Supporting Information for

Enantioselective Fluorination of 3-Indolinone-2-carboxylates with NFSI Catalyzed by Chiral Bisoxazolines

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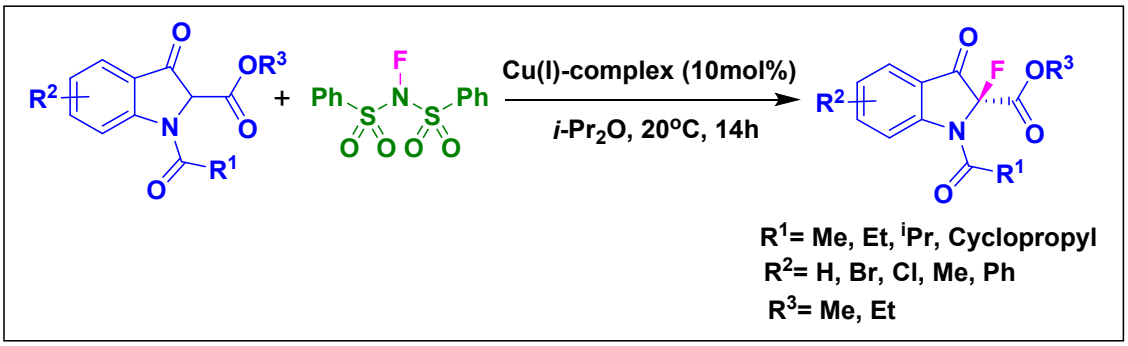
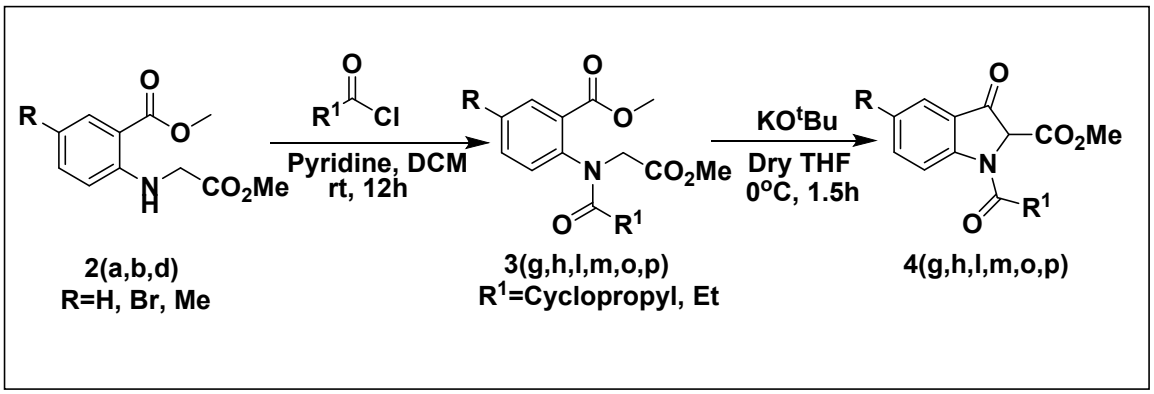


1.General information

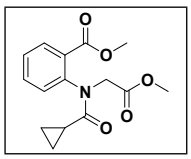
All reactions were performed in oven-dried round bottom flasks, and the flasks were fitted with rubber septa and the reactions were conducted under a nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel 100-200 mesh. Thin layer chromatography (TLC) plates were visualized by exposure to ultraviolet light at 254 nm, and by exposure to iodine vapours and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (approx. 250 °C). Organic solutions were concentrated on rotary evaporator at 35–40 °C. Melting points (MP) were obtained on Buchi B-540. ^{1}H, ^{13}C (proton decoupled) and ^{19}F NMR spectra were recorded in $CDCl_3$ using 300, 400 or 500 MHz (^{1}H), 101 MHz (^{13}C) and 376 or 377 MHz (^{19}F). Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra and HRMS were recorded on mass spectrometer by Electrospray ionization (ESI) and Atmosphericpressure chemical ionization (APCI) techniques. Infrared spectra (IR) were recorded with a thin film of solvated ($CHCl_3$) sample. Optical rotations were recorded on Perkin Elmer (model- 341) polarimeter. Enantiomeric excesses (ee) were determined by HPLC (Shimadzu) analysis by using DAICEL Chiralpak OD-H, OJ-H etc. columns.

2.(i) Experimental procedures and spectral data of compounds [3(g,h,l,m,o,p), 4(g,h,l,m,o,p)]:



Scheme-1. Preparation of 4(g,h,l,m,o,p)

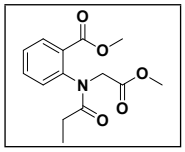
Methyl 2-(*N*-(2-methoxy-2-oxoethyl)cyclopropanecarboxamido)benzoate (3g):



To a stirred solution of **2a** (600 mg, 2.68 mmol, 1 equiv) in 20 mL dry CH_2Cl_2 was added anhydrous pyridine (0.8 mL,8.07 mmol, 3 equiv) at room temperature under nitrogen atmosphere. The resulting solution was stirred at 25 °Cfor 30 min, thencyclopropanecarbonyl chloride (0.5 mL, 5.38 mmol, 2 equiv) was added dropwise to the above solution at 0°C. After complete addition, the mixture was stirred at ambient temperature for overnight. Upon

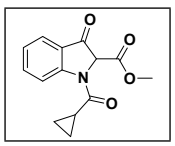
completion, the mixture was diluted with CH_2Cl_2 (10 mL), washed with 1N HCl (2x50 mL), and the organic layer was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane (1/1, v/v) mixture to afford the pure product **3g** (750 mg, 96% yield) as a colourless semi-solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.73 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.61 (td, *J* = 7.7, 1.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 4.98 (d, *J* = 17.4 Hz, 1H), 3.89 (s, 3H), 3.76 – 3.70 (m, 4H), 1.17 (ddd, *J* = 7.9, 4.5, 3.3 Hz, 1H), 1.08 – 0.91 (m, 2H), 0.66 – 0.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 170.1, 166.1, 142.3, 133.5, 131.7, 131.2, 129.3, 128.6, 52.6, 52.1, 51.4, 12.5, 8.6, 8.5. HRMS (*ESI Orbitrap*) calcd for $C_{15}H_{18}O_5N$ $[M+H]^+$:292.1179, Found: 292.1171.

Methyl 2-(*N*-(2-methoxy-2-oxoethyl)propionamido)benzoate (3h):



To a stirred solution of **2a** (500 mg, 2.24 mmol, 1 equiv) in 10 mL dry CH_2Cl_2 was added anhydrous pyridine (0.67 mL, 6.70 mmol, 3 equiv) at room temperature under nitrogen atmosphere. The resulting solution was stirred at 25 °C for 30 min, thenpropanoyl chloride (0.4mL, 4.5 mmol, 2 equiv) was added dropwise to the above solution at 0°C. After complete addition, the mixture was stirred at ambient temperature for overnight. Upon completion, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with 1N HCl (2x50 mL), and the organic layer was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane (1/1, v/v) mixture to afford the pure product **3h** (648 mg, 98.6% yield) as a very light yellow semi-solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.59 (td, *J* = 7.7, 1.5 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 4.97 (d, *J* = 17.4 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.68 (d, *J* = 17.4 Hz, 1H), 2.01 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 170.0, 165.9, 142.2, 133.5, 131.8, 131.2, 128.8, 52.7, 52.1, 51.1, 29.7, 27.2, 9.2.HRMS (*APCI Orbitrap*) calcd for $C_{14}H_{18}O_5N$ $[M+H]^+$: 280.1179, Found: 280.1178

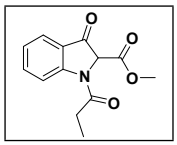
Methyl 1-(cyclopropanecarbonyl)-3-oxoindoline-2-carboxylate (4g):



To a stirred solution of **3g** (980 mg, 3.36 mmol, 1 equiv) in 20 mL dry THF at 0 °C was added a solution of ^{t}BuOK (453 mg, 4.03 mmol, 1.2 equiv in 20 mL dry THF) dropwise under argon atmosphere over 10 min. The resulting solution was allowed to stir at 25 °C for 1 h. The solvent THF was removed under reduced pressure at 40 °C to afford the residue, which was dissolved in 30 mL H_2O/AcOH (5:1) at 0 °C with a rapid stirring and extracted with EtOAc(2x50 mL). The combined extracts were washed with brine solution (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash

column chromatography on silica gel (60- 120 mesh) using ethyl acetate/*n*-hexane (3/7, v/v) mixture to afford the pure product **4g** (834 mg, 95.6% yield) as a colourless solid. mp.106^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 5.20 (s, 1H), 3.86 (s, 3H), 1.31-1.21 (m, 1H), 1.15 (s, 2H), 0.96 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 171.5, 165.0, 138.1, 124.7, 124.5, 118.9, 118.8, 118.7, 68.2, 53.7, 14.3, 9.8, 9.1. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{14}NO_4[M+H]^+$: 260.0761, Found: 260.0756.

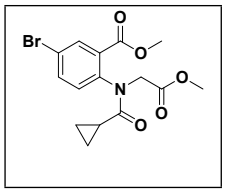
Methyl 3-oxo-1-propionylindoline-2-carboxylate (4h):



To a stirred solution of **3h** (800 mg, 2.73 mmol, 1 equiv) in 20 mL dry THF at 0 ^{o}C was added a solution of ^{t}BuOK (385 mg, 3.4 mmol, 1.2 equiv, in 20 mL dry THF) dropwise under argon atmosphere over 10 min. The resulting solution was allowed to stir at 25 °C for 1 h. THF was removed under reduced pressure at 40 ^{o}C to afford the residue, which was dissolved in 30 mL H_2O/AcOH (5:1) at 0 ^{o}C with a rapid stirring and extracted with EtOAc(2x50 mL). The combined extracts were washed with brine solution (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (60- 120 mesh) using ethyl acetate/*n*-hexane (3/7, v/v) mixture to afford the pure product **4h** (680 mg, 95.4% yield) as a colorless solid. mp.130^{o}C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.74 (d, *J*= 7.1 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.01 (s, 1H), 3.85 (s, 3H), 2.42 (s, 1H), 2.30 (s, 1H), 1.24 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 171.7, 164.9, 138.1, 124.7, 124.6, 122.5, 120.4, 118.8, 67.9, 53.8, 29.1, 8.6. HRMS (*ESI Orbitrap*) calcd for $C_{13}H_{14}O_4N$ $[M+H]^+$: 248.0917, Found: 248.0912.

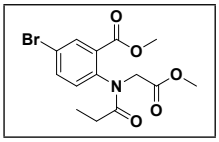
Similarly, all other starting materials like **4l**,**4m**,**4o** and **4p** were also prepared by following the same processes of **4g** and **4h:**

Methyl 5-bromo-2-(*N*-(2-methoxy-2-oxoethyl)cyclopropanecarboxamido)benzoate (3l):



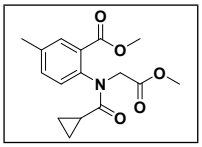
Yield (702 mg, 95%), pale yellow oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.72 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 4.98 (d, *J* = 17.5 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.70 (d, *J* = 17.5 Hz, 1H), 1.16 (tt, *J* = 7.9, 4.6 Hz, 1H), 1.09 – 1.01 (m, 1H), 0.94 (m, 1H), 0.68 – 0.58 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 170.0, 164.7, 141.3, 136.5, 134.6, 133.0, 130.9, 122.4, 52.9, 52.2, 51.2, 12.5, 9.1, 8.7, 8.6. HRMS (*ESI Orbitrap*) calcd for $C_{15}H_{17}O_5NBr$ $[M+H]^+$: 370.0285, Found:370.0273.

Methyl 5-bromo-2-(*N*-(2-methoxy-2-oxoethyl)propionamido)benzoate (3m):



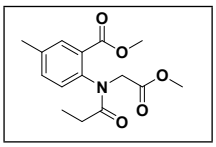
Yield (653 mg, 92%), pale yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 4.96 (d, *J* = 17.4 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H), 3.64 (d, *J* = 17.4 Hz, 1H), 2.13 – 1.91 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 170.0, 164.6, 141.2, 136.6, 134.7, 132.9, 130.5, 122.6, 53.0, 52.2, 50.9, 27.4, 9.2. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{17}O_5NBr$ $[M+H]^+$: 358.0285, Found: 358.0280.

Methyl 2-(*N*-(2-methoxy-2-oxoethyl)cyclopropanecarboxamido)-5-methylbenzoate (3o):



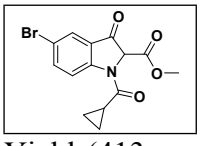
Yield (744 mg, 96%), colourless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.41 (dd, *J* = 1.5, 0.7 Hz, 1H), 4.97 (d, *J* = 17.4 Hz, 1H), 3.88 (s, 3H), 3.83 – 3.66 (m, 4H), 2.42 (s, 3H), 1.20 (ddd, *J* = 7.9, 4.5, 3.3 Hz, 1H), 1.10 – 0.98 (m, 1H), 0.96 – 0.88 (m, 1H), 0.67 – 0.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 170.2, 166.3, 139.7, 138.8, 134.1, 132.1, 131.0, 128.8, 52.6, 52.1, 51.4, 21.0, 12.4, 8.5, 8.4. HRMS (*ESI Orbitrap*) calcd for $C_{16}H_{20}O_5N$ $[M+H]^+$: 306.1336, Found: 306.1329.

Methyl 2-(*N*-(2-methoxy-2-oxoethyl)propionamido)-5-methylbenzoate (3p):



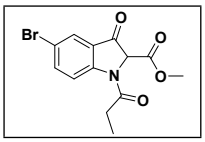
Yield (628 mg, 85%), colourless oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.0, 0.4 Hz, 1H), 5.07 – 4.84 (m, 1H), 3.88 (dd, *J* = 1.9, 0.9 Hz, 3H), 3.73 (dd, *J* = 2.1, 1.0 Hz, 3H), 3.66 (dd, *J* = 17.4, 0.8 Hz, 1H), 2.42 (d, *J* = 0.9 Hz, 3H), 2.15 – 1.81 (m, 2H), 1.03 (tdd, *J* = 7.4, 2.1, 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 170.1, 166.0, 139.6, 139.0, 134.2, 132.2, 130.8, 128.3, 52.6, 52.0, 51.1, 27.1, 21.0, 9.2. HRMS (*ESI Orbitrap*) calcd for $C_{15}H_{20}O_5N$ $[M+H]^+$: 294.1341, Found: 294.1339.

Methyl 5-bromo-1-(cyclopropanecarbonyl)-3-oxoindoline-2-carboxylate (4l):



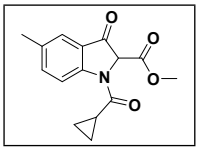
Yield (413 mg, 90%), pale yellow solid, mp.123^{o}C,^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.76 (dd, *J* = 8.8, 1.9 Hz, 1H), 5.22 (s, 2H), 3.86 (s, 6H), 1.21 (d, *J* = 6.1 Hz, 1H), 1.14 (s, 2H), 0.97 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 172.4, 171.4, 164.5, 140.9, 140.5, 127.2, 120.2, 117.5, 68.3, 54.5, 53.9, 10.0, 9.3. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{13}O_4NBr$ $[M+H]^+$: 337.9867, Found: 337.9870.

Methyl 5-bromo-3-oxo-1-propionylindoline-2-carboxylate (4m):



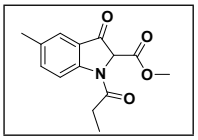
Yield (398 mg, 87%), white solid, mp.151°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.86 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 5.04 (s, 1H), 3.87 (s, 3H), 2.42 (s, 1H), 2.31 (s, 1H), 1.24 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 171.6, 171.6, 164.4, 140.6, 127.2, 120.3, 120.3, 117.6, 68.0, 54.0, 29.0, 8.6. HRMS (*ESI Orbitrap*) calcd for $C_{13}H_{13}O_4NBr$ $[M+H]^+$: 326.0010, Found: 326.0018.

Methyl 1-(cyclopropanecarbonyl)-5-methyl-3-oxoindoline-2-carboxylate (4o):



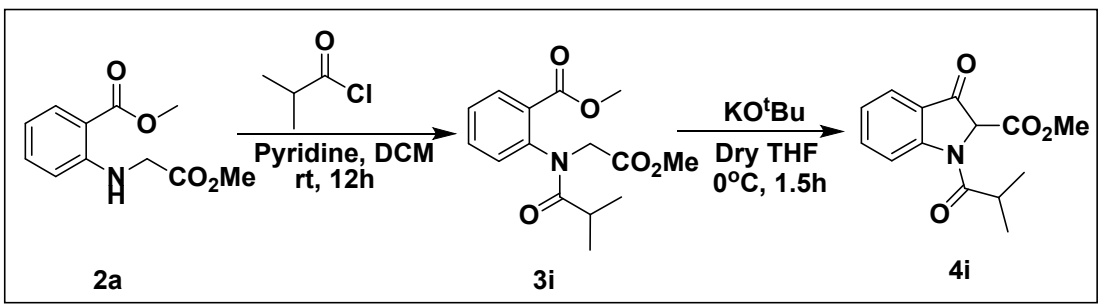
Yield (406 mg, 91%), paleyellow solid, mp.133°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.54 (s, 1H), 7.50 (dd, *J* = 8.5, 1.4 Hz, 1H), 5.19 (s, 1H), 3.84 (s, 3H), 2.38 (s, 3H), 1.24 (dd, J = 3.7, 2.2 Hz, 1H), 1.12 (s, 2H), 0.94 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 171.2, 165.1, 152.6, 139.2, 134.5, 124.2, 123.1, 118.4, 68.4, 53.6, 20.7, 14.1, 9.7, 8.9. HRMS (*ESI Orbitrap*) calcd for $C_{15}H_{16}O_4N$ $[M+H]^+$: 274.1071, Found: 274.1079.

Methyl 5-methyl-3-oxo-1-propionylindoline-2-carboxylate (4p):



Yield (397 mg, 85%), white solid, mp.130°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 5.00 (s, 1H), 3.85 (s, 3H), 2.38 (s, 3H), 2.30 (s, 1H), 1.75 (s, 1H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 171.4, 165.0, 152.6, 139.3, 134.7, 124.2, 122.9, 118.5, 68.1, 53.5, 28.9, 20.7, 8.6. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{16}O_4N$ $[M+H]^+$: 262.1074, Found: 262.1078.

2. (ii) Experimental procedures and spectral data of starting materials (3i,4i):



Scheme-2. Preparation of **4i**

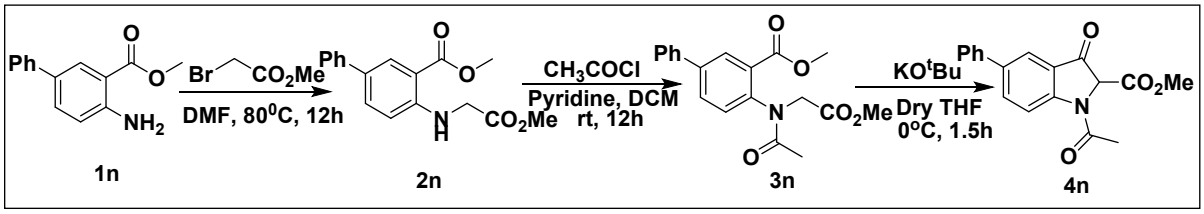
Methyl 2-(*N*-(2-methoxy-2-oxoethyl)isobutyramido)benzoate (3i):

To a stirred solution of **2a** (600 mg, 2.69 mmol, 1 equiv) in 10 mL dry CH_2Cl_2 was added anhydrous pyridine (0.8 mL,8.07 mmol, 3 equiv) at room temperature under nitrogen atmosphere. The resulting solution was stirred at 25 °C for 30 min, thenisobutyryl chloride (0.6 mL, 5.38 mmol, 2 eq) was added dropwise to the above solution at 0°C. After complete addition, the reaction mixture was stirred at ambient temperature for overnight. Upon completion, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with 1N HCl (2x50 mL) and the organic layer was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane (1/1, v/v) mixture to afford the pure product **3i** (yellow oil, 754mg, 95.6%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 1H), 7.67 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.61 (td, *J* = 7.6, 1.6 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 4.94 (d, *J* = 17.3 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.68 (d, *J* = 17.3 Hz, 1H), 2.33 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 170.0, 166.0, 142.3, 133.5, 131.8, 130.8, 128.9, 128.7, 52.6, 52.1, 51.2, 31.4, 19.7, 18.8. HRMS (*ESI Orbitrap*) calcd for $C_{15}H_{20}O_5N$ $[M+H]^+$: 294.1336, Found: 294.1325.

Methyl 1-isobutyryl-3-oxoindoline-2-carboxylate (4i):

To a stirred solution of **3i** (850 mg, 2.90 mmol, 1.0 equiv) in 20 mL dry THF at 0 °C was added a solution of ^{t}BuOK (390 mg, 3.48 mmol, 1.2 equiv, in 20 mL dry THF) dropwise under argon atmosphere over 10 min. The resulting solution was allowed to stir at 25 °C for 1 h. THF was removed under reduced pressure at 40 °C to afford the residue, which was dissolved in 30 mL H_2O/AcOH (5:1) at 0 °C with a rapid stirring and extracted with EtOAc(2x50 mL). The combined extracts were washed with brine solution (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (60- 120 mesh) using ethyl acetate/*n*-hexane (3/7, v/v) mixture to afford the pure product **4i** (710 mg, 93.8% yield) as a dark green oil, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.77 (d, *J* = 7.0 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 5.06 (s, 1H), 3.86 (s, 3H), 2.50 (s, 1H), 1.23 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 175.6, 165.0, 138.1, 124.6, 123.3, 123.2, 119.1, 119.1, 67.9, 53.8, 34.2, 20.0, 18.8. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{16}O_4N$ $[M+H]^+$: 262.1772, Found: 262.1780.

2.(iii) Experimental procedures and spectral data of starting materials (2n,3n,4n):



Scheme-3. Preparation of 4n

Methyl 4-((2-methoxy-2-oxoethyl)amino)-[1,1'-biphenyl]-3-carboxylate (2n):

To a stirred solution of **1n** (500 mg, 2.2 mmol, 1 equiv) in (30 mL) DMF was added methyl bromoacetate (0.3 mL, 3.30 mmol, 1.5 equiv) at room temperature under nitrogen atmosphere for 5 min. The resulting solution was stirred for 12 h at 80 ^{o}C .Then the mixture was allowed to stir at 25 °C and poured into ice water (100 mL).The resulting solution was extracted with EtOAc (2x100 mL). The combined extracts were washed with a saturated solution of$NaHCO_3$ (2x100 mL), water(3x100 mL) followed by a brine solution (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Purification of the crude product was carried out by flash column chromatography on silica gel (60-120 mesh) using ethyl acetate/*n*-hexane (1/4, v/v) mixture to afford the pure product **2n** (560mg, 85% yield) as a white solid, mp. 127°C,^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (t, *J* = 4.8 Hz, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 7.63 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 3H), 7.40 (t, *J* = 7.7 Hz, 3H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 4.07 (d, *J* = 5.4 Hz, 3H), 3.91 (s, 4H), 3.81 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 168.8, 149.2, 140.3, 133.3, 130.2, 128.8, 128.7, 126.5, 126.3, 111.7, 111.3, 52.4, 51.8, 45.0. HRMS (*ESI Orbitrap*) calcd for $C_{17}H_{18}O_4N$ $[M+H]^+$: 300.1230, Found: 300.1219.

Methyl 4-(*N*-(2-methoxy-2-oxoethyl)acetamido)-[1,1'-biphenyl]-3-carboxylate (3n):

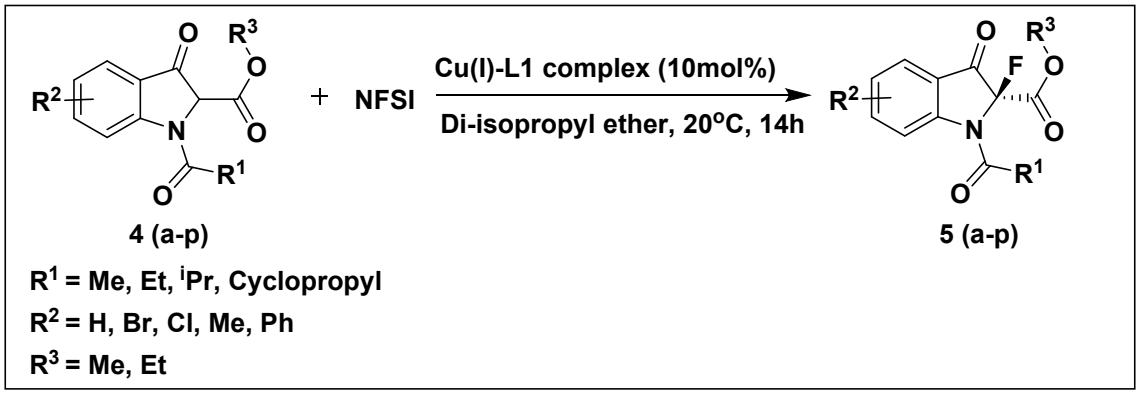
To a stirred solution of **2n** (400 mg, 1.34 mmol, 1 equiv) in 10 mL dry CH_2Cl_2 was added anhydrous pyridine (0.32 mL, 4.01 mmol, 3 equiv) at room temperature under nitrogen atmosphere. The resultant solution was stirred at 25 °C for 30 min, then acetyl chloride (0.2 mL, 2.67 mmol, 2 equiv) was added dropwise to the above solution at 0^{o}C. After complete addition, the reaction mixture was stirred at ambient temperature for overnight. Upon completion, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with 1N HCl (2x50 mL) and the organic layer was dried over Na_2SO_4. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane (1/1, v/v) mixture to afford the pure product **3n** (420 mg, 92% yield) as a semi-solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.2 Hz, 1H), 7.80 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.38 (m, 1H), 5.00 (d, *J* = 17.4 Hz, 1H), 3.93 (s, 3H), 3.73 (d, *J* = 19.3 Hz, 4H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.0, 165.9, 142.0, 141.5, 138.9, 131.9, 131.5, 130.4, 129.1, 128.9, 128.4, 127.1, 52.8, 52.2, 51.0, 22.1. HRMS (*ESI Orbitrap*) calcd for $C_{19}H_{20}O_5N$ $[M+H]^+$: 342.1336, Found: 342.1327.

Methyl 1-acetyl-3-oxo-5-phenylindoline-2-carboxylate (4n):

To a stirred solution of **3n** (400 mg, 1.17 mmol, 1eq.) in 20 mL dry THF at 0 ^{o}C was added a solution of t-BuOK (157mg, 1.4 mmol, 1.2 eq, in 20 mL dry THF) dropwise under argon atmosphere over 10 min. The resulting solution was allowed to stir at 25 °C for 1 h. THF was removed under reduced pressure at 40 ^{o}C to afford the residue, which was dissolved in30 mL H_2O/AcOH (5:1) at 0 ^{o}C with a rapid stirring and extracted with EtOAc(2x50 mL). The combined extracts were washed with a brine solution (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by a flash column chromatography on silica gel (60- 120 mesh) using ethyl acetate/*n*-hexane (3/7, v/v) mixture to afford the pure

product **4n**(330mg, 91% yield) as a yellow solid, mp. 152°C,^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 5.06 (s, 1H), 3.89 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 168.3, 164.8, 153.2, 138.9, 138.1, 137.1, 129.1, 128.0, 126.9, 123.5, 122.4, 119.1, 68.9, 54.0, 23.8. HRMS (*ESI Orbitrap*) calcd for $C_{18}H_{16}O_4N$ $[M+H]^+$: 310.1074, Found: 310.1079.

2. (iv) Experimental procedure and characterization data of products:



Enantioselective electrophilic fluorination (4a):

Preparation of racemic compounds:

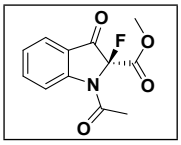
A flame dried 20 mL screw cap reaction tube with a stir bar was evacuated, and back filled with nitrogen. To this tube was charged with a fluorinating agent *N*-fluorobenzenesulfonimide (NFSI) (54 mg, 0.17 mmol, 0.8 equiv) and 10 mL di-isopropyl ether followed by the addition of substrate **4a**(50 mg, 0.22 mmol, 1 equiv) and Potassium carbonate (0.6 equiv). The reaction mixture was stirred for overnight at room temperature and upon consumption of the starting material, the solvent was evaporated to provide the crude product, which was purified by column chromatography using ethyl acetate/*n*-hexane (1/19 to 1/9 v/v) mixture to afford the pure product **5a**(43 mg) as a white solid.

Preparation of chiral compounds:

A flame dried 20 mL screw cap reaction tube with a stir bar was evacuated, and back filled with nitrogen. To this tube was charged with a fluorinating agent *N*-fluorobenzenesulfonimide (NFSI) (54 mg, 0.17 mmol, 0.8 equiv) and 10 mL di-isopropyl ether followed by 10 mol% of Cu(I)-ligand (L1) complex under nitrogen atmosphere. After stirring for 30 min at room temperature, the substrate **4a** (50 mg, 0.22 mmol, 1 equiv) was added and themixture was stirred at20°C for 14h. The reaction was monitored by TLC. Upon consumption of the starting material, the solvent was evaporated to provide the crude

product, which was purified by column chromatography using ethyl acetate/*n*-hexane (1/19 to 1/9 v/v) mixture to afford the pure product **5a** (40 mg) as a white solid.

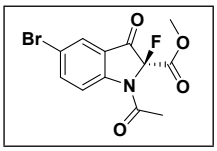
Methyl (*S*)-1-acetyl-2-fluoro-3-oxoindoline-2-carboxylate (5a):



Yield (40 mg, 90%), white solid, mp.118°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.80 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.75 (ddd, *J* = 8.6, 7.4, 1.4 Hz, 1H), 7.31 (td, *J* = 7.6, 0.7 Hz, 1H), 3.91 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9 (d, J_{C-F} = 16.5 Hz), 168.3, 163.5 (d, J_{C-F} = 35.8 Hz), 153.7, 139.1, 125.6, 125.5, 119.6, 118.4, 94.7 (d, J_{C-F} = 229.9 Hz), 54.4, 23.8. ^{19}F NMR (377 MHz, 3>) δ -138.38. IR (thin film): ν_{max}/cm^{-1} 1756, 1701, 1582, 1496, 1365, 1174, 1148, 762. HRMS (*ESI Orbitrap*) calcd for $C_{12}H_{11}O_4NF$ $[M+H]^+$:252.0667, Found: 252.0666. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (23.78 min), major (27.34 min), 95% ee; $[\alpha]_D^{20}$ +38.4 (*c* = 0.8, $CHCl_3$).

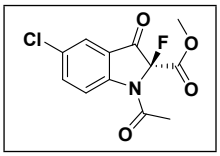
Similarly, all other reactions were carried out according to general procedure to provide fluoro compounds **5b-u**:

Methyl (*S*)-1-acetyl-5-bromo-2-fluoro-3-oxoindoline-2-carboxylate (5b):



Yield (48 mg, 92%),pale yellow solid, mp. 132°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.90 (d, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.91 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.7 (d, J_{C-F} = 16.8 Hz), 168.2, 163.0 (d, J_{C-F} = 35.8 Hz), 152.6, 141.5, 128.1, 121.2 119.9, 118.5, 94.6 (d, J_{C-F} = 231.6 Hz), 54.5, 23.7. ^{19}F NMR (377 MHz, 3>) δ -137.95. HRMS (*ESI Orbitrap*) calcd for $C_{12}H_{10}O_4NBrF$ $[M+H]^+$: 329.9766, Found: 329.9761. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (23.24 min), major (33.15 min), 97% ee; $[\alpha]_D^{20}$ +40.5 (*c* =0.7, $CHCl_3$).

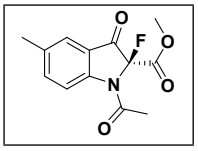
Methyl (*S*)-1-acetyl-5-chloro-2-fluoro-3-oxoindoline-2-carboxylate (5c):



Yield (45 mg, 85%), white solid, mp.98°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.75 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.91 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9 (d, J_{C-F} = 17.0 Hz), 168.2, 163.1 (d, J_{C-F} = 35.8 Hz), 152.2, 138.7, 131.3, 125.0, 120.9, 119.6, 94.8 (d, J_{C-F} = 231.3 Hz), 54.5, 23.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -137.92. IR (thin film): ν_{max}/cm^{-1} 1778, 1712, 1598, 1432, 1338, 1269, 1193, 1124, 1071, 770. HRMS (*ESI Orbitrap*) calcd for $C_{12}H_{10}O_4NClF$ $[M+H]^+$:286.0271, Found: 286.0269.

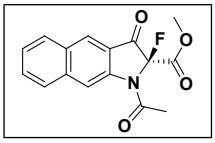
HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (26.71 min), major (34.71 min), 77% ee; $[\alpha]_D^{20}$ +10.3 (c =0.2, $CHCl_3$).

Methyl (*S*)-1-acetyl-2-fluoro-5-methyl-3-oxoindoline-2-carboxylate (5d):



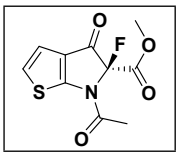
Yield (50 mg, 93%), white solid, mp. 114°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.58 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0 (d, J_{C-F} = 16.4 Hz), 168.1, 163.5 (d, J_{C-F} = 36.1 Hz), 140.1, 135.7, 125.3, 119.6, 118.2, 118.1, 95.0 (d, J_{C-F} = 230.0 Hz), 54.3, 23.7, 20.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -138.44. IR (thin film): ν_{max}/cm^{-1} 1783, 1744, 1705, 1492, 1379, 1329, 1246,1198, 764. HRMS (*ESI Orbitrap*) calcdfor $C_{13}H_{13}O_4NF$ $[M+H]^+$: 266.0823, Found: 266.0830. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (16.96 min), major (22.72 min), 98% ee; $[\alpha]_D^{20}$ +40.5 (*c* =0.7, $CHCl_3$).

Methyl (*S*)-1-acetyl-2-fluoro-3-oxo-2,3-dihydro-1*H*-benzo[*f*]indole-2-carboxylate (5e):



Yield (47 mg, 88%),pale yellow solid, mp. 156°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.40 (s, 1H), 7.93 (t, *J* = 9.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 3.91 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2 (d, J_{C-F} = 17.1 Hz), 168.9, 163.7 (d, J_{C-F} = 36.8 Hz), 145.4, 139.2, 131.0, 130.6, 130.3, 128.8, 128.3, 126.7, 119.4, 115.0, 95.4 (d, J_{C-F} = 230.1 Hz), 54.4, 23.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -135.86. IR (thin film): ν_{max}/cm^{-1} 1775, 1701, 1624, 1378, 1315, 1160, 760. HRMS (*ESI Orbitrap*) calcd for $C_{16}H_{13}O_4NF$ $[M+H]^+$: 302.0823, Found: 302.0836. HPLC analysis (DAICEL Chiralpak OD-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (11.73 min), major (12.62 min), 85% ee; $[\alpha]_D^{20}$ +50.6 (*c* =0.8, $CHCl_3$).

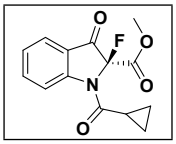
Methyl (*S*)-6-acetyl-5-fluoro-4-oxo-5,6-dihydro-4*H*-thieno[2,3-*b*]pyrrole-5-carboxylate (5f):



Yield (48 mg, 89%), white solid, mp. 138°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 14.8, 5.5 Hz, 2H), 3.93 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0 (d, J_{C-F} = 17.3 Hz), 170.3, 164.8, 162.5 (d, J_{C-F} = 34.8 Hz), 125.0, 123.1, 117.9, 98.7 (d, J_{C-F} = 236.9 Hz), 54.5, 21.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -138.78. IR (thin film): ν_{max}/cm^{-1} 1777, 1729, 1697, 1346, 1284, 1187, 756. HRMS (*ESI Orbitrap*) calcd for $C_{10}H_9O_4NFS$ $[M+H]^+$: 258.0231, Found: 258.0232. HPLC analysis (DAICEL Chiralpak OD-H, *n*-hexane/2- PrOH =

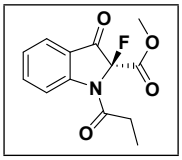
92/8, 1mL/min, 254 nm, minor (12.41 min), major (15.47 min), 83% ee; $[\alpha]_D^{20}$ +74.3 (*c* =0.8, $CHCl_3$).

Methyl (*S*)-1-(cyclopropanecarbonyl)-2-fluoro-3-oxoindoline-2-carboxylate (5g):



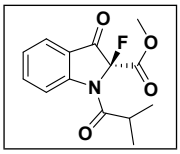
Yield (51 mg, 95%), white solid, mp.141°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1H), 7.80 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.32 – 7.26 (m, 1H), 3.88 (s, 3H), 1.99 – 1.78 (m, 1H), 1.46 – 1.34 (m, 1H), 1.07 – 0.97 (m, 2H), 0.97 – 0.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1 (d, J_{C-F} = 17.2 Hz), 172.1 (d, J_{C-F} = 2.6 Hz), 163.5 (d, J_{C-F} = 36.3 Hz), 154.1, 139.0, 125.6, 125.3, 119.5, 118.4, 94.8 (d, J_{C-F} = 228.2 Hz), 54.1, 14.0 (d, J_{C-F} = 4.5 Hz), 10.8, 9.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.56. IR (thin film): ν_{max}/cm^{-1} 1778, 1742, 1697, 1406, 1292, 1100, 760. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{13}O_4NF$ $[M+H]^+$: 278.0823, Found: 278.0831. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 95/5, 0.8mL/min, 254 nm, minor (25.49 min), major (33.34 min), 93% ee; $[\alpha]_D^{20}$ +21.2 (*c* =0.7, $CHCl_3$).

Methyl (*S*)-2-fluoro-3-oxo-1-propionylindoline-2-carboxylate (5h):



Yield (44 mg, 82%), white solid, mp.106°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 2.66 (dq, *J* = 14.7, 7.2 Hz, 1H), 2.34 (dd, *J* = 15.3, 7.1 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1 (d, J_{C-F} = 16.6 Hz), 172.2 (d, J_{C-F} = 2.1 Hz), 163.5 (d, J_{C-F} = 35.7 Hz), 153.9, 139.1, 125.8, 125.4, 119.6, 118.2, 94.6 (d, J_{C-F} = 229.7 Hz), 54.3, 29.1, 8.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.20. IR (thin film): ν_{max}/cm^{-1} 1783, 1744, 1469, 1374, 1292, 1185, 762. HRMS (*ESI Orbitrap*) calcd for $C_{13}H_{13}O_4NF$ $[M+H]^+$: 266.0846, Found: 266.0853. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2- PrOH = 90/10, 1mL/min, 254 nm, minor (14.27 min), major (22.45 min), 93% ee; $[\alpha]_D^{20}$ +11.8 (*c* =1.0, $CHCl_3$).

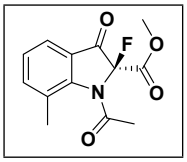
Methyl (*S*)-2-fluoro-1-isobutyryl-3-oxoindoline-2-carboxylate (5i):



Yield (31 mg, 58%), colourless liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.80 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 3.89 (s, 3H), 2.76 (s, 1H), 1.28 (d, *J* = 6.5 Hz, 3H), 1.16 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0 (d, J_{C-F} = 16.7 Hz), 176.6, 163.6 (d, J_{C-F} = 35.5 Hz), 154.0, 139.1, 125.7, 125.5, 119.9, 118.6, 94.7 (d, J_{C-F} = 229.7 Hz), 54.3, 34.6 (d, J_{C-F} = 1.7 Hz), 20.5, 18.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.54. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{15}O_4NF$ $[M+H]^+$= 280.0980, Found:

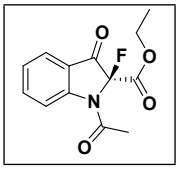
280.0973. HPLC analysis (DAICEL Chiralpak OJ-H, n-hexane/2- PrOH = 90/10, 1mL/min, 254 nm, minor (9.63 min), major (10.94 min), 59% ee; $[\alpha]_D^{20}$ +1.8 (*c* =1.9, $CHCl_3$).

Methyl (*S*)-1-acetyl-2-fluoro-7-methyl-3-oxoindoline-2-carboxylate (5j):



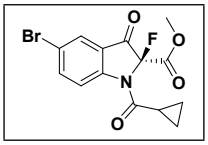
Yield (36 mg, 67%),light pink solid, mp.116°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 1H), 2.31 (d, *J* = 0.7 Hz, 1H), 2.29 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8 (d, *J* = 17.3 Hz), 168.0, 163.8 (d, *J* = 36.2 Hz), 153.0, 141.6, 129.8, 126.2, 123.3, 121.9, 95.7 (d, *J* = 230.7 Hz), 54.3, 24.0 (d, *J* = 2.4 Hz), 21.2.^{19}F NMR (377 MHz, $CDCl_3$) δ -136.29.HRMS (*ESI Orbitrap*) calcd for $C_{13}H_{13}O_4NF$ $[M+H]^+$: 266.0823, Found: 266.0827. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (20.79 min), major (25.05 min), 91% ee; $[\alpha]_D^{20}$+36.2 (*c*=1.2, $CHCl_3$).

Ethyl (*S*)-1-acetyl-2-fluoro-3-oxoindoline-2-carboxylate (5k):



Yield (32 mg, 60%),pale yellow liquid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.75 (ddd, *J* = 8.6, 7.4, 1.4 Hz, 1H), 7.31 (td, *J* = 7.7, 0.7 Hz, 1H), 4.46 – 4.28 (m, 2H), 2.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1 (d, $J_{C\text{-}F}$ = 16.6 Hz), 168.3 (d, $J_{C\text{-}F}$ = 1.0 Hz), 163.0 (d, $J_{C\text{-}F}$ = 35.4 Hz), 139.0, 129.2, 128.0, 125.7, 125.5, 119.6, 118.3, 94.7 (d, $J_{C\text{-}F}$ = 230.3 Hz), 64.1, 23.8, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.35. HRMS (*ESI Orbitrap*) Exact mass calcd for $C_{13}H_{13}O_4NF$ $[M+H]^+$: 266.0828, Found: 266.0822. HPLC analysis (DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1mL/min, 254 nm, minor (12.29 min), major (14.88 min), 84% ee, $[\alpha]_D^{20}$+23.5 (*c*=1.1, $CHCl_3$).

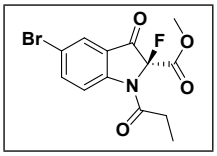
Methyl (*S*)-5-bromo-1-(cyclopropanecarbonyl)-2-fluoro-3-oxoindoline-2-carboxylate (5l):



Yield (50 mg, 95%), white solid, mp.135°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.9 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.80 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.88 (s, 3H), 1.86 (qdd, *J* = 7.8, 4.6, 1.3 Hz, 1H), 1.40 (ddt, *J* = 9.2, 7.0, 4.0 Hz, 1H), 1.08 – 0.97 (m, 2H), 0.97 – 0.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.0 (d, $J_{C\text{-}F}$ = 17.3 Hz), 172.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 163.1 (d, $J_{C\text{-}F}$ = 36.2 Hz), 152.9, 141.4, 128.0, 121.1, 120.0,118.3, 94.7 (d, $J_{C\text{-}F}$ = 229.5 Hz), 54.3, 13.9 (d, $J_{C\text{-}F}$ = 4.6 Hz), 11.0, 9.5.^{19}F NMR (377 MHz, $CDCl_3$) δ -136.09. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{12}O_4NBrF$ $[M+H]^+$: 358.0285, Found: 358.0280. HPLC analysis

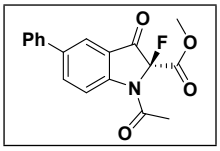
(DAICEL Chiralpak OJ-H, *n*-hexane/2- PrOH = 93/7, 0.8 mL/min, 254 nm, minor (18.44 min), major (29.97 min), 99% ee; $[\alpha]_D^{20}$ -13.4 (*c* =1.8, $CHCl_3$).

Methyl (*S*)-5-bromo-2-fluoro-3-oxo-1-propionylindoline-2-carboxylate (5m):



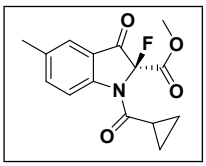
Yield (46 mg, 87%) white solid, mp.128°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.82 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.90 (s, 3H), 2.66 (dq, *J* = 21.9, 7.2 Hz, 1H), 2.33 (dd, *J* = 16.3, 7.4 Hz, 1H), 1.23 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9 (d, J_{C-F} = 16.7 Hz), 172.1, 163.1 (d, J_{C-F} = 35.7 Hz), 152.8, 141.5, 128.1, 121.2, 119.9, 118.4, 94.5 (d, J_{C-F} = 230.8 Hz), 54.5, 29.0, 8.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -137.67. IR (thin film): ν_{max}/cm^{-1} 1783, 1748, 1711, 1464, 1371, 1301, 1185, 1118, 771. HRMS (*ESI Orbitrap*) calcd for $C_{13}H_{12}O_4NBrF$ $[M+H]^+$: 344.1298, Found: 344.1304. HPLC analysis DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1 mL/min, 254 nm, minor (12.67 min), major (20.32 min), 95% ee; $[\alpha]_D^{20}$ -1.0 (*c* =0.3, $CHCl_3$).

Methyl (*S*)-1-acetyl-2-fluoro-3-oxo-5-phenylindoline-2-carboxylate (5n)



Yield (42 mg, 79%),pale yellow solid, mp.168°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.99 (s, 1H), 7.97 (d, *J* = 2.1 Hz, 1H), 7.58 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 3.92 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0 (d, J_{C-F} = 16.6 Hz), 168.2, 163.4 (d, J_{C-F} = 35.8 Hz), 152.9, 139.0, 138.5, 137.9, 129.2, 128.2, 126.9, 123.5, 120.2, 120.1, 118.6, 118.5, 95.1 (d, J_{C-F} = 229.9 Hz), 54.4, 23.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -138.08. IR (thin film): ν_{max}/cm^{-1} 1779, 1745, 1712, 1476, 1378, 1324, 1179, 1124, 1073, 772. HRMS (*ESI Orbitrap*) calcd for $C_{18}H_{15}FNO_4$ $[M+H]^+$: 328.0982, Found: 328.0977. HPLC analysis DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1 mL/min, 254 nm, minor (43.11 min), major (58.35 min), 92% ee; $[\alpha]_D^{20}$ -4.0 (*c* =0.3, $CHCl_3$).

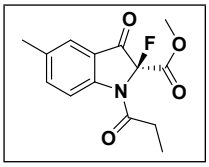
Methyl (*S*)-1-(cyclopropanecarbonyl)-2-fluoro-5-methyl-3-oxoindoline-2-carboxylate (5o):



Yield (48 mg, 90%),pale yellow solid, mp.98°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.54 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.87 (s, 3H), 2.40 (s, 3H), 1.94 – 1.82 (m, 1H), 1.50 – 1.33 (m, 1H), 1.09 – 0.97 (m, 2H), 0.95 – 0.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2 (d, J_{C-F} = 17.0 Hz), 171.9 (d, J_{C-F} = 2.6 Hz), 163.6 (d, J_{C-F} = 36.4 Hz), 152.3, 140.0, 135.5, 125.3, 119.6, 118.2, 95.0 (d, J_{C-F} = 228.0 Hz), 54.1, 20.7, 13.9 (d, J_{C-F} = 4.3 Hz),10.6, 9.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -136.64. IR (thin film): ν_{max}/cm^{-1} 1781, 1744, 1698, 1489, 1443, 1407, 1312, 1191, 1095, 776. HRMS (*ESI Orbitrap*) Exact mass

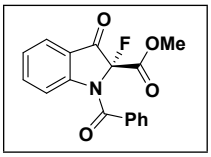
calcd for $C_{15}H_{15}O_4NF$ $[M+H]^+$: 292.0967, Found: 292.0962. HPLC analysis DAICEL Chiralpak OJ-H, *n*-hexane/2- PrOH = 90/10, 1 mL/min, 254 nm, minor (13.24 min), major (17.22 min), 92% ee; $[\alpha]_D^{20}$ +14.8 (*c* =0.3, $CHCl_3$).

Methyl (*S*)-2-fluoro-5-methyl-3-oxo-1-propionylindoline-2-carboxylate (5p):



Yield (46 mg, 86%), white solid, mp.88°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.58 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.67 (dq, *J* = 14.5, 7.1 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 1H), 1.23 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1 (d, J_{C-F} = 16.6 Hz), 172.0 (d, J_{C-F} = 2.2 Hz), 163.6 (d, J_{C-F} = 35.7 Hz), 152.1, 140.1, 135.5, 125.4, 119.7, 118.0, 94.9 (d, J_{C-F} = 229.6 Hz), 54.2, 29.4 (d, *J* = 75.1 Hz), 20.7, 8.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -138.20. IR (thin film): ν_{max}/cm^{-1} 1782, 1744, 1706, 1489, 1376, 1302, 1194, 1117, 1068, 768. HRMS (*ESI Orbitrap*) calcd for $C_{14}H_{15}O_4NF$ $[M+H]^+$: 280.0972, Found: 280.0977. HPLC analysis DAICEL Chiralpak OJ-H, *n*-hexane/2-PrOH = 90/10, 1 mL/min, 254 nm, minor (12.11 min), major (19.53 min), 95% ee; $[\alpha]_D^{20}$ +10.0 (*c* =0.3, $CHCl_3$).

Methyl (*R*)-1-benzoyl-2-fluoro-3-oxoindoline-2-carboxylate (5u):



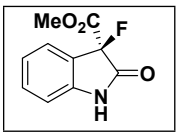
Yield (32 mg, 60%), yellowish white solid, mp. 159°C**,** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.78 (s, 1H), 7.70 – 7.65 (m, 1H), 7.64 (dd, *J* = 7.2, 1.0 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.28 (m, 1H), 3.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3 (d, J_{C-F} = 18.7 Hz), 169.0, 162.5 (d, J_{C-F} = 34.1 Hz), 153.8, 138.4, 133.9, 132.3, 128.7, 128.3 (d, J_{C-F} = 1.7 Hz), 125.9, 125.7, 120.3, 118.5, 94.8 (d, J_{C-F} = 230.6 Hz), 53.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -131.10. HRMS (*ESI Orbitrap*) calcd for $C_{17}H_{12}O_4NF$ $[M+H]^+$: 314.0823, Found**:** 314.0828, HPLC analysis DAICEL Chiralpak OD-H, *n*-hexane/2-PrOH = 90/10, 1 mL/min, 254 nm, major (13.78 min), minor (23.82 min), 58% ee; $[\alpha]_D^{20}$ +22.9 (*c* =0.6, $CHCl_3$).

Enantioselective electrophilic fluorination of methyl 2-oxoindoline-3-carboxylate (6)

A flame dried 20 mL screw cap reaction tube with a stir bar was evacuated, and back filled with nitrogen. To this tube was charged with a fluorinating agent *N*-fluorobenzenesulfonimide (NFSI) (66 mg, 0.21 mmol, 0.8 equiv) and 10 mL di-isopropyl ether followed by 10 mol% of Cu(I)-ligand (L1) complex under nitrogen atmosphere. After stirring for 30 min at room temperature, the substrate **6** (50 mg, 0.26 mmol, 1 equiv) was added and themixture was stirred at 20°C for 14h. The reaction was monitored by TLC. Upon consumption of the starting material, the solvent was evaporated to provide the crude

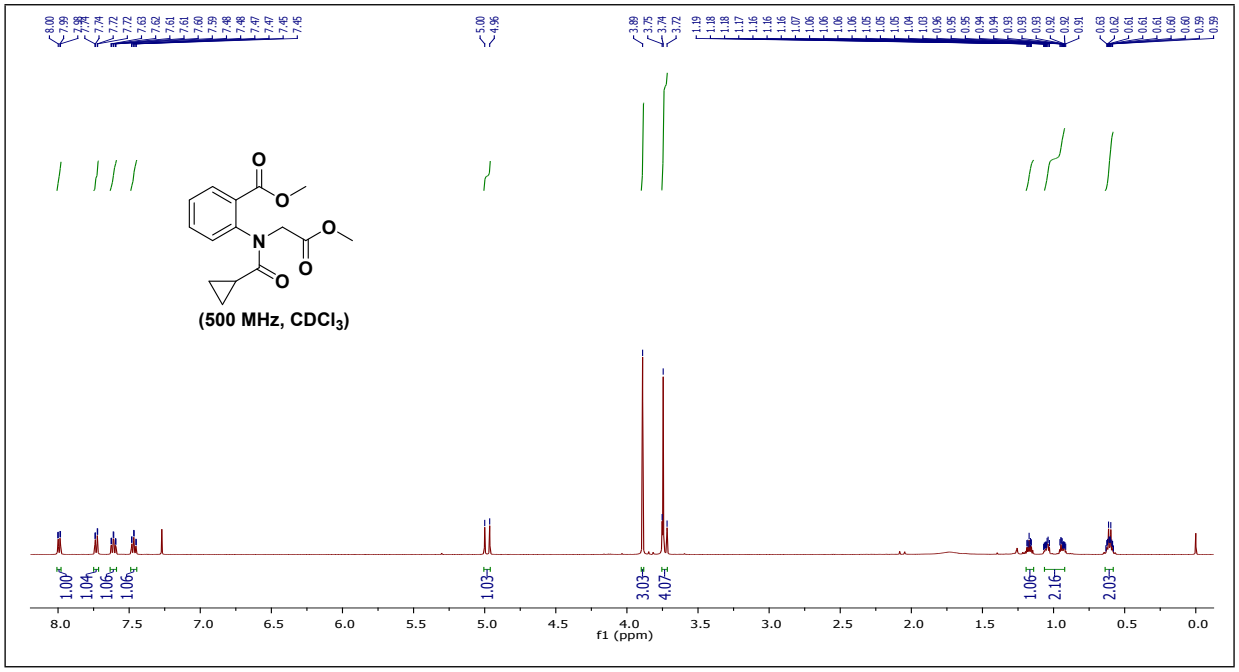
product, which was purified by column chromatography using ethyl acetate/*n*-hexane (1/19 to 1/9 v/v) mixture to afford the pure product **7** (36 mg) as a white solid.

Methyl (*R*)-3-fluoro-2-oxoindoline-3-carboxylate (7):

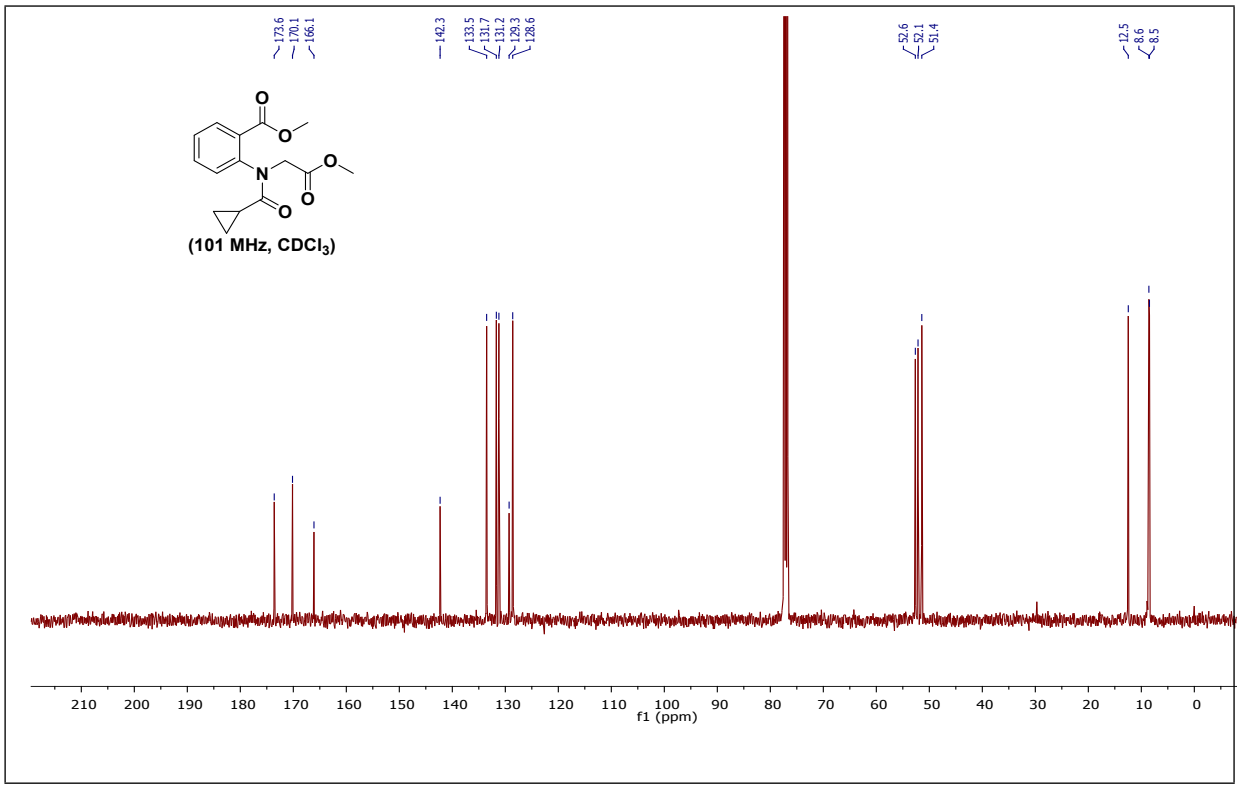


Yield (36 mg, 66%), orange white solid, mp. 132°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.40 (t, *J* = 7.0 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 165.6 (d, $J_{C\text{-}F}$ = 31.6 Hz), 142.3 (d, $J_{C\text{-}F}$ = 5.3 Hz), 132.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 125.3, 123.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 123.3 (d, $J_{C\text{-}F}$ = 19.4 Hz), 111.2, 90.4 (d, $J_{C\text{-}F}$ = 202.3 Hz), 53.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -164.40. HRMS (*ESI Orbitrap*) calcd for $C_{10}H_9O_3NF$ $[M+H]^+$: 210.0490, Found**:** 210.0485. HPLC analysis DAICEL Chiralpak OD-H, *n*-hexane/2-PrOH = 88/12, 1 mL/min, 254 nm, minor (7.83 min), major (9.76 min), 59% ee; $[\alpha]_D^{20}$ +34.2 (*c* =0.5, $CHCl_3$).

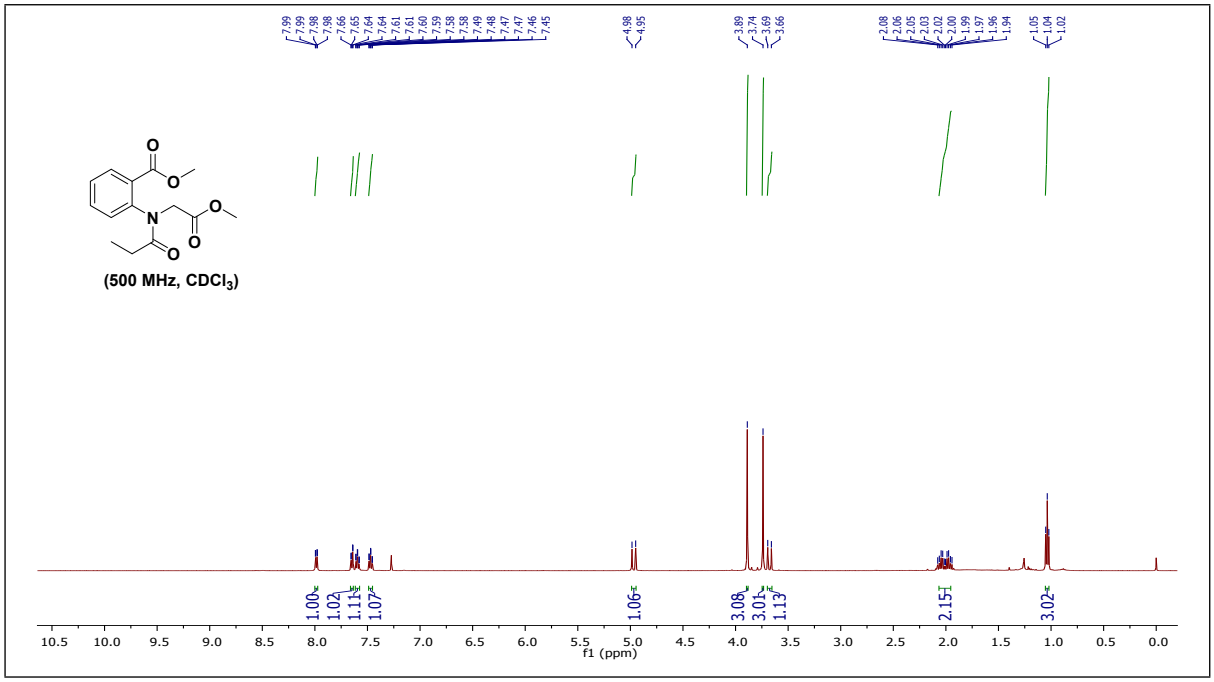
3.^{1}H & ^{13}C NMR spectra of starting materials: ^{1}H NMR spectrum of **3g:**



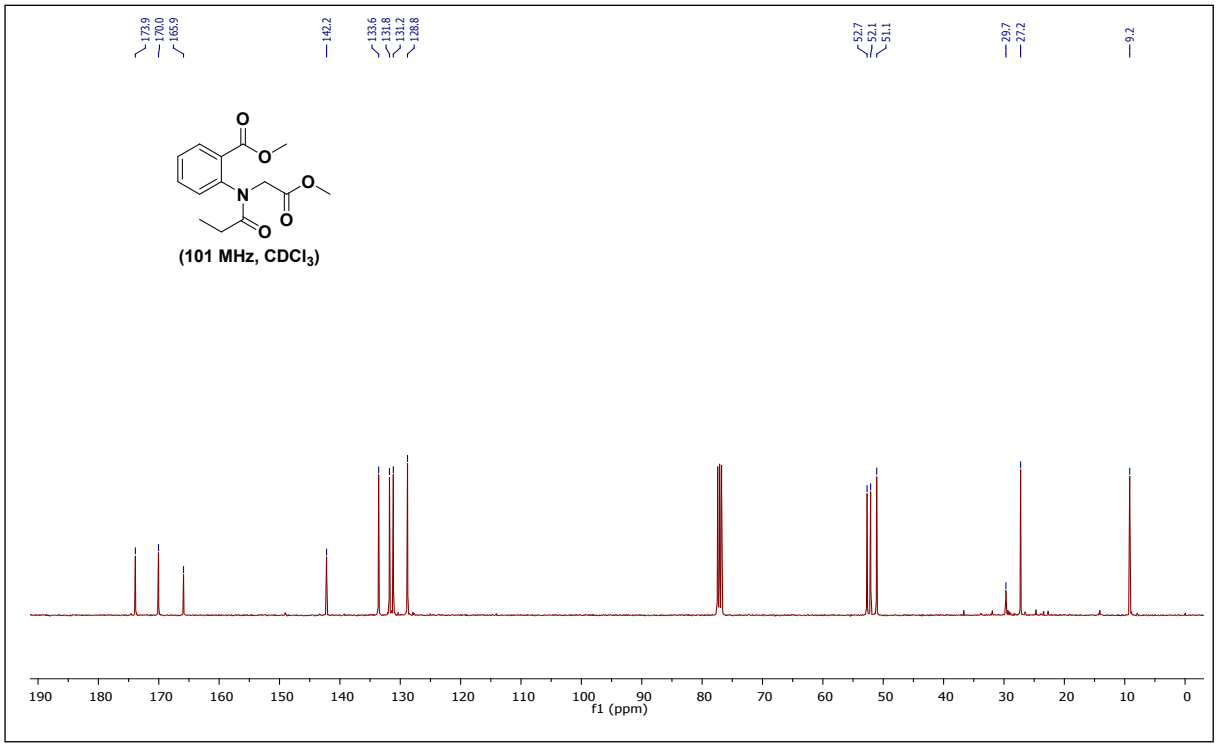
^{13}C NMR spectrum of **3g**:



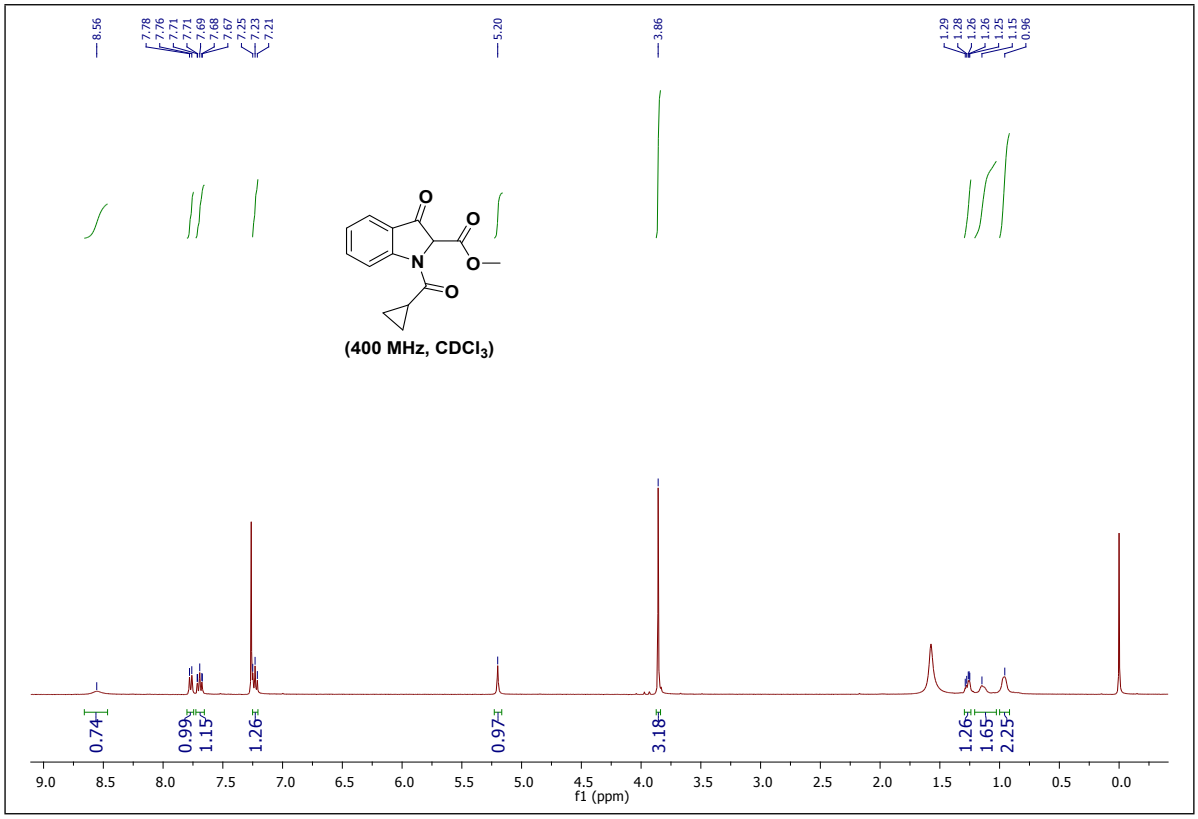
^{1}H NMR spectrum of **3h**:



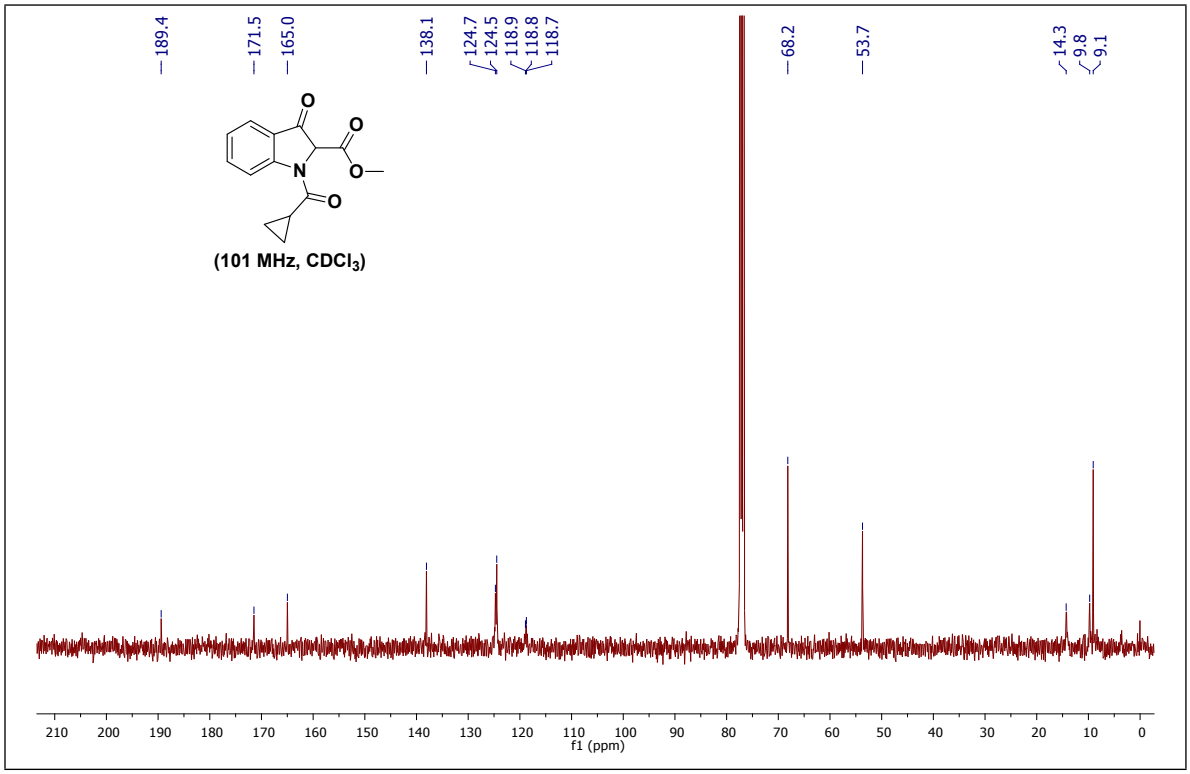
^{13}C NMR spectrum of **3h**:



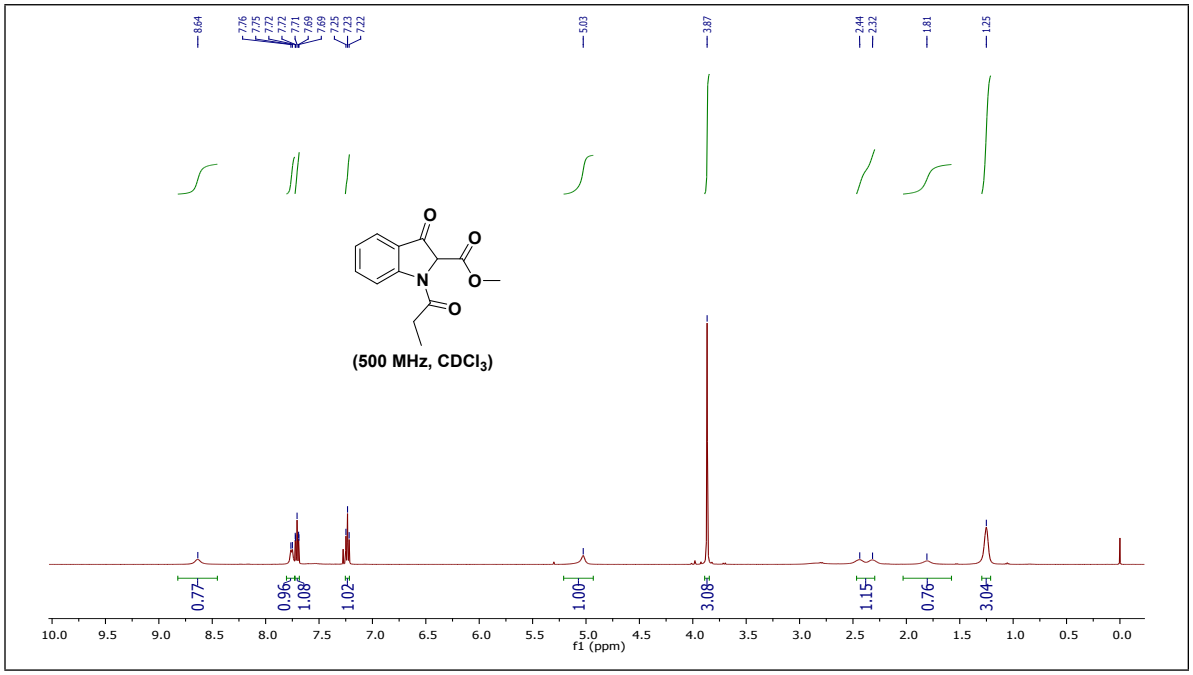
^{1}H NMR spectrum of **4g**:



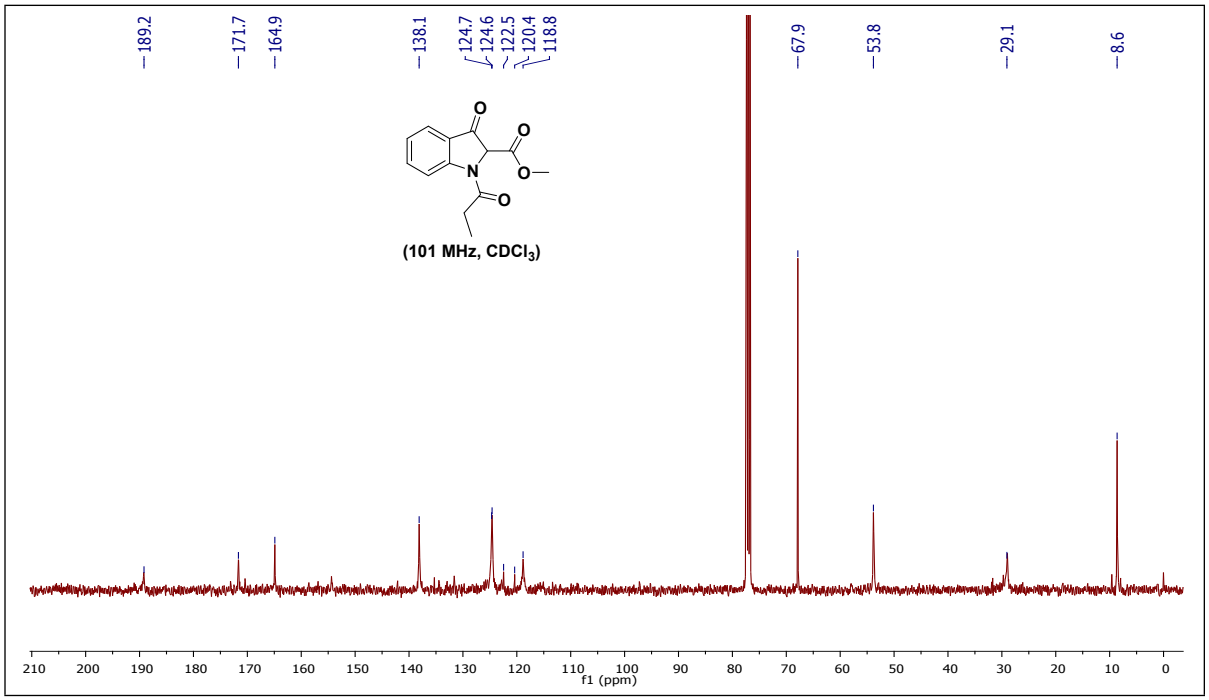
^{13}C NMR spectrum of **4g**:



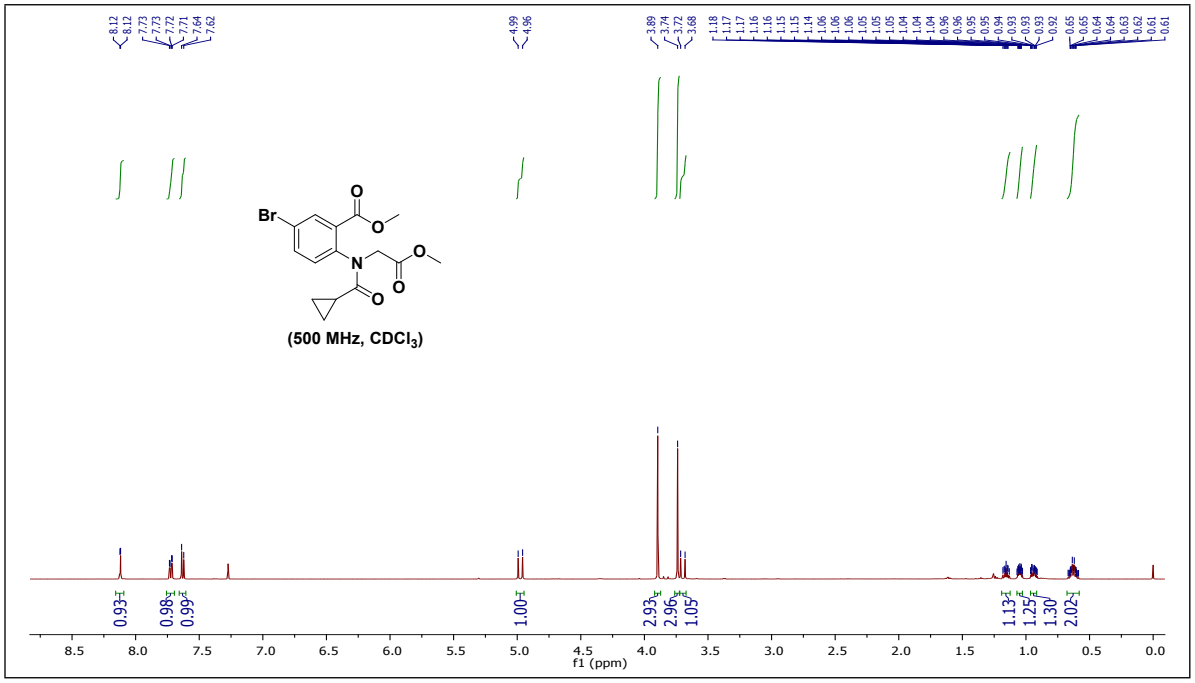
^{1}H NMR spectrum of **4h**:



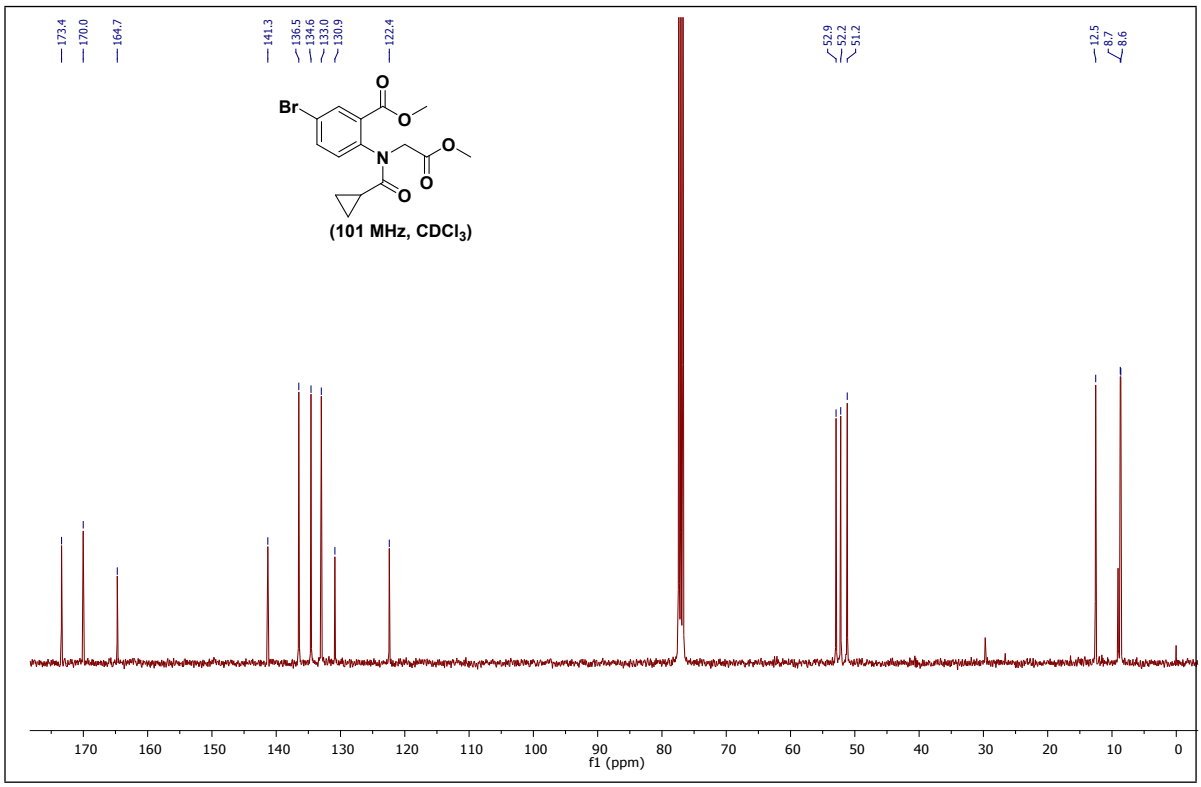
^{13}C NMR spectrum of **4h**:



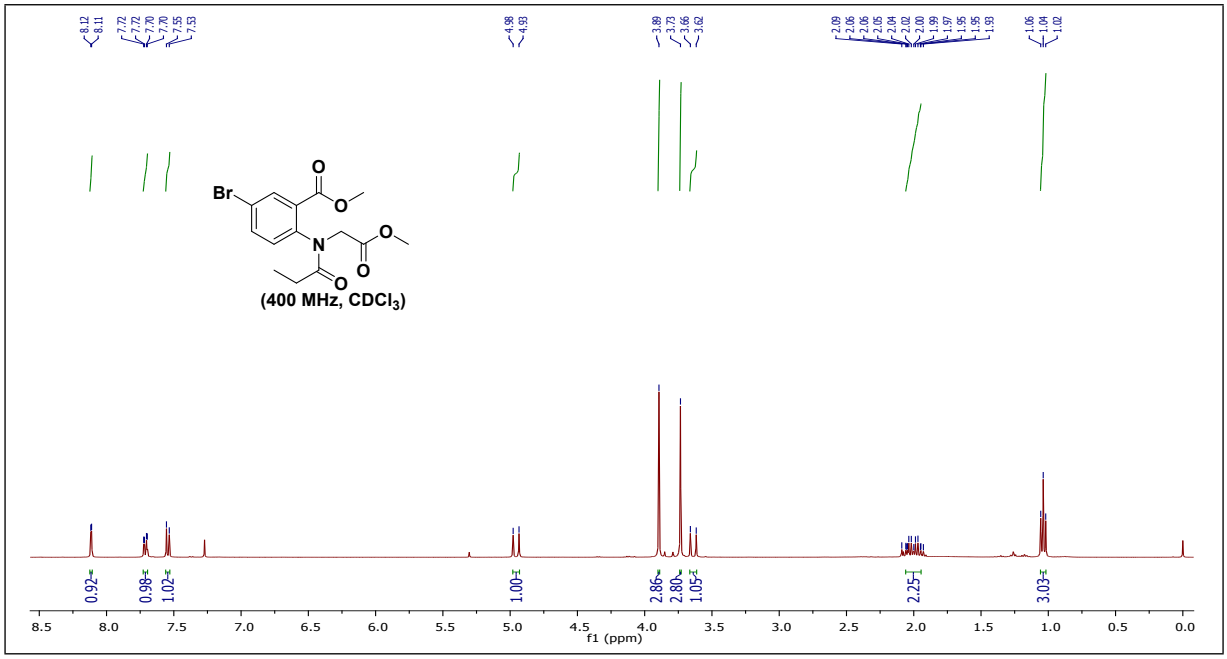
^{1}H NMR spectrum of **3l**:



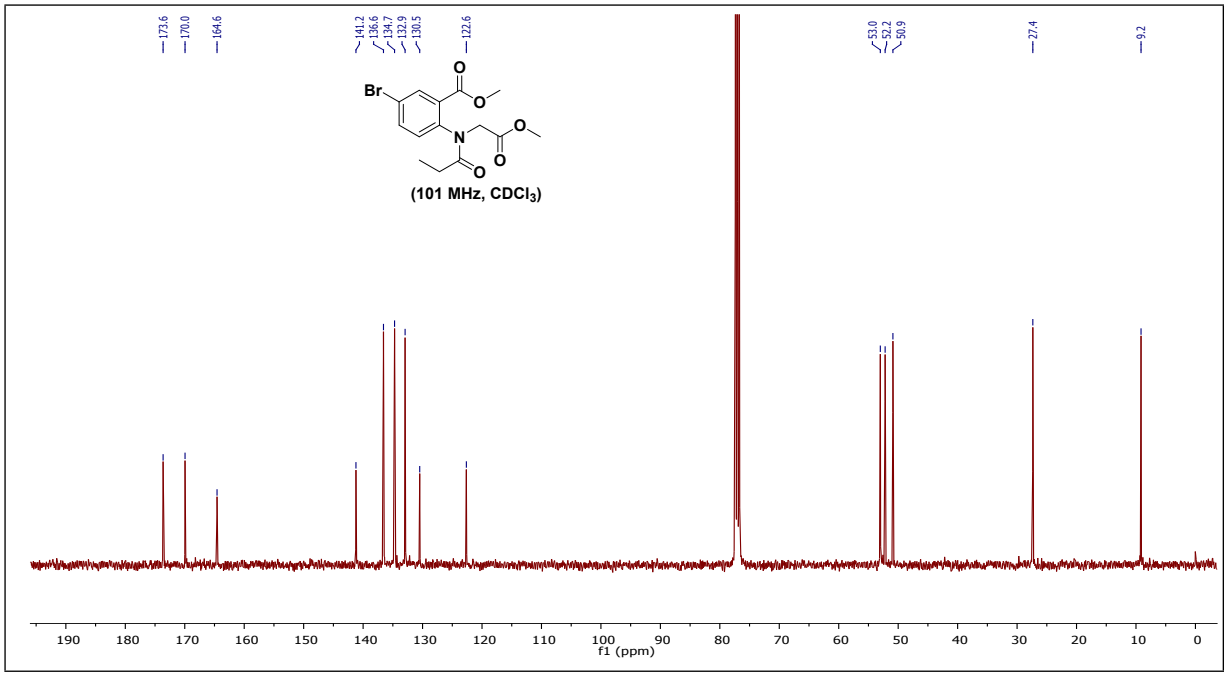
^{13}C NMR spectrum of **3l**:



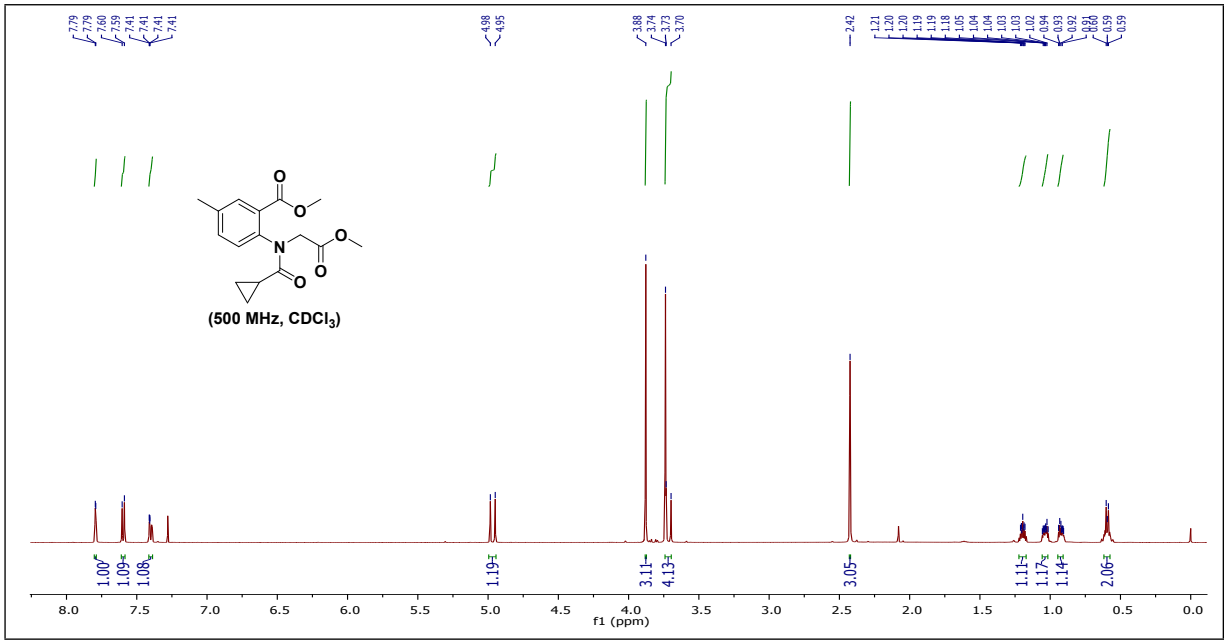
^{1}H NMR spectrum of **3m**:



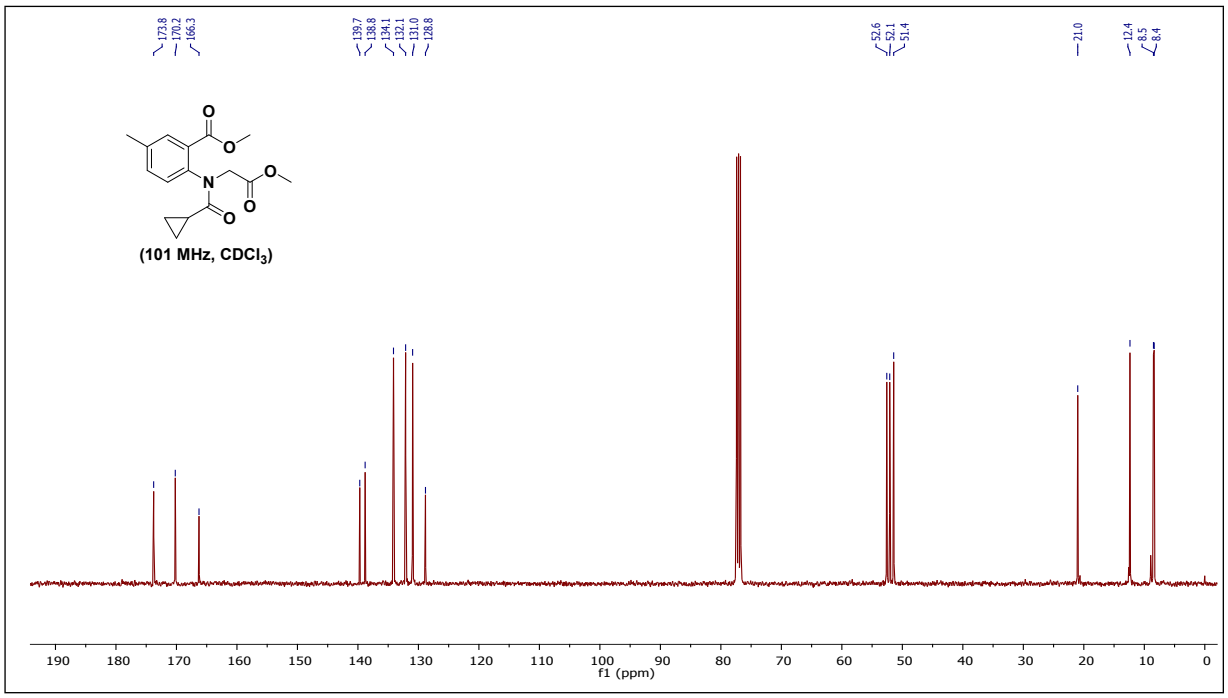
^{13}C NMR spectrum of **3m**:



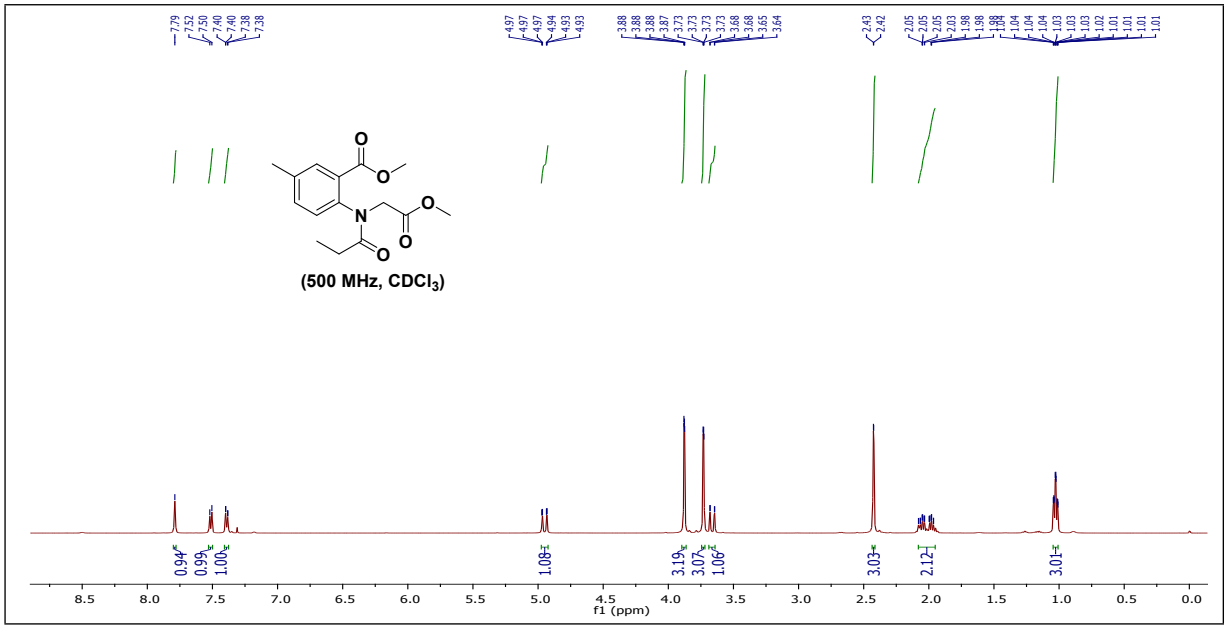
^{1}H NMR spectrum of **3o**:



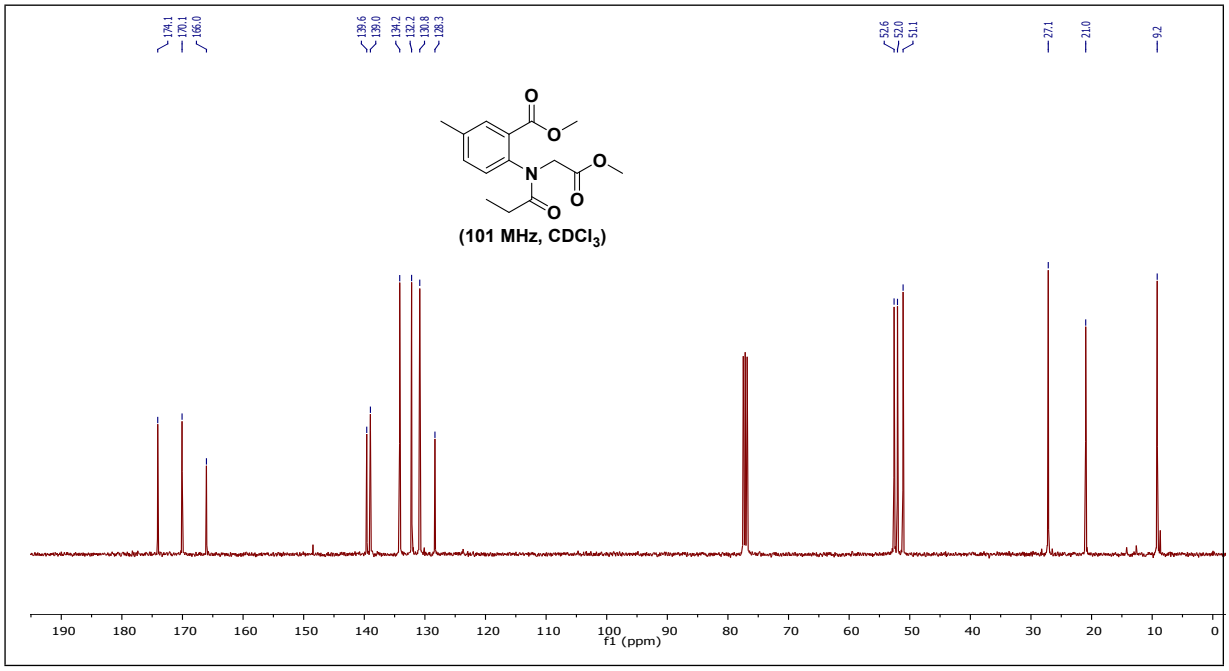
^{13}C NMR spectrum of **3o**:



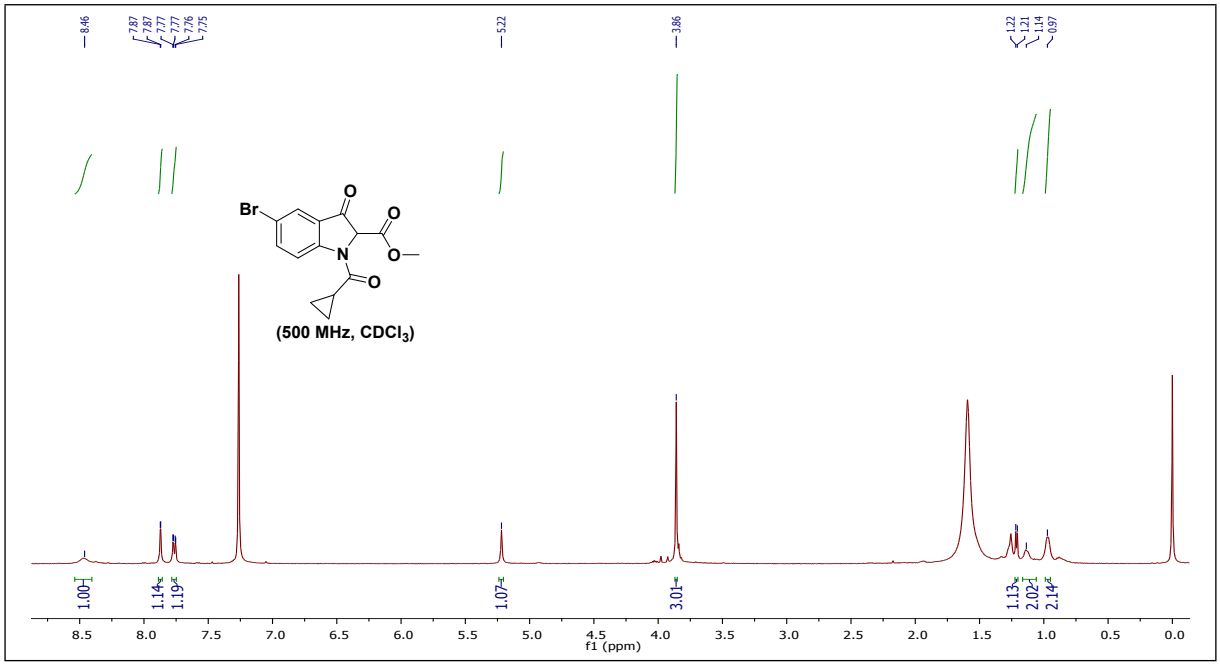
^{1}H NMR spectrum of **3p**:



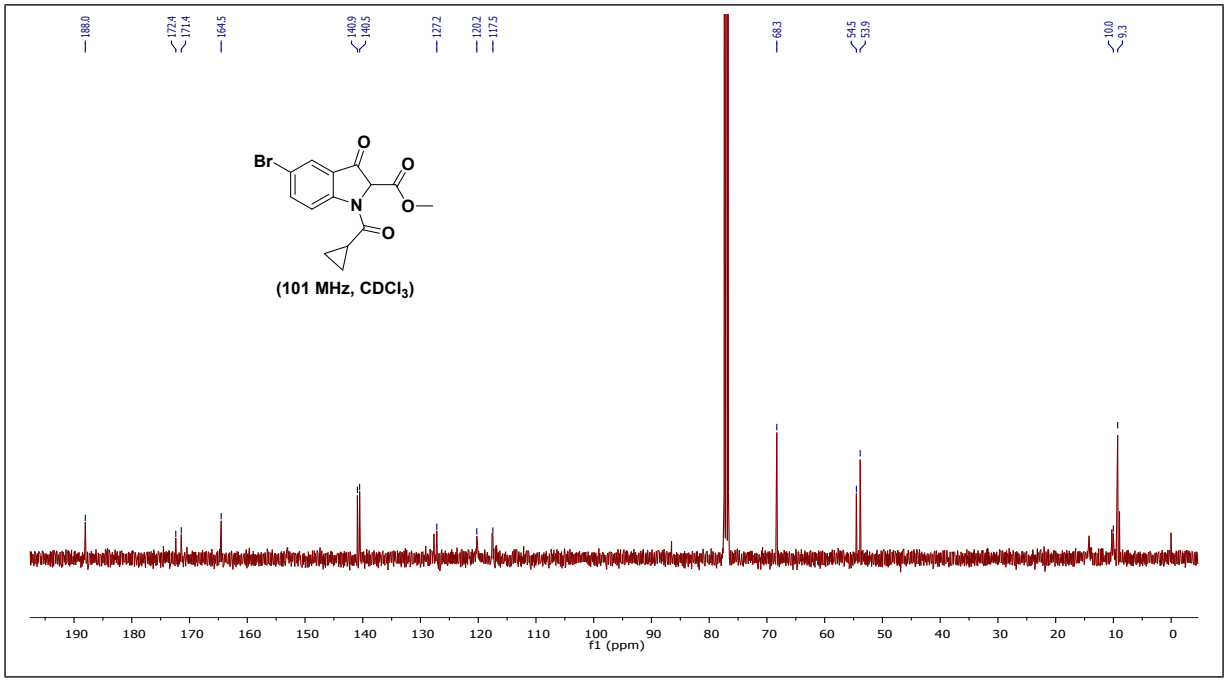
^{13}C NMR spectrum of **3p**:



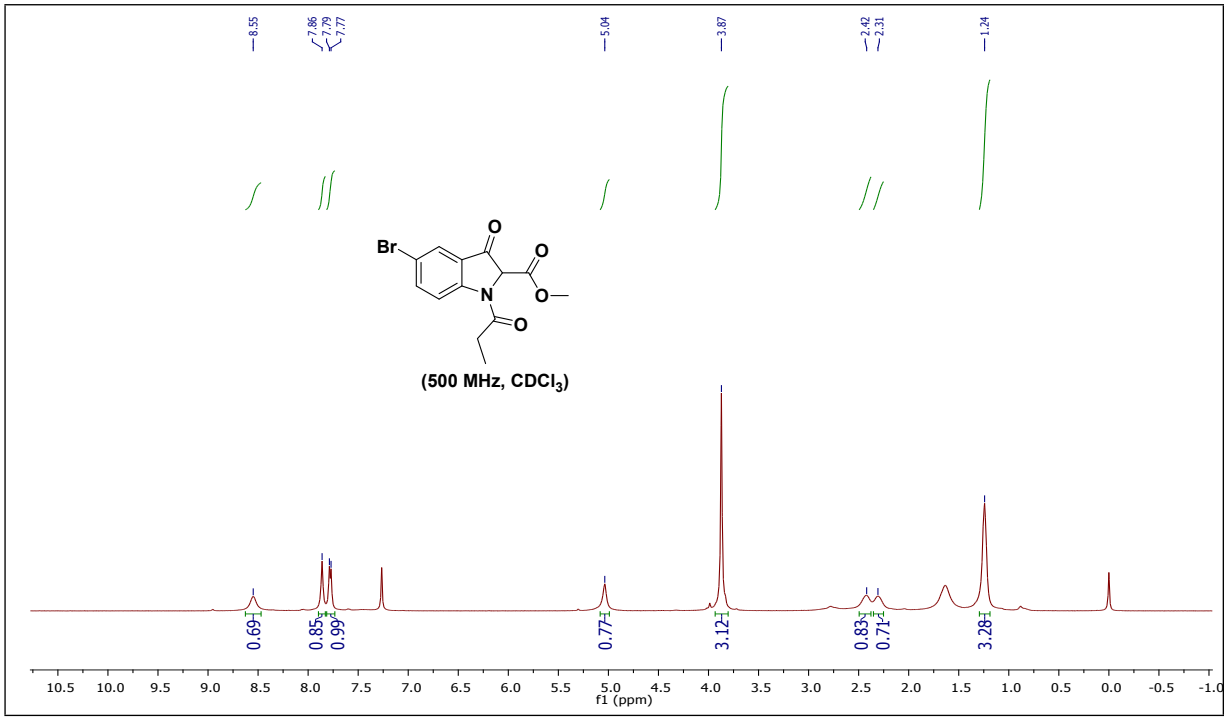
^{1}H NMR spectrum of **4l**:



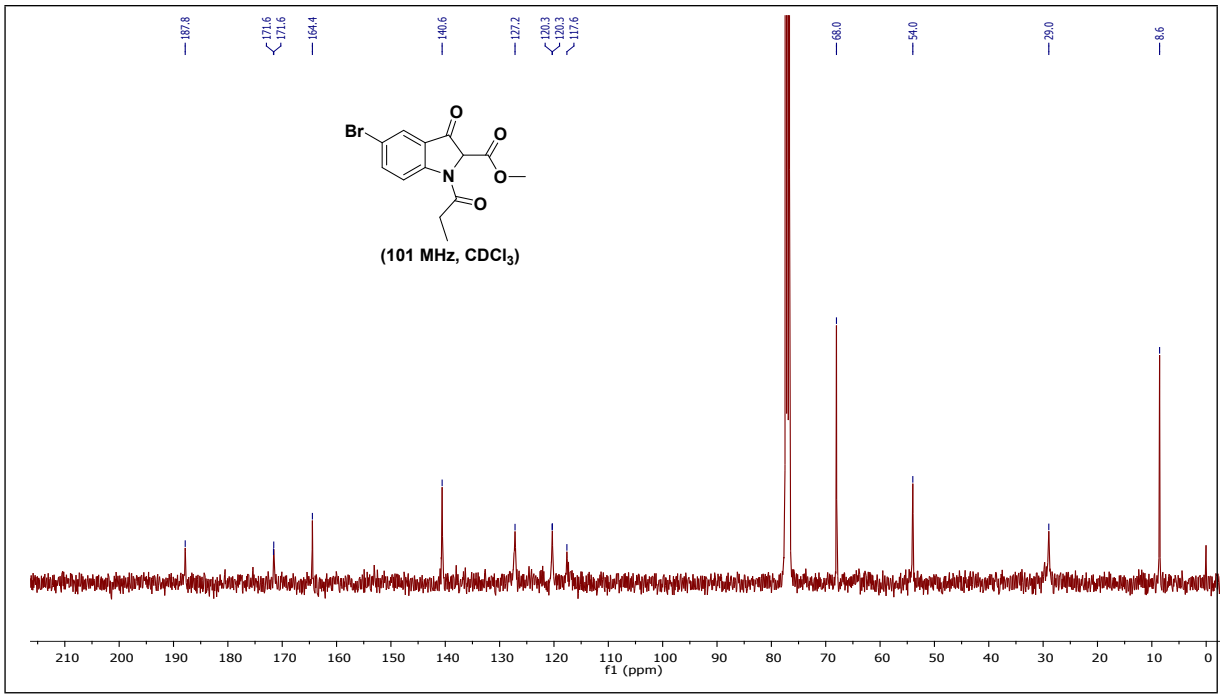
^{13}C NMR spectrum of **4l**:



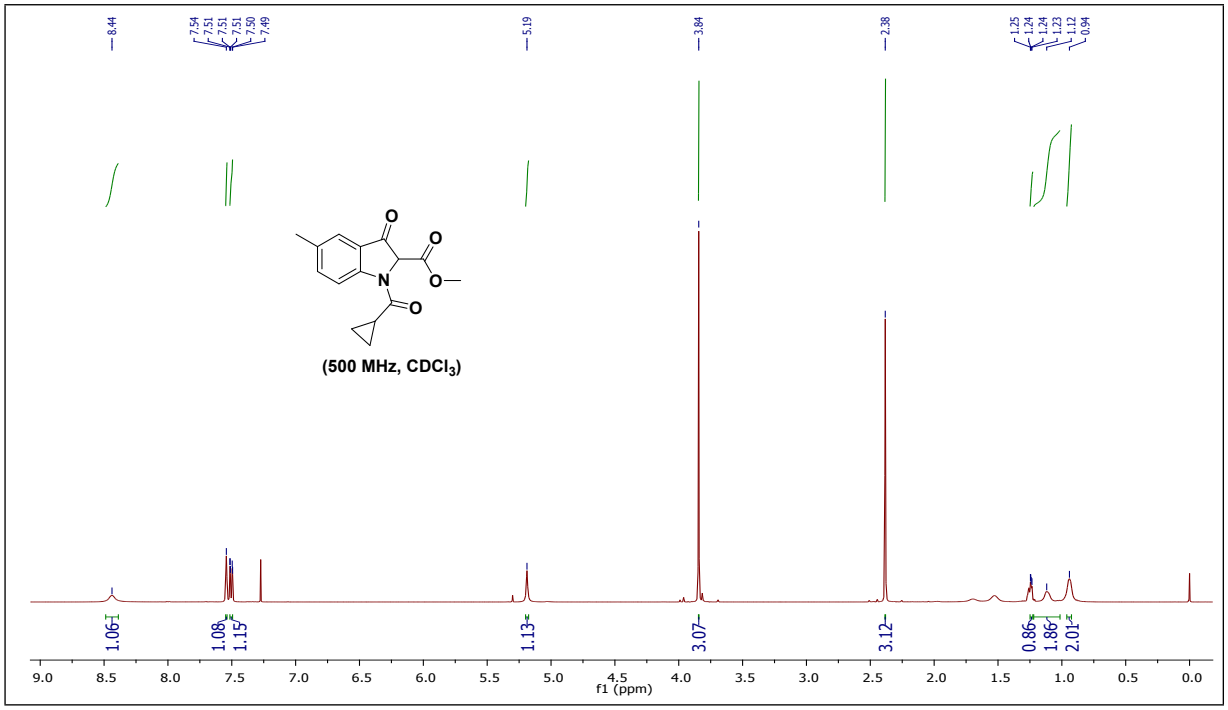
^{1}H NMR spectrum of **4m**:



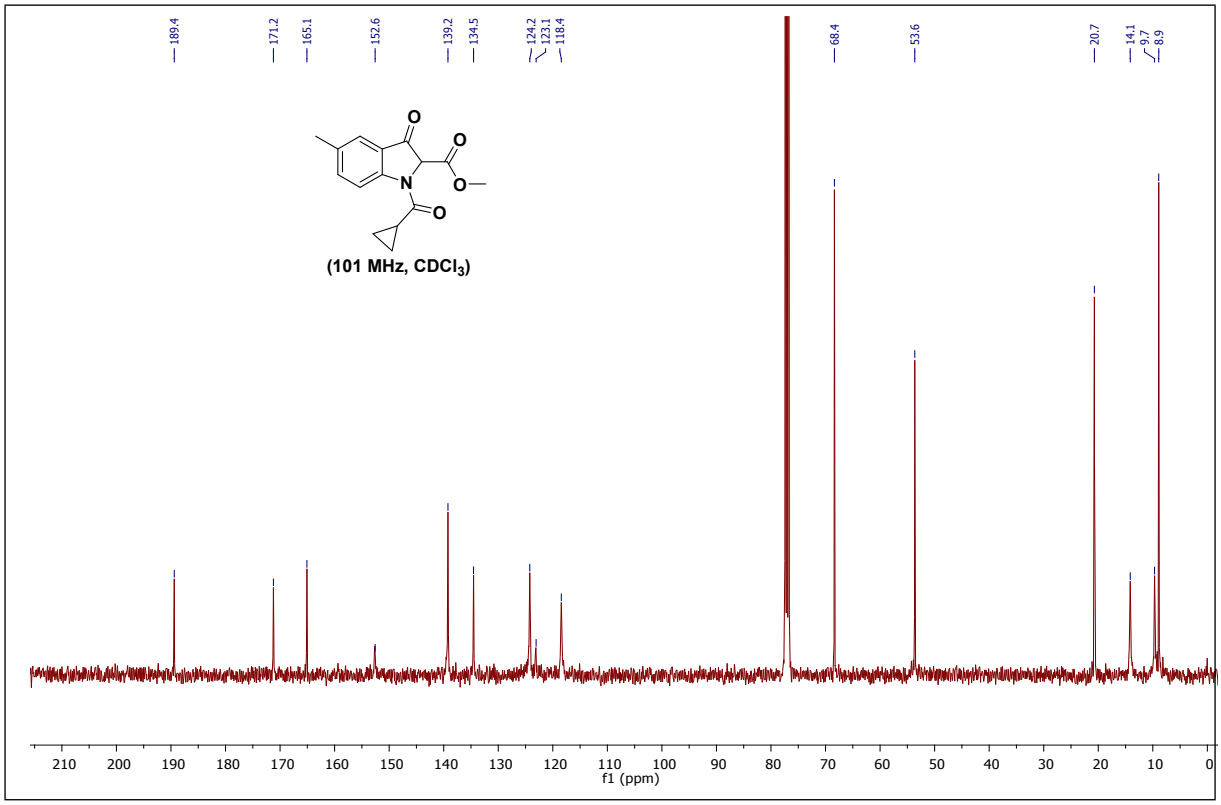
^{13}C NMR spectrum of **4m**:



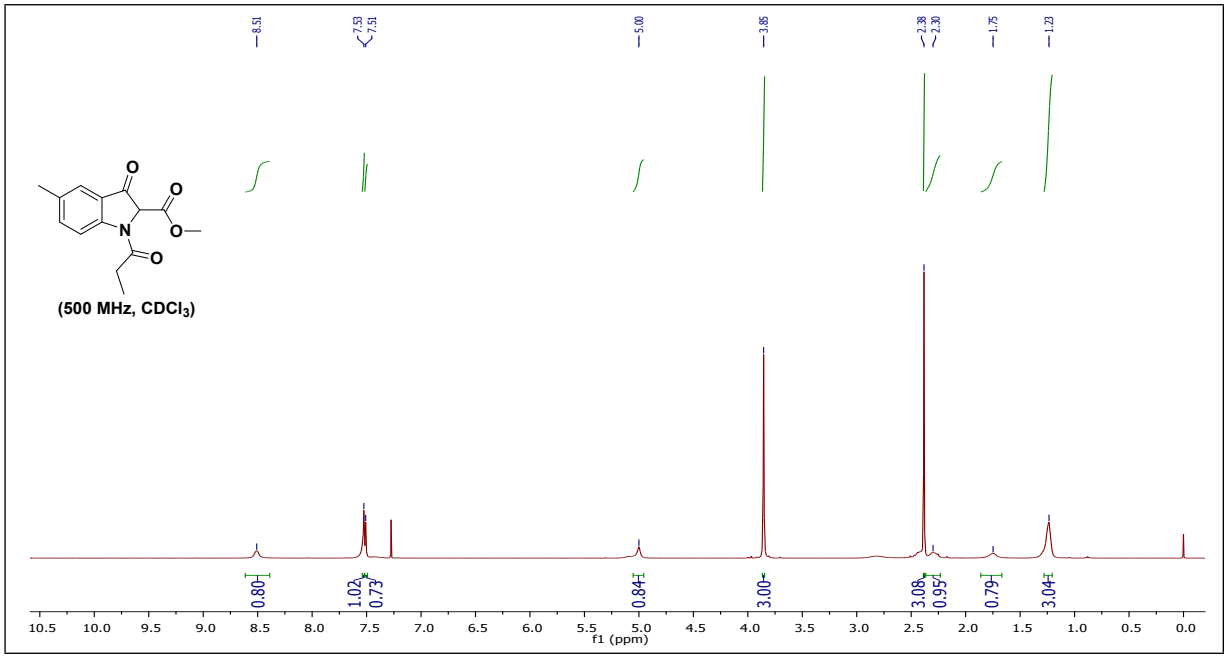
^{1}H NMR spectrum of **4o**:



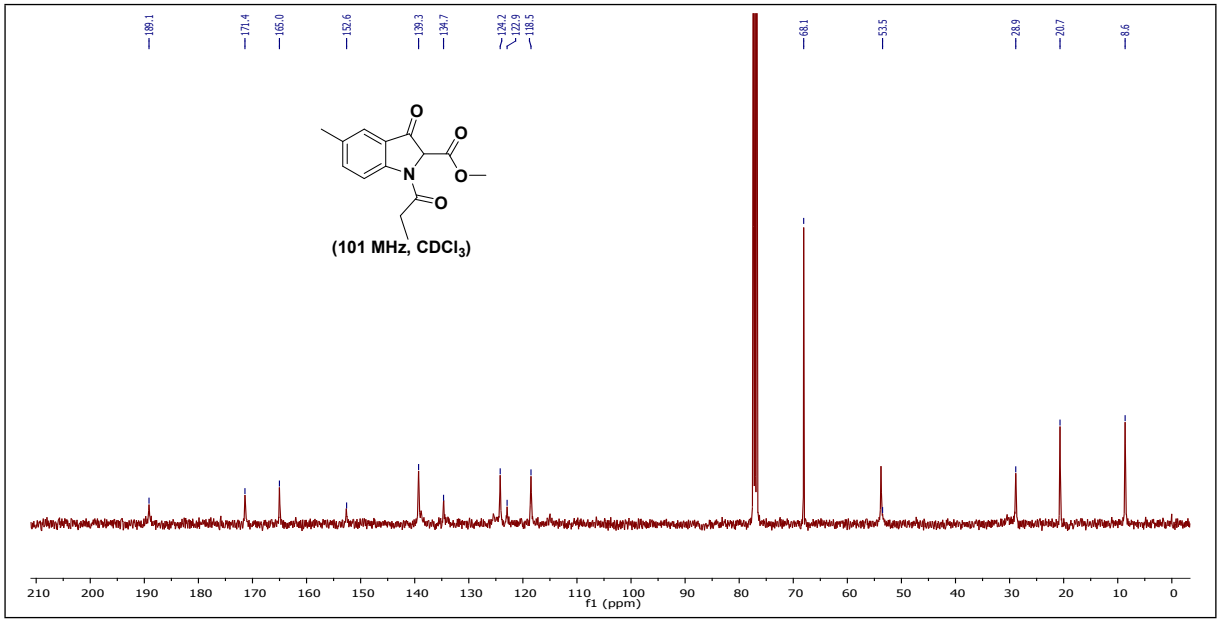
^{13}C NMR spectrum of **4o**:



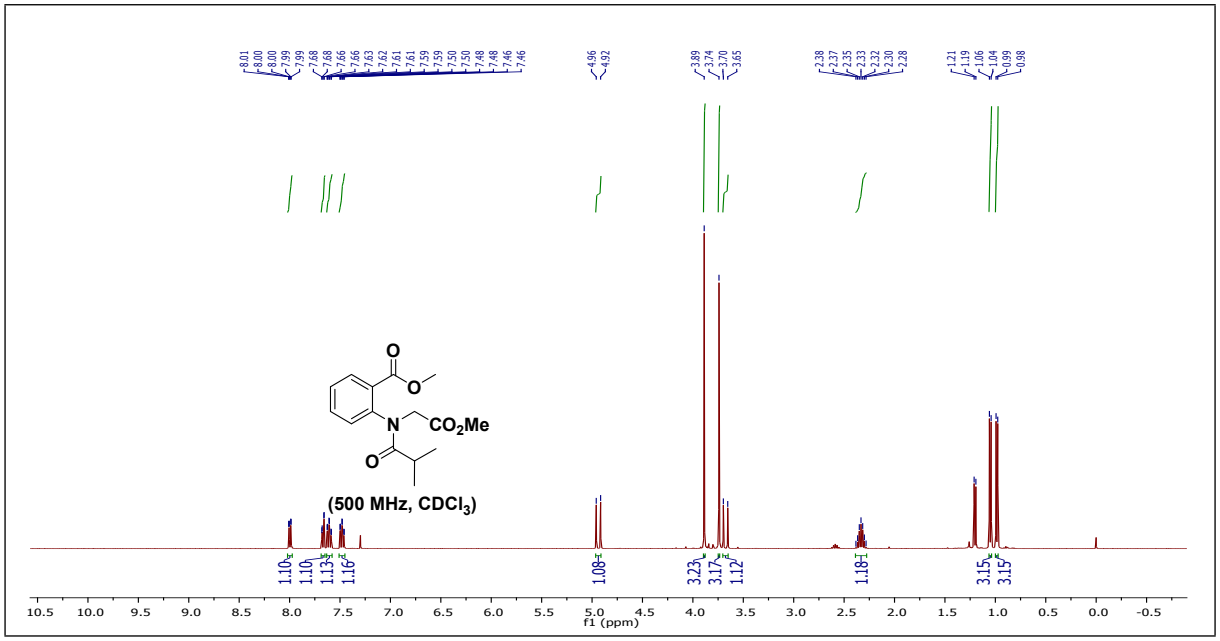
^{1}H NMR spectrum of **4p**:



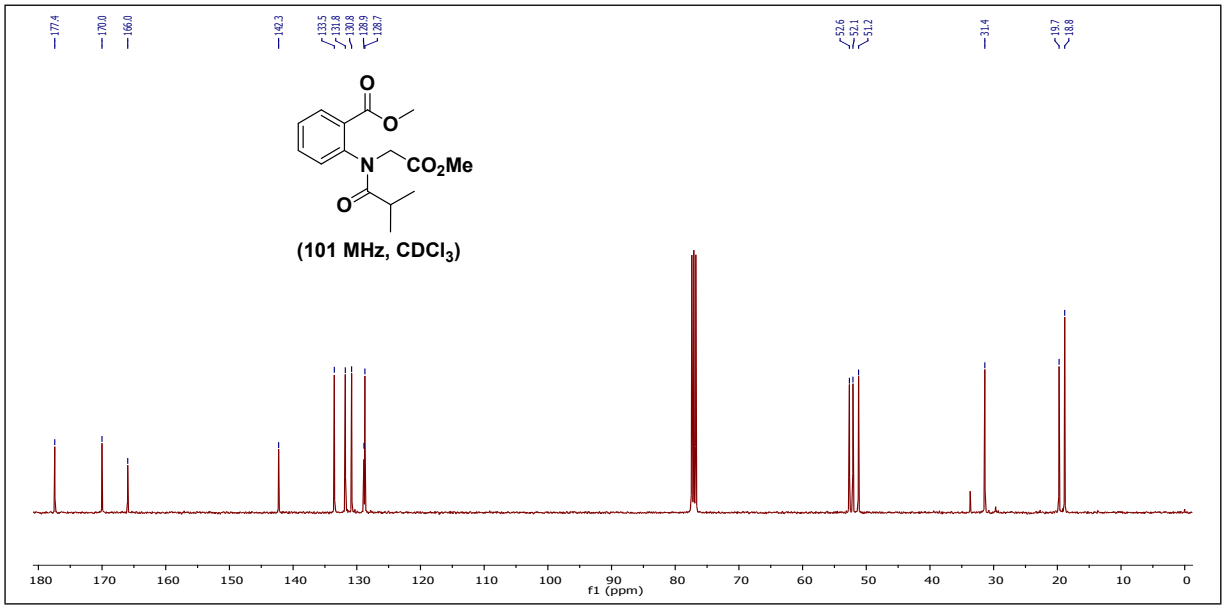
^{13}C NMR spectrum of **4p**:



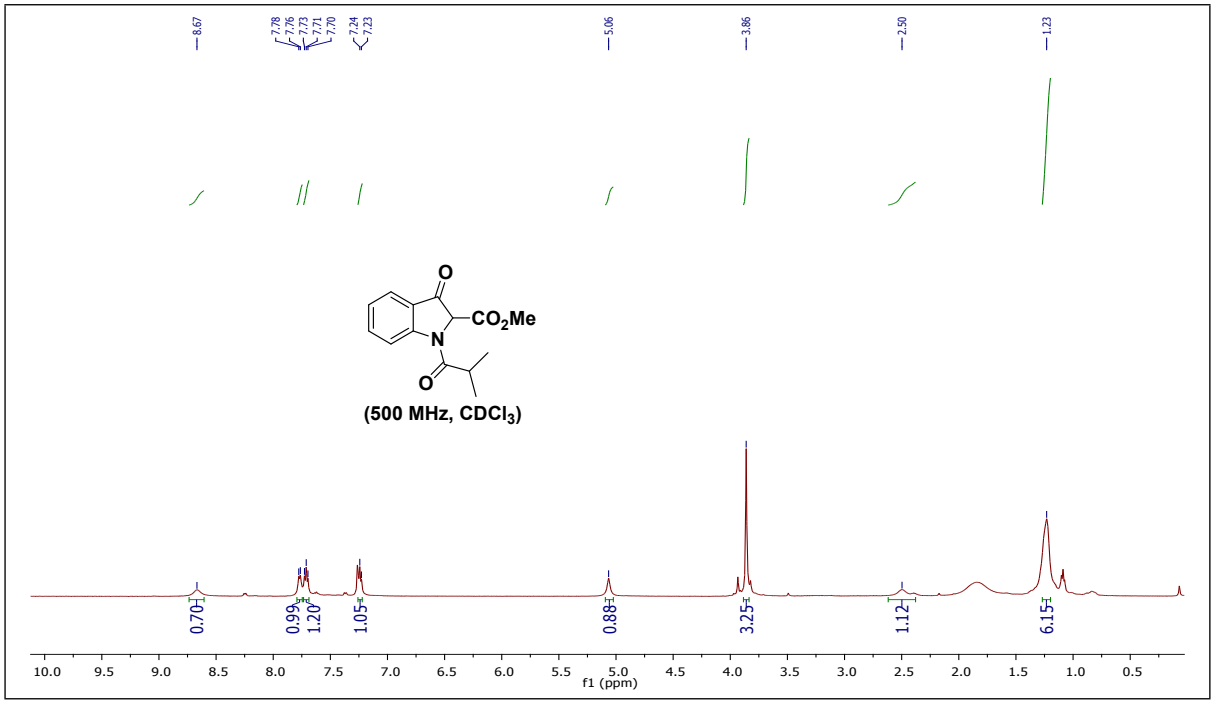
^{1}H NMR spectrum of **3i**:



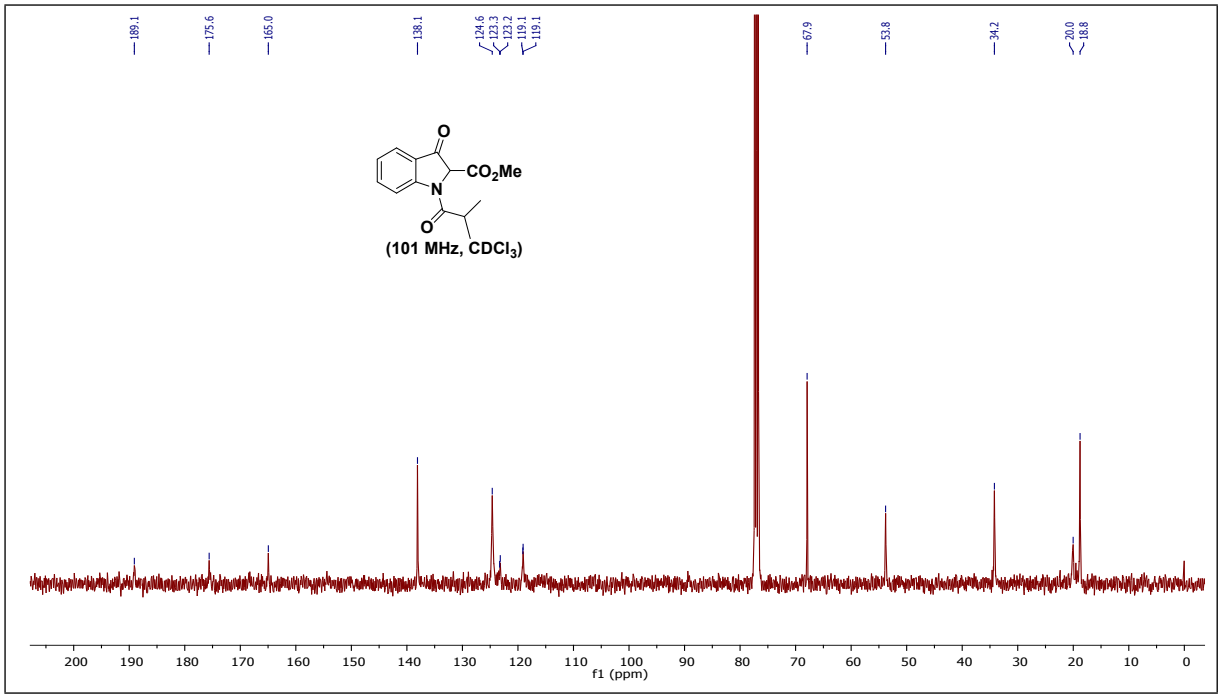
^{13}C NMR spectrumof **3i**:



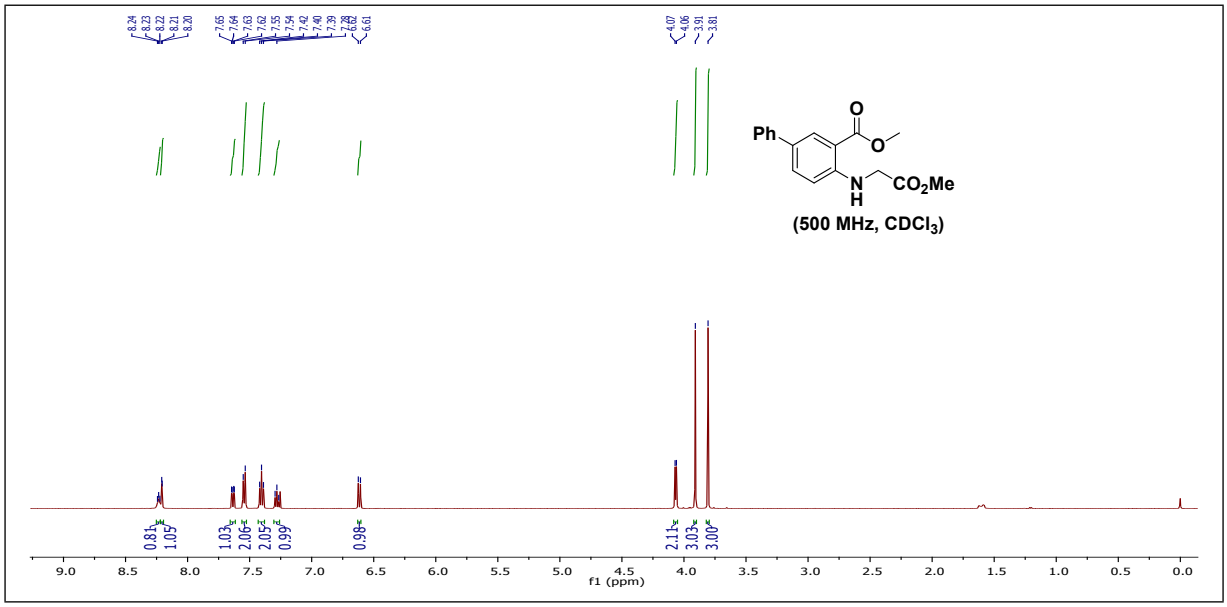
^{1}H NMR spectrum of **4i**:



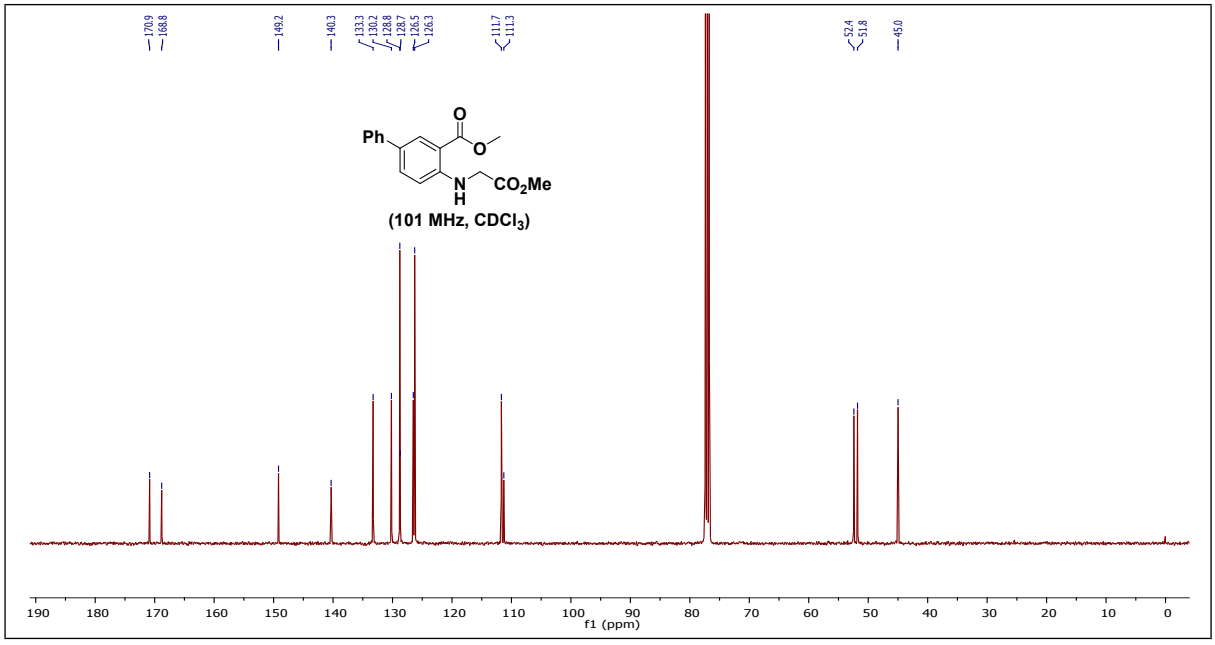
^{13}C NMR spectrum of **4i**:



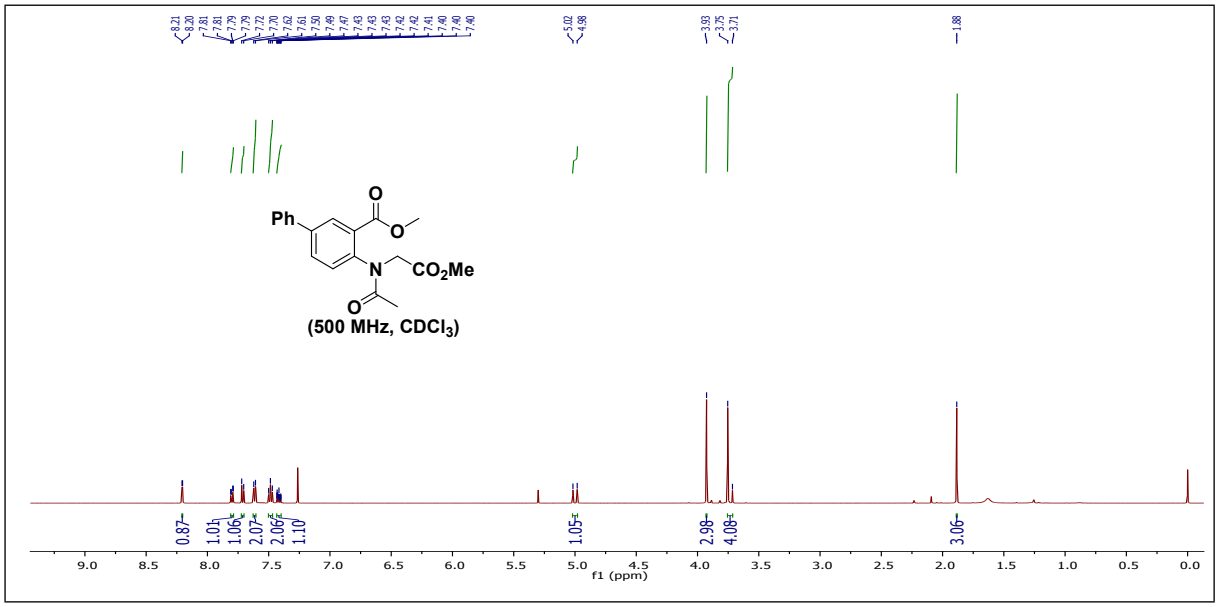
^{1}H NMR spectrum of **2n**:



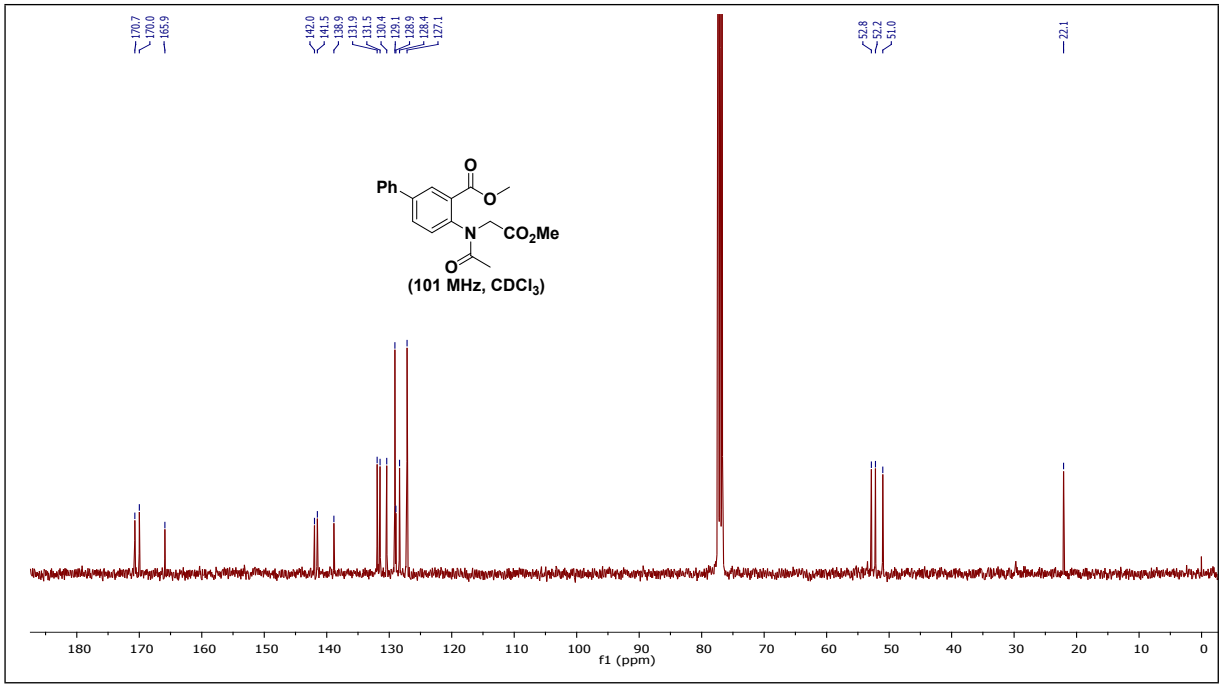
^{13}C NMR spectrum of **2n**:



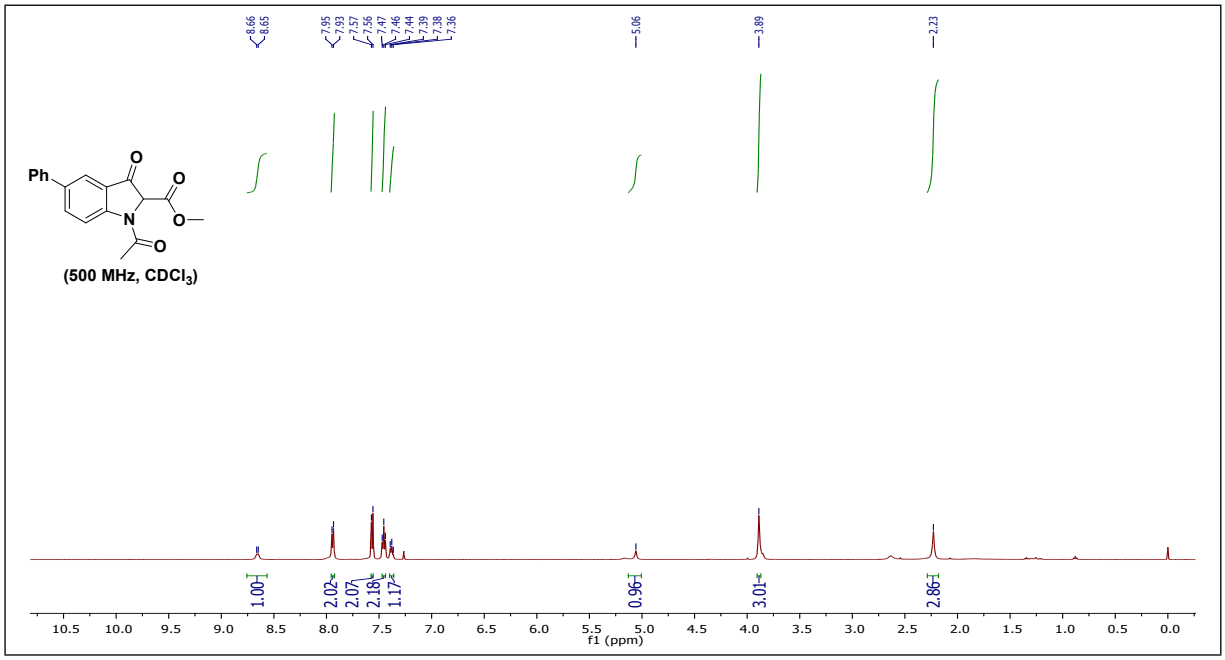
[1]H NMR spectrum of **3n**:



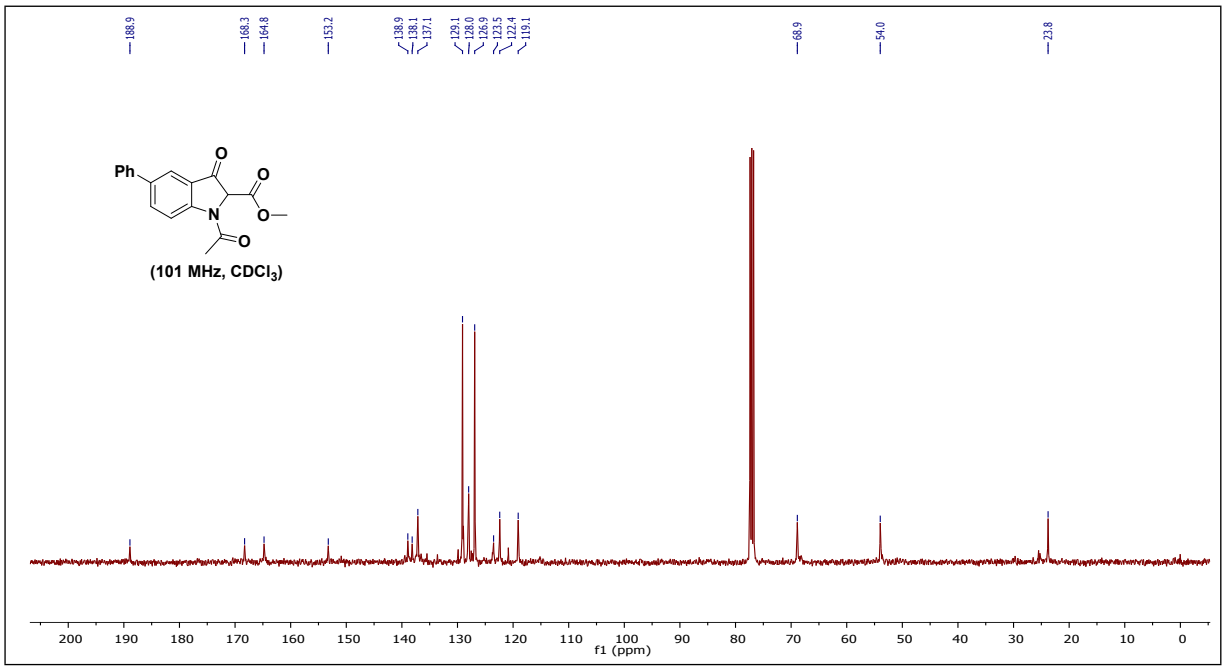
[13]C NMR spectrum of **3n**:



[1]H NMR spectrum of **4n**:

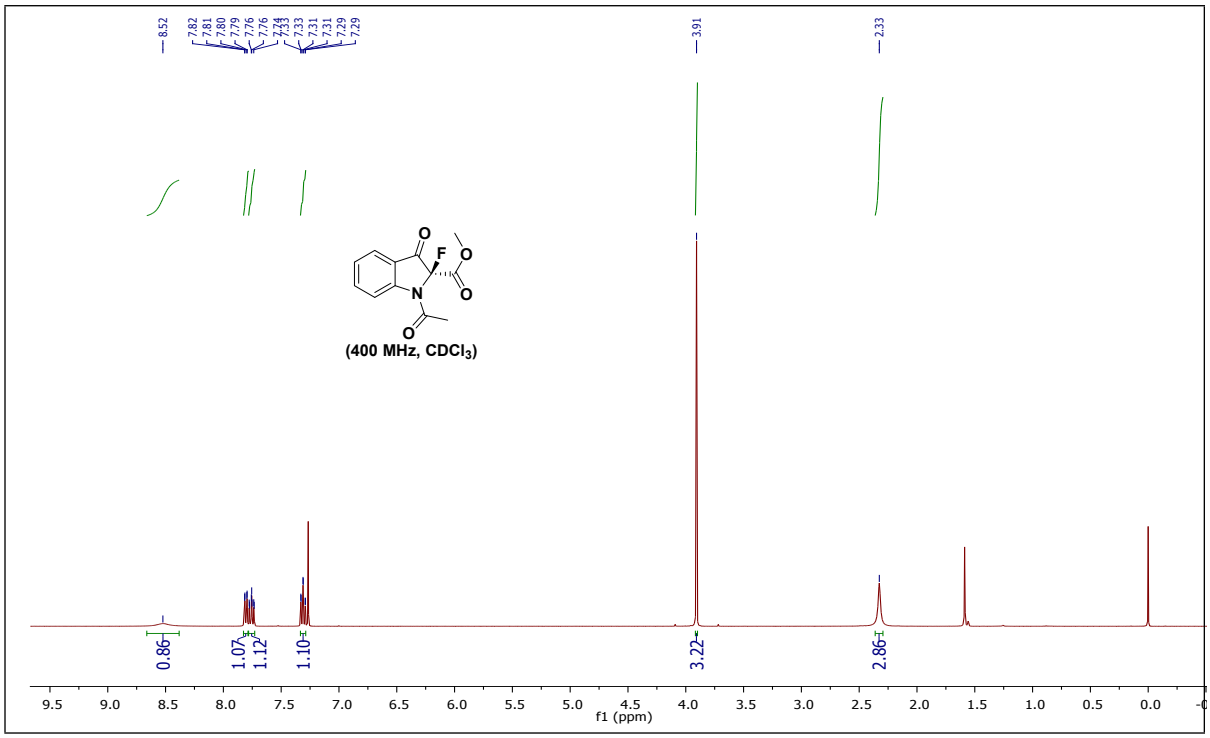


[13]C NMR spectrum of **4n**:

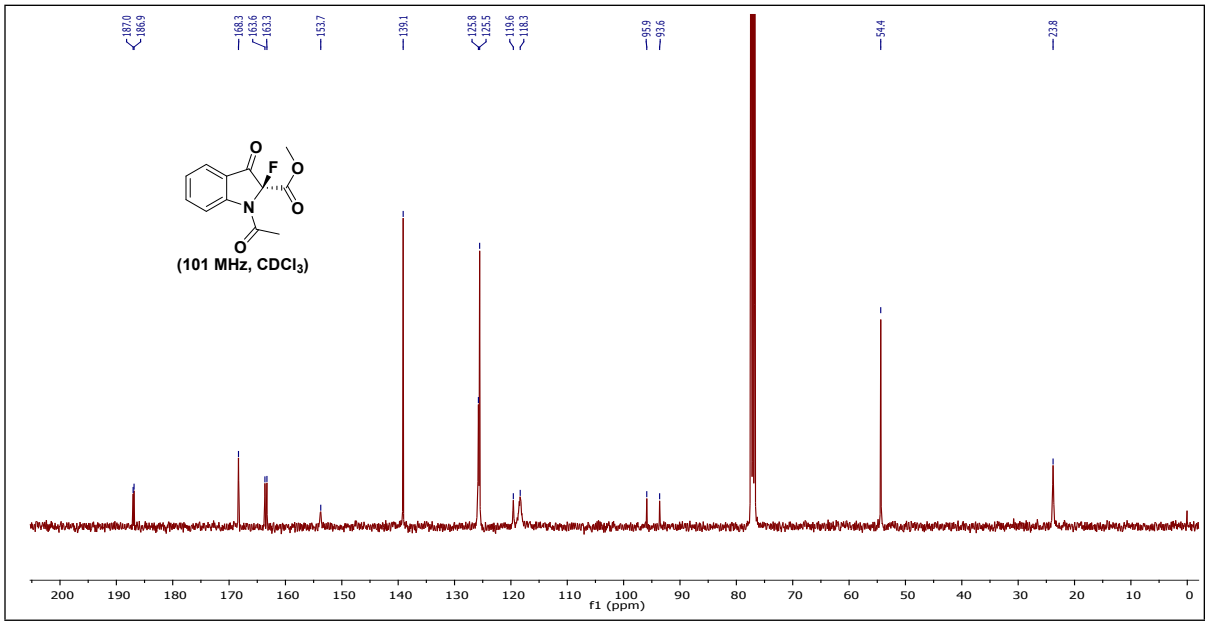


^{1}H, ^{13}C ,^{19}F NMR spectra and HPLC chromatograms of final fluorinated products (5a-5p):

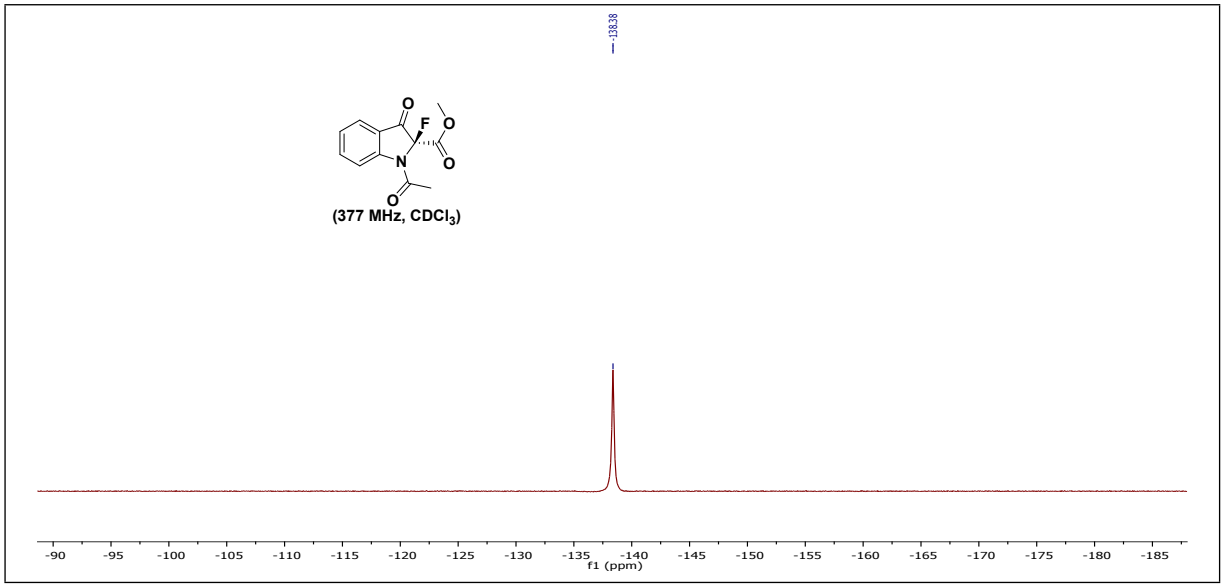
^{1}H NMR spectrum of **5a**:



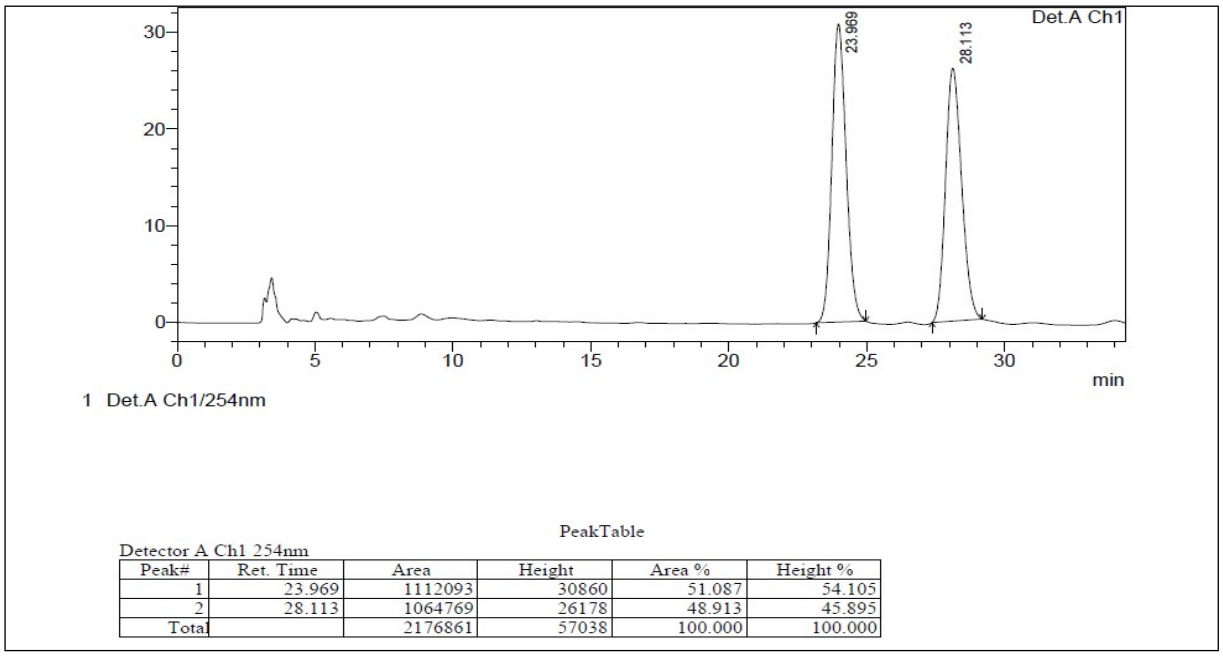
^{13}C NMR spectrum of **5a**:



^{19}F NMR spectrum of **5a**:



HPLC chromatogram of **5a**-racemic:

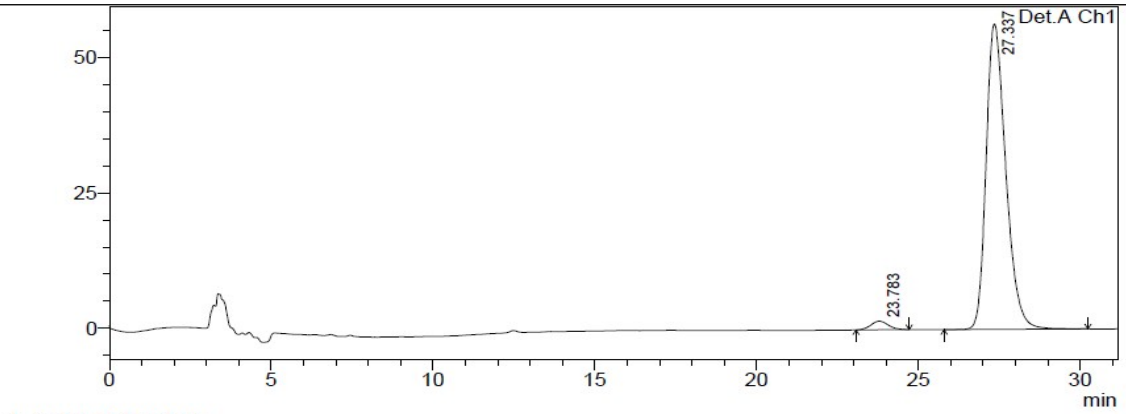


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.969	1112093	30860	51.087	54.105
2	28.113	1064769	26178	48.913	45.895
Total		2176861	57038	100.000	100.000

HPLC chromatogram of **5a**-chiral:



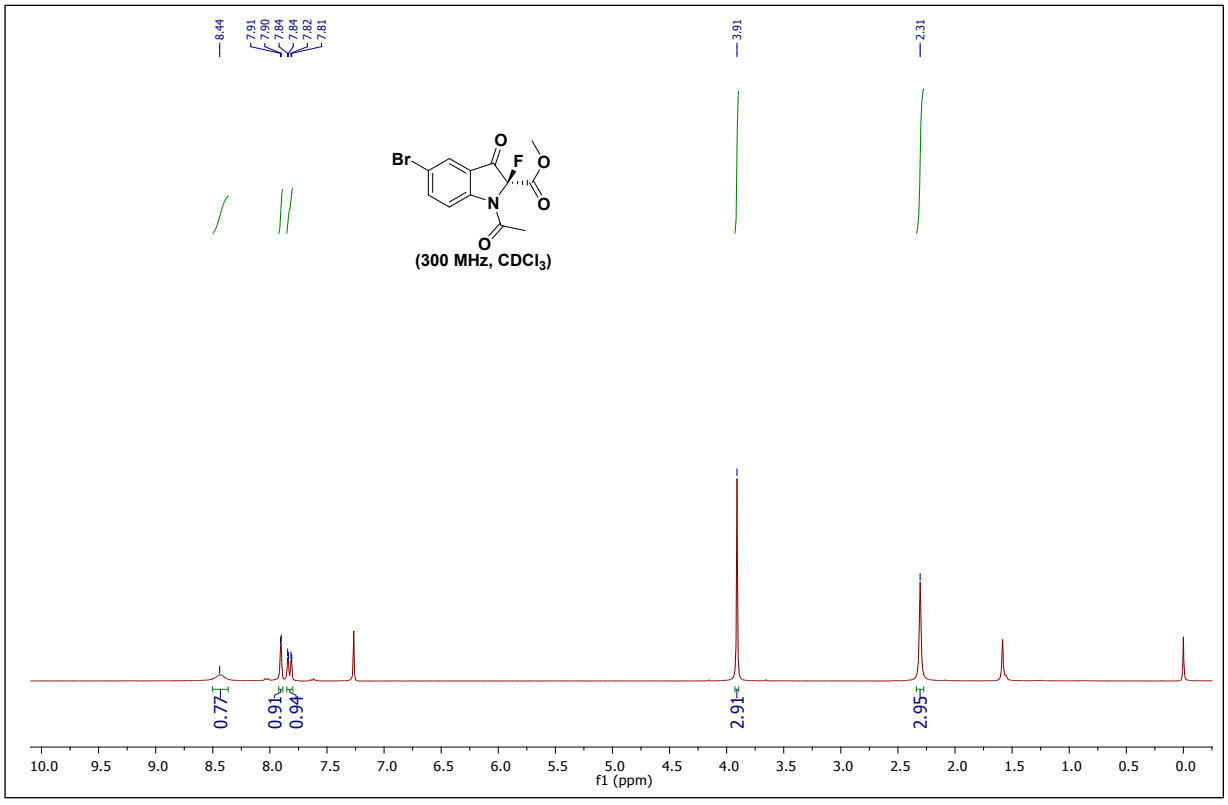
1 Det.A Ch1/254nm

PeakTable

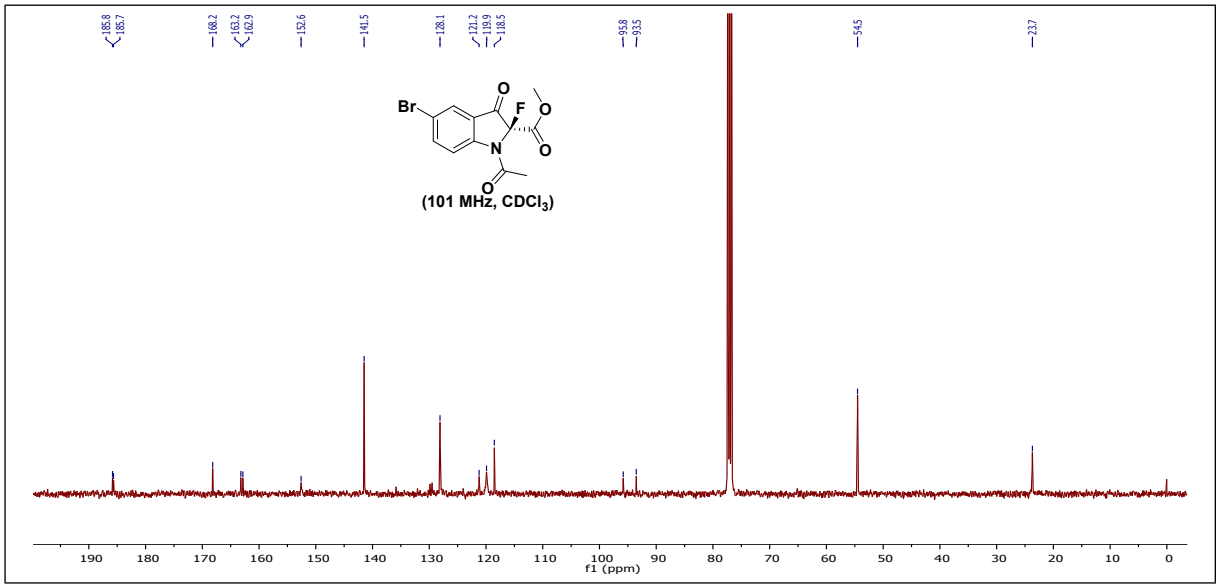
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.783	59192	1584	2.413	2.728
2	27.337	2393801	56471	97.587	97.272
Total		2452993	58055	100.000	100.000

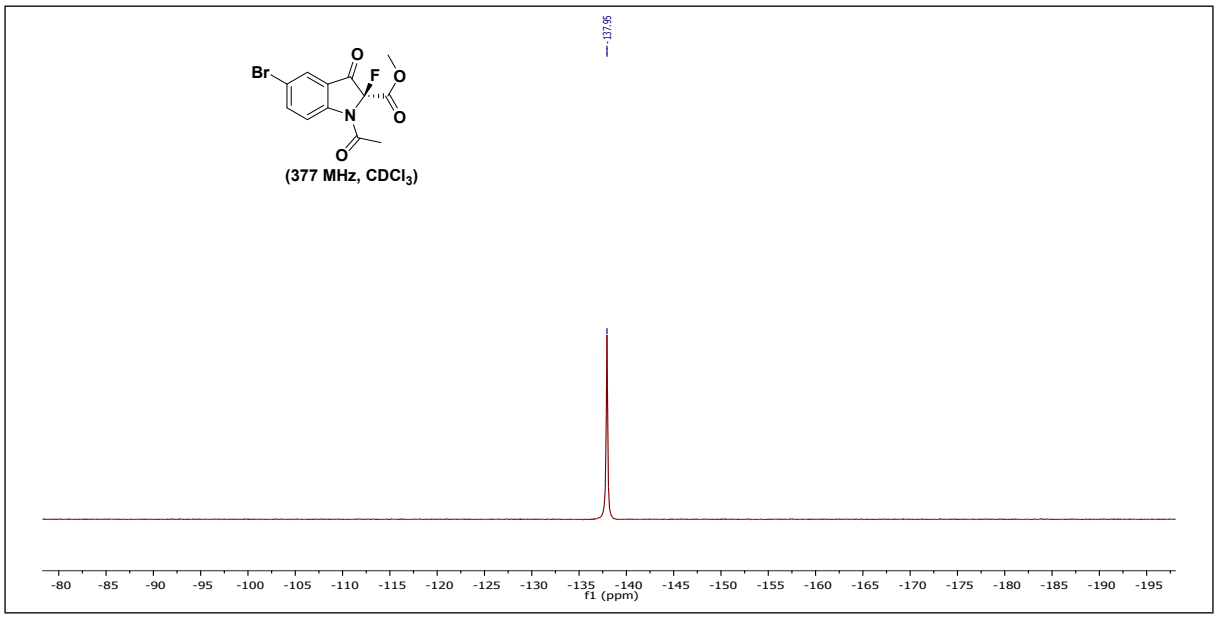
^{1}H NMR spectrum of **5b**:



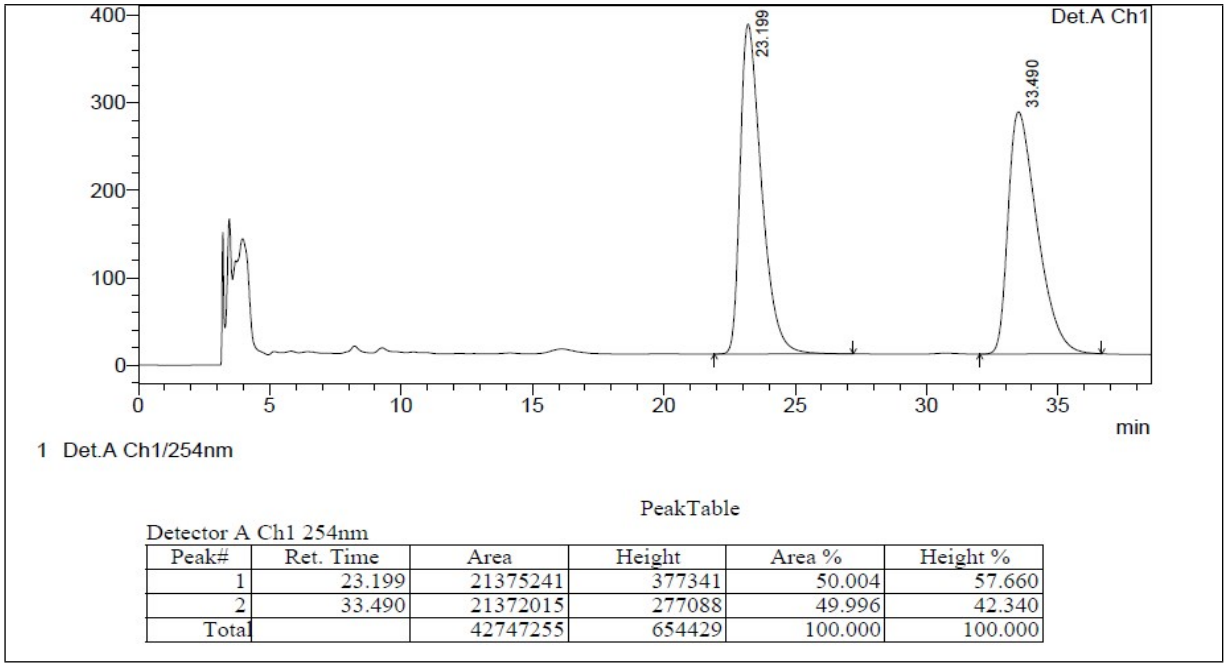
^{13}C NMR spectrum of **5b**:



^{19}F NMR spectrum of **5b**:



HPLC chromatogram of **5b**-racemic:

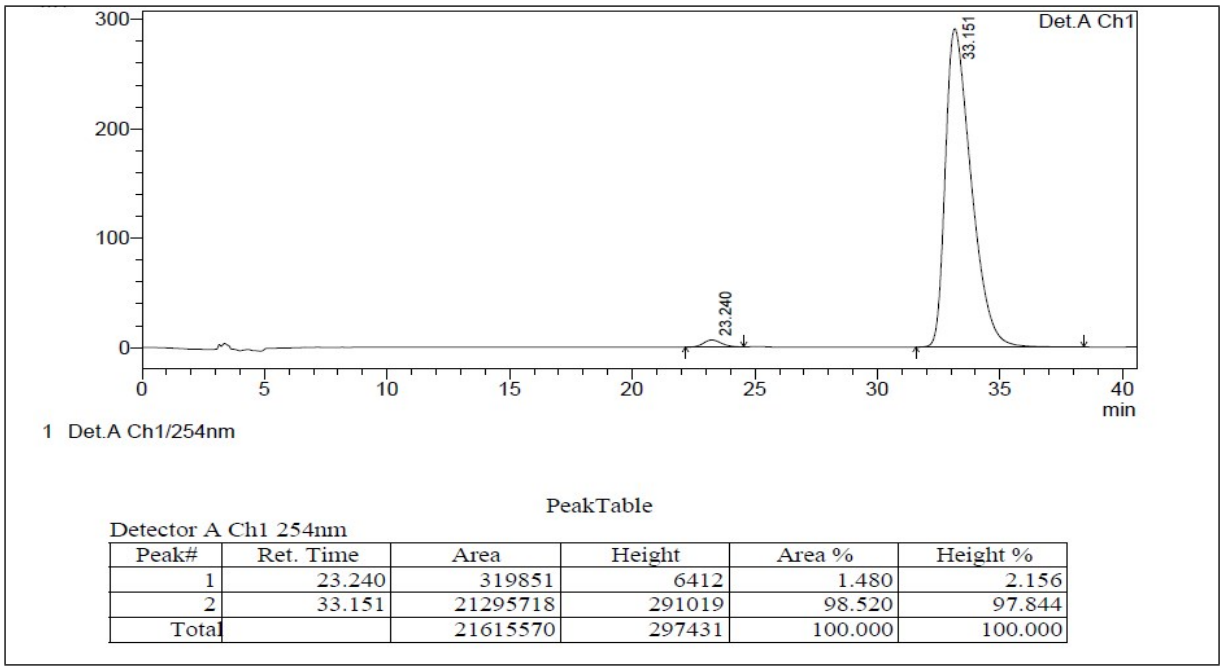


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.199	21375241	377341	50.004	57.660
2	33.490	21372015	277088	49.996	42.340
Total		42747255	654429	100.000	100.000

HPLC chromatogram of **5b**-chiral:

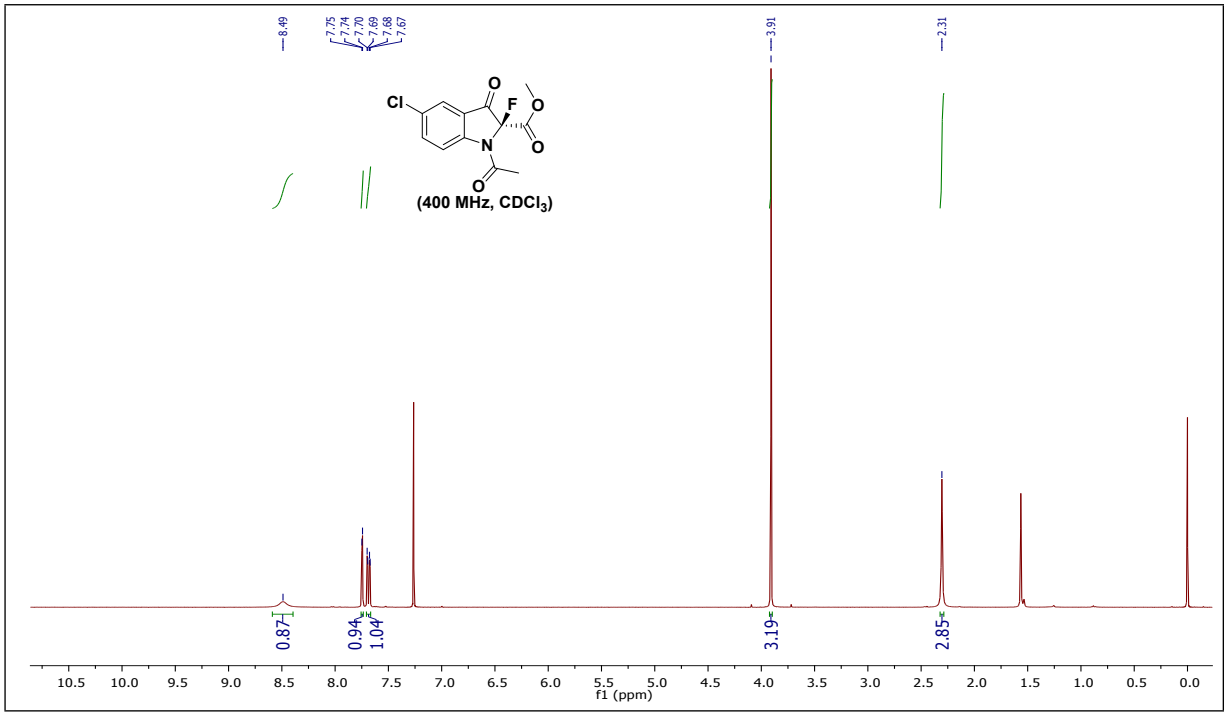


PeakTable

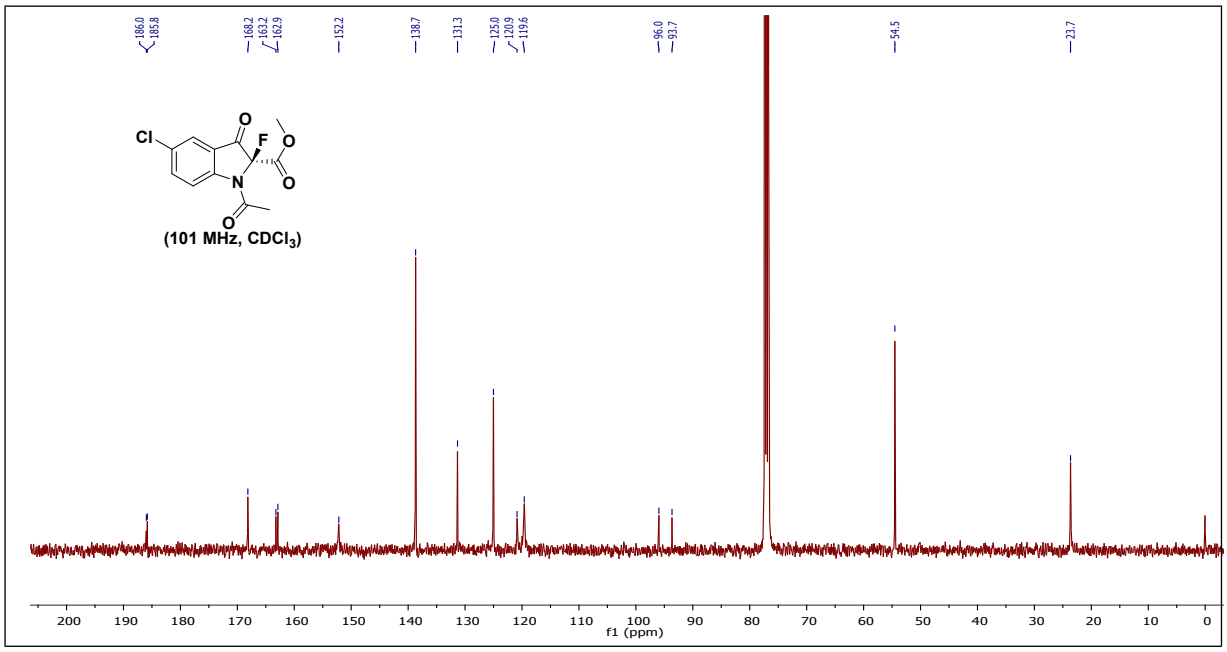
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.240	319851	6412	1.480	2.156
2	33.151	21295718	291019	98.520	97.844
Total		21615570	297431	100.000	100.000

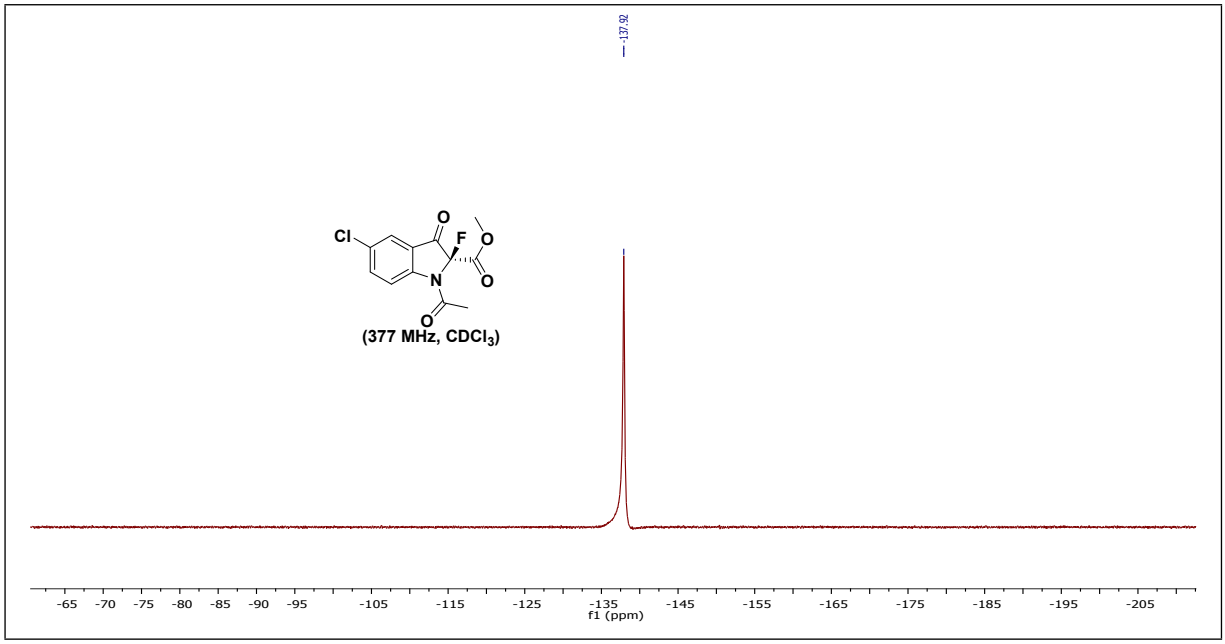
^{1}H NMR spectrum of **5c**:



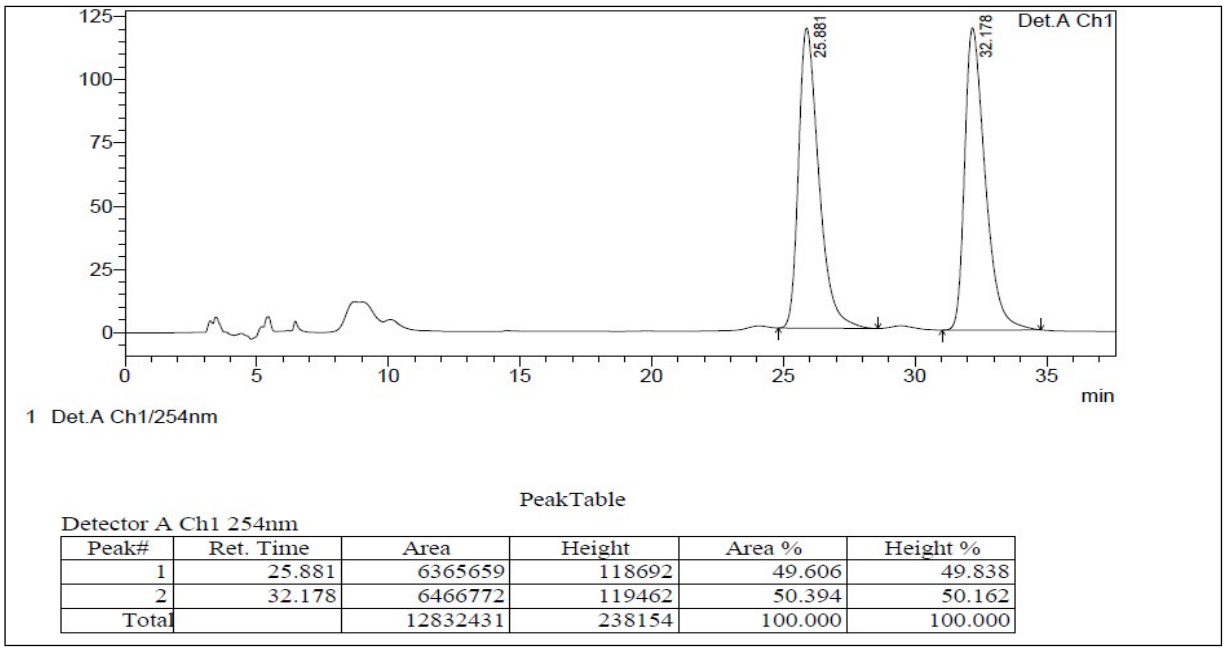
^{13}C NMR spectrum of **5c**:



^{19}F NMR spectrum of **5c:**



HPLC chromatogram of **5c**-racemic:

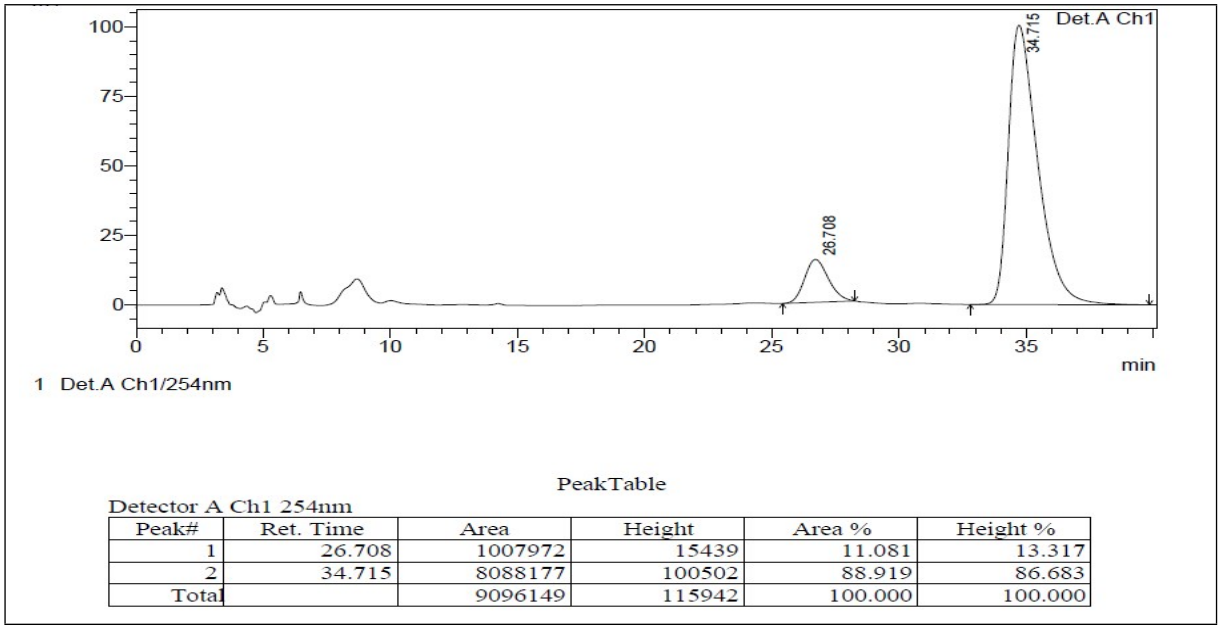


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.881	6365659	118692	49.606	49.838
2	32.178	6466772	119462	50.394	50.162
Total		12832431	238154	100.000	100.000

HPLC chromatogram of **5c**-chiral:

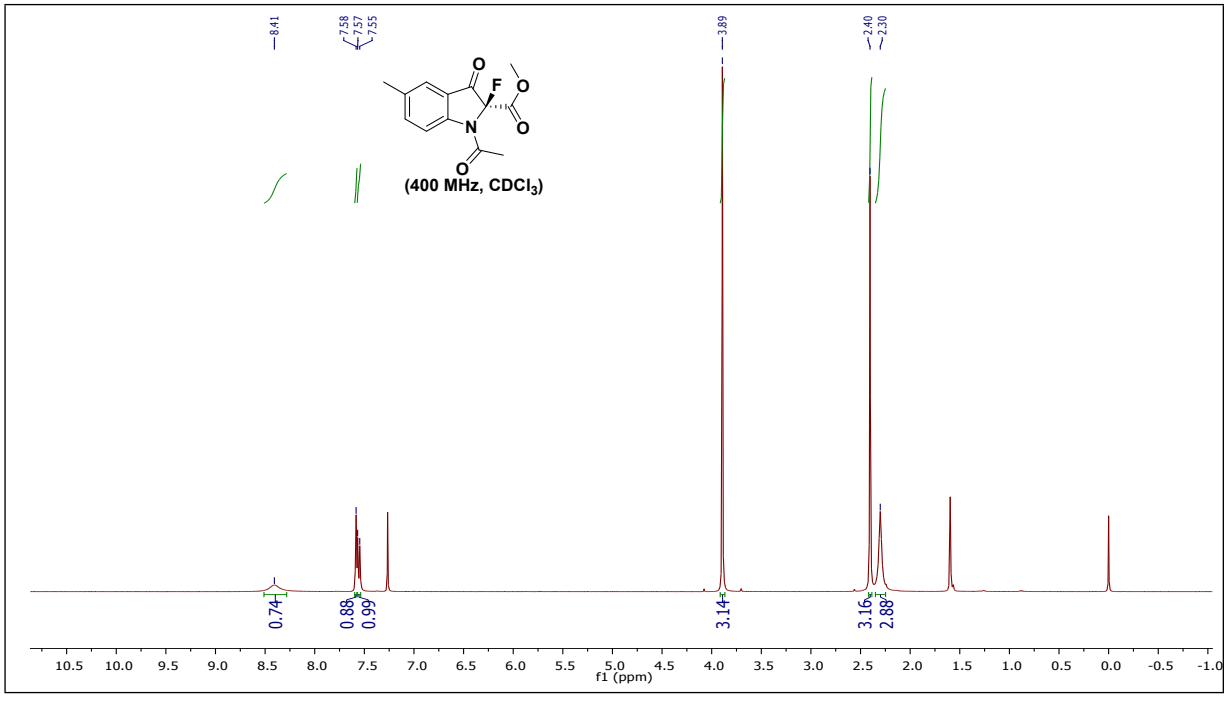


PeakTable

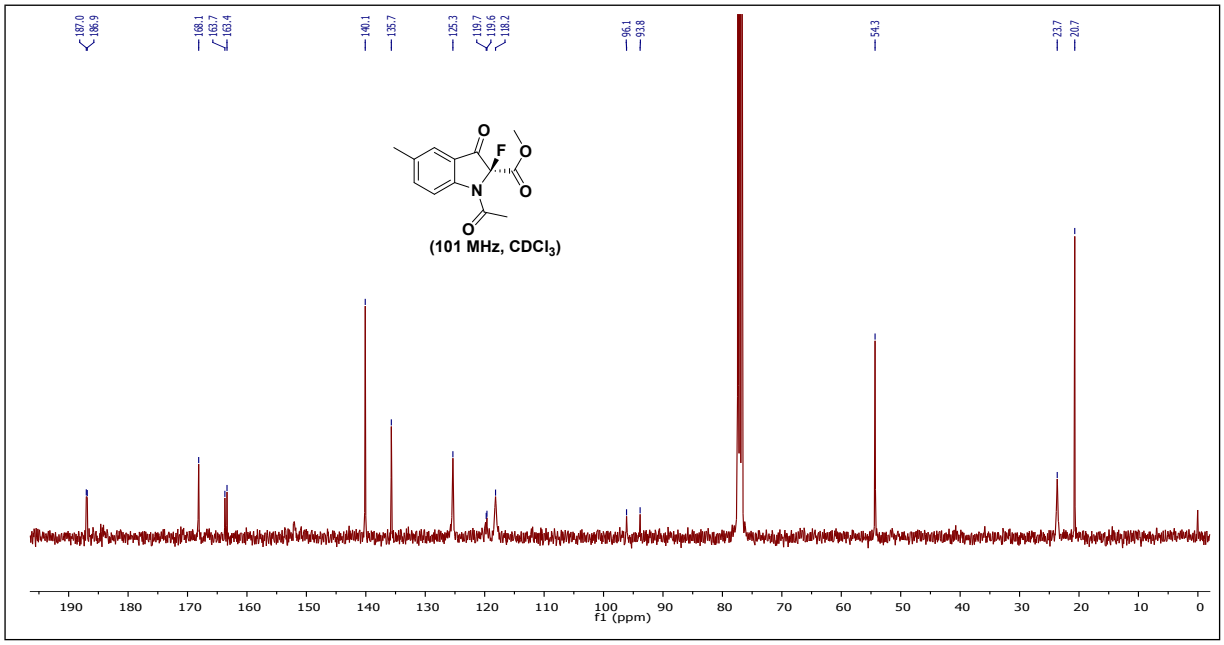
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.708	1007972	15439	11.081	13.317
2	34.715	8088177	100502	88.919	86.683
Total		9096149	115942	100.000	100.000

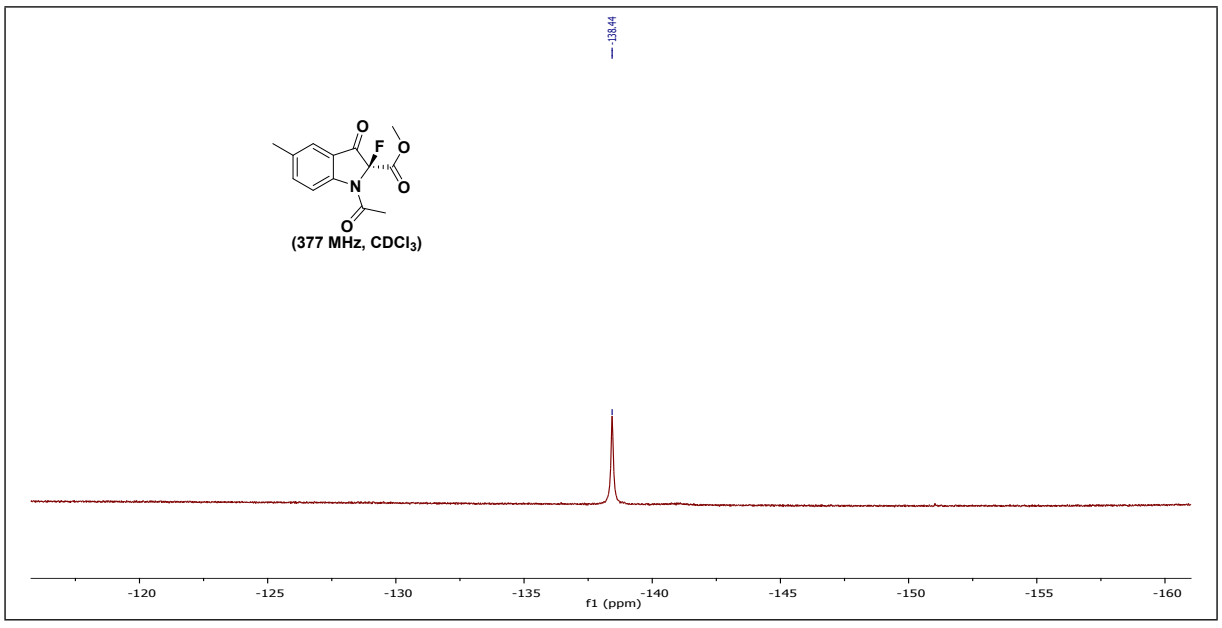
^{1}H NMR spectrum of **5d**:



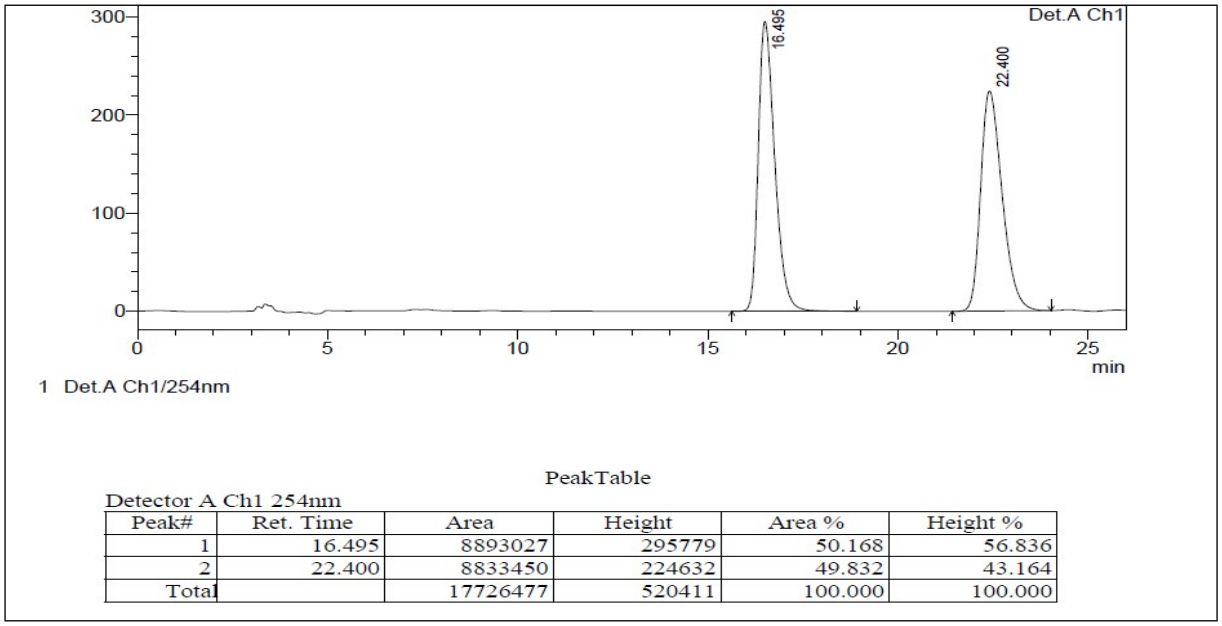
^{13}C NMR spectrum of **5d**:



^{19}F NMR spectrum of **5d**:



HPLC chromatogram of **5d**-racemic:

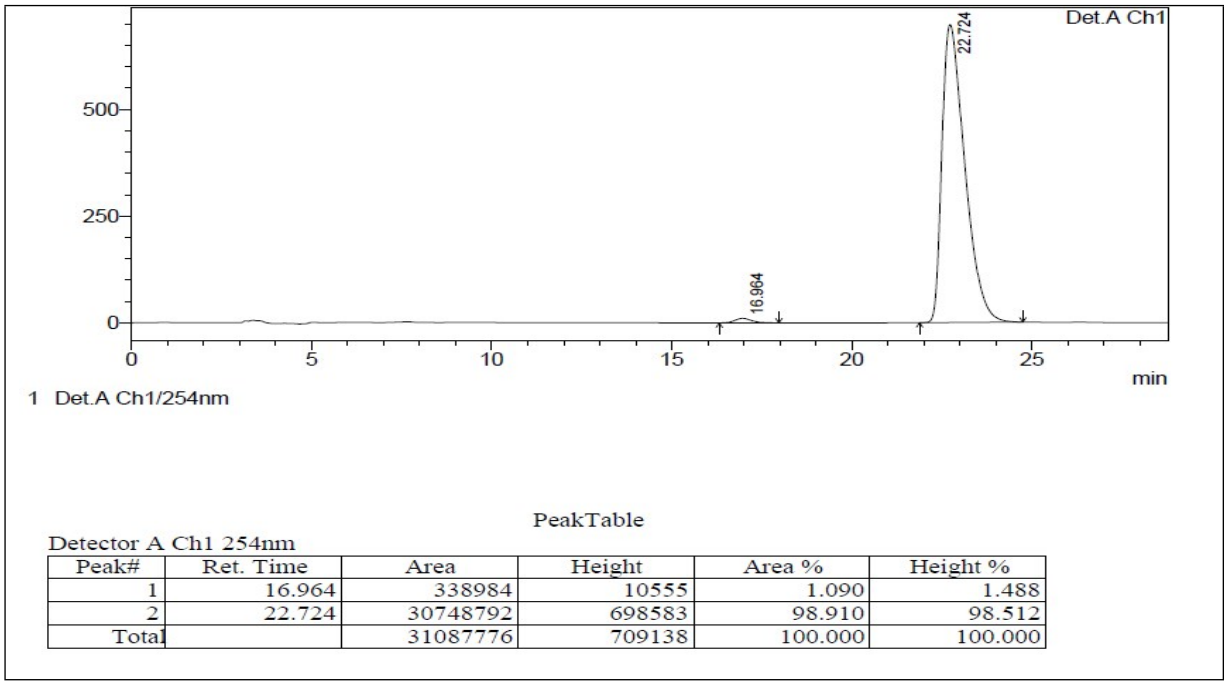


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.495	8893027	295779	50.168	56.836
2	22.400	8833450	224632	49.832	43.164
Total		17726477	520411	100.000	100.000

HPLC chromatogram of **5d**-chiral:

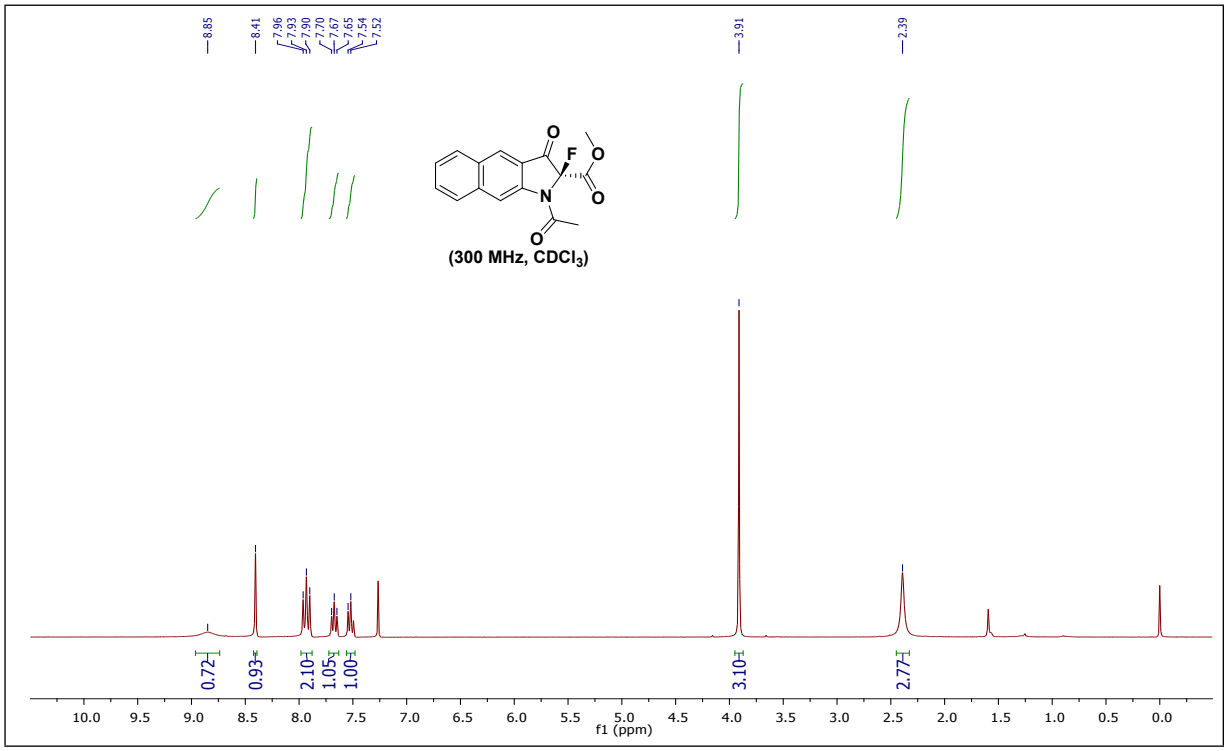


PeakTable

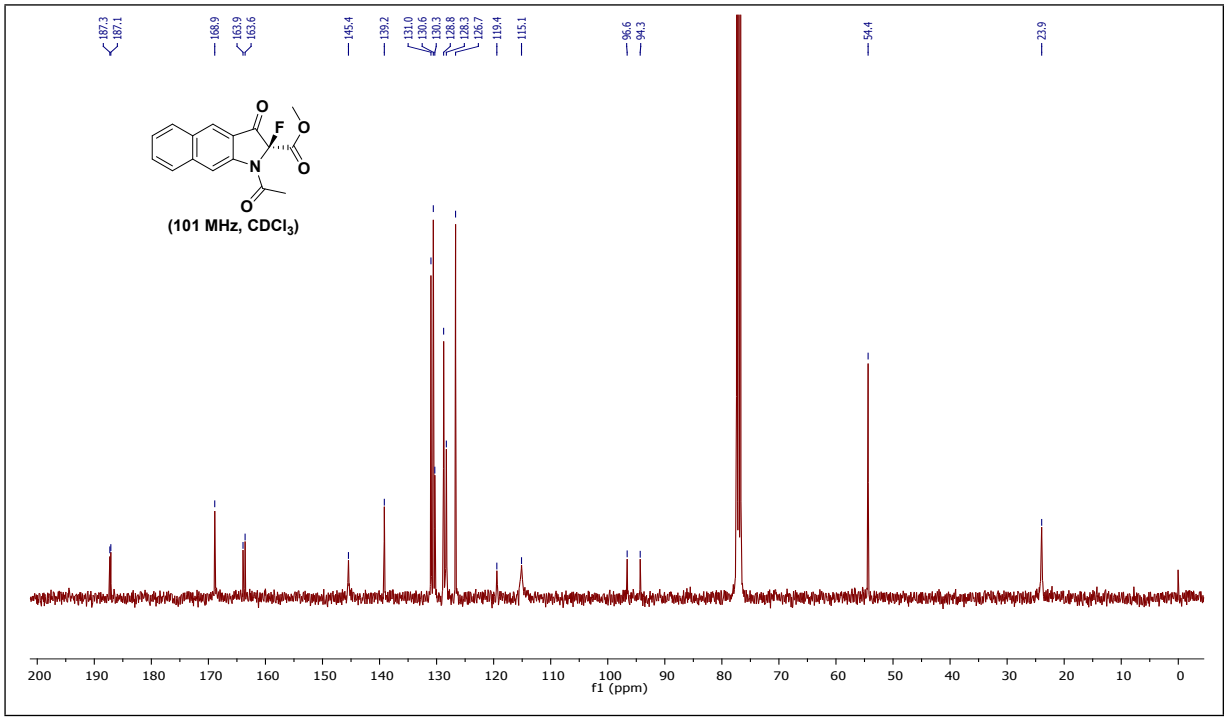
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.964	338984	10555	1.090	1.488
2	22.724	30748792	698583	98.910	98.512
Total		31087776	709138	100.000	100.000

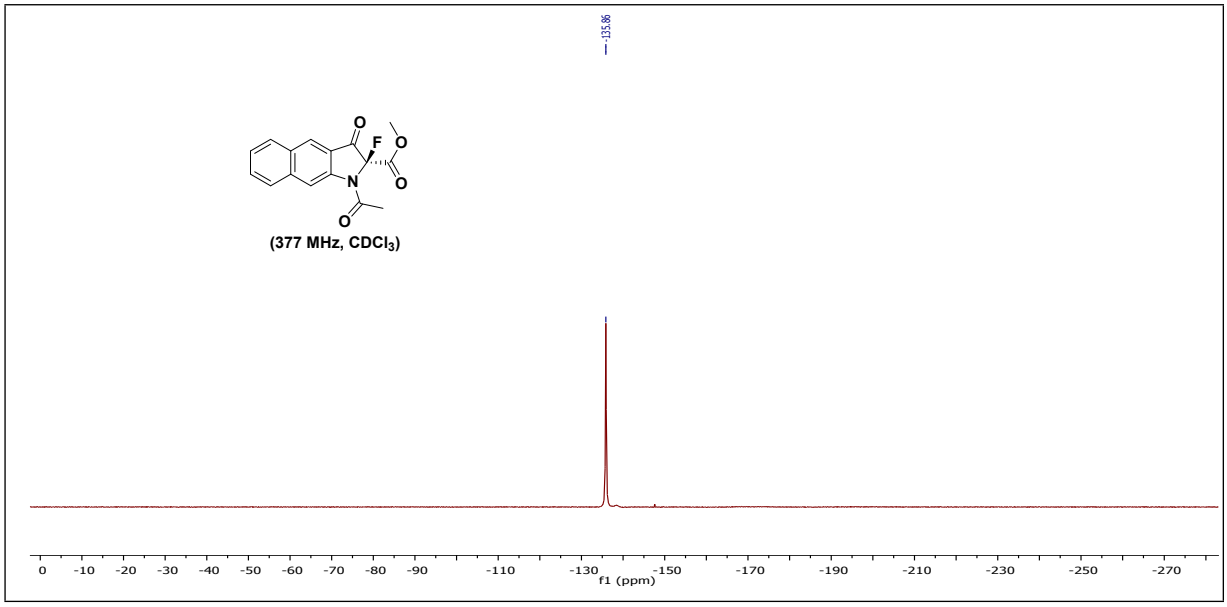
^{1}H NMR spectrum of **5e**:



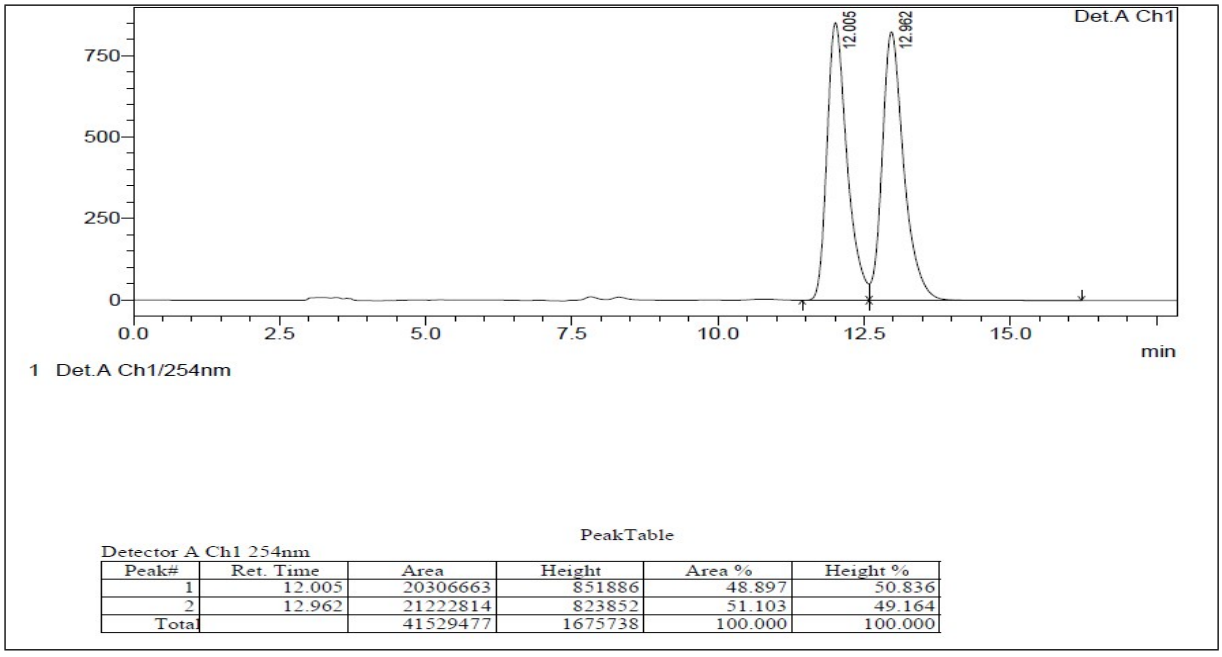
^{13}C NMR spectrum of **5e**:



^{19}F NMR spectrum of **5e**:



HPLC chromatogram of **5e**-racemic:

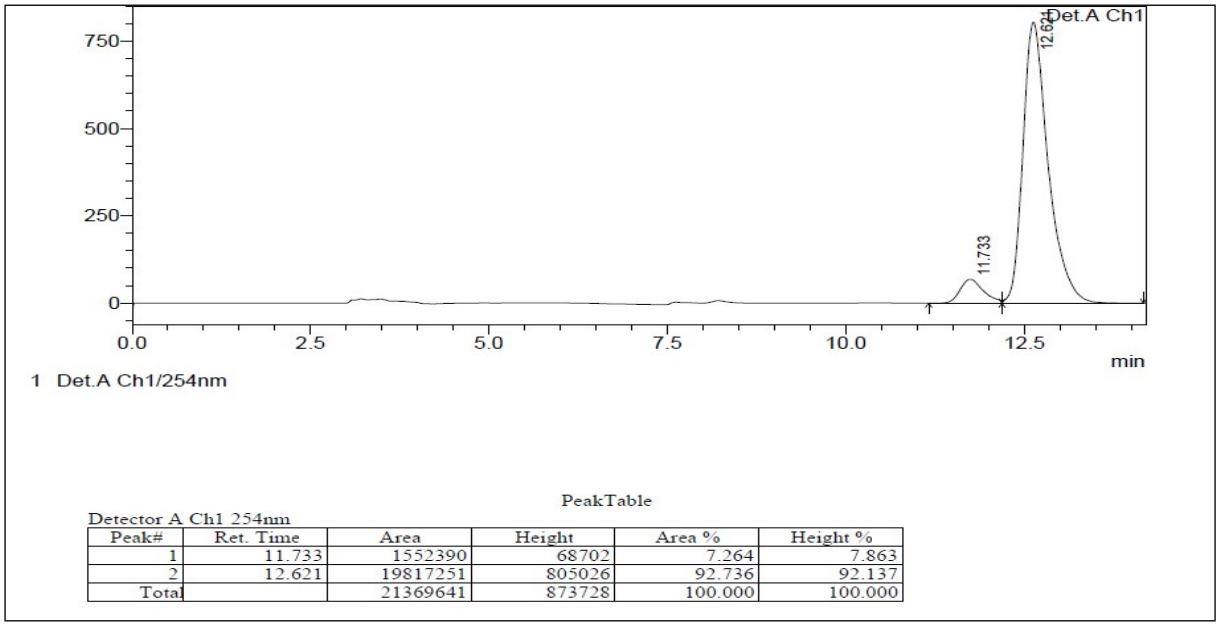


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.005	20306663	851886	48.897	50.836
2	12.962	21222814	823852	51.103	49.164
Total		41529477	1675738	100.000	100.000

HPLC chromatogram of **5e**-chiral:

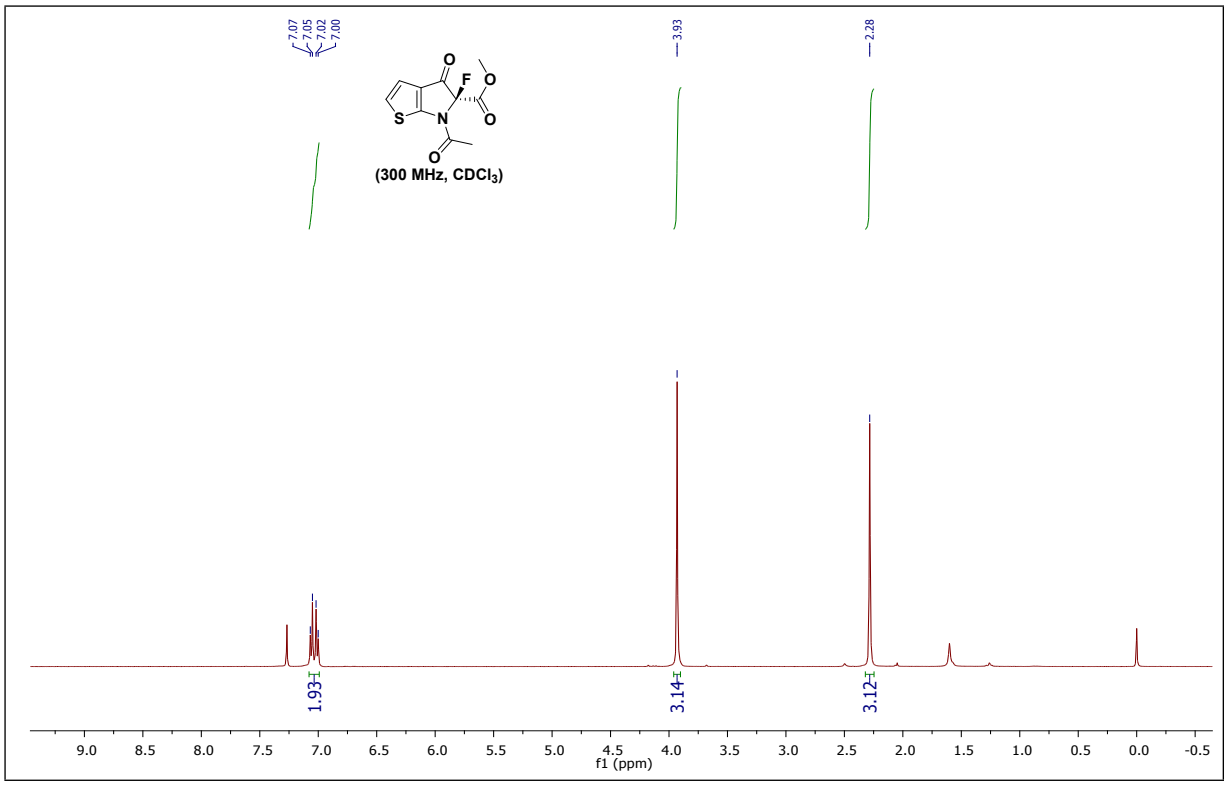


PeakTable

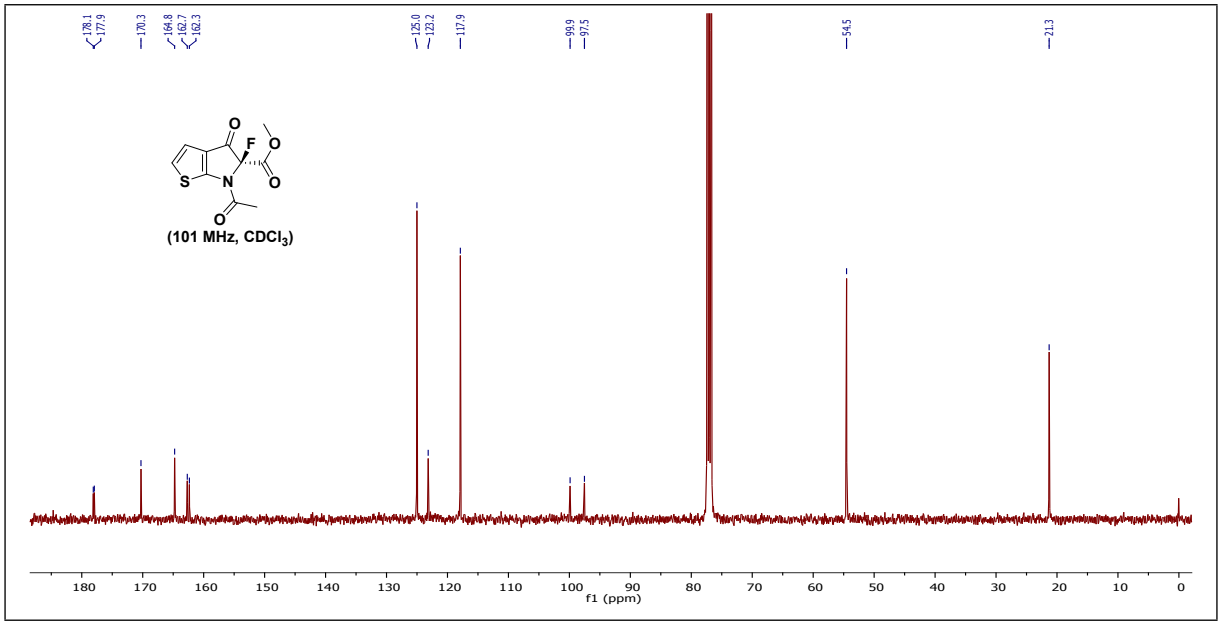
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.733	1552390	68702	7.264	7.863
2	12.621	19817251	805026	92.736	92.137
Total		21369641	873728	100.000	100.000

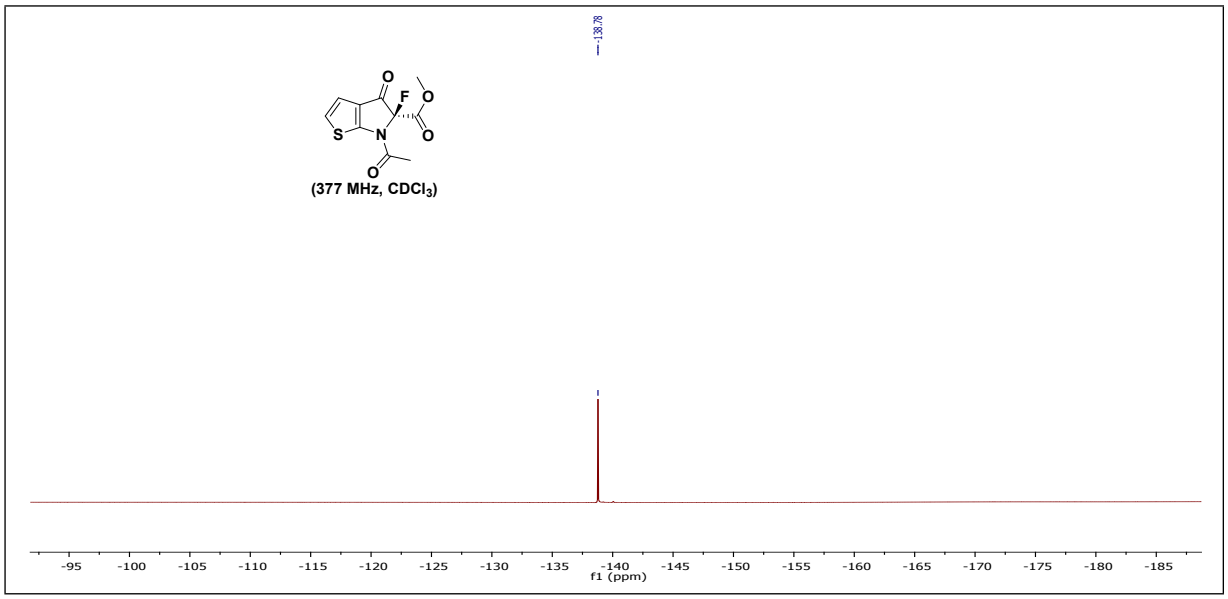
^{1}H NMR spectrum of **5f**:



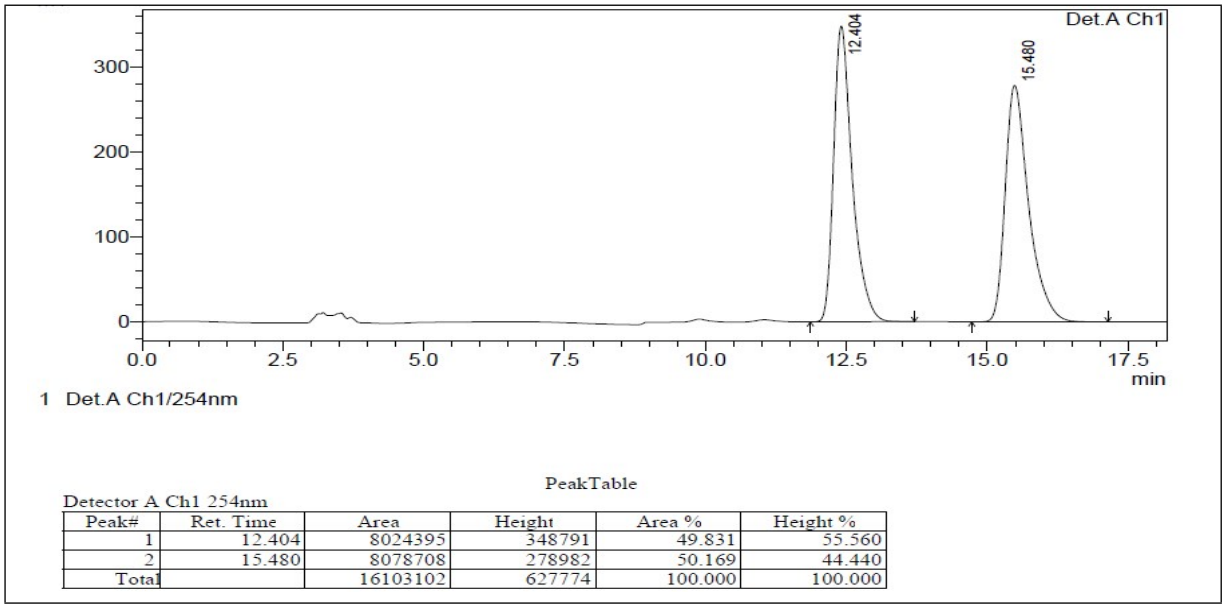
^{13}C NMR spectrum of **5f**:



^{19}F NMR spectrum of **5f**:



HPLC chromatogram of **5f**-racemic:

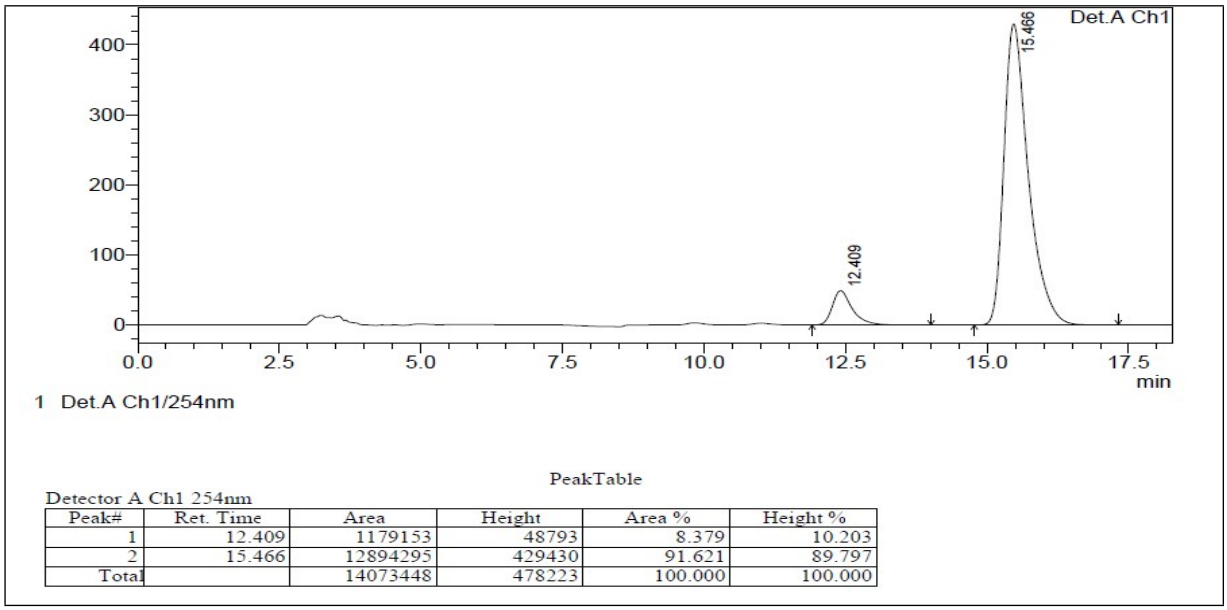


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.404	8024395	348791	49.831	55.560
2	15.480	8078708	278982	50.169	44.440
Total		16103102	627774	100.000	100.000

HPLC chromatogram of **5f**-chiral:

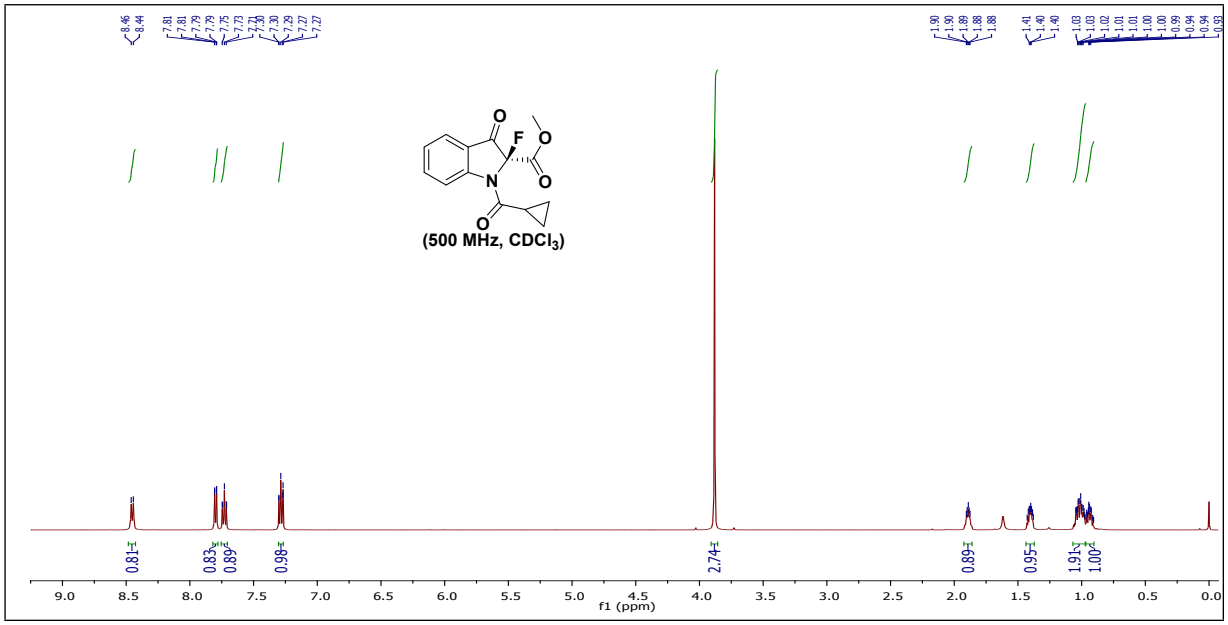


PeakTable

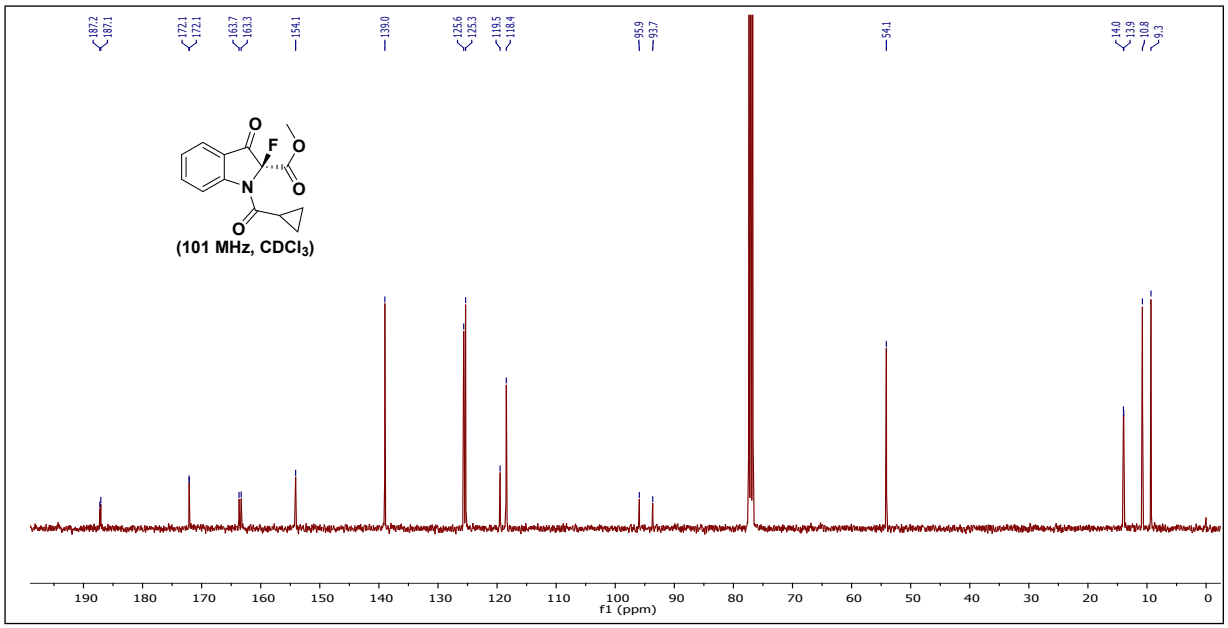
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.409	1179153	48793	8.379	10.203
2	15.466	12894295	429430	91.621	89.797
Total		14073448	478223	100.000	100.000

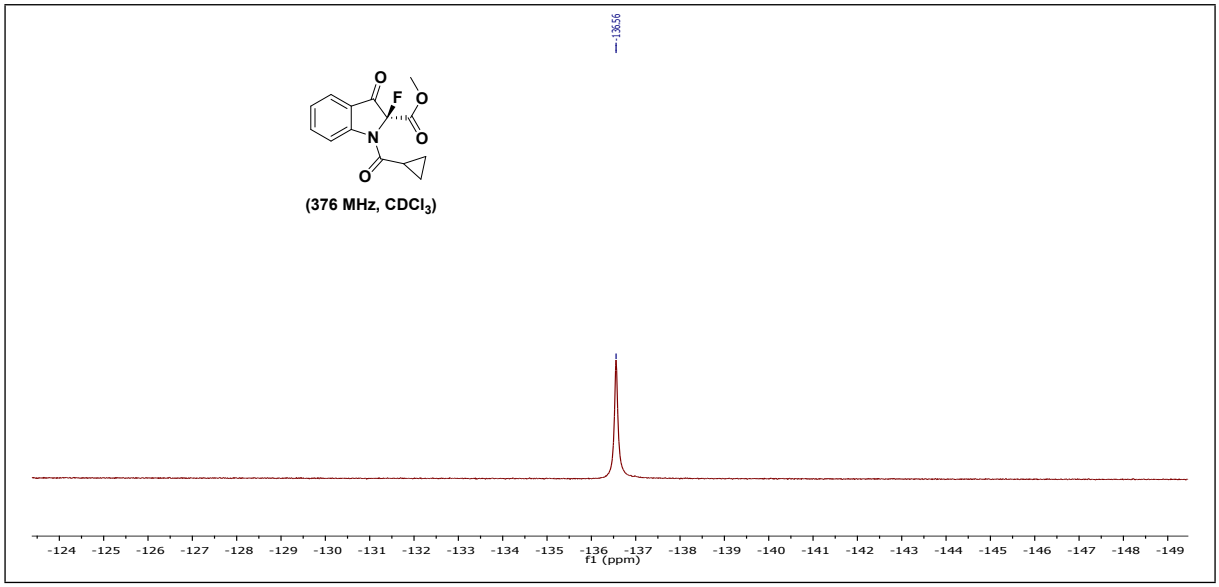
^{1}H NMR spectrum of **5g**:



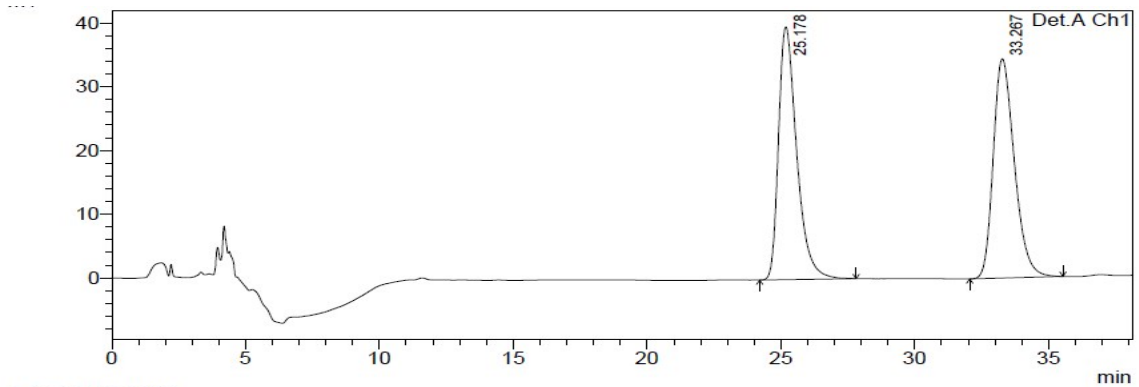
^{13}C NMR spectrum of **5g**:



^{19}F NMR spectrum of **5g**:



HPLC chromatogram of **5g**-racemic:

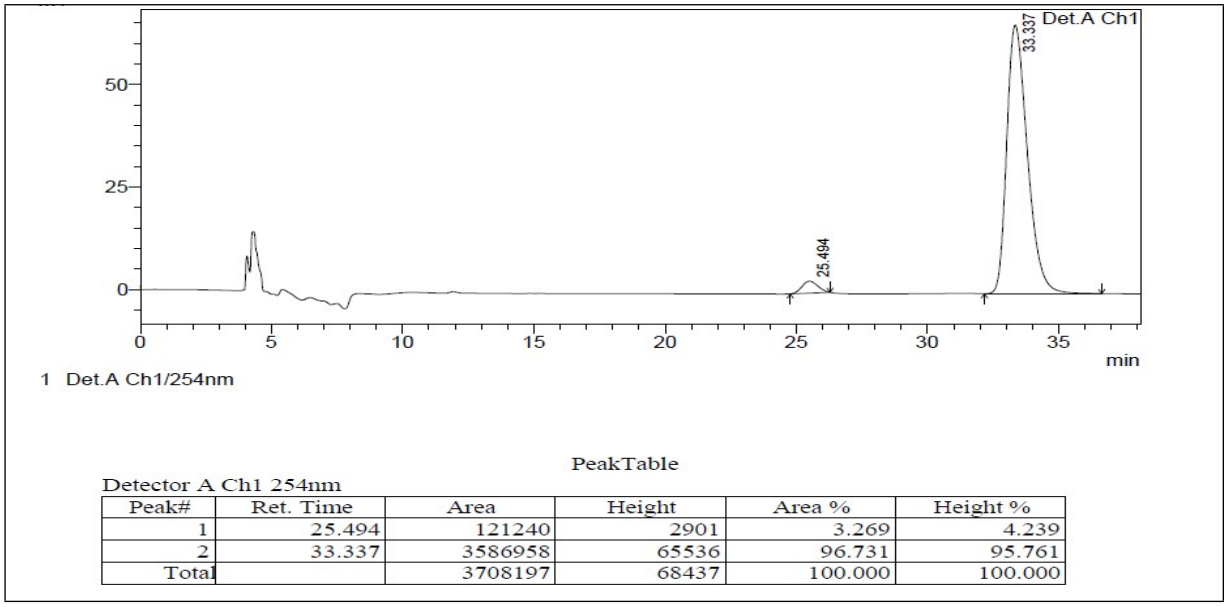


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.178	1872409	39626	49.846	53.556
2	33.267	1883957	34364	50.154	46.444
Total		3756366	73990	100.000	100.000

HPLC chromatogram of **5g**-chiral:

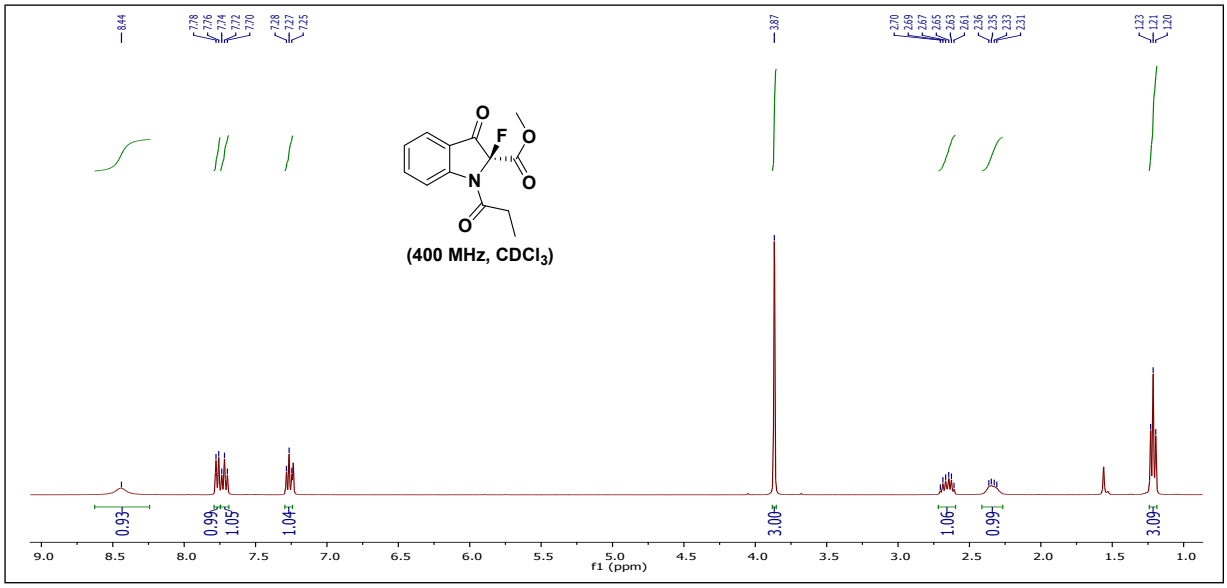


PeakTable

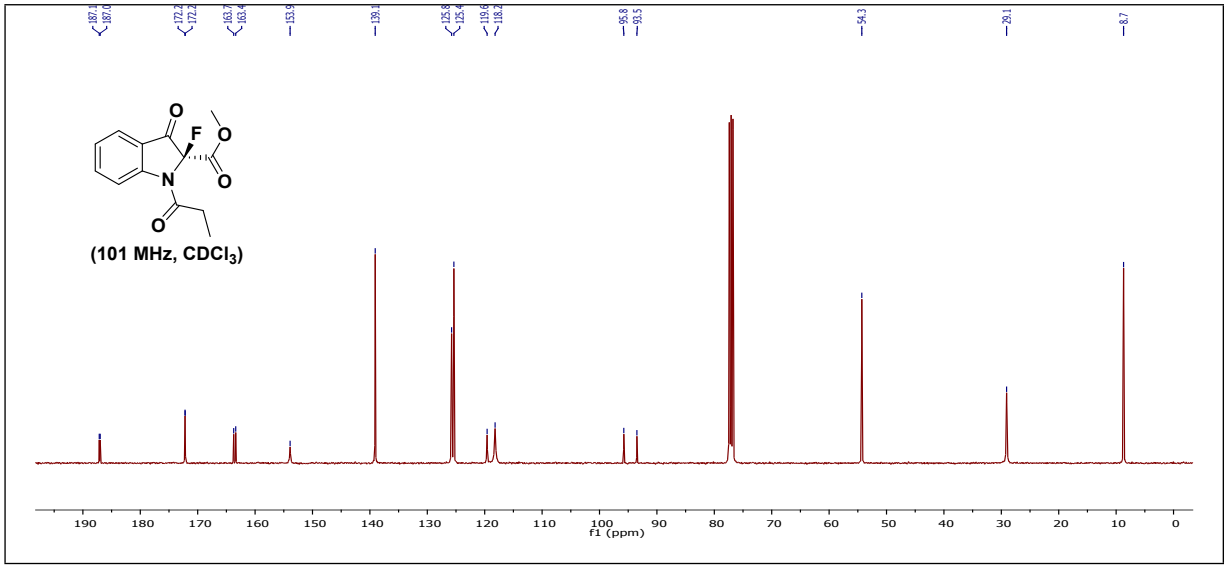
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.494	121240	2901	3.269	4.239
2	33.337	3586958	65536	96.731	95.761
Total		3708197	68437	100.000	100.000

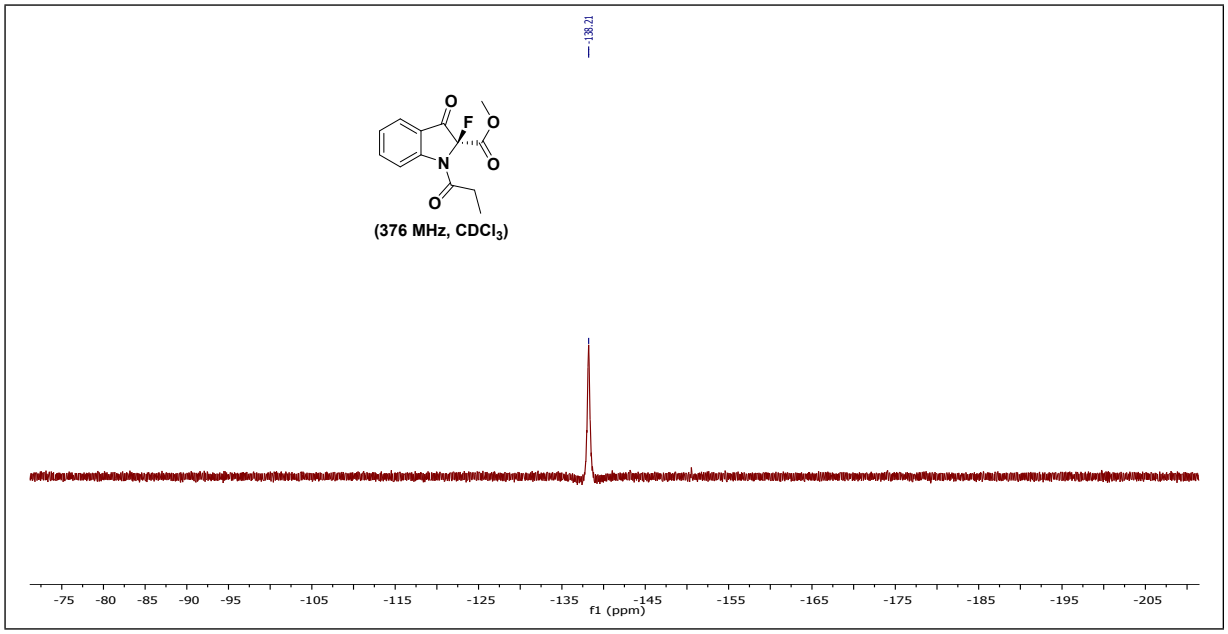
[1]H NMR spectrumof **5h**:



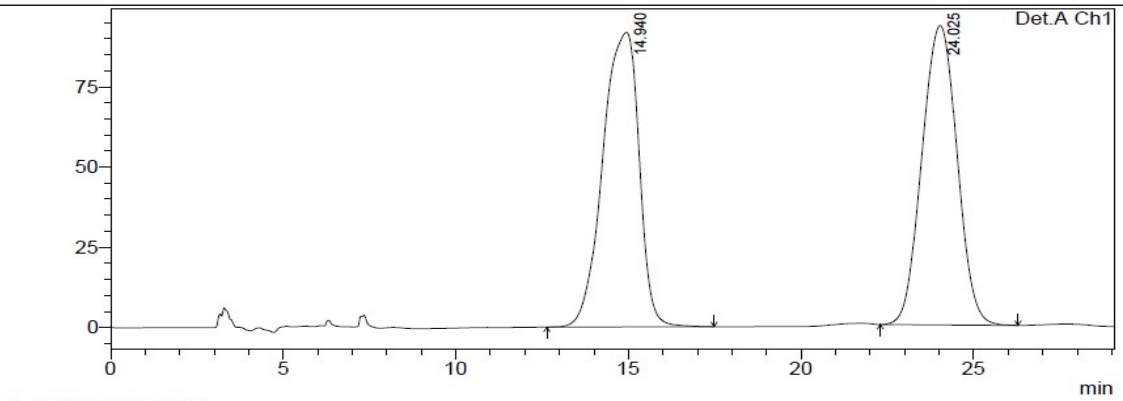
[13]C NMR spectrumof **5h**:



[19]F NMR spectrumof **5h**:



HPLC chromatogram of **5h**-racemic:

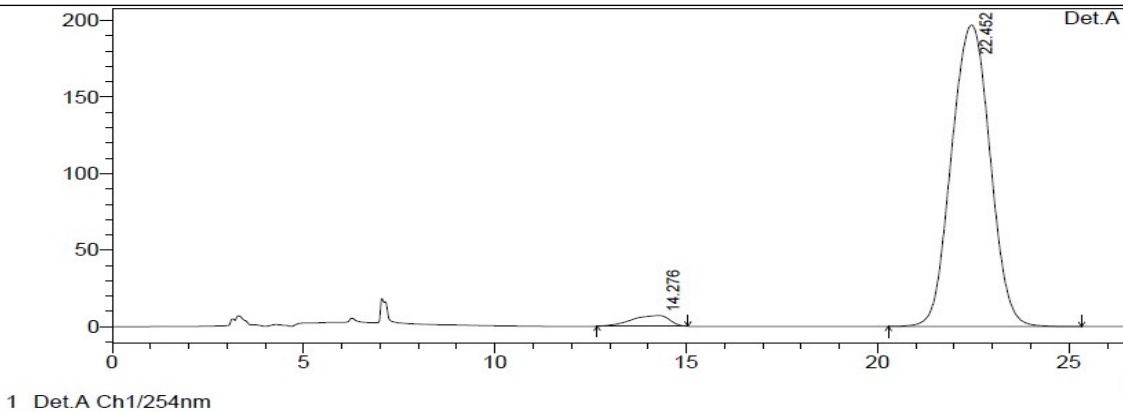


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.940	6697487	91755	50.329	49.589
2	24.025	6610002	93276	49.671	50.411
Total		13307489	185031	100.000	100.000

HPLC chromatogram of **5h**-chiral:

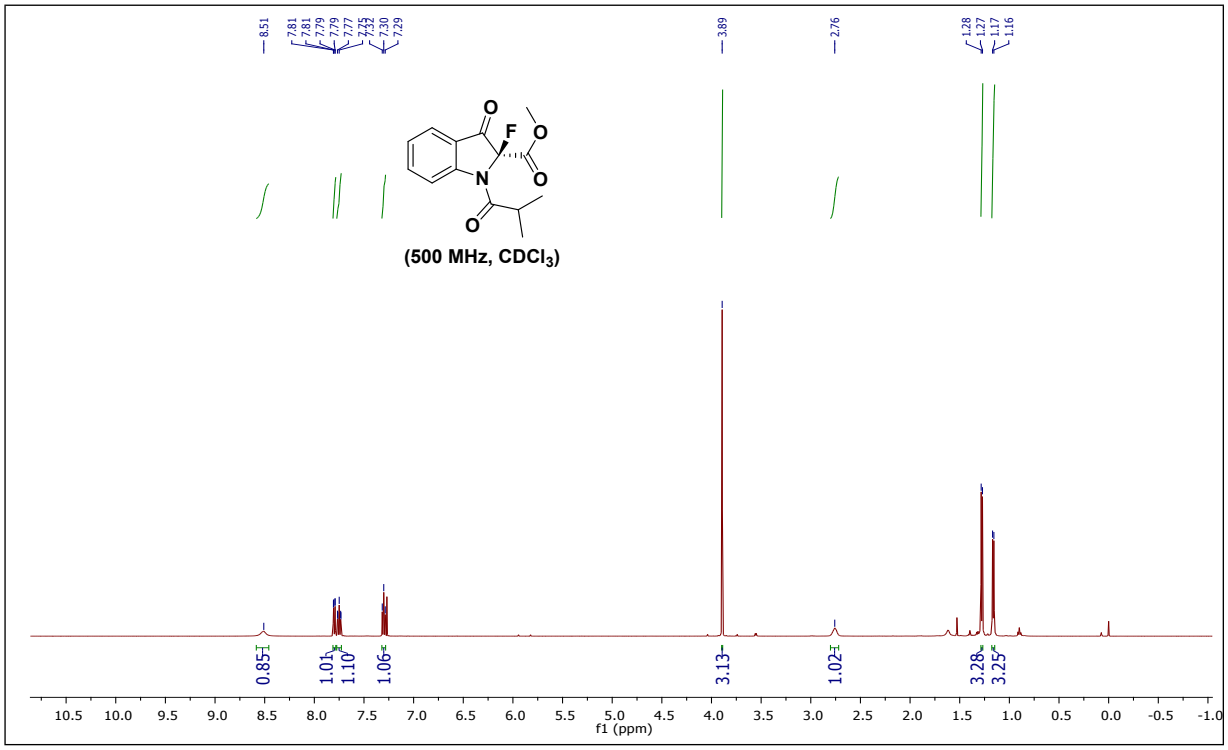


PeakTable

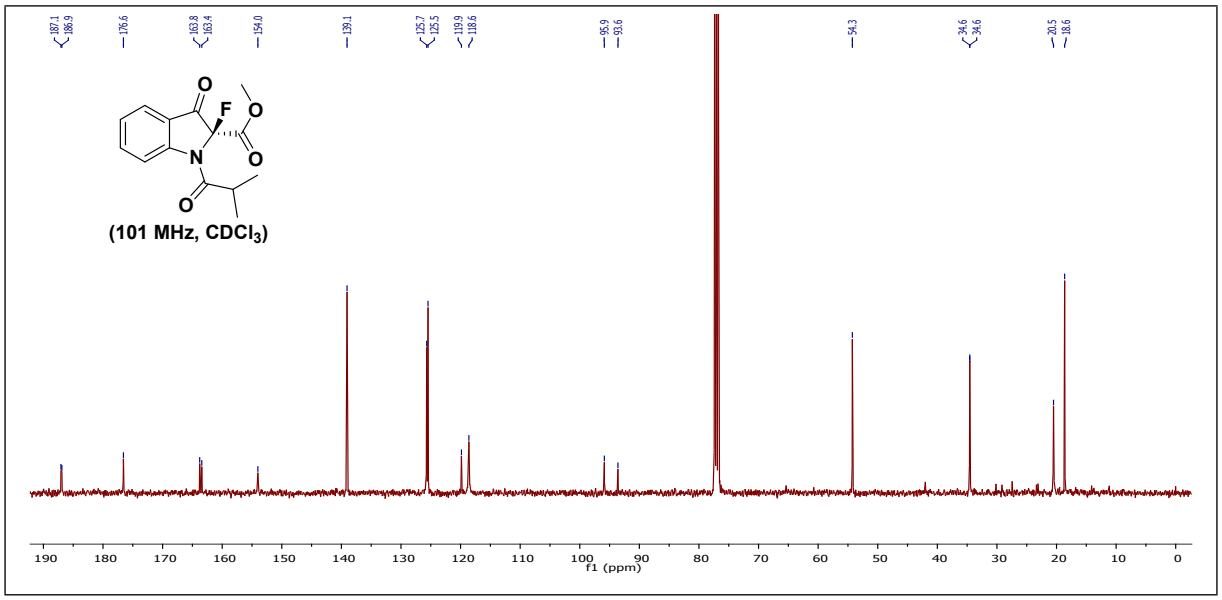
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.276	474975	6927	3.327	3.401
2	22.452	13800436	196751	96.673	96.599
Total		14275411	203678	100.000	100.000

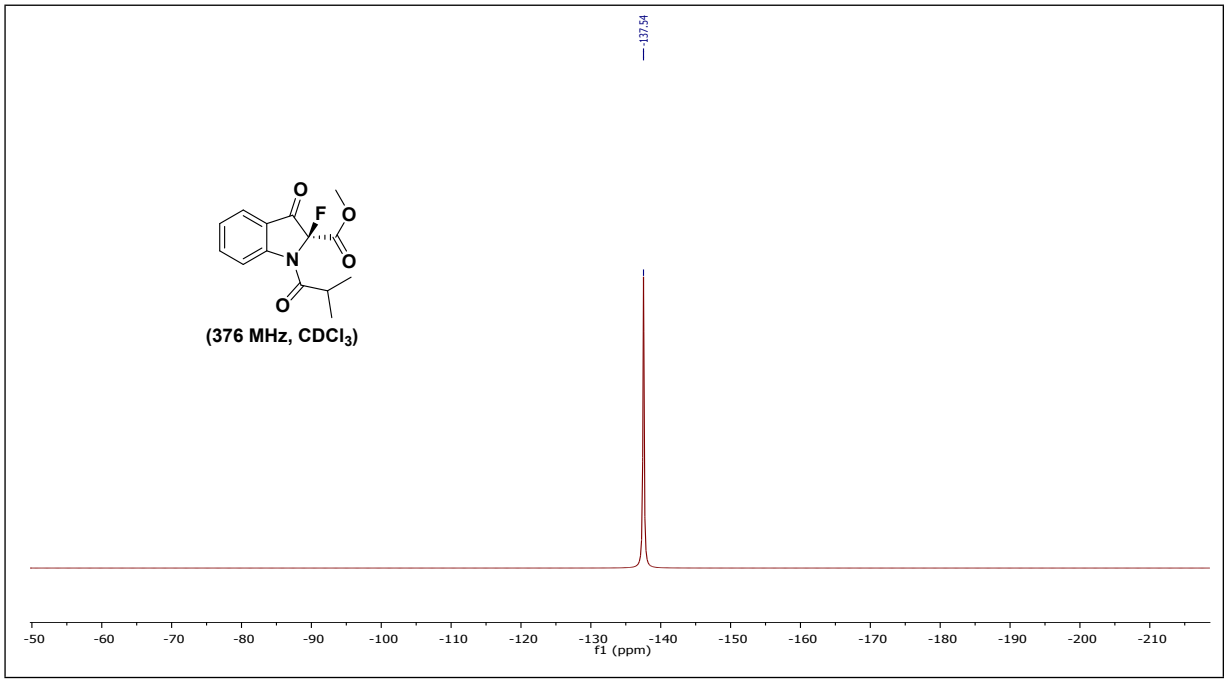
[1]H NMR spectrum of **5i**:



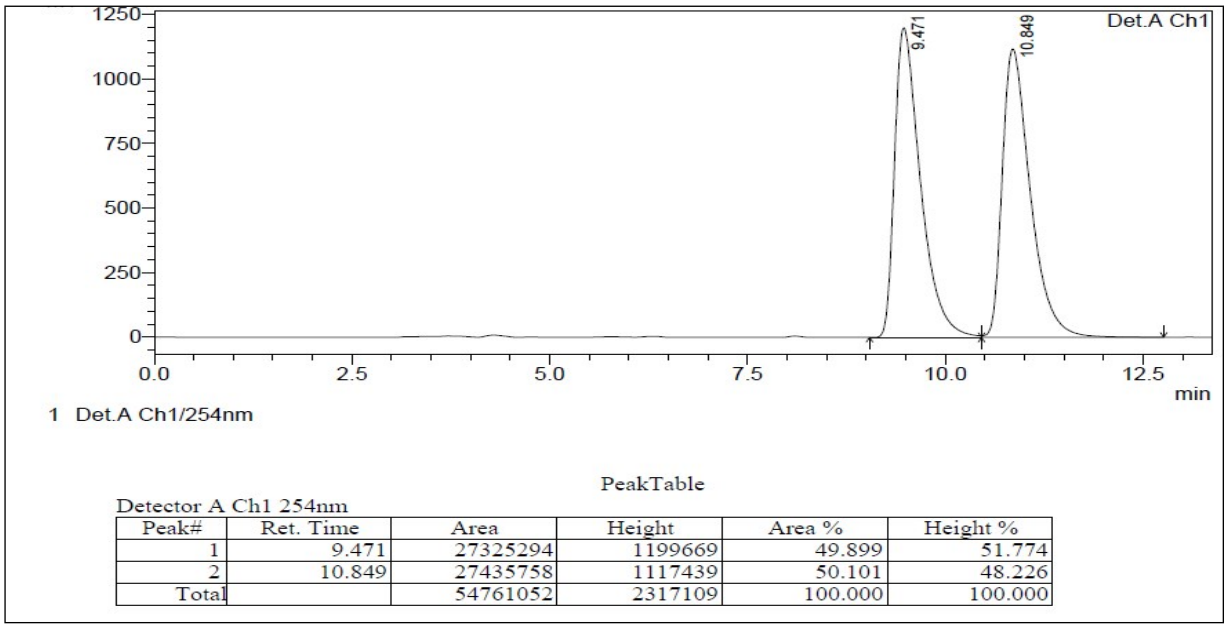
[13]C NMR spectrum of **5i**:



^{19}F NMR spectrum of **5i**:



HPLC chromatogram of **5i**-racemic:

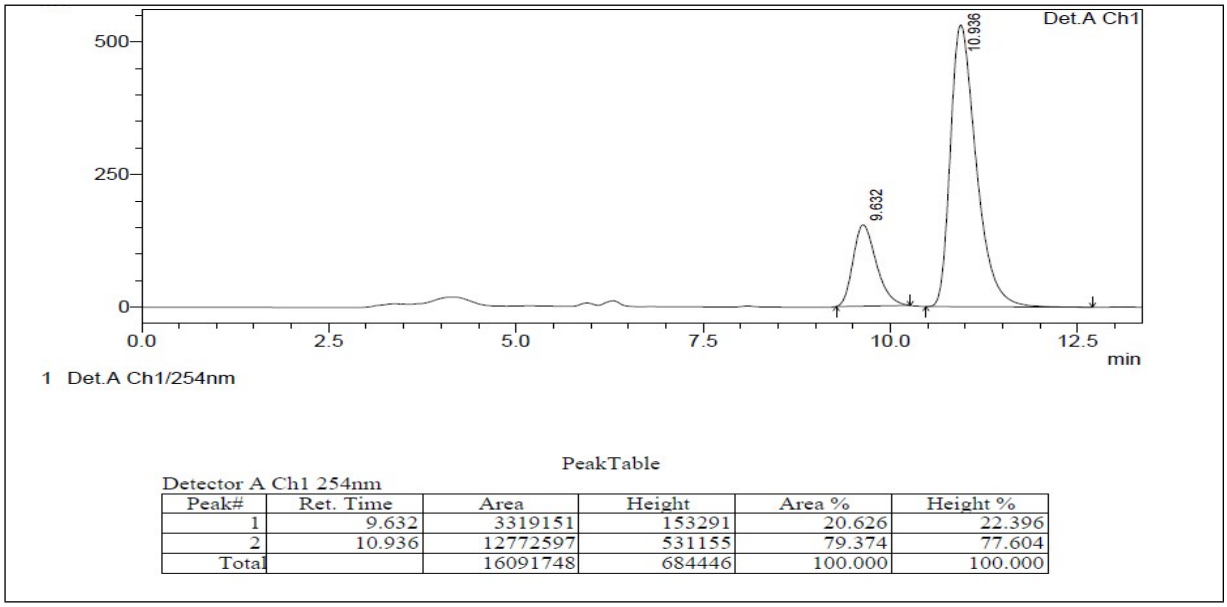


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.471	27325294	1199669	49.899	51.774
2	10.849	27435758	1117439	50.101	48.226
Total		54761052	2317109	100.000	100.000

HPLC chromatogram of **5i**-chiral:

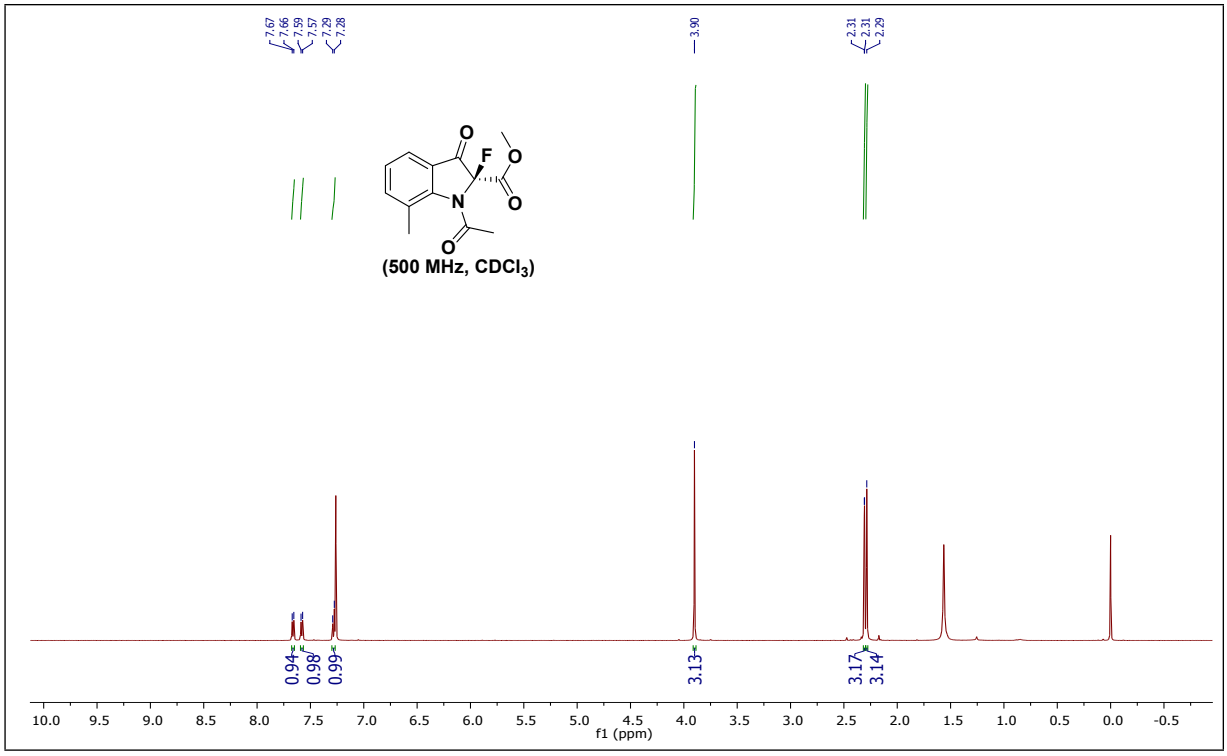


PeakTable

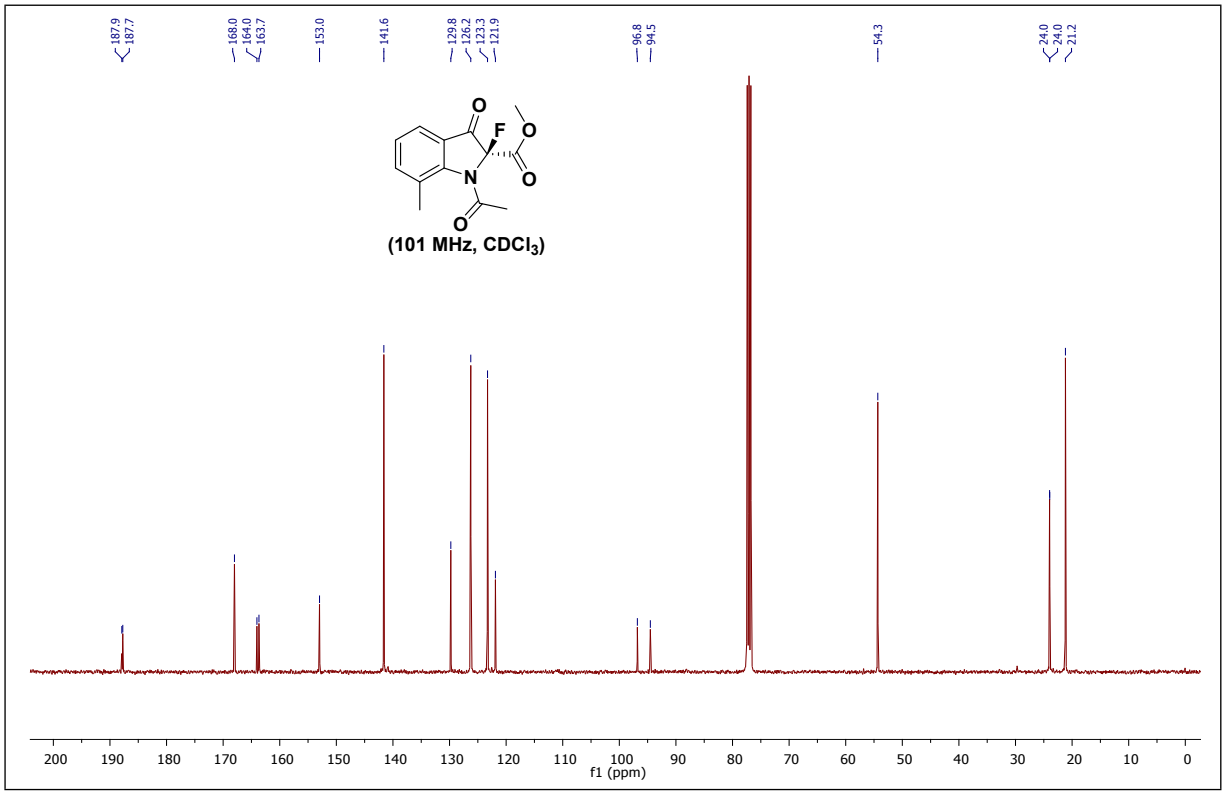
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.632	3319151	153291	20.626	22.396
2	10.936	12772597	531155	79.374	77.604
Total		16091748	684446	100.000	100.000

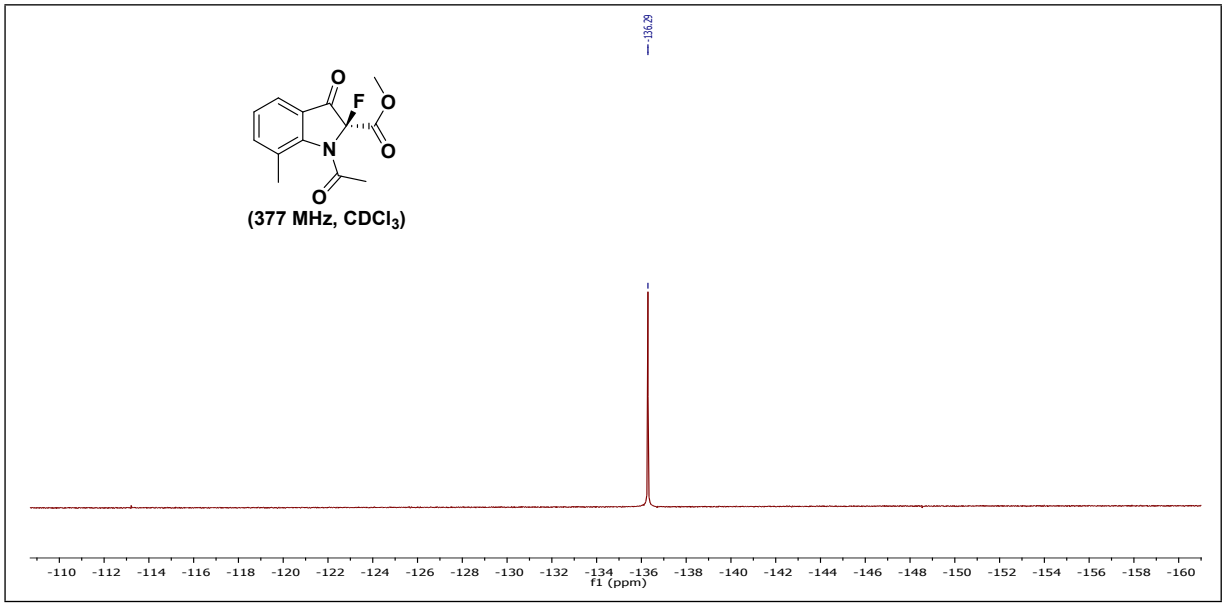
^{1}H NMR spectrum of **5j**:



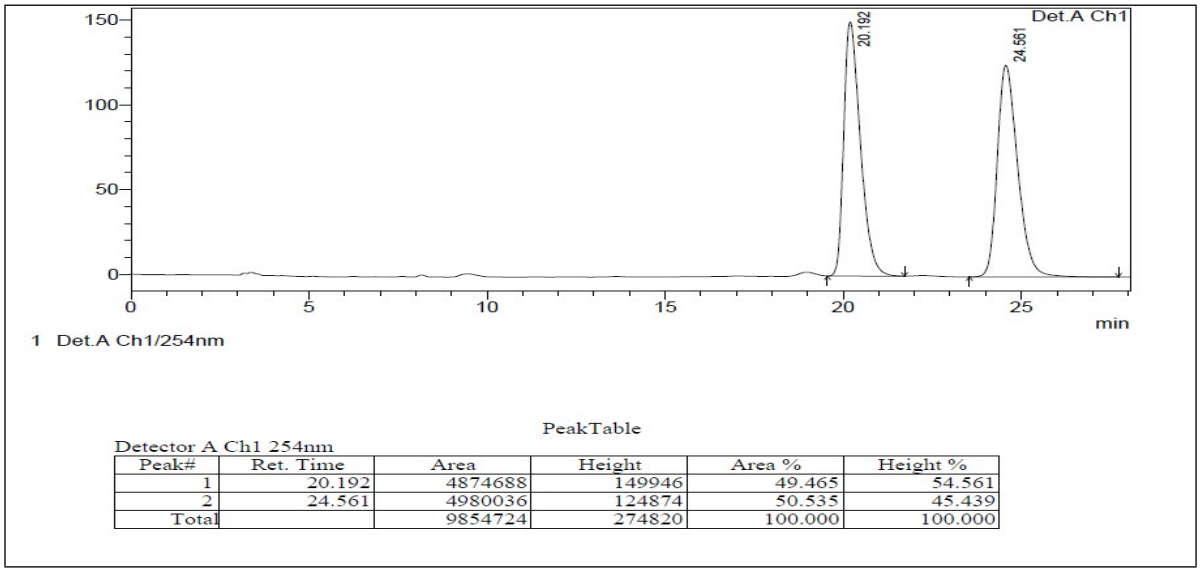
^{13}C NMR spectrum of **5j**:



^{19}F NMR spectrum of **5j**:



HPLC chromatogram of **5j**-racemic:

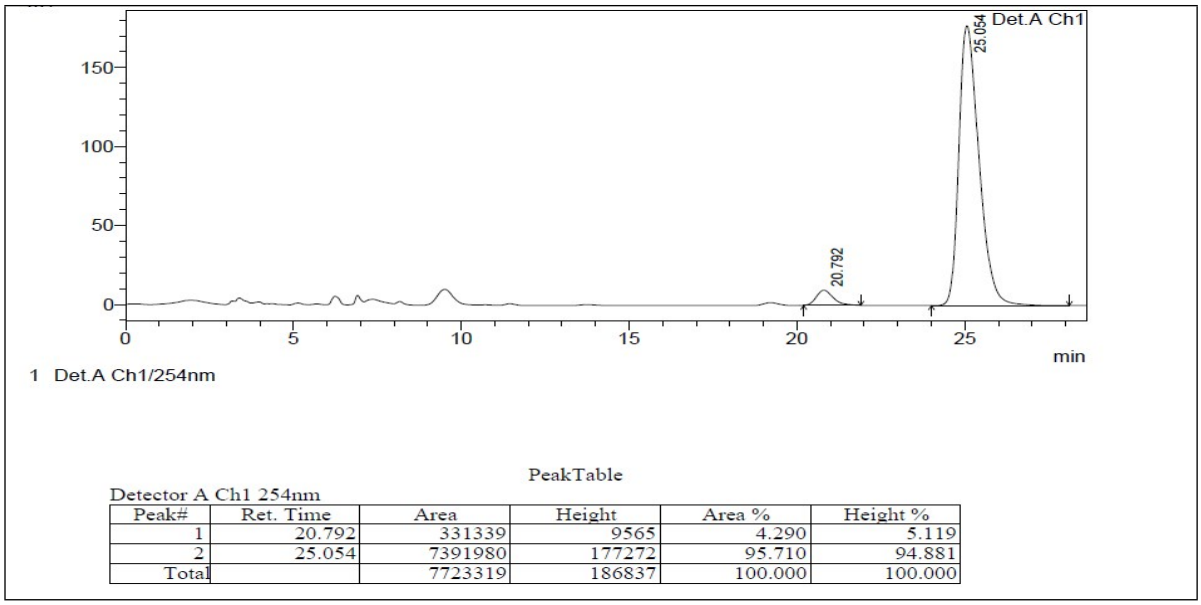


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.192	4874688	149946	49.465	54.561
2	24.561	4980036	124874	50.535	45.439
Total		9854724	274820	100.000	100.000

HPLC chromatogram of **5j**-chiral:

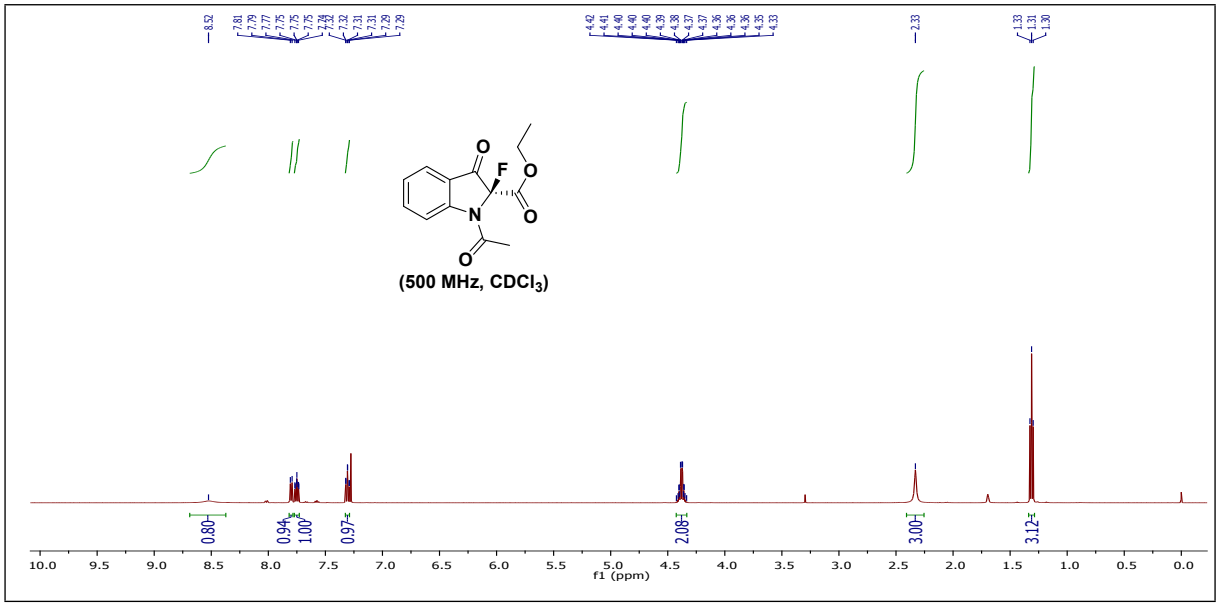


PeakTable

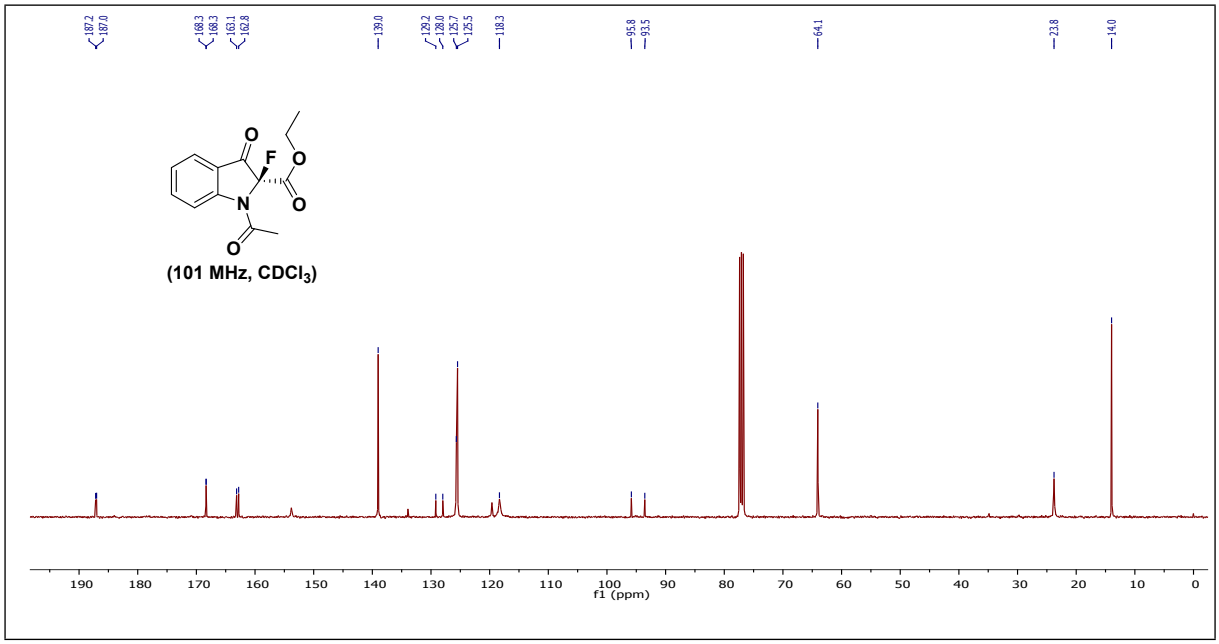
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.792	331339	9565	4.290	5.119
2	25.054	7391980	177272	95.710	94.881
Total		7723319	186837	100.000	100.000

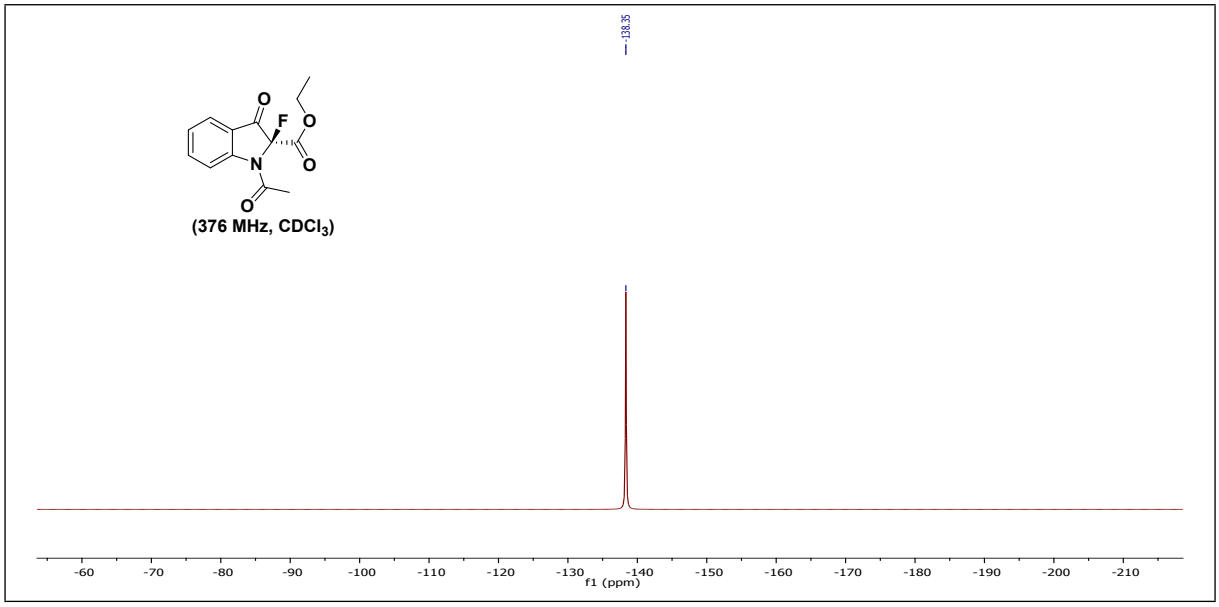
^{1}H NMR spectrum of **5k**:



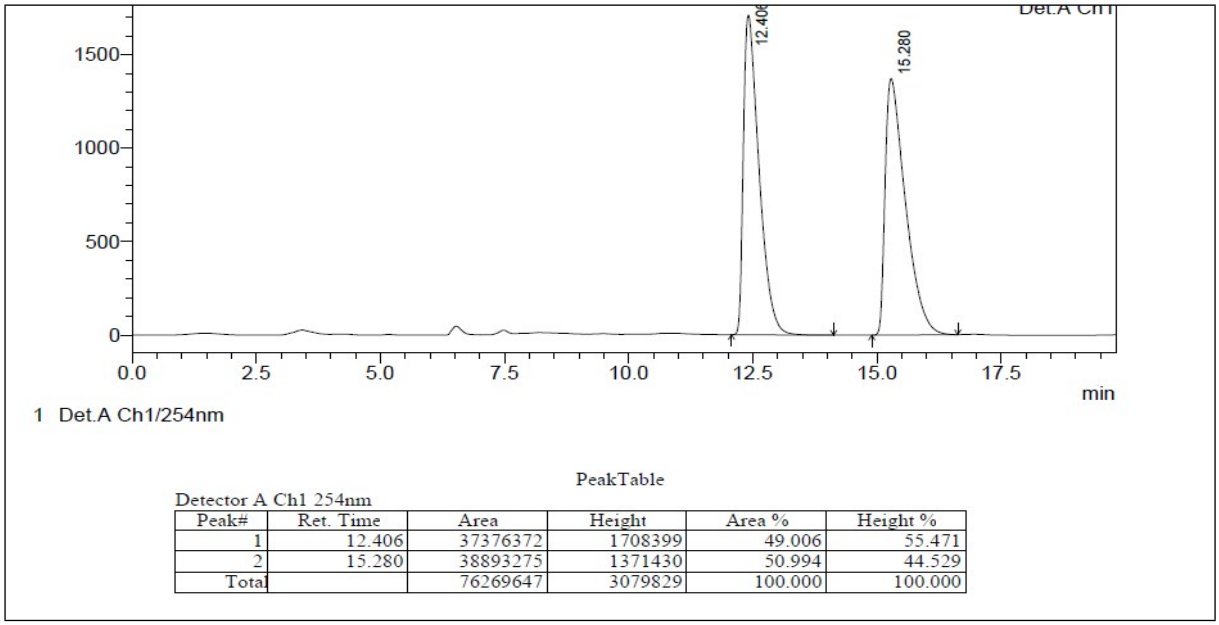
^{13}C NMR spectrum of **5k**:



^{19}F NMR spectrum of **5k**:



HPLC chromatogram of **5k**-racemic:

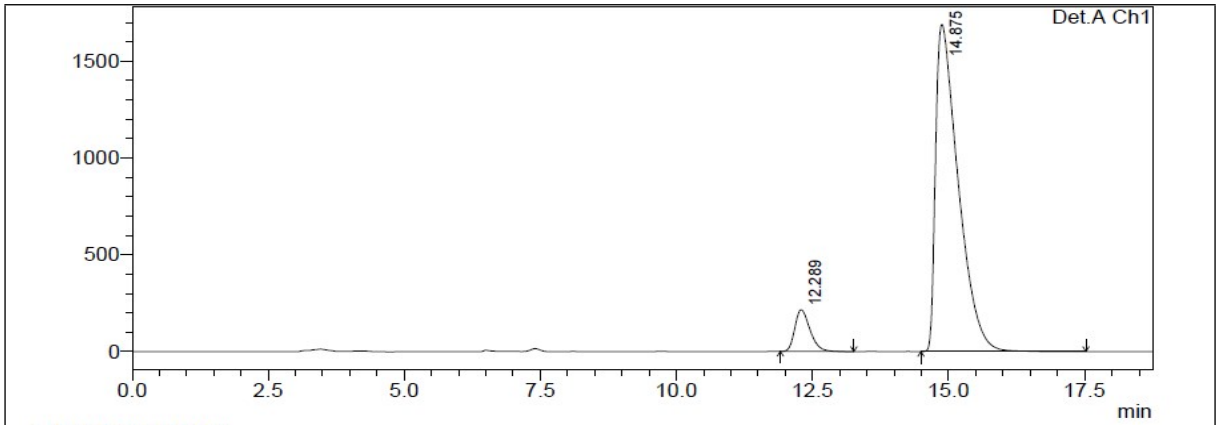


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.406	37376372	1708399	49.006	55.471
2	15.280	38893275	1371430	50.994	44.529
Total		76269647	3079829	100.000	100.000

HPLC chromatogram of **5k**- chiral:

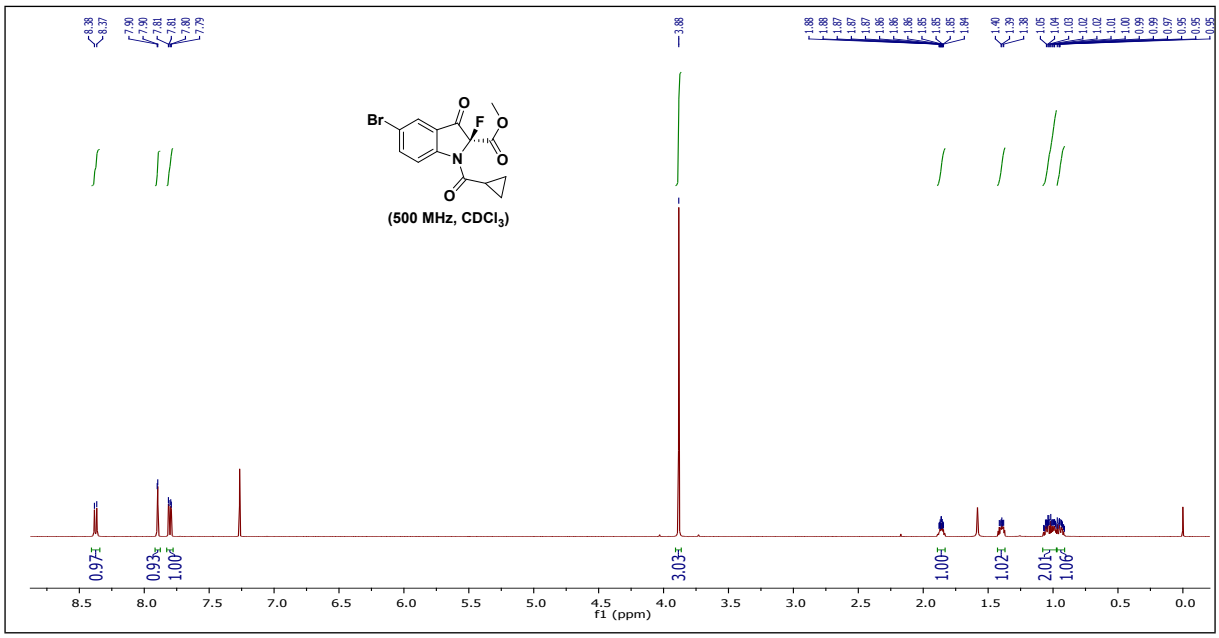


PeakTable

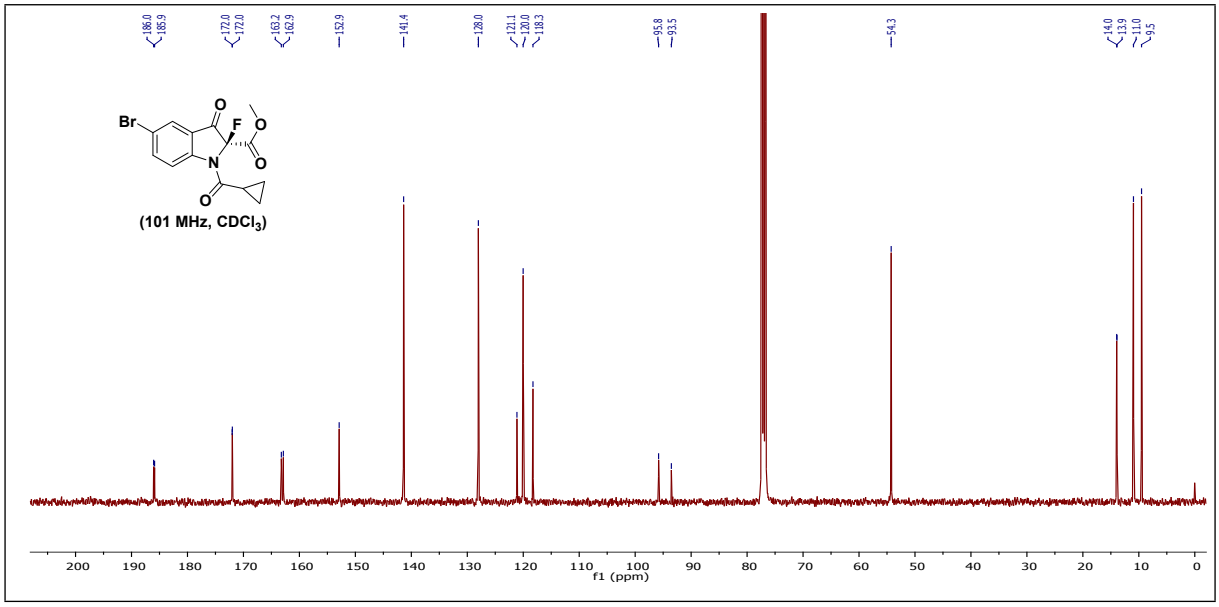
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.289	4166597	215365	7.860	11.306
2	14.875	48845281	1689569	92.140	88.694
Total		53011878	1904934	100.000	100.000

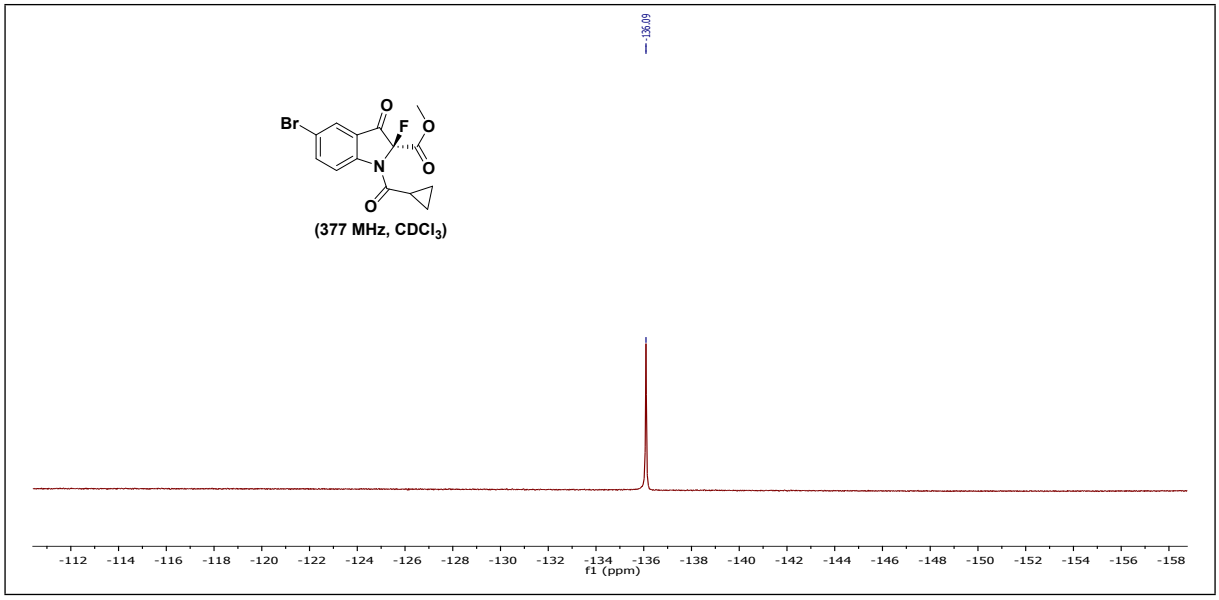
^{1}H NMR spectrum of **5l**:



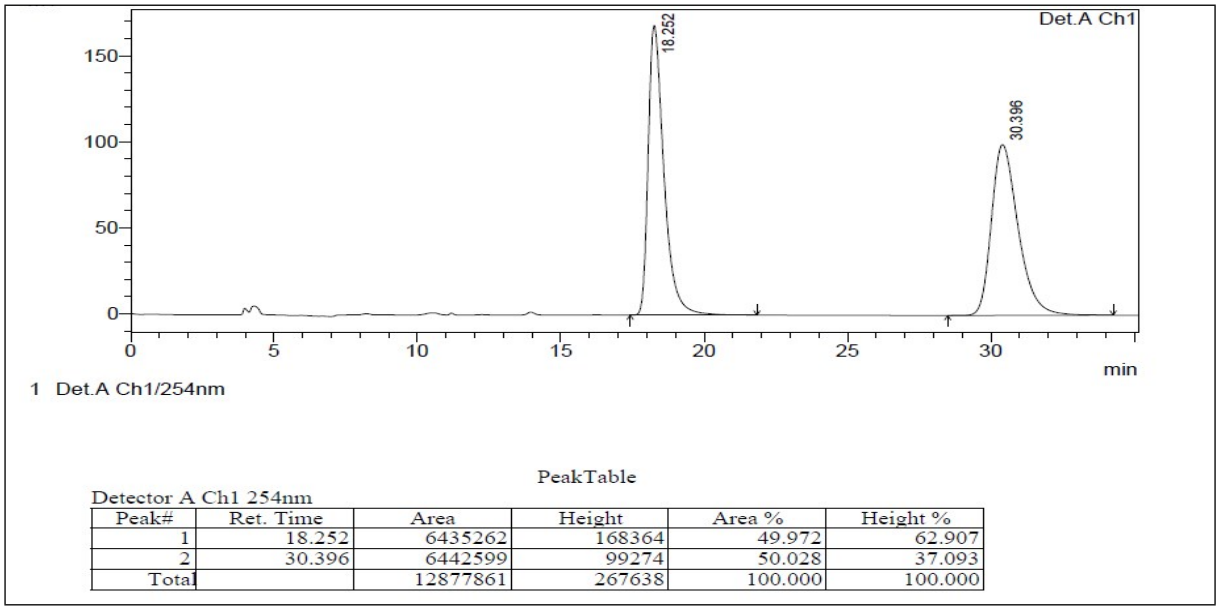
^{13}C NMR spectrum of **5l**:



^{19}F NMR spectrum of **5l**:



HPLC chromatogram of **5l**-racemic:

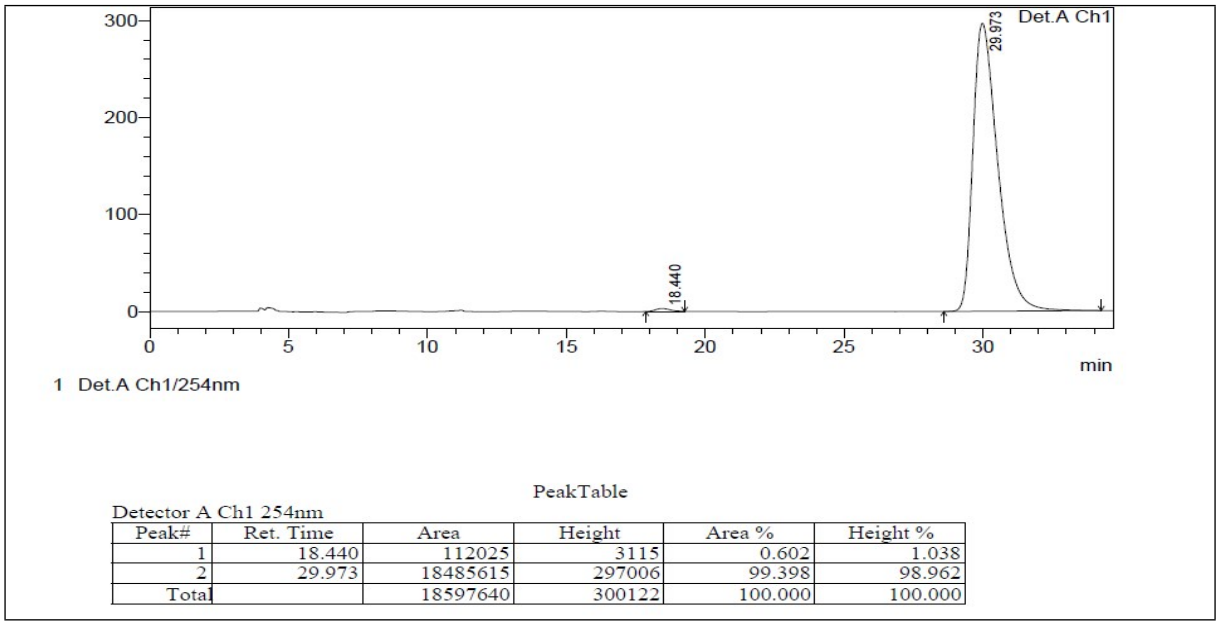


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.252	6435262	168364	49.972	62.907
2	30.396	6442599	99274	50.028	37.093
Total		12877861	267638	100.000	100.000

HPLC chromatogram of **5l**-chiral:

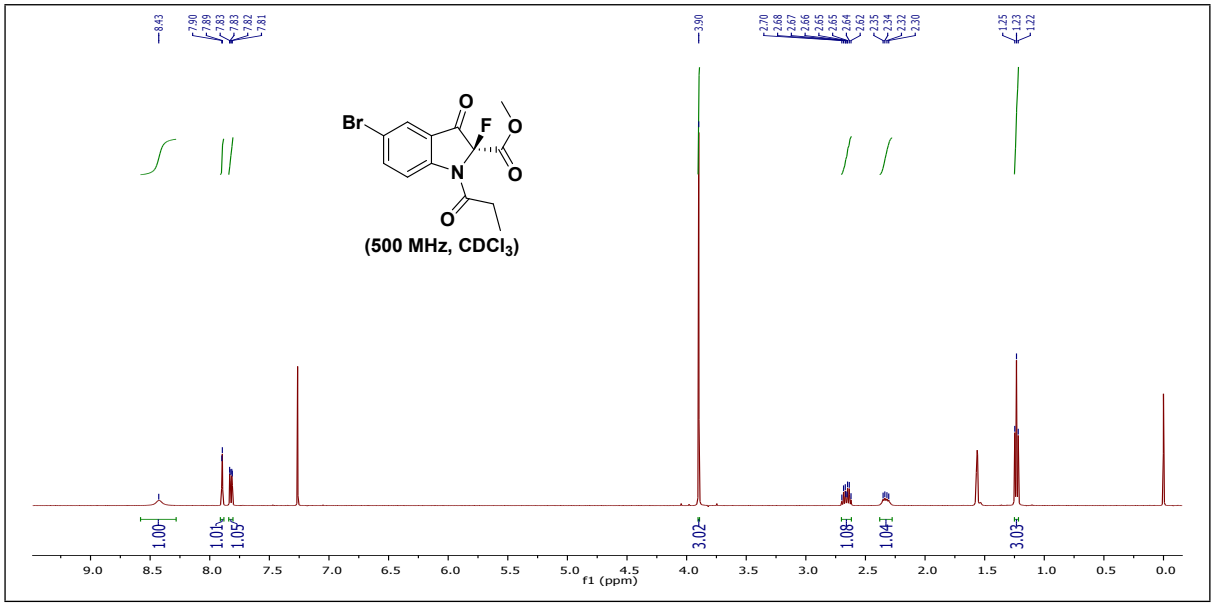


PeakTable

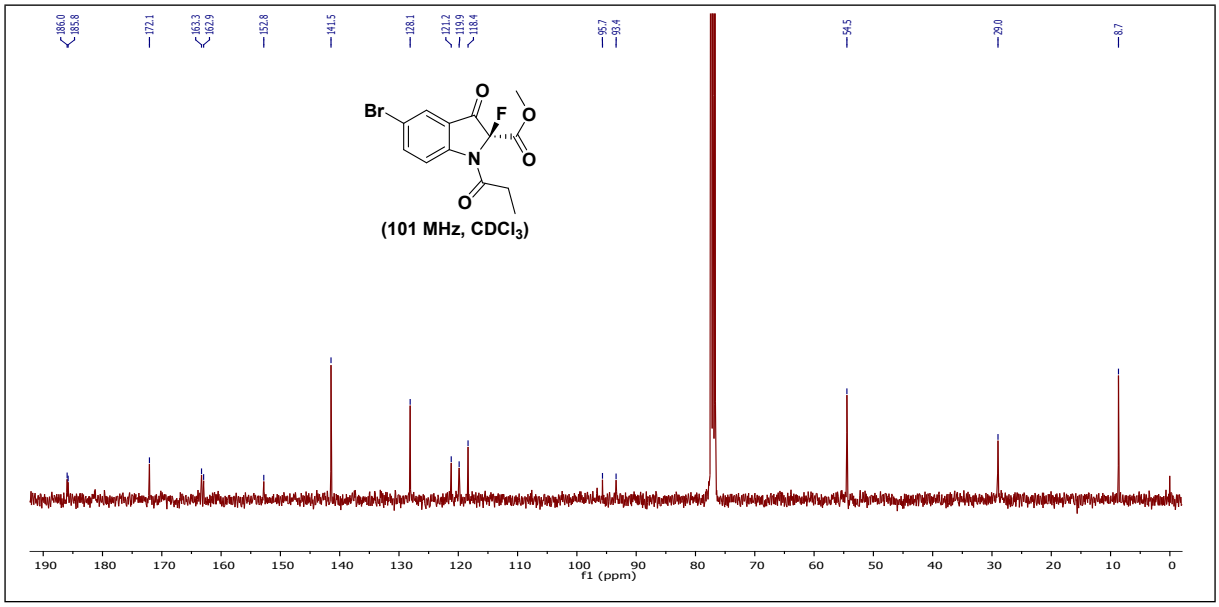
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.440	112025	3115	0.602	1.038
2	29.973	18485615	297006	99.398	98.962
Total		18597640	300122	100.000	100.000

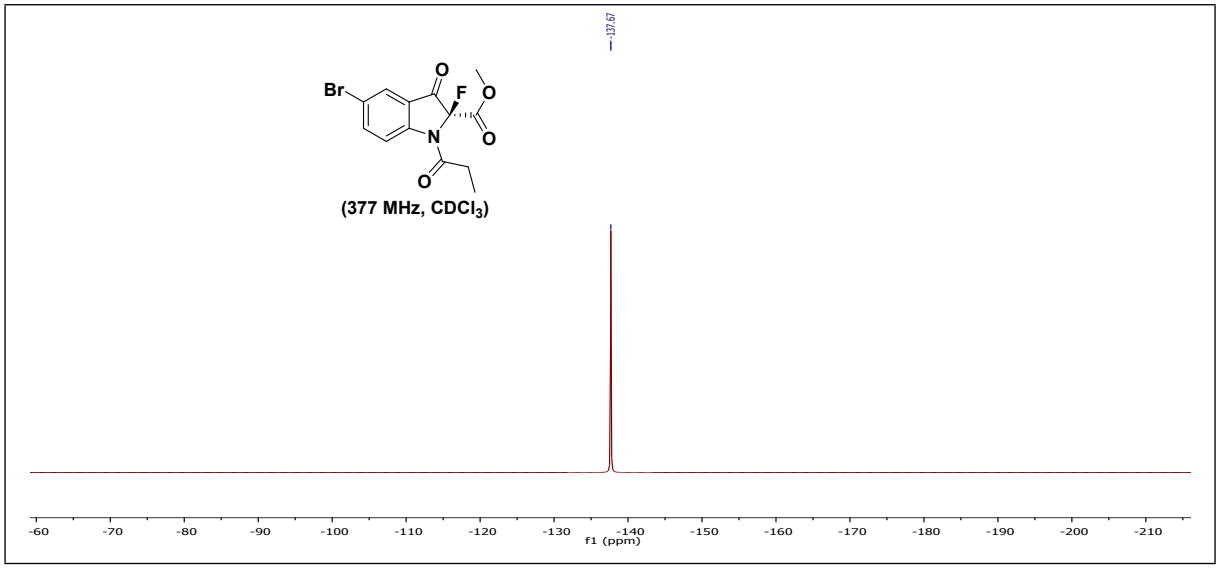
^{1}H NMR spectrum of **5m**:



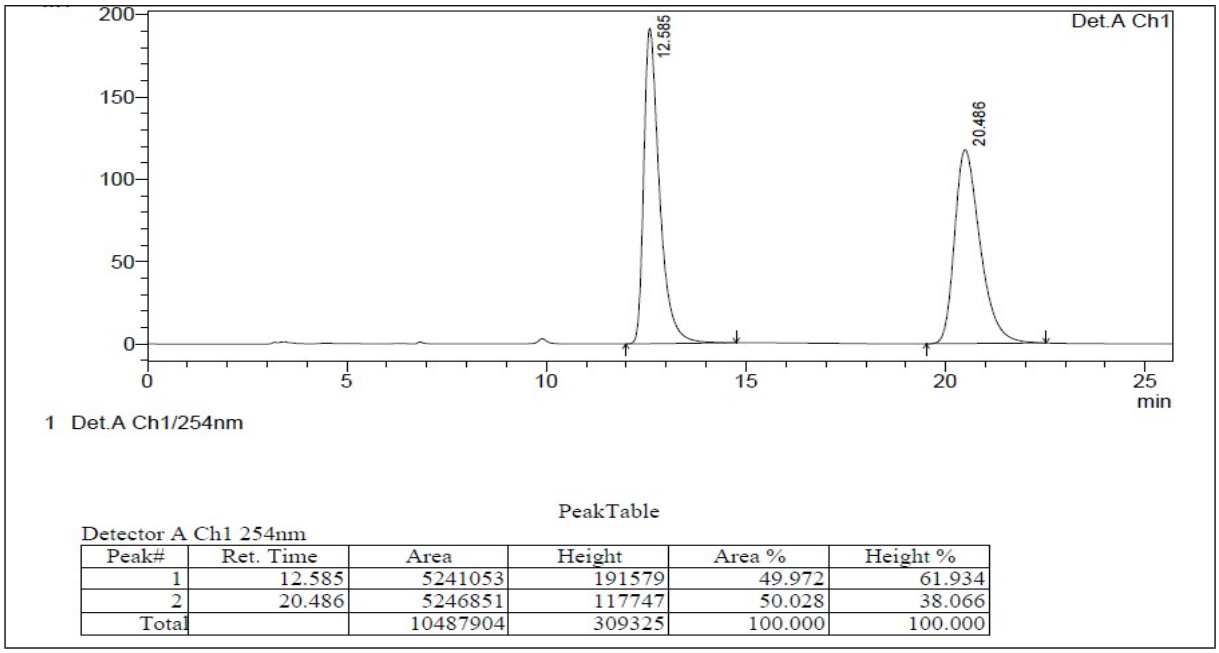
^{13}C NMR spectrum of **5m**:



^{19}F NMR spectrum of **5m**:



HPLC chromatogram of **5m**-racemic:

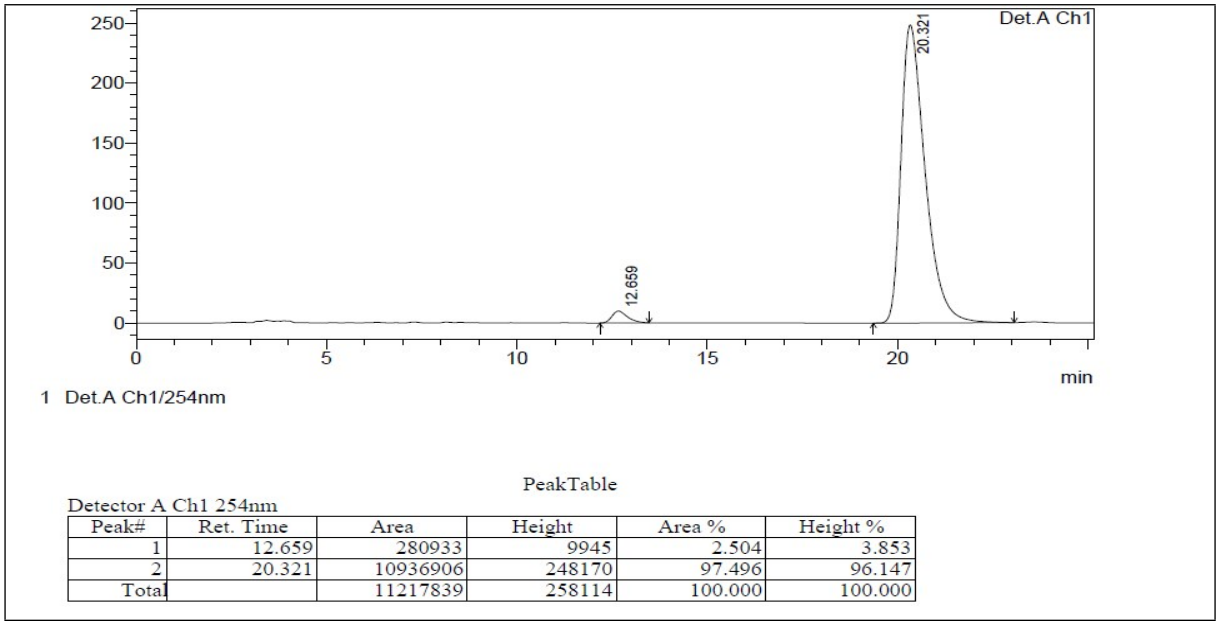


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.585	5241053	191579	49.972	61.934
2	20.486	5246851	117747	50.028	38.066
Total		10487904	309325	100.000	100.000

HPLC chromatogram of **5m**-chiral:

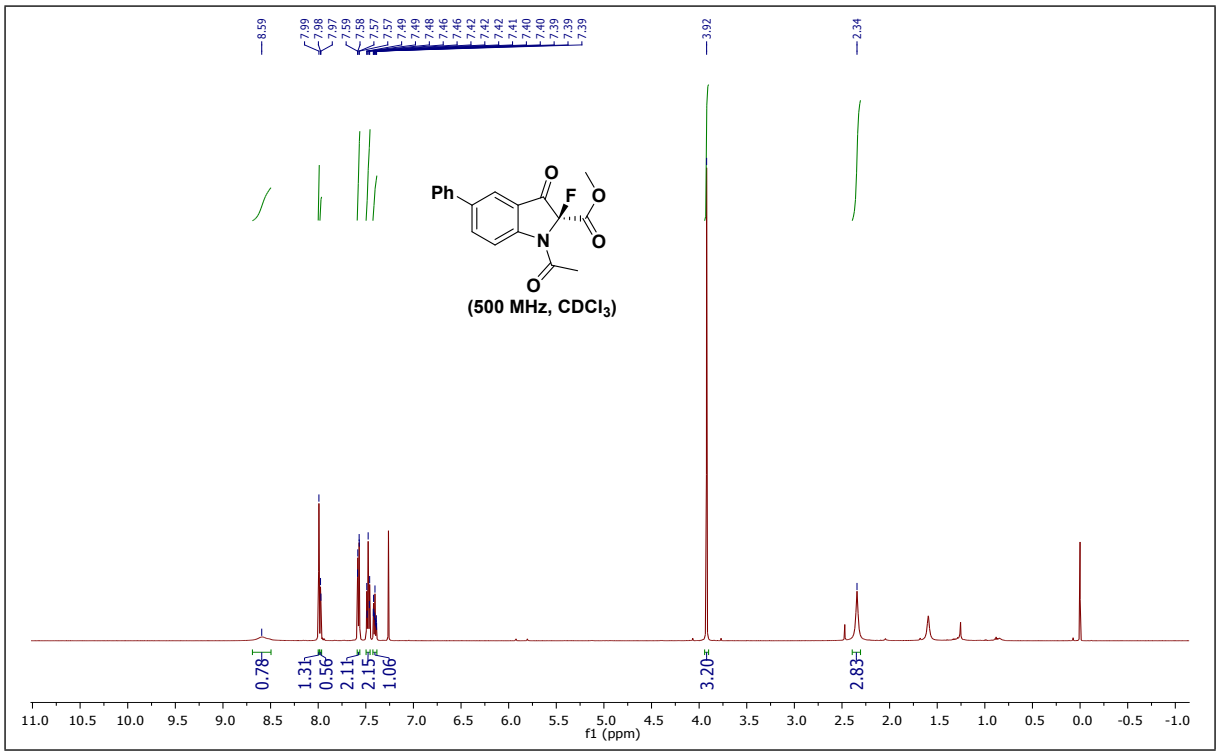


PeakTable

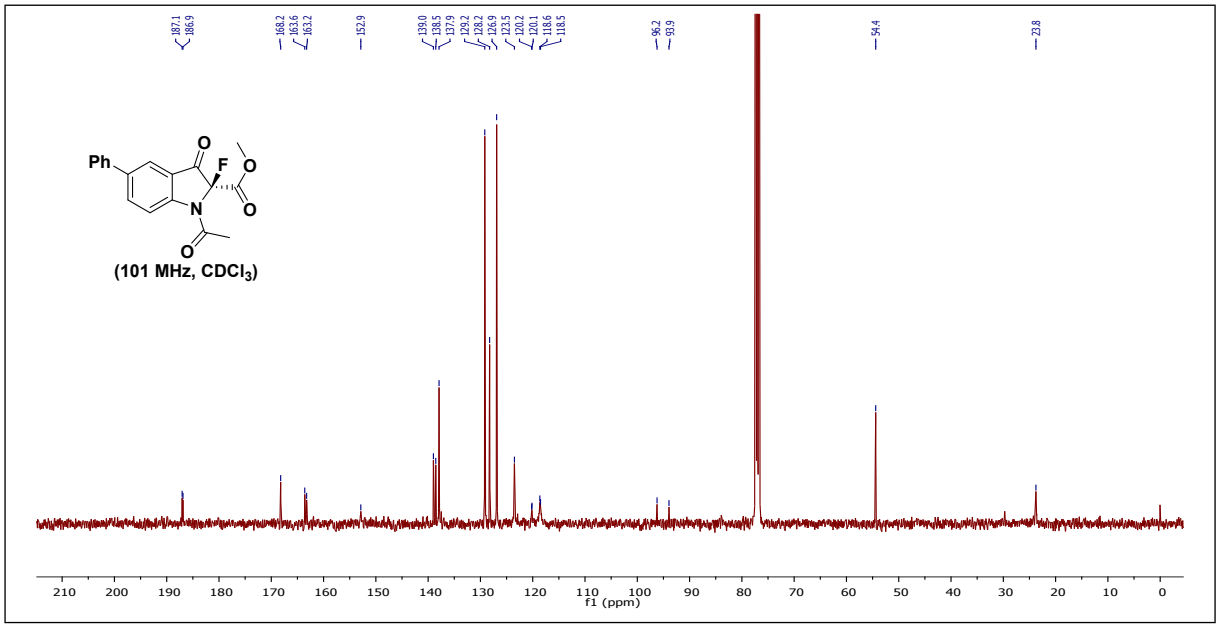
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.659	280933	9945	2.504	3.853
2	20.321	10936906	248170	97.496	96.147
Total		11217839	258114	100.000	100.000

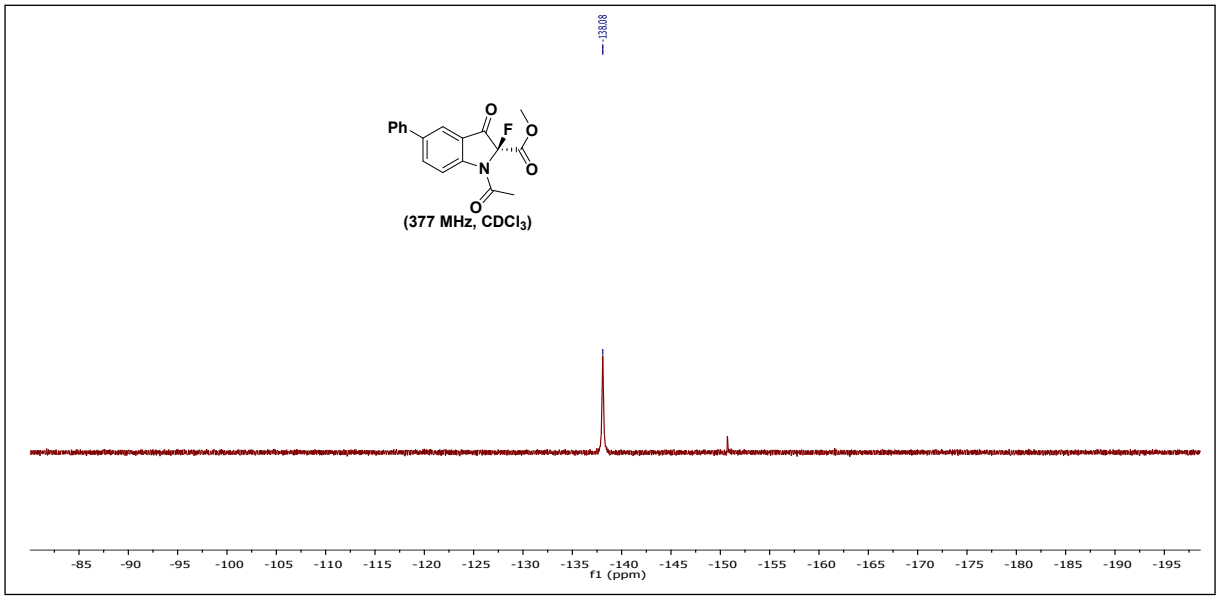
^{1}H NMR spectrum of **5n**:



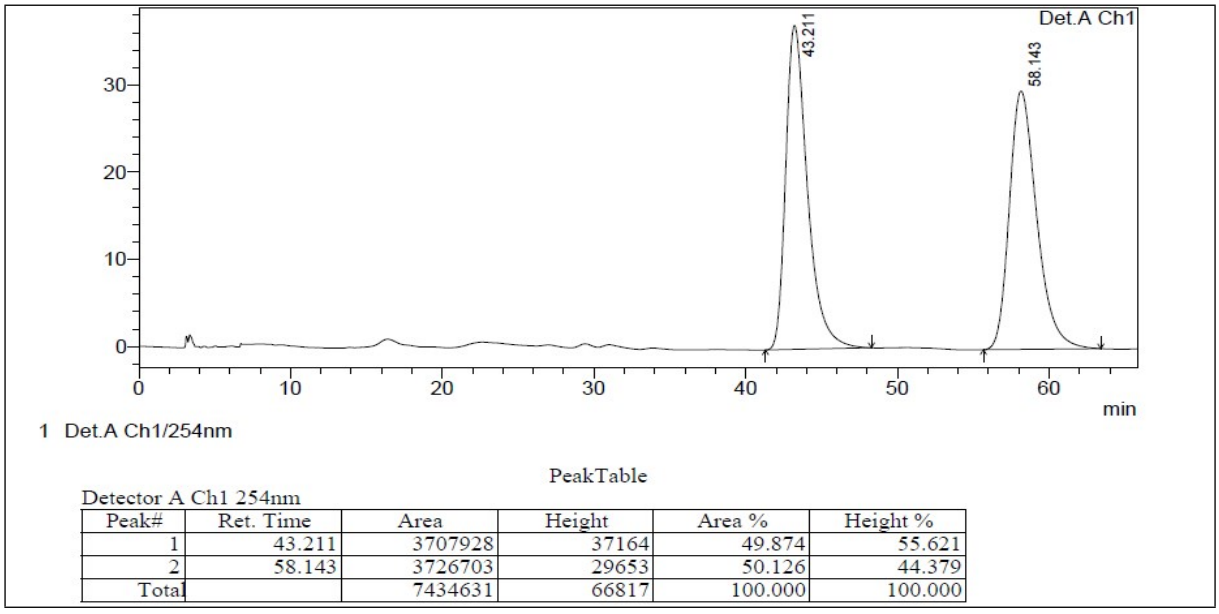
^{13}C NMR spectrum of **5n**:



^{19}F NMR spectrum of **5n**:



HPLC chromatogram of **5n**-racemic:

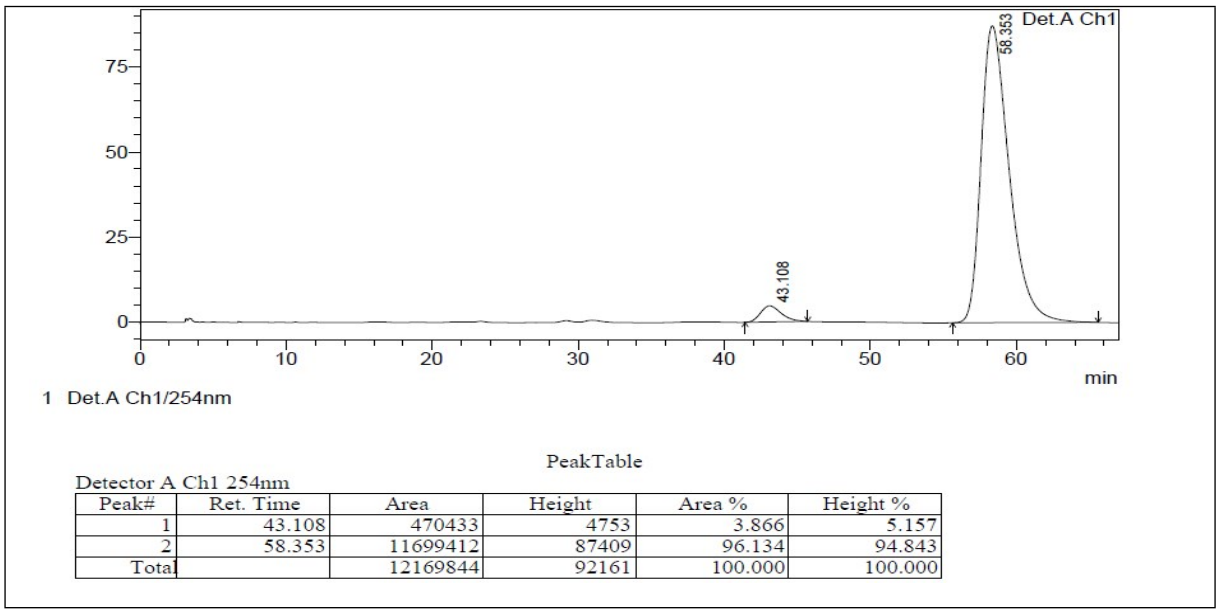


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.211	3707928	37164	49.874	55.621
2	58.143	3726703	29653	50.126	44.379
Total		7434631	66817	100.000	100.000

HPLC chromatogram of **5n**-chiral:

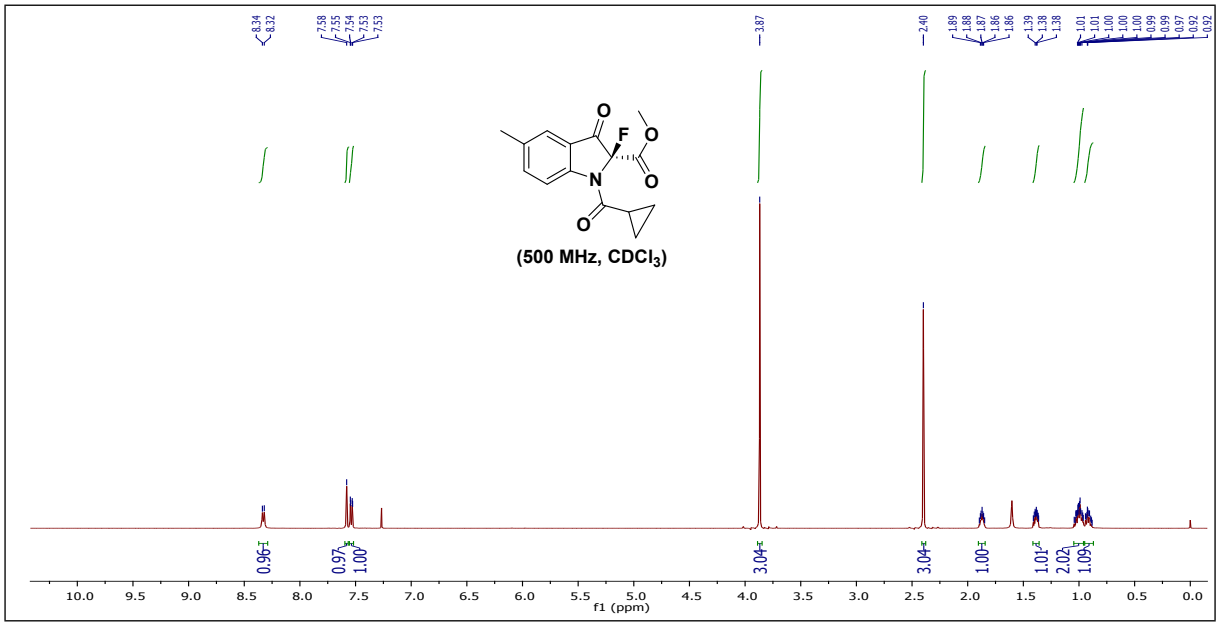


PeakTable

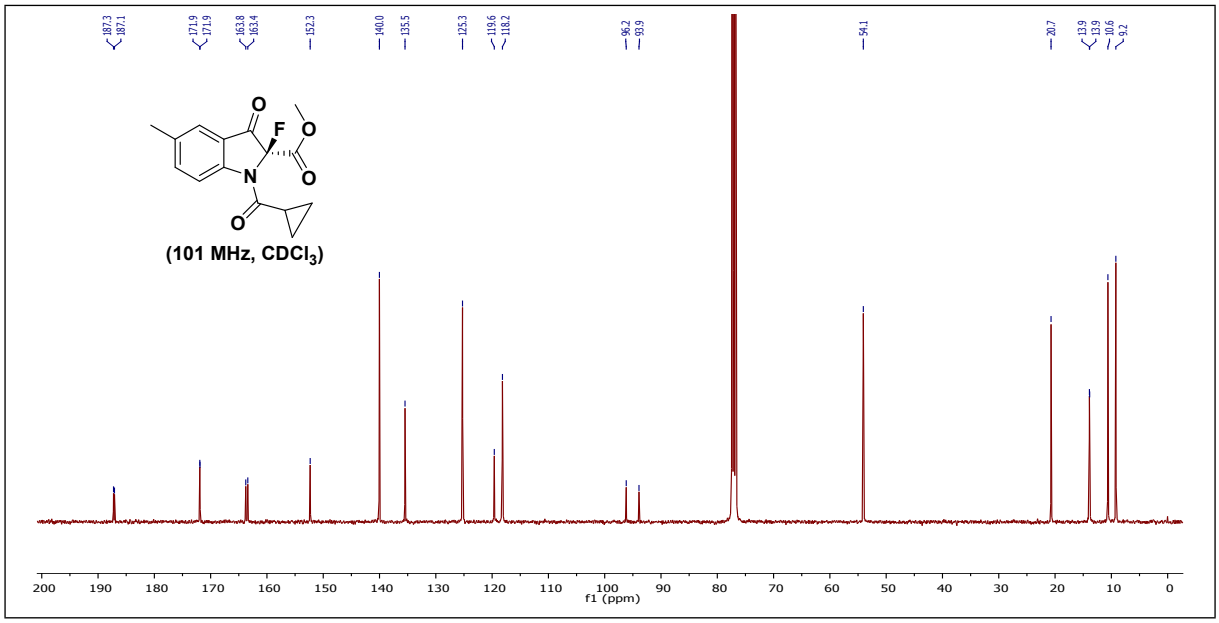
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.108	470433	4753	3.866	5.157
2	58.353	11699412	87409	96.134	94.843
Total		12169844	92161	100.000	100.000

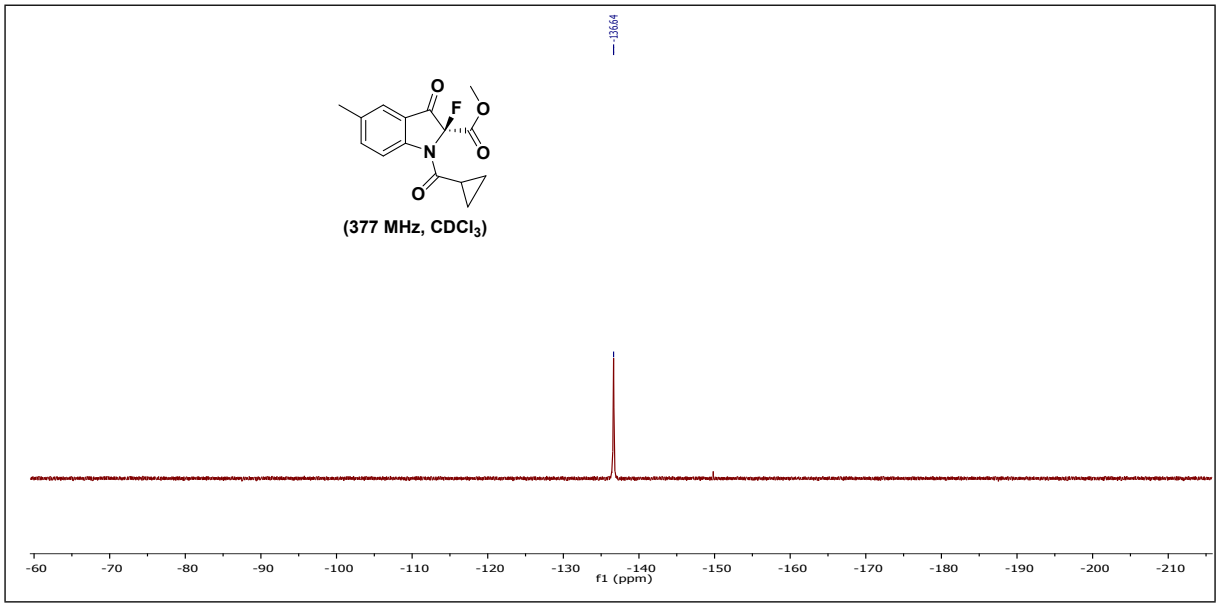
[1]H NMR spectrum of **5o**:



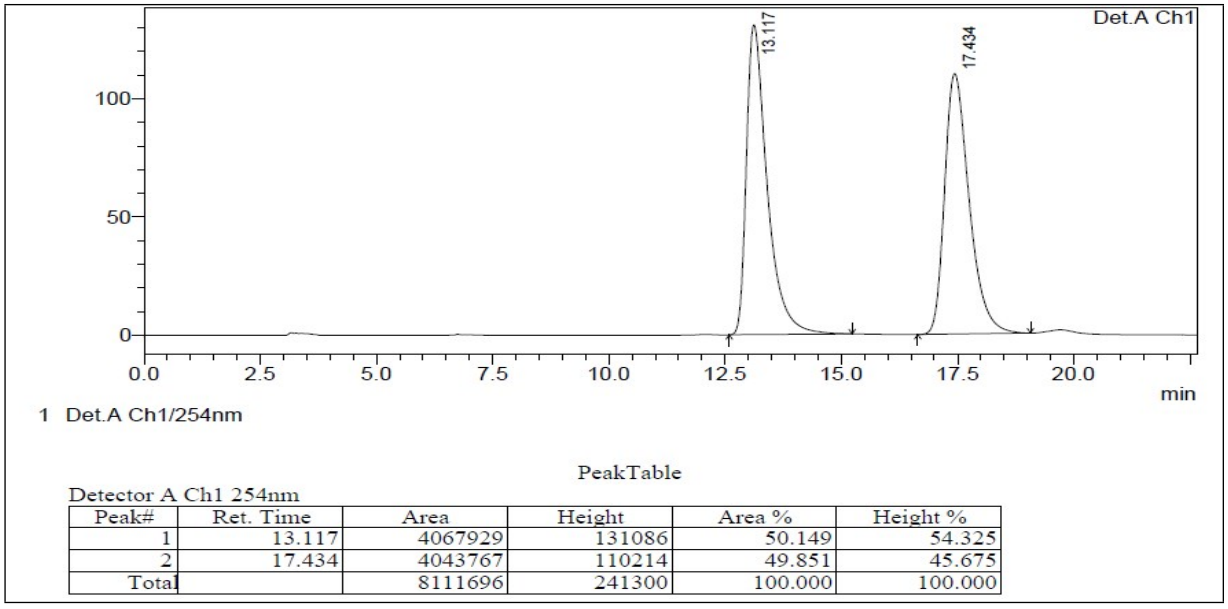
[13]C NMR spectrum of **5o**:



^{19}F NMR spectrum of **5o**:



HPLC chromatogram of **5o**-racemic:

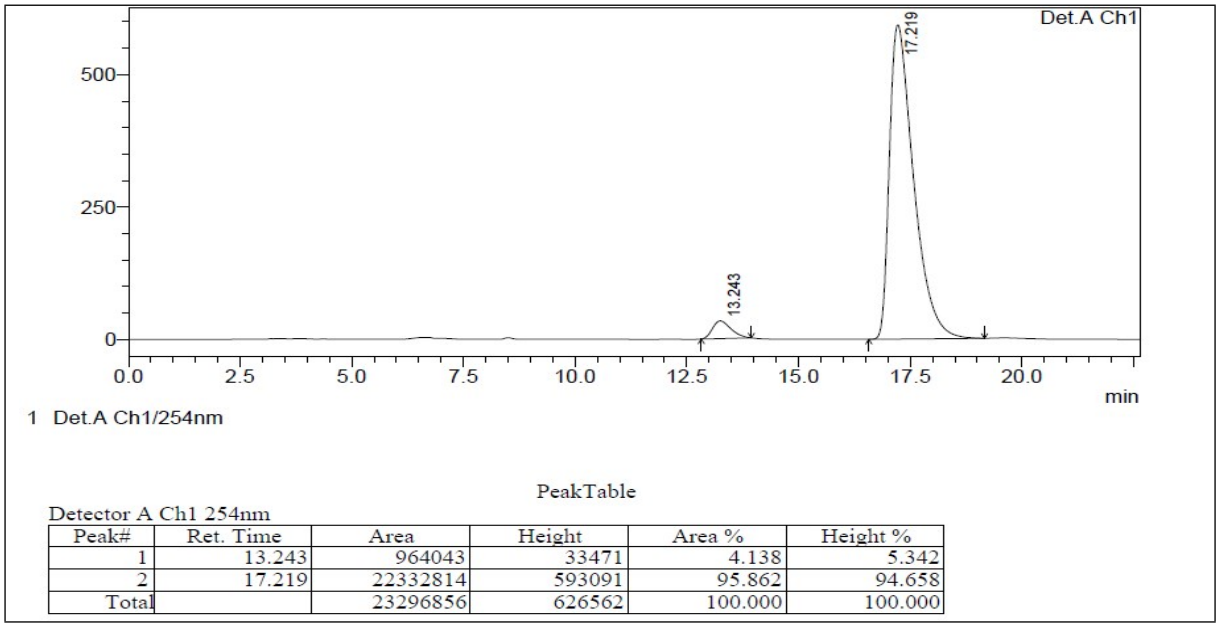


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.117	4067929	131086	50.149	54.325
2	17.434	4043767	110214	49.851	45.675
Total		8111696	241300	100.000	100.000

HPLC chromatogram of **5o**-chiral:

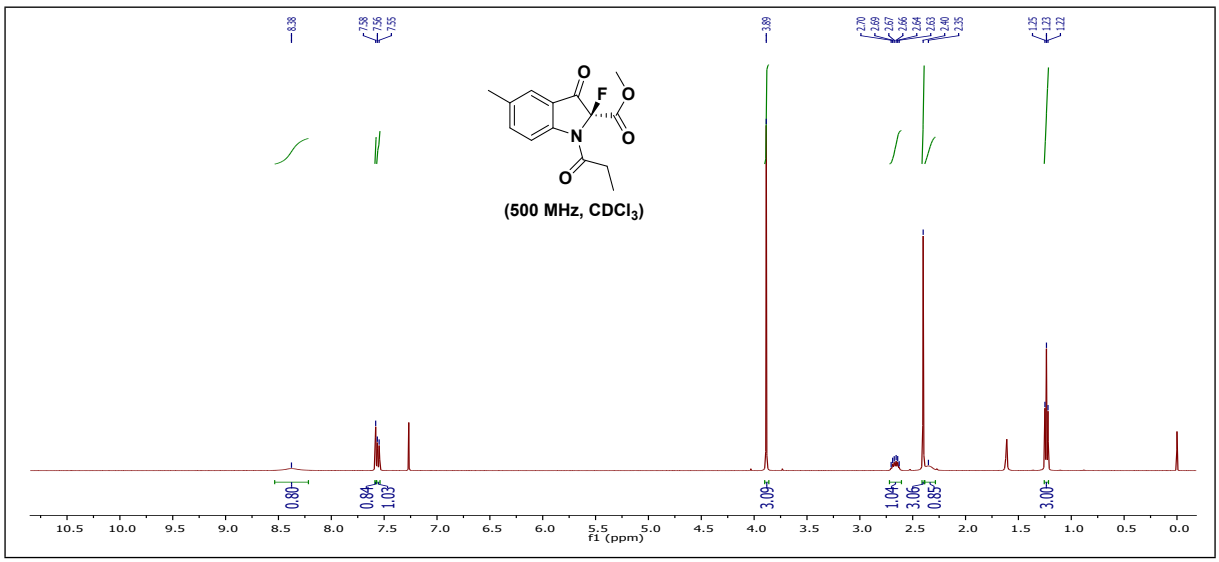


PeakTable

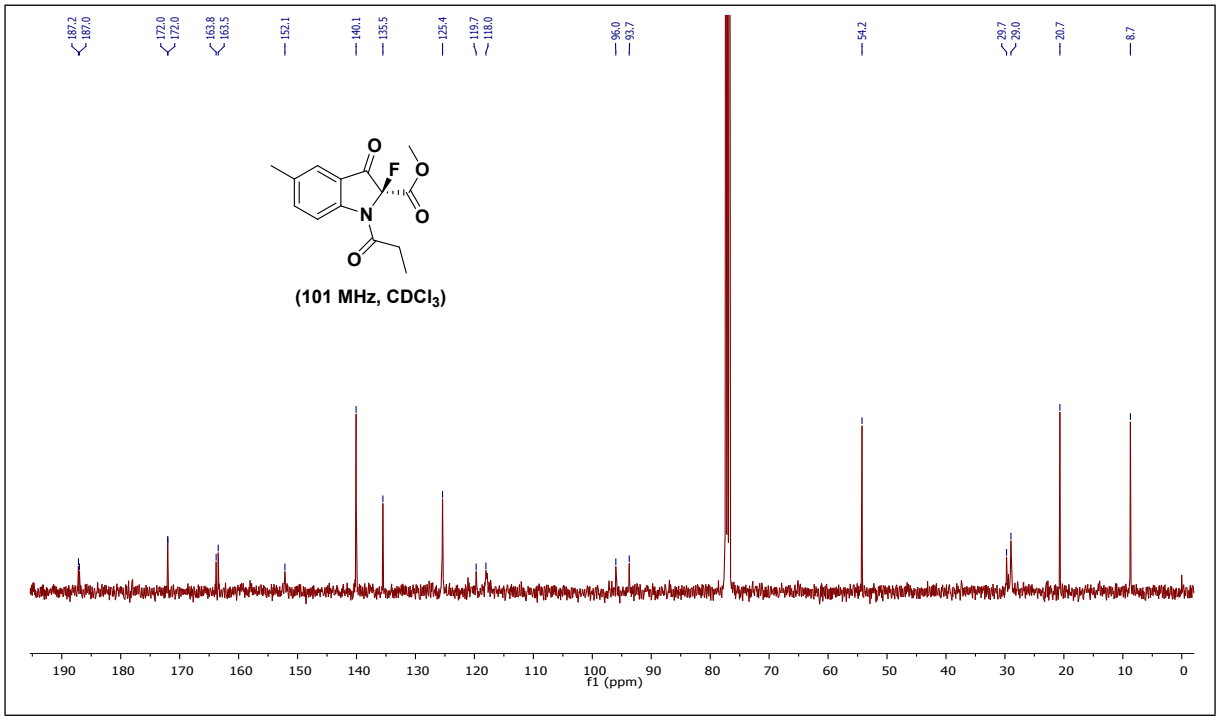
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.243	964043	33471	4.138	5.342
2	17.219	22332814	593091	95.862	94.658
Total		23296856	626562	100.000	100.000

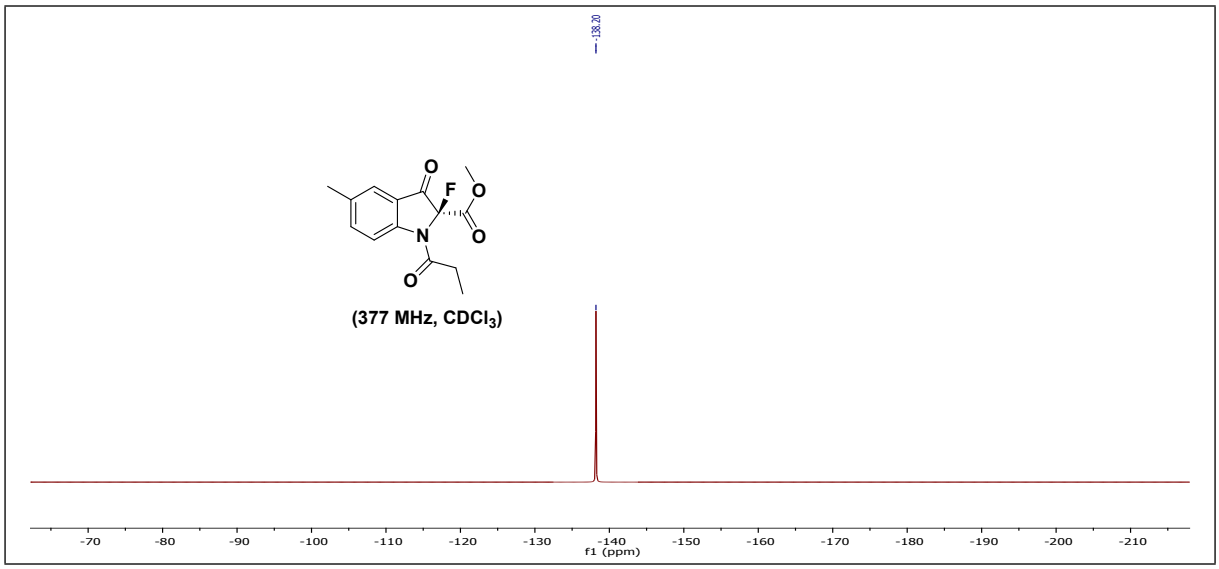
^{1}H NMR spectrum of **5p**:



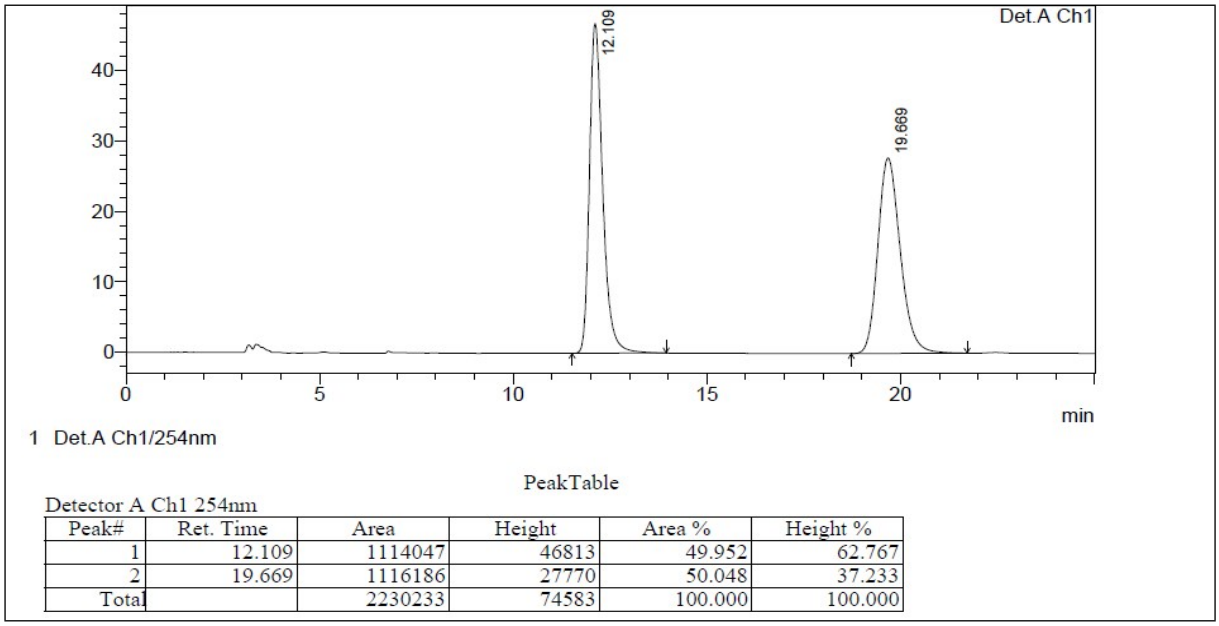
^{13}C NMR spectrum of **5p**:



^{19}F NMR spectrum of **5p**:



HPLC chromatogram of **5p**-racemic:

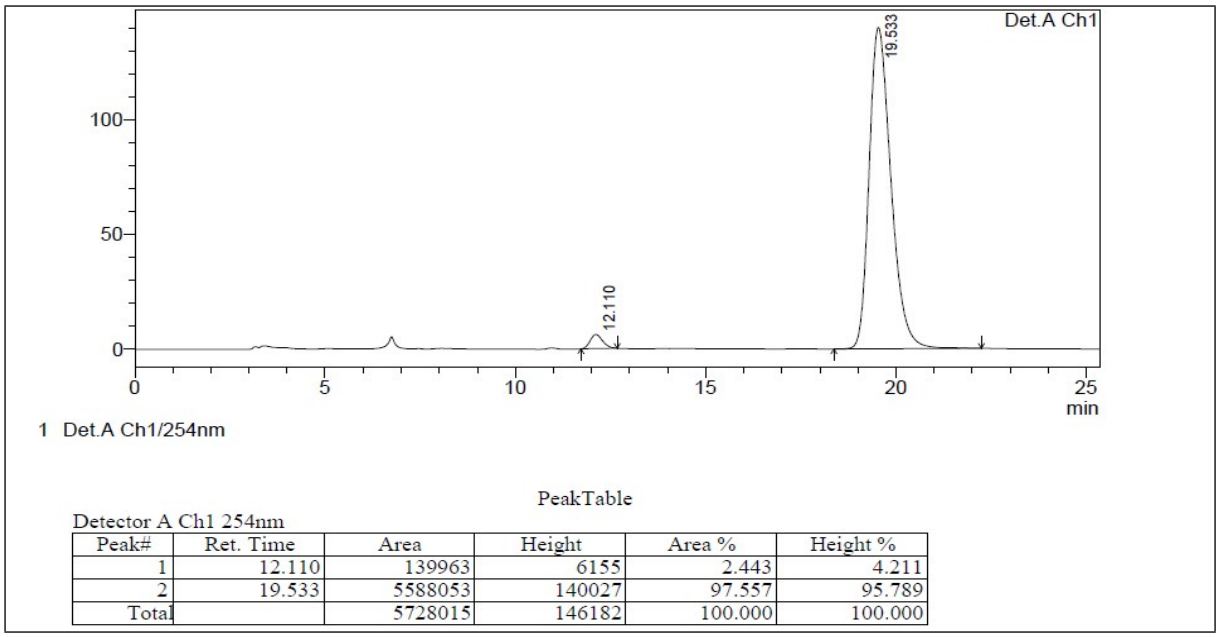


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.109	1114047	46813	49.952	62.767
2	19.669	1116186	27770	50.048	37.233
Total		2230233	74583	100.000	100.000

HPLC chromatogram of **5p**-chiral:

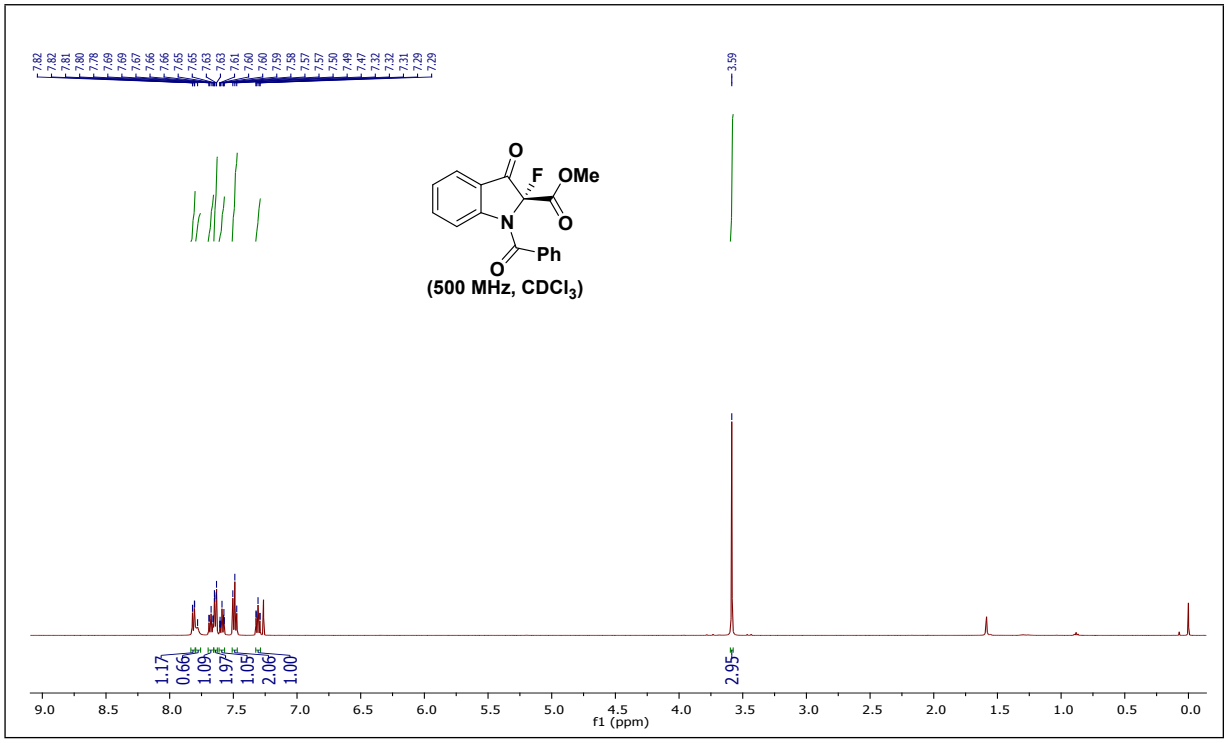


PeakTable

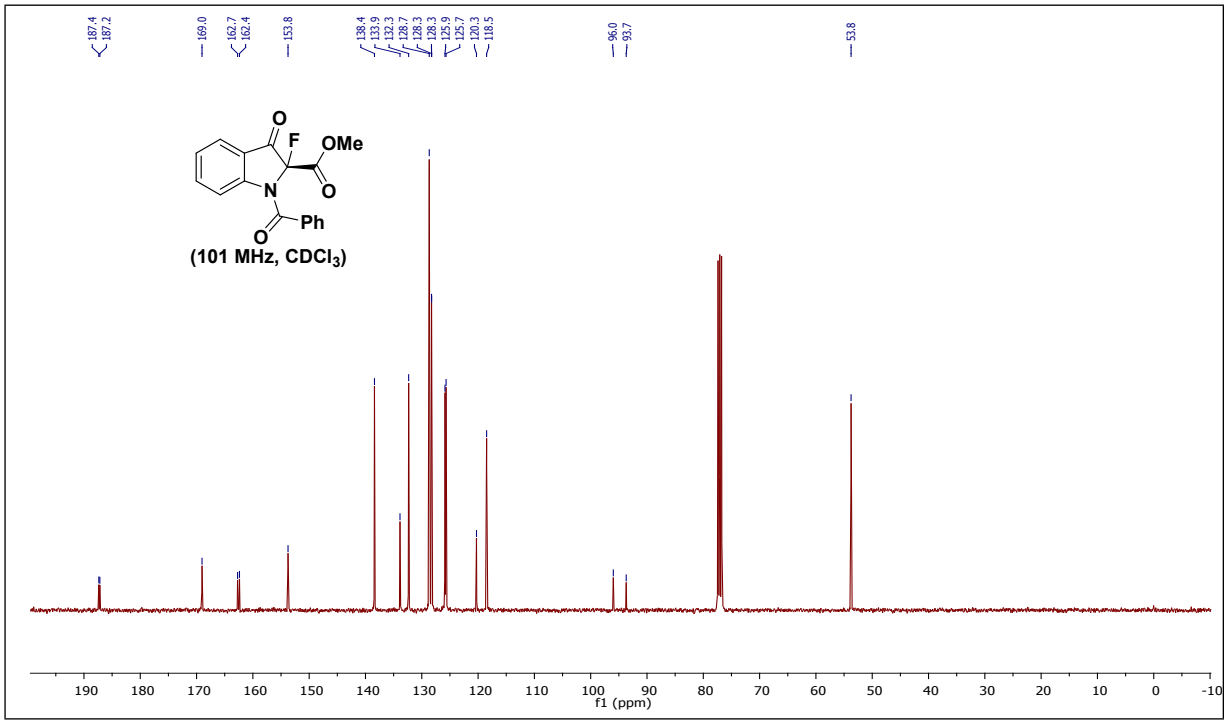
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.110	139963	6155	2.443	4.211
2	19.533	5588053	140027	97.557	95.789
Total		5728015	146182	100.000	100.000

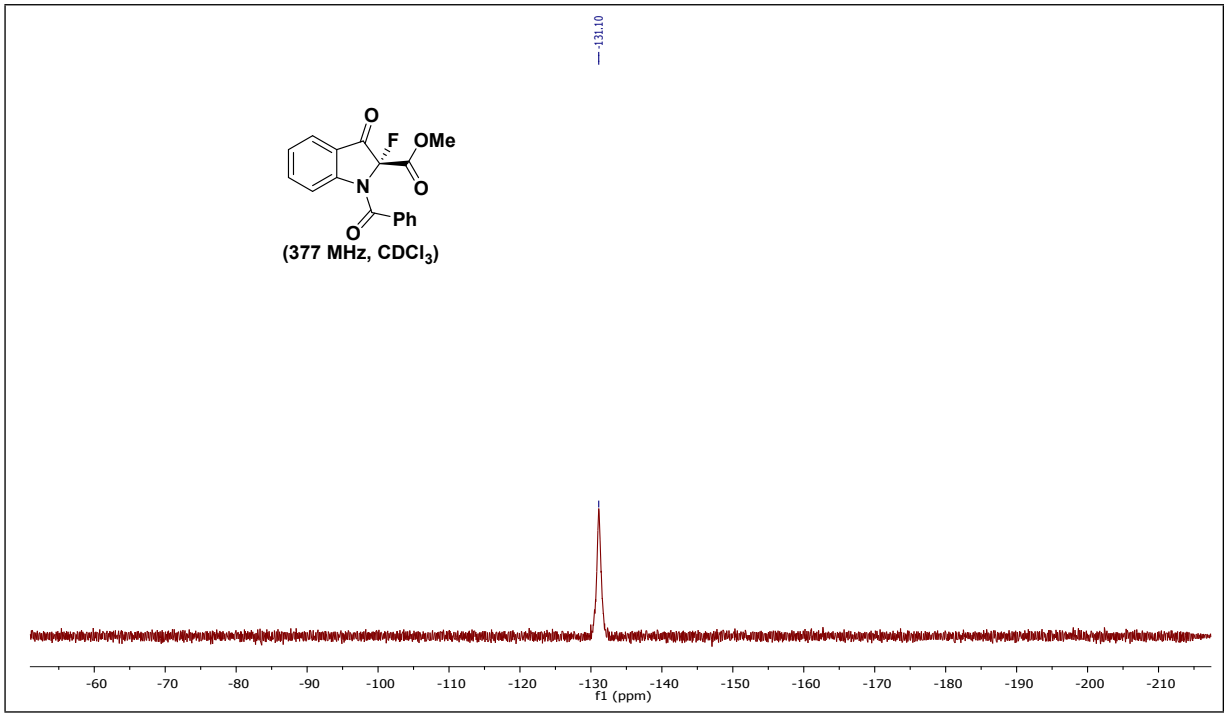
^{1}H NMR spectrum of **5u**:



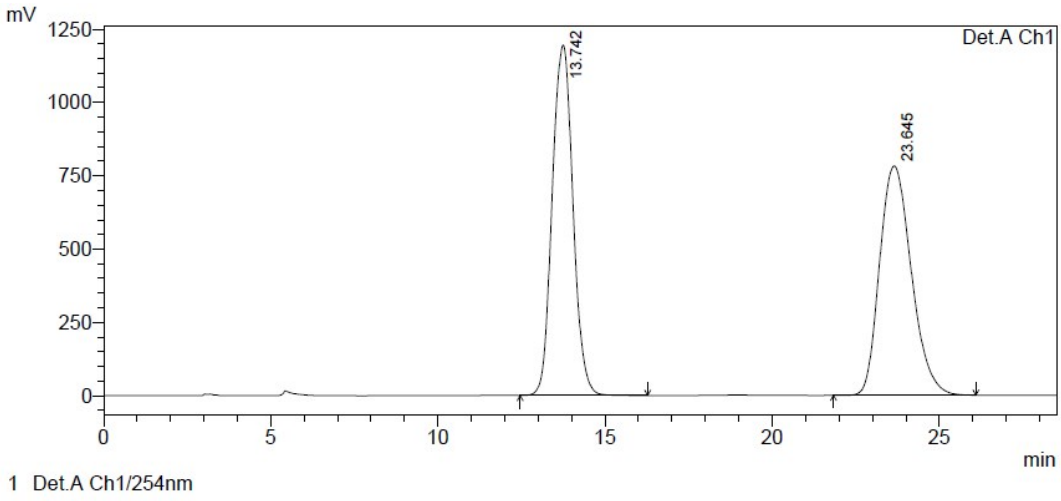
^{13}C NMR spectrum of **5u**:



^{19}F NMR spectrum of **5u**:



HPLC chromatogram of **5u**-racemic:



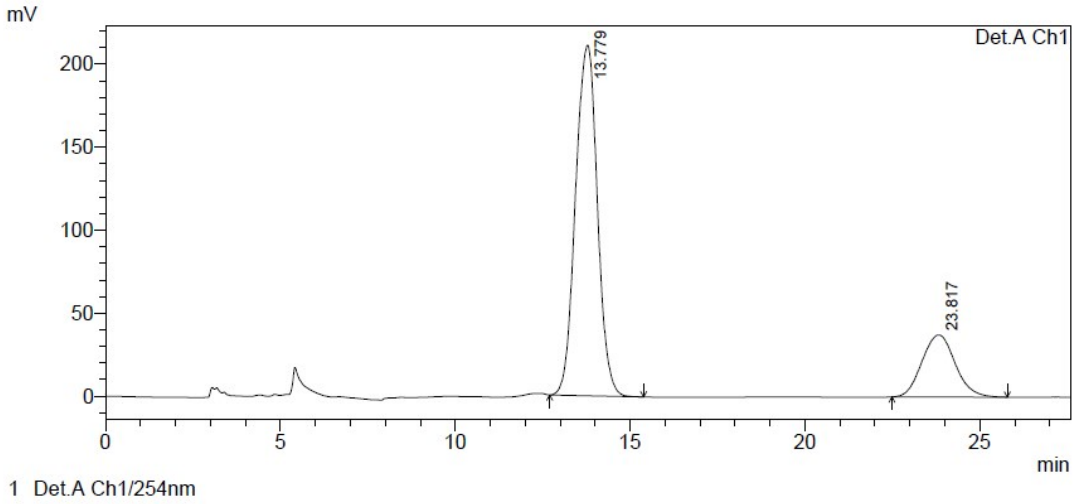
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.742	51582060	1194835	49.930	60.437
2	23.645	51726345	782154	50.070	39.563
Total		103308405	1976989	100.000	100.000

HPLC chromatogram of **5u**-chiral:



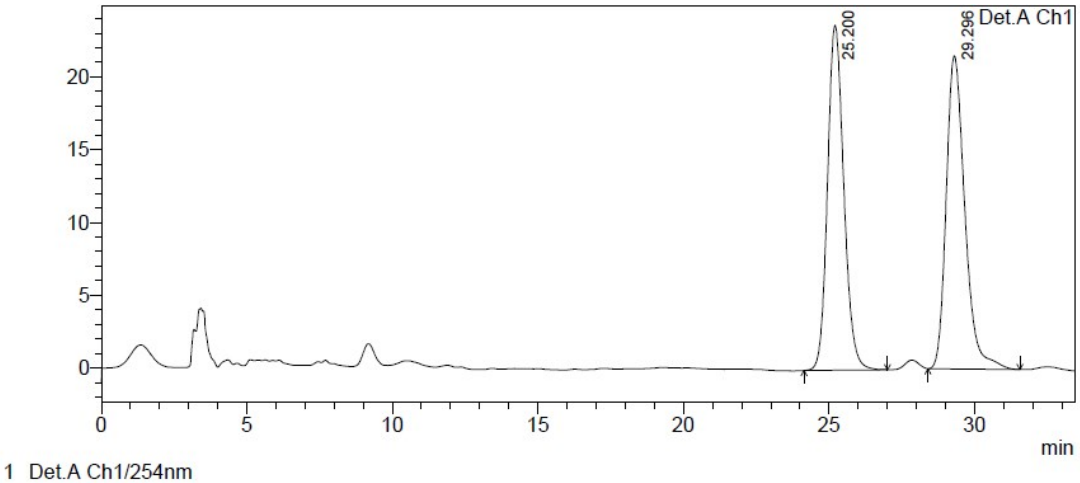
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.779	9171247	211142	78.800	84.970
2	23.817	2467362	37349	21.200	15.030
Total		11638608	248492	100.000	100.000

Gram scale reaction:

HPLC chromatogram of **5a**-racemic (1g batch):

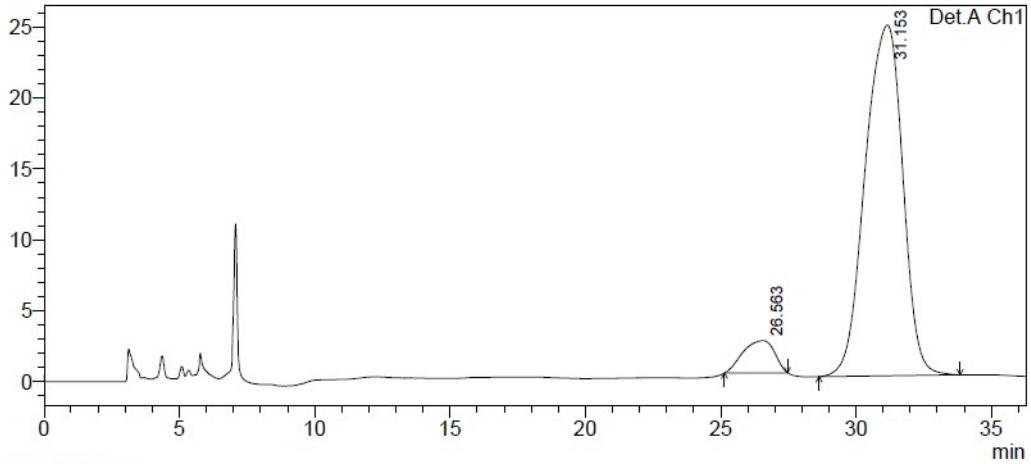


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.200	921474	23693	49.035	52.422
2	29.296	957738	21504	50.965	47.578
Total		1879212	45197	100.000	100.000

HPLC chromatogram of **5a**-chiral (1g batch):



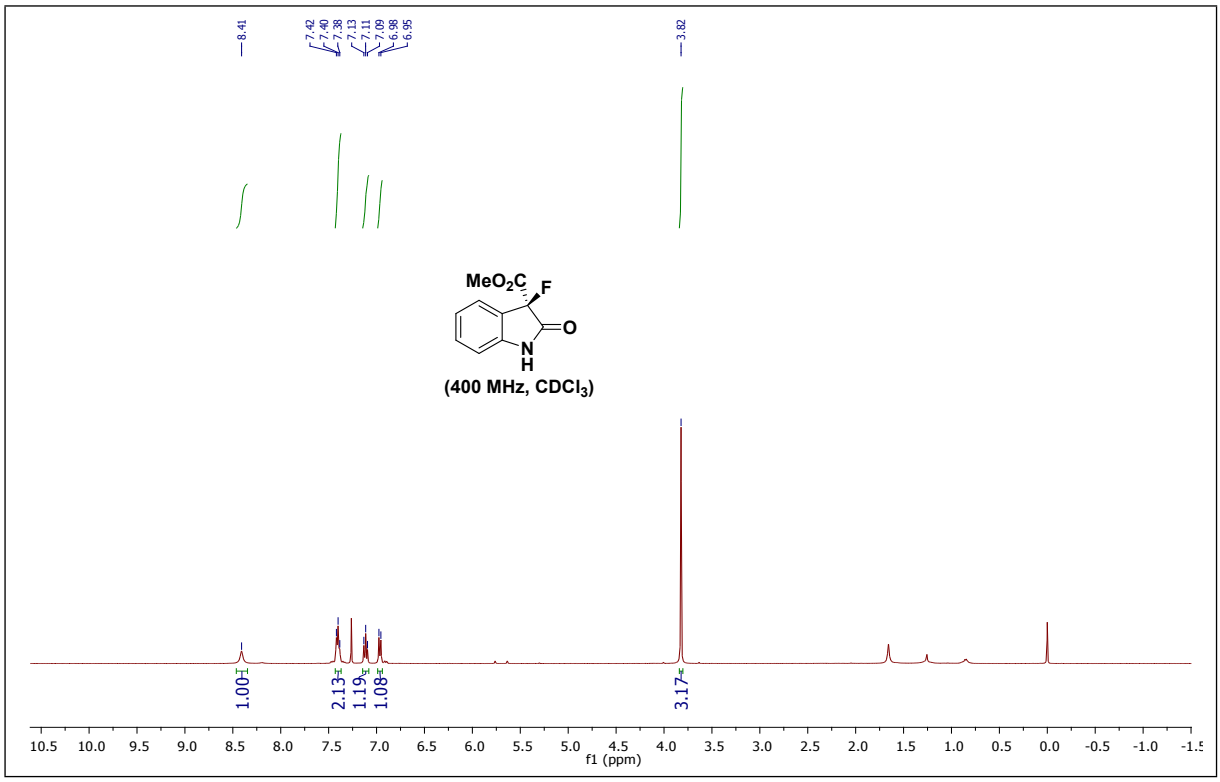
1 Det.A Ch1/254nm

PeakTable

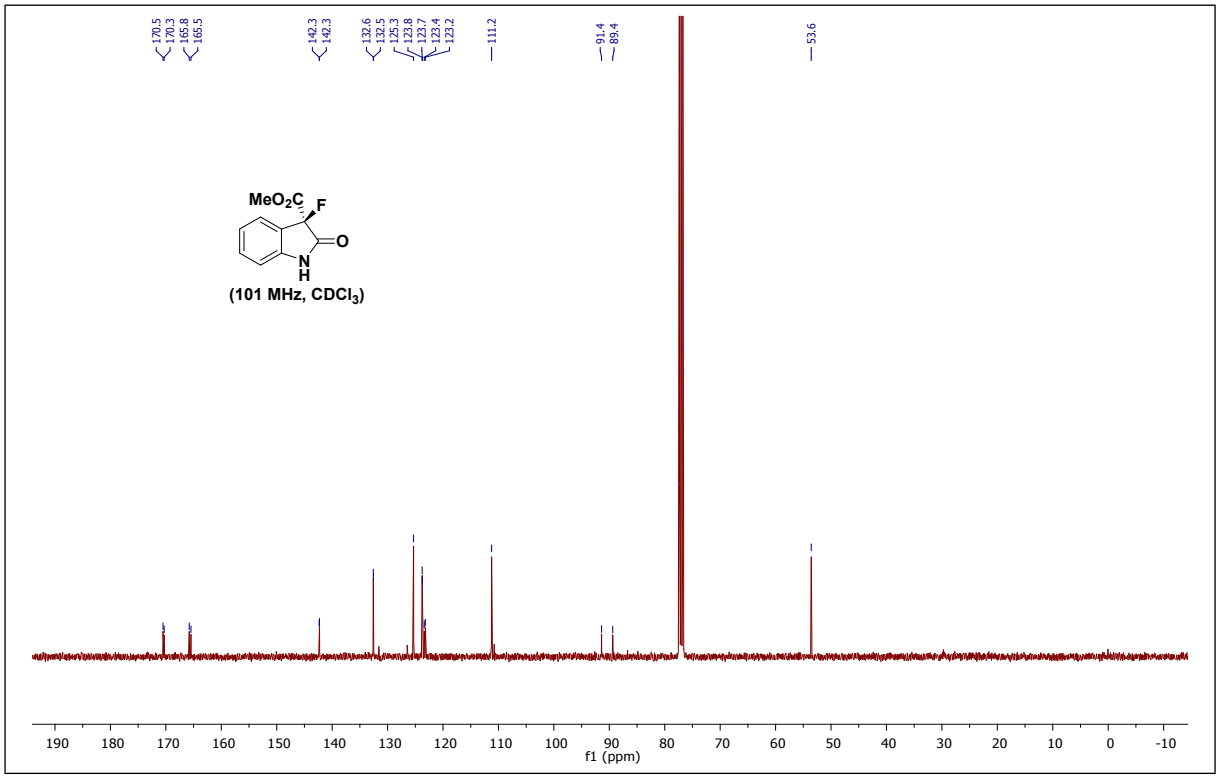
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.563	184409	2274	7.186	8.430
2	31.153	2381814	24701	92.814	91.570
Total		2566223	26975	100.000	100.000

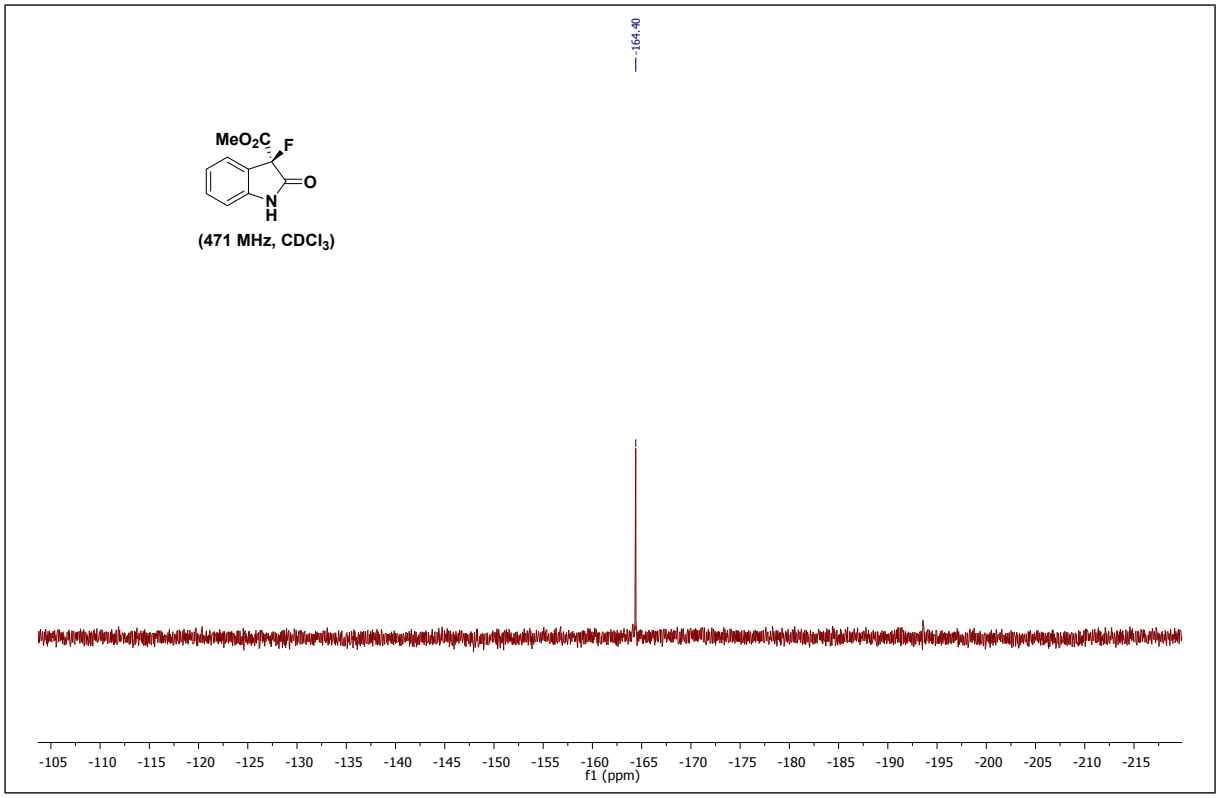
^{1}H NMR spectrum of **7**:



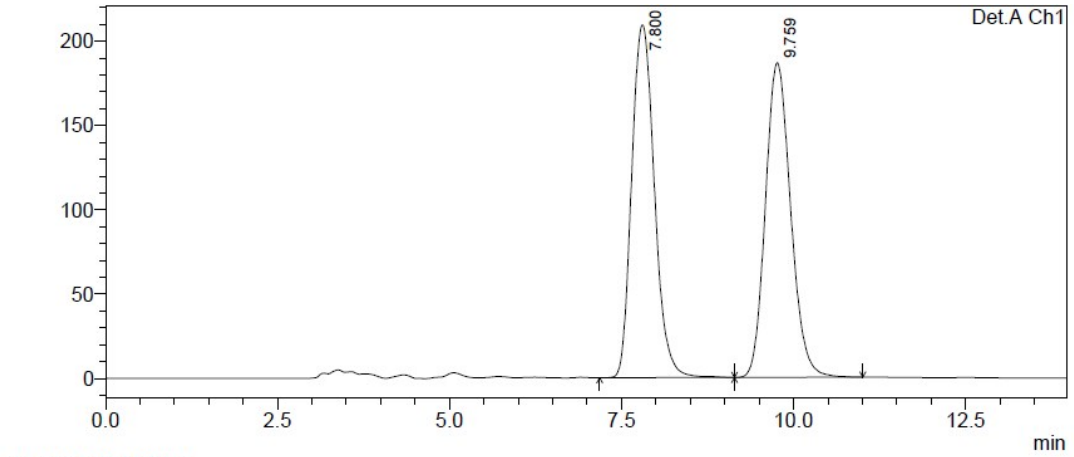
^{13}C NMR spectrum of **7**:



^{19}F NMR spectrum of **7**:



HPLC chromatogram of **7**-racemic:



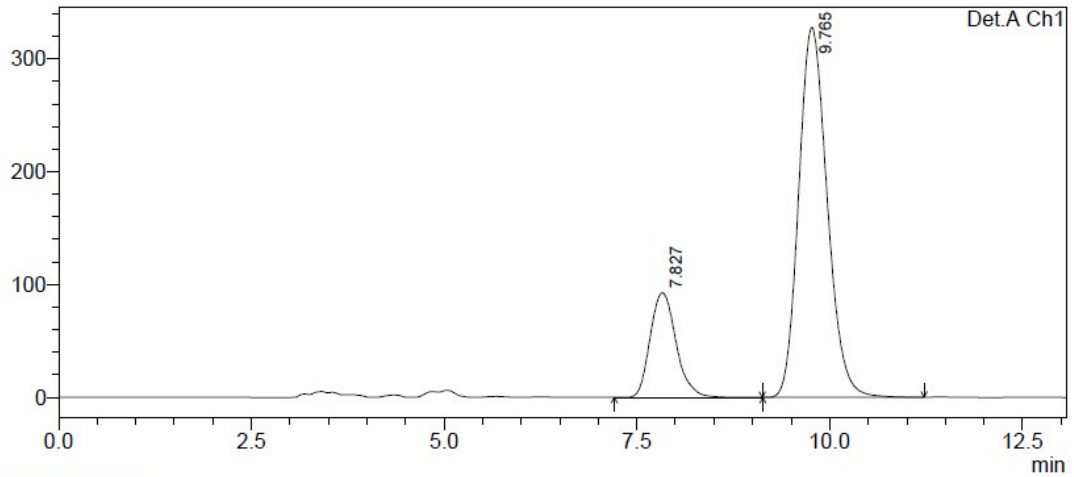
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.800	4808938	209108	50.236	52.838
2	9.759	4763817	186642	49.764	47.162
Total		9572755	395750	100.000	100.000

HPLC chromatogram of **7**-chiral:



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.827	2182246	92774	20.549	22.050
2	9.765	8437217	327974	79.451	77.950
Total		10619463	420748	100.000	100.000

4. X-ray Crystallography.

X-ray data for compound **5d** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$ for other H atoms].

Crystal structure determination of 5d

Crystal Data for $C_{13}H_{12}NO_4F$ (M =265.24 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.7100(7) Å, b = 9.8223(10) Å, c = 16.1672(13) Å, V = 1224.34(19) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.117 mm^{-1}, *Dcalc* = 1.439 g/cm^3, 11447 reflections measured (4.852° ≤ 2Θ ≤ 61.062°), 3688 unique (R_{int} = 0.0475, R_{sigma} = 0.0565) which were used in all calculations. The final R_1 was 0.0473 (I >2σ(I)) and wR_2 was 0.1287 (all data). CCDC 2047903 contains supplementary Crystallographic data for the structure of **5d**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** ActaCrystallography C71: 3-8.