Supporting Information

Visible Light-Induced C-F Bond Activation for the Difluoroalkylation of Indoles

Scott T. Shreiber, Albert Granados,† Bianca Matsuo,† Jadab Majhi,† Mark W. Campbell, Shivani Patel, Gary A. Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

† These authors contributed equally

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

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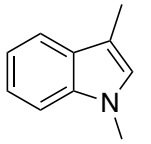
1. General Considerations

All chemical transformations requiring inert atmospheric conditions were carried out using Schlenk line techniques with a 4- or 5-port dual-bank manifold. For blue light irradiation, Kessil PR160L-blue LED lamps (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) was placed 2 inches away from the reaction vials. NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K using 400, 500 and 600 MHz spectrometers. ^{19}F NMR (376 MHz) and ^{13}C NMR spectra are ^{1}H decoupled unless otherwise noted. ^{1}H and ^{13}C NMR Spectra are referenced to the residual non-deuterated solvent peak. Data is presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, dd = doublet of doublets, qd = quartet of doublets, dq = doublet of quartets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant *J* (Hz) and integration. Reactions were monitored by GC/MS, ^{1}H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using potassium permanganate stain, and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm. Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. IR spectra were recorded on an FT-IR using either neat oil or solid products. Melting points (°C) are uncorrected.

2. Source of Indoles and Fluorinated Esters and Arenes

1 and **2** were either purchased and used as received or prepared according to established procedures.



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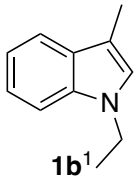

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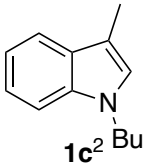

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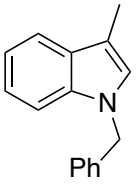

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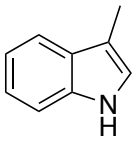

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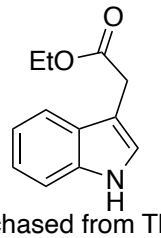

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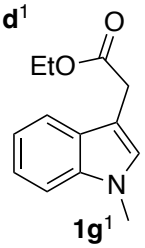

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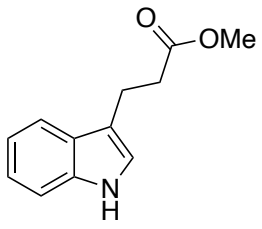

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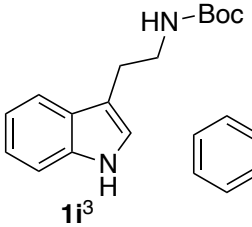

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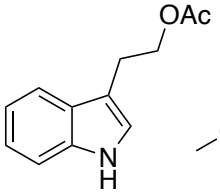

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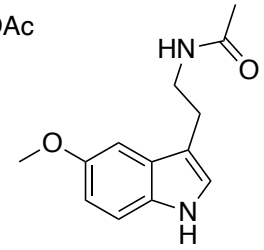

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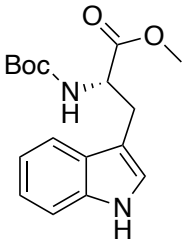

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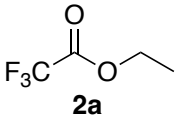

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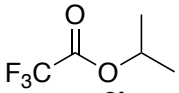

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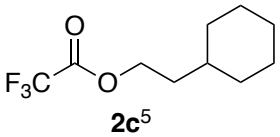

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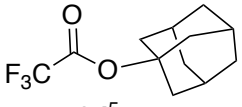

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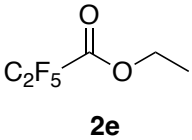

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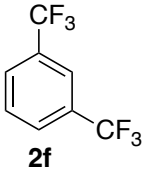

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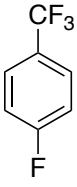

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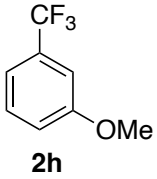
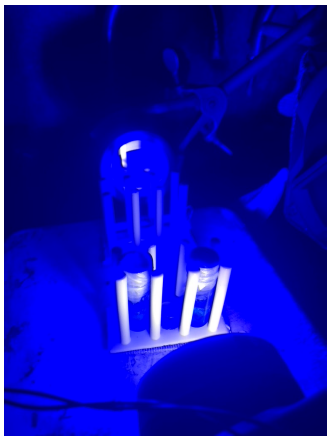


2h

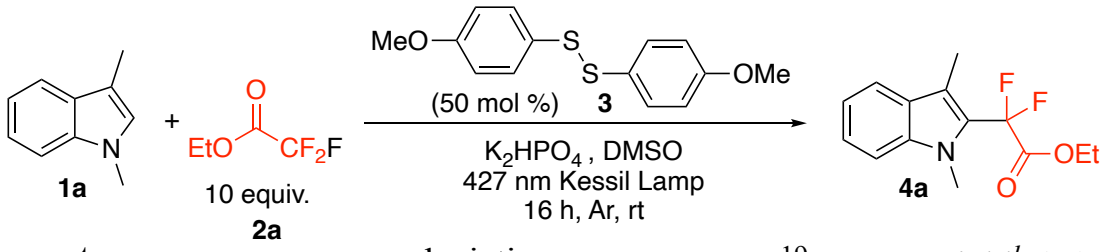
3. Synthesis of Fluorinated Indoles

a. Reaction Workflow



Photoredox reactions were performed with Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) with a distance of 2 inches from the vials. Two fans were used to keep reactions near room temperature in a fume hood. A typical reaction setup is shown.

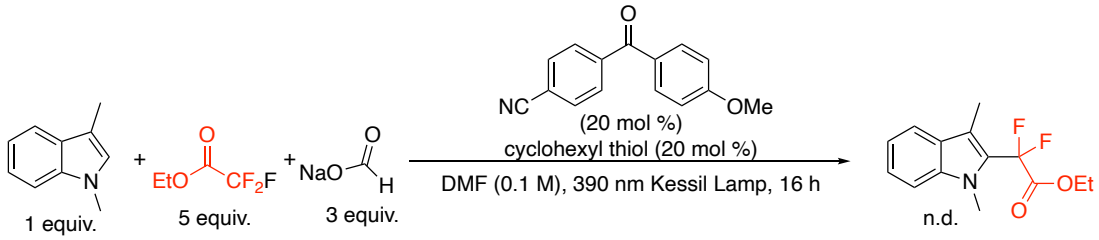
b. Optimization Table



entry	deviation	^{19}F NMR Yield[b] (%)
1	none	63
2	no Kessil	n.d.
3	390 nm Kessil	13
4	open to air	40
5	no base	n.d.
6	Na_2CO_3	58
7	K_2CO_3	52
8	MeCN	12
9	no **3**	n.d.
10	4-methoxybenzenethiol (100 mol %)	61
11	$Ir(ppy)_3$ (5 mol %)	n.d.
12	**3** (25 mol %)	45
13	**3** (100 mol %)	72 (63)[c]

[a]Reaction conditions: indole **1a** (0.1 mmol), **2a** (1.0 mmol), K_2HPO_4 (0.2 mmol), **3** (0.05 mmol) in DMSO (1 mL), stirred 16 h under 427 nm Kessil light irradiation at rt using a fan. [b]Yields were determined by ^{19}F NMR analysis using 2-bromo-5-(trifluoromethyl)pyridine as an internal standard. [c] Isolated yield.

The conditions used in our groups prior C-F activation methodology found no detectable product for the difluoroalkylation of indoles. (*J. Am. Chem. Soc.* **2021**, *143*, 19649-29654)

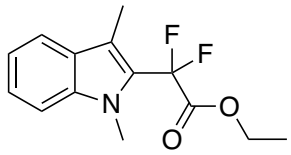


c. General Procedure

An 8 mL vial equipped with a magnetic stir bar was charged with indole (0.5 mmol, 1 equiv), bis(4-methoxybenzene)disulfide (139 mg, 0.5 mmol, 1 equiv), and K_2HPO_4 (174 mg, 1.0 mmol, 2 equiv). The vial was purged with argon, and 5 mL of anhyd DMSO were added. After purging an additional 2 min, the fluorinated substrate (5.0 mmol, 10 equiv) was added *via* syringe, and the reaction vial was sealed with Parafilm. The reaction was then irradiated with light (as described in Reaction Workflow) for 16 h. The reaction was quenched with H_2O (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with H_2O (30 mL), followed by brine (30 mL), and dried over Na_2SO_4. The solvent was removed *via* rotary evaporation, and the crude mixture was purified by automatic flash column chromatography.

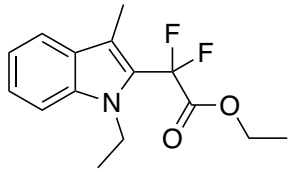
d. Characterization Data

Ethyl 2-(1,3-Dimethyl-1*H*-indol-2-yl)-2,2-difluoroacetate (4a)



Prepared according to the *General Procedure* from the corresponding indole **1a** (73 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **4a** was obtained as a colorless oil (84 mg, 0.32 mmol, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 7.65 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.23 (m, 2H), 7.19 – 7.15 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 2.47 (t, *J* = 3.1 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -98.0. Spectral Data agreed with previously reported.[1]

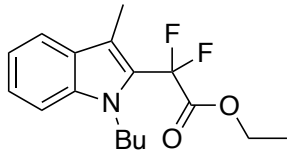
Ethyl 2-(1-Ethyl-3-methyl-1*H*-indol-2-yl)-2,2-difluoroacetate (4b)



Prepared according to the *General Procedure* from the corresponding indole **1b** (80 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **4b** was obtained as a colorless oil (45 mg, 0.16 mmol, 32%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 7.64 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.28 (m, 2H), 7.20 – 7.14 (m, 1H), 4.34 (q, *J* =

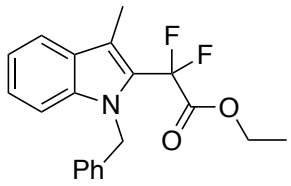
6.9 Hz, 4H), 2.45 (t, J = 3.0 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -98.1. Spectral Data agreed with previously reported.[1]

Ethyl 2-(1-Butyl-3-methyl-1*H*-indol-2-yl)-2,2-difluoroacetate (4c)



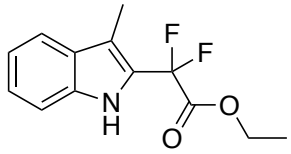
Prepared according to the *General Procedure* from the corresponding indole **1c** (94 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4c** was obtained as a colorless oil **4c** (73 mg, 0.24 mmol, 47%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 7.64 (dt, J = 8.0, 1.0 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.16 (ddd, J = 8.0, 6.3, 1.7 Hz, 1H), 4.33 (q, J = 7.4 Hz, 2H), 4.25 (t, J = 7.9 Hz, 2H), 2.45 (t, J = 3.0 Hz, 3H), 1.83 – 1.74 (m, 2H), 1.48 – 1.40 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -97.9. **^{13}C NMR** (101 MHz, $CDCl_3$), δ (ppm) 164.0 (t, J_{CF} = 35.9 Hz), 137.7, 128.2, 124.6 (t, J_{CF} = 28.8 Hz), 124.2, 120.2, 119.9, 114.5 (t, J_{CF} = 4.0 Hz), 112.8 (t, J = 251.1 Hz), 110.3, 63.7, 45.4 (t, J = 3.6 Hz), 32.7, 20.6, 14.2, 14.1, 9.3 (t, J_{CF} = 3.1 Hz). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2961, 2934, 2873, 1763, 1557, 1460, 1418, 1370, 1352, 1284, 1232, 1200, 1101, 1068, 1018, 948, 845. **HRMS (ESI)** calcd for $C_{17}H_{22}F_2NO_2$ $[M+H]^+$: 310.1619, found 310.1603.

Ethyl 2-(1-Benzyl-3-methyl-1*H*-indol-2-yl)-2,2-difluoroacetate (4d)



Prepared according to the *General Procedure* from the corresponding indole **1d** (111 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4d** was obtained as a colorless oil (57 mg, 0.17 mmol, 33%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 7.66 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.15 (m, 6H), 6.93 (d, *J* = 7.2 Hz, 2H), 5.51 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.50 (t, *J* = 3.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -97.8. Spectral Data agreed with previously reported.[1]

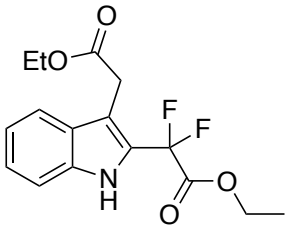
Ethyl 2,2-Difluoro-2-(3-methyl-1*H*-indol-2-yl)acetate (4e)



Prepared according to the *General Procedure* from the corresponding indole **1e** (66 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 10% EtOAc in hexanes), the title compound **4e** was obtained as a colorless oil (65 mg, 0.26 mmol, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 8.40 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.6

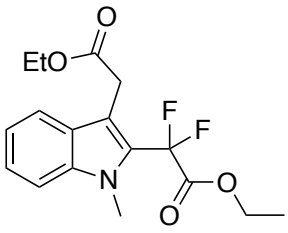
Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -101.4. Spectral Data agreed with previously reported.[1]

Ethyl 2-(3-(2-Ethoxy-2-oxoethyl)-1*H*-indol-2-yl)-2,2-difluoroacetate (4f)



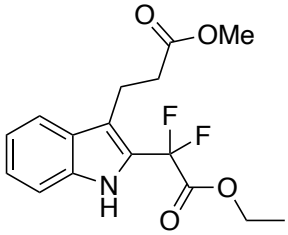
Prepared according to the *General Procedure* from the corresponding indole **1f** (102 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4f** was obtained as a yellow oil (86 mg, 0.27 mmol, 53%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) 8.51 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.93 (s, 2H) 1.33 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -101.5. **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 170.9, 163.2 (t, J_{CF} = 35.4 Hz), 135.5, 127.9, 124.8 (t, J_{CF} = 29.8 Hz), 124.5, 120.7, 119.9, 111.7, 111.1 (t, J_{CF} = 251.7 Hz), 110.5 (t, J_{CF} = 3.3 Hz), 63.9, 60.9, 29.9, 14.2, 13.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3245, 1805, 1680, 1541, 1244, 1165, 1129, 1082. **HRMS (EI)** calcd for $C_{16}H_{18}F_2NO_4$ $[M+H]^+$: 326.1204, found 326.1207.

Ethyl 2-(3-(2-Ethoxy-2-oxoethyl)-1-methyl-1*H*-indol-2-yl)-2,2-difluoroacetate (4g)



Prepared according to the *General Procedure* from the corresponding indole **1g** (109 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4g** was obtained as a yellow oil (85 mg, 0.25 mmol, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) 7.62 (d, J = 8.0 Hz, 1H), 7.38 – 7.24 (m, 2H), 7.17 (ddd, J = 7.9, 6.2, 1.7 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.95 (s, 2H), 3.86 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -98.7. **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 171.3, 163.3 (t, J_{CF} = 35.8 Hz), 138.0, 127.1, 126.2 (t, J_{CF} = 28.9 Hz), 124.2, 120.3, 119.7, 115.3, 112.1 (t, J_{CF} = 252.3 Hz), 109.8, 63.5, 60.8, 31.6, 30.1, 14.2, 13.9. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1804, 1677, 1554, 1251, 1169, 1130, 1090. **HRMS (EI)** calcd for $C_{17}H_{19}F_2NO_4$ $[M]^+$: 339.1282, found 339.1284.

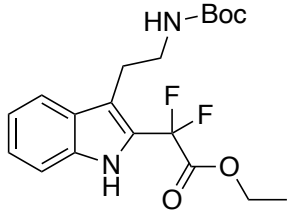
Methyl 3-(2-(2-Ethoxy-1,1-difluoro-2-oxoethyl)-1*H*-indol-3-yl)propanoate (4h)



Prepared according to the *General Procedure* from the corresponding indole **1h** (102 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification

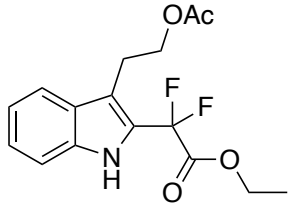
by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4h** was obtained as a colorless oil (90 mg, 0.28 mmol, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ (ppm) 8.58 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.3, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 3.32 – 3.20 (m, 2H), 2.71 – 2.64 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -101.2. Spectral Data agreed with previously reported.[1]

Ethyl 2-(3-(2-((*tert*-Butoxycarbonyl)amino)ethyl)-1*H*-indol-2-yl)-2,2-difluoroacetate (4i)



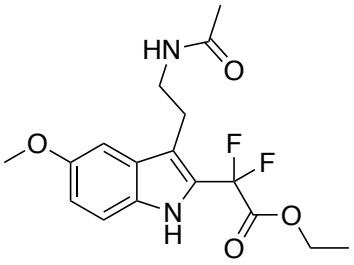
Prepared according to the *General Procedure* from the corresponding indole **1i** (174 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4i** was obtained as a light-yellow solid (117 mg, 0.31 mmol, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.57 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 4.66 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.45 – 3.35 (m, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 1.43 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 163.6 (t, J_{CF} = 35.7 Hz), 156.1, 135.8, 128.2, 124.6, 124.1 (t, J_{CF} = 30.0 Hz), 120.6, 120.3, 115.5, 111.7, 111.4 (t, J_{CF} = 251.5 Hz), 79.2, 63.8, 41.5, 28.5, 24.7, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -100.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3409, 3231, 1748, 1682, 1532, 1122. **mp** = 105 – 107 °C. **HRMS (ESI)** calcd for $C_{19}H_{24}F_2N_2O_4Na$ $[M+Na]^+$: 405.1602, found 405.1592.

Ethyl 2-(3-(2-Acetoxyethyl)-1*H*-indol-2-yl)-2,2-difluoroacetate (4j)



Prepared according to the *General Procedure* from the corresponding indole **1j** (102 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4j** was obtained as a colorless oil (82 mg, 0.25 mmol, 50%). **^{1}H NMR** (500 MHz, $CDCl_3$), δ (ppm) 8.46 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 4.34 (q, *J* = 7.5 Hz, 2H), 4.30 (t, *J* = 7.1 Hz, 2H) 3.24 (t, *J* = 7.2 Hz, 2H), 2.02 (s, 3H), 1.34 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -101.1. Spectral Data agreed with previously reported.[1]

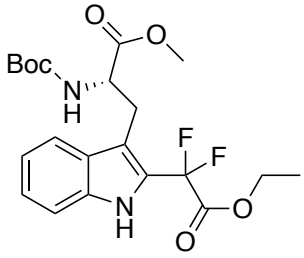
Ethyl 2-(3-(2-Acetamidoethyl)-5-methoxy-1*H*-indol-2-yl)-2,2-difluoroacetate (4k)



Prepared according to the *General Procedure* from the corresponding indole **1k** (116 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4k** was obtained as a colorless oil (74 mg, 0.21 mmol, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 9.15 (s, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.02 (t, *J* = 5.9 Hz, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 4.00 (s, 3H), 3.72 (q, *J* = 6.5 Hz, 2H), 3.26 (t, *J* = 6.4 Hz, 2H),

2.10 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H). One NH signal is not observed. **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm)170.5, 163.6 (t, J_{CF} = 36.2 Hz), 154.7, 131.1, 128.4, 124.7 (t, J_{CF} = 29.8 Hz), 115.6, 114.6 (t, J_{CF} = 3.2 Hz), 112.9, 111.5 (t, J_{CF} = 251.5 Hz),100.6, 63.8, 55.9, 40.3, 24.0, 23.3, 14.0. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -100.4. **FT-IR** (cm^{-1}, neat, ATR) $\tilde{\nu}$ = 3265, 2939, 1760, 1651, 1556, 1490, 1288, 1246, 1217, 1089 **HRMS (ESI)** calcd for $C_{17}H_{21}F_2N_2O_4$ $[M+H]^+$: 355.1469, found 355.1482.

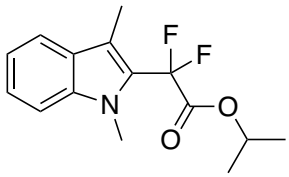
Methyl (*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-(2-(2-ethoxy-1,1-difluoro-2-oxoethyl)-1*H*-indol-3-yl)propanoate (4l)



Prepared according to the *General Procedure* from the corresponding indole **1l** (159 mg, 0.50 mmol, 1.0 equiv) and ethyl trifluoroacetate **2a** (710 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **4l** was obtained as a colorless oil (130 mg, 0.30 mmol, 60%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.64 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 5.15 (d, J = 8.3 Hz, 1H), 4.65 (q, J = 7.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.66 (s, 3H), 3.42 – 3.38 (m, 1H), 3.31 (dd, J = 14.5, 7.7 Hz, 1H), 1.35 (s, 9H), 1.33 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 207.5, 173.0, 164.0, 163.7 (t, J = 35.6 Hz), 155.4, 136.1, 128.2, 124.9 (t, J = 30.2 Hz), 124.8, 120.9, 120.3, 112.8, 112.0, 111.5 (t, J = 251.5 Hz), 80.0, 64.1, 54.5, 52.5, 28.5, 27.7, 14.2. **^{9}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -100.65

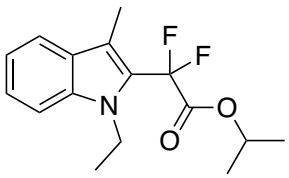
(d, J = 268.0, 1F) , -100.81 (d, J = 268.0, 1F). **FT-IR** (cm^{-1}, neat, ATR) $\tilde{\nu}$ = 3800, 2980, 1749, 1695, 1504, 1447, 1392, 1367, 1288, 1245, 1202, 1161, 1094. **HRMS (ESI)** calcd for $C_{21}H_{26}F_2N_2O_6Na$ $[M+Na]^+$: 463.1657, found 463.1647.

Isopropyl 2-(1,3-Dimethyl-1*H*-indol-2-yl)-2,2-difluoroacetate (5)



Prepared according to the *General Procedure* from the corresponding indole **1a** (73 mg, 0.50 mmol, 1.0 equiv) and isopropyl 2,2,2-trifluoroacetate (781 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **5** was obtained as a colorless oil (59 mg, 0.21 mmol, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 7.63 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 4.0 Hz, 2H), 7.20 – 7.09 (m, 1H), 5.16 – 5.10 (m, 1H), 3.84 (s, 3H), 2.45 (s, 3H), 1.31 (d, J = 6.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 163.2 (t, J_{CF} = 35.7 Hz), 138.0, 127.6, 125.0 (t, J_{CF} = 28.9 Hz), 123.9, 119.8, 119.6, 114.2 (t, J_{CF} = 4.0 Hz), 112.4 (t, J_{CF} = 251.8 Hz), 109.5, 71.9, 31.4, 21.5, 9.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -98.2. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2928, 1758, 1556, 1468, 1287, 738. **HRMS (ESI)** calcd for $C_{15}H_{18}F_2NO_2$ $[M+H]^+$: 282.1306, found 282.1316.

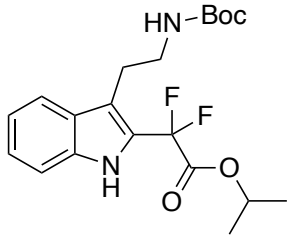
Isopropyl 2-(1-Ethyl-3-methyl-1*H*-indol-2-yl)-2,2-difluoroacetate (6)



Prepared according to the *General Procedure* from the corresponding indole **1a** (80 mg, 0.50 mmol, 1.0 equiv) and isopropyl 2,2,2-trifluoroacetate (781 mg, 5.0 mmol, 10 equiv). After

purification by automated flash column chromatography (from hexanes to 5% EtOAc in hexanes), the title compound **6** was obtained as a colorless oil (50 mg, 0.17 mmol, 34%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 7.64 (d, *J* = 8.0, 1H), 7.37 – 7.29 (m, 2H), 7.19 – 7.13 (m, 1H), 5.14 – 5.10(m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.45 (t, *J* = 3.0 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 163.4 (t, J_{CF} = 35.7 Hz), 137.0, 128.1, 124.4 (t, J_{CF} = 28.9 Hz), 124.0, 120.1, 120.0, 114.2 (t, J_{CF} = 3.8 Hz), 112.6 (t, J_{CF} = 250.0 Hz), 109.9, 72.0, 40.0, 21.6, 15.5, 9.1. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -98.3. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1757, 1288, 1212, 1093, 1083. **HRMS (ESI)** calcd for $C_{16}H_{20}F_2NO_2$ $[M+H]^+$: 296.1462, found 296.1473.

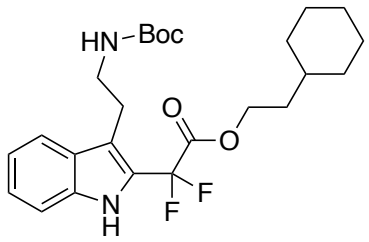
Isopropyl 2-(3-(2-((*tert*-Butoxycarbonyl)amino)ethyl)-1*H*-indol-2-yl)-2,2-difluoroacetate (7)



Prepared according to the *General Procedure* from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and isopropyl 2,2,2-trifluoroacetate (781 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **7** was obtained as a light-yellow solid (127 mg, 0.31 mmol, 62%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.49 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 5.18 – 5.10 (m, 1H), 4.64 (s, 1H), 3.41 (s, 2H), 3.09 (t, *J* = 7.0 Hz, 2H), 1.44 (s, 9H), 1.31 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 163.1 (t, J_{CF} = 35.4 Hz), 156.1, 135.8, 128.2, 124.5, 124.3, 120.6, 120.4, 115.5, 111.7, 111.4 (t, J_{CF} = 251.8 Hz), 79.2, 72.4, 41.6, 28.5, 24.7, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm)-

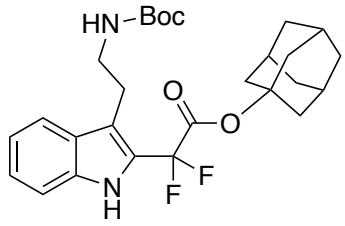
100.8. **mp** = 97 – 99 °C. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3389, 3229, 1748, 1685, 1541, 1296, 1114. **HRMS (ESI)** calcd for $C_{20}H_{26}F_2N_2O_4Na$ $[M+Na]^+$: 419.1758, found 419.1747.

2-Cyclohexylethyl 2-(3-(2-((*tert*-Butoxycarbonyl)amino)ethyl)-1*H*-indol-2-yl)-2,2-difluoroacetate (8)



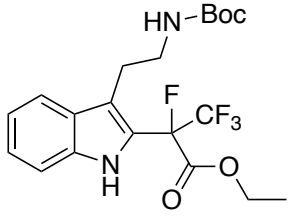
Prepared according to the *General Procedure* from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and 2-cyclohexylethyl 2,2,2-trifluoroacetate (1.12 g, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **8** was obtained as a dense colorless oil (142 mg, 0.31 mmol, 61%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.49 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.19 – 7.13 (m, 1H), 4.64 (s, 1H), 4.31 (t, *J* = 6.9 Hz, 2H), 3.46 – 3.33 (m, 2H), 3.22 – 2.98 (m, 2H), 1.64 – 1.51 (m, 7H), 1.44 (s, 9H), 1.27 – 1.18 (m, 1H), 1.14 – 1.04 (m, 3H), 0.91 – 0.82 (m, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz), δ (ppm) 163.6 (t, J_{CF} = 35.7 Hz), 156.0, 135.8, 128.2, 124.6, 124.2 (t, J_{CF} = 30.0 Hz), 120.6, 120.3, 115.5, 111.7, 111.5 (t, J_{CF} = 251.2 Hz), 79.2, 66.0, 41.6, 35.6, 34.5, 33.1, 28.6, 26.4, 26.1, 24.7. **^{19}F NMR** ($CDCl_3$, 376 MHz), δ (ppm) -101.2. **FT-IR** (cm^{-1}, neat, ATR) 3361 (br w), 2922 (s), 2851 (m), 1746 (m), 1682 (m), 1247 (m), 749 (m). **HRMS** (ESI) calcd for $C_{25}H_{35}F_2N_2O_4$ $[M + H]^+$: 465.2565, found: 465.2563.

(3*s*,5*s*,7*s*)-Adamantan-1-yl 2-(3-(2-((*tert*-Butoxycarbonyl)amino)ethyl)-1*H*-indol-2-yl)-2,2-difluoroacetate (9)



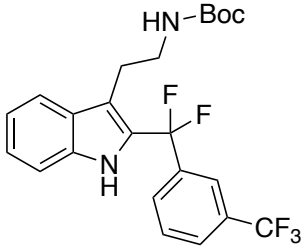
Prepared according to the *General Procedure* from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and (3*s*,5*s*,7*s*)-adamantan-1-yl 2,2,2-trifluoroacetate (1.24 g, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **9** was obtained as a dense colorless oil (154 mg, 0.32 mmol, 63%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.70 (s, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 4.69 (t, J = 6.2 Hz, 1H), 3.62 – 3.27 (m, 2H), 3.11 (t, J = 7.0 Hz, 2H), 2.21 – 2.16 (m, 3H), 2.12 (d, J = 3.5 Hz, 6H), 1.65 (t, J = 3.2 Hz, 6H), 1.46 (s, 9H). **^{13}C NMR** ($CDCl_3$, 151 MHz), δ (ppm) 162.0 (t, J_{CF} = 34.9 Hz), 156.1, 135.7, 128.2, 124.8 (t, J_{CF} = 30.0 Hz), 120.4, 120.3, 115.0, 111.7, 111.2 (t, J_{CF} = 252.3 Hz), 85.9, 79.1, 41.6, 35.9, 31.0, 28.5, 24.6. **^{19}F NMR** ($CDCl_3$, 376 MHz), δ (ppm) -100.6. **FT-IR** (cm^{-1}, neat, ATR) 3288 (br w), 2914 (m), 1751 (m), 1690 (s), 1167 (s), 1093 (s), 1043 (s), 742 (s). **HRMS** (ESI) calcd for $C_{27}H_{34}F_2N_2NaO_4$ $[M + Na]^+$: 511.2384, found: 511.2386.

Ethyl 2-(3-(2-((*tert*-Butoxycarbonyl)amino)ethyl)-1*H*-indol-2-yl)-2,3,3,3-tetrafluoropropanoate (10)



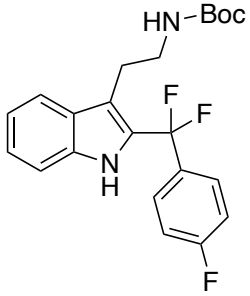
Prepared according to the *General Procedure* from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and ethyl pentafluoropropionate (960 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **10** was obtained as a dense colorless oil (138 mg mg, 0.32 mmol, 64%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.73 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.17 (t, J = 7.5 Hz, 1H), 4.64 (t, J = 6.7 Hz, 1H), 4.51 – 4.39 (m, 2H), 3.48 – 3.29 (m, 2H), 3.14 – 3.04 (m, 2H), 1.44 (s, 9H), 1.39 (t, J = 7.2, 3H). **^{13}C NMR** ($CDCl_3$, 151 MHz), δ (ppm) 164.1 (d, J_{CF} = 21.8 Hz), 156.1, 135.9, 128.4, 124.3, 121.2 (qd, J_{CF} = 287.8, 30.5 Hz), 120.5, 120.2 – 120.0 (m), 116.1, 111.5, 91.1 (dq, J_{CF} = 205.4, 33.8 Hz), 79.2, 64.4, 41.6, 28.5, 24.9, 14.0. **^{19}F NMR** ($CDCl_3$, 376 MHz), δ (ppm) -77.5 (d, J = 9.7 Hz, 3H), -173.8 (q, J = 9.7 Hz, 1H). **FT-IR** (cm^{-1}, neat, ATR) 3420 (br w), 2980 (w), 1693 (s), 1251 (s), 1160 (s), 743 (s). **HRMS** (ESI) calcd for $C_{20}H_{25}F_4N_2O_4$ $[M+H]^+$: 433.1750, found: 433.1731.

***tert*-Butyl (2-(2-(Difluoro(3-(trifluoromethyl)phenyl)methyl)-1*H*-indol-3-yl)ethyl)carbamate (11)**



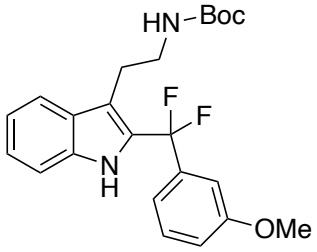
Prepared according to the *General Procedure,* with the addition of sodium formate (51 mg, 0.75 mmol, 1.5 equiv.), from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and 1,3-bis(trifluoromethyl)benzene (1.07 g, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **11** was obtained as a light-yellow oil (93 mg, 0.21 mmol, 41%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.25 (s, 1H), 7.86 (s, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 8.9 Hz, 2H), 7.58 (t, J = 7.9 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.0 Hz, 1H), 4.54 (s, 1H), 3.33 – 3.27 (m, 2H), 2.88 – 2.82 (m, 2H), 1.42 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 154.8, 136.3 (t, J_{CF} = 28.9 Hz), 134.2, 130.4 (q, J_{CF} = 32.7 Hz), 128.4, 127.2, 126.9 (t, J_{CF} = 31.3 Hz), 126.6, 123.4, 123.2, 122.6 (q, J_{CF} = 268.1 Hz), 121.8 (q, J_{CF} = 4.4 Hz), 119.5, 119.1, 116.9 (t, J_{CF} = 239.5 Hz), 113.1, 110.5, 78.1, 40.1, 27.4, 23.8. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -62.7 (s, 3F), -84.2 (s, 2F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3300, 2979, 1689, 1511, 1454, 1165, 1128. **HRMS (ESI)** calcd for $C_{23}H_{24}F_5N_2O_2$ $[M+H]^+$: 455.1758, found 455.1764.

***tert*-Butyl (2-(2-(Difluoro(4-fluorophenyl)methyl)-1*H*-indol-3-yl)ethyl)carbamate (12)**



Prepared according to the *General Procedure,* with the addition of sodium formate (51 mg, 0.75 mmol, 1.5 equiv), from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and 1-fluoro-4-(trifluoromethyl)benzene (821 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **12** was obtained as a colorless oil (42 mg, 0.11 mmol, 21%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.24 (s, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.38 (d, J = 8.3 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 8.6 Hz, 2H), 4.52 (s, 1H), 3.31 (q, J = 6.9 Hz, 2H), 2.85 (t, J = 7.0 Hz, 2H), 1.42 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 165.0, 163.3, 156.0, 135.2, 132.5 (dt, J_{CF} = 28.6, 3.3 Hz), 128.7 (t, J_{CF} = 31.6 Hz), 128.4 (t, J_{CF} = 4.6 Hz), 128.3 (t, J_{CF} = 4.9 Hz), 124.2, 120.6, 120.2, 118.4 (t, J_{CF} = 238.7 Hz), 116.0 (d, J_{CF} = 22.3 Hz), 113.9, 111.6, 41.3, 28.5, 24.9. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -82.5 (s, 2F), -109.3 (s, 1F). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ =3250, 2975, 2930, 1690, 1605, 1160. **HRMS (ESI)** calcd for $C_{22}H_{24}F_3N_2O_2$ $[M+H]^+$: 405.1790, found 405.1787.

***tert*-Butyl (2-(2-(Difluoro(3-methoxyphenyl)methyl)-1*H*-indol-3-yl)ethyl)carbamate (13)**

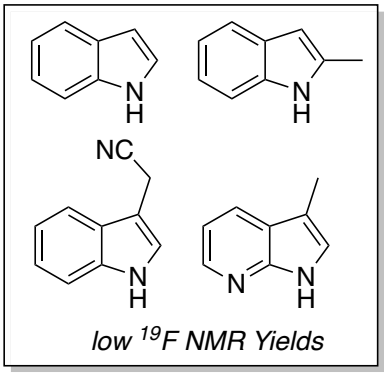


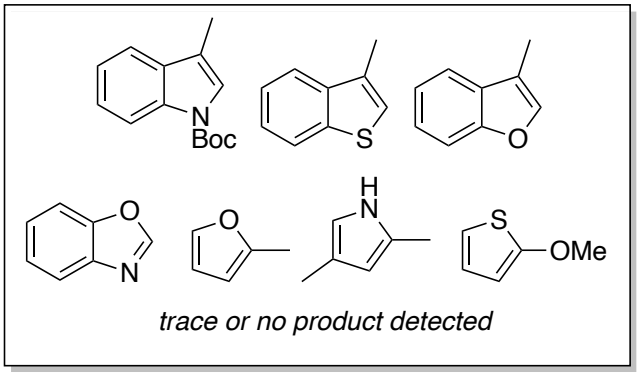
Prepared according to the *General Procedure,* with the addition of sodium formate (51 mg, 0.75 mmol, 1.5 equiv.), from the corresponding indole **1l** (130 mg, 0.50 mmol, 1.0 equiv) and 1-methoxy-3-(trifluoromethyl)benzene (881 mg, 5.0 mmol, 10 equiv). After purification by automated flash column chromatography (from hexanes to 20% EtOAc in hexanes), the title compound **13** was obtained as a light yellow oil (44 mg, 0.10 mmol, 20%) **^{1}H NMR** (600 MHz, $CDCl_3$), δ (ppm) 8.21 (s, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 5.0 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.09 (s, 2H), 7.00 (d, J = 7.8 Hz, 1H), 4.53 (s, 1H), 3.80 (s, 3H), 3.35 – 3.27 (m, 2H), 2.88 (t, J = 7.1 Hz, 2H), 1.41 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$), δ (ppm) 159.9, 156.0, 137.7 (t, J_{CF} = 28.1 Hz), 135.1, 130.0, 129.0 (t, J_{CF} = 32.2 Hz), 128.5, 124.0, 120.4, 120.2, 118.6 (t, J_{CF} = 239.9 Hz), 118.3 (t, J_{CF} = 5.2 Hz), 116.5, 113.7, 111.6, 111.5 (t, J_{CF} = 5.0 Hz), 79.1, 55.6, 41.3, 29.8, 28.5. **^{19}F NMR** (376 MHz, $CDCl_3$), δ (ppm) -83.9. **FT-IR** (cm^{-1}, neat, ATR), ṽ = 3300, 1689, 1587, 1272, 1245, 1161. **HRMS (ESI)** calcd for $C_{23}H_{26}F_2N_2O_3Na$ $[M+Na]^+$: 439.1809, found 439.1815.

e. Gram Scale Synthesis Reaction

A 500 mL round bottom flask was charged with a magnetic stir bar, 1,3-dimethylindole (1.16 g, 8.0 mmol, 1 equiv), bis(4-methoxybenzene) disulfide (2.23 g, 8.0 mmol, 1 equiv), and K_2HPO_4 (174 mg, 16 mmol, 2 equiv). The round bottom flask was sealed with a septum and purged with argon. Anhyd DMSO (80 mL) was added with additional purging for 3 min. Ethyl trifluoroacetate (4.8 mL, 40 mmol, 5 equiv) was added and the septum-sealed round bottom flask was wrapped with Parafilm. The round bottom flask was placed in between two Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) with a distance of 2 inches from the sides of the round bottom flask, and two fans were used on the other side to keep the reaction near room temperature. The reaction workflow is pictured below. After monitoring by ^{19}F NMR, the reaction was quenched with H_2O (100 mL) after 24 h and extracted with EtOAc (3 x 110 mL). The combined organic layers were washed with H_2O (100 mL), followed by brine (100 mL), and dried (Na_2SO_4). The solvent was removed by rotary evaporation, and the crude mixture was purified by automatic flash column chromatography (from hexanes to 5% EtOAc in hexanes). The product **4a** was obtained as a colorless oil (650 mg, 2.4 mmol), and starting material (1,3-dimethylindole) was also recovered (300 mg, 2.1 mmol). Calculating the yield based on recovered starting material (8.0 mmol starting – 2.1 mmol recovered = **5.9 mmol**), furnishes a 41% yield of **4a**.

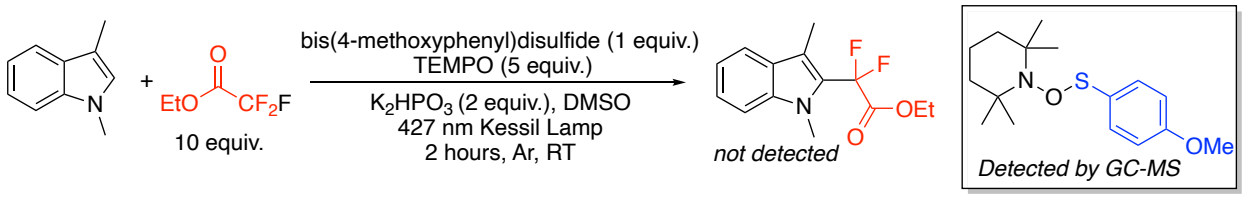
f) Unsuccessful Substrate Examples



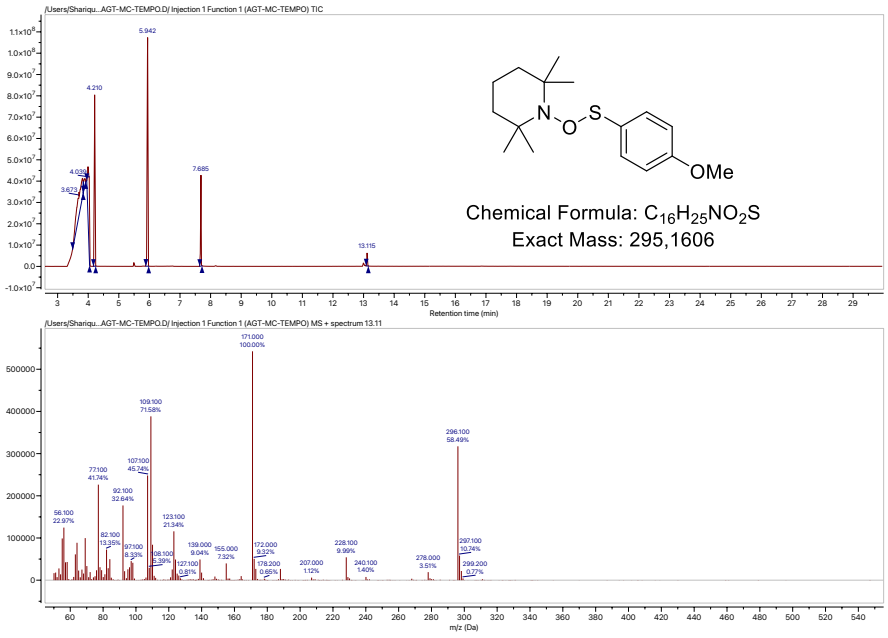


4. Mechanistic Experiments

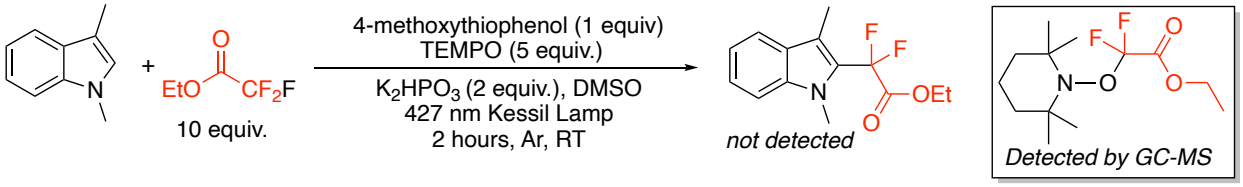
a. TEMPO Trapping with bis(4-methoxybenzen)disulfide



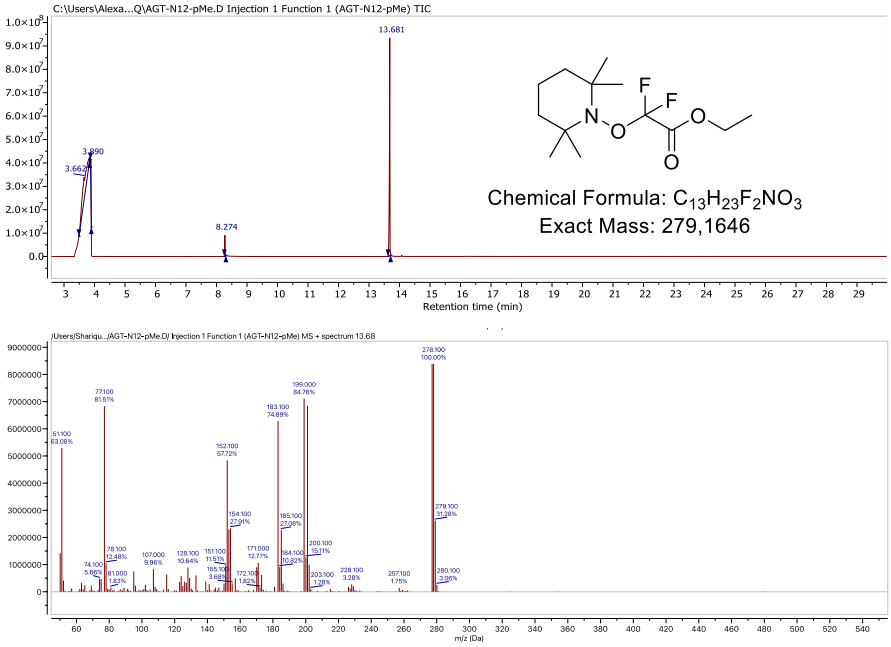
To a flame-dried 4 mL vial equipped with a magnetic stir bar, indole **1a** (14.5 mg, 0.1 mmol, 1.0 equiv), TEMPO (78.1 mg, 0.5 mmol, 5 equiv), K_2HPO_4 (34.8 mg, 0.2 mmol, 2.0 equiv) and bis(4-methoxyphenyl) disulfide (27.8 mg, 1 equiv) were added, and the vial was subjected to 3 cycles of vacuum/argon degassing. Subsequently, 1.0 mL of dry DMSO was added under inert atmosphere followed by 10 equiv of ethyltrifluoroacetate (142 mg, 0.12 mL, 1 mmol). The reaction mixture was irradiated with Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) for 2 h, as described in the "Workflow" section. The temperature of the reaction was maintained at approximately 25 °C via a fan. The crude analysis by GCMS did not show the formation of product **4a**, thus the presence of TEMPO inhibits the product formation. Additionally, we detected the *p*-methoxythiophenol-TEMPO adduct.



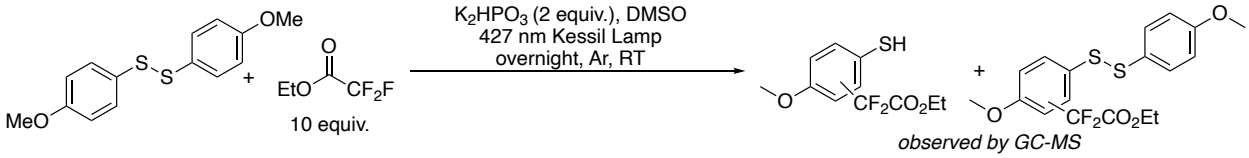
b. TEMPO Trapping with 4-methoxybenzenethiol



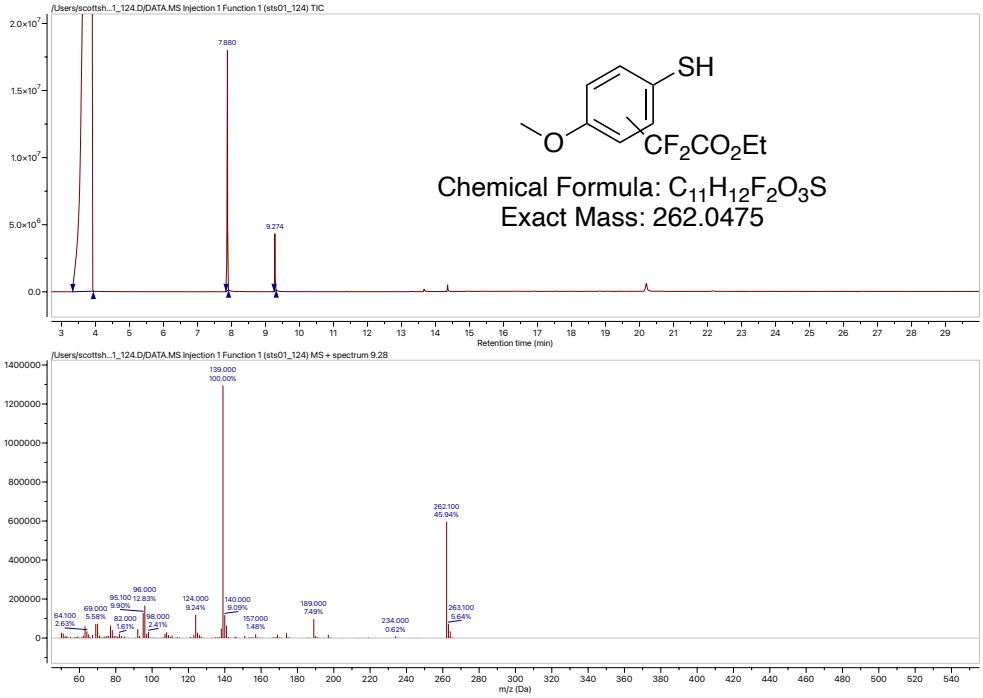
To a flame-dried 4 mL vial equipped with a magnetic stir bar, indole **1a** (14.5 mg, 0.1 mmol, 1.0 equiv), TEMPO (78.1 mg, 0.5 mmol, 5 equiv), K_2HPO_4 (34.8 mg, 0.2 mmol, 2.0 equiv) and 4-methoxythiophenol (14 mg, 1 equiv) were added, and the vial was subjected to 3 cycles of vacuum/argon degassing. Subsequently, 1.0 mL of dry DMSO were added under inert atmosphere followed by 10 equiv of ethyltrifluoroacetate (142 mg, 0.12 mL, 1 mmol). The reaction mixture was irradiated with Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) for 2 h, as described in the "Workflow" section. The temperature of the reaction was maintained at approximately 25 °C via a fan. The crude analysis by GCMS did not show the formation of product **4a**, thus the presence of TEMPO inhibits the product formation. Additionally, we detected the difluoroethylacetate-TEMPO adduct.

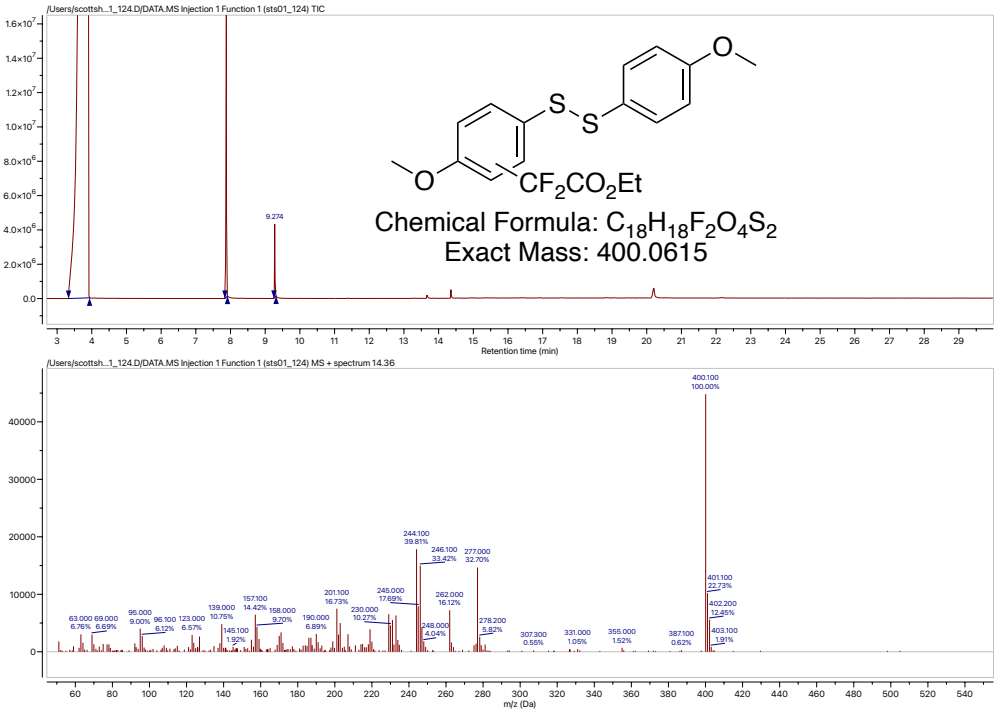


c) Control Reaction without Substrate

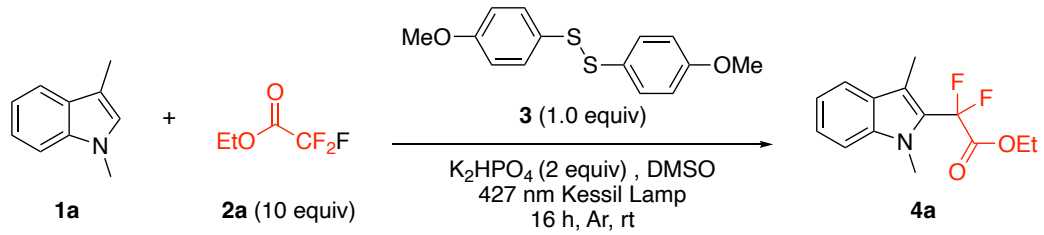


To a 4 mL vial charged with a stir bar, K_2HPO_4 (34.8 mg, 0.2 mmol, 2.0 equiv) and 1,2-bis(4-methoxyphenyl) disulfide (27.8 mg, 1 equiv) were added. The vial was purged with argon, and 1 mL of anhyd DMSO was added. The vial was sealed with Parafilm and irradiated with a Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) (as described in Workflow) overnight. Trimethoxybenzene was added, and the reaction was analyzed by GC-MS. The difluoroalkylated 4-methoxybenzenethiol and difluoroalkylated bis(4-methoxybenzene)disulfide were detected.

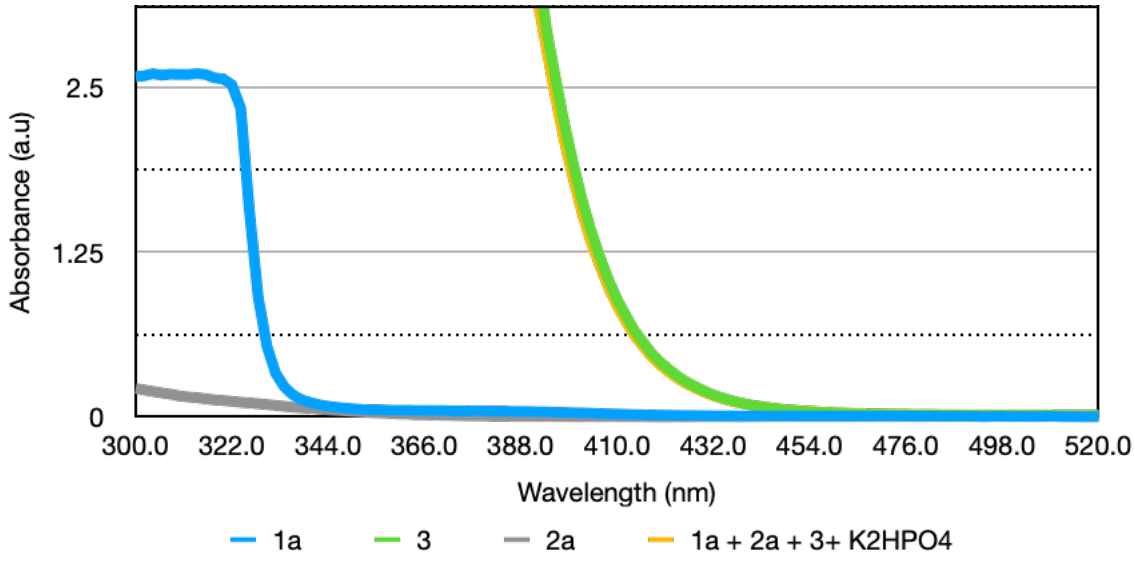

/Users/scottsh...1_124.D/DATA.MS Injection 1 Function 1 (sts01_124) TIC
7.880
9.274
Retention time (min)
SH
O
CF2CO2Et
Chemical Formula: C11H12F2O3S
Exact Mass: 262.0475
/Users/scottsh...1_124.D/DATA.MS Injection 1 Function 1 (sts01_124) MS + spectrum 9.28
139.000 100.00%
262.100 45.94%
96.000 12.83%
95.100 9.90%
124.000 9.24%
140.000 9.09%
189.000 7.49%
69.000 5.58%
82.000 1.67%
98.000 2.41%
157.000 1.48%
234.000 0.62%
263.100 5.64%
64.100 2.63%
m/z (Da)


/Users/scottsh...1_124.D/DATA.MS Injection 1 Function 1 (sts01_124) TIC
9.274
Retention time (min)
O
S
S
O
CF2CO2Et
Chemical Formula: C18H18F2O4S2
Exact Mass: 400.0615
/Users/scottsh...1_124.D/DATA.MS Injection 1 Function 1 (sts01_124) MS + spectrum 14.36
400.100 100.00%
244.100 39.81%
277.000 32.70%
246.100 33.42%
401.100 22.73%
157.100 14.42%
158.000 9.70%
201.100 16.73%
245.000 17.69%
262.000 16.12%
230.000 10.27%
402.200 12.45%
139.000 10.75%
190.000 6.89%
248.000 4.04%
278.200 5.82%
403.100 1.91%
63.000 6.76%
69.000 6.69%
95.000 9.00%
96.100 6.12%
123.000 6.57%
145.100 1.92%
307.300 0.55%
331.000 1.05%
355.000 1.52%
387.100 0.62%
m/z (Da)

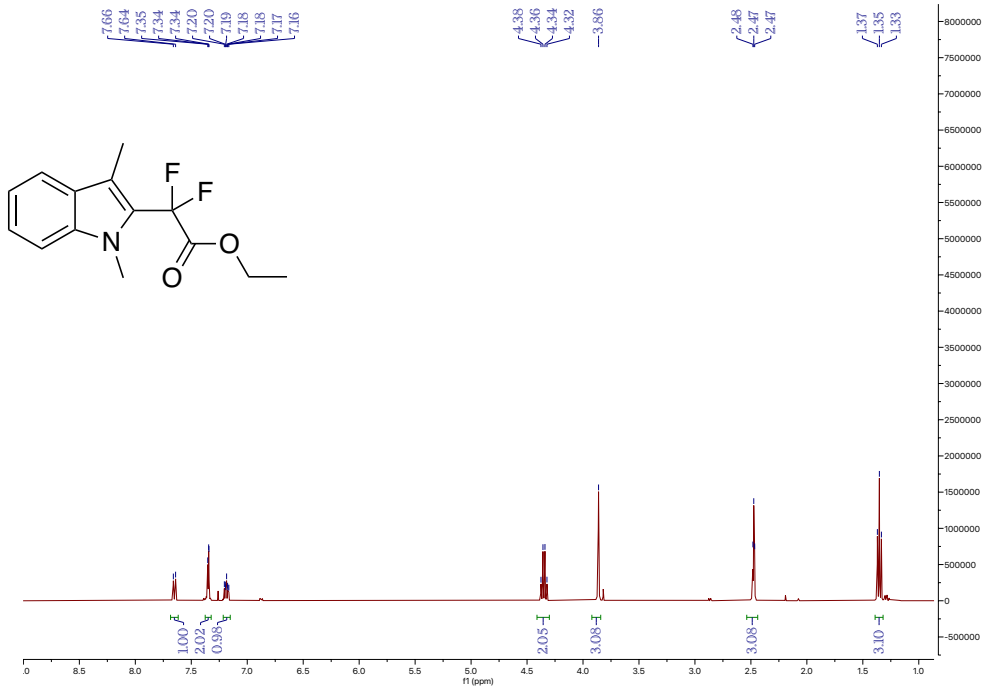
d) UV-Vis Data



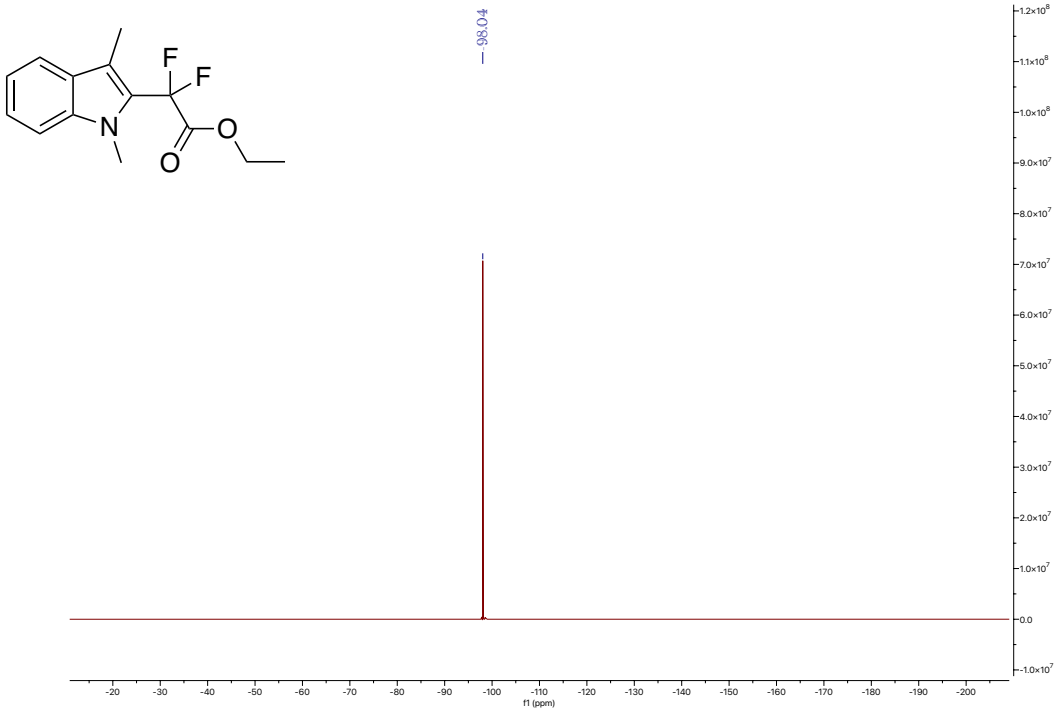
Individual solutions of **1a**, **2a**, **3**, and a mixture of **1a**, **2a**, **3**, and **base** in DMSO were prepared at 0.05 M concentration and used for the UV-Vis absorption spectroscopic measurements. The solutions were prepared in the presence of air.



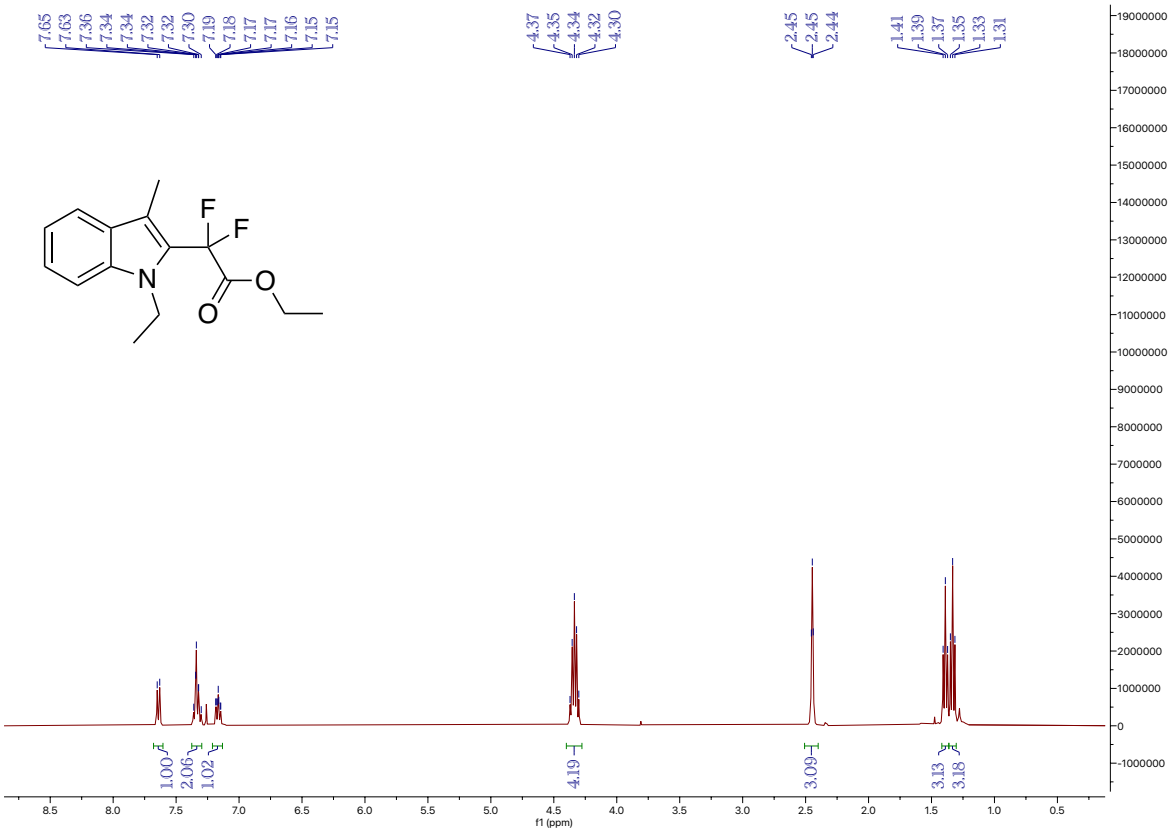
5. NMR Spectra



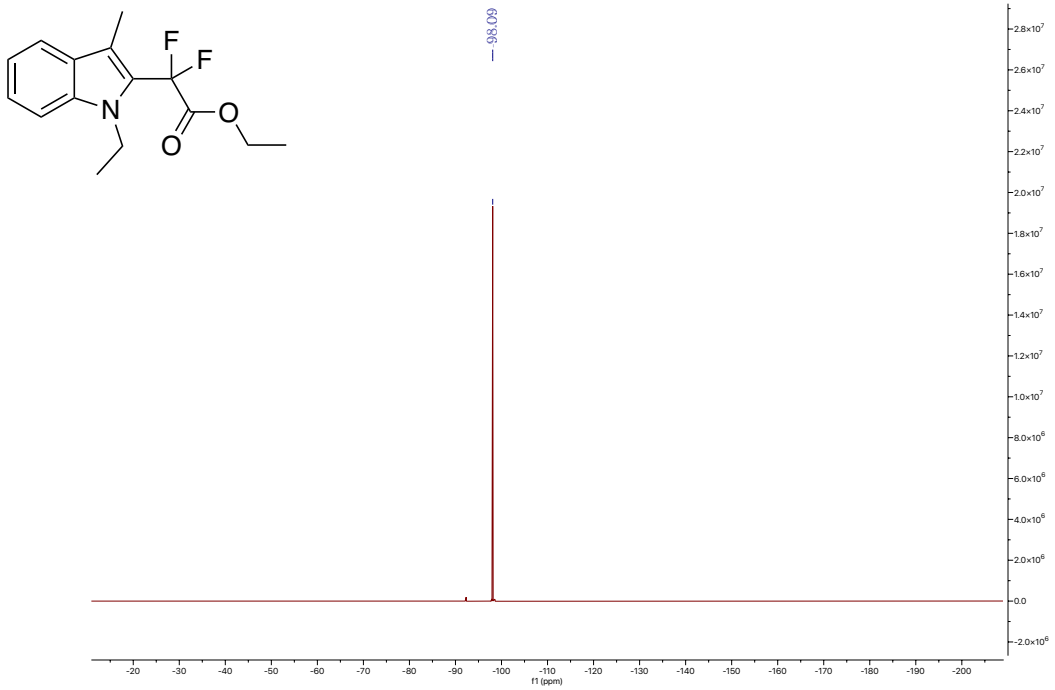
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**.



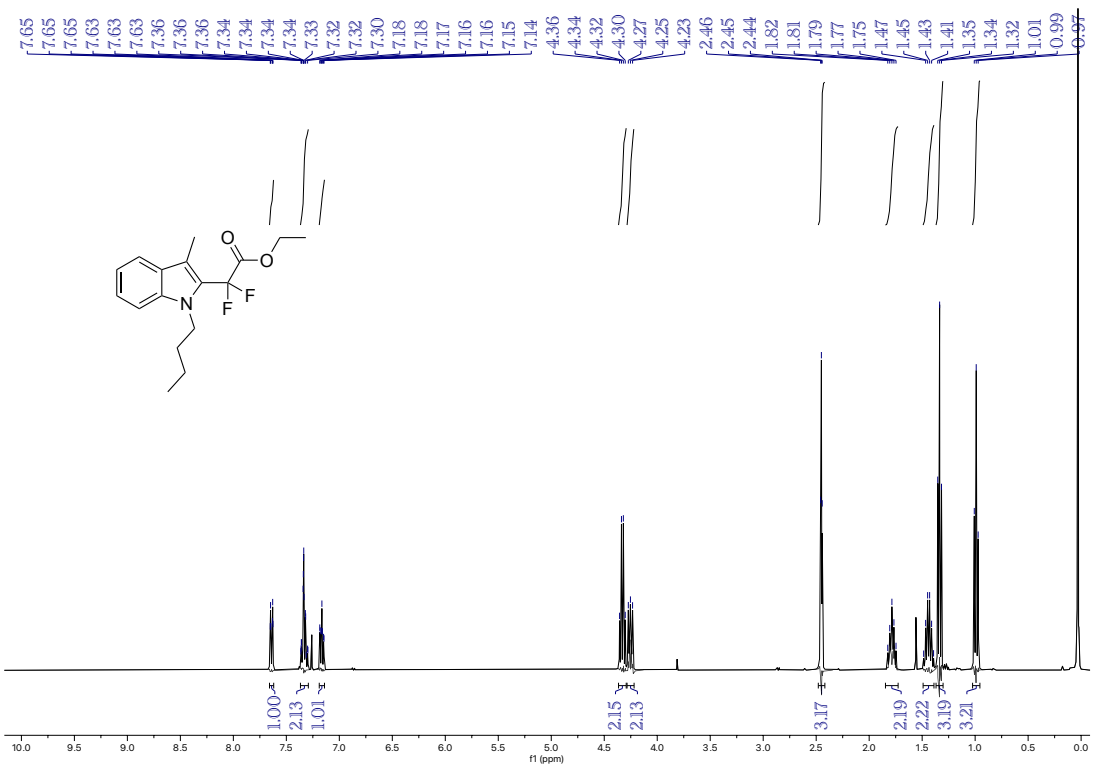
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4a**.



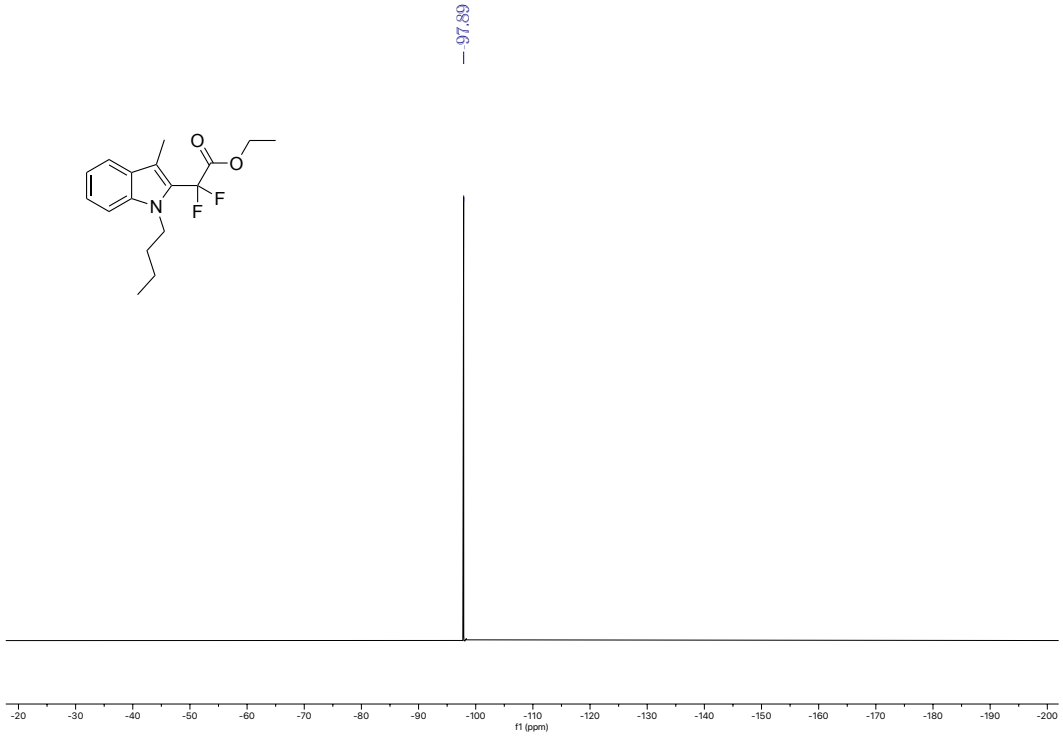
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**.



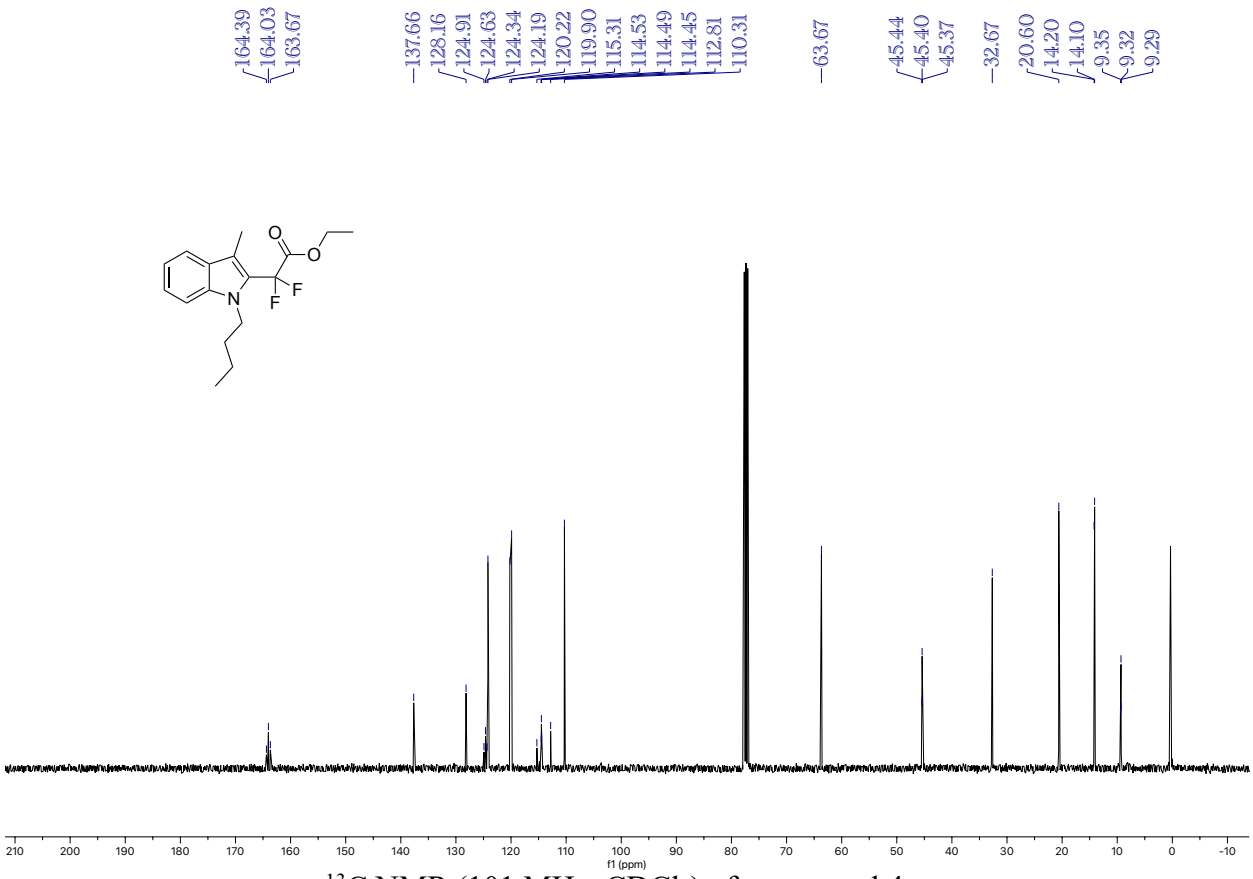
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4b**.



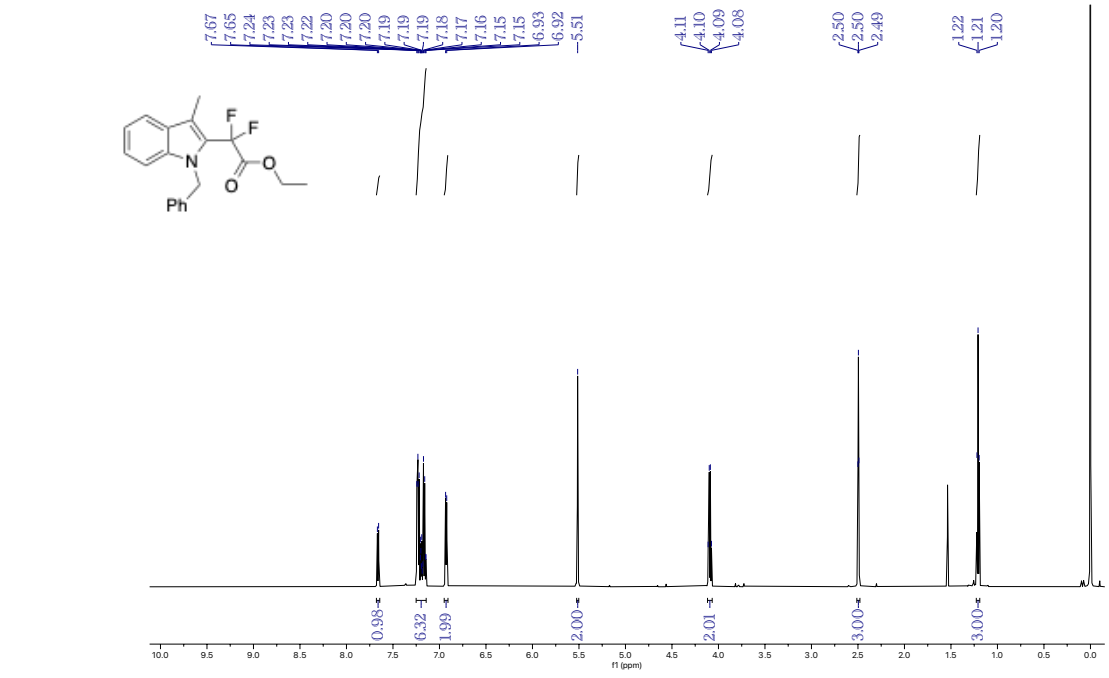
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4c**.



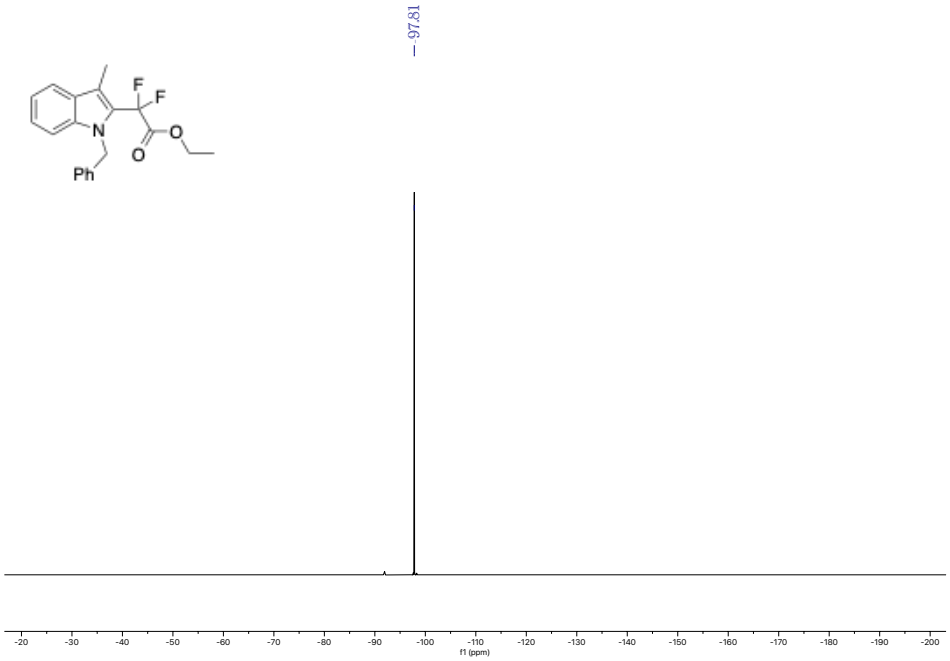
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4c**.



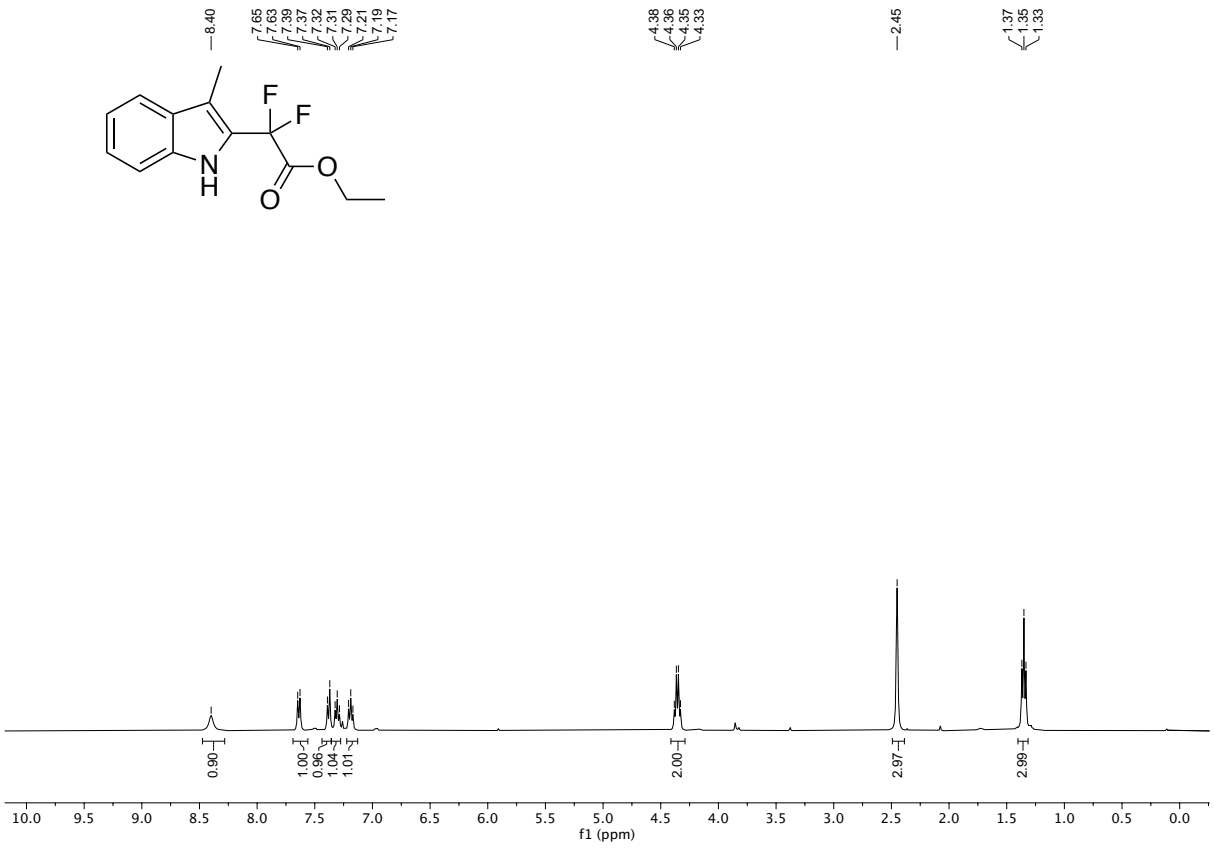
^{13}C NMR (101 MHz, $CDCl_3$) of compound **4c**.



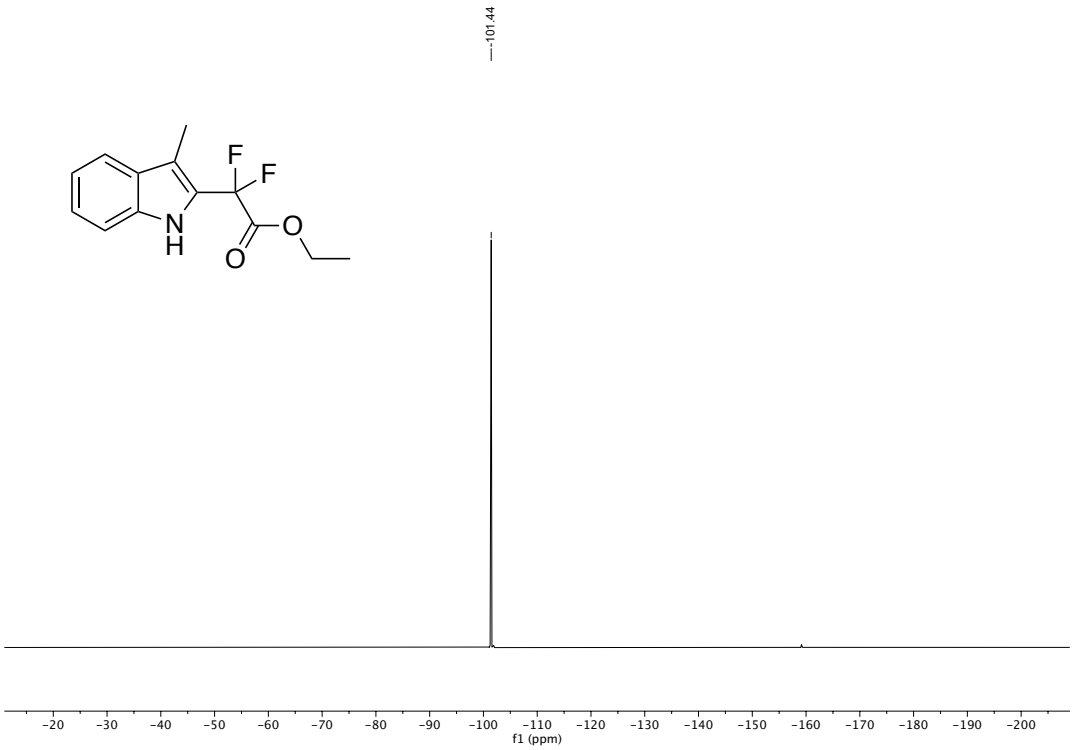
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4d**.



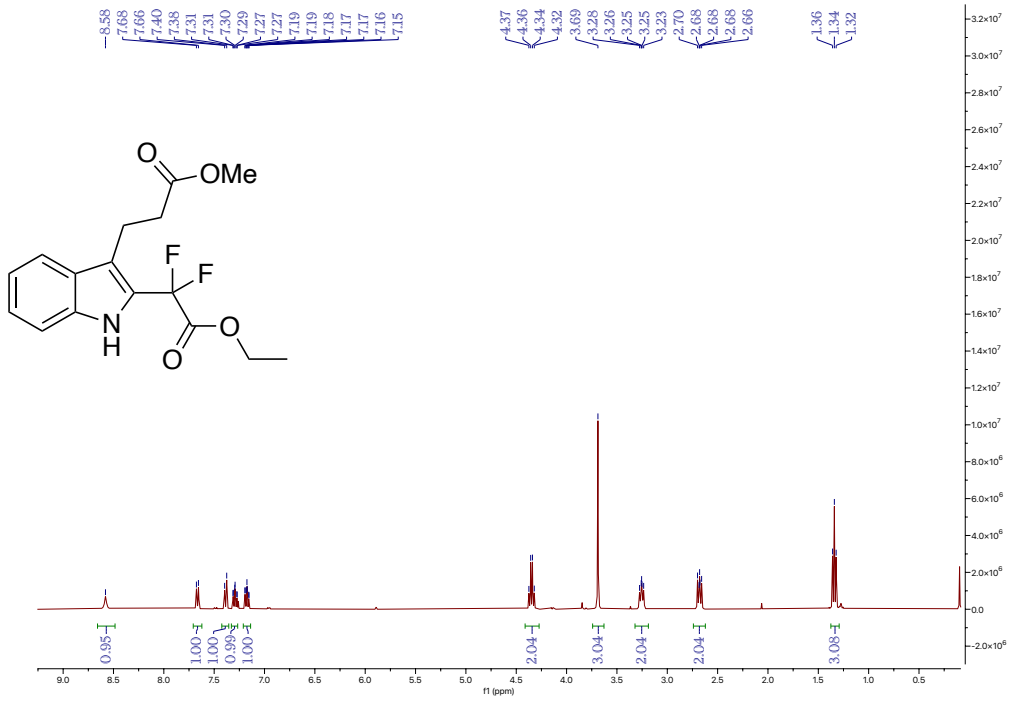
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4d**.



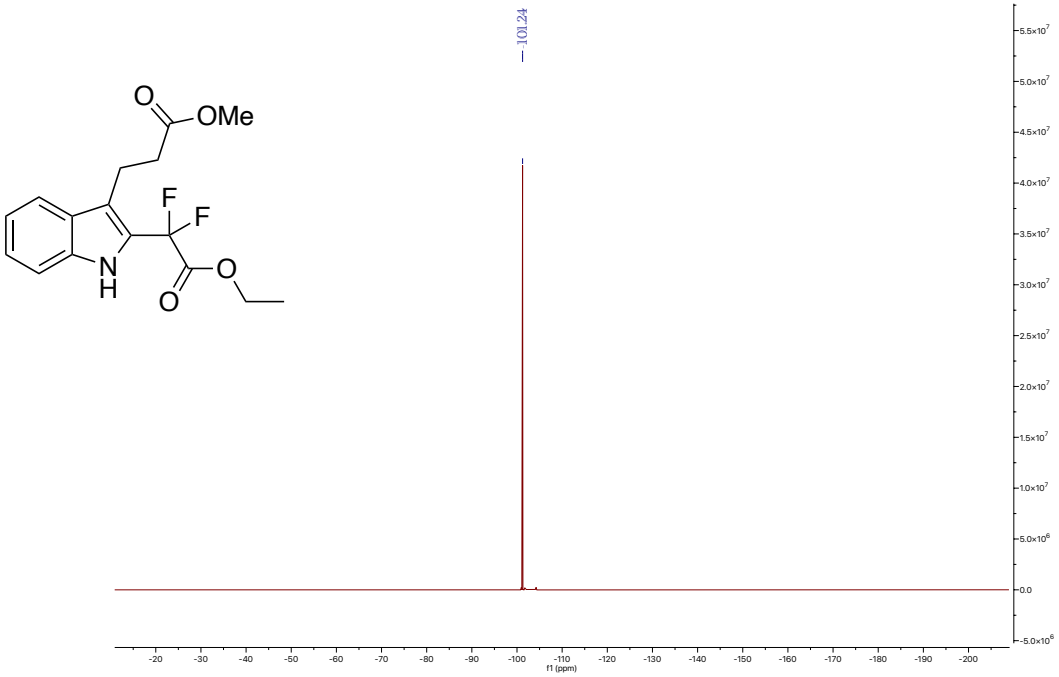
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4e**.



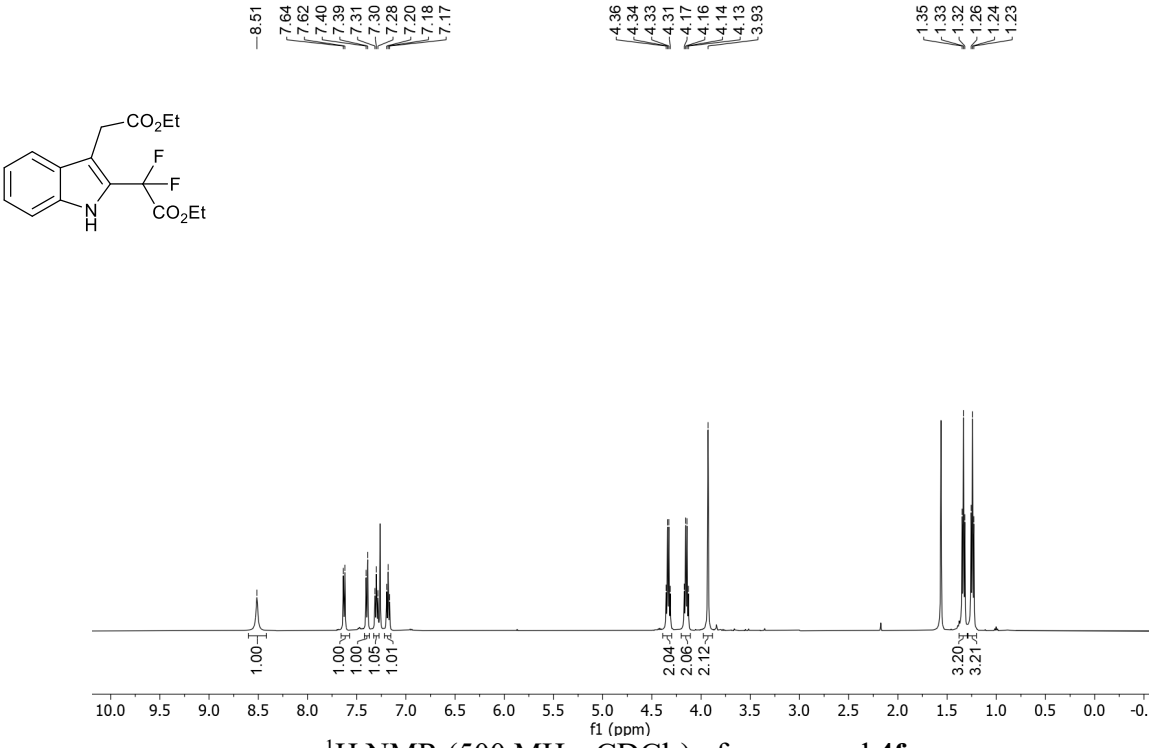
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4e**.



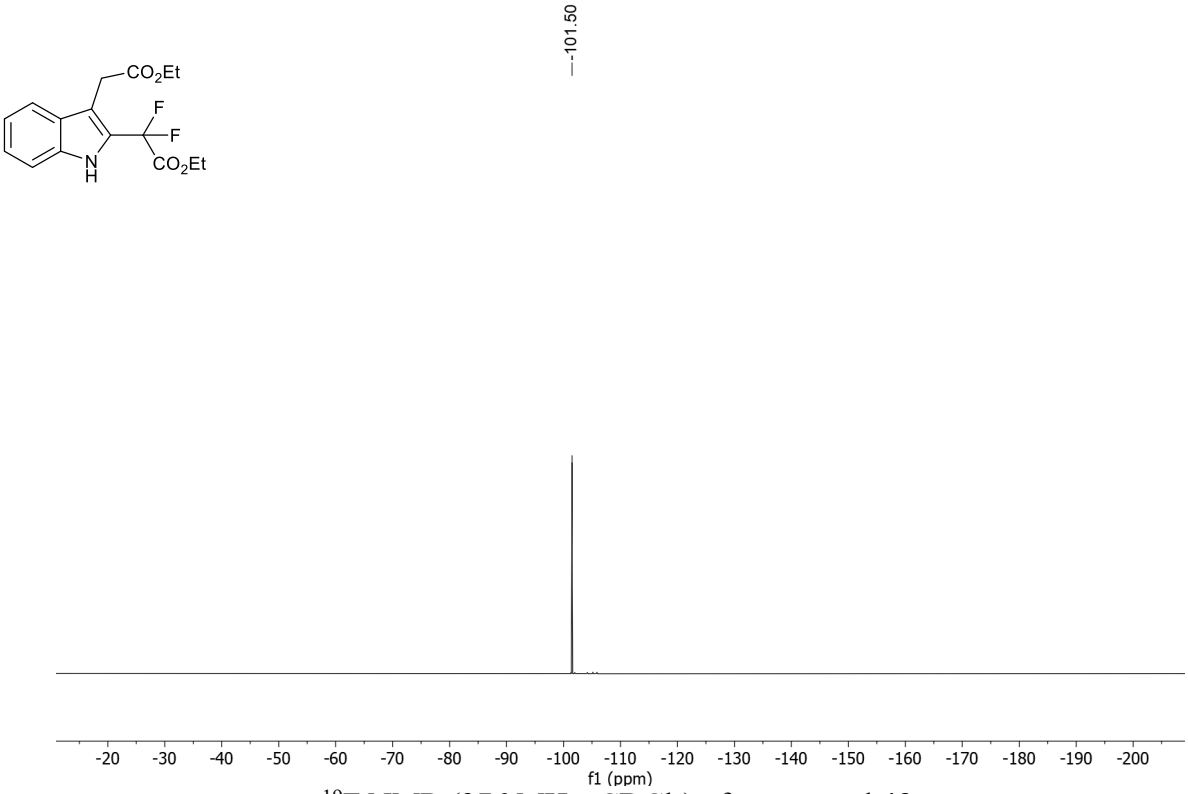
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4h**.



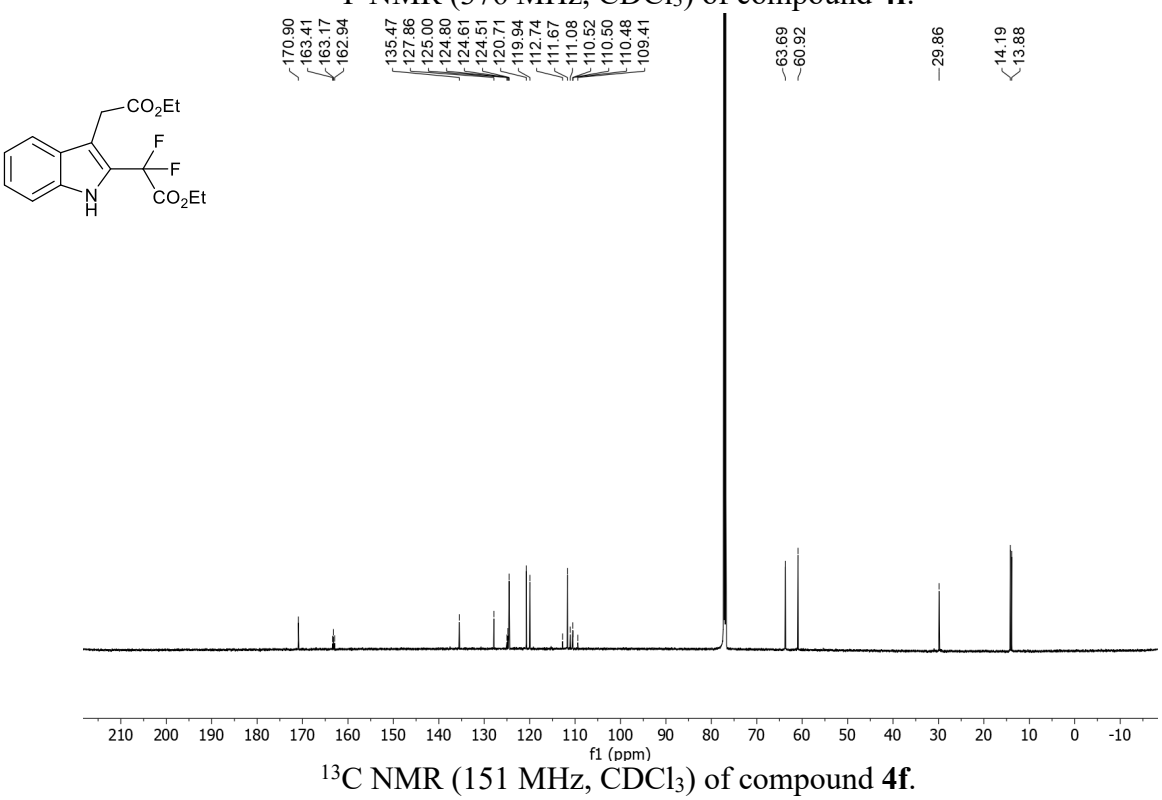
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4h**.



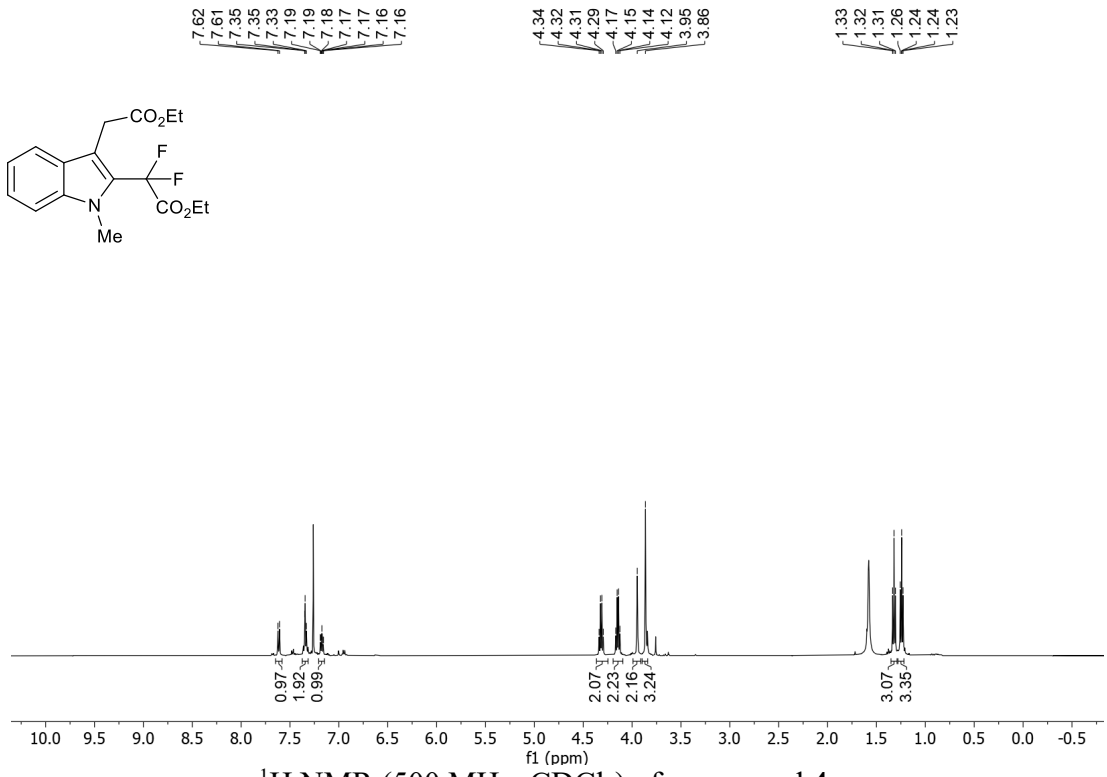
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4f**.



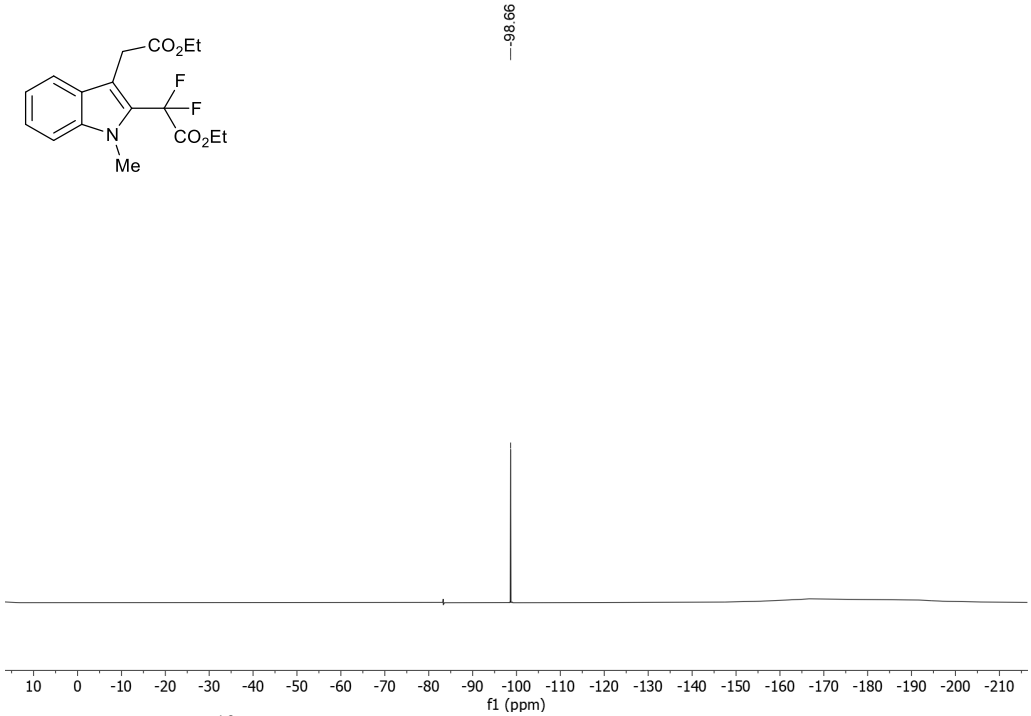
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4f**.



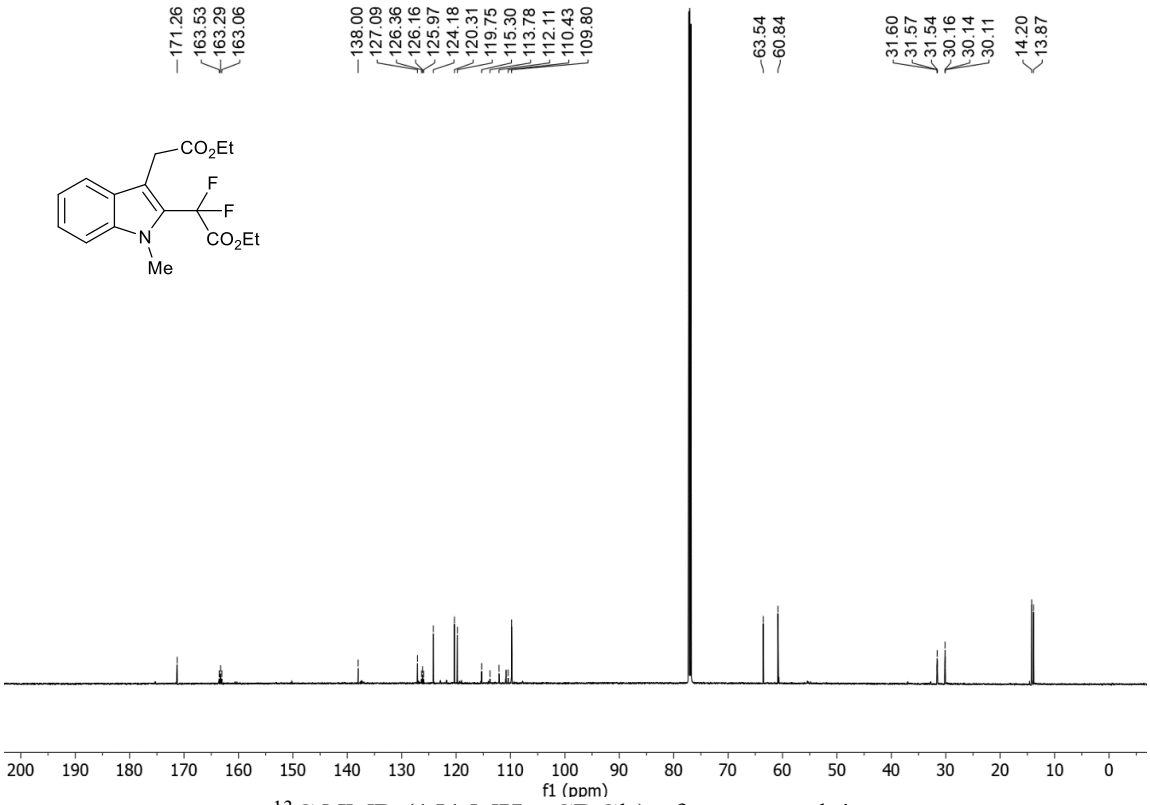
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4f**.



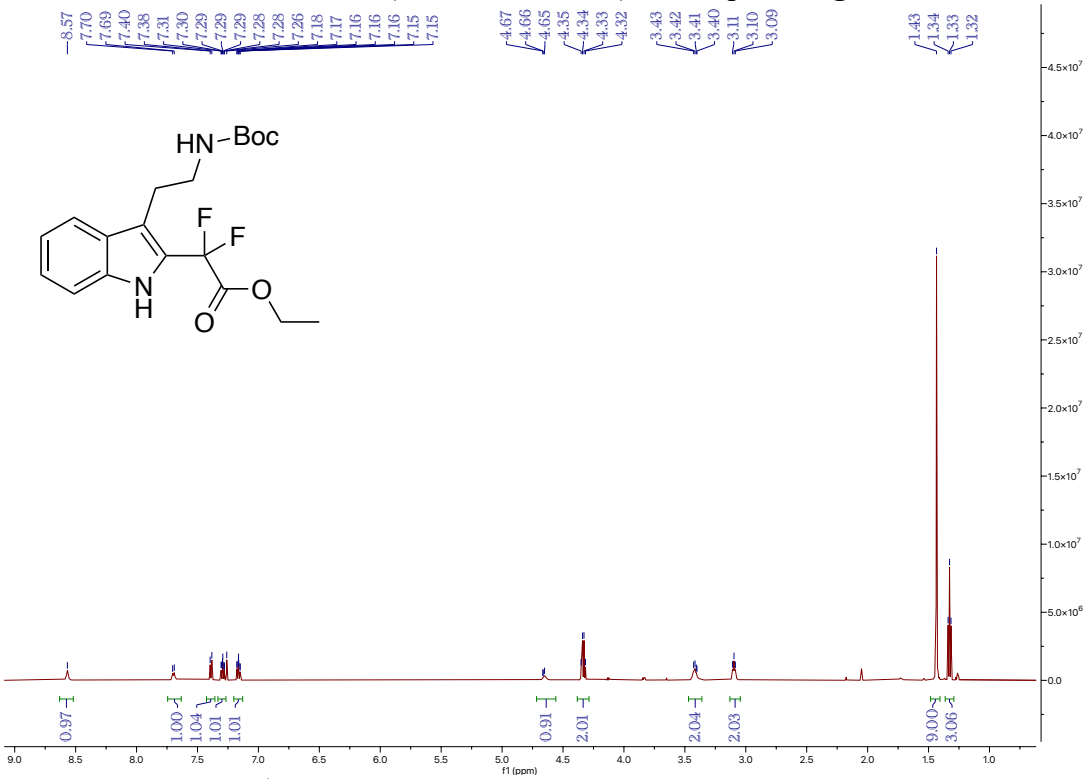
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**.



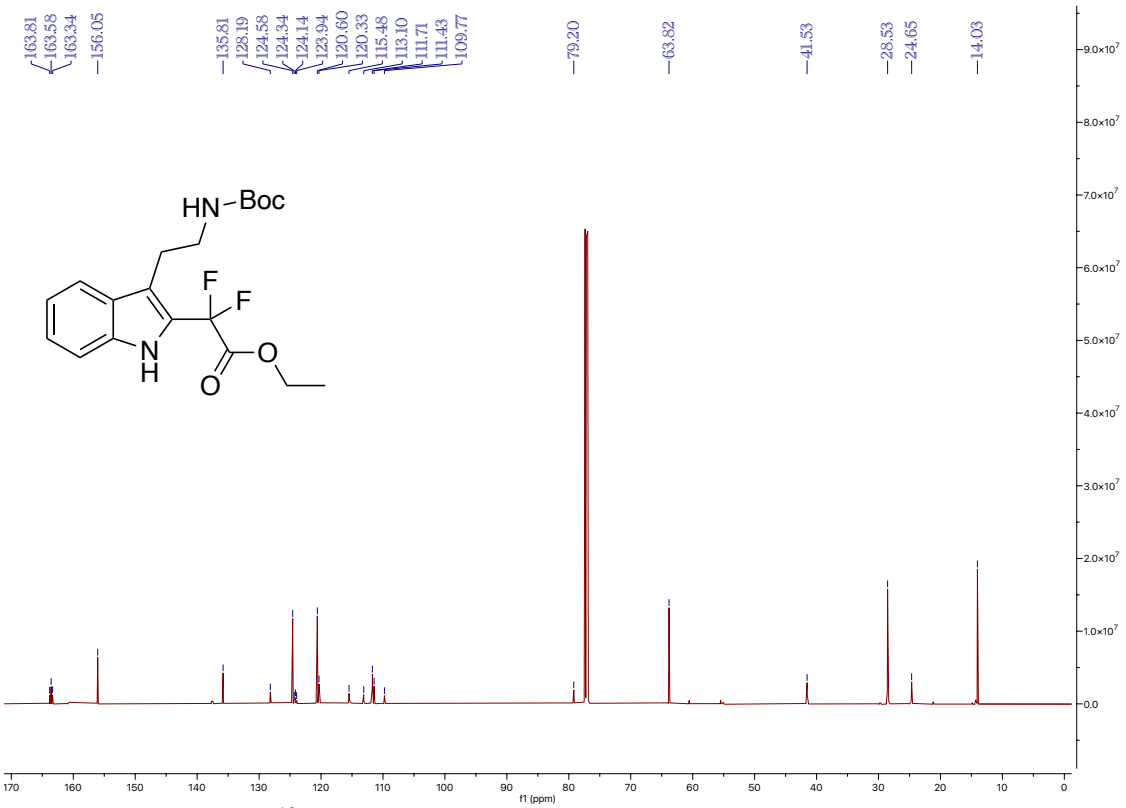
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4g**.



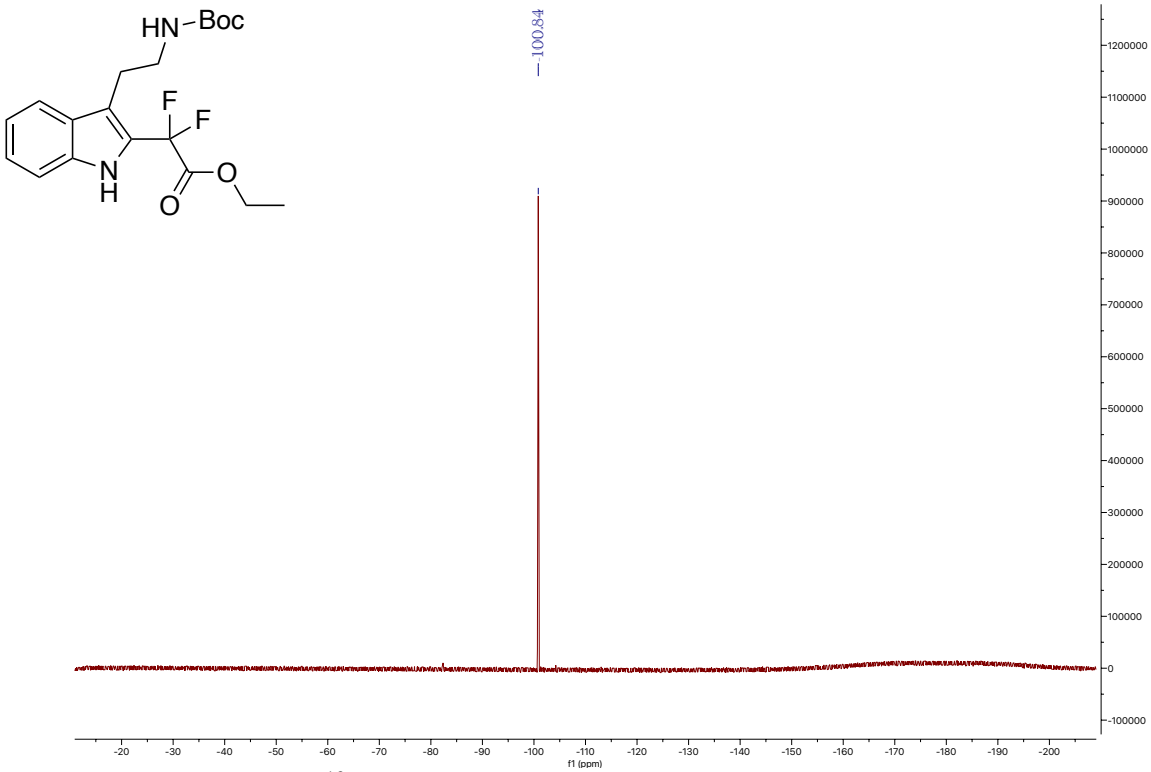
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4g**.



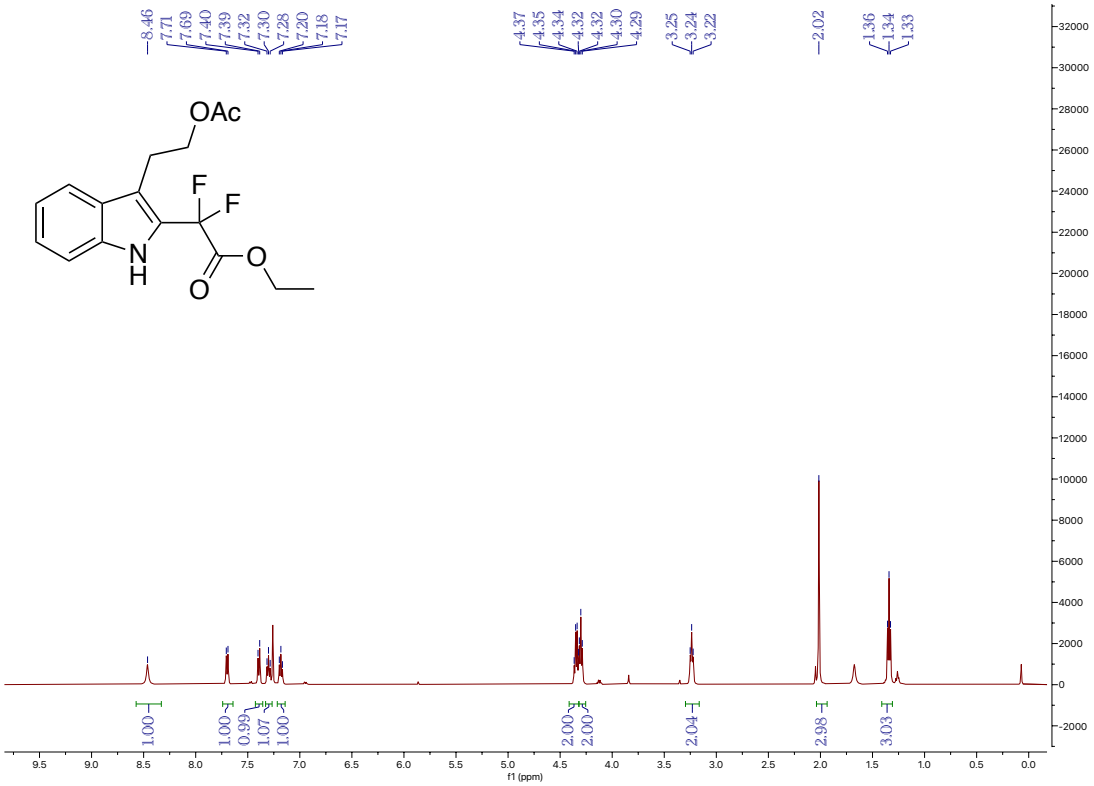
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4i**.



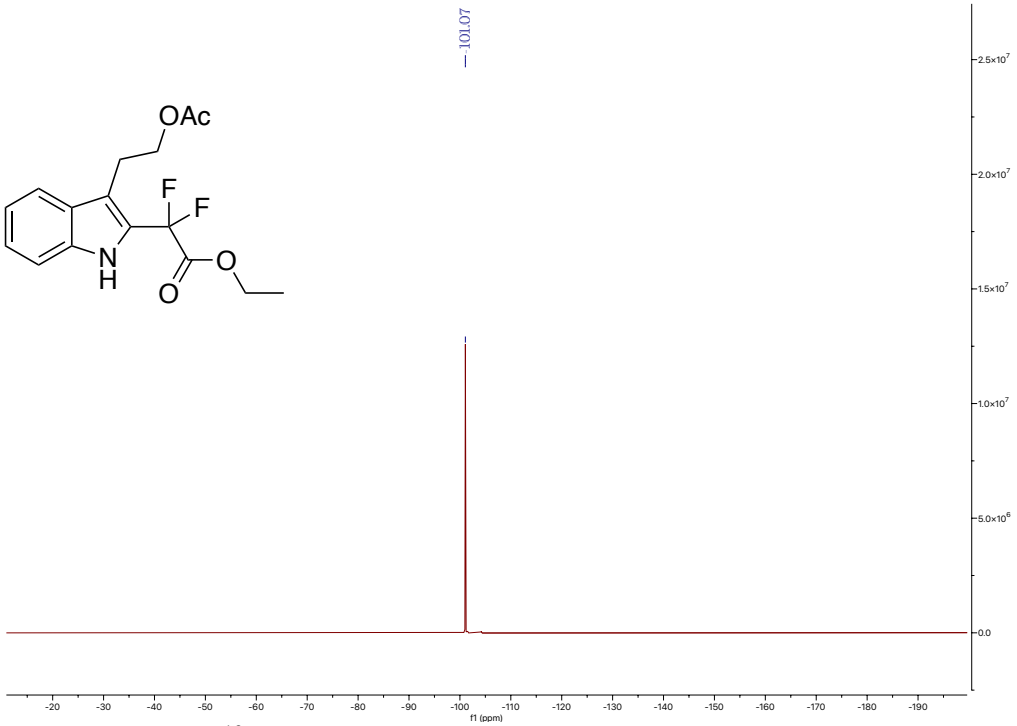
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4i**.



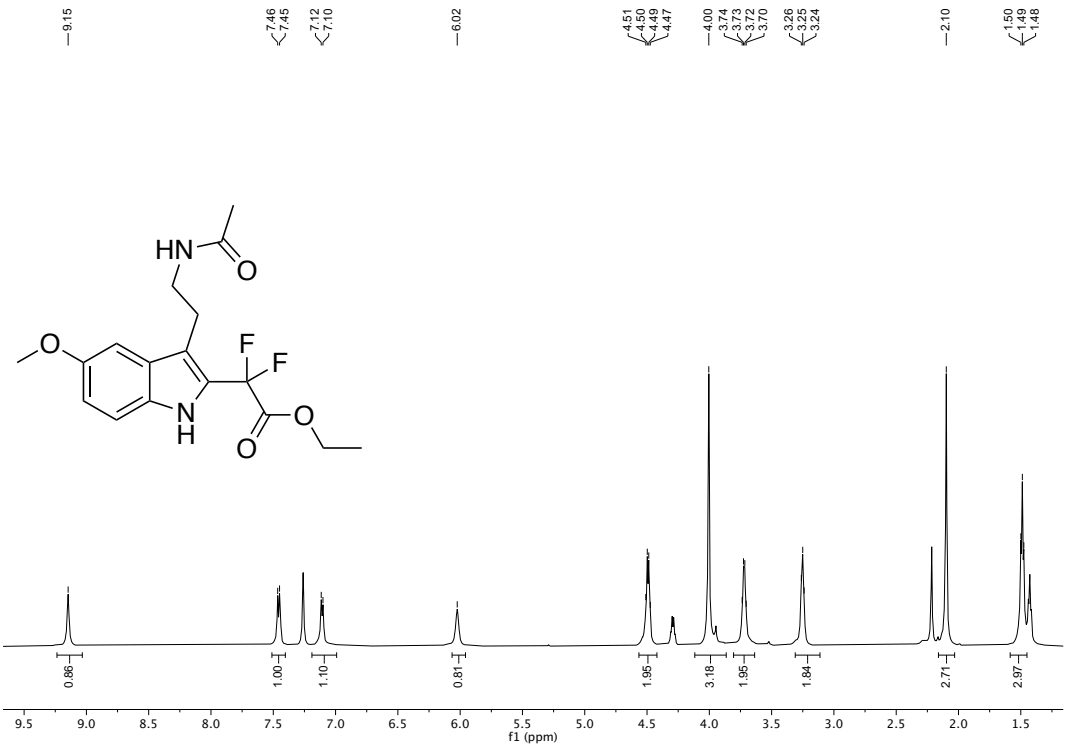
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4i**.



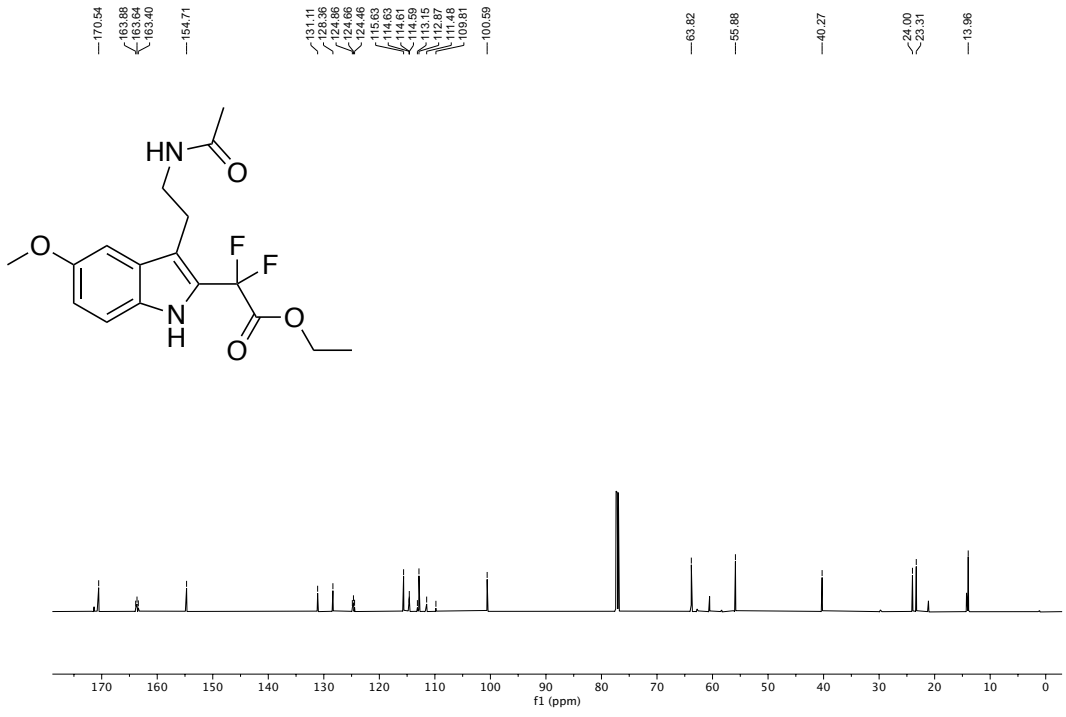
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4j**.



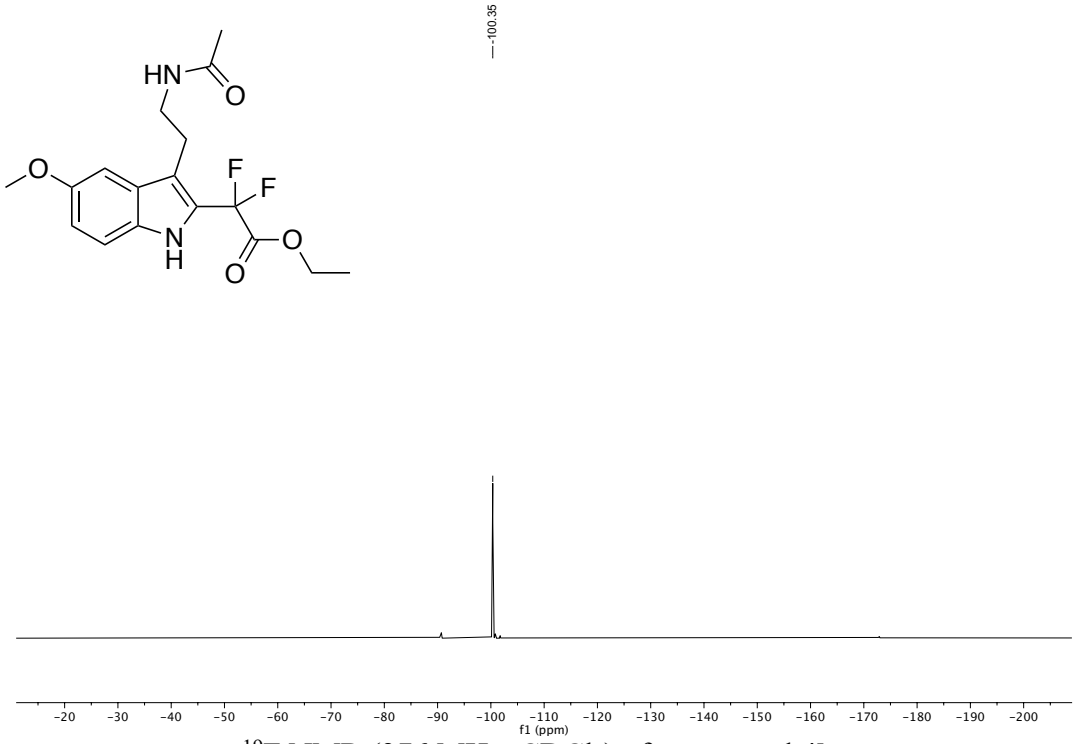
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4j**.



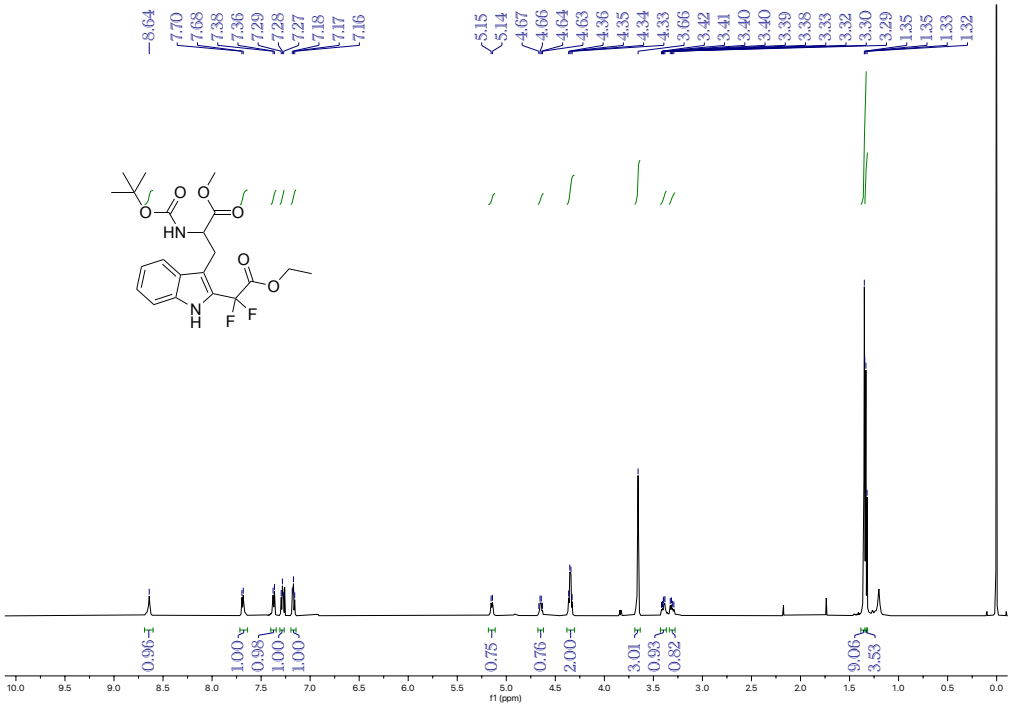
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4k**.



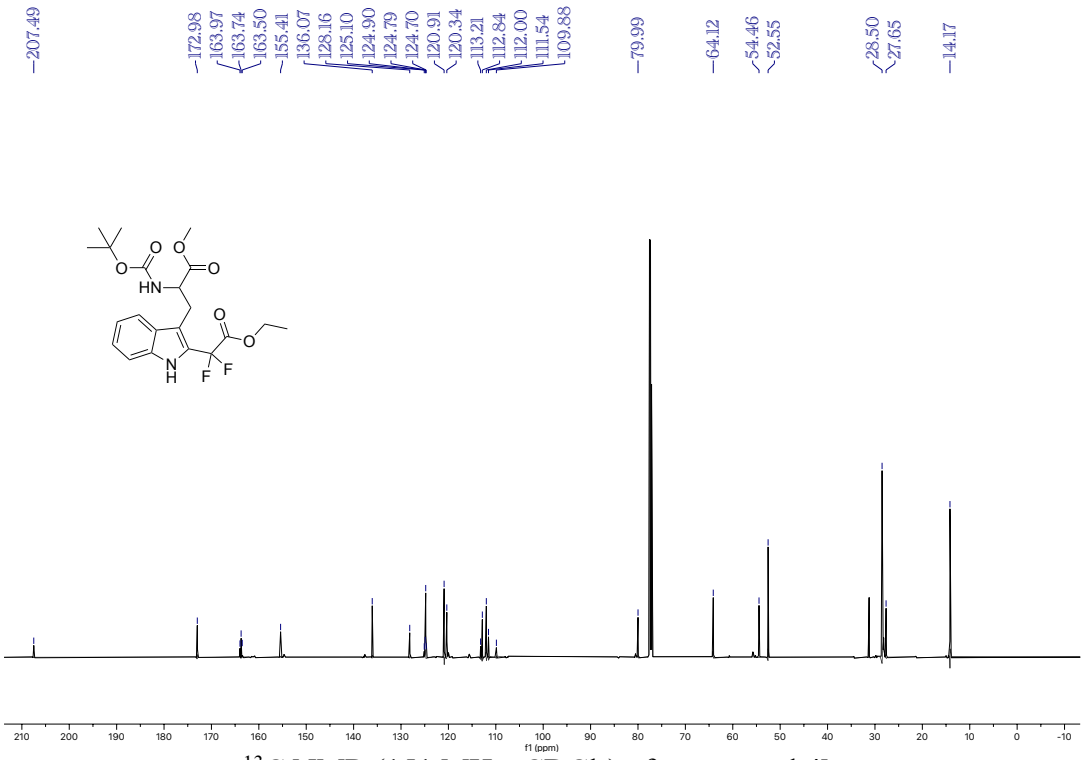
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4k**.



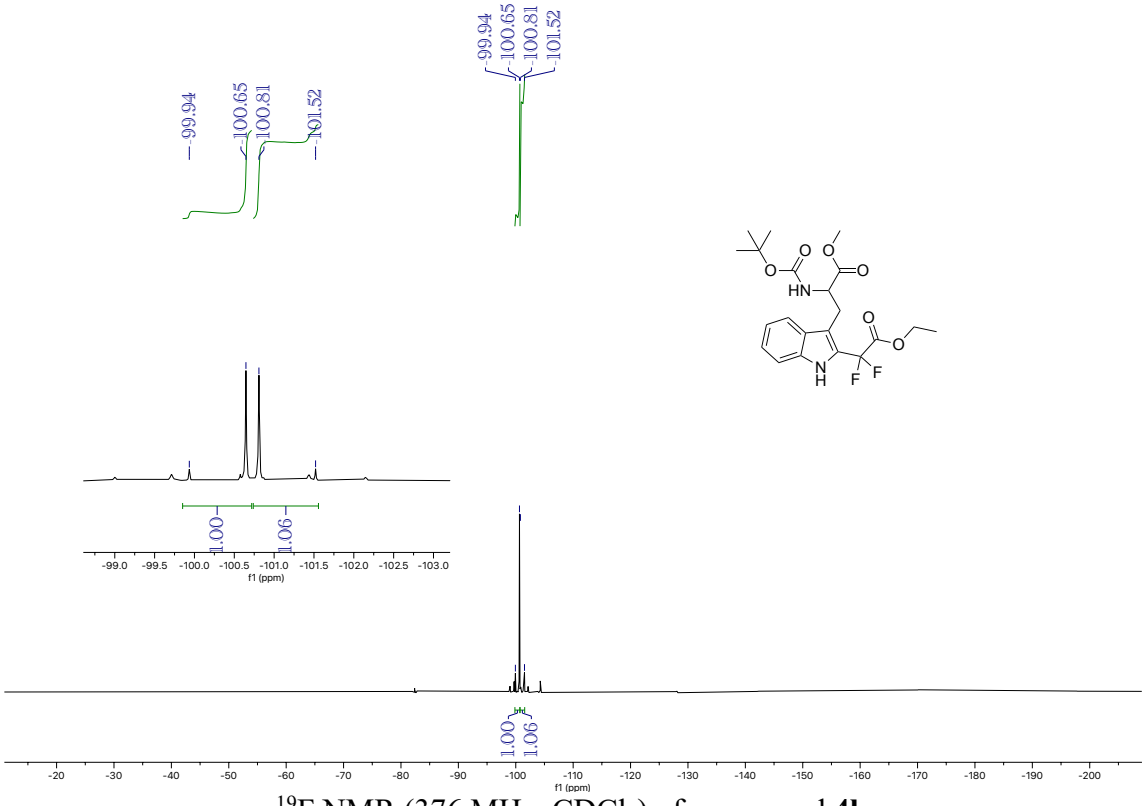
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4k**.



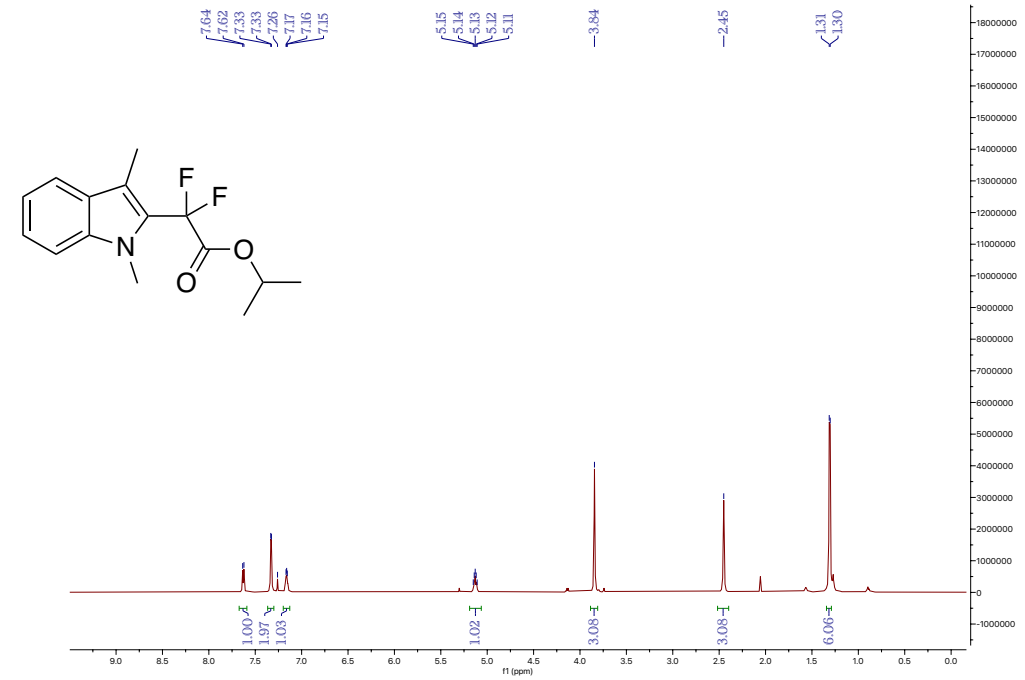
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4l**.



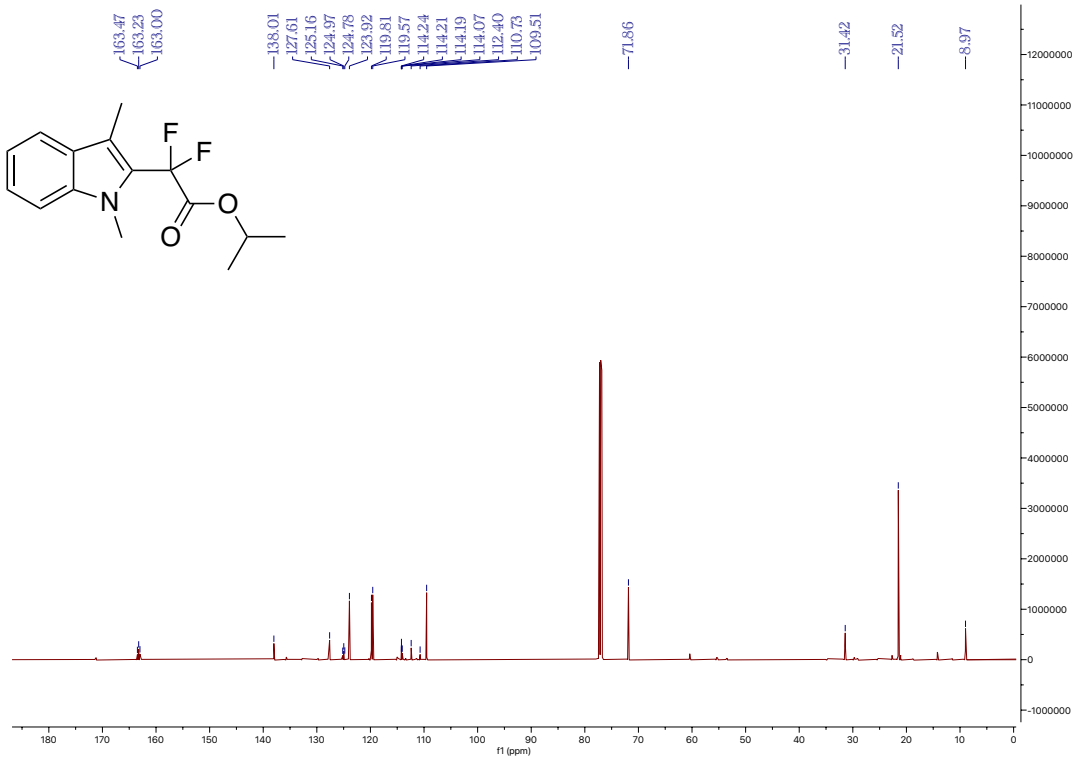
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4l**.



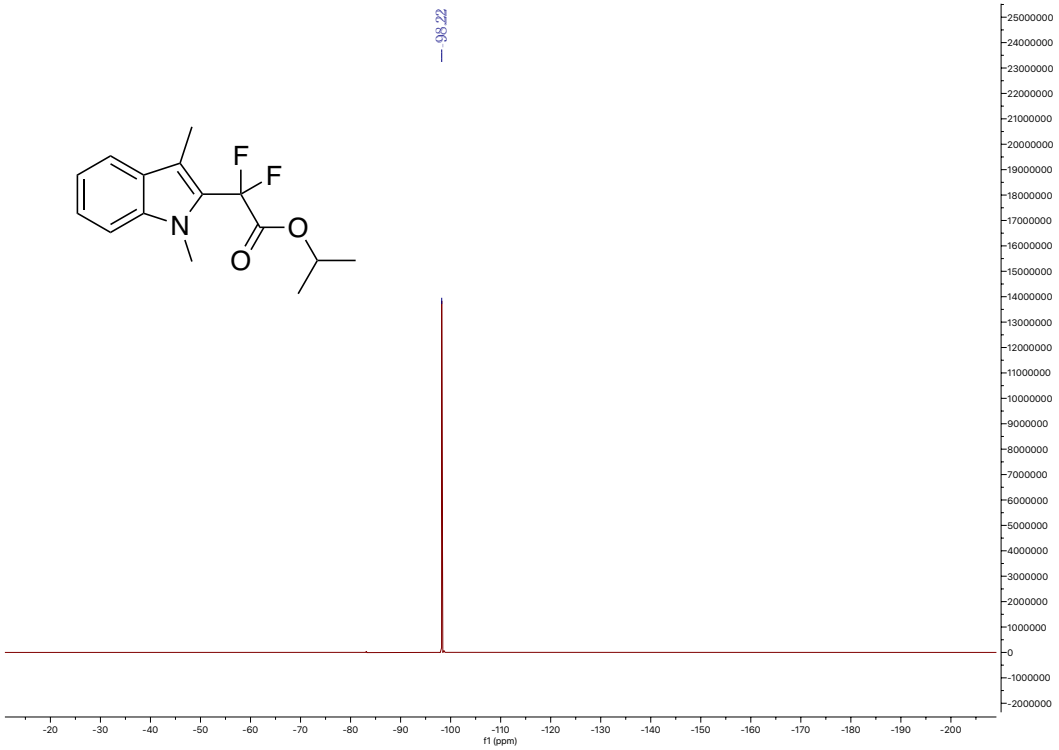
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4l**.



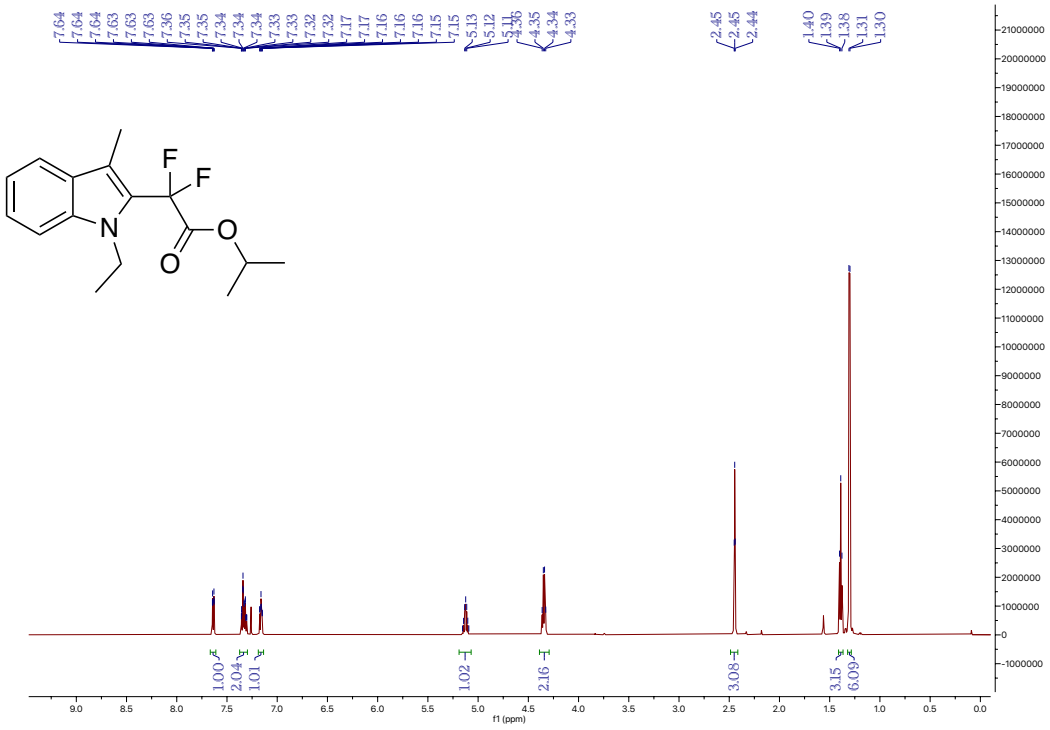
^{1}H NMR (600 MHz, $CDCl_3$) of compound **5**.



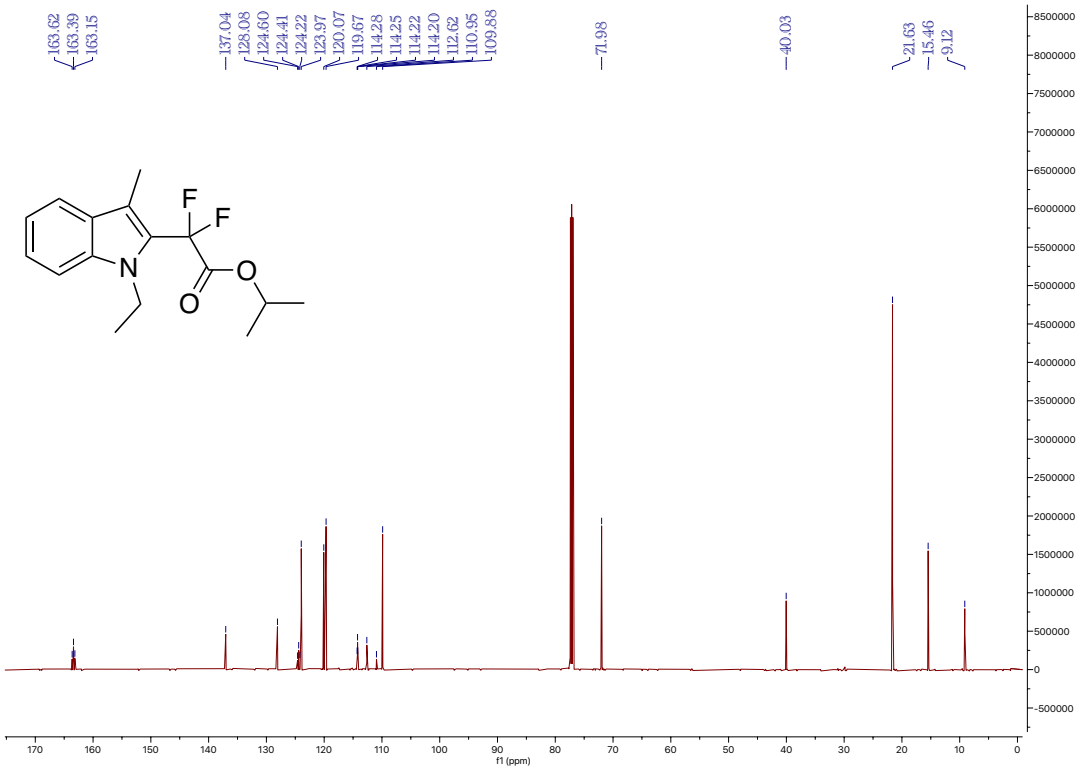
^{13}C NMR (151 MHz, $CDCl_3$) of compound **5**.



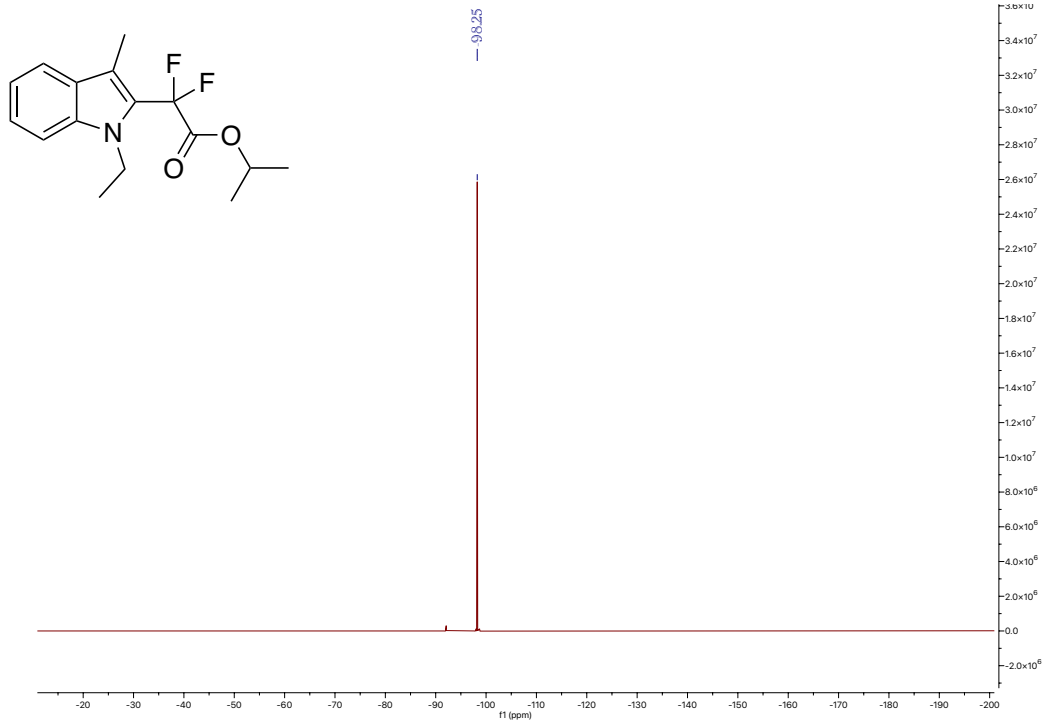
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5**.



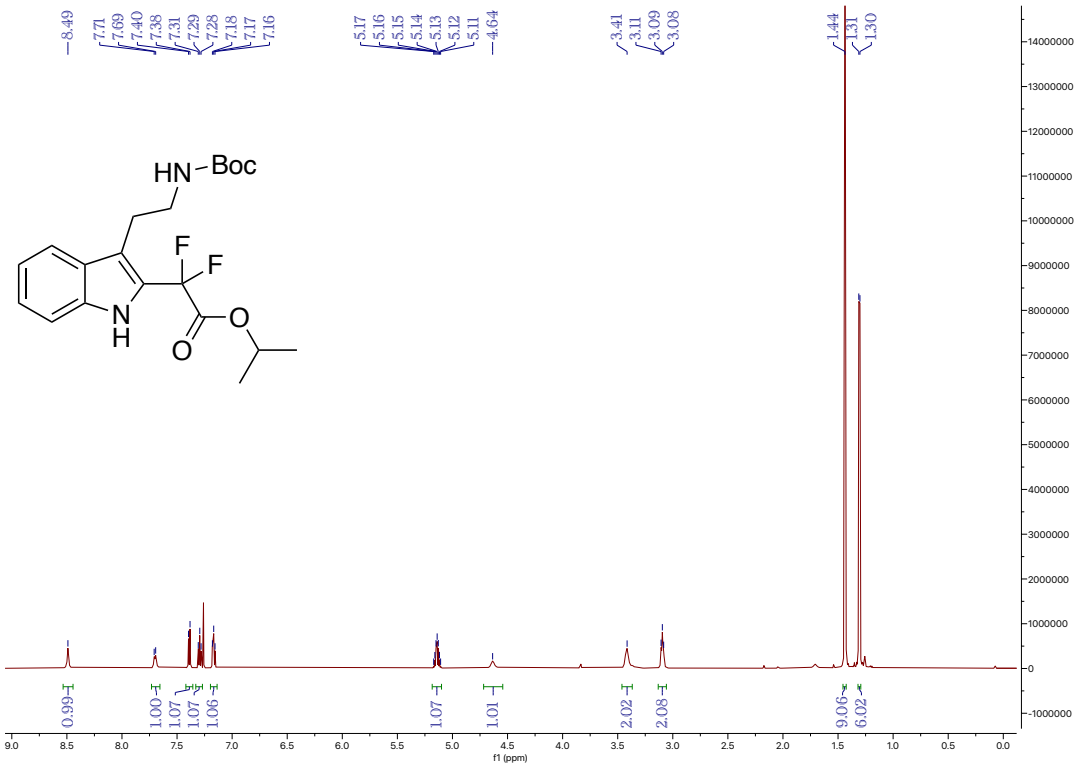
^{1}H NMR (600 MHz, $CDCl_3$) of compound **6**.



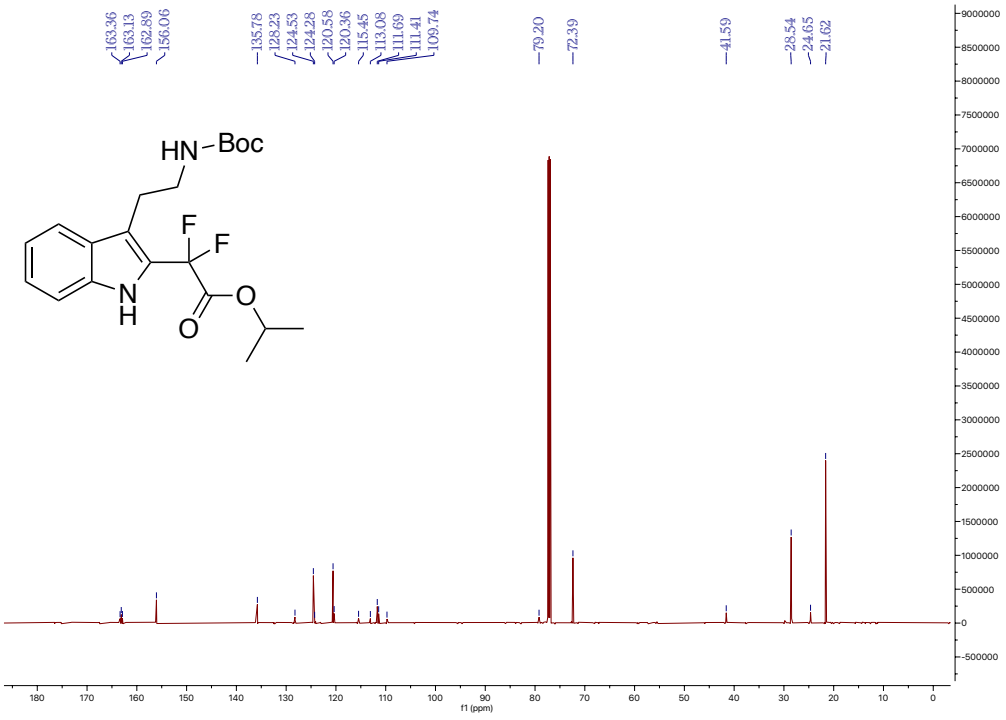
^{13}C NMR (151 MHz, $CDCl_3$) of compound **6**.



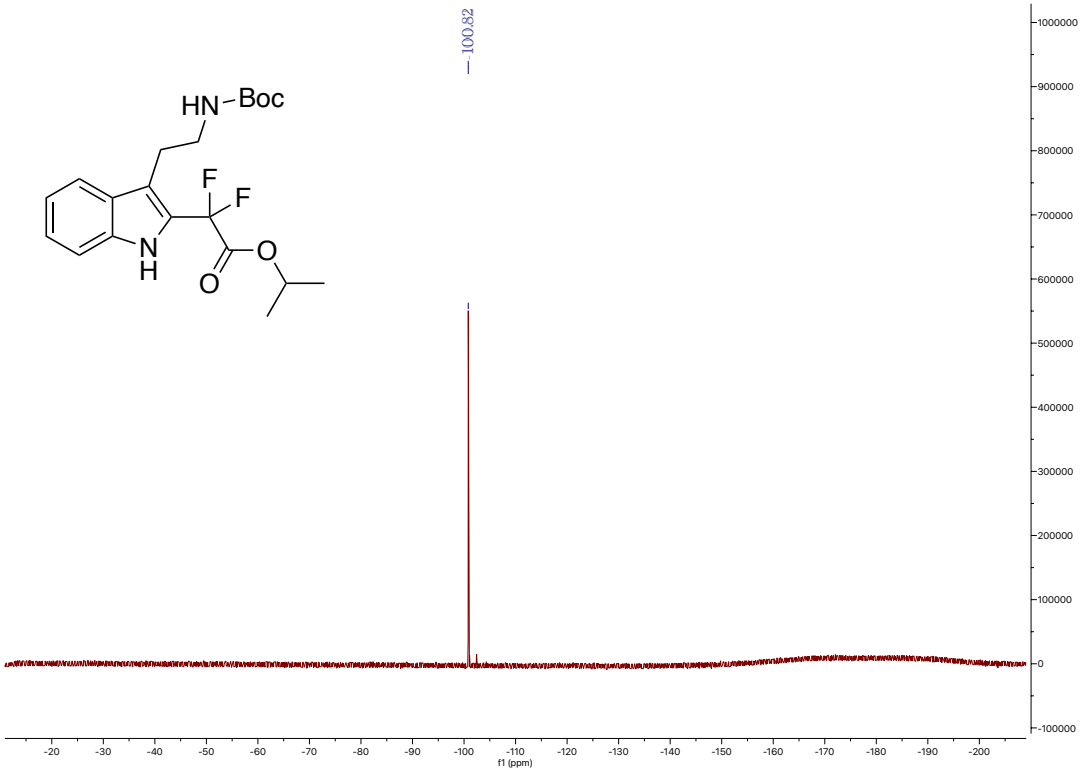
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6**.



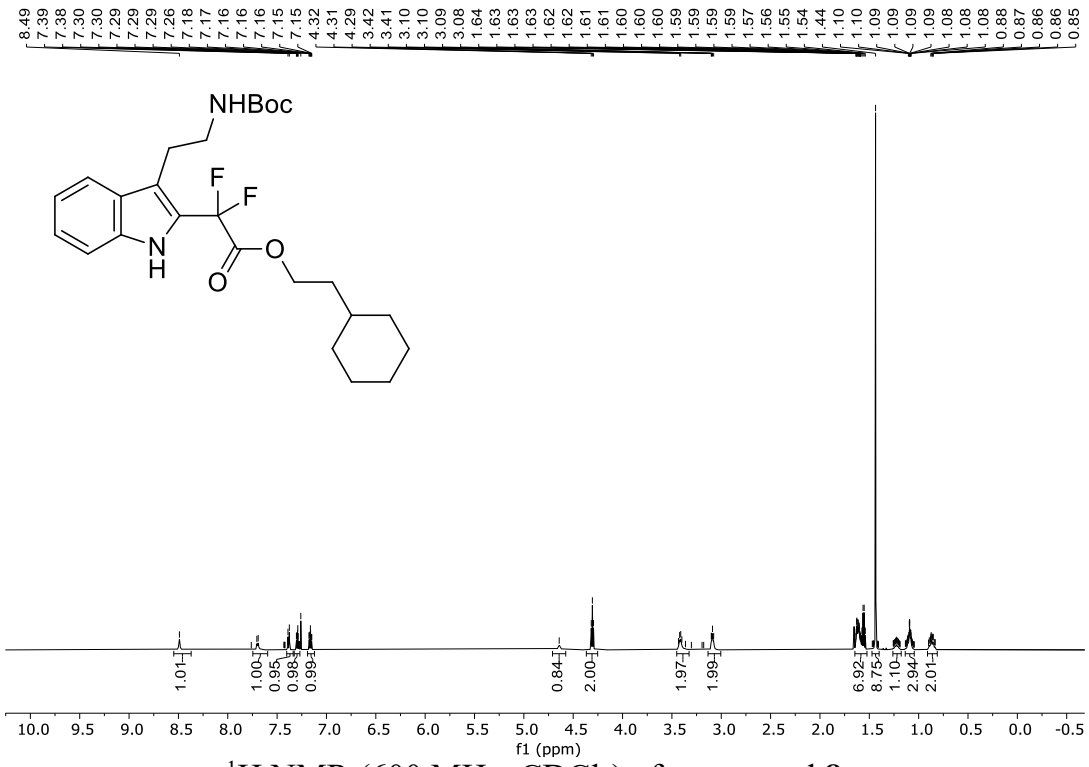
^{1}H NMR (600 MHz, $CDCl_3$) of compound **7**.



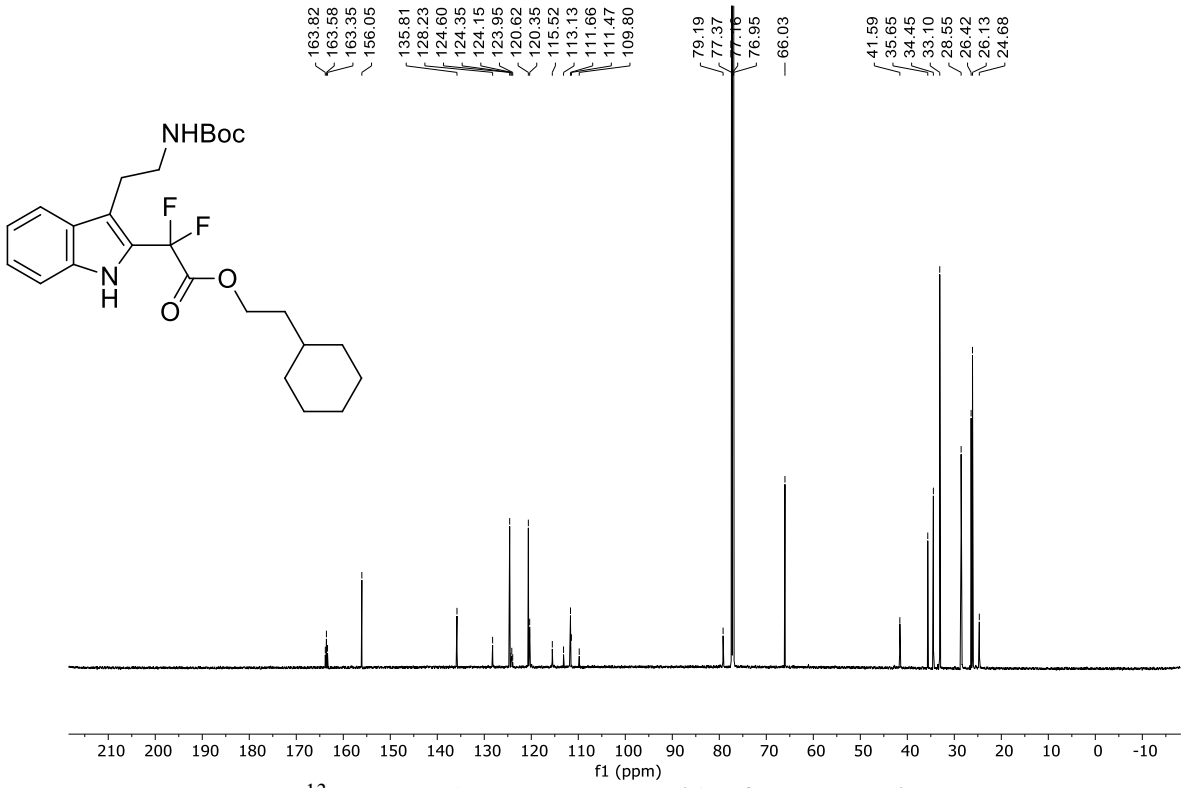
^{13}C NMR (151 MHz, $CDCl_3$) of compound **7**.



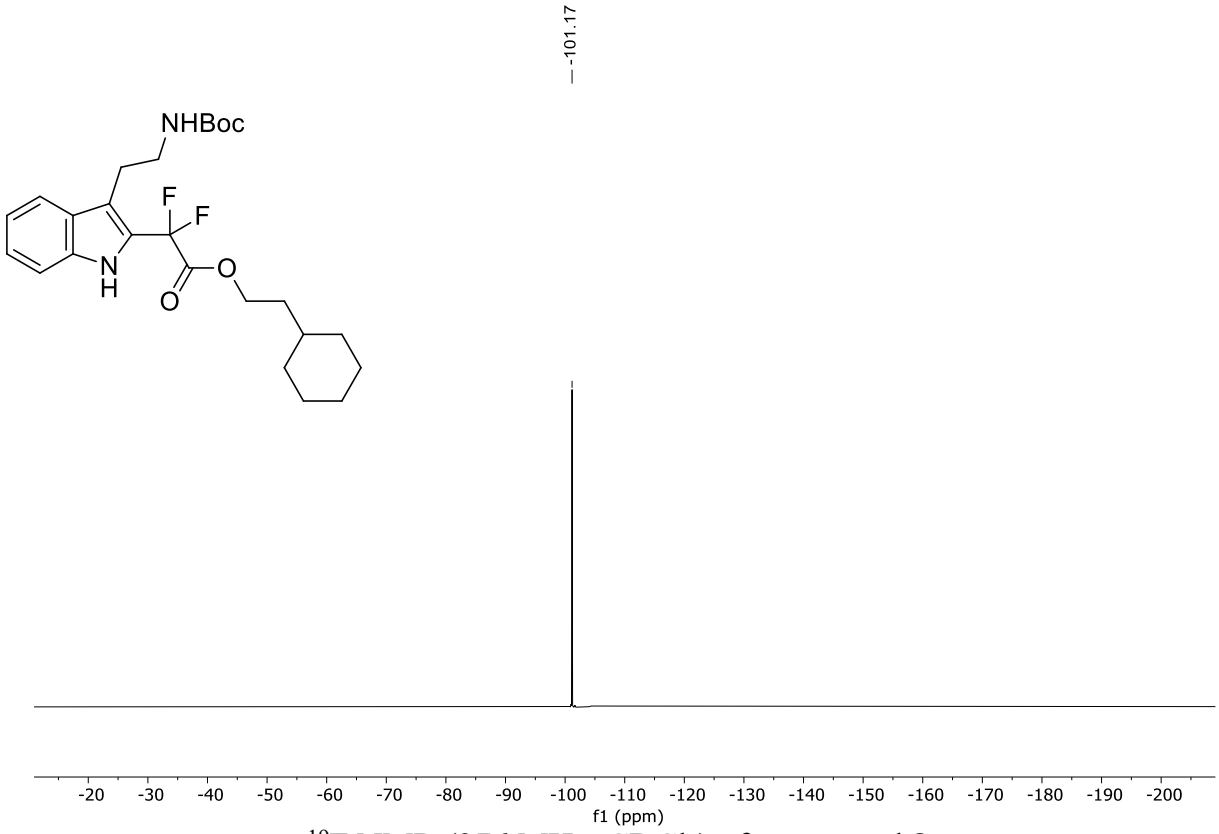
^{19}F NMR (376 MHz, $CDCl_3$) of compound **7**.



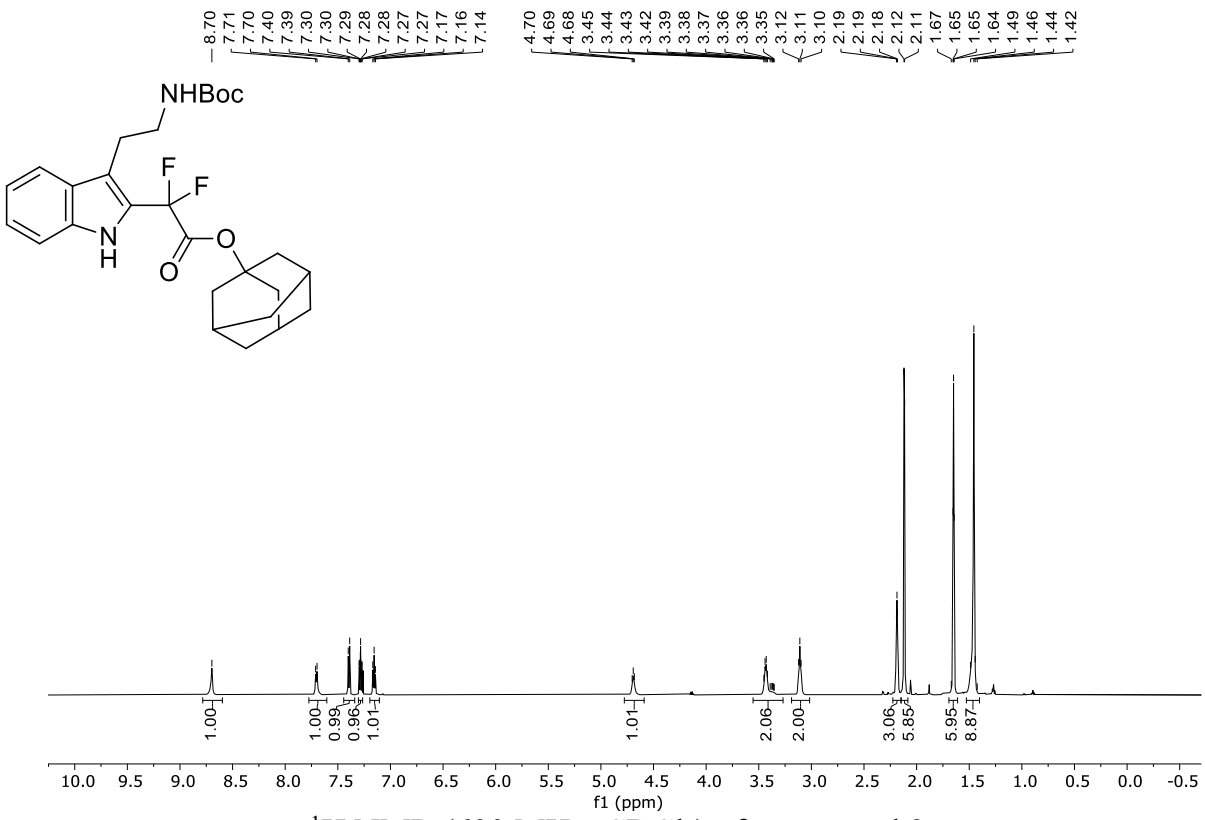
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8**.



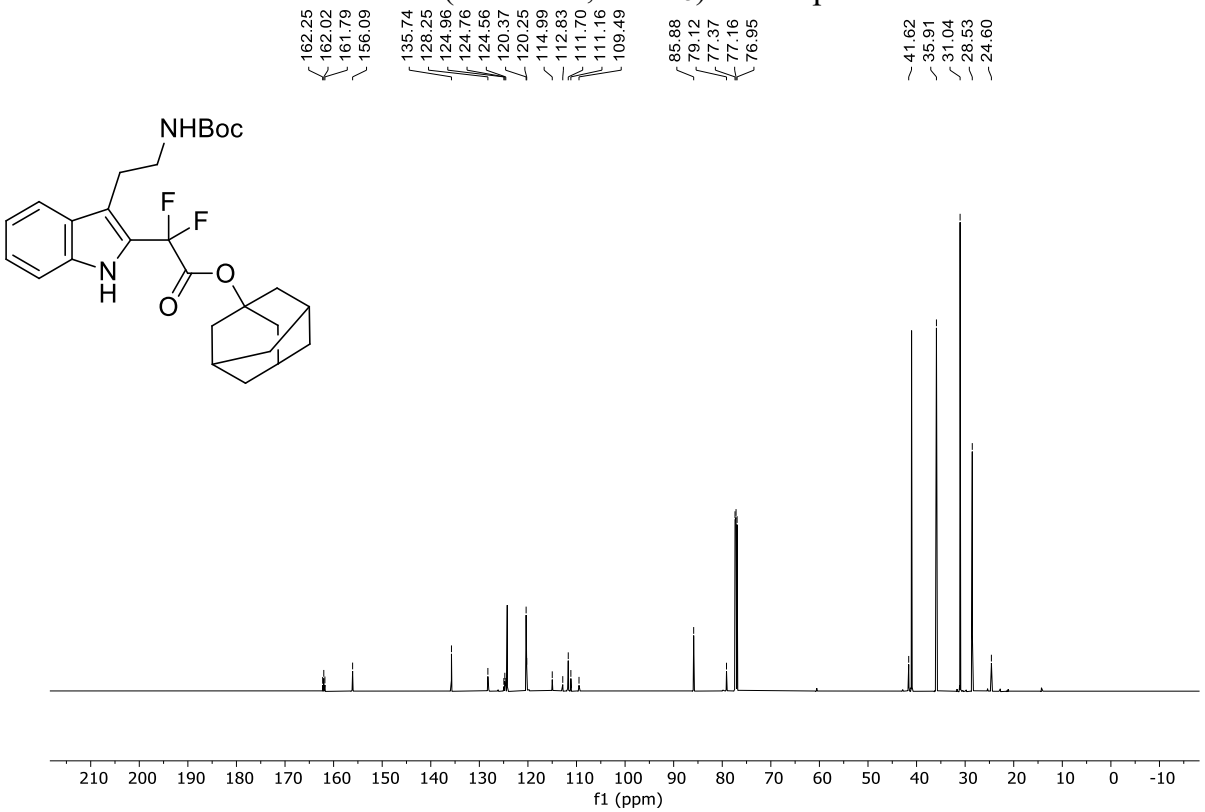
^{13}C NMR (151 MHz, $CDCl_3$) of compound **8**.



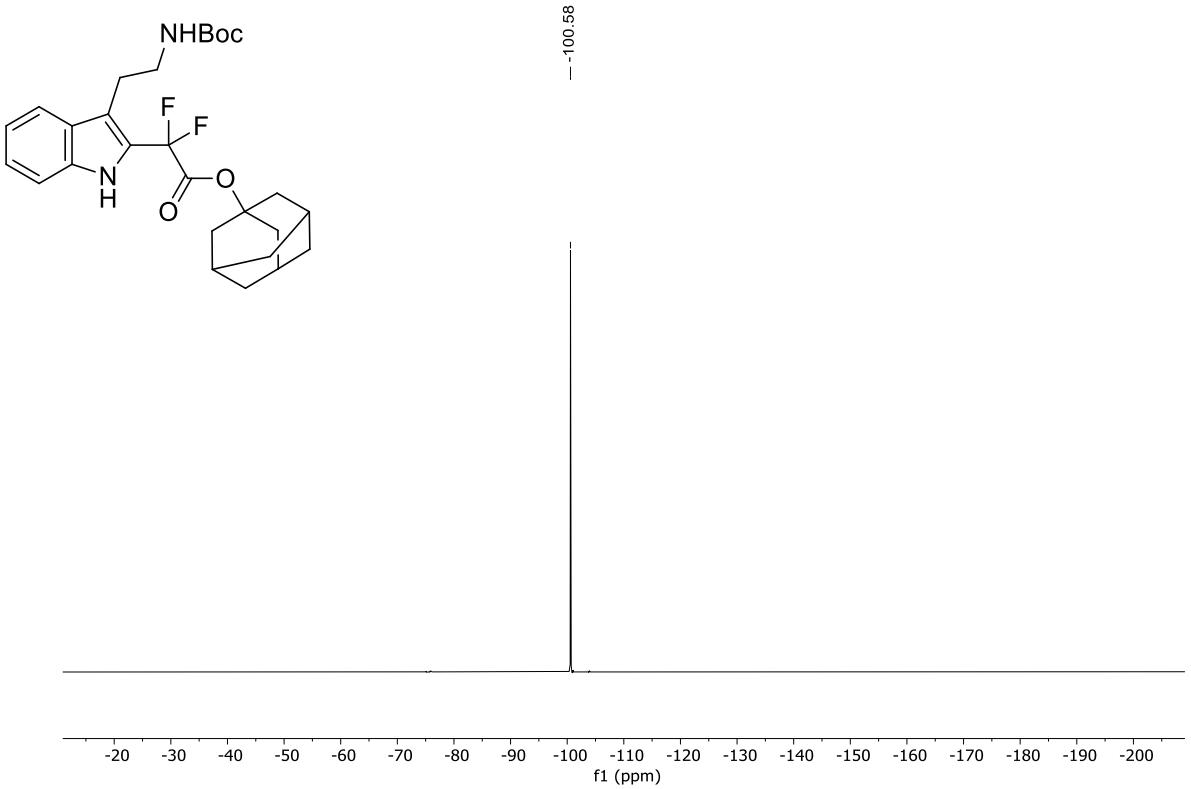
^{19}F NMR (376 MHz, $CDCl_3$) of compound **8**.



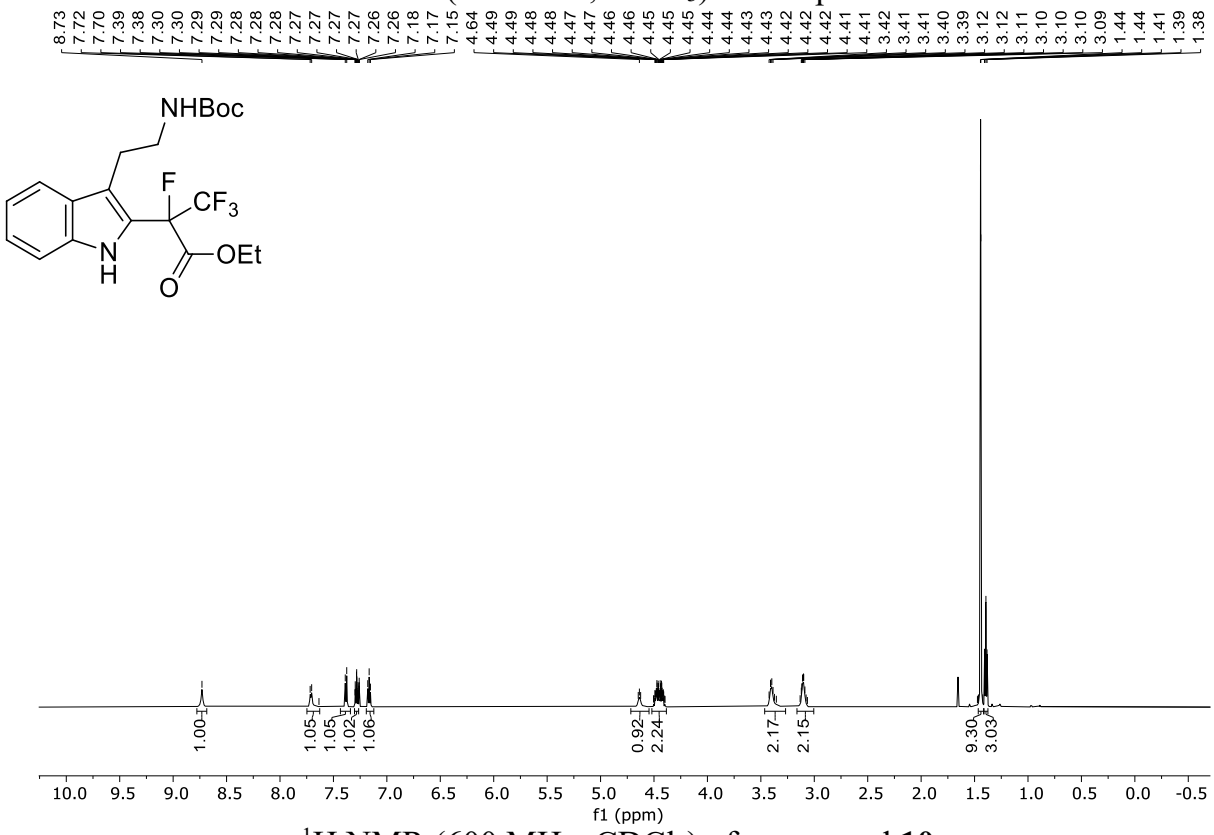
^{1}H NMR (600 MHz, $CDCl_3$) of compound **9**.



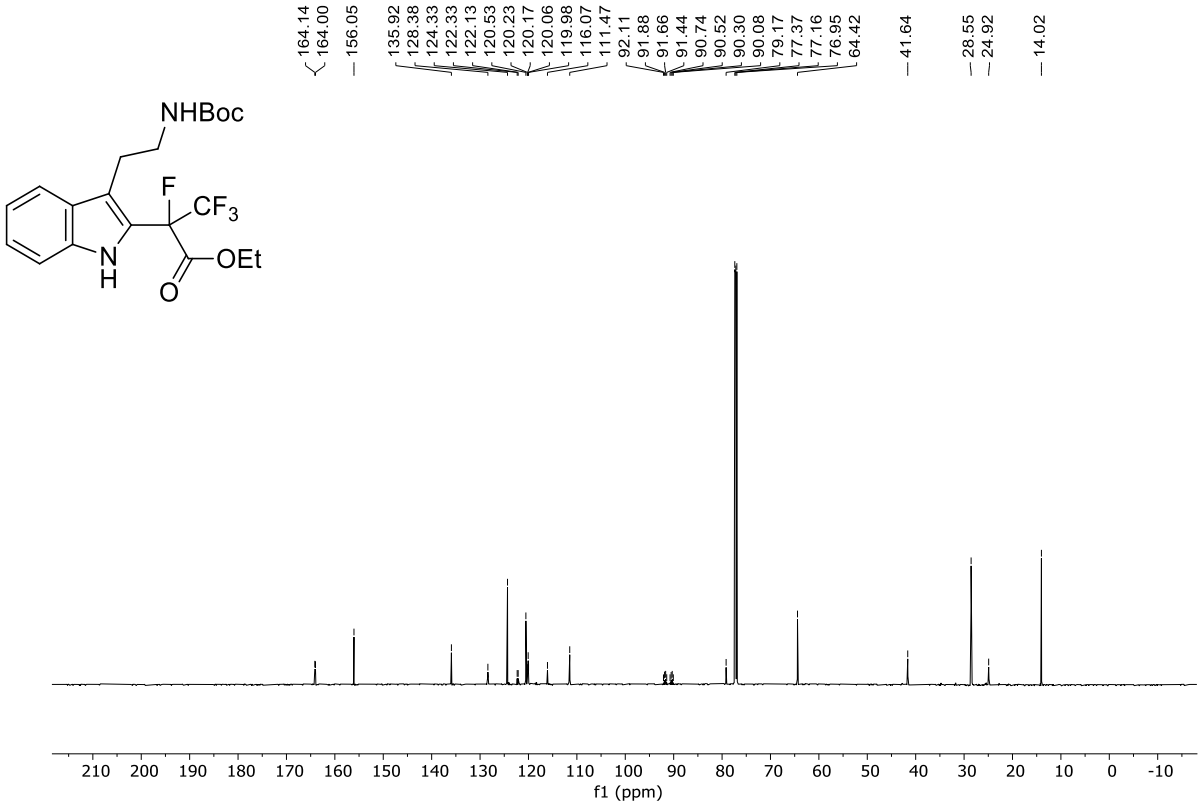
^{13}C NMR (151 MHz, $CDCl_3$) of compound **9**.



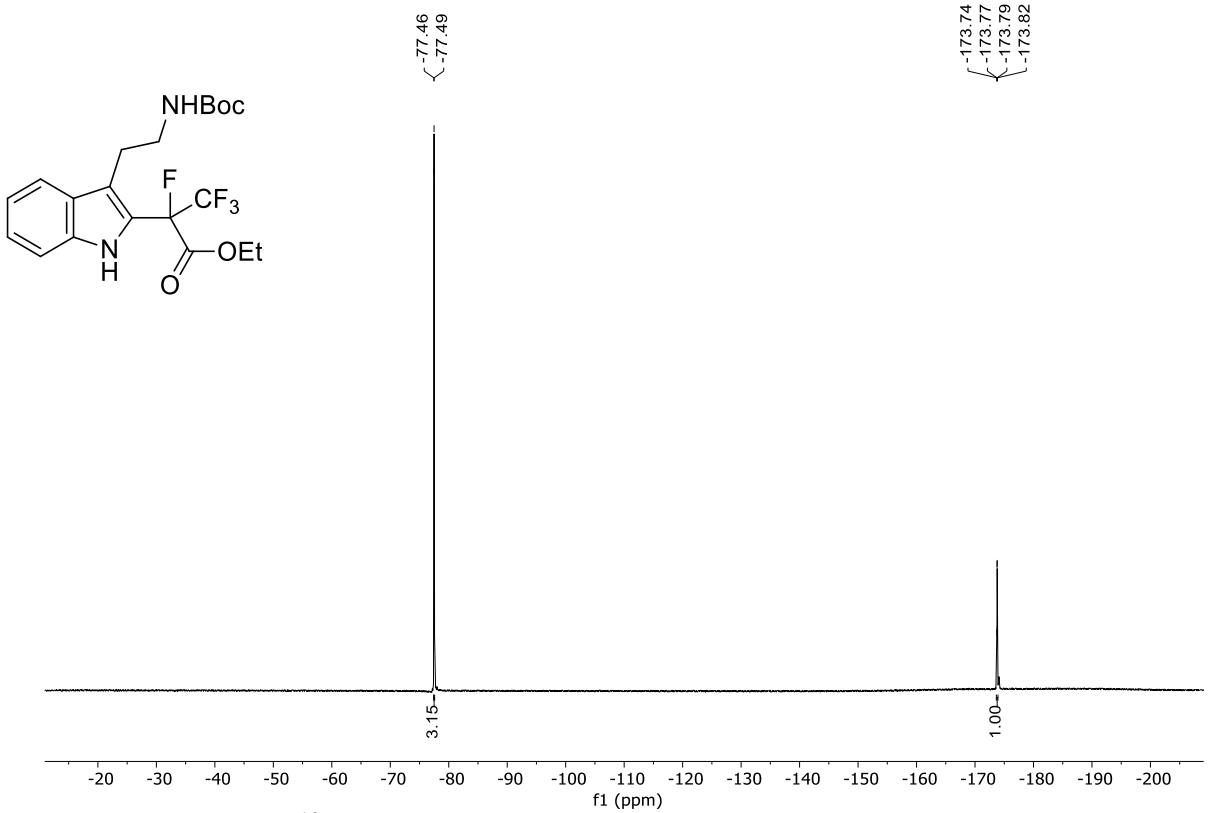
^{19}F NMR (376 MHz, $CDCl_3$) of compound **9**.



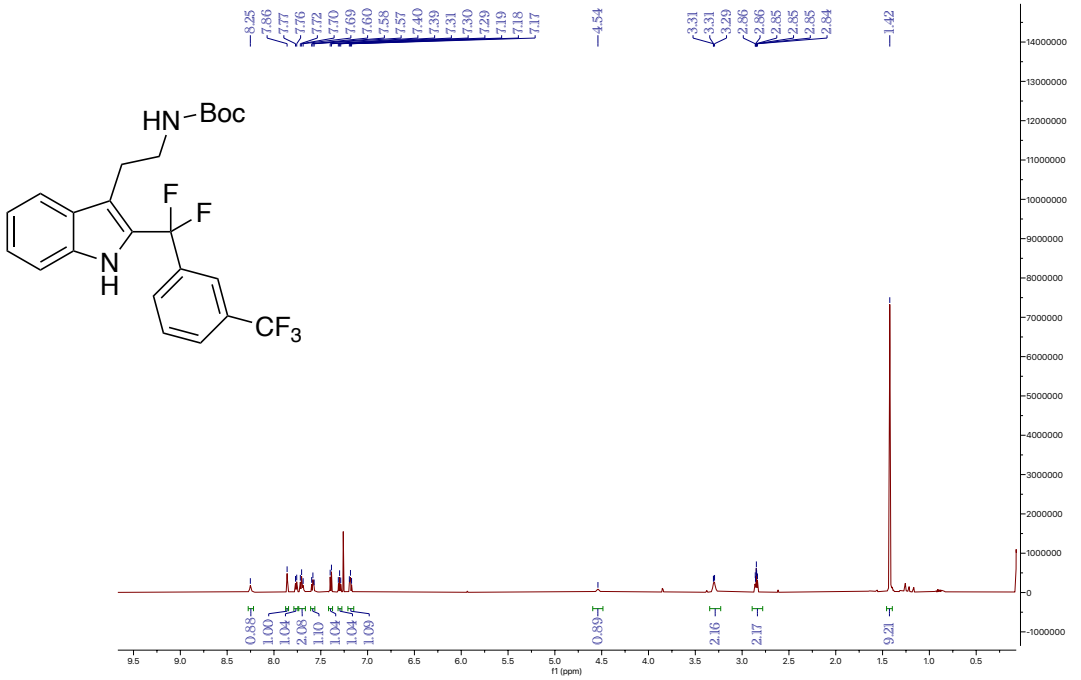
^{1}H NMR (600 MHz, $CDCl_3$) of compound **10**.



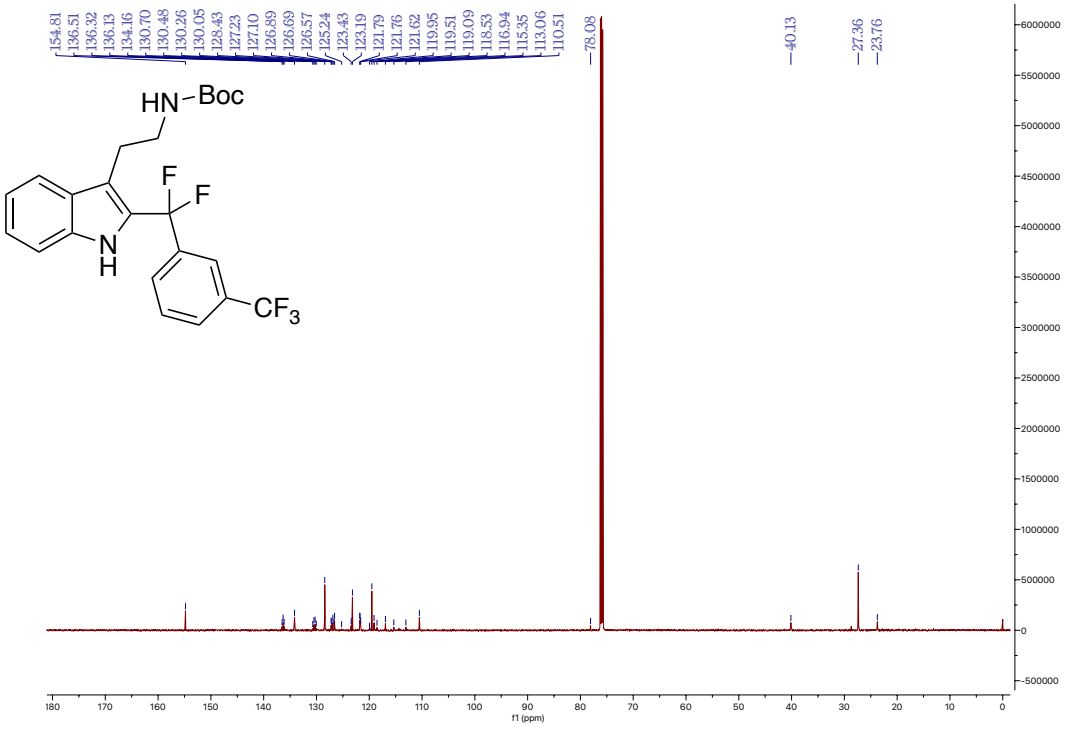
^{13}C NMR (151 MHz, $CDCl_3$) of compound **10**.



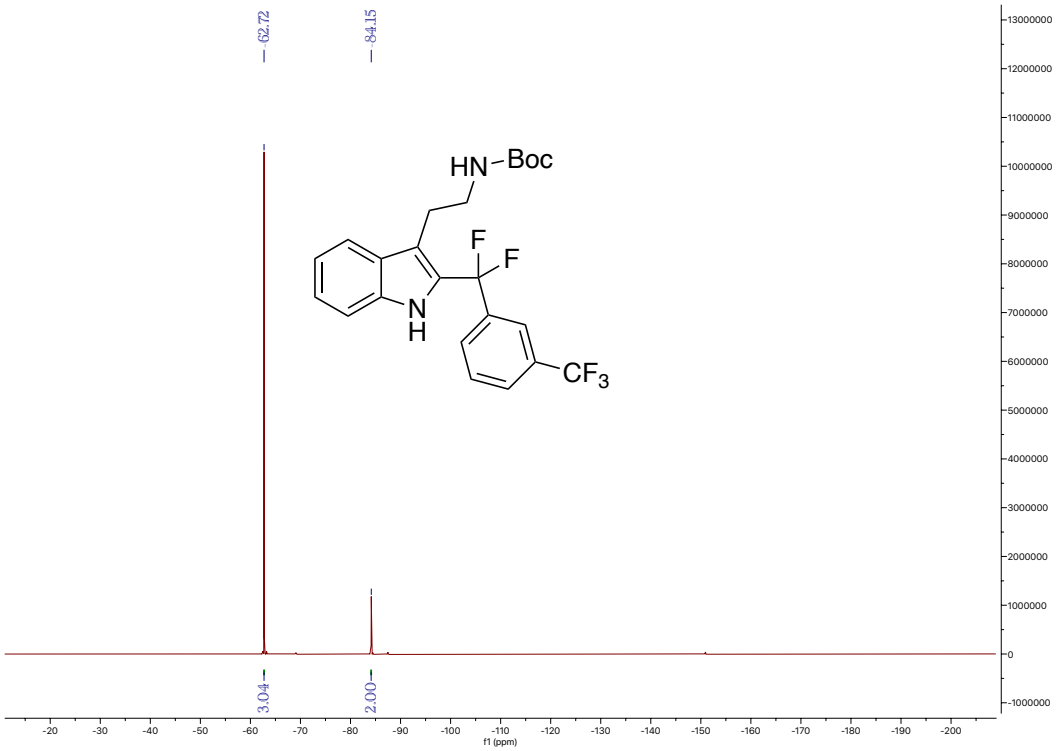
^{19}F NMR (376 MHz, $CDCl_3$) of compound **10**.



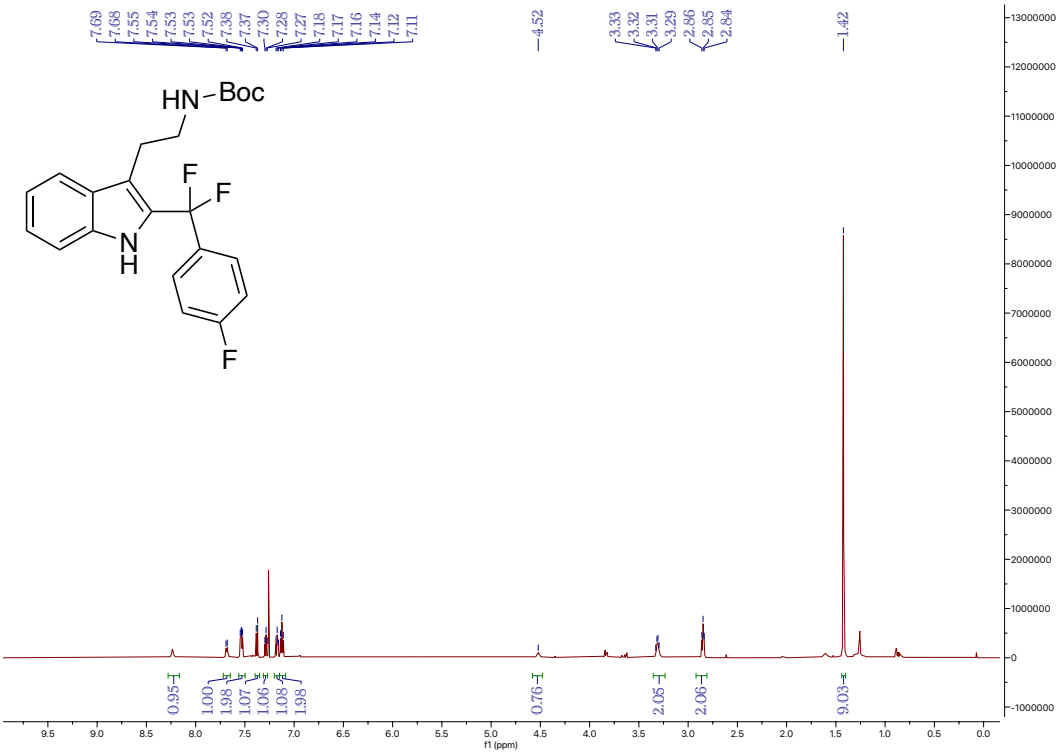
^{1}H NMR (600 MHz, $CDCl_3$) of compound **11**.



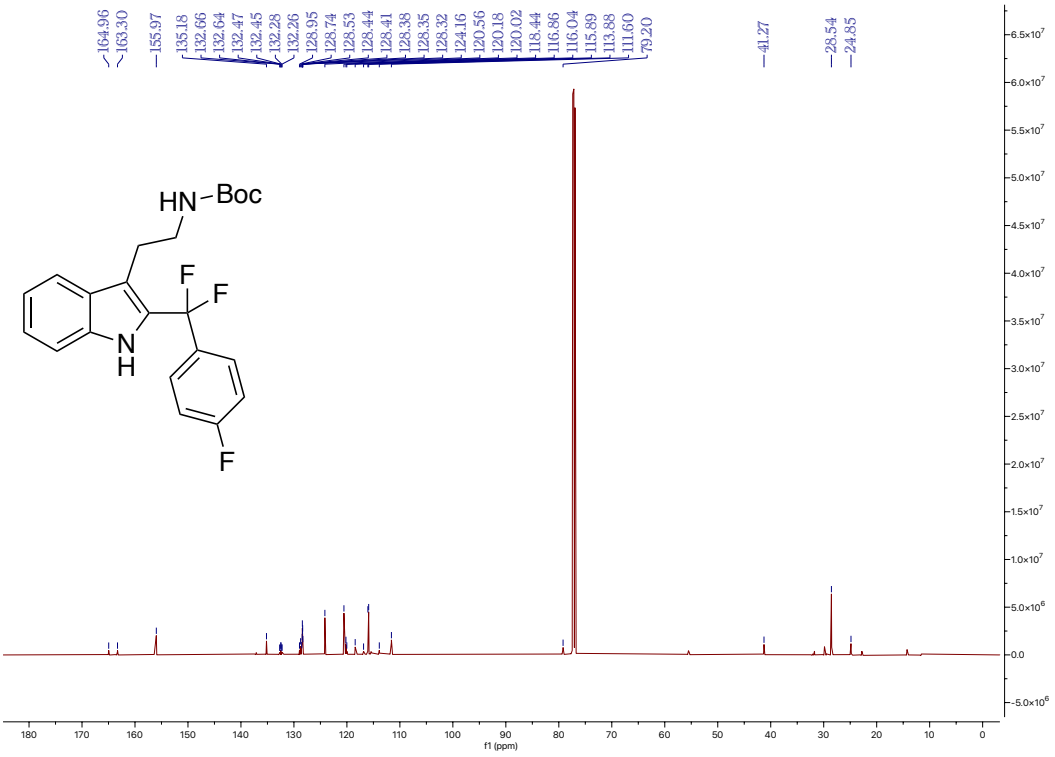
^{13}C NMR (151 MHz, $CDCl_3$) of compound **11**.



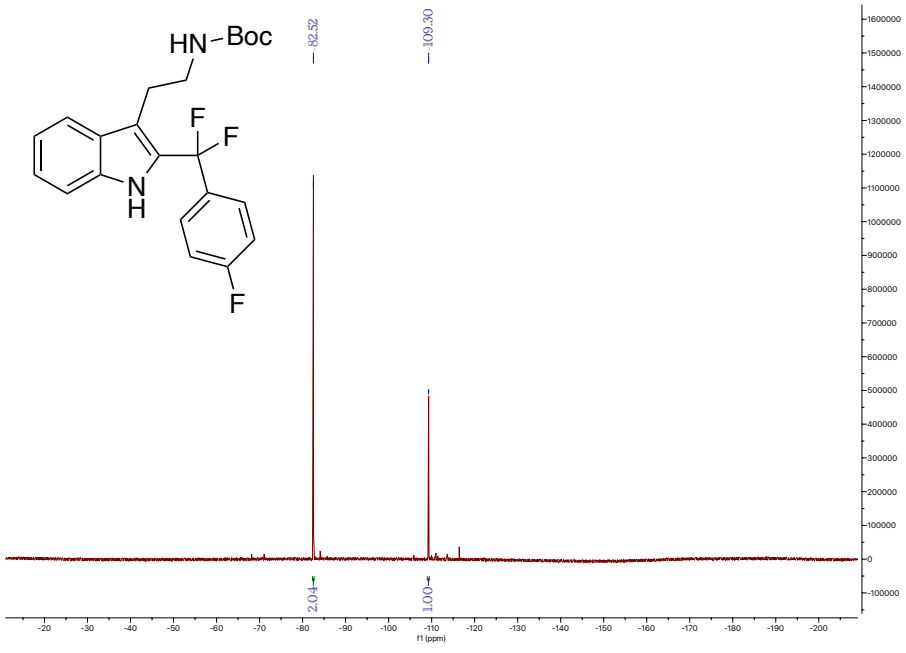
^{19}F NMR (376 MHz, $CDCl_3$) of compound **11**.



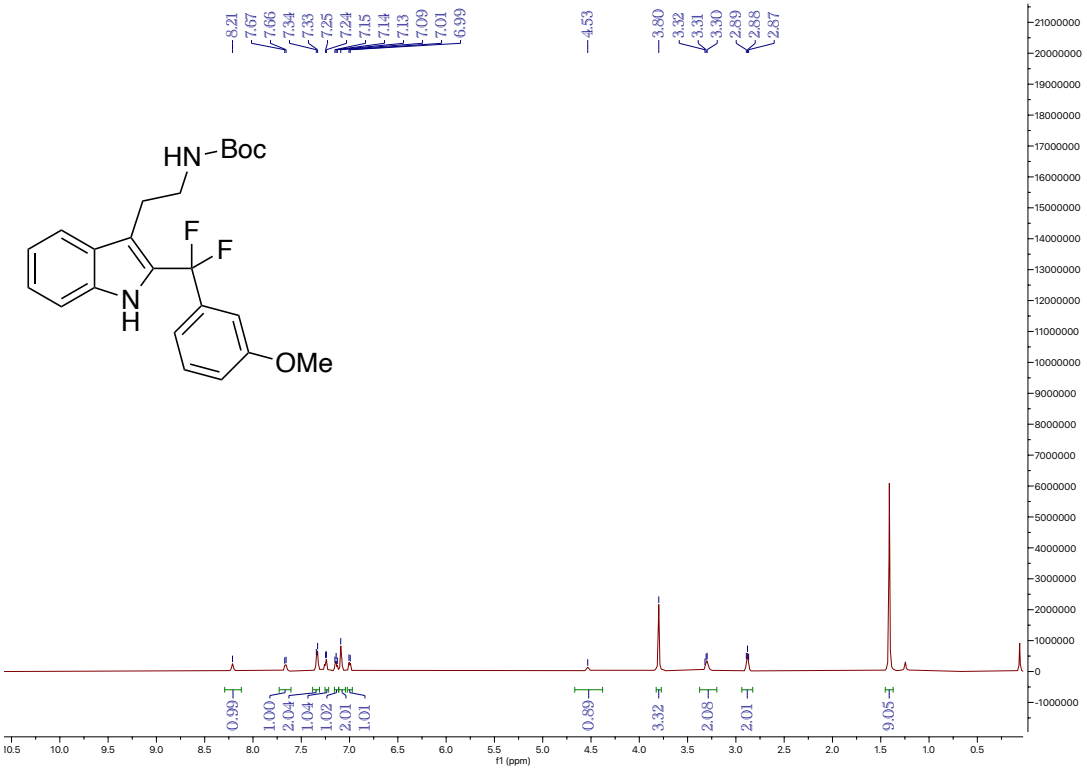
^{1}H NMR (600 MHz, $CDCl_3$) of compound **12**.



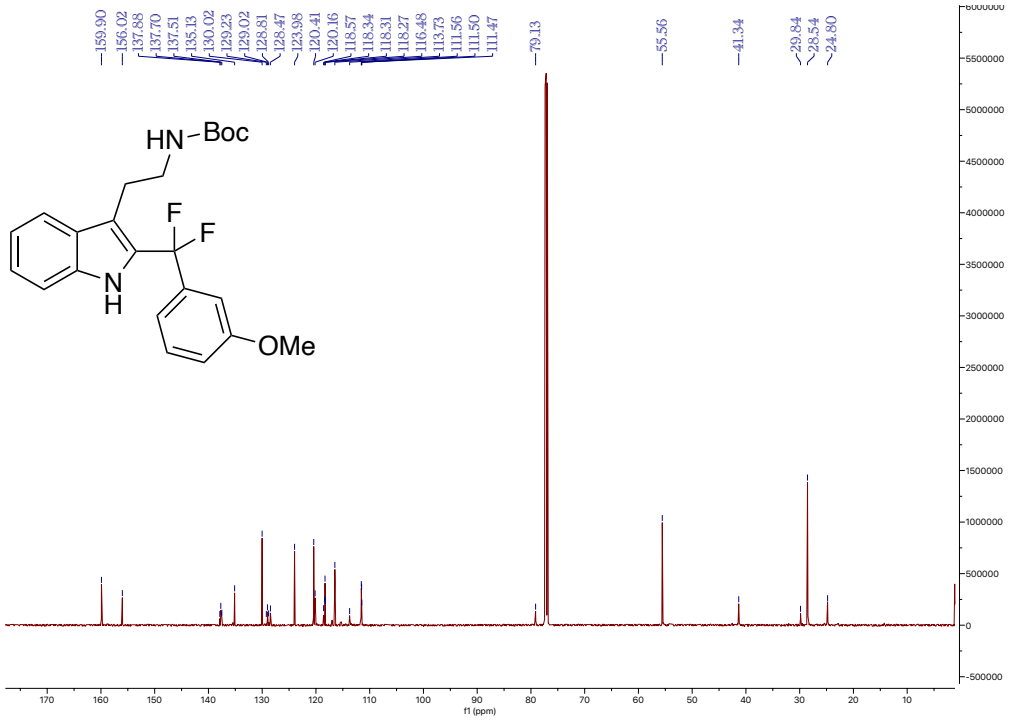
^{13}C NMR (151 MHz, $CDCl_3$) of compound **12**.



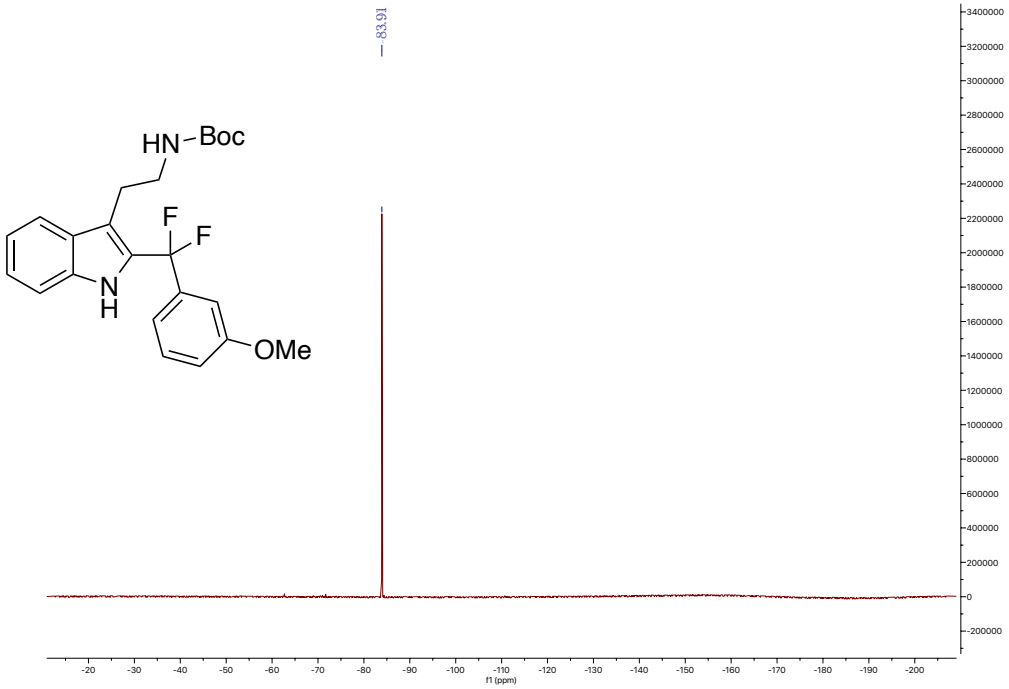
^{19}F NMR (376 MHz, $CDCl_3$) of compound **12**.



^{1}H NMR (600 MHz, $CDCl_3$) of compound **13**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **13**.



^{19}F NMR (376 MHz, $CDCl_3$) of compound **13**.

6. References

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