Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Photocatalytic C2-Trifluoroethylation and Perfluoroalkylation of 3-Substituted Indoles Using Fluoroalkyl Halides

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Supporting Information

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1. General Information

Unless otherwise noted, all chemicals were purchased from commercial sources and used without further purification. Yields refer to chromatographically pure material. All solvents were used as purchased, without purification. DMSO was used as after drying. Reactions were monitored by thin-layer chromatography (TLC) performed on 0.25 mm Merck silica gel plates (60F-254) using UV light. Merck silica gel (mesh size 100-200) was used for flash column chromatography. NMR spectra were recorded on JEOL 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer in $CDCl_3$ having TMS 0.03% as internal standard. ^{19}F NMR were recorded using $CDCl_3$. Mass spectrometric data were obtained using WATERS-Q-TOF Premier-ESI-MS and GC-MS.Crystal structure data for **3a** has been deposited in the Cambridge Crystallographic Data Centre with ID: CCDC No. 2322591. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of doublet, m = multiplet. All starting materials were prepared according to the literature reports.[12]

The photocatalytic device was made by wrapping an LED strip around a 250 mL beaker. The emission of the LED was recorded and is shown below (425- 500 nm). Total power was computed to be 18W.

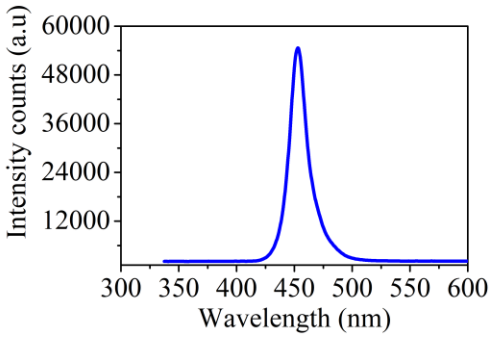
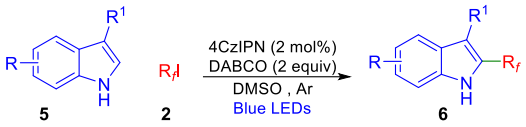


Figure 1: Emission profile of the LEDs

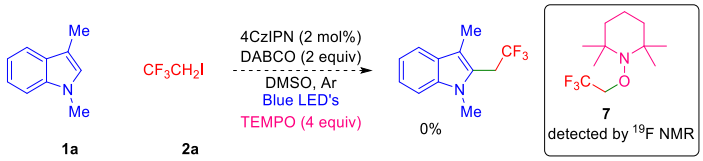
2. General Procedure



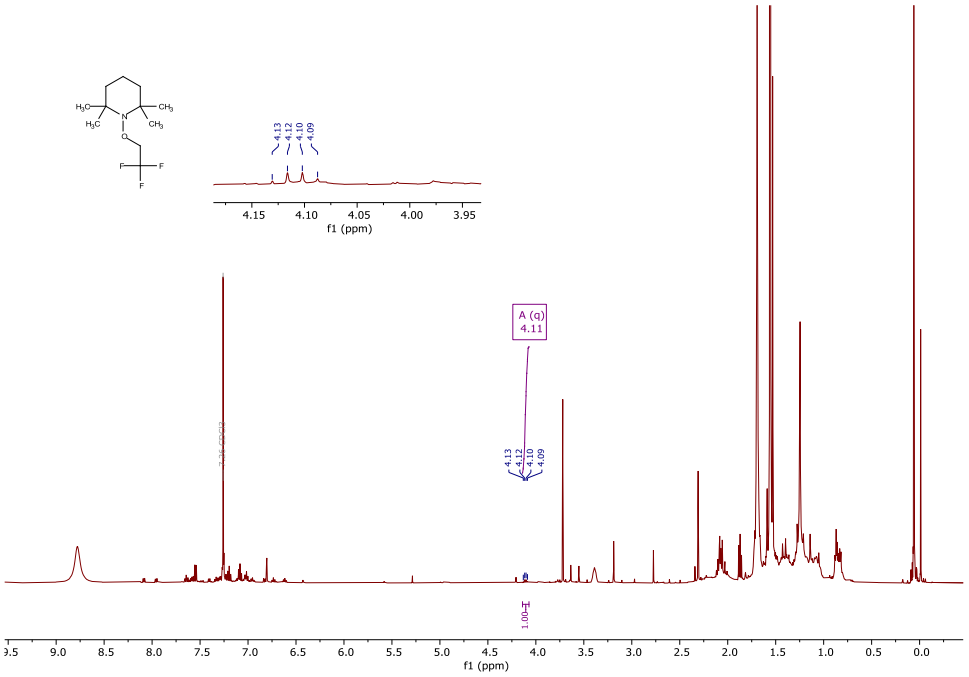
An oven dried reaction vial equipped with magnetic stir bar was charged with the indole derivative (1 equiv.), trifluoroethyliodide or perfluoroalkyliodide (2.0 equiv.), DABCO (2 equiv.), 4CzIPN (2 mol%), and then dry DMSO (2 mL) was added. The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LEDs. After completion of reaction (confirmed by TLC), reaction mixture was concentrated in vacuum. The residue was purified by column chromatography on silica gel using ethyl acetate in petroleum ether to afford the desired product.

3. Control Experiments

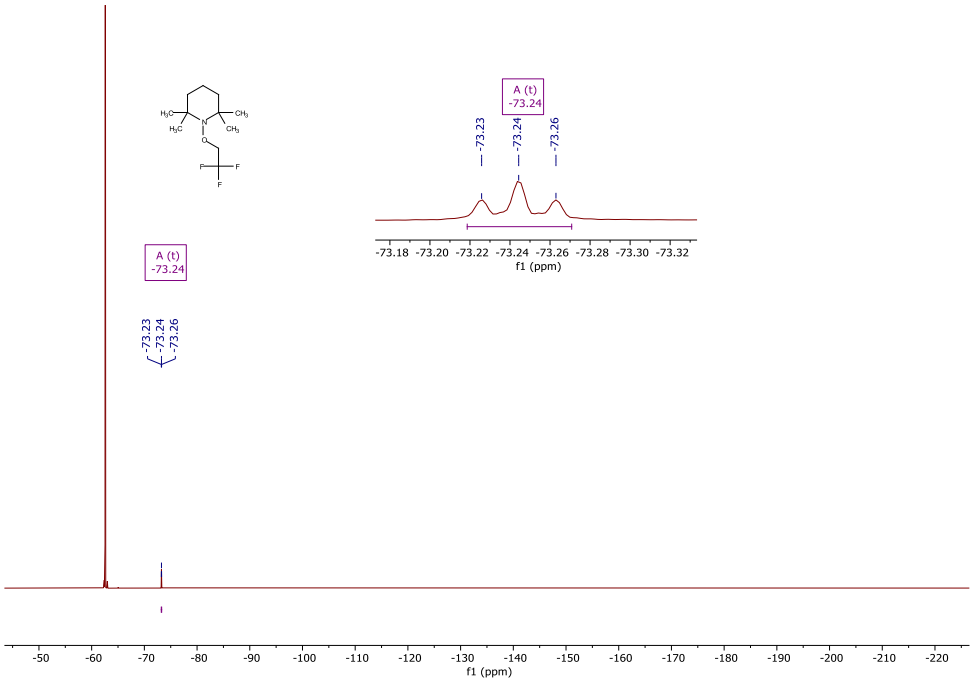
3.1. Procedure for Experiment with TEMPO:



Procedure: In an oven dried reaction vial equipped with a magnetic stir bar, **1a** (50 mg, 0.34 mmol), **2a** (2 equiv), DABCO (2 equiv), TEMPO (4 equiv) and 4CzIPN catalyst (2 mol%) were dissolved in 2 mL of dry DMSO. The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LED's. After 24 h TLC (Thin layer chromatography) no product formation was observed with TEMPO. We were able to detect TEMPO adduct **7** using ^{1}H and ^{19}F NMR spectroscopy of a crude sample.

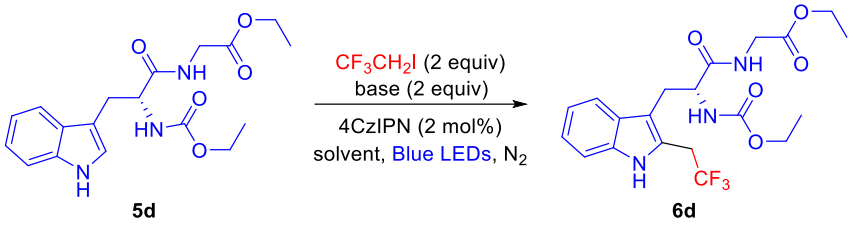


^{1}H NMR (500 MHz) spectrum of compound **7** in $CDCl_3$



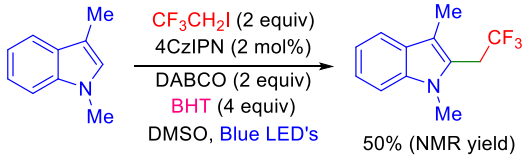
^{19} F NMR (471 MHz) spectrum of compound **7** in $CDCl_3$ with $PhCF_3$ as reference standard.

3.2 Additional Optimization for Trifluoroethylation of Peptides



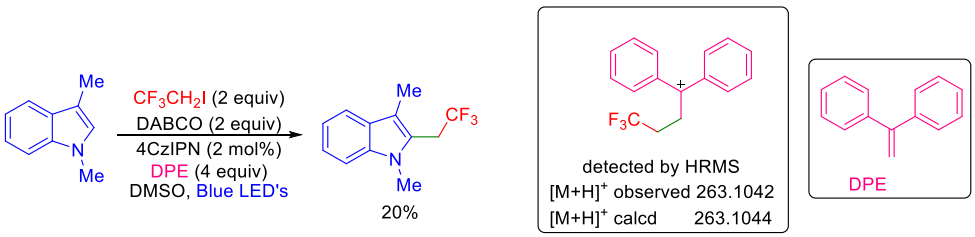
S.No.	Solvent	Base	Yield (%)
1	DMSO	K_2CO_3	29
2	DMSO	Cs_2CO_3	20
3	DMSO	Na_2CO_3	29
4	DMSO	DIPEA	00
5	THF	DABCO	00
6	DCE	DABCO	10
7	MeCN	DABCO	20

3.3. Procedure for Experiment with BHT:



Procedure: In an oven dried reaction vial equipped with a magnetic stir bar, **1a** (50mg, 0.34 mmol), **2a** (2 equiv), DABCO (2 equiv), BHT (4 equiv) and 4CzIPN catalyst (2 mol%) were dissolved in 2 mL of dry DMSO. The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LED's. After 24 h TLC (Thin layer chromatography) product formation was observed with BHT but with lower yield.

3.4. Procedure for Experiment with Diphenylethylene:



Procedure: In an oven dried reaction vial equipped with a magnetic stir bar, **1a** (50mg, 0.34 mmol), **2a** (2 equiv), DABCO (2 equiv), DPE (4 equiv) and 4CzIPN catalyst (2 mol%) were dissolved in 2 mL of dry DMSO. The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LED's. After 24 h TLC (Thin layer chromatography) product formation was observed with DPE but with lower yield and the adduct of Diphenylethylene with trifluoroethyliodide was observed and detected by HRMS.

4. Fluorescence Quenching Experiments:

Fluorescence spectra was recorded using Horiba Fluoromax spectrofluorometer. The Stern-Volmer fluorescence quenching studies were run with freshly prepared 4 CzIPN (2µM solution in MeCN) at room temperature. The solution was irradiated at 450 nm and fluorescence was measured from 480 to 700 nm. Control experiment showed that 4CzIPN fluorescence was quenched by DABCO and indole.

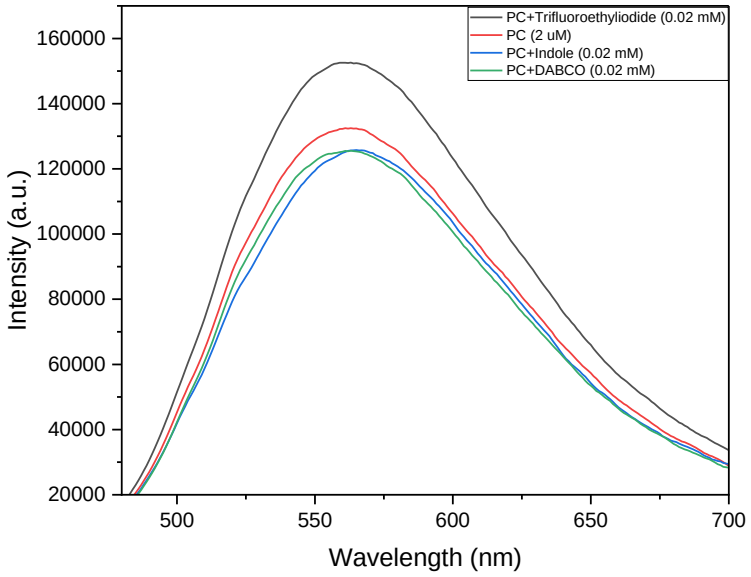


Figure S1: Fluorescence intensity of a 4CzIPN solution (2 µM solution in MeCN) containing 1,3-dimethyl-2-(2,2,2-trifluoroethyl)-1*H*-indole, trifluoroethyliodide, DABCO in MeCN (excitation wavelength: 450 nm). Peak descriptors: 4CzIPN (2µM) in MeCN (red line), indole (0.02mM) in MeCN (blue line), DABCO (0.02mM) in MeCN (green line), trifluoroethyliodide (0.02 mM) in MeCN (black line).

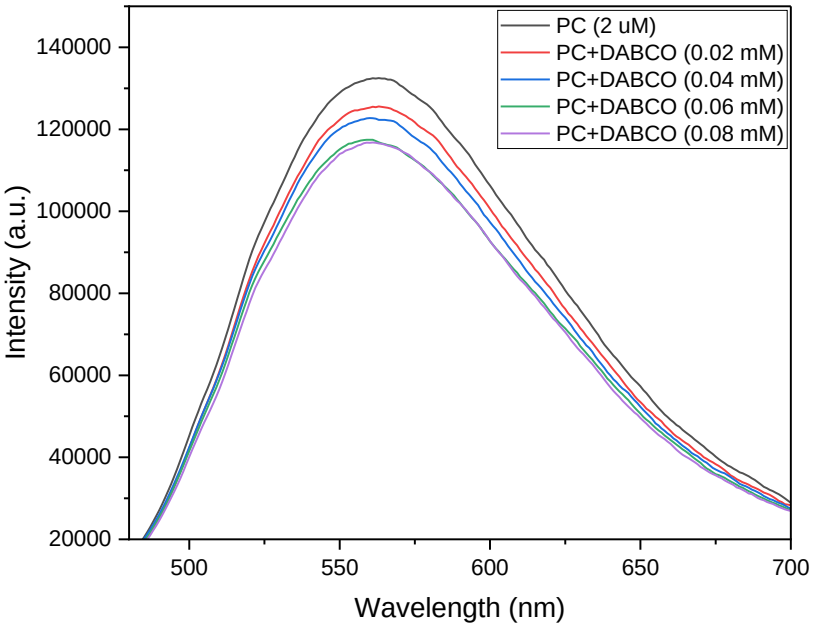


Figure S2: Fluorescence intensity of a 4CzIPN solution (2μM solution in MeCN) containing varying amount of DABCO (excitation wavelength 450 nm).

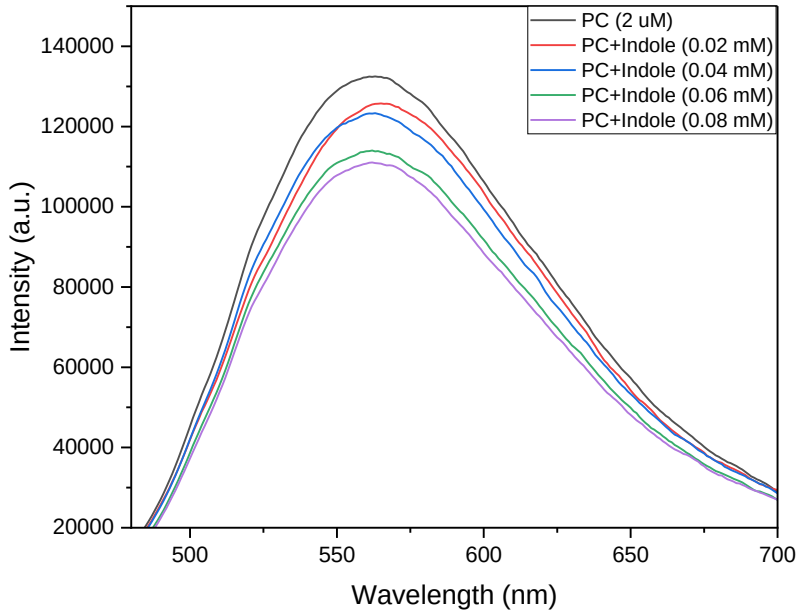


Figure S3: Fluorescence intensity of a 4CzIPN solution (2μM solution in MeCN) containing varying amount of indole (excitation wavelength 450 nm).

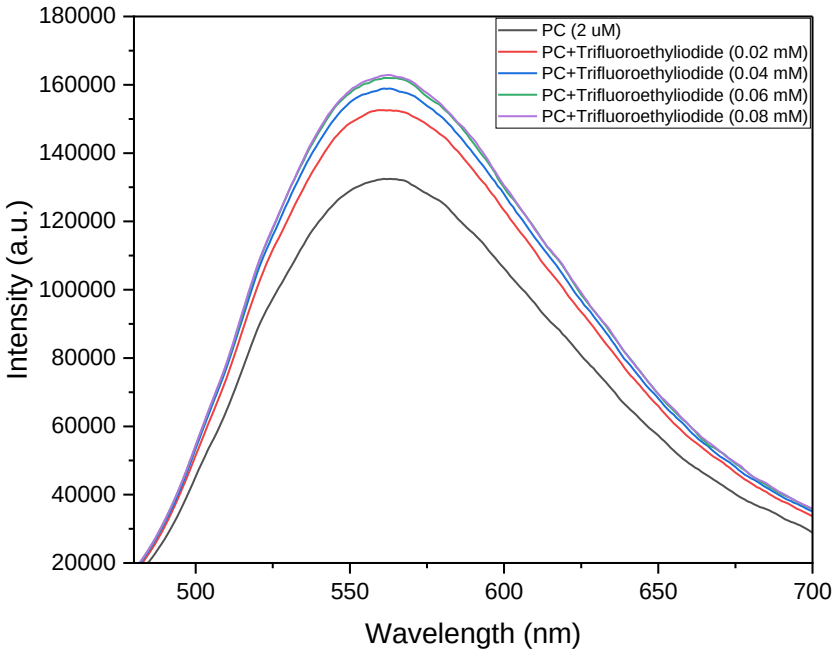


Figure S4: Fluorescence intensity of a 4CzIPN solution (2µM solution in MeCN) containing varying amount of trifluoroethyliodide (excitation wavelength 450 nm).

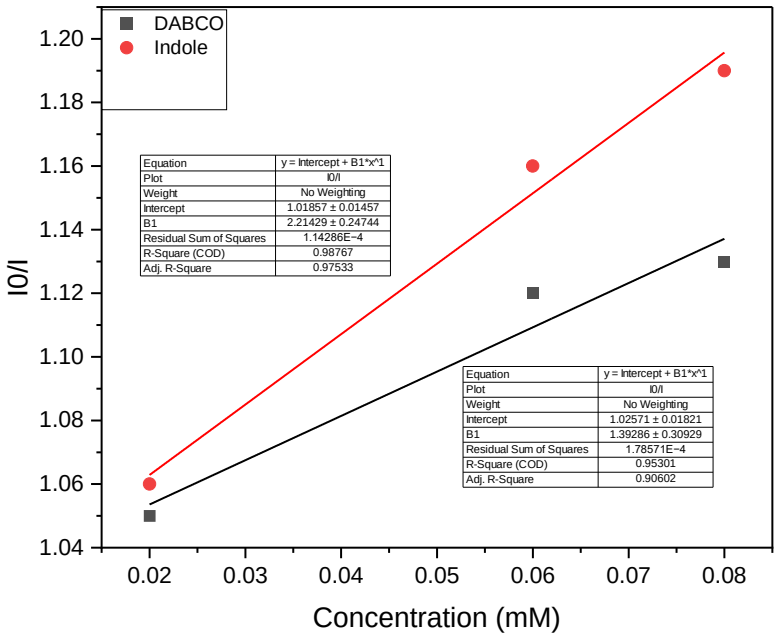
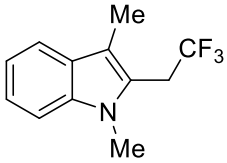
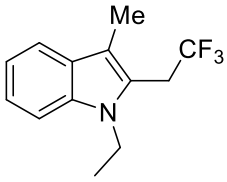


Figure S5: Stern Volmer Plot for fluorescence quenching studies of 4CzIPN by DABCO (black marks) and indole (red marks).

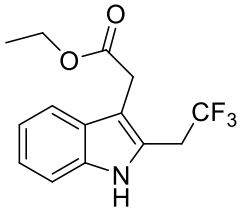
5. Analytical Data of Synthesized Products

1,3-Dimethyl-2-(2,2,2-trifluoroethyl)-1*H*-indole (3a): According to the general procedure **2**, 

1,3-dimethyl-1*H*-indole (50 mg, 0.34 mmol), trifluoroethyliodide (2 equiv, 0.69 mmol), DABCO (2 equiv, 0.69 mmol) provided **3a** after flash column chromatography as white solid (56 mg, 72%). Mp = 76-78 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 3.70 (s, 3H), 3.58 (q, *J* = 10.3 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} (100 MHz, Chloroform-*d*) δ 137.2, 127.8, 126.9, 124.7, 124.2, 122.2, 119.2, 118.9, 111.6, 109.2, 33.8 – 26.3 (m), 8.9. ^{19}F NMR (471 MHz, Chloroform-d) δ -64.9 (t, *J* = 11.1 Hz). HRMS (ESI) m/z: $[M+H]^{+}$calcd for $C_{12}H_{13}F_3N$ 228.0995 ; found 228.0992.

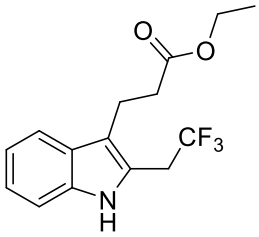


1-Ethyl-3-methyl-2-(2,2,2-trifluoroethyl)-1*H*-indole (3b): According to the general procedure **2**, 1-ethyl-3-methyl-1*H*-indole (50 mg, 0.31 mmol), trifluoroethyliodide (2 equiv, 0.63 mmol), DABCO (2 equiv, 0.63 mmol) provided **3b** after flash column chromatography as yellowish liquid (45 mg, 59%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.59 (q, *J* = 10.3 Hz, 2H), 2.32 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 136.0, 128.1, 126.9, 123.8, 122.2, 119.2, 119.0, 111.8, 109.4, 38.1, 29.9 (q, *J* = 31.7 Hz), 15.2, 9.0. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.7 (t, *J* = 10.3 Hz). HRMS (ESI) m/z: $[M+H]^{+}$calcd for $C_{13}H_{15}F_3N$ 242.1151 ; found 242.1148.

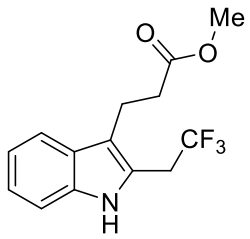


Ethyl 2-(2-(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) acetate (3c): According to the general procedure **2**, ethyl 2-(1*H*-indol-3-yl)acetate (50 mg, 0.25 mmol), trifluoroethyliodide (2 equiv, 0.49 mmol), DABCO (2 equiv, 0.49 mmol) provided **3c** after flash column chromatography as yellowish liquid (40 mg, 57%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 2H), 3.60

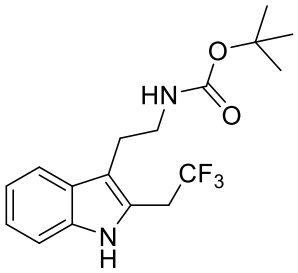
(q, *J* = 10.6 Hz, 2H), 1.23 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 171.5, 135.8, 127.7, 124.5, 123.9, 122.9, 120.2, 119.1, 111.0, 109.0, 61.1, 32.2 – 31.1 (m), 30.3, 14.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.7 (t, *J* = 10.5 Hz). HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{14}H_{15}F_3NO_2$ 286.1049; found 286.1046.



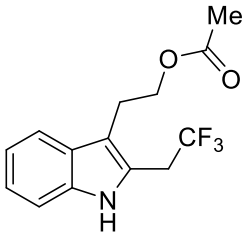
Ethyl 3-(2-(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) propanoate (3d): According to the general procedure **2**, ethyl 3-(1*H*-indol-3-yl) propanoate (50 mg, 0.23 mmol), trifluoroethyliodide (2 equiv, 0.46 mmol), DABCO (2 equiv, 0.46 mmol) provided **3d** after flash column chromatography as yellowish liquid (28 mg, 41%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.14 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.65 (q, *J* = 10.6 Hz, 2H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.22 (t, *J*= 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, Chloroform-*d*) δ 173.4, 136.1, 127.4, 126.5, 123.4, 122.7, 119.8, 118.8, 114.8, 111.0, 60.6, 35.0, 31.5 (q, *J* = 31.3 Hz), 19.4, 14.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.8 (t, *J* = 10.0 Hz). HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{15}H_{17}F_3NO_2$ 300.1206; found 300.1214.



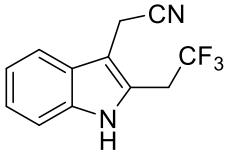
Methyl 3-(2-(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) propanoate (3e): According to the general procedure **2**, methyl 3-(1*H*-indol-3-yl)propanoate (50 mg, 0.25 mmol), trifluoroethyliodide (2 equiv, 0.49 mmol), DABCO (2 equiv, 0.49 mmol) provided **3e** after flash column chromatography as colourless oil (25 mg, 36%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 3.69 – 3.56 (m, 5H), 3.06 (t, *J* = 7.5 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, Chloroform-*d*) δ 173.7, 136.1, 127.4, 123.4, 122.8, 119.9, 118.8, 114.8, 111.0, 51.7, 34.7, 31.5 (q, *J* = 31.2 Hz), 19.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.8 (t, *J* = 10.7 Hz). HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{14}H_{15}F_3NO_2$ 286.1049 found 286.1042.



***tert*-Butyl (2-(2-(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) ethyl) carbamate (3f):** According to the general procedure **2**, *tert*-butyl (2-(1*H*-indol-3-yl)ethyl)carbamate (50 mg, 0.19 mmol), trifluoroethyliodide (2 equiv, 0.38 mmol), DABCO (2 equiv, 0.38 mmol) provided **3f** after flash column chromatography as yellowish liquid (35 mg, 53%). ^{1}H NMR (395 MHz, Chloroform d) δ 8.12 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.15 – 7.11 (m, 1H), 4.61 (s, 1H), 3.57 (q, *J* = 10.5 Hz, 2H), 3.42 – 3.35 (m, 2H), 2.94 (t, *J* = 6.9 Hz, 2H), 1.45 (s, 9H).^{13}C{^{1}H} NMR (125 MHz, Chloroform d) δ 156.0, 136.1, 127.7, 122.9, 122.2, 119.9, 119.5, 119.0, 113.3, 111.0, 79.3, 41.0, 31.5 (q, *J* = 31.4 Hz), 28.5, 24.8.^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.6 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: [M+Na]$^{+}$calcd for $C_{17}H_{21}F_3N_2NaO_2$ 365.1447; found 365.1449.

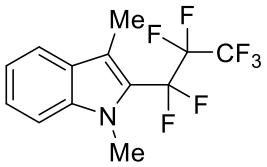


2-(2-(2,2,2-Trifluoroethyl)-1*H*-indol-3-yl) ethyl acetate (3g): According to the general procedure **2**, 2-(1*H*-indol-3-yl) ethyl acetate (50 mg, 0.25 mmol), trifluoroethyliodide (2 equiv, 0.49 mmol), DABCO (2 equiv, 0.49 mmol) provided **3g** after flash column chromatography as yellowish solid (26 mg, 37%). Mp = 104-106 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.15 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 3.60 (q, *J* = 10.5 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.2, 136.0, 127.7, 126.7, 123.9, 122.9, 120.0, 118.9, 112.1, 111.0, 64.4, 31.5 (q, *J* = 31.4 Hz), 23.8, 21.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.7 (t, *J* = 10.5 Hz). HRMS (ESI) m/z: [M+Na]$^{+}$calcd for $C_{14}H_{14}F_3NNaO_2$ 308.0869 found 308.0857.

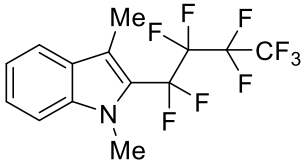


2-(2-(2,2,2-Trifluoroethyl)-1*H*-indol-3-yl)acetonitrile (3h): According to the general procedure **2**, 2-(1*H*-indol-3-yl)acetonitrile (50 mg, 0.32 mmol), trifluoroethyliodide (2 equiv, 0.64 mmol), DABCO (2 equiv, 0.64 mmol) provided **3h** after flash column chromatography as yellowish solid (15 mg, 20%). Mp = 140-143 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 3.82 (s, 2H), 3.63 (q, *J* = 10.3 Hz, 2H).^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 135.7, 126.7, 124.4, 123.8, 120.9, 118.4, 117.5,

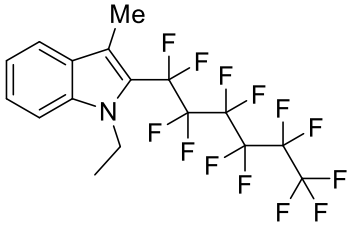
111.4, 104.5, 31.8 (q, *J* = 31.6 Hz), 13.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.8 (t, *J* = 10.3 Hz, 3F). HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{12}H_8F_3N_2$ 237.0645 found 237.0640.



1,3-Dimethyl-2-(perfluoropropyl)-1*H*-indole (3i): According to the general procedure **2**, 1,3-dimethyl-1*H*-indole (50 mg, 0.34 mmol), heptafluoropropyl iodide (2 equiv, 0.69 mmol), DABCO (2 equiv, 0.69 mmol) provided **3i** after flash column chromatography as colourless oil (80 mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 16.1, 8.2 Hz, 1H), 7.52 – 7.39 (m, 1H), 7.37 (d, *J* = 5.8 Hz, 1H), 7.19 (ddd, *J* = 8.0, 6.0, 1.8 Hz, 1H), 3.80 (s, 3H), 2.46 (t, *J* = 3.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 138.5, 127.4, 124.8, 123.2, 122.1 (t, *J* = 10.2 Hz), 120.1 (d, *J* = 11.7 Hz), 117.7, 117.6, 114.4, 109.8, 31.7, 9.2. ^{19} F NMR (471 MHz, Chloroform-*d*) δ -79.8 (t, *J* = 10.3 Hz, 2F), -79.9 (t, *J* = 10.3 Hz, 3F), -80.1 (m, 2F). HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{13}H_{11}F_7N$ 314.0774 ; found 314.0771.

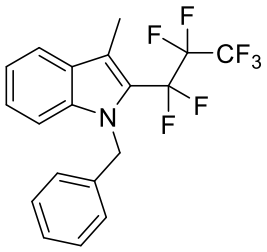


1,3-Dimethyl-2-(perfluorobutyl)-1*H*-indole (3j): According to the general procedure **2**, 1,3-dimethyl-1*H*-indole (50 mg, 0.34 mmol), nonafluorobutyliodide (2 equiv, 0.69 mmol), DABCO (2 equiv, 0.69 mmol) provided **3j** after flash column chromatography as colourless liquid (40 mg, 32%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.41 (m, 3H), 3.87 (s, 3H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 139.7, 124.8, 124.1, 123.2, 122.2, 120.1, 120.0, 117.4, 114.5, 109.8, 32.3, 11.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.8 (dt, *J* = 29.6, 9.0 Hz), -120.0 (q, *J* = 9.9 Hz), -121.7 – -122.0 (m), -125.4 – -126.0 (m). HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{14}H_9F_9N$ 362.0597 found 362.0594.

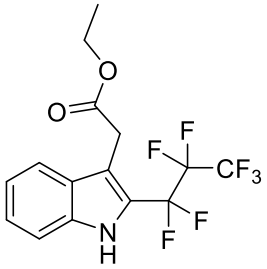


1-Ethyl-3-methyl-2-(perfluorohexyl)-1*H*-indole (3k): According to the general procedure **2**, 1-ethyl-3-methyl-1*H*-indole (50 mg, 0.31 mmol), decatrifluorohexyliodide (2 equiv, 0.63 mmol), DABCO (2 equiv, 0.63 mmol) provided **3k** after flash column chromatography as colourless oil (100 mg, 67%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.22 (ddd, *J* = 8.0, 4.5, 3.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.48 (t, *J* = 2.9 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 138.6, 137.4, 127.9, 124.7, 123.2, 120.3, 117.9 – 117.5 (m), 116.7 – 115.4 (m),

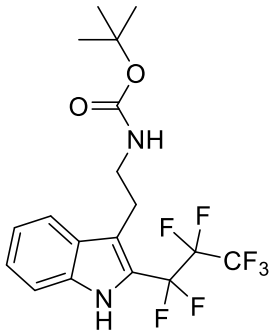
110.1, 40.4, 15.3, 9.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.3 – -80.9 (m), -100.5, -101.9 – -102.7 (m), -104.0 (t, *J* = 16.9 Hz), -121.3 – -122.9 (m), -125.8 – -126.3 (m). HRMS(ESI) m/z: $[M+H]^+$calcd for $C_{17}H_{13}F_{13}N$ 478.0835; found 478.0815.



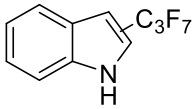
1-Benzyl-3-methyl-2-(perfluoropropyl)-1*H*-indole (3l): According to the general procedure **2**, 1-benzyl-3-methyl-1*H*-indole (50 mg, 0.23 mmol), heptafluoropropyliodide (2 equiv, 0.45 mmol), DABCO (2 equiv, 0.45 mmol) provided **3l** after flash column chromatography as colourless oil (35 mg, 40%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.16 (m, 4H), 6.94 (d, *J* = 6.9 Hz, 2H), 5.45 (s, 2H), 2.51 (t, *J* = 2.9 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.3, 137.8, 128.7, 127.8, 127.3, 125.6, 125.1, 120.4, 120.2, 118.2, 110.8, 48.8, 9.4. ^{19}F NMR (373 MHz, Chloroform-*d*) δ -79.8 (t, *J* = 10.4 Hz), -79.9 (t, *J* = 10.1 Hz), -79.9 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{19}H_{13}F_7N$ 388.0942 found 388.0934.



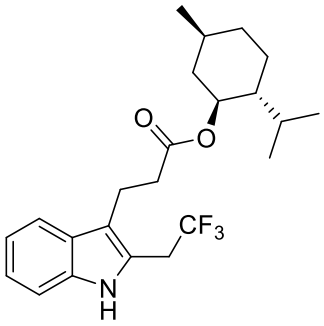
Ethyl 2-(2-(perfluoropropyl)-1*H*-indol-3-yl) acetate (3m): According to the general procedure **2**, ethyl 2-(1*H*-indol-3-yl)acetate (50 mg, 0.25 mmol), heptafluoropropyliodide (2 equiv, 0.49 mmol), DABCO (2 equiv, 0.49 mmol) provided **3m** after flash column chromatography as colourless oil (55 mg, 60%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.7, 136.0, 127.7, 125.3, 121.1, 120.4, 113.2, 111.8, 61.1, 30.1, 14.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.0 (t, *J* = 9.6 Hz, 3F), -109.0 (q, *J* = 9.1 Hz, 2F), -126.3 (m, 2F). HRMS (ESI) m/z: $[M+Na]^+$calcd for $C_{15}H_{12}F_7NNaO_2$ 394.0648 found 394.0648.



***tert*-Butyl (2-(2-(perfluoropropyl)-1*H*-indol-3-yl)ethyl)carbamate (3n):** According to the general procedure **2**, *tert*-butyl (2-(1*H*-indol-3-yl)ethyl)carbamate (50 mg, 0.19 mmol), heptafluoropropyliodide (2 equiv, 0.38 mmol), DABCO (2 equiv, 0.38 mmol) provided **3n** after flash column chromatography as colourless oil (50 mg, 61%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 4.67 (s, 1H), 3.45 – 3.37 (m, 2H), 3.08 (t, *J* = 6.9 Hz, 2H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 156.0, 136.2, 127.8, 125.1, 123.5, 120.8, 120.5, 119.9 (t, *J* = 29.2 Hz), 116.7 (d, *J* = 23.1 Hz), 111.8, 79.4, 41.4, 28.4, 24.9. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.0 (t, *J* = 9.9 Hz, 3F), -108.3 (q, *J* = 9.9, 9.5 Hz, 2F), -126.3 (s, 2F). HRMS (ESI) m/z: [M+Na]$^{+}$calcd for $C_{18}H_{19}F_7N_2NaO_2$ 451.1227; found 451.1221.

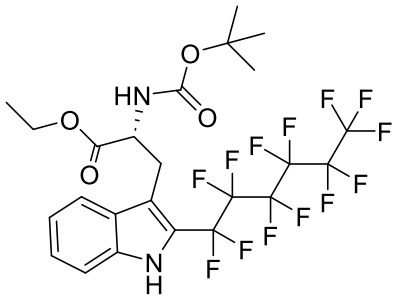


3-(Perfluoropropyl)-1*H*-indole or 2-(perfluoropropyl)-1*H*-indole (3o): According to the general procedure **2**, indole (50 mg, 0.43 mmol), heptafluoropropyliodide (2 equiv, 0.85 mmol), DABCO (2 equiv, 0.85 mmol) provided **3o** after flash column chromatography as colourless liquid (50 mg, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 8.41 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 5.8 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.29 (dd, *J* = 14.9, 7.4 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.99 (s, 1H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) δ 136.0, 130.9, 126.2, 125.0, 124.0, 123.0, 122.2, 121.3, 111.9, 111.8, 77.3, 77.1, 76.8.^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.0 (t, *J* = 9.5 Hz, 3F), -109.0 (q, *J* = 9.9 Hz, 2F), -125.2 (m, 2F). HRMS(ESI) m/z: [M+H]$^{+}$calcd for $C_{11}H_7F_7N$ 286.0461 found 286.0465.

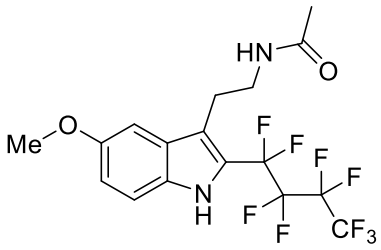


(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 3-(2(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) propanoate (6a): According to the general procedure **2**, (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(1*H*-indol-3-yl) propanoate (50 mg, 0.15 mmol), trifluoroethyliodide (2 equiv, 0.31 mmol), DABCO (2 equiv, 0.31 mmol) provided **6a** after flash column chromatography as colourless oil (25 mg, 40%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.15

(dt, *J* = 31.9, 7.3 Hz, 2H), 4.62 (td, *J* = 10.9, 4.4 Hz, 1H), 3.74 – 3.51 (m, 2H), 3.09 – 3.00 (m, 2H), 2.62 (td, *J* = 7.5, 3.1 Hz, 2H), 1.89 (d, *J* = 11.9 Hz, 1H), 1.64 – 1.56 (m, 4H), 1.44 (dddt, *J* = 12.2, 9.9, 6.8, 3.4 Hz, 1H), 1.00 (dd, *J* = 12.9, 3.2 Hz, 1H), 0.96 – 0.83 (m, 5H), 0.77 (d, *J* = 7.0 Hz, 3H), 0.63 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 172.9, 136.1, 127.4, 123.3, 122.7, 119.8, 118.9, 114.9, 110.9, 74.3, 47.0, 40.9, 35.2, 34.3, 32.1 – 31.0 (m), 26.3, 23.6, 22.1, 20.7, 19.6, 16.4. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.8 (t, *J* = 10.7 Hz, 3F). HRMS (ESI) m/z: $[M-H]^-$calcd for $C_{23}H_{29}F_3NO_2$ 408.2156 found 408.2152.

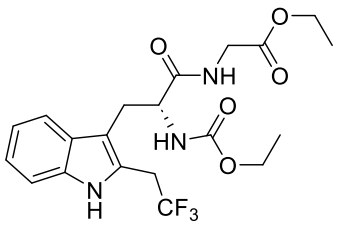


Ethyl 2-((*tert*-butoxycarbonyl)amino)-3-(2-(perfluorohexyl)-1*H*-indol-3-yl)propanoate (6b): According to the general procedure **2**, ethyl (*tert*-butoxycarbonyl)tryptophanate (50 mg, 0.15 mmol), decatrifluorohexyliodide (2 equiv, 0.30 mmol), DABCO (2 equiv, 0.30 mmol) provided **6b** after flash column chromatography as colourless liquid (40 mg, 41%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 5.13 (d, *J* = 8.2 Hz, 1H), 4.64 (d, *J* = 7.5 Hz, 1H), 4.14 – 4.08 (m, 1H), 4.05 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.32 (td, *J* = 16.5, 15.4, 6.8 Hz, 2H), 1.36 (s, 9H), 1.12 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 172.0, 155.0, 136.1, 127.7, 125.3, 121.0, 120.5, 115.8, 111.7, 79.8, 61.5, 54.3, 28.2, 13.8. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.3 – -81.2 (m), -106.9 (t, *J* = 13.6 Hz), -107.5 (t, *J* = 13.6 Hz), -121.6, -122.6, -126.0. HRMS(ESI) m/z: $[M+Na]^+$calcd for $C_{24}H_{23}F_{13}N_2NaO_4$ 673.1342; found 673.1341.

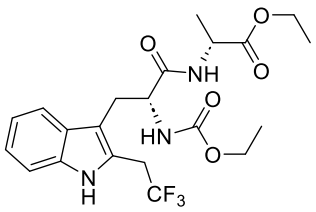


***N*-(2-(5-Methoxy-2-(perfluorobutyl)-1*H*-indol-3-yl) ethyl) acetamide (6c):** According to the general procedure **2**, melatonin (50 mg, 0.22 mmol), nonafluorobutyliodide (2 equiv, 0.43 mmol), DABCO (2 equiv, 0.43 mmol) provided **6c** after flash column chromatography as colourless oil (25 mg, 26%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.3 Hz, 1H), 5.65 (s, 1H), 3.86 (s, 3H), 3.55 (q, *J* = 6.8 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 1.94 (s, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, Chloroform-*d*) δ 170.4, 154.9, 131.4, 128.1, 120.4 (t, *J* = 28.7 Hz), 117.3, 116.6, 112.8, 100.7, 55.9, 40.3, 24.4, 23.3. ^{19}F NMR (471 MHz, Chloroform-*d*) δ

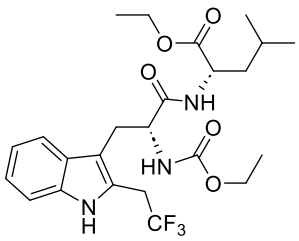
-80.8 (t, *J* = 9.7 Hz, 3F), -105.7 – -109.1 (m, 2F), -122.7 (m, 2F), -124.3 – -127.6 (m, 2F). HRMS(ESI) m/z: $[M+H]^+$calcd for $C_{17}H_{16}F_9N_2O_2$ 451.1063; found 451.1061.



Ethyl 2-(2-(ethoxycarbonylamino)-3-(2-(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) propanamido) acetate (6d): According to the general procedure **2**, ethyl (ethoxycarbonyl)tryptophylglycinate (50 mg, 0.14 mmol), trifluoroethyliodide (2 equiv, 0.28 mmol), DABCO (2 equiv, 0.28 mmol) provided **6d** after flash column chromatography as white solid (19 mg, 31%).Mp = 218-220 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.02 (s, 1H), 5.43 (s, 1H), 4.49 (s, 1H), 4.17 – 4.06 (m, 4H), 3.88 (dd, *J* = 18.3, 5.3 Hz, 1H), 3.75 (dd, *J* = 18.3, 5.1 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.34 (d, *J* = 15.3 Hz, 1H), 3.16 (dd, *J* = 14.5, 9.0 Hz, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.23 – 1.18 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 171.3, 169.2, 136.0, 127.7, 125.1, 123.1, 120.4, 118.9, 111.1, 110.6, 61.6, 55.3, 41.5, 31.4 (d, *J* = 31.4 Hz), 27.5, 14.6, 14.1.^{19} F NMR (471 MHz, Chloroform-*d*) δ -64.5 (t, *J* = 10.3 Hz, 3F). HRMS (ESI) m/z: $[M+Na]^+$calcd for $C_{20}H_{24}F_3N_3NaO_5$ 466.1560 found 466.1560.

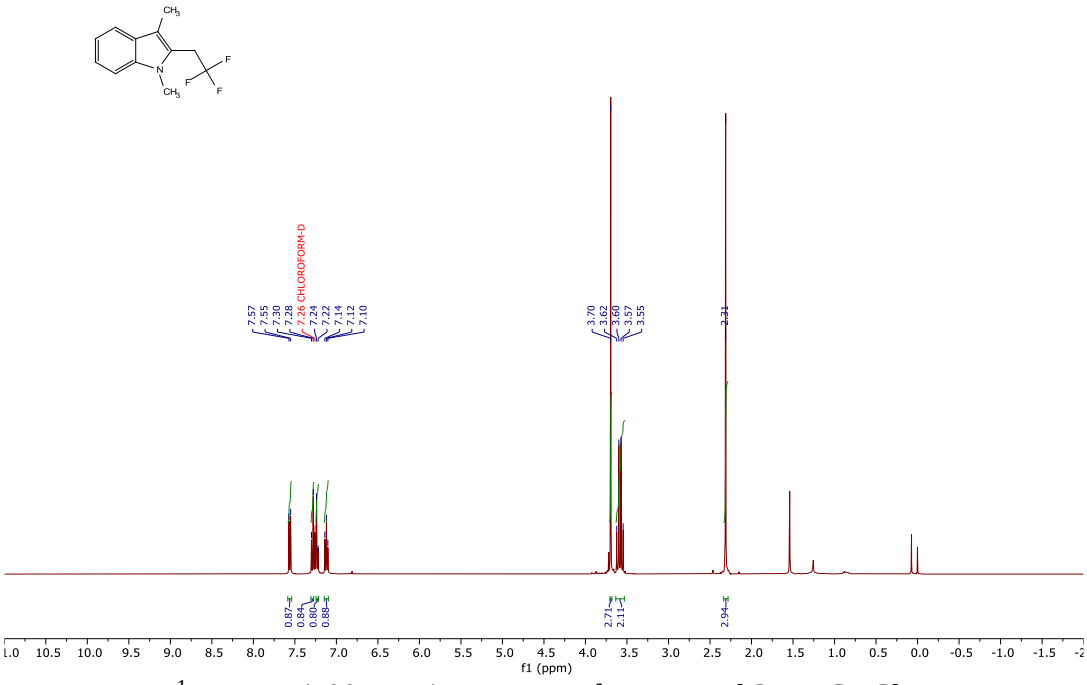


Ethyl2-(2-(ethoxycarbonylamino)-3-(2-(2,2,2-trifluoroethyl)-1*H*-indol-3-yl) propanamido) propanoate (6e): According to the general procedure **2**, ethyl (ethoxycarbonyl)tryptophylalaninate (50 mg, 0.13 mmol), trifluoroethyliodide (2 equiv, 0.27 mmol), DABCO (2 equiv, 0.27 mmol) provided **6e** after flash column chromatography as yellowish-white solid (18 mg, 30%). Mp = 142-144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.05 (d, *J* = 6.4 Hz, 1H), 5.50 (s, 1H), 4.42 (s, 1H), 4.34 – 4.25 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.08 – 3.97 (m, 2H), 3.69 – 3.59 (m, 2H), 3.29 (s, 1H), 3.17 – 3.06 (m, 1H), 1.67 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 172.1, 170.6, 136.1, 127.7, 125.0, 123.0, 120.2, 118.9, 111.0, 110.7, 61.5, 55.4, 48.4, 31.5, 29.8, 27.8, 18.4, 14.6, 14.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.5 (t, *J* = 10.3 Hz, 3F). HRMS(ESI) m/z: $[M+H]^+$calcd for $C_{21}H_{27}F_3N_3O_5$ 458.1897 found 458.1899.

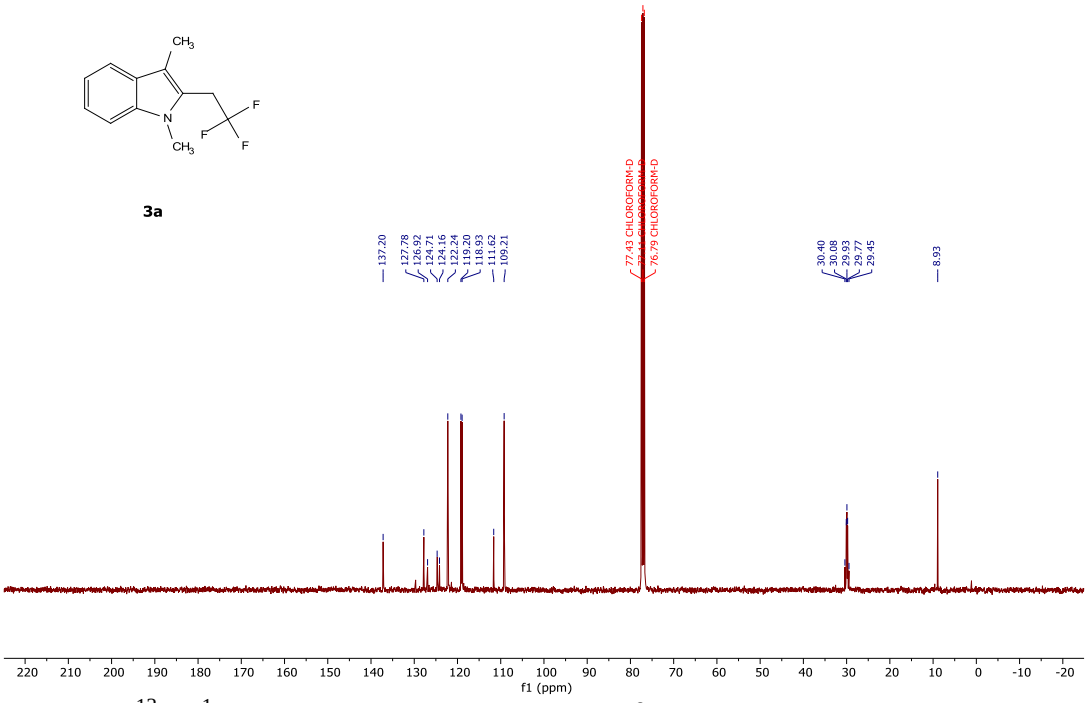


Ethyl 2-(2-(ethoxycarbonylamino)-3-(2-(2,2,2trifluoroethyl)-1*H*-indol-3-yl)propanamido)-4-methylpentanoate (6f): According to the general procedure **2**, ethyl (ethoxycarbonyl)tryptophylleucinate (50 mg, 0.12 mmol), trifluoroethyliodide (2 equiv, 0.24 mmol), DABCO (2 equiv, 0.24 mmol) provided **6f** after flash column chromatography as viscous yellowish solid (18 mg, 30%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J*= 7.6 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 5.88 (s, 1H), 5.44 (s, 1H), 4.60 – 4.27 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.05 – 3.97 (m, 2H), 3.60 (ddt, *J* = 15.6, 10.8, 7.1 Hz, 3H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.12 (dd, *J* = 14.4, 9.3 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 6H), 0.82 (d, *J* = 2.5 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 172.0, 170.8, 136.1, 127.7, 125.1, 122.9, 120.2, 119.0, 111.0, 110.7, 61.3, 51.1, 41.7, 31.5, 31.2, 29.8, 24.7, 22.7, 22.1, 14.6, 14.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.5 (t, *J* = 10.6 Hz, 3F). HRMS(ESI) m/z: $[M+Na]^{+}$calcd for $C_{24}H_{32}F_3N_3NaO_5$ 522.2186 found 522.2190.

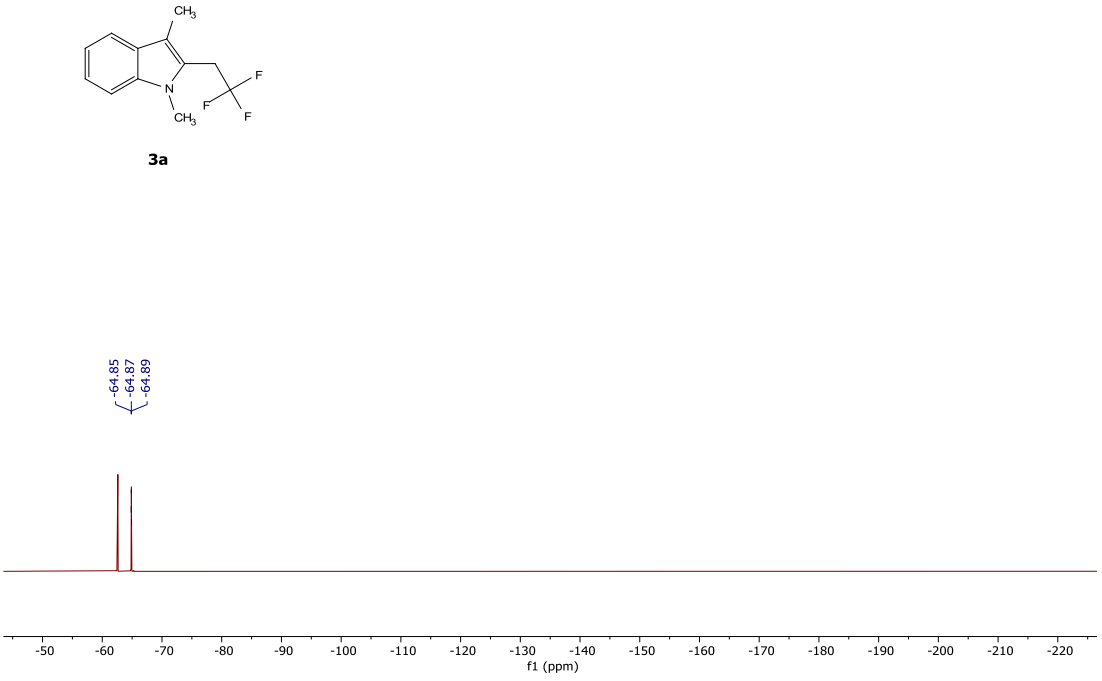
6. ^{1}H ,^{13}C & ^{19}F Spectra of Products



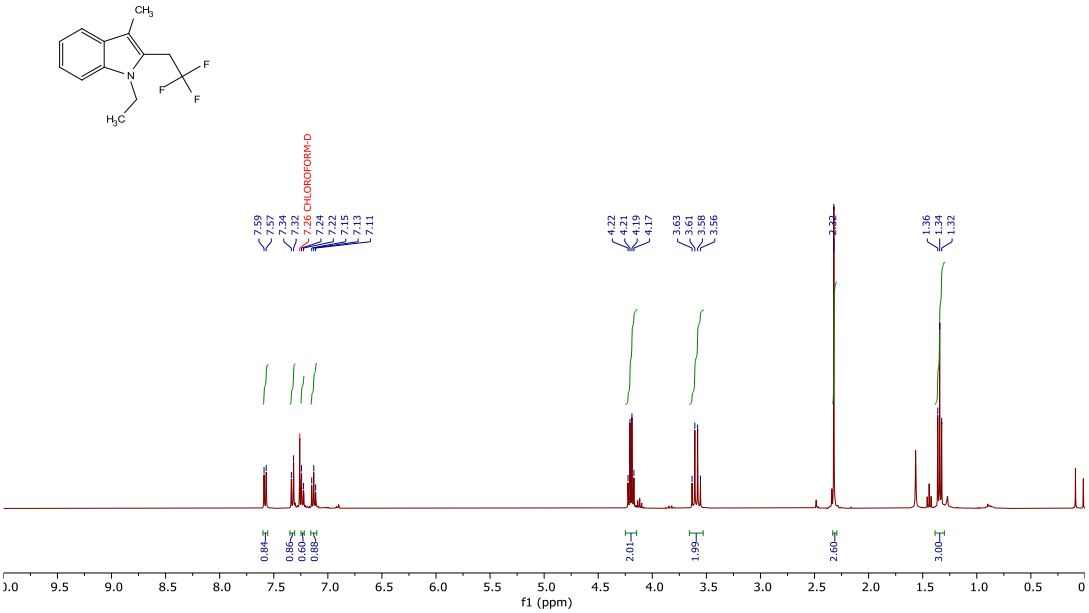
^{1}H NMR (400 MHz) spectrum of compound **3a** in $CDCl_3$



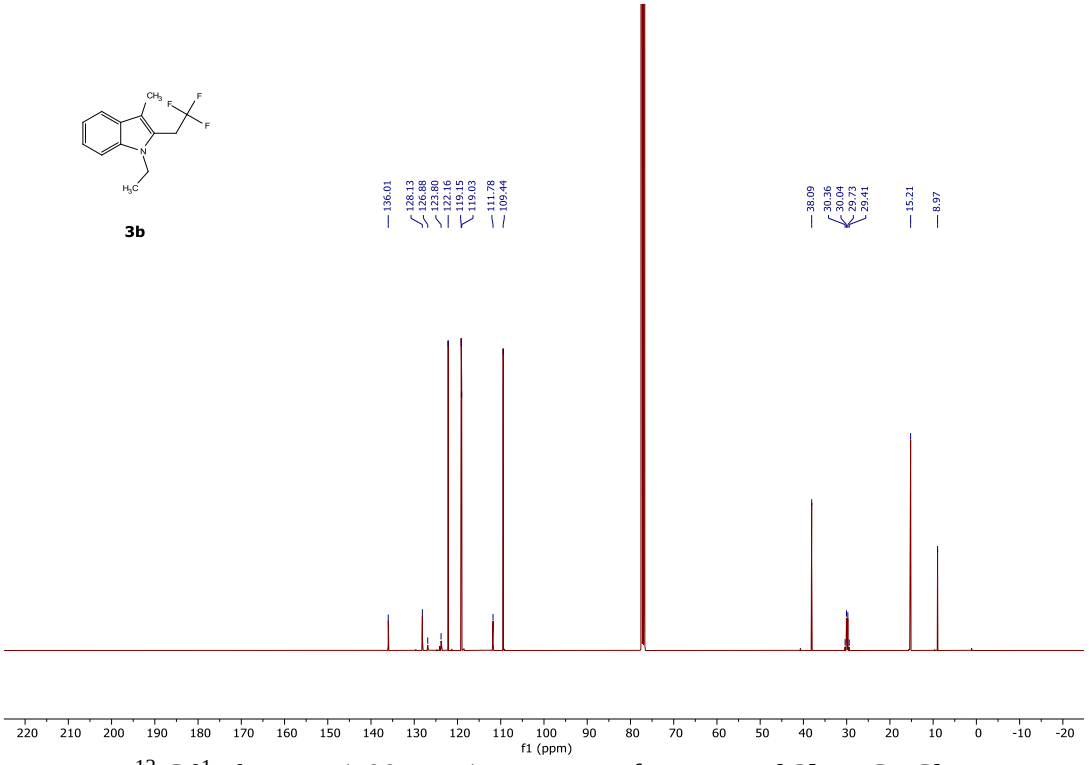
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3a** in $CDCl_3$



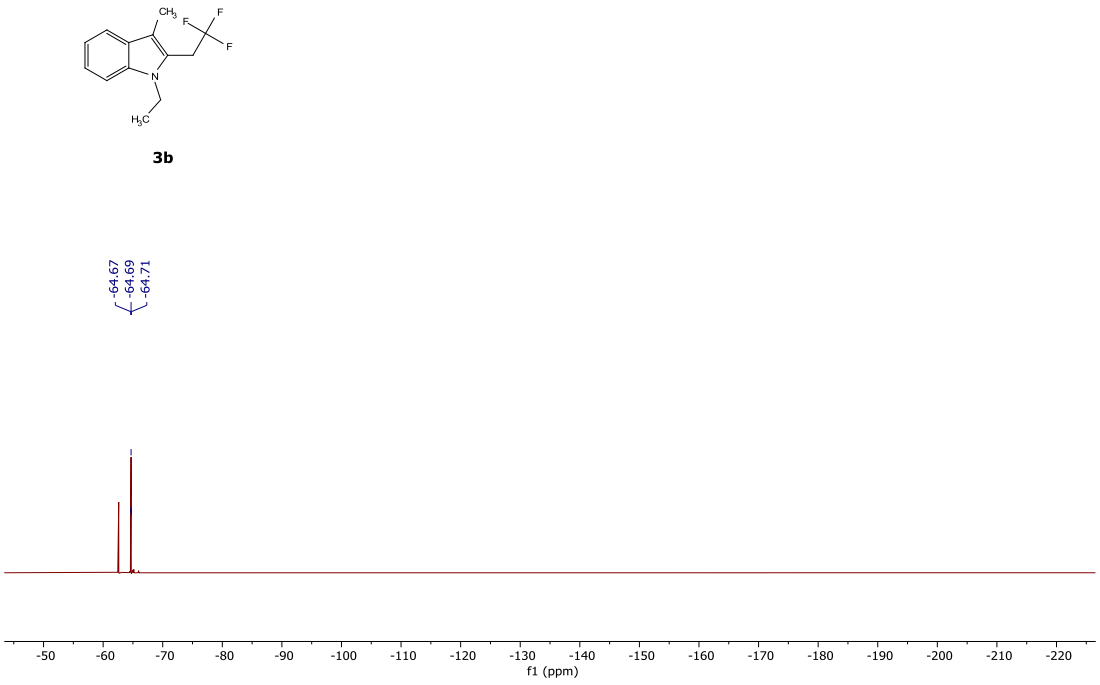
^{19}F NMR (471 MHz) spectrum of compound **3a** in $CDCl_3$ with $PhCF_3$ as reference standard



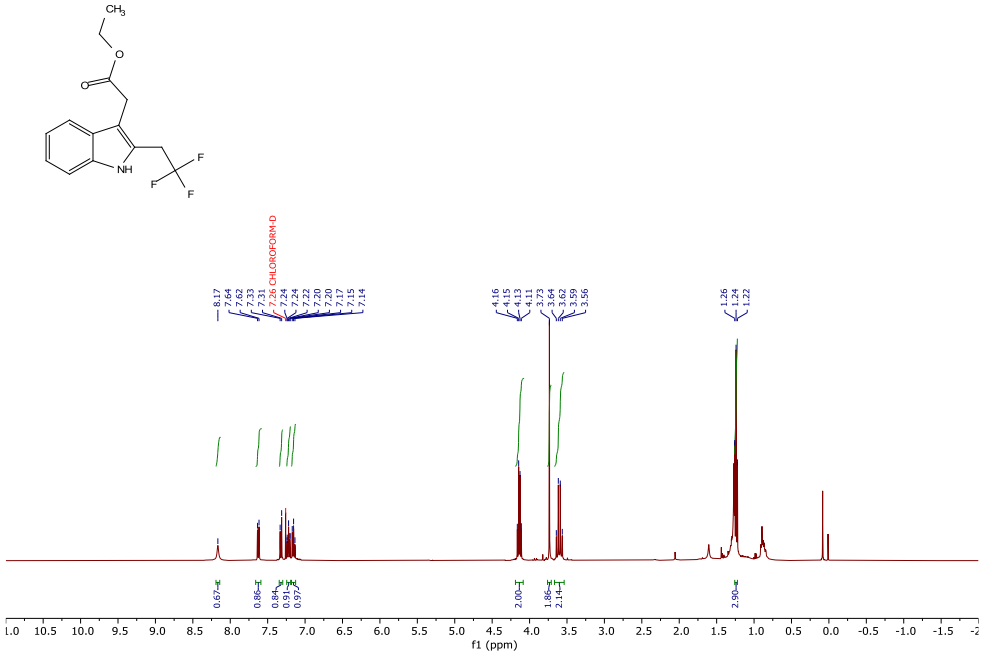
^{1}H NMR (400 MHz) spectrum of compound **3b** in $CDCl_3$



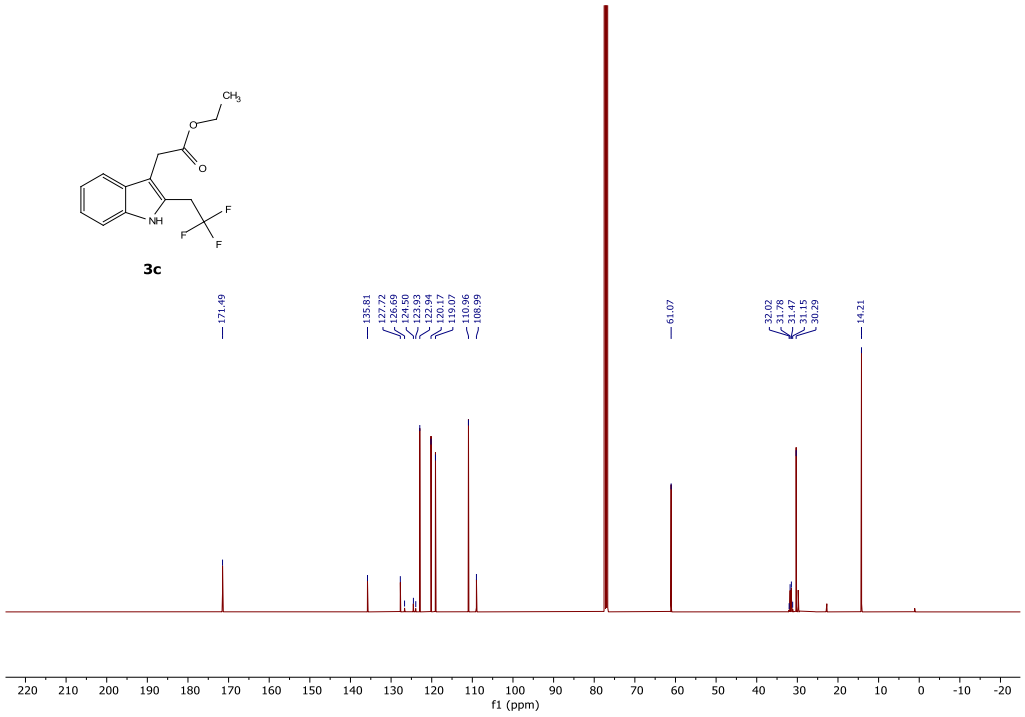
^{13} C{^{1}H} NMR (100 MHz) spectrum of compound **3b** in $CDCl_3$



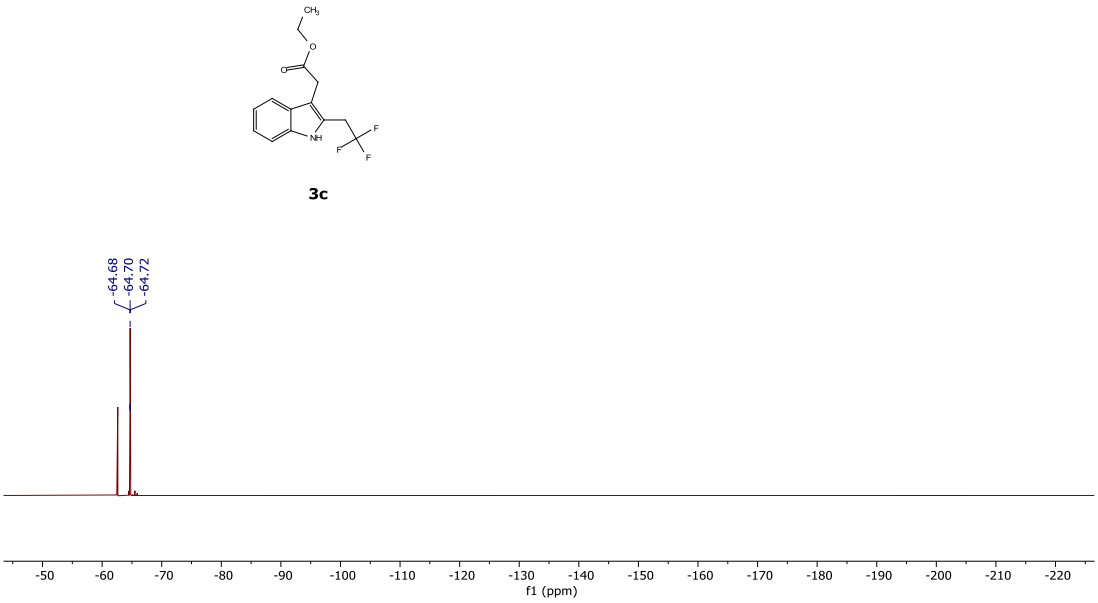
^{19}F NMR (471 MHz) spectrum of compound **3b** in $CDCl_3$ with $PhCF_3$ as reference standard



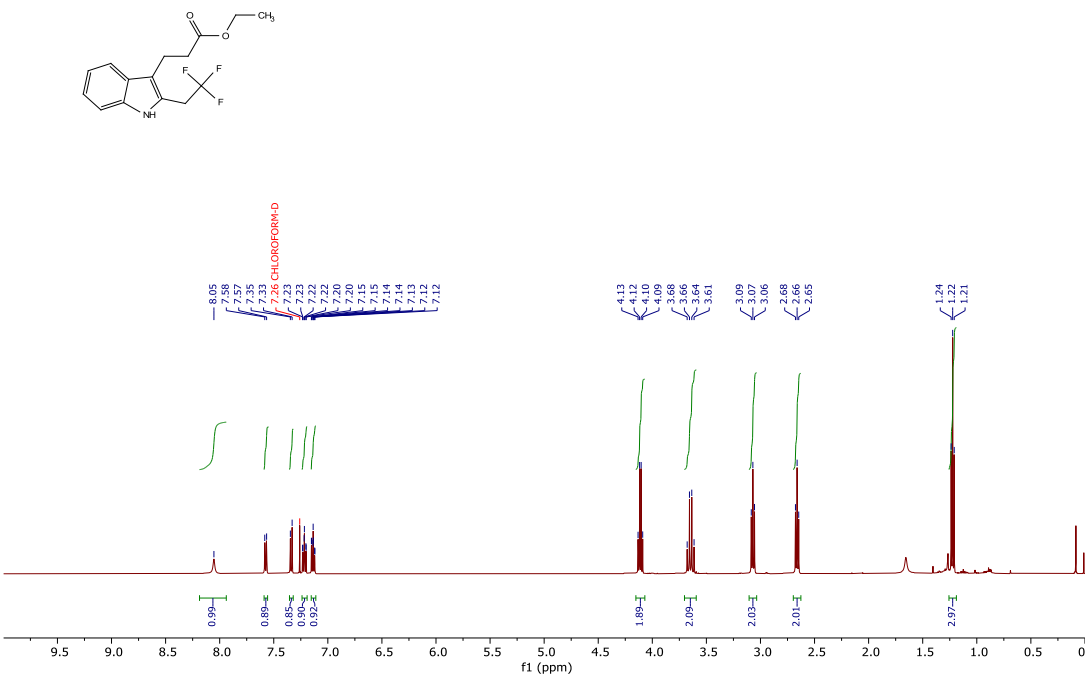
^{1}H NMR (400 MHz) spectrum of compound **3c** in $CDCl_3$



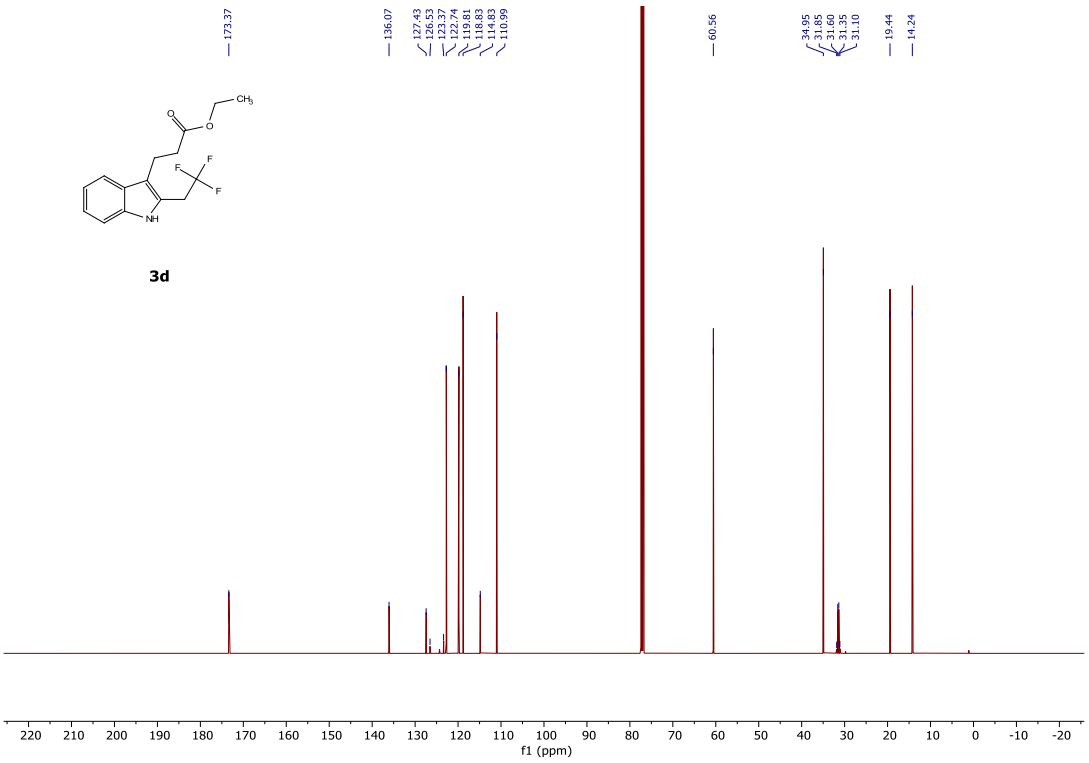
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3c** in $CDCl_3$



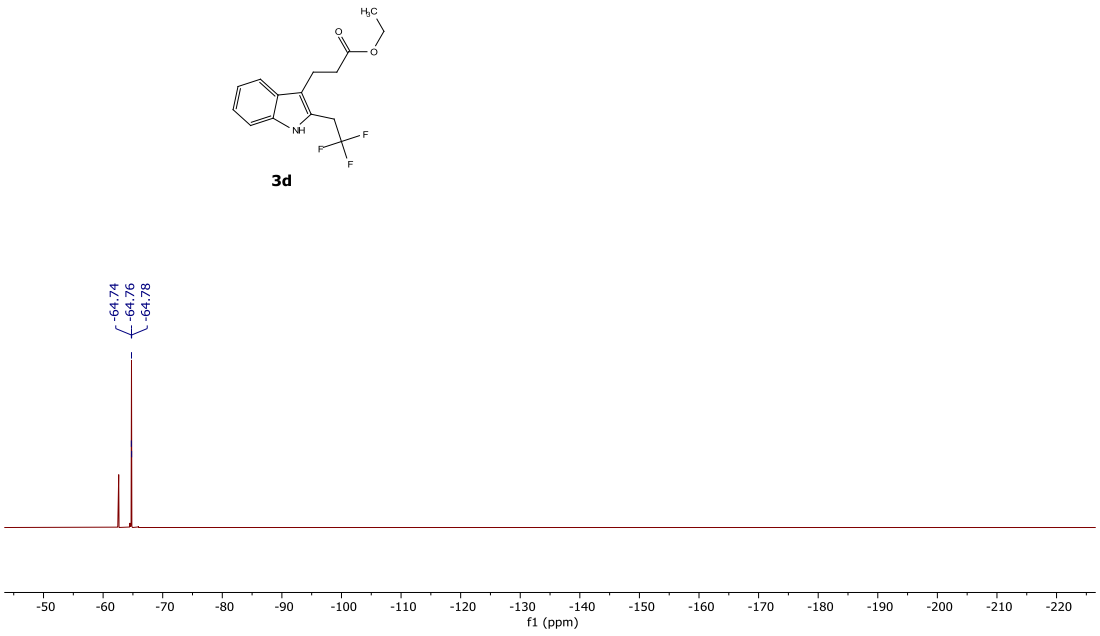
^{19}F NMR (471 MHz) spectrum of compound **3c** in $CDCl_3$ with $PhCF_3$ as reference standard



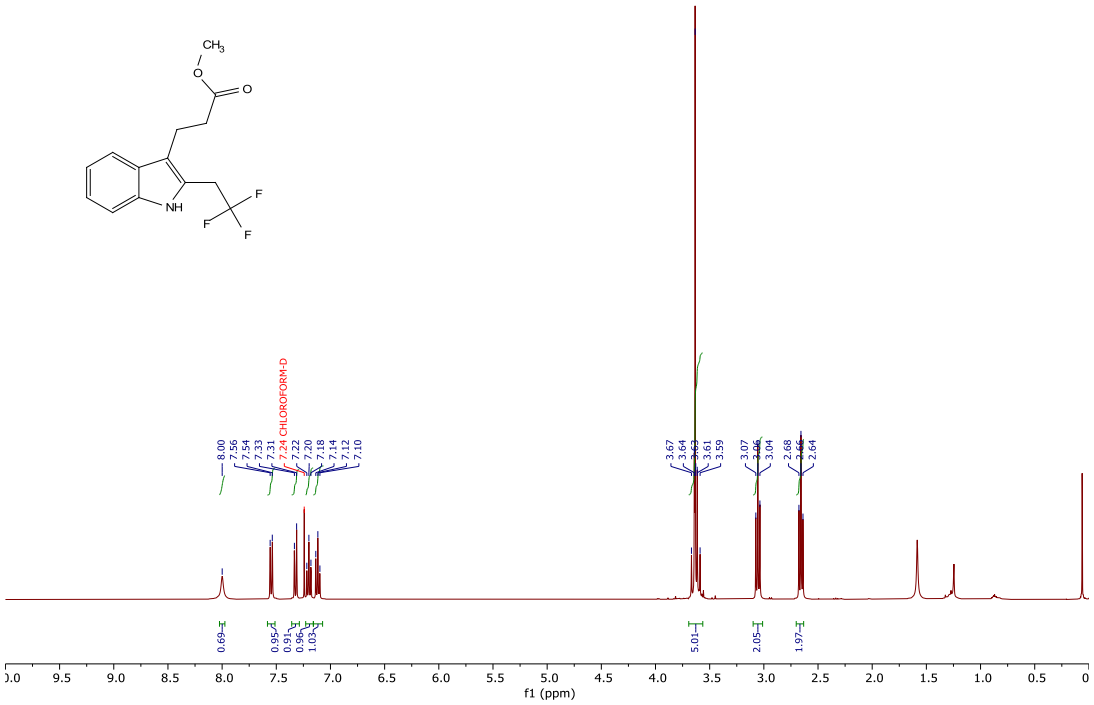
^{1}H NMR (500 MHz) spectrum of compound **3d** in $CDCl_3$



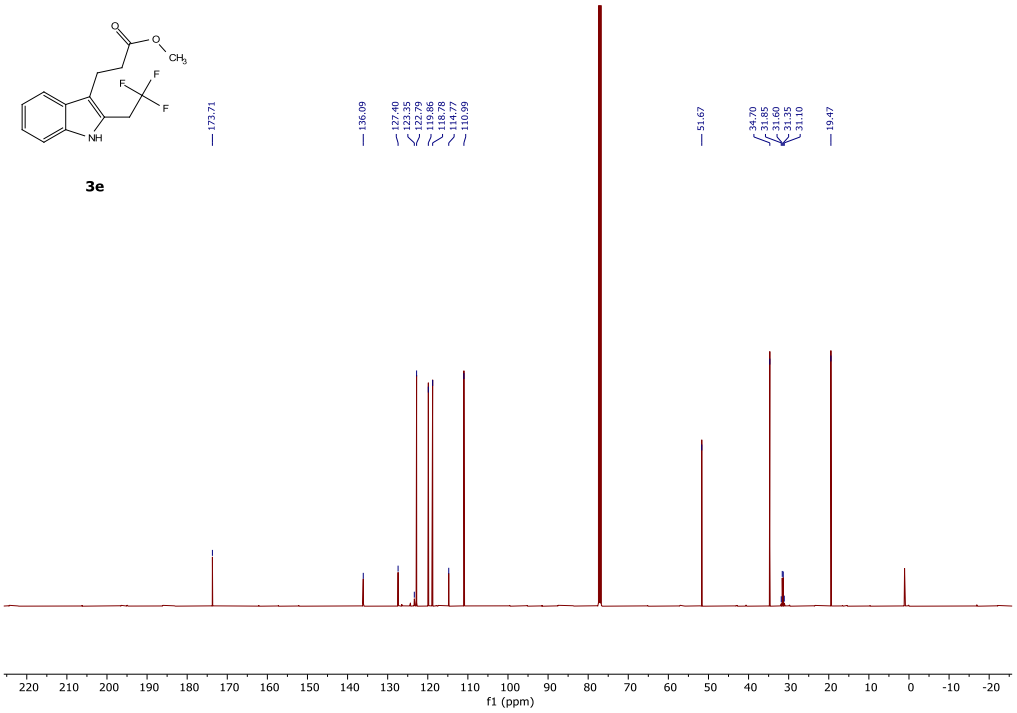
^{13}C{^{1}H} NMR (125 MHz) spectrum of compound **3d** in $CDCl_3$



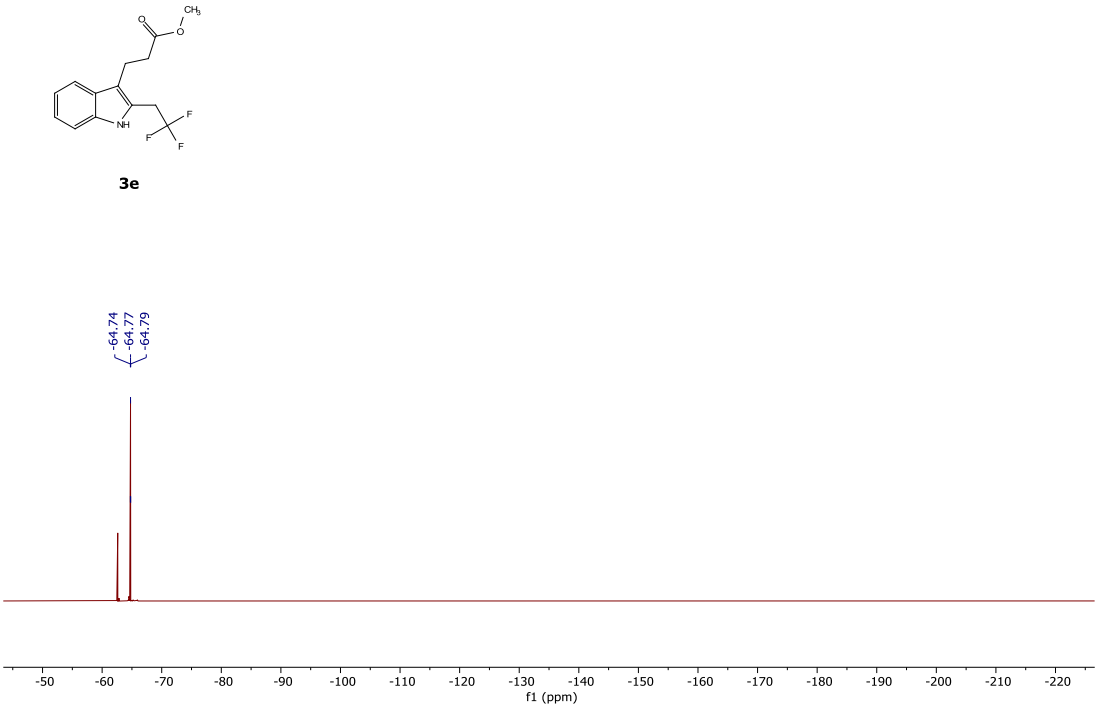
^{19}F NMR (471 MHz) spectrum of compound **3d** in $CDCl_3$ with $PhCF_3$ as reference standard



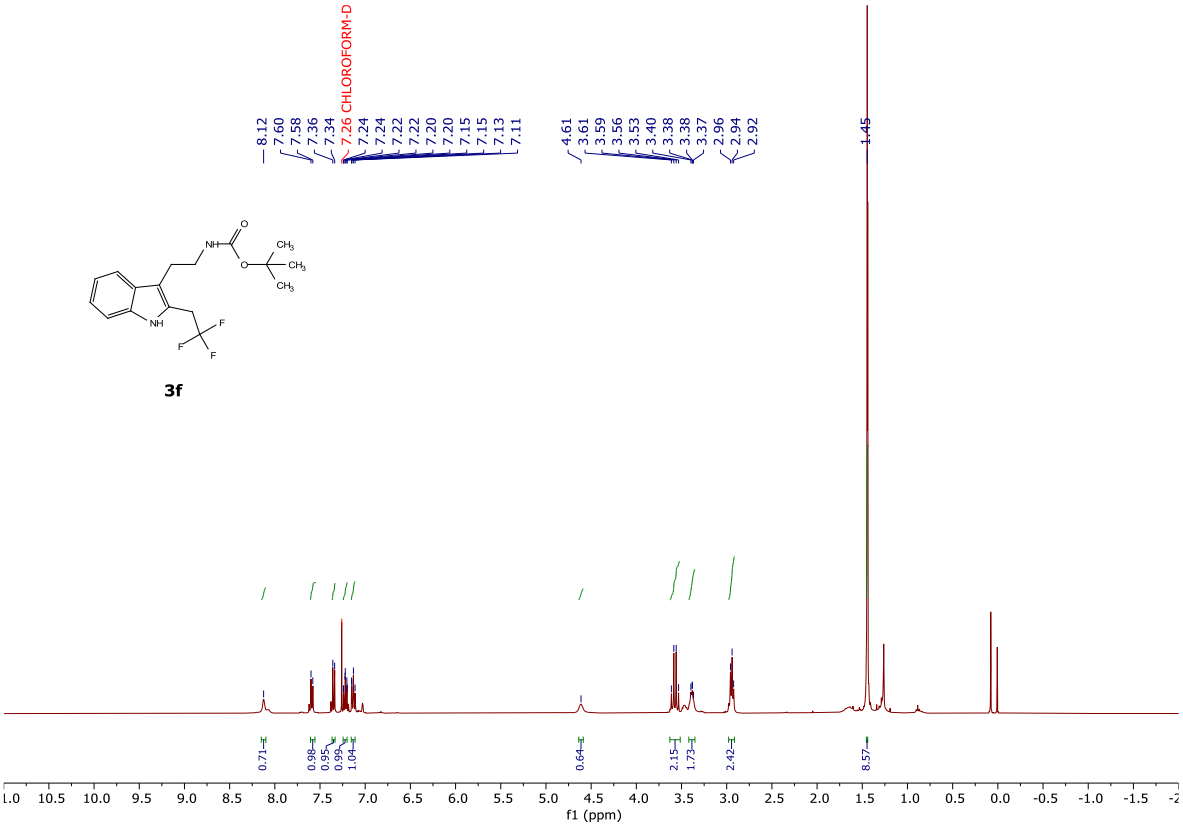
^{1}H NMR (400 MHz) spectrum of compound **3e** in $CDCl_3$



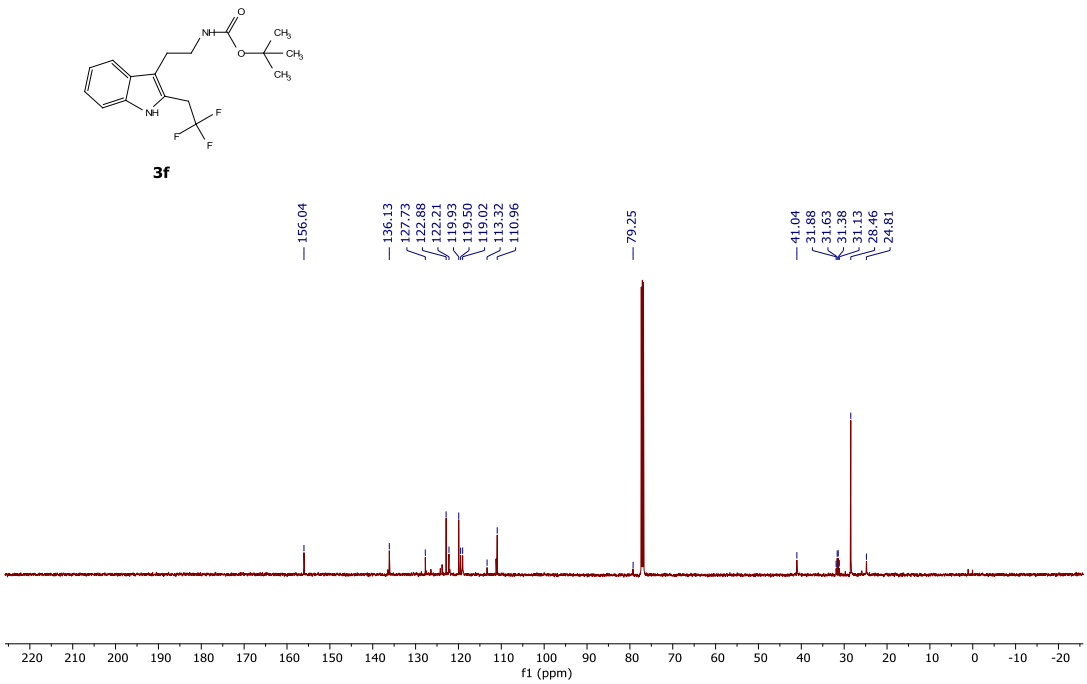
$^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of compound **3e** in $CDCl_3$



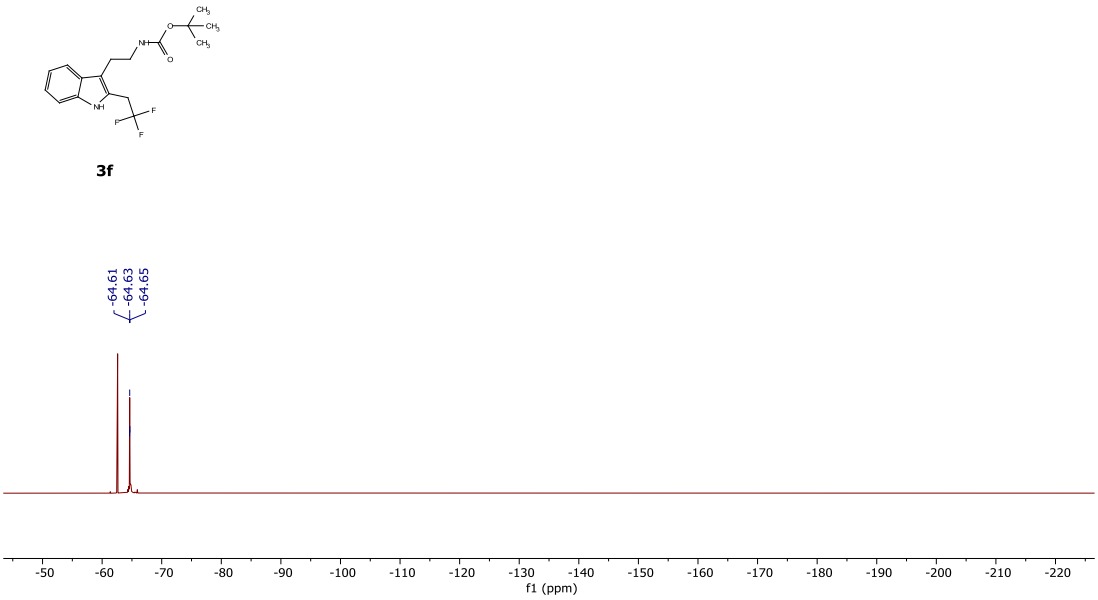
^{19}F NMR (471 MHz) spectrum of compound **3e** in $CDCl_3$ with $PhCF_3$ as reference standard



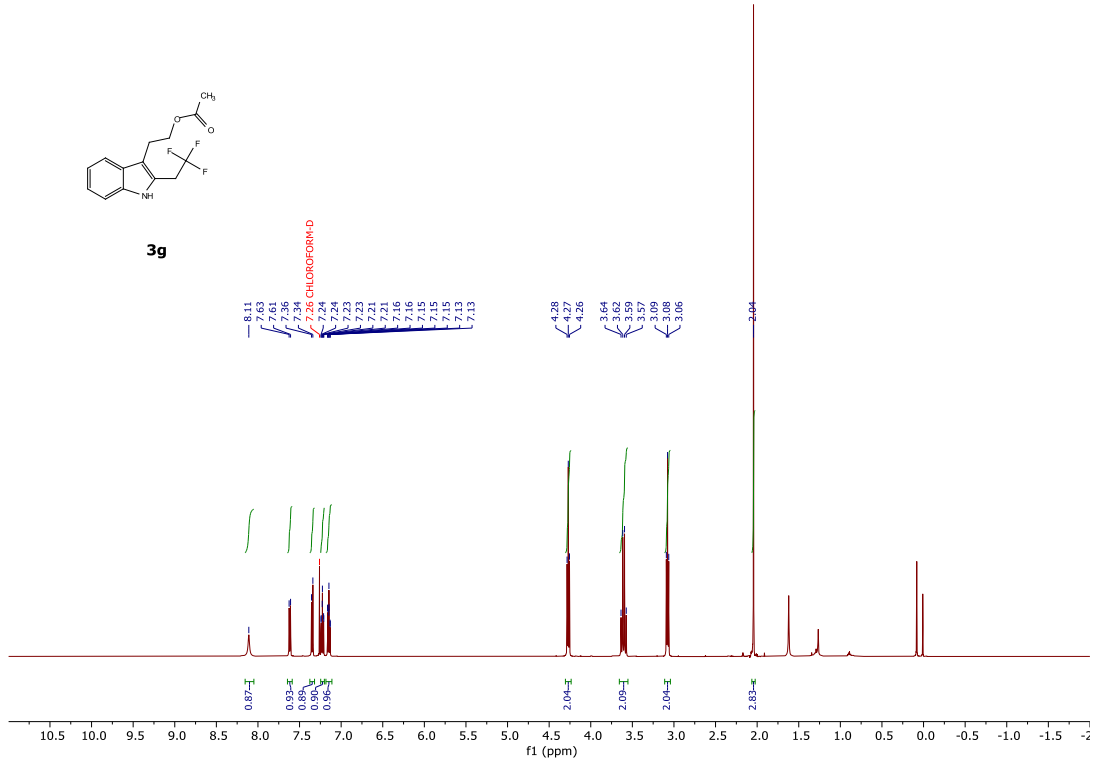
^{1}H NMR (396 MHz) spectrum of compound **3f** in $CDCl_3$



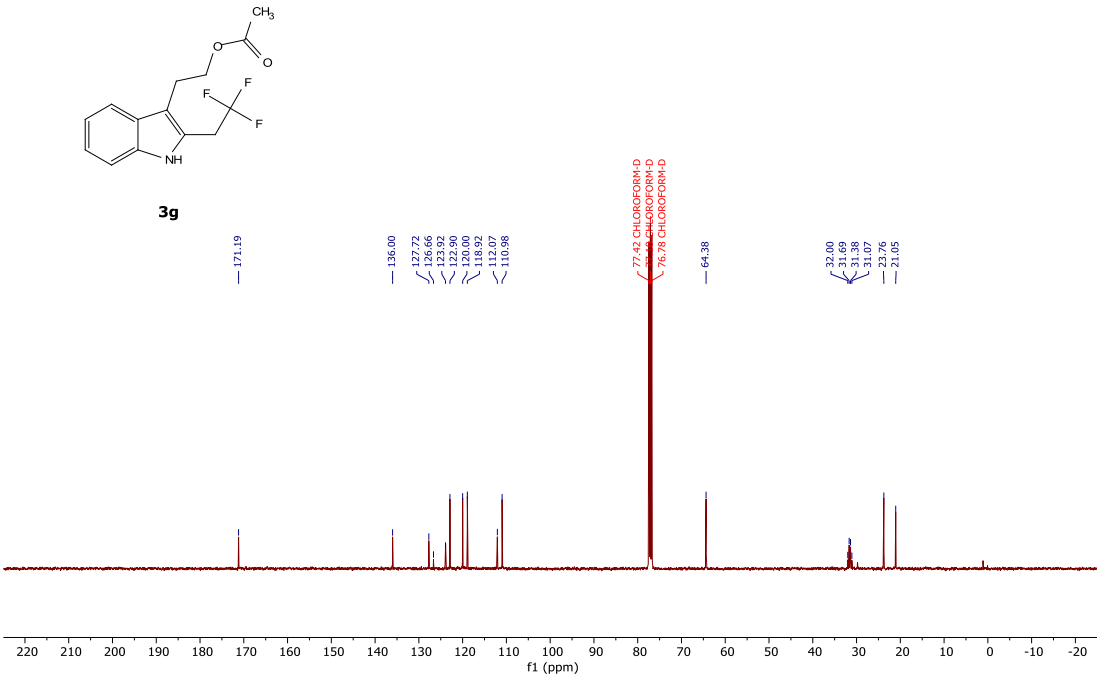
^{13}C{^{1}H} NMR (125 MHz) spectrum of compound **3f** in $CDCl_3$



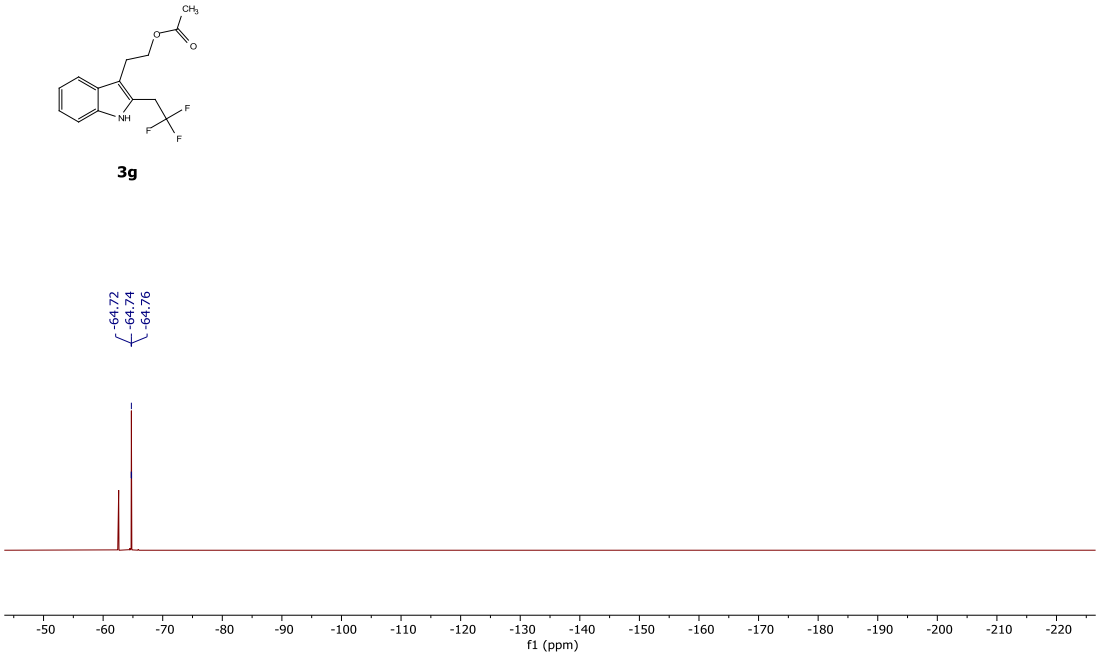
^{19}F NMR (471 MHz) spectrum of compound **3f** in $CDCl_3$ with $PhCF_3$ as reference standard



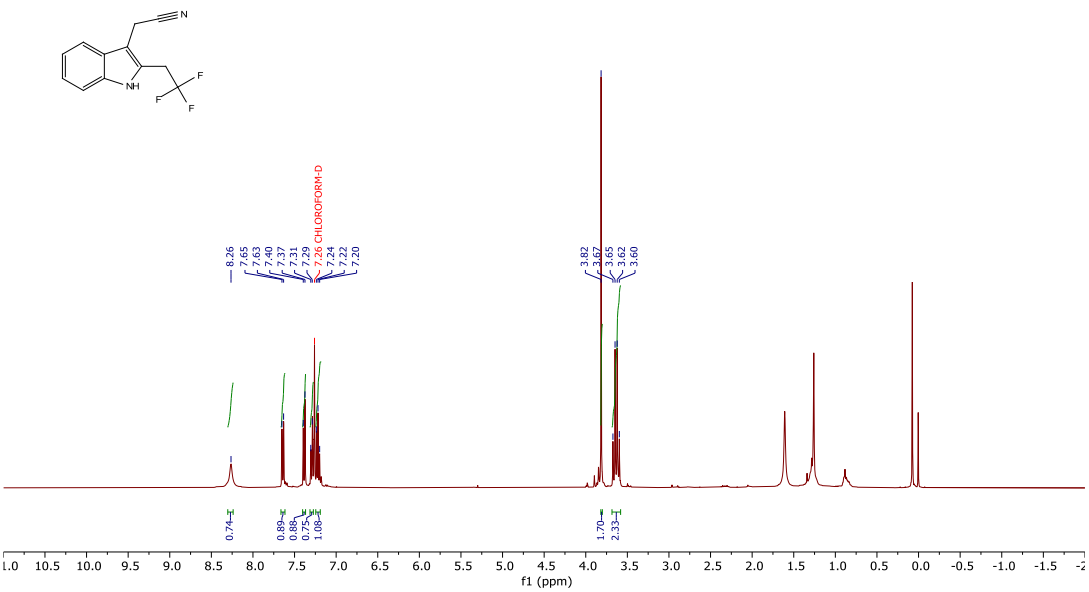
^{1}H NMR (500 MHz) spectrum of compound **3g** in $CDCl_3$



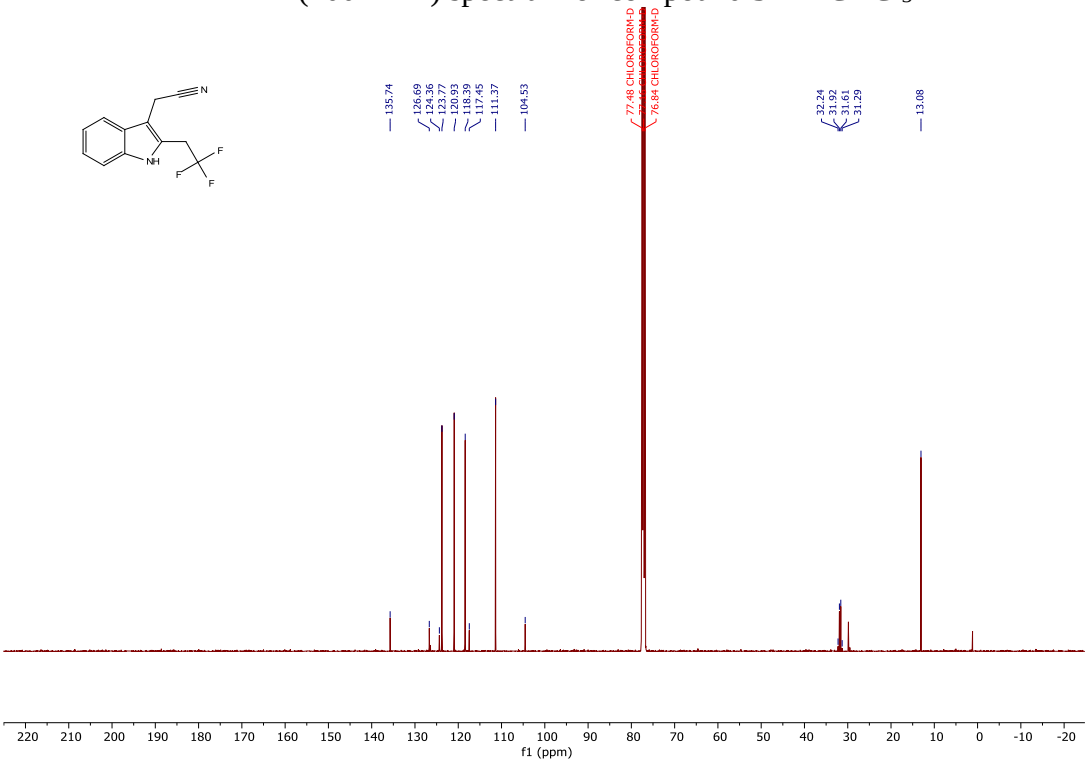
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3g** in $CDCl_3$



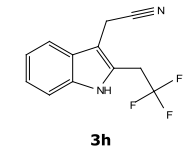
^{19}F NMR (471 MHz) spectrum of compound **3g** in $CDCl_3$ with $PhCF_3$ as reference standard



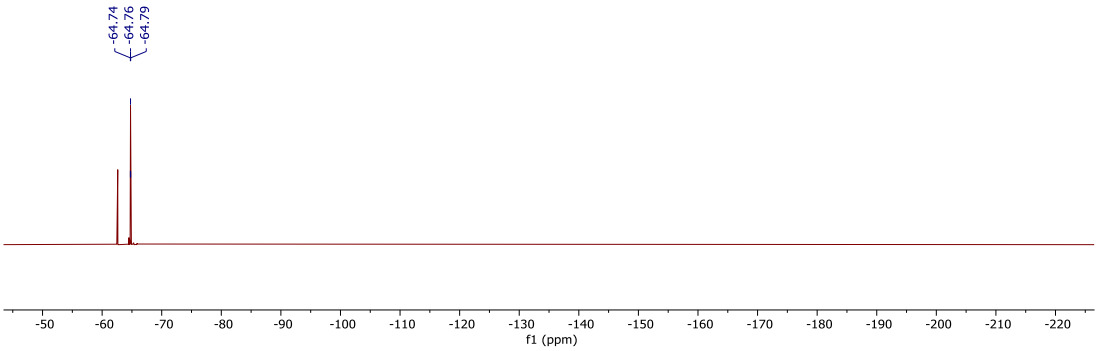
^{1}H NMR (400 MHz) spectrum of compound **3h** in $CDCl_3$



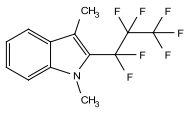
^{13} C{^{1}H} NMR (100 MHz) spectrum of compound **3h** in $CDCl_3$

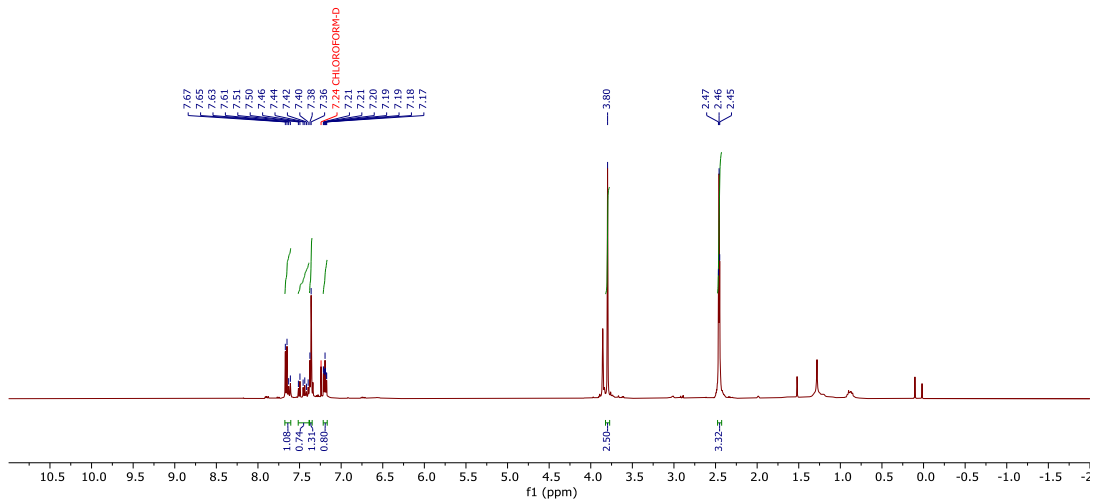


3h

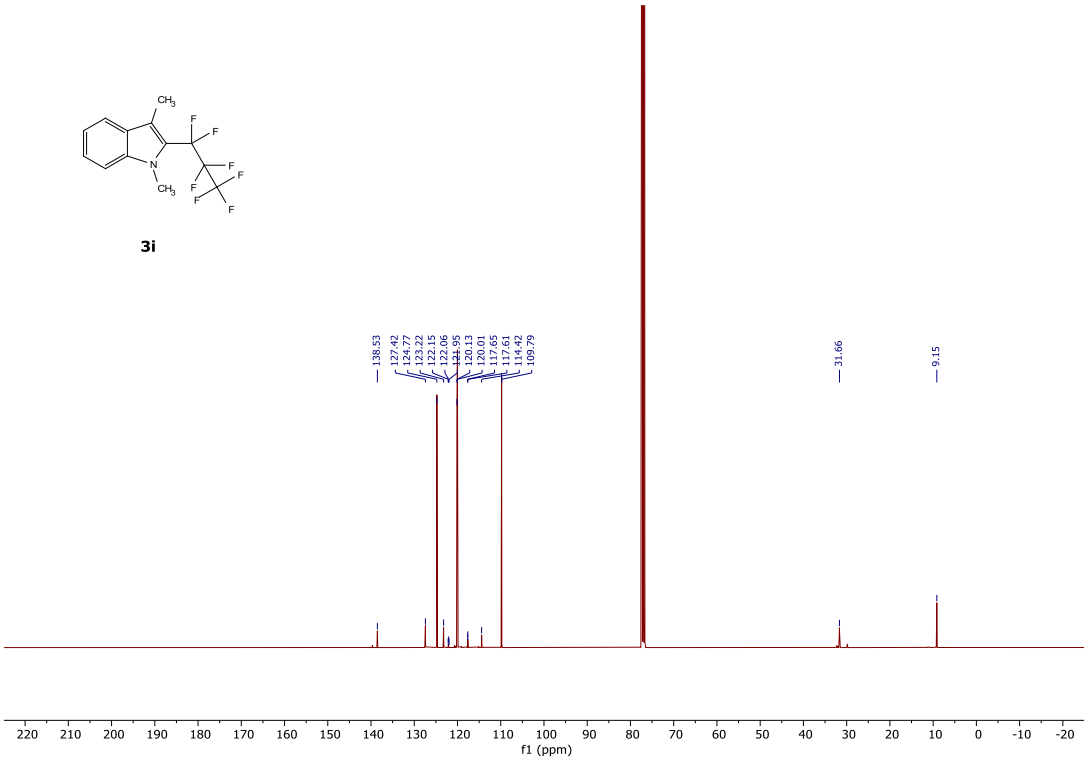


^{19}F NMR (471 MHz) spectrum of compound **3h** in $CDCl_3$ with $PhCF_3$ as reference standard

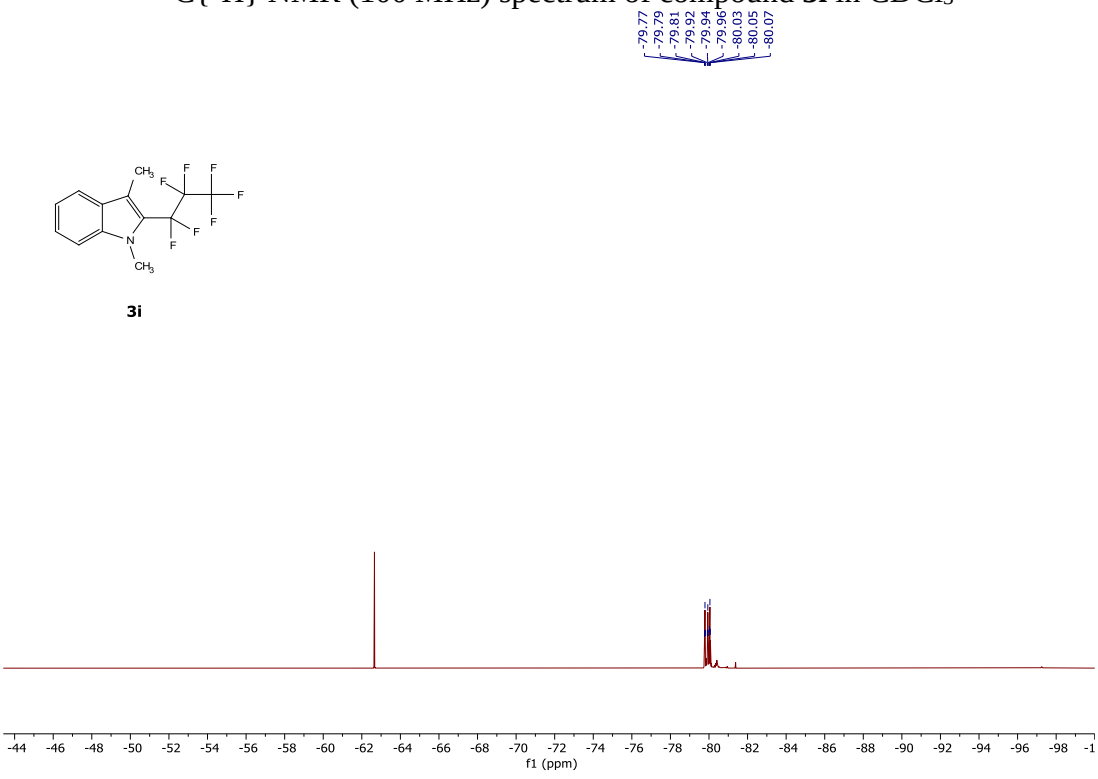




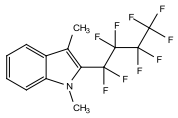
^{1}H NMR (400 MHz) spectrum of compound **3i** in $CDCl_3$

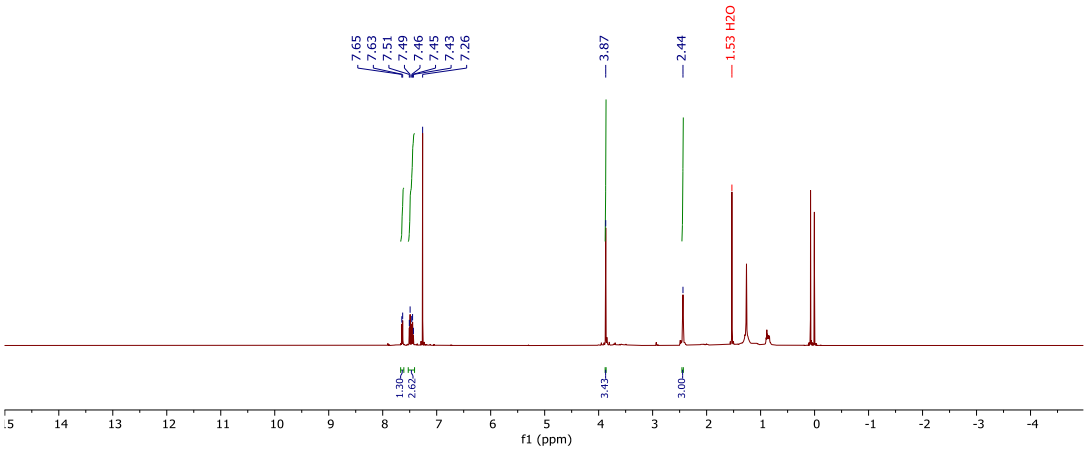


$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3i** in $CDCl_3$

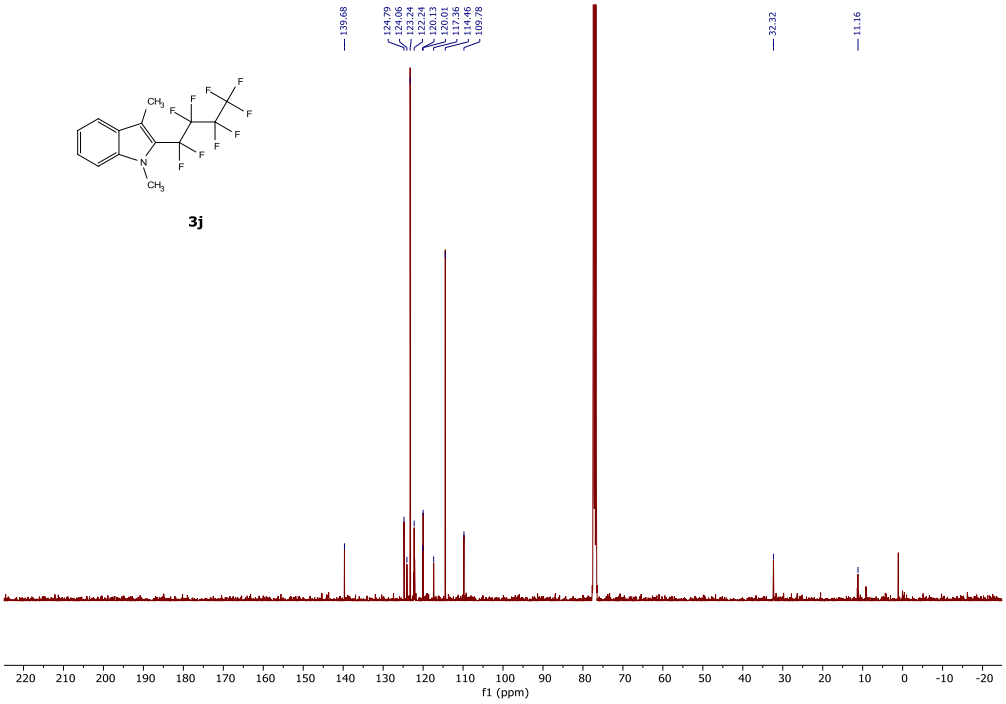


^{19}F NMR (471 MHz) spectrum of compound **3i** in $CDCl_3$ with $PhCF_3$ as reference standard

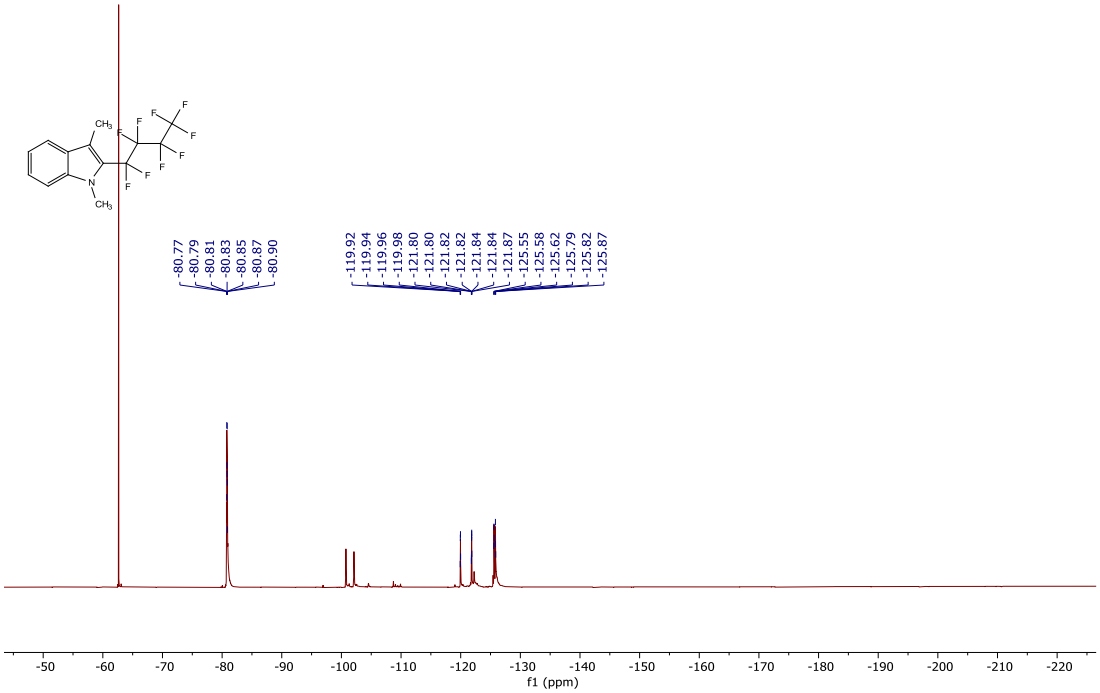




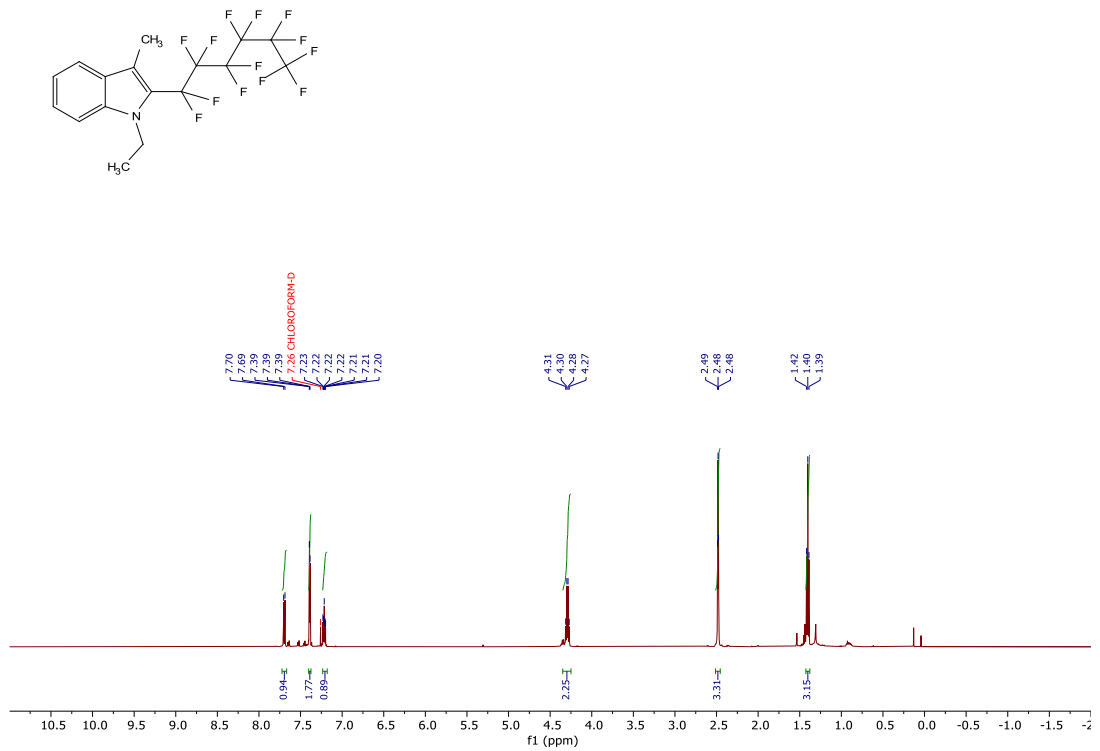
^{1}H NMR (500 MHz) spectrum of compound **3j** in $CDCl_3$



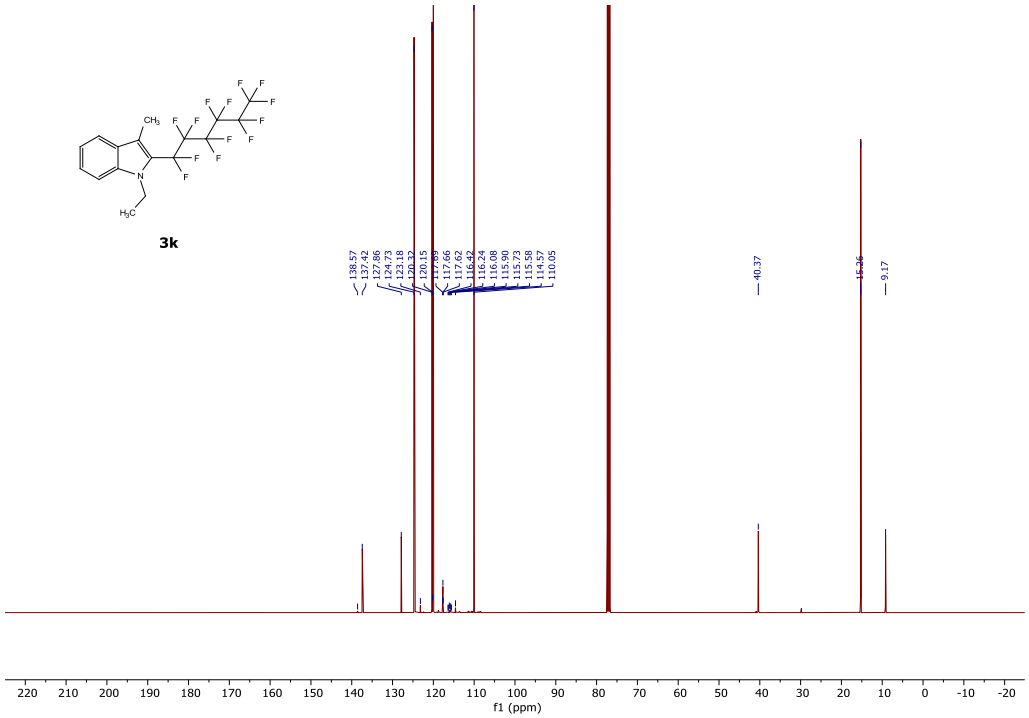
^{13}C{^{1}H} NMR (100 MHz) spectrum of compound **3j** in $CDCl_3$



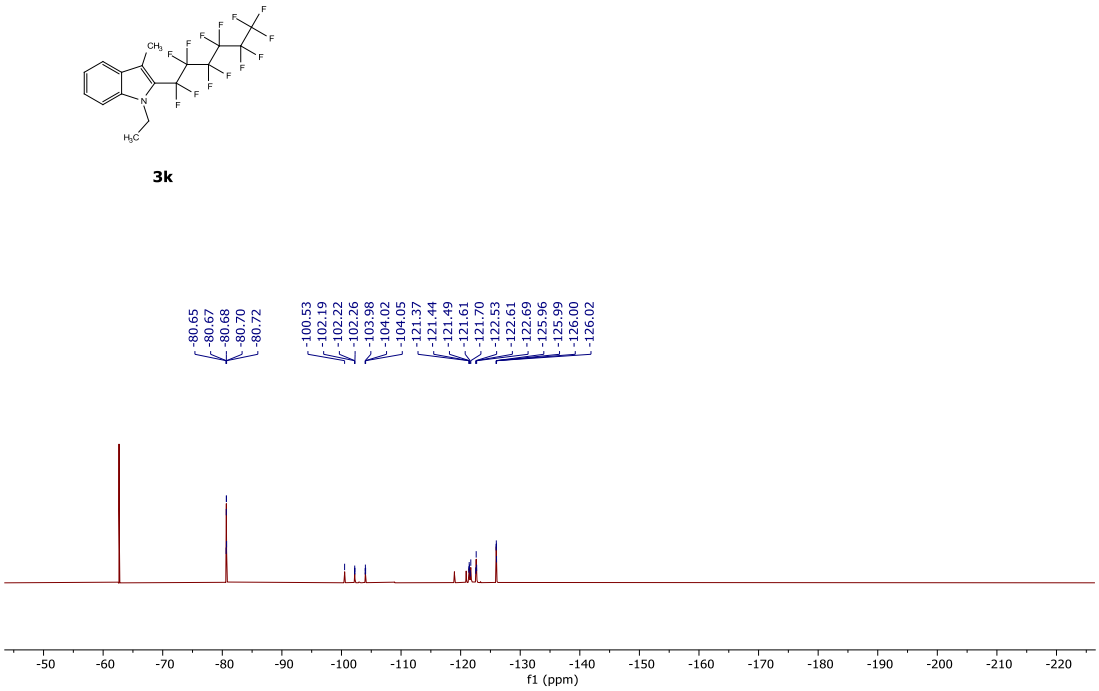
^{19}F NMR (471 MHz) spectrum of compound **3j** in $CDCl_3$ with $PhCF_3$ as reference standard



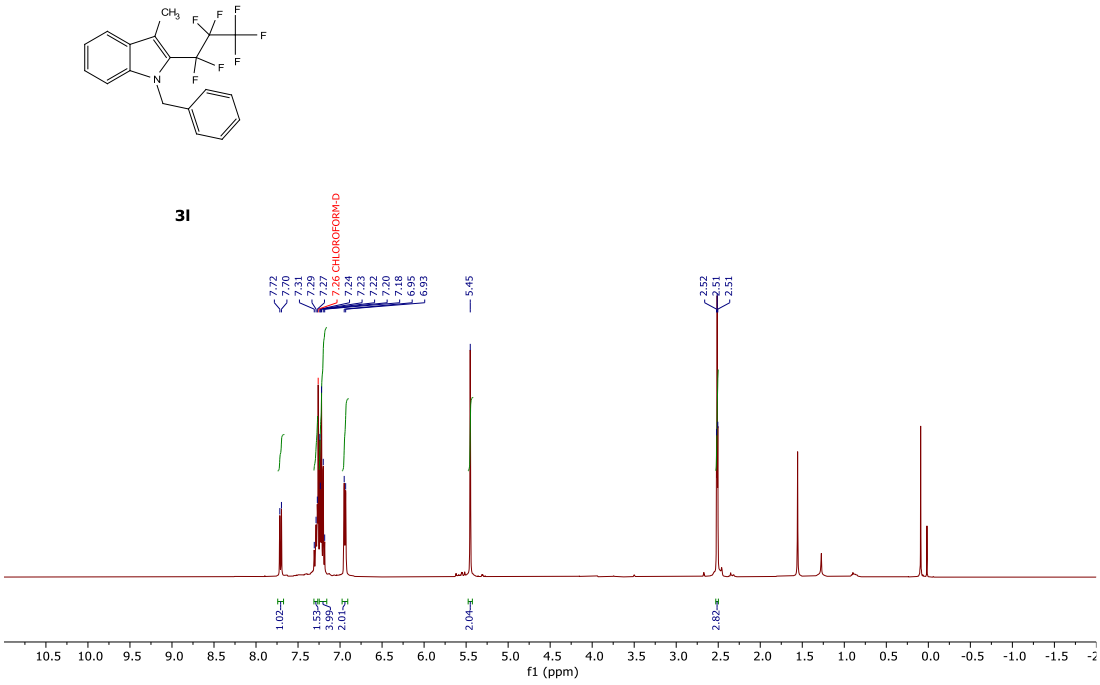
^{1}H NMR (500 MHz) spectrum of compound **3k** in $CDCl_3$



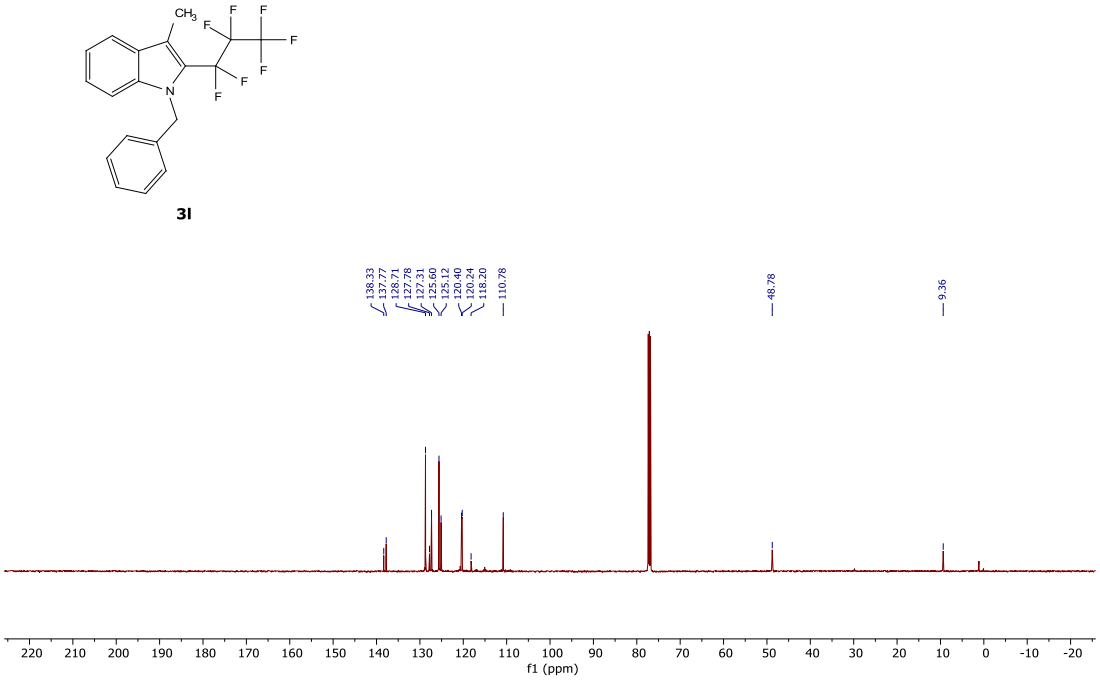
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3k** in $CDCl_3$



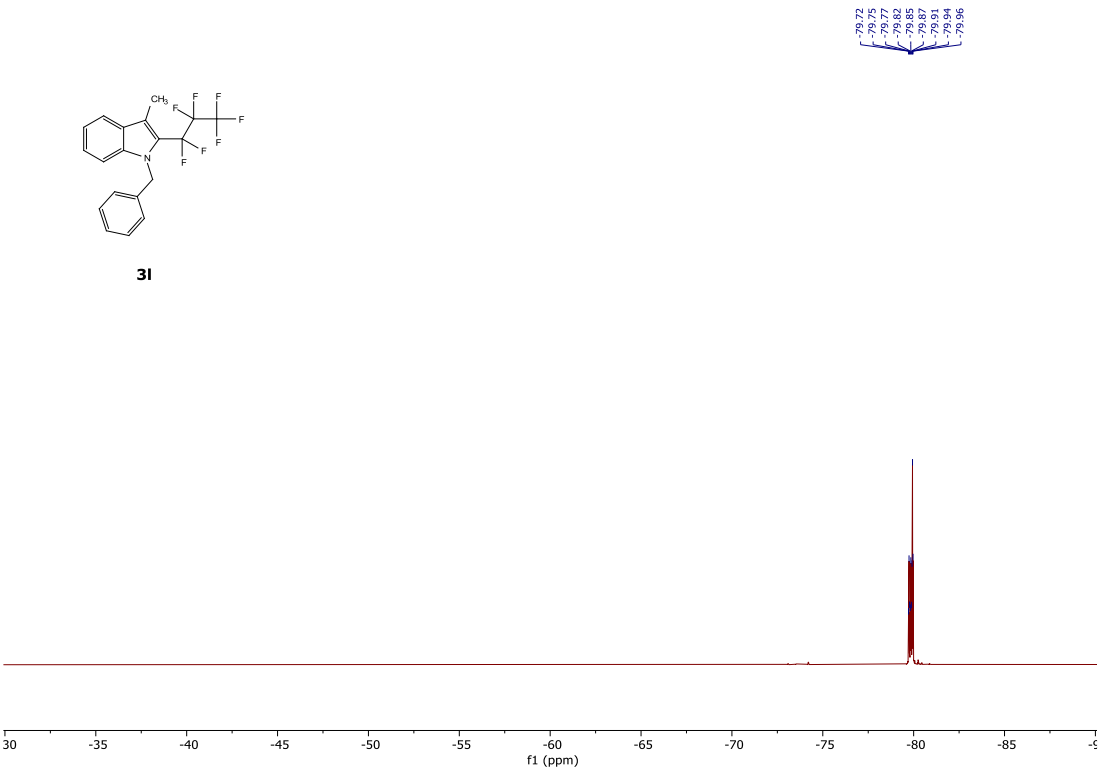
^{19}F NMR (471 MHz) spectrum of compound **3k** in $CDCl_3$ with $PhCF_3$ as reference standard



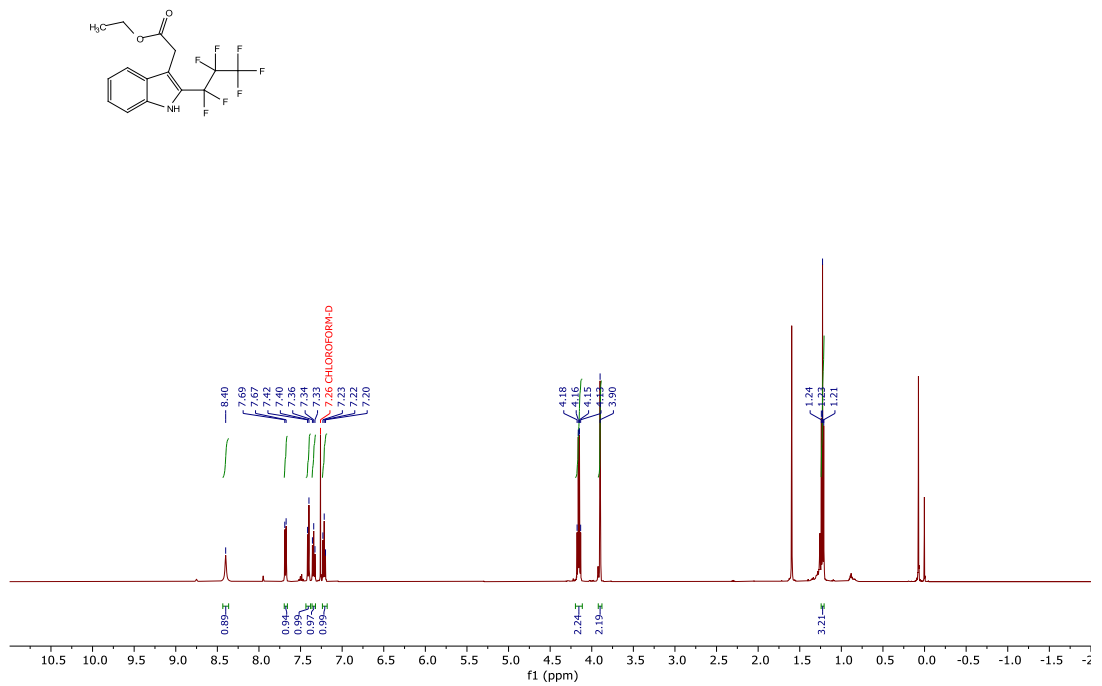
^{1}H NMR (400 MHz) spectrum of compound **3l** in $CDCl_3$



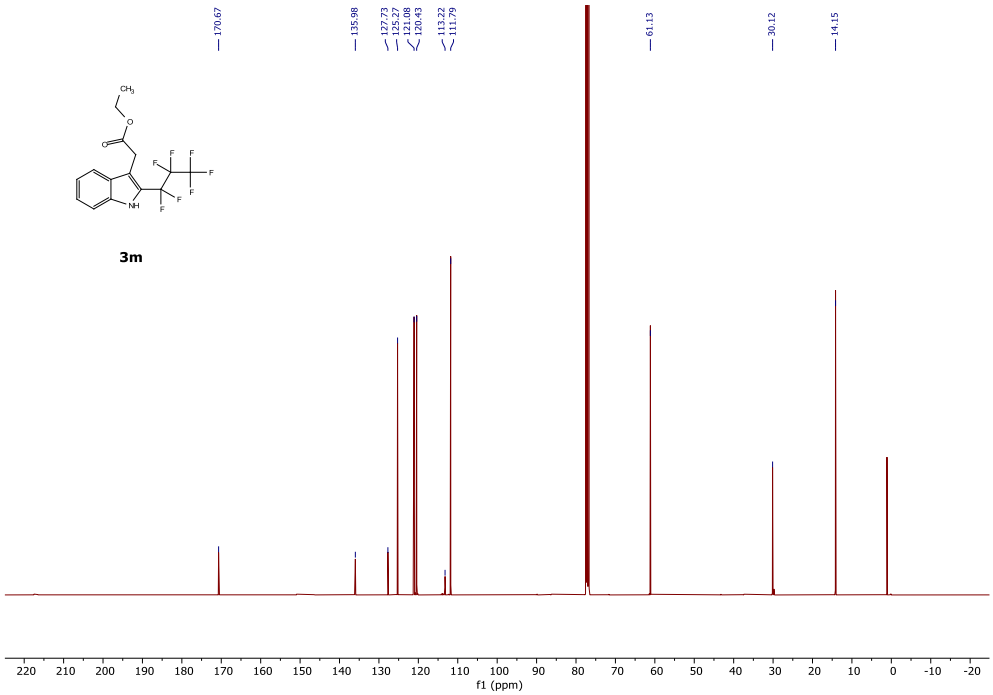
^{13} C{^{1}H} NMR (100 MHz) spectrum of compound **3l** in $CDCl_3$



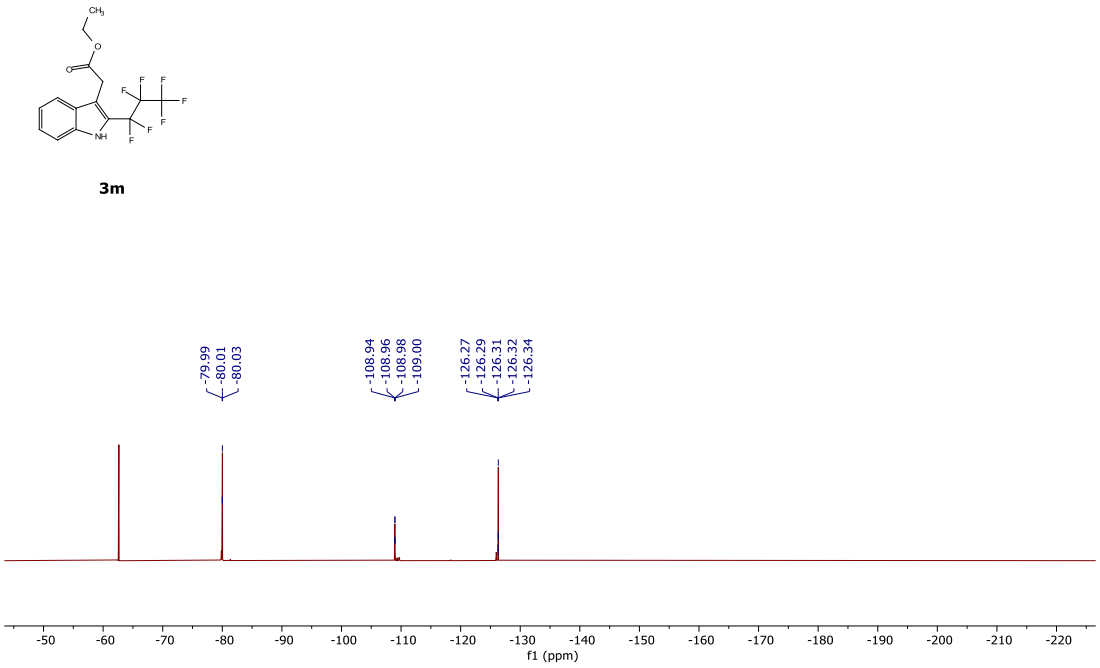
^{19}F NMR (373 MHz) spectrum of compound **3l** in $CDCl_3$



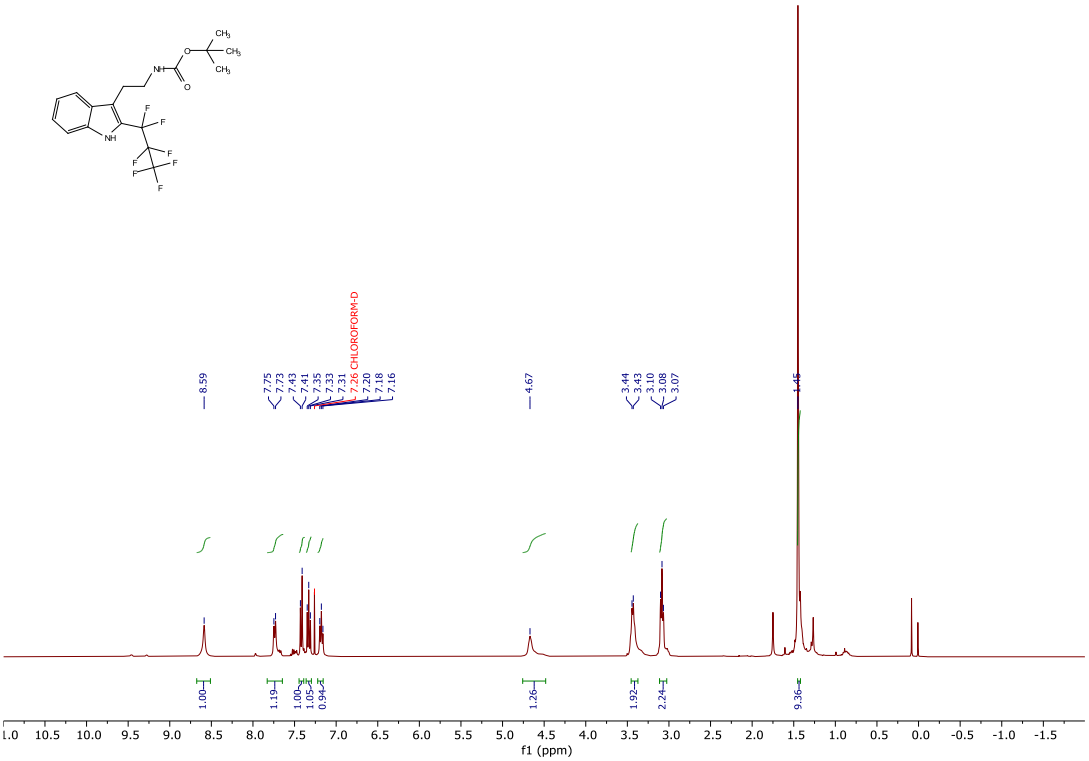
^{1}H NMR (500 MHz) spectrum of compound **3m** in $CDCl_3$



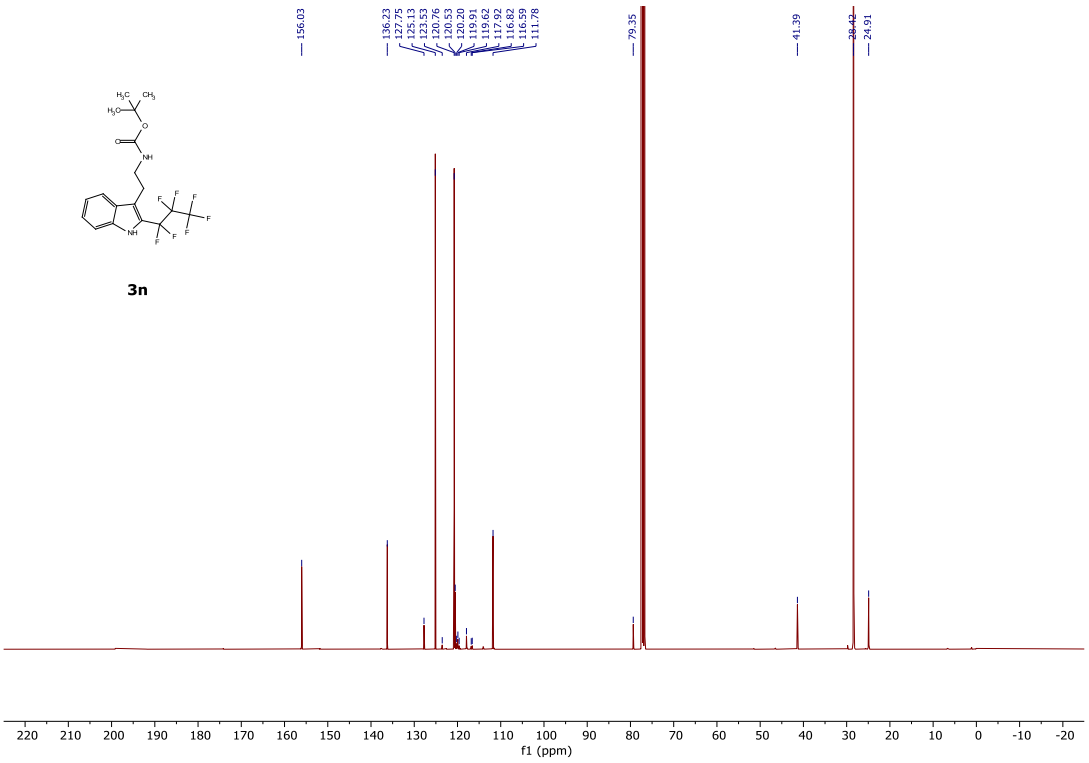
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3m** in $CDCl_3$



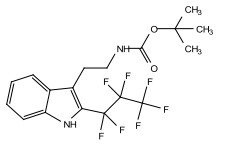
^{19}F NMR (471 MHz) spectrum of compound **3m** in $CDCl_3$ with $PhCF_3$ as reference standard



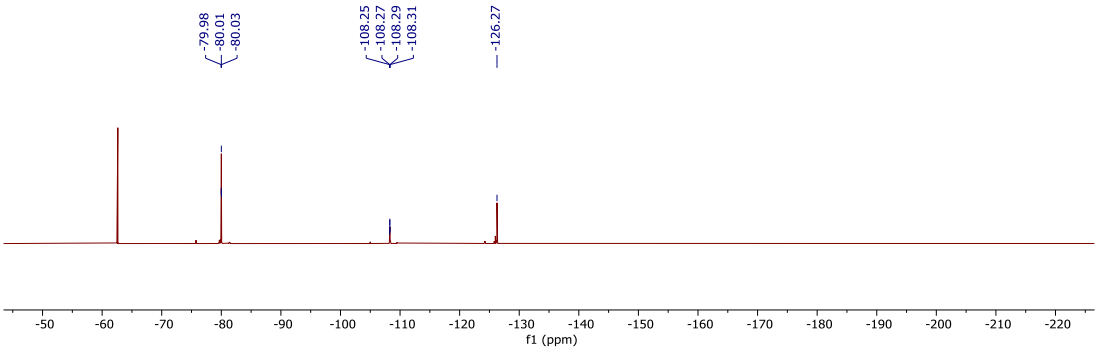
^{1}H NMR (400 MHz) spectrum of compound **3n** in $CDCl_3$



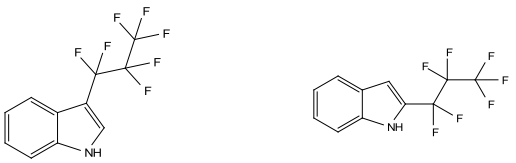
^{13} C{^{1}H} NMR (100 MHz) spectrum of compound **3n** in $CDCl_3$

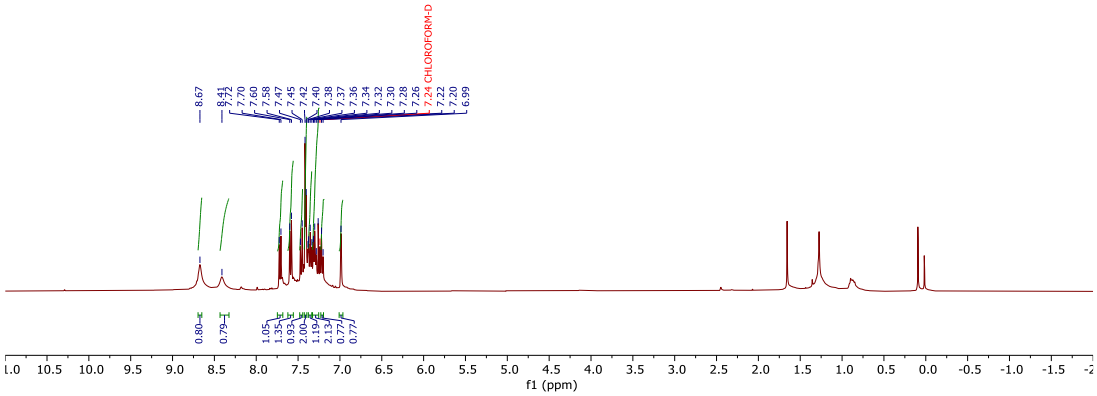


3n

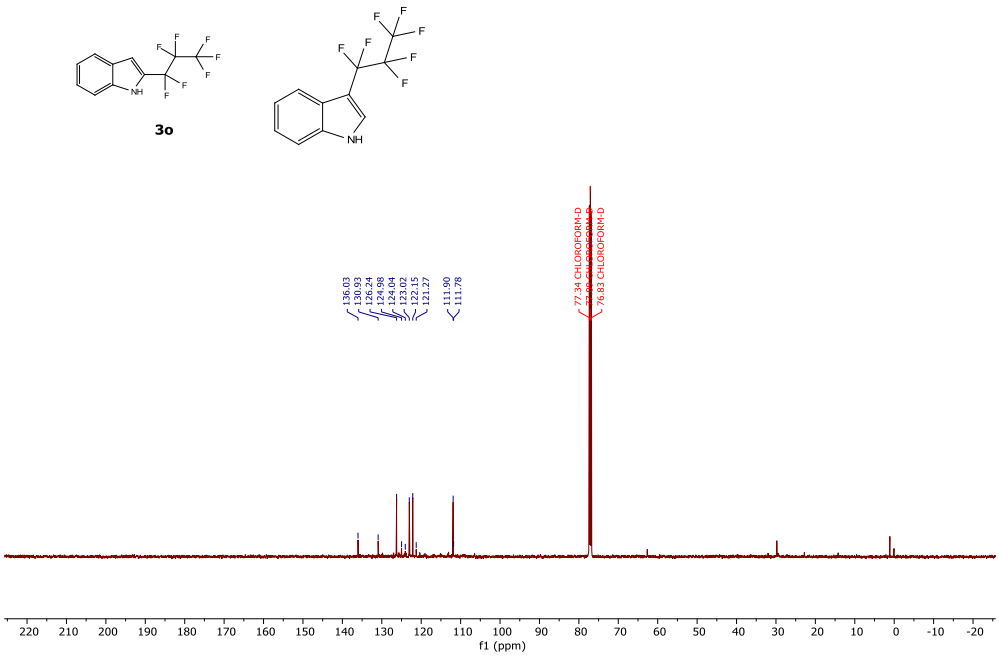


^{19}F NMR (471 MHz) spectrum of compound **3n** in $CDCl_3$ with $PhCF_3$ as reference standard

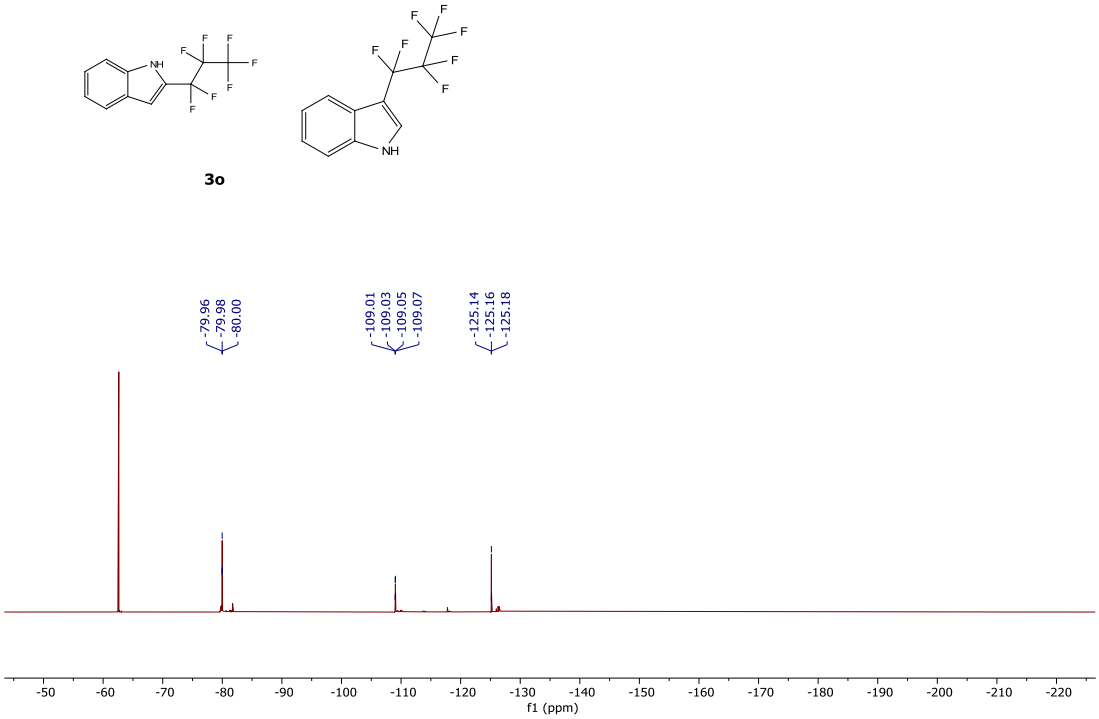




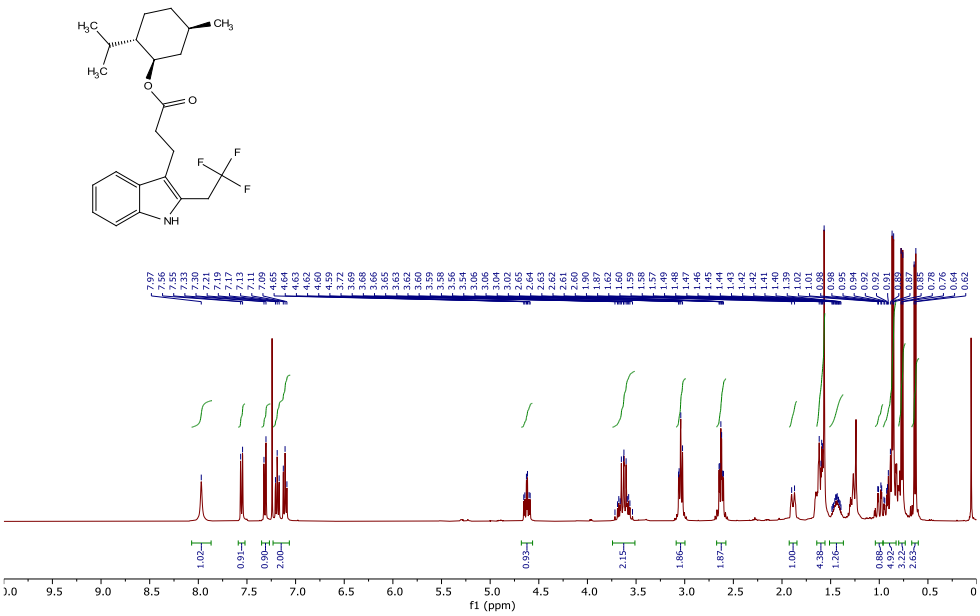
^{1}H NMR (400 MHz) spectrum of compound **3o** in $CDCl_3$



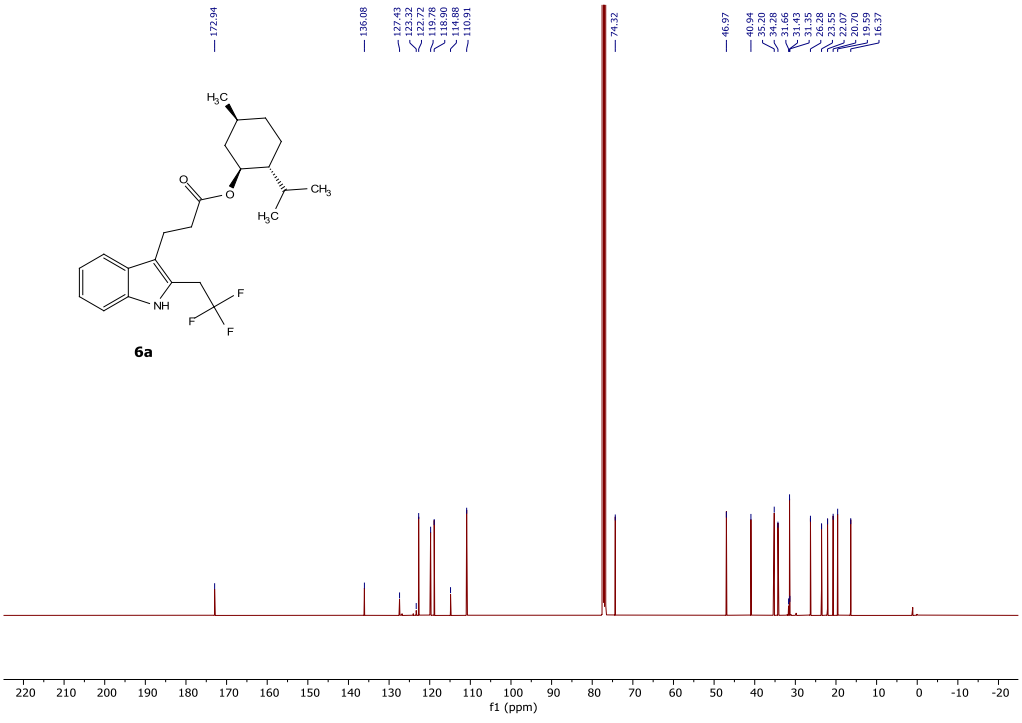
$^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of compound **3o** in $CDCl_3$



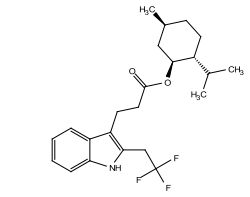
^{19}F NMR (471 MHz) spectrum of compound **3o** in $CDCl_3$ with $PhCF_3$ as reference standard



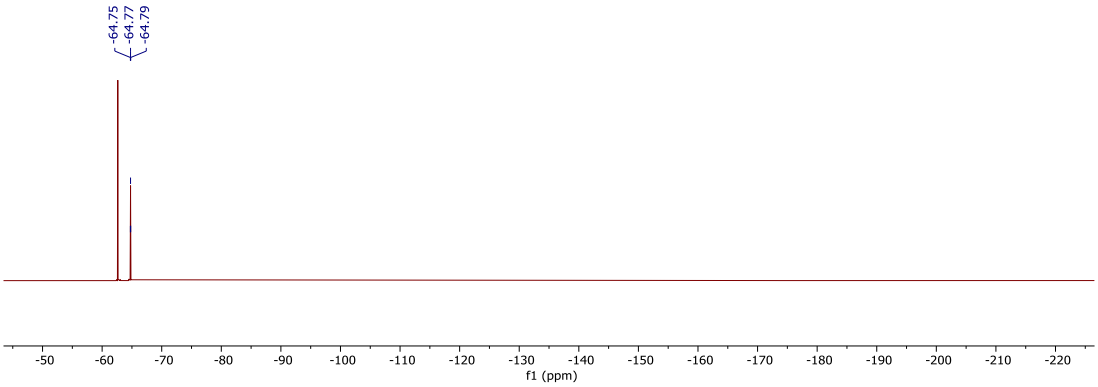
^{1}H NMR (400 MHz) spectrum of compound **6a** in $CDCl_3$



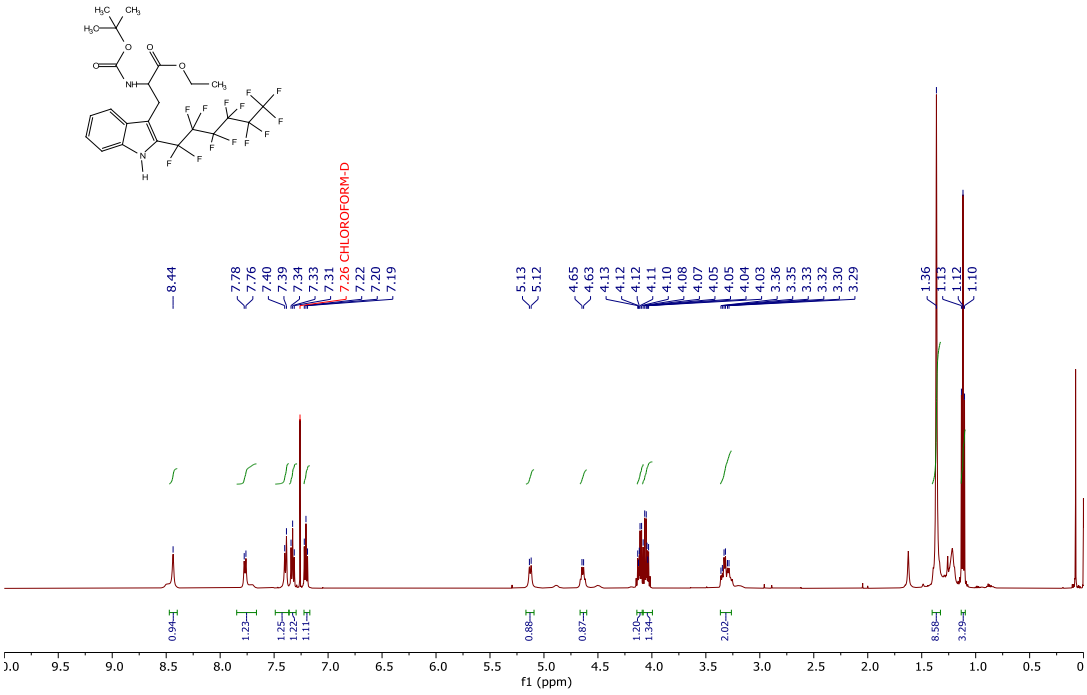
^{13}C{^{1}H} NMR (100 MHz) spectrum of compound **6a** in $CDCl_3$



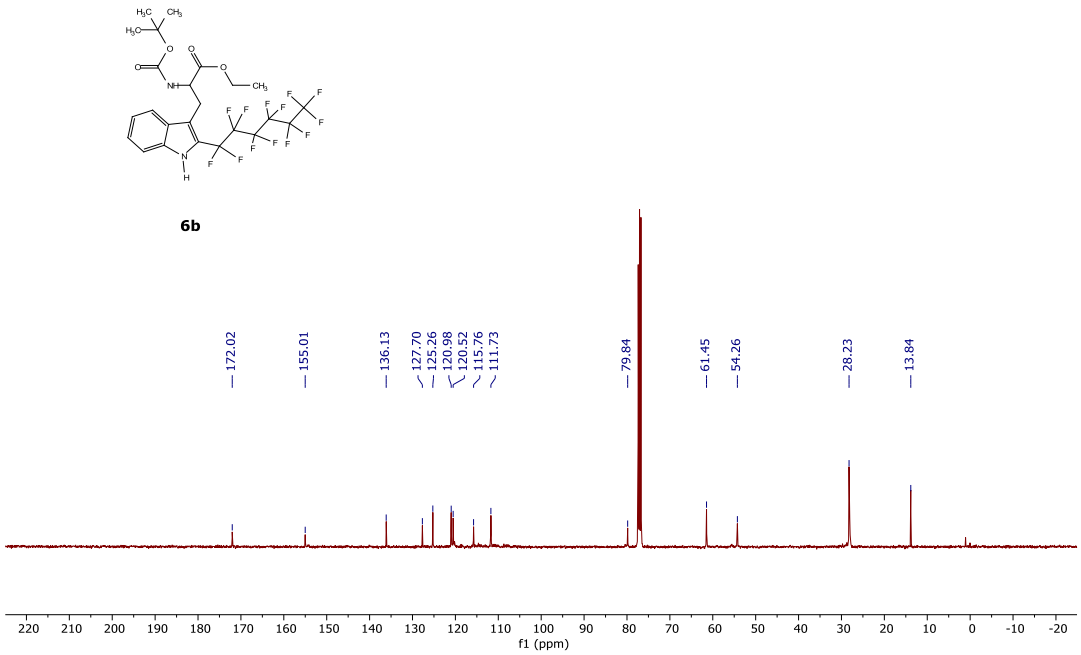
6a



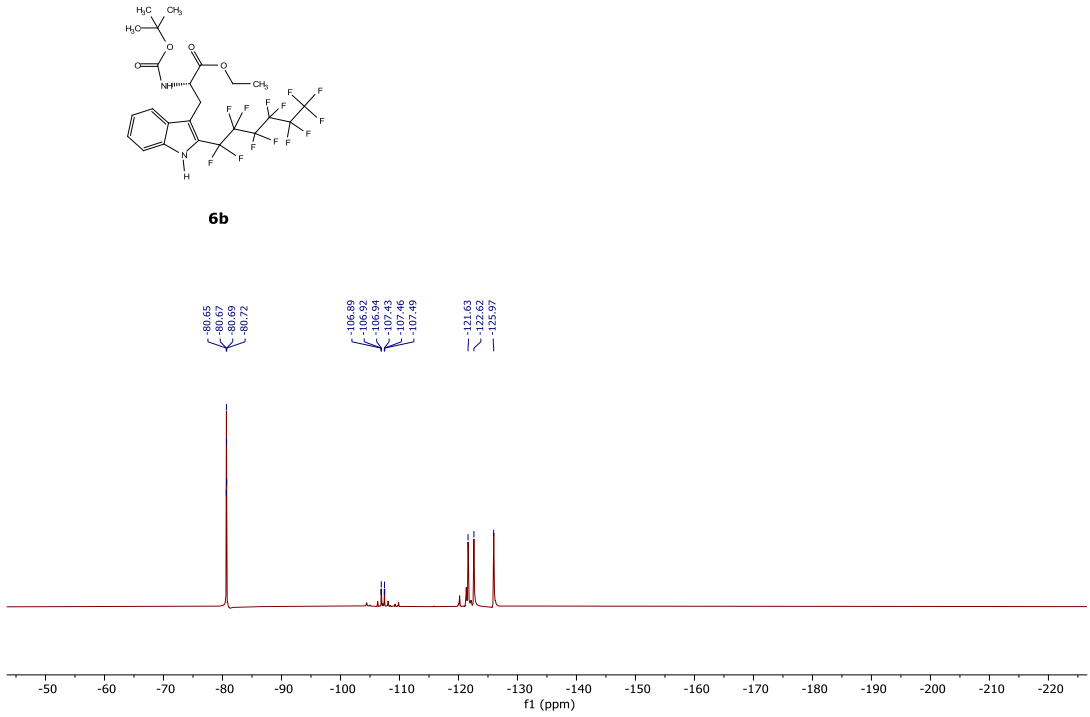
^{19}F NMR (471 MHz) spectrum of compound **6a** in $CDCl_3$ with $PhCF_3$ as reference standard



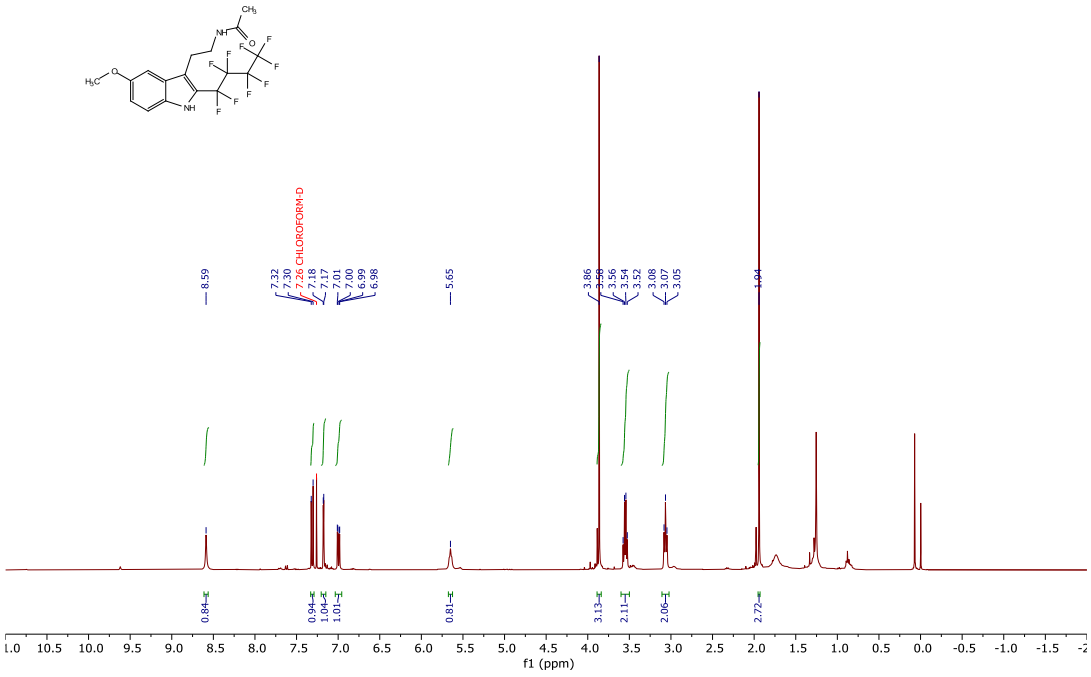
^{1}H NMR (500 MHz) spectrum of compound **6b** in $CDCl_3$



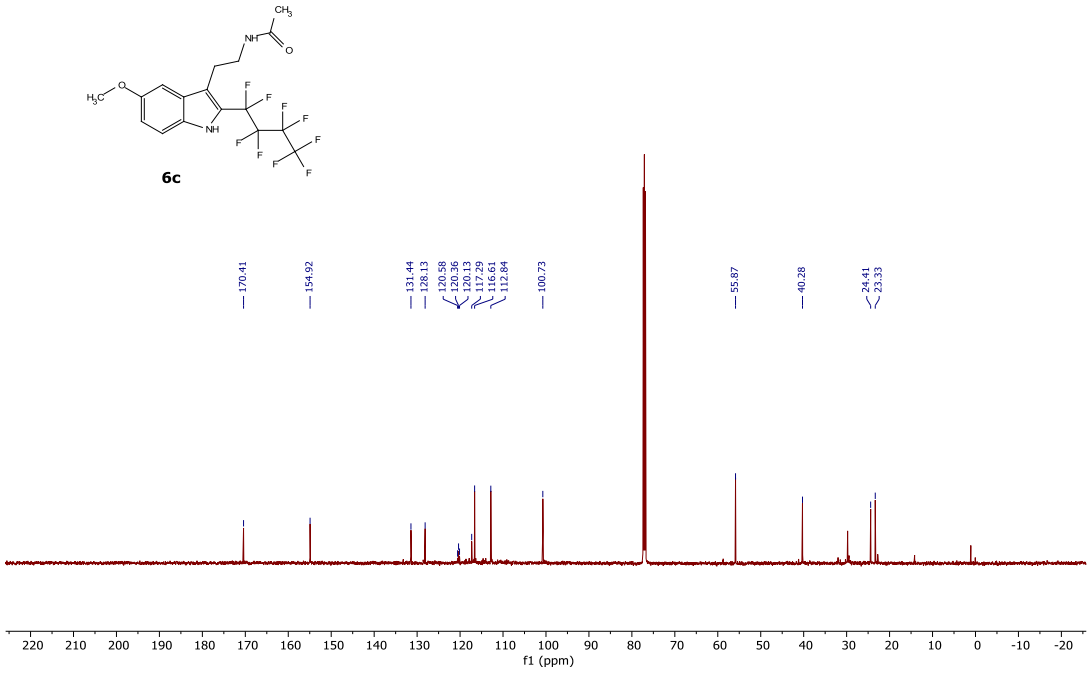
^{13} C{^{1}H} NMR (100 MHz) spectrum of compound **6b** in $CDCl_3$



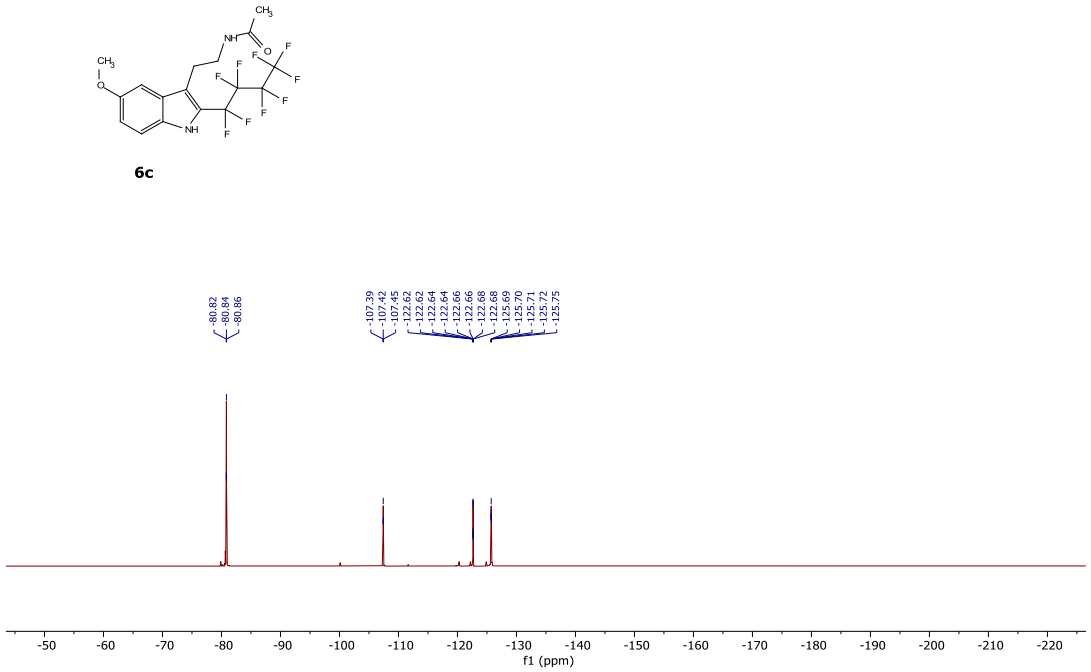
^{19}F NMR (471 MHz) spectrum of compound **6b** in $CDCl_3$



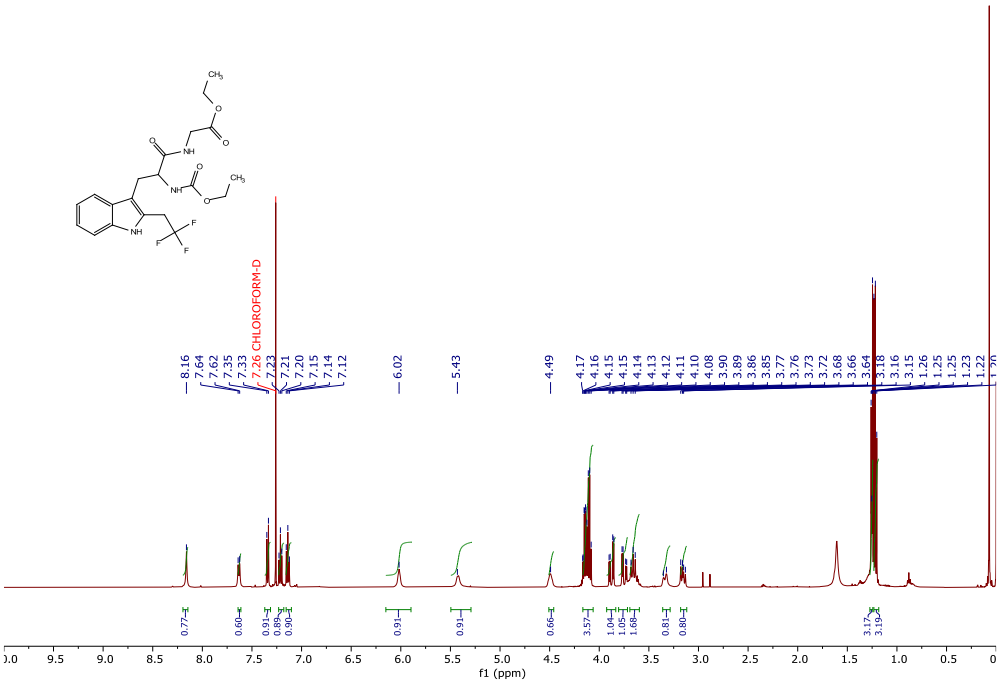
^{1}H NMR (400 MHz) spectrum of compound **6c** in $CDCl_3$



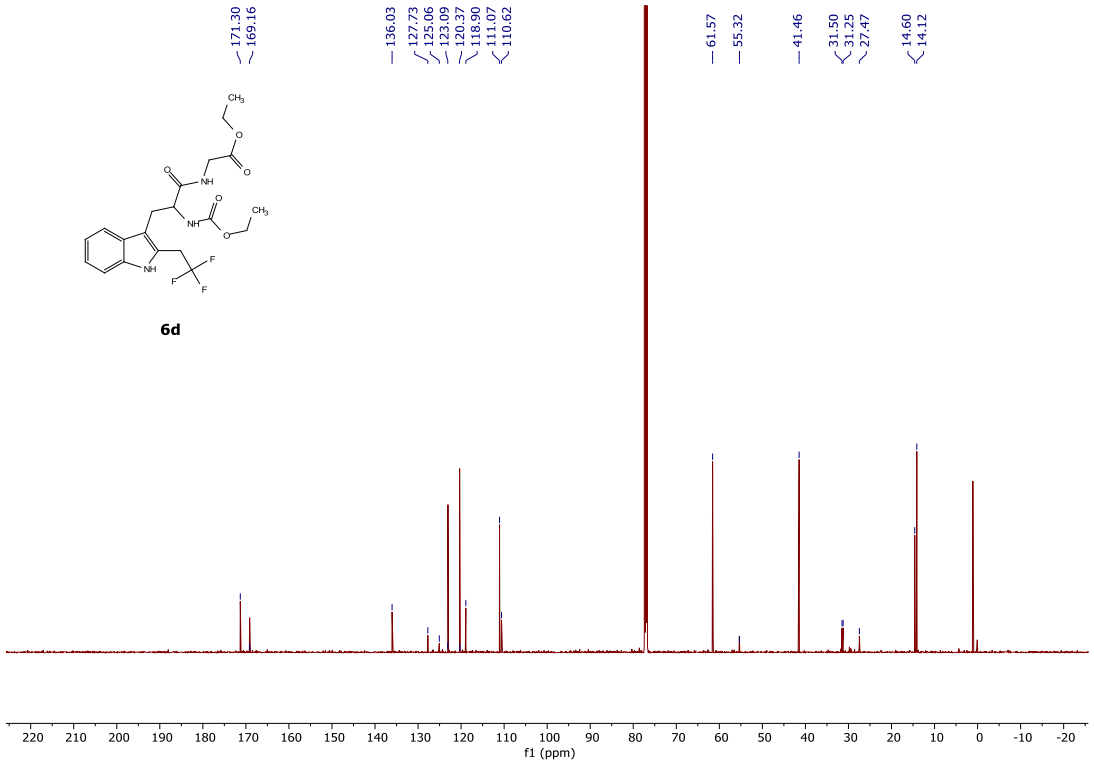
^{13}C{^{1}H} NMR (125 MHz) spectrum of compound **6c** in $CDCl_3$



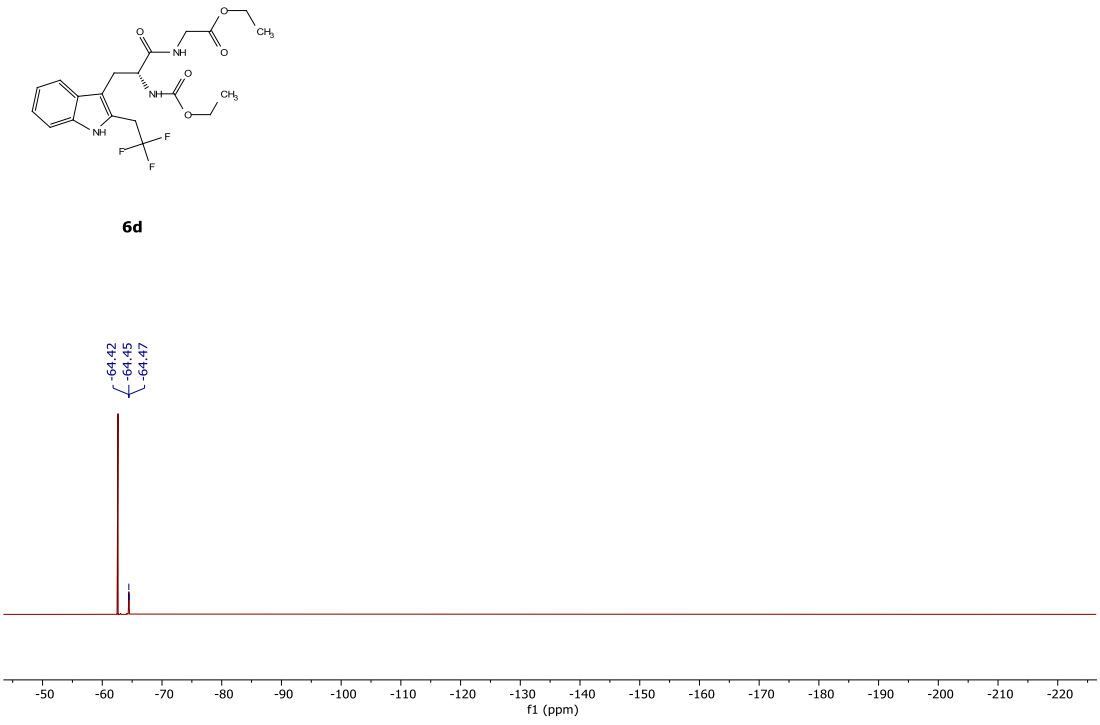
^{19}F NMR (471 MHz) spectrum of compound **6c** in $CDCl_3$



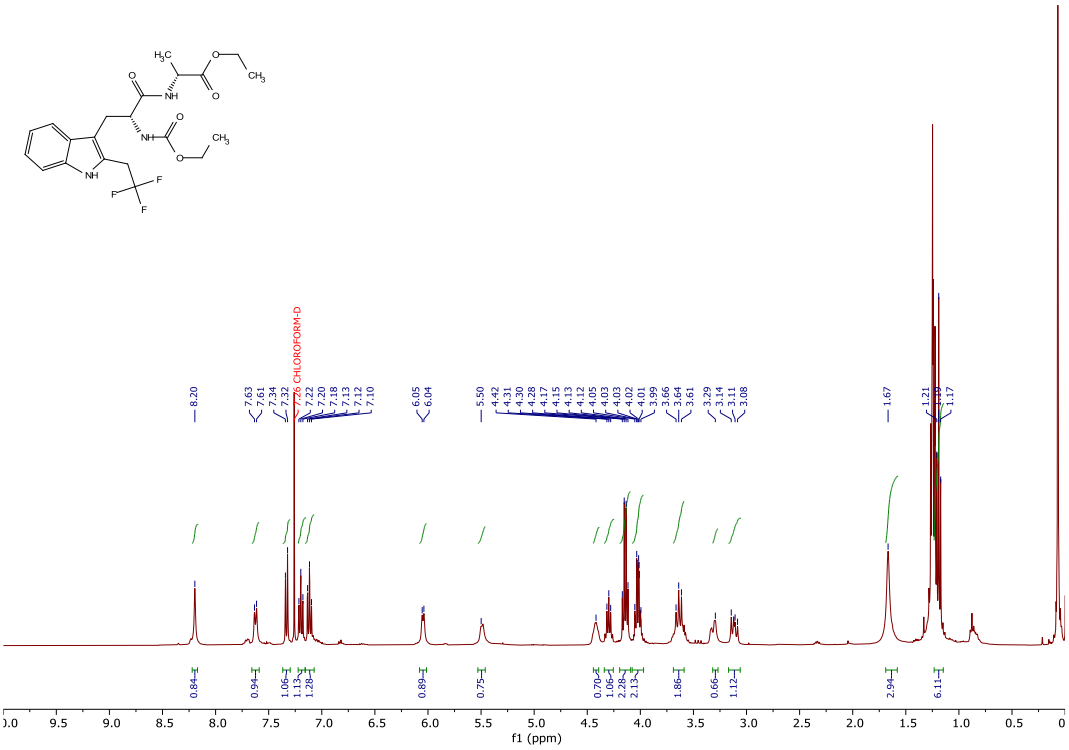
^{1}H NMR (500 MHz) spectrum of compound **6d** in $CDCl_3$



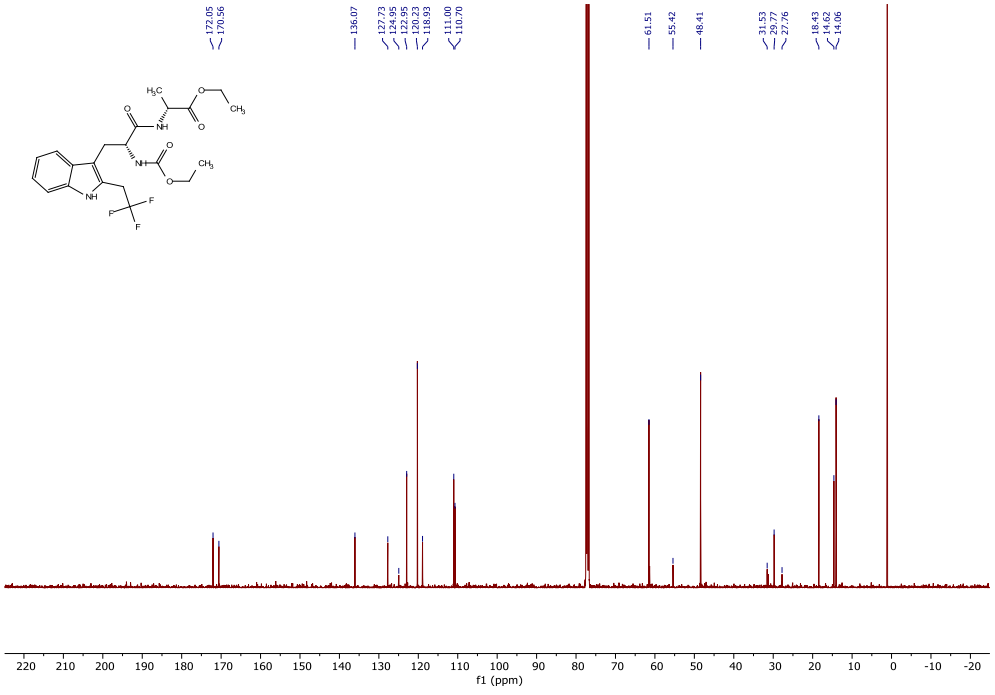
$^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of compound **6d** in $CDCl_3$



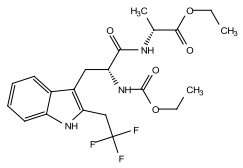
^{19}F NMR (471 MHz) spectrum of compound **6d** in $CDCl_3$ with $PhCF_3$ as reference standard



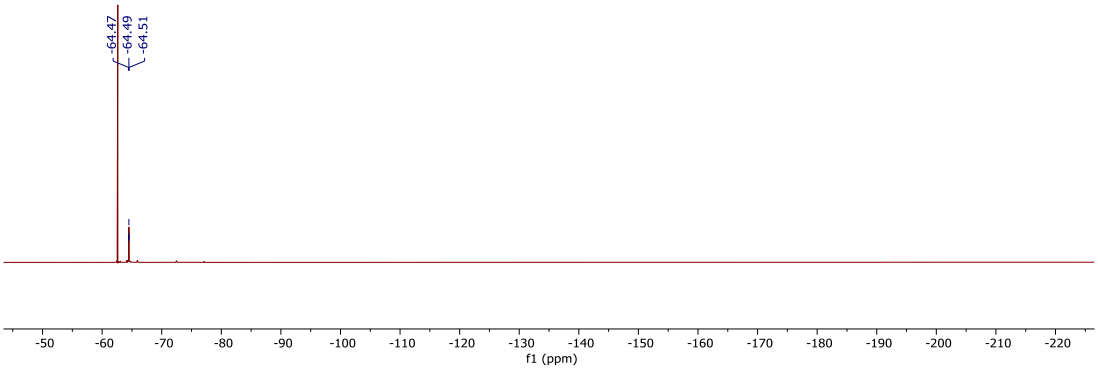
^{1}H NMR (400 MHz) spectrum of compound **6e** in $CDCl_3$



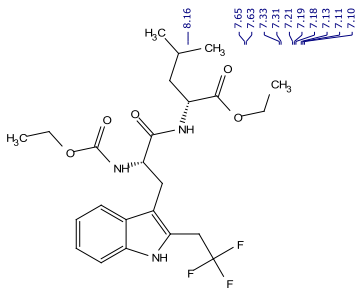
^{13} C{^{1}H} NMR (100 MHz) spectrum of compound **6e** in $CDCl_3$



6e

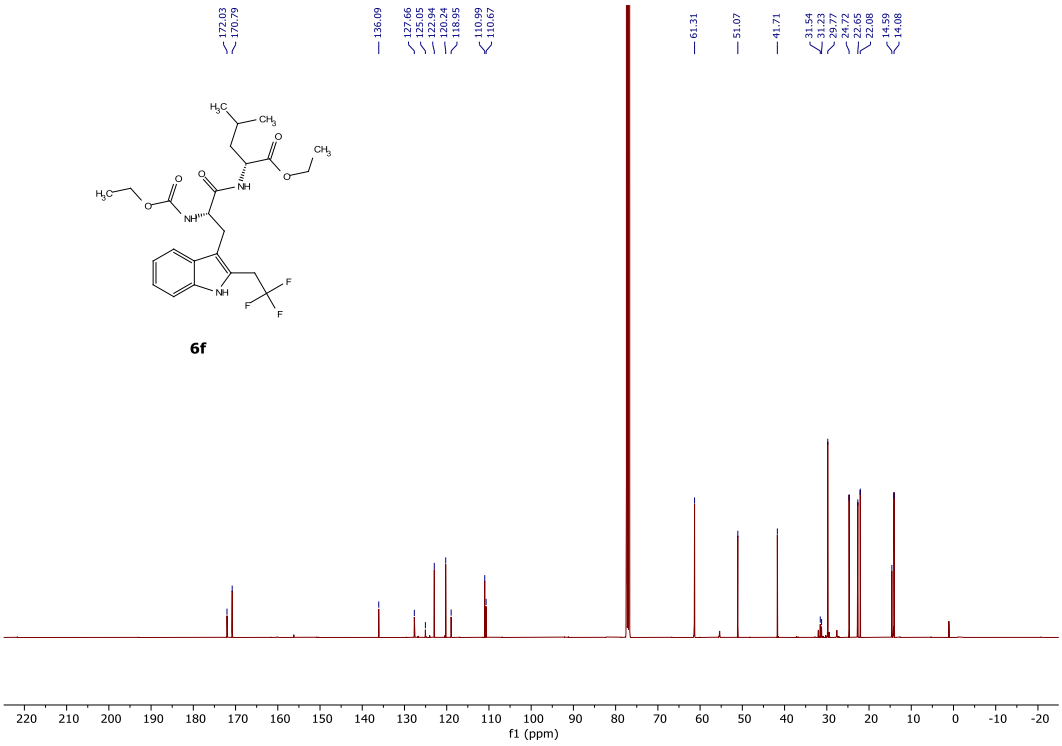


^{19}F NMR (471 MHz) spectrum of compound **6e** in $CDCl_3$ with $PhCF_3$ as reference standard

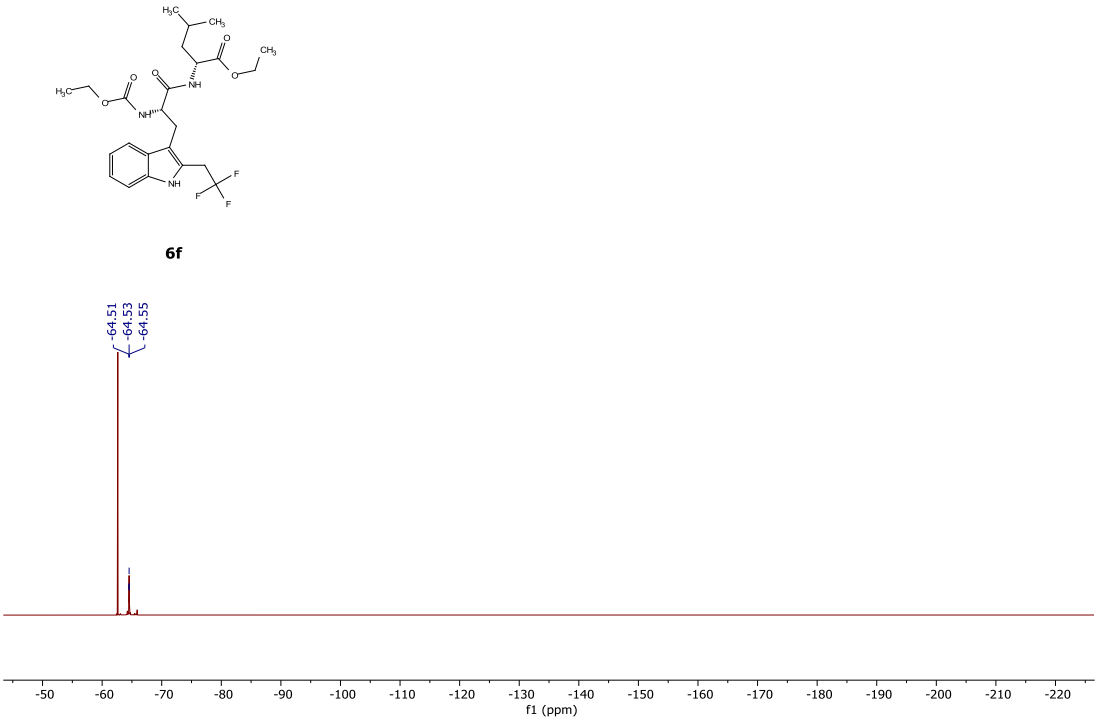


6f

^{1}H NMR (500 MHz) spectrum of compound **6f** in $CDCl_3$



$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **6f** in $CDCl_3$



^{19}F NMR (471 MHz) spectrum of compound **6f** in $CDCl_3$ with $PhCF_3$ as reference standard

7. Crystal Structure of 3a (CCDC No.: 2322591)