Preparation of Hexafluoroisopropyl Esters by Oxidative Esterification of Aldehydes using Sodium Persulfate

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SUPPORTING INFORMATION

General Considerations

NMR spectra (^{1}H, ^{13}C, and ^{19}F) were performed at 300 K on a Bruker DRX-400 400 MHz spectrometer. ^{1}H-NMR spectra were referenced to residual $CHCl_3$ (7.26 ppm) in $CDCl_3$. ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.16 ppm). ^{19}F-NMR spectra were referenced to hexafluorobenzene (−164.9 ppm). High-resolution mass spectra were collected on an Applied Biosystems QSTAR Elite instrument equipped with an electrospray ionization (ESI) source, calibrated using Agilent LC/MS tuning mix. Reactions were monitored by an Agilent Technologies 7820A gas chromatograph attached to a 5975 Mass Spectrometer, ^{1}H-NMR, and/or by TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using UV light. Silica plugs utilized Dynamic Adsorbents Inc. Flash Silica Gel (60 Å porosity, 32-63 μm).

Chemicals

Deuterated chloroform ($CDCl_3$) was purchased from Cambridge Isotope Laboratories. 4-Acetamido-TEMPO (ACT, **2**) was prepared using a previously reported protocol.[1] 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Oakwood Chemicals. Pyridine were purchased from J. T. Baker. Pentane and sodium persulfate were purchased from Sigma-Aldrich. All the aldehydes used were purchased from Oakwood Chemicals, Sigma-Aldrich or Alfa Aesar and distilled before use if required.

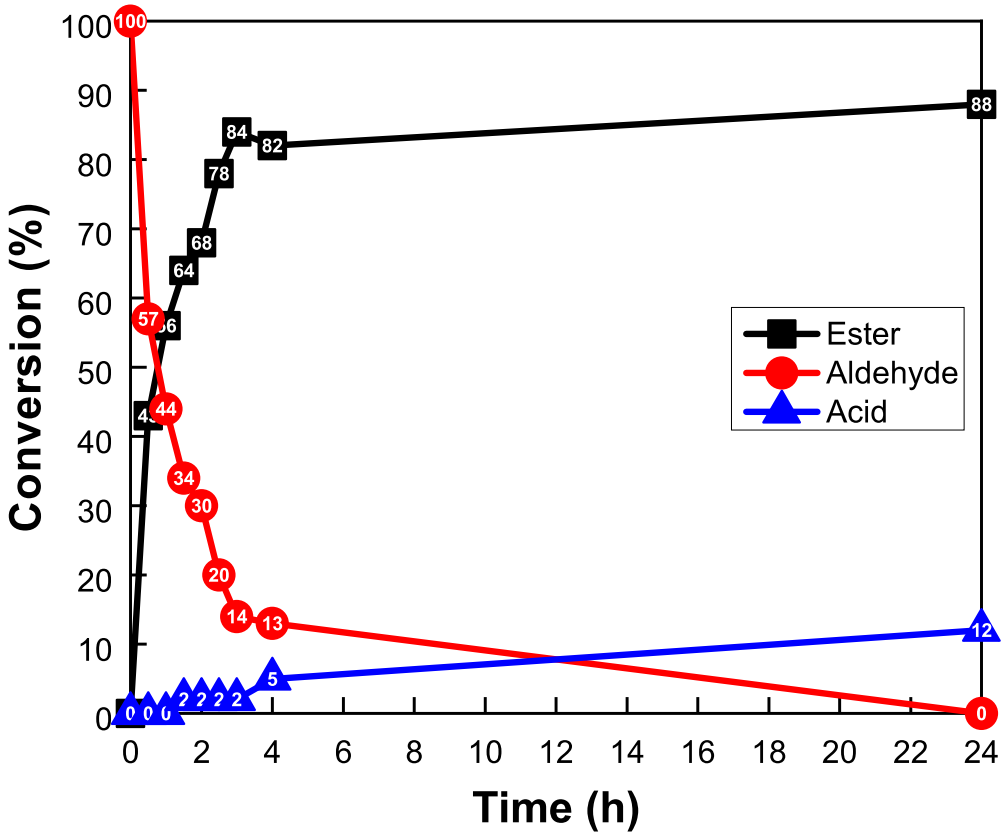
Photochemistry

LEDs were configured as outlined in the "Photochemical Reactor Design" section of a previous article.[2] A fan was employed to ensure reactions remained at or near room temperature (rt) when using LEDs. The LED-based photoreactors are designed with LED strips (Blue LEDs: 39.4 inch strips, 470 nm blue light, 32,918 mcd ft^{-1}), power supply (12 V DC power supply, 60 W), connectors (LC2 locking male connector CPS adapter cable), clip fan (2-speed clip fan, 6 in), Pyrex crystallizing dishes (150 × 75 mm), aluminum foil, and duct tape. The light components were purchased from SuperBright LEDs.

Representative Procedure for the Synthesis of Hexafluoroisopropyl Esters

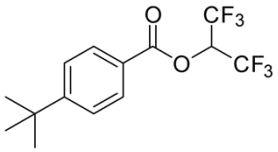
To a 4-dram reaction vial equipped with a stir bar were added the corresponding aldehyde (1 mmol, 1 equiv.), pyridine (404 µL, 5 equiv.), MeCN (2 mL), AcNH-TEMPO, **2**, (63 mg, 0.30 equiv.), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (264 µL, 2.5 equiv.), and $Na_2S_2O_8$ (1.190 g, 5 equiv.). The vial was closed tightly. The contents of the vial were then heated in an oil bath at 50 ºC for 24 h. Upon completion of the heating step, the reaction mixture was quenched with pentane (10 mL) and the vial contents transferred to a glass separatory funnel, rinsing the reaction vial with an additional 50 mL of pentane. The contents of the separatory funnel were diluted with deionized water (25 mL). The layers were separated, and the aqueous layer removed. The organic layer was washed with 0.5 M HCl (25 mL), and saturated aqueous sodium carbonate (Na_2CO_3, 15 mL). The organic layer was dried over sodium sulfate (Na_2SO_4), and the solvent removed *in-vacuo* to afford the product.

Kinetic Experiment for the Synthesis of 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-(tert-butyl)benzoate (5a)

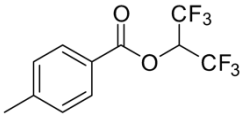


4-*tert*-Butylbenzaldehyde (0.162 g, 1 mmol, 1 equiv.), pyridine (404 µL, 5 equiv.), MeCN (2 mL), **2** (63 mg, 0.30 equiv.), HFIP (264 µL, 2.5 equiv.), and $Na_2S_2O_8$ (1.190 g, 5 equiv.) were added to a 4-dram vial. The vial was closed and then heated in an oil bath at 50 ºC. Aliquots of the reaction mixture were taken at different times. These aliquots were diluted with acetonitrile and the samples were analyzed via GC-MS. The reaction was followed for 24 h.

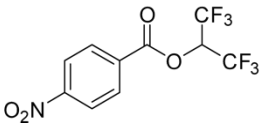
Product Characterization



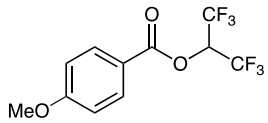
1,1,1,3,3,3-Hexafluoropropan-2-yl 4-(tert-butyl)benzoate (5a). Obtained as a colorless oil (257 mg, 78%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.20 – 7.85 (m, 2H), 7.69 – 7.41 (m, 2H), 6.01 (hept, *J* = 6.1 Hz, 1H), 1.36 (s, 9H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 163.37, 159.03, 130.60, 126.05, 125.02, 119.96 (q, *J* = 283.4 Hz), 66.95 (hept, *J* = 34.5 Hz), 35.49, 31.15. **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.38 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



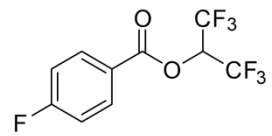
1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methylbenzoate (5b). Obtained as a clear white solid (222 mg, 78%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.01 (hept, *J* = 6.1 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 163.45, 146.10, 130.70, 129.73, 124.26, 120.80 (q, *J* = 283.4 Hz), 66.96 (hept, *J* = 34.8 Hz), 21.94.**^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.35 (d, *J* = 6.2 Hz). Spectral data for this compound is consistent with that previously reported.[3]



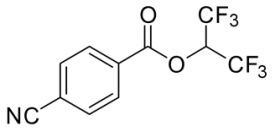
1,1,1,3,3,3-Hexafluoropropan-2-yl 4-nitrobenzoate (5c). Obtained as a colorless oil (209 mg, 66%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.46 – 8.34 (m, 2H), 8.33 – 8.18 (m, 2H), 6.02 (hept, *J* = 6.0 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 161.85, 151.74, 132.21, 131.81, 124.13, 120.50 (q, *J* = 283.7 Hz), 67.67 (hept, *J* = 35.0 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.23 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



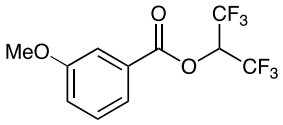
1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methoxybenzoate (5d). Obtained as a colorless oil (209 mg, 69%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.26 – 7.83 (m, 2H), 7.12 – 6.84 (m, 2H), 6.00 (hept, *J* = 6.2 Hz, 1H), 3.90 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 164.85, 162.86, 132.73, 120.68 (q, *J* = 283.4, 282.9 Hz), 118.98, 114.17, 66.70 (hept, *J* = 34.6 Hz), 55.54. **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.39 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



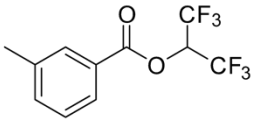
1,1,1,3,3,3-Hexafluoropropan-2-yl 4-fluorobenzoate (5e). Obtained as a white solid (140 mg, 48%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.22 – 8.11 (m, 2H), 7.26 – 7.18 (m, 2H), 6.02 (hept, *J* = 6.1 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 166.85 (d, *J* = 257.3 Hz), 162.29, 133.25 (d, *J* = 9.7 Hz), 123.09 (d, *J* = 3.2 Hz), 120.53 (q, *J* = 283.9, 283.4 Hz), 116.25 (d, *J* = 22.3 Hz), 67.01 (hept, *J* = 35.5, 35.0 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.31 (d, *J* = 6.0 Hz), -104.92 (tt, *J* = 8.3, 5.4 Hz). Spectral data for this compound is consistent with that previously reported.[3]



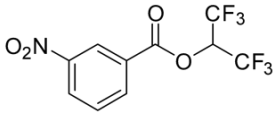
1,1,1,3,3,3-Hexafluoropropan-2-yl 4-cyanobenzoate (5f). Obtained as a white solid (205 mg, 69%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 6.03 (hept, *J* = 6.0 Hz, 0H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 161.89, 132.63, 130.88, 130.54, 120.35 (q, *J* = 281.9 Hz), 118.27, 117.38, 67.40 (hept, *J* = 35.0 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -75.95 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



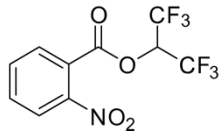
1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methoxybenzoate (5g). Obtained as a colorless oil (190 mg, 63%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.72 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.60 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.22 (ddd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 6.01 (hept, *J* = 6.1 Hz, 1H), 3.88 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 163.37, 159.99, 130.08, 128.20, 123.00, 121.36, 120.78 (q, *J* = 281.9, 281.2 Hz), 115.08, 67.15 (hept, *J* = 34.7 Hz), 55.69. **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.34 (d, *J* = 6.8 Hz). Spectral data for this compound is consistent with that previously reported.[3]



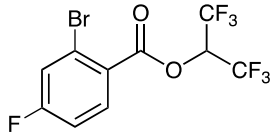
1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methylbenzoate (5h). Obtained as a yellow oil (133 mg, 46%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 6.04 (hept, *J* = 6.1 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 163.43, 138.85, 135.51 (d, *J* = 2.5 Hz), 130.88, 128.70, 127.63, 126.81, 120.65 (q, *J* = 282.4 Hz), 66.88 (hept, *J* = 34.9 Hz), 21.04. **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.23 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



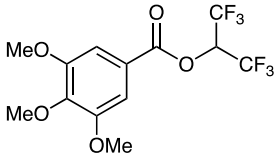
1,1,1,3,3,3-Hexafluoropropan-2-yl 3-nitrobenzoate (5i). Obtained as a colorless oil (190 mg, 60%).**^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.93 (t, *J* = 2.0 Hz, 1H), 8.55 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 8.44 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 6.04 (hept, *J* = 6.0 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 161.67, 148.69, 135.99, 130.47, 129.26, 128.73, 125.53, 120.48 (q, *J* = 283.0, 280.9 Hz), 67.65 (hept, *J* = 35.3 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.20 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



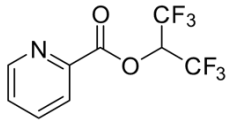
1,1,1,3,3,3-Hexafluoropropan-2-yl 2-nitrobenzoate (5j). Obtained as a colorless oil (214 mg, 67%) **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.13 – 8.06 (m, 1H), 7.88 – 7.66 (m, 3H), 6.01 (hept, *J* = 5.9 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 162.48, 133.45, 133.19, 129.87, 124.70, 124.50, 120.22 (q, *J* = 281.8 Hz), 67.64 (hept, *J* = 35.2 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -75.97 (d, *J* = 6.0 Hz) . Spectral data for this compound is consistent with that previously reported.[3]



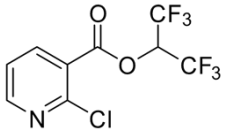
1,1,1,3,3,3-Hexafluoropropan-2-yl 2-bromo-4-fluorobenzoate (5k). Obtained as a white solid (158 mg, 54%) **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 8.8, 5.9 Hz, 1H), 7.51 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.17 (ddd, *J* = 8.8, 7.5, 2.5 Hz, 1H), 5.99 (hept, *J* = 6.0 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 165.13 (d, *J* = 260.7 Hz), 161.37, 134.66 (d, *J* = 9.9 Hz), 125.14 (d, *J* = 10.4 Hz), 124.40 (d, *J* = 3.4 Hz), 122.98 (d, *J* = 24.8 Hz), 120.59 (q, *J* = 284.1, 283.5, 280.3 Hz), 115.23 (d, *J* = 21.7 Hz), 67.28 (hept, *J* = 33.8 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.05 (d, *J* = 5.5 Hz), -105.00 – -105.08 (m). Spectral data for this compound is consistent with that previously reported.[3]



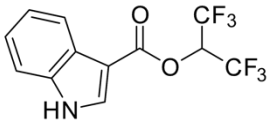
1,1,1,3,3,3-Hexafluoropropan-2-yl 3,4,5-trimethoxybenzoate (5l). Obtained as a yellow solid (130 mg, 36%) **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 7.37 (s, 2H), 6.02 (h, *J* = 6.1 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 6H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 162.95, 153.24, 144.02, 121.43, 120.25 (q, *J* = 283.6, 282.8 Hz), 107.81, 67.02 (hept, *J* = 34.3, 32.5 Hz), 61.03, 56.37. **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.33 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]



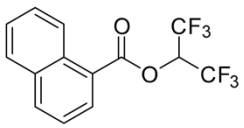
1,1,1,3,3,3-Hexafluoropropan-2-yl picolinate (5m). Obtained as a colorless oil (164 mg, 60%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.80 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.15 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.88 (td, *J* = 7.8, 1.8 Hz, 1H), 7.54 (ddd, *J* = 7.7, 4.7, 1.2 Hz, 1H), 6.05 (hept, *J* = 6.0 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 161.74, 150.57, 145.01, 137.28, 128.17, 126.22, 120.39 (q, *J* = 284.1, 282.6 Hz), 67.36 (hept, *J* = 35.0 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -75.92 (d, *J* = 6.3 Hz). Spectral data for this compound is consistent with that previously reported.[3]



1,1,1,3,3,3-Hexafluoropropan-2-yl 2-chloronicotinate (5n). Obtained as a yellow oil (84 mg, 27%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.64 (ddd, *J* = 4.9, 3.0, 1.8 Hz, 1H), 8.29 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.44 (ddd, *J* = 7.8, 4.8, 1.7 Hz, 1H), 6.02 (hept, *J* = 6.0 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 160.91, 153.51, 151.21, 141.02, 123.43, 122.31, 120.29 (q, *J* = 283.1 Hz), 67.31 (hept, *J* = 35.2, 34.3 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -75.97 (d, *J* = 5.8 Hz). **HRMS (ESI)** calculated for $C_9H_5ClF_6NO_2$ $[M+H]^+$ 307.9913, found 307.9935.



1,1,1,3,3,3-Hexafluoropropan-2-yl 1H-indole-3-carboxylate (5o). Obtained as a yellow solid (120 mg, 39%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.20 – 8.14 (m, 1H), 8.11 (d, *J* = 3.2 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.41 – 7.32 (m, 2H), 6.11 (hept, *J* = 6.3 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 160.90, 136.26, 133.10, 125.77, 124.21, 123.21, 121.50, 121.02 (q, *J* = 282.1 Hz), 111.97, 105.68, 66.04 (hept, *J* = 34.8 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.34 (d, *J* = 6.1 Hz). **HRMS (ESI)** calculated for $C_{12}H_6F_6NO_2$ $[M-H]^-$ 310.0308, found 310.0331.



1,1,1,3,3,3-Hexafluoropropan-2-yl 1-naphthoate (5p). Obtained as a yellow solid (137 mg, 43%). **^{1}H-NMR** (400 MHz, Chloroform-*d*) δ 8.93 (d, *J* = 8.7 Hz, 0H), 8.37 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 0H), 7.70 (ddd, *J* = 8.6, 6.9, 1.4 Hz, 1H), 7.64 – 7.52 (m, 2H), 6.14 (hept, *J* = 6.1 Hz, 1H). **^{13}C-NMR** (101 MHz, Chloroform-*d*) δ 163.41, 135.81, 134.02, 132.10, 131.83, 129.04, 128.96, 126.93, 125.38, 124.65, 123.10, 120.90 (q, *J* = 282.1, 281.7 Hz), 66.87 (hept, *J* = 34.8 Hz). **^{19}F-NMR** (376 MHz, Chloroform-*d*) δ -76.17 (d, *J* = 6.1 Hz). Spectral data for this compound is consistent with that previously reported.[3]

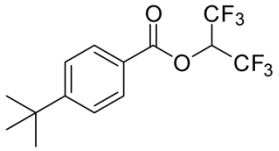
Scale-up of the Synthesis of 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-(tert-butyl)benzoate (5a)

To a 50-mL round-bottom flask equipped with a stir bar were added 4-*tert*-butylbenzaldehyde (1.622 g, 10 mmol, 1 equiv.), pyridine (3.95 g, 50 mmol, 5 equiv.), MeCN (20 mL), **2** (0.63 g, 3 mmol, 0.30 equiv.), HFIP (4.2 g, 25 mmol, 2.5 equiv.), and $Na_2S_2O_8$ (11.90 g, 50 mmol, 5 equiv.). The flask was closed with a septum. The reaction mixture was heated in an oil bath at 50 ºC for 24 h. Upon completion of the heating step, the reaction mixture was quenched with pentane (40 mL) and the content transferred to a glass separatory funnel rinsing the flask with an additional 80 mL of pentane. The contents of the separatory funnel were then diluted with deionized water (250 mL). The layers were separated, and the aqueous layer removed. The organic layer was washed with 0.5 M HCl (100 mL), and saturated aqueous sodium carbonate (Na_2CO_3, 30 mL). The organic layer was dried over sodium sulfate (Na_2SO_4), and the solvent removed *in-vacuo* to afford the product. Analytically pure **5a** was obtained as a colorless oil (2.996 g, 91%); characterized by ^{1}H-NMR spectroscopy.

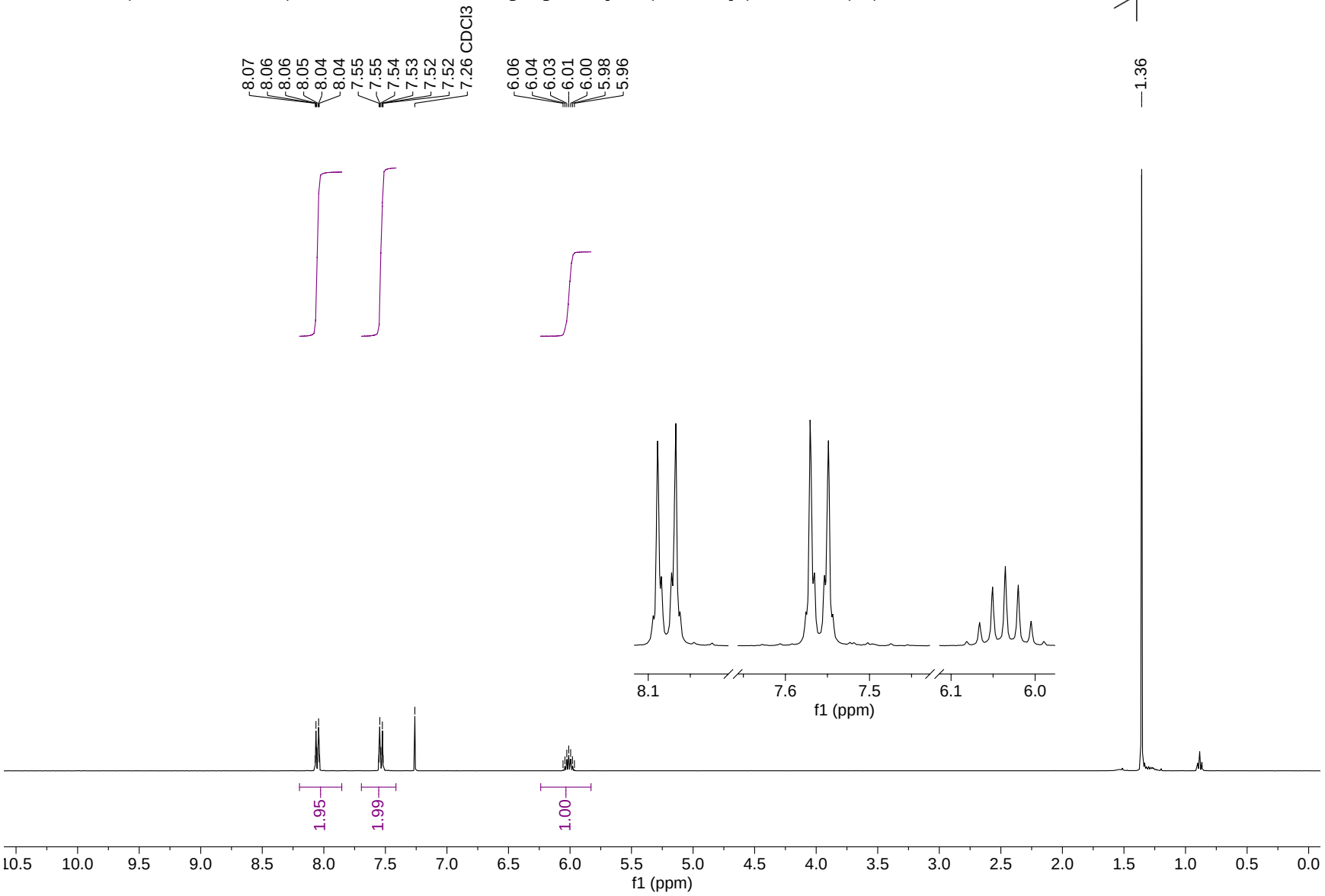
References

1. M. A. Mercadante, C. B. Kelly, J. M. Bobbitt, L. J. Tilley and N. E. Leadbeater, *Nat. Protoc.*, 2013, **8**, 666.
2. For information regarding these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**, *18*, 876.
3. C. B. Kelly, M. A. Mercadante, R. J. Wiles and N. E. Leadbeater, *Org. Lett.*, 2013, **15**, 2222.

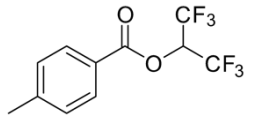
^{1}H-, ^{13}C- and ^{19}F-NMR Spectra of Compounds Prepared



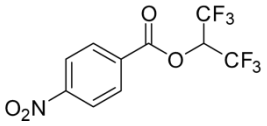
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-(tert-butyl)benzoate (5a)



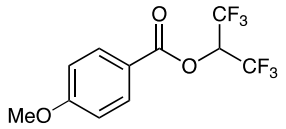
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methylbenzoate (5b)



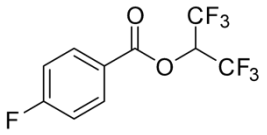
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-nitrobenzoate (5c)



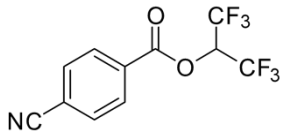
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methoxybenzoate (5d)



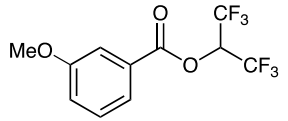
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-fluorobenzoate (5e)



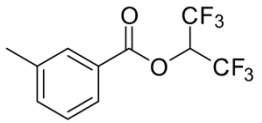
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-cyanobenzoate (5f)



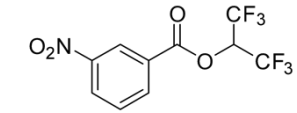
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methoxybenzoate (5g)



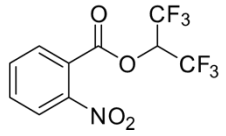
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methylbenzoate (5h)



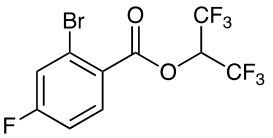
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-nitrobenzoate (5i)

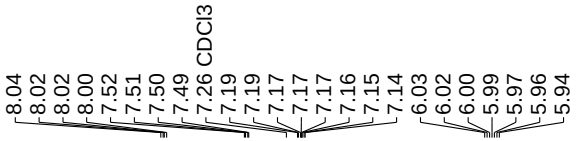


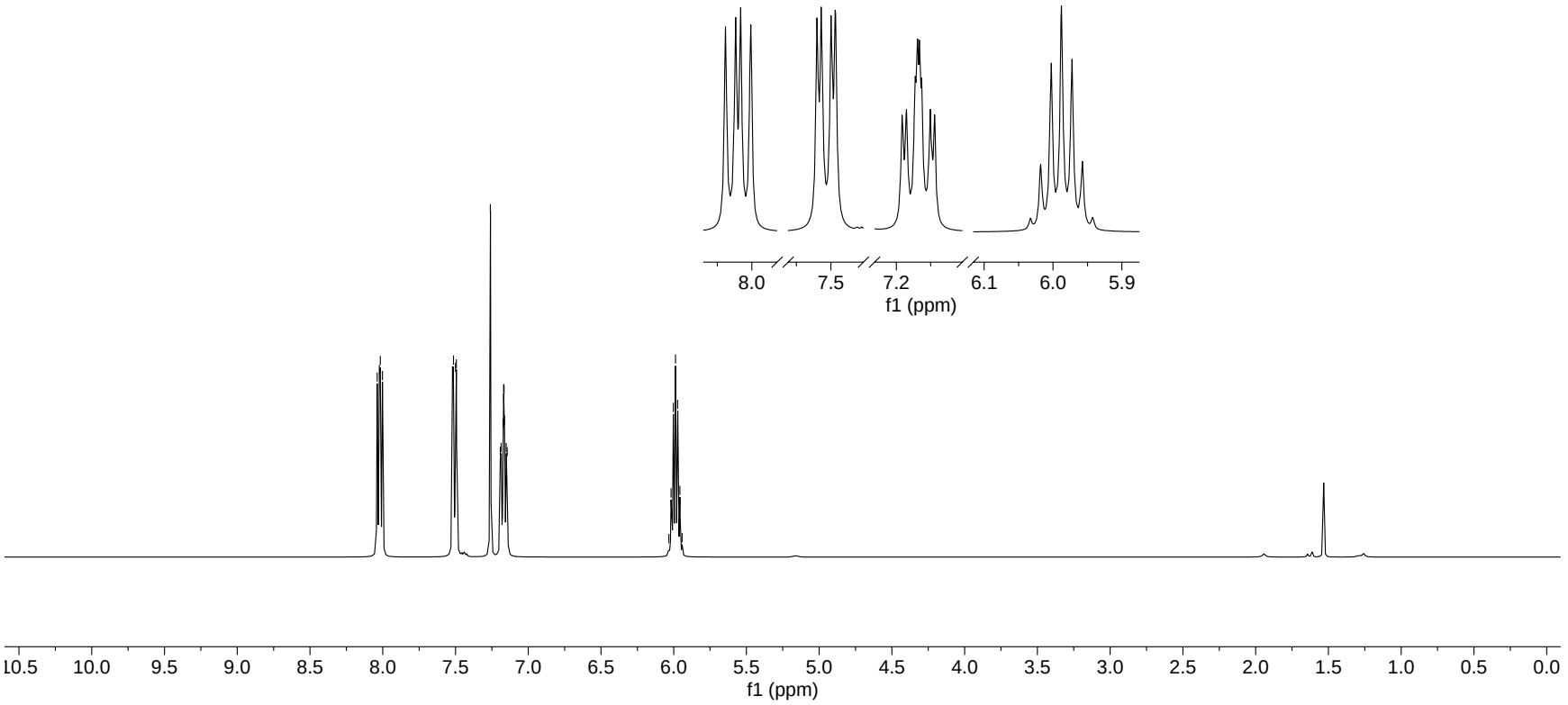
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-nitrobenzoate (5j)



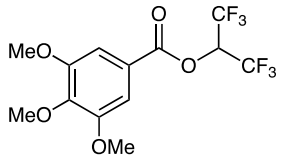
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-bromo-4-fluorobenzoate (5k)



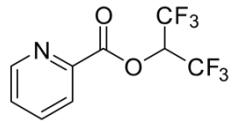




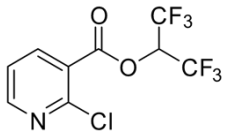
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3,4,5-trimethoxybenzoate (5l)



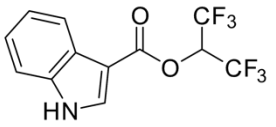
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl picolinate (5m)



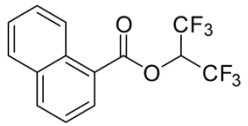
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-chloronicotinate (5n)



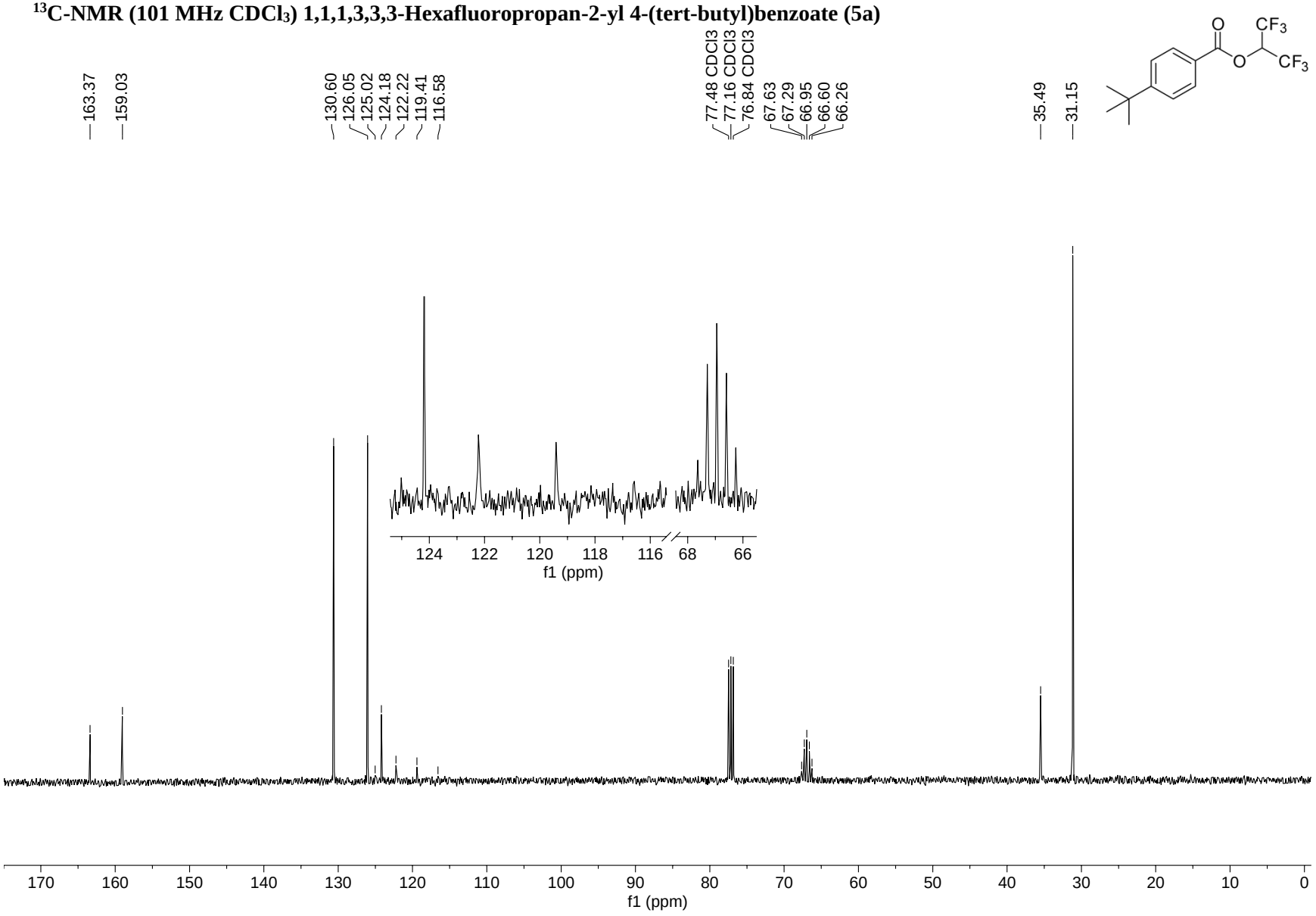
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 1H-indole-3-carboxylate (5o)



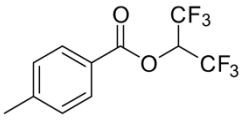
^{1}H-NMR (400 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 1-naphthoate (5p)



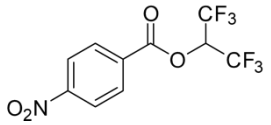
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-(tert-butyl)benzoate (5a)



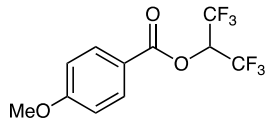
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methylbenzoate (5b)

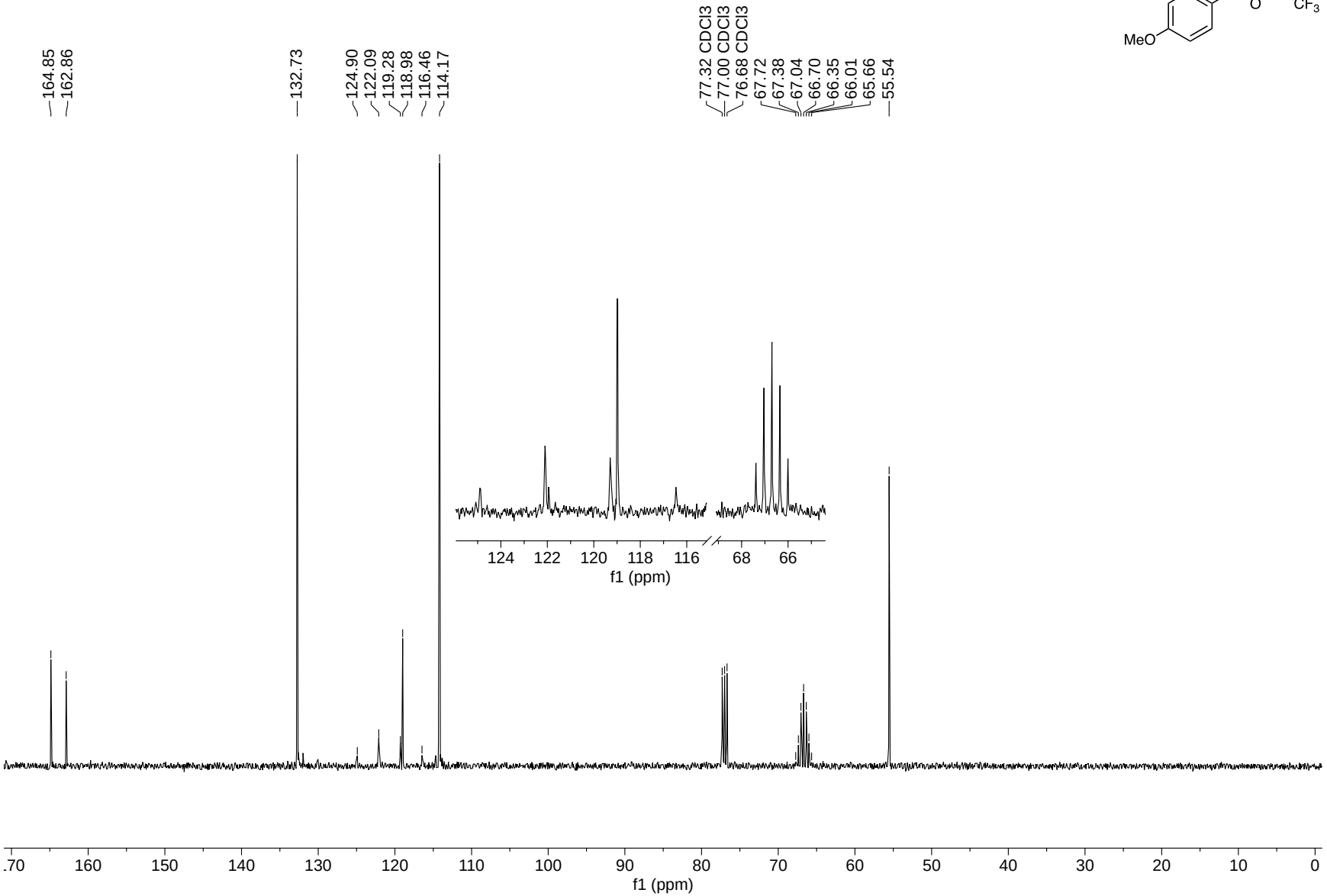


^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-nitrobenzoate (5c)

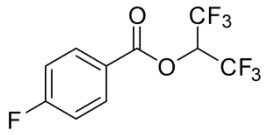


^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methoxybenzoate (5d)

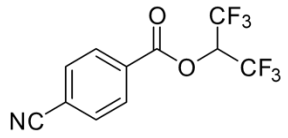




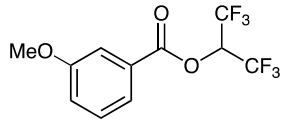
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-fluorobenzoate (5e)



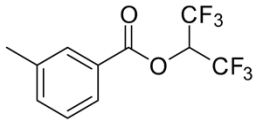
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-cyanobenzoate (5f)



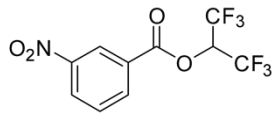
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methoxybenzoate (5g)



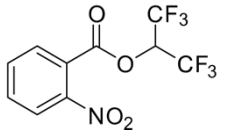
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methylbenzoate (5h)



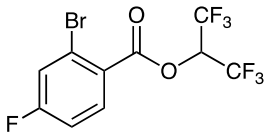
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-nitrobenzoate (5i)



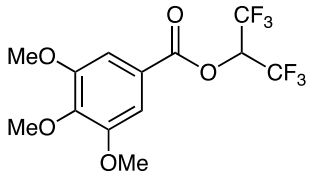
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-nitrobenzoate (5j)



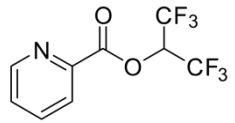
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-bromo-4-fluorobenzoate (5k)



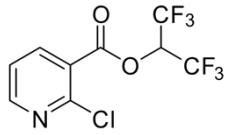
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3,4,5-trimethoxybenzoate (5l)



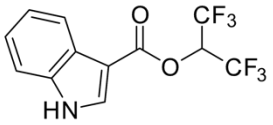
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl picolinate (5m)



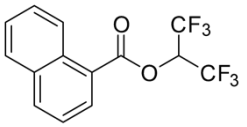
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-chloronicotinate (5n)



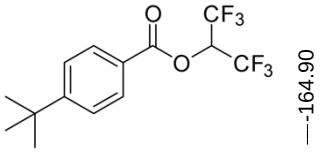
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 1H-indole-3-carboxylate (5o)



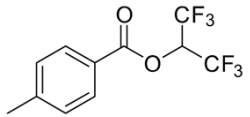
^{13}C-NMR (101 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 1-naphthoate (5p)

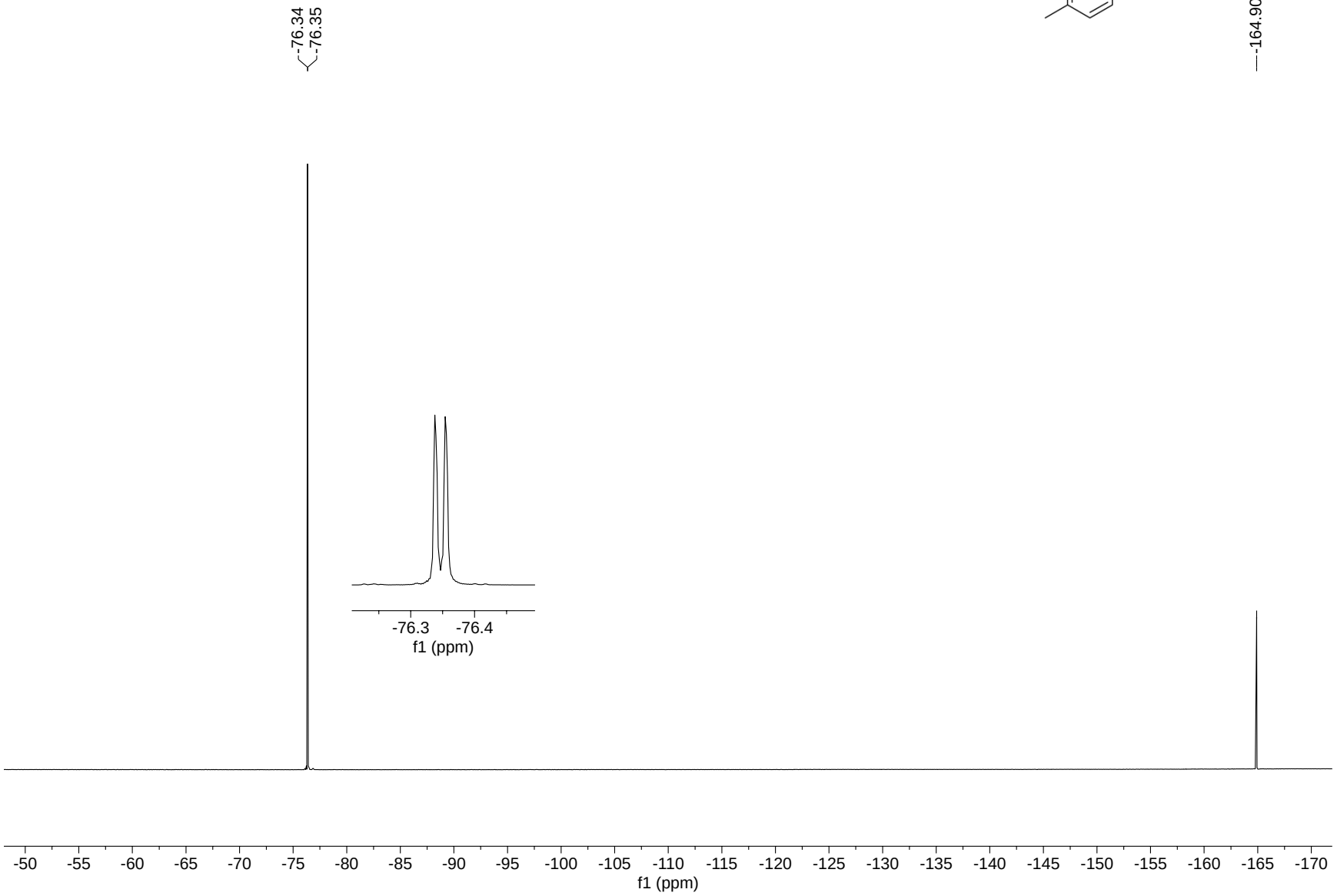


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-(tert-butyl)benzoate (5a)

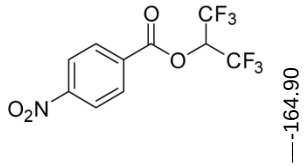


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methylbenzoate (5b)

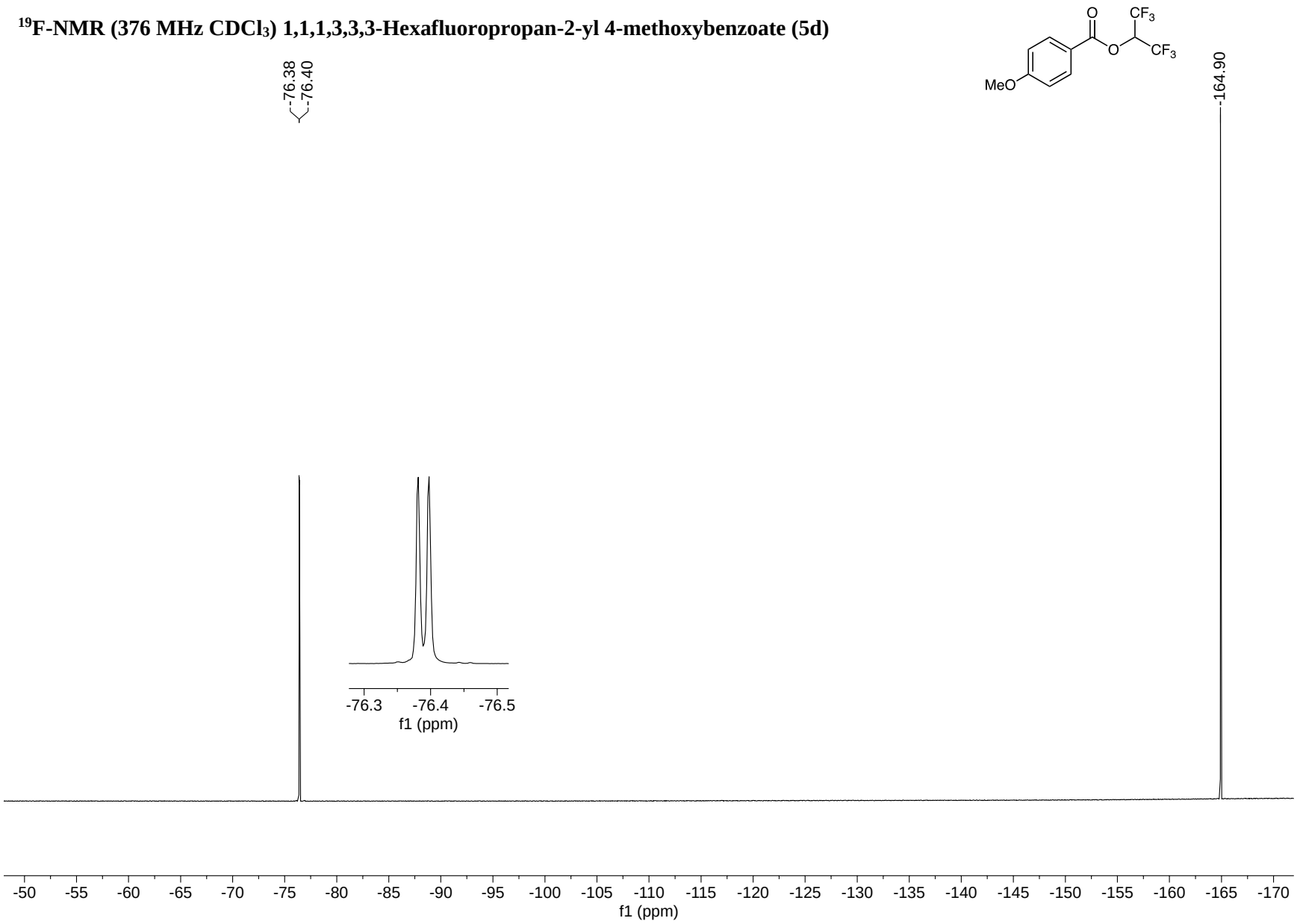




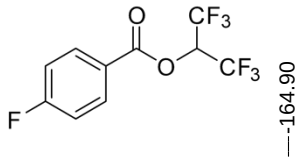
^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-nitrobenzoate (5c)

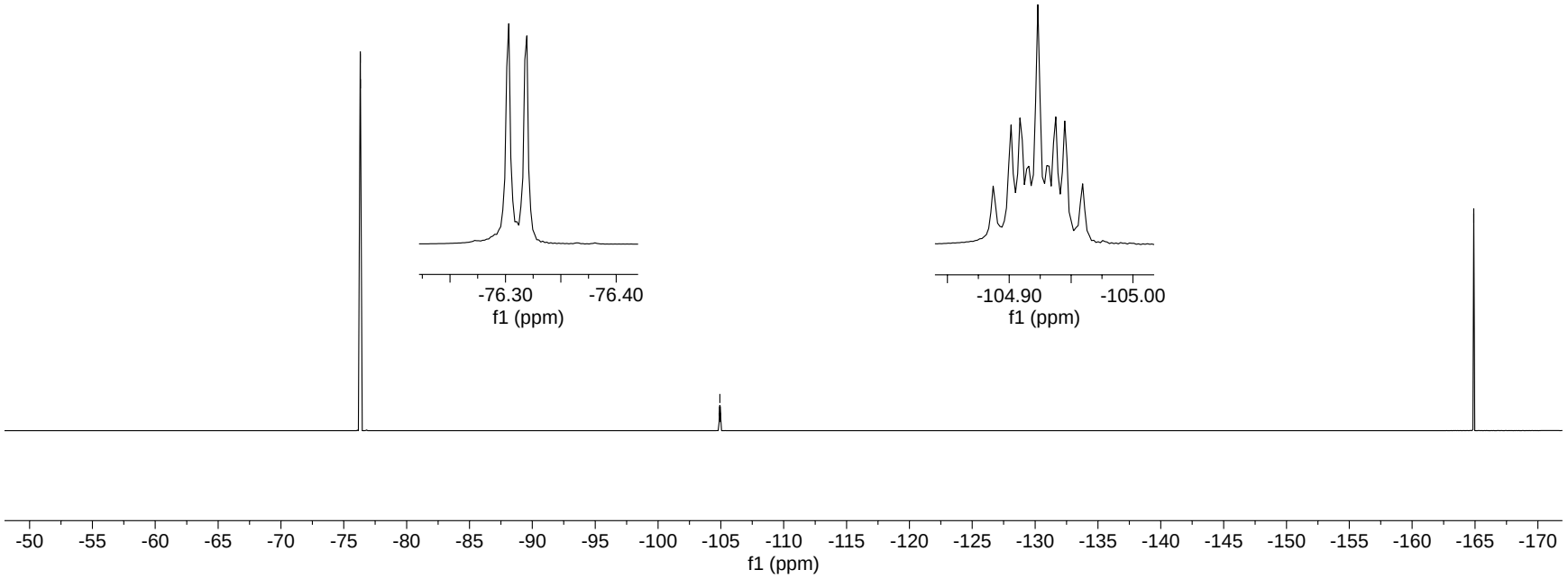


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-methoxybenzoate (5d)

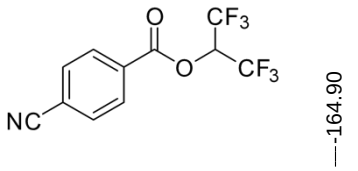


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-fluorobenzoate (5e)

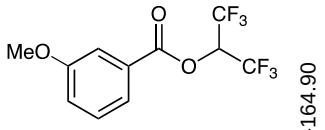


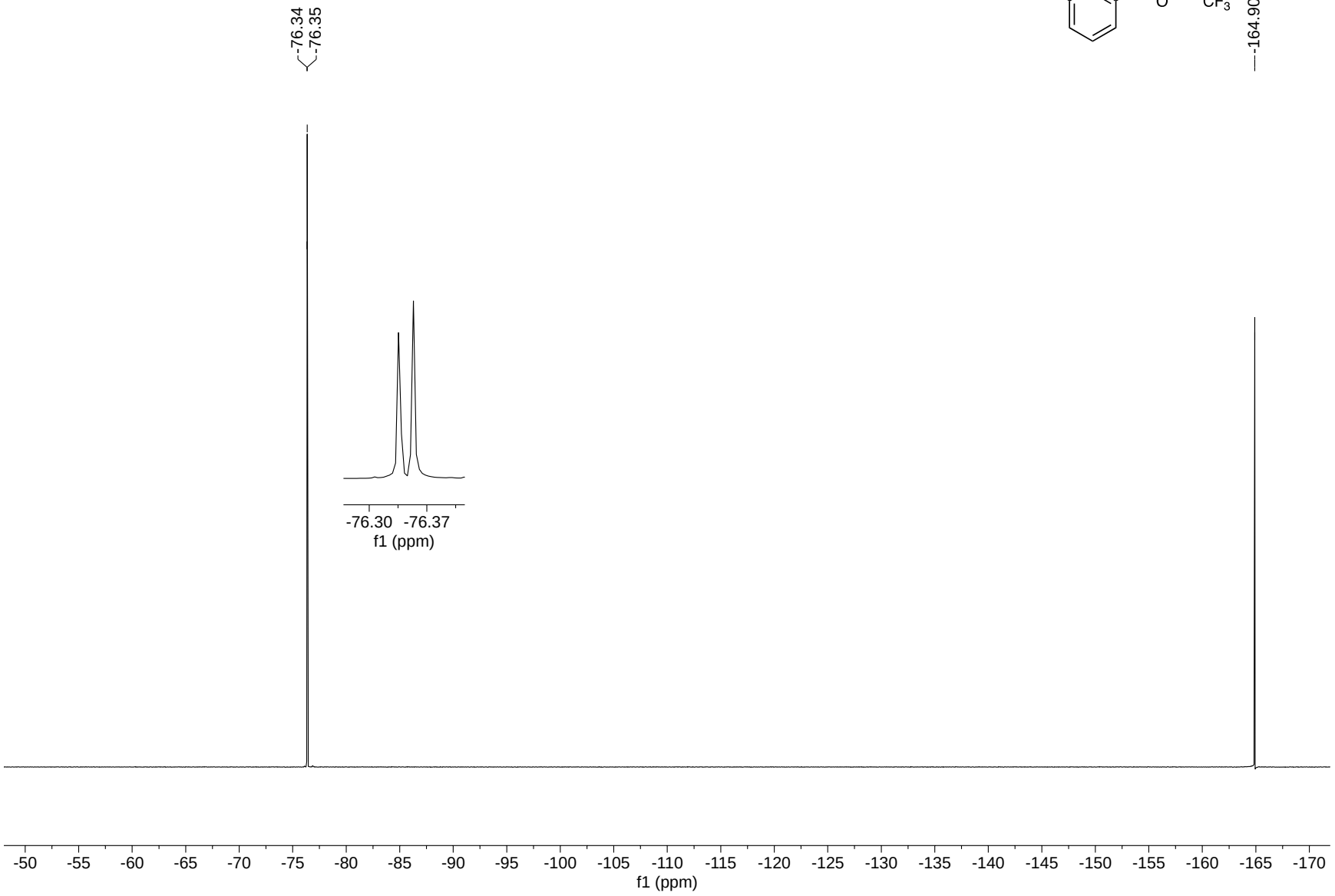


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 4-cyanobenzoate (5f)

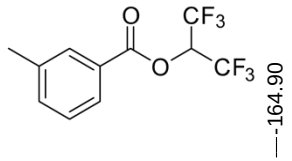


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methoxylbenzoate (5g)

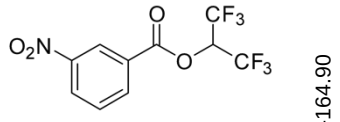


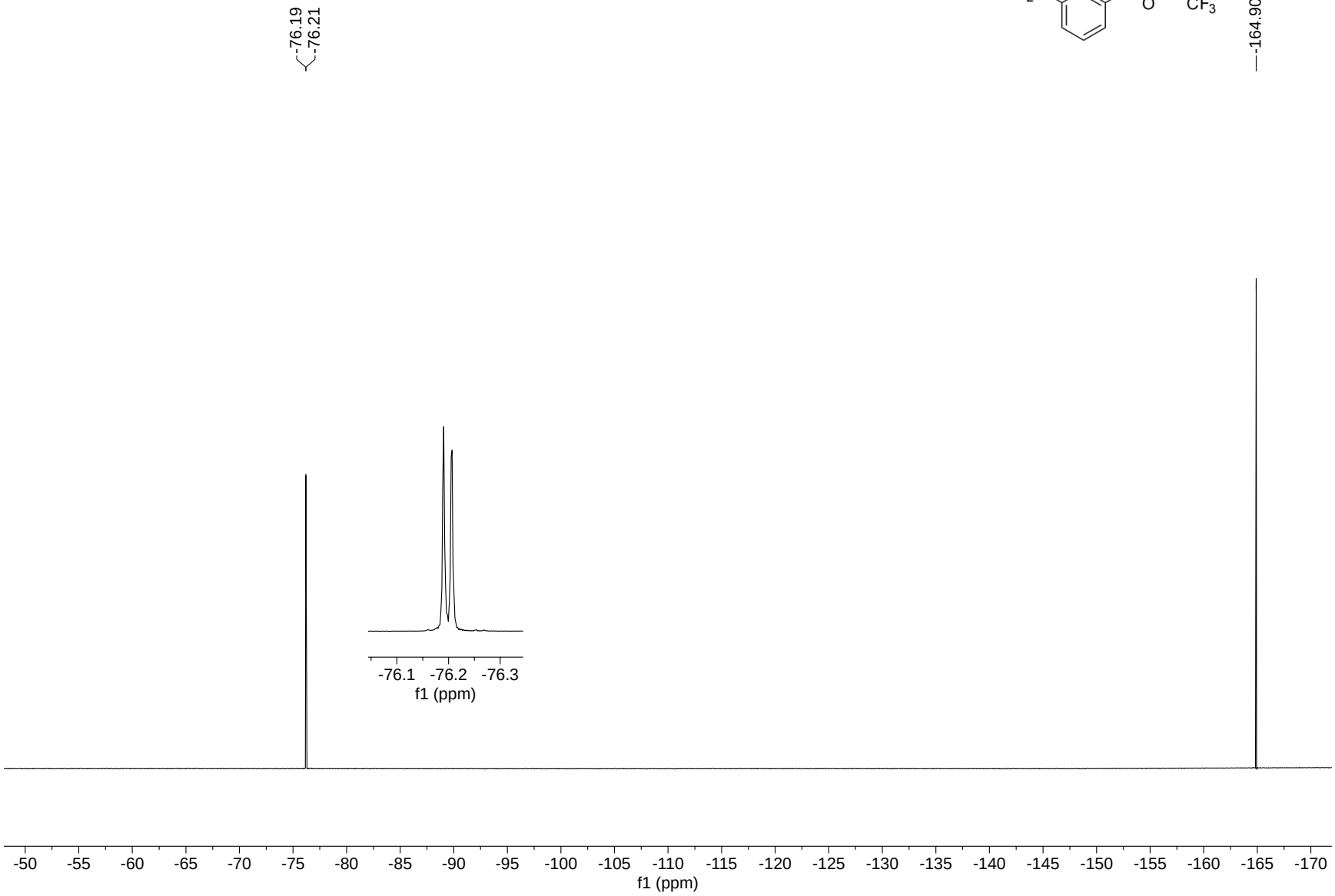


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methylbenzoate (5h)

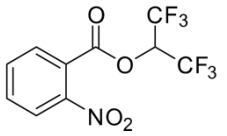


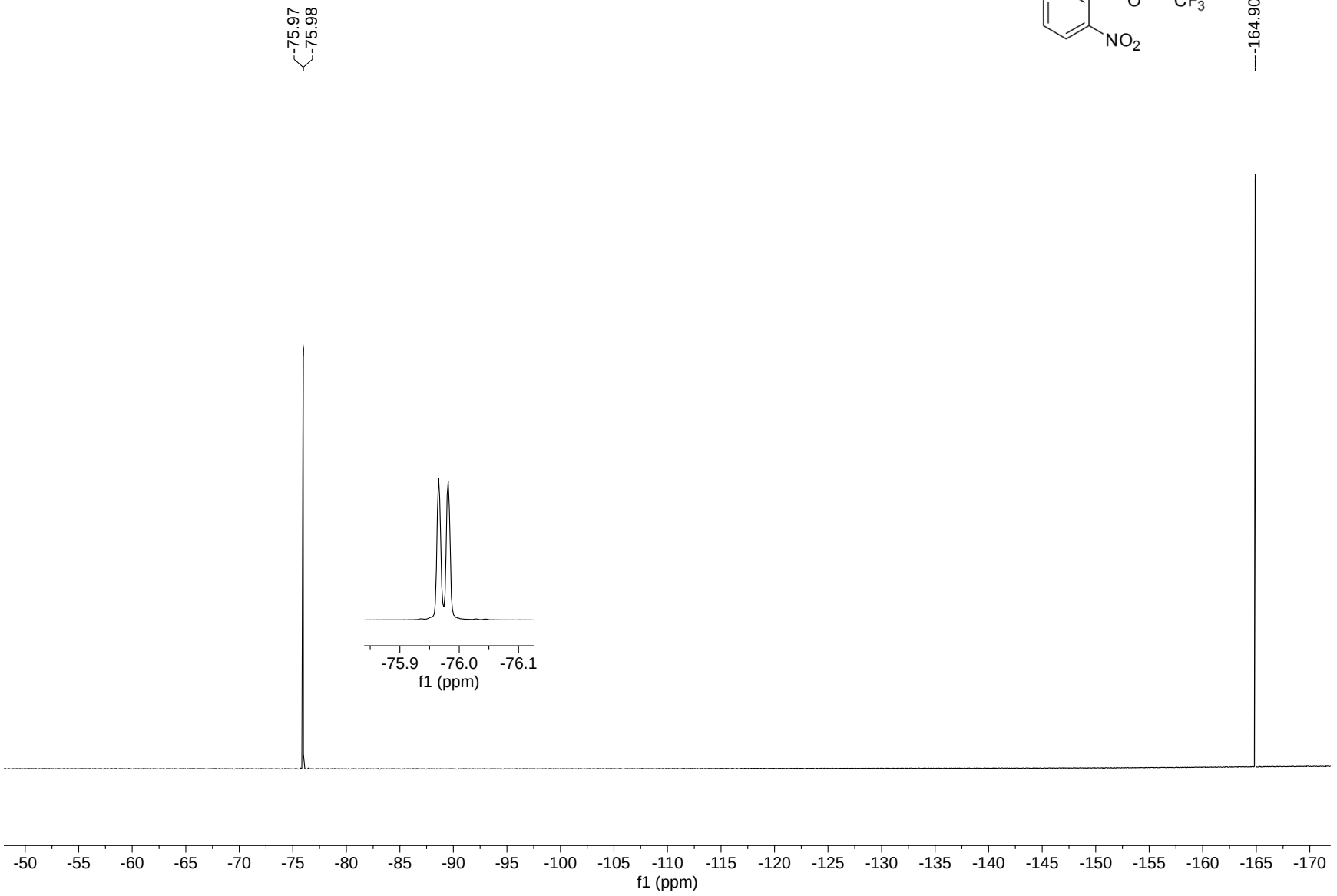
^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3-nitrobenzoate (5i)



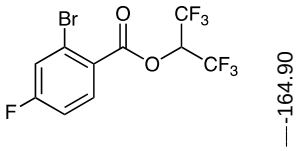


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-nitrobenzoate (5j)

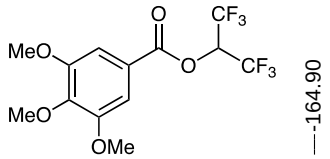




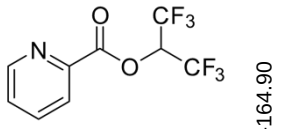
^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-bromo-4-fluorobenzoate (5k)

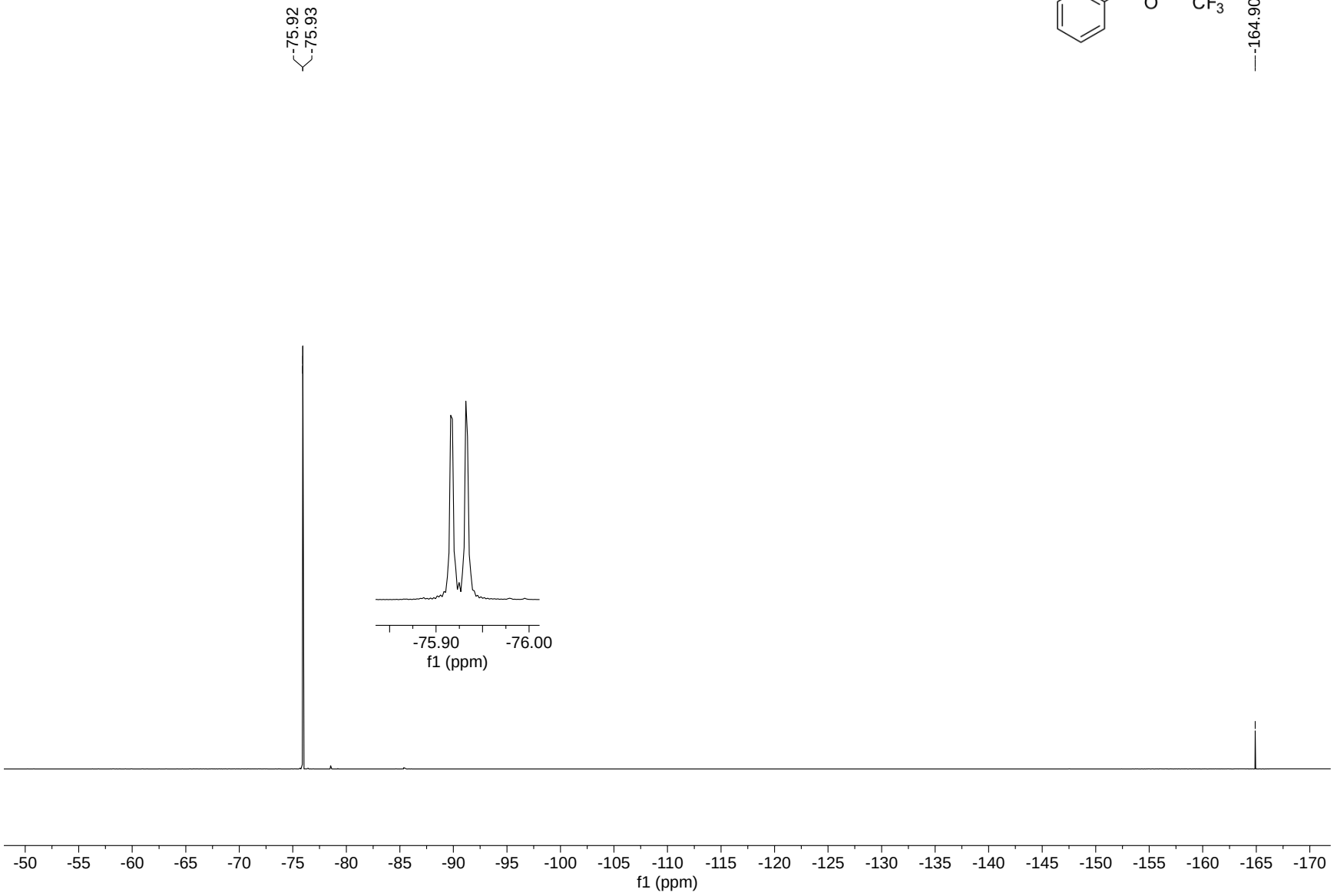


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 3,4,5-trimethoxybenzoate (5l)

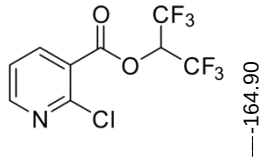


^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl picolinate (5m)

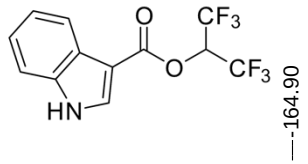




^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 2-chloronicotinate (5n)



^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 1H-indole-3-carboxylate (5o)



^{19}F-NMR (376 MHz $CDCl_3$) 1,1,1,3,3,3-Hexafluoropropan-2-yl 1-naphthoate (5p)