

Heptafluoroisopropyl diazomethane (*i*-C₃F₇CHN₂):

***in situ* generation and synthesis of pyrazoles**

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Supporting Information

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(A) Experimental part

1. General details

Solvents were purified according to standard procedures. Other starting materials were taken at Enamine at the highest commercial quality and used without further purification. Melting points are uncorrected. ¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance 500 or 400 spectrometer (at 500 MHz or 400 and 125 or 101 MHz, respectively). ¹⁹F-NMR spectra were recorded on a Varian Unity Plus 400 spectrometer (at 376 Hz). Chemical shifts are reported in ppm downfield from Me₄Si (¹H, ¹³C) or upfield from CFCl₃ (¹⁹F) using conventional deuterium lock referencing as internal standards.

3a. General procedure for generating *i*C₃F₇CHN₂ (**9**)

A suspension of C₃F₇CH₂NH₂*HCl (38 mg, 0.16 mmol, 1.0 equiv) and NaNO₂ (18 mg, 0.26 mmol, 1.6 equiv) in CDCl₃ (1.0 mL)/H₂O (0.1 mL) was vigorously stirred during 1 h at room temperature. The organic layer was separated, dried over Na₂SO₄ and filtered off. NMR spectra of crude *i*C₃F₇CHN₂ (**9**) in CDCl₃ (ca. 80% purity) were measured.

¹H NMR (400 MHz, CDCl₃) δ 4.25 (s, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -77.1 (6F, d, *J* = 11.3 Hz), -158.5 (1F, heptet (7 lines), *J* = 11.3 Hz).

3b. General procedure for [3+2]-cycloaddition

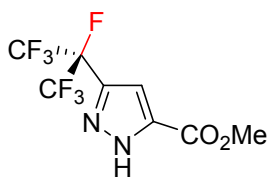
To a stirred suspension of C₃F₇CH₂NH₂*HCl (113 mg, 0.48 mmol, 3.0 equiv) in CH₂Cl₂ (4.0 mL) / water (0.2 mL), sodium nitrite (54 mg, 0.78 mmol, 5.0 equiv) and alkyne (0.16 mmol, 1.0 equiv) was added. The reaction mixture was vigorously stirred 1 h at RT and then heated 72 h at 35 °C. Water (1.0 mL) and CH₂Cl₂ (3 mL) were added. The organic layer was separated. The aqueous layer was washed with CH₂Cl₂ (2 × 3 mL). The combined organic layers were dried over Na₂SO₄ and evaporated under *vacuum* to provide the pure product.

4. General procedure for oxidation

To a stirred solution of **35a** (1.3 g, 4.2 mmol, 1 equiv) in benzene, MnO₂ (3.65 g, 42 mmol, 10 equiv.) was added. Then the reaction mixture was heated to reflux. After 5 h stirring, the obtained reaction mixture was cooled down to room temperature and then treated by filtering. The filtrate was evaporated under *vacuum*. The formed residue was purified by column chromatography on silica gel (Hex/MTBE = 3/1) to afford the desired product **13a** (0.55 g, 1.8 mmol, 43% yield) as a white solid, m.p. 46-47 °C.

(B) Data description

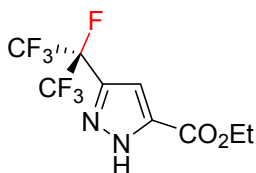
Methyl 3-(perfluoropropan-2-yl)-1H-pyrazole-5-carboxylate (10a)



Yield: 94%; white solid, m.p. 46-47 °C.

^1H NMR (400 MHz, CDCl_3) δ 11.92 (br s, 1H), 7.12 (s, 1H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.7 (d, $J = 8.9$ Hz), -181.3 (p, $J = 8.8$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 159.2 (s), 140.9 (d, $J = 26.4$ Hz), 135.6 (s), 120.2 (dm), 109.2 (s), 90.4-85.7 (m), 52.9 (s). Anal. calcd. for $\text{C}_8\text{H}_5\text{F}_7\text{N}_2\text{O}_2$: C, 32.67; H, 1.71; N, 9.52. Found: C, 32.51; H, 1.91; N, 9.72.

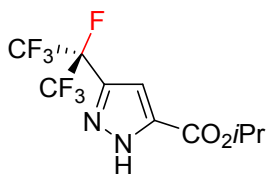
Ethyl 3-(perfluoropropan-2-yl)-1H-pyrazole-5-carboxylate (13a)



Yield: 91%; white solid, m.p. 46-47 °C.

^1H NMR (500 MHz, CDCl_3) δ 7.11 (s, 1H), 4.44 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.7 (d, $J = 9.0$ Hz), -181.2 (p, $J = 8.7$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 158.8 (s), 140.9 (d, $J = 26.0$ Hz), 135.9 (s), 125.0-115.4 (dm), 109.0 (s), 91.1-87.6 (m), 62.4 (s), 14.3 (s). Anal. calcd. for $\text{C}_9\text{H}_7\text{F}_7\text{N}_2\text{O}_2$: C, 35.08; H, 2.29; N, 9.09. Found: C, 35.37; H, 2.01; N, 8.75.

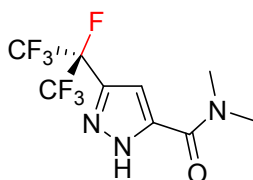
Isopropyl 3-(perfluoropropan-2-yl)-1H-pyrazole-5-carboxylate (14a)



Yield: 95%; yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 7.09 (s, 1H), 5.30 (m, 1H), 1.39 (d, $J = 6.3$ Hz, 6H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.7 (d, $J = 8.9$ Hz), -181.3 (p, $J = 8.8$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 158.5 (s), 140.7 (d, $J = 25.9$ Hz), 136.3 (s), 124.5 – 114.9 (dm), 109.0 (d, $J = 4.0$ Hz), 92.5-85.2 (m), 70.7 (s), 21.8 (s). Anal. calcd. for $\text{C}_{10}\text{H}_9\text{F}_7\text{N}_2\text{O}_2$: C, 37.28; H, 2.82; N, 8.70. Found: C, 37.42; H, 2.64; N, 8.97.

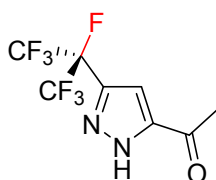
***N,N*-dimethyl-3-(perfluoropropan-2-yl)-1*H*-pyrazole-5-carboxamide (15a)**



Yield: 87%; white solid, m.p. 120-122 °C.

^1H NMR (500 MHz, CDCl_3) δ 6.85 (s, 1H), 3.28 (s, 3H), 3.04 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.7 (d, $J = 9.0$ Hz), -181.2 (p, $J = 8.7$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 160.1 (s), 139.8 (d, $J = 26.0$ Hz), 137.1 (s), 121.7 – 118.6 (dm), 90.3 – 87.9 (m), 106.6 (d, $J = 2.0$ Hz), 38.8 (s), 36.6 (s). Anal. calcd. for $\text{C}_9\text{H}_8\text{F}_7\text{N}_3\text{O}$: C, 35.19; H, 2.63; N, 13.68. Found: C, 35.45; H, 2.33; N, 13.84.

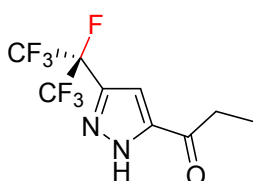
1-(3-(Perfluoropropan-2-yl)-1*H*-pyrazol-5-yl)ethan-1-one (16a)



Yield: 94%; yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 7.07 (s, 1H), 2.60 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.7 (d, $J = 8.9$ Hz), -181.0 (app, $J = 8.8$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 188.5 (s), 142.4 (s), 140.9 (d, $J = 26.3$ Hz), 124.3-116.2 (dm), 108.8 (s), 90.3 – 87.9 (m), 27.2 (s). Anal. calcd. for $\text{C}_8\text{H}_5\text{F}_7\text{N}_2\text{O}$: C, 34.55; H, 1.81; N, 10.07. Found: C, 34.27; H, 1.62; N, 10.31.

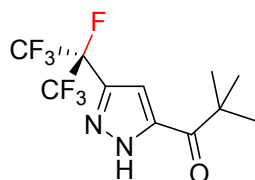
1-(3-(Perfluoropropan-2-yl)-1*H*-pyrazol-5-yl)propan-1-one (17a)



Yield: 89%; white solid, m.p. 65-66 °C.

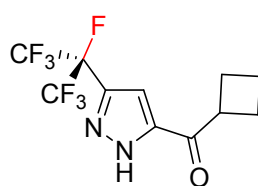
^1H NMR (500 MHz, CDCl_3) δ 10.91 (br s, 1H), 7.06 (s, 1H), 2.95 (q, $J = 7.3$ Hz, 2H), 1.25 (t, $J = 7.3$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.7 (d, $J = 8.4$ Hz), -181.0 (p, $J = 8.3$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 191.8 (s), 142.0 (s), 140.8 (d, $J = 26.2$ Hz), 123.9-116.0 (dm), 108.1 (s), 90.7 – 87.9 (m), 33.1 (s), 7.7 (s). Anal. calcd. for $\text{C}_9\text{H}_7\text{F}_7\text{N}_2\text{O}$: C, 37.00; H, 2.42; N, 9.59. Found: C, 37.21; H, 2.68; N, 9.14.

2,2-Dimethyl-1-(3-(perfluoropropan-2-yl)-1H-pyrazol-5-yl)propan-1-one (18a)



Yield: 81%; white solid, m.p. 67-68 °C.

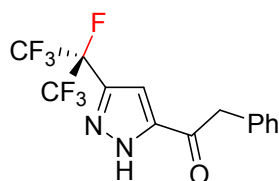
^1H NMR (500 MHz, CDCl_3) δ 7.04 (s, 1H), 1.38 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.6 (d, J = 8.8 Hz), -180.8 (app, J = 8.7 Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 196.6 (s), 141.0 (d, J = 26.5 Hz), 139.2 (s), 124.2–116.0 (dm), 108.1 (s), 90.5 – 88.1 (m), 43.8 (s), 27.4 (s). Anal. calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_7\text{N}_2\text{O}$: C, 41.26; H, 3.46; N, 8.75. Found: C, 41.58; H, 3.23; N, 8.91.



Cyclobutyl(3-(perfluoropropan-2-yl)-1H-pyrazol-5-yl)methanone (19a)

Yield: 83%; white solid, m.p. 103-105 °C.

^1H NMR (500 MHz, CDCl_3) δ 11.57 (br s, 1H), 6.94 (s, 2H), 3.83 (p, J = 8.3 Hz, 1H), 2.51 – 2.40 (m, 2H), 2.38 – 2.24 (m, 2H), 2.21 – 2.06 (m, 1H), 2.02 – 1.89 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.6 (d, J = 8.3 Hz), -180.7 – -180.9 (m). ^{13}C NMR (126 MHz, CDCl_3) δ 192.0 (s), 141.0 (d, J = 16.1 Hz), 123.9 – 116.5 (dm), 108.0 (s), 90.6 – 87.7 (m), 43.0 (s), 24.9 (s), 18.4 (s). Anal. calcd. for $\text{C}_{11}\text{H}_9\text{F}_7\text{N}_2\text{O}$: C, 41.52; H, 2.85; N, 8.80. Found: C, 41.85; H, 2.68; N, 8.91.

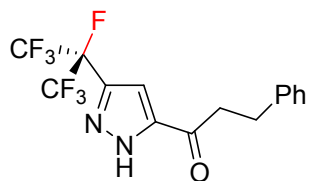


1-(3-(Perfluoropropan-2-yl)-1H-pyrazol-5-yl)-2-phenylethan-1-one (20a)

Yield: 78%; white solid, m.p. 62-63 °C.

^1H NMR (500 MHz, CDCl_3) δ 7.37 (t, J = 7.2 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.06 (s, 1H), 4.20 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.6 (d, J = 8.4 Hz), 180.9 (p, J = 8.9 Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 188.3 (s), 141.9 (s), 140.8 (d, J = 26.2 Hz), 132.5 (s), 129.6 (s), 129.1 (s), 127.8 (s), 124.1 – 116.4 (dm), 108.7 (s), 90.5 – 87.7 (m), 46.6 (s). Anal. calcd. for $\text{C}_{14}\text{H}_9\text{F}_7\text{N}_2\text{O}$: C, 47.47; H, 2.56; N, 7.91. Found: C, 47.25; H, 2.36; N, 8.12.

1-(3-(Perfluoropropan-2-yl)-1H-pyrazol-5-yl)-3-phenylpropan-1-one (21a)

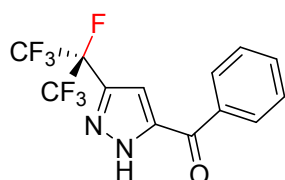


Yield: 91%; yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 7.32 (m, 2H), 7.25 (m, 3H), 7.24 (s, 1H), 3.10 (t, $J = 7.5$ Hz, 2H), 3.25 (t, $J = 7.5$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -76.6 (d, $J = 8.4$ Hz), -180.9 (p, $J = 8.2$ Hz).

hAnal. calcd. for $\text{C}_{15}\text{H}_{11}\text{F}_7\text{N}_2\text{O}$: C, 48.92; H, 3.01; N, 7.61. Found: C, 48.71; H, 3.34; N, 7.85.

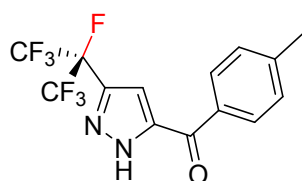
(3-(Perfluoropropan-2-yl)-1H-pyrazol-5-yl)(phenyl)methanone (22a)



Yield: 97%; white solid, m.p. 75-76 °C.

^1H NMR (500 MHz, DMSO-d_6) δ 14.95 (br s, 1H), 7.94 (d, $J = 7.4$ Hz, 2H), 7.74 (t, $J = 7.3$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 2H), 7.27 (s, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -75.8 (d, $J = 9.0$ Hz), -178.6 (br s). ^{13}C NMR (126 MHz, DMSO-d_6) δ 183.6 (s), 141.1 (s), 138.4 (d, $J = 26.6$ Hz), 136.1 (s), 133.7 (s), 129.2 (s), 129.0 (s), 124.6 – 115.3 (dm), 109.9 (s), 91.2 – 87.0 (m). Anal. calcd. for $\text{C}_{13}\text{H}_7\text{F}_7\text{N}_2\text{O}$: C, 45.90; H, 2.07; N, 8.23. Found: C, 45.80; H, 2.26; N, 8.44.

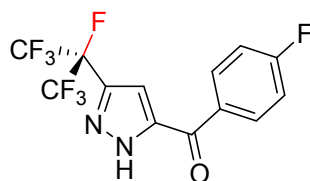
(3-(Perfluoropropan-2-yl)-1H-pyrazol-5-yl)(*p*-tolyl)methanone (23a)



Yield: 96%; white solid, m.p. 72-73 °C.

^1H NMR (500 MHz, DMSO-d_6) δ 14.91 (br s, 1H), 7.86 (d, $J = 7.5$ Hz, 2H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.40 (s, 1H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -75.8 (d, $J = 9.0$ Hz), -178.7 (br s). ^{13}C NMR (126 MHz, DMSO-d_6) δ 183.2 (s), 145.8 (s), 144.4 (s), 129.7 (s), 129.5 (s), 129.4 (s), 129.3 (s), 121.3 – 118.5 (dm), 109.6 (s), 21.2 (s). Anal. calcd. for $\text{C}_{14}\text{H}_9\text{F}_7\text{N}_2\text{O}$: C, 47.47; H, 2.56; N, 7.91. Found: C, 47.15; H, 2.81; N, 7.73.

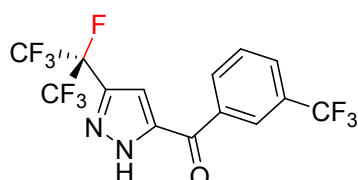
(4-Fluorophenyl)(3-(perfluoropropan-2-yl)-1H-pyrazol-5-yl)methanone (24a)



Yield: 94%; white solid, m.p. 100-101 °C.

¹H NMR (500 MHz, DMSO-d₆) δ 14.95 (s, 1H), 8.04 (dd, *J* = 7.8, 5.6 Hz, 2H), 7.43 (t, *J* = 8.7 Hz, 2H), 7.30 (s, 1H). ¹⁹F NMR (376 MHz, DMSO-d₆) δ -75.9 (d, *J* = 9.2 Hz), -105.5 (s), -178.7 (br s). ¹³C NMR (101 MHz, DMSO-d₆) δ 182.2 (s), 165.3 (d, *J* = 252.6 Hz), 141.0 (s), 138.5 (d, *J* = 26.7 Hz), 132.7 (d, *J* = 2.7 Hz), 132.3 (d, *J* = 9.6 Hz), 124.5 – 116.4 (dm), 116.1 (d, *J* = 22.1 Hz), 110.0 (s), 90.8 – 87.3 (m). Anal. calcd. for C₁₃H₆F₈N₂O: C, 43.59; H, 1.69; N, 7.82. Found: C, 43.80; H, 1.91; N, 7.51.

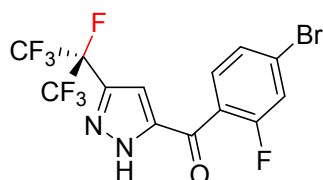
(3-(Perfluoropropan-2-yl)-1H-pyrazol-5-yl)(3-(trifluoromethyl)phenyl)methanone (25a)



Yield: 88%; white solid, m.p. 80-81 °C.

¹H NMR (500 MHz, DMSO-d₆) δ 15.04 (s, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 8.14 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.31 (s, 1H). ¹⁹F NMR (376 MHz, DMSO-d₆) δ -62.0 (br s), -75.9 (d, *J* = 6.5 Hz), -178.6 (br s). ¹³C NMR (101 MHz, DMSO-d₆) δ 182.6 (s), 140.8 (s), 138.6 (d, *J* = 26.9 Hz), 137.0 (s), 133.3 (s), 130.3 (s), 129.9 – 129.7 (m), 129.5 (s), 125.5 (d, *J* = 3.9 Hz), 124.6 – 115.1 (dm), 123.7 (q, *J* = 272.3 Hz), 110.4 (s), 91.1 – 86.2 (m). Anal. calcd. for C₁₄H₆F₁₀N₂O: C, 41.19; H, 1.48; N, 6.86. Found: C, 41.35; H, 1.22; N, 6.99.

(4-Bromo-2-fluorophenyl)(3-(perfluoropropan-2-yl)-1H-pyrazol-5-yl)methanone (26a)

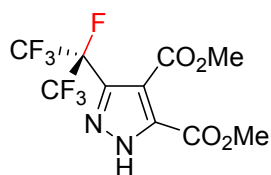


Yield: 91%; white solid, m.p. 102-103 °C.

¹H NMR (500 MHz, DMSO-d₆) δ 15.06 (s, 1H), 7.81 (d, *J* = 9.5 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.25 (s, 1H). ¹⁹F NMR (376 MHz, DMSO-d₆) δ -75.9 (d, *J* = 9.0 Hz), -110.9 (t, *J* = 9.6 Hz), -178.8 (br s). ¹³C NMR (101 MHz, DMSO-d₆) δ 180.7 (s), 159.5 (d, *J* = 257.2

Hz), 141.9 (s), 138.6 (d, $J = 26.8$ Hz), 132.3 (s), 128.3 (s), 126.9 (d, $J = 9.9$ Hz), 124.5 (d, $J = 13.5$ Hz), 120.3 (d, $J = 24.9$ Hz), 123.9 – 113.8 (dm), 110.7 (s), 91.6 – 85.3 (m). Anal. calcd. for $C_{13}H_5BrF_8N_2O$: C, 35.72; H, 1.15; N, 6.41. Found: C, 35.97; H, 1.04; N, 6.68.

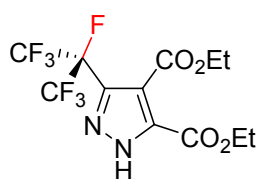
Dimethyl 3-(perfluoropropan-2-yl)-1H-pyrazole-4,5-dicarboxylate (30a)



Yield: 53%; yellow oil.

1H NMR (500 MHz, $CDCl_3$) δ 3.96 (s, 3H), 3.94 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.7 (d, $J = 8.9$ Hz), -181.3 (p, $J = 8.8$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (s), 158.0 (s), 137.8 (d, $J = 28.0$ Hz), 133.5 (s), 121.7 – 117.7 (dm), 118.3 (s), 89.8 – 88.1 (m), 53.3 (s), 53.2 (s). Anal. calcd. for $C_{10}H_7F_7N_2O_4$: C, 34.11; H, 2.00; N, 7.95. Found: C, 34.45; H, 2.25; N, 7.58.

Diethyl 3-(perfluoropropan-2-yl)-1H-pyrazole-4,5-dicarboxylate (31a)



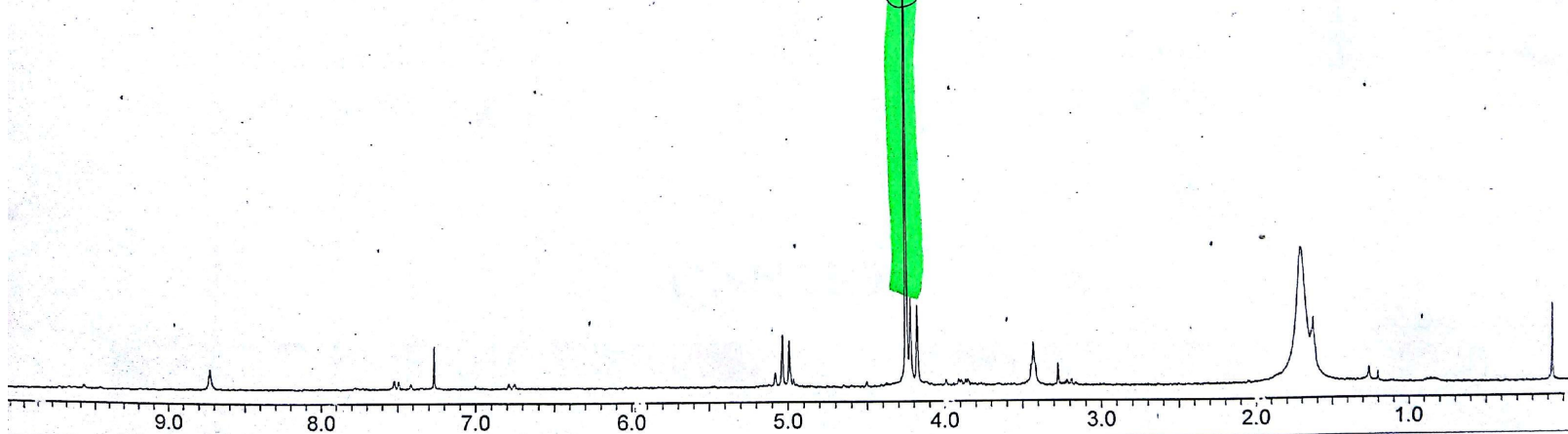
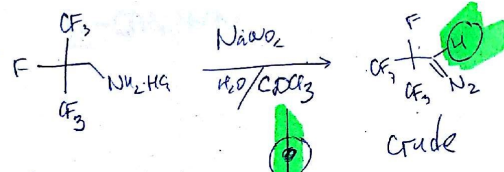
Yield: 59%; yellow oil.

1H NMR (500 MHz, $CDCl_3$) δ 4.43-4.39 (m, 4H), 1.39-1.38 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.7 (d, $J = 8.9$ Hz), -181.3 (p, $J = 8.9$ Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (s), 157.7 (s), 137.6 (s), 133.6 (s), 124.7 – 117.3 (dm), 62.6 (s), 62.5 (s), 14.1 (s), 14.0 (s). Anal. calcd. for $C_{12}H_{11}F_7N_2O_4$: C, 37.91; H, 2.92; N, 7.37. Found: C, 37.57; H, 3.29; N, 7.50.

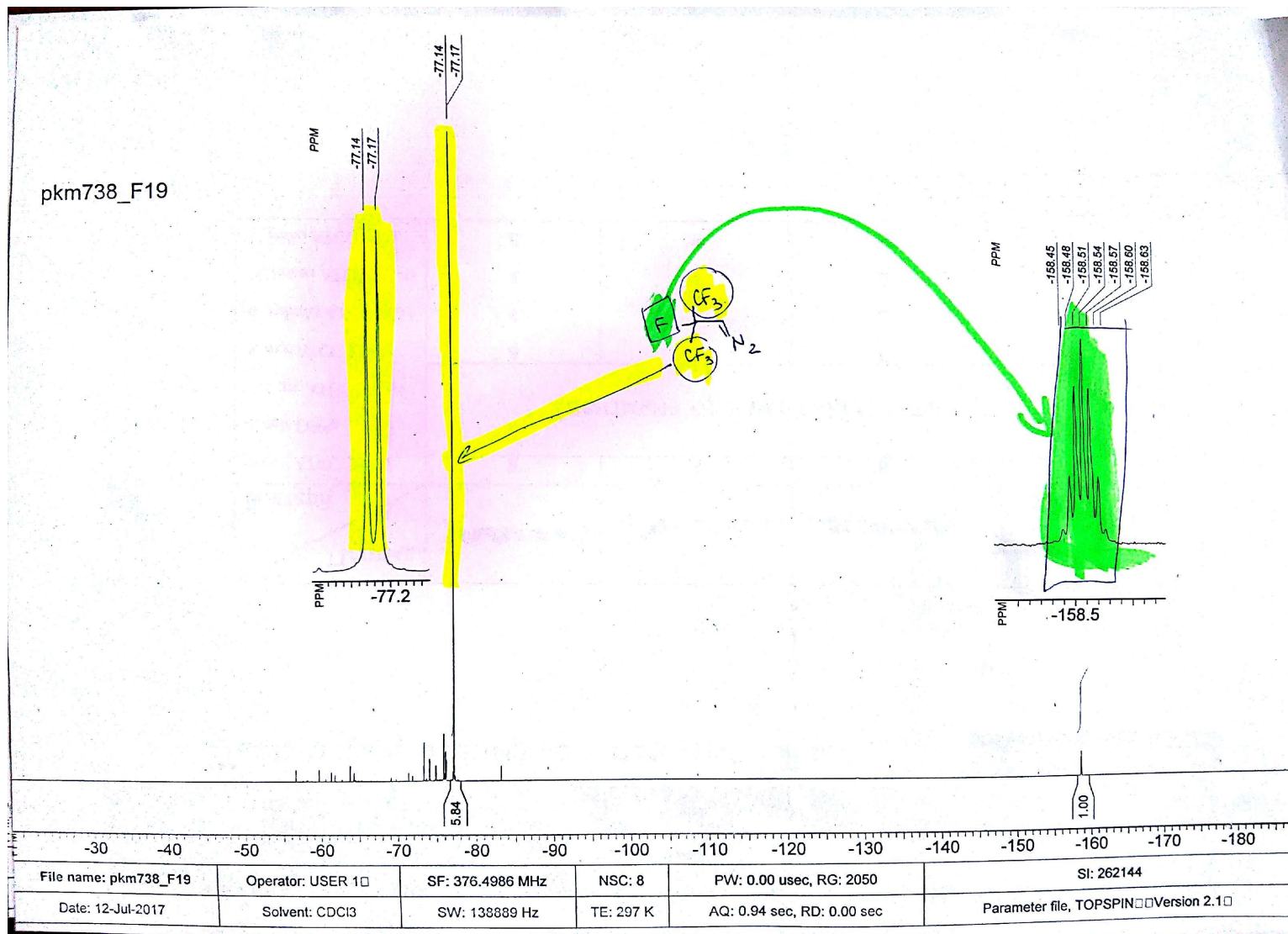
(C) Copies of ^1H , ^{19}F and ^{13}C NMR spectra

Crude $i\text{C}_3\text{F}_7\text{CHN}_2$ (**9**)/ CDCl_3

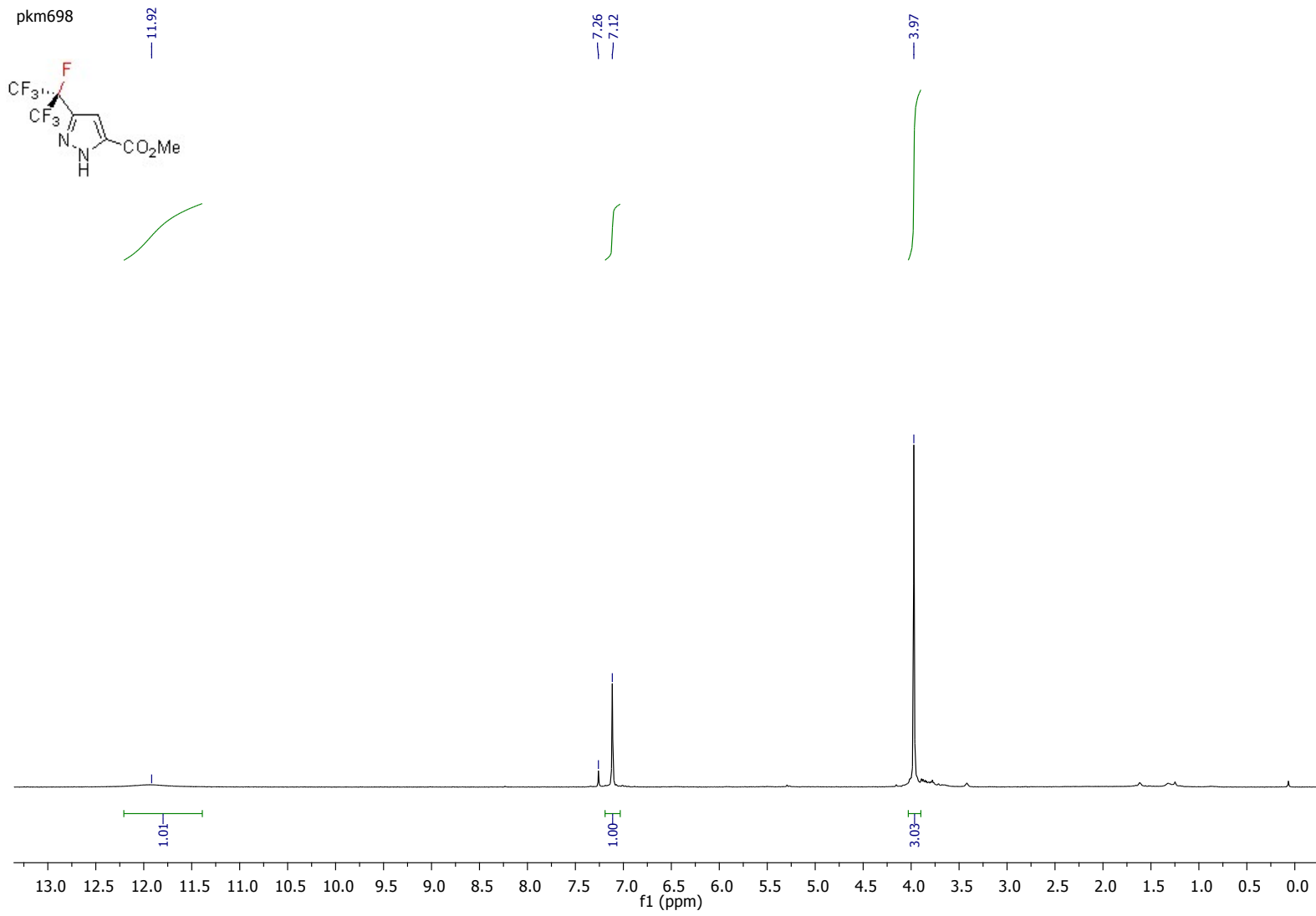
pkm738



File name: pkm738	Operator: USER 1	SF: 400.1300 MHz	NSC: 1	PW: 9.00 usec, RG: 25	SI: 32768
Date: 12-Jul-2017	Solvent: CDCl3	SW: 8224 Hz	TE: 297 K	AQ: 1.99 sec, RD: 0.00 sec	Parameter file, TOPSPIN Version 2.1

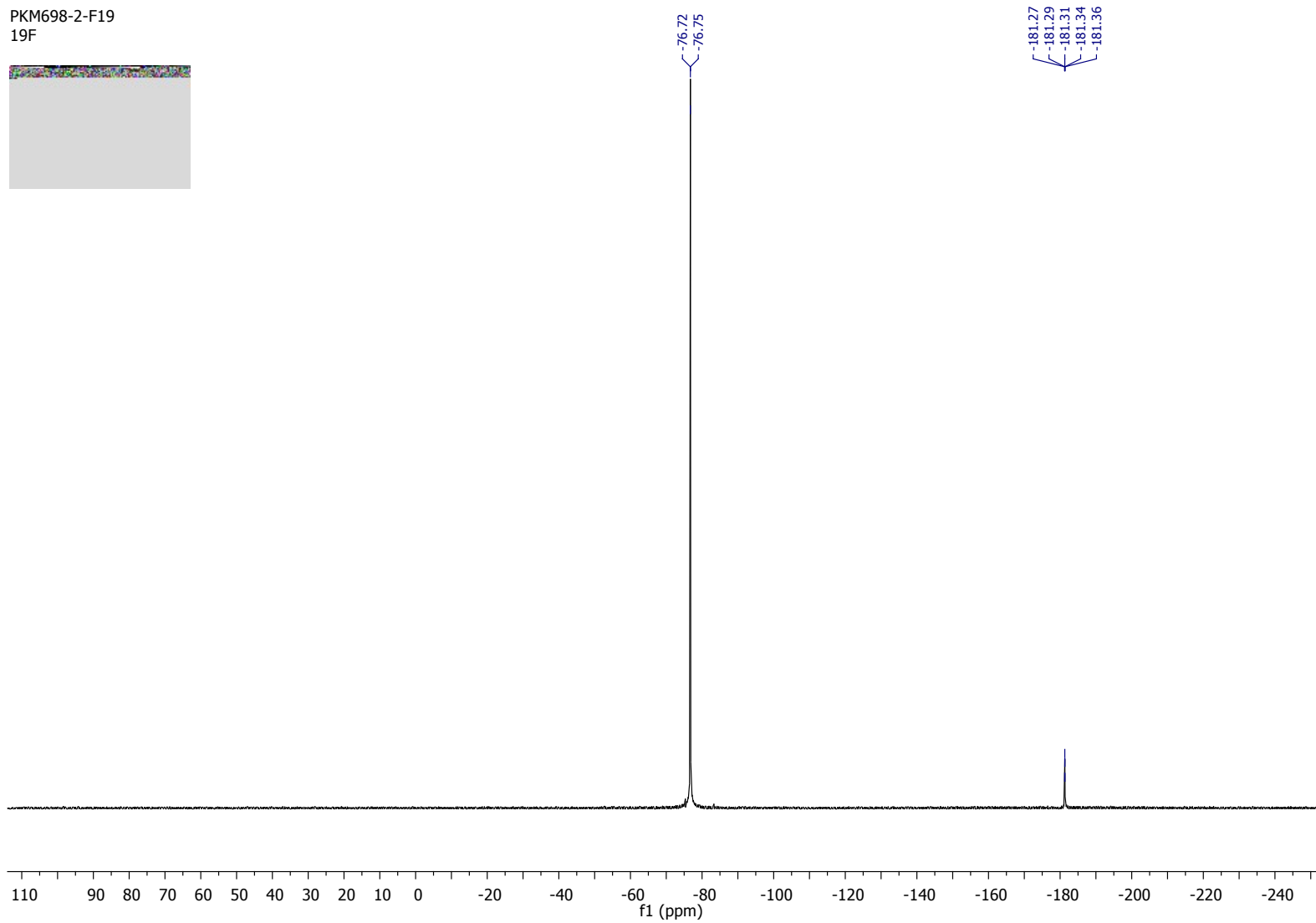


Compound **10a**



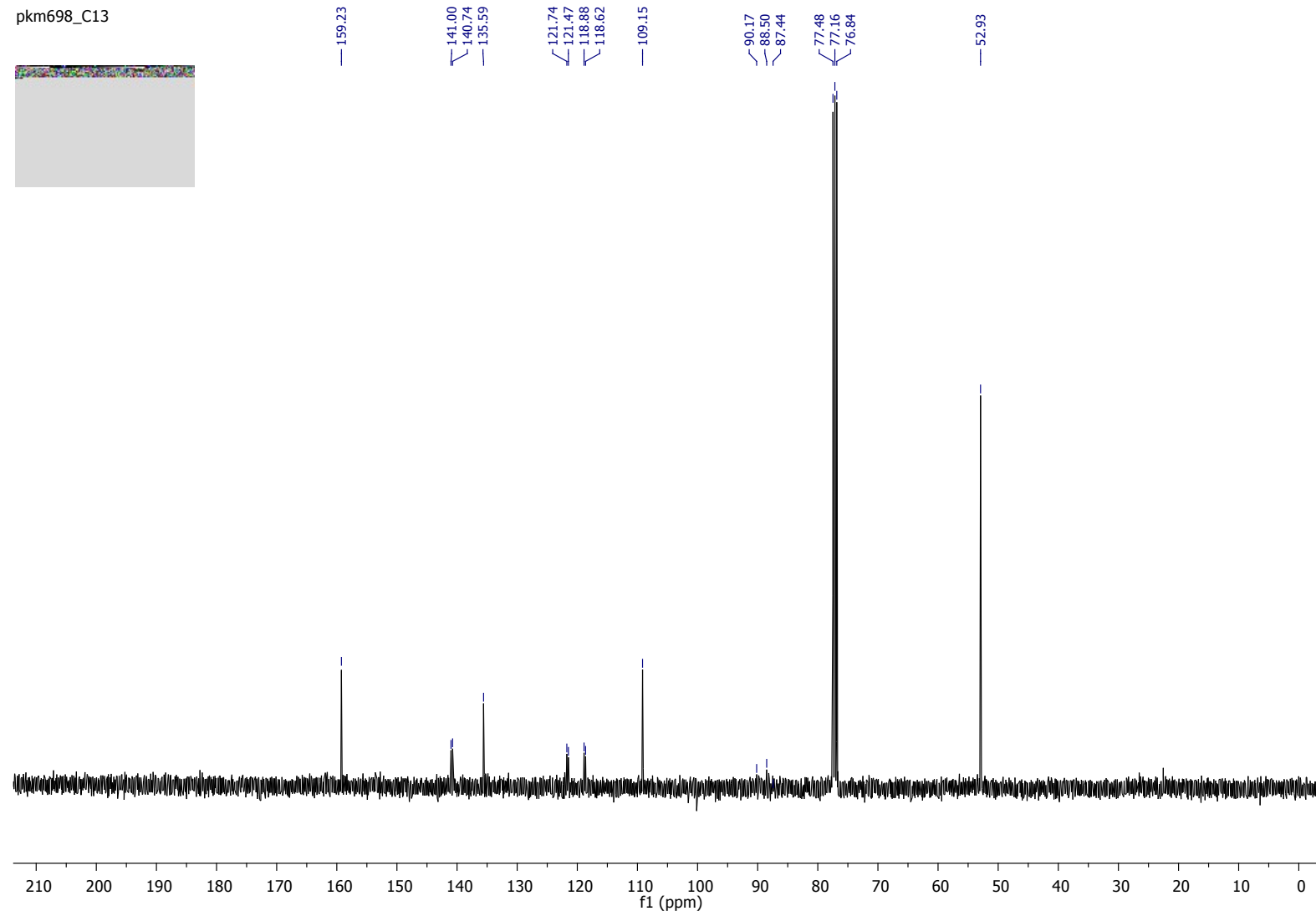
Compound 10a

PKM698-2-F19
19F



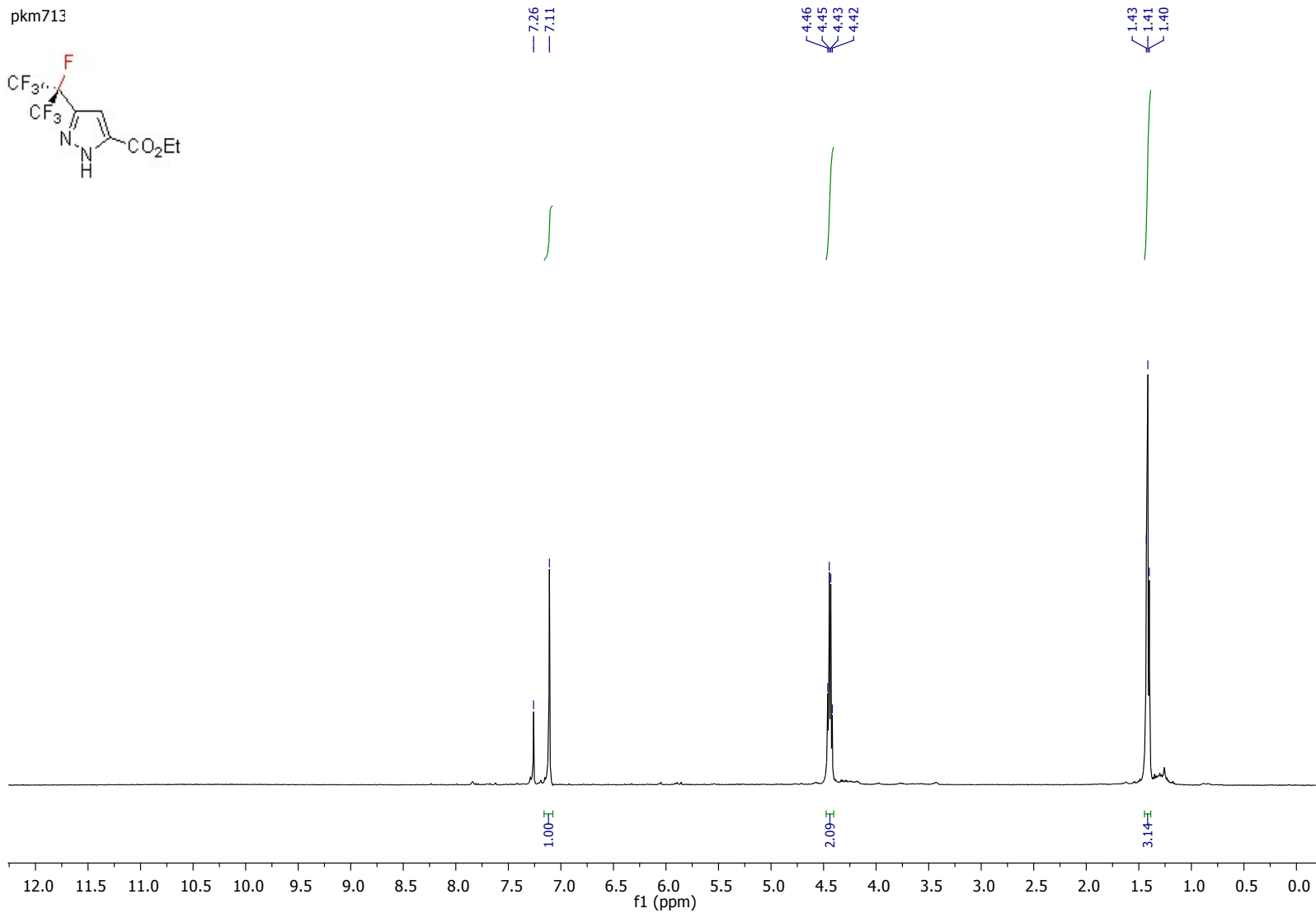
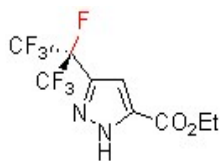
Compound **10a**

pkm698_C13



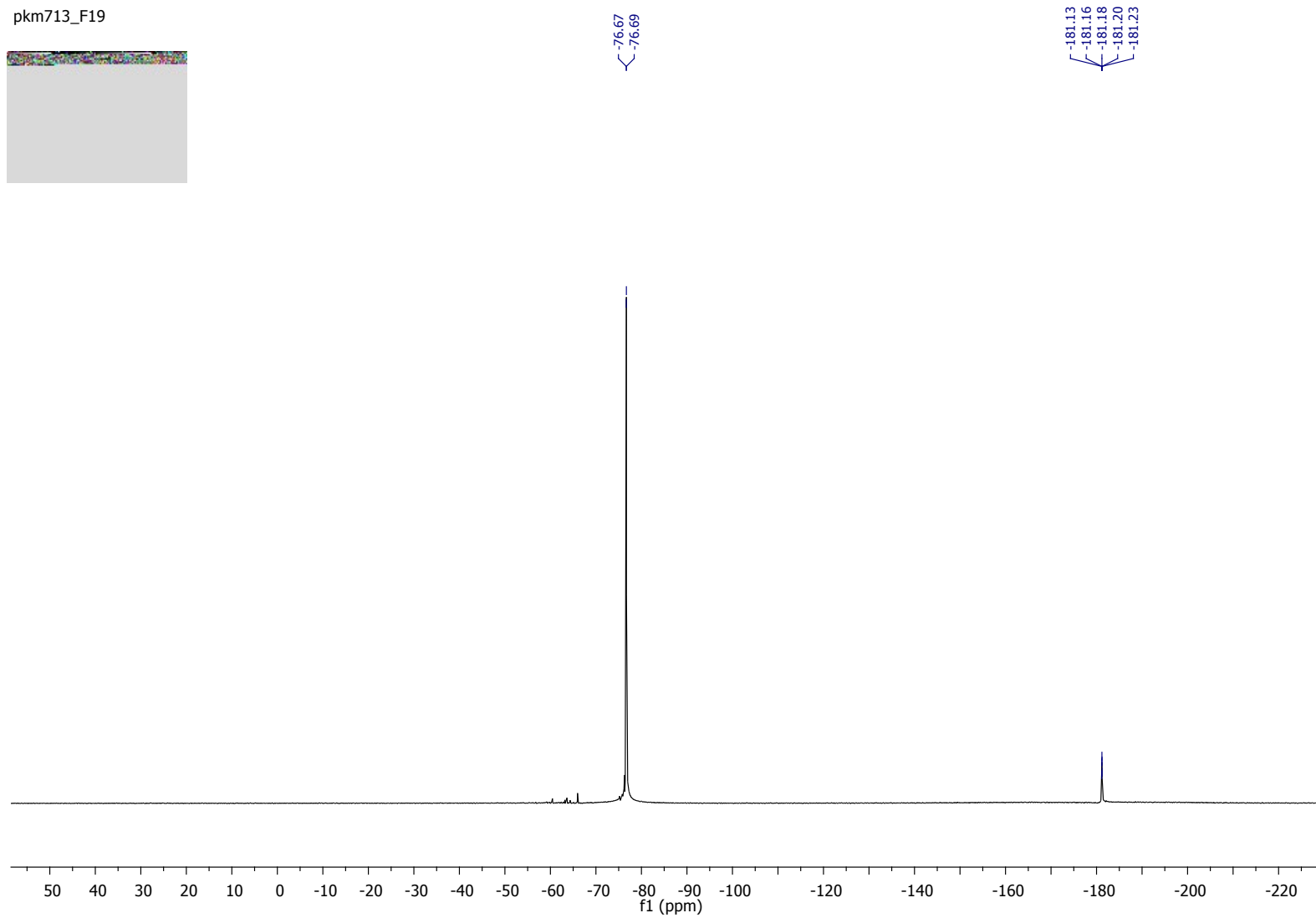
Compound 13a

pkm713



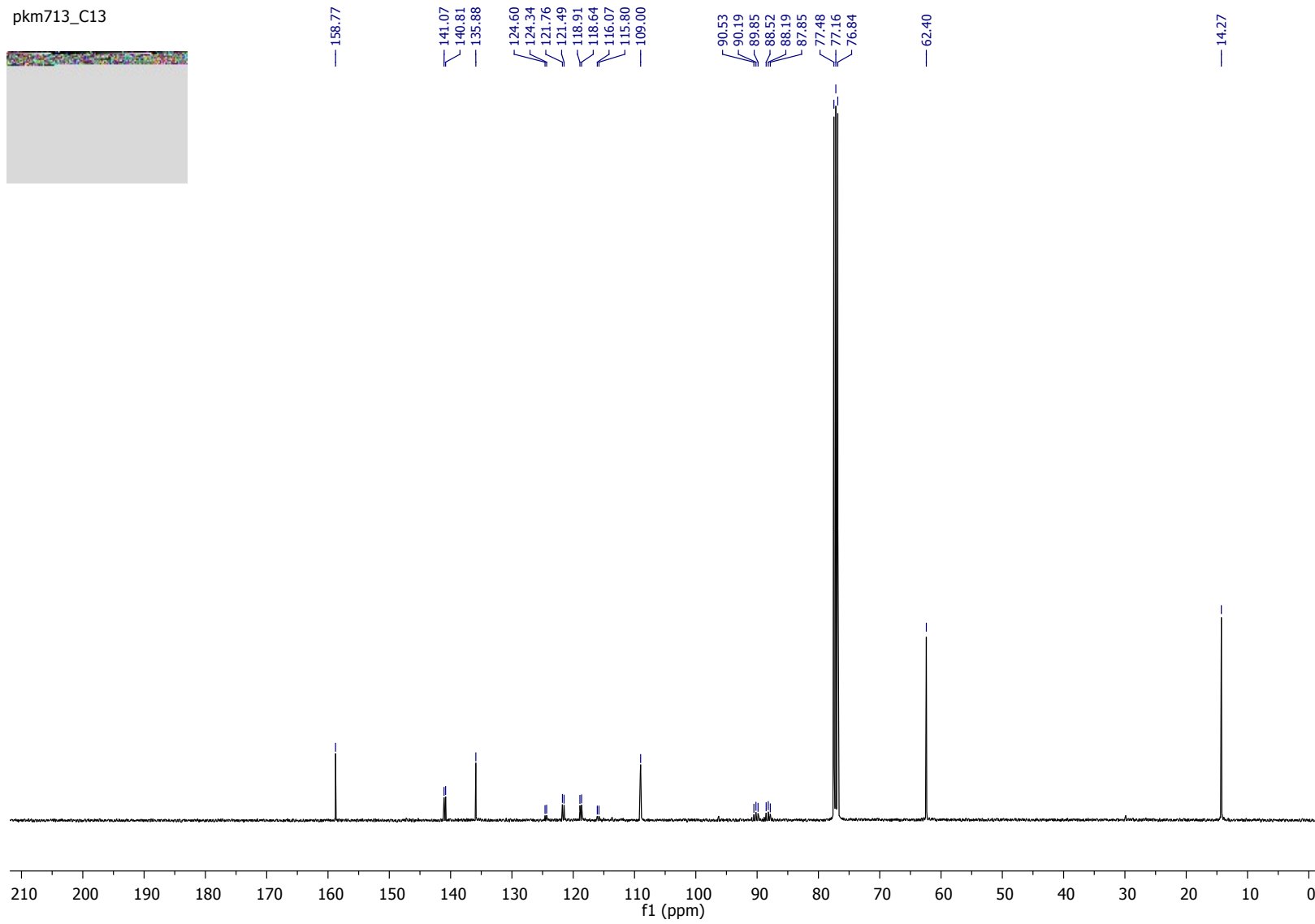
Compound 13a

pkm713_F19



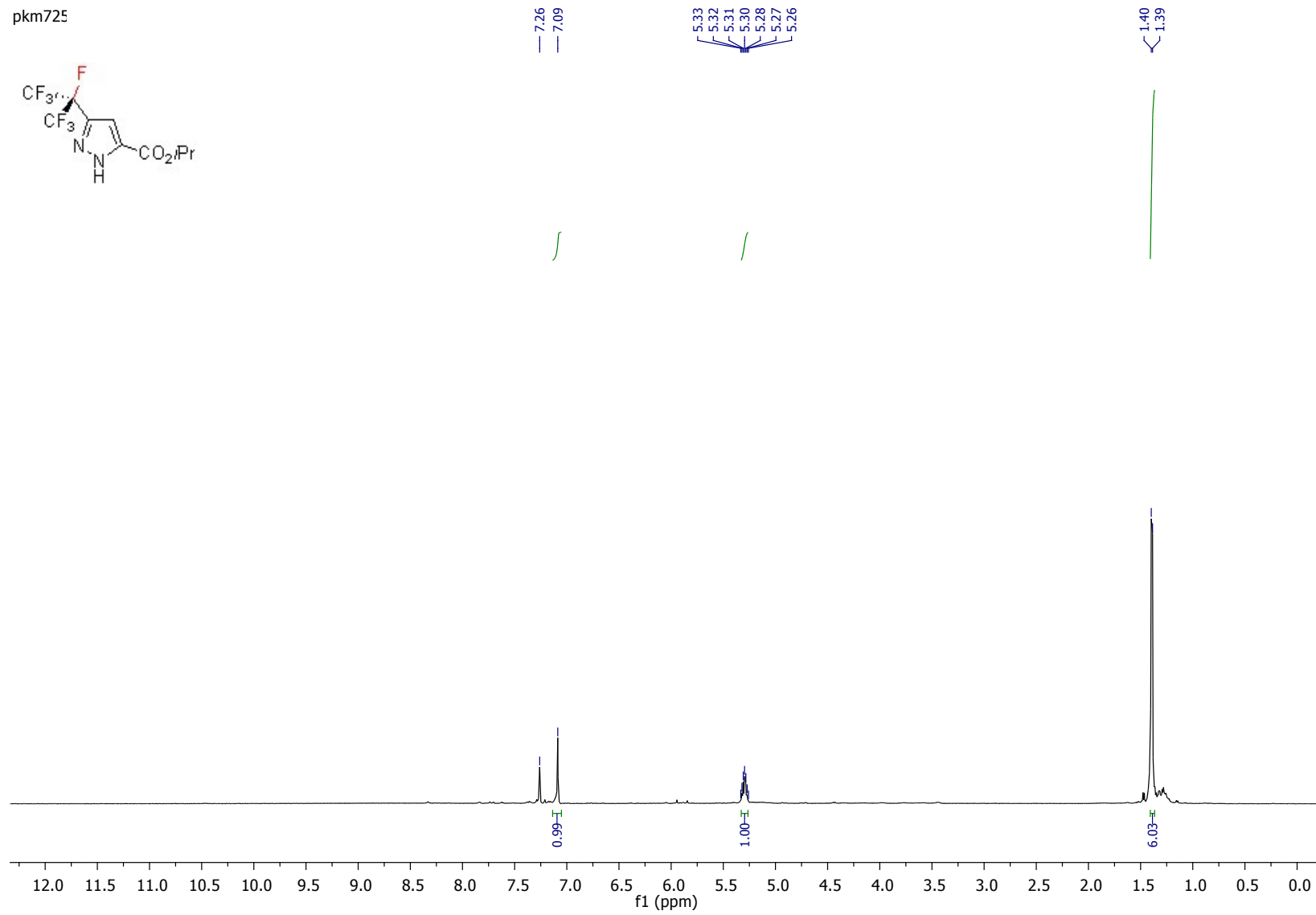
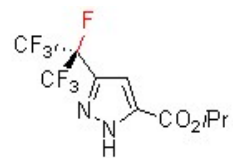
Compound **13a**

pkm713_C13



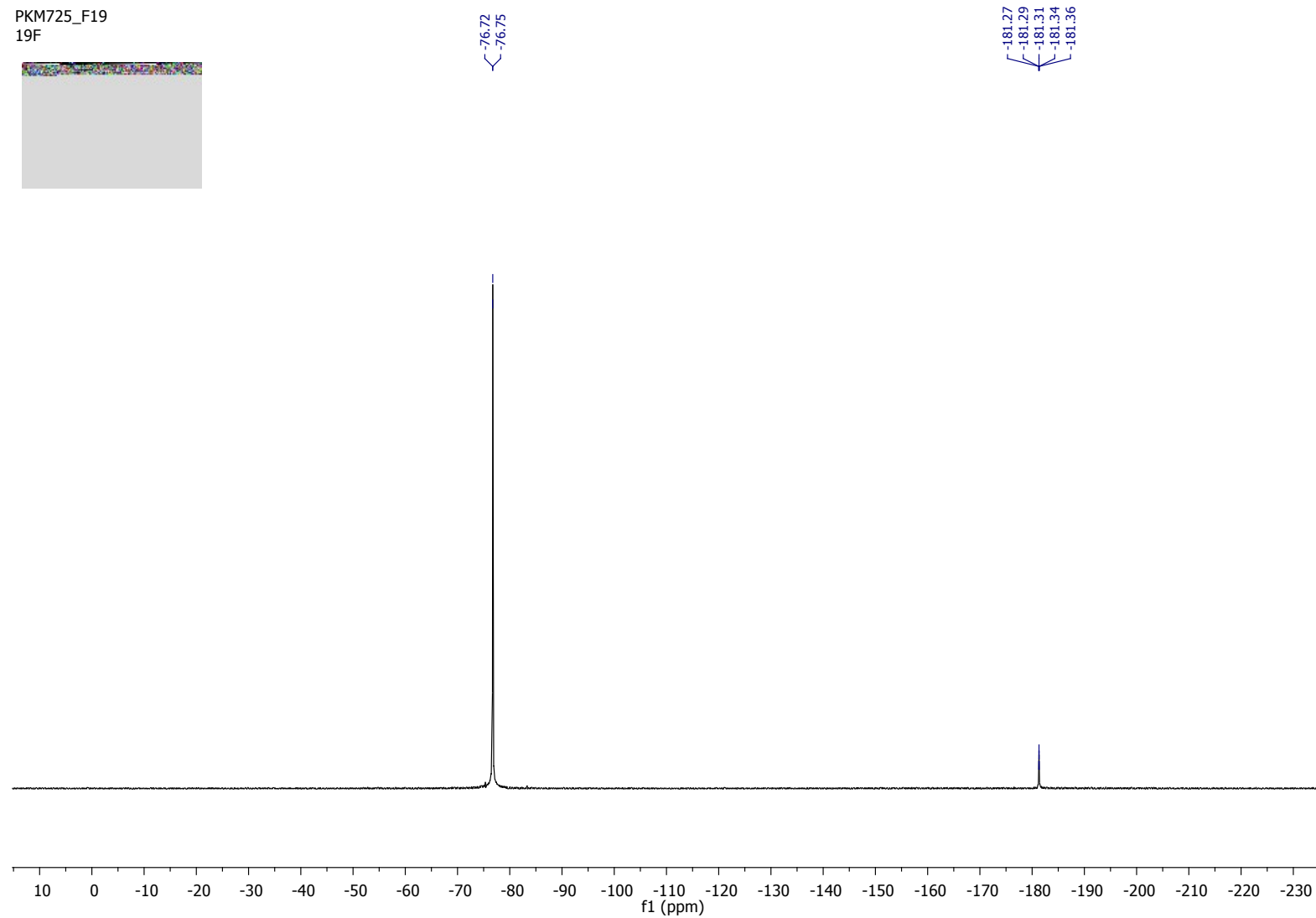
Compound **14a**

pkm725



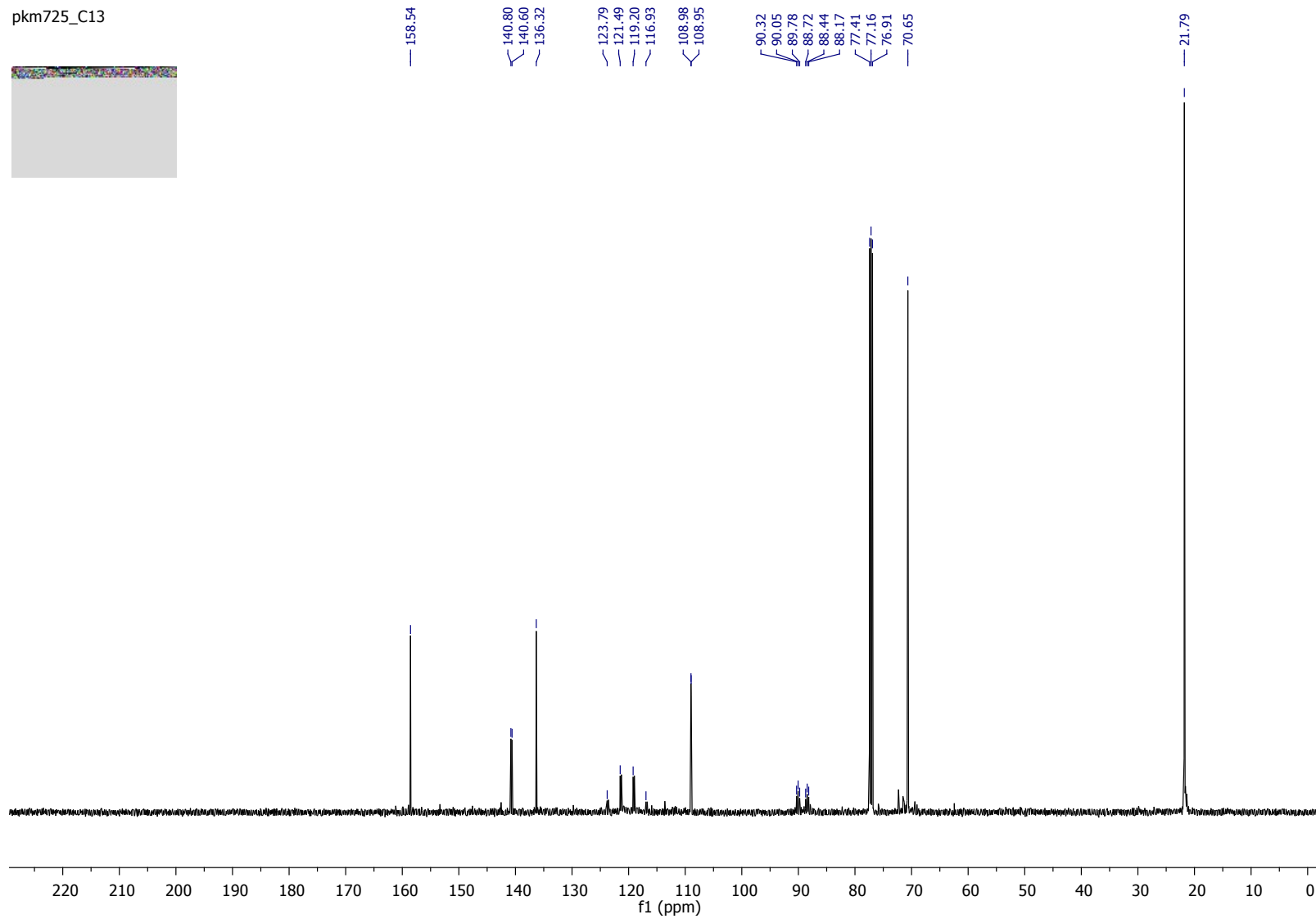
Compound 14a

PKM725_F19
19F



Compound **14a**

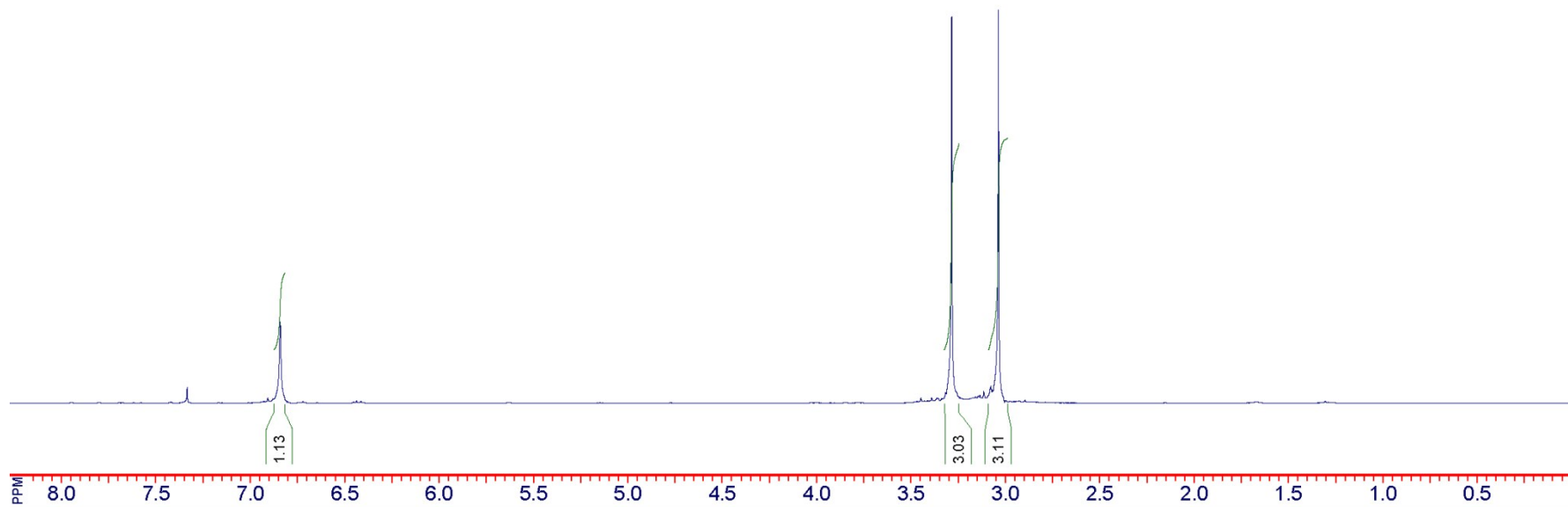
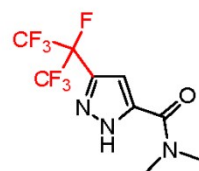
pkm725_C13



Compound 15a

PPM

pkm726



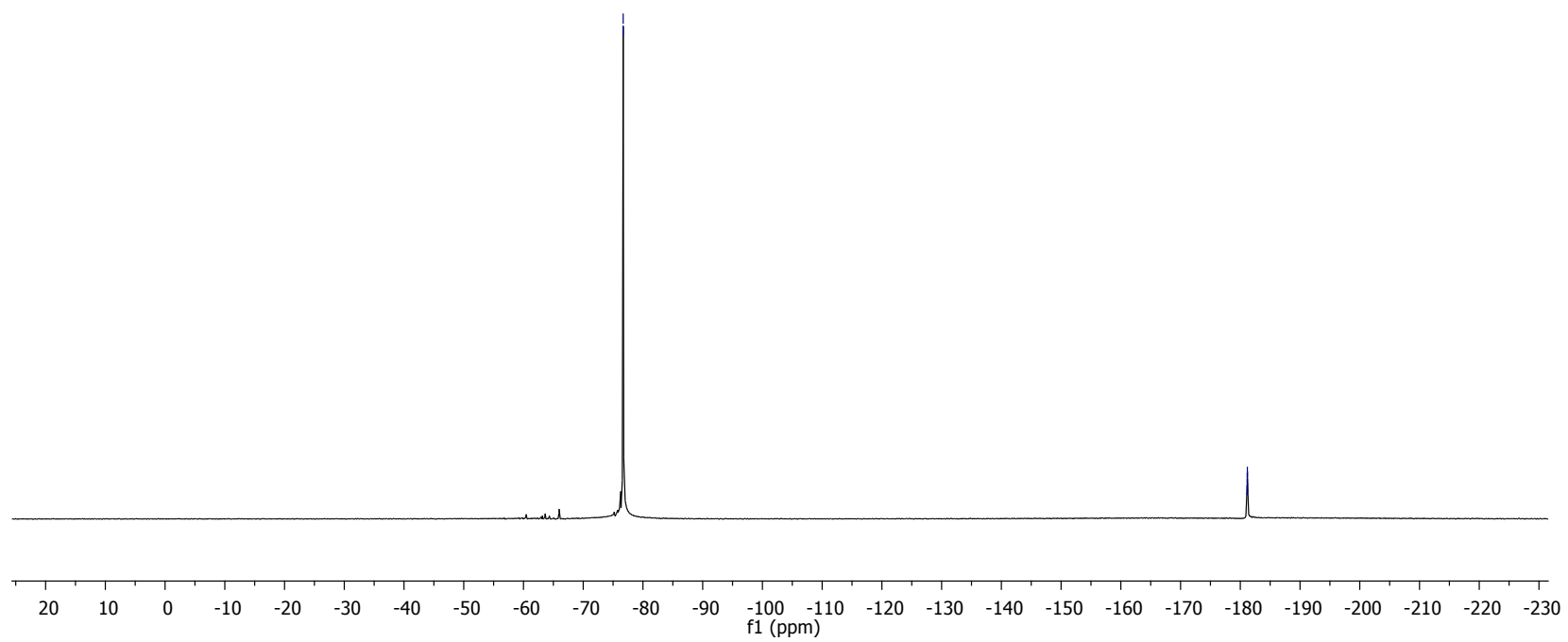
Compound 15a

pkm736_F19

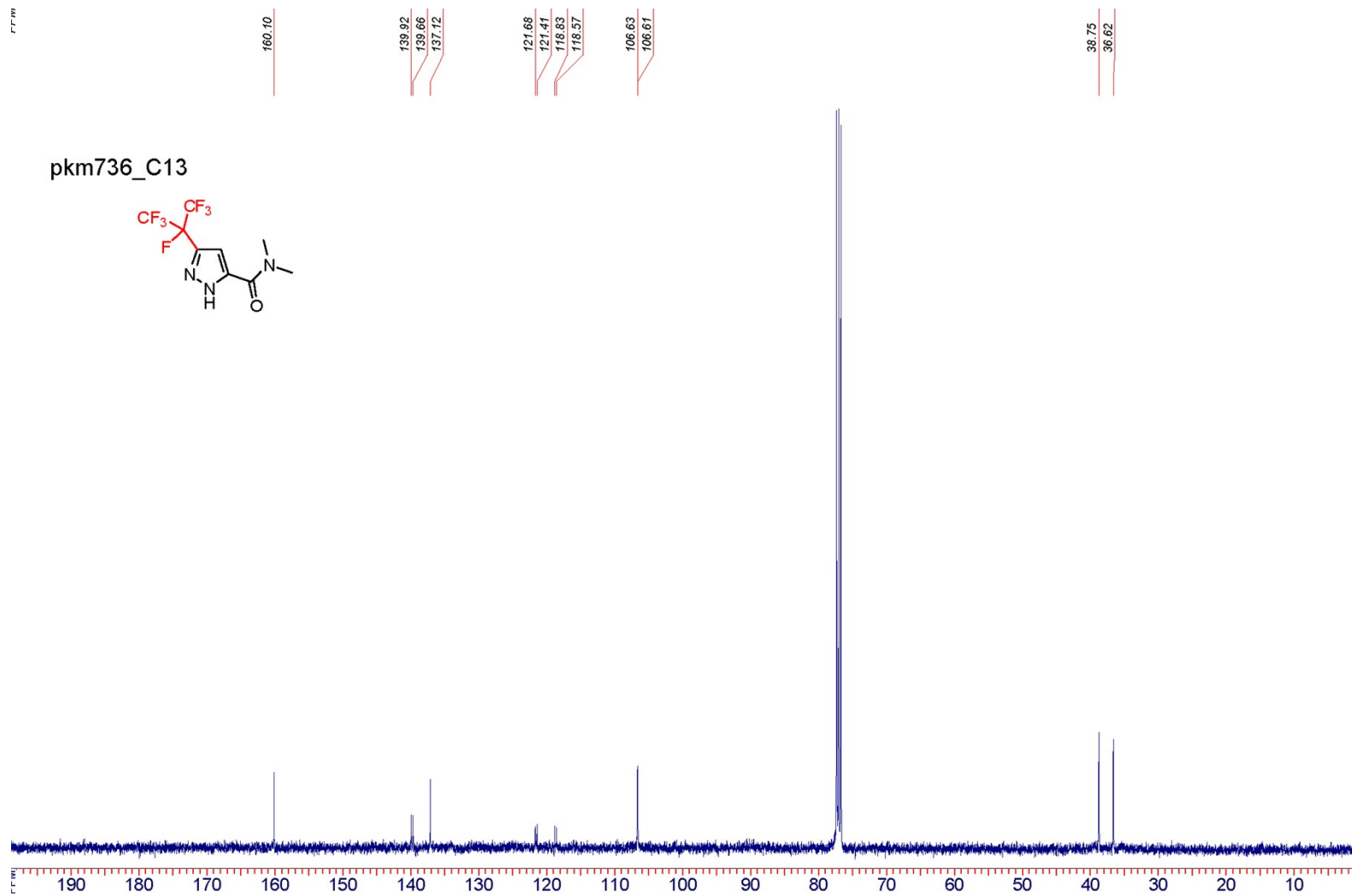


-76.67
-76.69

-181.13
-181.16
-181.18
-181.20
-181.23

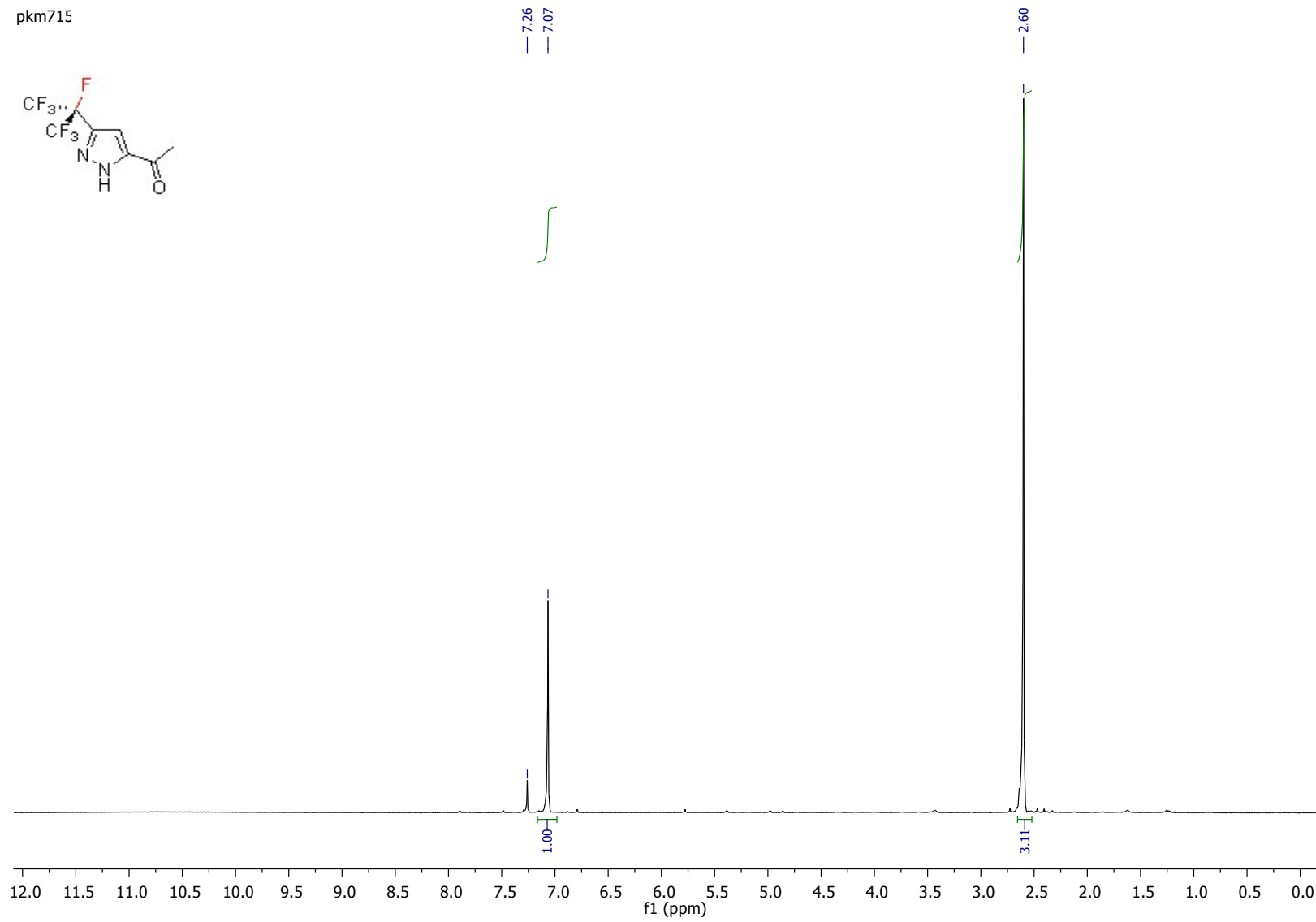
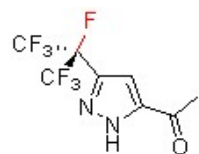


Compound **15a**



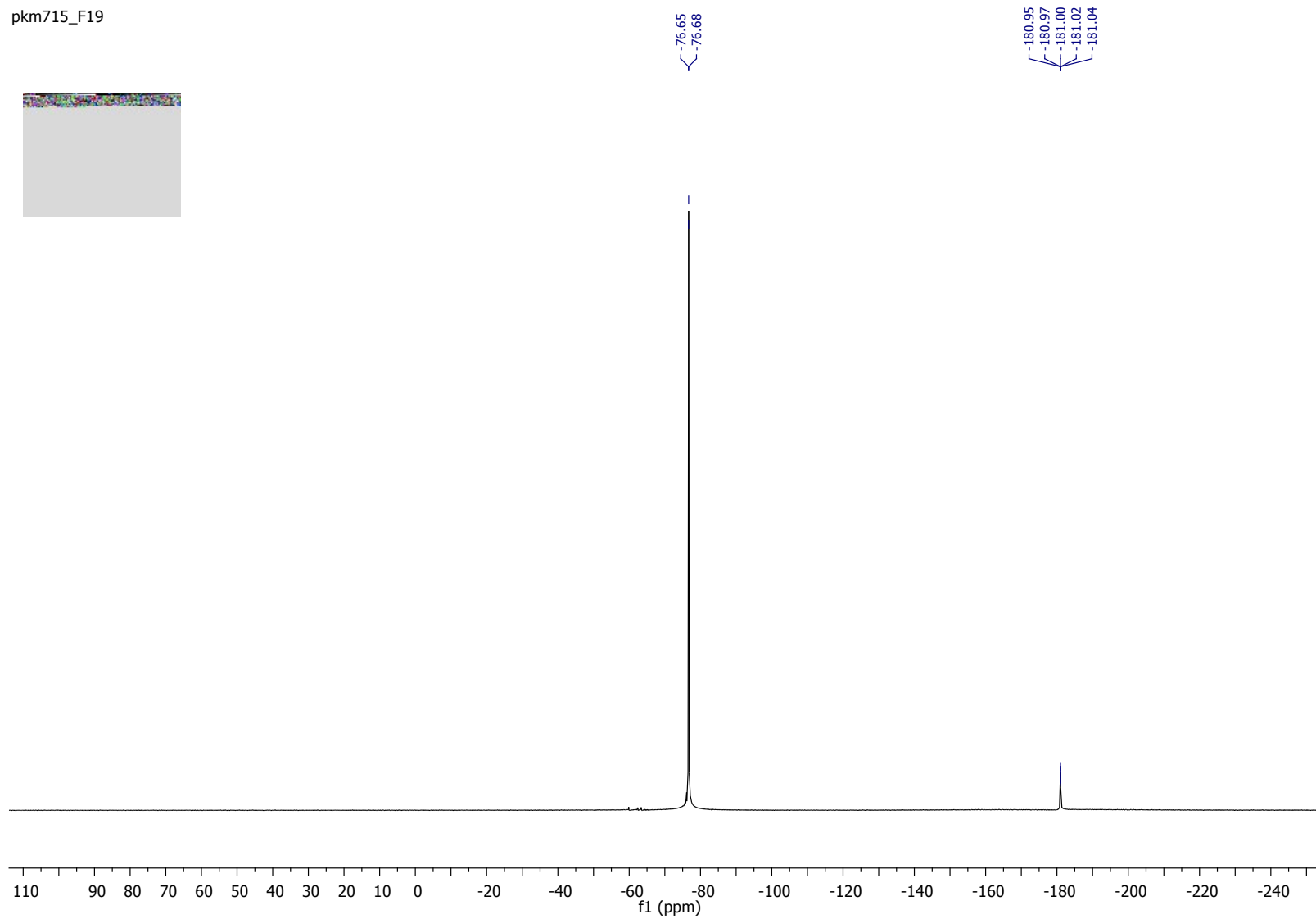
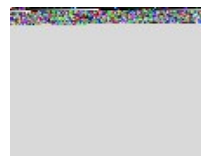
Compound **16a**

pkm715



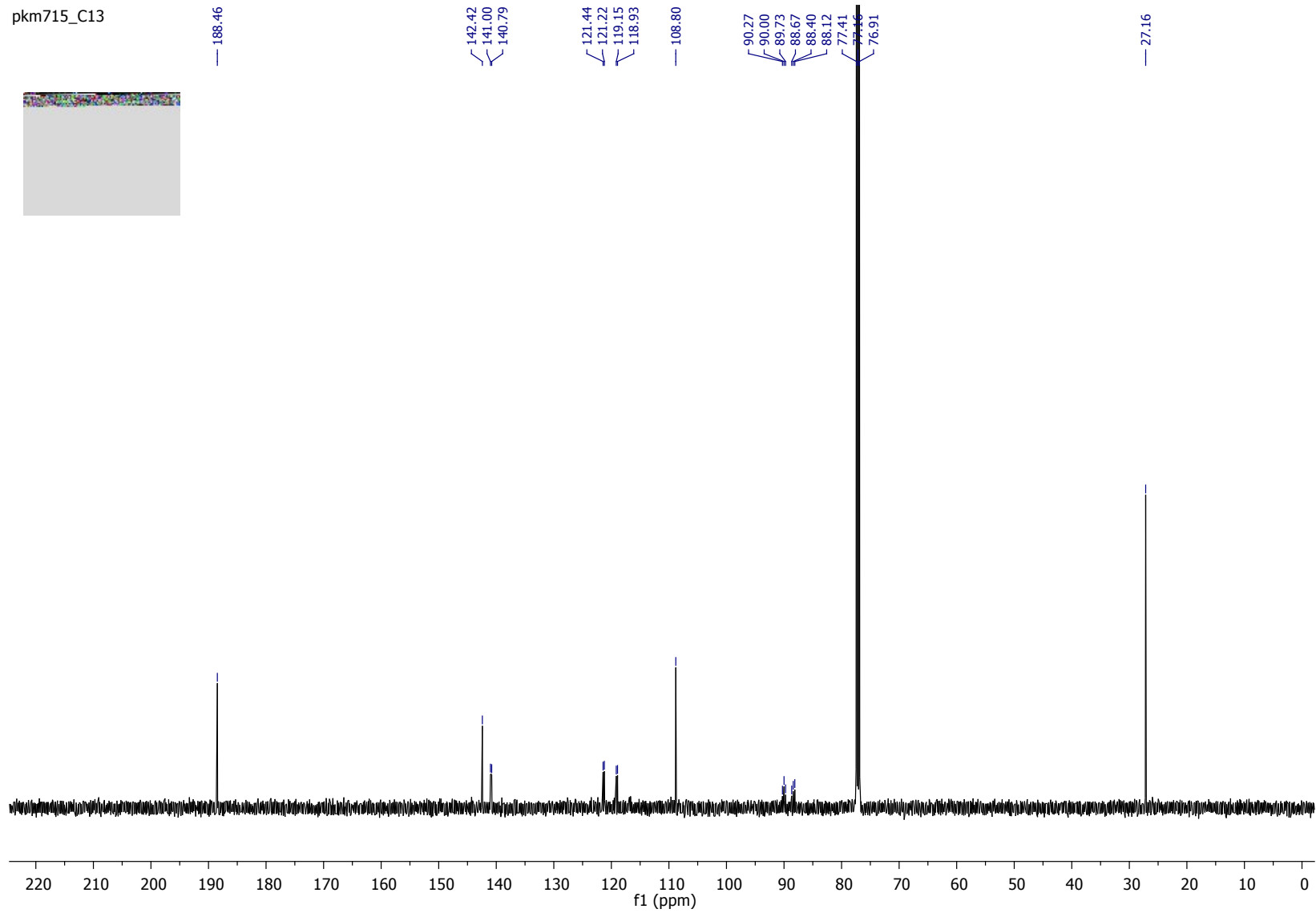
Compound **16a**

pkm715_F19



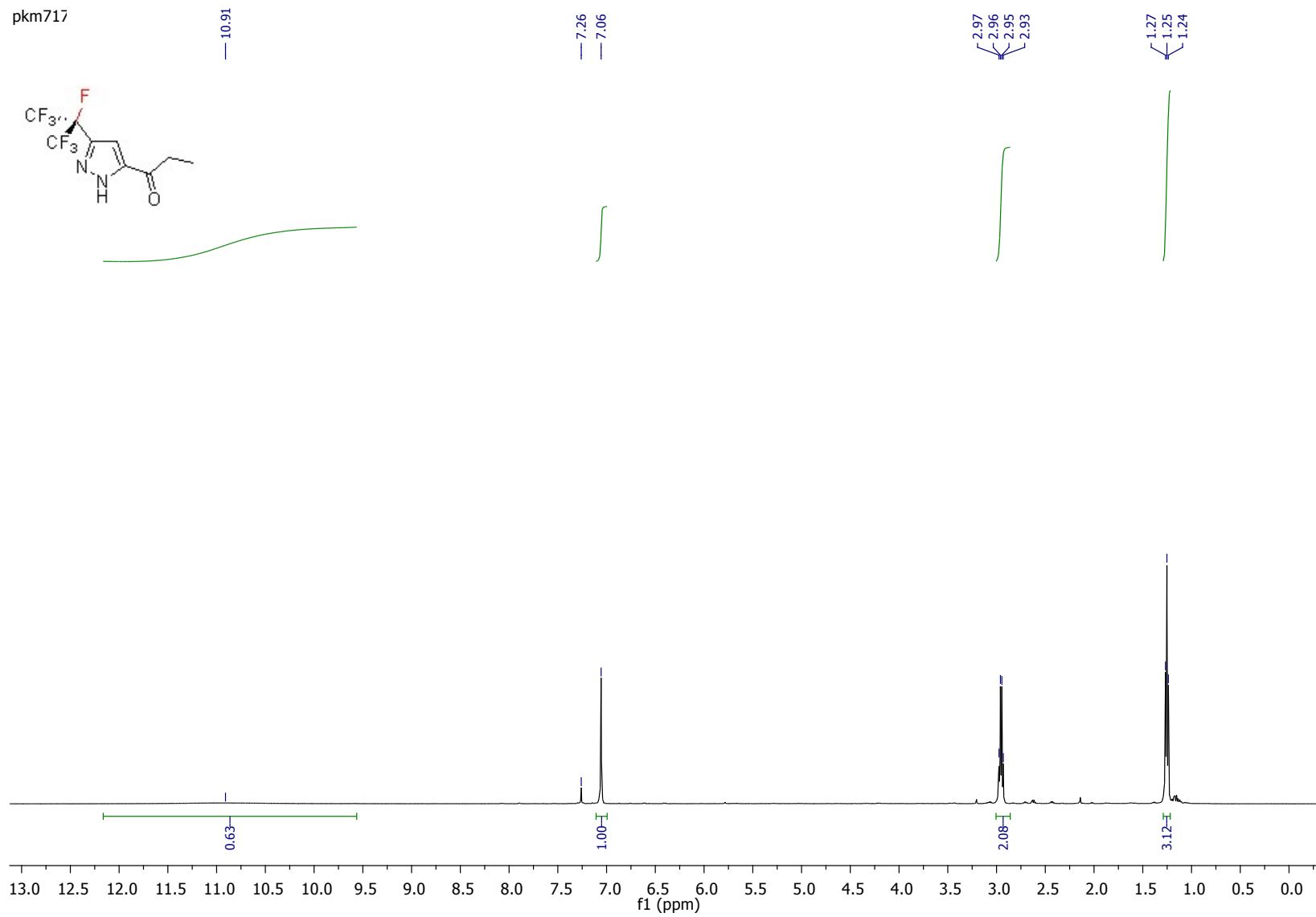
Compound **16a**

pkm715_C13



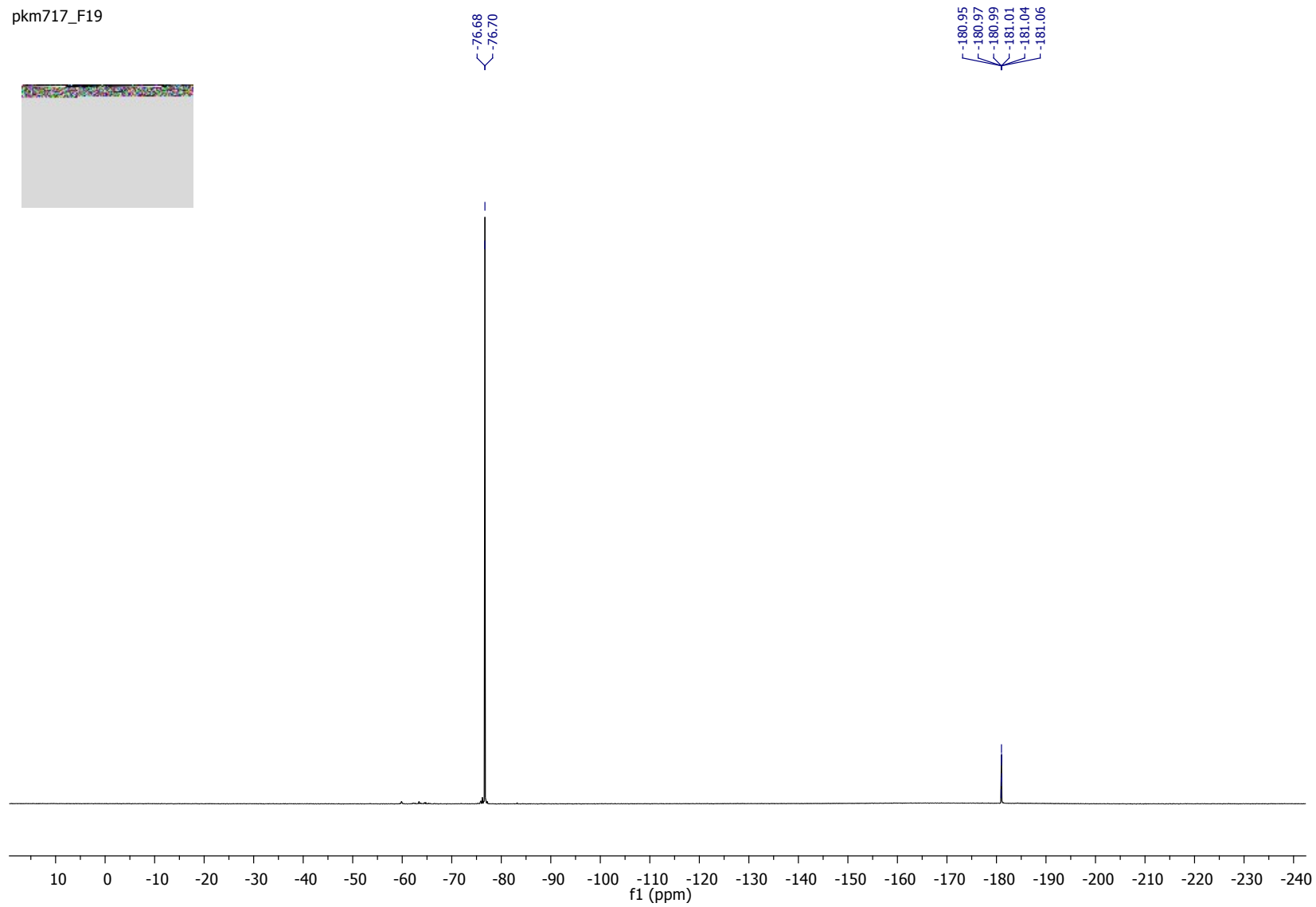
Compound 17a

pkm717



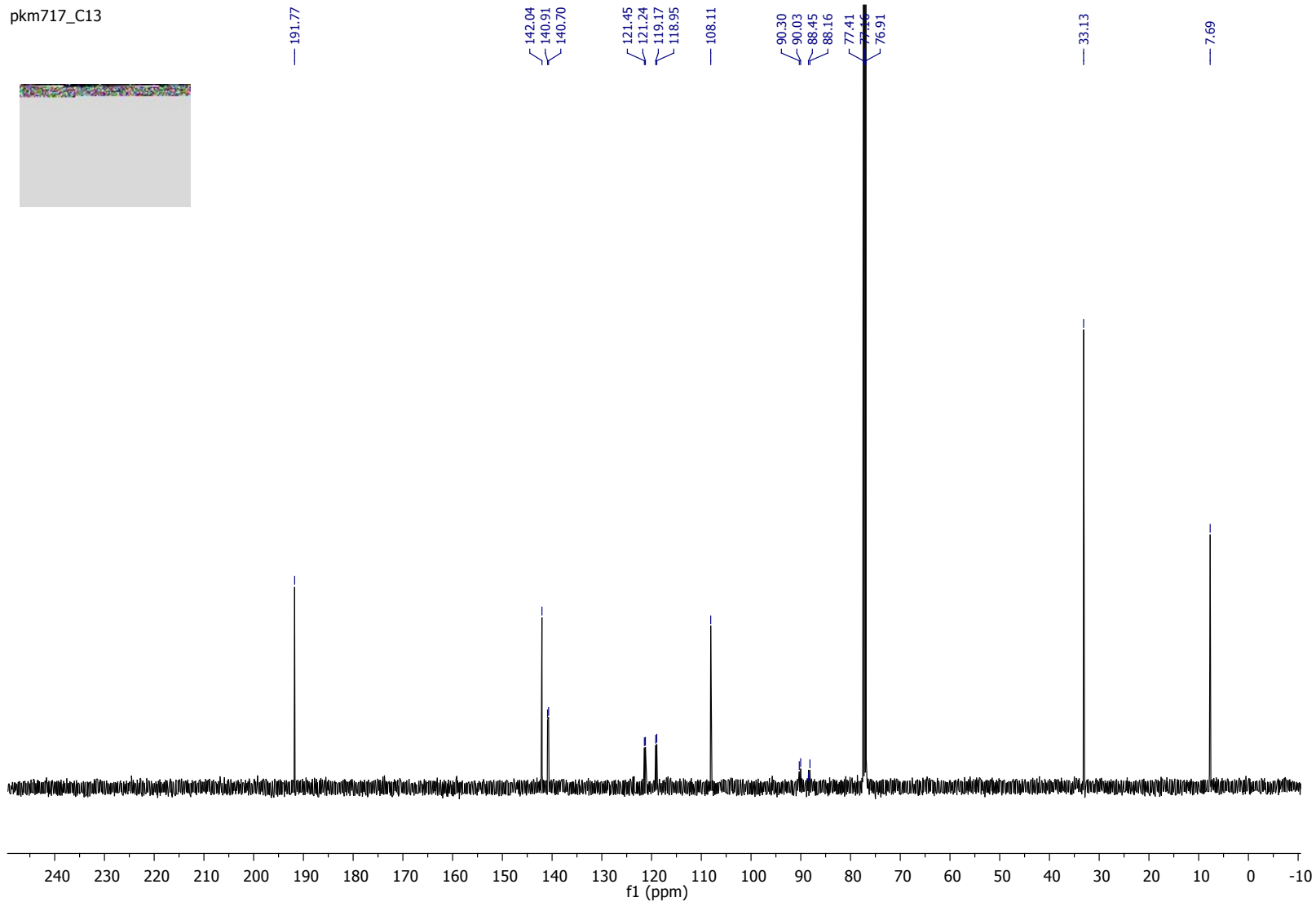
Compound 17a

pkm717_F19



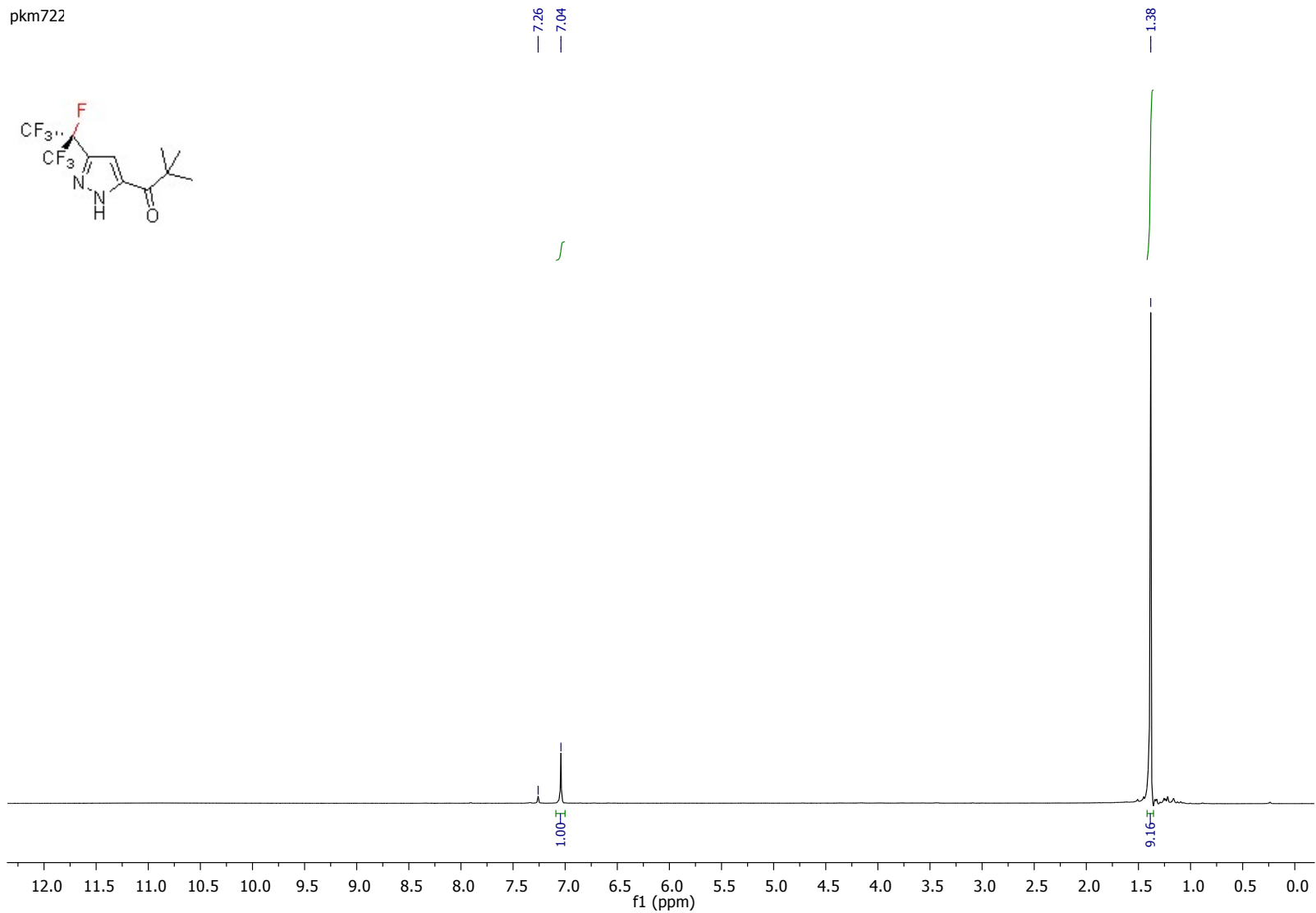
Compound 17a

pkm717_C13



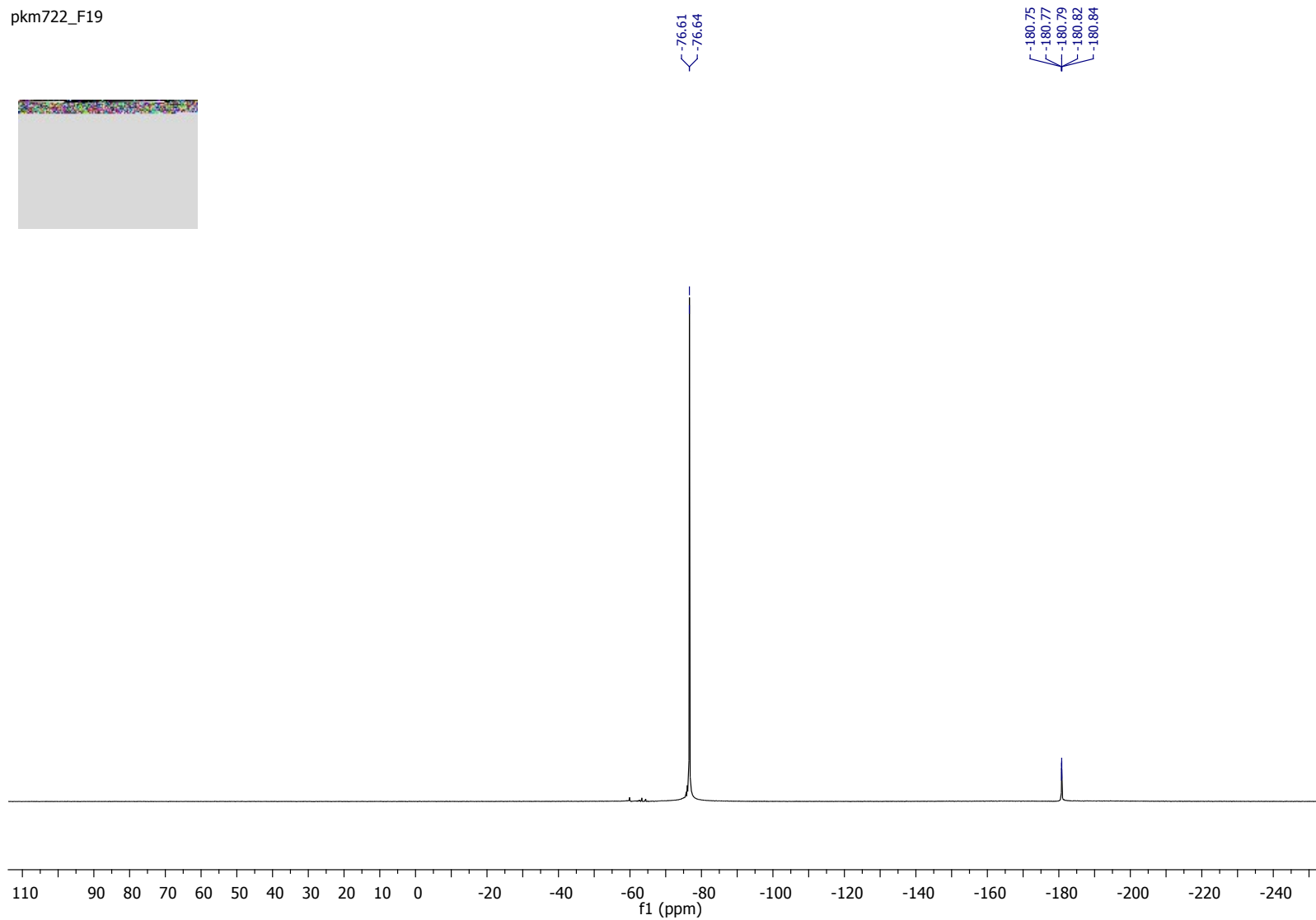
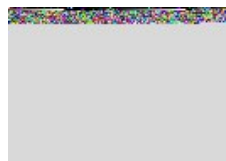
Compound 18a

pkm722



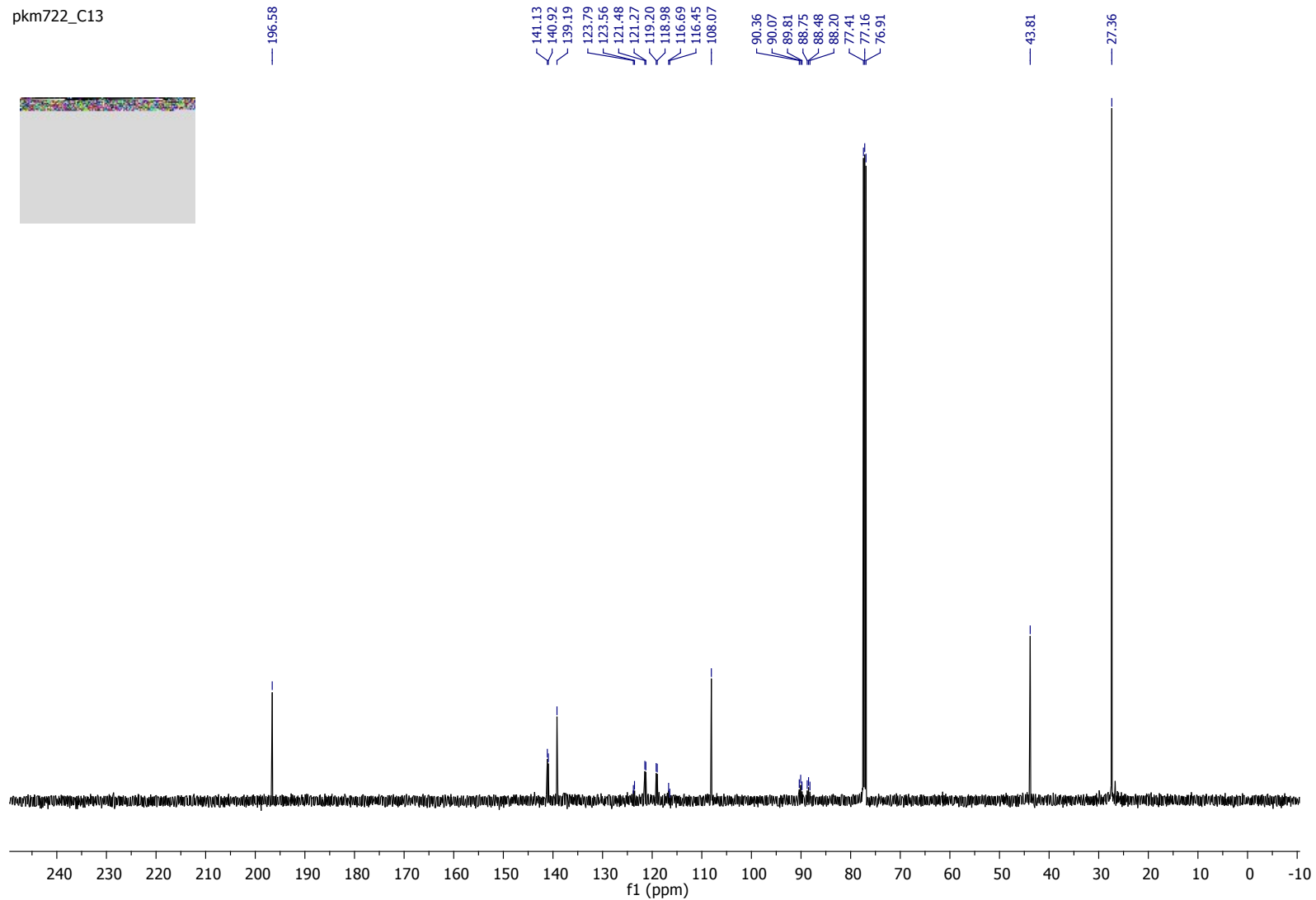
Compound **18a**

pkm722_F19



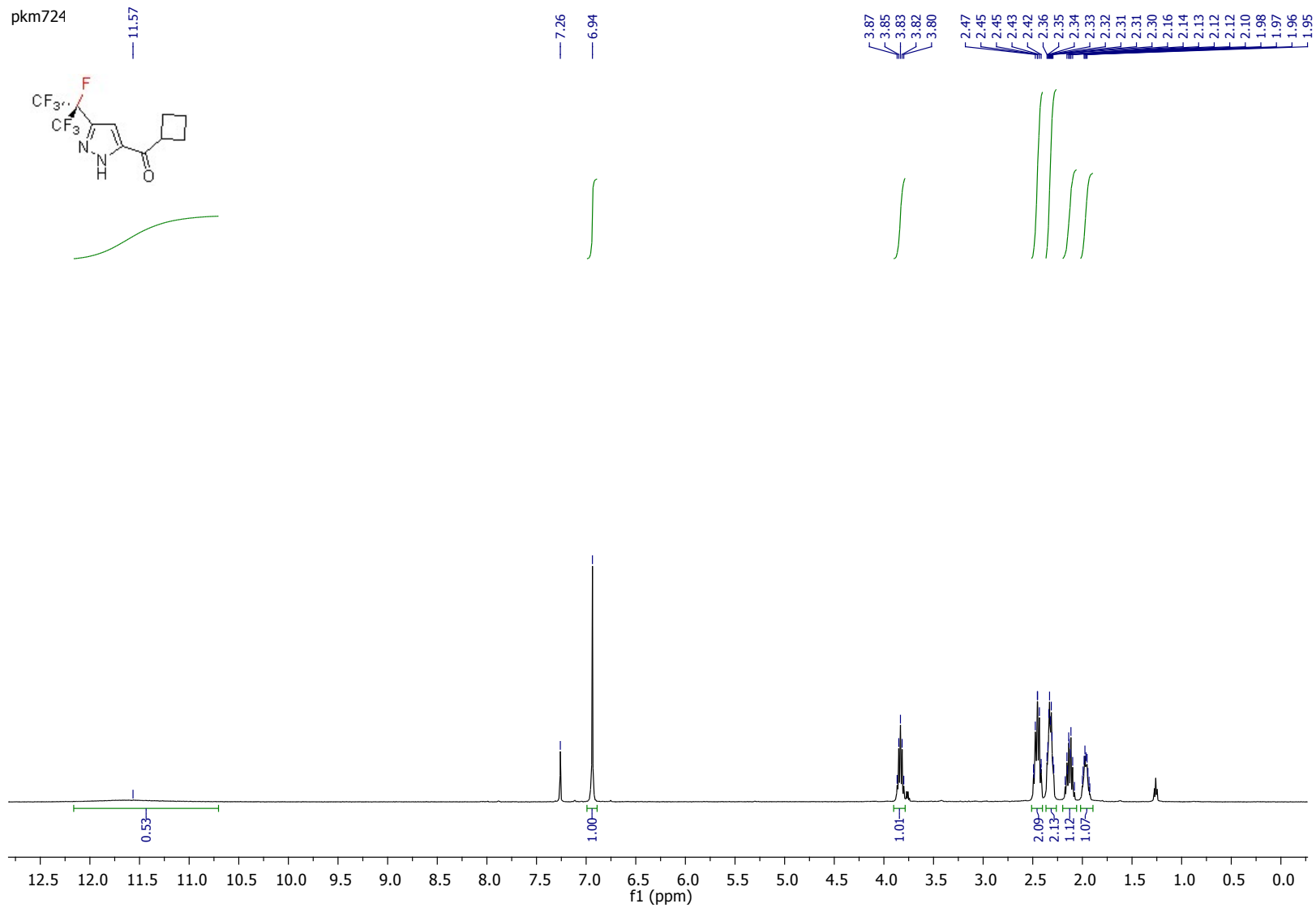
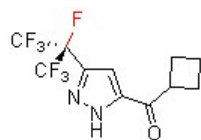
Compound **18a**

pkm722_C13



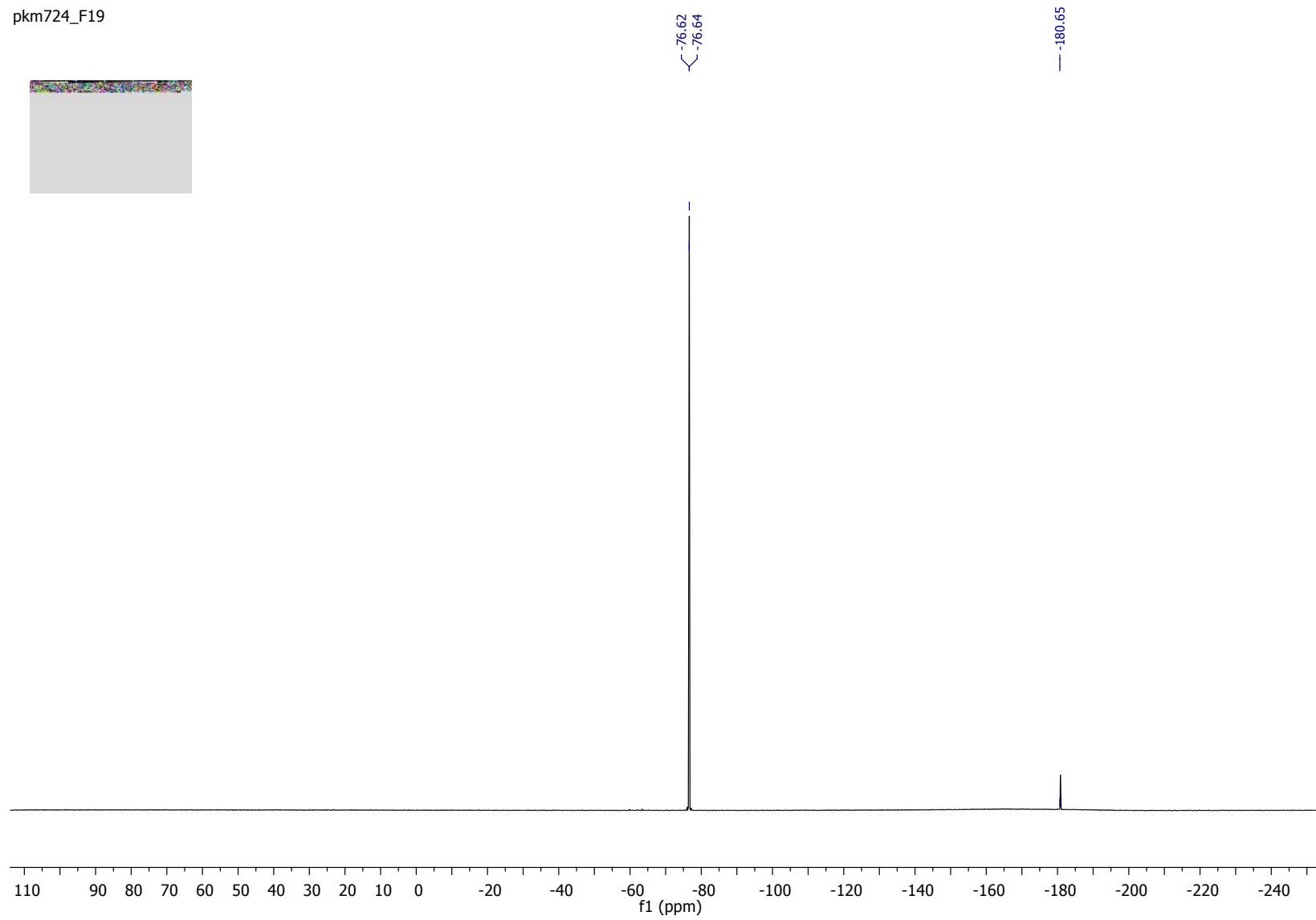
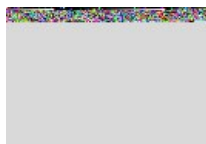
Compound 19a

pkm724



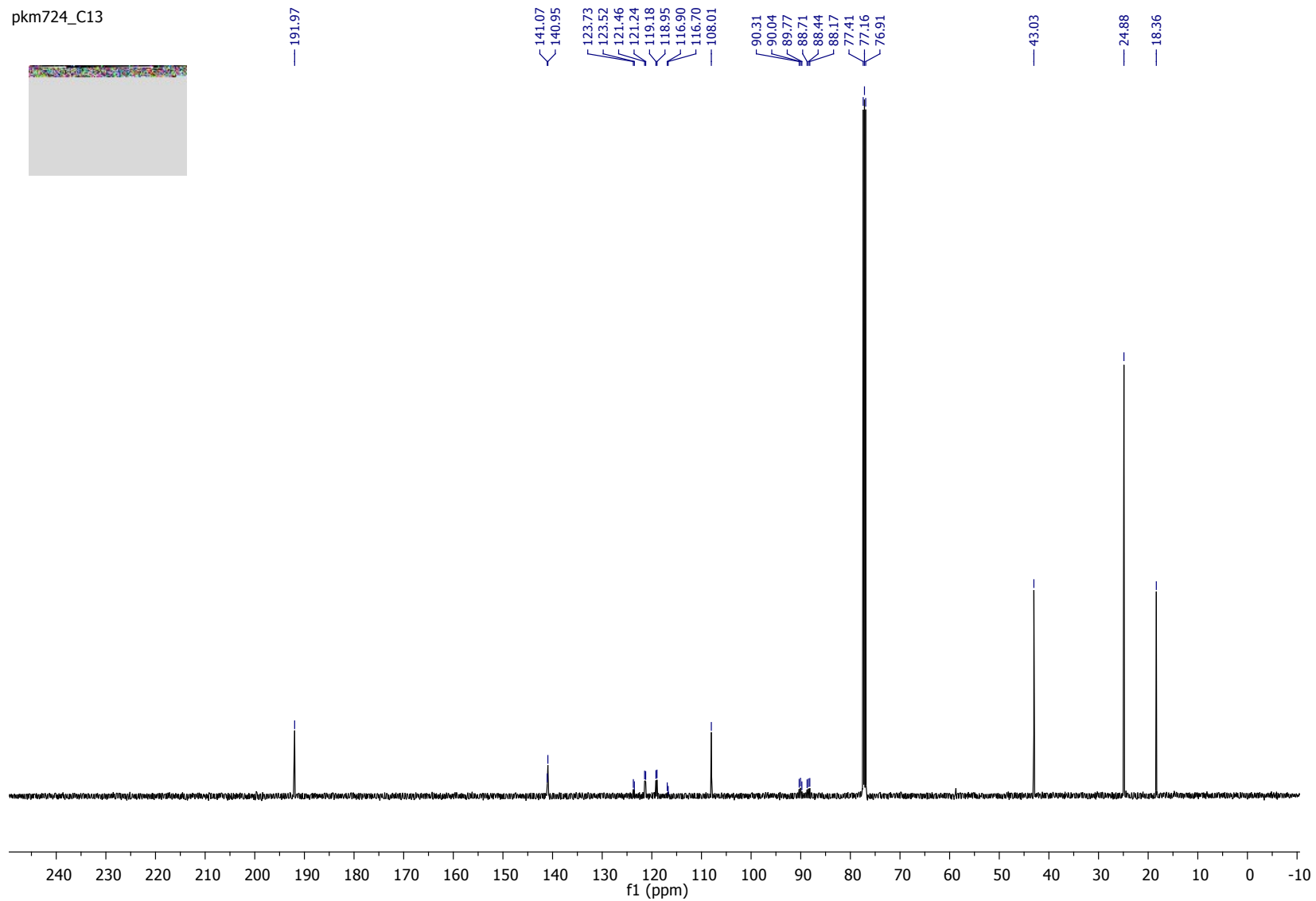
Compound 19a

pkm724_F19



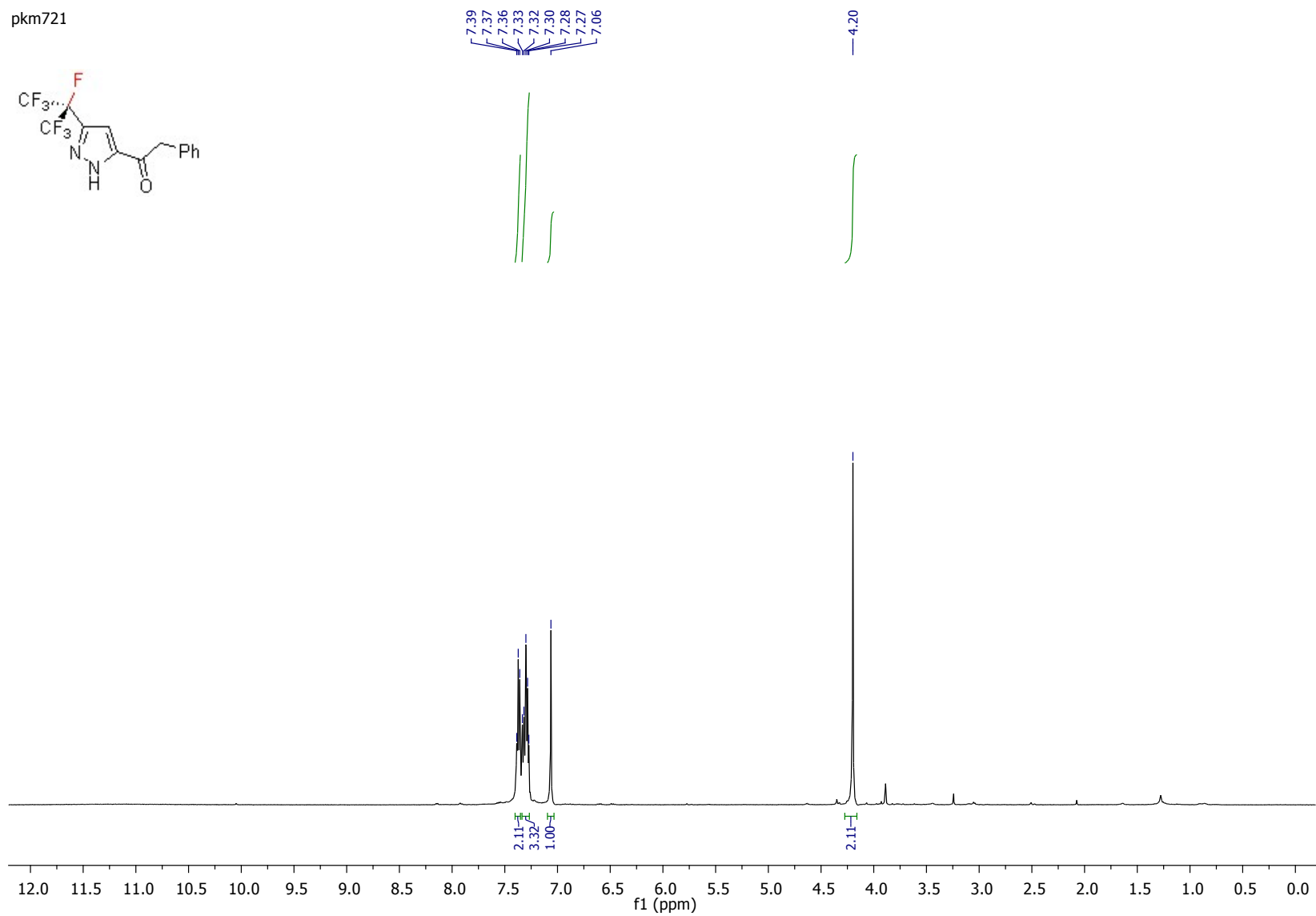
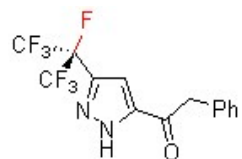
Compound 19a

pkm724_C13



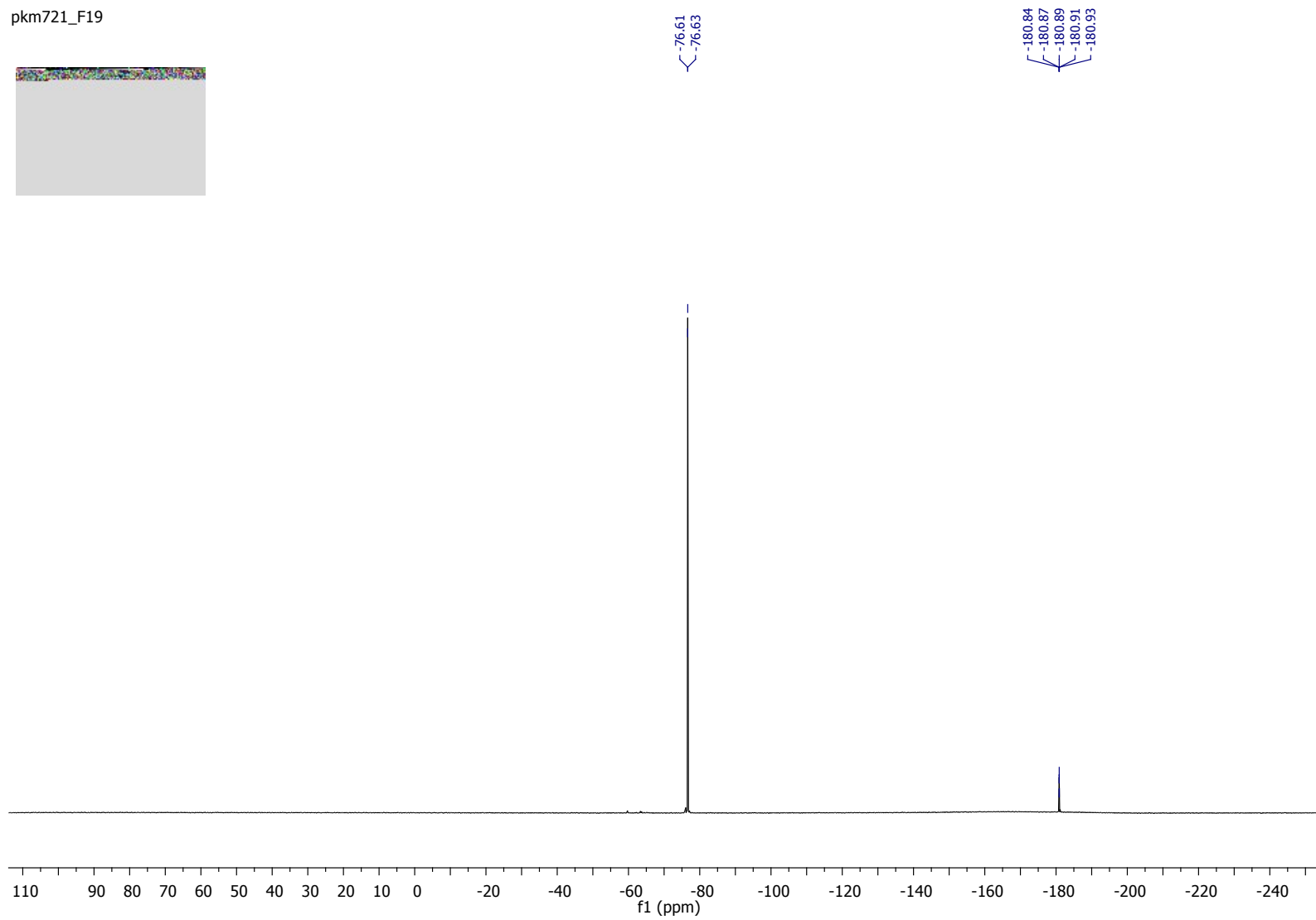
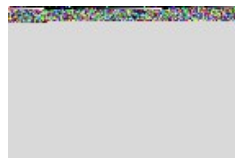
Compound 20a

pkm721



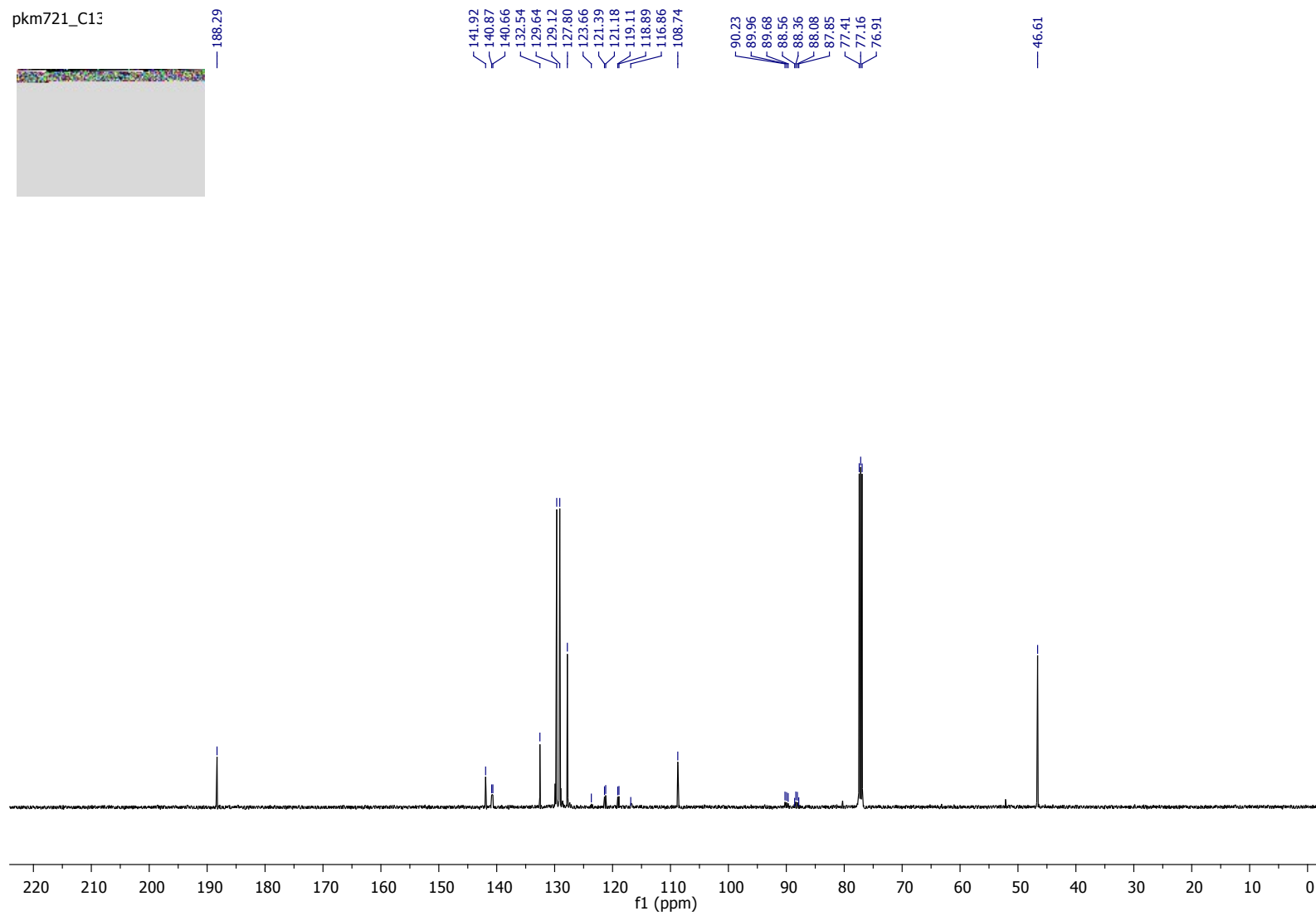
Compound 20a

pkm721_F19



Compound 20a

pkm721_C13

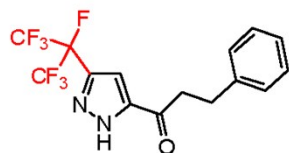


Compound 21a

PF

7.318
7.303
7.259
7.244

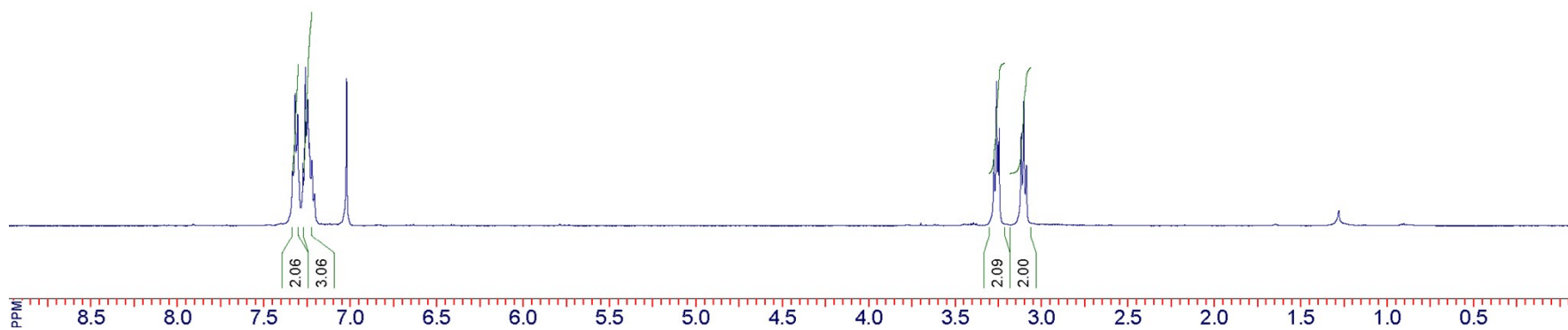
pkm723



3.275
3.260
3.252
3.245

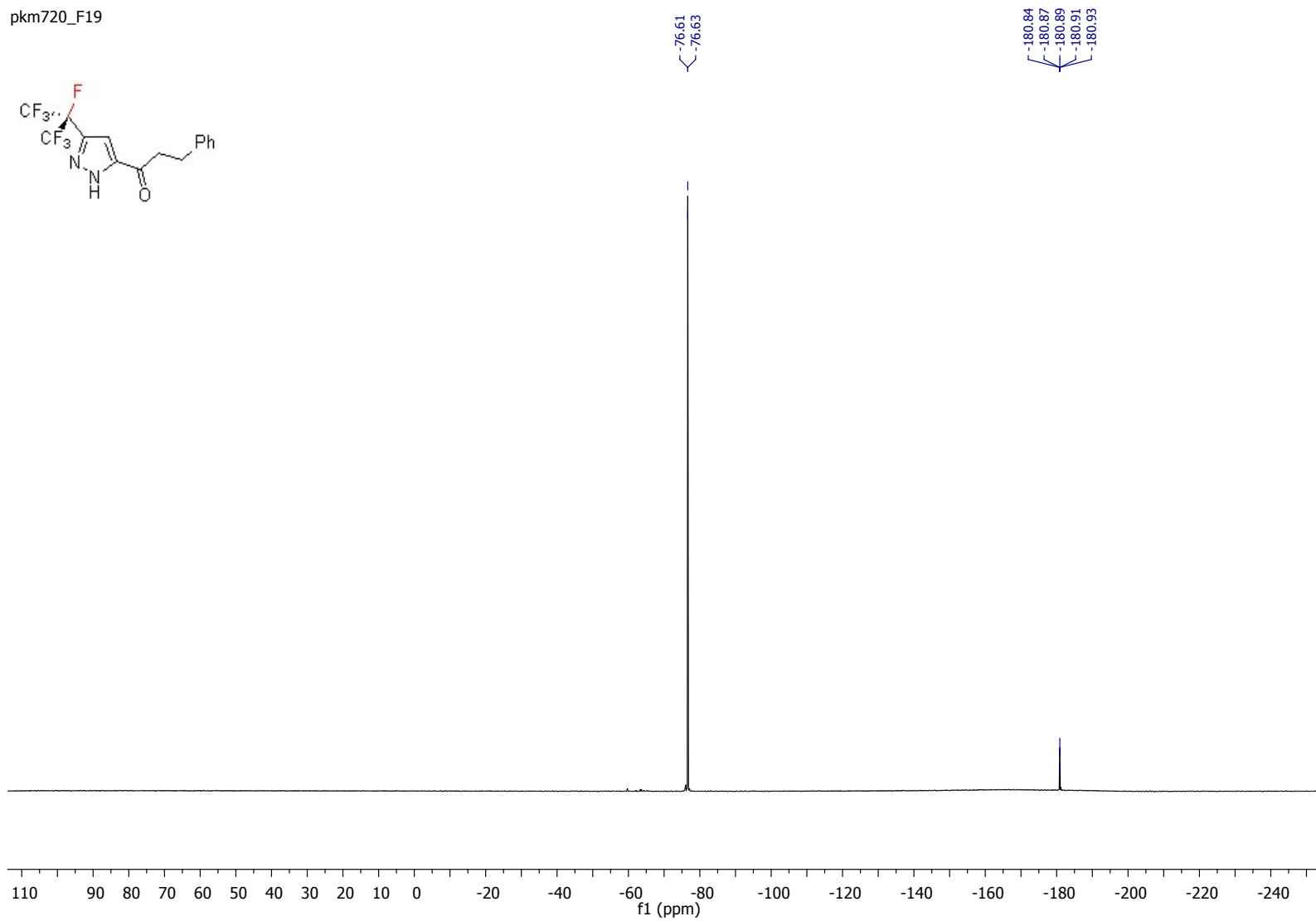
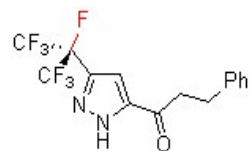
PPM
3.117
3.102
3.087

PPM
3.10

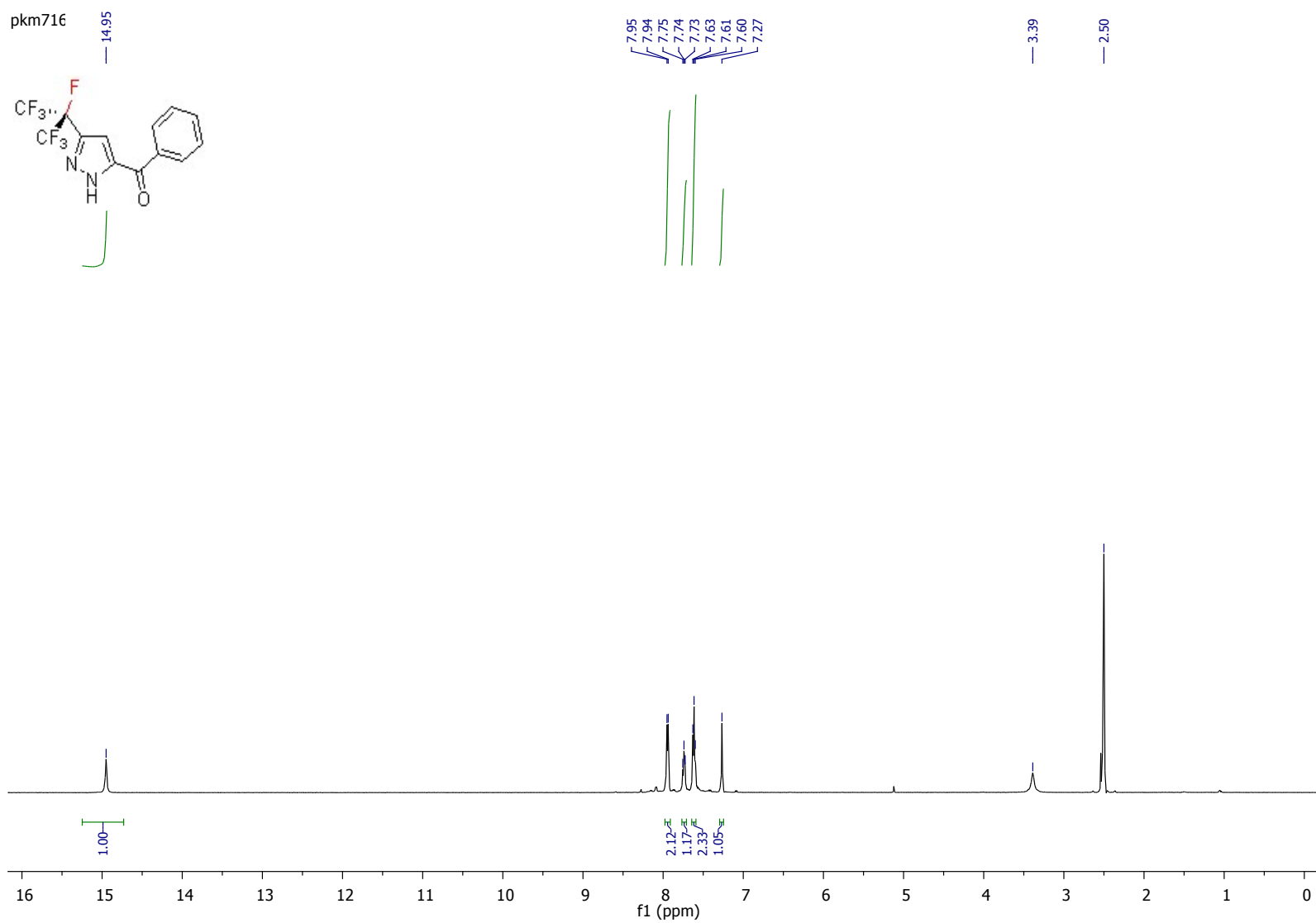


Compound 21a

pkm720_F19

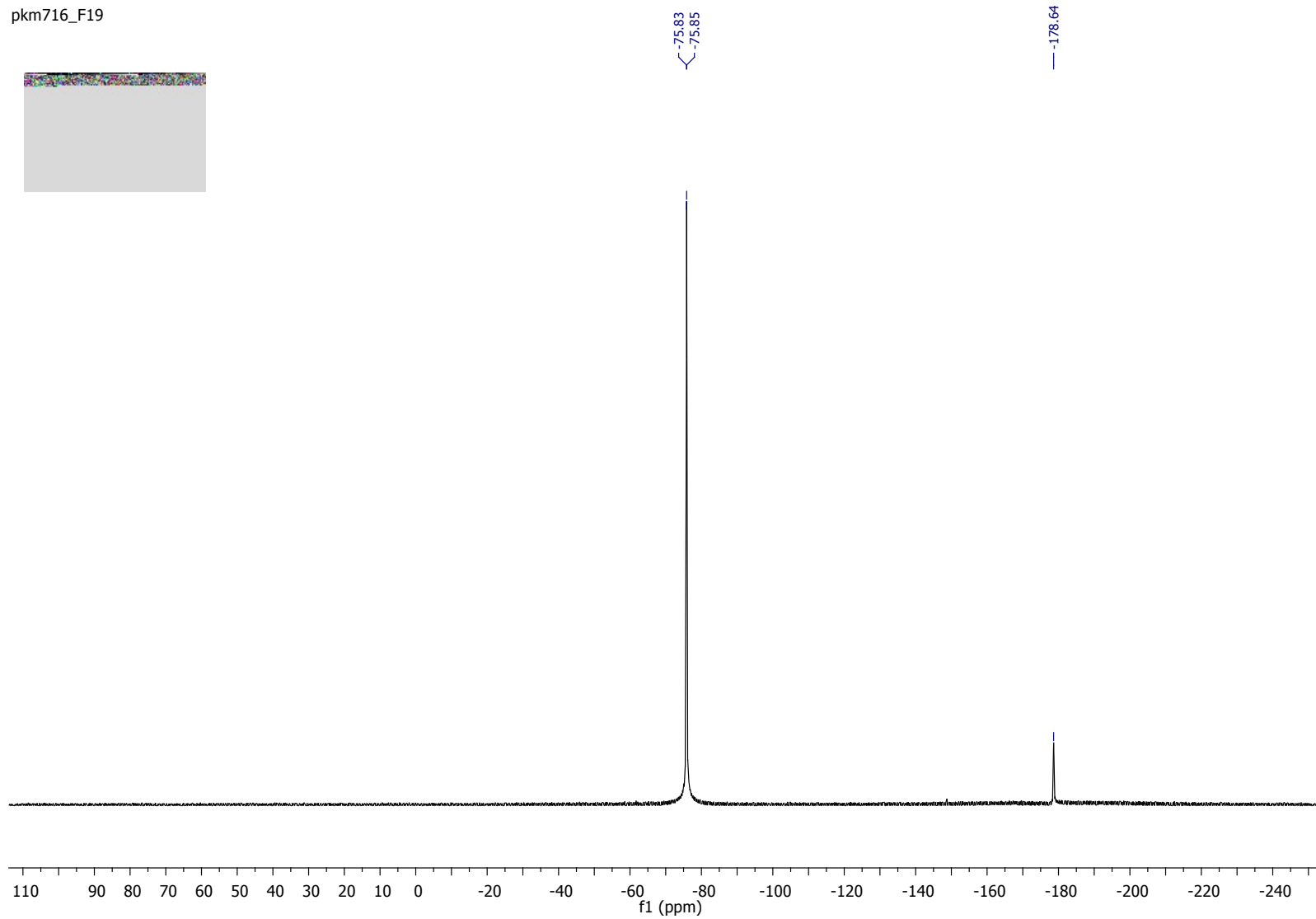


Compound 22a

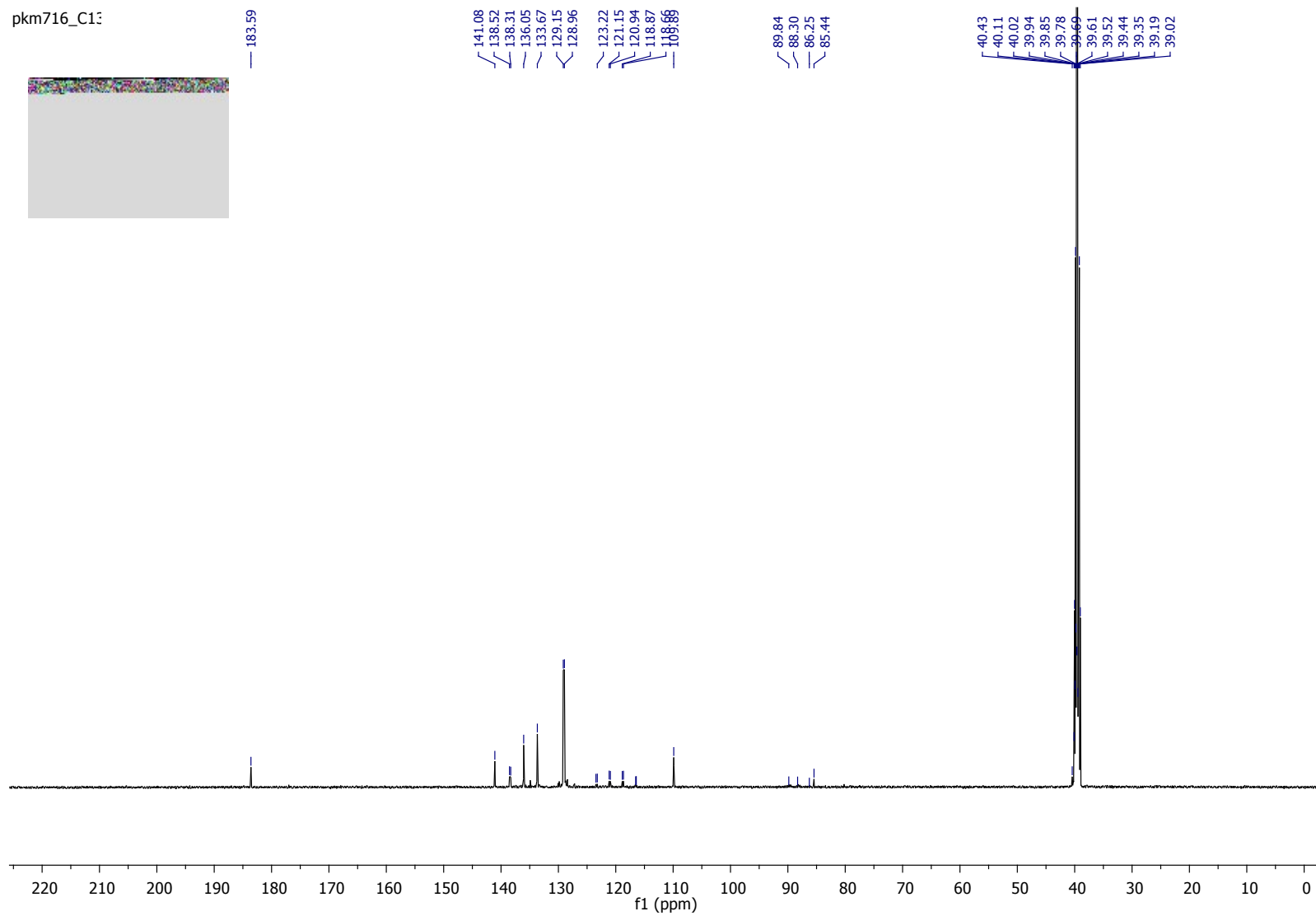


Compound 22a

pkm716_F19



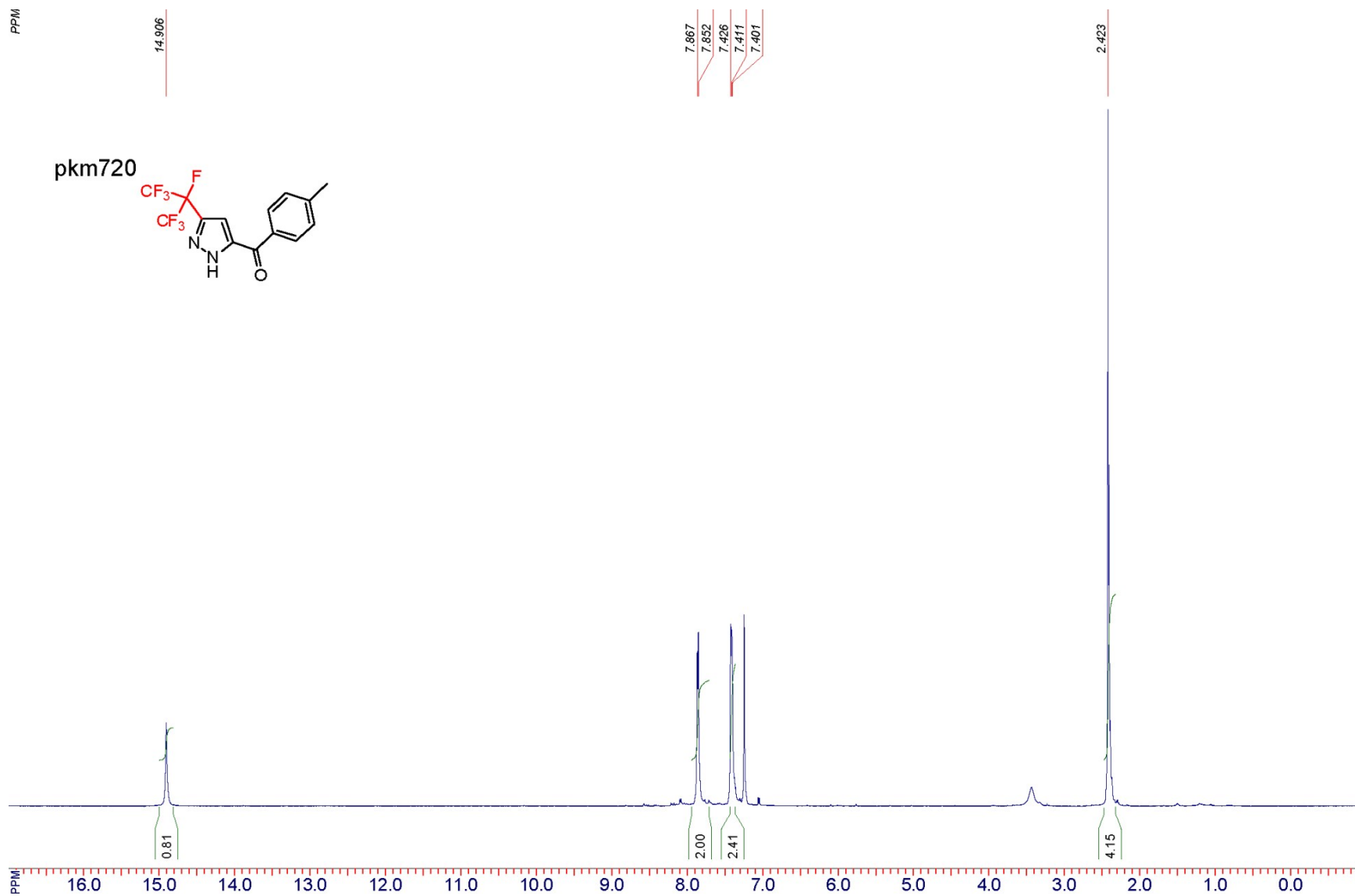
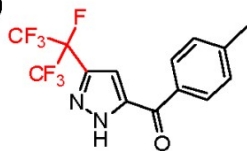
Compound 22a



Compound 23a

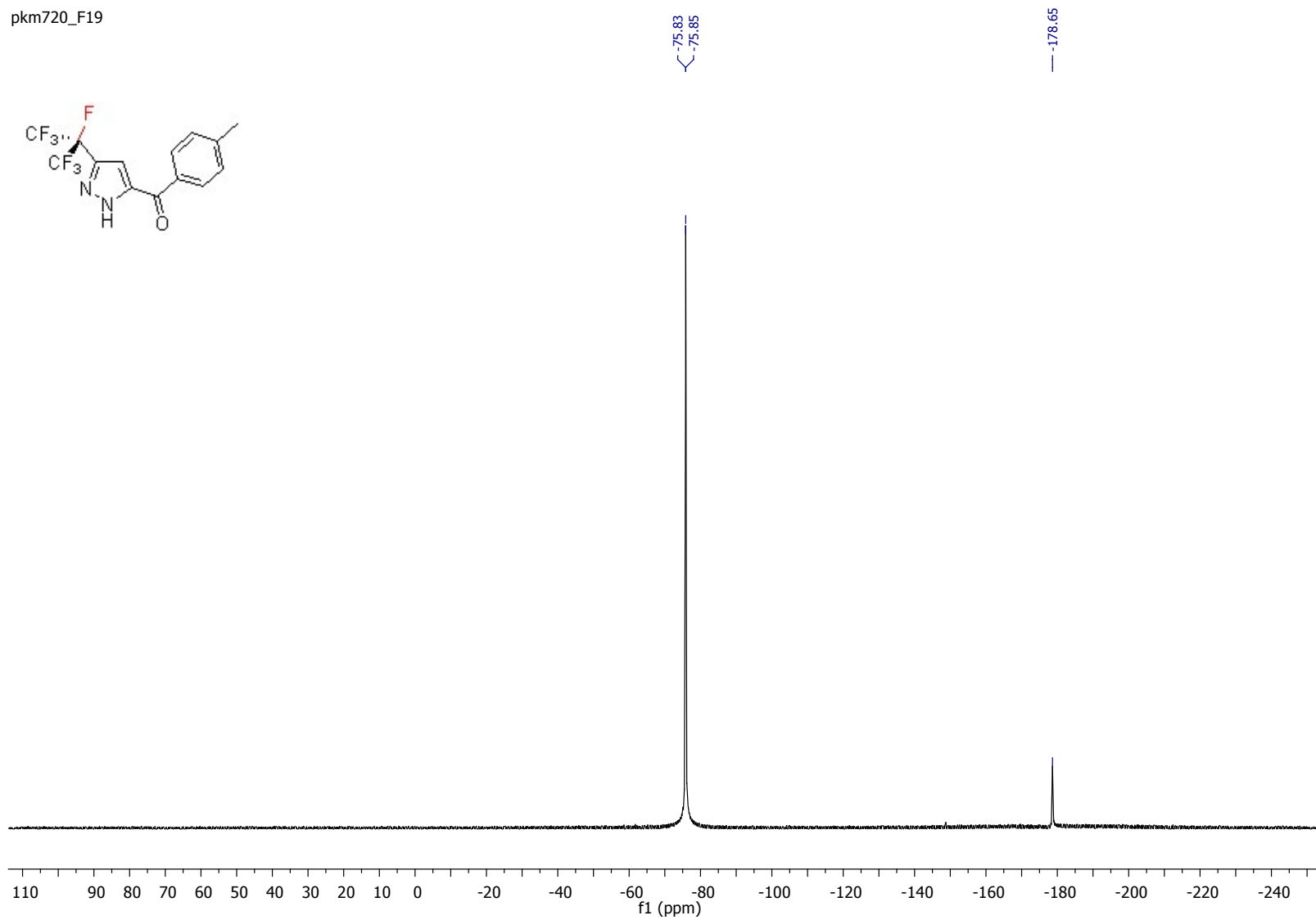
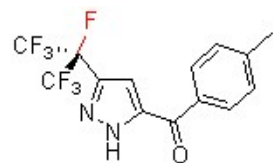
PPM

pkm720



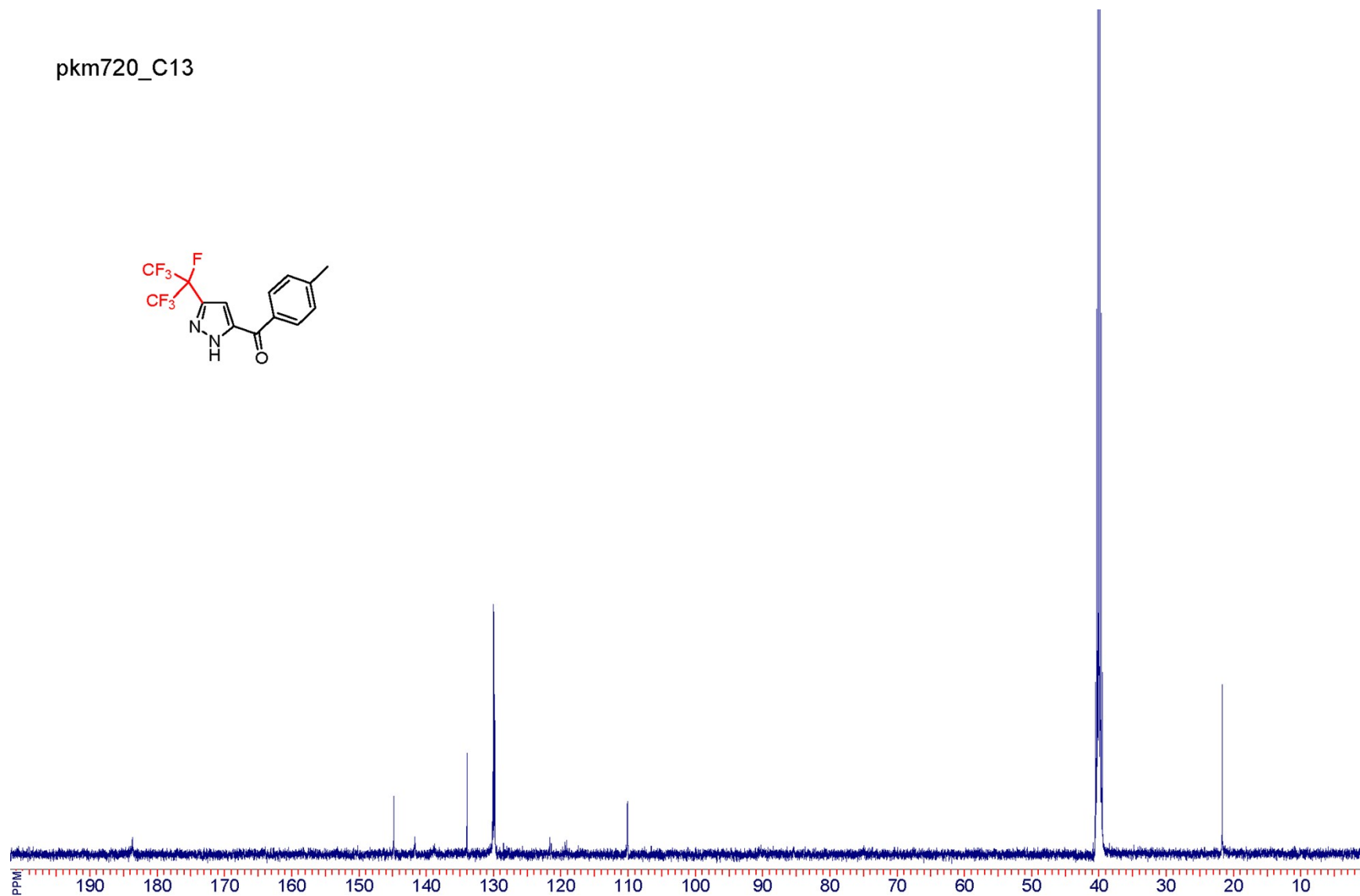
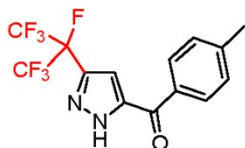
Compound 23a

pkm720_F19

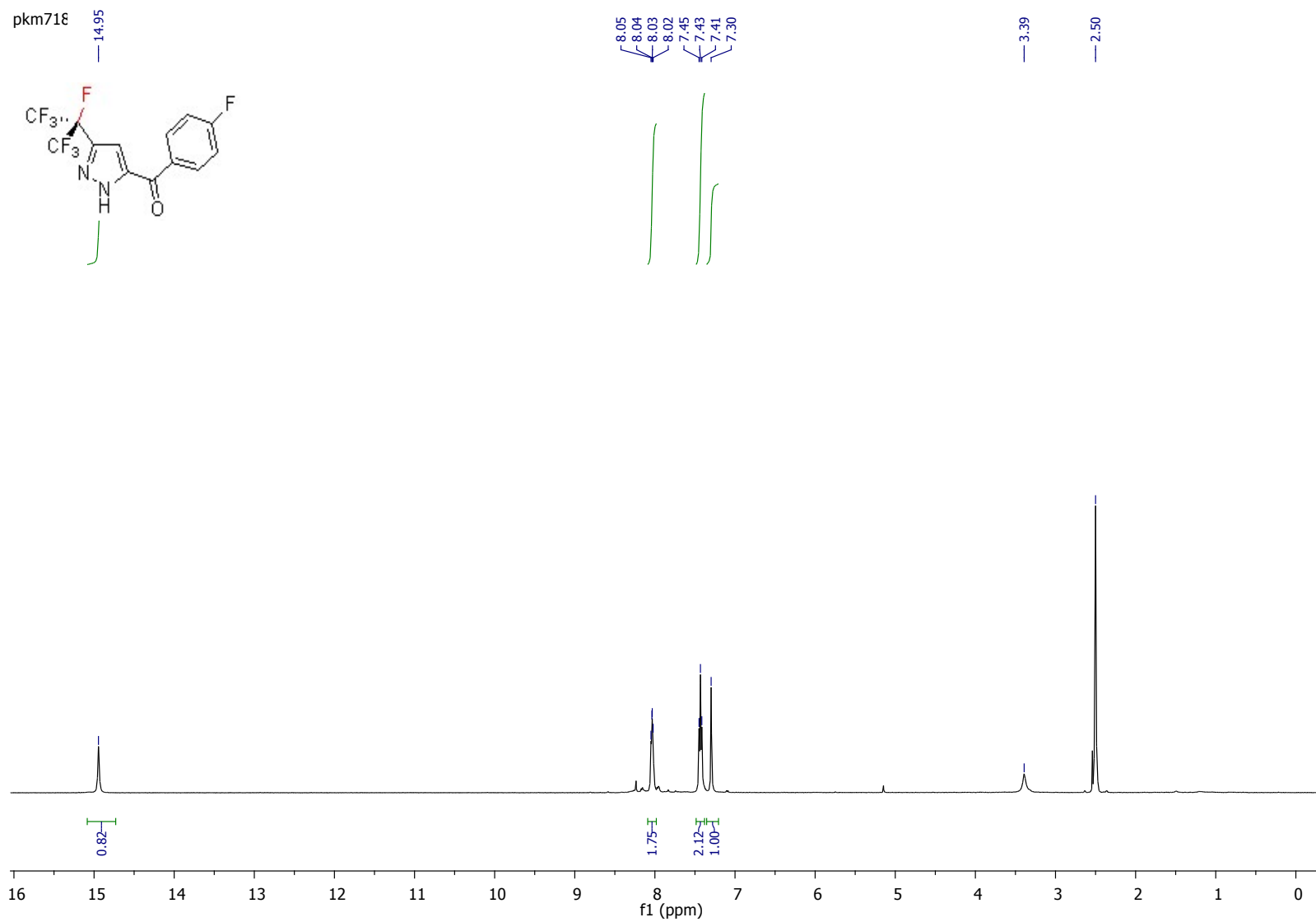


Compound 23a

pkm720_C13

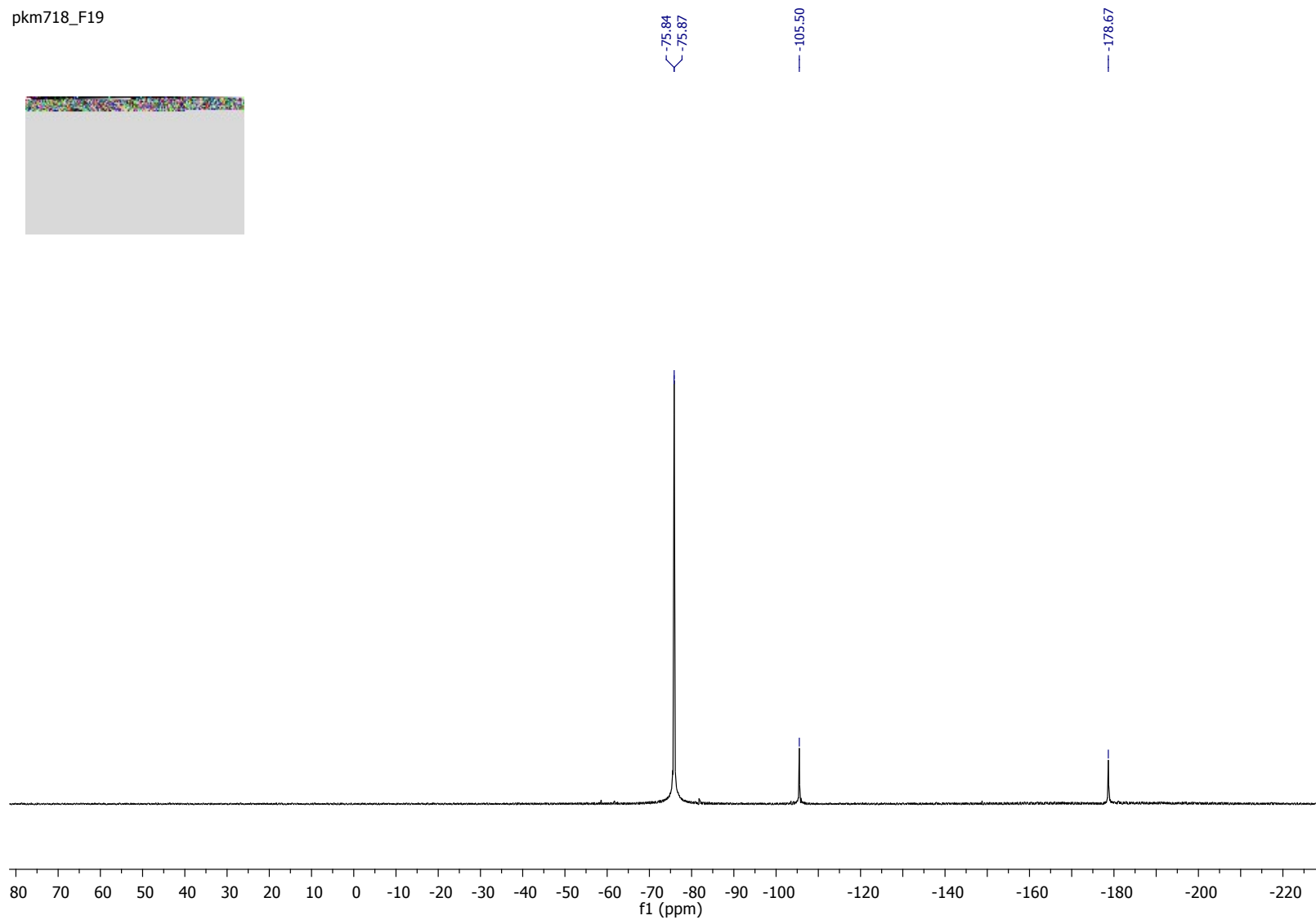


Compound 24a

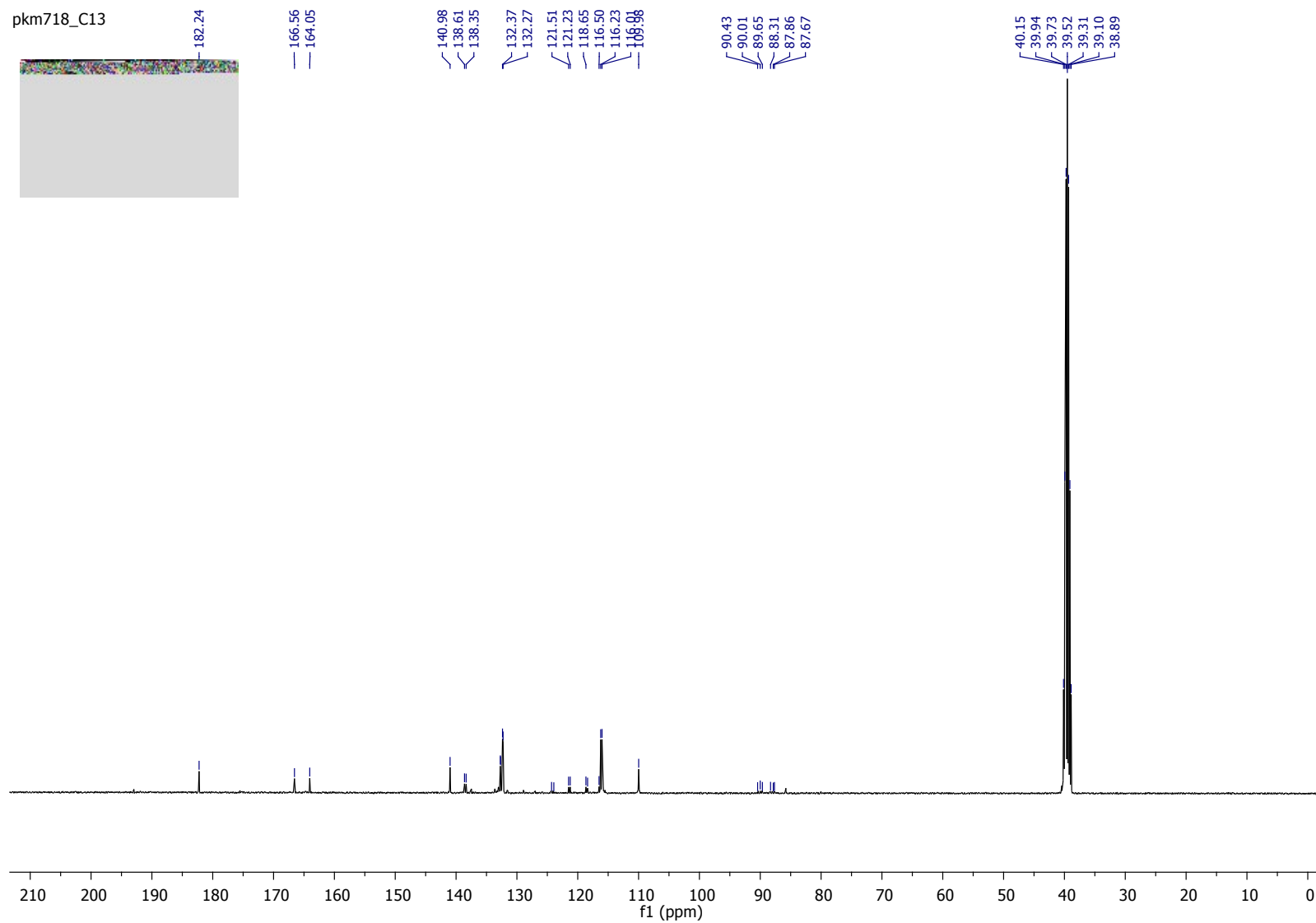


Compound 24a

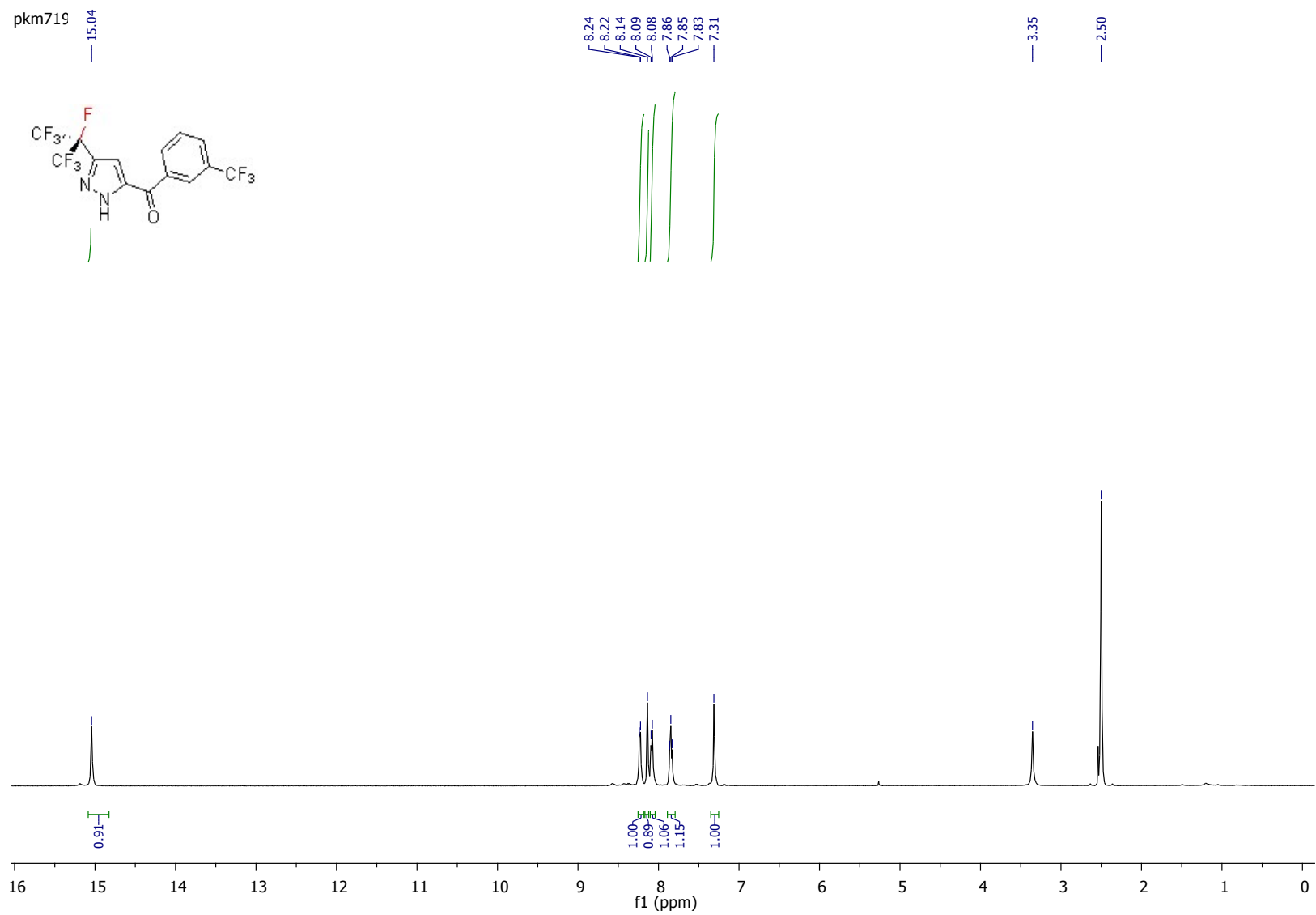
pkm718_F19



Compound 24a

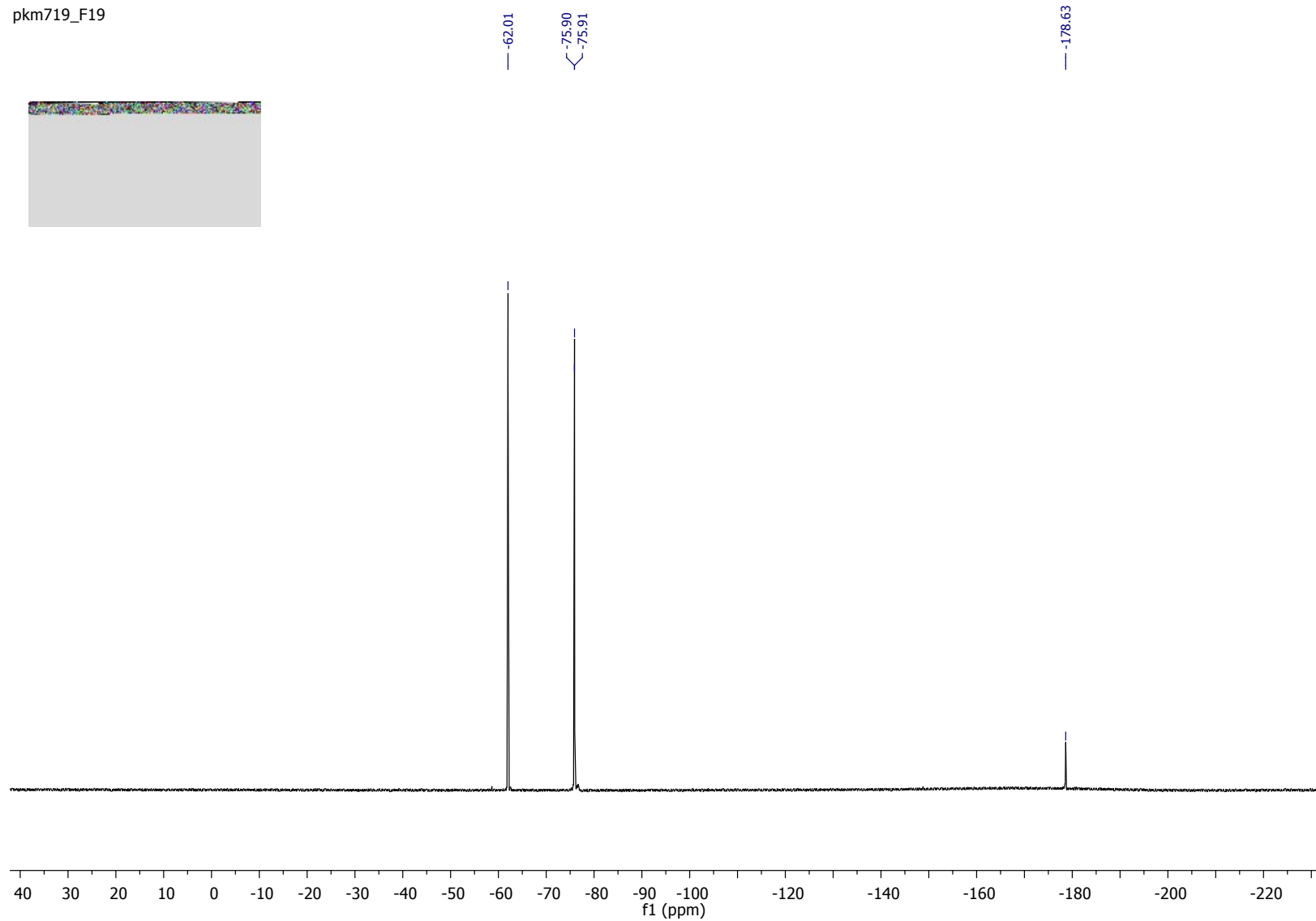


Compound 25a



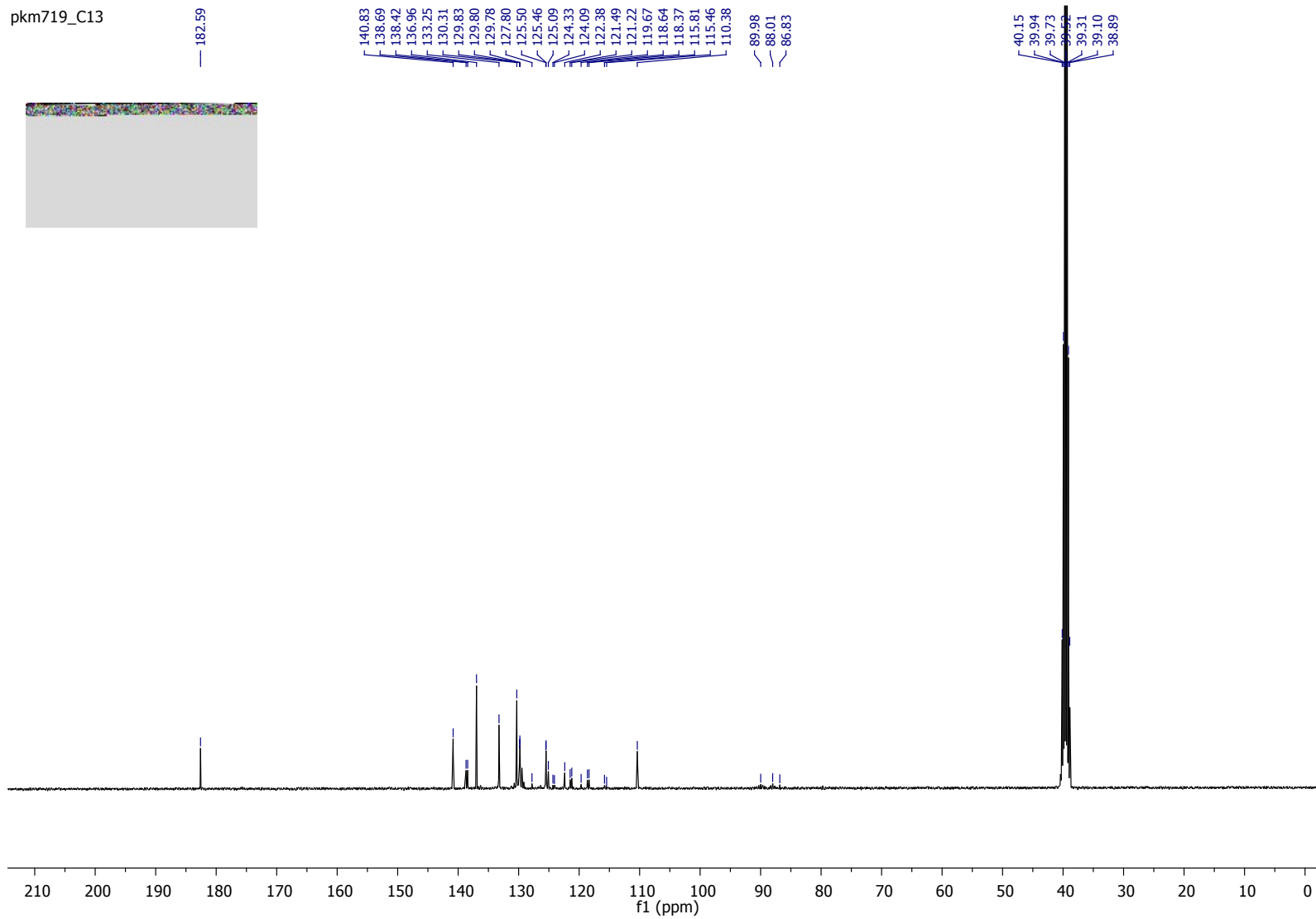
Compound 25a

pkm719_F19

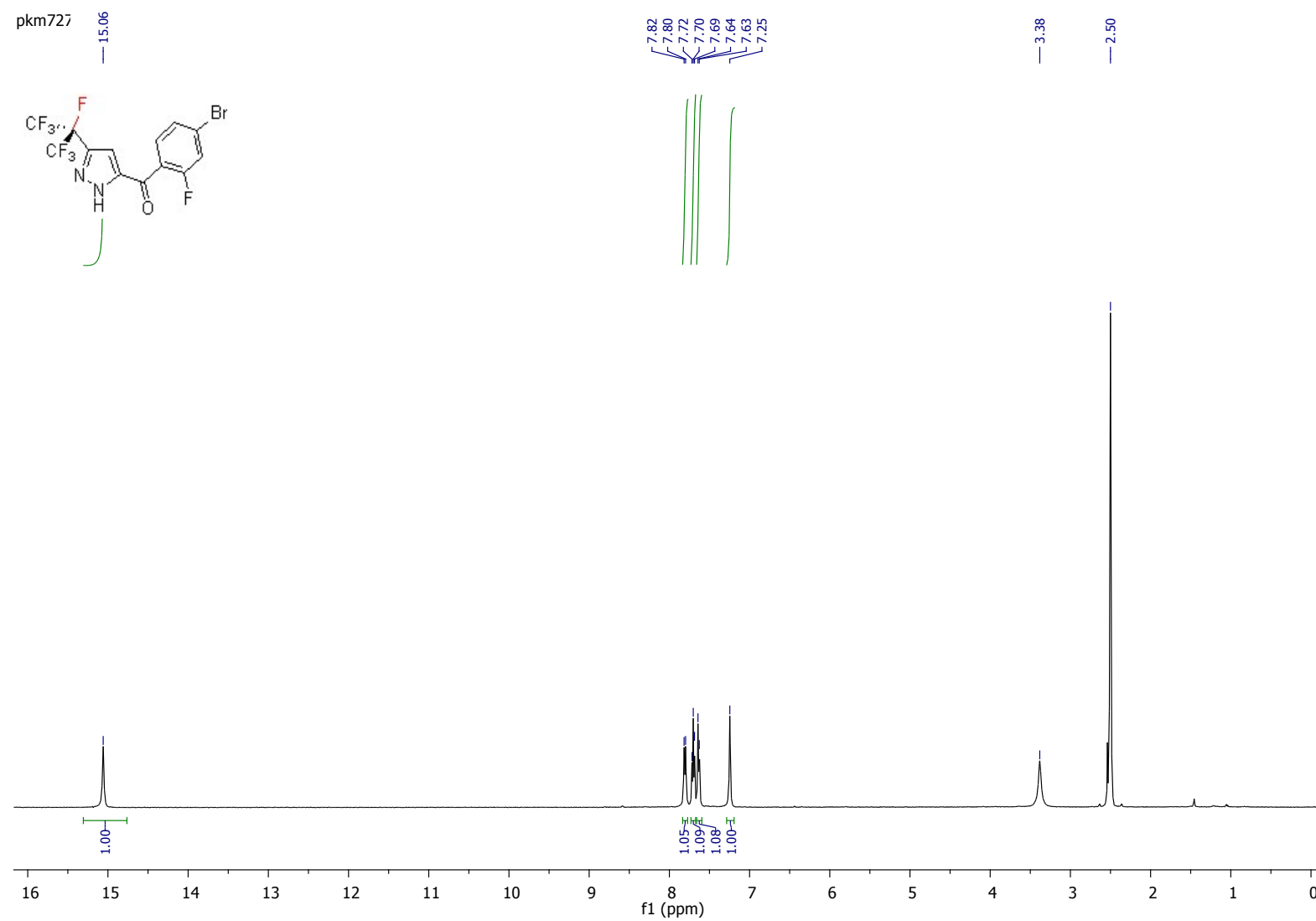


Compound 25a

pkm719_C13

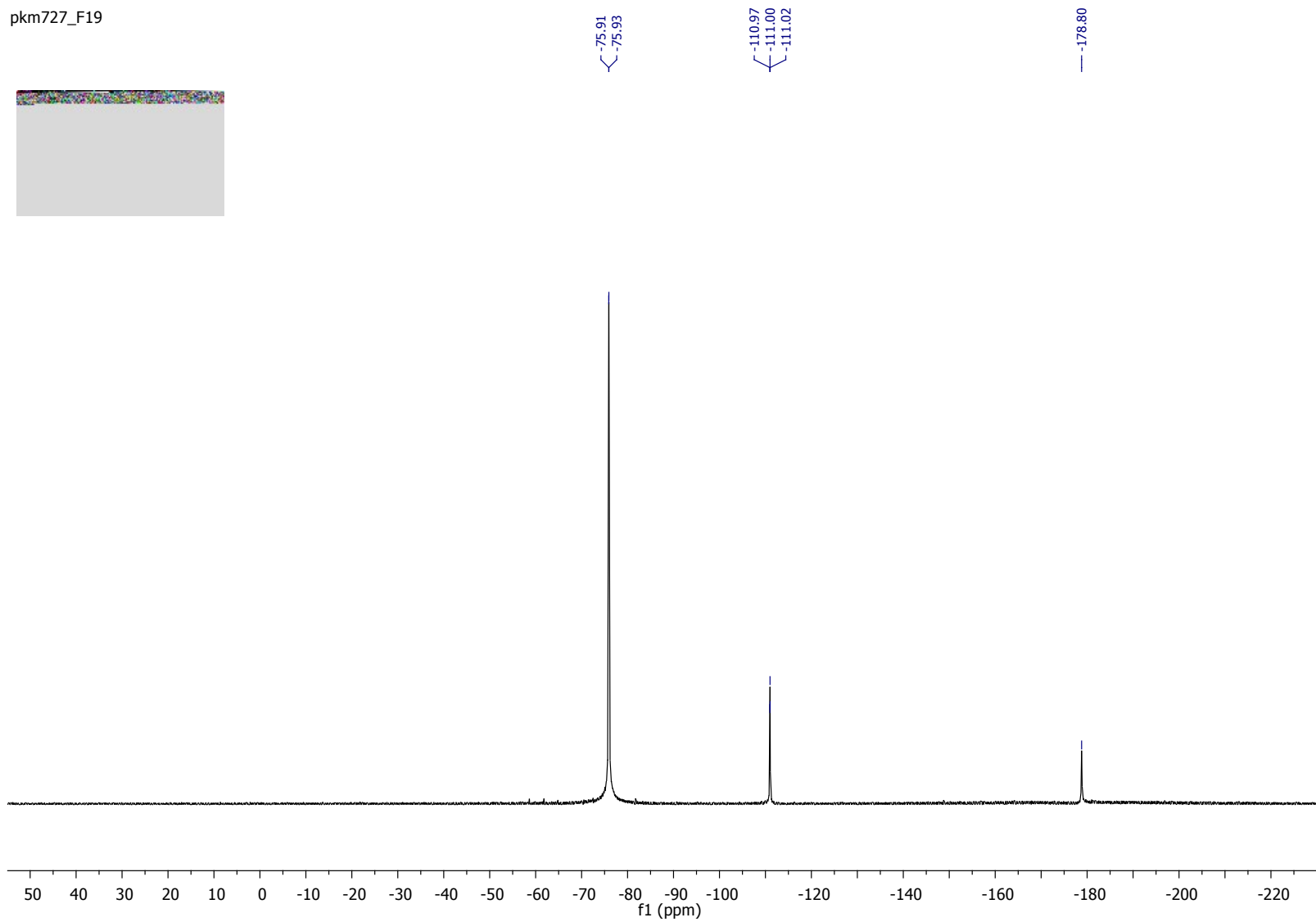
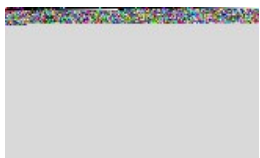


Compound 26a

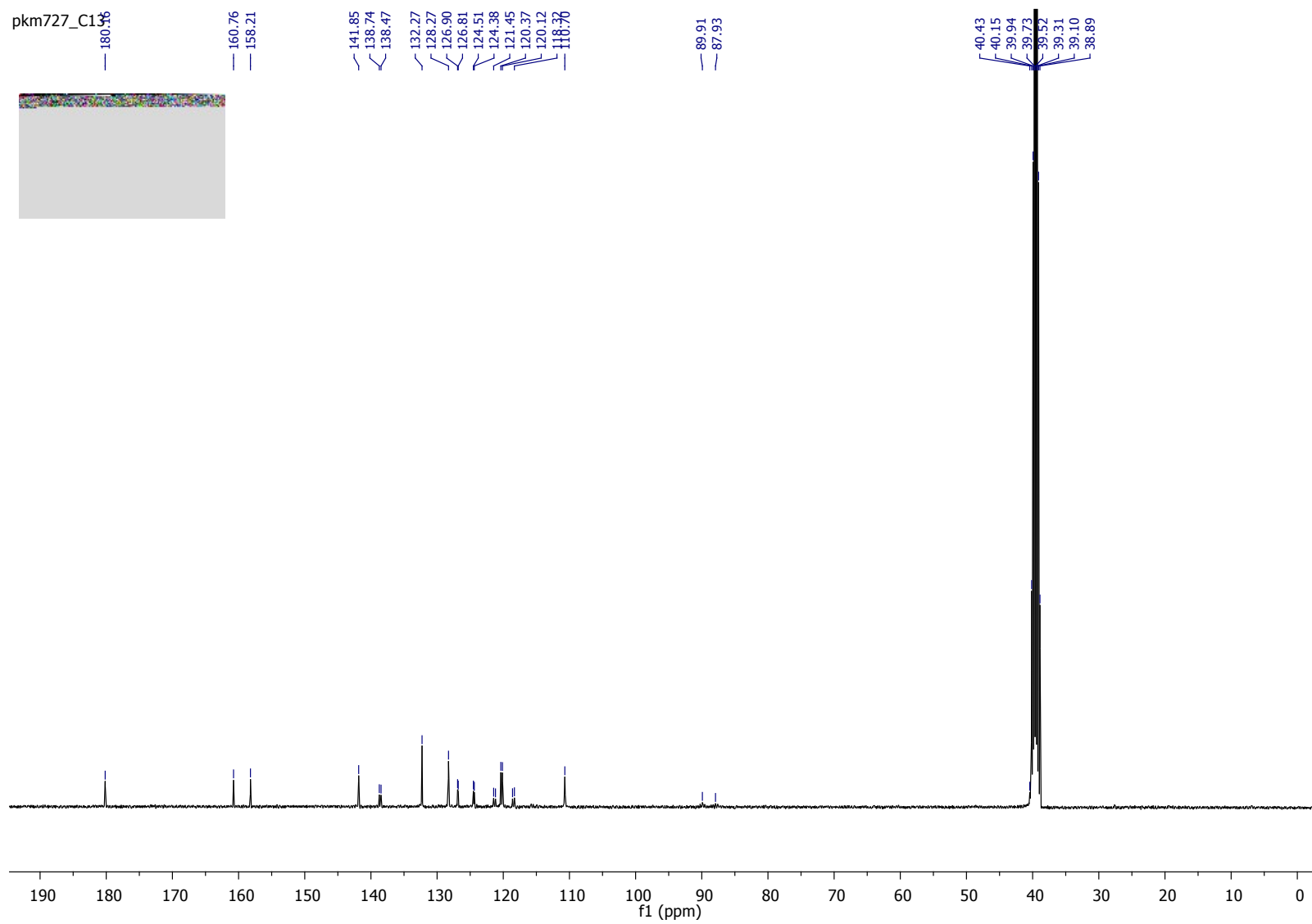


Compound 26a

pkm727_F19



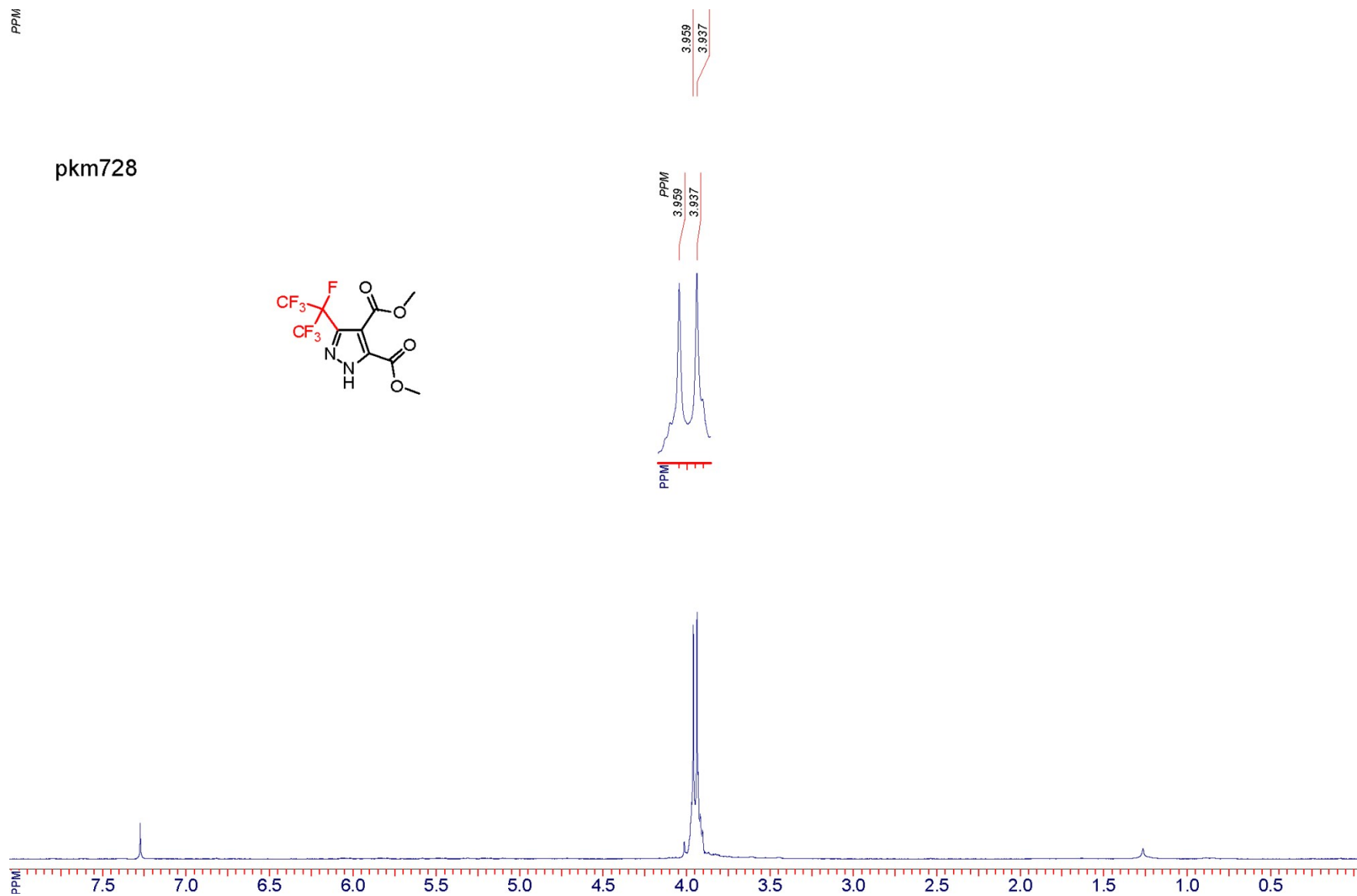
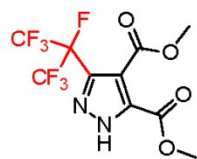
Compound 26a



Compound 30a

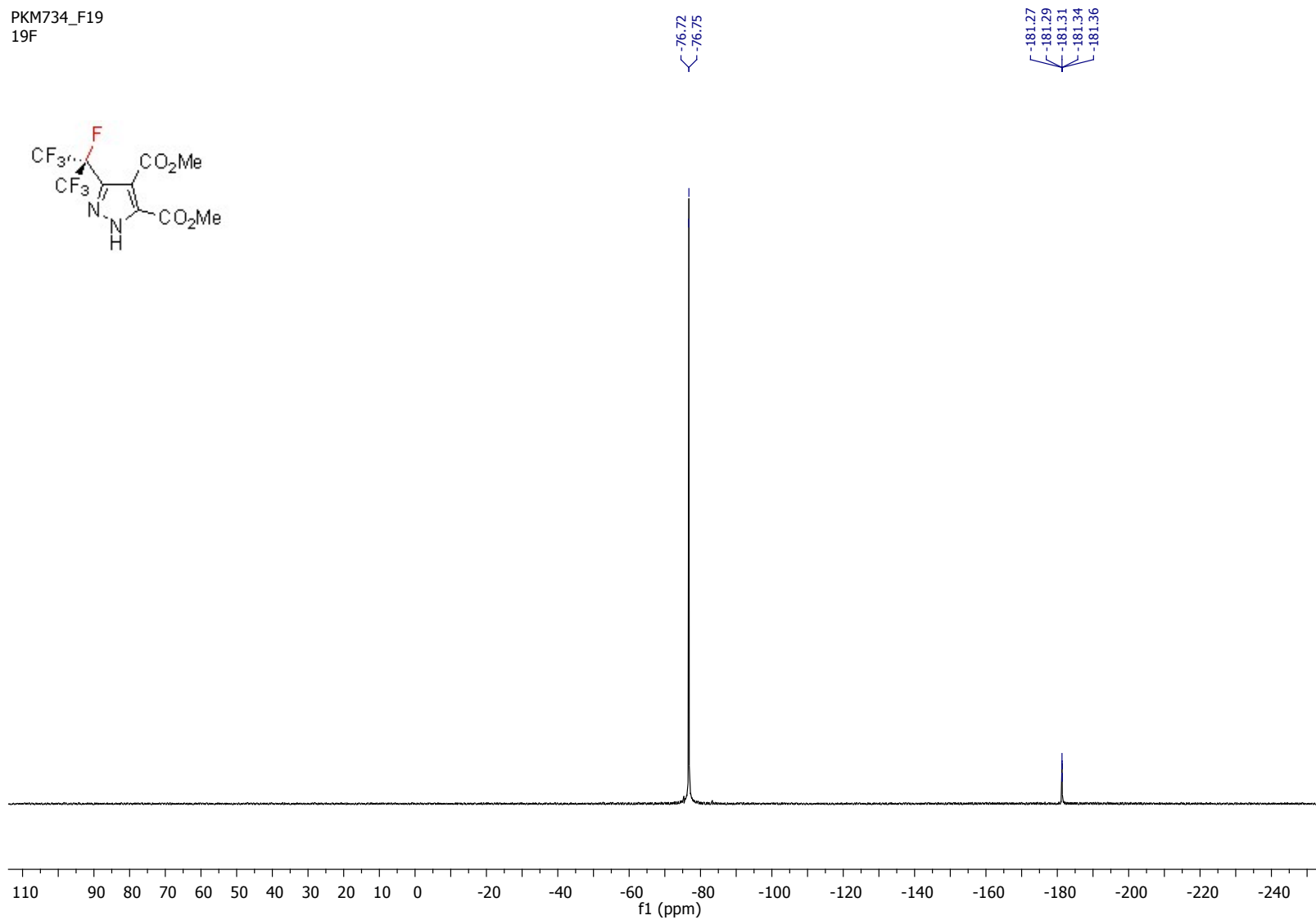
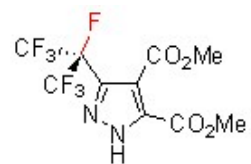
PPM

pkm728



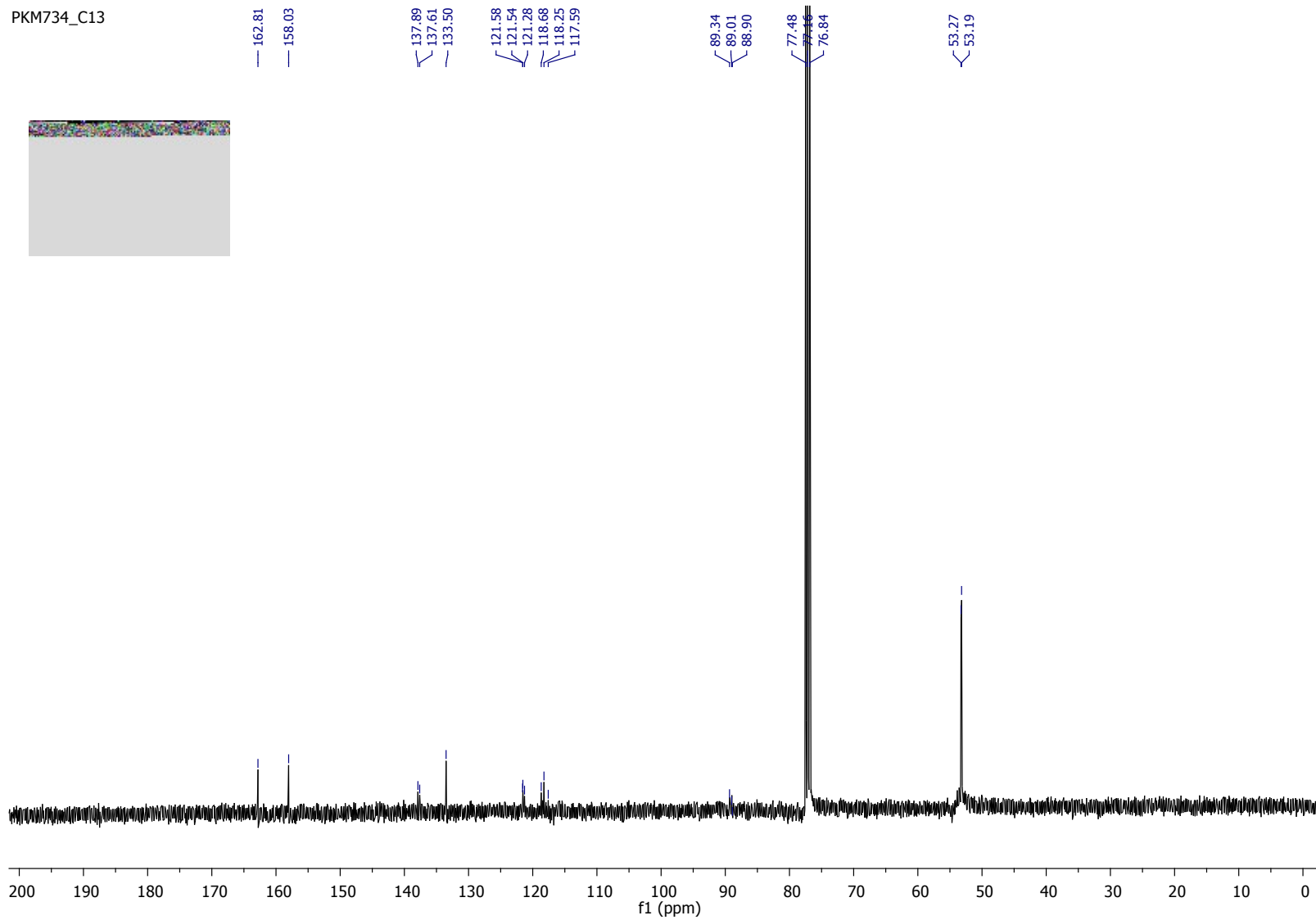
Compound 30a

PKM734_F19
19F



Compound 30a

PKM734_C13



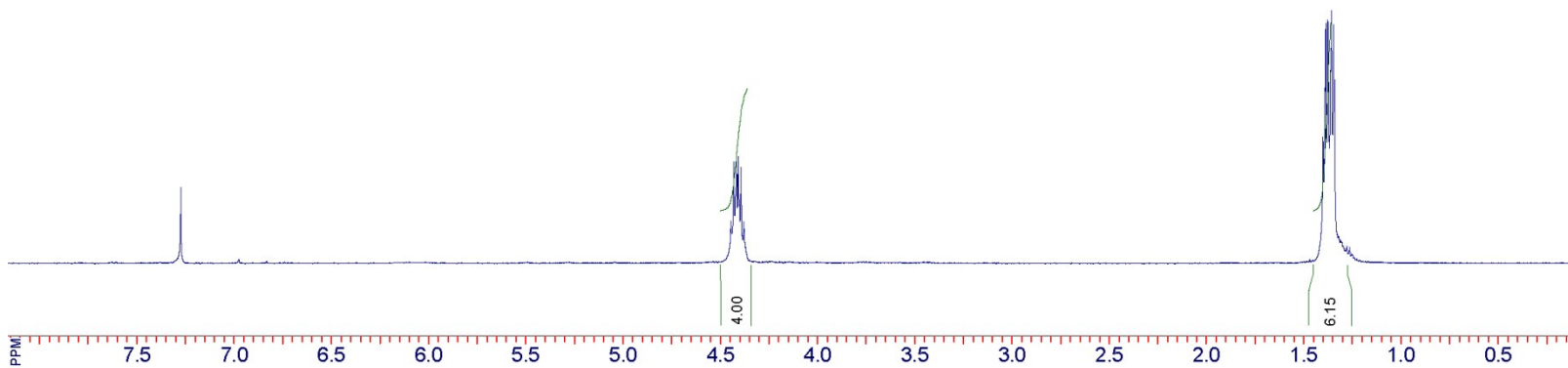
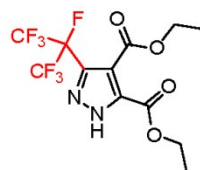
Compound 31a

PPM

4.431
4.416
4.407
4.393

1.386
1.376

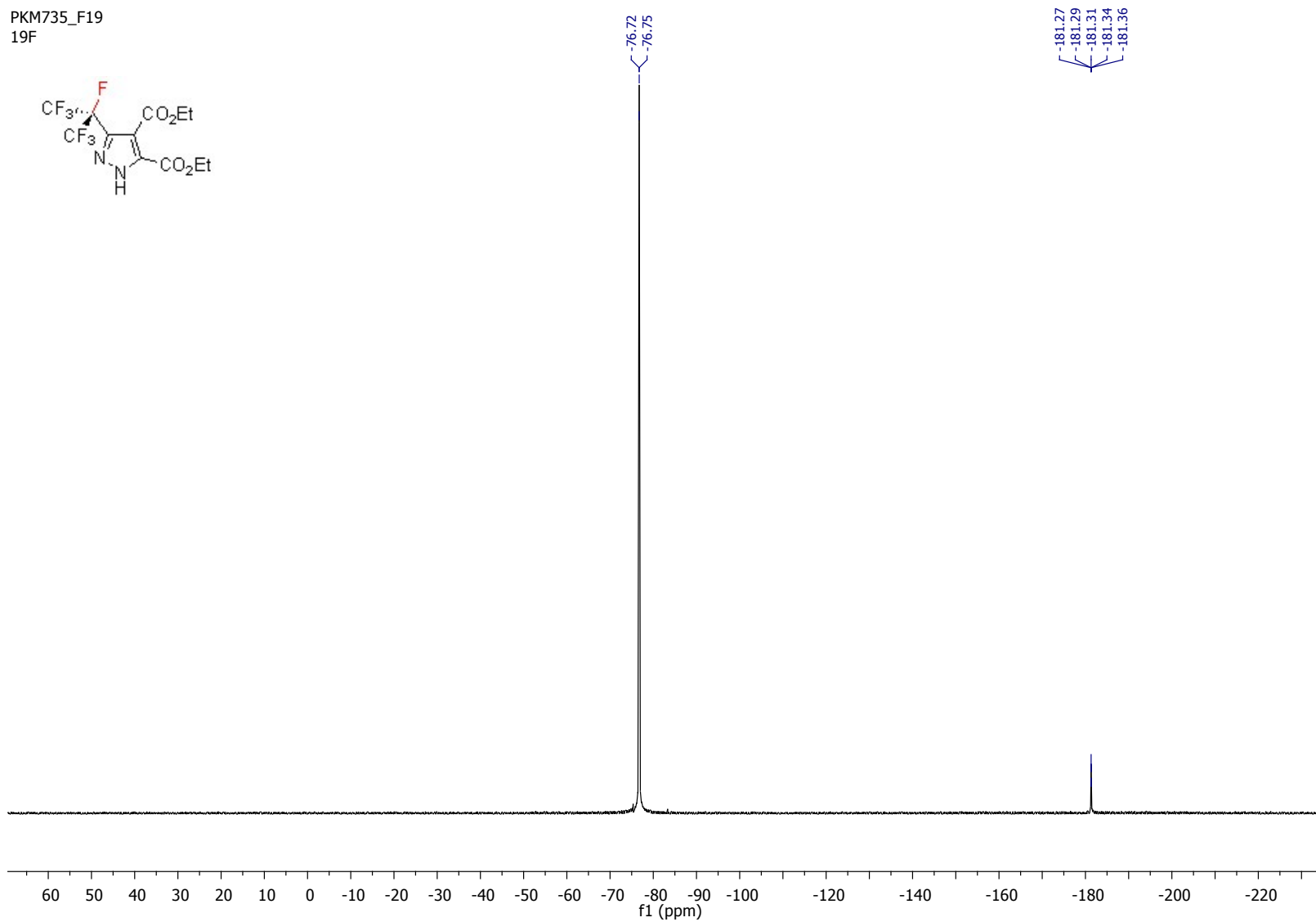
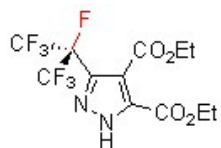
pkm729



File name: pkm729	Operator: root	SF: 499.9500 MHz	NSC: 1	PW: 0.00 usec, RG: 32	SI: 32768
Date: 30-Jan-2017	Solvent: CDCl3	SW: 8993 Hz	TE: 683 K	AQ: 1.82 sec, RD: 0.00 sec	

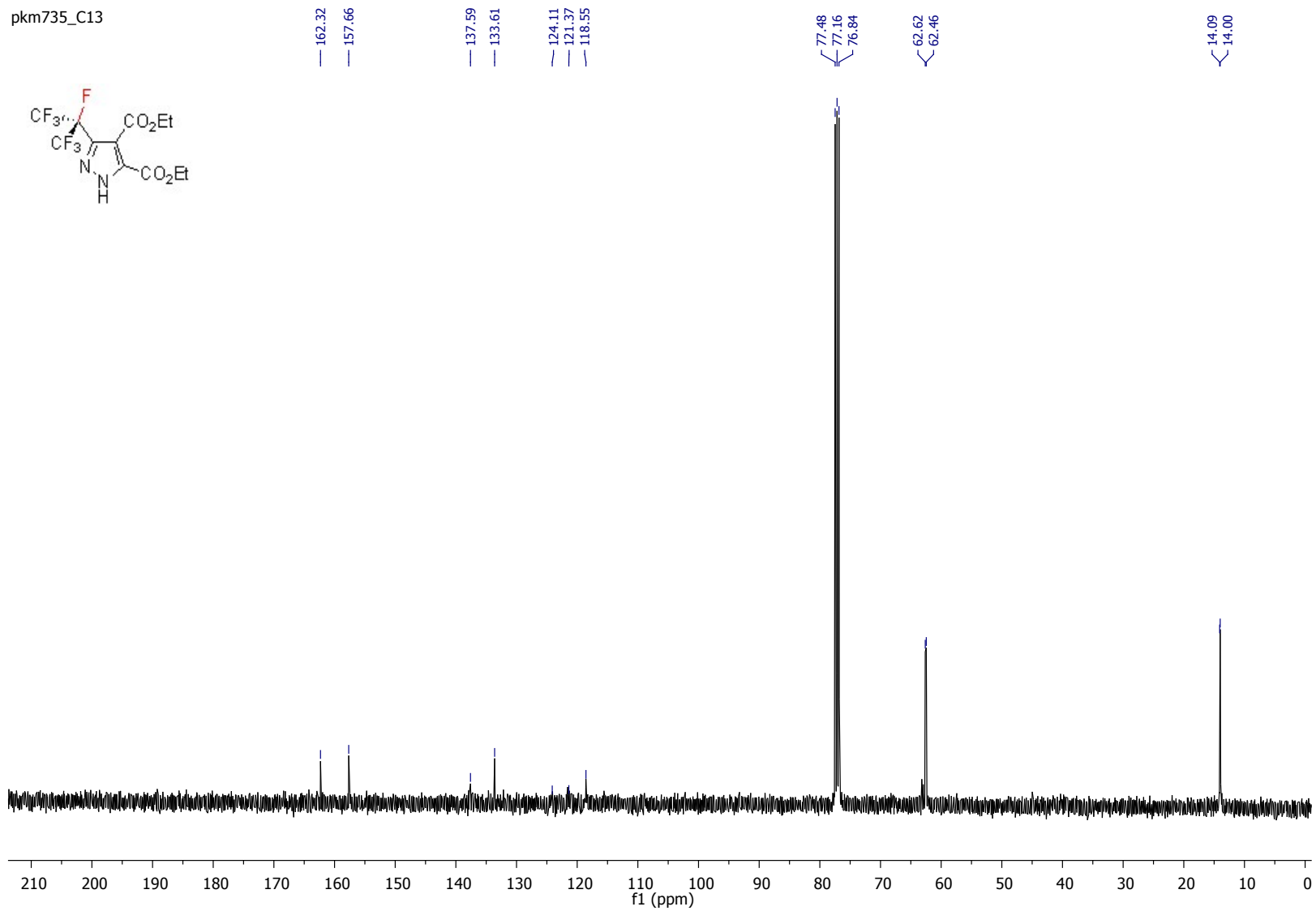
Compound 31a

PKM735_F19
19F



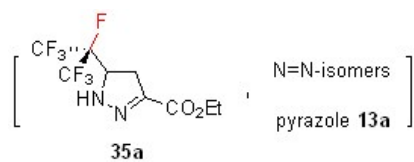
Compound 31a

pkm735_C13



Crude product 35a

pkm714



crude

