Haloalkane Driven Dichotomous Reactivity of Aryl Radical as Halogen and Hydrogen Atom Transfer Agent: Photocatalytic Olefin and Alkyne Functionalization Cascades

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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. DCE 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 $CDCl_3$ and $PhCF_3$ as reference standard. Mass spectrometric data were obtained using WATERS-Q-TOF Premier-ESI-MS and GC-MS. 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[1-6].

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.

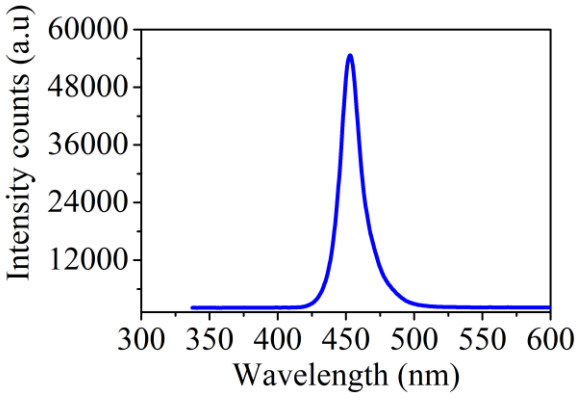
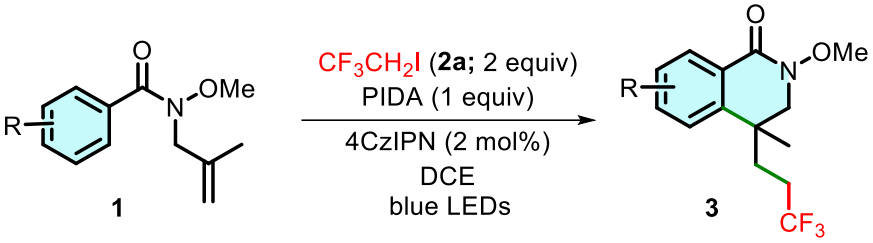


Figure S1: Emission profile of Blue LEDs & Photocatalytic set up

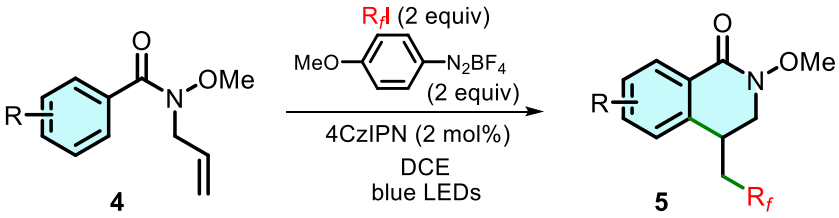
2. General Procedures:

2.1. General Procedure 1:



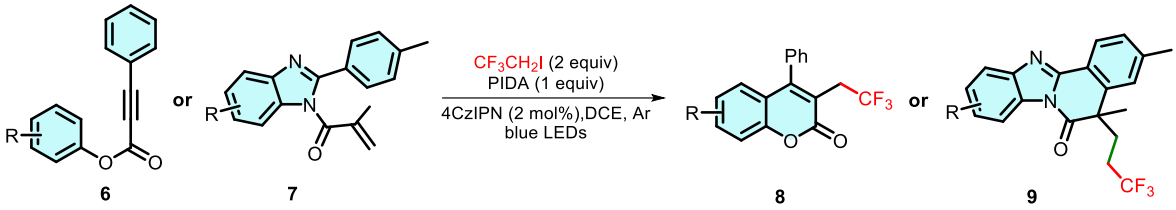
An oven dried reaction vial equipped with magnetic stir bar was charged with the weinreb amide **1** (1.0 equiv.), PIDA (1 equiv.), 4CzIPN (2 mol%) and dry DCE (0.24 M). The reaction mixture was sparged with Ar for 15 minutes and then trifluoroethyl iodide **2a** (2 equiv) was added and the reaction mixture was irradiated under 18 W Blue LEDs. After completion of reaction (confirmed by TLC), reaction mixture was concentrated and the residue was purified by column chromatography on silica gel using ethyl acetate in petroleum ether to afford the desired product **3**.

2.2. General Procedure 2:



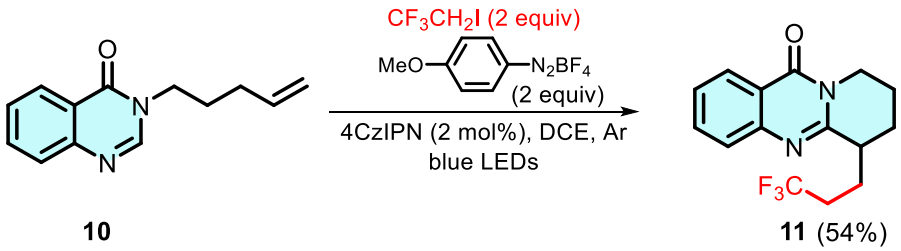
An oven dried reaction vial equipped with magnetic stir bar was charged with the weinreb amide **4** (1.0 equiv.), 4-methoxyphenyl diazonium tetrafluoroborate (2 equiv.), 4CzIPN (2 mol%) and dry DCE (0.24 M). The reaction mixture was purged with Ar for 15 minutes and then trifluoroethyl iodide or perfluoroalkyl iodide (2 equiv) was added 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 **5**.

2.3. General Procedure 3:



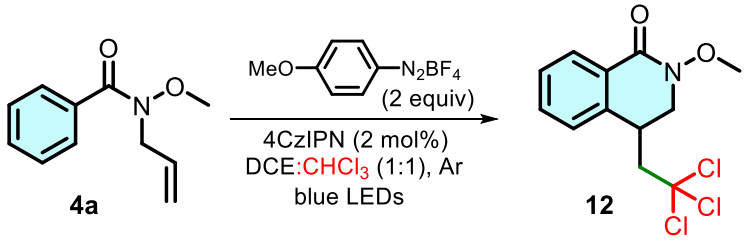
An oven dried reaction vial equipped with magnetic stir bar was charged with **6** or **7** (1.0 equiv.), PIDA (1 equiv.), 4CzIPN (2 mol%) and dry DCE (0.24 M). The reaction mixture was purged with Ar for 15 minutes and then trifluoroethyl iodide (2 equiv) was added and irradiated under 18 W Blue LED's. 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 **8** or **9**.

2.4. General Procedure 4:



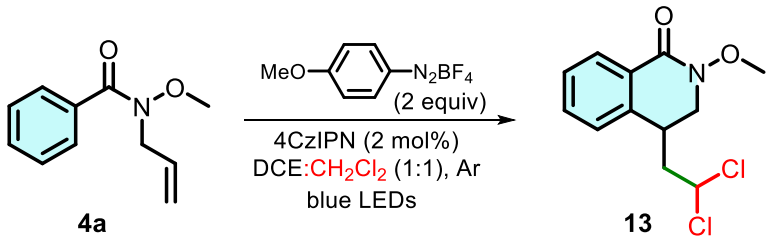
An oven dried reaction vial equipped with magnetic stir bar was charged with **10** (1.0 equiv.), 4-methoxy phenyl diazonium salt (2 equiv.), 4CzIPN (2 mol%) and dry DCE (1 mL). The reaction mixture was purged with Ar for 15 minutes and then trifluoroethyl iodide (2 equiv) was added and irradiated under 18 W Blue LED's. 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 **11**.

2.5. General Procedure 5:



An oven dried reaction vial equipped with magnetic stir bar was charged with Weinreb amide **4a** (1.0 equiv.), 4-methoxy phenyl diazonium salt (2 equiv.), 4CzIPN (2 mol%) and dry DCE and $CHCl_3$ (1:1, 2ml). The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LED's. 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 **12** (35 mg, 43%).

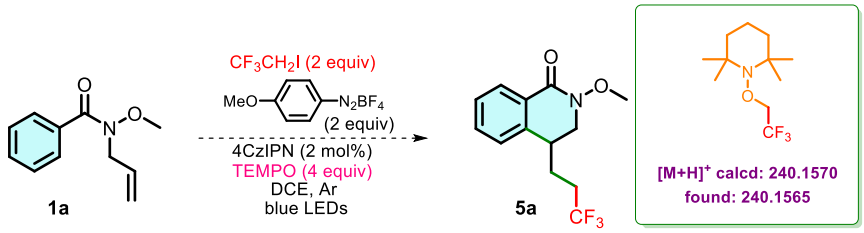
2.6. General Procedure 6:



An oven dried reaction vial equipped with magnetic stir bar was charged with Weinreb amide **4a** (1.0 equiv.), 4- methoxy phenyl diazonium salt (2 equiv.), 4CzIPN (2 mol%) and dry DCE and CH_2Cl_2 (1 mL: 1 mL). The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LED's. 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 **13** (32 mg, 45%).

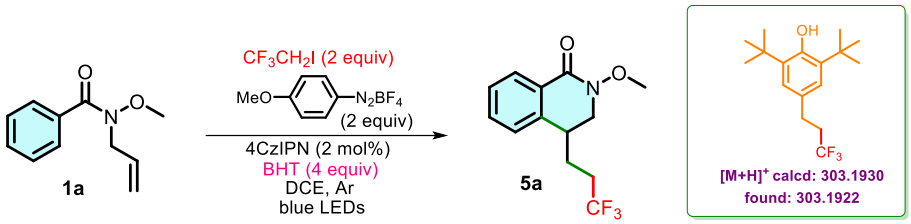
3. Control Experiments:

3.1. Procedure for the experiment with TEMPO:



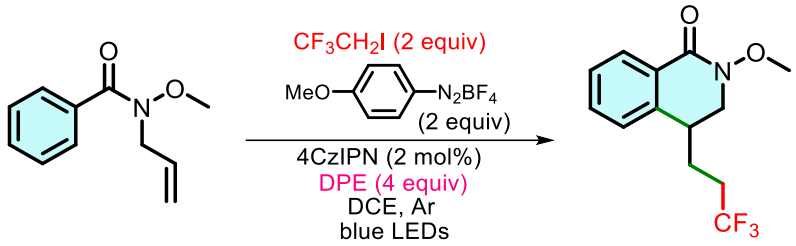
In an oven dried reaction vial equipped with a magnetic stir bar, **1a** (50 mg, 0.26 mmol), **2a** (2 equiv), 4-methoxy phenyl diazonium salt (2 equiv), TEMPO (4 equiv) and 4CzIPN catalyst (2 mol%) were dissolved in 1 mL of dry DCE. The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LED's. After 24 h TLC (Thin layer chromatography) no product formation was observed with TEMPO.

3.2. Procedure for Experiment with BHT:



In an oven dried reaction vial equipped with a magnetic stir bar, **1a** (50 mg, 0.26 mmol), **2a** (2 equiv), 4-methoxyphenyl diazonium tetrafluoroborate (2 equiv), BHT (4 equiv) and 4CzIPN catalyst (2 mol%) were dissolved in DCE (0.24 M). The reaction mixture was purged with Ar for 15 minutes and irradiated under 18 W Blue LEDs. After 24 h, TLC (thin layer chromatography) indicated product formation. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel using ethyl acetate in petroleum ether to afford the desired product **3a** (27 mg, 39%).

3.3 Procedure for Experiment with Diphenylethylene:



In an oven dried reaction vial equipped with a magnetic stir bar, **1a** (50 mg, 0.26 mmol), **2a** (2 equiv),4-methoxy phenyl diazonium salt (2 equiv), 1,1 diphenylethylene (4 equiv) and 4CzIPN catalyst (2 mol%) were dissolved in 1 mL of dry DCE. 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) indicated product formation. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel using ethyl acetate in petroleum ether to afford the desired product **3a** (15 mg, 21%).

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 (4 μM solution in DCE) at room temperature. The solution was irradiated at 350 nm and fluorescence was measured from

400 to 650 nm. Control experiment showed that 4CzIPN fluorescence was quenched by 4-methoxy phenyl diazonium salt.

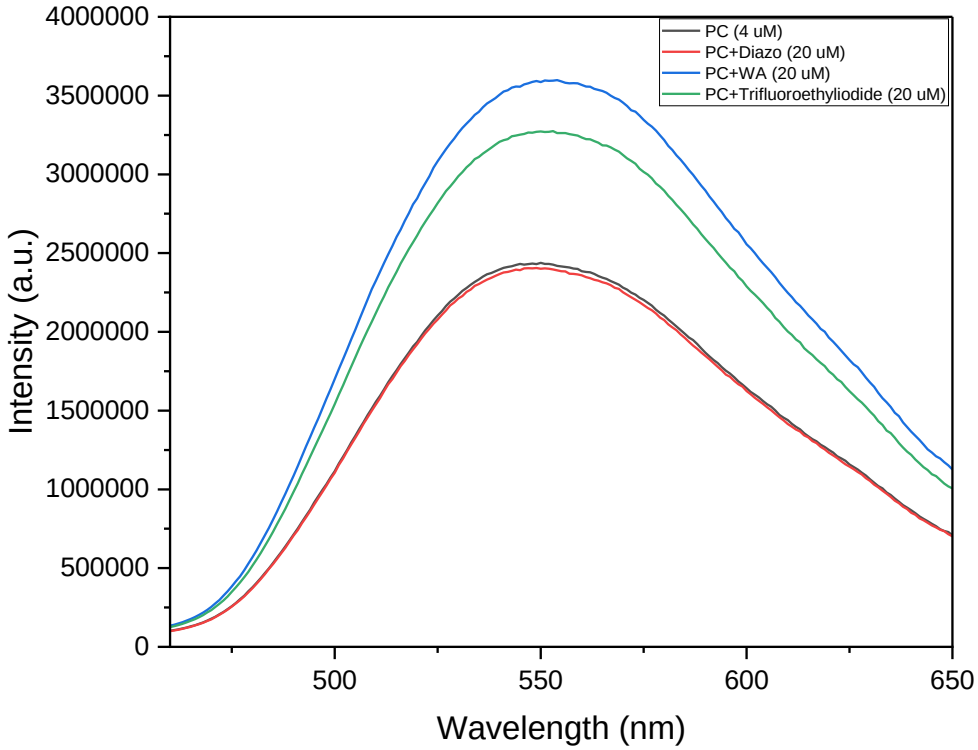


Figure S2: Fluorescence intensity of 4CzIPN solution (4 μM solution in DCE) containing 4-methoxy phenyl diazonium salt, weinreb amide, trifluoroethyl iodide in DCE (excitation wavelength: 350 nm). Peak descriptors: 4CzIPN (4 μM) in DCE (black line), 4-methoxy phenyl diazonium salt (20 μM) in DCE (red line), trifluoroethyl iodide (20 μM) in DCE (green line), weinreb amide (20 μM) in DCE (blue line).

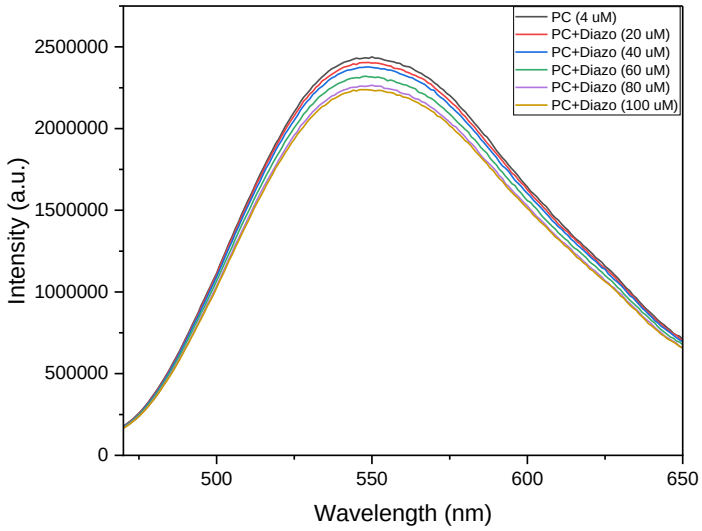


Figure S3: Fluorescence intensity of 4CzIPN solution (4 μM solution in DCE) containing varying amounts of 4-methoxy phenyl diazonium salt (excitation wavelength: 350 nm)

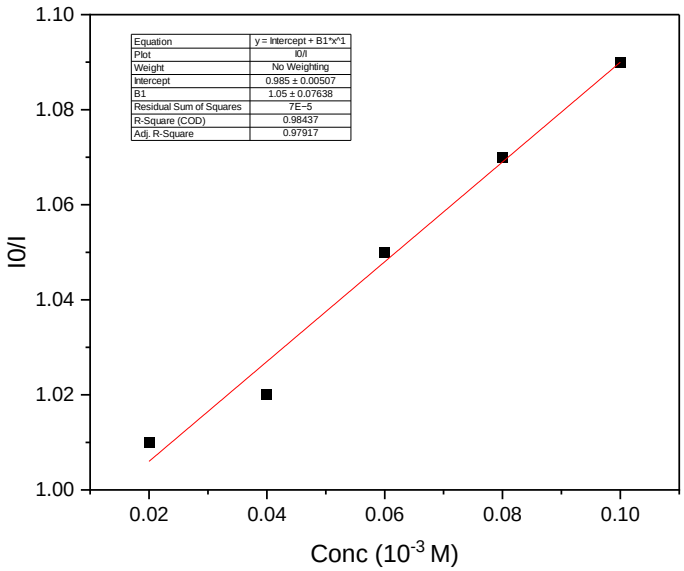
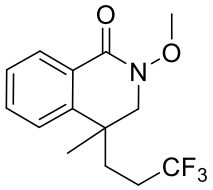
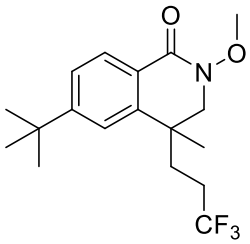


Figure S4: Stern Volmer plot for the fluorescence quenching studies of 4CzIPN by 4-methoxy phenyl diazonium salt.

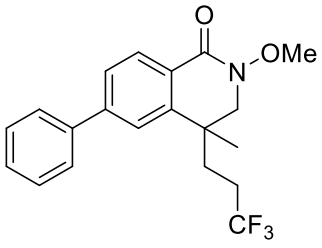
5. Analytical Data of Synthesized Products:



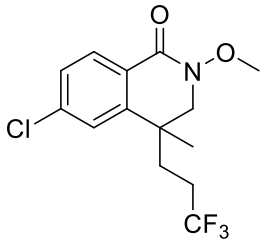
2-Methoxy-4-methyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3a): According to general procedure **2.1**, *N*-methoxy-*N*-(2-methylallyl) benzamide (1 equiv, 0.24 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.49 mmol), PIDA (1 equiv, 0.24 mmol) provided **3a** after flash column chromatography as colourless oil (46 mg, 66%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.22 (d, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.70 (d, *J* = 11.8 Hz, 1H), 3.57 (d, *J* = 11.8 Hz, 1H), 2.08 – 1.87 (m, 4H), 1.42 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 162.9, 143.1, 132.9, 129.2, 127.8 (2C), 127.0 (q, *J* = 276.6 Hz), 124.5, 61.8, 57.9, 38.2, 31.6, 29.7 (q, *J* = 28.6 Hz), 24.1. ^{19} F NMR (471 MHz, Chloroform-*d*) δ -66.33 (t, *J* = 8.7 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{17}F_3NO_2$ 288.1206 found 288.1207.



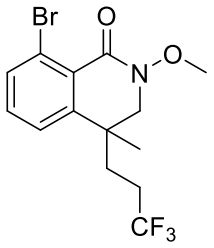
6-(*tert*-Butyl)-2-methoxy-4-methyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3b): According to general procedure **2.1**, 4-(*tert*-butyl)-*N*-methoxy-*N*-(2-methylallyl) benzamide (1 equiv, 0.19 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.38 mmol), PIDA (1 equiv, 0.19 mmol) provided **3b** after flash column chromatography as colourless oil (50 mg, 76%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.20 (s, 1H), 3.88 (s, 3H), 3.66 (d, *J* = 11.3 Hz, 1H), 3.57 (d, *J* = 11.8 Hz, 1H), 2.07 – 1.94 (m, 4H), 1.43 (s, 3H), 1.33 (s, 9H). ^{13}C {^{1}H}NMR (100 MHz, Chloroform-*d*) δ 163.3, 156.6, 142.8, 129.7, 129.1, 127.1 (q, *J* = 276.6 Hz), 125.0, 121.2, 66.7, 61.7, 57.9, 38.4, 35.4, 31.3, 29.7 (q, *J* = 28.6 Hz), 24.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.34 (t, *J* = 9.5 Hz, 3F). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{24}F_3NNaO_2$ 366.1651 found 366.1659.



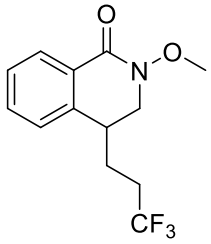
2-Methoxy-4-methyl-6-phenyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3c): According to general procedure **2.1**, *N*-methoxy-*N*-(2-methylallyl)-[1,1'-biphenyl]-4-carboxamide (1 equiv, 0.18 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.36 mmol), PIDA (1 equiv, 0.18 mmol) provided **3c** after flash column chromatography as colourless oil (49 mg, 76%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.58 (m, 3H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.44 – 7.39 (m, 2H), 3.92 (s, 3H), 3.74 (d, *J* = 11.6 Hz, 1H), 3.61 (d, *J* = 11.8 Hz, 1H), 2.15 – 1.96 (m, 4H), 1.49 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.0, 145.8, 143.7, 140.1, 129.9, 129.2, 128.5, 127.5, 126.7, 123.3, 61.9, 58.0, 49.3, 38.4, 31.7, 29.8 (q, *J* = 27.8 Hz), 24.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.26 (t, *J* = 9.9 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{21}F_3NO_2$ 364.1519 found: 364.1528.



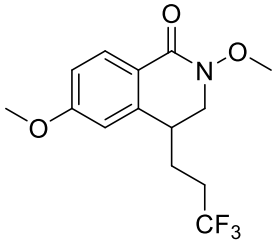
6-Chloro-2-methoxy-4-methyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3d): According to general procedure **2.1**, 4-chloro-*N*-methoxy-*N*-(2-methylallyl) benzamide (1 equiv, 0.21 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.42 mmol), PIDA (1 equiv, 0.21 mmol) provided **3d** after flash column chromatography as colourless oil (32 mg, 48%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 3.88 (s, 3H), 3.70 (d, *J* = 12.2 Hz, 1H), 3.56 (d, *J* = 11.8 Hz, 1H), 2.11 – 1.92 (m, 4H), 1.42 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 162.2, 145.2, 139.4, 129.5 (q, *J* = 247 Hz), 130.9, 128.3, 126.4, 124.9, 61.9, 57.7, 38.3, 31.6 (q, *J* = 2.9 Hz), 29.7, 23.8. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.29 (t, *J* = 9.5 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{16}ClF_3NO_2$ 322.0816 found: 322.0819.



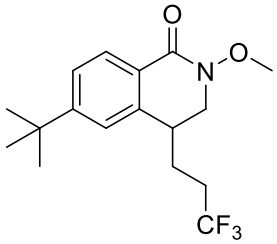
8-Bromo-2-methoxy-4-methyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3e): According to general procedure **2.1**, 2-bromo-*N*-methoxy-*N*-(2-methylallyl) benzamide (1 equiv, 0.18 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.35 mmol), PIDA (1 equiv, 0.18 mmol) provided **3e** after flash column chromatography as colourless oil (34 mg, 53%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 7.8, 1.1 Hz, 1H), 3.91 (s, 3H), 3.76 (d, *J* = 12.8 Hz, 1H), 3.56 (d, *J* = 12.8 Hz, 1H), 2.11 – 1.87 (m, 4H), 1.38 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 160.1, 146.3, 135.2, 132.5, 127.1, 126.9 (q, *J* = 246.43 Hz), 124.0, 123.9, 62.3, 57.7, 38.5, 31.1, 29.5 (q, *J* = 28.9 Hz), 23.4. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.25 (t, *J* = 9.9 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{16}BrF_3NO_2$ 366.0311 found 366.0312.



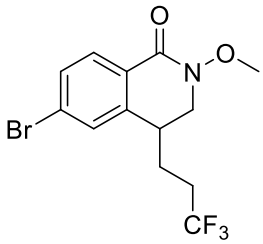
2-Methoxy-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5a): According to general procedure **2.2**, *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.52 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.52 mmol) provided **5a** after flash column chromatography as colourless oil (50 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.8 Hz, 1H), 7.48 (td, *J* = 7.4, 1.2 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 4.06 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.88 (s, 3H), 3.62 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.07 (dq, *J* = 7.3, 4.5, 4.1 Hz, 1H), 2.19 – 2.08 (m, 2H), 2.07 – 1.96 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 162.7, 139.6, 132.6, 129.0, 128.0, 127.2, 126.9 (q, *J* = 276.4 Hz), 125.8, 61.8, 52.1, 37.8, 31.5 (q, *J* = 29.0 Hz), 26.3. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.91 (t, *J* = 10.3 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{15}F_3NO_2$ 274.1049 found 274.1051.



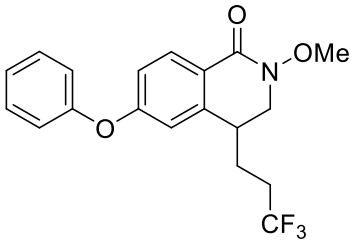
2,6-Dimethoxy-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5b): According to general procedure **2.2**, *N*-allyl-*N*,4-dimethoxybenzamide (1 equiv, 0.23 mmol), trifluoroethyliodide **2a** (2 equiv, 0.45 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.45 mmol) provided **5b** after flash column chromatography as colourless oil (42 mg, 61%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.8 Hz, 1H), 6.88 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 4.00 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.58 (dd, *J* = 11.6, 3.1 Hz, 1H), 3.15 – 2.88 (m, 1H), 2.24 – 2.09 (m, 2H), 2.07 – 1.93 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.3, 163.0, 141.9, 131.3, 130.6 (q, *J* = 250 Hz), 120.7, 112.9, 112.8, 61.9, 55.6, 52.2, 38.1, 31.6 (q, *J* = 29.0 Hz), 26.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.90 (t, *J* = 10.5 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{17}F_3NO_3$ 304.1155 found 304.1163.



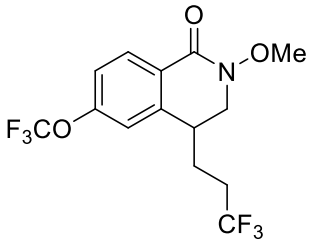
6-(*tert*-Butyl)-2-methoxy-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5c): According to general procedure **2.2**, *N*-allyl-4-(*tert*-butyl)-*N*-methoxybenzamide (1 equiv, 0.20 mmol), trifluoroethyliodide **2a** (2 equiv, 0.40 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.40 mmol) provided **5c** after flash column chromatography as colourless oil (55 mg, 83%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 4.05 (dd, *J* = 11.7, 4.5 Hz, 1H), 3.86 (s, 3H), 3.60 (dd, *J* = 11.7, 2.8 Hz, 1H), 3.10 – 2.97 (m, 1H), 2.23 – 1.92 (m, 4H), 1.32 (s, 9H).^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.0, 156.4, 139.4, 128.9, 127.0 (q, *J* = 276.4 Hz), 125.4, 125.1, 124.1, 61.8, 52.2, 38.2, 35.2, 31.6 (q, *J* = 28.9 Hz)), 31.2, 26.4. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.84 (t, *J* = 10.7 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{23}F_3NO_2$ 330.1675 found 330.1674.



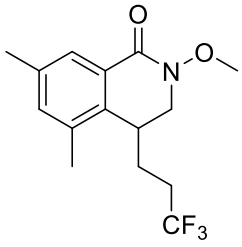
6-Bromo-2-methoxy-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5d): According to general procedure **2.2**, *N*-allyl-4-bromo-*N*-methoxybenzamide (1 equiv, 0.19 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.37 mmol), 4-methoxyphenyl diazonium tetrafluoroborate (2 equiv, 0.37 mmol) provided **5d** after flash column chromatography as colourless oil (38 mg, 58%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.32 (d, *J* = 1.9 Hz, 1H), 4.10 – 4.00 (m, 1H), 3.87 (s, 3H), 3.61 (dd, *J* = 11.9, 3.0 Hz, 1H), 3.04 (tt, *J* = 7.4, 3.9 Hz, 1H), 2.25 – 2.10 (m, 2H), 2.07 – 1.95 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, Chloroform-*d*) δ 162.1, 141.6, 131.5, 130.8, 130.1, 127.5, 127.1, 62.0, 51.9, 37.7, 31.6 (q, *J* = 29.6 Hz), 26.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.86 (t, *J* = 9.9 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{14}BrF_3NO_2$ 352.0155 found 352.0155.



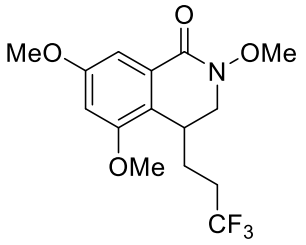
2-Methoxy-6-phenoxy-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5e): According to general procedure **2.2**, *N*-allyl-*N*-methoxy-4-phenoxybenzamide (1 equiv, 0.18 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.35 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.35 mmol) provided **5e** after flash column chromatography as colourless oil (48 mg, 74%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.73 (d, *J* = 2.3 Hz, 1H), 4.04 (dd, *J* = 11.7, 4.5 Hz, 1H), 3.87 (s, 3H), 3.60 (dd, *J* = 11.8, 3.1 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.19 – 2.08 (m, 2H), 2.05 – 1.97 (m, 2H).^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 162.8, 161.5, 155.5, 142.1, 131.3, 130.2, 126.9 (q, *J* = 276.4), 124.8, 122.5, 120.2, 116.9, 115.9, 61.9, 52.1, 38.0, 31.6 (q, *J* = 29.0 Hz), 26.2.^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.94 (t, *J* = 10.3 Hz, 3F). HRMS (ESI) *m/z*: [M+H]$^{+}$ calcd for $C_{19}H_{19}F_3NO_3$ 366.1312 found 366.1315.



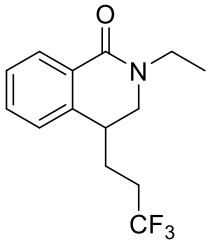
2-Methoxy-6-(trifluoromethoxy)-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5f): According to general procedure **2.2**, *N*-allyl-*N*-methoxy-4-(trifluoromethoxy) benzamide (1 equiv, 0.18 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.36 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.36 mmol) provided **5f** after flash column chromatography as colourless oil (37 mg, 57 %). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 1H), 4.09 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.90 (s, 3H), 3.67 (dd, *J* = 12.1, 3.0 Hz, 1H), 3.16 (tt, *J* = 7.2, 3.6 Hz, 1H), 2.28 – 1.94 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 161.3, 140.5, 134.4 (q, *J* = 27.8 Hz), 131.3, 129.8, 127.1 (q, *J* = 276.4 Hz), 125.0 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 3.6 Hz), 123.6 (q, *J* = 272.8 Hz), 62.0, 51.7, 37.8, 31.5 (q, *J* = 29.0 Hz), 26.3. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.95, -65.87 (t, *J* = 10.3 Hz, 3F). HRMS (ESI) *m/z*: [M+H]$^{+}$ calcd for $C_{14}H_{14}F_6NO_3$ 358.0872 found 358.0861.



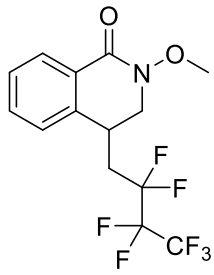
2-Methoxy-5,7-dimethyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5g): According to general procedure **2.2**, *N*-allyl-*N*-methoxy-3,5-dimethylbenzamide (1 equiv, 0.23 mmol), trifluoroethyliodide **2a** (2 equiv, 0.46 mmol), 4-methoxy phenyldiazonium salt (2 equiv, 0.46 mmol) provided **5g** after flash column chromatography as colourless oil (47 mg, 68%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.16 (s, 1H), 3.99 (dd, *J* = 12.0, 4.2 Hz, 1H), 3.87 (s, 3H), 3.64 (dd, *J* = 12.0, 1.7 Hz, 1H), 3.15 (dt, *J* = 8.4, 4.2 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.28 – 2.17 (m, 2H), 2.05 – 1.96 (m, 1H), 1.81 – 1.73 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.1, 137.5, 135.8, 135.6, 134.3, 128.1, 127.2, 126.9 (q, *J* = 265.6 Hz), 61.7, 50.4, 34.4, 31.8 (q, *J* = 29.0 Hz), 24.5, 21.0, 18.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.93 (t, *J* = 10.7 Hz, 3F). HRMS (ESI) *m/z*: [M+H]$^{+}$ calcd for $C_{15}H_{19}F_3NO_2$ 302.1362 found 302.1364.



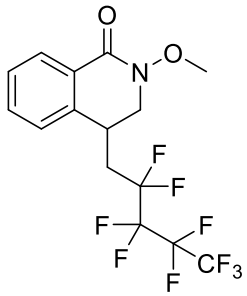
2,5,7-Trimethoxy-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5h): According to general procedure **2.2**, *N*-allyl-*N*,3,5-trimethoxybenzamide (1 equiv, 0.2 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.4 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.4 mmol) provided **5h** after flash column chromatography as colourless oil (45 mg, 68%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 2.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 3.97 (dd, *J* = 12.0, 4.6 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.58 (dd, *J* = 11.9, 1.6 Hz, 1H), 3.34 – 3.29 (m, 1H), 2.28 – 2.16 (m, 1H), 2.12 – 2.00 (m, 1H), 1.97 – 1.83 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 162.6, 160.2, 156.7, 129.9, 127.1 (q, *J* = 276.4 Hz), 121.5, 103.2, 102.8, 61.7, 55.9, 52.0, 31.8 (q, *J* = 29.0 Hz), 31.2, 25.5. ^{19} F NMR (471 MHz, Chloroform-*d*) δ -66.27 (t, *J* = 10.3 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{19}F_3NO_4$ 334.1261 found 334.1267.



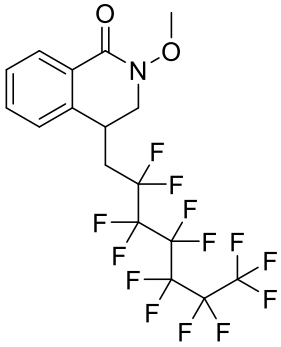
2-Ethyl-4-(3,3,3-trifluoropropyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5hh): According to general procedure **2.2**, *N*-allyl-*N*-ethylbenzamide (1 equiv, 0.26 mmol), trifluoroethyl iodide **2a** (2 equiv, 0.53 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.53 mmol) provided **5hh** after flash column chromatography as colourless oil (26 mg, 36%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 (dd, *J* = 7.6, 1.5 Hz, 1H), 3.85 (dd, *J* = 12.6, 4.2 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.60 – 3.51 (m, 1H), 3.48 (s, 1H), 3.30 (dd, *J* = 12.6, 2.7 Hz, 1H), 2.89 (td, *J* = 7.2, 4.0 Hz, 1H), 2.17 – 1.99 (m, 2H), 1.91 (dt, *J* = 6.9, 2.5 Hz, 1H), 1.21 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.7, 140.1, 131.8, 129.0, 128.9, 127.8, 127.7 (q, *J* = 253.7 Hz), 126.8, 49.9, 42.3, 36.6, 31.7, 26.0 (q, *J* = 3.8 Hz), 12.6. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.85 (t, *J* = 10.3 Hz). HRMS (ESI): m/z: $[M+H]^+$ calcd for $C_{14}H_{17}F_3NO^+$: 272.1257, found 272.1266.



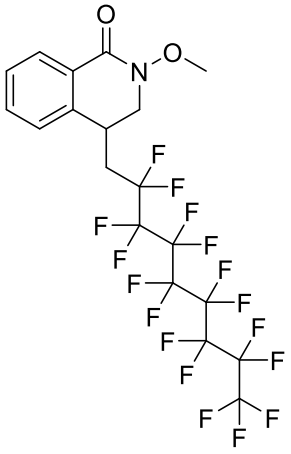
4-(2,2,3,3,4,4,4-Heptafluorobutyl)-2-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (5i): According to general procedure **2.2**, *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), heptafluoropropyl iodide (2 equiv, 0.52 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.52 mmol) provided **5i** after flash column chromatography as colourless oil (47 mg, 50%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (td, *J* = 7.4, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 4.08 (dd, *J* = 12.2, 4.0 Hz, 1H), 3.89 (s, 3H), 3.84 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.62 – 3.54 (m, 1H), 2.80 – 2.61 (m, 1H), 2.35 – 2.17 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.3, 139.5, 133.2, 129.1, 128.5, 128.2, 127.0, 62.0, 51.9 (d, *J* = 3.6 Hz), 34.3 – 33.4 (m), 32.8. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.21 (t, *J* = 9.9 Hz), -111.47 – -116.27 (m), -127.63. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{13}F_7NO_2$ 360.0829 found 360.0837.



2-Methoxy-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5j): According to general procedure **2.2**, *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), nonafluorobutyl iodide (2 equiv, 0.52 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.52 mmol) provided **5j** after flash column chromatography as colourless oil (61 mg, 57%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 4.08 (dd, *J* = 12.1, 3.9 Hz, 1H), 3.89 (s, 3H), 3.84 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.62 – 3.55 (m, 1H), 2.79 – 2.64 (m, 1H), 2.35 – 2.20 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.3, 139.6, 133.2, 129.1, 128.5, 128.2, 127.0, 62.0, 51.9 (d, *J* = 3.6 Hz), 34.3 – 33.4 (m), 32.9. ^{19}FNMR (471 MHz, Chloroform-*d*) δ -80.97 (t, *J* = 10.3 Hz), -111.21 – -114.59 (m), -124.36 (d, *J* = 9.9 Hz), -125.54 – -125.91 (m). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}F_9NO_2$ 410.0797 found 410.0809.

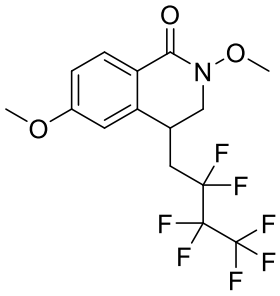


2-Methoxy-4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5k): According to general procedure **2.2**, *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), tridecafluorohexyl iodide (2 equiv, 0.52 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.52 mmol) provided **5k** after flash column chromatography as colourless oil (50 mg, 38%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (td, *J* = 7.6, 1.5 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 4.08 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.89 (s, 3H), 3.84 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.61 – 3.55 (m, 1H), 2.79 – 2.65 (m, 1H), 2.35 – 2.21 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.3, 139.6, 133.2, 129.1, 128.5, 128.2, 127.0, 62.0, 51.9 (d, *J* = 3.6 Hz), 34.5 – 33.6 (m), 32.9. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.69 (t, *J* = 11.5 Hz), -111.32 – -114.22 (m), -121.55, -122.69, -123.35, -125.98. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{13}F_{13}NO_2$ 510.0733 found 510.0735.

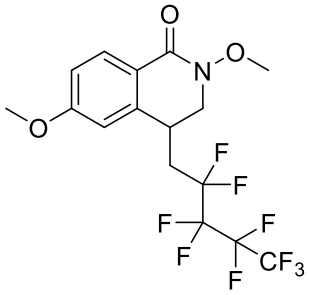


4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-2-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (5l): According to general procedure **2.2**., *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-8-iodooctane (2 equiv, 0.52 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.52 mmol) provided **5l** after flash column chromatography as colourless oil (68 mg, 43%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 9.2 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 4.08 (dd, *J* = 12.2, 3.7 Hz, 1H), 3.89 (s, 3H), 3.84 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.58 (dq, *J* = 10.4, 3.7 Hz, 1H), 2.82 – 2.62 (m, 1H), 2.36 – 2.19 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.3, 139.6, 133.2, 129.1, 128.5, 128.2, 127.0, 62.0, 51.9, 34.6 – 33.6 (m), 32.9. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.81 (t, *J* = 9.9 Hz), -110.96 – -114.27 (m), -

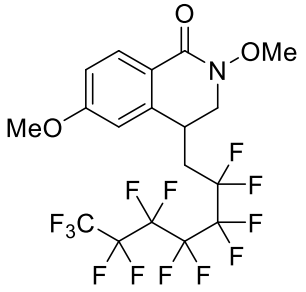
121.40, -121.84, -122.64, -123.36, -126.07. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{13}F_{17}NO_2$ 610.0669 found 610.0661.



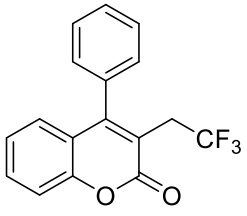
4-(2,2,3,3,4,4,4-Heptafluorobutyl)-2,6-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (5m): According to general procedure **2.2**, *N*-allyl-*N*,4-dimethoxybenzamide (1 equiv, 0.23 mmol), heptafluoropropyl iodide (2 equiv, 0.45 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.45 mmol) provided **5m** after flash column chromatography as colourless oil (45 mg, 51%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 4.02 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.79 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.54 – 3.47 (m, 1H), 2.79 – 2.63 (m, 1H), 2.33 – 2.18 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 159.6, 159.2, 137.5, 127.1, 116.5, 109.4, 107.9, 57.8, 51.5, 47.8, 29.5 (t, *J* = 21.7 Hz), 28.8. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.23 (t, *J* = 9.9 Hz), -112.29 – -115.24 (m), -127.62. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{14}F_7NNaO_3$ 412.0754 found: 412.0761.



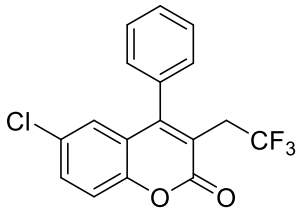
2,6-Dimethoxy-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5n): According to general procedure **2.2**., *N*-allyl-*N*,4-dimethoxybenzamide (1 equiv, 0.23 mmol), nonafluorobutyl iodide (2 equiv, 0.45 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.45 mmol) provided **5n** after flash column chromatography as colourless oil (57 mg, 57%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.5 Hz, 1H), 6.92 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.68 (d, *J* = 3.1 Hz, 1H), 4.02 (dd, *J* = 12.2, 3.7 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.79 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.51 (dq, *J* = 10.4, 3.7 Hz, 1H), 2.82 – 2.62 (m, 1H), 2.38 – 2.16 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.9, 163.4, 141.7, 131.3, 120.7, 113.7, 112.2, 62.0, 55.7, 52.0, 33.9 (t, *J* = 21.1 Hz), 33.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.93 (t, *J* = 11.5 Hz), -111.53 – -114.35 (m), -124.32 (d, *J* = 9.9 Hz), -125.54 – -125.79 (m). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{15}F_9NO_3$ 440.0903 found 440.0912.



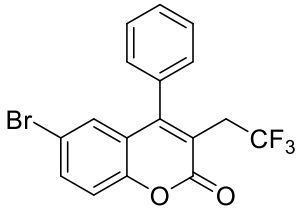
2,6-Dimethoxy-4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5o): According to general procedure **2.2**, *N*-allyl-*N*,4-dimethoxybenzamide (1 equiv, 0.23 mmol), tridecafluorohexyl iodide (2 equiv, 0.45 mmol), 4-methoxy phenyl diazonium salt (2 equiv, 0.45 mmol) provided **5o** after flash column chromatography as colourless oil (59 mg , 48%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 4.02 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.79 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.51 (dq, *J* = 9.9, 3.5 Hz, 1H), 2.80 – 2.64 (m, 1H), 2.35 – 2.16 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 163.9, 163.4, 141.8, 131.3, 113.7, 112.2, 55.7, 52.0, 34.0 (t, *J* = 21.7 Hz), 33.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -80.73, -110.83 – -115.14 (m), -121.58, -122.74, -123.39, -126.04. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}F_{13}NO_3$ 540.0839 found 540.0845.



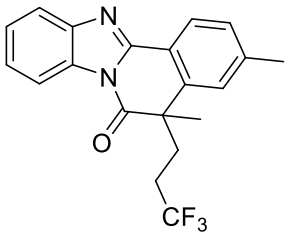
4-Phenyl-3-(2,2,2-trifluoroethyl)-2*H*-chromen-2-one (8a): According to general procedure **2.3**, phenyl 3-phenylpropiolate (1 equiv, 0.22 mmol), trifluoroethyl iodide (2 equiv, 0.45 mmol), PIDA (1 equiv, 0.22 mmol) provided **8a** after flash column chromatography as colourless oil (28 mg, 41%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.50 (m, 4H), 7.38 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.24 (dd, *J* = 7.9, 2.0 Hz, 2H), 7.18 – 7.12 (m, 1H), 6.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.33 (q, *J* = 10.1 Hz, 2H). ^{13}C {^{1}H} NMR (125 MHz, Chloroform-*d*) δ 161.1, 156.2, 153.1, 133.6, 132.3, 129.3, 129.1, 128.3, 128.1, 125.3 (q, *J* = 278.8 Hz), 124.5, 120.5, 116.9, 116.3, 32.8 (q, *J* = 32.6 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.24 (t, *J* = 10.3 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{12}F_3O_2$ 305.0784 found: 305.0789.



6-Chloro-4-phenyl-3-(2,2,2-trifluoroethyl)-2*H*-chromen-2-one (8b): According to general procedure **2.3**., 3-chlorophenyl 3-phenylpropiolate (1 equiv, 0.19 mmol), trifluoroethyl iodide (2 equiv, 0.39 mmol), PIDA (1 equiv, 0.19 mmol) provided **8b** after flash column chromatography as colourless oil (31 mg, 47%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 6.9 Hz, 3H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.12 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 3.31 (q, *J* = 10.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 160.5, 155.6, 153.4, 138.4, 133.2, 129.6, 129.3, 129.1, 128.3, 125.2 (q, *J* = 278.9 Hz), 125.1, 119.2, 117.2, 33.0 (q, *J* = 31.4 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.24 (t, *J* = 9.9 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{11}ClF_3O_2$ 339.0394 found : 339.0391

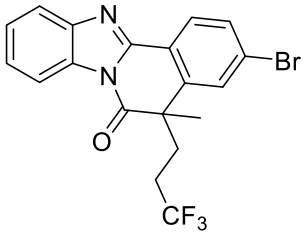


6-Bromo-4-phenyl-3-(2,2,2-trifluoroethyl)-2*H*-chromen-2-one (8c): According to general procedure **2.3**., 4-bromophenyl 3-phenylpropiolate (1 equiv, 0.17 mmol), trifluoroethyl iodide (2 equiv, 0.33 mmol), PIDA (1 equiv, 0.17 mmol) provided **8c** after flash column chromatography as colourless oil (37 mg, 58%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 4H), 7.27 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.21 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 1H), 3.31 (q, *J* = 10.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 160.4, 155.6, 153.2, 133.1, 129.5, 129.2, 129.1, 128.2, 127.9, 126.3, 123.7, 120.1, 119.5, 116.5, 32.9. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.23 (t, *J* = 9.9 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{11}BrF_3O_2$ 382.9889 found: 382.9898.

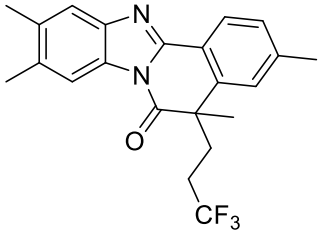


3,5-Dimethyl-5-(3,3,3-trifluoropropyl) benzo [4,5] imidazo[2,1-a] isoquinolin-6(5*H*)-one (9a): According to general procedure **2.3,** 2-methyl-1-(2-(*p*-tolyl)-1*H*-benzo[d]imidazol-1-yl)prop-2-en-1-one (1 equiv, 0.18 mmol), trifluoroethyl iodide (2 equiv, 0.36 mmol), PIDA (1 equiv, 0.18 mmol) provided **9a** after flash column chromatography as colourless oil (46 mg, 71%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.34 – 8.31 (m, 1H), 7.80 (dd, *J* = 6.3, 1.3 Hz, 1H),

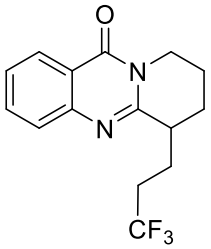
7.47 – 7.39 (m, 3H), 7.33 (d, J = 8.0 Hz, 1H), 2.71 (td, J = 12.8, 4.7 Hz, 2H), 2.48 (s, 3H), 2.24 (td, J = 13.2, 3.8 Hz, 2H), 1.74 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, Chloroform-*d*) δ 172.3, 149.7, 144.2, 143.2, 140.1, 131.3, 129.6, 126.4, 126.2, 126.12, 125.7, 48.4, 33.5, 29.9 (q, J = 21.1 Hz), 22.1. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.41 (t, J = 9.9 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{18}F_3N_2O$ 359.1366 found: 359.1369.



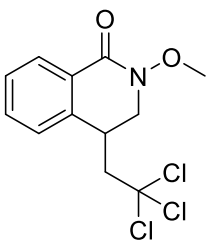
3-Bromo-5-methyl-5-(3,3,3-trifluoropropyl) benzo[4,5]imidazo[2,1-a]isoquinolin-6(5*H*)-one (9b): According to general procedure **2.3**, 1-(2-(4-bromophenyl)-1*H*-benzo[d]imidazol-1-yl)-2-methylprop-2-en-1-one (1 equiv, 0.15 mmol), trifluoroethyl iodide (2 equiv, 0.29 mmol), PIDA (1 equiv, 0.15 mmol) provided **9b** after flash column chromatography as colourless oil (43 mg, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 – 8.31 (m, 2H), 7.84 – 7.80 (m, 1H), 7.68 (dd, J = 8.5, 2.4 Hz, 1H), 7.63 (d, J = 2.4 Hz, 1H), 7.48 – 7.45 (m, 2H), 2.72 (td, J = 13.1, 4.6 Hz, 2H), 2.22 (td, J = 13.4, 4.0 Hz, 2H), 1.76 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 171.4, 141.9, 132.1, 131.3, 129.1, 127.9, 127.1, 126.5, 126.3, 122.2, 120.2, 115.8, 48.5, 33.6, 30.9 – 29.0 (m). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.31 (t, J = 10.7 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{15}BrF_3N_2O$ 423.0314 found: 423.0318.



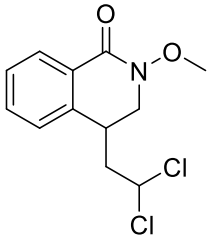
3,5,9,10-Tetramethyl-5-(3,3,3-trifluoropropyl) benzo[4,5]imidazo[2,1-a]isoquinolin-6(5*H*)-one (9c): According to general procedure **2.3**, 1-(5,6-dimethyl-2-(*p*-tolyl)-1*H*-benzo[d]imidazol-1-yl)-2-methylprop-2-en-1-one (1 equiv, 0.16 mmol), trifluoroethyl iodide (2 equiv, 0.33 mmol), PIDA (1 equiv, 0.16 mmol) provided **9c** after flash column chromatography as colourless oil (46 mg, 72%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.33 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H), 7.54 (s, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.23 (s, 1H), 2.68 (td, J = 13.3, 4.7 Hz, 2H), 2.47 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H), 2.27 – 2.17 (m, 2H), 1.72 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, Chloroform-*d*) δ 172.3, 149.0, 142.8, 142.7, 139.9, 135.2, 135.1, 129.7, 129.5, 126.6 (q, J = 276.4 Hz), 126.2, 126.1, 120.8, 120.2, 116.0, 48.3, 30.2 (q, J = 22.9 Hz), 29.9, 22.1, 20.6, 20.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.37 (t, J = 10.7 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{22}F_3N_2O$ 387.1679 found 387.1672.



6-(3,3,3-Trifluoropropyl)-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-b] quinazolin-11-one (11): According to general procedure **2.4**, 3-(pent-4-en-1-yl) quinazolin-4(3*H*)-one (1 equiv, 0.23 mmol), trifluoroethyl iodide (2 equiv, 0.47 mmol), 4-methoxyphenyl diazonium tetrafluoroborate (2 equiv, 0.47 mmol) provided **11** after flash column chromatography as colourless oil (37 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, J = 7.9 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 4.37 – 4.26 (m, 1H), 3.89 (dt, J = 14.0, 6.7 Hz, 1H), 2.95 – 2.83 (m, 1H), 2.52 – 2.24 (m, 3H), 2.14 (dq, J = 12.8, 6.1 Hz, 1H), 1.99 (dq, J = 12.8, 6.4 Hz, 3H), 1.69 – 1.55 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 162.2, 156.3, 147.3, 134.3, 127.4 (q, J = 276.6 Hz), 127.1, 126.8, 126.6, 120.4, 41.4, 39.3, 31.9 (q, J = 28.6 Hz), 25.4, 20.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -66.20 (t, J = 11.5 Hz, 3F). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{16}F_3N_2O$ 297.1209 found : 297.1210



2-Methoxy-4-(2,2,2-trichloroethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (12): According to general procedure **2.5**, *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), chloroform (48 equiv, 1 mL), 4-methoxyphenyl diazonium tetrafluoroborate (2 equiv, 0.52 mmol) and DCE (1 mL) provided **12** after flash column chromatography as colourless oil (35 mg, 43%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.9 Hz, 1H), 7.52 (td, *J* = 7.3, 1.8 Hz, 1H), 7.44 – 7.33 (m, 2H), 4.12 (d, *J* = 3.1 Hz, 2H), 3.92 (s, 3H), 3.68 – 3.61 (m, 1H), 3.38 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.89 (dd, *J* = 15.3, 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 163.4, 140.0, 133.2, 128.86, 128.2, 128.1, 127.0, 98.5, 62.0, 57.6, 52.4, 37.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{13}Cl_3NO_2$ 308.0006 found 308.0015.



4-(2,2-Dichloroethyl)-2-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (13): According to general procedure **2.6**, *N*-allyl-*N*-methoxybenzamide (1 equiv, 0.26 mmol), 4-methoxyphenyl diazonium tetrafluoroborate (2 equiv, 0.52 mmol), dichloromethane (60 equiv, 1 mL) and DCE (1 mL) provided **13** after flash column chromatography as colourless oil (32 mg, 45%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 9.5 Hz, 1H), 7.51 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.28 (d, *J* = 6.3 Hz, 1H), 5.58 (t, *J* = 6.6 Hz, 1H), 4.13 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.90 (s, 3H), 3.66 (dd, *J* = 11.8, 2.3 Hz, 1H), 3.44 – 3.37 (m, 1H), 2.63 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, Chloroform-*d*) δ 162.6, 138.6, 132.7, 129.3, 128.4, 128.2, 127.0, 71.2, 61.9, 52.5, 47.4, 36.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{14}Cl_2NO_2$ 274.0396 found : 274.0396.

6. References:

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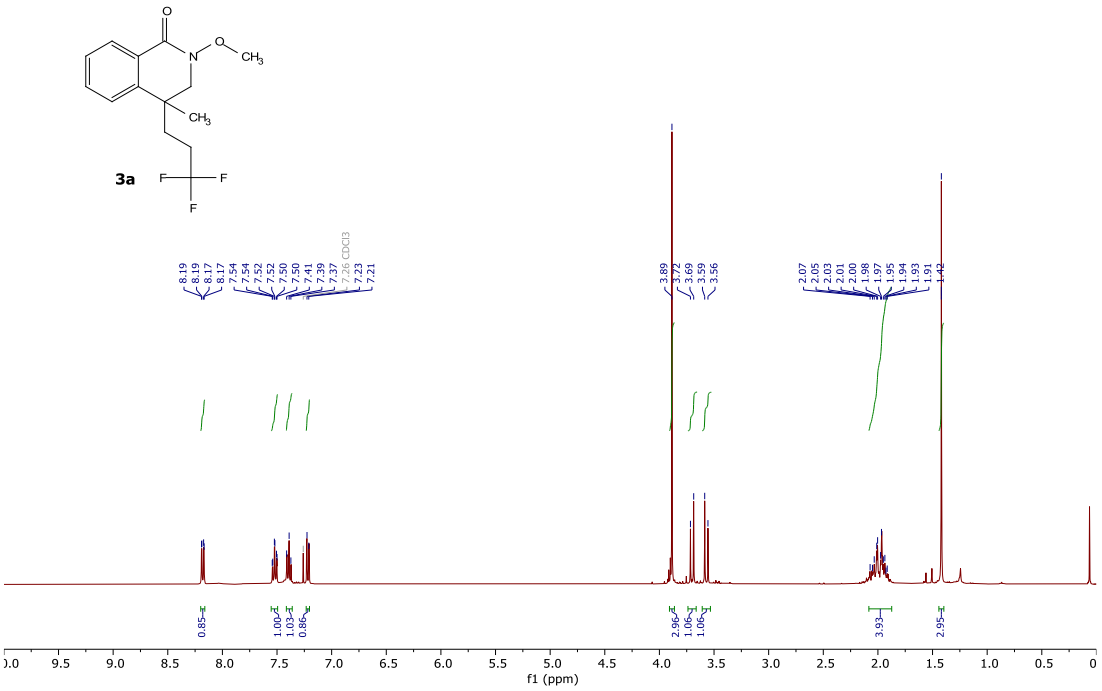
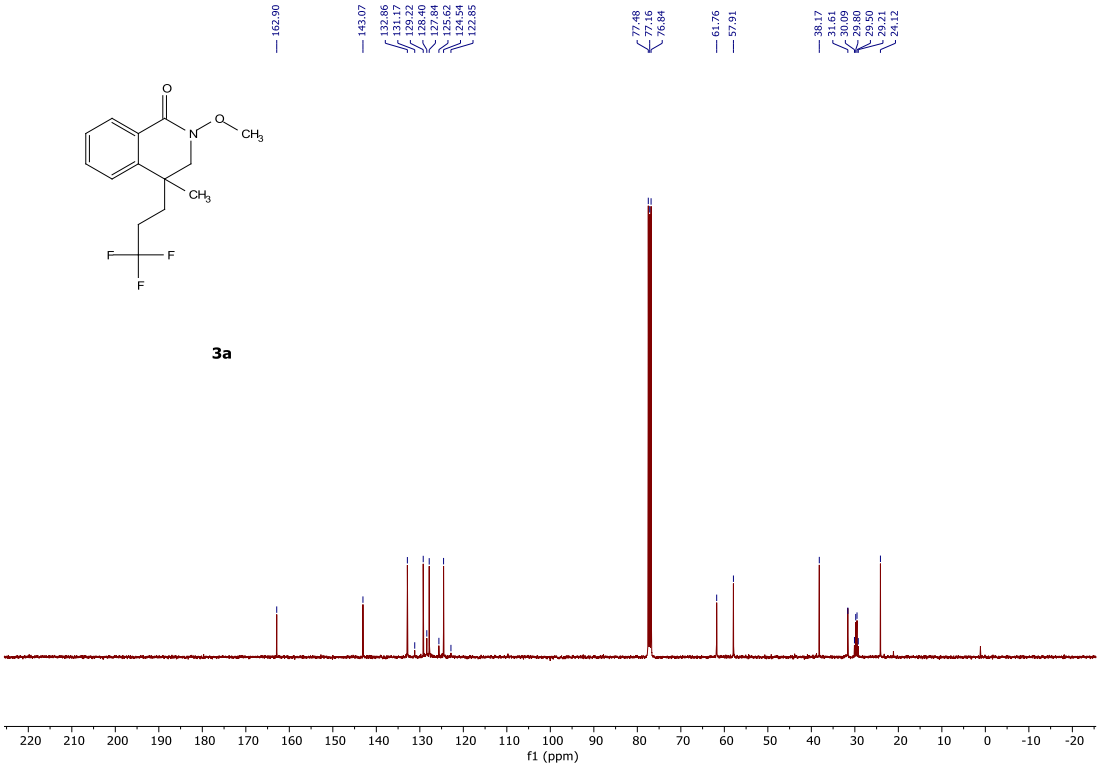
6. Yuan, J.; Qu, H.; Jia, W.; Li, J.; Yang, L.; Xiao, Y.; Yin, Y.; Qu, L. Photoredox-Catalyzed Radical Difluoromethylation/Cyclization of *N*-Acryloyl-2-arylbenzimidazole to Access CF2H-Substituted Benzimidazo[2,1-*a*]isoquinolin-6(5*H*)-ones. *Org. Biomol. Chem.* **2024**

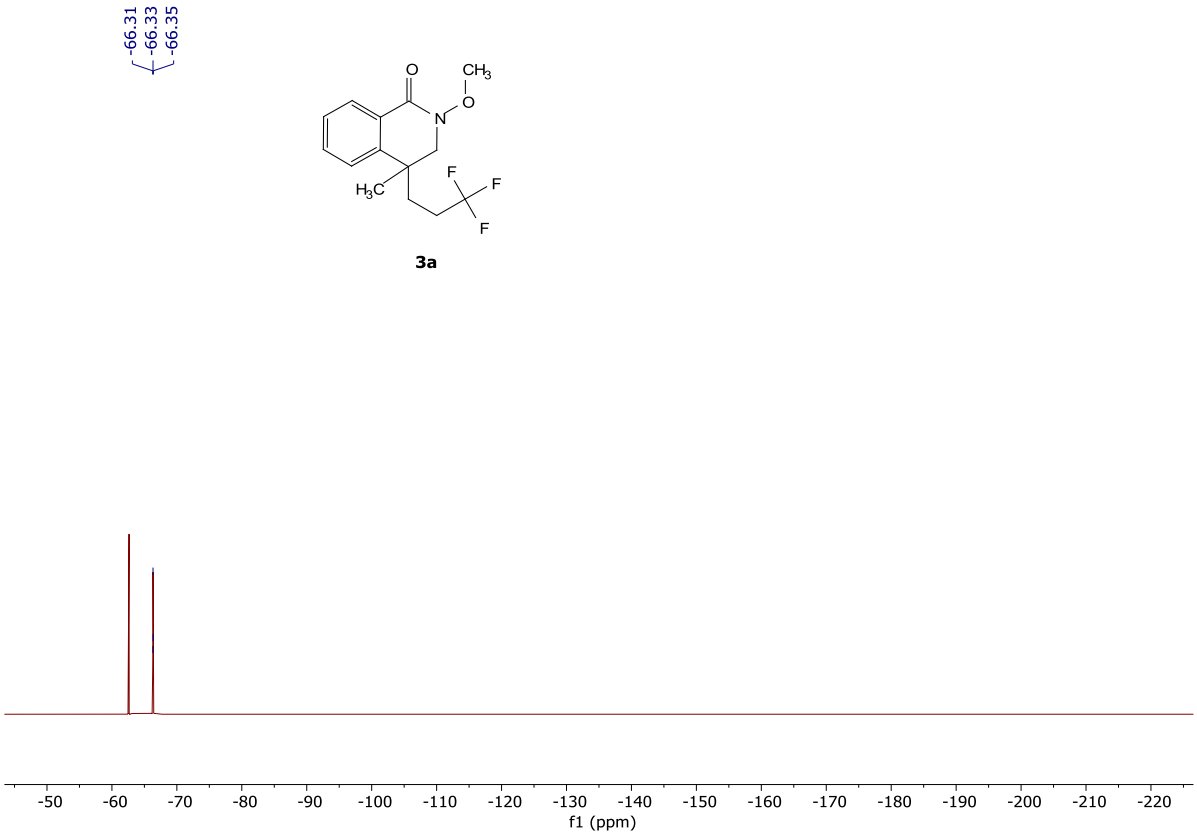
7. ^{1}H, ^{13}C{1H} and ^{19}F Spectra of Products:



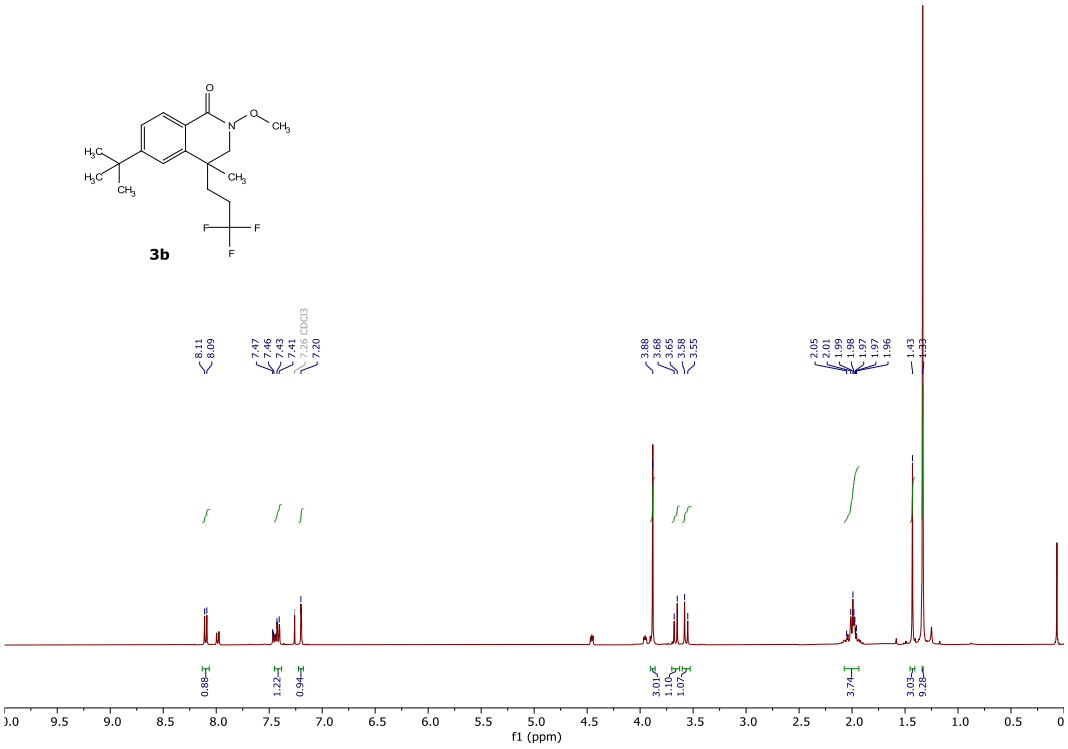
^{1}H NMR (400 MHz) spectrum of compound **3a** in $CDCl_3$



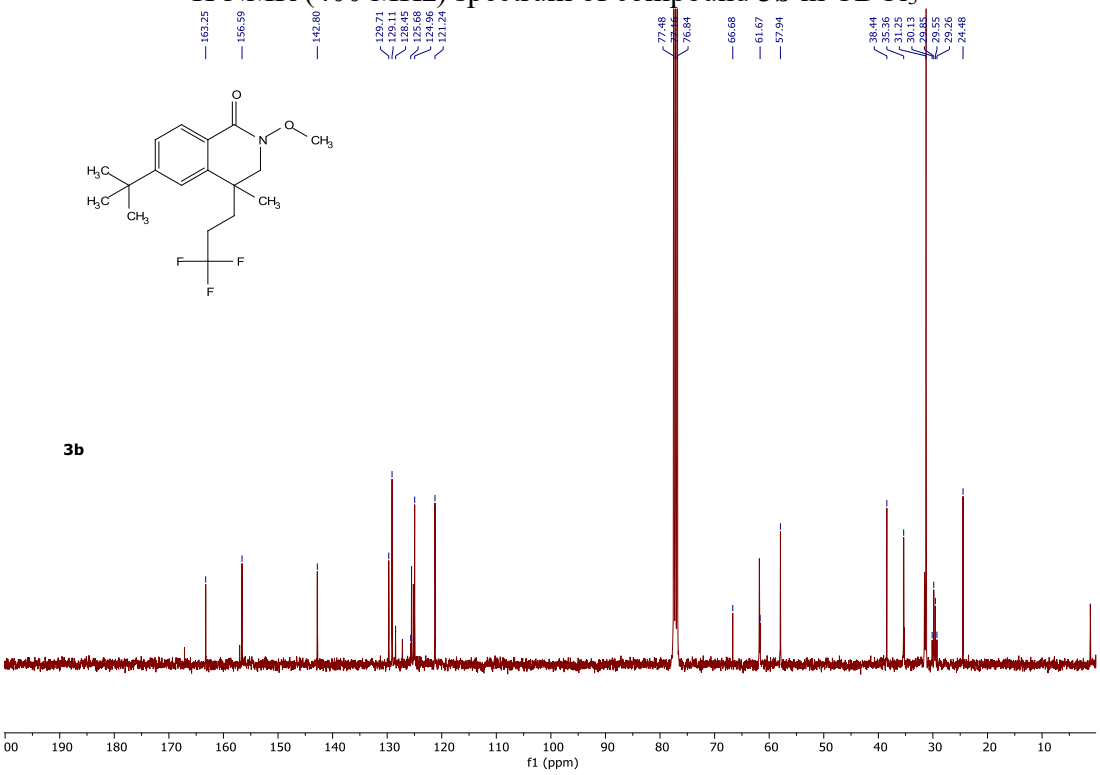
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound **3a** in $CDCl_3$



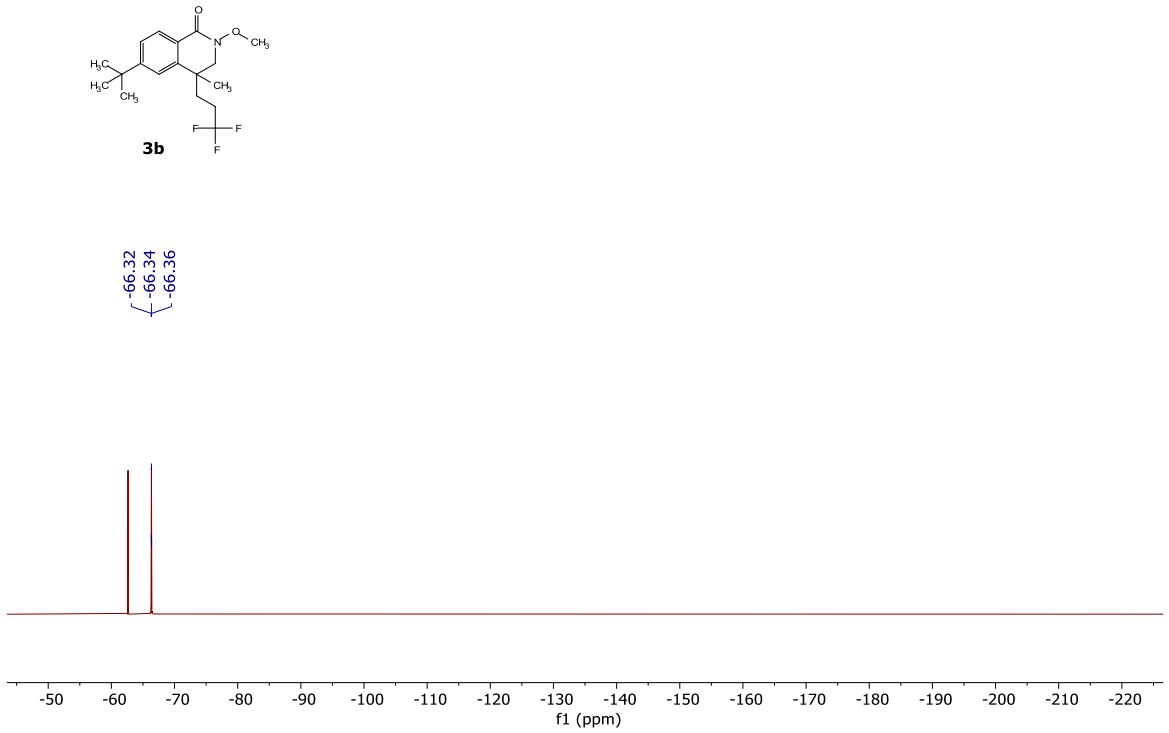
^{19}F NMR (471 MHz) spectrum of compound **3a** in $CDCl_3$ with $PhCF_3$ as reference standard



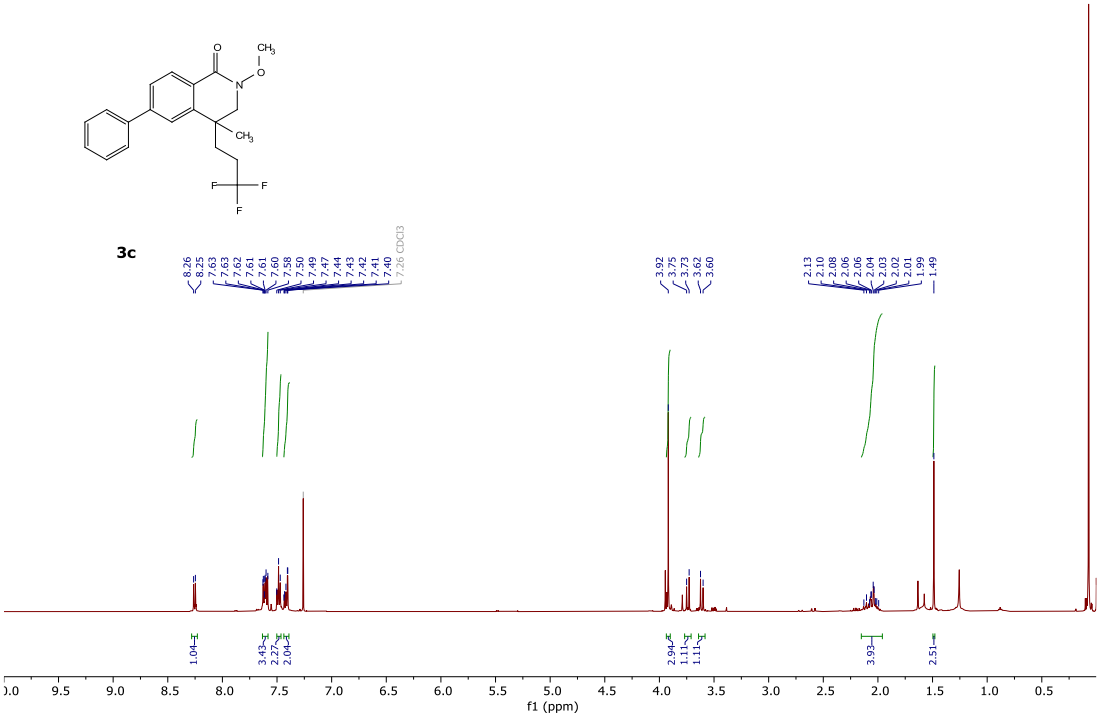
^{1}H NMR (400 MHz) spectrum of compound **3b** in $CDCl_3$



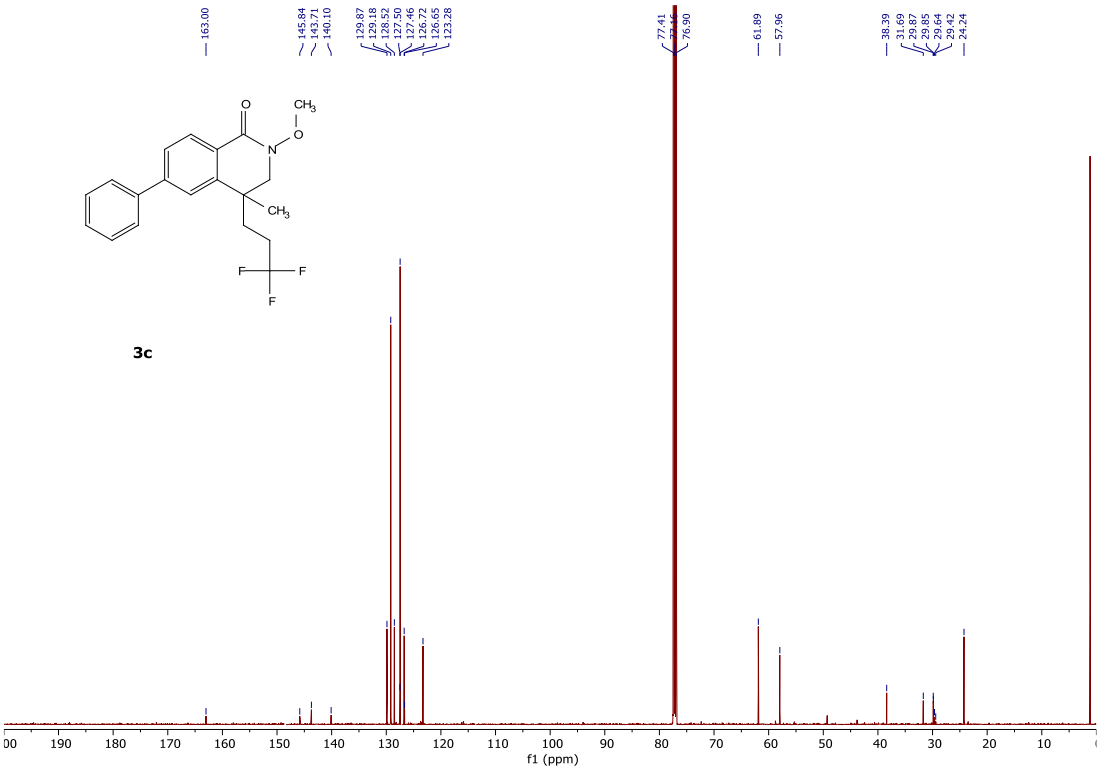
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **3b** in $CDCl_3$



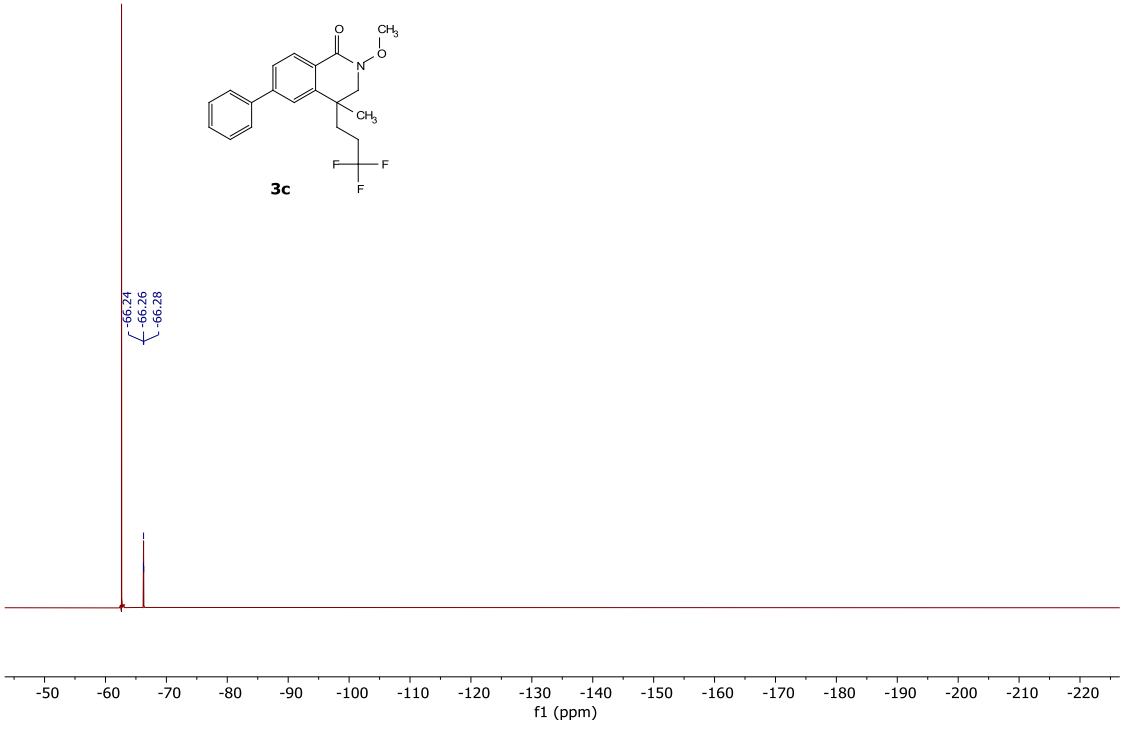
^{19} F NMR (471 MHz) spectrum of compound **3b** in $CDCl_3$ with $PhCF_3$ as reference standard



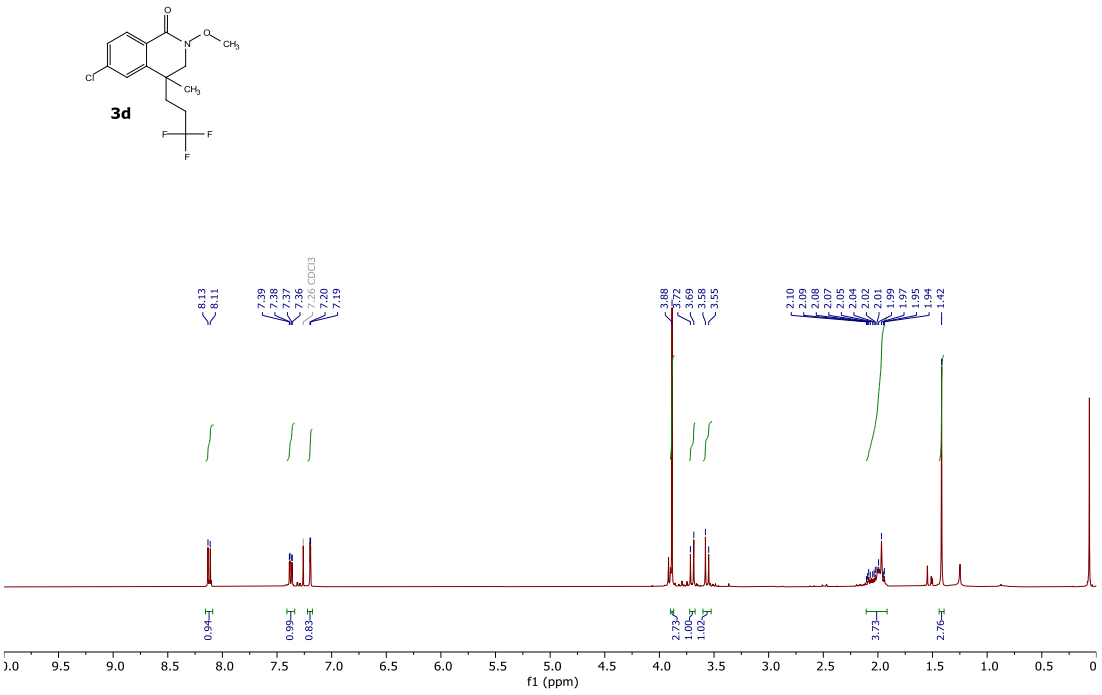
^{1}H NMR (500 MHz) spectrum of compound **3c** in $CDCl_3$



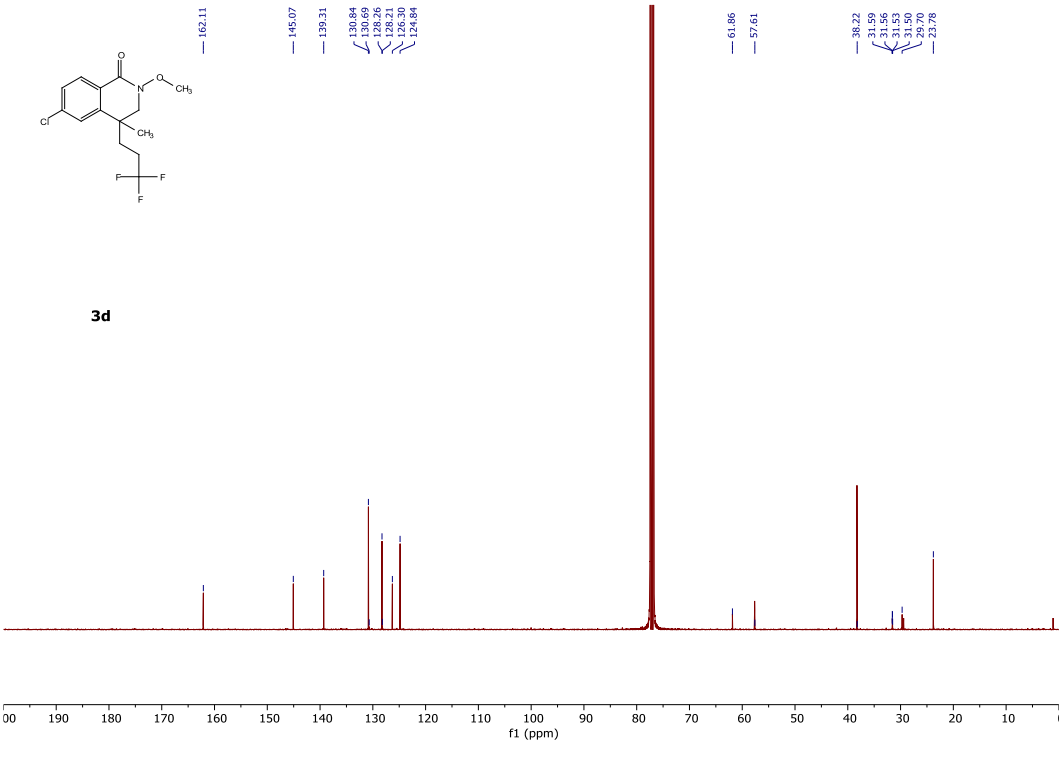
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **3c** in $CDCl_3$



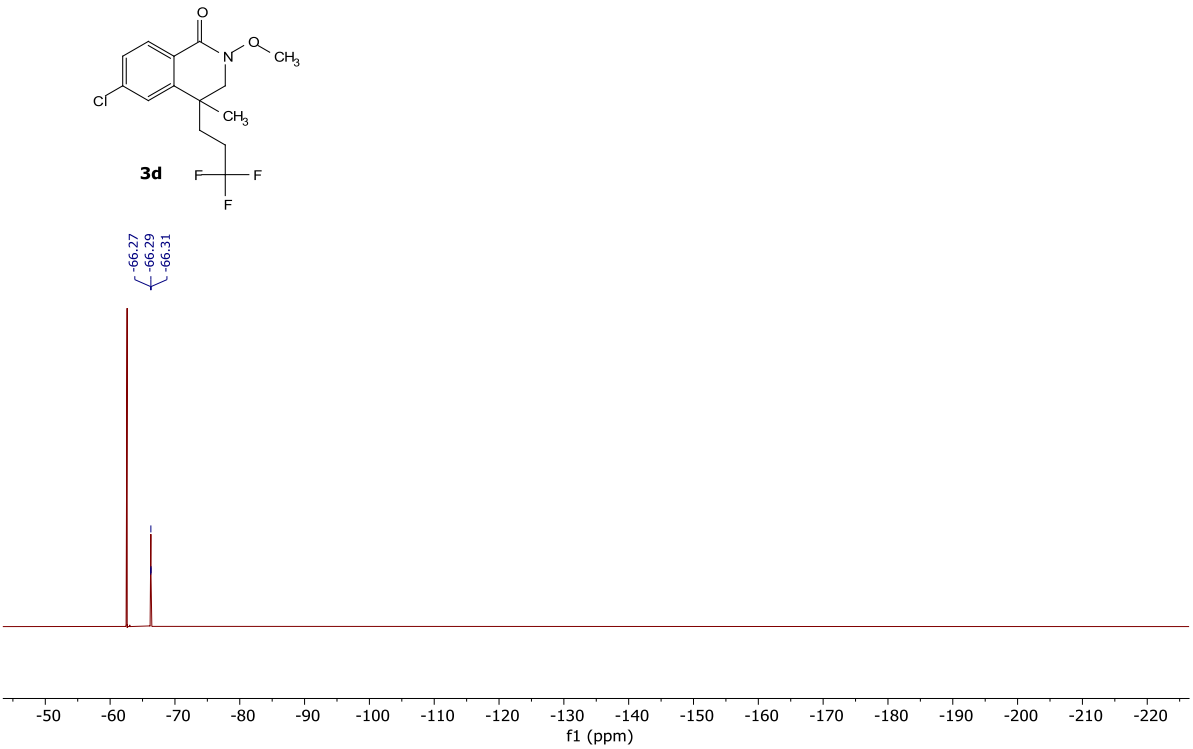
^{19}F NMR (471 MHz) spectrum of compound **3c** in $CDCl_3$ with $PhCF_3$ as reference standard



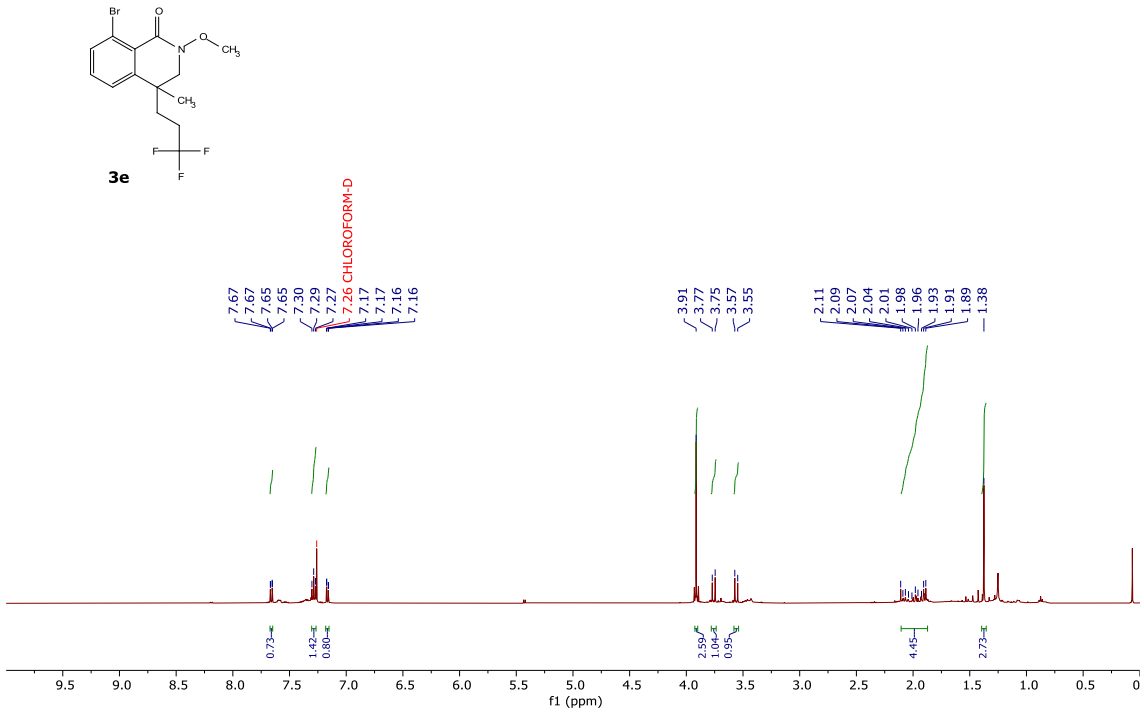
^{1}H NMR (396 MHz) spectrum of compound **3d** in $CDCl_3$



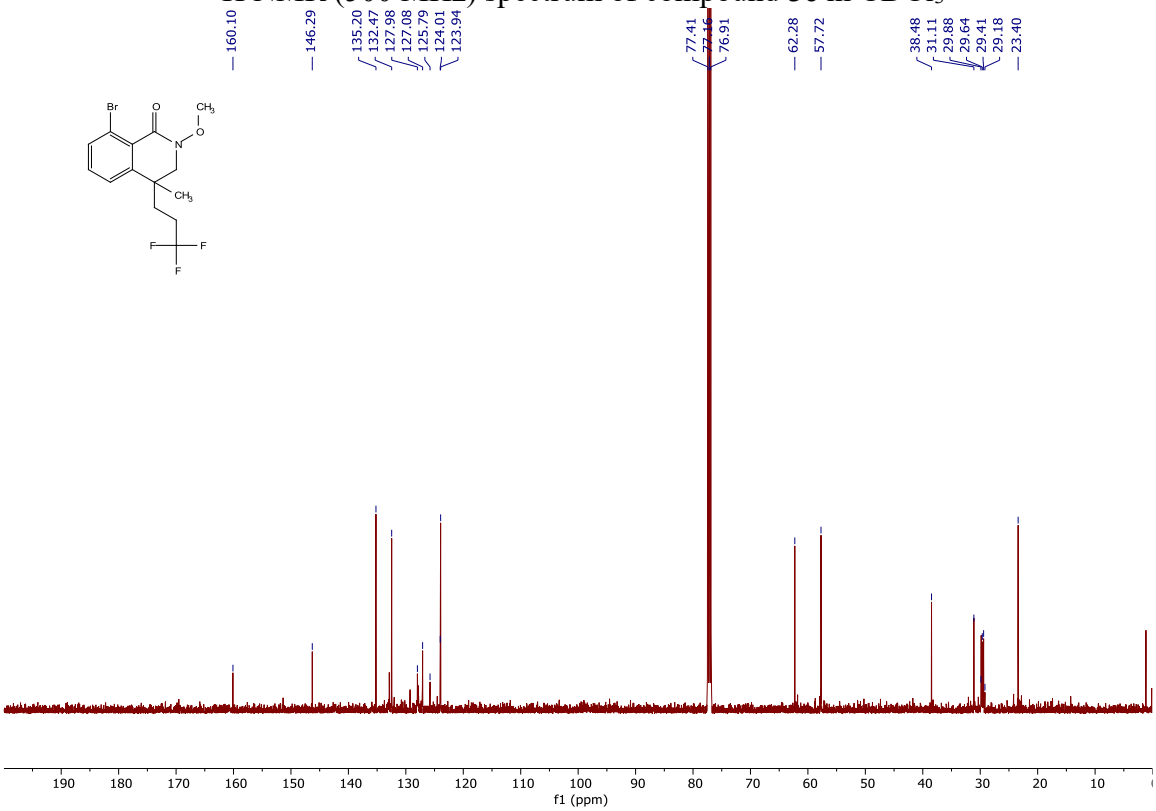
^{13} C {^{1}H} NMR (100 MHz) spectrum of compound **3d** in $CDCl_3$



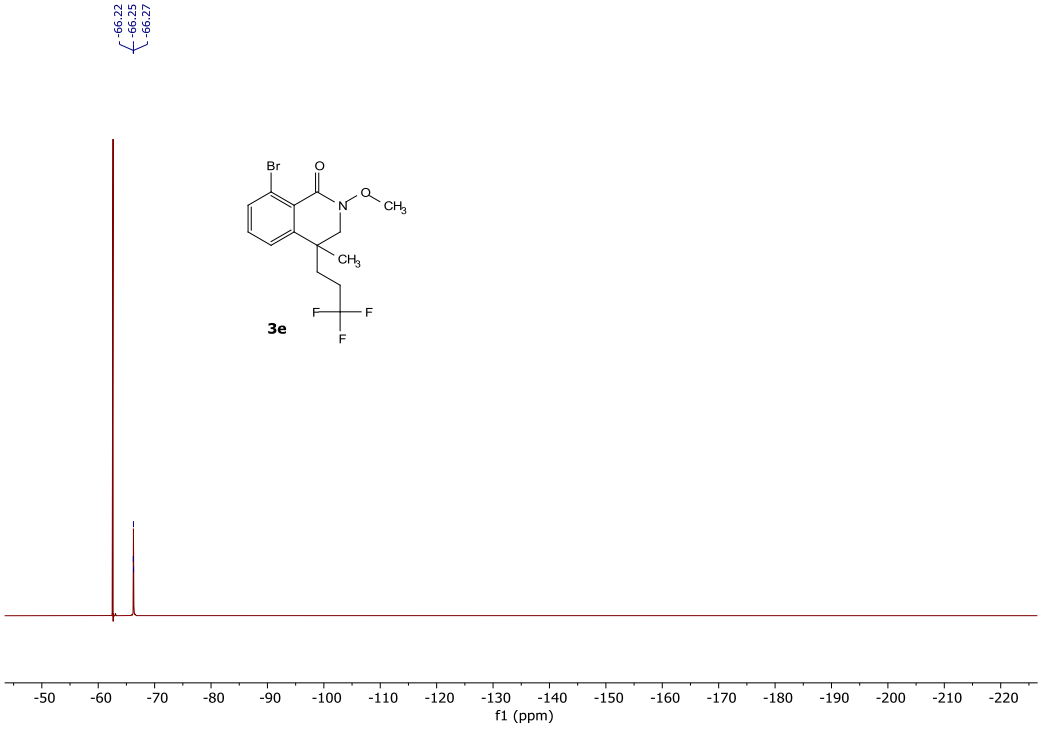
^{19} F NMR (471 MHz) spectrum of compound **3d** in $CDCl_3$ with $PhCF_3$ as reference standard



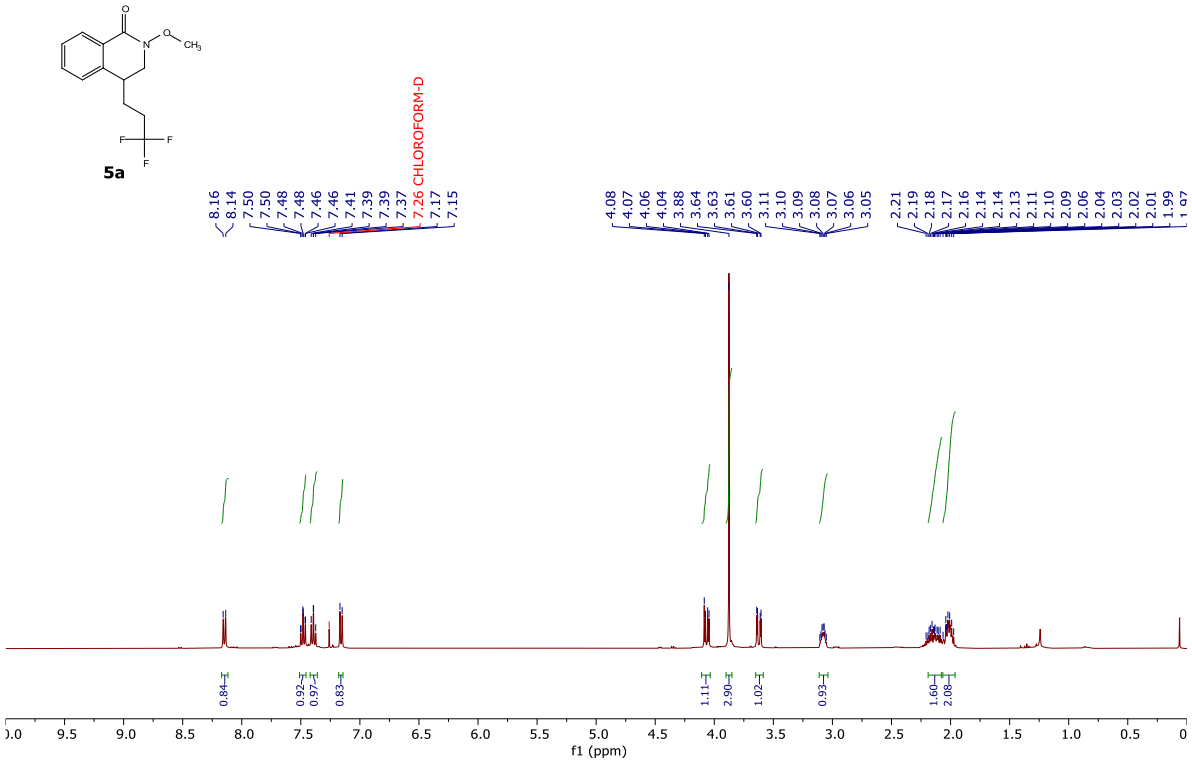
^{1}H NMR (500 MHz) spectrum of compound **3e** in $CDCl_3$



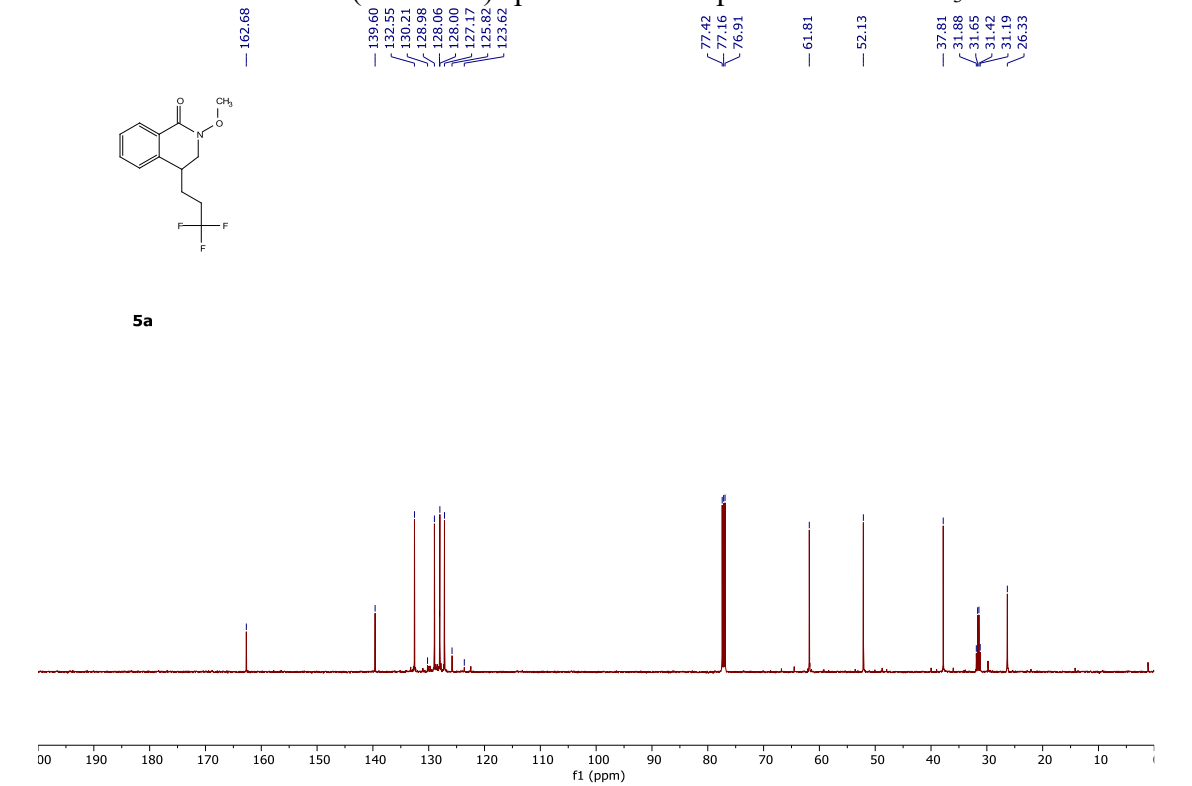
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **3e** in $CDCl_3$



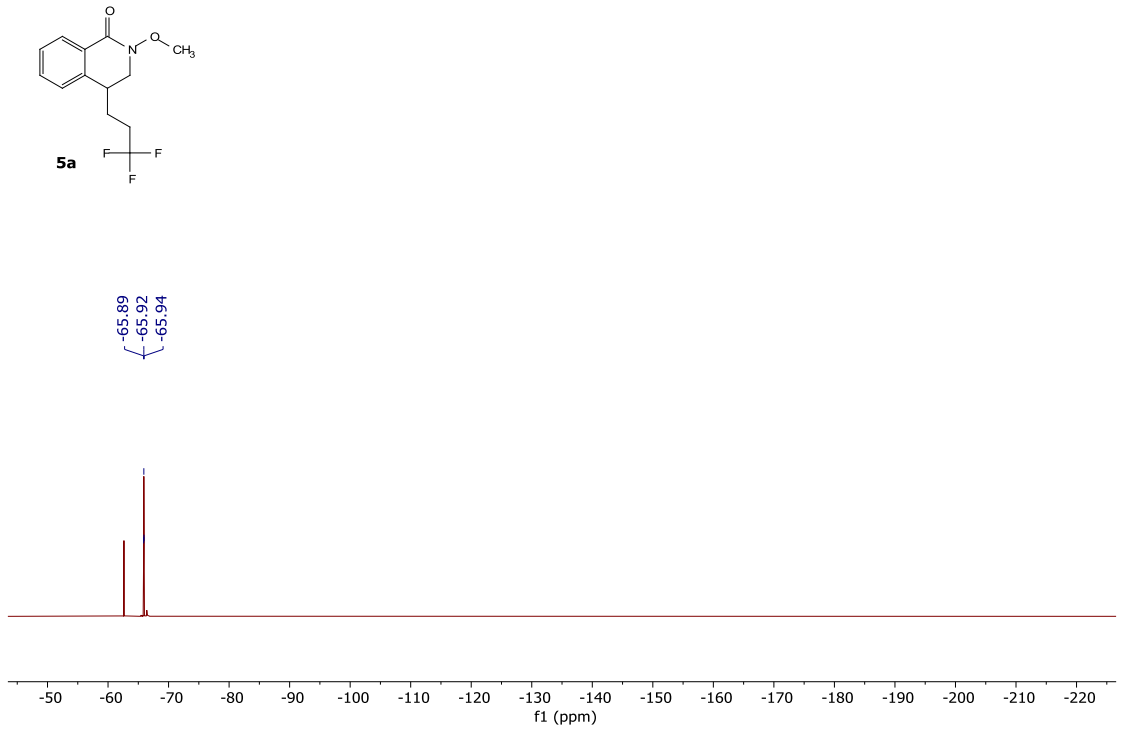
^{19} F NMR (471 MHz) spectrum of compound **3e** in $CDCl_3$ with $PhCF_3$ as reference standard



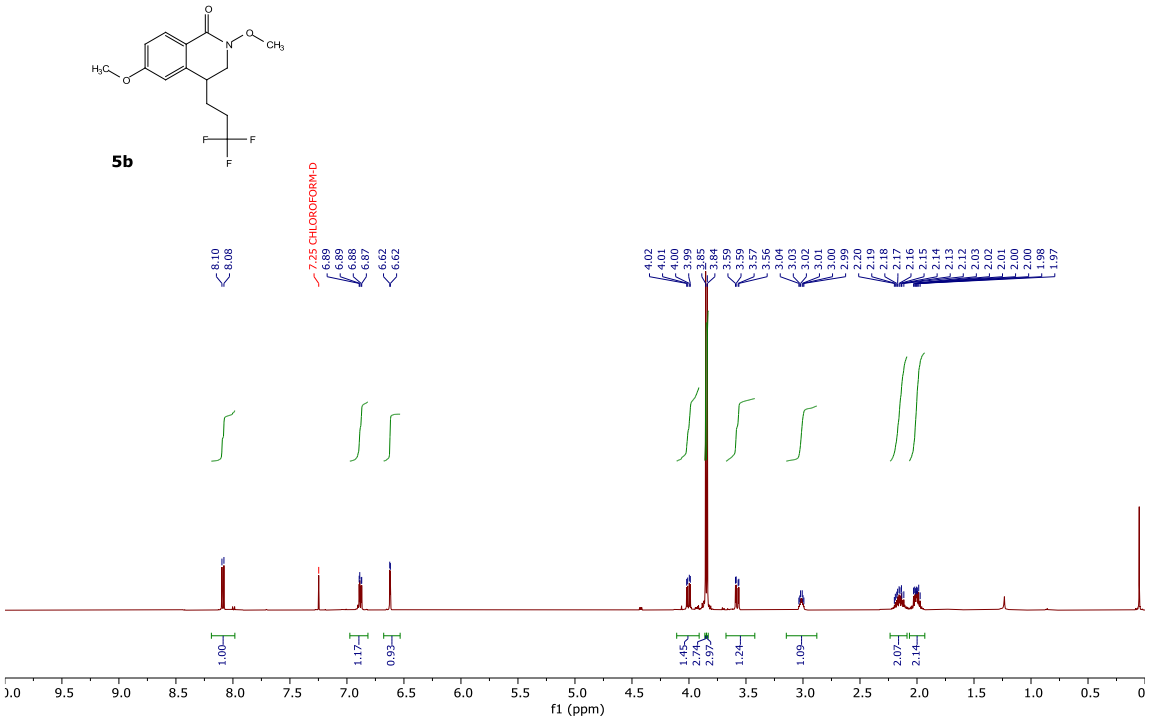
^{1}H NMR (400 MHz) spectrum of compound **5a** in $CDCl_3$



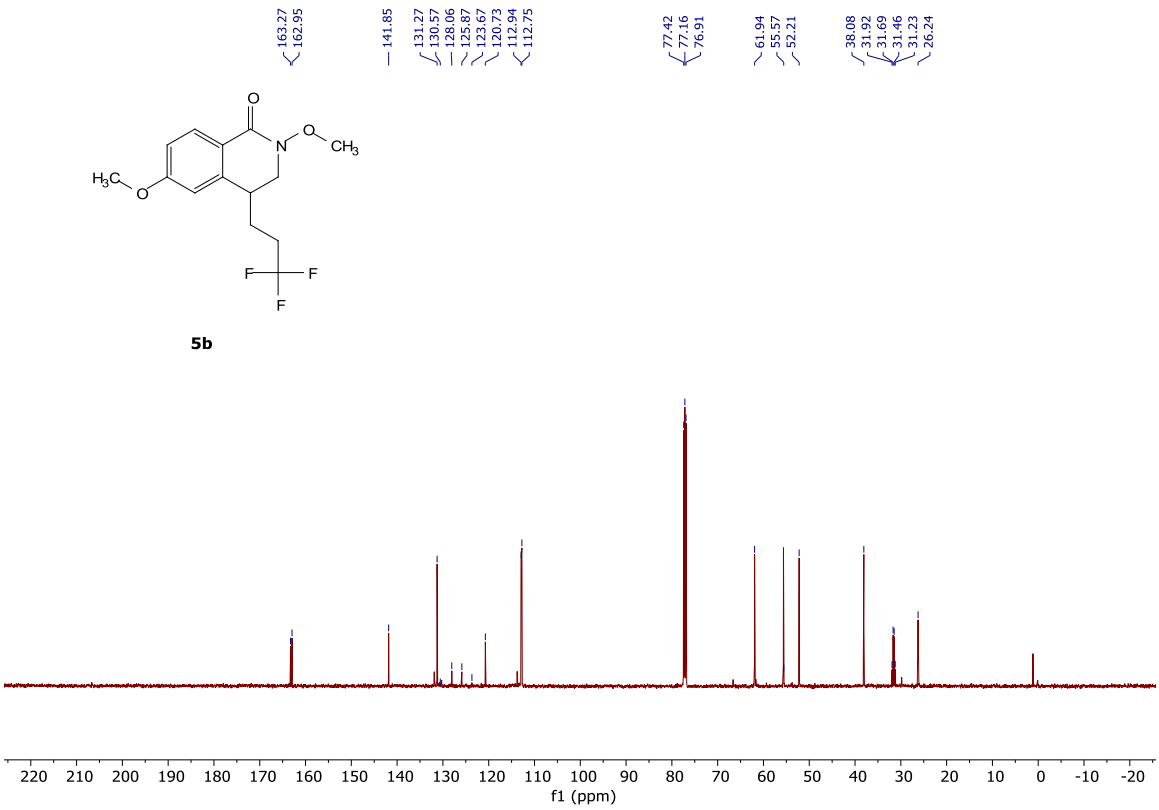
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **5a** in $CDCl_3$



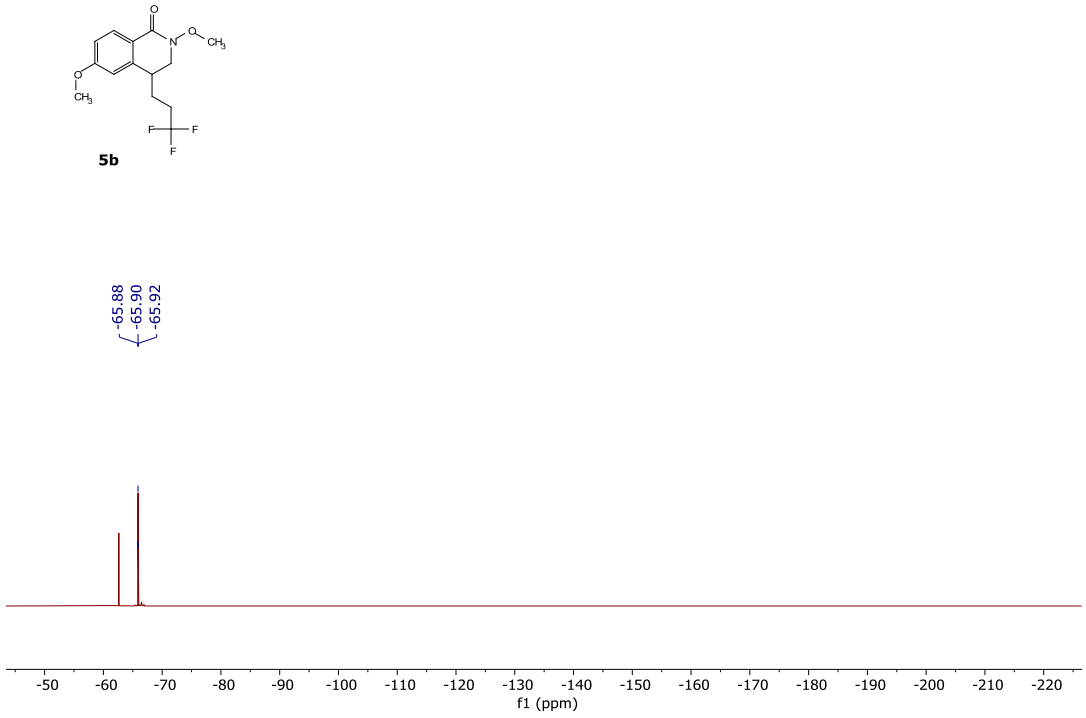
^{19} F NMR (471 MHz) spectrum of compound **5a** in $CDCl_3$ with $PhCF_3$ as reference standard



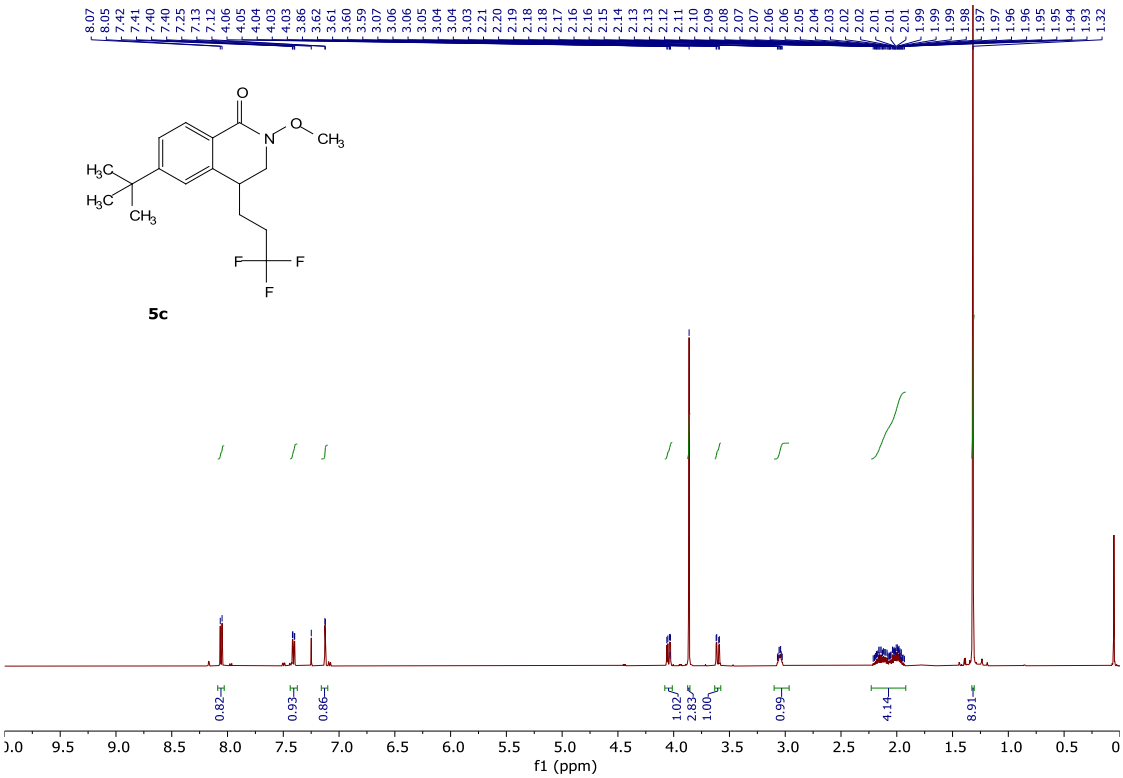
^{1}H NMR (500 MHz) spectrum of compound **5b** in $CDCl_3$



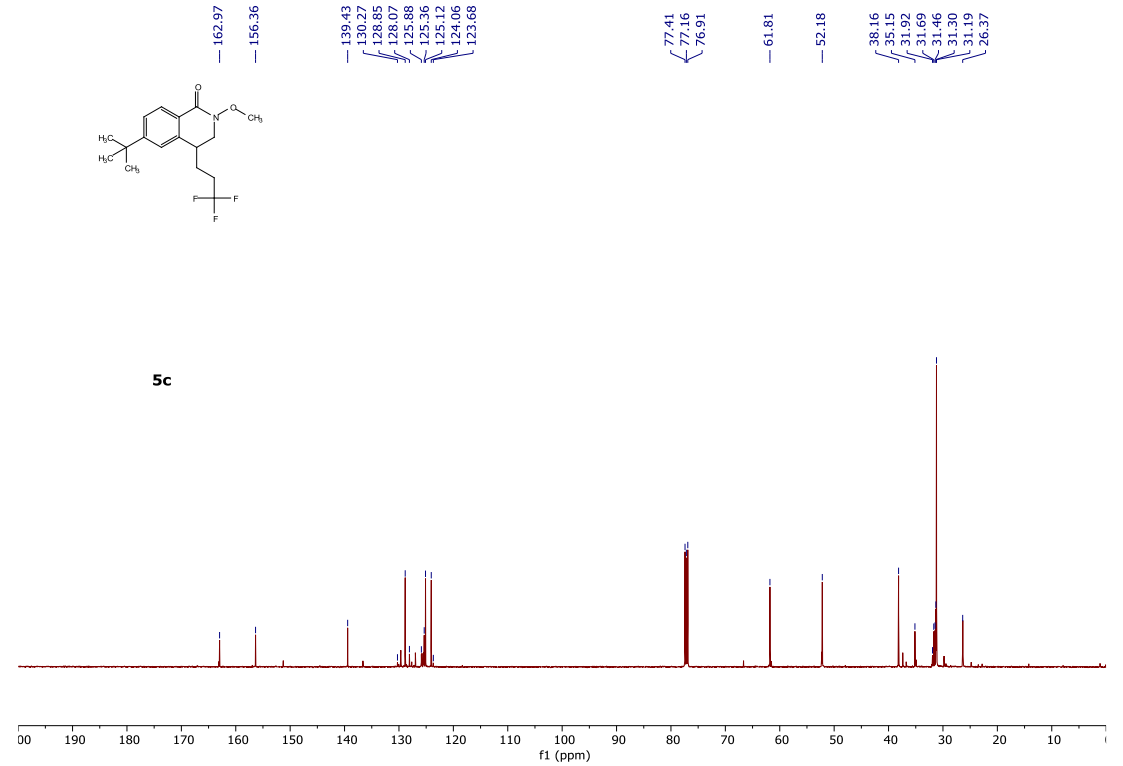
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **5b** in $CDCl_3$



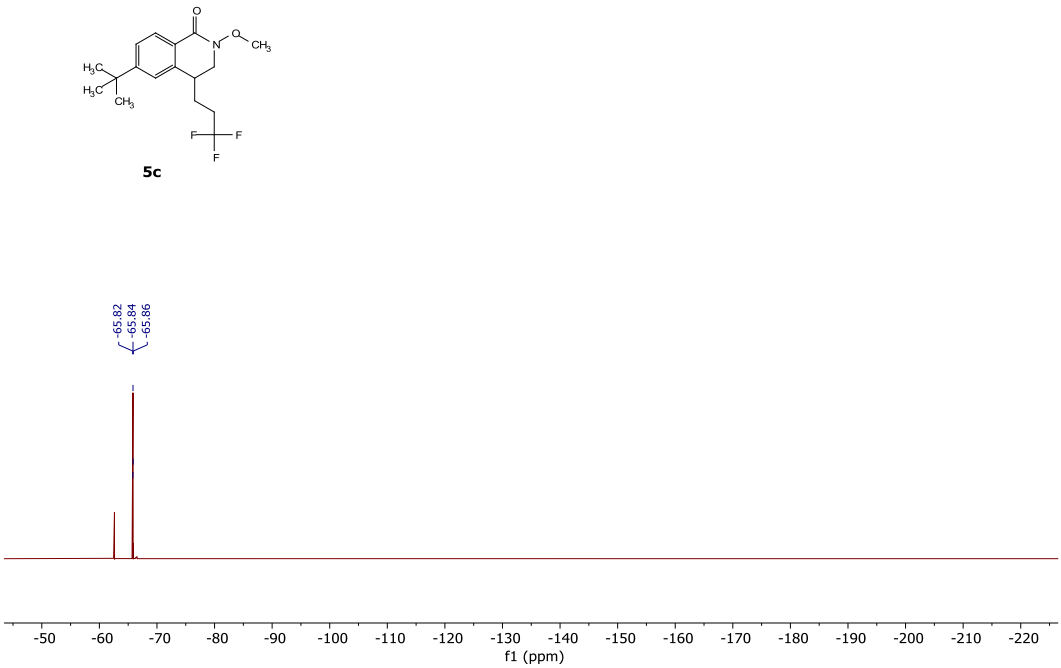
^{19} F NMR (471 MHz) spectrum of compound **5b** in $CDCl_3$ with $PhCF_3$ as reference standard



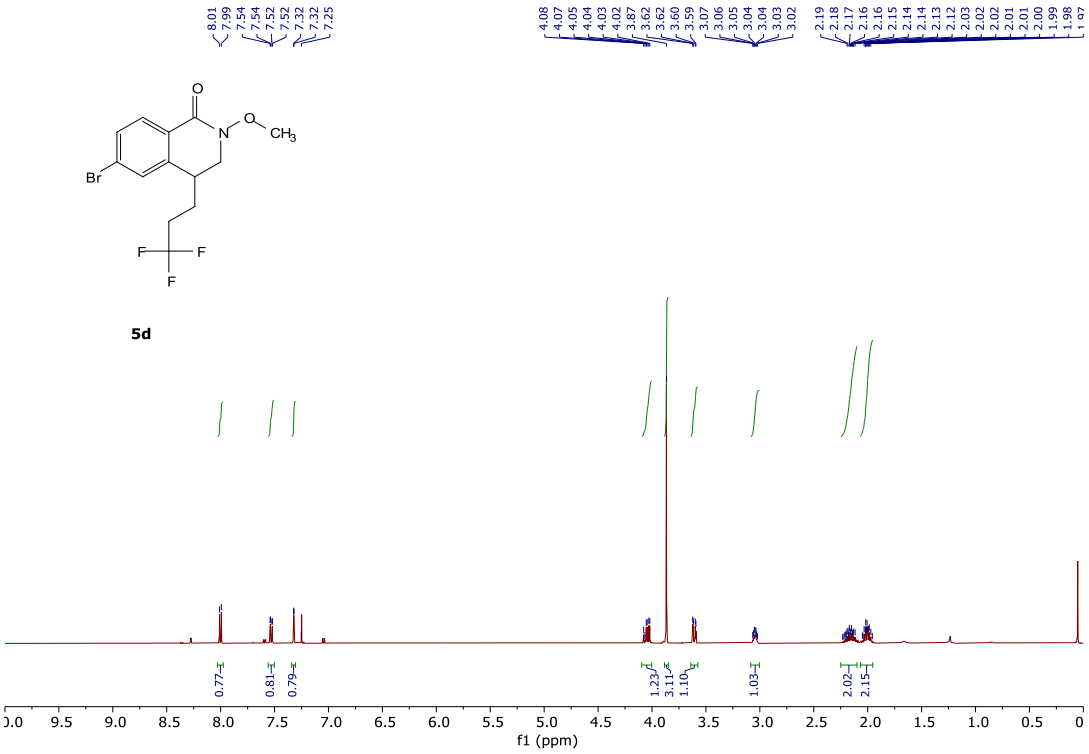
^{1}H NMR (500 MHz) spectrum of compound **5c** in $CDCl_3$



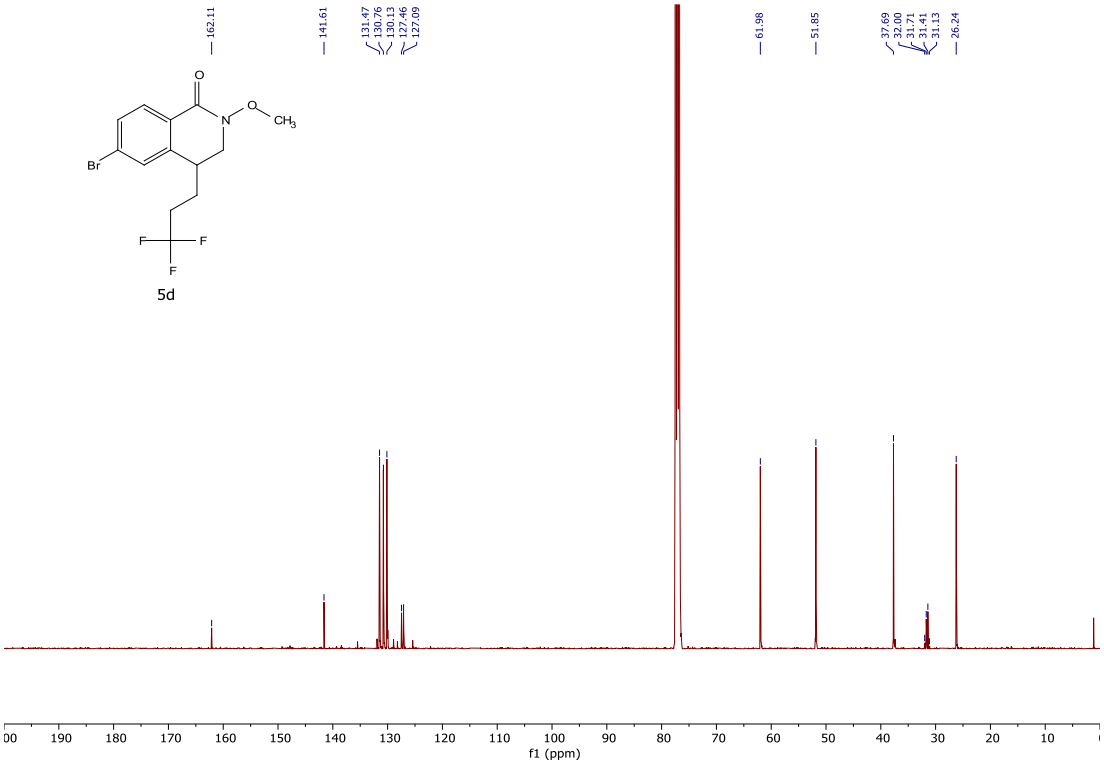
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5c** in $CDCl_3$



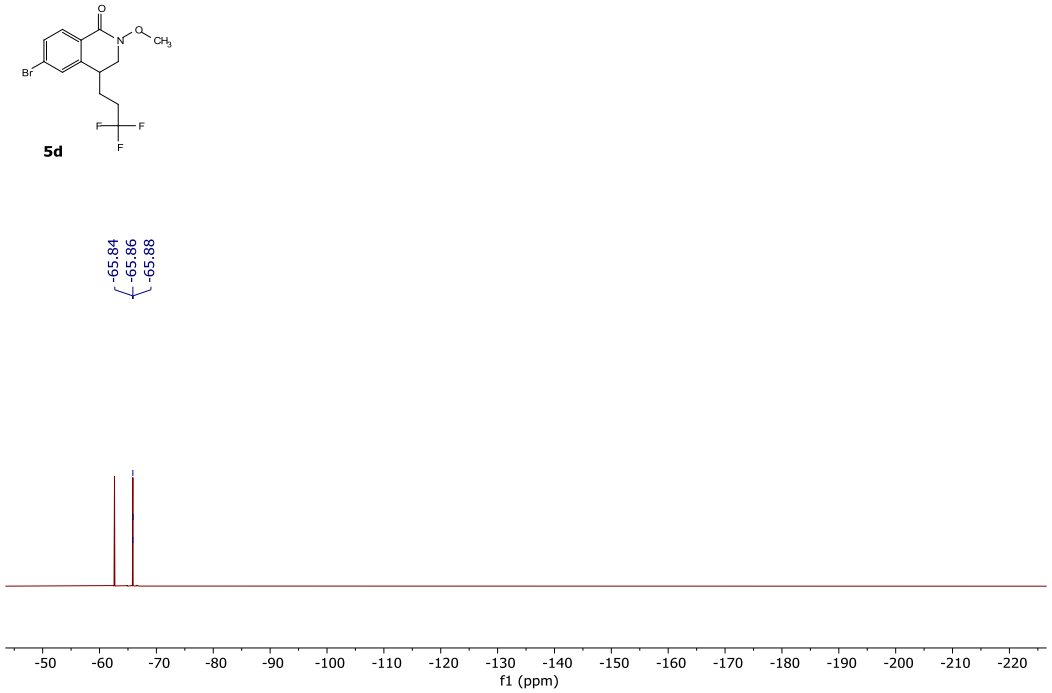
^{19}F NMR (471 MHz) spectrum of compound **5c** in $CDCl_3$ with $PhCF_3$ as reference standard



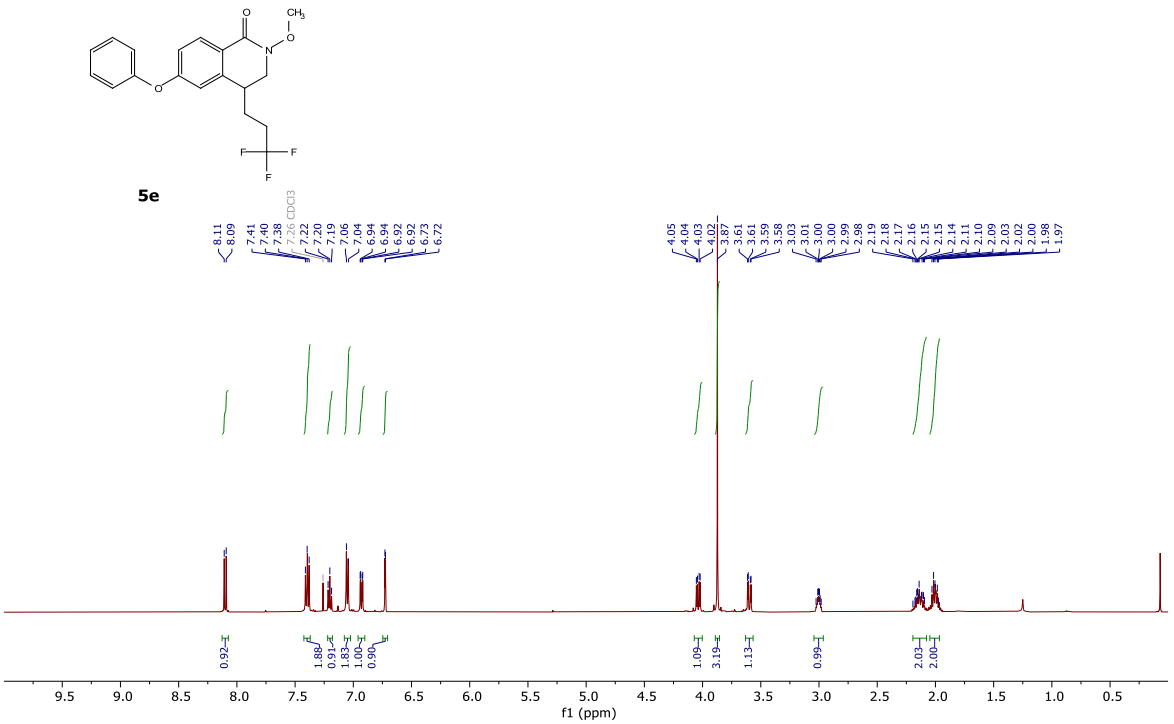
^{1}H NMR (500 MHz) spectrum of compound **5d** in $CDCl_3$



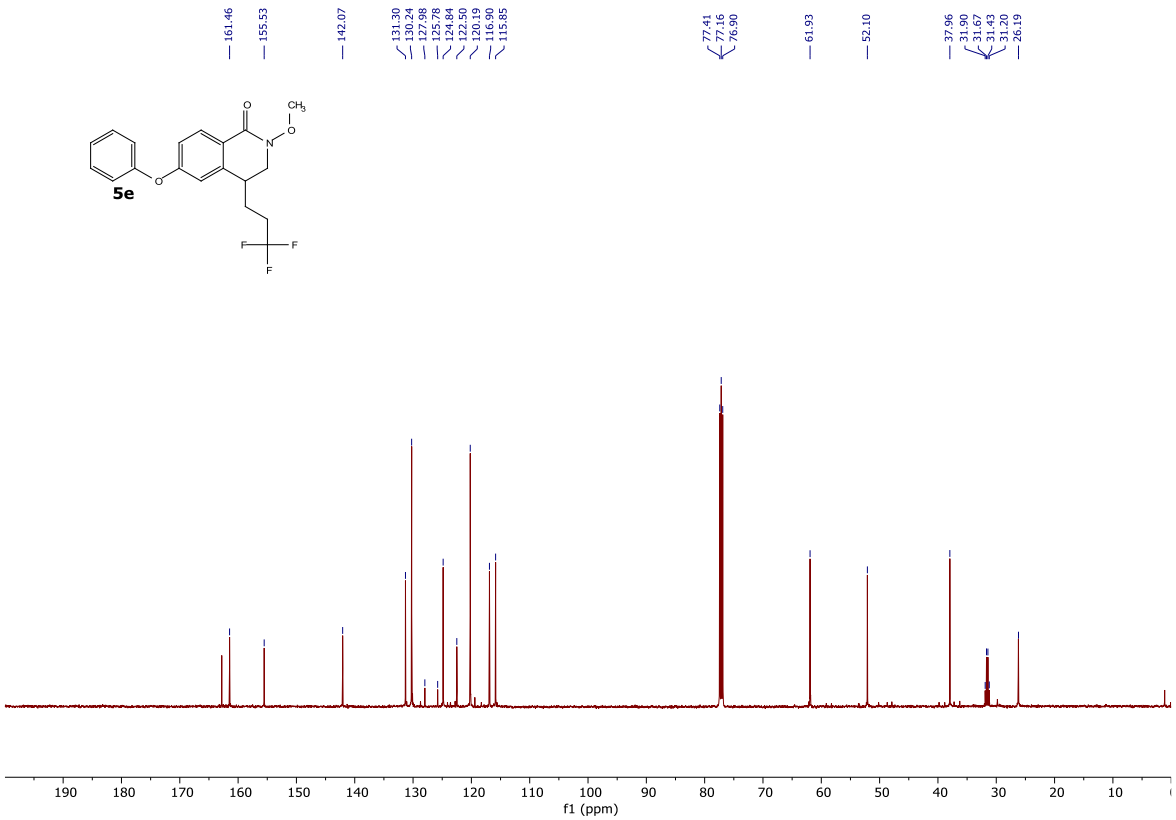
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5d** in $CDCl_3$



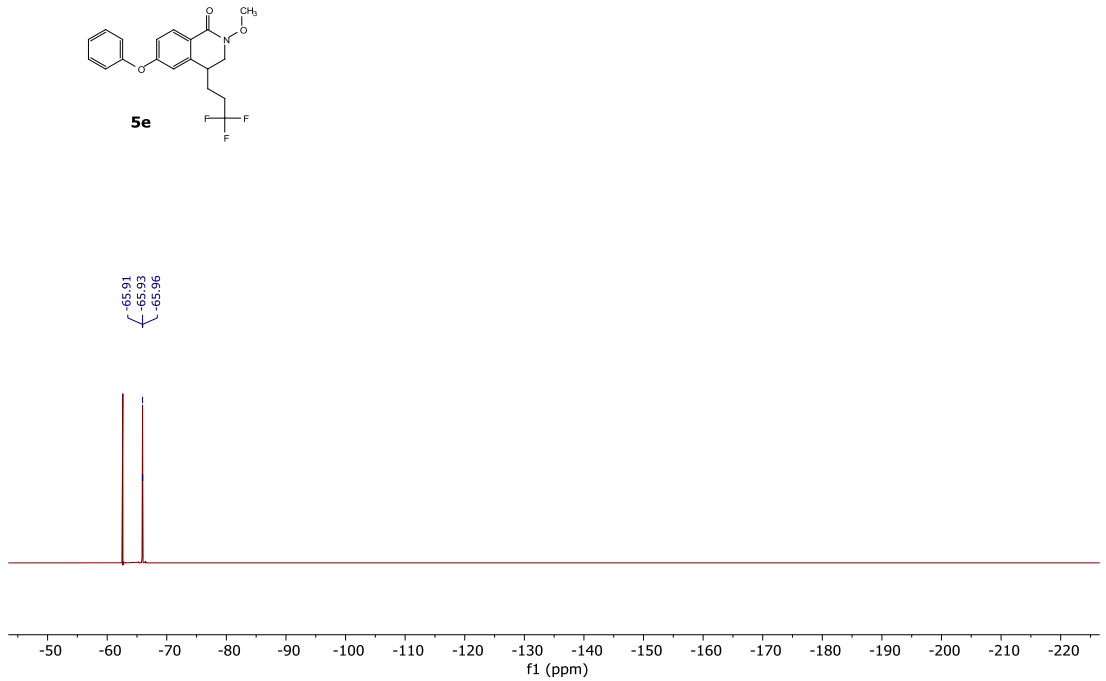
^{19} F NMR (471 MHz) spectrum of compound **5d** in $CDCl_3$ with $PhCF_3$ as reference standard



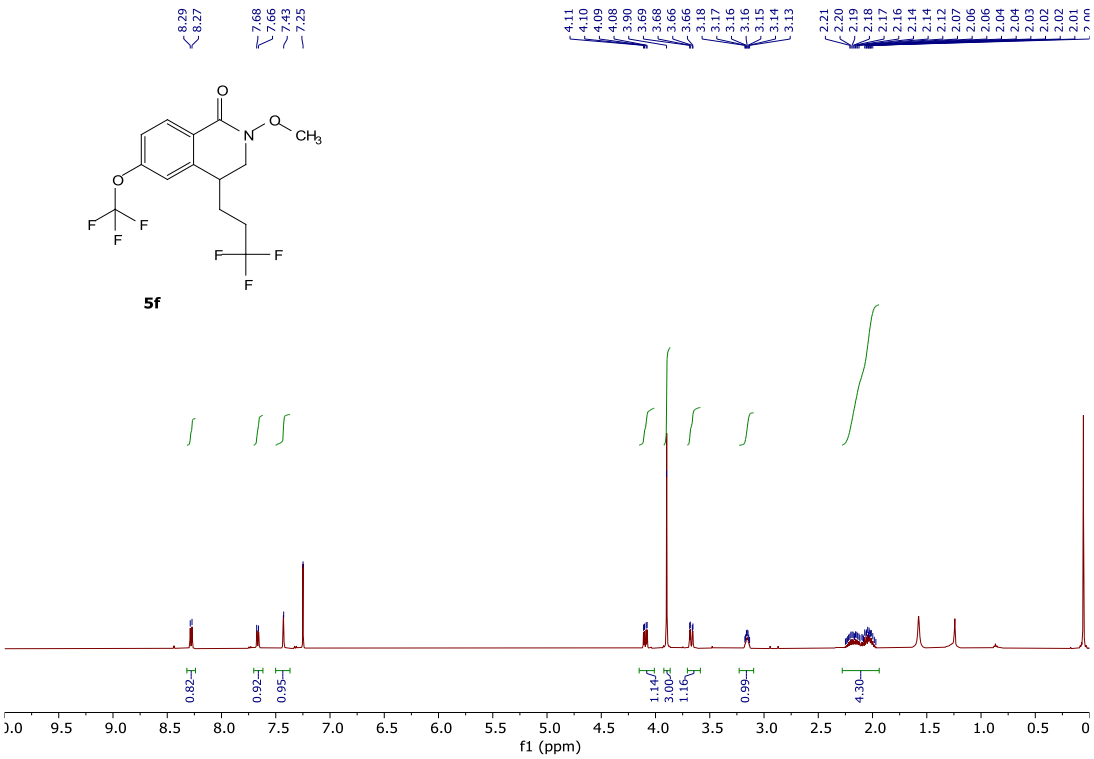
^{1}H NMR (500 MHz) spectrum of compound **5e** in $CDCl_3$



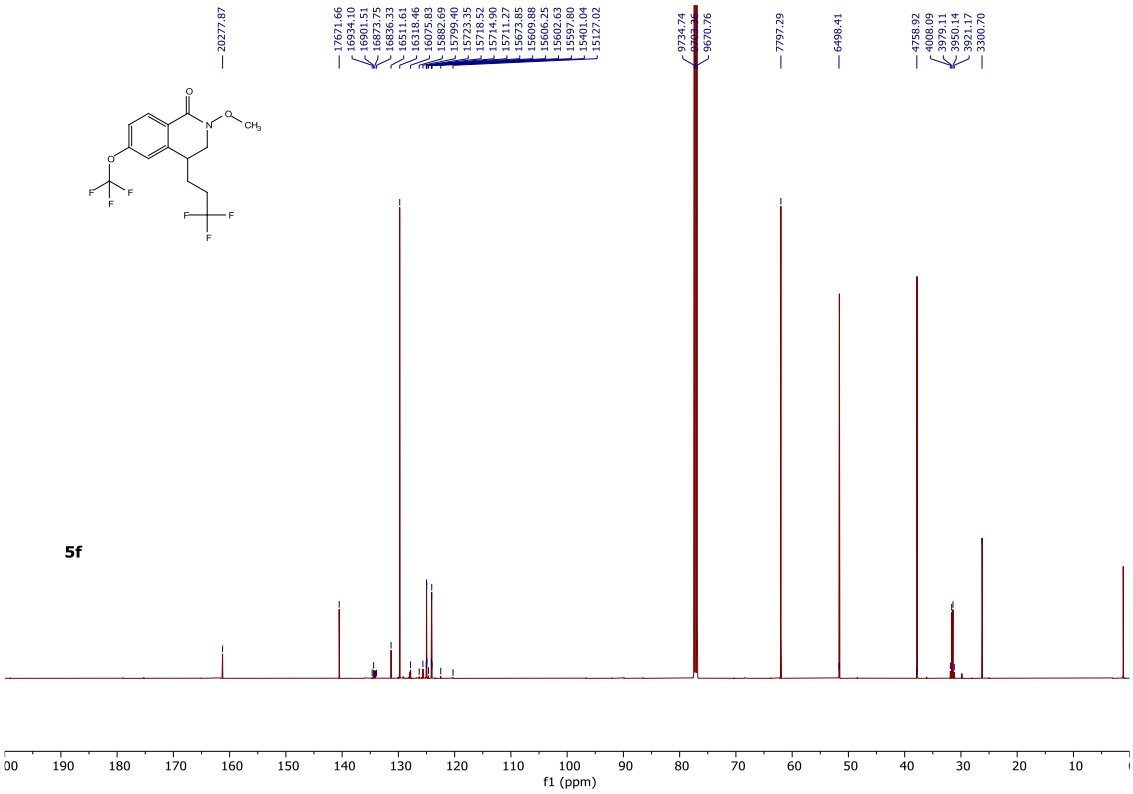
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **5e** in $CDCl_3$



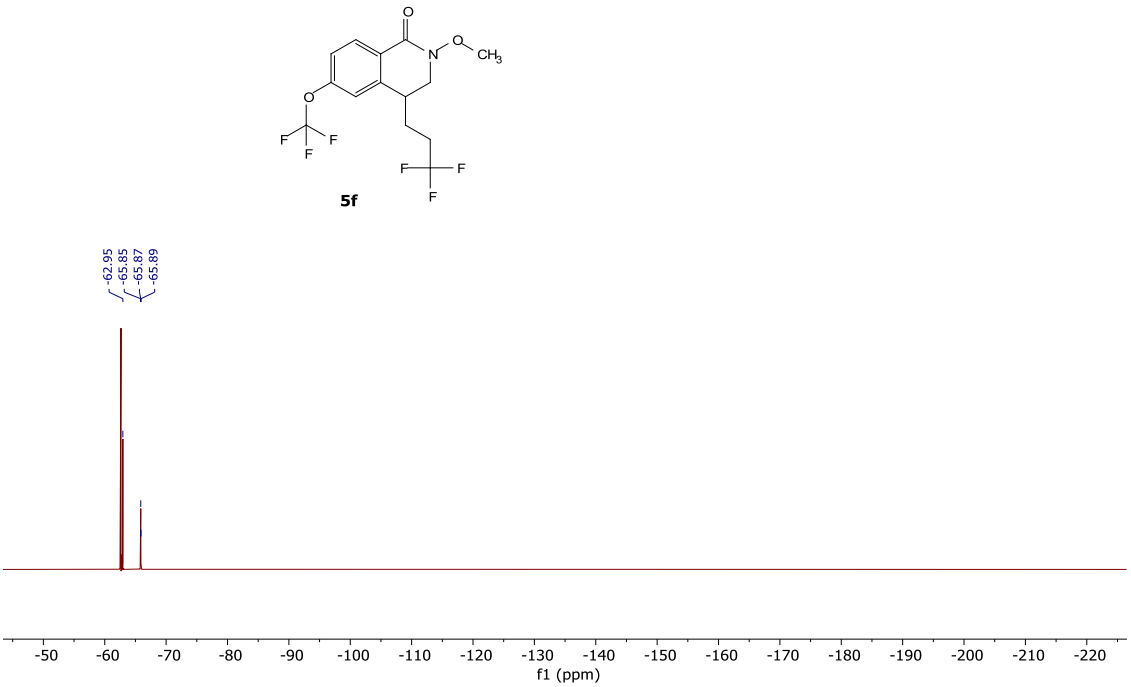
^{19} F NMR (471 MHz) spectrum of compound **5e** in $CDCl_3$ with $PhCF_3$ as reference standard



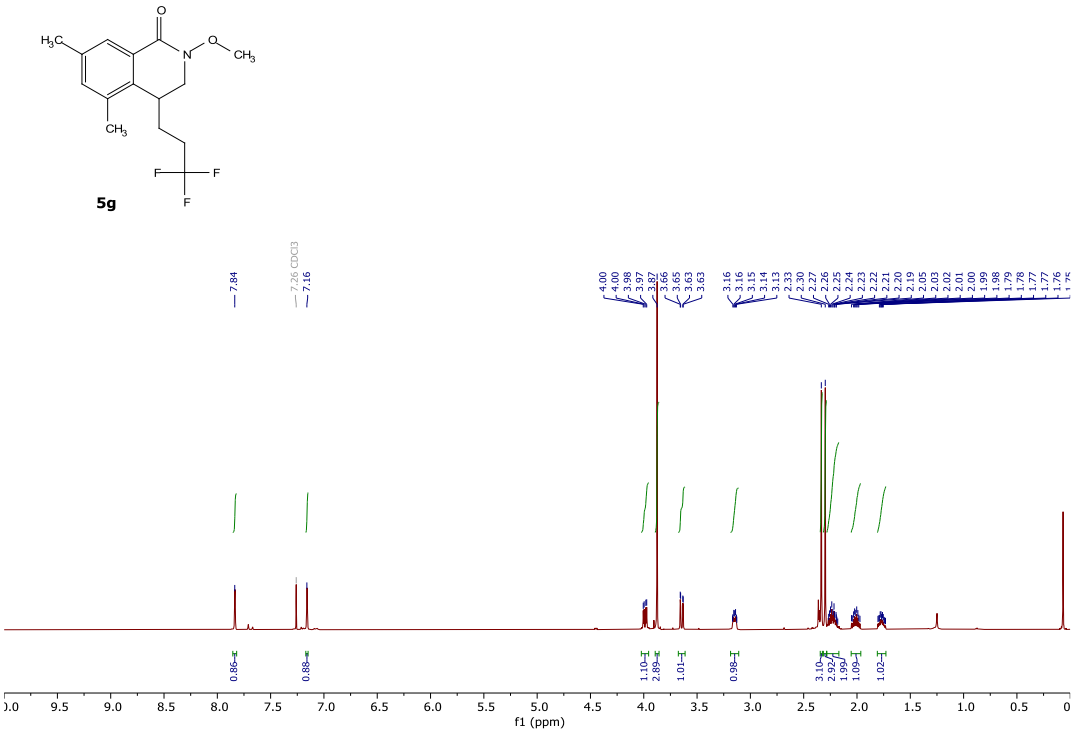
^{1}H NMR (500 MHz) spectrum of compound **5f** in $CDCl_3$



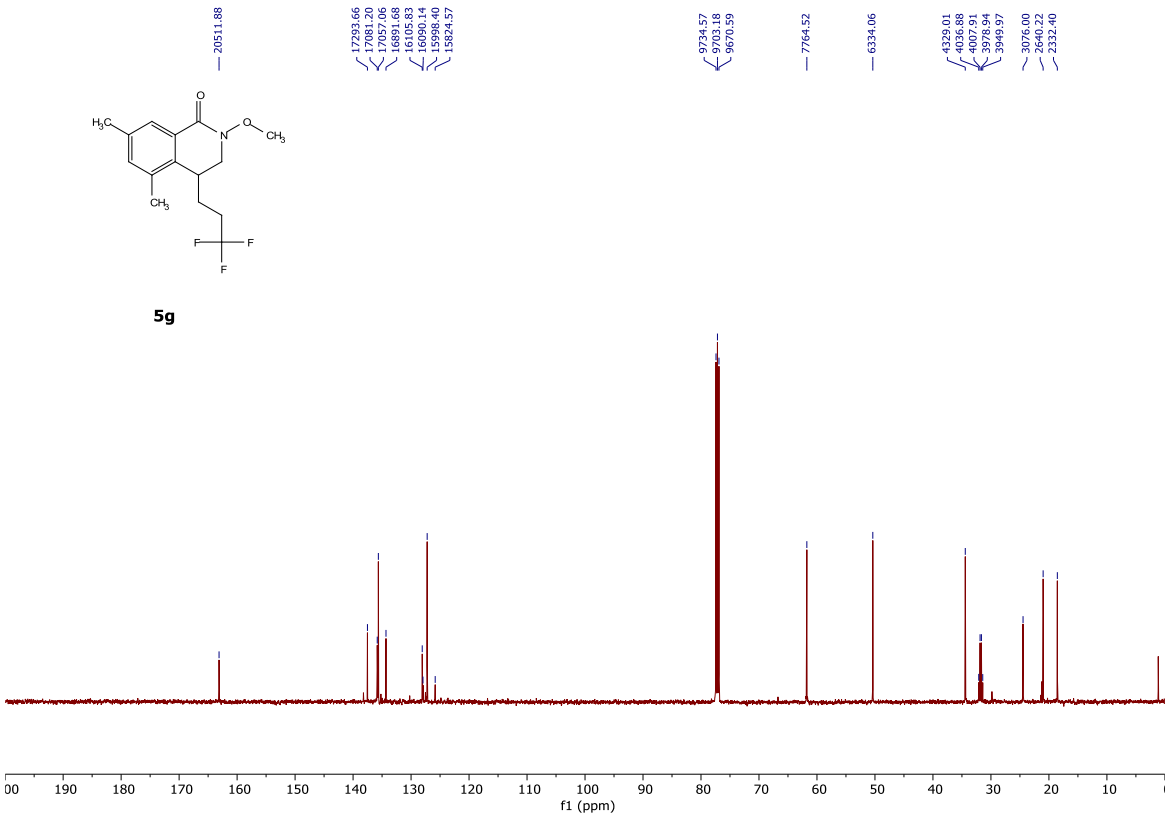
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5f** in $CDCl_3$



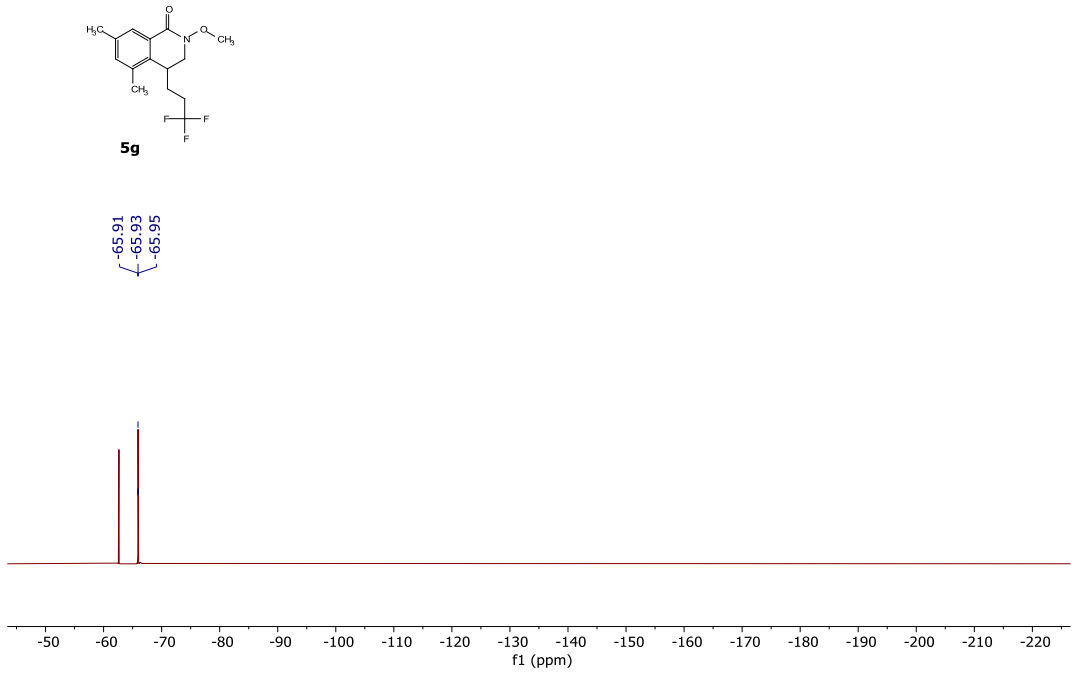
^{19} F NMR (471 MHz) spectrum of compound **5f** in $CDCl_3$ with $PhCF_3$ as reference standard



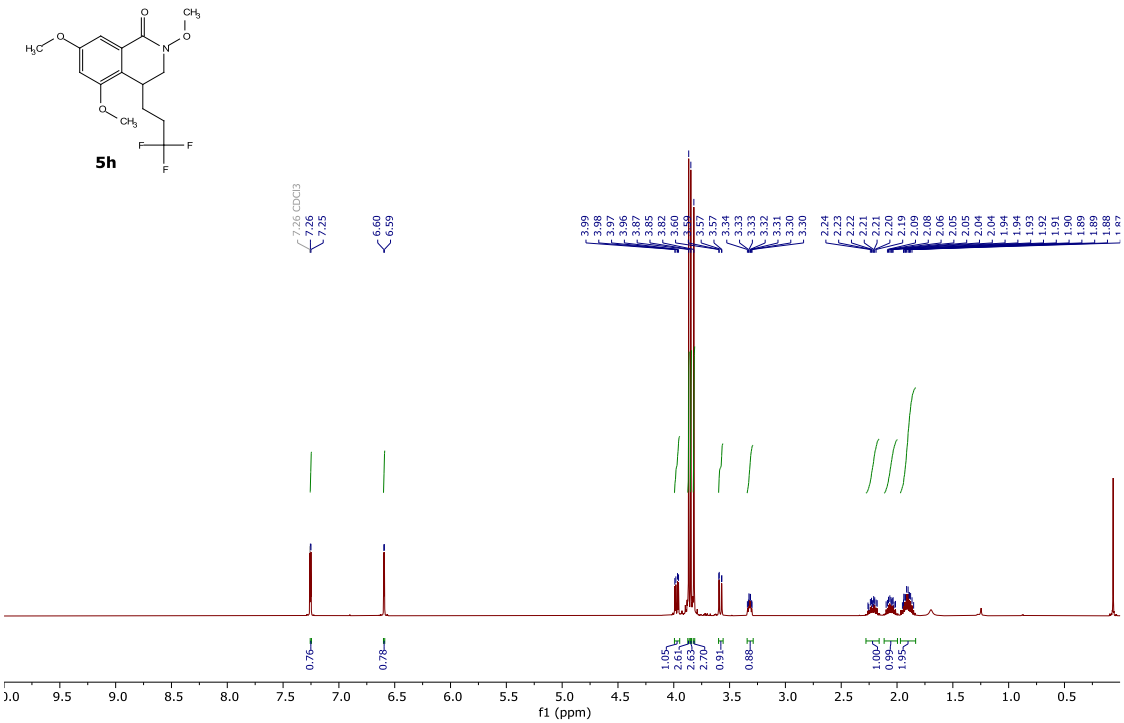
^{1}H NMR (500 MHz) spectrum of compound **5g** in $CDCl_3$



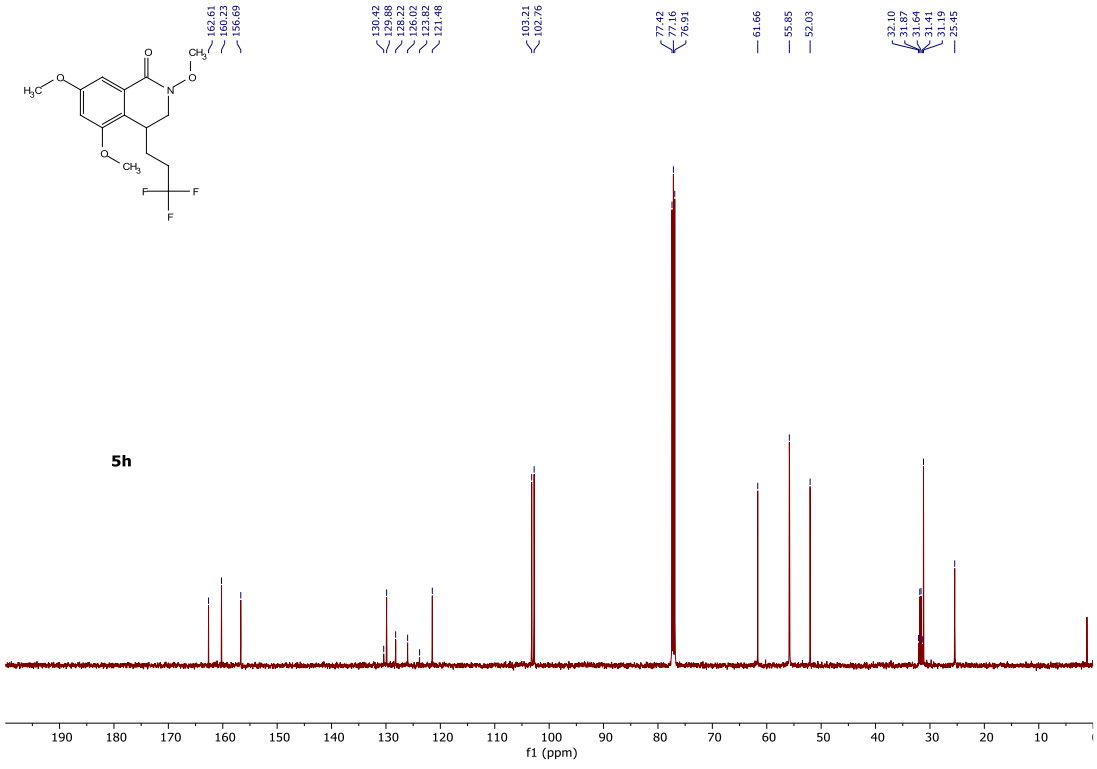
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5g** in $CDCl_3$



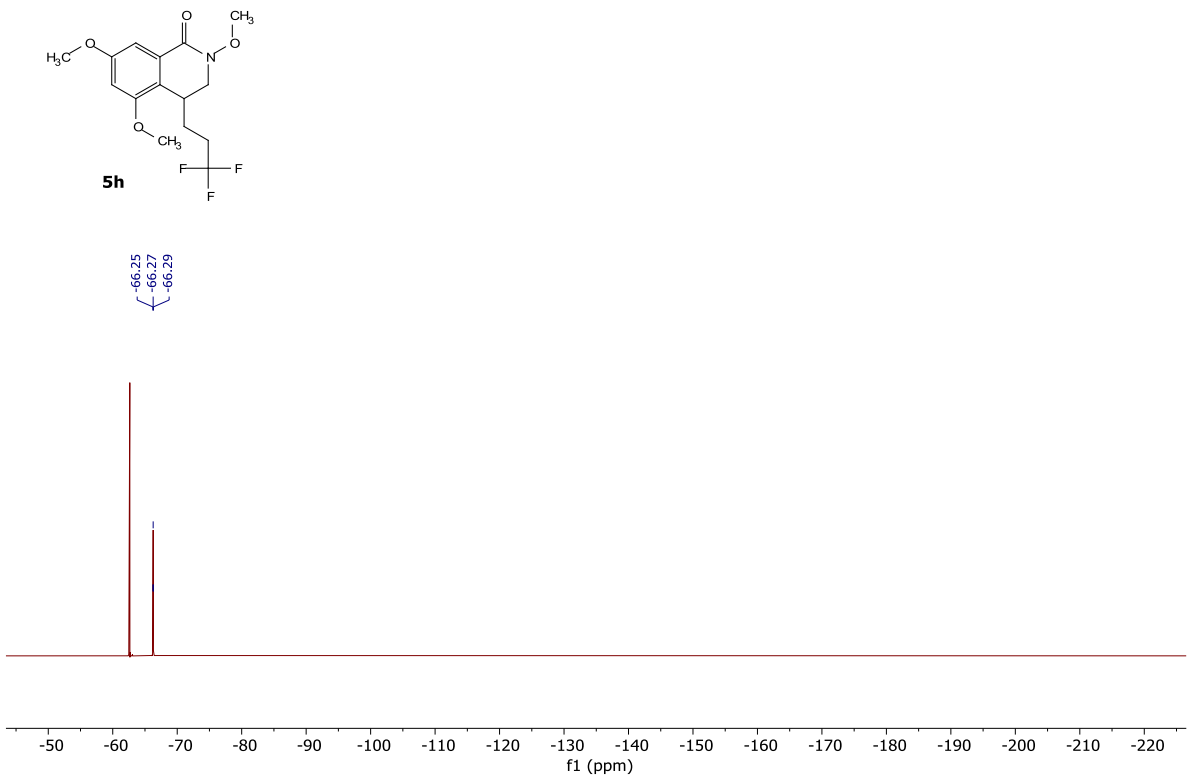
^{19}F NMR (471 MHz) spectrum of compound **5g** in $CDCl_3$ with $PhCF_3$ as reference standard



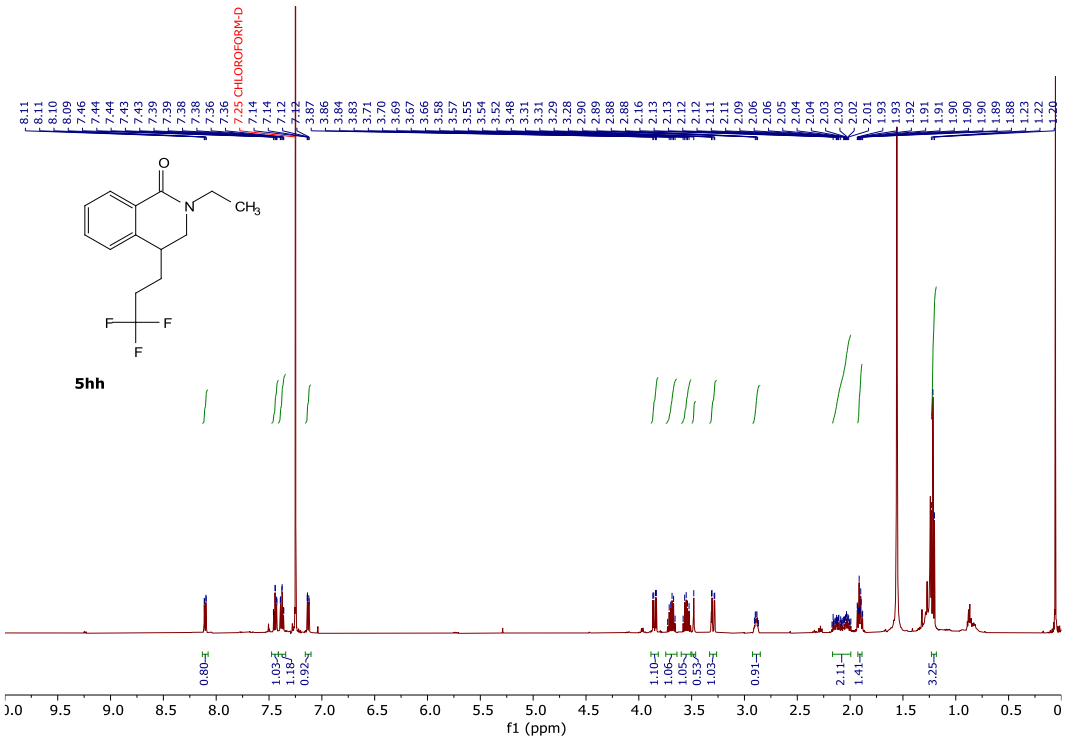
^{1}H NMR (500 MHz) spectrum of compound **5h** in $CDCl_3$



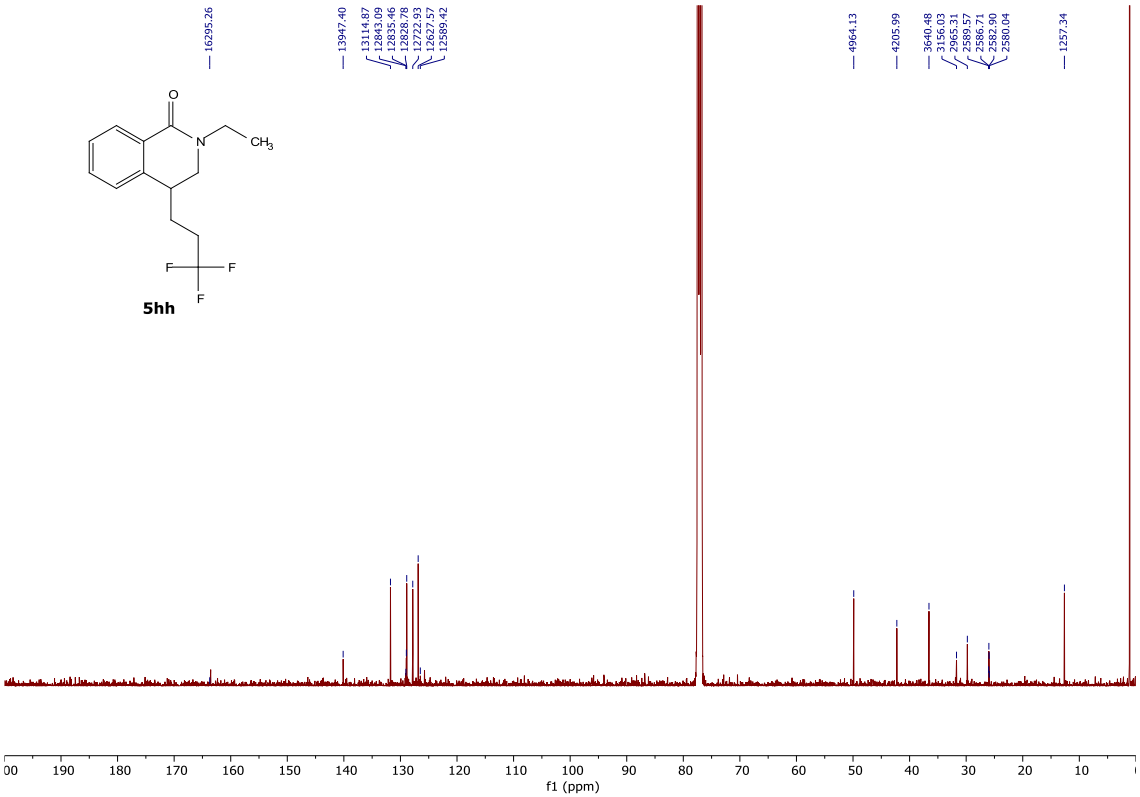
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5h** in $CDCl_3$



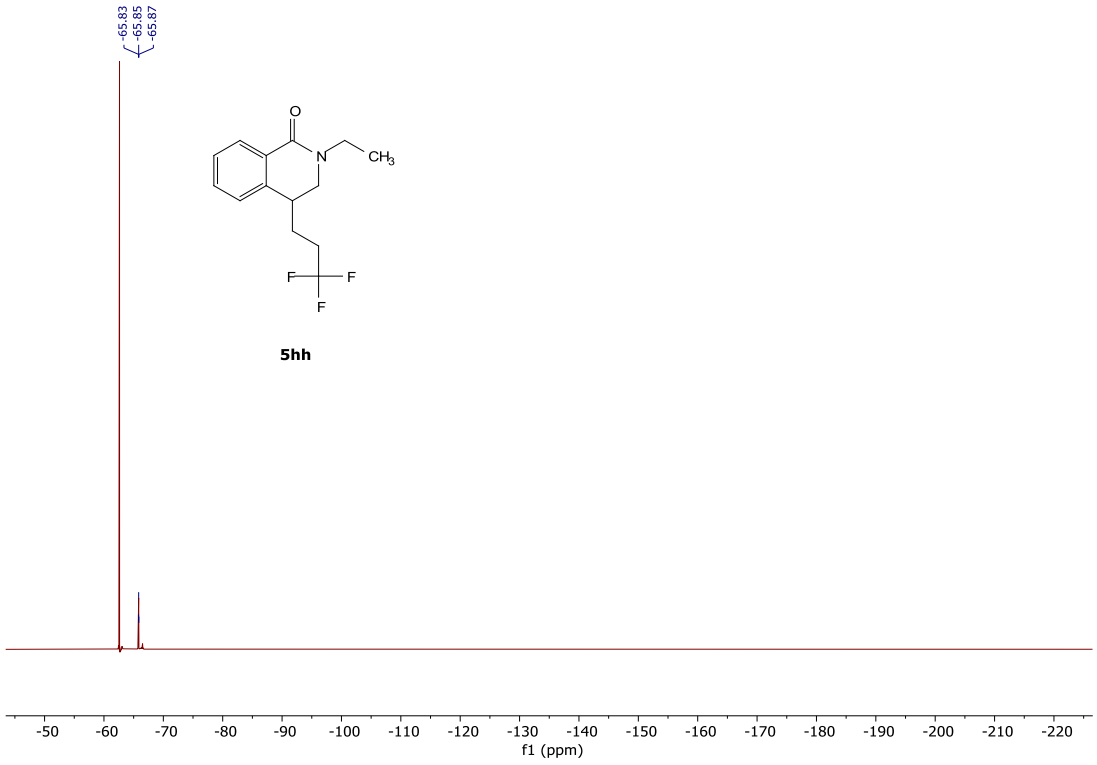
^{19} F NMR (471 MHz) spectrum of compound **5h** in $CDCl_3$ with $PhCF_3$ as reference standard



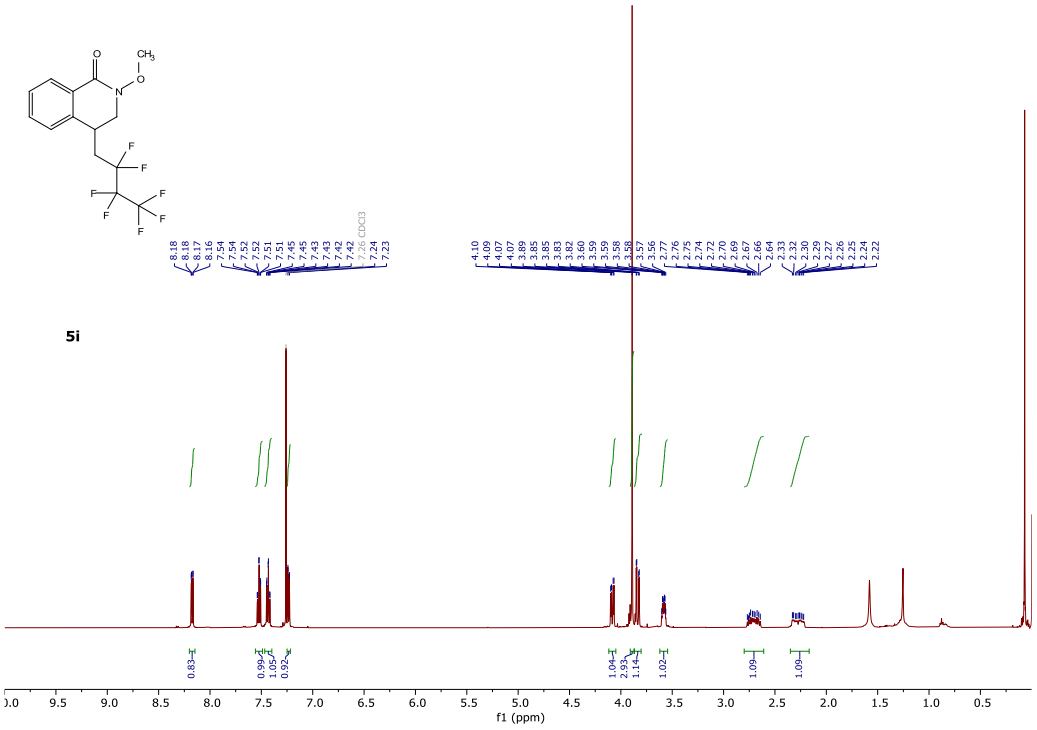
^{1}H NMR (500 MHz) spectrum of compound **5hh** in $CDCl_3$



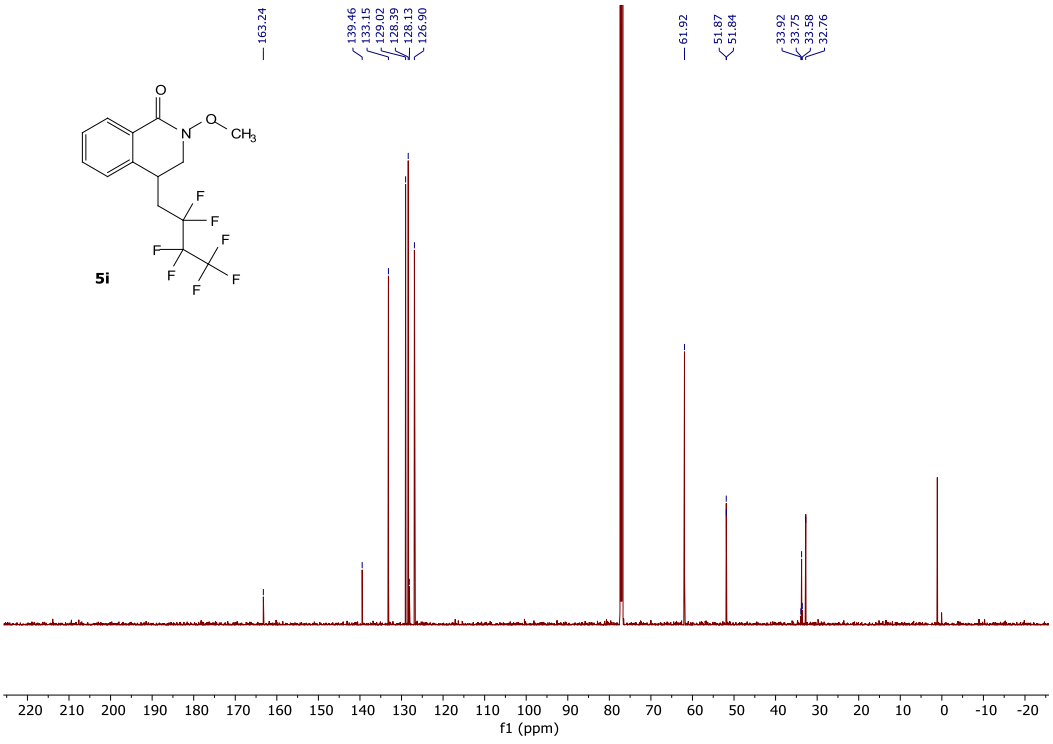
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5hh** in $CDCl_3$



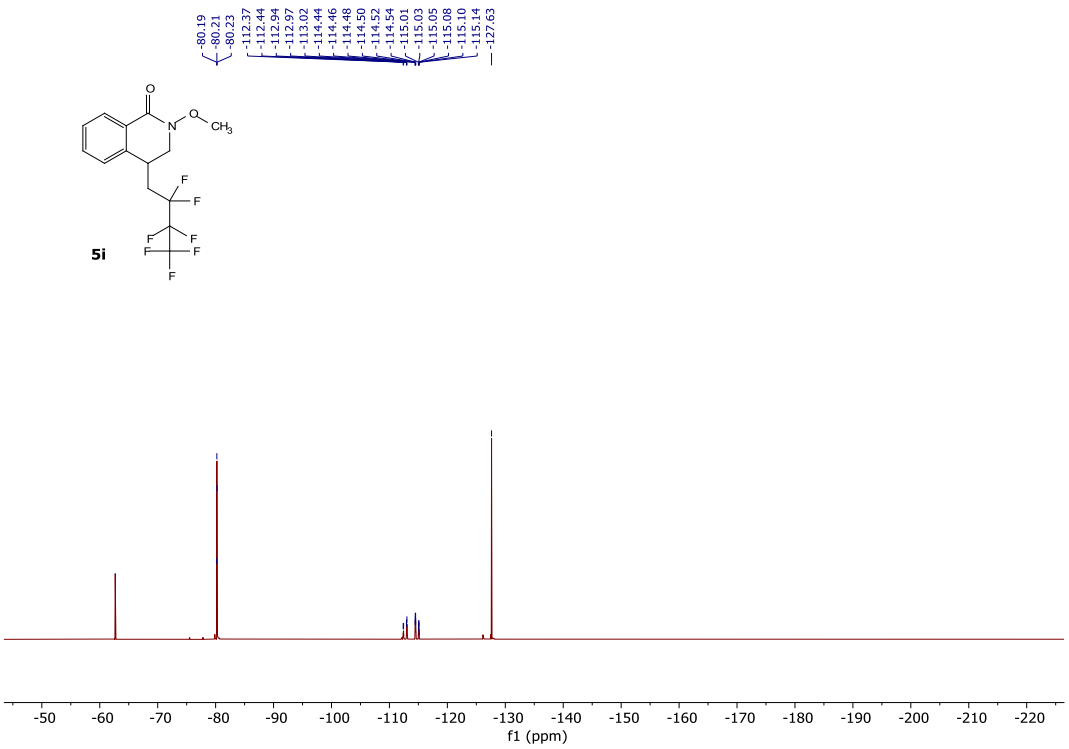
^{19}F NMR (471 MHz) spectrum of compound **5hh** in $CDCl_3$ with $PhCF_3$ as reference standard



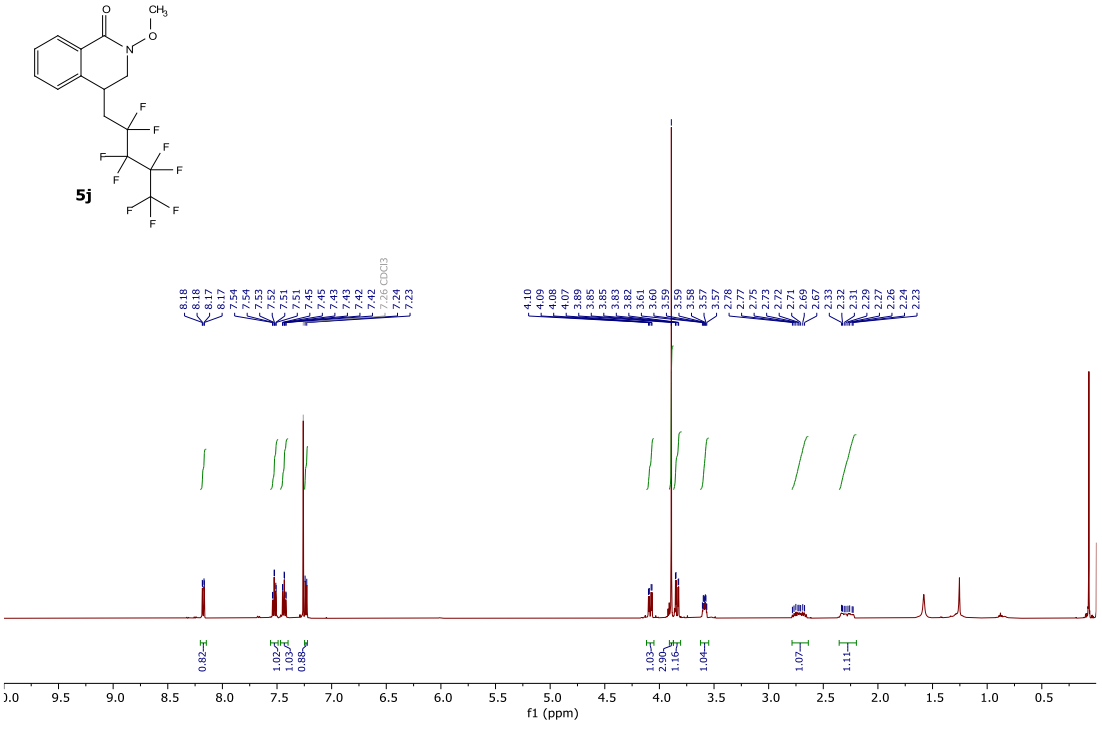
^{1}H NMR (500 MHz) spectrum of compound **5i** in $CDCl_3$



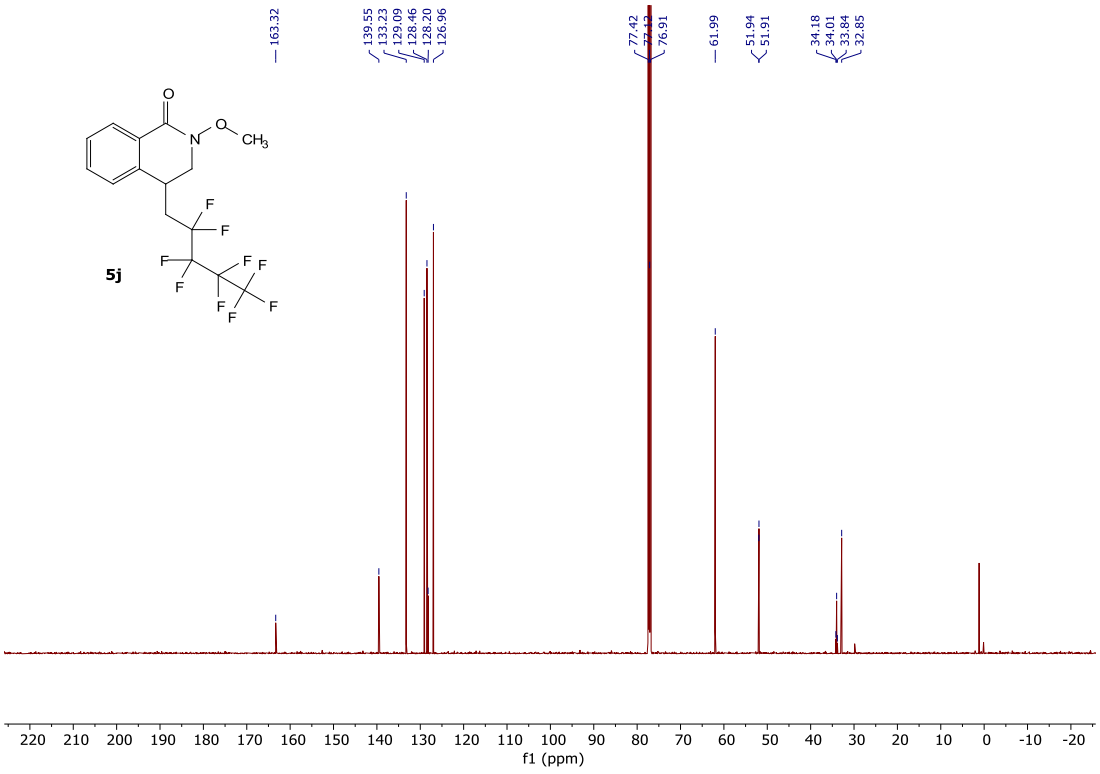
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5i** in $CDCl_3$



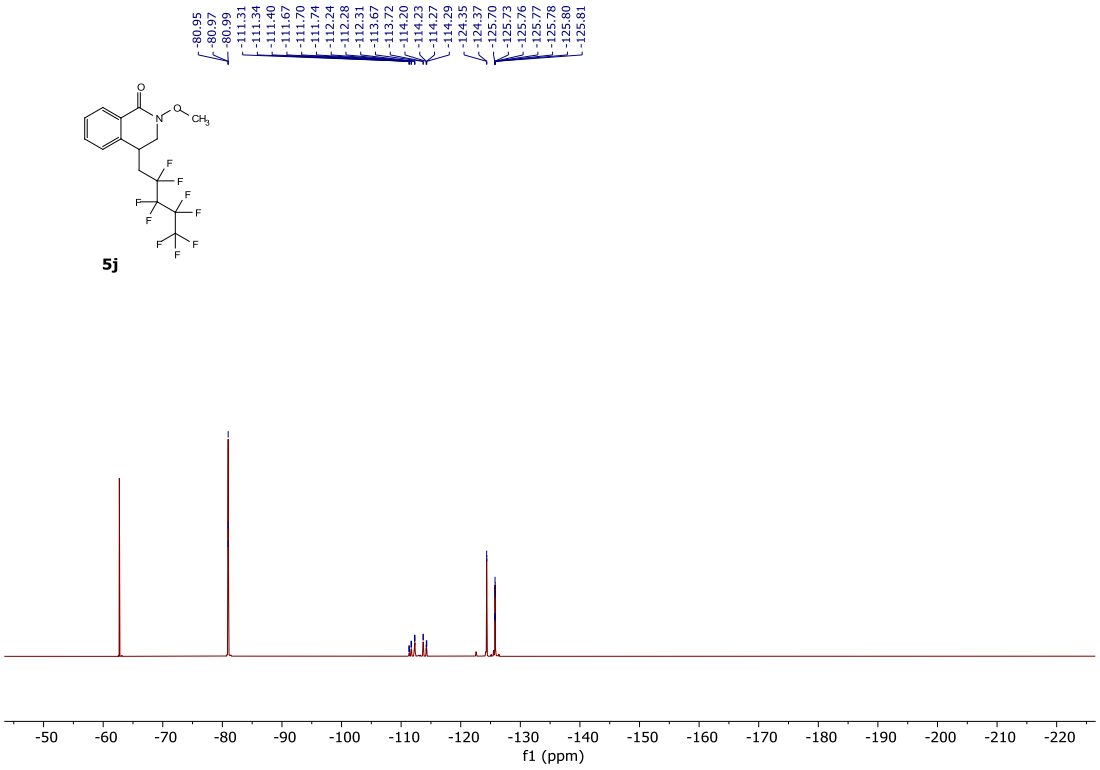
^{19} F NMR (471 MHz) spectrum of compound **5i** in $CDCl_3$ with $PhCF_3$ as reference standard



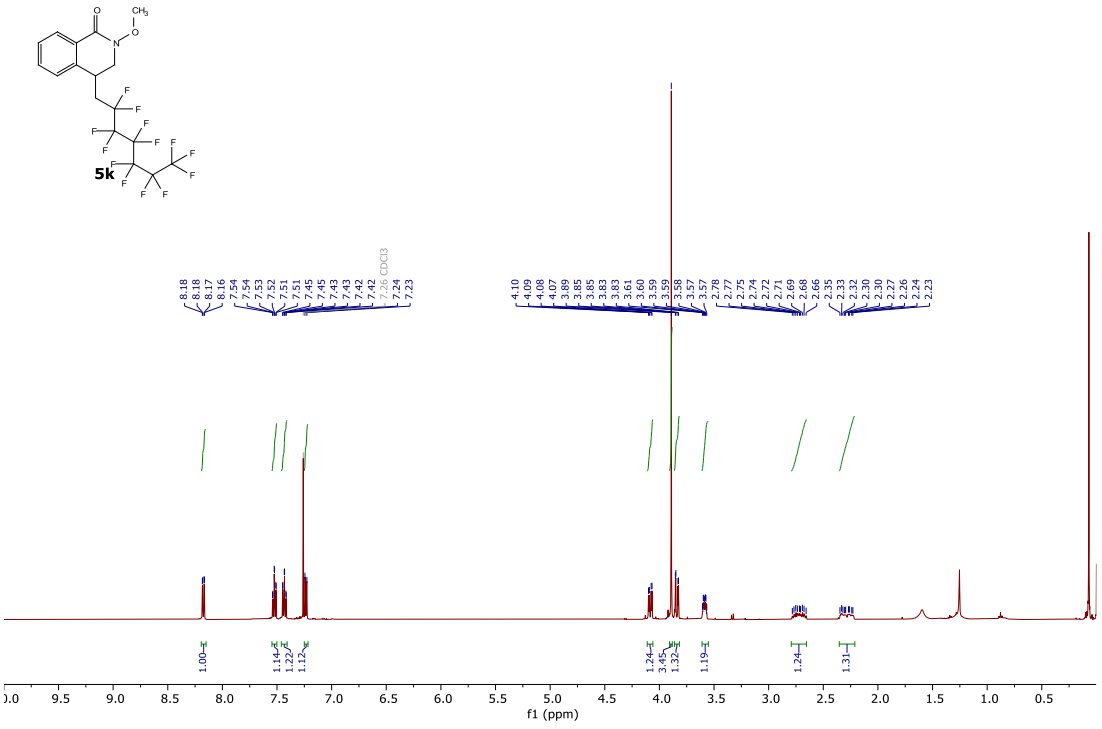
^{1}H NMR (500 MHz) spectrum of compound **5j** in $CDCl_3$



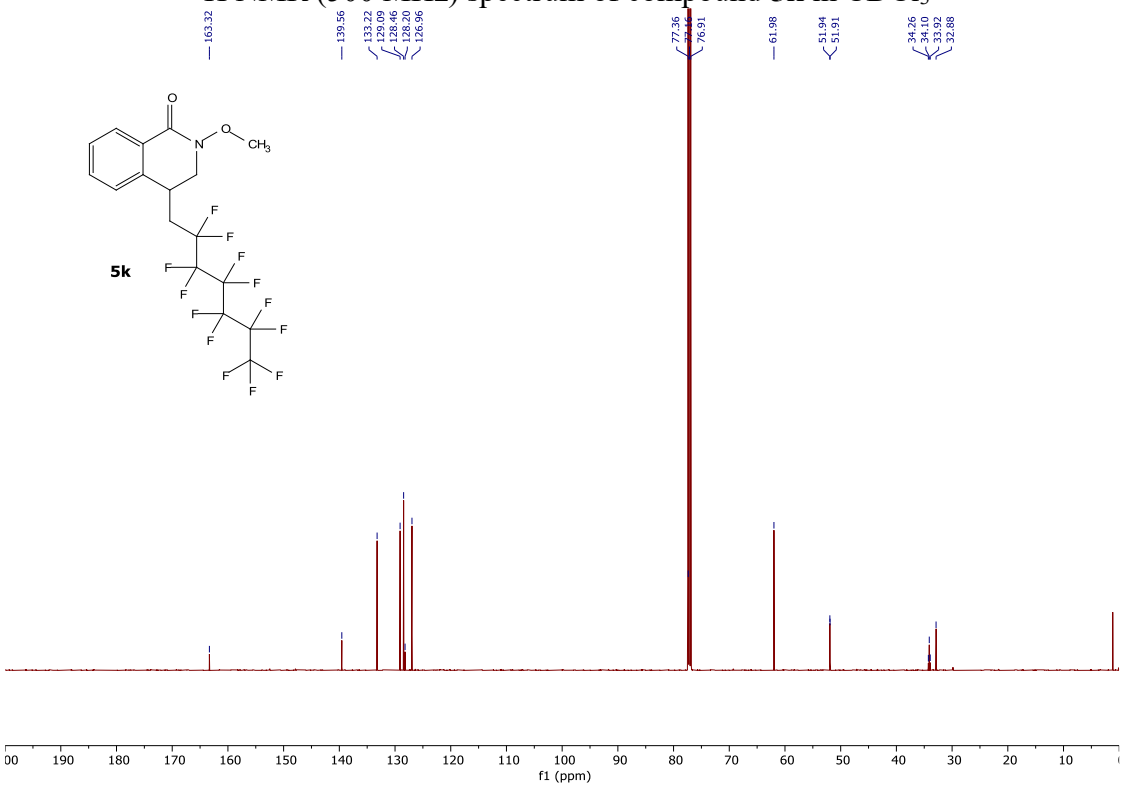
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **5j** in $CDCl_3$



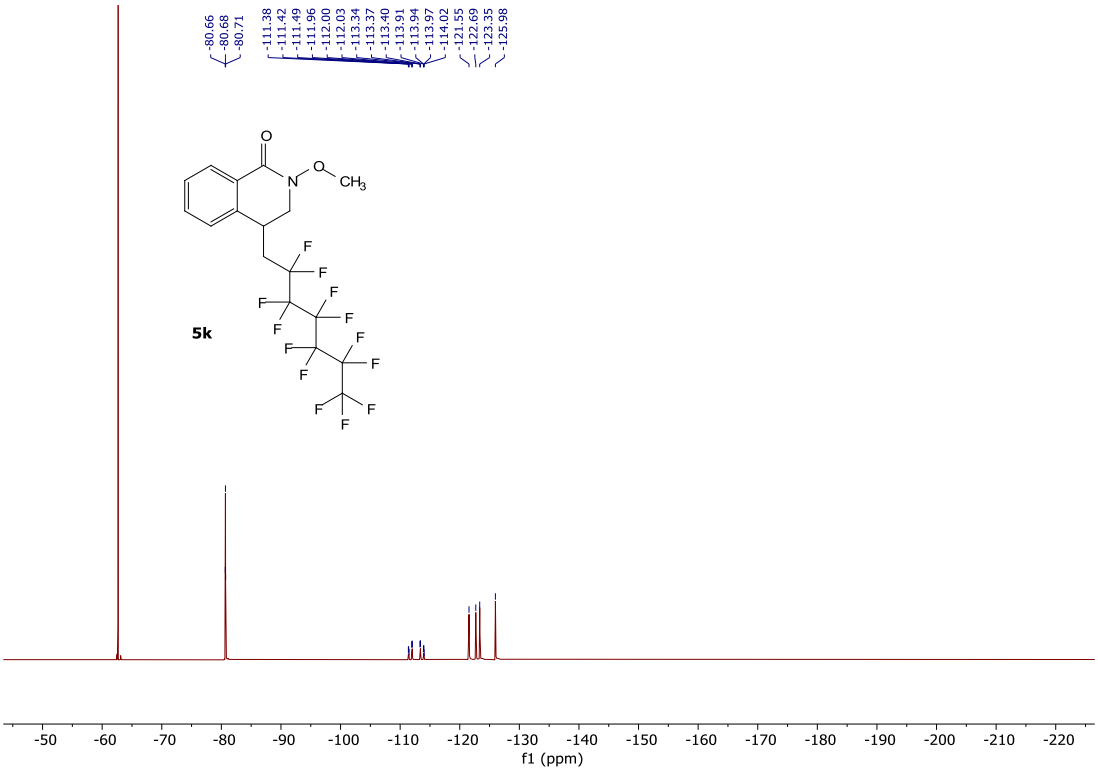
^{19} F NMR (471 MHz) spectrum of compound **5j** in $CDCl_3$ with $PhCF_3$ as reference standard



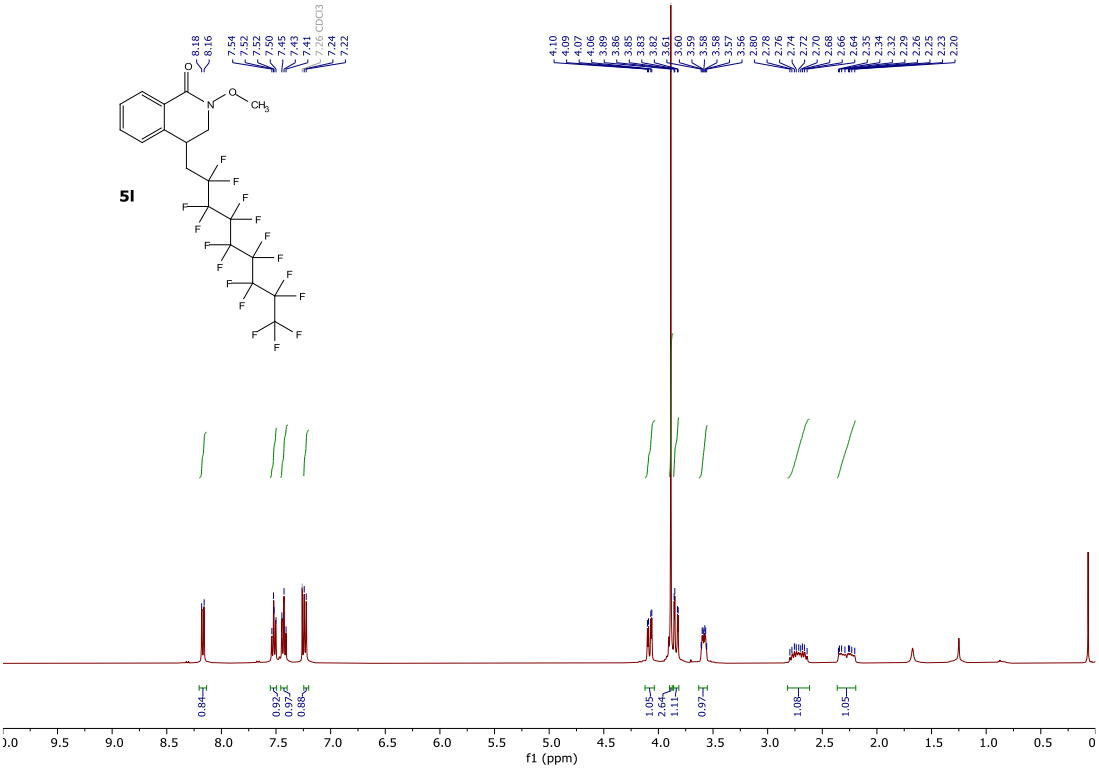
^{1}H NMR (500 MHz) spectrum of compound **5k** in $CDCl_3$



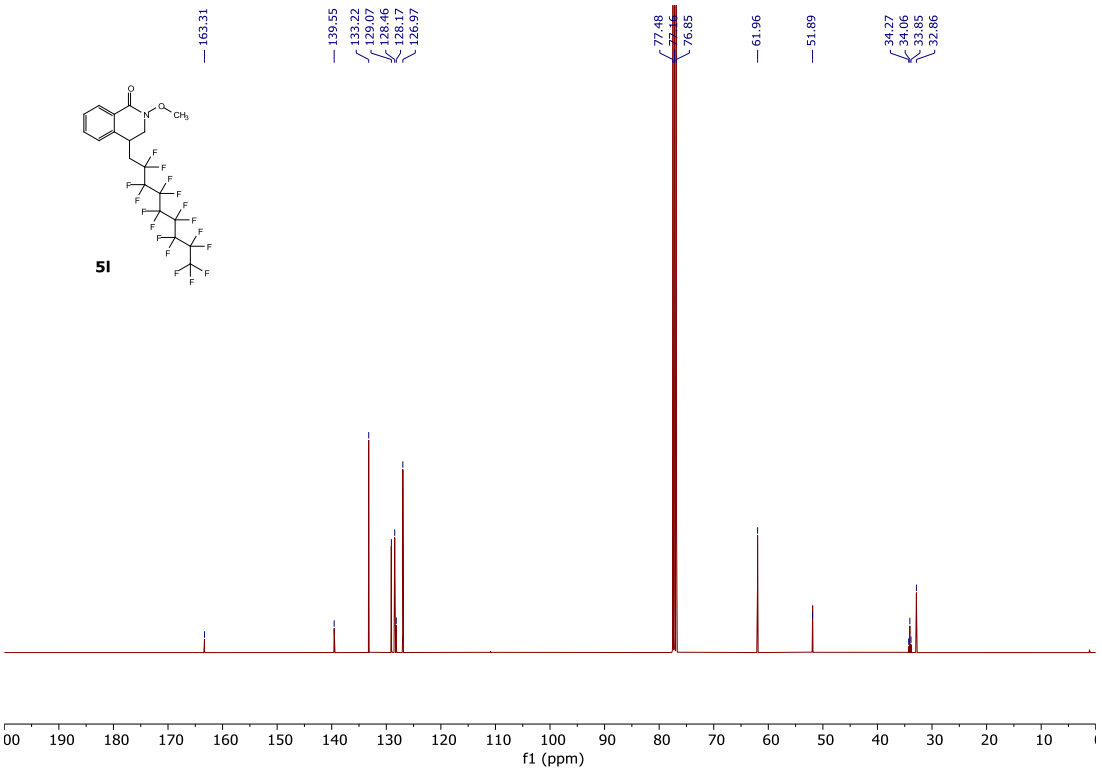
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **5k** in $CDCl_3$



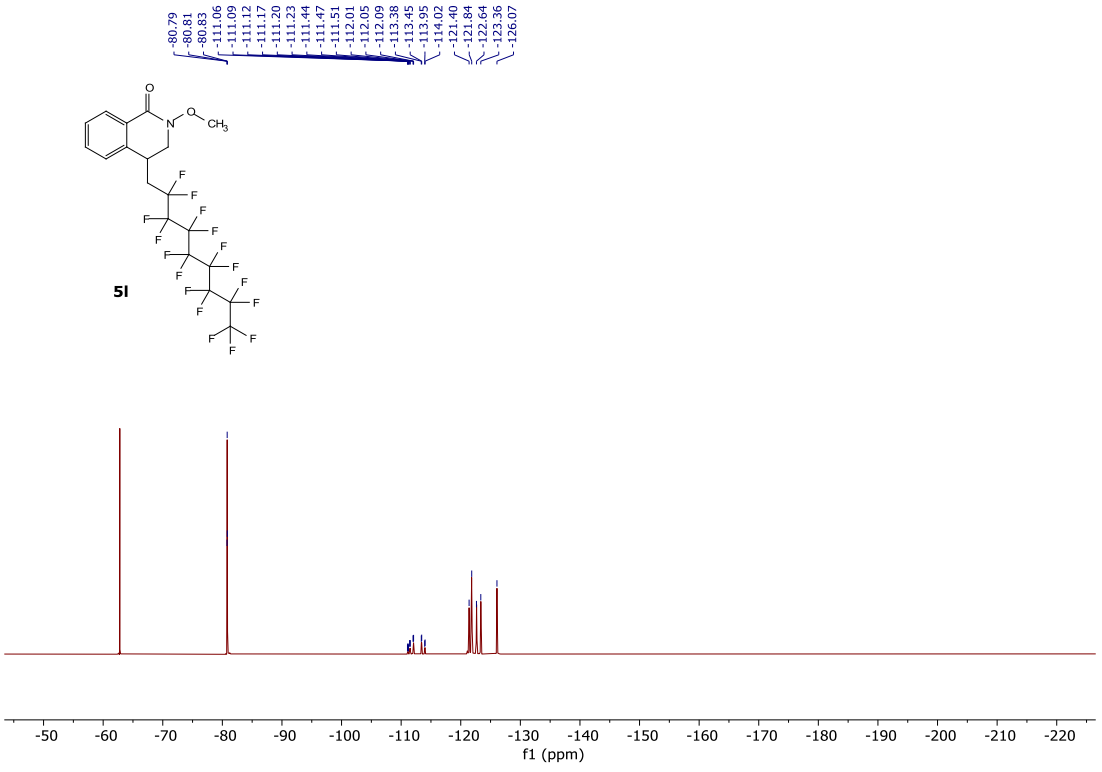
^{19} F NMR (471 MHz) spectrum of compound **5k** in $CDCl_3$ with $PhCF_3$ as reference standard



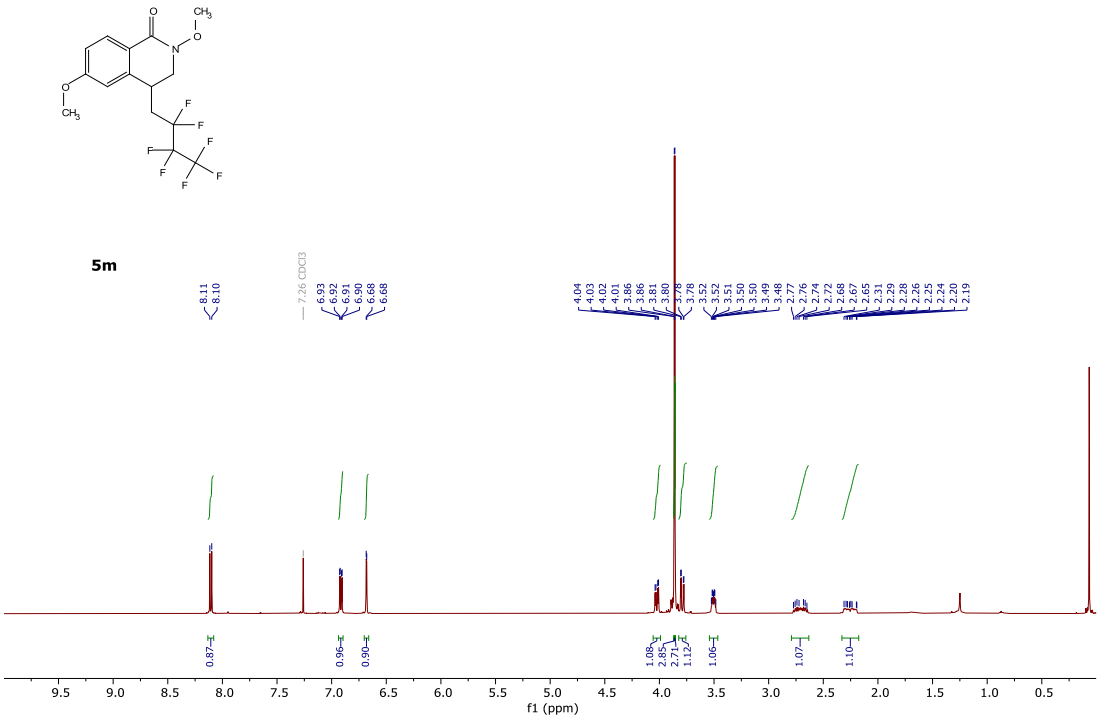
^{1}H NMR (400 MHz) spectrum of compound **5l** in $CDCl_3$



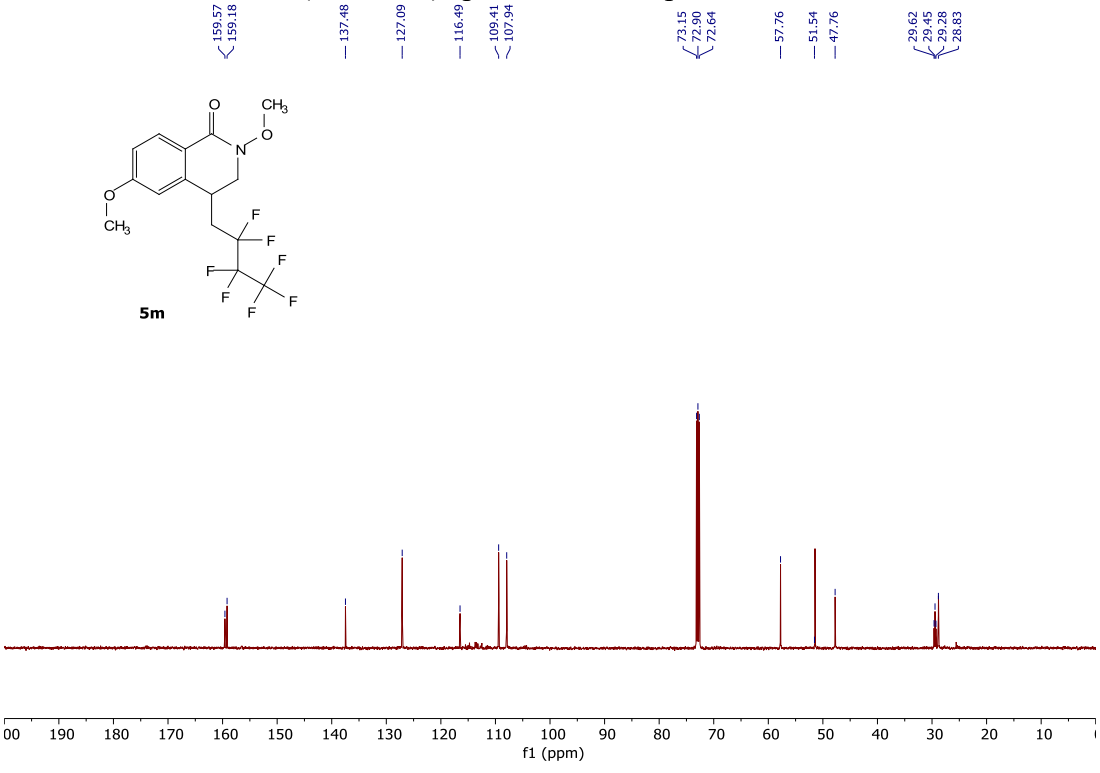
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **5l** in $CDCl_3$



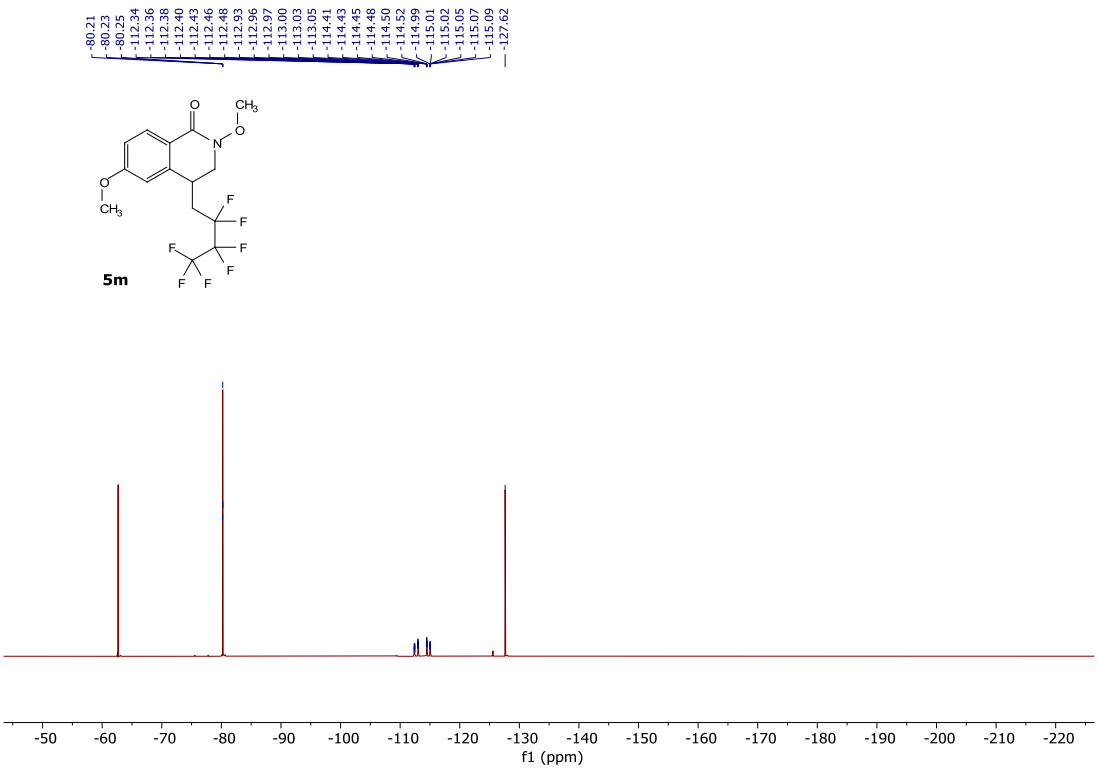
^{19}F NMR (471 MHz) spectrum of compound **5l** in $CDCl_3$ with $PhCF_3$ as reference standard



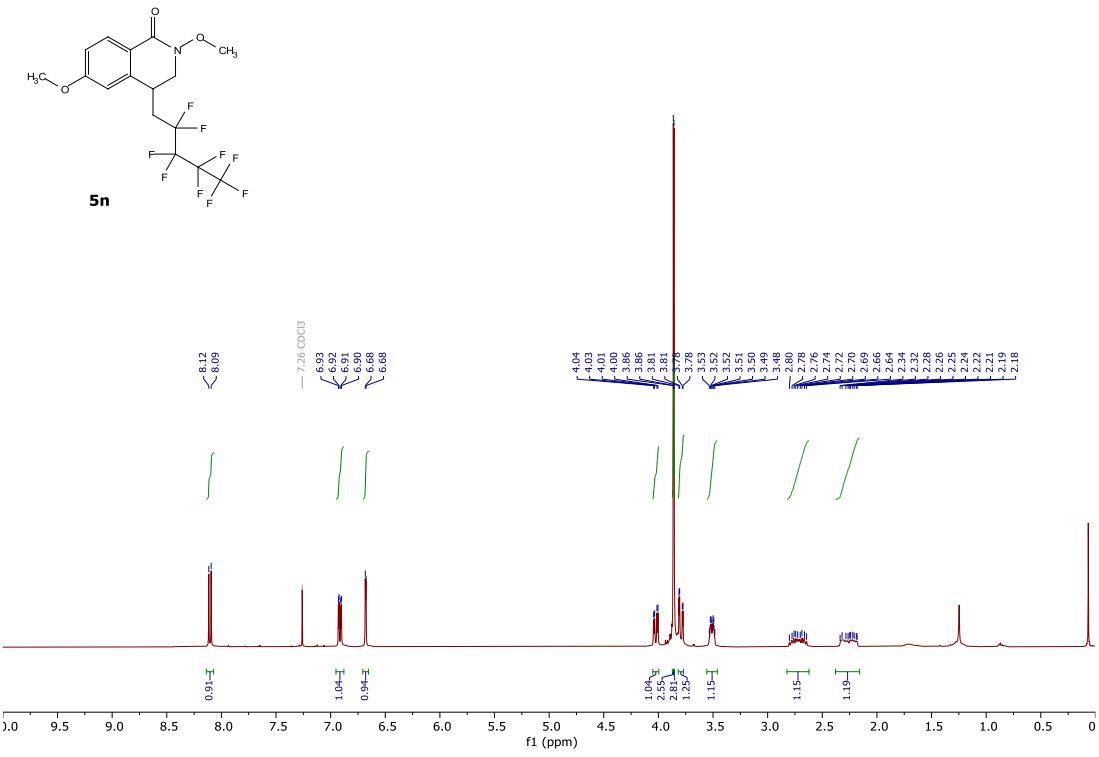
^{1}H NMR (500 MHz) spectrum of compound **5m** in $CDCl_3$



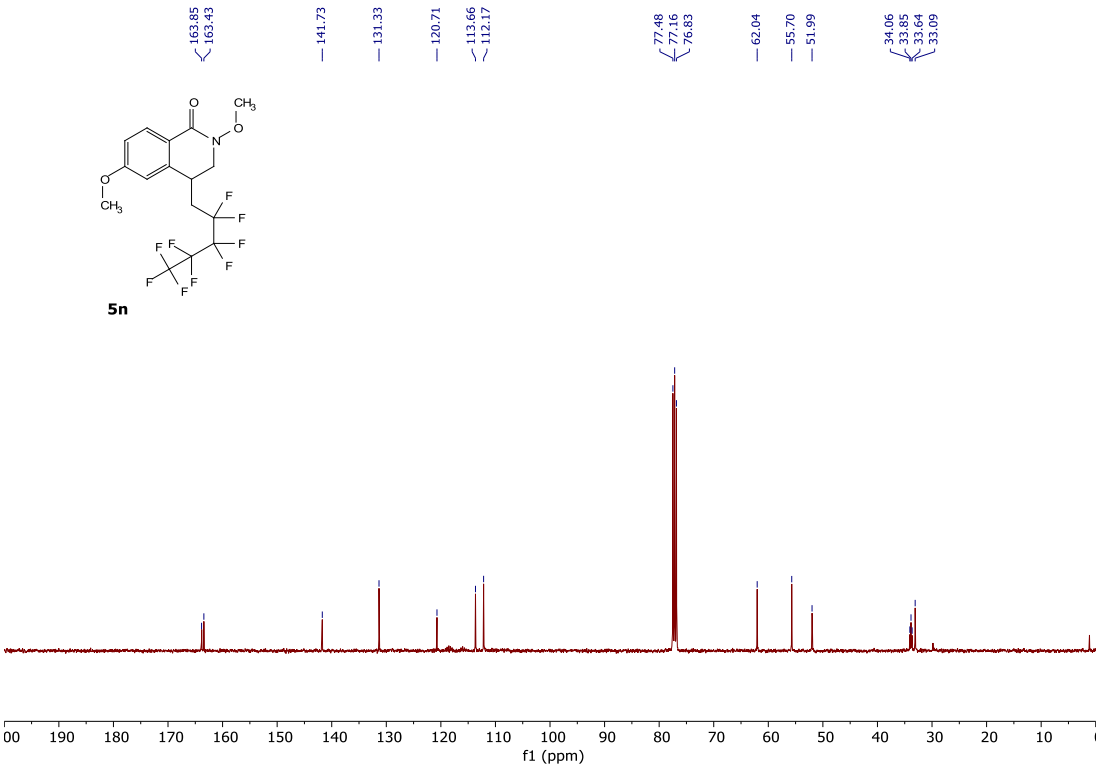
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **5m** in $CDCl_3$



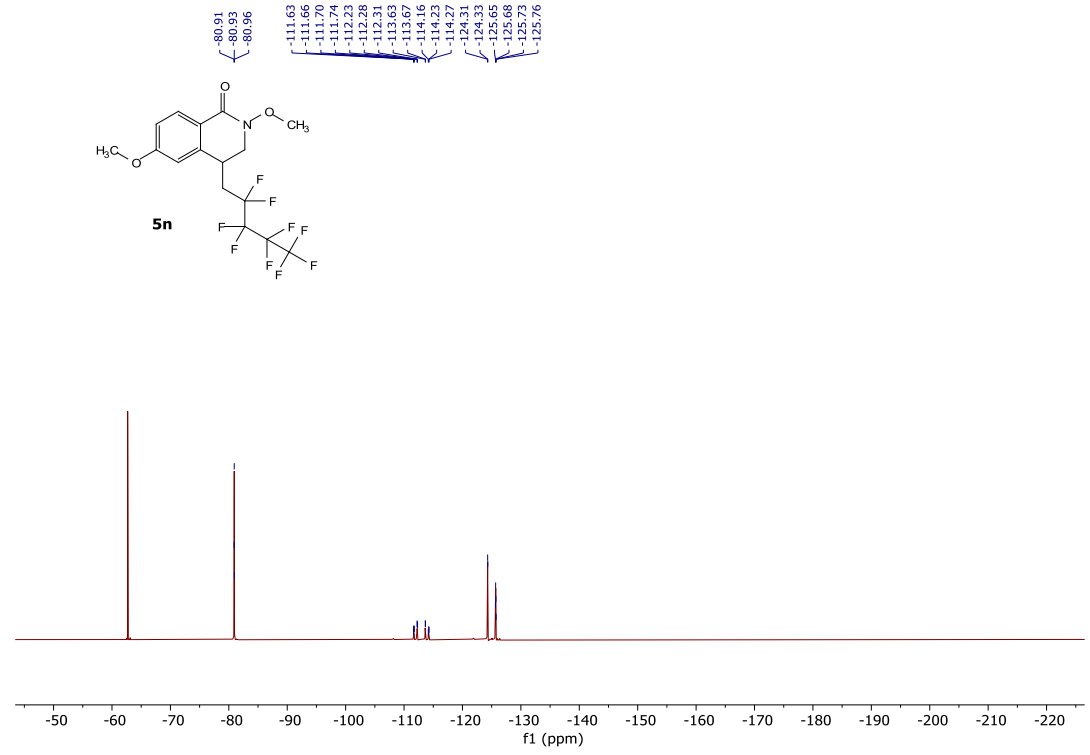
^{19} F NMR (471 MHz) spectrum of compound **5m** in $CDCl_3$ with $PhCF_3$ as reference standard



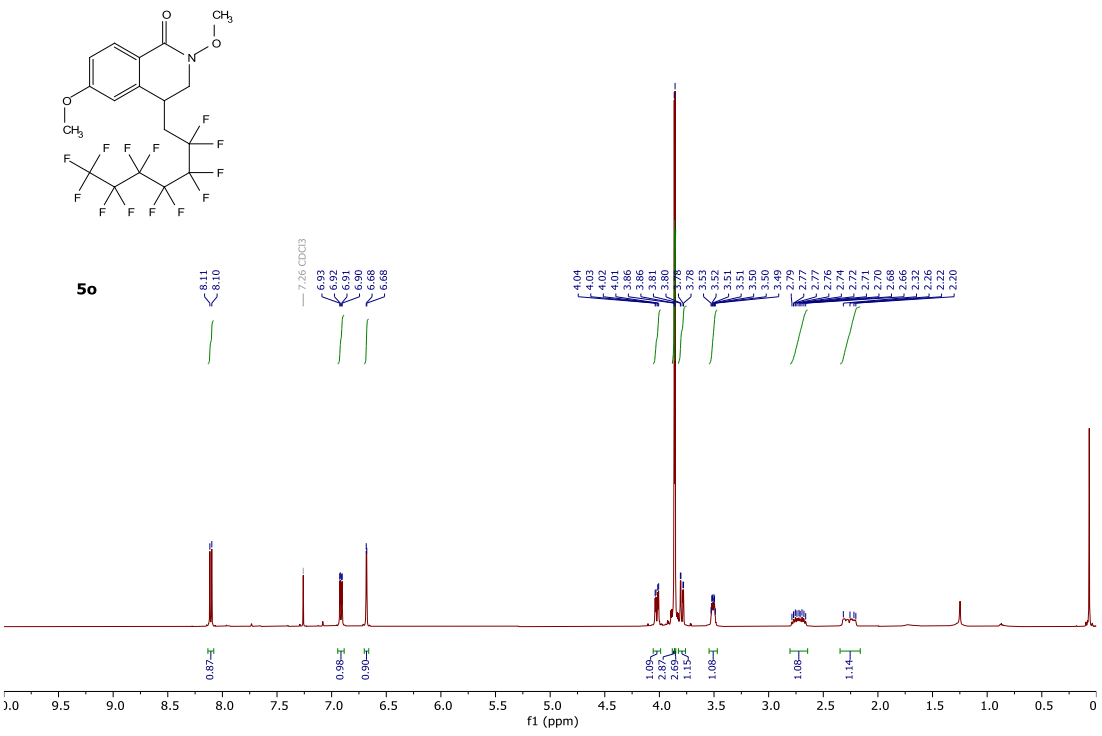
^{1}H NMR (400 MHz) spectrum of compound **5n** in $CDCl_3$



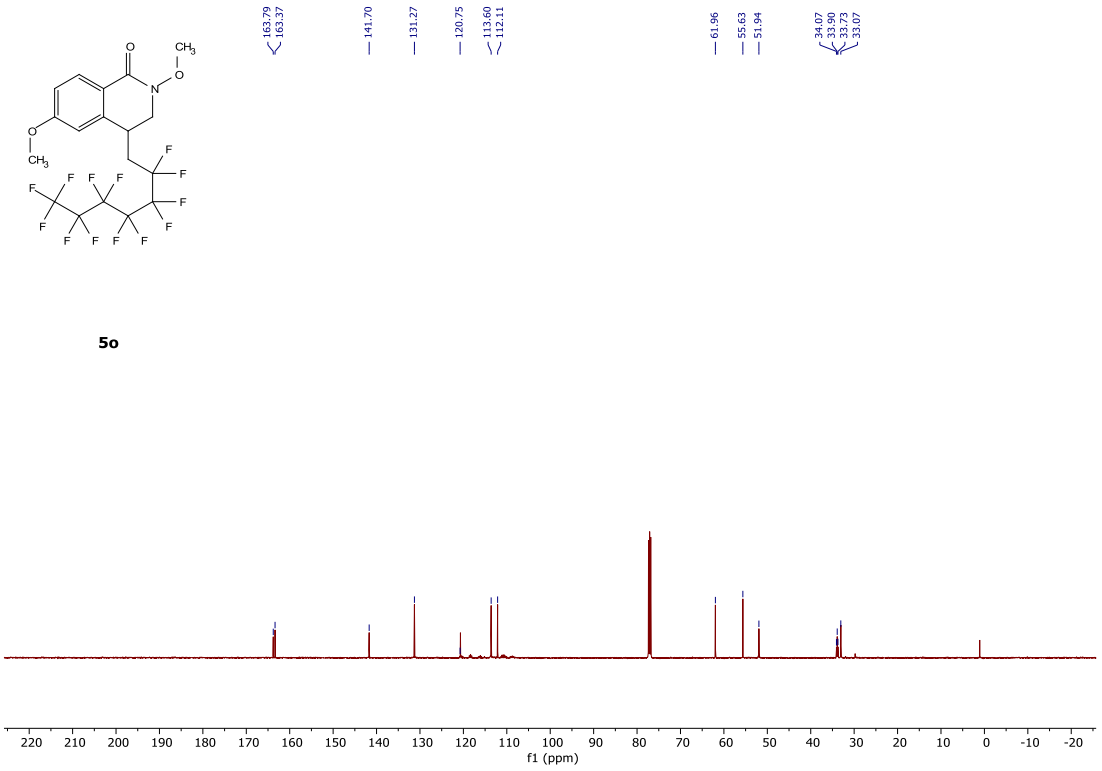
^{13} C {^{1}H} NMR (100 MHz) spectrum of compound **5n** in $CDCl_3$



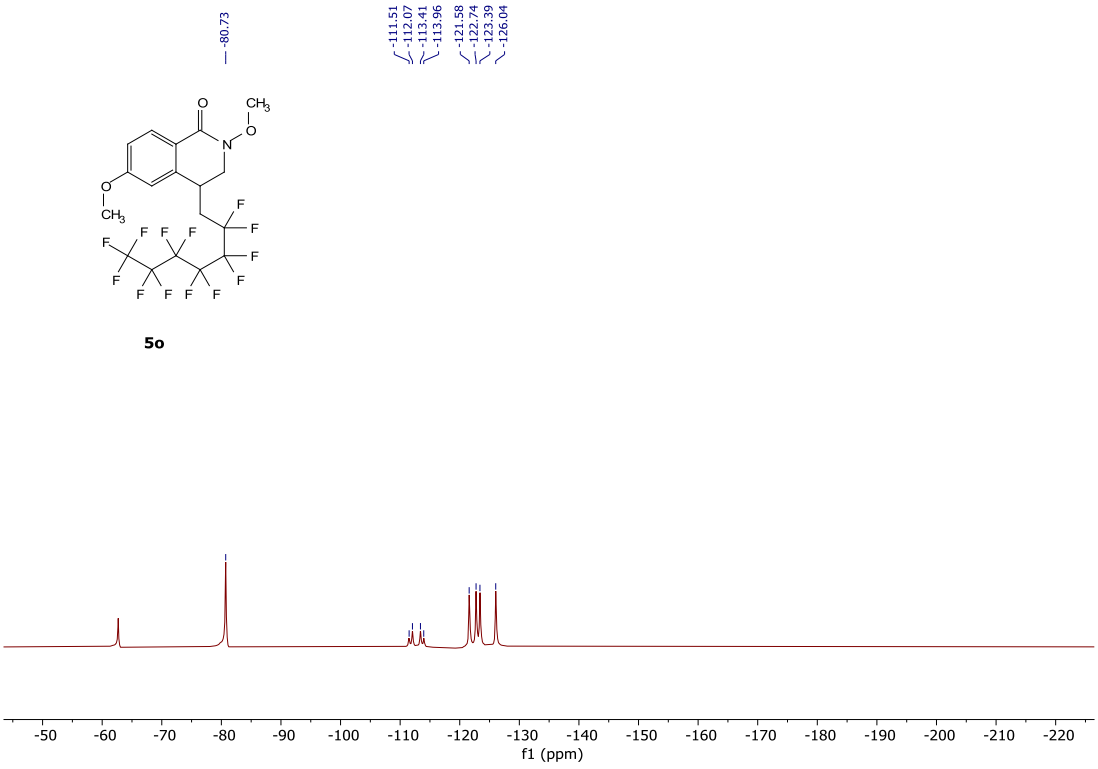
^{19} F NMR (471 MHz) spectrum of compound **5n** in $CDCl_3$ with $PhCF_3$ as reference standard



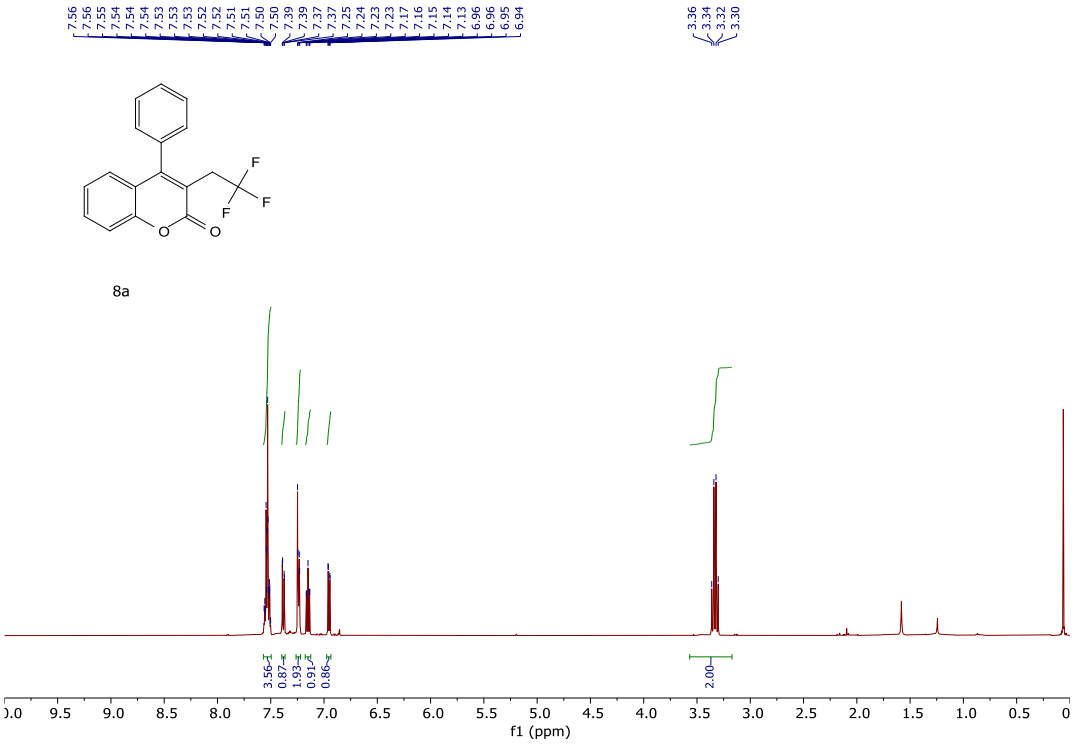
^{1}H NMR (500 MHz) spectrum of compound **5o** in $CDCl_3$



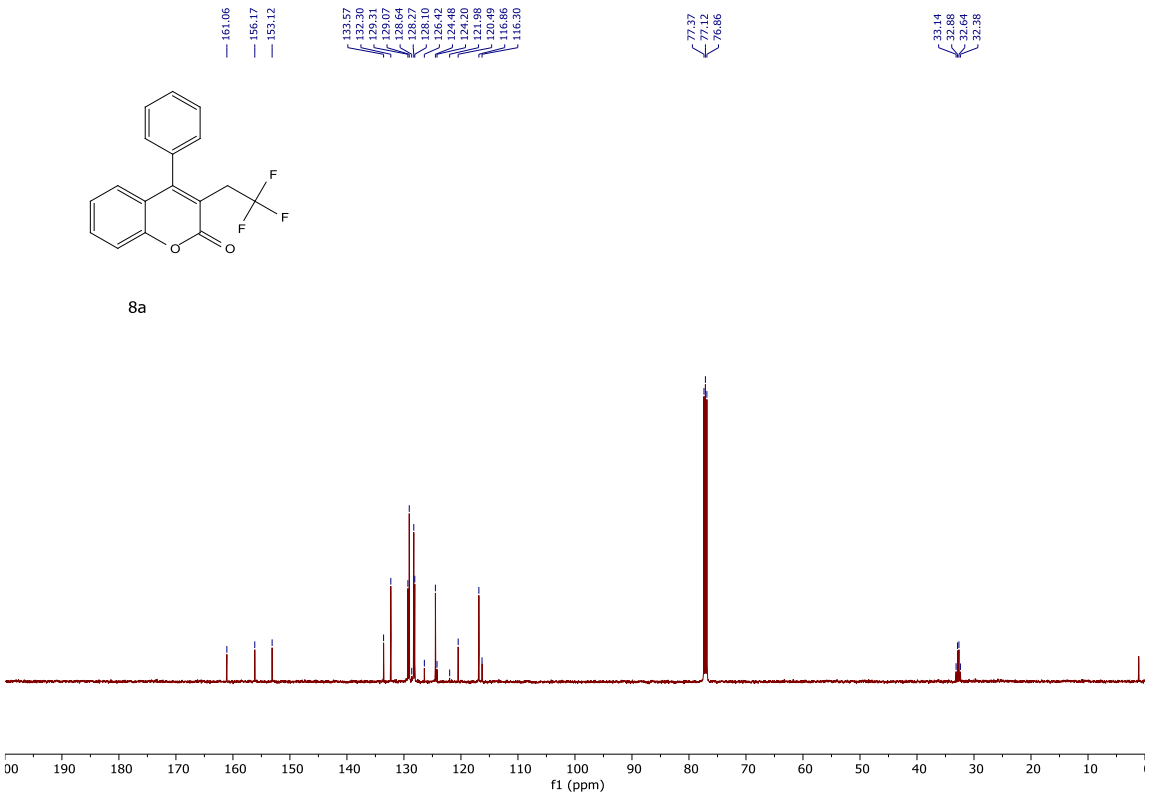
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **5o** in $CDCl_3$



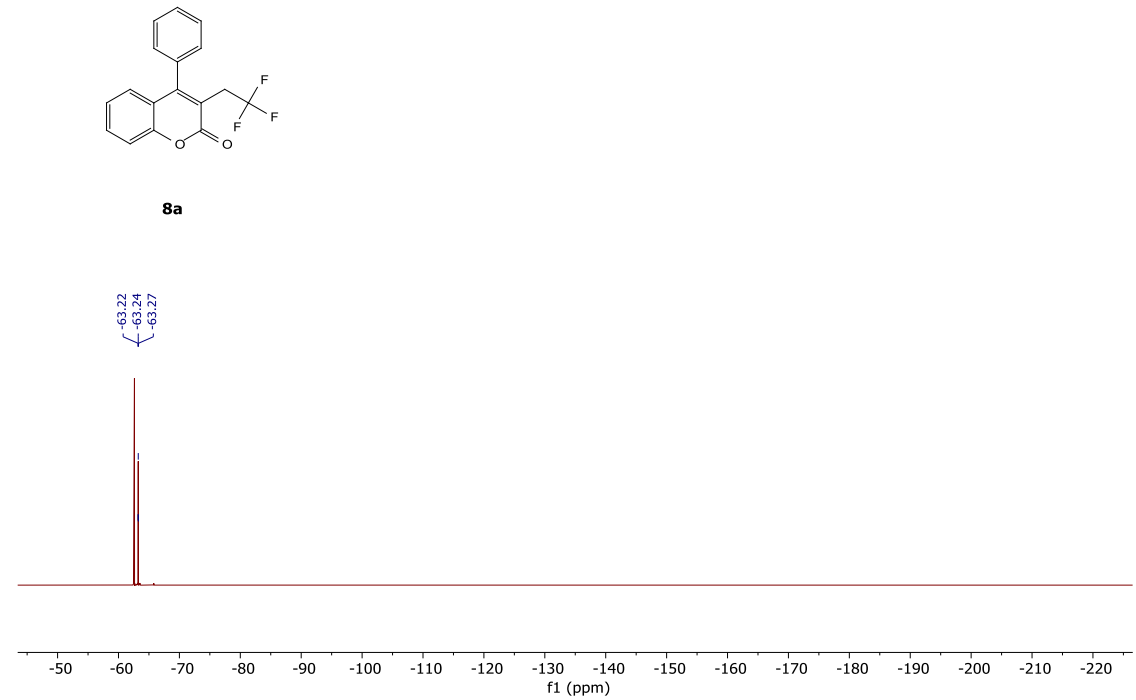
^{19} F NMR (471 MHz) spectrum of compound **5o** in $CDCl_3$ with $PhCF_3$ as reference standard



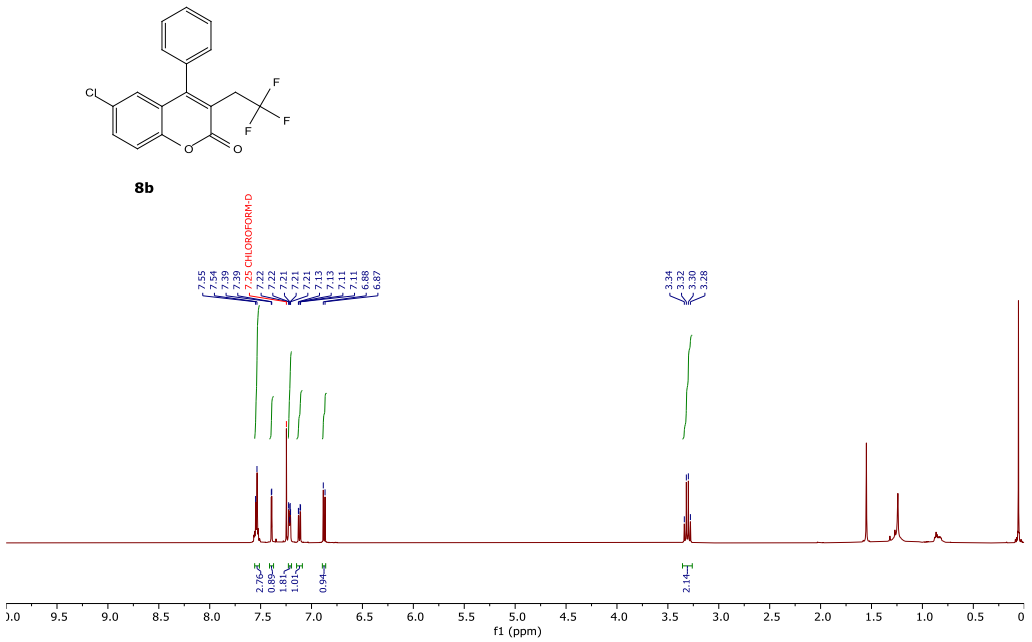
^{1}H NMR (500 MHz) spectrum of compound **8a** in $CDCl_3$



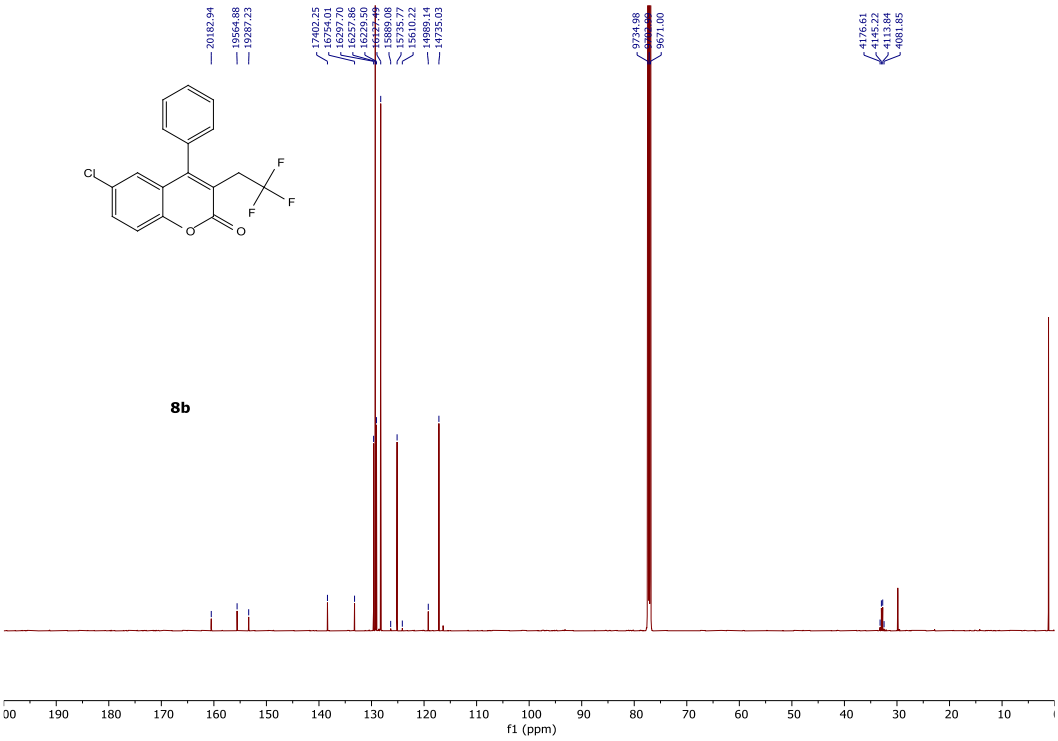
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **8a** in $CDCl_3$



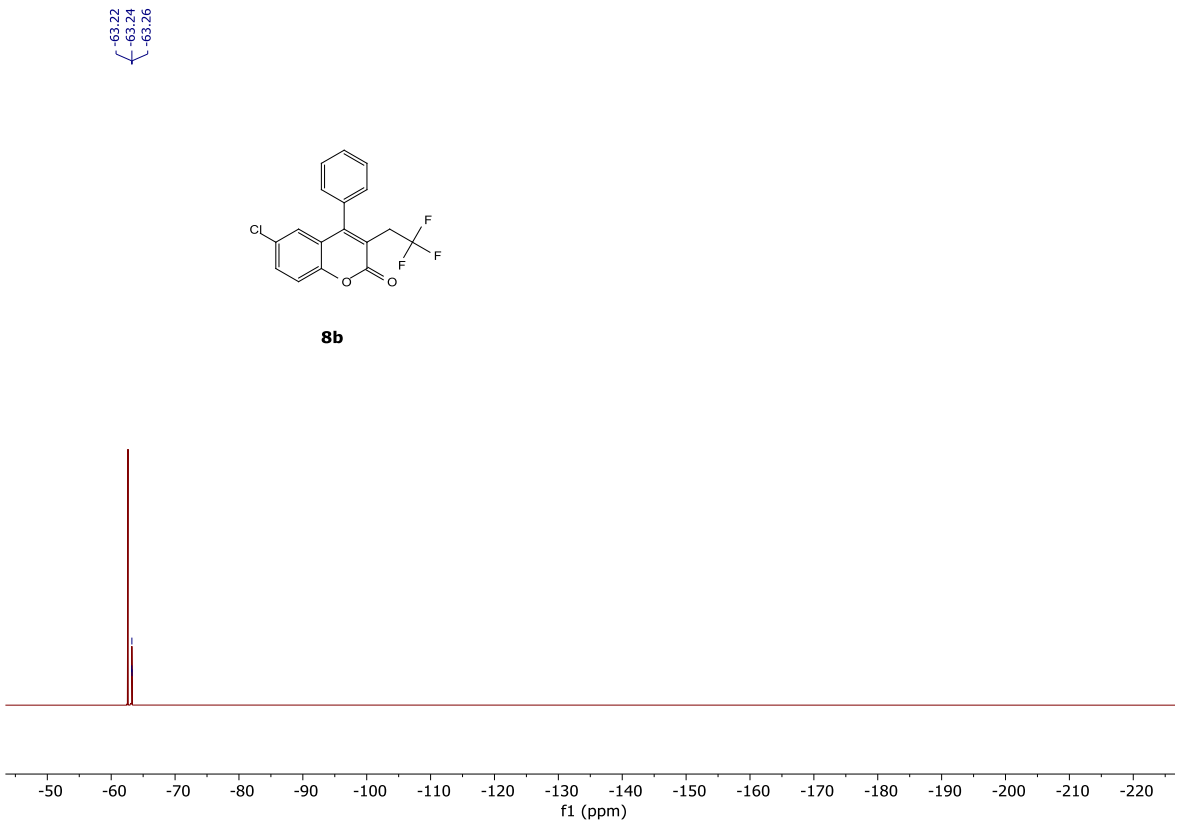
^{19} F NMR (471 MHz) spectrum of compound **8a** in $CDCl_3$ with $PhCF_3$ as reference standard



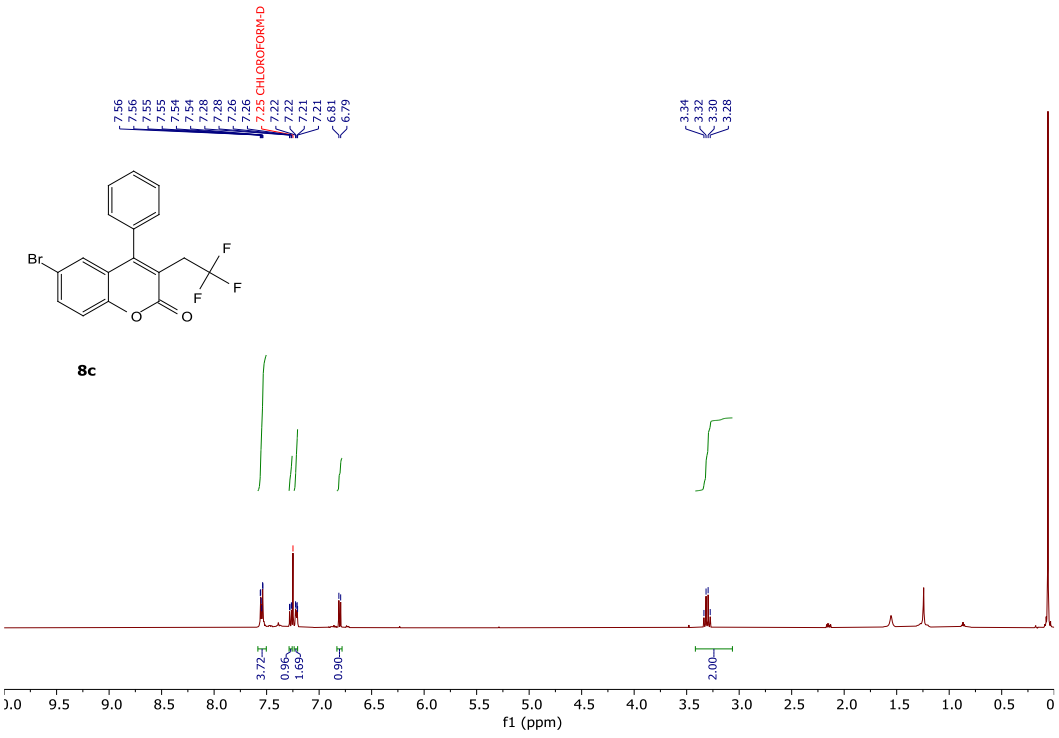
^{1}H NMR (500 MHz) spectrum of compound **8b** in $CDCl_3$



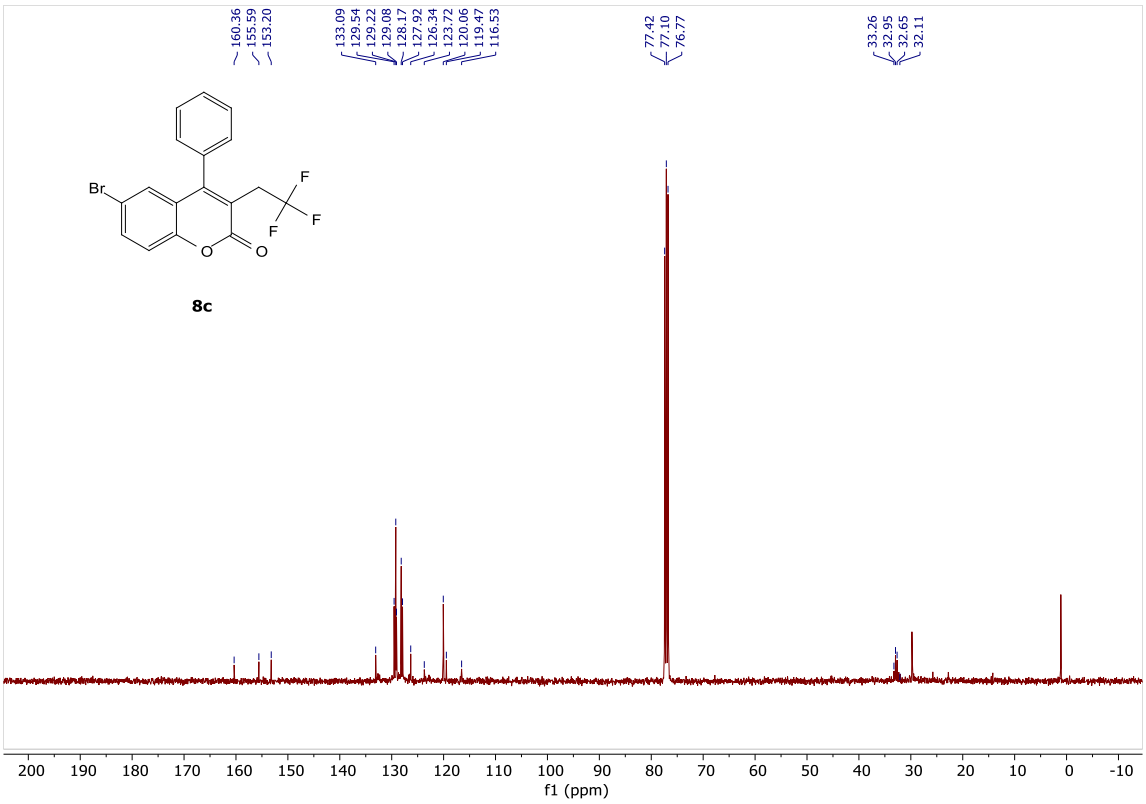
^{13} C {^{1}H} NMR (125 MHz) spectrum of compound **8b** in $CDCl_3$



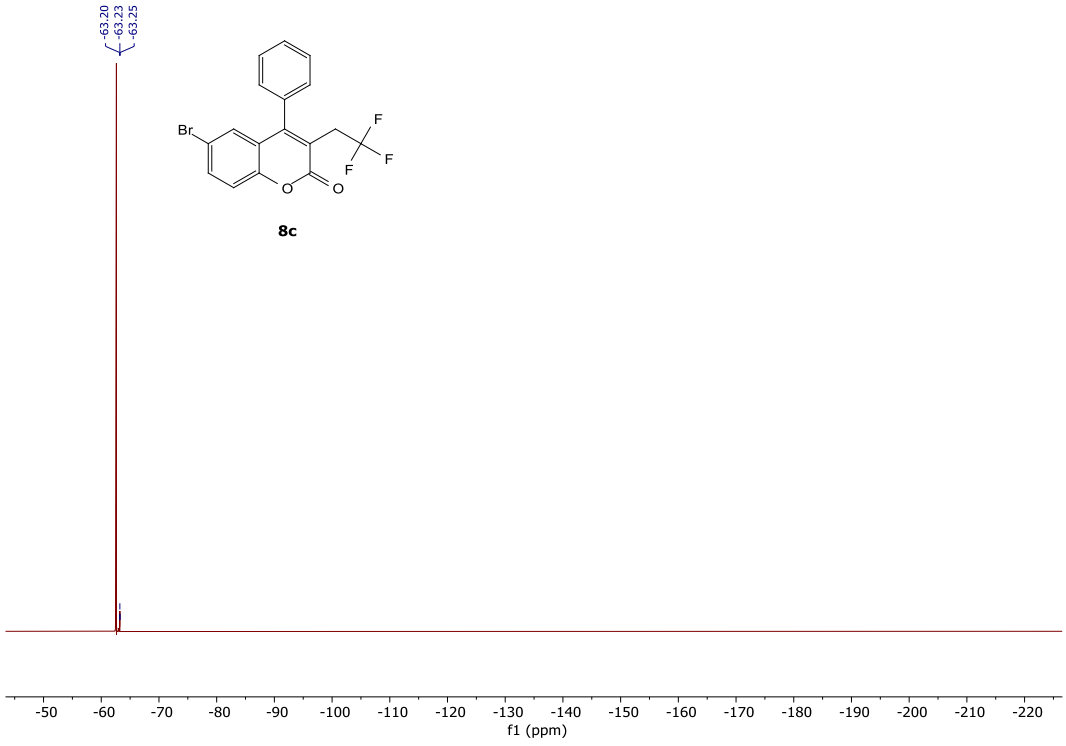
^{19} F NMR (471 MHz) spectrum of compound **8b** in $CDCl_3$ with $PhCF_3$ as reference standard



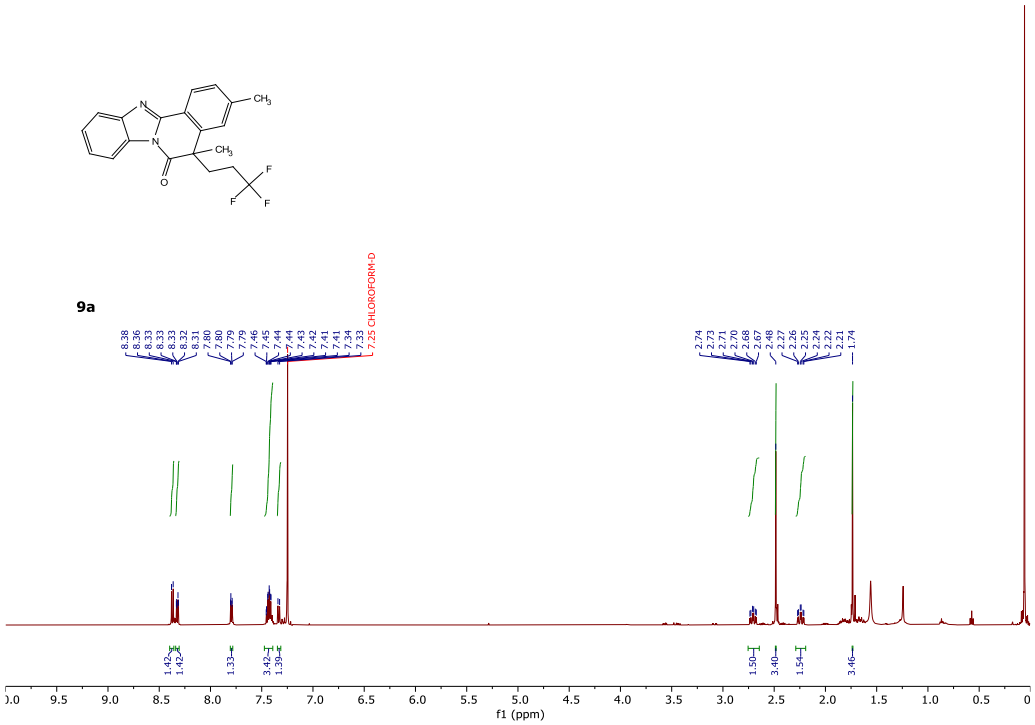
^{1}H NMR (500 MHz) spectrum of compound **8c** in $CDCl_3$



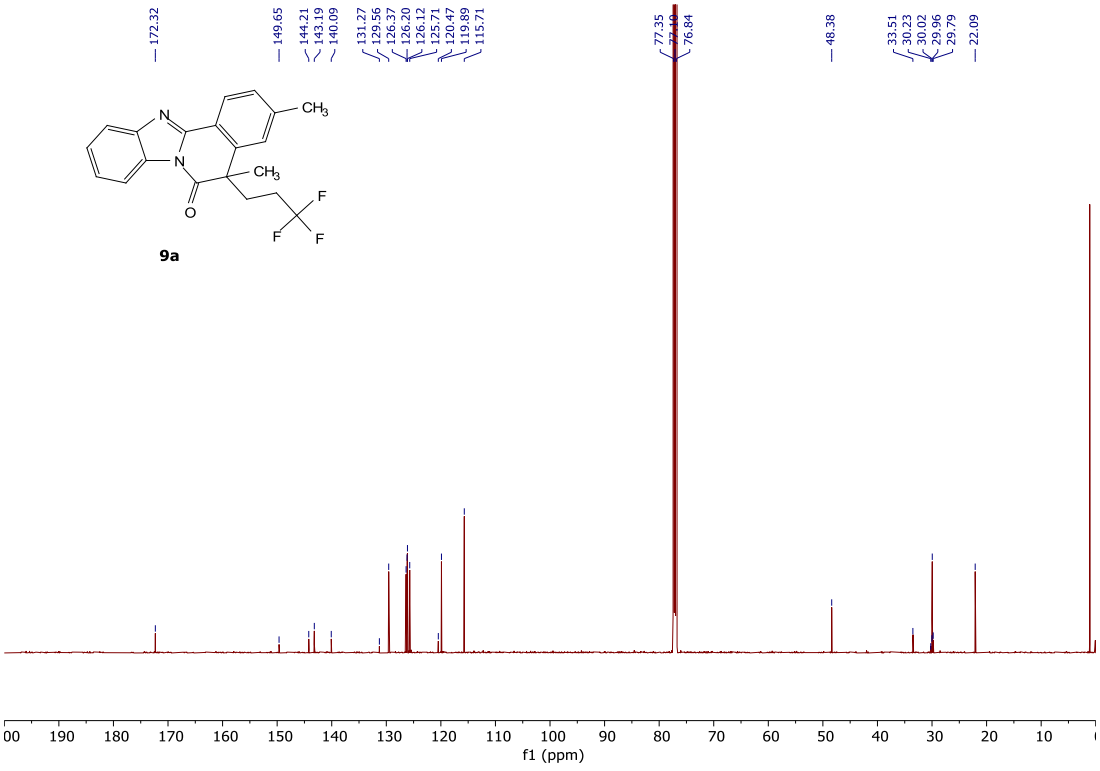
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **8c** in $CDCl_3$



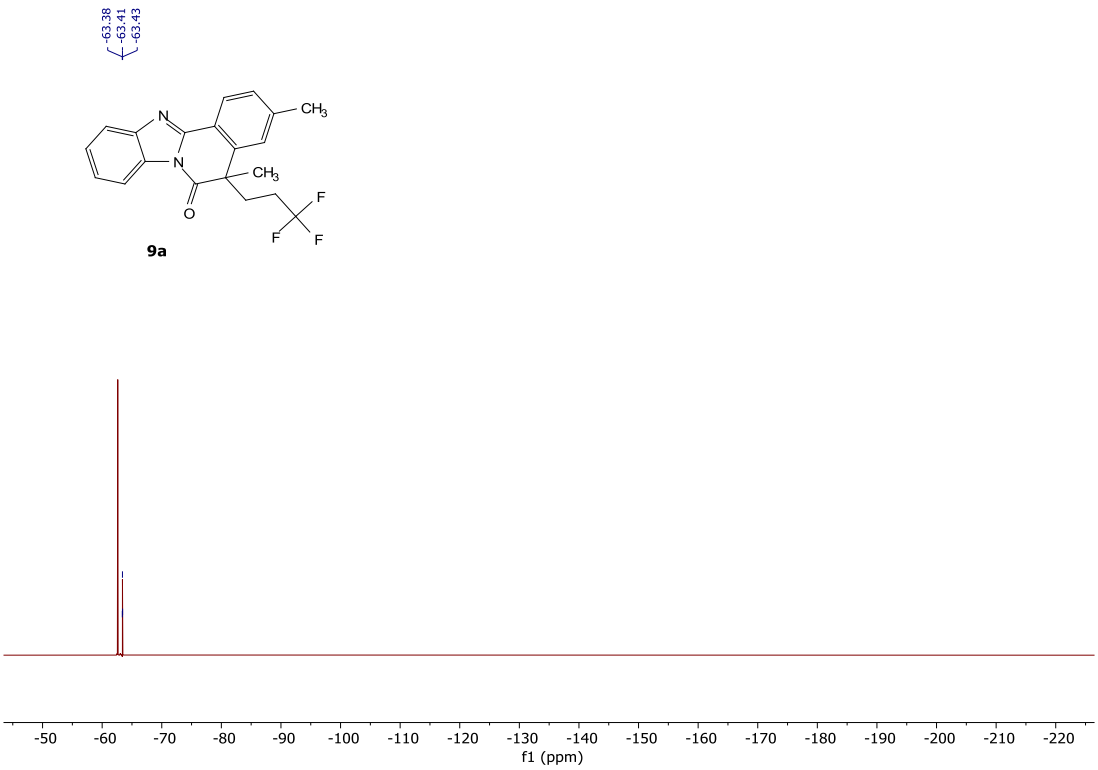
^{19}F NMR (471 MHz) spectrum of compound **8c** in $CDCl_3$ with $PhCF_3$ as reference standard



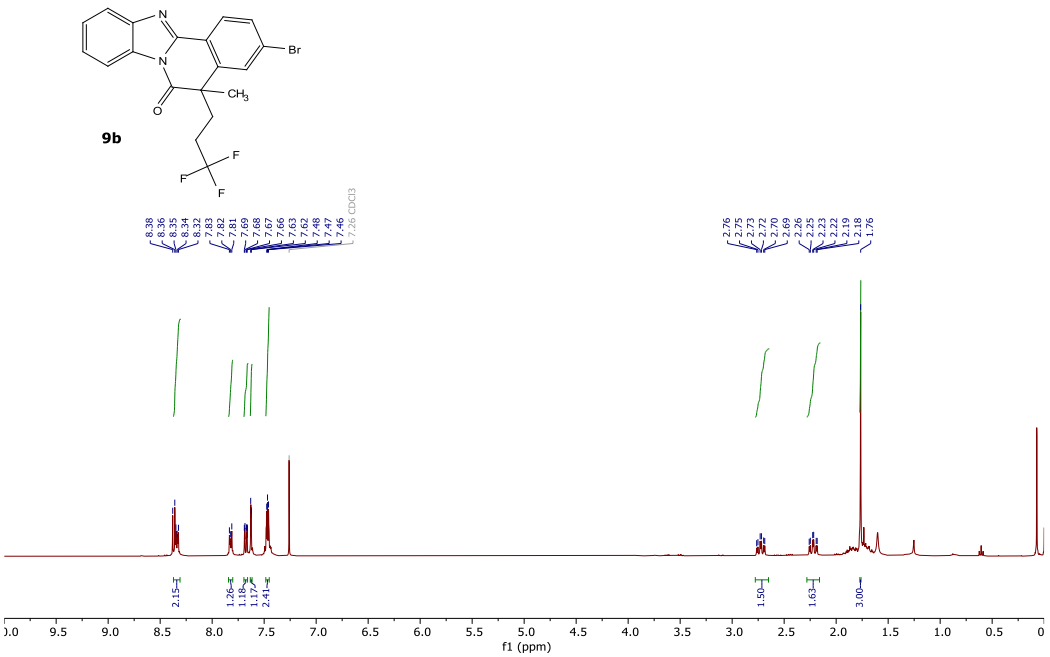
^{1}H NMR (500 MHz) spectrum of compound **9a** in $CDCl_3$



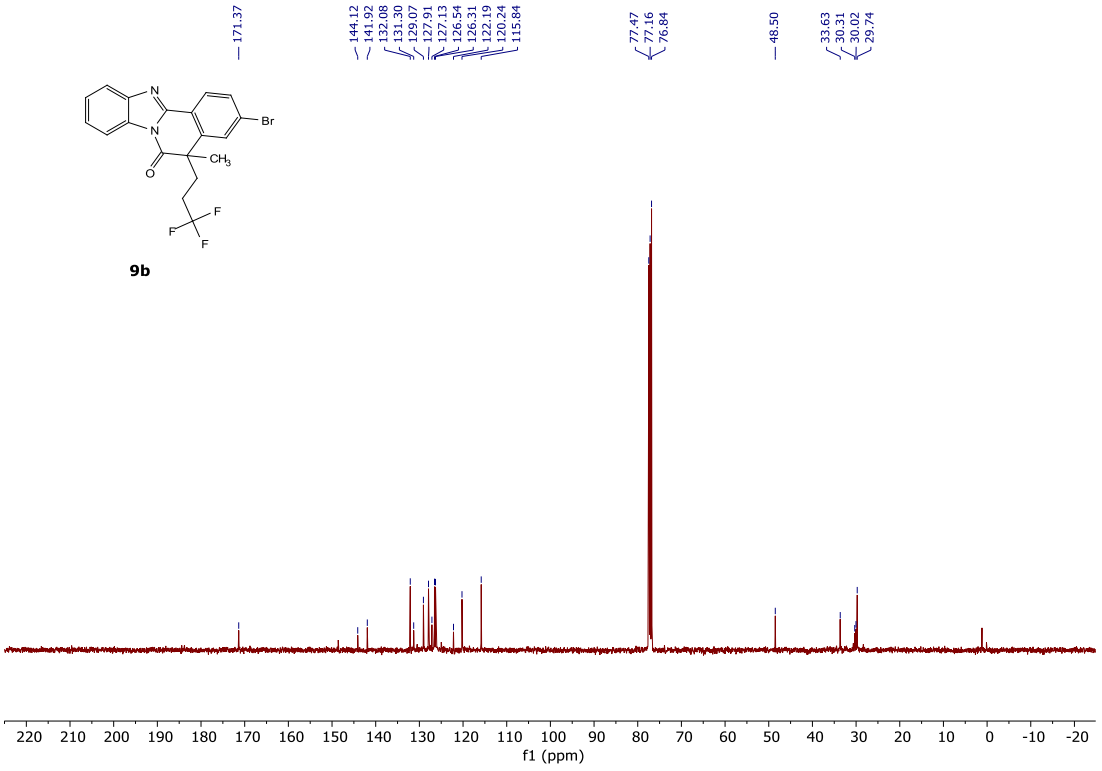
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **9a** in $CDCl_3$



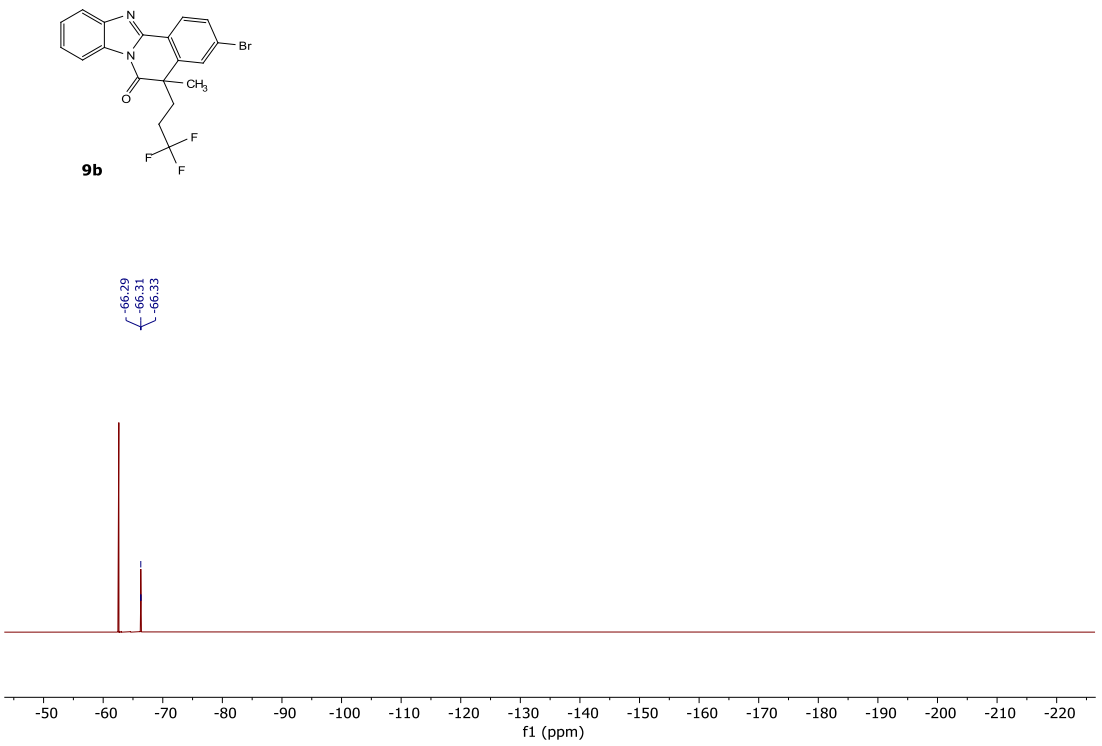
^{19} F NMR (471 MHz) spectrum of compound **9a** in $CDCl_3$ with $PhCF_3$ as reference standard



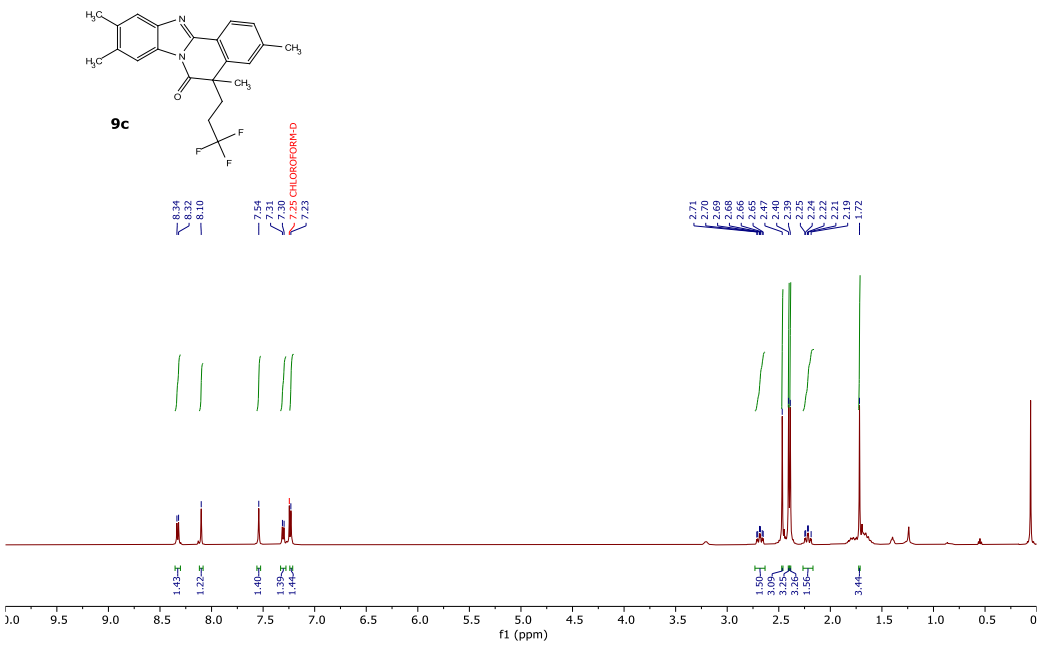
^{1}H NMR (400 MHz) spectrum of compound **9b** in $CDCl_3$



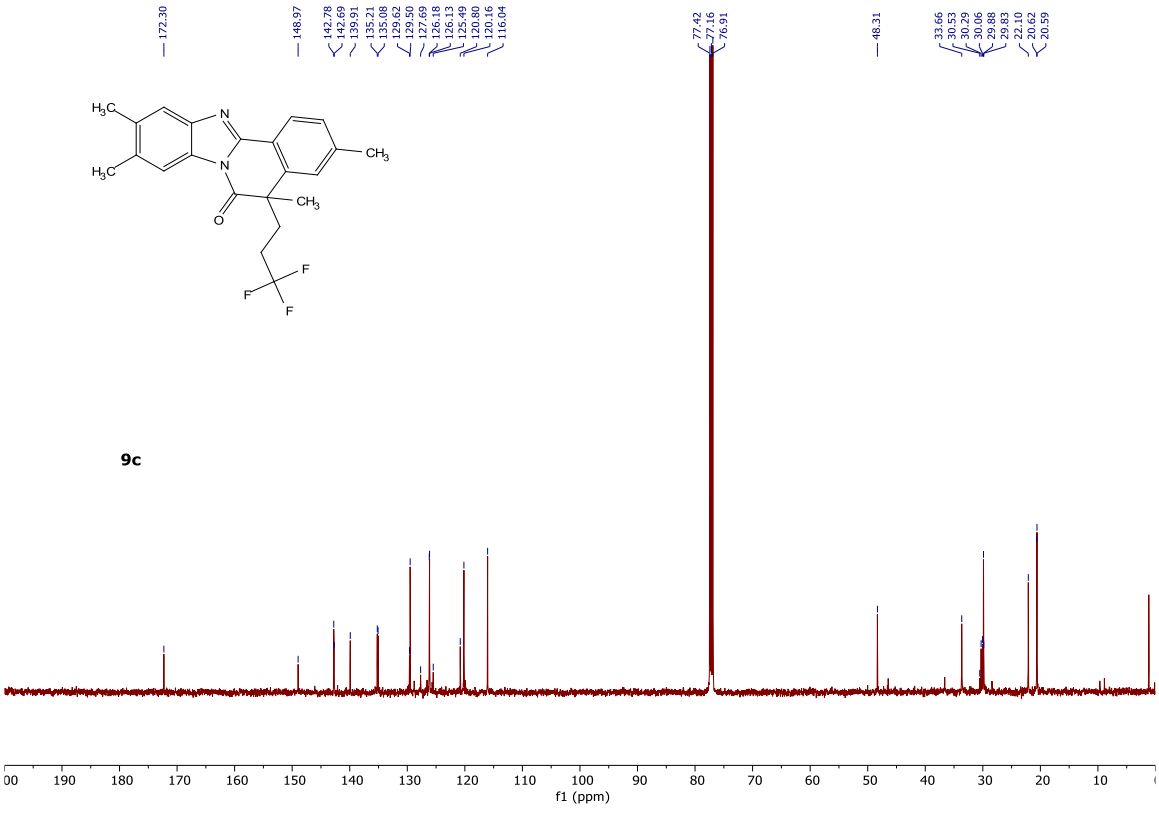
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **9b** in $CDCl_3$



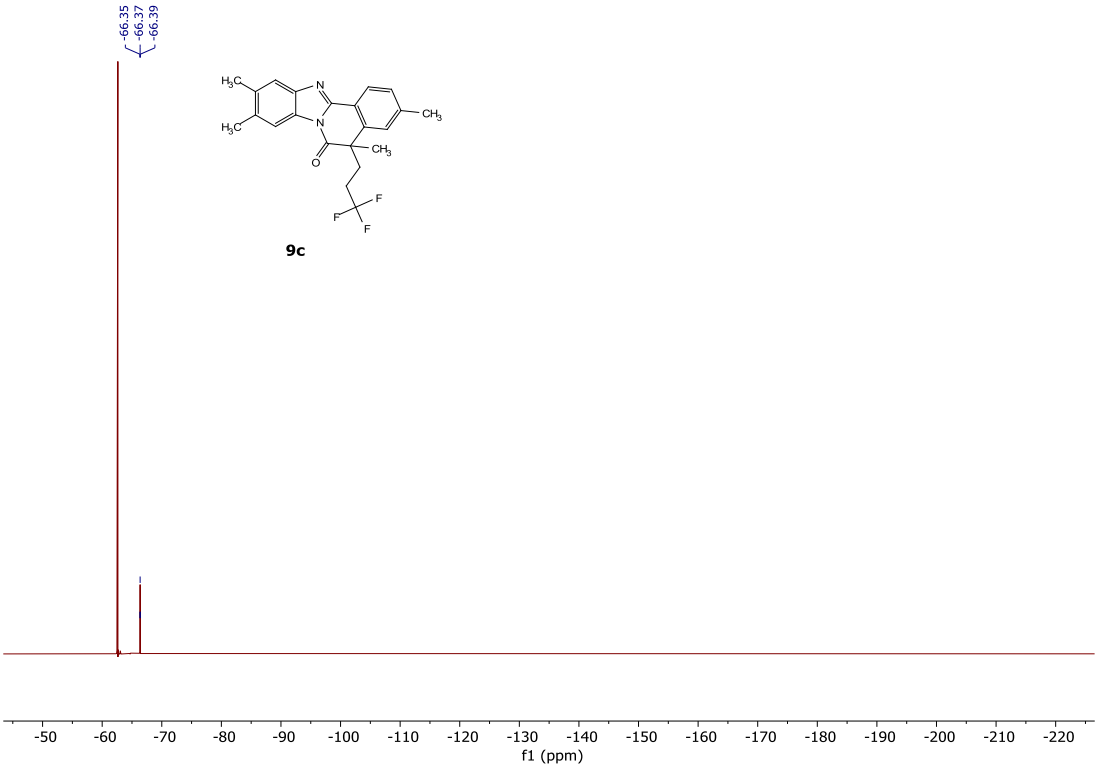
^{19}F NMR (471 MHz) spectrum of compound **9b** in $CDCl_3$ with $PhCF_3$ as reference standard



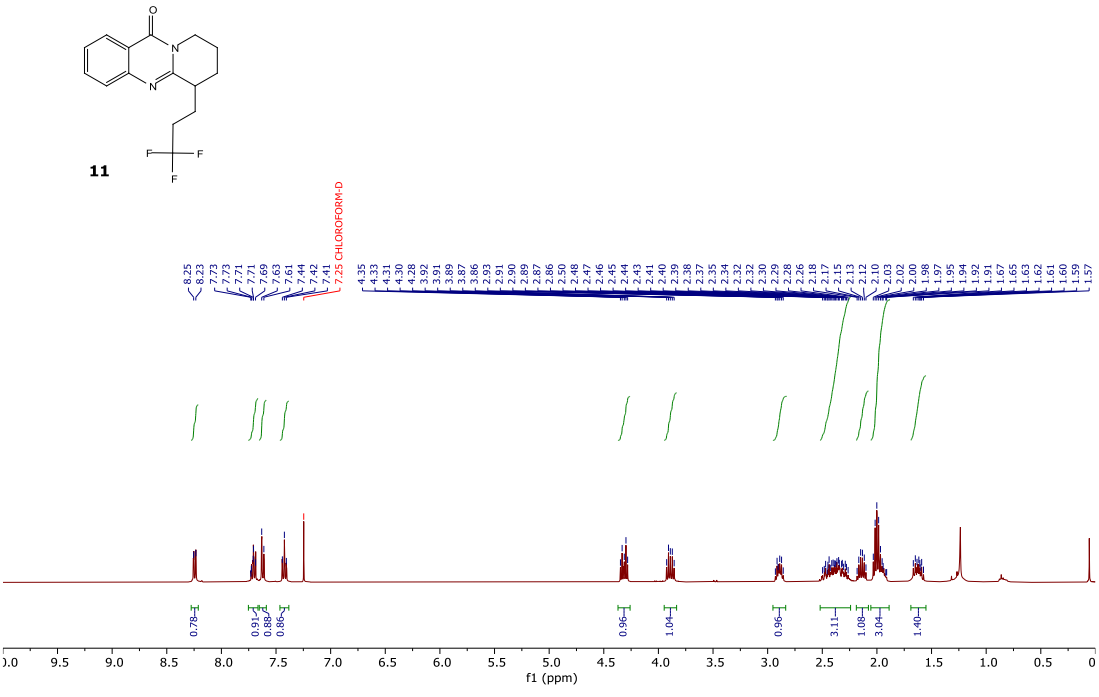
^{1}H NMR (500 MHz) spectrum of compound **9c** in $CDCl_3$



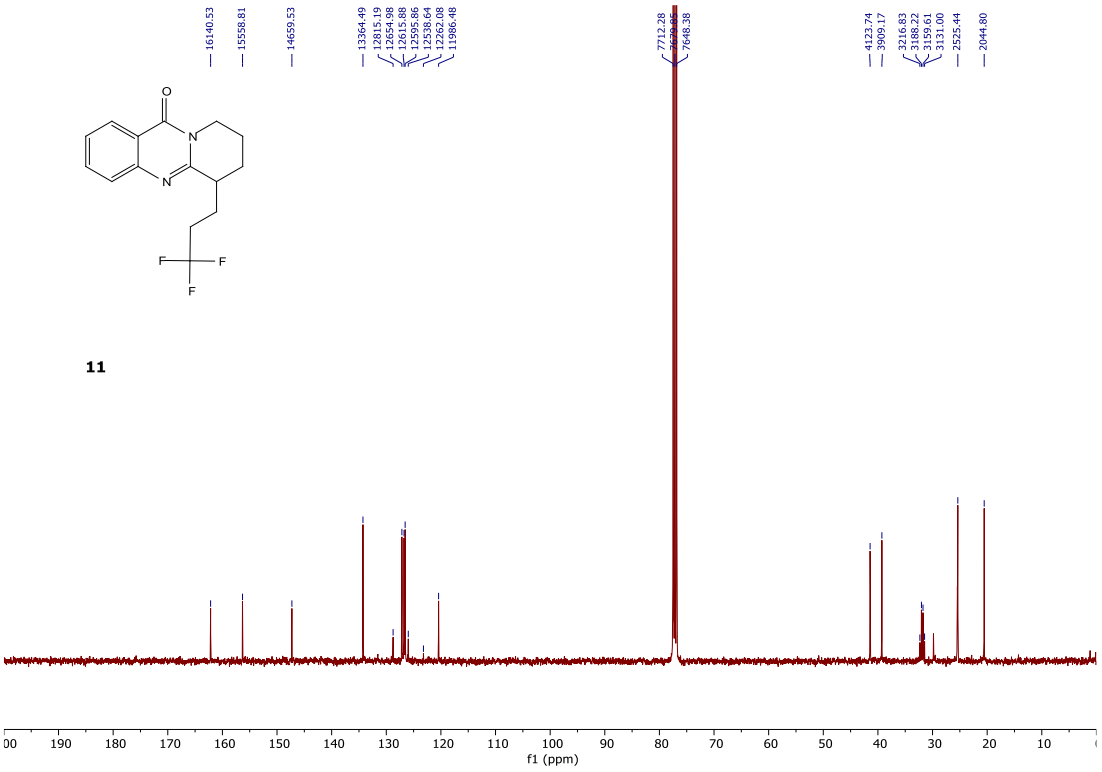
^{13}C {^{1}H} NMR (125 MHz) spectrum of compound **9c** in $CDCl_3$



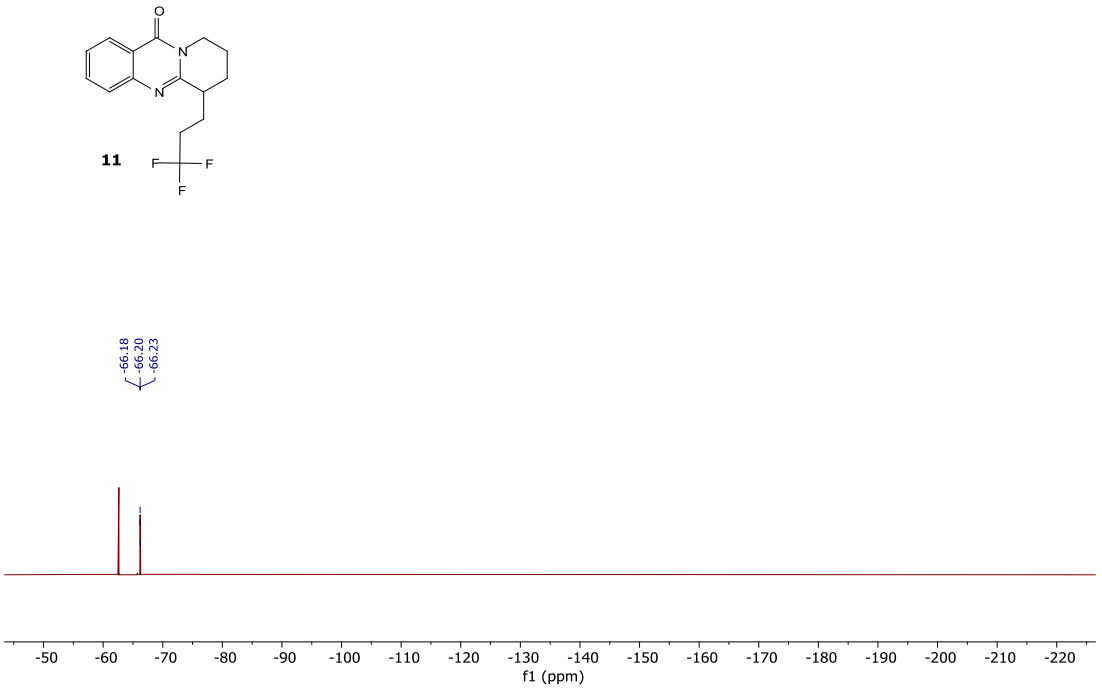
^{19} F NMR (471 MHz) spectrum of compound **9c** in $CDCl_3$ with $PhCF_3$ as reference standard



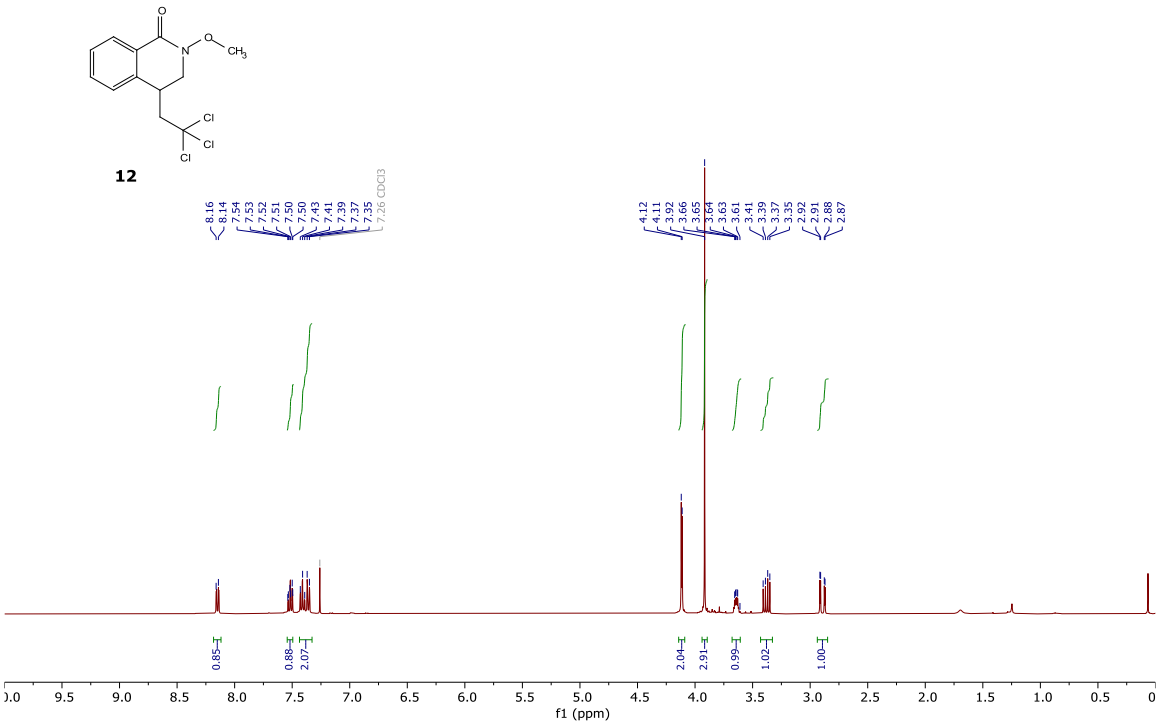
^{1}H NMR (400 MHz) spectrum of compound **11** in $CDCl_3$



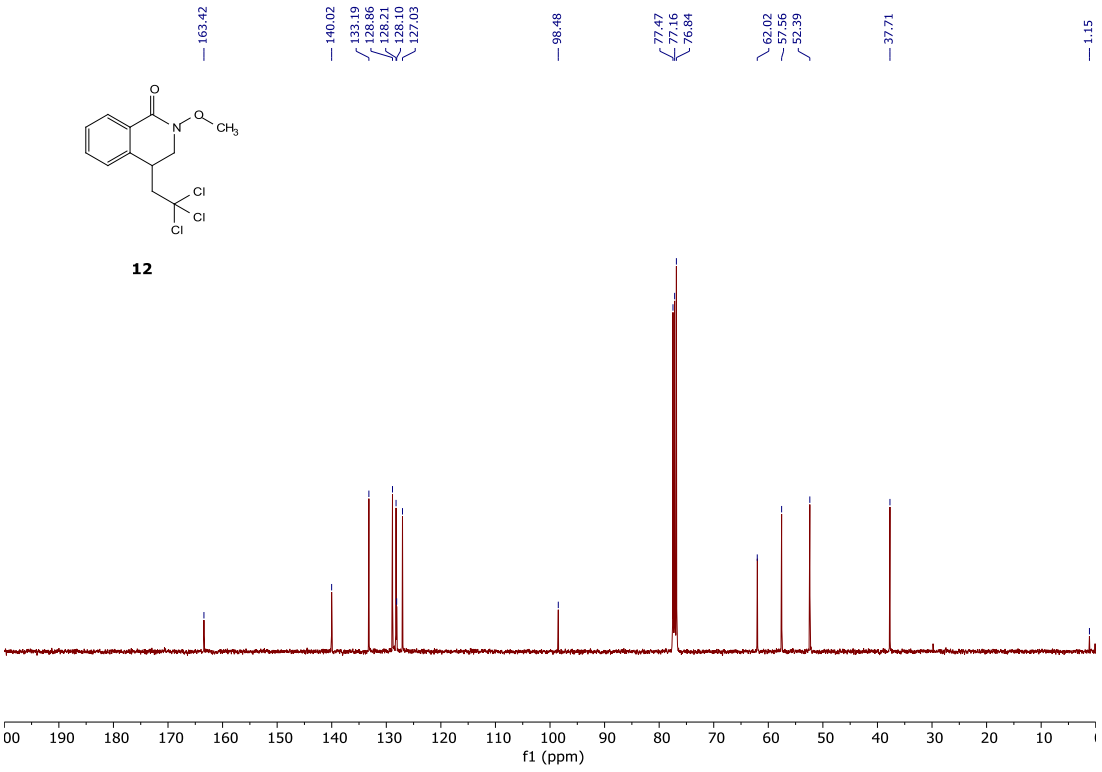
^{13}C {^{1}H} NMR (100 MHz) spectrum of compound **11** in $CDCl_3$



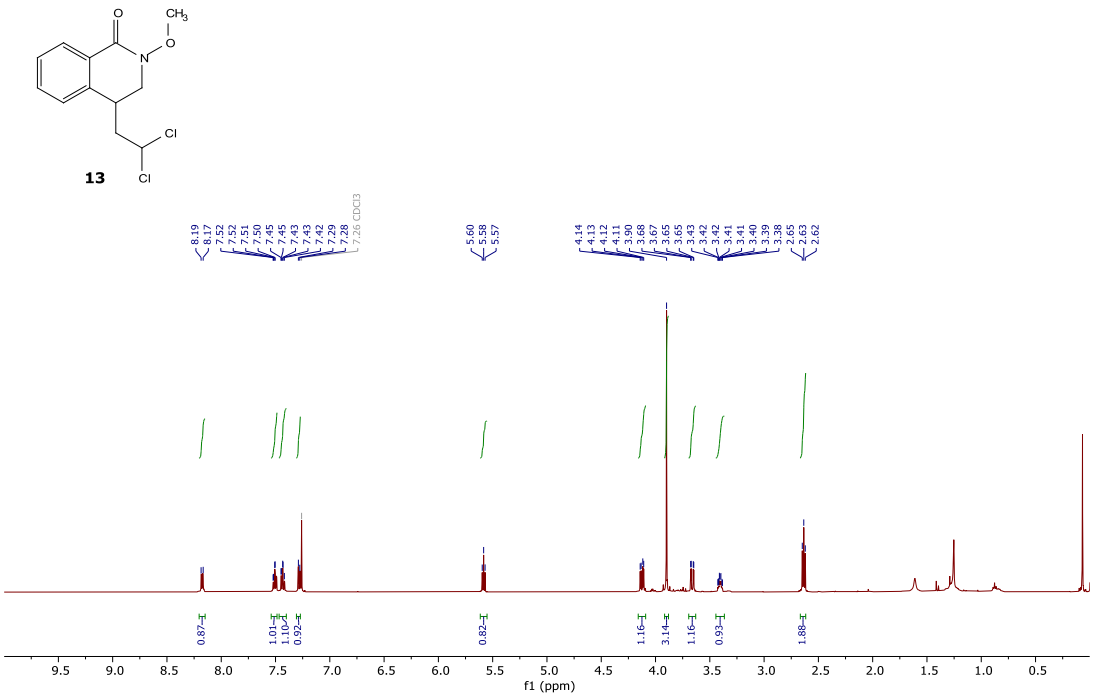
^{19}F NMR (471 MHz) spectrum of compound **11** in $CDCl_3$ with $PhCF_3$ as reference standard



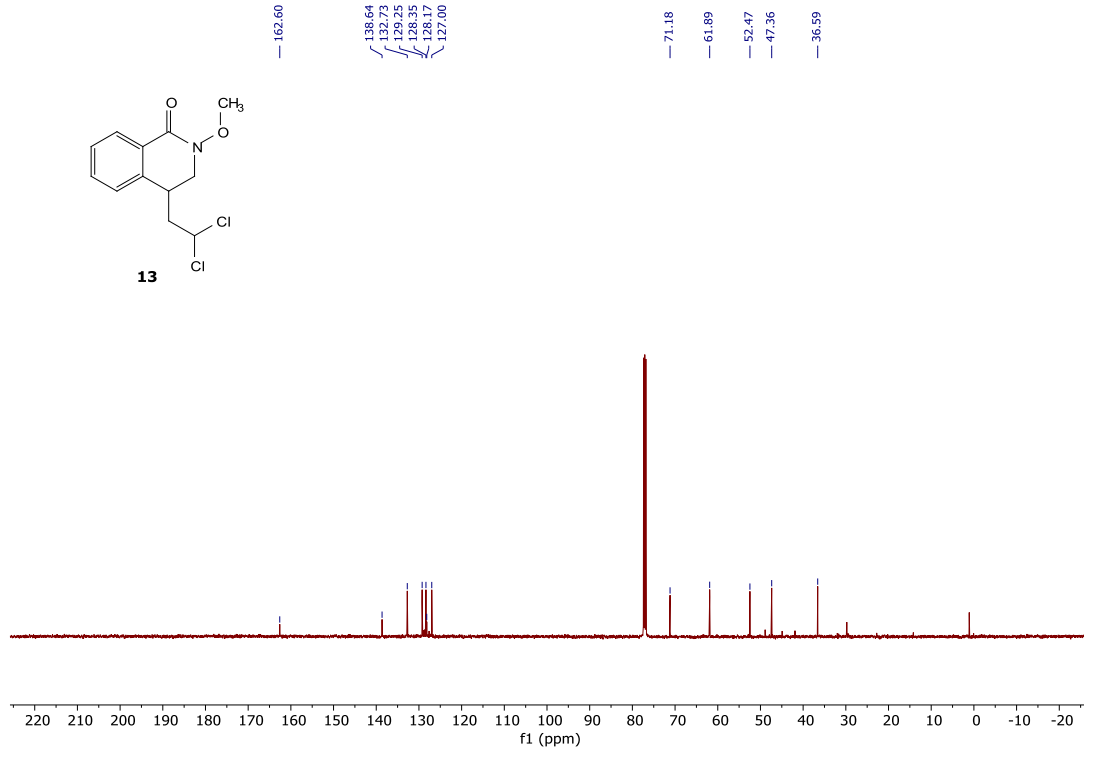
^{1}H NMR (400 MHz) spectrum of compound **12** in $CDCl_3$



^{13} C {^{1}H} NMR (100 MHz) spectrum of compound **12** in $CDCl_3$



^{1}H NMR (500 MHz) spectrum of compound **13** in $CDCl_3$



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