Electronic Supplementary Material (ESI) for Chemical Communications

Cascade fluorofunctionalisation of 2,3-unsubstituted indoles by means of electrophilic fluorination

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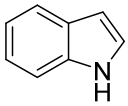
SUPPLEMENTARY INFORMATION

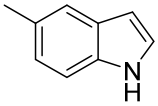
I) Experimental Section

Experimental Data for Compounds

General Procedures. All reactions were carried out under a nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. Dry tetrahydrofuran (THF), hexane, diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), and toluene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Methanol (MeOH), benzene, and *N*,*N*'-dimethylformamide (DMF) were purchased in anhydrous form and used without further purification. Water, ethyl acetate (EtOAc), diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), and hexanes were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of ammonium molybdate, anisaldehyde, potassium permanganate and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-400 or Bruker AV-600 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, pent = pentet, hex = hexet, br = broad. When necessary, the structures of novel compounds were confirmed unambiguously using 2D NMR techniques: ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC. Infrared (IR) spectra were recorded on a Perkin−Elmer Spectrum One FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on an Agilent ESI TOF (time of flight) mass spectrometer at 3500 V emitter voltage. Reactions at low temperature were carried out using Julabo FT901 Cryostats.

List of starting indoles (11) used in this study


11a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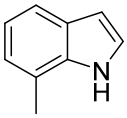
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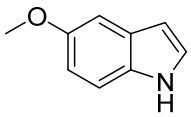
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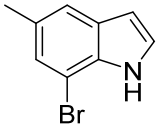
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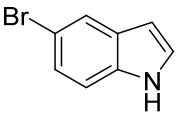
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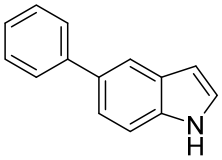
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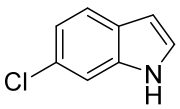
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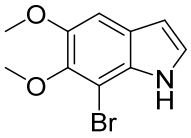
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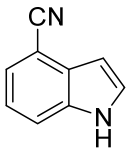
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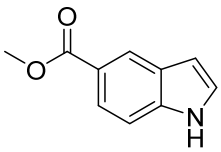
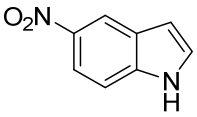
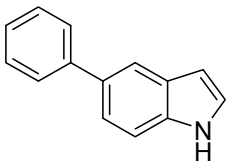
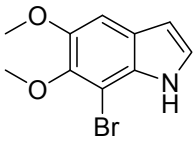

11n


11o



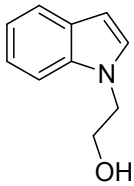
5-phenylindole **11j**. To the solution of 5-bromoindole **11i** (1.50 g, 7.65 mmol, 1 equiv) and phenylboronic acid (1.87 g, 15.3 mmol) in THF (15 mL) was added a 0.5 M aqueous solution of K_3PO_4 (30.6 mL, 15.3 mmol). The mixture was degassed with a flow of argon for 5 min, followed by an addition of the 2nd generation Buchwald XPhos precatalyst (121 mg, 0.15 mmol). The reaction mixture was stirred at 50 ^oC overnight and water was then added. The crude was extracted with CH_2Cl_2 (3 times) and the combined organic layers were dried with $MgSO_4$. After concentration in *vacuo*, purification by silica gel chromatography column 5-10% EtOAc:petroleum ether gave the desired product (1.20 g, 80%). All physical characteristics were identical to those reported in the literature.[1]



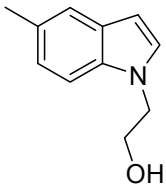
7-bromo-5,6-dimethoxyindole **11l** was synthesized according to the reported procedure.[2]

General procedure A for the preparation of compounds 2. To the solution of respective indole **11** (1 equiv), potassium hydroxide or sodium hydroxide (5 equiv) and tetrabutylammonium iodide (5 mol%) in DMF (0.5 M of **11**) was added either 2-chloroethanol (1.2 equiv). The reaction mixture was stirred overnight at 70 °C. Water was then added and the crude was extracted with diethyl ether (3 times). The combined organic layer was washed repeatedly with water (3 times) to remove DMF, dried with $MgSO_4$ and concentrated in *vacuo* to give the crude product. Purification by silica gel column chromatography

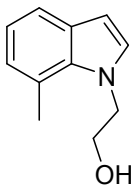
using EtOAc:hexanes afforded the desired product.



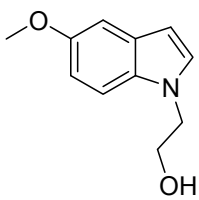
Compound **1a:** Following general procedure A, indole **11a** (7 g, 60 mmol, 1 equiv) gave **1a** (6.6 g, 68%) as a red oil. All physical characteristics were identical to those reported in the literature.[3]



Compound **1e:** Following general procedure A, indole **11e** (200 mg, 1.52 mmol, 1 equiv) gave 2-indolylethanol **1e** (200 mg, 75%) as a white amorphous solid. IR (neat) ν_{max} 3363, 2921, 2872, 1487, 1359, 1332, 1298, 1060, 866, 791, 759, 717 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.43 (s, 1H), 7.27 (s, 1H), 7.26 (s, 1H), 7.11 (d, *J* = 1.9 Hz, 1H), 7.08–7.02 (m, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 4.25 (s, 2H), 3.93 (s, 2H), 2.46 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 134.8, 129.4, 129.2, 128.7, 123.7, 121.1, 109.3, 101.4, 62.4, 49.1, 21.7 ppm; HRMS (ESI-TOF) calcd for $C_{11}H_{14}NO^+$ $[M+H]^+$, 176.1075 found 176.1066.

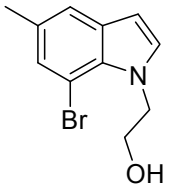


Compound **1f:** Following general procedure A, **11f** (131.2 mg, 1 mmol, 1 equiv) gave **1f** (86.1 mg, 49%) as a yellow amorphous solid. FTIR (neat) ν_{max} 3374, 2956, 1582, 1523, 1489, 1450, 1417, 1393, 1358, 1331, 1310, 1217, 1186, 1060, 864, 783, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48 (ddd, *J* = 7.5, 1.4, 0.6 Hz, 1H), 7.10 (d, *J* = 3.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 3.0 Hz, 1H), 4.51 (t, *J* = 5.4 Hz, 2H), 3.93 (t, *J* = 5.4 Hz, 2H), 2.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.8, 130.1, 129.9, 125.0, 120.8, 119.9, 119.4, 102.2, 63.7, 50.9, 20.5 ppm; HRMS (ESI-TOF) calcd for $C_{11}H_{13}NONa$ $[M + Na]^+$, 198.0889 found 198.0889.

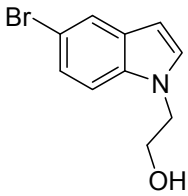


Compound **1g:** Following general procedure A, **11g** (769 mg, 5.23 mmol, 1 equiv) gave **1g** (600 mg, 60%) as a white crystalline solid. FTIR (neat) ν_{max} 3410, 2940, 2832, 1619, 1488, 1449, 1238, 1151, 1062, 1031, 799, 720; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 2.5 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.44 (d, *J* = 2.5 Hz, 1H), 4.23 (t, *J* = 5.3 Hz, 1H), 3.92 (t, *J* = 5.3 Hz, 1H), 3.85 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 131.6, 129.3, 129.0, 112.1, 110.2, 102.9, 101.3, 62.2,

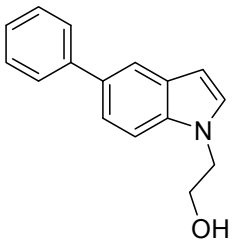
56.1, 49.1 ppm. HRMS (ESI-TOF) calcd for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.1019; found 192.1025.



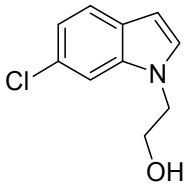
Compound **1h:** Following general procedure A, **11h** (200 mg, 0.95 mmol, 1 equiv) gave **1h** (155 mg, 64%) as a white amorphous solid. IR (film) ν_{max} 3331, 2923, 2868, 1548, 1410, 1356, 1318, 1300, 1176, 1062, 844, 713 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 0.6 Hz, 1H), 7.21 (s, 1H), 7.11 (d, *J* = 3.1 Hz, 1H), 6.40 (d, *J* = 3.1 Hz, 1H), 4.67 (s, 2H), 4.00 (s, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 132.8, 132.2, 130.7, 130.7, 128.7, 120.6, 103.4, 101.5, 63.8, 50.7, 21.1 ppm; HRMS (ESI): calcd for $C_{11}H_{12}{}^{79}BrNONa^+$ $[M+Na]^+$ 276.000; found 275.9983; calcd for $C_{11}H_{12}{}^{81}BrNONa$ $[M+Na]^+$ 277.9979; found 277.9962.



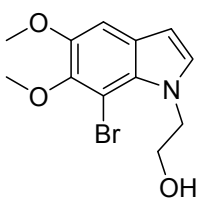
Compound **1i:** Following general procedure A, **11i** (2.94 g, 15 mmol, 1 equiv) gave **1i** (2.3 g, 63%) as a yellow amorphous solid. All physical characteristics were identical to those reported in the literature.[4]



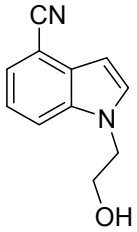
Compound **1j:** Following general procedure A, **11j** (658 mg, 3.40 mmol, 1 equiv) gave **1j** (680 mg, 84%) as a beige amorphous solid. FTIR (neat) ν_{max} 3288, 2931, 1477, 1455, 1357, 1068, 754, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.66–7.62 (m, 2H), 7.49–7.42 (m, 4H), 7.33– 7.28 (m, 1H), 7.20 (s, 1H), 6.58 (s, 1H), 4.32 (dd, *J* = 5.6, 4.9 Hz, 2H), 4.00 (dd, *J* = 5.6, 4.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.6, 135.8, 133.4, 129.4, 129.1, 128.8, 127.5, 126.5, 121.8, 119.8, 109.7, 102.2, 62.2, 49.0 ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{15}NONa$ $[M + Na]^+$, 260.1046 found 260.1048.



Compound **1k:** Following general procedure A, **11k** (250 mg, 1.65 mmol, 1 equiv) gave **1k** (280 mg, 86%) as a brown oil. IR (neat) ν_{max} 3429, 2898, 1607, 1467, 1318, 1064, 904, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.39–7.34 (m, 1H), 7.15 (d, *J* = 3.2 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.49 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.24 (t, *J* = 5.3 Hz, 2H), 3.96 (t, *J* = 5.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.7, 129.2, 127.9, 127.4, 122.0, 120.4, 109.6, 102.0, 62.0, 48.9 ppm; HRMS (ESI-TOF) calcd for $C_{10}H_{11}ClNO$ $[M+H]^+$ 196.0524 ; found 196.0531.



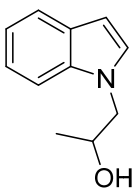
Compound **1l:** Following general procedure A, **11l** (652 mg, 2.57 mmol, 1 equiv) gave **1l** (600 mg, 78%) as a beige amorphous solid. IR (neat) ν_{max} 3456, 2920, 2850, 1737, 1553, 1453, 1249, 1040, 829, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.08 (d, *J* = 3.1 Hz, 1H), 7.05 (s, 1H), 6.38 (d, *J* = 3.1 Hz, 1H), 4.67 (t, *J* = 5.4 Hz, 2H), 3.99 (t, *J* = 5.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.7, 143.9, 131.9, 127.5, 127.1, 102.8, 101.4, 100.4, 63.5, 61.0, 56.6, 50.5 ppm; HRMS (ESI-TOF) calcd for $C_{12}H_{14}{}^{79}BrNNaO_3$ $[M + Na]^+$ 322.0049; found 322.0055; calcd for $C_{12}H_{14}{}^{81}BrNNaO_3$ $[M + Na]^+$ 324.0030; found 324.0034.



Compound **1m:** Following general procedure A, **11m** (500 mg, 3.52 mmol, 1 equiv) gave **1m** (370 mg, 56%) as a white amorphous solid. IR (film) ν_{max} 3455, 2879, 2224, 1604, 1505, 1436, 1343, 1295, 1057, 749 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.3 Hz, 1H), 7.47 (d, *J* = 6.5 Hz, 1H), 7.36 (d, *J* = 3.2 Hz, 1H), 7.25–7.22 (m, 1H), 6.74 (d, *J* = 4.0 Hz, 1H), 4.33 (s, 2H), 3.99 (s, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.3, 131.3, 130.3, 125.4, 121.6, 119.0, 114.6, 103.7, 101.1, 62.3, 49.2 ppm; HRMS (ESI-TOF) calcd for $C_{11}H_{10}N_2ONa^+$ $[M+Na]^+$ 209.0691; found 209.0679.

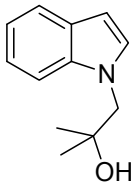
General procedure B for the preparation of compounds 1b, 1c, 1n, 1o

To a 0.2 M solution of respective indole **11** (1 equiv) in dry DMF was added portionwise NaH (1.2 equiv) at 0 °C under a flow of argon. Propylene oxide (2 equiv) or isobutylene oxide (2 equiv) was added, and the resulting mixture was allowed to warm up to room temperature under stirring overnight. Cold water was then added and the crude was extracted with diethyl ether. The combined organic layers were washed with water, dried with $MgSO_4$ and concentrated in *vacuo*. Purification by silica gel column chromatography using EtOAc:hexanes afforded the desired product.

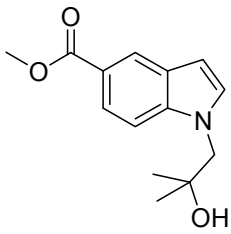


Compound **1b:** Following general procedure B with propylene oxide (1.07 mL, 15. 3 mmol), indole **11a** (1.0 g, 8.54 mmol, 1 equiv) gave **1b** (569 mg, 76%) as a yellow oil. IR (film) ν_{max} 3379, 2973, 1512, 1463, 1314, 1255, 1199, 1134, 1083, 1012, 937 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.26 (s, 1H), 7.17 (d, *J*

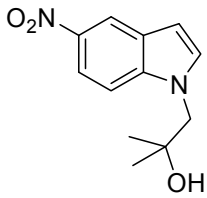
= 3.1 Hz, 2H), 6.55 (dd, *J* = 3.0, 0.5 Hz, 1H), 4.17 (t, *J* = 8.5 Hz, 3H), 4.05 (s, 1H), 1.27 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 136.6, 129.0, 128.9, 122.0, 121.4, 119.9, 109.8, 101.9, 67.6, 54.1, 20.8 ppm; HRMS (ESI): calcd for $C_{11}H_{14}NO$ $[M + H]^+$ 176.1070, found 176.1076.



Compound **1c:** Following general procedure B with isobutylene oxide (1.06 mL, 11.94 mmol), indole **11a** (1 g, 8.53 mmol) provided alcohol **1c** (1.29 g, 80%) as a light yellow oil. IR (film) ν_{max} 3436, 2934, 1735, 1612, 1552, 1478, 1466, 1368, 1335, 1304, 1277, 1254, 1210, 1189, 1156, 1143, 1103, 1083, 1073, 1036, 1020, 998, 974, 965 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.22 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.17 (d, *J* = 1.9 Hz, 1H), 7.14–7.09 (m, 1H), 6.58–6.52 (m, 1H), 4.10 (s, 2H), 1.28 (s, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 137.3, 129.7, 128.6, 122.0, 121.2, 119.7, 110.4, 102.0, 72.5, 57.2, 27.7 (2C) ppm; HRMS (ESI-TOF) calcd for $C_{12}H_{16}NO$ $[M+H]^+$ 190.1226; found 190.1235

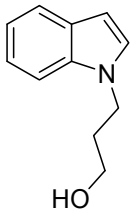


Compound **1n:** Following general procedure B with isobutylene oxide (0.51 mL, 5.70 mmol), indole **11n** (500 mg, 2.85 mmol, 1 equiv) gave **1n** (290 mg, 41%) as a white amorphous solid. IR (neat) ν_{max} 3502, 1693, 1610, 1432, 1280, 1202, 1131, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (dd, *J* = 1.1, 0.5 Hz, 1H), 7.90 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 6.63 (dd, *J* = 3.2, 0.5 Hz, 1H), 4.12 (s, 2H), 3.93 (s, 3H), 1.27 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.3, 139.7, 130.9, 128.0, 124.1, 123.2, 121.7, 109.9, 103.4, 72.3, 57.2, 52.0, 27.7 (2C) ppm; HRMS (ESI-TOF) calcd for $C_{14}H_{18}NO_3$ 248.1281 $[M+H^+$; found 248.1292.



Compound **1o:** Following general procedure B with isobutylene oxide (1.07 mL, 11.84 mmol), indole **11o** (960 mg, 5.92 mmol, 1 equiv) gave **1o** (1.03 g, 74%) as a yellow amorphous solid. IR (neat) ν_{max} 3475, 2975, 2934, 1609, 1577, 1511, 1479, 1329, 1070, 902, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (dd, *J* = 2.3, 0.5 Hz, 1H), 8.10 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 3.3 Hz, 1H), 6.71 (dd, *J* = 3.3, 0.5 Hz, 1H), 4.14 (s, 2H), 1.29 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 140.1, 132.8, 127.7, 118.2,

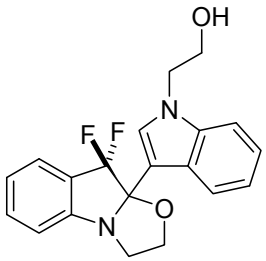
117.4, 110.3, 104.3, 72.2, 57.3, 27.7 (2C) ppm; HRMS (ESI-TOF) calcd for $C_{12}H_{15}N_2O_3$ $[M+H]^+$ 235.1077; found 235.1082.



3-indol-1-ylpropan-1-ol **1d** was synthesized by following a reported procedure starting from indole **11a**.[3] All physical characteristics were identical to those reported in the literature.

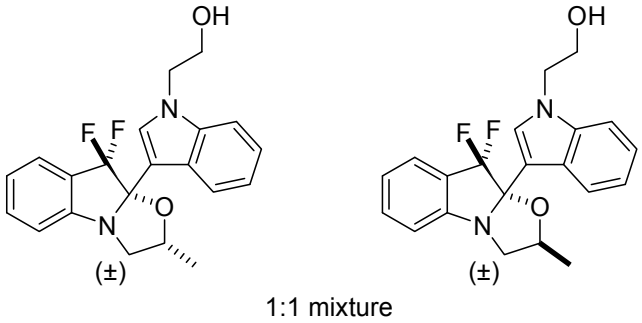
Cascade fluorofunctionalization (CFF) of indoles – General procedure C

A 0.05 M solution of respective indole **1** (1 equiv) in a mixture of HPLC grade solvents [MeCN:MeOH (1:1) or MeCN:EtOH (1:1) or MeCN:toluene (1:1)] was stirred at a specific temperature under argon for 10 min and NFSI (3 equiv) was then added. The reaction mixture was maintained at the same temperature for a specific period of time as determined by TLC monitoring. After the completion, the reaction was quenched with TEA (10 equiv) and the crude was concentrated to dryness in *vacuo*. Purification by silica gel column chromatography using EtOAc:hexanes or MeCN:CH_2Cl_2 afforded the desired product **2**.

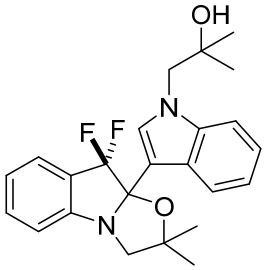


Compound **2a**: Following general procedure C with indole **1a** (102 mg; 0.64 mmol), NFSI (600 mg) in a mixture of MeCN:MeOH (1:1, 12.8 mL) at -20 ^oC for 20 h, **2a** was purified by column chromatography using 2% MeCN:CH_2Cl_2 and was obtained as a white foam (61 mg, 54%). IR (neat) ν_{max} 3412, 2926, 2856, 1613, 1552, 1470, 1302, 1077, 984, 745 cm^{-1}; ^1H NMR (400 MHz, Acetone-d_6) δ = 7.79 (d, J = 8.0 Hz, 1H), 7.57–7.49 (m, 2H), 7.53 (s, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.19–7.09 (m, 3H), 7.04 (td, J = 7.5, 0.9 Hz, 1H), 4.34–4.26 (m, 2H), 4.02 (s, 1H), 3.93 (t, J = 5.3 Hz, 2H), 3.91–3.77 (m, 3H), 3.51 (dt, J = 11.1, 7.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6) δ = 154.0 (dd, J = 9, 6 Hz), 138.4, 134.0 (d, J = 1 Hz), 130.1, 127.9, 127.87, 125.1, 124.87 (dd, J = 28, 25 Hz), 124.84, 123.7 (dd, J = 256, 239 Hz), 123.0, 122.2, 121.9, 110.9, 109.4, 104.0 (dd, J = 35, 18 Hz), 66.5, 61.8, 51.3 (d, J = 3 Hz), 49.6 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -90.18 (d, J = 256.0 Hz, 1F), 113.52 (d, J = 256.0 Hz, 1F) ppm;

HRMS (ESI-TOF) calcd for $C_{20}H_{19}F_2N_2O_2$ [M+H] 357.1409; found 357.1426.

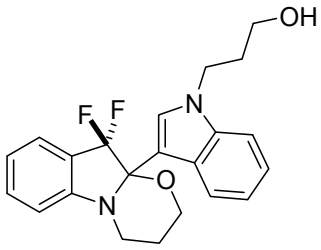


Isomeric mixture **2b**: Following general procedure C with indole **1b** (126 mg, 0.72 mmol, 1 equiv), NFSI (680 mg) in a mixture of MeCN:MeOH (1:1, 14.4 mL) at -20 °C for 20 h, isomeric mixture **2b** (1:1), which could not be separable by normal chromatographic methods, was obtained as a white foam (80 mg, 58%). IR (neat) ν_{max} 3412, 2971, 1614, 1469, 1380, 1305, 1075, 993, 745 cm^{-1}; ^1H NMR (400 MHz, Acetone-d_6) δ = 7.80 (m, 1H), 7.75 (m, 1H), 7.56-7.43 (m, 8H), 7.20-6.99 (m, 8H), 4.30-4.10 (m, 7H), 4.10-3.99 (m, 4H), 3.70 (dd, J = 11.3, 7.5 Hz, 1H), 3.36 (ddd, J = 11.3, 5.1, 1.3 Hz, 1H), 3.07-2.99 (m, 1H), 1.22-1.13 (m, 9H), 1.11 (dd, J = 6.2, 0.9 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6): very complex due to C-F couplings; ^{19}F NMR (376 MHz, CD_3CN) δ = -88.95 (dd, J = 255.7, 7.5 Hz, 1F), -90.68 (dd, J = 255.7, 3.8 Hz, 1F), -112.46 (dd, J = 255.7, 22.6 Hz, 1F), -112.65 (d, J =255.7 Hz, 1F) ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{23}F_2N_2O_2$ $[M + H]^+$ 385.1722; found 385.1730; calcd for $C_{22}H_{22}F_2N_2O_2Na$ $[M + H]^+$ 407.1542; found 407.1560.

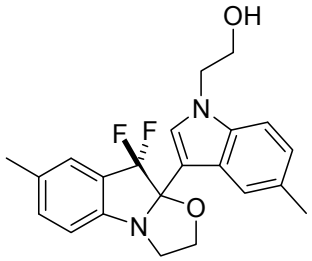


Compound **2c**: Following general procedure C with indole **1c** (100 mg, 0.53 mmol), NFSI (500 mg, 1.59 mmol) in a mixture MeCN:MeOH (1:1, 10 mL) at −20 °C for 72 h. Flash column chromatography using hexanes:EtOAc (4:1) afforded **2c** (69 mg, 63%) as an orange solid. IR (film) ν_{max} 3436, 2934, 1735, 1612, 1552, 1478, 1466, 1368, 1335, 1304, 1277, 1254, 1210, 1189, 1156, 1143, 1103, 1083, 1073, 1036, 1020, 998, 974, 965, 910, 869, 828, 794, 741, 692 cm^{-1}; ^1H NMR (600 MHz, CD_3CN): δ = 7.71 (d, J = 7.9 Hz, 1H), 7.54–7.50 (m, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.45 (s, 1H), 7.18 (d, J = 1.3 Hz, 1H), 7.11–7.01 (m, 3H), 4.11 (s, 2H), 3.79 (dd, J = 12.4, 2.4 Hz, 1H), 3.34 (d, J = 12.4 Hz, 1H), 1.17 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H), 0.96 (s, 3H) ppm; ^{13}C NMR (150 MHz, CD_3CN): δ = 154.7 (dd, J = 9.0, 6.0 Hz), 139.1, 134.4 (d, J = 3 Hz), 130.9, 127.4, 125.2, 124.0 (dd, J = 256.5, 238.5 Hz), 123.8 (dd, J =

27.0, 24.0 Hz), 123.0, 122.4, 121.7, 120.1, 114.3, 111.8, 110.7, 104.1 (dd, *J* = 36.0, 18.0 Hz), 83.9, 72.1, 62.3 (d, *J* = 3.0 Hz), 57.2, 29.5, 28.6, 27.69, 27.67 ppm; ^{19}F NMR (376 MHz, CD_3CN): δ = −90.48 (d, *J* = 254.93 Hz), −113.76 (d, *J* = 254.93 Hz) ppm; HRMS (ESI): calcd for $C_{24}H_{27}F_2N_2O_2$ $[M+H]^+$ 413.2035; found 413.2035.

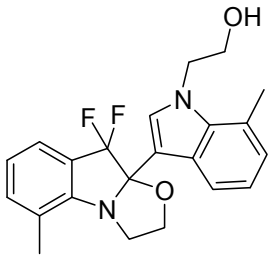


Compounds **2d**: Following general procedure C with indole **1d** (159 mg, 0.91 mmol, 1 equiv), NFSI (855 mg) in a mixture of MeCN:MeOH (1:1, 18.2 mL) at -20 °C for 20 h, **2d** was purified by column chromatography using 2% MeCN:CH_2Cl_2 and was obtained as a white foam (75 mg, 43%). IR (neat) ν_{max} 3390, 2960, 1617, 1546, 1469, 1262, 1088, 1017, 868, 745 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ = 7.79 (brm, 1H), 7.75-7.48 (m, 3H), 7.47 (s, 1H), 7.26 (ddd, *J* = 8.4, 7.5, 1.2 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (dd, *J* =8.4, 1.5 Hz, 1H), 7.00-6.96 (m, 1H), 4.35 (t, *J* = 6.9 Hz, 2H), 3.92-3.81 (m, 2H), 3.51 (td, *J* = 6.9, 5.0 Hz, 2H), 2.73 (t, *J* = 5.0 Hz, 1H), 2.10-2.00 (m, 2H), 1.93-1.83 (m, 1H), 1.27-1.22 (brm, 1H) ppm; ^{13} C NMR (100 MHz, CD_3CN) δ = 152.0 (dd, *J* = 7, 5 Hz), 138.0, 134.0 (d, *J* = 3 Hz), 131.8 (brs), 128.1 (brs), 124.8, 124.4 (dd, *J* = 257, 239 Hz), 124.0 (dd, *J* = 27, 24 Hz), 122.7, 121.7 (brs), 120.8, 120.6 (d, *J* = 2 Hz), 111.6, 111.1, 106.8, 96.7 (dd, *J* = 36, 19 Hz), 63.6, 59.4, 43.9, 40.9, 33.6, 22.7 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -91.29 (brm), -125.64 to -131.8 9(brm) ppm (rotamers); HRMS (ESI-TOF) calcd for $C_{22}H_{22}F_2N_2O_2$ $[M]^+$ 384.1644; found 384.1656; calcd for $C_{22}H_{22}F_2N_2NaO_2$ $[M+Na]^+$ 407.1542; found 407.1561.

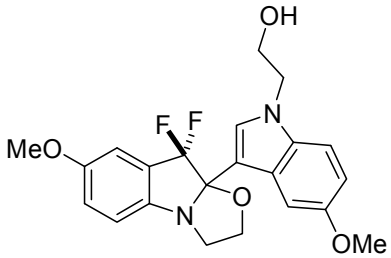


Compound **2e**: Following general procedure C with indole **1e** (102 mg, 0.58 mmol), NFSI (551 mg, 1.74 mmol) in a mixture MeCN:MeOH (1:1, 11.6 mL) at −20 °C for 48 h. Flash column chromatography using hexanes:EtOAc (4:1) afforded **2e** (45 mg, 40%) as a yellow oil. IR (film) ν_{max} 3416, 2924, 1622, 1493, 1276, 1163, 1075, 789 cm^{-1}; ^{1}H NMR (600 MHz, CD_3CN) δ = 7.51 (s, 1H), 7.38 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.33–7.30 (m, 2H), 7.03 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 4.19 (td, *J* = 5.4, 3.1 Hz, 2H), 3.86–3.77 (m, 4H), 3.73 (dtd, *J* = 11.2, 4.6, 2.4 Hz, 1H), 3.43 (dt, *J* =

11.9, 8.0 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (150 MHz, CD_3CN): δ = 152.1 (dd, *J* = 8.9, 5.9 Hz), 136.7, 135.1, 133.3, 130.3, 129.5, 127.9, 125.0, 124.4 (dd, *J* = 247.4, 238.4 Hz), 124.2 (dd, *J* = 24.2, 23.9 Hz), 124.14, 121.3, 114.8 (d, *J* = 3 Hz), 110.7, 108.8, 104.3 (dd, *J* = 36.2, 18.6 Hz), 66.7, 61.7, 51.6 (d, *J* = 3.0 Hz), 49.6, 21.6, 20.8 (d, *J* = 2 Hz) ppm; ^{19}F NMR (376 MHz, CD_3CN): δ = −89.96 (d, *J* = 255.68 Hz), −113.67 (d, *J* = 255.68 Hz) ppm; HRMS (ESI): calcd for $C_{22}H_{23}F_2N_2O_2$ $[M + H]^+$ 385.1722, found 385.1738.

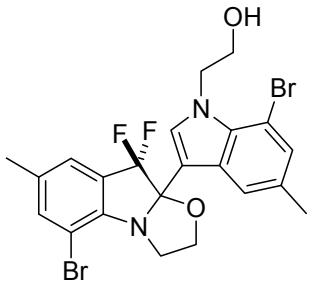


Compound **2f**: Following general procedure C with indole **1f** (95.3 mg, 0.54 mmol, 1 equiv), NFSI (514.5 mg) in a mixture of toluene:MeCN (1:1, 10.9 mL) at -20 °C for 20 h, **2f** was purified by column chromatography using 30% EtOAc:petroleum ether and was obtained as a brown amorphous solid (54 mg, 52%). IR (neat) ν_{max} 3564, 2958, 2927, 2891, 1605, 1552, 1453, 1281, 1077, 1043, 1017, 791 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6) δ = 7.63 (d, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.92–6.88 (m, 2H), 4.50 (td, *J* = 5.8, 2.7 Hz, 2H), 4.05– 4.00 (m, 2H), 3.92–3.85 (m, 3H), 3.75-3.67 (m, 1H), 3.66–3.58 (m, 1H), 2.71 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 152.5 (dd, *J* = 8, 6 Hz), 137.0, 136.0 (t, *J* = 2 Hz), 131.5, 128.9, 125.7, 125.4, 125.3 (dd, *J* = 28, 24 Hz), 125.0, 123.8 (dd, *J* = 257, 239 Hz), 123.5 (t, *J* = 2 Hz), 122.3, 121.7, 120.2, 110.4 (dd, *J* = 2 Hz), 103.5 (dd, *J* = 35, 19 Hz), 67.2, 66.1, 63.4, 51.6 (d, *J* = 3 Hz), 20.3, 18.0 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -91.16 (dd, *J* = 255.68, 3.76 Hz), -106.22 (dd, *J* = 255.68, 3.76 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{23}F_2N_2O_2$ $[M+H]^+$ 385.1722; found 385.1706; calcd for $C_{22}H_{22}F_2N_2O_2Na$ $[M + Na]^+$ 407.1542; found 407.1547.

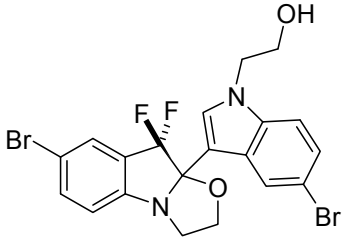


Compound **2g**: Following general procedure C with indole **1g** (153.8 mg, 0.80 mmol), NFSI (760 mg) in a mixture of MeCN:EtOH (1:1, 16 mL) at -40 °C for 40 h, **2g** was purified by column chromatography using 2-5% MeCN:CH_2Cl_2 and was obtained as a white amorphous solid (85 mg, 51%). IR (neat) ν_{max} 3440, 2936, 2836, 1622, 1577, 1548, 1488, 1271, 1215, 1178, 1077,

1034, 984 cm^{-1}; ^1H NMR (400 MHz, Acetone-d_6) δ = 7.46 (s, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.13-7.04 (m, 3H), 6.83 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.26 (t, *J* = 5.4 Hz, 2H), 3.99 (t, *J* = 5.4 Hz, 1H), 3.93 – 3.81 (m, 4H), 3.83 (s, 3H), 3.80-3.72 (m, 1H), 3.76 (s, 3H), 3.46 (dt, *J* = 11.6, 8.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 156.7 (dd, *J* = 2.0, 1.4 Hz), 155.0, 147.8 (dd, *J* = 9.0, 6.0 Hz), 133.7, 130.5, 128.4, 125.5 (dd, *J* = 27.0, 24.0 Hz), 123.8 (dd, *J* = 256.0, 239.0 Hz), 120.9 (d, *J* = 2 Hz), 115.8, 112.2, 111.3, 109.2, 108.9, 104.7 (dd, *J* = 36.0, 19.0 Hz), 104.1, 66.4, 61.9, 56.3, 56.0, 51.8 (d, *J* = 3 Hz), 49.7 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -90.18 (d, *J* = 255.7 Hz), -113.81 (d, *J* = 255.7 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{23}F_2N_2O_4$ 417.1620; found 417.1638.

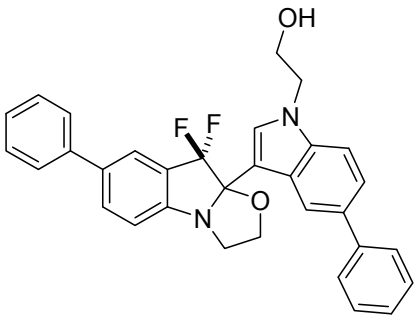


Compound **2h**: Following general procedure C with indole **1h** (75 mg, 0.30 mmol), NFSI (279 mg, 0.89 mmol) in a mixture MeCN:MeOH (1:1, 6 mL) at −20 °C for 48 h. Flash column chromatography (silica gel, hexanes:EtOAc 80:20) afforded **2h** (35 mg, 44%) as a yellow oil. IR (film) ν_{max} 3445, 2924, 1708, 1569, 1478, 1267, 1073, 985, 740 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ = 7.58 (d, *J* = 1.0 Hz, 1H), 7.49 (d, *J* = 1.4 Hz, 1H), 7.41 (s, 1H), 7.32 (s, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 4.64–4.50 (m, 2H), 4.06–3.95 (m, 2H), 3.90 – 3.77 (m, 3H), 3.61–3.50 (m, 1H), 2.36 (d, *J* = 0.8 Hz, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (150 MHz, CD_3CN): δ = 148.8 (dd, *J* = 9.0, 6.0 Hz), 138.9, 136.1, 134.1, 132.6, 131.6, 131.1, 129.4, 127.1 (dd, *J* = 29.0, 25.5 Hz), 124.8, 123.3 (dd, *J* = 258.0, 240.0 Hz), 121.0, 109.1 (d, *J* = 3.0 Hz), 108.9, 103.8, 103.4 (dd, *J* = 33.0, 18.0 Hz), 67.7, 62.9, 51.7 (d, *J* = 2.0 Hz), 51.3, 20.9, 20.4 ppm; ^{19}F NMR (376 MHz, CD_3CN): δ = −91.54 (d, *J* = 254.18 Hz), −106.50 (d, *J* = 254.18 Hz) ppm; HRMS (ESI) calcd for $C_{22}H_{21}{}^{79}Br_2F_2N_2O_2$ $[M+H]^+$ 540.9932; found 540.9937; calcd for $C_{22}H_{20}{}^{79}Br_2F_2N_2O_2$ $[M+Na]^+$ 562.9752; found 562.9780.

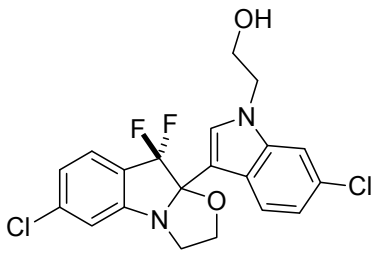


Compound **2i**: Following general procedure C with indole **1i** (96.6 mg, 0.20 mmol), NFSI (380 mg) in a mixture of MeCN:MeOH (1:1, 4 mL) at -20 °C for 48 h, **2i** was purified by column chromatography using 2-5% MeCN:CH_2Cl_2 and was obtained as a white amorphous solid (56 mg,

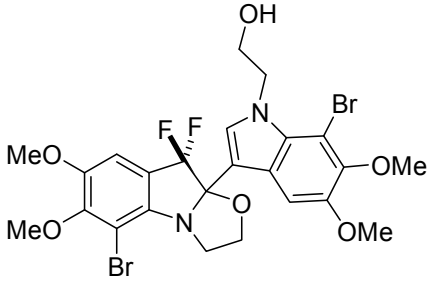
54%). IR (neat) ν_{max} 3444, 2967, 2899, 1610, 1545, 1256, 1080, 988, 706 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6) δ = 7.89 (s, 1H), 7.71-7.66 (m, 2H), 7.59 (s, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.28 (dd, J = 8.8, 1.7 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 4.33 (t, J = 5.3 Hz, 2H), 4.05 (t, J = 5.3 Hz, 1H), 3.98–3.80 (m, 5H), 3.51 (dt, J = 11.5, 7.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 153.6 (dd, J = 9.0, 6.0 Hz), 137.2, 137.1 (d, J = 2.0 Hz), 131.8, 129.3 (d, J = 1 Hz), 127.8, 126.8 (dd, J = 27.0, 25.0 Hz), 125.0, 123.9, 122.8 (dd, J = 258.0, 240.0 Hz), 117.1, 114.6, 113.3, 113.0, 108.6, 104.0 (dd, J = 36.0, 19.0 Hz), 66.8, 61.8, 51.3 (d, J = 3.0 Hz), 49.9 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -90.74 (d, J = 259.4 Hz), -114.17 (d, J = 259.4 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{20}H_{17}{}^{79}Br_2F_2N_2O_2$ $[M+H]^+$ 512.9619; found 512.9637; calcd for $C_{20}H_{17}{}^{81}Br_2F_2N_2O_2$ $[M+H]^+$ 514.9600; found 514.9624.



Compound **2j**: Following general procedure C with indole **1j** (148.6 mg, 0.63 mmol), NFSI (592 mg) in a mixture of toluene:MeCN (1:1, 12.6 mL) at -20 °C for 70 h, **2j** was purified by column chromatography using 0-2% MeCN:CH_2Cl_2 and was obtained as a white amorphous solid (72 mg, 45%). IR (neat) ν_{max} 3488, 2958, 2930, 1621, 1548, 1477, 1309, 1080, 755 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6) δ = 8.09 (s, 1H), 7.84 (dd, J = 8.4, 1.6 Hz, 1H), 7.79 (s, 1H), 7.69 (dd, J = 8.3, 1.2 Hz, 2H), 7.63 (dd, J = 8.3, 1.2 Hz, 2H), 7.60 (s, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.52–7.39 (m, 5H), 7.38–7.32 (m, 1H), 7.31–7.22 (m, 2H), 4.41–4.32 (m, 2H), 4.10–4.03 (m, 1H), 4.01–3.86 (m, 5H), 3.59 (dt, J = 10.9, 6.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 153.9 (dd, J = 9.0, 6.0 Hz, 1H), 143.6, 141.1, 138.1, 136.5, 133.7, 132.9, 130.1, 129.8 (2C), 129.6 (2C), 128.4, 128.0, 127.9 (2C), 127.5 (2C), 127.1, 125.6 (dd, J = 27.0, 25.0 Hz), 123.7 (dd, J = 257.0, 240.0 Hz), 123.1, 121.9, 120.2, 115.3, 111.3, 109.8, 104.4 (dd, J = 36.0, 19.0 Hz), 66.7, 61.2, 51.4 (d, J = 2 Hz), 49.8 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -90.41 (d, J = 255.7 Hz), -113.87 (d, J = 255.7 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{32}H_{27}F_2N_2O_2$ $[M+H]^+$ 509.2035; found 509.2057.



Compound **2k**: Following general procedure C with indole **1k** (113 mg, 0.58 mmol), NFSI (546 mg) in a mixture of MeCN:MeOH (1:1, 11.6 mL) at -25 °C for 96 h, **2k** was purified by column chromatography using 2-5% MeCN:CH_2Cl_2 and was obtained as a brown foam (49 mg, 40%). IR (neat) ν_{max} 3486, 2929, 2874, 1609, 1542, 1472, 1426, 1284, 1069, 991, 957, 812 cm^{-1}; ^1H NMR (400 MHz, Acetone-d_6) δ = 7.71 (d, J = 8.5 Hz, 1H), 7.57(s, 1H), 7.56 (m, 1H), 7.53 (dt, J = 8.1, 1.5 Hz, 1H), 7.23 (d, J = 1.5 Hz, 1H), 7.14 (dd, J = 8.1, 1.5 Hz, 1H), 7.06 (dd, J = 8.5, 1.9 Hz, 1H), 4.33 (td, J = 5.1, 0.9 Hz, 2H), 4.09 (t, J = 5.5 Hz, 1H), 3.99–3.85 (m, 5H), 3.57–3.46 (m, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 155.8 (dd, J = 9.0, 6.0 Hz), 139.5 (d, J = 2 Hz), 138.9, 131.3, 128.0, 126.3, 123.5 (dd, J = 28.0, 25.0 Hz), 123.4, 122.9 (dd, J = 257.0, 240.0 Hz), 122.8, 120.7, 120.4, 115.2, 111.0, 109.3, 103.9 (dd, J = 36.0, 19.0 Hz), 66.8, 61.9, 51.2 (d, J = 2 Hz), 49.8 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -90.51 (d, J = 259.4 Hz), -113.51 (d, J = 259.4 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{20}H_{17}Cl_2F_2N_2O_2$ $[M+H]^+$ 425.0630; found 425.0642.

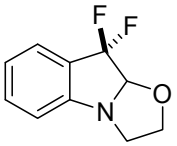


Compound **2l**: Following general procedure C with indole **1l** (152 mg, 0.51 mmol), NFSI (479 mg) in a mixture of MeCN:MeOH (1:1, 10.2 mL) at -20 °C for 20 h, **2l** was purified by column chromatography using 2-5% MeCN:CH_2Cl_2 and was obtained as a white foam (50 mg, 50%). IR (neat) ν_{max} 3465, 3003, 2942, 1618, 1523, 1462, 1340, 1210, 1077, 739 cm^{-1}; ^1H NMR (400 MHz, Acetone-d_6) δ = 7.45 (s, 1H), 7.30 (s, 1H), 7.21 (s, 1H), 4.75–4.59 (m, 2H), 4.13–4.04 (m, 1H), 4.00–3.86 (m, 5H), 3.93 (s, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.67–3.53 (m, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 152.2, 151.2, 149.3, 145.9 (dd, J = 8.0, 7.0 Hz), 144.7, 133.4, 129.3, 125.9, 123.5 (dd, J = 259.0, 240.0 Hz), 121.1 (dd, J = 28.0, 25.0 Hz), 109.7 (d, J = 2 Hz), 108.2, 105.9, 103.9, 103.7 (dd, J = 34.0, 18.0 Hz), 100.5, 67.6, 63.1, 60.9, 60.8, 57.2, 56.7, 52.1 (d, J = 2 Hz), 51.3 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -91.55 (d, J = 251.9 Hz), -133.93 (d, J = 251.9 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{24}H_{25}Br_2F_2N_2O_6$ $[M+H]^+$ 633.0042; found 633.0063;

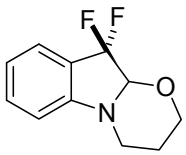
calcd for $C_{24}H_{24}Br_2F_2N_2NaO_6$ $[M+Na]^+$ 654.9861, found 654.9921.

Difluorocyclization of indoles at high temperature – General procedure D

A 0.05 M solution of respective indole **1** (1 equiv) in a mixture of HPLC grade solvents toluene:MeCN (4:1) was stirred at 90 ^oC for 10 min and NFSI (2.5 equiv) was then added. The reaction mixture was maintained at the same temperature for a specific period of time as determined by TLC monitoring. After the completion, the reaction was quenched with TEA (5 equiv) and the crude was concentrated to dryness in *vacuo*. Purification by silica gel column chromatography using EtOAc:hexanes or EtOAc:petroleum ether afforded the desired oxazolidine **3**. In general, oxindoles **10** were also formed in 15-20% yields as determined by ^{19}F NMR from the crude mixtures. As an example, oxindole **9i** (see below) was isolated and fully characterized.



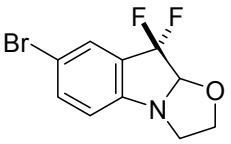
Oxazolidine **3a**: Following general procedure D with indole **1a** (300 mg, 1.86 mmol), NFSI (1.47 g) for 1 h, **3a** was purified by column chromatography using 10-20% EtOAc:petroleum ether and was obtained as a colorless oil (147 mg, 40%). IR (neat) ν_{max} 2956, 2893, 1616, 1469, 1371, 1322, 1294, 1181, 1039, 987, 776 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 7.54–7.39 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.01 (ddt, *J* = 7.5, 1.6, 0.8 Hz, 1H), 5.05 (d, *J* = 11.7 Hz, 1H), 3.98–3.86 (m, 1H), 3.73–3.57 (m, 2H), 3.57–3.30 (m, 1H) ppm; ^{13}C NMR (100 MHz, CD_3CN) δ = 154.9 (dd, *J* = 9.0, 5.0 Hz), 134.8 (dd, *J* = 2.0, 1.0 Hz), 124.8, 124.4 (dd, *J* = 254.0, 235.0 Hz), 124.2 (dd, *J* = 25.0, 24.0 Hz), 123.3 (t, *J* = 2 Hz), 115.1 (d, *J* = 1.0 Hz), 97.7 (dd, *J* = 45.0, 17.0 Hz), 67.1, 51.9 (d, *J* = 2.0 Hz) ppm; ^{19}F NMR (376 MHz, CD_3CN) δ =-93.87 (d, *J* = 267.0 Hz), -109.41 (d, *J* = 267.0 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{10}H_{10}F_2NO$ $[M+H]^+$ 198.0725; found 198.0724.



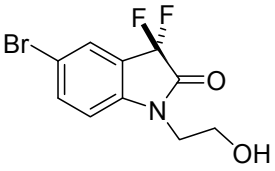
Tetrahydro-1,3-oxazine **3d**: Following general procedure D with indole **1d** (264.4 mg, 1.50 mmol), NFSI (1.18 g) for 1 h, **3d** was obtained as a white amorphous solid (127 mg, 40%). IR (neat) ν_{max} 2921, 2860, 1618, 1484, 1397, 1315, 1272, 1177, 1017, 988, 924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.39–7.34 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.18–4.01 (m, 1H), 3.80 (td, *J* = 12.7, 2.2

Hz, 1H), 3.73 (ddd, *J* = 14.2, 4.6, 1.7 Hz, 1H), 3.32 (ddd, *J* = 14.2, 12.7, 3.3 Hz, 1H), 1.93–1.78 (m, 1H), 1.34 (ddd, *J* = 13.5, 3.3, 1.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.5 (dd, *J* = 8.0, 5.0 Hz), 133.2 (d, *J* = 2 Hz), 124.5, 122.8 (dd, *J* = 254.0, 239.0 Hz), 122.3 (dd, *J* = 26.0, 23.0 Hz), 119.2 (t, *J* = 3 Hz), 108.6, 91.6 (dd, *J* = 44.0, 20.0 Hz), 67.0, 41.9, 23.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -93.87 (d, *J* = 267.0 Hz), -109.41 (d, *J* = 267.0 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{11}H_{12}F_2NO$ 212.0881; found 212.0890.

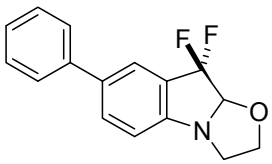
Oxazolidine **3i** and oxindole **7i**: Following general procedure D with indole **1i** (155.7 mg, 0.65 mmol), NFSI (511 mg) for 2 h, **3i** was purified by column chromatography using 10-20% EtOAc:petroleum ether and was obtained as a colorless oil (105 mg, 40%). It should be noted that oxindole **7i** was also obtained as yellow oil (18 mg, 10%).



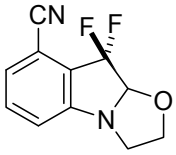
Oxazolidine **3i**: IR (neat) ν_{max} 2955, 2890, 1610, 1471, 1367, 1293, 1183, 1042, 986, 820 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ = 7.67–7.57 (m, 2H), 6.98–6.92 (m, 1H), 5.07 (d, *J* = 11.8 Hz, 1H), 3.99–3.93 (m, 1H), 3.75–3.60 (m, 2H), 3.45 (ddd, *J* = 11.5, 8.3, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ = 154.1 (dd, *J* = 9.0, 6.0 Hz), 137.6 (t, *J* = 2.0 Hz), 127.7, 126.3 (dd, *J* = 27.0, 24.0 Hz), 123.6 (dd, *J* = 254.0, 236.0 Hz), 117.1, 114.6 (t, *J* = 2 Hz), 97.7 (dd, *J* = 45.0, 18.0 Hz), 67.3, 51.8 (d, *J* = 3 Hz) ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -94.75 (d, *J* = 263.2 Hz), -109.06 (d, *J* = 263.2 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{10}H_9{}^{79}BrF_2NO$ $[M+H]^+$ 275.9830; found 275.9832; calcd for $C_{10}H_9{}^{81}BrF_2NO$ $[M+H]^+$ 277.9810; found 277.9815.



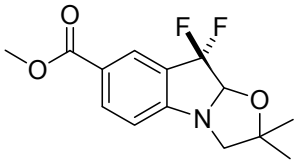
Oxindole **7i**. IR (neat) ν_{max} 3420, 2936, 2885, 1740, 1616, 1486, 1283, 1089, 817, 721 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ = 7.78 (q, *J* = 1.8 Hz, 1H), 7.72–7.66 (m, 1H), 7.09 (dt, *J* = 8.5, 1.4 Hz, 1H), 3.81–3.65 (m, 4H), 3.04 (t, *J* = 5.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, CD_3CN) δ = 165.8 (t, *J* = 29.0 Hz), 144.7 (t, *J* = 3.0 Hz), 137.6, 128.4, 122.3 (t, *J* = 23.0 Hz), 116.5 (t, *J* = 3.0 Hz), 114.1, 111.6 (t, *J* = 247.0 Hz), 59.5, 44.1 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -113.08 ppm; HRMS (ESI-TOF) calcd for $C_{10}H_9{}^{79}BrF_2NO_2$ $[M+H]^+$ 291.9779; found 291.9778; calcd for $C_{10}H_9{}^{81}BrF_2NO_2$ $[M+H]^+$ 293.9758, found 293.9767.



Oxazolidine **3j**: Following general procedure D with indole **1j** (242 mg, 1.02 mmol), NFSI (801.6 mg) for 2 h, **3j** was purified by column chromatography using 10-20% EtOAc:petroleum ether and was obtained as a white amorphous solid (131 mg, 47%). IR (neat) ν_{max} 2964, 2883, 1620, 1478, 1372, 1310, 1221, 1182, 1041, 757 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 7.80–7.71 (m, 2H), 7.64–7.57 (m, 2H), 7.45 (m, 2H), 7.39–7.30 (m, 1H), 7.09 (dq, *J* = 8.3, 0.9 Hz, 1H), 5.11 (d, *J* = 11.6 Hz, 1H), 4.03–3.92 (m, 1H), 3.77–3.64 (m, 2H), 3.55–3.41 (m, 1H) ppm; ^{13}C NMR (100 MHz, CD_3CN) δ = 154.3 (dd, *J* = 9.0, 5.0 Hz), 140.9, 136.6 (t, *J* = 2Hz), 133.7 (t, *J* = 2 Hz), 130.0 (2C), 128.3, 127.7 (2C), 125.0 (dd, *J* = 27.0, 24.0 Hz), 124.4 (dd, *J* = 254.0, 236.0 Hz), 123.1, 115.5 (d, *J* = 1 Hz), 98.0 (dd, *J* = 46.0, 18.0 Hz), 67.2, 51.9 (d, *J* = 3 Hz) ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -94.09 (d, *J* = 263.2 Hz), -109.54 (d, *J* = 263.2 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{16}H_{14}F_2NO$ $[M+H]^+$ 274.1038; found 274.1044.

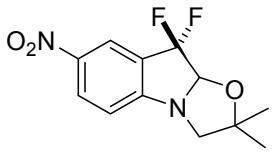


Oxazolidine **3m**: Following general procedure D with indole **1m** (210 mg, 1.13 mmol) and NFSI (891 mg) in dry toluene/MeCN (4:1, 22.5 mL) for 16 h. Flash column chromatography using petroleum ether:CH_2Cl_2 (1:3) afforded oxazolidine **3m** (124 mg, 49%) as a red oil. IR (film) ν_{max} 2898, 2235, 1604, 1450, 1292, 1220, 1180, 1057, 1005, 801, 751 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 7.68–7.59 (m, 1H), 7.40 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.33–7.28 (m, 1H), 5.15 (d, *J* = 12.2 Hz, 1H), 4.10–3.88 (m, 1H), 3.79–3.63 (m, 2H), 3.54–3.44 (m, 1H) ppm; ^{13}C NMR (100 MHz, CD_3CN) δ = 155.8 (dd, *J* = 8.0, 6.0 Hz), 135.7 (t, *J* = 1.0 Hz), 127.7 (t, *J* = 1.5 Hz), 125.3 (dd, *J* = 25.5, 24.0 Hz), 123.3 (dd, *J* = 255.0, 237.0 Hz), 120.3, 116.1, 108.7, 97.3 (dd, *J* = 45.0, 18.0 Hz), 67.5, 51.7 (d, *J* = 2 Hz) ppm; ^{19}F NMR (376 MHz, CD_3CN): δ = -97.10 (d, *J* = 267.0 Hz), -108.32 (d, *J* = 267.0 Hz) ppm; HRMS (ESI): calcd for $C_{11}H_8F_2N_2NaO$ $[M+Na]^+$ 245.0502, found 245.0507.



Oxazolidine **3n**: Following general procedure D with indole **1n** (50.5 mg, 0.20 mmol), NFSI (160.3 mg) for 16 h, **3n** was purified by column chromatography using 10-20% EtOAc:petroleum ether and was obtained as a white amorphous solid (29 mg, 50%). IR (neat) ν_{max} 2964, 2883, 1723, 1623, 1494, 1311, 1252, 1045,

777 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 8.16–7.89 (m, 2H), 7.08–6.79 (m, 1H), 5.24 (d, *J* = 12.9 Hz, 1H), 3.85 (s, 3H), 3.59 (dd, *J* = 11.7, 1.6 Hz, 1H), 3.36 (d, *J* = 11.7 Hz, 1H), 1.37 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (100 MHz, CD_3CN) δ = 166.8, 159.4 (dd, *J* = 8.0, 5.0 Hz), 136.4, 126.8, 124.9 (t, *J* = 2 Hz), 123.9 (dd, *J* = 255.0, 213.0 Hz), 123.8 (dd, *J* = 27.0, 25.0 Hz), 113.9, 97.3 (dd, *J* = 46.0, 18.0 Hz), 84.4, 62.0 (d, *J* = 2 Hz), 52.7, 28.3, 26.8 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -95.40 (d, *J* = 267.0 Hz), -108.32 (d, *J* = 267.0 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{14}H_{16}F_2NO_3$ $[M+H]^+$ 284.1093; found 284.1090.

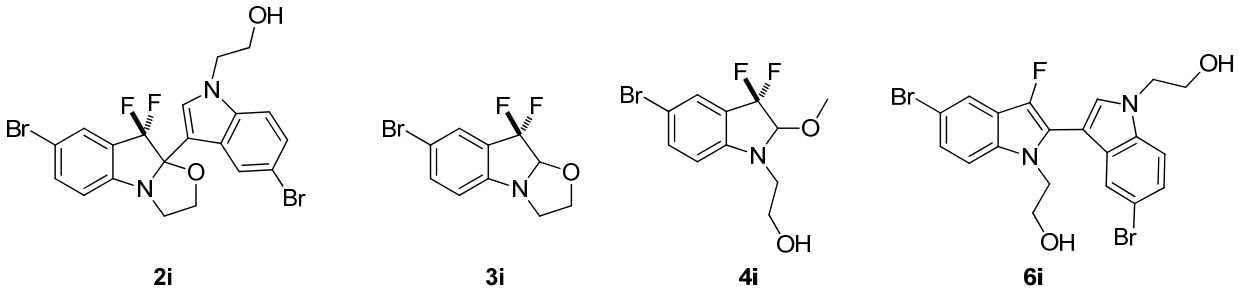


Oxazolidine **3o**: Following general procedure D with indole **1o** (97 mg, 0.41 mmol), NFSI (325 mg) for 16 h, **3o** was purified by column chromatography using 20-30% EtOAc:petroleum ether and was obtained as a yellow amorphous solid (68 mg, 61%). IR (neat) ν_{max} 2973, 2838, 1620, 1519, 1338, 1233, 1092, 1051, 740 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ = 8.42–8.30 (m, 2H), 7.04 (dd, *J* = 9.5, 1.5 Hz, 1H), 5.31 (d, *J* = 13.1 Hz, 1H), 3.63 (dd, *J* = 11.8, 1.6 Hz, 1H), 3.41 (d, *J* = 11.8 Hz, 1H), 1.39 (s, 3H), 1.03 (s, 3H) ppm; ^{13}C NMR (100 MHz, CD_3CN) δ = 160.4 (dd, *J* = 7.5, 5.0 Hz), 143.4, 131.1 (t, *J* = 1 Hz), 124.0 (dd, *J* = 27.0, 25.0 Hz), 123.3 (dd, *J* = 256.0, 237.0 Hz), 122.0, 113.9, 97.30 (dd, *J* = 46.0, 18.0), 84.9, 61.7 (d, *J* = 2 Hz), 28.2, 26.7 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -96.52 (d, *J* = 270.7 Hz), -107.59 (d, *J* = 270.7 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{12}H_{13}F_2N_2O_3$ $[M+H]^+$ 271.0889; found 271.0888.

Isolation and characterization of intermediates and side-products of the cascade C-F/C-C/C-O bond forming reaction of indoles

To a 0.05 M solution of **1i** (160 mg, 0.67 mmol, 1 equiv) in a mixture of HPLC MeCN:MeOH (1:1, 13.4 mL) was added NFSI (357 mg, 1.7 equiv) under air. The reaction mixture was stirred at room temperature for 16 h and concentrated to dryness. ^{19}F NMR in $CDCl_3$ of the crude mixture showed the presence of **2i**, **3i**, **6i** and **9i** in 4:1:1:1 ratio as shown in Figure 1 below. It should be noted that oxindole **9i**[5] was observed in trace amounts together with other unknown minor products. Purification by column chromatography with 10-80% EtOAc:petroleum ether afforded **2i**, **3i**, **6i** in 18%, 5%, 4% yields,

respectively.



2i **3i** **4i** **6i**

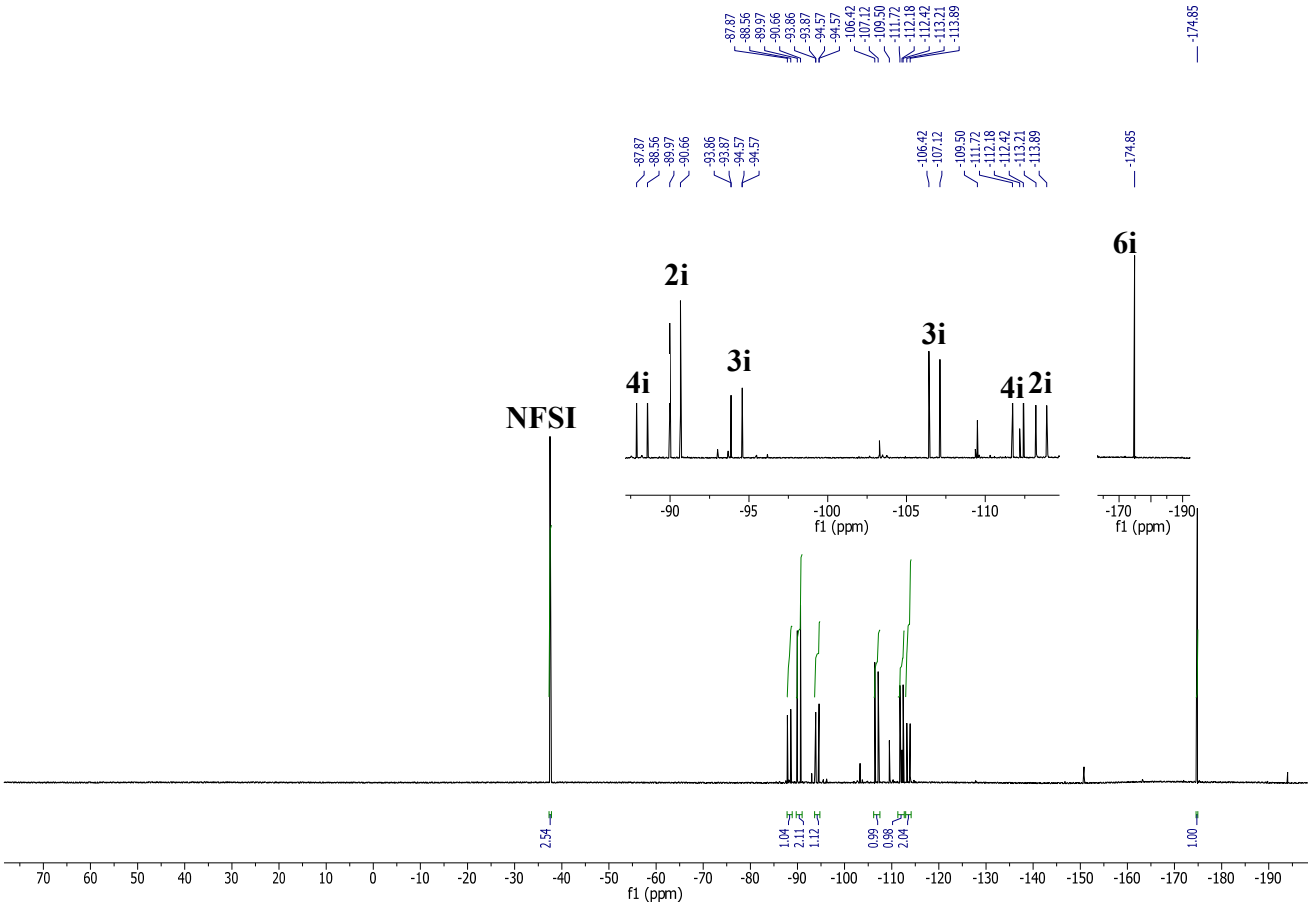
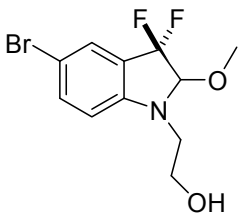
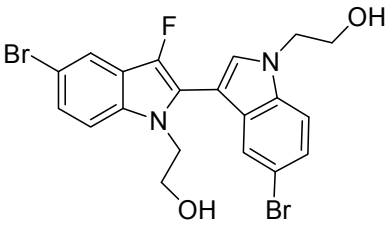


Figure 1. ^{19}F NMR of the reaction of indole **1i** with NFSI (1.7 equiv) at room temperature



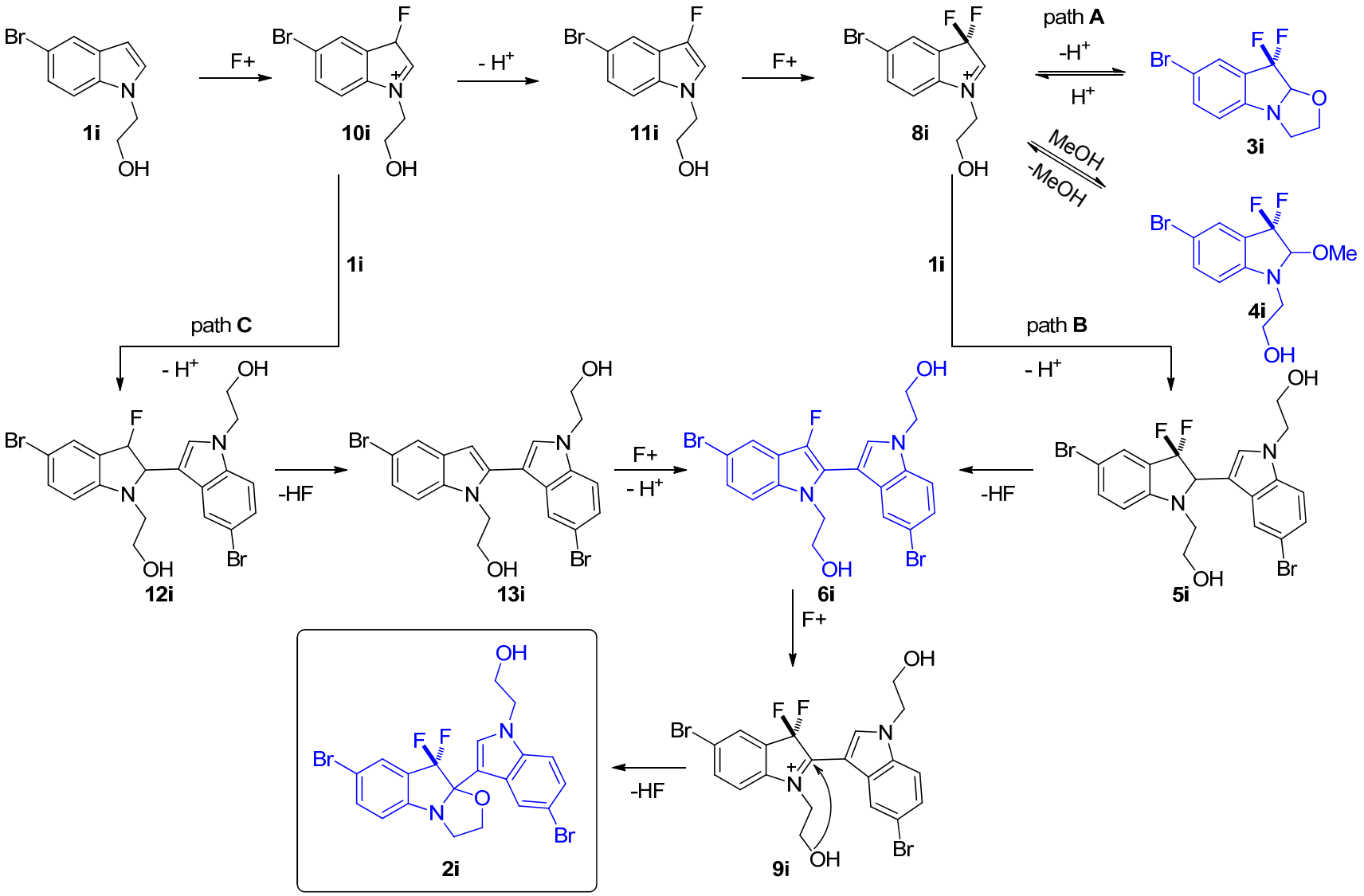
Compound **4i**: An analytically pure sample of **4i** could not be obtained despite several chromatographic purifications, due to the similar polarity with those of the remaining starting material **1i** and other minor side products. The structure of **4i** was suggested based on ^{1}H NMR, ^{19}F NMR and HRMS analyses. ^{1}H NMR (400

MHz, $CDCl_3$) δ = 7.52–7.47 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 6.48 (d, *J* = 8.6 Hz, 1H), 4.64 (dd, *J* = 15.4, 2.3 Hz, 1H), 3.76 (dt, *J* = 10.9, 6.6 Hz, 2H), 3.65–3.41 (m, 1H), 3.58 (s, 3H), 3.34 (ddd, *J* = 14.9, 7.3, 3.7 Hz, 2H), 2.54 (s, 1H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -88.00 (d, *J* = 260.2 Hz), -112.26 (d, *J* = 260.2 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{11}H_{13}{}^{79}Br_2F_2NO_2$ $[M+H]^+$ 308.0092; found 308.0084; $C_{11}H_{12}{}^{79}Br_2F_2NNaO_2$ $[M+H]^+$ 329.9912; found 329.9919.



Compound **6i**: IR (neat) ν_{max} 3460, 2925, 2878, 1628, 1445, 1229, 1074, 743 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6) δ = 7.86 (s, 1H), 7.76–7.66 (m, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.36 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.31 (dd, *J* = 8.8, 1.9 Hz, 1H), 4.45 (t, *J* = 5.3 Hz, 2H), 4.30 (t, *J* = 5.7 Hz, 2H), 4.15 (t, *J* = 5.5 Hz, 1H), 4.02–3.96 (m, 3H), 3.78 (q, *J* = 5.7 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6) δ = 140.6 (d, *J* = 240.0 Hz), 135.5, 132.1 (d, *J* = 6.0 Hz), 131.6, 129.4, 124.6, 124.5, 122.1 (d, *J* = 3.0 Hz), 118.9 (d, *J* = 23.0 Hz), 118.4 (d, *J* = 16.0 Hz), 117.9 (d, *J* = 3.0 Hz), 113.0, 112.6 (d, *J* = 1.0 Hz), 112.4, 112.2, 101.4 (d, *J* = 3.0 Hz), 60.9, 60.7, 49.2, 46.1 ppm; ^{19}F NMR (376 MHz, CD_3CN) δ = -174.13 (s) ppm; HRMS (ESI-TOF) calcd for $C_{20}H_{18}{}^{79}Br_2FN_2O_2$ $[M+H]^+$ 494.9714; found 494.9703; calcd for $C_{20}H_{18}{}^{79}Br^{81}Br\,FN_2O_2$ $[M+H]^+$ 496.9694; found 496.9687; calcd for $C_{20}H_{18}{}^{81}Br_2FN_2O_2$ $[M+H]^+$ 498.9672; found 498.9670.

Proposed Possible Pathways for the Cascade Fluorofunctionalization Leading to 2i



II) Abbreviations

NFSI = *N*-Fluorobenzenesulfonimide

TLC = thin layer chromatography

equiv = equivalents

EtOAc = ethyl acetate

h = hour

HPLC = high performance liquid chromatography

HRMS = high-resolution mass spectra

M = molar

min = minute

NMR = nuclear magnetic resonance

brs = broad singlet

brm = broad multiplet

TEA = triethylamine

DMF = *N*,*N*'-dimethylformamide

DCE = 1,2-dichloroethane

THF = tetrahydrofuran

Et = ethyl

Me = methyl

Bu = butyl

Ac = acetyl

Bu = butyl

Bn = benzyl

III) References

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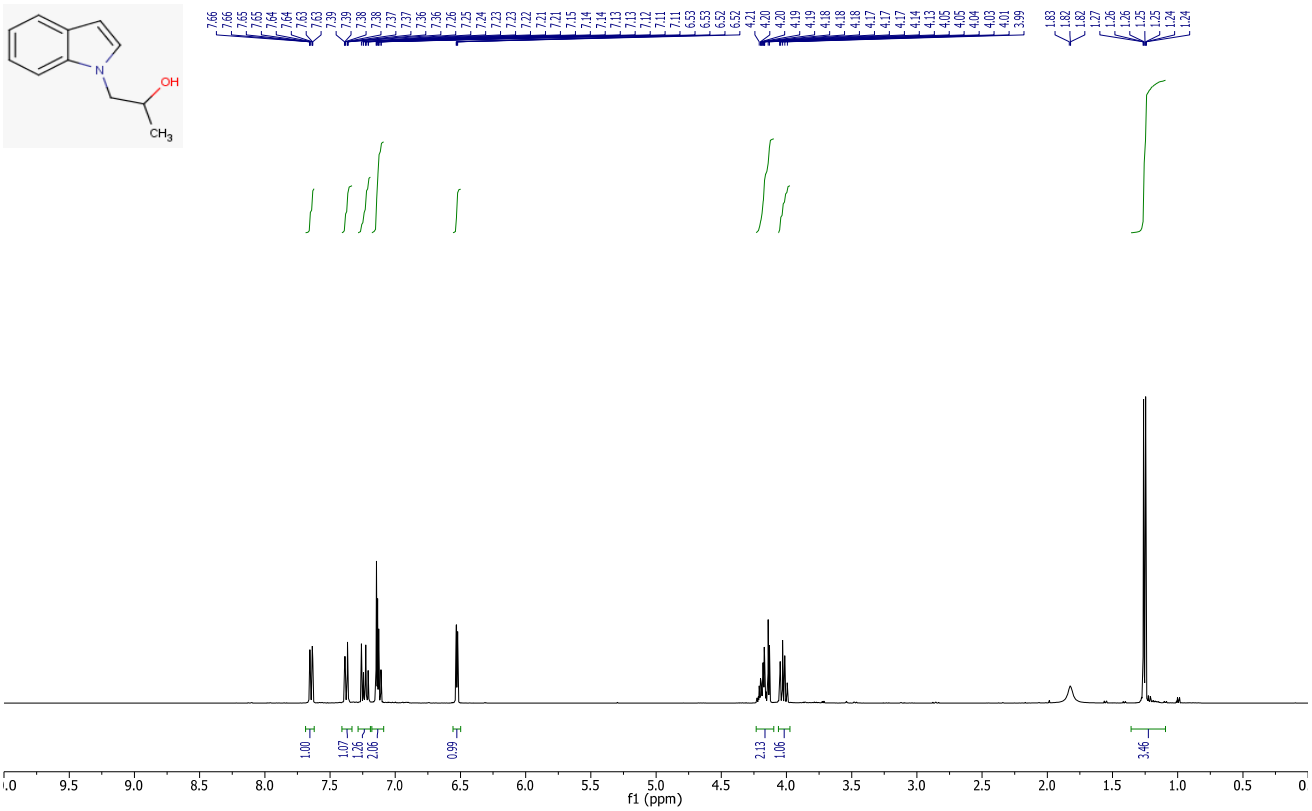
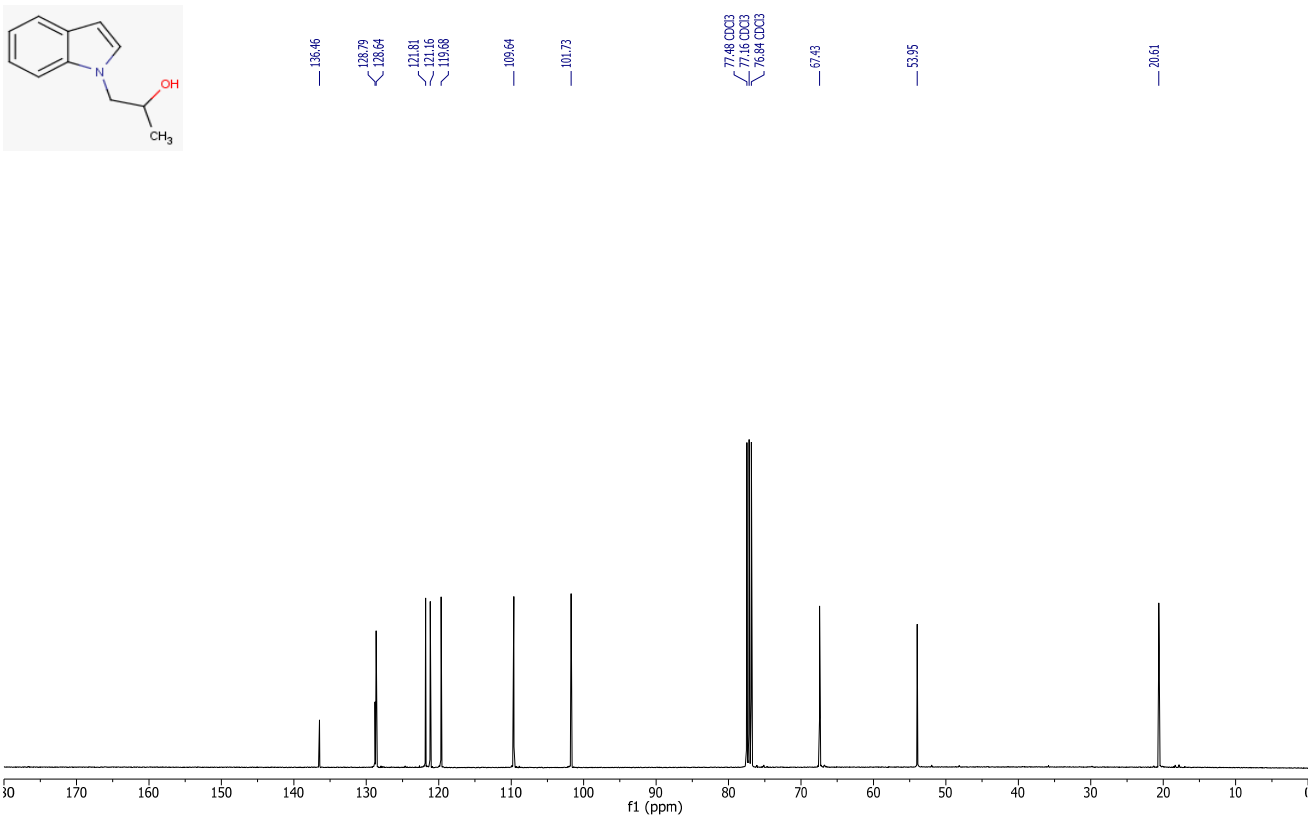
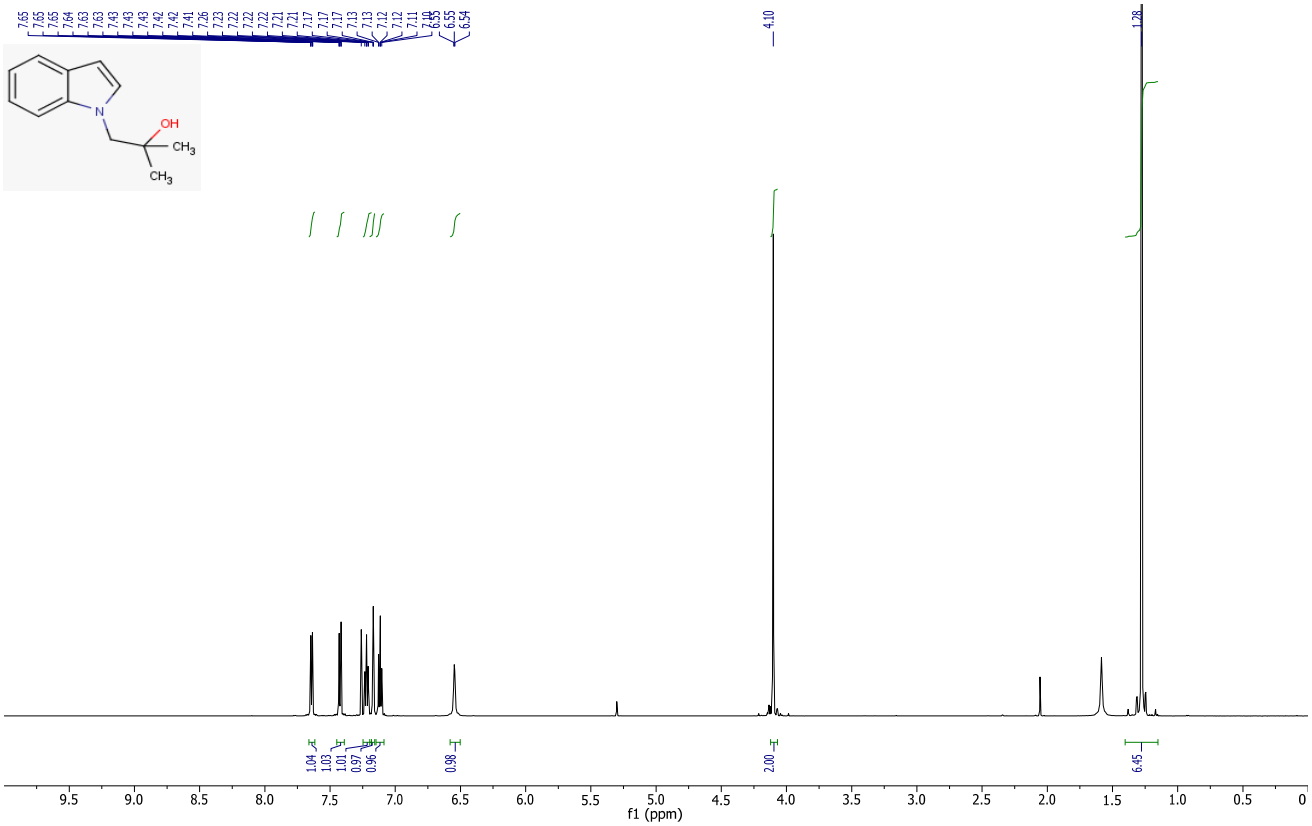
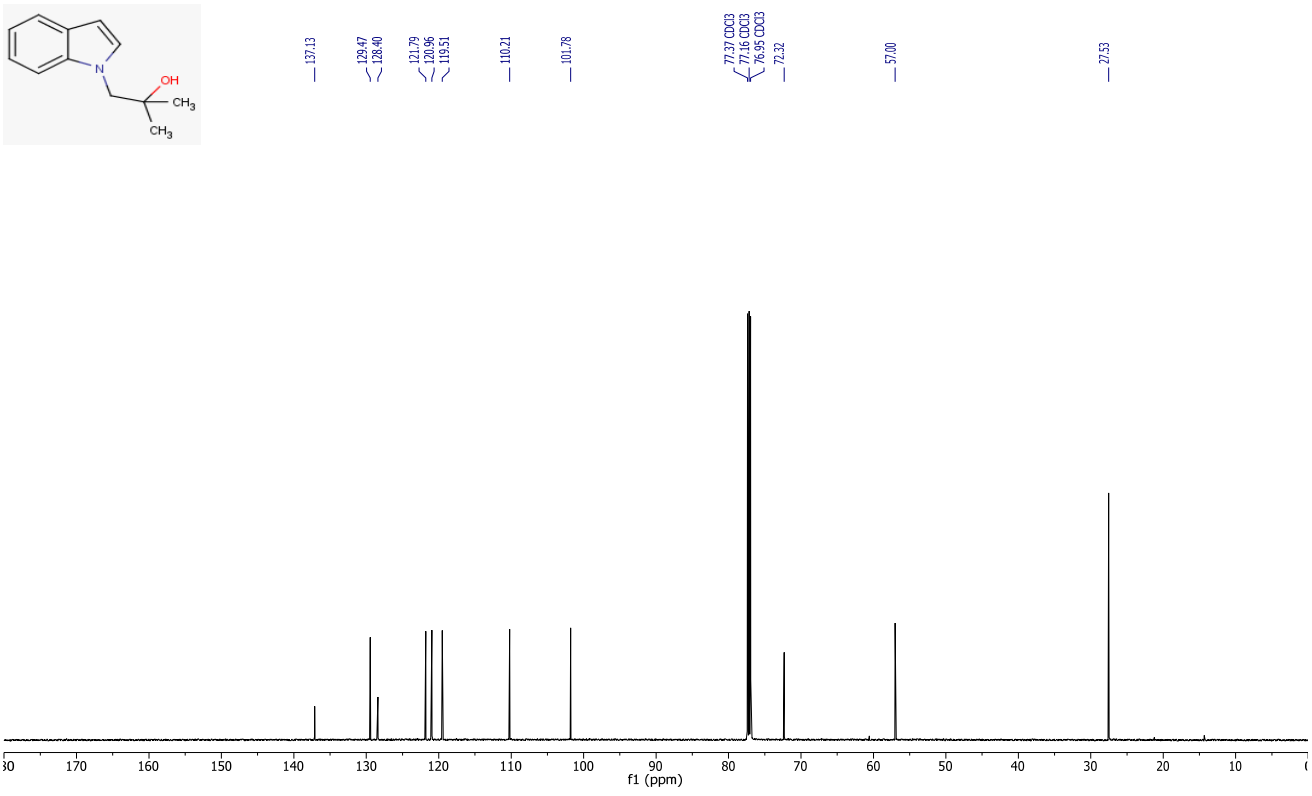
^{1}H and ^{13}C NMR of compound 1b



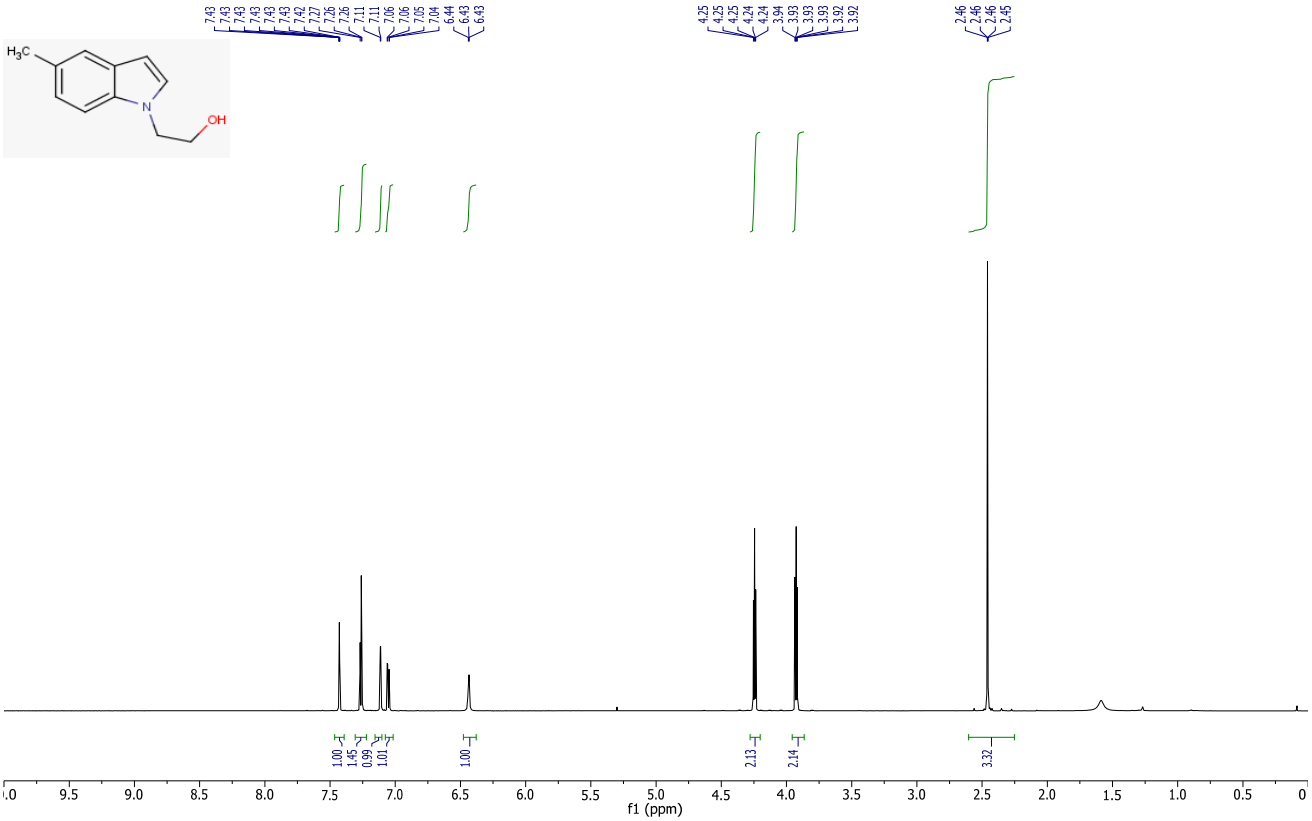


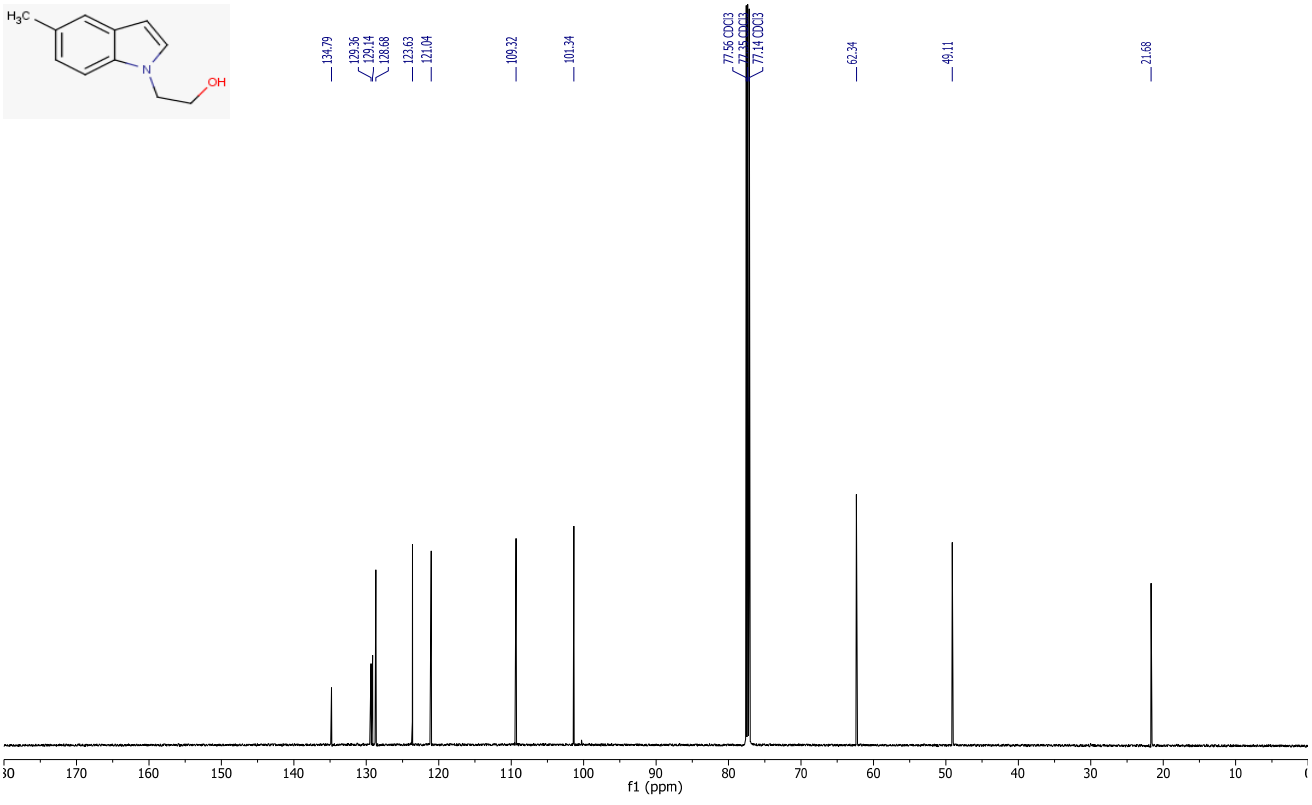
^{1}H and ^{13}C NMR of compound 1c



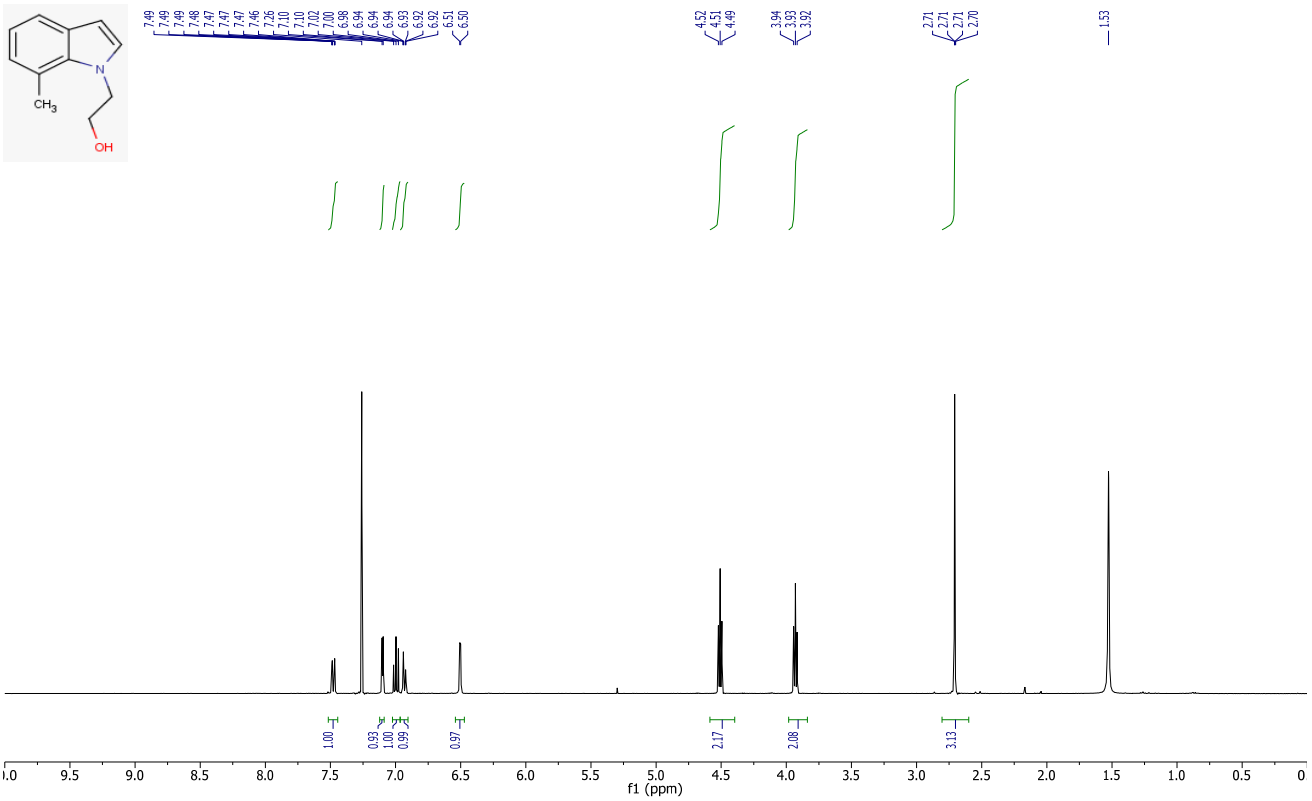


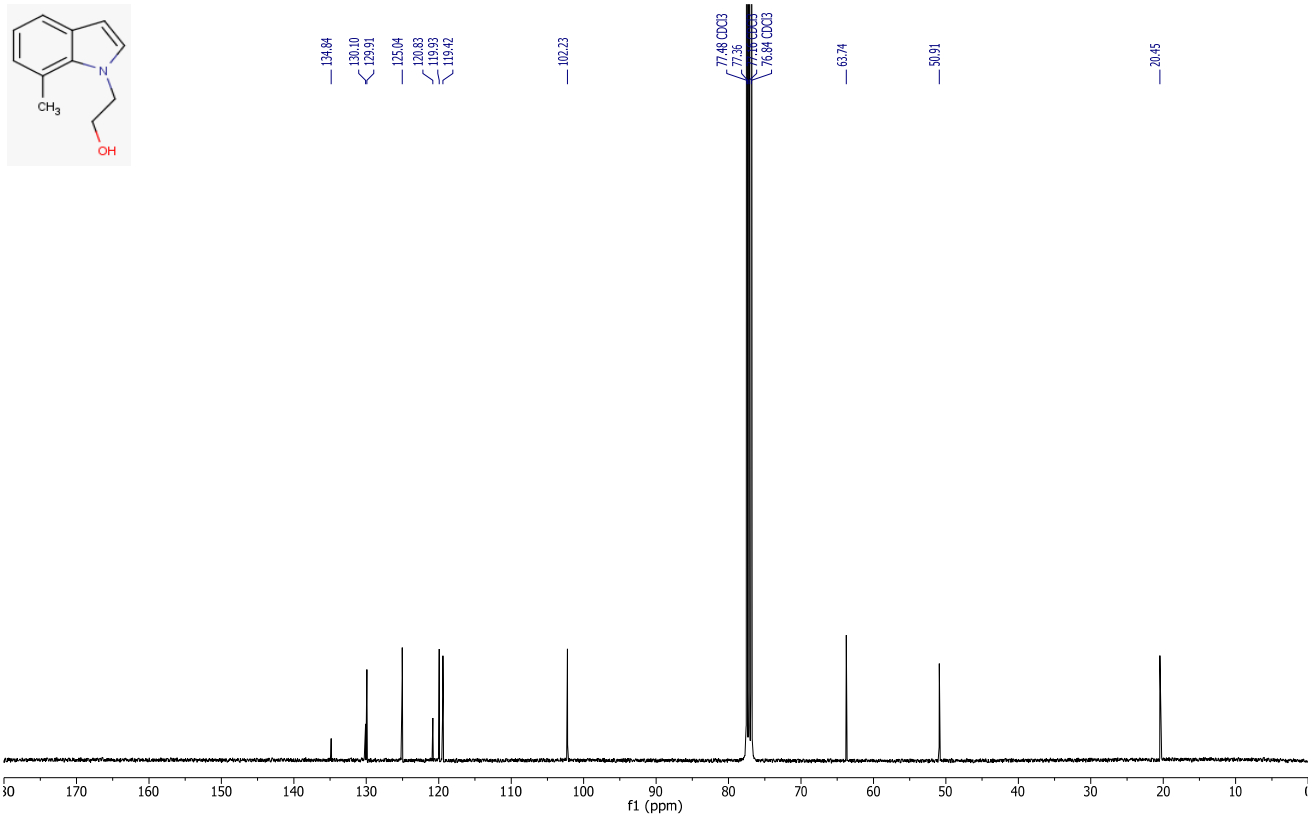
^{1}H and ^{13}C NMR of compound 1e



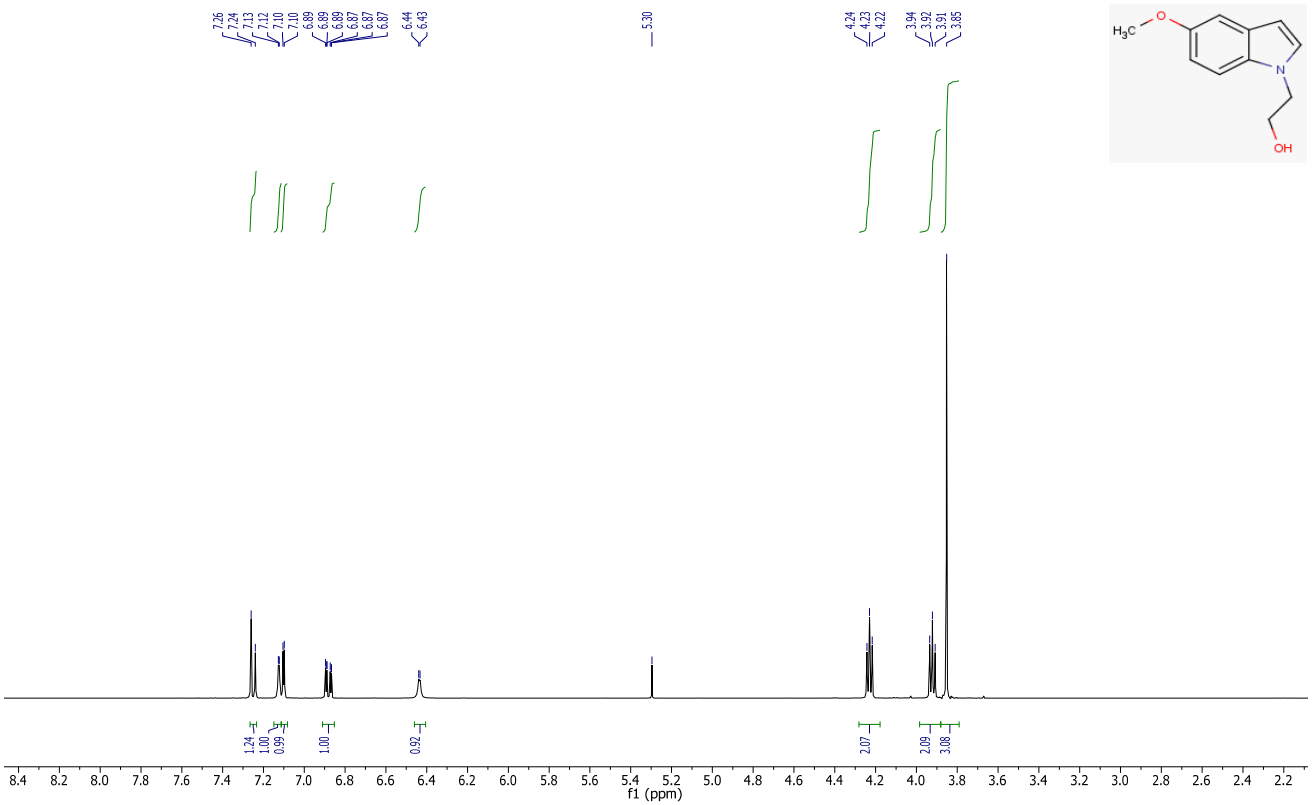


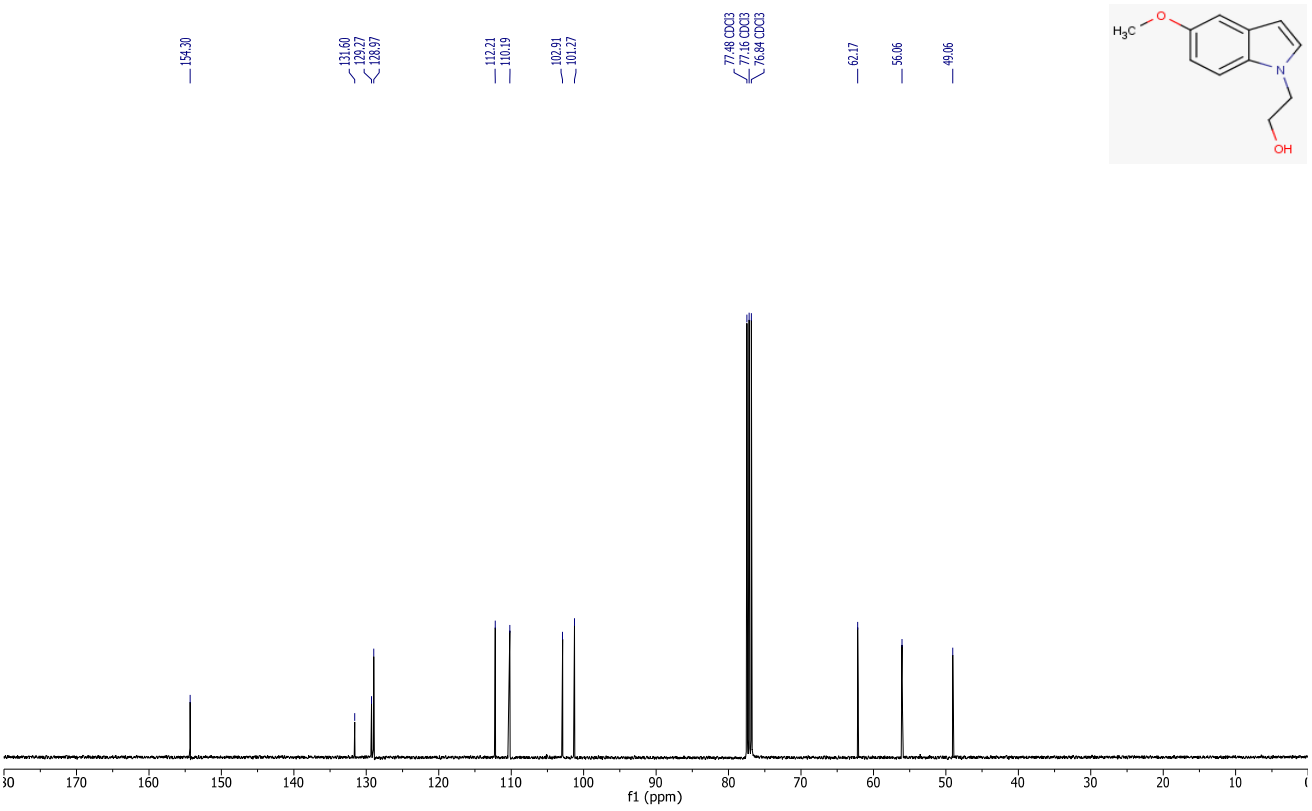
^{1}H and ^{13}C NMR of compound 1f



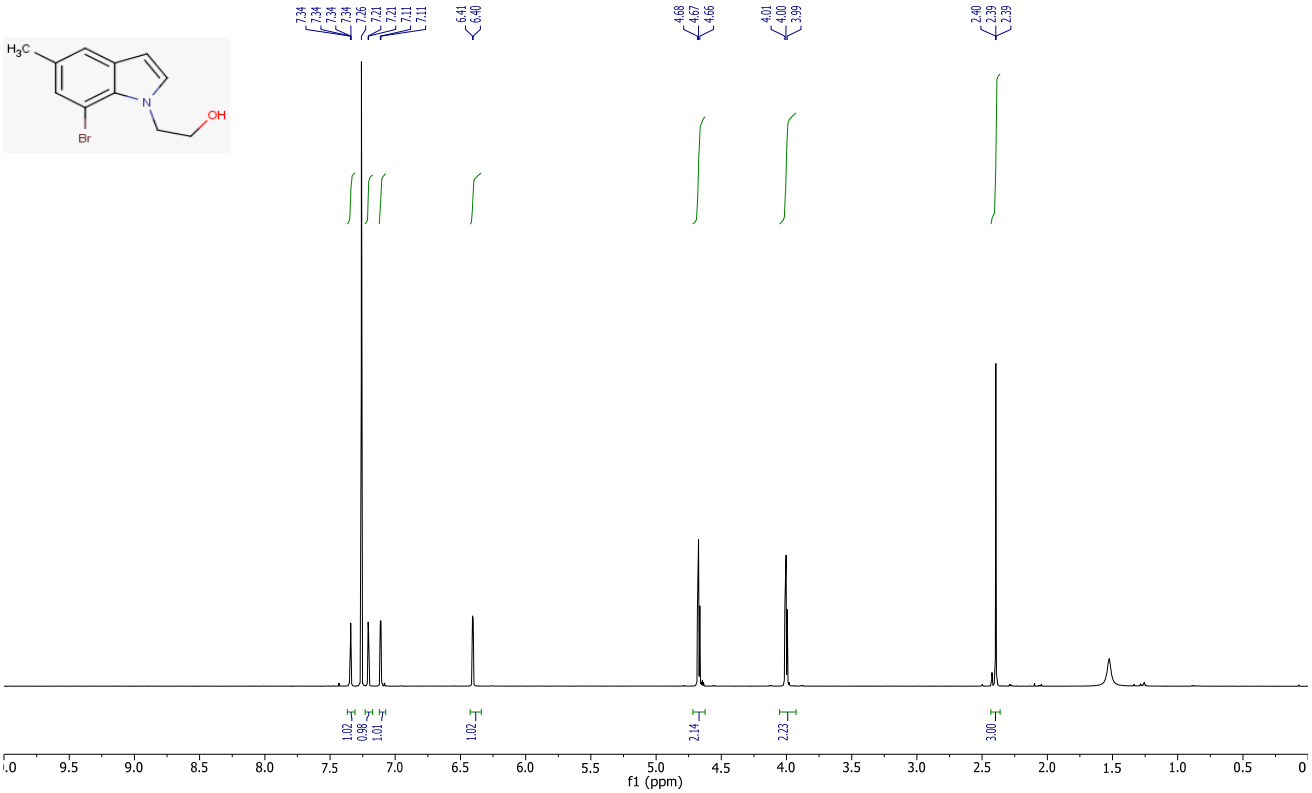


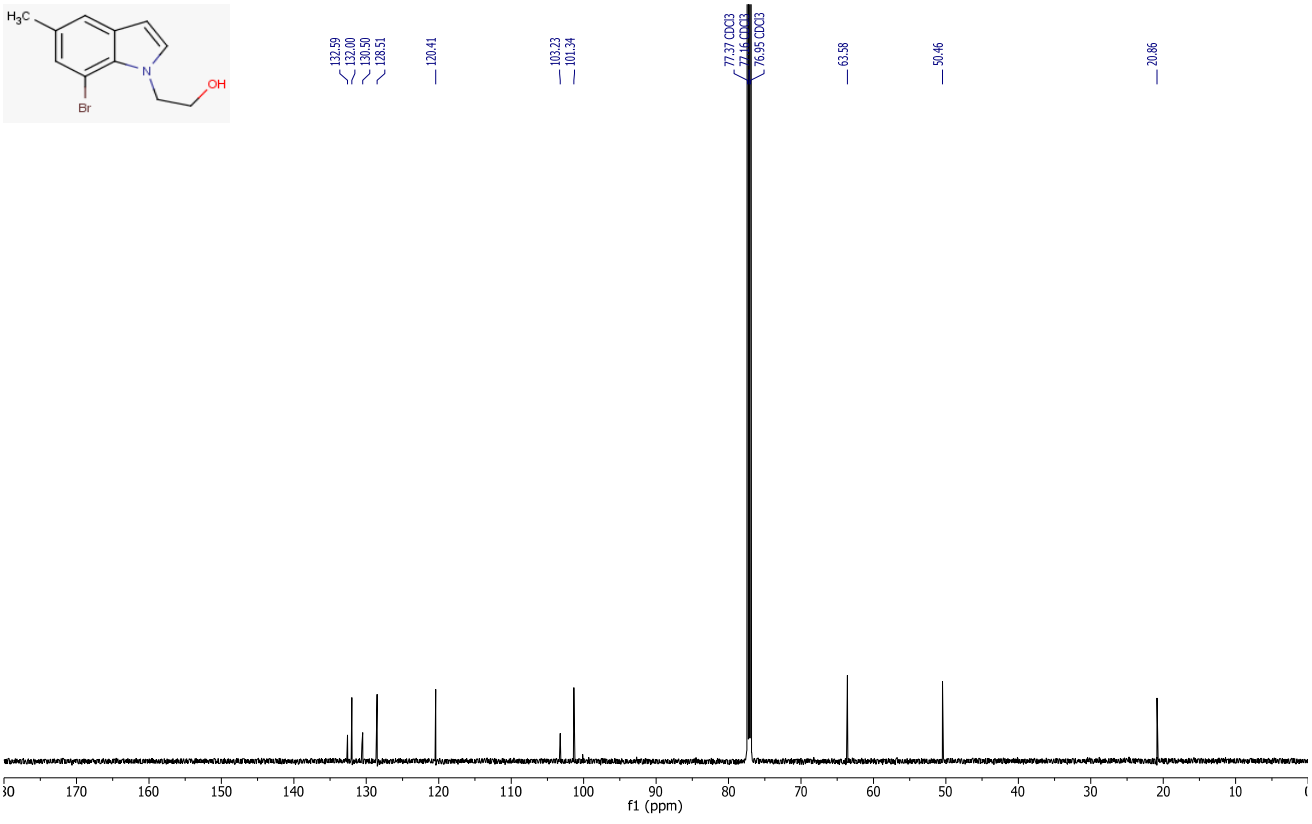
^{1}H and ^{13}C NMR of compound 1g





^{1}H and ^{13}C NMR of compound 1h





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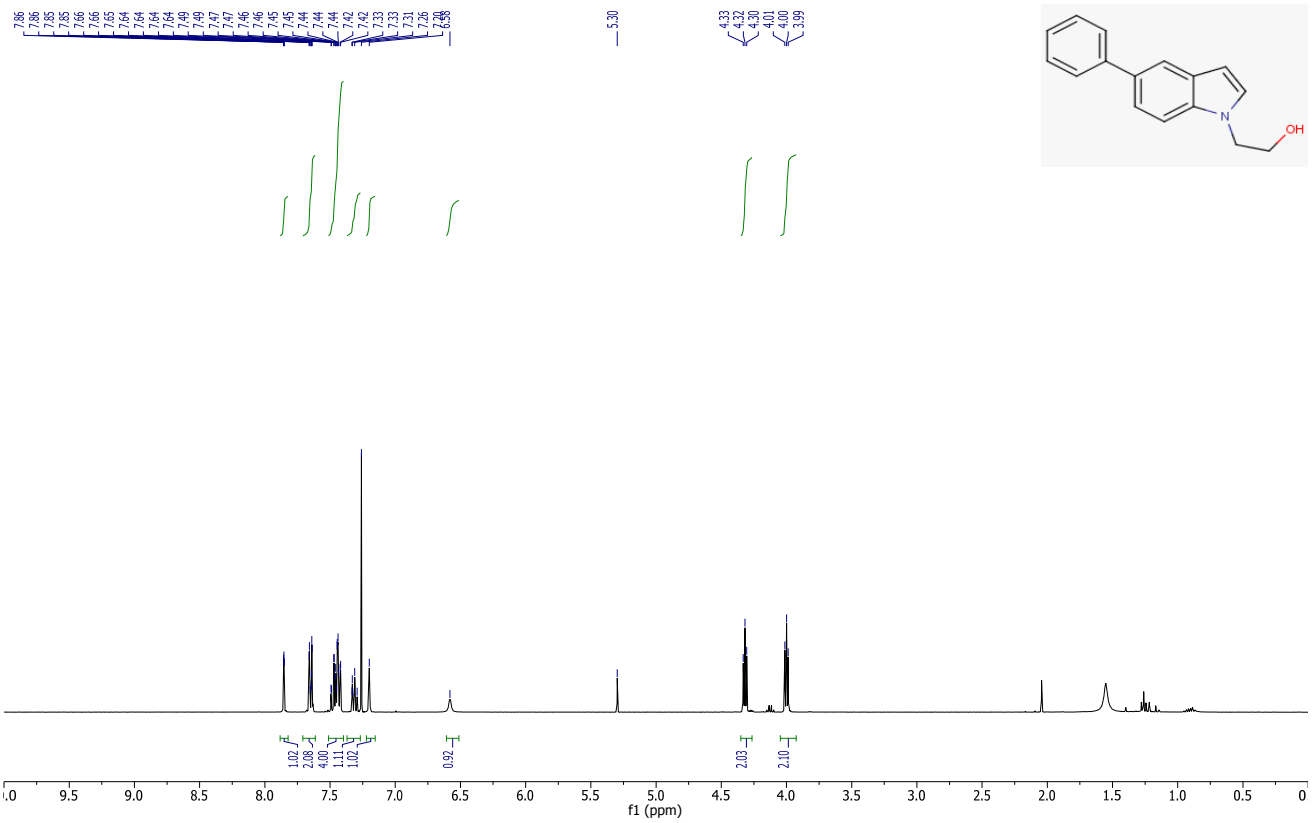
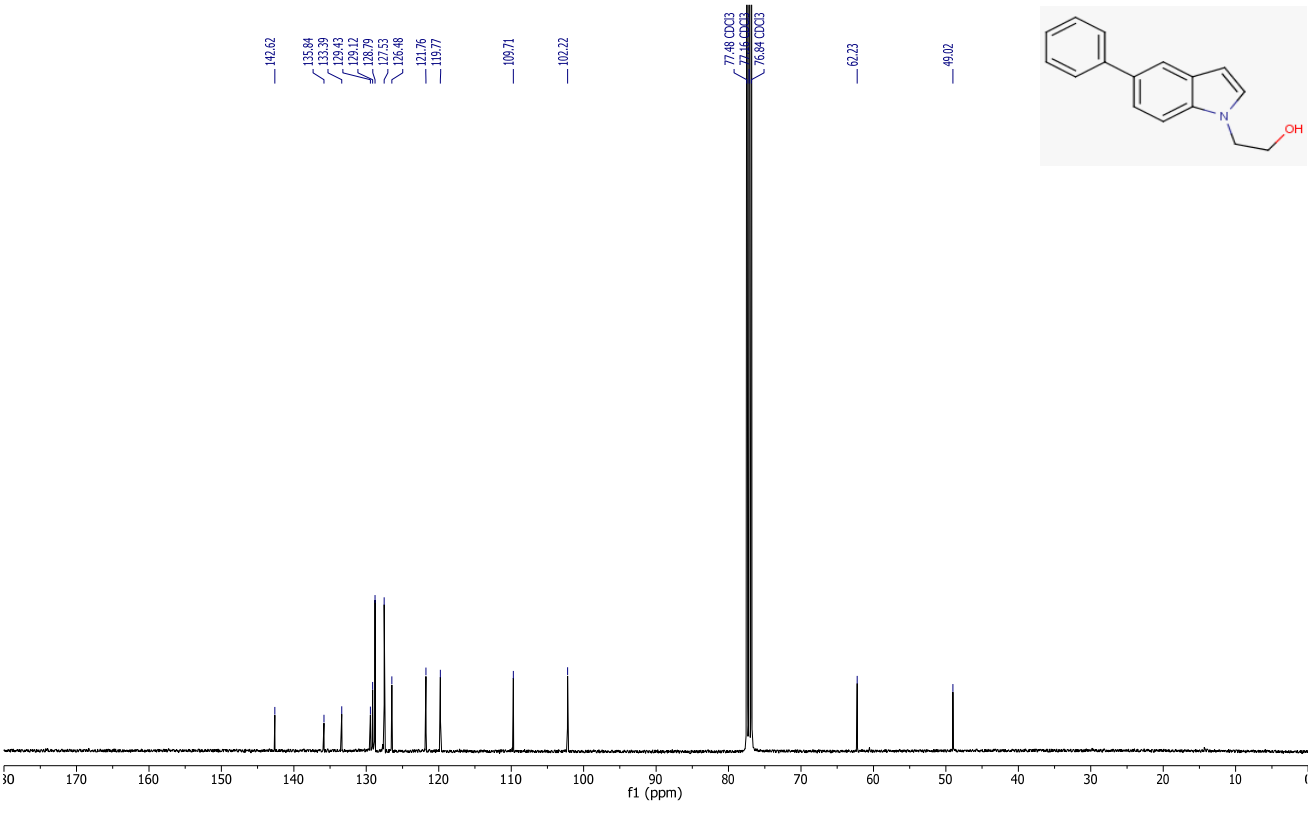
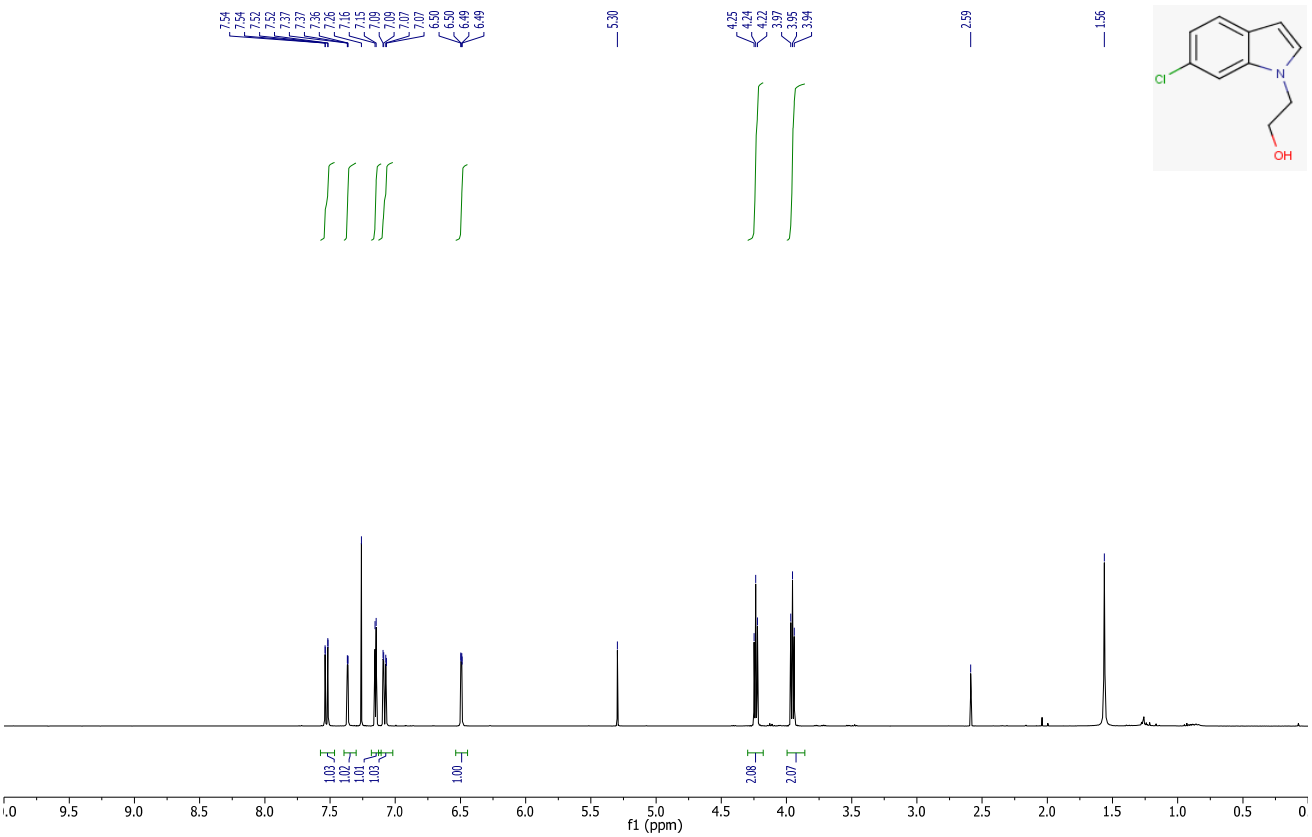
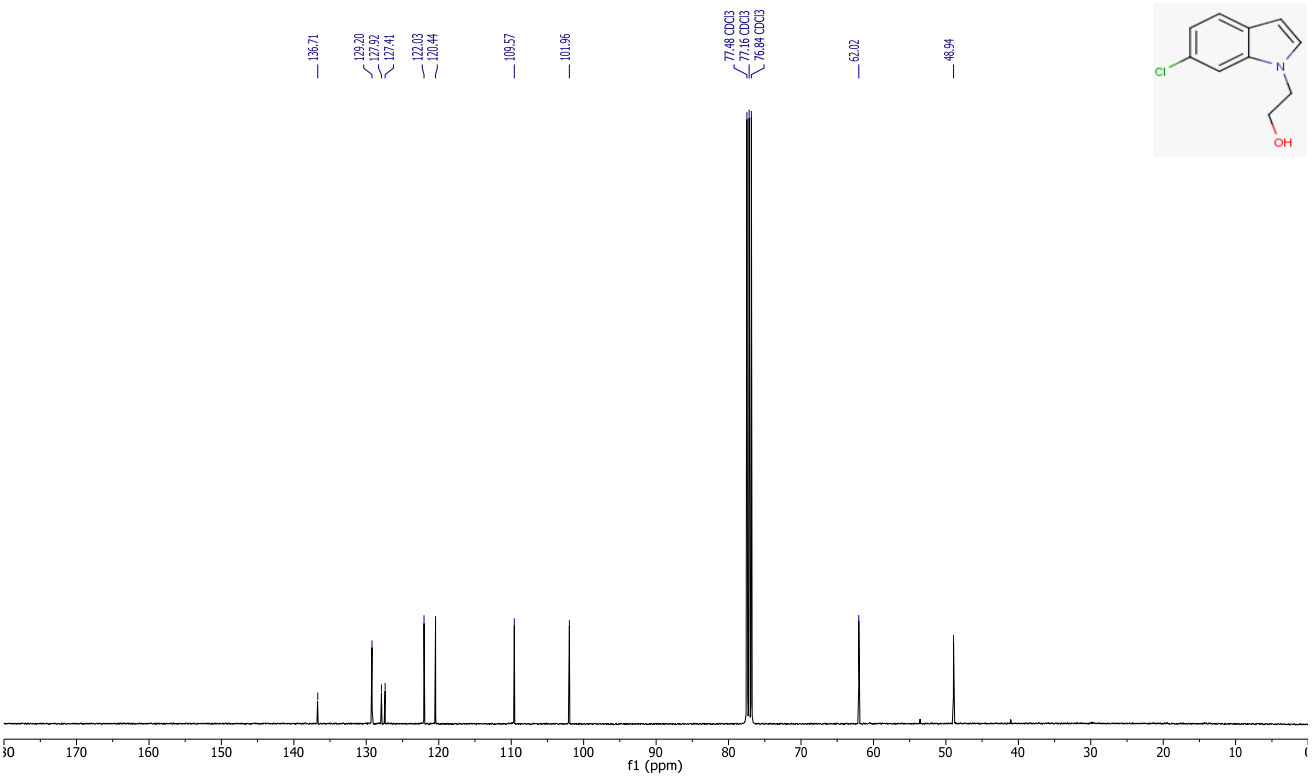


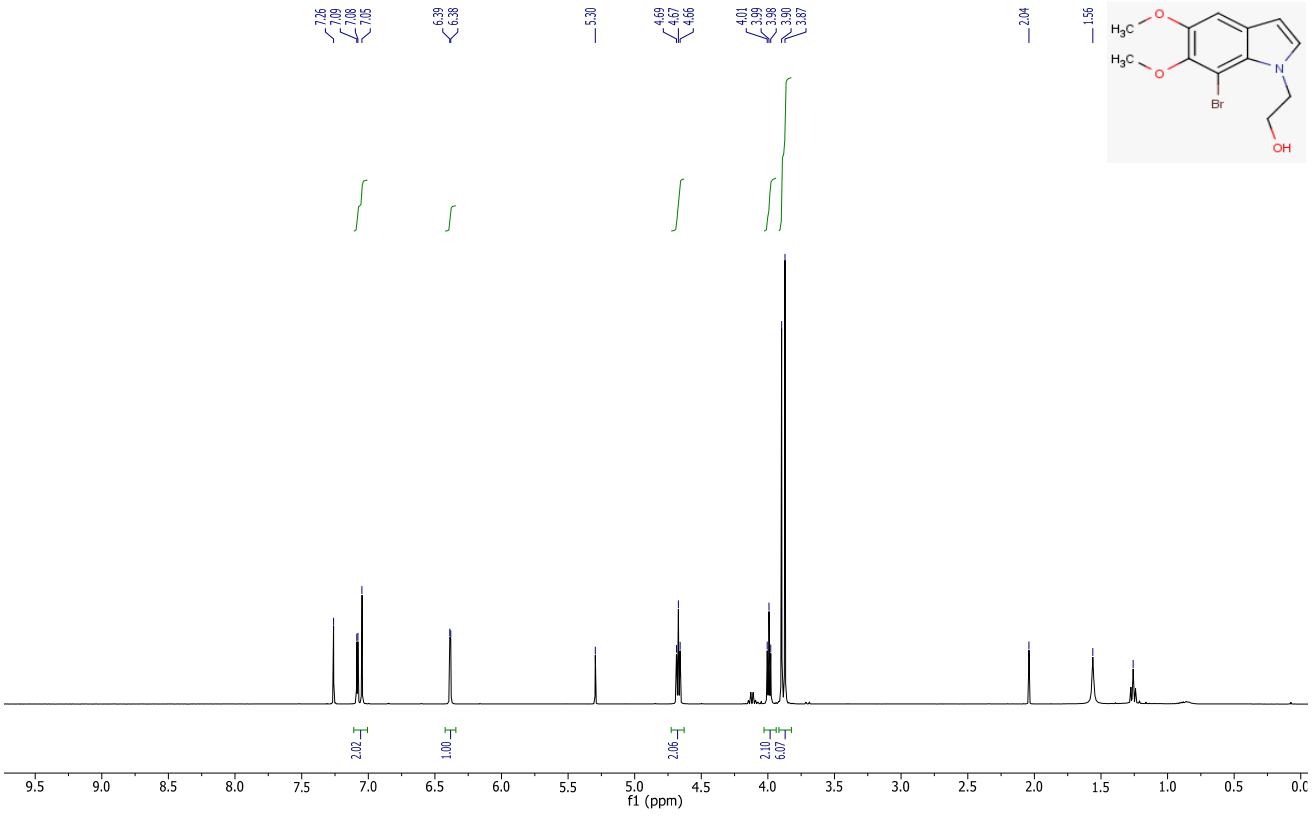


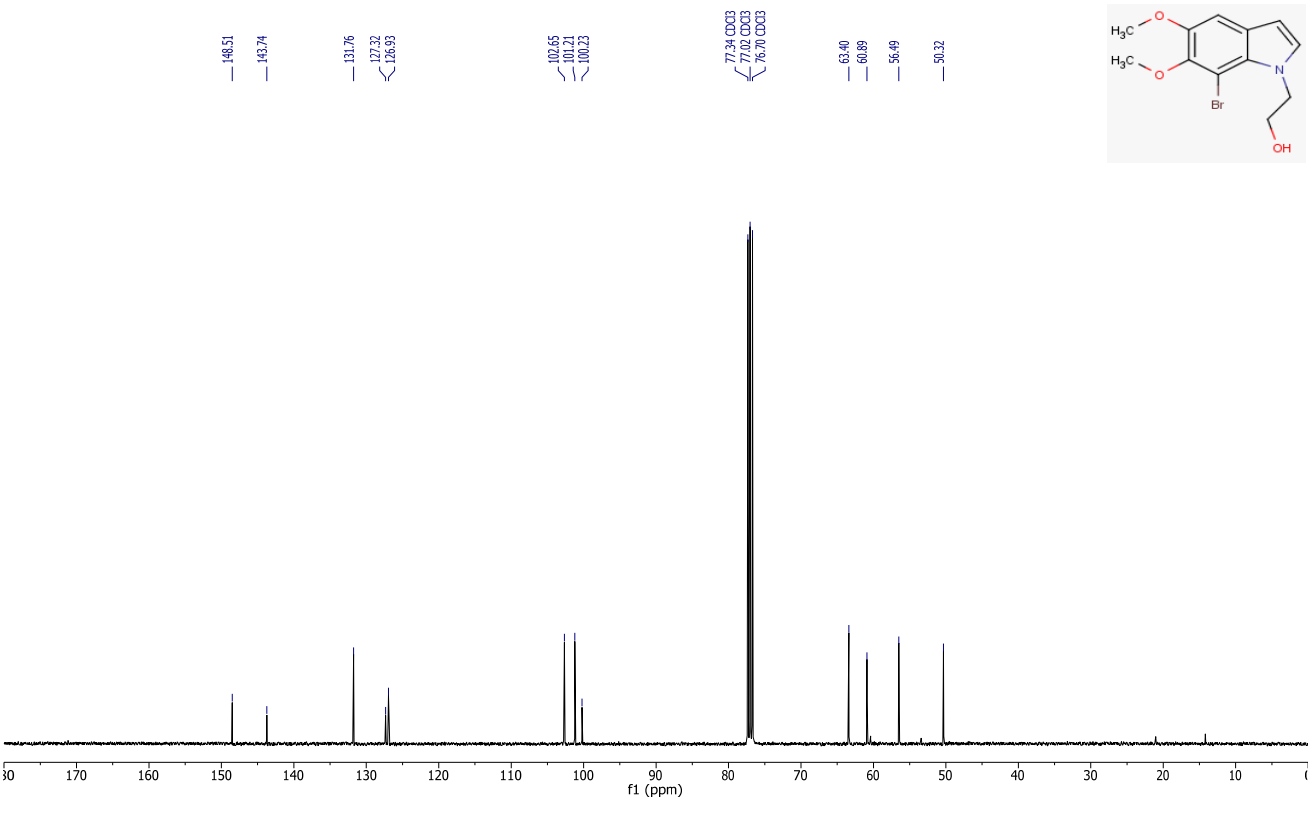
^{1}H and ^{13}C NMR of compound 1k



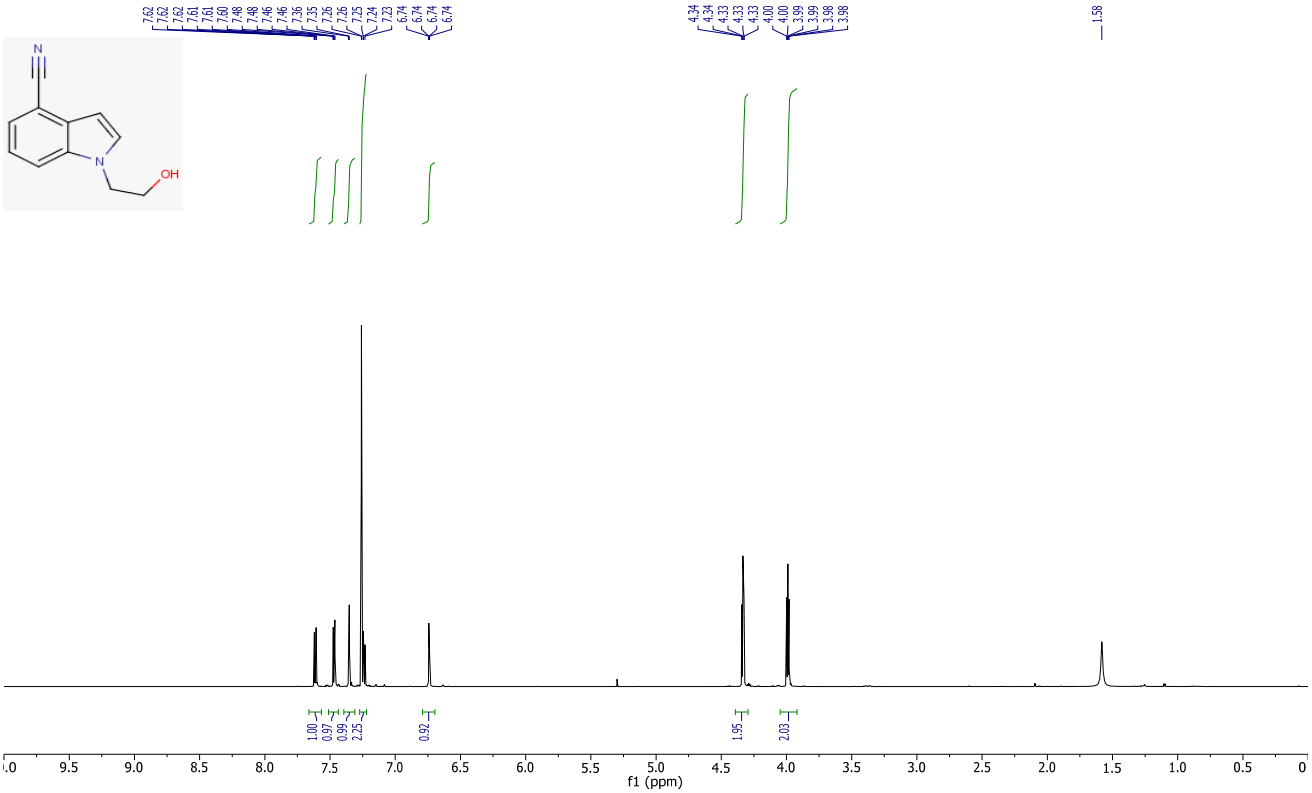


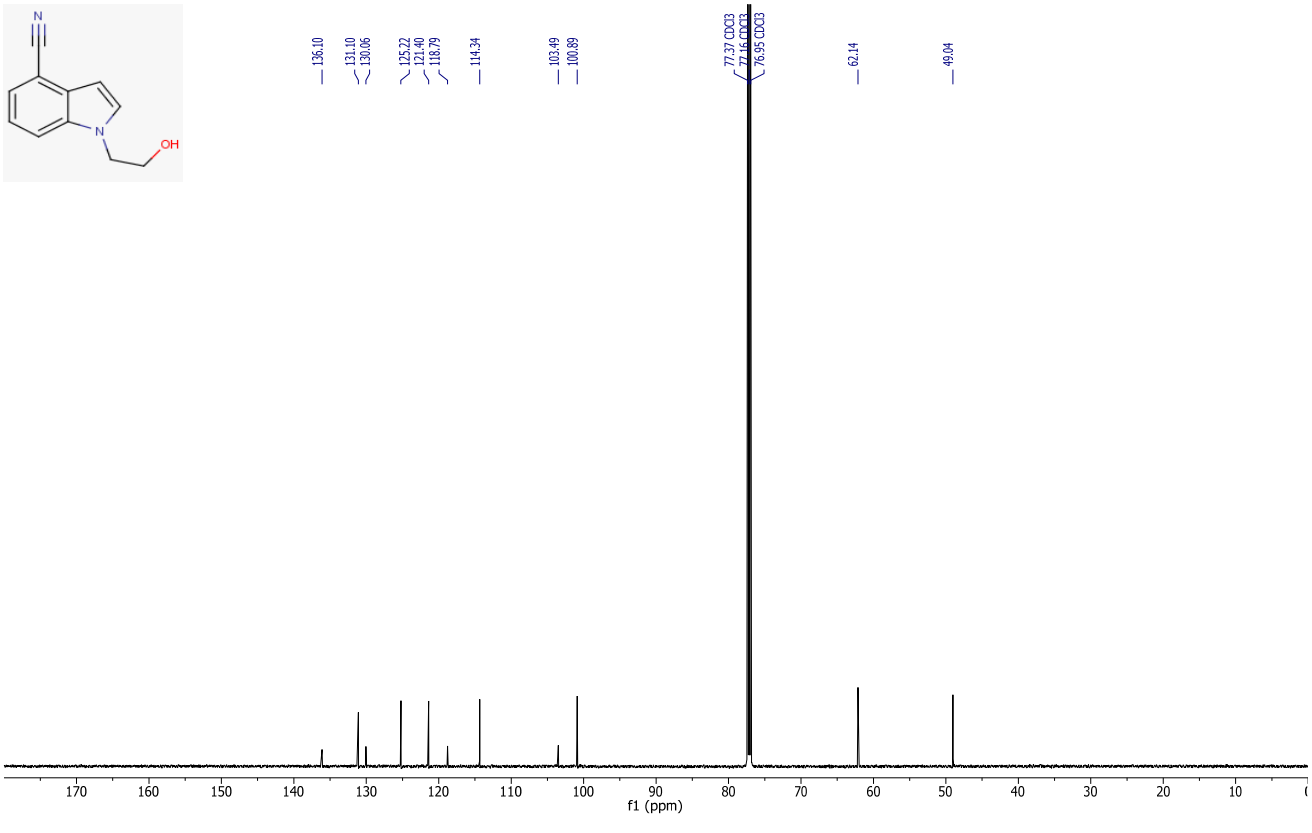
^{1}H and ^{13}C NMR of compound 1l





^{1}H and ^{13}C NMR of compound 1m





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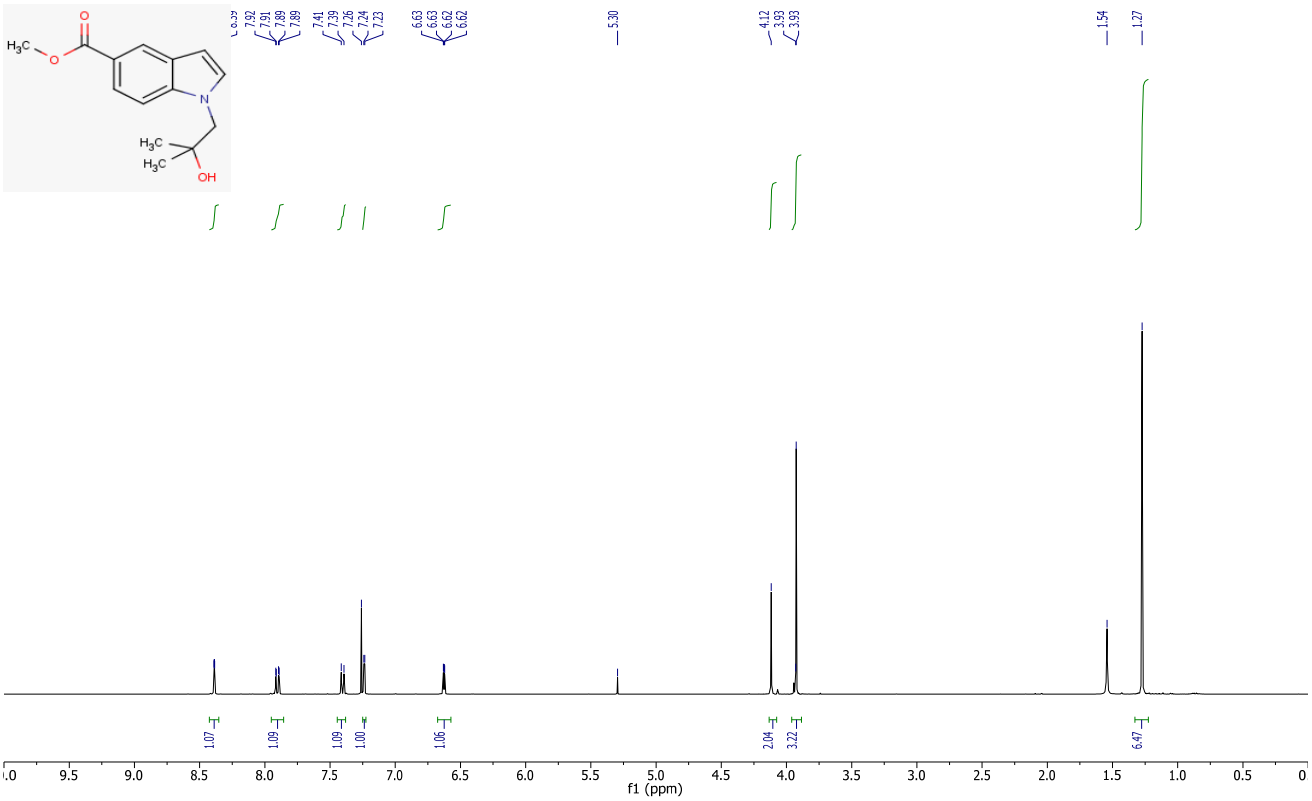
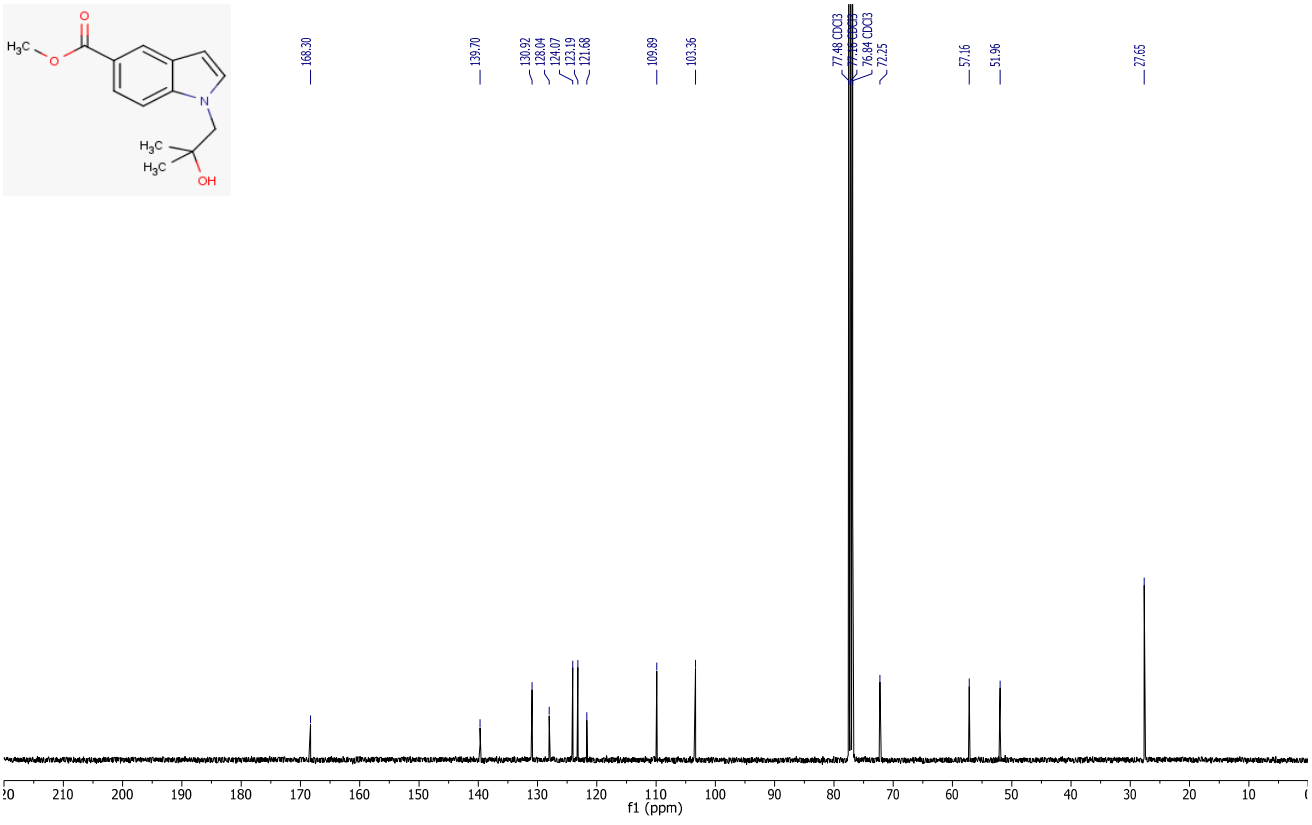
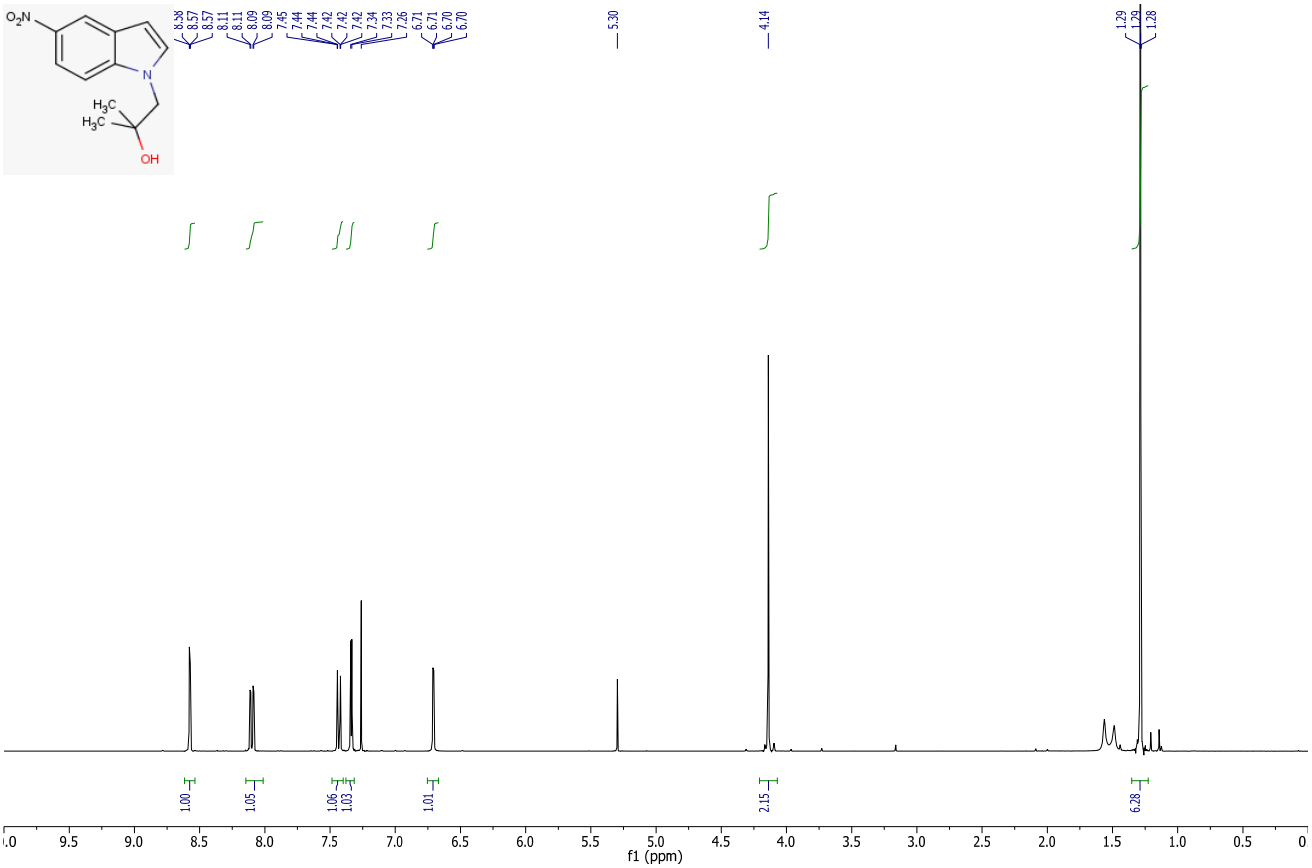
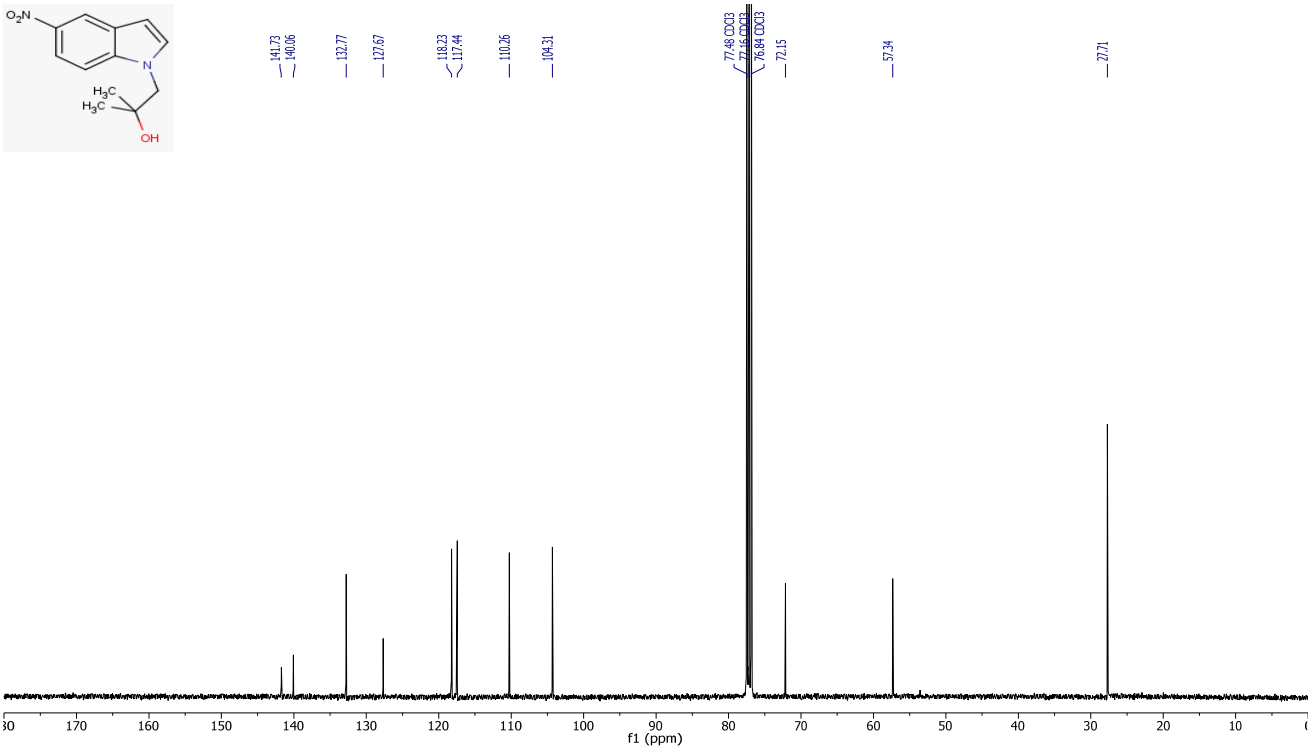


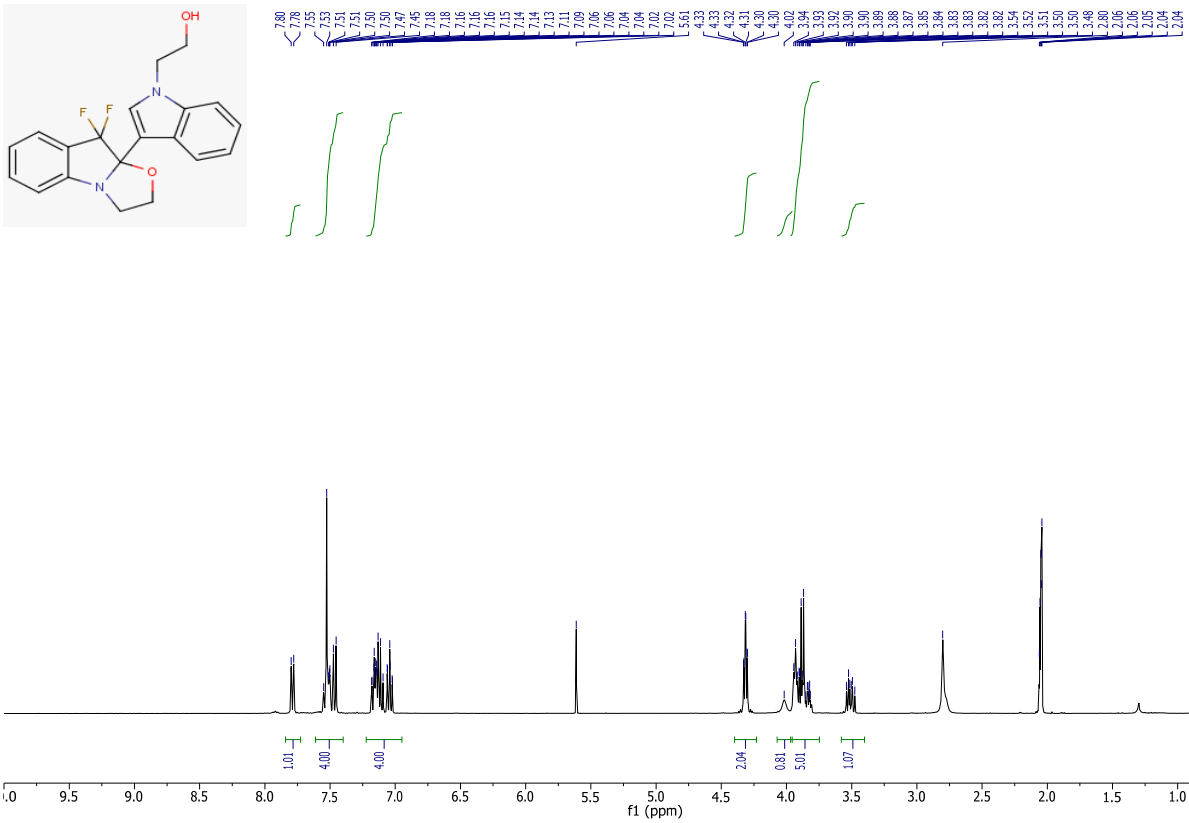


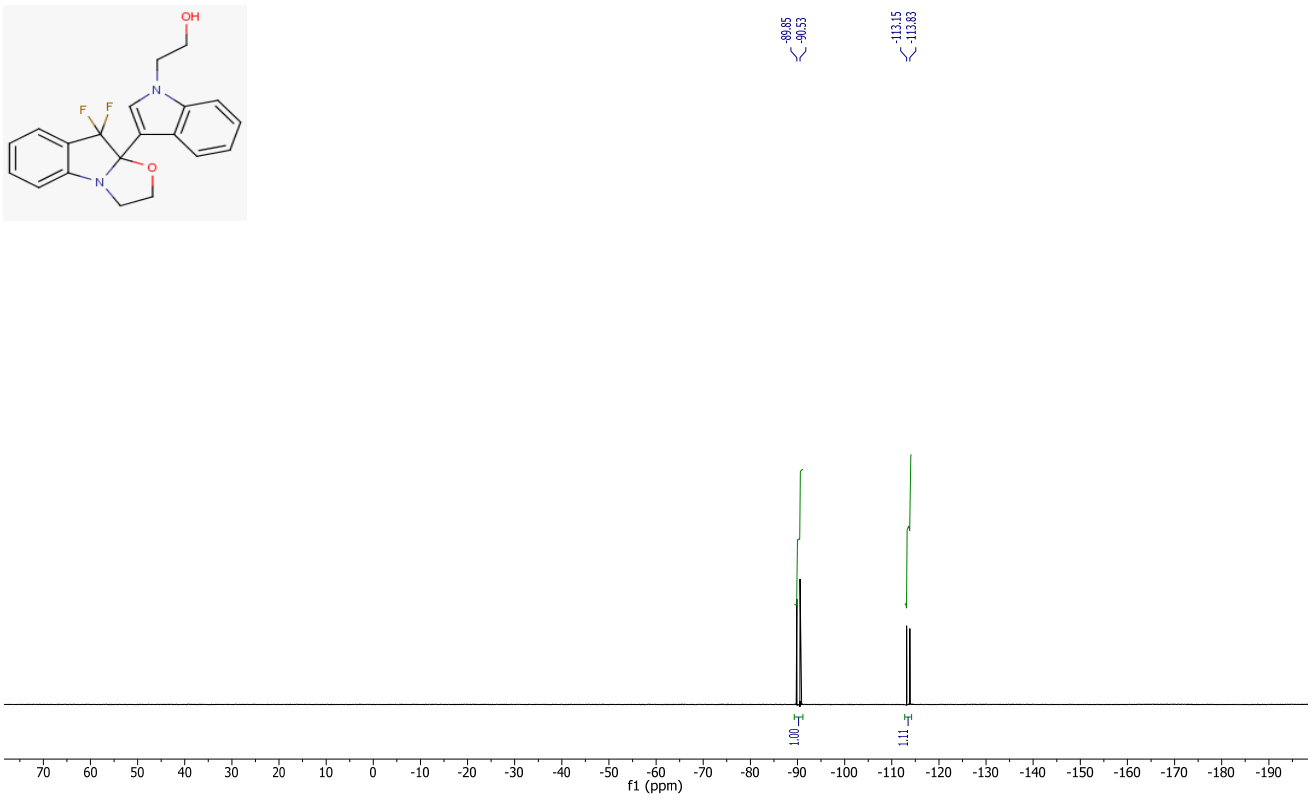
^{1}H and ^{13}C NMR of compound 1o



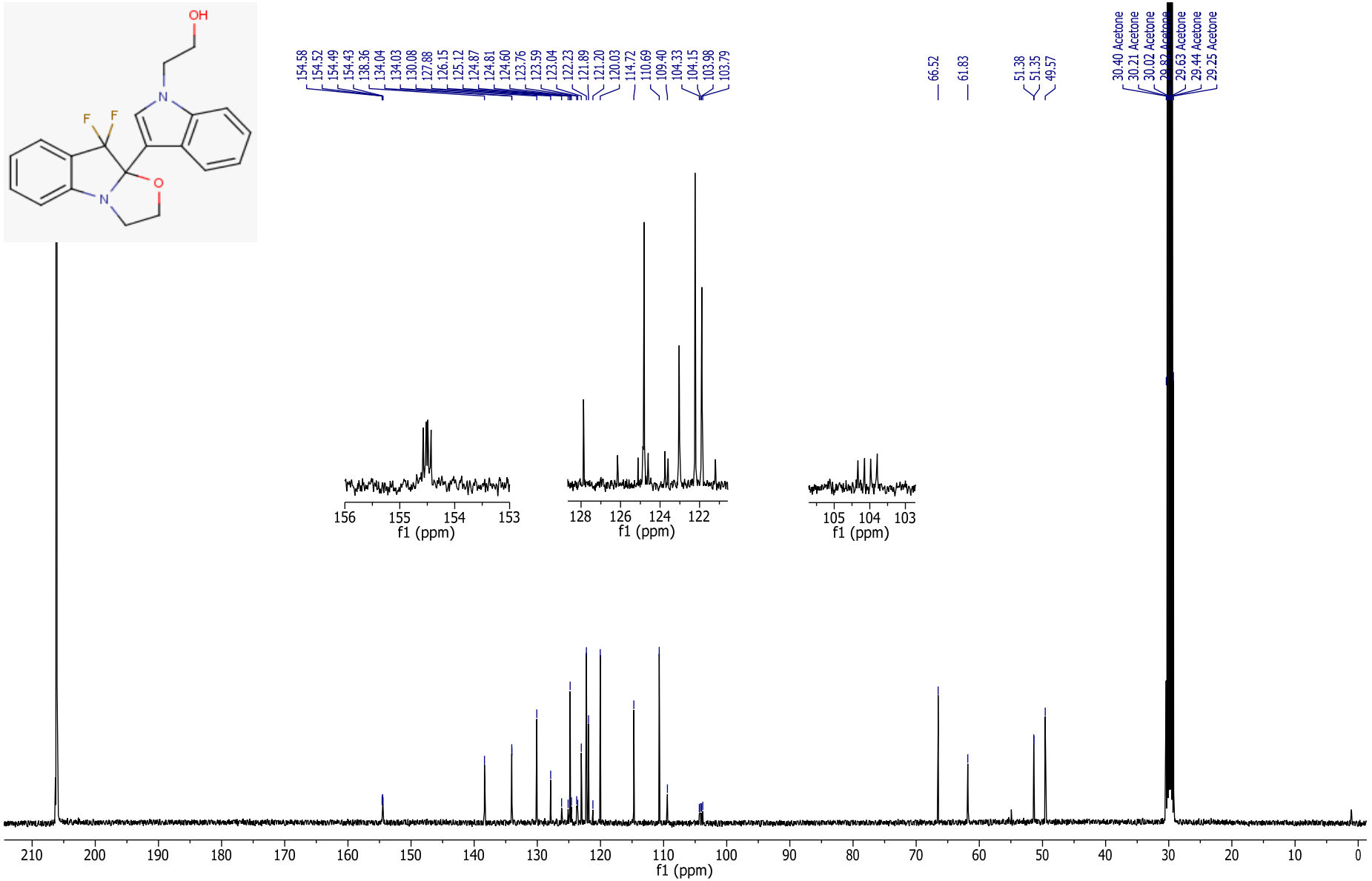


^{1}H and ^{19}F NMR of compound 2a

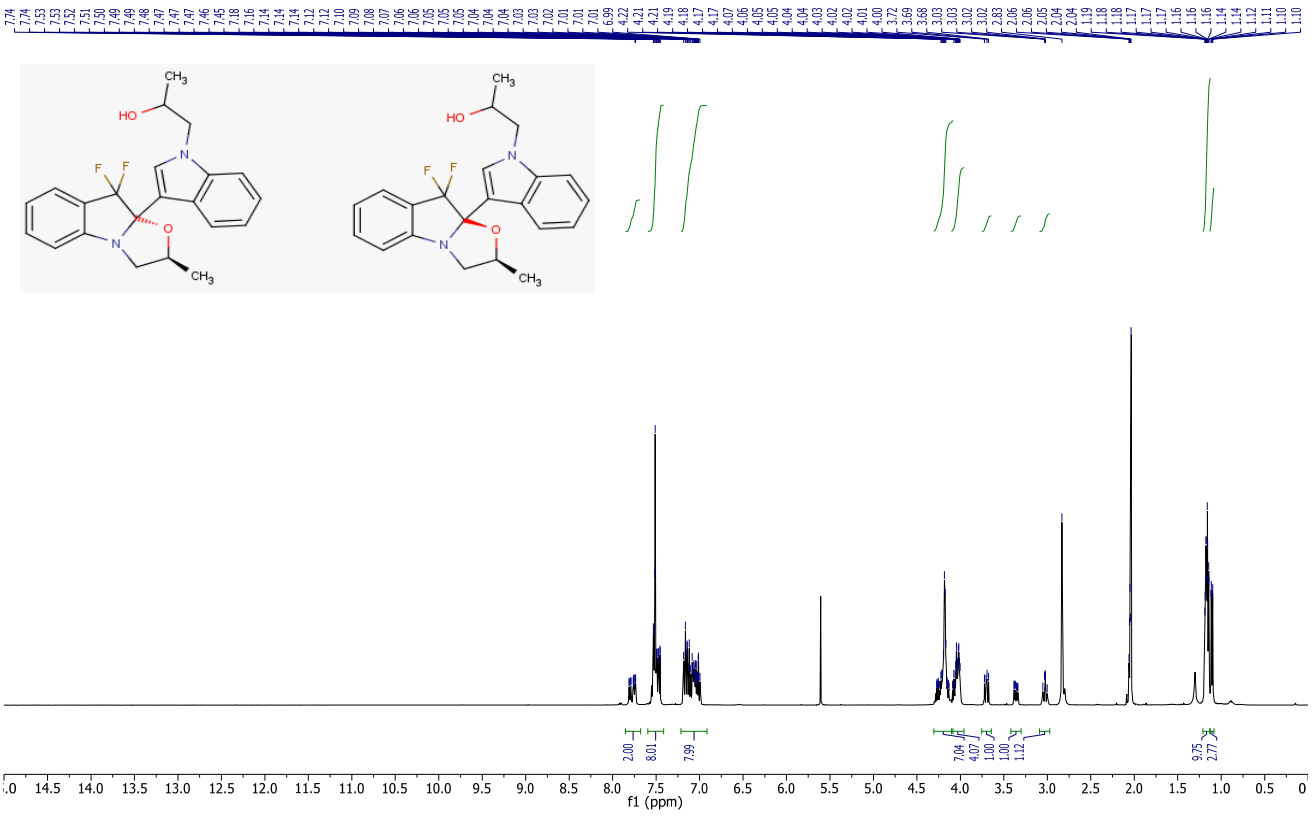


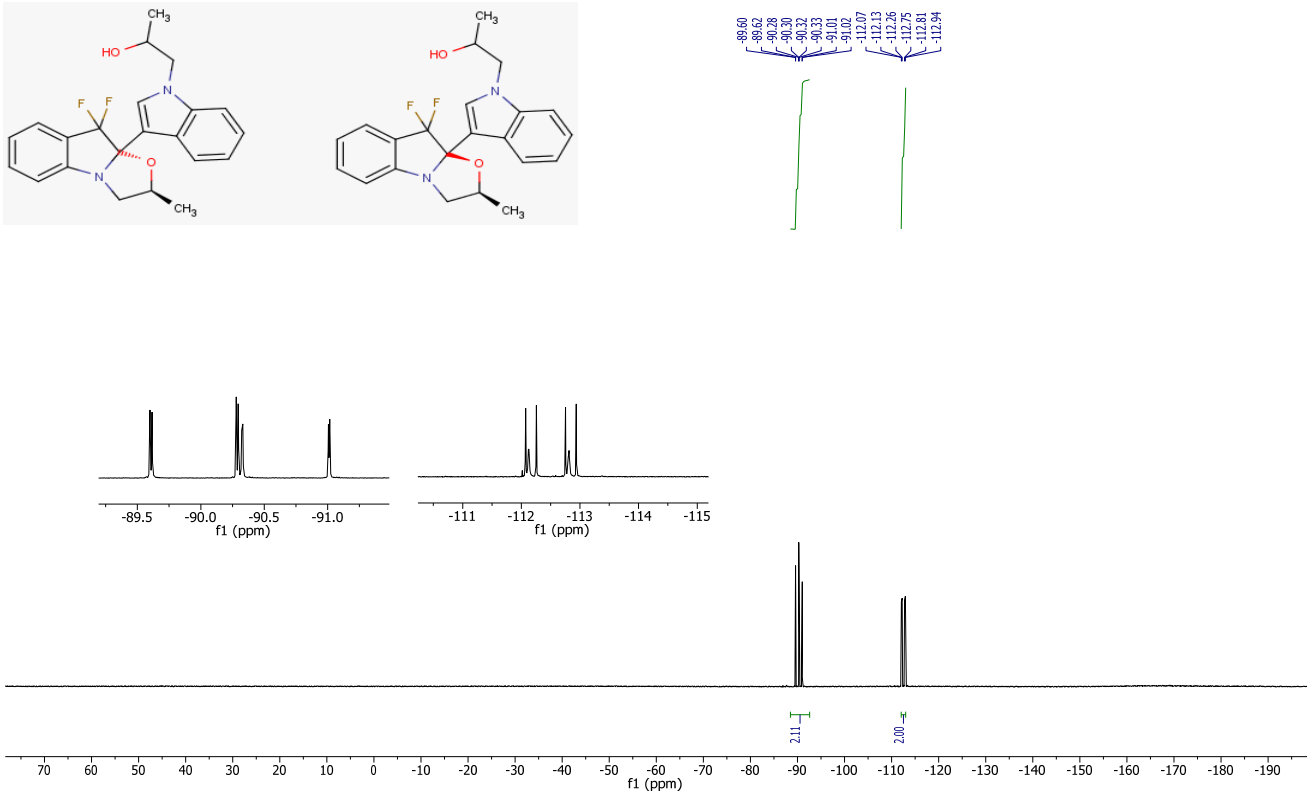


^{13}C NMR of compound 2a



^{1}H and ^{19}F NMR of compound 2b





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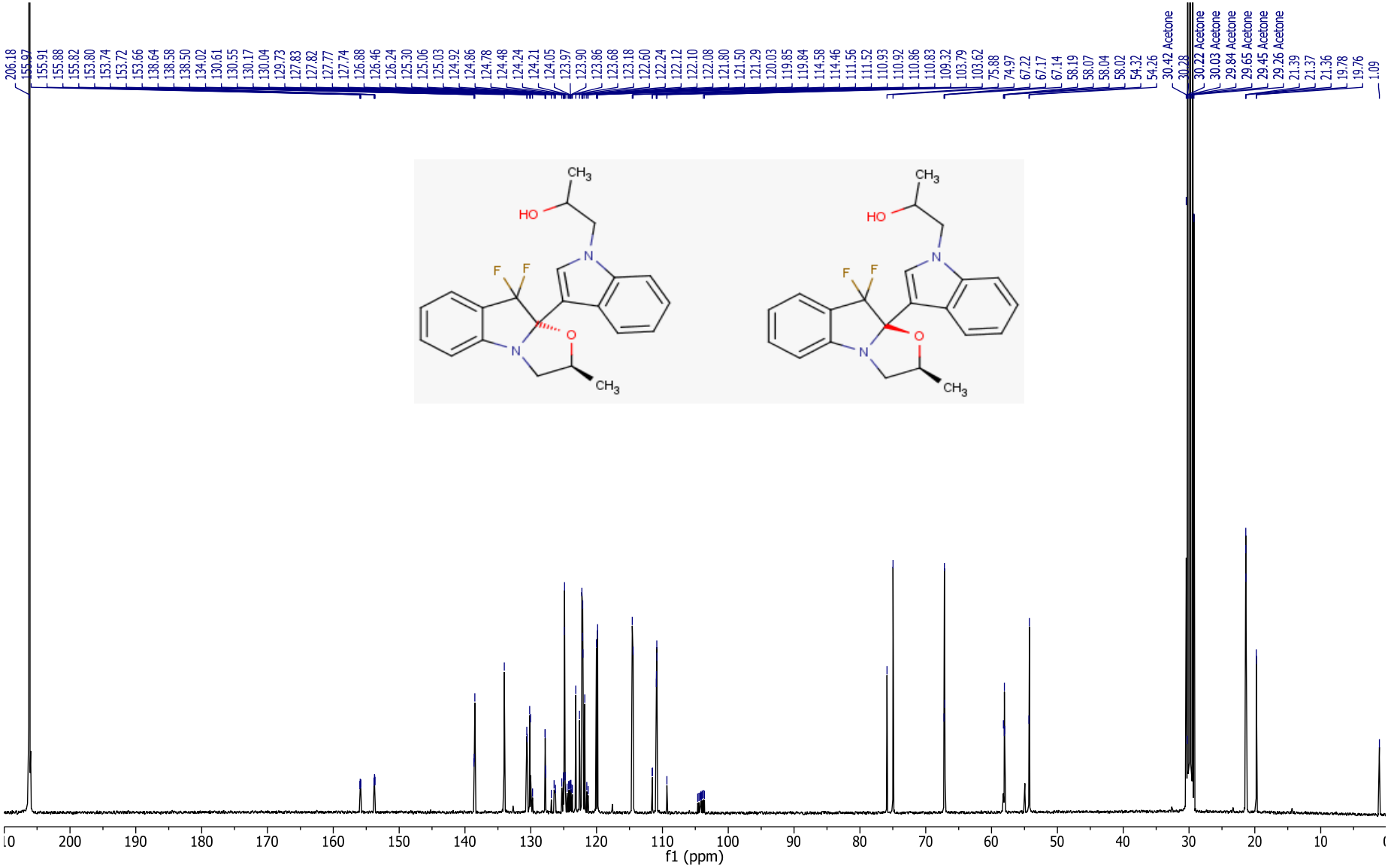
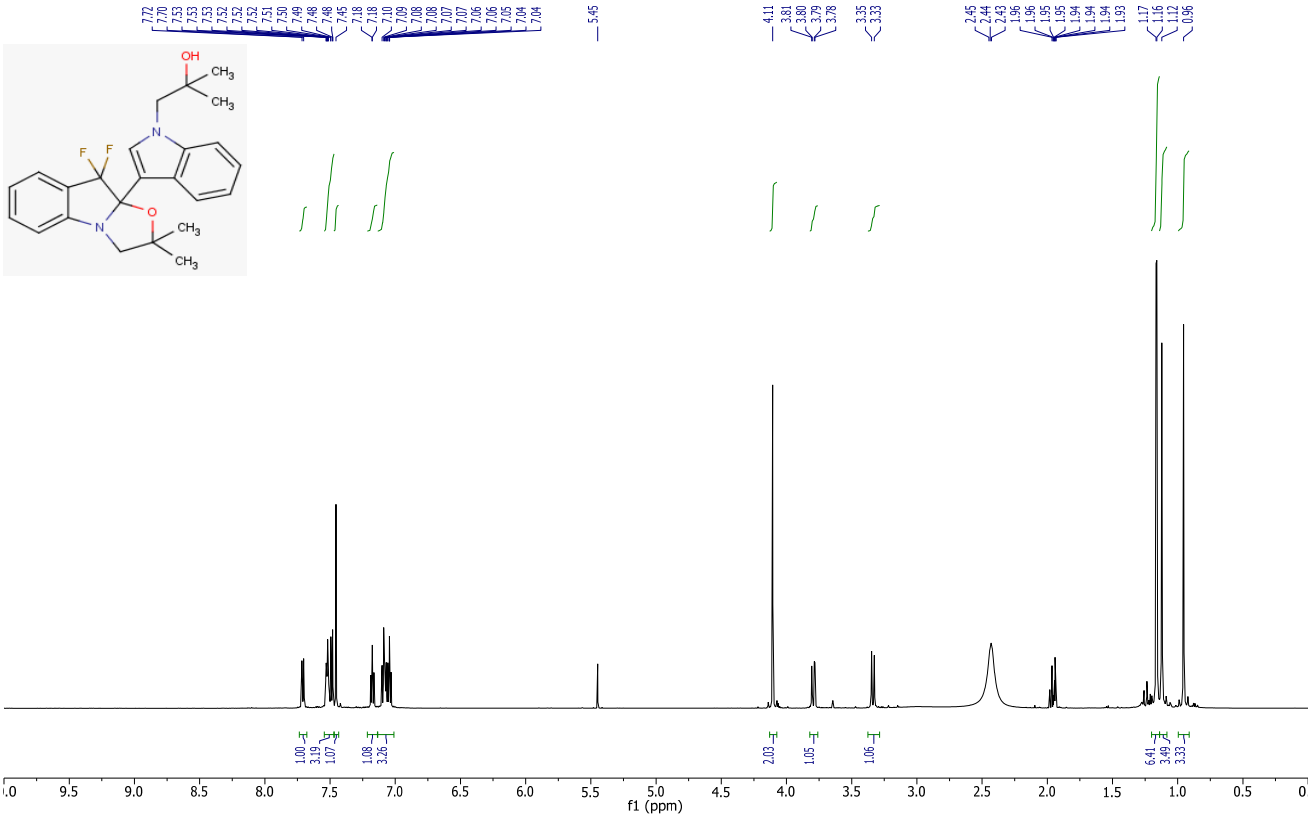
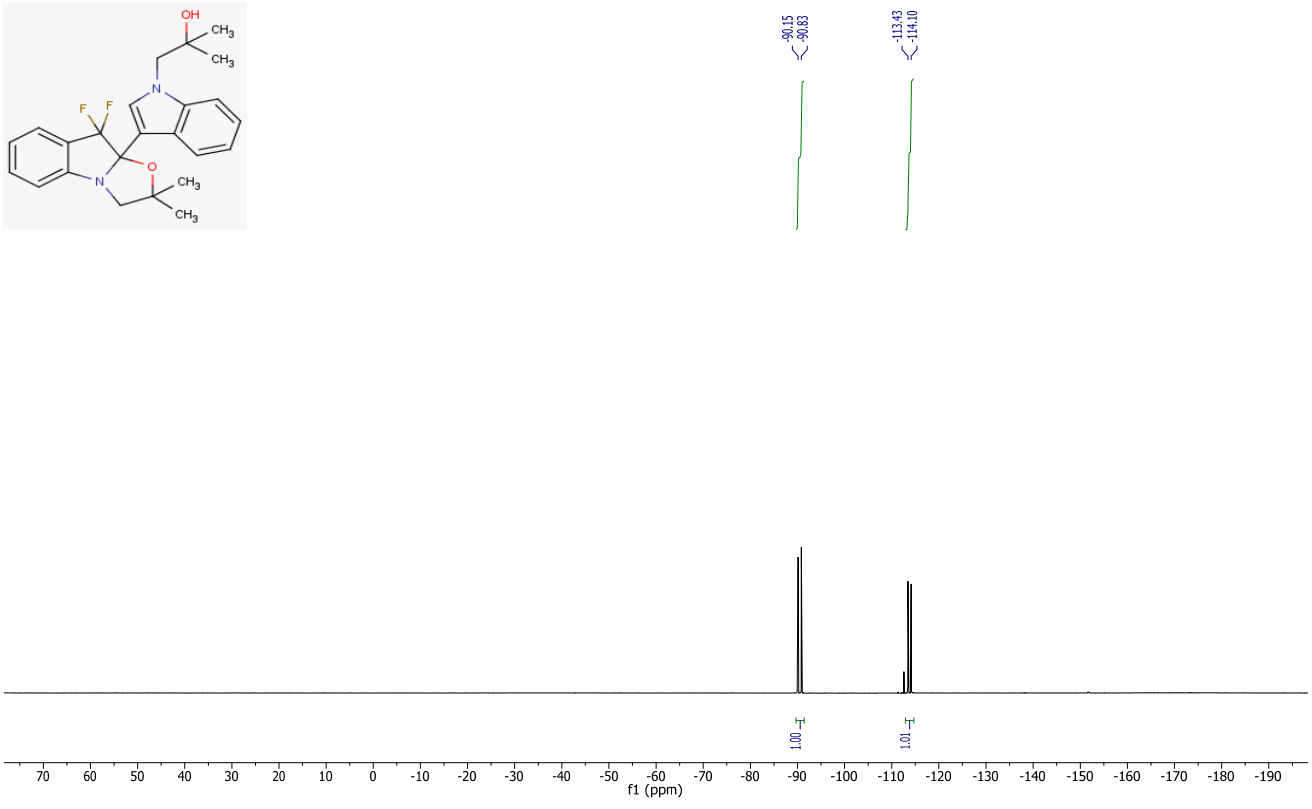
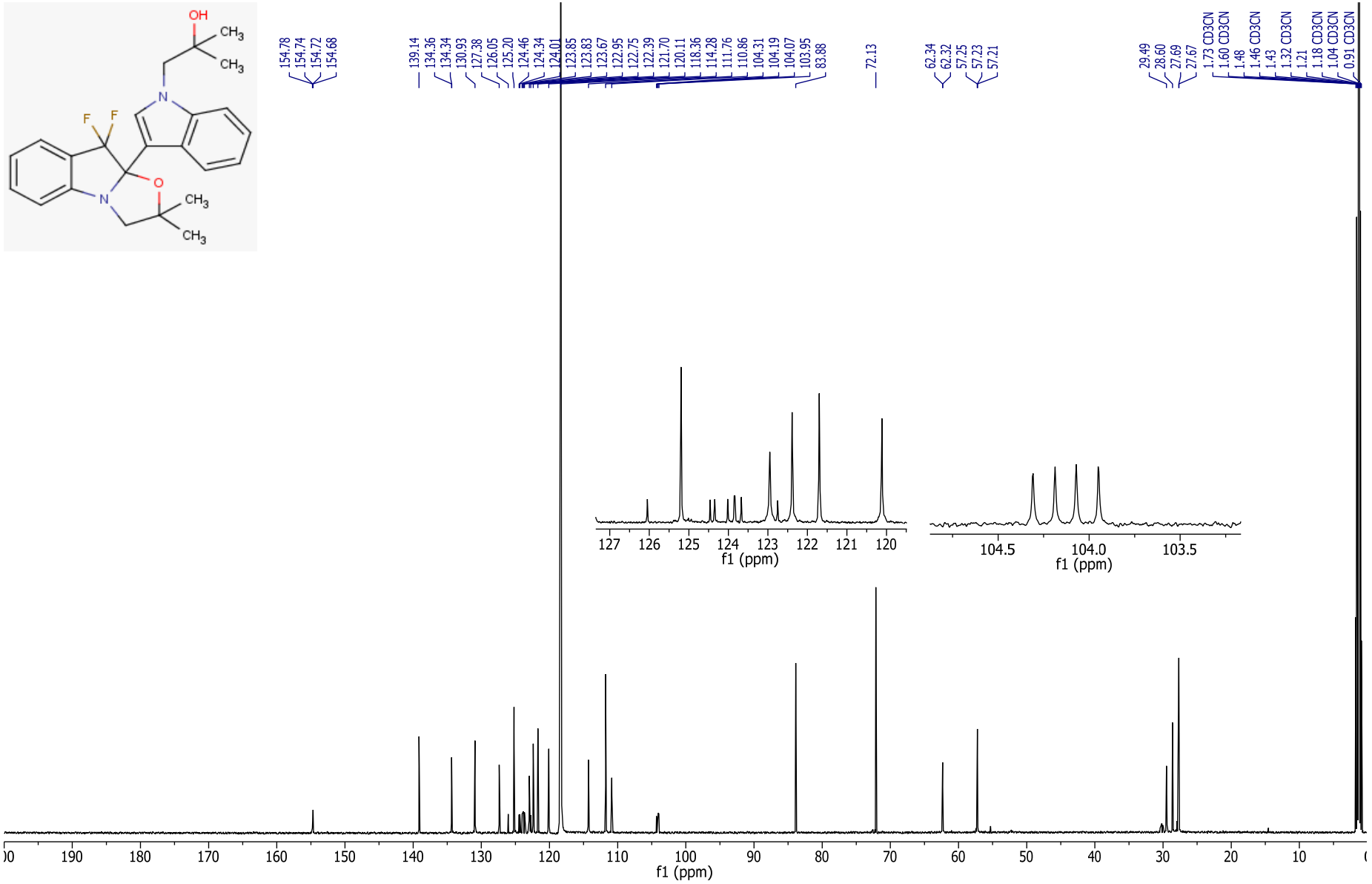


^{1}H and ^{19}F NMR of compound 2c

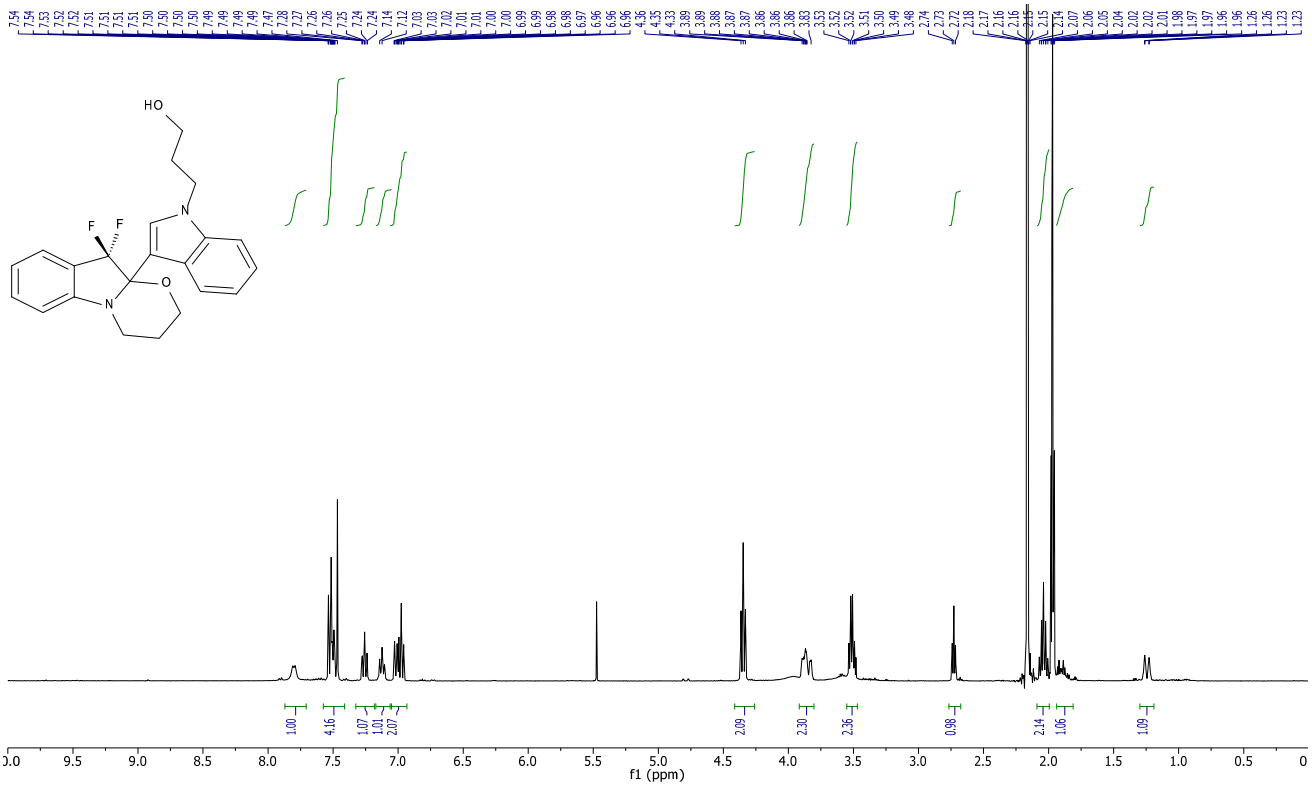


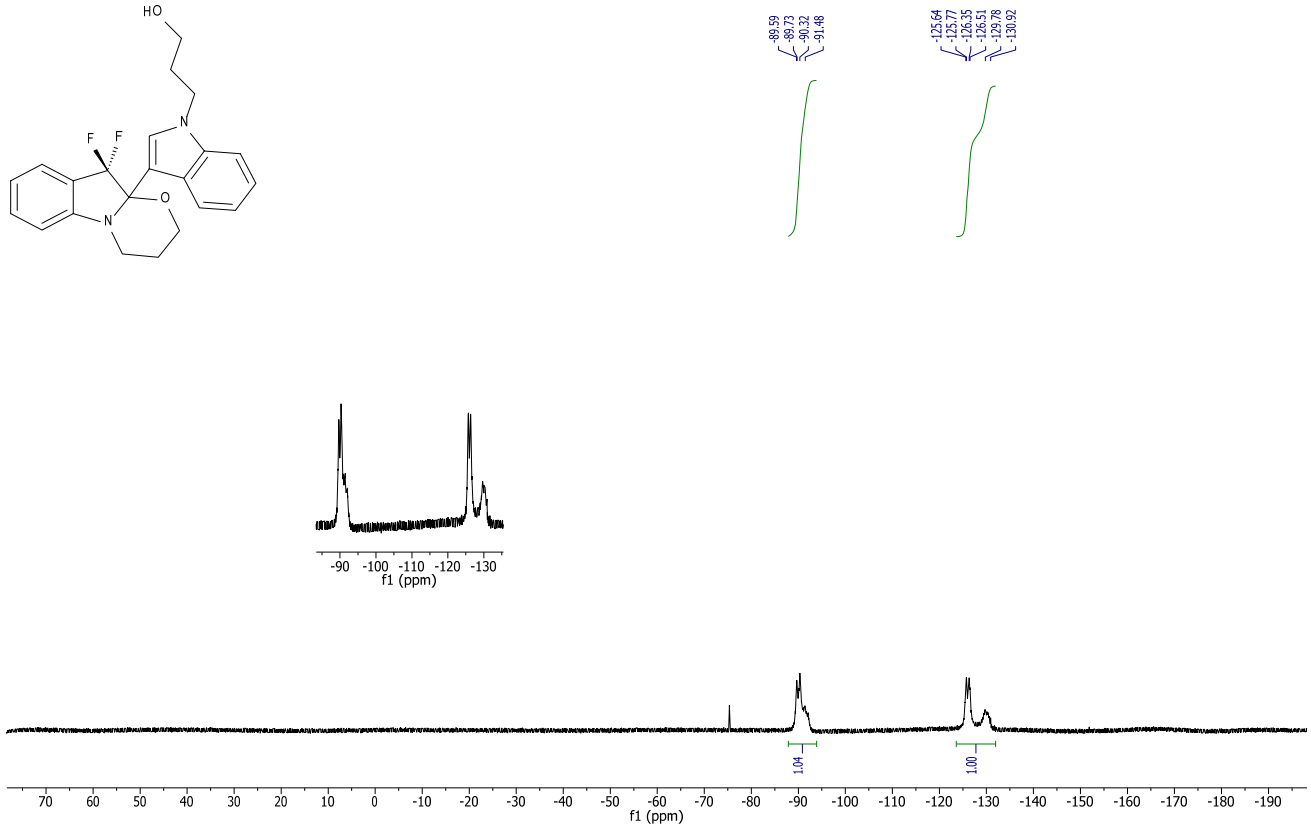


^{13}C NMR of compound 2c

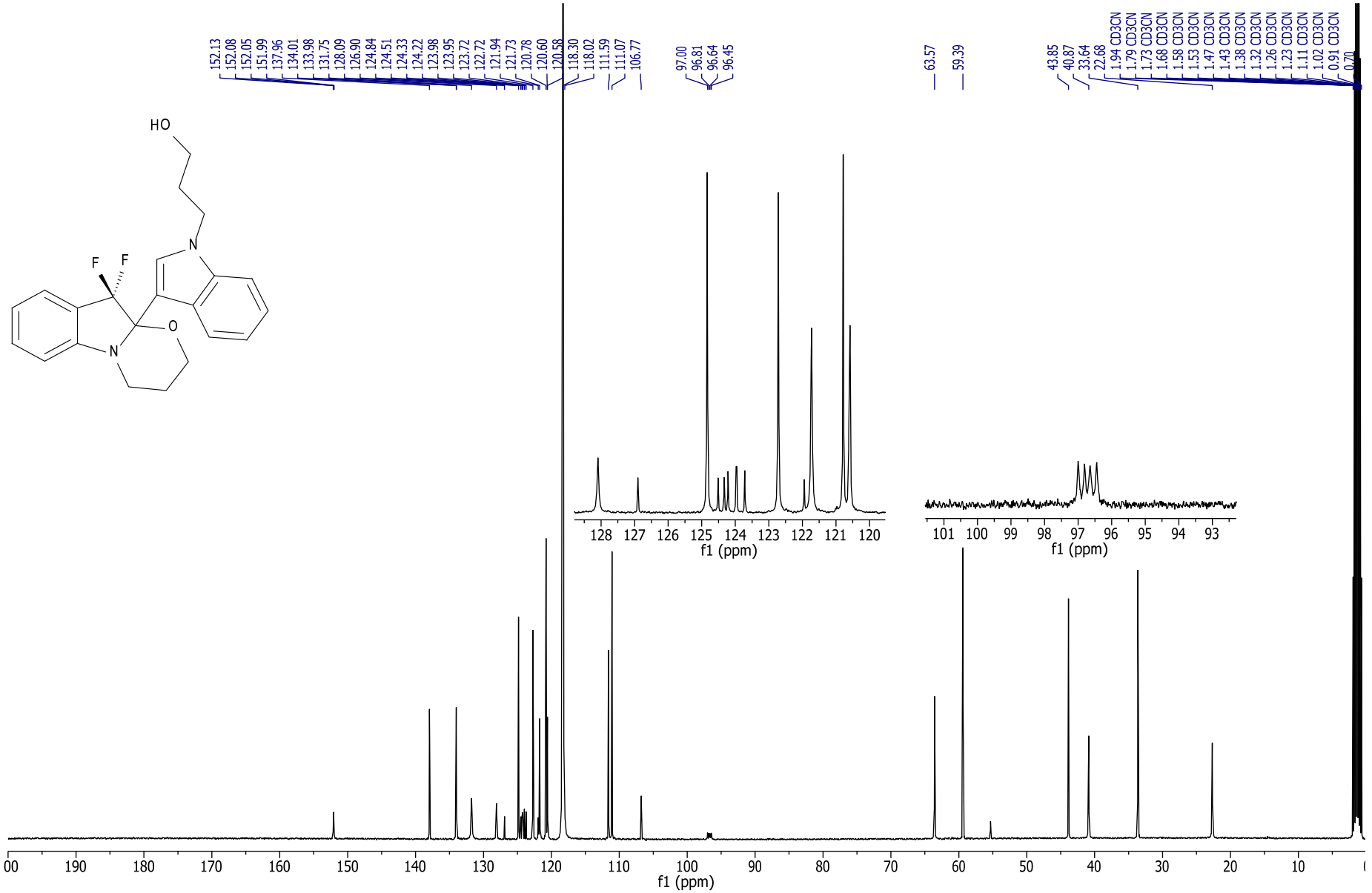


^{1}H and ^{19}F NMR of compound 1d

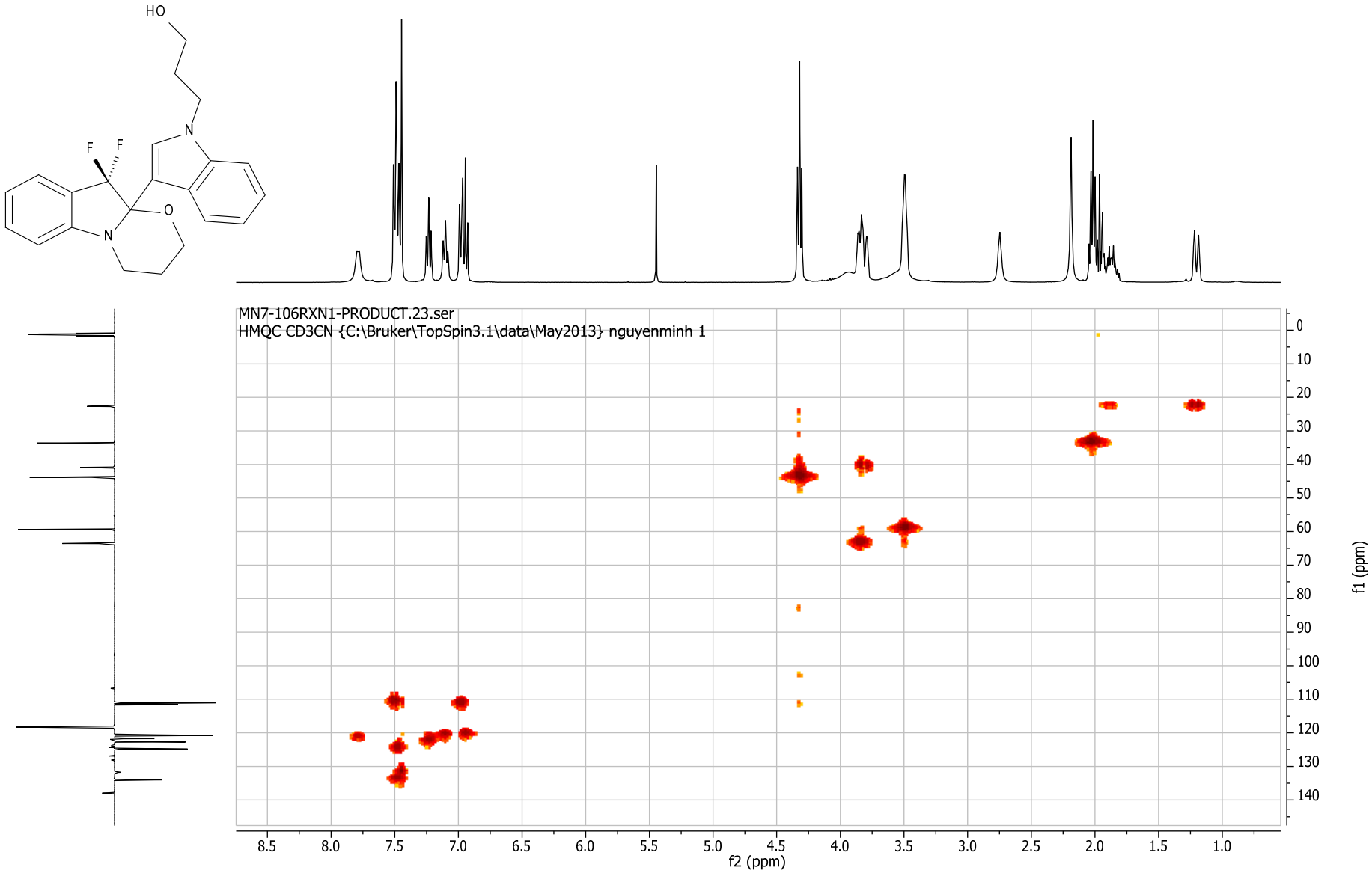




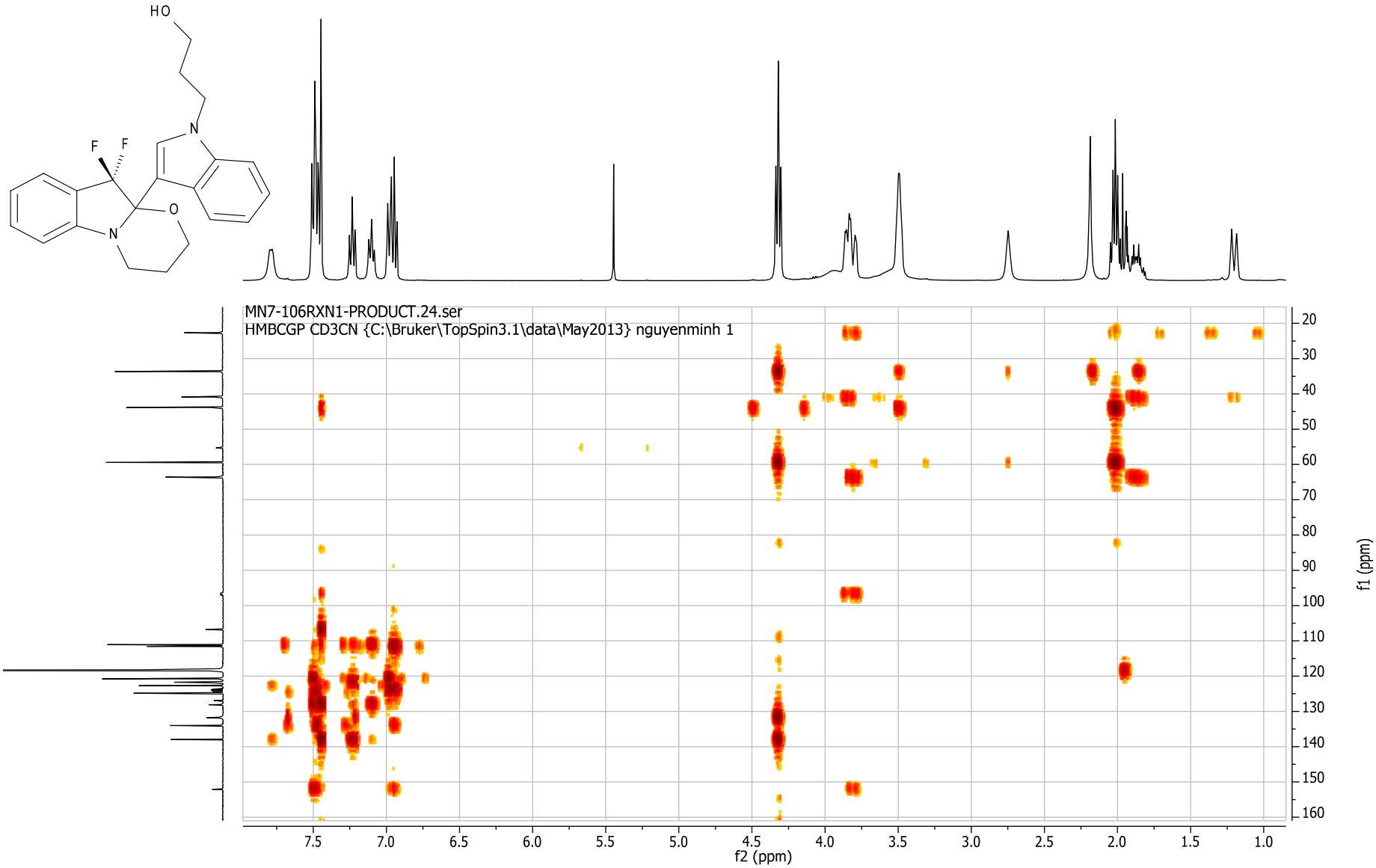
^{13}C NMR of compound 1d



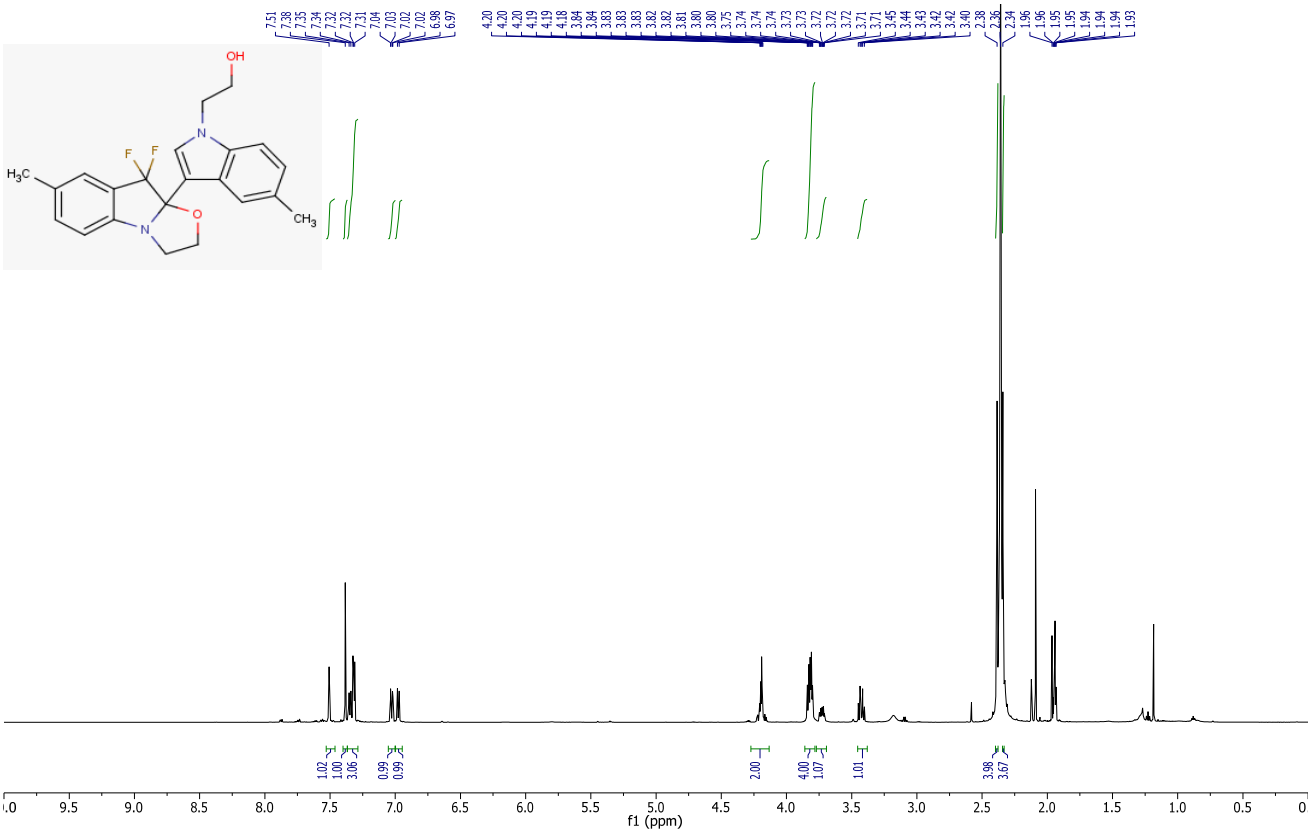
^{1}H- ^{13}C HMQC of compound 1d

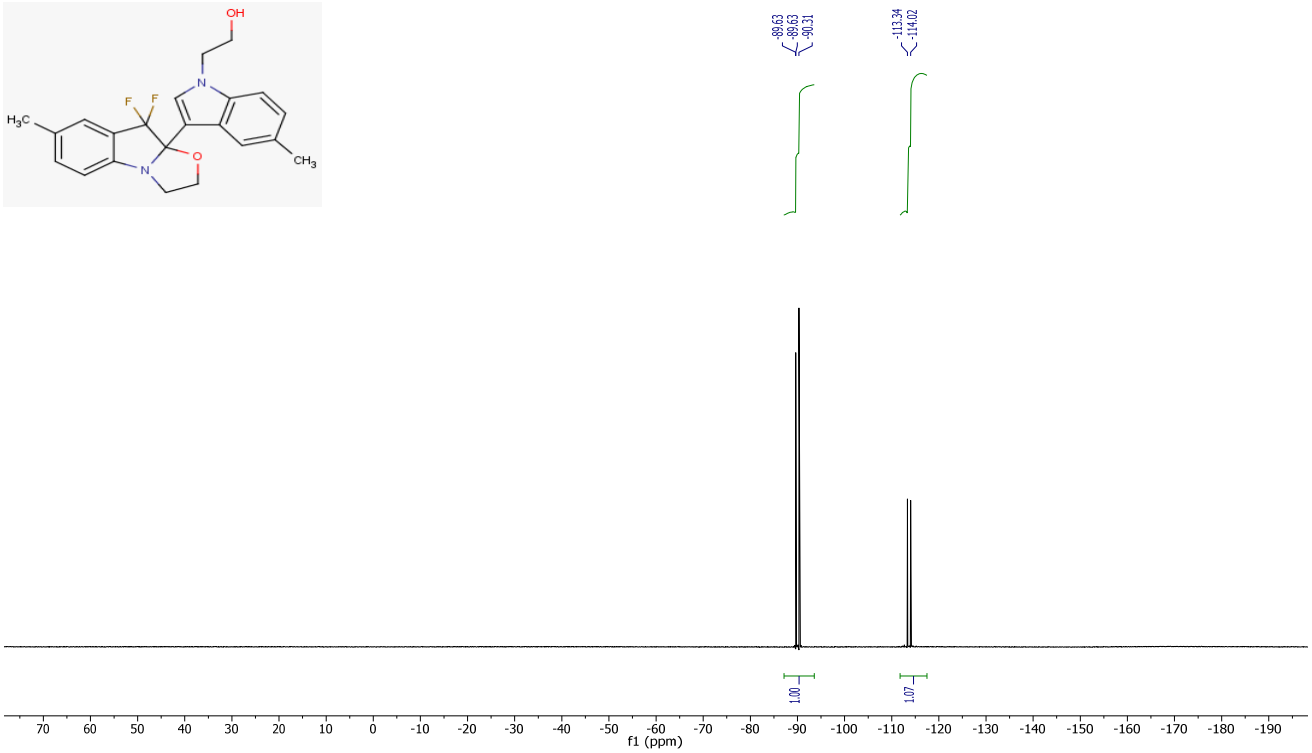


^{1}H- ^{13}C HMBC of compound 1d

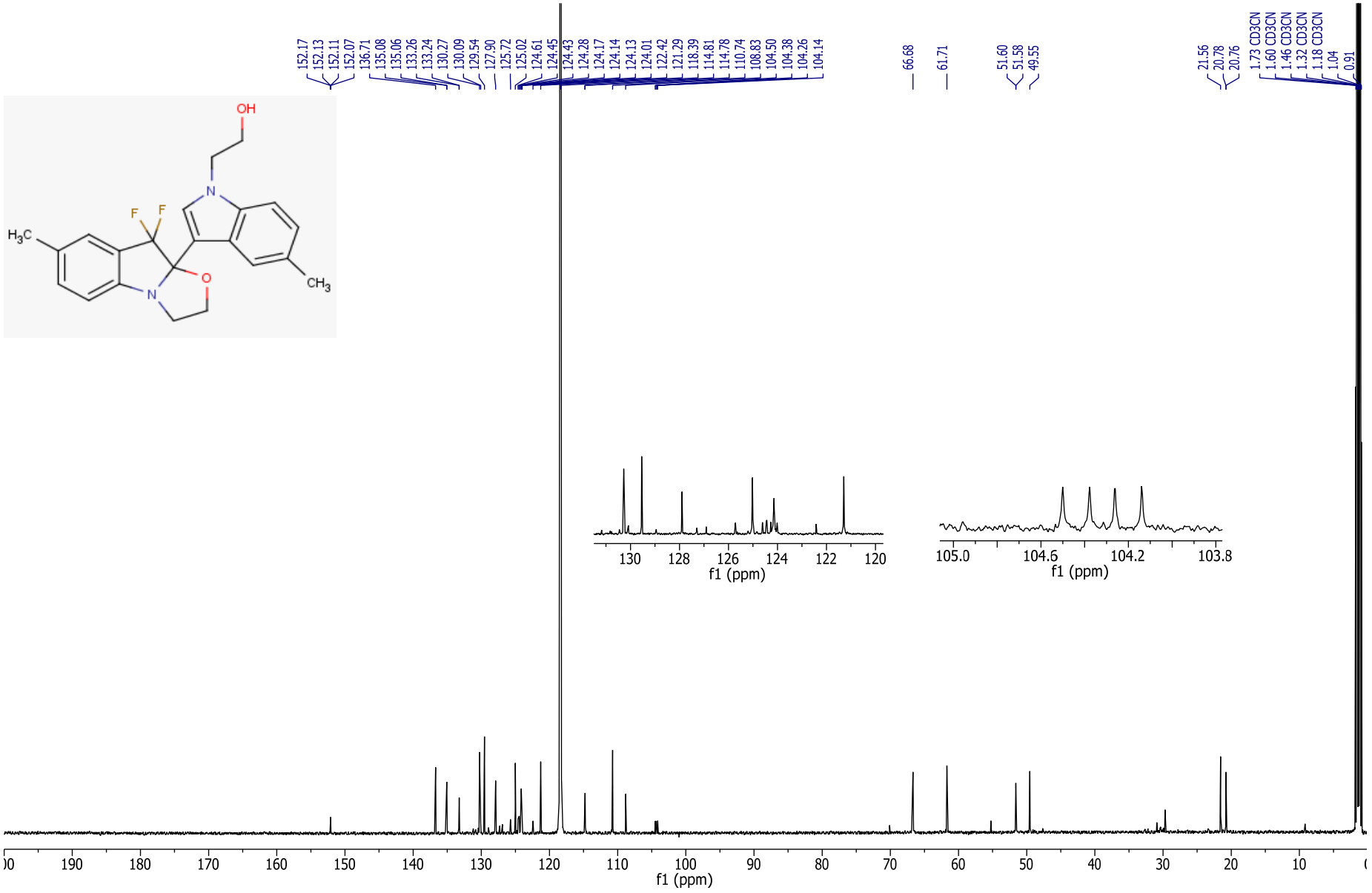


^{1}H and ^{19}F NMR of compound 1e

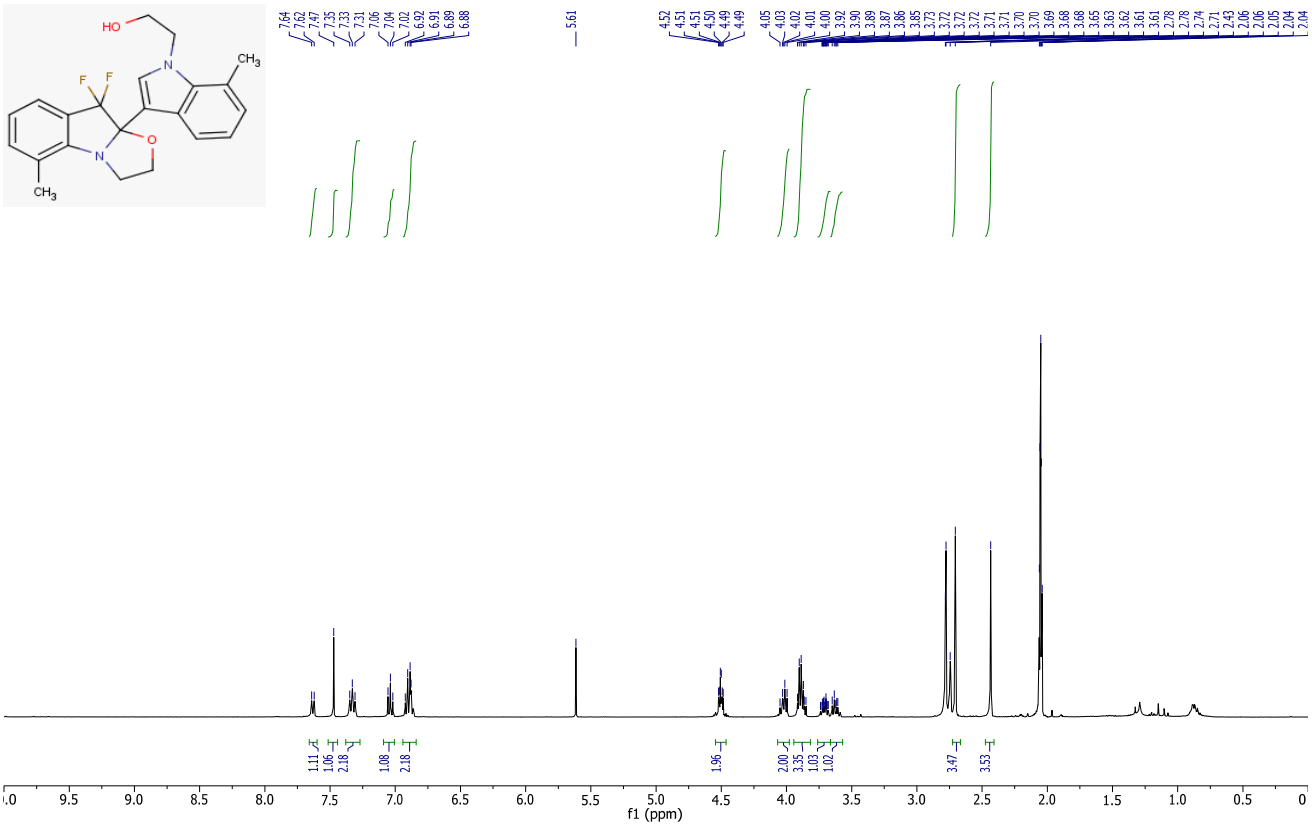


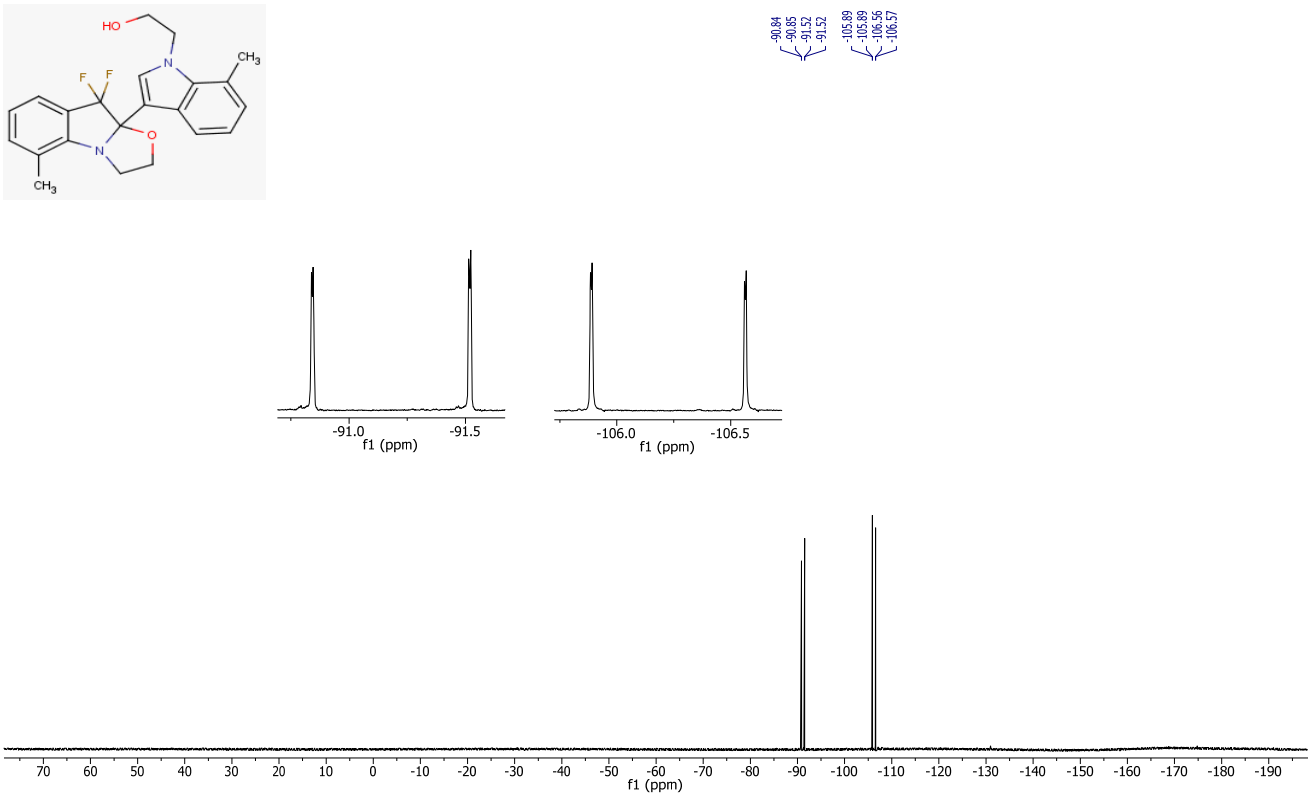


^{13}C NMR of compound 1e

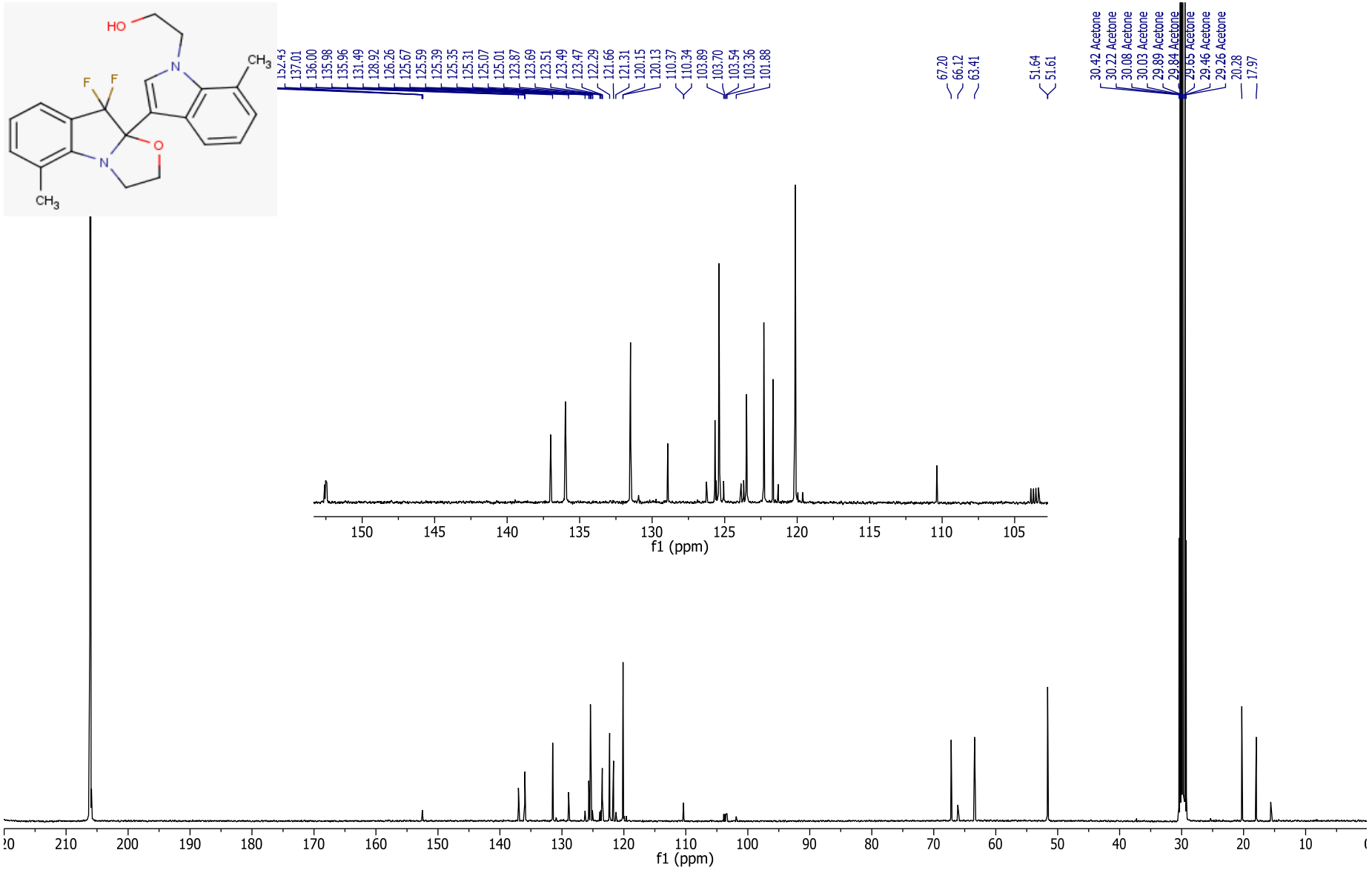


^{1}H and ^{19}F NMR of compound 1f

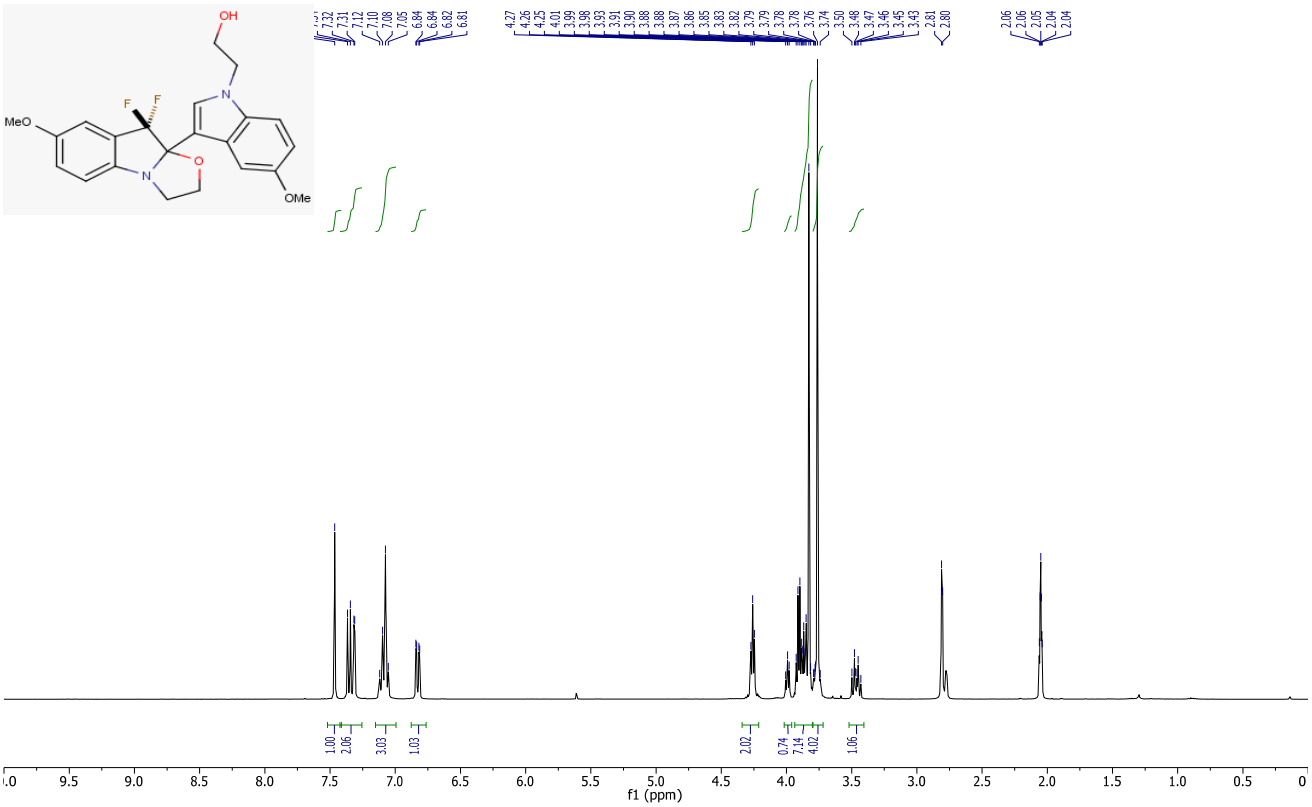


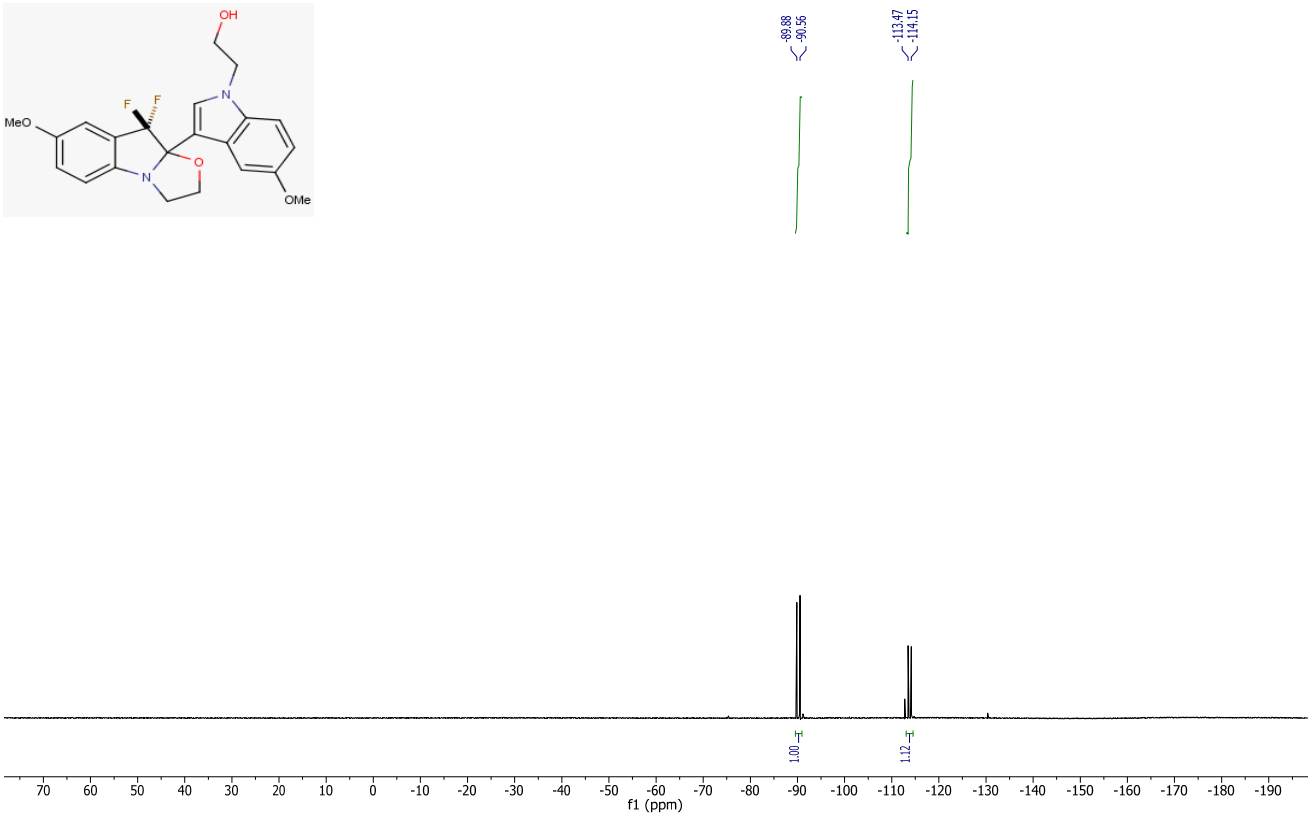


^{13}C NMR of compound 1f



^{1}H and ^{19}F NMR of compound 2g





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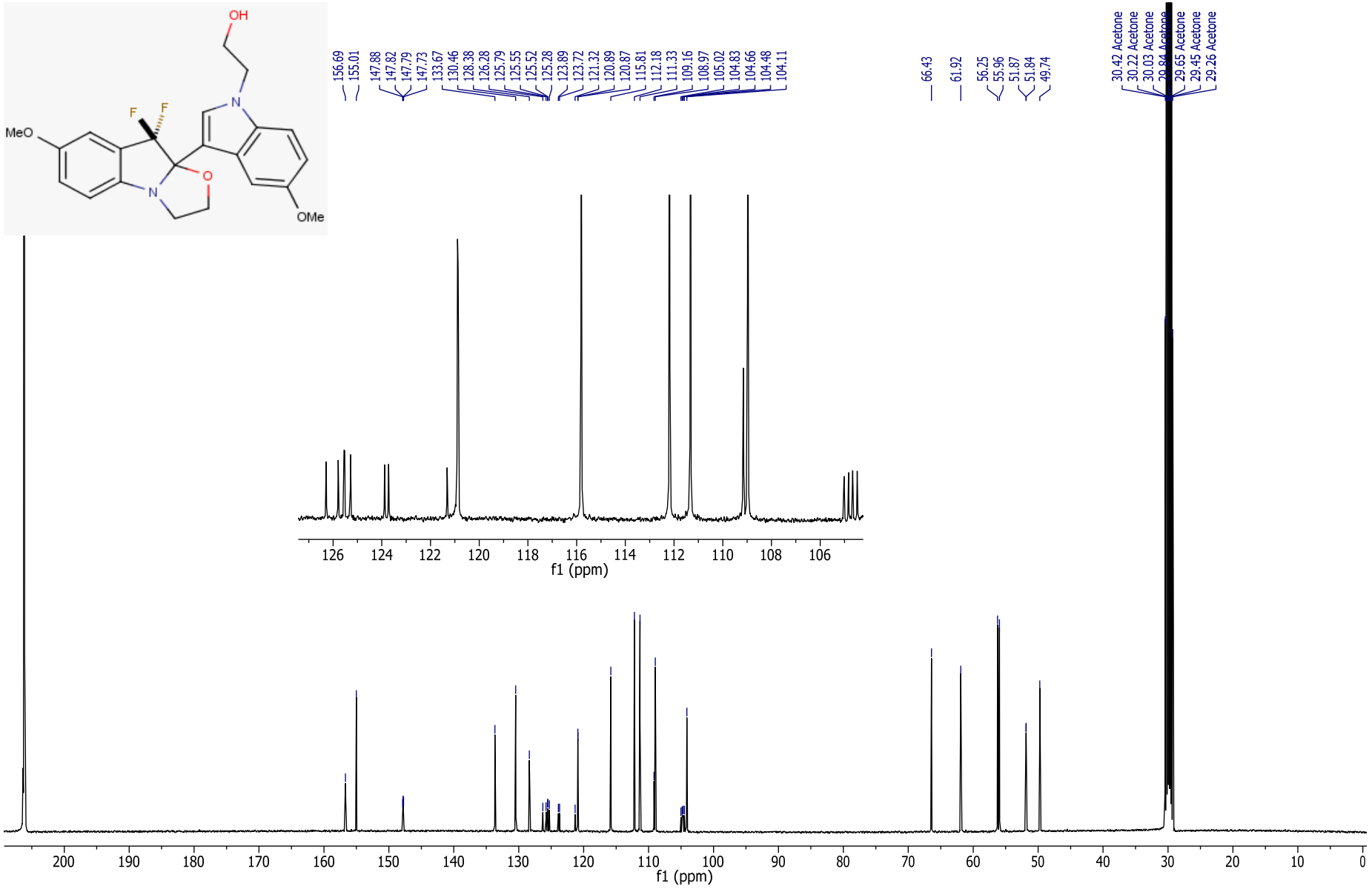
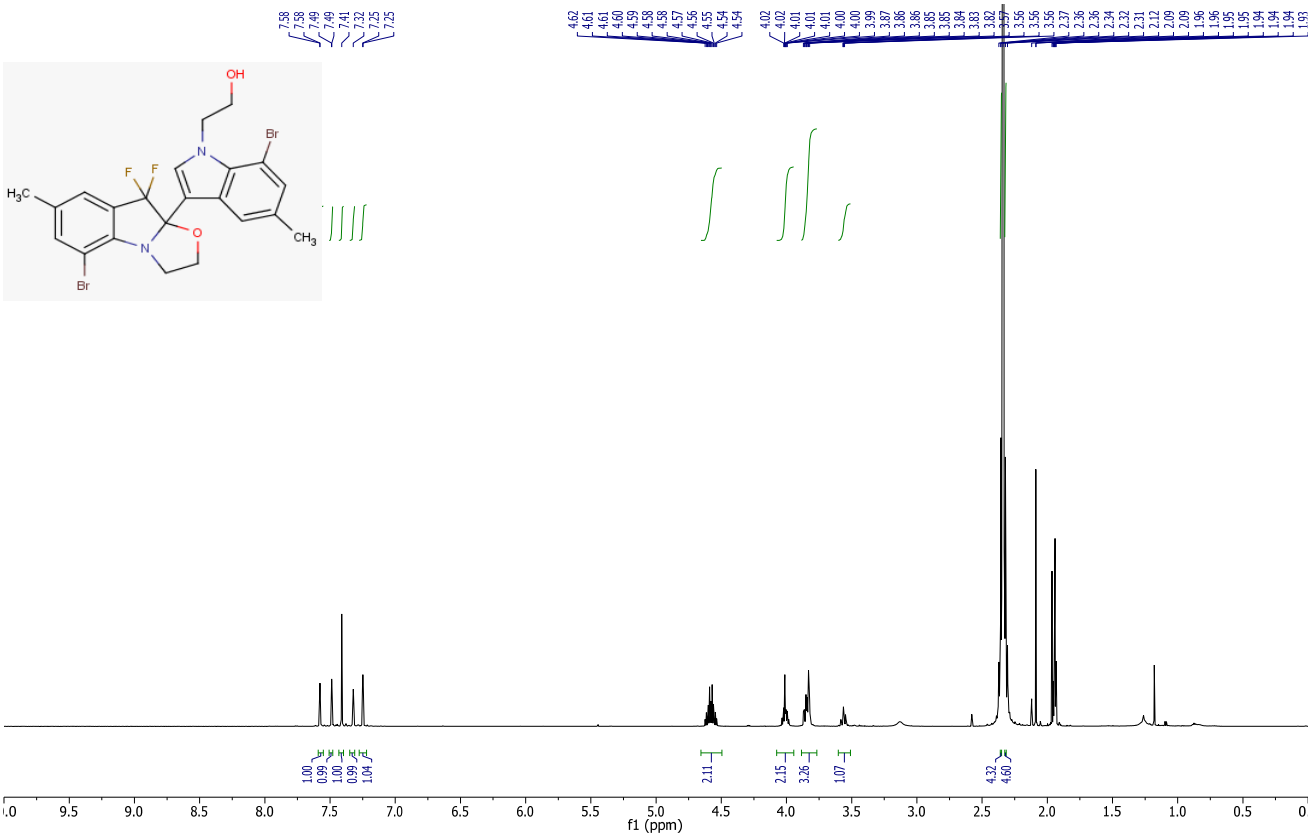
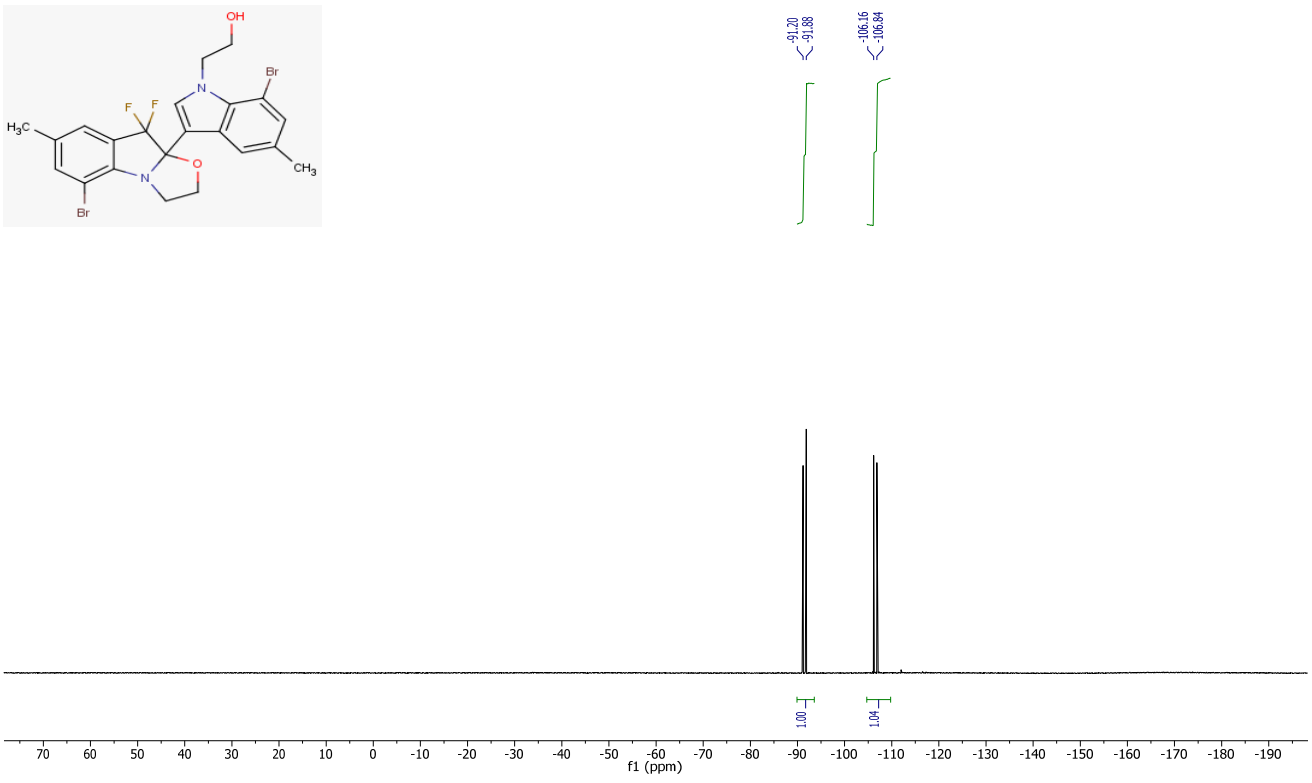


^{1}H and ^{19}F NMR of compound 2h





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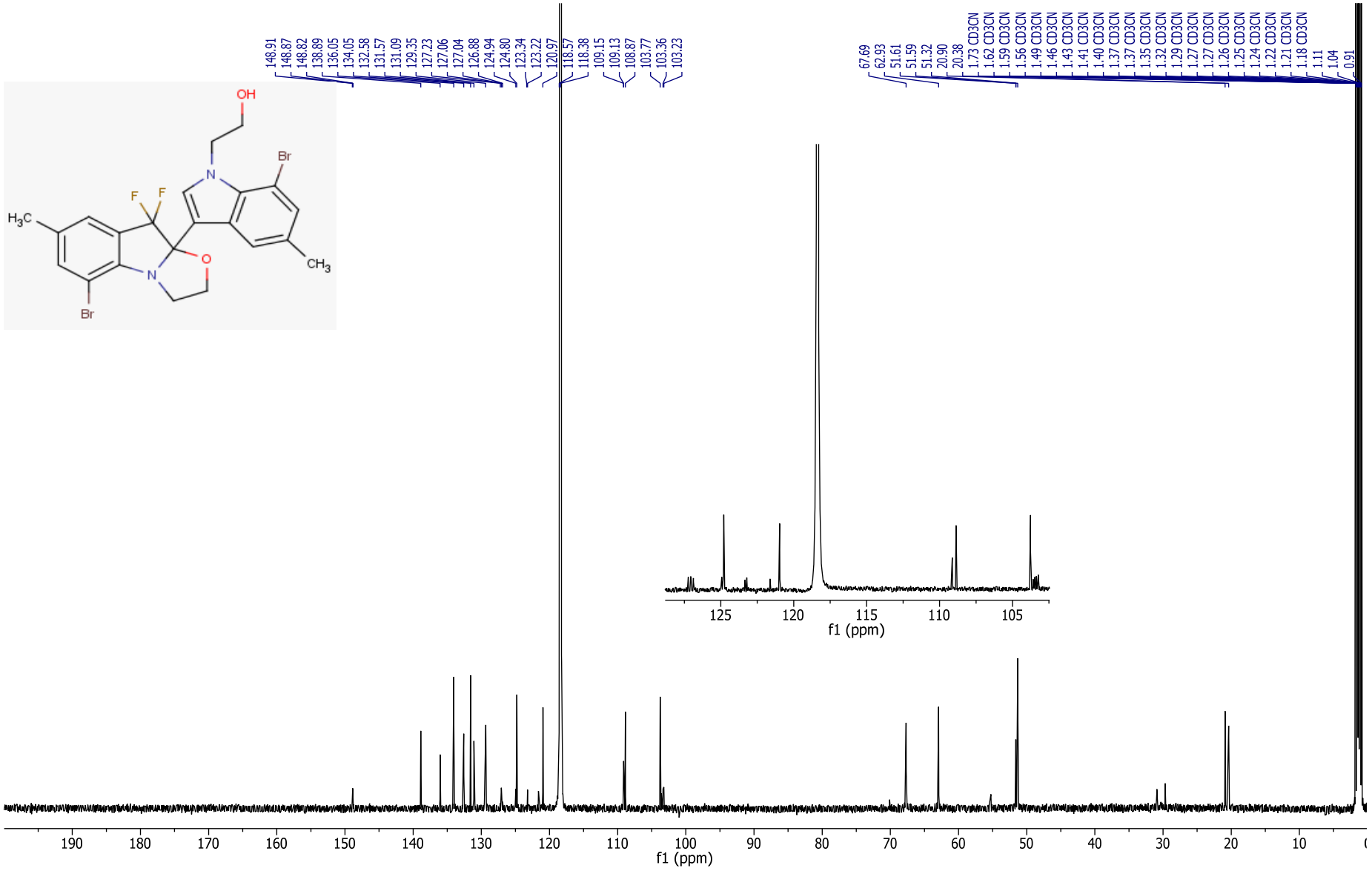
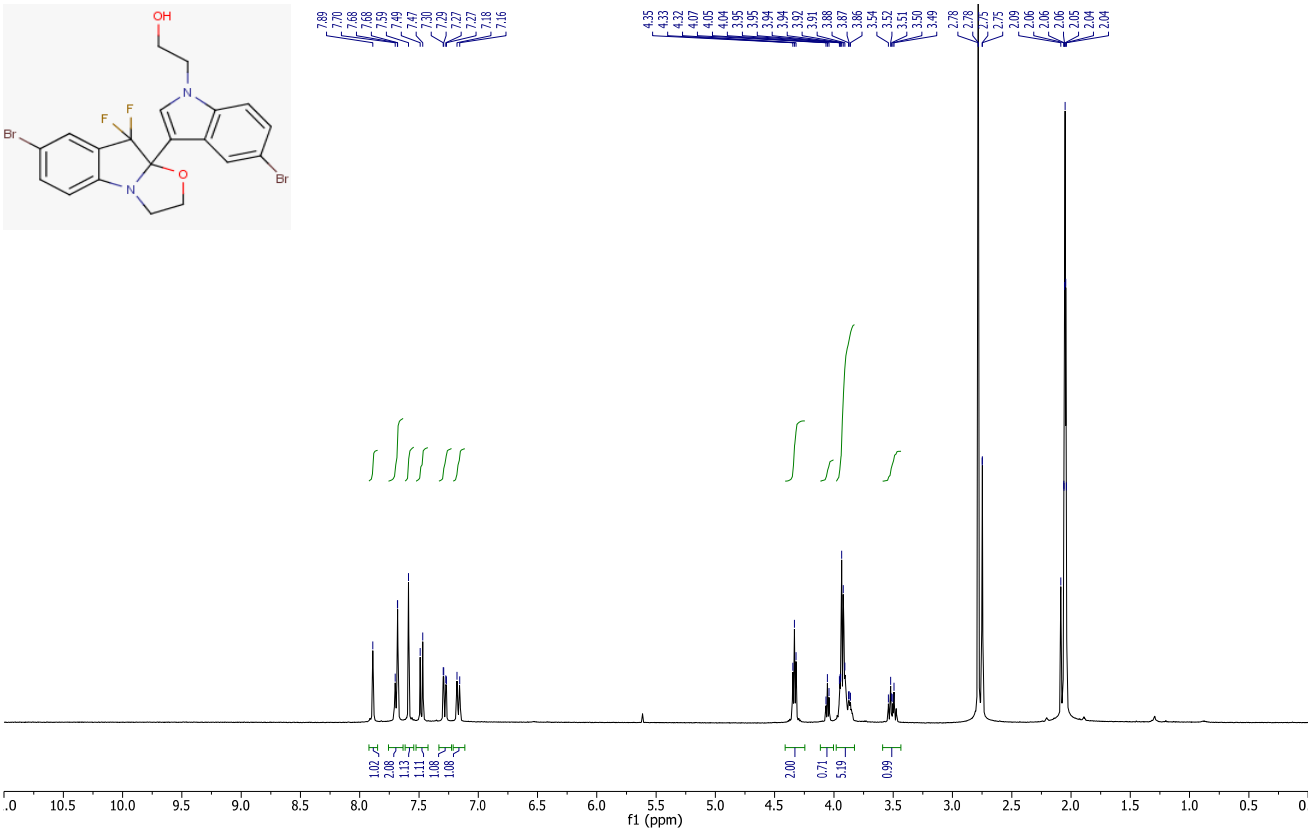
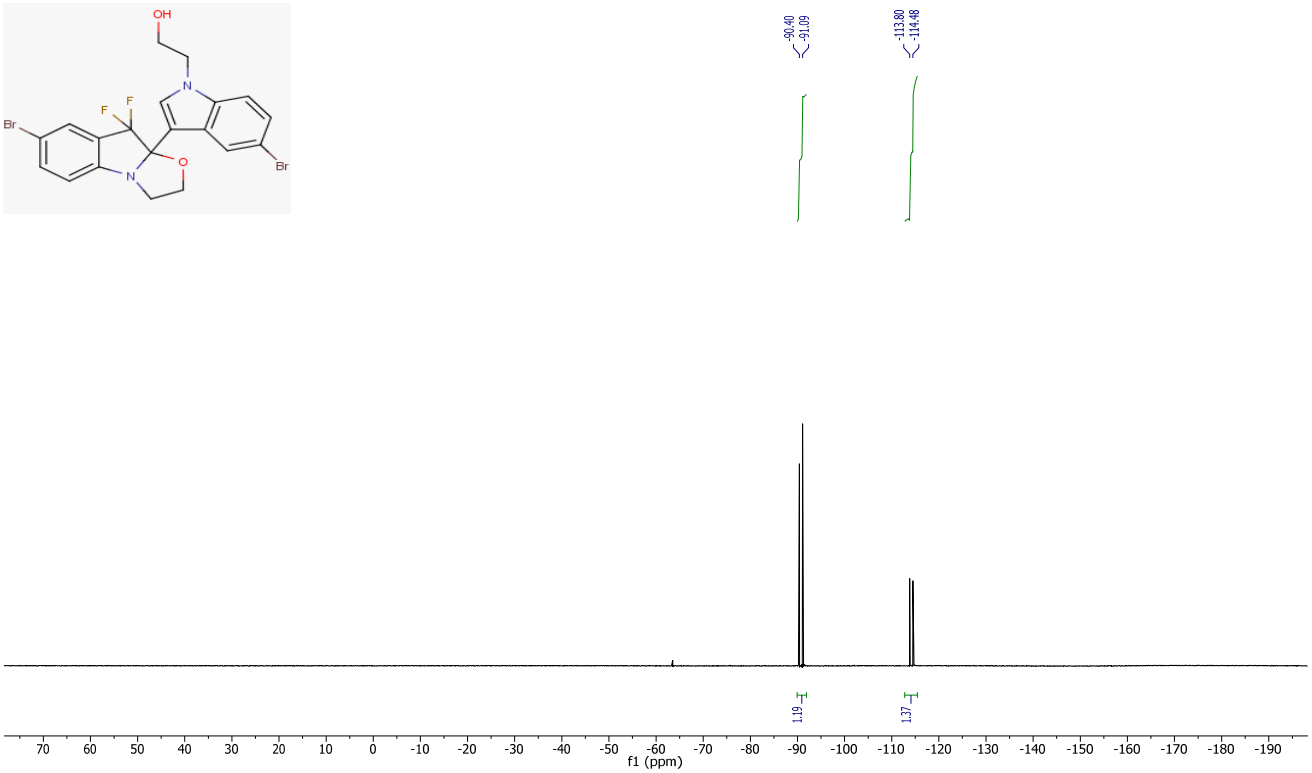
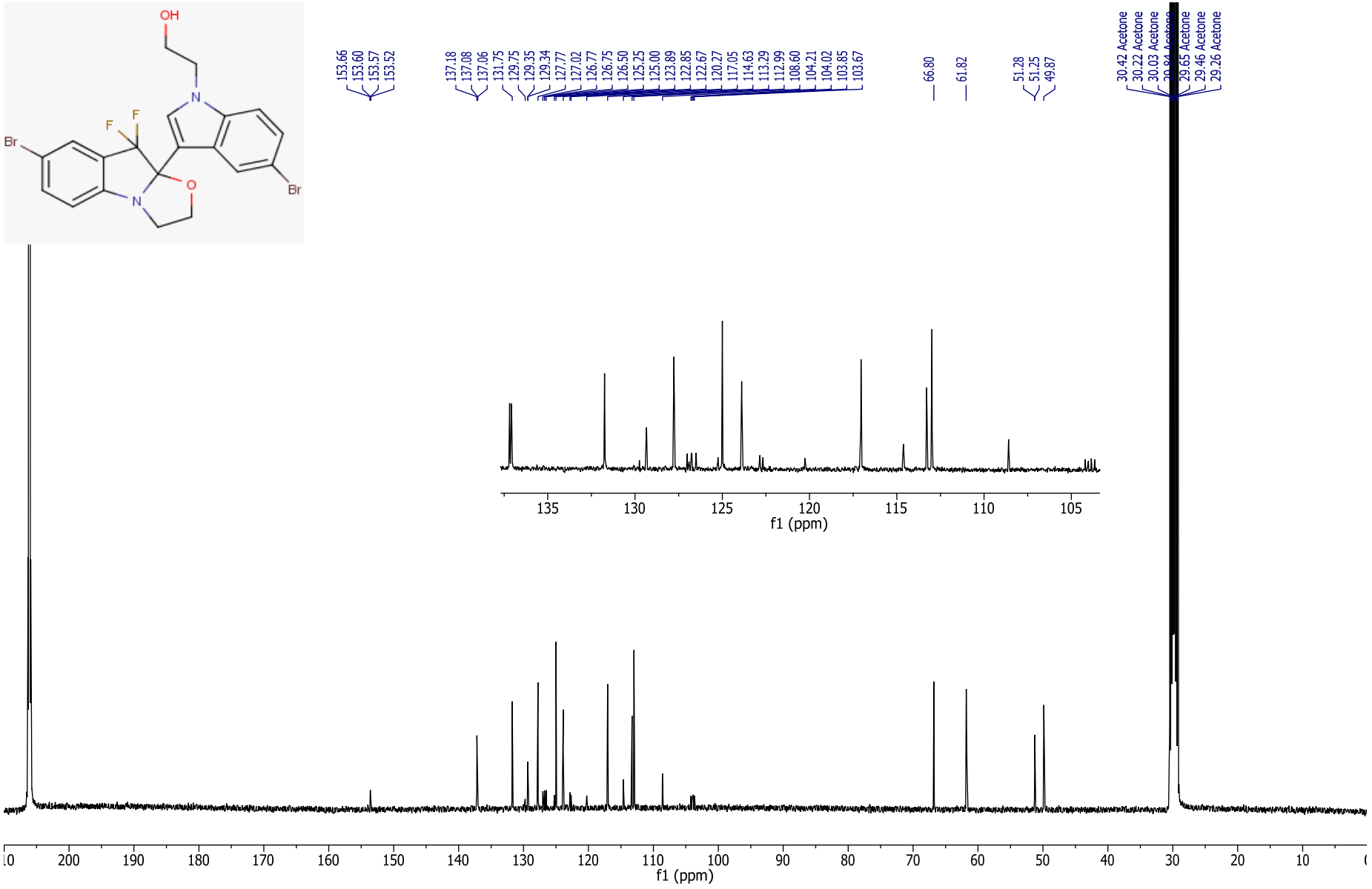


^{1}H and ^{19}F NMR of compound 2i

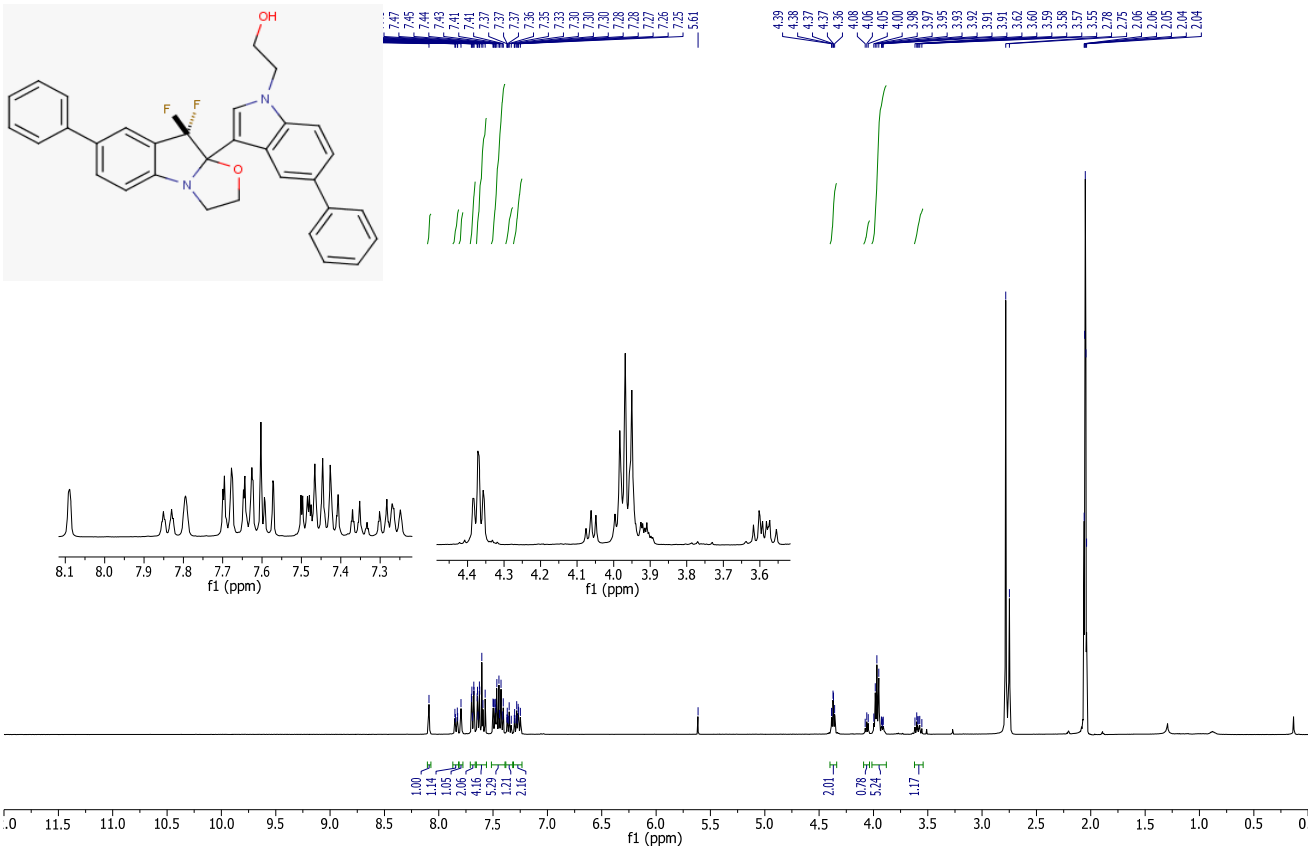


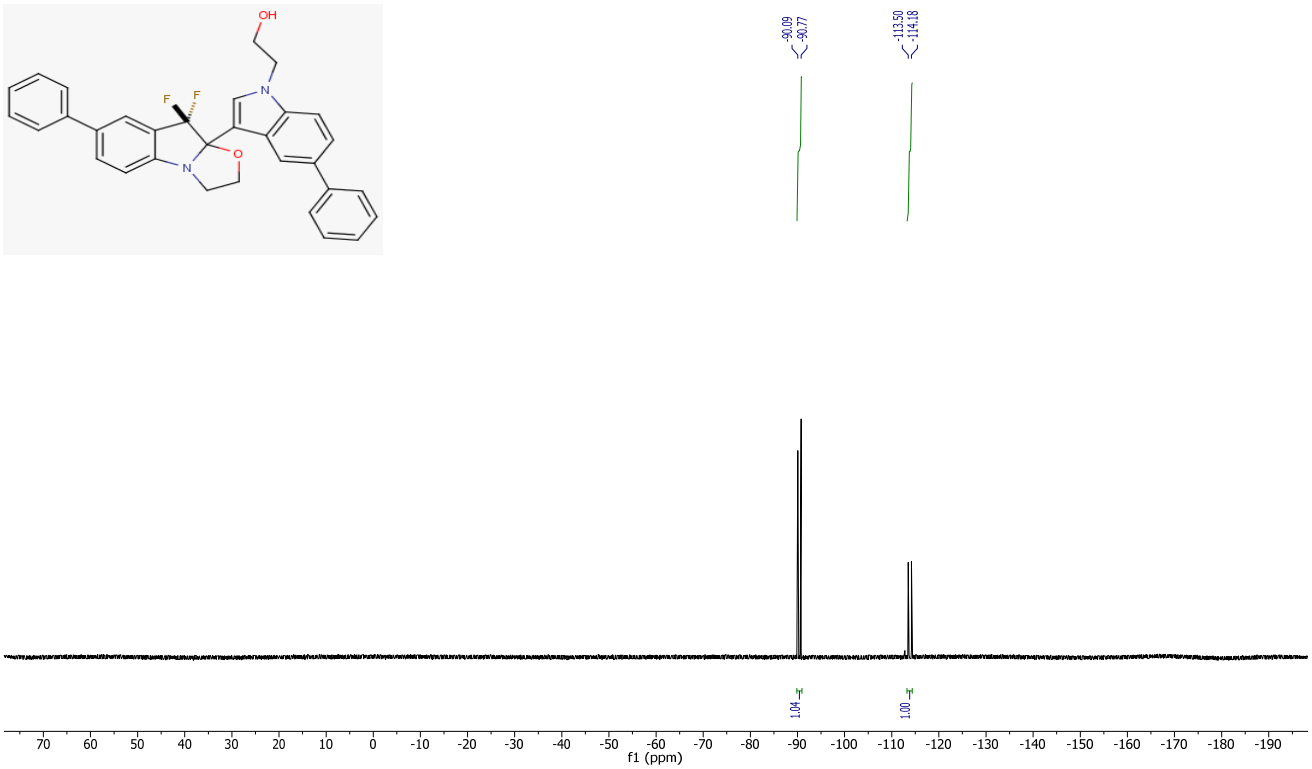


^{13}C NMR of compound 2i



^{1}H and ^{19}F NMR of compound 2j





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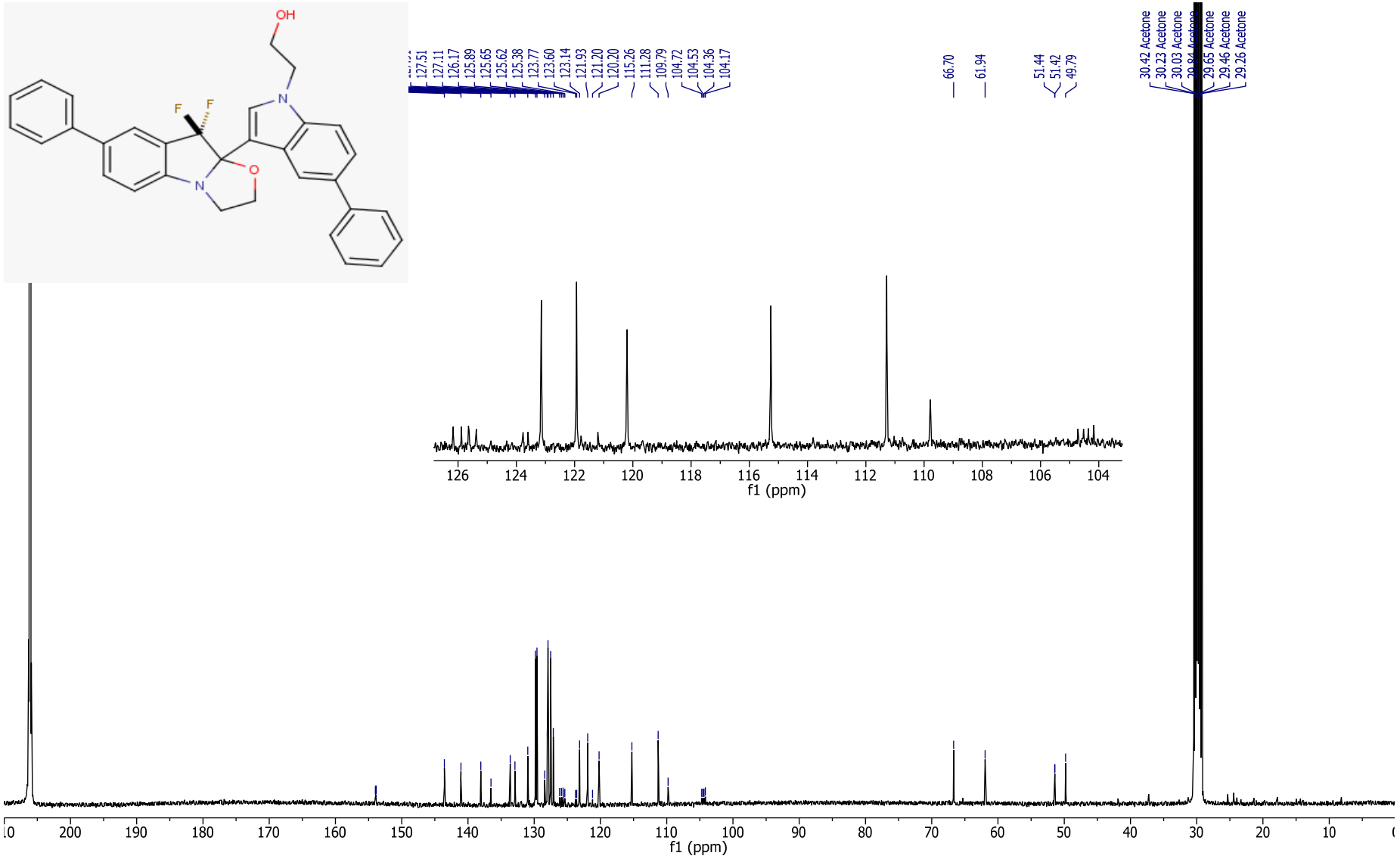
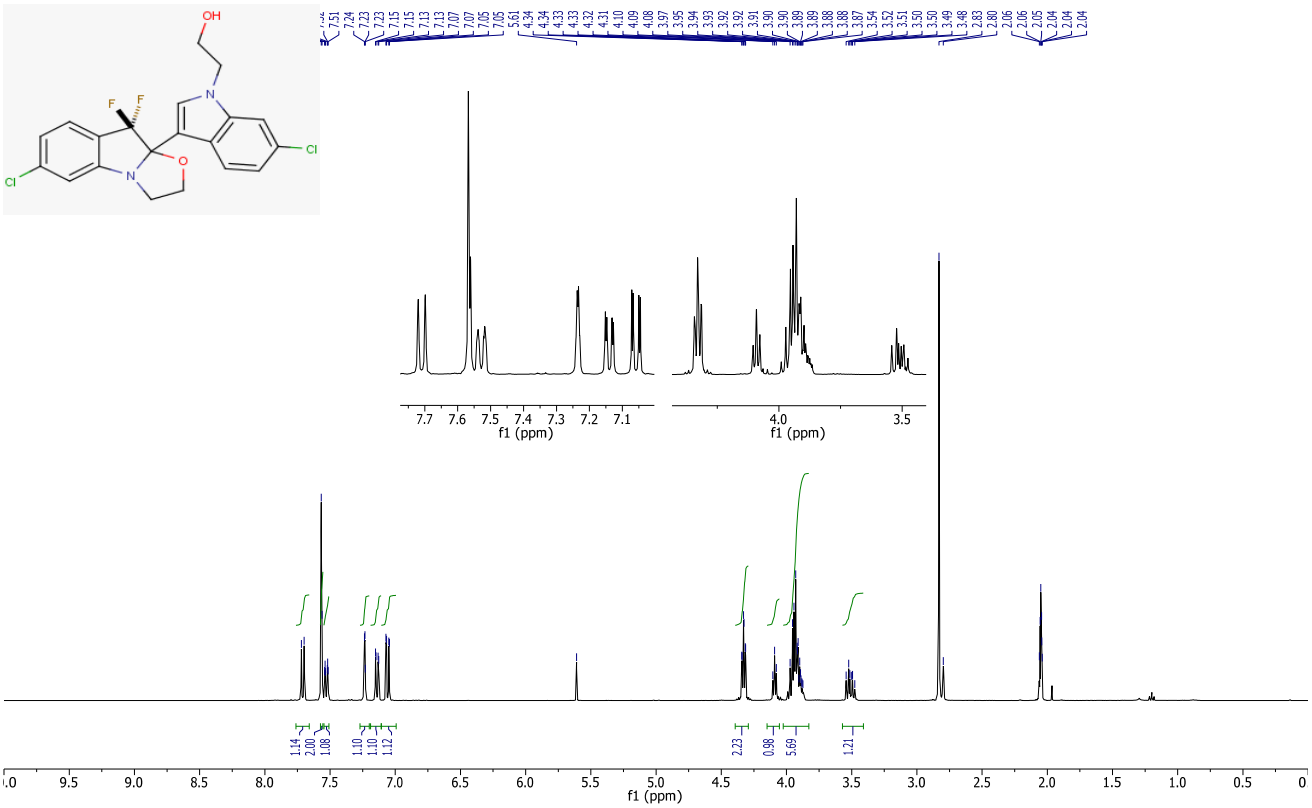
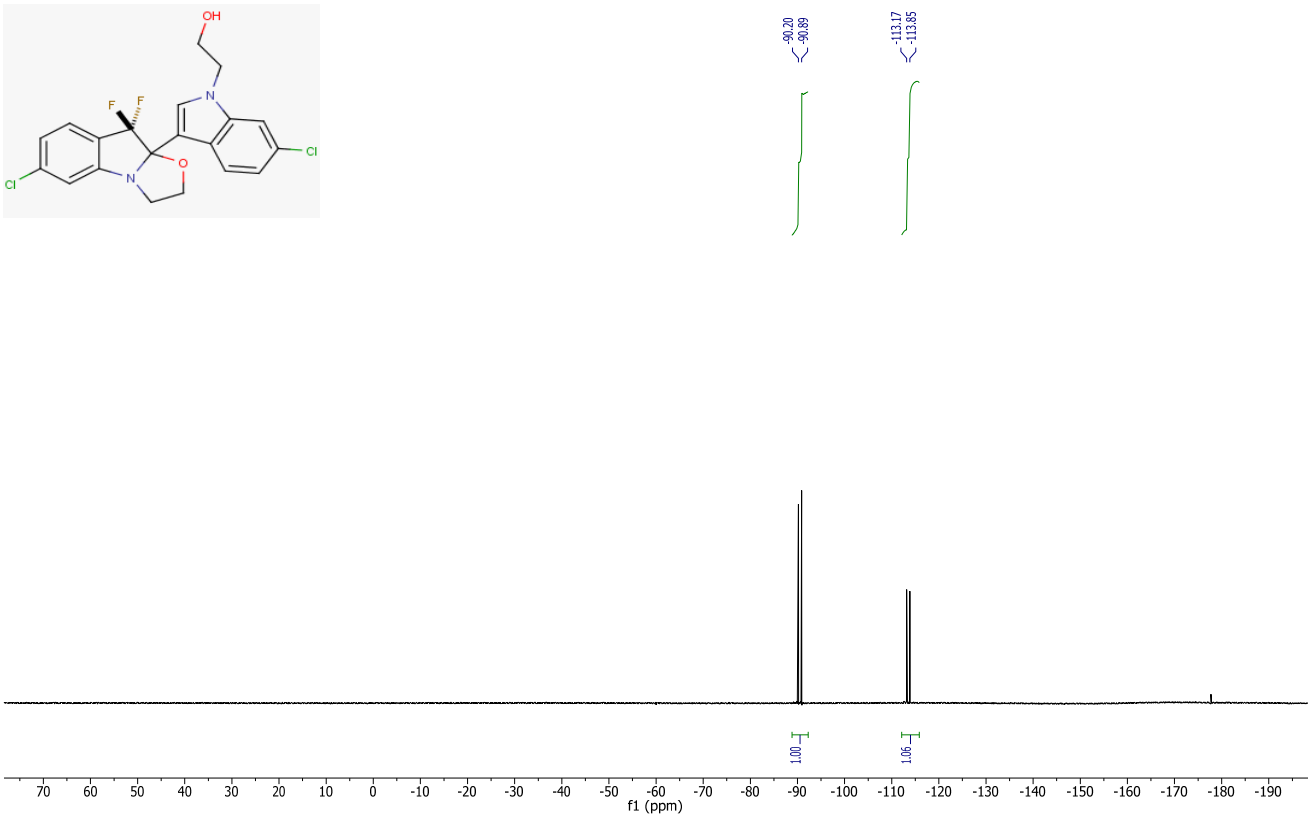


^{1}H and ^{19}F NMR of compound 2k





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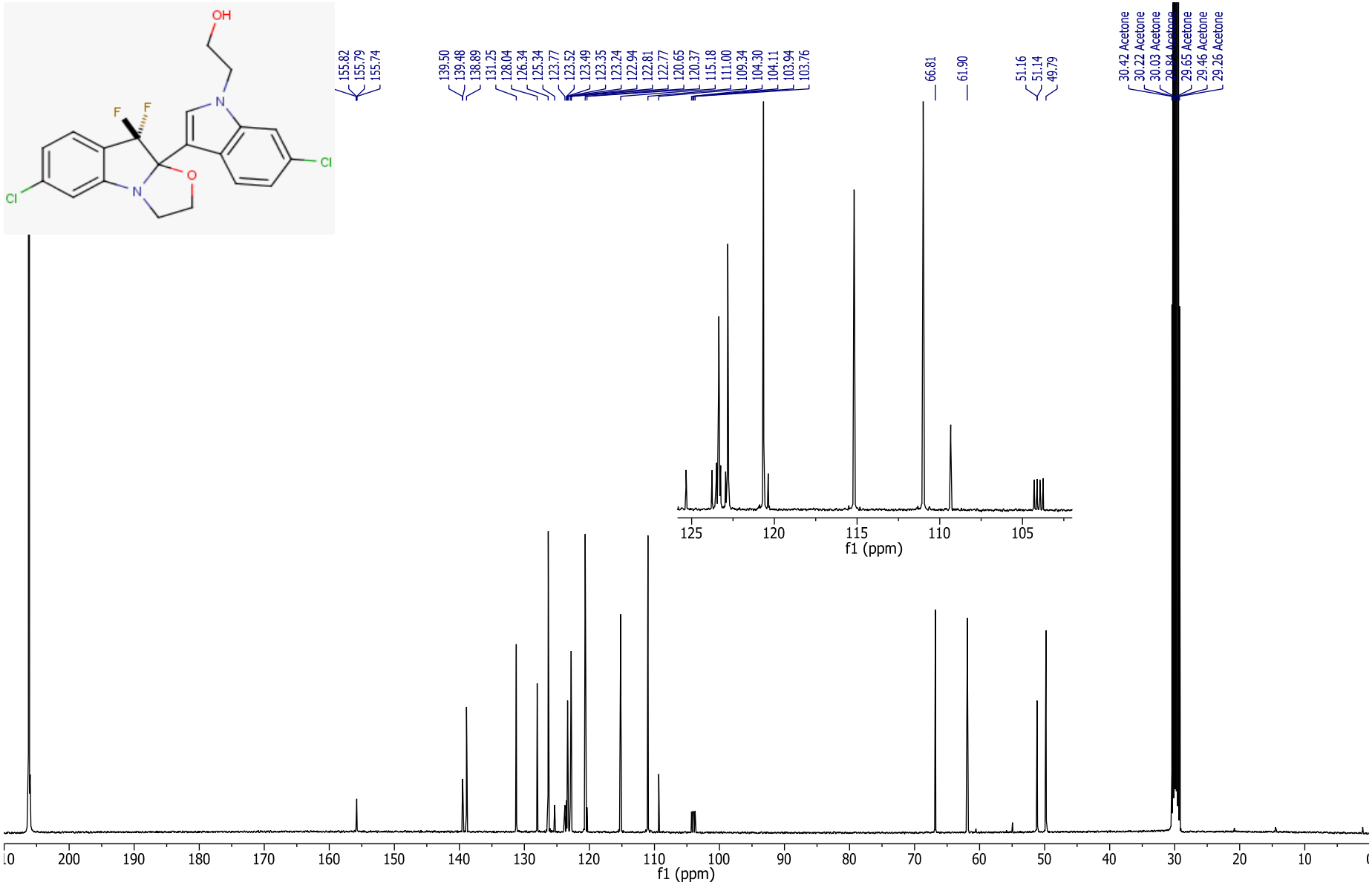
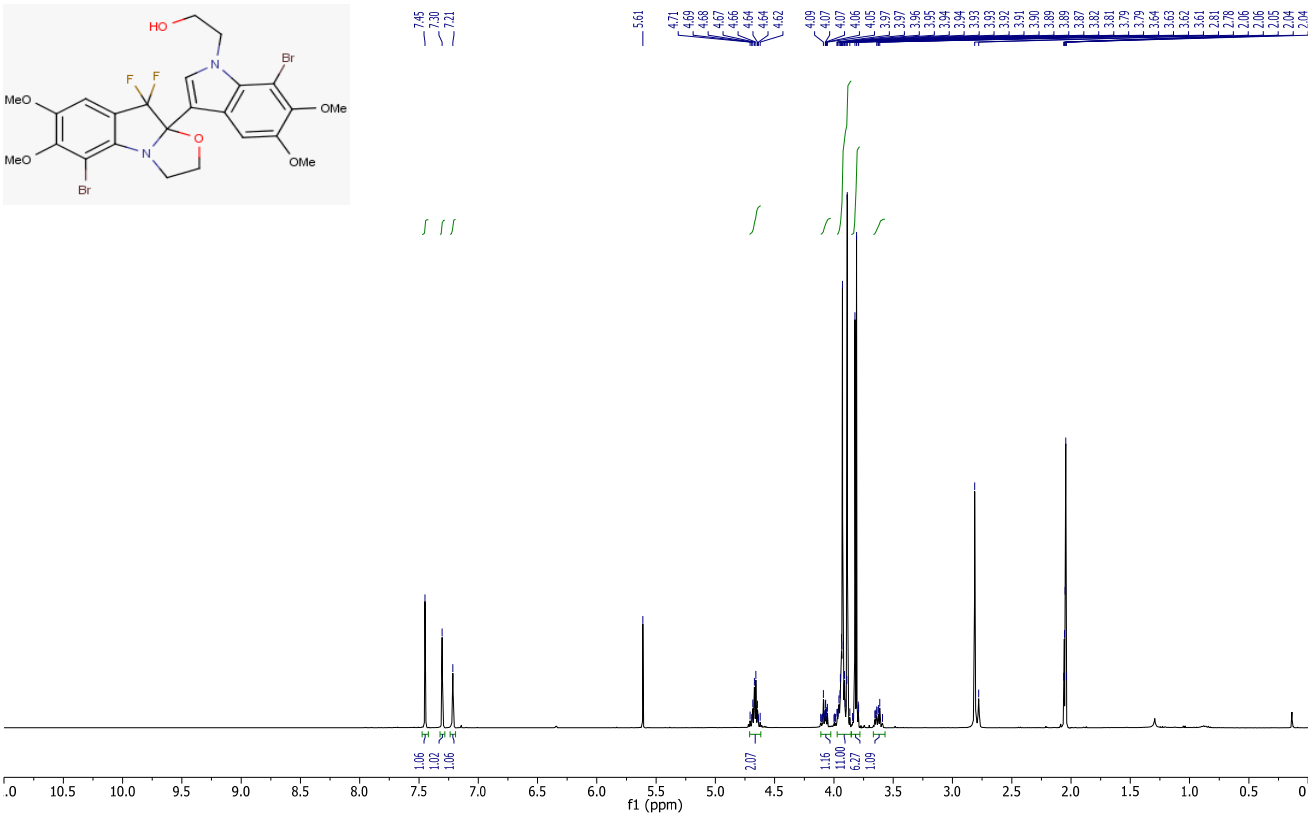
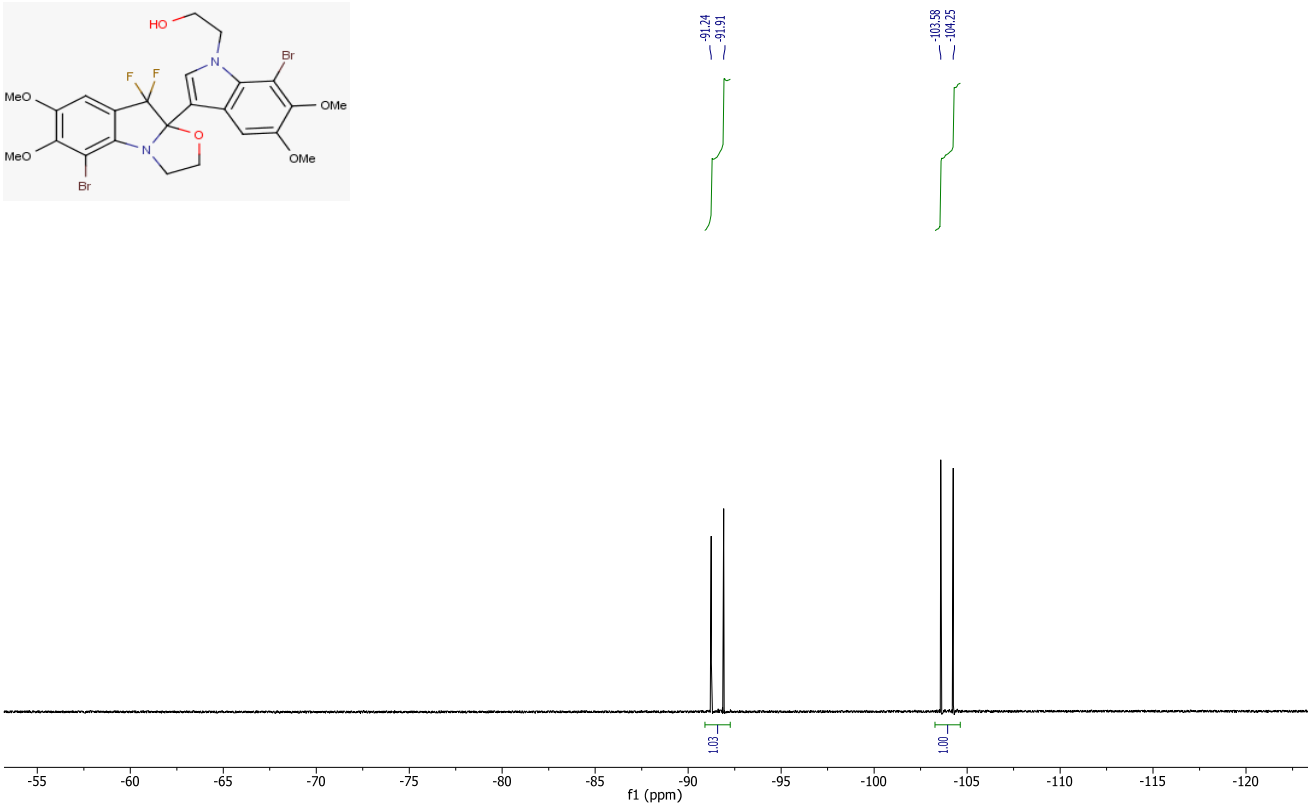


^{1}H and ^{19}F NMR of compound 2l





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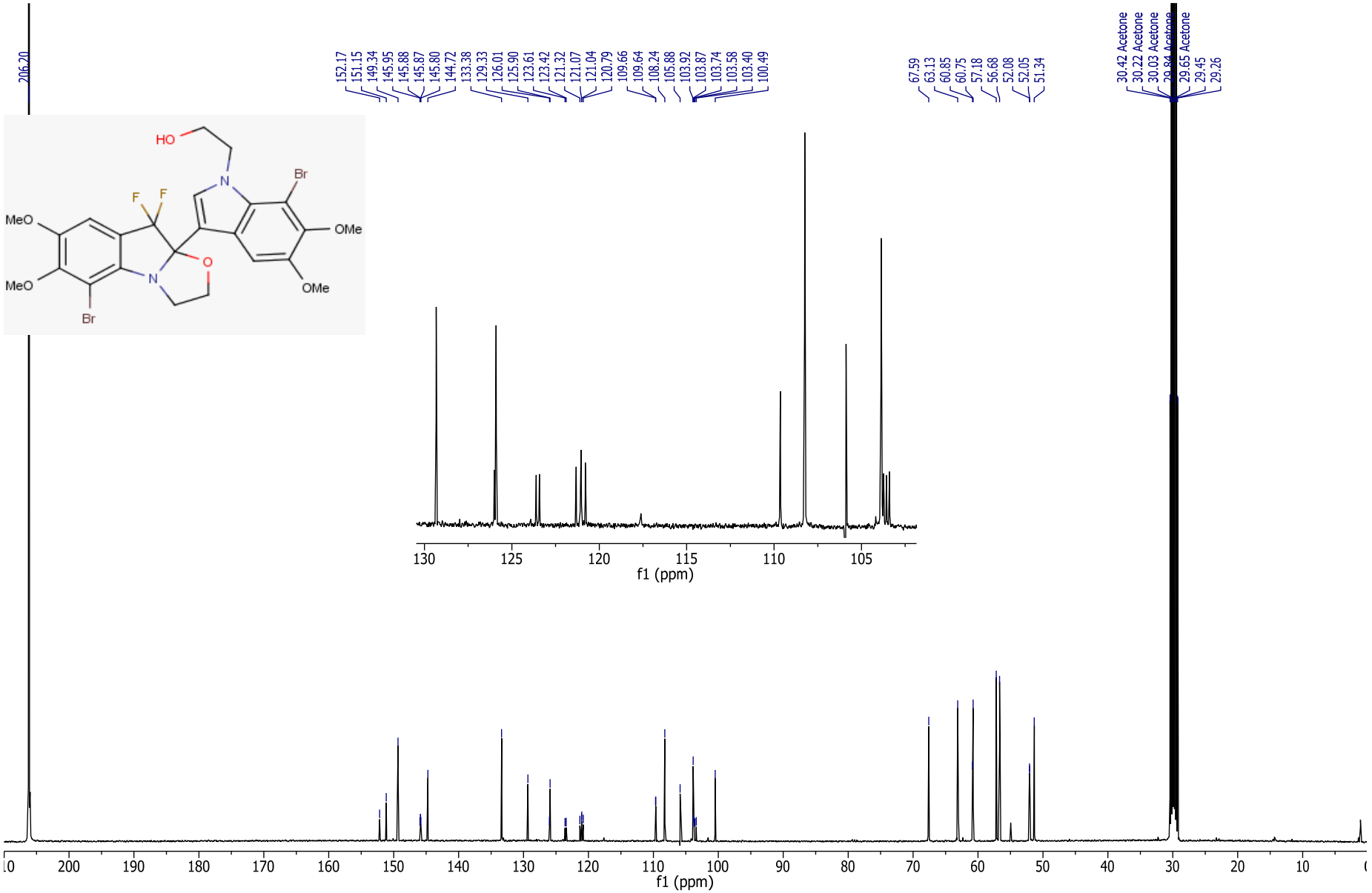
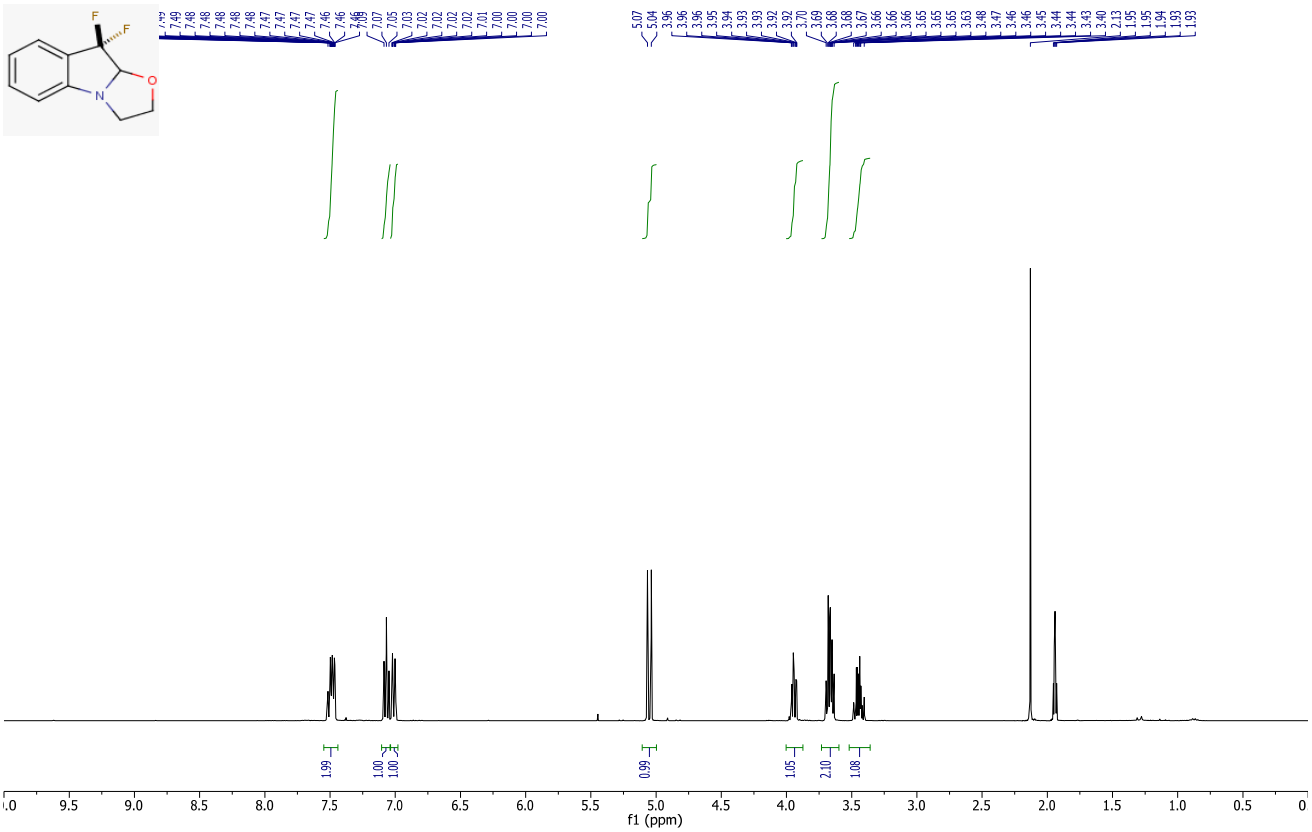
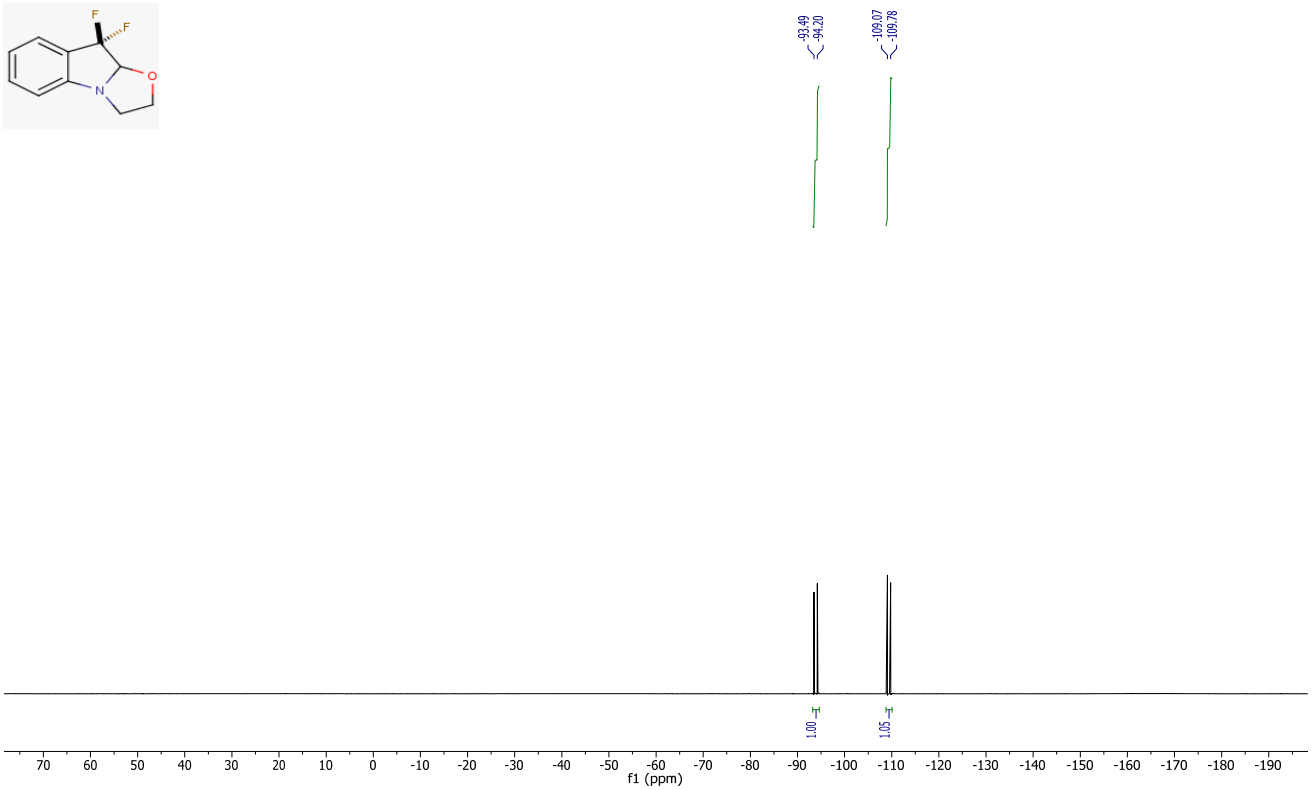
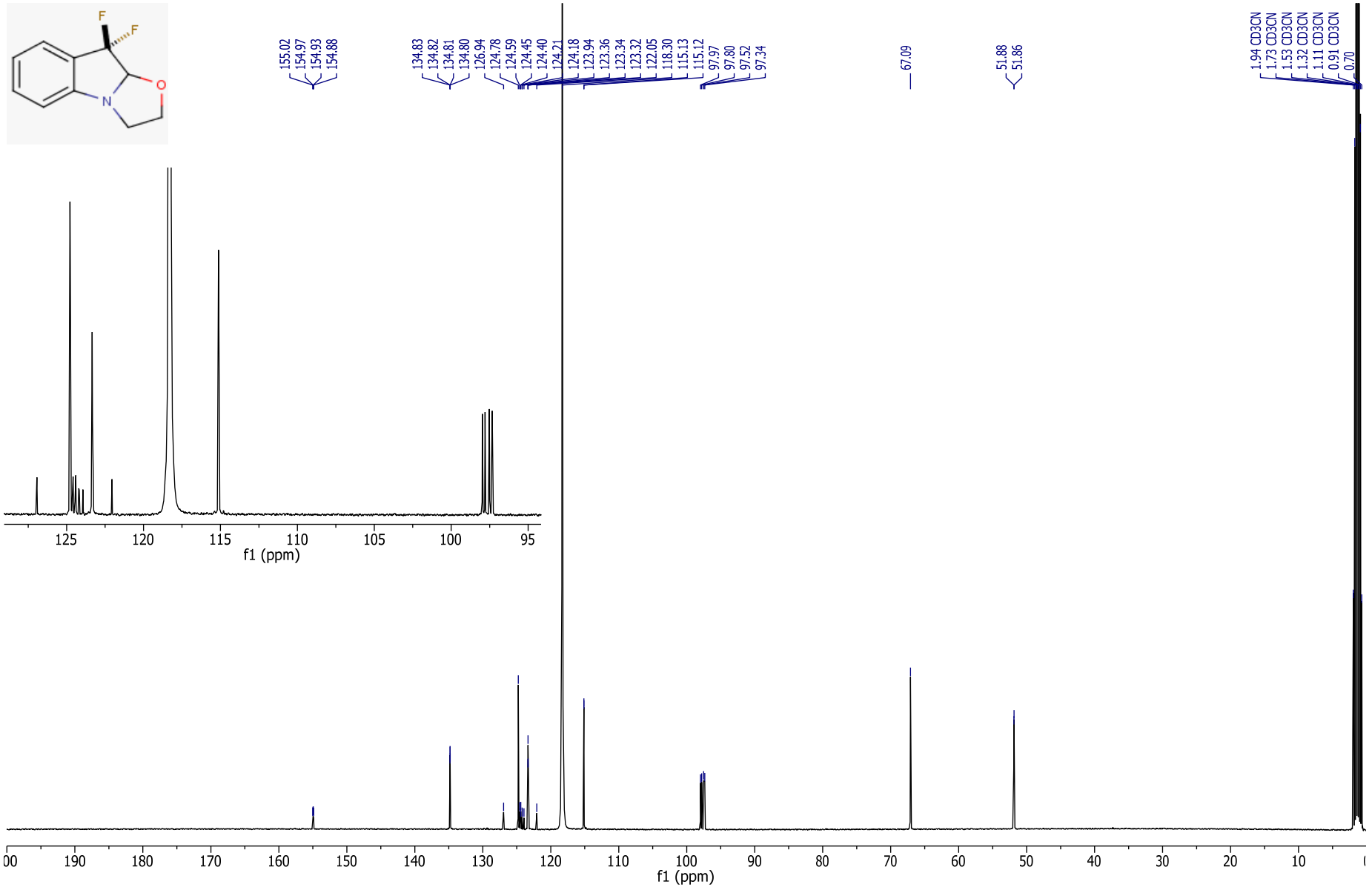


^{1}H and ^{19}F NMR of compound 3a

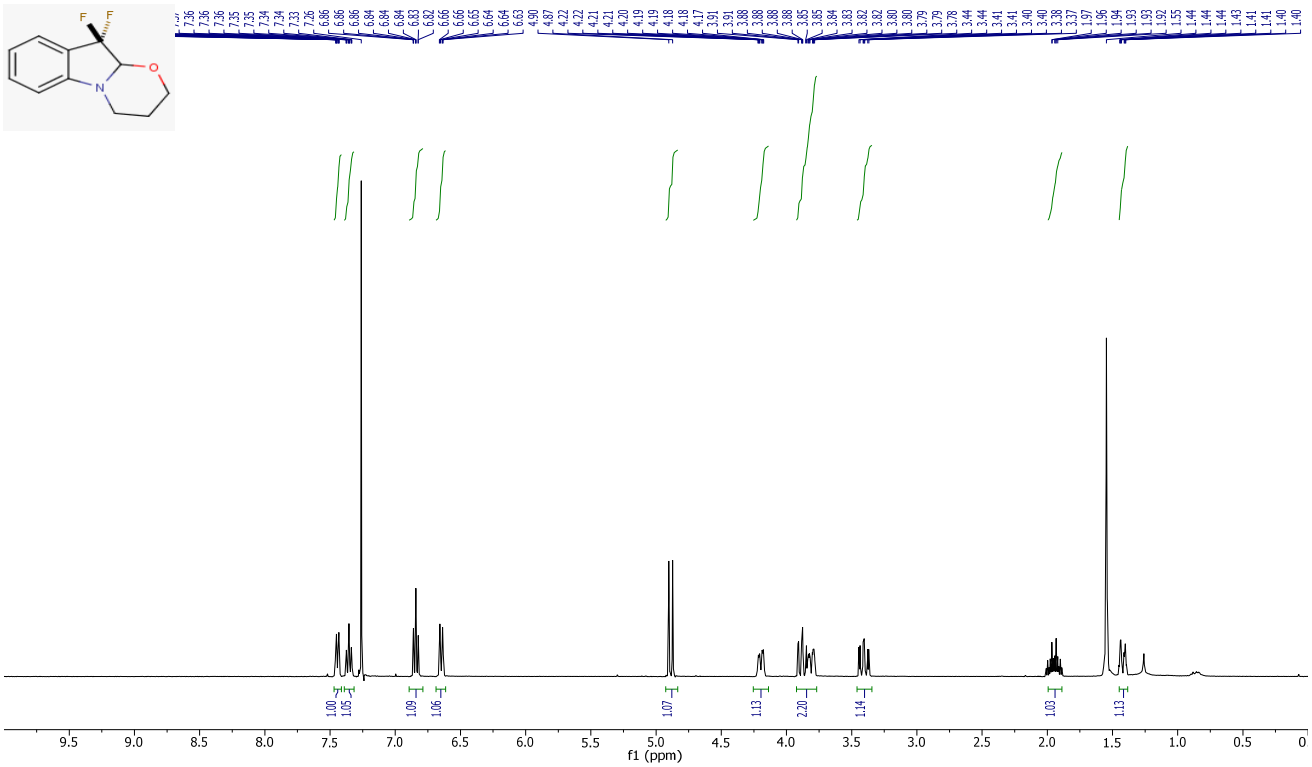


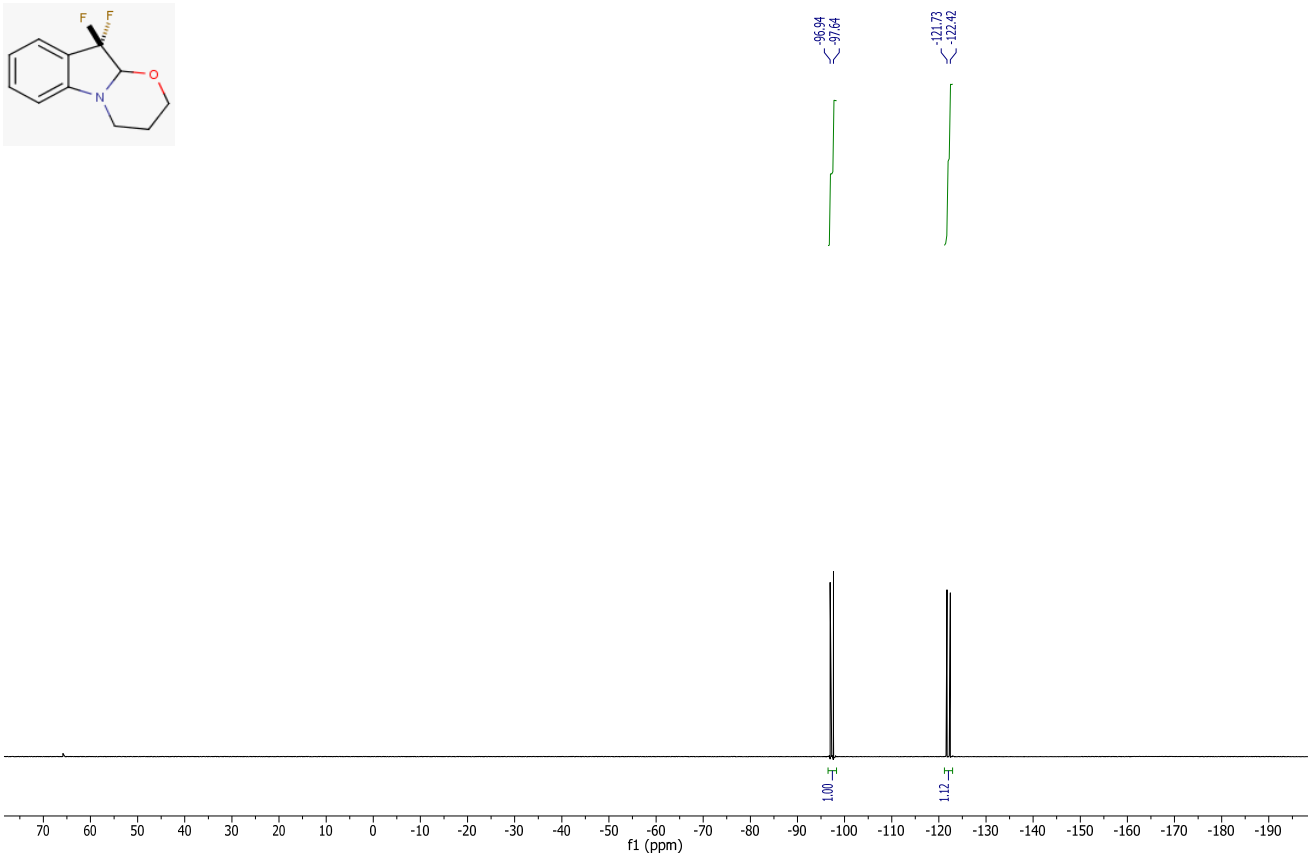


^{13}C NMR of compound 3a

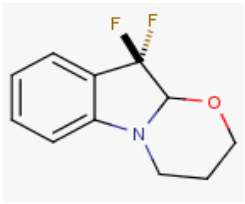


^{1}H and ^{19}F NMR of compound 3d





^{13}C NMR of compound 3d



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150.55
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150.47
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133.15
129.80
128.55
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124.45
122.86
122.71
122.50
122.27
122.24
122.01
120.32
119.26
119.24
119.22
108.59
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77.48 CDCl3
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76.84 CDCl3
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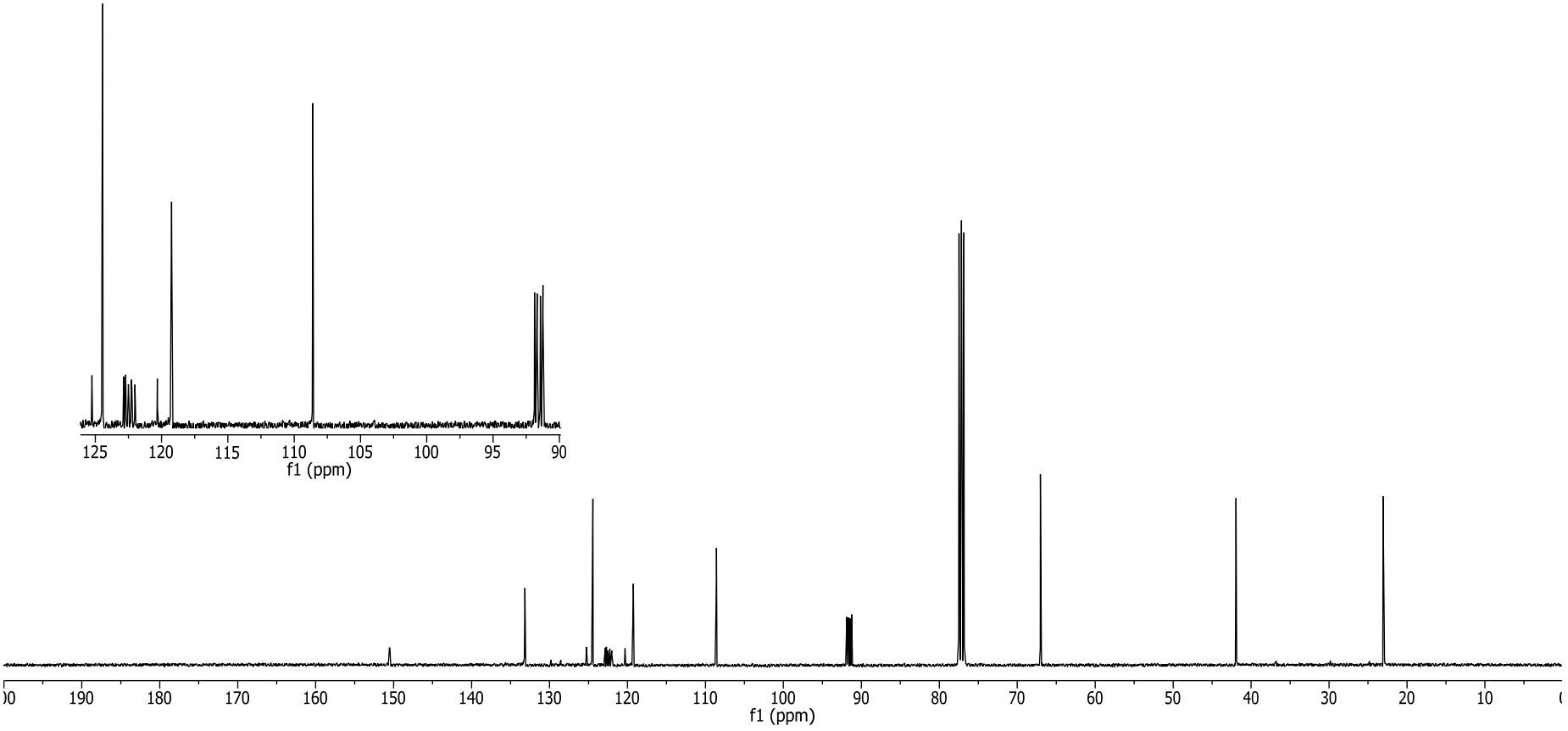
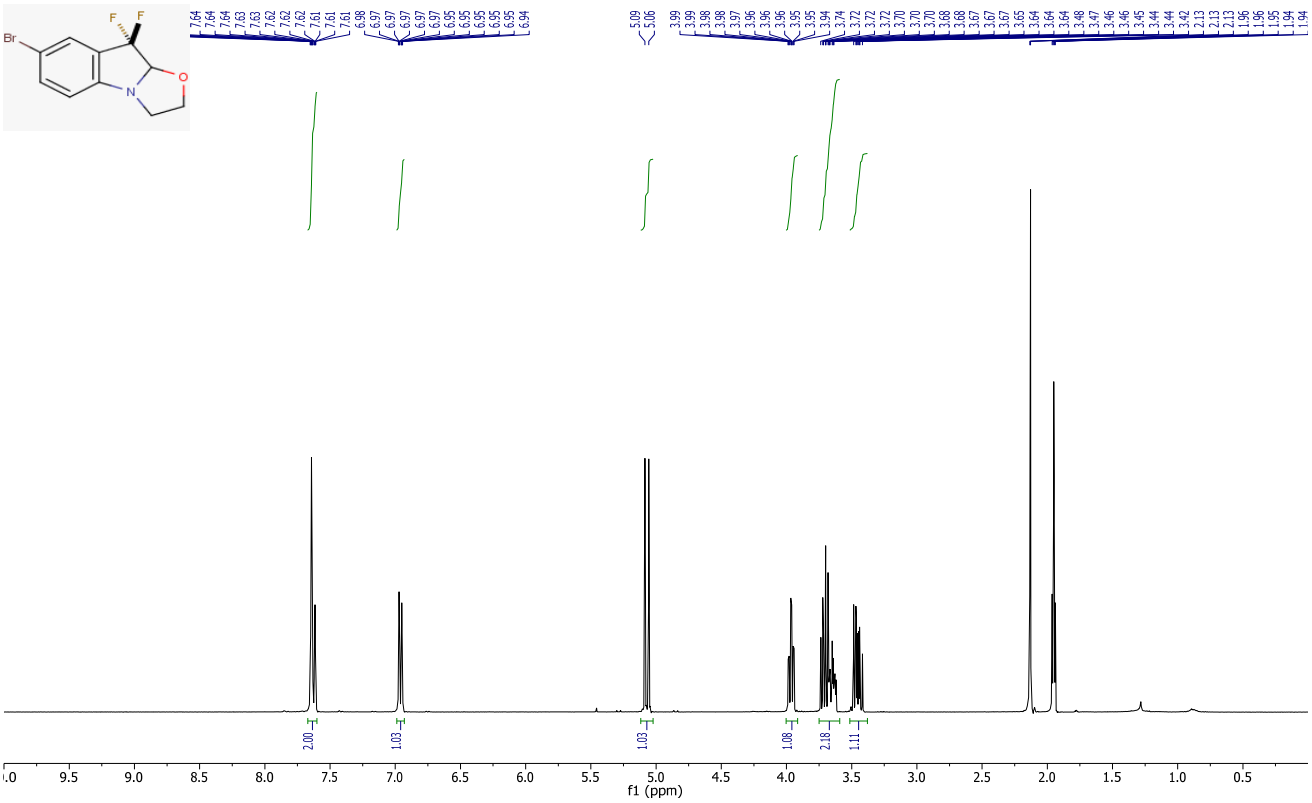
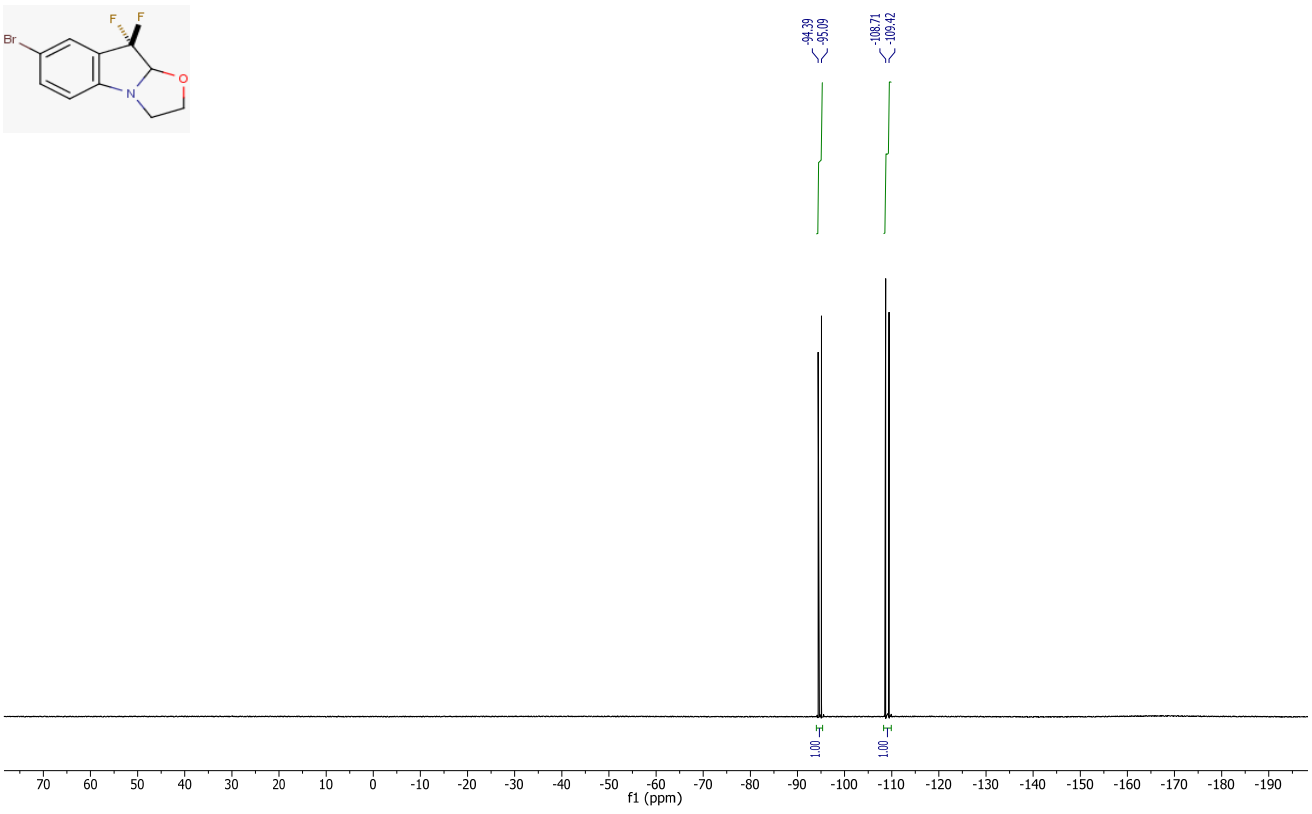
23.08

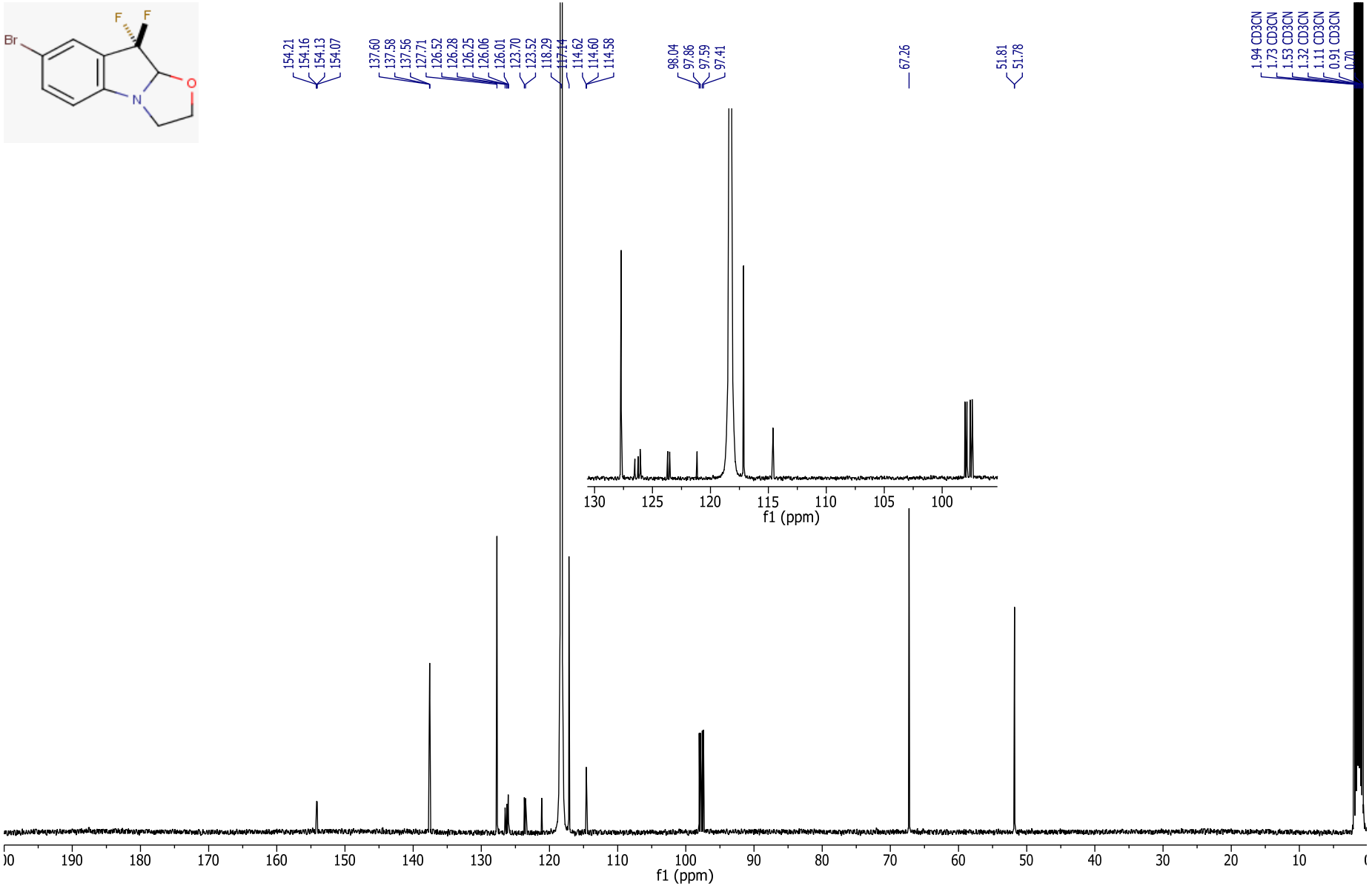


^{1}H and ^{19}F NMR of compound 3i

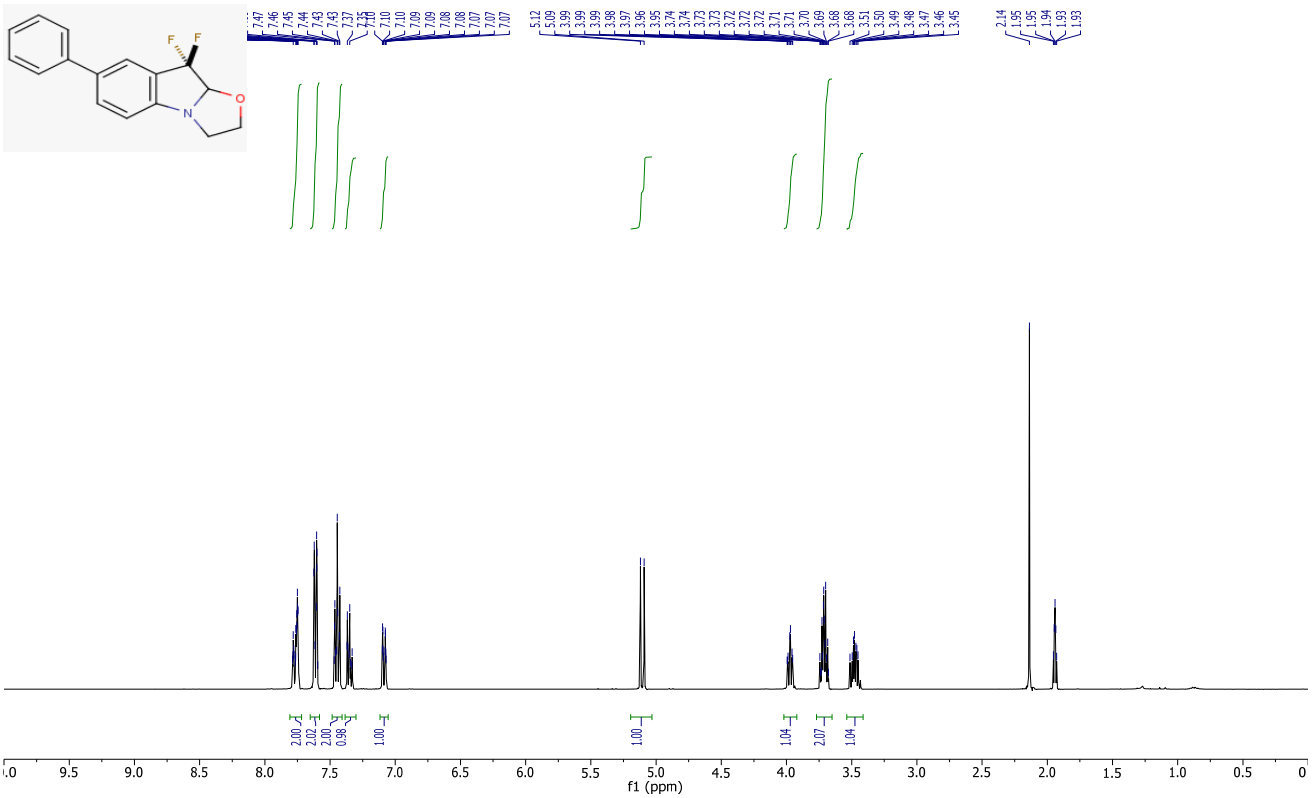


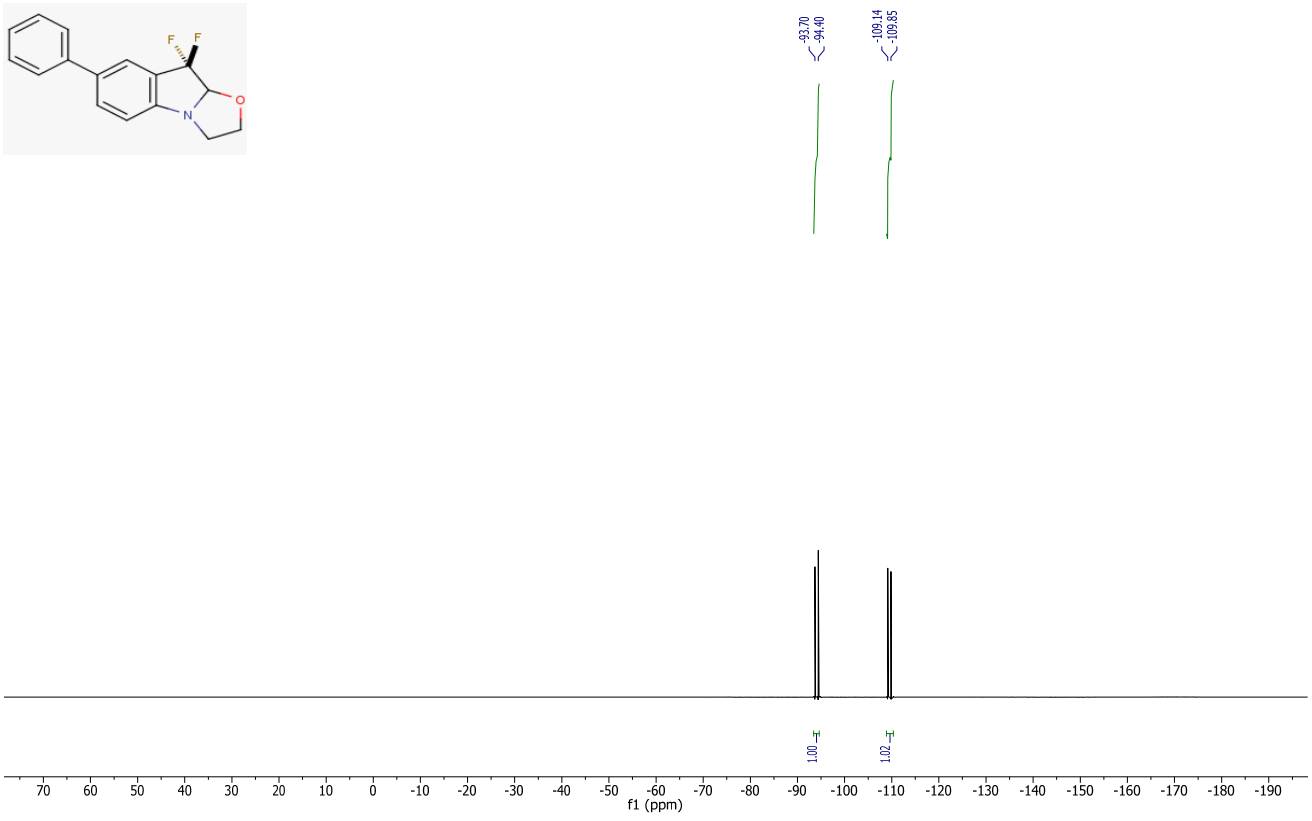


^{13}C NMR of compound 3i

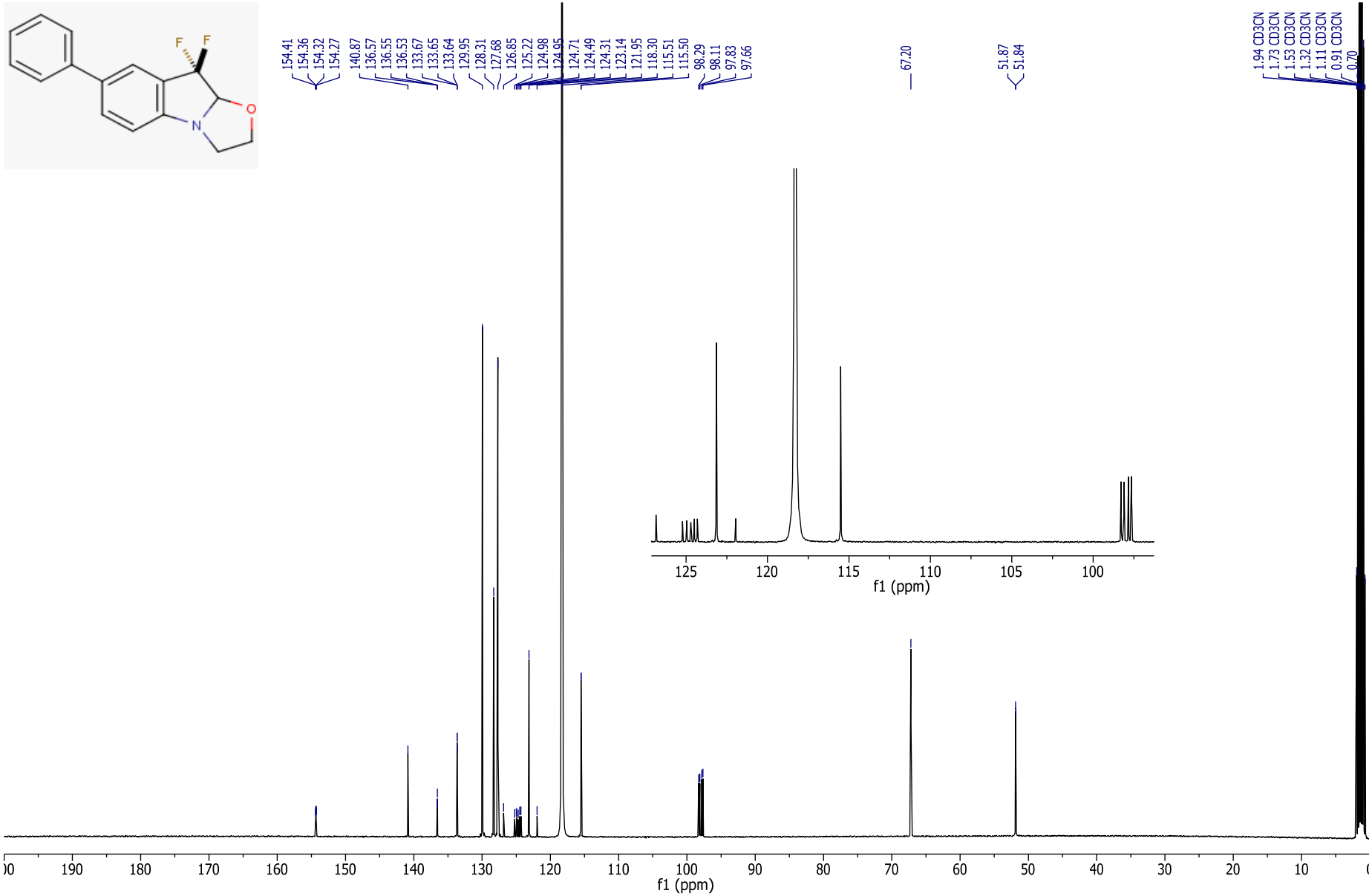


^{1}H and ^{19}F NMR of compound 3j

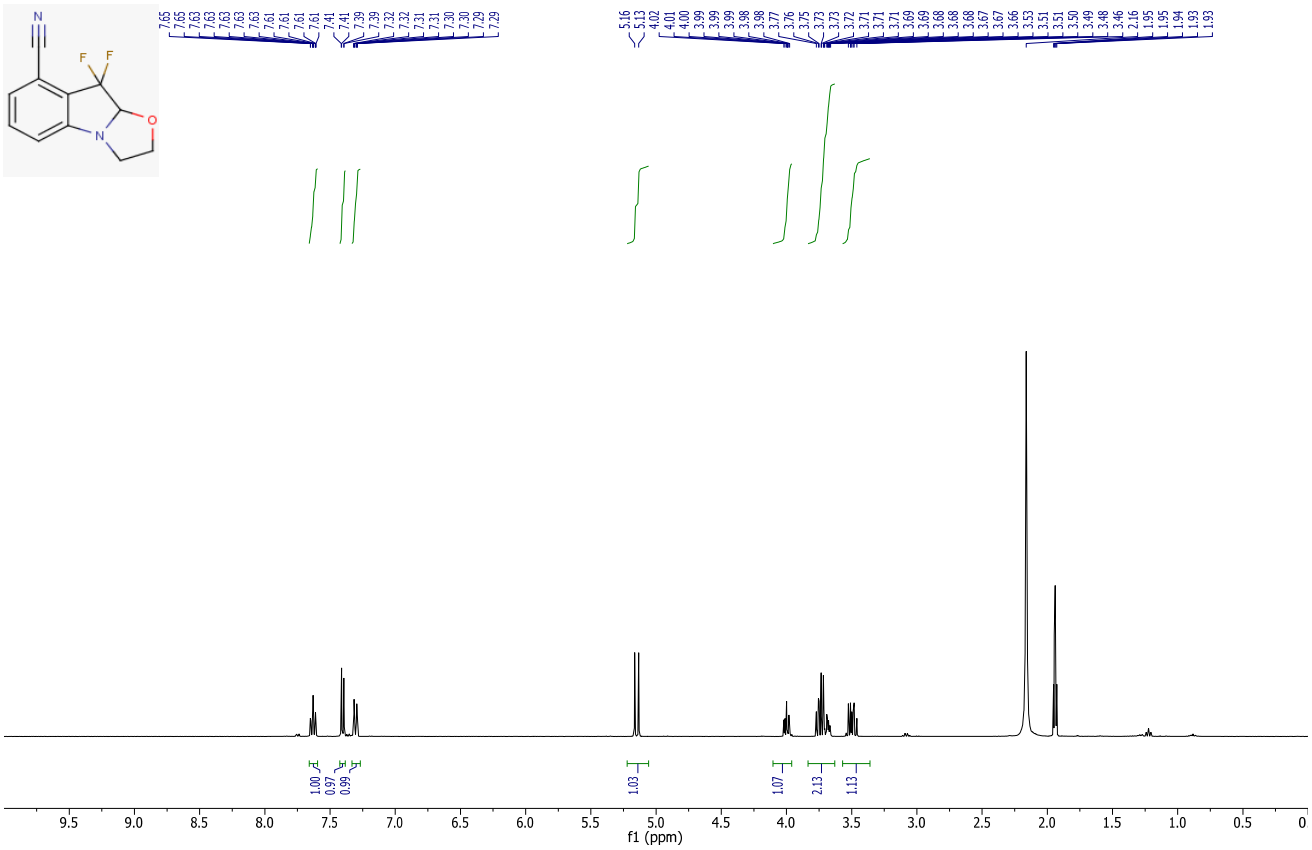


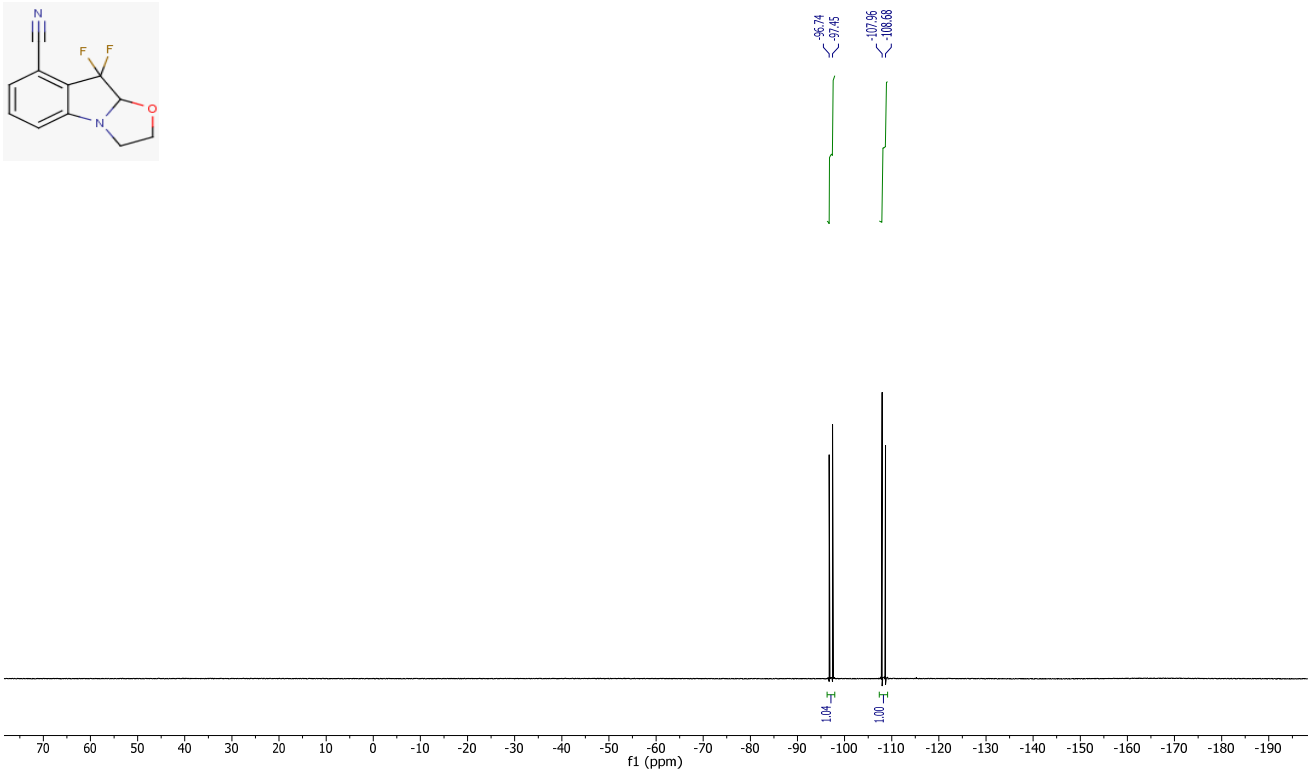


^{13}C NMR of compound 3j



^{1}H and ^{19}F NMR of compound 3m





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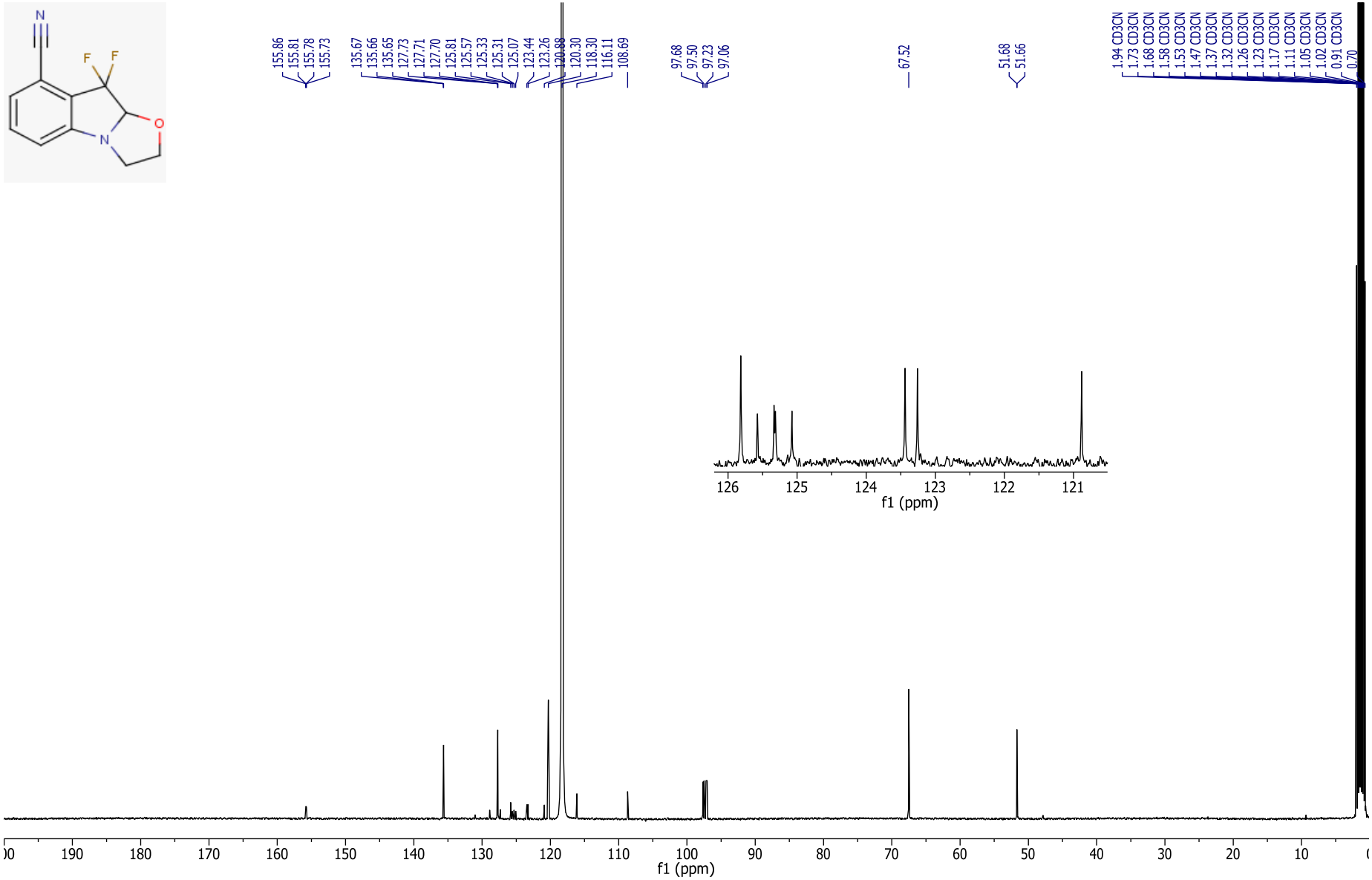

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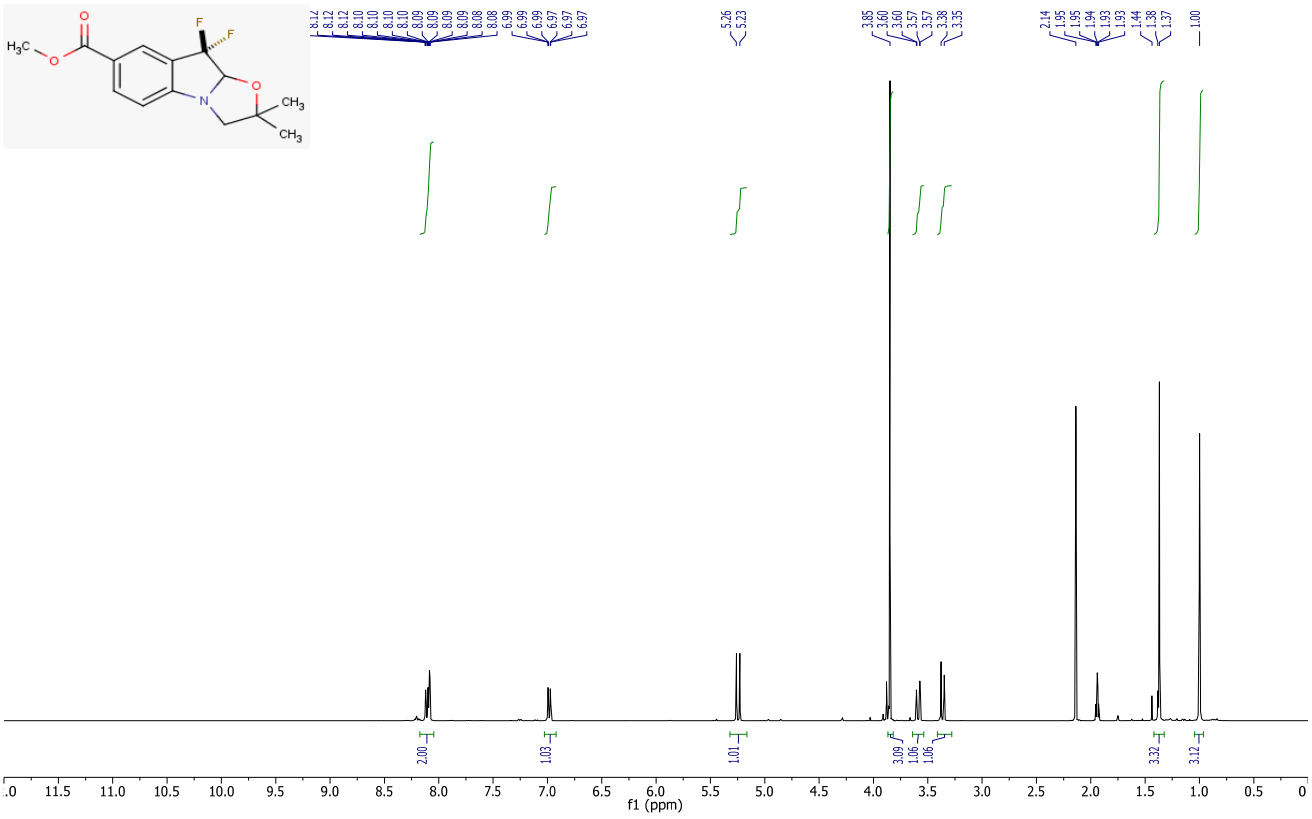
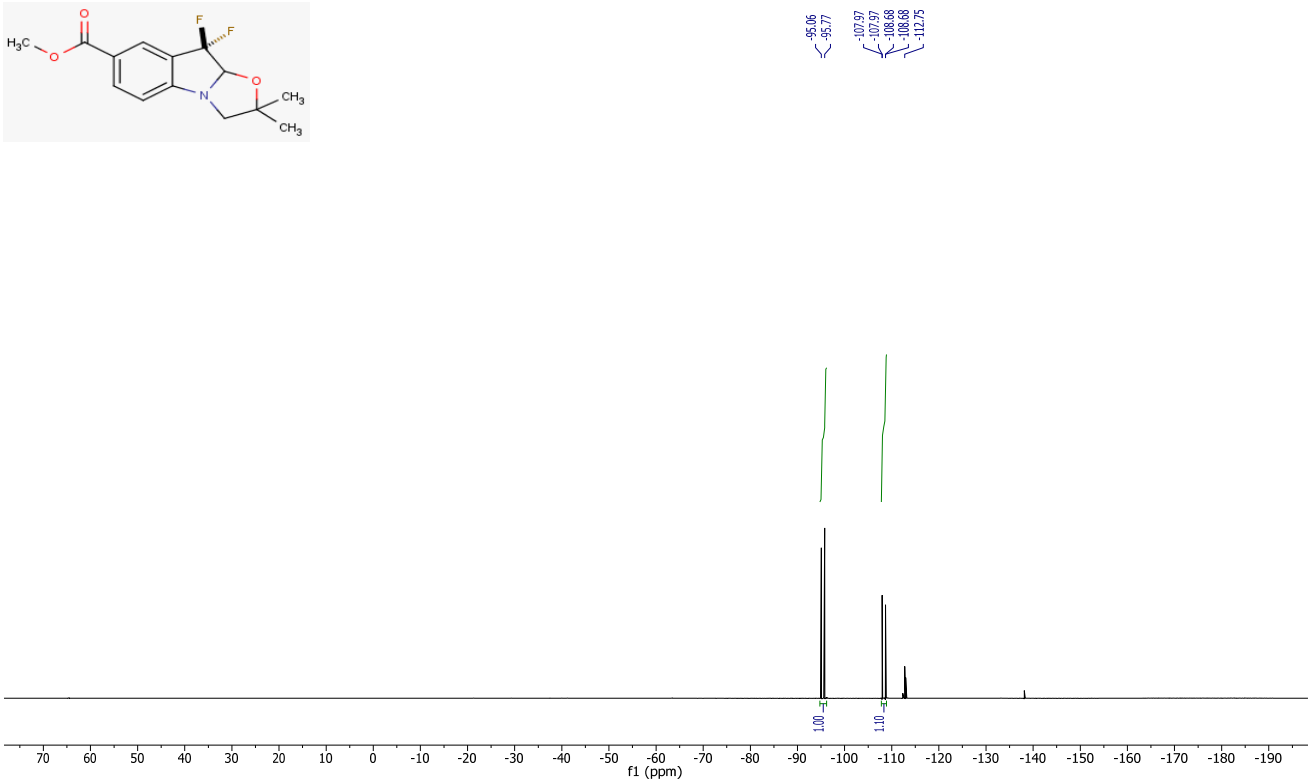
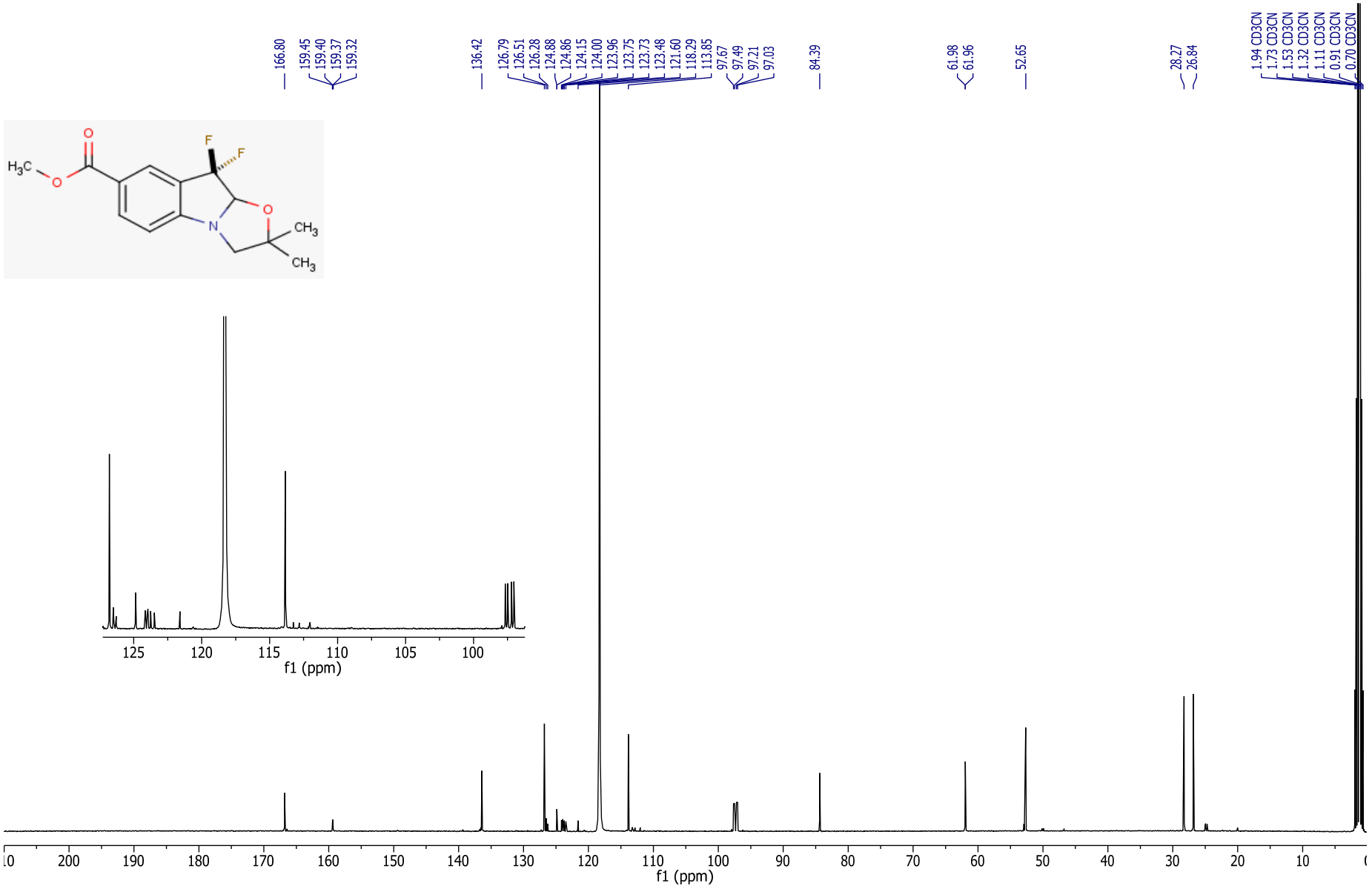
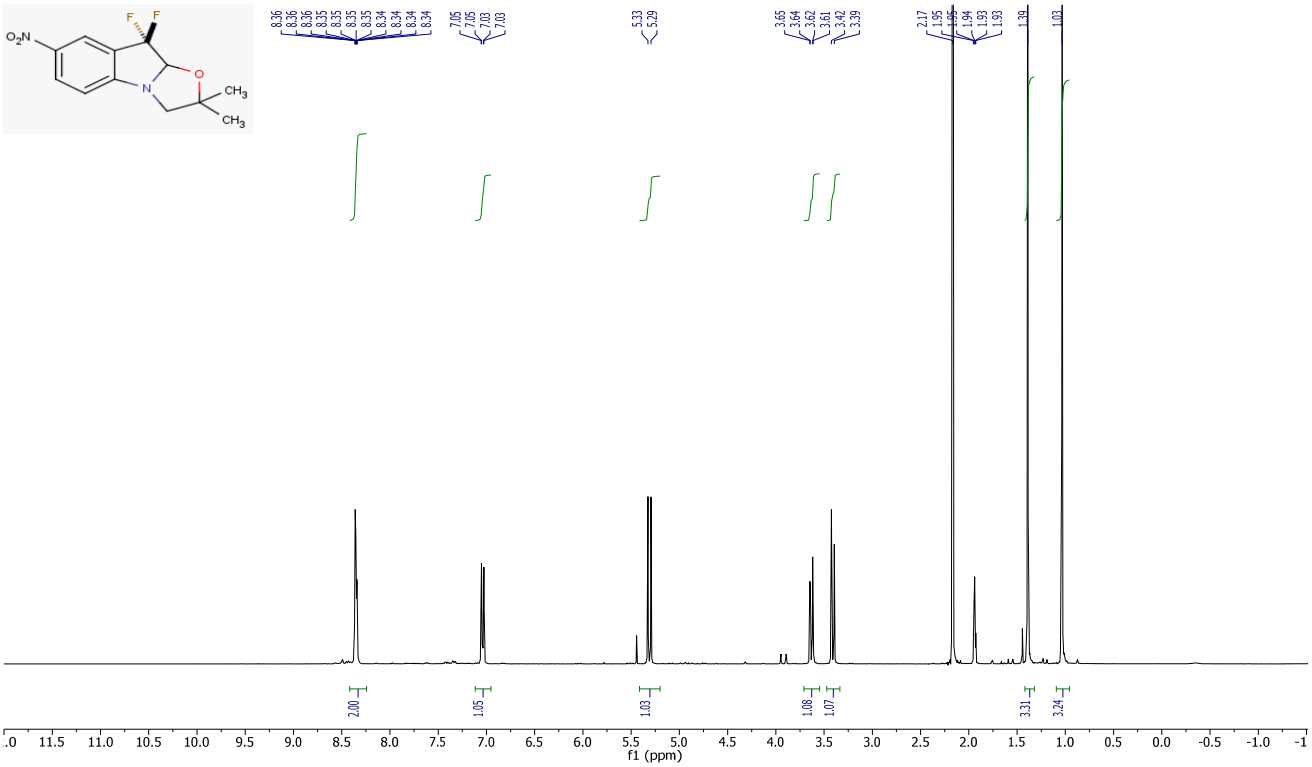


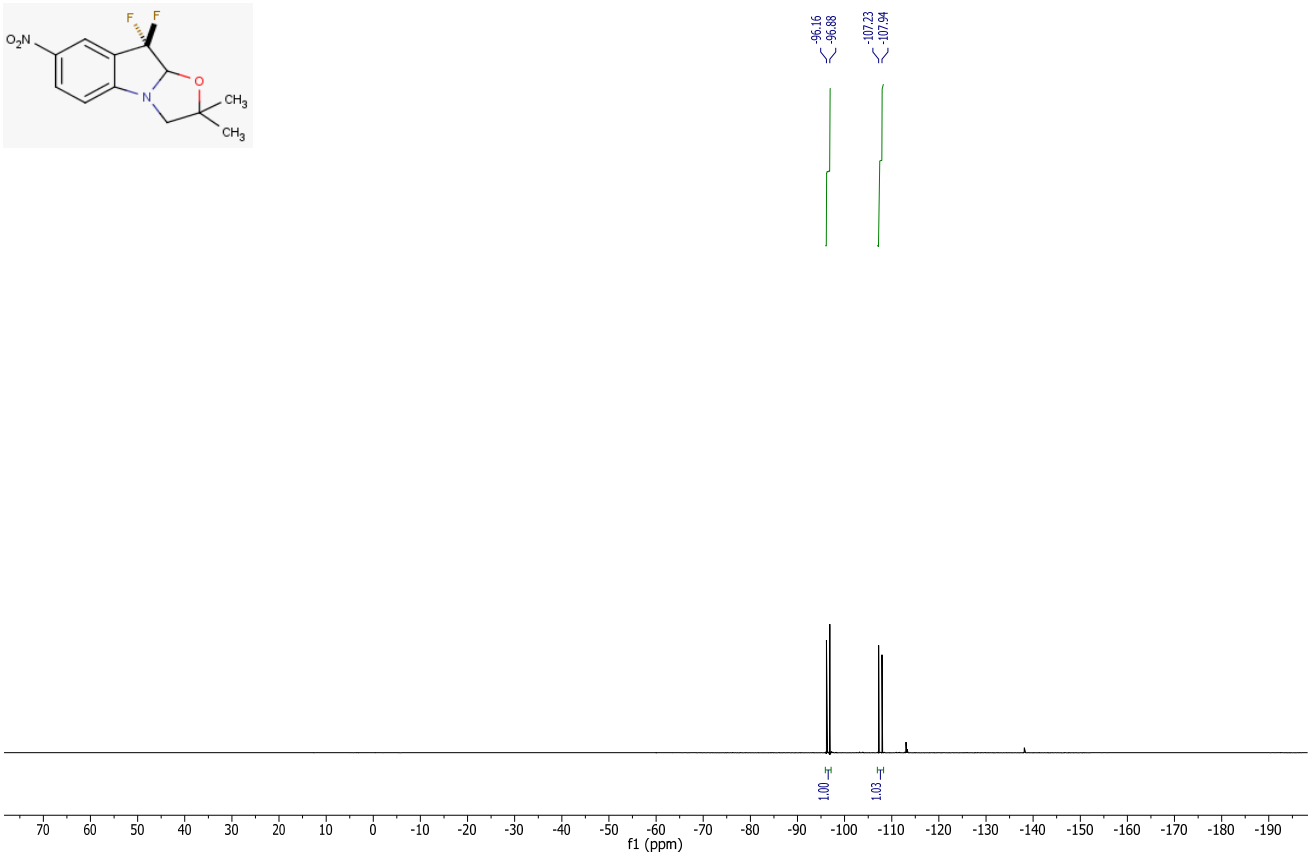


^{13}C NMR of compound 3n



^{1}H and ^{19}F NMR of compound 3o





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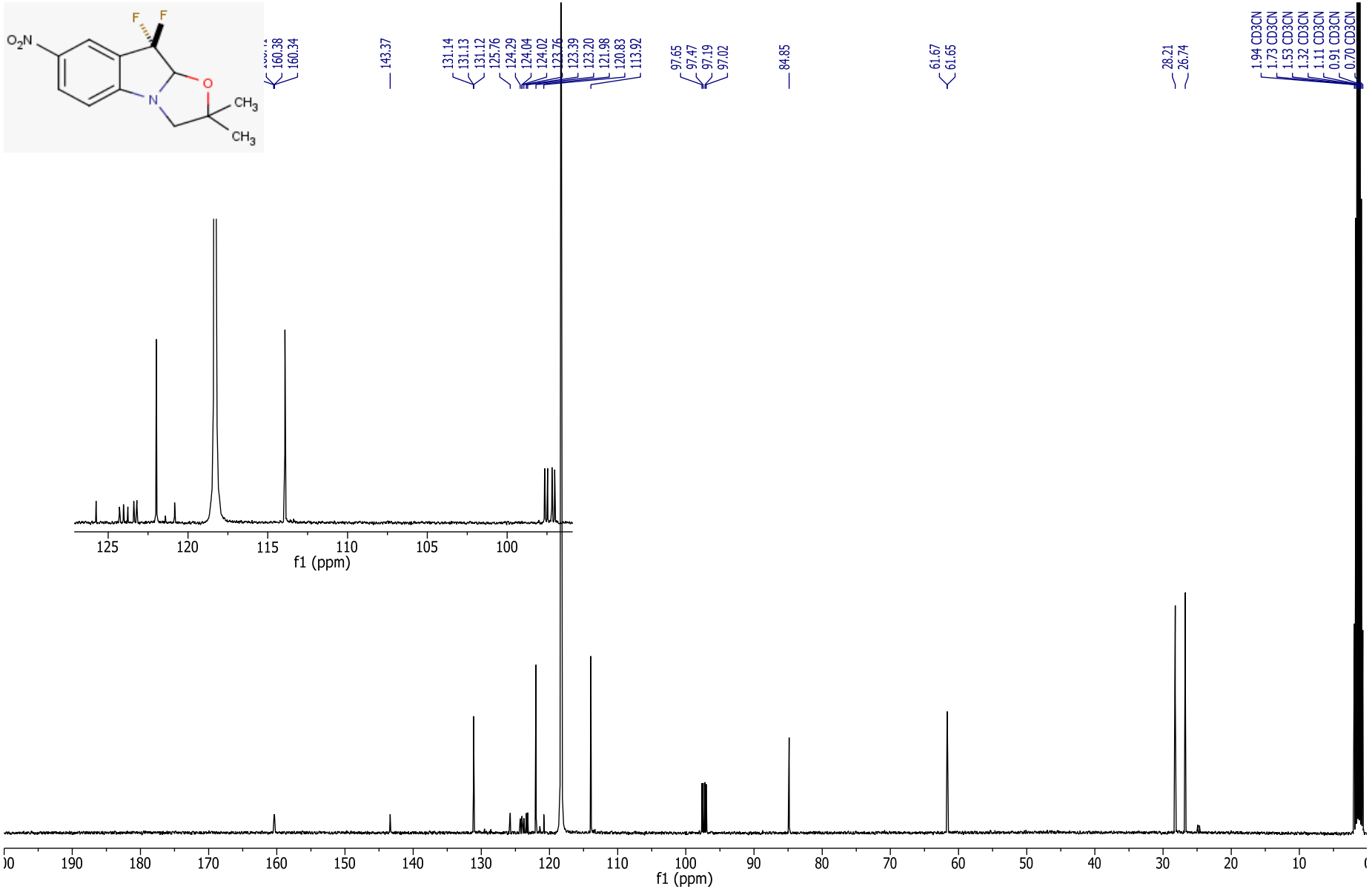
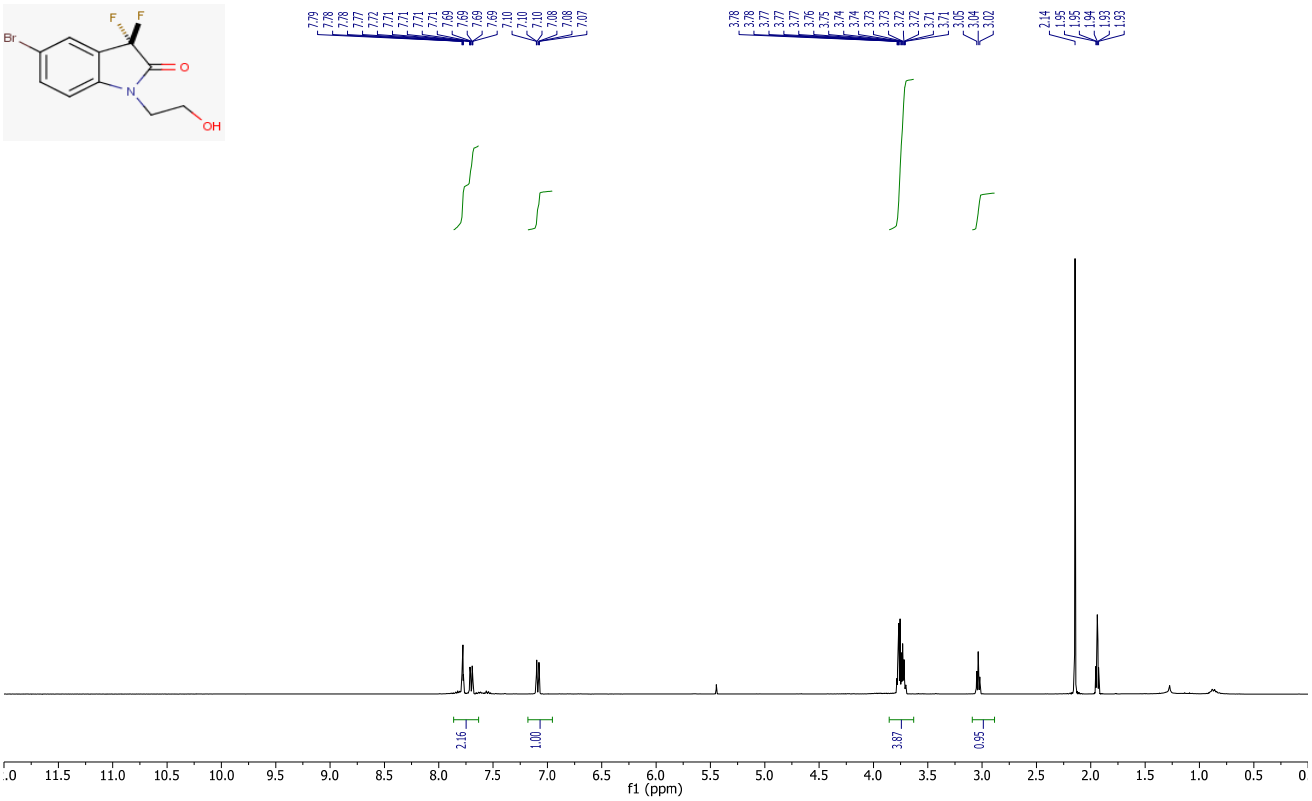
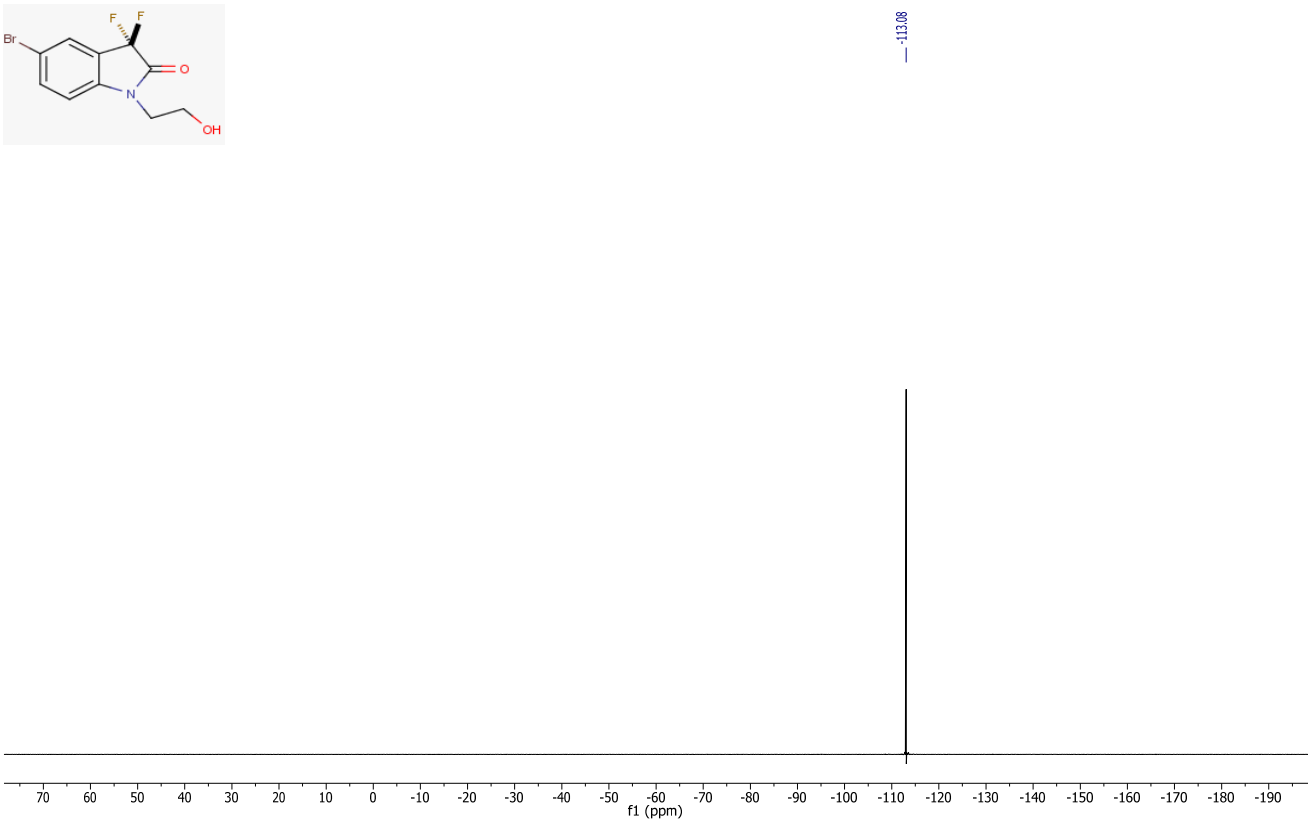


^{1}H and ^{19}F NMR of compound 7i





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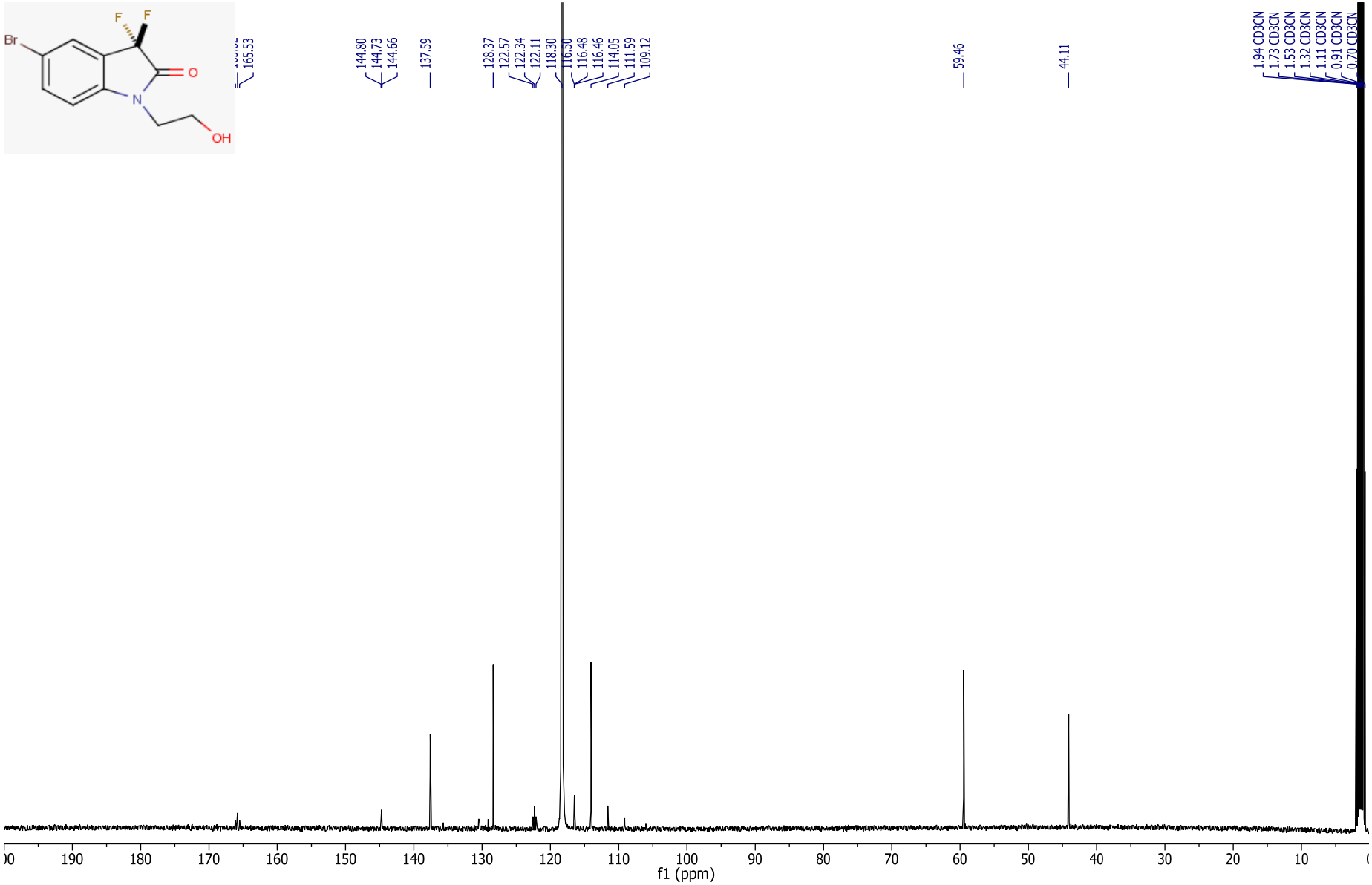
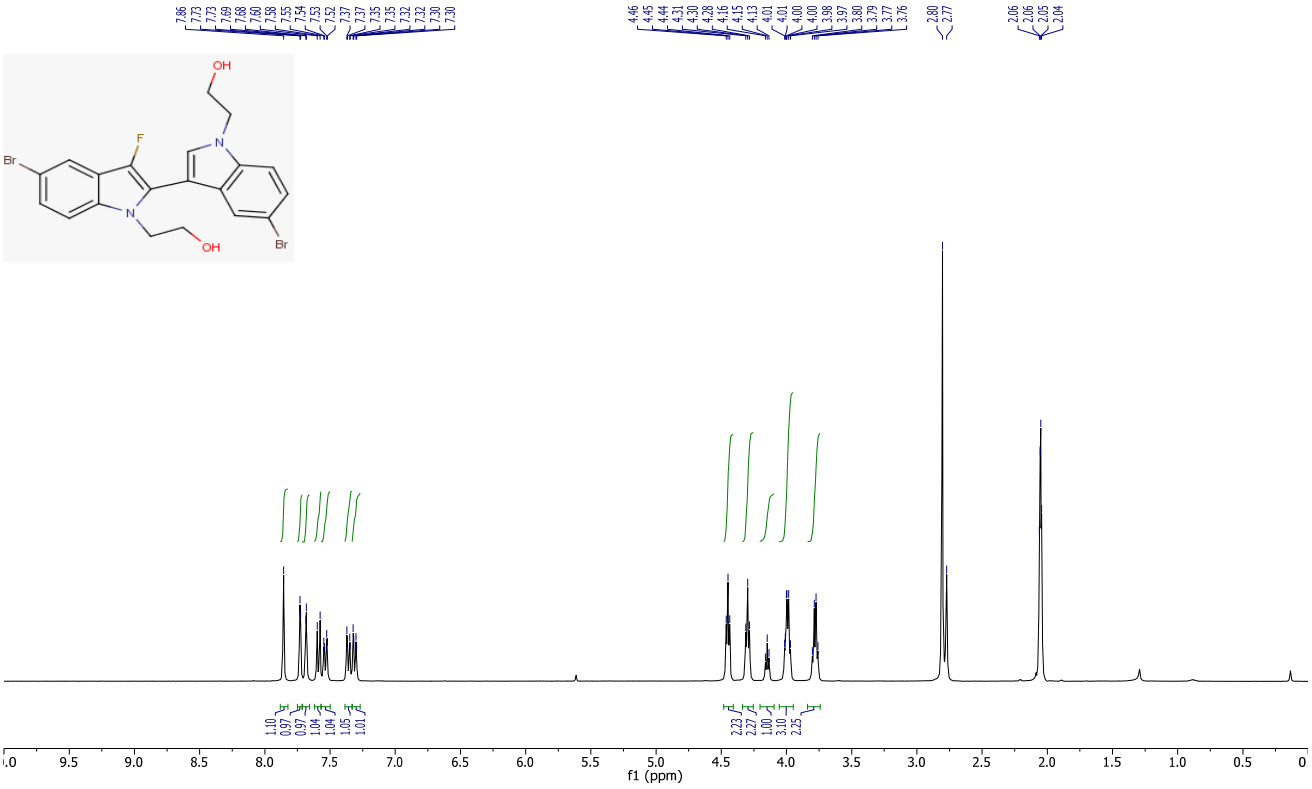
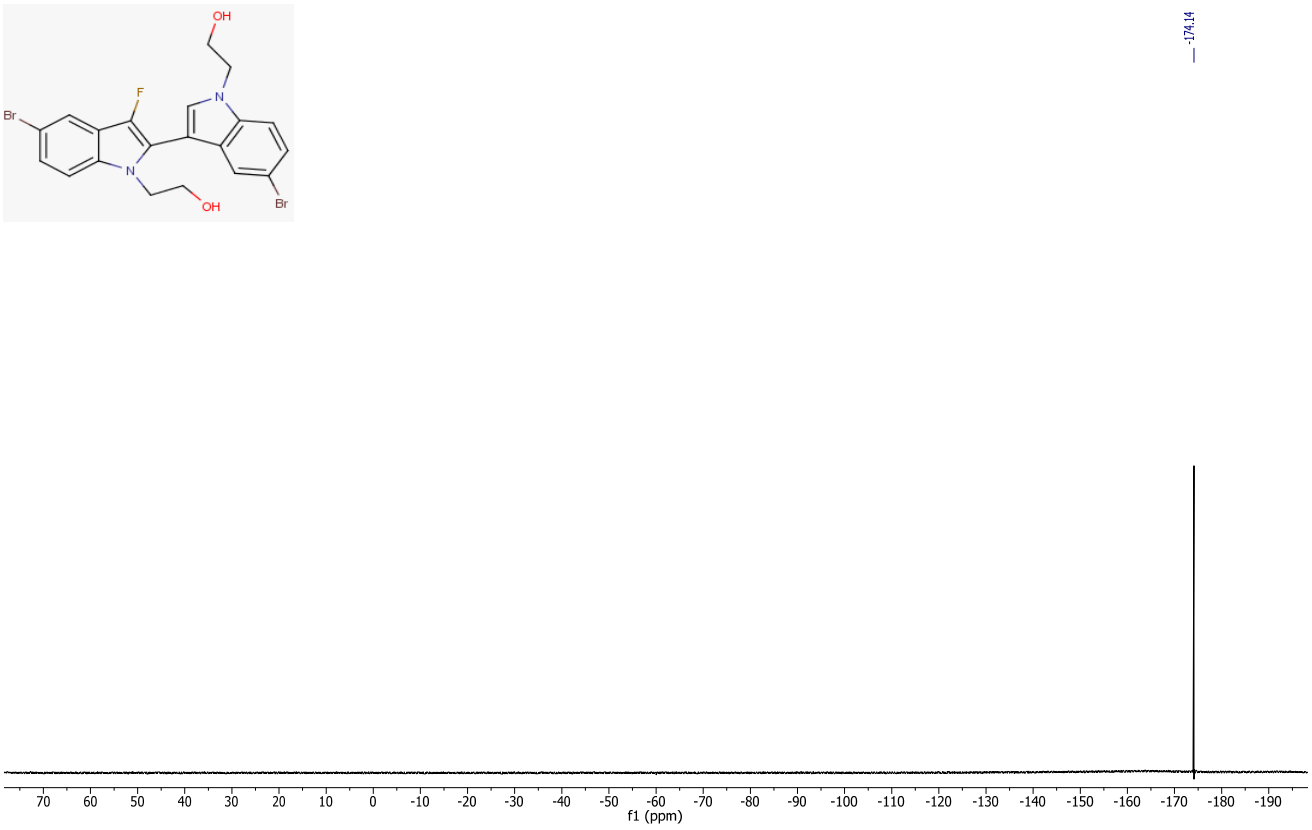


^{1}H and ^{19}F NMR of compound 6i





^{13}C NMR of compound 6i