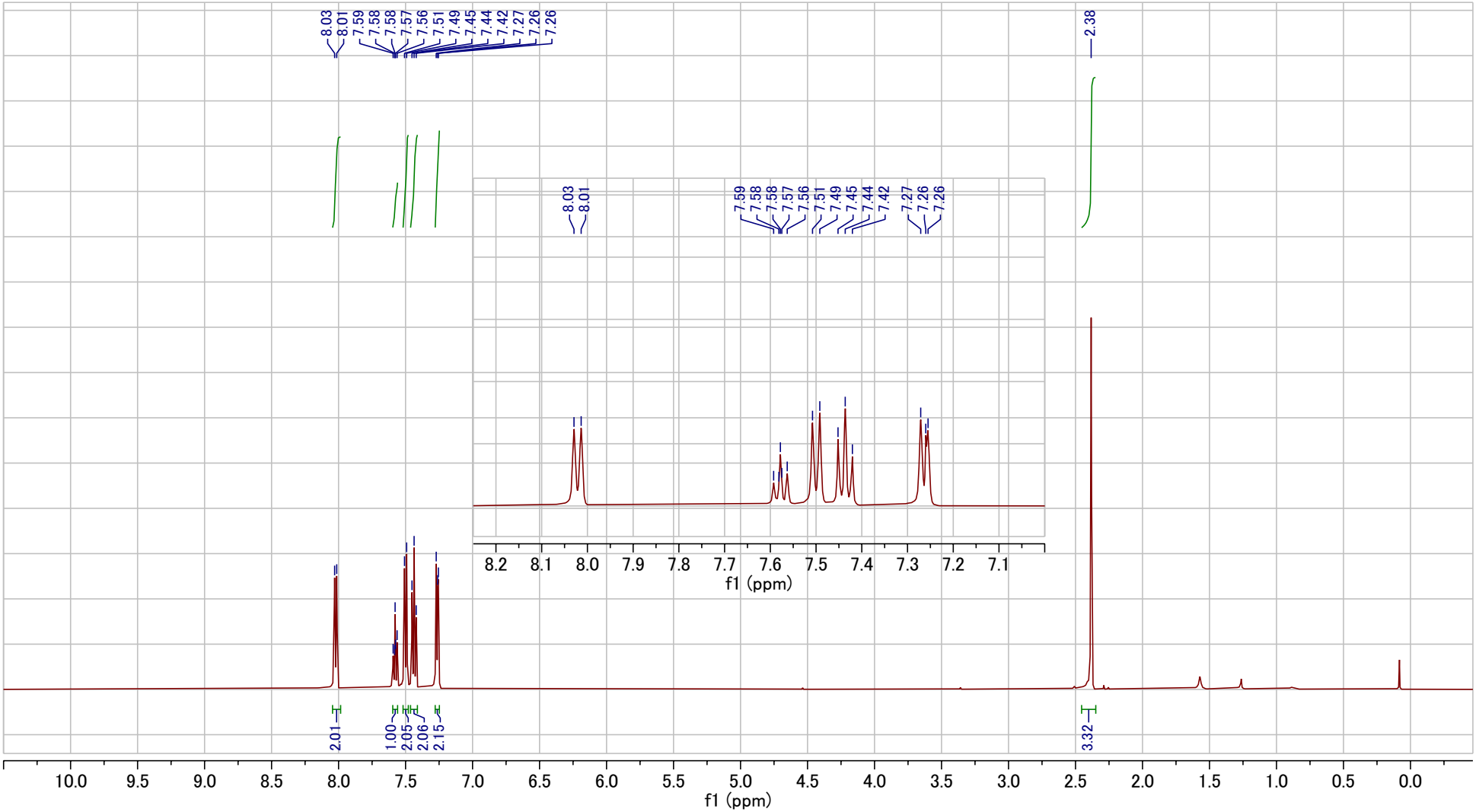

$^{13}C$ NMR (126 MHz, $CDCl_3$)



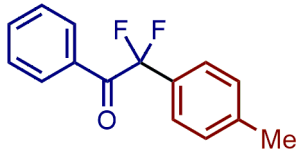
2,2-Difluoro-2-(4-methylphenyl)-1-phenylethan-1-one (3ah)



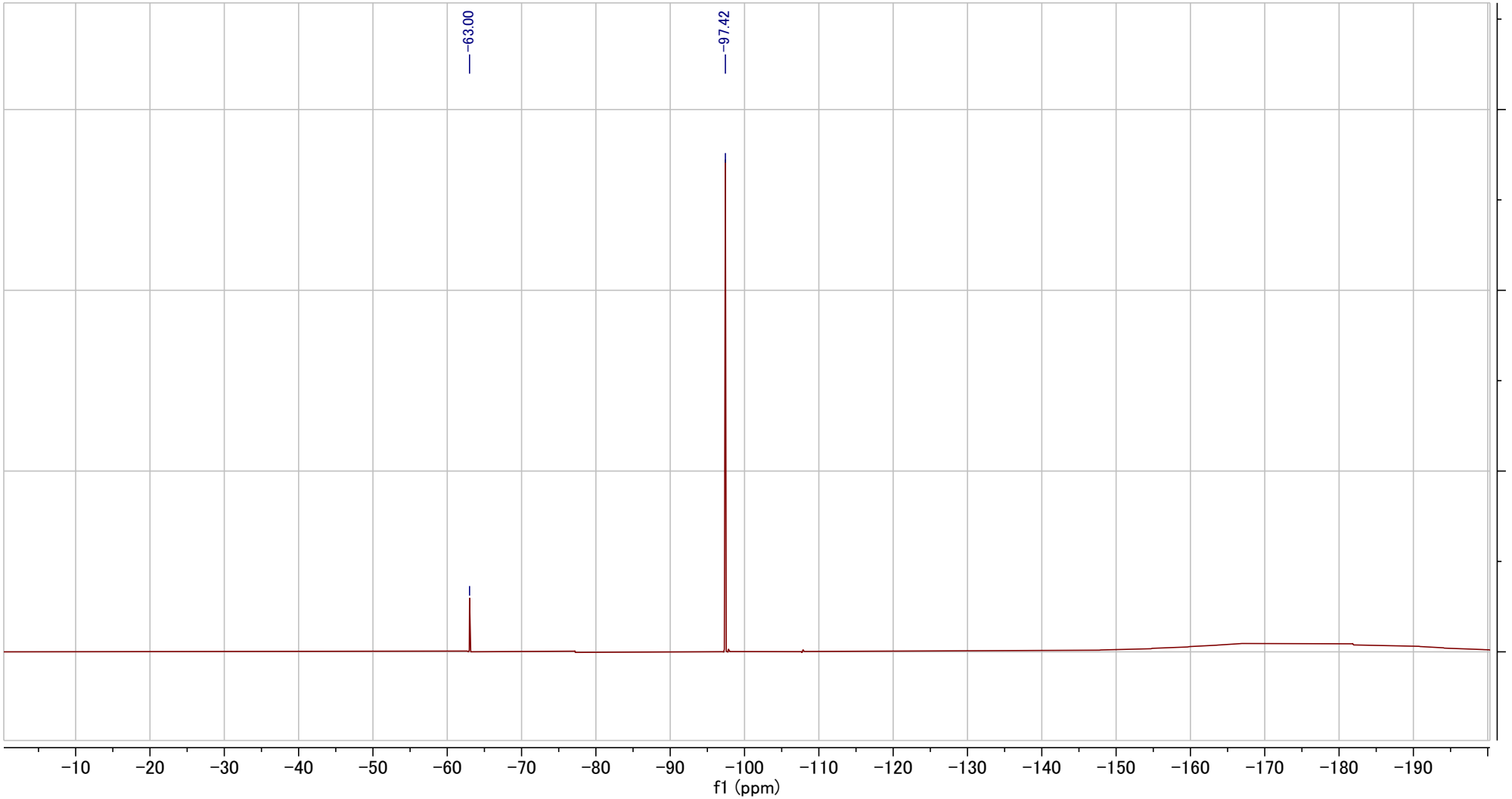

$^1$H NMR (500 MHz, $CDCl_3$)



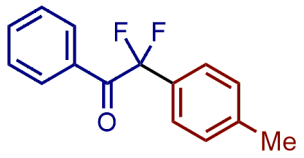
2,2-Difluoro-2-(4-methylphenyl)-1-phenylethan-1-one (3ah)



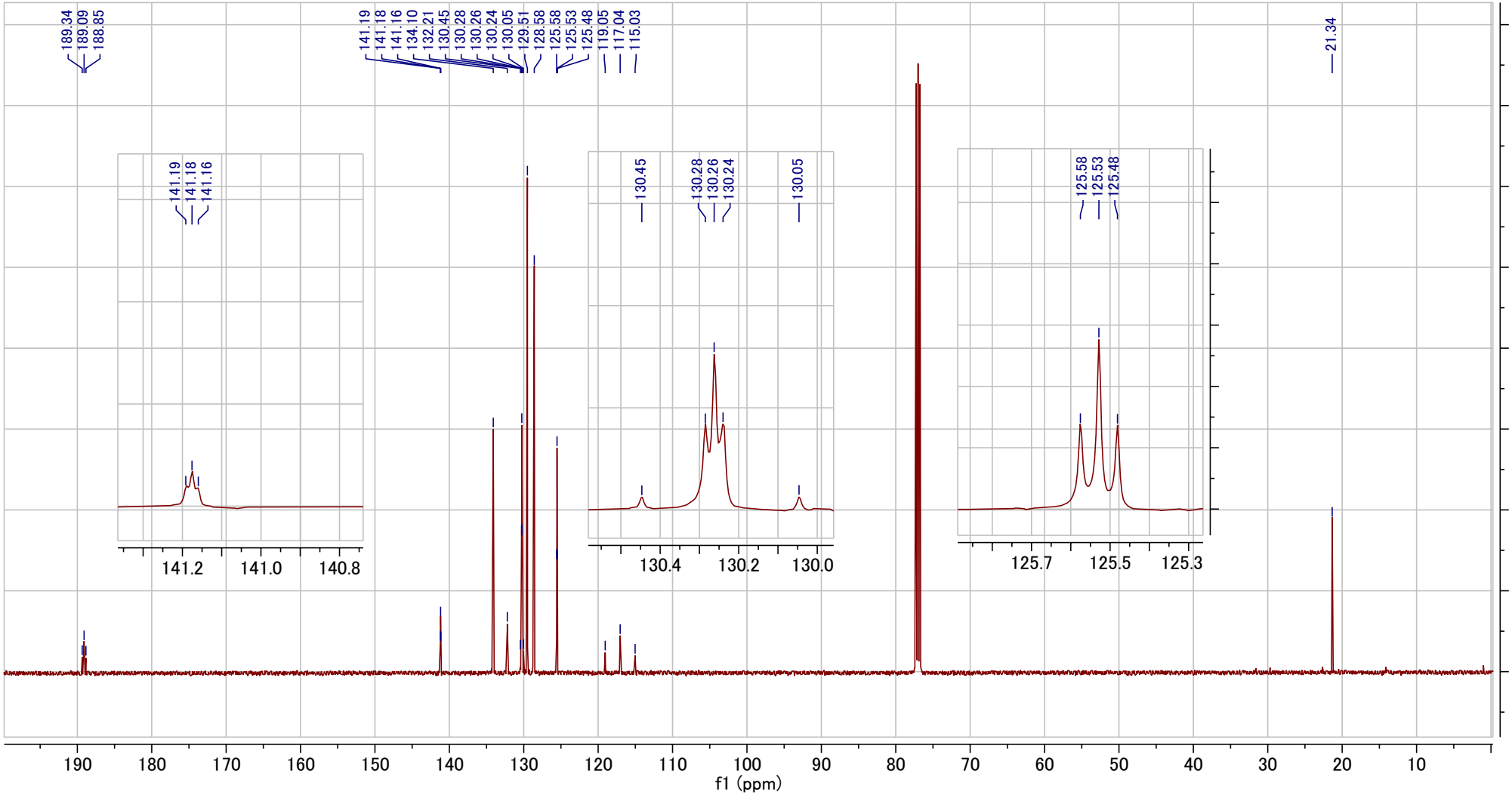

$^{19}F$ NMR (471 MHz, $CDCl_3$)



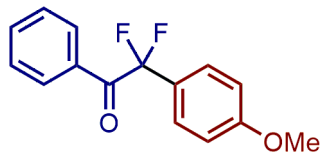
2,2-Difluoro-2-(4-methylphenyl)-1-phenylethan-1-one (3ah)



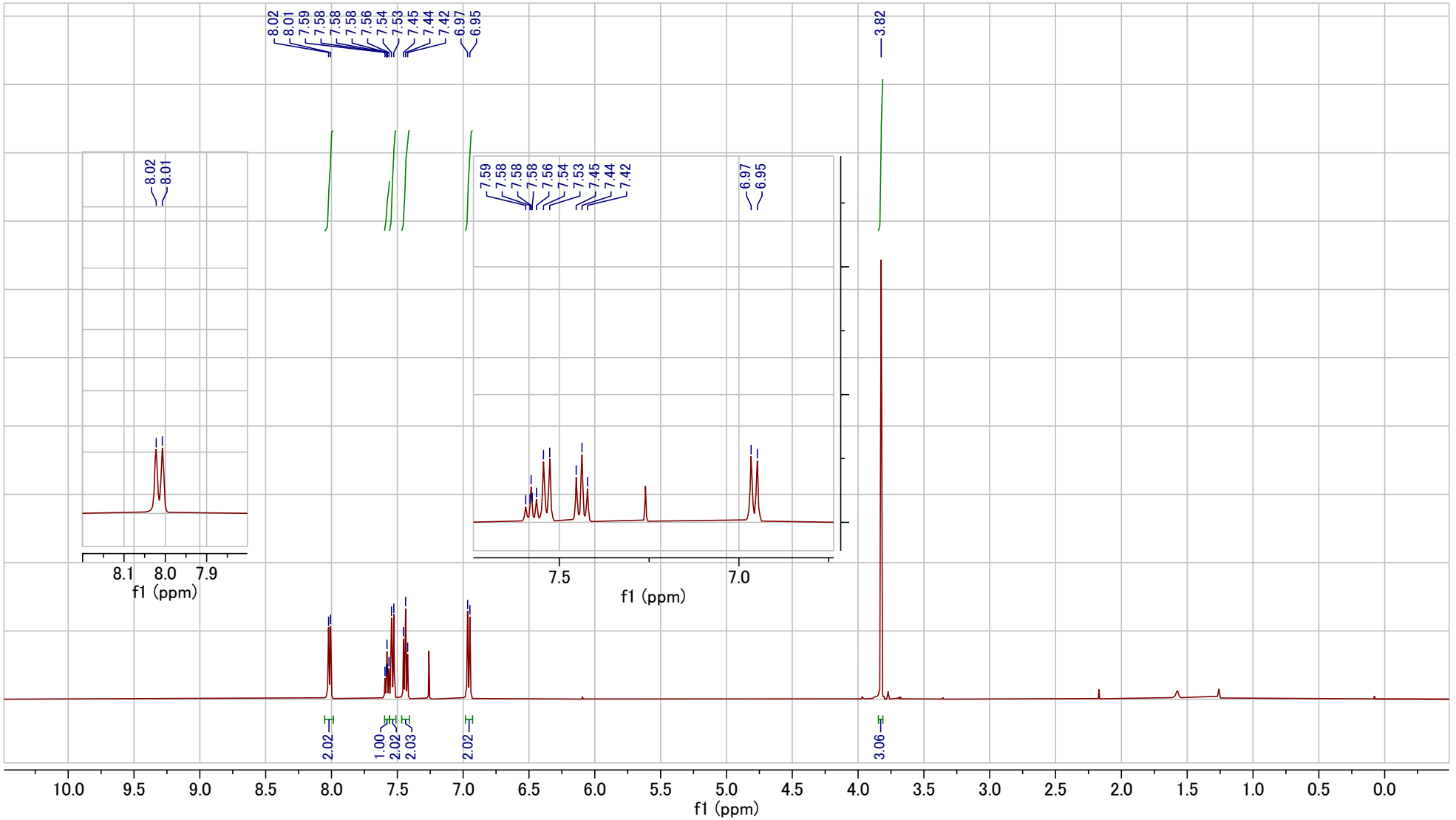

$^{13}C$ NMR (126 MHz, $CDCl_3$)



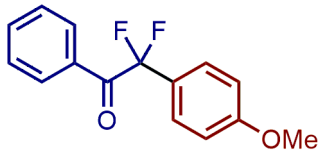
2,2-Difluoro-2-(4-methoxyphenyl)-1-phenylethan-1-one (3ai)



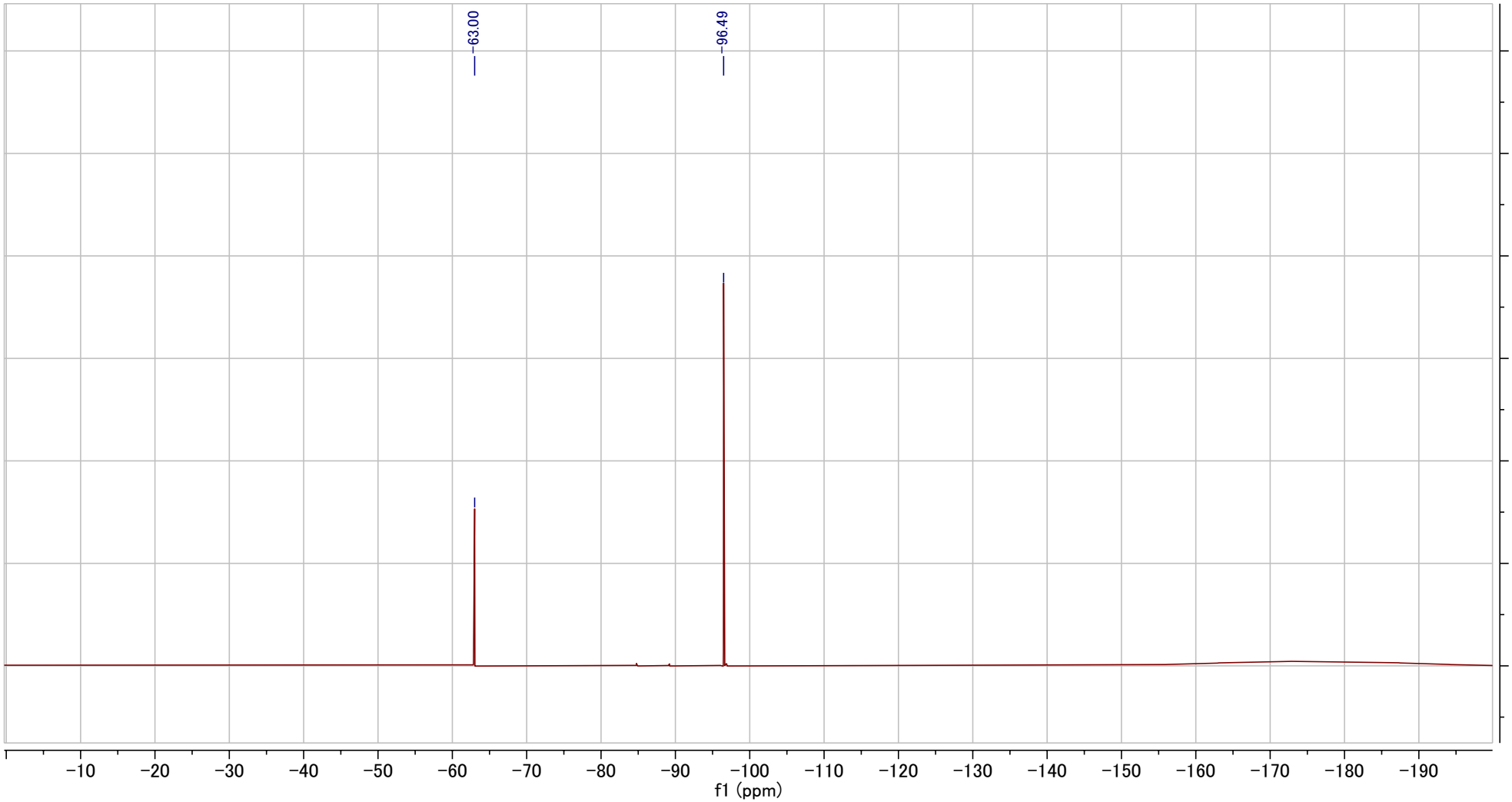

$^1$H NMR (500 MHz, $CDCl_3$)



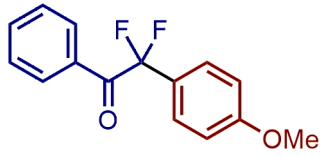
2,2-Difluoro-2-(4-methoxyphenyl)-1-phenylethan-1-one (3ai)



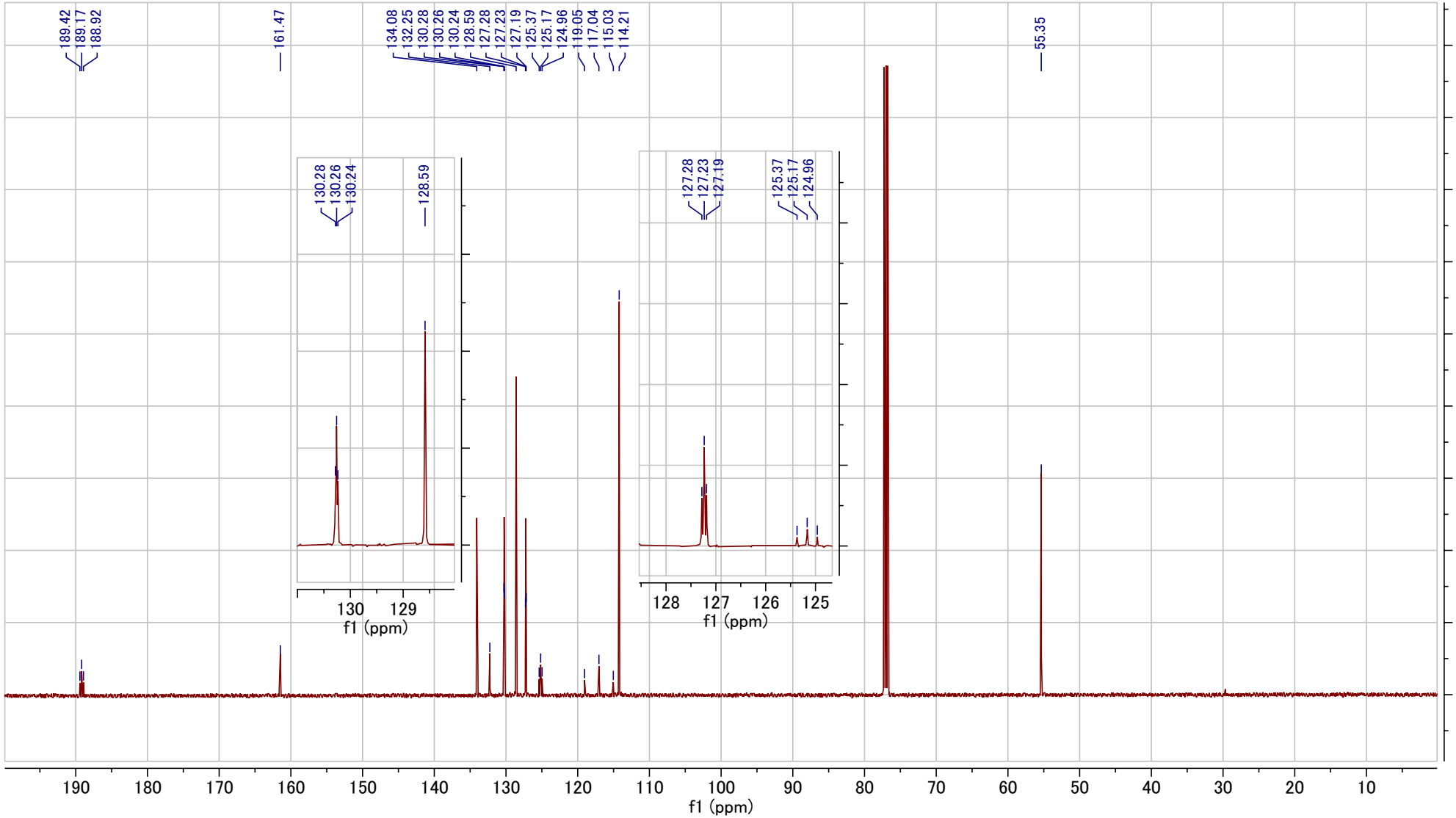

$^{19}F$ NMR (471 MHz, $CDCl_3$)



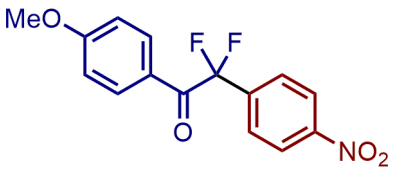
2,2-Difluoro-2-(4-methoxyphenyl)-1-phenylethan-1-one (3ai)



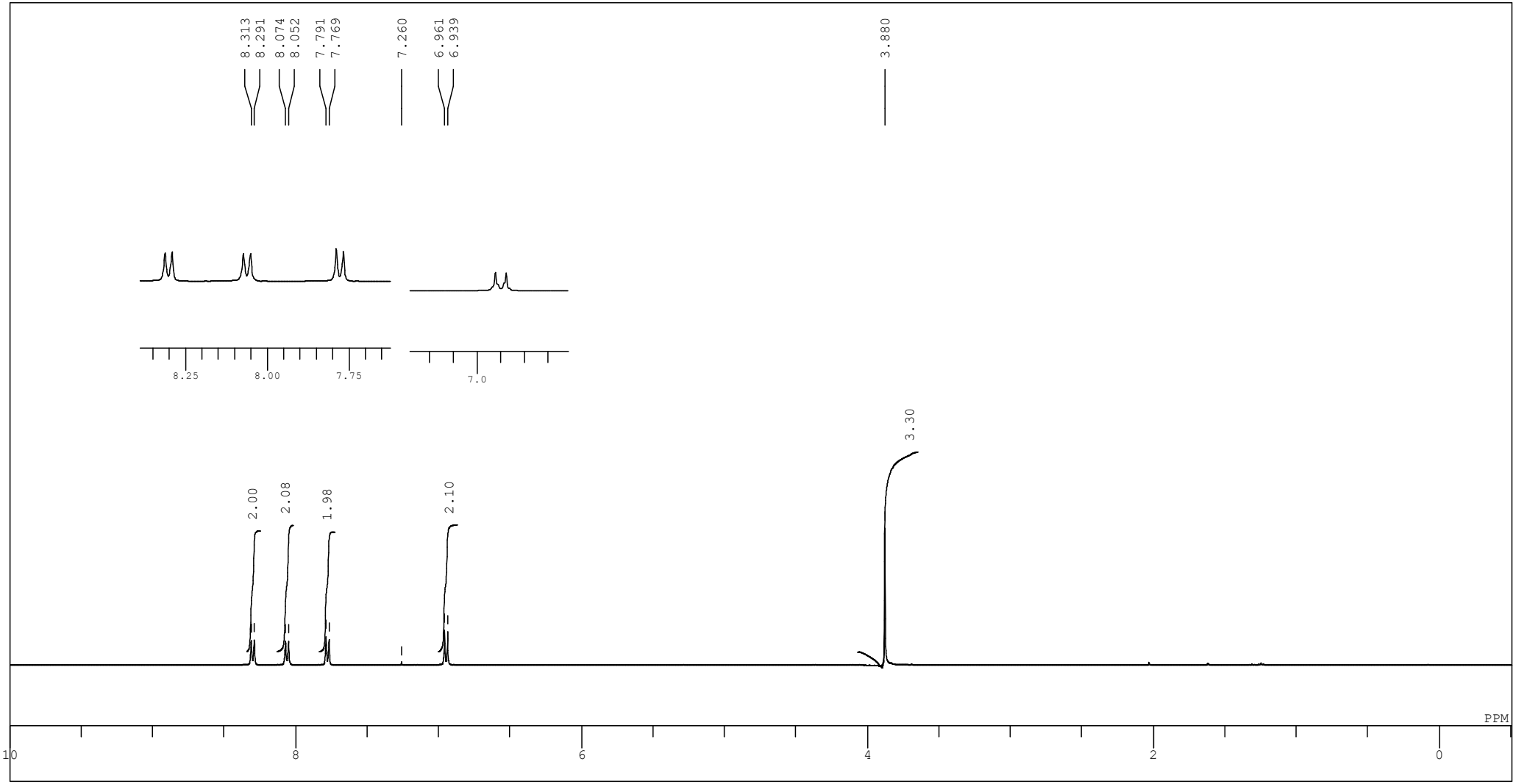

$^{13}C$ NMR (126 MHz, $CDCl_3$)



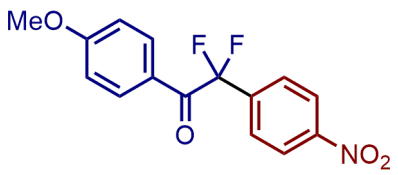
2,2-Difluoro-1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (3ba)



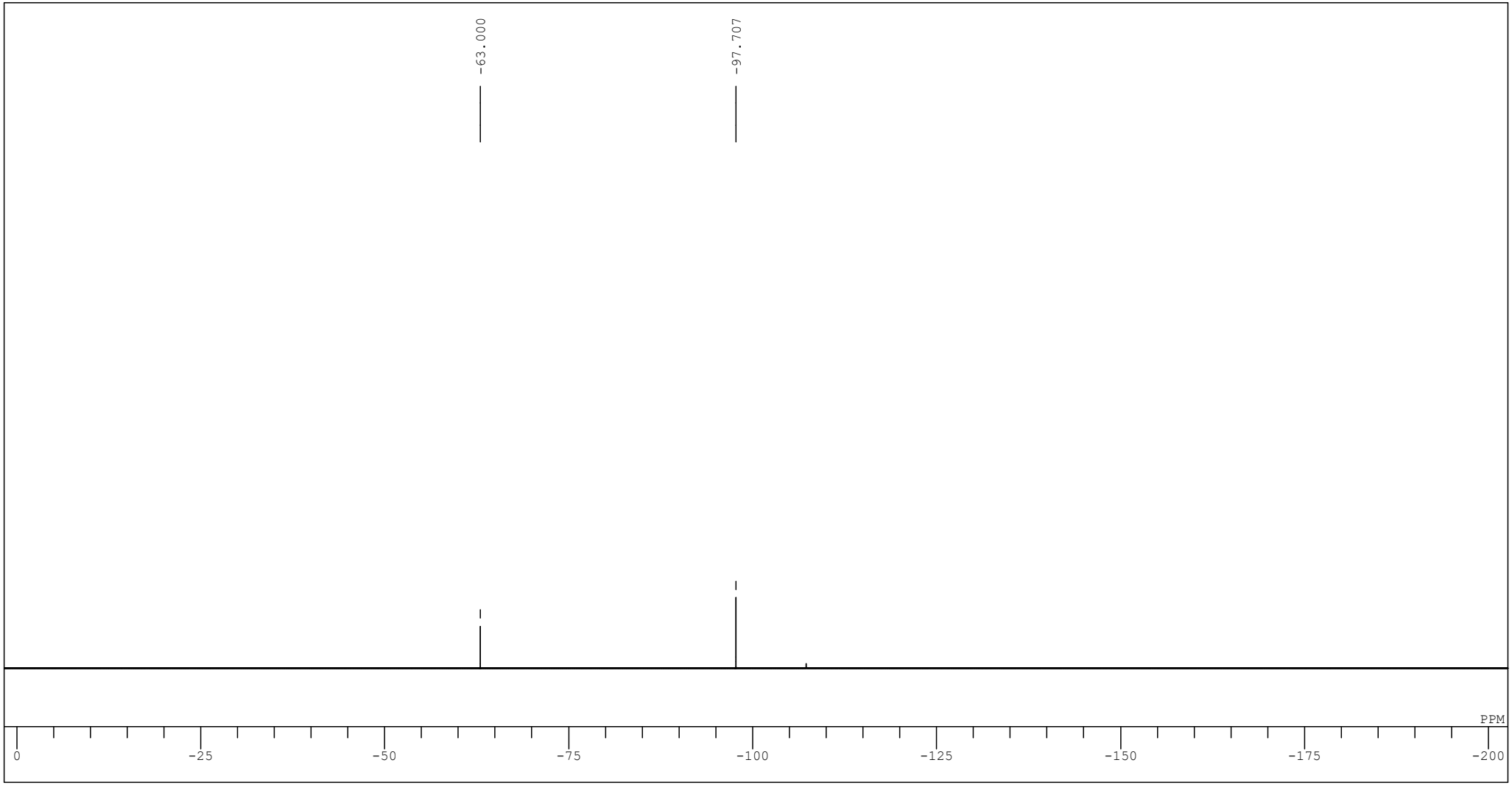

$^1$H NMR (400 MHz, $CDCl_3$)



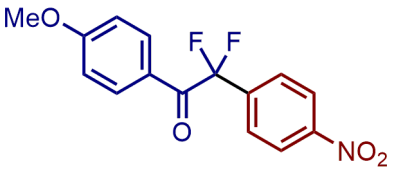
2,2-Difluoro-1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (3ba)



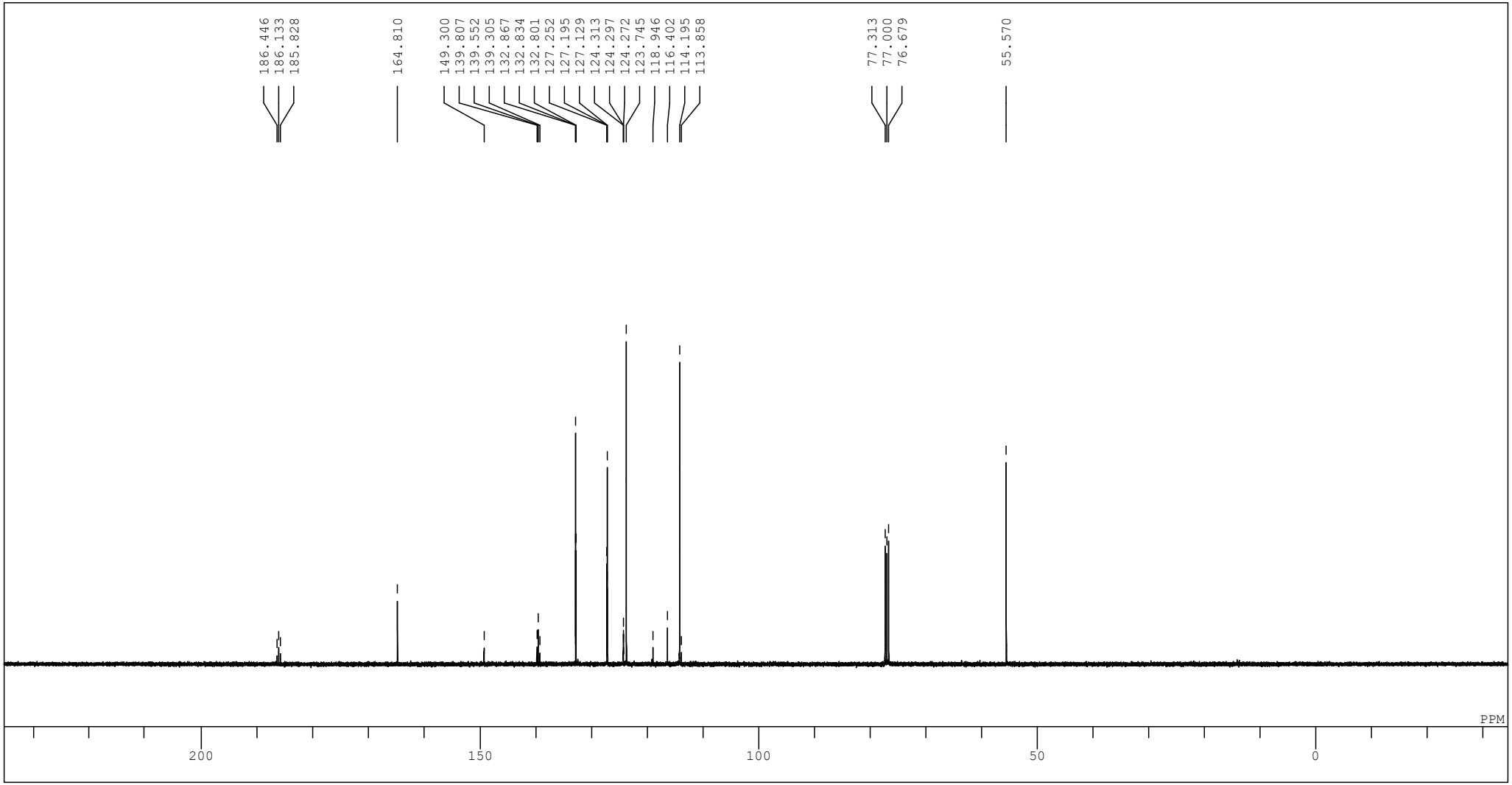

$^{19}F$ NMR (376 MHz, $CDCl_3$)



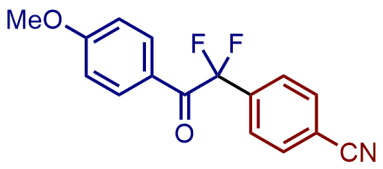
2,2-Difluoro-1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (3ba)



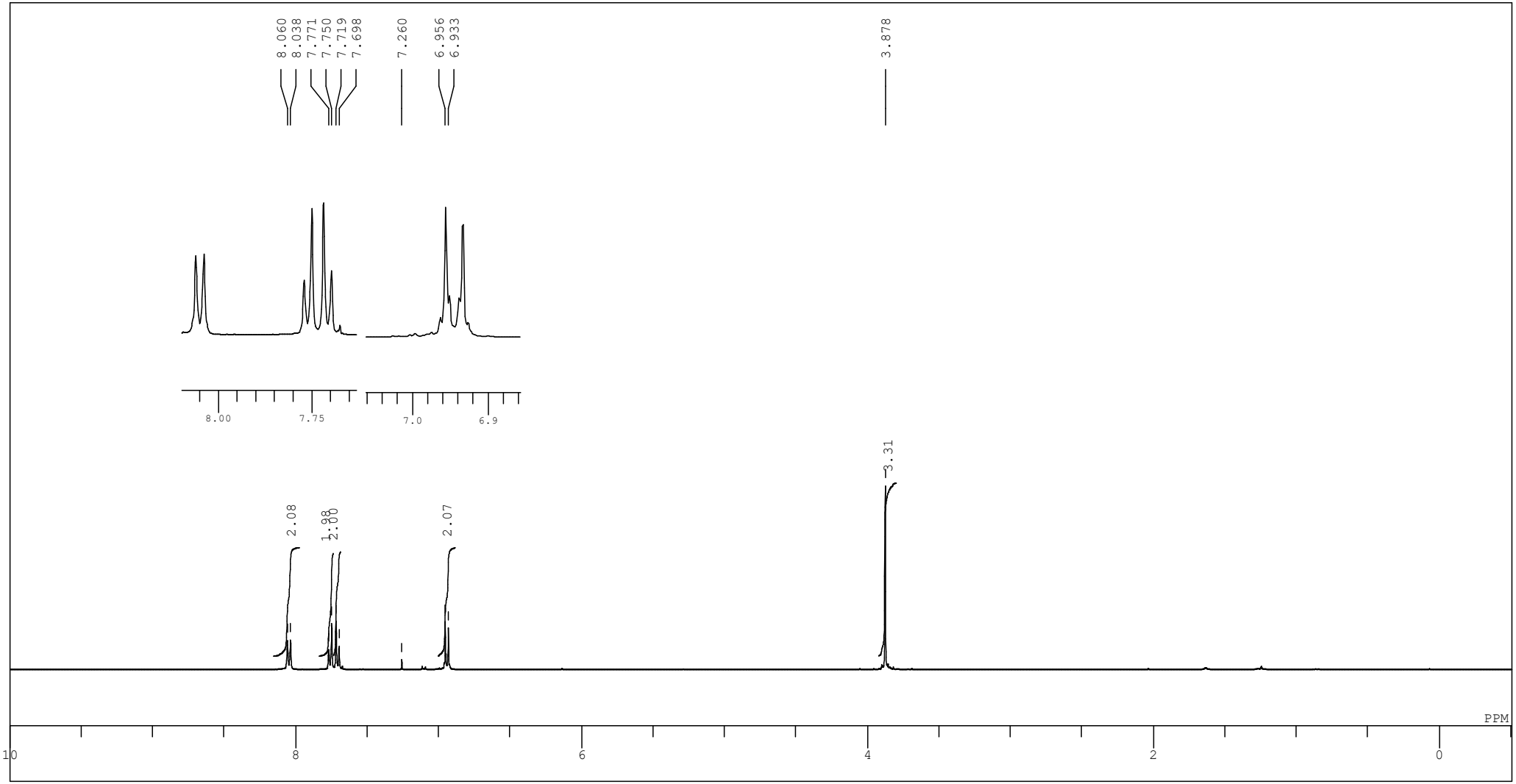

$^{13}C$ NMR (100 MHz, $CDCl_3$)



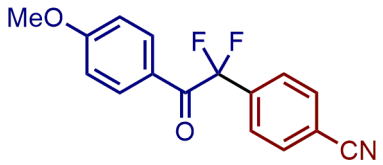
4-(1,1-Difluoro-2-(4-methoxyphenyl)-2-oxoethyl)benzonitrile (3bb)



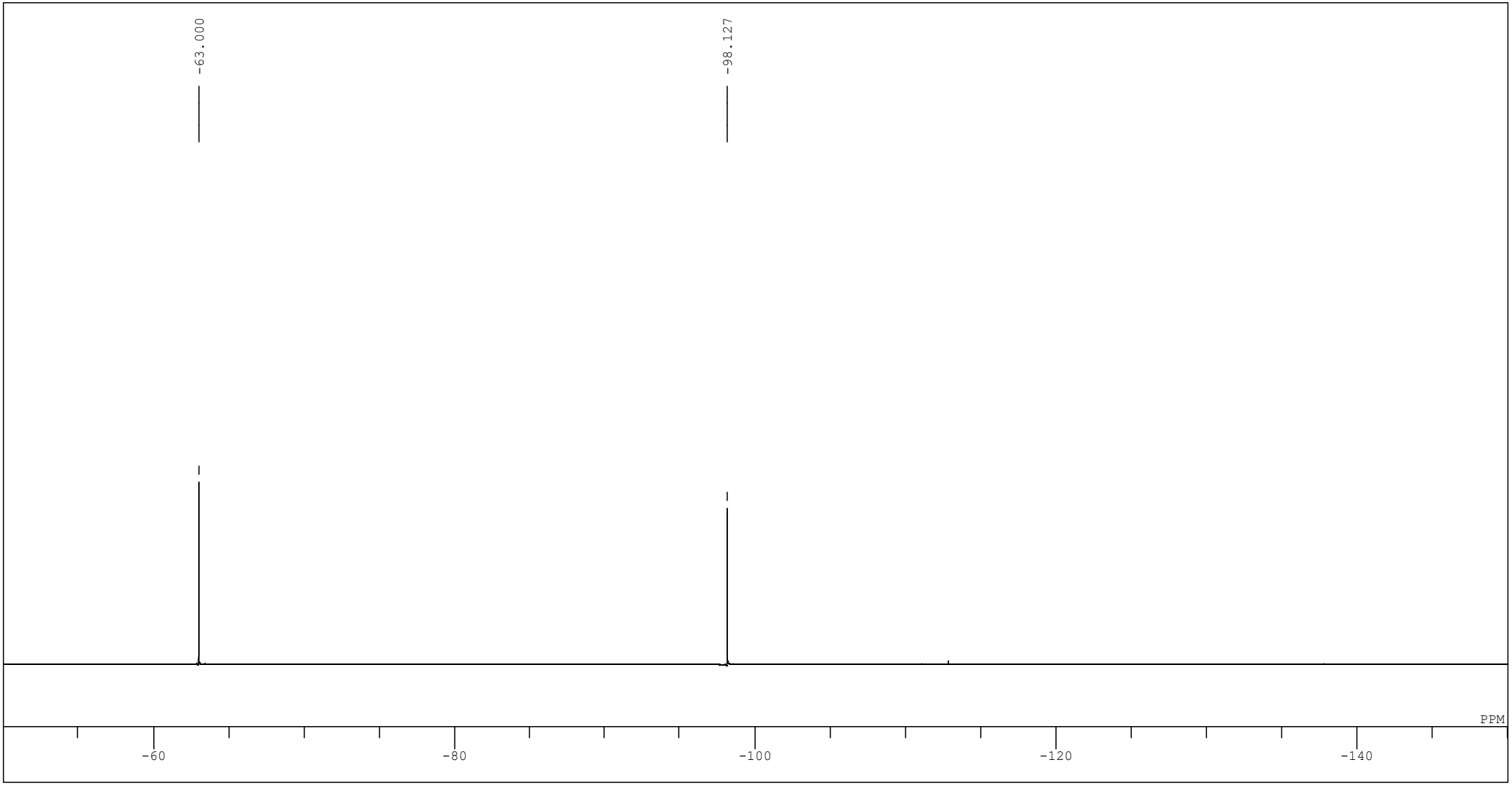

$^1$H NMR (400 MHz, $CDCl_3$)



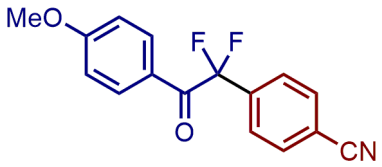
4-(1,1-Difluoro-2-(4-methoxyphenyl)-2-oxoethyl)benzonitrile (3bb)



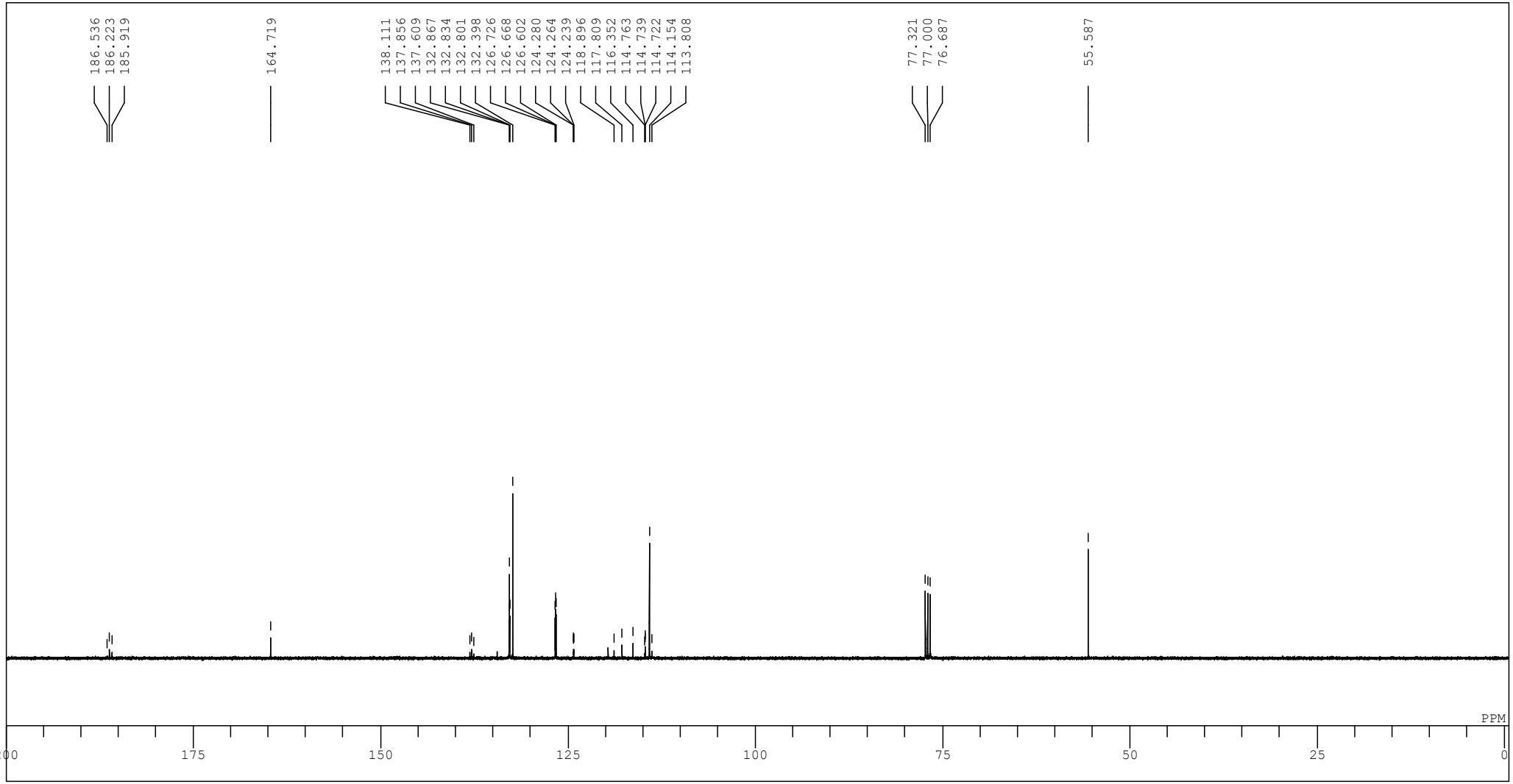

$^{19}F$ NMR (471 MHz, $CDCl_3$)



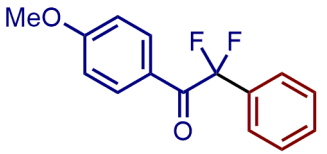
4-(1,1-Difluoro-2-(4-methoxyphenyl)-2-oxoethyl)benzonitrile (3bb)



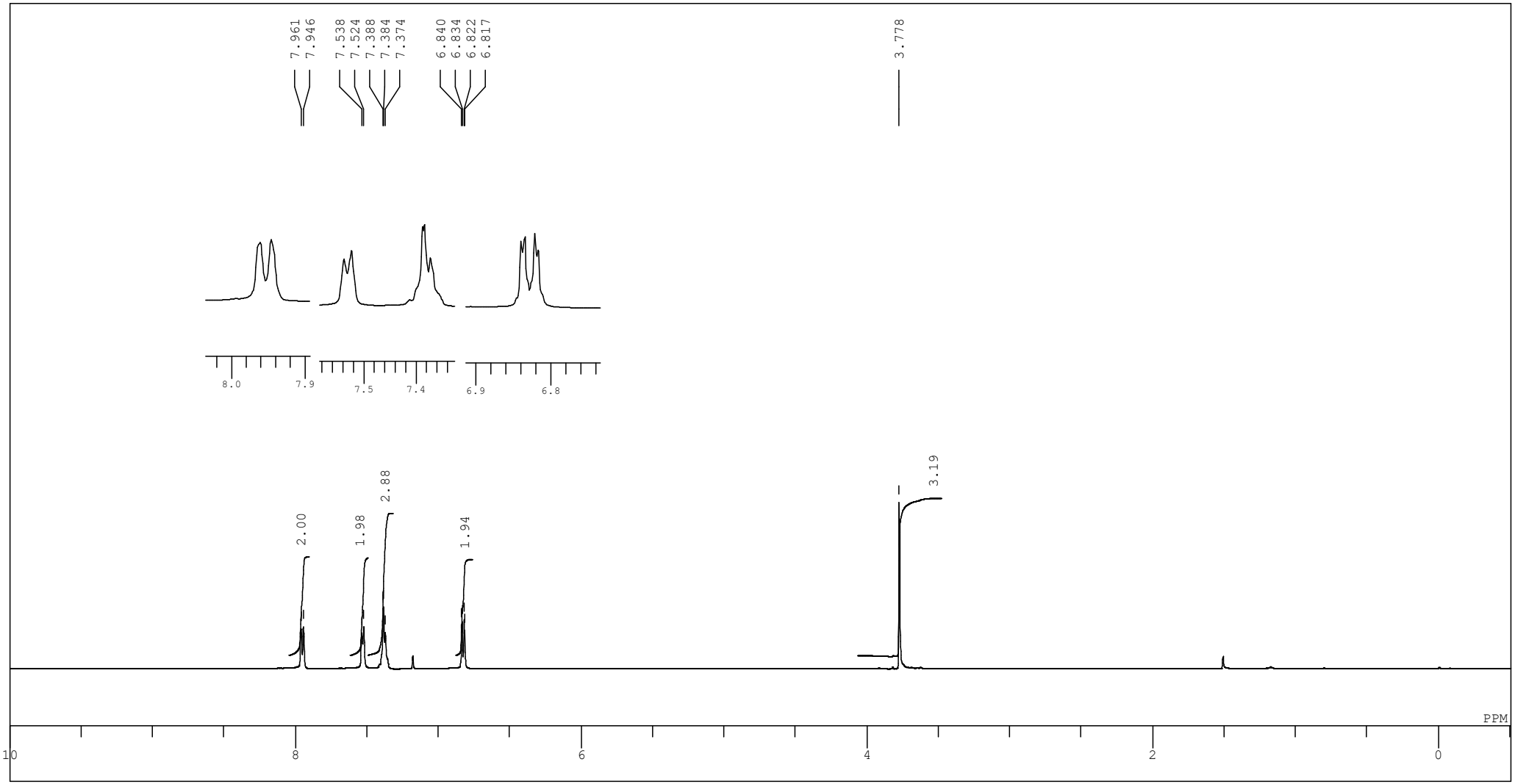

$^{13}C$ NMR (100 MHz, $CDCl_3$)



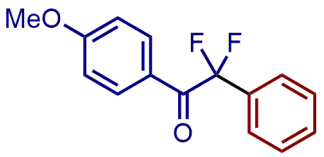
2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylethan-1-one (3bj)



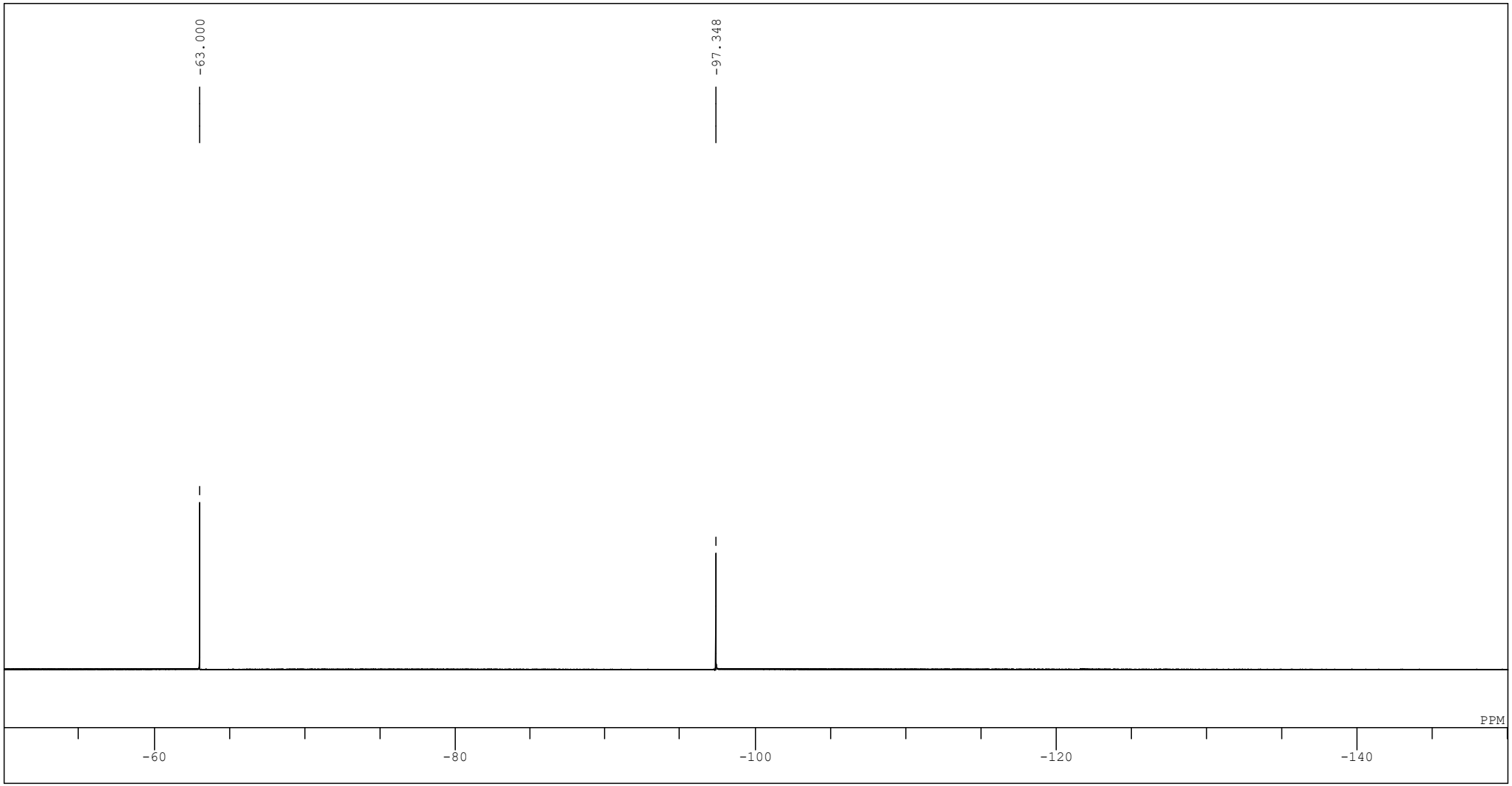

$^1$H NMR (500 MHz, $CDCl_3$)



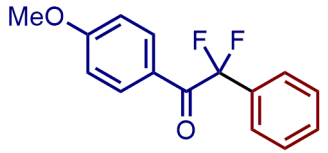
2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylethan-1-one (3bj)



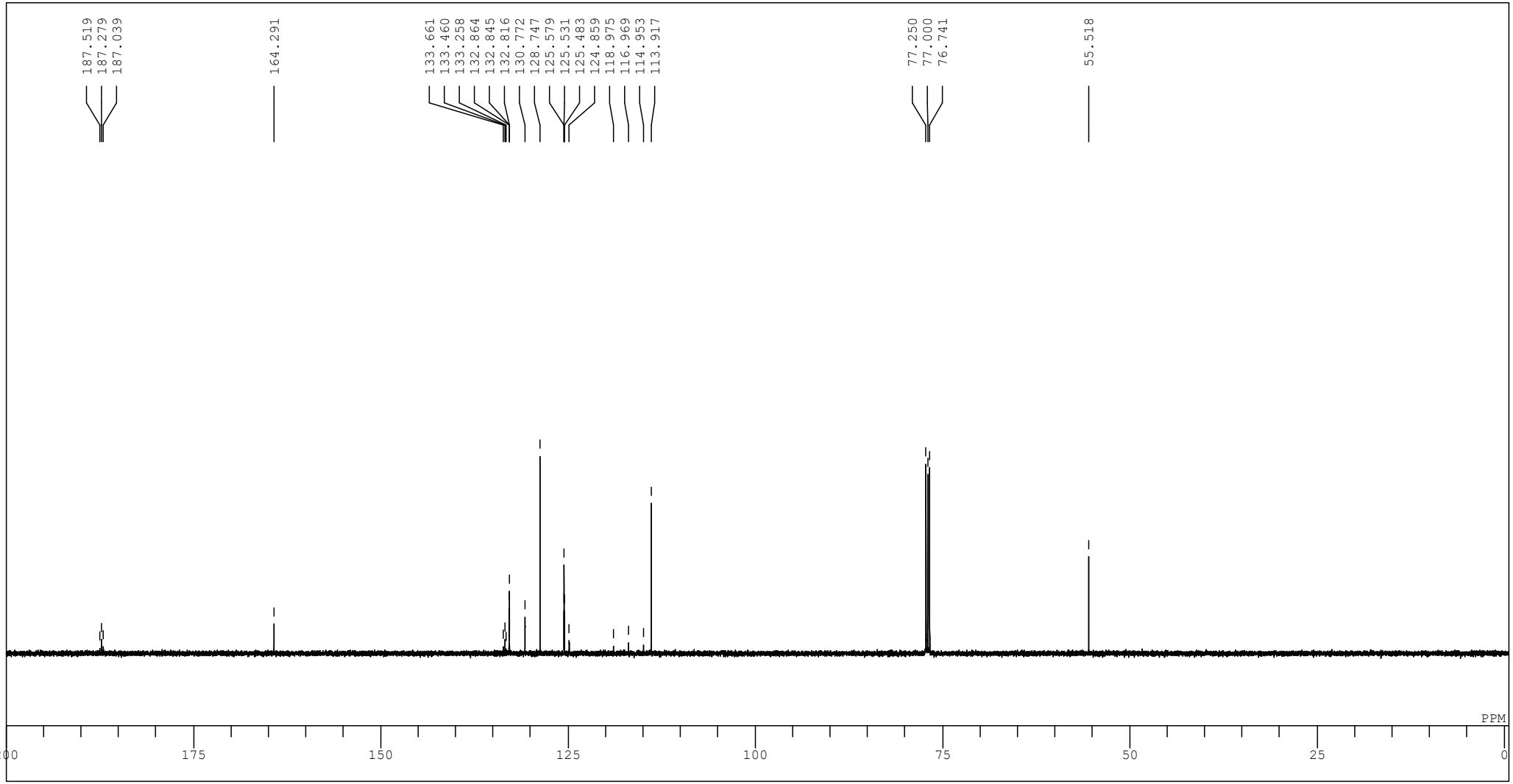

$^{19}F$ NMR (471 MHz, $CDCl_3$)



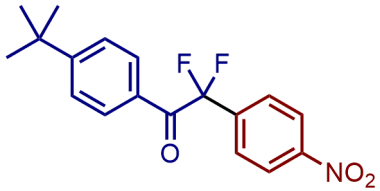
2,2-Difluoro-1-(4-methoxyphenyl)-2-phenylethan-1-one (3bj)



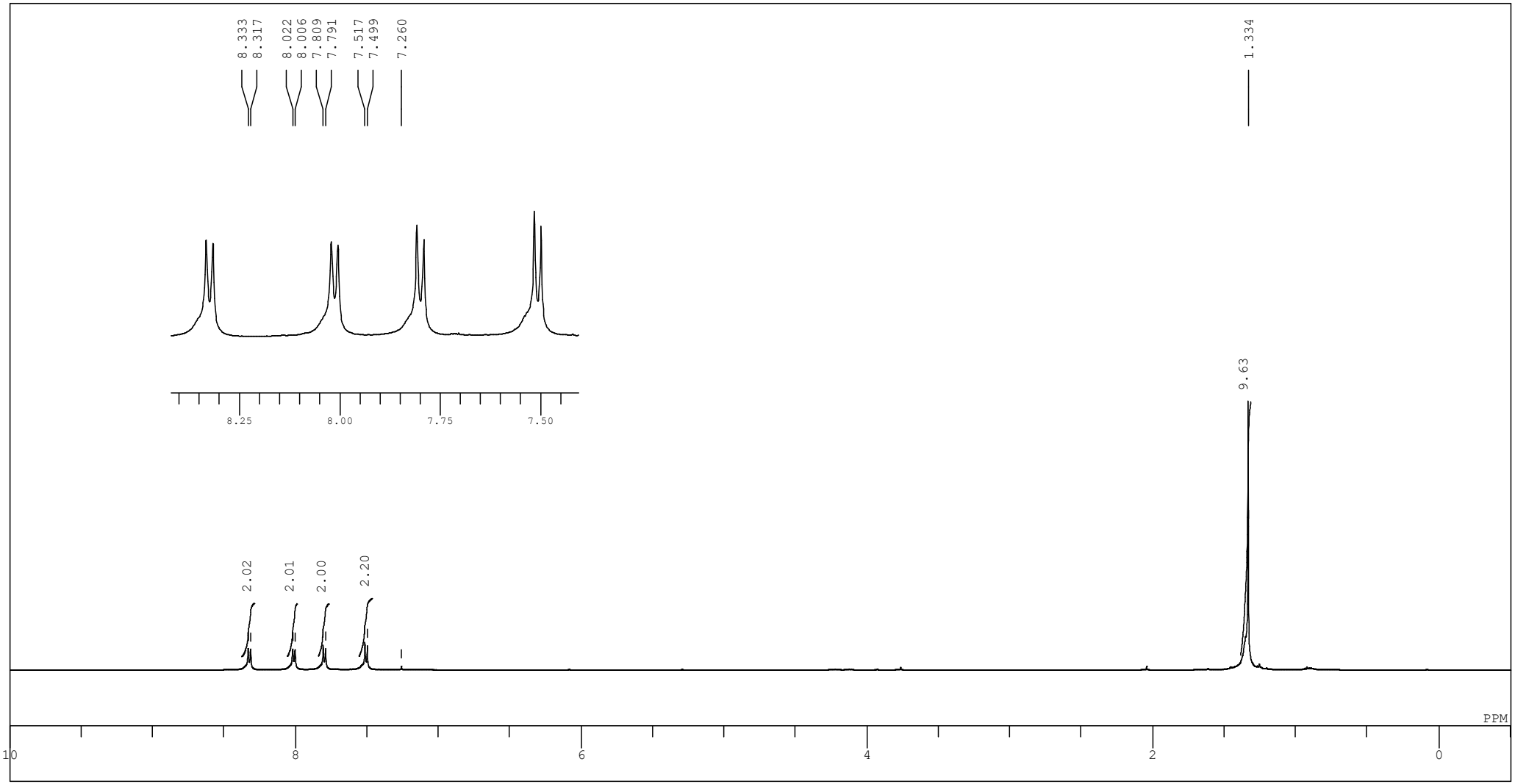

$^{13}C$ NMR (126 MHz, $CDCl_3$)



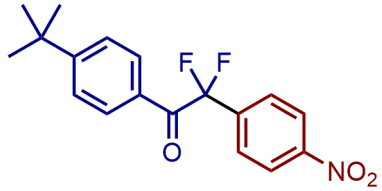
1-(4-(*tert*-Butyl)phenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ca)



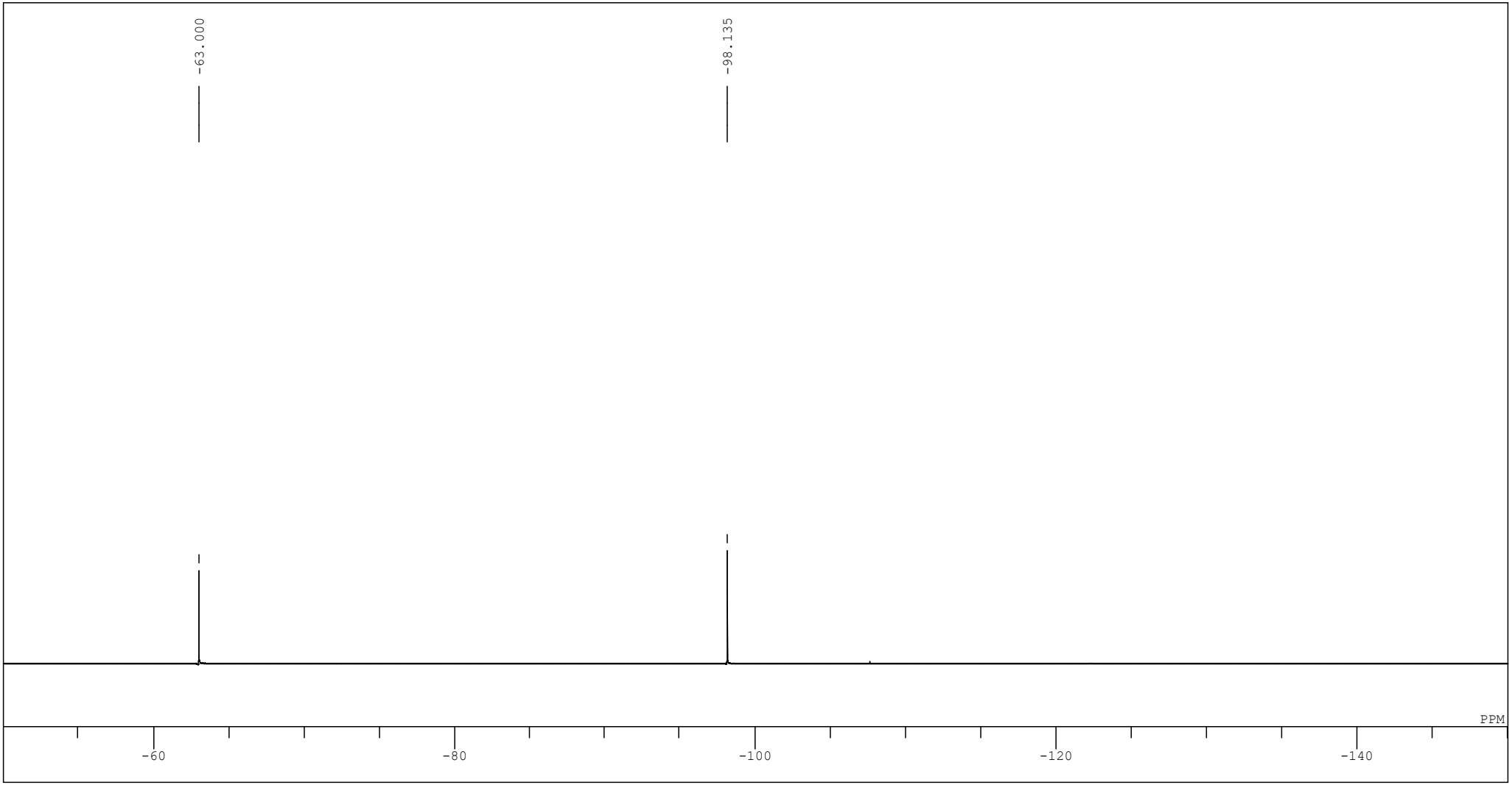

$^1$H NMR (500 MHz, $CDCl_3$)



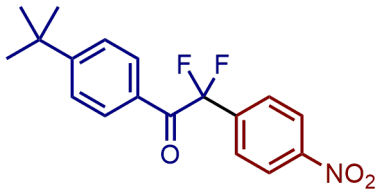
1-(4-(*tert*-Butyl)phenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ca)



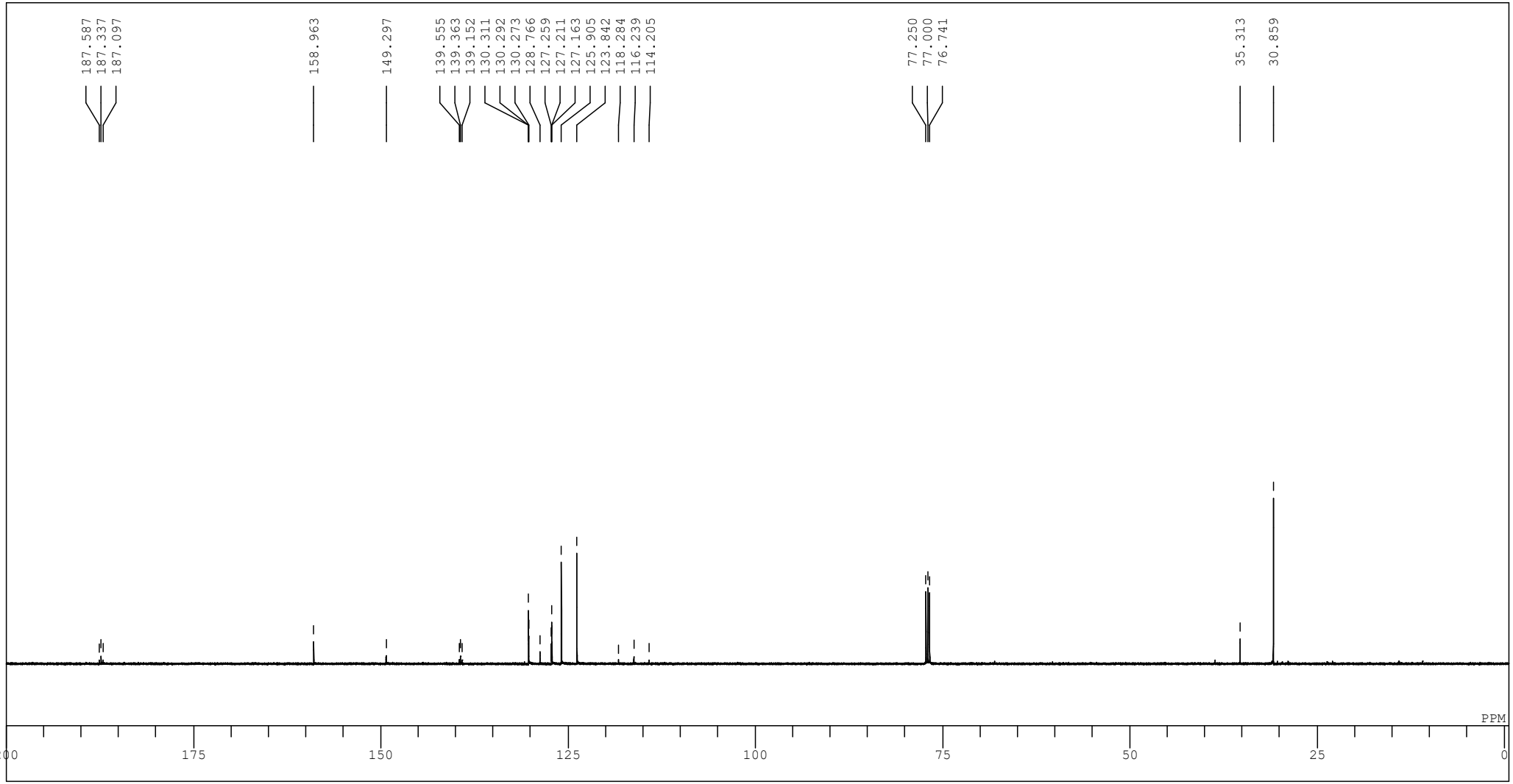

$^{19}F$ NMR (471 MHz, $CDCl_3$)



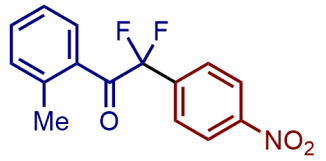
1-(4-(*tert*-Butyl)phenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ca)



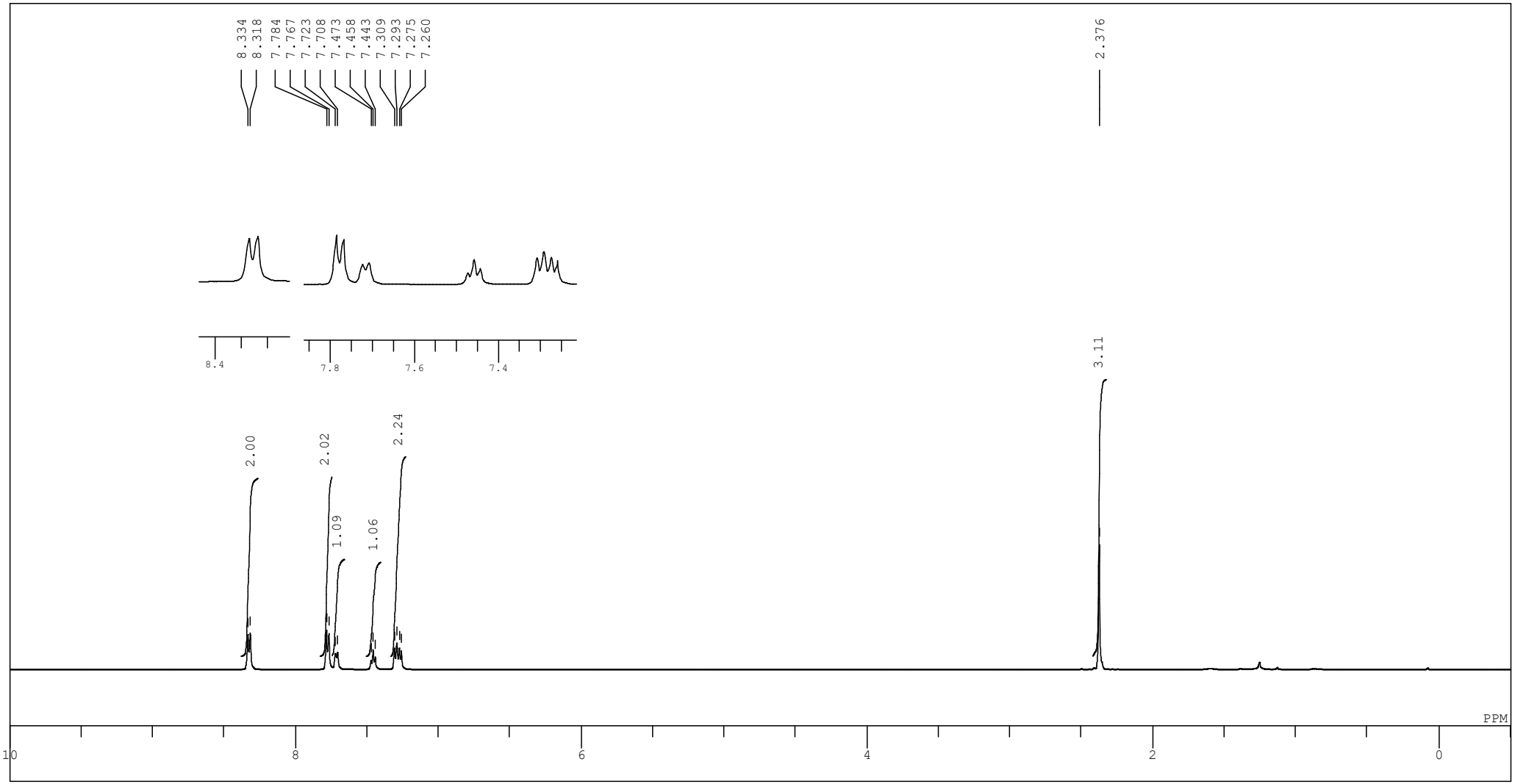

$^{13}C$ NMR (126 MHz, $CDCl_3$)



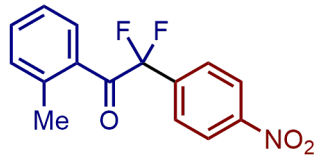
2,2-Difluoro-1-(4-methylphenyl)-2-(4-nitrophenyl)ethan-1-one (3da)



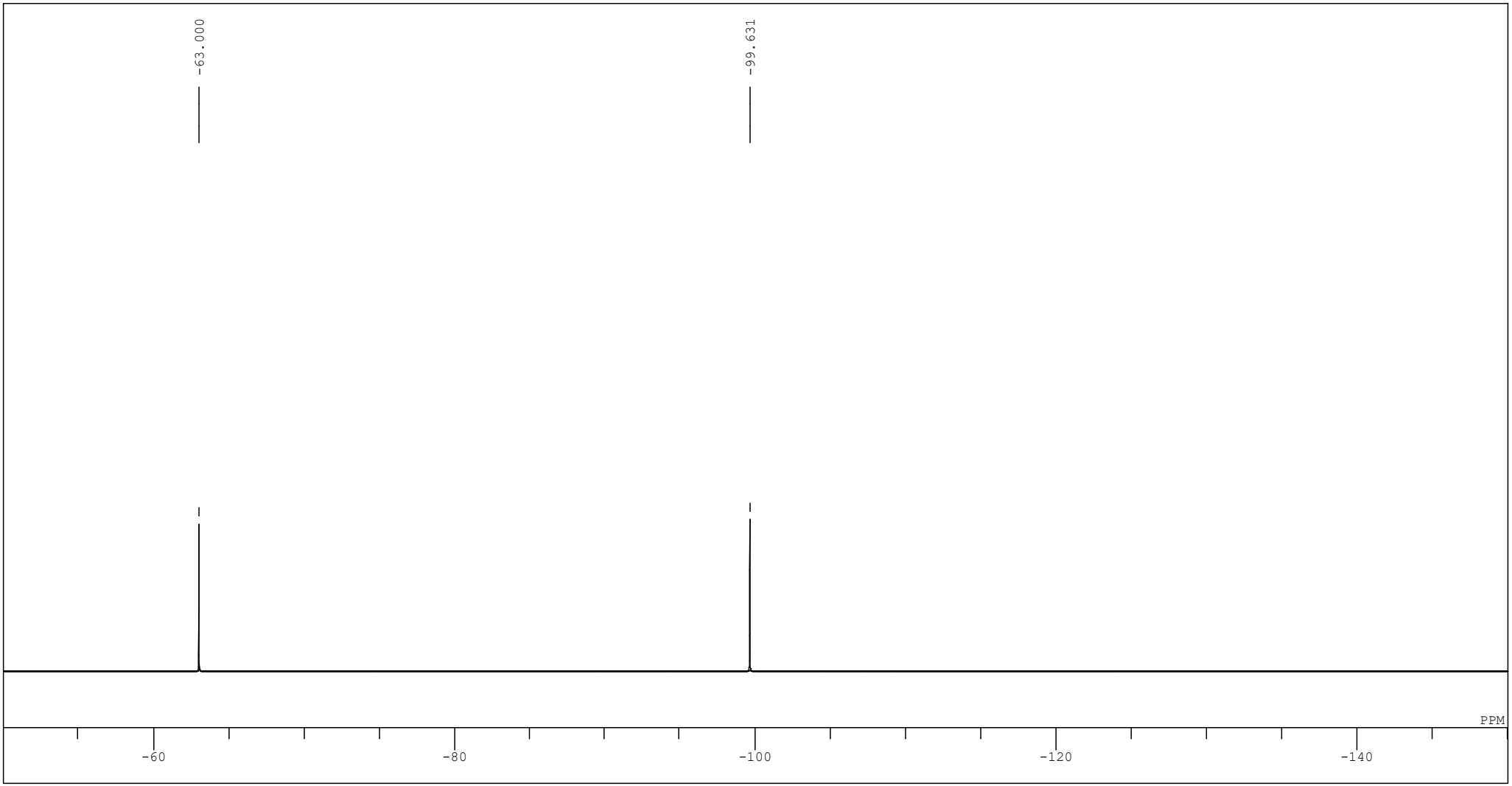

$^1$H NMR (500 MHz, $CDCl_3$)



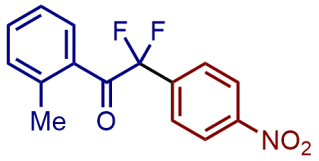
2,2-Difluoro-1-(4-methylphenyl)-2-(4-nitrophenyl)ethan-1-one (3da)



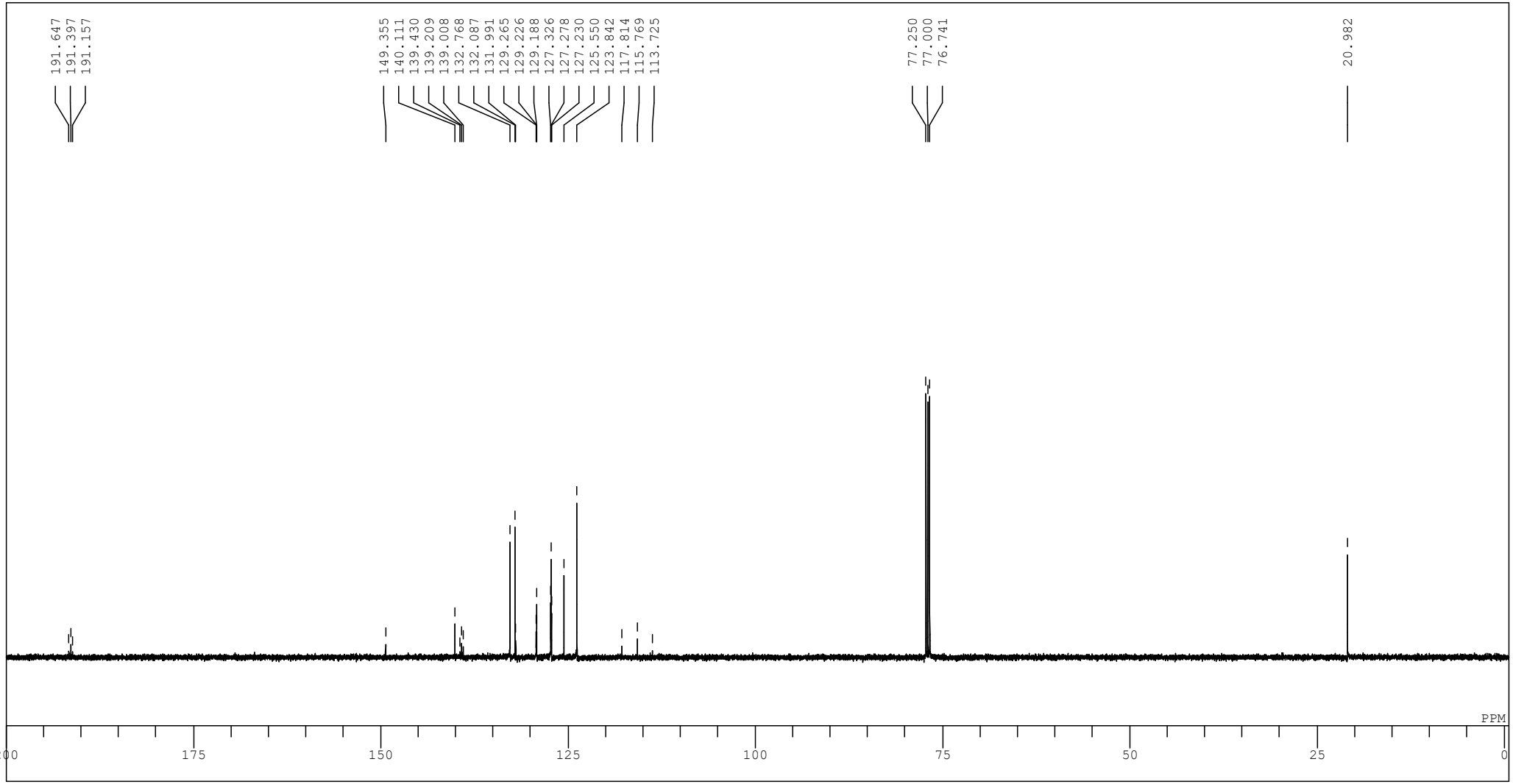

$^{19}F$ NMR (471 MHz, $CDCl_3$)



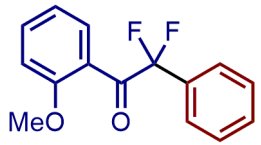
2,2-Difluoro-1-(4-methylphenyl)-2-(4-nitrophenyl)ethan-1-one (3da)



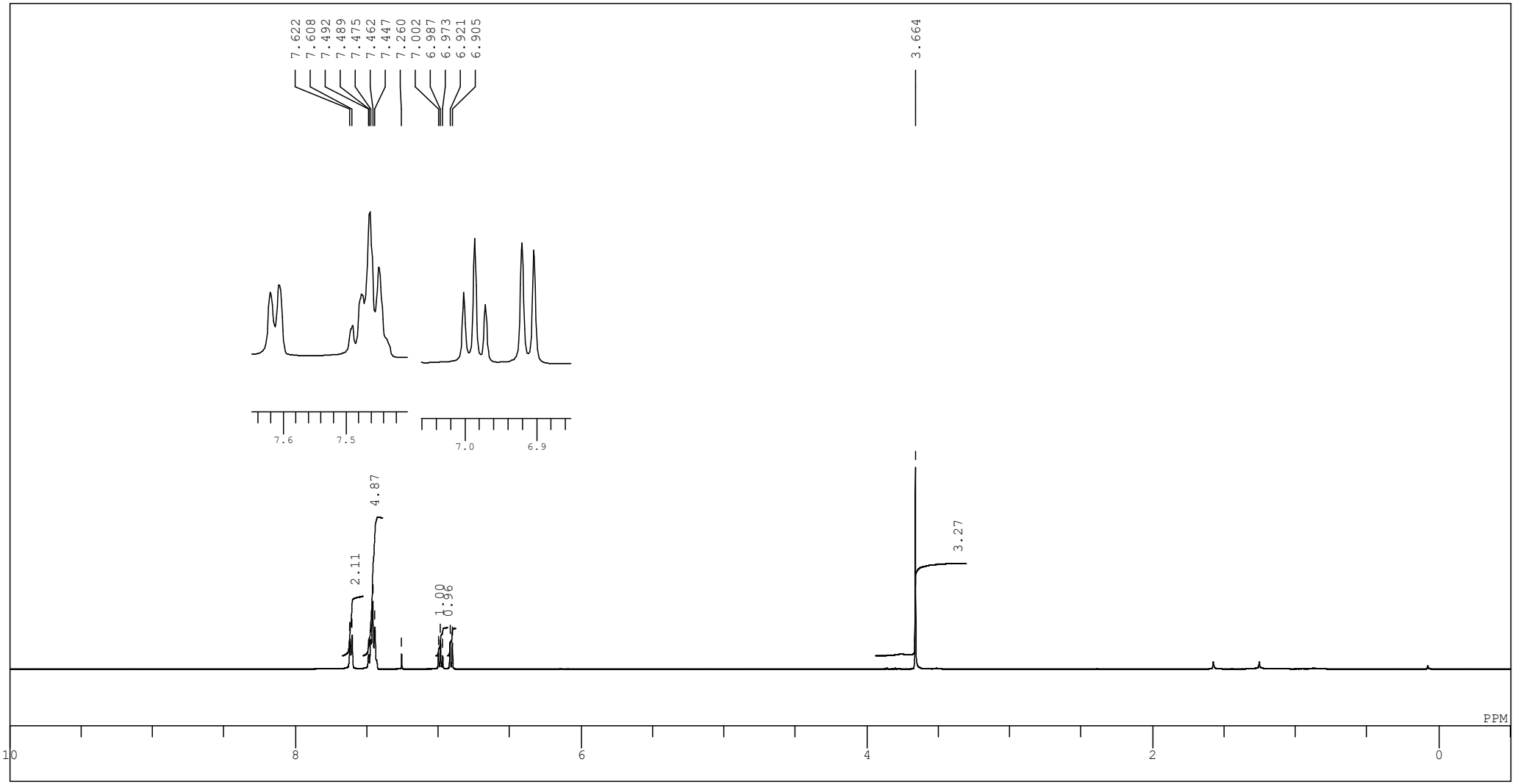

$^{13}C$ NMR (126 MHz, $CDCl_3$)



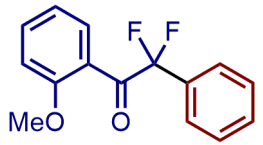
2,2-Difluoro-1-(2-methoxyphenyl)-2-phenylethan-1-one (3ej)



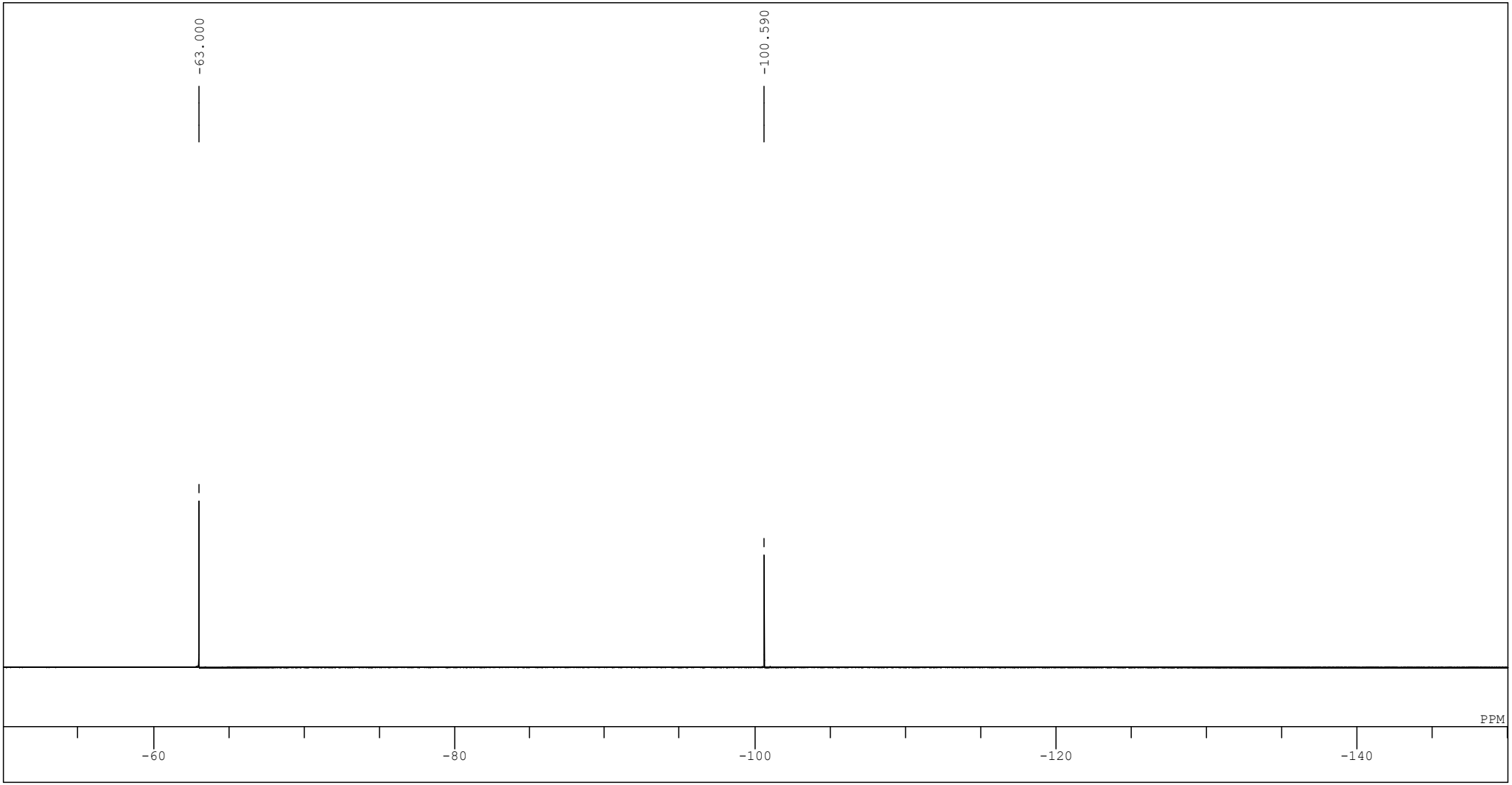

$^1$H NMR (500 MHz, $CDCl_3$)



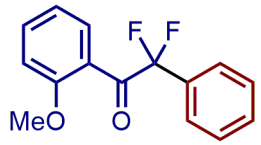
2,2-Difluoro-1-(2-methoxyphenyl)-2-phenylethan-1-one (3ej)



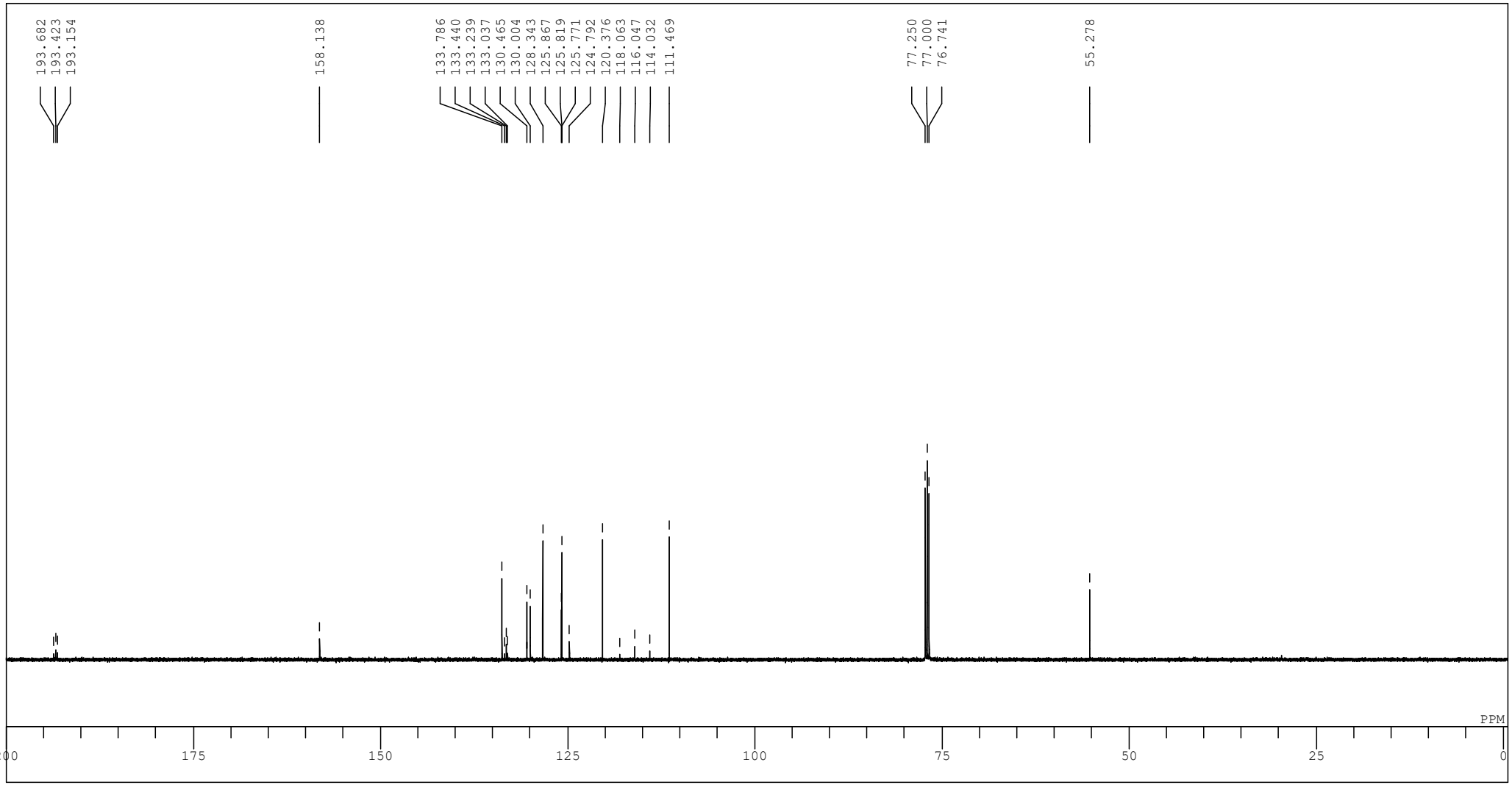

$^{19}F$ NMR (471 MHz, $CDCl_3$)



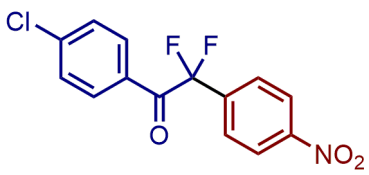
2,2-Difluoro-1-(2-methoxyphenyl)-2-phenylethan-1-one (3ej)



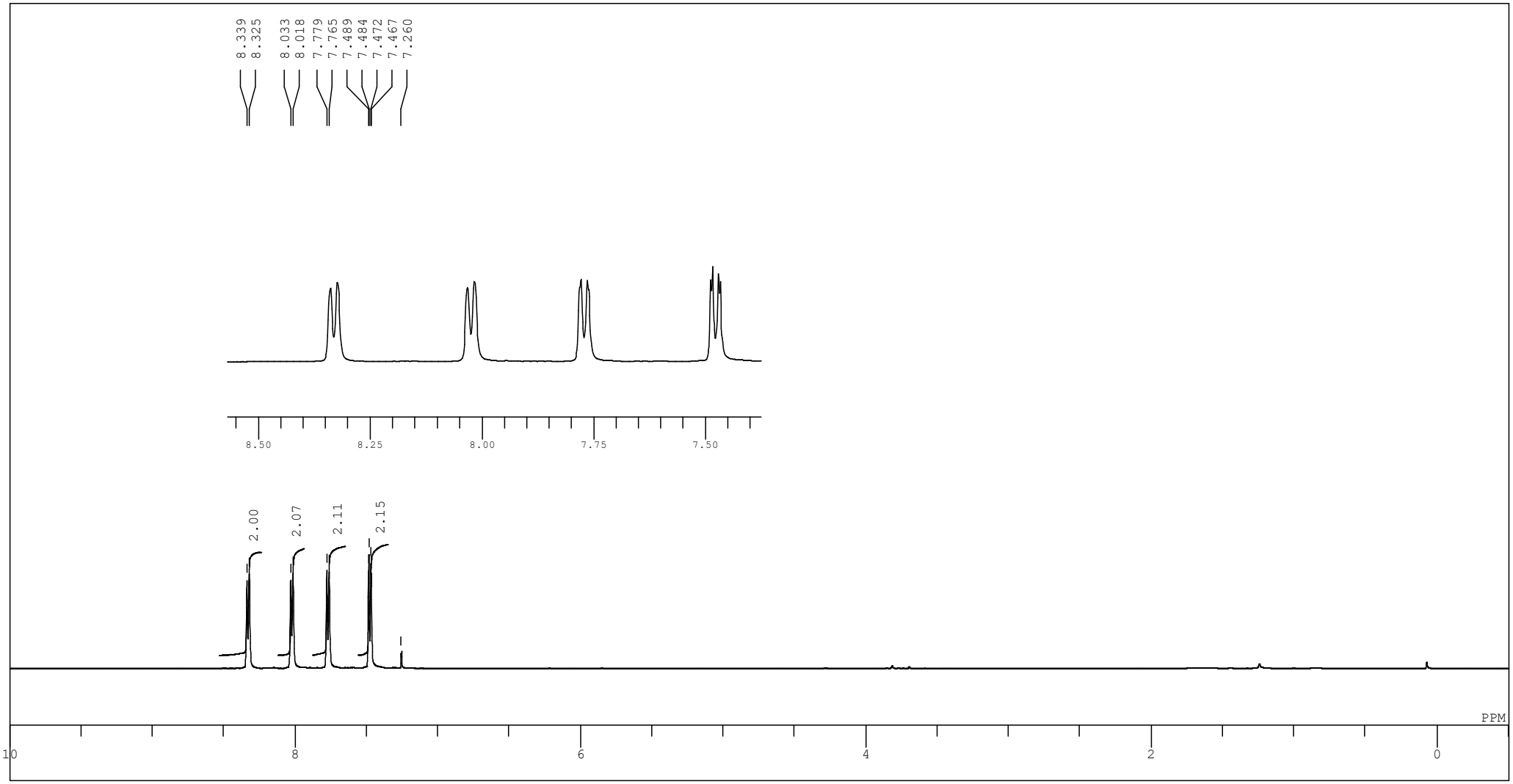

$^{13}C$ NMR (126 MHz, $CDCl_3$)



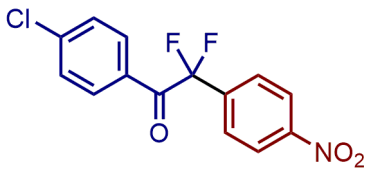
1-(4-Chlorophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3fa)



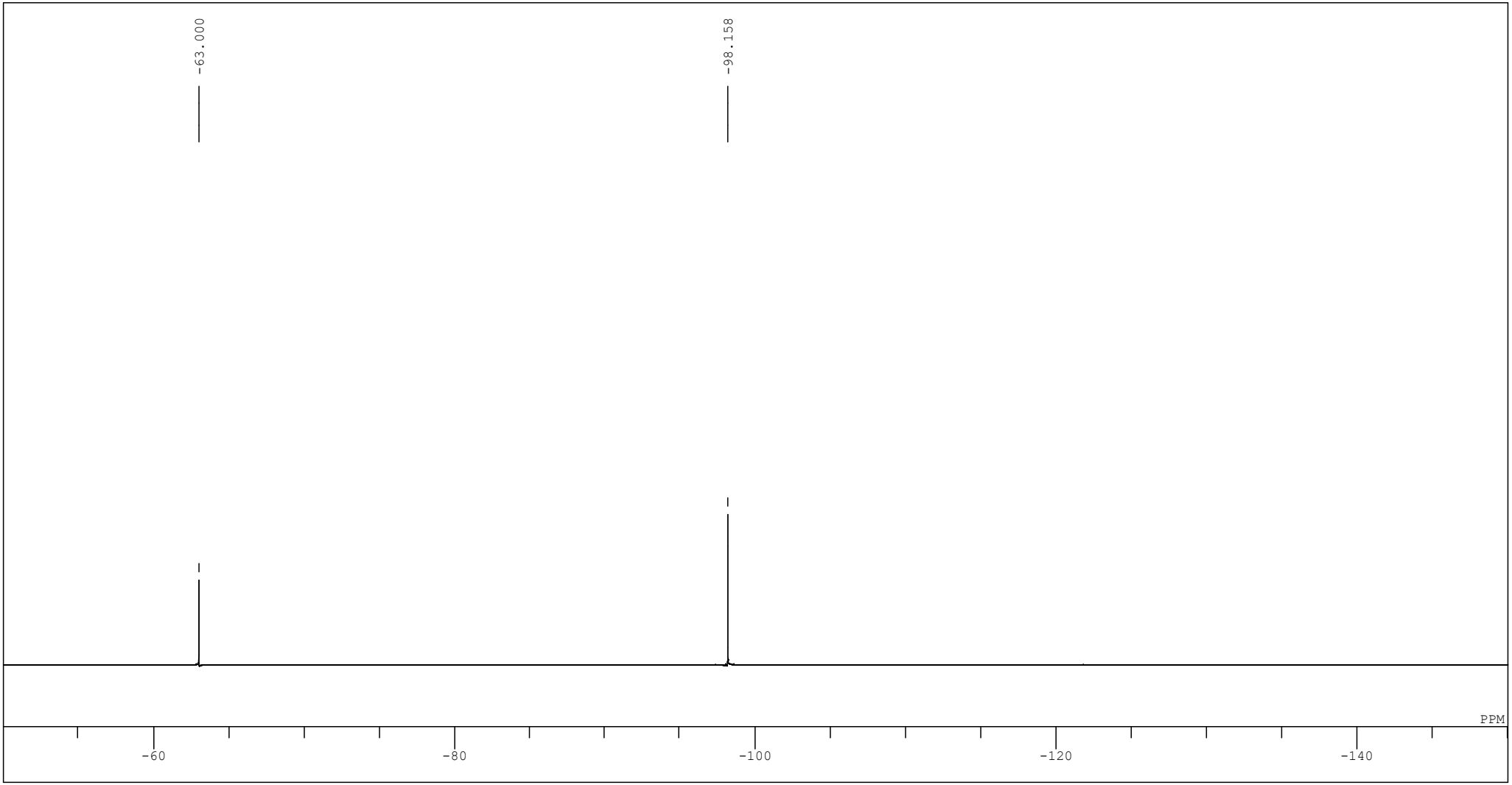

$^1$H NMR (500 MHz, $CDCl_3$)



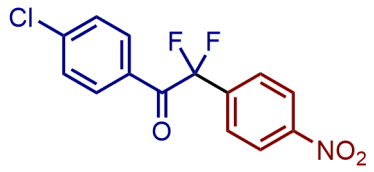
1-(4-Chlorophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3fa)



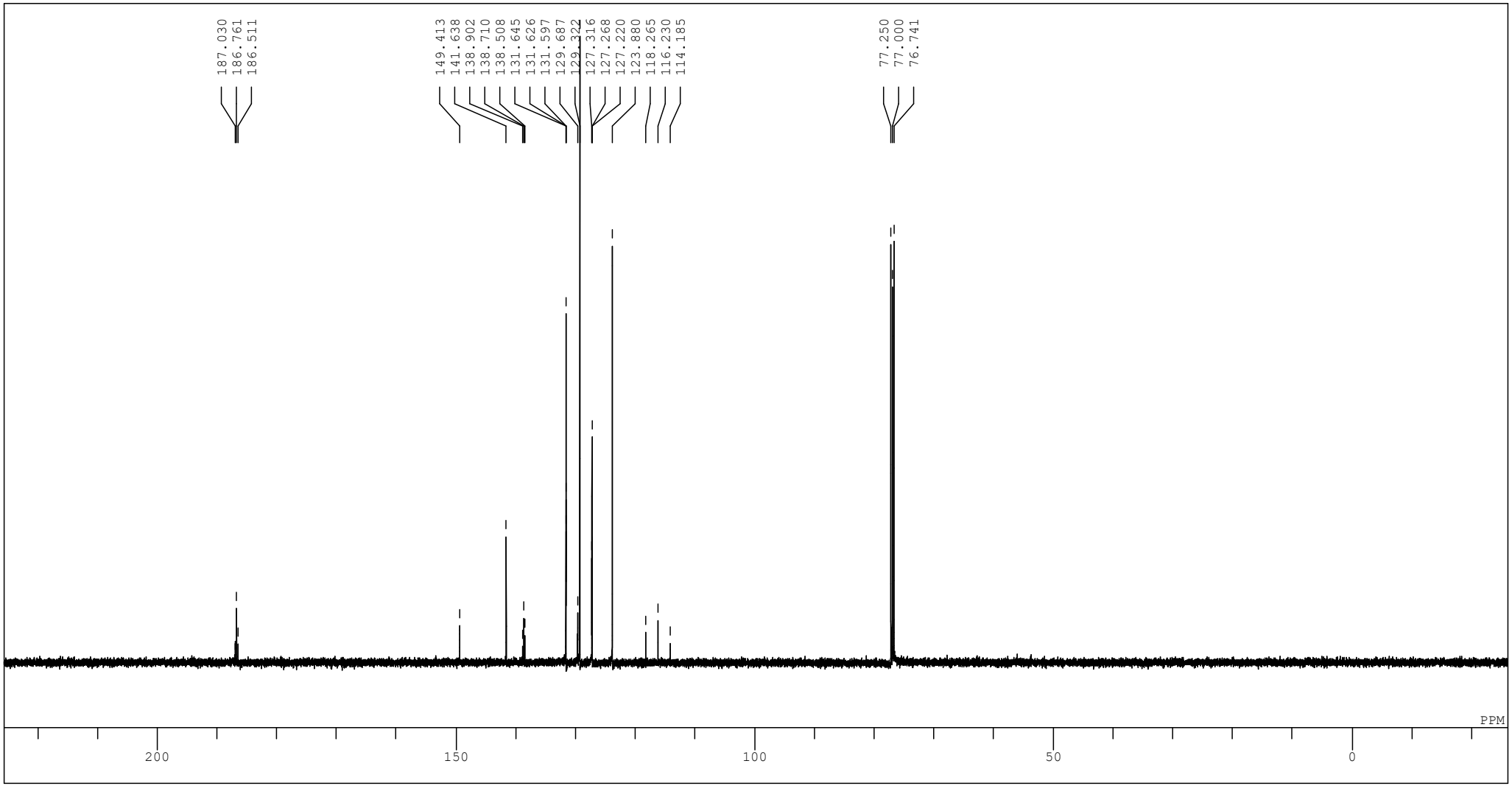

$^{19}F$ NMR (471 MHz, $CDCl_3$)



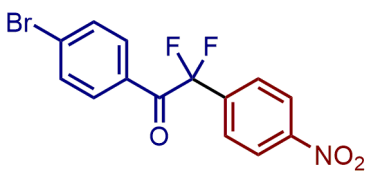
1-(4-Chlorophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3fa)



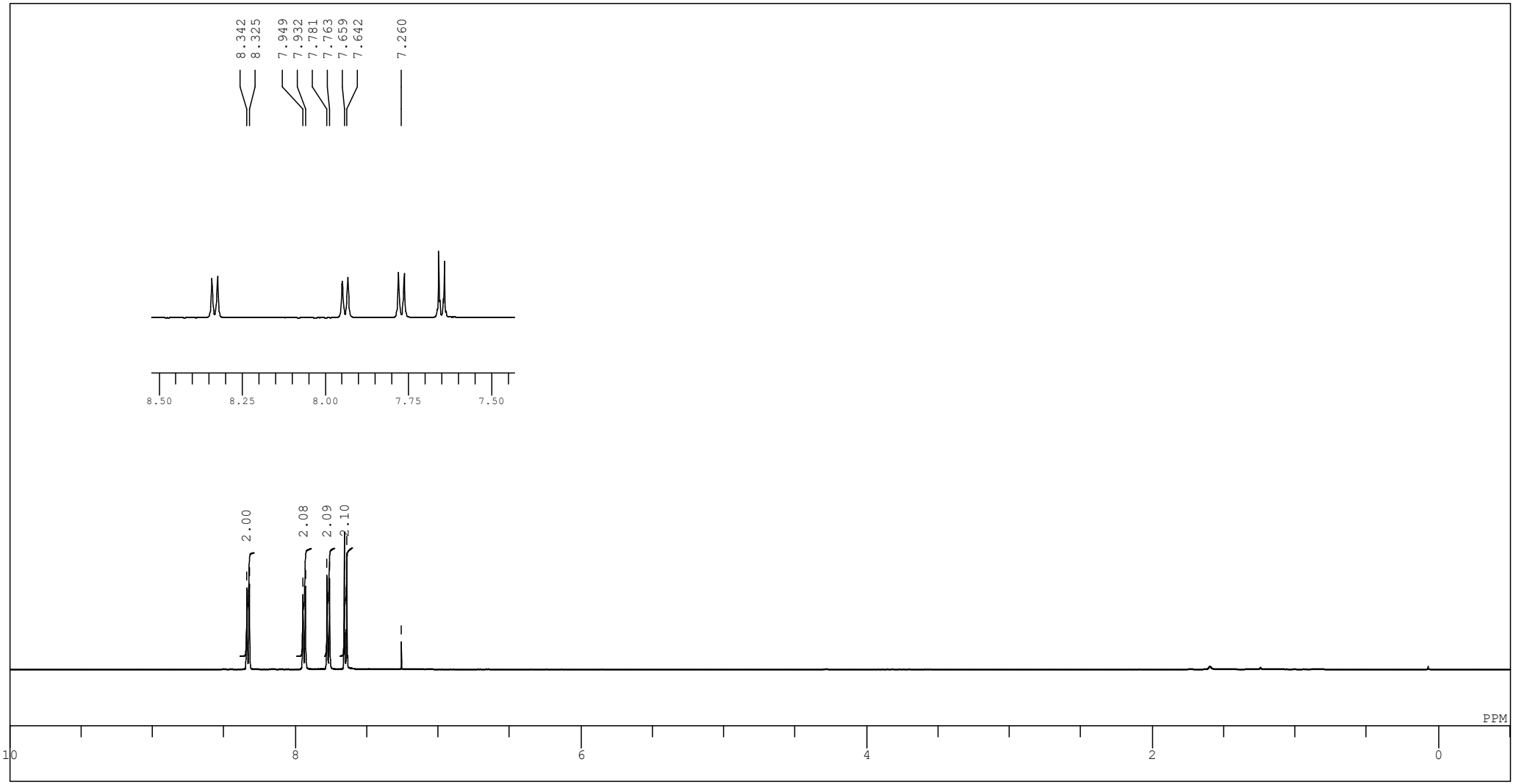

$^{13}C$ NMR (126 MHz, $CDCl_3$)



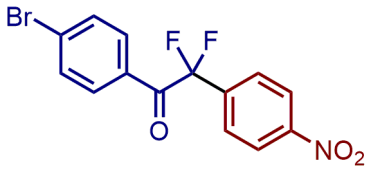
1-(4-Bromophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ga)



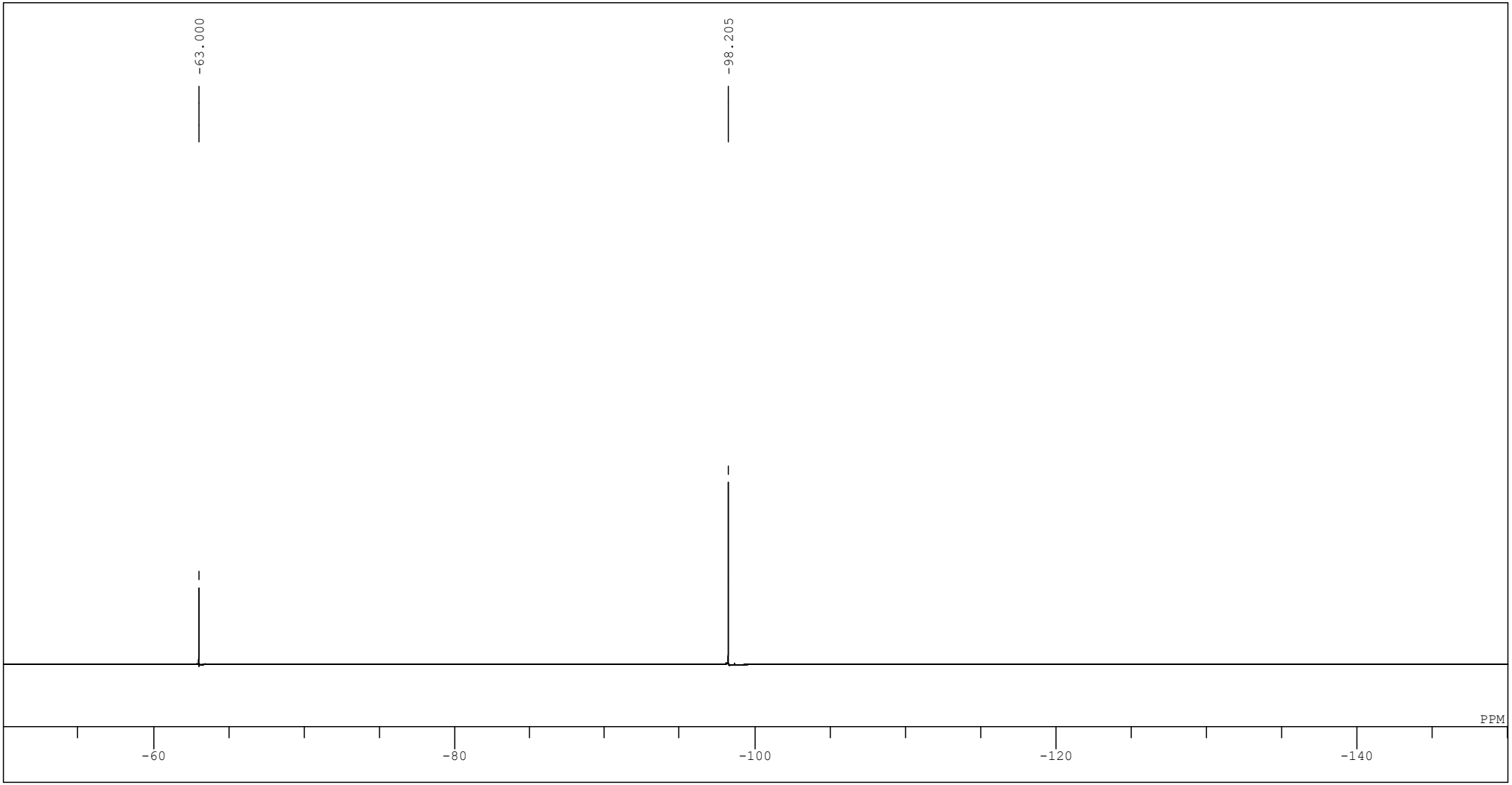

$^1$H NMR (500 MHz, $CDCl_3$)



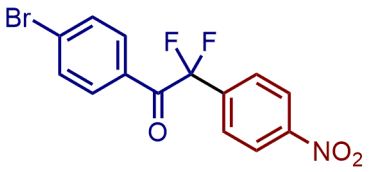
1-(4-Bromophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ga)



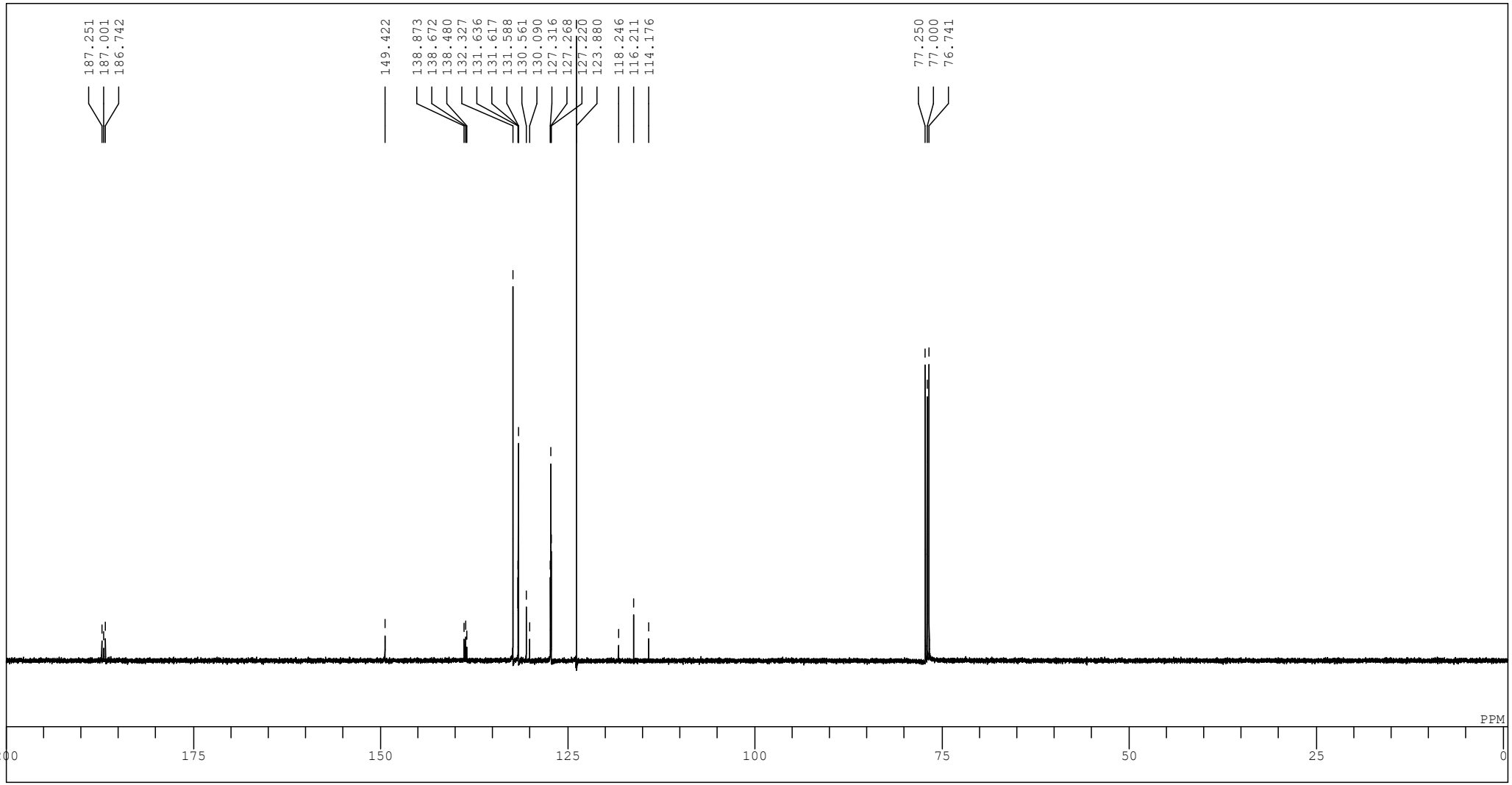

$^{19}F$ NMR (471 MHz, $CDCl_3$)



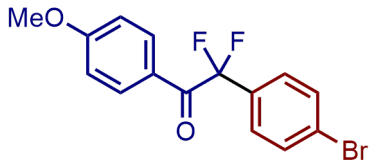
1-(4-Bromophenyl)-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ga)



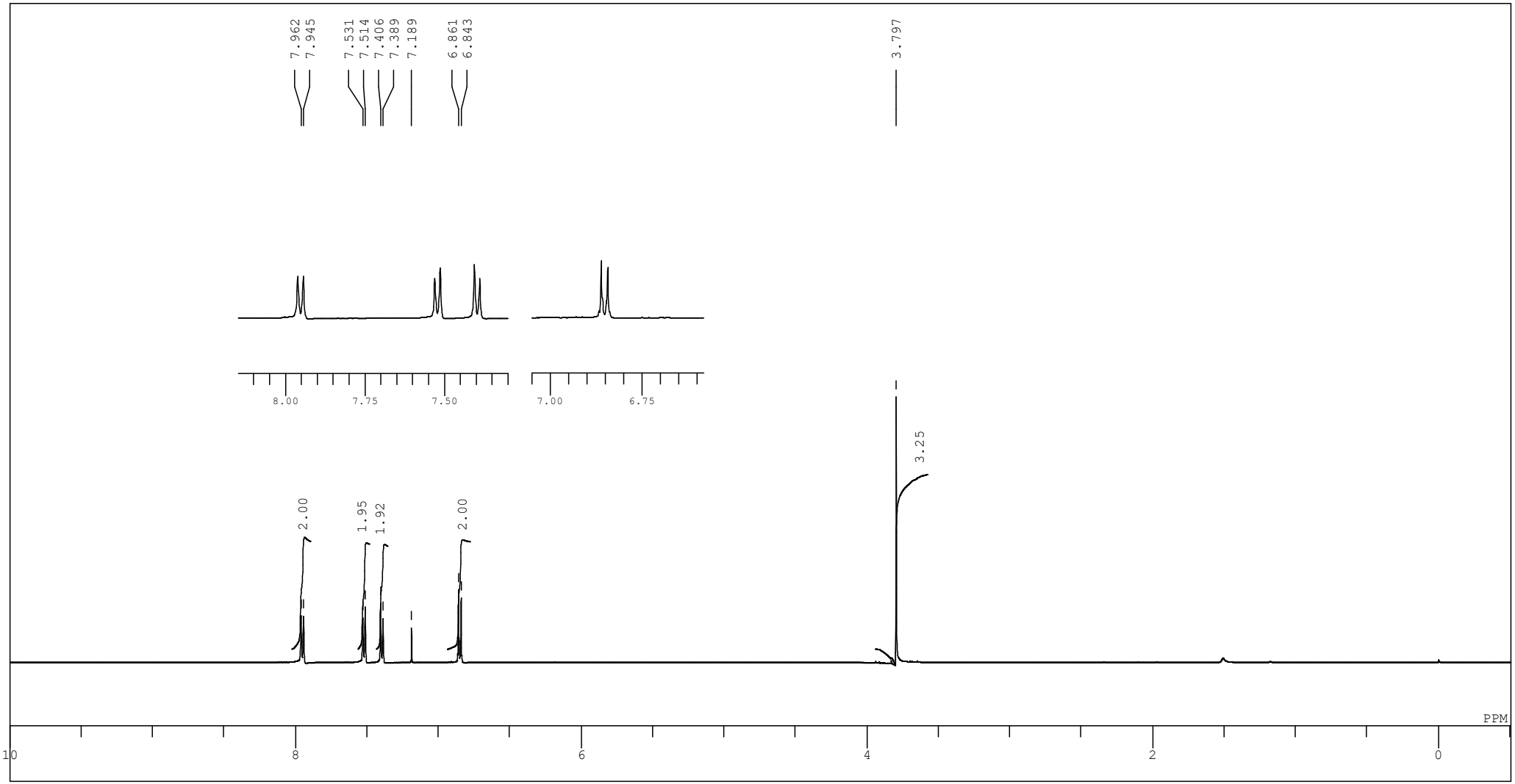

$^{13}C$ NMR (126 MHz, $CDCl_3$)



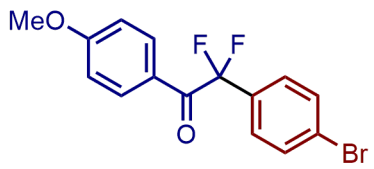
2-(4-Bromophenyl)-2,2-difluoro-1-(4-methoxyphenyl)ethan-1-one (3bk)



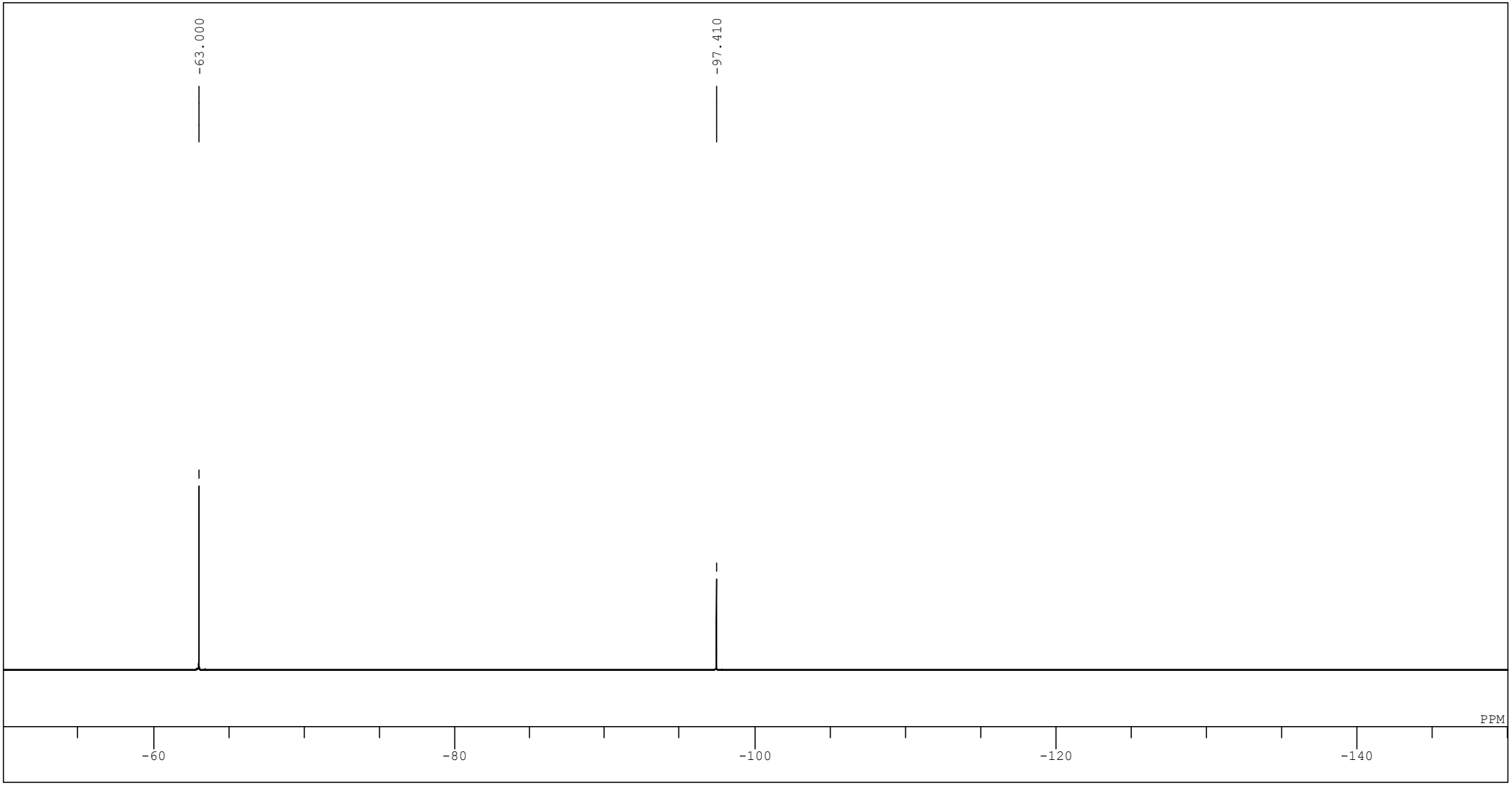

$^1$H NMR (500 MHz, $CDCl_3$)



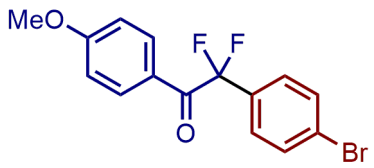
2-(4-Bromophenyl)-2,2-difluoro-1-(4-methoxyphenyl)ethan-1-one (3bk)



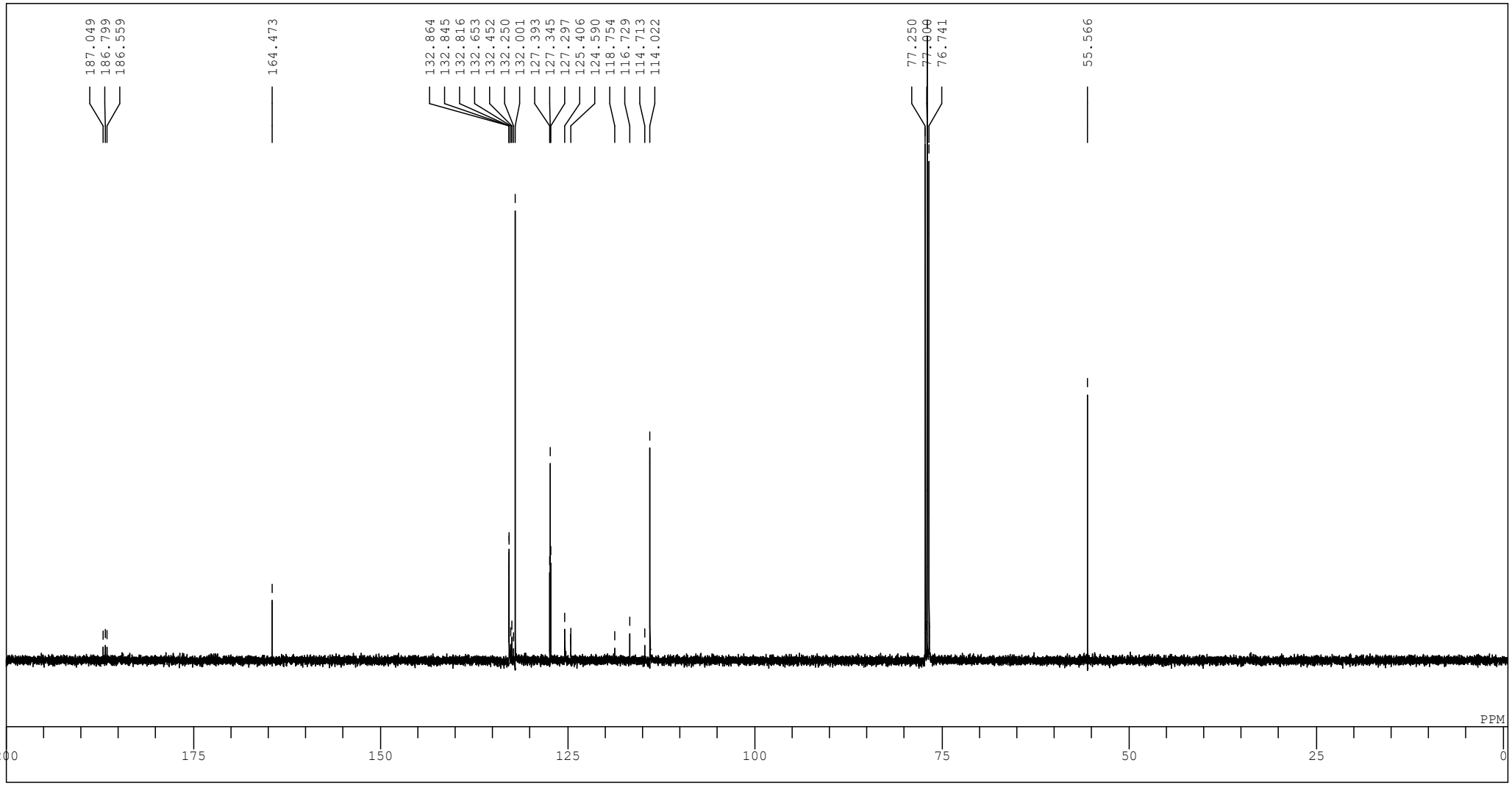

$^{19}F$ NMR (471 MHz, $CDCl_3$)



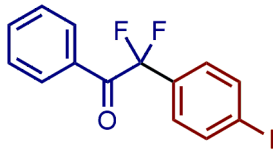
2-(4-Bromophenyl)-2,2-difluoro-1-(4-methoxyphenyl)ethan-1-one (3bk)



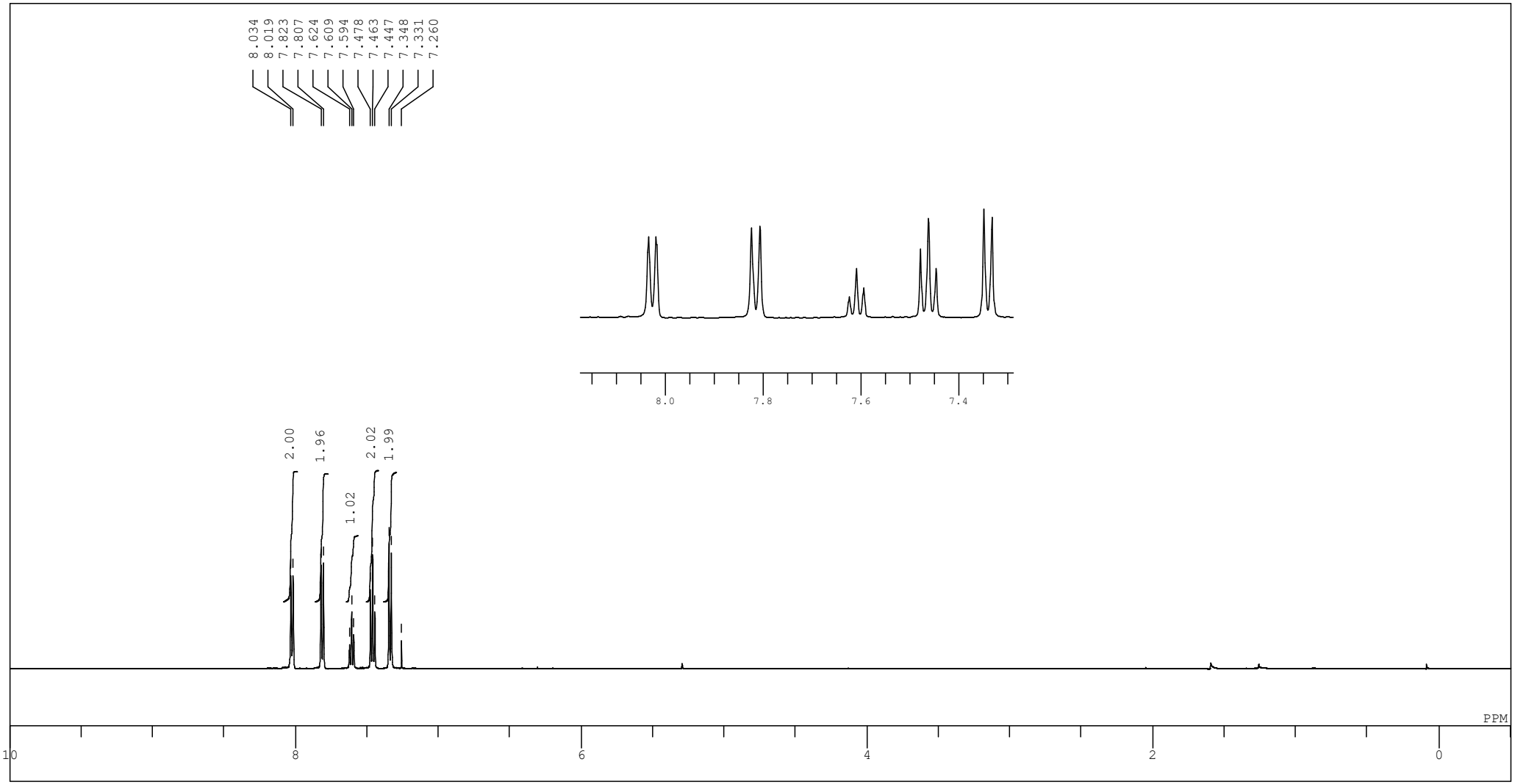

$^{13}C$ NMR (126 MHz, $CDCl_3$)



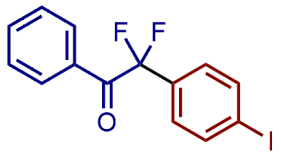
2,2-Difluoro-2-(4-iodophenyl)-1-phenylethan-1-one (3al)



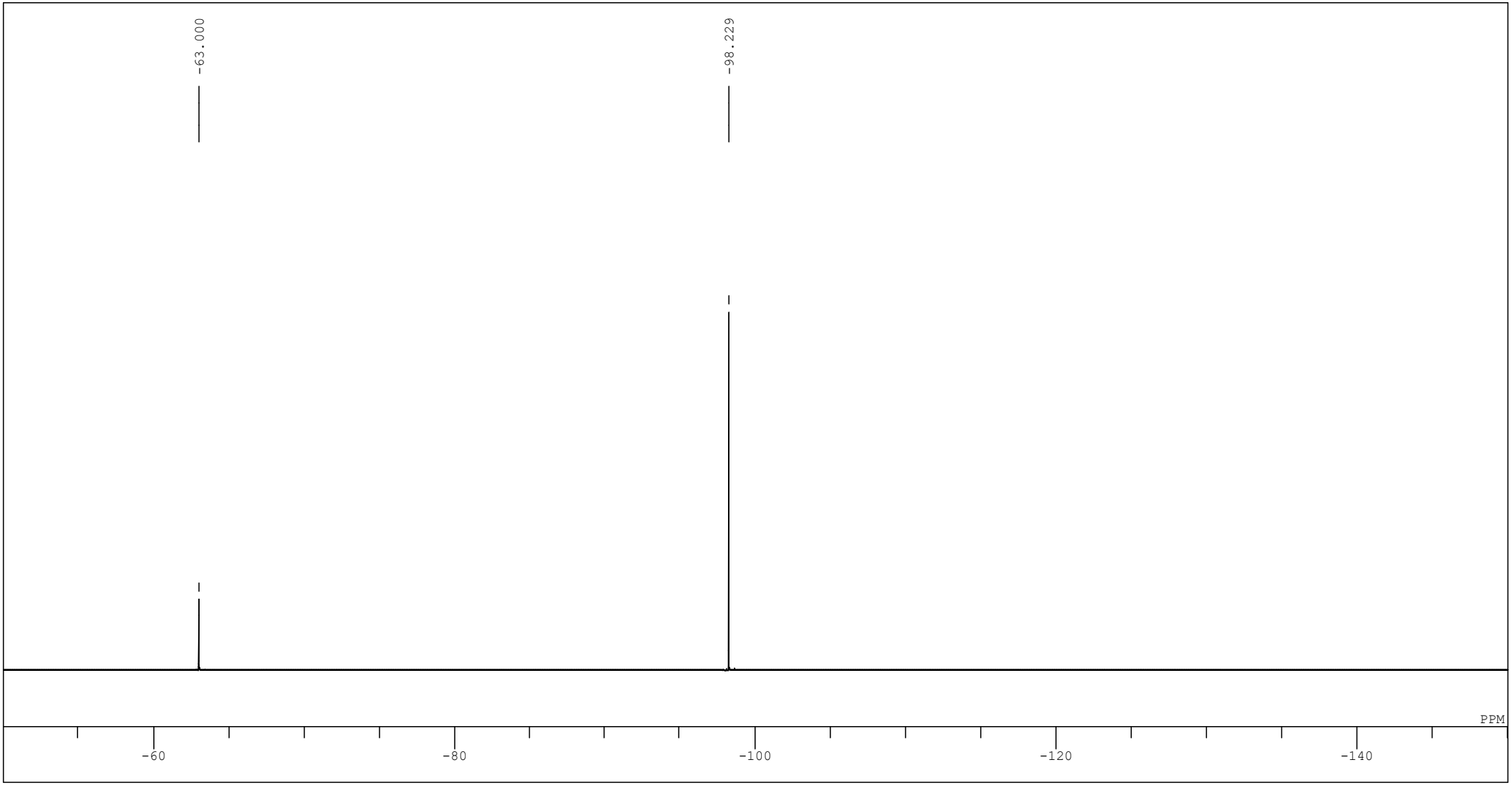

$^1$H NMR (500 MHz, $CDCl_3$)



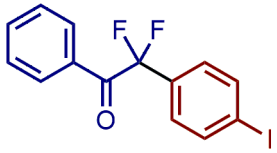
2,2-Difluoro-2-(4-iodophenyl)-1-phenylethan-1-one (3al)



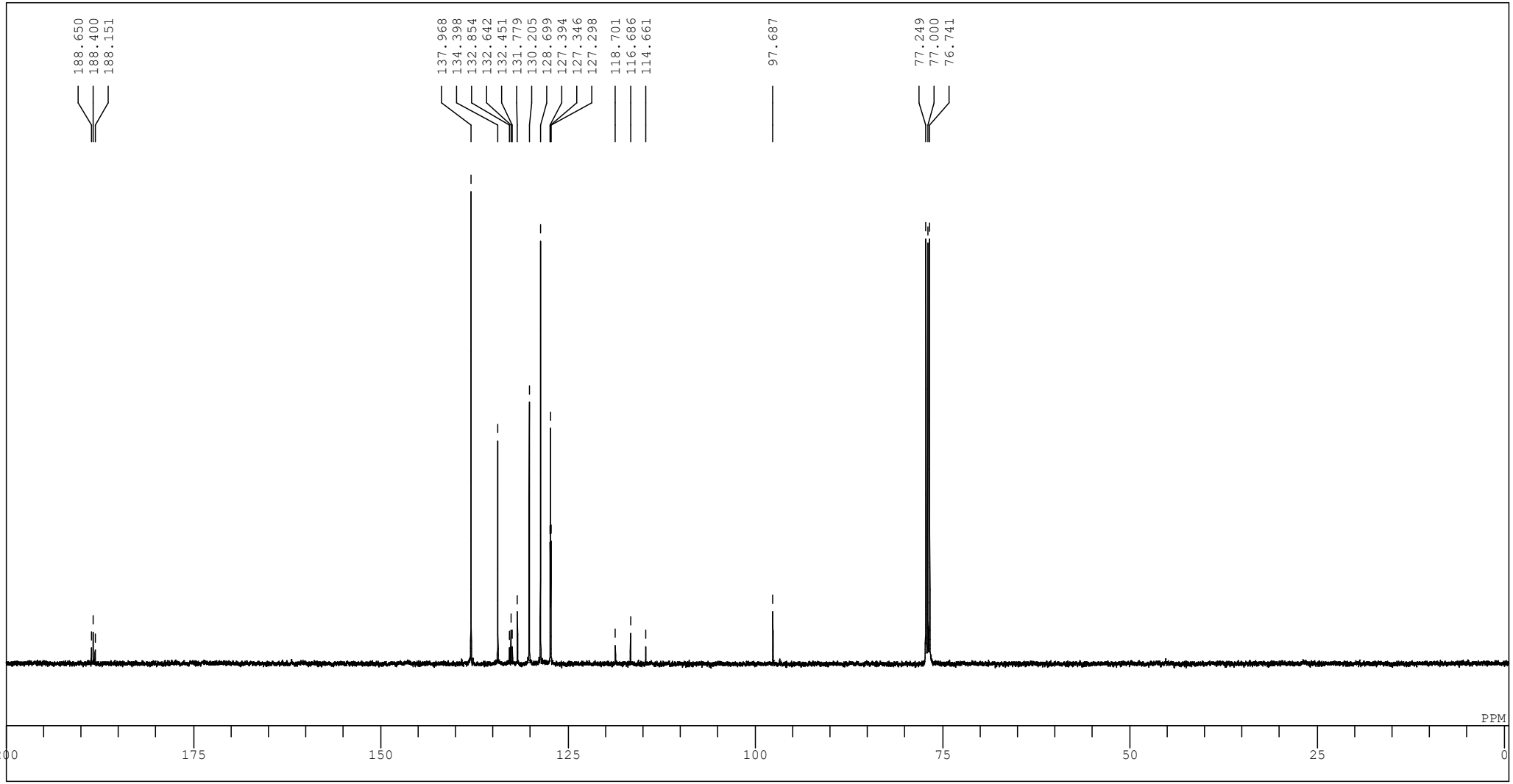

$^{19}F$ NMR (471 MHz, $CDCl_3$)



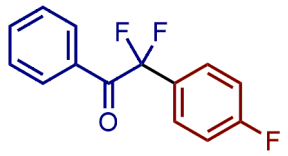
2,2-Difluoro-2-(4-iodophenyl)-1-phenylethan-1-one (3al)



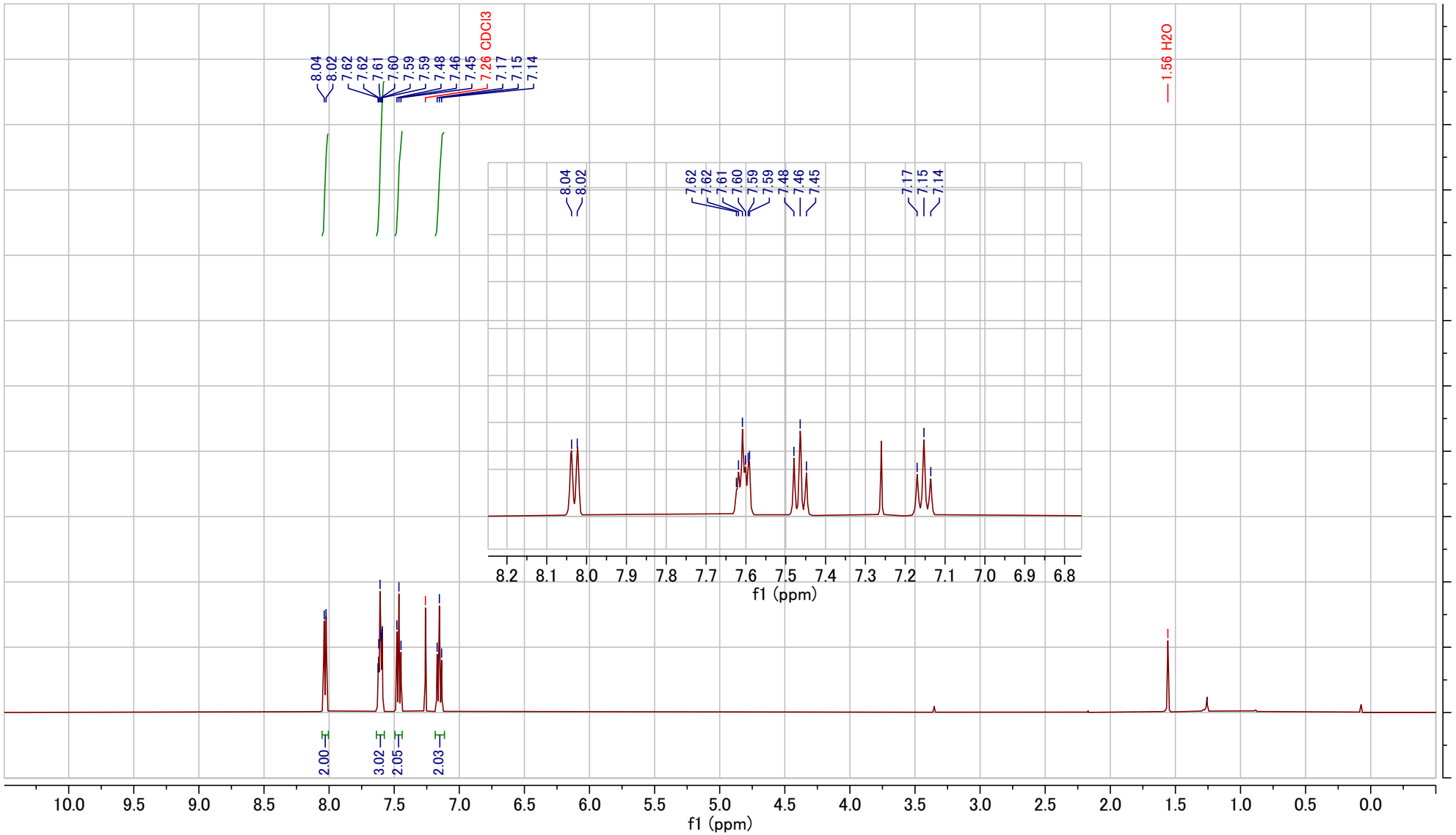

$^{13}C$ NMR (126 MHz, $CDCl_3$)



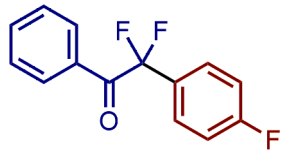
2,2-difluoro-2-(4-fluorophenyl)-1-phenylethan-1-one (3am)



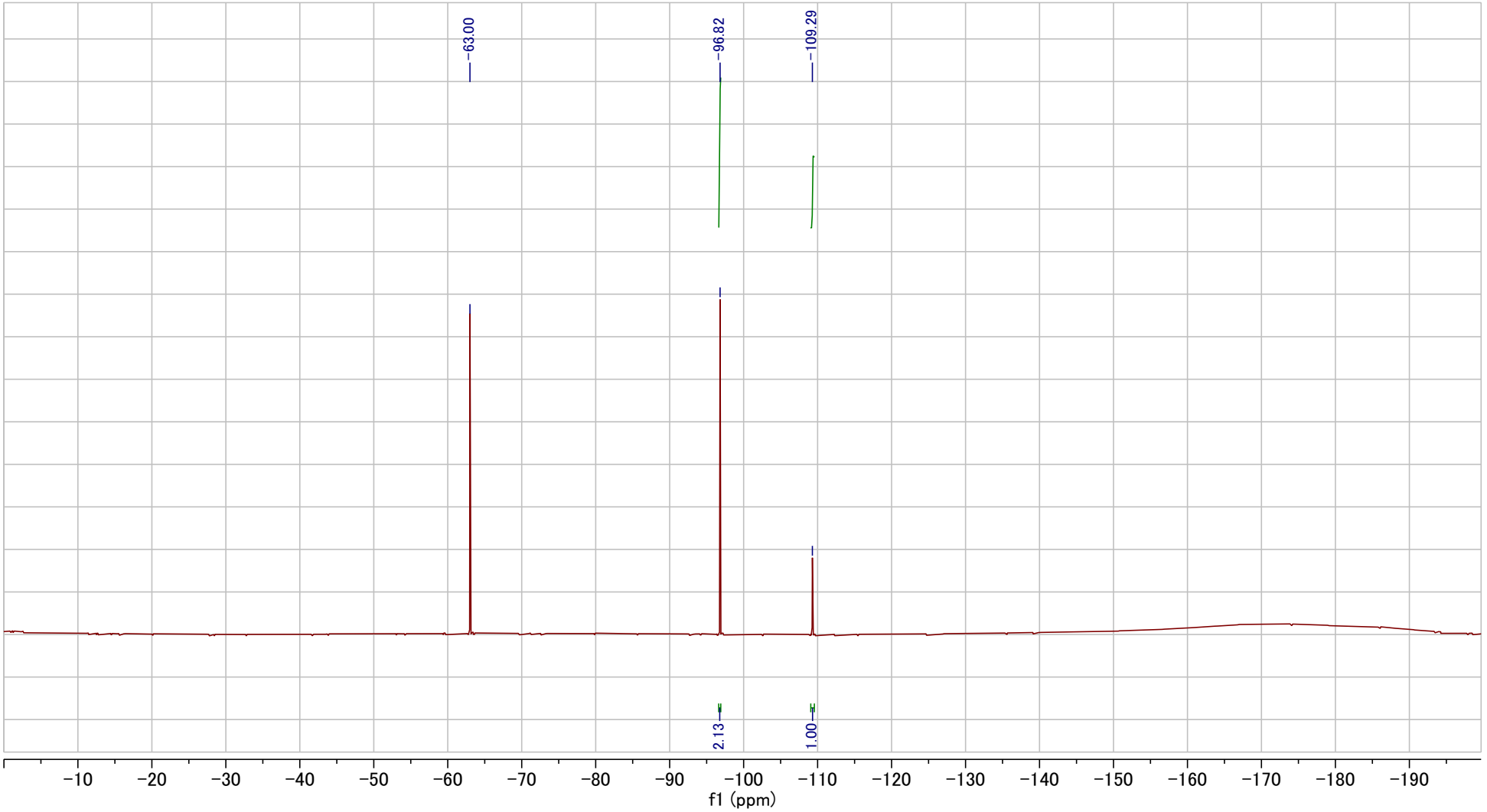

$^1$H NMR (500 MHz, $CDCl_3$)



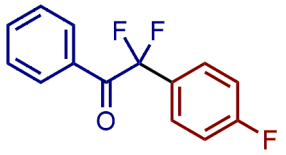
2,2-difluoro-2-(4-fluorophenyl)-1-phenylethan-1-one (3am)



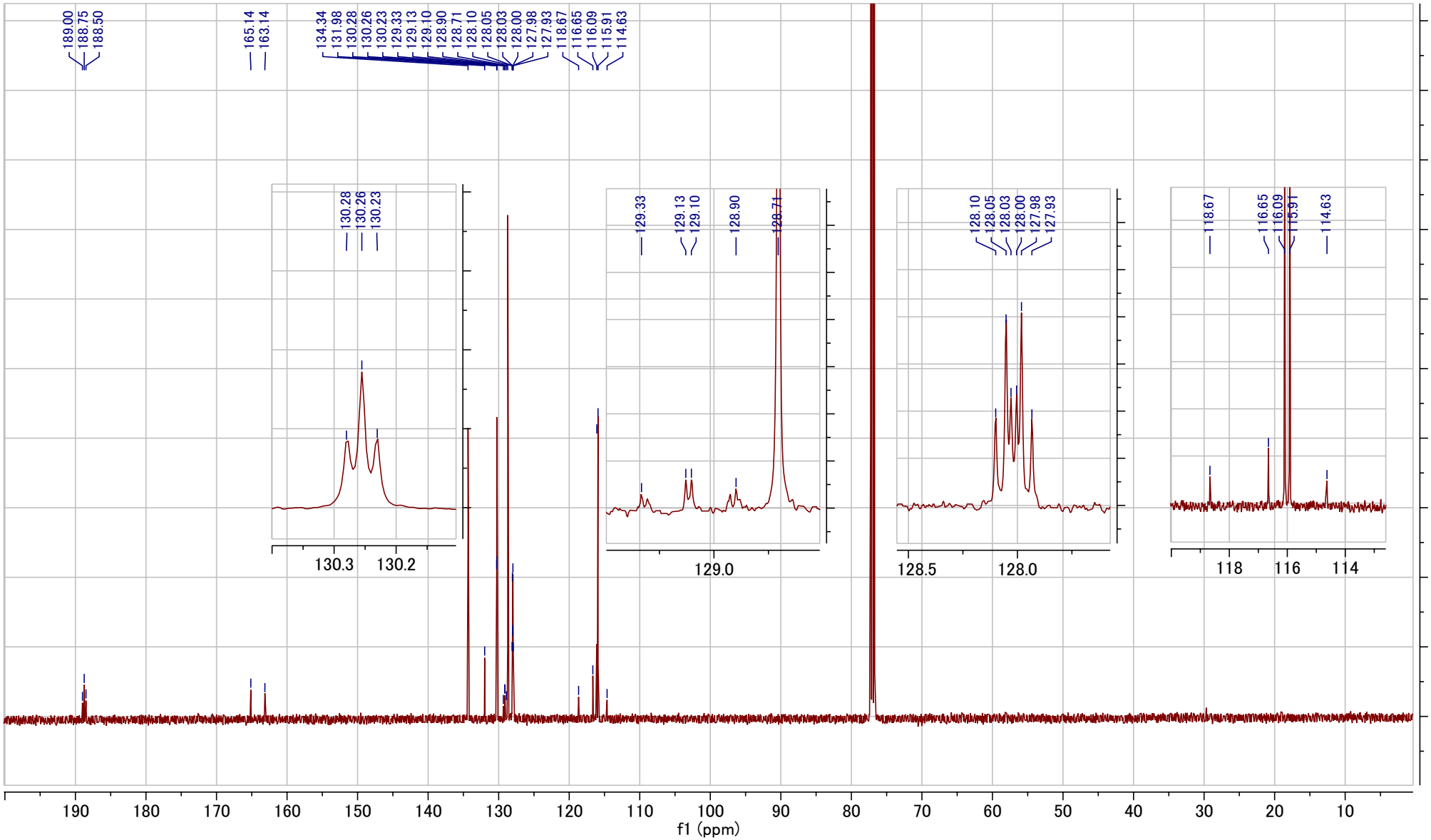

$^{19}F$ NMR (471 MHz, $CDCl_3$)



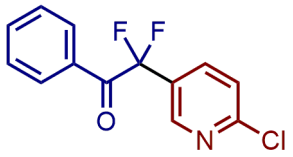
2,2-difluoro-2-(4-fluorophenyl)-1-phenylethan-1-one (3am)



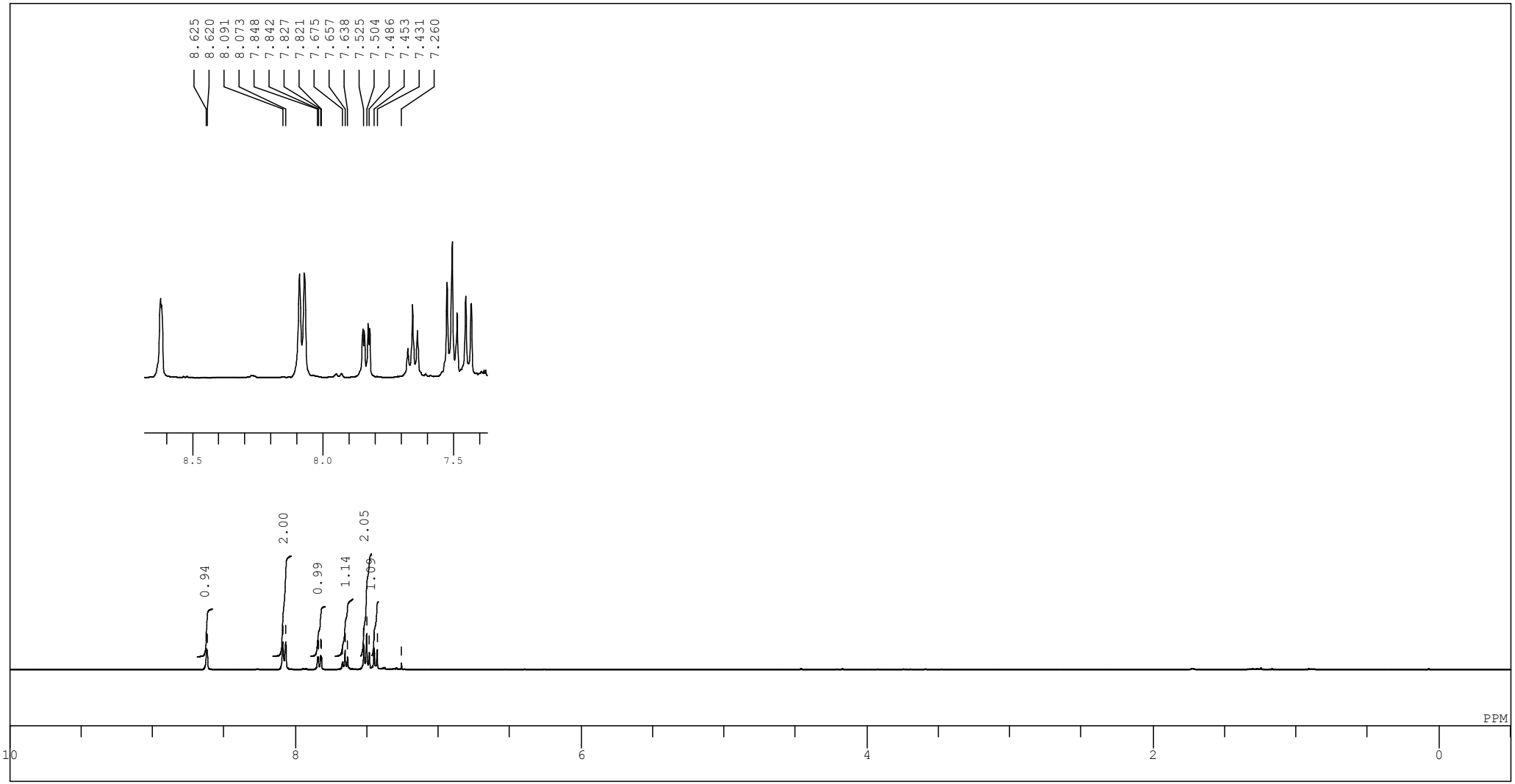

$^{13}C$ NMR (126 MHz, $CDCl_3$)



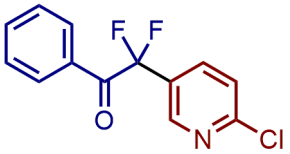
2-(6-Chloropyridin-3-yl)-2,2-difluoro-1-phenylethan-1-one (3an)



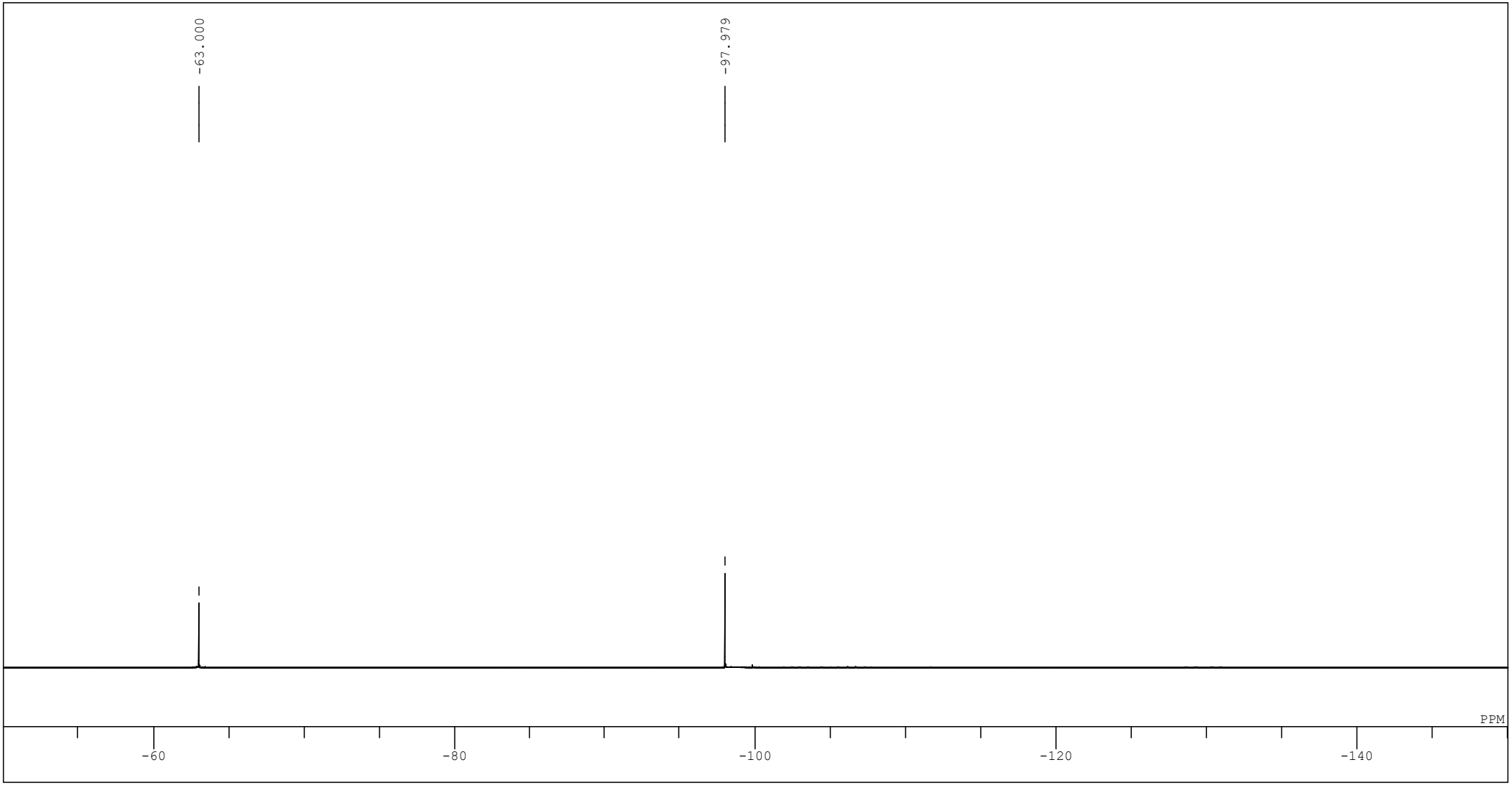

$^1$H NMR (400 MHz, $CDCl_3$)



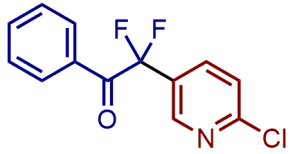
2-(6-Chloropyridin-3-yl)-2,2-difluoro-1-phenylethan-1-one (3an)



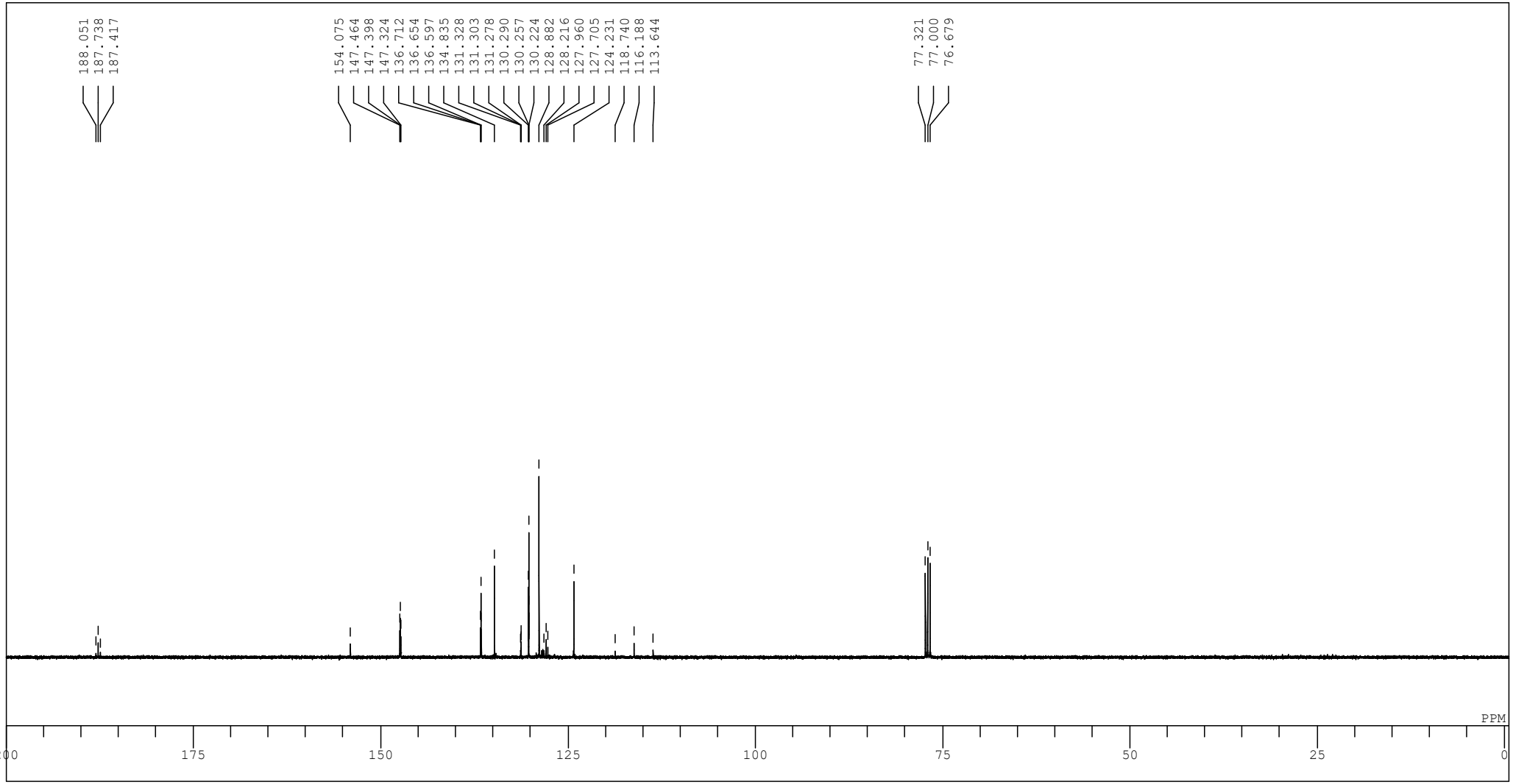

$^{19}F$ NMR (376 MHz, $CDCl_3$)



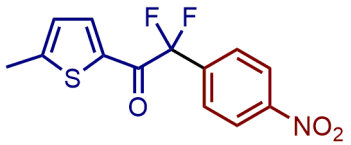
2-(6-Chloropyridin-3-yl)-2,2-difluoro-1-phenylethan-1-one (3an)



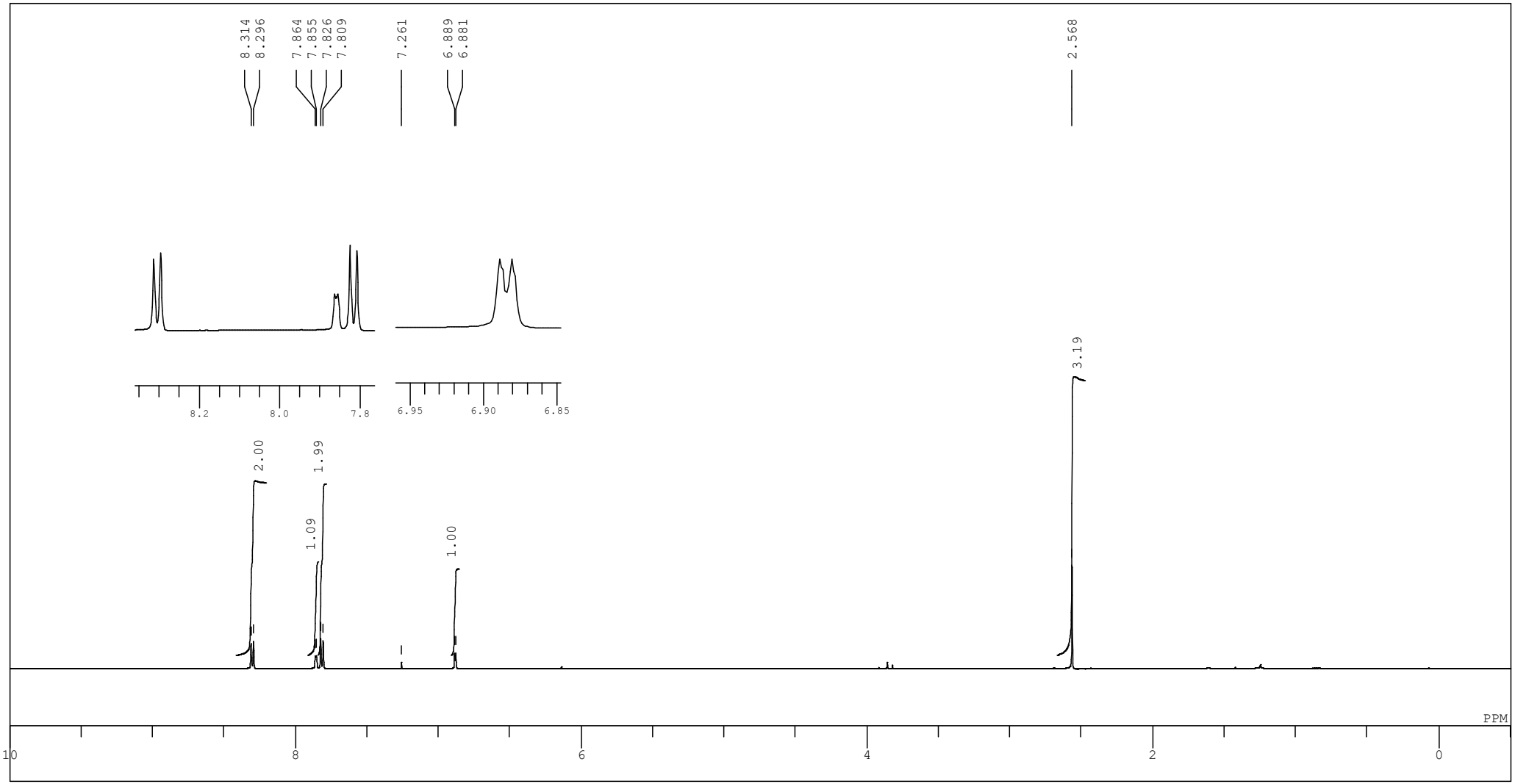

$^{13}C$ NMR (100 MHz, $CDCl_3$)



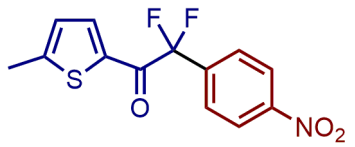
2,2-Difluoro-1-(5-methylthiophen-2-yl)-2-(4-nitrophenyl)ethan-1-one (3ha)



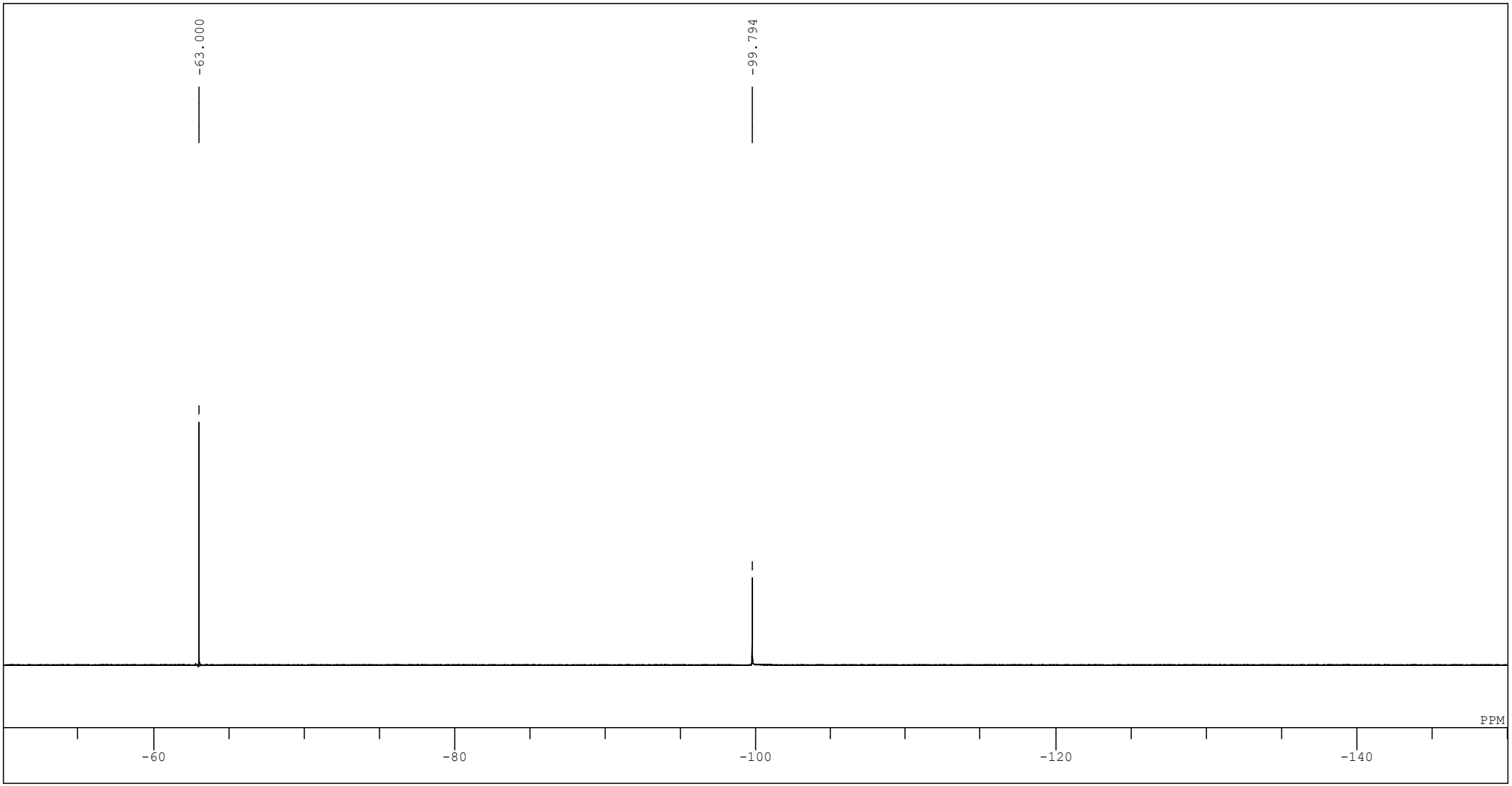

$^1$H NMR (500 MHz, $CDCl_3$)



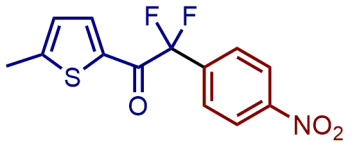
2,2-Difluoro-1-(5-methylthiophen-2-yl)-2-(4-nitrophenyl)ethan-1-one (3ha)



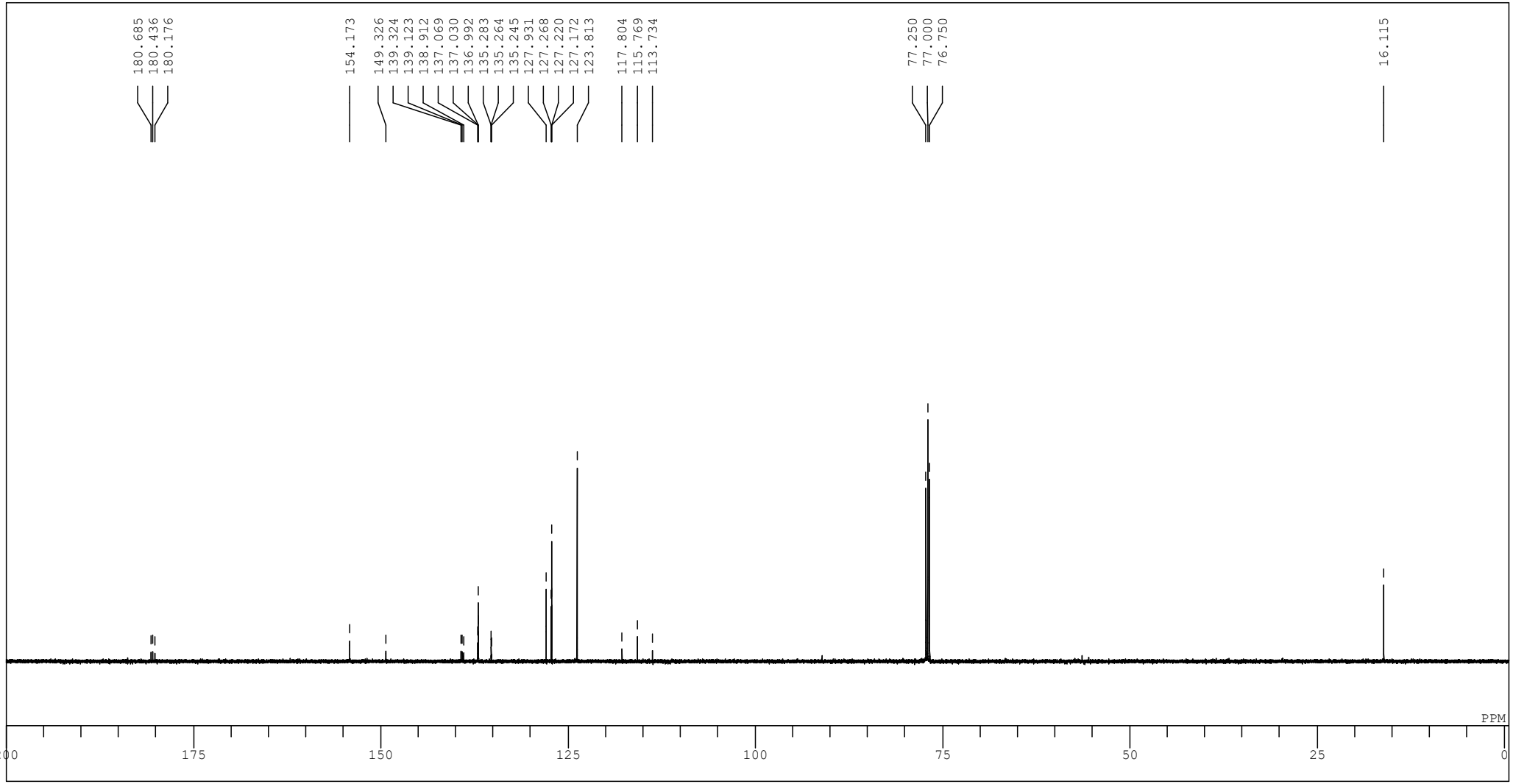

$^{19}F$ NMR (471 MHz, $CDCl_3$)



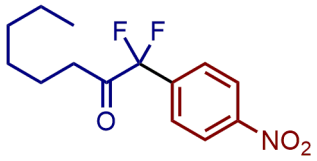
2,2-Difluoro-1-(5-methylthiophen-2-yl)-2-(4-nitrophenyl)ethan-1-one (3ha)



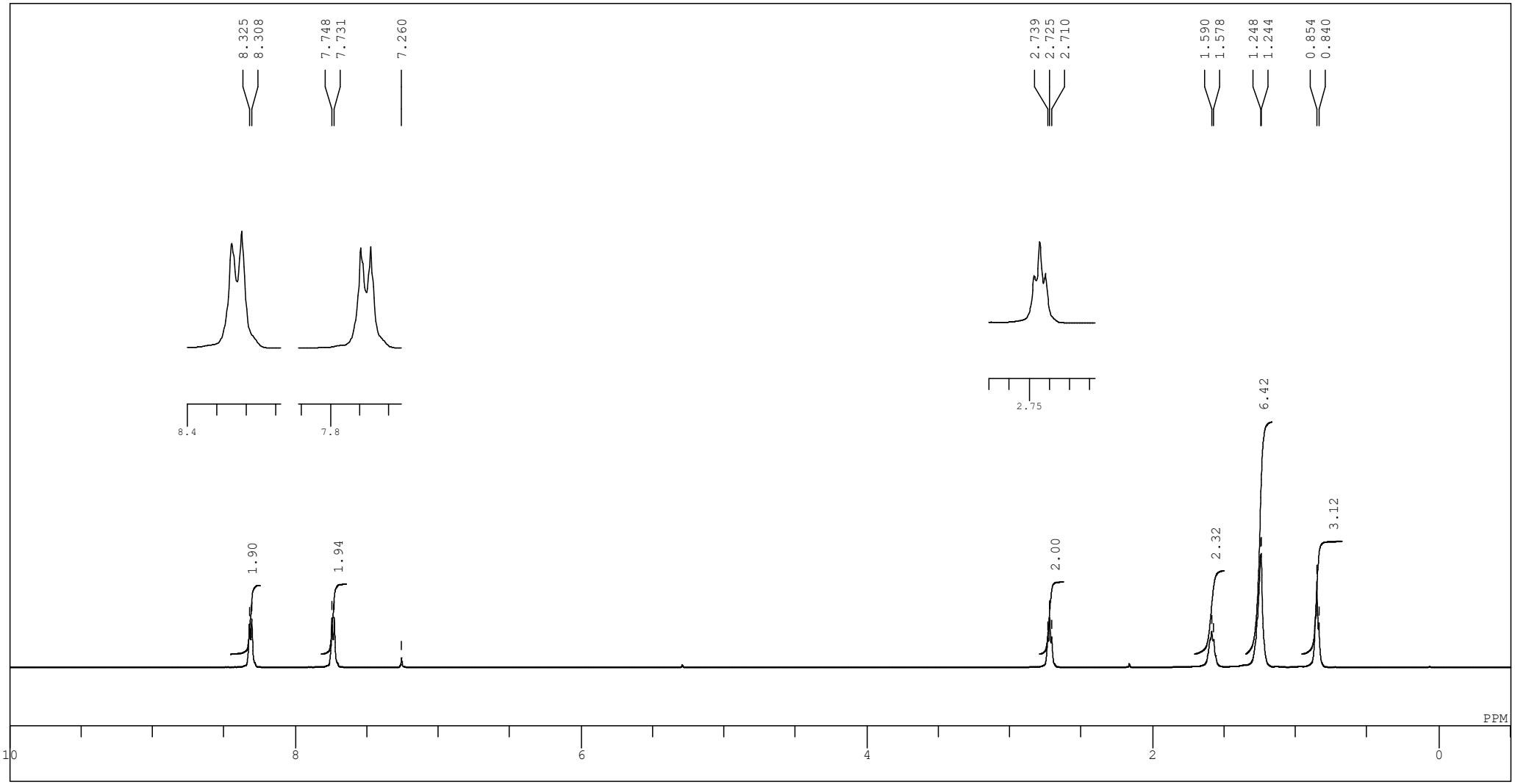

$^{13}C$ NMR (126 MHz, $CDCl_3$)



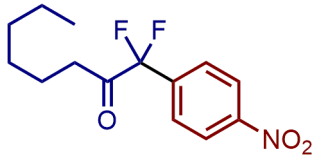
1,1-Difluoro-1-(4-nitrophenyl)octan-2-one (3ia)



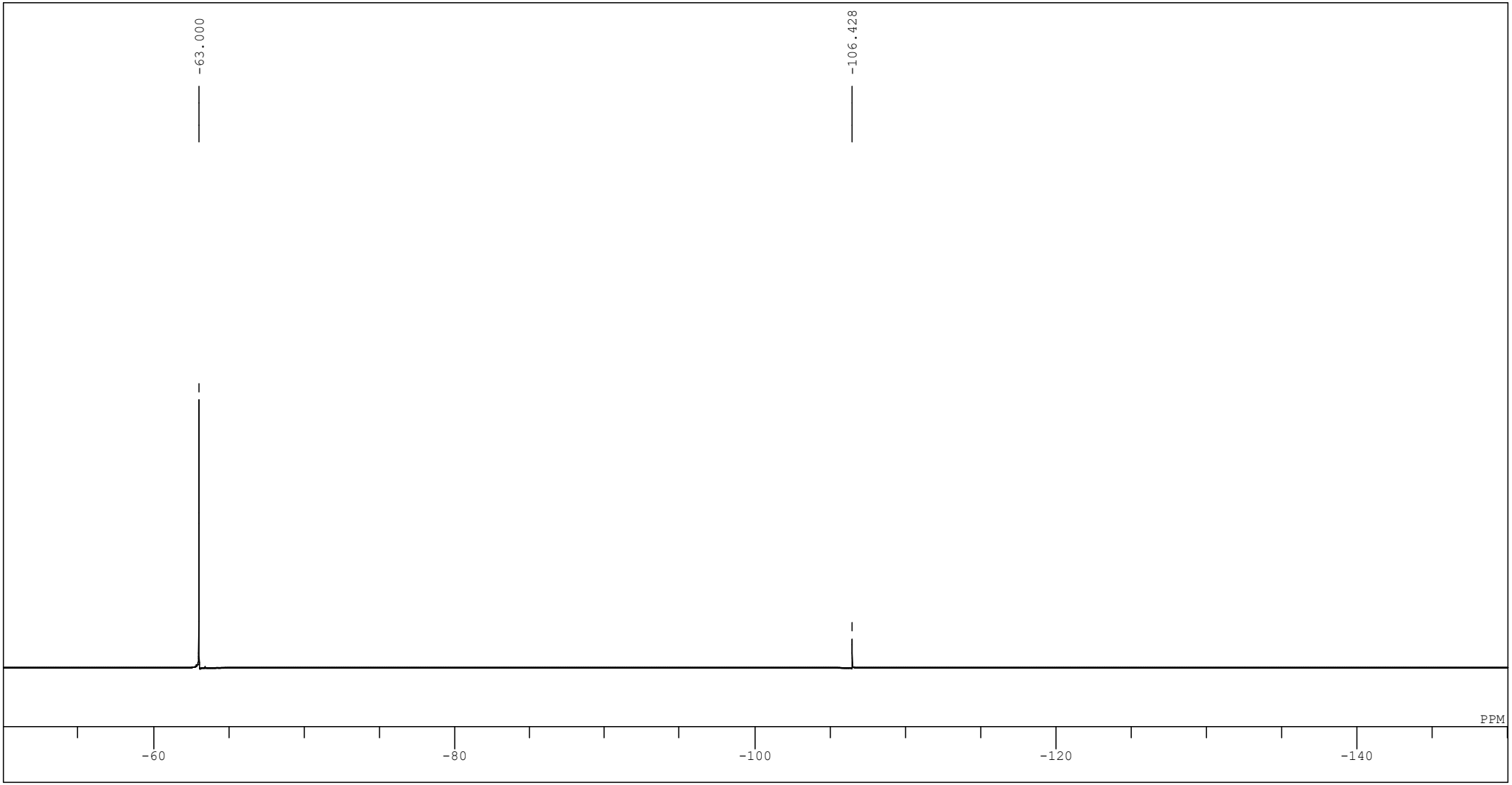

$^1$H NMR (500 MHz, $CDCl_3$)



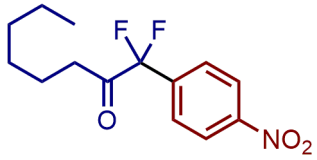
1,1-Difluoro-1-(4-nitrophenyl)octan-2-one (3ia)



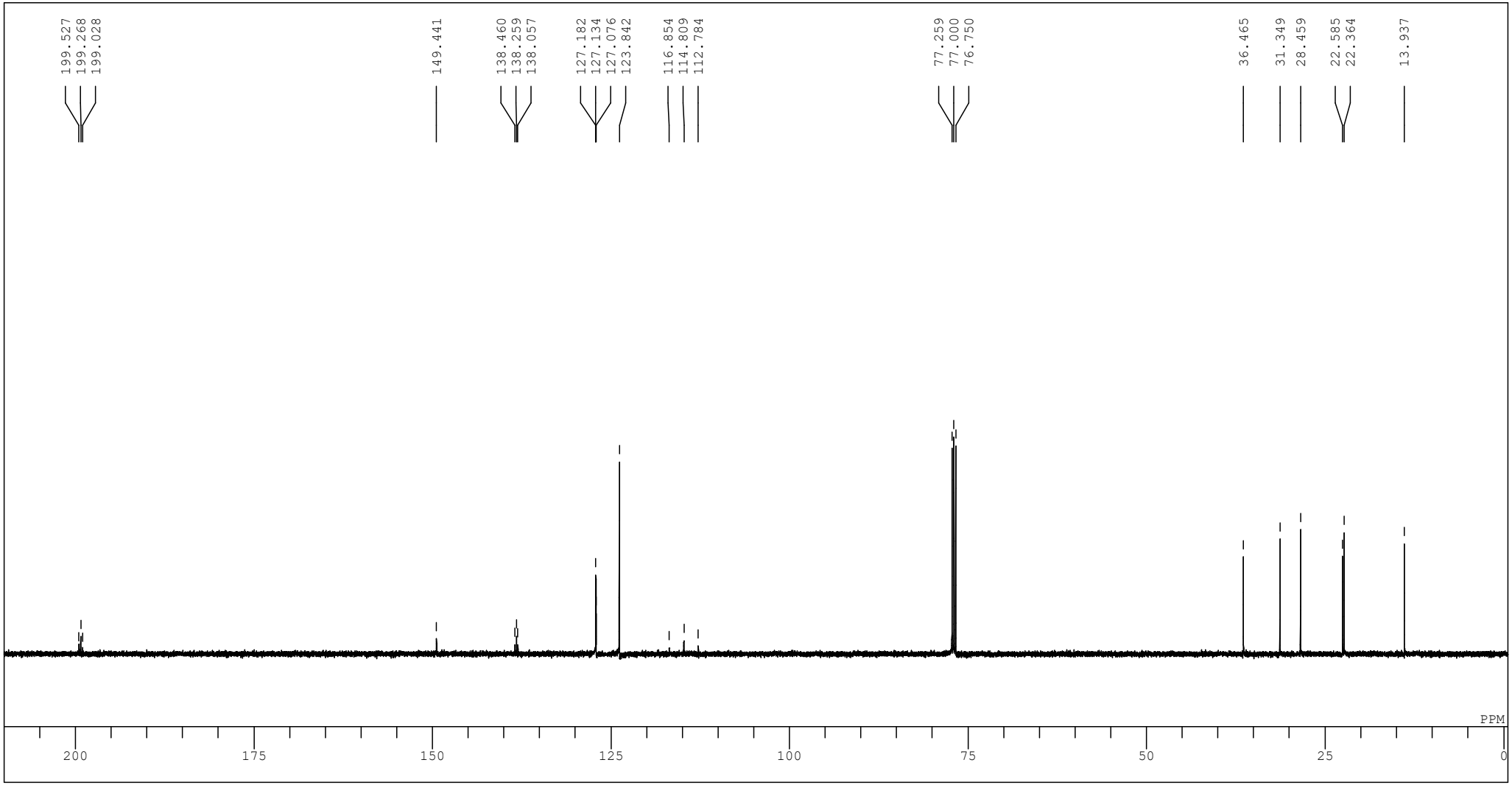

$^{19}F$ NMR (471 MHz, $CDCl_3$)



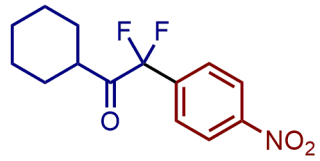
1,1-Difluoro-1-(4-nitrophenyl)octan-2-one (3ia)



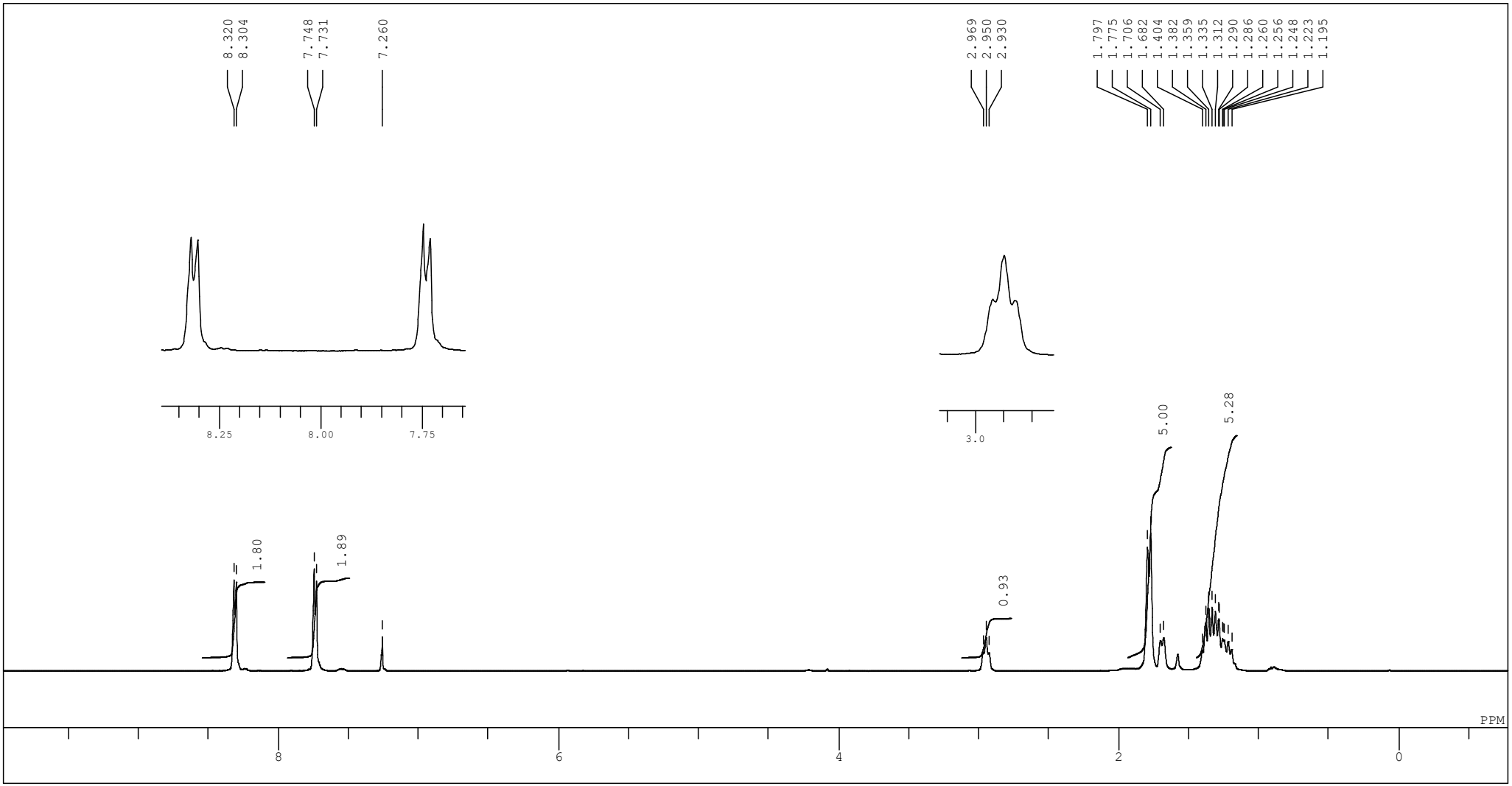

$^{13}C$ NMR (126 MHz, $CDCl_3$)



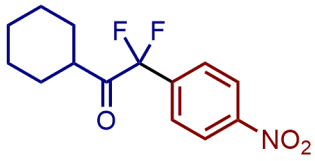
1-Cyclohexyl-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ja)



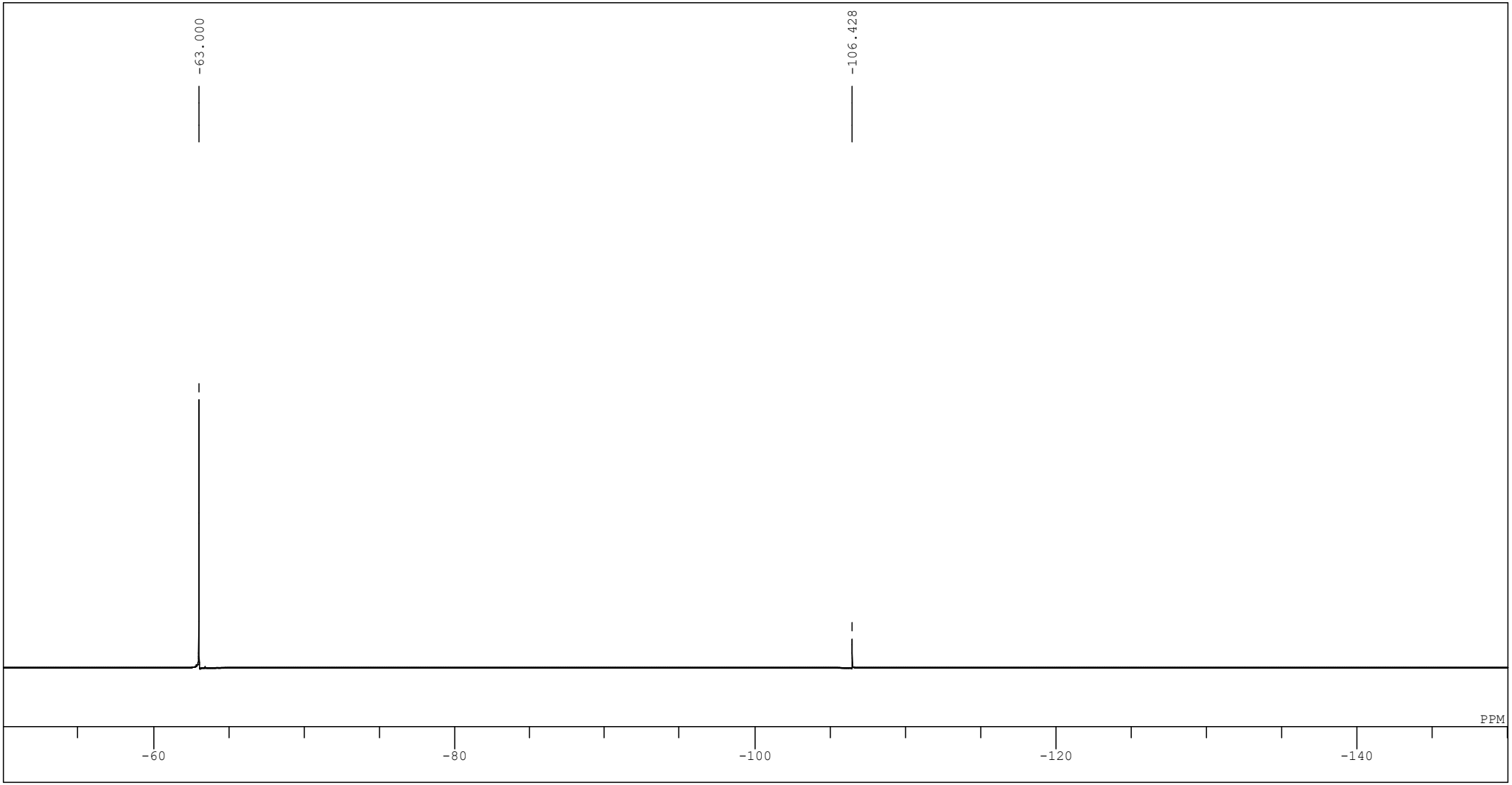

$^1$H NMR (500 MHz, $CDCl_3$)



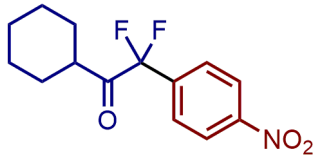
1-Cyclohexyl-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ja)



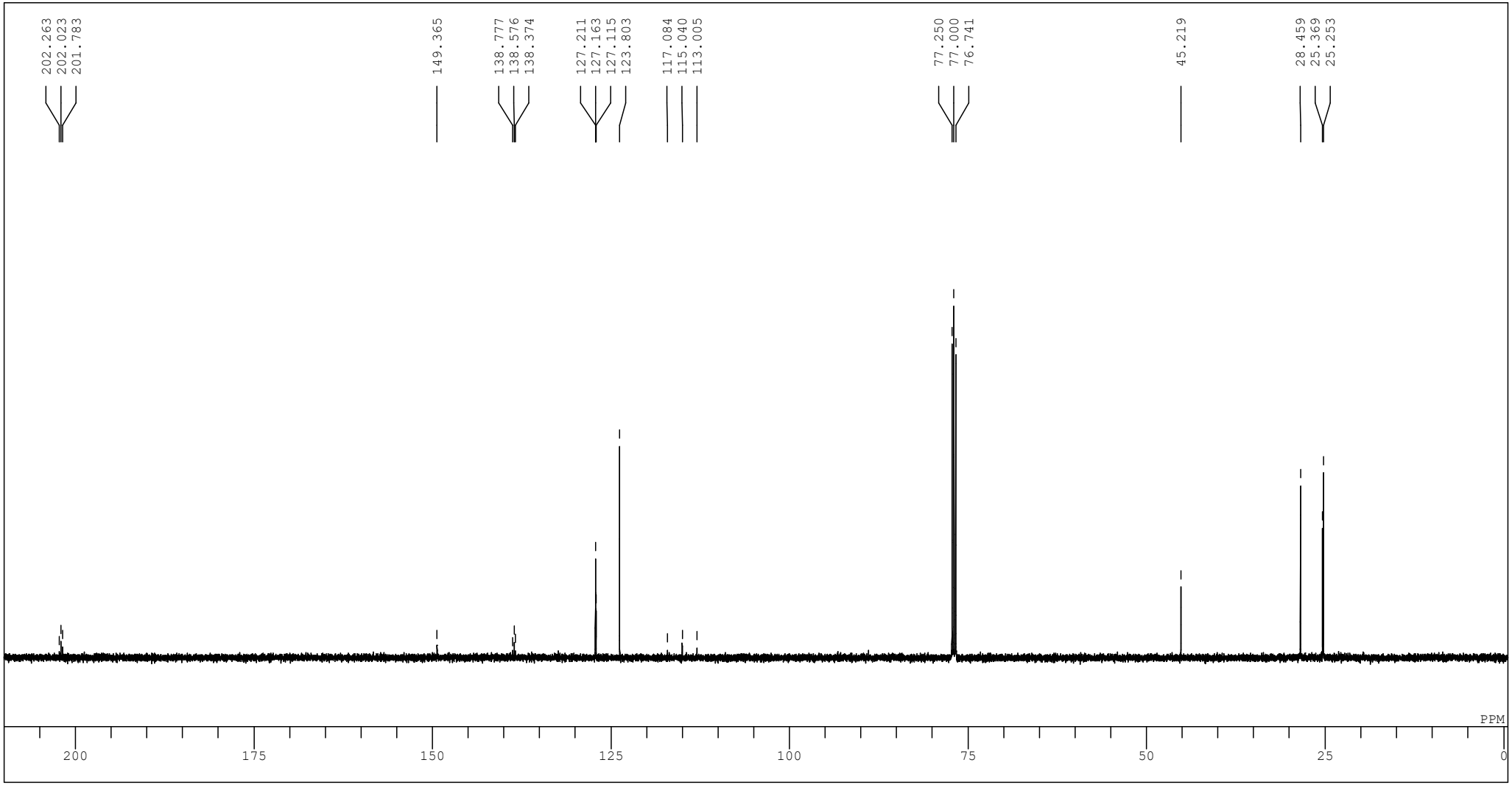

$^{19}F$ NMR (471 MHz, $CDCl_3$)



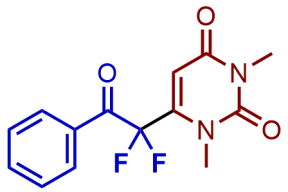
1-Cyclohexyl-2,2-difluoro-2-(4-nitrophenyl)ethan-1-one (3ja)



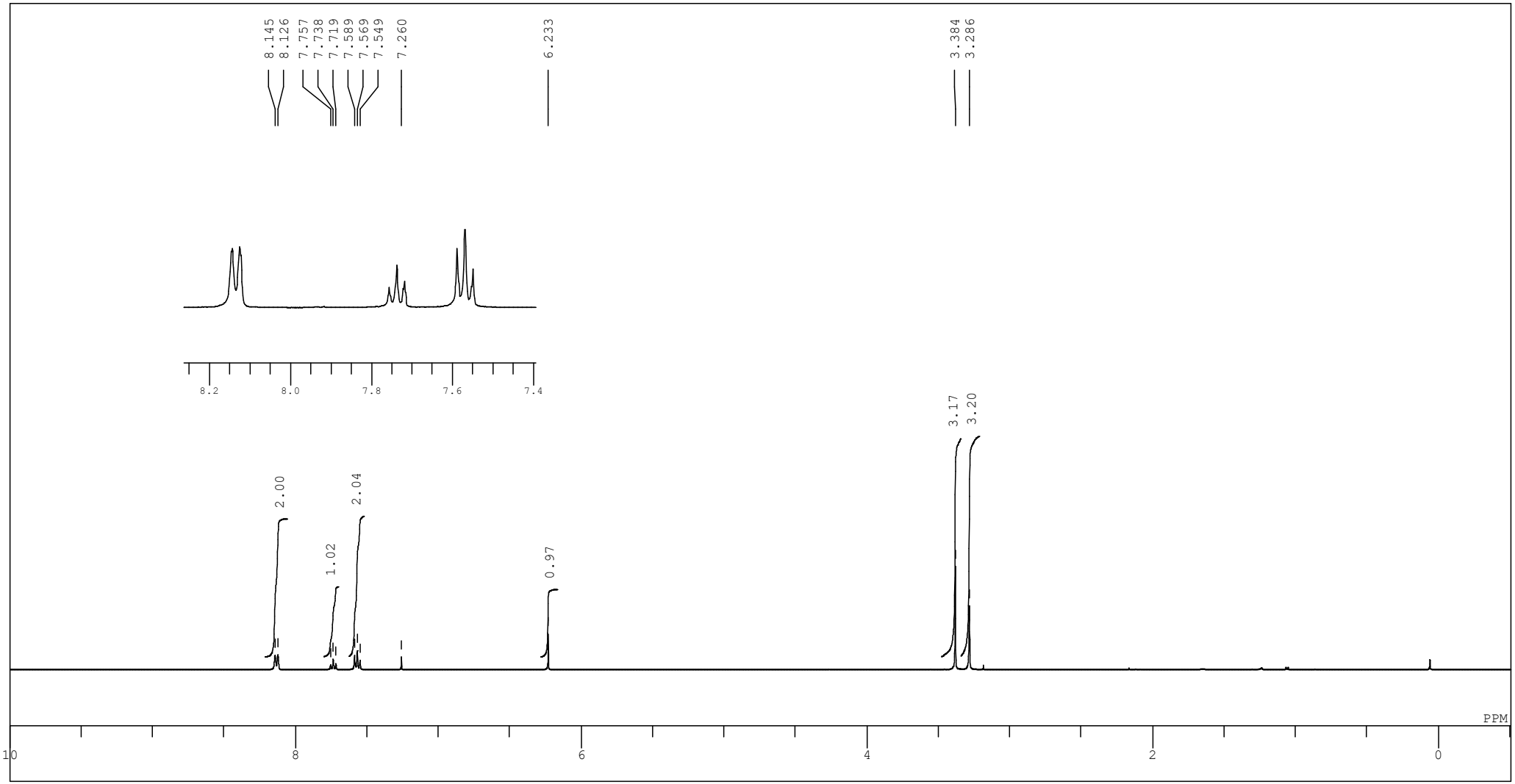

$^{13}C$ NMR (126 MHz, $CDCl_3$)



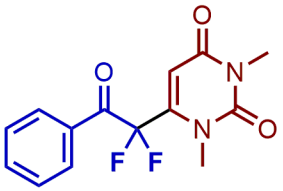
6-(1,1-Difluoro-2-oxo-2-phenylethyl)-*N*,*N*-dimethyluracil (3ao)



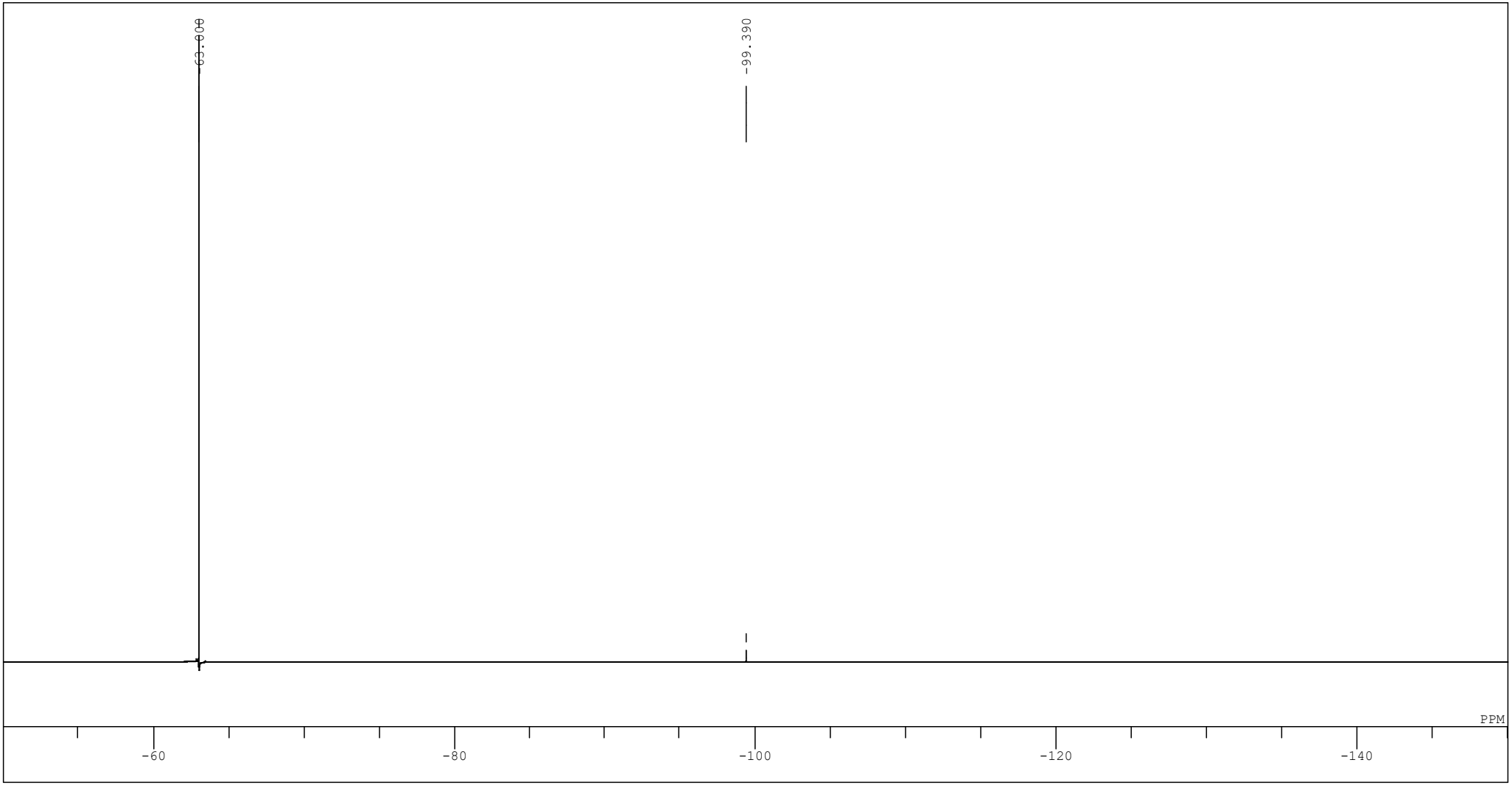

$^1$H NMR (400 MHz, $CDCl_3$)



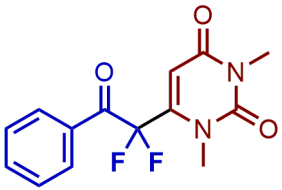
6-(1,1-Difluoro-2-oxo-2-phenylethyl)-*N*,*N*-dimethyluracil (3ao)



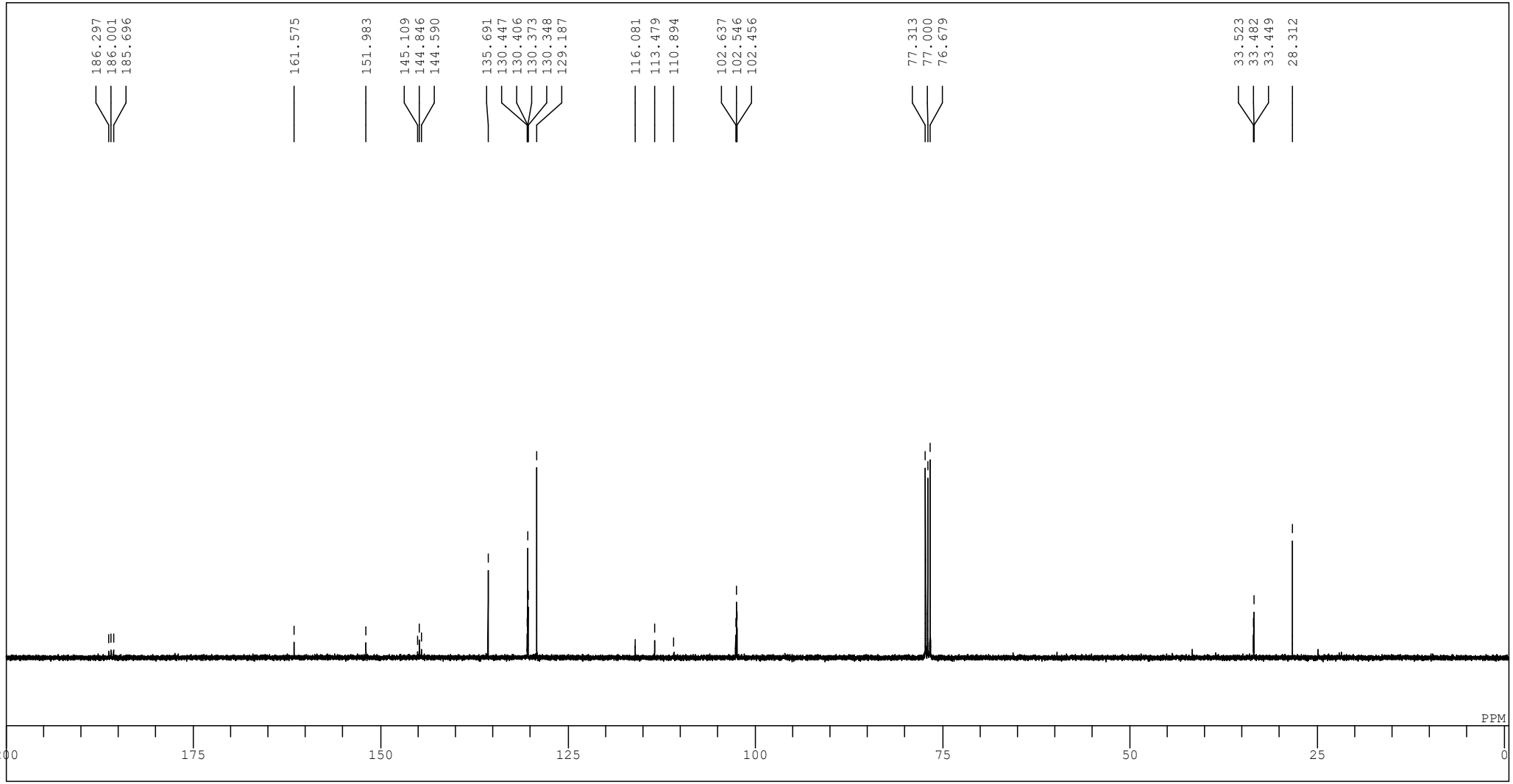

$^{19}$F NMR (471 MHz, $CDCl_3$)



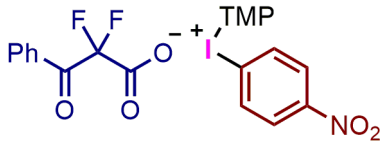
6-(1,1-Difluoro-2-oxo-2-phenylethyl)-*N*,*N*-dimethyluracil (3ao)



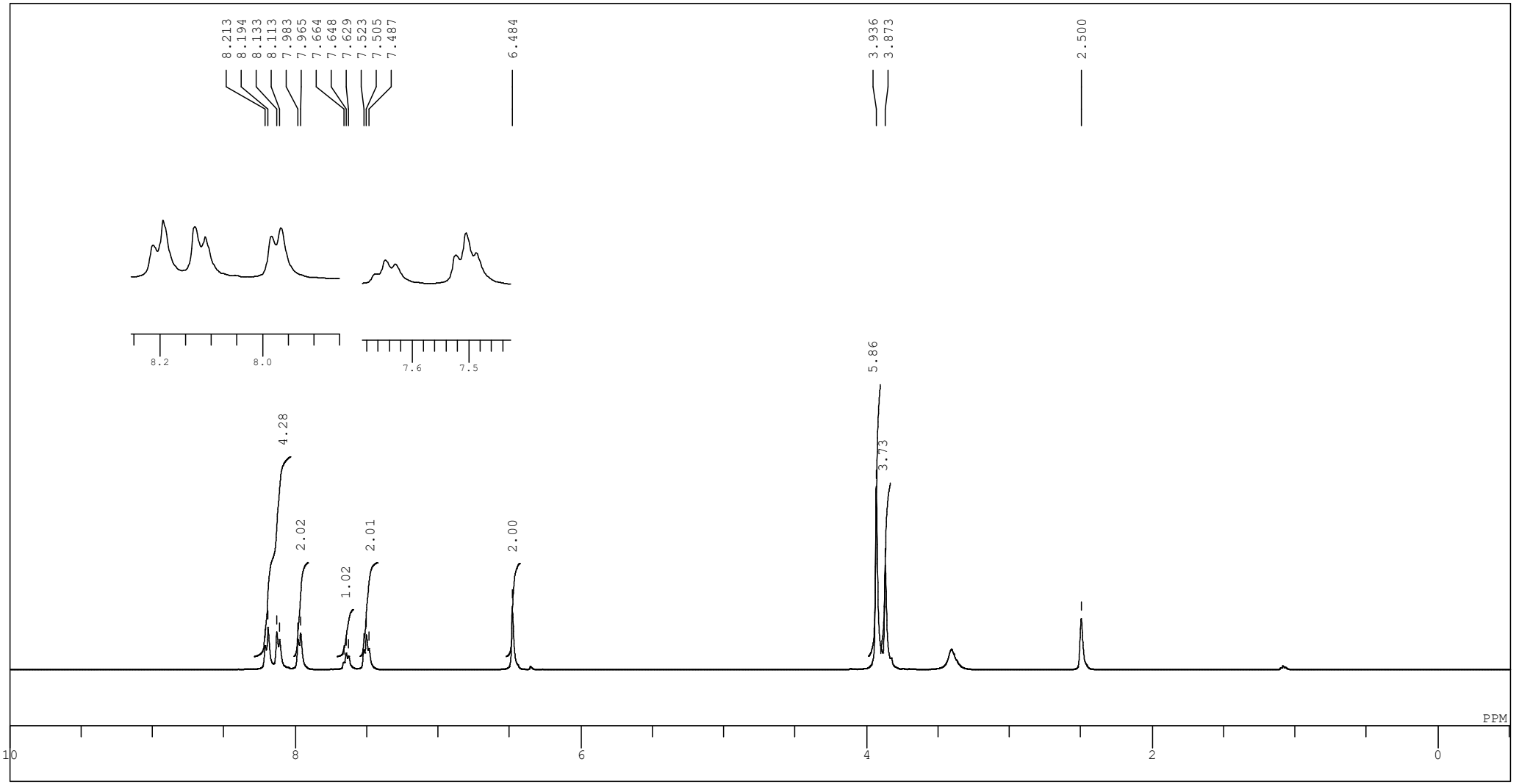

$^{13}C$ NMR (100 MHz, $CDCl_3$)



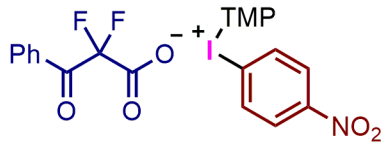
(4-Nitrophenyl)(TMP)iodonium 2,2-difluoro-3-oxo-3-phenylpropanoate (1a2a-TMP)



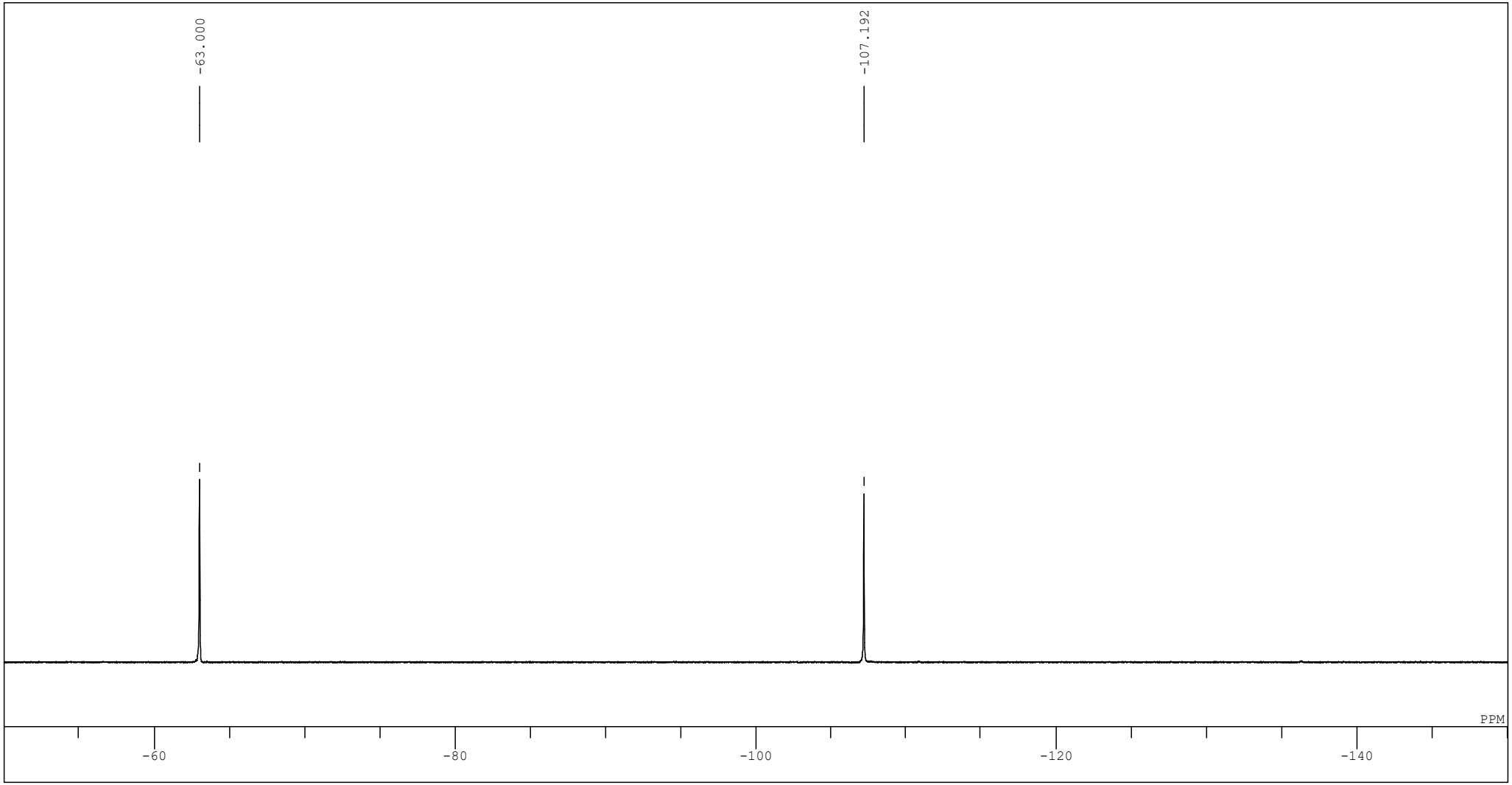

$^1$H NMR (400 MHz, DMSO-$d_6$)



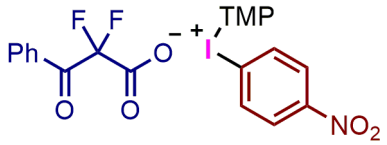
(4-Nitrophenyl)(TMP)iodonium 2,2-difluoro-3-oxo-3-phenylpropanoate (1a2a-TMP)



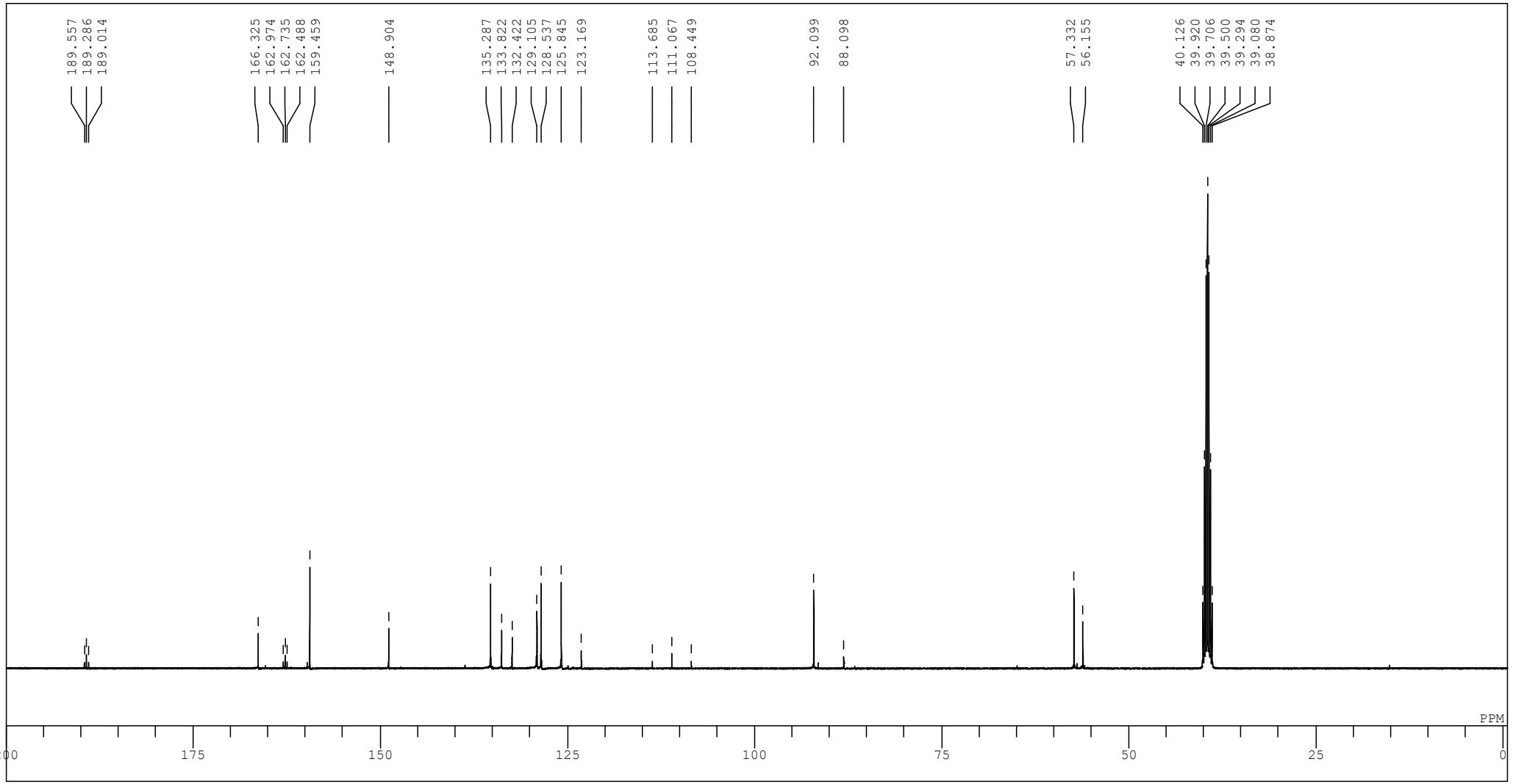

$^{19}$F NMR (376 MHz, DMSO-$d_6$)



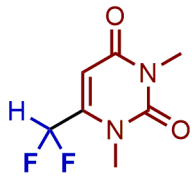
(4-Nitrophenyl)(TMP)iodonium 2,2-difluoro-3-oxo-3-phenylpropanoate (1a2a-TMP)



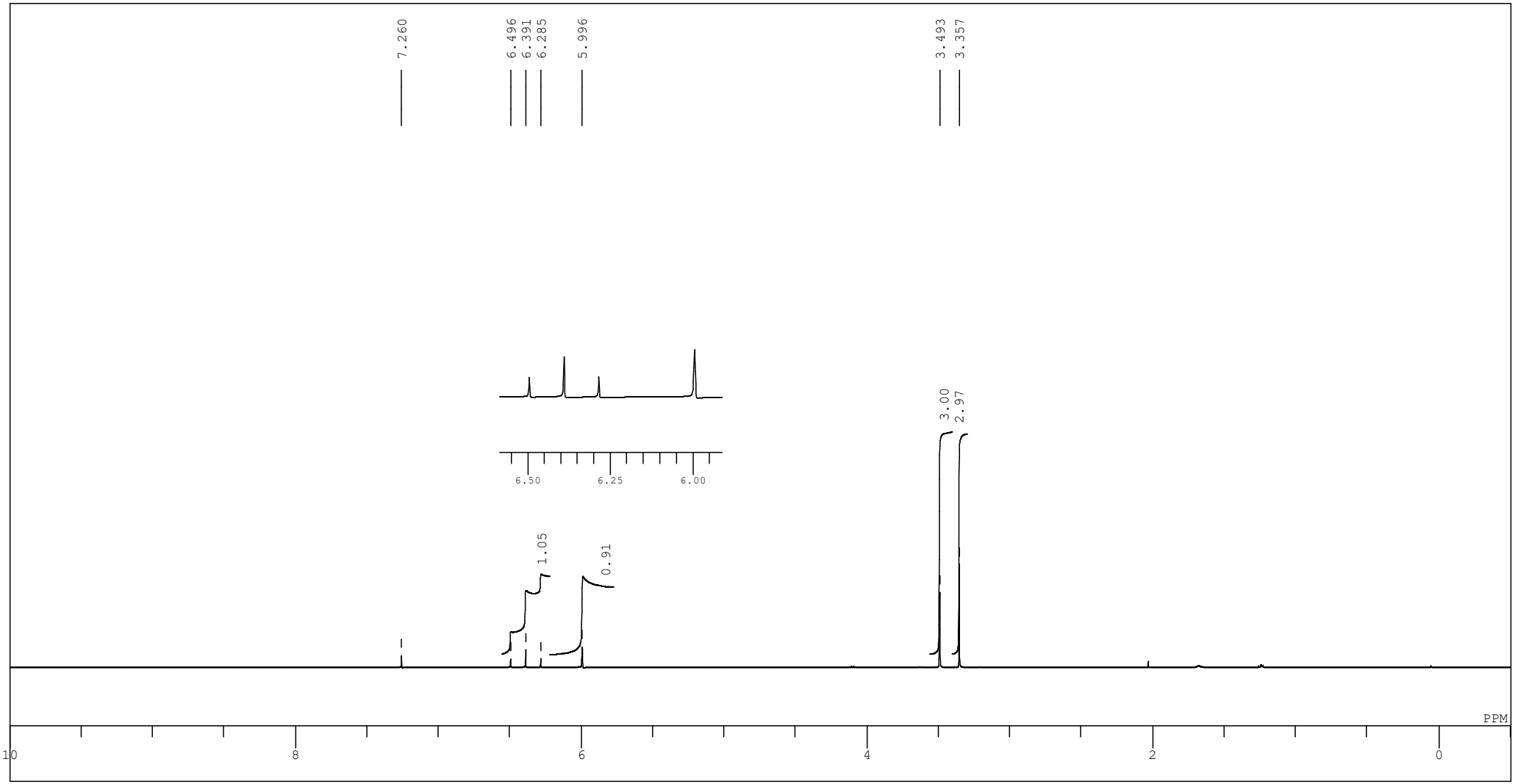

$^{13}$C NMR (100 MHz, DMSO-$d_6$)



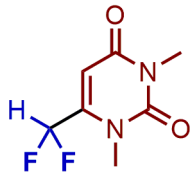
6-Difluoromethyl-*N*,*N*-dimethyluracil (4o)



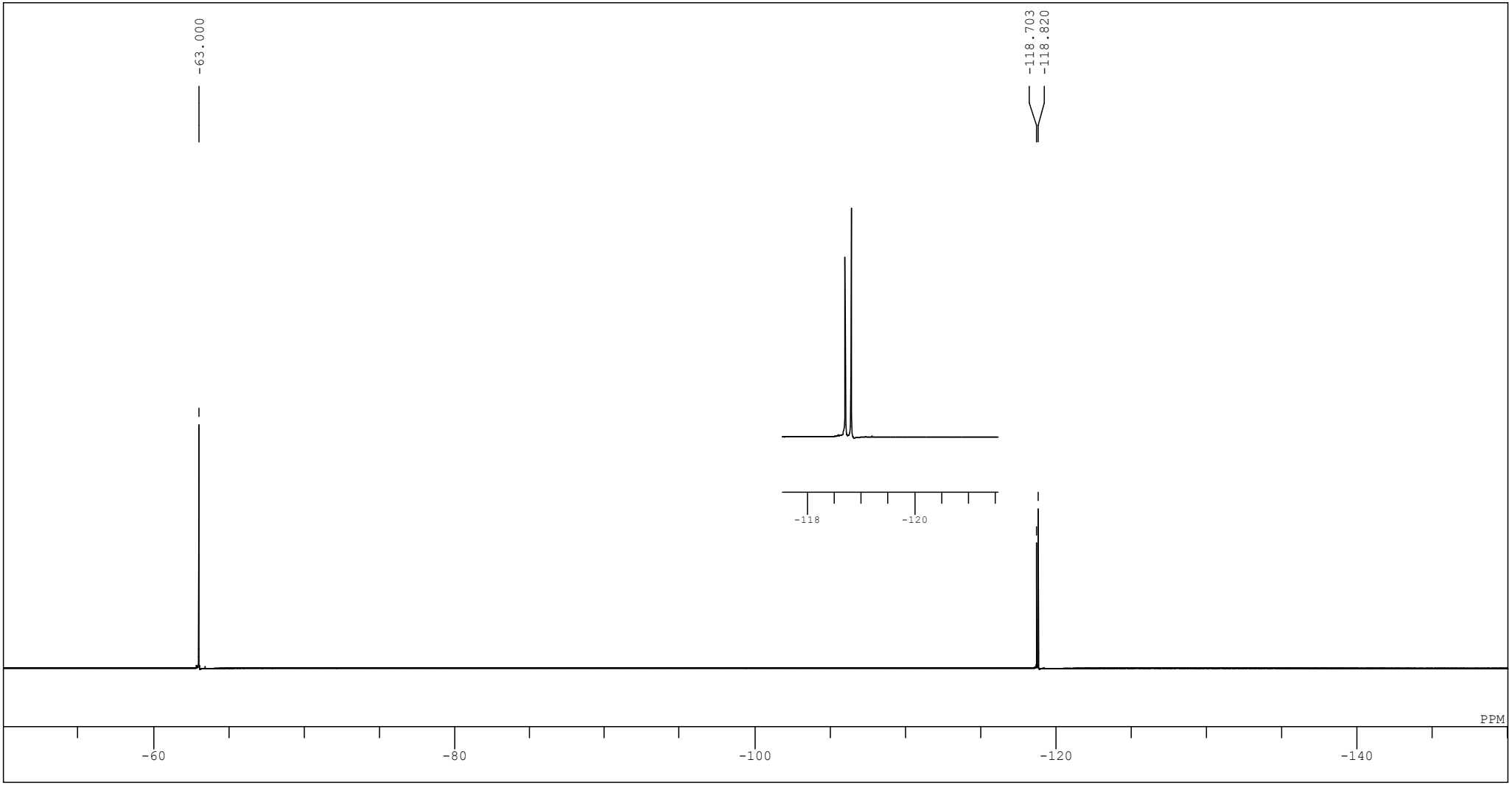

$^{1}$H NMR (500 MHz, $CDCl_3$)



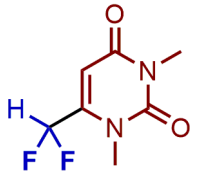
6-Difluoromethyl-*N*,*N*-dimethyluracil (4o)



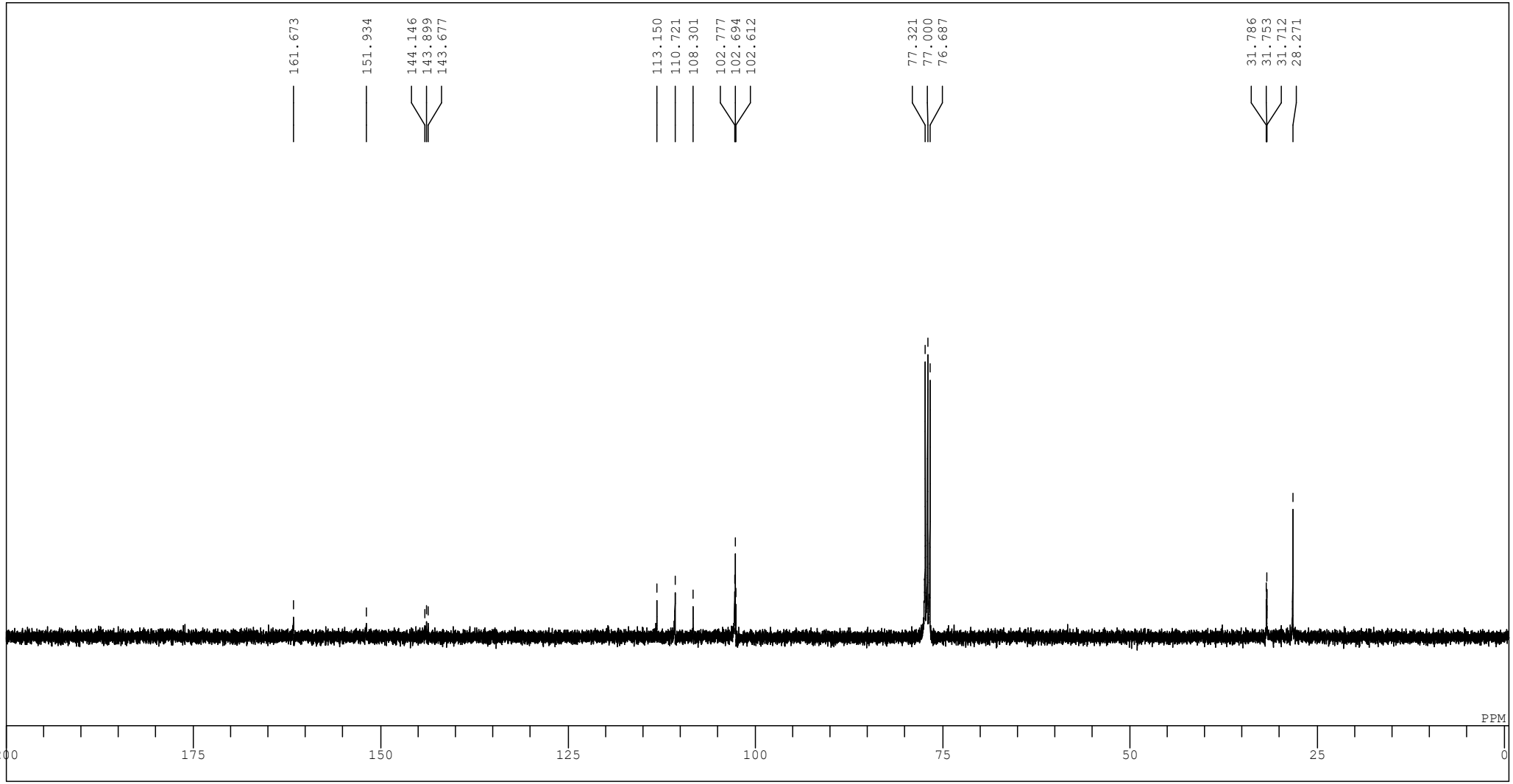

$^{19}F$ NMR (471 MHz, $CDCl_3$)



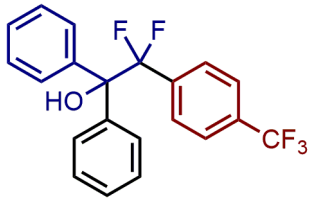
6-Difluoromethyl-*N*,*N*-dimethyluracil (4o)



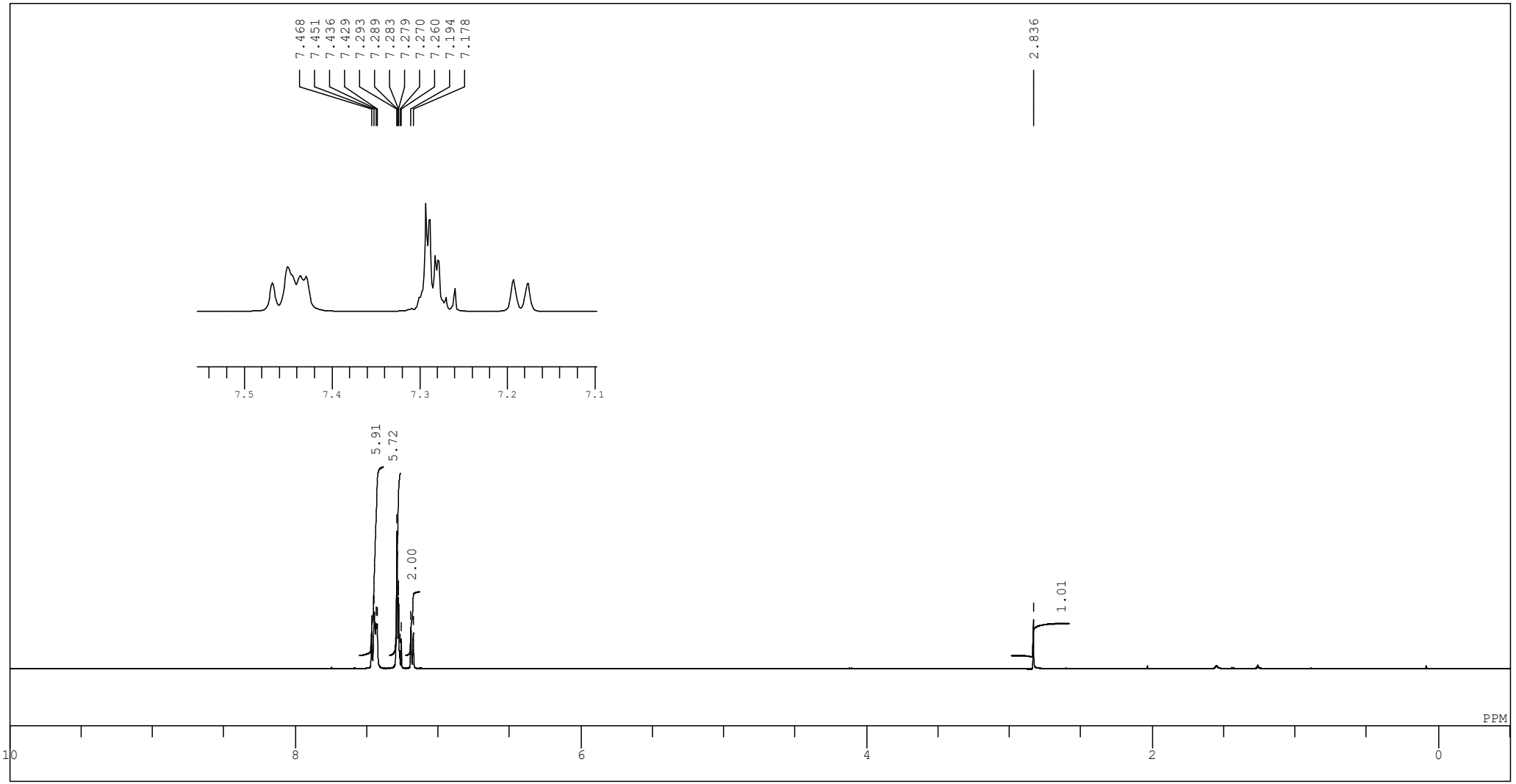

$^{13}C$ NMR (100 MHz, $CDCl_3$)



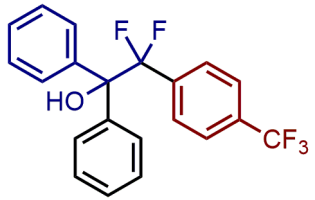
2,2-Difluoro-1,1-diphenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (5aeb)



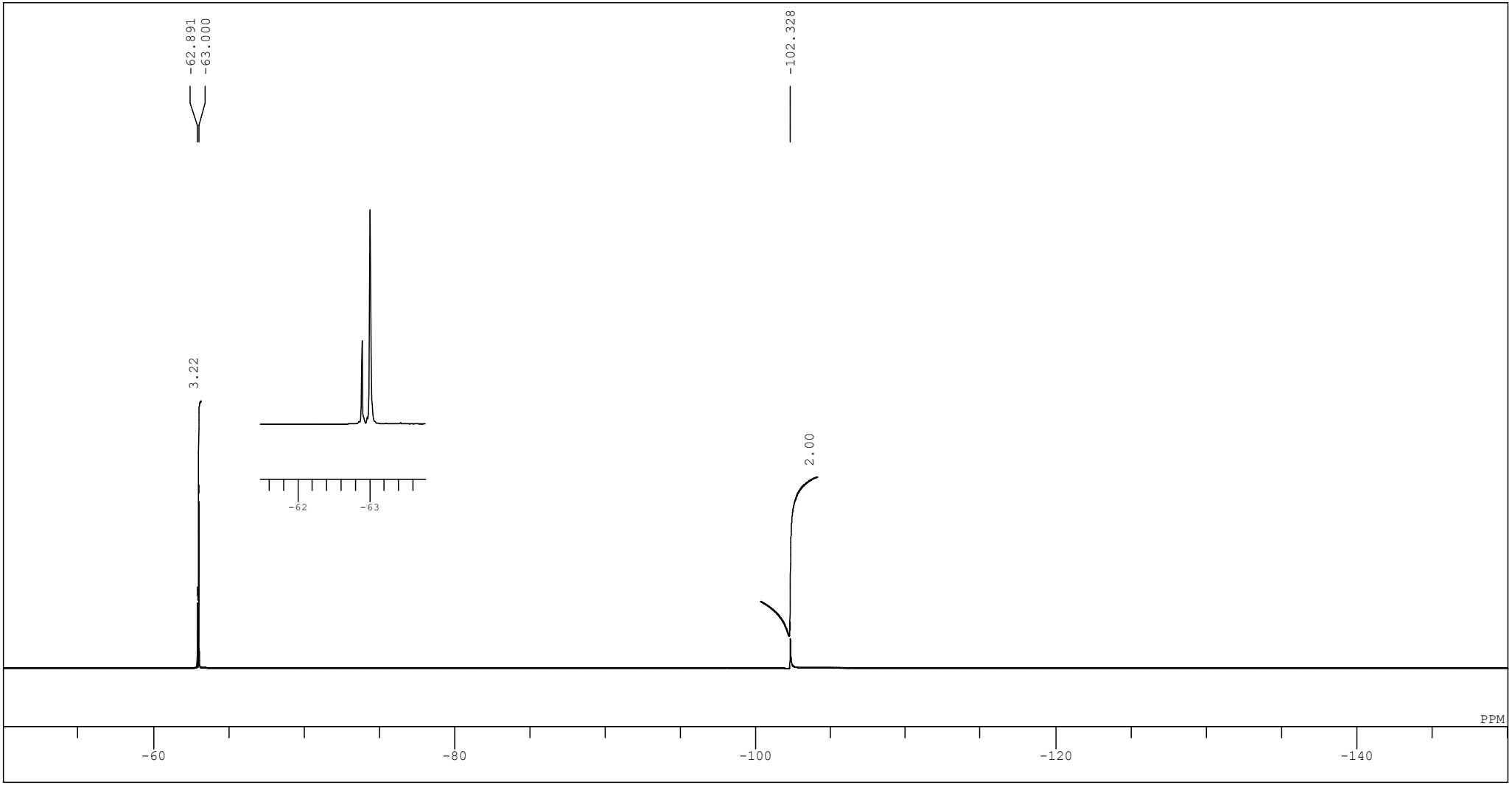

$^1$H NMR (500 MHz, $CDCl_3$)



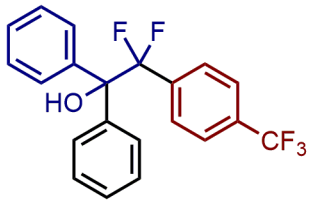
2,2-Difluoro-1,1-diphenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (5aeb)



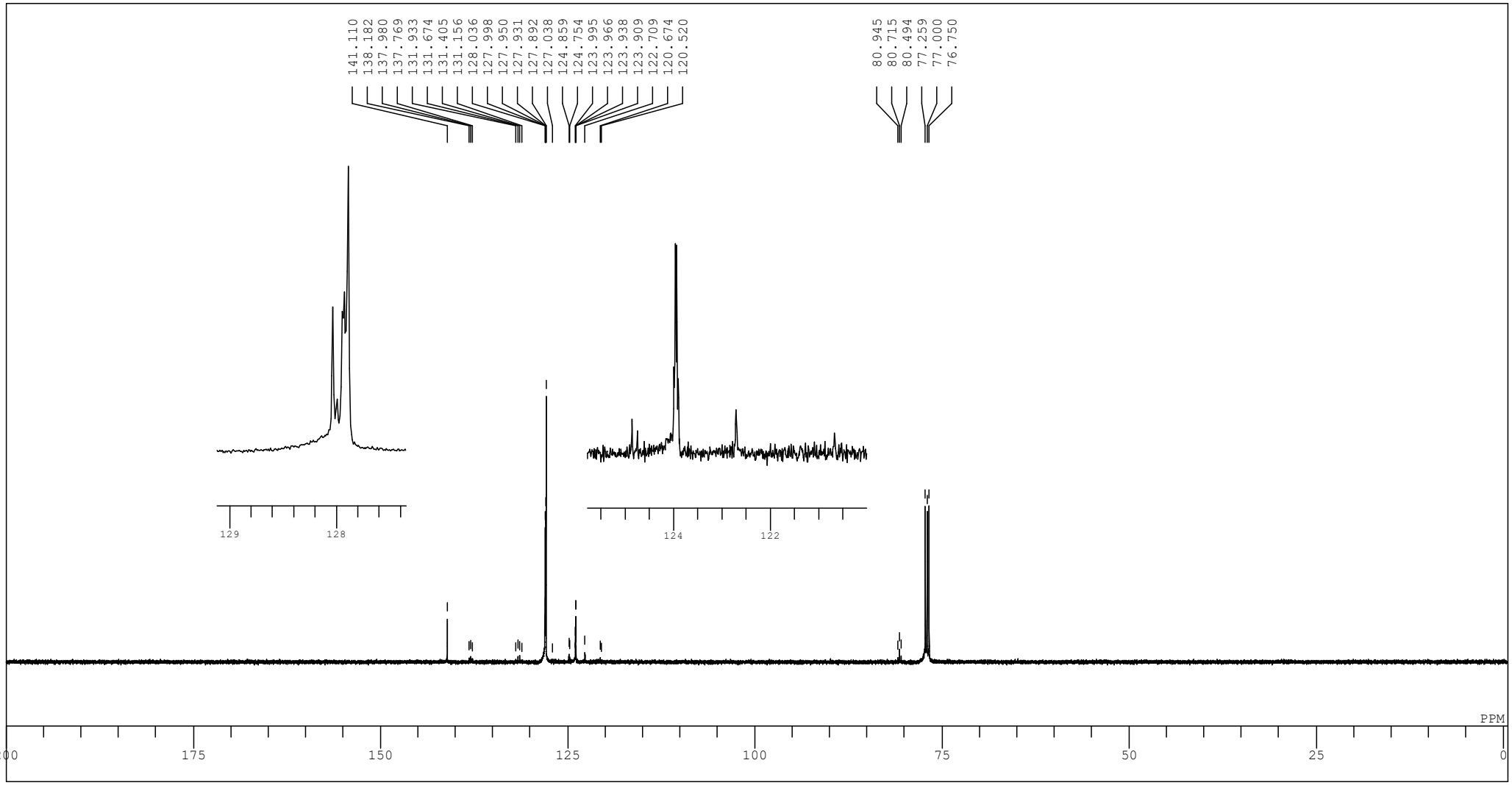

$^{19}F$ NMR (471 MHz, $CDCl_3$)



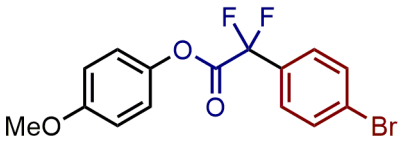
2,2-Difluoro-1,1-diphenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (5aeb)



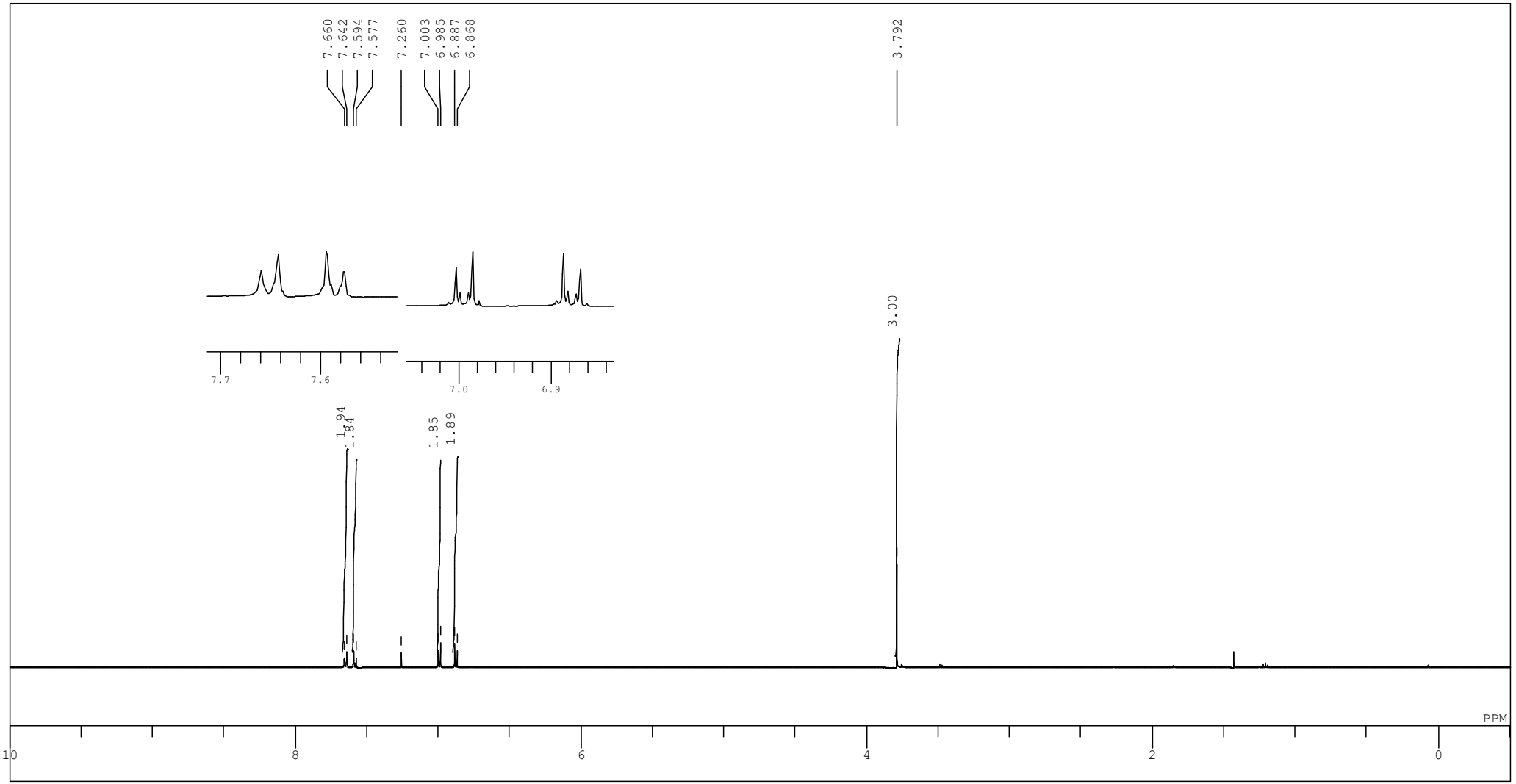

$^{13}C$ NMR (126 MHz, $CDCl_3$)



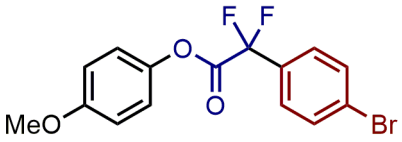
4-Methoxyphenyl 2-(4-bromophenyl)-2,2-difluoroacetate (6bk)



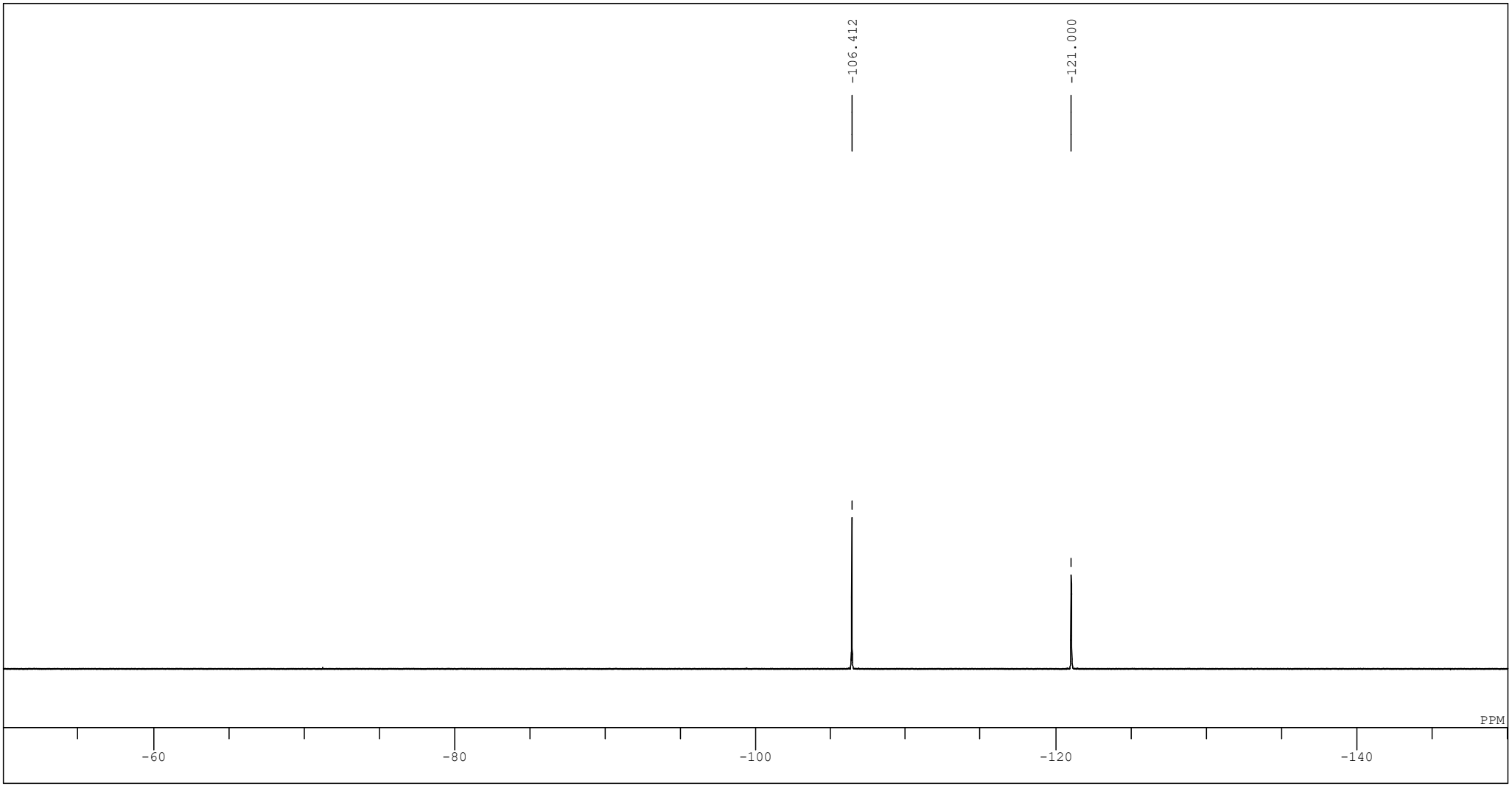

$^1$H NMR (500 MHz, $CDCl_3$)



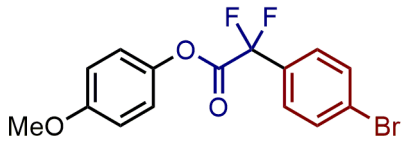
4-Methoxyphenyl 2-(4-bromophenyl)-2,2-difluoroacetate (6bk)



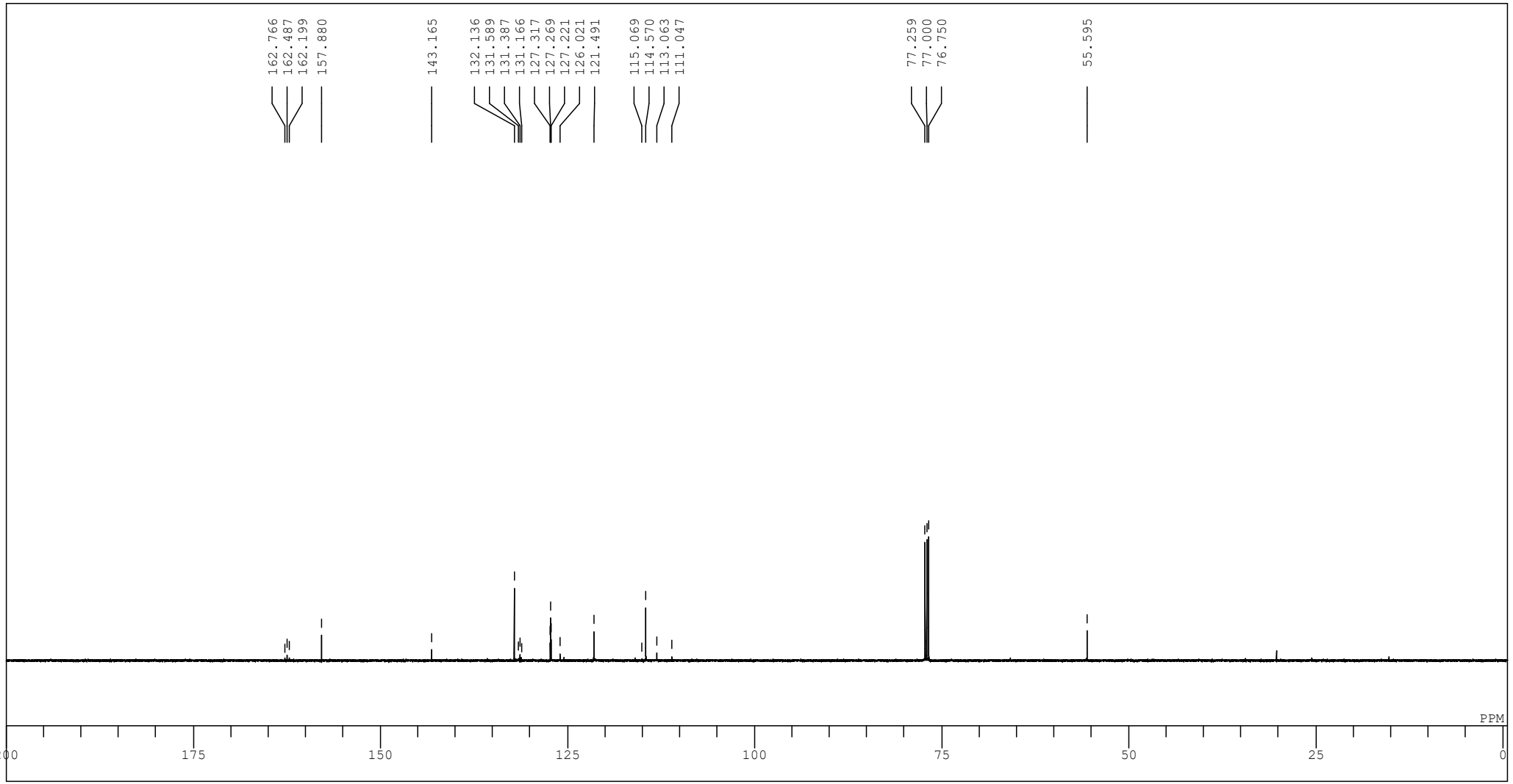

$^{19}F$ NMR (471 MHz, $CDCl_3$)



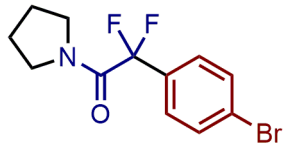
4-Methoxyphenyl 2-(4-bromophenyl)-2,2-difluoroacetate (6bk)



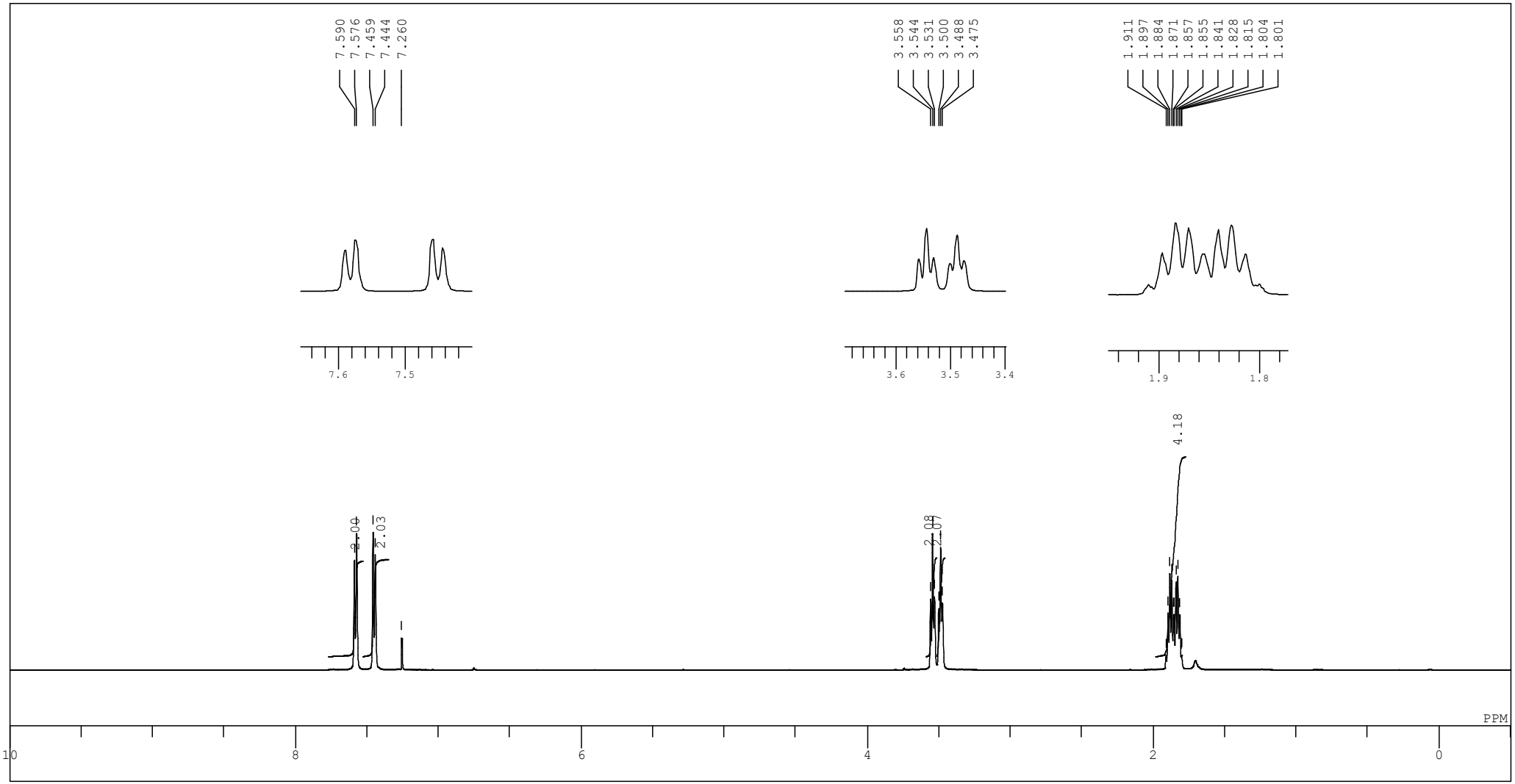

$^{13}C$ NMR (126 MHz, $CDCl_3$)



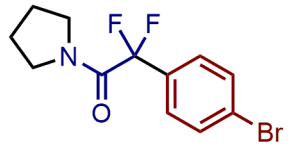
2-(4-Bromophenyl)-2,2-difluoro-1-(pyrrolidin-1-yl)ethan-1-one (7k)



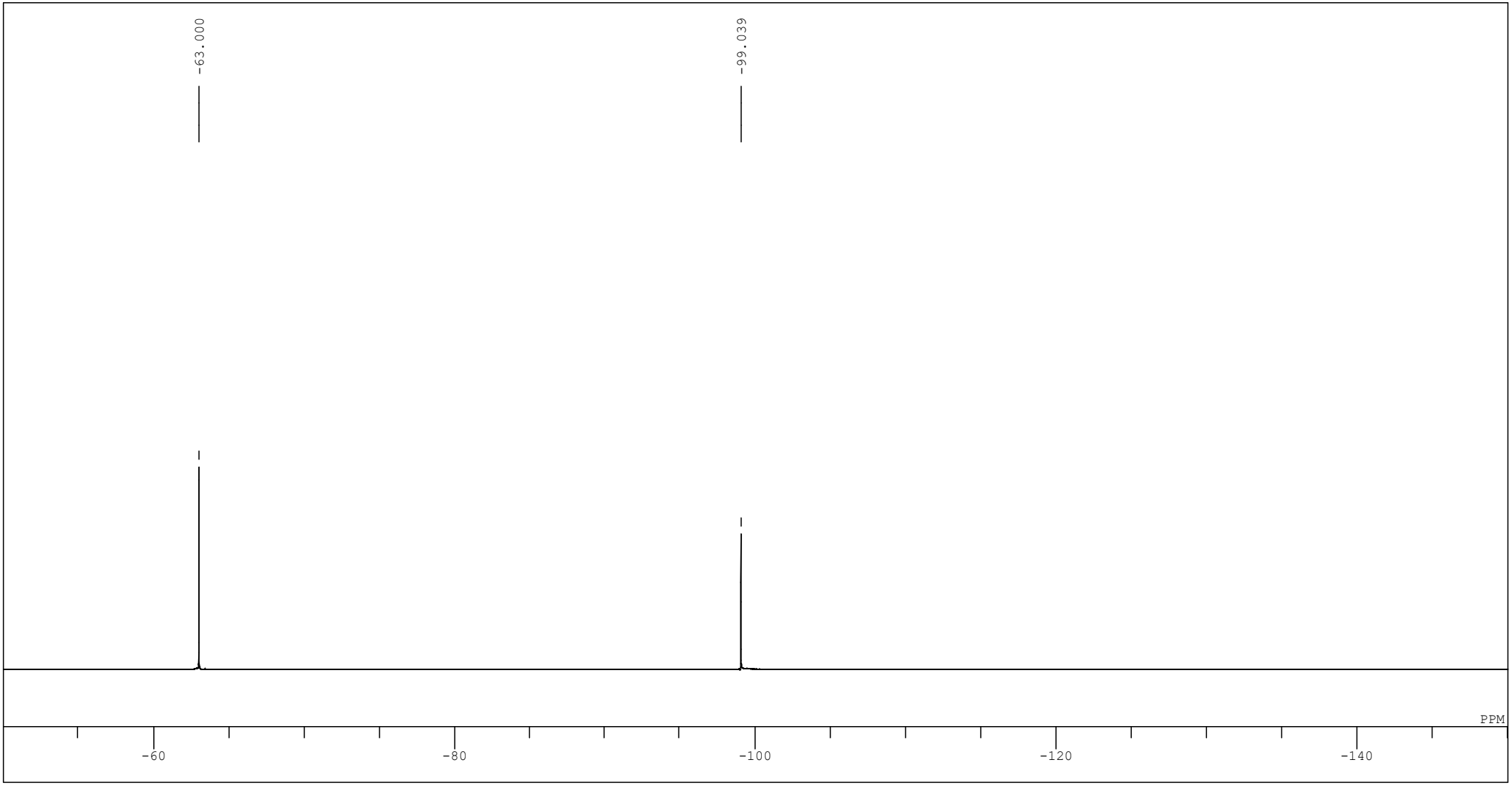

$^1$H NMR (500 MHz, $CDCl_3$)



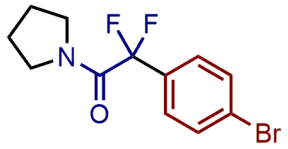
2-(4-Bromophenyl)-2,2-difluoro-1-(pyrrolidin-1-yl)ethan-1-one (7k)



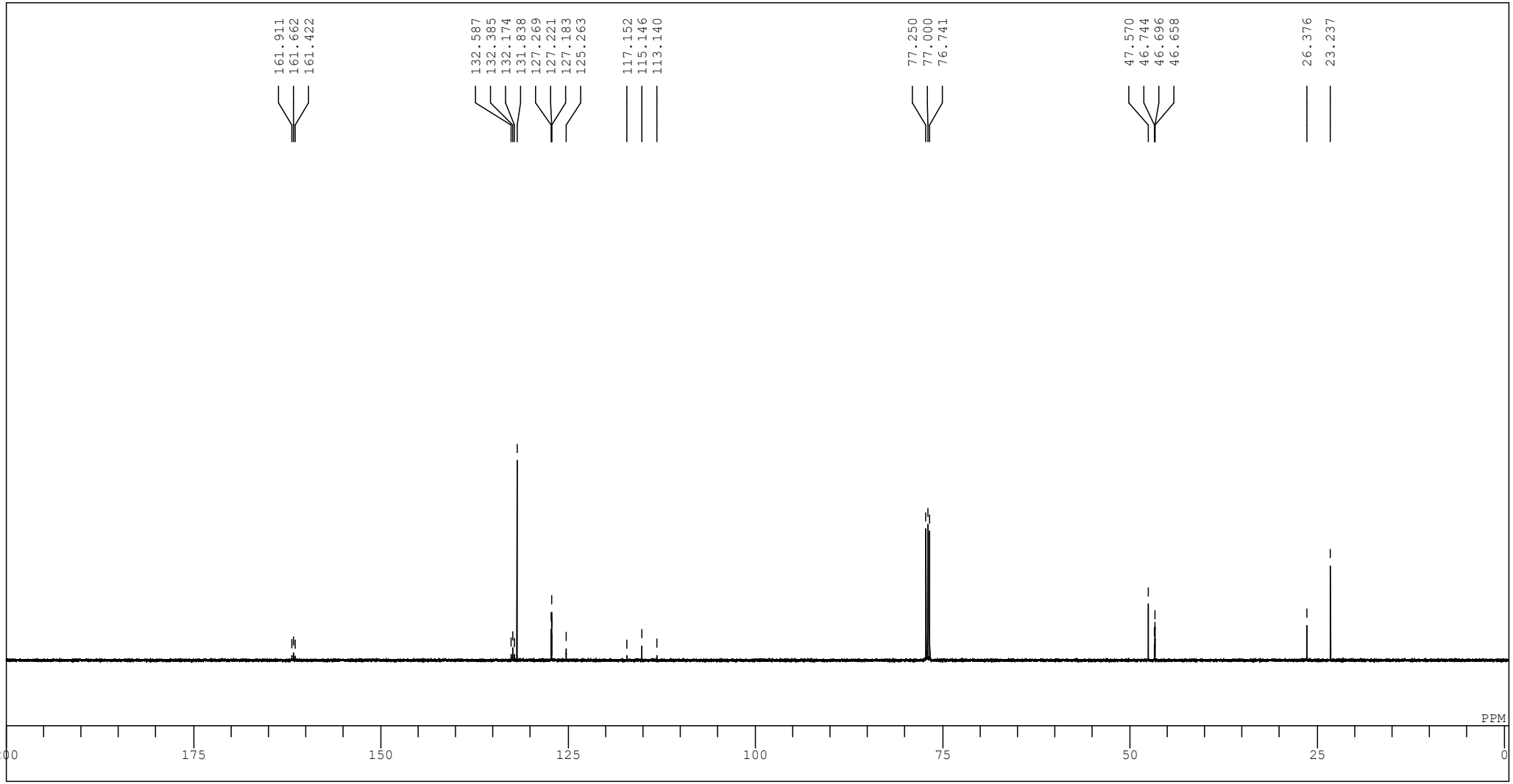

$^{19}F$ NMR (471 MHz, $CDCl_3$)



2-(4-Bromophenyl)-2,2-difluoro-1-(pyrrolidin-1-yl)ethan-1-one (7k)

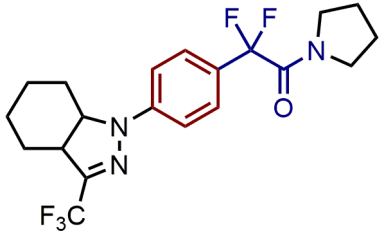


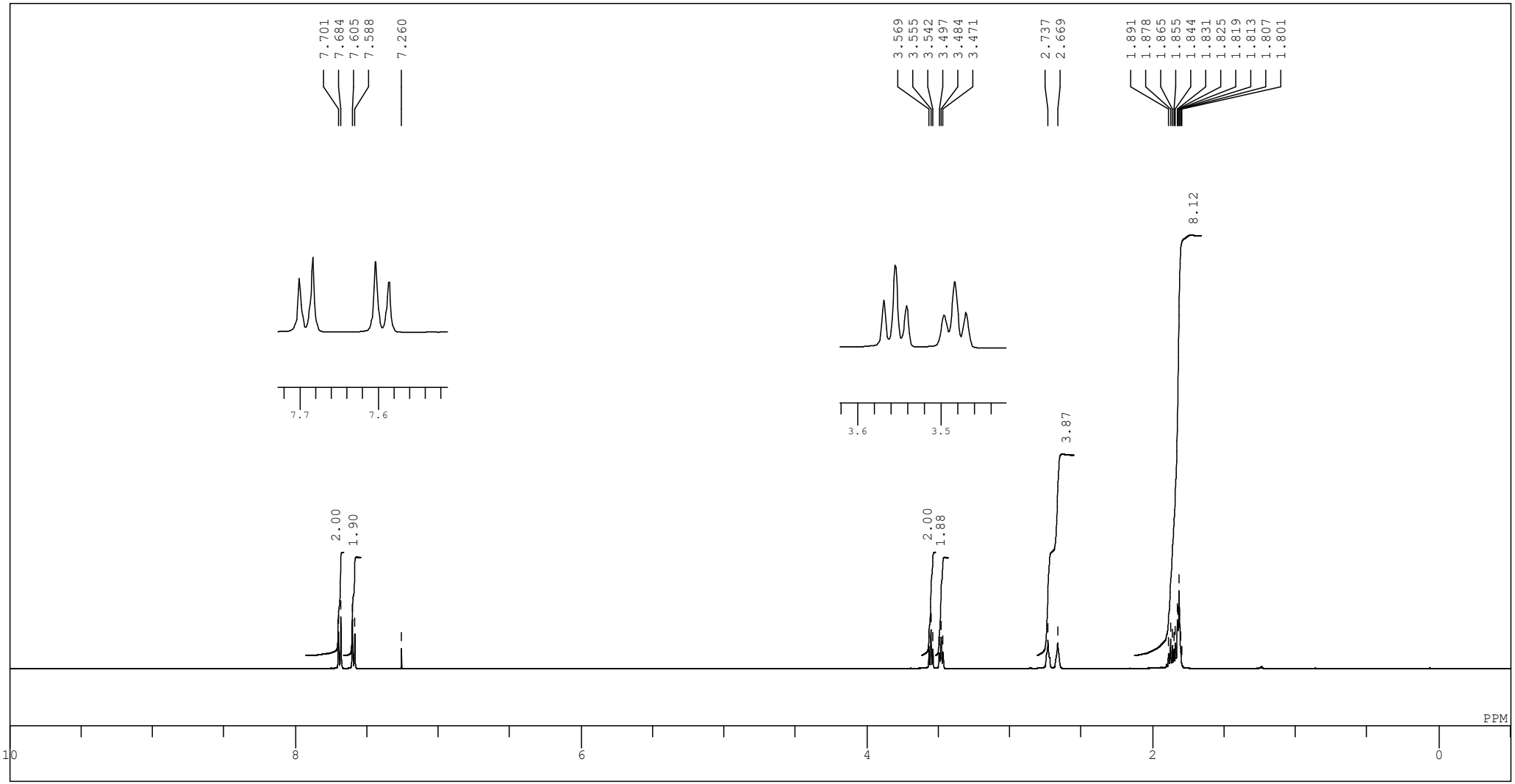

$^{13}C$ NMR (126 MHz, $CDCl_3$)



Compound 8

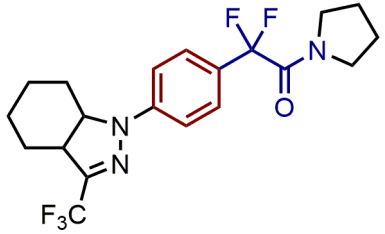
$^1$H NMR (500 MHz, $CDCl_3$)

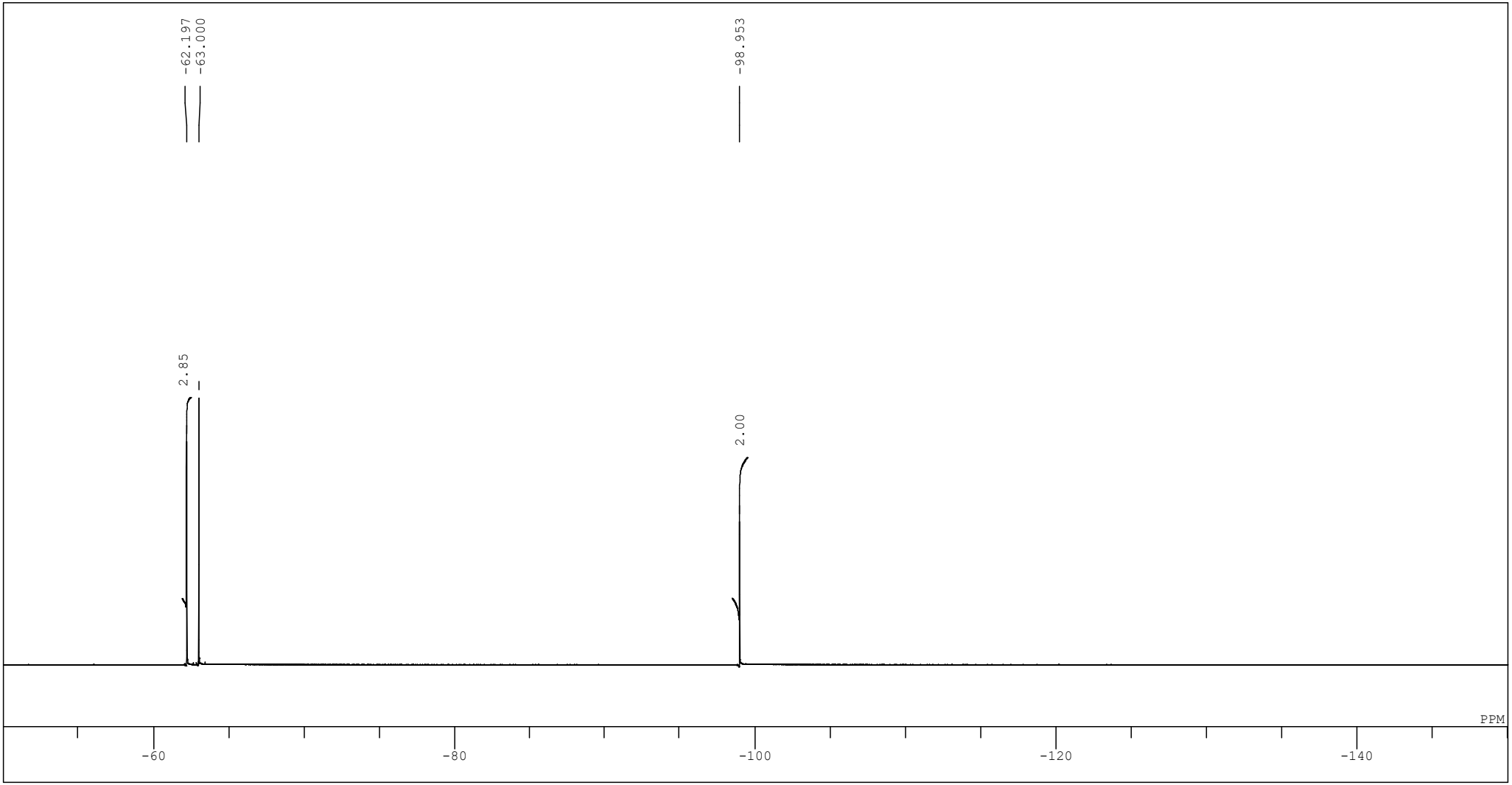


Compound 8

$^{19}F$ NMR (471 MHz, $CDCl_3$)



Compound 8

$^{13}C$ NMR (126 MHz, $CDCl_3$)