Supporting Information

Diastereodivergent Synthesis of Fully Disubstituted Spiro[indoline-3,2'-pyrrolidin]-2-ones via Tuneable Lewis base/Brønsted base-promoted (3+2) Cycloadditions

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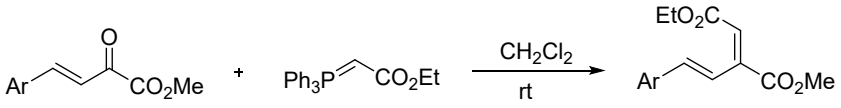
1. General experimental details.

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. All commercially available reagents were used without further purification.

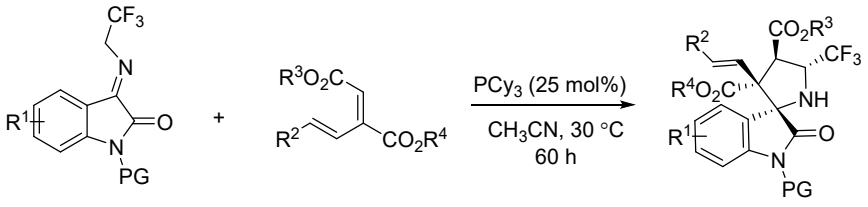
2. General procedure for synthesis of diene [1].



2

The general procedure was followed at r.t. with β, γ-unsaturated α-keto esters **1** (5 mmol, 1.0 equiv) and ylide (5 mmol, 1.0 equiv) in 50 mL of DCM. When completed, the resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30 - 60 ºC, 4 × 30 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 20% EtOAc in petroleum ether) to provide the diene **2** as yellow oil.

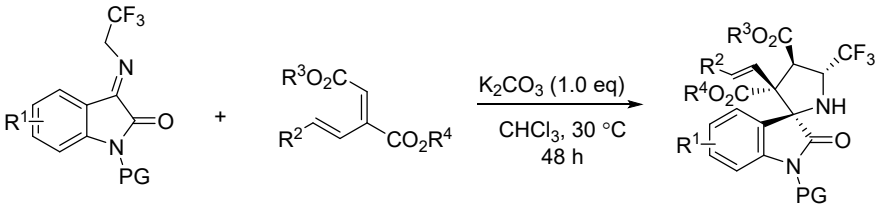
3. General Procedure for Reactions



1 **2** ***endo*-3**

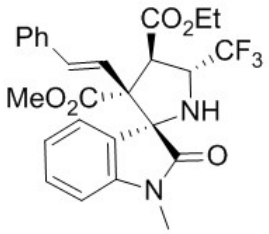
To a dry flask filled with nitrogen were added **1**[2] (0.15 mmol) and **2** (0.23 mmol) in 2 mL CH_3CN, PCy_3 (0.037 mmol) was next added. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After

the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: EtOAc / petroleum ether = 6:1) to afford ***endo*-3**.



1 **2** ***exo*′-4**

To a dry flask filled with nitrogen were added **1**[2] (0.15 mmol) and **2** (0.23 mmol) in 2 mL $CHCl_3$, K_2CO_3 (0.15 mmol) was next added. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: EtOAc / petroleum ether = 6:1) to afford **4**.

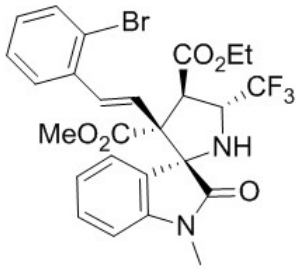


4'-Ethyl 3'-methyl 1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3a.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3a** (49.7 mg, 66% yield).

Yellow solid. **MP**: 91.2-92.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43-7.21 (m, 8H), 7.07 (dd, *J* = 11.1, 4.2 Hz, 1H), 6.81 (dd, *J* = 12.0, 9.1 Hz, 2H, CH=C), 6.14 (d, *J* = 16.4 Hz, 1H, C=CH), 4.89-4.78 (m, 1H, CH), 4.45 (d, *J* = 10.1 Hz, 1H, CH), 4.07 (q, *J* = 7.1 Hz, 2H, CH_2), 3.17 (s, 3H, OCH_3), 3.14 (s, 3H, N-CH_3), 1.13 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.4 (s, C=O), 169.0 (s, C=O), 168.0 (s, C=O), 143.2 (s, C), 136.4 (s, C), 131.6 (s, CH), 130.0 (s, C), 129.7 (s, CH), 128.6 (s, 2CH, CH, =CH), 128.0 (s, CH), 126.7 (s, 2CH, CH, =CH), 125.7 (q, *J* = 278.2 Hz,

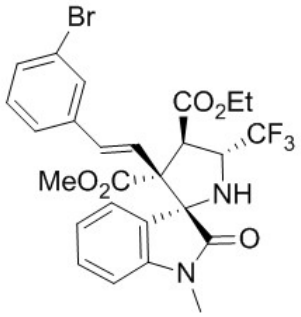
CF_3),124.6 (s, CH), 123.3 (s, CH), 123.0 (s, CH), 108.0 (s, CH), 73.3 (s, C), 68.8 (s, C), 61.8 (s, CH_2), 61.0 (s, OCH_3) ,60.6 (s, CH), 52.0 (s, N-CH_3), 26.9 (s, CH), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.17 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{26}F_3N_2O_5$ 503.1788; Found 503.1791.



4'-Ethyl 3'-methyl 3'-((E)-2-bromostyryl)-1-methyl-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3b.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (76.1 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3b** (57.4 mg, 66% yield).

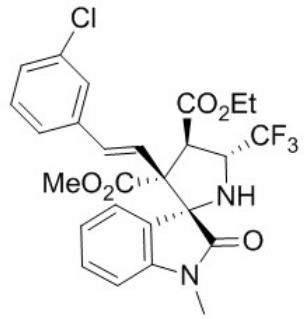
Yellow solid. **MP**: 116.7-117.5 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (d, J = 6.9 Hz, 1H), 7.46 (dd, J = 16.9, 7.7 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.10 (dd, J = 15.1, 7.2 Hz, 2H), 6.78 (dd, J = 18.2, 12.0 Hz, 2H, ArH, CH=C), 6.50 (d, J = 16.3 Hz, 1H, C=CH), 4.93-4.77 (m, 1H, CH), 4.47 (d, J = 10.0 Hz, 1H, CH), 4.16 (dd, J = 13.7, 6.9 Hz, 2H, CH_2), 3.18 (d, J = 3.5 Hz, 6H, N-CH_3, OCH_3), 2.86 (s, 1H, NH), 1.20 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.3 (s, C=O), 168.7 (s, C=O), 168.1 (s, C=O), 143.2 (s, C), 136.5 (s, C), 133.2 (s, C), 132.6 (s, CH), 130.5 (s, CH), 129.8 (s, CH), 129.3 (s, CH), 127.8 (d, J = 2.5 Hz, 2CH), 127.1 (q, J = 273.0 Hz, CF_3), 126.3 (s, CH), 124.6 (d, J = 3.0 Hz, CH), 123.5 (s, C), 123.1 (s, CH), 108.0 (s, CH), 73.5 (s, C), 68.7 (s, C), 62.1 (s, CH_2), 62.0 (s, OCH_3), 52.0 (s, CH), 51.8 (s, N-CH_3), 26.9 (s, CH), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.09 (d, J = 5.6 Hz, 2F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}BrF_3N_2O_5$ 581.0893; Found 581.0915.



4'-Ethyl 3'-methyl 3'-((E)-3-bromostyryl)-1-methyl-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3c.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (76.1 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3c** (57.4 mg, 66% yield).

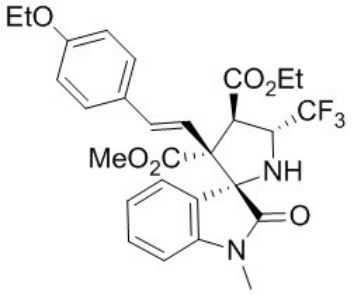
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.45-7.28 (m, 4H), 7.13 (dt, *J* = 28.4, 7.7 Hz, 2H), 6.89-6.77 (m, 2H, ArH, CH=C), 6.08 (d, *J* = 16.4 Hz, 1H, C=CH), 4.91-4.72 (m, 1H, CH), 4.44 (d, *J* = 10.2 Hz, 1H, CH), 4.10 (q, *J* = 7.1 Hz, 2H, CH_2), 3.26 (d, *J* = 10.0 Hz, 1H, NH), 3.17 (d, *J* = 7.7 Hz, 6H, N-CH_3, OCH_3), 1.15 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.2 (s, C=O), 168.7 (s, C=O), 168.0 (s, C=O), 143.2 (s, C), 138.5 (s, C), 130.9 (s, CH), 130.2 (s, CH), 130.0 (s, CH), 129.9 (s, C), 129.8 (s, CH), 129.6 (s, CH), 128.7 (q, *J* = 273.0 Hz, CF_3), 125.2 (s, CH), 125.1 (s, CH), 124.5 (d, *J* = 2.2 Hz, CH), 123.5 (s, CH), 122.8 (s, C), 108.1 (s, CH), 73.3 (s, C), 68.7 (s, C), 61.9 (s, CH_2), 60.7 (s, OCH_3), 52.1(s, CH), 51.9 (s, N-CH_3), 26.9 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.12 (d, *J* = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}BrF_3N_2O_5$ 581.0893; Found 581.0887.



4'-Ethyl 3'-methyl 3'-((E)-3-chlorostyryl)-1-methyl-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3d.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (66.1 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3d** (49.0 mg, 61% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65-7.28 (m, 4H), 7.23 (dd, *J* = 4.0, 2.2 Hz, 2H), 7.14-7.04 (m, 1H), 6.82 (dd, *J* = 11.9, 7.6 Hz, 2H, ArH, CH=C), 6.09 (d, *J* = 16.4 Hz, 1H, C=CH), 4.81 (dd, *J* = 15.3, 7.6 Hz, 1H, CH), 4.44 (d, *J* = 10.1 Hz, 1H, CH), 4.09 (q, *J* = 7.1 Hz, 2H, CH_2), 3.16 (d, *J* = 7.8 Hz, 6H, N-CH_3, OCH_3), 1.15 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.2 (s, C=O), 168.7 (s, C=O), 168.0 (s, C=O), 143.2 (s, C), 138.2 (s, C), 134.6 (s, C), 130.1 (s, CH), 129.9 (s, C), 129.8 (d, *J* = 4.5 Hz, 2CH), 128.0 (s, CH), 127.1 (q, *J* = 275.3 Hz, CF_3), 126.6 (s, CH), 125.1 (s, CH), 124.8 (s, CH), 124.6 (d, *J* = 3 Hz, CH), 123.0 (s, CH), 108.1 (s, CH), 73.3 (s, C), 68.7 (s, C), 61.8 (s, CH_2), 61.0 (s, OCH_3), 52.1 (s, CH), 51.9 (s, N-CH_3), 26.9 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.12 (d, *J* = 8.5 Hz, 2F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClF_3N_2O_5$ 537.1399; Found 537.1392.

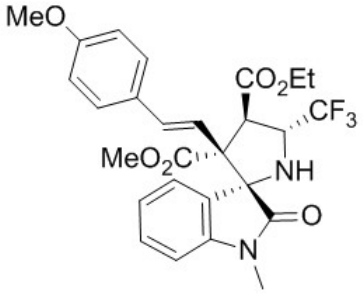


4'-Ethyl 3'-methyl 3'-((E)-4-ethoxystyryl)-1-methyl-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3e.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (68.4 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3e** (35.2 mg, 43% yield).

Yellow solid. **MP**: 124.3-125.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44-7.28 (m, 4H), 7.13-7.02 (m, 1H), 6.87-6.76 (m, 3H), 6.68 (d, *J* = 16.4 Hz, 1H, CH=C), 6.06 (d, *J* = 16.4 Hz, 1H, C=CH), 4.90-4.76 (m, 1H, CH), 4.43 (d, *J* = 10.1 Hz, 1H, CH), 4.04 (dq,

J = 13.8, 7.0 Hz, 4H, $2CH_2$), 3.24 (d, *J* = 8.8 Hz, 1H, NH), 3.16 (s, 3H, OCH_3), 3.12 (s, 3H, N-CH_3), 1.41 (t, *J* = 7.0 Hz, 3H, CH_3), 1.12 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.4 (s, C=O), 169.1 (s, C=O), 168.0 (s, C=O), 158.9 (s, C), 143.2 (s, C), 131.0 (s, CH), 130.1 (s, C), 129.7 (s, CH), 129.0 (s, C), 127.9 (q, *J* = 276.7 Hz, CF_3), 127.9 (s, 2CH), 124.6 (d, *J* = 3.0 Hz, CH), 122.9 (s, CH), 120.8 (s, CH), 114.6 (s, 2CH), 107.9 (s, CH), 73.3 (s, C), 68.9 (s, C), 63.5 (s, CH_2), 61.7 (s, CH_2), 61.0 (s, OCH_3), 52.1 (s, CH), 52.0 (s, N-CH_3), 26.9 (s, CH), 14.8 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.17 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}F_3N_2O_6$ 547.2050; Found 547.2069.

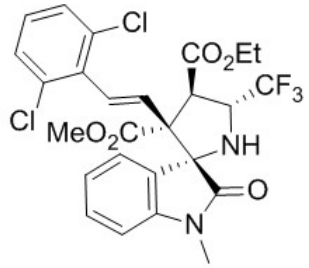


4'-Ethyl 3'-methyl 3'-((E)-4-methoxystyryl)-1-methyl-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3f.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (65.3 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3f** (42.3 mg, 53% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.09-6.97 (m, 2H), 6.85-6.78 (m, 3H), 6.69 (d, *J* = 16.4 Hz, 1H, CH=C), 6.07 (d, *J* = 16.4 Hz, 1H, C=CH), 4.88-4.80 (m, 1H, CH), 4.43 (d, *J* = 10.1 Hz, 1H, CH), 4.07 (q, *J* = 7.1 Hz, 2H, CH_2), 3.80 (s, 3H, OCH_3), 3.67 (s, 1H, NH), 3.15 (d, *J* = 10.4 Hz, 6H, N-CH_3, OCH_3), 1.12 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.3 (s, C=O), 169.1 (s, C=O), 168.0 (s, C=O), 159.6 (s, C), 143.3 (s, C), 131.0 (s, CH), 130.0 (s, C), 129.7 (s, CH), 129.2 (s, C), 127.9 (s, 2CH), 125.7 (q, *J* = 273.0 Hz, CF_3), 124.6 (d, *J* = 3 Hz, CH), 123.0 (s, CH), 120.9 (s, CH), 114.0 (s, 2CH), 108.0 (s, CH), 73.3 (s, C), 68.8 (s, C), 61.7 (s, CH_2), 55.3 (s, OCH_3), 55.2 (s, OCH_3), 52.1 (s, CH), 52.0 (s, N-CH_3), 26.9 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz,

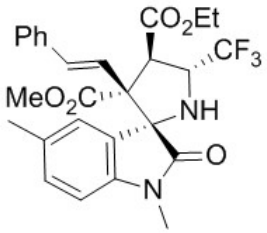
$CDCl_3$) δ -75.02 (d, J = 8.5 Hz, 2F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}F_3N_2O_6$ 533.1894; Found 533.1905.



4'-Ethyl 3'-methyl 3'-((E)-2,6-dichlorostyryl)-1-methyl-2-oxo-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3g.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (73.8 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3g** (47.0 mg, 55% yield).

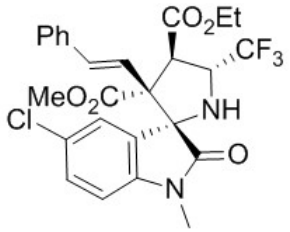
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 1H), 7.35-7.23 (m, 3H), 7.06 (dd, J = 16.6, 9.3 Hz, 3H), 6.80 (d, J = 7.7 Hz, 1H, CH=C), 6.35 (d, J = 16.8 Hz, 1H, C=CH), 4.81 (s, 1H, CH), 4.50 (d, J = 10.2 Hz, 1H, CH), 4.18 (tt, J = 7.8, 4.0 Hz, 2H, CH_2), 3.24 (s, 1H, NH), 3.18 (s, 6H, N-CH_3, OCH_3), 1.20 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.1 (s, C=O), 168.7 (s, C=O), 167.7 (s, C=O), 143.3 (s, C), 138.2 (s, C), 134.4 (s, 2C), 132.8 (s, C), 131.7 (s, CH), 129.8 (s, CH), 128.7 (s, 2CH), 128.5 (s, CH), 126.8 (s, CH), 125.7 (q, J = 278.2 Hz, CF_3), 124.8 (d, J = 2.2 Hz, CH), 122.9 (s, CH), 107.9 (s, CH), 73.6 (s, C), 69.4 (s, C), 61.9 (s, CH_2), 60.9 (s, OCH_3), 52.0(s, CH), 51.8 (s, N-CH_3), 26.8 (s, CH), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.90 (d, J = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}Cl_2F_3N_2O_5$ 571.1009; Found 571.0993.



4'-Ethyl 3'-methyl 1,5-dimethyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3h.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (38.4 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3h** (41.0 mg, 53% yield).

Yellow solid. **MP**: 130.6-131.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.28 (m, 4H), 7.24 (d, *J* = 3.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 16.4 Hz, 1H, CH=C), 6.69 (d, *J* = 7.9 Hz, 1H, ArH), 6.14 (d, *J* = 16.4 Hz, 1H, C=CH), 4.85-4.81 (m, 1H, CH), 4.46 (d, *J* = 10.1 Hz, 1H, CH), 4.09 (q, *J* = 7.1 Hz, 2H, CH_2), 3.14 (s, 6H, N-CH_3, OCH_3), 2.34 (s, 3H, CH_3), 1.14 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.3 (s, C=O), 169.0 (s, C=O), 168.0 (s, C=O), 140.8 (s, C), 138.7 (s, C), 136.4 (s, C), 132.6 (s, C), 131.4 (s, CH), 129.9 (s, CH), 128.6 (s, 2CH), 128.2 (q, *J* = 273.0 Hz, CF_3), 128.0 (s, CH), 126.7 (s, 2CH), 125.4 (d, *J* = 3 Hz, CH), 123.4 (s, CH), 107.7 (s, CH), 73.4 (s, C), 68.8 (s, C), 61.8 (s, CH_2), 60.6 (s, OCH_3), 52.1 (s, CH), 52.0 (s, N-CH_3), 26.9 (s, CH), 21.2 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.03 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}F_3N_2O_5$ 517.1945; Found 517.1957.

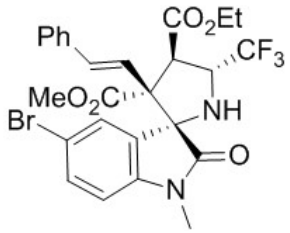


4'-Ethyl 3'-methyl 5-chloro-1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3i.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (44.1 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3i** (37.8 mg, 47% yield).

Yellow solid. **MP**: 116.8-117.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (ddd, *J* = 17.6, 8.5, 2.0 Hz, 6H), 7.23 (d, *J* = 7.1 Hz, 1H), 6.75 (dd, *J* = 14.6, 12.4 Hz, 2H, ArH, CH=C), 6.16 (d, *J* = 16.4 Hz, 1H, C=CH), 4.84 (dd, *J* = 15.7, 8.6 Hz, 1H, CH), 4.39 (d, *J* = 10.1 Hz, 1H, CH), 4.08 (q, *J* = 7.1 Hz, 2H, CH_2), 3.24 (s, 3H, OCH_3), 3.15 (s, 3H, N-CH_3), 1.13 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.0 (s, C=O), 168.7 (s, C=O), 167.8 (s, C=O), 141.8 (s, C), 136.2 (s, C), 131.8 (s, CH), 131.7

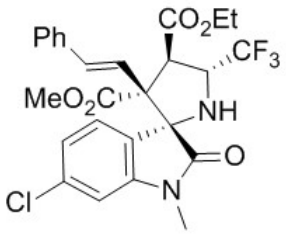
(s, C), 129.6 (s, CH), 128.7 (s, 2CH), 128.4 (s, C), 128.2 (s, CH), 126.9 (q, J = 271.5 Hz, CF_3), 126.7 (s, 2CH), 125.1 (d, J = 2.2 Hz, CH), 122.9 (s, CH), 108.9 (s, CH), 73.4 (s, C), 68.7 (s, C), 61.9 (s, CH_2), 60.6 (s, OCH_3), 52.2 (s, CH), 51.9 (s, N-CH_3), 27.0 (s, CH), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.26 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClF_3N_2O_5$ 537.1399; Found 537.1409.



4'-Ethyl 3'-methyl 5-bromo-1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3j.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (48.0 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3j** (40.0 mg, 46% yield).

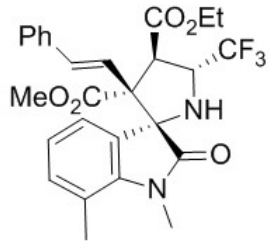
Yellow solid. **MP**: 137.1-138.0 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55-7.27 (m, 6H), 7.23 (d, J = 7.0 Hz, 1H), 6.72 (dd, J = 25.9, 12.3 Hz, 2H, ArH, CH=C), 6.16 (d, J = 16.4 Hz, 1H, C=CH), 4.86 (dt, J = 16.5, 8.2 Hz, 1H, CH), 4.39 (d, J = 10.1 Hz, 1H, CH), 4.08 (q, J = 7.1 Hz, 2H, CH_2), 3.24 (s, 3H, OCH_3), 3.14 (s, 3H, N-CH_3), 1.13 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.9 (s, C=O), 168.7 (s, C=O), 167.8 (s, C=O), 142.3 (s, C), 136.2 (s, C), 132.5 (s, CH), 132.1 (s, C), 131.8 (s, CH), 128.6 (s, 2CH), 128.2 (s, CH), 127.8 (d, J = 2.2 Hz, CH), 126.8 (q, J = 278.2 Hz, CF_3), 126.7 (s, 2CH), 112.9 (s, CH), 115.6 (s, C), 109.4 (s, CH), 73.4 (s, C), 68.7 (s, C), 61.9 (s, CH_2), 61.1 (s, OCH_3), 52.2 (s, CH), 51.9 (s, N-CH_3), 27.0 (s, CH), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -76.71 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}BrF_3N_2O_5$ 581.0893; Found 581.0937.



4'-Ethyl 3'-methyl 6-chloro-1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3k.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (41.4 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3k** (77.2 mg, 96% yield).

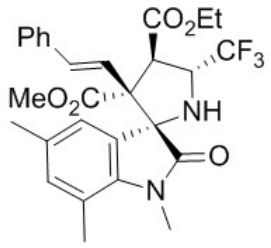
Yellow solid. **MP**: 151.5-152.3 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44-7.30 (m, 5H), 7.27 (t, *J* = 5.7 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.79 (d, *J* = 16.3 Hz, 2H, ArH, CH=C), 6.15 (d, *J* = 16.4 Hz, 1H, C=CH), 4.84 (dd, *J* = 14.5, 7.4 Hz, 1H, CH), 4.40 (d, *J* = 10.1 Hz, 1H, CH), 4.08 (q, *J* = 7.1 Hz, 2H, CH_2), 3.23 (s, 3H, OCH_3), 3.15 (s, 3H, N-CH_3), 1.13 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.3 (s, C=O), 168.9 (s, C=O), 167.8 (s, C=O), 144.5 (s, C), 136.3 (s, C), 135.6 (s, C), 131.8 (s, CH), 128.6 (s, 2CH), 128.5 (s, C), 128.1 (s, CH), 126.7 (s, 2CH), 126.4 (q, *J* = 276.0 Hz, CF_3), 125.6 (d, *J* = 3.7 Hz, CH), 122.9 (s, CH), 122.7 (s, CH), 108.7 (s, CH), 73.0 (s, C), 68.8 (s, C), 61.9 (s, CH_2), 60.6 (s, OCH_3), 52.2 (s, CH), 52.0 (s, N-CH_3), 27.0 (s, CH), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.22 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClF_3N_2O_5$ 537.1399; Found 537.1392.



4'-Ethyl 3'-methyl 1,7-dimethyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3l.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (38.4 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3l** (48.0 mg, 62% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.09-7.01 (m, 5H), 6.96-6.94 (m, 2H), 6.85 (d, *J* = 6.7 Hz, 2H, C=CH), 5.35 (s, 1H, NH), 4.78 (d, *J* = 7.9 Hz, 1H, CH), 4.40 (d, *J* = 8.4 Hz, 1H, CH), 4.23 (dt, *J* = 10.8, 3.7 Hz, 2H, CH_2), 3.89 (s, 3H, OCH_3), 3.07 (s, 3H, N-CH_3), 2.26 (s, 3H, CH_3), 1.26 (dd, *J* = 8.9, 5.3 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.3 (s, C=O), 169.0 (s, C=O), 168.0 (s, C=O), 144.0 (s, CH), 143.2 (s, C), 138.1 (s, C), 136.6 (s, C), 131.7 (s, C), 130.1 (s, CH), 129.7 (s, CH), 128.9 (s, CH), 128.5 (s, CH), 127.2 (q, *J* = 275.2 Hz, CF_3), 127.1 (s, CH), 124.6 (d, *J* = 2.2 Hz, CH), 124.0 (s, CH), 122.9 (s, CH), 122.8 (s, CH), 73.3 (s, C), 68.9 (s, C), 61.8 (s, CH_2), 61.0 (s, OCH_3), 52.0 (s, CH), 51.9 (s, N-CH_3), 26.9 (s, CH), 21.4 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -76.75 (d, *J* = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}F_3N_2O_5$ 517.1945; Found 517.1959.

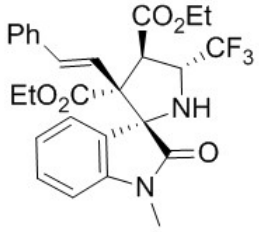


4'-Ethyl 3'-methyl 1,5,7-trimethyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3m.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (40.5 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3m** (54.9 mg, 69% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39-7.30 (m, 4H), 7.24-7.21 (m, 1H), 7.06 (s, 1H), 6.85-6.80 (m, 2H, ArH, CH=C), 6.13 (d, *J* = 16.4 Hz, 1H, C=CH), 4.85-4.76 (m, 1H, CH), 4.43 (d, *J* = 10.2 Hz, 1H, CH), 4.06 (q, *J* = 7.0 Hz, 2H, CH_2), 3.40 (s, 3H, OCH_3), 3.18 (s, 3H, N-CH_3), 2.47 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.12 (t, *J* = 1.8 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 175.6 (s, C=O), 167.0 (s, C=O),

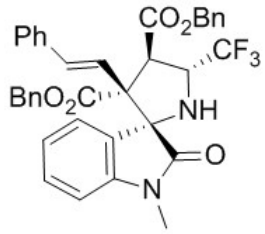
168.0 (s, C=O), 138.5 (s, C), 136.5 (s, C), 133.7 (s, CH), 132.4 (s, C), 131.3 (s, CH), 131.0 (s, C), 128.6 (s, 2CH), 128.0 (s, CH), 127.7 (q, J = 278.7 Hz, CF_3), 126.7 (s, 2CH), 123.7 (s, CH), 123.3 (d, J = 2.2 Hz, CH), 119.2 (s, C), 72.9 (s, C), 68.7 (s, C), 61.7 (s, CH_2), 60.6 (s, OCH_3), 52.0 (s, CH), 51.9 (s, N-CH_3), 30.4 (s, CH), 20.9 (s, CH_3), 18.9 (s, CH_3), 14.0 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.00 (d, J = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}F_3N_2O_5$ 531.2101; Found 531.2090.



Diethyl 1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3n.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (61.7 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3n** (70.4 mg, 91% yield).

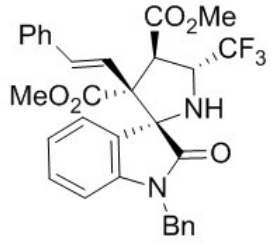
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.29 (m, 5H), 7.25 (d, J = 3.2 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H, CH=C), 6.86-6.76 (m, 3H), 6.07 (d, J = 16.4 Hz, 1H, C=CH), 4.88 (d, J = 10.5 Hz, 1H, CH), 4.63 (s, 1H, CH), 4.30-4.08 (m, 4H, CH_2), 3.15 (s, 3H, N-CH_3), 2.52 (s, 1H, NH), 1.25 (t, J = 7.1 Hz, 3H, CH_3), 1.17 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.9 (s, C=O), 170.1 (s, C=O), 169.8 (s, C=O), 145.0 (s, C), 136.2 (s, C), 132.9 (s, CH), 130.2 (s, CH), 128.7 (s, 2CH), 128.2 (s, CH), 128.0 (q, J = 272.2 Hz, CF_3), 126.7 (s, 2CH), 126.4 (s, C), 126.0 (s, CH), 123.6 (s, CH), 121.9 (s, CH), 108.2 (s, CH), 72.1 (s, C), 66.4 (s, C), 61.6 (s, CH_2), 61.3 (s, CH_2), 60.9 (s, CH), 49.1 (s, N-CH_3), 26.2 (s, CH), 14.0 (s, CH_3), 13.7 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.00 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}F_3N_2O_5$ 517.1945; Found 517.1934.



Dibenzyl 1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline- 3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3o.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (85.6 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3o** (61.5 mg, 64% yield).

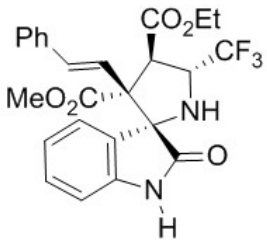
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.25 (dd, *J* = 6.6, 4.9 Hz, 10H), 7.07 (dd, *J* = 10.7, 4.6 Hz, 3H), 6.85-6.73 (m, 2H), 6.68 (d, *J* = 7.7 Hz, 1H, CH=C), 5.92 (d, *J* = 16.4 Hz, 1H, C=CH), 5.11 (dd, *J* = 12.3, 4.8 Hz, 2H, CH_2), 5.00 (d, *J* = 10.4 Hz, 1H), 4.89 (dd, *J* = 18.9, 12.3 Hz, 2H, CH_2), 4.69 (s, 1H, NH), 4.62 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.94 (s, 3H, N-CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.7 (s, C=O), 169.1 (s, C=O), 169.9 (s, C=O), 145.0 (s, C), 135.9 (s, C), 135.3 (s, C), 134.7 (s, C), 133.1 (s, CH), 130.1 (s, CH), 128.7 (s, 2CH), 128.6 (s, CH), 128.5 (s, 2CH), 128.4 (s, 2CH), 128.3 (s, 2CH), 128.2 (s, CH), 128.1 (s, 2CH), 127.0 (s, CH), 126.7 (s, 2CH), 126.3 (s, C), 125.9 (s, CH), 125.3 (q, *J* = 278.3 Hz, CF_3), 123.2 (s, CH), 121.9 (s, CH), 108.4 (s, CH), 72.0 (s, C), 67.3 (s, CH_2), 67.1 (s, CH_2), 66.4 (s, C), 61.2 (s, CH), 49.2 (s, N-CH_3), 26.0 (s, CH). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.00 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{37}H_{32}F_3N_2O_5$ 641.2258; Found 641.2237.



Dimethyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline- 3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3p.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (55.4 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3p** (60.1 mg, 71% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43-7.26 (m, 10H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 16.4 Hz, 1H, CH=C), 6.71 (d, *J* = 7.7 Hz, 1H), 6.20 (d, *J* = 16.4 Hz, 1H, C=CH), 5.16 (d, *J* = 15.4 Hz, 1H, CH), 4.87 (s, 1H, CH), 4.50 (dd, *J* = 12.8, 6.8 Hz, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.30 (s, 1H, NH), 2.83 (s, 3H, OCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 174.8 (s, C=O), 169.0 (s, C=O), 168.7 (s, C=O), 142.3 (s, C), 136.5 (s, C), 135.3 (s, C), 131.7 (s, CH), 130.1 (s, C), 129.5 (s, CH), 128.7 (s, 2CH), 128.6 (s, 2CH), 128.1 (s, CH), 127.8 (s, CH), 127.7 (s, 2CH), 126.7 (s, 2CH), 125.7 (q, *J* = 277.5 Hz, CF_3), 124.7 (d, *J* = 2.2 Hz, CH), 123.5 (s, CH), 123.0 (s, CH), 108.8 (s, CH), 73.4 (s, C), 68.9 (s, C), 61.2 (s, CH), 52.8 (s, OCH_3), 52.1 (s, CH), 51.8 (s, OCH_3), 44.4 (s, CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.25 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{28}F_3N_2O_5$ 565.1945; Found 565.1933.

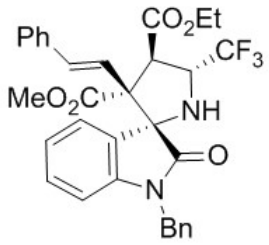


4'-Ethyl 3'-methyl 2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3q.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (40.5 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3q** (71.0 mg, 97% yield).

Yellow solid. **MP**: 201.7-202.5 ^{o}C. **^{1}H NMR** (300 MHz, DMSO-d6) δ 10.62 (s, 1H, NH), 7.92-7.75 (m, 1H), 7.65-7.54 (m, 1H), 7.43-7.32 (m, 4H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.99-6.81 (m, 3H, 2ArH, CH=C), 6.09 (d, *J* = 16.5 Hz, 1H, C=CH), 4.96-4.83 (m, 1H, NH), 4.41 (d, *J* = 10.3 Hz, 1H, CH), 4.26 (d, *J* = 10.2 Hz, 1H, CH), 3.96 (q, *J* = 7.1 Hz, 2H, CH_2), 3.11 (s, 3H, OCH_3), 1.02 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75

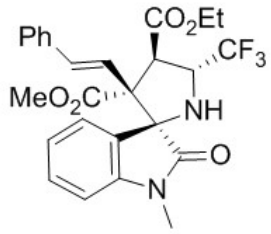
MHz, DMSO-d6) δ 175.2 (s, C=O), 169.0 (s, C=O), 168.6 (s, C=O), 142.1 (s, C), 137.1 (s, C), 130.6 (s, C), 130.1 (s, CH), 129.8 (s, CH), 129.0 (s, 2CH), 128.2 (s, CH), 127.6 (q, J = 274.5 Hz, CF_3), 126.9 (s, 2CH), 125.4 (s, CH), 124.9 (d, J = 3.7 Hz, CH), 121.9 (s, CH), 110.0 (s, CH), 73.8 (s, C), 69.1 (s, C), 61.5 (s, CH_2), 52.2 (s, OCH_3), 51.9 (s, CH), 27.7 (s, CH), 14.3 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -73.28 (s, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}F_3N_2O_5$ 489.1632; Found 489.1637.



4'-Ethyl 3'-methyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *endo*-3r.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***endo*-3r** (76.3 mg, 88% yield).

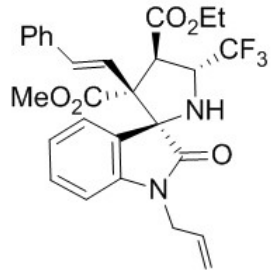
Yellow solid. **MP**: 89.1-91.0 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.2, 2.9 Hz, 3H), 7.35-7.28 (m, 5H), 7.24 (t, J =2.0 Hz, 3H), 7.17 (td, J = 7.7, 0.7 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 16.4 Hz, 1H, CH=C), 6.71 (d, J = 7.7 Hz, 1H), 6.20 (d, J = 16.4 Hz, 1H, C=CH), 5.16 (d, J = 15.4 Hz, 1H, CH), 4.86 (dt, J = 16.7, 8.5 Hz, 1H, CH), 4.49 (dd, J = 19.4, 12.8 Hz, 2H, CH_2), 4.09 (q, J = 7.1 Hz, 2H, CH_2), 3.30 (d, J = 9.6 Hz, 1H, NH), 2.84 (s, 3H, OCH_3), 1.13 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.8 (s, C=O), 168.9 (s, C=O), 168.0 (s, C=O), 142.3 (s, C), 136.5 (s, C), 135.3 (s, C), 131.6 (s, CH), 130.2 (s, C), 129.5 (s, CH), 128.7 (s, 2CH), 128.6 (s, 2CH), 128.1 (s, CH), 127.8 (s, CH), 127.7 (s, 2CH), 126.7 (s, 2CH), 125.7 (q, J = 277.5 Hz, CF_3), 124.6 (d, J = 1.5 Hz, CH), 123.6 (s, CH), 123.0 (s, CH), 108.8 (s, CH), 73.4 (s, C), 68.9 (s, C), 61.8 (s, CH_2), 52.0 (s, CH), 51.7 (s, CH), 51.8 (s, N-CH_3), 44.4 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.21 (d, J = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{30}F_3N_2O_5$ 579.2101; Found 579.2112.



4'-Ethyl 3'-methyl 1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4a.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo′*-4a** (67.9 mg, 90% yield).

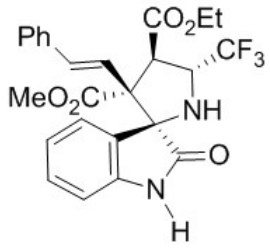
Yellow solid. **MP**: 137.6-138.5 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.41-7.28 (m, 6H), 7.05 (d, *J* = 7.3 Hz, 1H, CH=C), 6.87-6.75 (m, 3H), 6.04 (d, *J* = 16.4 Hz, 1H, C=CH), 4.87 (d, *J* = 10.4 Hz, 1H, CH), 4.68-4.58 (m, 1H, C=CH), 4.20 (q, *J* = 7.1 Hz, 2H, CH_2), 3.66 (s, 3H, OCH_3), 3.16 (s, 3H, N-CH_3), 1.24 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.9 (s, C=O), 170.3 (s, C=O), 170.0 (s, C=O), 145.0 (s, C), 136.1 (s, C), 133.1 (s, CH), 130.2 (s, CH), 129.1 (q, *J* = 277.5 Hz, CF_3), 128.8 (s, 2CH, CH, =CH), 128.3 (s, CH), 126.7 (s, 2CH, CH), 126.3 (s, C=CH), 126.1 (s, CH), 123.5 (s, CH), 121.9 (s, CH), 108.2 (s, CH), 72.1 (s, C), 66.6 (s, C), 61.3 (s, CH_2), 60.9(s, OCH_3) , 52.4 (s, CH), 49.0 (s, N-CH_3), 26.2 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.02 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{26}F_3N_2O_5$ 503.1788; Found 503.1798.



4'-Ethyl 3'-methyl 1-allyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4b.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (42.9 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4b** (52.3 mg, 66% yield).

Yellow solid. **MP**: 114.1-115.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 – 7.21 (m, 6H), 7.06 (d, *J* = 7.0 Hz, 1H, C=CH), 6.85-6.75 (m, 3H), 6.07 (d, *J* = 16.4 Hz, 1H, CH=C), 5.83 (ddd, *J* = 22.4, 10.6, 5.5 Hz, 1H, C=CH), 5.31 (ddd, *J* = 13.8, 11.4, 1.1 Hz, 2H, CH_2), 4.88 (d, *J* = 10.4 Hz, 1H, CH), 4.68-4.43 (m, 2H, C=CH_2), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2), 4.09 (dd, *J* = 16.2, 5.9 Hz, 1H, CH), 3.66 (s, 3H, OCH_3), 1.24 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.6 (s, C=O), 170.2 (s, C=O), 170.0 (s, C=O), 144.2 (s, C), 136.1 (s, C), 133.1 (s, CH), 131.3 (s, CH), 130.1 (s, CH), 128. 8 (s, 2CH), 128.3 (s, CH), 126.7 (s, 2CH), 126.6 (q, *J* = 276.0 Hz, CF_3), 126.3 (s, C), 126.1 (s, CH), 123.5 (s, CH), 121.9 (s, CH), 118.1 (s, C=CH_2), 109.2 (s, CH), 72.0 (s, C), 66.6 (s, C), 61.3 (s, CH_2), 52.5 (s, OCH_3), 49.1 (s, CH), 42.5 (s, CH_2), 30.9 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.09 (d, *J* = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{28}F_3N_2O_5$ 529.1945; Found 529.1935.

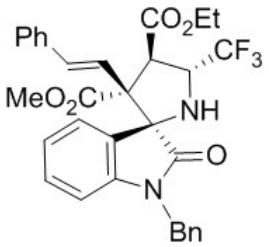


4'-Ethyl 3'-methyl 2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)- spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4c.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (40.5 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4c** (43.2 mg, 59% yield).

Yellow solid. **MP**: 100.3-101.2 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.39 (s, 1H, NH), 7.42-7.29 (m, 5H), 7.21 (td, *J* = 7.8, 1.0 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H, CH=C), 6.87-6.76 (m, 3H), 6.10 (d, *J* = 16.4 Hz, 1H, C=CH), 4.83 (d, *J* = 10.4 Hz, 1H, CH), 4.71-4.59 (m, 1H, CH), 4.21 (q, *J* = 7.1 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 2.57 (d, *J* = 8.1 Hz, 1H, NH), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ*

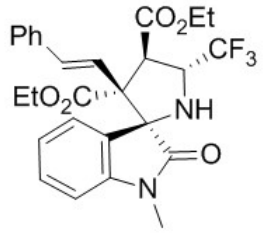
179.1 (s, C=O), 170.4 (s, C=O), 170.0 (s, C=O), 142.2 (s, C), 136.0 (s, C), 133.0 (s, CH), 130.2 (s, CH), 128.8 (s, 2CH), 128.3 (s, CH), 127.8 (q, J = 270.0 Hz, CF_3), 126.9 (s, C), 126.7 (s, 2CH), 126.3 (s, CH), 123.4 (s, CH), 122.0 (s, CH), 110.2 (s, CH), 72.6 (s, C), 66.6 (s, C), 61.4 (s, CH_2), 52.5 (s, OCH_3), 49.4 (s, CH), 31.0 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.05 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}F_3N_2O_5$ 489.1632; Found 489.1626.



4'-Ethyl 3'-methyl -1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4d.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4d** (83.2 mg, 96% yield).

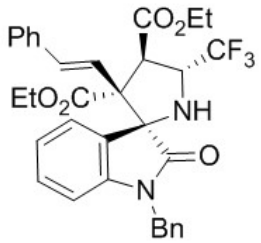
Yellow solid. **MP**: 93.4-94.3 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 9H), 7.25-7.23 (m, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 6.78 (dd, J = 12.2, 4.2 Hz, 2H), 6.69 (d, J = 7.8 Hz, 1H, CH=C), 6.09 (d, J = 16.4 Hz, 1H, C=CH), 4.97 (dd, J = 24.2, 13.0 Hz, 2H, CH_2), 4.64 (d, J = 15.6 Hz, 2H, CH), 4.19 (q, J = 7.1 Hz, 2H, CH_2), 3.55 (s, 3H, OCH_3), 2.55 (s, 1H, NH), 1.23 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0 (s, C=O), 170.2 (s, C=O), 170.1 (s, C=O), 142.2 (s, C), 136.1 (s, C), 135.7 (s, C), 133.0 (s, CH), 130.1 (s, CH), 128.8 (s, 2CH), 128.7 (s, 2CH), 128.3 (s, CH), 127.9 (q, J = 276.7 Hz, CF_3), 127.8 (s, 2CH), 127.6 (s, CH), 126.7 (s, 2CH), 126.4 (s, C), 126.1 (s, CH), 123.5 (s, CH), 122.1 (s, CH), 109.3 (s, CH), 72.1 (s, C), 66.5 (s, C), 61.4 (s, CH_2), 52.4 (s, OCH_3), 49.2 (s, CH), 44.0 (s, CH_2), 29.8 (s, CH), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.02 (d, J = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{30}F_3N_2O_5$ 579.2101; Found 579.2127.



Diethyl 1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline- 3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4e.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (36.3 mg, 0.15 mmol, 1.0 equiv) and diene (61.7 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4e** (49.5 mg, 64% yield).

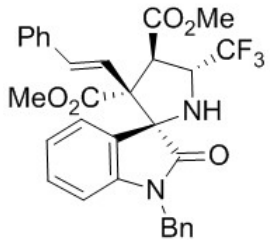
Yellow solid. **MP**: 89.1-91.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29-7.40 (m, 5H), 7.26 (s, 1H), 7.05 (d, *J* = 7.4 Hz, 1H, CH=C), 6.86-6.76 (m, 3H), 6.07 (d, *J* = 16.4 Hz, 1H, C=CH), 4.88 (d, *J* = 10.5 Hz, 1H, CH), 4.64-4.57 (m, 1H, CH), 4.30-4.08 (m, 4H, $2CH_2$), 3.15 (s, 3H, N-CH_3), 2.51 (s, 1H, NH), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 1.17 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.9 (s, C=O), 170.2 (s, C=O), 169.8 (s, C=O), 145.0 (s, C), 136.1 (s, C), 132.9 (s, CH), 130.2 (s, CH), 129.1 (q, *J* = 278.2 Hz, CF_3), 128.8 (s, 2CH), 128.2 (s, CH), 126.7 (s, 2CH), 126.4 (s, C), 126.0 (s, CH), 123.6 (s, CH), 121.9 (s, CH), 108.2 (s, CH), 72.0 (s, C), 66.4 (s, C), 61.6 (s, CH_2), 61.3 (s, CH_2), 60.9(s, CH), 49.0 (s, N-CH_3), 26.2 (s, CH), 14.0 (s, CH_3), 13.8 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.08 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}F_3N_2O_5$ 517.1945; Found 517.1922.



Diethyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline- 3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4f.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (61.7 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4f** (68.4 mg, 77% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 (dt, *J* = 22.3, 7.3 Hz, 10H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.80 (dd, *J* = 15.7, 6.9 Hz, 2H), 6.66 (d, *J* = 7.8 Hz, 1H, CH=C), 6.13 (d, *J* = 16.3 Hz, 1H, C=CH), 5.05-4.91 (m, 2H, CH_2), 4.69 (d, *J* = 15.7 Hz, 1H, CH), 4.19 (dddd, *J* = 17.6, 10.2, 9.0, 5.2 Hz, 4H, $2CH_2$), 4.07-3.96 (m, 1H, CH), 2.54 (d, *J* = 6.3 Hz, 1H, NH), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 1.15 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 177.1 (s, C=O), 170.2 (s, C=O), 169.8 (s, C=O), 144.3 (s, C), 136.2 (s, C), 135.7 (s, C), 133.0 (s, CH), 130.0 (s, CH), 129.7 (q, *J* = 276.0 Hz, CF_3), 128.8 (s, 2CH), 128.7 (s, 2CH), 128.2 (s, CH), 127.6 (s, 2CH), 127.5 (s, CH), 126.7 (s, 2CH), 126.5 (s, C), 126.1 (s, CH), 123.6 (s, CH), 122.0 (s, CH), 109.3 (s, CH), 72.1 (s, C), 66.3 (s, C), 61.7 (s, CH_2), 61.3 (s, CH_2), 49.0 (s, CH), 44.0 (s, CH_2), 39.4 (s, CH), 14.0 (s, CH_3), 13.8 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -74.95 (d, *J* = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{32}F_3N_2O_5$ 593.2258; Found 593.2272.

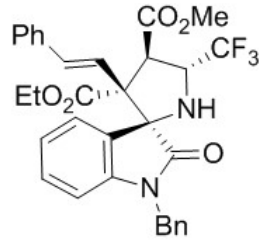


Dimethyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline- 3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4g.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (55.3 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4g** (64.3 mg, 76% yield).

Yellow solid. **MP**: 82.7-83.5 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.27 (m, 10H), 7.18-7.06 (m, 2H), 6.79 (dd, *J* = 15.8, 7.8 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H, CH=C), 6.09 (d, *J* = 16.4 Hz, 1H, C=CH), 5.04-4.91 (m, 2H, CH_2), 4.66 (d, *J* = 15.6 Hz, 2H, 2CH), 3.73 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 2.55 (s, 1H, NH). **^{13}C NMR** (75 MHz,

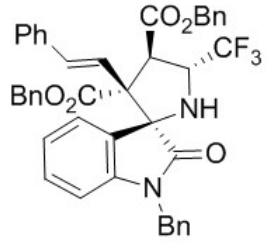
$CDCl_3$) δ 176.9 (s, C=O), 170.7 (s, C=O), 170.2 (s, C=O), 144.2 (s, C), 136.1 (s, C), 135.7 (s, C), 133.1 (s, CH), 130.1 (s, CH), 129.0 (q, J = 272.2 Hz, CF_3), 128.8 (s, 2CH), 128.7 (s, 2CH), 128.3 (s, CH), 127.8 (s, 2CH), 127.6 (s, CH), 126.7 (s, 2CH), 126.4 (s, C), 126.1 (s, CH), 123.4 (s, CH), 122.1 (s, CH), 109.3 (s, CH), 72.0 (s, C), 66.4 (s, C), 61.3 (s, CH), 52.5 (s, $2CH_3$), 49.1 (s, CH), 44.0 (s, CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.04 (d, J = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{28}F_3N_2O_5$ 565.1945; Found 565.1949.



3'-Ethyl 4'-methyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4h.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4h** (48.5 mg, 56% yield).

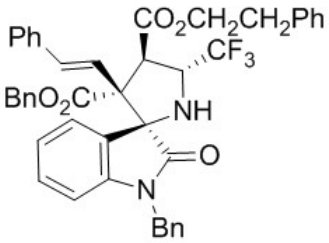
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.27 (m, 10H), 7.12 (ddd, J = 20.5, 13.6, 4.1 Hz, 2H), 6.83-6.76 (m, 2H), 6.66 (d, J = 7.7 Hz, 1H, CH=C), 6.13 (d, J = 16.4 Hz, 1H, C=CH), 5.01-4.91 (m, 2H, CH_2), 4.64 (ddd, J = 15.3, 13.5, 11.2 Hz, 2H, CH_2), 4.16 (dq, J = 10.8, 7.1 Hz, 1H, CH), 4.00 (dq, J = 10.7, 7.1 Hz, 1H,CH), 3.73 (s, 3H, OCH_3), 2.45 (s, 1H, NH), 1.14 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0 (s, C=O), 170.8 (s, C=O), 169.7 (s, C=O), 144.3 (s, C), 136.2 (s, C), 135.7 (s, C), 133.2 (s, CH), 130.0 (s, CH), 129.5 (q, J = 270.7 Hz, CF_3), 128.8 (s, 2CH), 128.7 (s, 2CH), 128.3 (s, CH), 127.6 (s, 2CH), 127.5 (s, CH), 126.7 (s, 2CH), 126.4 (s, C), 126.1 (s, CH), 123.4 (s, CH), 122.0 (s, CH), 109.3 (s, CH), 72.0 (s, C), 66.3 (s, C), 61.8 (s, CH_2), 61.3 (s, CH), 52.4 (s, OCH_3), 48.9 (s, CH), 44.0 (s, CH_2), 13.7 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.06 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{30}F_3N_2O_5$ 579.2101; Found 579.2120.



Dibenzyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro- [indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4i.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (89.6 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo′*-4i** (77.3 mg, 72% yield).

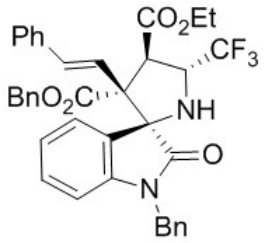
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 (tdd, *J* = 16.5, 9.3, 4.9 Hz, 16H), 7.21 (s, 1H), 7.16-7.05 (m, 4H), 6.79 (td, *J* = 11.3, 6.8 Hz, 3H), 6.64 (dd, *J* = 12.9, 7.8 Hz, 1H, CH=C), 6.12 (dd, *J* = 16.4, 3.8 Hz, 1H, C=CH), 5.10 (dd, *J* = 22.0, 9.8 Hz, 1H, CH), 4.97-4.91 (m, 1H, CH), 4.72-4.59 (m, 2H, CH_2), 4.21-3.87 (m, 2H, CH_2), 3.73 (s, 2H ,CH_2), 2.52 (s, 1H, NH). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.9 (s, C=O), 170.8 (s, C=O), 169.7 (s, C=O), 144.2 (s, C), 136.1 (s, C), 135.9 (s, C), 135.7 (s, C), 135.3 (s, C), 133.3 (s, CH), 133.2 (s, CH), 130.1 (s, CH), 129.1 (s, CH), 128.8 (s, 2CH), 128.7 (s, CH), 128.7 (s, 2CH), 128.5 (s, CH), 128.4 (s, CH), 128.4 (dd, *J* = 6.0 Hz, 2.2 Hz, 4CH), 128.2 (s, CH), 128.1 (s, CH), 127.7 (s, CH), 127.6 (s, 2CH), 126.7 (s, 2CH), 126.7 (s, CH), 126.1 (s, CH), 125.7 (q, *J* = 276.7 Hz, CF_3), 123.4 (s, CH), 122.0 (s, CH), 109.3 (s, CH), 72.0 (s, C), 67.2 (s, CH_2), 66.3 (s, C), 61.8 (s, CH_2), 52.4 (s, CH), 44.0 (s, CH_2), 13.7 (s, CH). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.06 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{43}H_{36}F_3N_2O_5$ 717.2571; Found 717.2570.



3'-Benzyl 4'-phenethyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro-[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4j.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (92.7 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4j** (63.5 mg, 58% yield).

Yellow solid. **MP**: 115.2-116.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.9 Hz, 2H), 7.31 (dt, *J* = 7.5, 3.6 Hz, 3H), 7.26-7.04 (m, 15H), 6.85-6.78 (m, 3H), 6.74-6.60 (m, 2H, ArH, CH=C), 5.90 (d, *J* = 16.4 Hz, 1H, C=CH), 5.15-4.77 (m, 4H, CH_2, 2CH), 4.65 (dd, *J* = 15.3, 9.2 Hz, 2H, CH_2), 4.07 (ddt, *J* = 46.7, 10.7, 6.8 Hz, 2H, CH_2), 2.61-2.36 (m, 3H, CH_2, NH). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.9 (s, C=O), 169.9 (s, C=O), 169.6 (s, C=O), 144.3 (s, C), 137.3 (s, C), 136.0 (s, C), 135.7 (s, C), 135.4 (s, C), 133.3 (s, CH), 130.2 (s, CH), 128.8 (s, 2CH), 128.8 (s, 2CH), 128.7 (s, 2CH), 128.5 (s, 2CH), 128.4 (s, 2CH), 128.3 (s, 2CH), 128.3 (s, CH), 128.2 (s, CH), 127.9 (s, 2CH),127.8 (q, *J* = 272.2 Hz, CF_3), 127.7 (s, CH), 126.8 (s, 2CH), 126.5 (s, 2CH), 126.2 (s, CH), 123.1 (s, CH), 122.1 (s, CH), 109.3 (s, CH), 72.1 (s, C), 67.3 (s, CH_2), 66.4 (s, CH_2), 66.3 (s, C), 60.9 (s, CH), 49.3 (s, CH), 44.1 (s, CH_2), 34.4 (s, CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -74.81 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{44}H_{38}F_3N_2O_5$ 731.2727; Found 731.2760.

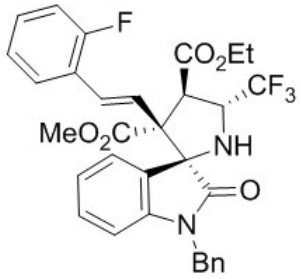


3'-Benzyl 4'-ethyl 1-benzyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro-[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4k.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (75.6 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4k** (61.8 mg, 63% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.4, 3.0 Hz, 6H), 7.32-7.28 (m, 8H), 7.15-7.04 (m, 3H), 6.78 (dt, *J* = 12.9, 4.3 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 1H, CH=C), 6.12 (d, *J* = 16.4 Hz, 1H, C=CH), 5.15 (s, 2H, CH_2), 5.06-4.91 (m, 2H, CH_2), 4.69-4.61 (m, 2H, 2CH), 4.09-3.85 (m, 2H, CH_2), 2.53 (s, 1H, NH), 1.00 (t, *J* = 7.1

Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0 (s, C=O), 170.0 (s, C=O), 169.7 (s, C=O), 144.3 (s, C), 136.1 (s, C), 135.7 (s, C), 135.4 (s, C), 133.2 (s, CH), 130.6 (s, CH), 128.8 (s, 2CH), 128.7 (s, 2CH), 128.5 (s, 2CH), 128.4 (s, 2CH), 128.3 (s, CH), 128.3 (s, CH), 128.2 (q, J = 279.7 Hz, CF_3), 127.6 (s, 2CH), 127.5 (s, CH), 126.7 (s, 2CH), 126.4 (s, C), 126.0 (s, CH), 123.4 (s, CH), 122.0 (s, CH), 109.3 (s, CH), 72.2 (s, C), 67.3 (s, CH_2), 66.4 (s, C), 61.8 (s, CH_2), 52.4 (s, CH), 49.1 (s, CH), 44.0 (s, CH_2), 13.7 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.86 (d, J = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{38}H_{34}F_3N_2O_5$ 655.2414; Found 655.2401.

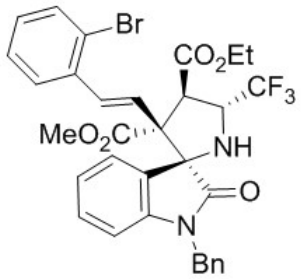


4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-2-fluorostyryl)-2-oxo-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4l.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (62.6 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4l** (66.2 mg, 74% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (td, J = 7.6, 1.5 Hz, 1H), 7.34 (dt, J = 14.0, 6.7 Hz, 5H), 7.20-7.12 (m, 3H), 7.07-7.01 (m, 2H), 6.94-6.82 (m, 2H), 6.71 (d, J = 7.7 Hz, 1H, CH=C), 6.19 (d, J = 16.6 Hz, 1H, C=CH), 5.03-4.91 (m, 2H), 4.67 (d, J = 15.6 Hz, 1H, CH), 4.20 (q, J = 7.1 Hz, 2H, CH_2), 3.76 (dt, J = 14.1, 5.7 Hz, 1H, CH), 3.54 (s, 3H, OCH_3), 2.58 (s, 1H, NH), 1.24 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8 (s, C=O), 170.0 (s, C=O), 169.9 (s, C=O), 162.0 (d, J = 249.0 Hz, C-F), 144.2 (s, C), 135.7 (s, C), 130.1 (s, CH), 129.6 (d, J = 8.2 Hz, CH), 128.7 (s, 2CH), 128.1 (d, J = 3.7 Hz, CH), 127.8 (s, 2CH), 127.6 (s, CH), 127.2 (q, J = 279.0 Hz, CF_3), 126.3 (s, CH), 125.9 (s, CH), 124.4 (d, J = 3.0 Hz, CH), 123.9 (s, C), 123.7 (s, C), 122.1 (s, CH), 116.1 (s, CH), 115.8 (s, CH), 109.3 (s, CH), 72.0 (s, C), 66.8 (s, C), 61.4 (s, CH_2), 61.2 (s, CH), 52.4 (s, OCH_3), 49.4 (s, CH), 44.0 (s,

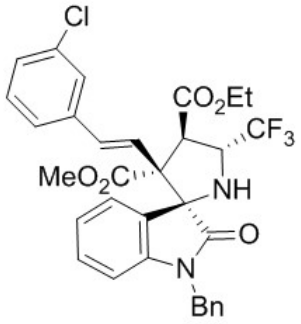
CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.85 (d, J = 5.6 Hz, 3F), 117.16 (q, J = 5.6 Hz, F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{29}F_4N_2O_5$ 597.2007; Found 597.2047.



4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-2-bromostyryl)-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4m.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (76.0 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo′*-4m** (61.0 mg, 62% yield).

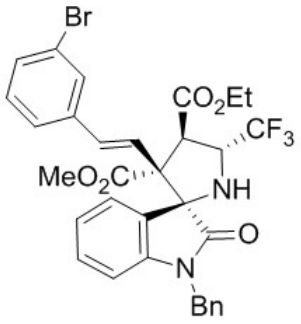
Yellow solid. **MP**: 134.1-135.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.8, 1.4 Hz, 1H), 7.52 (dd, J = 8.0, 1.0 Hz, 1H), 7.40-7.27 (m, 6H), 7.21-7.07 (m, 3H), 6.88 (dt, J = 8.3, 4.1 Hz, 1H, CH=C), 6.71 (dd, J = 12.0, 6.1 Hz, 2H), 6.42 (d, J = 16.3 Hz, 1H, C=CH), 5.00-4.91 (m, 2H, CH_2), 4.73-4.58 (m, 2H, CH), 4.22 (q, J = 7.1 Hz, 2H, CH_2), 3.53 (s, 3H, OCH_3), 2.56 (d, J = 8.6 Hz, 1H, NH), 1.26 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8 (s, C=O), 170.1 (s, C=O), 169.9 (s, C=O), 144.1 (s, C), 136.4 (s, C), 135.7 (s, C), 132.9 (s, CH), 132.0 (s, CH), 130.1 (s, CH), 129.5 (s, CH), 128.7 (s, 2CH), 127.9 (s, CH), 127.8 (s, 2CH), 127.6 (d, J = 2.2 Hz, 2CH), 127.2 (q, J = 276.0 Hz, CF_3), 126.7 (s, CH), 126.2 (s, C), 125.9 (s, CH), 123.7 (s, C), 122.3 (s, CH), 109.3 (s, CH), 71.8 (s, C), 66.5 (s, C), 61.5 (s, CH_2), 61.3 (s, CH), 52.4 (s, OCH_3), 49.3 (s, CH), 44.0 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.90 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{29}BrF_3N_2O_5$ 657.1206; Found 675.1238.



4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-3-chlorostyryl)-2-oxo-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4n.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (66.1 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4n** (51.4 mg, 56% yield).

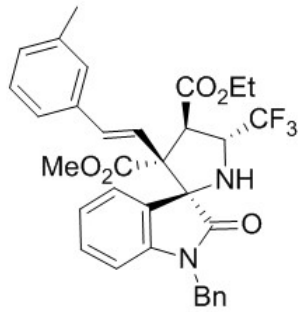
Yellow solid. **MP**: 81.7-82.6 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 (dt, *J* = 14.2, 5.5 Hz, 6H), 7.26 (s, 3H), 7.20-7.14 (m, 1H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.84-6.79 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H, CH=C), 6.02 (d, *J* = 16.4 Hz, 1H, C=CH), 4.98 (dd, *J* = 28.0, 13.0 Hz, 2H, CH_2), 4.66 (d, *J* = 15.6 Hz, 2H, 2CH), 4.21 (q, *J* = 7.1 Hz, 2H, CH_2), 3.56 (s, 3H, OCH_3), 2.54 (s, 1H, NH), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.8 (s, C=O), 170.0 (s, C=O), 170.0 (s, C=O), 144.3 (s, C), 137.9 (s, C), 135.6 (s, C), 134.8 (s, C), 131.6 (s, CH), 130.2 (s, CH), 130.1 (s, CH), 128.7 (s, 2CH), 128.3 (s, CH), 127.7 (s, 2CH), 127.6 (s, CH), 127.2 (q, *J* = 271.5 Hz, CF_3), 126.5 (s, CH), 126.3 (s, C), 125.9 (s, CH), 125.2 (s, CH), 125.0 (s, CH), 122.1 (s, CH), 109.4 (s, CH), 72.0 (s, C), 66.4 (s, C), 61.4 (s, CH_2), 60.8 (s, CH), 52.5 (s, OCH_3), 49.1 (s, CH), 44.0 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -74.99 (d, *J* = 8.5 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{29}ClF_3N_2O_5$ 613.1712; Found 613.1751.



4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-3-bromostyryl)-2-oxo-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4o.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (76.0 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4o** (59.0 mg, 60% yield).

Yellow solid. **MP**: 82.6-83.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.43-7.30 (m, 6H), 7.25-7.14 (m, 3H), 7.02 (d, *J* = 7.1 Hz, 1H), 6.85-6.78 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H, CH=C), 6.01 (d, *J* = 16.4 Hz, 1H, C=CH), 4.98 (dd, *J* = 27.8, 13.0 Hz, 2H, CH_2), 4.66 (d, *J* = 15.7 Hz, 2H, 2CH), 4.21 (q, *J* = 7.1 Hz, 2H, CH_2), 3.55 (s, 3H, OCH_3), 2.54 (s, 1H, NH), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.8 (s, C=O), 170.0 (d, *J* = 1.5 Hz, 2C, C=O), 144.3 (s, C), 138.2 (s, C), 135.6 (s, C), 131.5 (s, CH), 131.2 (s, CH), 130.4 (s, CH), 130.2 (s, CH), 129.4 (s, CH), 128.7 (s, 2CH), 128.3 (q, *J* = 270.7 Hz, CF_3), 127.7 (s, 2CH), 127.6 (s, CH), 126.3 (s, C), 125.9 (s, CH), 125.4 (s, CH), 125.2 (s, CH), 123.0 (s, C), 122.1 (s, CH), 109.4 (s, CH), 72.0 (s, C), 66.4 (s, C), 61.4 (s, CH_2), 61.2 (s, CH), 52.5 (s, OCH_3), 49.1 (s, CH), 44.0 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -74.97 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{29}BrF_3N_2O_5$ 657.1206; Found 657.1237.

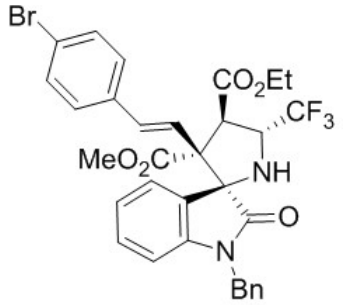


4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-3-methylstyryl)-2-oxo-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4p.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (61.7 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4p** (66.6 mg, 75% yield).

Yellow solid. **MP**: 82.7-83.4 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.24 (m, 7H), 7.17-7.06 (m, 4H), 6.79 (dd, *J* = 16.0, 9.0 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 1H, CH=C),

6.05 (d, J = 16.4 Hz, 1H, C=CH), 5.05-4.90 (m, 2H), 4.65 (d, J = 15.6 Hz, 2H, 2CH), 4.20 (q, J = 7.1 Hz, 2H, CH_2), 3.55 (s, 3H, OCH_3), 2.55 (s, 1H, NH), 2.36 (s, 3H, CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0 (s, C=O), 170.2 (s, C=O), 170.0 (s, C=O), 144.2 (s, C), 138.4 (s, C), 136.0 (s, C), 135.7 (s, C), 133.2 (s, CH), 130.0 (s, CH), 129.1 (s, CH), 128.7 (s, 2CH), 127.8 (s, 2CH), 127.6 (s, CH), 127.3 (s, 2CH), 127.2 (q, J = 273.7 Hz, CF_3), 126.5 (s, C), 126.1 (s, CH), 123.9 (s, CH), 123.1 (s, CH), 122.1 (s, CH), 109.3 (s, CH), 72. 1 (s, C), 66.5 (s, C), 61.3 (s, CH_2), 60.8 (s, CH), 52.4 (s, OCH_3), 49.2 (s, CH), 44.0 (s, CH_2), 21.4 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.95 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{32}F_3N_2O_5$ 593.2258; Found 593.2272.

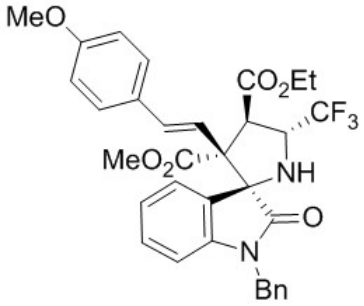


4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-4-bromostyryl)-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4q.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (76.0 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo′*-4q** (45.3 mg, 46% yield).

Yellow solid. **MP**: 137.4-138.3 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41-7.28 (m, 9H), 7.17 (td, J = 7.8, 1.1 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.83-6.78 (m, 2H), 6.71 (d, J = 7.7 Hz, 1H, CH=C), 6.04 (d, J = 16.4 Hz, 1H, C=CH), 5.05-4.91 (m, 2H, CH_2), 4.64 (dd, J = 16.3, 7.8 Hz, 2H, 2CH), 4.20 (q, J = 7.1 Hz, 2H, CH_2), 3.56 (s, 3H, OCH_3), 2.53 (s, 1H, NH), 1.25 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.9 (s, C=O), 170.1 (s, 2C=O), 144.3 (s, C), 135.6 (s, C), 134.6 (s, C), 134.0 (s, C), 131.7 (s, CH), 130.2 (s, CH), 129.0 (s, 2CH), 128.7 (s, 2CH), 127.9 (s, 2CH), 127.8 (s, 2CH), 127.6 (s, CH), 127.2 (q, J = 271.5 Hz, CF_3), 126.4 (s, C), 126.0 (s, CH), 124.3 (s, CH), 122.0 (s, CH), 109.4 (s, CH), 72.0 (s, C), 66.4 (s, C), 61.4 (s, CH_2), 60.9 (s,

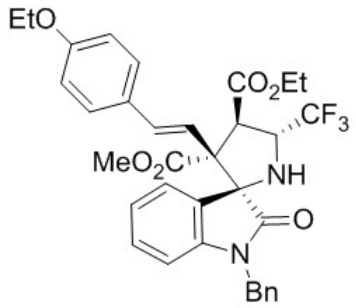
CH), 52.5 (s, OCH_3), 49.1 (s, CH), 44.0 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.00 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{28}BrF_3N_2NaO_5$ 679.1026; Found 679.0938.



4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-4-methoxystyryl)-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4r.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (65.3 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo′*-4r** (49.3 mg, 54% yield).

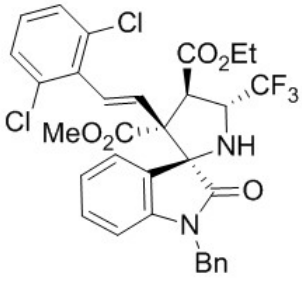
Yellow solid. **MP**: 194.9-195.7 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.27 (m, 7H), 7.17-7.06 (m, 2H), 6.89-6.78 (m, 3H), 6.67 (dd, J = 16.3, 12.1 Hz, 2H, ArH, CH=C), 6.03 (d, J = 16.4 Hz, 1H, C=CH), 4.97 (dd, J = 32.3, 13.0 Hz, 2H, CH_2), 4.65 (d, J = 15.6 Hz, 2H, 2CH), 4.19 (q, J = 7.1 Hz, 2H, CH_2), 3.81 (s, 3H, OCH_3), 3.55 (s, 3H, CH_3), 2.52 (s, 1H, NH), 1.24 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.9 (s, C=O), 170.3 (s, C=O), 170.0 (s, C=O), 159.8 (s, C), 144.3 (s, C), 135.7 (s, C), 132.5 (s, CH), 130.0 (s, CH), 128.8 (s, C), 128.7 (s, 2CH), 128.5 (q, J = 272.2 Hz, CF_3), 127.9 (s, 2CH), 127.8 (s, 2CH), 127.6 (s, CH), 126.5 (s, C), 126.1 (s, CH), 122.0 (s, CH), 121.2 (s, CH), 114.2 (s, 2CH), 109.3 (s, CH), 72.2 (s, C), 66.4 (s, C), 61.3 (s, CH_2), 60.9 (s, CH), 55.3 (s, OCH_3), 52.4 (s, CH_3), 49.2 (s, CH), 44.0 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -74.96 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{33}H_{32}F_3N_2O_6$ 609.2207; Found 609.2183.



4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-4-ethoxystyryl)-2-oxo-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4s.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (68.4 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo′*-4s** (45.7 mg, 49% yield).

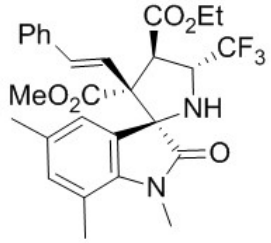
Yellow solid. **MP**: 83.7-84.2 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 15.4, 7.1 Hz, 7H), 7.18-7.06 (m, 2H), 6.88-6.78 (m, 3H), 6.66 (dd, *J* = 18.5, 12.1 Hz, 2H, ArH, CH=C), 6.02 (d, *J* = 16.4 Hz, 1H, C=CH), 5.05-4.90 (m, 2H, CH_2), 4.65 (d, *J* = 15.6 Hz, 2H, 2CH), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2), 4.04 (q, *J* = 6.9 Hz, 2H, CH_2), 3.55 (s, 3H, OCH_3), 2.53 (s, 1H, NH), 1.42 (t, *J* = 7.0 Hz, 3H, CH_3), 1.24 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 177.0 (s, C=O), 170.3 (s, C=O), 170.0 (s, C=O), 159.2 (s, C), 144.2 (s, C), 135.7 (s, C), 132.6 (s, CH), 131.2 (s, C), 130.0 (s, CH), 128.7 (s, 2CH), 127.9 (s, 2CH), 127.7 (s, 2CH), 127.6 (s, CH), 127.2 (q, *J* = 273.0 Hz, CF_3), 126.5 (s, C), 126.2 (s, CH), 122.0 (s, CH), 121.0 (s, CH), 114.7 (s, 2CH), 109.2 (s, CH), 72.1 (s, C), 66.4 (s, C), 63.5 (s, CH_2), 61.3 (s, CH_2), 60.9 (s, CH), 52.3 (s, OCH_3), 49.2 (s, CH), 44.0 (s, CH_2), 14.8 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -74.95 (d, *J* = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{34}H_{34}F_3N_2O_6$ 623.2363; Found 623.2382.



4'-Ethyl 3'-methyl 1-benzyl-3'-((E)-2,6-dichlorostyryl)-2-oxo-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo′*-4t.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (47.7 mg, 0.15 mmol, 1.0 equiv) and diene (73.8 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4t** (36.8 mg, 38% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.7, 6.2 Hz, 9H), 7.16-7.11 (m, 3H), 6.72 (d, *J* = 7.8 Hz, 1H, CH=C), 6.33 (d, *J* = 16.9 Hz, 1H, C=CH), 4.95 (d, *J* = 15.1 Hz, 2H, CH_2), 4.70 (d, *J* = 15.7 Hz, 1H, CH), 4.22 (dd, *J* = 7.1, 2.9 Hz, 2H, CH_2), 3.75 (s, 1H, CH), 3.54 (s, 3H, OCH_3), 2.57 (s, 1H, NH), 1.26 (t, *J* = 7.2 Hz, 3H. CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.7 (s, C=O), 169.9 (s, C=O), 169.6 (s, C=O), 144.1 (s, C), 138.3 (s, C), 135.7 (s, C), 134.4 (s, C), 132.2 (s, C), 130.8 (s, CH), 130.1 (s, CH), 129.0 (s, CH), 128.9 (s, 2CH), 128.7 (s, 2CH), 127.8 (s, 2CH), 127.6 (s, CH), 127.4 (s, CH), 127.1 (q, *J* = 270.0 Hz, CF_3), 126.1 (s, CH), 126.0 (s, C), 122.2 (s, CH), 109.2 (s, CH), 72.2 (s, C), 66.9 (s, C), 61.4 (s, CH_2), 60.7 (s, CH), 52.4 (s, OCH_3), 49.4 (s, CH), 44.0 (s, CH_2), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -72.89 (d, *J* = 8.5 Hz, F), -72.89 (d, *J* = 8.5 Hz, F), -73.26 (d, *J* = 8.5 Hz, F), -74.69 (d, *J* = 8.5 Hz, F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{28}Cl_2F_3N_2O_5$ 647.1322; Found 647.1303.

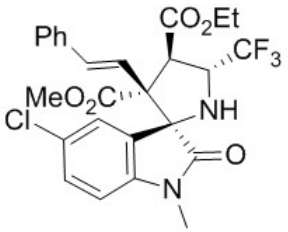


4'-Ethyl 3'-methyl 1,5,7-trimethyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4u.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (40.5 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4u** (50.9 mg, 64% yield).

Yellow solid. **MP**: 117.1-178.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 6.881-6.72 (m, 3H, 2ArH, CH=C), 6.04 (d, *J* = 16.4 Hz, 1H, C=CH), 4.89 (d, *J* = 10.5 Hz, 1H, CH), 4.61 (d, *J* = 8.8 Hz, 1H, CH), 4.20 (q, *J* = 7.1 Hz, 2H, CH_2), 3.67 (s, 3H, OCH_3), 3.41 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 2.43 (d, *J* = 6.1 Hz, 1H, NH), 1.97 (s,

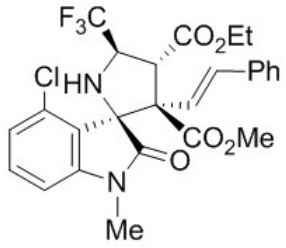
3H, CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.7 (s, C=O), 170.4 (s, C=O), 170.2 (s, C=O), 140.2 (s, C), 136.1 (s, C), 134.4 (s, CH), 133.0 (s, CH), 130.9 (s, C), 128.7 (s, 2CH), 128.2 (s, CH), 126.9 (s, C), 126.5 (s, 2CH), 125.4 (q, J = 277.5 Hz, CF_3), 125.3 (s, CH), 123.9 (s, CH), 119.5 (s, C), 71.8 (s, C), 66.8 (s, C), 61.3 (s, CH_2), 60.9 (s, CH), 52.5 (s, OCH_3), 48.9 (s, CH), 29.8 (s, CH_3), 20.6 (s, CH_3), 19.0 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.14 (d, J = 8.5 Hz, F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}F_3N_2O_5$ 531.2101; Found 531.2103.



4'-Ethyl 3'-methyl 5-chloro-1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4v.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (41.4 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4v** (38.6 mg, 48% yield).

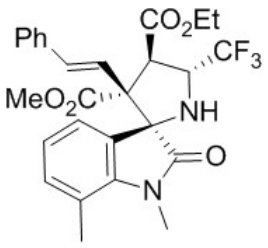
Yellow solid. **MP**: 197.3-198.0 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 7.26 (s, 1H), 7.05 (d, J = 2.0 Hz, 1H, CH=C), 6.75-6.69 (m, 2H), 6.09 (d, J = 16.4 Hz, 1H, C=CH), 4.83 (d, J = 10.4 Hz, 1H, CH), 4.65-4.57 (m, 1H, CH), 4.21 (q, J = 7.1 Hz, 2H, CH_2), 3.67 (s, 3H, OCH_3), 3.16 (s, 3H, CH_3), 2.47 (d, J = 7.5 Hz, 1H, NH), 1.25 (t, J = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.5 (s, C=O), 170.2 (s, C=O), 169.8 (s, C=O), 143.6 (s, C), 135.8 (s, C), 134.0 (s, CH), 130.0 (s, CH), 128.8 (s, 2CH), 128.4 (s, CH), 127.9 (s, C), 127.1(s, C), 127.0 (s, CH), 126.7 (s, 2CH), 125.6 (q, J = 272.2 Hz, CF_3), 123.1 (s, CH), 109.1 (s, CH), 72.1 (s, C), 66.6 (s, C), 61.4 (s, CH_2), 60.9 (s, CH), 52.6 (s, OCH_3), 48.7 (s, CH), 26.3 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -75.05 (d, J = 5.6 Hz, 3F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClF_3N_2O_5$ 537.1399; Found 537.1389.



4'-Ethyl 3'-methyl 4-chloro-1-methyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4w.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (41.4 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4w** (37.0 mg, 46% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 4.1 Hz, 4H), 7.23 (d, *J* = 5.1 Hz, 2H), 7.08 (d, *J* = 16.4 Hz, 1H), 6.76 (dd, *J* = 15.4, 7.9 Hz, 2H, ArH, CH=C), 5.98 (d, *J* = 16.3 Hz, 1H, C=CH), 4.65 (s, 1H, CH), 4.20 (q, *J* = 7.1 Hz, 2H, CH_2), 3.66 (s, 3H, CH_3), 3.15 (s, 3H, OCH_3), 2.97 (d, *J* = 21.8 Hz, 1H, CH), 1.66 (s, 1H, NH), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 176.8 (s, C=O), 170.3 (s, C=O), 169.6 (s, C=O), 147.1 (s, C), 136.3 (s, C), 131.8 (s, C), 131.5 (s, CH), 131.1 (s, CH), 128.5 (s, 2CH), 128.0 (s, CH), 126.8 (s, 2CH), 125.2 (q, *J* = 276.7 Hz, CF_3), 124.2 (s, CH), 123.3 (s, CH), 122.4 (s, C), 107.1 (s, CH), 74.3 (s, C), 68.4 (s, C), 61.7 (s, CH), 61.3 (s, CH_2), 52.6 (s, OCH_3), 48.1 (s, CH), 26.5 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -75.28(s, CF_3) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClF_3N_2O_5$ 537.1399; Found 537.1393.



4'-Ethyl 3'-methyl 1,7-dimethyl-2-oxo-3'-((E)-styryl)-5'-(trifluoromethyl)-spiro[indoline-3,2'-pyrrolidine]-3',4'-dicarboxylate *exo'*-4x.

The reaction N-2,2,2-Trifluoroethylisatin ketimines (38.4 mg, 0.15 mmol, 1.0 equiv) and diene (58.5 mg, 0.23 mmol, 1.5 equiv), after a flash column chromatography (petroleum : AcOEt = 6:1), afforded the product ***exo'*-4x** (50.3 mg, 65% yield).

Yellow solid. **MP**: 171.2-172.0 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H, CH=C), 6.74 (dd, *J* = 15.9, 8.3 Hz, 2H), 6.03 (d, *J* = 16.4 Hz, 1H, C=CH), 4.89 (d, *J* = 10.5 Hz, 1H, CH), 4.64-4.59 (m, 1H, CH), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2), 3.67 (s, 3H, OCH_3), 3.44 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.43 (s, 1H, NH), 1.24 (t, *J* = 7.1 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) *δ* 177.8 (s, C=O), 170.4 (s, C=O), 170.1 (s, C=O), 142.7 (s, C), 136.1 (s, C), 134.0 (s, CH), 133.0 (s, CH), 128.8 (s, 2CH), 128.2 (s, CH), 126.9 (s, C), 126.7 (s, 2CH), 125.7 (q, *J* = 273.7 Hz, CF_3), 124.1 (s, CH), 123.5 (s, CH), 121.8 (s, CH), 119.9 (s, C), 71.5 (s, C), 66.9 (s, C), 61.3 (s, CH), 60.8 (s, CH_2), 52.5 (s, OCH_3), 49.1 (s, CH), 29.8 (s, CH_3), 19.2 (s, CH_3), 14.1 (s, CH_3). **^{19}F NMR** (282 MHz, $CDCl_3$) *δ* -74.95 (d, *J* = 5.6 Hz, 2F), -117.16 (q, *J* = 5.6 Hz, F) ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}F_3N_2O_5$ 517.1945; Found 517.1990.

4. HRMS study

Dectection of intermediate C： To a dry flask filled with nitrogen were added **1** (0.2 mmol) in 2 mL CH_3CN，then PBu_3 (0.05 mmol) were added. This solution was stirred at room temperature for 10 mins. Then a small aliquot was injected in the machine for mass spectrometry. As shown in Figure S1, the proposed intermediate **C** can be found with MW = 705.3620 ([M+H]+).

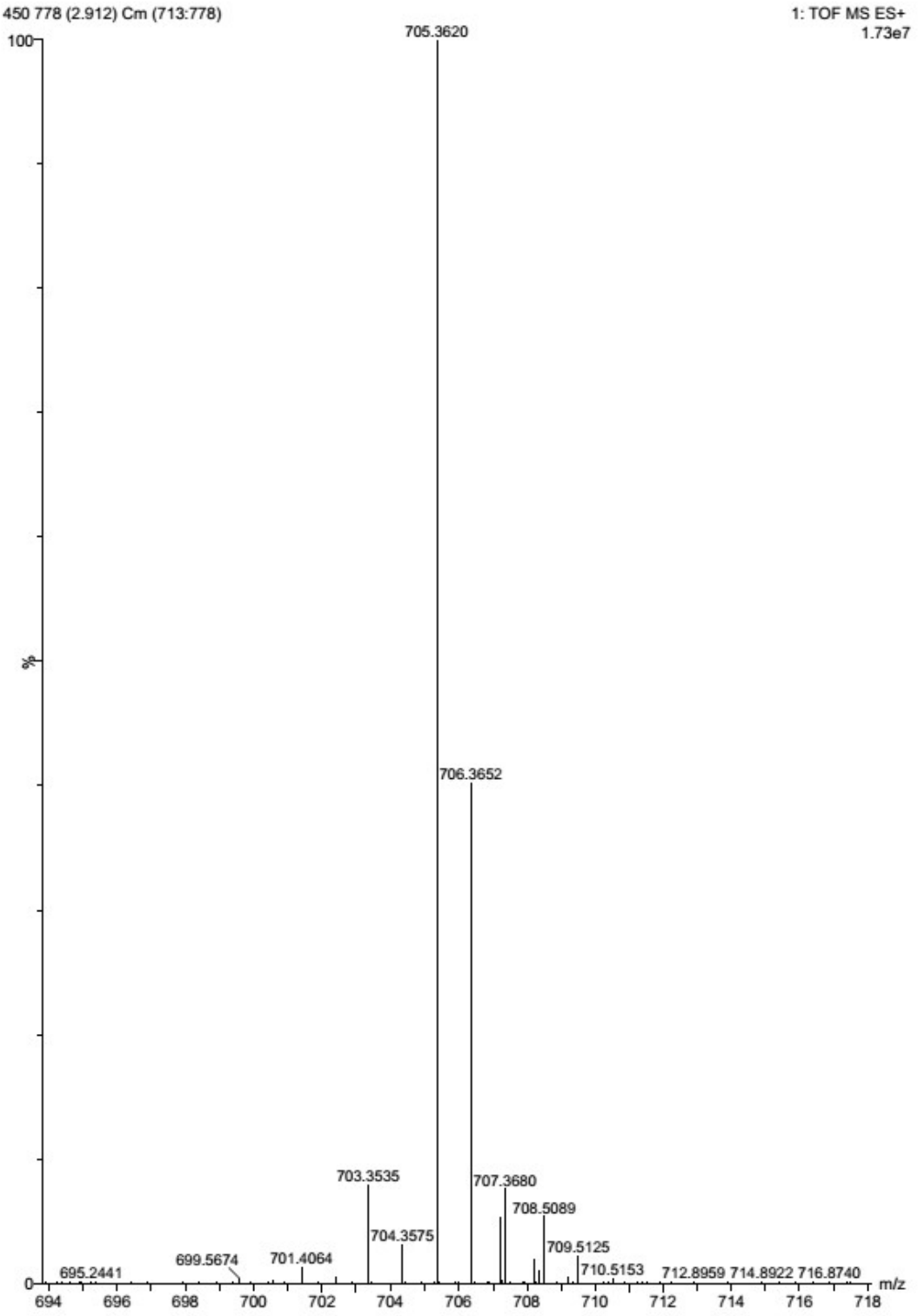
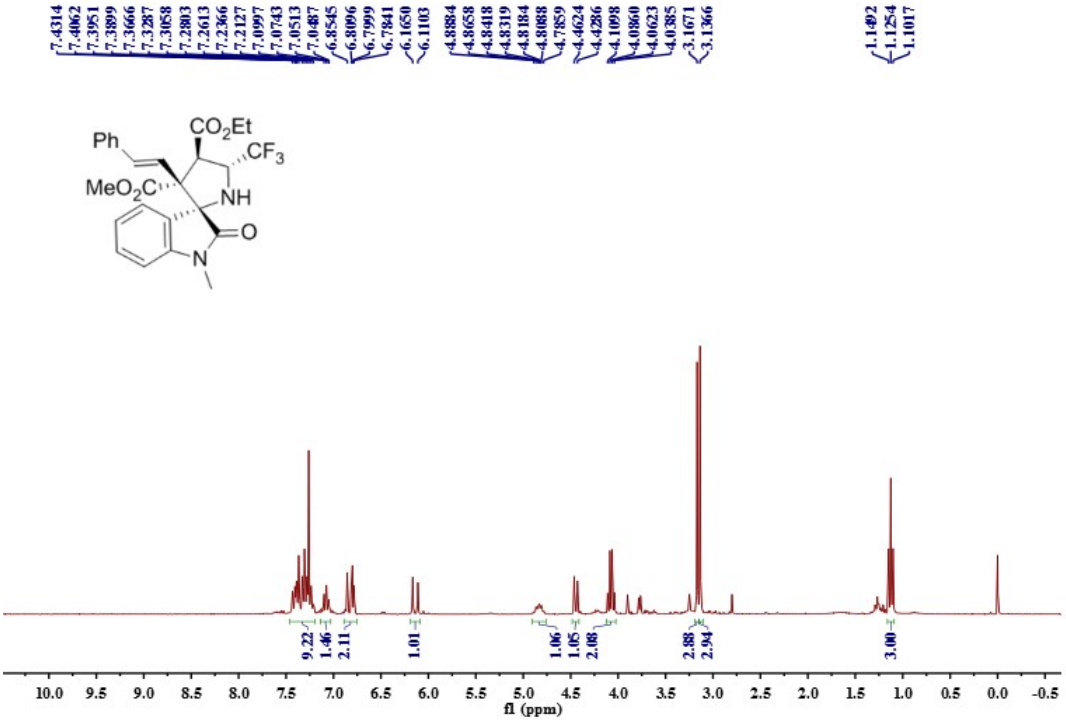
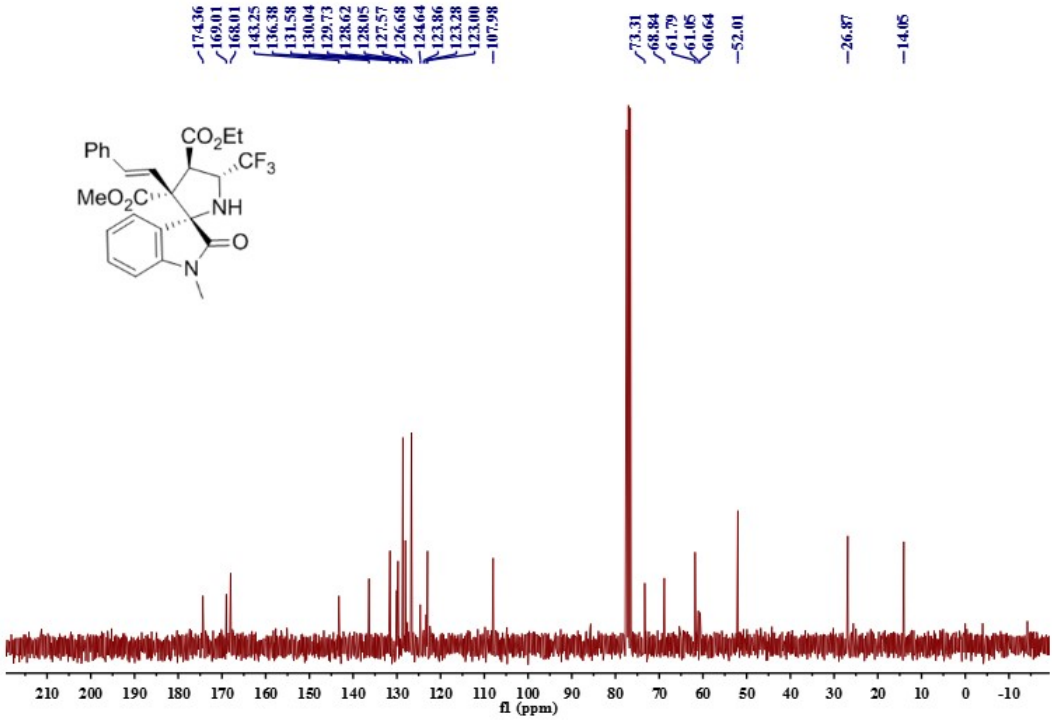


Figure S1. HRMS analysis of the intermediate **C.**

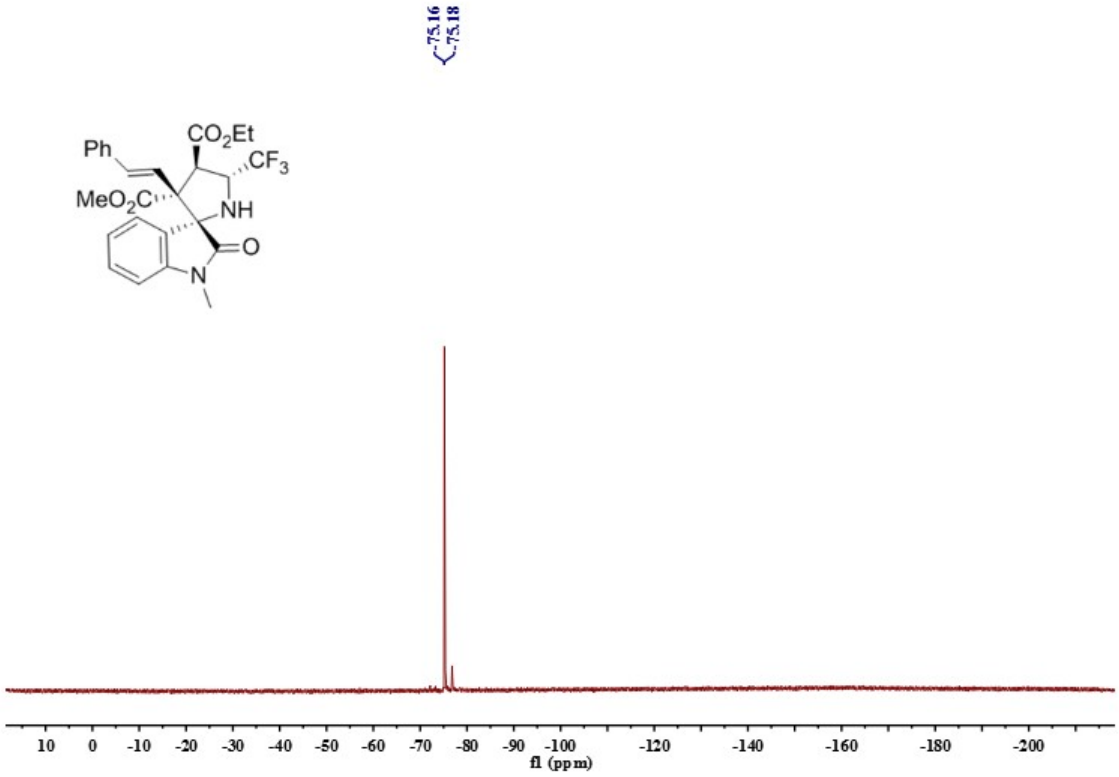
5. Copies of ^{1}H NMR, ^{13}C NMR spectra



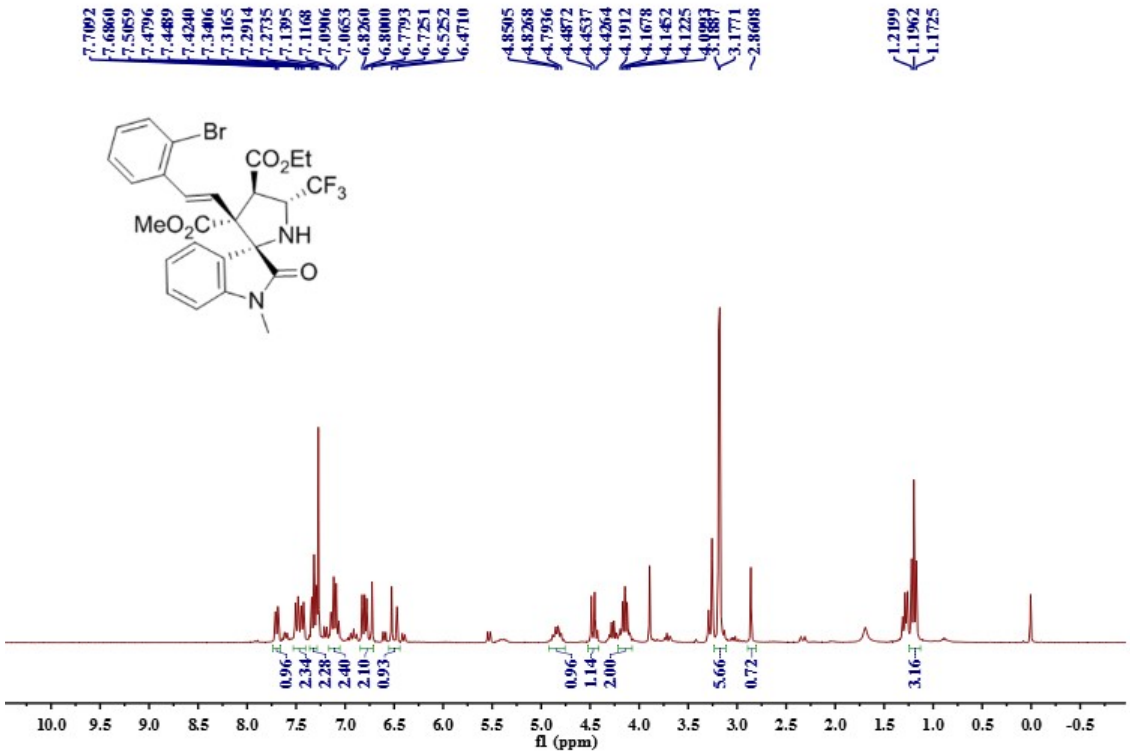
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3a



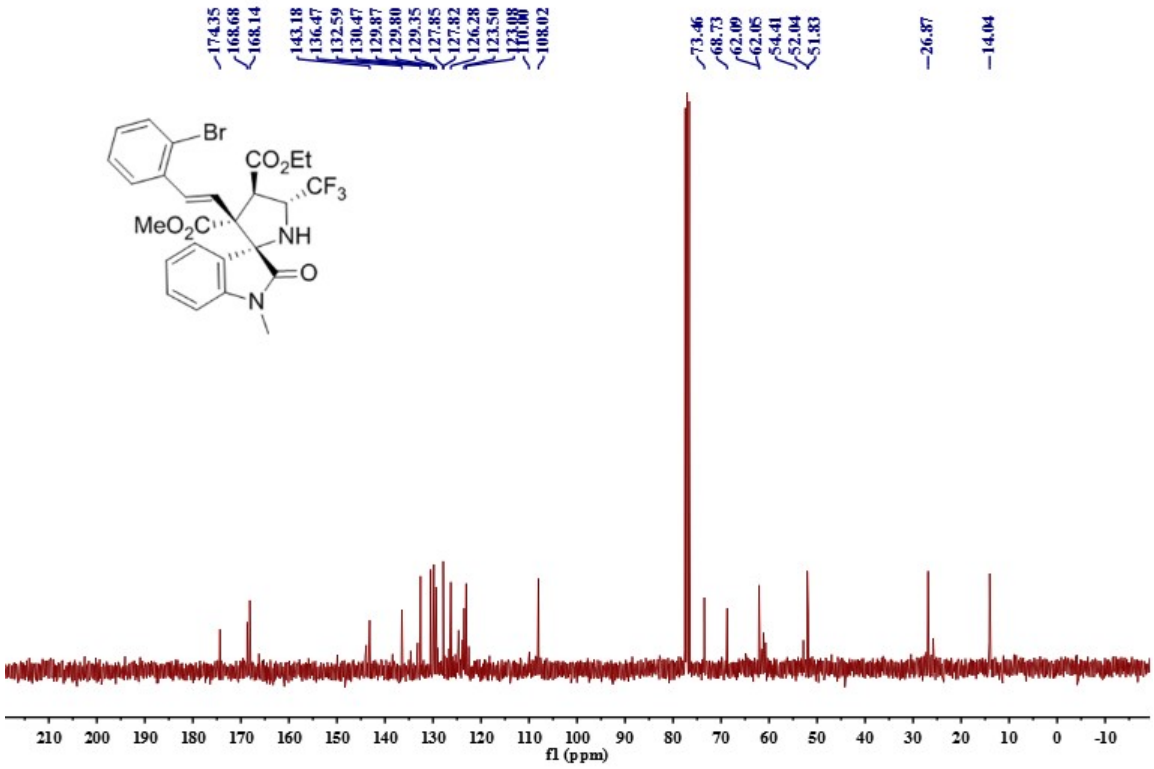
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3a



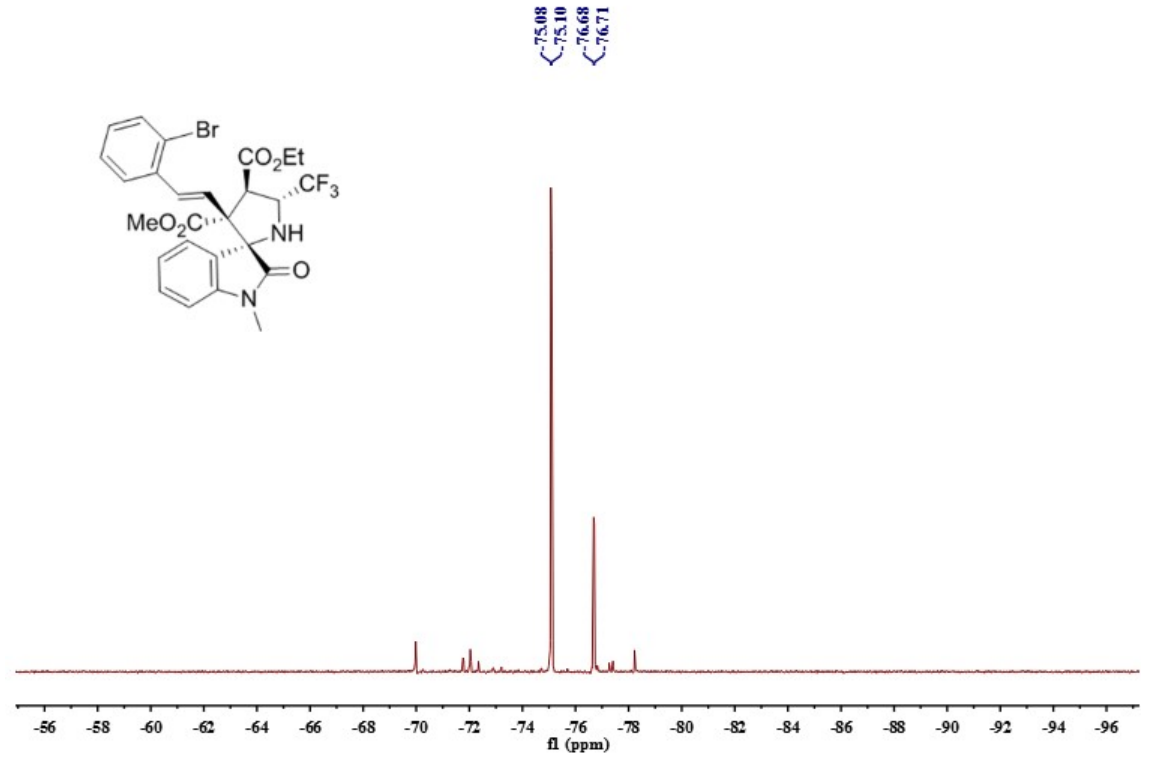
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3a



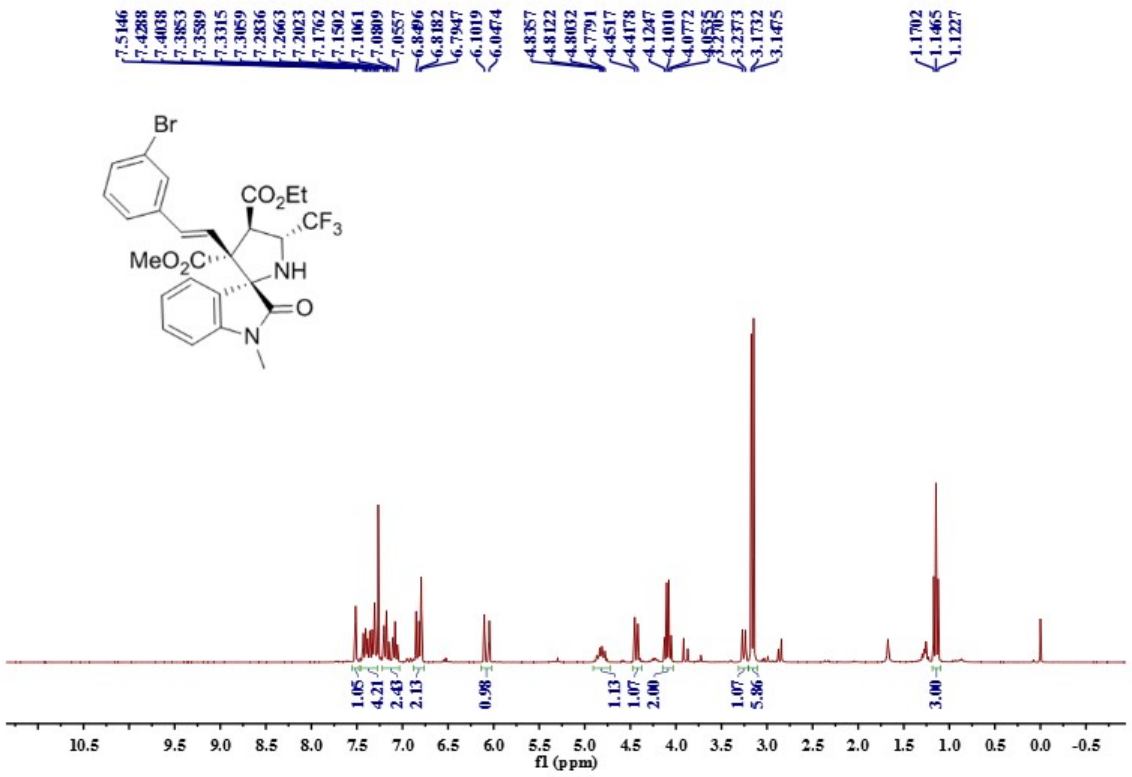
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3b



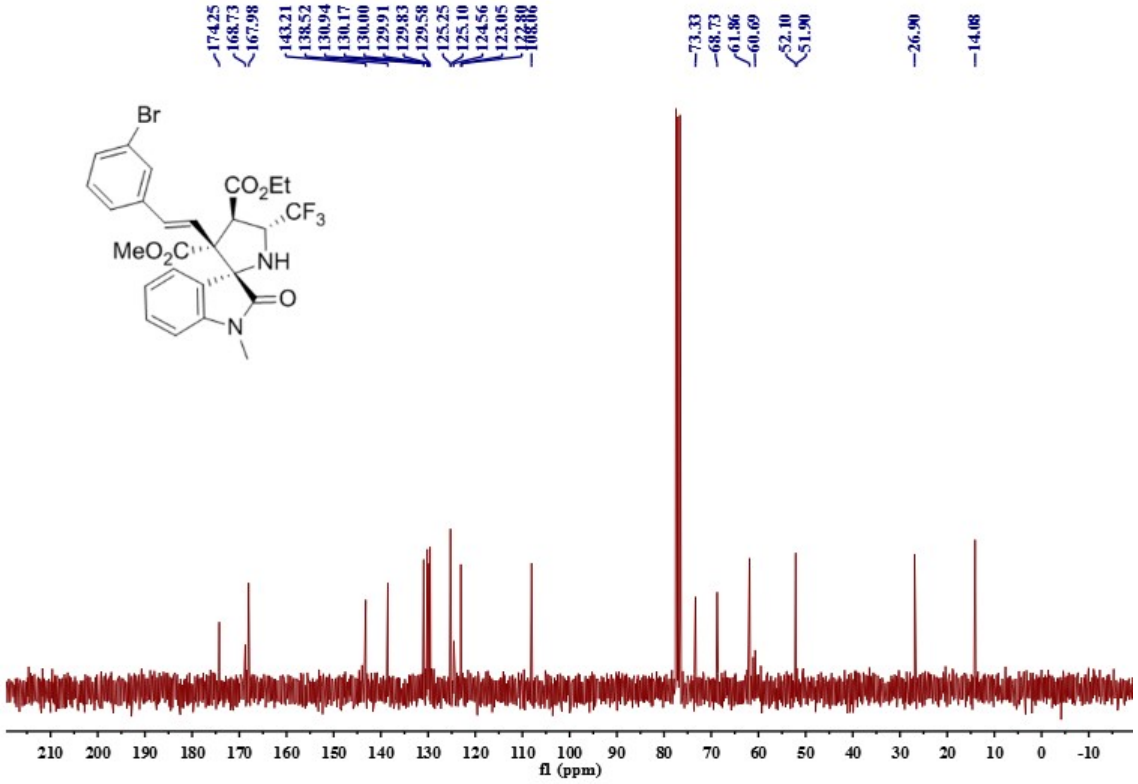
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3b



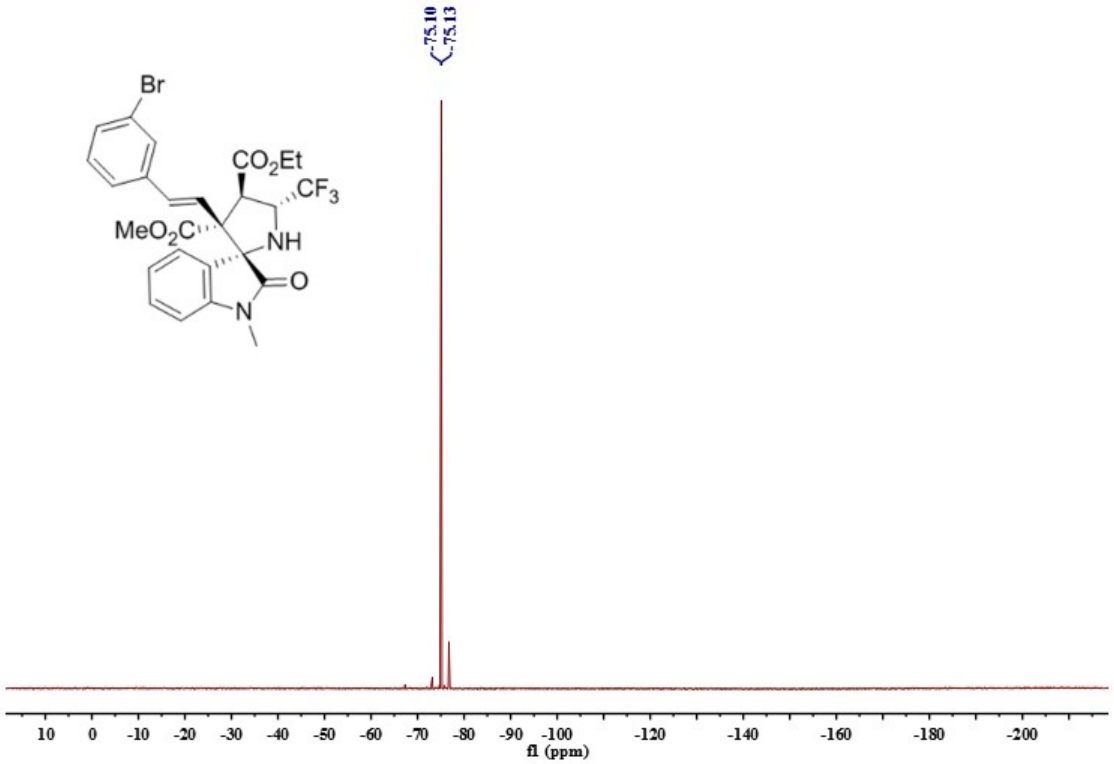
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3b



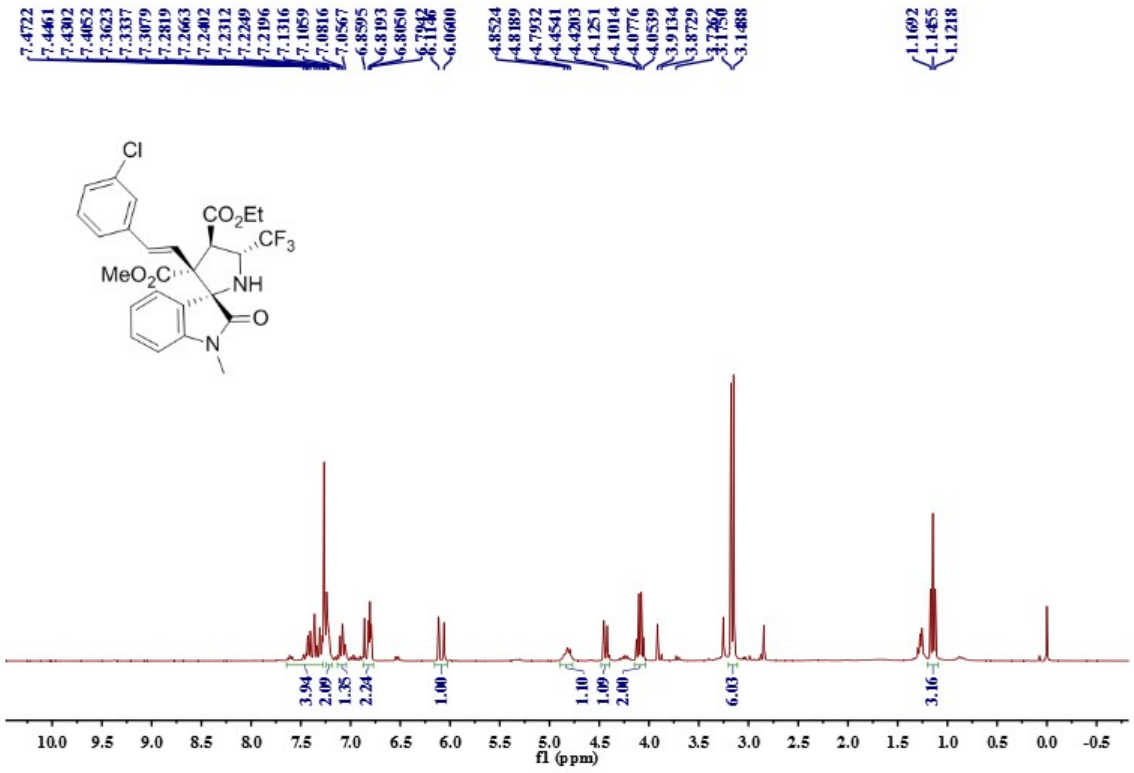
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3c



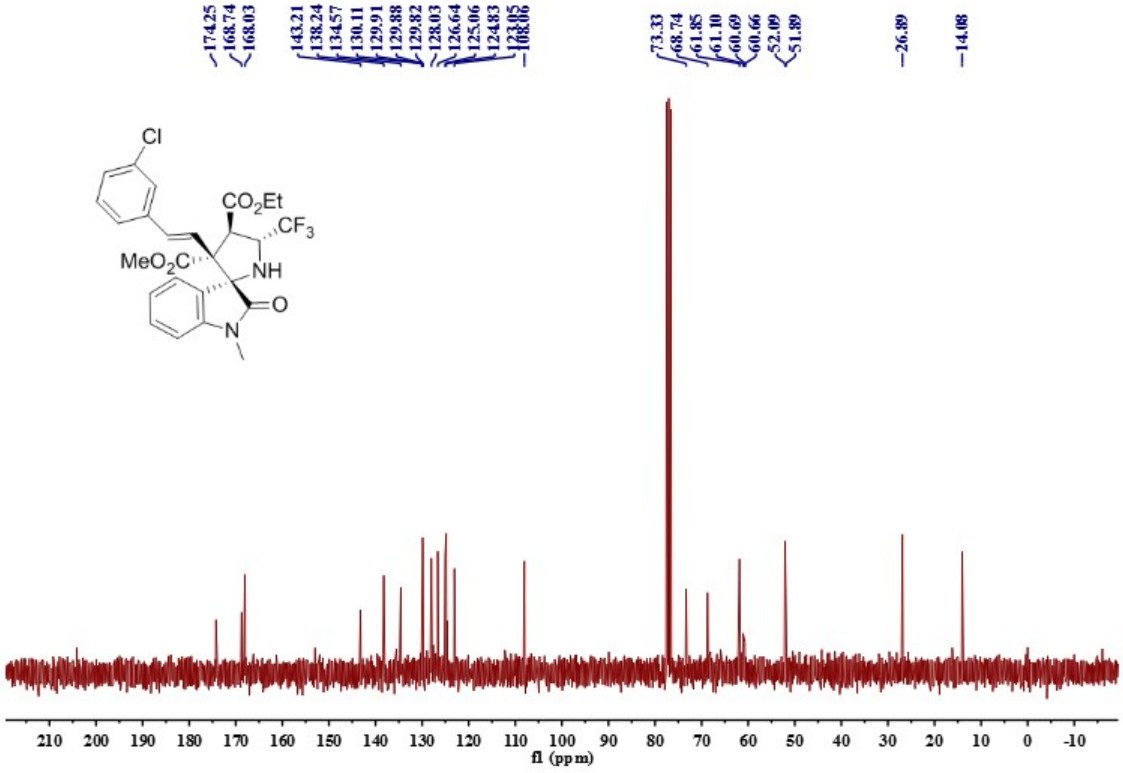
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3c



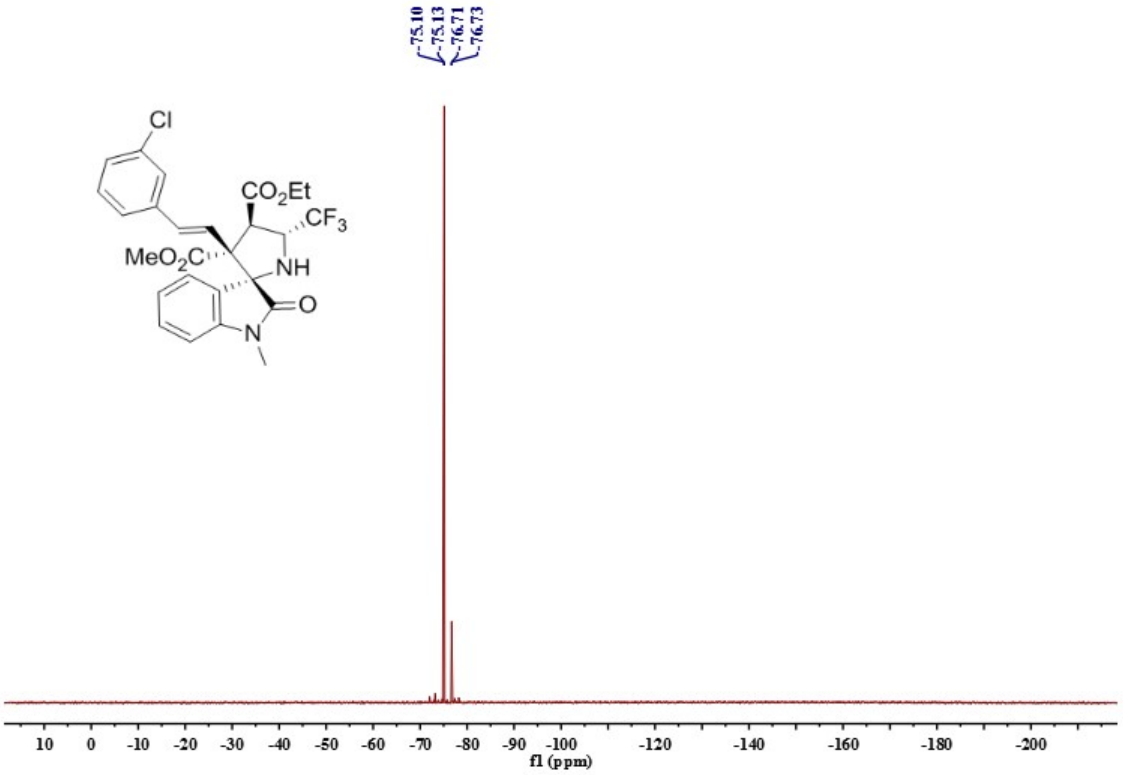
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3c



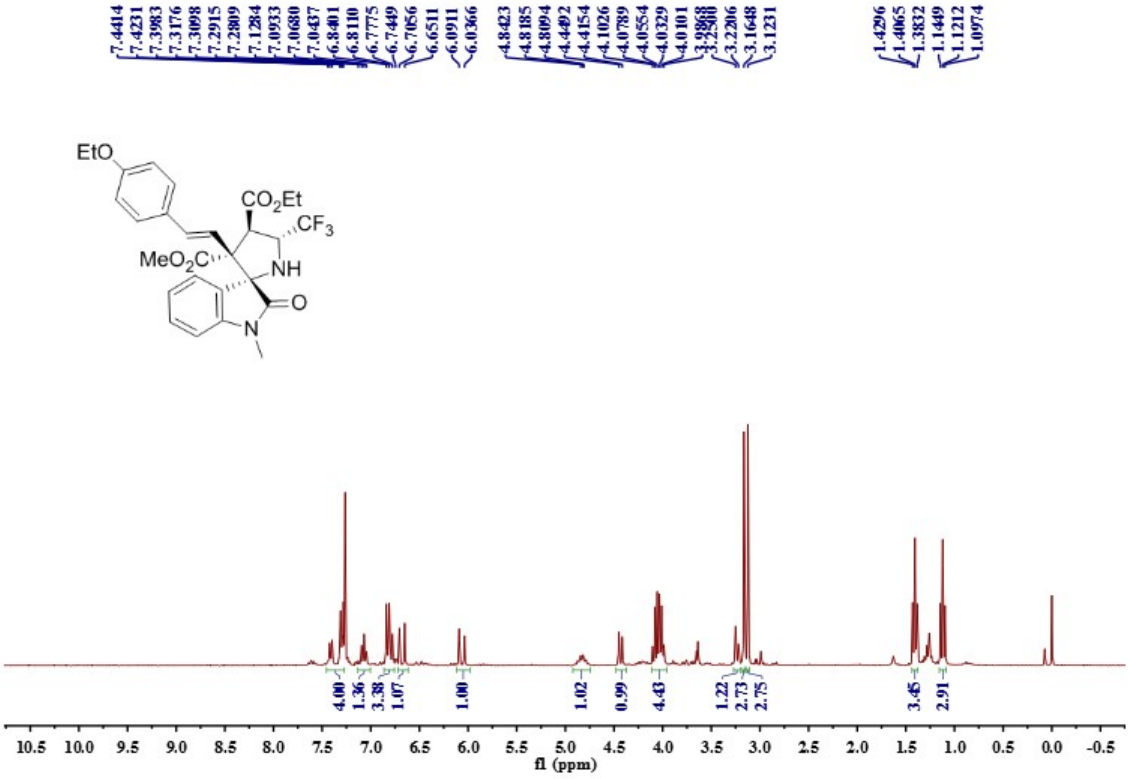
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3d



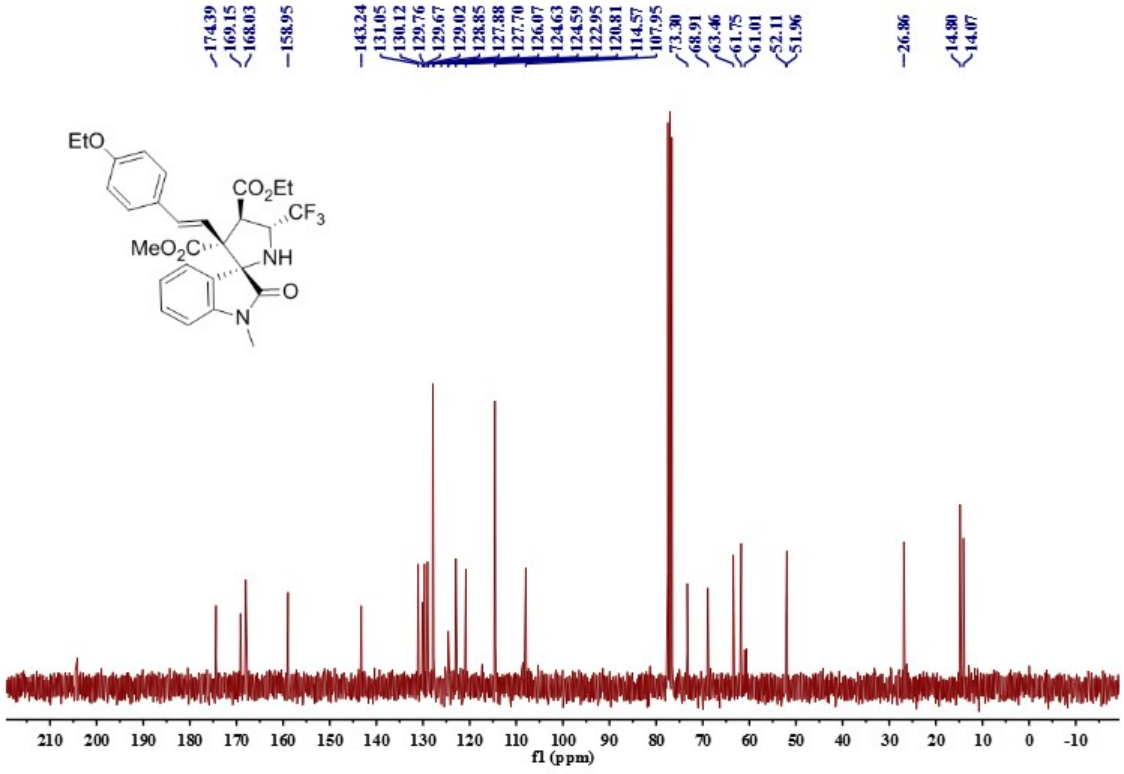
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3d



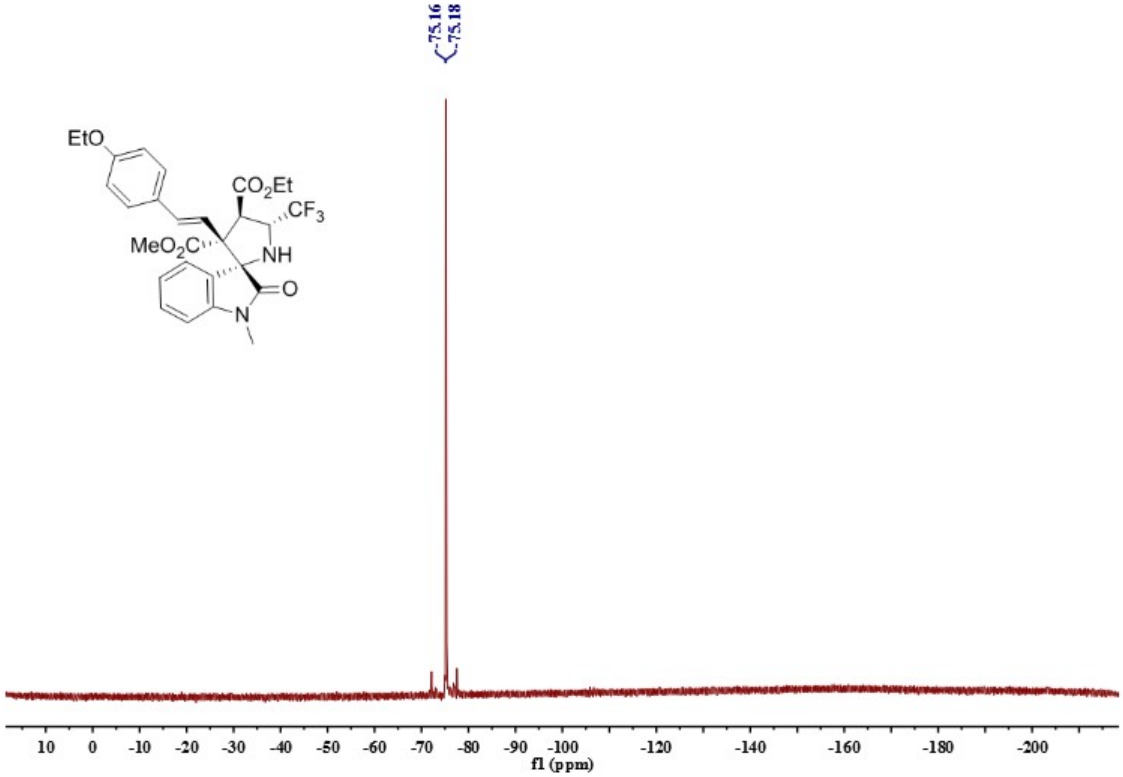
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3d



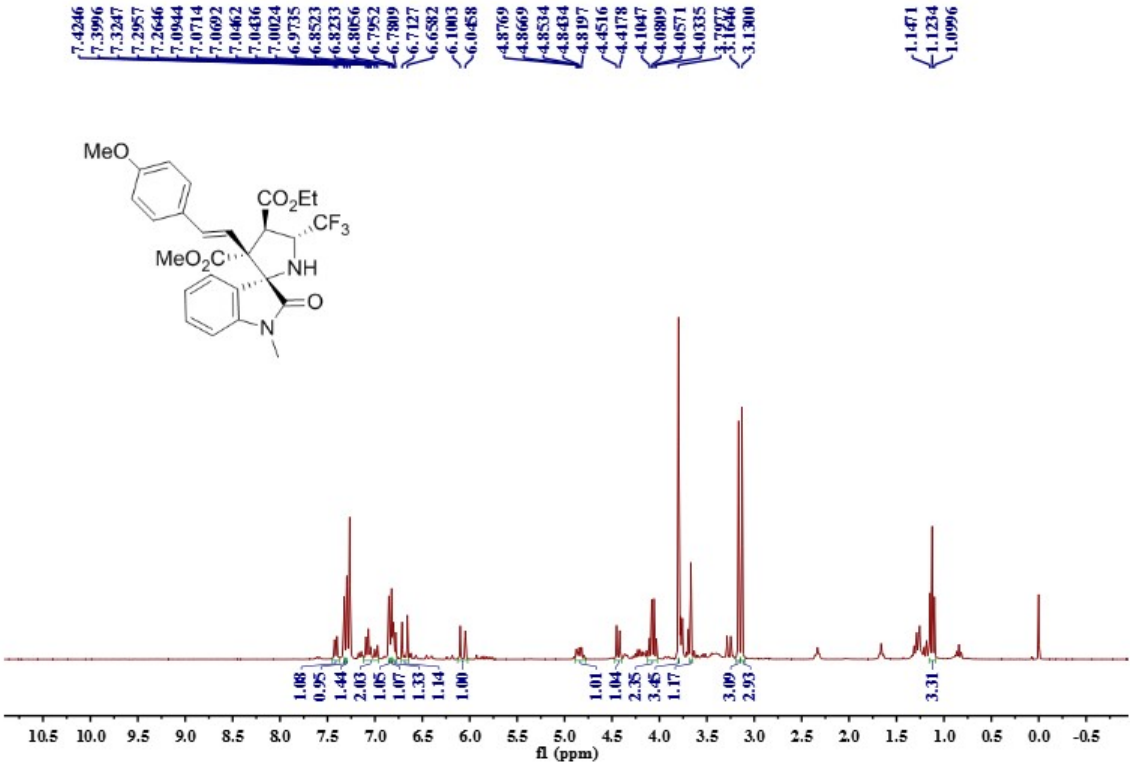
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3e



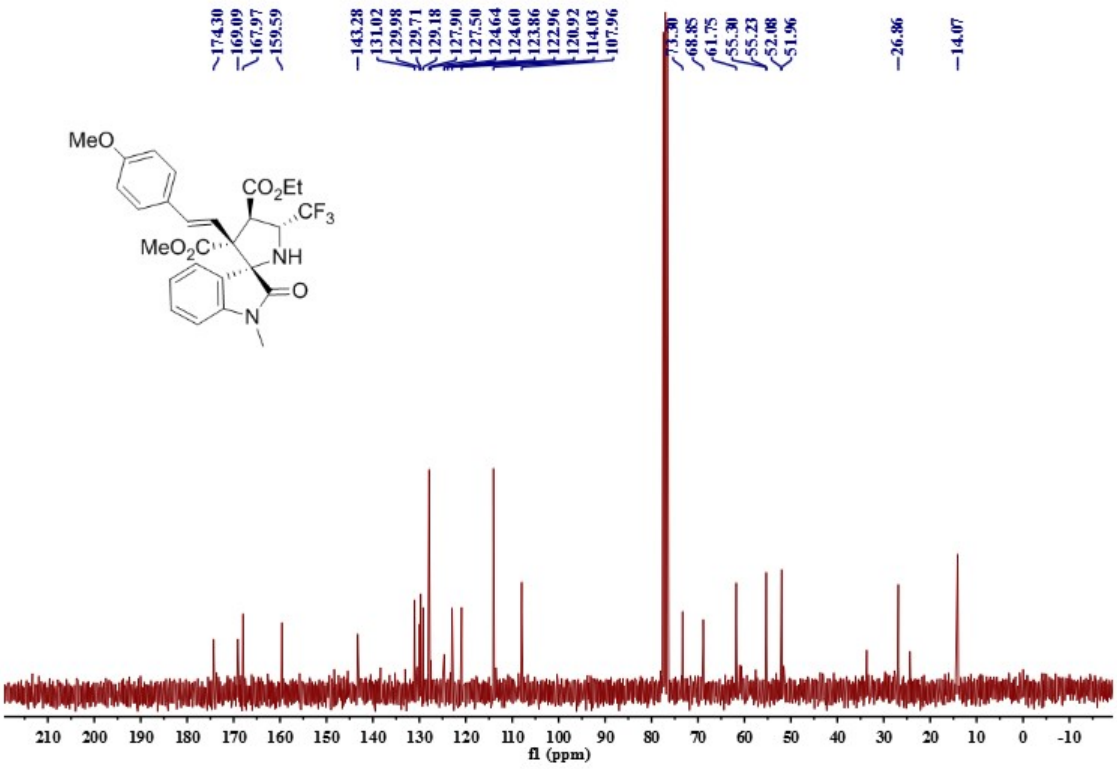
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3e



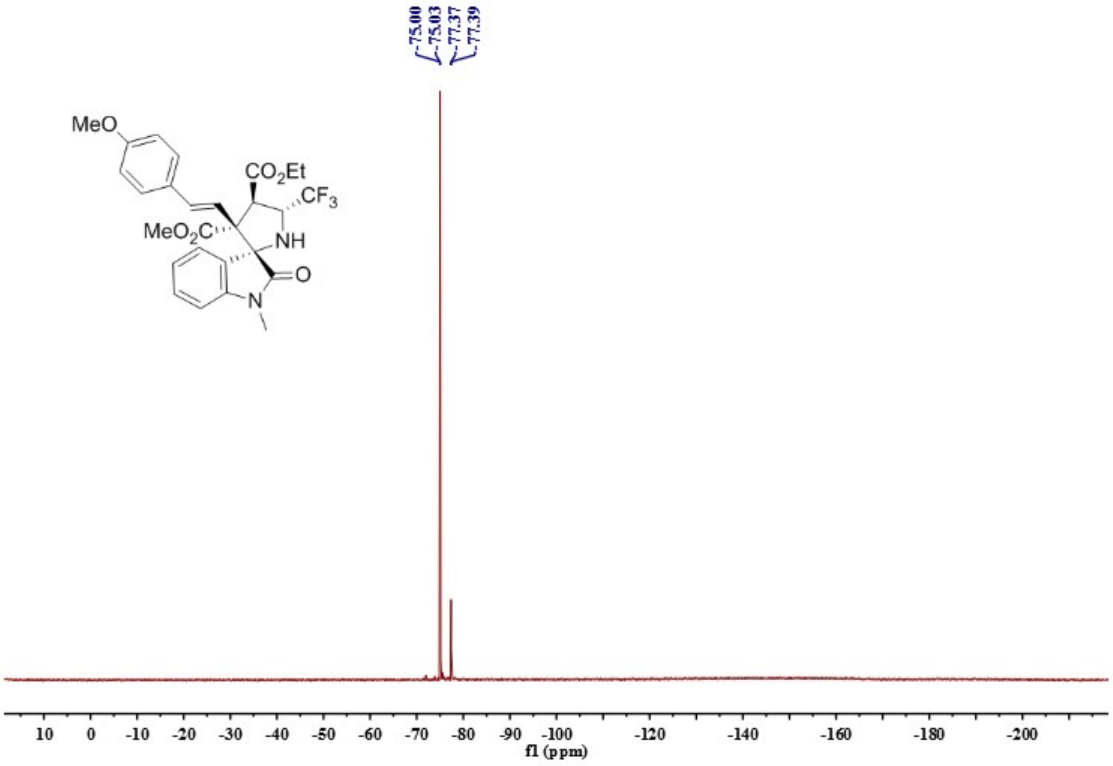
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3e



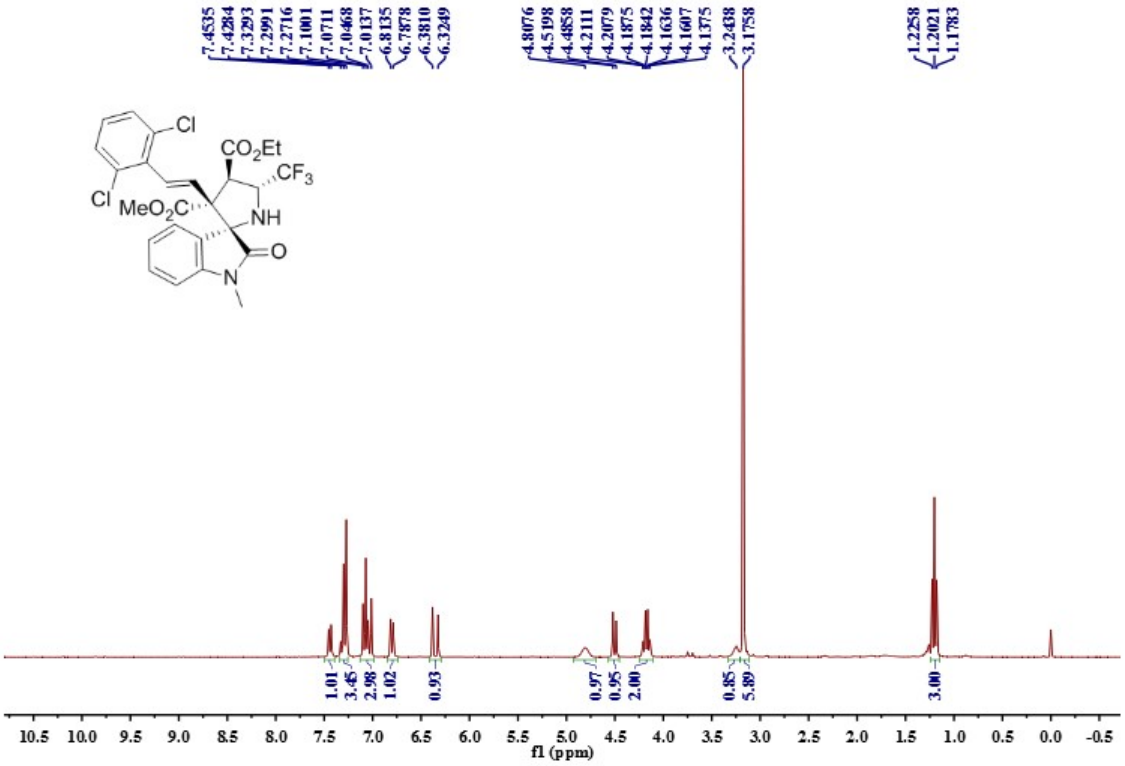
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3f



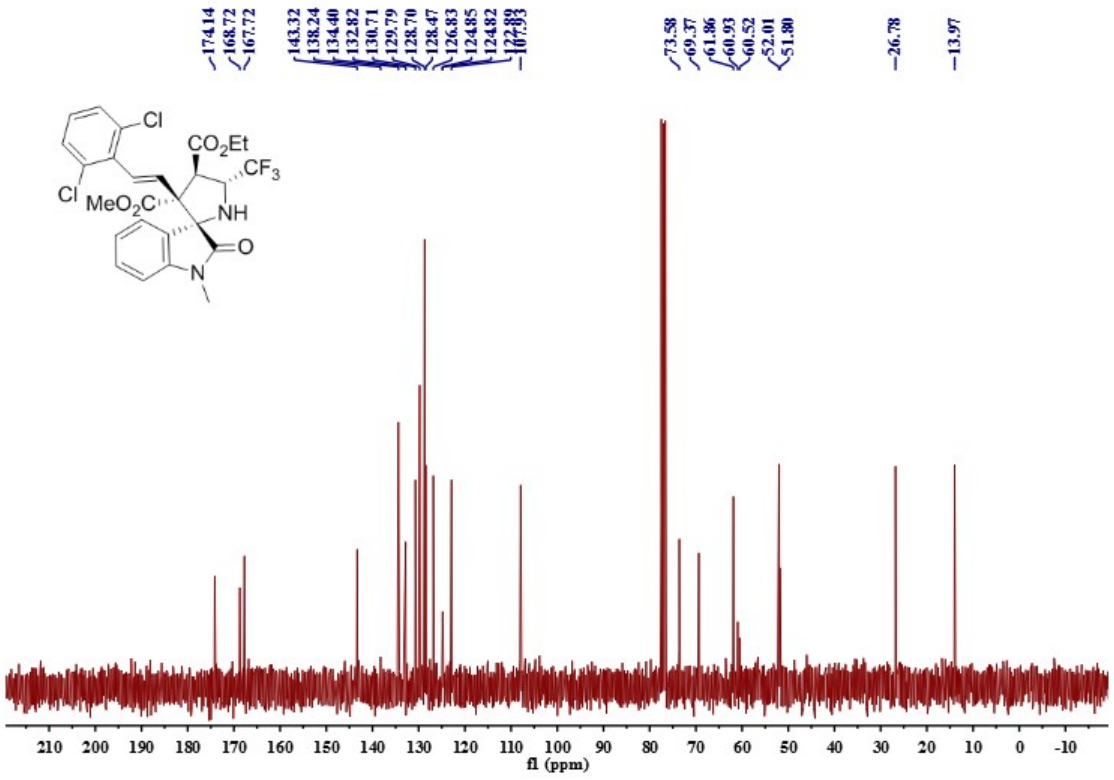
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3f



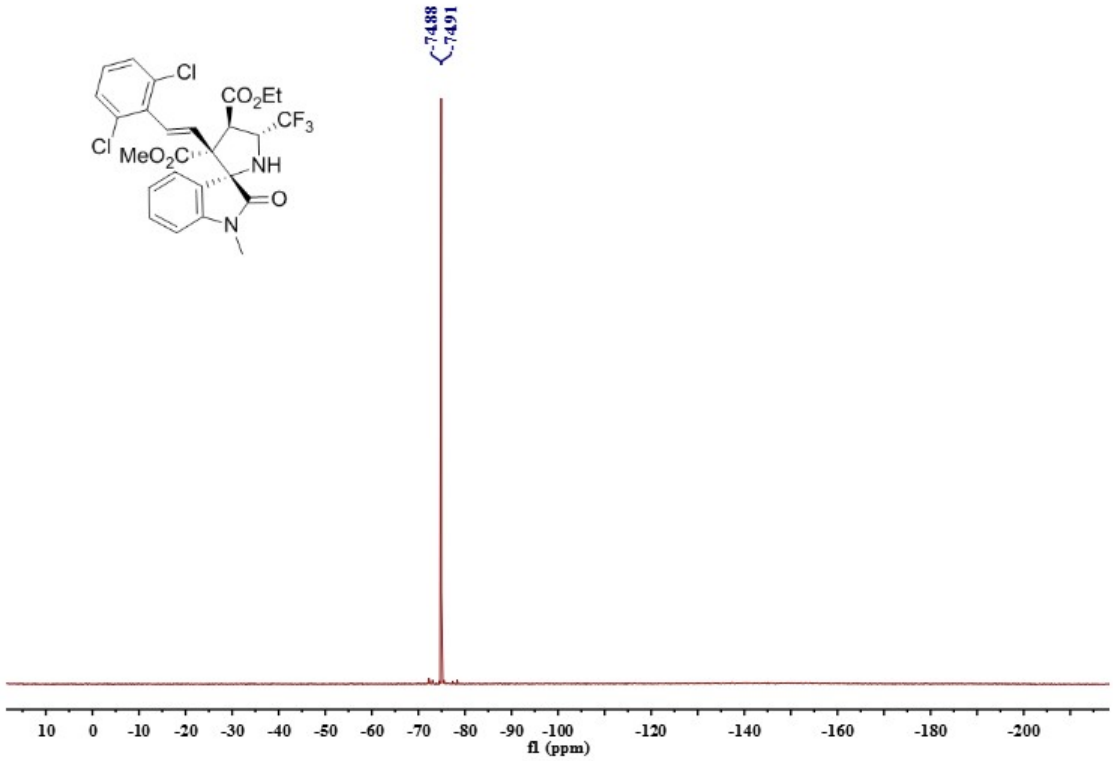
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3f



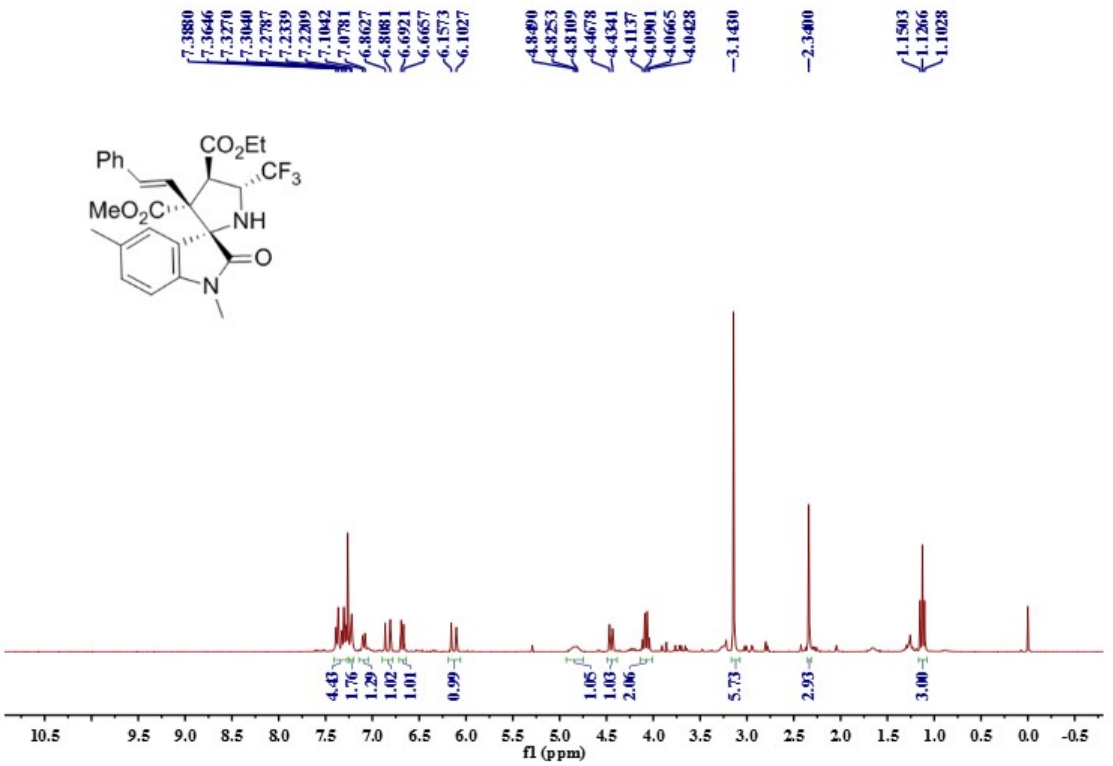
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3g



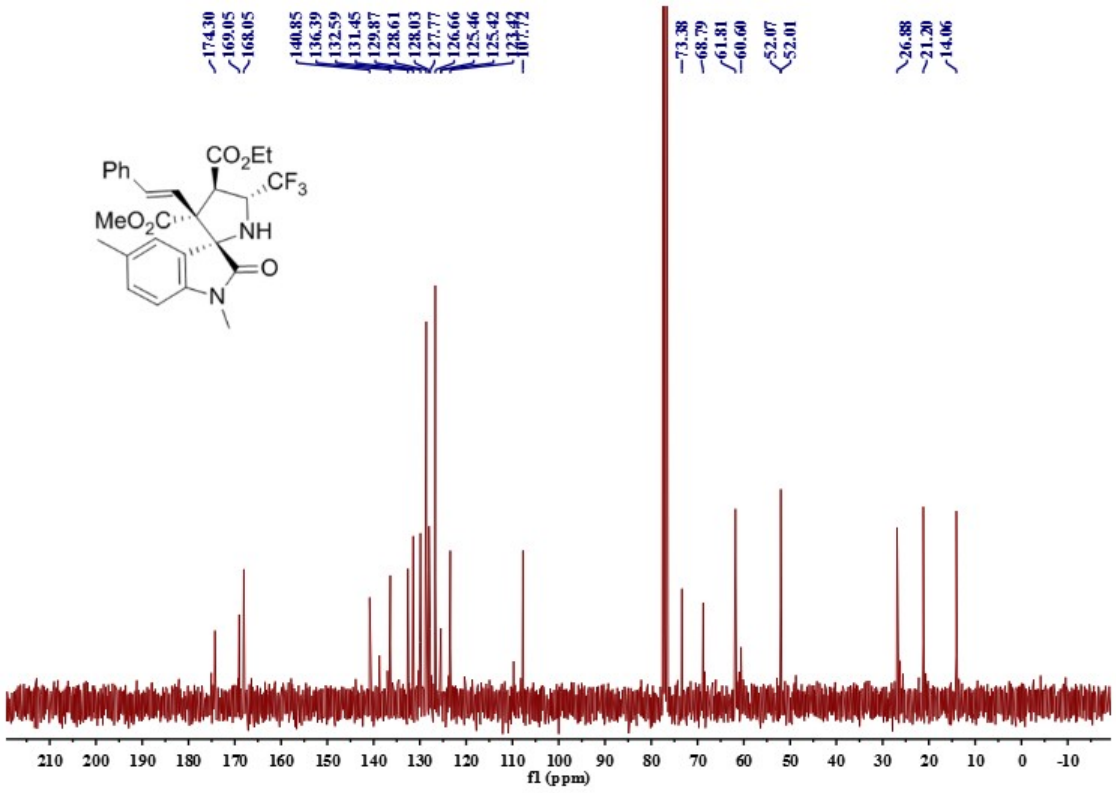
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3g



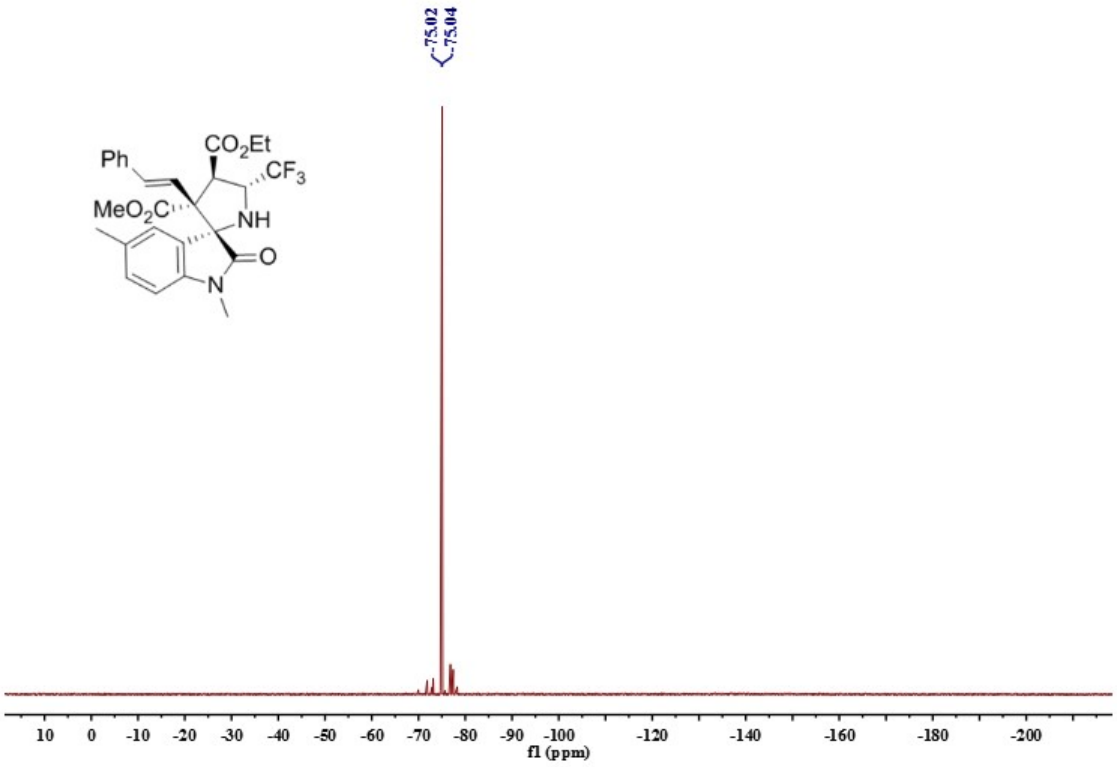
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3g



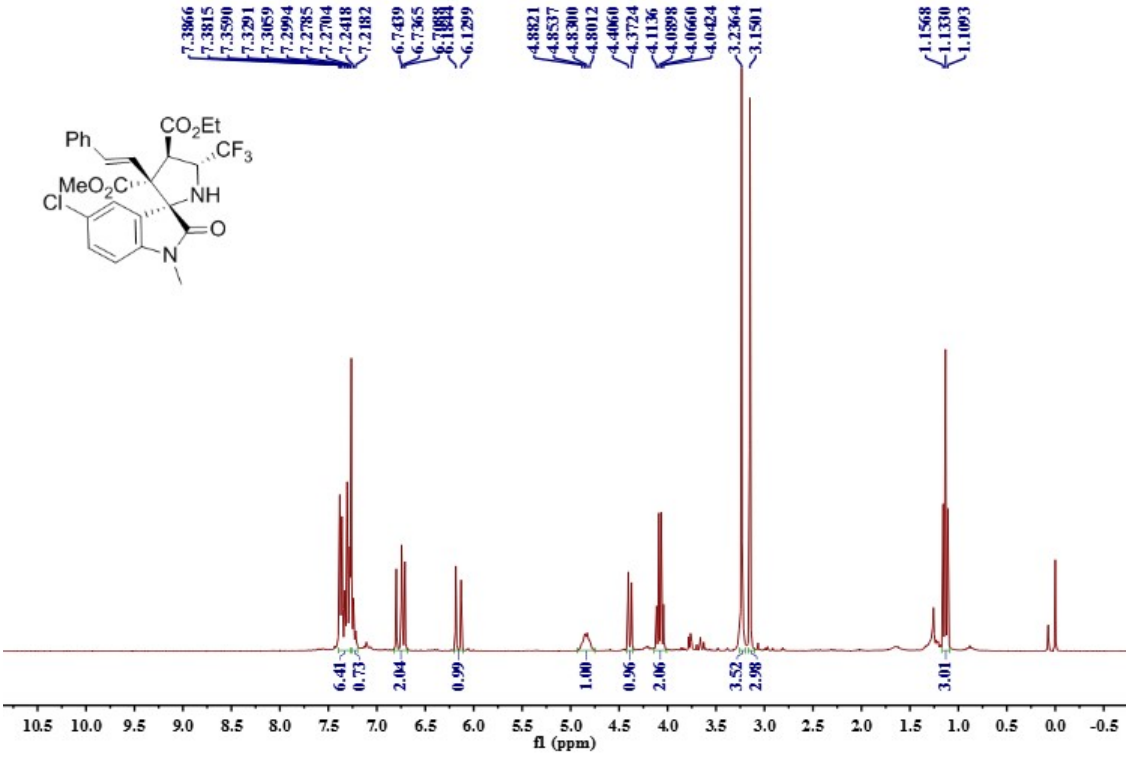
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3h



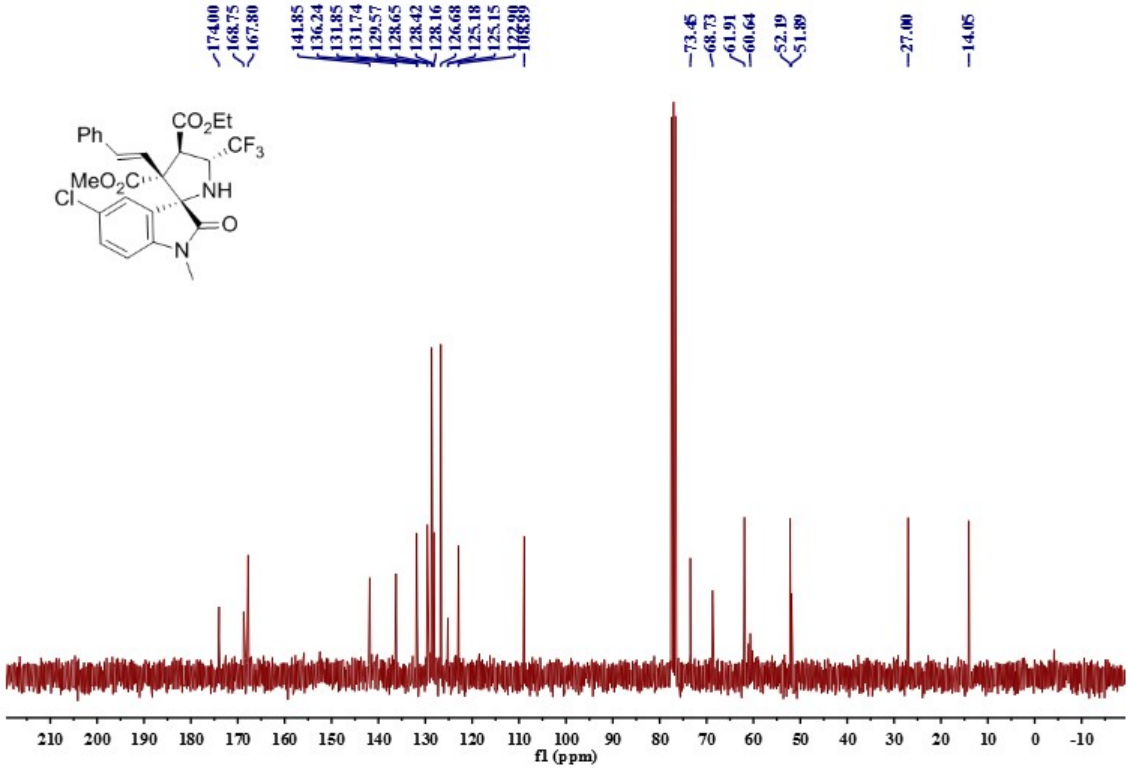
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3h



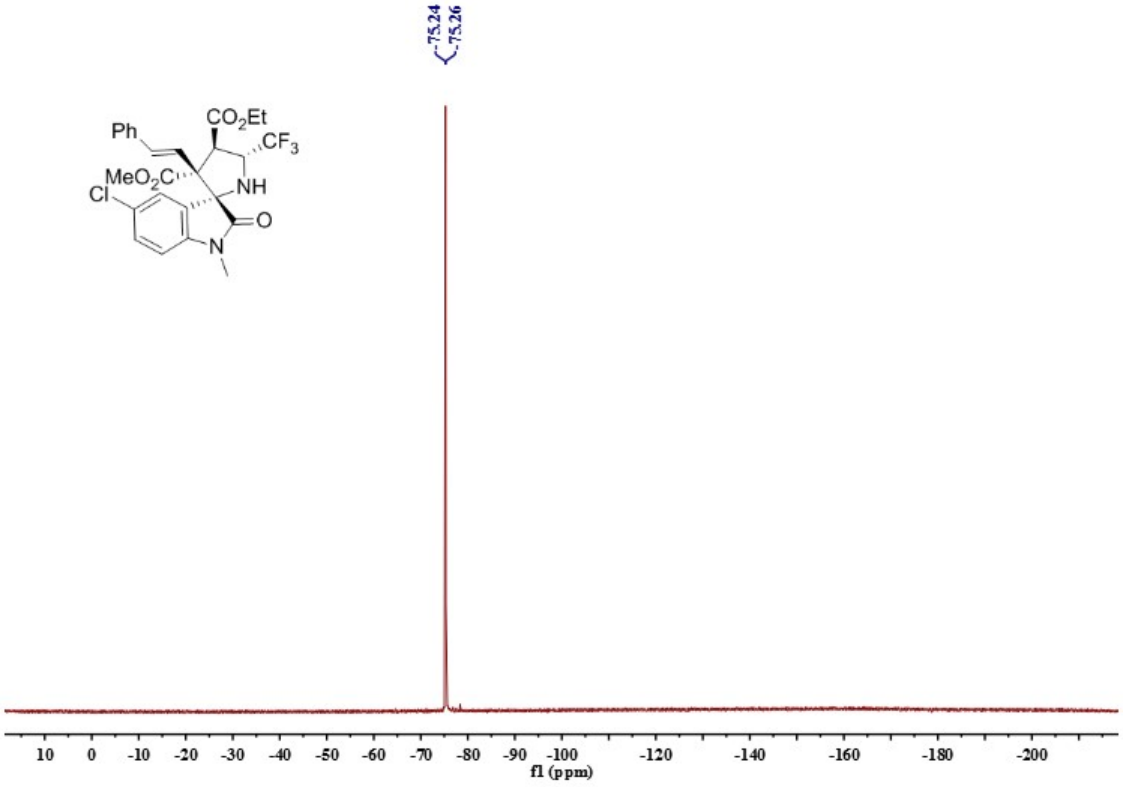
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3h



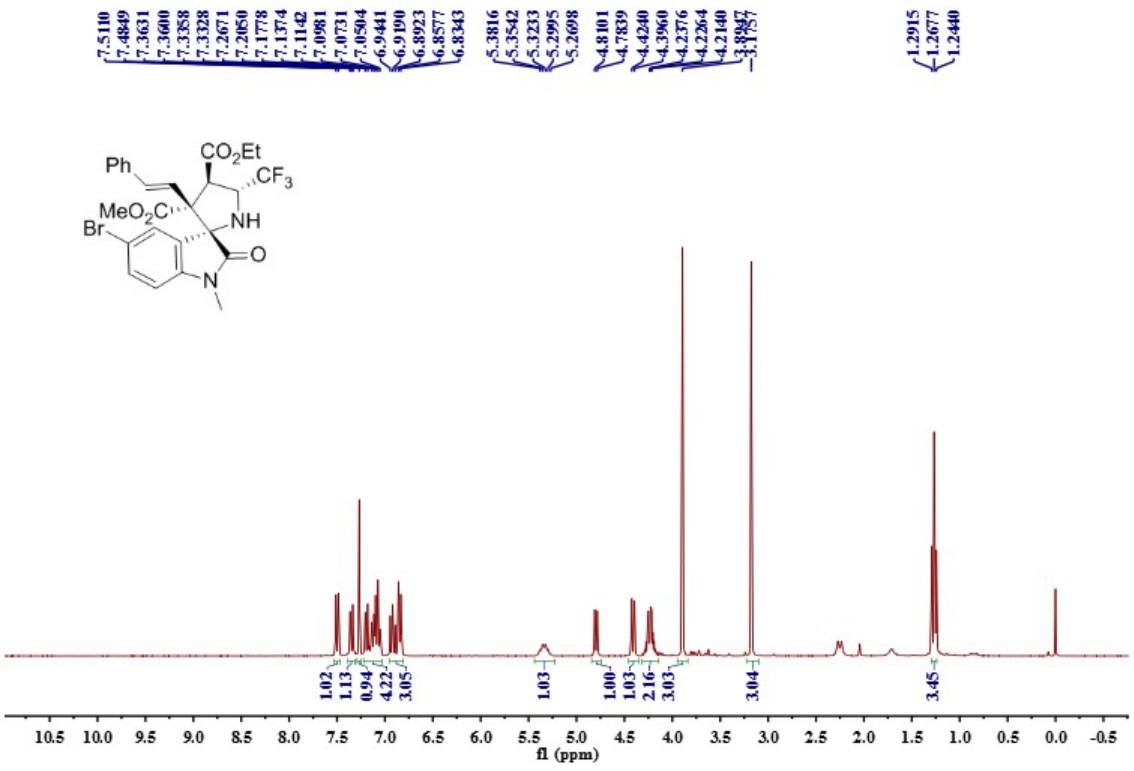
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3i



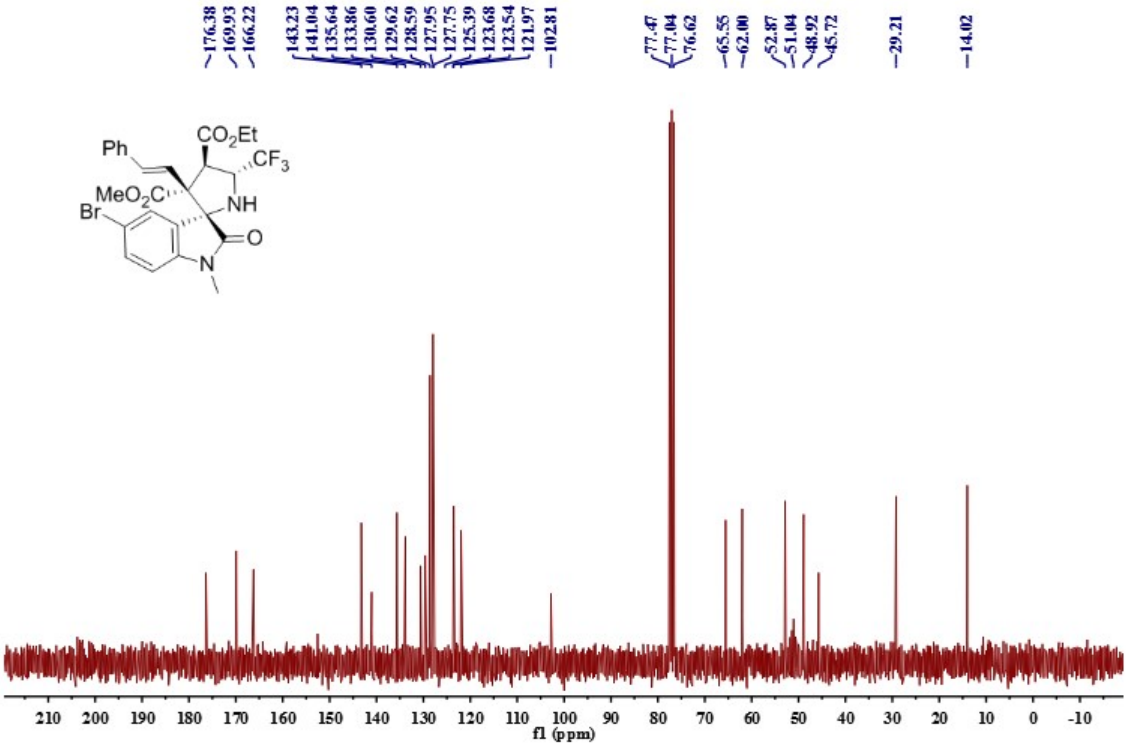
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3i



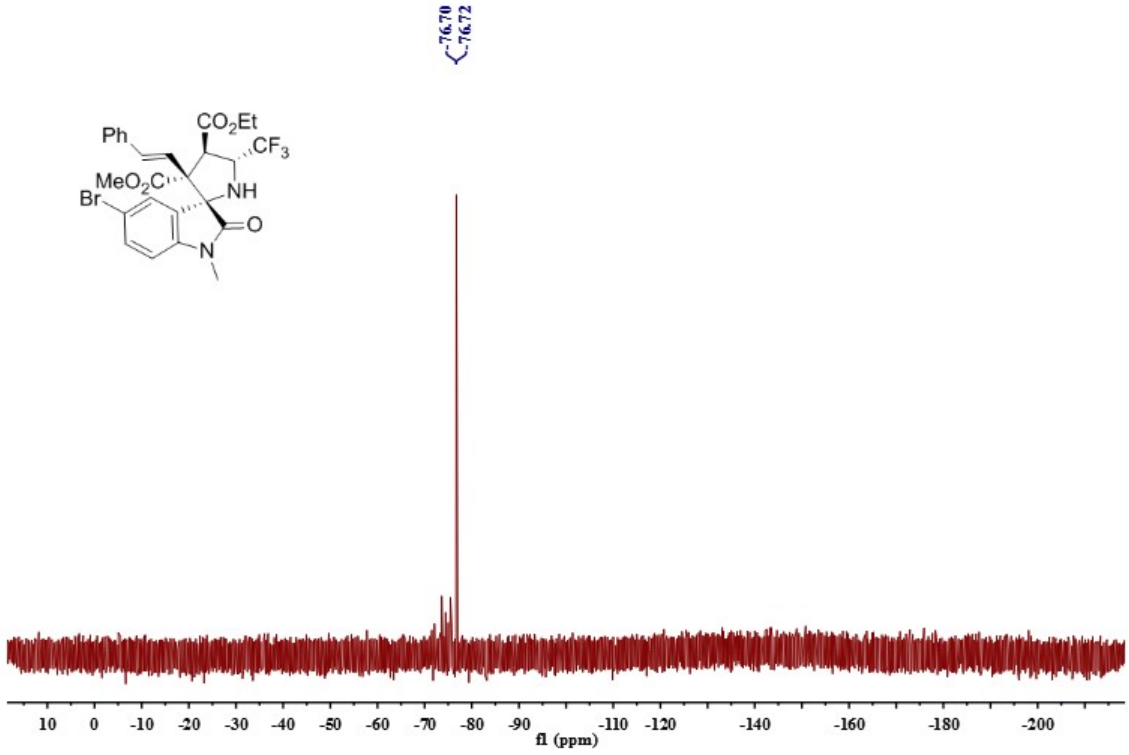
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3i



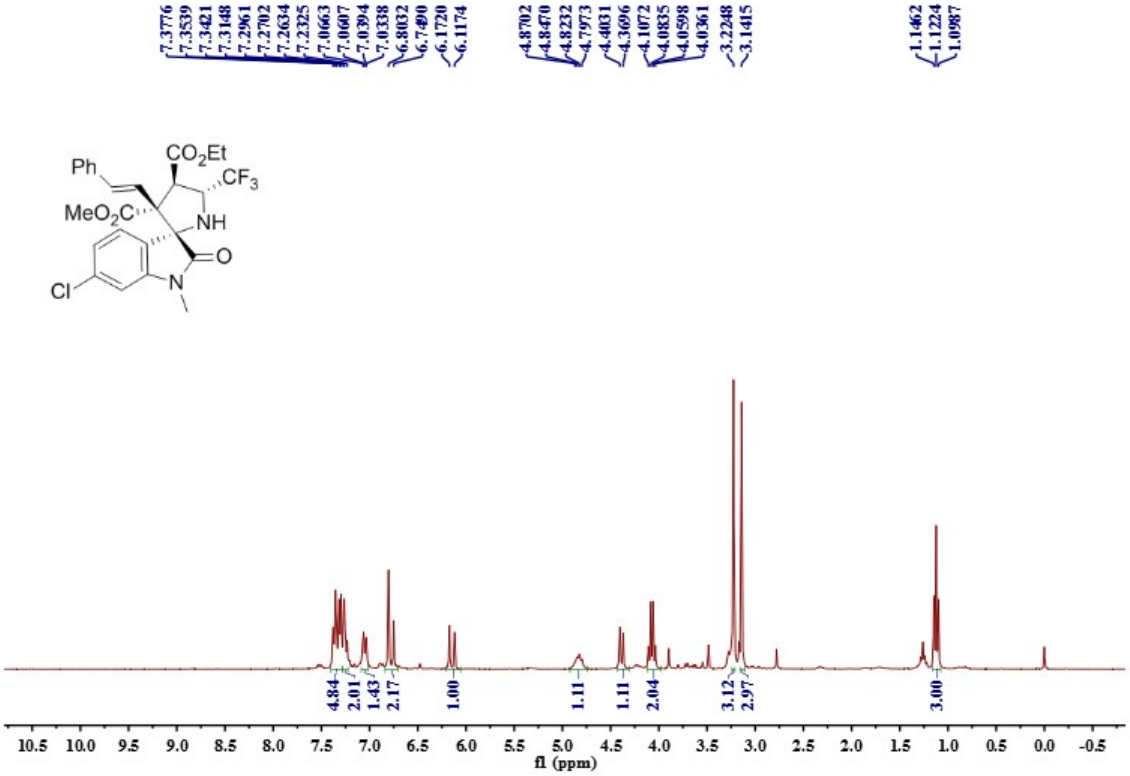
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3j



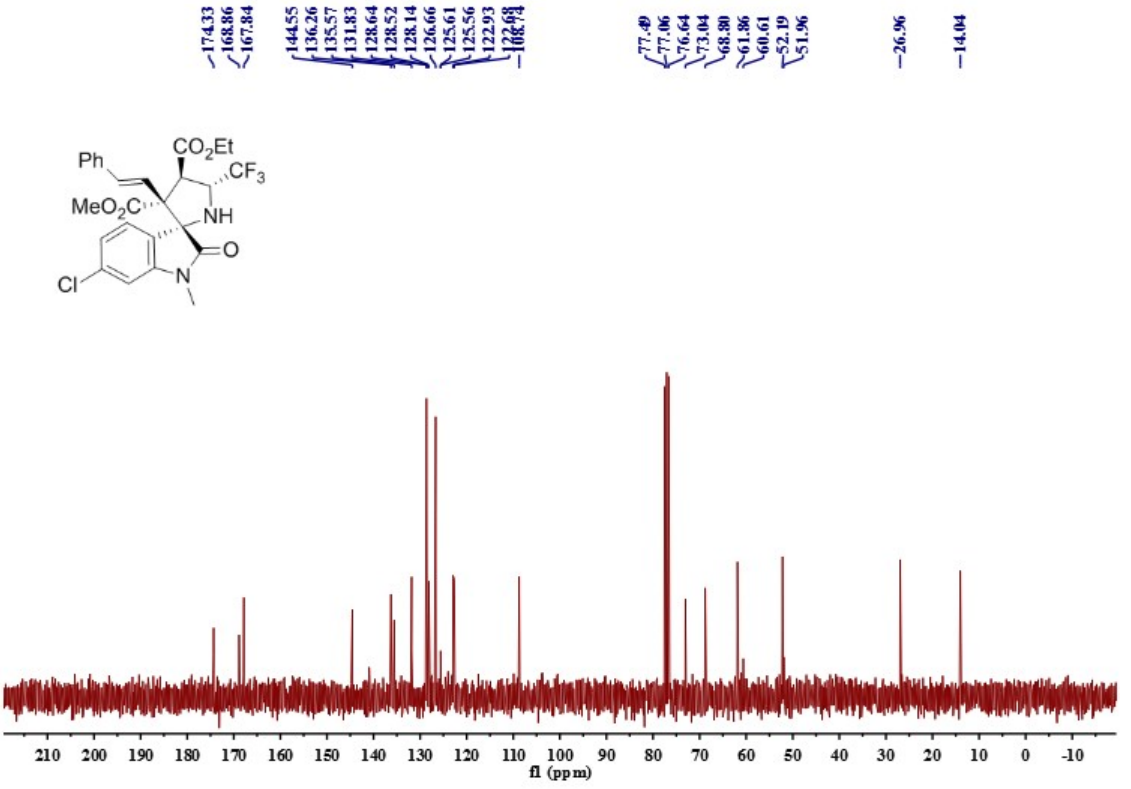
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3j



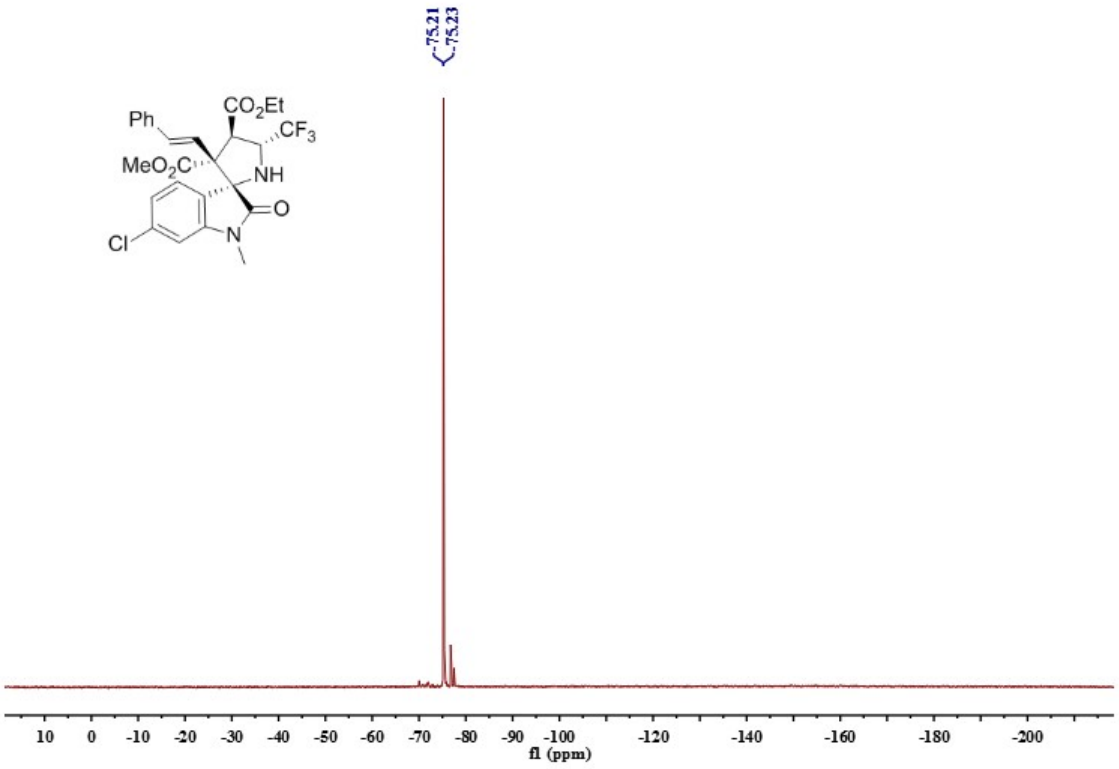
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3j



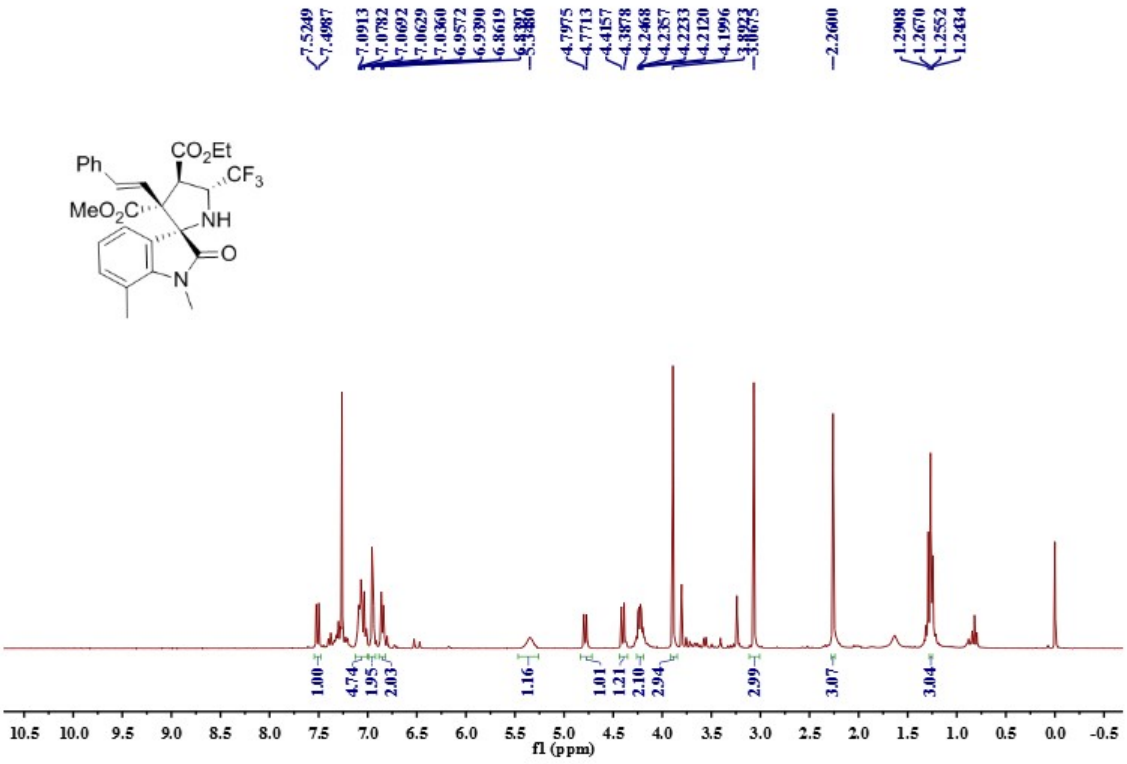
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3k



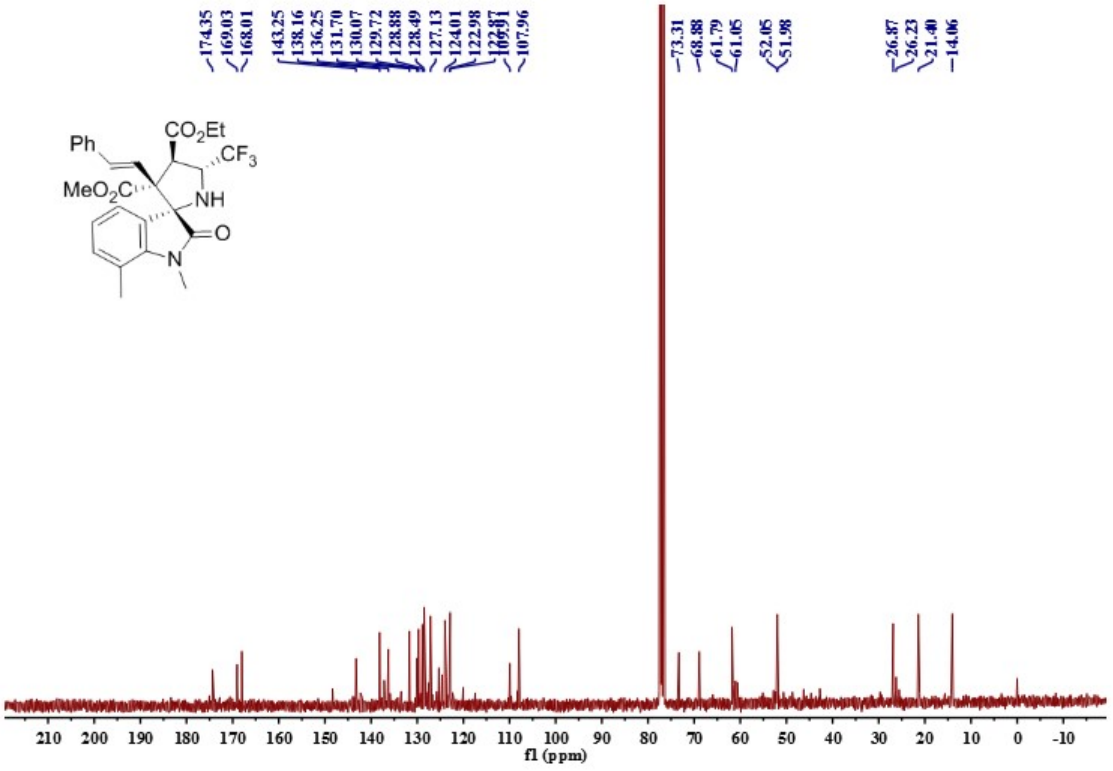
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3k



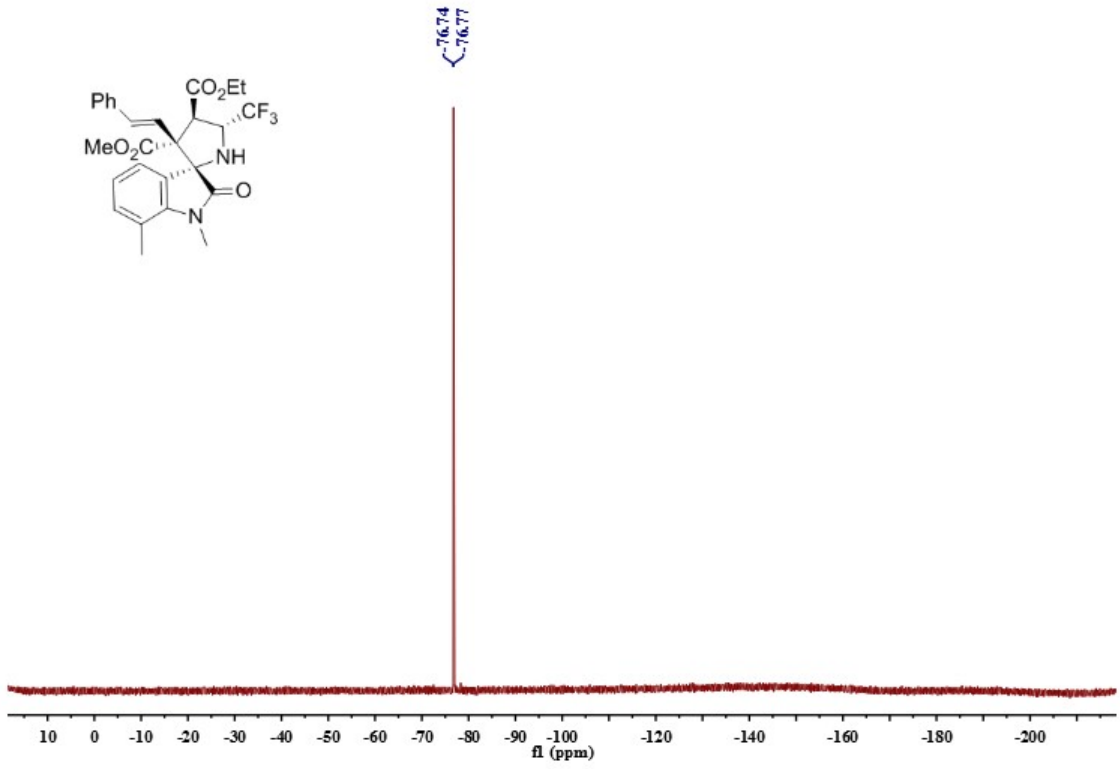
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3k



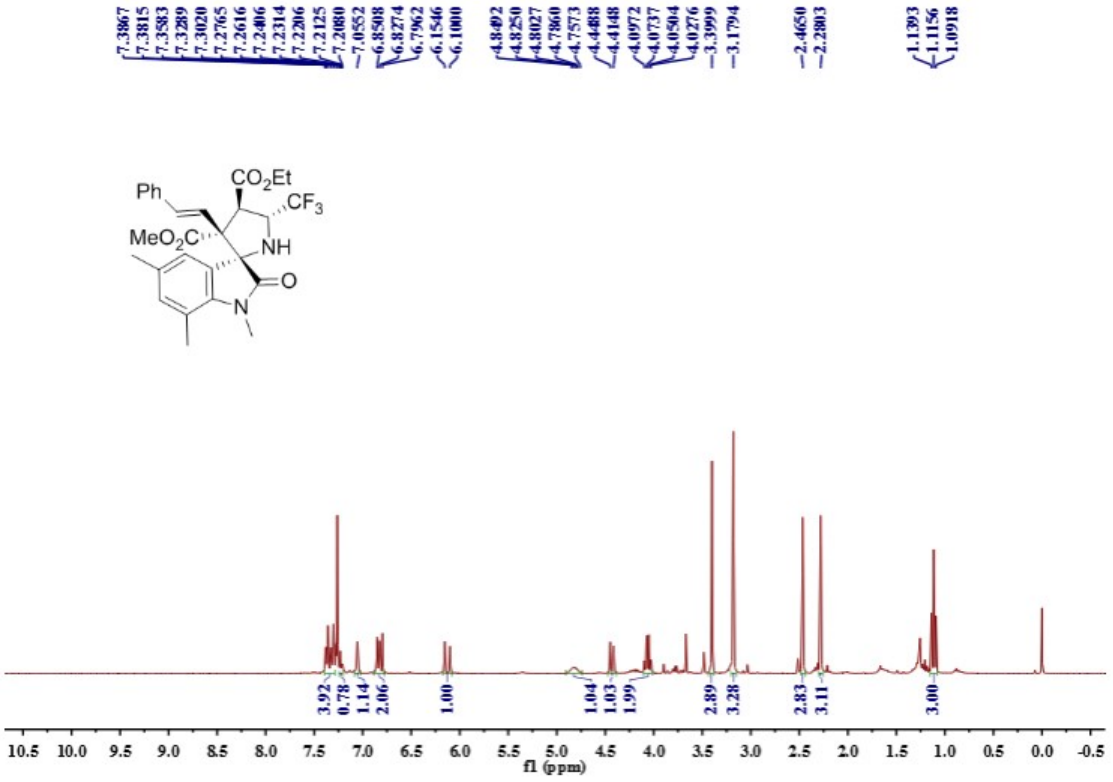
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3l



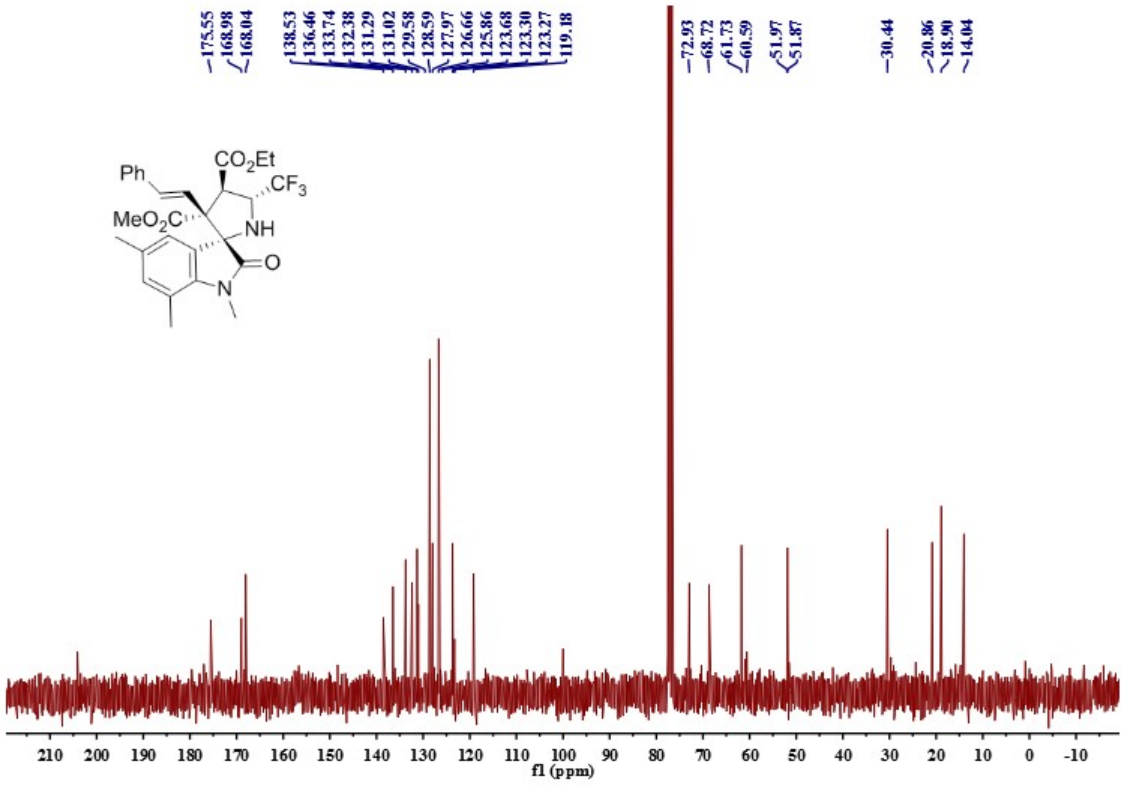
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3l



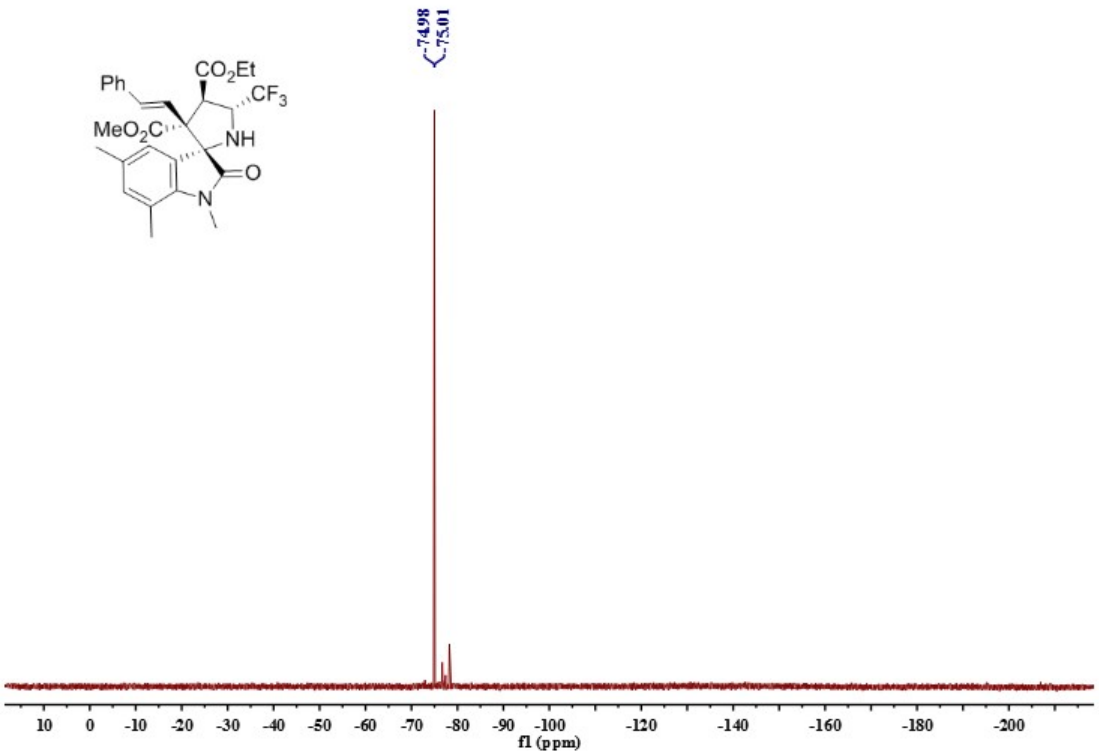
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3l



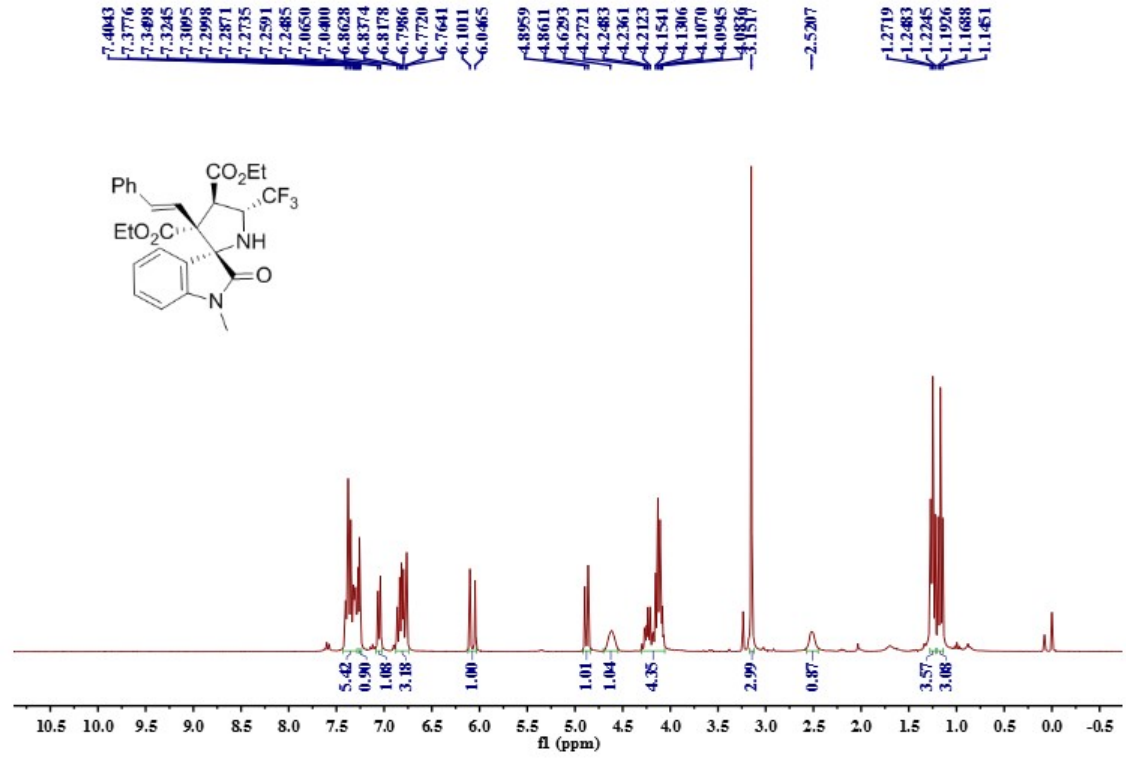
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3m



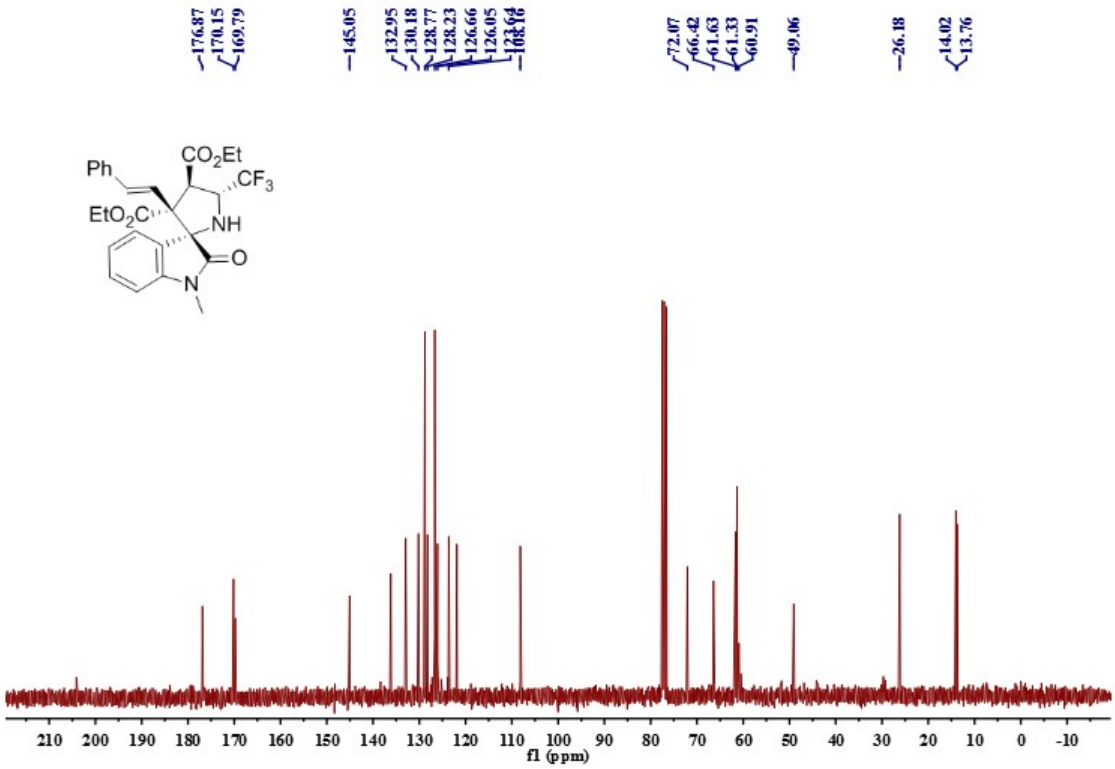
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3m



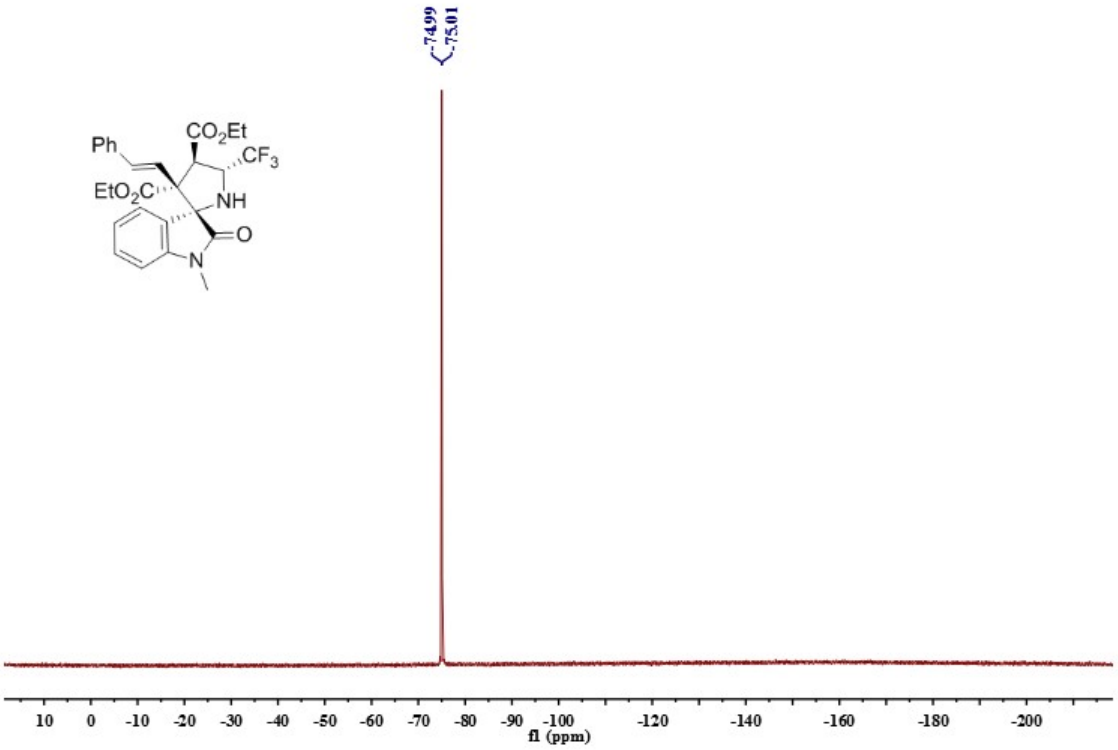
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3m



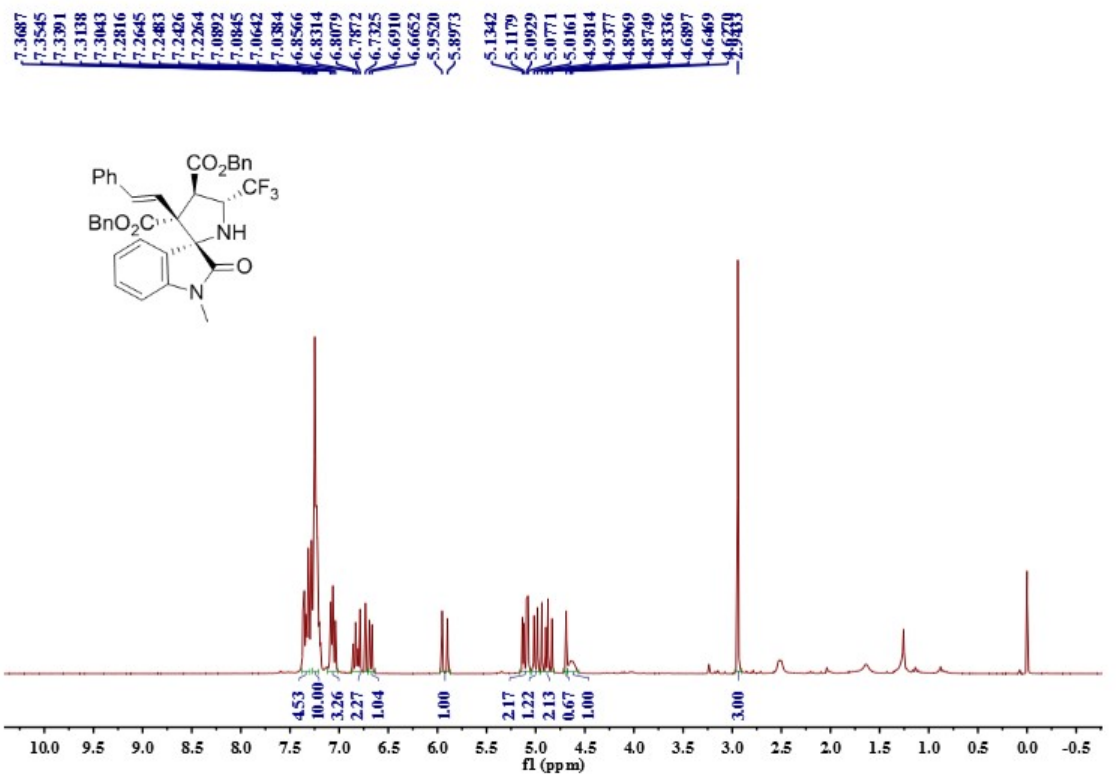
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3n



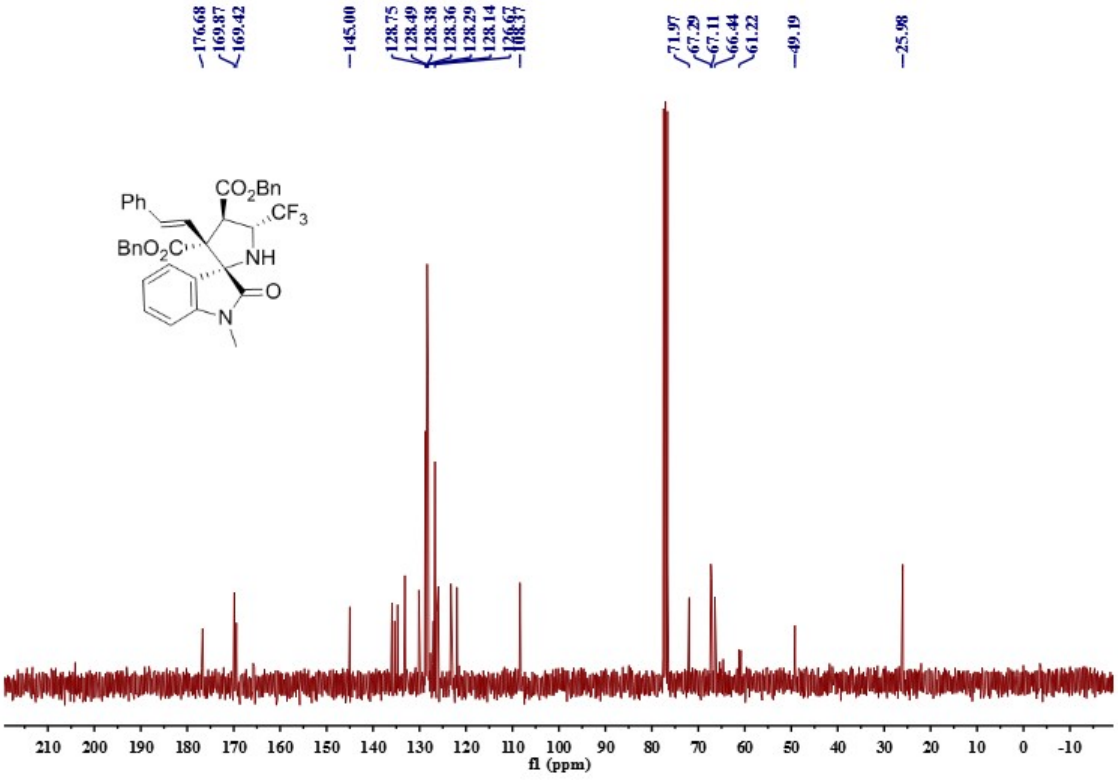
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3n



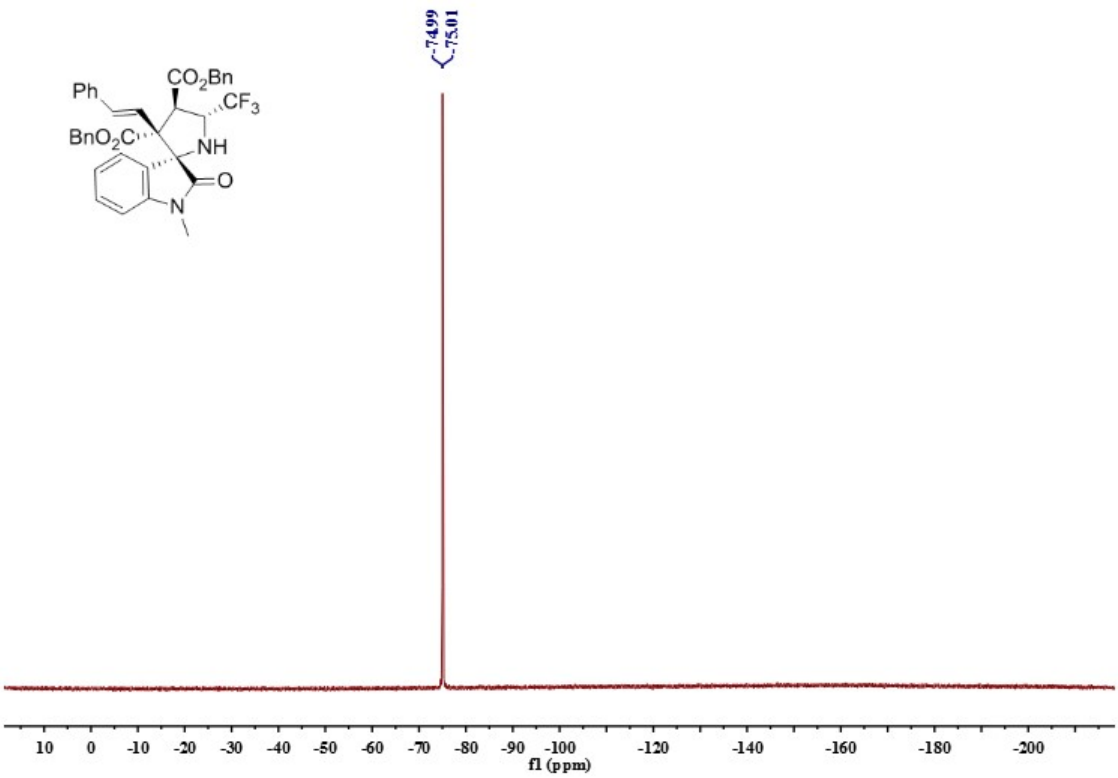
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3n



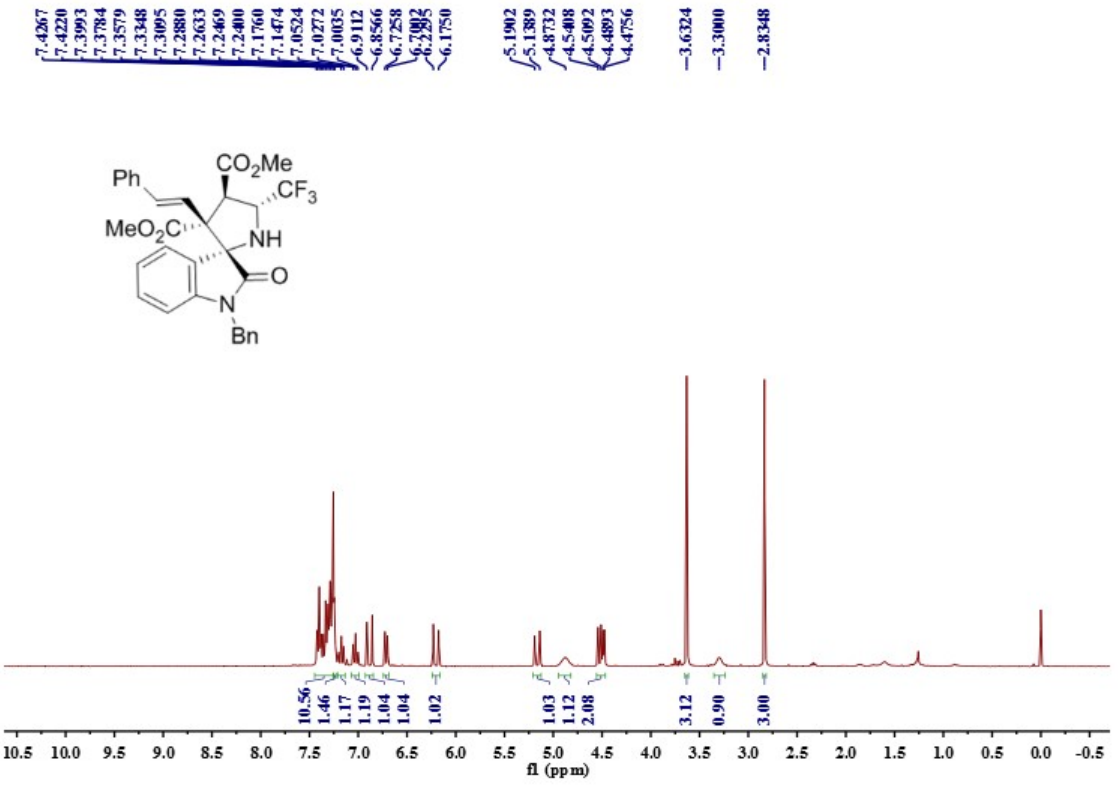
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3o



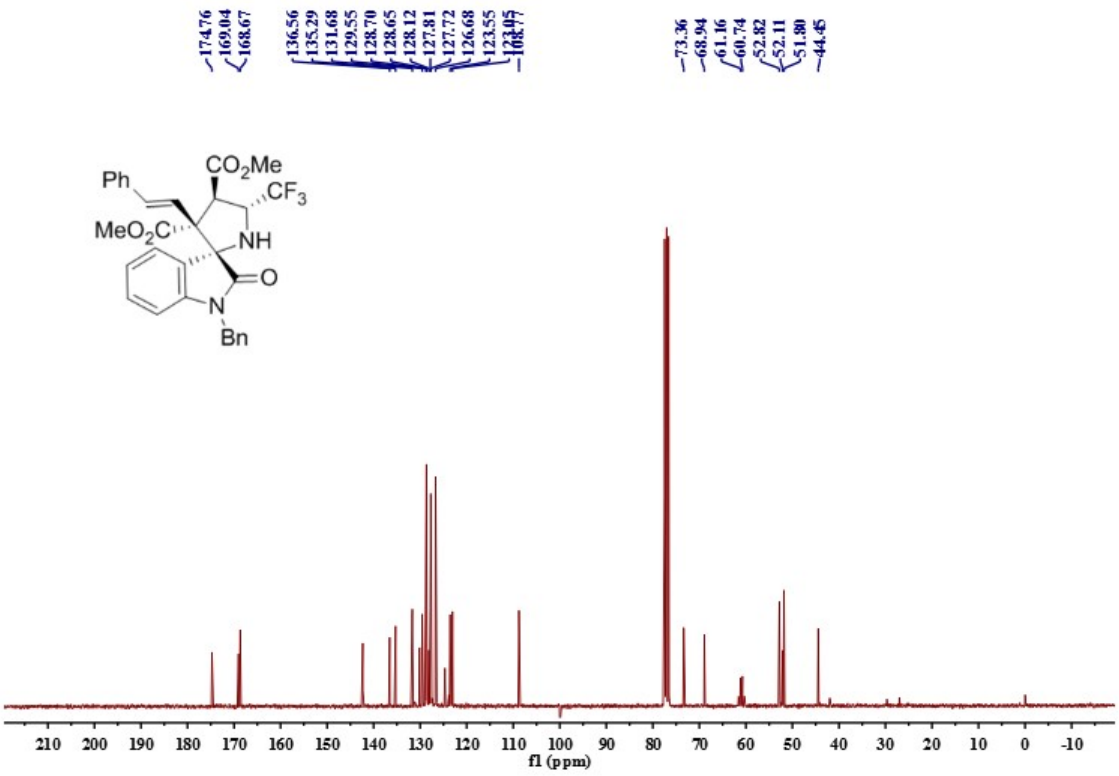
^{13}C($CDCl_3$, 75 MHz) NMR of compound *endo*-3o



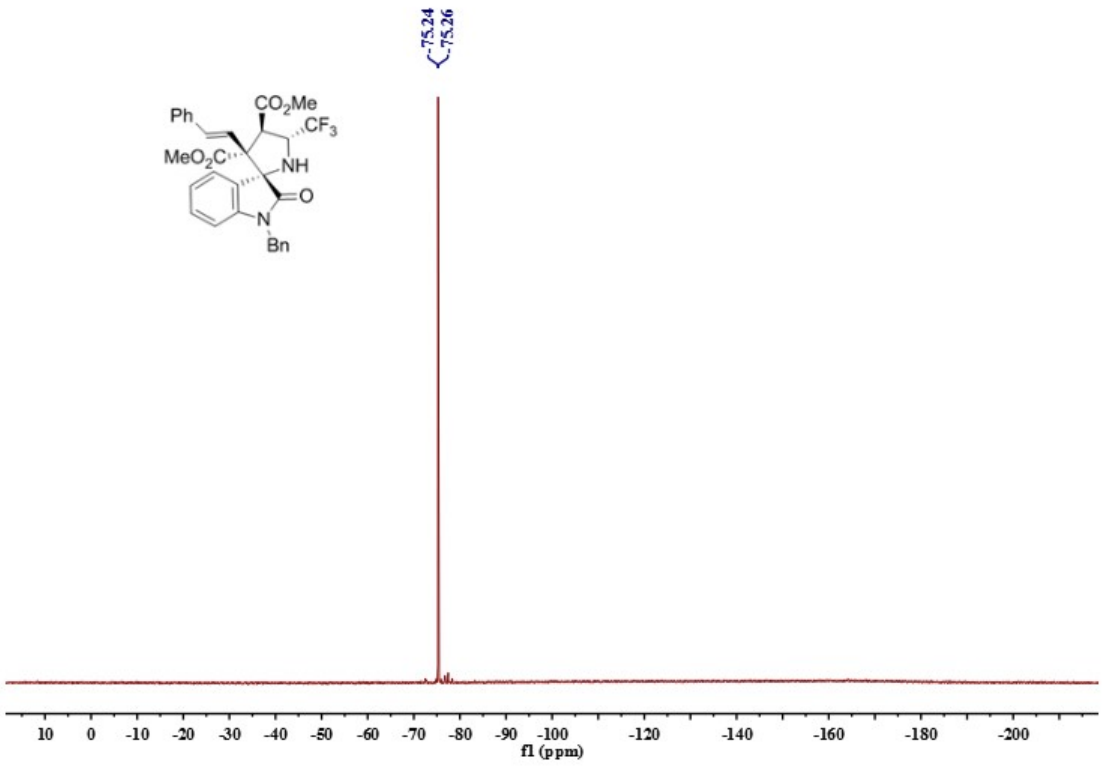
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3o



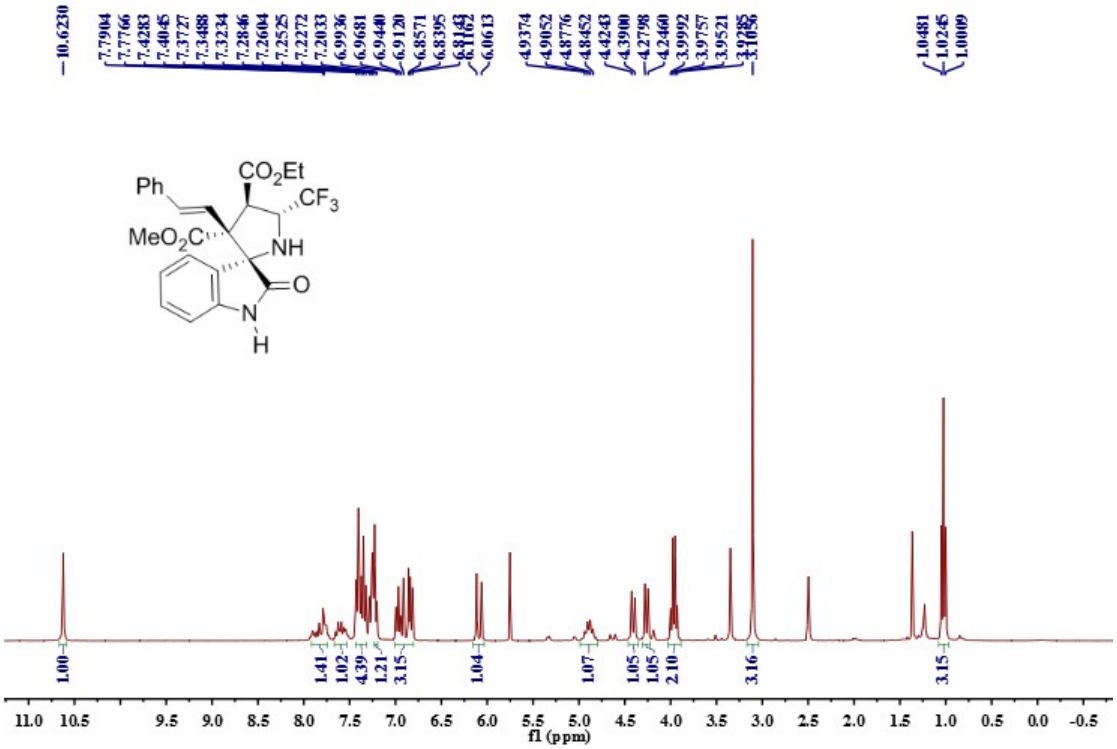
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *endo*-3p



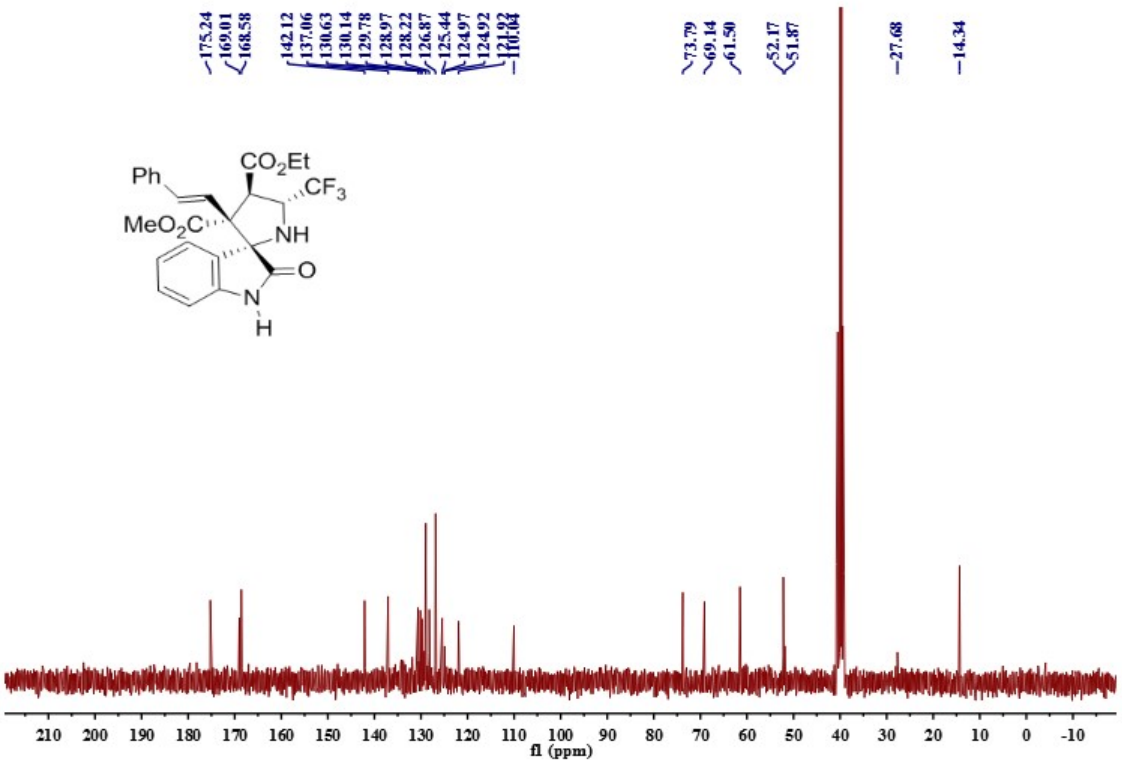
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3p



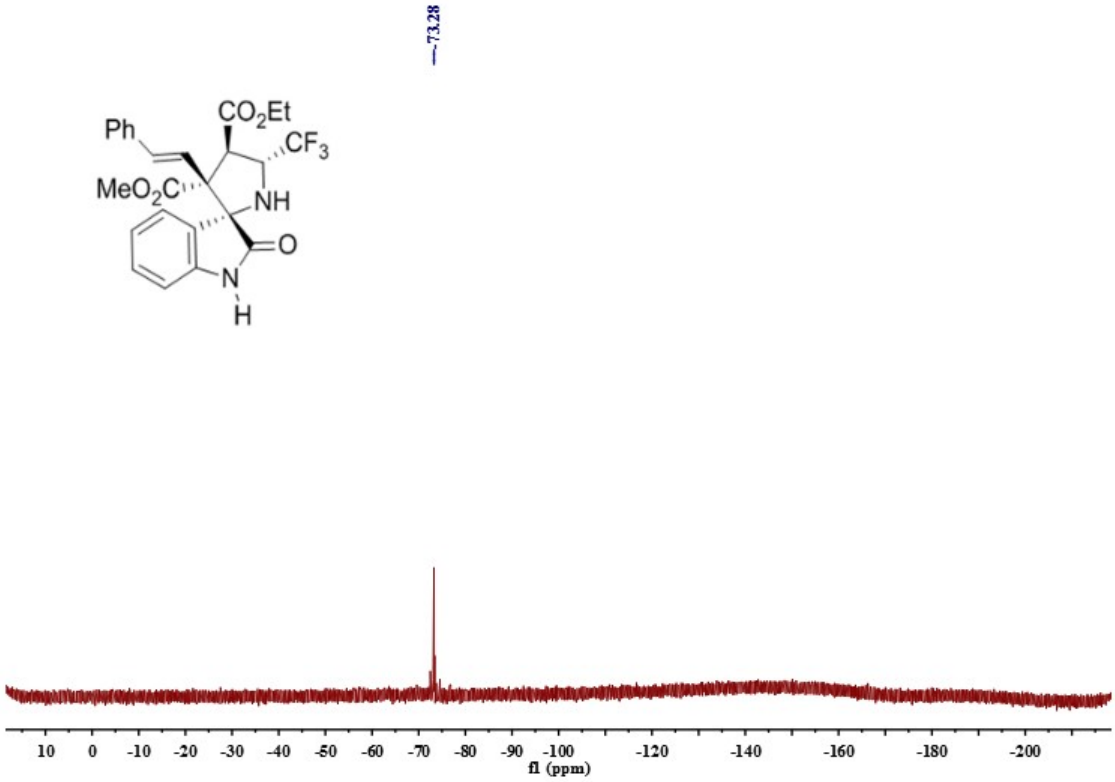
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3p



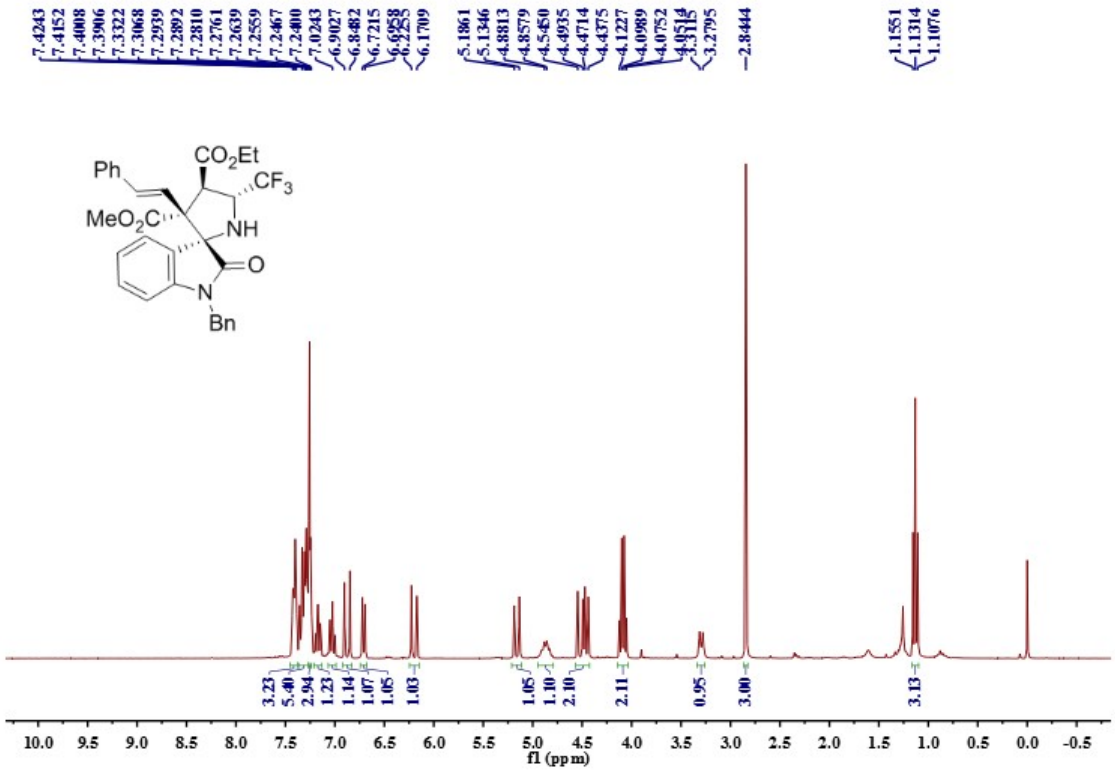
^{1}H(DMSO-d6, 300 MHz) NMR of compound *endo*-3q



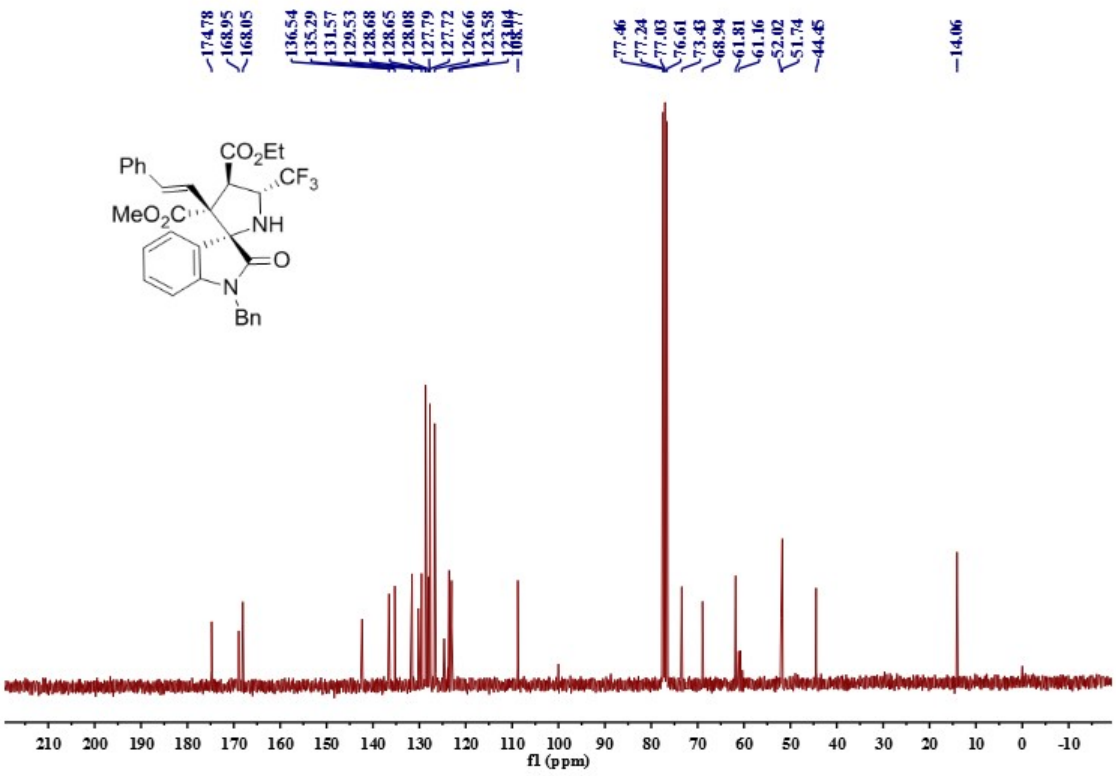
^{13}C(DMSO-d6, 300 MHz) NMR of compound *endo*-3q



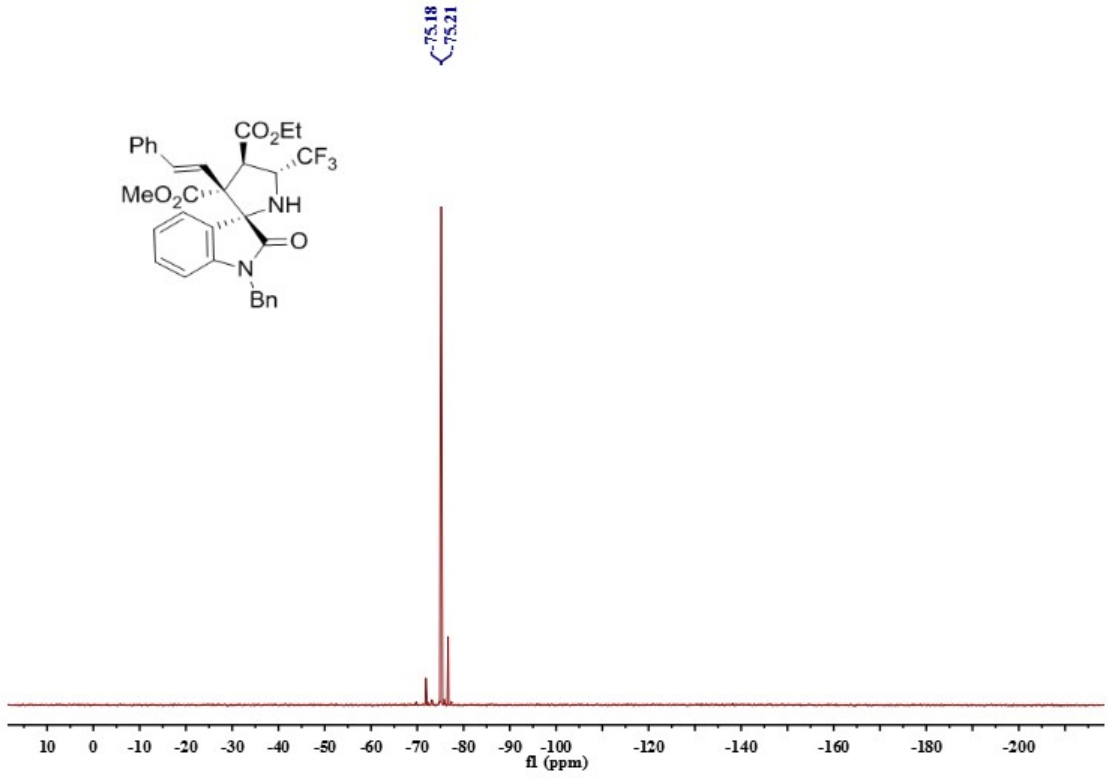
^{19}F(DMSO-d6, 282 MHz) NMR of compound *endo*-3q



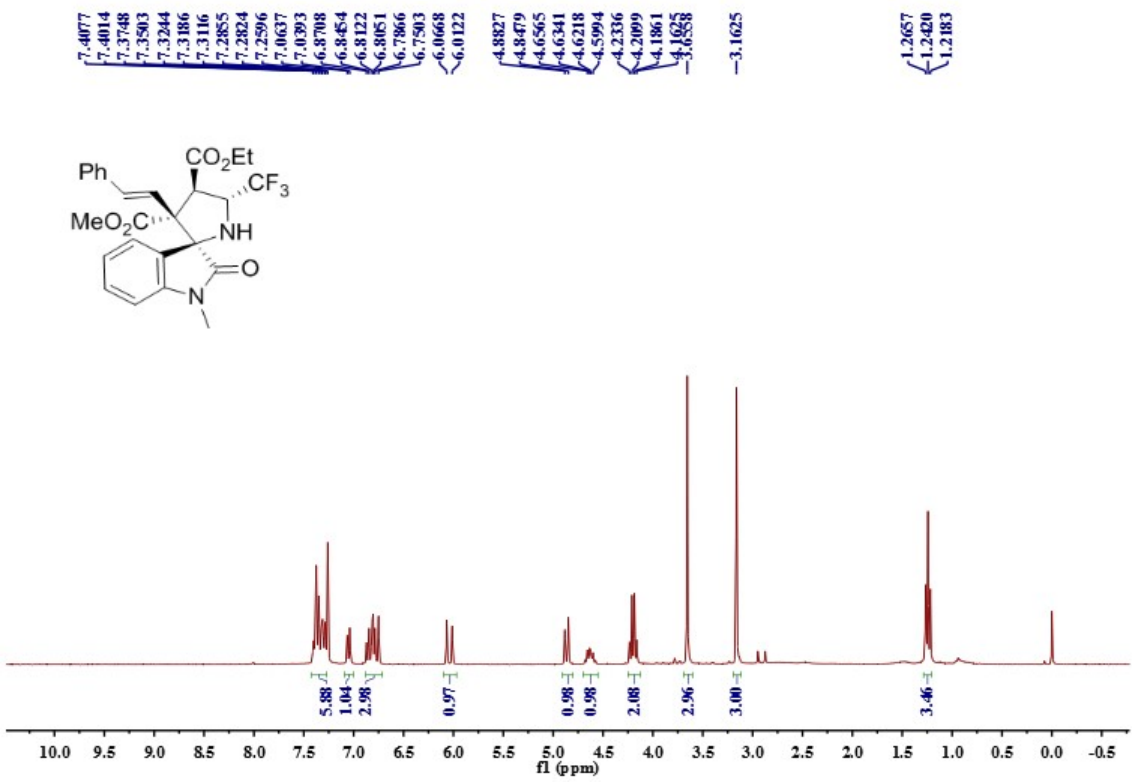
^{1}H($CDCl_3$, 300 MHz) NMR of compound *endo*-3r



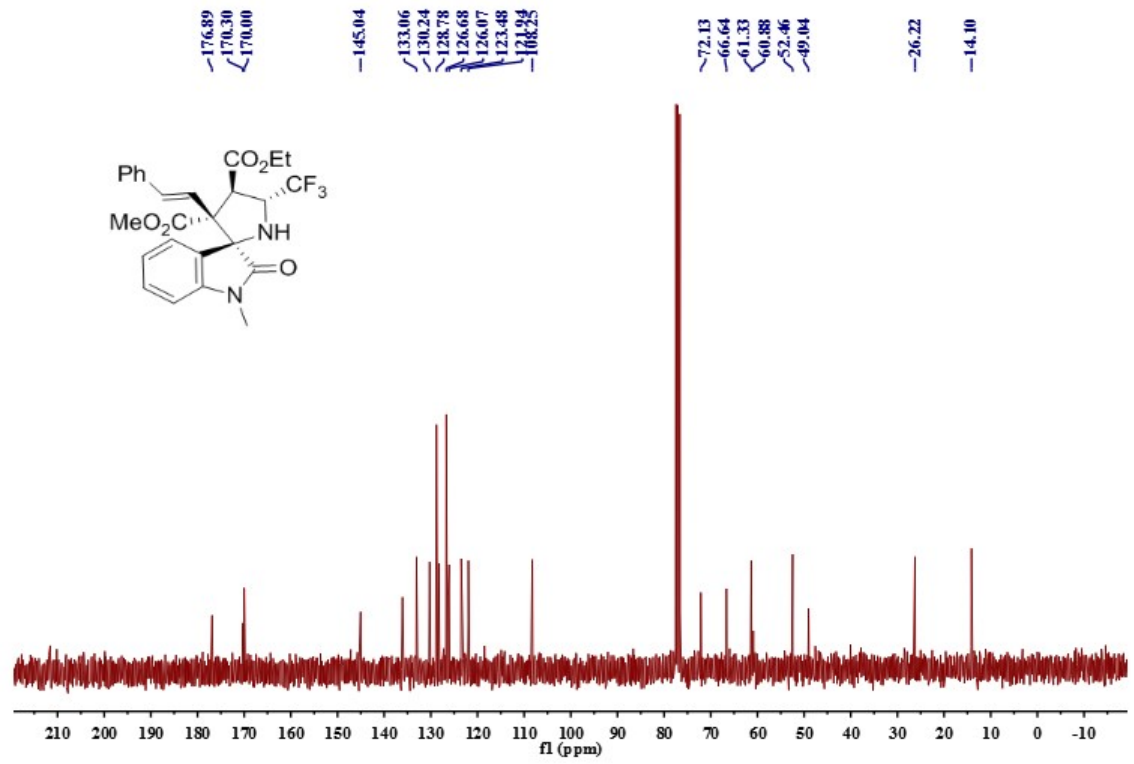
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *endo*-3r



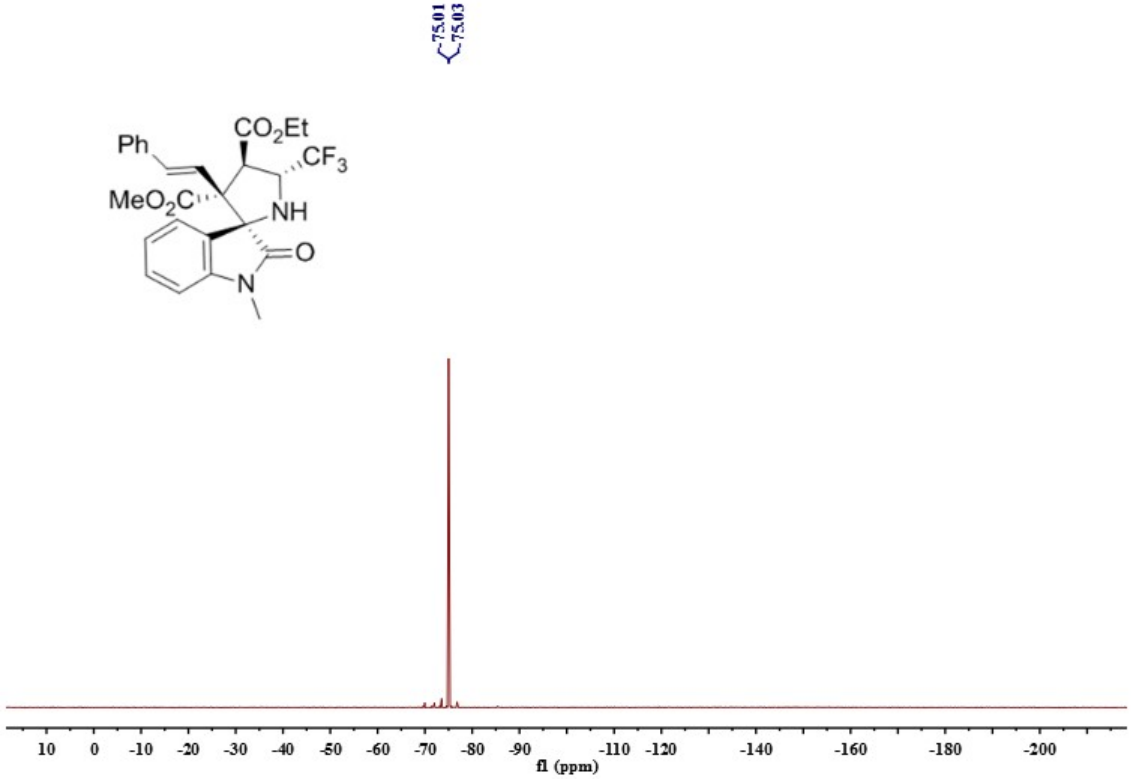
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *endo*-3r



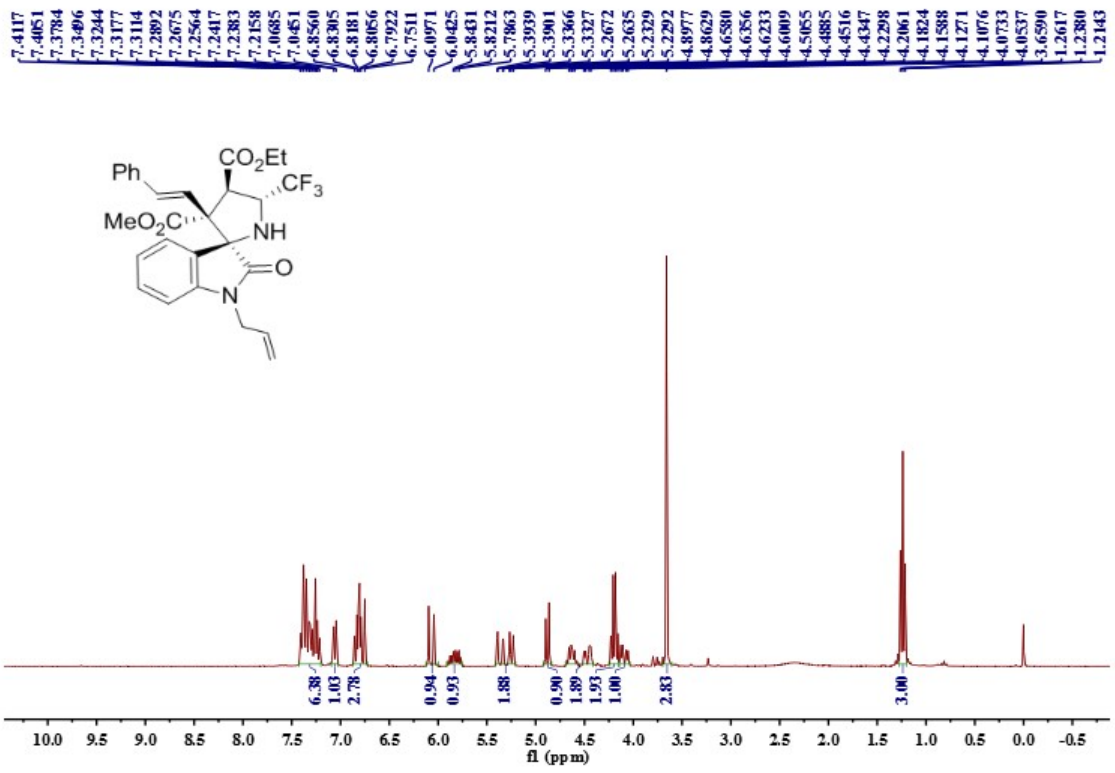
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4a



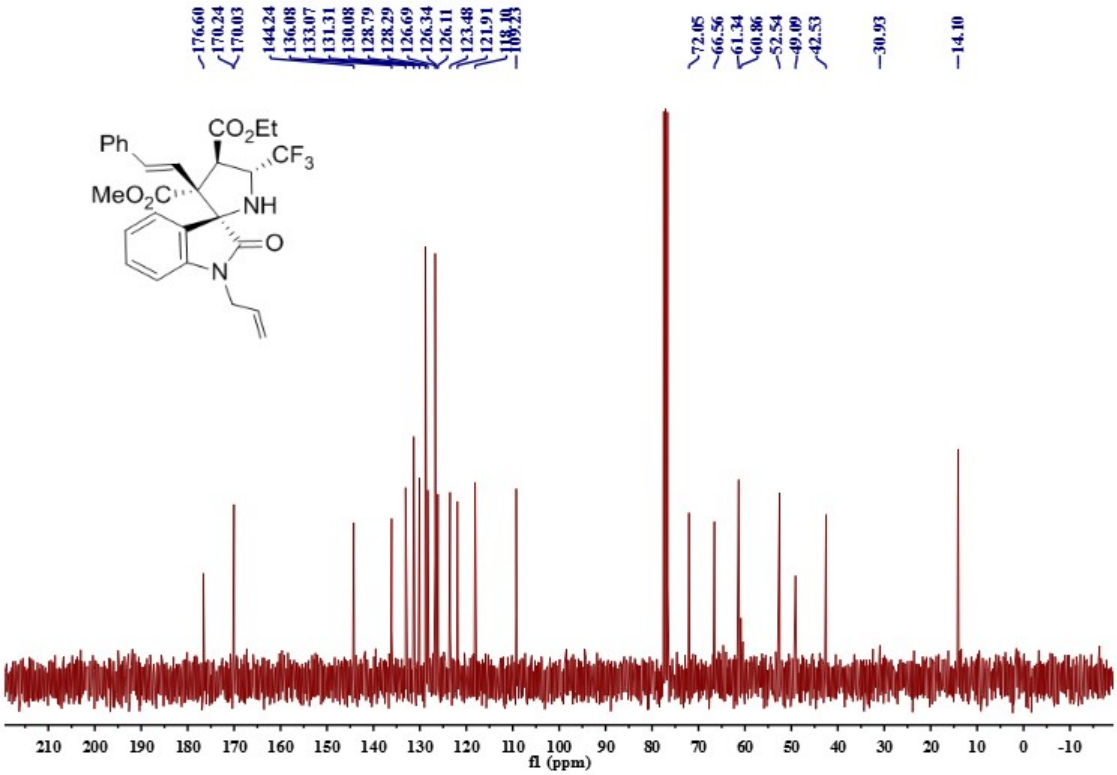
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4a



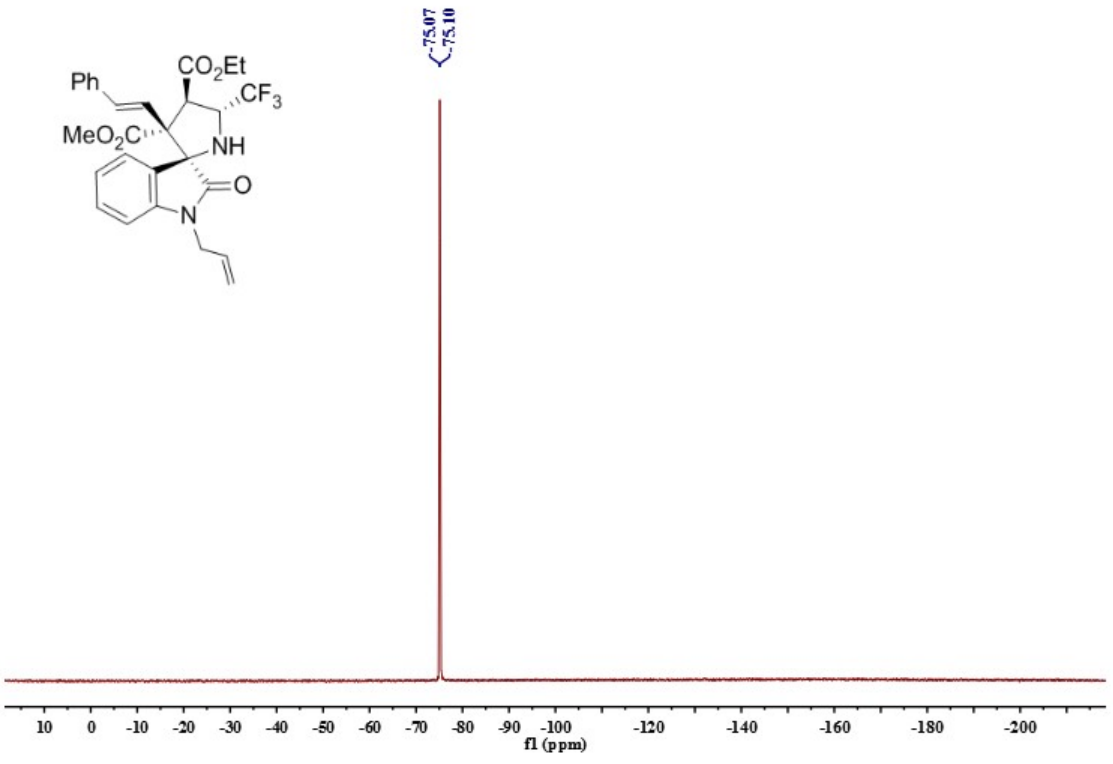
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo′*-4a



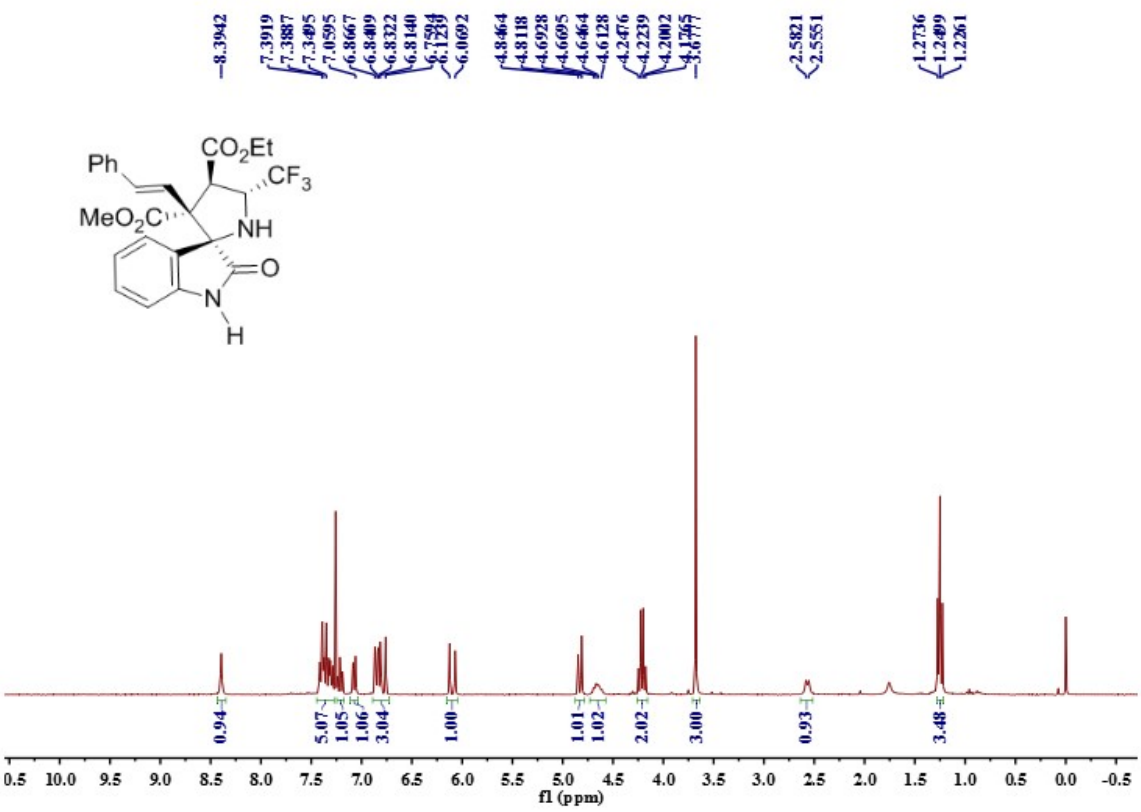
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo′*-4b



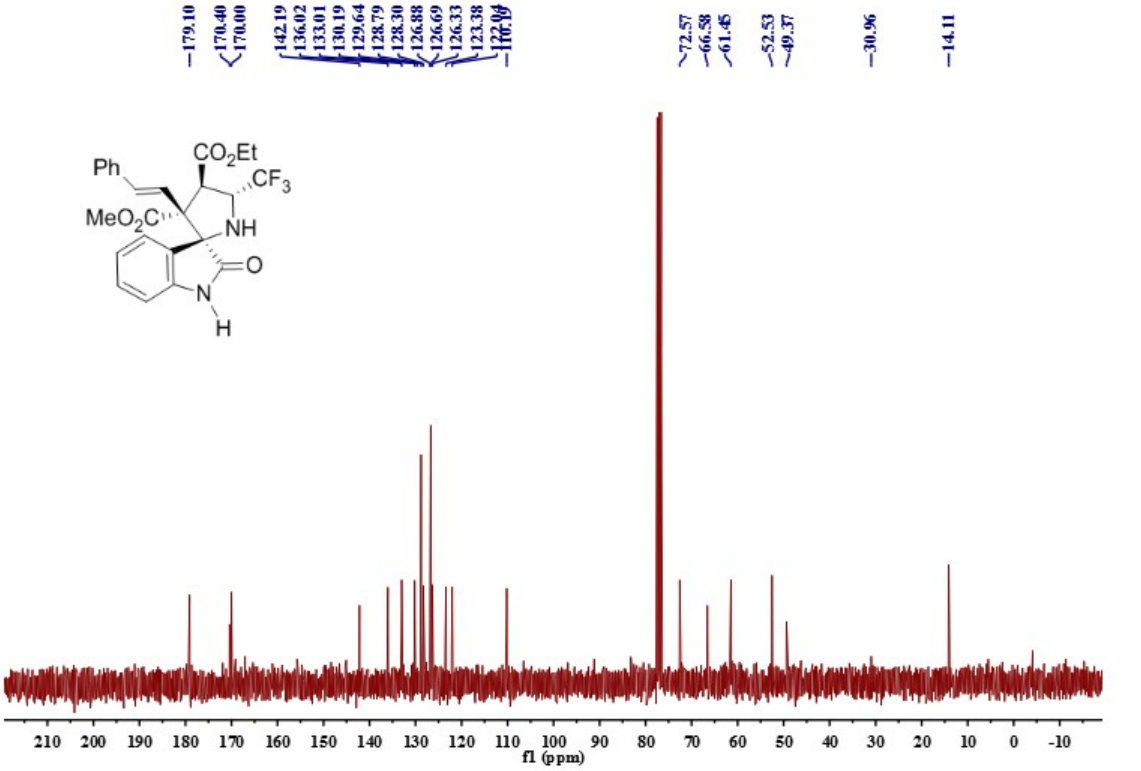
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4b



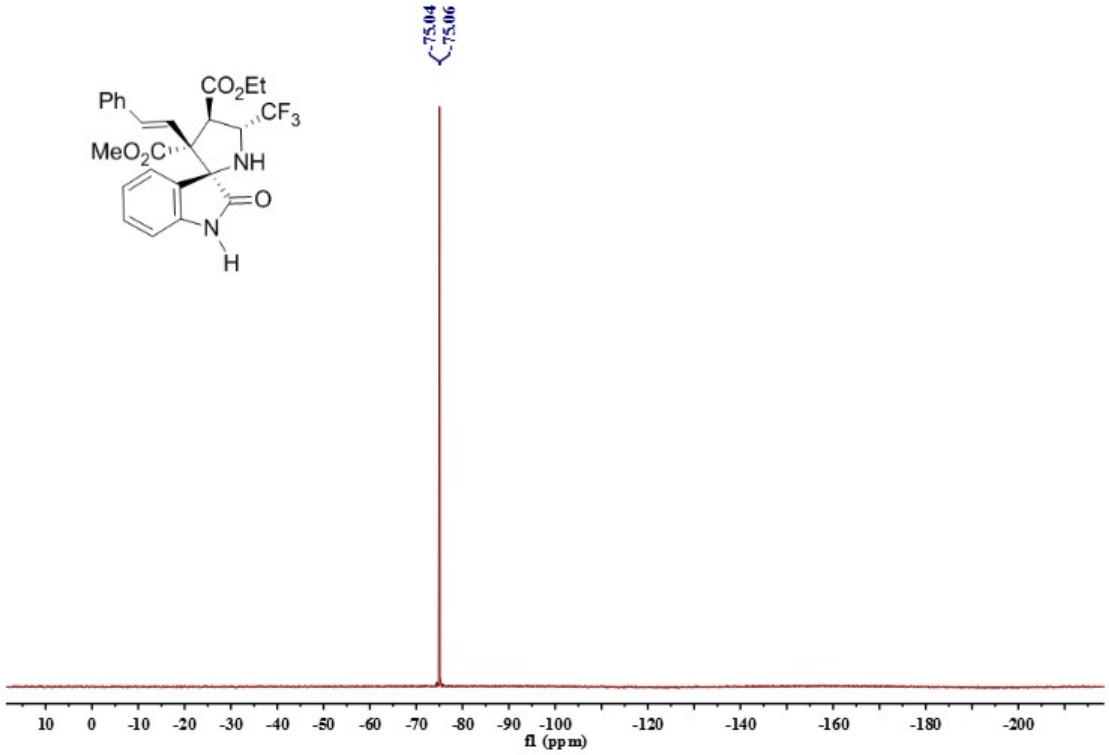
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4b



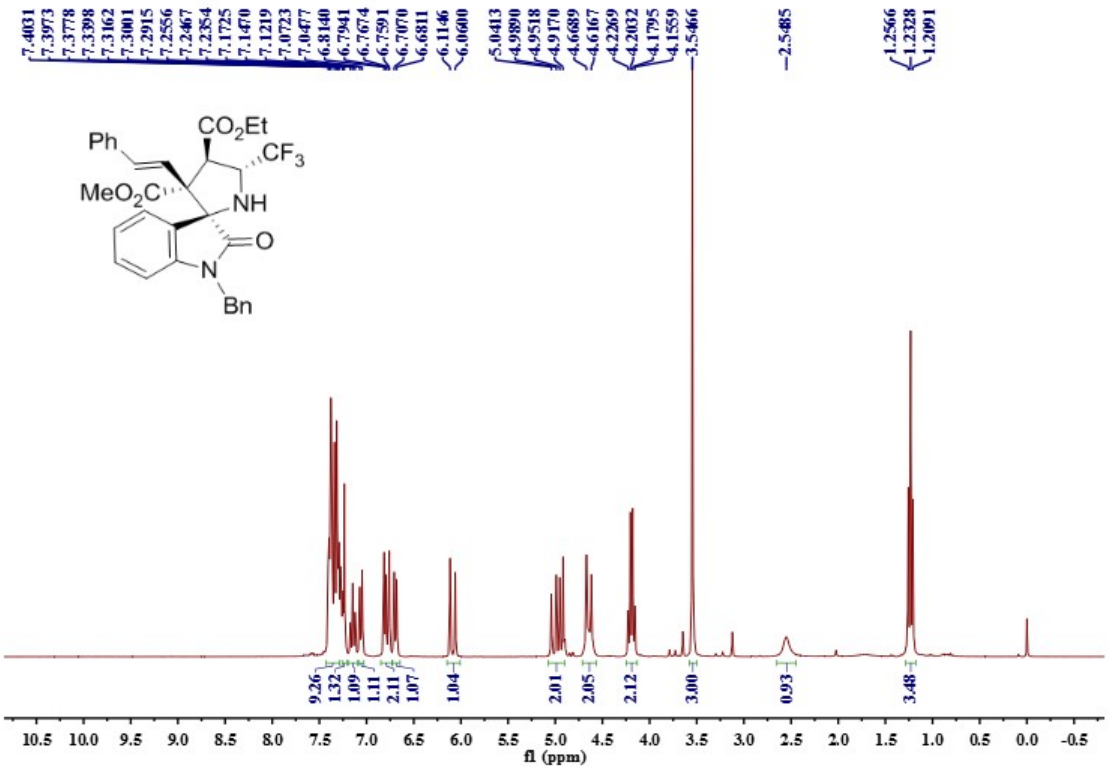
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4c



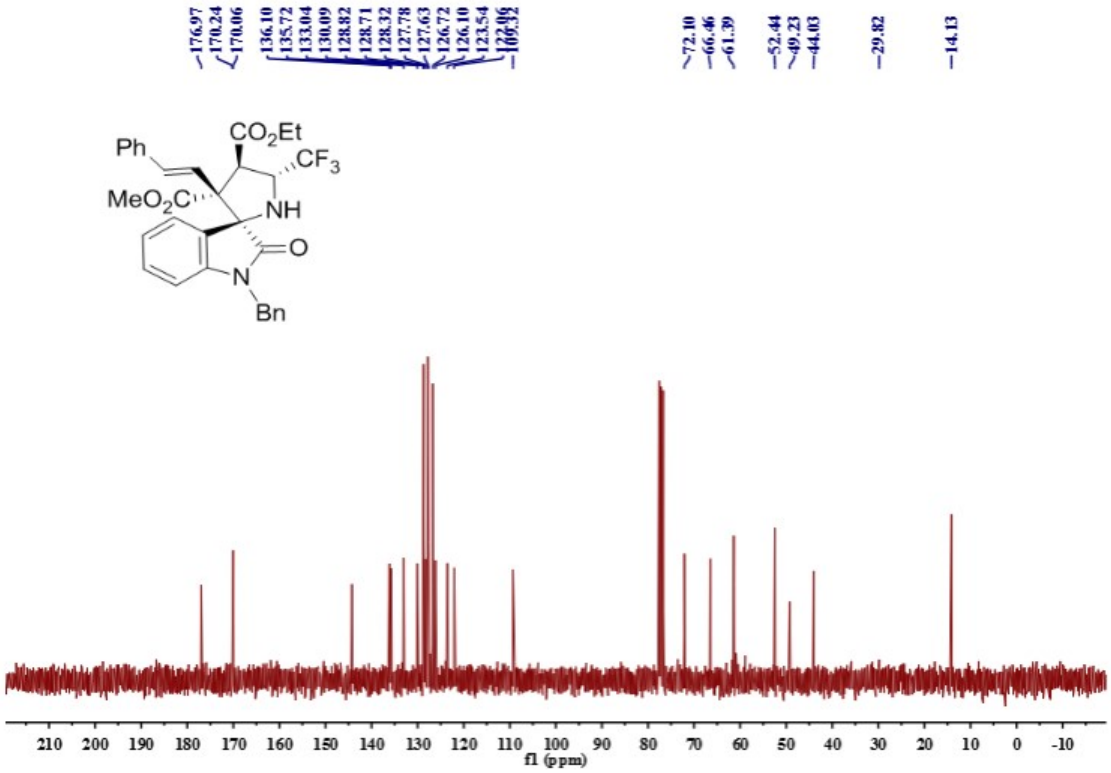
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4c



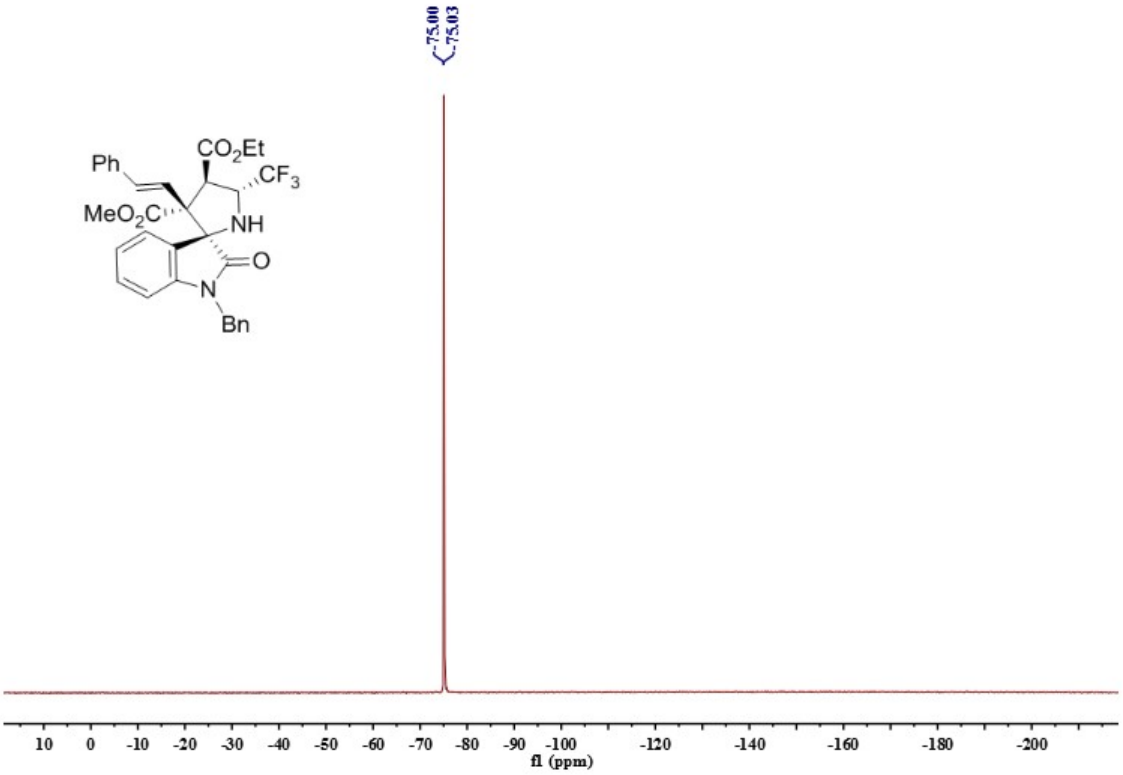
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4c



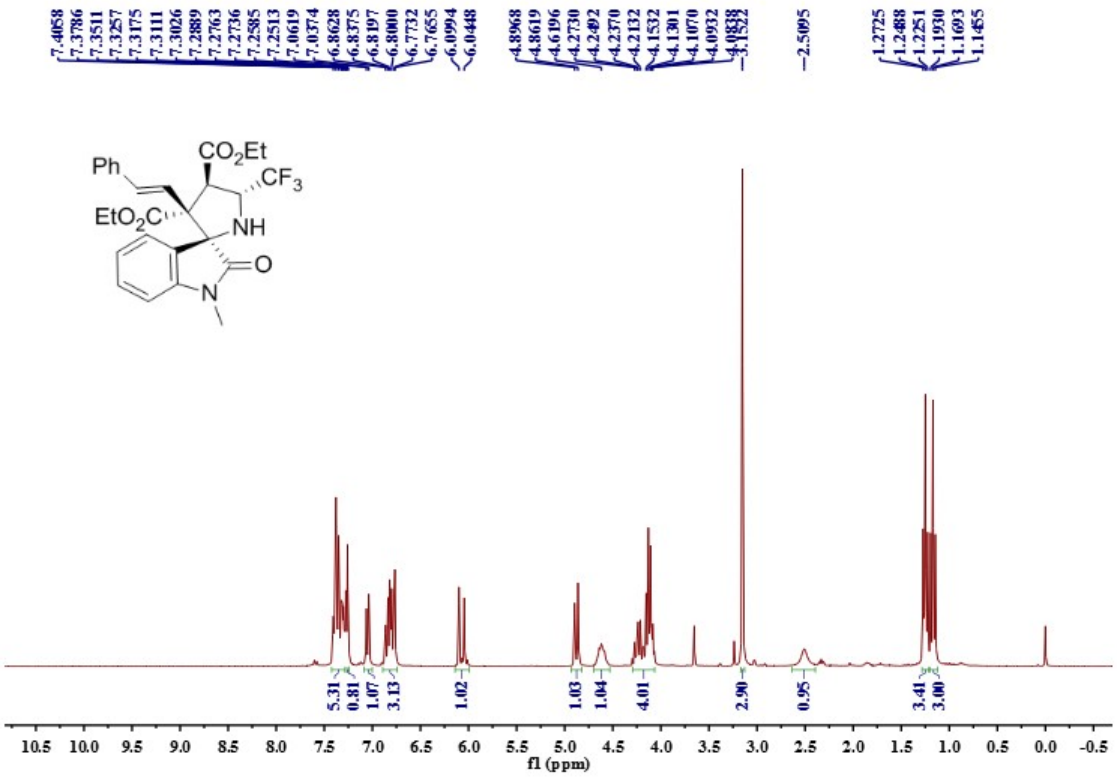
$^{1}H(CDCl_3, 300\ MHz)$ NMR of Compound *exo'*-4d



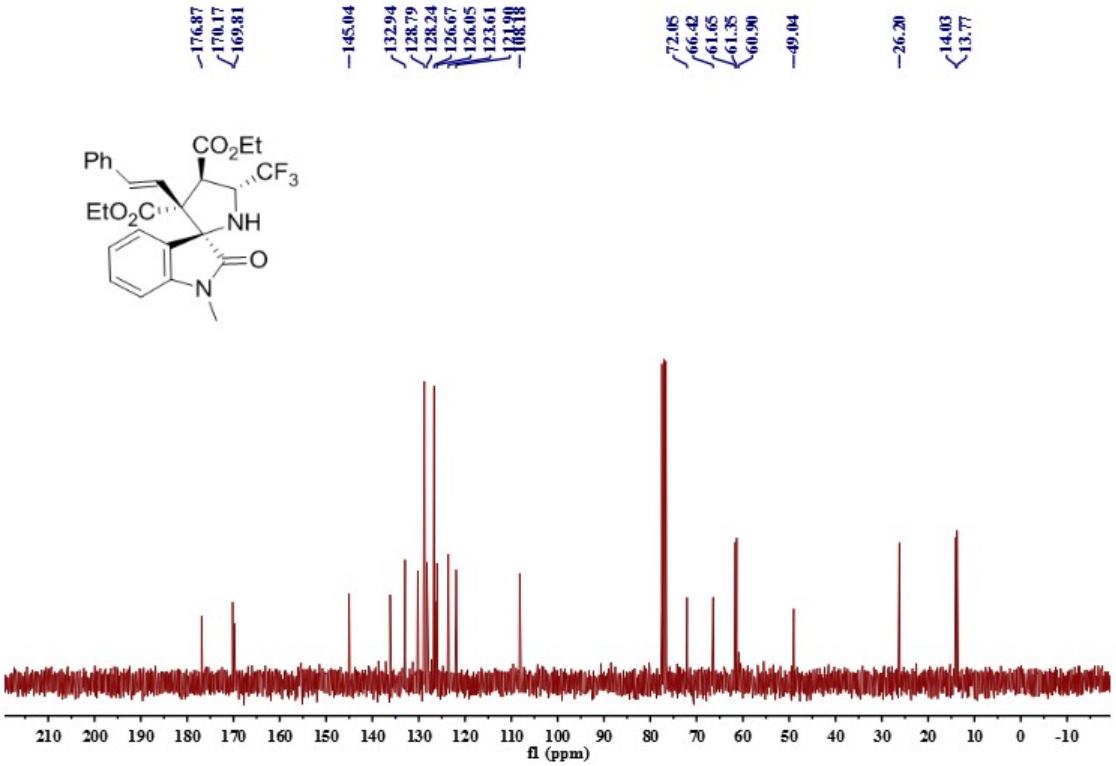
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4d



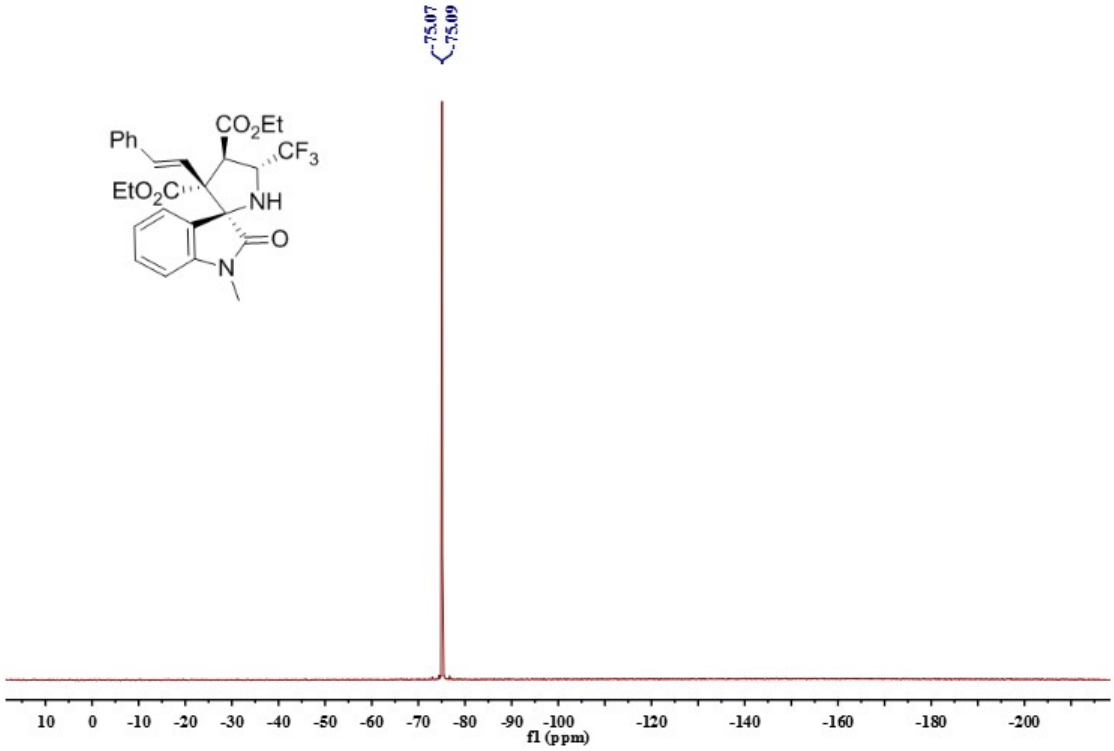
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4d



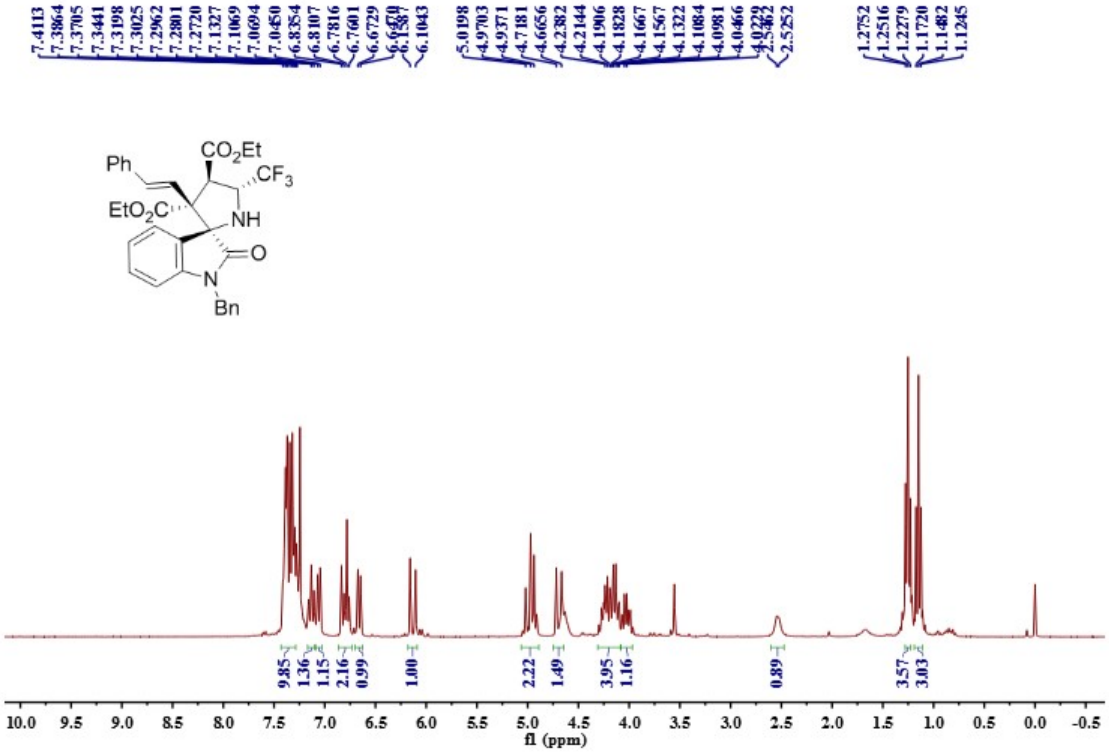
$^{1}H(CDCl_3, 300\ MHz)$ of compound *exo'*-4e



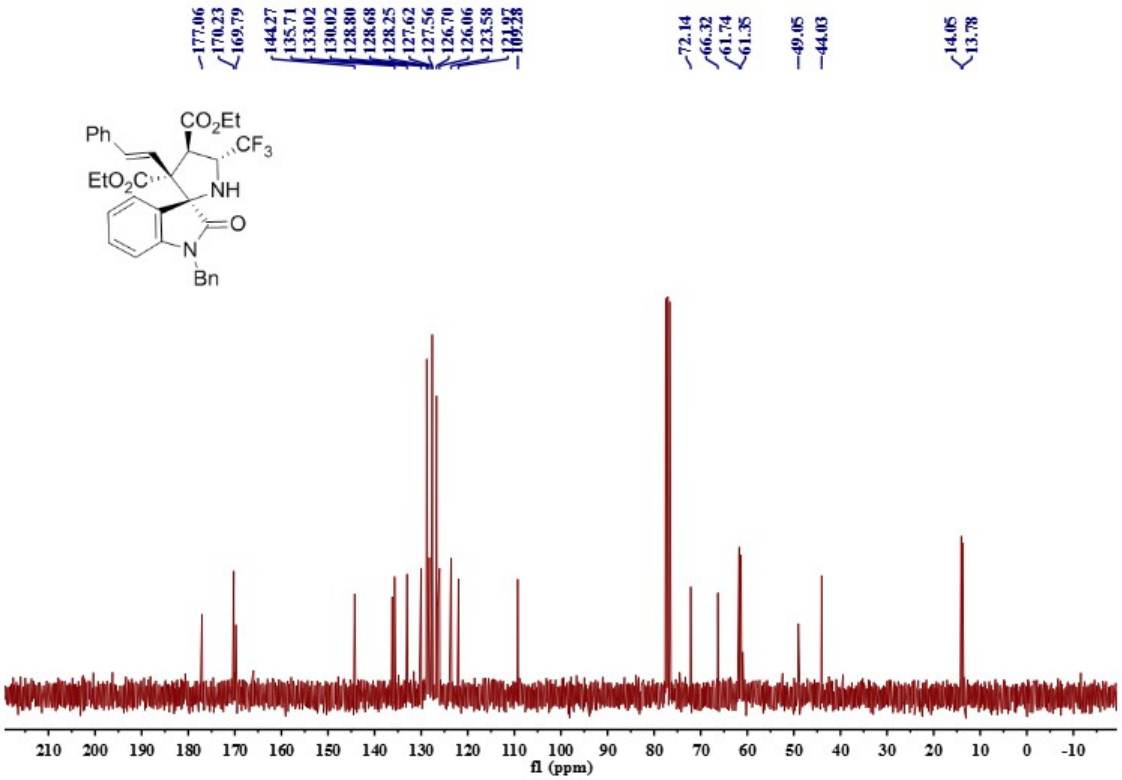
$^{13}C(CDCl_3, 75\ MHz)$ NMR of Compound *exo'*-4e



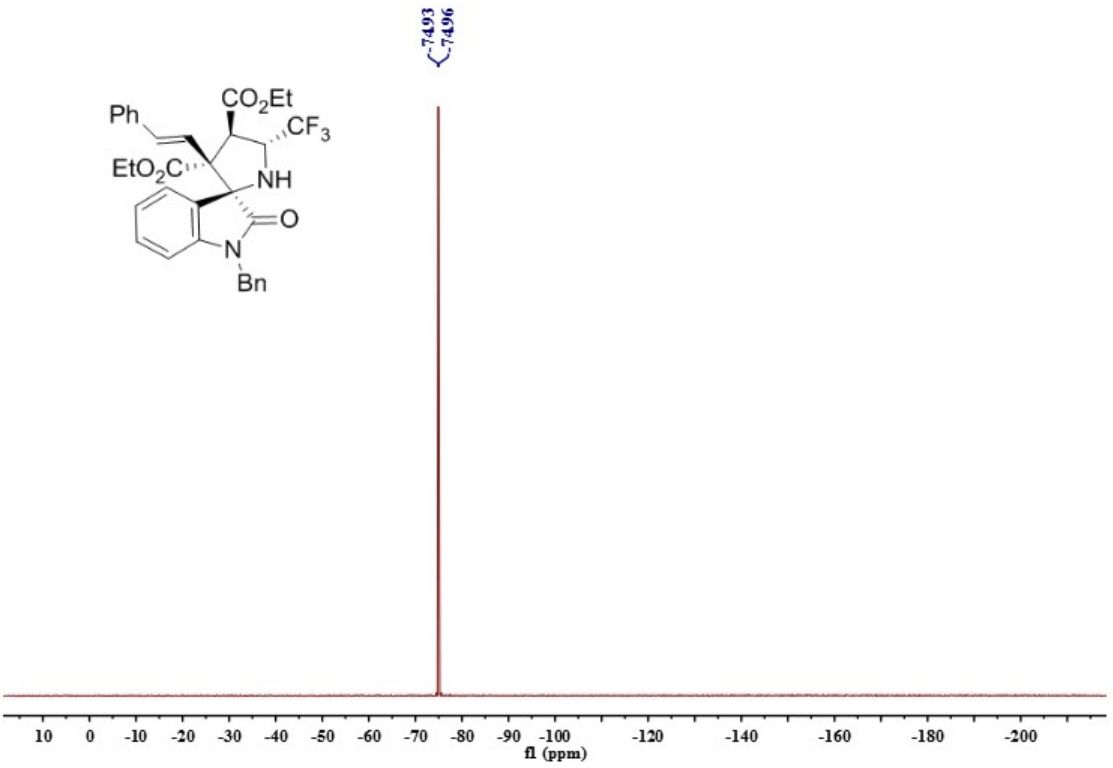
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4e



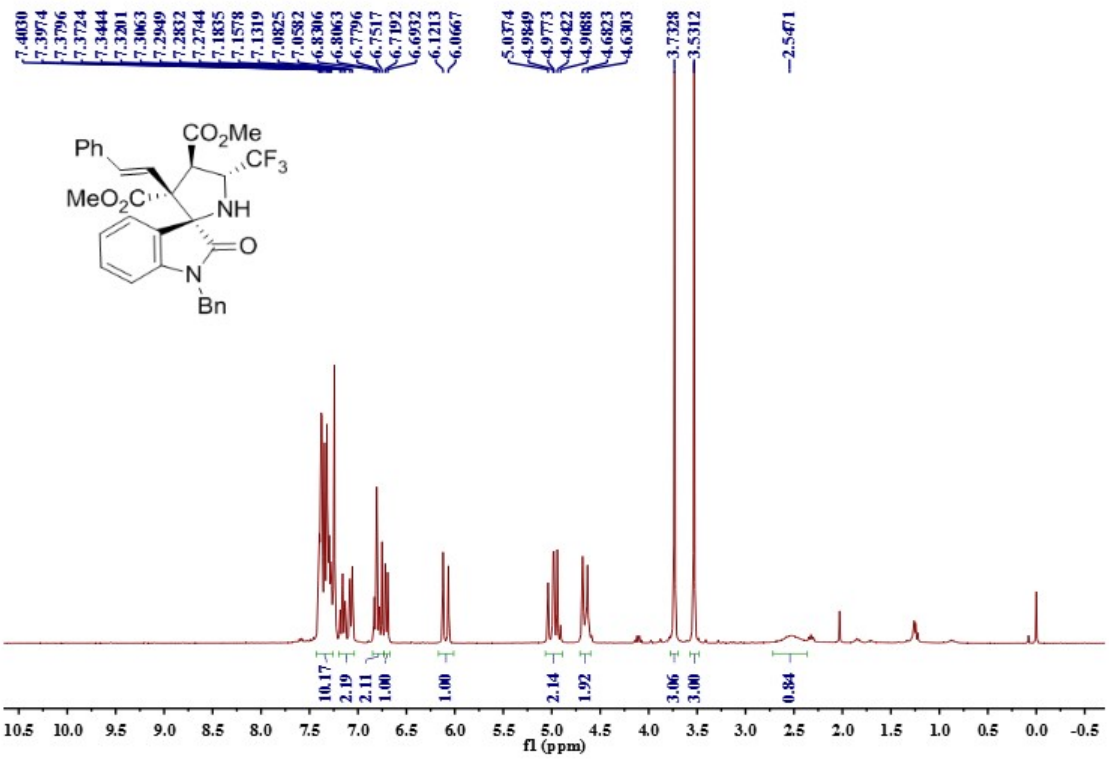
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4f



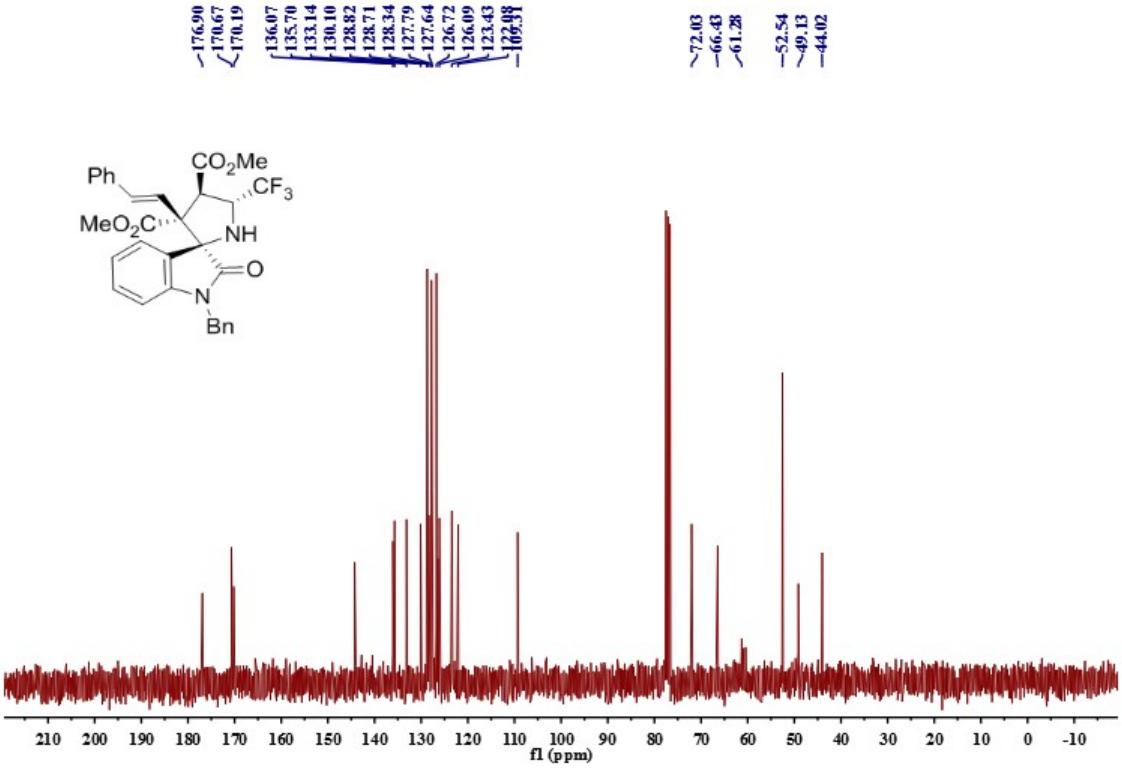
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4f



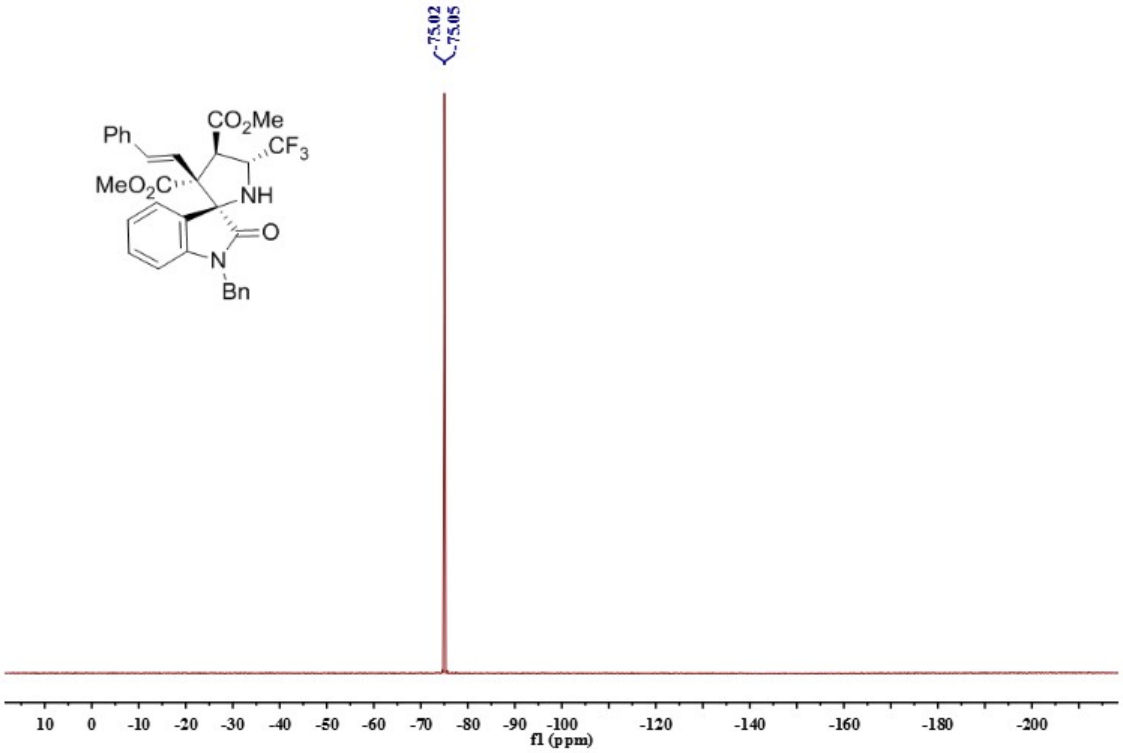
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4f



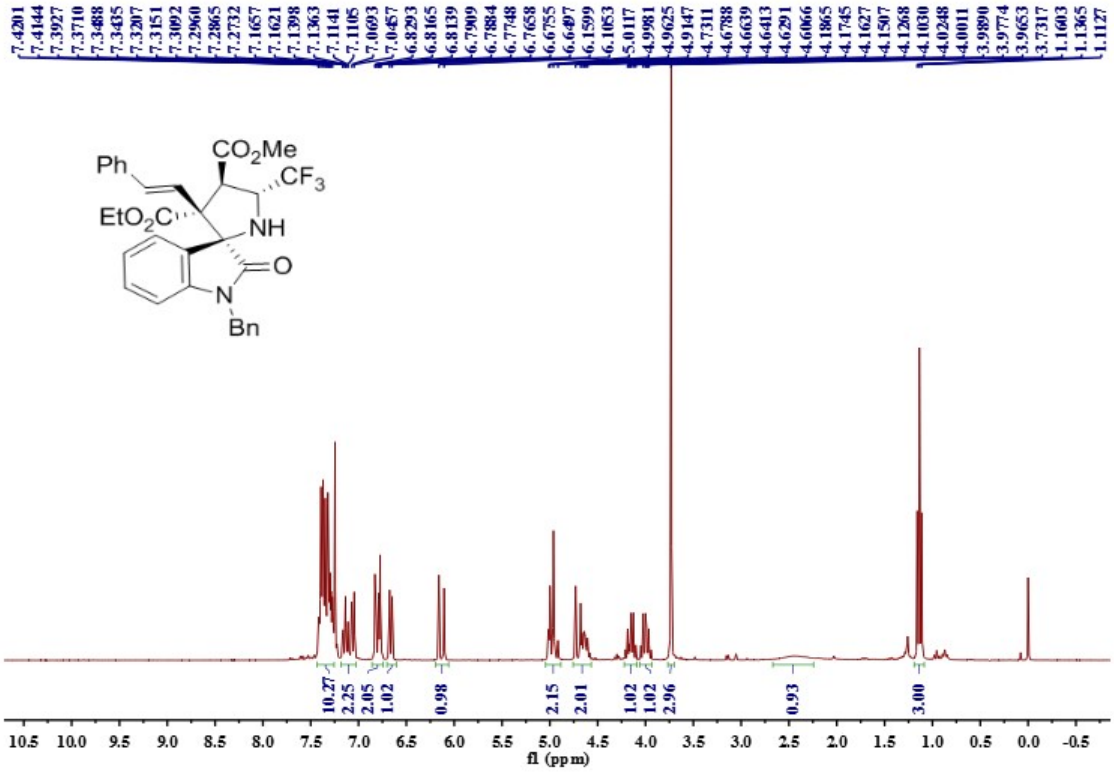
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4g



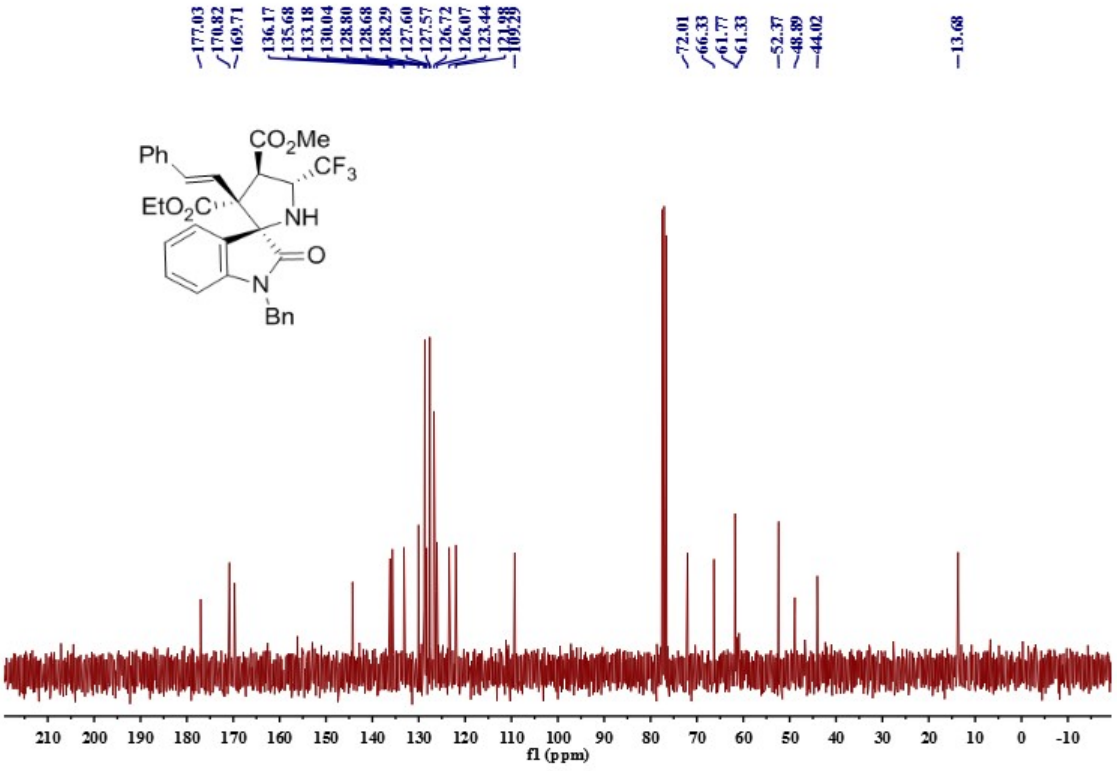
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4g



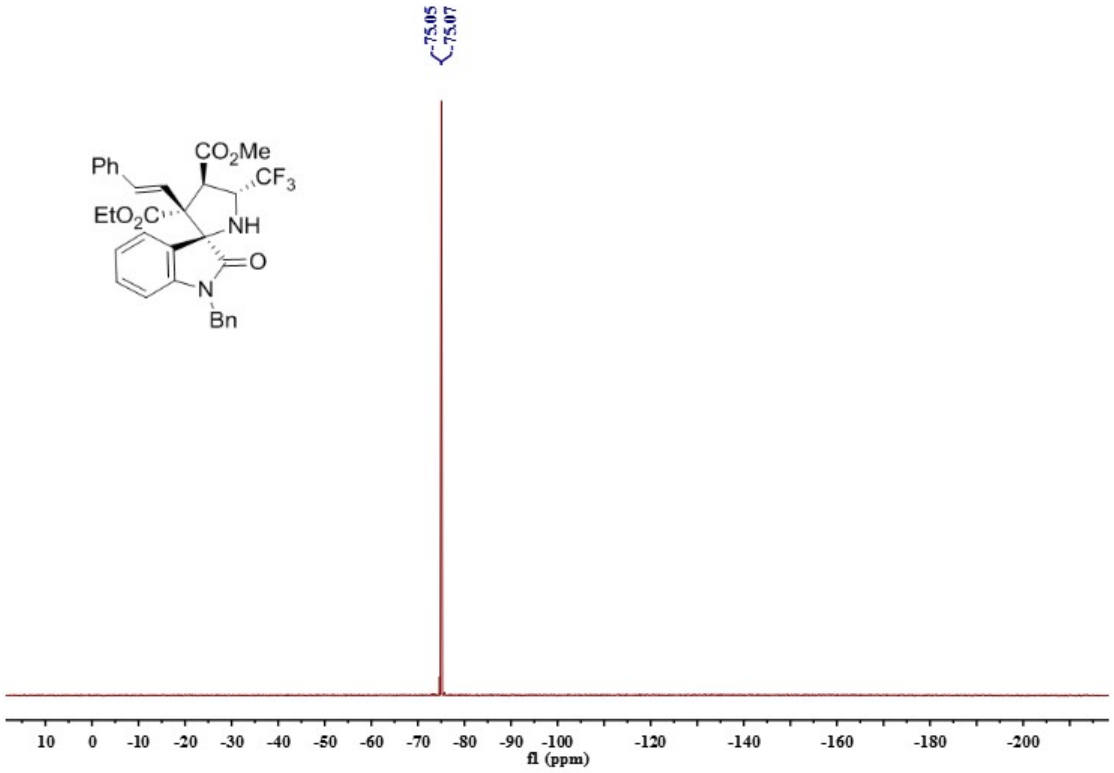
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4g



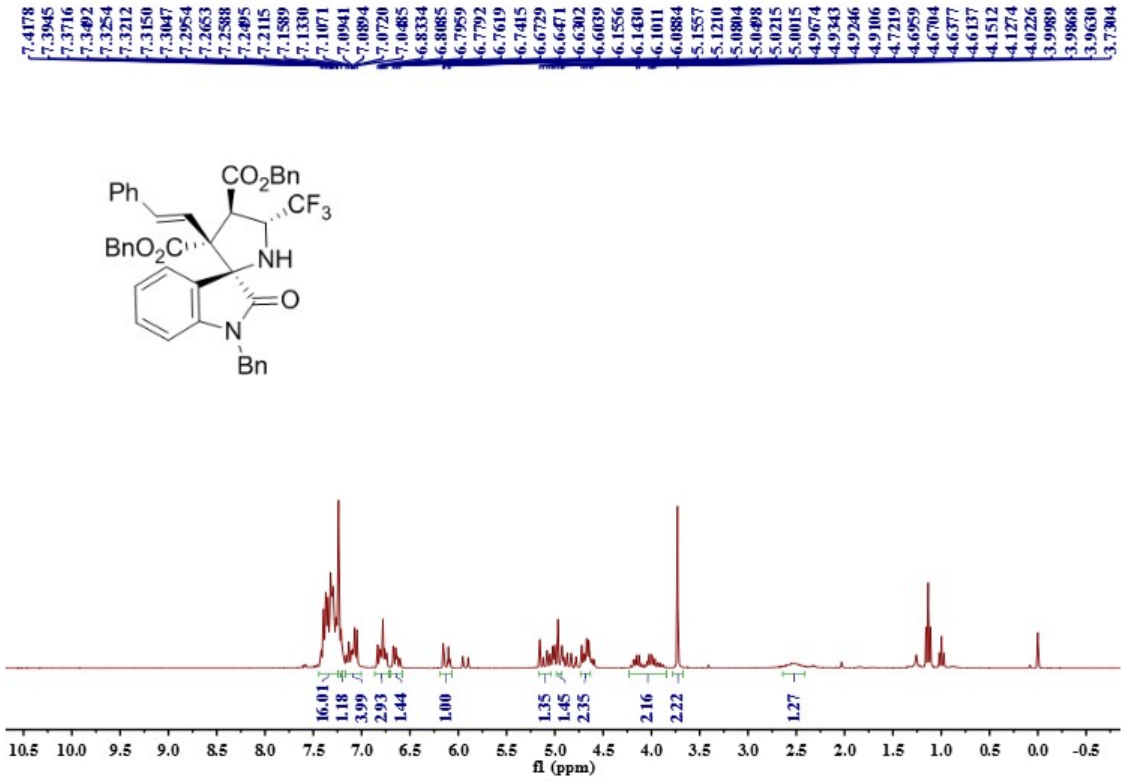
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4h



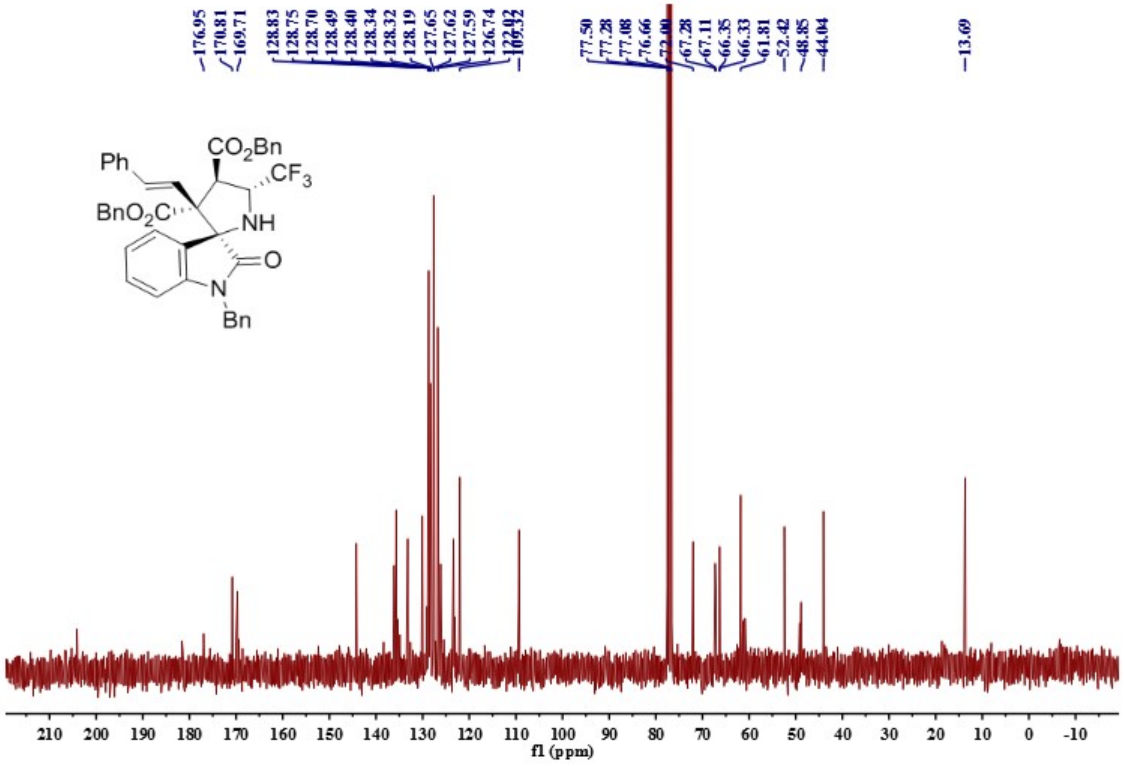
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4h



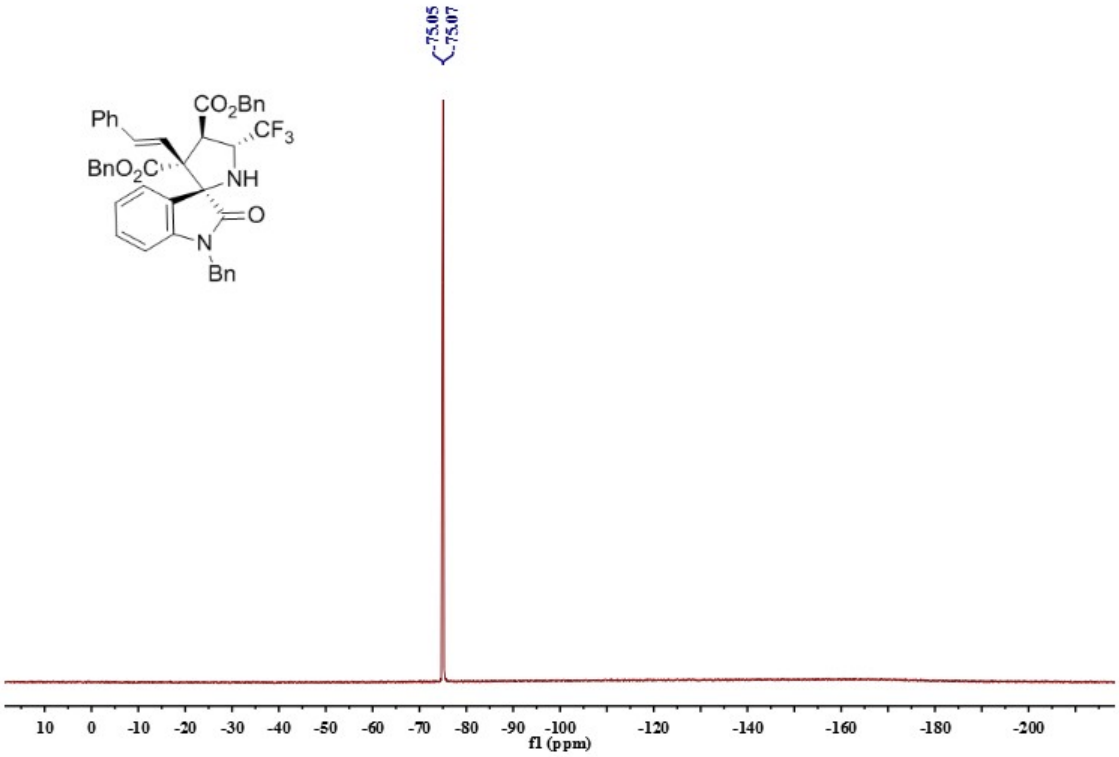
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4h



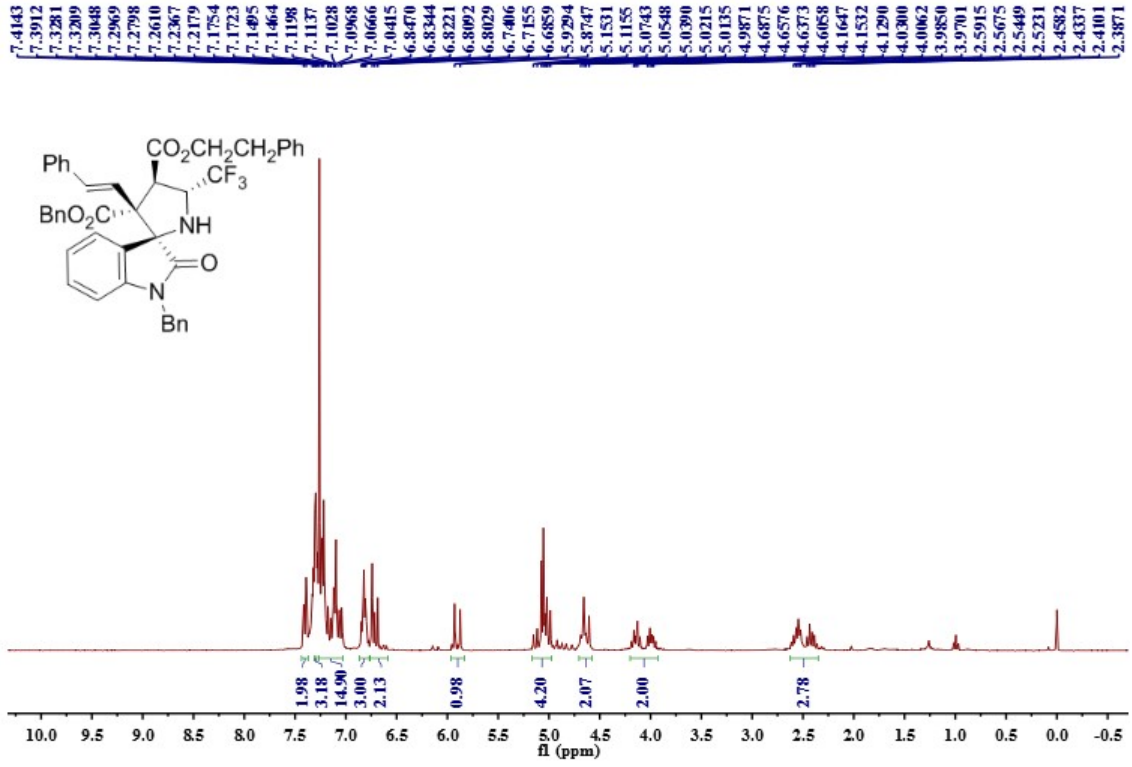
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo′*-4i



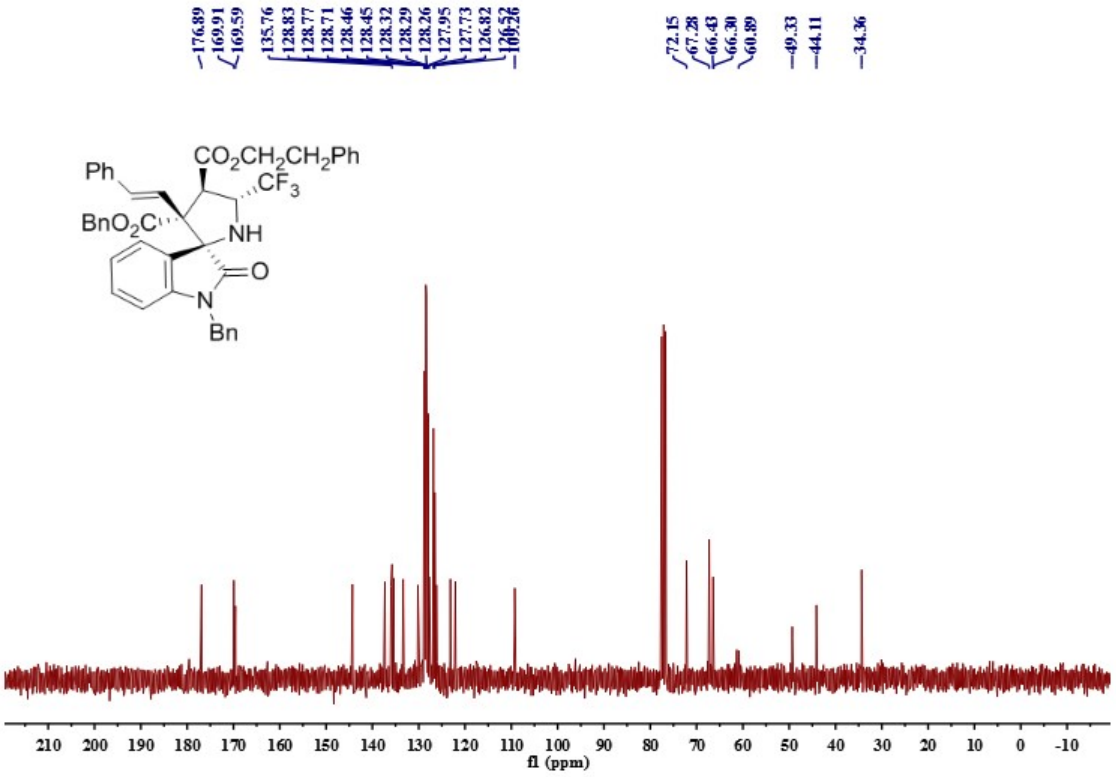
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo′*-4i



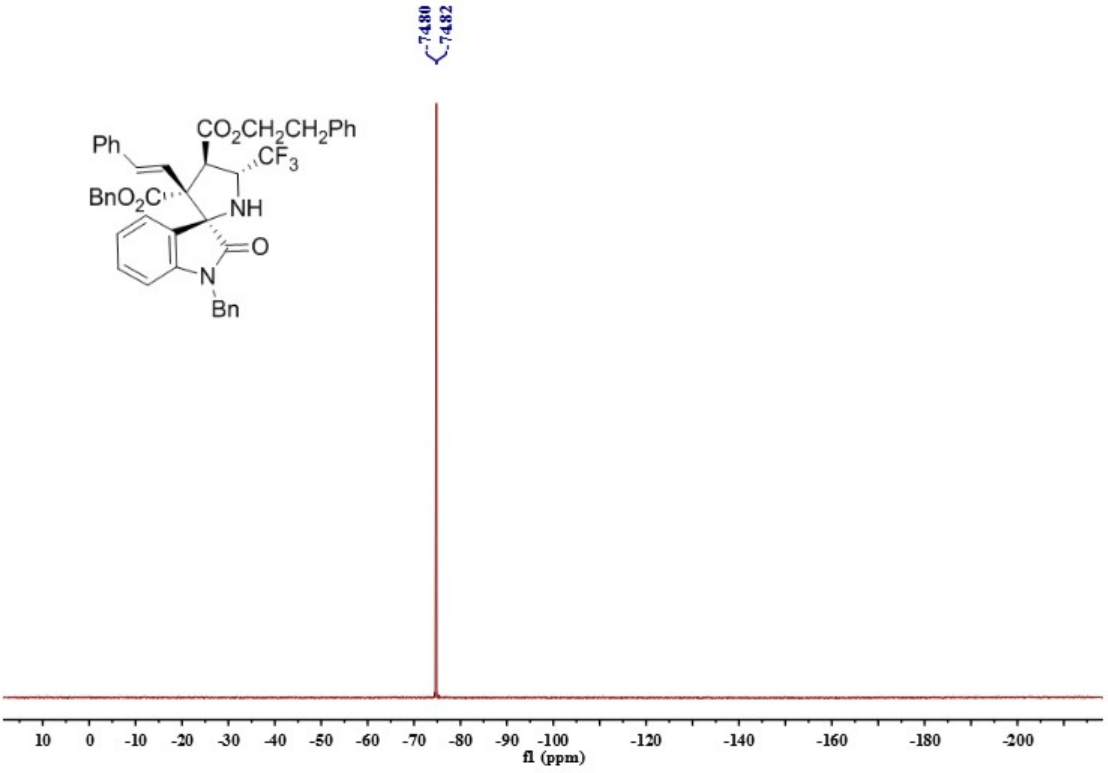
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4i



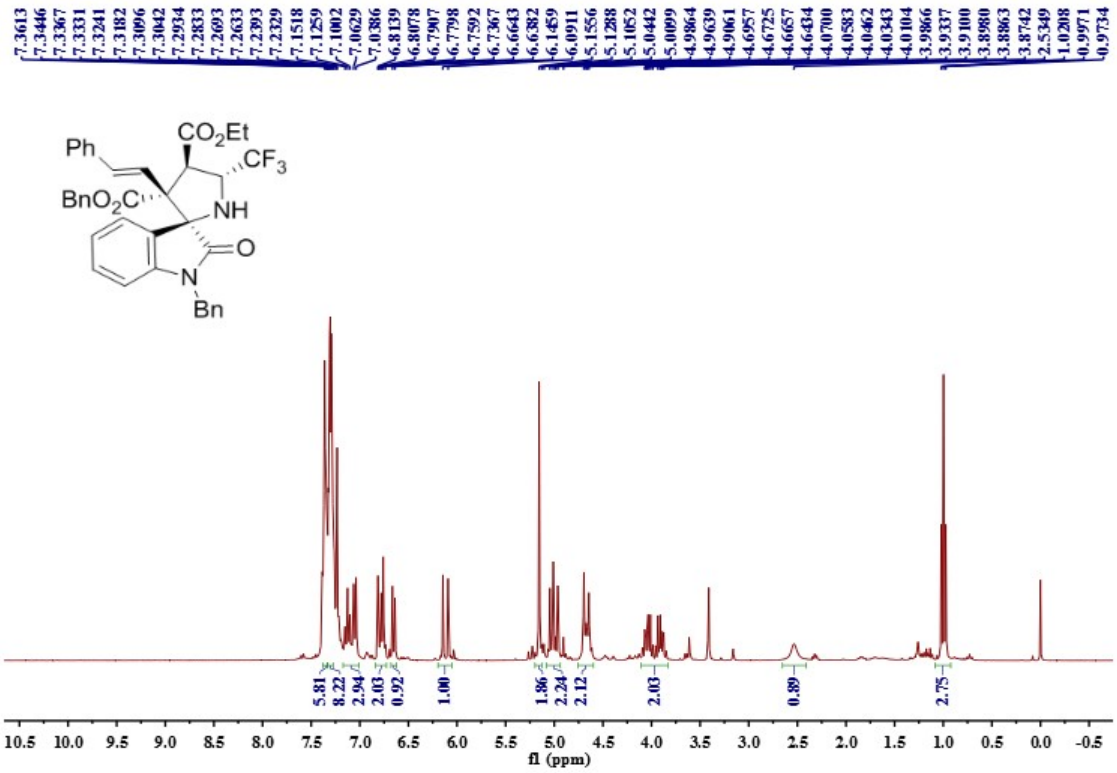
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4j



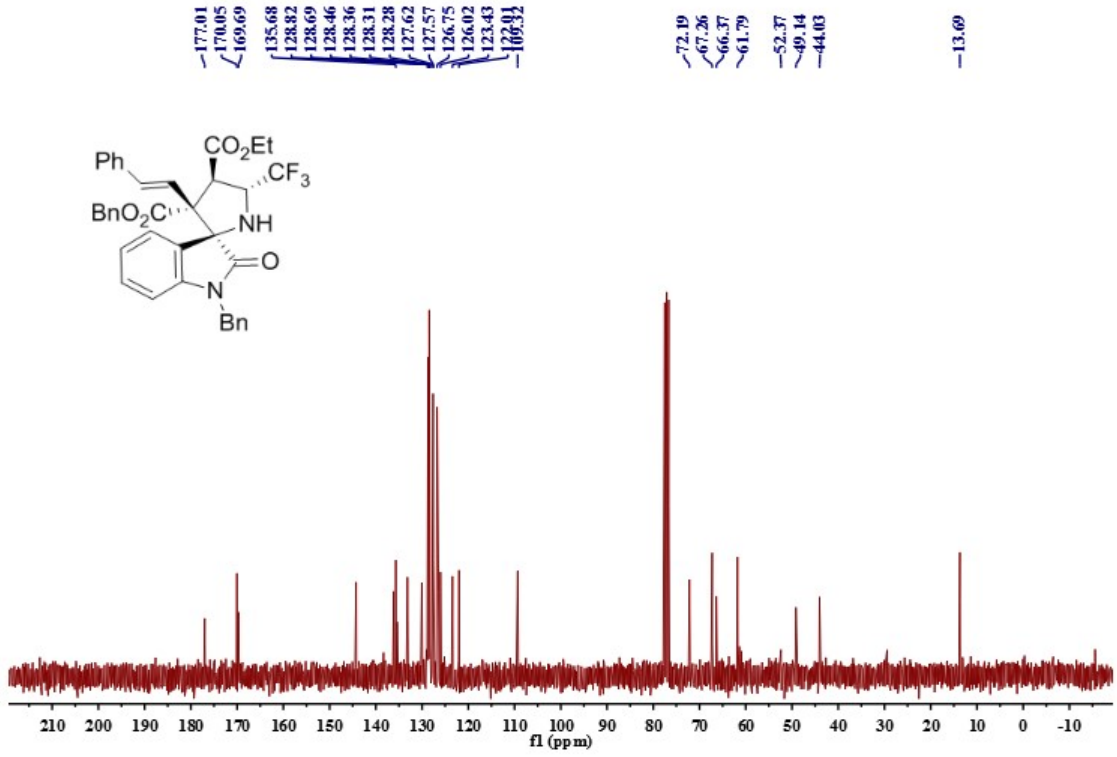
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4j



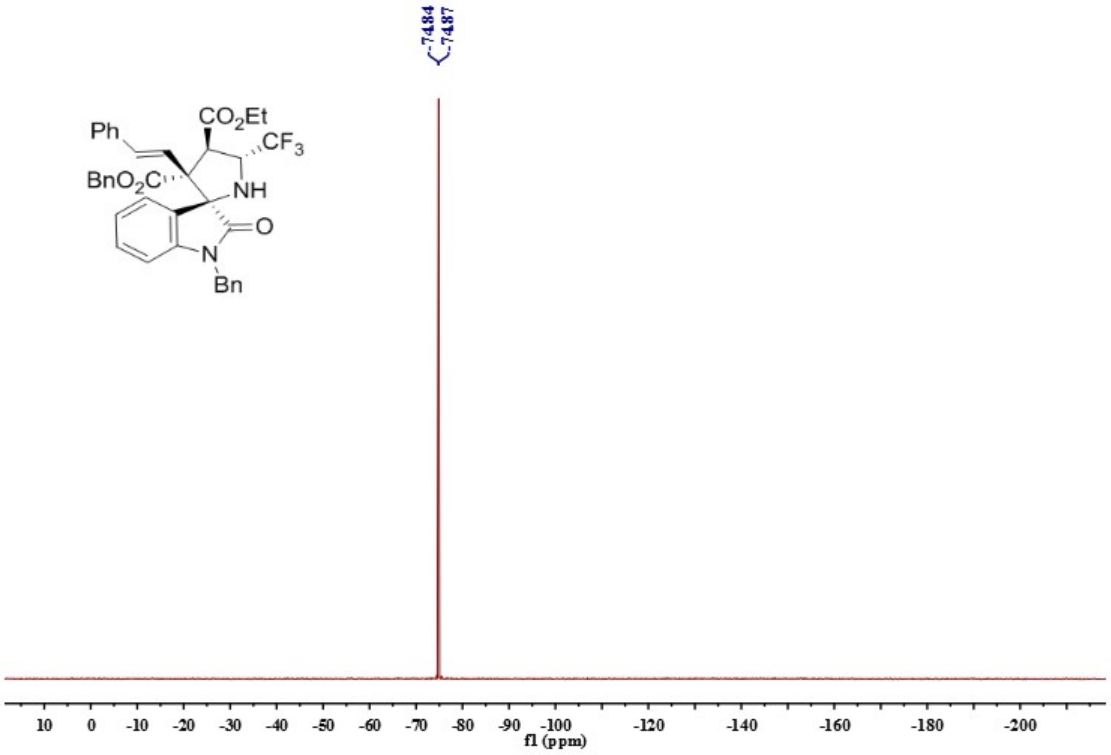
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4j



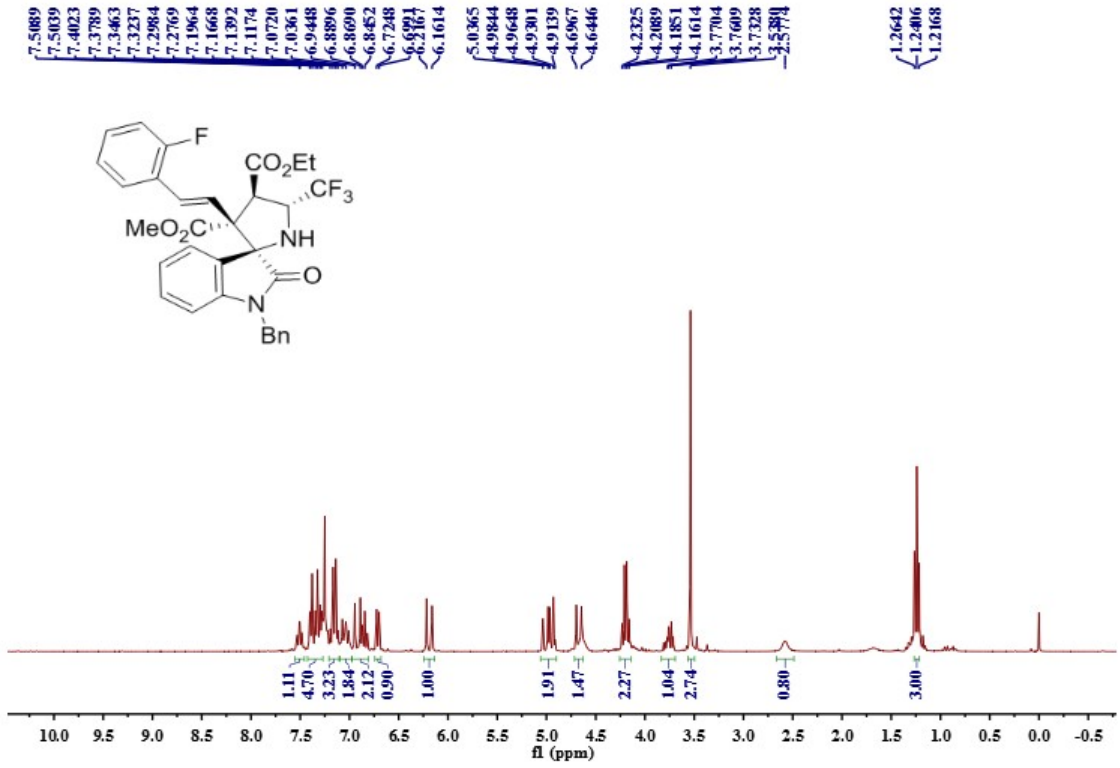
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4k



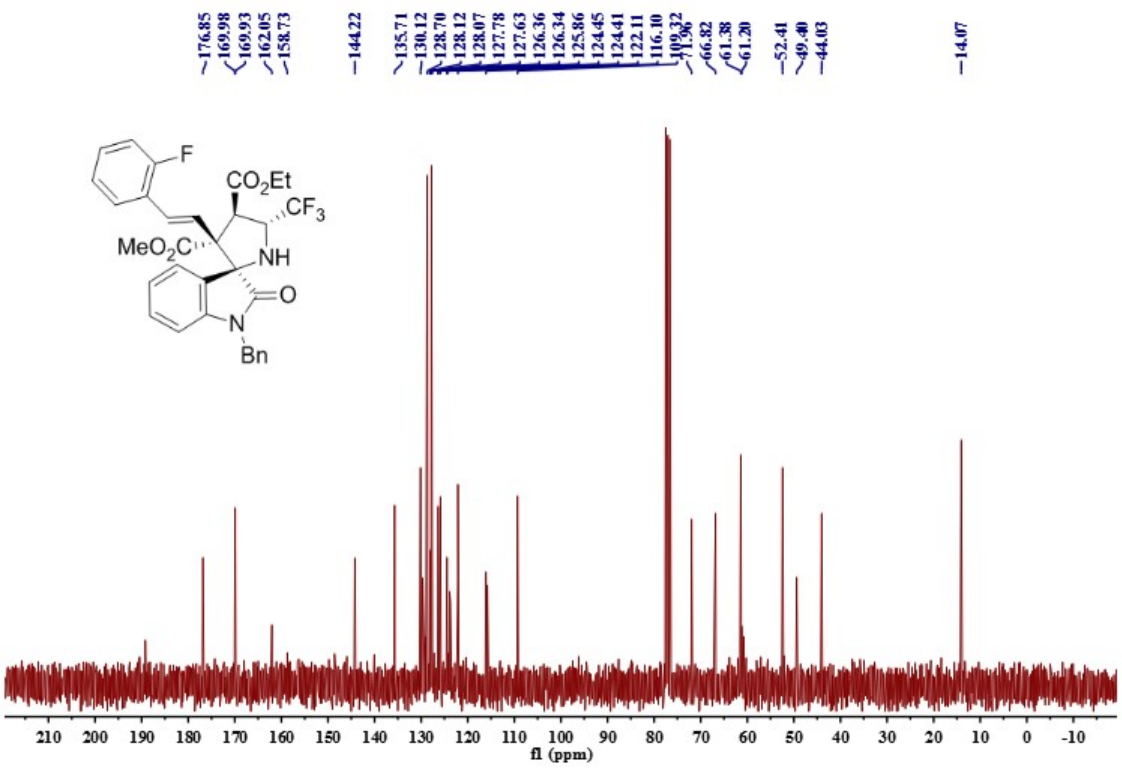
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4k



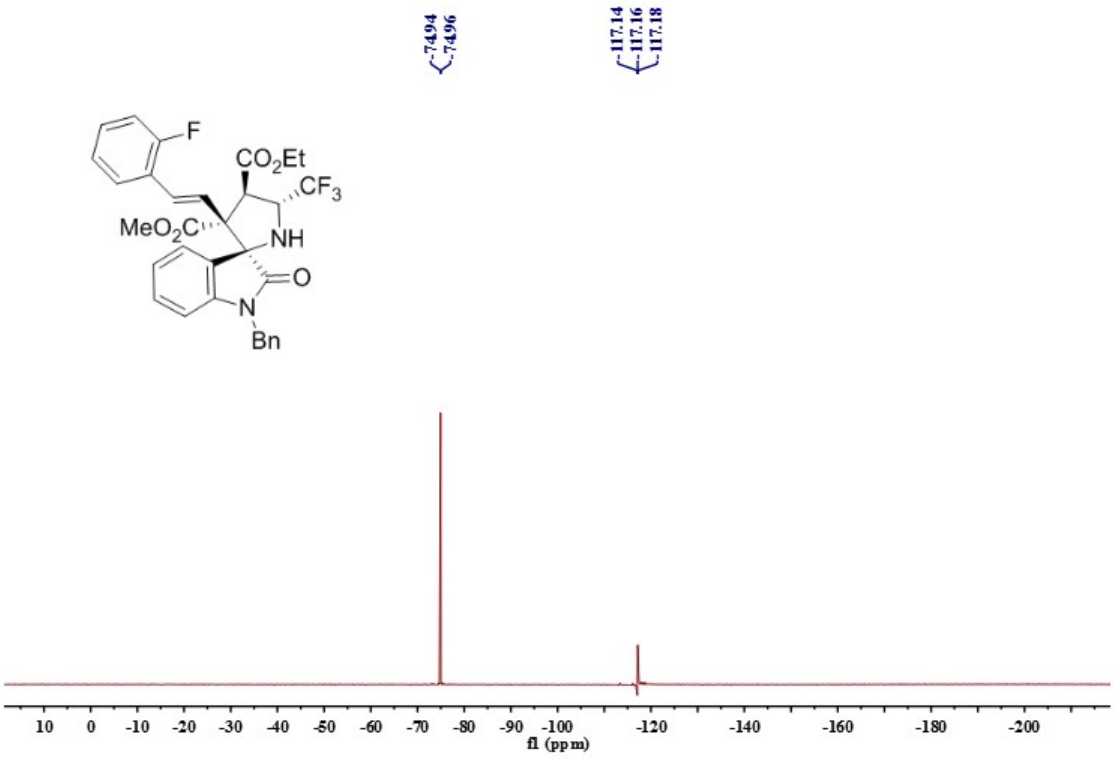
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo′*-4k



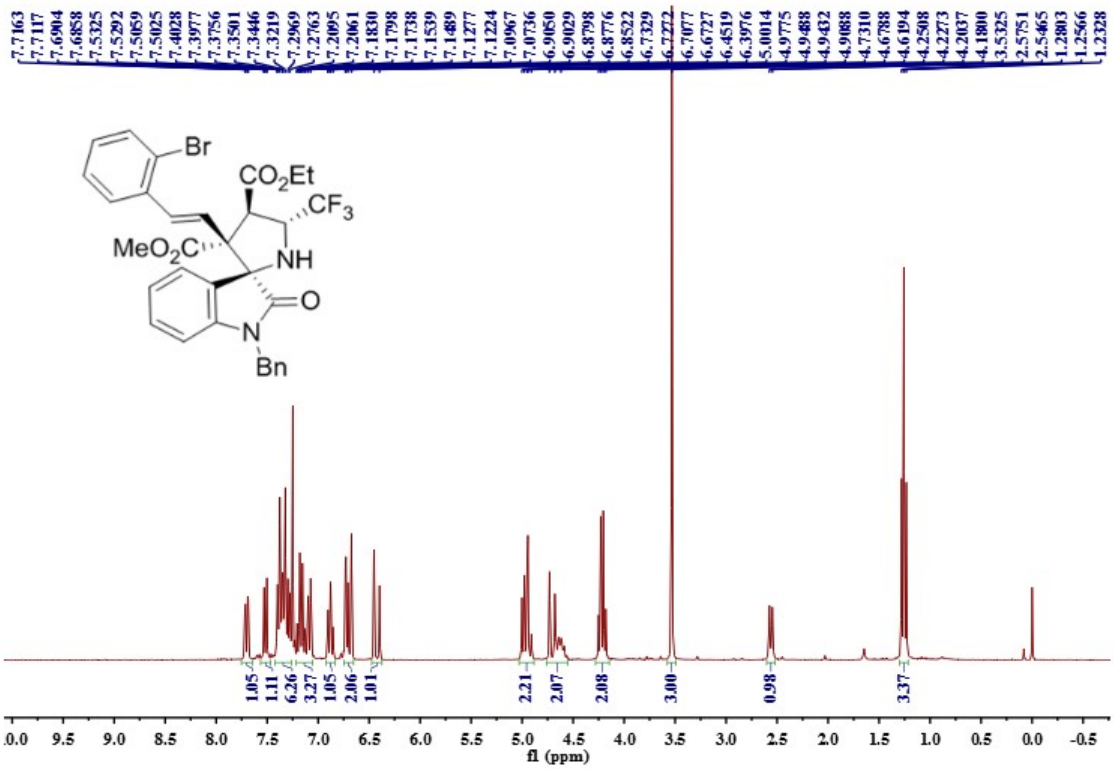
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo′*-4l



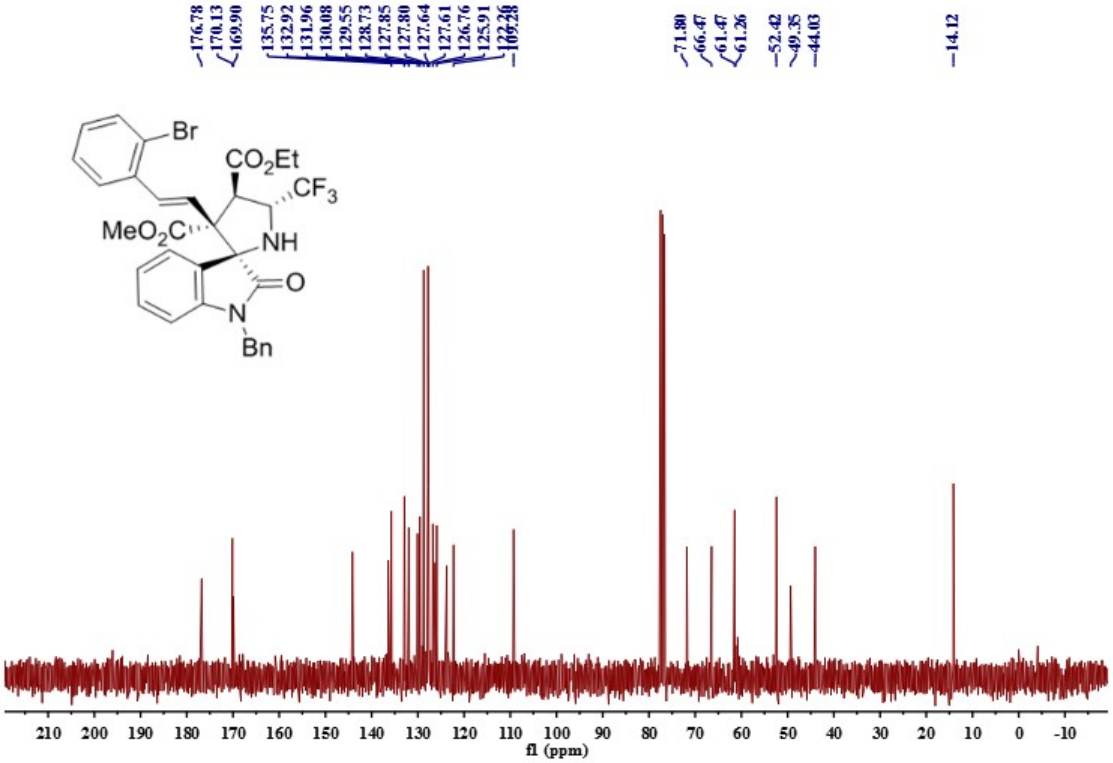
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4l



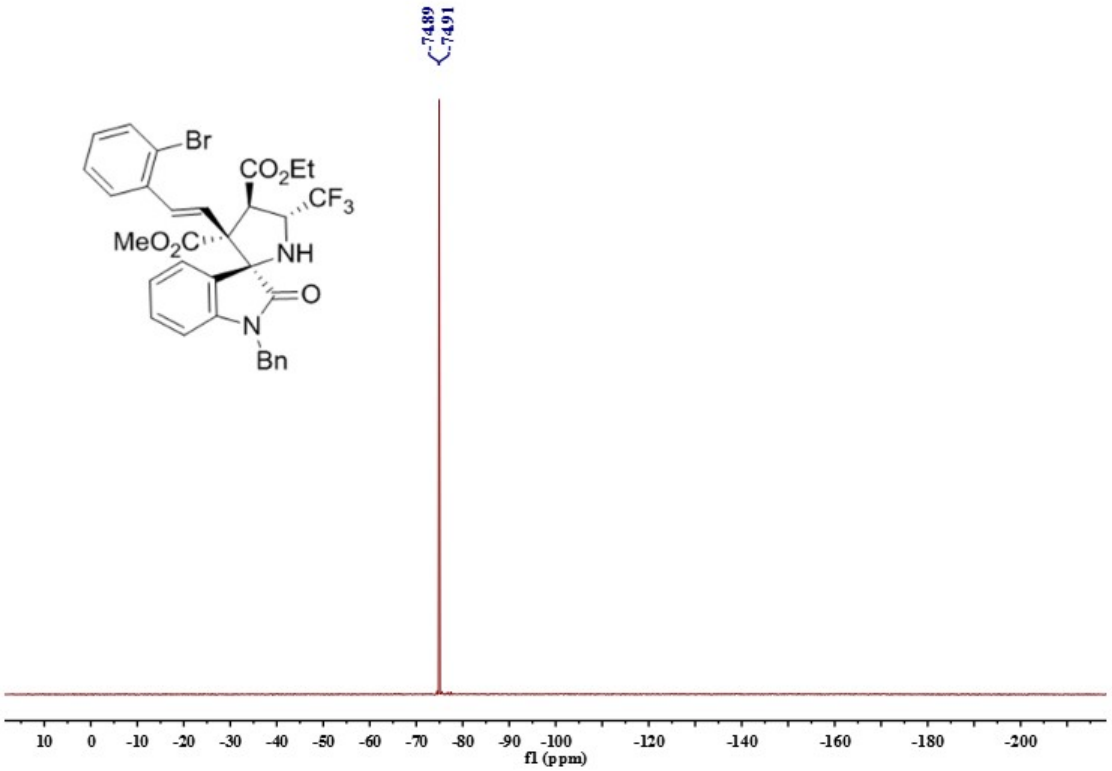
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4l



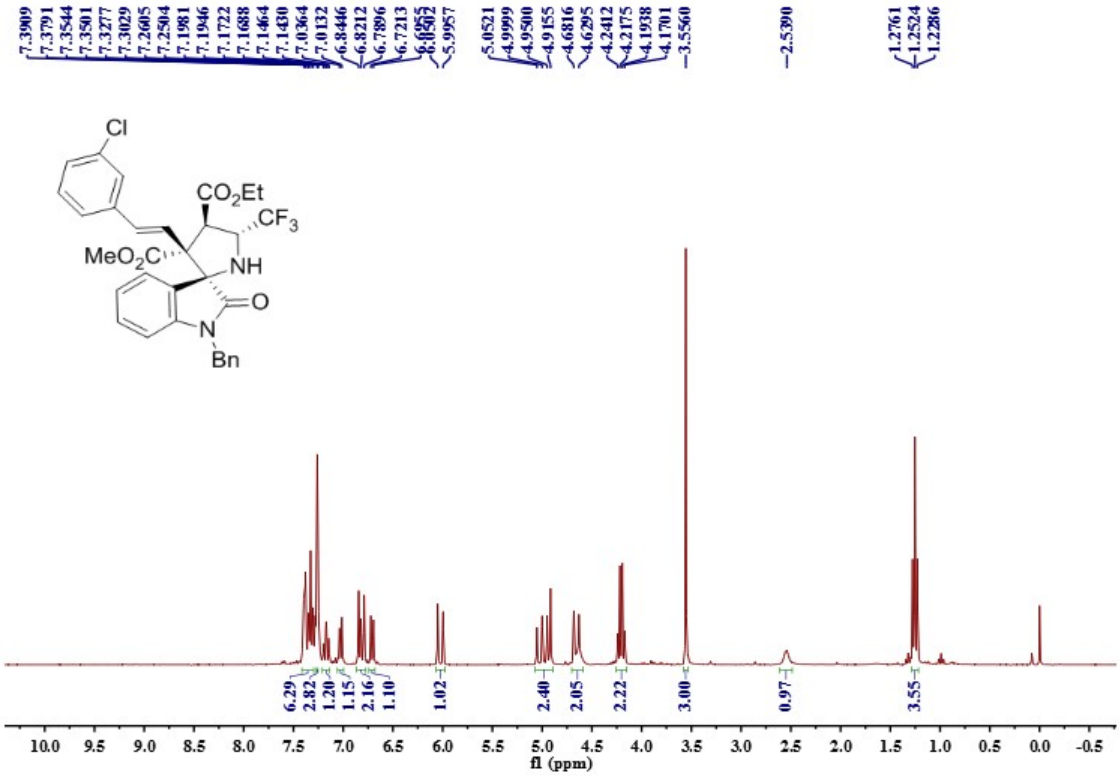
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4m



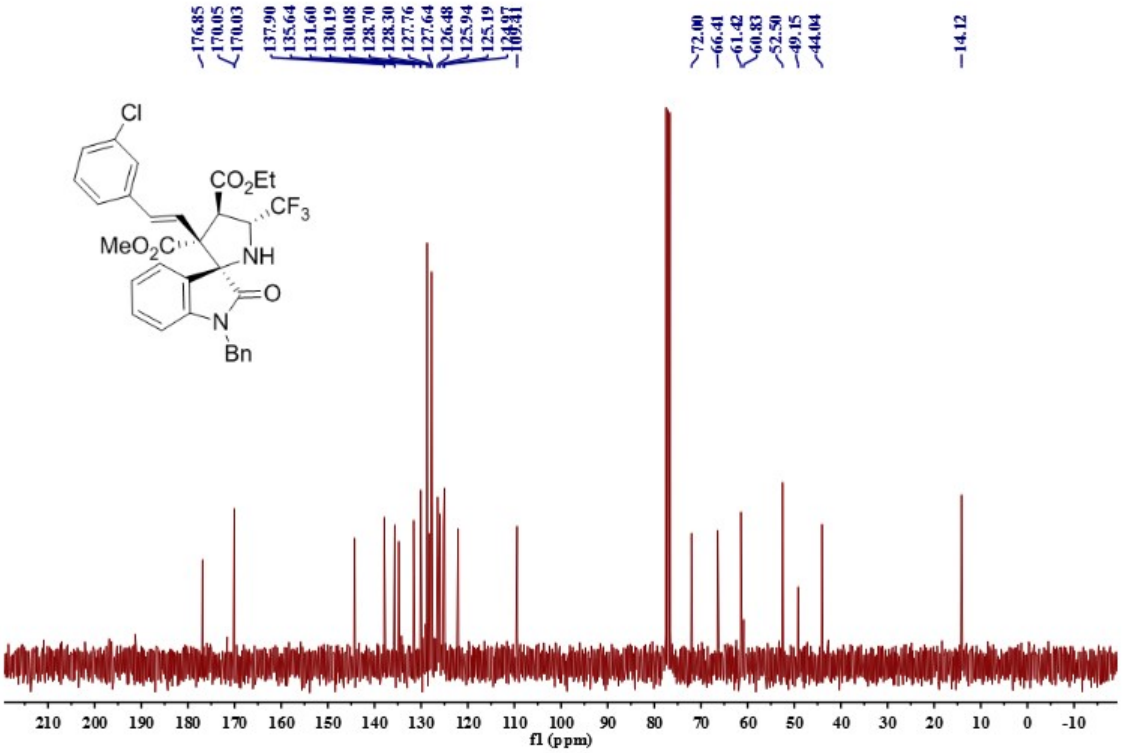
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4m



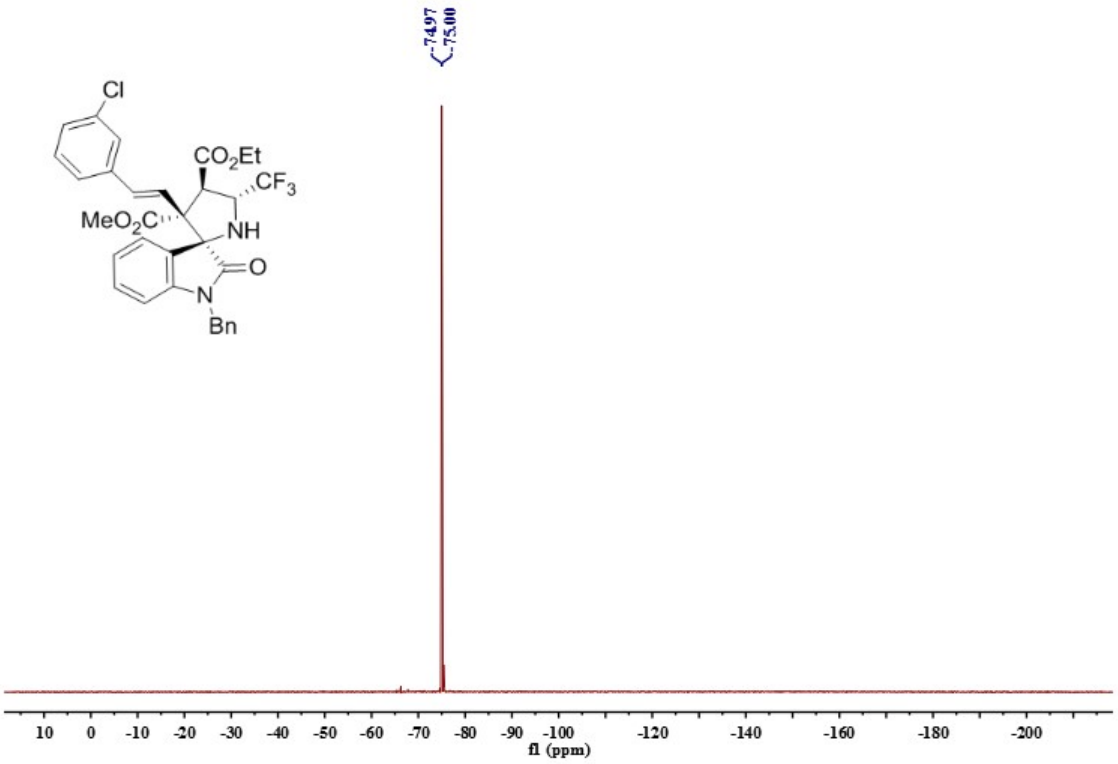
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4m



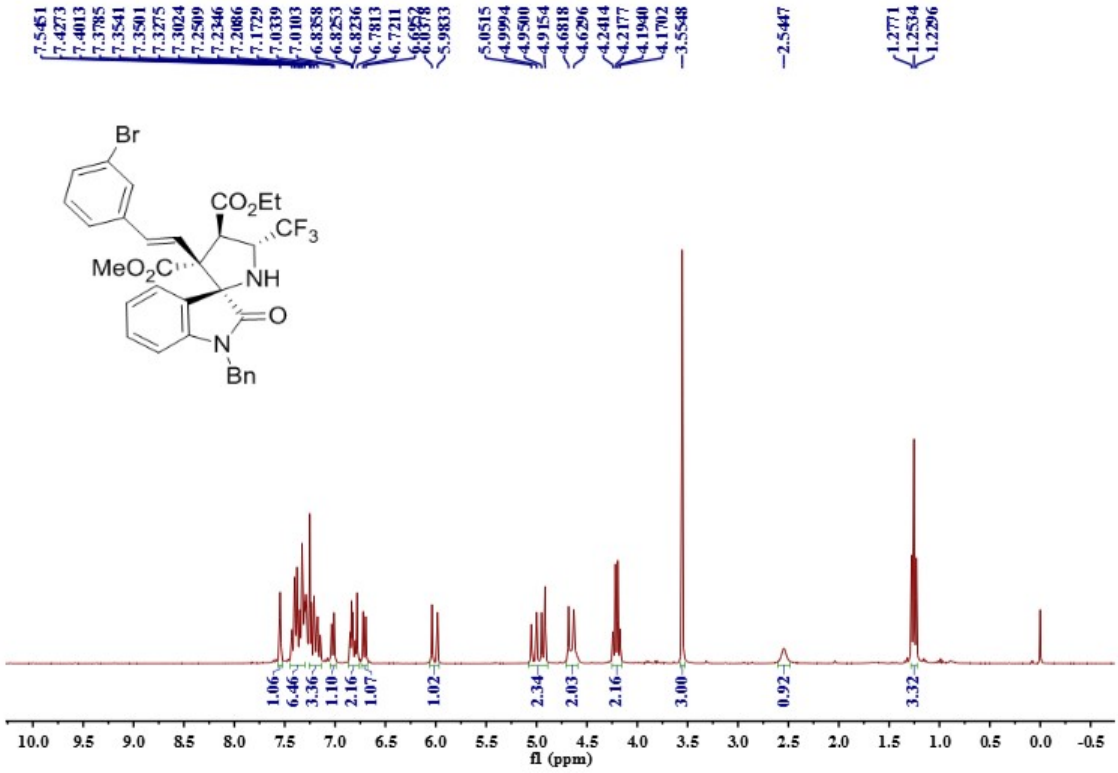
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4n



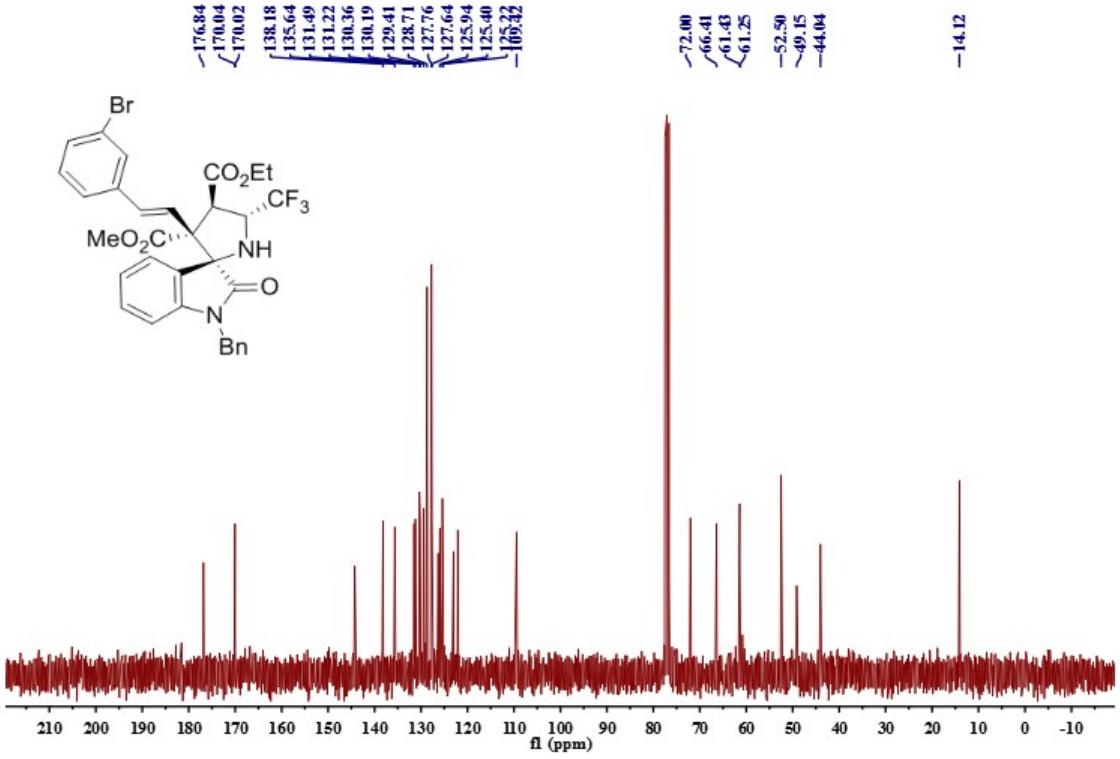
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4n



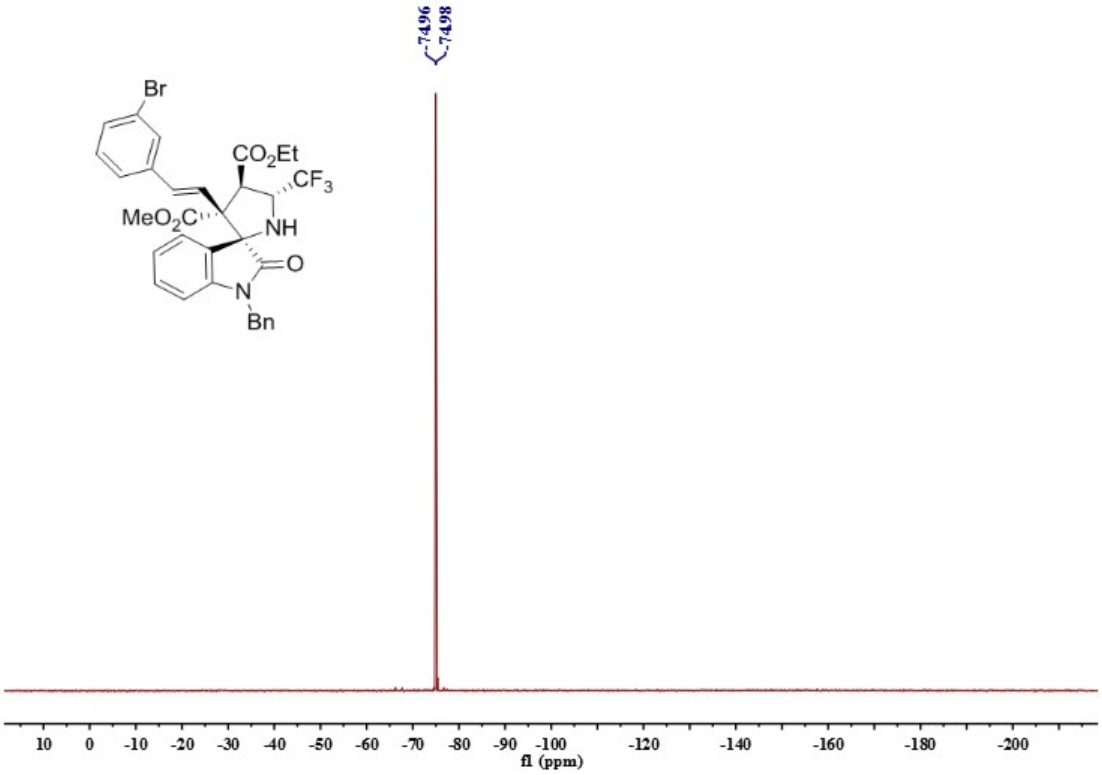
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4n



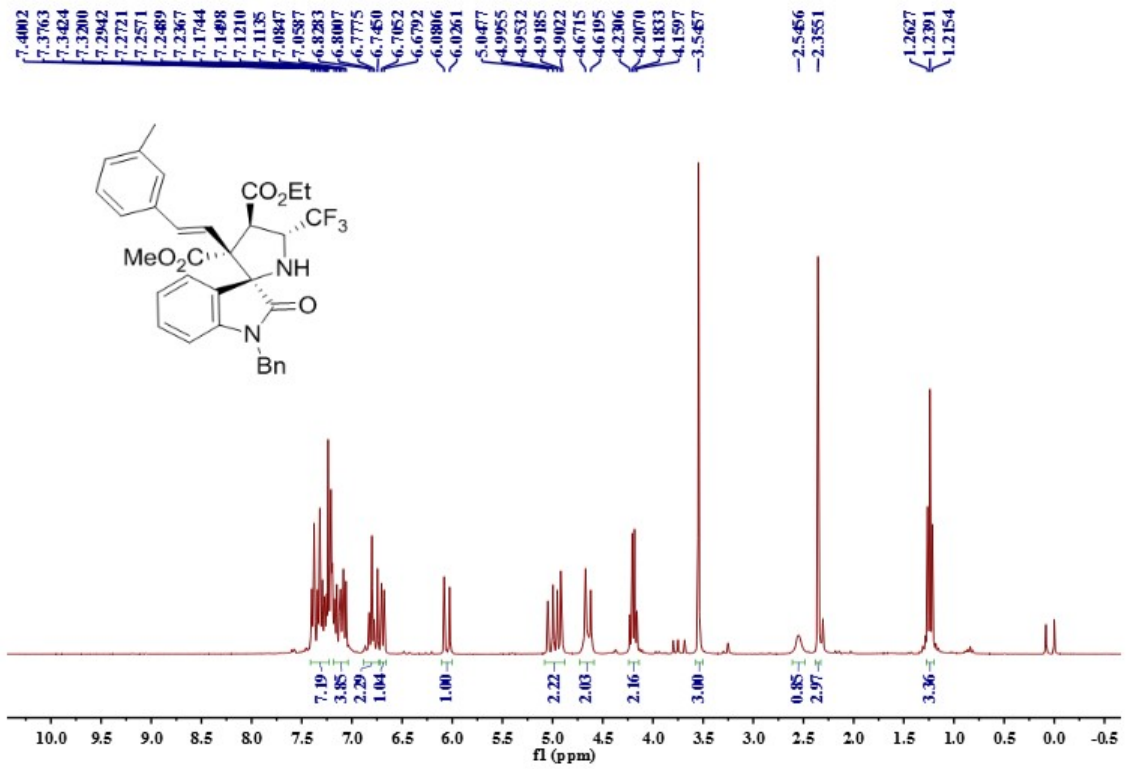
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4o



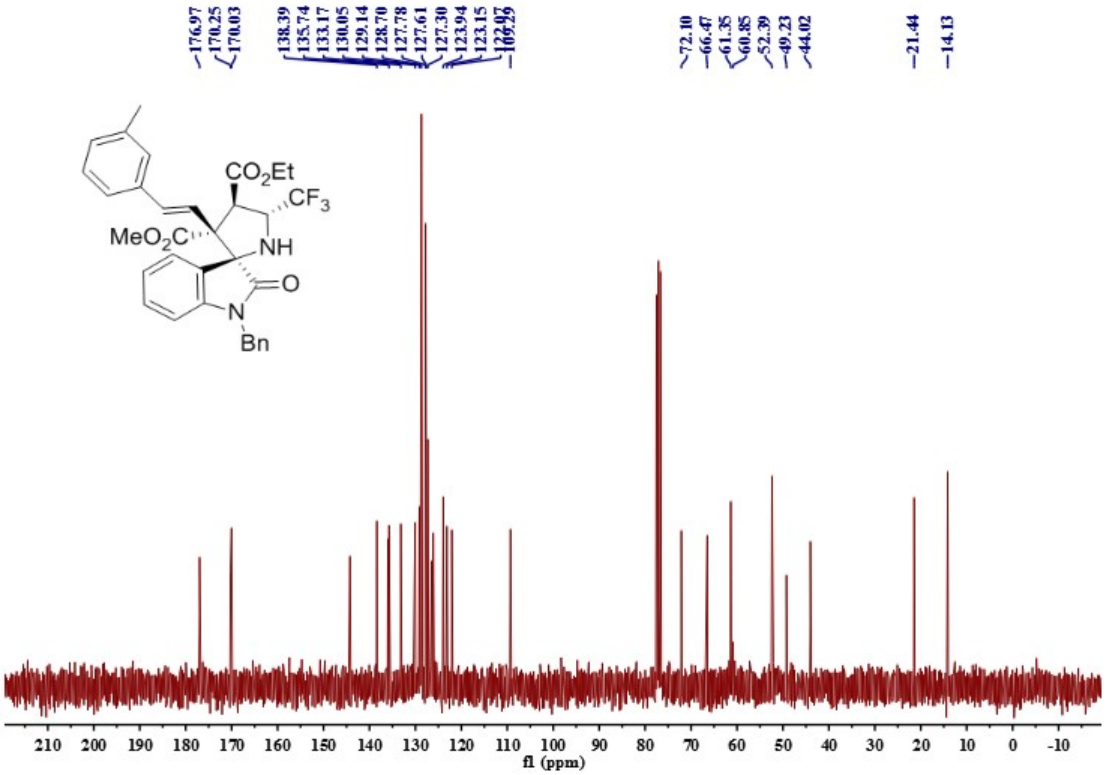
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4o



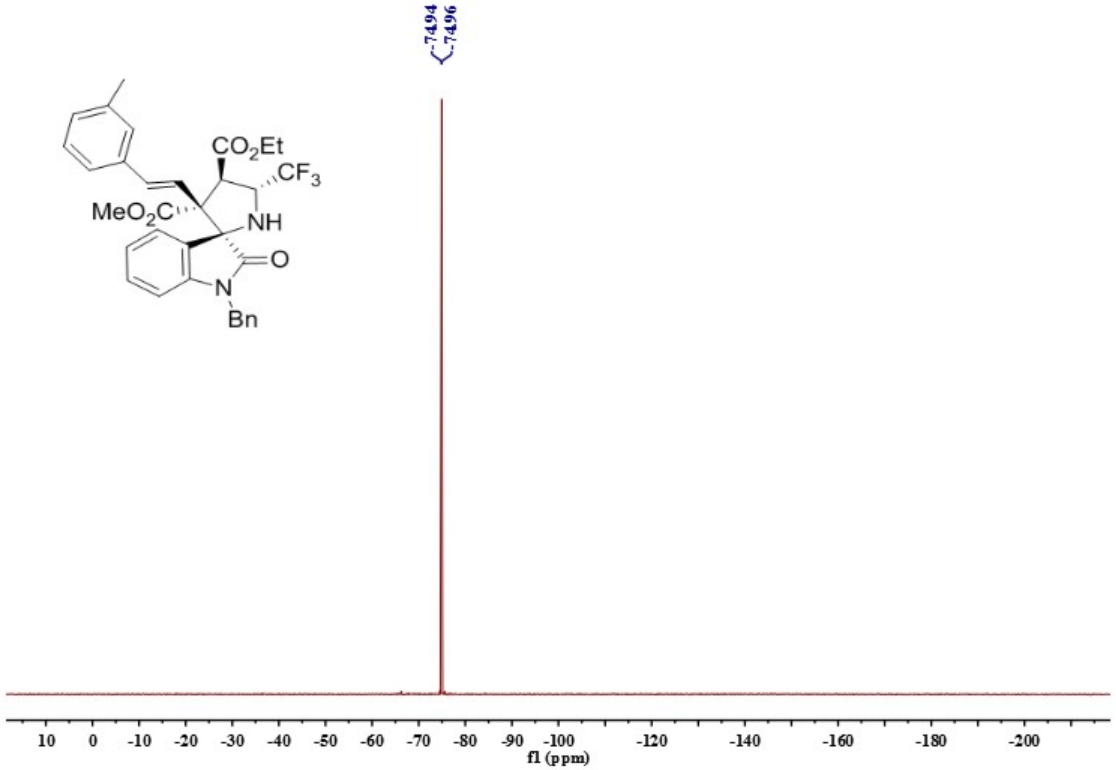
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo′*-4o



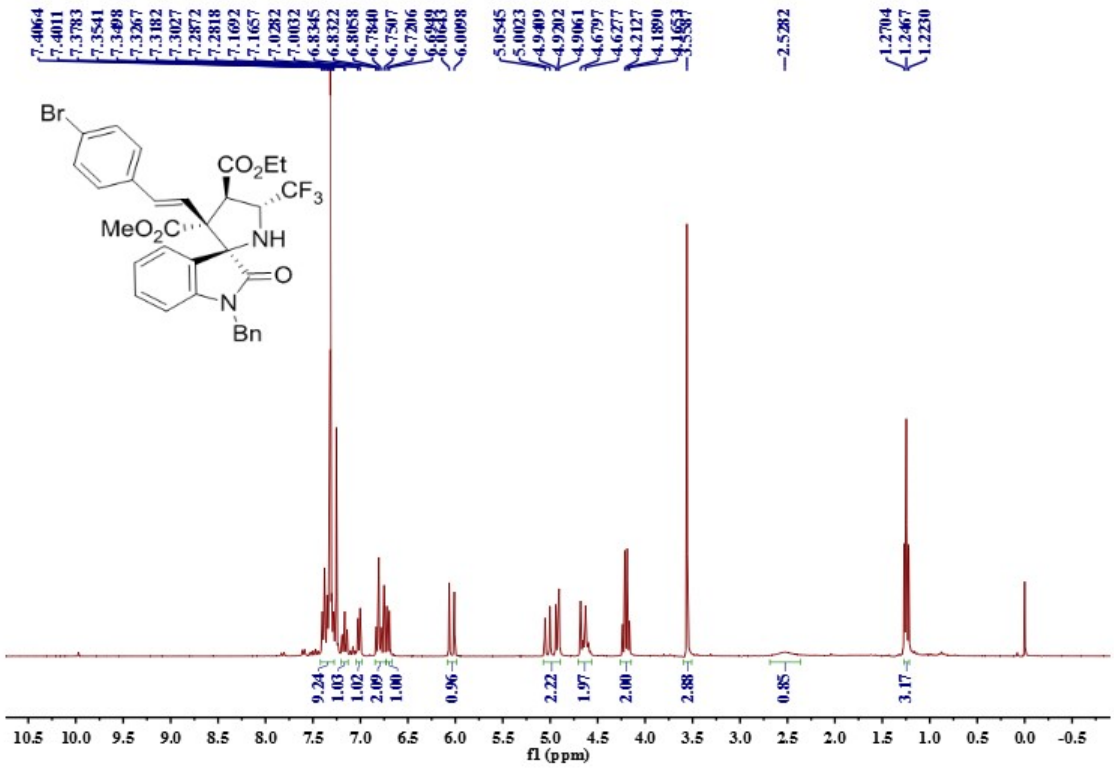
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo′*-4p



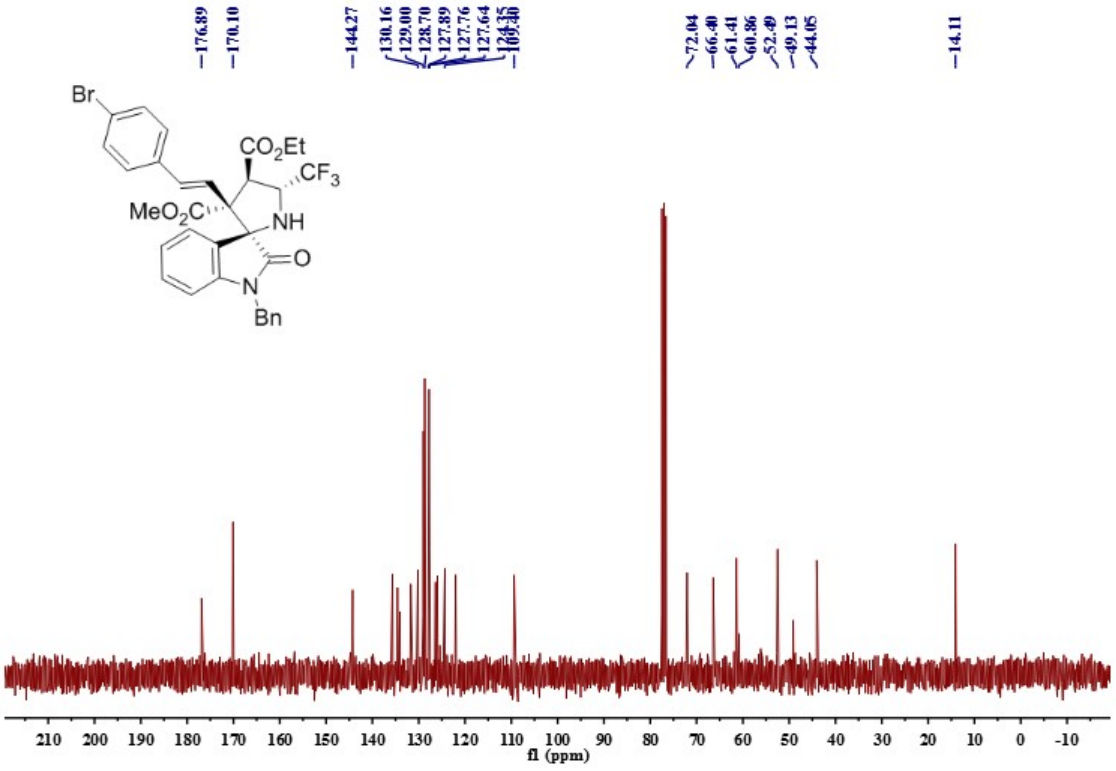
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4p



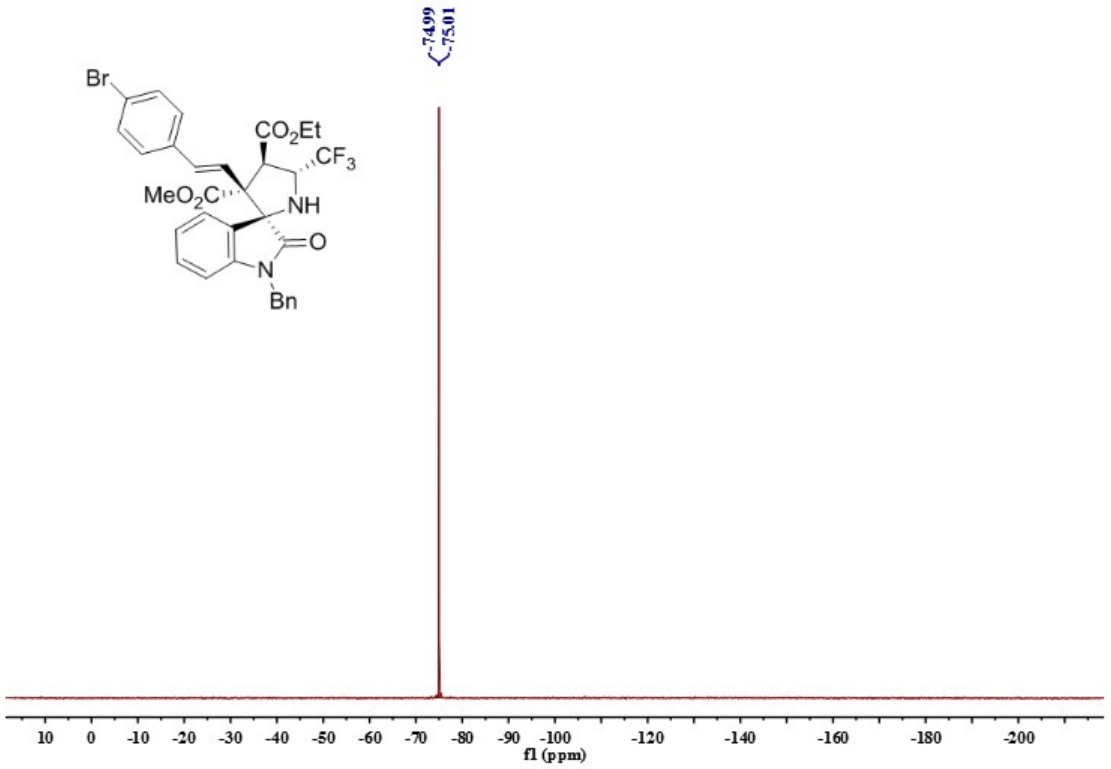
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4p



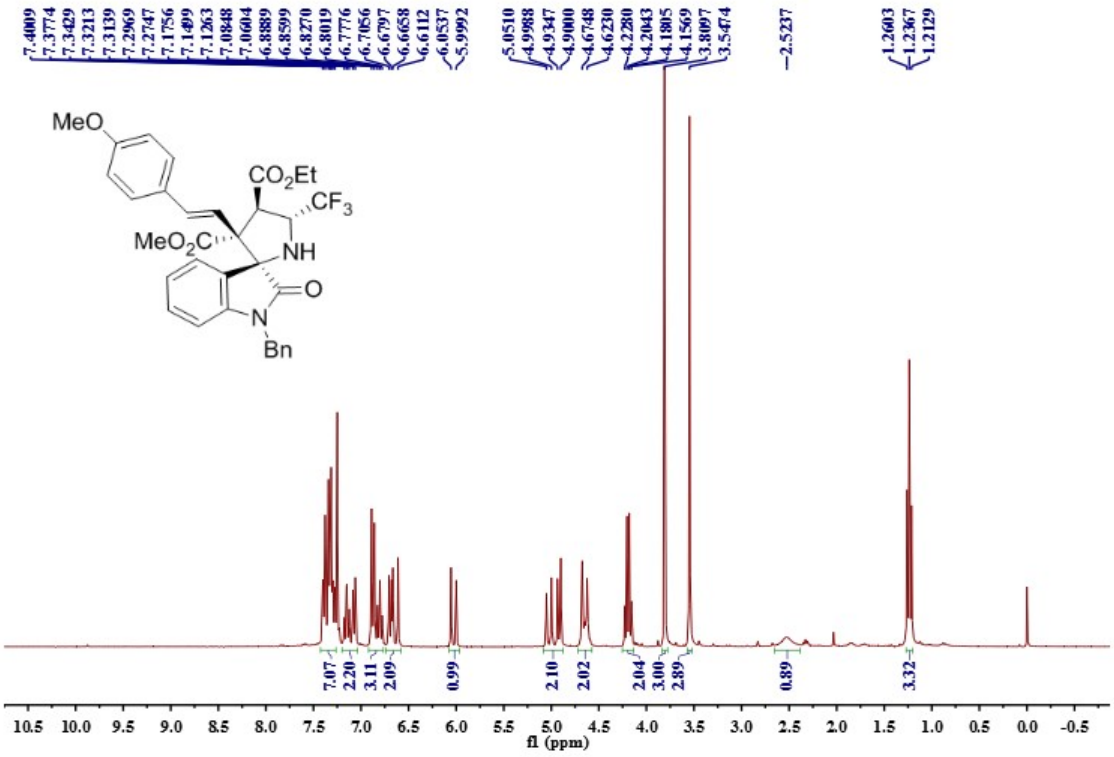
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4q



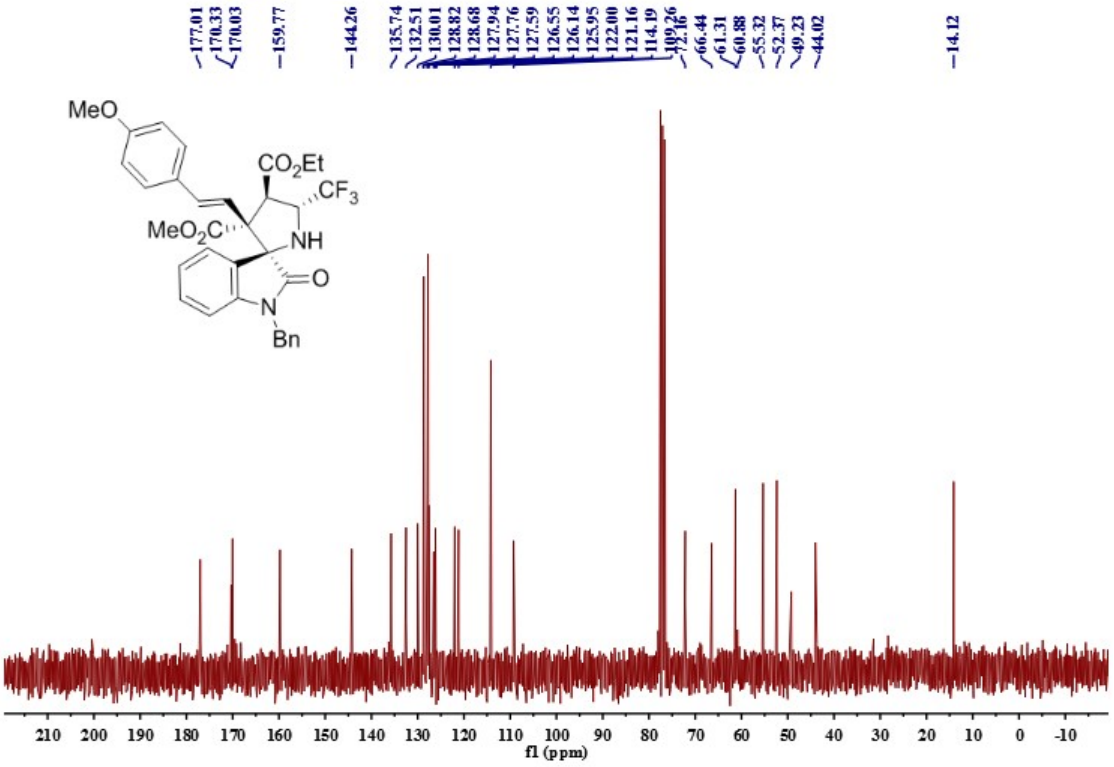
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4q



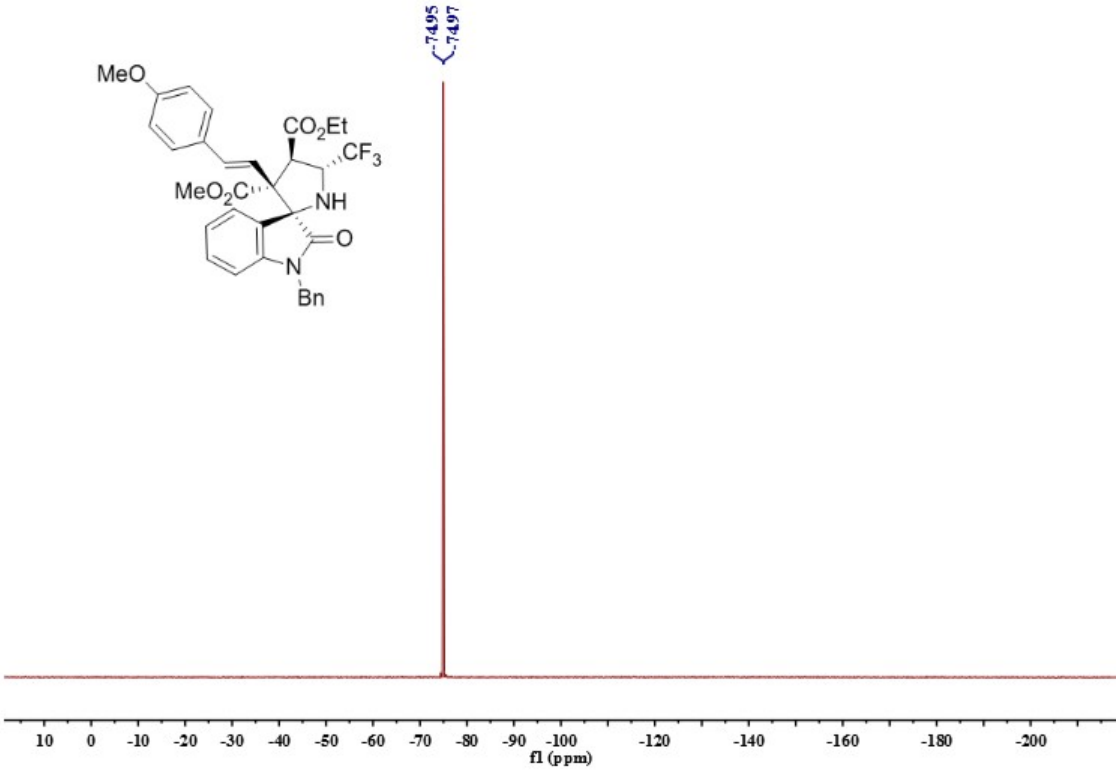
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo′*-4q



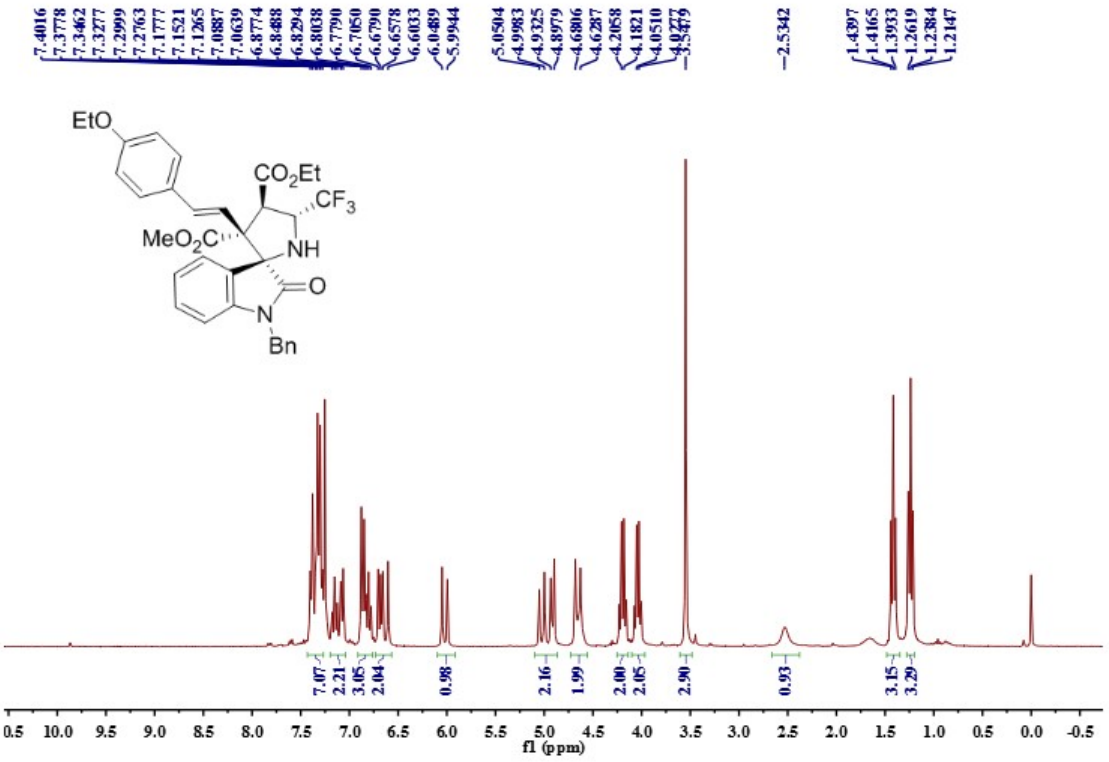
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo′*-4r



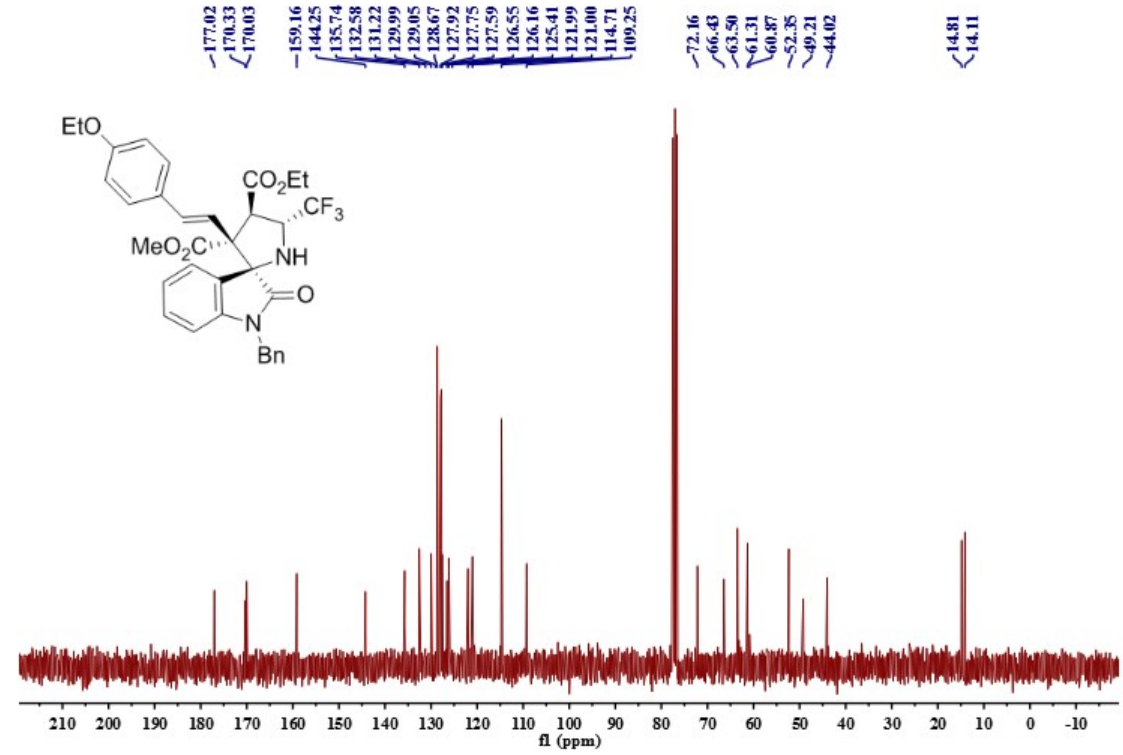
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4r



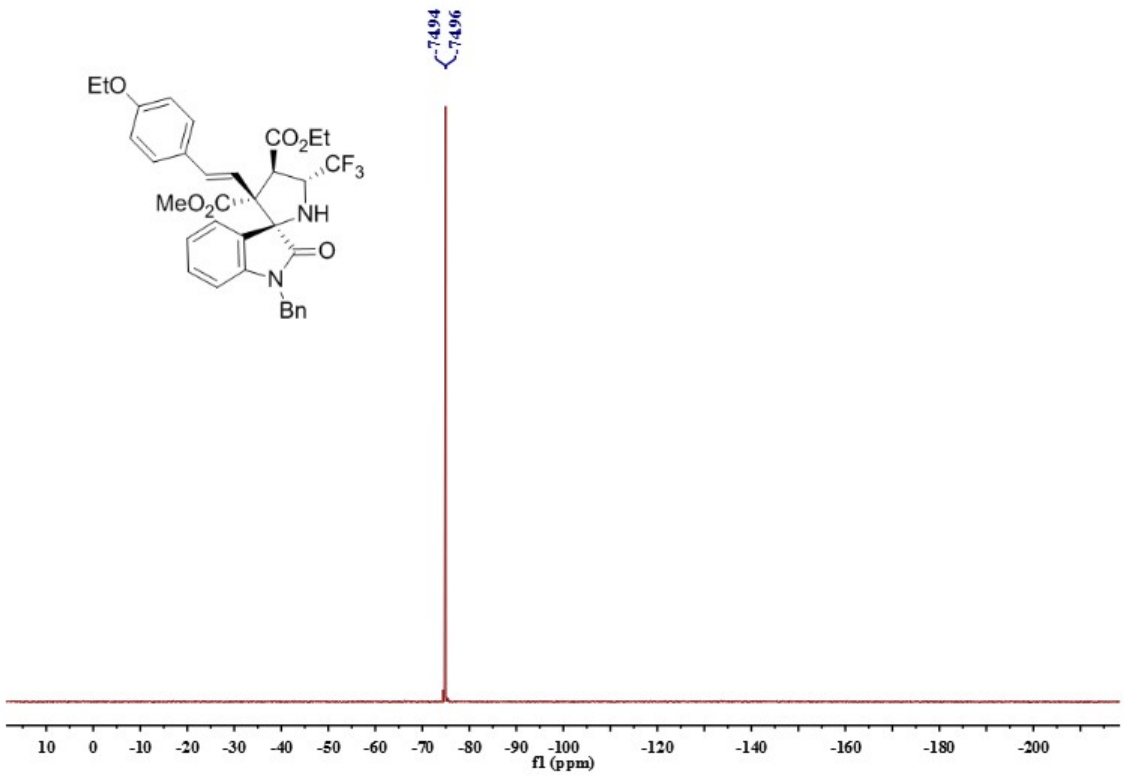
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4r



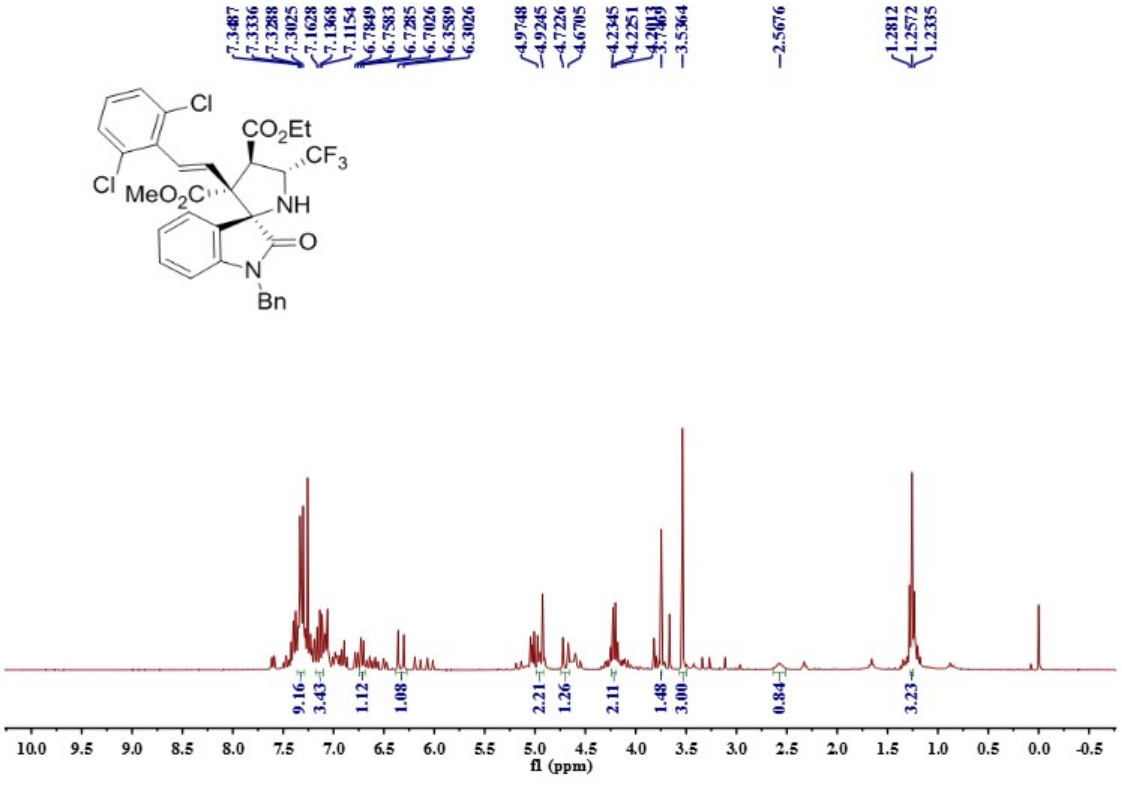
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4s



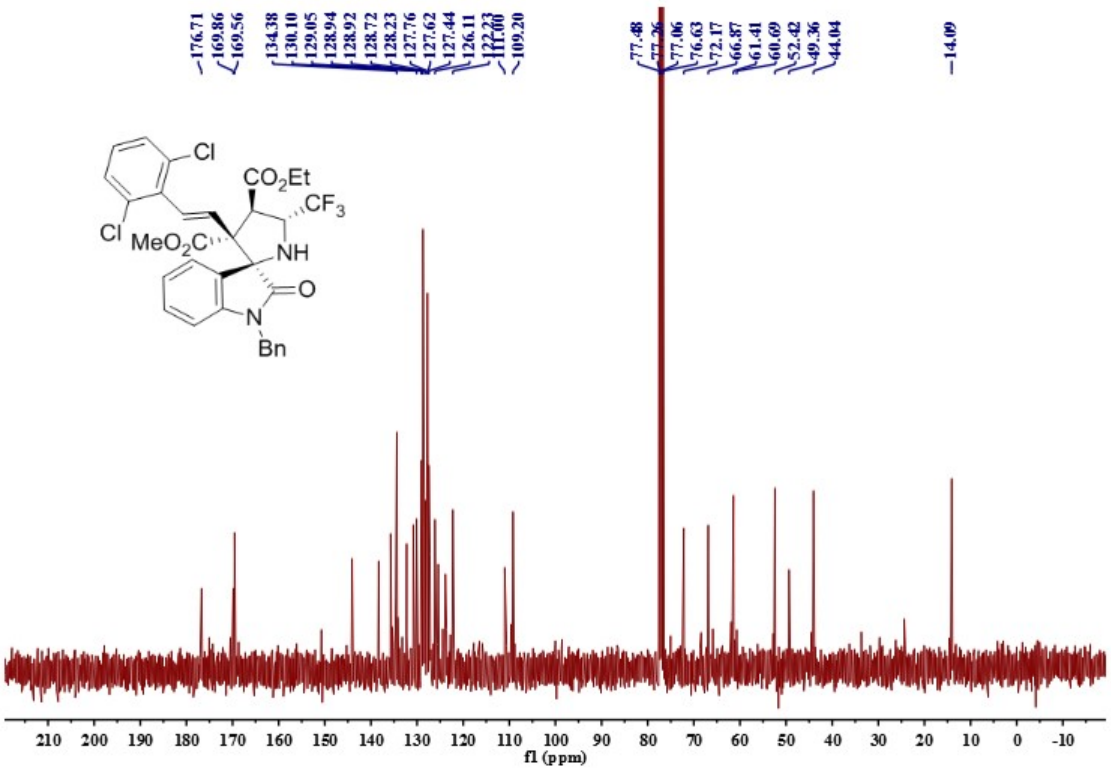
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4s



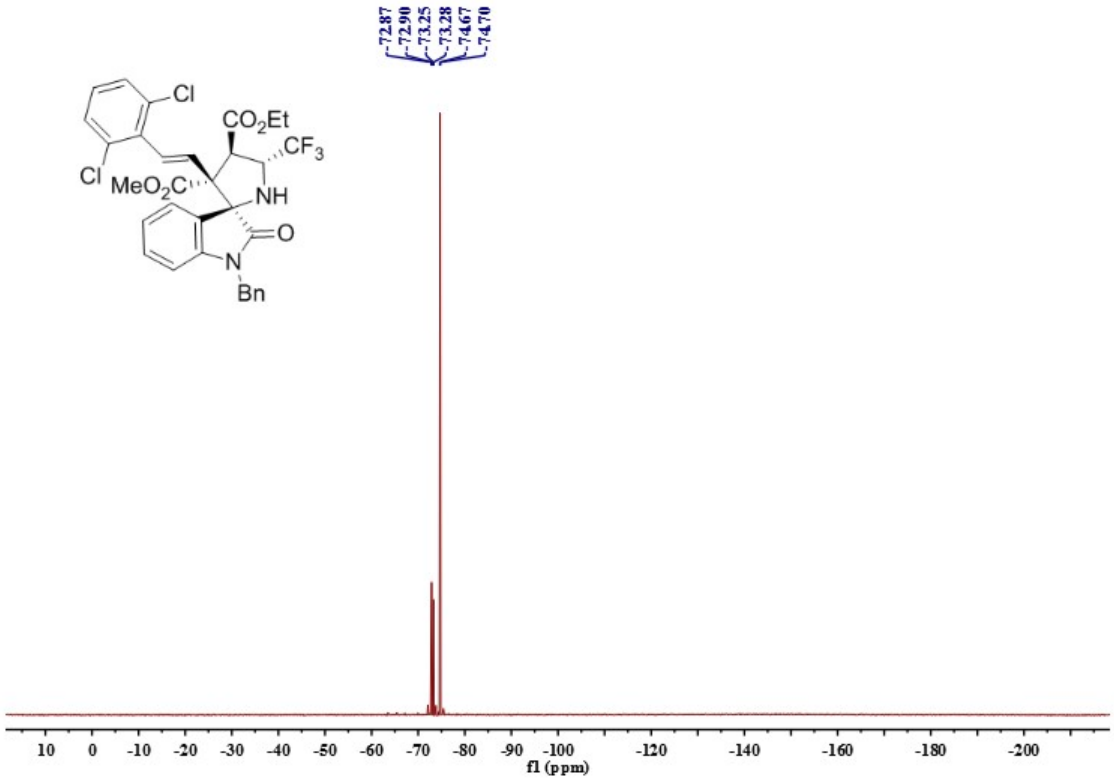
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4s



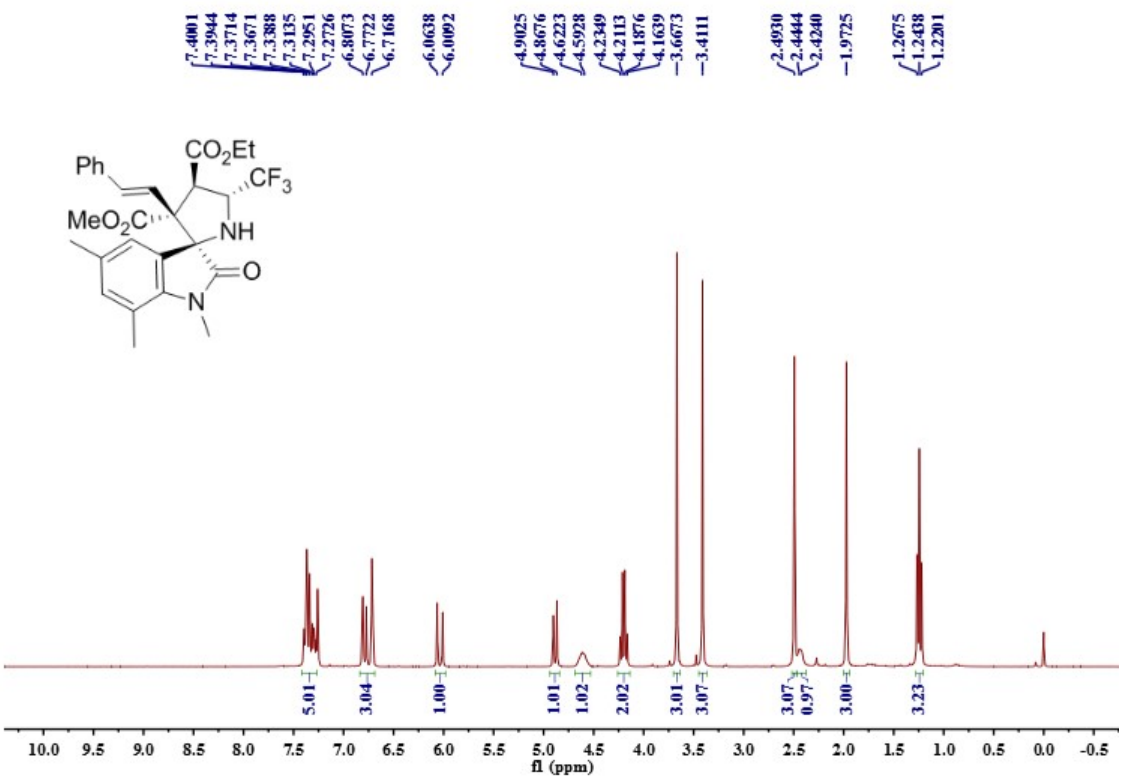
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4t



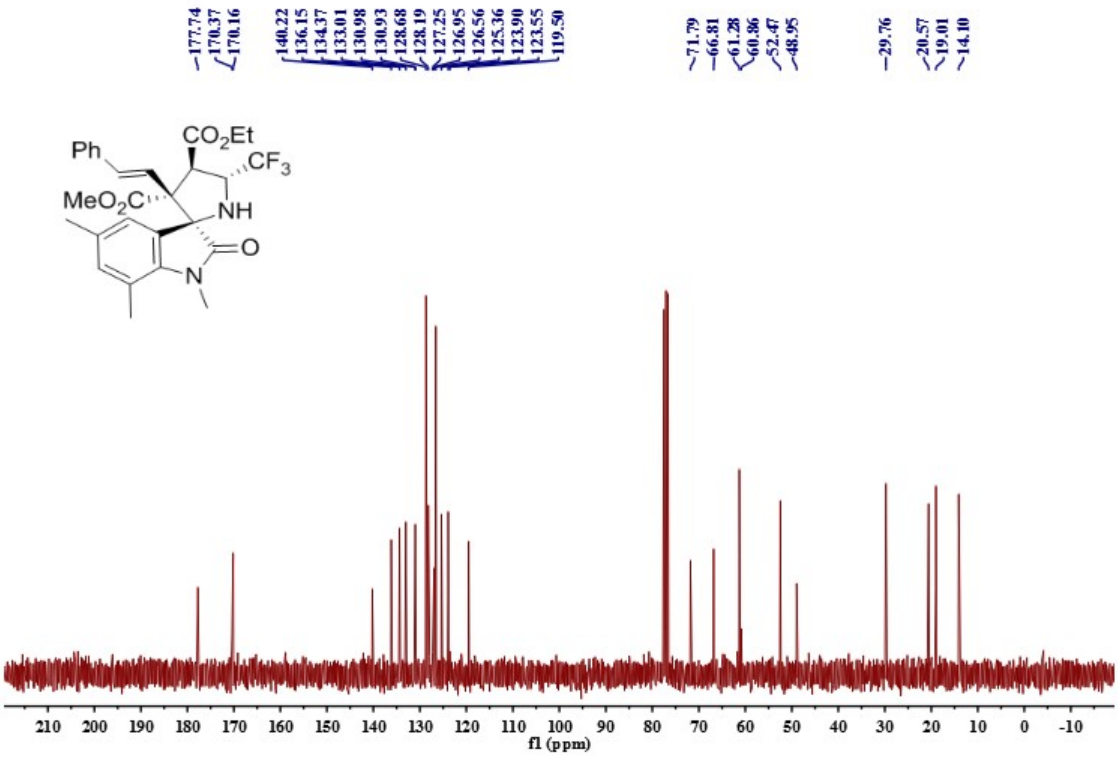
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4t



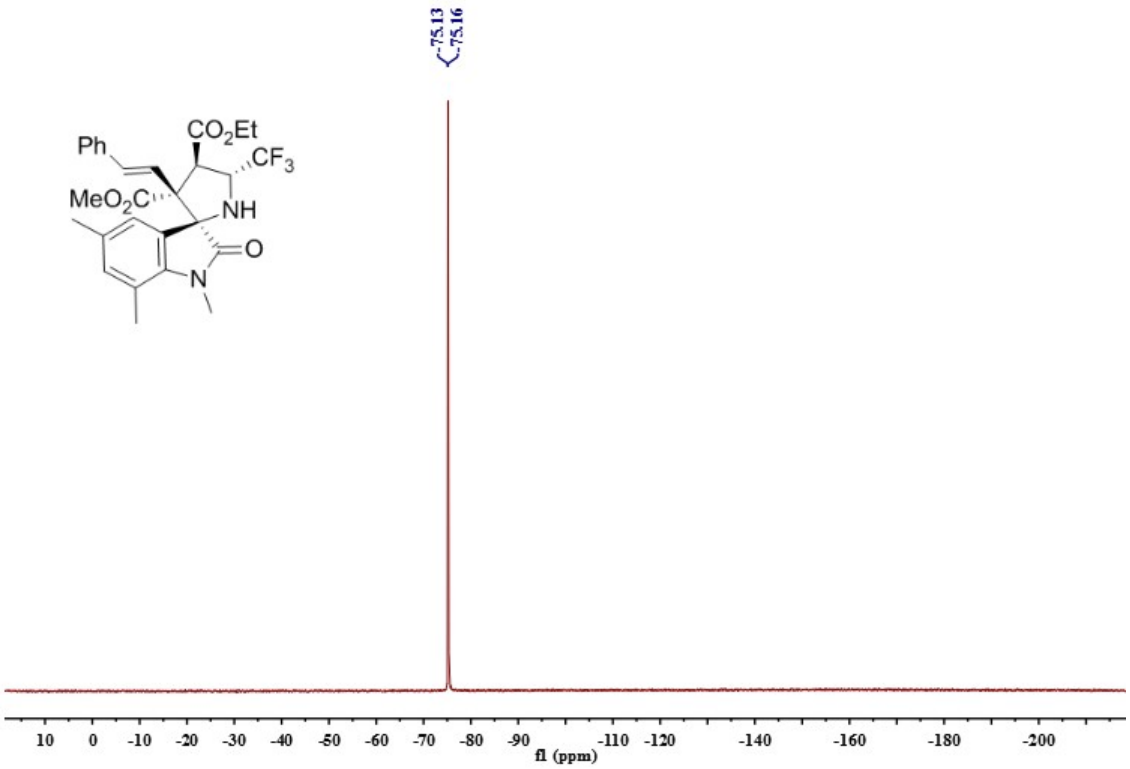
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4t



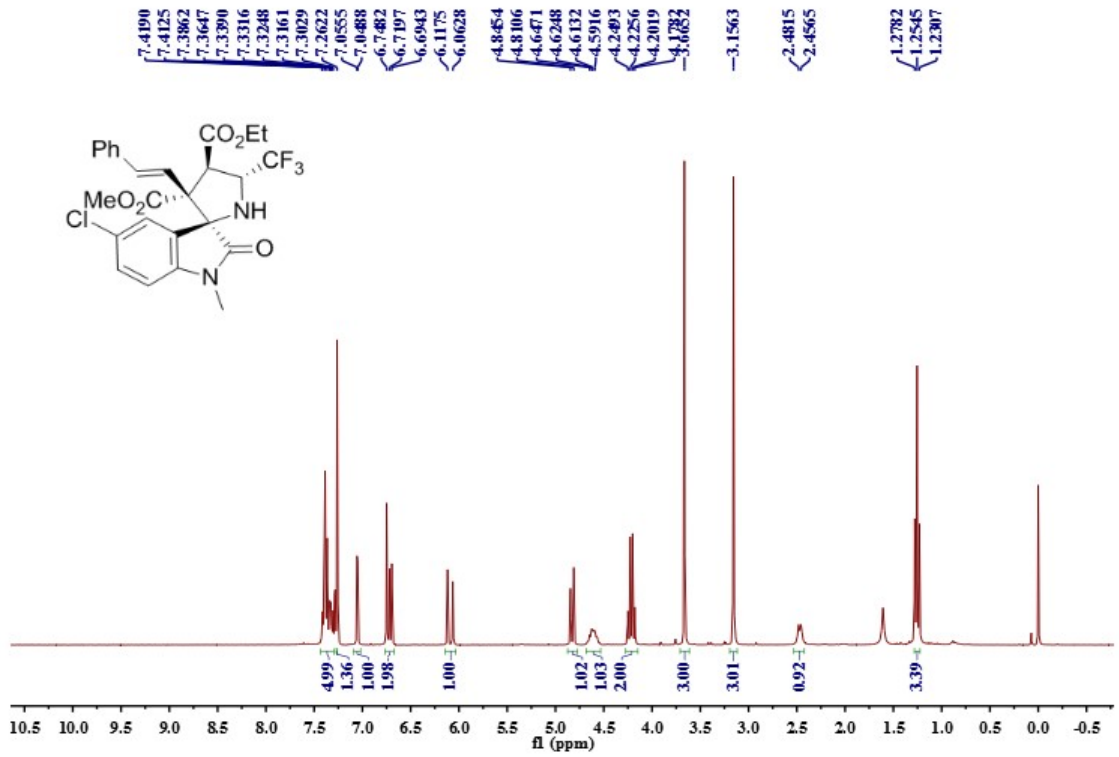
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4u



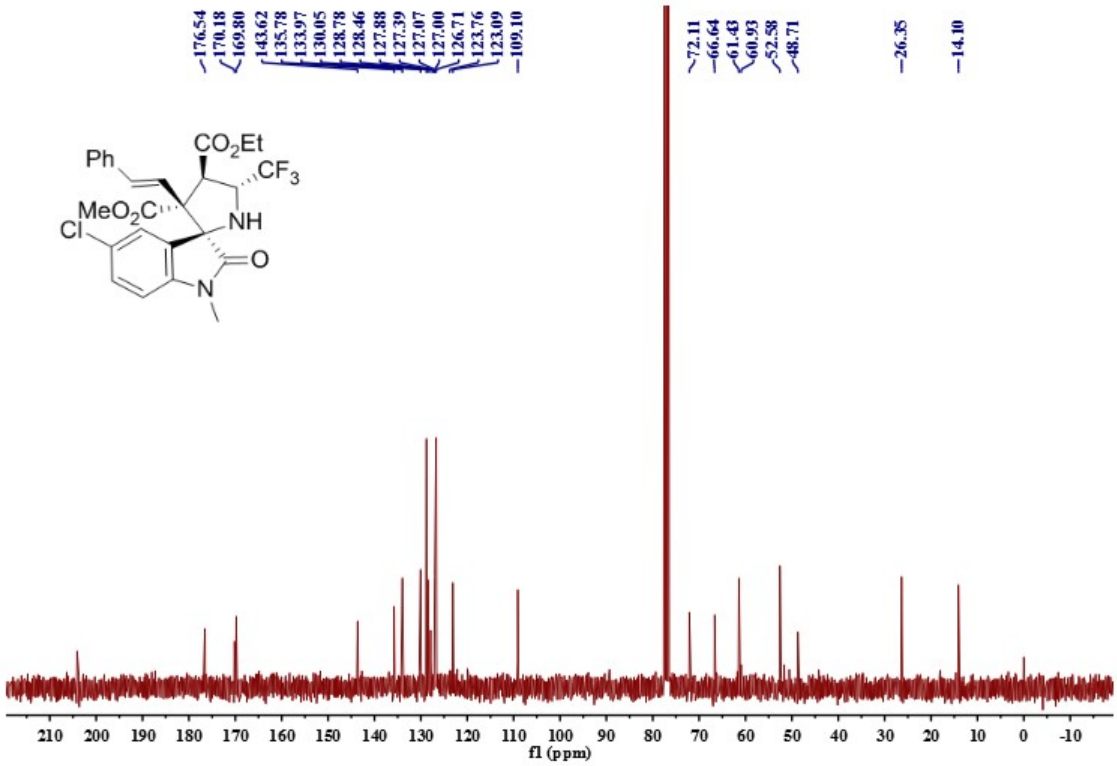
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4u



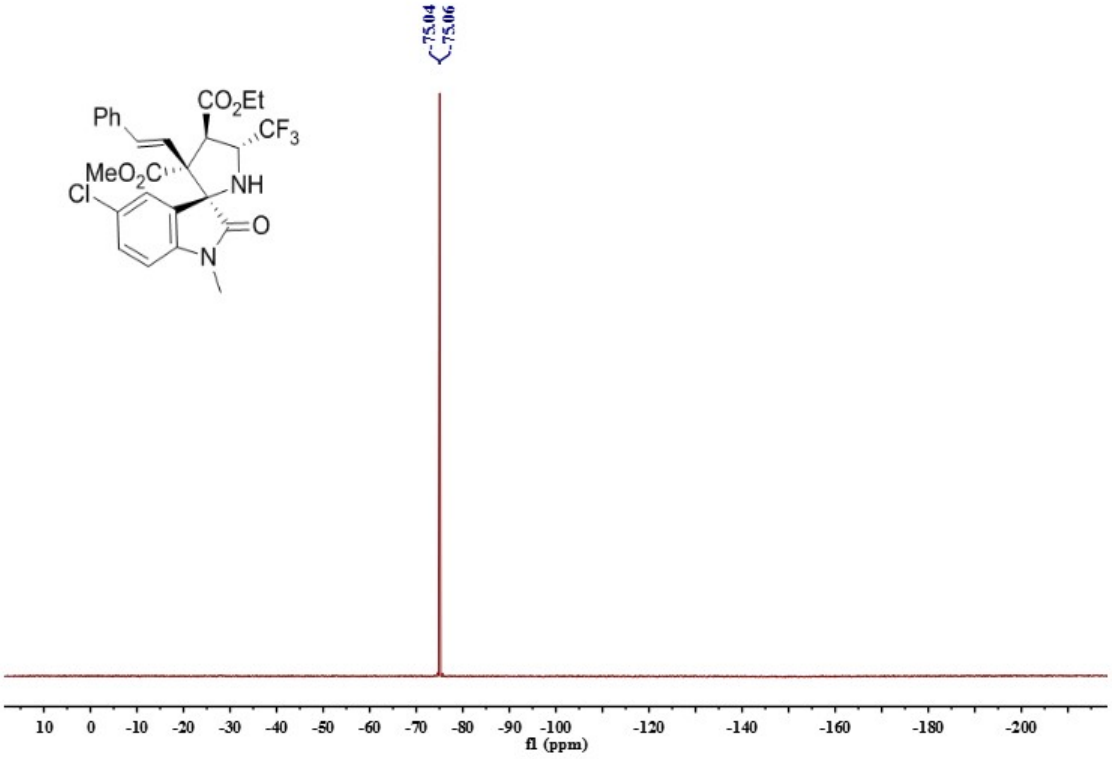
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo′*-4u



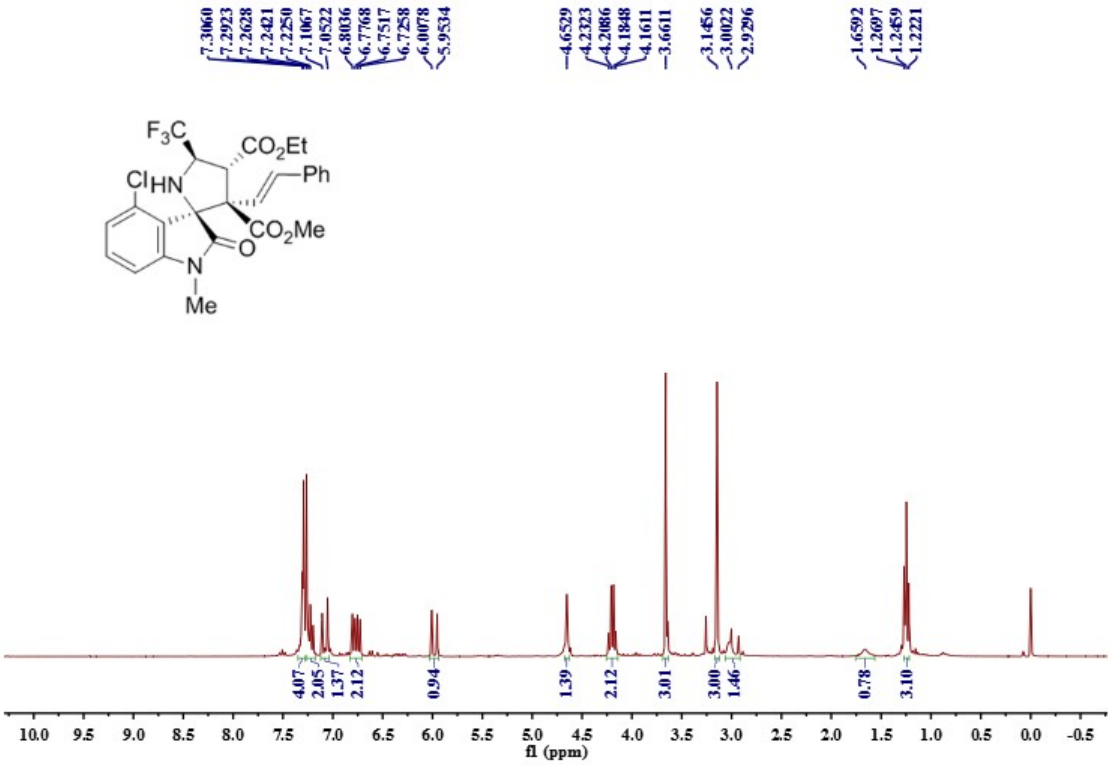
$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo′*-4v



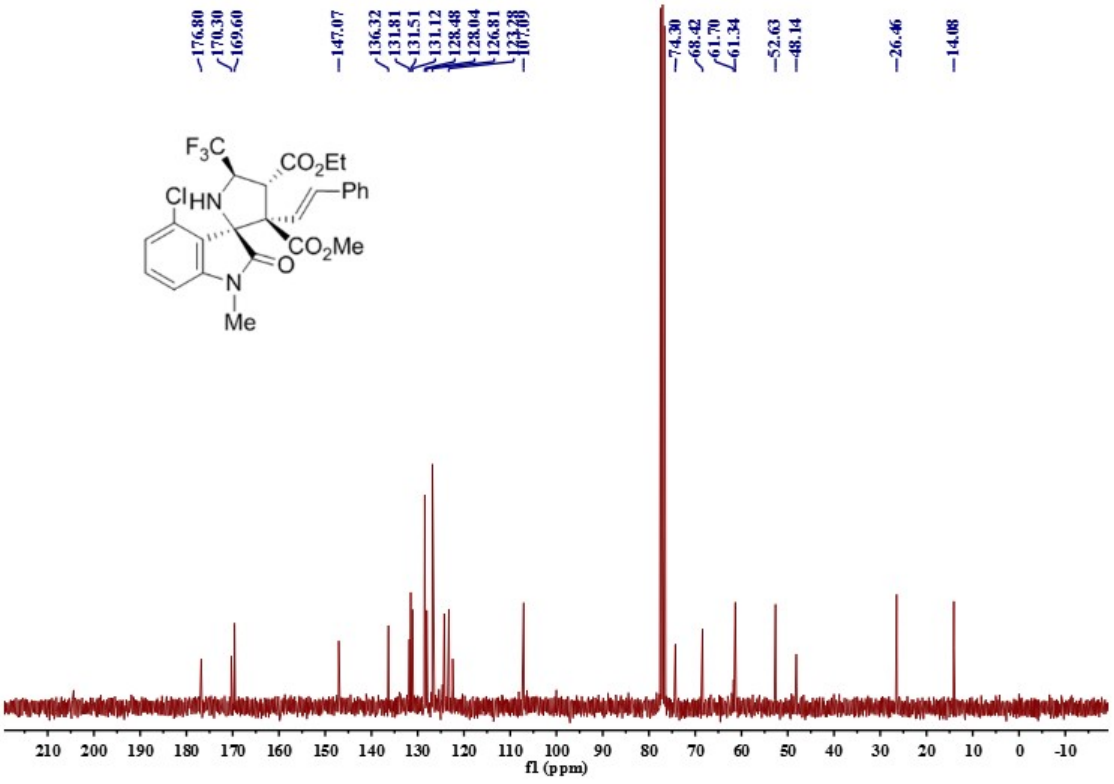
$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4v



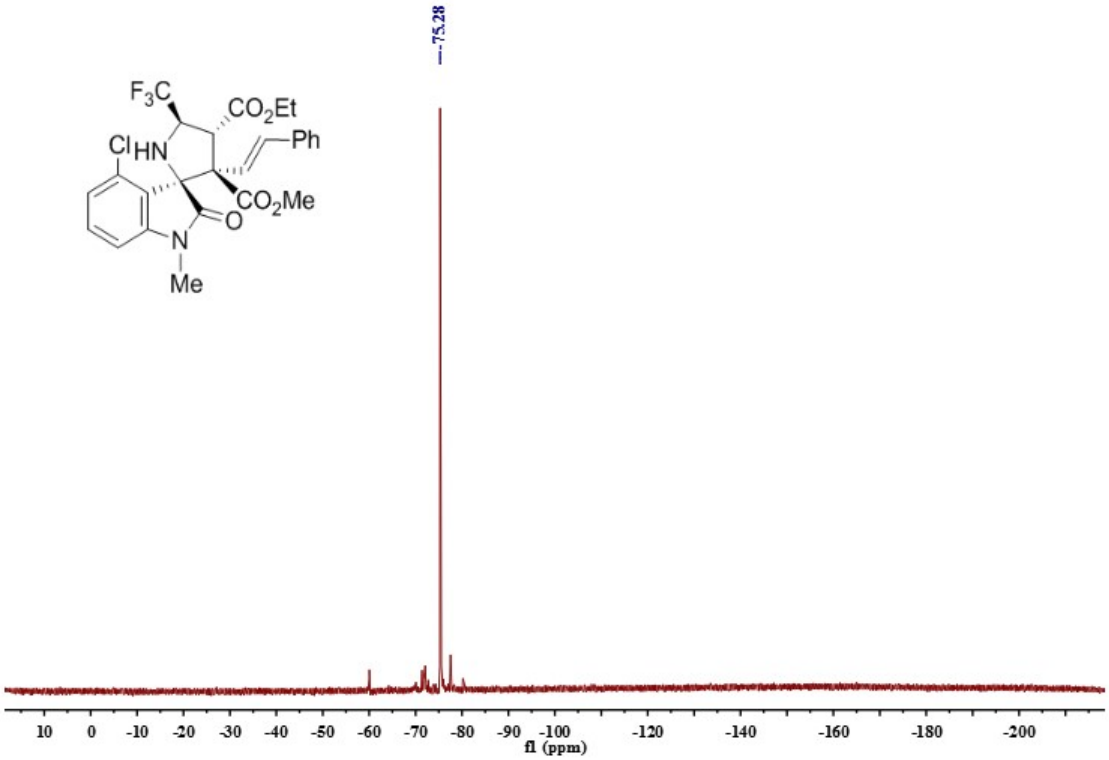
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4v



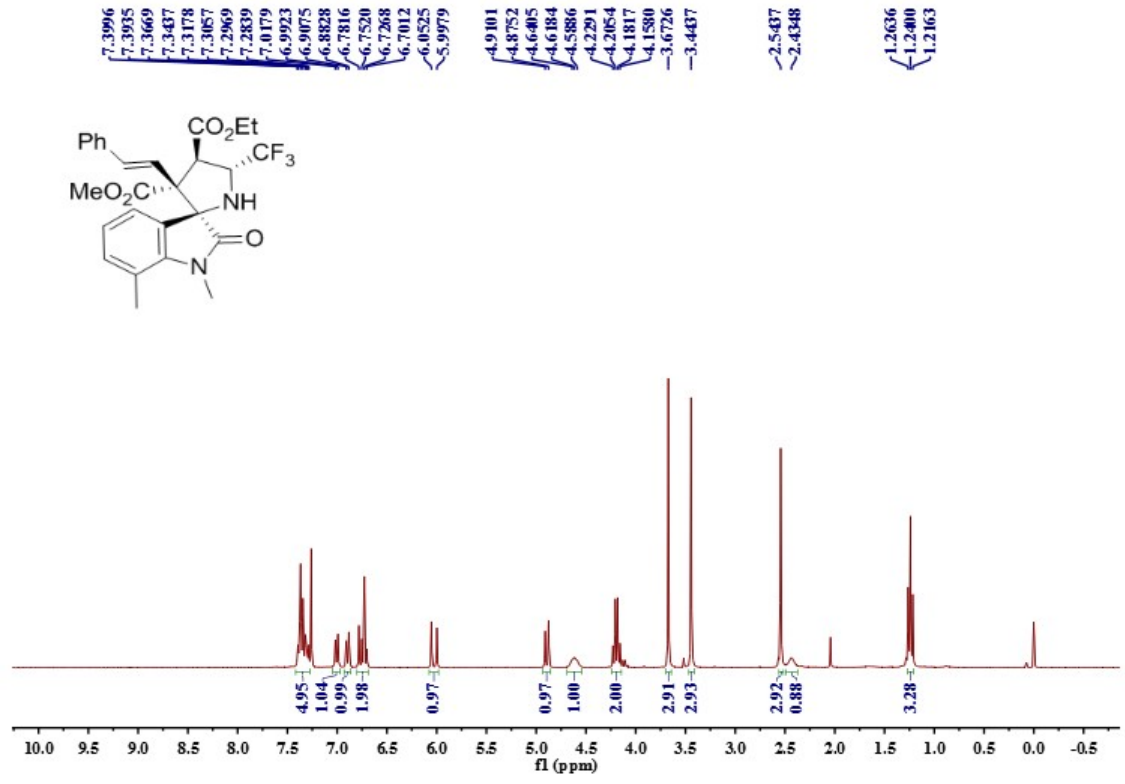
^{1}H($CDCl_3$, 300 MHz) NMR of compound *exo'*-4w



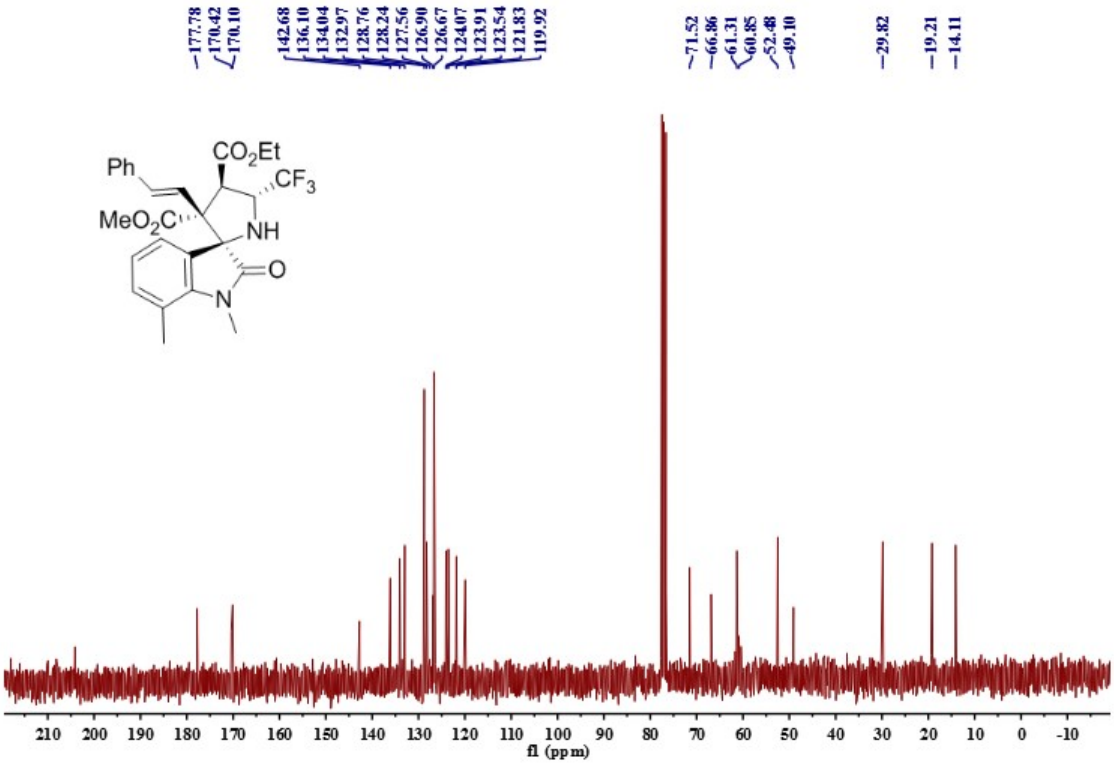
^{13}C($CDCl_3$, 75 MHz) NMR of compound *exo'*-4w



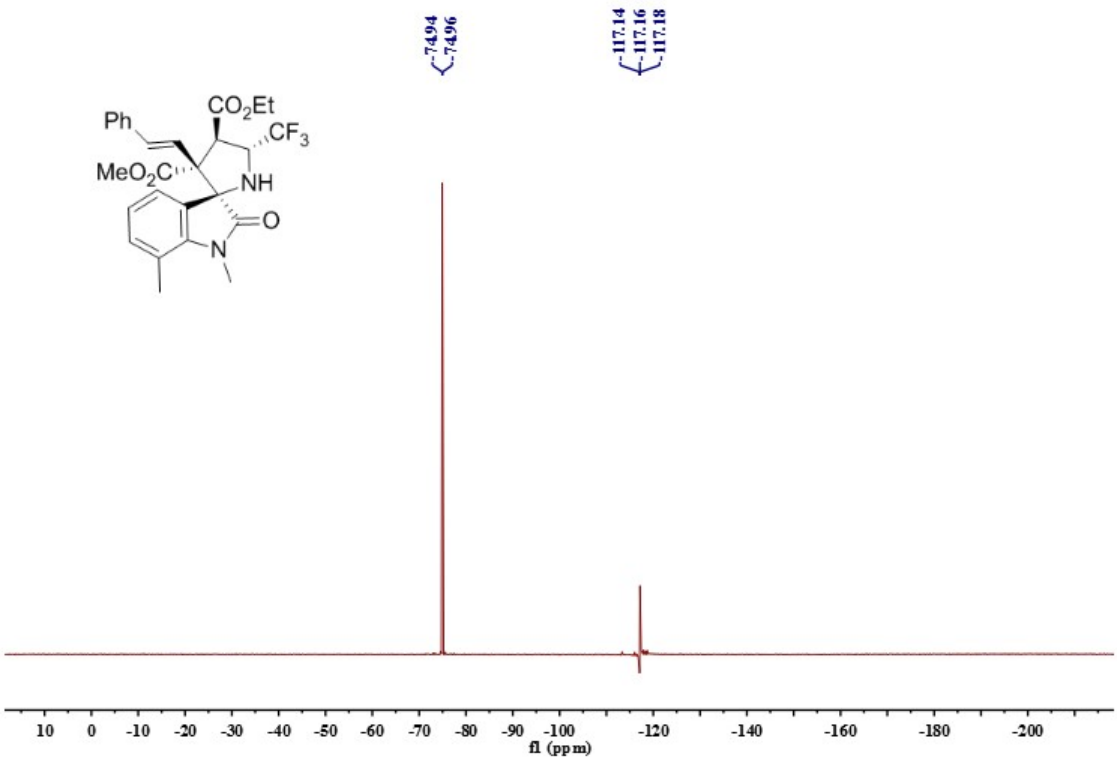
$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4w



$^{1}H(CDCl_3, 300\ MHz)$ NMR of compound *exo'*-4x



$^{13}C(CDCl_3, 75\ MHz)$ NMR of compound *exo'*-4x



$^{19}F(CDCl_3, 282\ MHz)$ NMR of compound *exo'*-4x

6. References

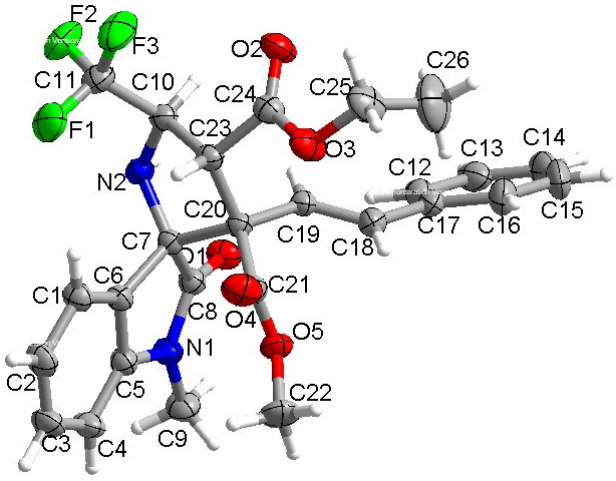
[1] Z. Gan, Y. Gong, Y. Chu, E.-Q. Li, Y. Huang, Z. Duan, Phosphine-catalyzed regiodivergent annulations of γ-substituted allenoates with conjugated dienes. *Chem. Commun.* **2019**, *55*, 10120-10123.

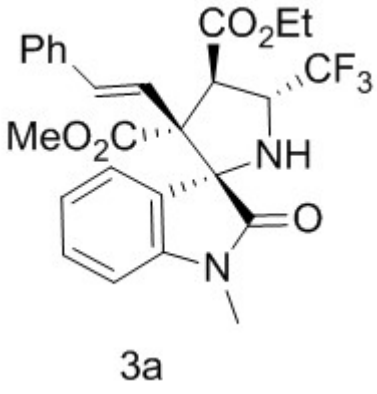
7. X-ray crystal structures

The X-ray crystallographic structures for ***endo*-3a, *exo*′-4a**. ORTEP view of the molecules of complex ***endo*-3a, *exo*′-4a**, showing ellipsoids at 30% probability level. Crystal data have been deposited to CCDC, number 2057244 **(*endo*-3a),** 2050077 **(*exo*′-4a)**.

A summary of the fundamental crystal and refinement data are given in the Table S**1** of the Supporting Information. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files.

Yellow crystals suitable for X-ray diffraction (Gemini E) were grown by n-hexane/dichloromethane solution of ***endo*-3a, *exo*′-4a** inside a penicillin bottle.





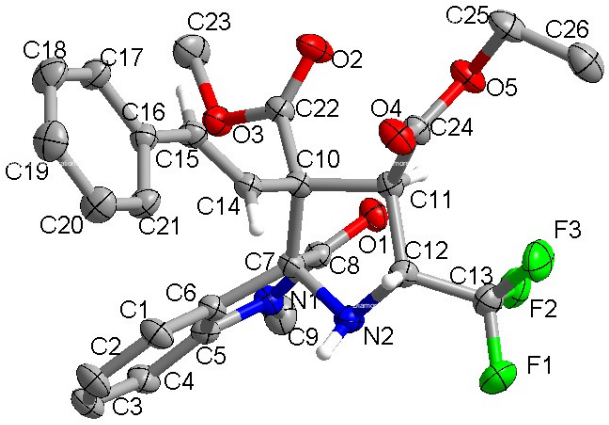
3a

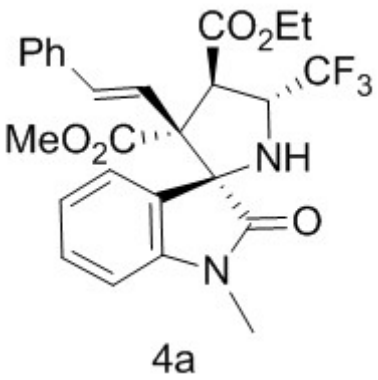
Crystal structure of 3a (CCDC 2057244)

Table 1 Crystal data and structure refinement for *endo*-3a

Identification code	202012310A

Empirical formula	$C_{26}H_{25}F_3N_2O_5$
Formula weight	502.48
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.2180(8)
b/Å	18.6769(8)
c/Å	10.1474(4)
α/°	90
β/°	91.226(4)
γ/°	90
Volume/Å^3	2883.5(2)
Z	4
ρ_{calc}g/cm^3	1.157
μ/mm^{-1}	0.793
F(000)	1048.0
Crystal size/mm^3	0.18 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.494 to 134.13
Index ranges	-18 ≤ h ≤ 17, -22 ≤ k ≤ 22, -10 ≤ l ≤ 12
Reflections collected	11695
Independent reflections	5131 [R_{int} = 0.0311, R_{sigma} = 0.0400]
Data/restraints/parameters	5131/0/332
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1652
Final R indexes [all data]	R_1 = 0.0762, wR_2 = 0.1833
Largest diff. peak/hole / e Å^{-3}	0.24/-0.22





4a

Crystal structure of 3ba (CCDC 2050077)

Table 1 Crystal data and structure refinement for *exo′*-4a.

Identification code	202012294
Empirical formula	$C_{26}H_{25}F_3N_2O_5$
Formula weight	502.48
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.1670(2)
b/Å	13.05385(18)
c/Å	19.7407(3)
α/°	90
β/°	94.4125(12)
γ/°	90
Volume/Å^3	4924.52(11)
Z	8
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.928
F(000)	2096.0
Crystal size/mm^3	0.15 × 0.1 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.128 to 134.146
Index ranges	$-22 \le h \le 22$, $-10 \le k \le 15$, $-23 \le l \le 21$
Reflections collected	20632
Independent reflections	8792 [R_{int} = 0.0307, R_{sigma} = 0.0367]
Data/restraints/parameters	8792/0/663
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1223
Final R indexes [all data]	R_1 = 0.0709, wR_2 = 0.1391

Largest diff. peak/hole / e $Å^{-3}$ 0.26/-0.20