Supporting Information

Palladium/copper-cocatalyzed three-component tandem cyclization of *o*-alkenyl arylisocyanides, sulfur ylides with alcohols: direct synthesis of spiro 3,3'-cyclopropyl oxindoles

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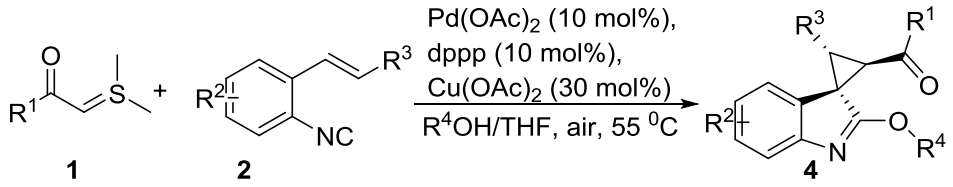
I. General Information:

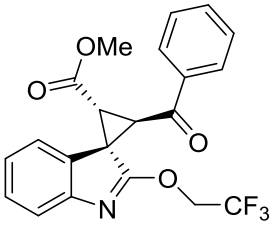
All reagents were commercial and were used without further purification. *o*-Alkenyl arylisocyanide **2** were synthesized according to known literature procedure.[1] Sulfur ylides **1** were prepared according to the previous method reported.[2] Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz, 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compounds **4ai** and **7a** were glued on a glass fiber. Data were collected at 293 K using graphite-monochromated Mo Kradiation ($\lambda = 0.71073$Å) and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. Synthetic Procedures and Analytical Data of Compounds 4 (4aa as example):



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (108.2 mg, 0.6 mmol), **2a** (37.4 mg, 0.2 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), dppp (8.2 mg 0.02 mmol) and $Cu(OAc)_2$ (10.8 mg 0.06 mmol), then 2.0 mL solution of anhydrous THF and CF_3CH_2OH (2.0 mL, V/V = 1/6) were added under air. The reaction was stirred at 55 ℃ for 12 h. After the reaction was completed, the reaction mixture was extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic extracts were dried over anhydrous $NaSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (EtOAc/petroleum ether = 1/10, V/V) to give **4aa** (62.9 mg, 78%) as a yellow liquid.

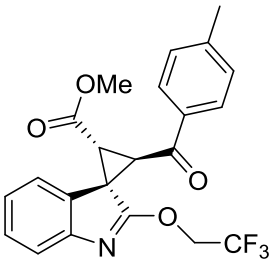
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-in -dole]-3-carboxylate (4aa):



Following the general procedure, **4aa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (62.9 mg, 78% yield, 6:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.93 – 4.79 (m, 2H), 4.23 (d, *J* = 7.9 Hz, 1H), 3.68 (s, 3H), 3.66 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.60, 172.59, 165.35, 150.63, 135.36, 132.91, 130.22, 127.81, 127.56, 127.31, 123.47, 121.73(q, *J* = 277.7 Hz), 120.57, 118.38, 64.14 (q, *J* = 36.8 Hz), 51.66, 39.72, 35.84, 32.48; ^{19}F NMR (565

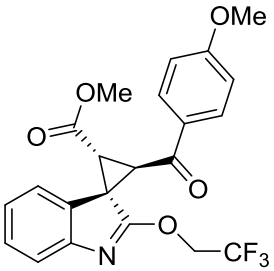
MHz, $CDCl_3$) δ = -73.90 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}F_3NO_4^+$ 404.1104; Found 404.1105.

Methyl (1*S*,2*R*,3*R*)-3-(4-methylbenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-2-carboxylate (4ba):



Following the general procedure, **4ba** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (61.8 mg, 74% yield, 4:1 dr); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 4.98 – 4.88 (m, 2H), 4.28 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.72 (d, *J* = 7.9 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.07, 173.68, 166.47, 151.62, 145.05, 133.92, 131.33, 129.52, 128.50, 128.46, 124.46, 122.75(q, *J* = 277.4 Hz), 121.57, 119.33, 65.12 (q, *J* = 36.8 Hz), 40.62, 38.94, 36.84, 33.44, 21.69; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.91 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_4^+$ 418.1261; Found 418.1251.

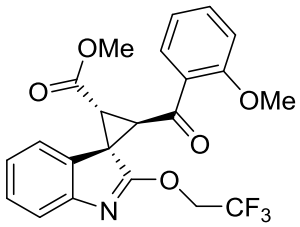
Methyl (1*S*,2*R*,3*R*)-3-(4-methoxybenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopr-opane-1,3'-indole]-2-carboxylate (4ca):



Following the general procedure, **4ca** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a yellow solid (65.0 mg, 75% yield, 4:1 dr); ^1H NMR (600 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.15 (m, , 1H), 7.04 – 7.01 (m, 1H), 6.97 – 6.93 (m, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 4.90 – 4.80 (m,

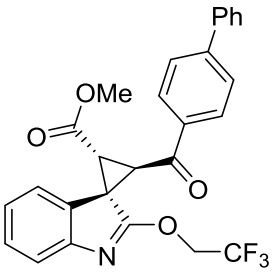
2H), 4.19 (d, *J* = 7.9 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.64 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 188.73, 173.74, 166.53, 164.20, 151.62, 131.43, 130.74, 129.45, 128.46, 124.44, 122.77(q, *J* = 277.6 Hz), 121.59, 119.31, 114.05, 65.12 (q, *J* = 37.0 Hz), 55.51, 52.64, 40.52, 36.71, 33.45; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.89 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_5^+$ 434.1210; Found 434.1213.

Methyl (1*S*,2*R*,3*R*)-3-(2-methoxybenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopr -pane-1,3'-indole]-2-carboxylate (4da):



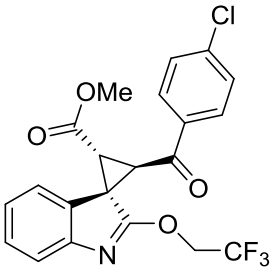
Following the general procedure, **4da** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a yellow solid (49.4 mg, 57% yield, 5:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.13 (d, J = 7.4 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.94 – 4.80 (m, 2H), 4.37 (d, *J* = 8.3 Hz, 1H), 3.77 (d, *J* = 8.3 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 191.57, 174.53, 166.79, 159.27, 151.72, 134.85, 132.03, 130.86, 128.19, 126.88, 124.34, 122.76 (q, *J* = 277.0 Hz), 121.70, 120.81, 119.12, 111.69, 65.09 (q, *J* = 36.8 Hz), 55.64, 52.54, 42.04, 40.90, 34.08; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.88 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_5^+$ 434.1210; Found 434.1213.

Methyl (1*S*,2*R*,3*R*)-2-([1,1'-biphenyl]-4-carbonyl)-2'-(2,2,2-trifluoroethoxy)spiro [cyclopropane-1,3'-indole]-3-carboxylate (4ea):



Following the general procedure, **4ea** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (70.0 mg, 73% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.54 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.27 – 7.24 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (td, J = 7.6, 0.9 Hz, 1H), 5.00 – 4.91 (m, 2H), 4.34 (d, J = 7.9 Hz, 1H), 3.76 (d, *J* = 6.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.10, 173.65, 166.42, 151.67, 146.68, 139.48, 135.02, 131.28, 128.98, 128.95, 128.61, 128.46, 127.46, 127.25, 124.52, 122.77 (q, *J* = 277.3 Hz), 121.61, 119.42, 65.16 (q, *J* = 36.8 Hz), 52.71, 40.75, 36.93, 33.50; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.86 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{21}F_3NO_4^+$ 480.1417; Found 480.1417.

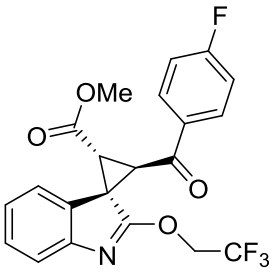
Methyl (1*S*,2*R*,3*R*)-3-(4-chlorobenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopro -pane-1,3'-indole]-2-carboxylate (4fa):



Following the general procedure, **4fa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (59.5 mg, 68% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.20 – 7.17 (m, 1H), 6.99 – 6.94 (m, 2H), 4.92 – 4.80 (m, 2H), 4.16 (d, *J* = 7.9 Hz, 1H), 3.69 (s, 3H), 3.65 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.49, 173.45, 166.24, 151.62, 140.61, 134.62, 131.00, 129.67, 129.21, 128.72, 124.54, 122.72 (q, *J* = 277.6 Hz), 121.44, 119.50, 65.16 (q, *J* = 36.9 Hz), 52.75, 40.68, 36.71, 33.41; ^{19}F NMR (565

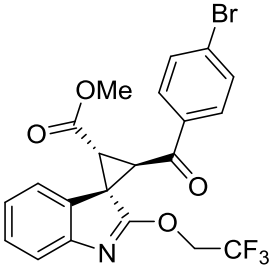
MHz, $CDCl_3$) δ = -73.89 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}ClF_3NO_4^+$ 438.0714; Found 438.0716.

Methyl (1*S*,2*R*,3*R*)-3-(4-fluorobenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropa-ne-1,3'-indole]-2-carboxylate (4ga):



Following the general procedure, **4ga** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (59.0 mg, 70% yield, 5:1 dr); ^1H NMR (500 MHz, $CDCl_3$) δ= 7.75 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.93 (m, 4H), 4.92 – 4.80 (m, 2H), 4.17 (d, *J* = 7.9 Hz, 1H), 3.68 (s, 3H), 3.65 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.03, 173.50, 166.28, 166.19 (d, *J* = 256.8 Hz), 151.64, 132.79 (d, *J* = 2.7 Hz), 131.09, 131.05 (d, *J* = 9.7 Hz), 128.67, 124.51, 122.73 (q, *J* = 277.5 Hz), 121.49, 119.46, 116.08 (d, *J* = 22.2 Hz), 65.15 (q, *J* = 36.9 Hz), 52.72, 40.64, 36.69, 33.44; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.90 (t, *J* = 8.3 Hz), -103.09 (tt, *J* = 8.4, 5.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}F_4NO_4^+$ 422.1010; Found 422.1015.

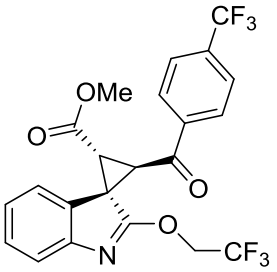
Methyl (1*S*,2*R*,3*R*)-2-(4-bromobenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-3-carboxylate (4ha):



Following the general procedure, **4ha** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (70.4 mg, 73% yield, 5:1 dr); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.20 – 7.17 (m, 1H), 6.97 (d, *J* = 6.6 Hz, 2H), 4.92 – 4.80 (m, 2H), 4.15 (d, *J*

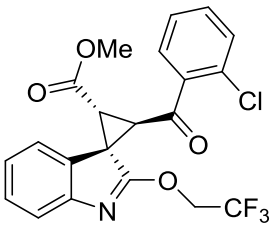
= 7.9 Hz, 1H), 3.68 (s, 3H), 3.64 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.72, 173.44, 166.23, 151.61, 135.01, 132.21, 130.98, 129.72, 129.41, 128.74, 124.55, 122.71 (q, *J* = 277.5 Hz), 121.43, 119.51, 65.16 (q, *J* = 36.8 Hz), 52.76, 40.68, 36.68, 33.39; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.89 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}BrF_3NO_4^+$ 482.0209; Found 482.0209.

Methyl (1*S*,2*R*,3*R*)-3-(4-fluorobenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropa-ne-1,3'-indole]-2-carboxylate (4ia):



Following the general procedure, **4ia** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (54.7 mg, 58% yield, 5:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 4.4 Hz, 1H), 6.97 (d, *J* = 6.0 Hz, 2H), 4.92 – 4.81 (m, 2H), 4.20 (d, *J* = 7.8 Hz, 1H), 3.69 (s, 3H), 3.67 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.99, 173.32, 166.10, 151.64, 138.87, 135.13 (q, *J* = 32.8 Hz), 130.80, 128.86, 128.62, 125.95 (q, *J* = 3.5 Hz), 124.60, 123.02 (q, *J* = 277.4 Hz), 121.87 (d, *J* = 25.8 Hz), 121.41, 119.60, 65.19 (q, *J* = 36.8 Hz), 52.81, 40.84, 36.88, 33.41; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -63.33, -63.35, -73.91 (t, *J* = 8.2 Hz), -74.16 (t, *J* = 8.1 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}F_6NO_4^+$ 472.0978; Found 472.0969.

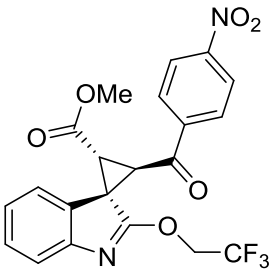
Methyl (1*S*,2*R*,3*R*)-3-(2-chlorobenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-2-carboxylate (4ja):



Following the general procedure, **4ja** was isolated by flash chromatography on silica

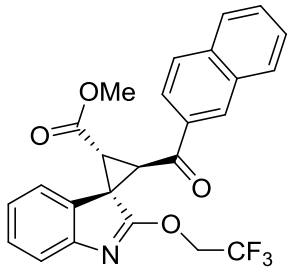
(EtOAc/PE = 1/5) as a yellow solid (46.4 mg, 53% yield, 6:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.27 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.02 (td, *J* = 7.6, 1.0 Hz, 1H), 4.90 – 4.84 (m, 1H), 4.72 – 4.66 (m, 1H), 4.14 (d, *J* = 7.9 Hz, 1H), 3.71 (d, *J* = 7.9 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 192.55, 173.72, 166.24, 151.86, 137.50, 133.25, 132.46, 131.25, 130.88, 130.55, 128.73, 127.18, 124.49, 122.67 (q, *J* = 277.5 Hz), 122.09, 119.40, 65.14 (q, *J* = 36.9 Hz), 52.71, 42.48, 40.56, 34.36; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.90 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}ClF_3NO_4^+$ 438.0714; Found 438.0715.

Methyl (1S,2R,3R)-3-(4-nitrobenzoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-indole]-2-carboxylate (4ka):



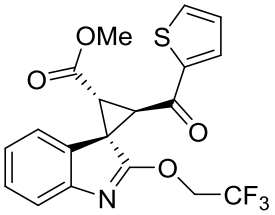
Following the general procedure, **4ka** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a white solid (34.1 mg, 38% yield, 4:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.05 (q, *J* = 6.8, 5.9 Hz, 2H), 5.00 – 4.90 (m, 2H), 4.27 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.75 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.60, 173.18, 165.94, 151.64, 150.69, 140.53, 130.58, 129.31, 129.01, 125.44, 124.66, 124.09, 122.68 (q, *J* = 277.5 Hz), 121.34, 119.70, 65.22 (q, *J* = 36.8 Hz), 52.90, 40.95, 36.94, 33.45; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.87 (t, *J* = 8.1 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}F_3N_2O_6^+$ 449.0955; Found 449.0950.

Methyl (1*S*,2*R*,3*R*)-2-(2-naphthoyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-indole]-3-carboxylate (4la):



Following the general procedure, **4la** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a yellow solid (49.0 mg, 54% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.80 (t, *J* = 7.1 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 5.01 – 4.94 (m, 1H), 4.91 – 4.83 (m, 1H), 4.39 (d, *J* = 7.9 Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.39, 173.69, 166.49, 151.64, 135.88, 133.66, 132.28, 131.28, 130.62, 129.74, 129.06, 128.81, 128.61, 127.77, 127.06, 124.51, 122.85 (q, *J* = 277.5 Hz), 123.50, 121.62, 119.41, 65.14 (q, *J* = 36.8 Hz), 52.74, 40.89, 37.00, 33.60; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.79 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{19}F_3NO_4^+$ 454.1261; Found 454.1262.

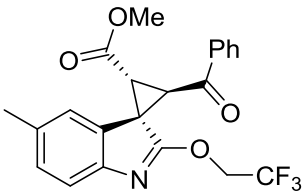
Methyl (1S,2R,3R)-3-(thiophene-2-carbonyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-indole]-2-carboxylate (4ma):



Following the general procedure, **4ma** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (52.4 mg, 64% yield, 5:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.69 – 7.62 (m, 2H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.22 – 7.20 (m, 1H), 7.07 (tt, *J* = 5.2, 3.0 Hz, 2H), 4.91 (td, *J* = 8.3, 4.2 Hz, 2H), 4.21 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.71 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 182.90, 173.53, 166.22, 151.71, 143.49, 135.23, 133.15, 131.22, 128.62, 128.49, 124.55, 122.73 (q, *J* = 277.5 Hz), 121.98, 119.36, 65.14 (q, *J* = 36.8 Hz), 52.72, 40.90, 37.31, 33.50; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.91 (t, *J* = 8.4 Hz); HRMS (ESI)

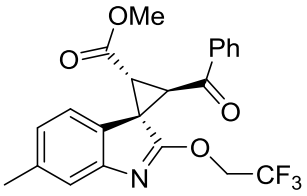
m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}F_3NO_4S^+$ 410.0668; Found 410.0682.

Methyl (1*S*,2*R*,3*R*)-2-benzoyl-5'-methyl-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-3-carboxylate (4ab):



Following the general procedure, **4ab** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (64.3 mg, 77% yield, 5:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.90 (s, 1H), 4.97 – 4.85 (m, 2H), 4.27 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.69 (d, *J* = 7.9 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.72, 172.98, 166.45, 149.25, 136.43, 134.32, 133.91, 131.26, 129.14, 128.83, 128.36, 122.76 (q, *J* = 277.4 Hz), 122.27, 118.95, 65.07 (q, *J* = 36.9 Hz), 52.68, 40.71, 36.86, 33.47, 21.45; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.92 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_4^+$ 418.1261; Found 418.1256.

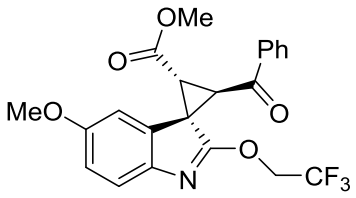
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-6'-methyl-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-3-carboxylate (4ac):



Following the general procedure, **4ac** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (54.3 mg, 65% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 – 7.70 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.10 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.92 – 4.78 (m, 2H), 4.20 (d, *J* = 7.9 Hz, 1H), 3.67 (s, 3H), 3.62 (d, *J* = 7.9 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.76, 173.76, 166.48, 151.78, 138.78, 136.40, 133.89, 128.82, 128.33, 128.19, 125.11, 122.76 (q, *J* = 277.5 Hz), 121.23, 120.27, 65.10 (q, *J*

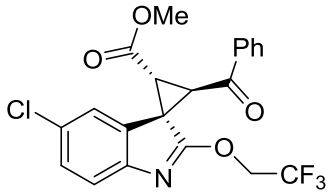
= 36.9 Hz), 52.66, 40.71, 36.71, 33.34, 21.58; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.89 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_4^+$ 418.1261; Found 418.1252.

Methyl (1*S*,2*R*,3*R*)-2-benzoyl-5'-methoxy-2'-(2,2,2-trifluoroethoxy)spiro[cyclopro -pane-1,3'-indole]-3-carboxylate (4ad):



Following the general procedure, **4ad** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a yellow solid (45.9 mg, 53% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 4.96 – 4.84 (m, 2H), 4.29 (d, *J* = 7.9 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.68 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.52, 172.15, 166.37, 157.10, 144.88, 136.38, 133.94, 132.48, 128.83, 128.36, 122.78 (q, *J* = 277.6 Hz), 119.70, 113.81, 108.06, 65.03 (q, *J* = 36.8 Hz), 55.70, 52.69, 40.88, 36.85, 33.65. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.92 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}F_3NO_5^+$ 434.1210; Found 434.1200.

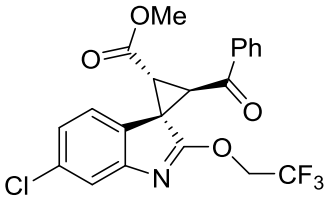
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-5'-chloro-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropa -ne-1,3'-indole]-3-carboxylate (4ae):



Following the general procedure, **4ae** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a yellow liquid (55.2 mg, 63% yield, 5:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.16 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 4.93 – 4.80 (m, 2H), 4.23 (d, *J* = 7.9 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 1H); ^{13}C NMR (151 MHz,

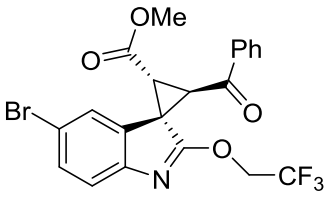
$CDCl_3$) δ = 190.62, 173.60, 166.38, 151.65, 136.35, 133.95, 131.24, 128.83, 128.59, 128.33, 124.49, 122.74 (q, *J* = 277.5 Hz), 121.59, 119.39, 65.15 (q, *J* = 37.0 Hz), 52.70, 40.73, 36.85, 33.48; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.90 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}ClF_3NO_4^+$ 438.0714; Found 438.0715.

Methyl (1*S*,2*R*,3*R*)-2-benzoyl-6'-chloro-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropa-ne-1,3'-indole]-3-carboxylate (4af):



Following the general procedure, **4af** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (54.3 mg, 62% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 1.5 Hz, 1H), 6.97 – 6.93 (m, 2H), 4.92 – 4.78 (m, 2H), 4.23 (d, J = 7.9 Hz, 1H), 3.69 (s, 3H), 3.65 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.48, 174.60, 166.10, 152.86, 136.18, 134.38, 134.14, 129.58, 128.92, 128.33, 124.44, 122.63 (q, *J* = 277.5 Hz), 122.44, 120.05, 65.30 (q, *J* = 37.0 Hz), 52.79, 40.48, 36.87, 33.62; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.86 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}ClF_3NO_4^+$ 438.0714; Found 438.0709.

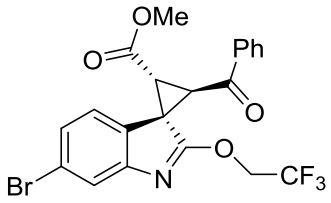
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-5'-bromo-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-3-carboxylate (4ag):



Following the general procedure, **4ag** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (57.9 mg, 60% yield, 4:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 – 7.74 (m, 2H), 7.50 – 7.47 (m, 1H), 7.37 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 4.90 – 4.78 (m, 2H), 4.24 (d, *J* = 8.0 Hz, 1H), 3.69 (s, 3H), 3.64 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.33, 173.65, 166.01, 150.72, 136.21, 134.15, 133.25, 131.66, 128.91,

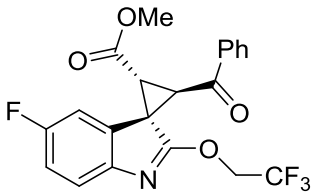
128.43, 125.03, 122.63 (q, J = 277.4 Hz), 120.74, 117.66, 65.27 (q, J = 37.1 Hz), 52.82, 40.58, 36.90, 33.92. ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.87 (t, J = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}BrF_3NO_4^+$ 482.0209; Found 482.0203.

Methyl (1*S*,2*R*,3*R*)-2-benzoyl-6'-bromo-2'-(2,2,2-trifluoroethoxy)spiro[cycloprop-ane-1,3'-indole]-3-carboxylate (4ah):



Following the general procedure, **4ah** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (63.6 mg, 66% yield, 4:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.80 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.50 (s, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 8.2 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 4.98 – 4.87 (m, 2H), 4.31 (d, J = 7.9 Hz, 1H), 3.76 (s, 3H), 3.73 (d, J = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.45, 174.46, 166.07, 153.04, 136.18, 134.15, 130.11, 128.92, 128.33, 127.32, 122.62 (q, J = 277.5 Hz), 122.92, 122.80, 122.24, 65.32 (q, J = 37.1 Hz), 52.79, 40.55, 36.86, 33.60; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.87 (t, J = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}BrF_3NO_4^+$ 482.0209; Found 482.0201.

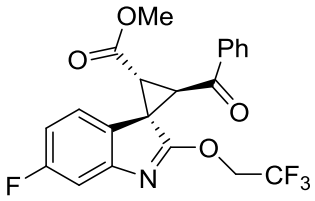
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-5'-fluoro-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropa-ne-1,3'-indole]-3-carboxylate (4ai):



Following the general procedure, **4ai** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (56.5 mg, 67% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 – 7.74 (m, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.8 Hz, 2H), 7.21 (dd, J = 8.5, 4.6 Hz, 1H), 6.87 (td, J = 9.1, 2.6 Hz, 1H), 6.82 (dd, J = 8.5, 2.5 Hz, 1H), 4.90 – 4.76 (m, 2H), 4.25 (d, J = 7.9 Hz, 1H), 3.69 (s, 3H), 3.63 (d, J = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.35, 173.23 (d, J = 2.6 Hz), 166.06, 160.07

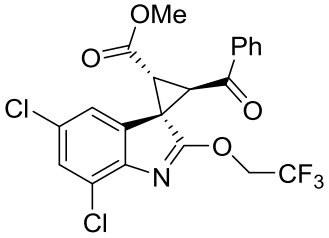
(d, *J* = 242.8 Hz), 147.61 (d, *J* = 2.4 Hz), 136.24, 134.10, 132.83 (d, *J* = 10.1 Hz), 128.89, 128.39, 122.69 (q, *J* = 277.4 Hz), 120.02 (d, *J* = 8.8 Hz), 115.11 (d, *J* = 23.6 Hz), 109.86 (d, *J* = 26.9 Hz), 65.17 (q, *J* = 37.1 Hz), 52.76, 40.84 (d, *J* = 2.7 Hz), 36.78, 33.85; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.91 (t, *J* = 8.2 Hz), -116.75 (td, *J* = 8.9, 4.6 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}F_4NO_4^+$ 422.1010; Found 422.0997.

Methyl (1*S*,2*R*,3*R*)-2-benzoyl-6'-fluoro-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropa-ne-1,3'-indole]-3-carboxylate (4aj):



Following the general procedure, **4aj** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (51.4 mg, 61% yield, 5:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.15 – 7.02 (m, 2H), 6.73 (td, *J* = 9.2, 2.3 Hz, 1H), 4.98 – 4.85 (m, 2H), 4.29 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.71 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.63, 174.94, 166.19, 163.34 (d, *J* = 245.4 Hz), 153.14 (d, *J* = 11.8 Hz), 136.27, 134.08, 128.89, 128.32, 126.68 (d, *J* = 2.7 Hz), 122.64 (q, *J* = 277.3 Hz), 122.51 (d, *J* = 9.7 Hz), 111.06 (d, *J* = 22.8 Hz), 107.63 (d, *J* = 24.8 Hz), 65.28 (q, *J* = 37.0 Hz), 52.76, 40.43, 36.74, 33.53; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.88 (t, *J* = 8.1 Hz), -112.41 (td, *J* = 9.2, 5.3 Hz); HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}F_4NNaO_4^+$ 444.0829; Found 444.0823.

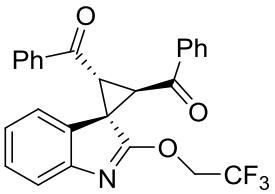
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-5',7'-dichloro-2'-(2,2,2-trifluoroethoxy)spiro[cyclop-ropane-1,3'-indole]-3-carboxylate (4ak):



Following the general procedure, **4ak** was isolated by flash chromatography on silica

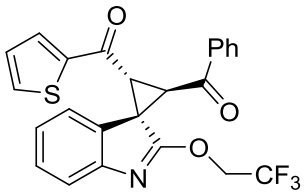
(EtOAc/PE = 1/10) as a white solid (36.8 mg, 39% yield, 4:1 dr); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 5.06 – 4.91 (m, 2H), 4.35 (d, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 3.74 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 189.97, 174.18, 165.63, 147.31, 136.01, 134.35, 133.98, 130.44, 129.00, 128.95, 128.46, 124.78, 122.55 (q, *J* = 277.2 Hz), 120.78, 65.65 (q, *J* = 37.1 Hz), 52.92, 41.15, 37.28, 34.27; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.84 (t, *J* = 8.1 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}Cl_2F_3NO_4^+$ 472.0325; Found 472.0327.

((2*R*,3*R*)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-indole]-2,3-diyl)bis(phenylmethanone) (4al):



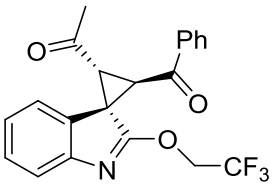
Following the general procedure, **4al** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (39.5 mg, 44% yield, >20:1 dr); mp 60-61 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.54 (q, *J* = 7.1 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 4.84 – 4.78 (m, 1H), 4.58 – 4.50 (m, 2H), 4.34 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 191.35, 190.05, 173.70, 152.03, 136.54, 135.70, 133.96, 133.90, 130.99, 128.84, 128.73, 128.46, 128.42, 124.64, 122.45 (q, *J* = 277.8 Hz), 121.66, 119.51, 64.79 (q, *J* = 37.1 Hz), 41.88, 38.30, 36.40; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -74.02 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{19}F_3NO_3^+$ 450.1312; Found 450.1315.

((1*S*,2*R*,3*R*)-2-benzoyl-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-indol]-3-yl)(thiophen-2-yl)methanone (4am):



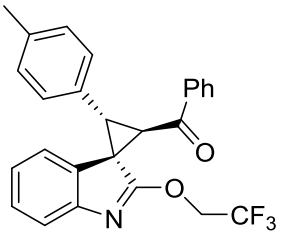
Following the general procedure, **4am** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (47.4 mg, 52% yield, 3:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 – 7.79 (m, 2H), 7.56 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.05 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.94 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.81 – 4.74 (m, 1H), 4.59 – 4.52 (m, 1H), 4.43 (d, *J* = 7.9 Hz, 1H), 4.24 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 191.10, 182.71, 173.63, 151.95, 142.93, 136.45, 134.81, 134.00, 133.05, 131.10, 128.86, 128.72, 128.47, 128.37, 124.63, 122.48 (q, *J* = 278.0 Hz), 121.60, 119.50, 64.86 (q, *J* = 36.8 Hz), 41.85, 38.69, 36.32; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -74.02 (t, *J* = 8.0 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{17}F_3NO_3S^+$ 456.0876; Found 456.0882.

1-((1*R*,2*R*,3*R*)-2-benzoyl-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-indol]-3-yl)ethan-1-one (4an):



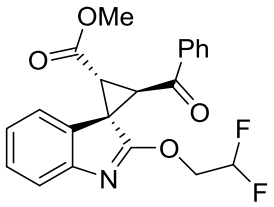
Following the general procedure, **4an** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (31.0 mg, 40% yield, 5:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 7.0 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.99 (td, *J* = 7.6, 1.1 Hz, 1H), 4.92 – 4.81 (m, 2H), 4.29 (d, *J* = 8.1 Hz, 1H), 3.77 (d, *J* = 8.0 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 197.75, 190.98, 173.59, 151.67, 136.38, 133.96, 131.36, 128.83, 128.61, 128.36, 124.51, 122.67 (q, *J* = 277.8 Hz), 121.55, 119.44, 64.87 (q, *J* = 37.0 Hz), 41.42, 40.84, 36.56, 30.25; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.90 (t, *J* = 8.0 Hz); HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{16}F_3NNaO_3^+$ 410.0974; Found 410.0976.

Phenyl ((1*R*,2*S*,3*R*)-2-(*p*-tolyl)-2'-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,3'-i-ndol]-3-yl)methanone (4ao):



Following the general procedure, **4ao** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (49.6 mg, 57% yield, >20:1 dr); mp 77-78 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.98 (m, 3H), 4.78 – 4.71 (m, 1H), 4.41 – 4.35 (m, 1H), 4.25 (d, *J* = 8.3 Hz, 1H), 4.20 (d, *J* = 8.3 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 192.26, 174.59, 151.70, 137.42, 136.96, 133.67, 132.94, 130.45, 128.95, 128.83, 128.67, 128.24, 127.71, 124.10, 122.55 (q, *J* = 277.5 Hz), 121.37, 119.07, 64.65 (q, *J* = 36.8 Hz), 43.15, 38.95, 37.86, 21.09; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -74.18 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}F_3NO_2^+$ 436.1519; Found 436.1517.

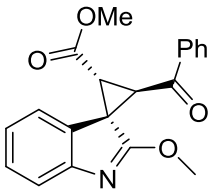
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-2'-(2,2-difluoroethoxy)spiro[cyclopropane-1,3'-indo -le]-3-carboxylate (4ap):



Following the general procedure, **4ap** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (37.8 mg, 49% yield, 3:1 dr);^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 – 7.78 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.09 (d, *J* = 7.1 Hz, 1H), 7.02 (td, *J* = 7.6, 0.9 Hz, 1H), 6.18 (tt, *J* = 55.0, 4.0 Hz, 1H), 4.82 – 4.62 (m, 2H), 4.28 (d, *J* = 7.9 Hz, 1H), 3.76 (s, 3H), 3.72 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.76, 174.12, 166.58, 152.07, 136.38, 133.92, 131.17, 128.82, 128.54, 128.36, 124.27, 121.53, 119.23, 112.32 (t, *J* = 241.5 Hz), 67.17 (t, *J* = 29.7 Hz), 52.71,

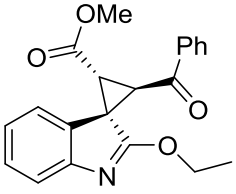
40.82, 36.86, 33.50; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -126.23 (td, *J* = 13.4, 5.6 Hz), -126.33 (td, *J* = 13.4, 5.7 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}F_2NO_4^+$ 386.1198; Found 386.1201.

Methyl (1*S*,2*R*,3*R*)-2-benzoyl-2'-methoxyspiro[cyclopropane-1,3'-indole]-3-carbo -xylate (4aq):



Following the general procedure, **4aq** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (31.5 mg, 47% yield, >20:1 dr); mp 55-56 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.22 (d, *J* = 7.8 Hz, 1H), 4.14 (s, 3H), 3.74 (s, 3H), 3.67 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 191.10, 175.76, 166.94, 152.86, 136.50, 133.82, 131.03, 128.77, 128.45, 128.38, 123.70, 121.35, 118.86, 56.92, 52.60, 41.04, 36.92, 33.42; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}NO_4^+$ 336.1230; Found 336. 1226.

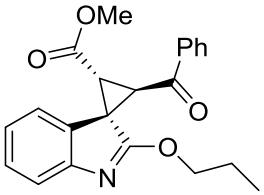
Methyl (1*S*,2*R*,3*R*)-2-benzoyl-2'-ethoxyspiro[cyclopropane-1,3'-indole]-3-carboxy -late (4ar):



Following the general procedure, **4ar** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (24.4 mg, 35% yield, >20:1 dr); mp 102-103 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 4.55 – 4.46 (m, 2H), 4.14 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 3H), 3.61 (d, *J* = 7.8 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz,

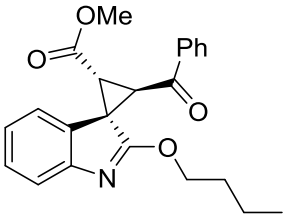
$CDCl_3$) δ = 191.22, 175.10, 166.85, 153.19, 136.56, 133.77, 130.85, 128.76, 128.40, 128.36, 123.53, 121.27, 118.74, 65.75, 52.45, 40.95, 36.92, 33.35, 14.40; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}NO_4^+$ 350.1387; Found 350.1387.

Methyl (1S,2R,3R)-2-benzoyl-2'-propoxyspiro[cyclopropane-1,3'-indole]-3-carboxylate (4as):



Following the general procedure, **4as** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (21.1 mg, 29% yield, >20:1 dr); mp 85-86 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.82 – 7.78 (m, 2H), 7.52 (td, *J* = 7.3, 1.3 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.22 (td, *J* = 7.6, 1.3 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.97 (td, *J* = 7.6, 1.1 Hz, 1H), 4.51 – 4.43 (m, 2H), 4.21 (d, *J* = 7.8 Hz, 1H), 3.75 (s, 3H), 3.68 (d, *J* = 7.8 Hz, 1H), 1.88 – 1.81 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 191.20, 175.27, 166.82, 153.17, 136.57, 133.76, 130.84, 128.76, 128.41, 128.33, 123.52, 121.26, 118.73, 71.49, 52.50, 41.16, 37.03, 33.32, 22.20, 10.32; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4^+$ 364.1543; Found 364.1545.

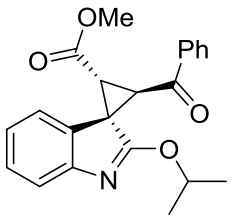
Methyl (1S,2R,3R)-2-benzoyl-2'-butoxyspiro[cyclopropane-1,3'-indole]-3-carboxylate (4at):



Following the general procedure, **4at** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (22.6 mg, 30% yield, >20:1 dr); mp 74-75 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.51 (t, *J* = 6.6 Hz, 2H), 4.20 (d, *J* = 7.8 Hz, 1H), 3.75 (s,

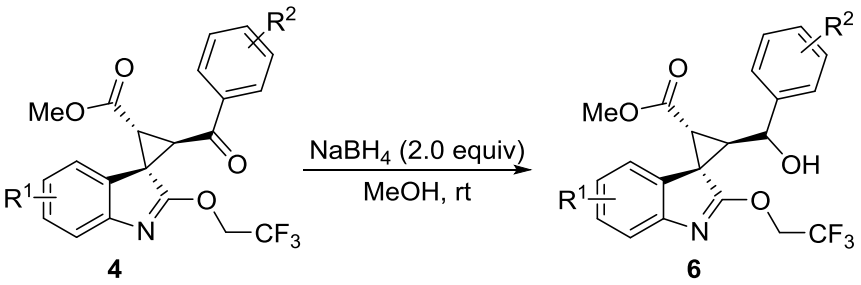
3H), 3.68 (d, *J* = 7.8 Hz, 1H), 1.80 (p, *J* = 6.8 Hz, 2H), 1.51 (dq, *J* = 14.1, 7.0 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.18, 174.26, 165.78, 152.14, 135.54, 132.74, 129.81, 127.73, 127.39, 127.31, 122.49, 120.24, 117.70, 68.71, 51.47, 40.12, 36.01, 32.28, 29.78, 17.97, 12.70; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}NO_4^+$ 378.1700; Found 378.1694.

Methyl (1S,2R,3R)-2-benzoyl-2'-isopropoxyspiro[cyclopropane-1,3'-indole]-3-carboxylate (4au):



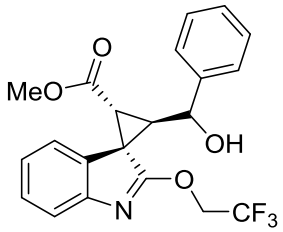
Following the general procedure, **4au** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (16.0 mg, 22% yield, >20:1 dr); mp 122-123 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.13 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 5.20 – 5.12 (m, 2H), 3.82 (s, 3H), 3.71 (d, *J* = 5.2 Hz, 1H), 1.52 (d, *J* = 5.2 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.40, 166.14, 160.06, 141.13, 137.71, 131.12, 130.57, 128.71, 128.64, 127.92, 127.42, 126.34, 121.93, 69.85, 52.78, 39.59, 28.38, 26.33, 21.79, 21.55; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_4^+$ 364.1543; Found 364.1540.

Ⅲ. Synthetic Procedures and Analytical Data of Compounds 6:



In a flame-dried Schlenk tube, sodium borohydride (22.8 mg, 0.6 mmol) was suspended in methanol (1.5 mL). Compounds **4** (0.2 mmol) dissolved in methanol (1.5 mL) was added via syringe and stirred for 3 h at room temperature and monitored by TLC analysis. After quenching with sat. $NaHCO_3$ (5.0 mL) the aqueous layer was extracted with DCM (5.0 mL × 3). The combined organic layers were dried over Na_2SO_4 and the crude product was purified by column chromatography (MeOH/DCM = 1:30) to give the separable pure products **6**.

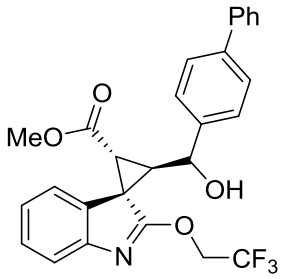
Methyl (1*S*,2*R*,3*R*)-3-((*R*)-hydroxy(phenyl)methyl)-2'-(2,2,2-trifluoroethoxy)spiro [cyclopropane-1,3'-indole]-2-carboxylate (6a):



Following the general procedure, **6a** was isolated by flash chromatography on silica (MeOH/DCM = 1:30) as a colorless solid (59.2 mg, 73% yield, >20:1 dr); mp 179-181 ^{o}C;^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.17 (s, 1H), 7.16 – 7.12 (m, 1H), 4.86 (d, *J* = 9.4 Hz, 1H), 4.74 – 4.67 (m, 1H), 4.08 – 4.01 (m, 1H), 3.57 (s, 3H), 3.09 (dd, *J* = 9.4, 8.4 Hz, 1H), 2.87 (d, *J* = 8.3 Hz, 1H), 2.75 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 175.17, 166.39, 152.03, 141.23, 132.71, 128.89, 128.58, 128.40, 126.13, 124.04, 122.53 (q, *J* = 277.2 Hz), 120.23, 119.82, 71.34, 64.93 (q, *J* = 36.9 Hz), 52.51, 40.09, 39.04, 35.85; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.79 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}F_3NNaO_4^+$ 428.1080; Found

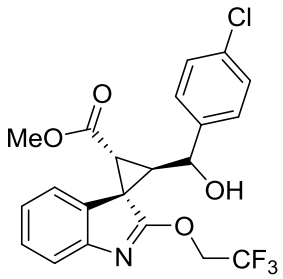
428.1071.

Methyl (1*S*,2*R*,3*R*)-2-((*R*)-[1,1'-biphenyl]-4-yl(hydroxy)methyl)-2'-(2,2,2-trifluoro-ethoxy)spiro[cyclopropane-1,3'-indole]-3-carboxylate (6b):



Following the general procedure, **6b** was isolated by flash chromatography on silica (MeOH/DCM = 1:30) as a colorless solid (85.7 mg, 89% yield, dr = 7:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 17.5, 6.3 Hz, 6H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.45 (q, *J* = 9.4, 8.5 Hz, 3H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 4.98 (d, *J* = 9.5 Hz, 1H), 4.71 – 4.63 (m, 1H), 3.75 (dd, *J* = 11.6, 8.6 Hz, 1H), 3.63 (s, 4H), 3.21 (t, *J* = 8.9 Hz, 1H), 2.98 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 175.24, 166.35, 151.90, 141.27, 140.66, 140.31, 132.65, 128.85, 128.71, 127.63, 127.48, 127.14, 126.62, 124.08, 122.44 (q, *J* = 277.0 Hz), 120.36, 119.77, 71.00, 64.90 (q, *J* = 36.9 Hz), 52.59, 40.29, 39.16, 35.88; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.70 (t, *J* = 8.2 Hz); HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{22}F_3NNaO_4^+$ 504.1393; Found 504.1381.

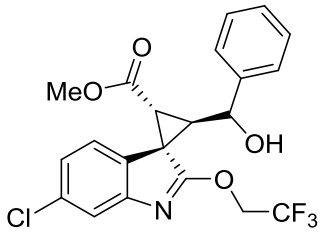
Methyl (1*S*,2*R*,3*R*)-3-((*R*)-(4-chlorophenyl)(hydroxy)methyl)-2'-(2,2,2-trifluoroet-hoxy)spiro[cyclopropane-1,3'-indole]-2-carboxylate (6c):



Following the general procedure, **6c** was isolated by flash chromatography on silica (MeOH/DCM = 1:20) as a colorless solid (72.1 mg, 82% yield, dr > 20:1); mp 147-148 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45 (dd, *J* = 12.1, 8.1 Hz, 3H), 7.35 (t,

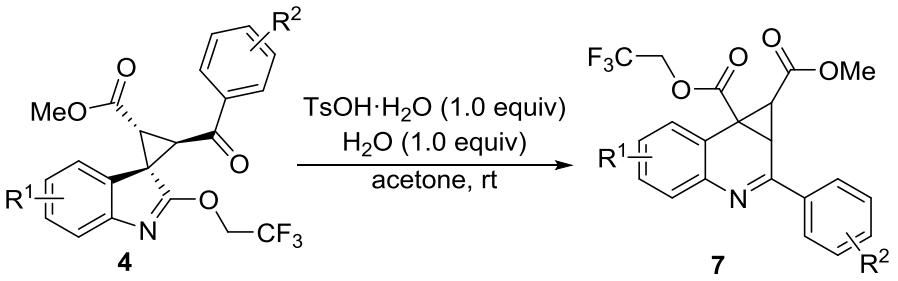
J = 8.1 Hz, 3H), 7.16 (d, *J* = 6.4 Hz, 2H), 4.84 (d, *J* = 9.4 Hz, 1H), 4.61 (td, *J* = 8.3, 4.0 Hz, 1H), 3.78 (p, *J* = 8.3 Hz, 1H), 3.57 (s, 3H), 3.28 (s, 1H), 3.01 (t, *J* = 8.9 Hz, 1H), 2.87 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 175.02, 166.28, 152.07, 139.65, 134.19, 132.47, 129.05, 128.71, 127.46, 124.14, 122.52 (q, *J* = 278.3 Hz), 120.11, 119.91, 70.77, 64.97 (q, *J* = 37.2 Hz), 52.62, 39.88, 38.86, 35.78; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.81 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}ClF_3NO_4^+$ 440.0871; Found 440.0872.

Methyl (1*S*,2*R*,3*R*)-6'-chloro-3-((*R*)-hydroxy(phenyl)methyl)-2'-(2,2,2-trifluoroet -hoxy)spiro[cyclopropane-1,3'-indole]-2-carboxylate (6d):



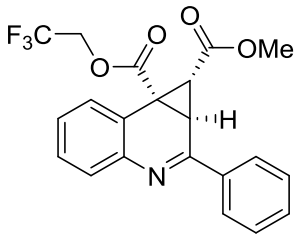
Following the general procedure, **6d** was isolated by flash chromatography on silica (MeOH/DCM = 1:20) as a colorless solid (71.2 mg, 81% yield, dr > 20:1); mp 175-176 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 (dd, *J* = 14.1, 6.9 Hz, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.16 (s, 2H), 4.94 – 4.85 (m, 2H), 4.51 (dq, *J* = 12.4, 8.2 Hz, 1H), 3.65 (s, 3H), 3.13 (t, *J* = 8.8 Hz, 1H), 2.94 (d, *J* = 8.4 Hz, 1H), 2.17 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 176.10, 166.30, 153.32, 141.04, 134.12, 131.27, 128.97, 128.58, 126.08, 123.95, 122.55 (q, *J* = 277.3 Hz), 121.03, 120.42, 71.53, 65.17 (q, *J* = 37.0 Hz), 52.62, 39.91, 38.80, 35.83; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.82 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}ClF_3NO_4^+$ 440.0871; Found 440.0867.

Ⅳ. Synthetic Procedures and Analytical Data of Compounds 7:



To a mixture compound of **4** (0.20 mmol) in acetone (2.0 mL), *p*-TsOH·H_2O (32 mg, 0.20 mmol) and water (36 μL, 0.20 mmol) was added. The reaction mixture was stirred for 0.5 h and monitored by TLC analysis. After the reaction was completed, the reaction mixture was extracted with DCM (5.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to give the separable pure products **7**.

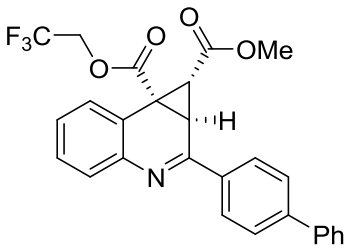
1-Methyl 7b-(2,2,2-trifluoroethyl) (1*R*,1a*R*,7b*S*)-2-phenyl-1,1a-dihydro-7b*H*-cycl -opropa[*c*]quinoline-1,7b-dicarboxylate (7a):



Following the general procedure, **7a** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow solid (65.3 mg, 81% yield); mp 80-82 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.12 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.69 (ddd, *J* = 27.2, 7.8, 1.1 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 4.63 – 4.53 (m, 2H), 3.82 (s, 3H), 3.75 (d, *J* = 5.3 Hz, 1H), 1.60 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.47, 165.31, 159.42, 141.01, 137.44, 131.31, 130.81, 129.17, 128.71, 128.20, 127.36, 126.19, 122.73 (q, *J* = 277.2 Hz), 120.42, 61.61 (q, *J* = 37.0 Hz), 53.04, 38.59, 28.40, 26.20; ^{19}F NMR (565 MHz, $CDCl_3$) δ =

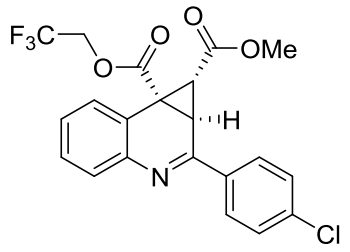
-73.32 (t, *J* = 8.4 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}F_3NO_4^+$ 404.1104; Found 404.1106.

1-Methyl 7b-(2,2,2-trifluoroethyl) (1*R*,1a*R*,7b*S*)-2-phenyl-1,1a-dihydro-7b*H*-cycl -opropa[*c*]quinoline-1,7b-dicarboxylate (7b):



Following the general procedure, **7b** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a colorless solid (90.1mg, 94% yield); mp 103-104 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.64 (m, 3H), 7.62 – 7.55 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.36 (td, *J* = 7.7, 1.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 (td, *J* = 7.6, 1.3 Hz, 1H), 4.57 – 4.47 (m, 2H), 3.75 (s, 3H), 3.72 (d, *J* = 5.3 Hz, 1H), 1.55 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.52, 165.34, 158.99, 144.02, 141.10, 140.18, 136.28, 130.81, 129.20, 128.95, 128.18, 127.98, 127.87, 127.36, 127.20, 126.22, 122.75 (q, *J* = 277.2 Hz), 120.41, 61.63 (q, *J* = 37.0 Hz), 53.07, 38.63, 28.35, 26.21; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.29 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{21}F_3NO_4^+$ 480.1417; Found 480.1415.

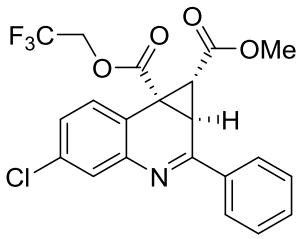
1-Methyl 7b-(2,2,2-trifluoroethyl) (1*R*,1a*R*,7b*S*)-2-(4-chlorophenyl)-1,1a-dihydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (7c):



Following the general procedure, **7c** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a colorless solid (70.0 mg, 80% yield); mp 74-75 ^oC; ^1H NMR

(500 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 4.55 – 4.48 (m, 2H), 3.75 (s, 3H), 3.62 (d, *J* = 5.3 Hz, 1H), 1.52 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.33, 165.22, 158.15, 140.83, 137.57, 135.83, 130.83, 129.25, 128.95, 128.65, 128.43, 126.25, 122.70 (q, *J* = 277.8 Hz), 120.35, 61.64 (q, *J* = 37.1 Hz), 53.11, 38.56, 28.09, 26.06; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.33 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}ClF_3NO_4^+$ 438.0714; Found 438.0720.

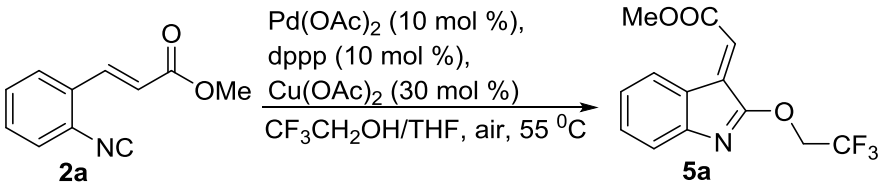
1-Methyl 7b-(2,2,2-trifluoroethyl) (1*R*,1a*R*,7b*S*)-5-chloro-2-phenyl-1,1a-dihydro-7b*H*-cyclopropa[*c*]quinoline-1,7b-dicarboxylate (7d):



Following the general procedure, **7d** was isolated by flash chromatography on silica (EtOAc/PE = 1/5) as a colorless solid (79.7 mg, 91% yield); mp 104-105 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.06 – 8.01 (m, 2H), 7.71 – 7.51 (m, 2H), 7.50 – 7.42 (m, 3H), 7.22 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.51 (q, *J* = 8.3 Hz, 2H), 3.75 (s, 3H), 3.68 (d, *J* = 5.3 Hz, 1H), 1.53 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.04, 165.11, 160.90, 142.23, 137.02, 134.68, 131.73, 130.45, 128.78, 127.99, 127.50, 127.39, 122.66 (q, *J* = 277.1 Hz), 118.89, 61.67 (q, *J* = 37.0 Hz), 53.15, 37.98, 28.31, 26.44; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.32 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}ClF_3NO_4^+$ 438.0714; Found 438.0715.

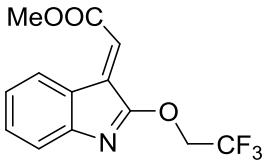
Ⅵ. The Mechanism Studies

Synthetic Procedure and Analytical Data of Compound 5a:



A solution of **2a** (37.4 mg, 0.2 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), dppp (8.2mg, 0.02 mmol), and $Cu(OAc)_2$ (10.8 mg, 0.06 mmol) in anhydrous THF and CF_3CH_2OH (2.0 mL, V/V = 1/6) was heated at 55 ℃ in a sealed tube under stirring for 12 h, then substrate **2a** was consumed as indicated by TLC. The resulting mixture was concentrated in vacuo, and purification of the crude product with flash column chromatography (ethyl acetate/petroleum ether = 1:20) gave **5a** (21.7 mg, 38 % yield) as an orange solid.

Methyl (*E*)-2-(2-(2,2,2-trifluoroethoxy)-3*H*-indol-3-ylidene)acetate 5a:



Following the general procedure, **5a** was isolated by flash chromatography on silica (EtOAc/PE = 1/20) as an orange solid (21.7 mg, 38% yield); mp 100-101 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.41 (d, *J* = 7.6 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 6.70 (s, 1H), 4.82 (q, *J* = 8.2 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 169.95, 165.51, 153.85, 139.79, 132.50, 128.07, 125.59, 125.29, 122.77 (q, *J* = 277.2 Hz), 121.36, 119.10, 64.99 (q, *J* = 36.9 Hz), 52.32; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -73.85 (t, *J* = 8.3 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{11}F_3NO_3^+$ 286.0686; Found 286.0683.

Ⅴ. The X-ray Analytical data of Compound 4ai and 7a:

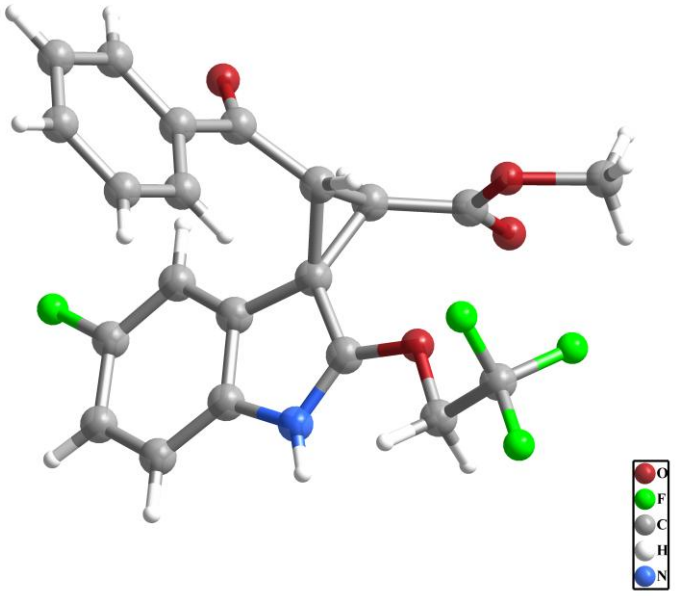


Figure 1. The ORTEP drawing of crystal (The ellipsoid contour percent probability level is 50%). Method of Crystallization: The **4ai** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

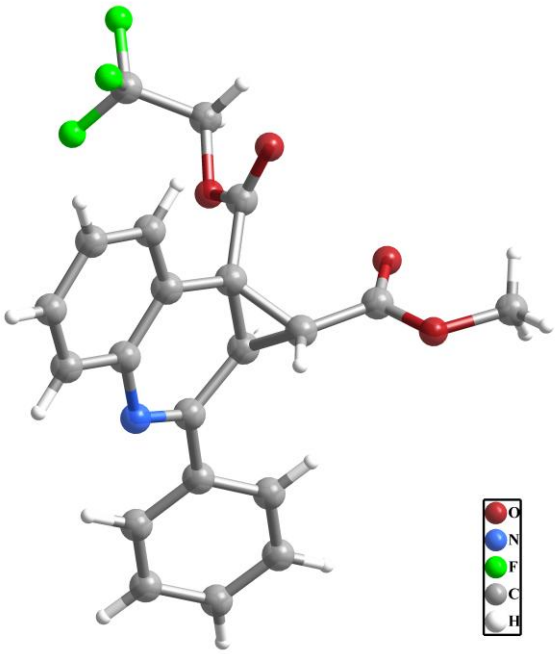


Figure 2. The ORTEP drawing of crystal (The ellipsoid contour percent probability level is 50%). Method of Crystallization: The **7a** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

Ⅶ. References:

1. (a) H. Tokuyama, Y. Kaburagi, X. Chen and T. Fukuyama, *Synthesis*, **2000**, 429; (b) T. Mamoru, F. Hirokazu, K. Keika and C. Naoto, *J. Org. Chem.*, **2010**, *75*, 4841.
2. (a) J. Quintana, M. Torres and F. Serratosa, *Tetrahedron.*, **1973**, *29*, 2065; (b) G. Payne, *J. Org. Chem.*, **1967**, *32*, 3351.

Ⅷ. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of 4-7:

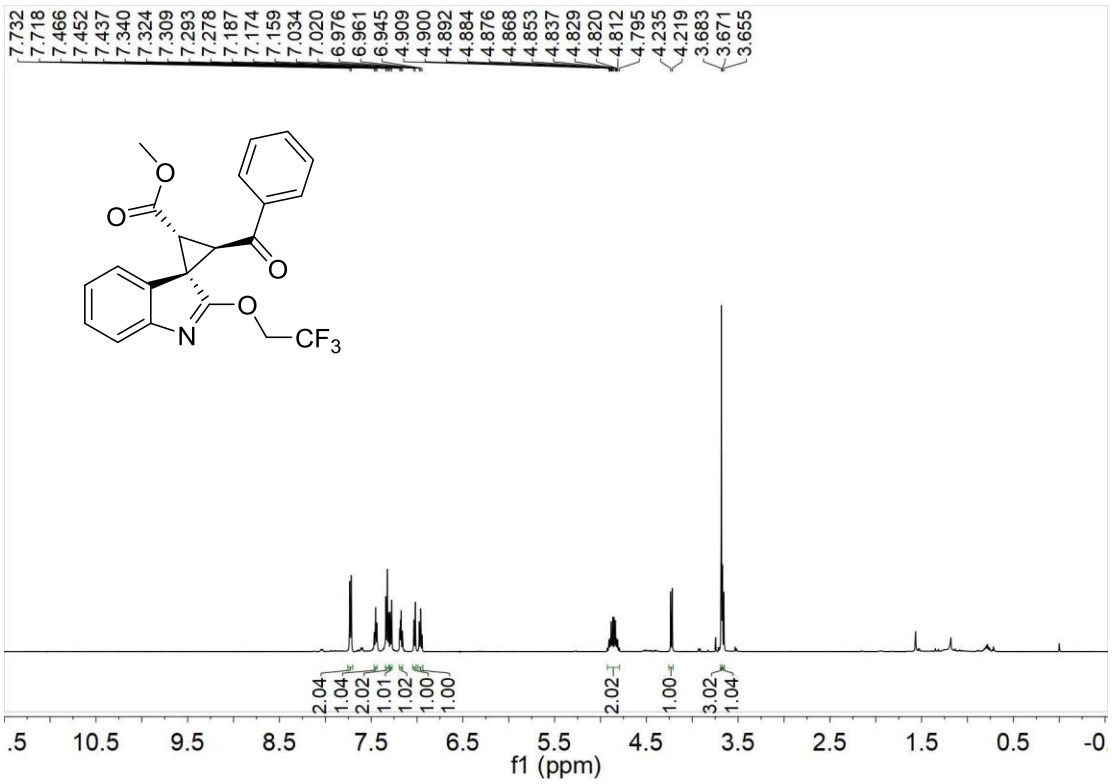


Figure 3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4aa**

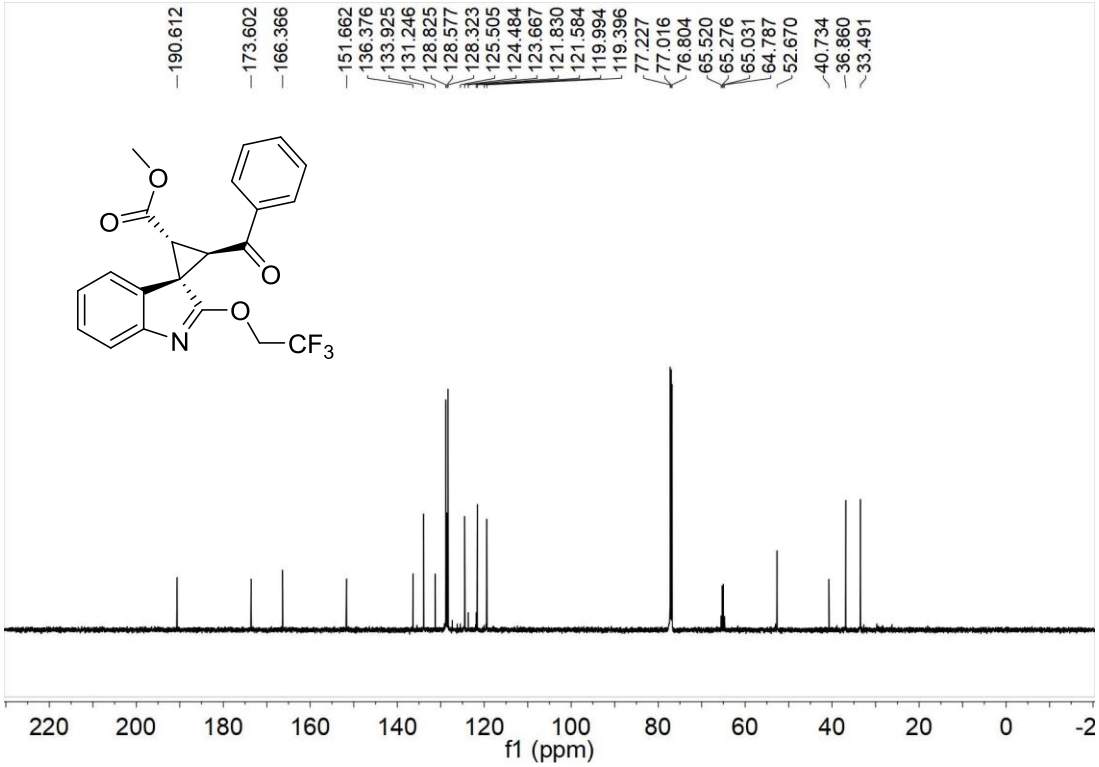


Figure 4. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4aa**

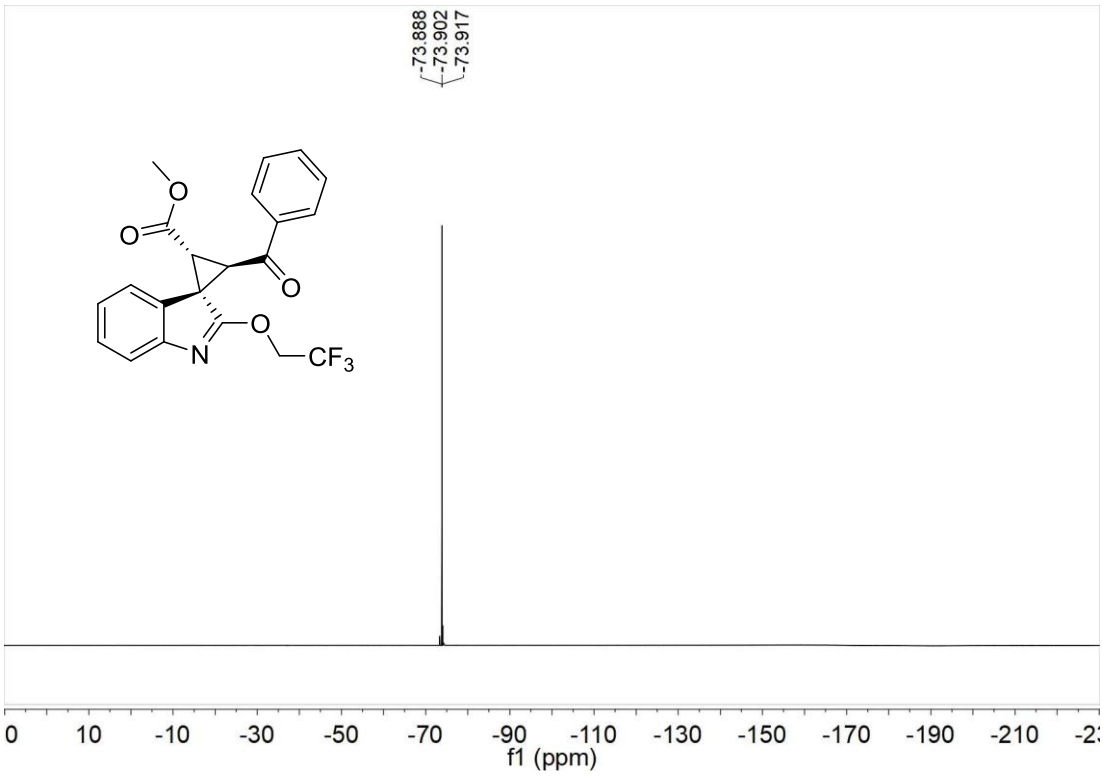


Figure 5. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4aa**

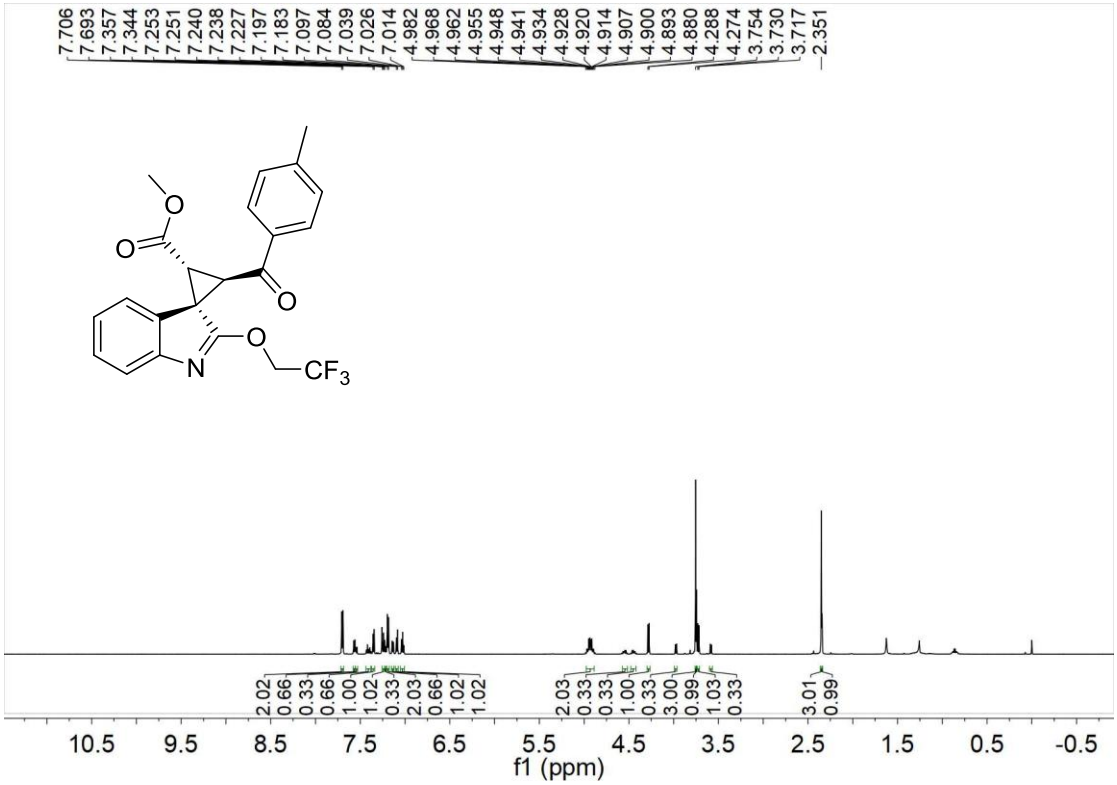


Figure 6. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ba**

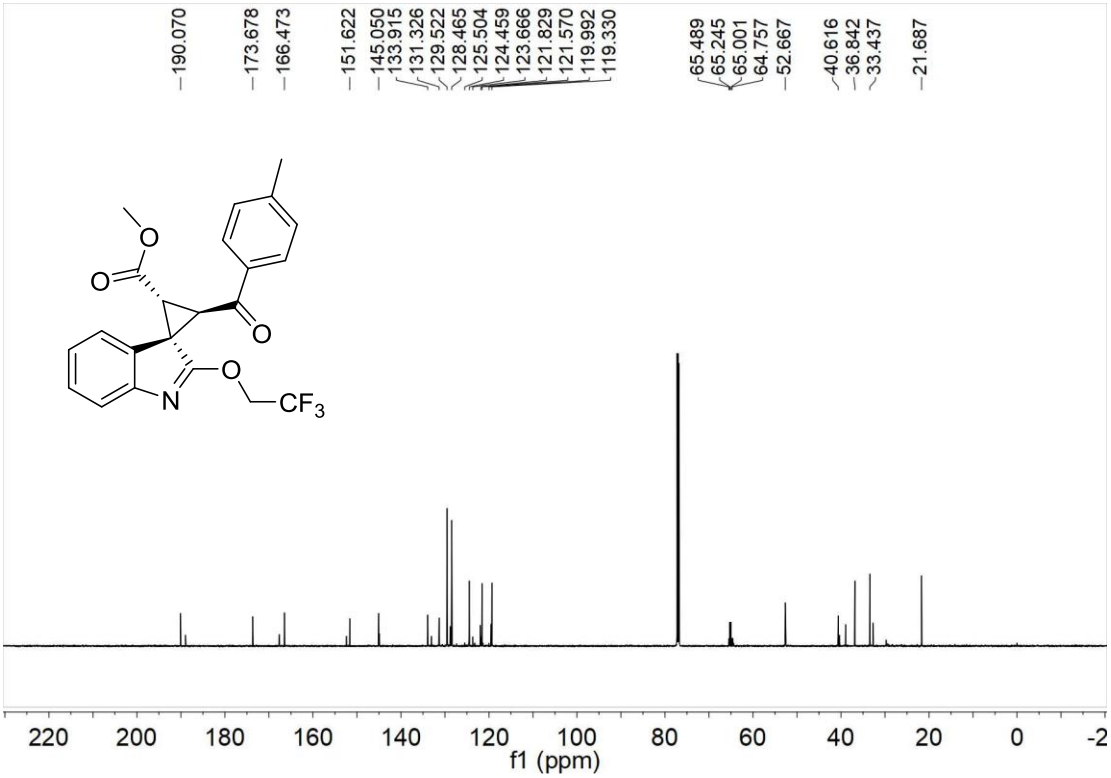


Figure 7. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ba**

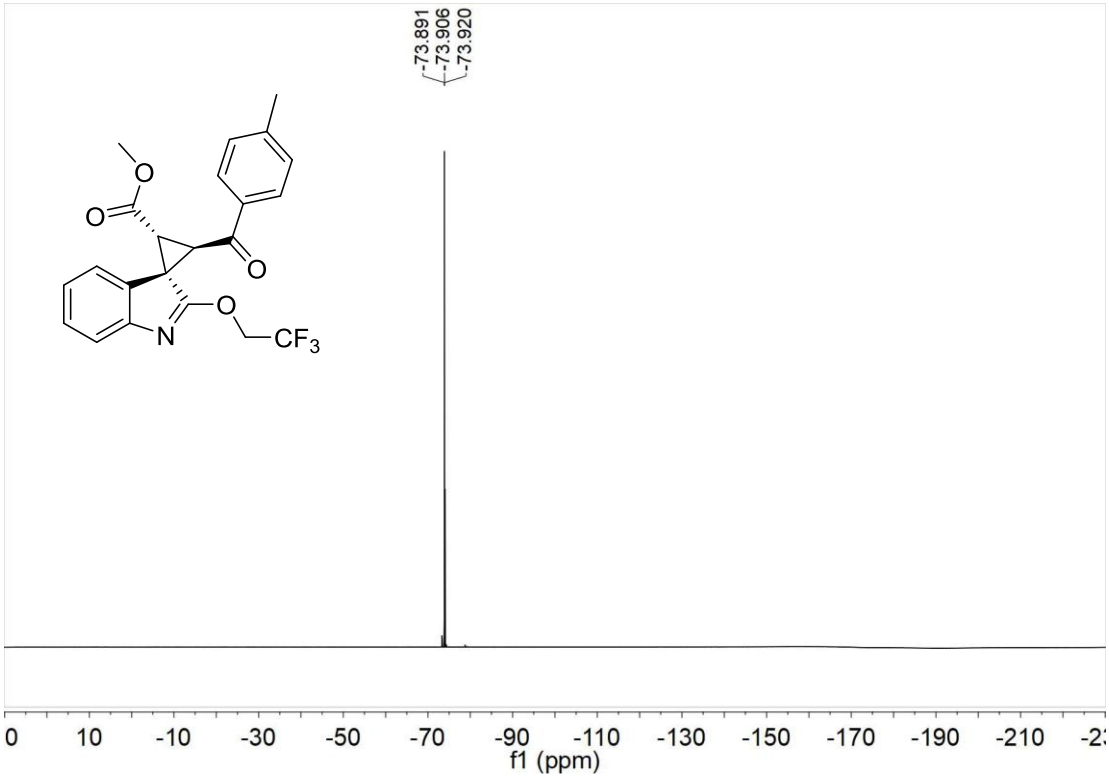


Figure 8. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ba**

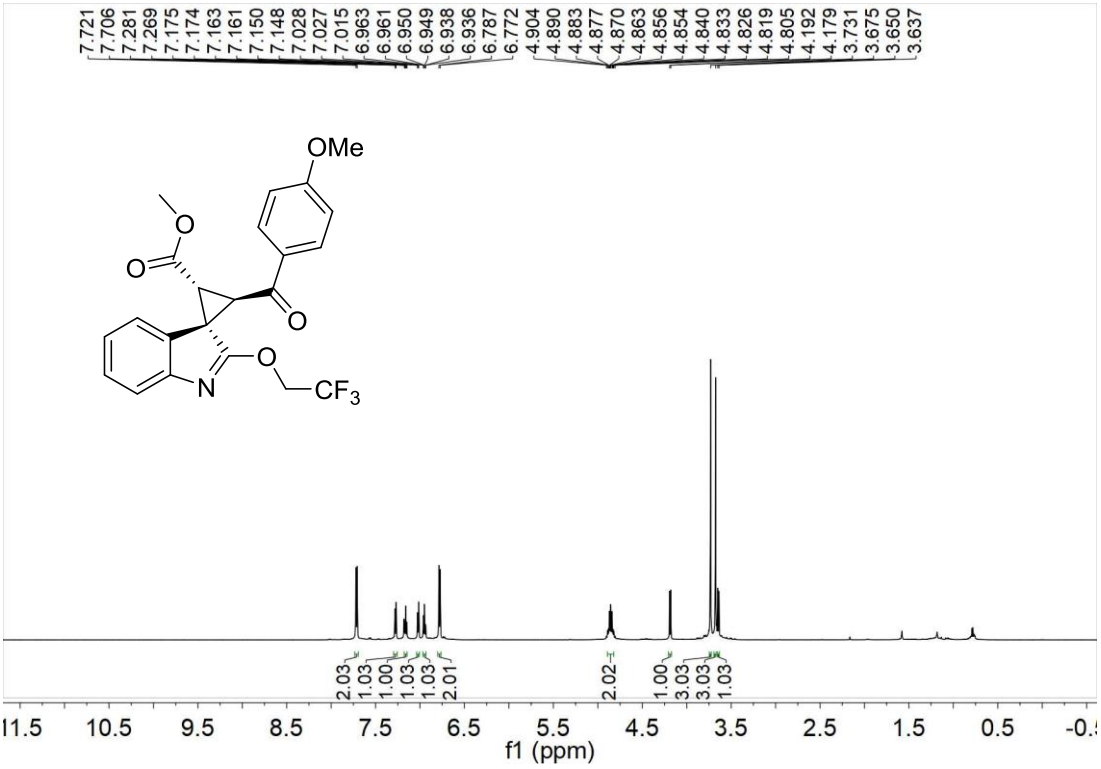


Figure 9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ca**

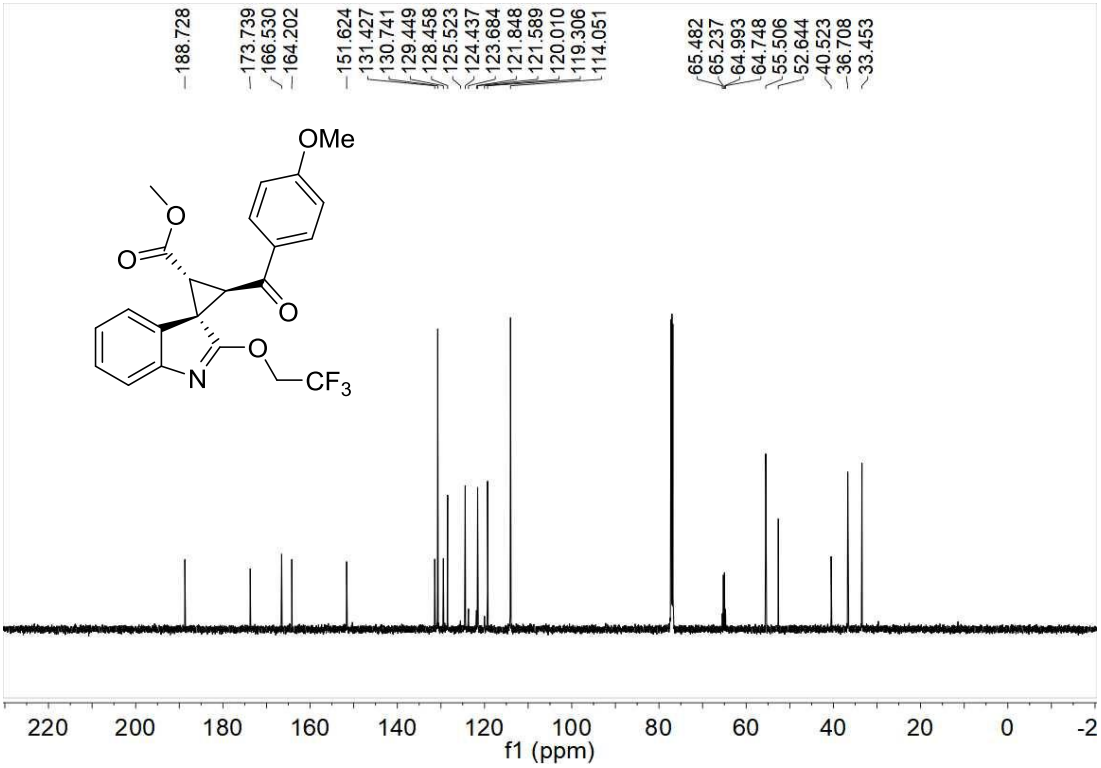


Figure 10. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ca**

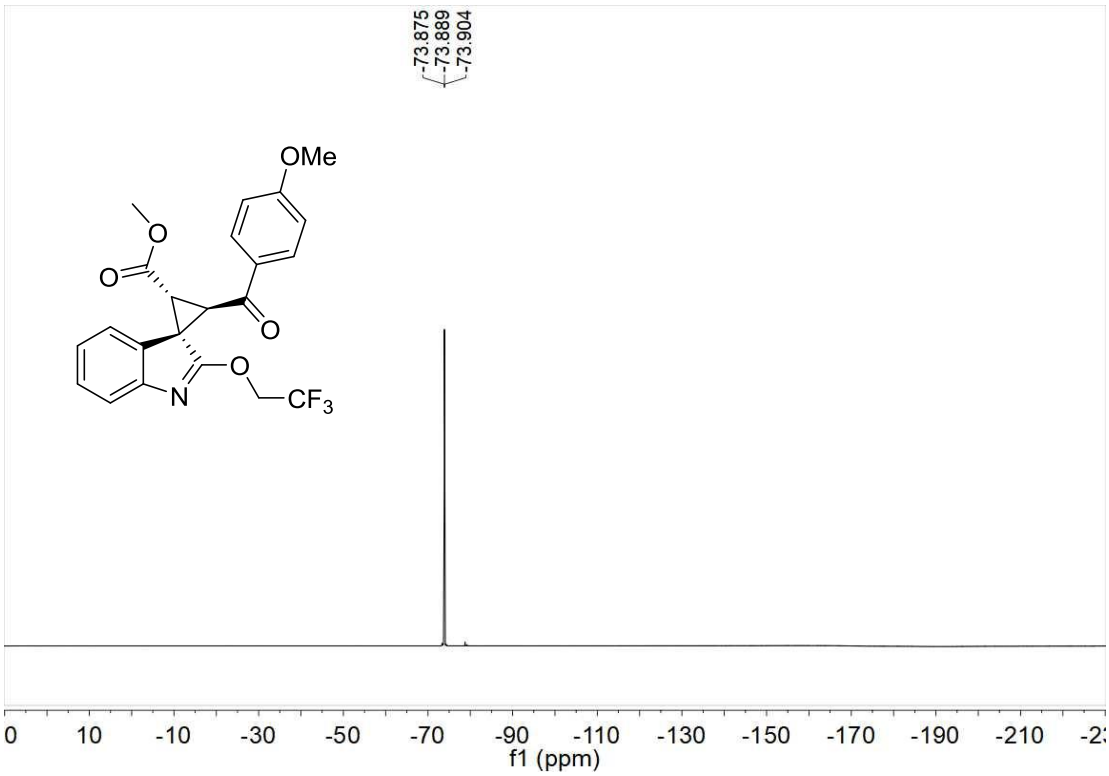


Figure 11. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ca**

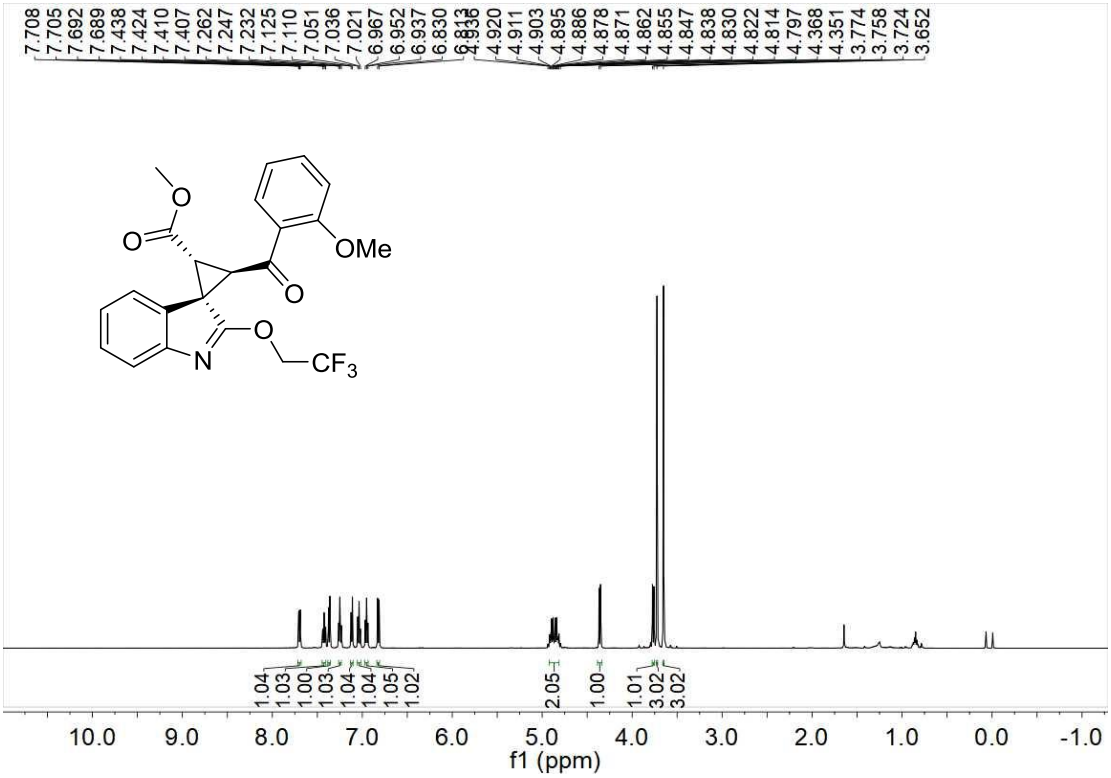


Figure 12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4da**

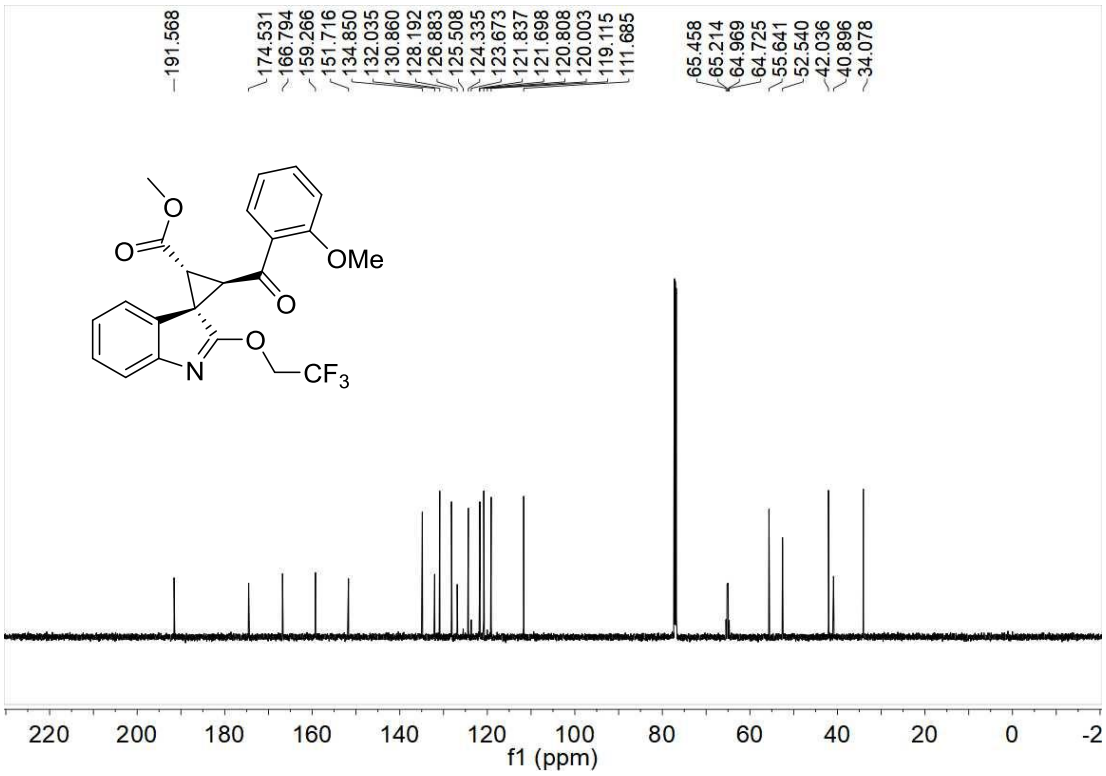


Figure 13. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4da**

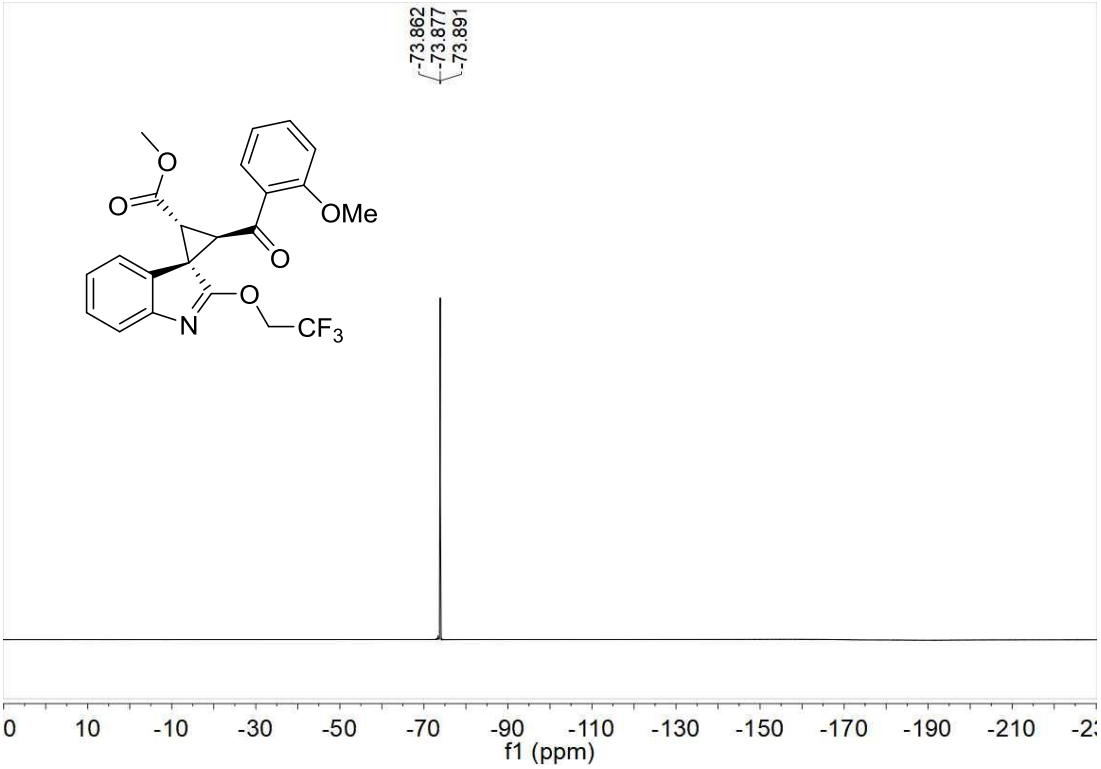


Figure 14. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4da**

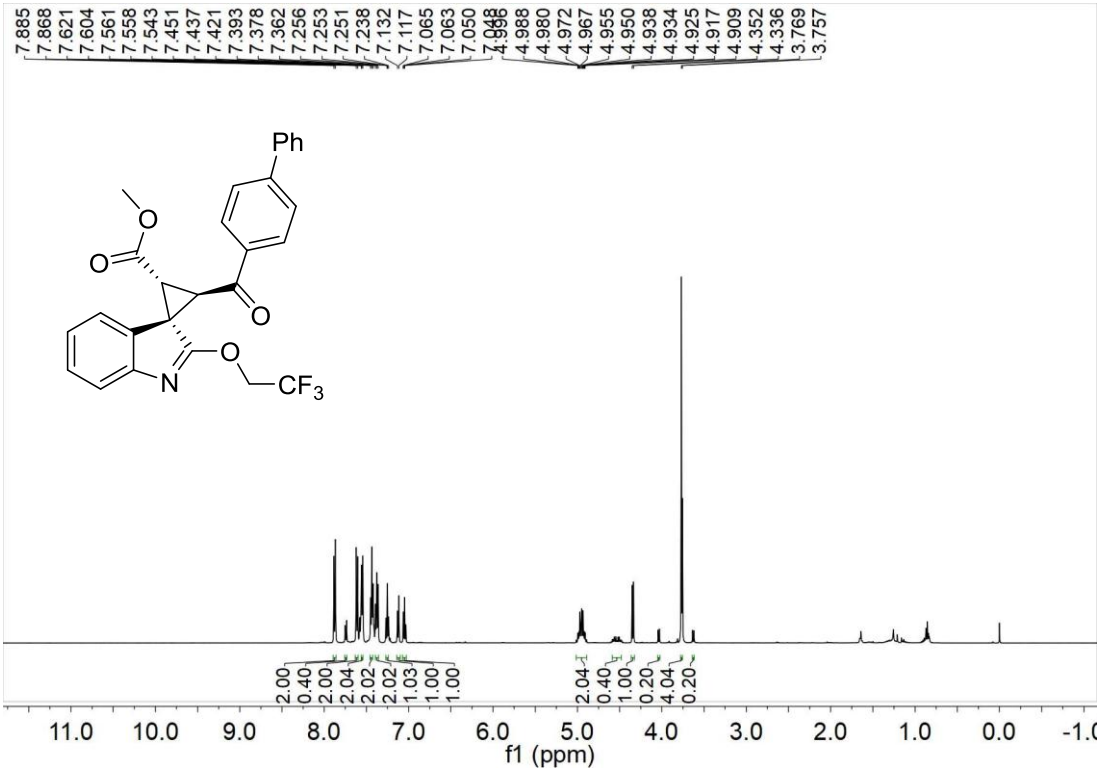


Figure 15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ea**

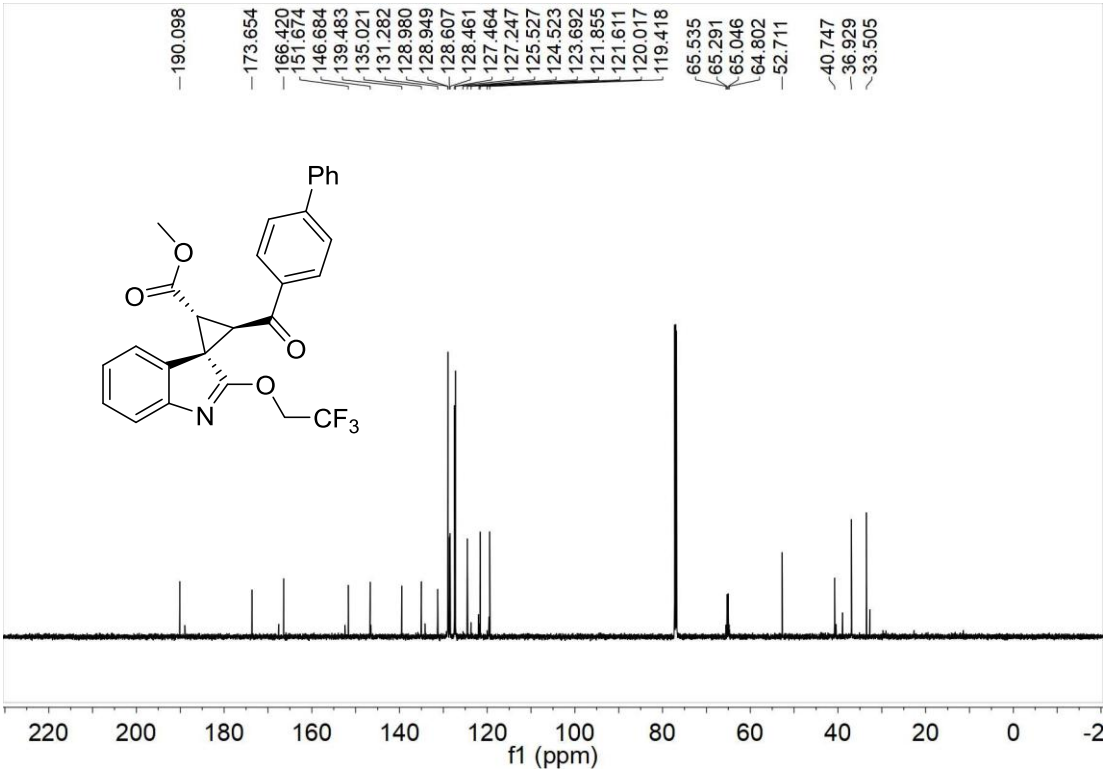


Figure 16. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ea**

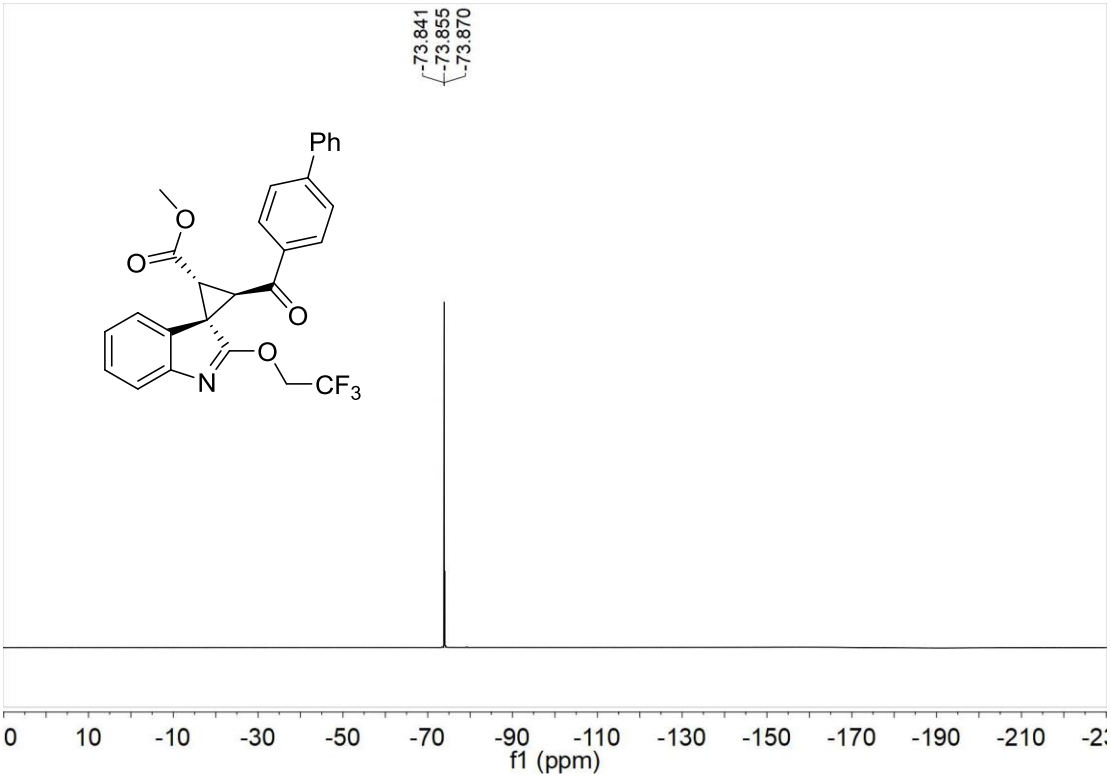


Figure 17. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ea**

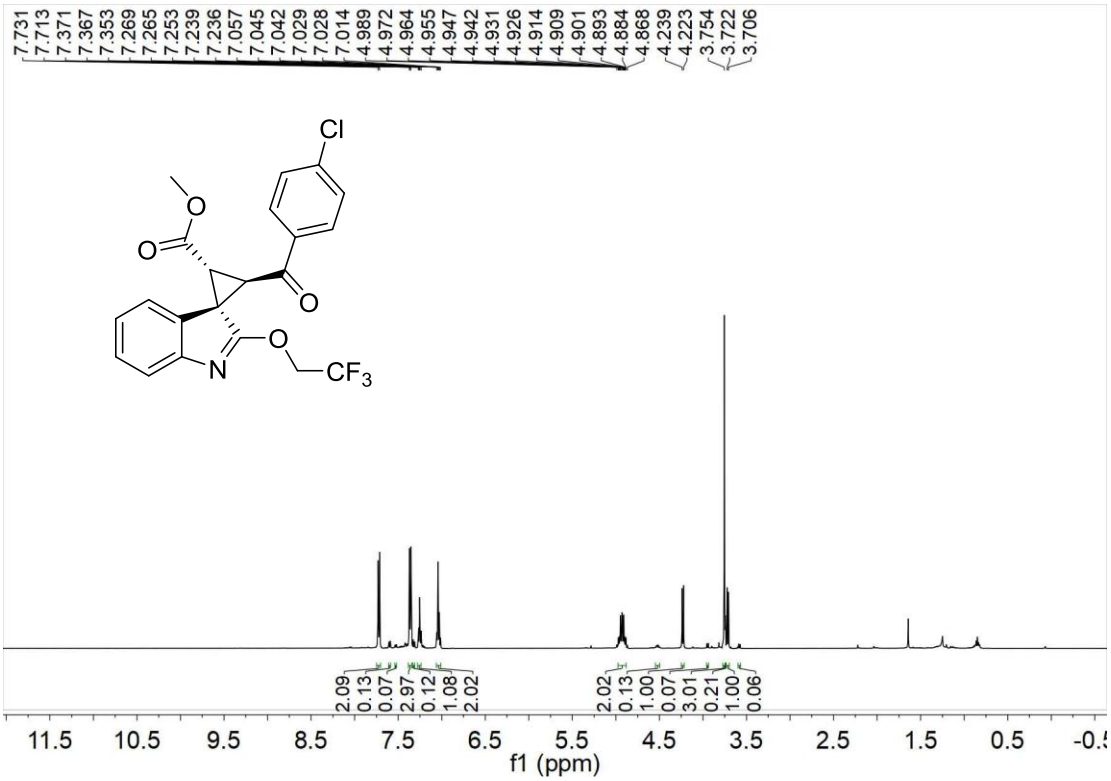


Figure 18. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4fa**

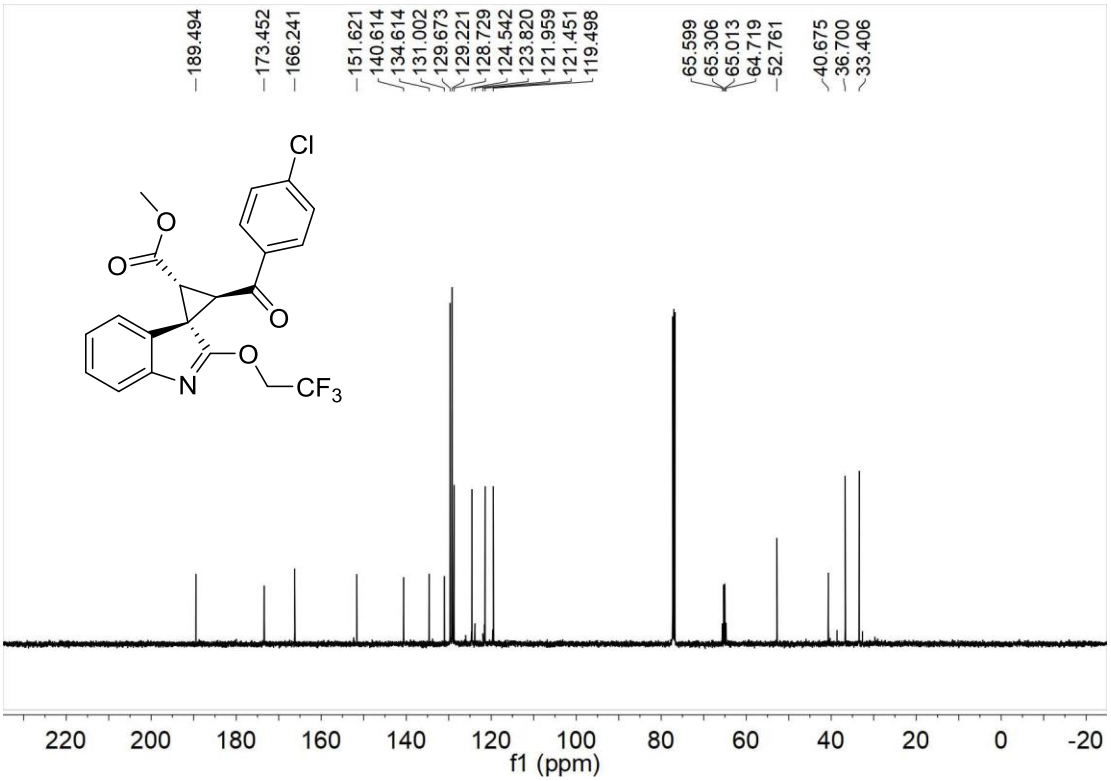


Figure 19. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4fa**

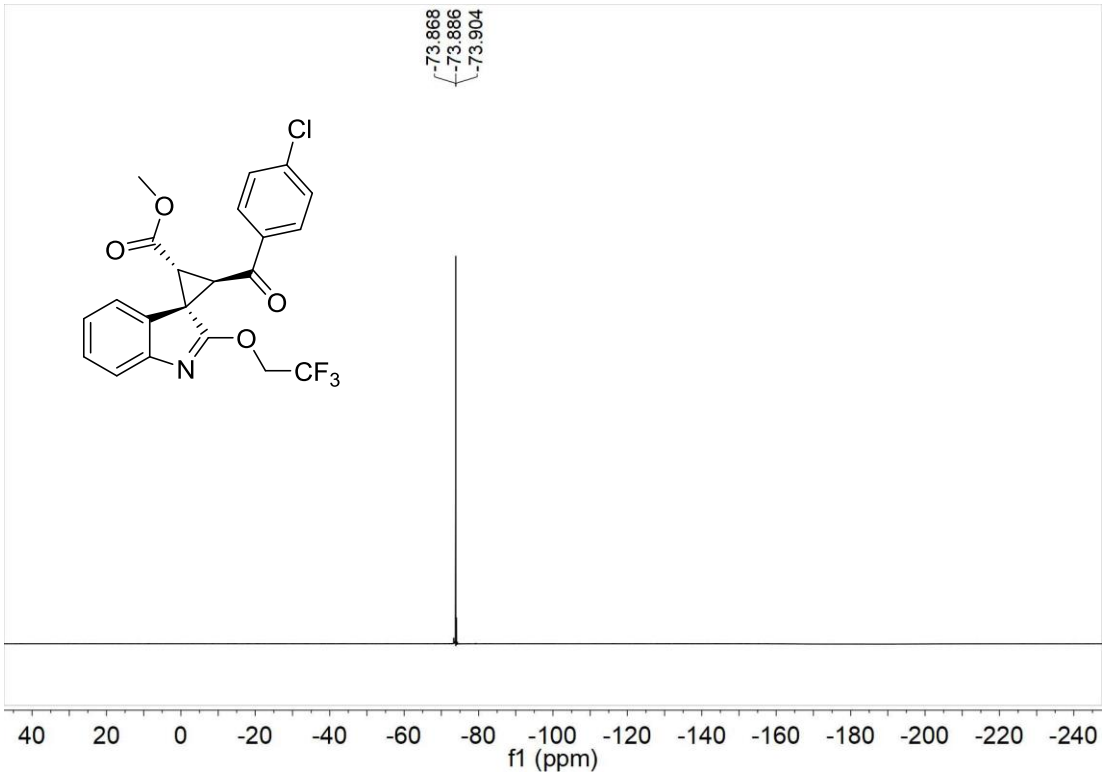


Figure 20. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4fa**

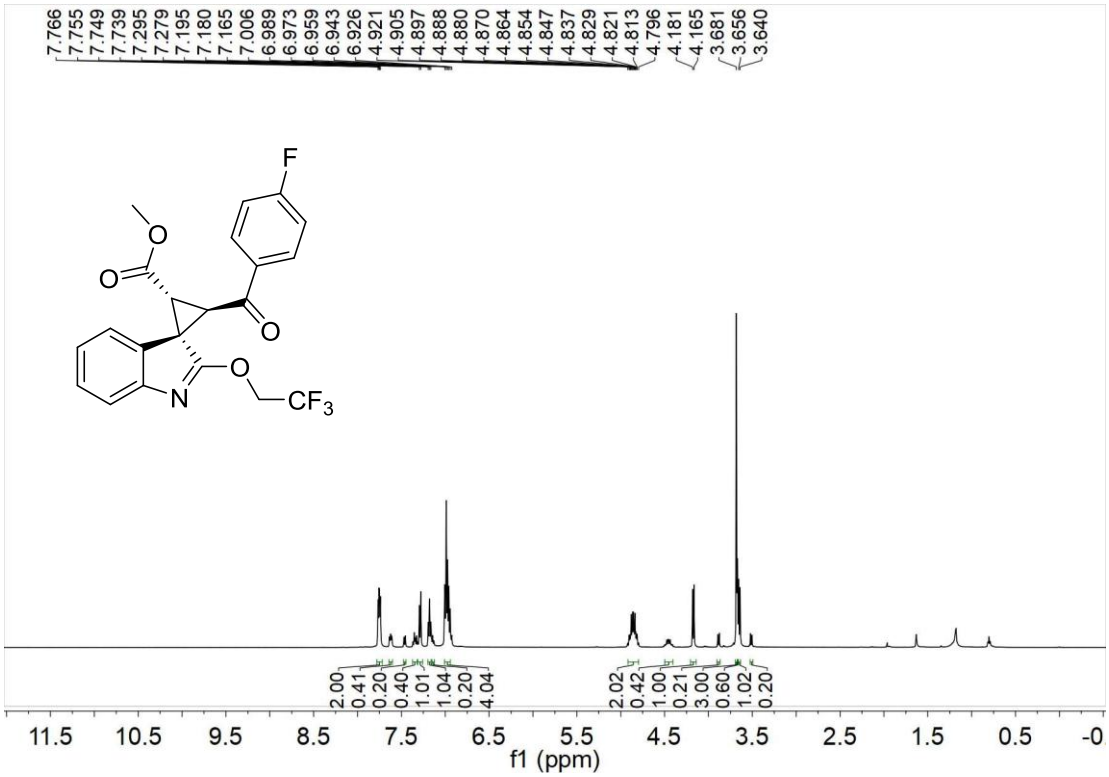


Figure 21. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ga**

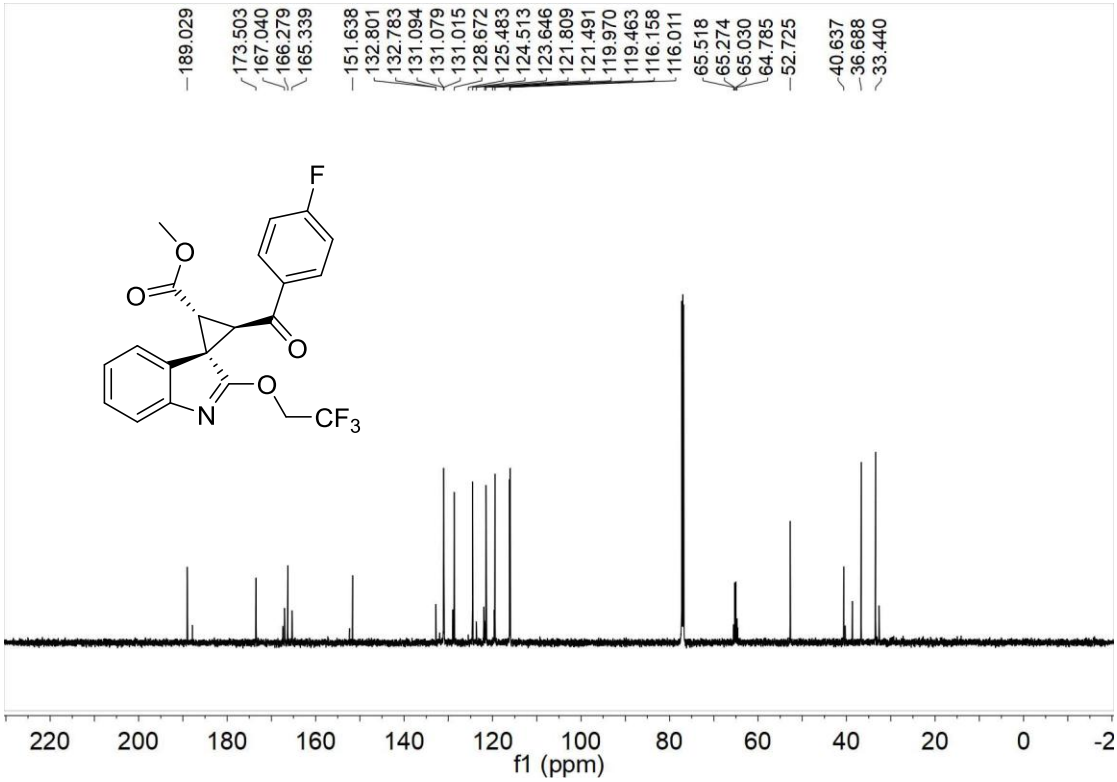


Figure 22. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ga**

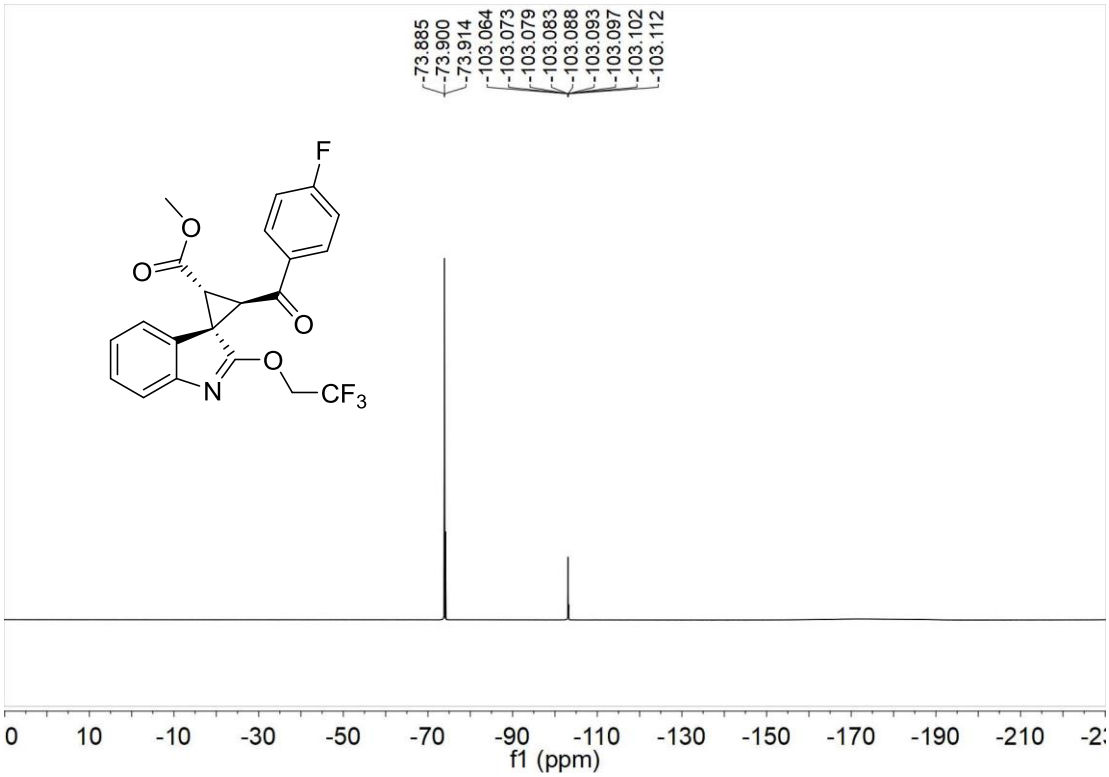


Figure 23. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ga**

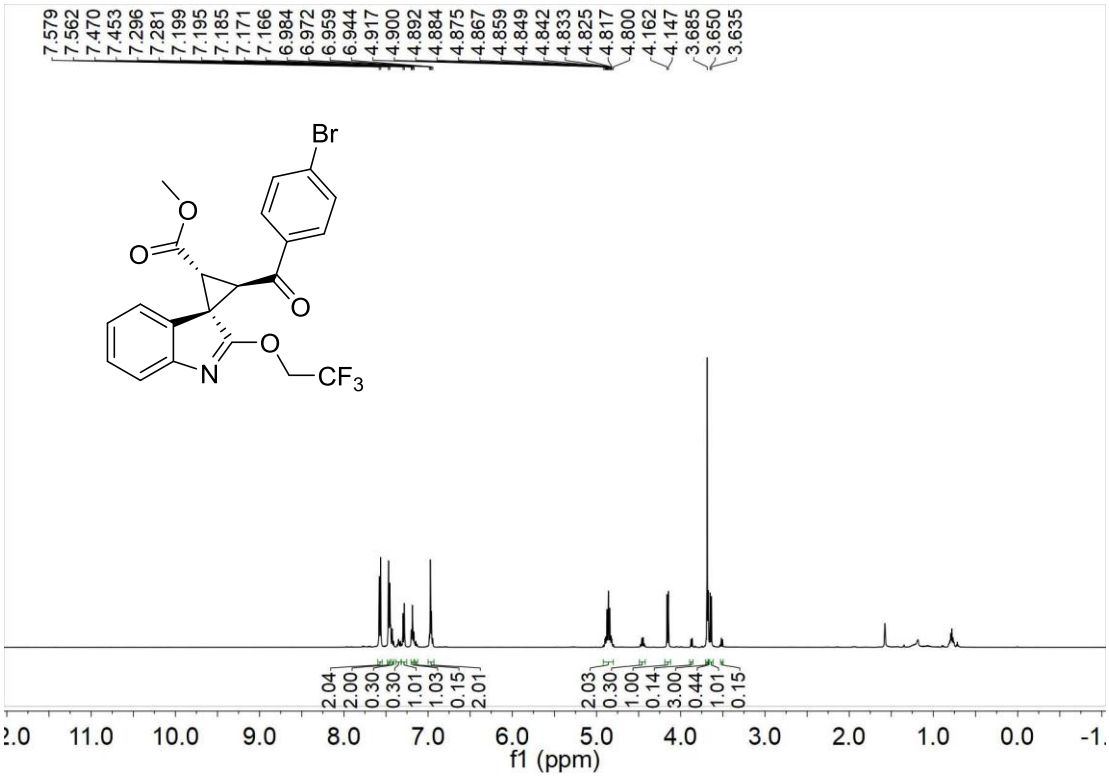


Figure 24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ha**

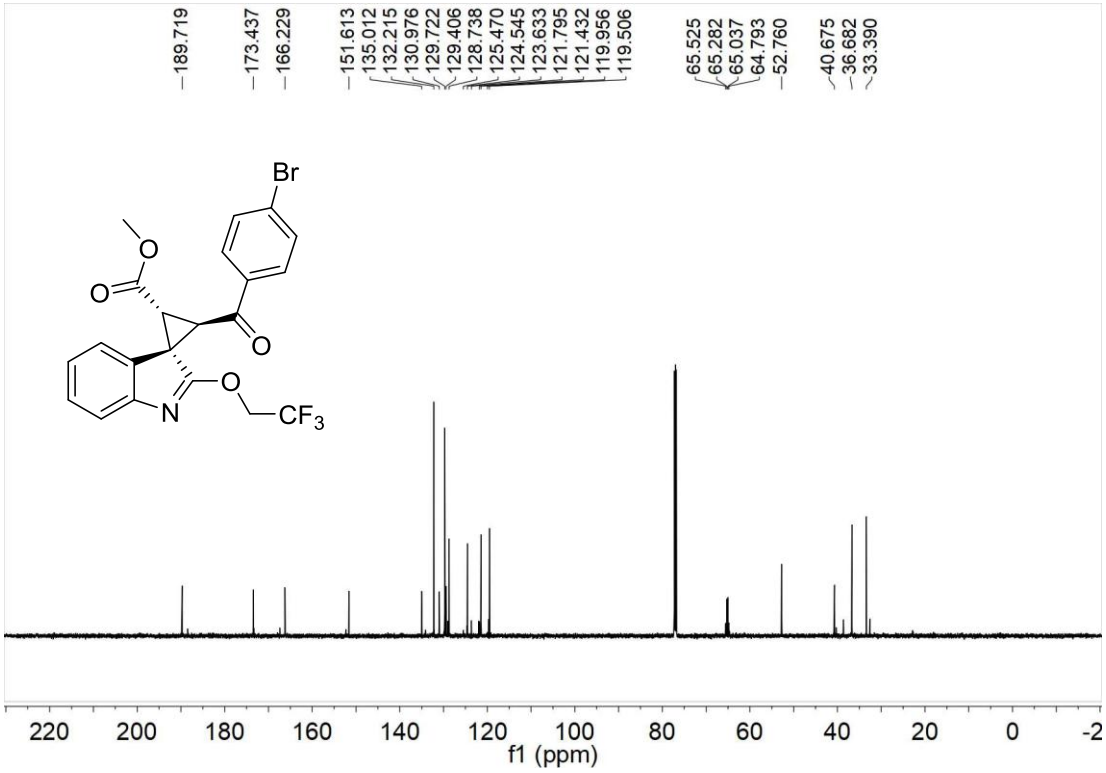


Figure 25. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ha**

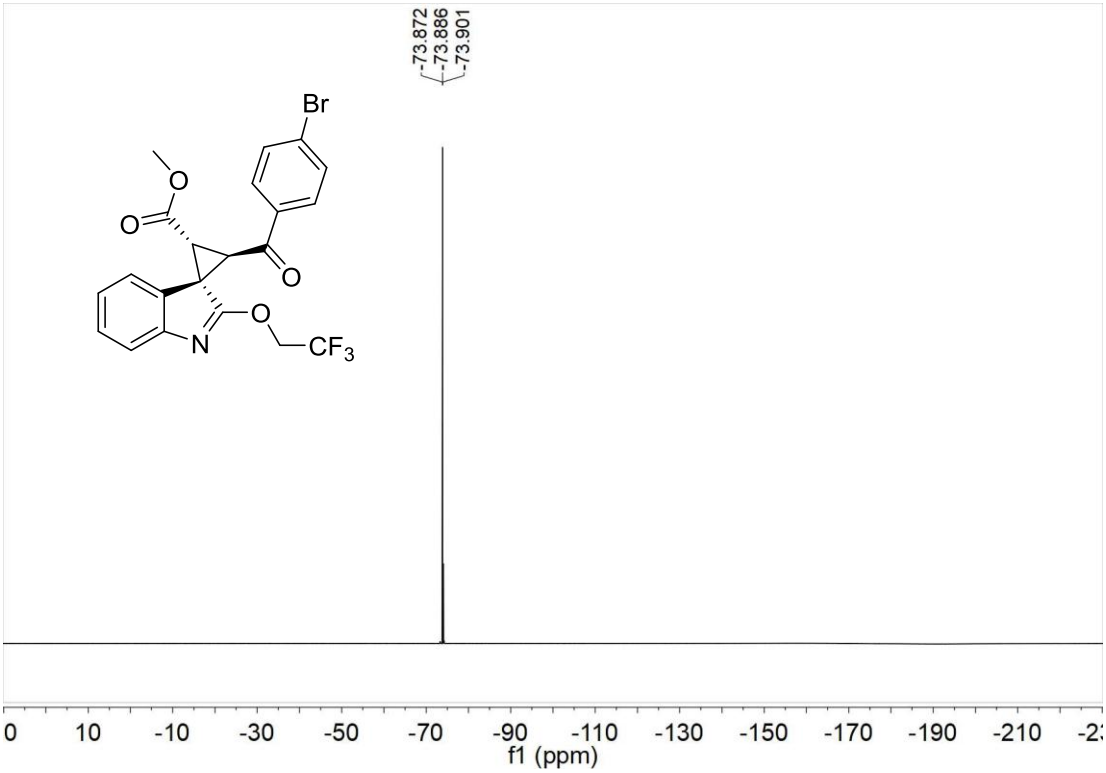


Figure 26. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ha**

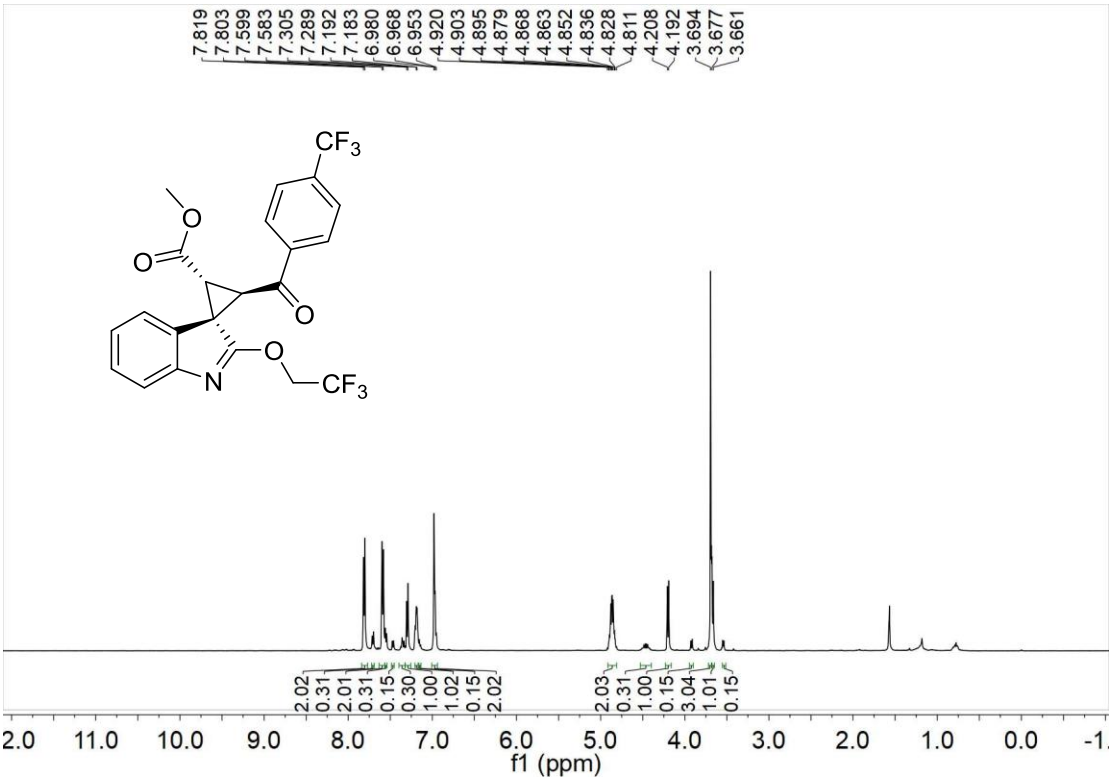


Figure 27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ia**

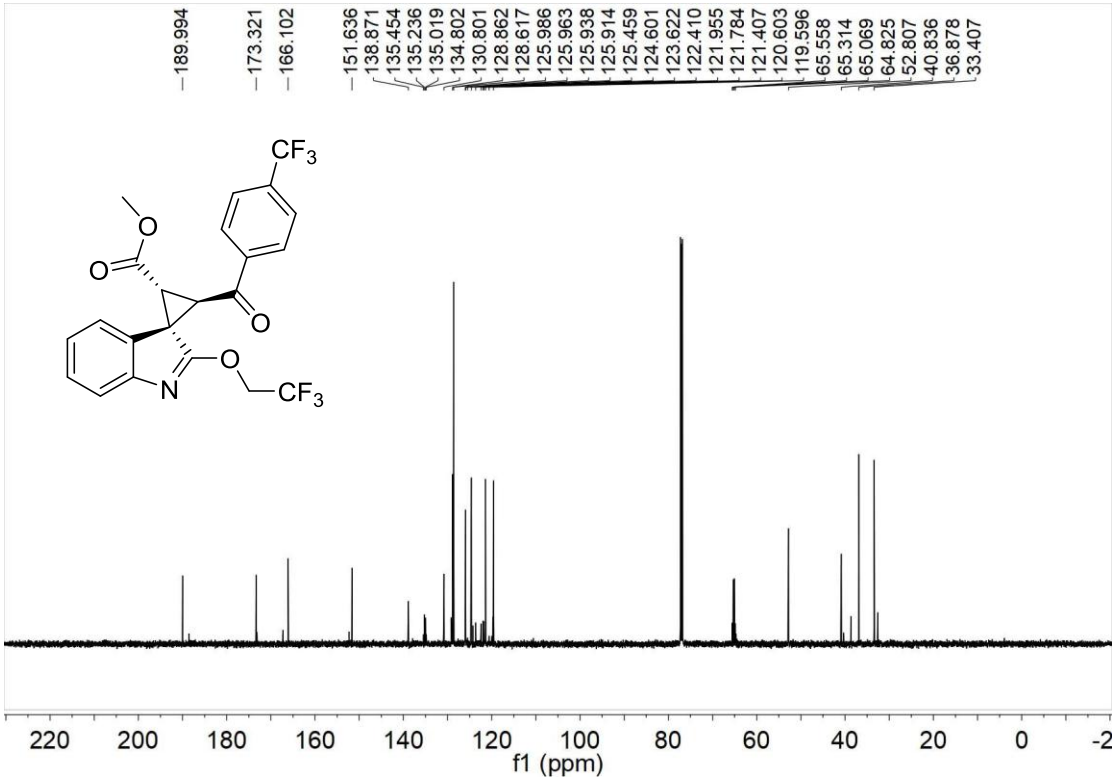


Figure 28. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ia**

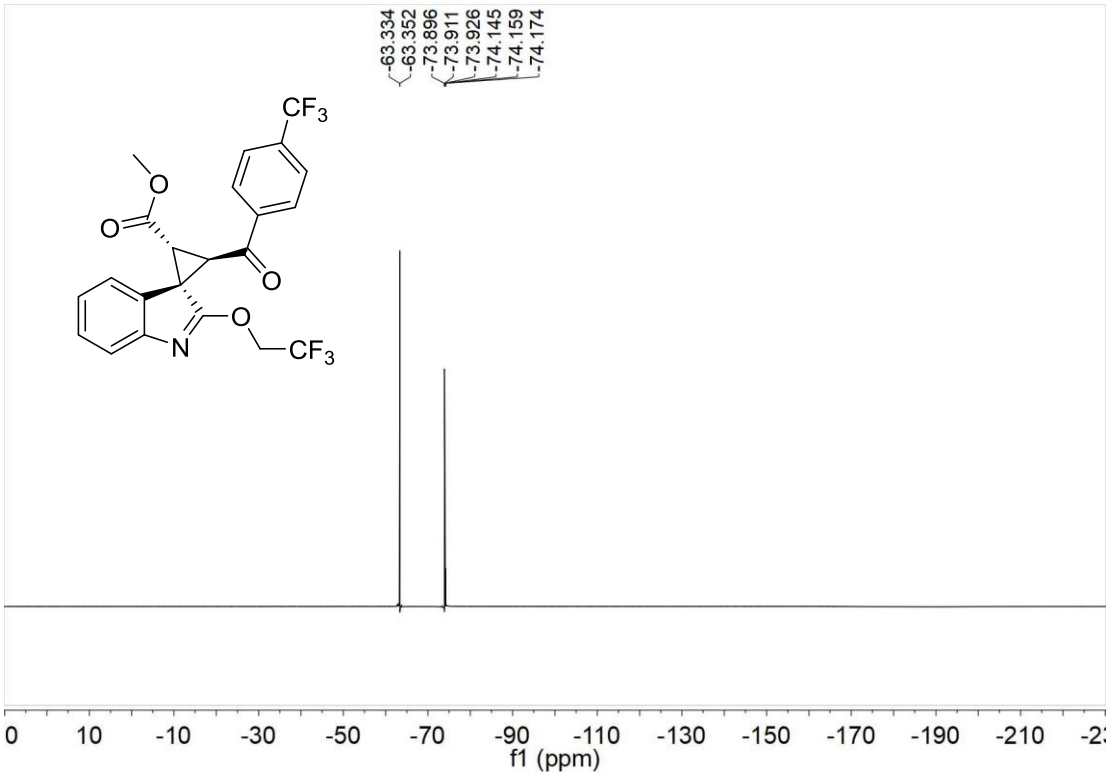


Figure 29. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ia**

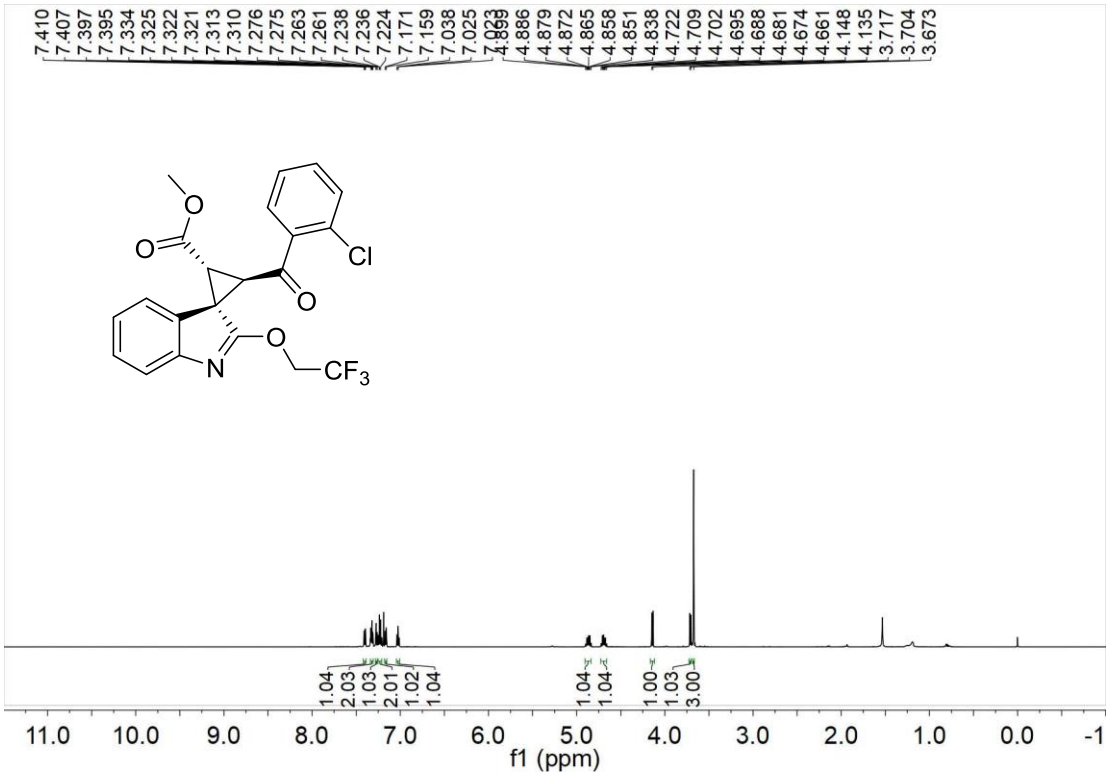


Figure 30. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ja**

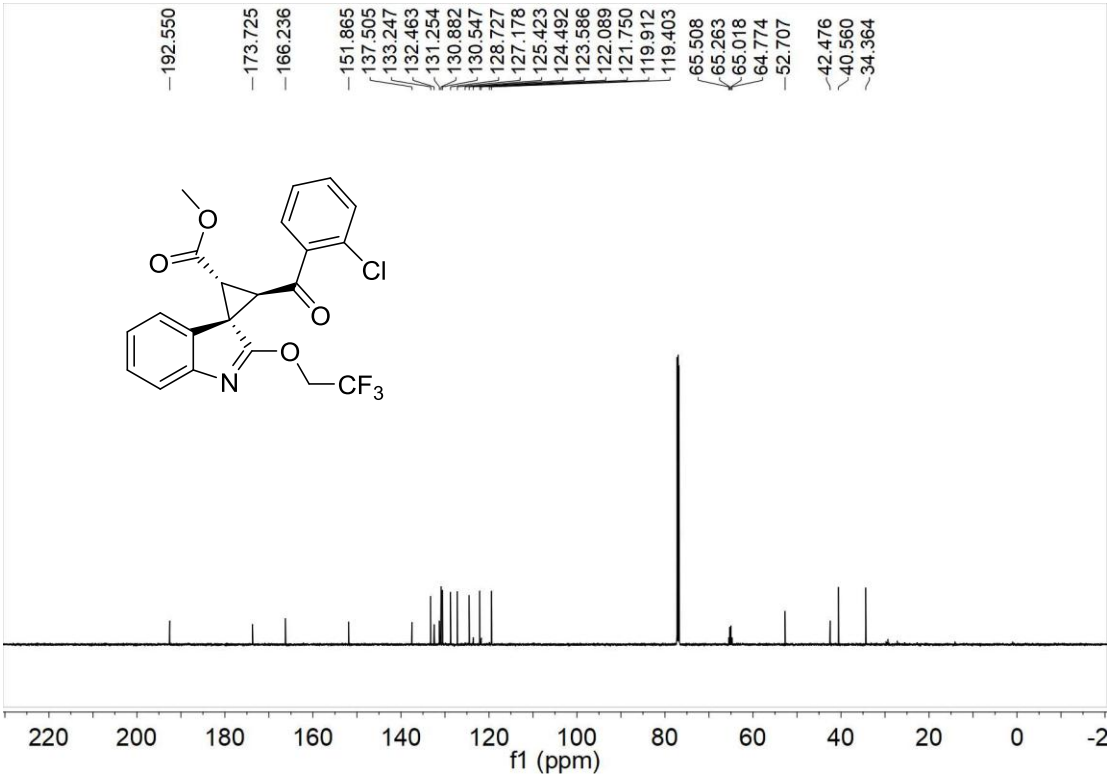


Figure 31. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ja**

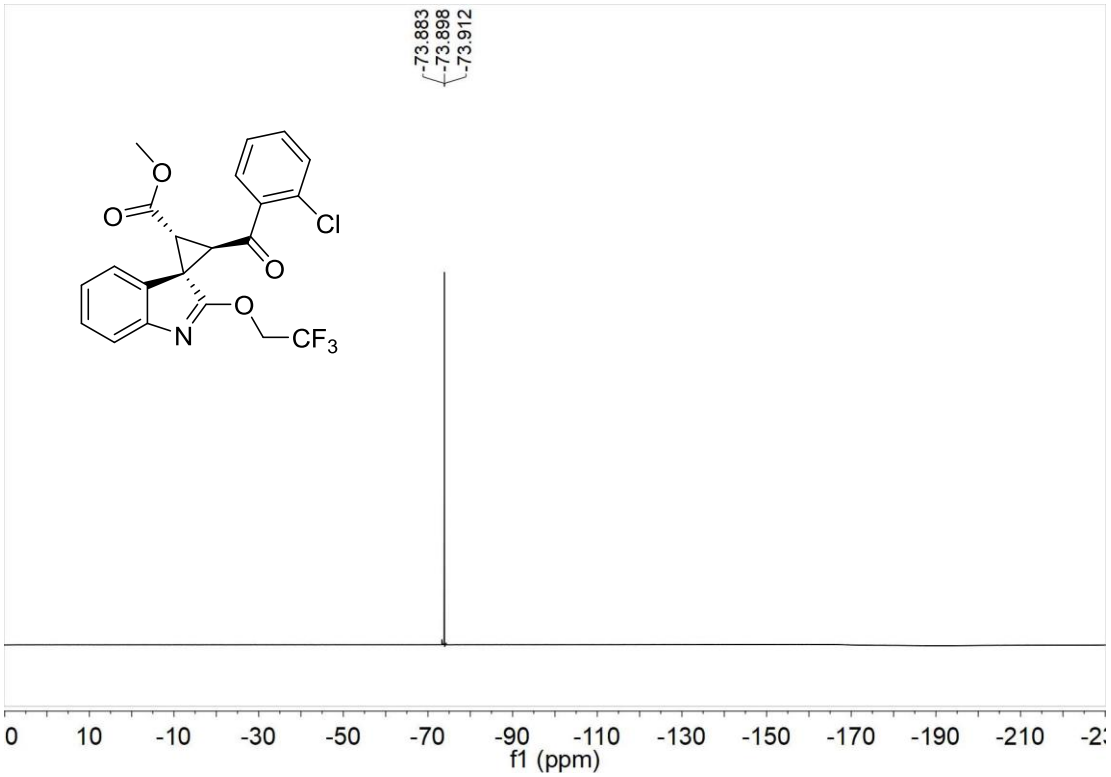


Figure 32. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ja**

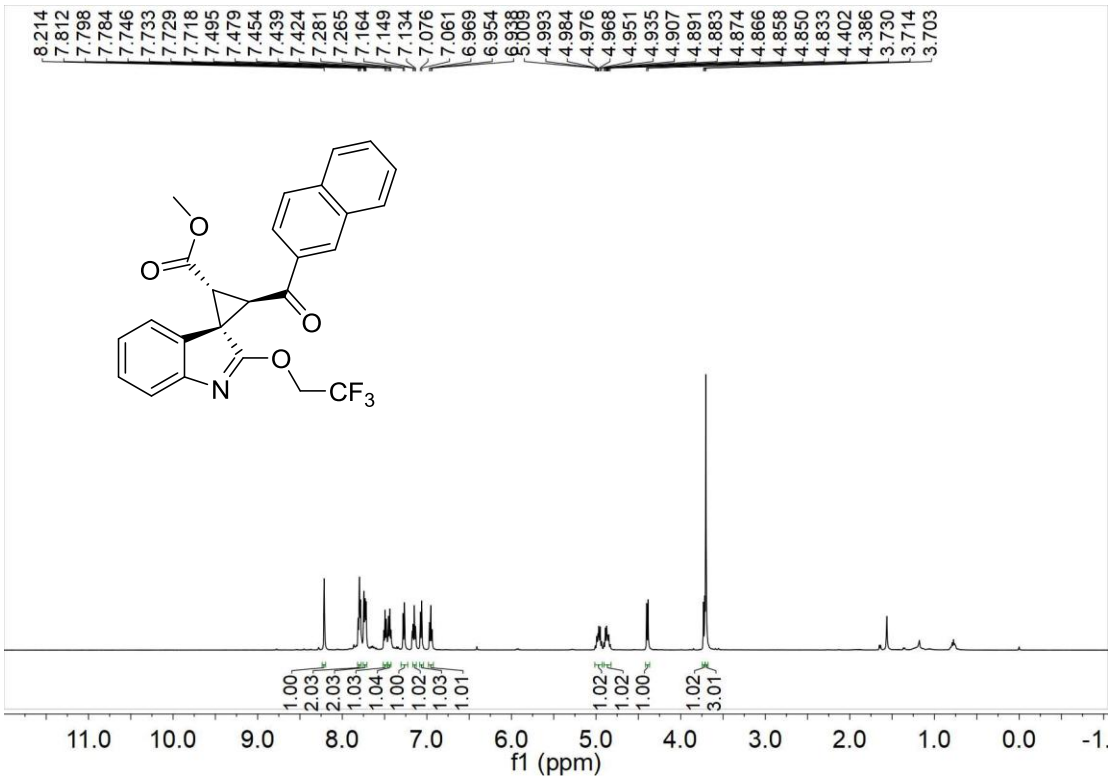


Figure 33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4la**

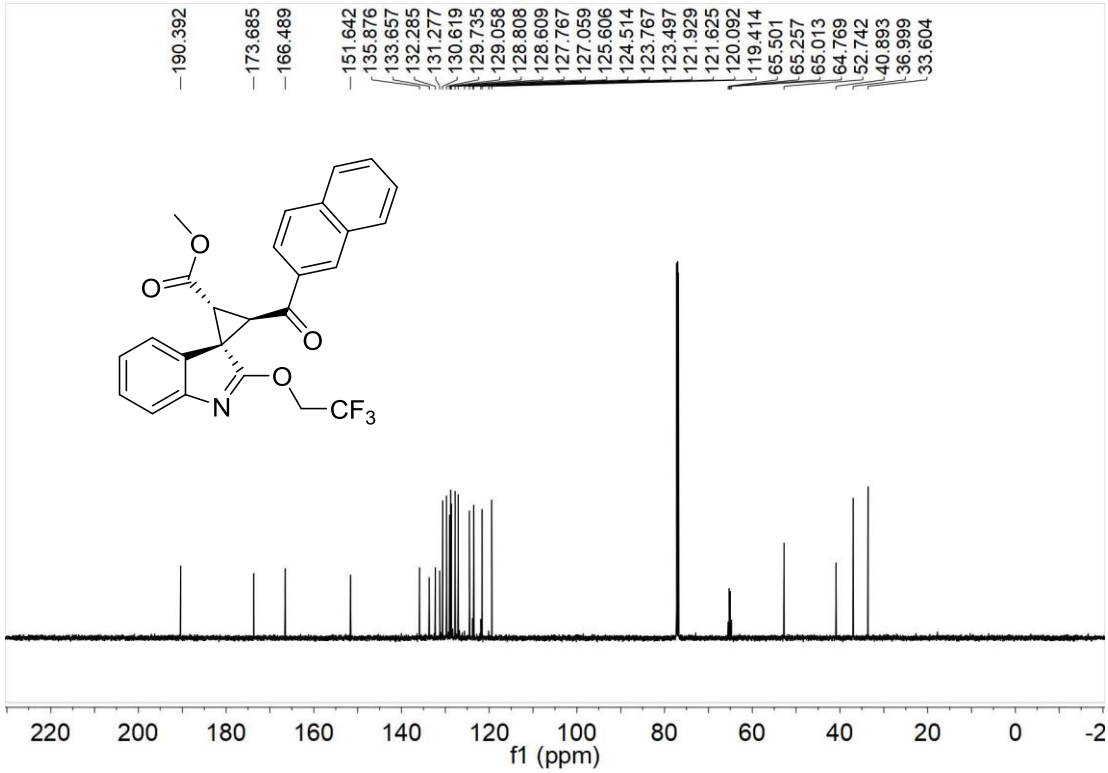


Figure 34. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4la**

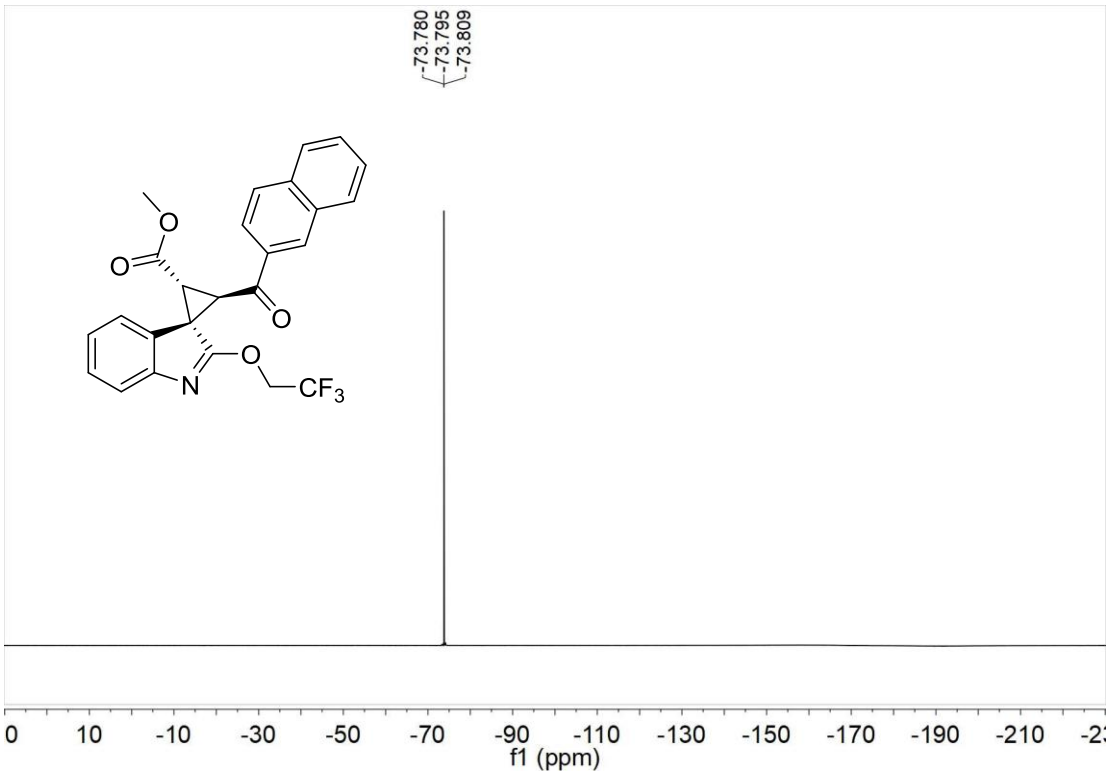


Figure 35. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4la**

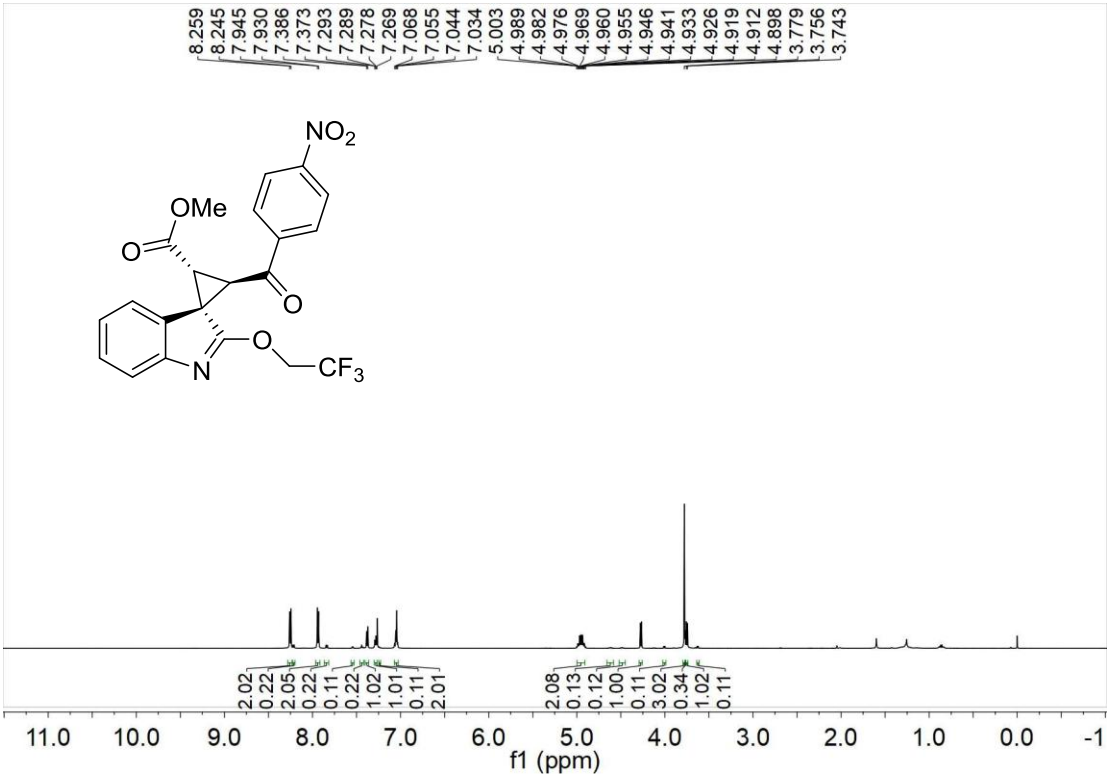


Figure 36. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ka**

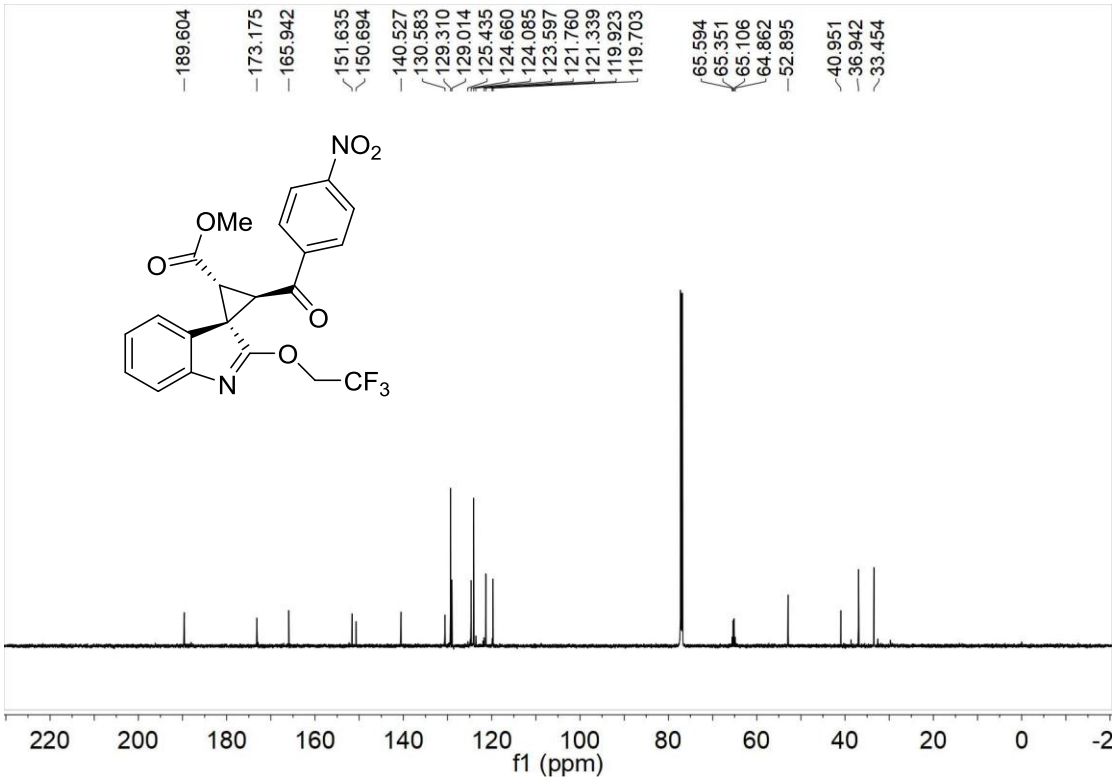


Figure 37. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ka**

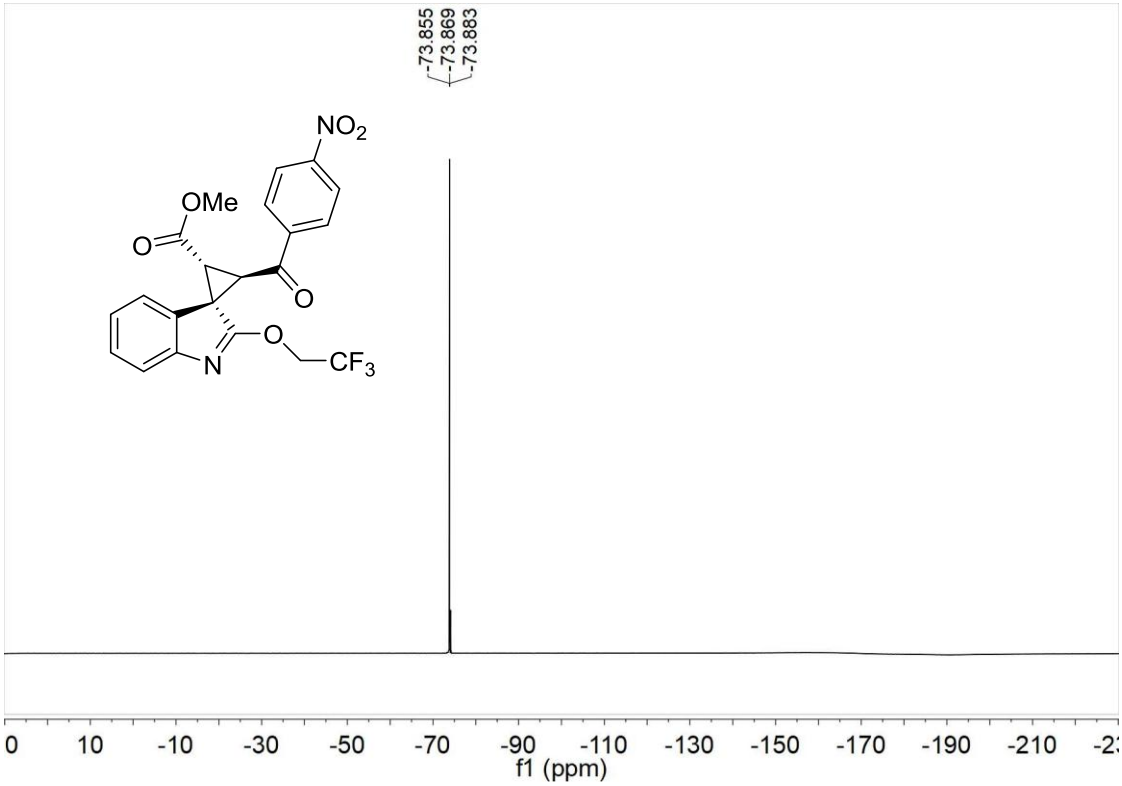


Figure 38. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ka**

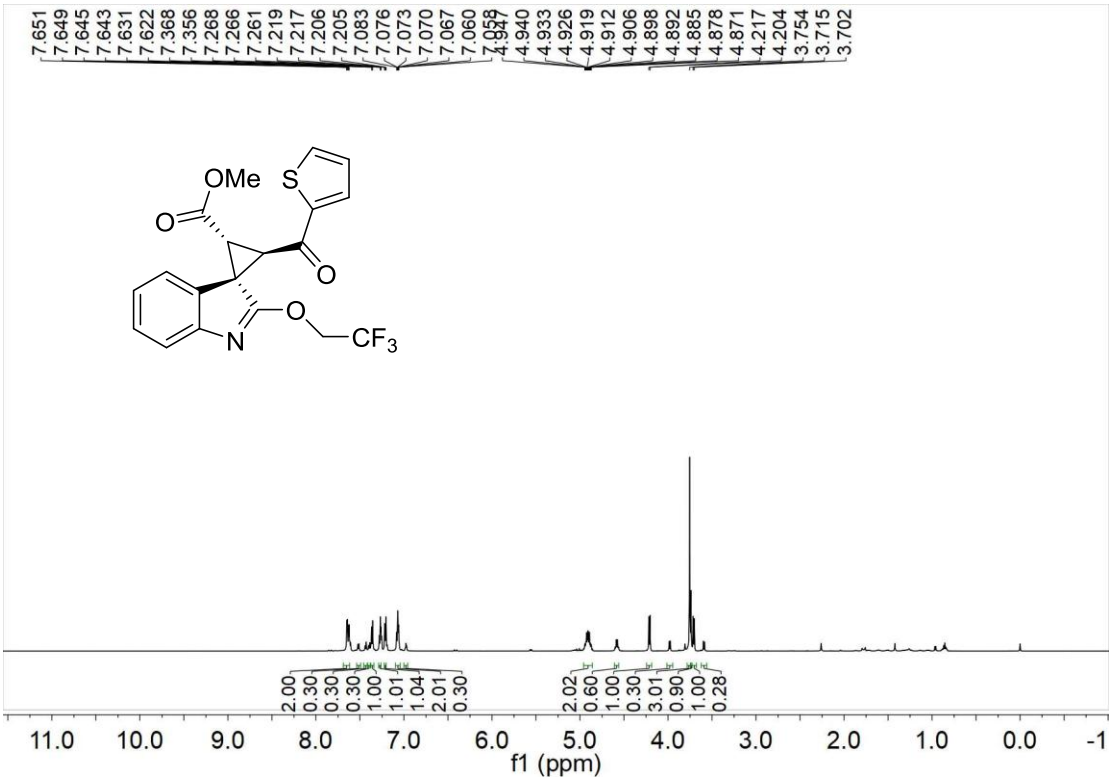


Figure 39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ma**

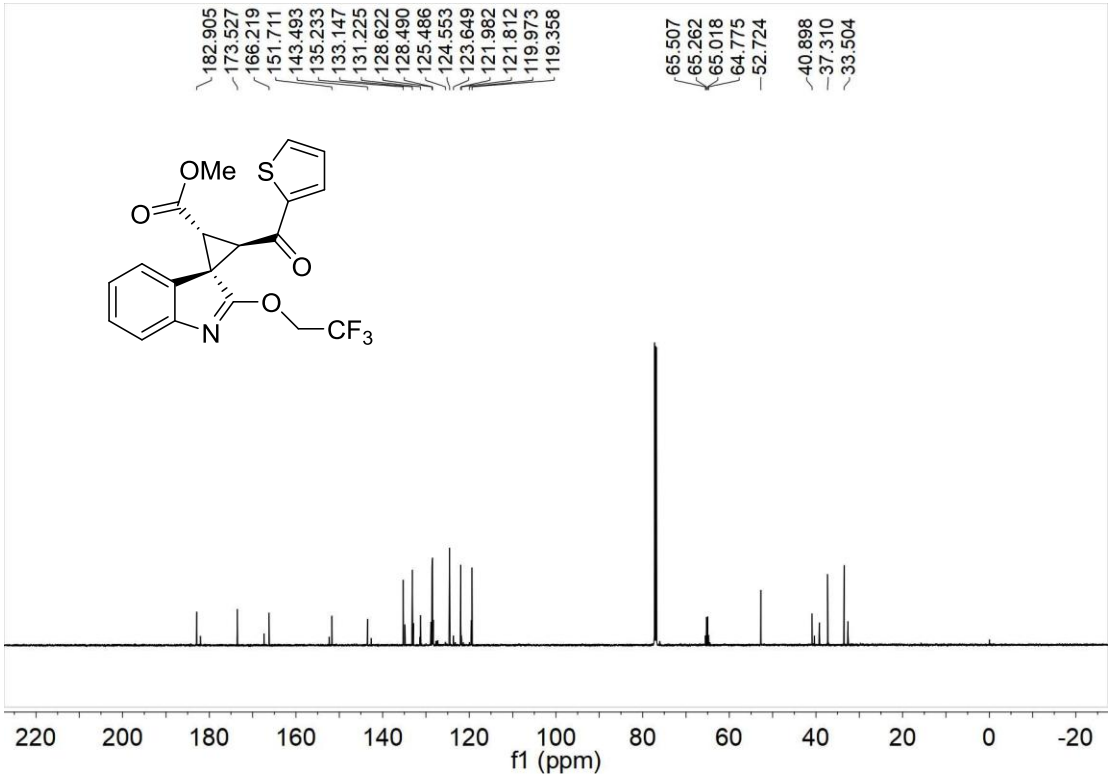


Figure 40. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ma**

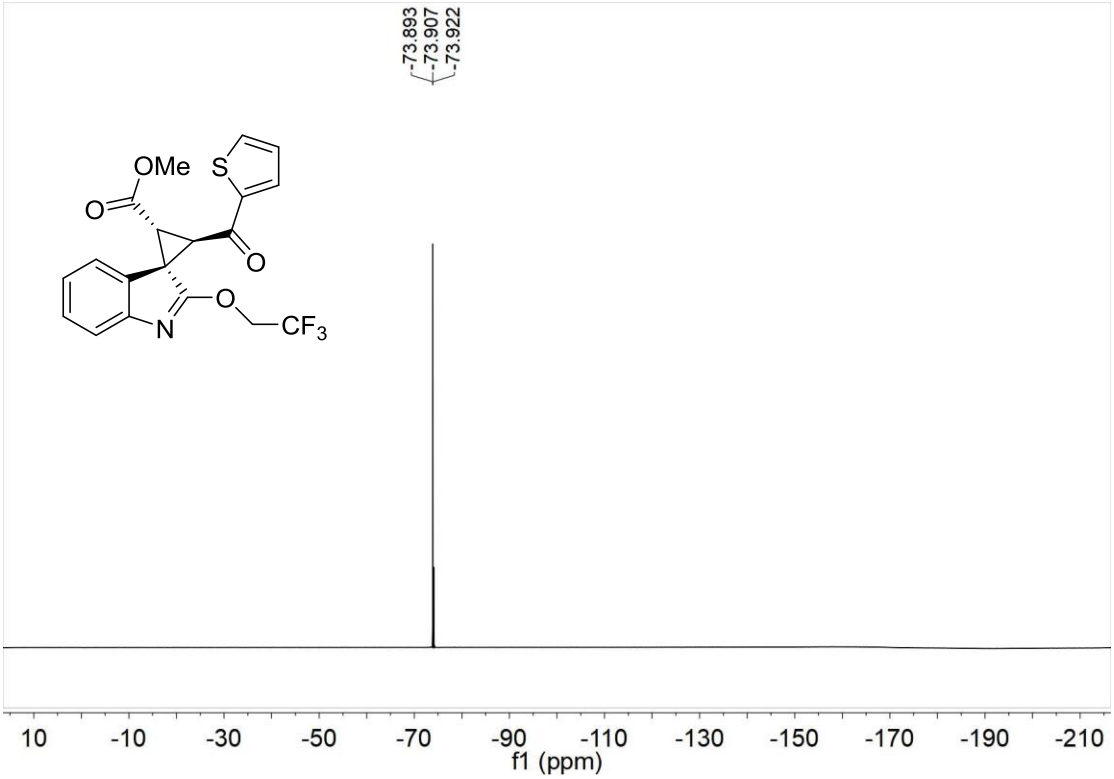


Figure 41. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ma**

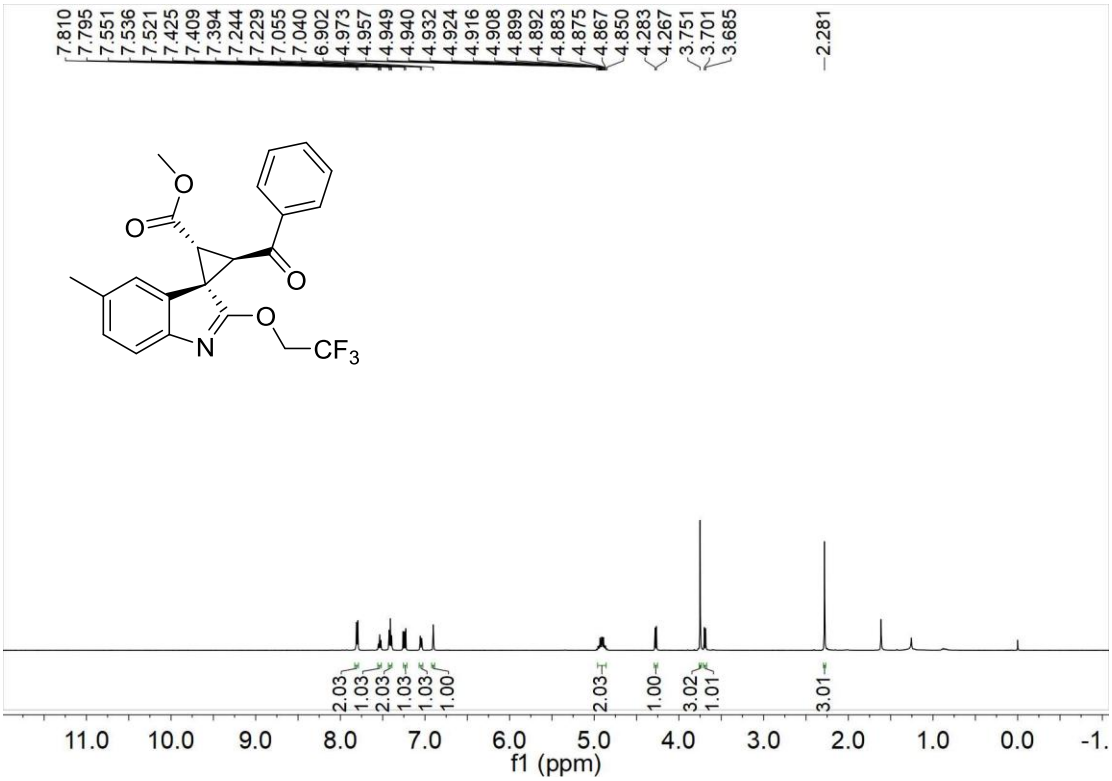


Figure 42. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ab**

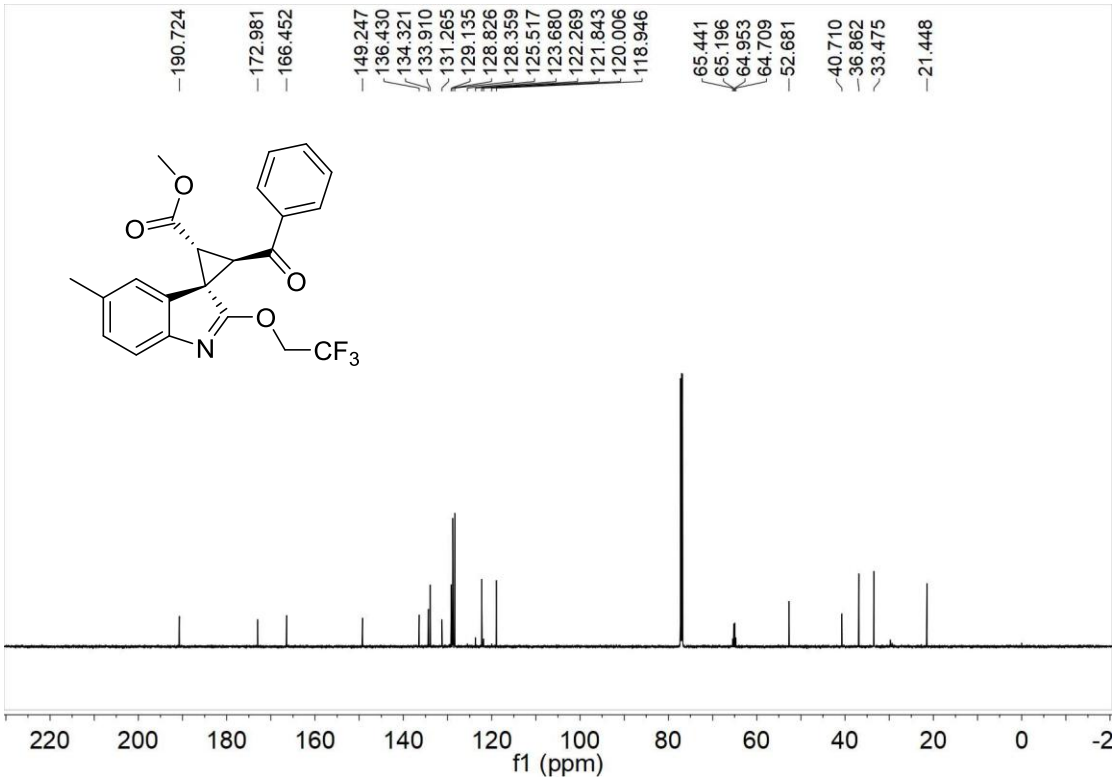


Figure 43. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ab**

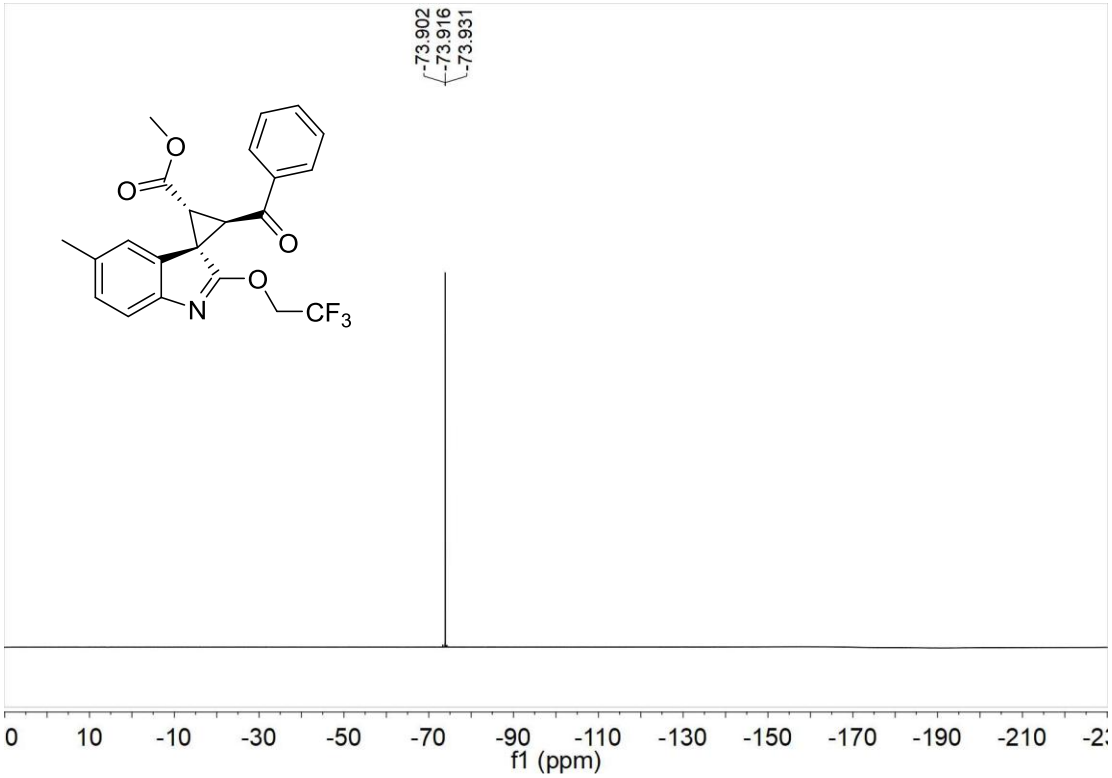


Figure 44. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ab**

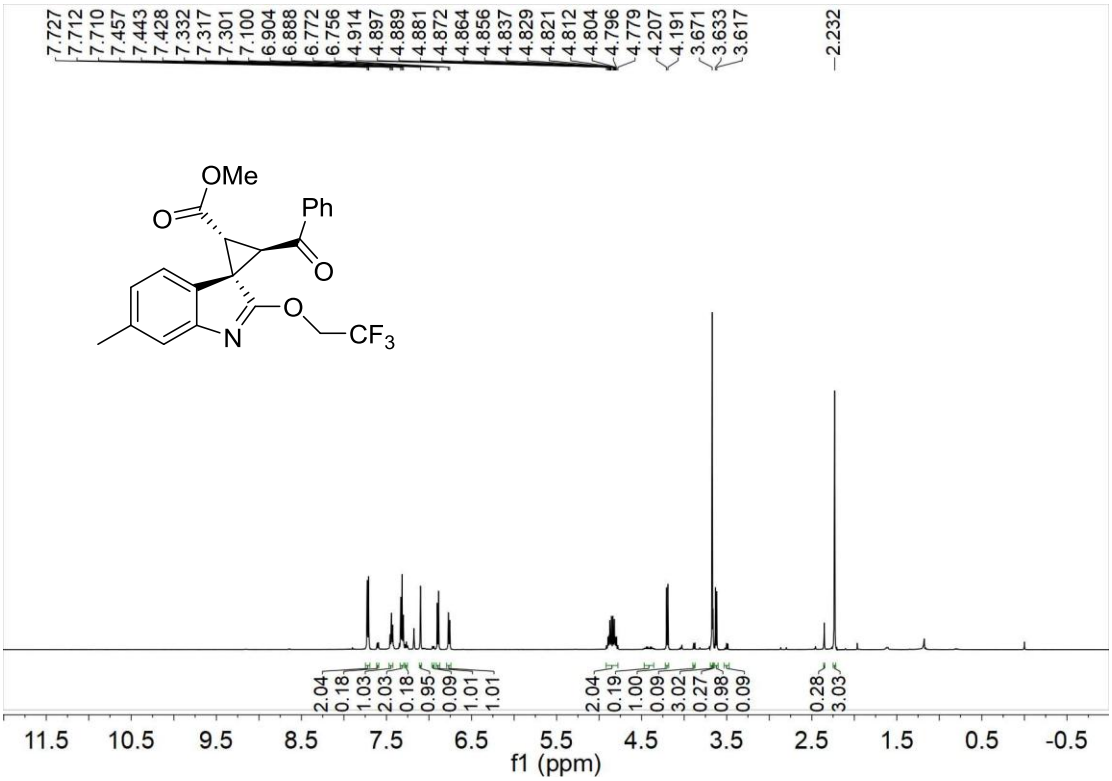


Figure 45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ac**

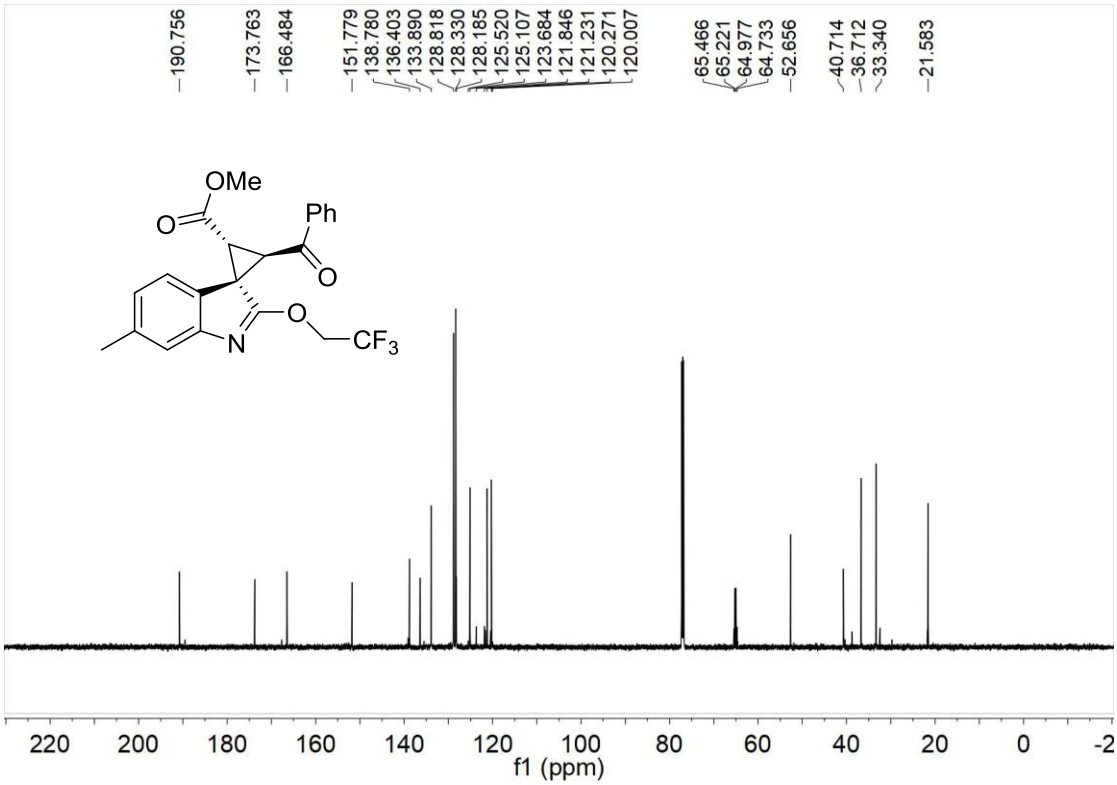


Figure 46. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ac**

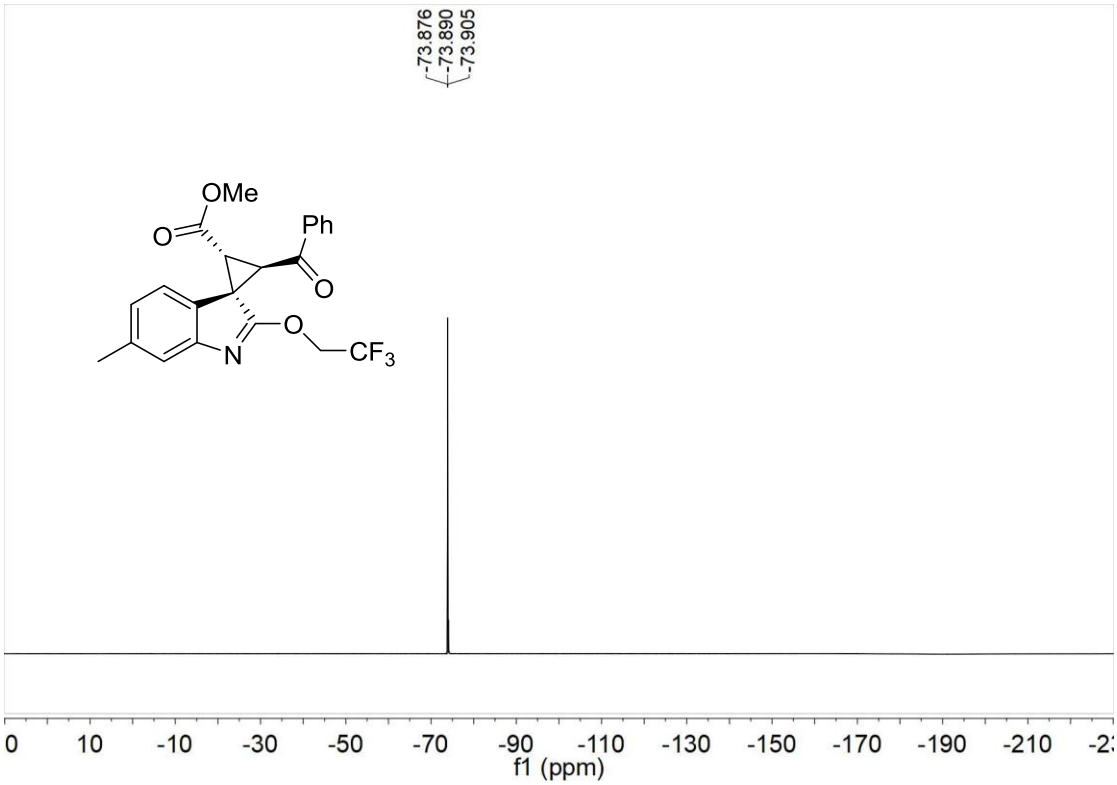


Figure 47. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ac**

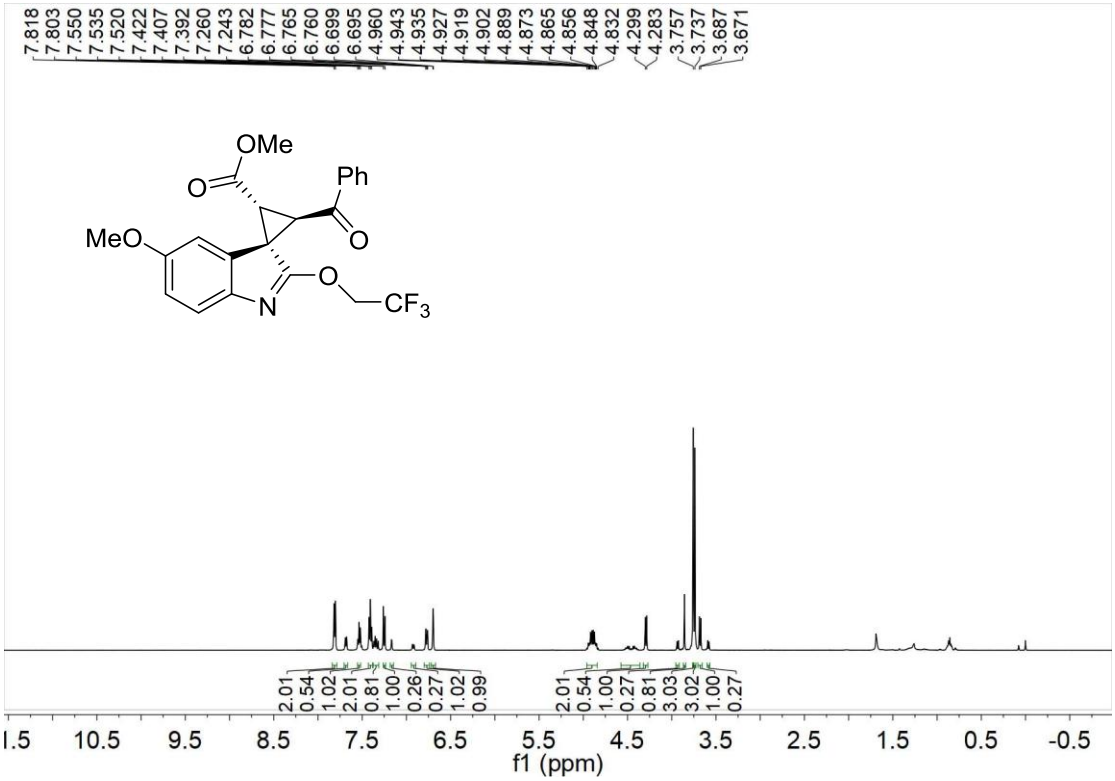


Figure 48. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ad**

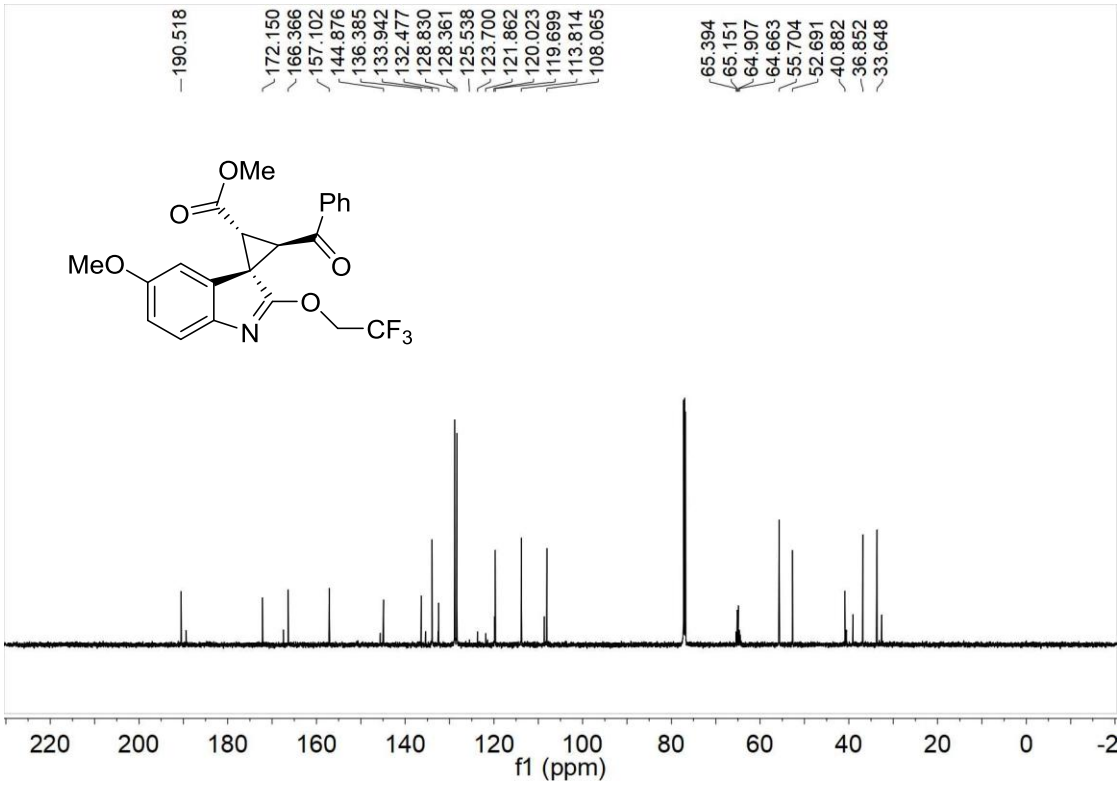


Figure 49. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ad**

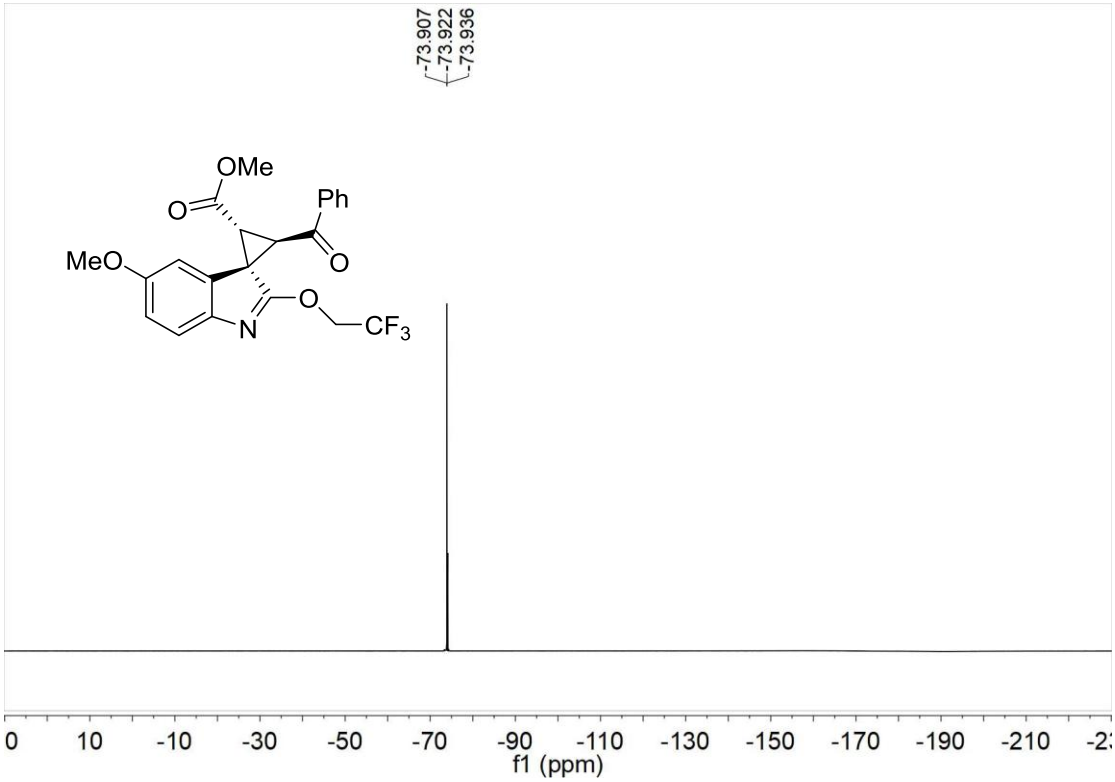


Figure 50. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ad**

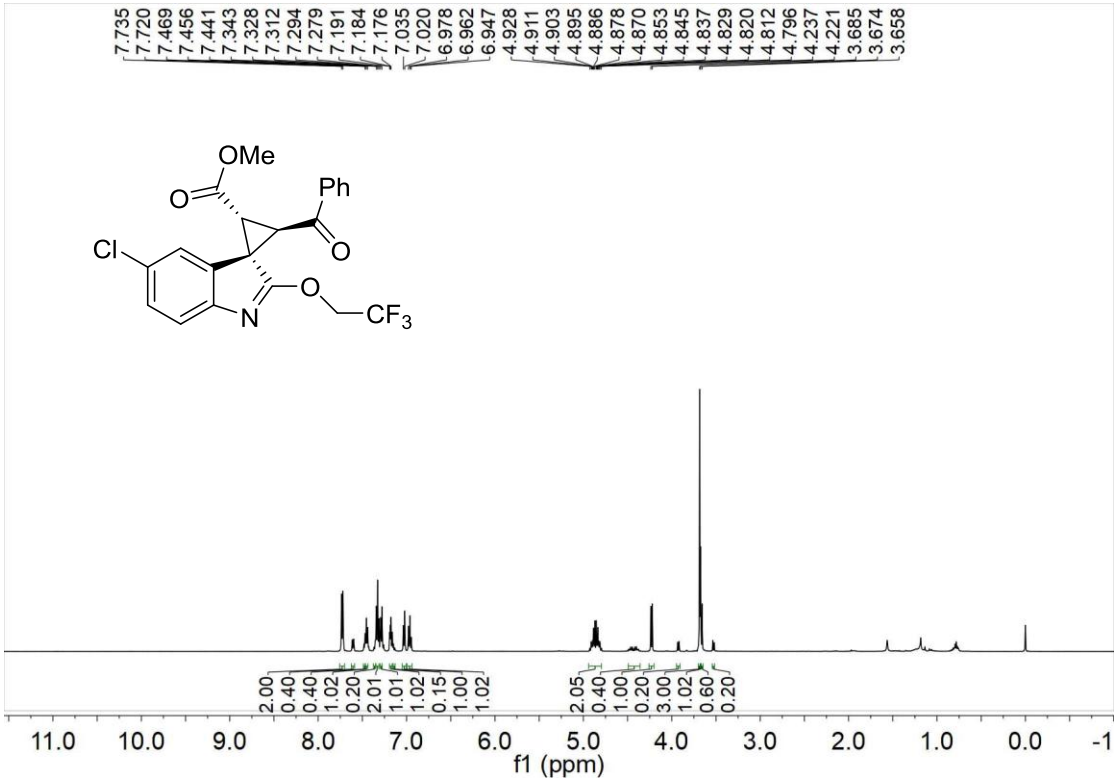


Figure 51. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ae**

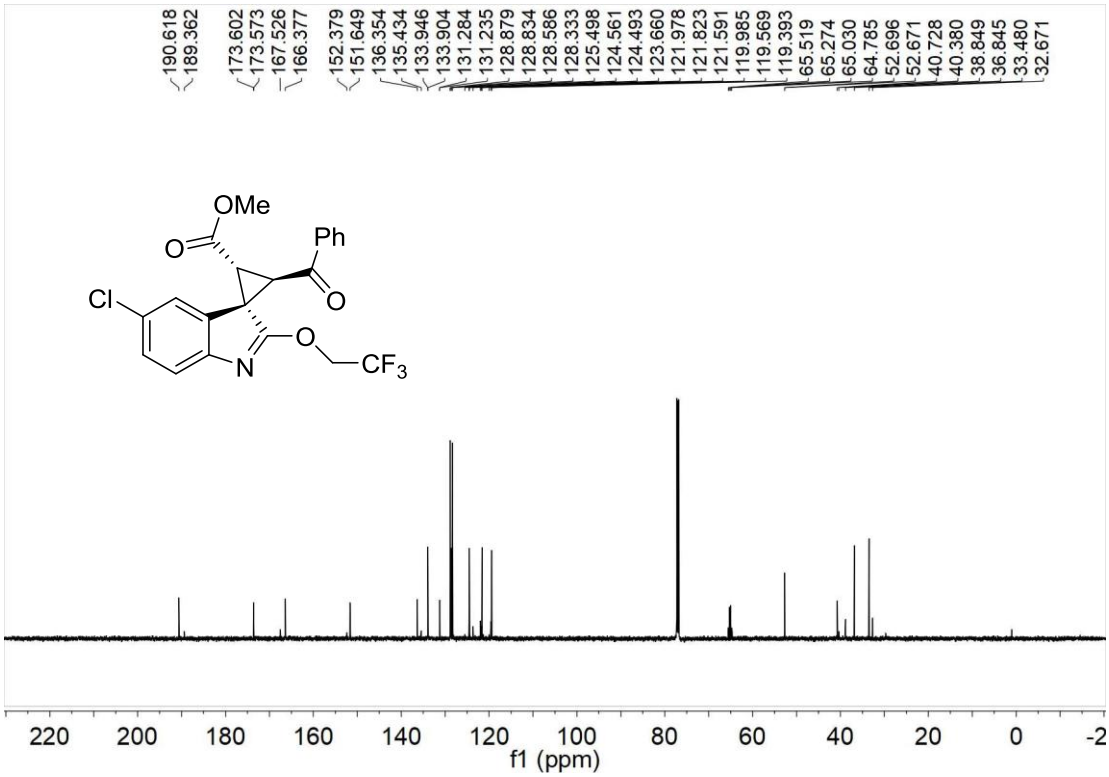


Figure 52. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ae**

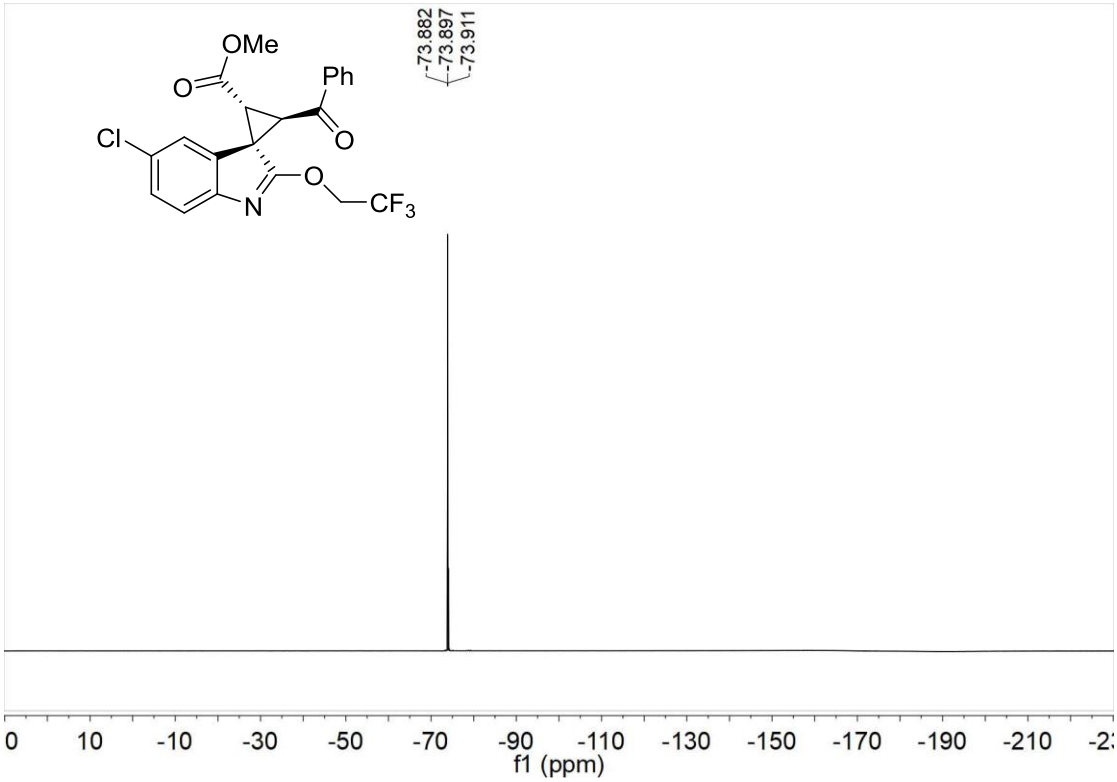


Figure 53. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ae**

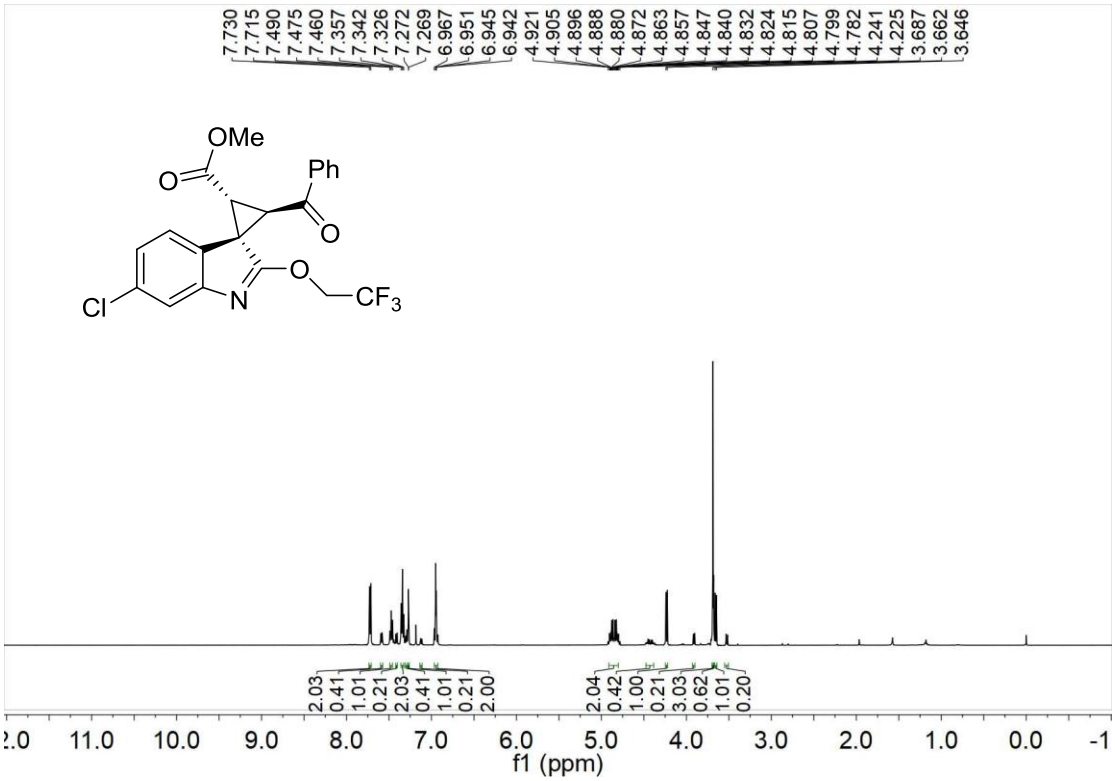


Figure 54. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4af**

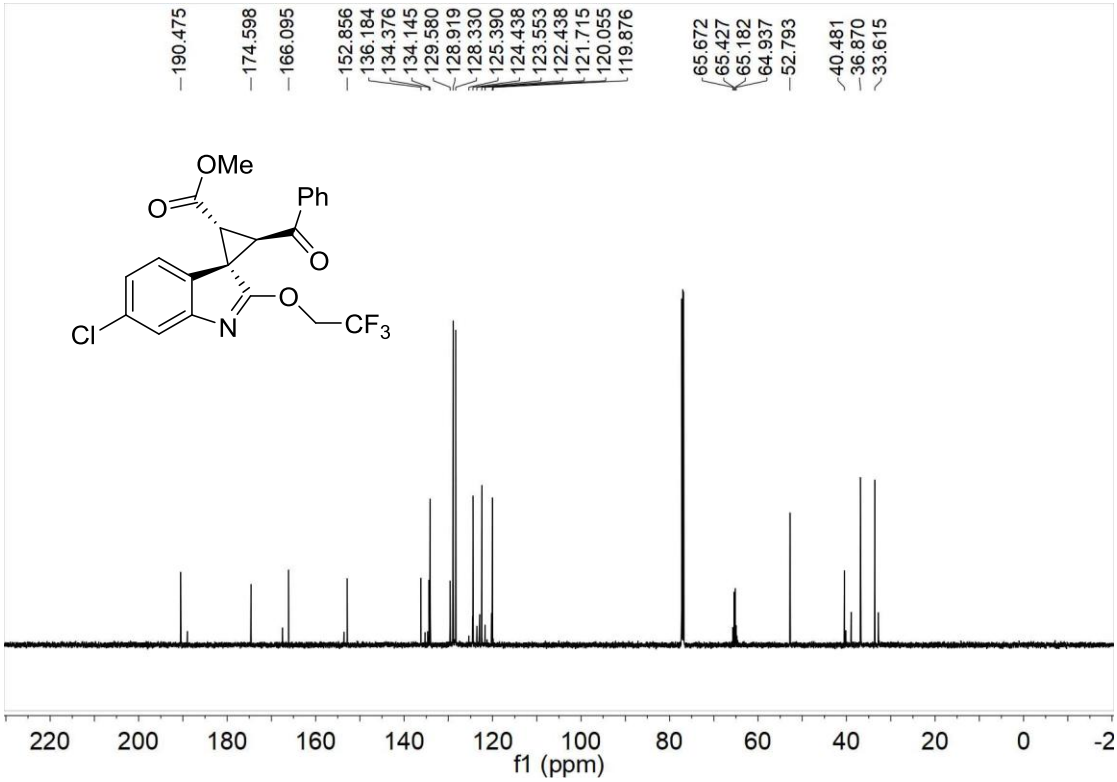


Figure 55. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4af**

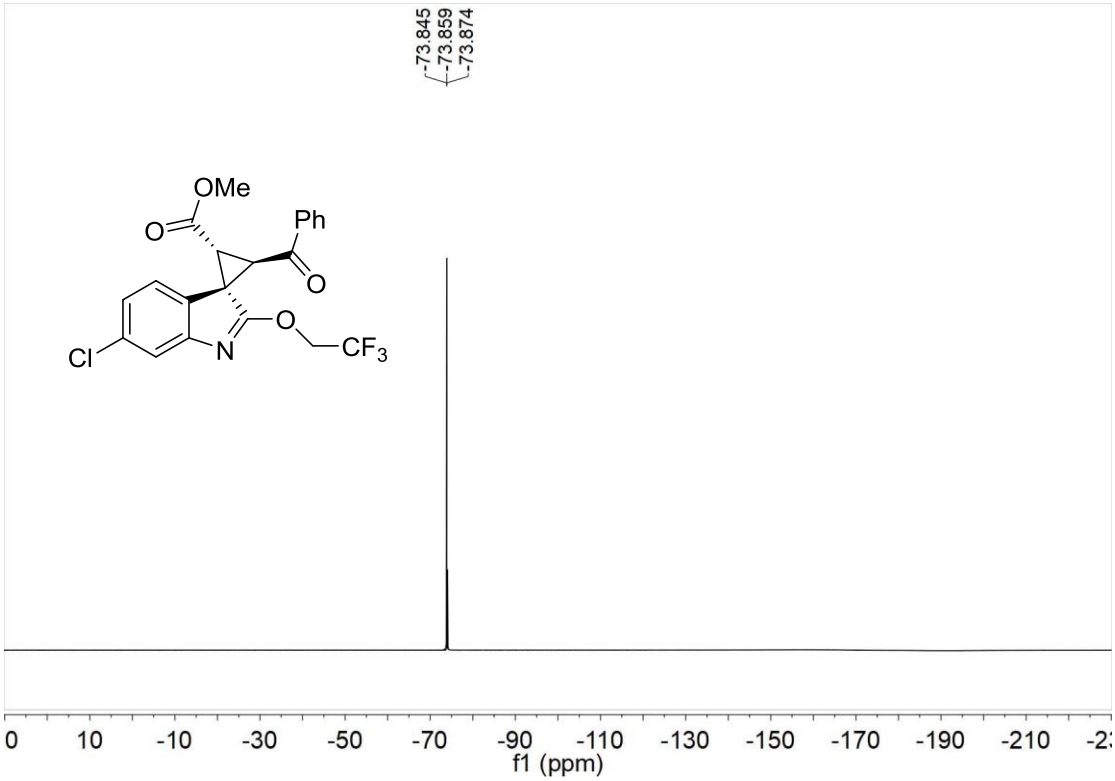


Figure 56. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4af**

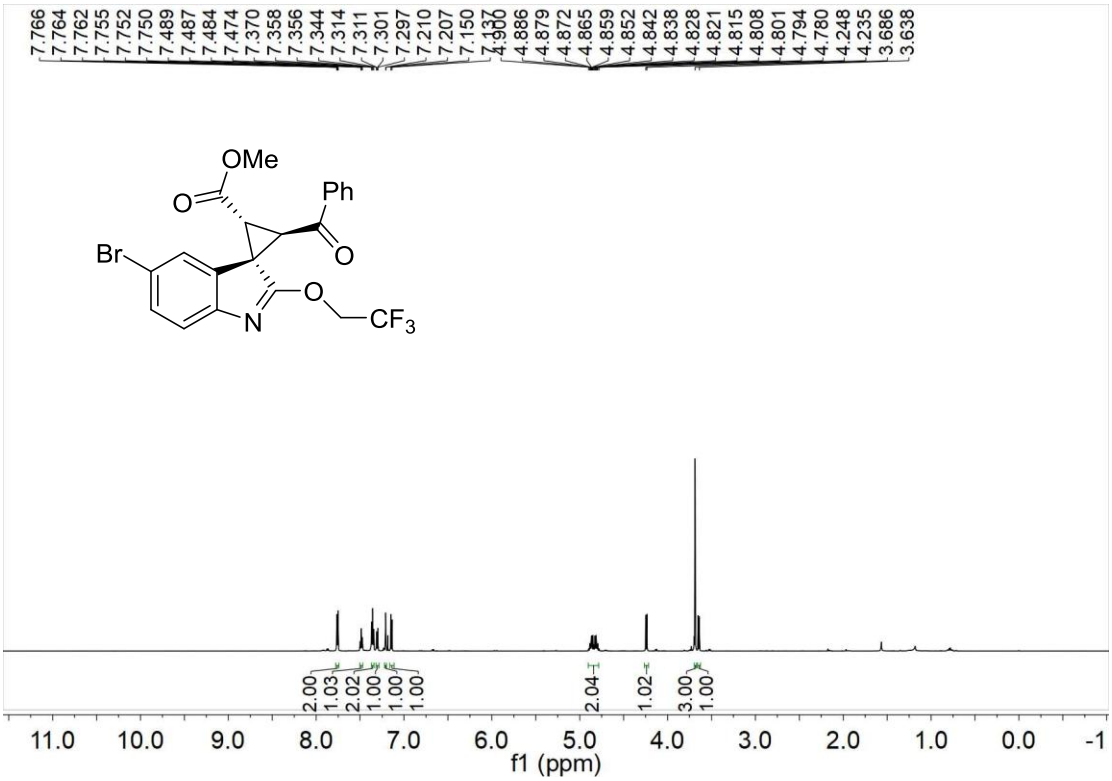


Figure 57. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ag**

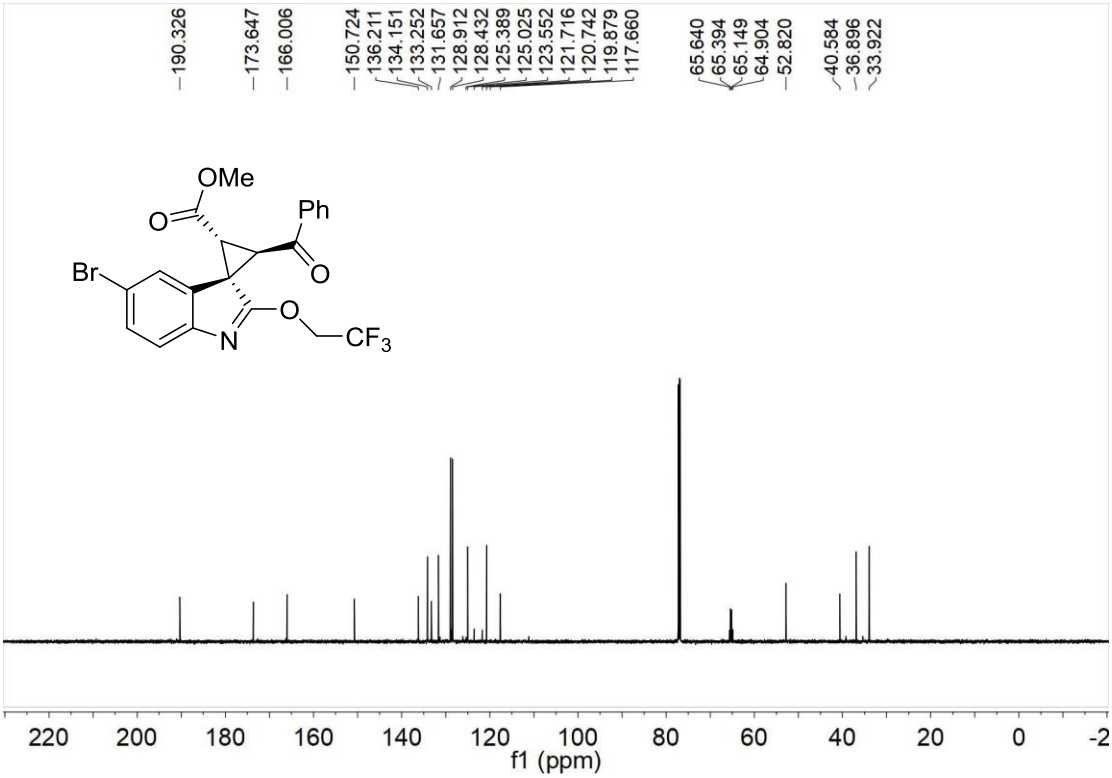


Figure 58. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ag**

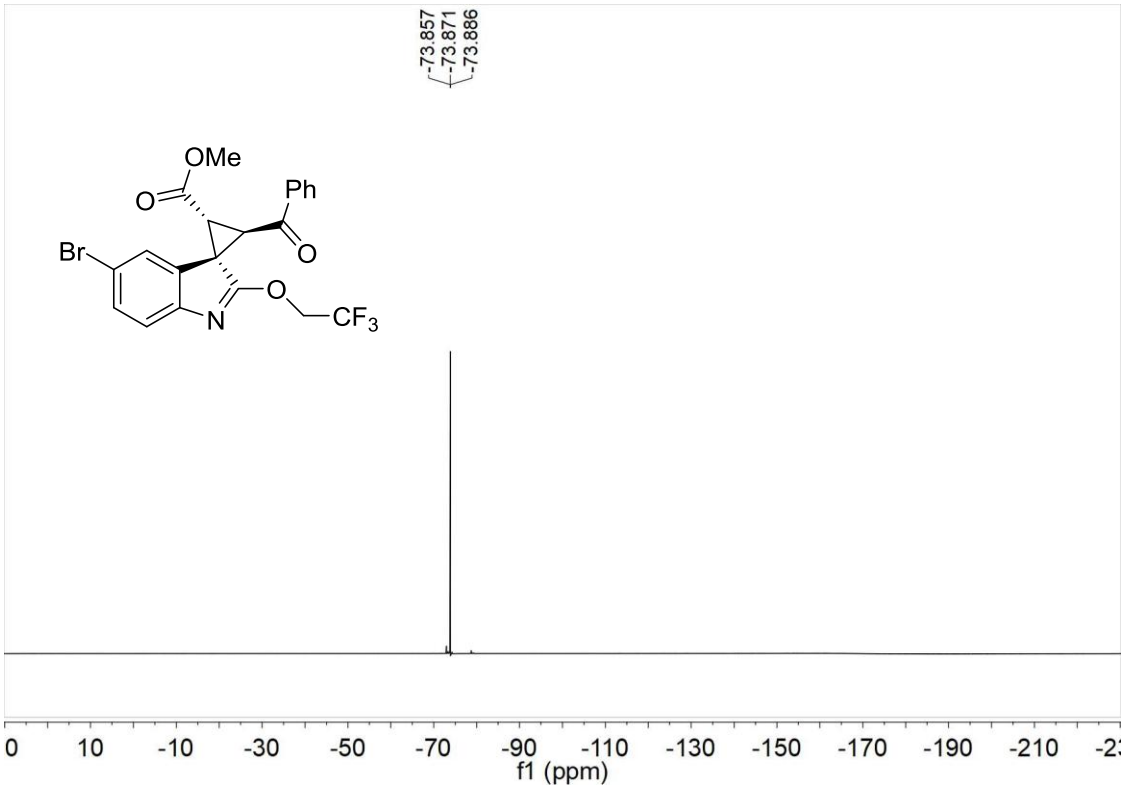


Figure 59. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ag**

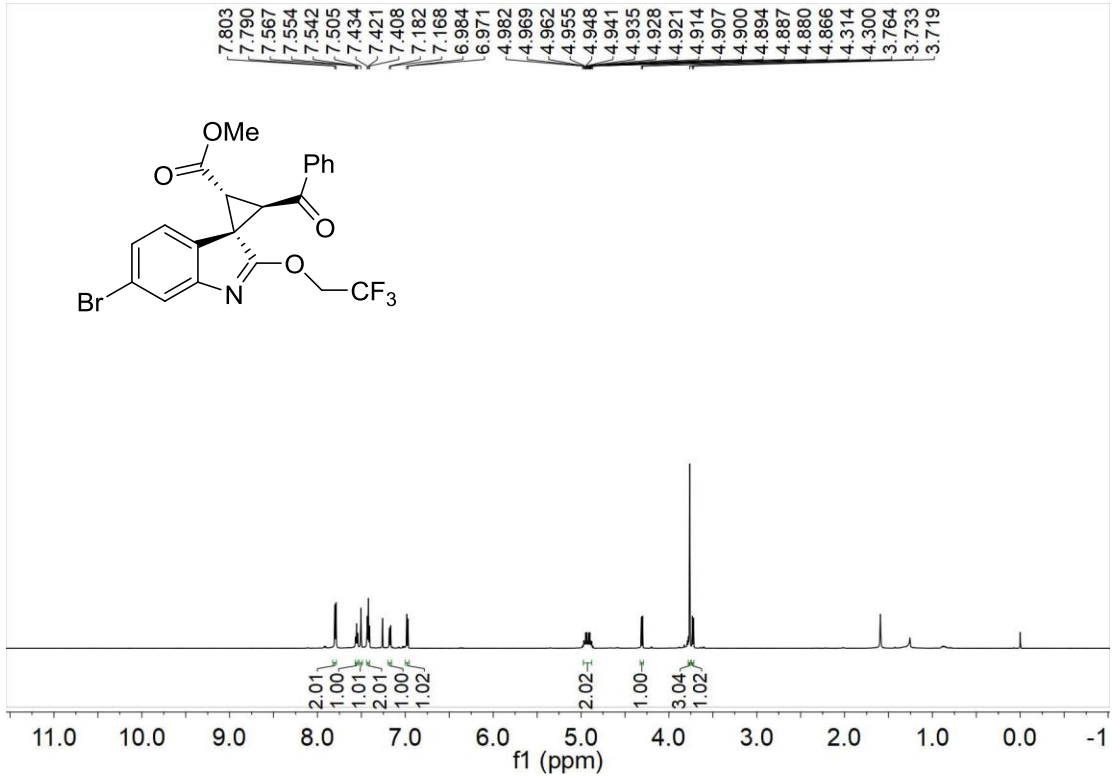


Figure 60. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ah**

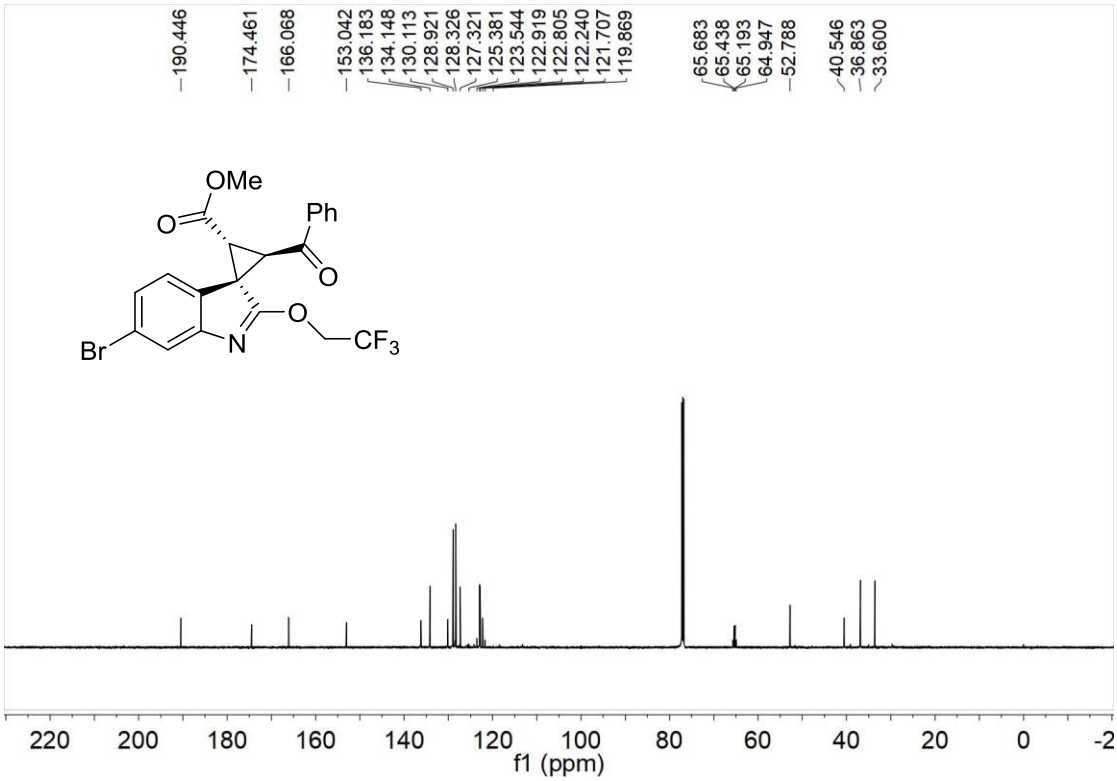


Figure 61. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ah**

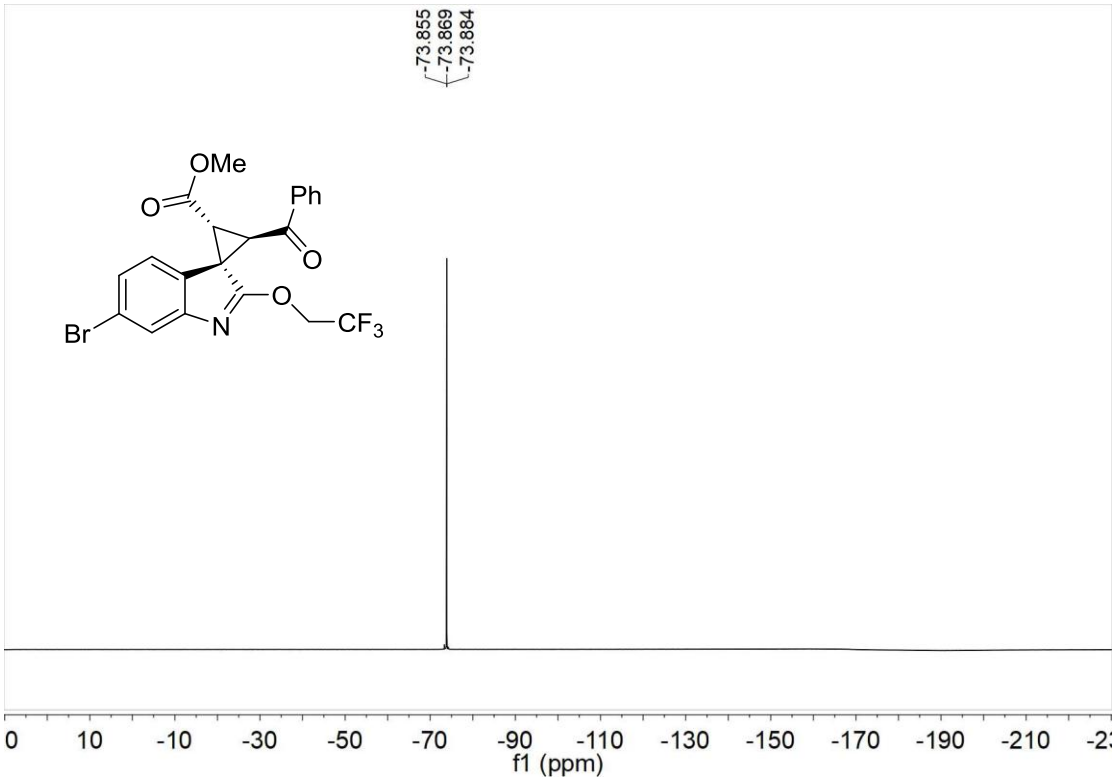


Figure 62. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ah**

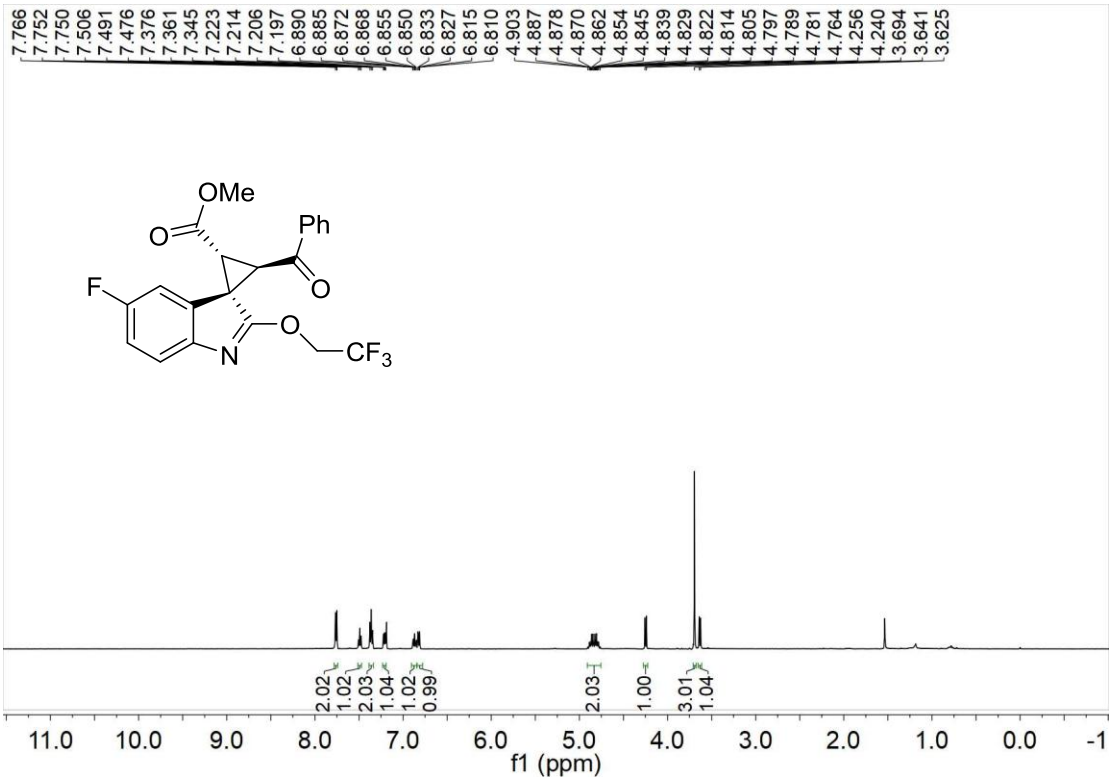


Figure 63. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ai**

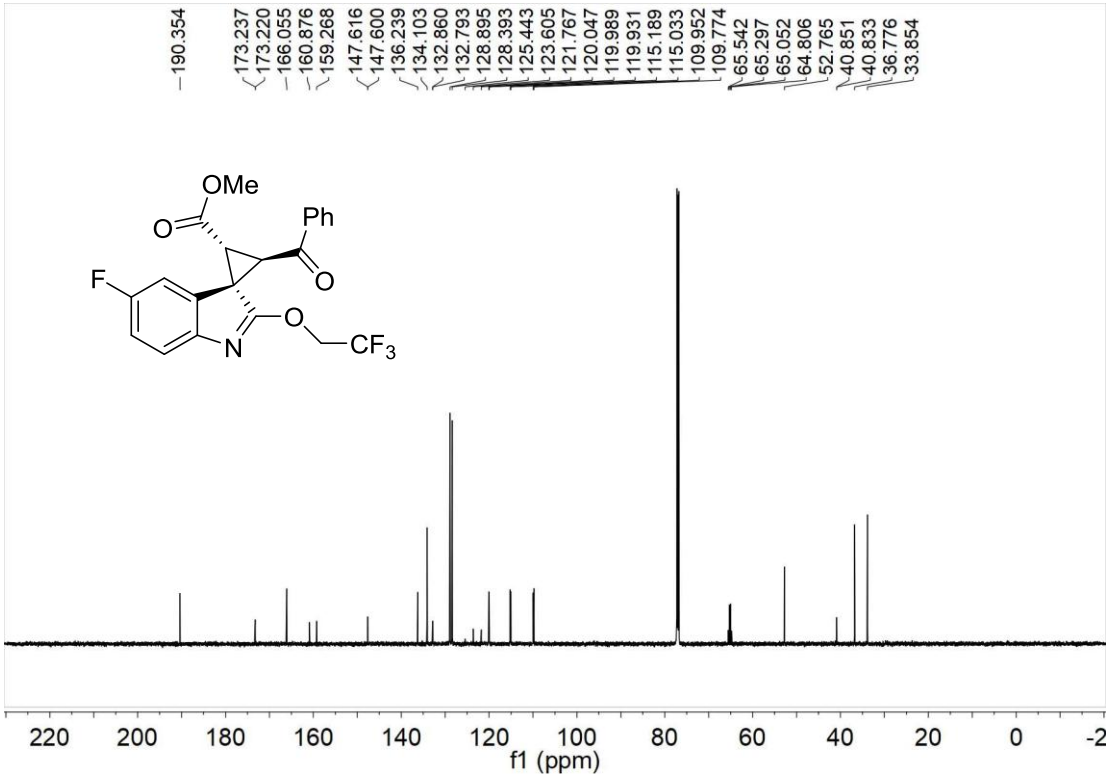


Figure 64. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ai**

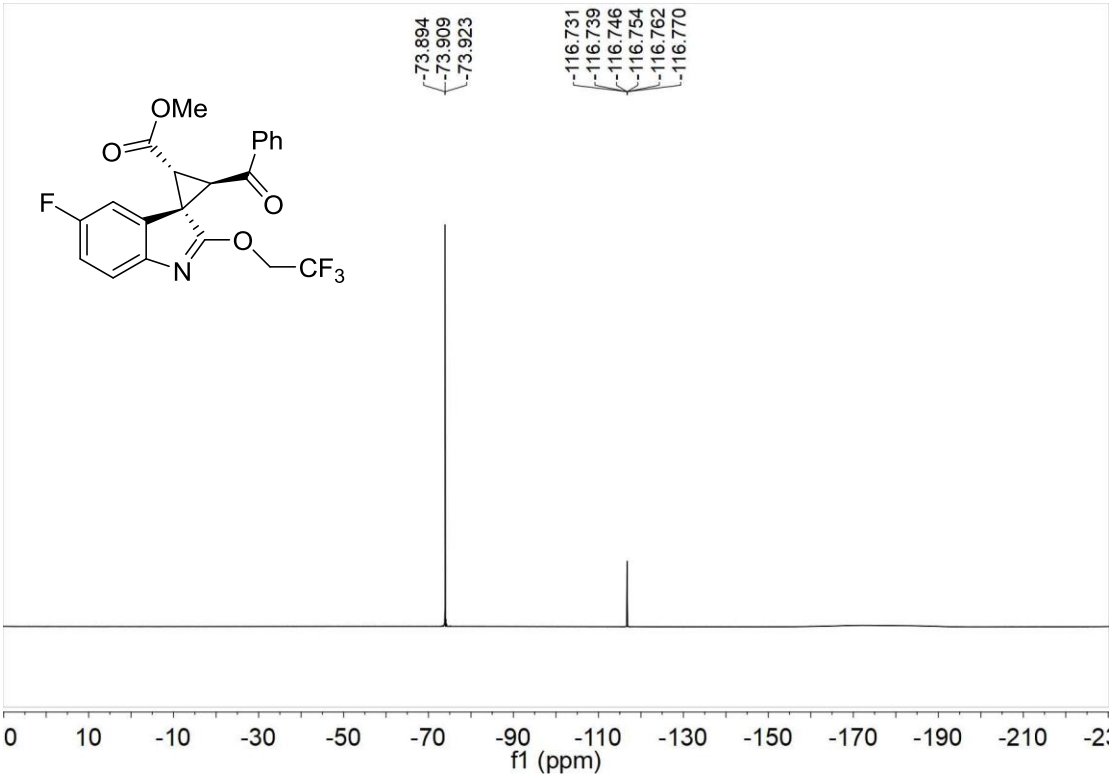


Figure 65. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ai**

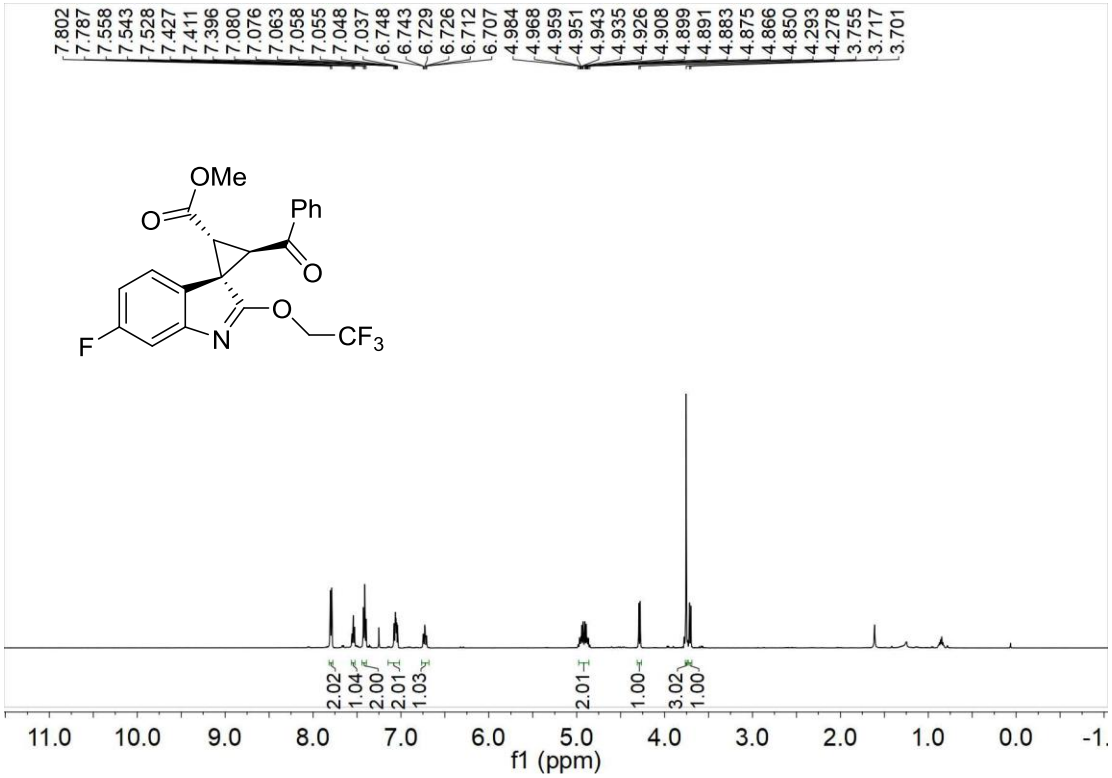


Figure 66. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4aj**

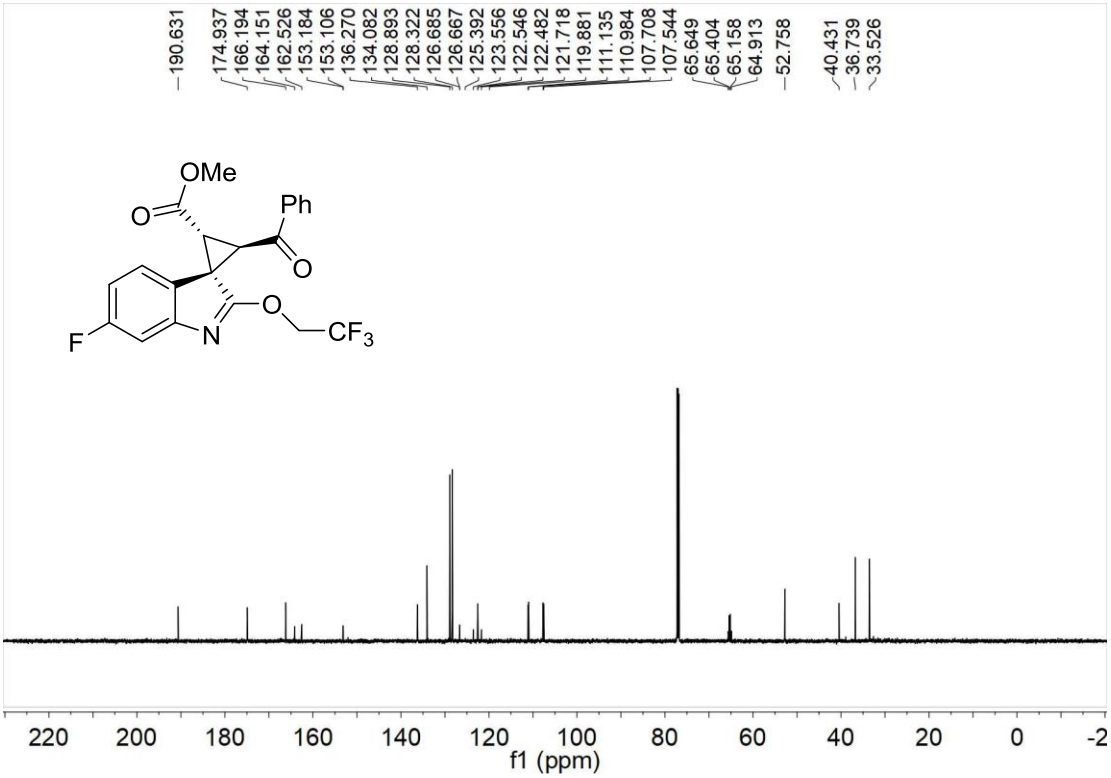


Figure 67. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4aj**

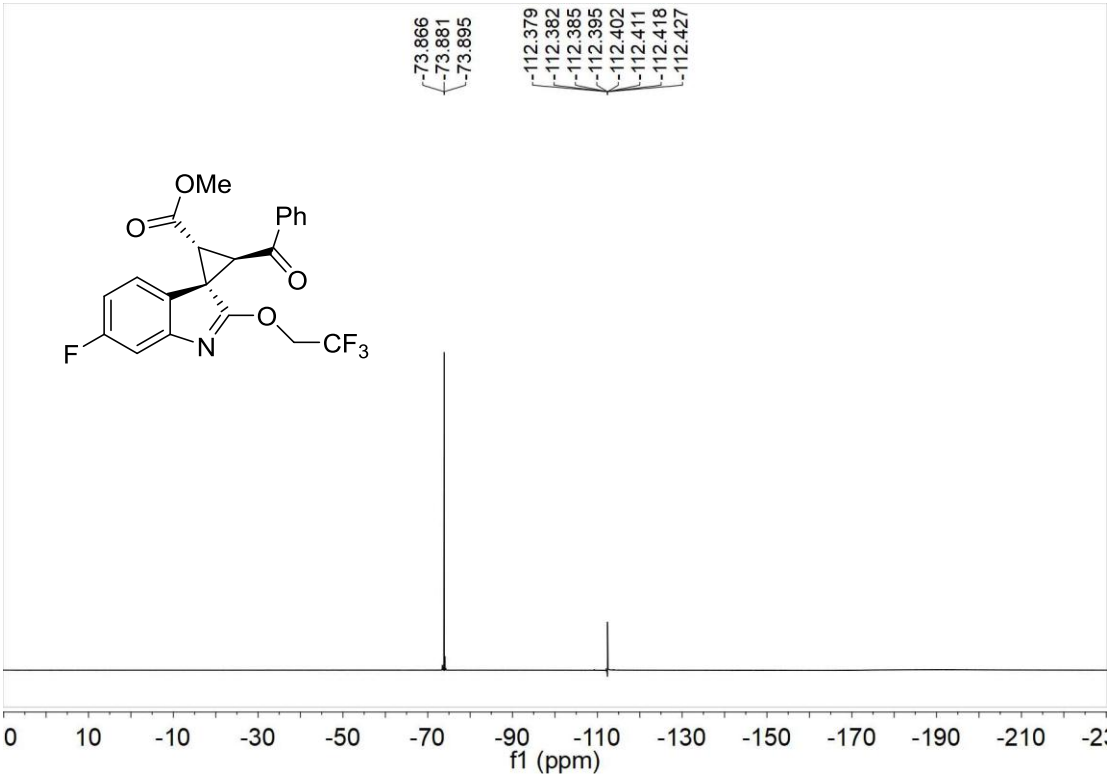


Figure 68. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4aj**

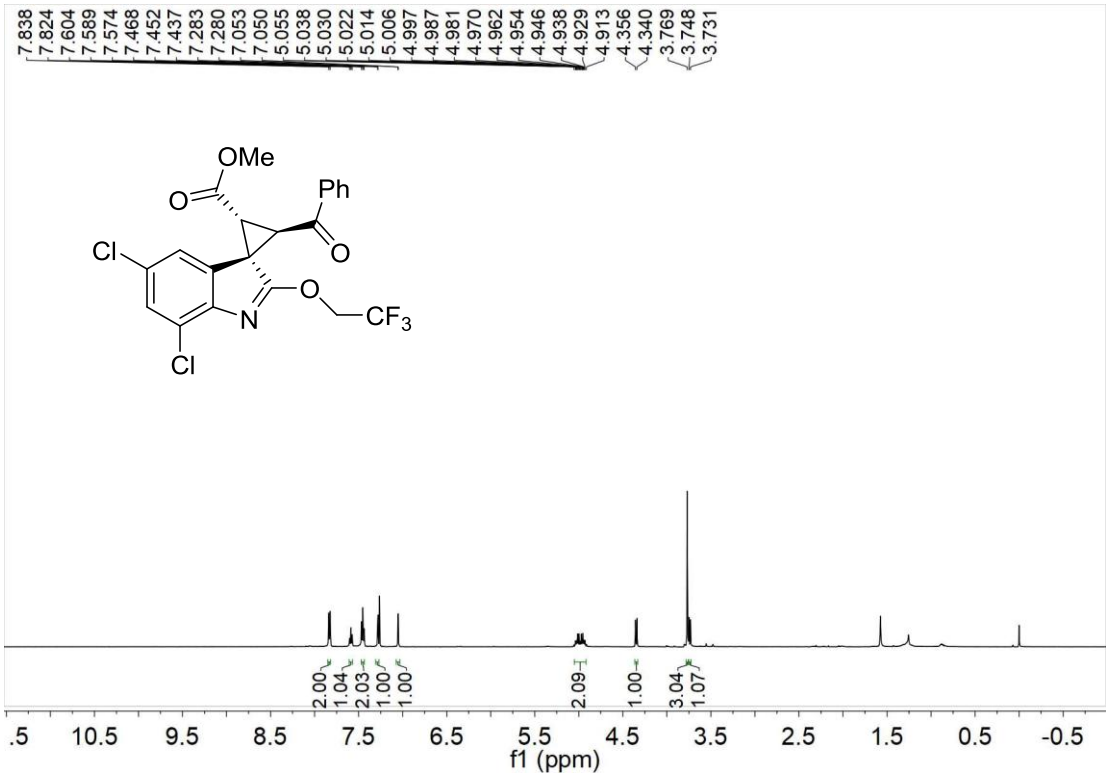


Figure 69. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ak**

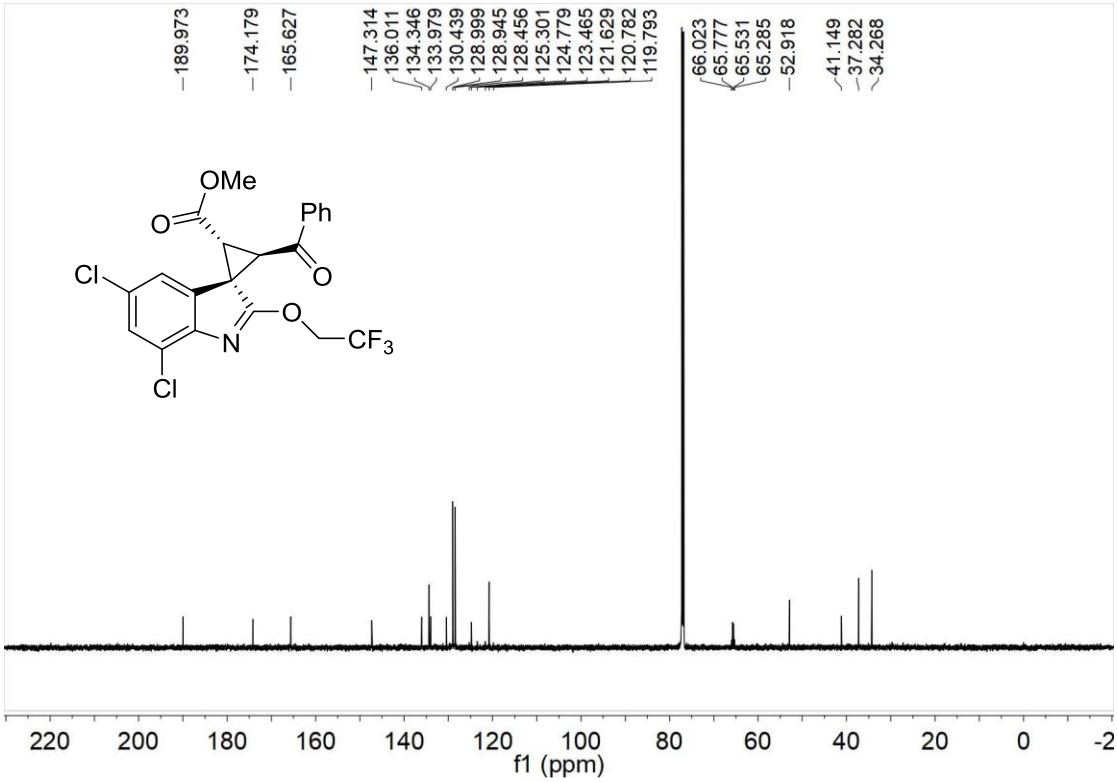


Figure 70. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ak**

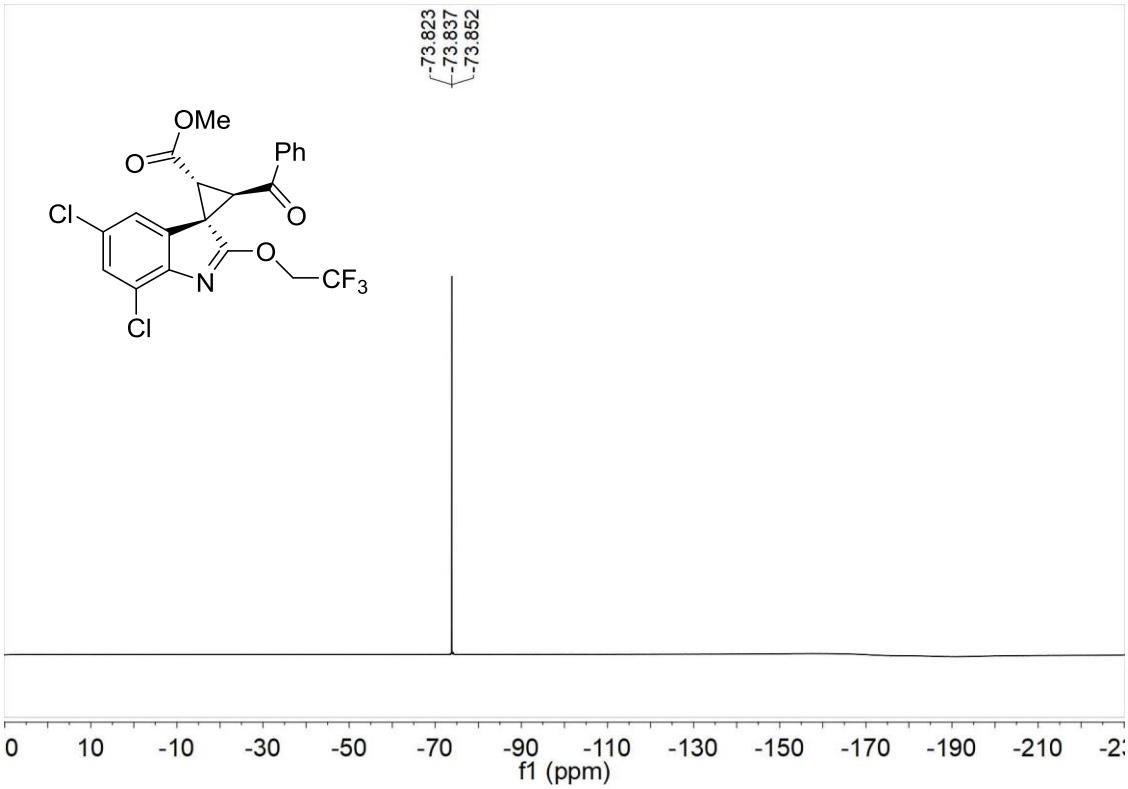


Figure 71. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ak**

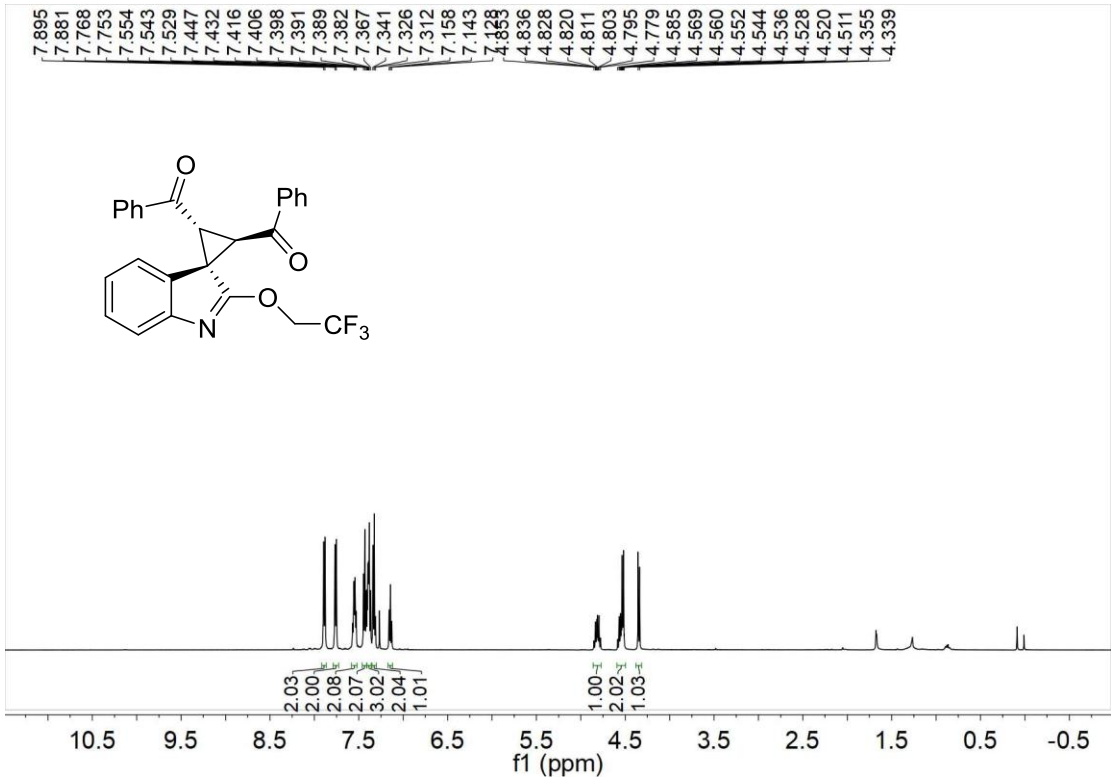


Figure 72. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4al**

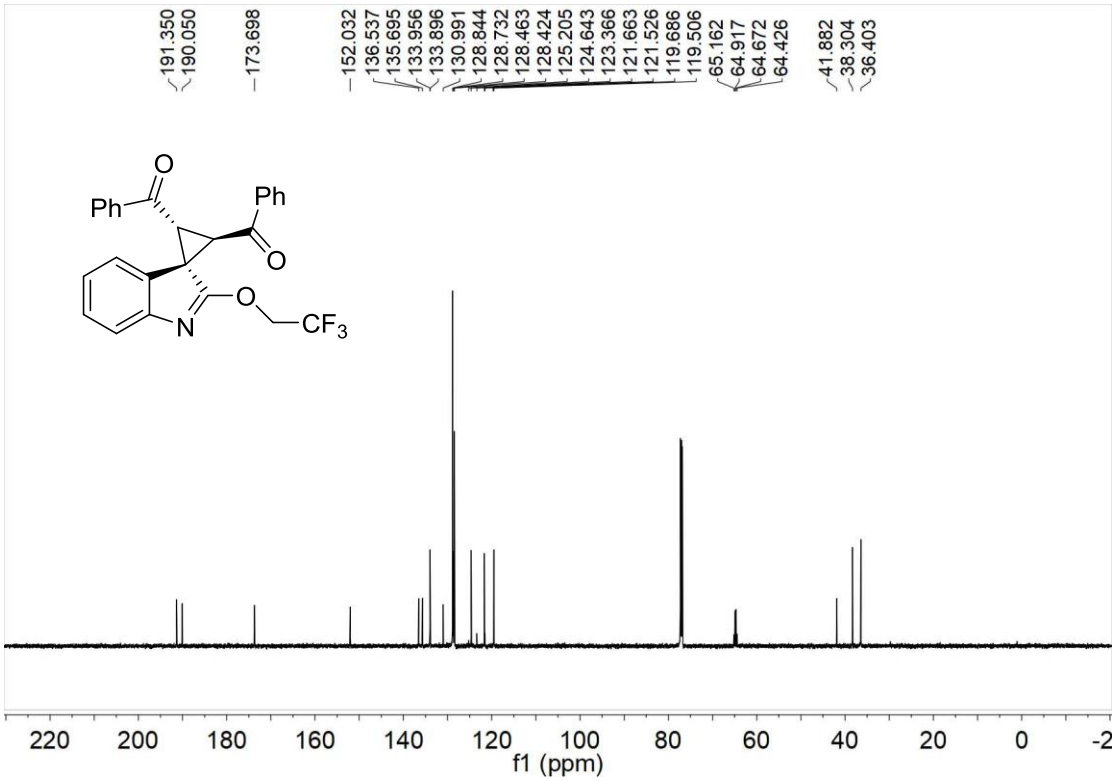


Figure 73. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4al**

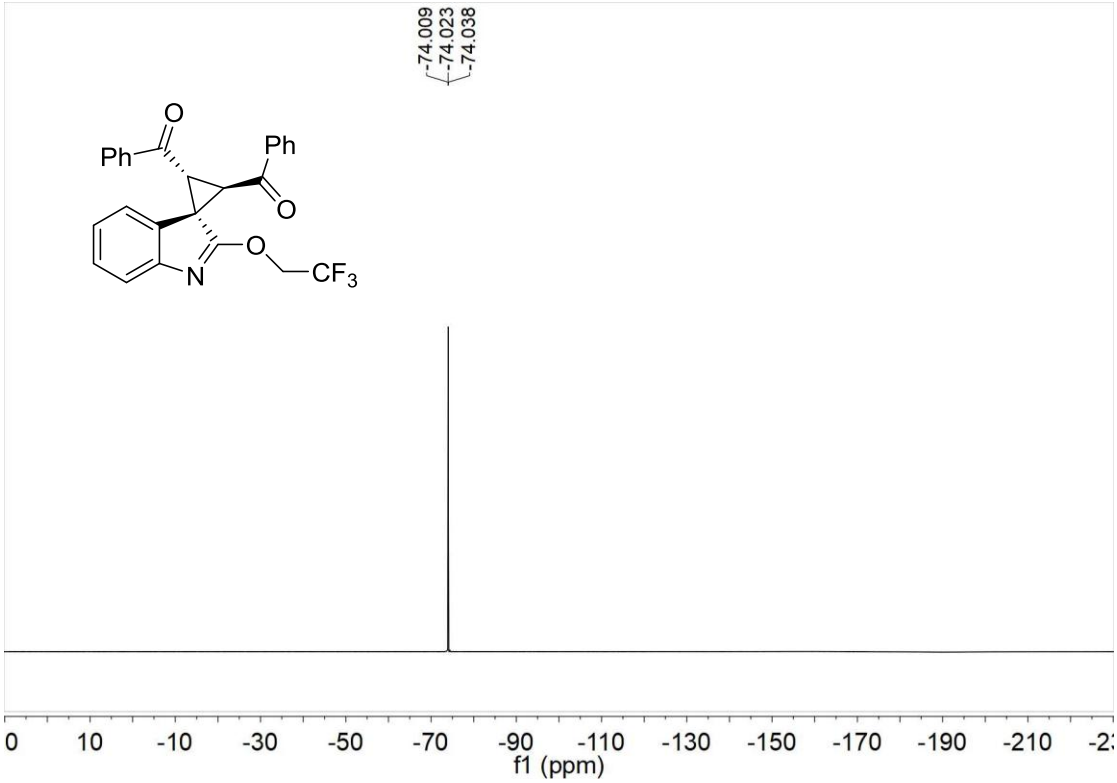


Figure 74. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4al**

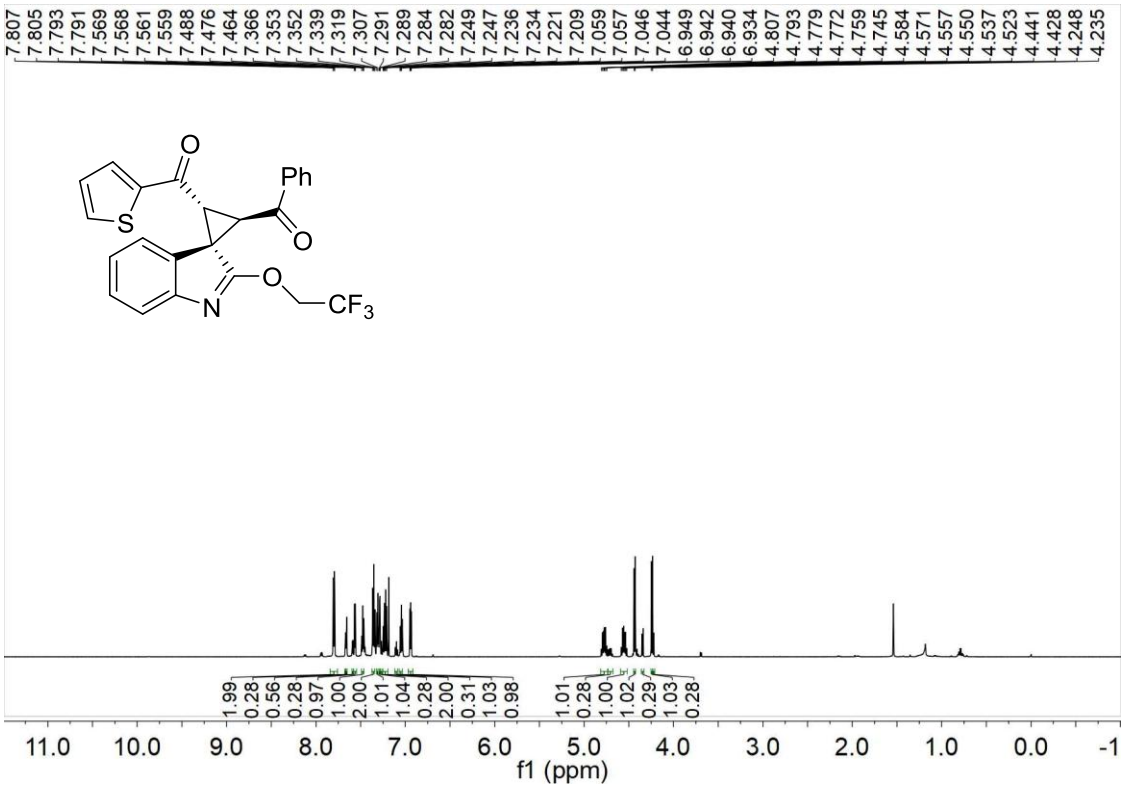


Figure 75. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4am**

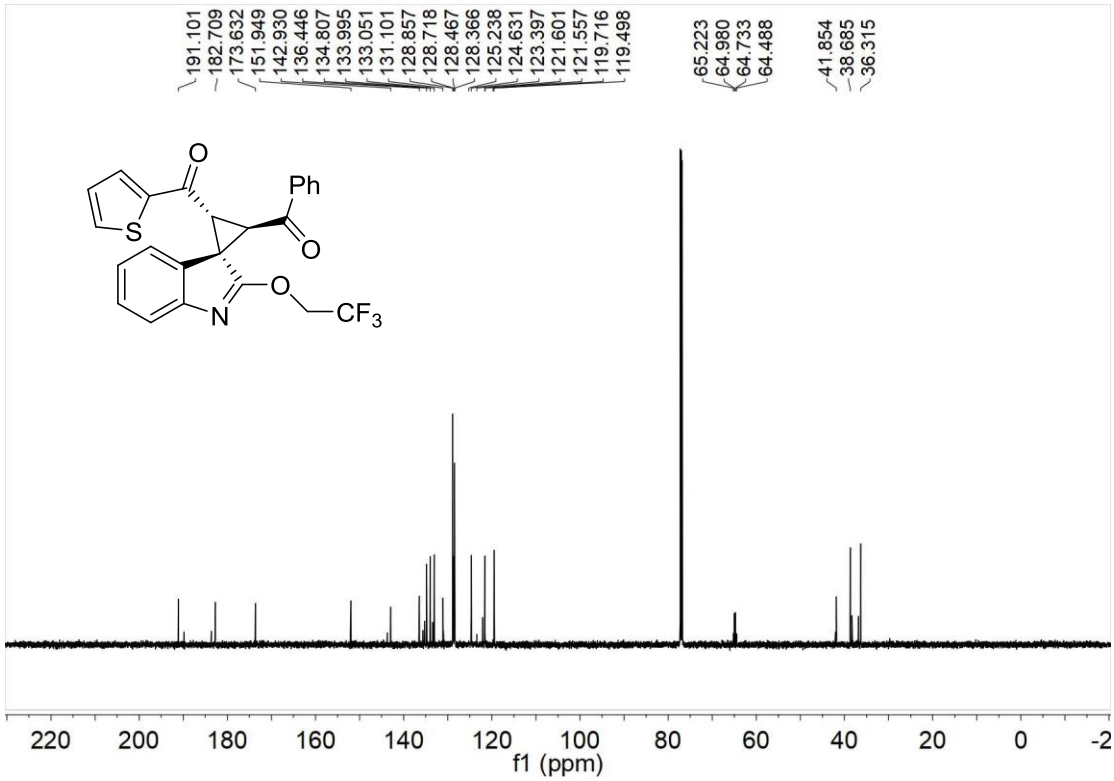


Figure 76. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4am**

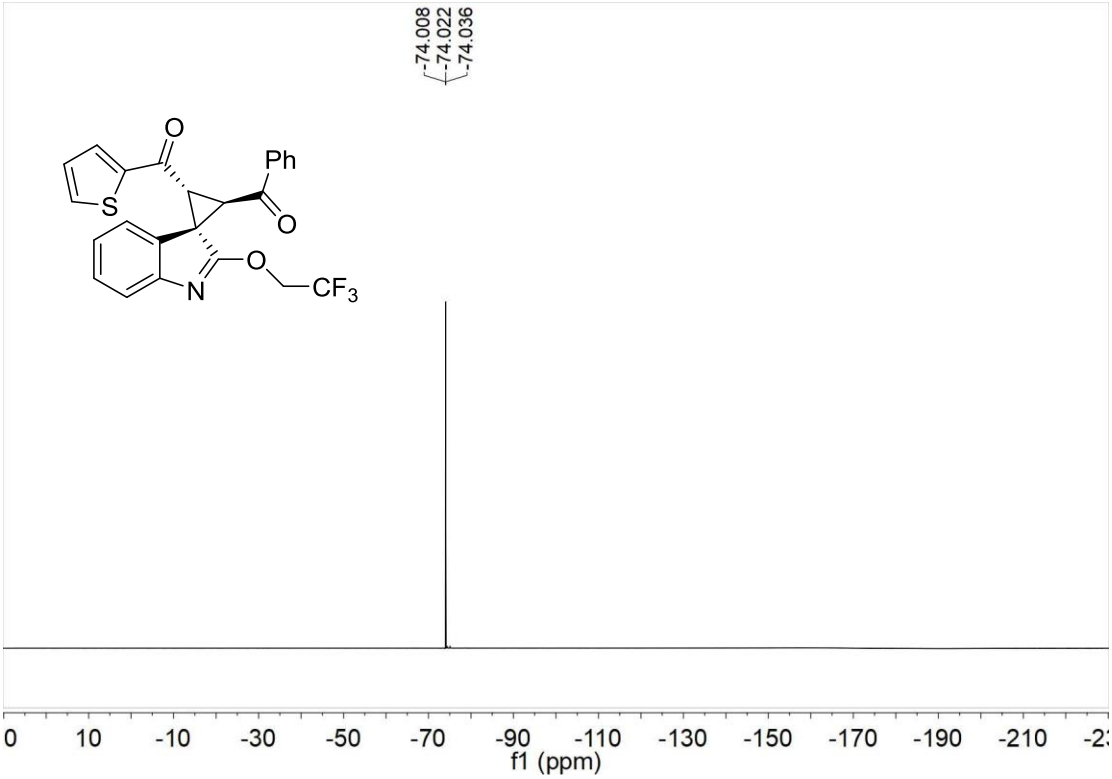


Figure 77. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4am**

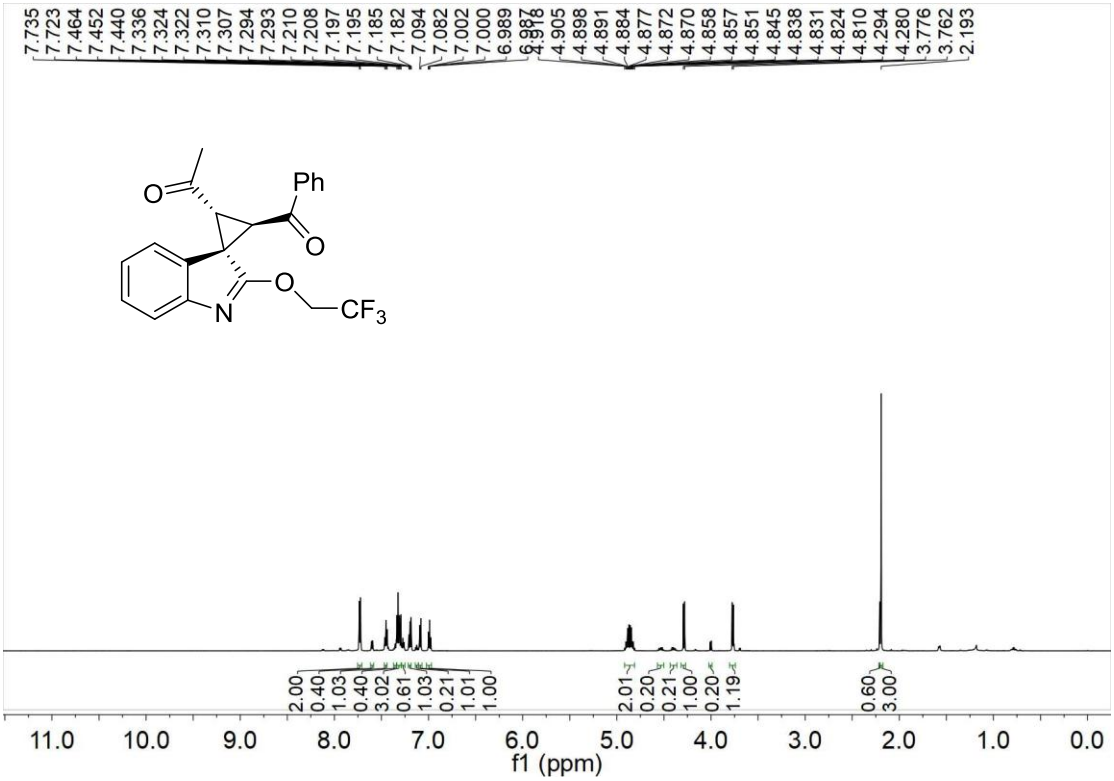


Figure 78. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4an**

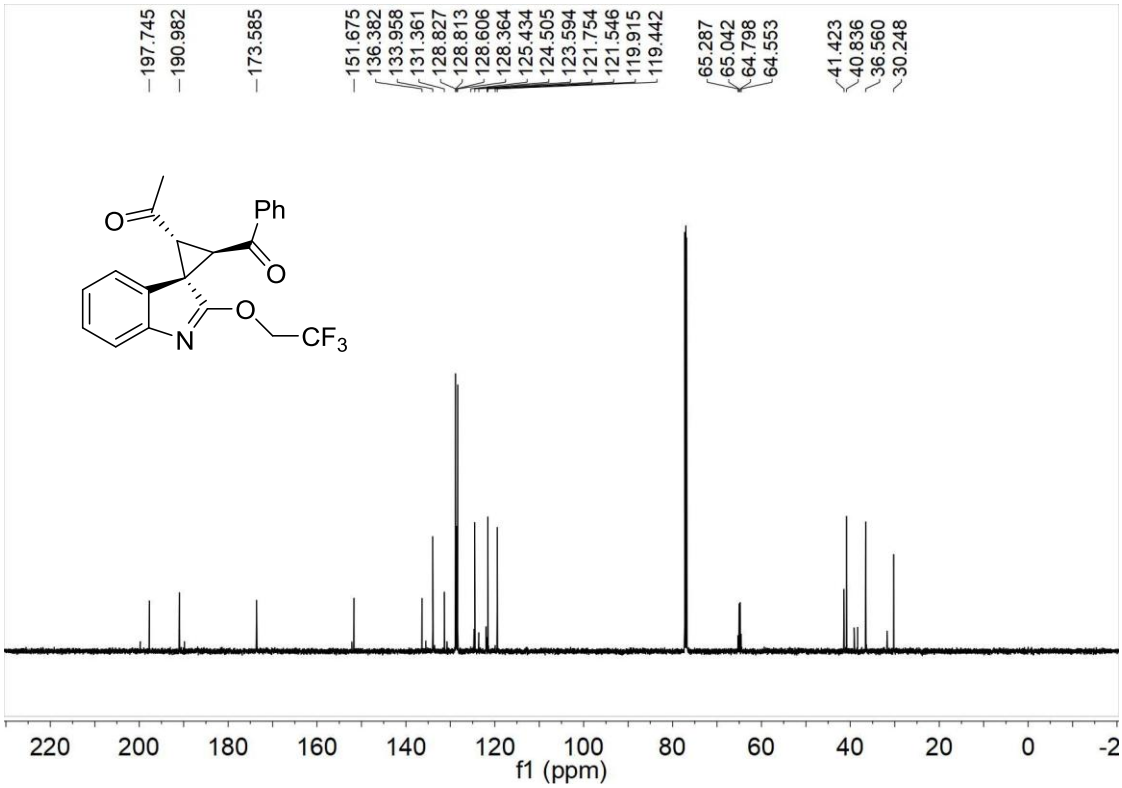


Figure 79. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4an**

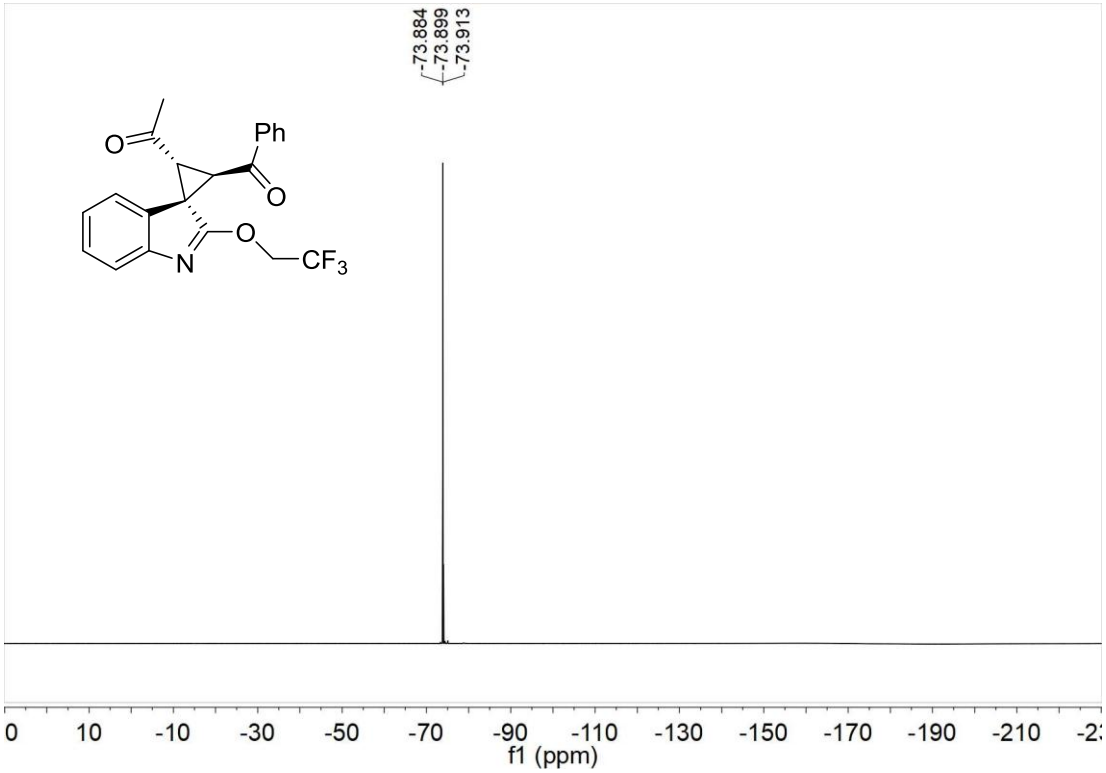


Figure 80. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4an**

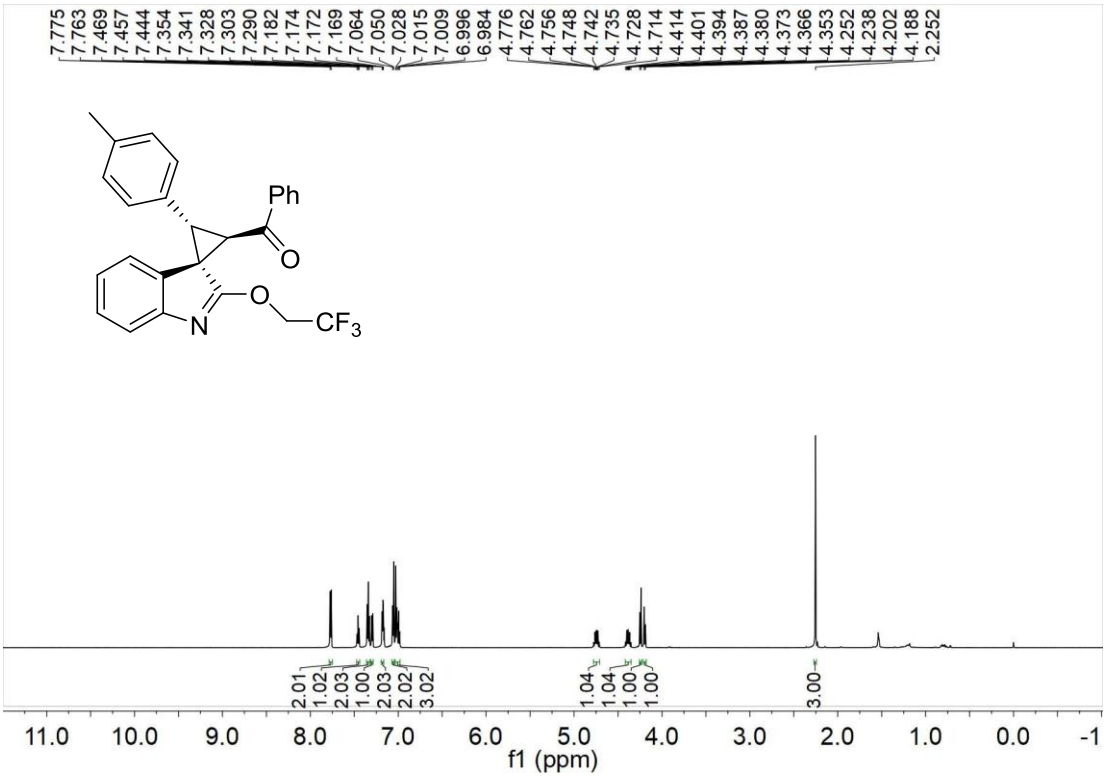


Figure 81. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **4ao**

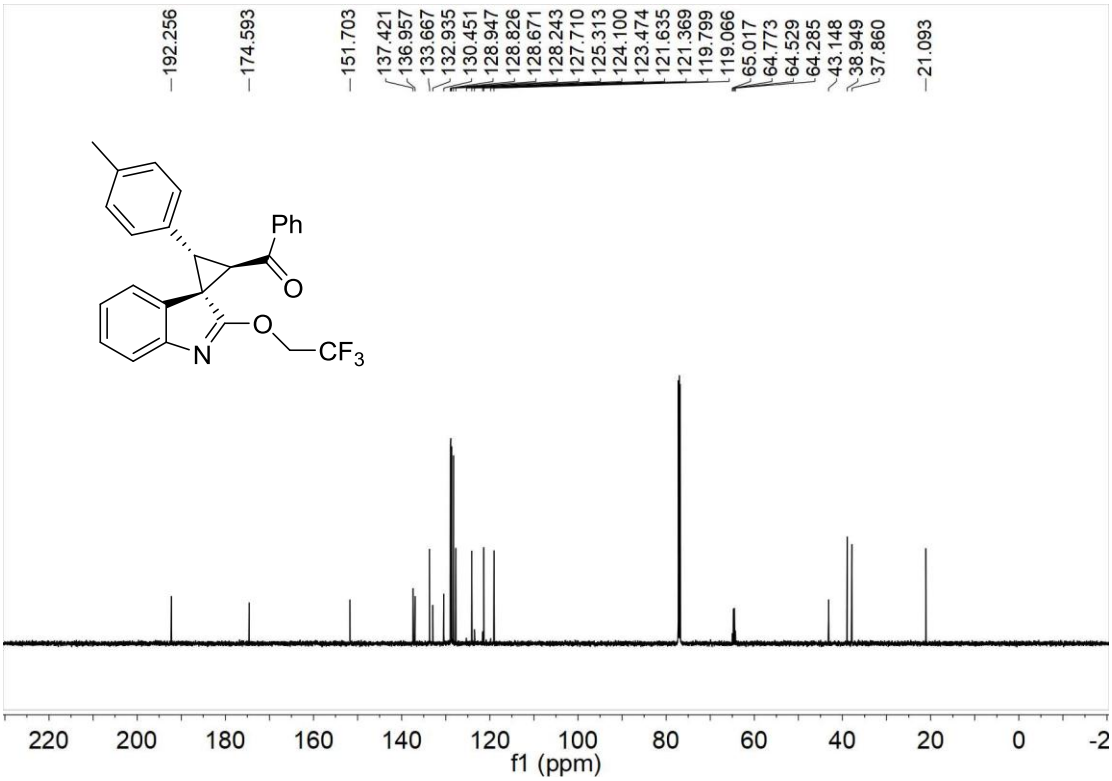


Figure 82. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ao**

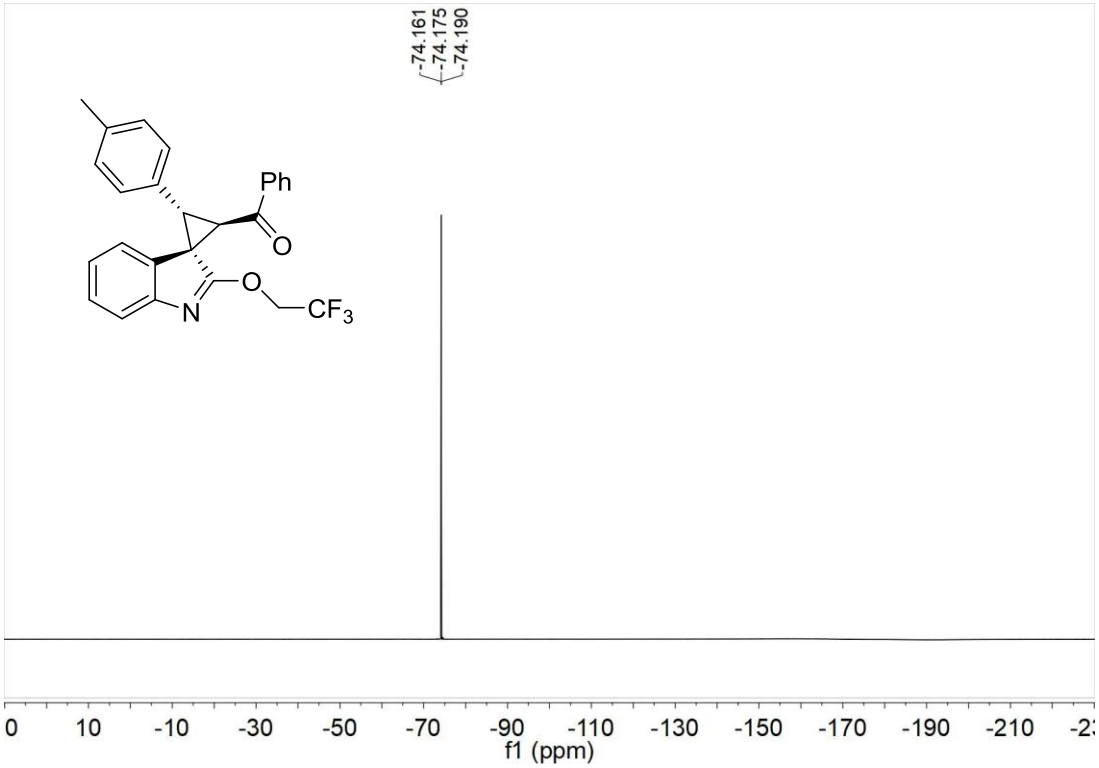


Figure 83. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ao**

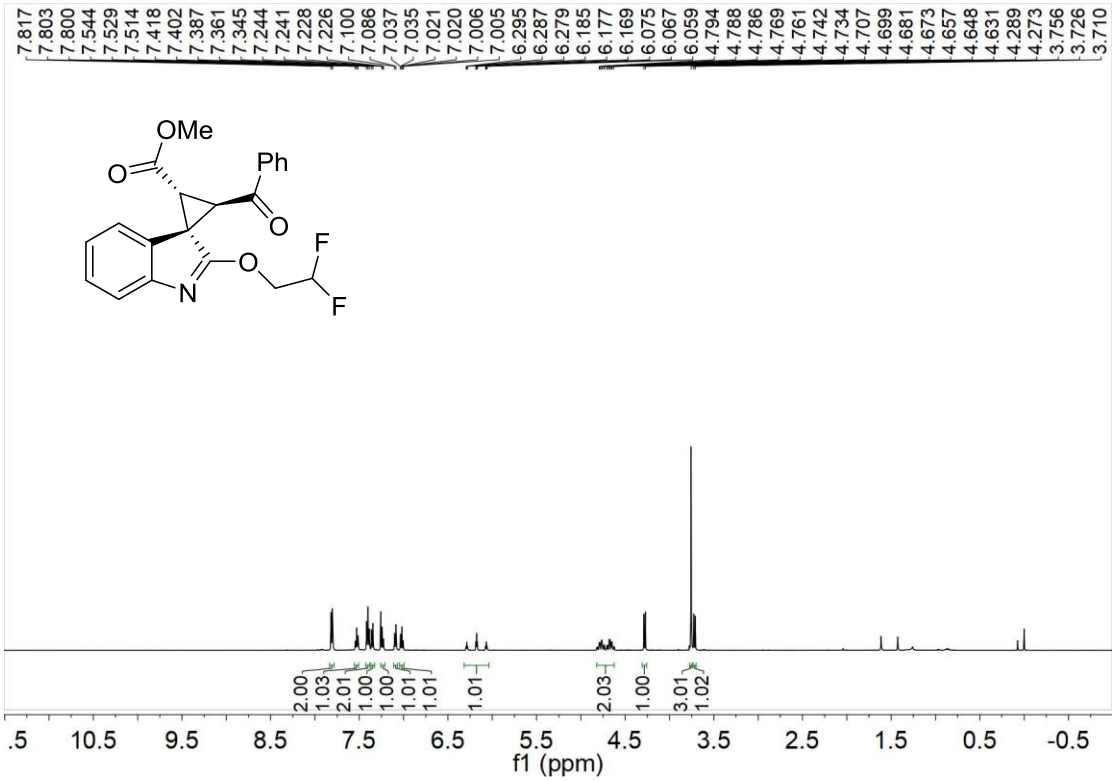


Figure 84. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ap**

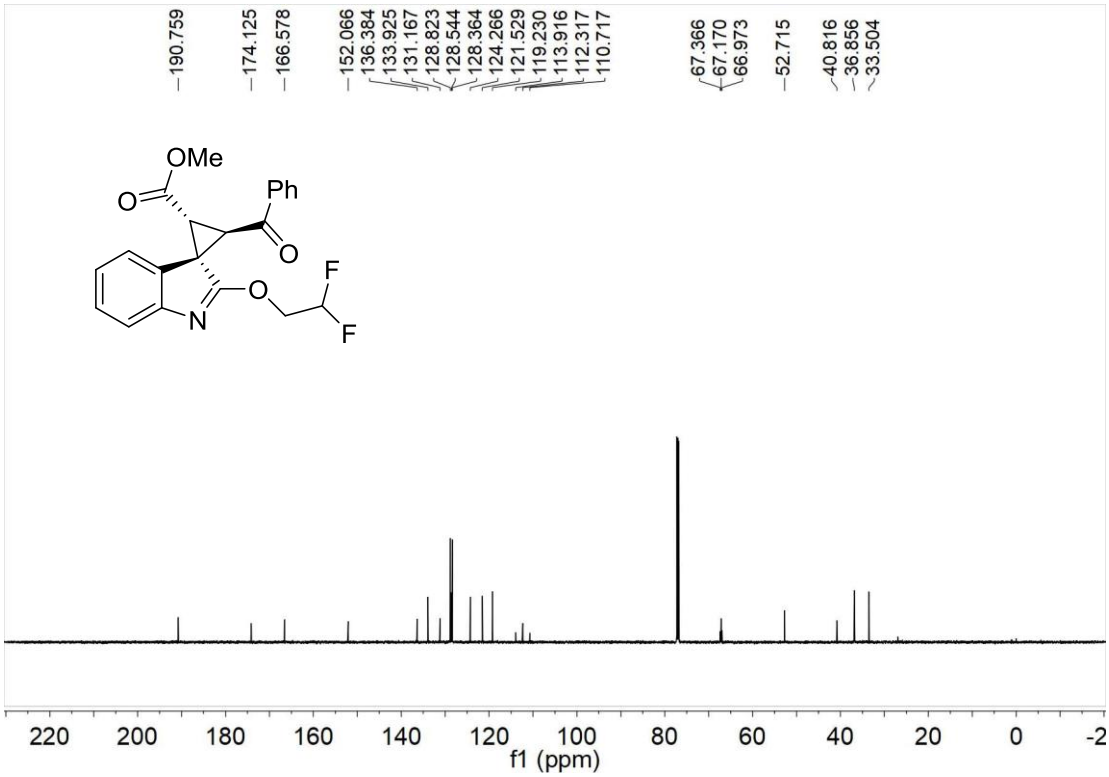


Figure 85. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ap**

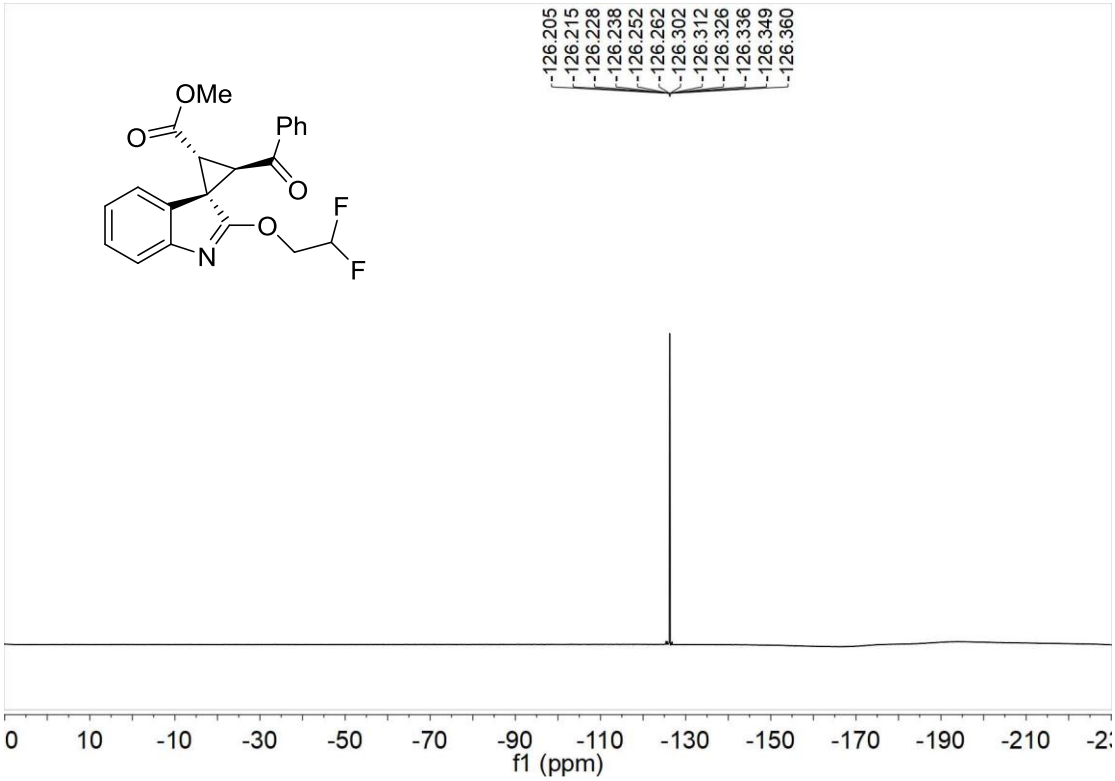


Figure 86. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **4ap**

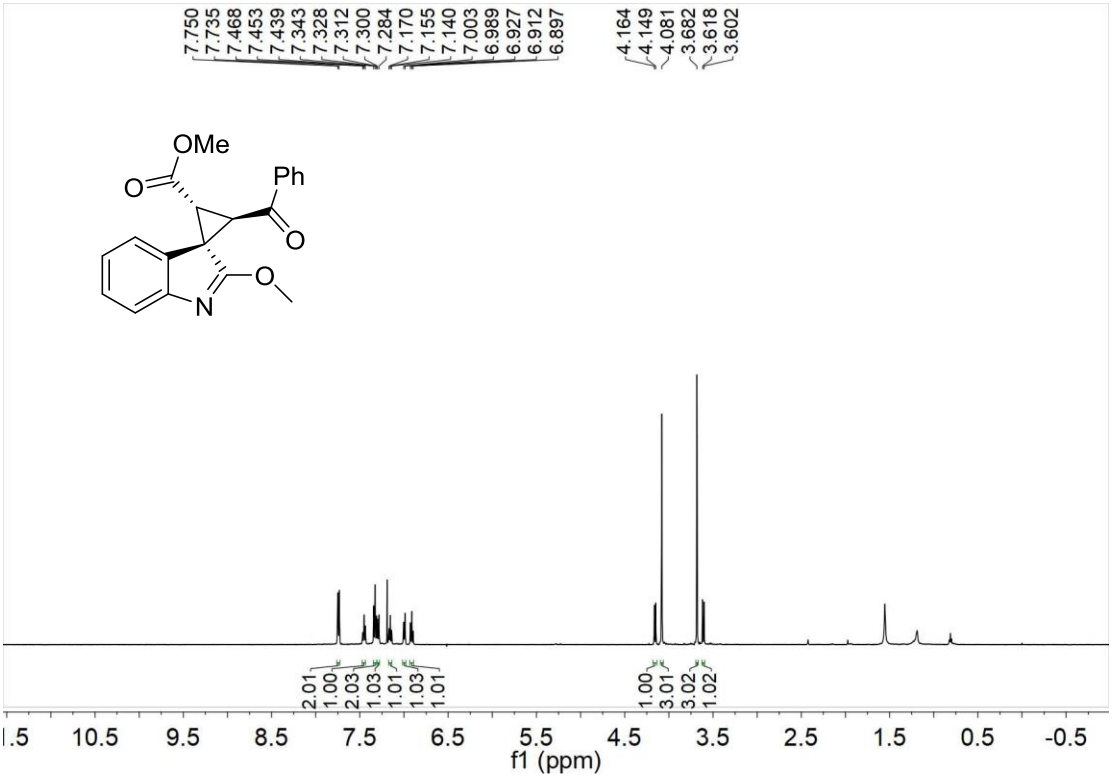


Figure 87. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4aq**

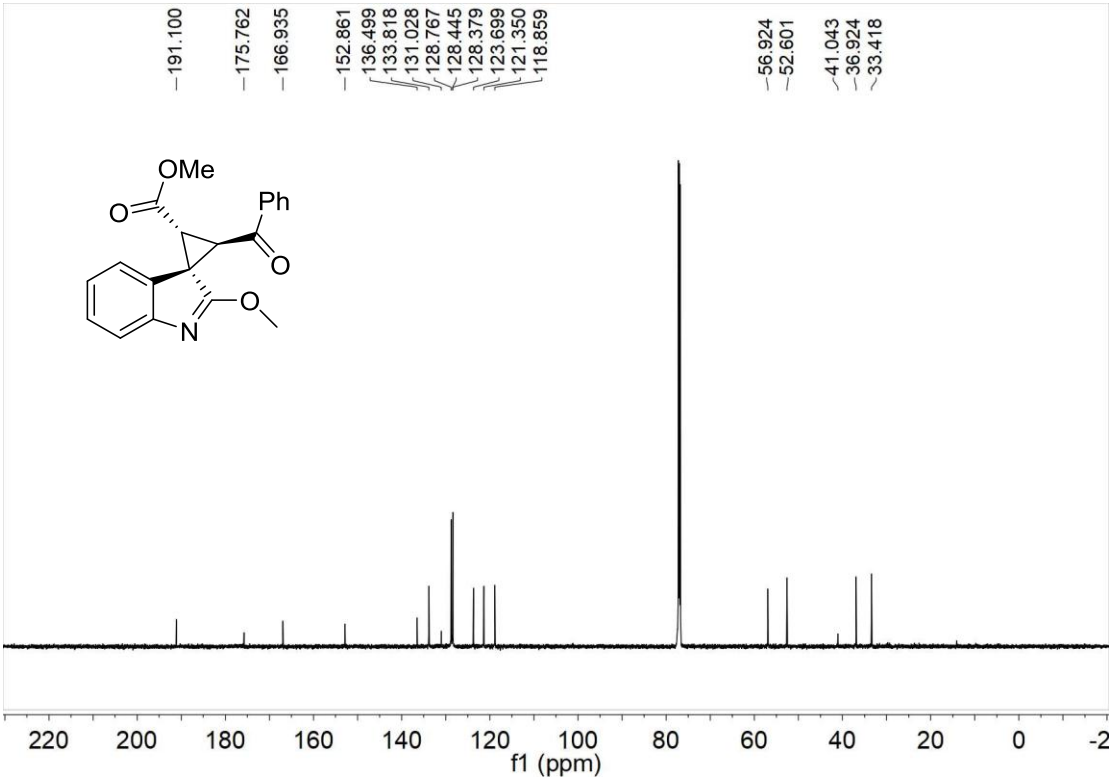


Figure 88. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4aq**

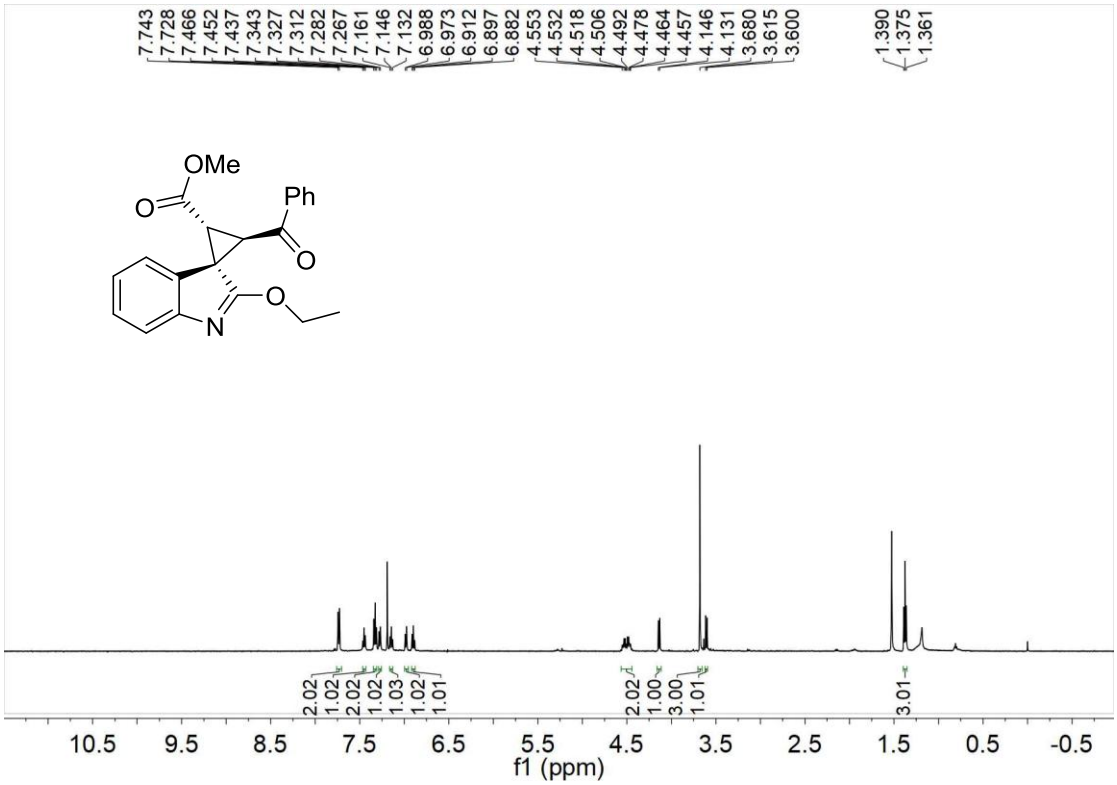


Figure 89. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4ar**

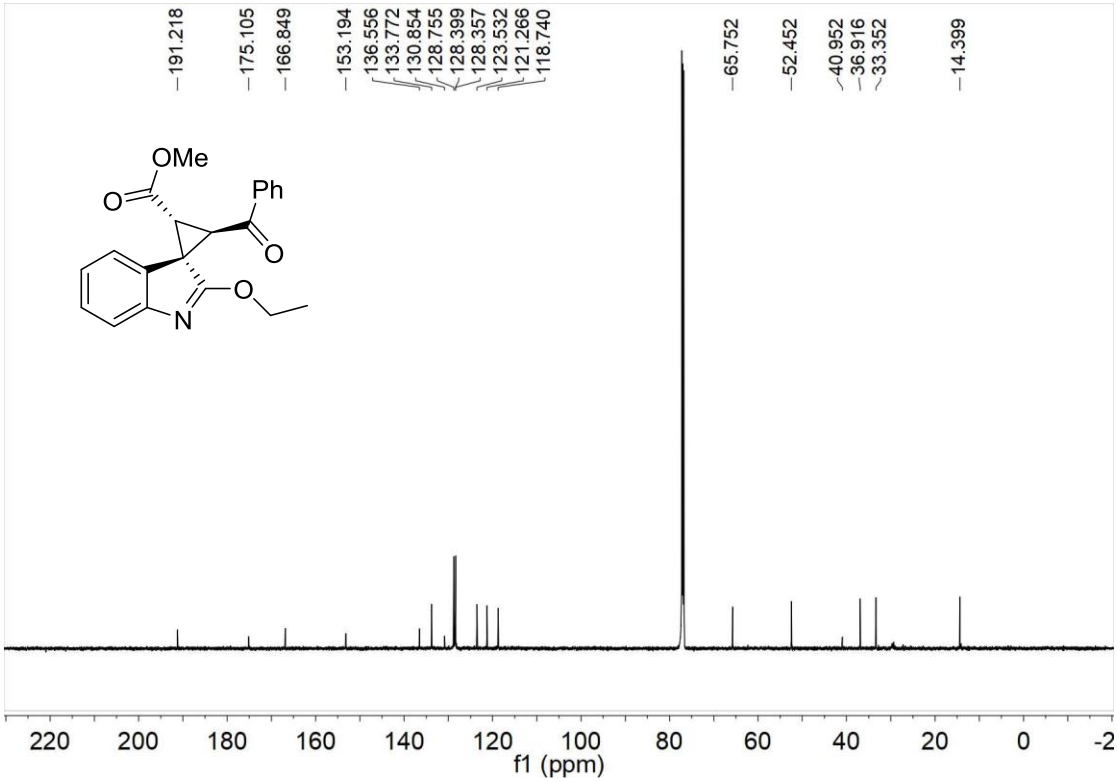


Figure 90. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4ar**

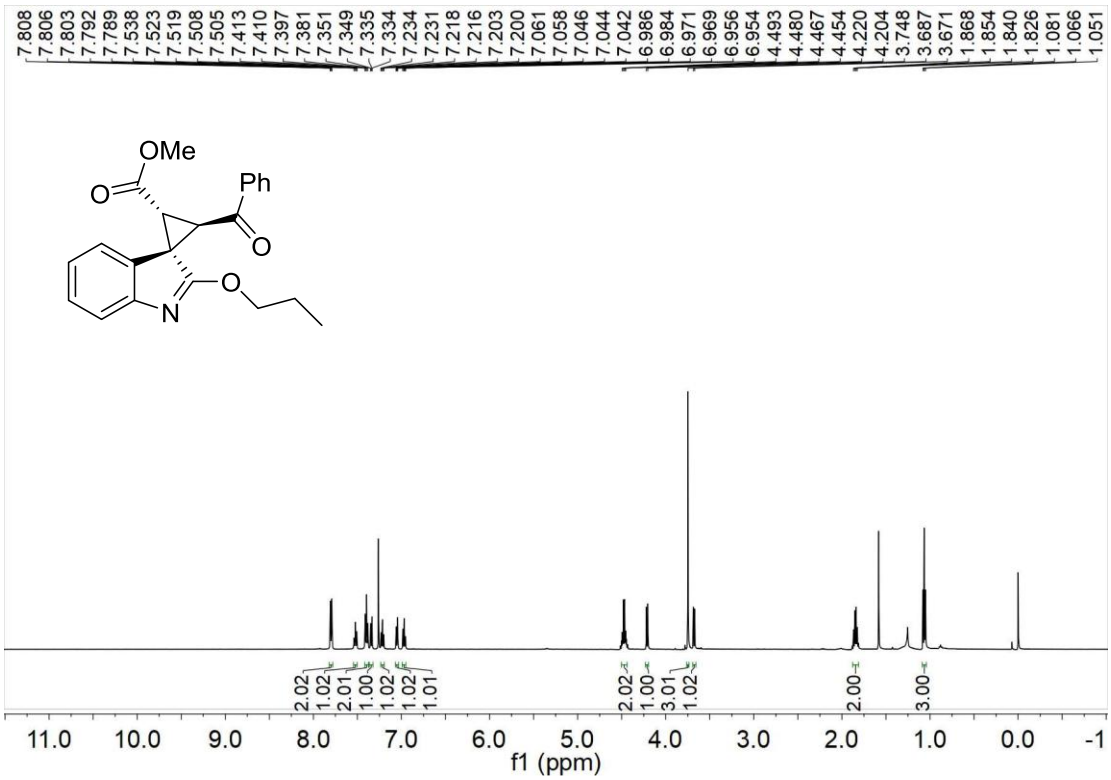


Figure 91. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4as**

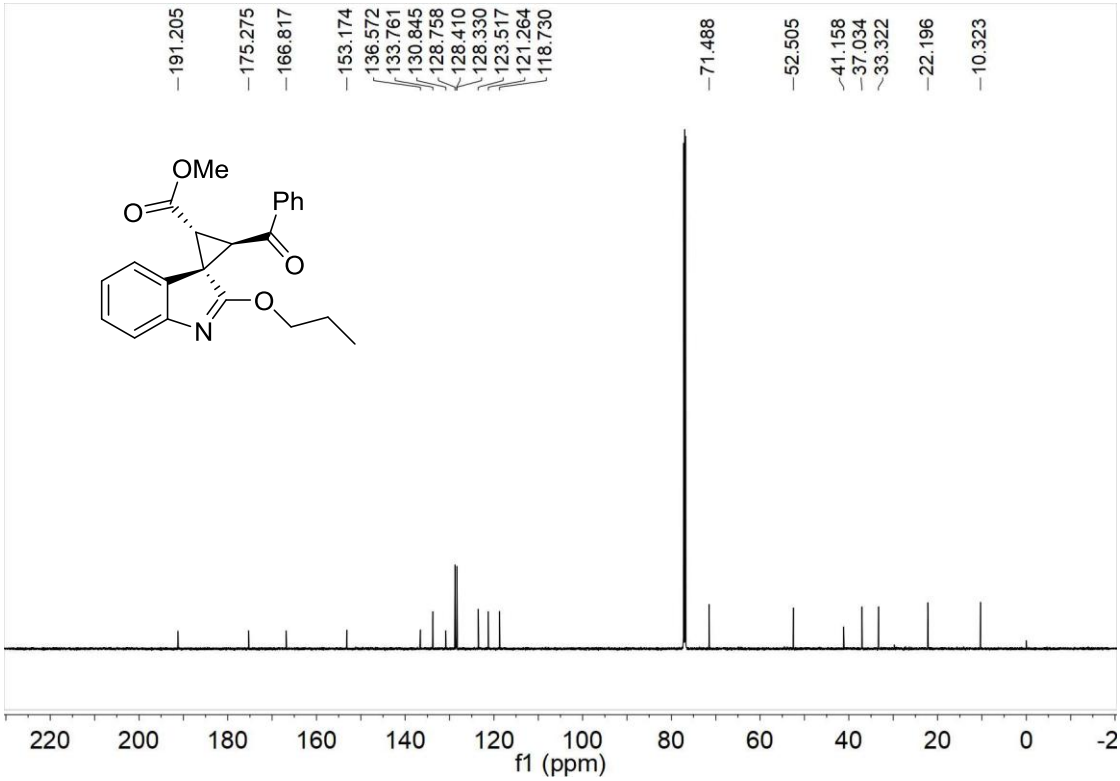


Figure 92. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4as**

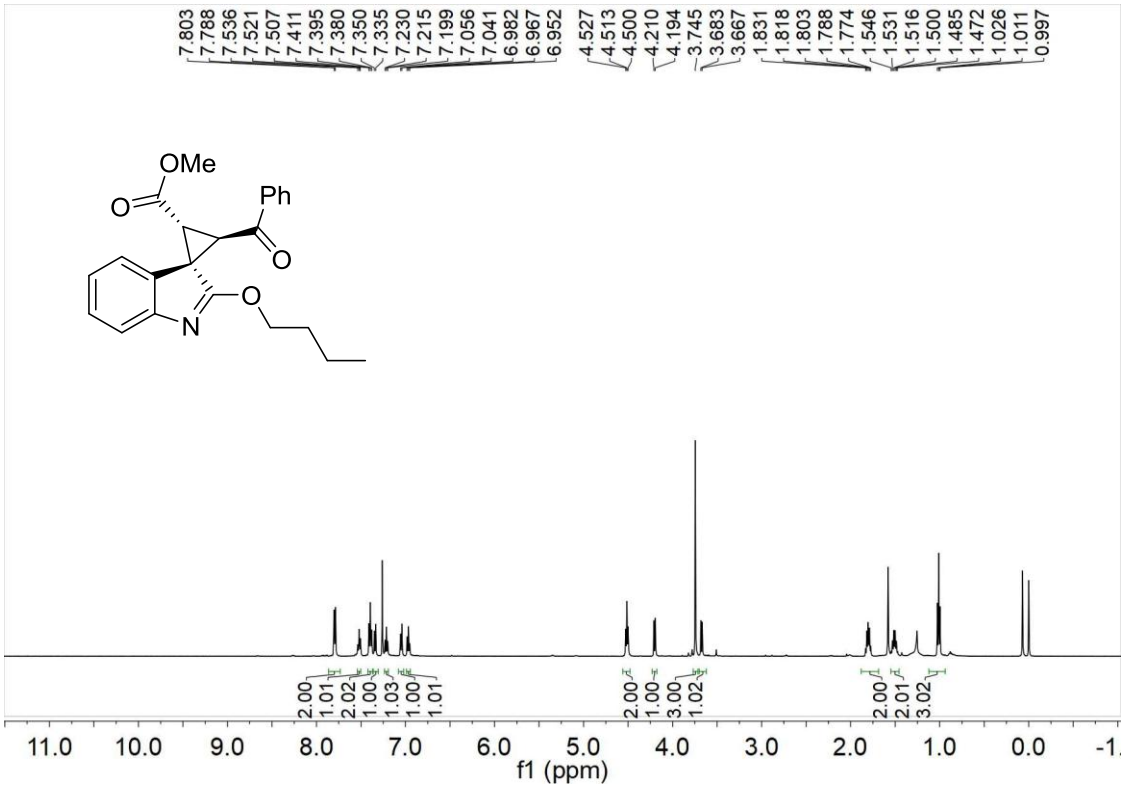


Figure 93. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4at**

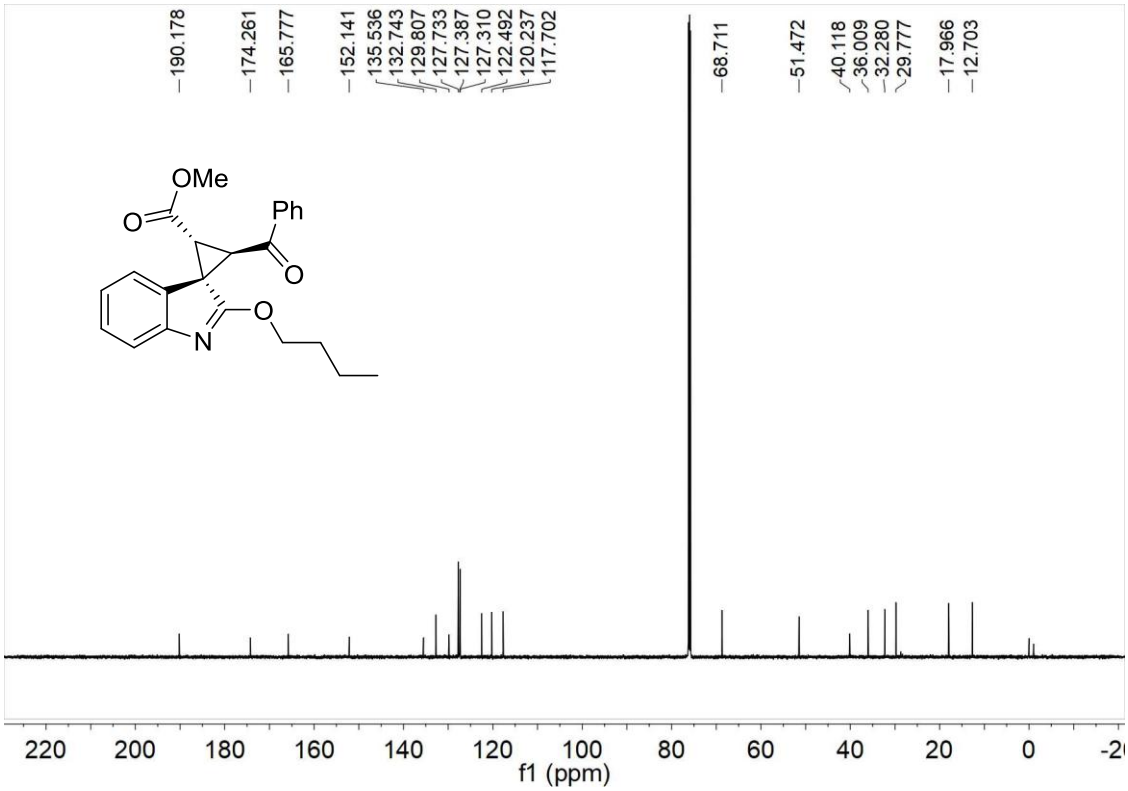


Figure 94. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4at**

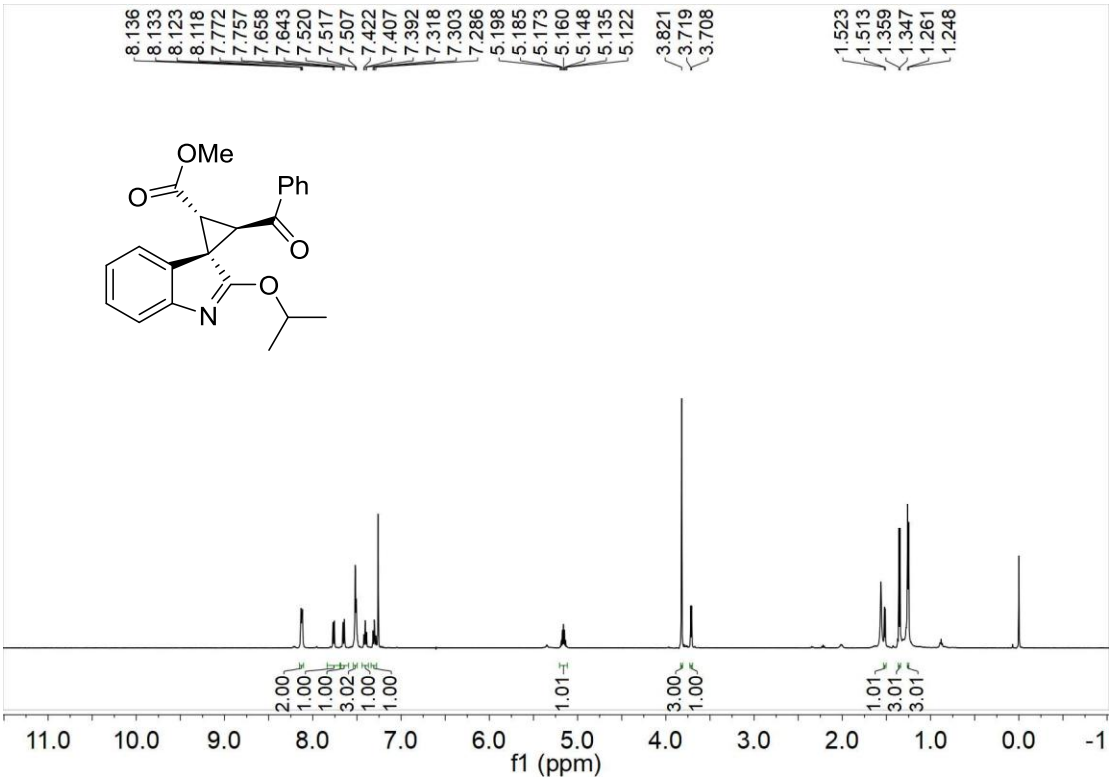


Figure 95. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4au**

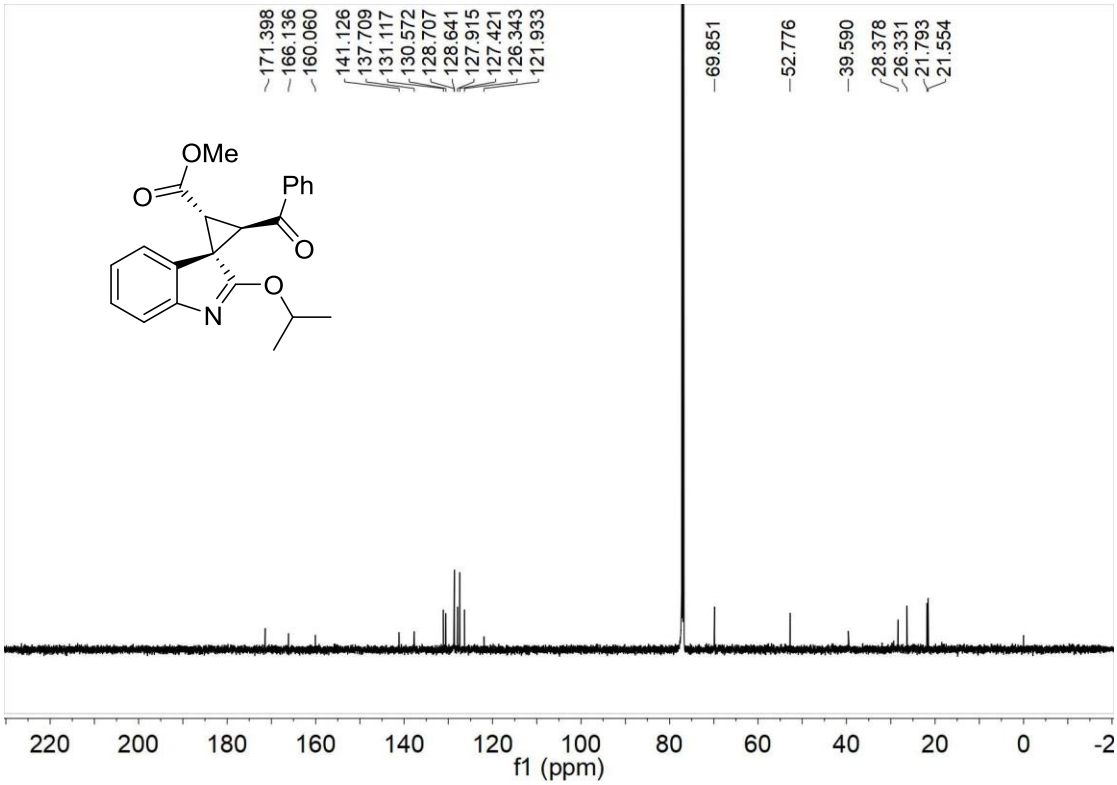


Figure 96. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4au**

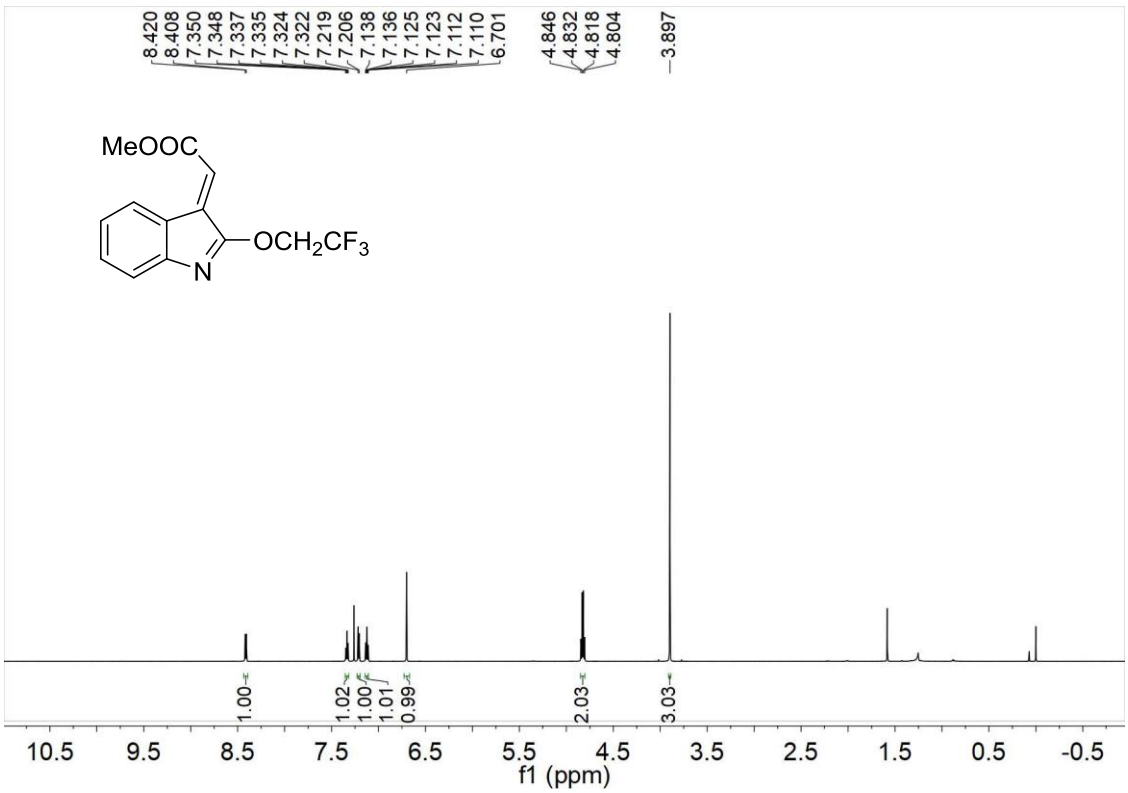


Figure 97. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **5a**

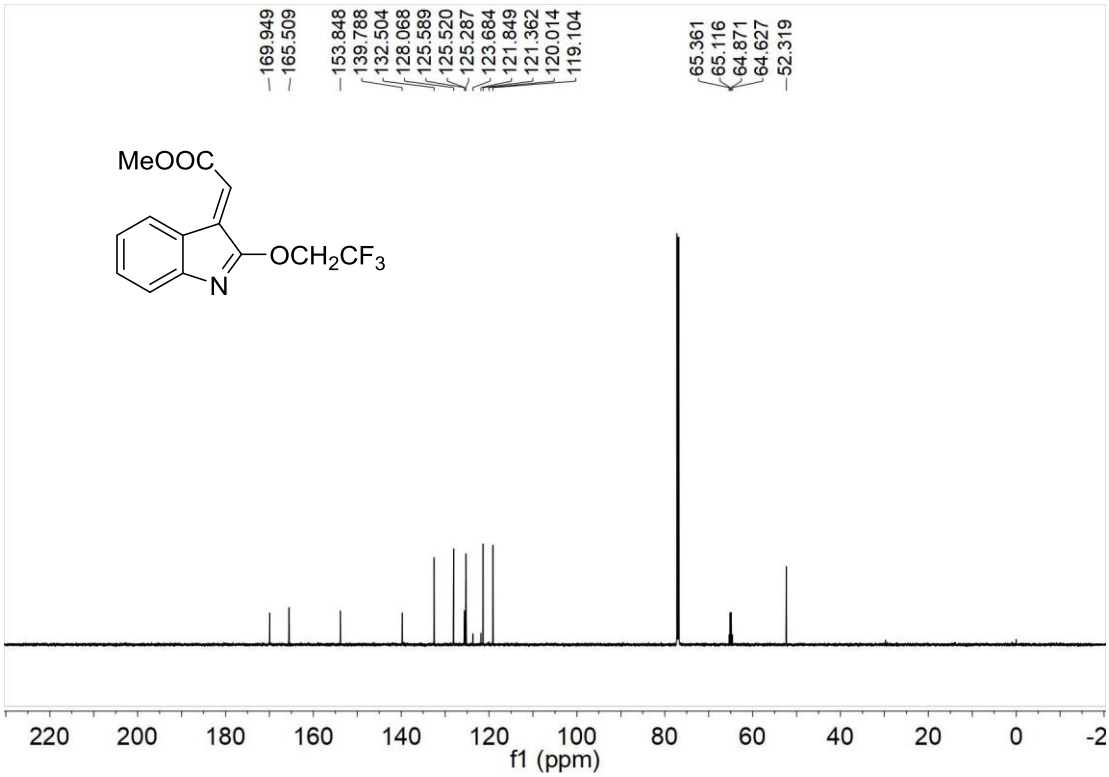


Figure 98. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **5a**

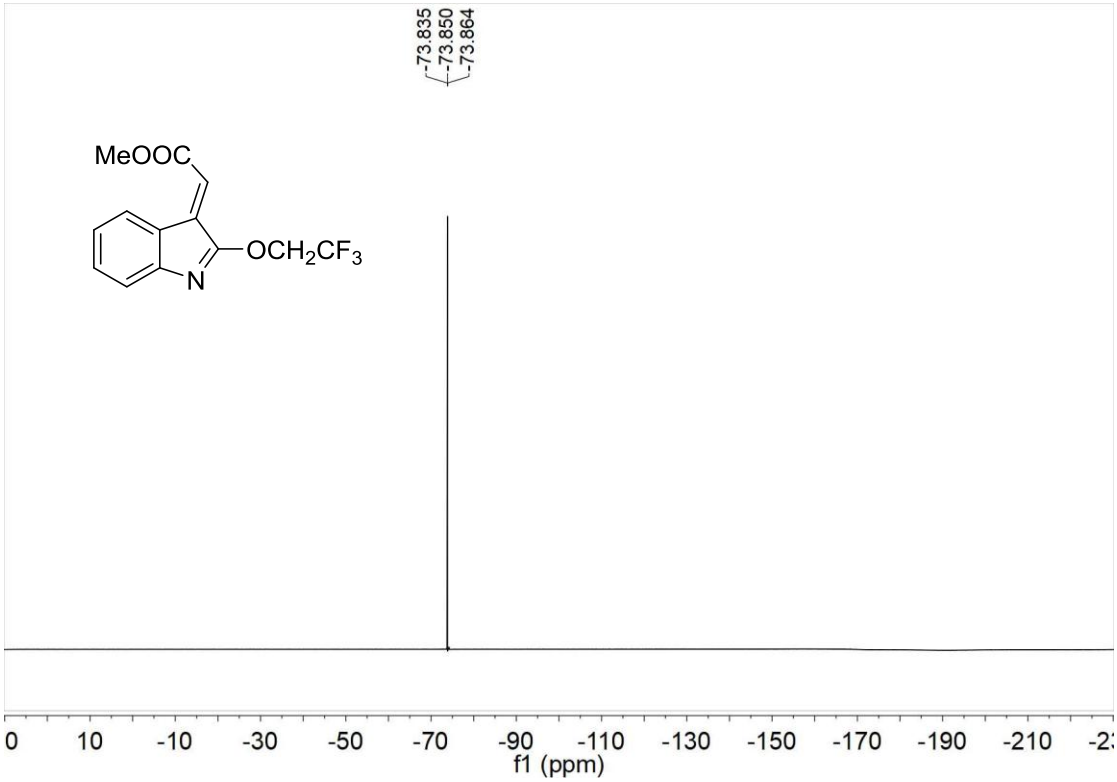


Figure 99. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **5a**

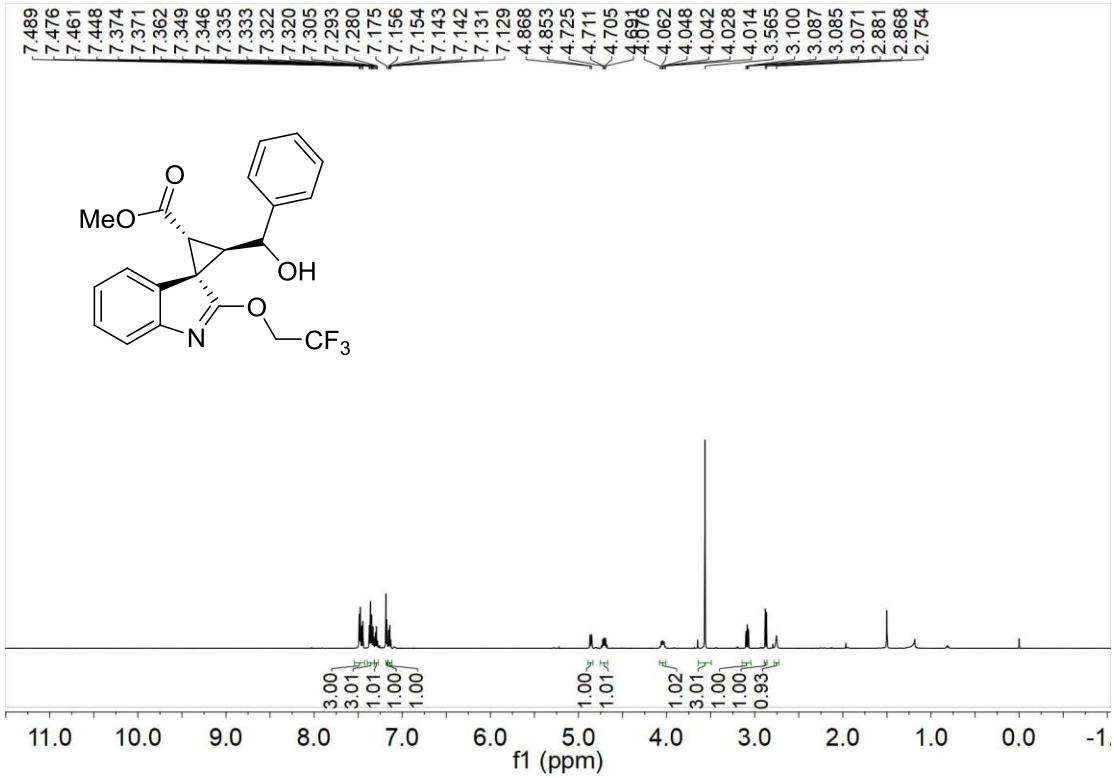


Figure 100. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **6a**

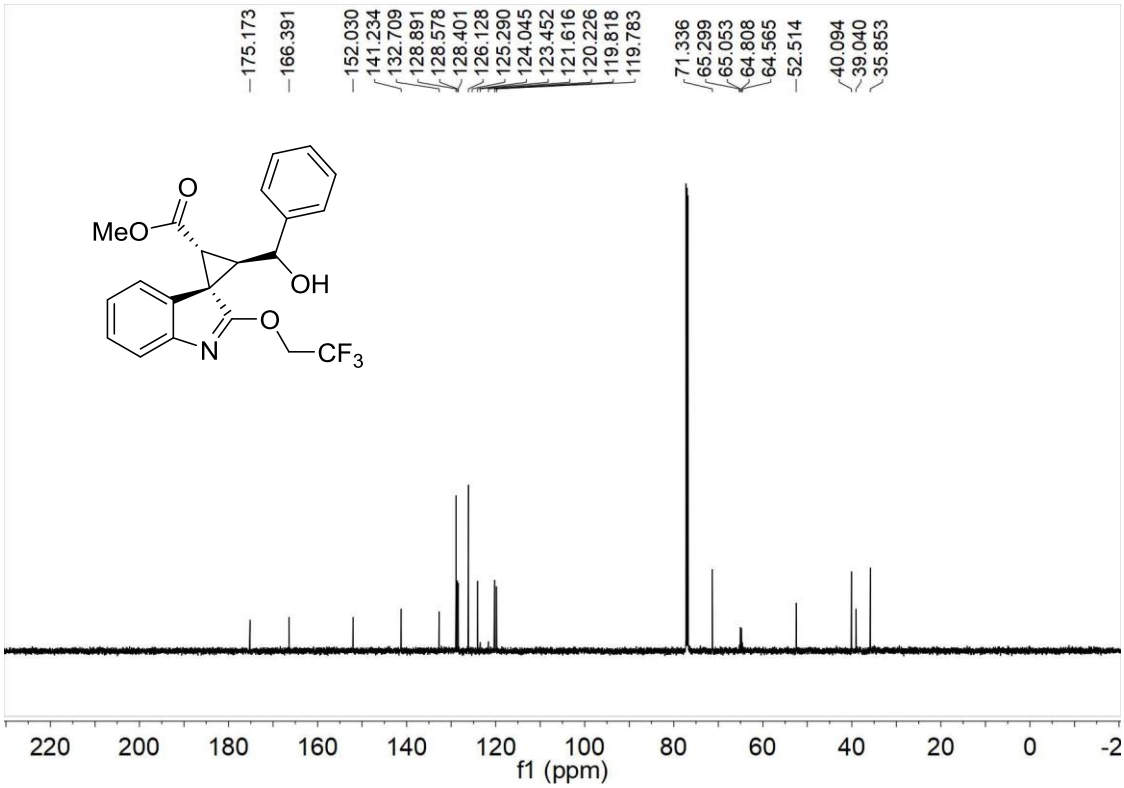


Figure 101. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **6a**

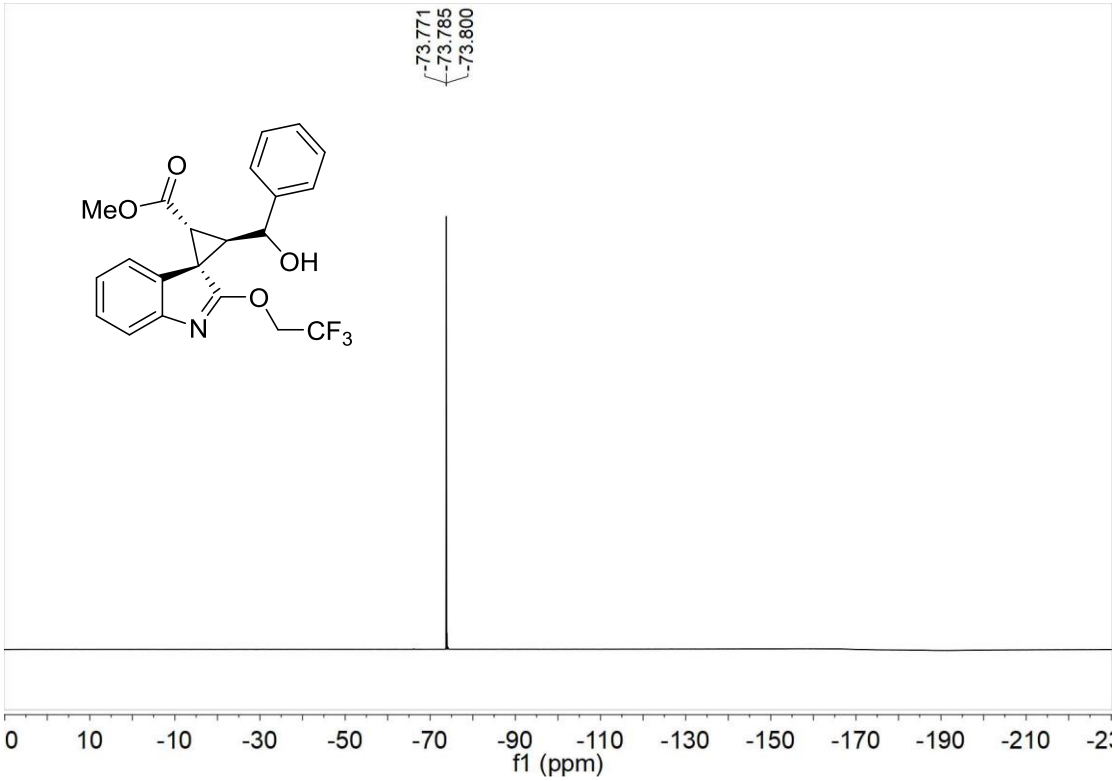


Figure 102. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **6a**

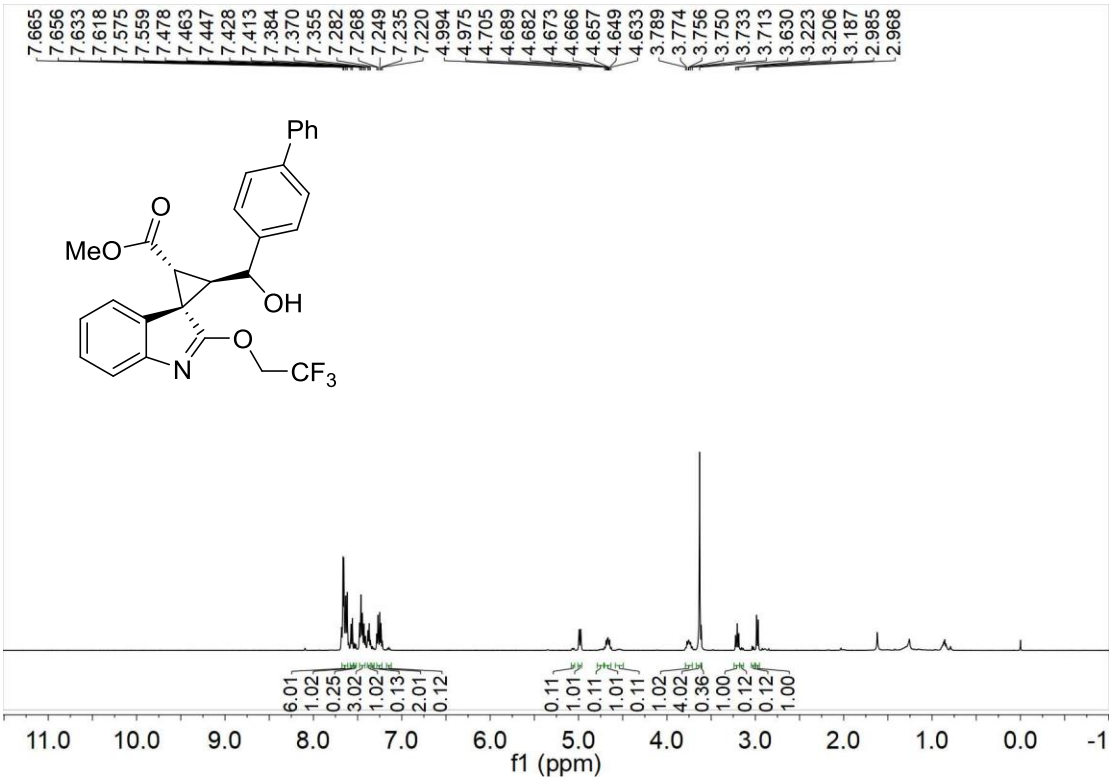


Figure 103. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6b**

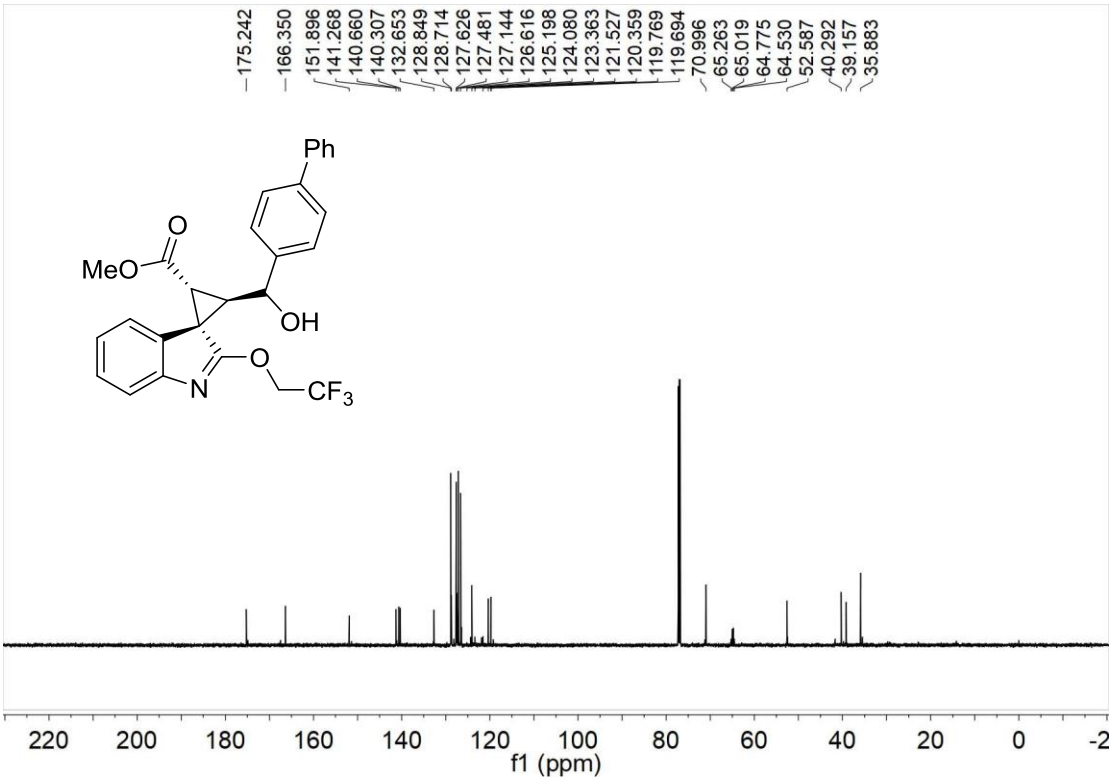


Figure 104. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **6b**

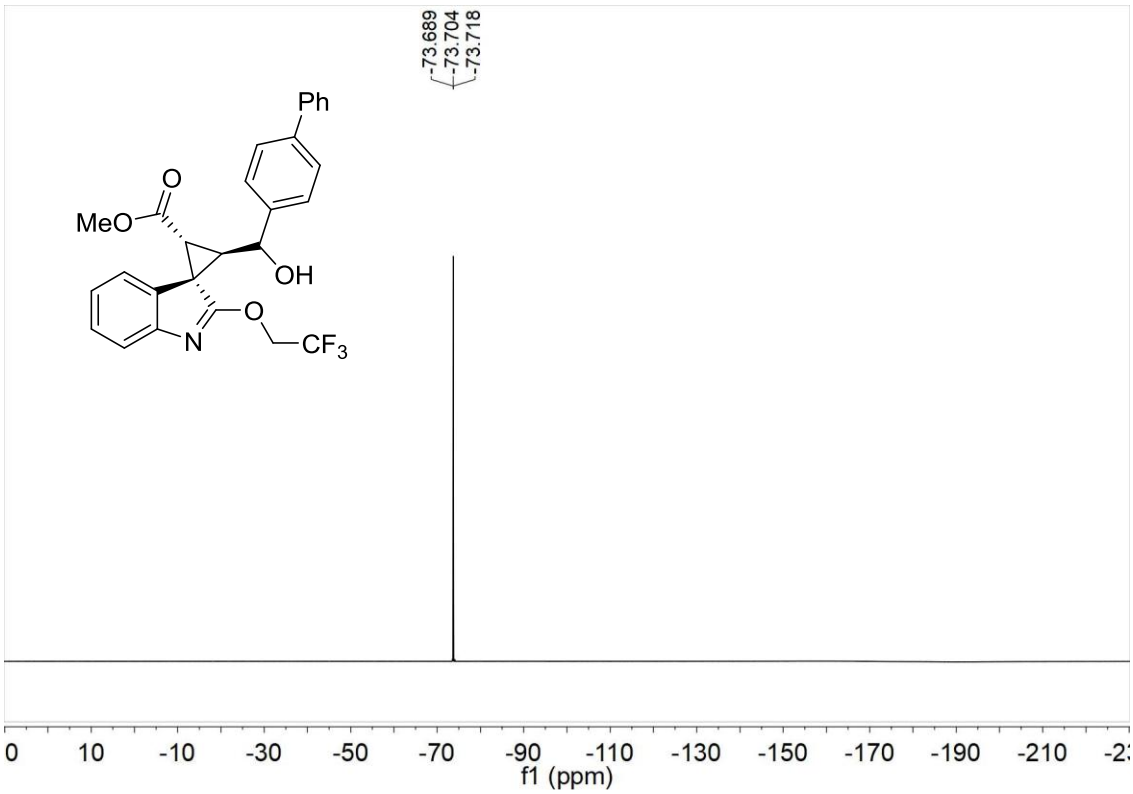


Figure 105. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **6b**

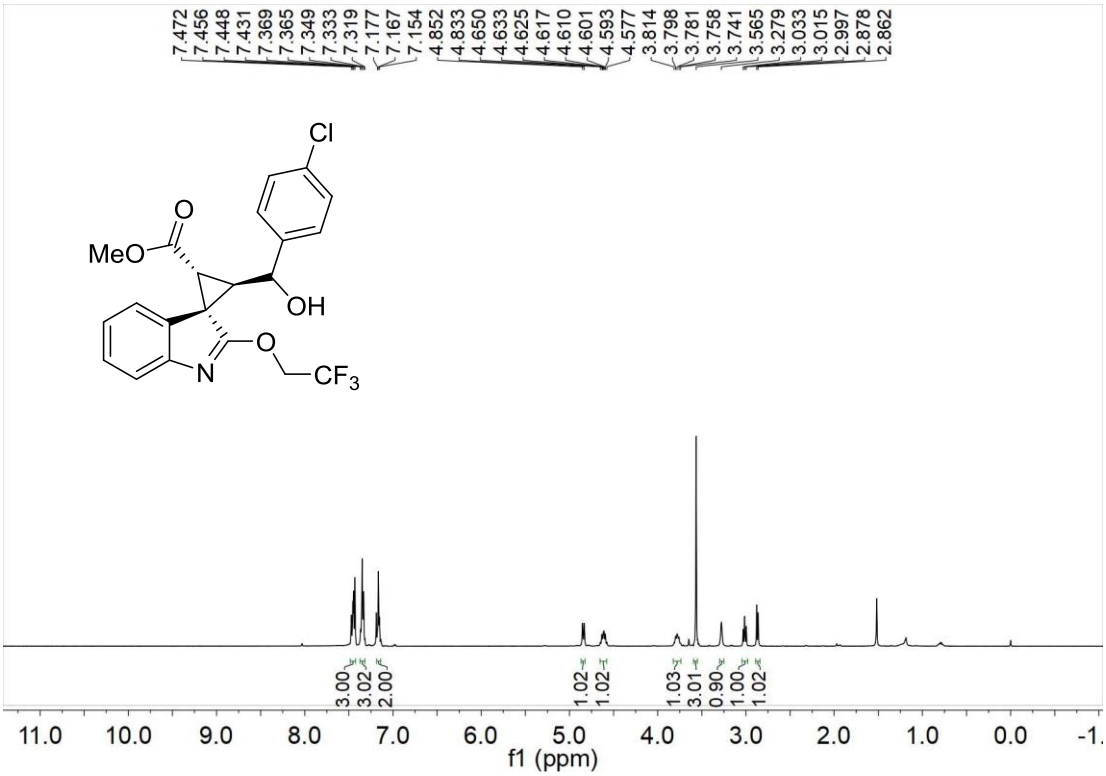


Figure 106. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6c**

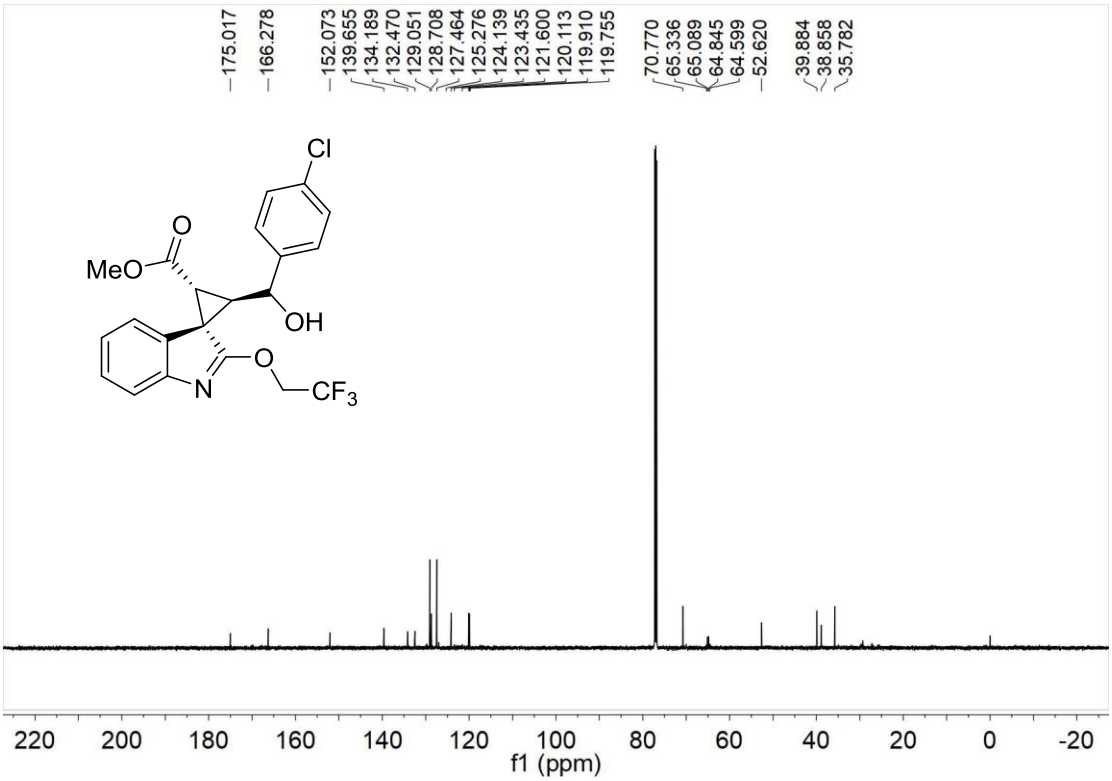


Figure 107. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **6c**

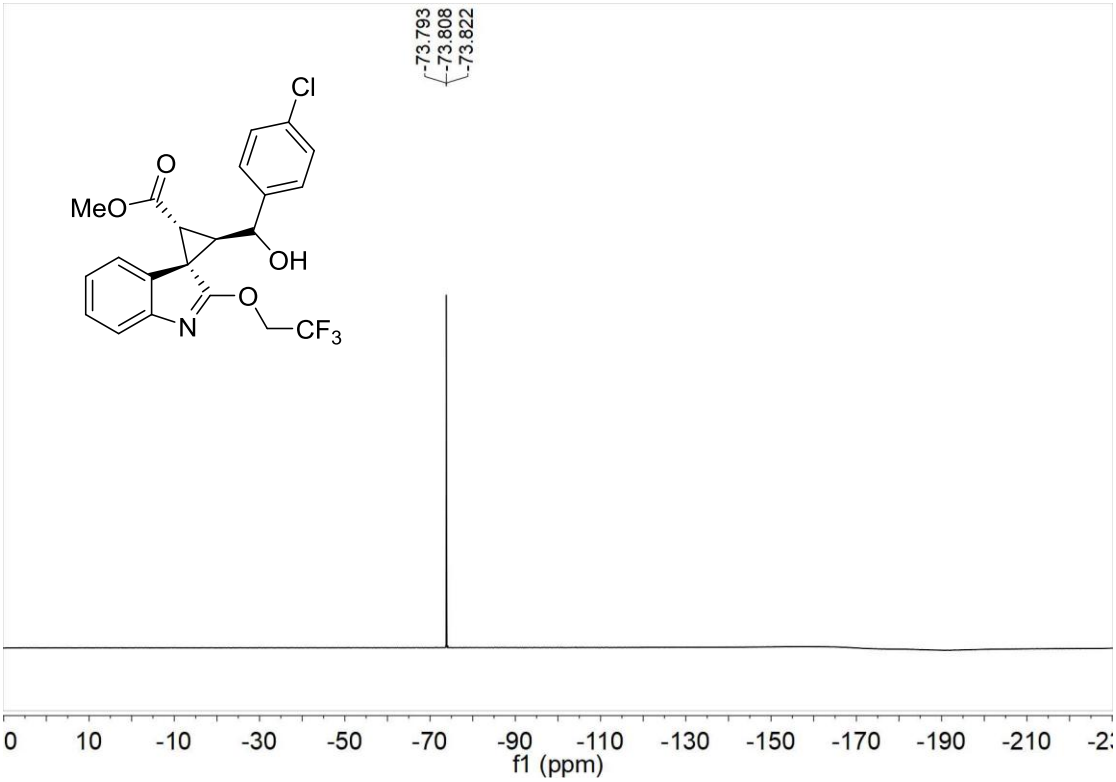


Figure 108. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **6c**

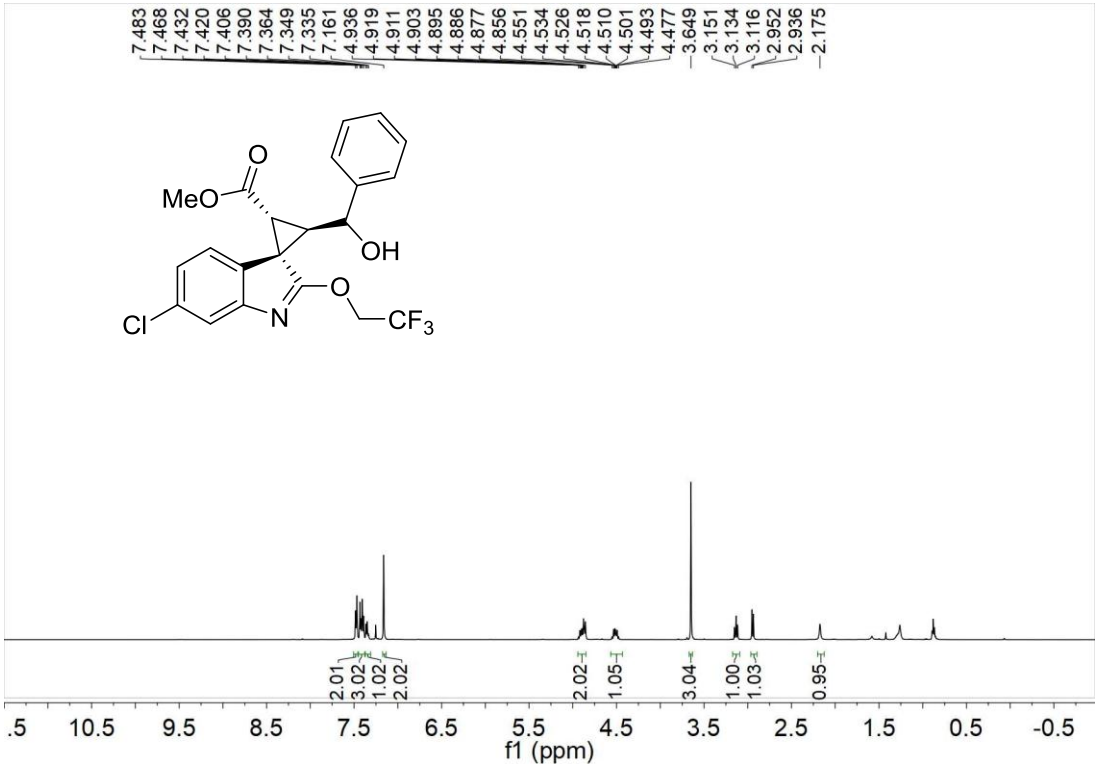


Figure 109. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6d**

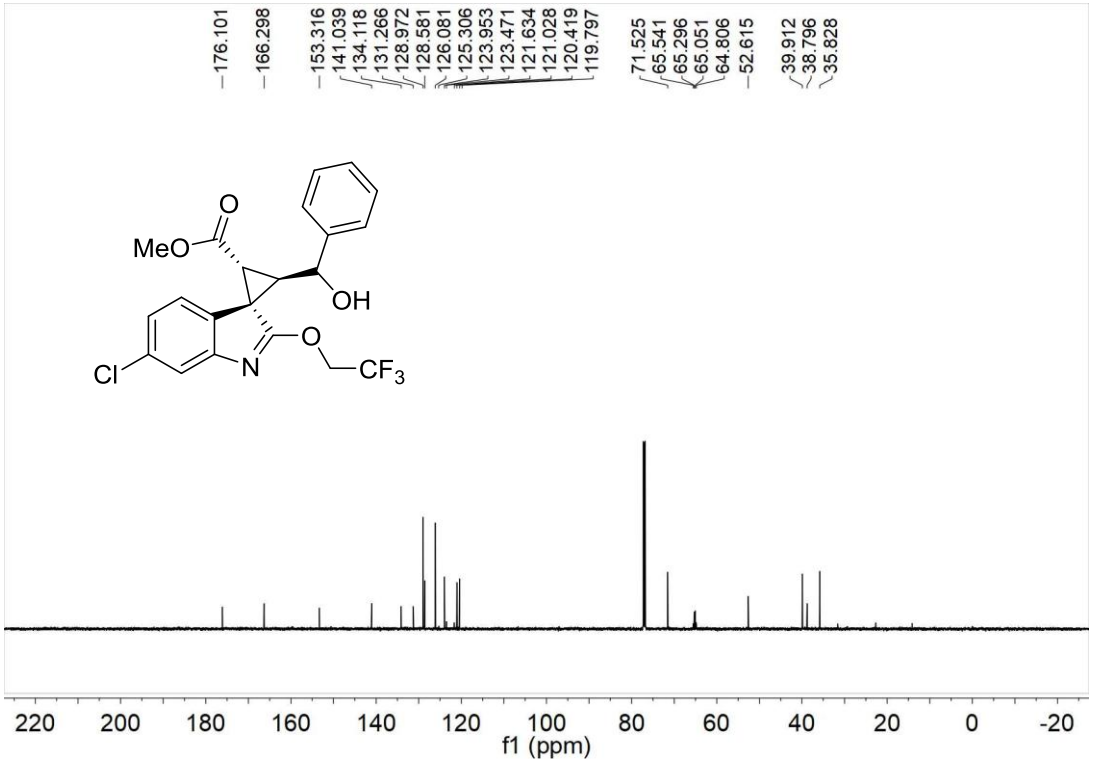


Figure 110. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **6d**

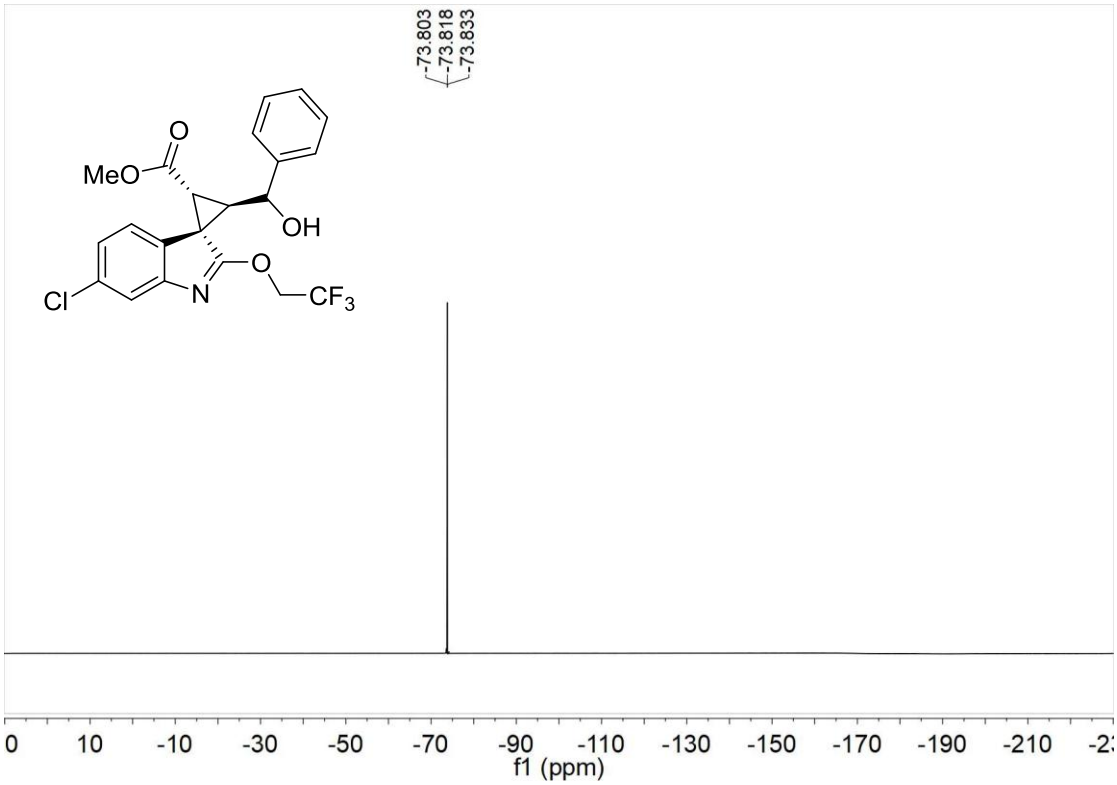


Figure 111. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **6d**

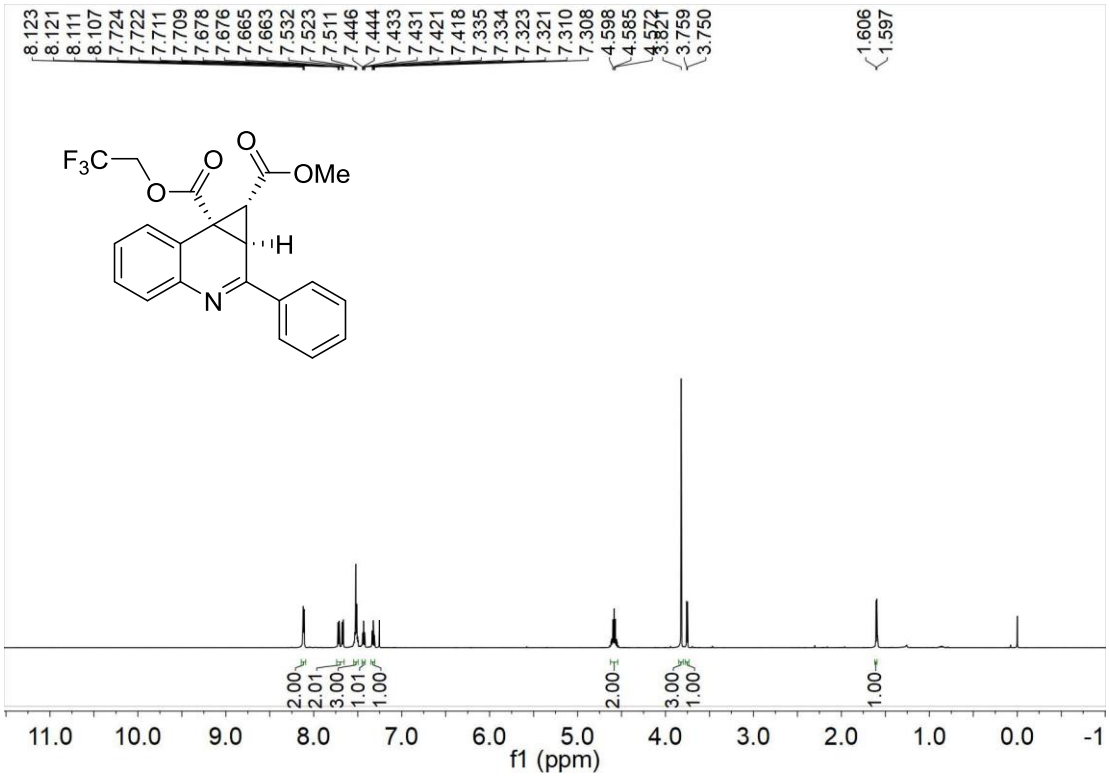


Figure 112. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **7a**

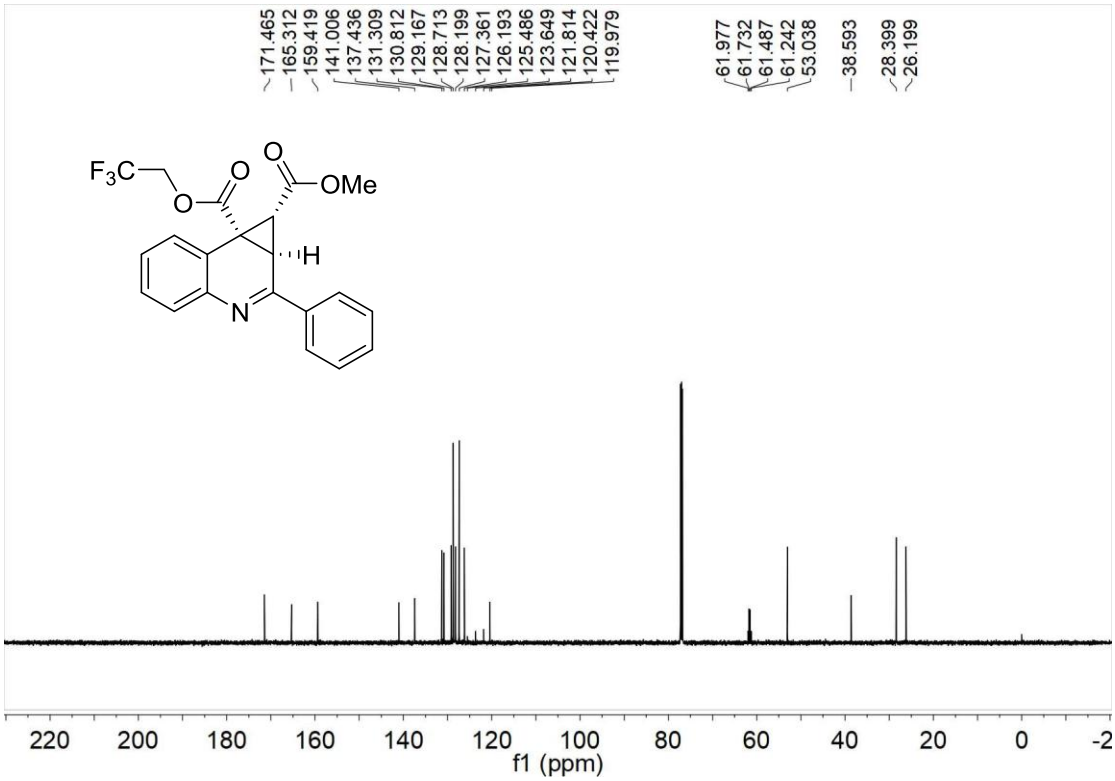


Figure 113. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7a**

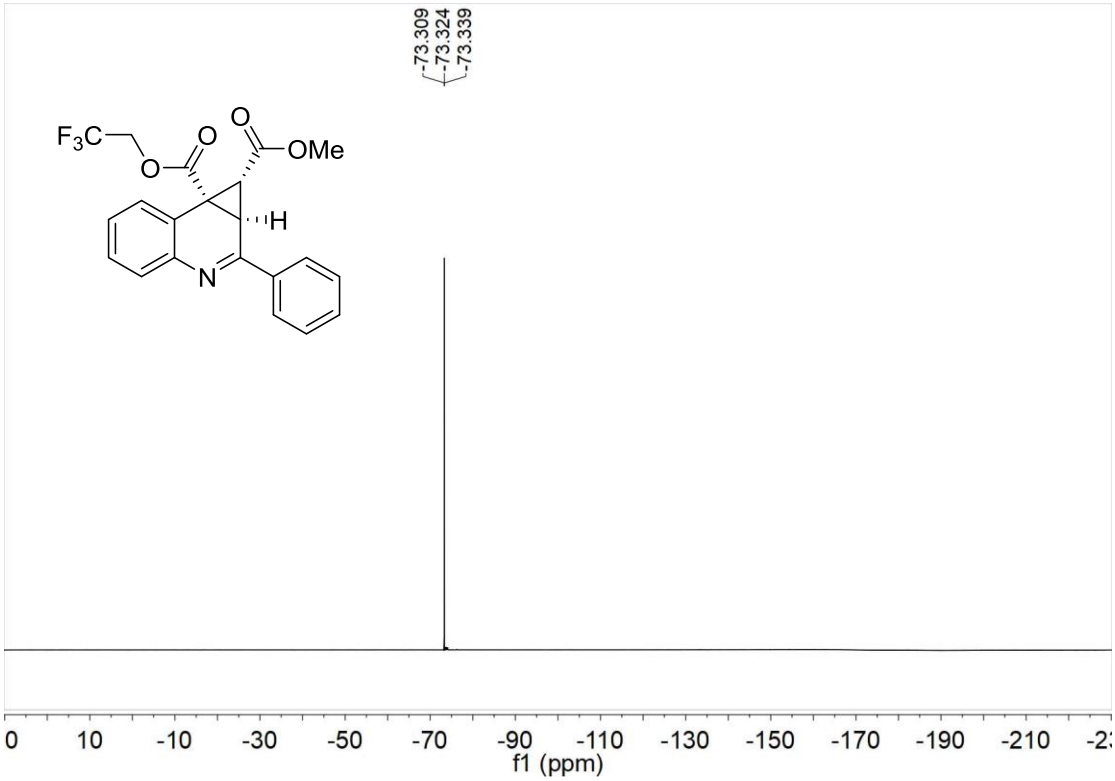


Figure 114. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **7a**

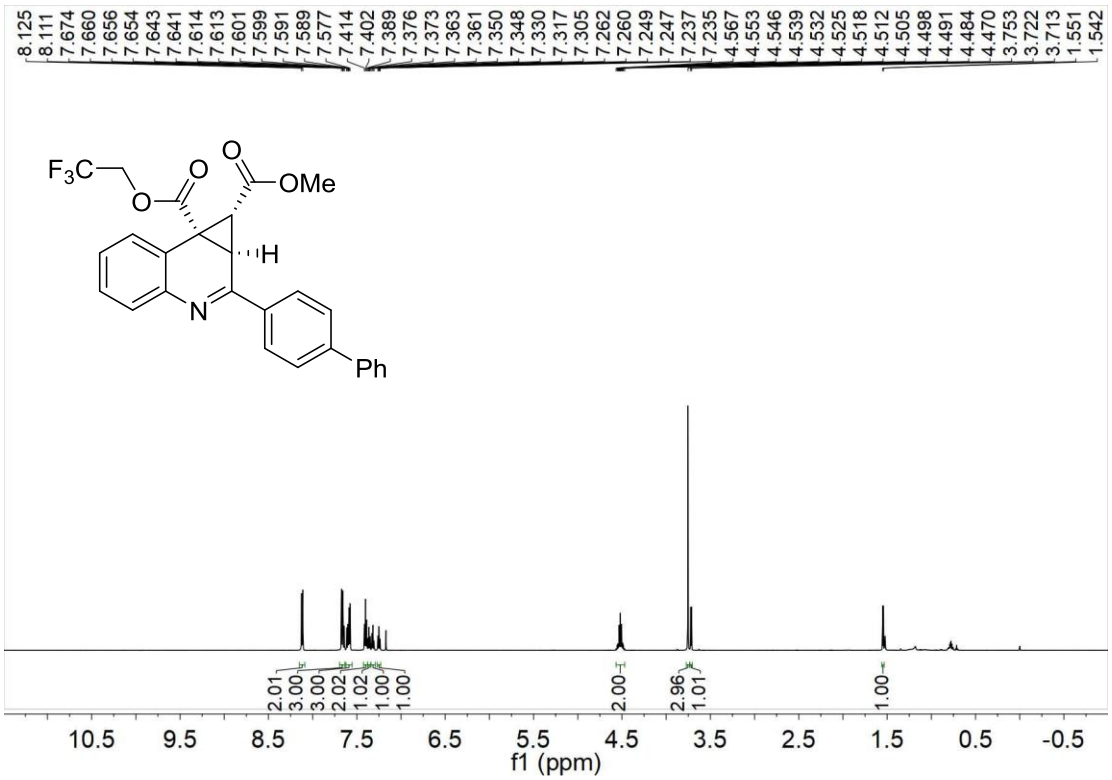


Figure 115. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7b**

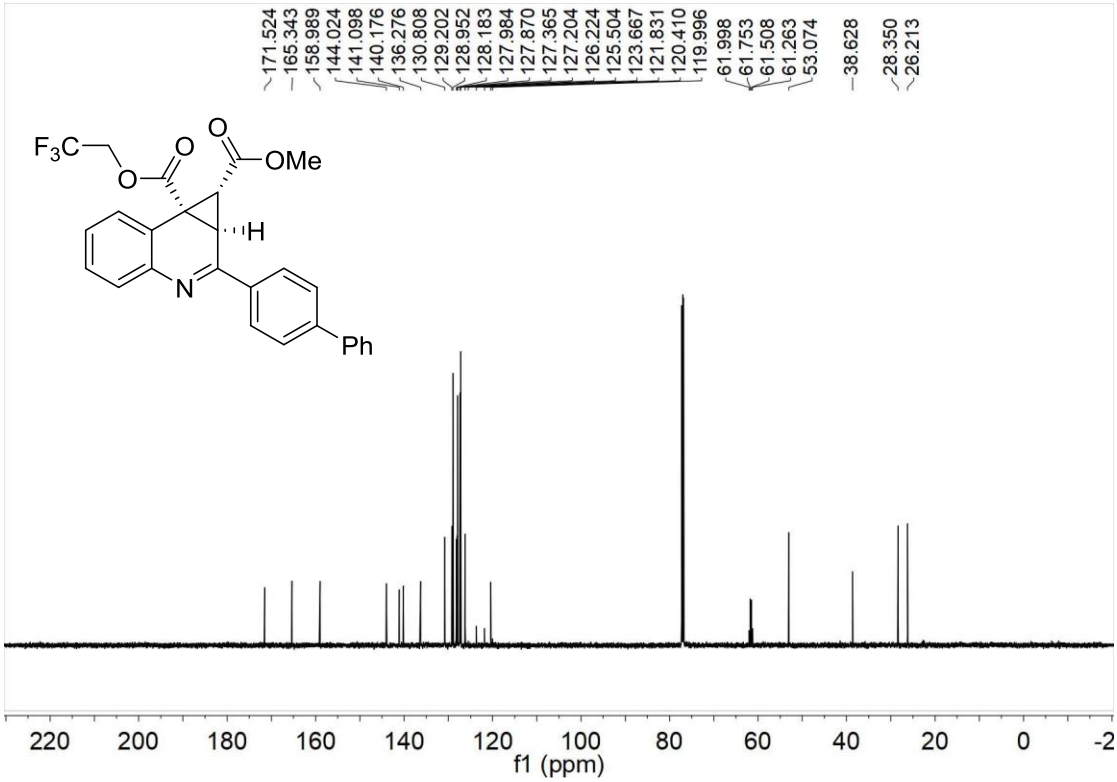


Figure 116. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7b**

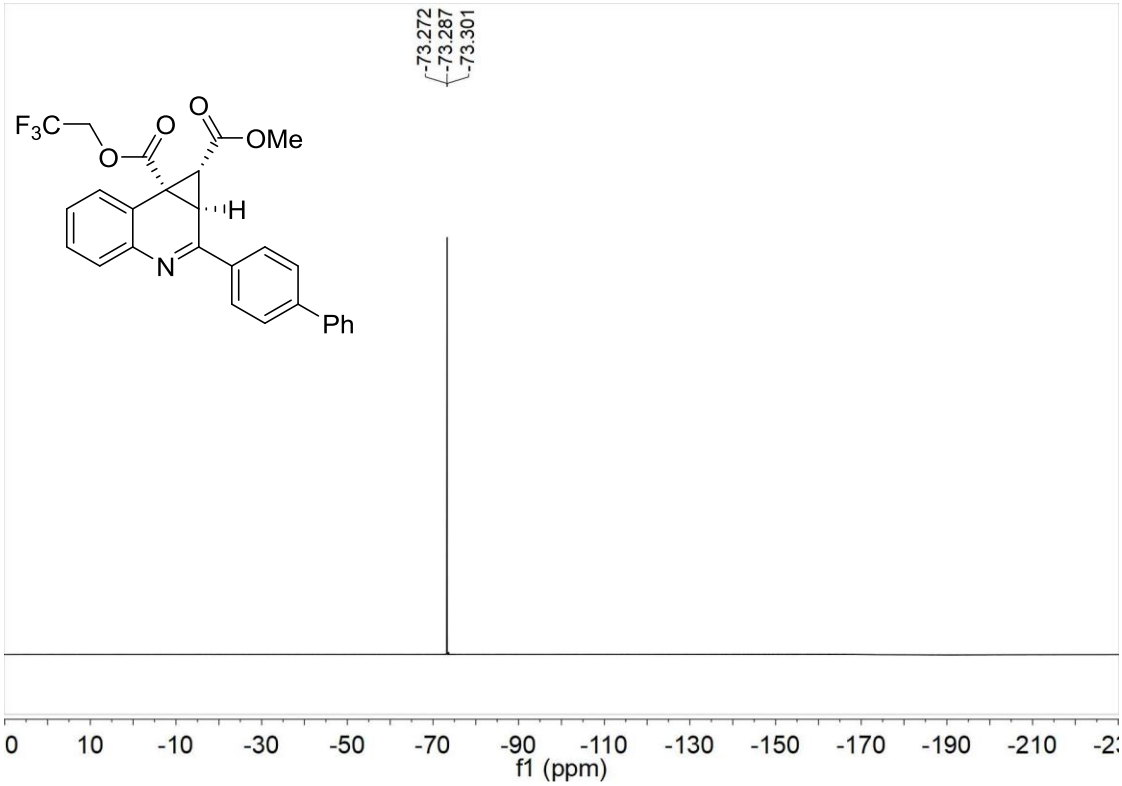


Figure 117. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **7b**

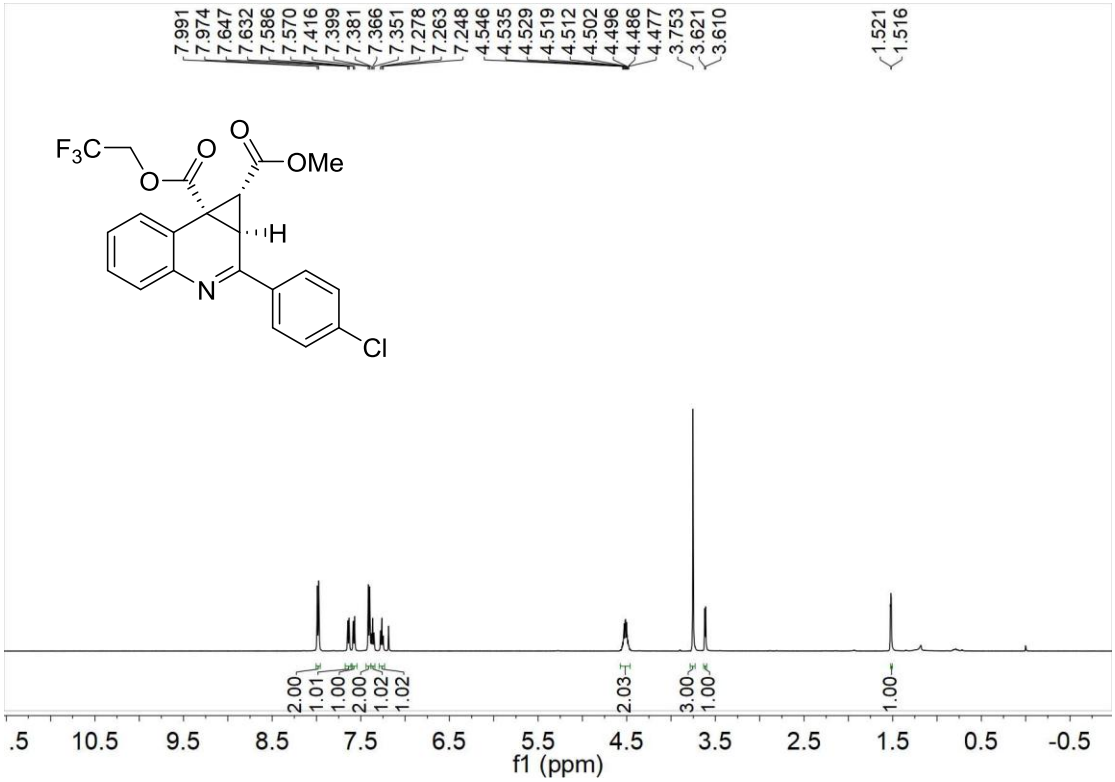


Figure 118. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7c**

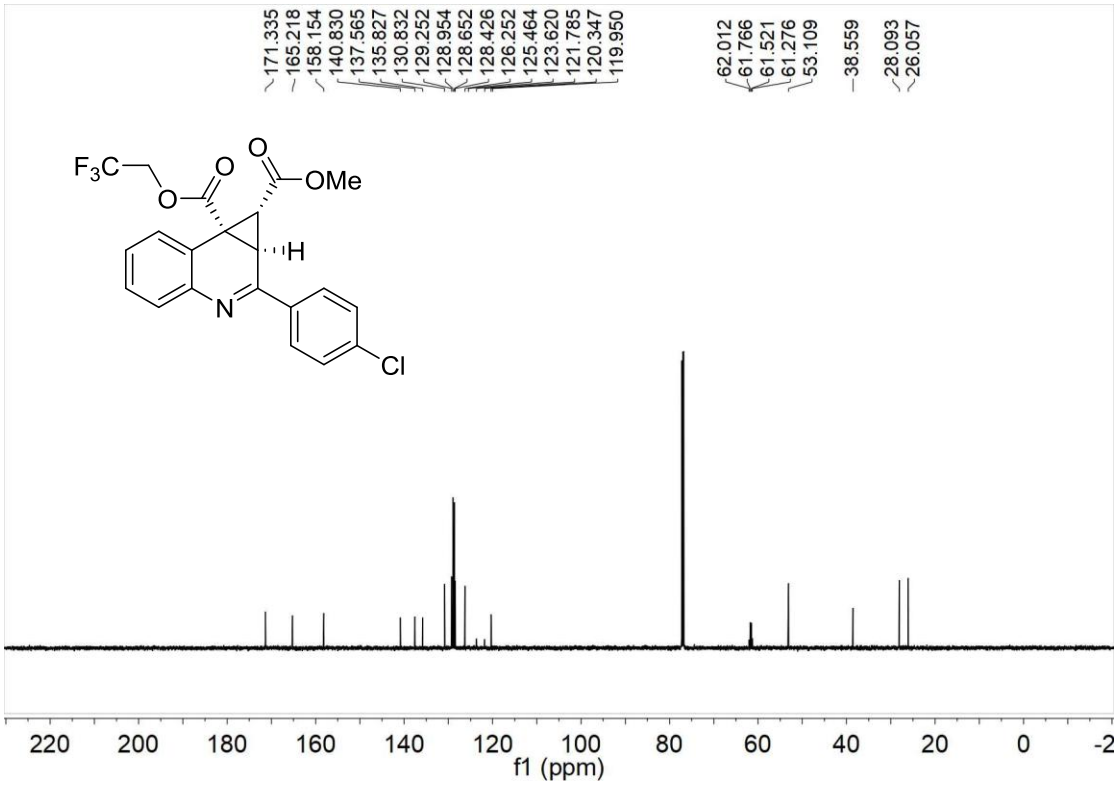


Figure 119. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7c**

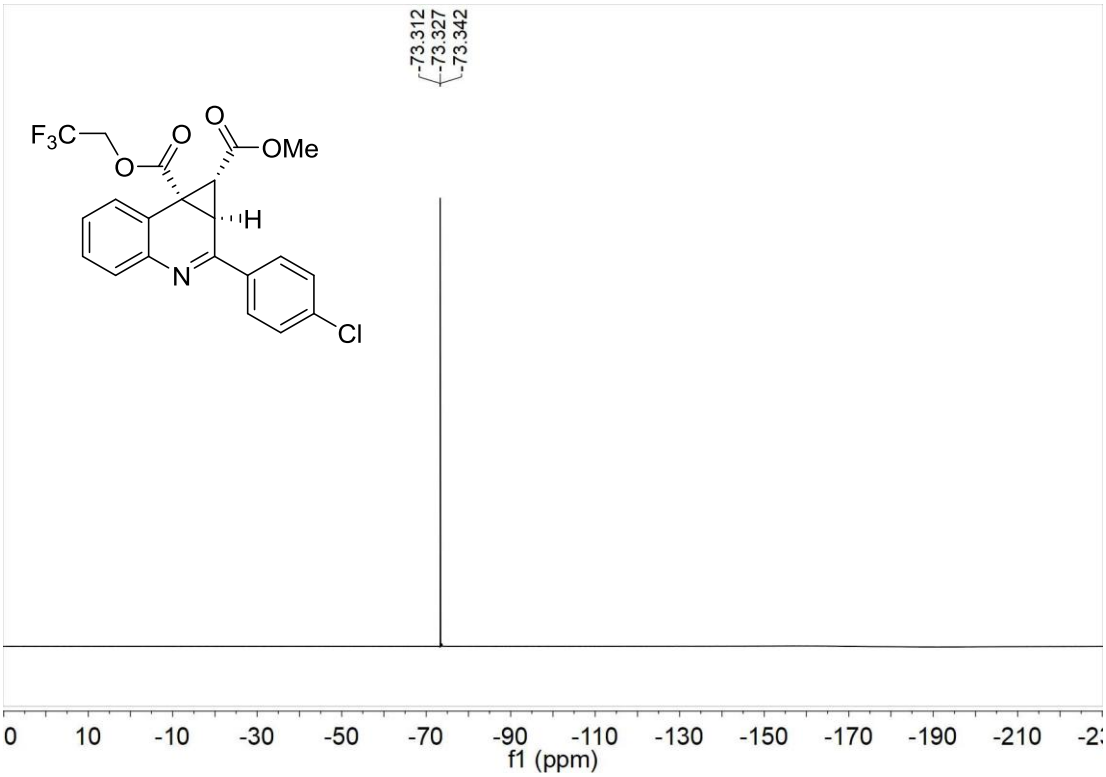


Figure 120. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **7c**

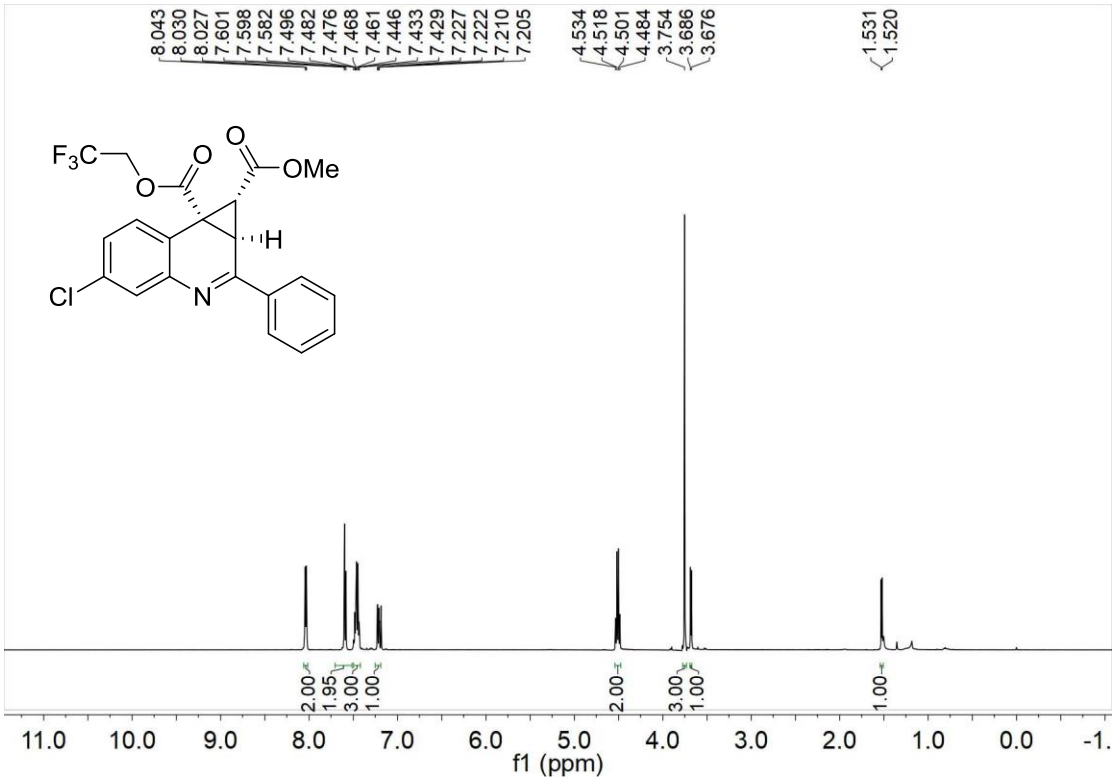


Figure 121. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7d**

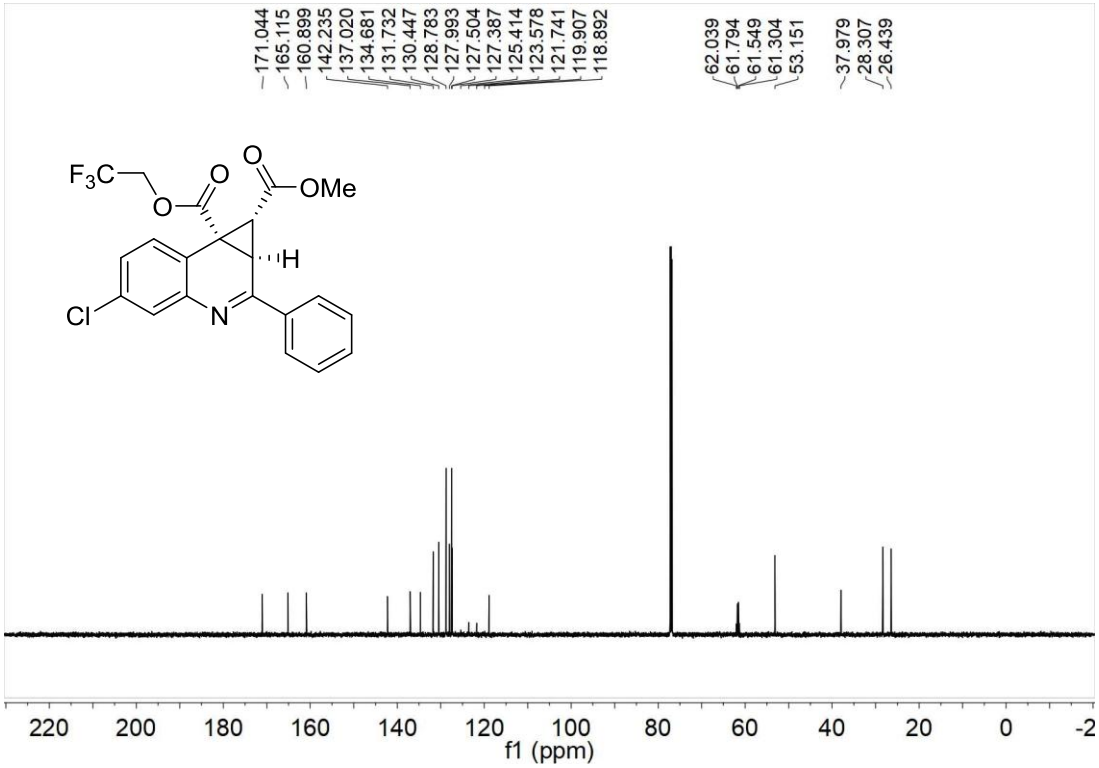


Figure 122. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **7d**

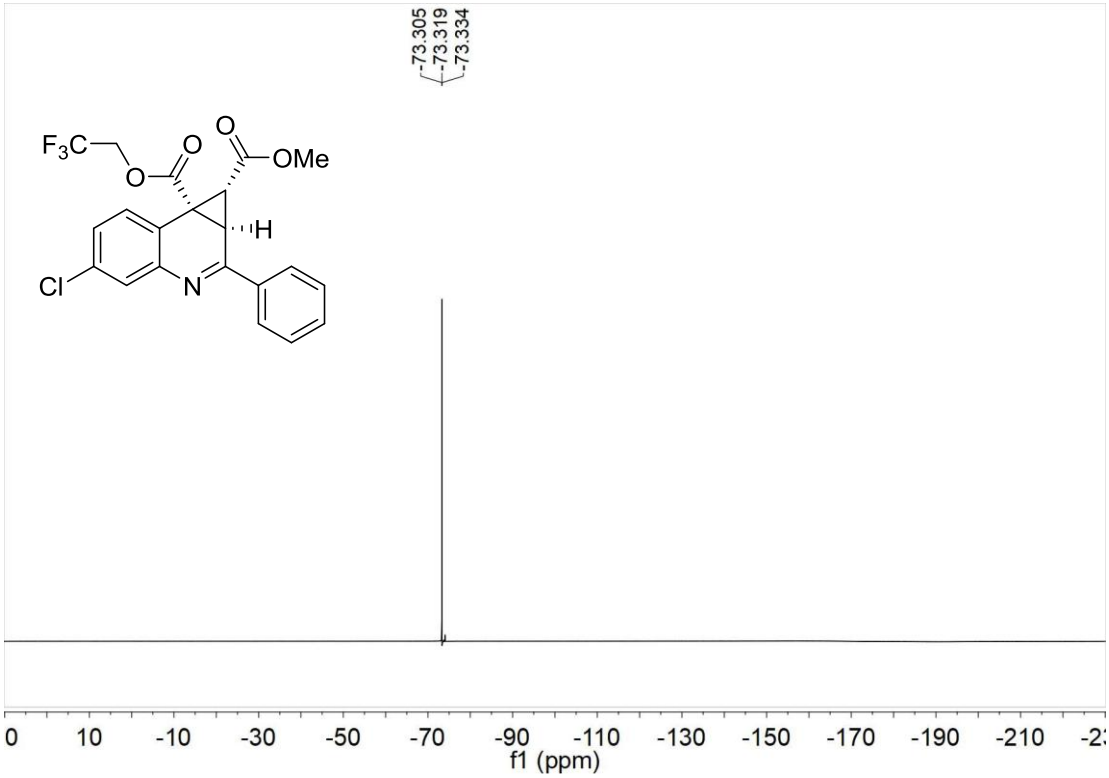


Figure 123. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **7d**