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Supporting Information

Asymmetric synthesis of C-F quaternary α-fluoro-β-amino-indolin-2-ones via Mannich addition reactions; facets of reactivity, structural generality and stereochemical outcome

Chen Xie, Wanxing Sha, Yi Zhu, Jianlin Han, Vadim A. Soloshonok and Yi Pan

1. General information

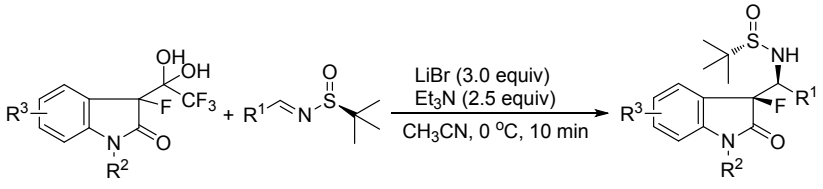
All commercial reagents were used without additional purification unless otherwise specified. *β*-keto-amides-hydrates **8** and **12** were synthesized according to literature.[1] Solvents were purified and dried according to standard methods prior to use. All experiments were monitored by thin layer chromatography (TLC) using UV light as visualizing agent. TLC was performed on pre-coated silica gel plated. Column chromatography was performed using silica gel 60 (300-400 mesh).

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were measured on Bruker AVANCE III-400. Chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm) or with the solvent reference relative to TMS employed as the internal standard. Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (br) and multiplet (m)], coupling constants [Hz], integration). ^{19}F NMR spectra were broadband decoupled from hydrogen nuclei. Melting points are uncorrected. Values of optical rotation were measured on Rudolph Automatic Polarimeter A21101 at the wavelength of the sodium D-line (589 nm). Infrared spectra were obtained on Bruker Vector 22 in KBr pellets. HRMS were recorded on a LTQ-Orbitrap XL (Thermofisher, U. S. A.). HPLC analysis were performed on Shimadzu SPD-20A using Daicel Chiralpak AD-H Column.

References:
1. Xie, C.; Zhang, L.; Sha, W.; Soloshonok, V. A.; Han, J.; Pan, Y. *Org. Lett.* **2016**, *18*, 3270-3273.

2. General synthetic procedures

2.1. General procedures for asymmetric detrifluoroacetylative Mannich reaction

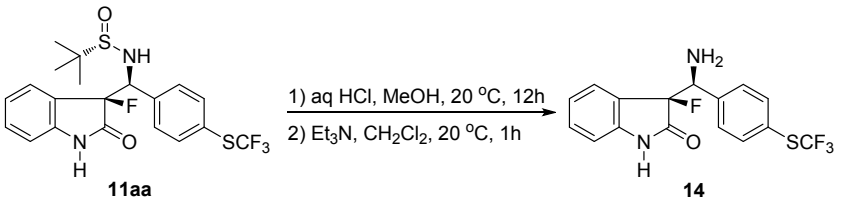


8, **12** **10** **11**, **13**

R^1 = non-fluorinated group

To a solution of *β*-keto-amides-hydrates **8** or **12** (0.6 mmol), non-fluorinated sulfinylimines **10** (0.5 mmol), and LiBr (156.3 mg, 1.8 mmol) in CH_3CN (5 mL) at 0 °C was added Et_3N (151.8 mg, 1.5 mmol) dropwise. After 10 min, the reaction was quenched with saturated aqueous NH_4Cl (5 mL) followed by H_2O (10 mL) and EtOAc (20 mL), then the mixture was brought to room temperature. The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with H_2O (2 × 20 mL) and brine solution (1 × 20 mL) and dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography (petroleum ether/ethyl acetate = 2:1 to 1:2) to afford the corresponding product **11** or **13**.

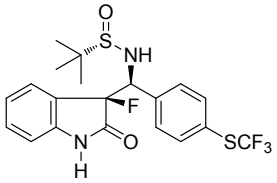
2.2. Procedures for the deprotection to affording the free amine



11aa (92.1 mg, 0.2 mmol) and MeOH (5 mL) were placed in a 25 mL round-bottom flask and aq HCl (36%, 1 mL) was added dropwise. The reaction was stirred at 20 °C for 12 h, during which the cleavage was monitored by TLC. Volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and Et_3N (1.52 g, 15 mmol) was added. The mixture was stirred at 20 °C for 1 h, then H_2O (10 mL) was added. The organic layer was taken, washed with H_2O (2 × 10 mL), dried with anhydrous Na_2SO_4, filtered and the solvent was removed to give the crude product, which was purified by column chromatography (petroleum ether/ethyl acetate = 1:1) to afford the corresponding deprotection product **14**.

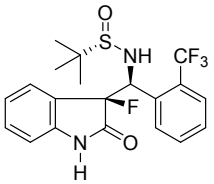
3. Characterization data of compounds

3.1. Characterization data of compounds 11 and 13



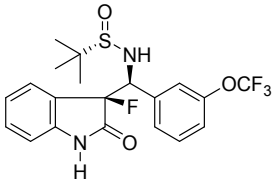
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (11aa)

White solid, 205.1 mg (89% yield), R_f = 0.26 (hexanes/ethyl acetate = 1:1), m.p. 192–193 °C, [α]20 D = +55.3 (c = 0.43, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.27 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.97 (d, *J* = 4.6 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.51 (s, 3F), -159.04 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7 (d, *J* = 21.6 Hz), 142.1 (d, *J* = 5.6 Hz), 137.9 (d, *J* = 4.6 Hz), 135.7, 132.1 (d, *J* = 2.8 Hz), 129.9, 129.5 (q, *J* = 308.2 Hz), 125.7, 124.8 (q, *J* = 1.9 Hz), 123.1 (d, *J* = 18.6 Hz), 123.1 (d, *J* = 2.4 Hz), 111.0, 92.6 (d, *J* = 199.9 Hz), 62.4 (d, *J* = 27.7 Hz), 56.7, 22.6. IR (cm^{-1}): 1732, 1720, 1625, 1477, 1157, 1117, 1085, 1046, 1015, 840, 756. HRMS (TOF MS ESI): calcd for $C_{20}H_{20}F_4N_2O_2S_2Na^+$ $[M+Na]^+$ 483.0795, found 483.0803.



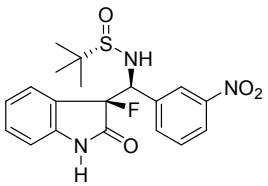
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(2-(trifluoromethyl)phenyl)methyl)-2-methylpropane-2-sulfinamide (11ab)

White solid, 137.6 mg (64% yield), R_f = 0.16 (hexanes/ethyl acetate = 1:1), m.p. 192–193 °C, [α]20 D = +58.1 (c = 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, MeOD) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.47 – 7.39 (m, 2H), 7.26 (tt, *J* = 7.8, 1.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.47 (d, *J* = 14.5 Hz, 1H), 4.87 (s, 2H), 1.07 (s, 9H); ^{19}F NMR (376 MHz, MeOD) δ -57.01 (d, *J* = 3.9 Hz, 3F), -159.93 (s, 1F); ^{13}C NMR (101 MHz, MeOD) δ 175.1 (d, *J* = 20.9 Hz), 143.9 (d, *J* = 5.8 Hz), 136.9 (dd, *J* = 3.6, 1.2 Hz), 133.3, 133.0 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 1.1 Hz), 129.9, 129.2 (q, *J* = 29.7 Hz), 127.8, 127.1 (q, *J* = 5.9 Hz), 125.5 (q, *J* = 273.9 Hz), 124.7 (d, *J* = 18.4 Hz), 123.6 (d, *J* = 2.5 Hz), 111.7, 93.8 (d, *J* = 195.8 Hz), 60.6 (dd, *J* = 29.5, 2.2 Hz), 57.9, 22.6. IR (cm^{-1}): 1716, 1616, 1473, 1311, 1164, 1121, 1032, 1012, 758. HRMS (TOF MS ESI): calcd for $C_{20}H_{20}F_4N_2O_2SNa^+$ $[M+Na]^+$ 451.1074, found 451.1075.



(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(3-(trifluoromethoxy)phenyl)methyl)-2-methylpropane-2-sulfinamide (11ac)

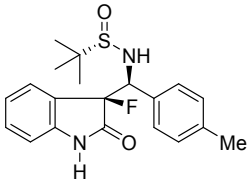
White solid, 188.9 mg (85% yield), R_f = 0.28 (hexanes/ethyl acetate = 1:1), m.p. 156–157 °C, [α]20 D = +47.2 (c = 0.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.15 (m, 2H), 7.12 – 6.99 (m, 4H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.25 (dd, *J* = 7.4, 4.7 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.93 (s, 3F), -159.12 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 (d, *J* = 21.6 Hz), 148.9 (q, *J* = 1.7 Hz), 141.9 (d, *J* = 5.6 Hz), 137.2 (d, *J* = 4.7 Hz), 132.1 (d, *J* = 2.8 Hz), 129.5, 127.7, 125.7, 123.2, 123.1 (d, *J* = 20.4 Hz), 121.5, 121.3, 120.4 (q, *J* = 257.5 Hz), 110.9, 92.6 (d, *J* = 199.7 Hz), 62.3 (d, *J* = 27.7 Hz), 56.7, 22.6. IR (cm^{-1}): 1718, 1474, 1254, 1203, 1151, 1061, 1032, 755. HRMS (TOF MS ESI): calcd for $C_{20}H_{20}F_4N_2O_3SNa^+$ $[M+Na]^+$ 467.1023, found 467.1020.



(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(3-nitrophenyl)methyl)-2-methylpropane-2-sulfinamide (11ad)

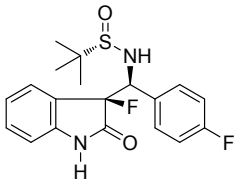
White solid, 194.3 mg (96% yield), R_f = 0.22 (hexanes/ethyl acetate = 1:1), m.p. 208–209 °C, [α]20 D = +72.2 (c = 0.42, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.10 – 8.00 (m,

2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 15.7, 7.7 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 5.38 – 5.32 (m, 1H), 5.06 (d, *J* = 4.3 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -159.21 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (d, *J* = 21.4 Hz), 147.9, 142.0 (d, *J* = 5.6 Hz), 137.3 (d, *J* = 4.6 Hz), 135.1, 132.4 (d, *J* = 2.7 Hz), 129.2, 125.6, 123.7, 123.6, 123.3 (d, *J* = 2.3 Hz), 122.7 (d, *J* = 18.6 Hz), 111.2, 92.4 (d, *J* = 200.3 Hz), 62.1 (d, *J* = 28.1 Hz), 56.9, 22.6. IR (cm^{-1}): 1733, 1626, 1528, 1478, 1348, 1198, 1037, 813. HRMS (TOF MS ESI): calcd for $C_{19}H_{20}FN_3O_4SNa^+$ $[M+Na]^+$ 428.1051, found 428.1059.



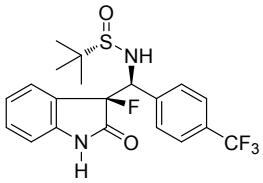
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(p-tolyl)methyl)-2-methylpropane-2-sulfinamide (11ae)

White solid, 148.0 mg (79% yield), R_f = 0.24 (hexanes/ethyl acetate = 1:1), m.p. 186–187 °C, [α]20 D = +46.3 (c = 0.38, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 7.01 – 6.90 (m, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.19 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.95 (s, 1H), 2.21 (s, 3H), 1.21 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.06 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2 (d, *J* = 21.6 Hz), 142.3 (d, *J* = 5.5 Hz), 138.1, 131.7 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 4.6 Hz), 128.8, 128.8, 125.7, 123.7 (d, *J* = 18.4 Hz), 122.7, 110.9, 92.9 (d, *J* = 197.9 Hz), 62.5 (d, *J* = 27.1 Hz), 56.5, 22.7, 21.2. IR (cm^{-1}): 1714, 1623, 1473, 1198, 1059, 1032, 826, 755. HRMS (TOF MS ESI): calcd for $C_{20}H_{23}FN_2O_2SNa^+$ $[M+Na]^+$ 397.1356, found 397.1360.



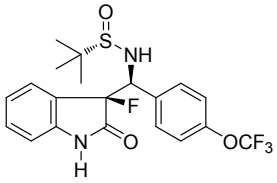
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(4-fluorophenyl)methyl)-2-methylpropane-2-sulfinamide (11af)

White solid, 160.4 mg (85% yield), R_f = 0.24 (hexanes/ethyl acetate = 1:1), m.p. 183–184 °C, [α]20 D = +60.5 (c = 0.17, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.23 (dd, *J* = 7.4, 4.4 Hz, 1H), 4.98 (d, *J* = 3.9 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.14 (s, 1F), -158.96 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9 (d, *J* = 21.7 Hz), 162.6 (d, *J* = 247.7 Hz), 142.1 (d, *J* = 5.6 Hz), 131.9 (d, *J* = 2.7 Hz), 130.7 (d, *J* = 8.2 Hz), 130.3 (dd, *J* = 5.0, 3.2 Hz), 125.6, 123.5 (d, *J* = 18.5 Hz), 123.0 (d, *J* = 2.4 Hz), 115.1 (d, *J* = 21.6 Hz), 110.9, 92.8 (d, *J* = 198.8 Hz), 62.1 (d, *J* = 27.2 Hz), 56.6, 22.7. IR (cm^{-1}): 1724, 1623, 1509, 1474, 1227, 1204, 1190, 1048, 840, 756, 708. HRMS (TOF MS ESI): calcd for $C_{19}H_{20}F_2N_2O_2SNa^+$ $[M+Na]^+$ 401.1106, found 401.1106.



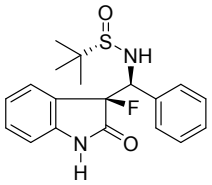
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(4-(trifluoromethyl)phenyl)methyl)-2-methylpropane-2-sulfinamide (11ag)

White solid, 194.7 mg (91% yield), R_f = 0.26 (hexanes/ethyl acetate = 1:1), m.p. 197–198 °C, [α]20 D = +59.9 (c = 0.45, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.29 (dd, *J* = 7.2, 4.7 Hz, 1H), 4.88 (d, *J* = 4.2 Hz, 1H), 1.23 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68 (s, 3F), -158.81 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (d, *J* = 21.6 Hz), 141.9 (d, *J* = 5.6 Hz), 138.8 (d, *J* = 3.6 Hz), 132.2 (d, *J* = 2.8 Hz), 130.6 (q, *J* = 32.6 Hz), 129.4, 125.7, 125.1 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 272.3 Hz), 123.2 (d, *J* = 2.5 Hz), 123.1 (d, *J* = 18.6 Hz), 111.0, 92.5 (d, *J* = 199.5 Hz), 62.4 (d, *J* = 27.5 Hz), 56.7, 22.7. IR (cm^{-1}): 1716, 1622, 1475, 1324, 1164, 1126, 1062, 1028, 1017, 849, 757. HRMS (TOF MS ESI): calcd for $C_{20}H_{20}F_4N_2O_2SNa^+$ $[M+Na]^+$ 451.1074, found 451.1072.



(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(4-(trifluoromethoxy)phenyl)methyl)-2-methylpropane-2-sulfinamide (11ah)

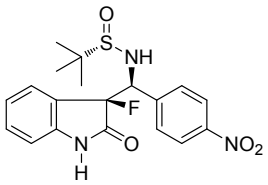
White solid, 189.2 mg (85% yield), R_f = 0.26 (hexanes/ethyl acetate = 1:1), m.p. 162–163 °C, [α]20 D = +59.2 (c = 0.45, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.22 – 7.13 (m, 3H), 7.02 – 6.94 (m, 3H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.26 (dd, *J* = 7.4, 4.8 Hz, 1H), 5.06 (d, *J* = 4.4 Hz, 1H), 1.21 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.80 (s, 3F), -158.80 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (d, *J* = 21.5 Hz), 149.1 (d, *J* = 1.6 Hz), 142.3 (d, *J* = 5.6 Hz), 133.3 (d, *J* = 4.9 Hz), 132.0 (d, *J* = 2.6 Hz), 130.4, 125.5, 123.2 (d, *J* = 18.5 Hz), 122.9 (d, *J* = 2.2 Hz), 120.4 (q, *J* = 257.6 Hz), 120.2, 111.0, 92.7 (d, *J* = 198.9 Hz), 62.1 (d, *J* = 27.6 Hz), 56.6, 22.6. IR (cm^{-1}): 1721, 1624, 1508, 1475, 1254, 1222, 1205, 1162, 1055, 1044, 1018, 850, 755. HRMS (TOF MS ESI): calcd for $C_{20}H_{20}F_4N_2O_3SNa^+$ $[M+Na]^+$ 467.1023, found 467.1021.



(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(phenyl)methyl)-2-methylpropane-2-sulfinamide (11ai)

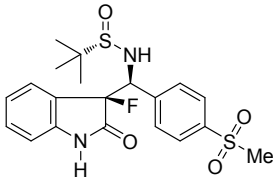
White solid, 149.3 mg (83% yield), R_f = 0.22 (hexanes/ethyl acetate = 1:1), m.p. 207–208 °C,

[α]20 D = +64.8 (c = 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.11 (m, 6H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.22 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.91 (d, *J* = 4.3 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.10 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (d, *J* = 21.7 Hz), 142.1 (d, *J* = 5.6 Hz), 134.6 (d, *J* = 4.6 Hz), 131.8 (d, *J* = 2.8 Hz), 129.0, 128.5, 128.1, 125.8, 123.6 (d, *J* = 18.5 Hz), 122.9 (d, *J* = 2.5 Hz), 110.8, 92.9 (d, *J* = 198.6 Hz), 62.8 (d, *J* = 27.1 Hz), 56.6, 22.7. IR (cm^{-1}): 1718, 1626, 1477, 1195, 1037, 745, 703. HRMS (TOF MS ESI): calcd for $C_{19}H_{21}FN_2O_2SNa^+$ $[M+Na]^+$ 383.1200, found 383.1207.



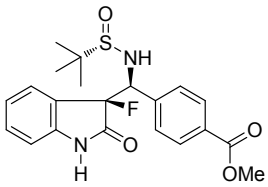
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(4-nitrophenyl)methyl)-2-methylpropane-2-sulfinamide (11aj)

White solid, 196.3 mg (97% yield), R_f = 0.21 (hexanes/ethyl acetate = 1:1), m.p. 217–218 °C, [α]20 D = +58.7 (c = 0.47, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 5.36 (dd, *J* = 7.6, 4.8 Hz, 1H), 5.12 (d, *J* = 4.5 Hz, 1H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.65 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 (d, *J* = 21.4 Hz), 147.7, 142.2 (d, *J* = 5.2 Hz), 132.3 (d, *J* = 2.1 Hz), 129.8, 125.5, 123.2, 123.1, 123.1, 122.8 (d, *J* = 18.3 Hz), 111.3, 92.2 (d, *J* = 199.7 Hz), 62.5 (d, *J* = 28.1 Hz), 56.8, 22.5. IR (cm^{-1}): 1716, 1623, 1525, 1473, 1346, 1196, 1059, 1025, 1012, 833, 758. HRMS (TOF MS ESI): calcd for $C_{19}H_{20}FN_3O_4SNa^+$ $[M+Na]^+$ 428.1051, found 428.1051.



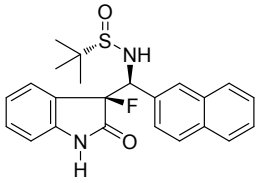
(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(4-(methylsulfonyl)phenyl)methyl)-2-methylpropane-2-sulfinamide (11ak)

White solid, 199.7 mg (91% yield), R_f = 0.19 (hexanes/ethyl acetate = 1:2), m.p. 200–201 °C, [α]20 D = +53.8 (c = 0.51, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 5.33 (dd, *J* = 7.5, 4.8 Hz, 1H), 5.09 (s, 1H), 2.99 (s, 3H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.31 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (d, *J* = 21.6 Hz), 142.1 (d, *J* = 5.4 Hz), 141.2 (d, *J* = 4.8 Hz), 140.4, 132.3 (d, *J* = 2.6 Hz), 130.0, 127.1, 125.5, 123.2, 122.9 (d, *J* = 18.5 Hz), 111.3, 92.3 (d, *J* = 199.6 Hz), 62.4 (d, *J* = 27.8 Hz), 56.8, 44.4, 22.7. IR (cm^{-1}): 1737, 1718, 1624, 1477, 1310, 1146, 1046, 1036, 956, 758. HRMS (TOF MS ESI): calcd for $C_{20}H_{23}FN_2O_4S_2Na^+$ $[M+Na]^+$ 461.0975, found 461.0975.



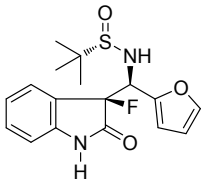
methyl 4-((S)-((S)-1,1-dimethylethylsulfinamido)((S)-3-fluoro-2-oxoindolin-3-yl)methyl)benzoate (11al)

White solid, 188.2 mg (90% yield), R_f = 0.21 (hexanes/ethyl acetate = 1:1), m.p. 204–205 °C, [α]20 D = +53.8 (c = 0.73, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.28 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.99 (d, *J* = 4.4 Hz, 1H), 3.85 (s, 3H), 1.21 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.45 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7 (d, *J* = 21.6 Hz), 166.8, 142.1 (d, *J* = 5.6 Hz), 139.9 (d, *J* = 4.7 Hz), 132.1 (d, *J* = 2.7 Hz), 130.2, 129.3, 129.0, 125.7, 123.2 (d, *J* = 18.6 Hz), 123.0 (d, *J* = 2.2 Hz), 111.0, 92.5 (d, *J* = 199.4 Hz), 62.7 (d, *J* = 27.6 Hz), 56.7, 52.3, 22.6. IR (cm^{-1}): 3256, 1723, 1623, 1471, 1264, 1111, 1080, 1058, 747, 723, 705. HRMS (TOF MS ESI): calcd for $C_{21}H_{23}FN_2O_4SNa^+$ $[M+Na]^+$ 441.1255, found 441.1254.



(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(naphthalen-2-yl)methyl)-2-methylpropane-2-sulfinamide (11am)

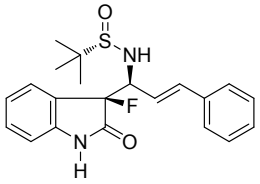
White solid, 174.3 mg (85% yield), R_f = 0.25 (hexanes/ethyl acetate = 1:1), m.p. 201–202 °C, [α]20 D = +66.3 (c = 0.66, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.77 – 7.60 (m, 4H), 7.47 – 7.39 (m, 3H), 7.28 – 7.23 (m, 1H), 7.16 (tt, *J* = 7.8, 1.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.40 (dd, *J* = 7.4, 4.3 Hz, 1H), 4.91 (d, *J* = 3.0 Hz, 1H), 1.23 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -158.21 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9 (d, *J* = 21.7 Hz), 141.9 (d, *J* = 5.8 Hz), 133.2, 132.9, 132.1 (d, *J* = 4.7 Hz), 131.9 (d, *J* = 2.8 Hz), 128.9, 128.2, 127.8, 127.7, 126.6, 126.3, 126.2, 125.8, 123.7 (d, *J* = 18.5 Hz), 123.0 (d, *J* = 2.1 Hz), 110.8, 92.9 (d, *J* = 198.8 Hz), 63.0 (d, *J* = 27.0 Hz), 56.6, 22.7. IR (cm^{-1}): 1718, 1475, 1205, 1037, 759, 751. HRMS (TOF MS ESI): calcd for $C_{23}H_{23}FN_2O_2SNa^+$ $[M+Na]^+$ 433.1356, found 433.1356.



(S)-N-((S)-((S)-3-fluoro-2-oxoindolin-3-yl)(furan-2-yl)methyl)-2-methylpropane-2-sulfinamide (11an)

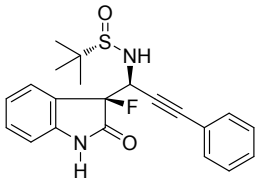
White solid, 140.4 mg (80% yield), R_f = 0.17 (hexanes/ethyl acetate = 1:1), m.p. 154–155 °C, [α]20 D = +72.7 (c = 0.20, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.26 (dd, *J* = 1.7,

0.7 Hz, 1H), 7.22 – 7.13 (m, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 6.24 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.32 (t, *J* = 7.2 Hz, 1H), 4.94 (d, *J* = 7.4 Hz, 1H), 1.16 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -156.74 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3 (d, *J* = 20.9 Hz), 148.9 (d, *J* = 4.6 Hz), 143.0 (d, *J* = 5.4 Hz), 142.7, 131.8 (d, *J* = 2.8 Hz), 125.7, 122.9 (d, *J* = 18.4 Hz), 122.7 (d, *J* = 2.6 Hz), 111.2, 110.7, 109.7 (d, *J* = 1.5 Hz), 91.6 (d, *J* = 197.1 Hz), 57.3 (d, *J* = 32.1 Hz), 56.8, 22.4. IR (cm^{-1}): 1722, 1623, 1473, 1206, 1037, 1012, 792, 752, 732. HRMS (TOF MS ESI): calcd for $C_{17}H_{19}FN_2O_3SNa^+$ $[M+Na]^+$ 373.0993, found 373.0998.



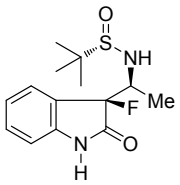
(S)-N-((S,E)-1-((S)-3-fluoro-2-oxoindolin-3-yl)-3-phenylallyl)-2-methylpropane-2-sulfinamide (11ao)

White solid, 168.4 mg (87% yield), R_f = 0.14 (hexanes/ethyl acetate = 1:1), m.p. 181–182 °C, [α]20 D = -88.7 (c = 0.37, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.18 (m, 6H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.03 (dd, *J* = 15.8, 6.9 Hz, 1H), 4.83 (q, *J* = 6.4 Hz, 1H), 4.49 (d, *J* = 6.0 Hz, 1H), 1.20 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -159.35 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3 (d, *J* = 21.2 Hz), 142.8 (d, *J* = 5.5 Hz), 136.0, 135.7, 131.9 (d, *J* = 2.8 Hz), 128.7, 128.3, 126.8, 125.5, 123.6 (d, *J* = 18.5 Hz), 123.0 (d, *J* = 2.3 Hz), 122.5 (d, *J* = 4.0 Hz), 111.2, 92.4 (d, *J* = 197.8 Hz), 61.0 (d, *J* = 28.8 Hz), 56.6, 22.7. IR (cm^{-1}): 1730, 1622, 1470, 1200, 1056, 973, 751. HRMS (TOF MS ESI): calcd for $C_{21}H_{23}FN_2O_2SNa^+$ $[M+Na]^+$ 409.1356, found 409.1351.



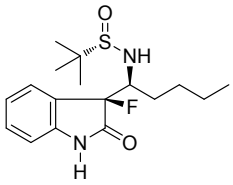
(S)-N-((S)-1-((S)-3-fluoro-2-oxoindolin-3-yl)-3-phenylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (11ap)

White solid, 161.7 mg (84% yield), R_f = 0.14 (hexanes/ethyl acetate = 1:1), m.p. 218–219 °C, [α]20 D = +155.4 (c = 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, MeOD) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.43 – 7.35 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.04 (d, *J* = 4.4 Hz, 1H), 4.90 (s, 2H), 0.97 (s, 9H); ^{19}F NMR (376 MHz, MeOD) δ -155.07 (s, 1F); ^{13}C NMR (101 MHz, MeOD) δ 174.4 (d, *J* = 20.1 Hz), 145.4 (d, *J* = 5.6 Hz), 133.3 (d, *J* = 3.1 Hz), 132.8, 130.2, 129.6, 128.0, 124.6 (d, *J* = 18.1 Hz), 123.8 (d, *J* = 2.7 Hz), 123.3, 111.9 (d, *J* = 1.0 Hz), 92.7 (d, *J* = 193.7 Hz), 89.8, 84.3, 57.0, 51.2 (d, *J* = 36.1 Hz), 22.8. IR (cm^{-1}): 1724, 1625, 1471, 1338, 1204, 1043, 759, 749. HRMS (TOF MS ESI): calcd for $C_{21}H_{21}FN_2O_2SNa^+$ $[M+Na]^+$ 407.1200, found 407.1210.



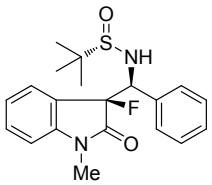
(S)-N-((S)-1-((S)-3-fluoro-2-oxoindolin-3-yl)ethyl)-2-methylpropane-2-sulfinamide (11aq)

White solid, 128.4 mg (86% yield), R_f = 0.24 (hexanes/ethyl acetate = 1:2), m.p. 190–191 °C, [α]20 D = +64.3 (c = 0.51, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 4.51 (d, *J* = 7.1 Hz, 1H), 4.22 – 4.12 (m, 1H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.18 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -160.09 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7 (d, *J* = 21.1 Hz), 143.0 (d, *J* = 5.6 Hz), 131.7 (d, *J* = 2.8 Hz), 125.1, 124.1 (d, *J* = 18.4 Hz), 123.0 (d, *J* = 2.5 Hz), 111.3, 93.0 (d, *J* = 194.0 Hz), 56.2, 55.2 (d, *J* = 28.2 Hz), 22.6, 16.4 (d, *J* = 3.5 Hz). IR (cm^{-1}): 1716, 1623, 1473, 1340, 1204, 1057, 1028, 763. HRMS (TOF MS ESI): calcd for $C_{14}H_{19}FN_2O_2SNa^+$ $[M+Na]^+$ 321.1043, found 321.1045.



(S)-N-((S)-1-((S)-3-fluoro-2-oxoindolin-3-yl)pentyl)-2-methylpropane-2-sulfinamide (11ar)

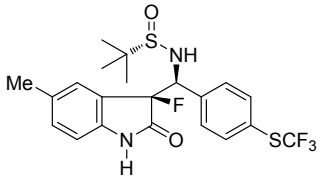
White solid, 127.5 mg (75% yield), R_f = 0.17 (hexanes/ethyl acetate = 1:1), m.p. 81–82 °C, [α]20 D = +41.6 (c = 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.80 (d, *J* = 8.3 Hz, 1H), 3.95 – 3.85 (m, 1H), 1.43 – 1.06 (m, 15H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -155.94 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2 (d, *J* = 21.2 Hz), 143.0 (d, *J* = 5.4 Hz), 131.7 (d, *J* = 2.9 Hz), 124.9, 124.5 (d, *J* = 18.4 Hz), 123.1 (d, *J* = 2.4 Hz), 111.5, 91.9 (d, *J* = 194.1 Hz), 60.6 (d, *J* = 26.6 Hz), 57.0, 30.4 (d, *J* = 2.8 Hz), 28.1, 23.0, 22.1, 13.9. IR (cm^{-1}): 1733, 1624, 1472, 1207, 1047, 746. HRMS (TOF MS ESI): calcd for $C_{17}H_{25}FN_2O_2SNa^+$ $[M+Na]^+$ 363.1513, found 363.1526.



(S)-N-((S)-((S)-3-fluoro-1-methyl-2-oxoindolin-3-yl)(phenyl)methyl)-2-methylpropane-2-sulfinamide (11bi)

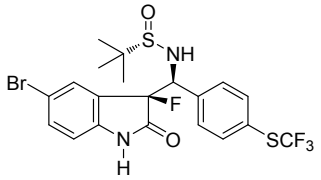
White solid, 153.6 mg (82% yield), R_f = 0.29 (hexanes/ethyl acetate = 1:1), m.p. 147–148 °C, [α]20 D = +78.8 (c = 0.07, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.17 – 7.02 (m, 6H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.19 (dd, *J* = 7.3, 4.3 Hz, 1H), 4.83 (d, *J* = 3.2 Hz, 1H), 2.95 (s, 3H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -162.03 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2 (d, *J* = 22.1 Hz), 144.1 (d, *J* = 5.3 Hz), 134.6 (d, *J* = 5.3 Hz),

131.8 (d, J = 2.7 Hz), 128.8, 128.4, 127.9, 125.1, 123.5 (d, J = 18.6 Hz), 123.2 (d, J = 2.4 Hz), 108.7, 92.9 (d, J = 199.6 Hz), 63.0 (d, J = 26.4 Hz), 56.5, 26.0, 22.7. IR (cm^{-1}): 1718, 1707, 1617, 1379, 1070, 700. HRMS (TOF MS ESI): calcd for $C_{20}H_{23}FN_2O_2SNa^+$ $[M+Na]^+$ 397.1356, found 397.1354.



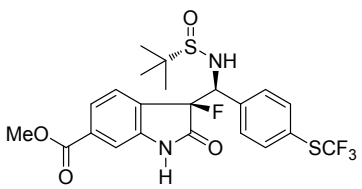
(S)-N-((S)-((S)-3-fluoro-5-methyl-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13a)

White solid, 201.4 mg (85% yield), R_f = 0.31 (hexanes/ethyl acetate = 1:1), m.p. 95–96 °C, [α]20 D = -4.8 (c = 0.25, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 6.98 – 6.92 (m, 2H), 6.52 (dd, J = 8.4, 0.8 Hz, 1H), 5.19 (dd, J = 7.5, 5.6 Hz, 1H), 4.99 (d, J = 5.2 Hz, 1H), 2.24 (s, 3H), 1.19 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.54 (s, 3F), -158.52 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (d, J = 21.4 Hz), 139.8 (d, J = 5.7 Hz), 138.0 (d, J = 3.9 Hz), 135.6, 132.6 (d, J = 2.6 Hz), 132.4 (d, J = 2.7 Hz), 129.9, 129.5 (q, J = 308.1 Hz), 126.2, 124.6 (d, J = 2.0 Hz), 122.8 (d, J = 18.5 Hz), 110.8, 92.8 (d, J = 199.6 Hz), 62.4 (d, J = 28.1 Hz), 56.7, 22.5, 21.1. IR (cm^{-1}): 1724, 1495, 1161, 1116, 906, 729. HRMS (TOF MS ESI): calcd for $C_{21}H_{22}F_4N_2O_2S_2Na^+$ $[M+Na]^+$ 497.0951, found 497.0959.



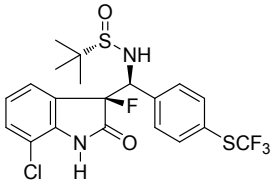
(S)-N-((S)-((S)-5-bromo-3-fluoro-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13b)

White solid, 248.4 mg (92% yield), R_f = 0.30 (hexanes/ethyl acetate = 1:1), m.p. 152–153 °C, [α]20 D = -54.6 (c = 0.52, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.56 (d, J = 8.6 Hz, 1H), 5.20 (dd, J = 7.7, 5.9 Hz, 1H), 5.07 (d, J = 5.6 Hz, 1H), 1.18 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.40 (s, 3F), -158.28 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5 (d, J = 21.2 Hz), 141.6 (d, J = 5.5 Hz), 137.4 (d, J = 4.1 Hz), 135.8, 134.9 (d, J = 2.2 Hz), 129.8, 129.4 (q, J = 308.3 Hz), 128.7, 125.0 (q, J = 1.9 Hz), 124.8 (d, J = 18.5 Hz), 115.3 (d, J = 3.0 Hz), 112.8, 92.3 (d, J = 200.9 Hz), 62.4 (d, J = 27.9 Hz), 56.8, 22.5. IR (cm^{-1}): 1735, 1619, 1474, 1114, 1084, 1015. HRMS (TOF MS ESI): calcd for $C_{20}H_{19}BrF_4N_2O_2S_2Na^+$ $[M+Na]^+$ 560.9900, found 560.9908.



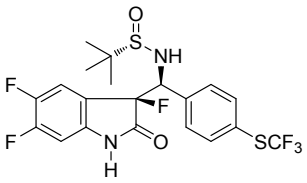
(S)-methyl 3-((S)-((S)-1,1-dimethylethylsulfinamido)(4-((trifluoromethyl)thio)phenyl)methyl)-3-fluoro-2-oxoindoline-6-carboxylate (13c)

White solid, 204.6 mg (79% yield), R_f = 0.27 (hexanes/ethyl acetate = 1:1), m.p. 113–114 °C, [α]20 D = +42.0 (c = 0.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 5.28 (t, *J* = 7.0 Hz, 1H), 5.04 (d, *J* = 4.3 Hz, 1H), 3.79 (s, 3H), 1.19 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.45 (s, 3F), -158.50 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7 (d, *J* = 21.0 Hz), 165.9, 143.1 (d, *J* = 5.4 Hz), 137.6 (d, *J* = 2.6 Hz), 135.8, 133.3, 129.8, 129.4 (q, *J* = 308.2 Hz), 127.3 (d, *J* = 18.1 Hz), 125.8, 125.0, 124.2, 111.9, 92.3 (d, *J* = 200.2 Hz), 62.4 (d, *J* = 28.4 Hz), 57.0, 52.5, 22.5. IR (cm^{-1}): 1723, 1631, 1456, 1283, 1221, 1116, 1086, 907, 729. HRMS (TOF MS ESI): calcd for $C_{22}H_{22}F_4N_2O_4S_2Na^+$ $[M+Na]^+$ 541.0849, found 541.0859.



(S)-N-((S)-((S)-7-chloro-3-fluoro-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13d)

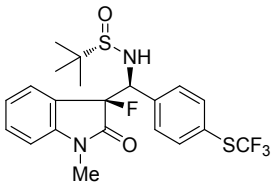
White solid, 225.6 mg (91% yield), R_f = 0.46 (hexanes/ethyl acetate = 1:1), m.p. 164–165 °C, [α]20 D = +103.4 (c = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 5.35 (dd, *J* = 7.9, 4.7 Hz, 1H), 5.19 (d, *J* = 4.0 Hz, 1H), 1.25 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.53 (s, 3F), -158.50 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (d, *J* = 21.5 Hz), 140.0 (d, *J* = 5.6 Hz), 137.3 (d, *J* = 4.7 Hz), 135.7, 131.9 (d, *J* = 2.3 Hz), 129.9, 129.4 (q, *J* = 308.2 Hz), 124.9 (q, *J* = 2.0 Hz), 124.6 (d, *J* = 18.8 Hz), 123.9 (d, *J* = 2.0 Hz), 123.8, 116.2, 93.1 (d, *J* = 201.3 Hz), 62.3 (d, *J* = 27.5 Hz), 56.7, 22.5. IR (cm^{-1}): 1735, 1623, 1476, 1118, 1074, 845, 796, 737. HRMS (TOF MS ESI): calcd for $C_{20}H_{19}ClF_4N_2O_2S_2Na^+$ $[M+Na]^+$ 517.0405, found 517.0426.



(S)-2-methyl-N-((S)-((S)-3,5,6-trifluoro-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)propane-2-sulfinamide (13e)

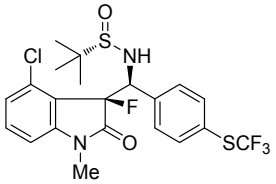
White solid, 206.2 mg (83% yield), R_f = 0.35 (hexanes/ethyl acetate = 1:1), m.p. 191–192 °C, [α]20 D = +61.0 (c = 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, MeOD) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.46 (ddd, *J* = 9.4, 7.9, 1.6 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.61 (ddd, *J* = 10.0, 6.4, 0.7 Hz, 1H), 5.37 (d, *J* = 8.9 Hz, 1H), 4.86 (s, 2H), 1.21 (s, 9H); ^{19}F NMR (376 MHz, MeOD) δ -44.60 (s, 3F), -133.73 (dd, *J* = 19.2, 5.2 Hz, 1F), -147.03 (d, *J* = 19.2 Hz, 1F), -158.05 (d, *J* = 5.1 Hz, 1F); ^{13}C NMR (101 MHz, MeOD) δ 174.4 (d, *J* = 21.2 Hz), 153.9 (ddd, *J* = 251.0, 14.0, 2.9 Hz), 147.8 (ddd, *J* = 243.0, 13.6, 3.0 Hz), 141.0 – 140.8 (m), 140.0 (d, *J* = 5.1 Hz), 137.0, 131.0, 131.0 (q, *J* = 306.9 Hz), 125.8 (q, *J* = 2.0 Hz), 120.4 (ddd, *J* = 19.0, 6.4, 4.1 Hz), 116.9 (d, *J* = 21.1 Hz), 101.8

(d, *J* = 23.3 Hz), 93.1 (d, *J* = 199.3 Hz), 63.7 (d, *J* = 28.4 Hz), 57.9, 22.7. IR (cm^{-1}): 1734, 1633, 1503, 1471, 1347, 1131, 1117, 1085, 1045, 777, 719. HRMS (TOF MS ESI): calcd for $C_{20}H_{18}F_6N_2O_2S_2Na^+$ $[M+Na]^+$ 519.0606, found 519.0629.



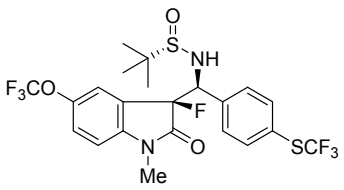
(S)-N-((S)-((S)-3-fluoro-1-methyl-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13f)

White solid, 206.5 mg (87% yield), R_f = 0.32 (hexanes/ethyl acetate = 1:1), m.p. 143–144 °C, [α]20 D = +56.4 (c = 0.55, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 3H), 7.30 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.14 – 7.07 (m, *J* = 7.9 Hz, 3H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.24 (dd, *J* = 6.9, 4.4 Hz, 1H), 4.93 (d, *J* = 3.3 Hz, 1H), 2.92 (s, 3H), 1.26 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.77 (s, 3F), -163.42 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7 (d, *J* = 22.0 Hz), 143.8 (d, *J* = 5.3 Hz), 137.8 (d, *J* = 5.2 Hz), 135.4, 132.0 (d, *J* = 2.6 Hz), 129.6, 129.4 (q, *J* = 308.2 Hz), 124.9, 124.5 (q, *J* = 2.0 Hz), 123.3 (d, *J* = 2.4 Hz), 122.9 (d, *J* = 18.7 Hz), 108.7, 92.5 (d, *J* = 201.7 Hz), 62.6 (d, *J* = 26.9 Hz), 56.5, 25.8, 22.6. IR (cm^{-1}): 1715, 1612, 1462, 1117, 1079, 1055, 1016, 754, 699. HRMS (TOF MS ESI): calcd for $C_{21}H_{22}F_4N_2O_2S_2Na^+$ $[M+Na]^+$ 497.0951, found 497.0964.



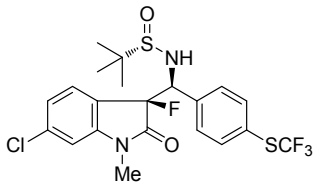
(S)-N-((S)-((S)-4-chloro-3-fluoro-1-methyl-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13g)

White solid, 218.7 mg (86% yield), R_f = 0.50 (hexanes/ethyl acetate = 1:1), m.p. 165–166 °C, [α]20 D = +45.8 (c = 0.26, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.55 (s, 1H), 5.23 (dd, *J* = 6.8, 4.7 Hz, 1H), 4.83 (d, *J* = 3.9 Hz, 1H), 2.93 (s, 3H), 1.25 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.68 (s, 3F), -161.98 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 (d, *J* = 22.0 Hz), 145.2 (d, *J* = 5.2 Hz), 138.1 (d, *J* = 3.0 Hz), 137.5 (d, *J* = 4.7 Hz), 135.6, 129.6, 129.4 (q, *J* = 308.1 Hz), 126.1, 124.9 (q, *J* = 1.8 Hz), 123.2 (d, *J* = 2.3 Hz), 121.1 (d, *J* = 19.0 Hz), 109.5, 92.1 (d, *J* = 201.9 Hz), 62.3 (d, *J* = 27.0 Hz), 56.6, 26.0, 22.5. IR (cm^{-1}): 1726, 1609, 1496, 1380, 1114, 1062, 1009, 907, 730. HRMS (TOF MS ESI): calcd for $C_{21}H_{21}ClF_4N_2O_2S_2Na^+$ $[M+Na]^+$ 531.0561, found 531.0579.



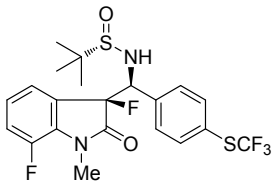
(S)-N-((S)-((S)-3-fluoro-1-methyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13h)

White solid, 234.3 mg (84% yield), R_f = 0.37 (hexanes/ethyl acetate = 1:1), m.p. 126–127 °C, [α]20 D = +38.8 (c = 0.49, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.27 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.50 (dd, *J* = 8.5, 0.9 Hz, 1H), 5.20 (dd, *J* = 7.5, 4.4 Hz, 1H), 4.84 (d, *J* = 4.1 Hz, 1H), 2.91 (s, 3H), 1.22 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.83 (s, 3F), -58.61 (s, 3F), -163.85 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5 (d, *J* = 22.1 Hz), 145.0 – 144.8 (m), 142.5 (d, *J* = 5.0 Hz), 137.4 (d, *J* = 5.2 Hz), 135.7, 129.5, 129.4 (q, *J* = 308.1 Hz), 125.3 (d, *J* = 0.9 Hz), 125.1 (q, *J* = 2.0 Hz), 124.3 (d, *J* = 18.8 Hz), 120.5 (q, *J* = 257.5 Hz), 119.2, 109.5, 92.2 (d, *J* = 203.5 Hz), 62.7 (d, *J* = 26.8 Hz), 56.7, 26.0, 22.6. IR (cm^{-1}): 1728, 1624, 1495, 1471, 1367, 1254, 1215, 1158, 1111, 1074, 1016, 732. HRMS (TOF MS ESI): calcd for $C_{22}H_{21}F_7N_2O_3S_2Na^+$ $[M+Na]^+$ 581.0774, found 581.0785.



(S)-N-((S)-((S)-6-chloro-3-fluoro-1-methyl-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13i)

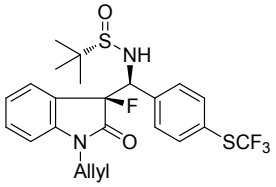
White solid, 229.2 mg (90% yield), R_f = 0.50 (hexanes/ethyl acetate = 1:1), m.p. 171–172 °C, [α]20 D = +41.6 (c = 0.38, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.08 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.55 (s, 1H), 5.21 (dd, *J* = 6.8, 4.5 Hz, 1H), 4.76 (d, *J* = 3.3 Hz, 1H), 2.93 (s, 3H), 1.25 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.66 (s, 3F), -162.23 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7 (d, *J* = 22.0 Hz), 145.3 (d, *J* = 5.2 Hz), 138.2 (d, *J* = 3.0 Hz), 137.5 (d, *J* = 4.8 Hz), 135.7, 129.7, 129.5 (q, *J* = 308.2 Hz), 126.1, 125.0 (q, *J* = 2.0 Hz), 123.3 (d, *J* = 2.4 Hz), 121.2 (d, *J* = 19.0 Hz), 109.6, 92.2 (d, *J* = 202.1 Hz), 62.4 (d, *J* = 26.9 Hz), 56.7, 26.0, 22.6. IR (cm^{-1}): 1722, 1623, 1473, 1340, 1206, 1037, 1012, 752, 732. HRMS (TOF MS ESI): calcd for $C_{21}H_{21}ClF_4N_2O_2S_2Na^+$ $[M+Na]^+$ 531.0561, found 531.0567.



(S)-N-((S)-((S)-3,7-difluoro-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13j)

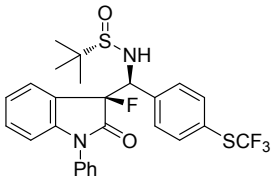
Colorless oil, 226.7 mg (92% yield), R_f = 0.51 (hexanes/ethyl acetate = 1:1), [α]20 D = +44.5 (c = 0.46, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.09 – 6.98 (m, 4H), 5.19 (dd, *J* = 7.0, 4.1 Hz, 1H), 4.90 (d, *J* = 3.2 Hz, 1H), 3.11 (d, *J* = 2.4 Hz, 3H), 1.26 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.76 (s, 3F), -135.00 (s, 1F), -162.39 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (d, *J* = 21.9 Hz), 147.5 (d, *J* = 246.5 Hz), 137.4 (d, *J* = 5.3 Hz), 135.7, 130.5 (dd, *J* = 8.9, 5.3 Hz), 129.7, 129.5 (q, *J* = 308.2 Hz), 125.8 (dd, *J* = 18.9, 3.1 Hz),

125.1 (q, *J* = 2.1 Hz), 124.3 (dd, *J* = 6.3, 2.3 Hz), 120.9 (d, *J* = 3.3 Hz), 120.1 (dd, *J* = 19.3, 2.4 Hz), 92.4 (dd, *J* = 202.5, 2.5 Hz), 62.7 (d, *J* = 26.7 Hz), 56.7, 28.4 (d, *J* = 5.8 Hz), 22.7. IR (cm^{-1}): 1727, 1634, 1481, 1373, 1244, 1114, 1078, 731. HRMS (TOF MS ESI): calcd for $C_{21}H_{21}F_5N_2O_2S_2Na^+$ $[M+Na]^+$ 515.0857, found 515.0865.



(S)-N-((S)-((S)-1-allyl-3-fluoro-2-oxoindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13k)

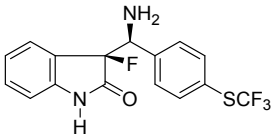
White solid, 217.9 mg (87% yield), R_f = 0.49 (hexanes/ethyl acetate = 1:1), m.p. 116–117 °C, [α]20 D = +45.8 (c = 0.72, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.05 (m, 3H), 6.51 (d, *J* = 7.9 Hz, 1H), 5.38 (ddd, *J* = 22.4, 10.4, 5.3 Hz, 1H), 5.24 (dd, *J* = 6.7, 4.0 Hz, 1H), 5.05 (d, *J* = 2.4 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 17.4 Hz, 1H), 4.27 – 4.17 (m, 1H), 3.85 (dd, *J* = 16.4, 5.5 Hz, 1H), 1.24 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.62 (s, 3F), -160.63 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4 (d, *J* = 22.0 Hz), 143.3 (d, *J* = 5.3 Hz), 137.7 (d, *J* = 5.6 Hz), 135.6, 132.0 (d, *J* = 2.7 Hz), 130.0, 129.9, 129.4 (q, *J* = 308.1 Hz), 125.0, 124.6 (q, *J* = 1.9 Hz), 123.4 (d, *J* = 2.5 Hz), 123.0 (d, *J* = 18.6 Hz), 118.0, 109.8, 92.2 (d, *J* = 200.4 Hz), 62.4 (d, *J* = 26.7 Hz), 56.6, 42.3, 22.6. IR (cm^{-1}): 1712, 1619, 1471, 1375, 1160, 1111, 1080, 850, 752. HRMS (TOF MS ESI): calcd for $C_{23}H_{24}F_4N_2O_2S_2Na^+$ $[M+Na]^+$ 523.1108, found 523.1131.



(S)-N-((S)-((S)-3-fluoro-2-oxo-1-phenylindolin-3-yl)(4-((trifluoromethyl)thio)phenyl)methyl)-2-methylpropane-2-sulfinamide (13l)

White solid, 241.6 mg (90% yield), R_f = 0.60 (hexanes/ethyl acetate = 1:1), m.p. 86–87 °C, [α]20 D = +120.3 (c = 0.36, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.35 (m, 5H), 7.24 – 7.14 (m, 4H), 6.94 (d, *J* = 7.7 Hz, 2H), 6.43 (d, *J* = 7.7 Hz, 1H), 5.35 (dd, *J* = 6.5, 3.7 Hz, 1H), 5.14 (dd, *J* = 3.6, 1.5 Hz, 1H), 1.28 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.62 (s, 3F), -162.91 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (d, *J* = 22.0 Hz), 143.9 (d, *J* = 5.1 Hz), 137.7 (dd, *J* = 5.3, 0.7 Hz), 135.6, 132.6, 131.9 (d, *J* = 2.4 Hz), 129.9, 129.8, 129.4 (q, *J* = 308.1 Hz), 128.7, 125.9, 125.1, 124.6, 123.8 (d, *J* = 2.3 Hz), 122.8 (d, *J* = 18.6 Hz), 109.8, 92.6 (d, *J* = 202.4 Hz), 62.8 (d, *J* = 26.6 Hz), 56.5, 22.6. IR (cm^{-1}): 1735, 1614, 1499, 1467, 1374, 1113, 1083, 755, 700. HRMS (TOF MS ESI): calcd for $C_{26}H_{24}F_4N_2O_2S_2Na^+$ $[M+Na]^+$ 559.1108, found 559.1114.

3.2. Characterization data of compounds 14



(S)-3-((S)-amino(4-((trifluoromethyl)thio)phenyl)methyl)-3-fluoroindolin-2-one (14)

Colorless oil, 63.5 mg (89% yield), R_f = 0.31 (hexanes/ethyl acetate = 1:1), [α]20 D = +33.6 (c = 0.93, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 8.4 Hz, 1H), 1.98 (br, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.65 (s, 3F), -158.41 (s, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9 (d, *J* = 20.8 Hz), 142.4 (d, *J* = 5.7 Hz), 140.8, 135.9, 131.8 (d, *J* = 2.8 Hz), 129.6 (q, *J* = 308.1 Hz), 129.2 (d, *J* = 1.7 Hz), 126.1, 124.3 (q, *J* = 2.0 Hz), 123.2 (d, *J* = 19.1 Hz), 123.0 (d, *J* = 2.4 Hz), 110.9, 94.0 (d, *J* = 194.9 Hz), 58.4 (d, *J* = 28.9 Hz). IR (cm^{-1}): 1722, 1620, 1472, 1114, 1087, 757. HRMS (TOF MS ESI): calcd for $C_{16}H_{13}F_4N_2OS^+$ $[M+H]^+$ 357.0679, found 357.0683. The ee values were determined by chiral stationary phase HPLC analysis using a Daicel Chiralpak AD-H column (90:10 hexanes/*i*-PrOH at 1.0 mL/min, λ = 254 nm).

4. X-ray crystallography for 11bi

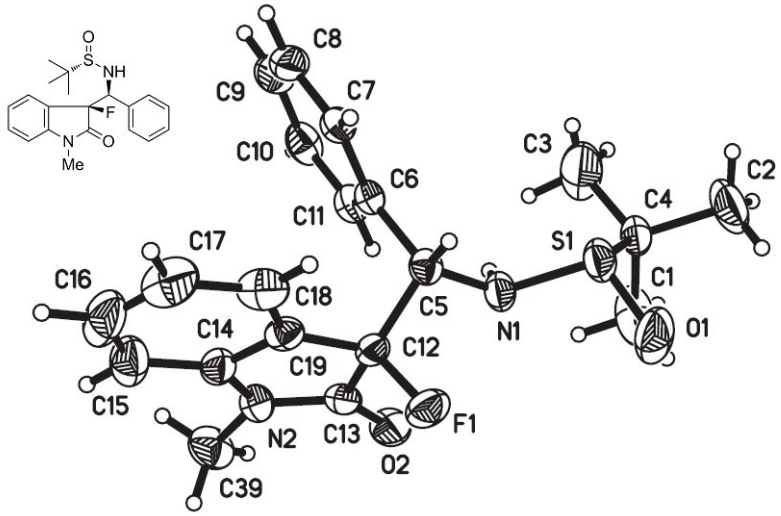
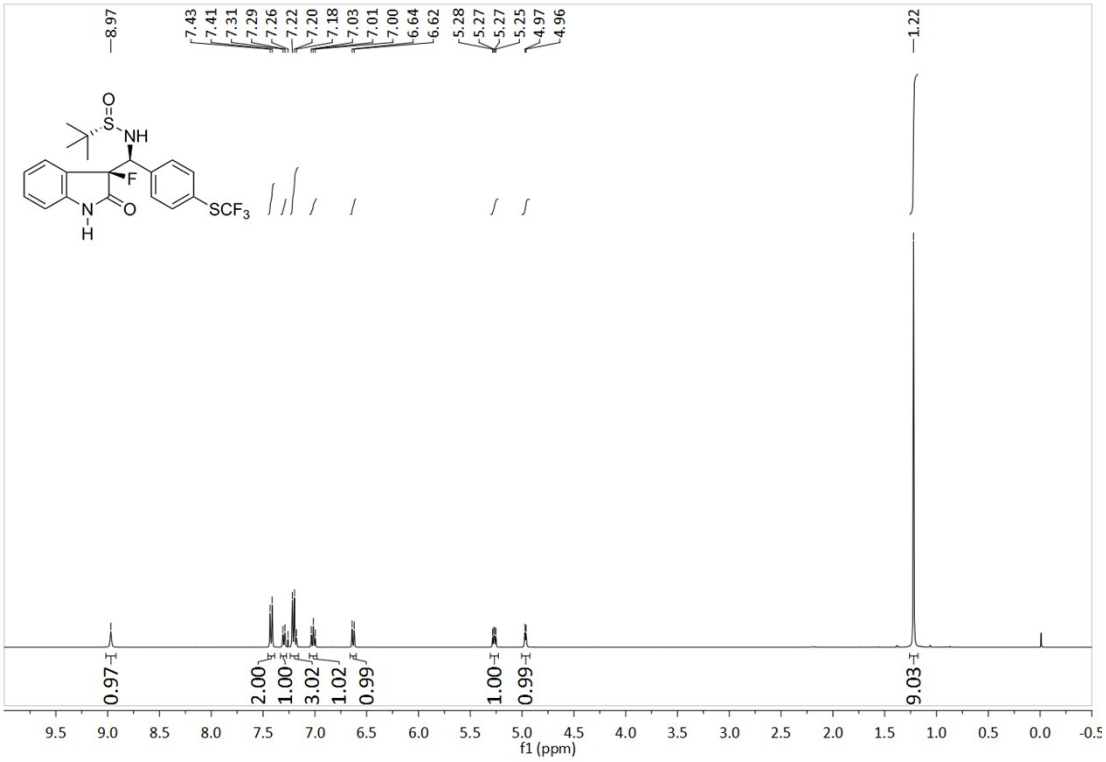


Figure 1 ORTEP structure of compound **11bi** (CCDC number 1457060)

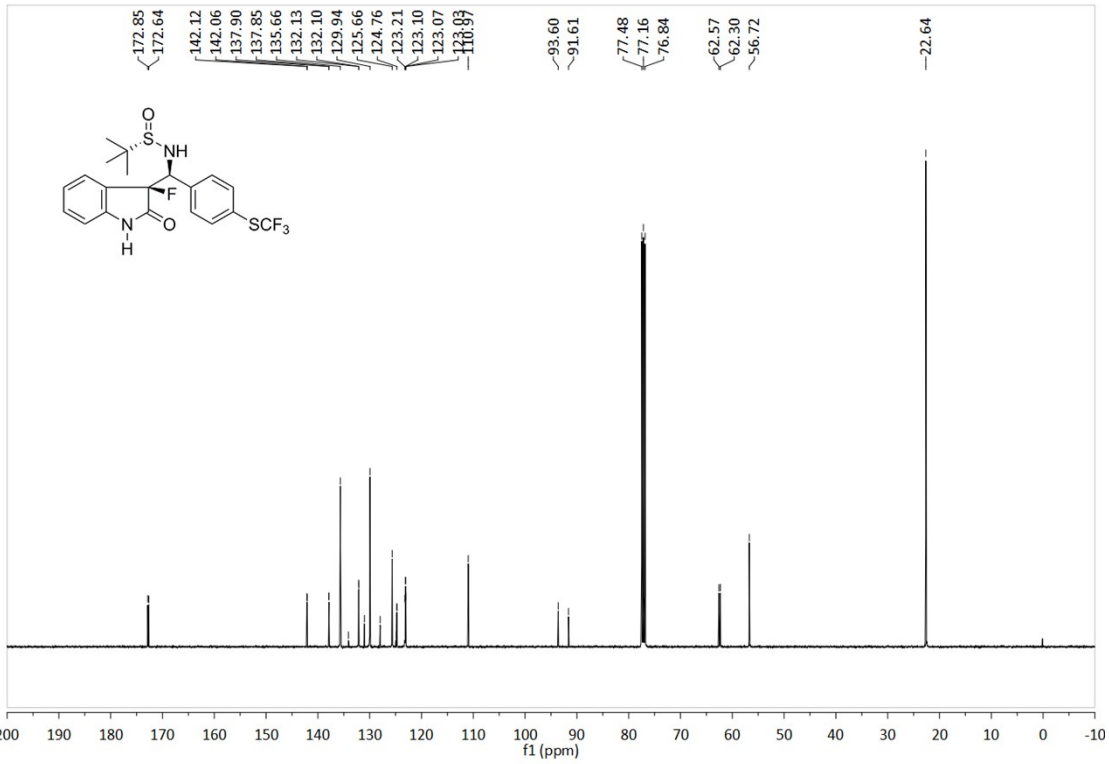
5. NMR spectra

5.1. NMR spectra of products 11 and 13

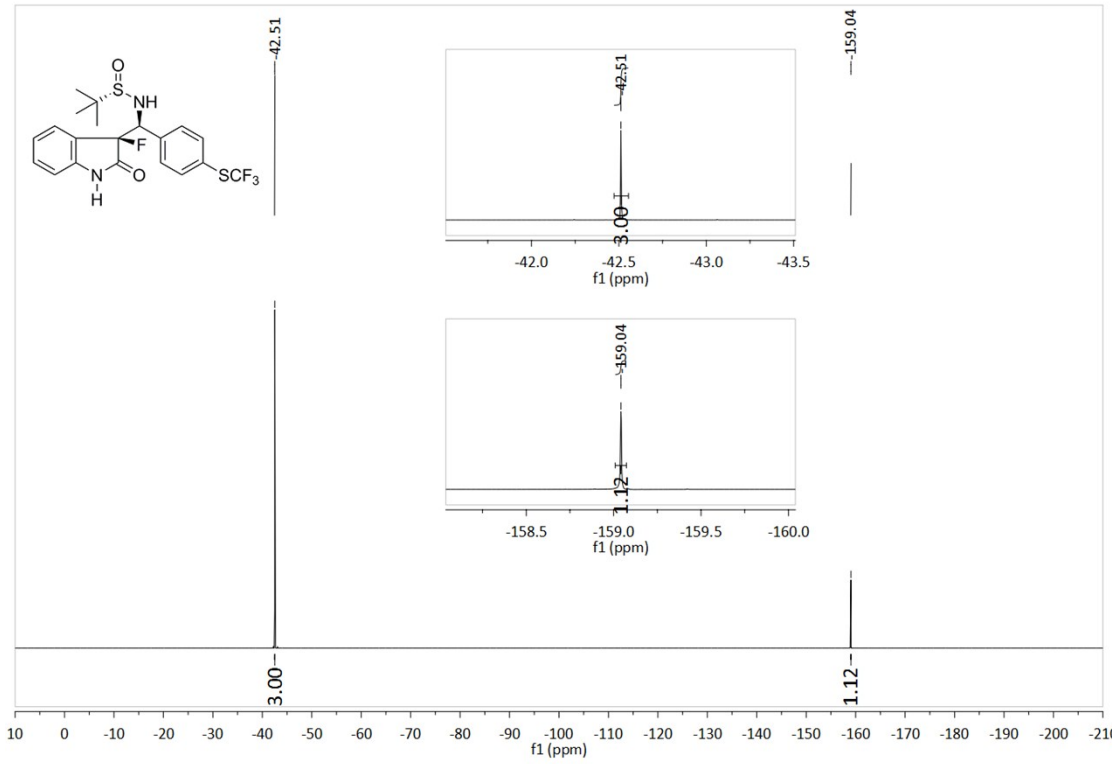
^{1}H NMR spectrum of **11aa**



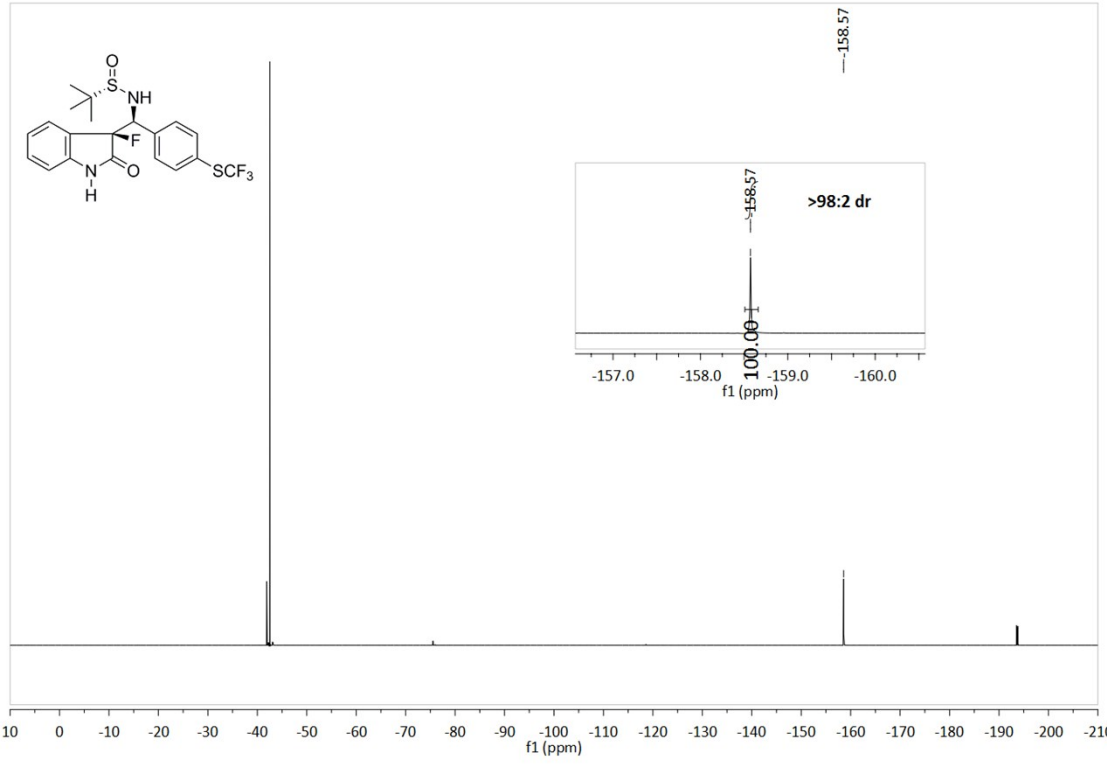
^{13}C NMR spectrum of **11aa**



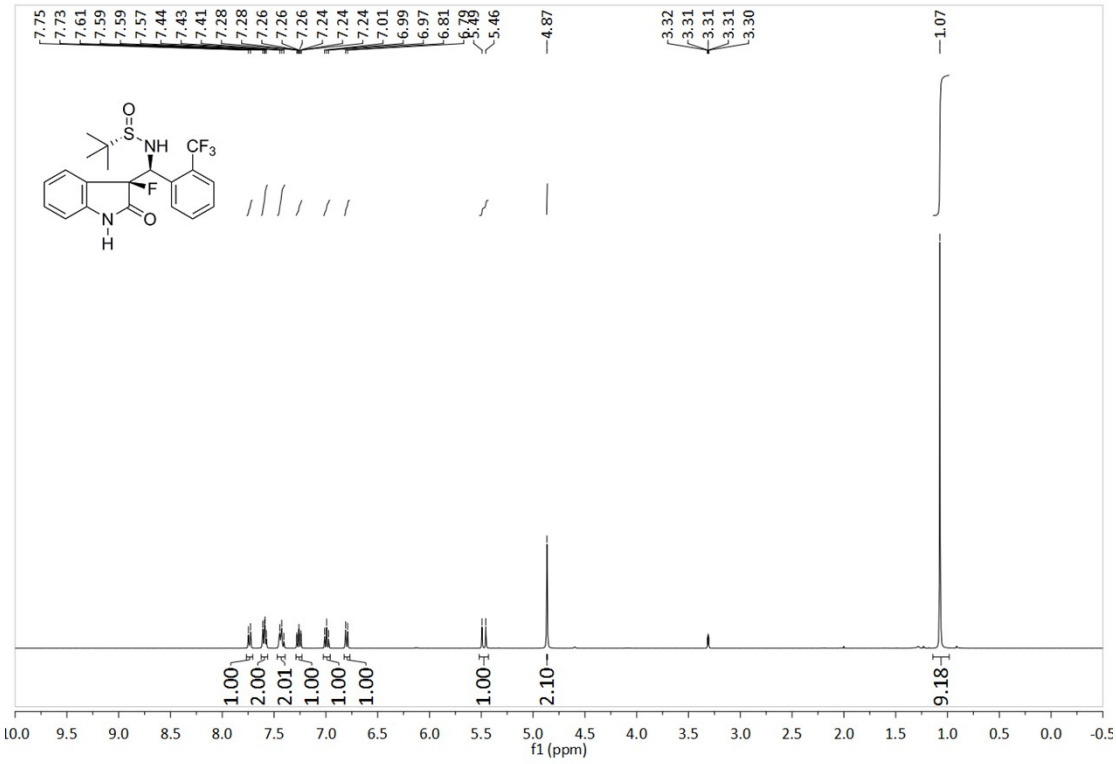
^{19}F NMR spectrum of **11aa**



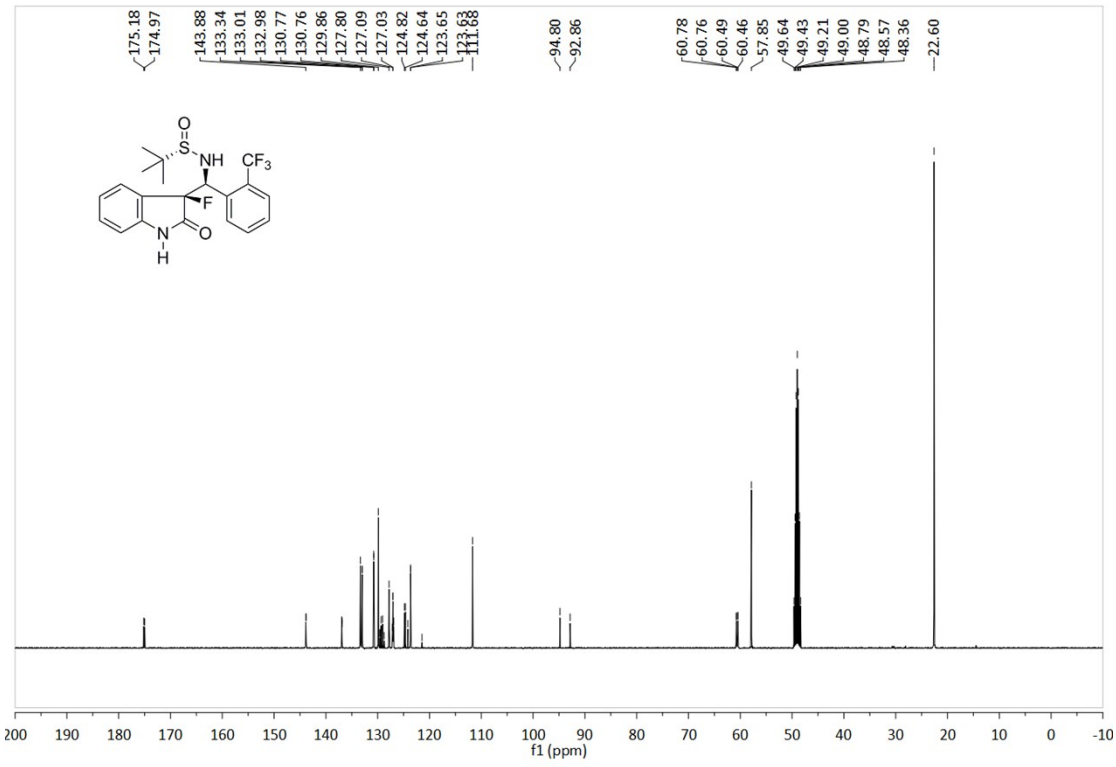
^{19}F NMR spectrum of the crude reaction mixture



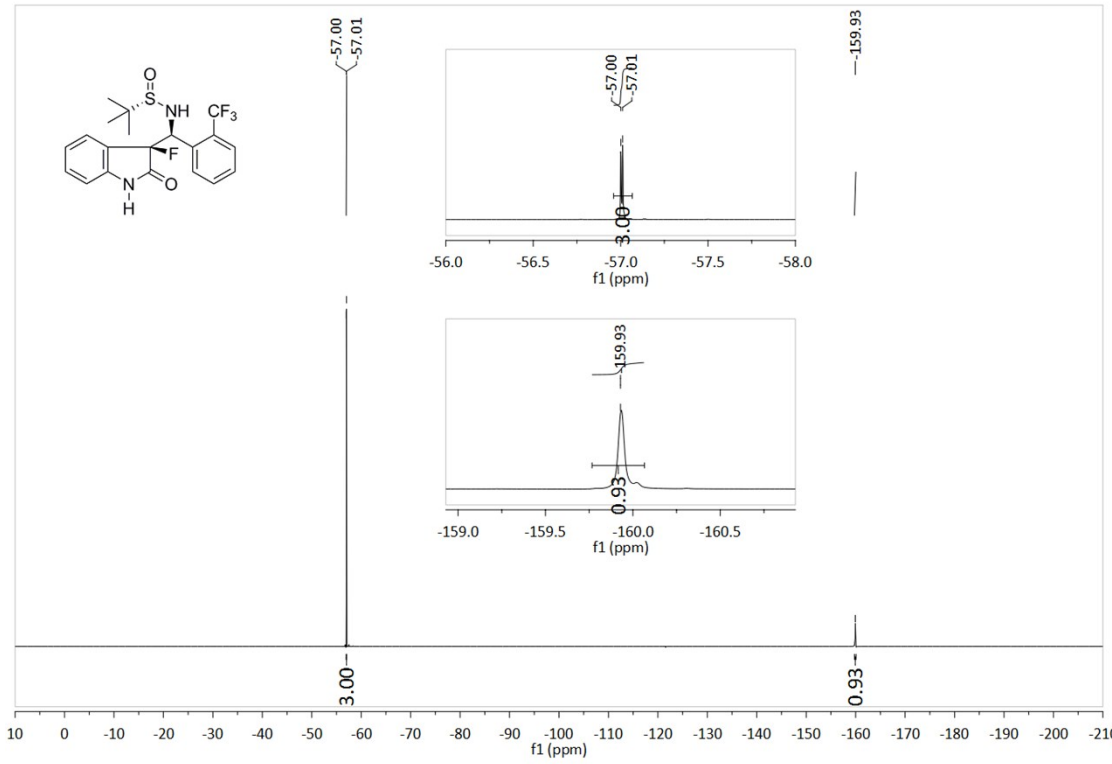
^{1}H NMR spectrum of **11ab**



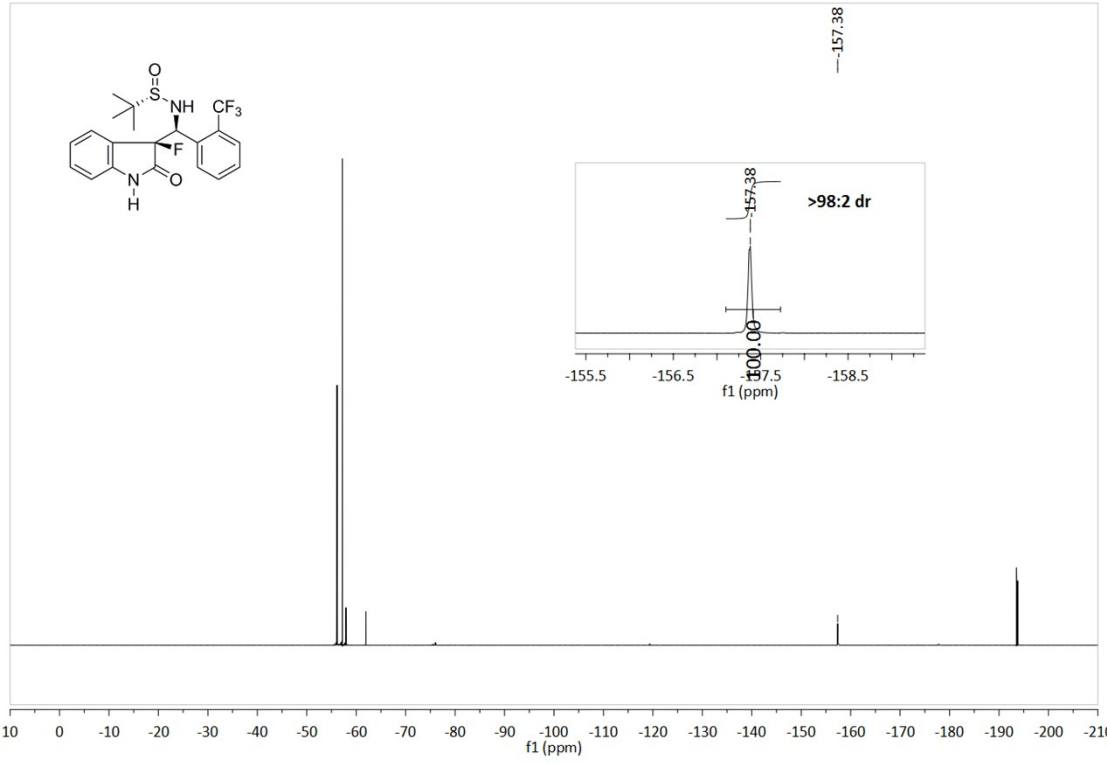
^{13}C NMR spectrum of **11ab**



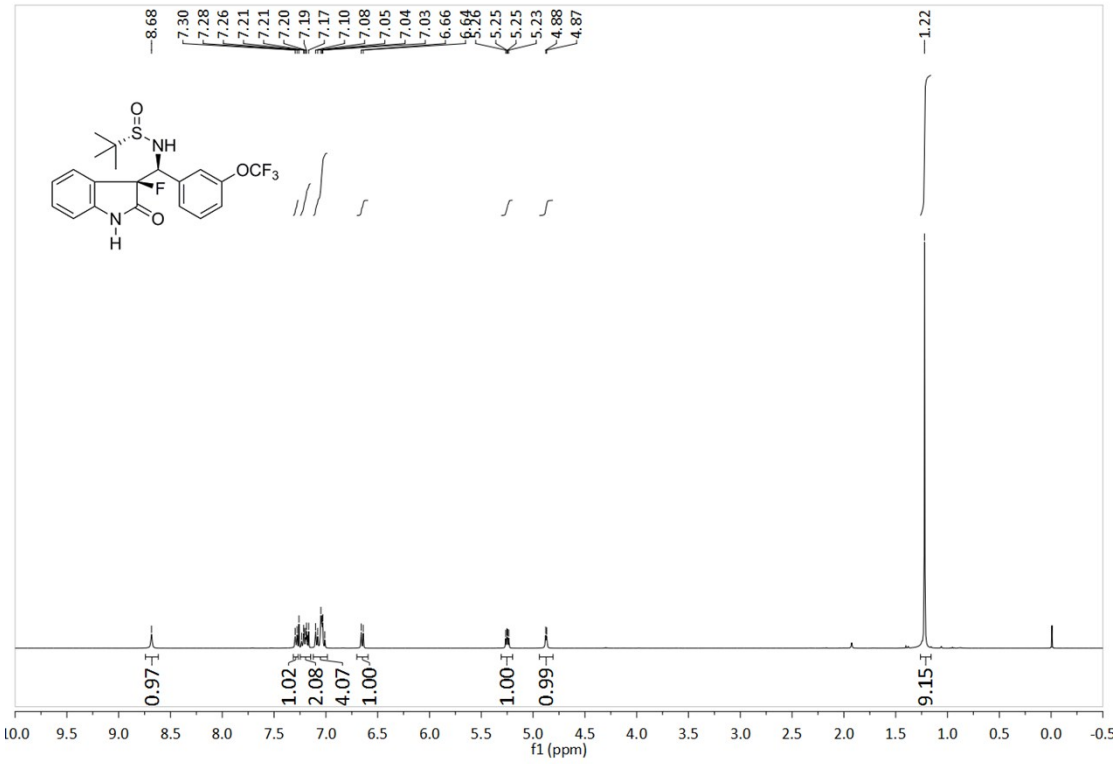
^{19}F NMR spectrum of **11ab**



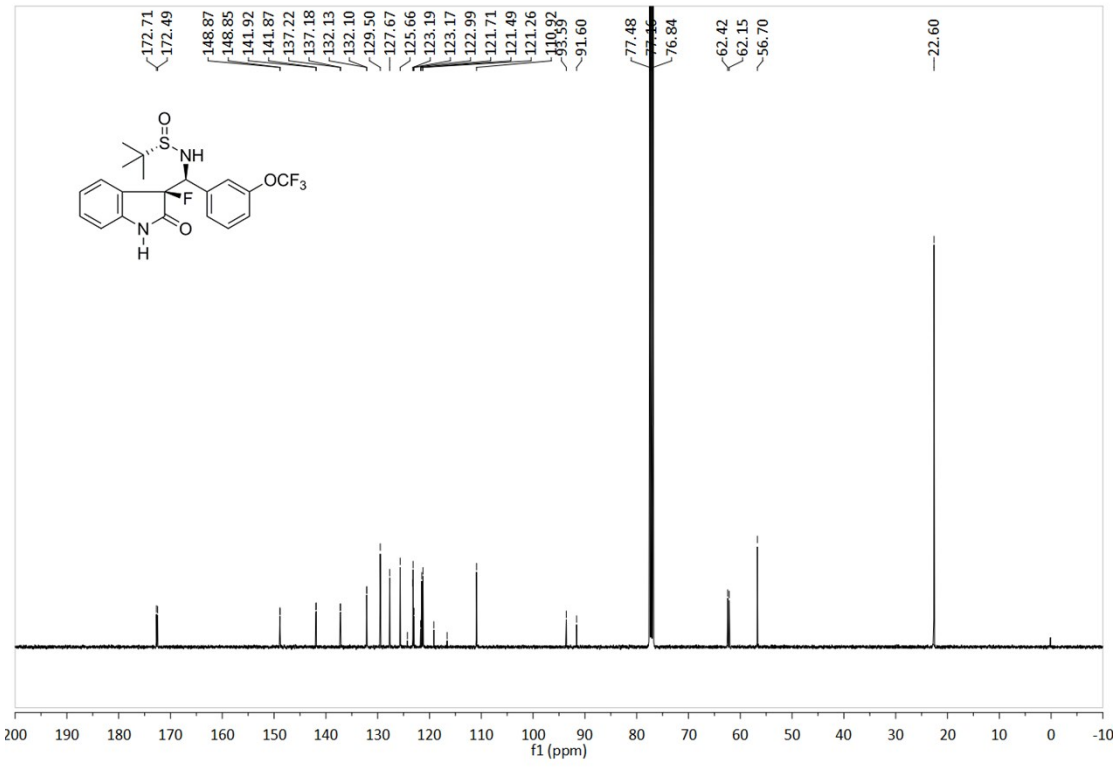
^{19}F NMR spectrum of the crude reaction mixture



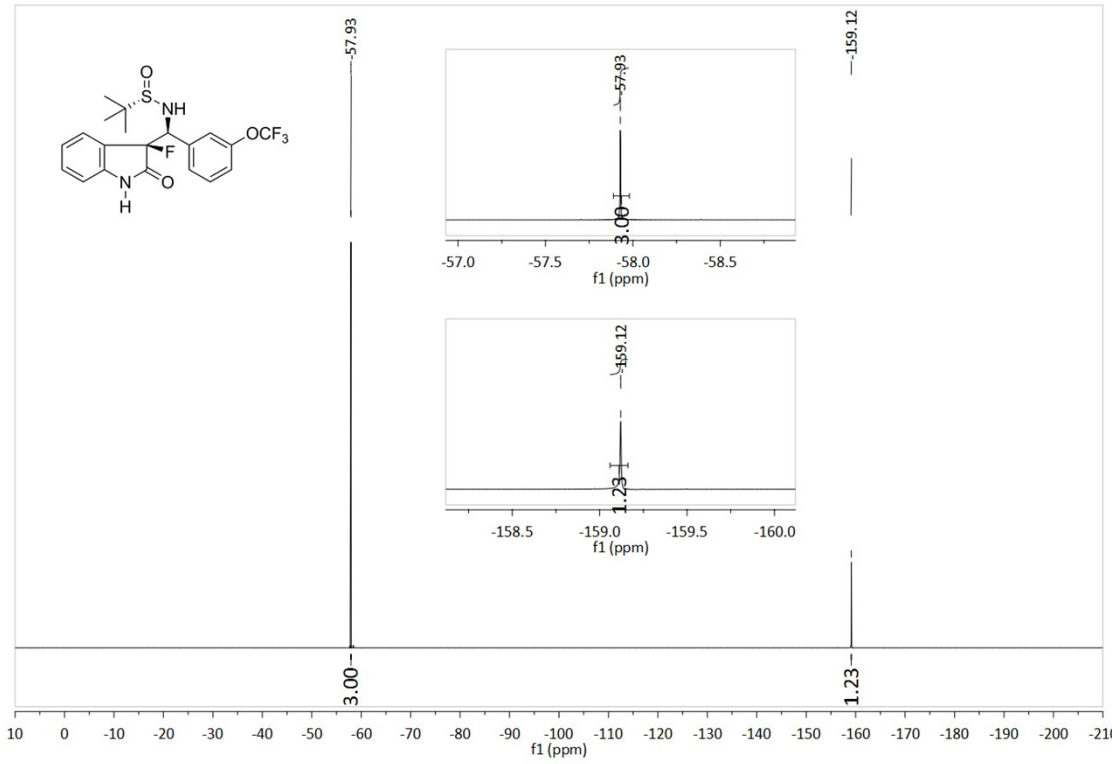
^{1}H NMR spectrum of **11ac**



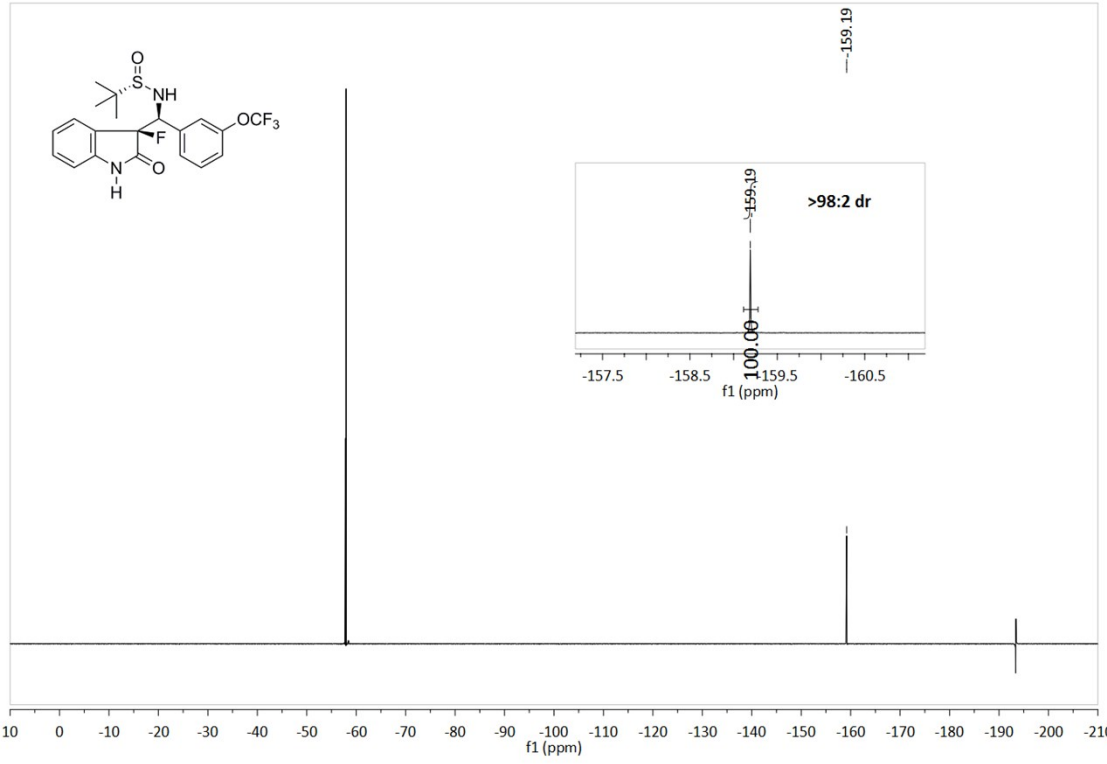
^{13}C NMR spectrum of **11ac**



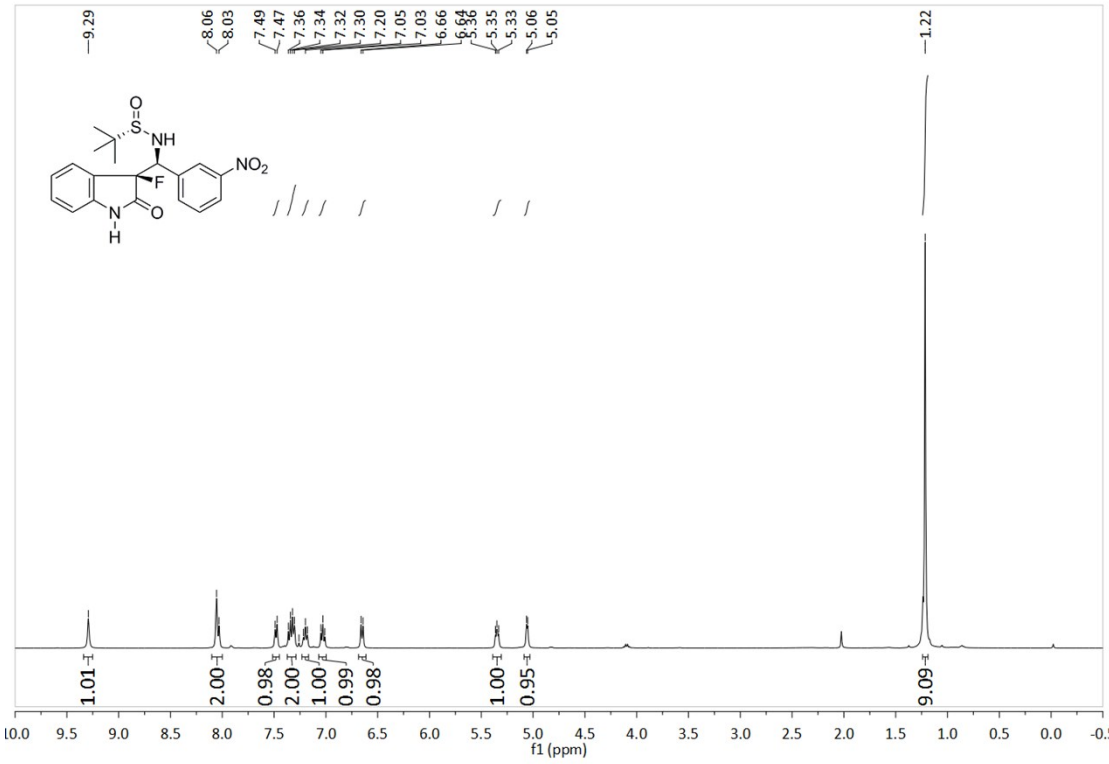
^{19}F NMR spectrum of **11ac**



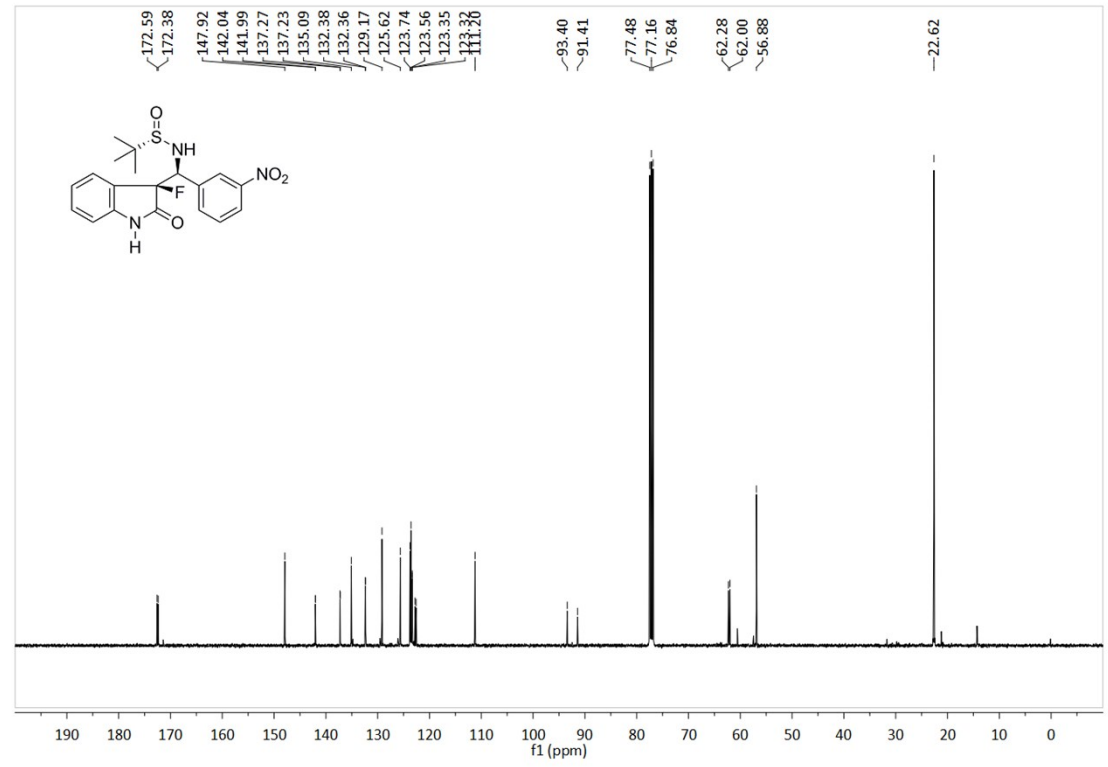
^{19}F NMR spectrum of the crude reaction mixture



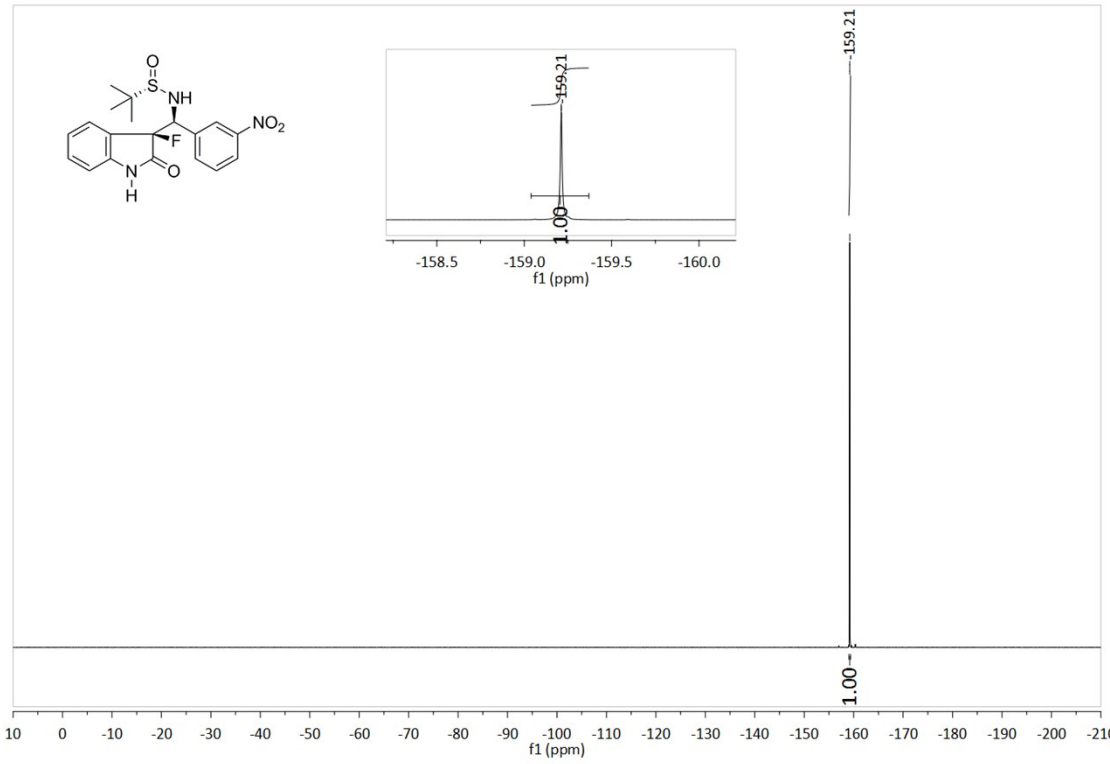
^{1}H NMR spectrum of **11ad**



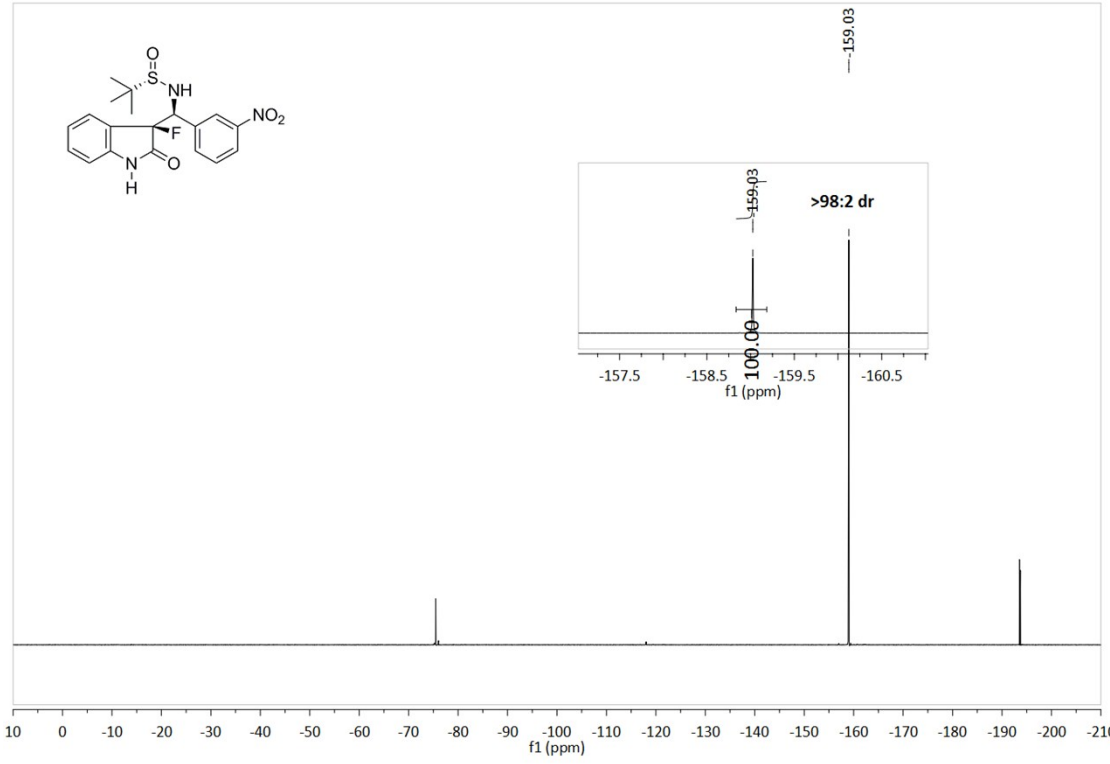
^{13}C NMR spectrum of **11ad**



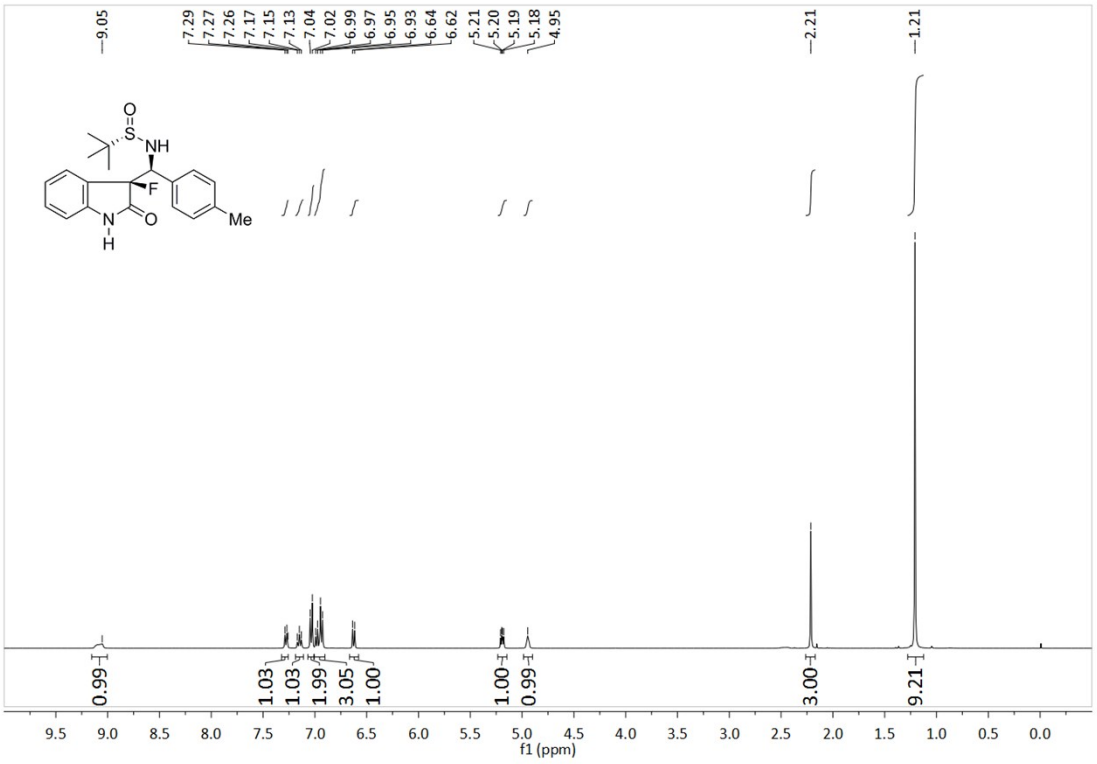
^{19}F NMR spectrum of **11ad**



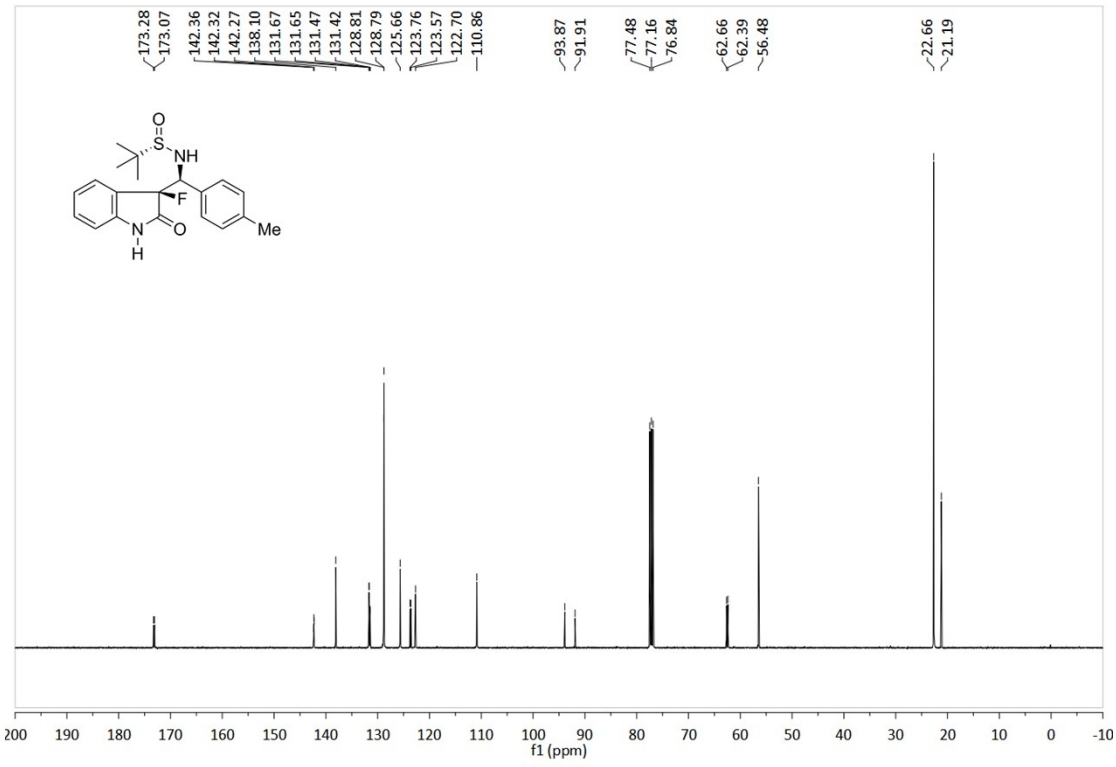
^{19}F NMR spectrum of the crude reaction mixture



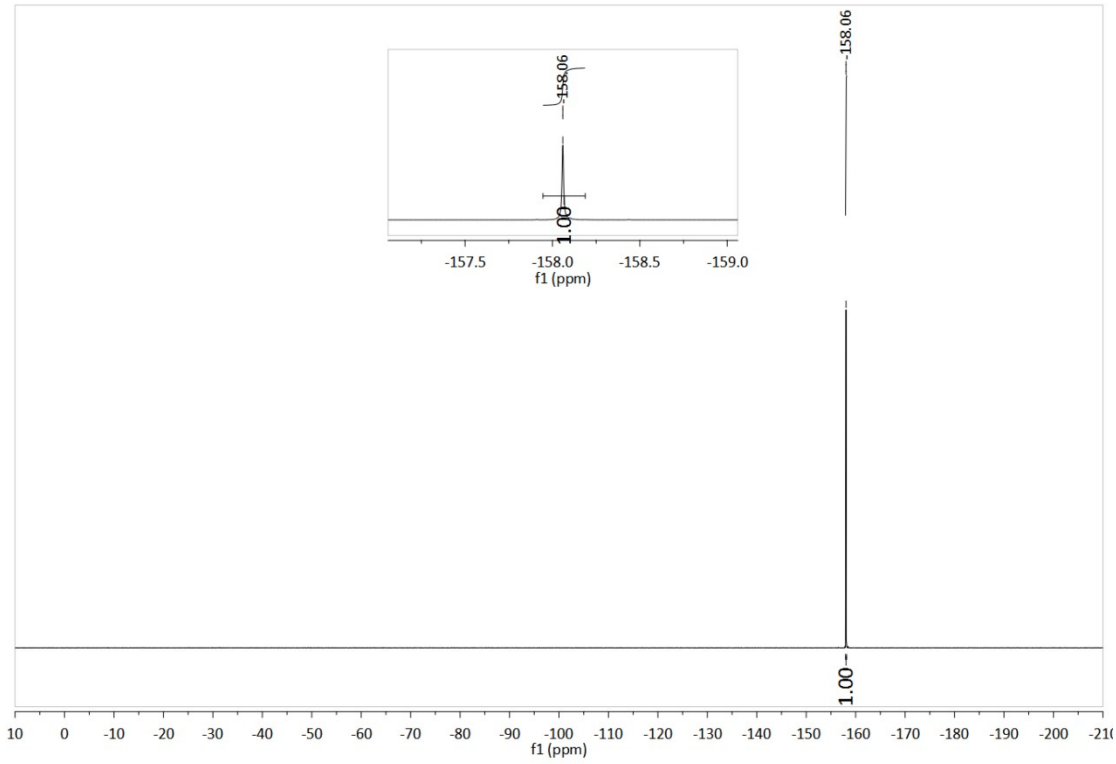
^{1}H NMR spectrum of **11ae**



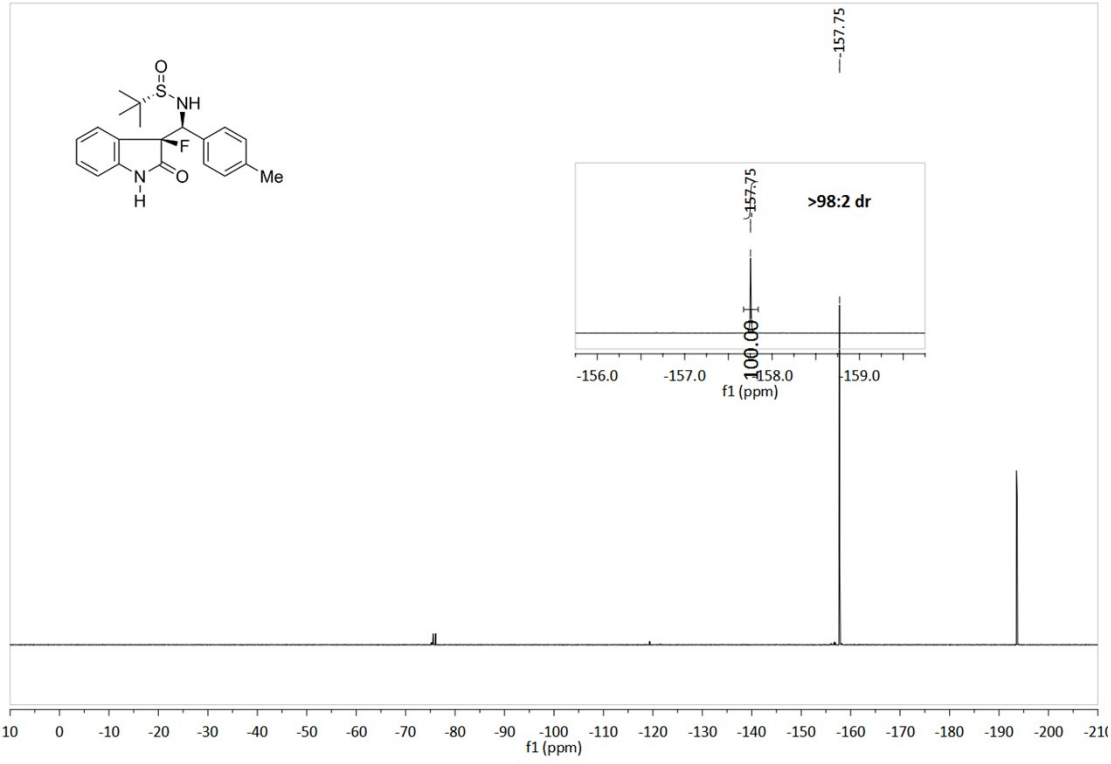
^{13}C NMR spectrum of **11ae**



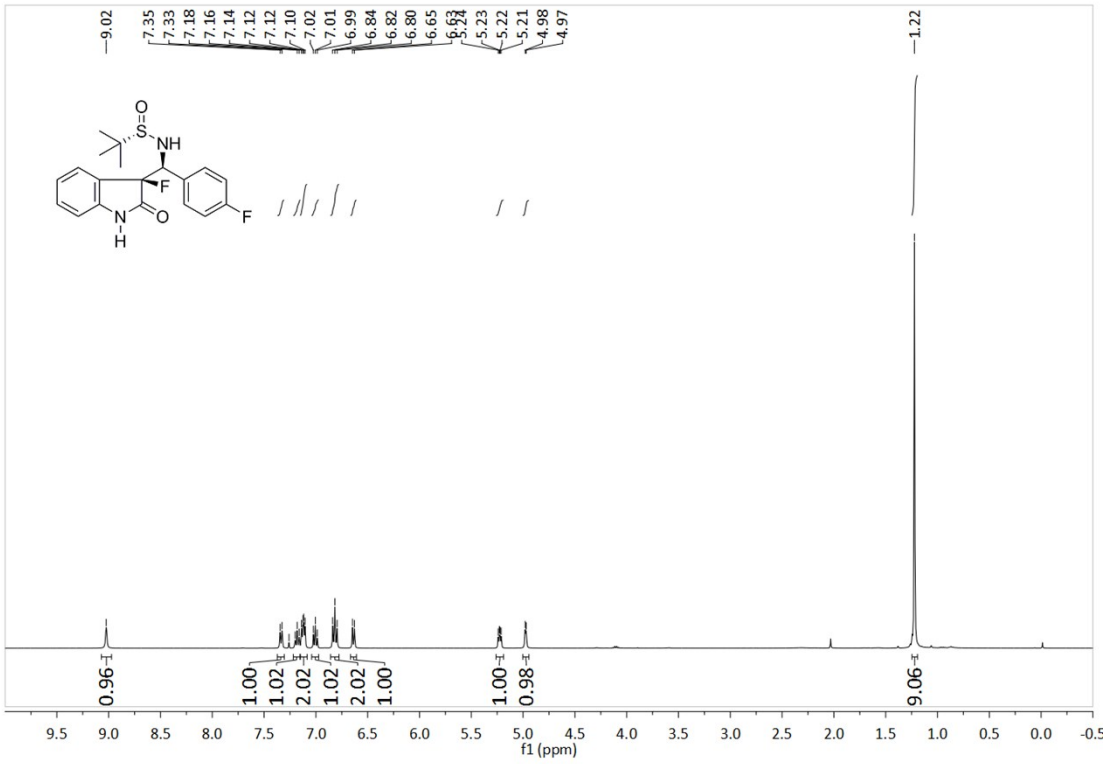
^{19}F NMR spectrum of **11ae**



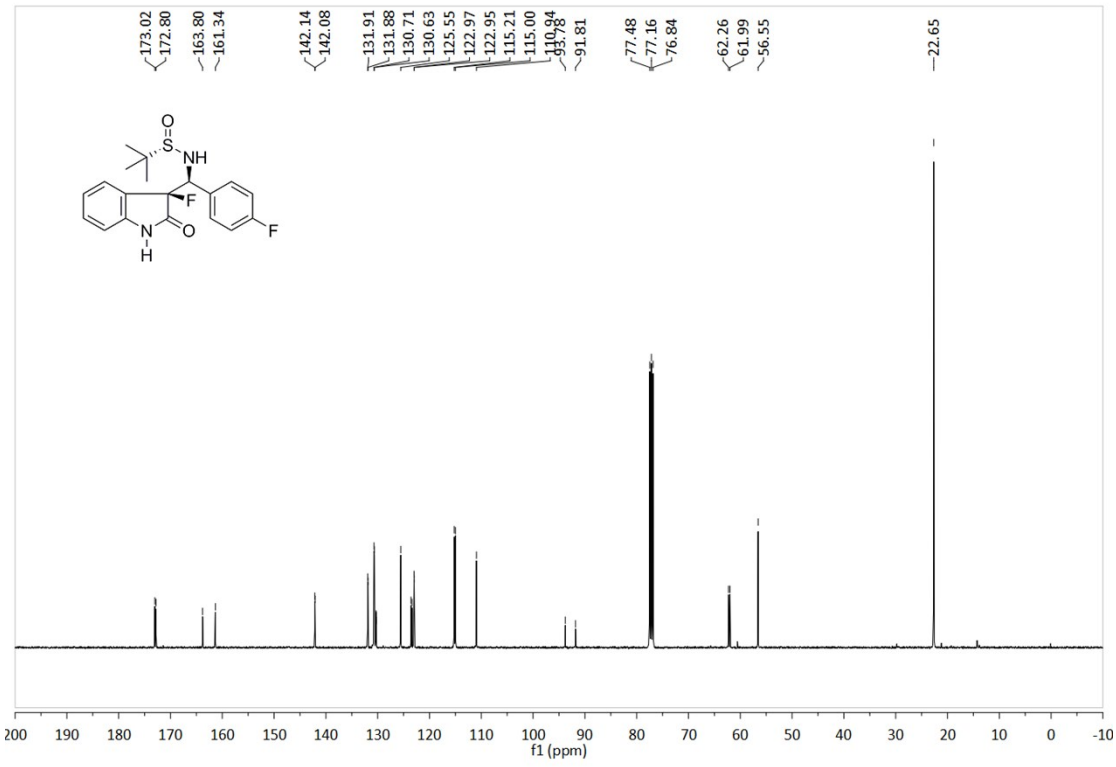
^{19}F NMR spectrum of the crude reaction mixture



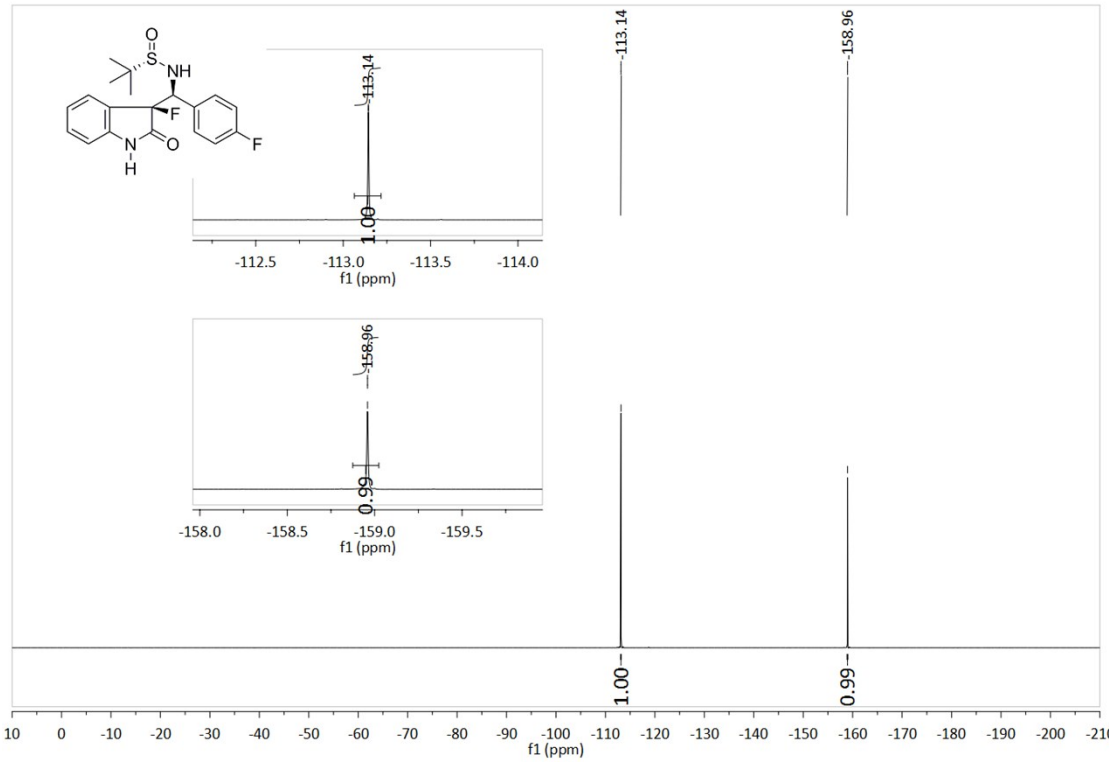
^{1}H NMR spectrum of **11af**



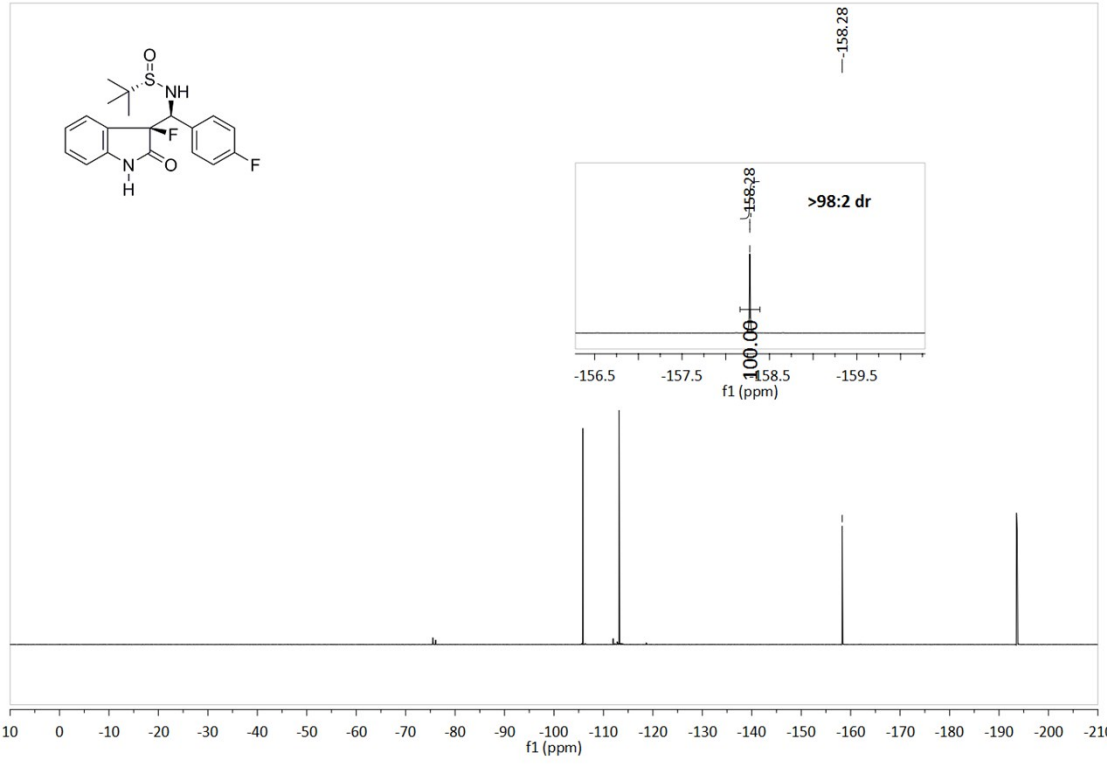
^{13}C NMR spectrum of **11af**



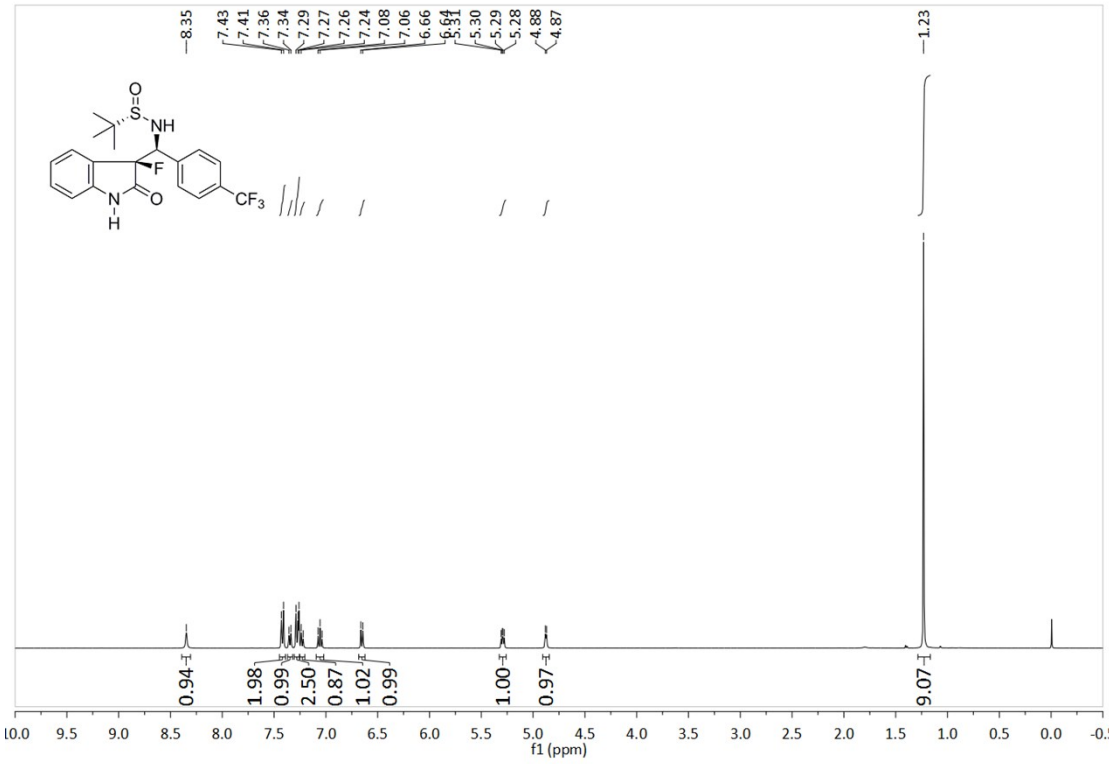
^{19}F NMR spectrum of **11af**



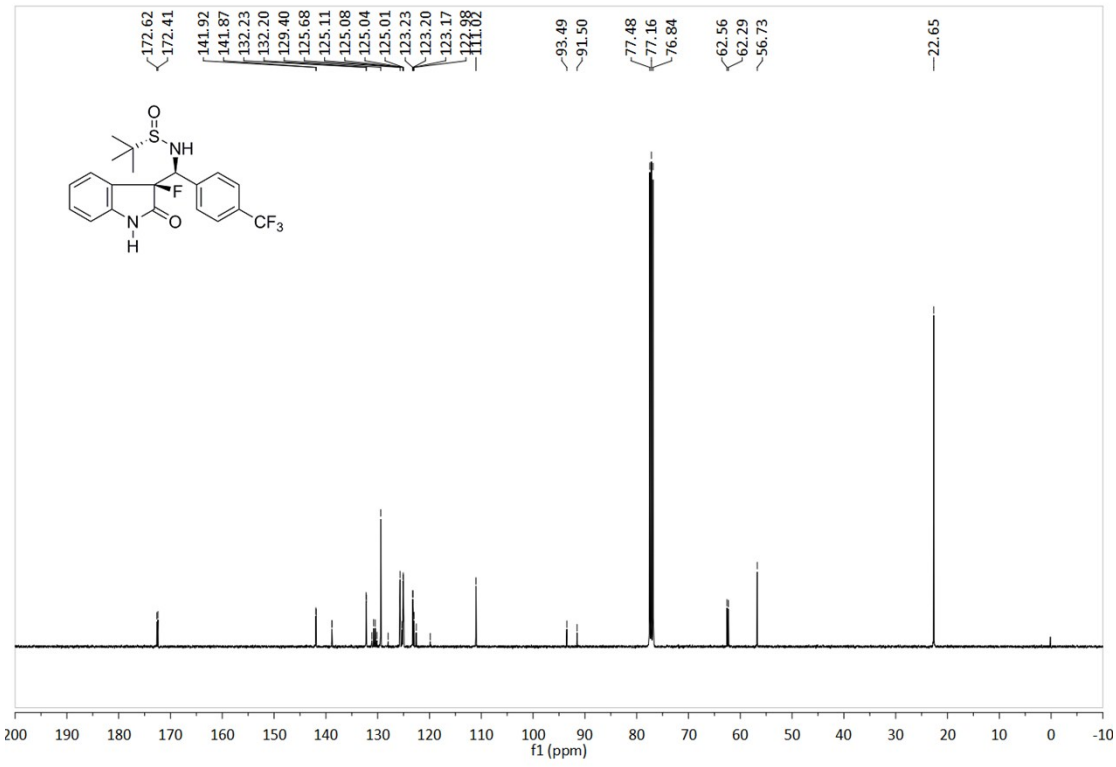
^{19}F NMR spectrum of the crude reaction mixture



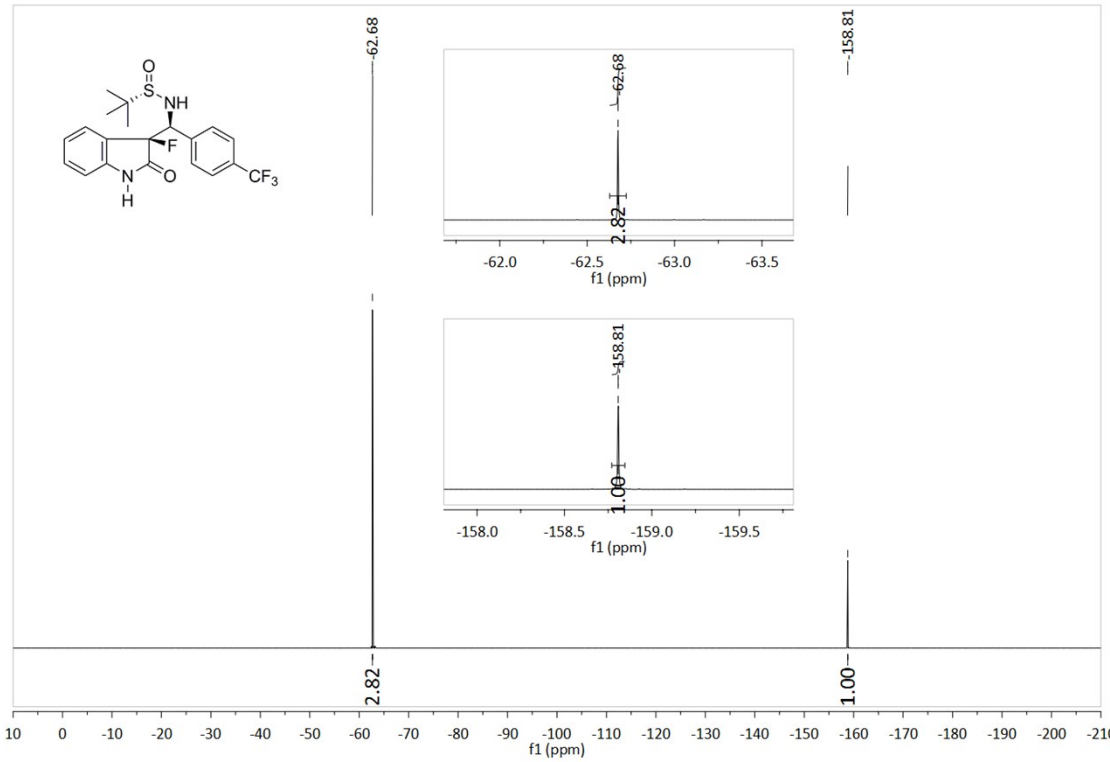
^{1}H NMR spectrum of **11ag**



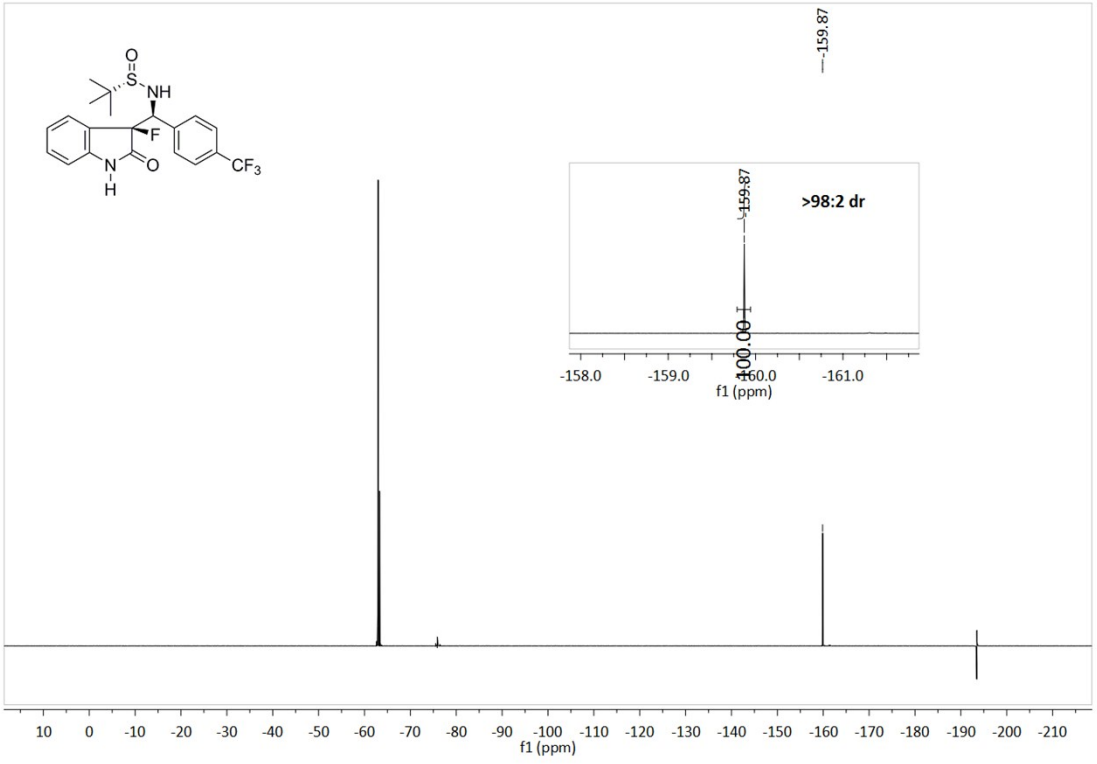
^{13}C NMR spectrum of **11ag**



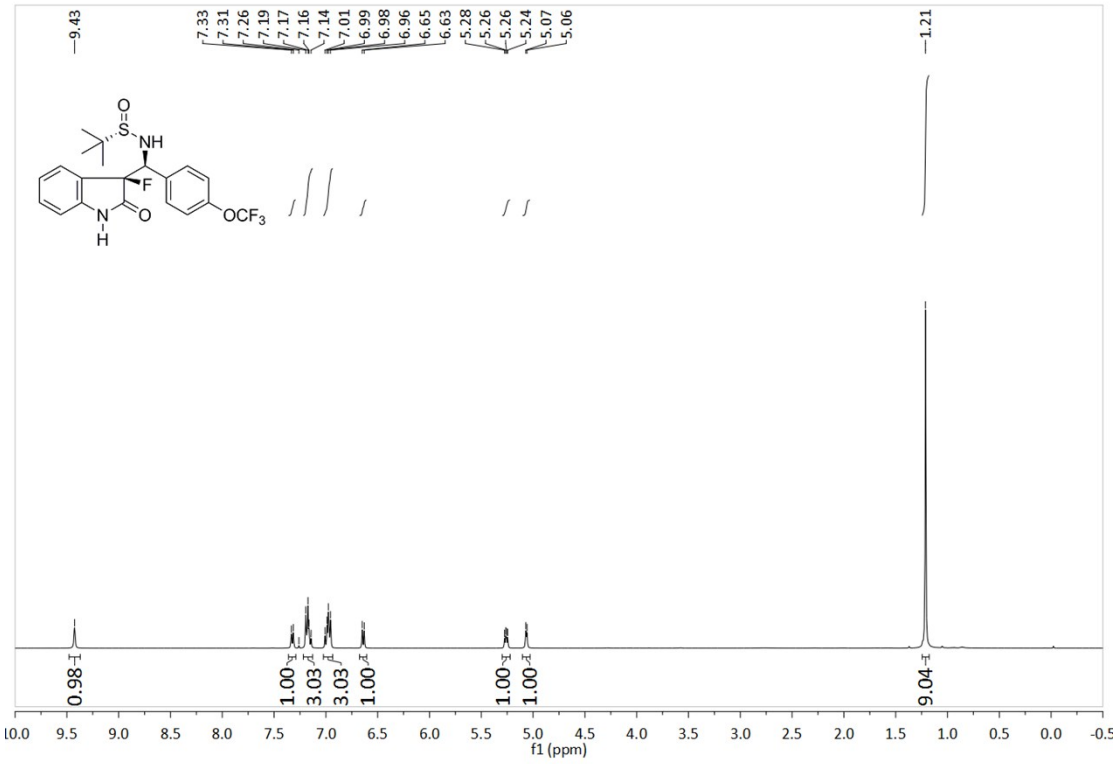
^{19}F NMR spectrum of **11ag**



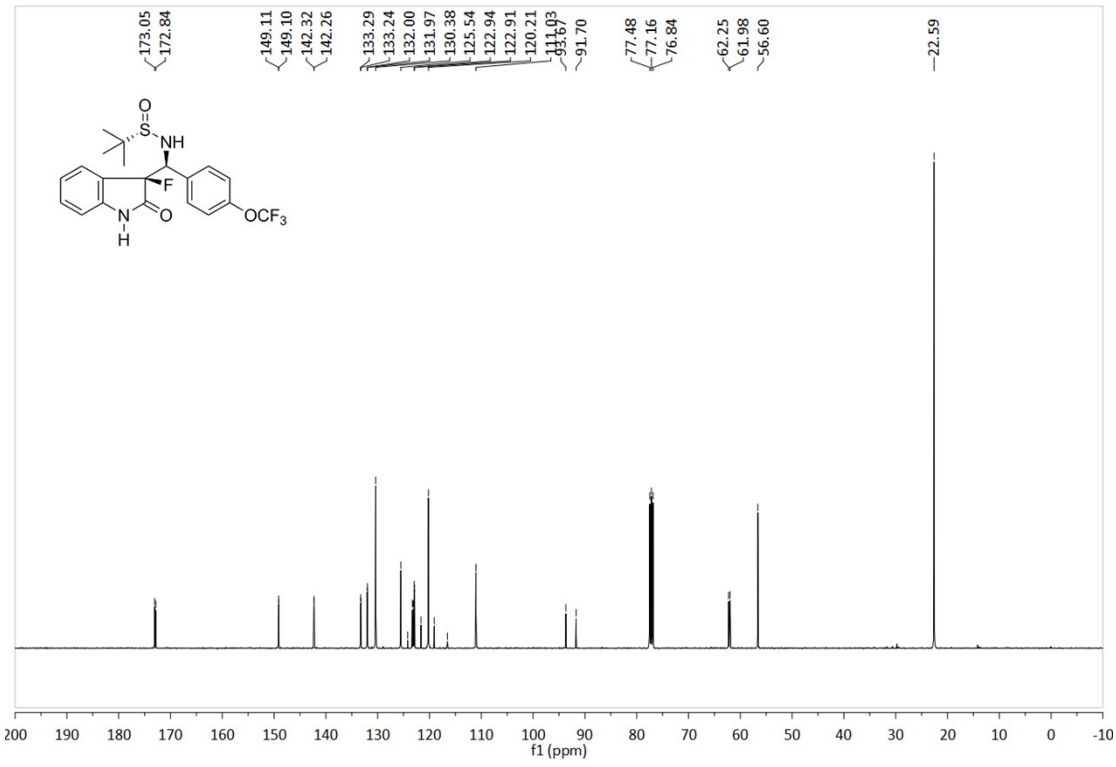
^{19}F NMR spectrum of the crude reaction mixture



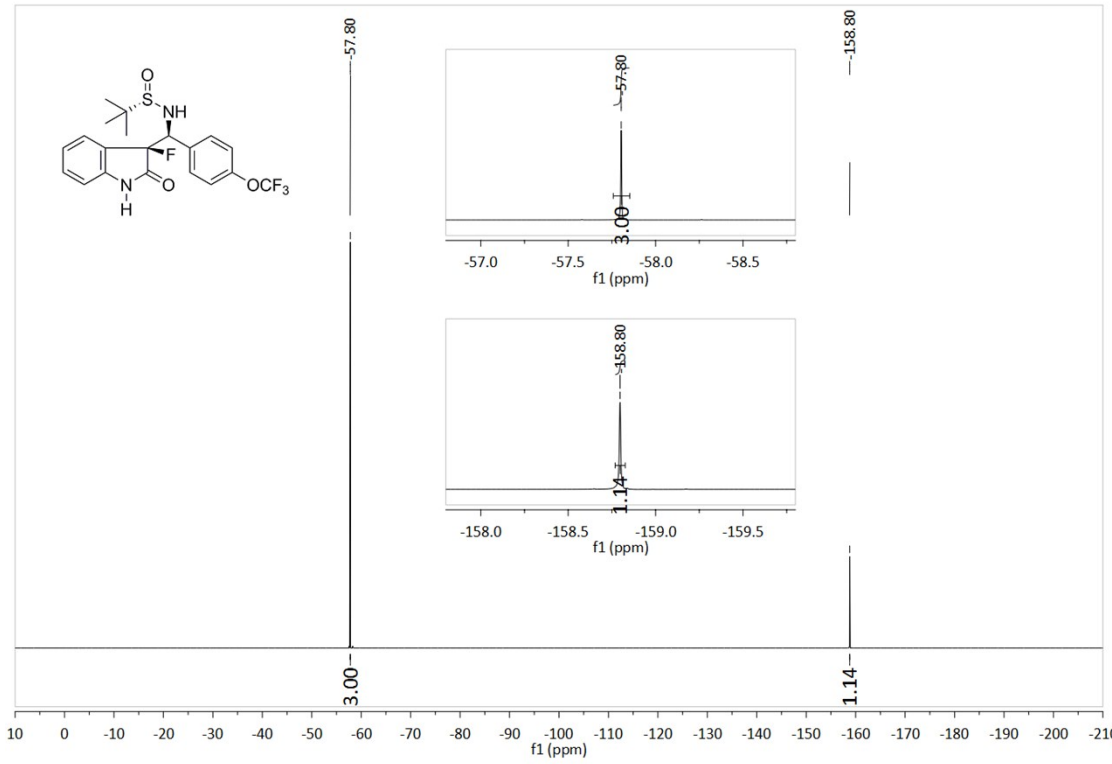
^{1}H NMR spectrum of **11ah**



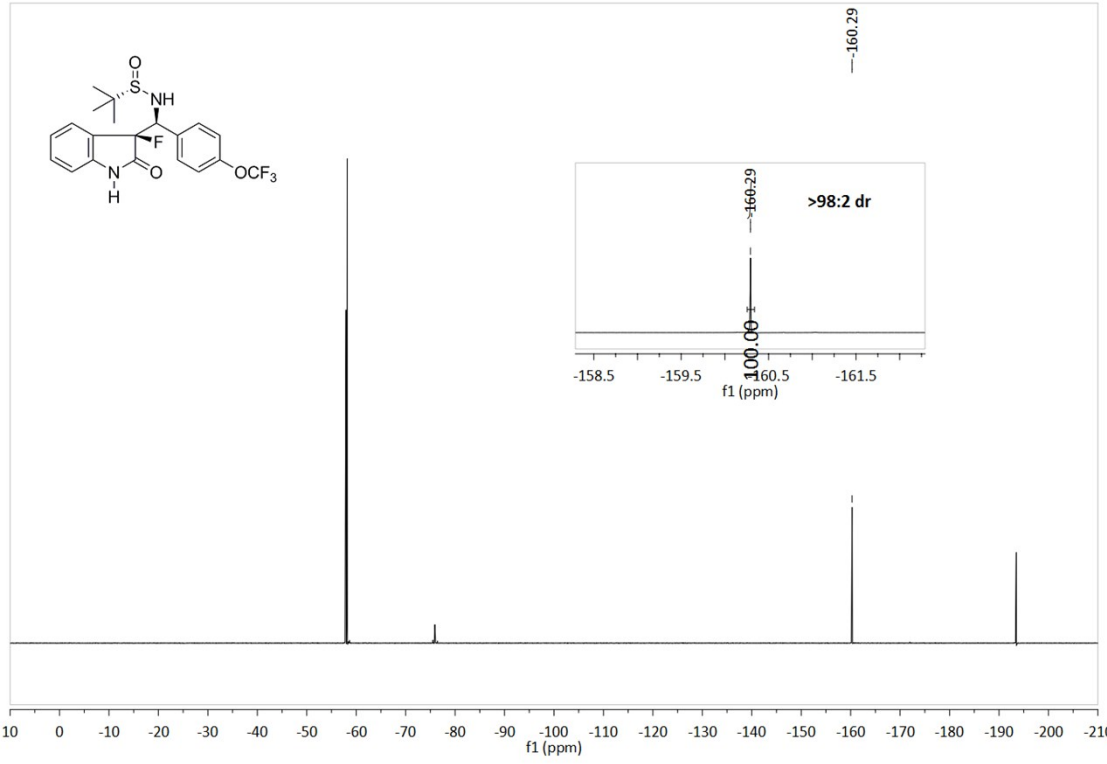
^{13}C NMR spectrum of **11ah**



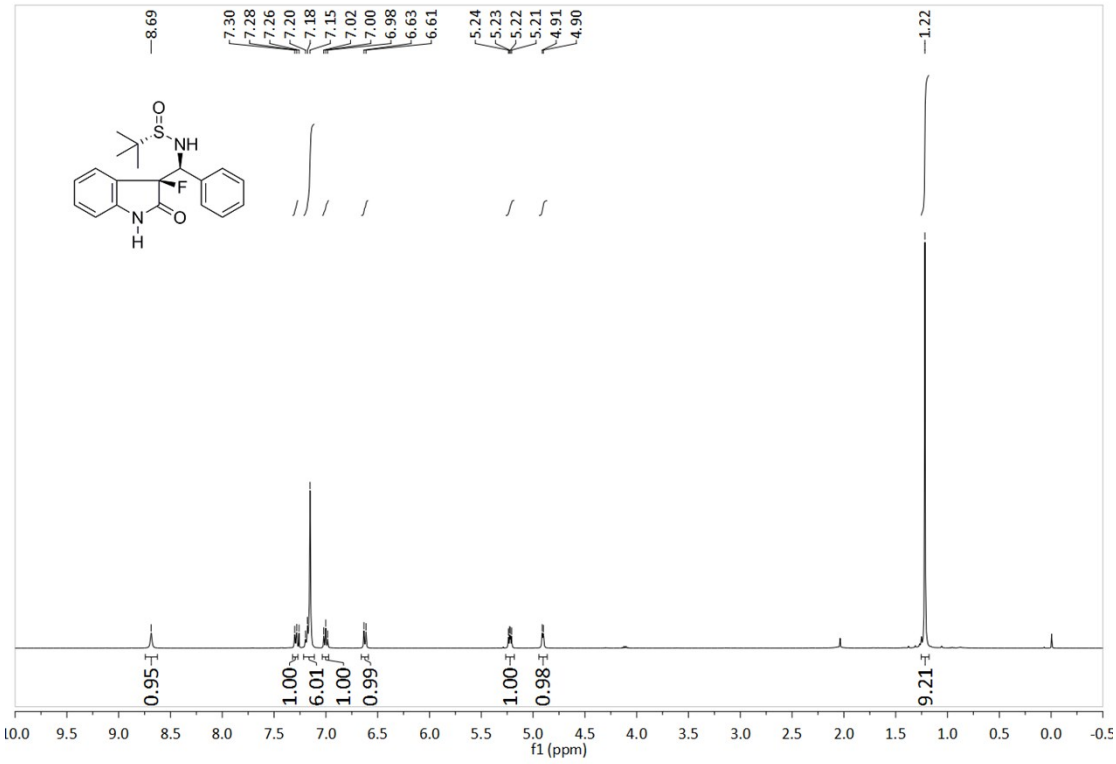
^{19}F NMR spectrum of **11ah**



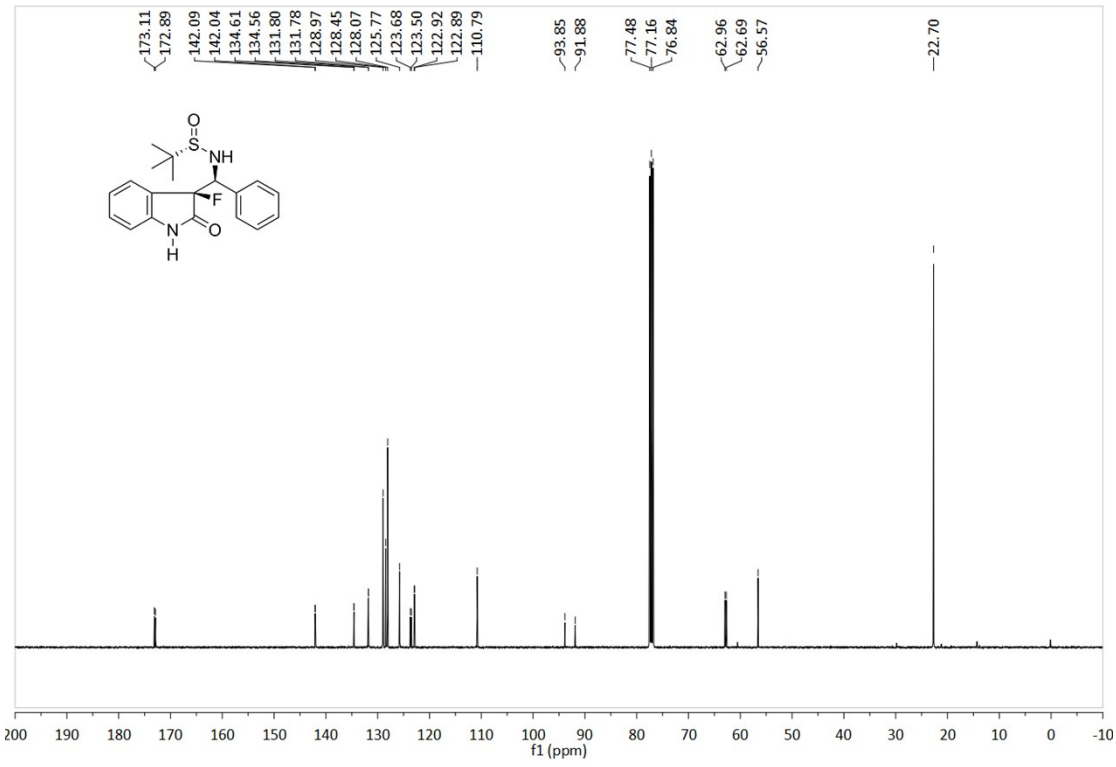
^{19}F NMR spectrum of the crude reaction mixture



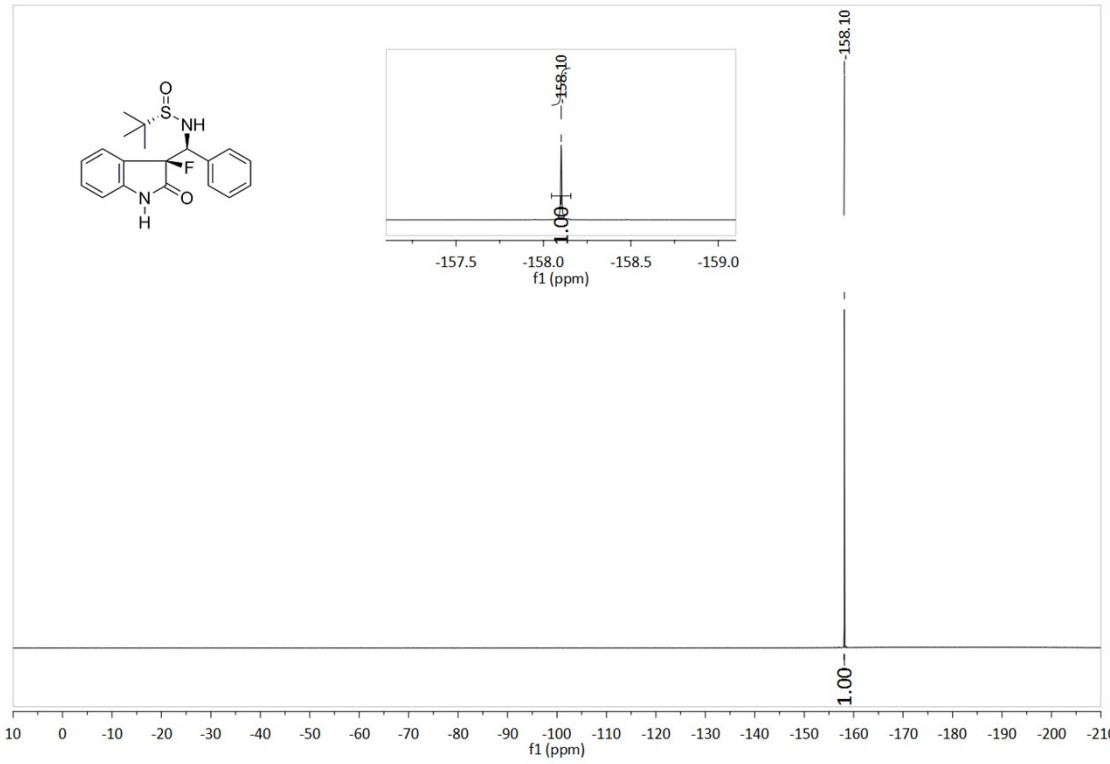
^{1}H NMR spectrum of **11ai**



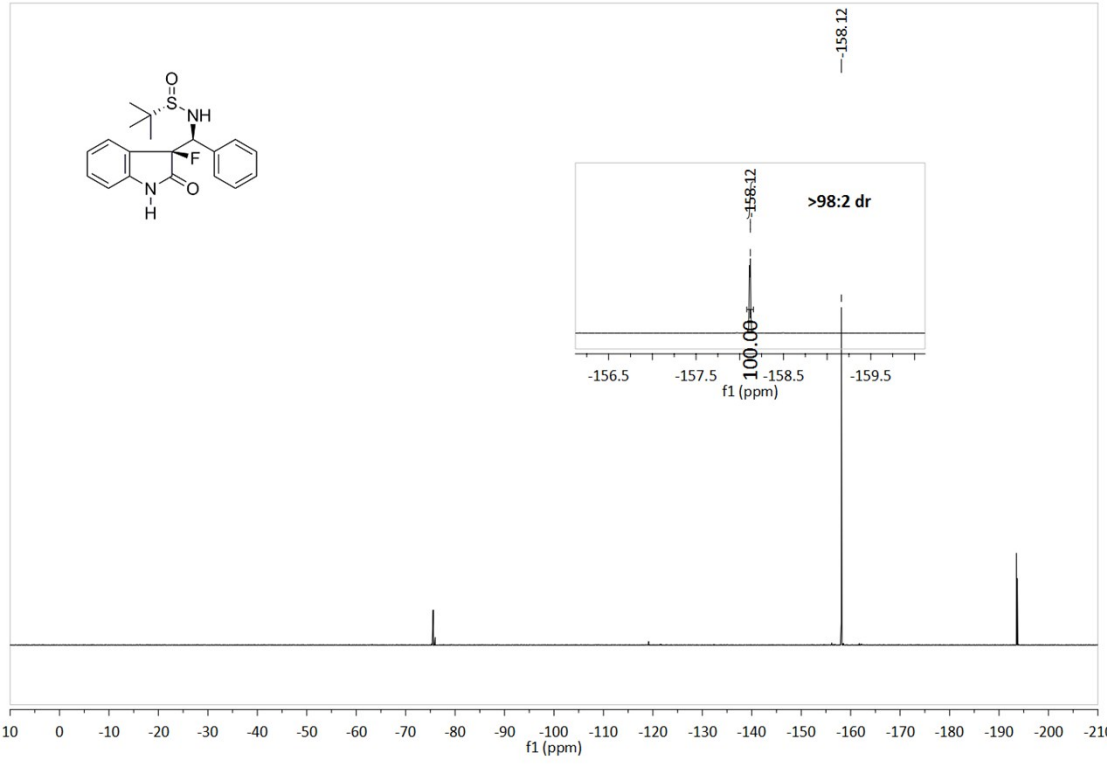
^{13}C NMR spectrum of **11ai**



^{19}F NMR spectrum of **11ai**



^{19}F NMR spectrum of the crude reaction mixture



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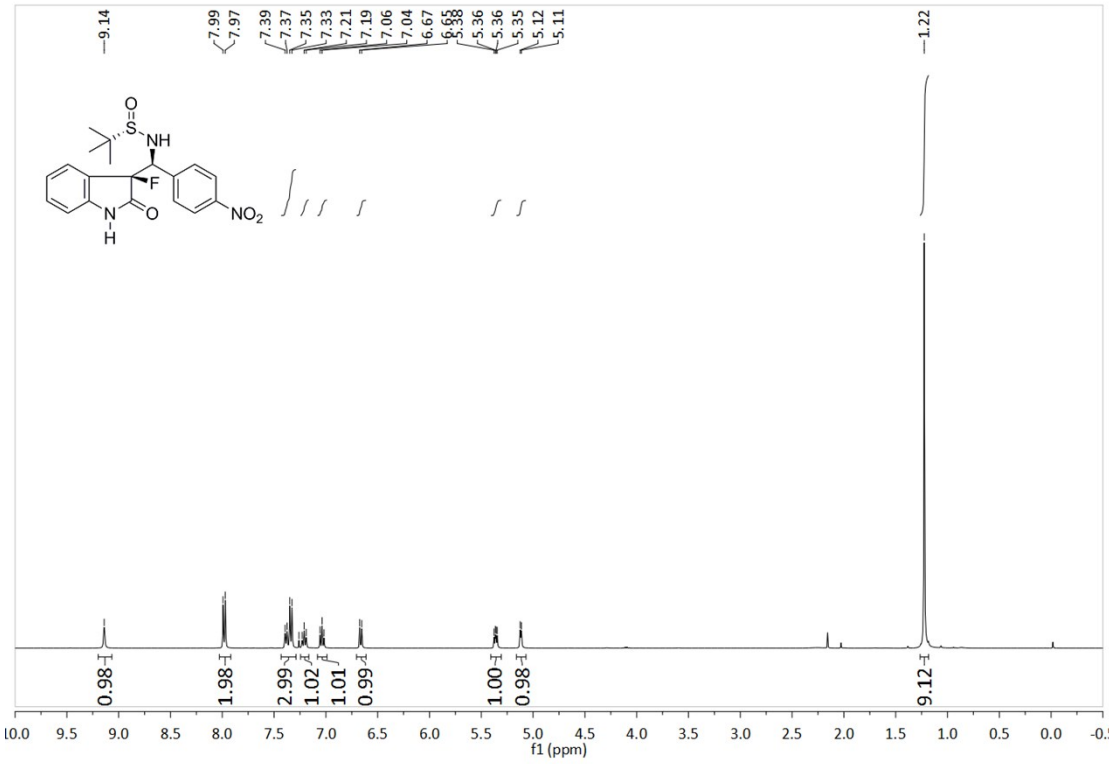
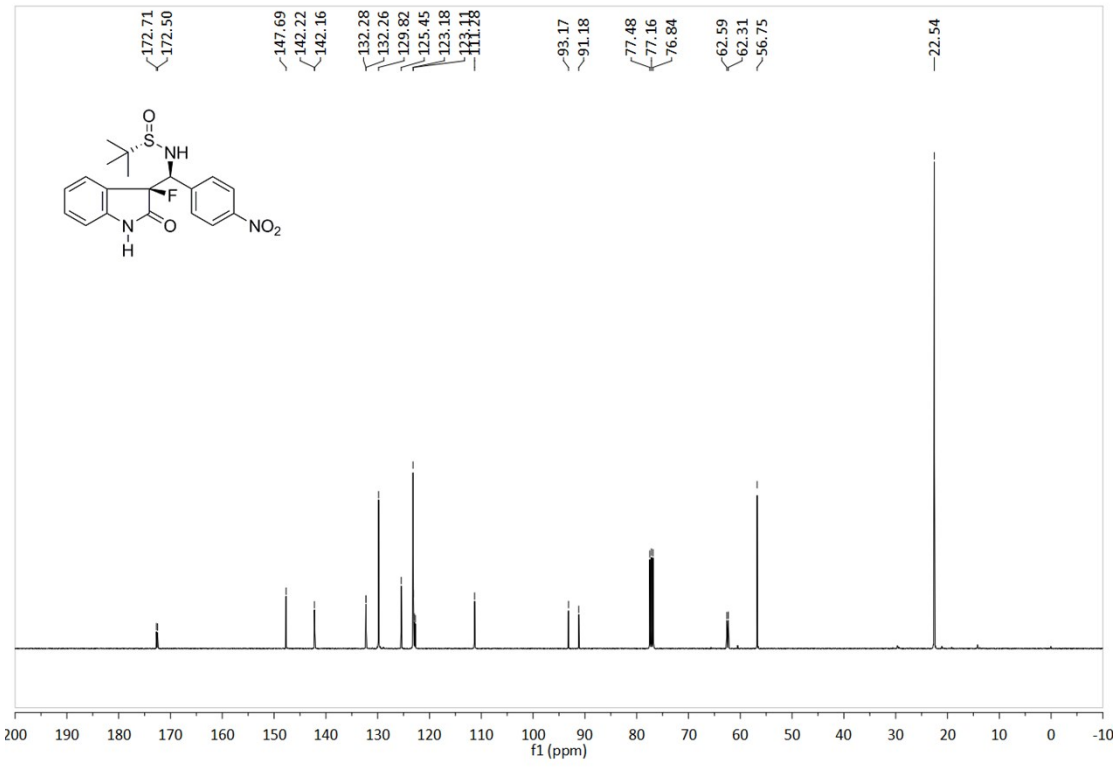
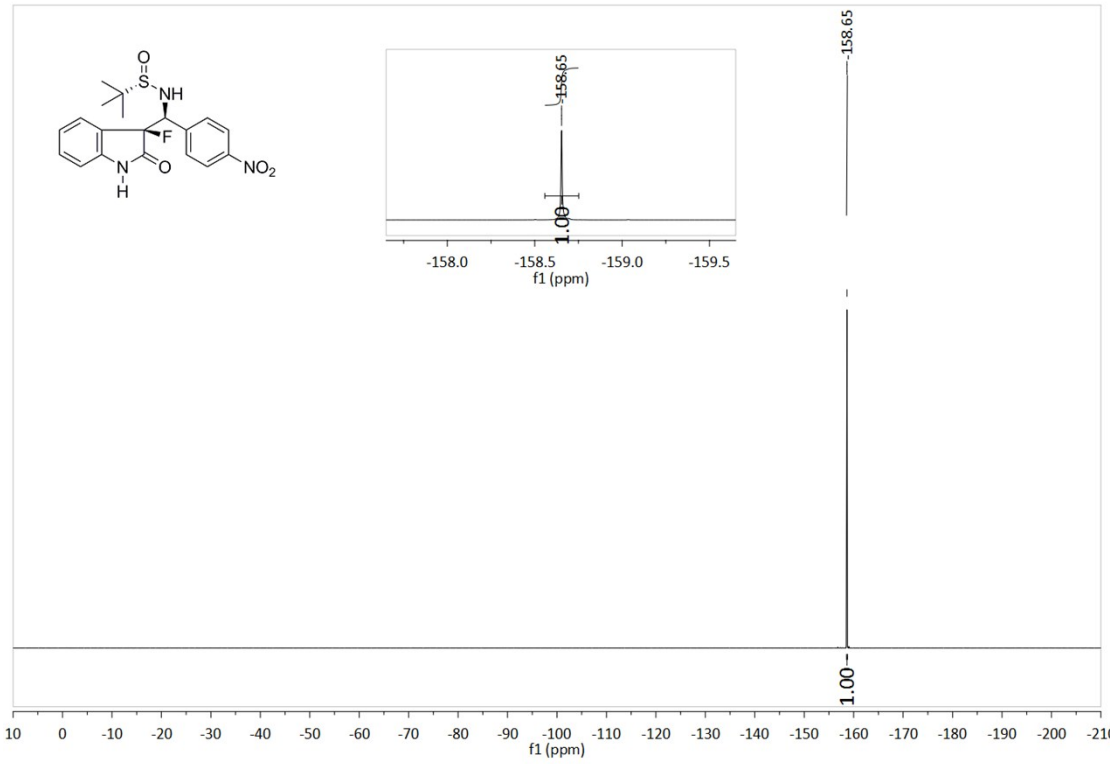


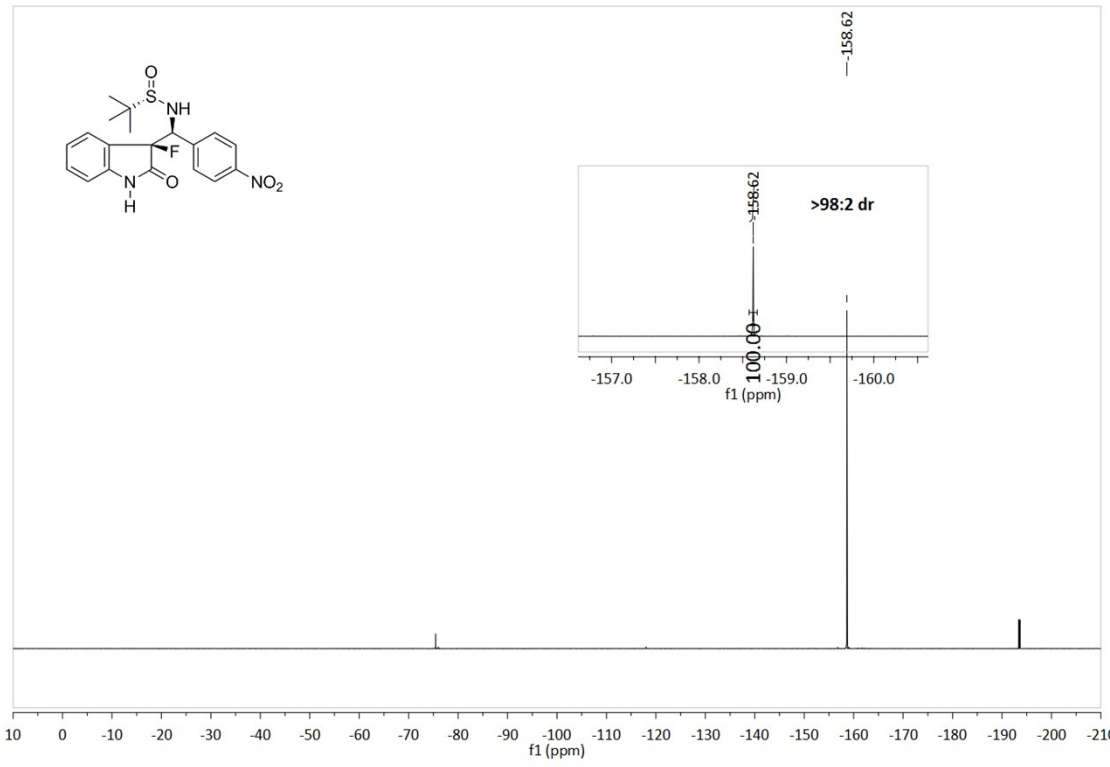
^{13}C NMR spectrum of **11aj**



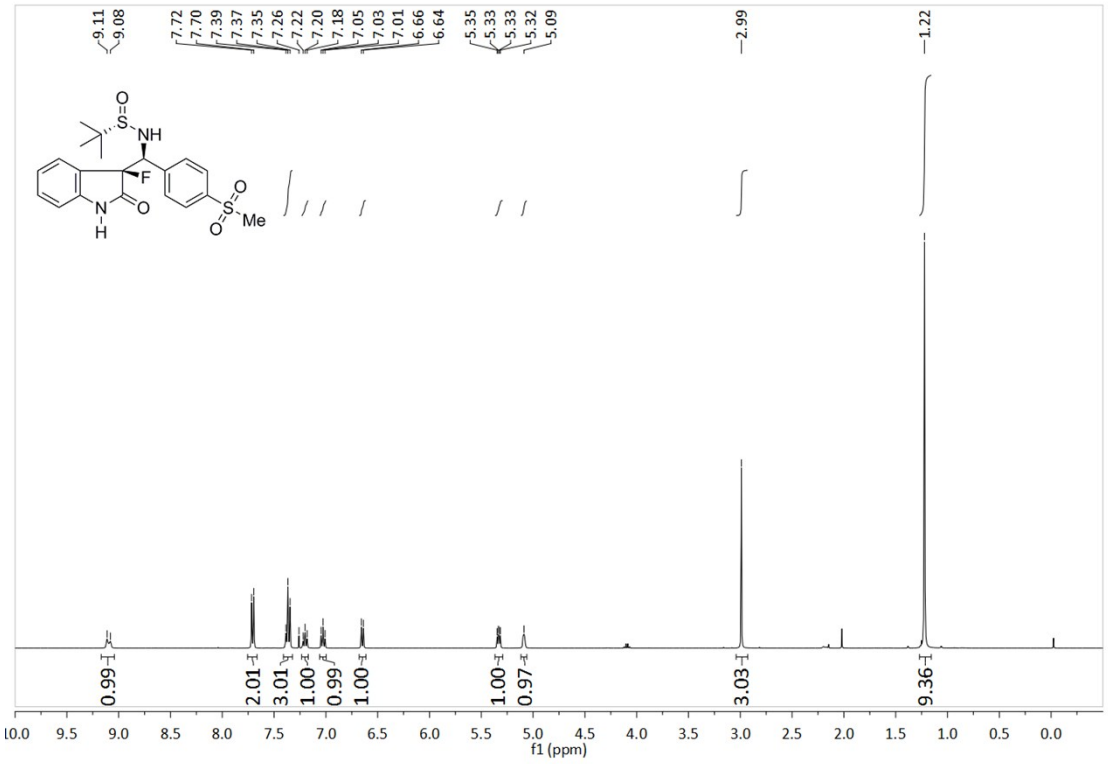
^{19}F NMR spectrum of **11aj**



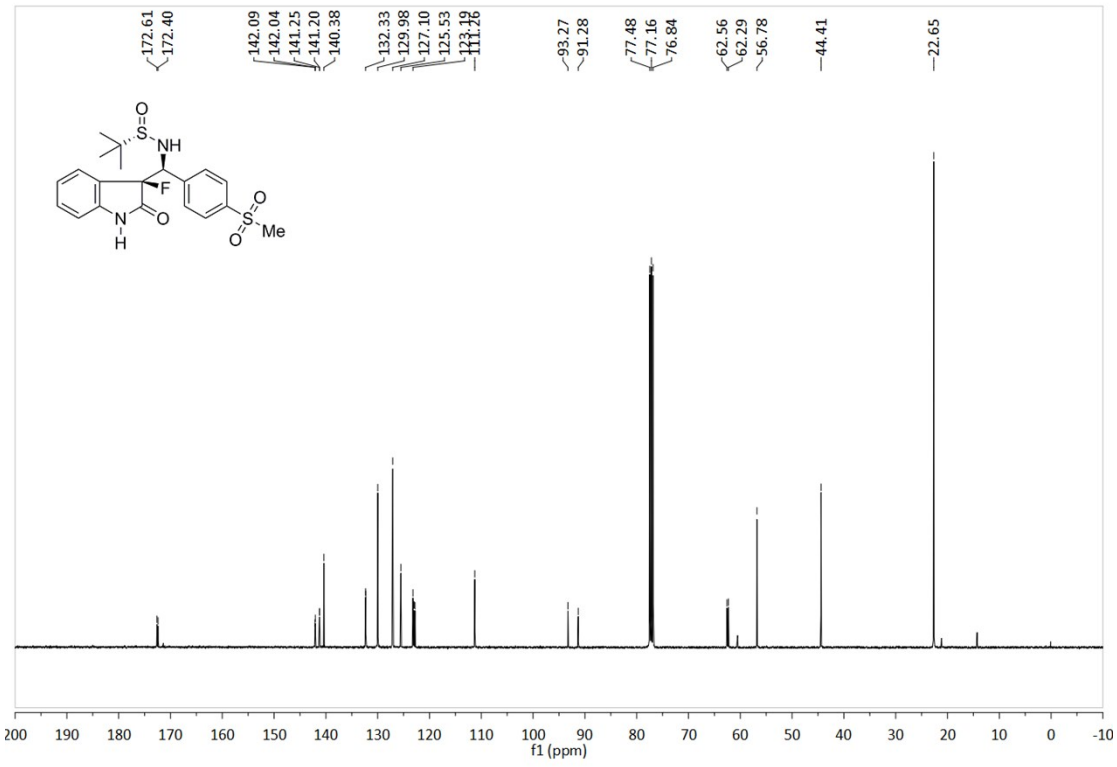
^{19}F NMR spectrum of the crude reaction mixture



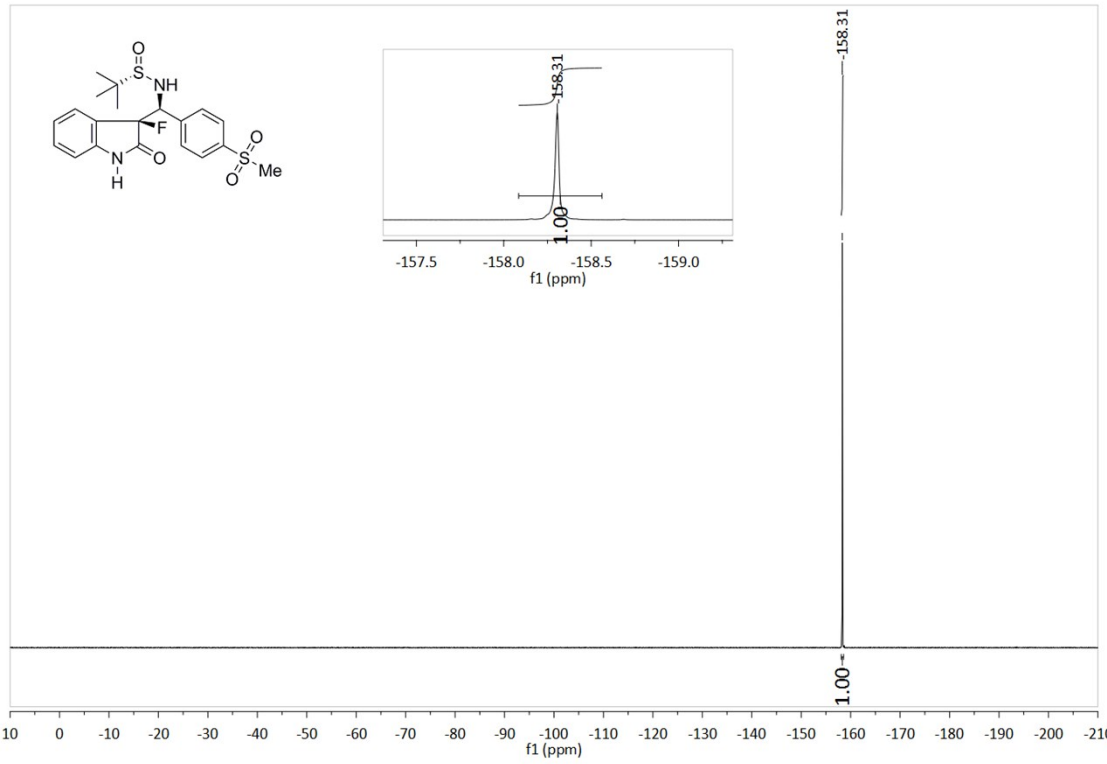
^{1}H NMR spectrum of **11ak**



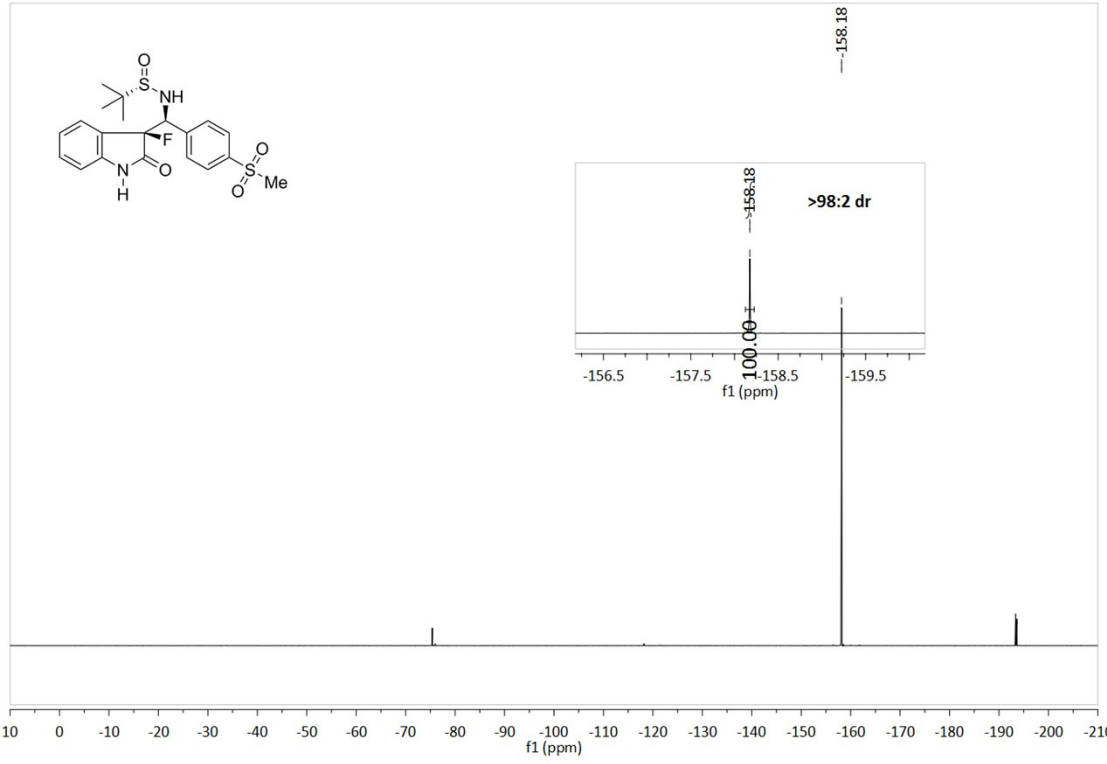
^{13}C NMR spectrum of **11ak**



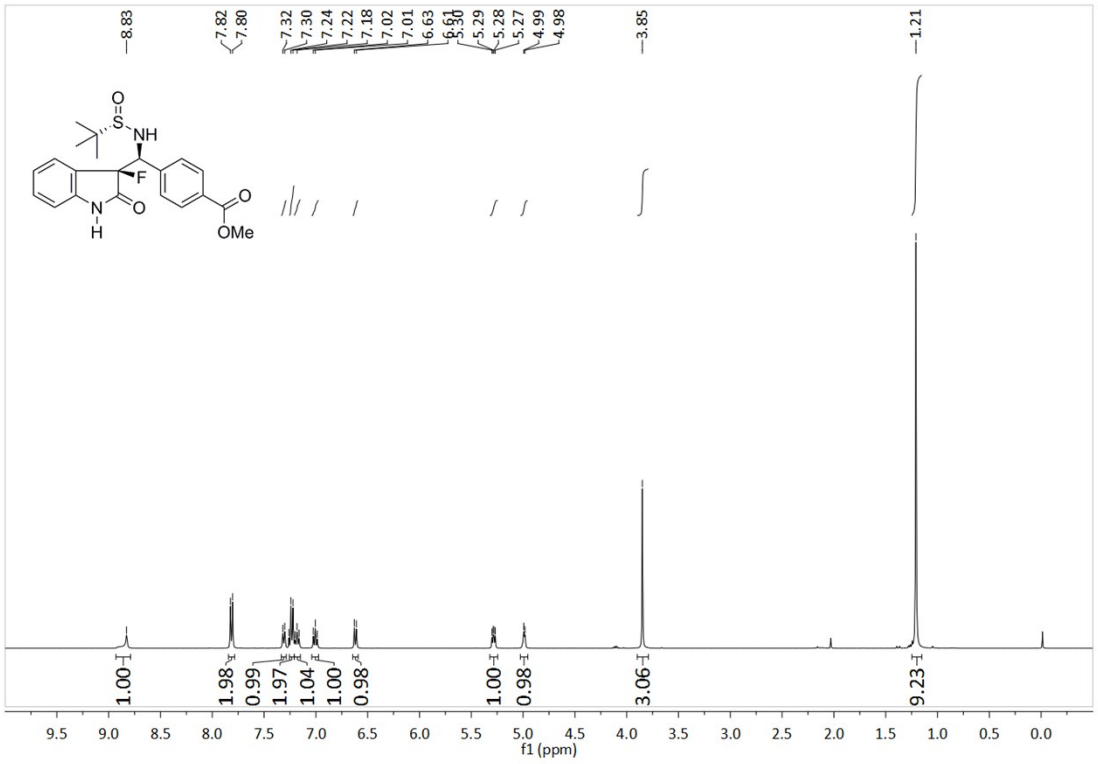
^{19}F NMR spectrum of **11ak**



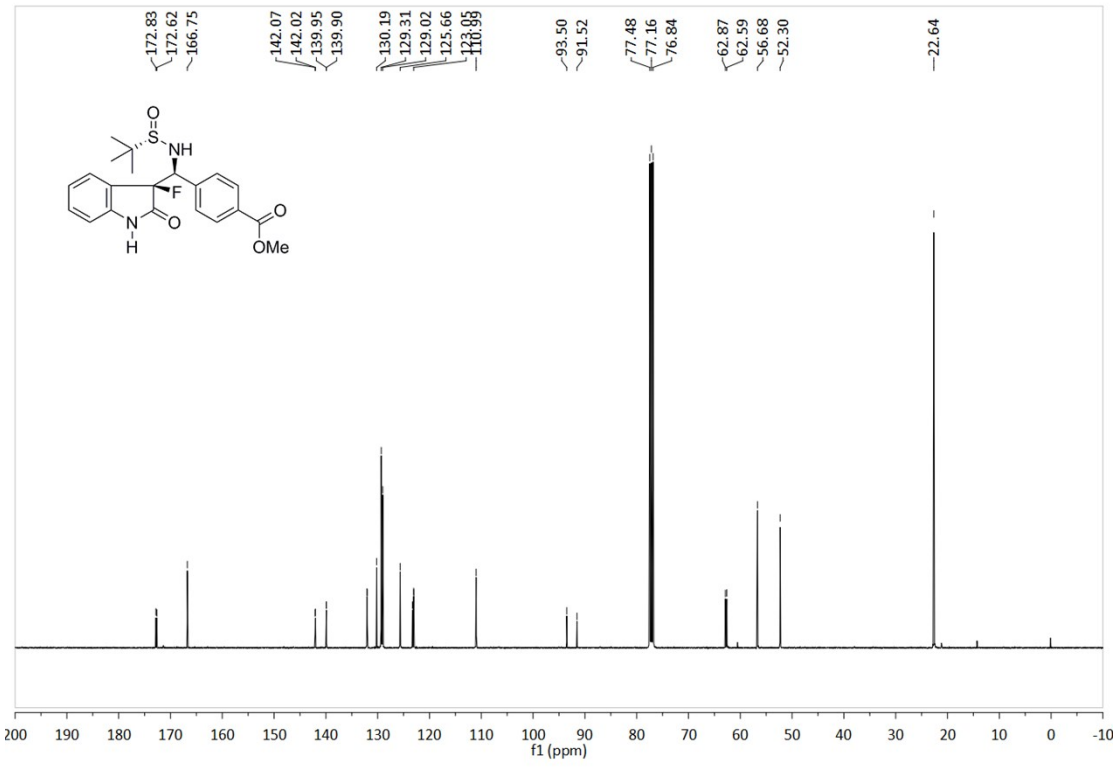
^{19}F NMR spectrum of the crude reaction mixture



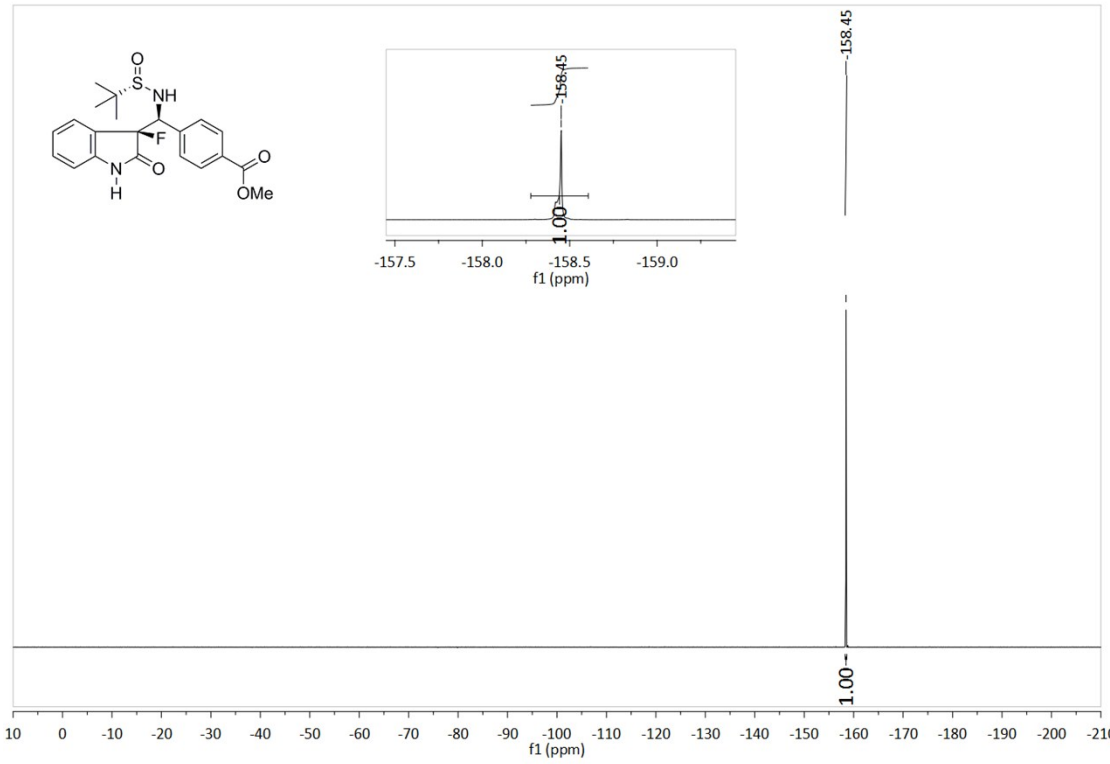
^{1}H NMR spectrum of **11al**



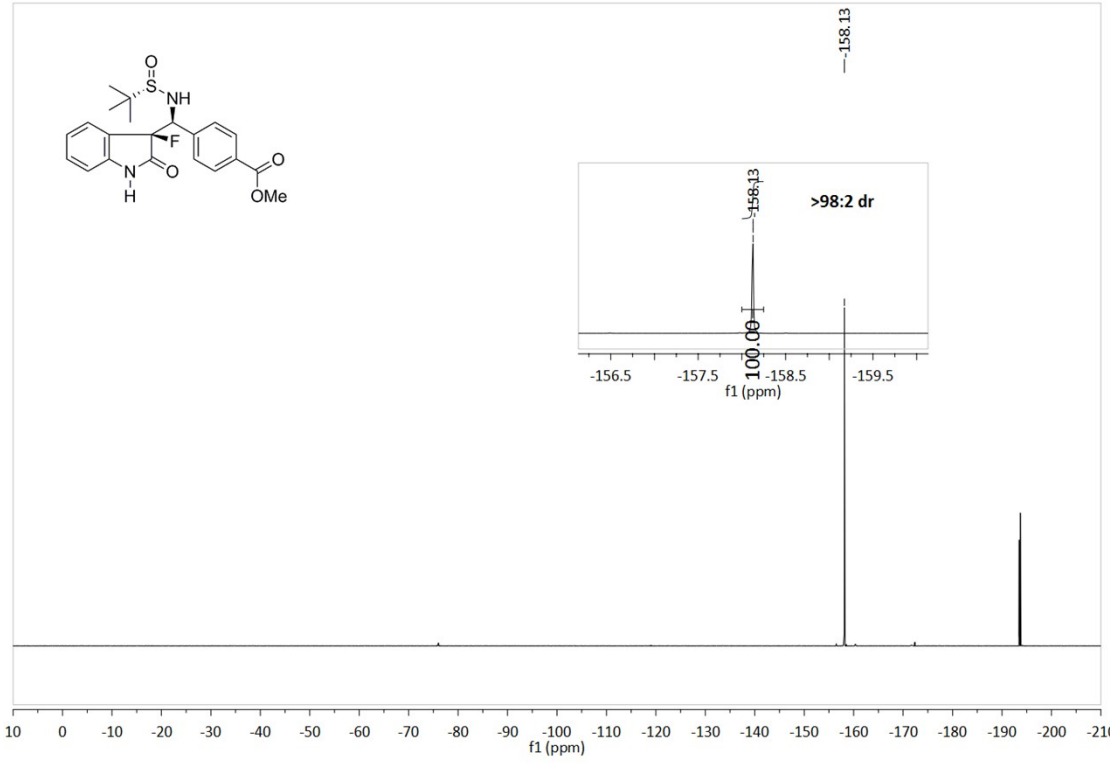
^{13}C NMR spectrum of **11al**



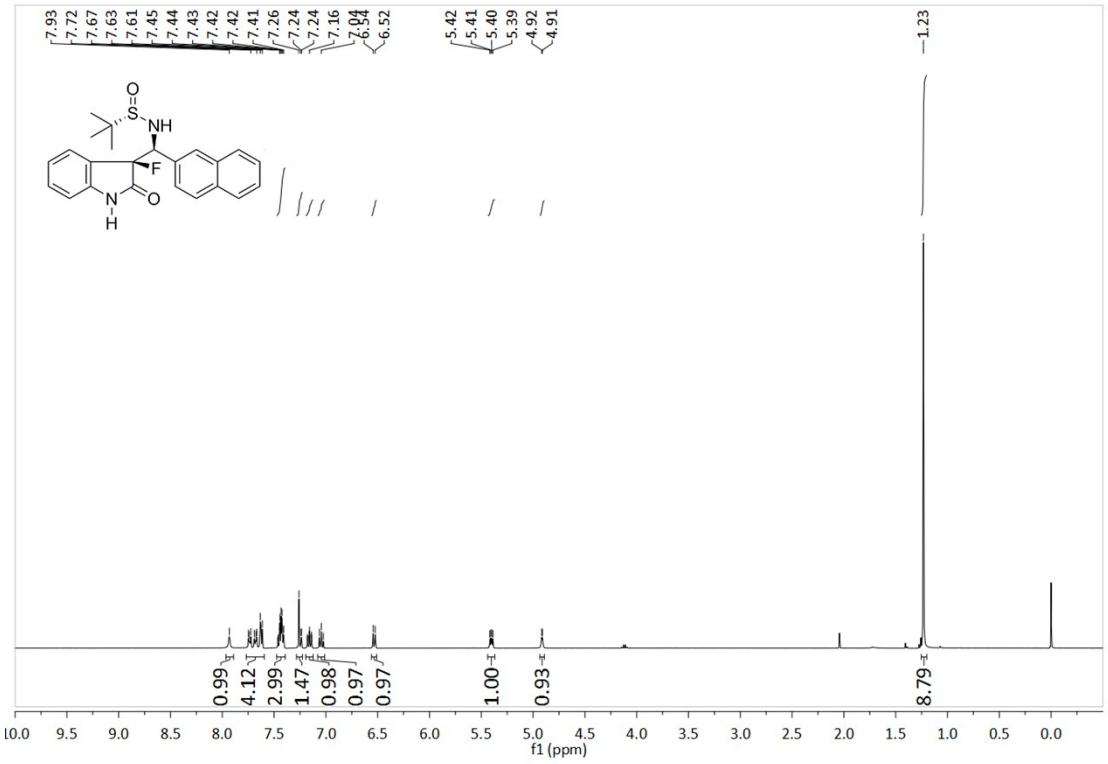
^{19}F NMR spectrum of **11al**



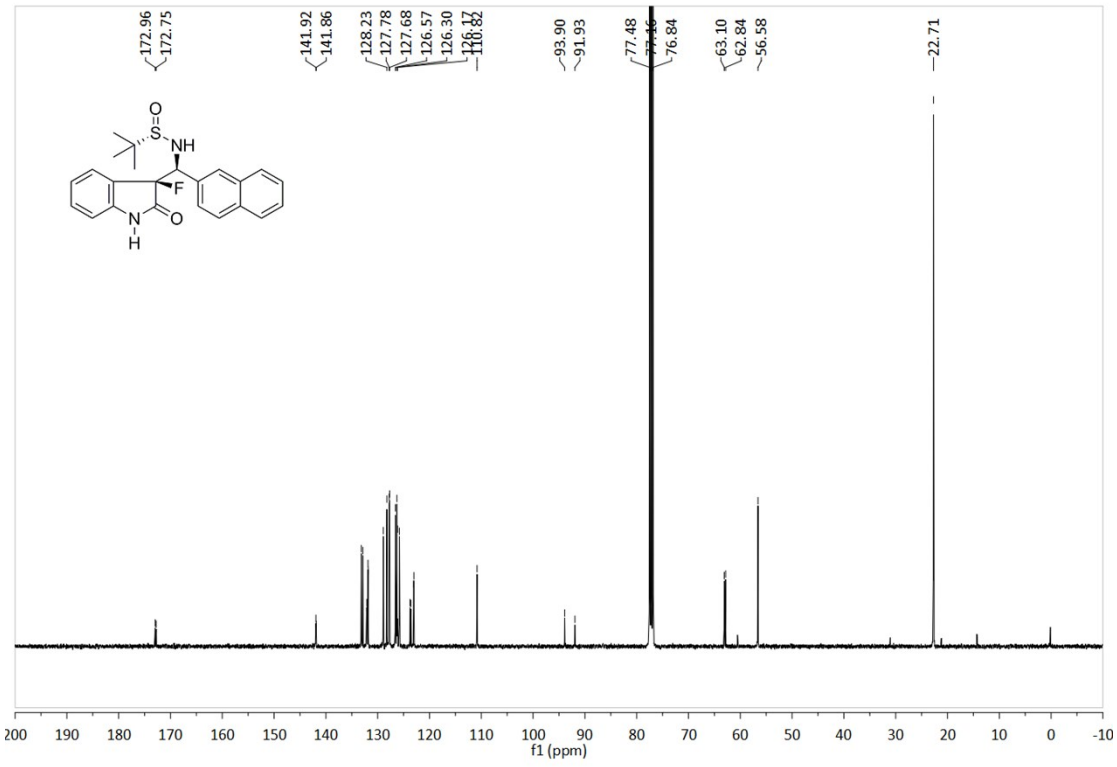
^{19}F NMR spectrum of the crude reaction mixture



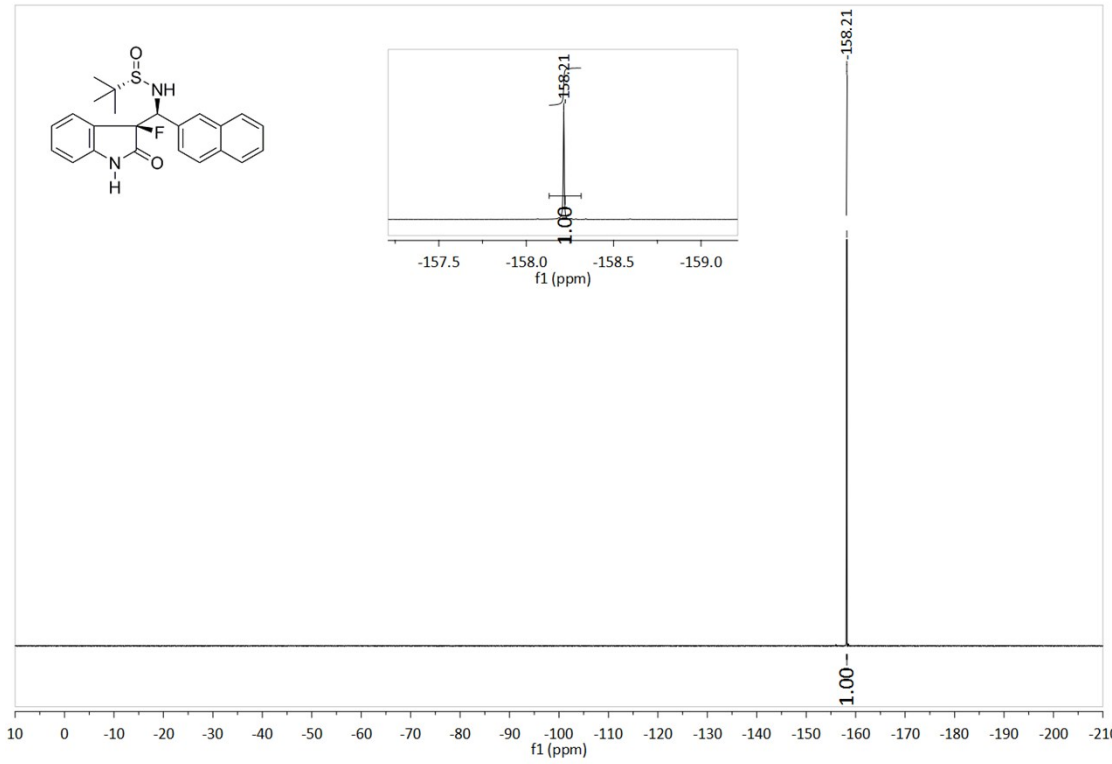
^{1}H NMR spectrum of **11am**



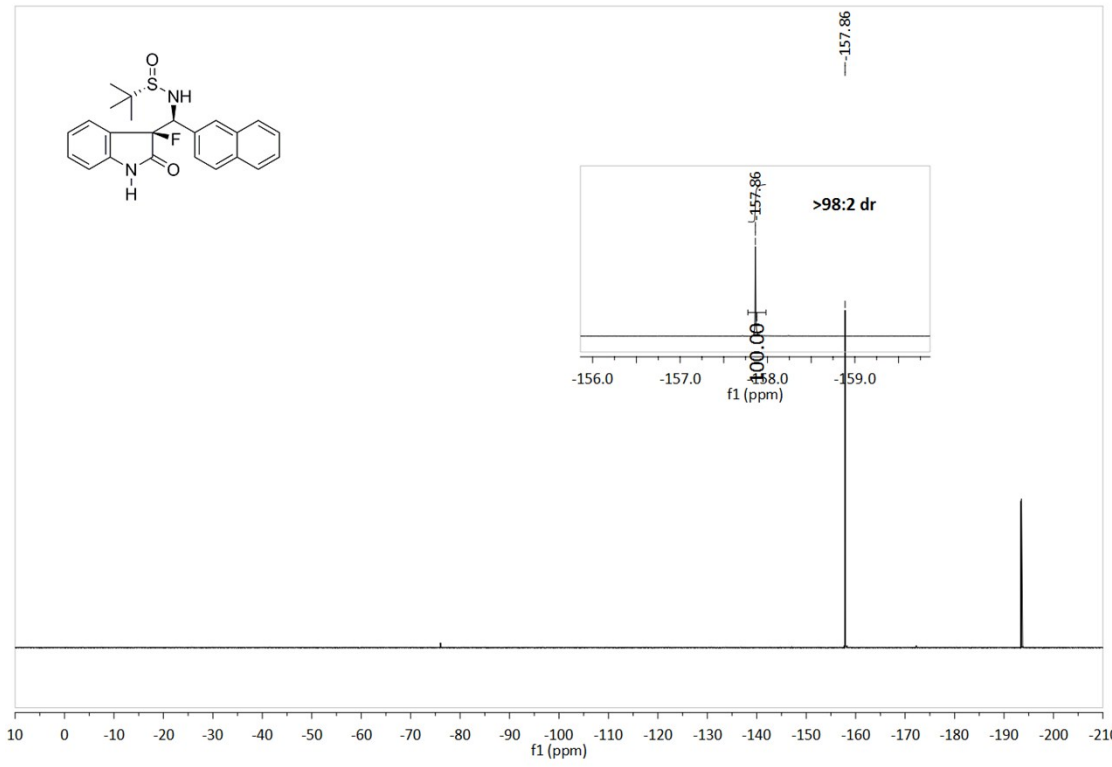
^{13}C NMR spectrum of **11am**



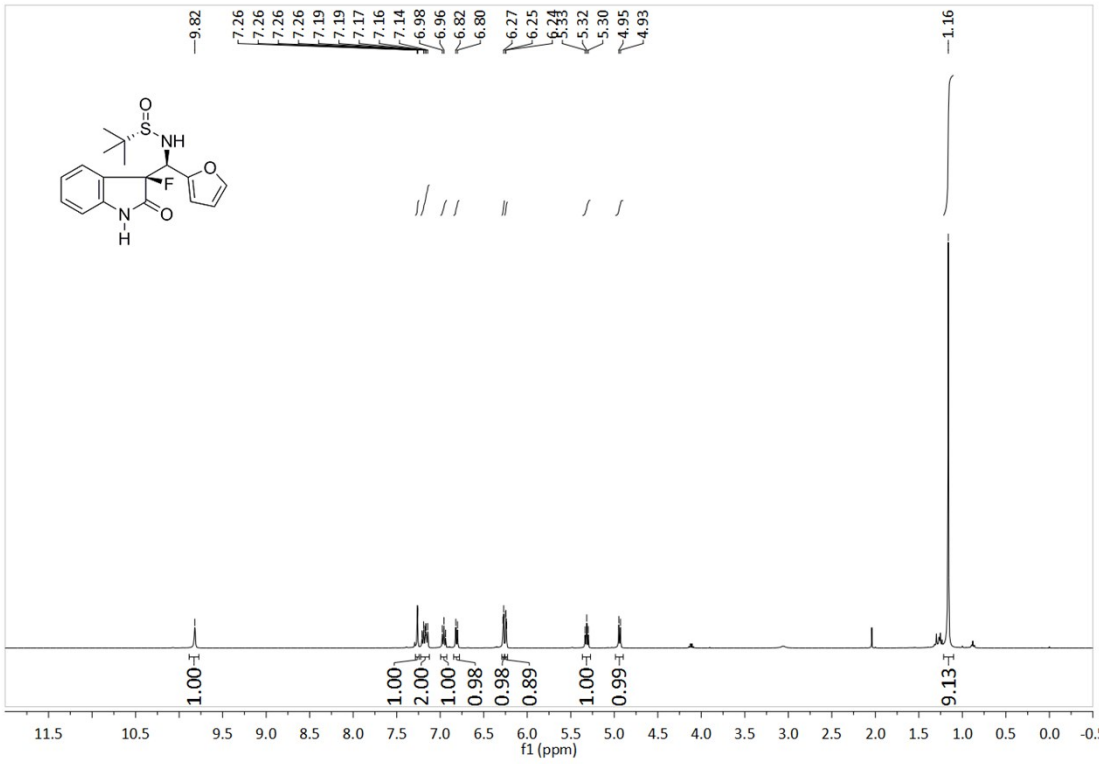
^{19}F NMR spectrum of **11am**



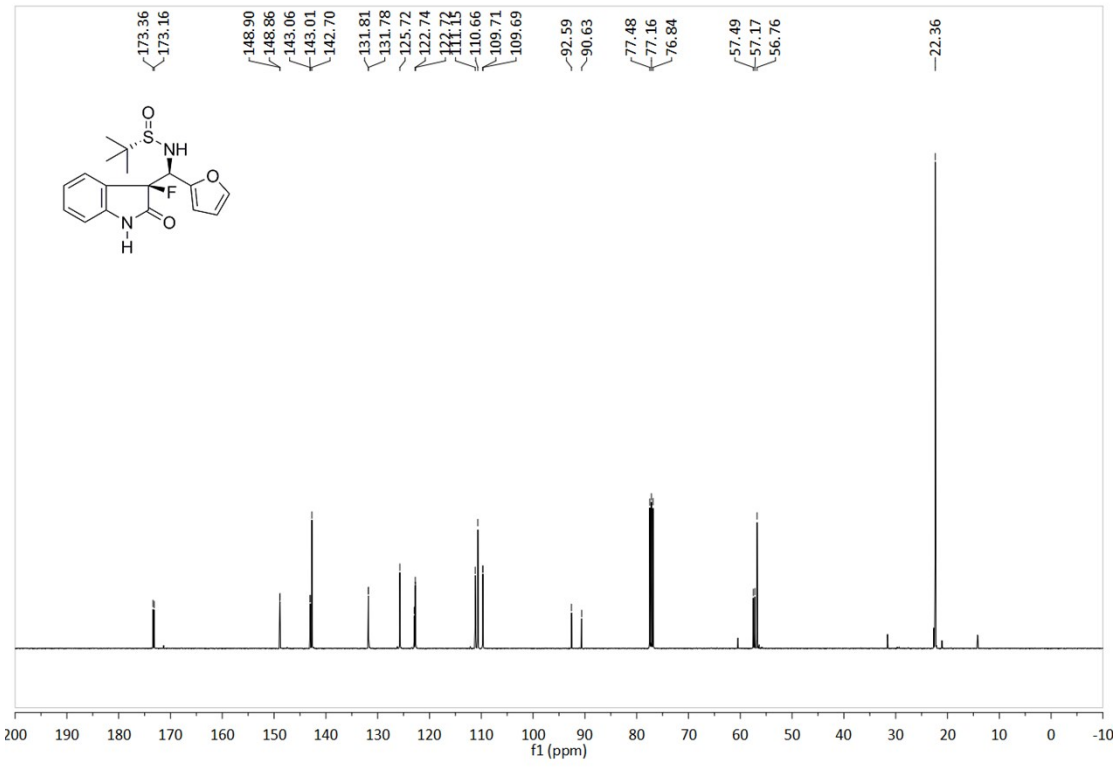
^{19}F NMR spectrum of the crude reaction mixture



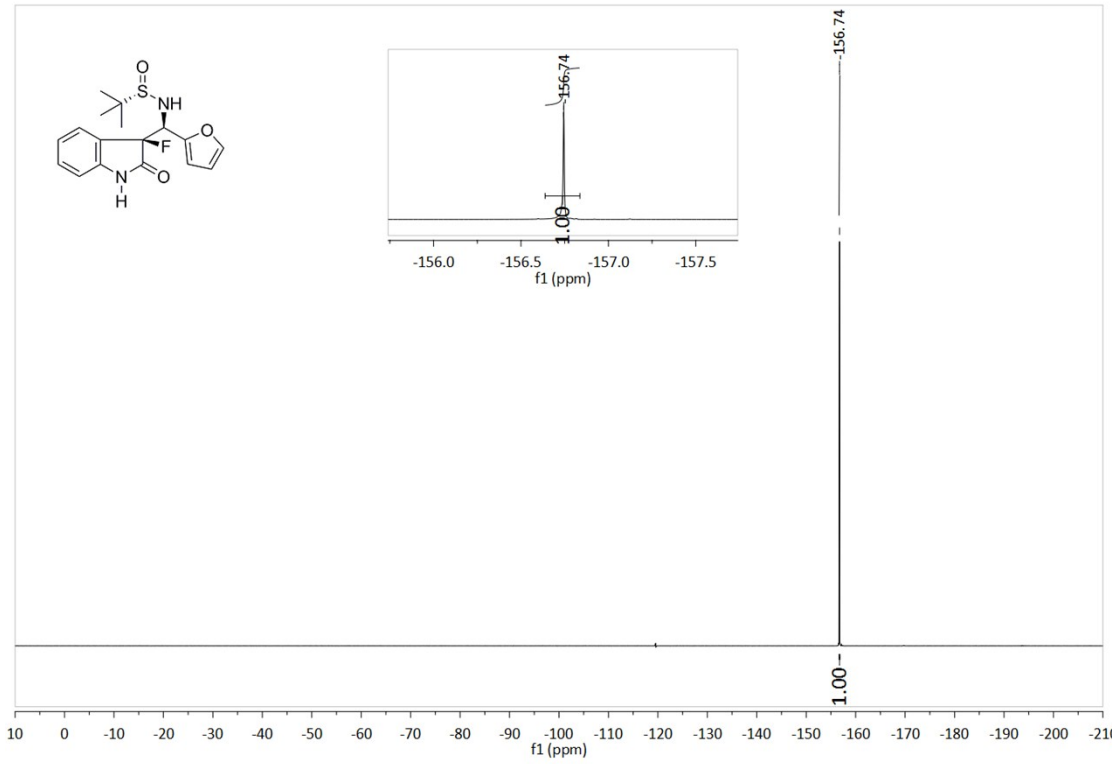
^{1}H NMR spectrum of **11an**



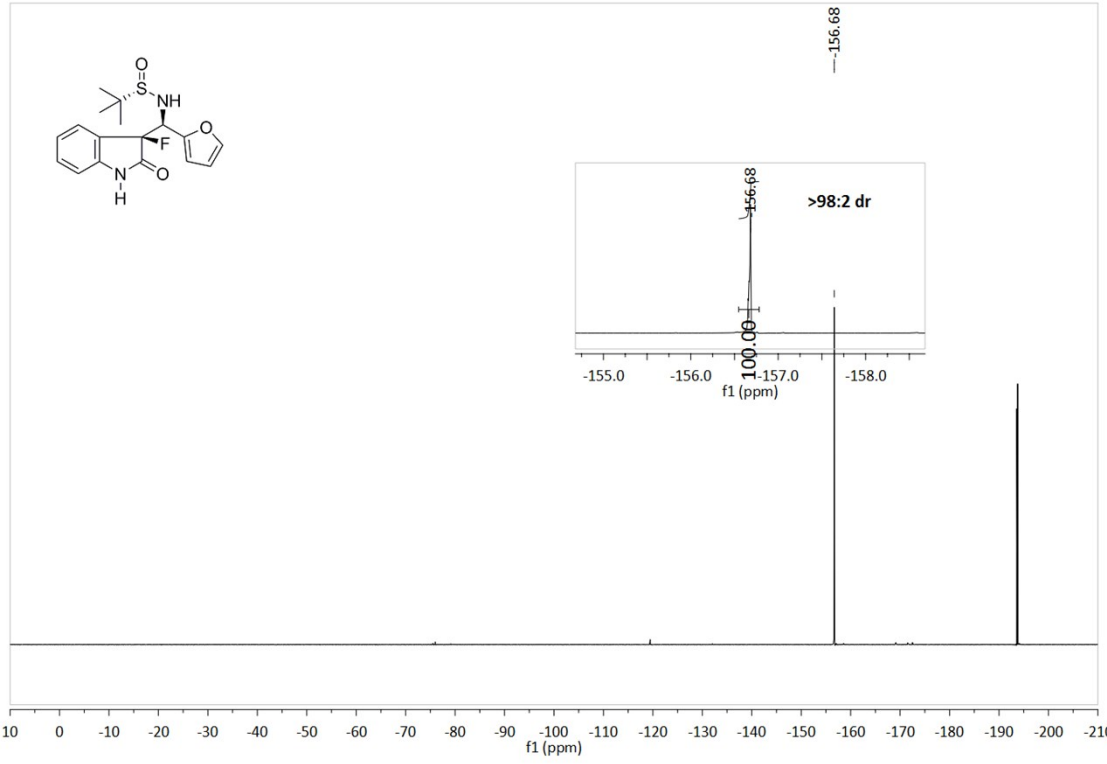
^{13}C NMR spectrum of **11an**



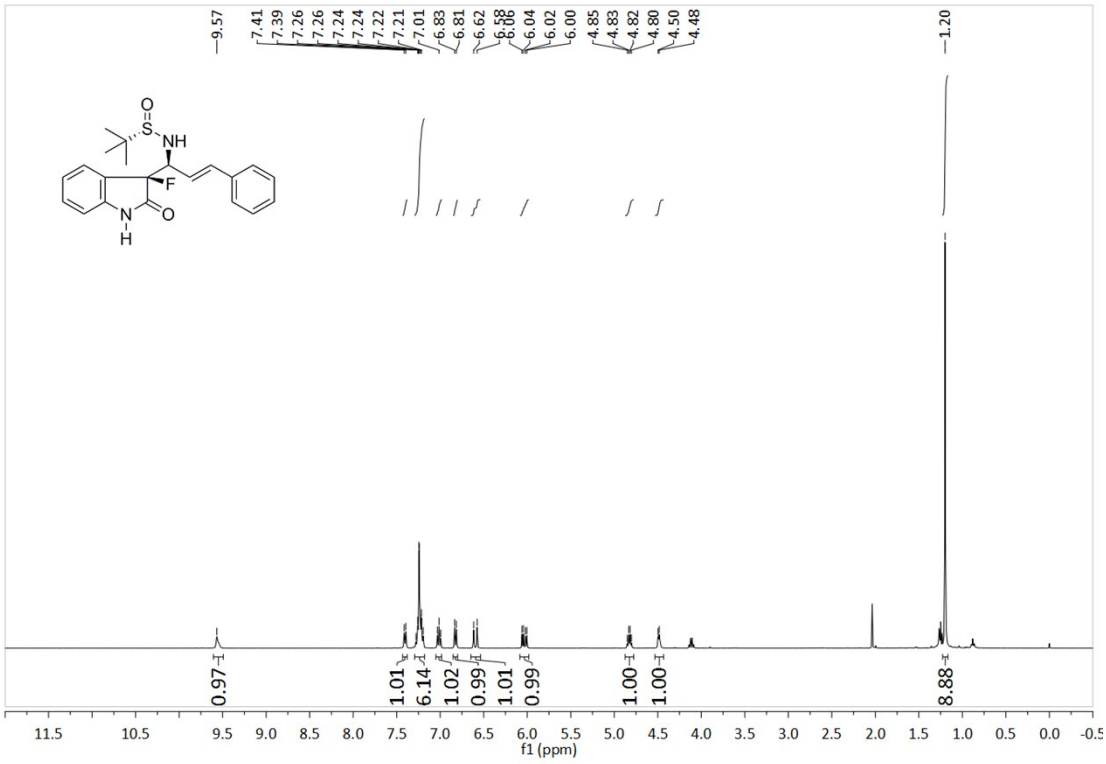
^{19}F NMR spectrum of **11an**



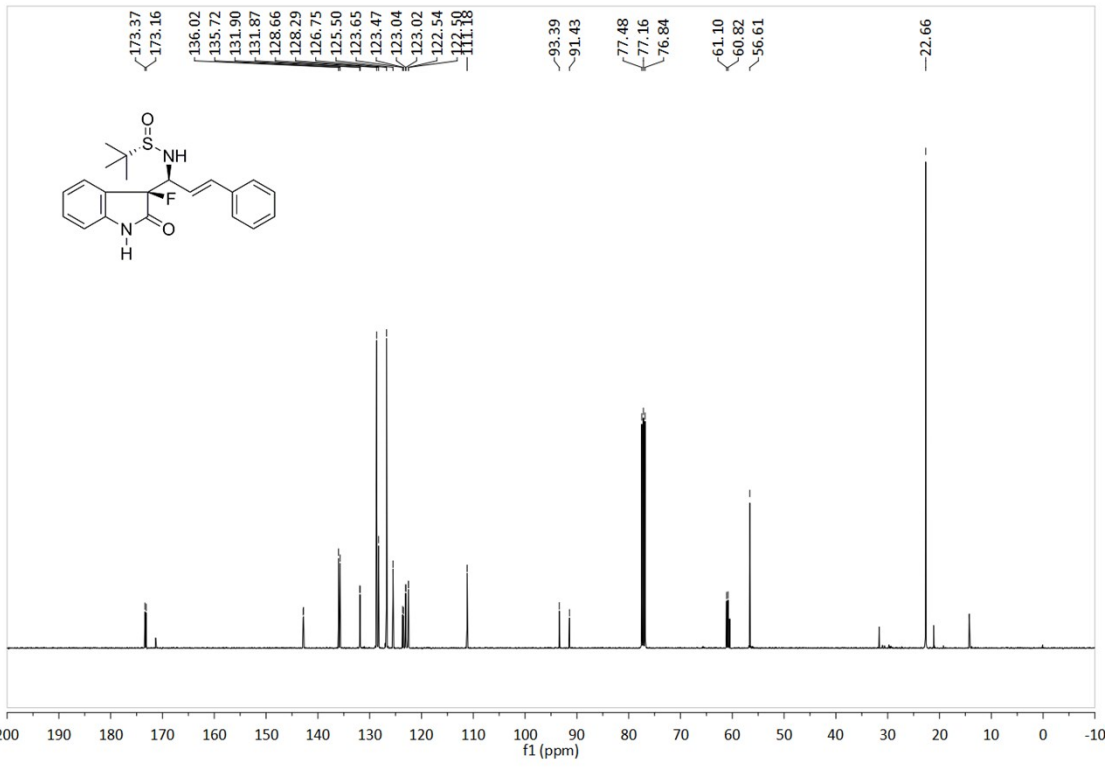
^{19}F NMR spectrum of the crude reaction mixture



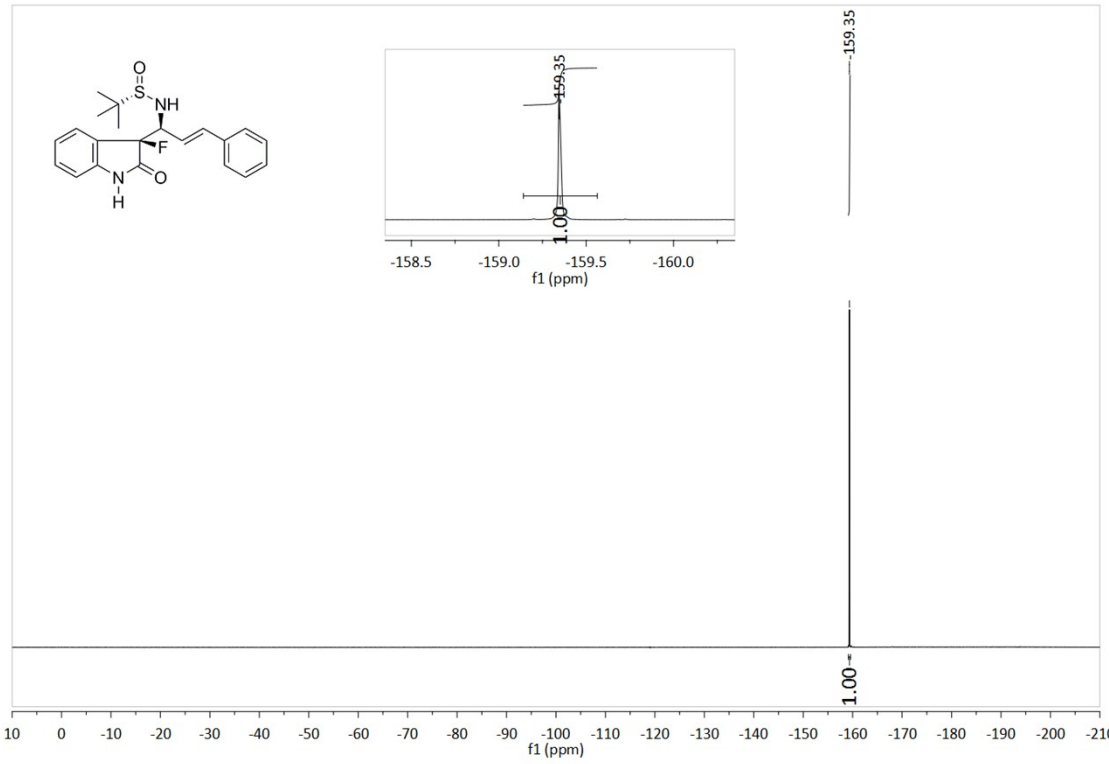
^{1}H NMR spectrum of **11ao**



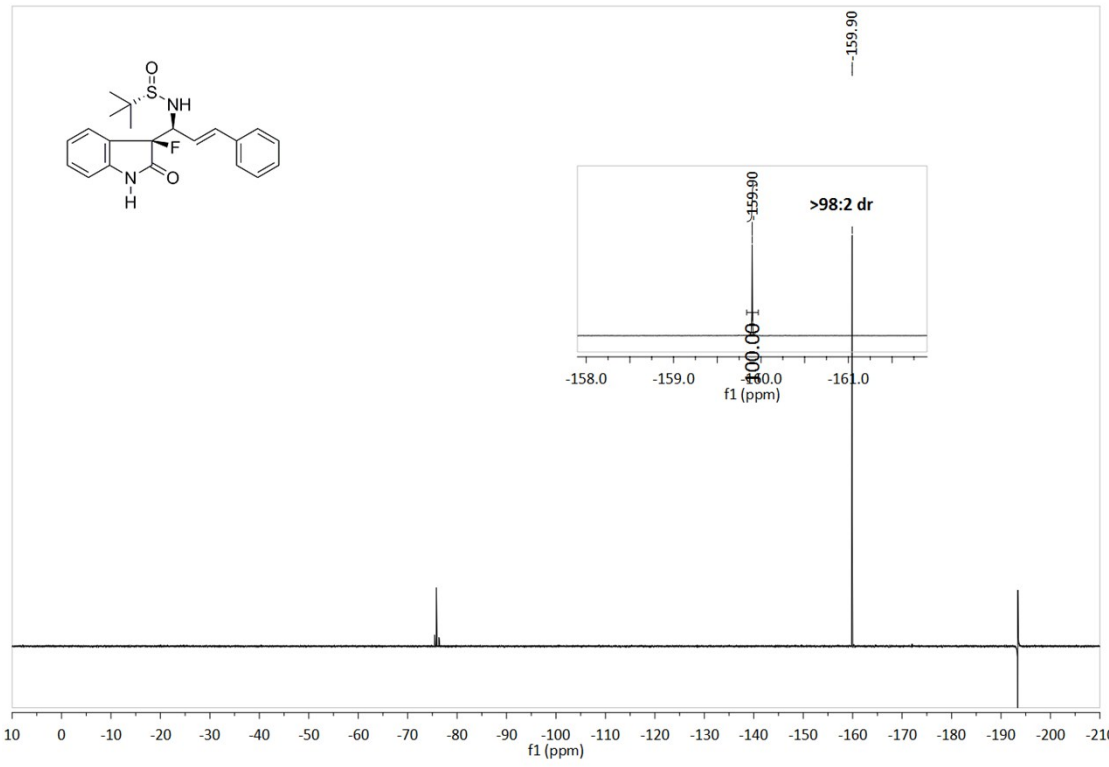
^{13}C NMR spectrum of **11ao**



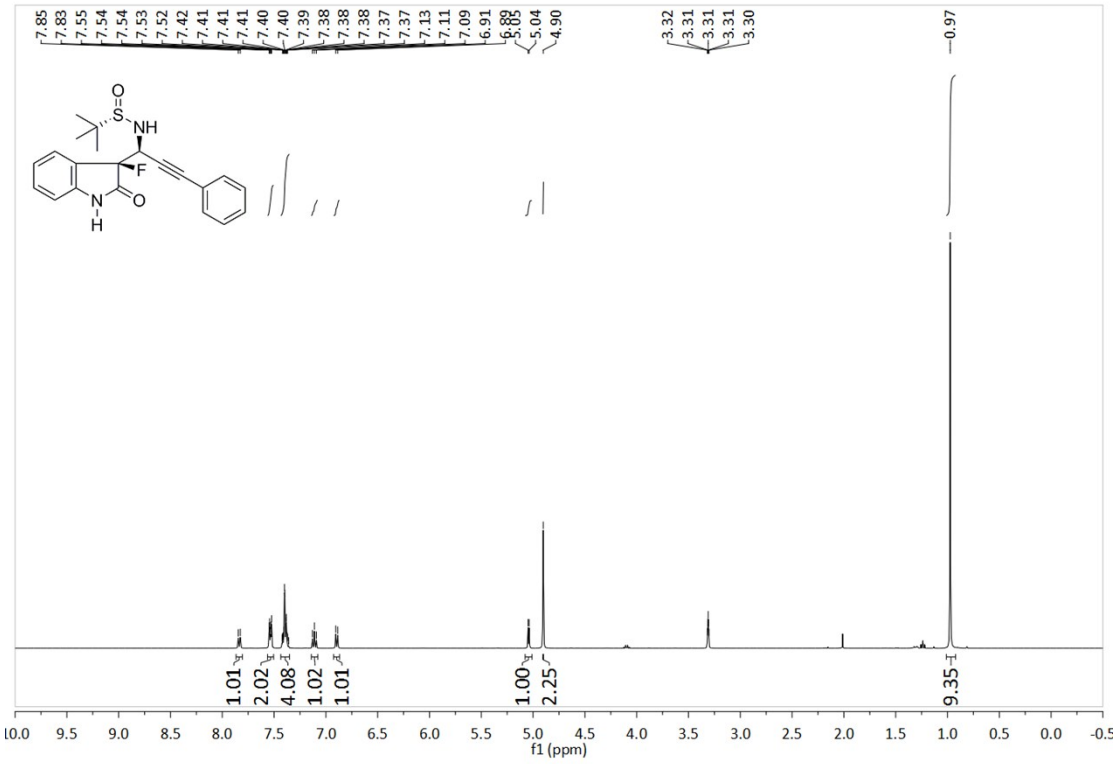
^{19}F NMR spectrum of **11ao**



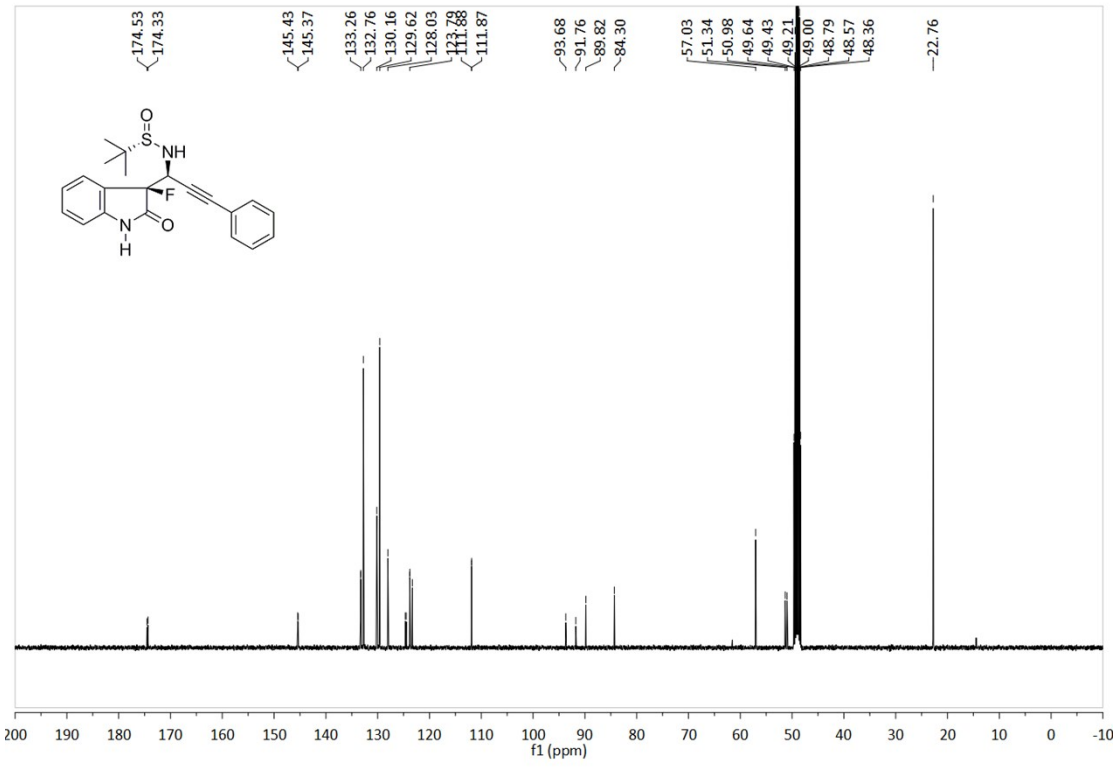
^{19}F NMR spectrum of the crude reaction mixture



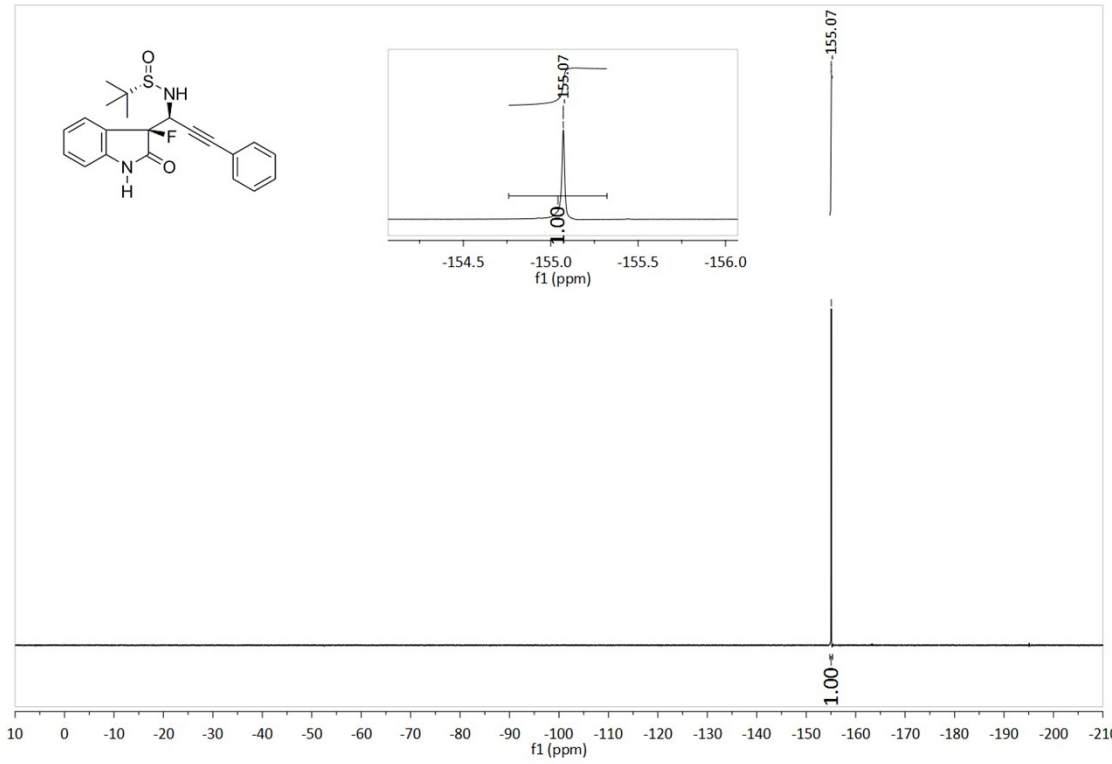
^{1}H NMR spectrum of **11ap**



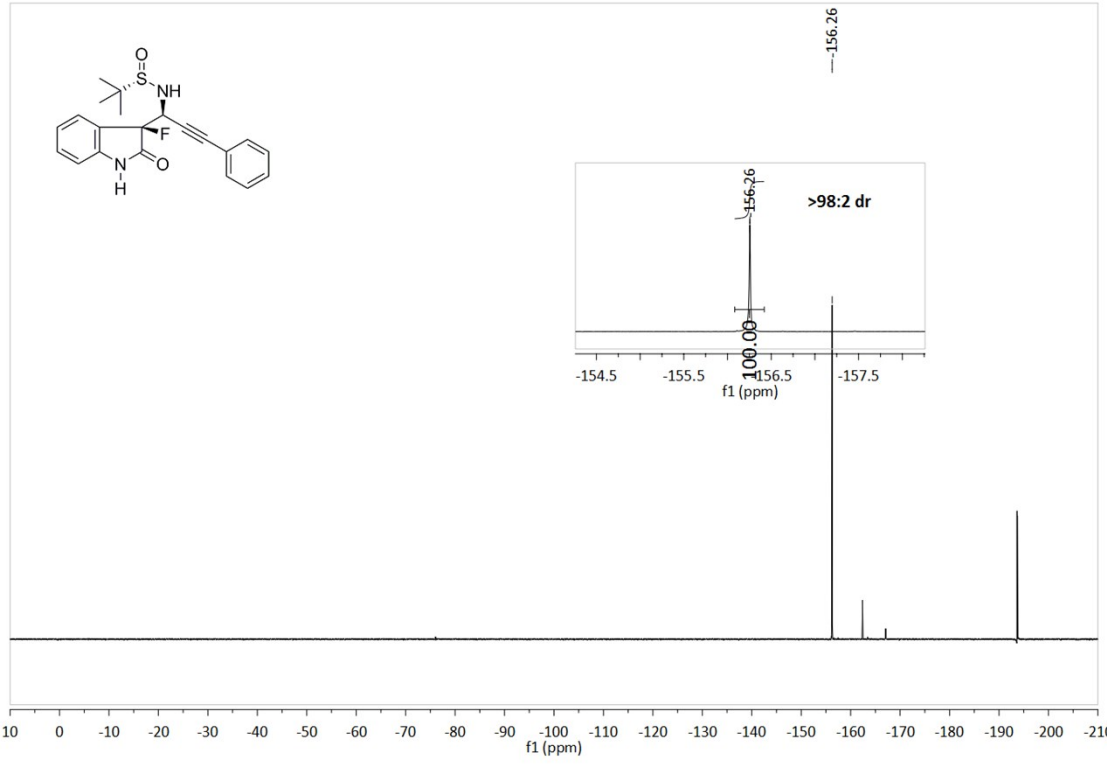
^{13}C NMR spectrum of **11ap**



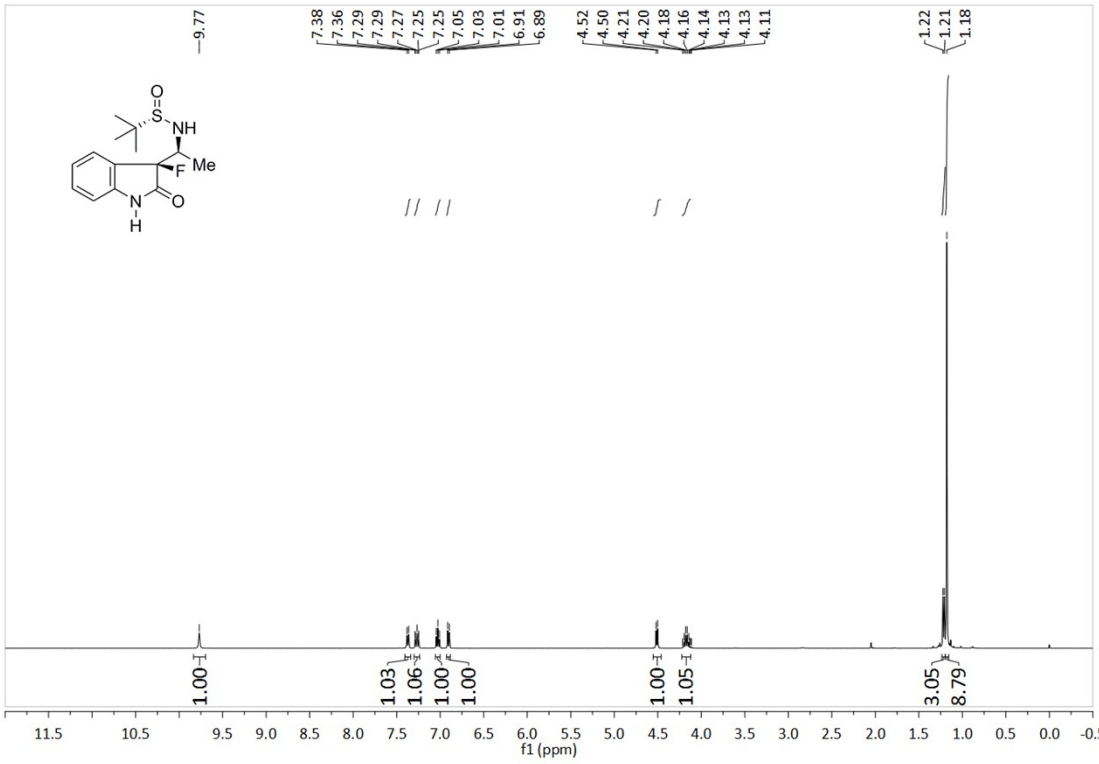
^{19}F NMR spectrum of **11ap**



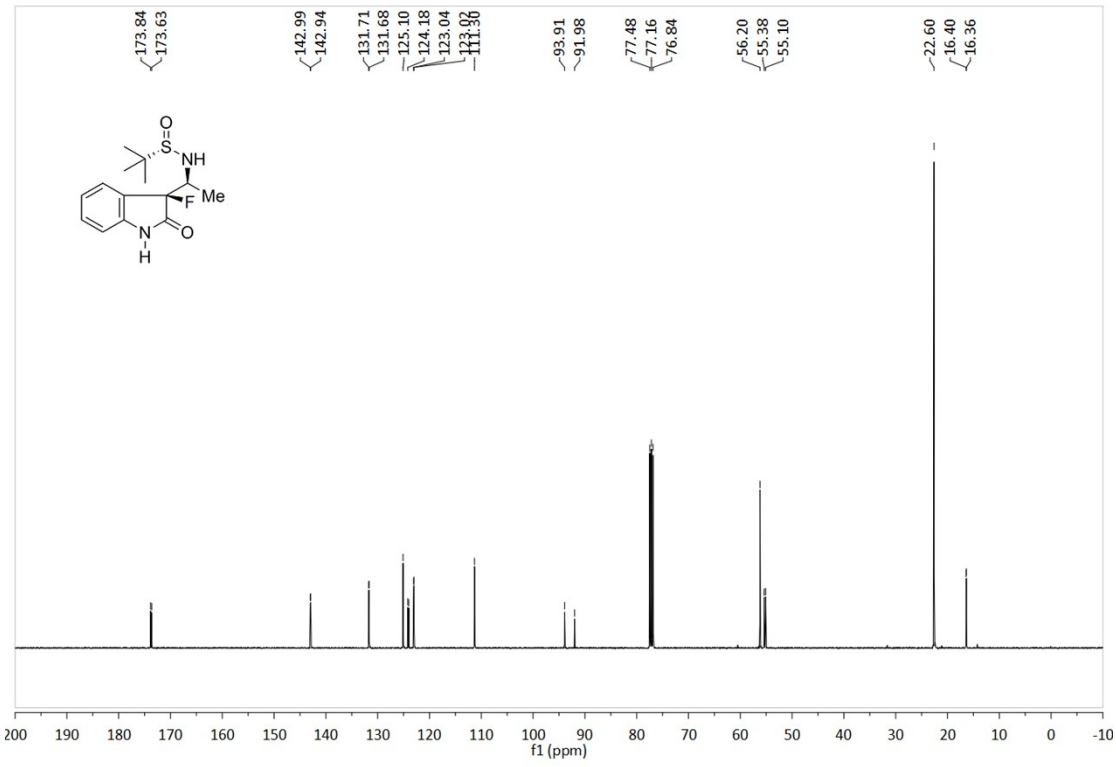
^{19}F NMR spectrum of the crude reaction mixture



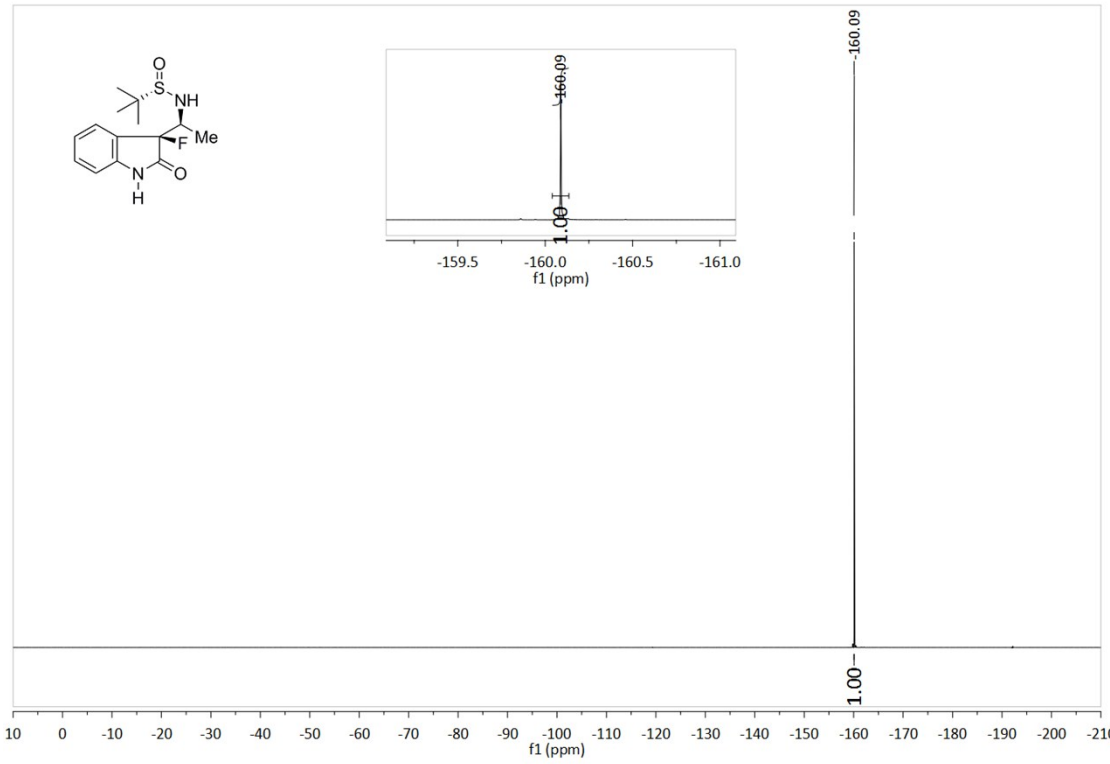
^{1}H NMR spectrum of **11aq**



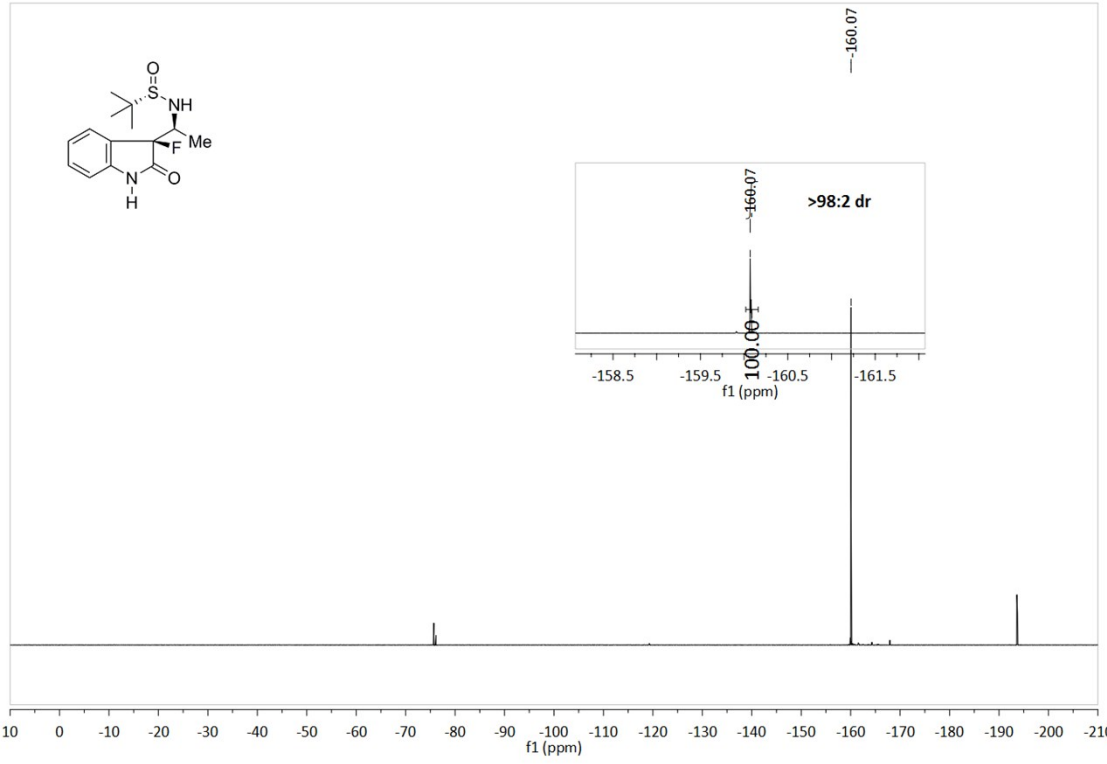
^{13}C NMR spectrum of **11aq**



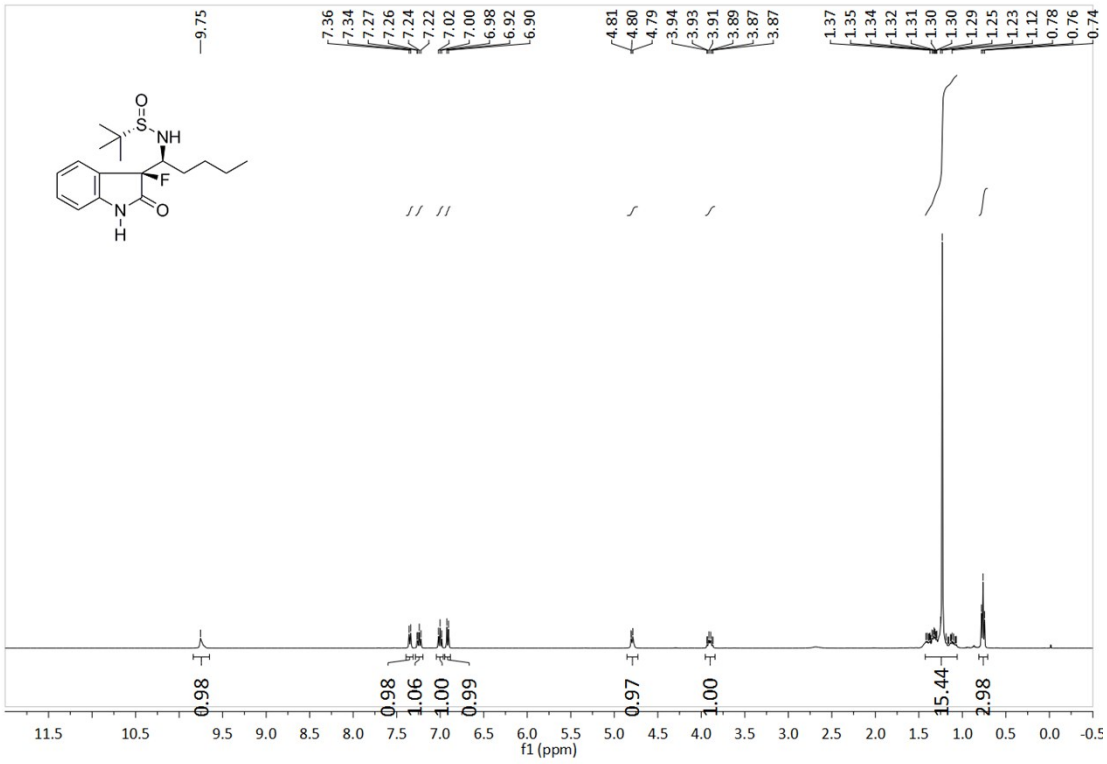
^{19}F NMR spectrum of **11aq**



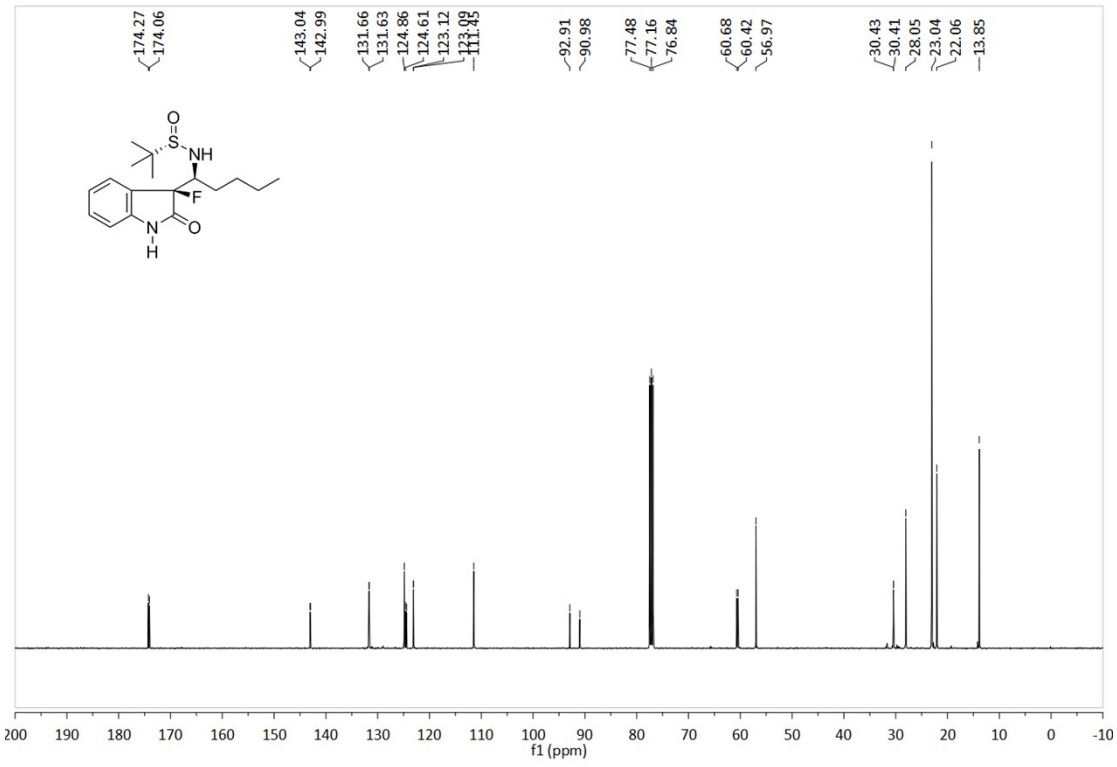
^{19}F NMR spectrum of the crude reaction mixture



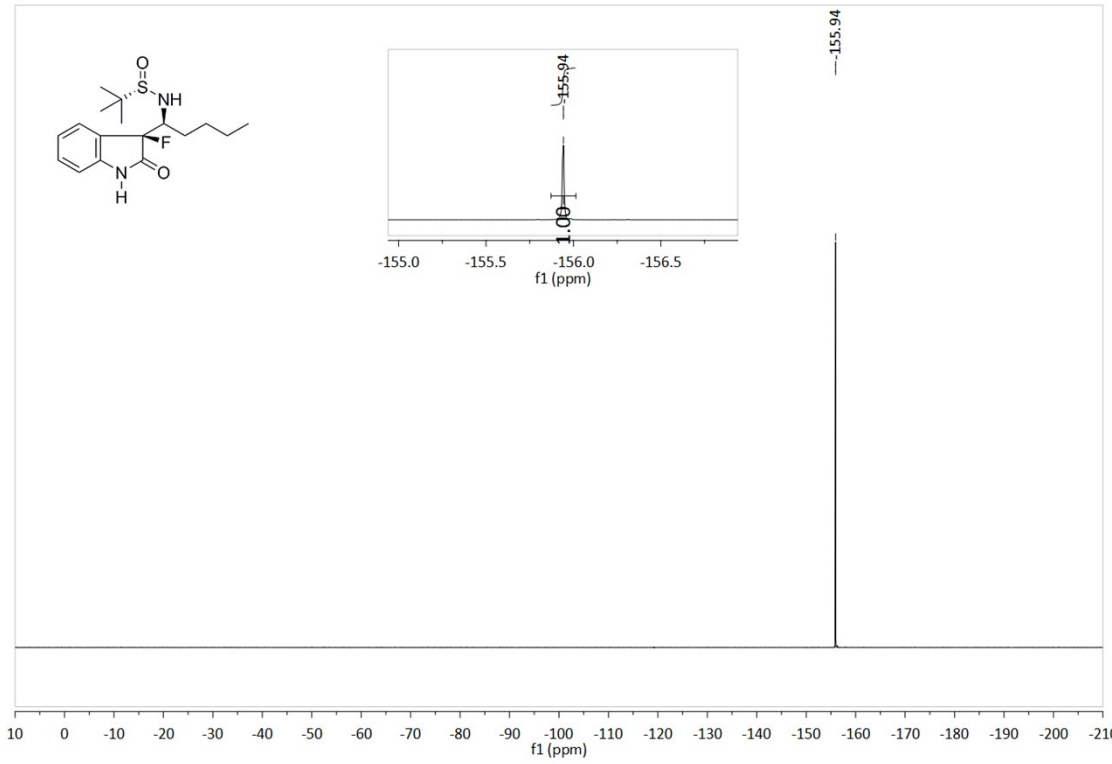
^{1}H NMR spectrum of **11ar**



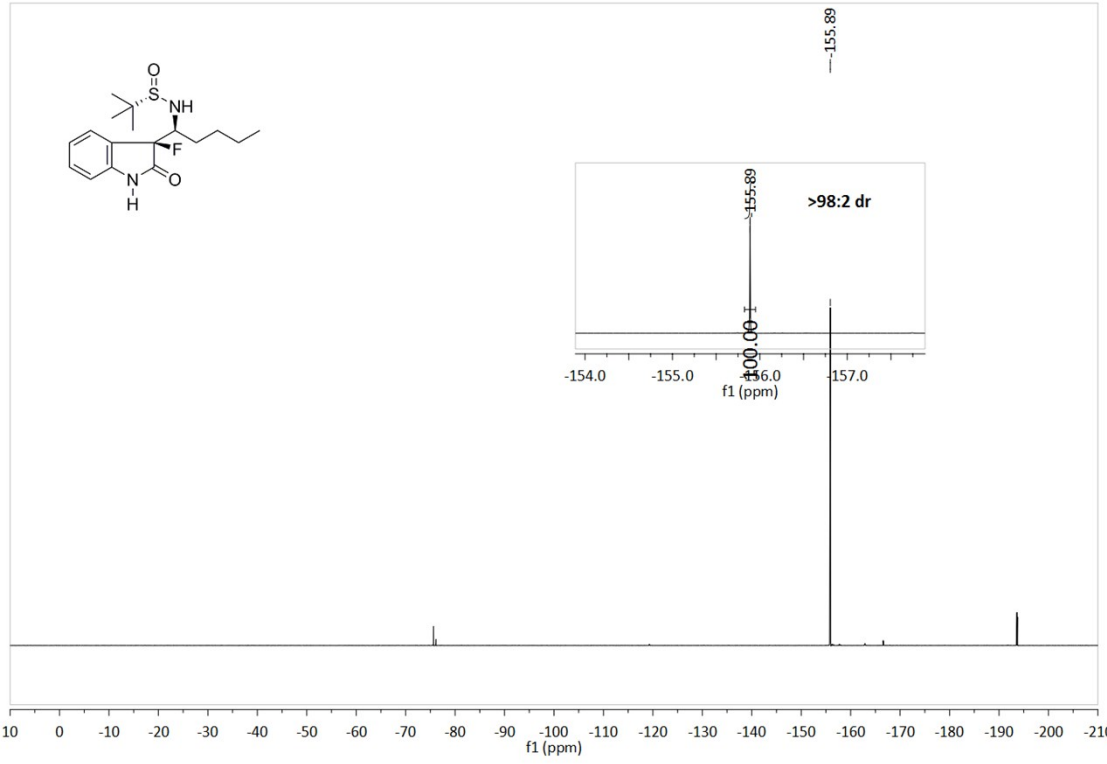
^{13}C NMR spectrum of **11ar**



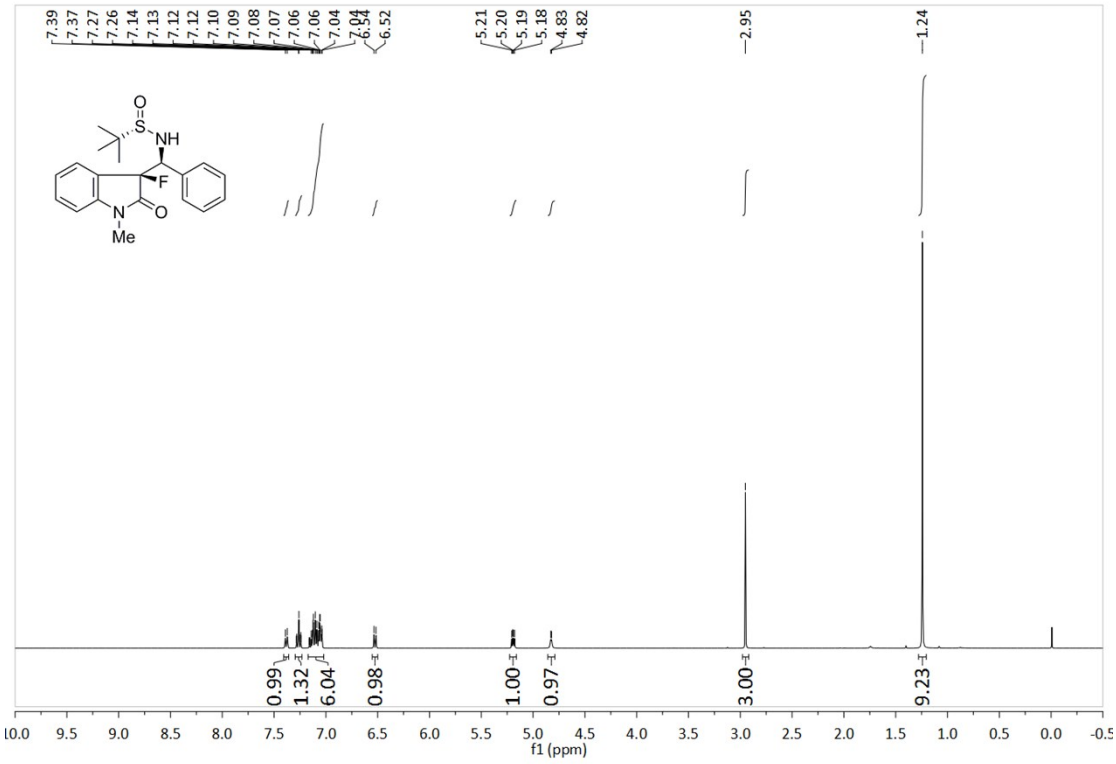
^{19}F NMR spectrum of **11ar**



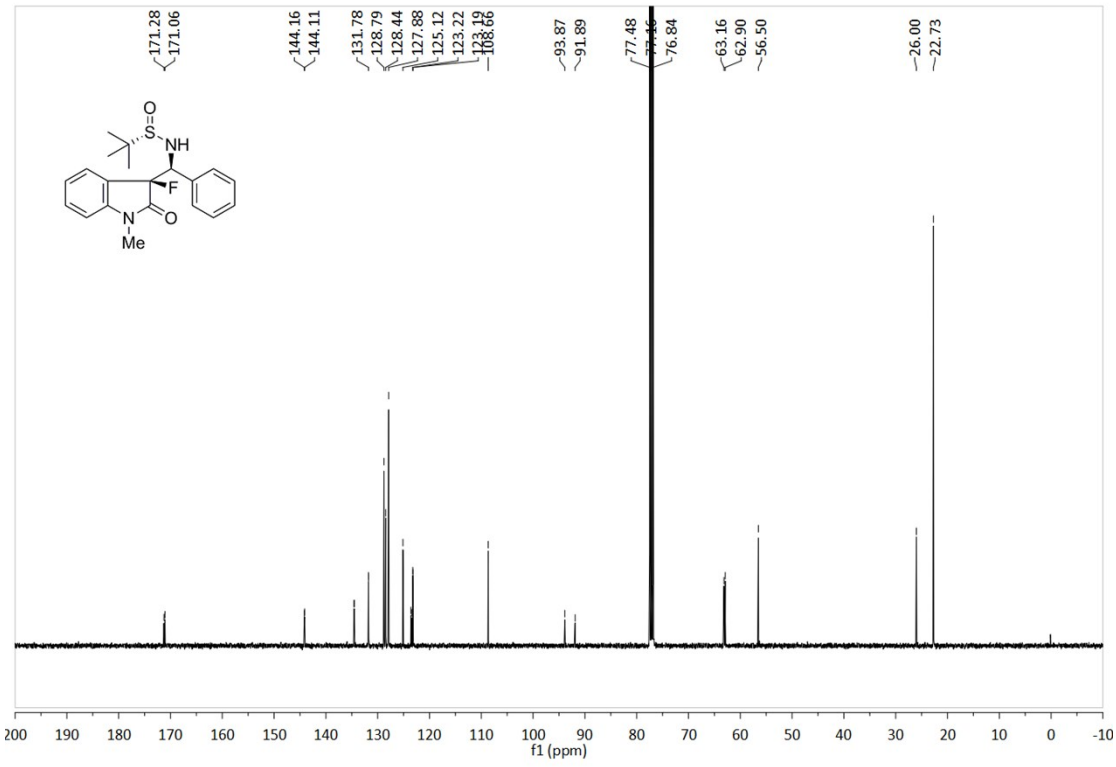
^{19}F NMR spectrum of the crude reaction mixture



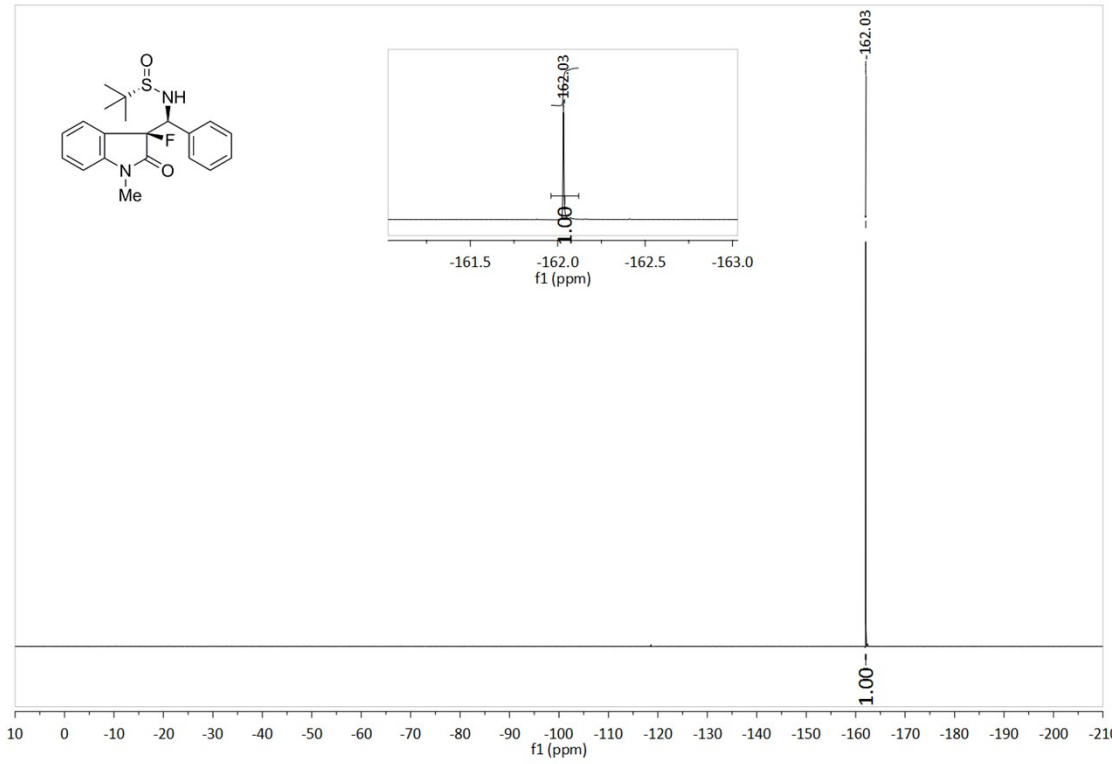
^{1}H NMR spectrum of **11bi**



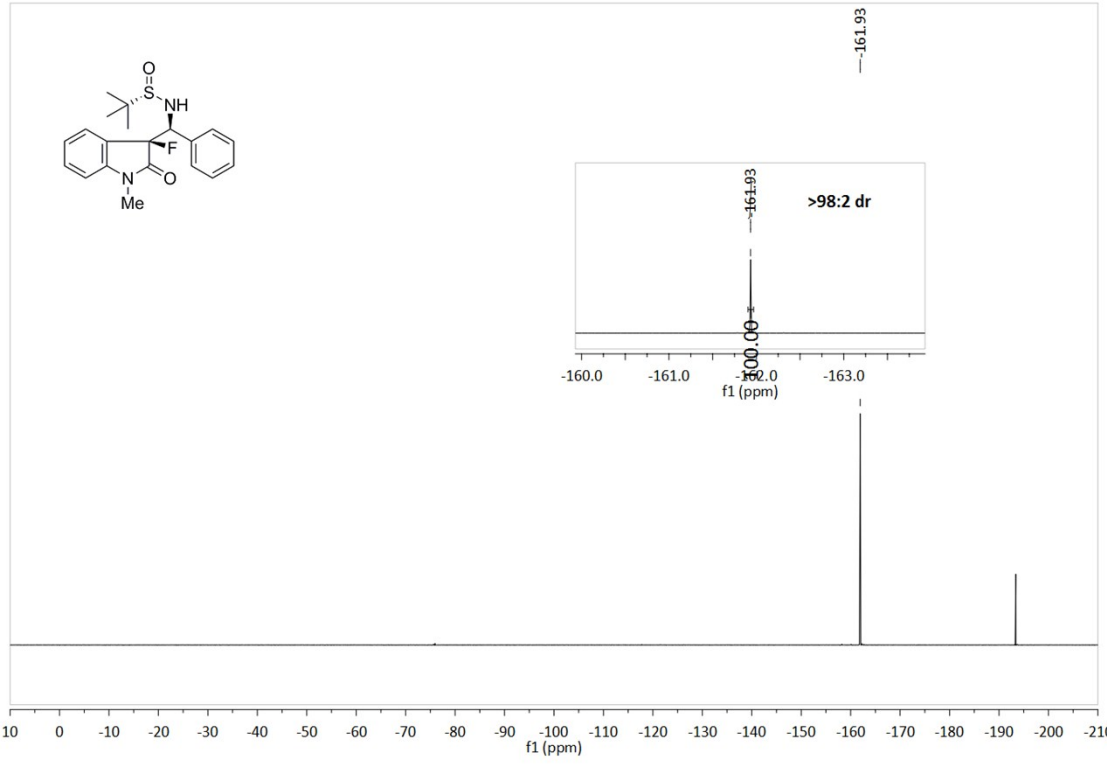
^{13}C NMR spectrum of **11bi**



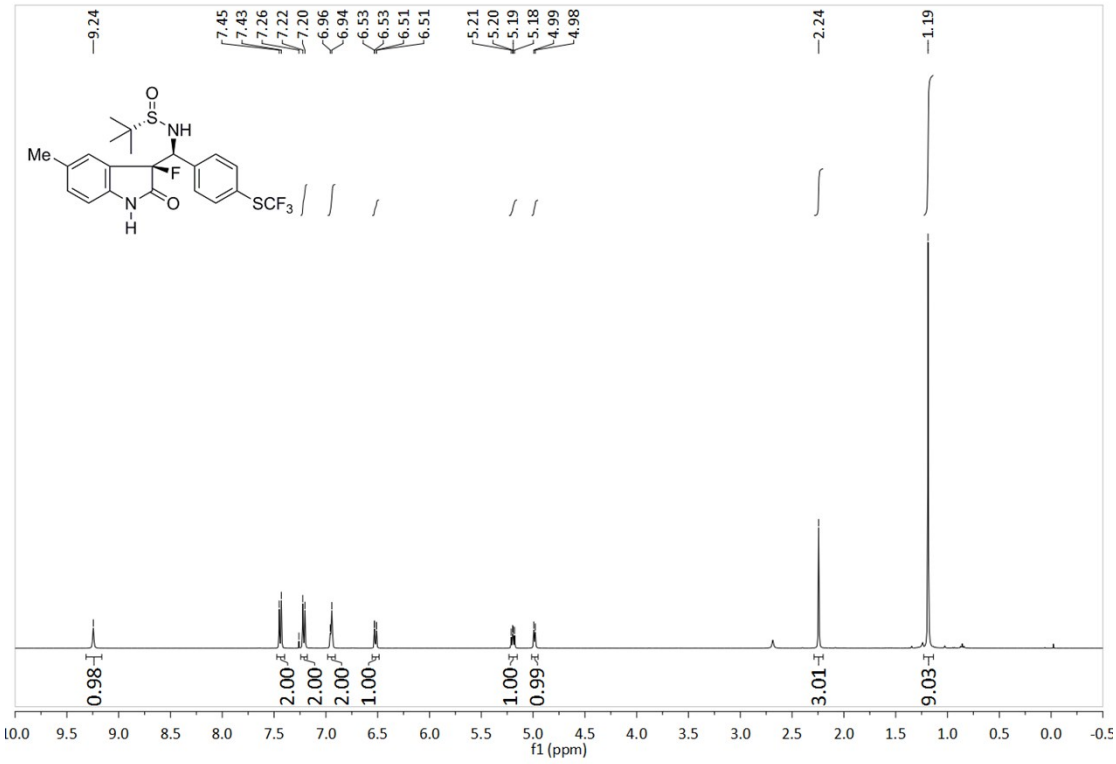
^{19}F NMR spectrum of **11bi**



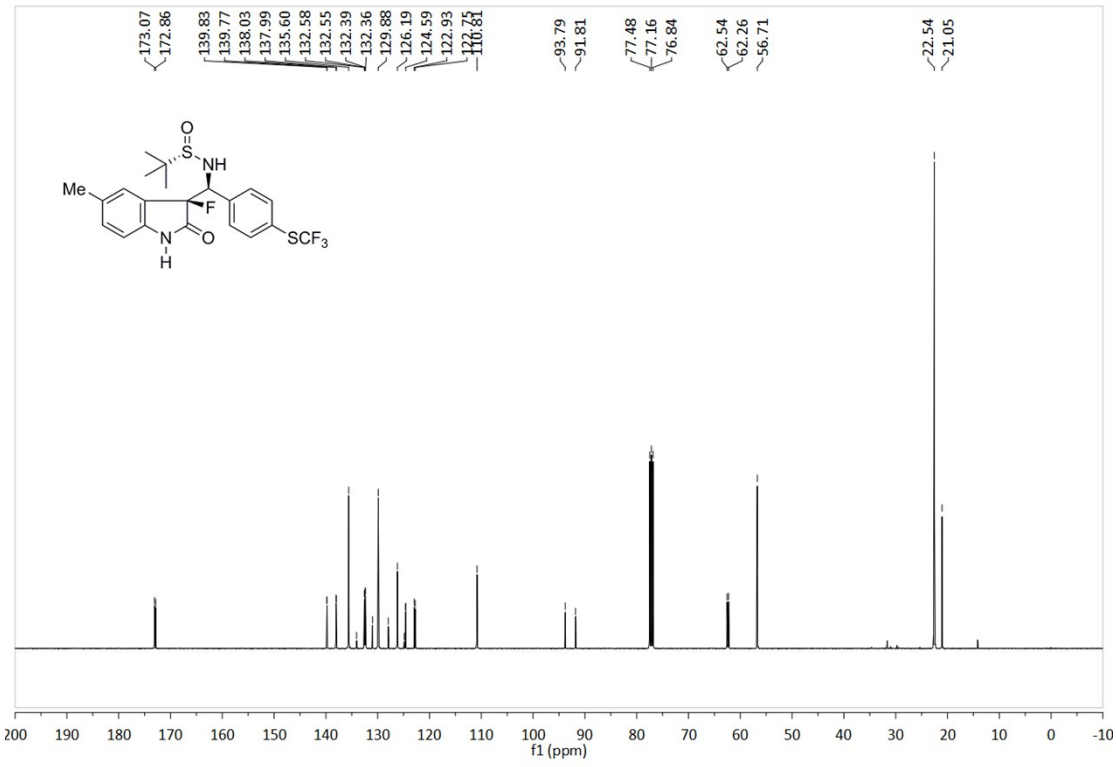
^{19}F NMR spectrum of the crude reaction mixture



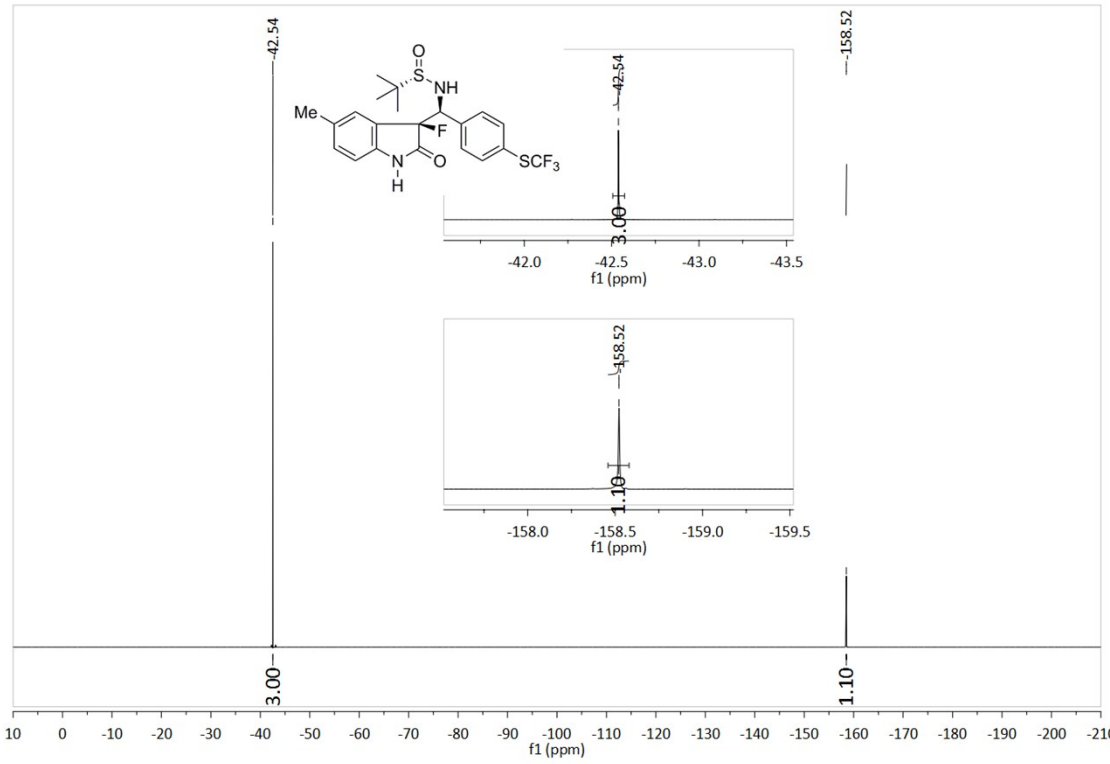
^{1}H NMR spectrum of **13a**



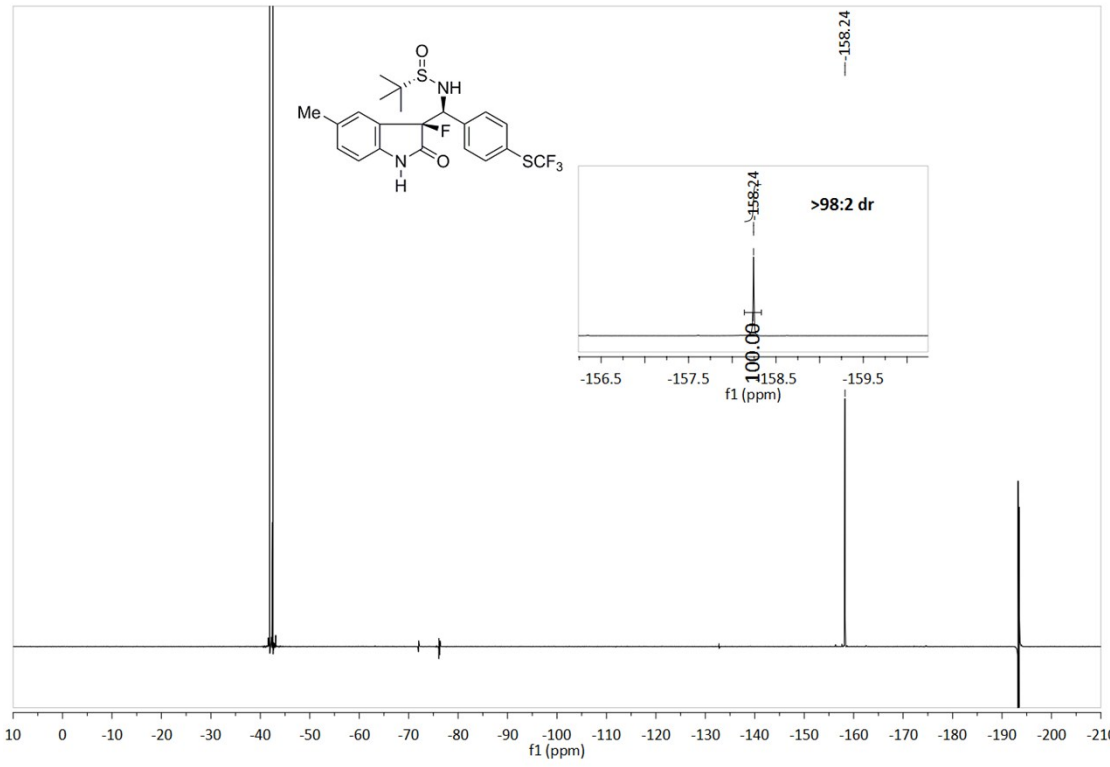
^{13}C NMR spectrum of **13a**



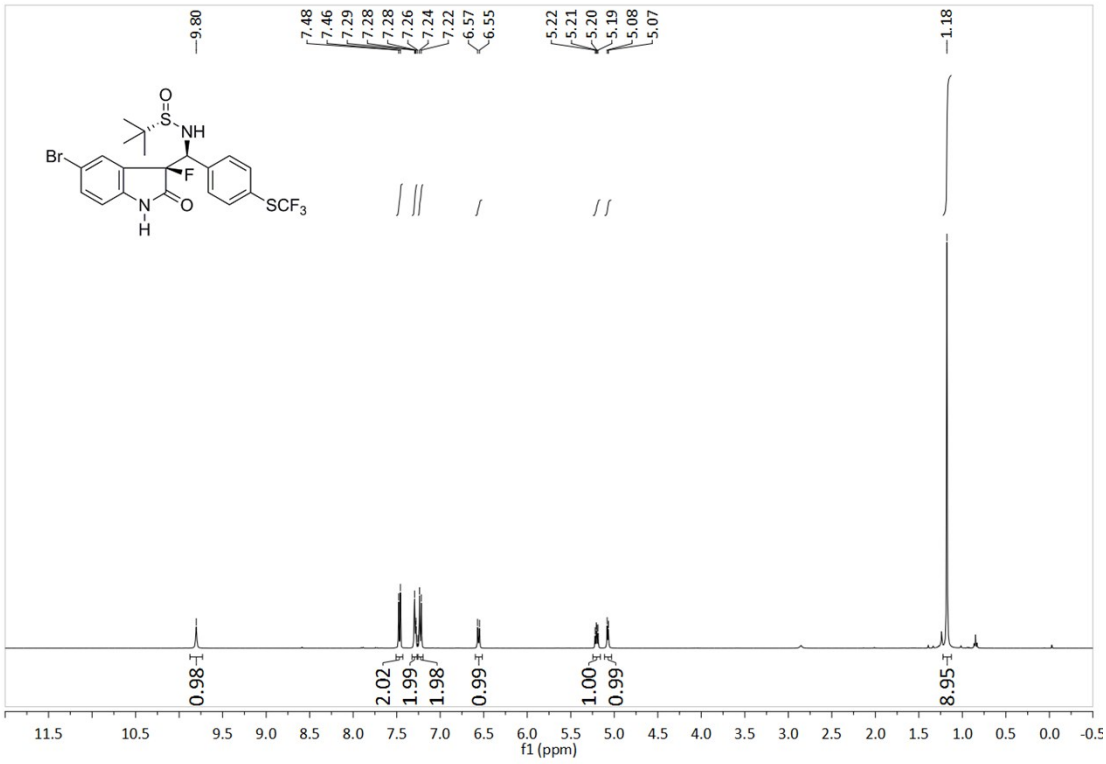
^{19}F NMR spectrum of **13a**



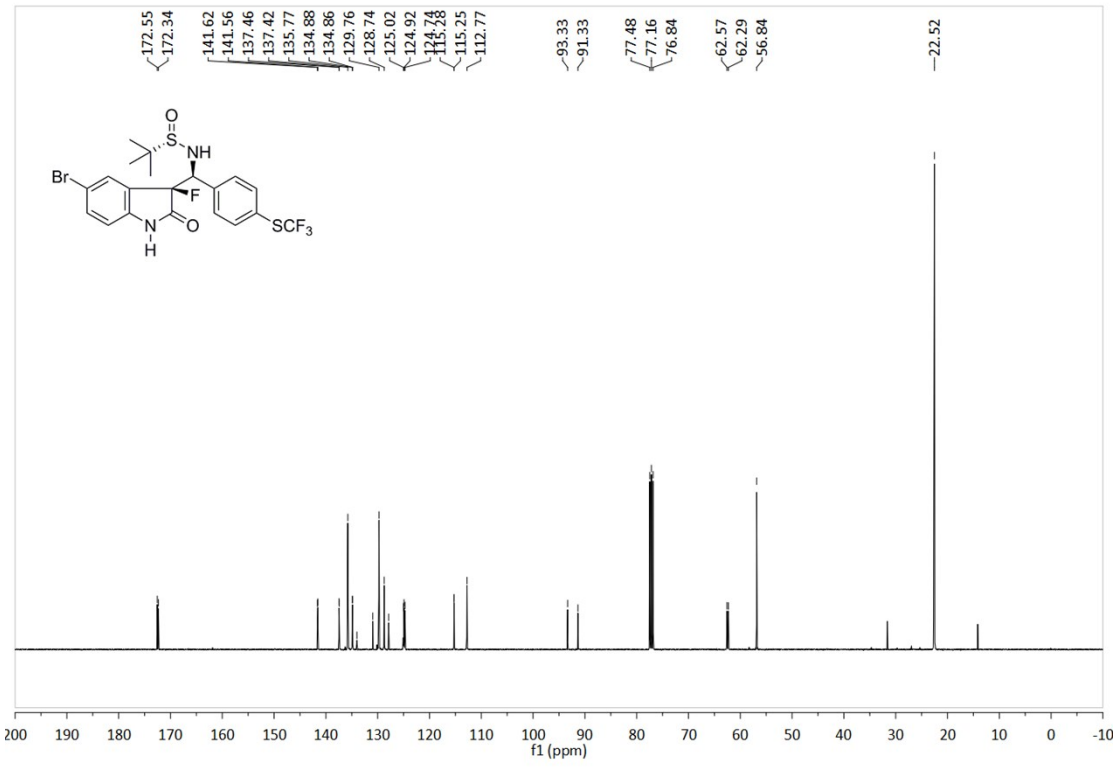
^{19}F NMR spectrum of the crude reaction mixture



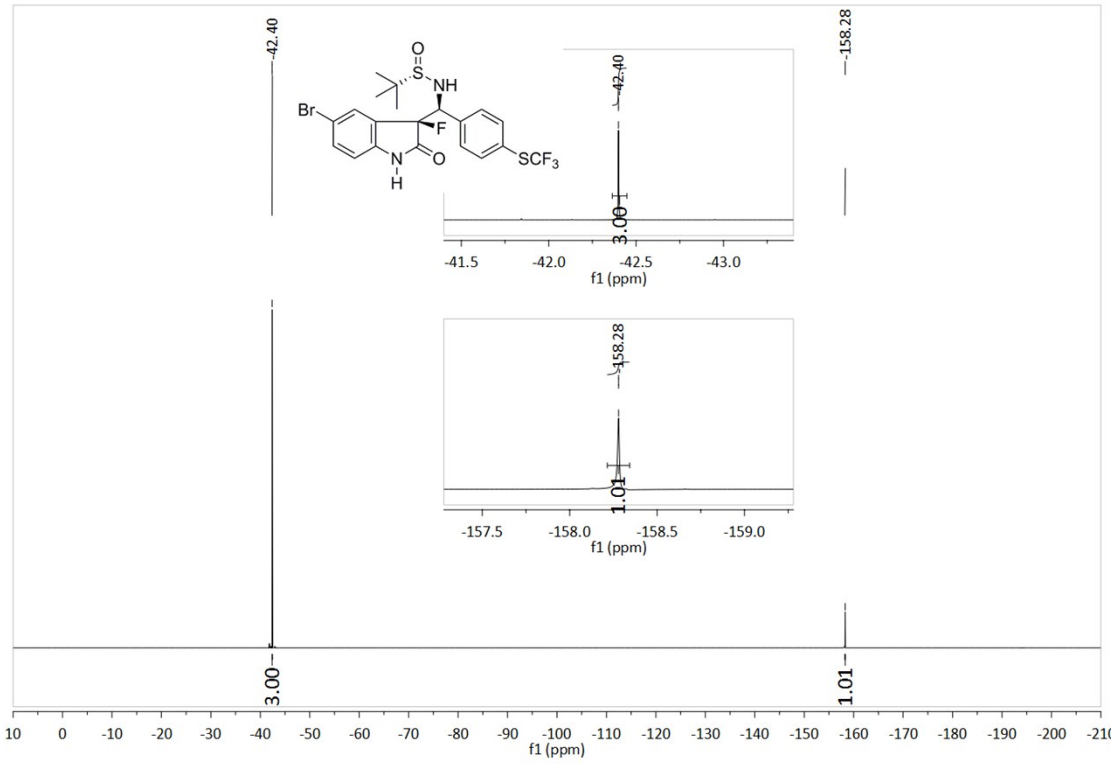
^{1}H NMR spectrum of **13b**



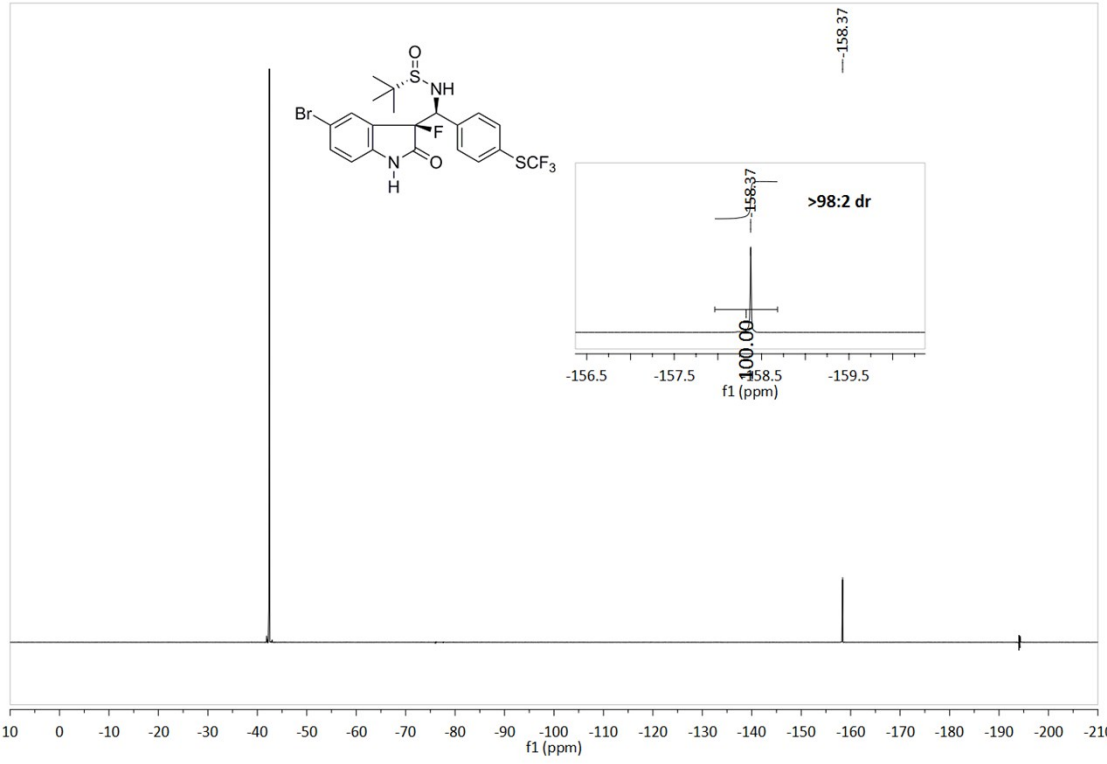
^{13}C NMR spectrum of **13b**



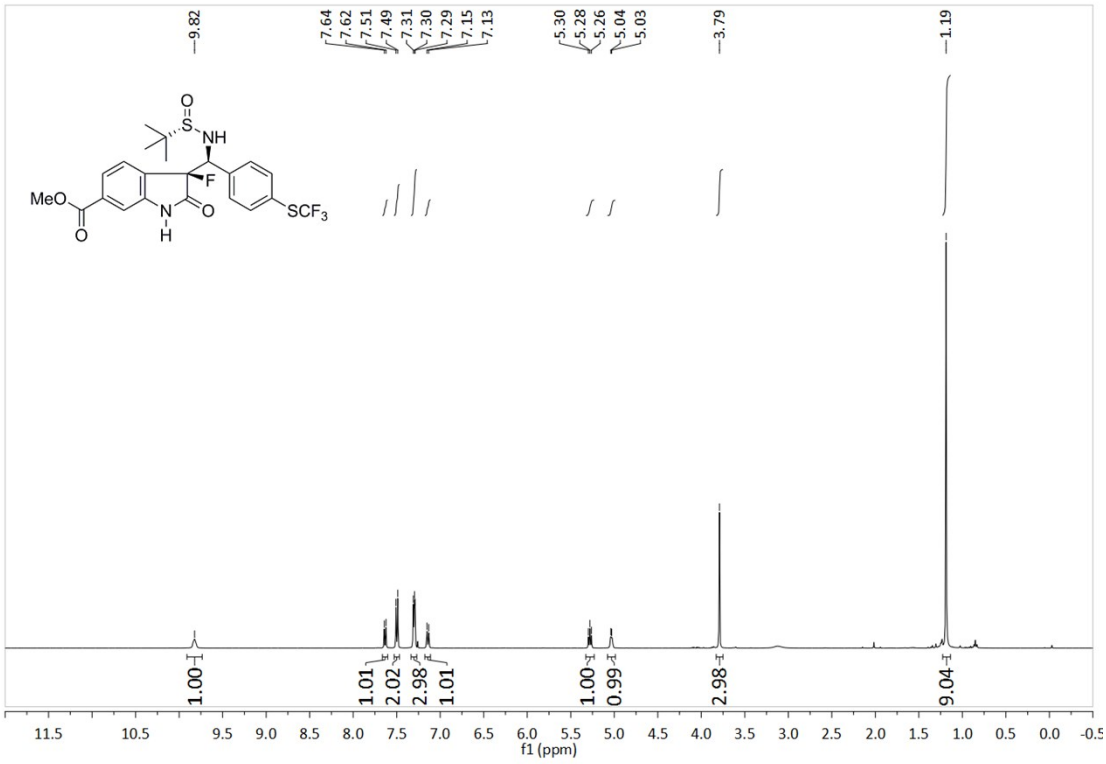
^{19}F NMR spectrum of **13b**



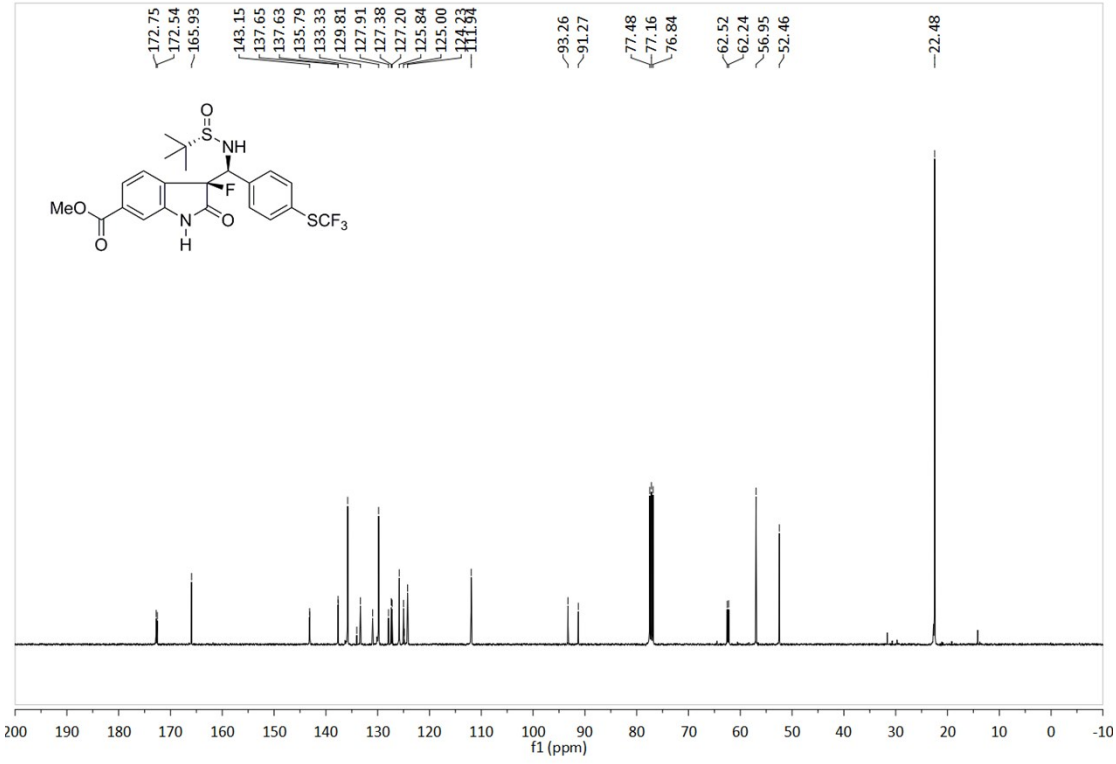
^{19}F NMR spectrum of the crude reaction mixture



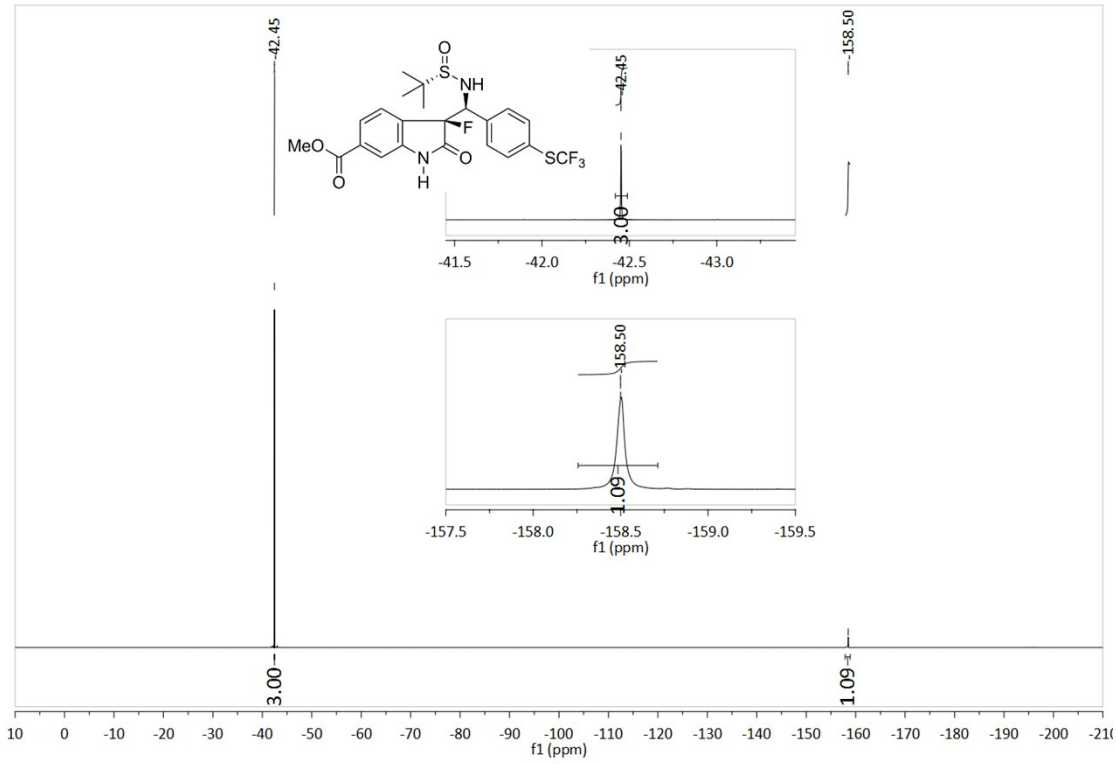
^{1}H NMR spectrum of **13c**



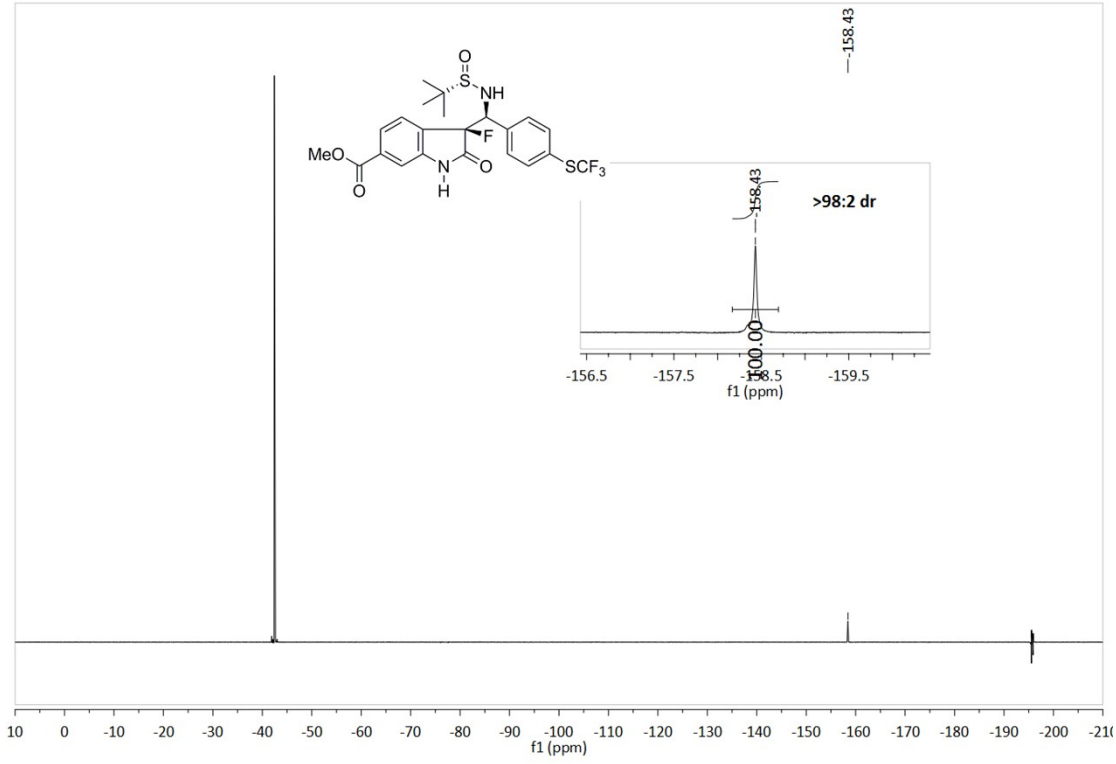
^{13}C NMR spectrum of **13c**



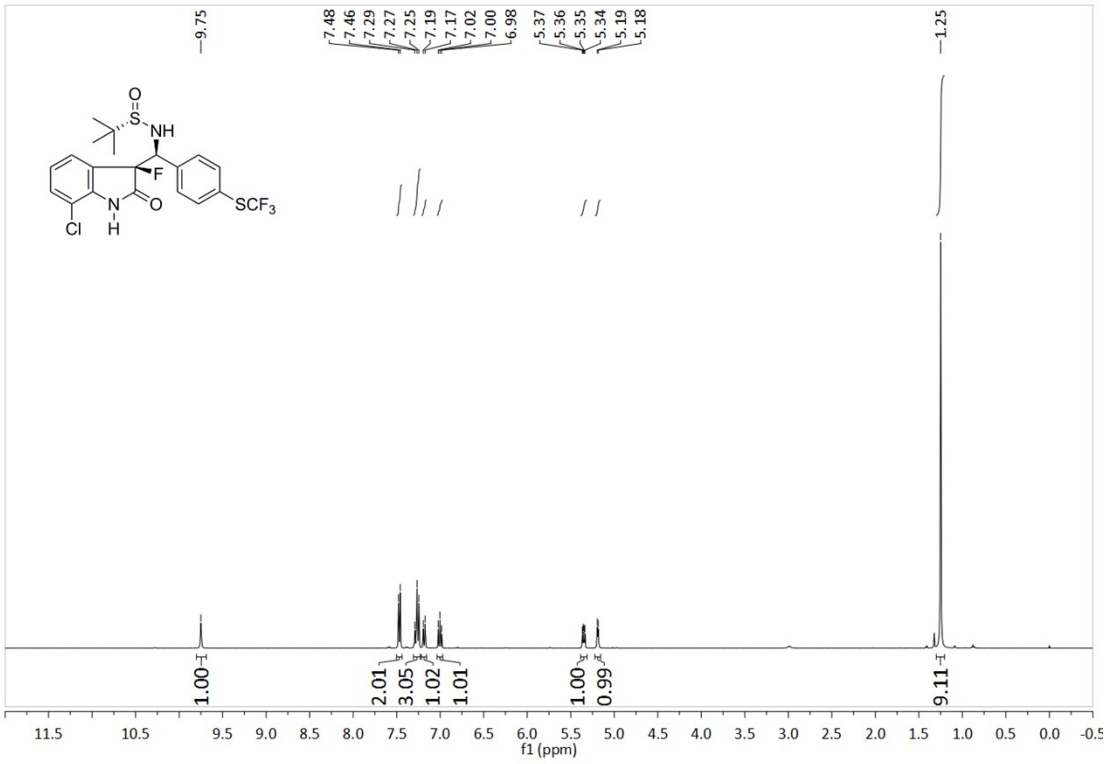
^{19}F NMR spectrum of **13c**



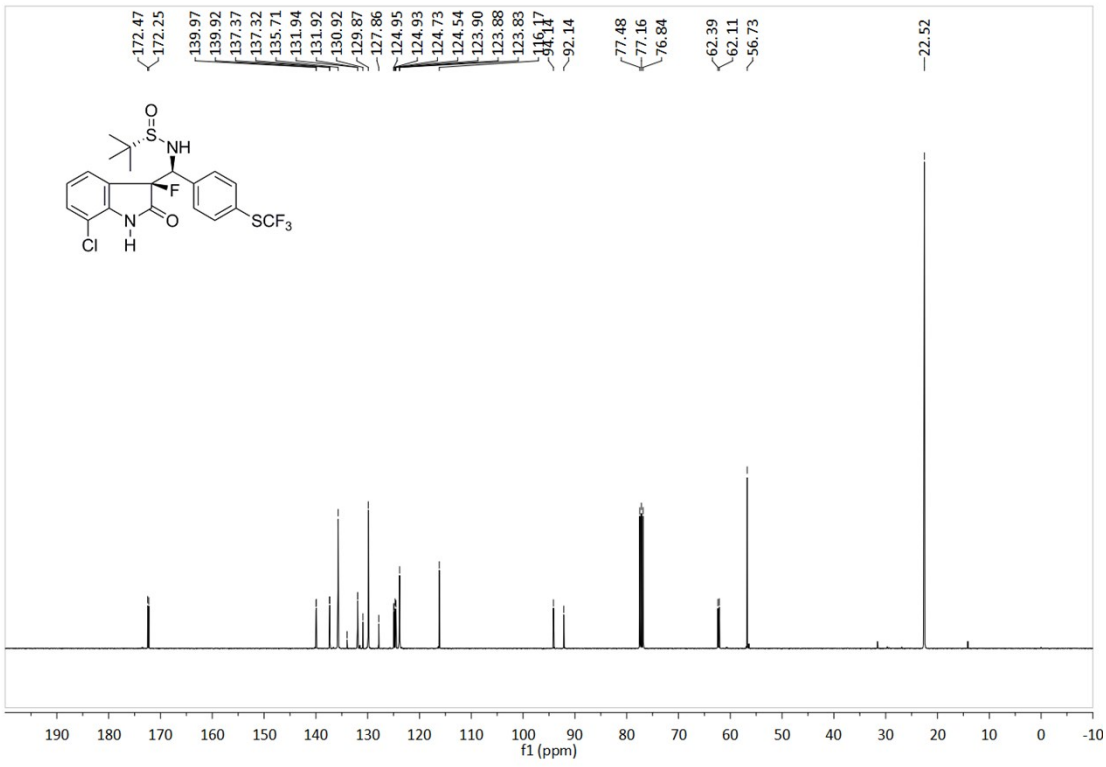
^{19}F NMR spectrum of the crude reaction mixture



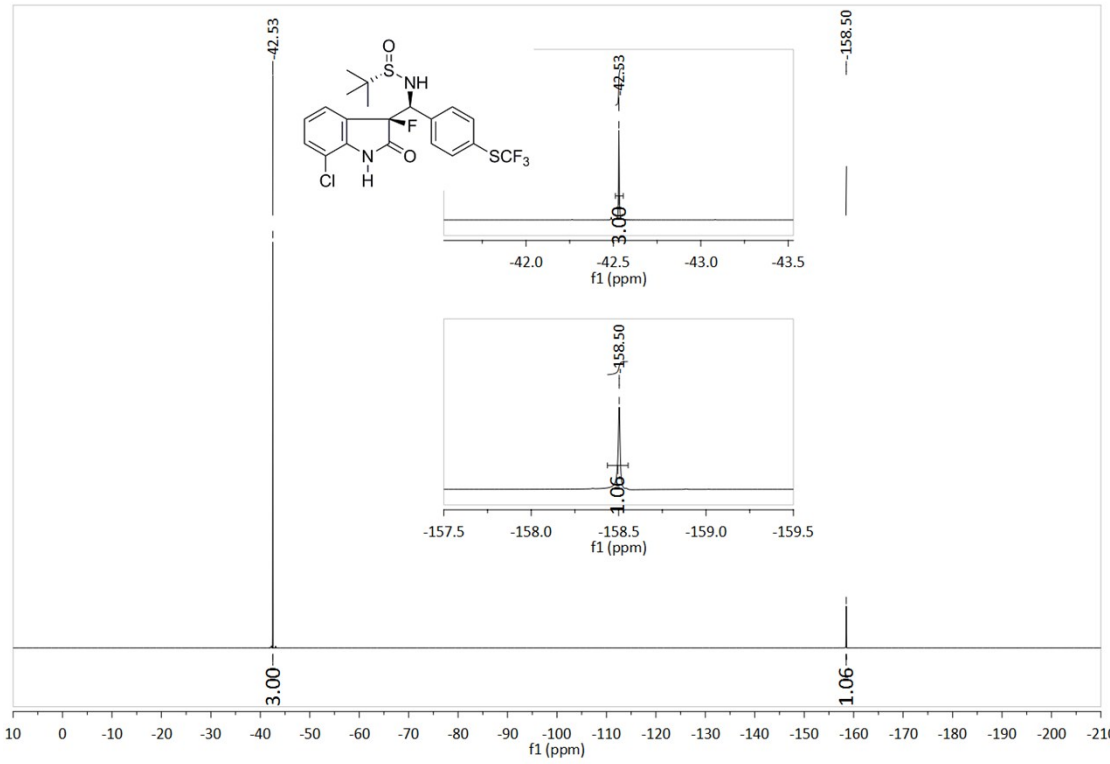
^{1}H NMR spectrum of **13d**



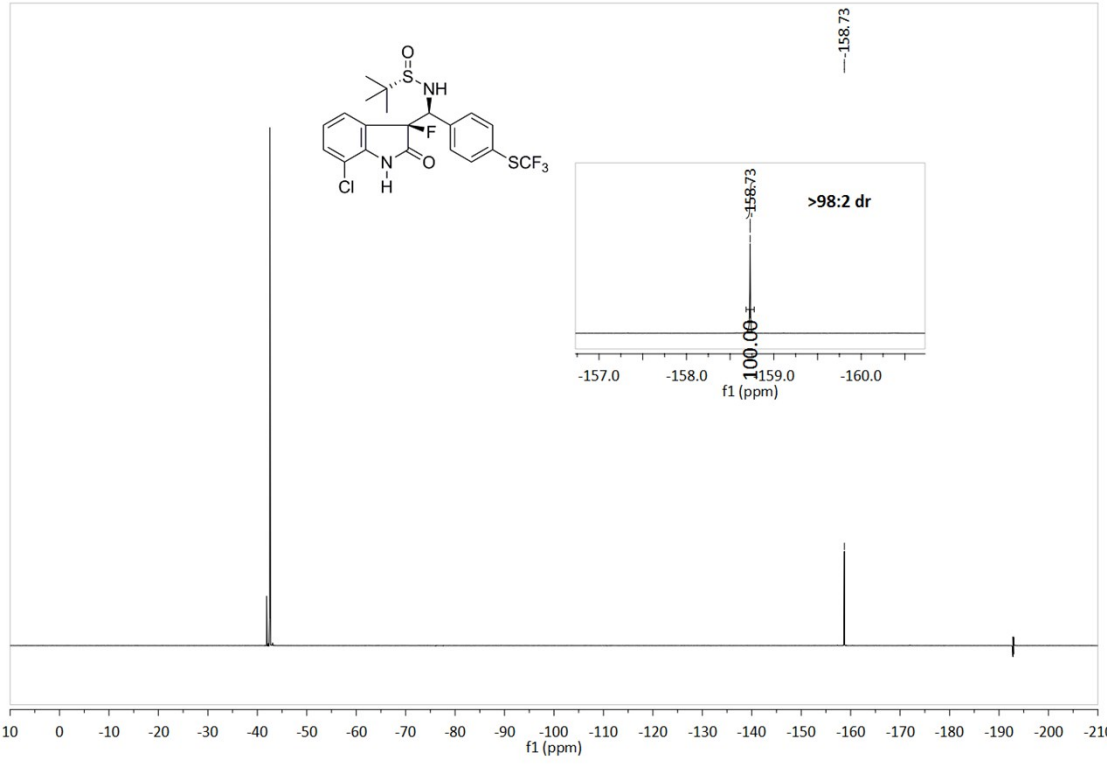
^{13}C NMR spectrum of **13d**



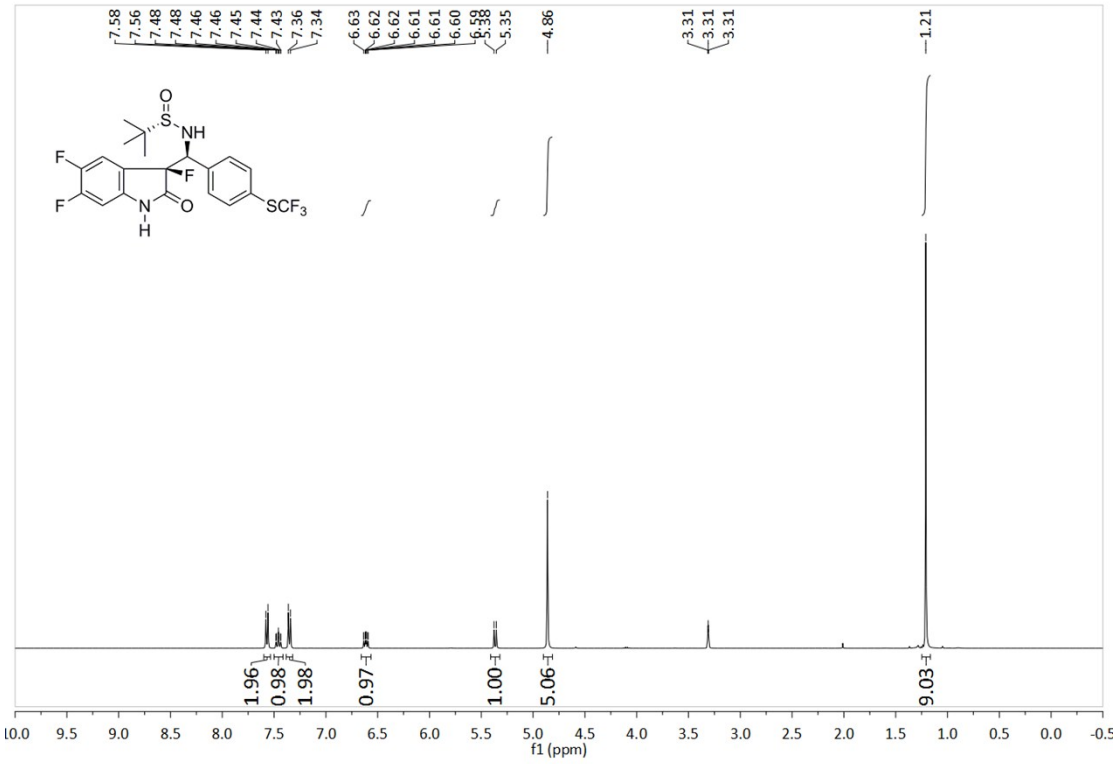
^{19}F NMR spectrum of **13d**



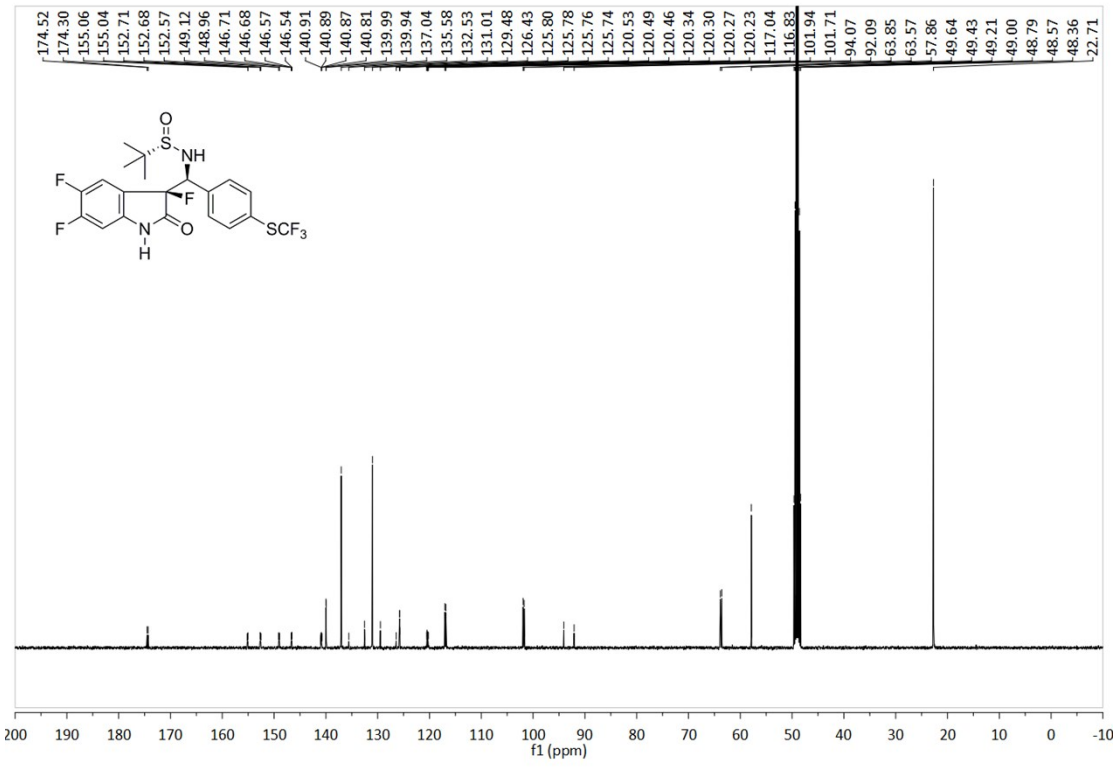
^{19}F NMR spectrum of the crude reaction mixture



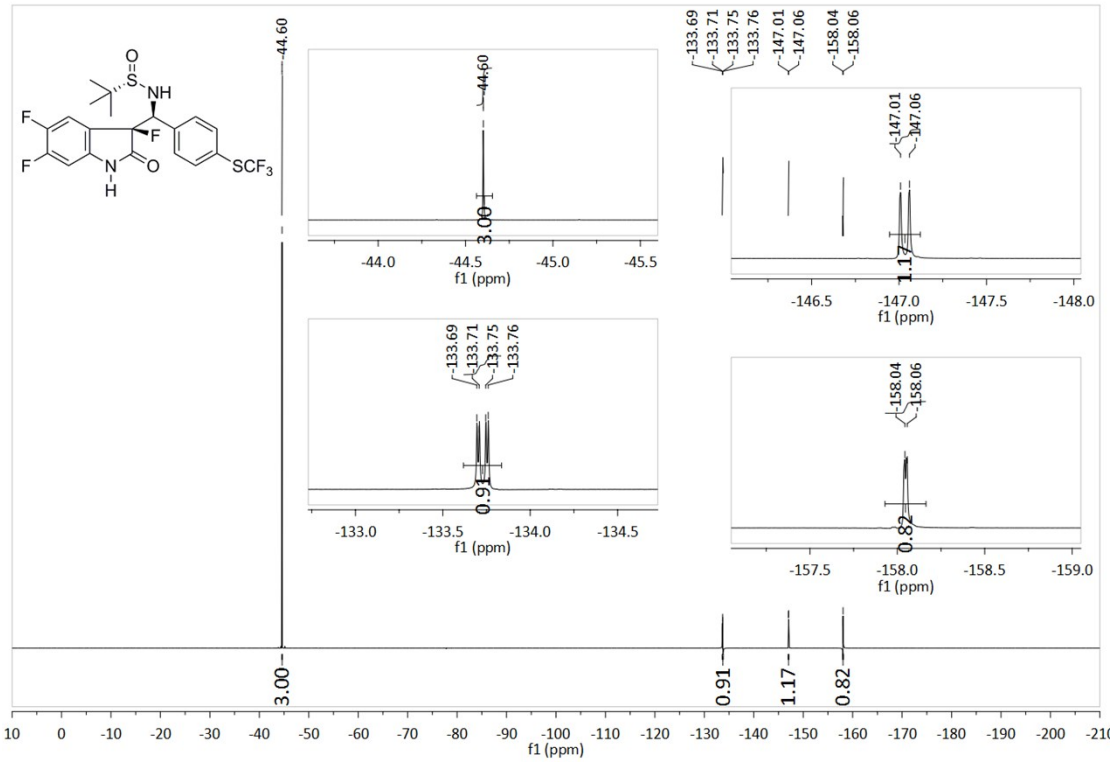
^{1}H NMR spectrum of **13e**



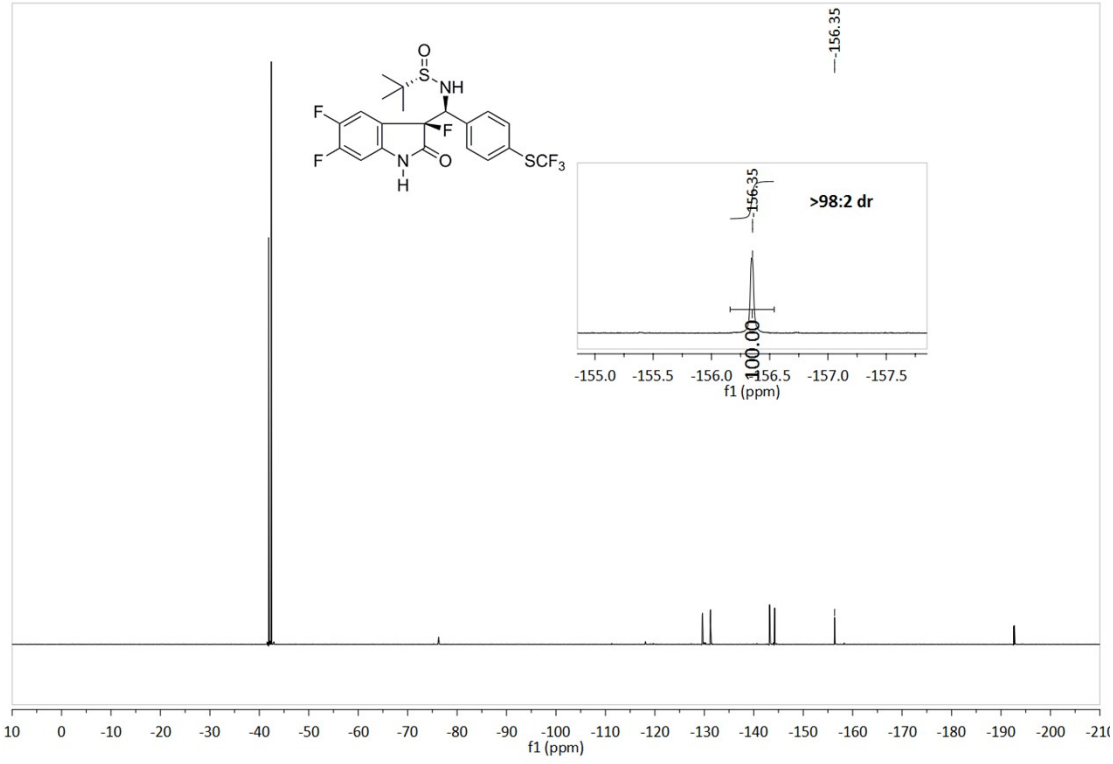
^{13}C NMR spectrum of **13e**



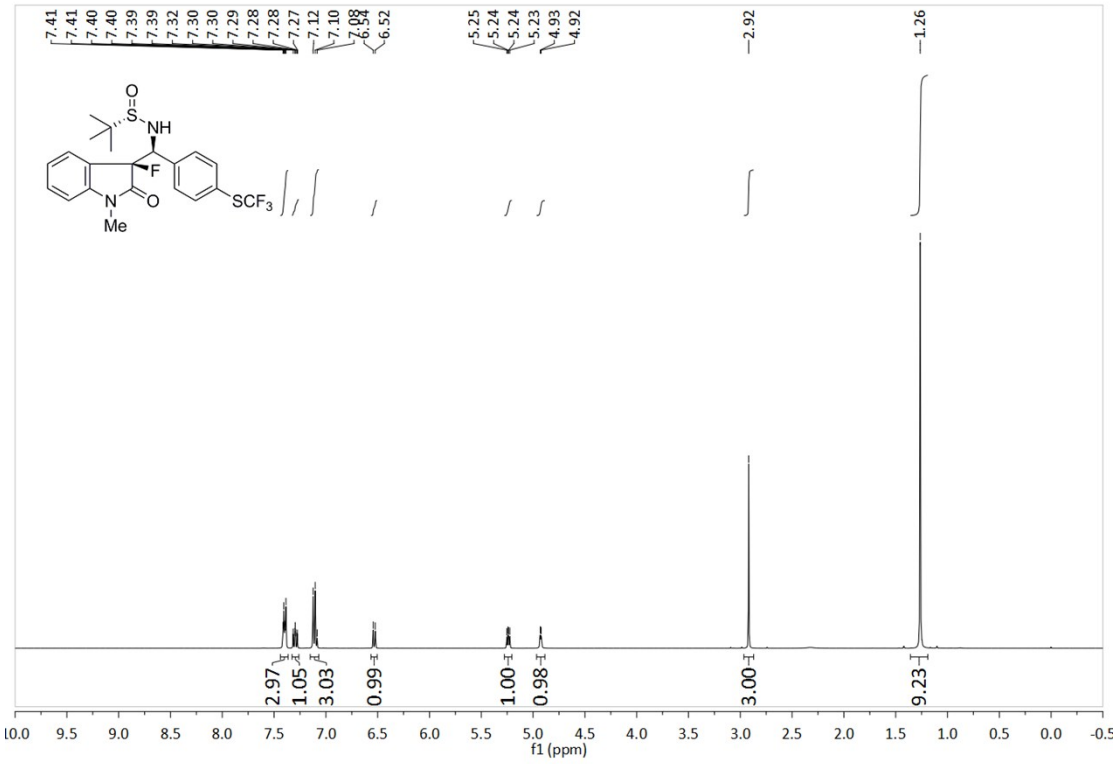
^{19}F NMR spectrum of **13e**



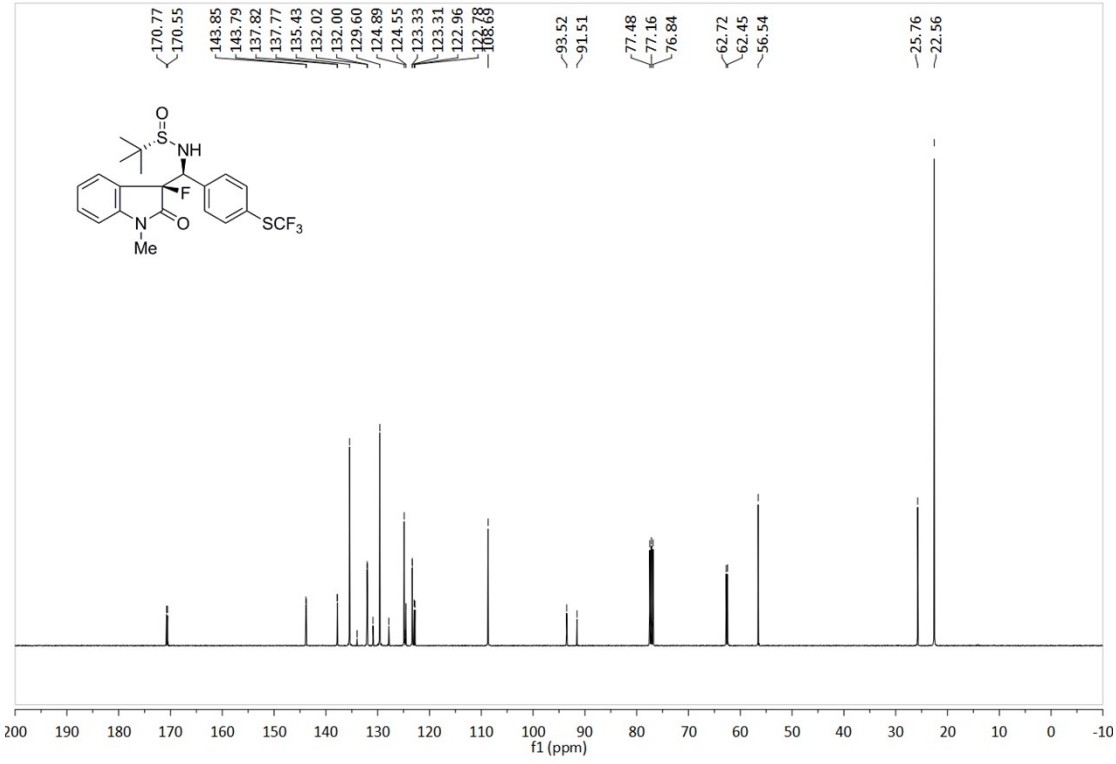
^{19}F NMR spectrum of the crude reaction mixture



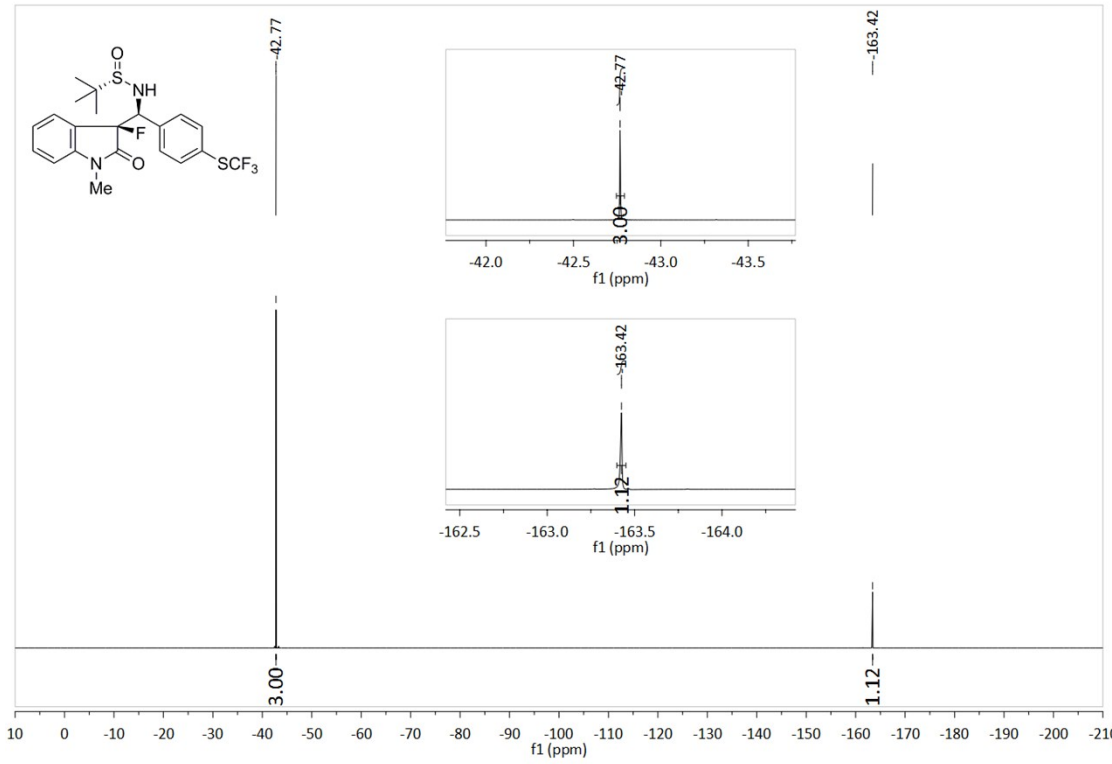
^{1}H NMR spectrum of **13f**



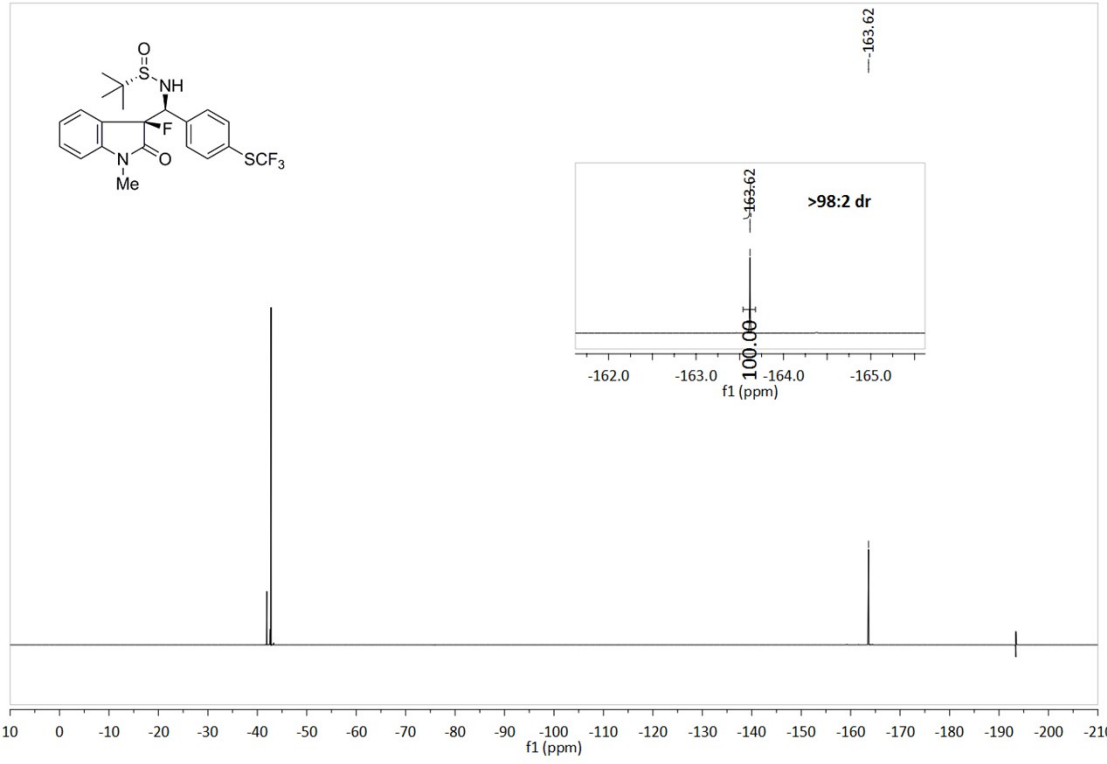
^{13}C NMR spectrum of **13f**



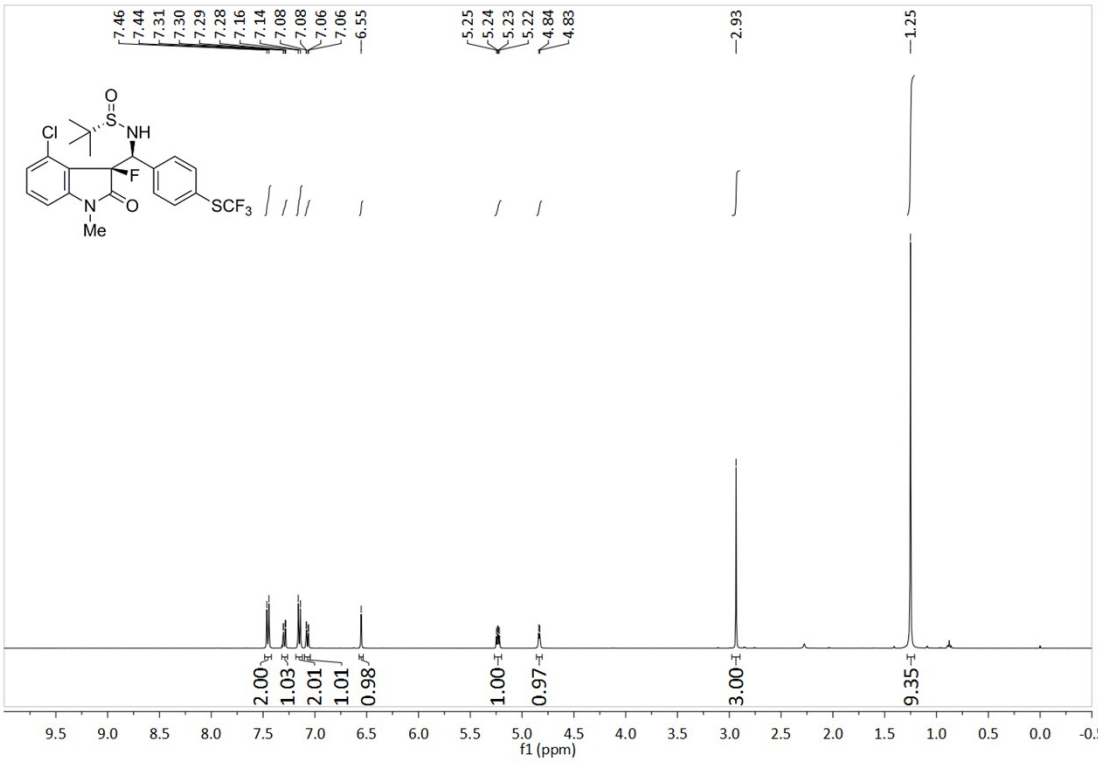
^{19}F NMR spectrum of **13f**



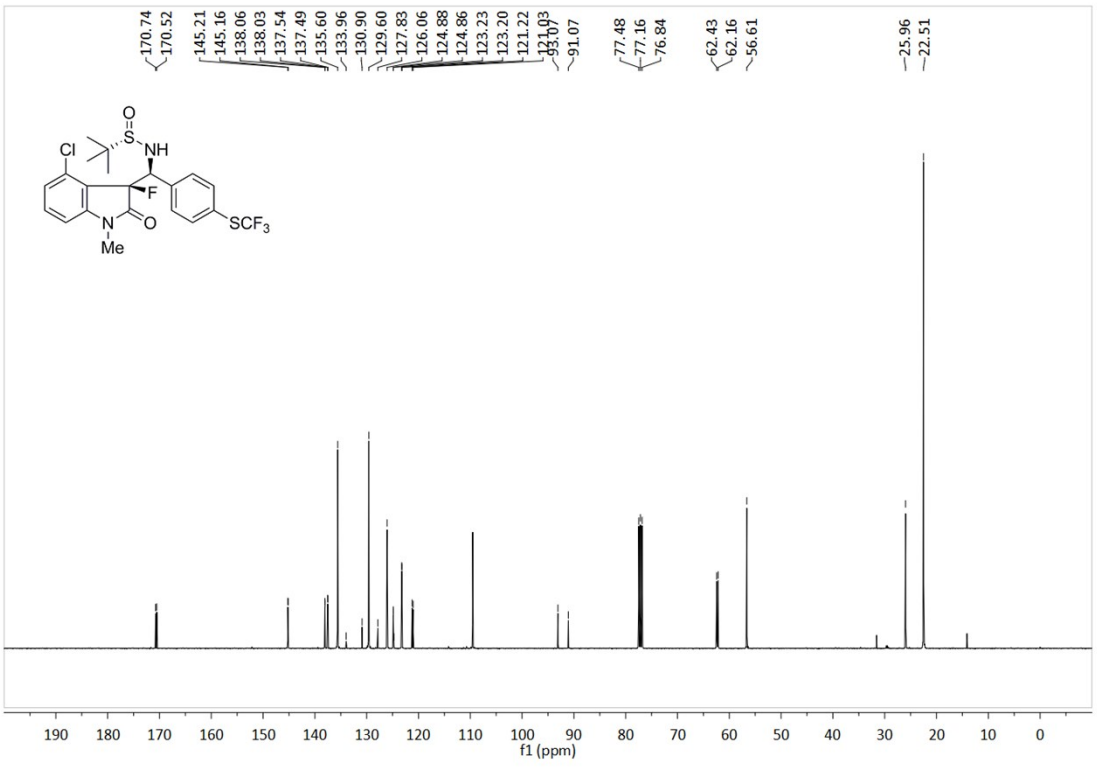
^{19}F NMR spectrum of the crude reaction mixture



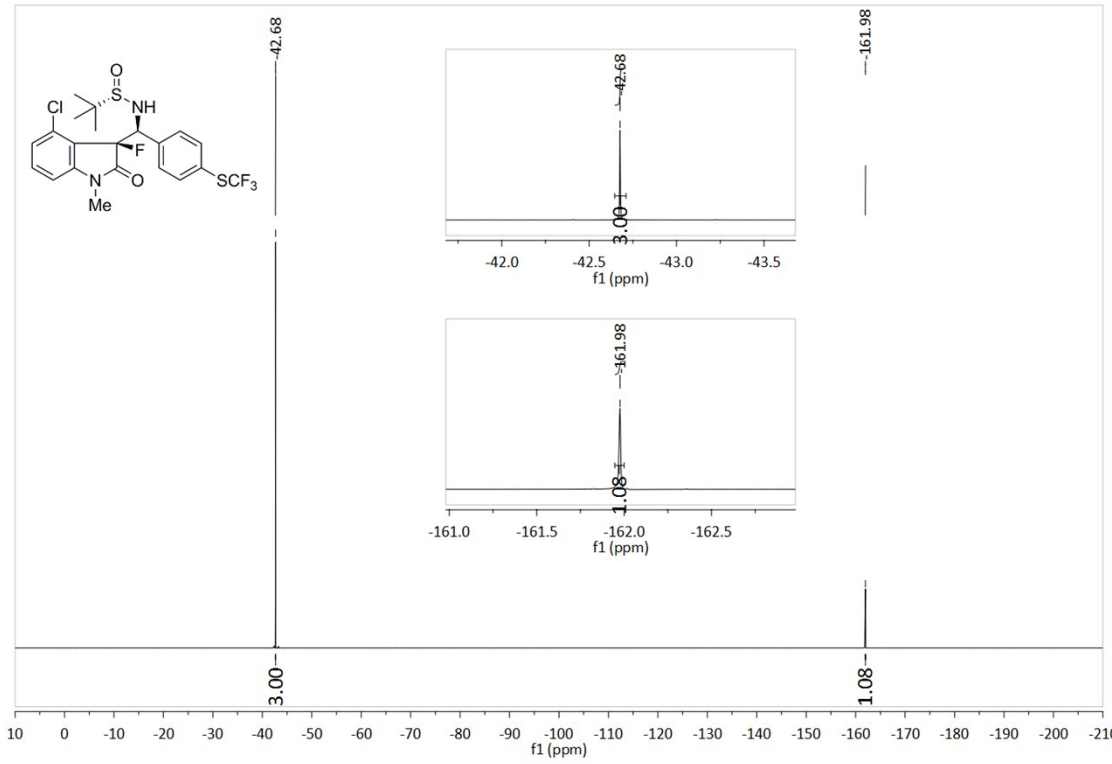
^{1}H NMR spectrum of **13g**



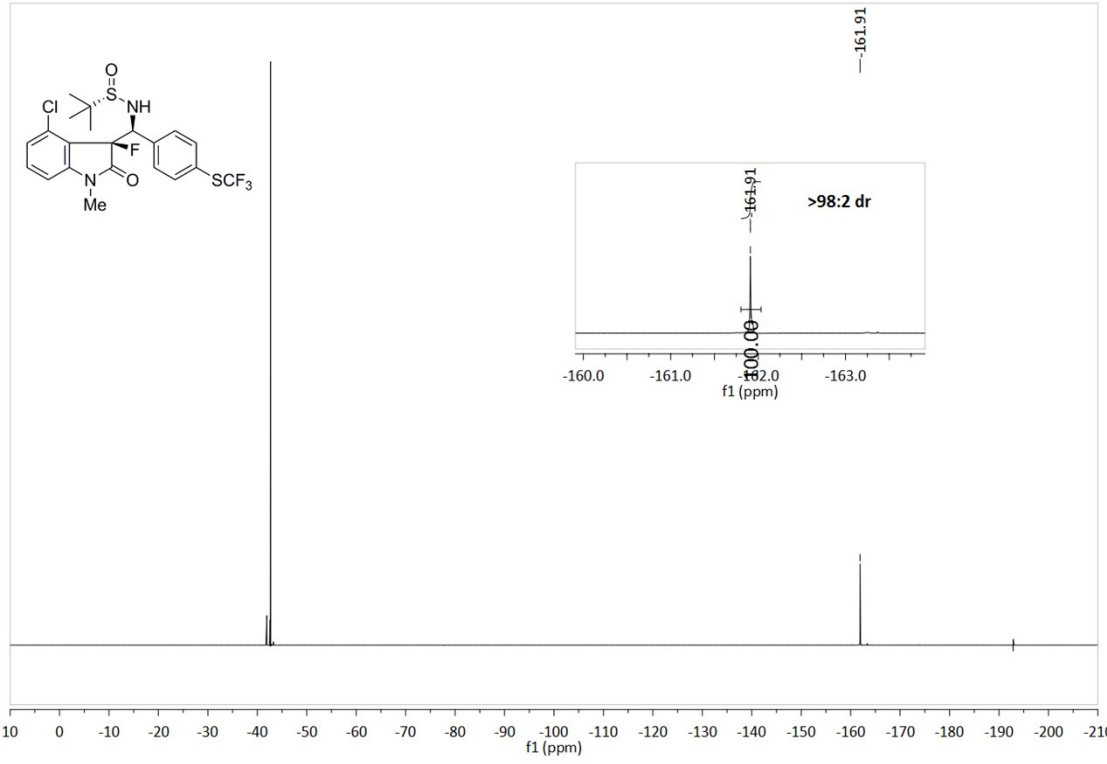
^{13}C NMR spectrum of **13g**



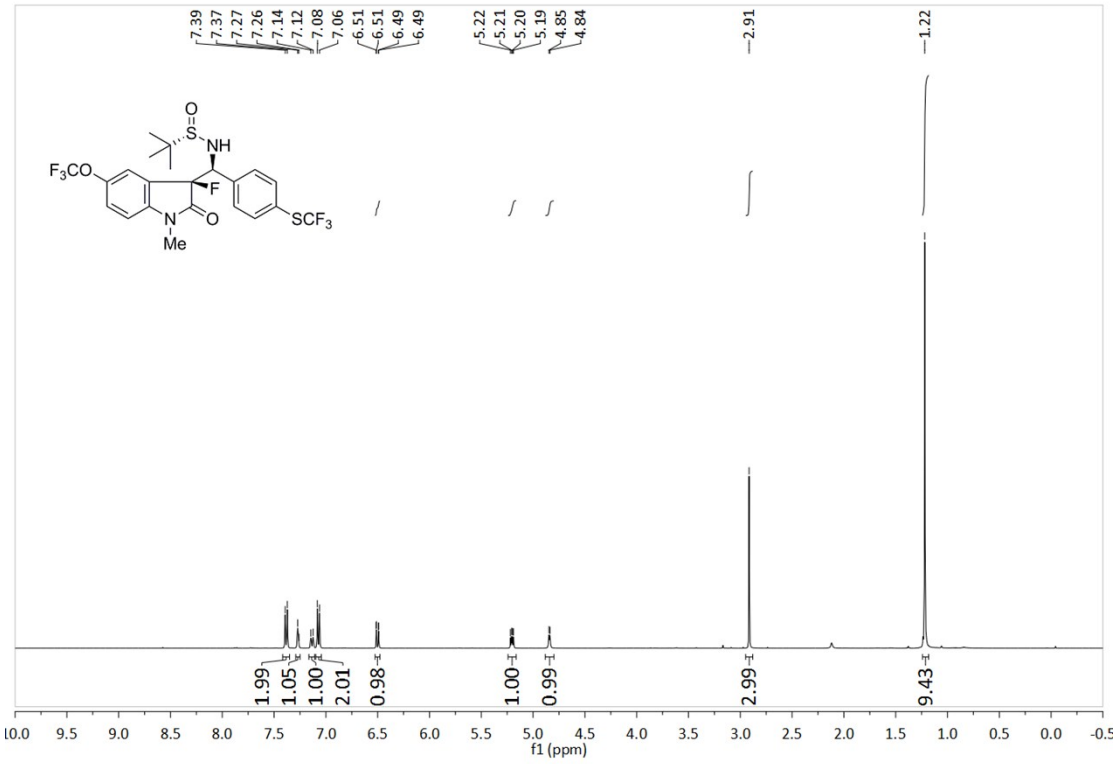
^{19}F NMR spectrum of **13g**



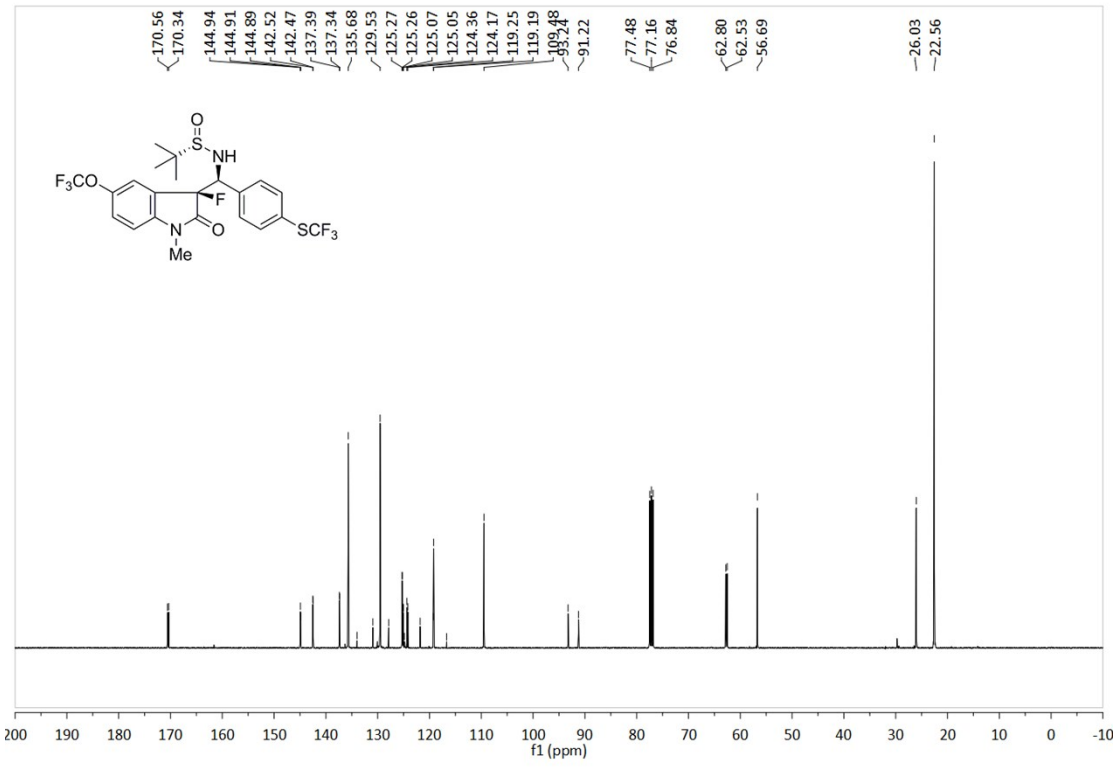
^{19}F NMR spectrum of the crude reaction mixture



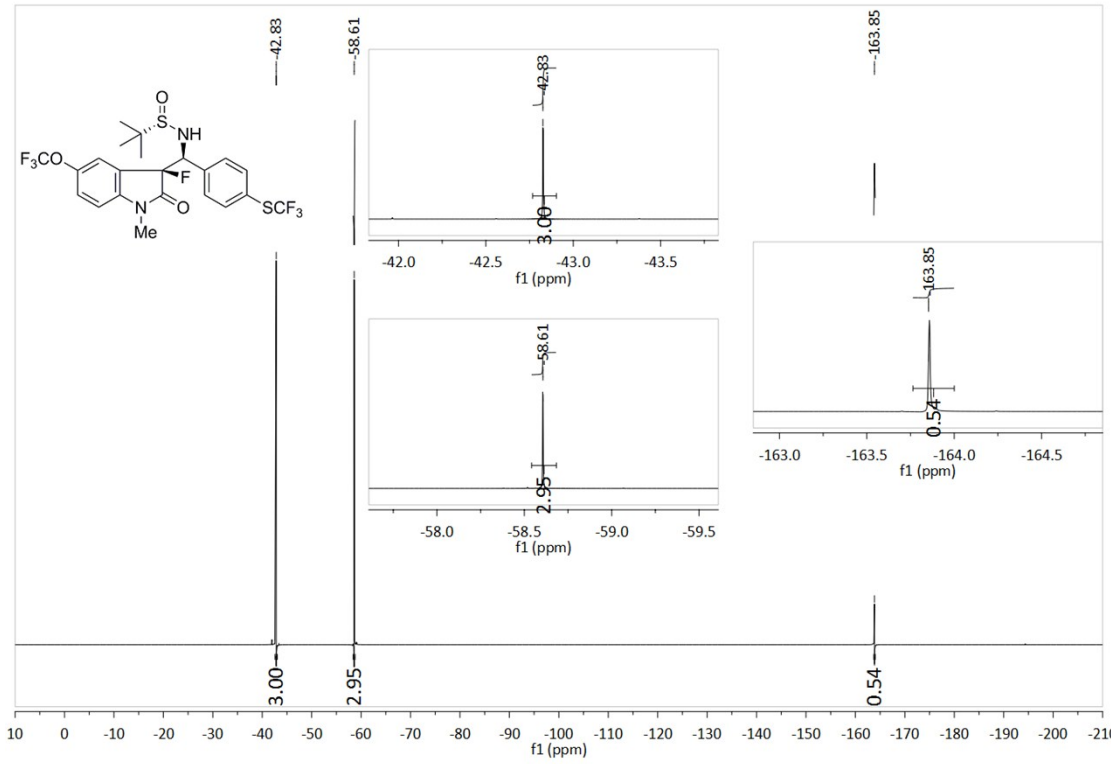
^{1}H NMR spectrum of **13h**



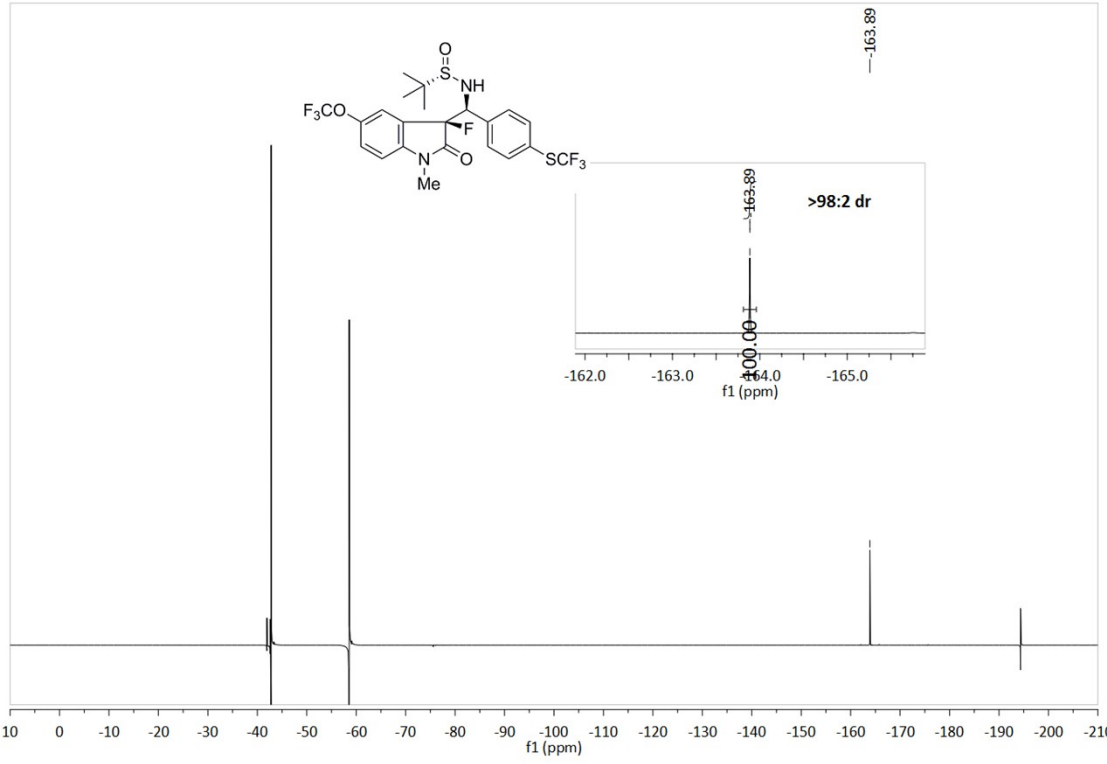
^{13}C NMR spectrum of **13h**



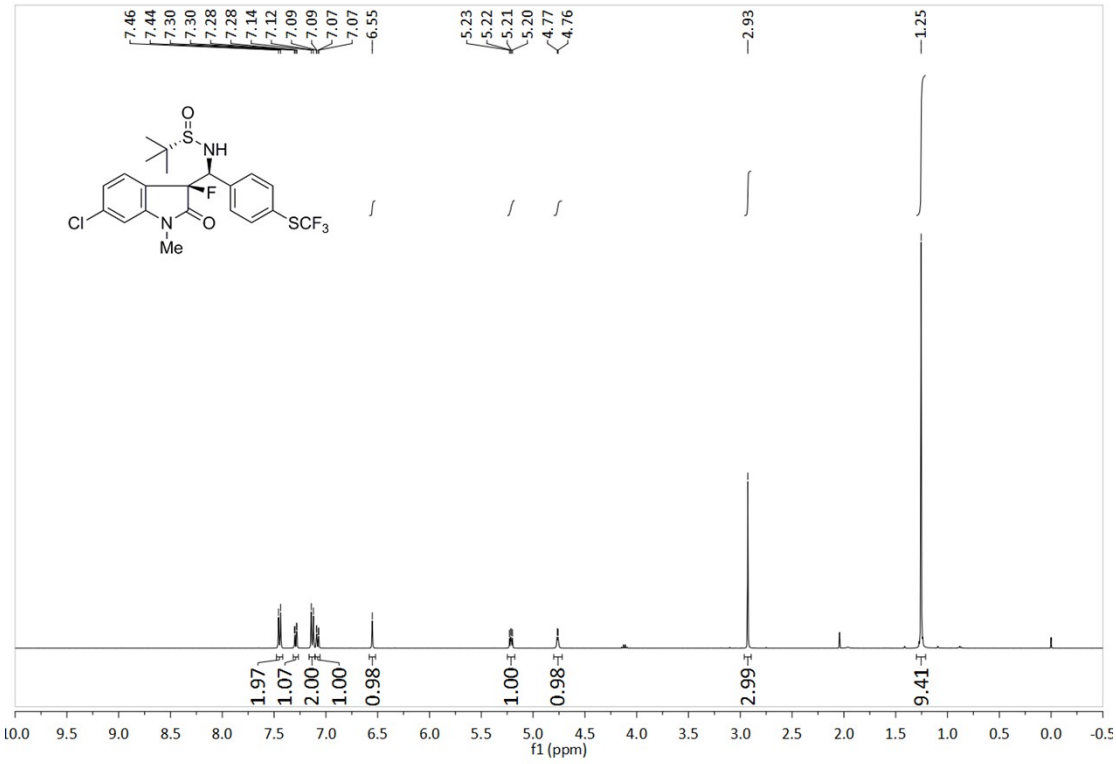
^{19}F NMR spectrum of **13h**



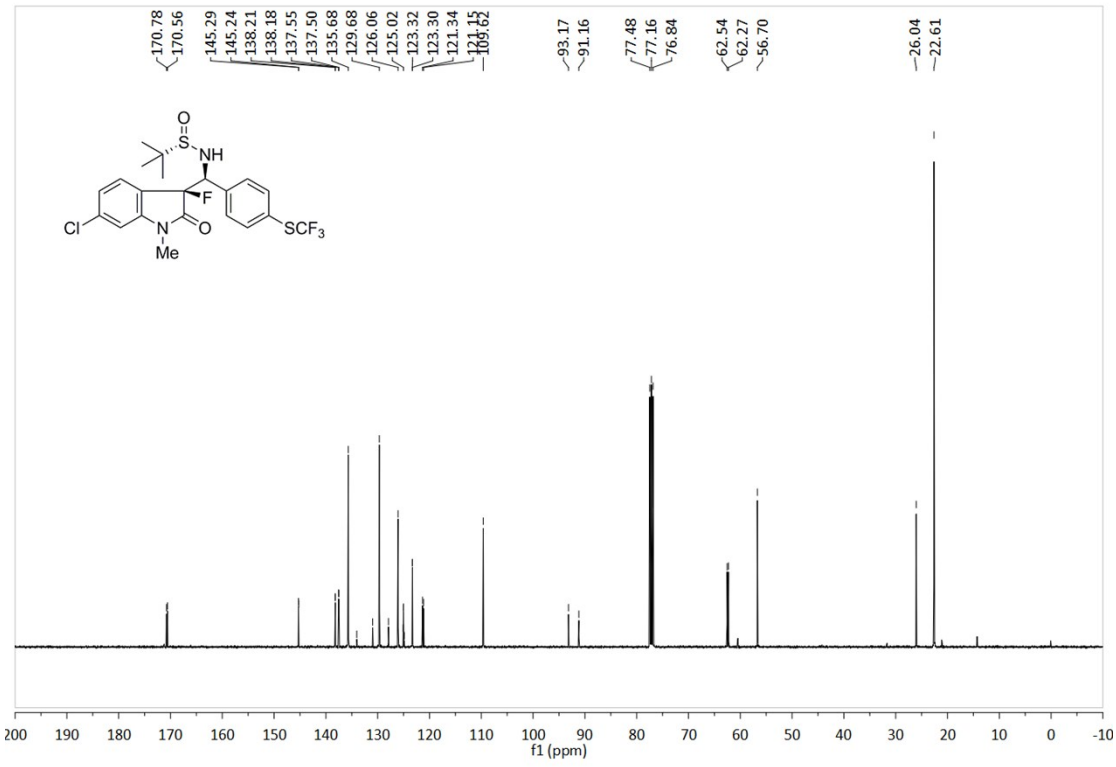
^{19}F NMR spectrum of the crude reaction mixture



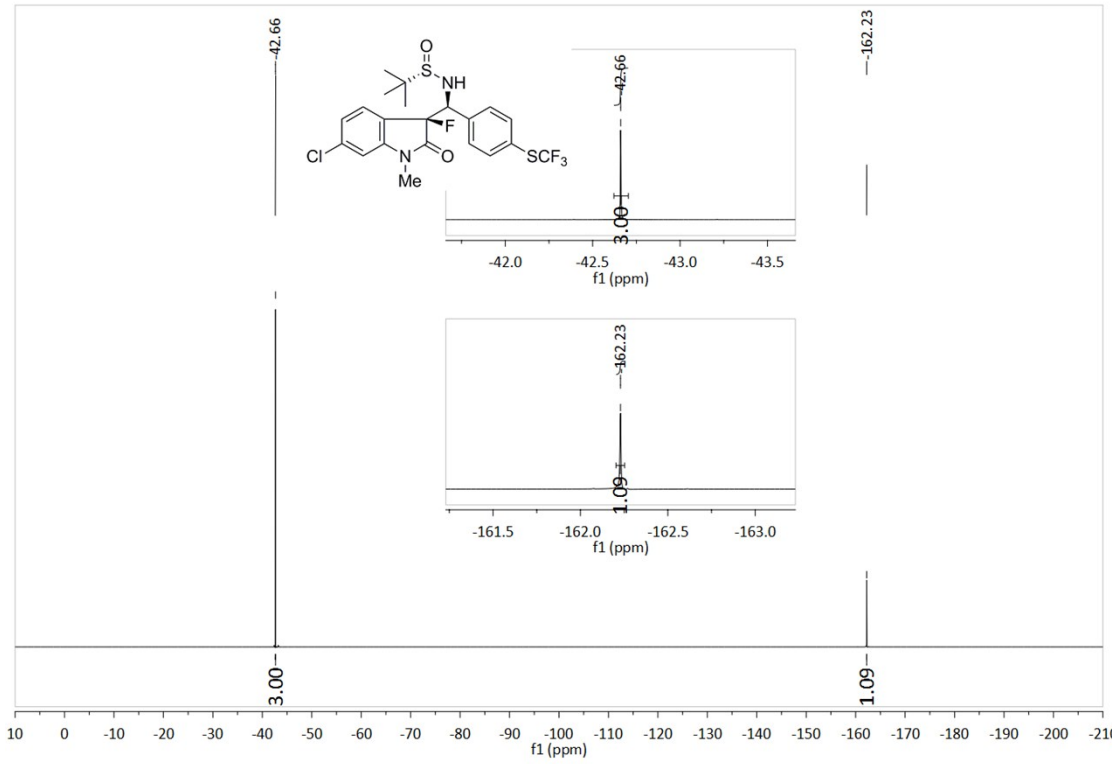
^{1}H NMR spectrum of **13i**



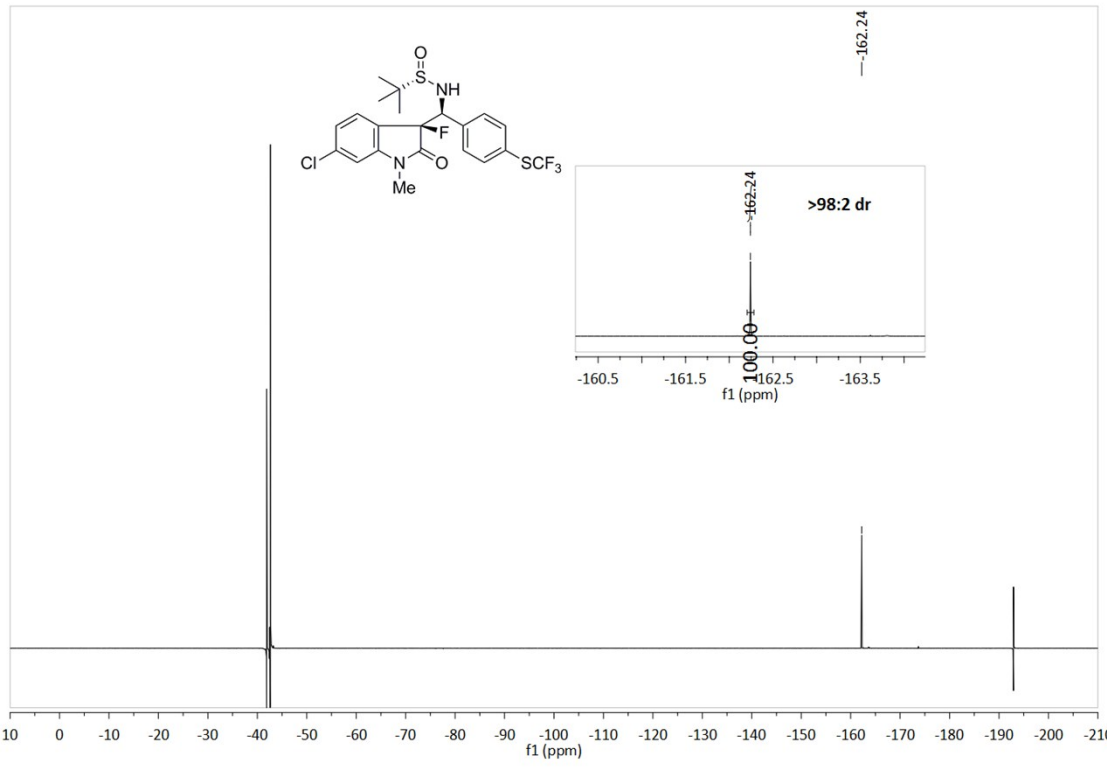
^{13}C NMR spectrum of **13i**



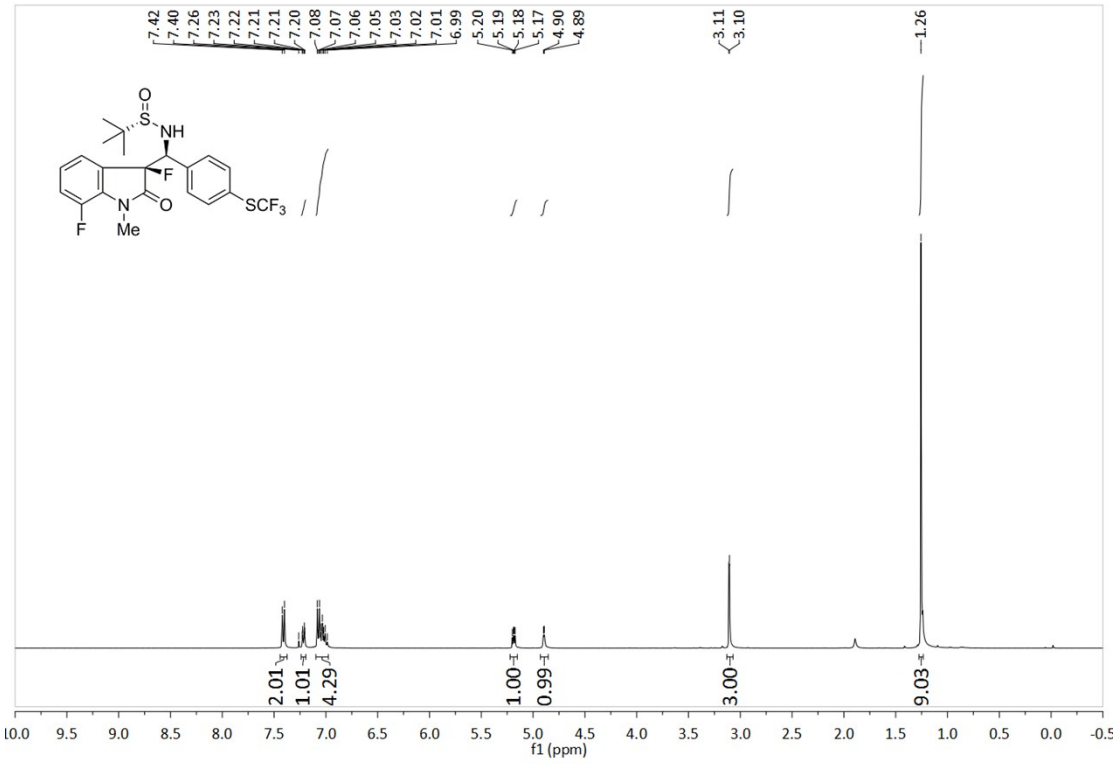
^{19}F NMR spectrum of **13i**



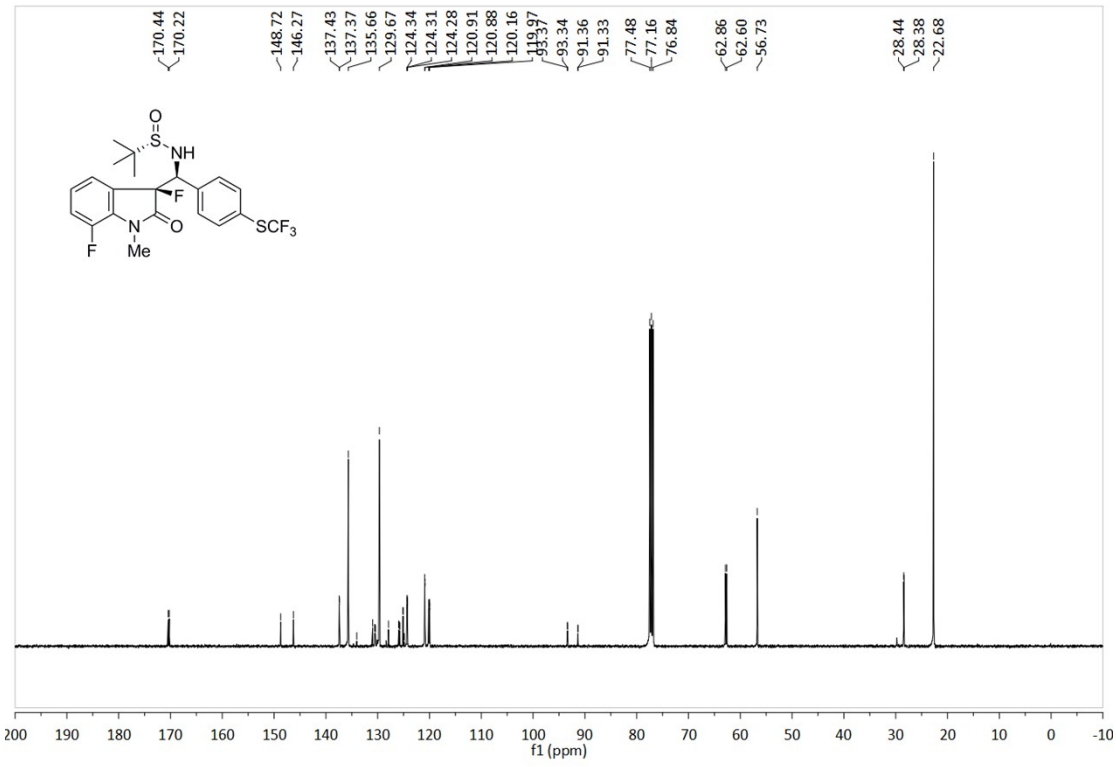
^{19}F NMR spectrum of the crude reaction mixture



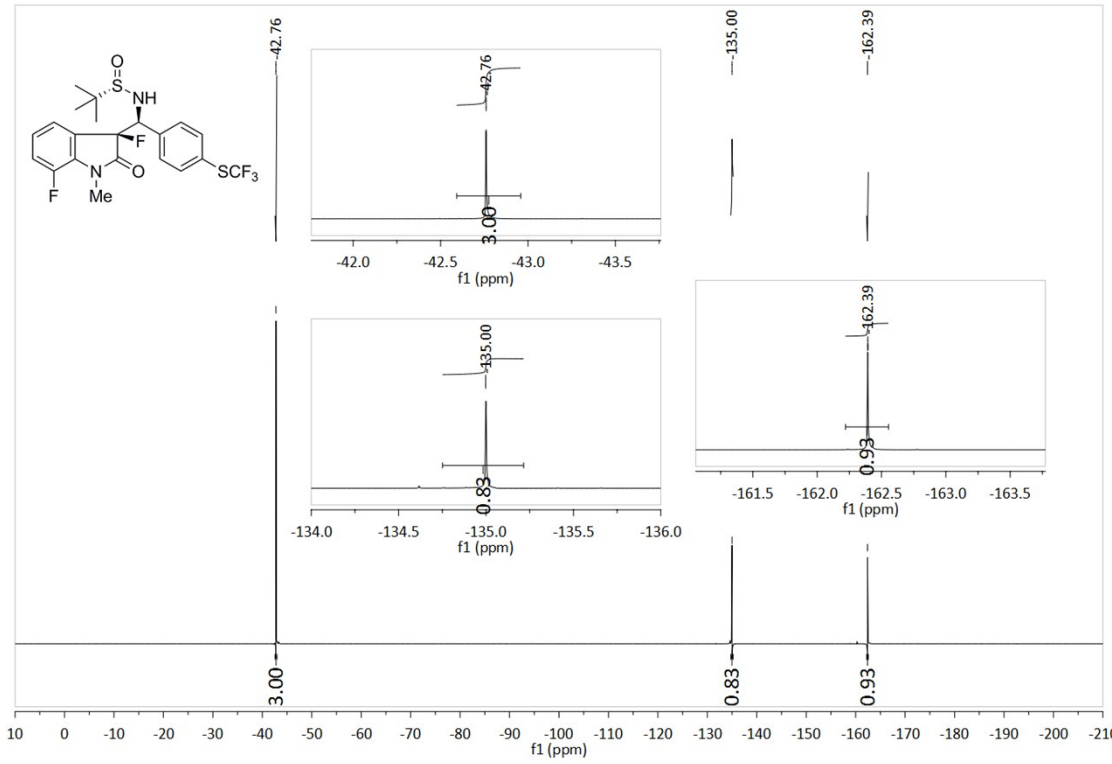
^{1}H NMR spectrum of **13j**



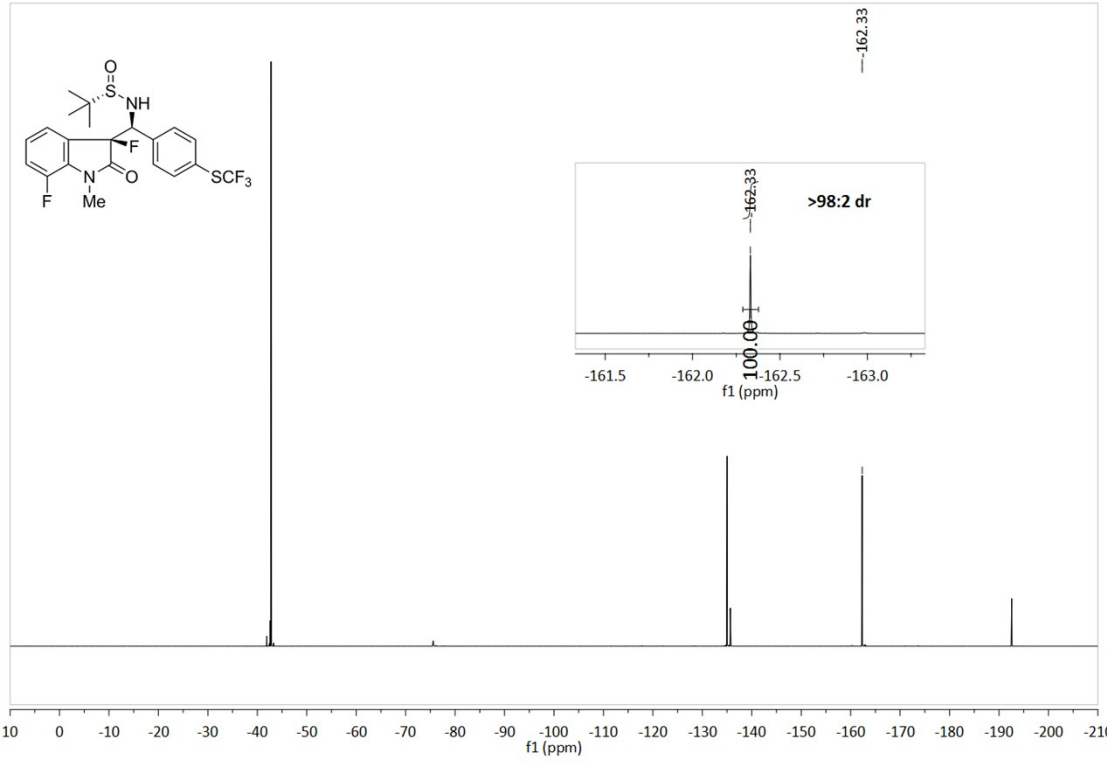
^{13}C NMR spectrum of **13j**



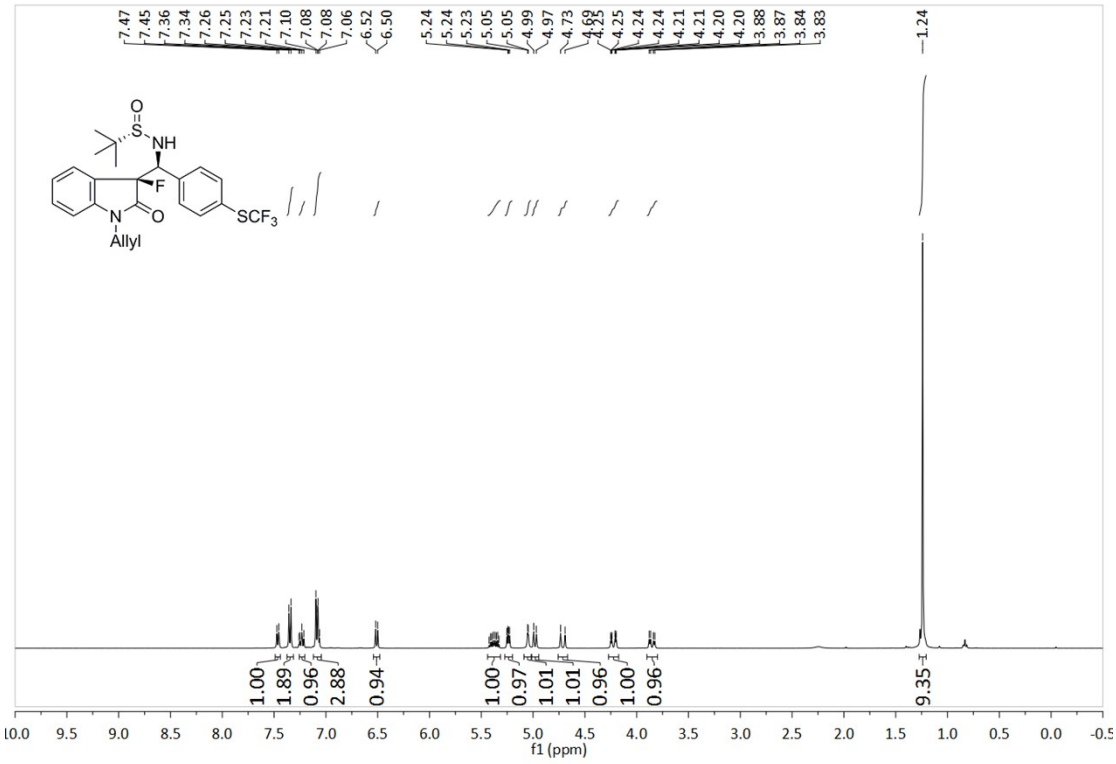
^{19}F NMR spectrum of **13j**



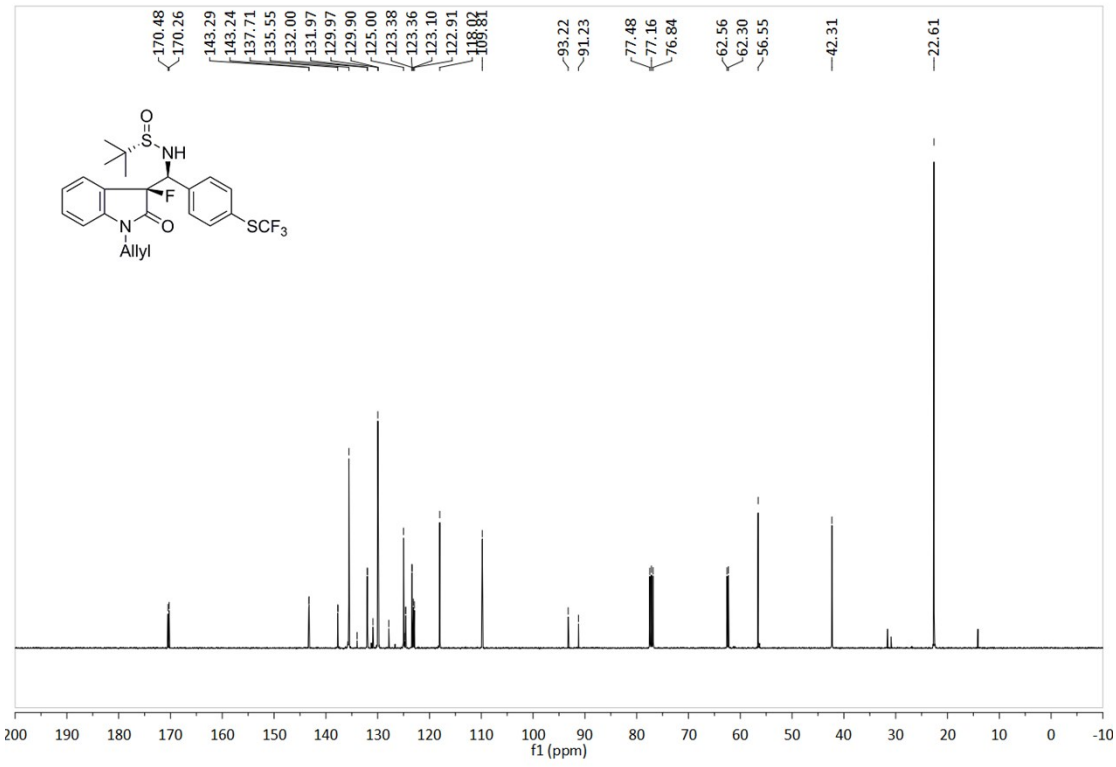
^{19}F NMR spectrum of the crude reaction mixture



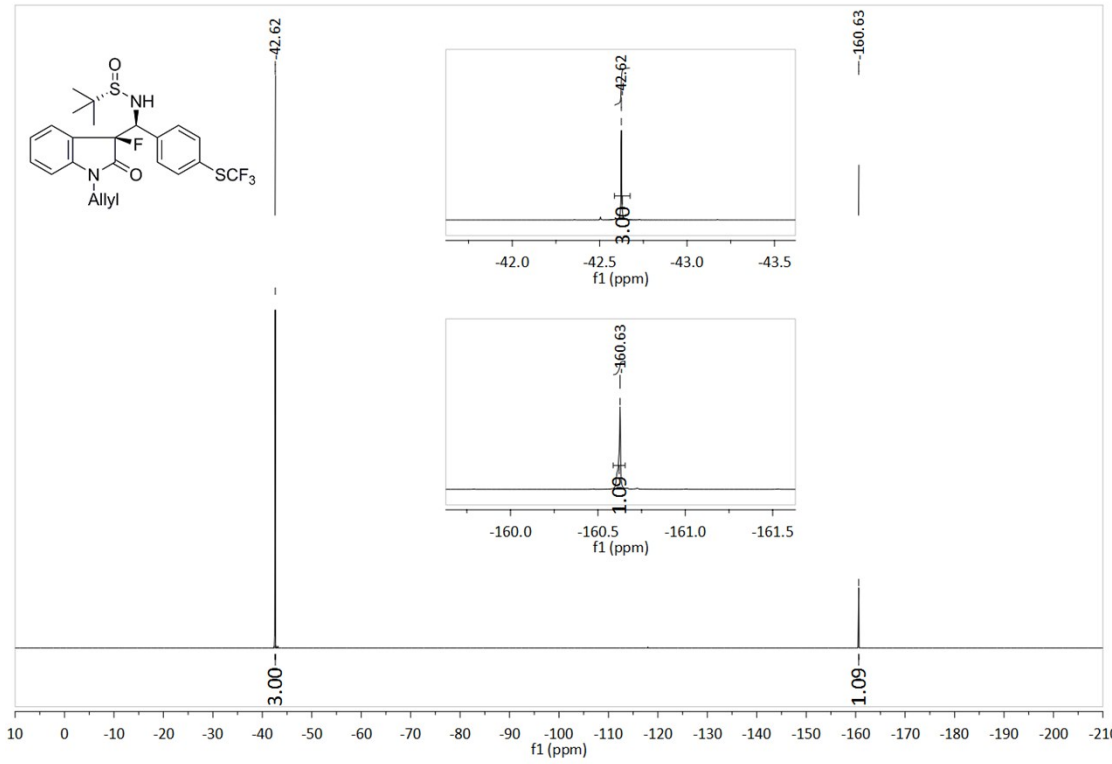
^{1}H NMR spectrum of **13k**



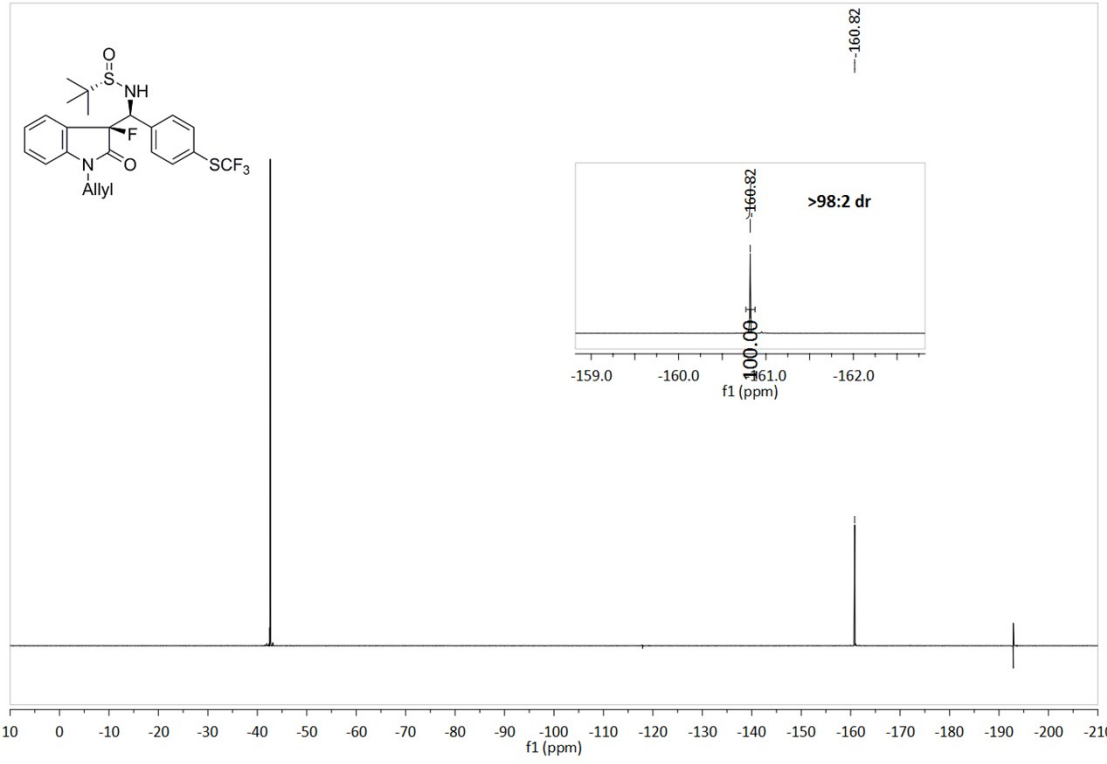
^{13}C NMR spectrum of **13k**



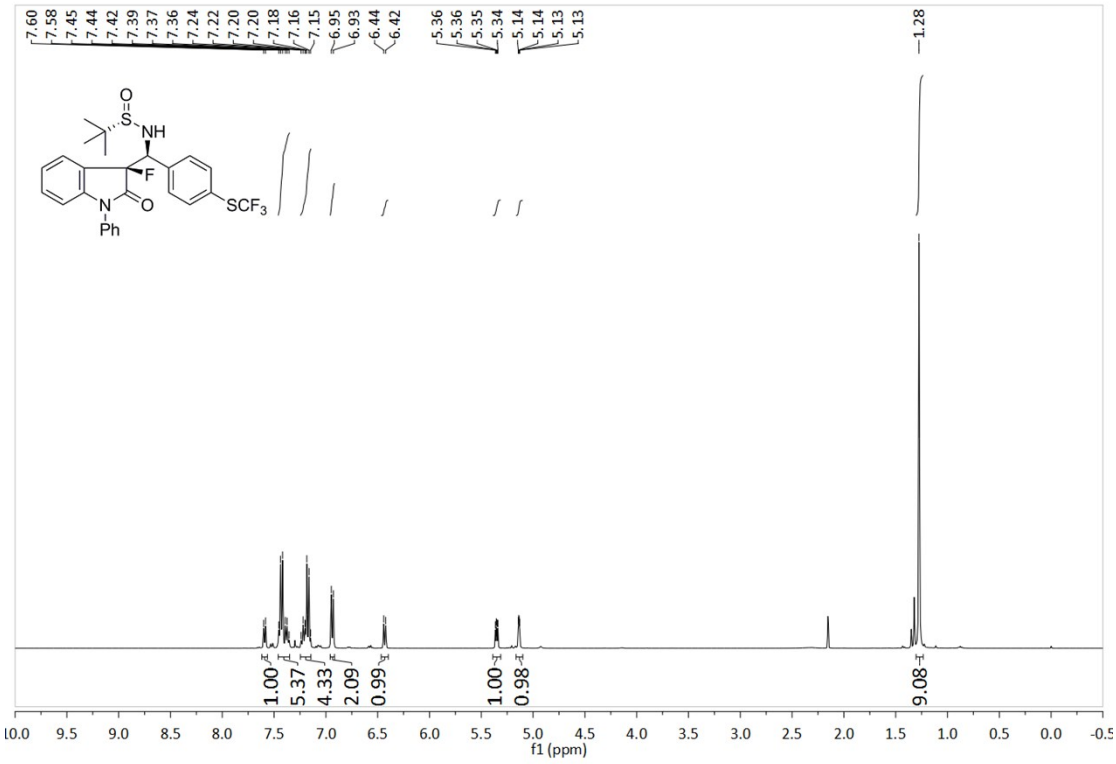
^{19}F NMR spectrum of **13k**



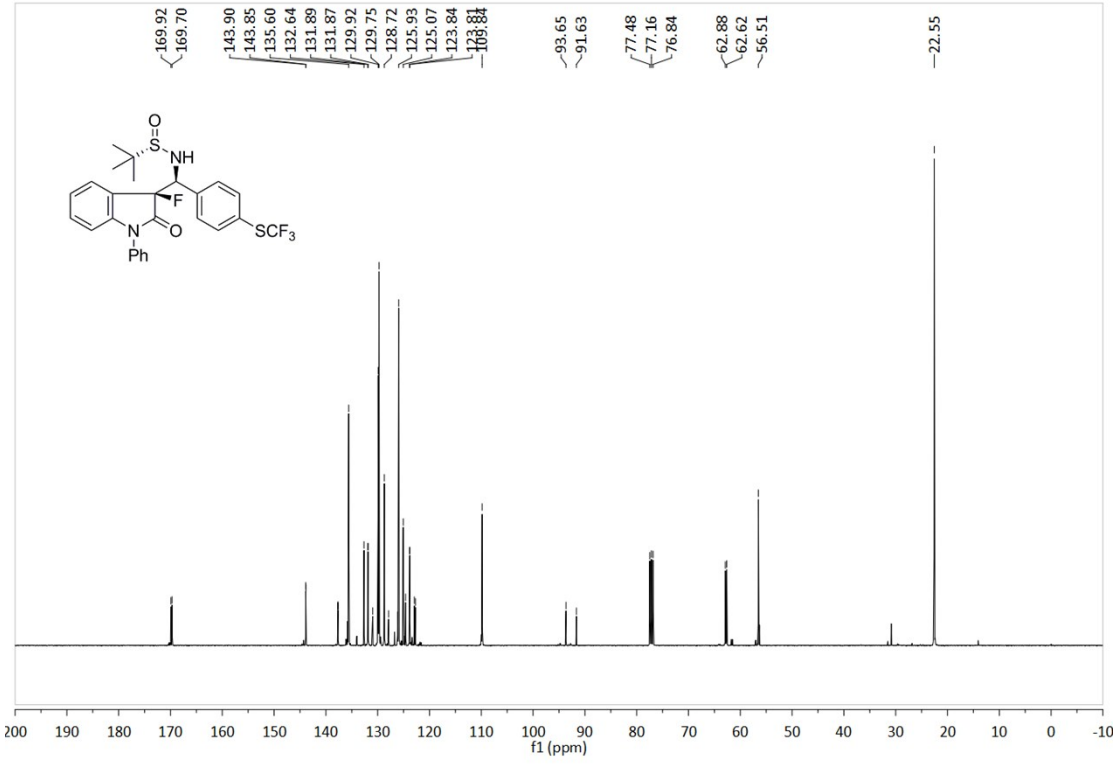
^{19}F NMR spectrum of the crude reaction mixture



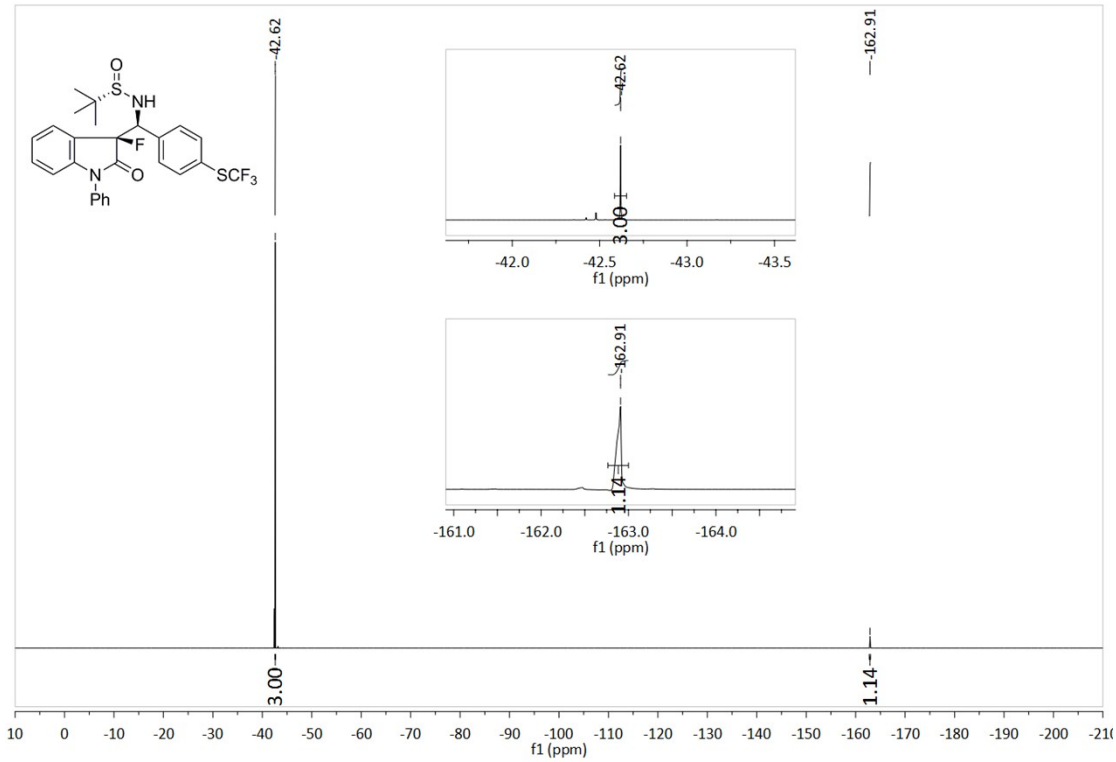
^{1}H NMR spectrum of **13l**



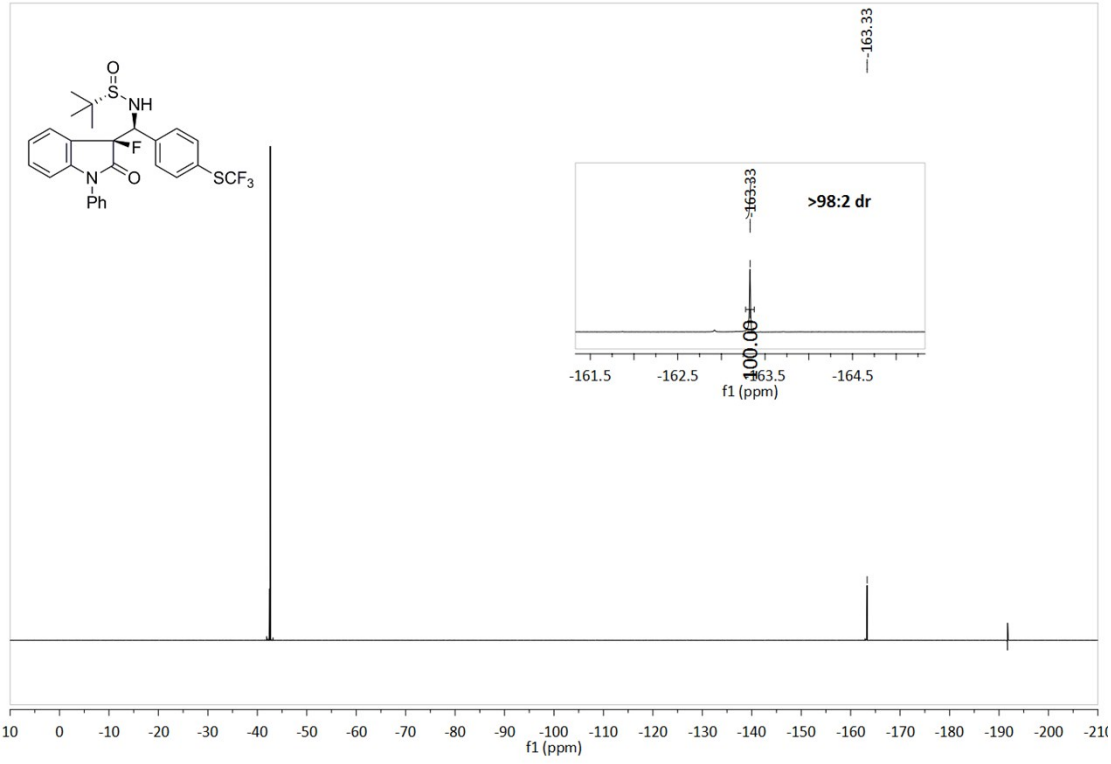
^{13}C NMR spectrum of **13l**



^{19}F NMR spectrum of **13l**

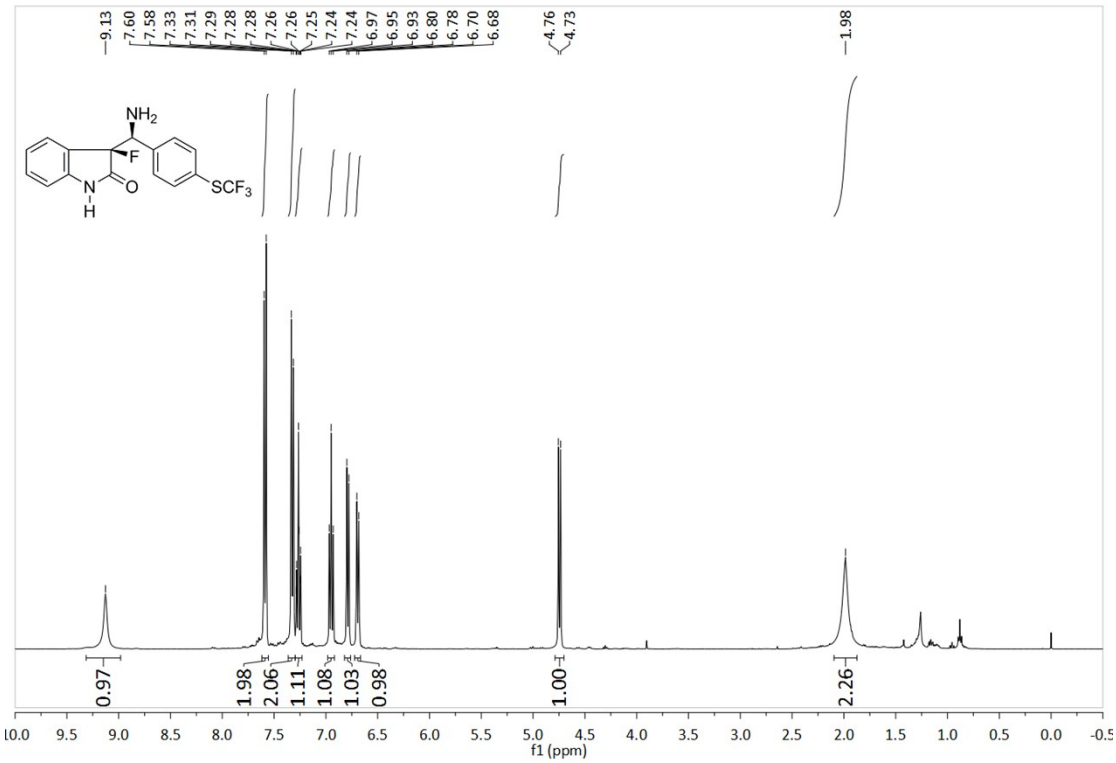


^{19}F NMR spectrum of the crude reaction mixture

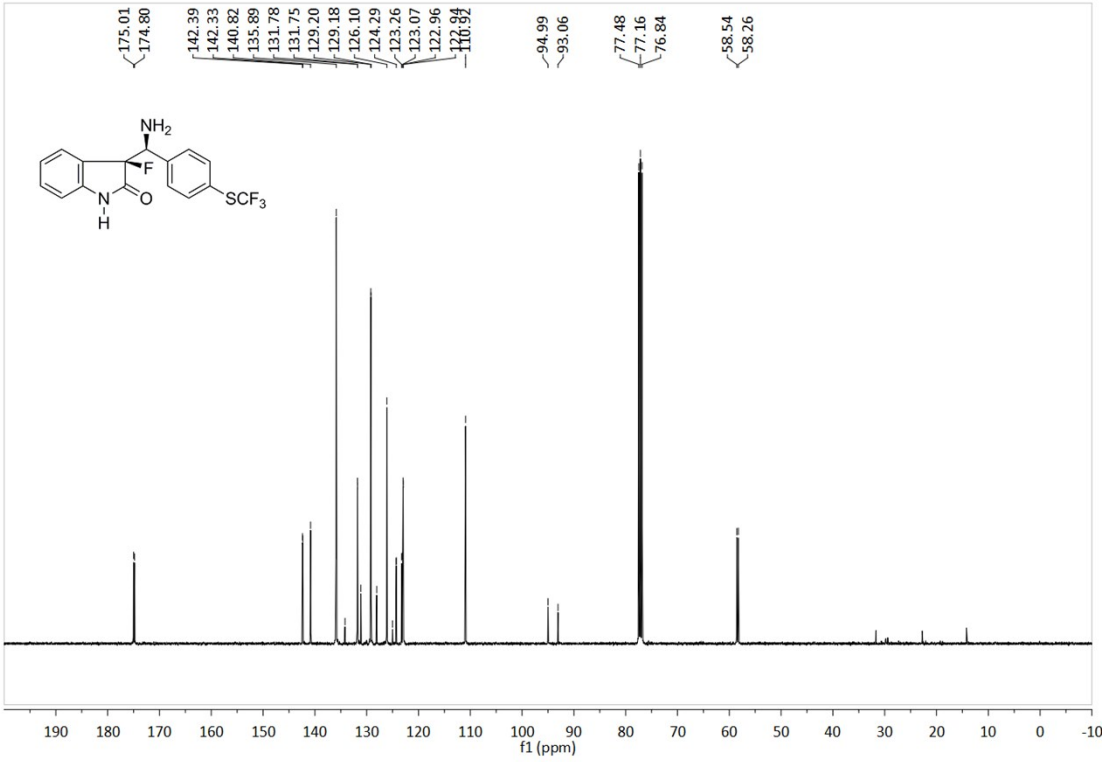


5.2. NMR spectra of deprotection product 14

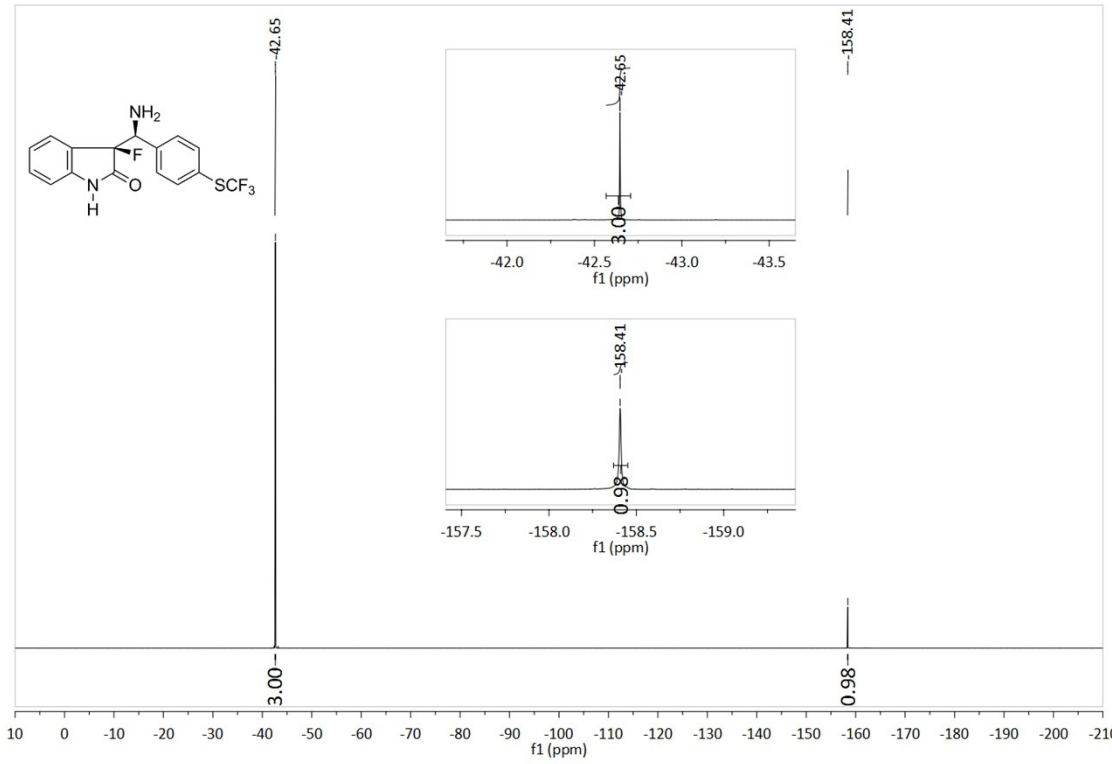
^{1}H NMR spectrum of **14**



^{13}C NMR spectrum of **14**

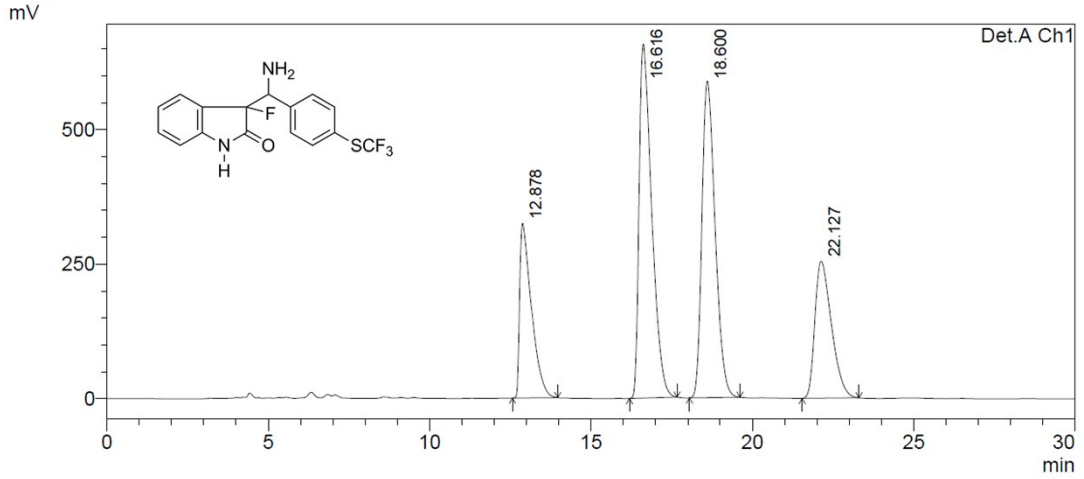


^{19}F NMR spectrum of **14**



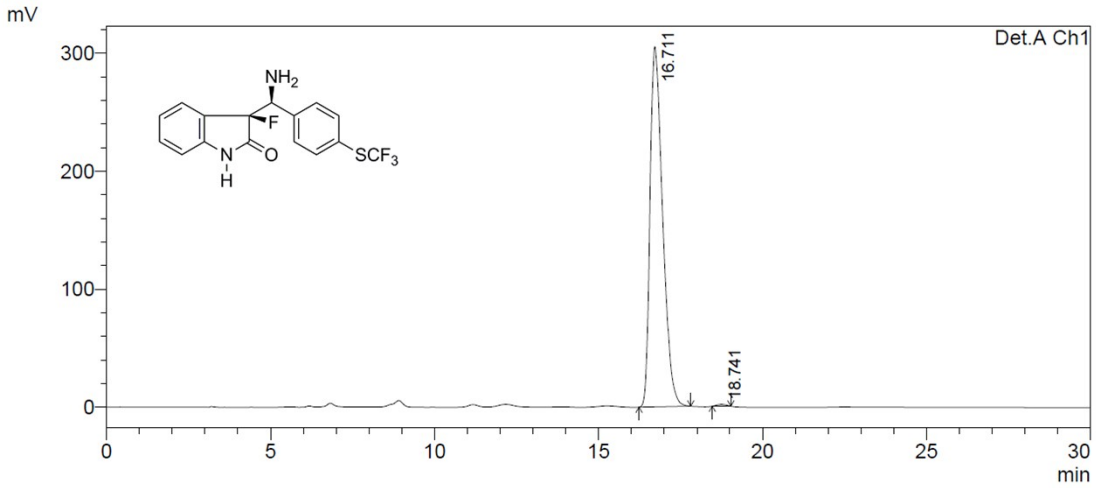
6. HPLC spectra of deprotection product 14

HPLC spectrum of **racemic-14**



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.878	8207660	324798	15.760	17.789
2	16.616	17944787	657839	34.456	36.029
3	18.600	16817207	588625	32.291	32.239
4	22.127	9110306	254578	17.493	13.943
Total		52079960	1825840	100.000	100.000

HPLC spectrum of **(3*S*, 2'*S*)-14**



Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.711	8146878	305552	99.622	99.493
2	18.741	30952	1557	0.378	0.507
Total		8177830	307109	100.000	100.000