Supporting Information

Palladium-Catalyzed Asymmetric (4+3) Cycloaddition of N-2,2,2-Trifluoroethylisatin Ketimines: Access to Optically Active Spirooxindoles

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College of Chemistry, Green Catalysis Center, Zhengzhou University, Zhengzhou 450001, P. R. China General Experimental Details.

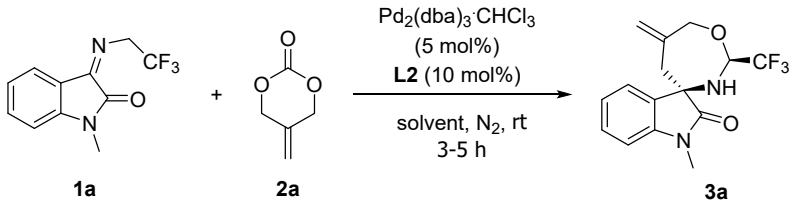
1. General Experimental Details

All reactions were performed under nitrogen using solvents dried by standardmethods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemicalshifts are expressed in parts per million (ppm) downfield from internal TMS. HRMSspectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini Ediffractometer. Melting Point: heating rate: 4°C/min, the thermometer was notcorrected. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IG/AD-H/IB-N-5 in comparison with the authentic racemates. Chiral HPLC analysisrecorded on Shanghaiyice instruments and Equipment Co. Ltd. and ShimadzuLC-20A. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification. The compound **1**[1] and **2a**[2] were prepared according to literature methods.

2. Optimization of the Reaction Conditions

2.1. Optimization of reaction conditions.

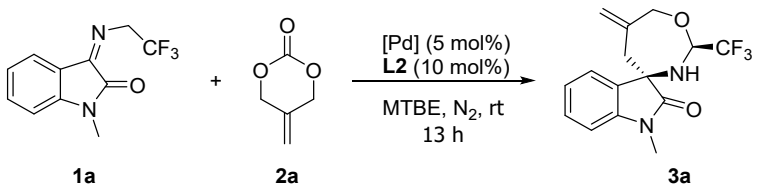
Table S1. Screening of the solvents. [a]



entry	solvent	yield [b]	dr [c]	ee [d]
1	THF	43%	>20:1	92%
2	MTBE	60%	>20:1	94%
3	Et_2O	55%	20:1	84%
4	1,4-dioxane	35%	>20:1	96%
5	EA	49%	>20:1	92%
6	toluene	30%	9:1	80%
7	DCM	38%	15:1	64%

[a] Reaction conditions: under N_2, the mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd_2(dba)_3$•$CHCl_3$ (5 mol%), **L2** (10 mol%) in solvent (1.0 mL) at room temperature for 3-20 h. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by HPLC analysis.

Table S2. Screening of the Pd catalysts. [a]

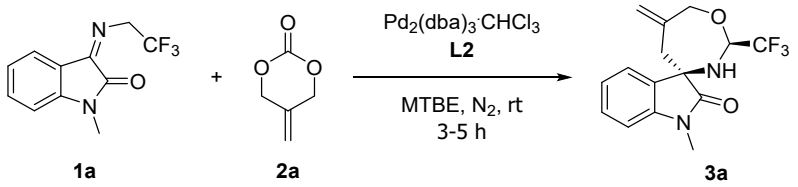


entry	[Pd]	yield [b]	dr [c]	ee [d]
1	$Pd_2(dba)_3·CHCl_3$	60%	>20:1	94%
2	$Pd_2(dba)_3$	44%	>20:1	80%

3	$Pd(dba)_2$	49%	>20:1	60%
4	$Pd(OAc)_2$	x	x	x
5	$[Pd(\eta\text{-allyl})Cl]_2$	x	x	x

[a] Reaction conditions: under N_2, the mixture of **1a** (0.1 mmol), **2a** (0.15 mmol), [Pd] (5 mol%), **L2** (10 mol%) in MBTE (1.0 mL) at room temperature for 13 h. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by HPLC analysis.

Table S3. Screening of loading of Pd catalysts. [a]

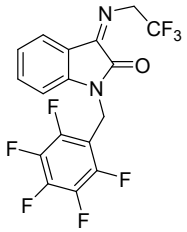


entry	$Pd_2(dba)_3\cdot CHCl_3$	L3	yield [b]	dr [c]	ee [d]
1	3 mol%	6 mol %	46%	>20:1	90%
2	4 mol %	8 mol %	44%	>20:1	84%
3	5 mol %	10 mol %	60%	>20:1	94%
4	5 mol %	15 mol %	41%	>20:1	94%
5	5.5 mol %	11 mol %	49%	>20:1	90%
6	6 mol %	12 mol %	55%	>20:1	92%
7	7 mol %	14 mol %	51%	>20:1	94%

[a] Reaction conditions: under N_2, the mixture of **1a,** (0.1 mmol), **2a** (0.15 mmol), in MBTE (1.0 mL) at room temperature for 13 h. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by HPLC analysis.

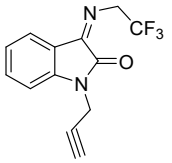
3. The data of compound 1j, 1k, 1p-1x.

The compounds 1j, 1k, 1p - 1x were prepared according to previous literature.[1]



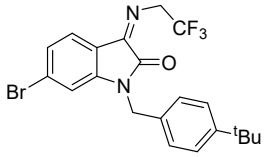
(*Z*)-1-((perfluorophenyl) methyl)-3-((2, 2, 2-trifluoroethyl) imino)indolin-2-one 1j.

Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, J = 6.9 Hz, 1H), 7.47 (td, J = 7.9, 1.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 5.02 (s, 2H), 4.85 (q, J = 9.7 Hz, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.0, 154.6, 150.6, 141.3, 136.2, 126.5, 125.7, 124.4, 121.7, 116.2, 53.8, 44.4, 34.5, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{17}H_9F_8N_2O^+$ $[M+Na]^+$: 431.0401, found 431.0402.



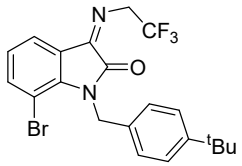
(*Z*)-1-(prop-2-yn-1-yl)-3-((2, 2, 2-trifluoroethyl)imino)indolin-2-one 1k.

Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, J = 7.5 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.20 – 7.15 (m, 1H), 7.08 (d, J = 7.9 Hz, 1H), 4.84 (q, J = 9.7 Hz, 2H), 4.53 (d, J = 2.4 Hz, 2H), 2.31 (t, J = 2.4 Hz, 1H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5, 155.2, 144.4, 133.8, 123.8, 123.2, 120.7, 109.8, 76.1, 72.9, 53.8, 53.6, 29.0 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{13}H_{10}F_3N_2O^+$ $[M+Na]^+$: 267.0740, found 267.0739.



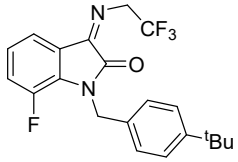
(*Z*)-6-bromo-1-(4-(tert-butyl) benzyl)-3-((2, 2, 2-trifluoroethyl) imino) indolin-2-one 1p.

Yellow solid. **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.60 (d, J = 8.0 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.29 – 7.25 (m, 3H), 6.99 (d, J = 1.4 Hz, 1H), 4.86 (m, 4H), 1.33 (s, 9H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 154.7, 151.3, 131.4, 128.0, 127.1, 126.6, 126.1, 124.2, 113.2, 53.9, 34.6, 31.3 ppm. **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{21}H_{21}BrF_3N_2O^+$: 453.0787, found 453.0784.



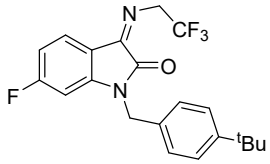
(*Z*)-7-bromo-1-(4-(tert-butyl) benzyl)-3-((2, 2, 2-trifluoroethyl) imino)indolin-2-one 1q.

Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (dd, J = 7.4, 0.9 Hz, 1H), 7.57 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.06 – 6.97 (m, 1H), 5.42 (s, 2H), 4.86 (q, *J* = 9.7 Hz, 2H), 1.32 (s, 9H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.2, 154.5, 150.5, 142.8, 139.5, 133.3, 126.4, 125.7, 124.7, 122.3, 103.2, 54.2, 53.9, 43.9, 34.5, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{21}H_{21}BrF_3N_2O^+$ $[M+H]^+$: 453.0784, found 453.0788.



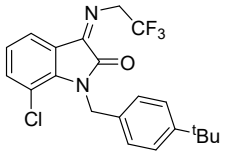
(*Z*)-1-(4-(tert-butyl)benzyl)-7-fluoro-3-((2, 2, 2-trifluoroethyl)imino)indolin-2-one 1r.

Yellow solid. **^{1}H NMR (400 MHz, CDCl3)** δ 7.61 – 7.49 (m, 1H), 7.44 – 7.25 (m, 4H), 7.18 (m, 1H), 7.10 – 6.94 (m, 1H), 5.04 (d, *J* = 19.0 Hz, 2H), 4.88 (m, 2H), 1.32 (d, *J* = 18.6 Hz, 9H) ppm; **^{13}C NMR (101 MHz, CDCl3)** δ 158.3, 158.3, 155.0, 151.0, 133.1, 133.0, 127.6, 125.7, 124.2, 124.1, 123.5, 122.0, 121.9, 121.8, 121.7, 119.1, 53.9, 53.6, 53.5, 45.2, 34.6, 34.5, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{21}H_{21}F_4N_2O^+$ $[M+H]^+$: 393.1585, found 393.1583.



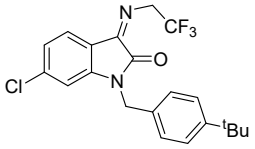
(*Z*)-1-(4-(tert-butyl)benzyl)-6-fluoro-3-((2, 2, 2-trifluoroethyl)imino)indolin-2-one 1s.

Yellow solid. **^{1}H NMR (400 MHz, CDCl3)** δ 7.73 (dd, *J* = 8.2, 5.6 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.82 – 6.73 (m, 2H), 6.55 (dd, *J* = 8.7, 1.7 Hz, 1H), 4.89 (m, 4H), 1.33 (s, 9H) ppm; **^{13}C NMR (101 MHz, CDCl3)** δ 167.6, 165.1, 154.3, 151.3, 147.6, 147.5, 131.4, 127.2, 126.0, 125.1, 125.0, 110.2, 110.0, 98.9, 98.6, 53.7, 53.4, 53.1, 43.5, 34.6, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{21}H_{21}F_4N_2O^+$ $[M+H]^+$: 393.1585, found 393.1588.



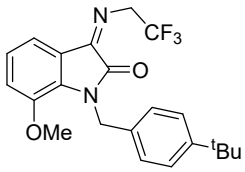
(*Z*)-1-(4-(*tert*-butyl)benzyl)-7-chloro-3-((2, 2, 2-trifluoroethyl)imino) indolin-2-one 1t.

Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 – 7.70 (m, 1H), 7.40 – 7.37 (m, 3H), 7.26 (d, J = 8.4 Hz, 2H), 7.09 – 7.05 (m, 1H), 5.37 (s, 2H), 4.88 (q, J = 9.7 Hz, 2H), 1.33 (s, 9H).; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.0, 154.6, 150.6, 141.3, 136.2, 126.5, 125.7, 124.4, 121.7, 116.2, 53.8, 44.4, 34.5, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{21}H_{21}ClF_3N_2O^+$ $[M+H]^+$: 409.1289, found 409.1292.



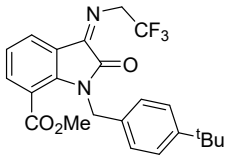
(*Z*)-1-(4-(tert-butyl) benzyl)-6-chloro-3-((2, 2, 2-trifluoroethyl) imino) indolin-2-one 1u.

Yellow solid. **^{1}H NMR (400MHz, CDCl3)** δ 7.67 (d, J = 8.0 Hz, 1H), 7.40 (m, J = 8.3 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.09 (dd, J = 8.0, 1.7 Hz, 1H), 6.82 (d, J = 1.6 Hz, 1H), 4.89 – 4.86 (m, 3H), 1.33 (s, 9H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 154.6, 127.1, 126.1, 124.1, 123.6, 119.1, 53.9, 53.6, 43.5, 34.6, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{21}H_{21}ClF_3N_2O^+$ $[M+H]^+$: 409.1289, found 409.1295.



(*Z*)-1-(4-(tert-butyl)benzyl)-7-methoxy-3-((2, 2, 2-trifluoroethyl)imino)indolin- 2-one 1w.

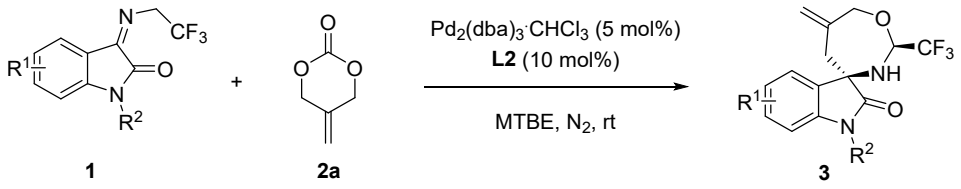
Yellow solid. **^{1}H NMR (400 MHz, CDCl3)** δ 7.39 – 7.35 (m, 3H), 7.31 (m, 2H), 7.07 – 7.01 (m, 2H), 5.17 (s, 2H), 4.88 (q, J = 9.5 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 9H) ppm; **^{13}C NMR (101 MHz, CDCl3)** δ 158.9, 156.1, 150.4, 145.2, 134.5, 133.7, 127.4, 125.4, 124.0, 122.3, 117.7, 115.6, 55.9, 54.2, 53.8, 53.5, 45.4, 34.5, 31.3 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{22}H_{24}F_3N_2O_2^+$ $[M+H]^+$: 405.1784, found 405.1784.



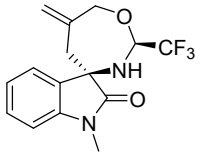
methyl (*Z*)-1-(4-(tert-butyl)benzyl)-2-oxo-3-((2, 2, 2-trifluoroethyl)imino)indoline -7-carboxylate 1x

Yellow solid. **^{1}H NMR (400 MHz, CDCl3)** δ 7.90 (dd, J = 7.4, 1.2 Hz, 1H), 7.60 – 7.52 (dd, J=8.0, 4.0 Hz, 1H), 7.28 (m, 3H, overlapped with the peak of chloroform), 7.12 (t, J = 7.7 Hz, 1H), 6.99 (d, J = 8.3 Hz, 2H), 5.25 (s, 2H), 4.89 (q, J = 9.8 Hz, 2H), 3.61 (s, 3H), 1.28 (s, 9H) ppm; **^{13}C NMR (101 MHz, CDCl3)** δ 166.3, 159.3, 154.4, 150.5, 143.3, 134.4, 131.7, 125.5, 122.7, 122.5, 118.0, 54.2, 53.8, 52.5, 44.5, 34.5, 31.3, 29.7 ppm; **HRMS** (m/z)(m/z) $[M+H]^+$ Calcd for $C_{22}H_{24}F_3N_2O_3^+$ $[M+H]^+$: 433.1734, found 433.1732.

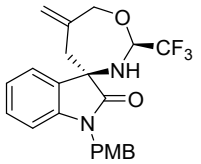
4. General Procedure for Reactions



To a flame dried sealing tube, $Pd_2(dba)_3 \bullet CHCl_3$(0.005 mmol, 5.2 mg), **L2** (0.01 mmol, 5.4 mg), freshly distilled anhydrous MTBE (1.0 mL) were added. The resulting mixture was allowed to stir for 30 min. Then, compound **1** (0.1 mmol) and compound **2a** (0.15 mmol) were added subsequently. The resulting reaction mixture was stirred at room temperature for 3 h (monitored by TLC). The residue was subjected to column chromatography on silica gel, using a mixture of petroleum ether and ethyl acetate as eluent, to give desired product **3**.

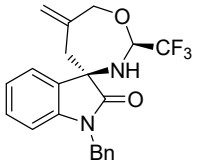


3a：Purified by silica gel chromatography using PE/EA 6:1, white solid, 60% yield, 18.7 mg, 94% ee, dr> 20:1; MP**:** 127.6-128.4°C. $[\alpha]_D$ = + 31 (*c* = 0.1, CH_2Cl_2, 32.1 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 7.37-7.32 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.40 (dd, *J* = 9.9, 4.8 Hz, 1H), 5.25 (s, 1H), 5.00 (s, 1H), 4.58 (d, *J* = 13.5 Hz, 1H), 4.37 (d, *J* = 13.2 Hz, 1H), 3.20 (s, 3H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.71 (d, *J* = 13.8 Hz, 1H), 2.44 (d, *J* = 10.2 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.1, 142.8, 140.6, 131.5, 129.6, 122.9, 122.5 (q, *J* = 279.75 Hz), 122.4, 119.1, 108.6, 82.2 (q, *J* = 33.00 Hz), 74.0, 59.6, 44.4, 26.2 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.86 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M+Na]^+$ Calcd for $C_{15}H_{15}F_3N_2NaO_2^+$ 335.0983, found 335.0984. **HPLC** (Chiralpak IG-H, *n*-hexane/*i*-propanol = 99.2/0.8, flow rate = 1.0 mL/min, l = 254 nm) tR = 34.48 min (major), 47.72 min (minor).

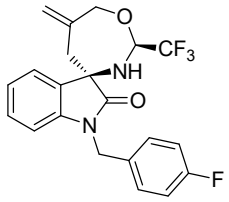


3b: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 58% yield, 24.2 mg, 88% ee, dr> 20:1; $[\alpha]_D$ = + 37 (*c* = 0.1, CH_2Cl_2, 33.0 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 7.32 (d, *J* = 7.3 Hz, 1H), 7.24-7.20 (m, 3H), 7.05-7.00 (m, 1H), 6.86-6.83 (m, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.45 (dd, *J* = 9.6, 4.5Hz, 2H), 5.26 (s, 1H), 5.01 (s, 1H), 4.88 (d, *J* = 15.3Hz, 1H), 4.77 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 13.2 Hz, 1H), 4.38 (d, *J* = 13.2 Hz, 1H), 3.77 (s, 3H), 2.92 (d, *J* = 14.1 Hz, 1H), 2.76 (d, *J* = 14.1 Hz, 1H), 2.47 (d, *J* = 5.1 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** *δ* 177.2, 159.1, 141.8, 140.6, 131.7, 129.4, 128.5, 127.6, 122.8, 122.5 (q, *J* = 279.00 Hz), 122.4, 119.2, 114.3, 109.6, 82.2 (q, *J* = 32.25 Hz), 74.1, 59.6, 55.3, 44.5, 43.0 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.87 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{22}H_{22}F_3N_2O_3^+$ 419.1583, found 419.1588. **HPLC** (Chiralpak AD-H, *n*-

hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =15.42 min (major), 19.71 min (minor).

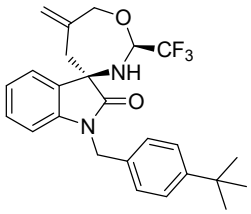


3c: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 53% yield, 22.5 mg, 91% ee, dr> 20:1; $[\alpha]_D$ = + 17 (*c* = 0.1, CH_2Cl_2,33.4 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.35-7.19 (m, 6H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.45 (dd, *J* = 10.2, 4.8 Hz, 1H), 5.26(s, 1H), 5.02 (s, 1H), 4.96 (d, *J* = 15.9Hz, 1H), 4.83 (d, *J* = 15.6Hz, 1H), 4.60 (d, *J* = 13.5Hz, 1H), 4.39 (d, *J* = 13.2Hz, 1H), 2.95 (d, *J* = 13.8Hz, 1H), 2.78 (d, *J* = 14.1Hz, 1H), 2.48 (d, *J* = 11.1 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.2, 141.8, 140.6, 135.6, 131.7, 129.5, 128.9, 127.7, 127.1, 122.9, 122.5(q, *J* = 279.75 Hz), 122.4, 119.2, 109.6, 82.2 (q, *J* = 33.00 Hz), 74.1, 59.6, 44.5, 43.5 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.81 (d, *J* = 2.8 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{20}F_3N_2O_2^+$ 389.1477, found 389.1484. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 98/2, flow rate = 1.0 mL/min, l = 254 nm) tR = 17.86 min (major), 25.72 min (minor).

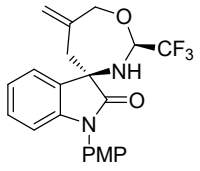


3d: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 73% yield, 29.6 mg, 88% ee, dr> 20:1; $[\alpha]_D$ = + 23 (*c* = 0.1, CH_2Cl_2, 33.3°C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.28-7.21 (m, 3H), 7.07-6.98 (m, 3H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.44 (td, *J* = 9.9, 5.1 Hz, 1H), 5.27 (s, 1H), 5.02 (s, 1H), 4.86 (dd, *J* = 20.4, 15.6 Hz, 2H), 4.60 (d, *J* =13.2 Hz, 1H),4.39 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 13.8 Hz, 1H), 2.77 (d, *J* = 14.1 Hz, 1H), 2.47 (d, *J* = 11.7 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.2, 162.2 (d, *J* = 250.50 Hz), 141.6, 140.5, 131.7, 131.3(d, *J* =3.75 Hz), 129.5, 128.9, 128.8, 123.0, 122.6, 122.5(q, *J* = 279.00 Hz), 119.3, 115.9, 115.7, 109.5, 82.1(q, *J* = 33.00 Hz), 74.1, 59.5, 44.4, 42.8 ppm. **^{19}F NMR** (**282 MHz,**

$CDCl_3$) δ -80.76 (d, J = 5.6 Hz), -115.39 (d, J = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{19}F_4N_2O_2^+$ 407.1383, found 407.1383. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =10.47 min (major), 14.39 min (minor).

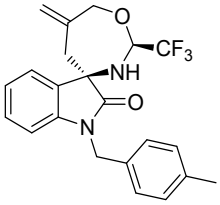


3e: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 78% yield, 34.6 mg, 94% ee, dr: 93:7; $[\alpha]_D$ = + 21 (*c* = 0.1, CH_2Cl_2, 29.8 °C). **^{1}H NMR** (**300 MHz, $CDCl_3$**): δ 7.35-7.32 (m, 3H), 7.21 (d, J = 8.1 Hz, 3H), 7.03 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.47 (dd, J = 10.5, 5.1 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.93 (d, J = 15.6 Hz, 1H), 4.77 (d, J = 15.6 Hz, 1H), 4.60 (d, J = 13.5 Hz, 1H), 4.38 (d, J = 13.2 Hz, 1H), 2.94 (d, J = 14.1 Hz, 1H), 2.77 (d, J = 13.8 Hz, 1H), 2.49 (d, J = 10.2 Hz, 1H), 1.28 (s, 9H) ppm. **^{13}C NMR** (**75 MHz, $CDCl_3$**) δ 177.2, 150.7, 142.0, 140.6, 132.6, 131.7, 129.5, 126.9, 125.8, 122.8, 122.6 (q, J = 279.75 Hz), 122.4, 119.2, 109.7, 82.2 (q, J = 32.25Hz), 74.1, 59.6, 44.6, 43.2, 34.5, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.99 (d, J = 5.6 Hz,) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{28}F_3N_2O_2^+$ 445.2103, found 445.2110. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR =24.38 min (major), 34.79 min (minor).

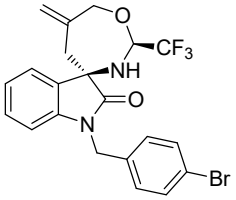


3f: Purified by silica gel chromatography using PE/EA 5:1, white solid, 50% yield, 20.2 mg, 92% ee, dr: 94 :6; MP: 102.5-104.3 °C. $[\alpha]_D$ = + 42 (*c* = 0.1, CH_2Cl_2, 29.4 °C). **^{1}H NMR** (**300 MHz, $CDCl_3$**): δ 7.41-7.24 (m, 4H), 7.12-7.02 (m, 3H), 6.82 (d, J = 7.8 Hz, 1H), 5.43 (dd, J =9.3, 4.5 Hz, 1H), 5.27 (s, 1H), 5.05 (s, 1H), 4.60 (d, J = 13.3 Hz, 1H), 4.38 (d, J = 13.2 Hz, 1H), 3.86 (s, 3H), 3.00 (d, J = 14.1 Hz, 1H), 2.83

(d, J = 13.8 Hz, 1H), 2.51 (d, J = 10.2 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 176.6, 159.2, 143.1, 140.5, 131.3, 129.5, 127.8, 126.5, 123.2, 122.7, 122.5(q, J = 279.75 Hz), 119.3, 114.9, 109.8, 82.2 (q, J = 32.25 Hz), 74.0, 59.6, 55.6, 44.7 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -80.83 (d, J = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{20}F_3N_2O_3^+$ 405.1426, found 405.1429. **HPLC** (Chiralpak AD, *n*-hexane/*i*-propanol = 80/20, flow rate = 1.0 mL/min, l = 254 nm) tR = 9.85 min (major), 12.63 min (minor).

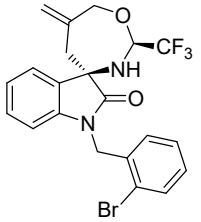


3g: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 65% yield, 26.1 mg, 94 % ee, dr: 97 :3; $[\alpha]_D$ = + 27 (c = 0.1, CH_2Cl_2, 30.9 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.32 (d, J = 7.5 Hz, 1H), 7.21-7.10 (m, 5H), 7.02 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 5.46 (dd, J = 10.5, 5.1 Hz, 1H), 5.26 (s, 1H), 5.01 (s, 1H), 4.92 (d, J = 15.6 Hz, 1H), 4.77 (d, J = 15.6 Hz, 1H), 4.59 (d, J = 13.2 Hz, 1H), 4.38 (d, J = 13.2 Hz, 1H), 2.93 (d, J = 13.8 Hz, 1H), 2.76 (d, J = 14.1 Hz, 1H), 2.48 (d, J = 10.2 Hz, 1H), 2.30 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.2, 141.9, 140.6, 137.4, 132.6, 131.7, 129.5, 129.4, 127.2, 122.8, 122.6 (q, J = 279.00 Hz), 122.4, 119.2, 109.7, 82.2 (q, J = 32.25 Hz), 74.1, 59.6, 44.5, 43.3, 21.1 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -80.86 (d, J = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{22}H_{22}F_3N_2O_2^+$ 403.1633, found 403.1640. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, flow rate = 1.0 mL/min, l = 254 nm) tR = 13.86 min (major), 19.24 min (minor).

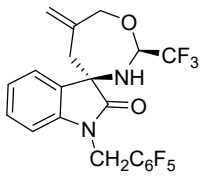


3h: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 67% yield, 31.2 mg, 88% ee, dr: 95 :5; $[\alpha]_D$ = + 21 (c = 0.1, CH_2Cl_2, 31 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.44 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H), 7.23-7.14 (m, 3H), 7.05

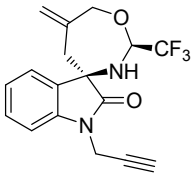
(t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.42 (s, 1H), 5.27 (s, 1H), 5.02 (s, 1H), 4.83 (dd, *J* = 20.4, 15.9 Hz, 2H), 4.60 (d, *J* = 13.3 Hz, 1H), 4.38 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 14.0 Hz, 1H), 2.78 (d, *J* = 14.0 Hz, 1H), 2.48 (d, *J* = 11.5 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.2, 141.5, 140.5, 134.6, 132.0, 131.6, 129.5, 128.9, 123.1, 122.6, 122.5(q, *J* = 279.75 Hz), 121.7, 119.3, 109.4, 82.1(q, *J* = 33.00 Hz), 74.1, 59.5, 44.4, 42.9 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -81.07 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{19}BrF_3N_2O_2^+$ 467.0582, found 467.0590. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =12.80 min (major), 19.43 min (minor).



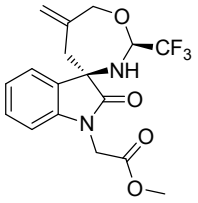
3i： Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 63% yield, 29.3 mg, 90% ee, dr: 90 : 10; $[\alpha]_D$ = + 14 (*c* = 0.1, CH_2Cl_2, 28.6 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 7.60-7.57 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.24-7.19 (m, 2H), 7.16-7.04 (m, 3H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.44 (td, *J* = 9.9, 4.8 Hz, 1H), 5.28 (s, 1H), 5.05 (s, 1H), 5.00-4.92 (m, 2H), 4.61 (d, *J* = 13.2 Hz, 1H), 4.39 (d, *J* = 13.2 Hz, 1H), 2.98 (d, *J* = 14.1 Hz, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.52 (d, *J* = 10.8 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.3, 141.6, 140.5, 134.2, 133.0, 131.6, 129.6, 129.2, 127.9, 127.7, 123.2, 122.8, 122.5(d, *J* = 279.75 Hz), 122.5, 119.4, 109.7, 82.1(q, *J* = 33.00 Hz), 74.1, 59.6, 44.4, 43.5 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -81.07 (d, *J* = 5.6 Hz,) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{19}BrF_3N_2O_2^+$ 467.0582, found 467.0590. **HPLC** (Chiralpak IG-H, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, l = 254 nm) tR =7.24 min (minor), 8.29 min (major).



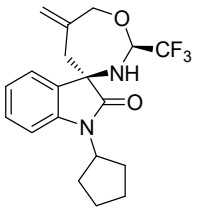
3j: Purified by silica gel chromatography using PE/EA 6:1, white solid, 66% yield, 31.5 mg, 92% ee, dr: 97 :3; MP**:** 108.2-110.8 °C. $[\alpha]_D$ = + 17 (*c* = 0.1, CH_2Cl_2, 29.6 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 7.36-7.27 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.41 (d, *J* = 5.7 Hz, 1H), 5.27 (s, 1H), 5.19 (d, *J* = 15.3 Hz, 1H), 5.00 (s, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 13.5 Hz, 1H), 4.39 (d, *J* = 13.5 Hz, 1H), 2.80 (dd, *J* = 27.3, 14.1 Hz, 2H), 2.44 (s, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 176.2, 147.4-147.0 (m), 144.1-143.7 (m), 140.7, 140.0, 139.7-139.1 (m), 136.2-135.8 (m), 131.5, 129.7, 123.4, 122.7, 122.5(q, *J* = 279.00 Hz), 119.4, 109.2-108.7 (m), 108.4, 81.9 (q, *J* = 33.00 Hz), 74.0, 59.5, 44.6, 31.8 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.91 (d, *J* = 5.6 Hz), -142.29-142.40 (m), -154.53 (t, *J* = 22.56 Hz), -162.09-162.27 (m) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{21}H_{15}F_8N_2O_2^+$ 479.1000, found 479.1013. **HPLC** (Chiralpak IB-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR =31.13 min (minor), 39.17 min (major).



3k: Purified by silica gel chromatography using PE/EA 5:1, white solid, 55% yield, 18.5 mg, 89 % ee, dr> 20:1; MP**:** 179.3-180.6 °C. $[\alpha]_D$ = + 53 (*c* = 0.1, CH_2Cl_2, 32.8 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 7.40-7.34 (m, 2H), 7.14-7.09 (m, 2H), 5.37 (dd, *J* = 10.5, 4.8 Hz, 1H), 5.25(s, 1H), 5.00(s, 1H), 4.67-4.56 (m, 2H), 4.38-4.31 (m, 2H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.72 (d, *J* = 14.1 Hz, 1H), 2.44 (d, *J* = 11.1 Hz, 1H), 2.27 (s, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 176.1, 140.9, 140.3, 131.4, 129.6, 123.3, 122.6, 122.5(q, *J* = 279.75 Hz), 119.3, 109.7, 82.2 (q, *J* = 33.00 Hz), 76.7, 74.0, 72.7, 59.7, 44.4, 29.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.88 (d, *J* = 2.8 Hz) ppm. **HRMS** (m/z) $[M+H]^+$ Calcd for $C_{17}H_{16}F_3N_2O_2^+$ 337.1164, found 337.1161. **HPLC** (Chiralpak IG-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR = 9.92 min (minor), 11.57 min (major).

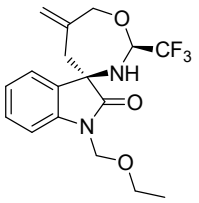


3l: Purified by silica gel chromatography using PE/EA 5:1, white solid；70% yield, 25.9 mg, 94% ee, dr: 95 :5; MP**:** 101.2-102.5 °C. $[\alpha]_D$ = + 37 (*c*= 0.1, CH_2Cl_2, 30.7 °C).**^{1}H NMR (300 MHz, $CDCl_3$)**:*δ* 7.37-7.29 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.38 (td, *J* = 9.9, 4.8 Hz, 1H), 5.24 (s, 1H), 5.00 (s, 1H), 4.69-4.57 (m, 2H), 4.37 (d, *J* = 13.2 Hz, 1H), 4.25 (d, *J* = 17.7 Hz, 1H), 3.77 (s, 3H), 2.90 (d, *J* = 14.1 Hz , 1H), 2.77 (d, *J* = 14.1 Hz , 1H), 2.48 (d, *J* = 11.4 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.0, 167.9, 141.3, 140.1, 131.3, 129.6, 123.3, 122.7, 122.5(q, *J* = 279.75 Hz), 119.4, 108.6, 82.1 (q, *J* = 32.25 Hz), 74.0, 59.7, 52.7, 44.7, 41.0 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.78 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M+H]^+$ Calcd for $C_{17}H_{18}F_3N_2O_4^+$ 371.1219, found 371.1221. **HPLC** (Chiralpak IB-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR = 16.53 min (major), 30.50 min (minor).

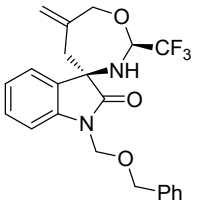


3m: Purified by silica gel chromatography using PE/EA 6:1, yellow oil, 62% yield, 22.7 mg, 94 % ee, dr> 20 :1; $[\alpha]_D$ = + 18 (*c* = 0.1, CH_2Cl_2, 33.1 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: *δ* 7.35-7.28 (m, 2H), 7.08-7.02 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 5.40 (d, *J* = 3.9 Hz, 1H), 5.24 (s, 1H), 4.98 (s, 1H), 4.77-4.65 (m, 1H), 4.57 (d, *J* = 13.2 Hz, 1H), 4.35 (d, *J* = 13.2 Hz, 1H), 2.87 (d, *J* = 14.1 Hz , 1H), 2.67 (d, *J* = 13.8 Hz , 1H), 2.40 (s, 1H), 2.12-2.03 (m, 2H), 1.99-1.89 (m, 4H), 1.77-1.70 (m, 2H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.2, 141.4, 140.7, 132.0, 129.2, 122.7, 122.5 (q, *J* = 279.00 Hz), 122.3, 118.9, 110.1, 82.3 (q, *J* = 33.00 Hz), 74.0, 59.3, 52.3, 44.6, 27.8, 27.5, 25.2 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.77 (d, *J* = 2.8 Hz) ppm. **HRMS** (m/z) $[M+H]^+$ Calcd for $C_{19}H_{22}F_3N_2O_2^+$ 367.1633, found 367.1624. **HPLC** (Chiralpak IG-H,

n-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR = 15.12 min (major), 19.43 min (minor).

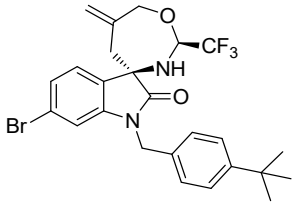


3n： Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 62% yield, 22.1 mg, 90 % ee, dr> 20 :1; $[\alpha]_D$ = +23 (*c* = 0.1, CH_2Cl_2, 31.5 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.38-7.33 (m, 2H), 7.14-7.08 (m, 2H), 5.37 (d, *J* = 3.3 Hz, 1H), 5.26 (s, 1H), 5.17 (dd, *J* = 19.5, 11.1 Hz, 2H), 5.01 (s, 1H), 4.59 (d, *J* = 13.2 Hz, 1H), 4.37 (d, *J* = 13.2 Hz, 1H), 3.55 (dd, *J* = 11.4, 7.2 Hz, 2H), 2.89 (d, *J* = 14.1 Hz, 1H), 2.76 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 1H), 1.18 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.5, 141.1, 140.4, 131.2, 129.7, 123.4, 122.5, 122.4(q, *J* = 279.75 Hz), 119.3, 110.2, 82.1 (q, *J* = 33.00 Hz), 74.1, 69.8, 64.3, 59.8, 44.5, 14.9 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.87 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{17}H_{20}F_3N_2O_3^+$ 357.1426, found 357.1435. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, flow rate = 1.0 mL/min, l = 254 nm) tR = 7.63 min (major), 9.15 min (minor).

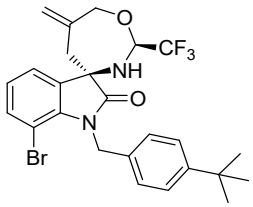


3o: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 69% yield, 28.8 mg, 84% ee, dr> 20 :1; $[\alpha]_D$ = + 28 (*c* = 0.1, CH_2Cl_2, 32.3 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.38-7.33 (m, 2H), 7.31-7.28 (m, 5H), 7.14-7.09 (m, 2H), 5.37 (td, *J* = 9.9, 4.8 Hz, 1H), 5.29-5.18 (m, 3H), 4.99 (s, 1H), 4.60-4.50 (m, 3H), 4.35 (d, *J* = 13.5 Hz, 1H), 2.85 (d, *J* = 14.1 Hz, 1H), 2.67 (d, *J* = 13.8 Hz, 1H), 2.44 (d, *J* = 11.4 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.6, 141.0, 140.4, 137.2, 131.2, 129.7, 128.4, 127.9, 123.4, 122.6, 122.4(q, *J* = 270.75 Hz), 119.3, 110.2, 82.1 (q, *J* = 32.25 Hz), 74.1, 70.6, 69.5, 59.8, 44.4 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.97 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{22}H_{22}F_3N_2O_3^+$ 419.1583, found

419.1591. **HPLC** (Chiralpak IG-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR = 24.13 min (minor), 27.02 min (major).

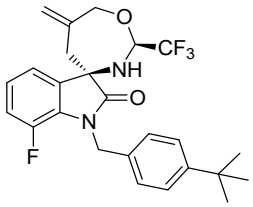


3p: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 47% yield, 24.5 mg, 86% ee, dr: 97 :3; $[\alpha]_D$ = + 9 (*c* = 0.1, CH_2Cl_2, 31.1 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.36 (d, *J* = 8.1Hz, 2H), 7.21-7.15 (m, 4H), 6.92 (d, *J* = 0.6 Hz, 1H), 5.41 (dd, *J* = 9.0, 4.2 Hz, 1H), 5.26 (s, 1H), 5.00 (s, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.74 (d, *J* = 15.9 Hz, 1H), 4.58 (d, *J* = 13.2 Hz, 1H), 4.36 (d, *J* = 13.2 Hz, 1H), 2.92 (d, *J* = 13.8 Hz, 1H), 2.72 (d, *J* = 14.1 Hz, 1H), 2.44 (d, *J* = 10.5 Hz, 1H), 1.29 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.0, 150.9, 143.4, 140.3, 132.0, 130.5, 126.8, 125.9, 125.7, 123.9, 123.2, 122.5 (q, *J* = 279.75 Hz), 119.4, 113.0, 82.2 (q, *J* = 33.00 Hz), 74.0, 59.4, 44.4, 43.3, 34.6, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.80 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{27}BrF_3N_2O_2^+$ 523.1208, found 523.1202. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =7.70 min (major), 10.20 min (minor).

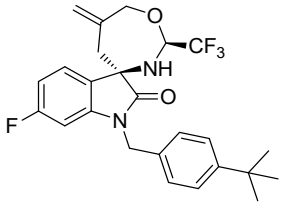


3q: Purified by silica gel chromatography using PE/EA 5:1, white solid, 63% yield, 32.9 mg, 97% ee, dr> 20 :1; MP: 102.6-103.8 °C. $[\alpha]_D$ = + 34 (*c* = 0.1, CH_2Cl_2, 30.8 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.38 (d, *J* = 8.4 Hz, 1H), 7.33-7.28 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 5.45-5.29 (m, 3H), 5.25 (s, 1H), 4.98 (s, 1H), 4.59 (d, *J* = 13.5 Hz, 1H), 4.38 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 13.8 Hz, 1H), 2.78 (d, *J* = 13.8 Hz, 1H), 2.45 (d, *J* = 10.8 Hz, 1H), 1.28 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: *δ* 177.8, 150.1, 140.2, 139.6, 135.4, 134.9, 134.0, 126.1, 125.5, 124.2, 122.5 (q, *J* = 279.75 Hz), 121.5, 119.5, 103.1, 82.0 (q, *J* = 32.25 Hz), 74.0, 58.9, 44.9, 43.9, 34.5, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) *δ* -80.83 (d, *J* = 5.6 Hz) ppm.

HRMS (m/z) $[M + H]^+$ Calcd for $C_{25}H_{27}BrF_3N_2O_2^+$ 523.1208, found 523.1202. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 97/3, flow rate = 1.0 mL/min, l = 254 nm) tR =9.35 min (major), 12.03min (minor).

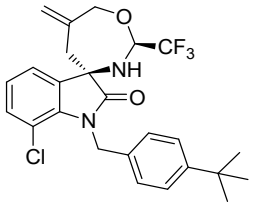


3r: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 64% yield, 29.5 mg, 93% ee, dr: 94 :6; $[\alpha]_D$ = + 23 (*c* = 0.1, CH_2Cl_2, 31.5 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.34-7.24 (m, 4H), 7.13-7.10 (m, 1H), 7.03-6.97 (m, 2H), 5.44 (dd, *J* = 9.4, 4.5 Hz, 1H), 5.26 (s, 1H), 5.05-4.94 (m, 3H), 4.59 (d, *J* = 13.3 Hz, 1H), 4.38 (d, *J* = 13.3 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.75 (d, *J* = 14.0 Hz, 1H), 2.45 (d, *J* = 10.9 Hz, 1H), 1.28 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 176.8, 150.6, 147.6 (d, *J* = 244.50 Hz), 140.2, 134.4(d, *J* = 3.00 Hz), 133.8, 128.7 (d, *J* = 9.00 Hz), 127.2 (d, *J* = 0.75 Hz), 125.6, 123.7 (d, *J* = 6.00 Hz), 122.5 (q, *J* = 278.25 Hz), 119.5, 118.3 (d, *J* = 3.75 Hz), 117.7 (d, *J* = 20.25 Hz), 82.0 (q, *J* = 32.25 Hz), 74.1, 59.7 (d, *J* = 1.50 Hz), 44.8 (d, *J* = 5.25 Hz), 44.6, 34.5, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.89 (d, *J* = 5.6 Hz,), -133.72 (d, *J* = 8.4 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{27}F_4N_2O_2^+$ 463.2009, found 463.2013. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol =80/20, flow rate = 1.0 mL/min, l = 254 nm) tR =5.18 min (major), 5.90 min (minor).

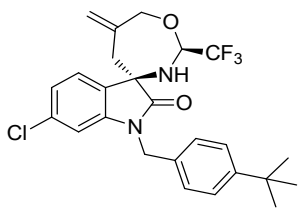


3s: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 61% yield, 28.2 mg, 86% ee, dr: 95 :5; $[\alpha]_D$ = + 20 (*c* = 0.1, CH_2Cl_2, 31.2 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.30-7.27 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.70 (td, *J* = 9.6, 2.4 Hz, 1H), 6.50 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.42 (s, 1H), 5.27 (s, 1H), 5.01 (s, 1H), 4.90 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 13.5 Hz,

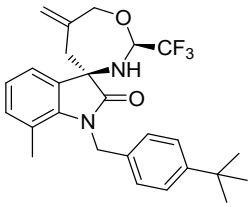
1H), 4.37 (d, *J* = 13.5 Hz, 1H), 2.94 (d, *J* = 14.1 Hz, 1H), 2.74 (d, J = 13.8 Hz, 1H), 2.45 (s, 1H), 1.29 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.4 , 163.6 (d, *J* = 245.25 Hz), 150.9, 143.7 (d, *J* = 12.00 Hz), 140.4, 132.0, 127.1 (d, *J* = 3.00 Hz), 126.9, 125.9, 123.7 (d, *J* = 9.75 Hz), 122.5 (q, *J* = 279.00 Hz), 119.3, 108.9 (d, *J* = 22.50 Hz), 98.5 (d, *J* = 27.75 Hz), 82.1 (q, *J* = 33.00 Hz), 74.0, 59.3, 44.5, 43.4, 34.5, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.82 (d, *J* = 5.6 Hz); -110.98 ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{27}F_4N_2O_2^+$ 463.2009, found 463.2012. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =8.05 min (major), 10.32 min (minor).



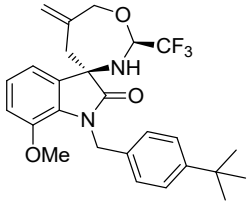
3t: Purified by silica gel chromatography using PE/EA 5:1, white solid, 54% yield, 25.8 mg, 94% ee, dr: 95 :5; **MP:** 111.3-112.5°C. $[\alpha]_D$ = + 47 (*c* = 0.1, CH_2Cl_2, 30.4°C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.26-7.24 (m, 1H), 7.09 (d, *J* =8.4 Hz, 2H), 7.21-7.16 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.43 (td, *J* = 9.6, 4.5 Hz, 1H), 5.37-5.24 (m, 3H), 4.99 (s, 1H), 4.59 (d, *J* = 13.2 Hz, 1H), 4.39 (d, *J* = 13.5 Hz, 1H), 2.90 (d, *J* = 13.8 Hz, 1H), 2.75 (d, *J* = 13.8 Hz, 1H), 2.45 (d, *J* = 11.4 Hz, 1H), 1.28 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.6, 150.2, 140.2, 138.1, 134.5, 134.2, 132.0, 126.3, 125.5, 123.8, 120.9, 122.6 (q, *J* = 278.25 Hz), 119.5, 116.1, 82.0 (q, *J* = 33.00 Hz), 74.1, 59.0, 44.8, 44.2, 34.5, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.83 (d, *J* = 5.6 Hz,) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{25}H_{27}ClF_3N_2O_2^+$ 479.1713, found 479.1718. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR =17.76 min (major), 24.71 min (minor).



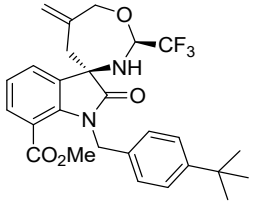
3u: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 57% yield, 27.2 mg, 86% ee, dr: 85:15; $[\alpha]_D$ = + 20 (*c* = 0.1, CH_2Cl_2, 33.1 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 9.9 Hz , 3H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.77 (s, 1H), 5.41 (s, 1H), 5.27 (s, 1H), 5.01 (s, 1H), 4.90 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 13.2 Hz, 1H), 4.37 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 14.1 Hz, 1H), 2.73 (d, *J* = 14.1 Hz, 1H), 2.43 (s, 1H), 1.30 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.1, 150.9, 143.3, 140.3, 135.4, 131.9, 129.9, 126.8, 125.9, 123.5, 122.7, 122.4 (q, *J* = 279.00 Hz), 119.4, 110.3, 82.2 (q, *J* = 33.00 Hz), 74.0, 59.4, 44.4, 43.3, 34.6, 31.3 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -80.90 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for$C_{25}H_{27}ClF_3N_2O_2^+$ 479.1713, found 479.1719. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 90/10, flow rate = 1.0 mL/min, l = 254 nm) tR =6.03 min (major), 7.64min (minor).



3v: Purified by silica gel chromatography using PE/EA 5:1, white solid, 68% yield, 31.1 mg, 92% ee, dr: 94 : 6; **MP:** 104.4-105.8 °C. $[\alpha]_D$ = + 25 (*c* = 0.1, CH_2Cl_2, 28.9 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (dd, *J* = 6.3, 1.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.00-6.93 (m, 2H), 5.47 (d, *J* = 4.2 Hz, 1H), 5.25 (s, 1H), 5.13 (s, 2H), 5.03 (s, 1H), 4.60 (d, *J* = 13.5 Hz, 1H), 4.40 (d, *J* = 13.5 Hz, 1H), 2.93 (d, *J* = 14.1 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.47 (s, 1H), 2.31 (s, 3H), 1.28 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 178.1, 150.2, 140.7, 139.9, 134.3, 133.3, 132.5, 125.8, 125.4, 123.0, 122.5 (q, *J* = 288.25 Hz), 120.7, 120.2, 119.2, 82.0 (q, *J* = 33.00 Hz), 74.1, 58.7, 45.0, 44.4, 34.5, 31.3, 19.0 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -81.10 (d, *J* = 5.6 Hz,) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{26}H_{30}F_3N_2O_2^+$ 459.2259, found 459.2266. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =6.69 min (major), 11.96min (minor).



3w: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 55% yield, 26.1 mg, 90% ee, dr: 90 : 10; $[\alpha]_D$ = + 14 (*c* = 0.1, CH_2Cl_2, 33.1 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.24-7.21 (m, 2H), 7.03-6.93 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.47 (td, *J* = 10.2, 4.8 Hz, 1H), 5.24 (s, 1H), 5.18-5.07 (m, 2H), 4.97 (s, 1H), 4.58 (d, *J* = 13.2 Hz, 1H), 4.38 (d, *J* = 13.2 Hz, 1H), 3.72 (s, 3H), 2.86 (d, *J* = 14.1 Hz, 1H), 2.75 (d, *J* = 13.8 Hz, 1H), 2.43 (d, *J* = 11.1 Hz, 1H), 1.28 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 177.4, 149.9, 145.4, 140.6, 135.2, 133.3, 130.0, 127.0, 125.3, 123.7, 122.6 (q, *J* = 279.75 Hz), 119.1, 114.8, 113.6, 82.0 (q, *J* = 33.00 Hz), 74.1, 59.5, 55.9, 45.1, 44.8, 34.5, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -81.07 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{26}H_{30}F_3N_2O_3^+$ 475.2209, found 475.2216. **HPLC** (Chiralpak AD-H, *n*-hexane/*i*-propanol = 95/5, flow rate = 1.0 mL/min, l = 254 nm) tR =8.96 min (major), 18.84 min (minor).

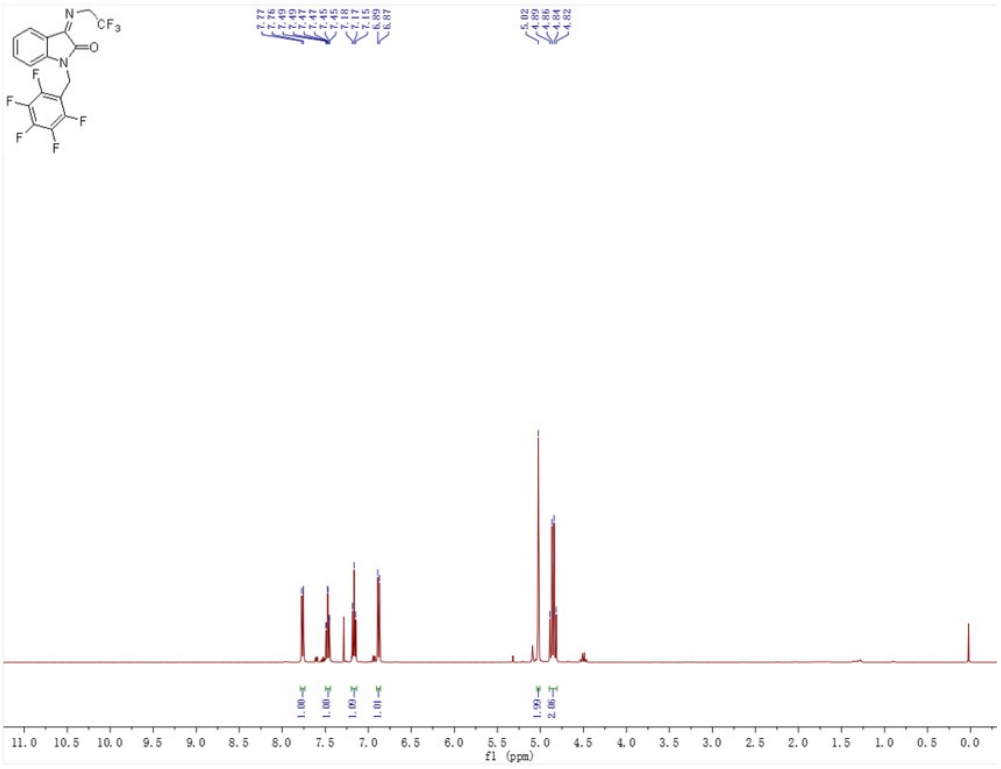


3x: Purified by silica gel chromatography using PE/EA 5:1, yellow oil, 49% yield, 24.6 mg, 92% ee, dr> 20 :1; $[\alpha]_D$ = + 27 (*c* = 0.1, CH_2Cl_2, 30.1 °C). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.48-7.39 (m, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.05 (t, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.48 (td, *J* = 9.9, 4.8 Hz, 1H), 5.37-5.28 (m, 2H), 5.06 (d, *J* = 18.0 Hz, 2H), 4.61 (d, *J* = 13.5 Hz, 1H), 4.41 (d, *J* = 13.2 Hz, 1H), 3.61 (s, 3H), 2.94 (d, *J* = 14.1 Hz, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.48 (d, *J* = 11.4 Hz, 1H), 1.25 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 178.0, 166.7, 150.2, 140.2, 139.9, 133.6, 132.2, 130.2, 126.5, 125.4, 124.9, 122.5 (q, *J* = 279.00 Hz), 122.2, 119.5, 117.6, 81.9 (q, *J* = 33.00 Hz), 74.1, 58.2, 52.4, 44.7, 44.2, 34.4, 31.3 ppm. **^{19}F NMR** (**282 MHz, $CDCl_3$**) δ -80.83 (d, *J* = 5.6 Hz) ppm. **HRMS** (m/z) $[M + H]^+$ Calcd for $C_{27}H_{30}F_3N_2O_4^+$

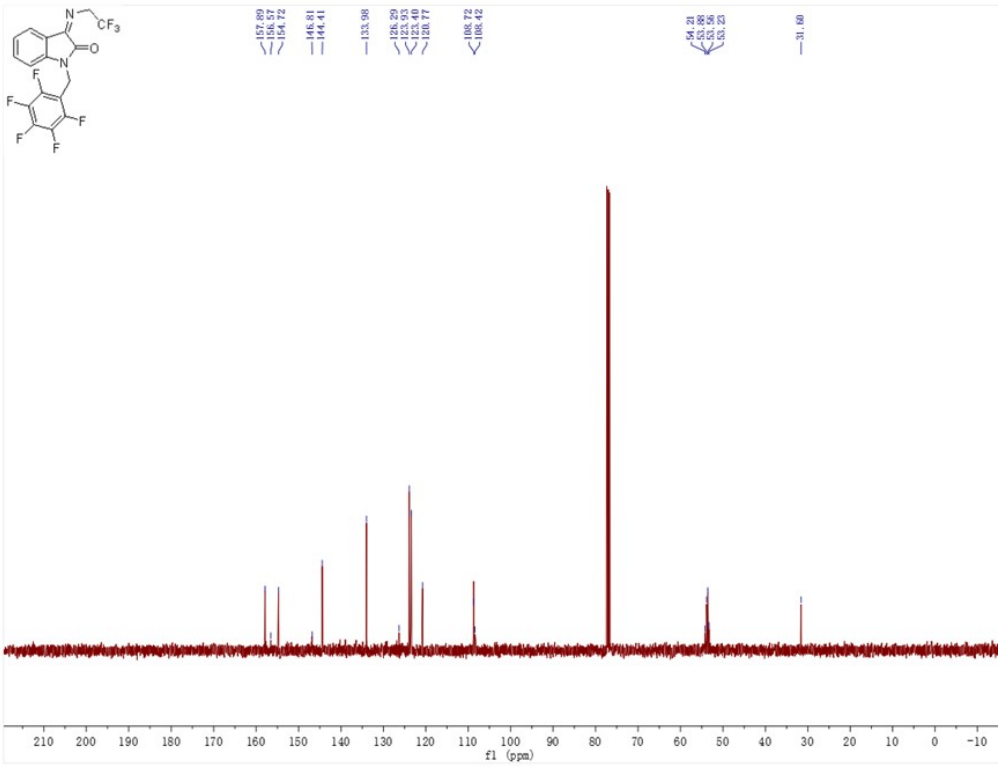
503.2158, found 503.2164. **HPLC** (Chiralpak IB-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR =13.00 min (minor), 16.04 min (major).

1. (a) Niu, B.; Wu, X.; Wei, Y.; Shi, M. Palladium-Catalyzed Diastereoselective Formal [5+3] Cycloaddition for the Construction of Spirooxindoles Fused with an EightMembered Ring. *Org. Lett*. **2019**, *21*, 4859-4863. (b) Li, X.; Shen, Z.; Yan, W.; Wang, K.; Wang, R. Synthesis of Chiral α-Trifluoromethylamines with 2,2,2-Trifluoroethylamine as a "Building Block". *Org. Lett*. **2016**, *18*, 956-959.
2. Mao, B.; Liu, H.; Yan, Z.; Xu, Y.; Xu, J.; Wang, W.; Wu, Y.; Guo, H. Palladium-Catalyzed Asymmetric [4+2] Cycloaddition of 2-Methylidenetrimethylene Carbonate with Alkenes: Access to Chiral Tetrahydropyran-Fused Spirocyclic Scaffolds. *Angew. Chem. Int. Ed*. **2020**, *59*, 11316-11320.

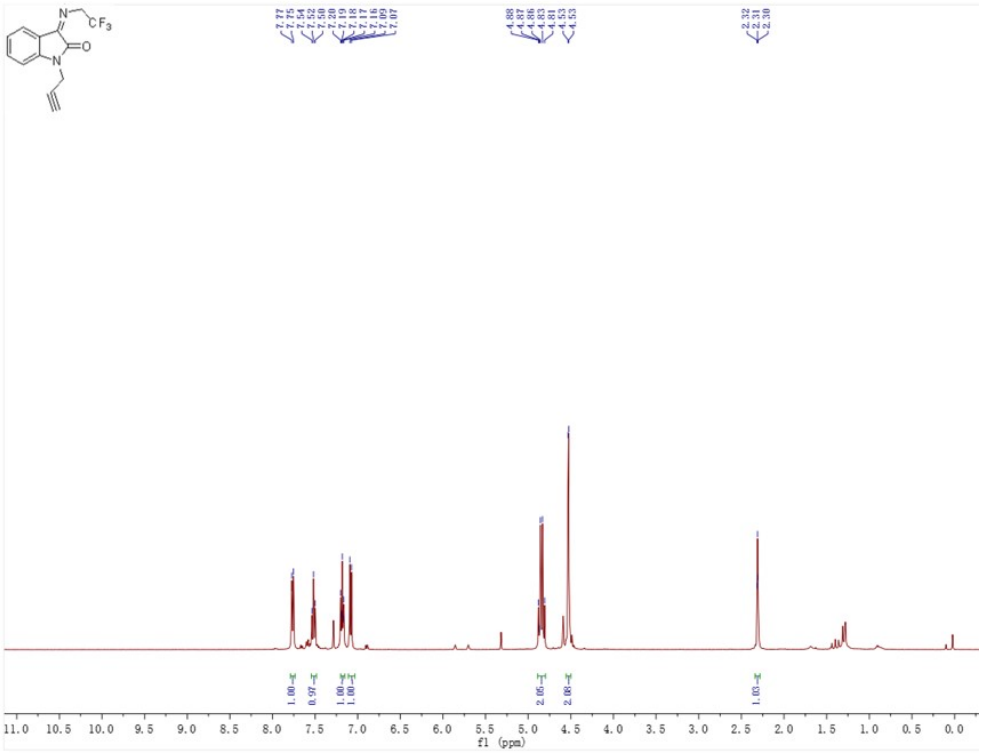
5. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra



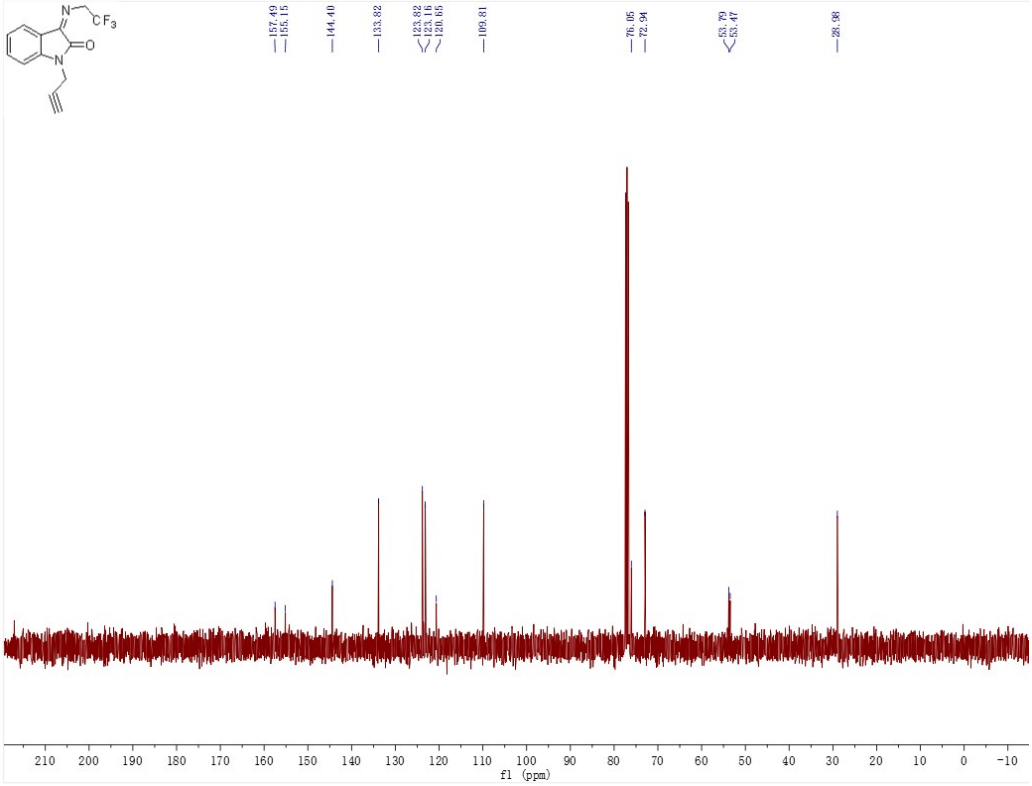
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1j**



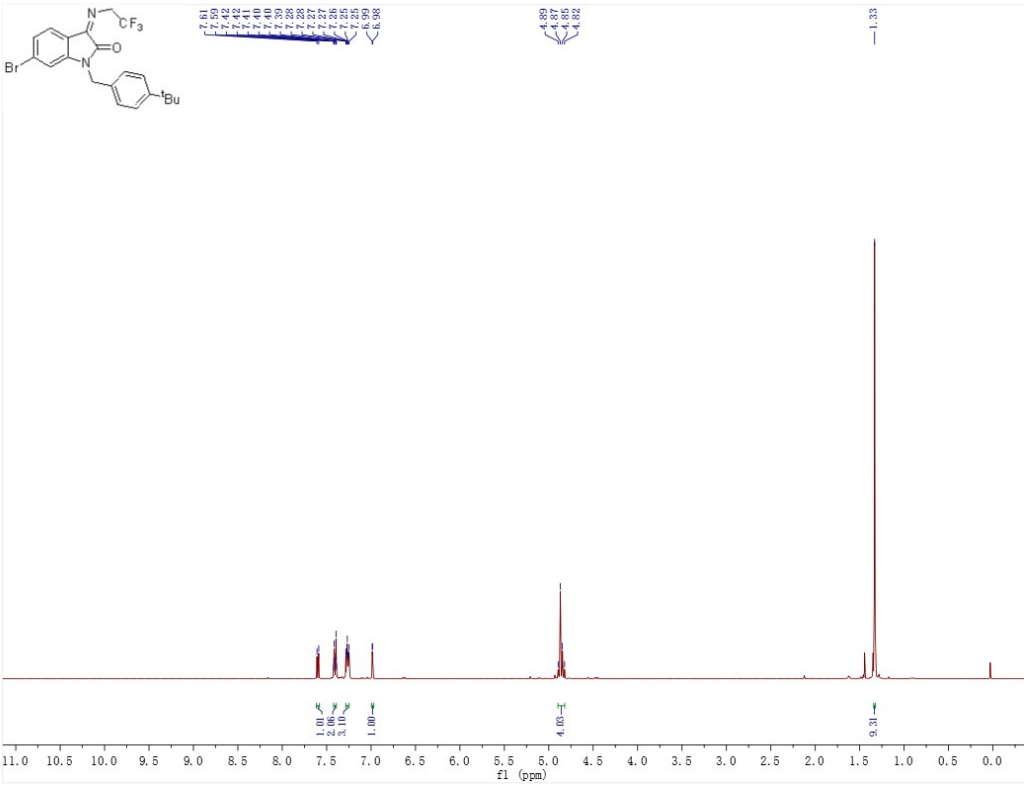
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1j**



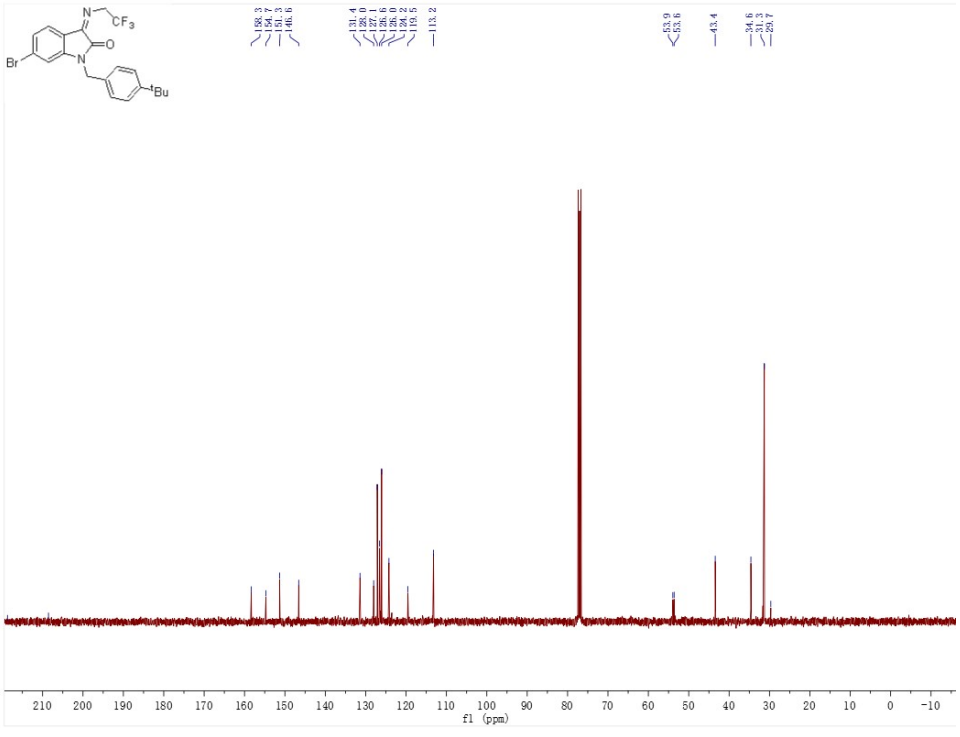
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1k**



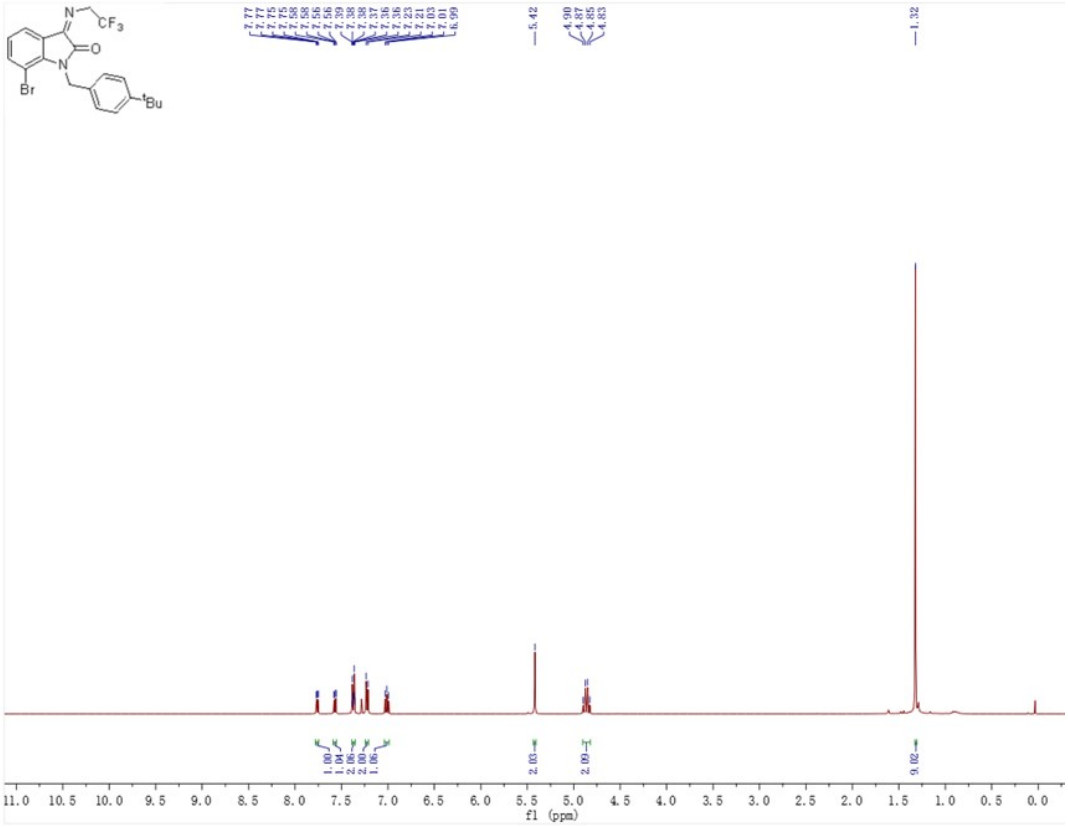
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1k**



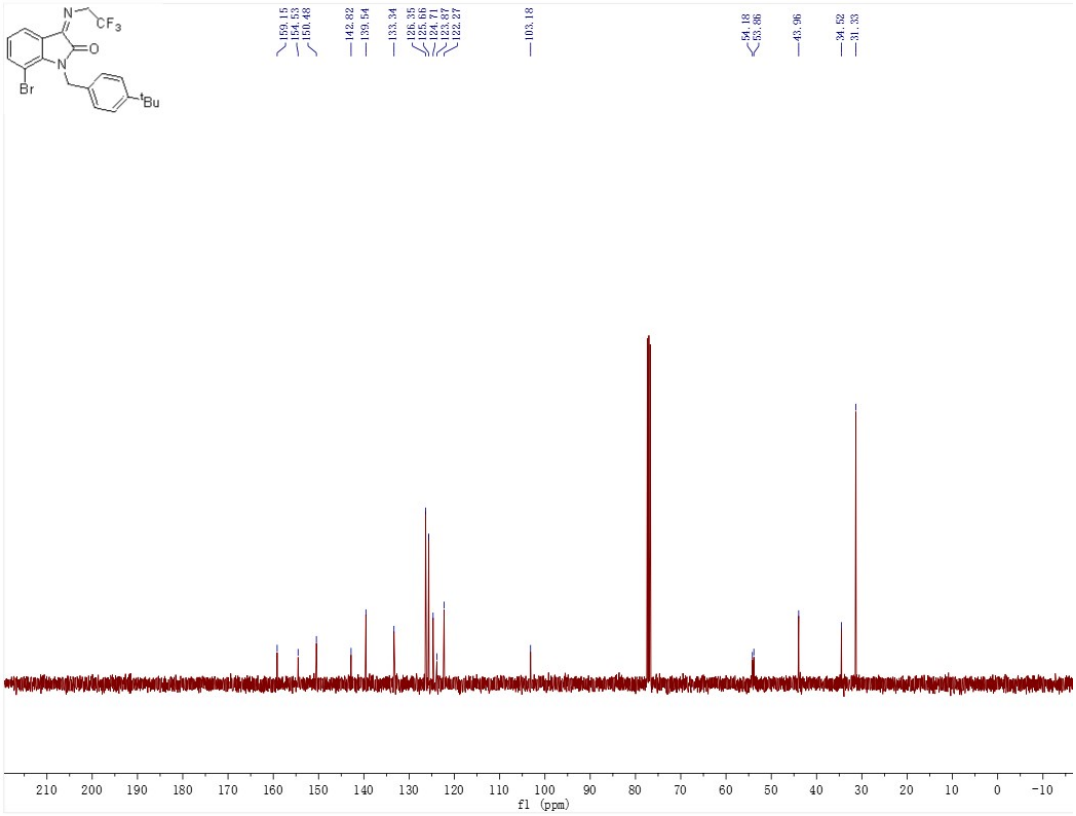
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1p**



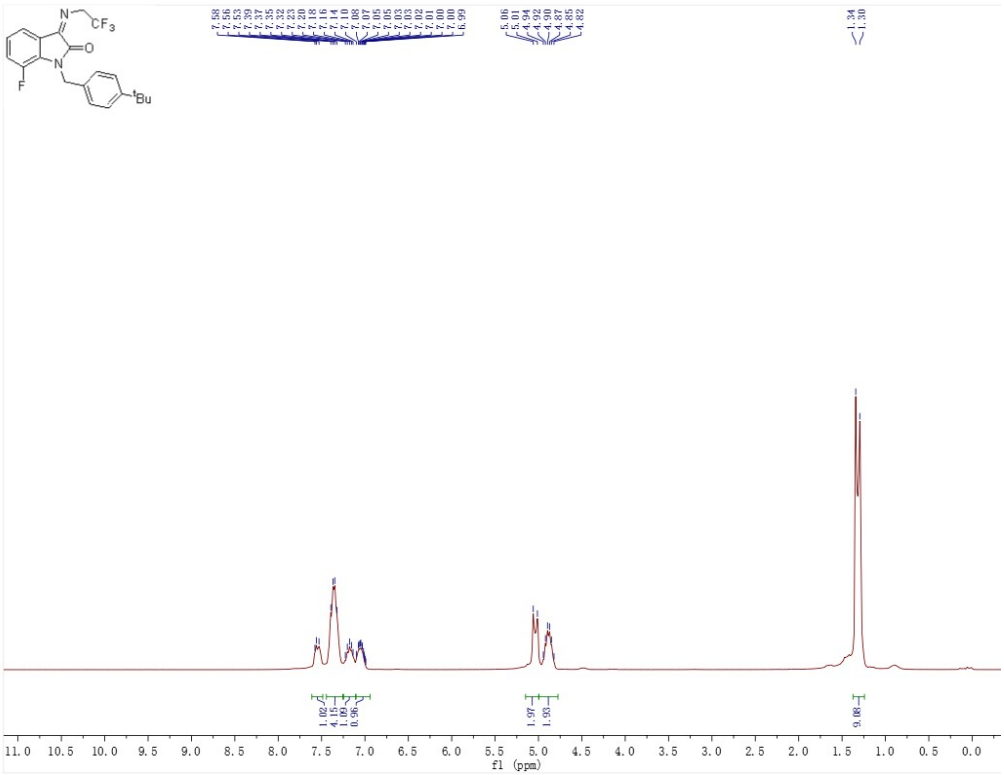
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1p**



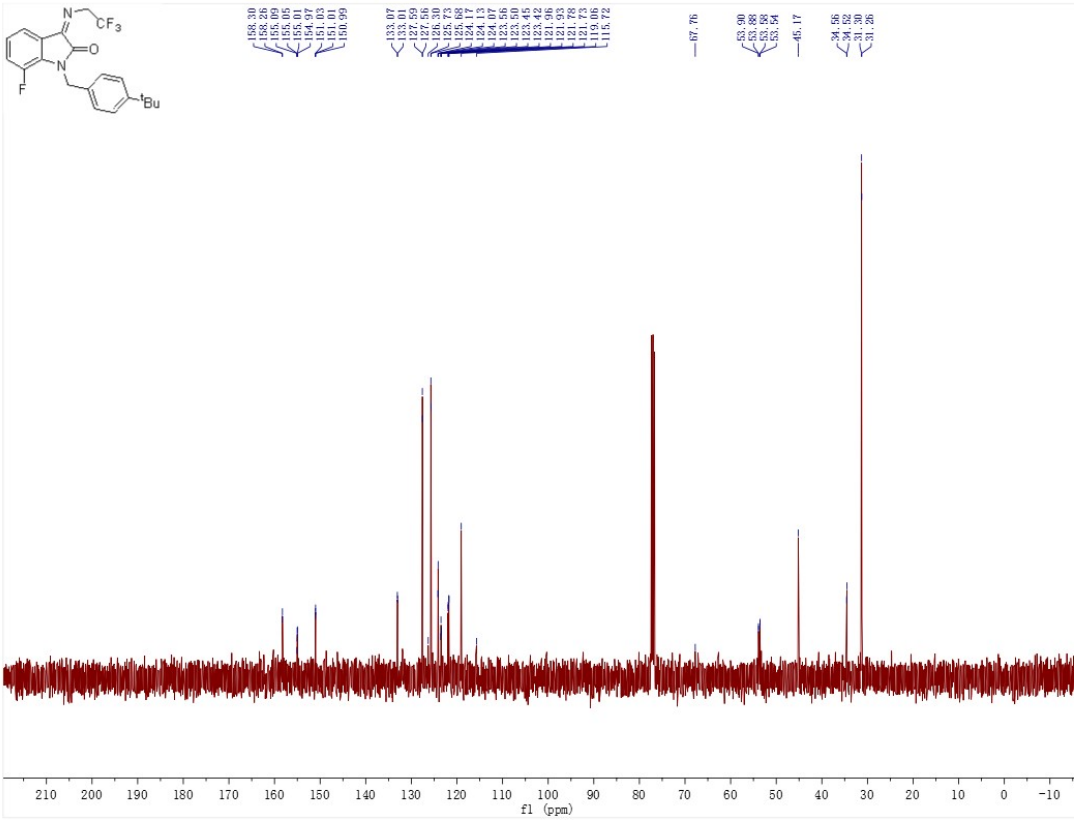
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1q**



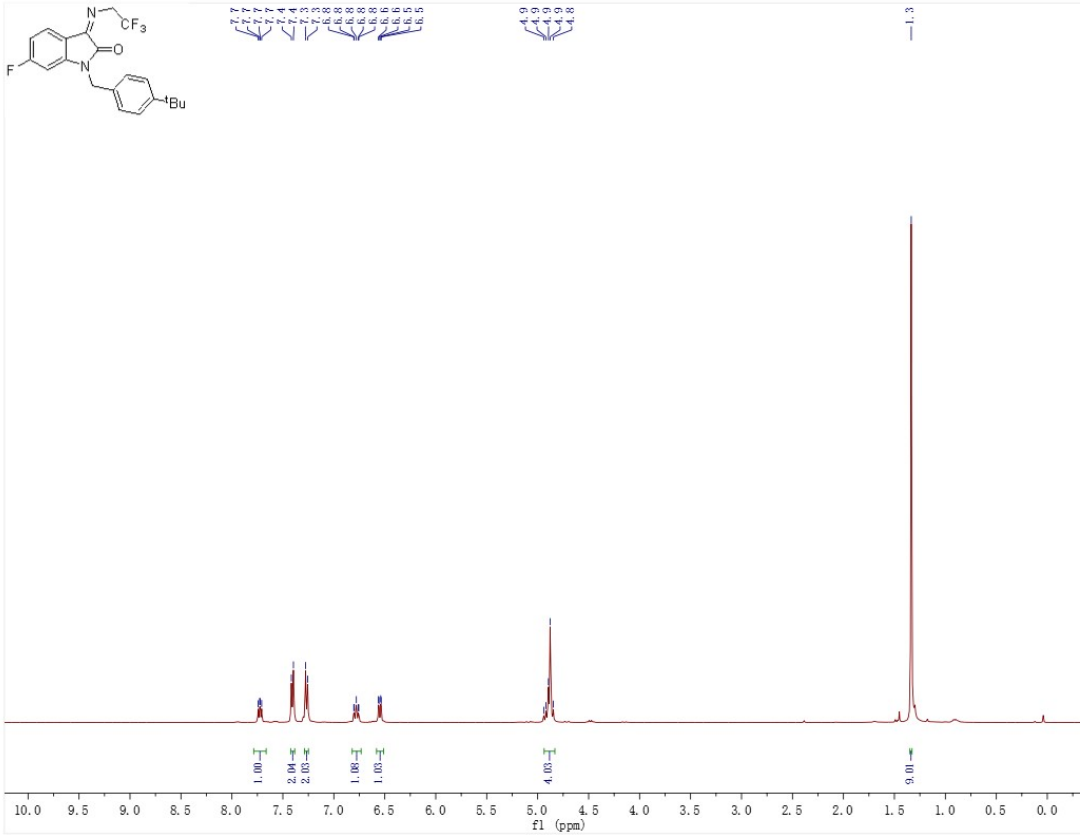
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1q**



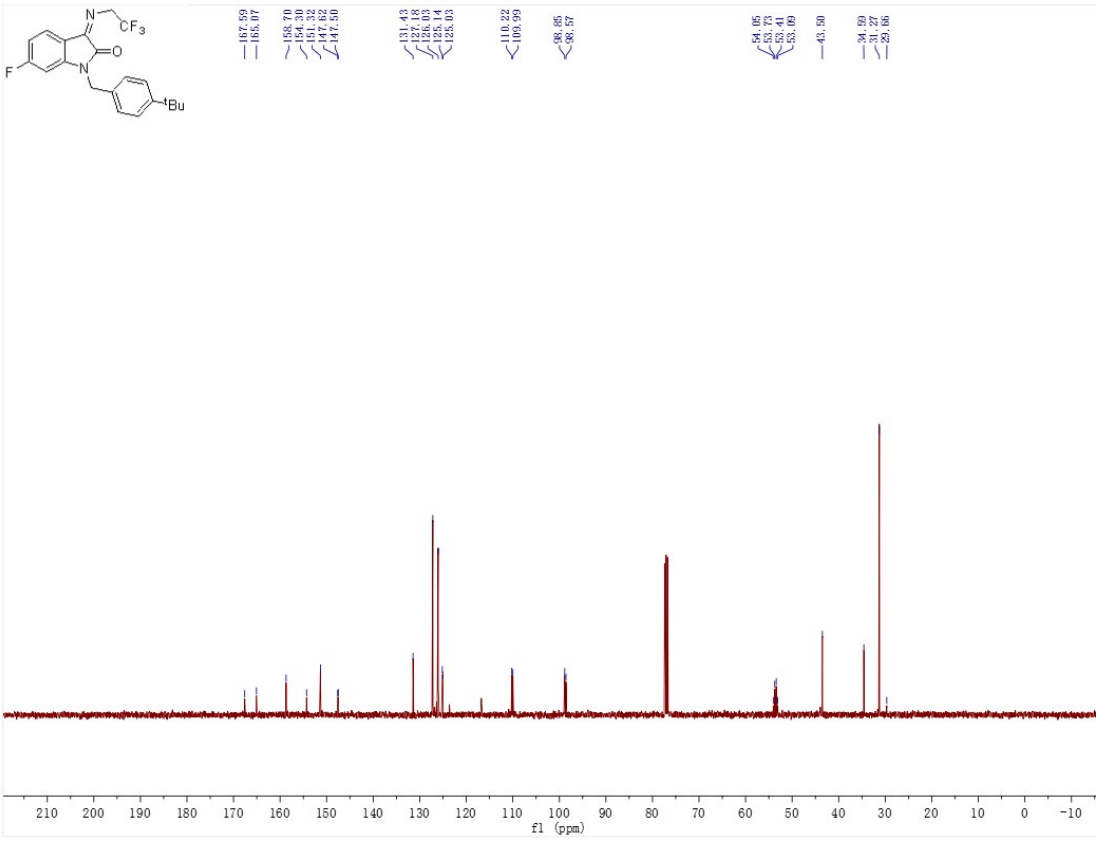
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1r**



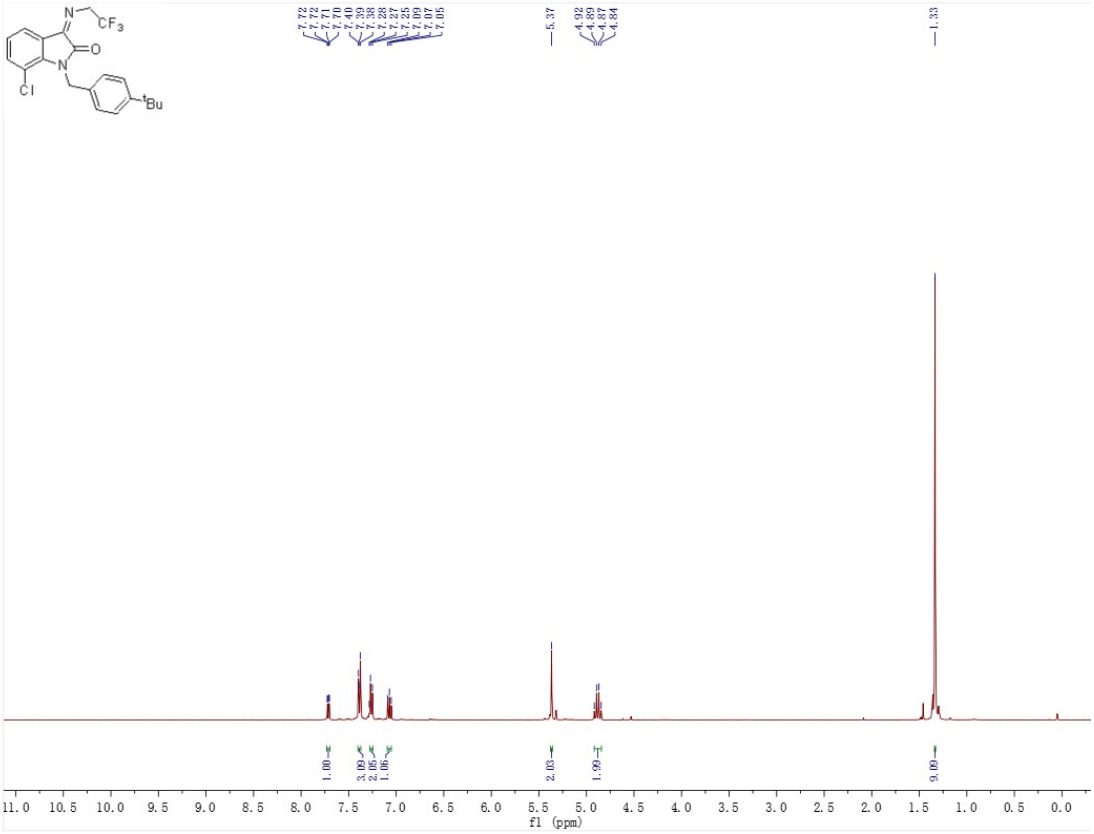
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1r**



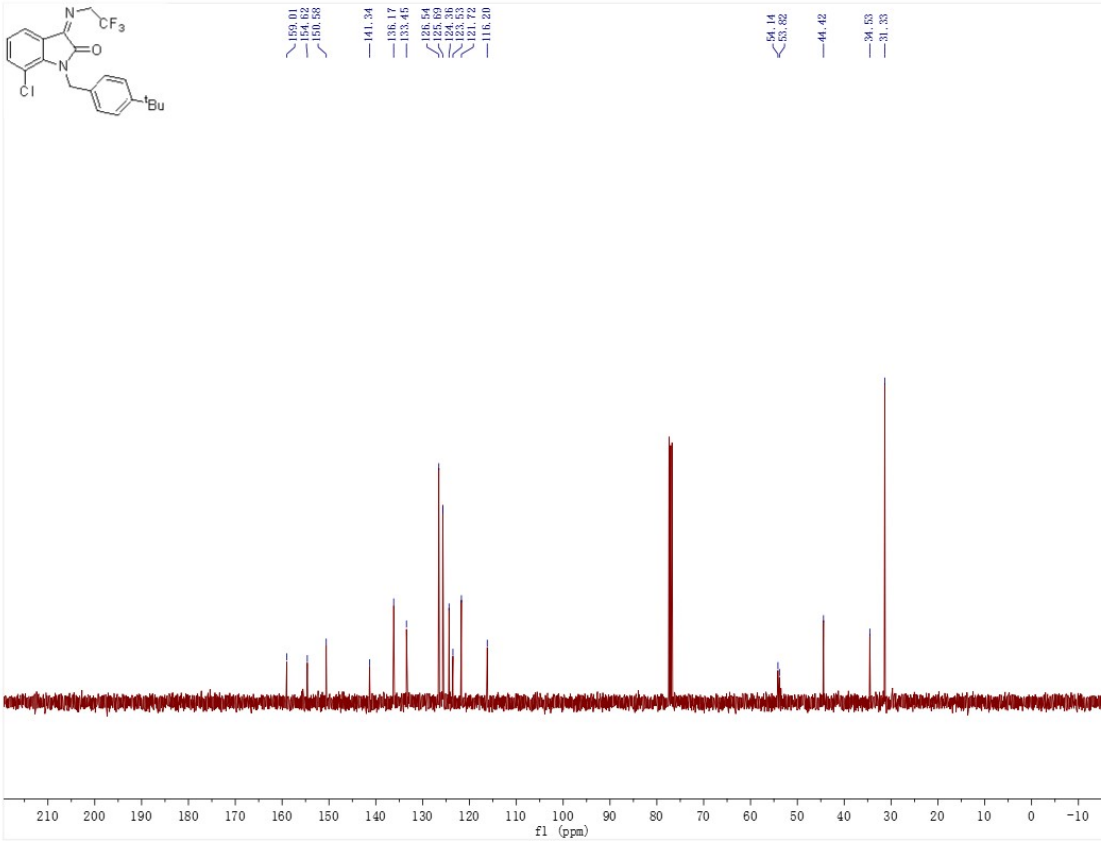
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1s**



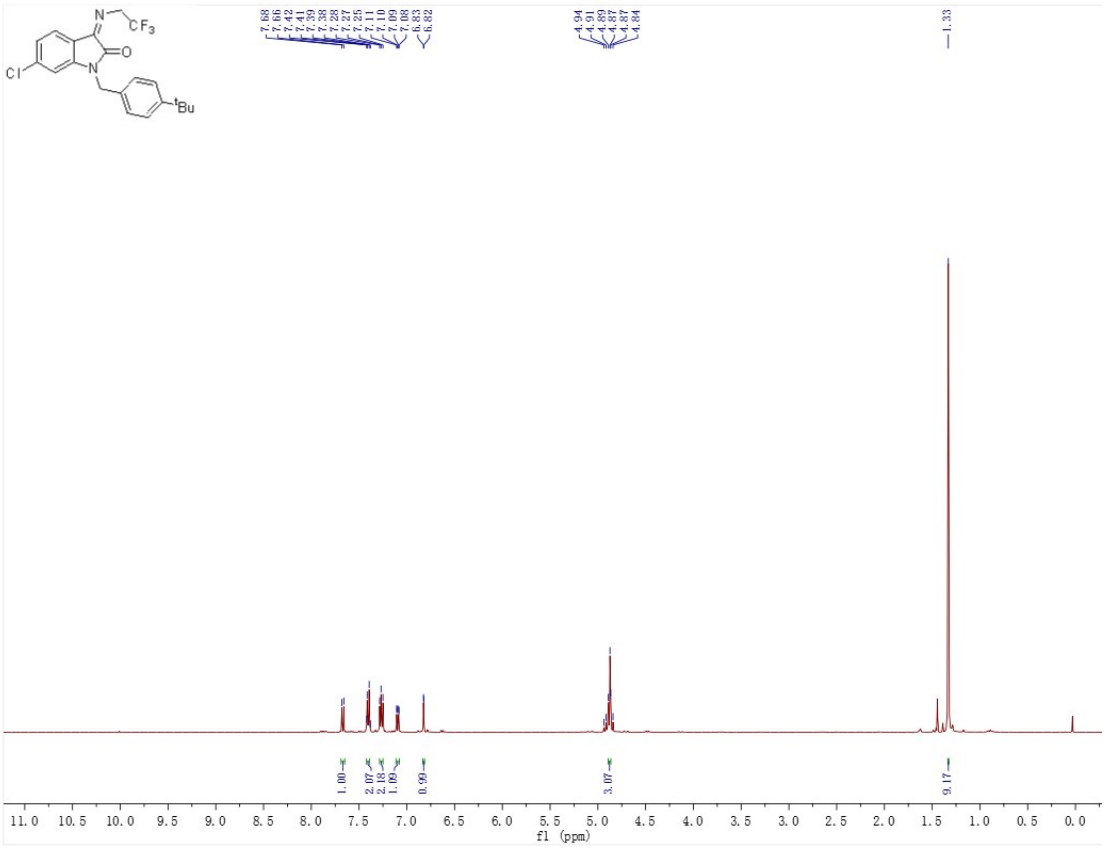
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1s**



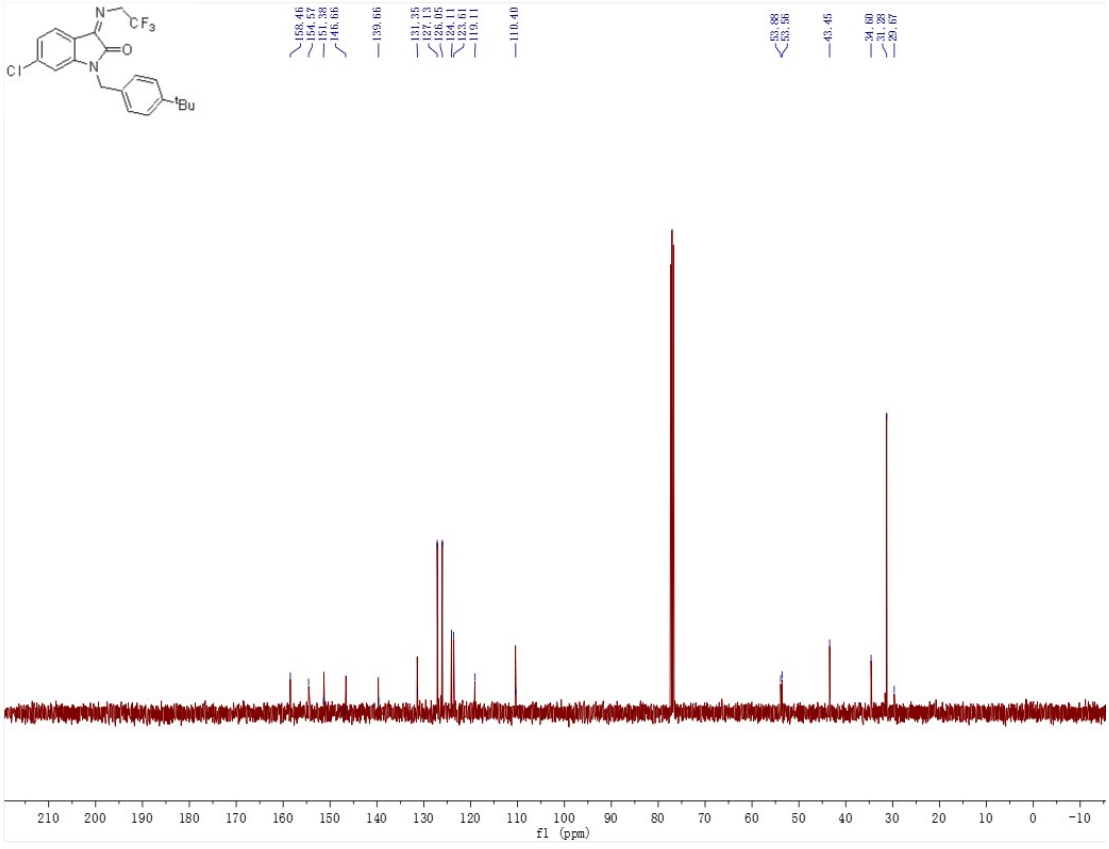
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1t**



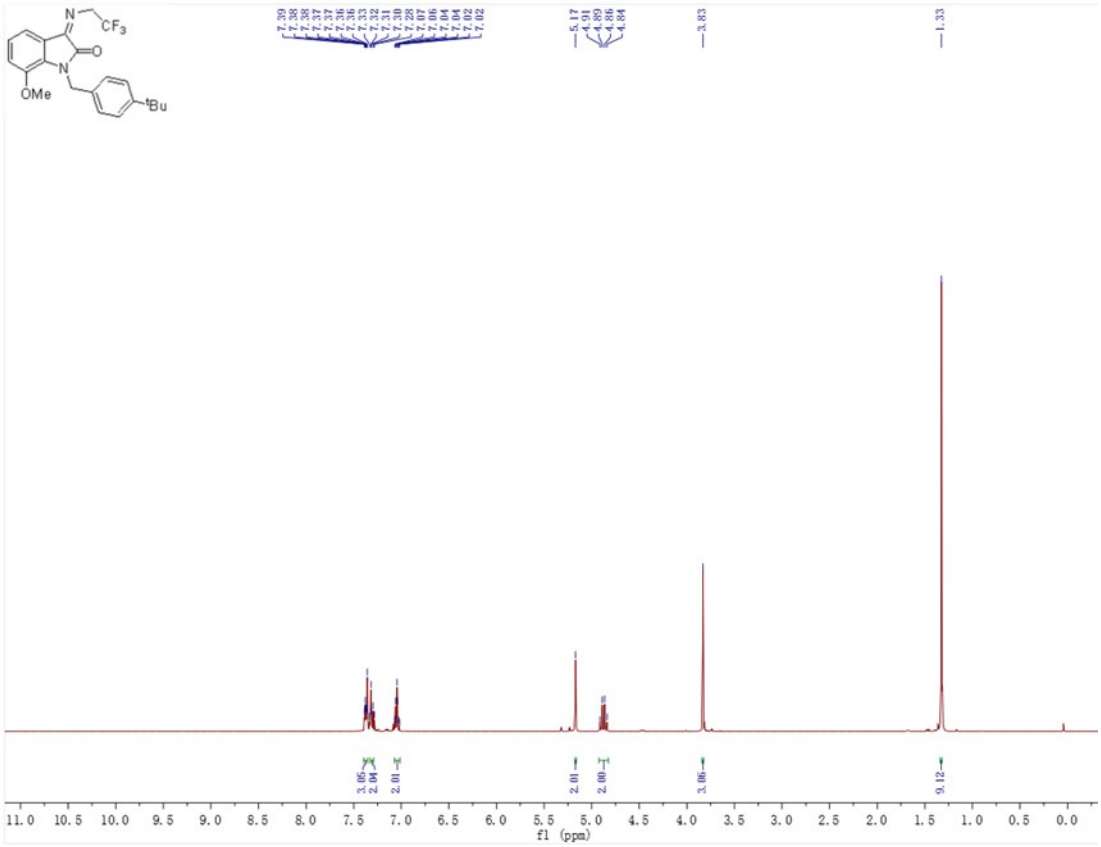
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1t**



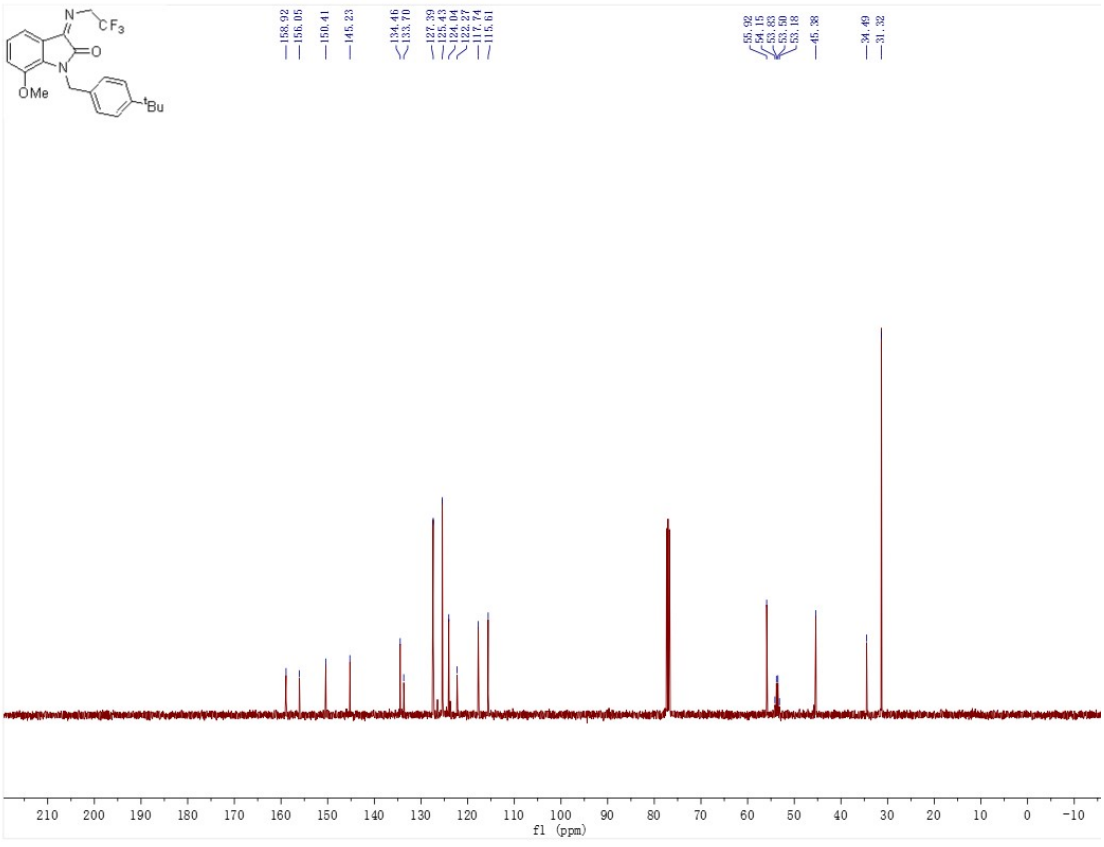
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1u**



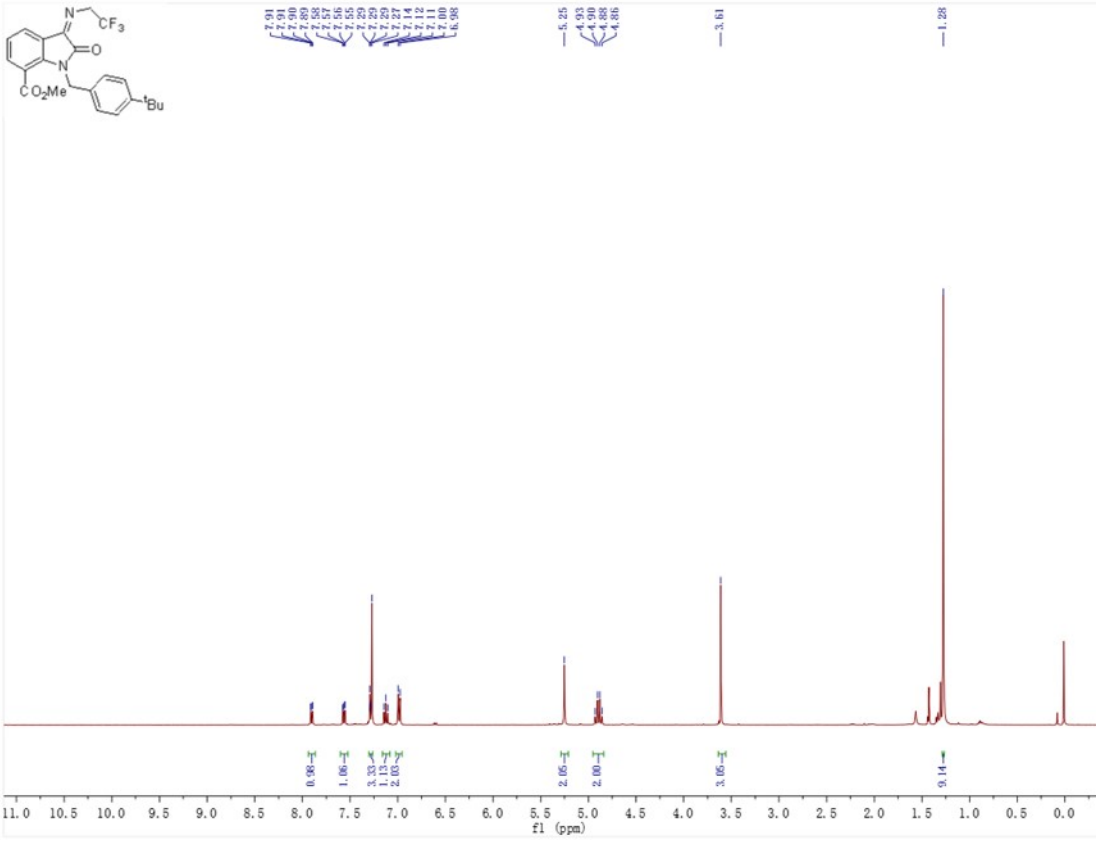
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1u**



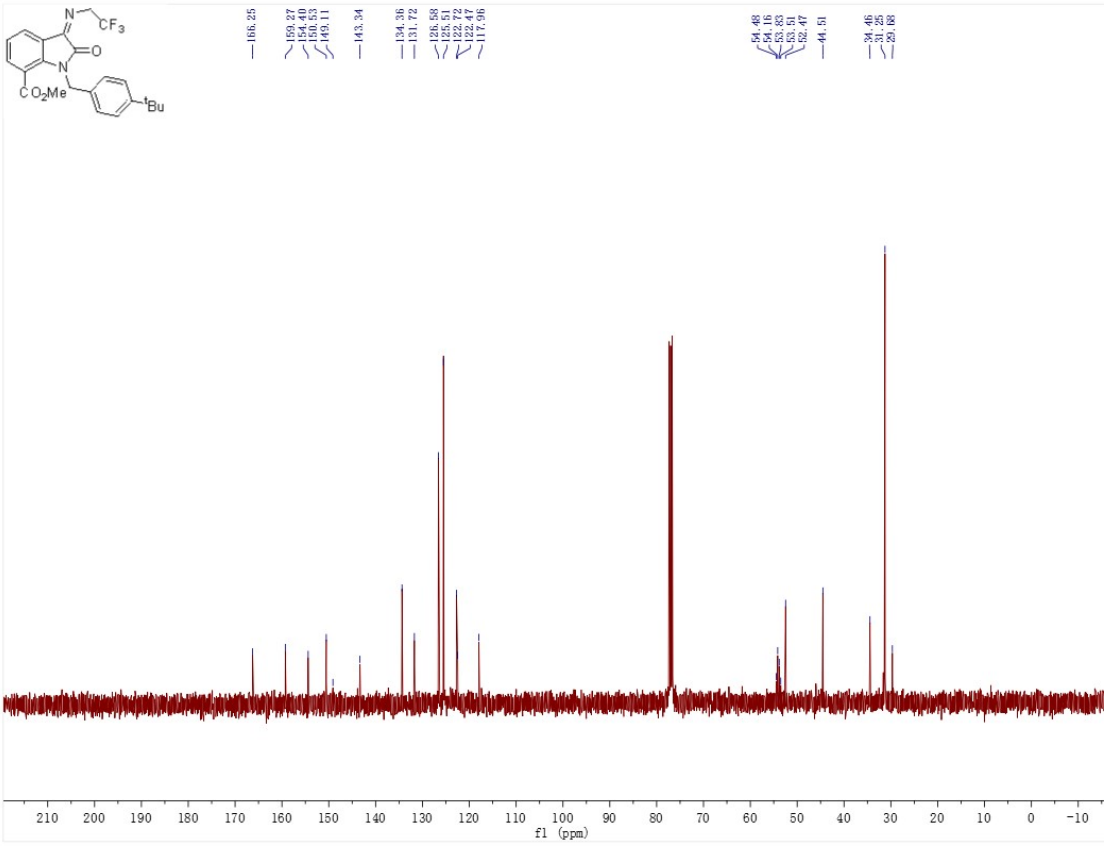
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1w**



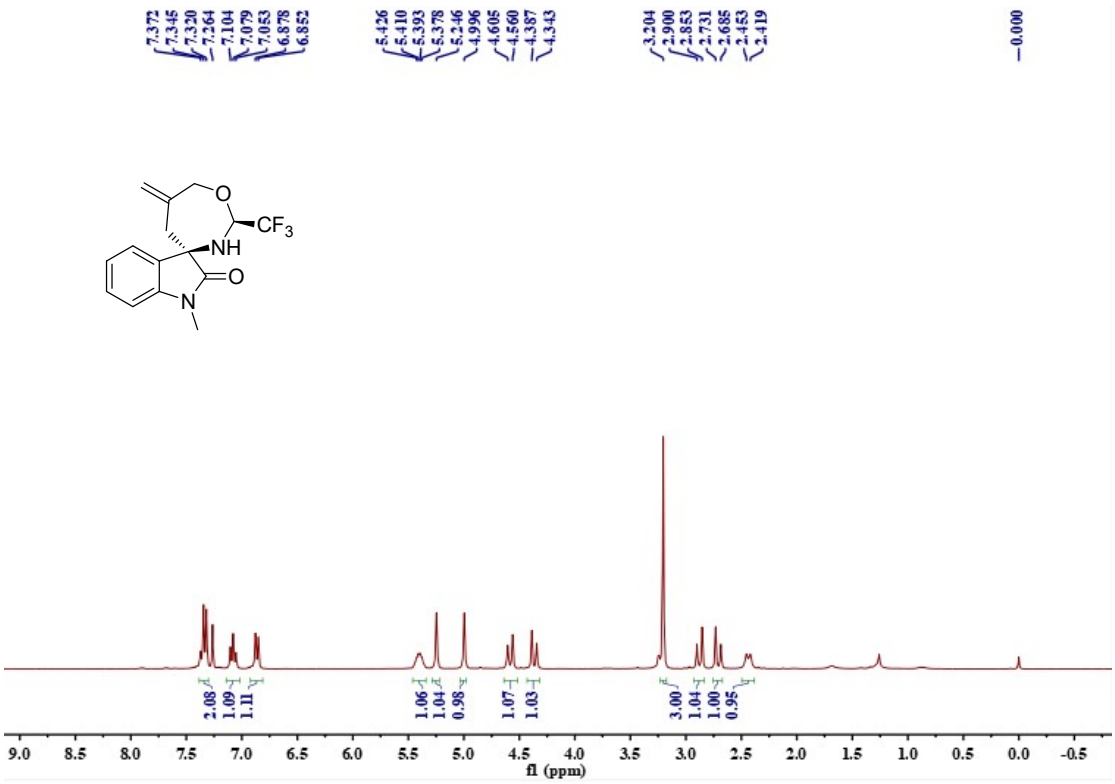
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1w**



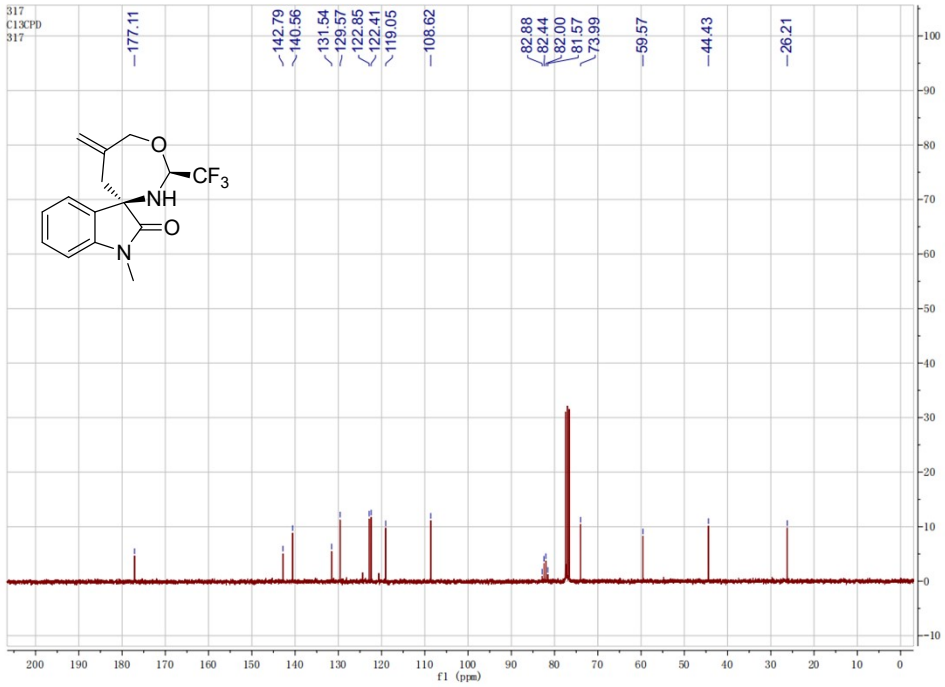
^{1}H NMR ($CDCl_3$, 400 MHz) NMR of **1x**



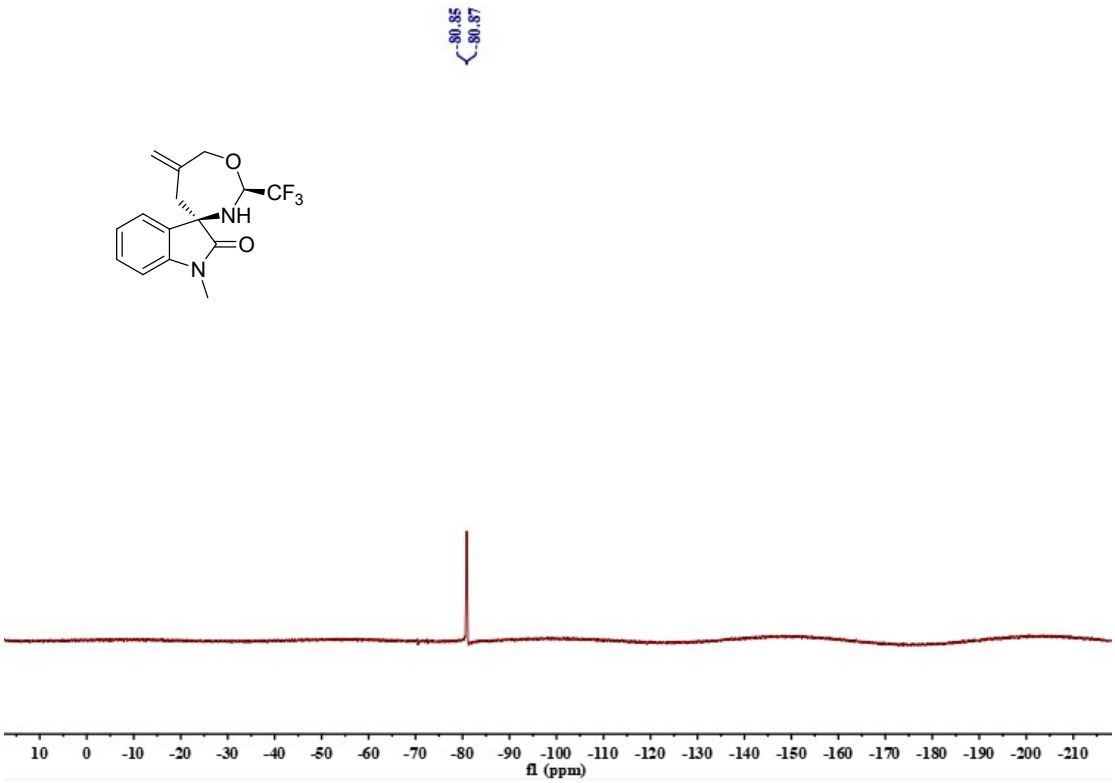
^{13}C NMR ($CDCl_3$, 101 MHz) NMR of **1w**



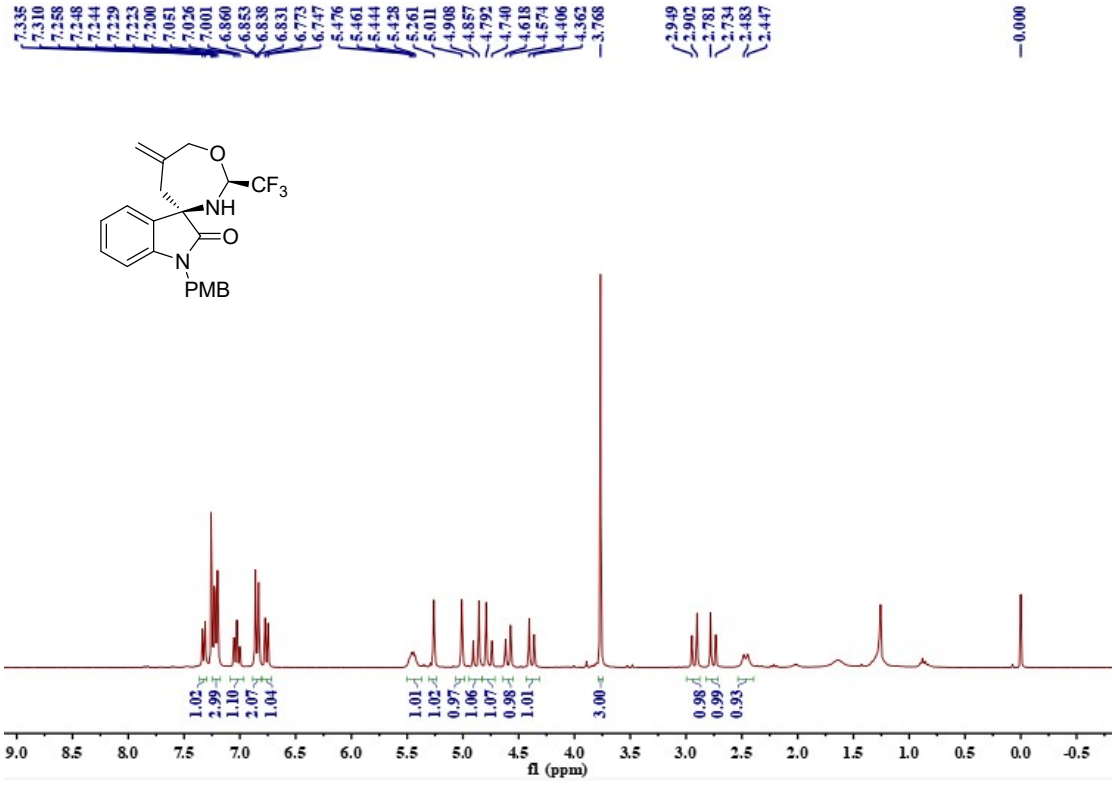
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3a**



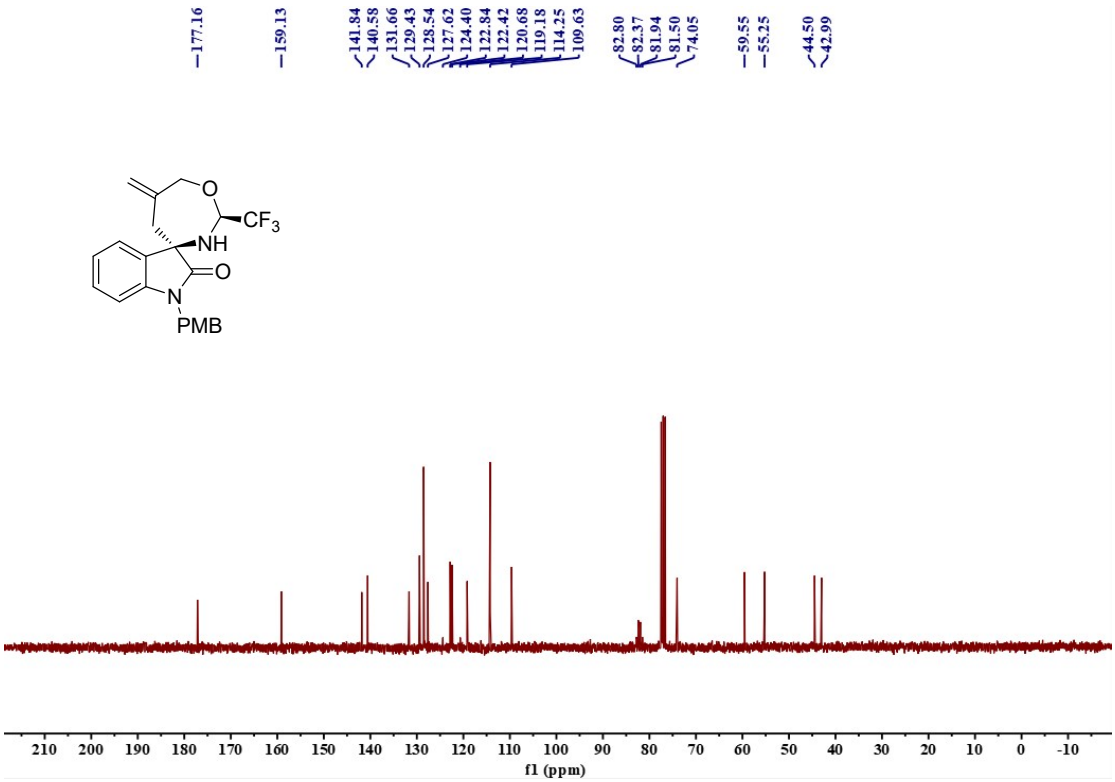
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3a**



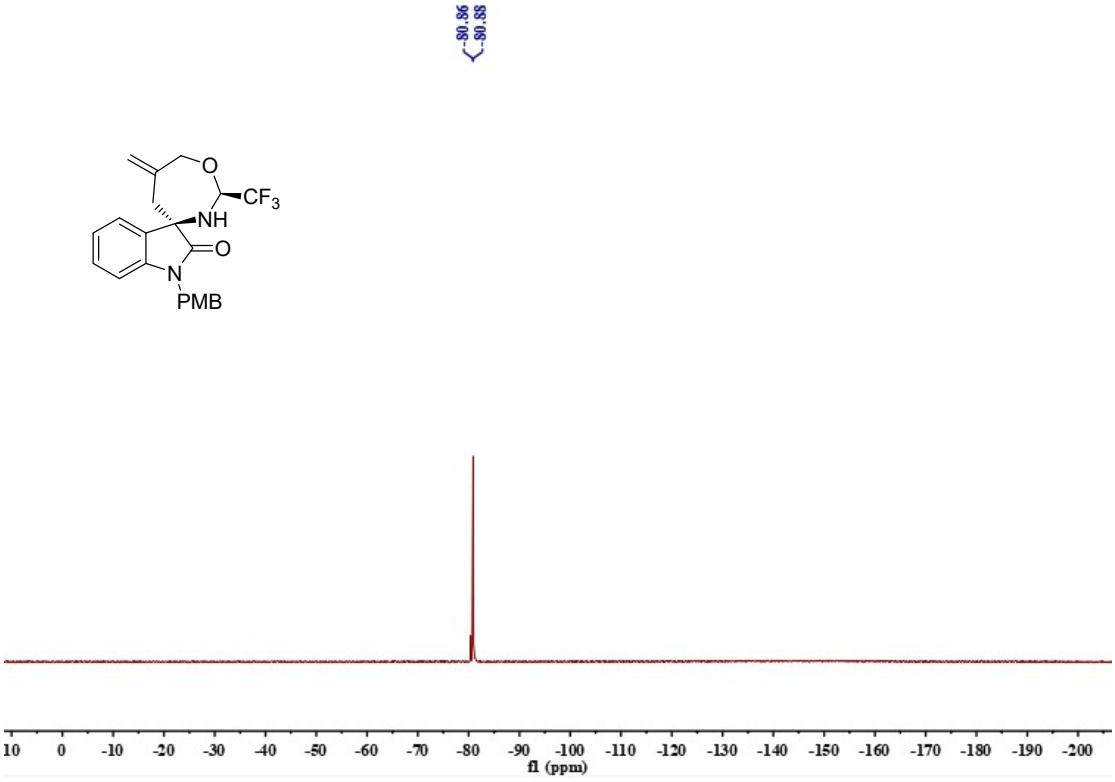
^{19}F NMR (CDCl3, 282 MHz) NMR of **3a**



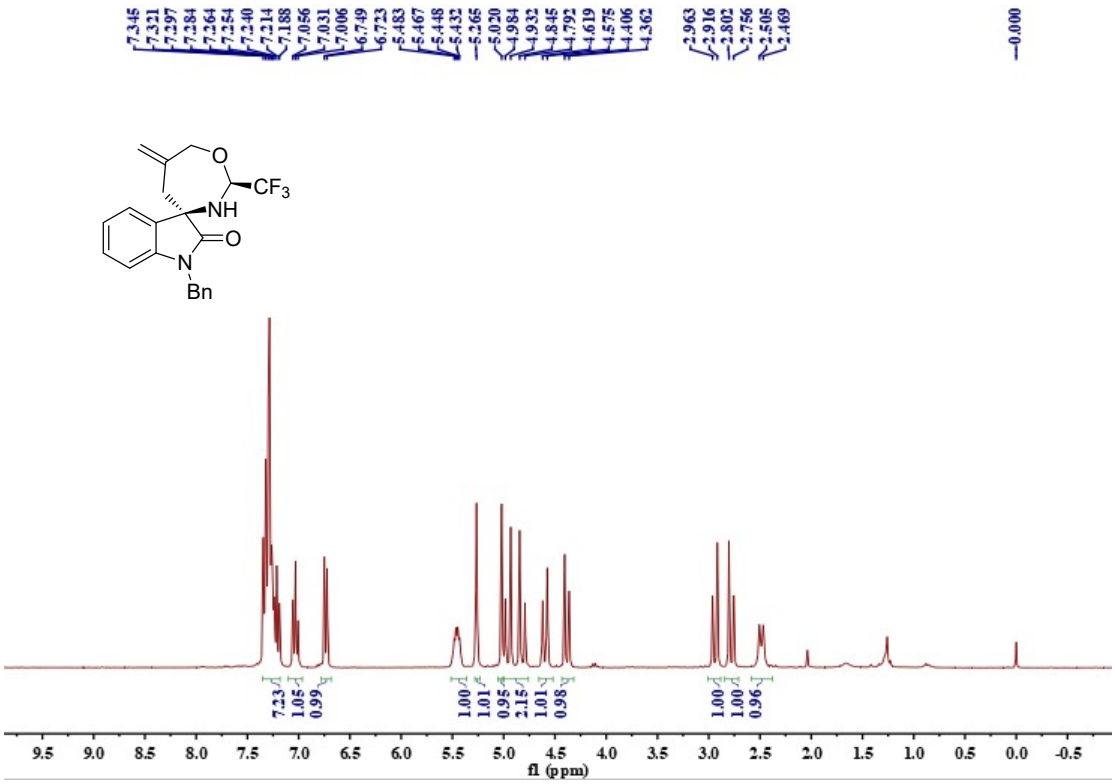
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3b**



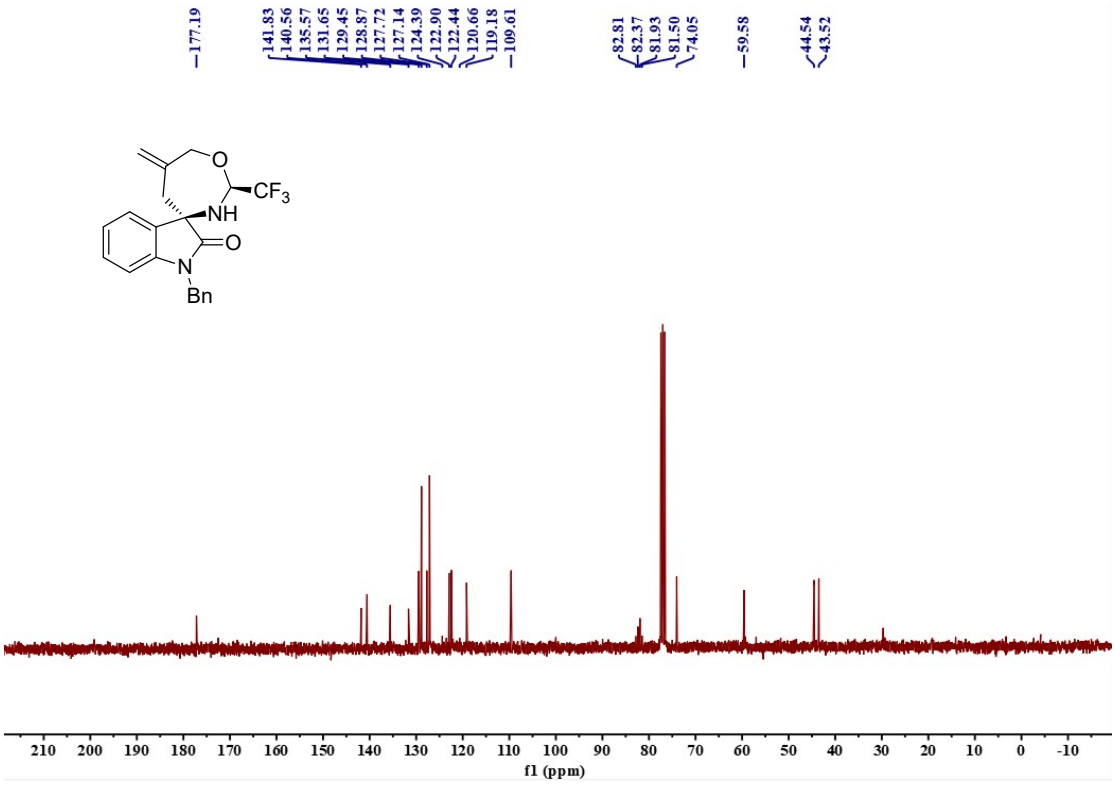
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3b**



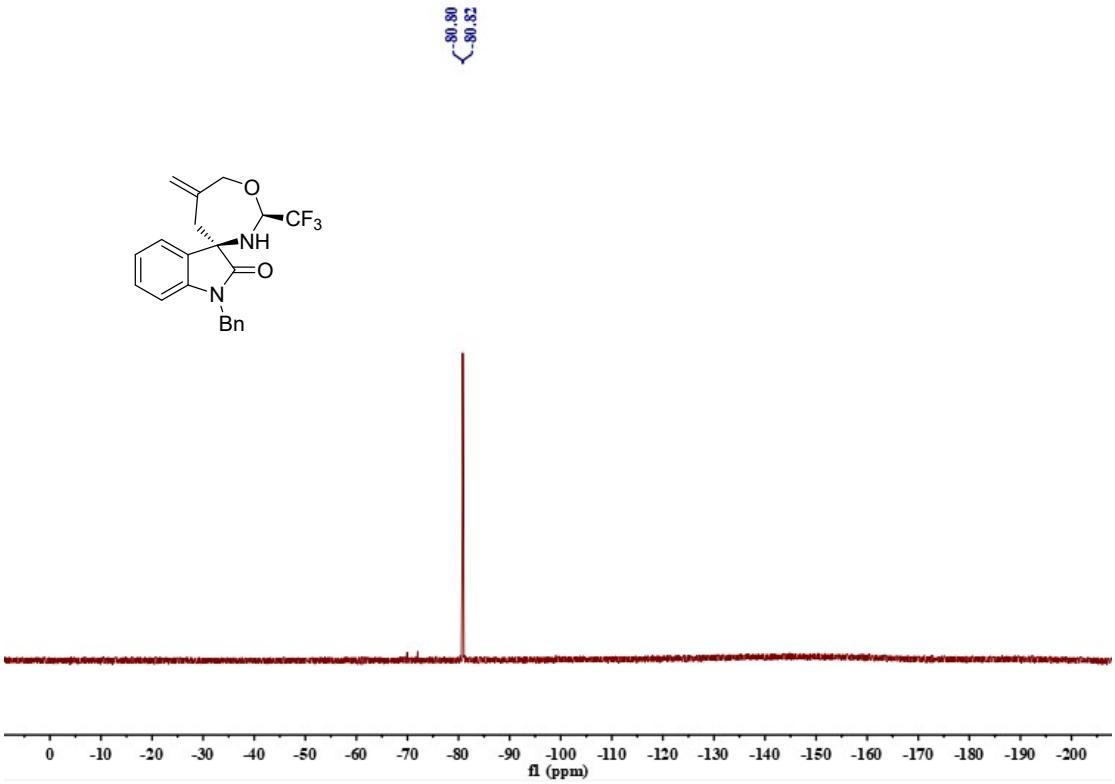
^{19}F NMR ($CDCl_3$, 282 MHz) NMR of **3b**



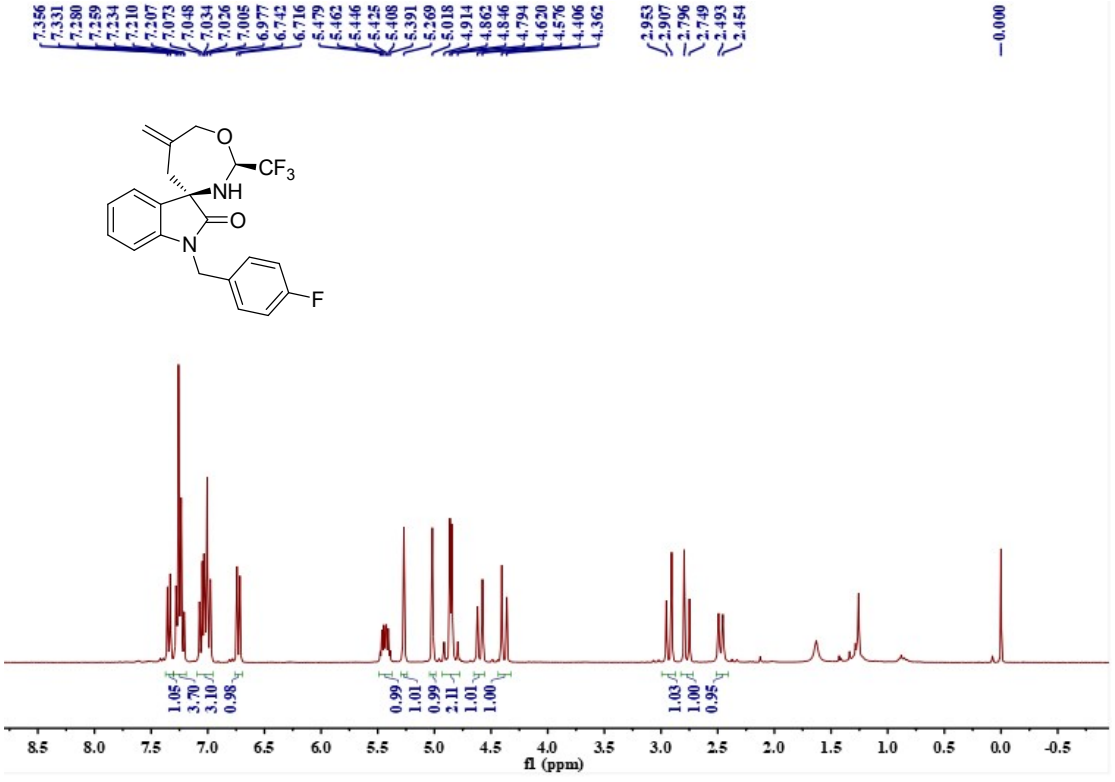
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3c**



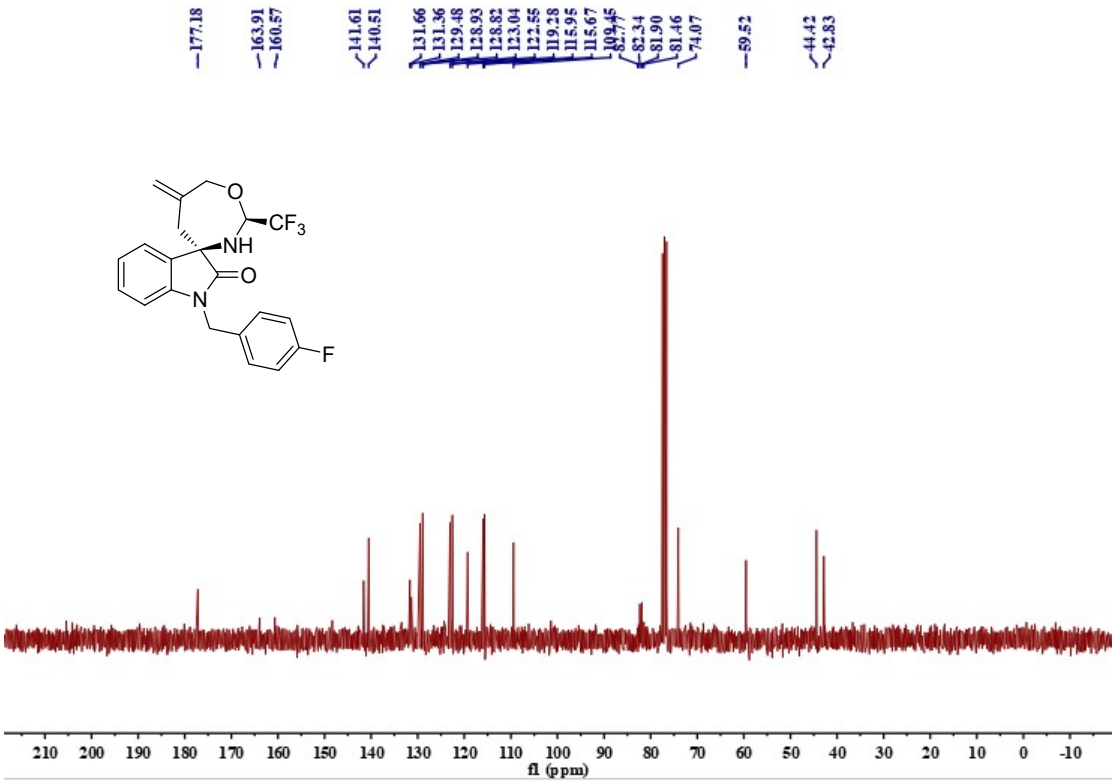
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3c**



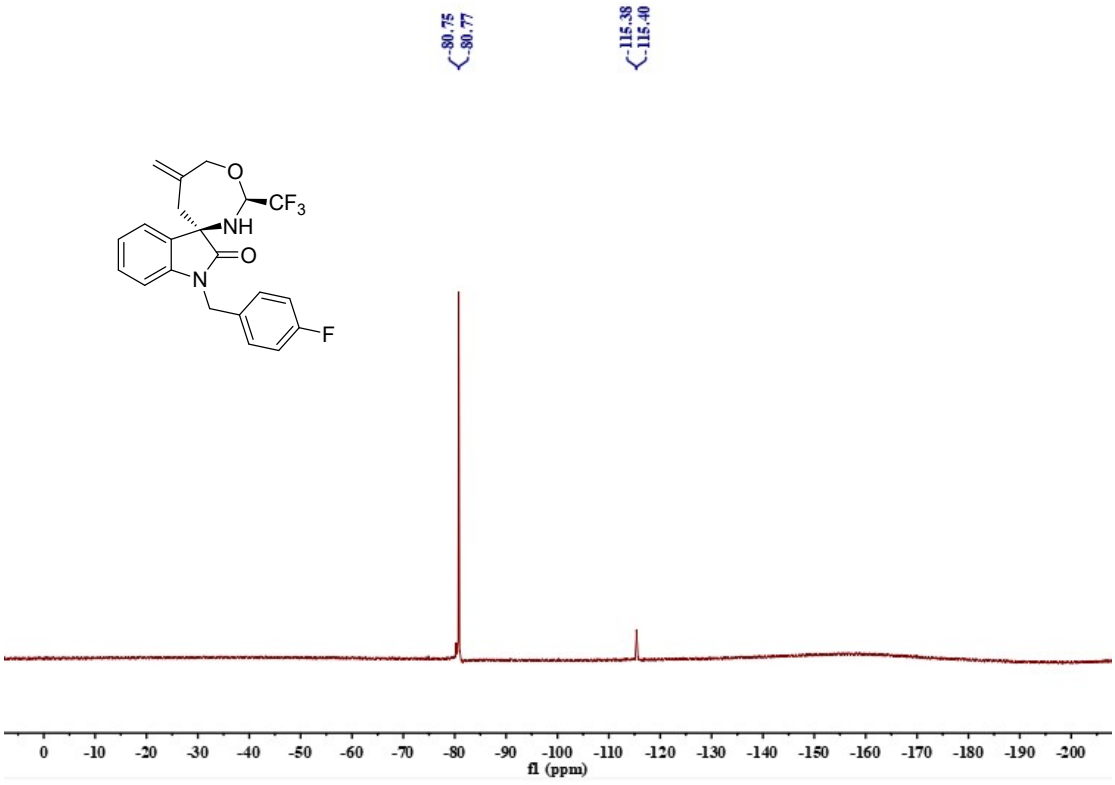
^{19}F NMR (CDCl3, 282 MHz) NMR of **3c**



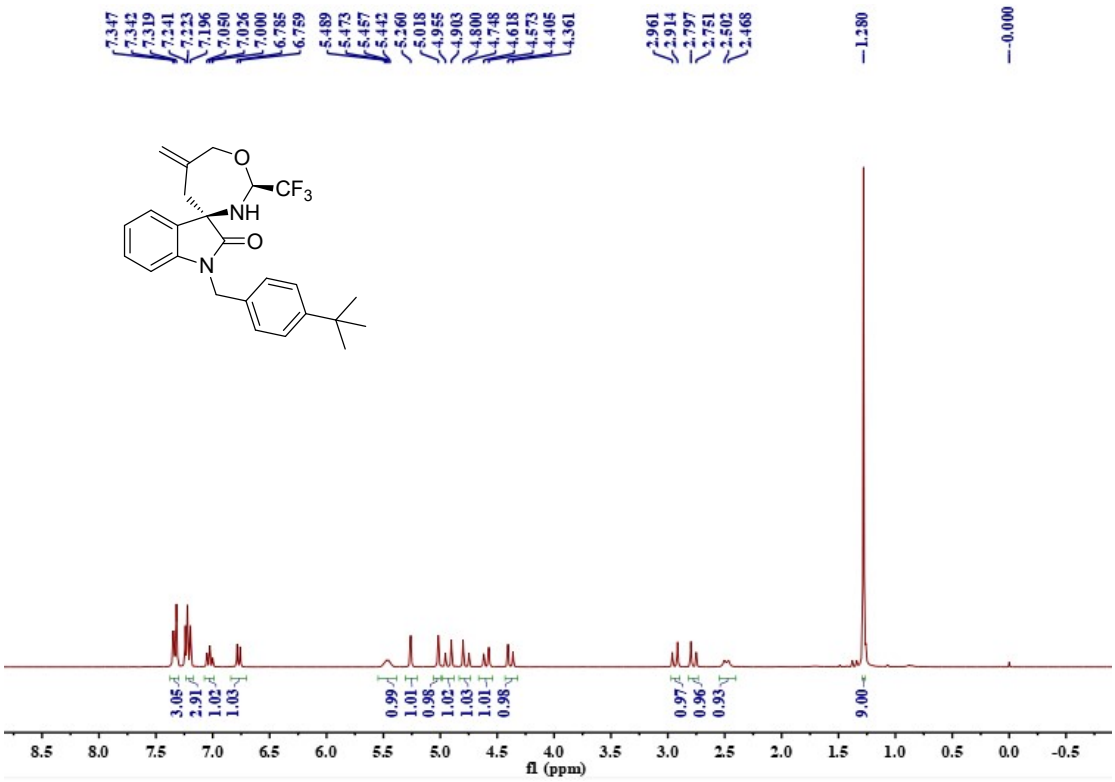
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3d**



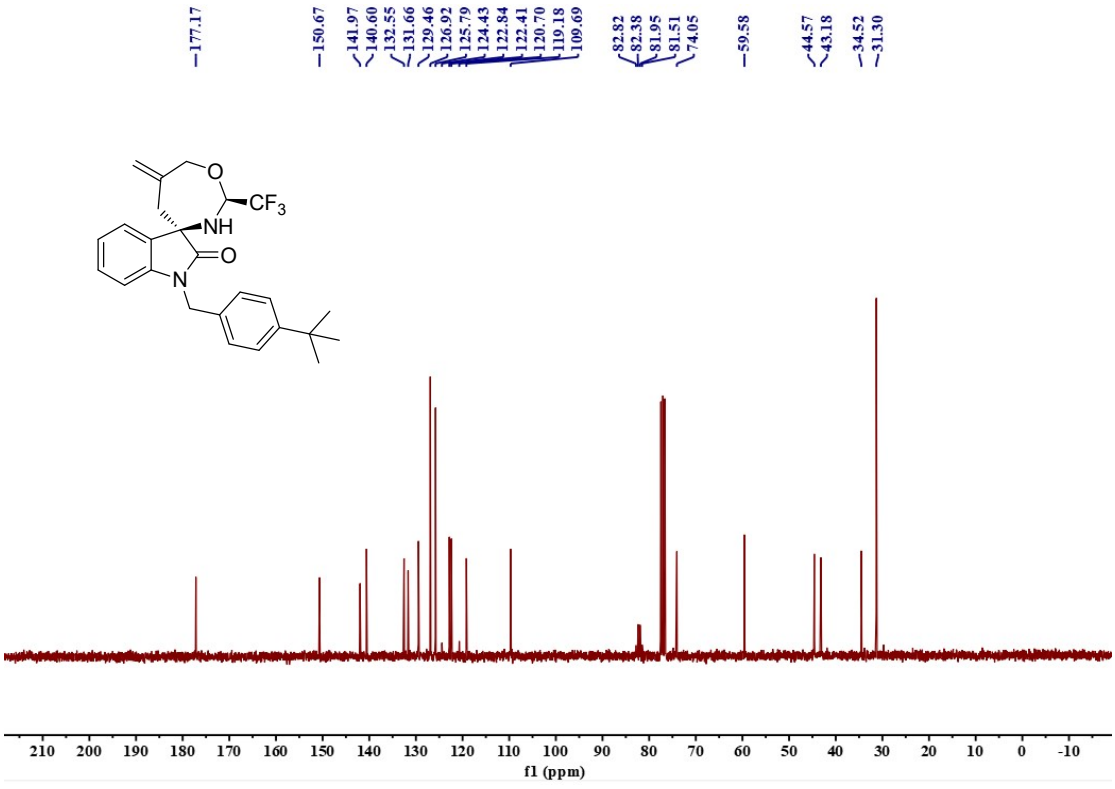
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3d**



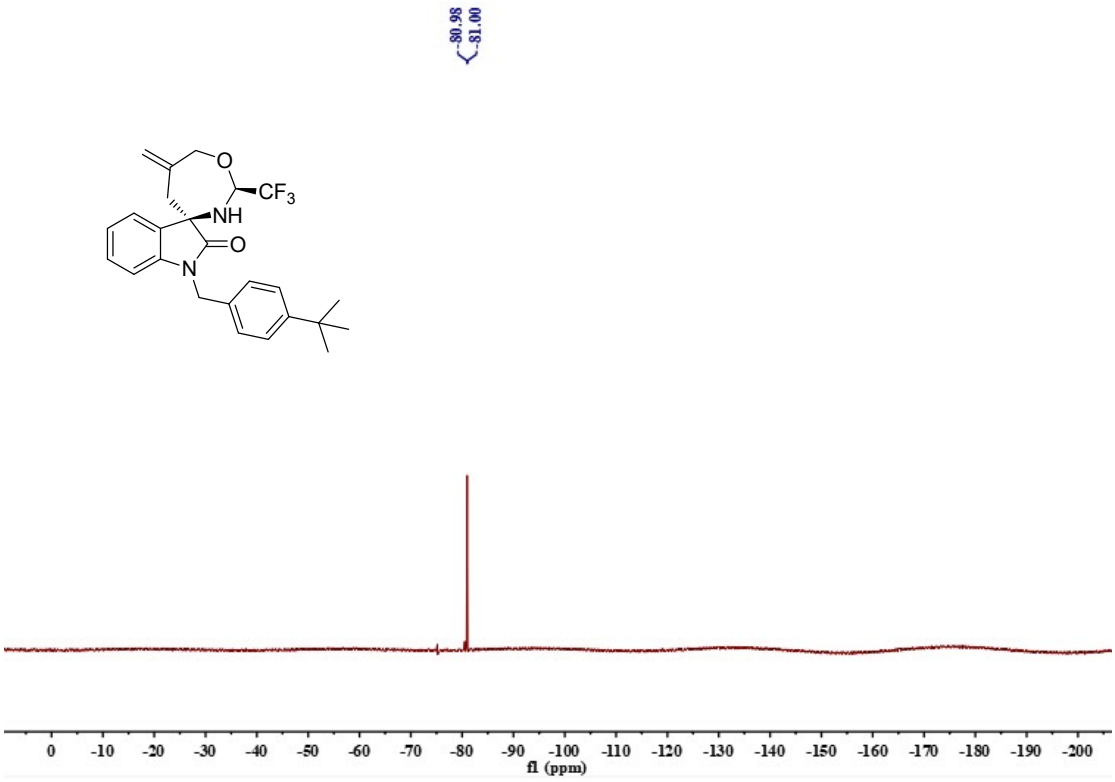
^{19}F NMR (CDCl3, 282 MHz) NMR of **3d**



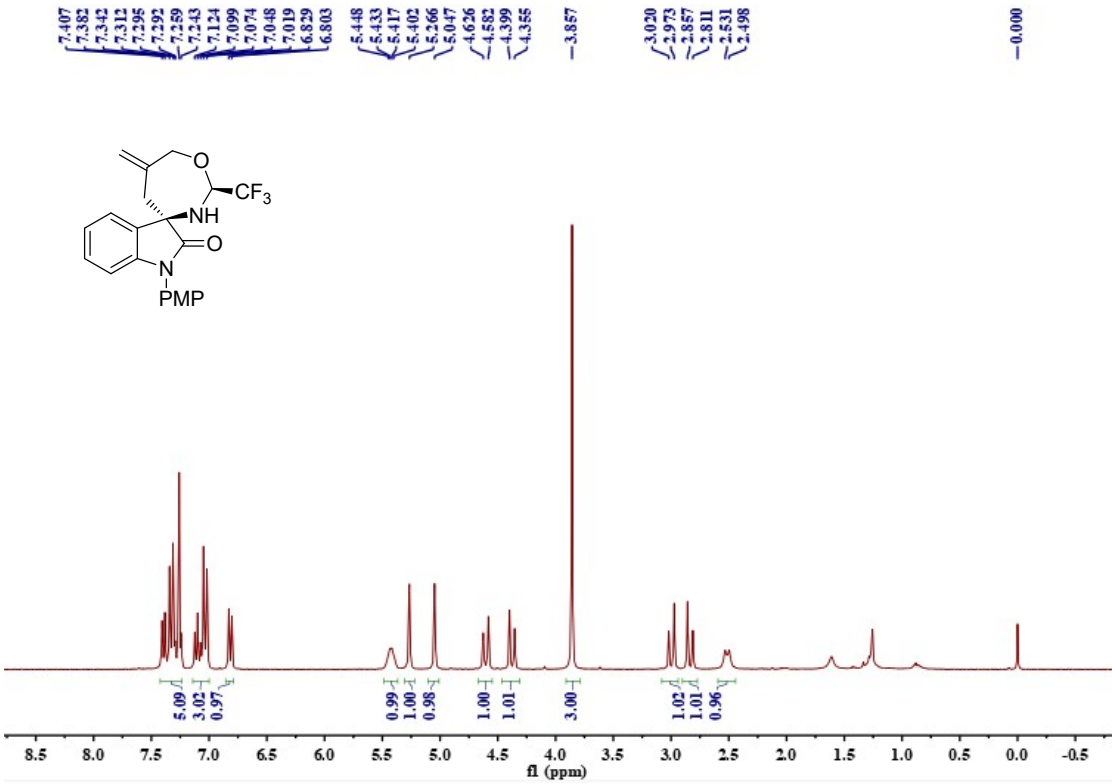
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3e**



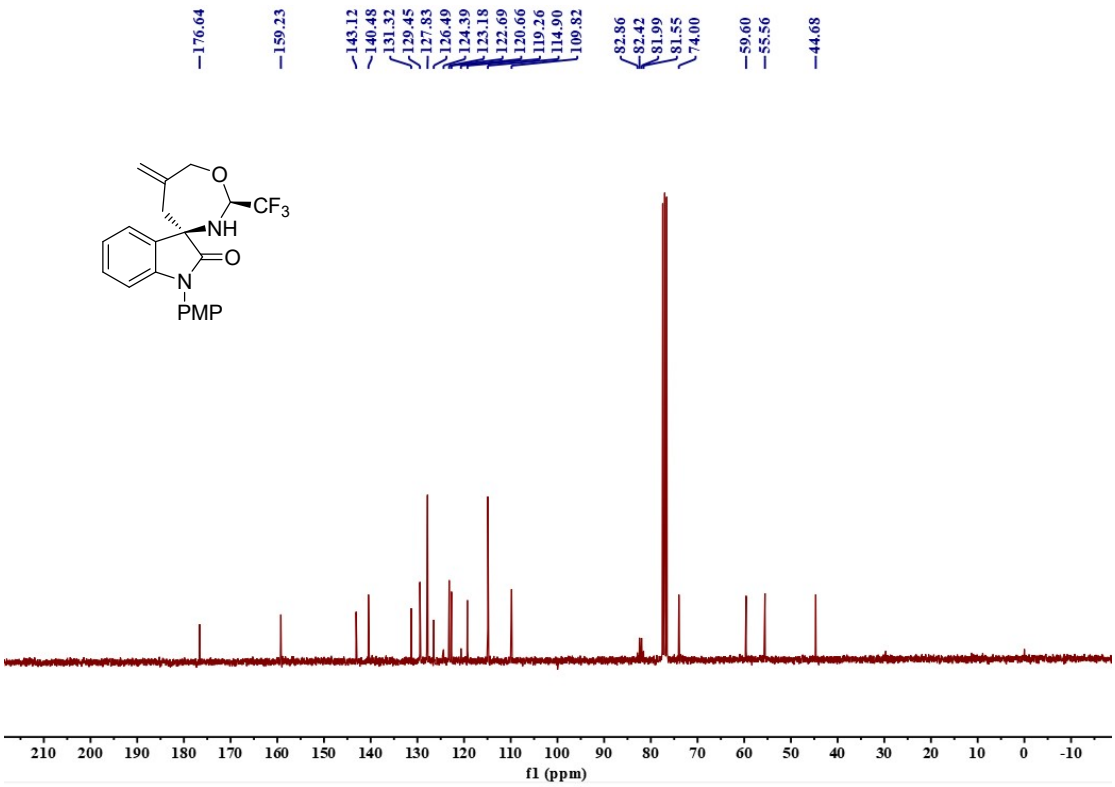
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3e**



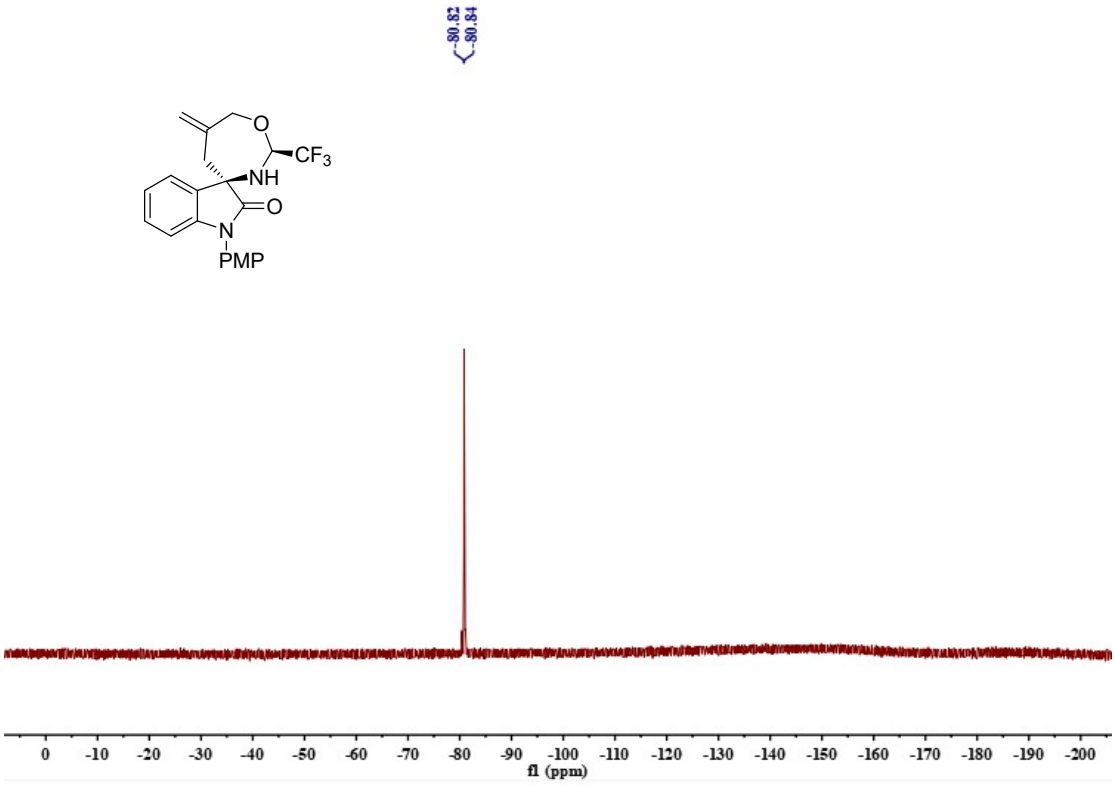
^{19}F NMR (CDCl3, 282 MHz) NMR of **3e**



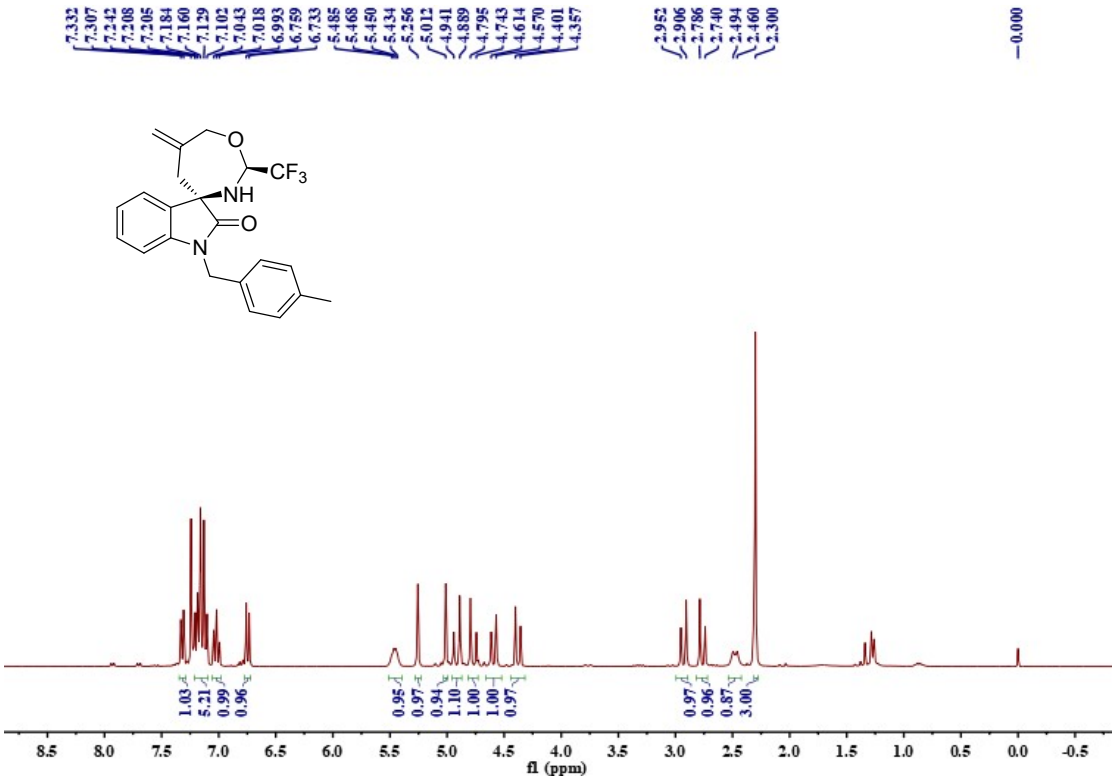
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3f**



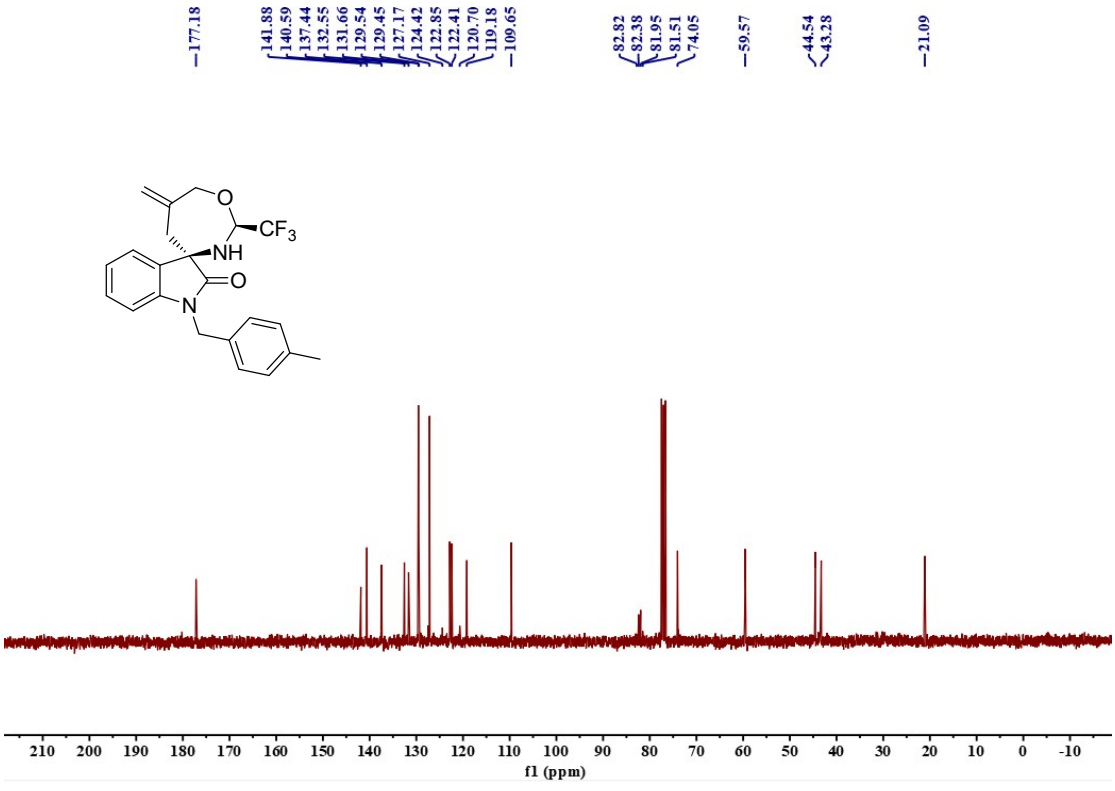
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3f**



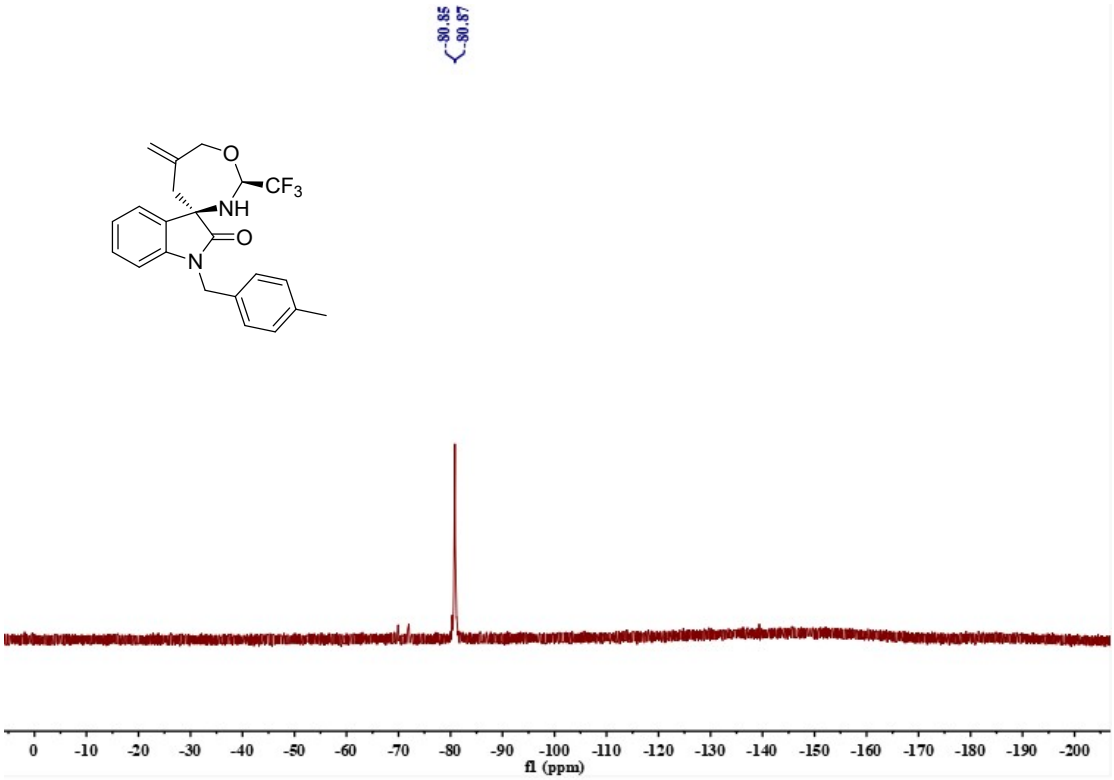
^{19}F NMR (CDCl3, 282 MHz) NMR of **3f**



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



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



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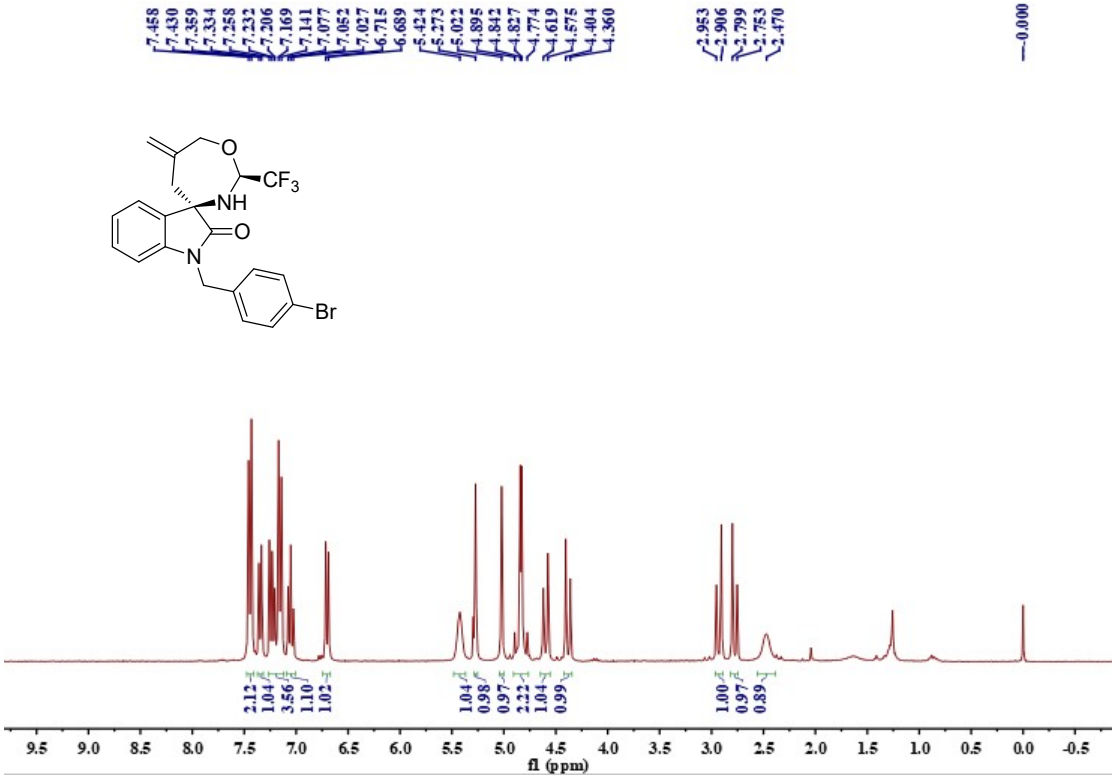
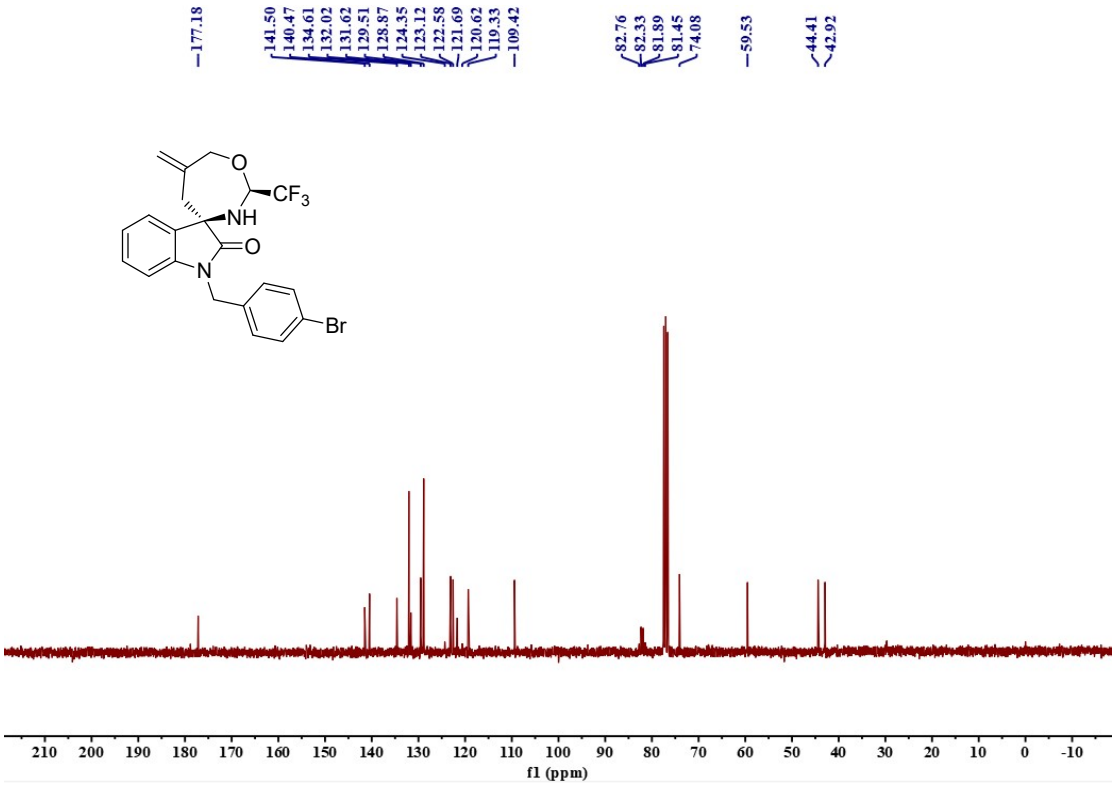
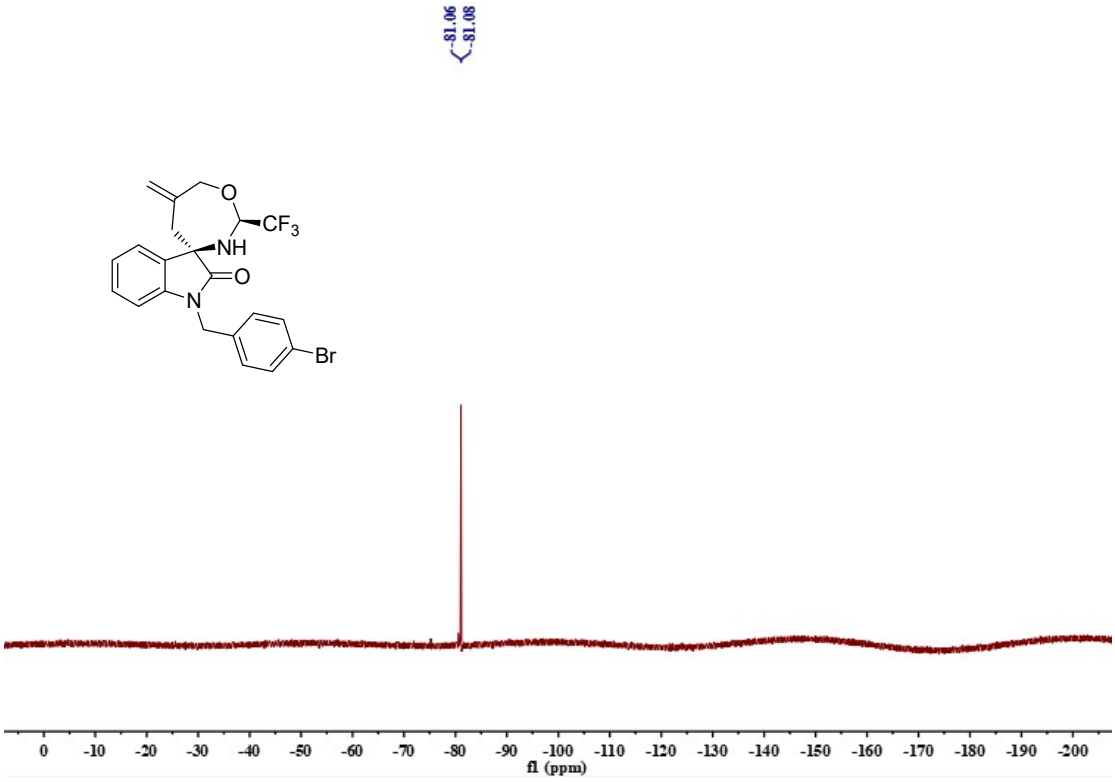


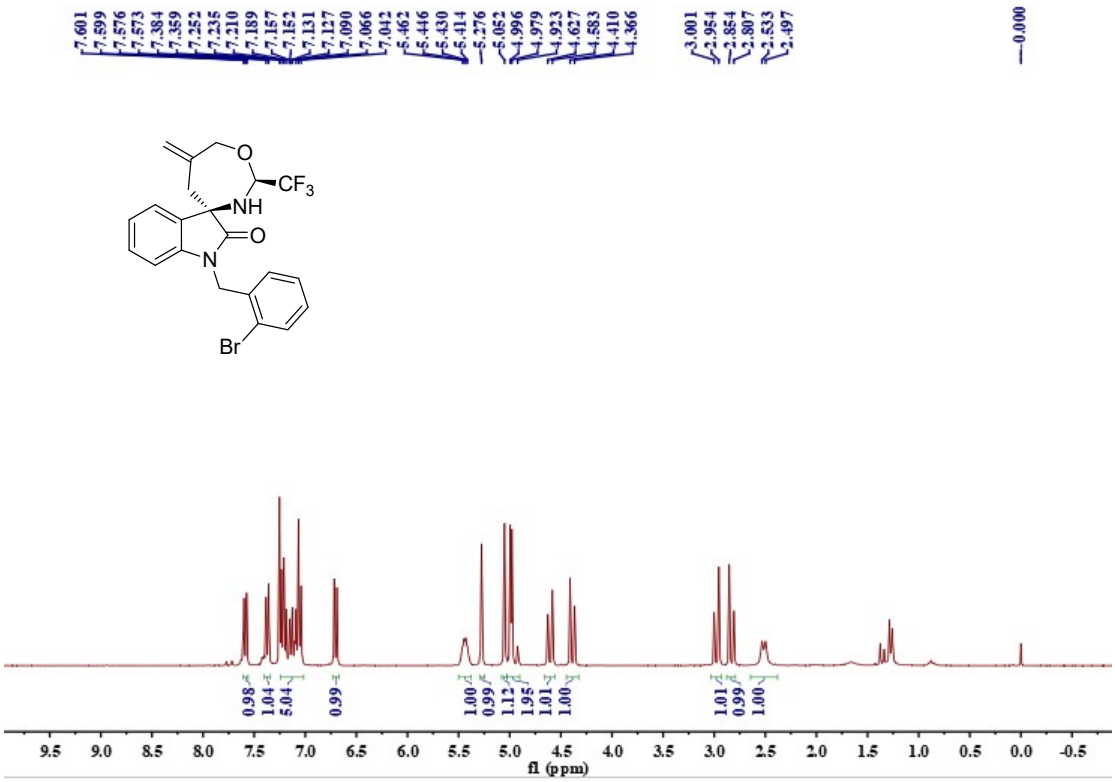
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3h**



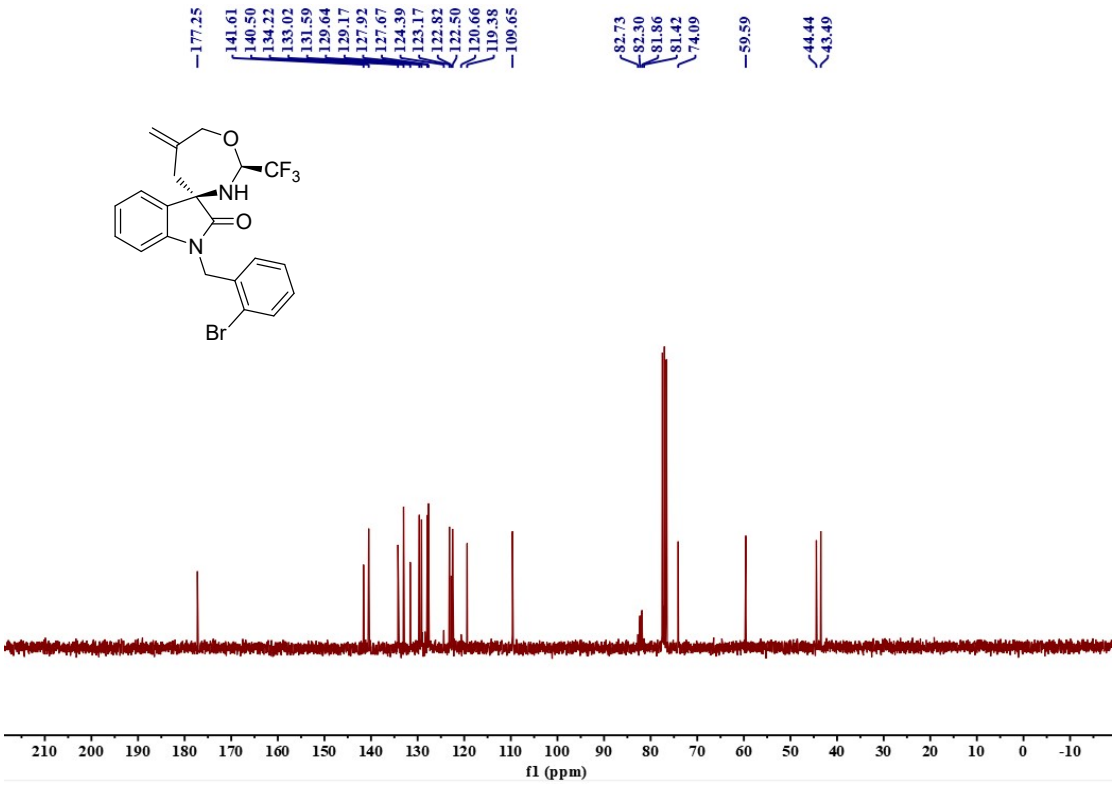
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3h**



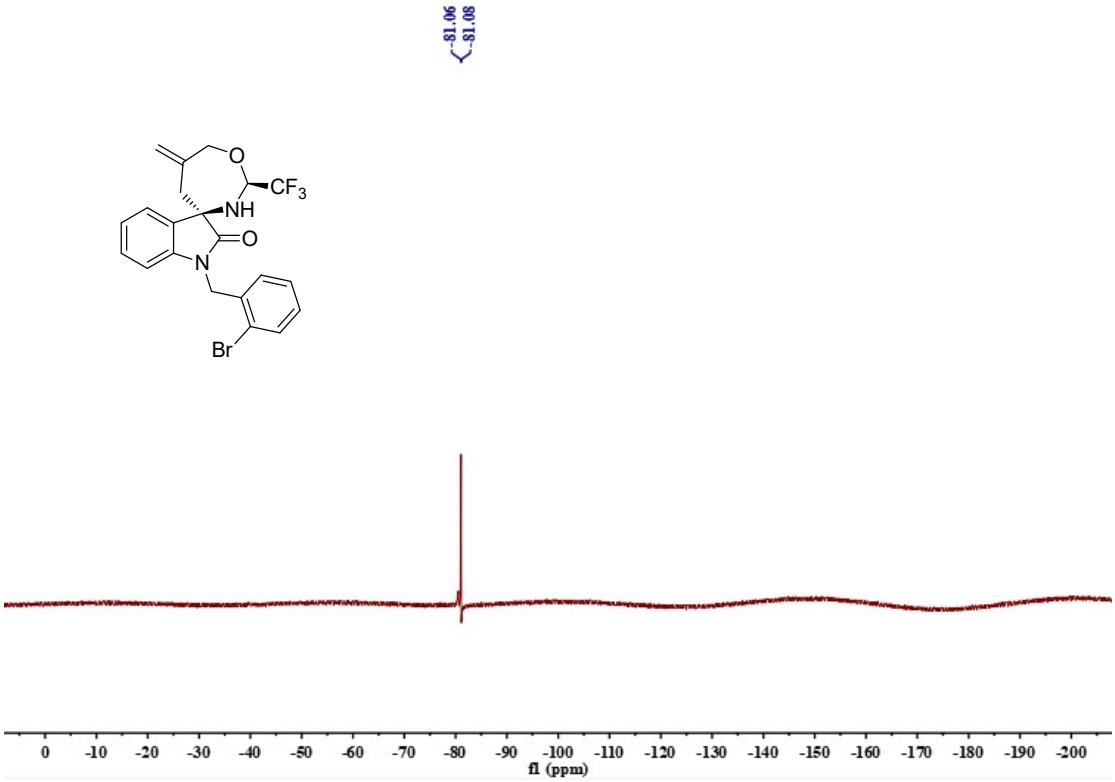
^{19}F NMR (CDCl3, 282 MHz) NMR of **3h**



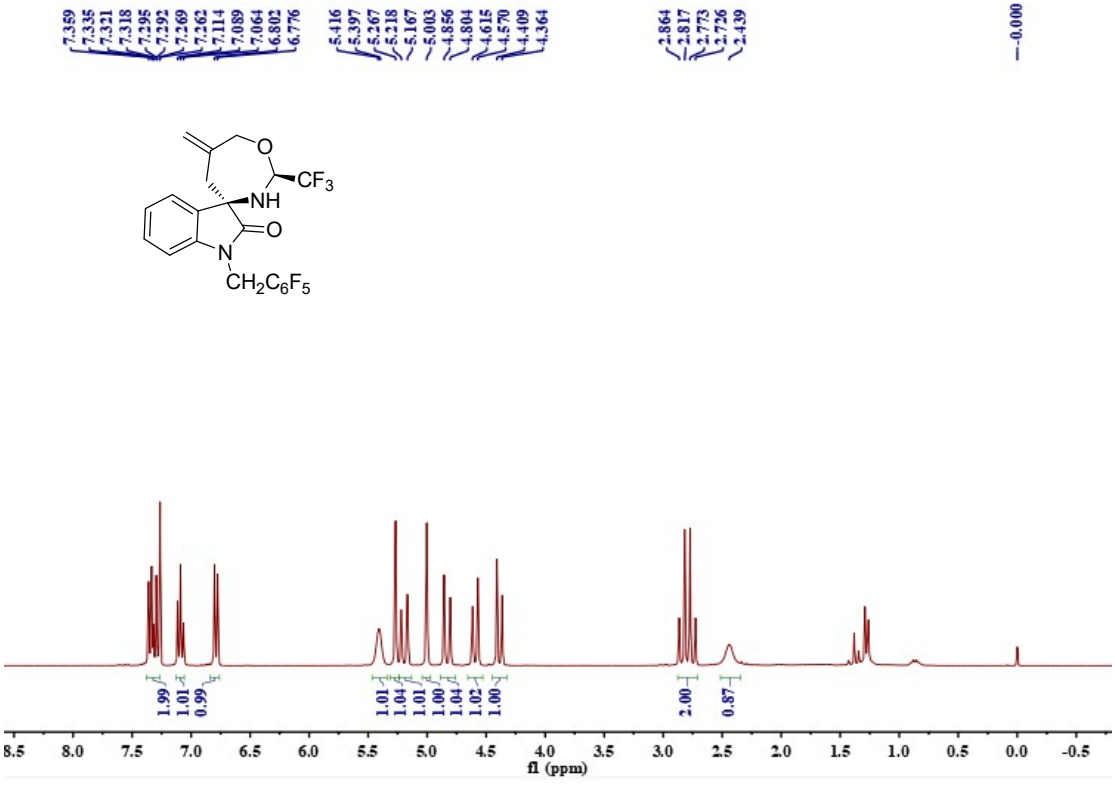
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3i**



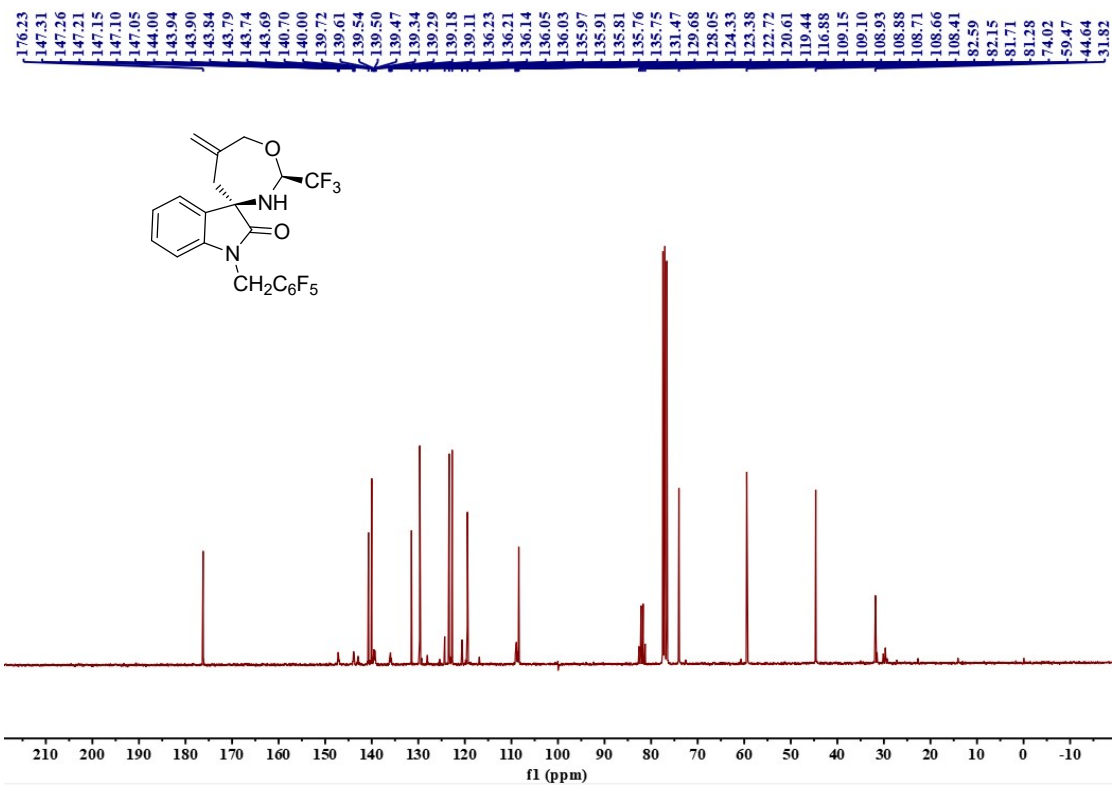
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3i**



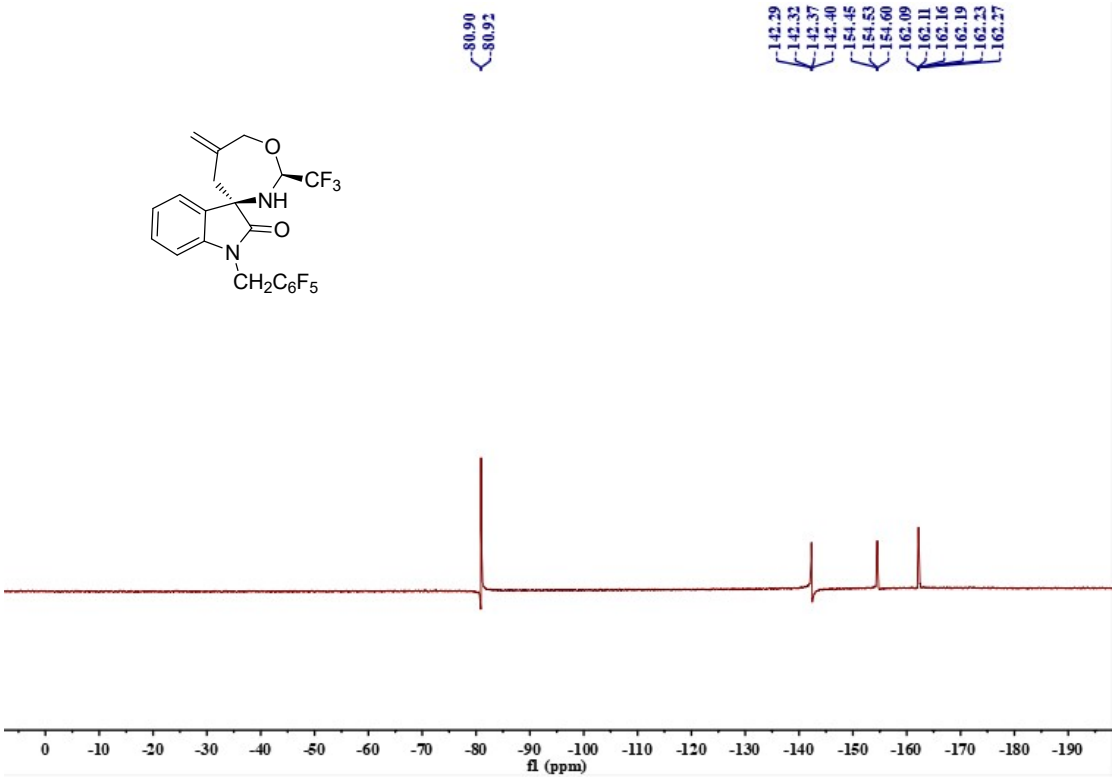
^{19}F NMR (CDCl3, 282 MHz) NMR of **3i**



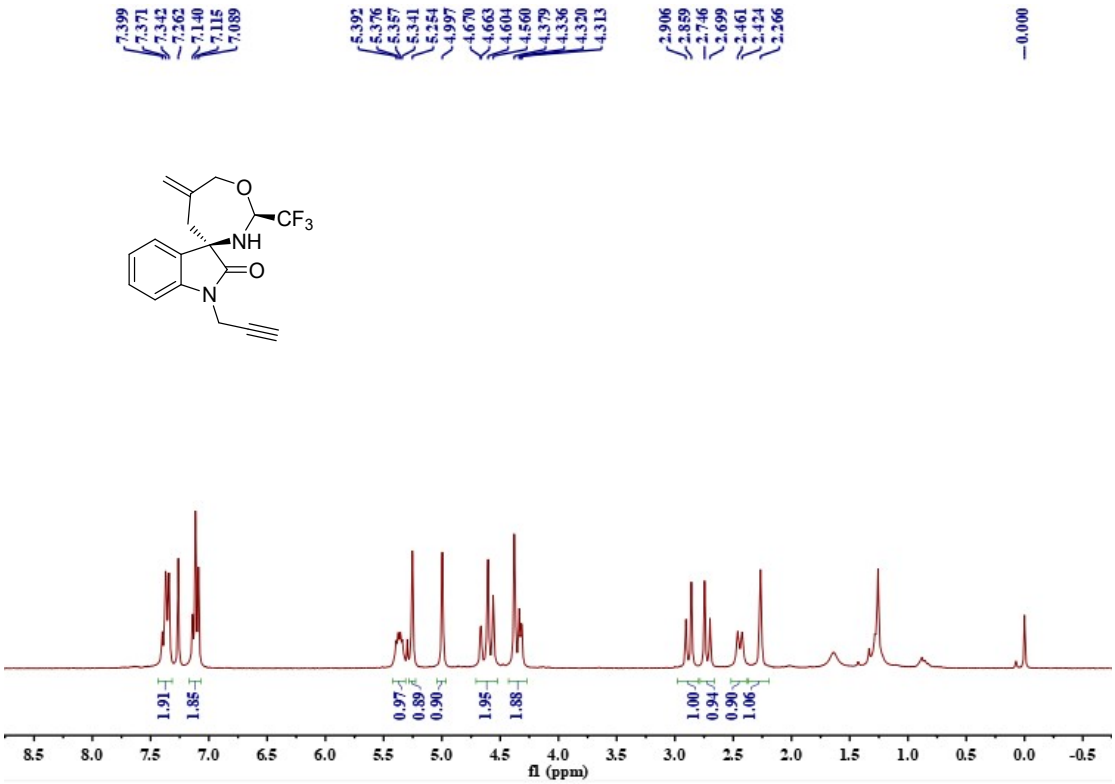
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3j**



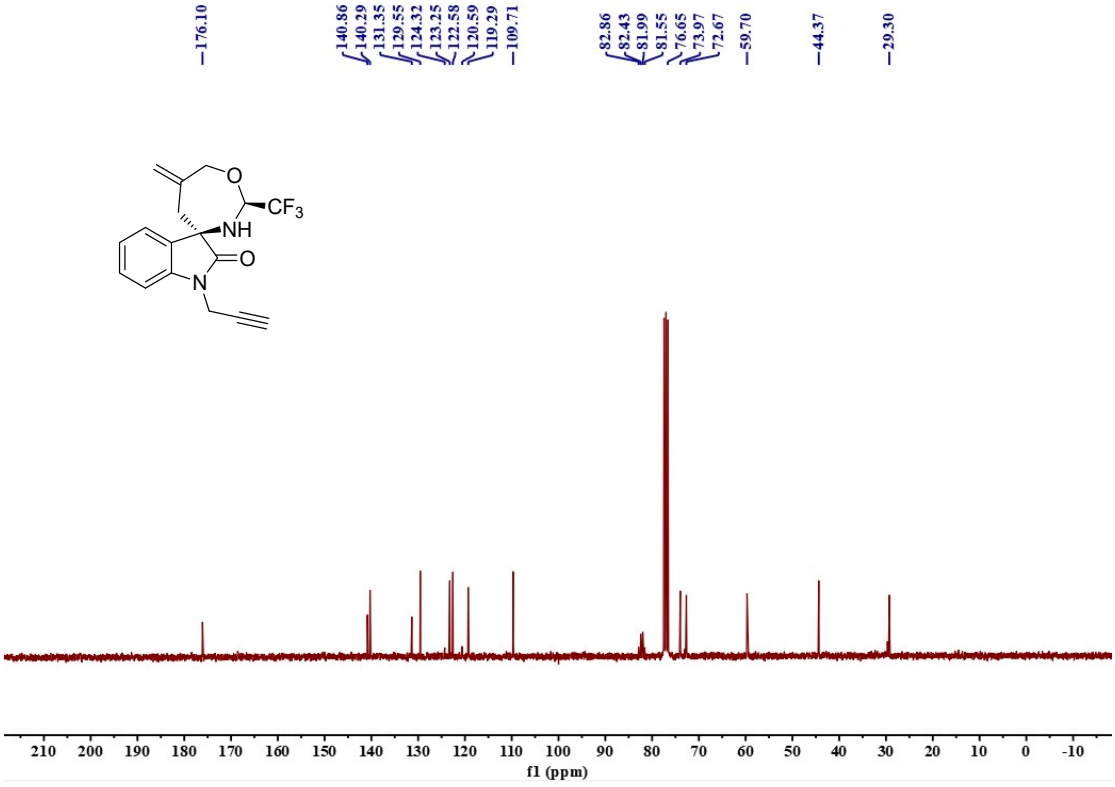
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3j**



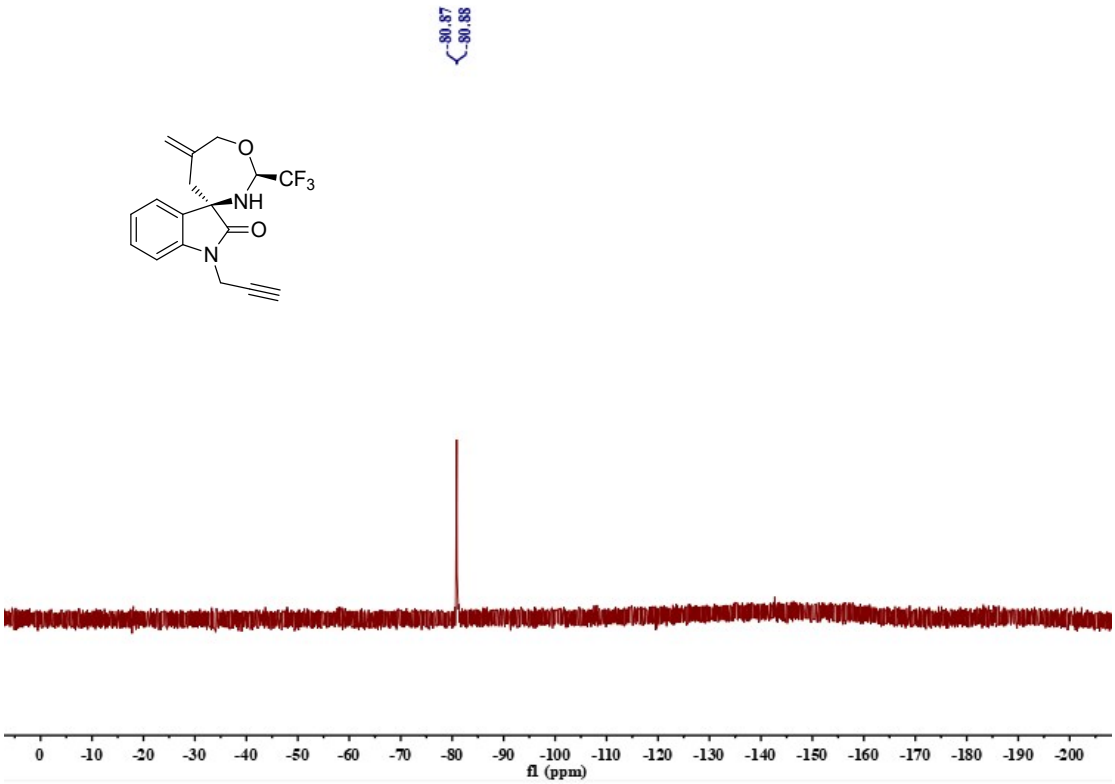
^{19}F NMR (CDCl3, 282 MHz) NMR of **3j**



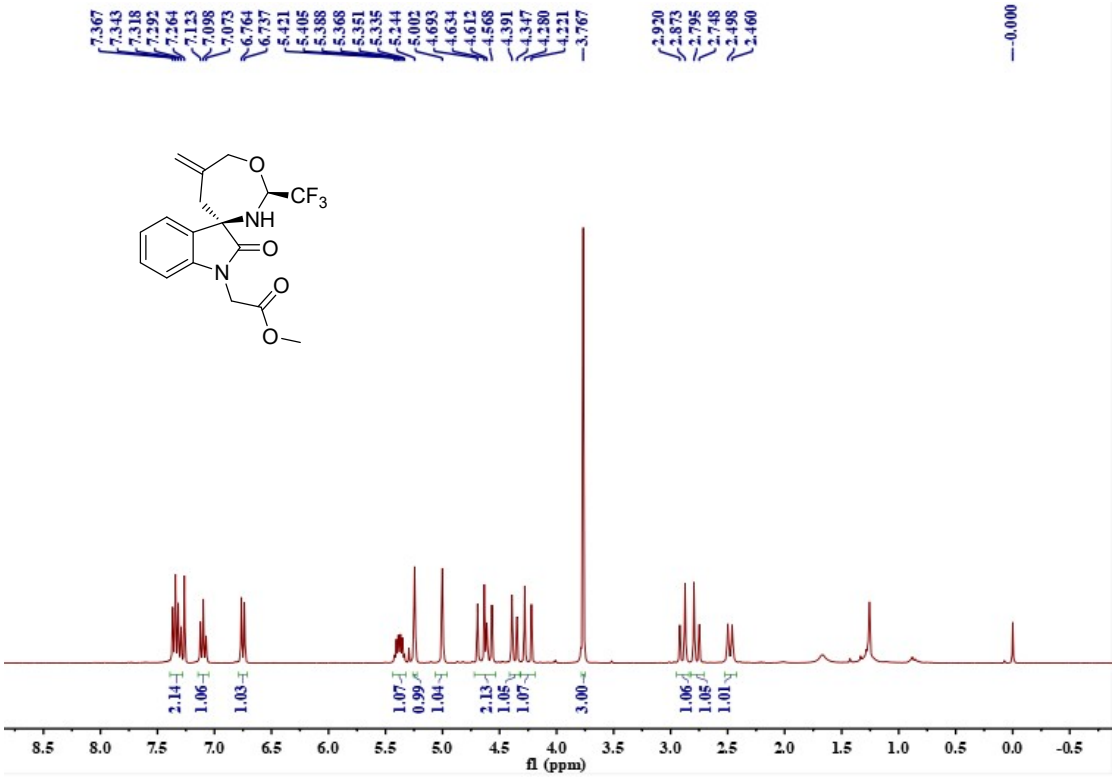
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3k**



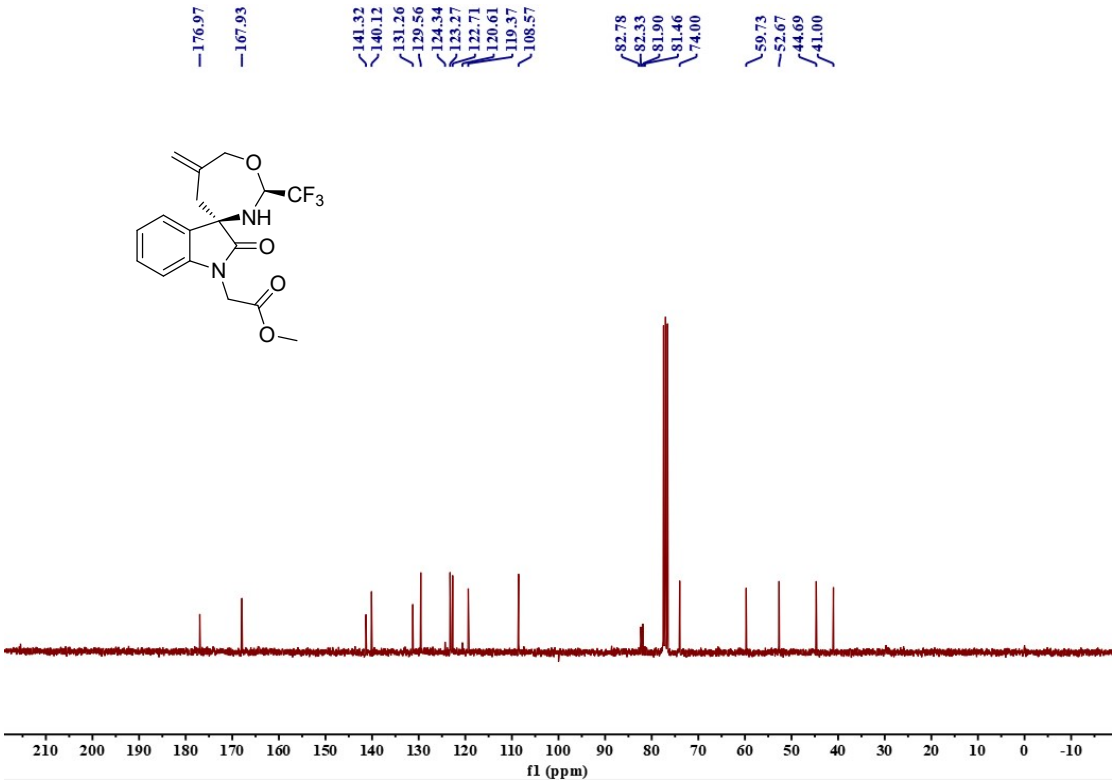
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3k**



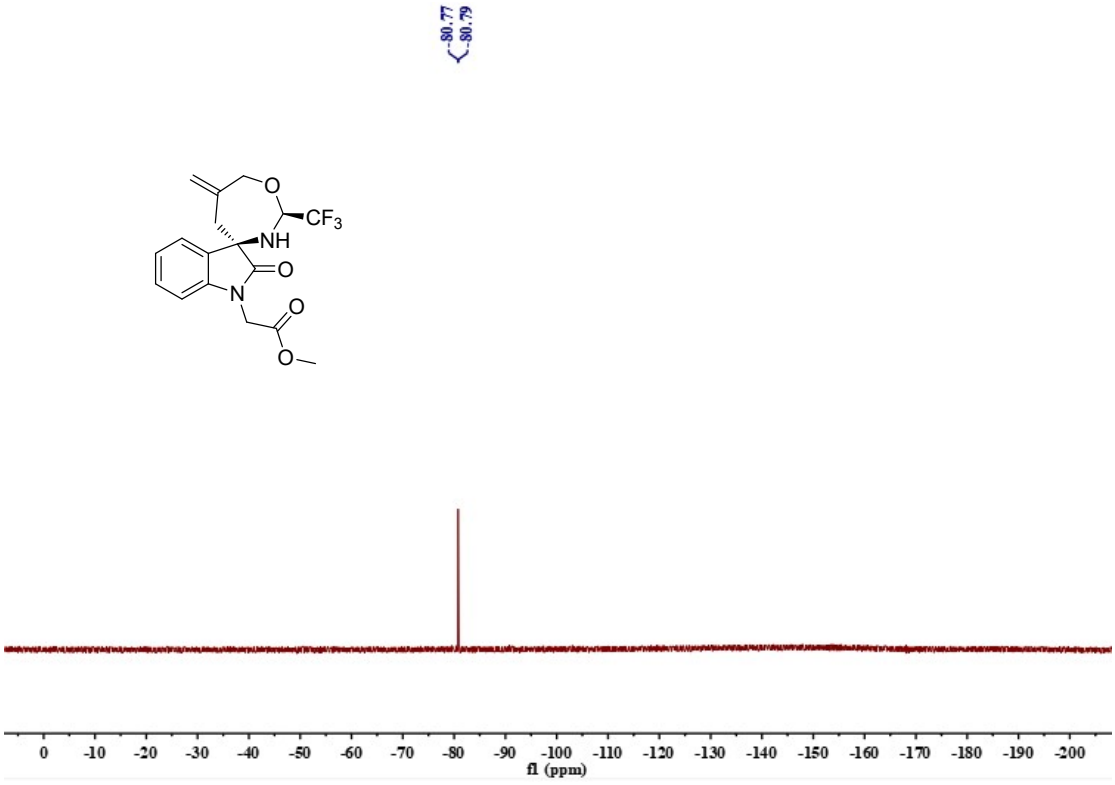
^{19}F NMR (CDCl3, 282 MHz) NMR of **3k**



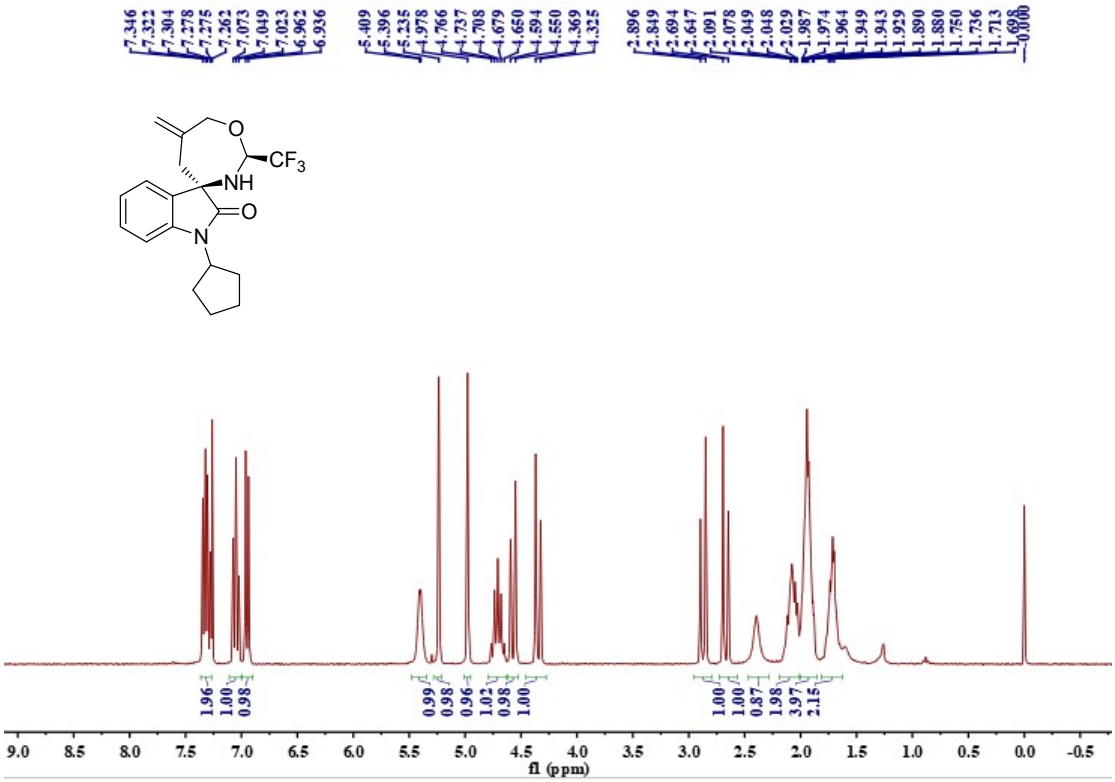
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3l**



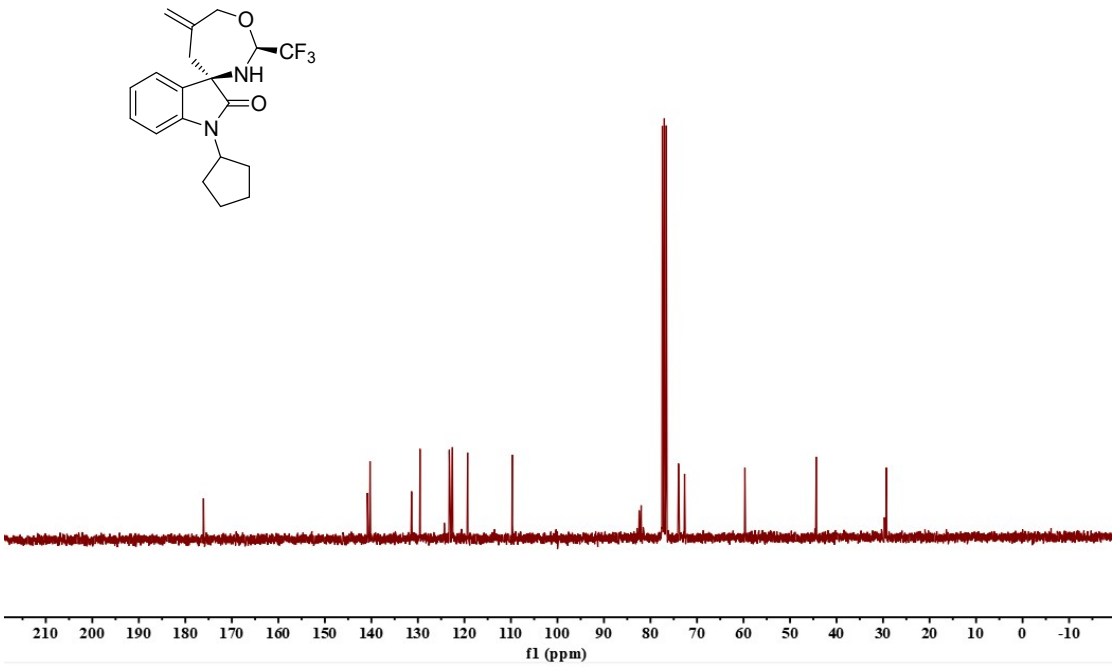
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3l**



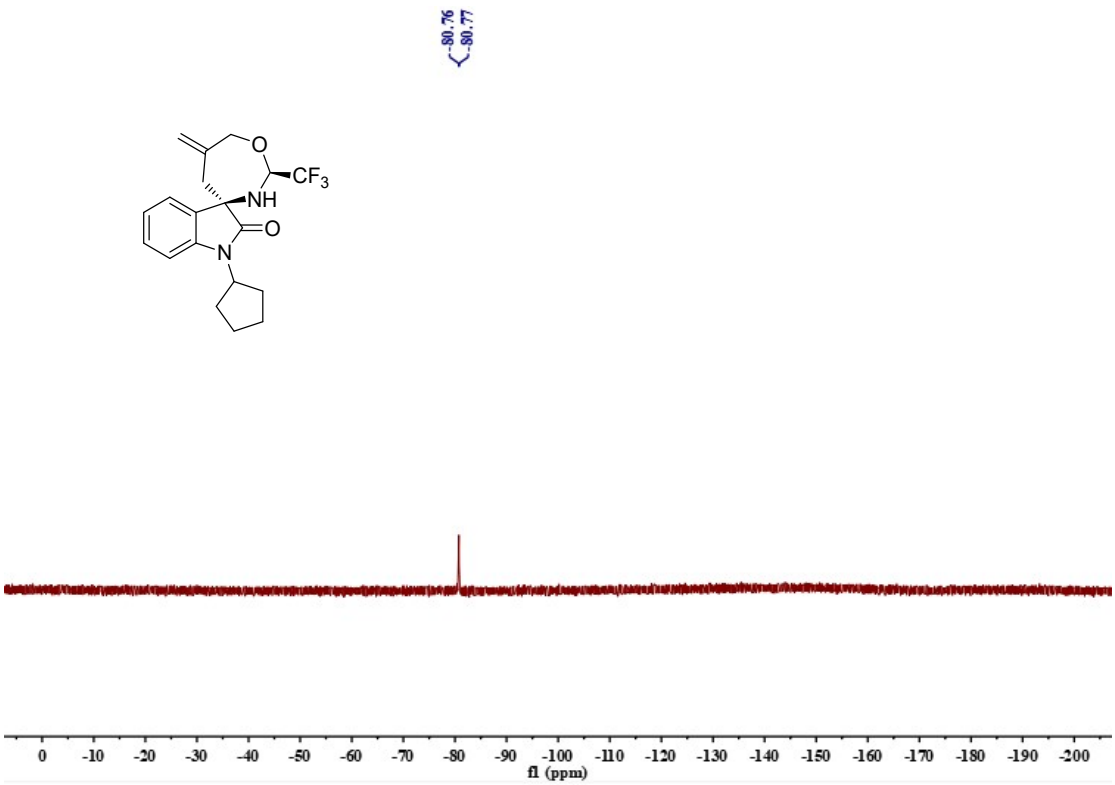
^{19}F NMR (CDCl3, 282 MHz) NMR of **3l**



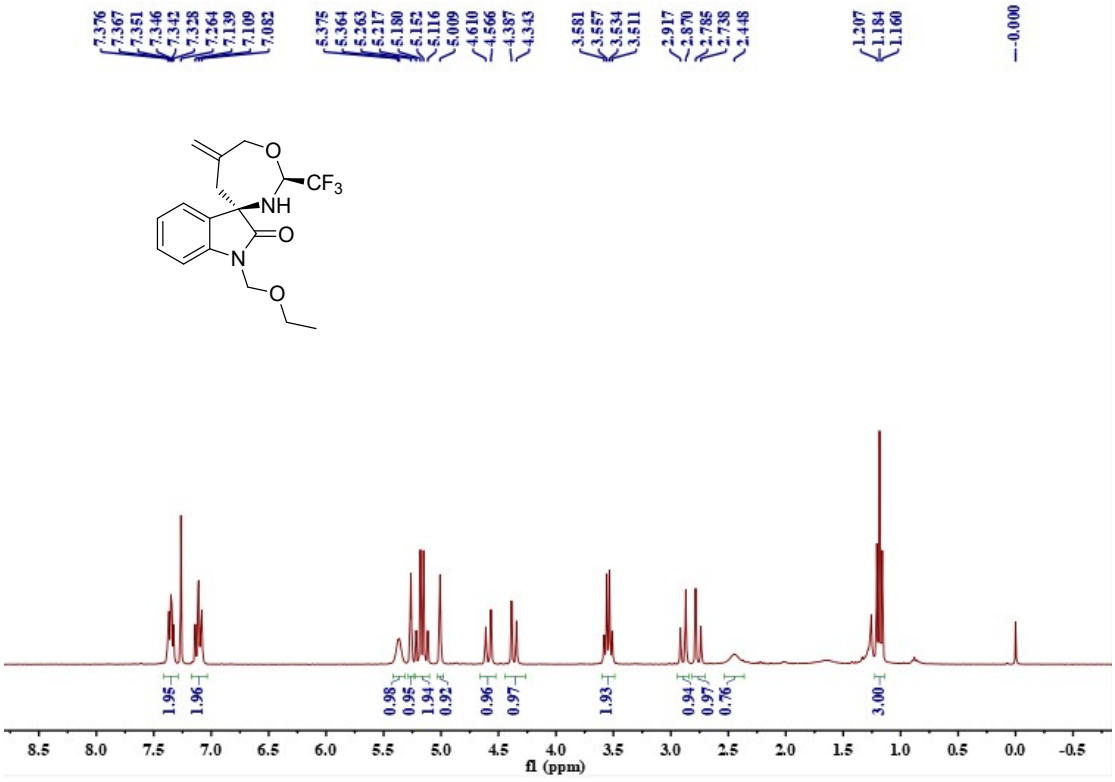
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3m**



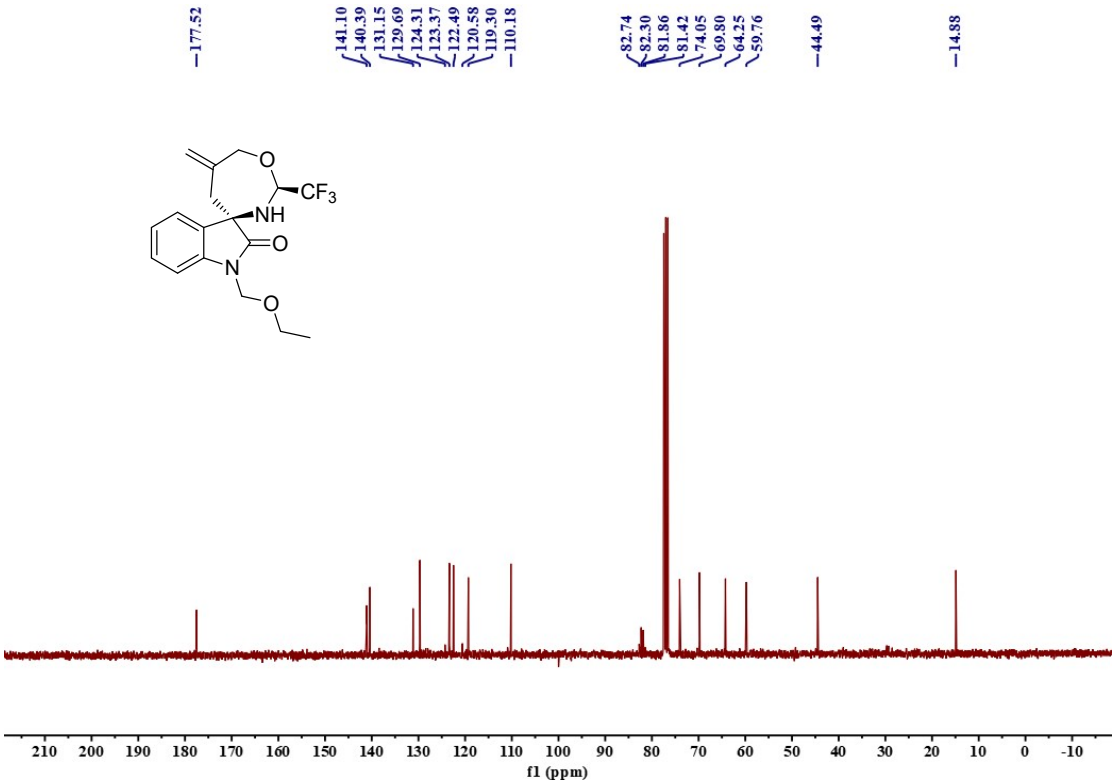
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3m**



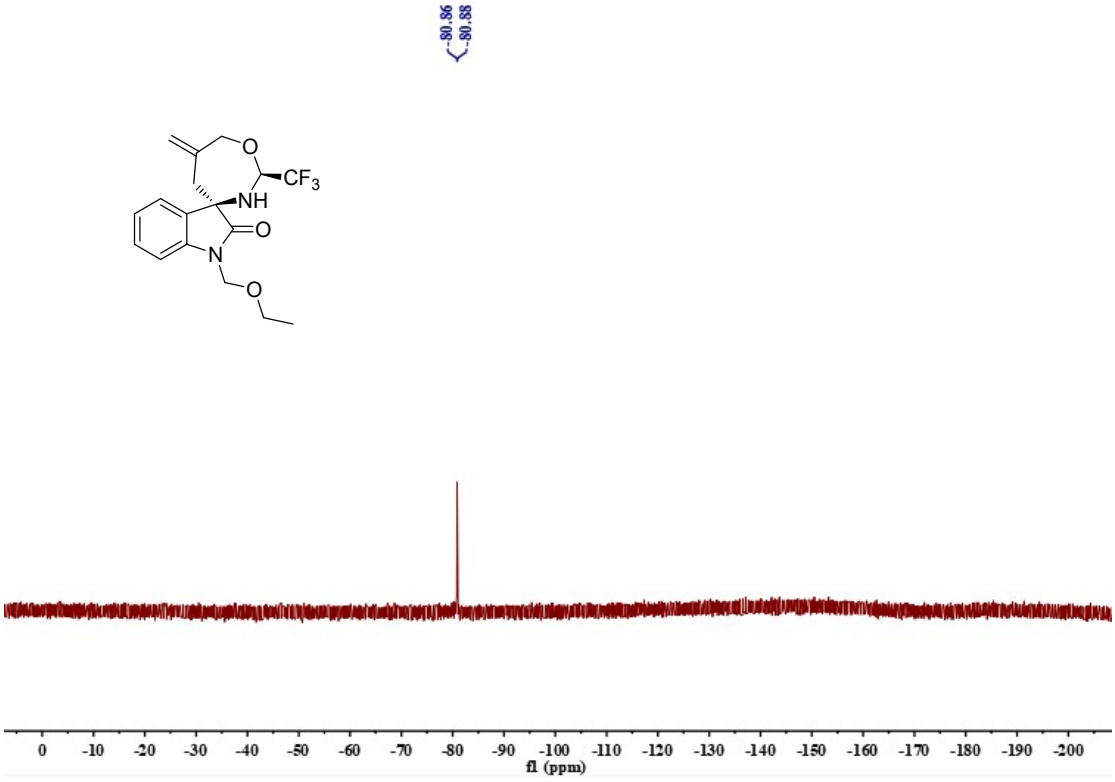
^{19}F NMR (CDCl3, 282 MHz) NMR of **3m**



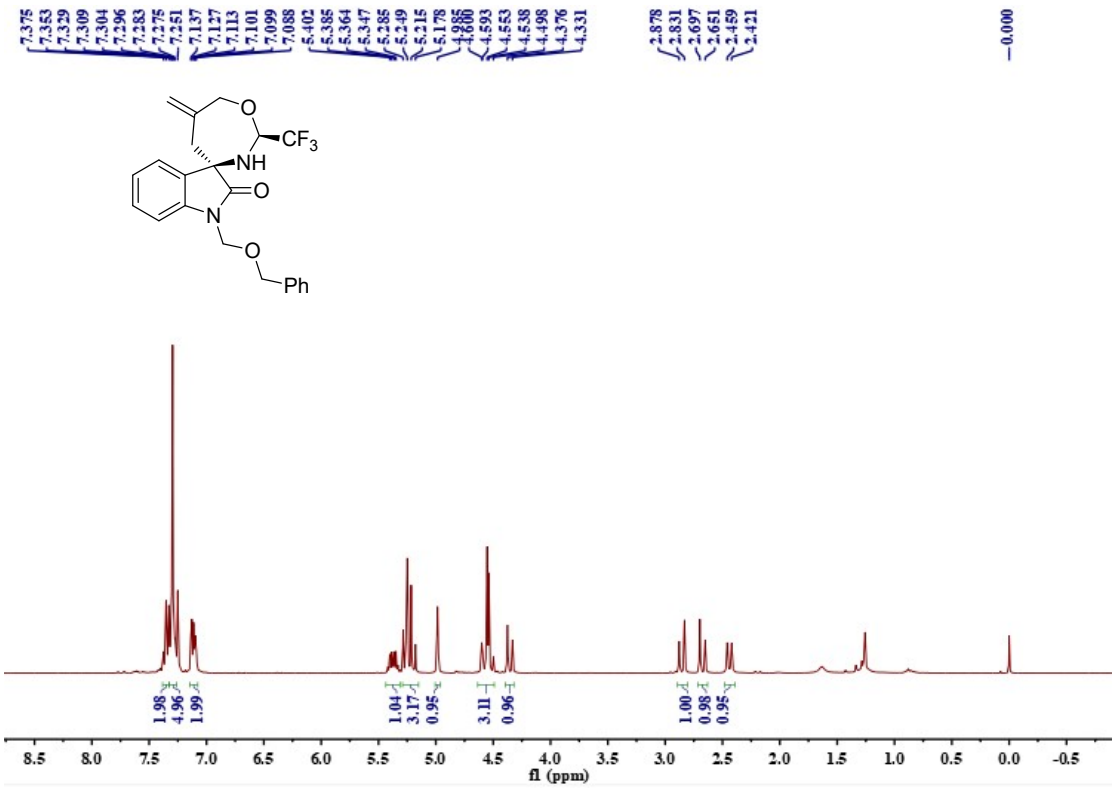
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3n**



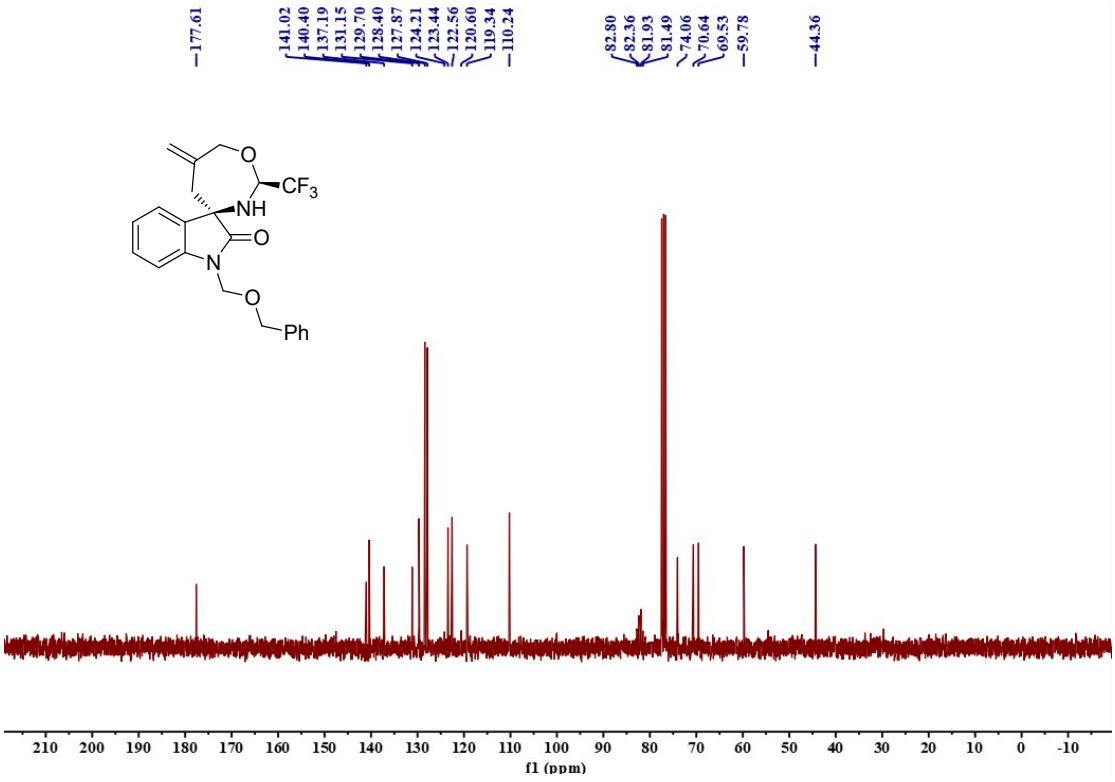
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3n**



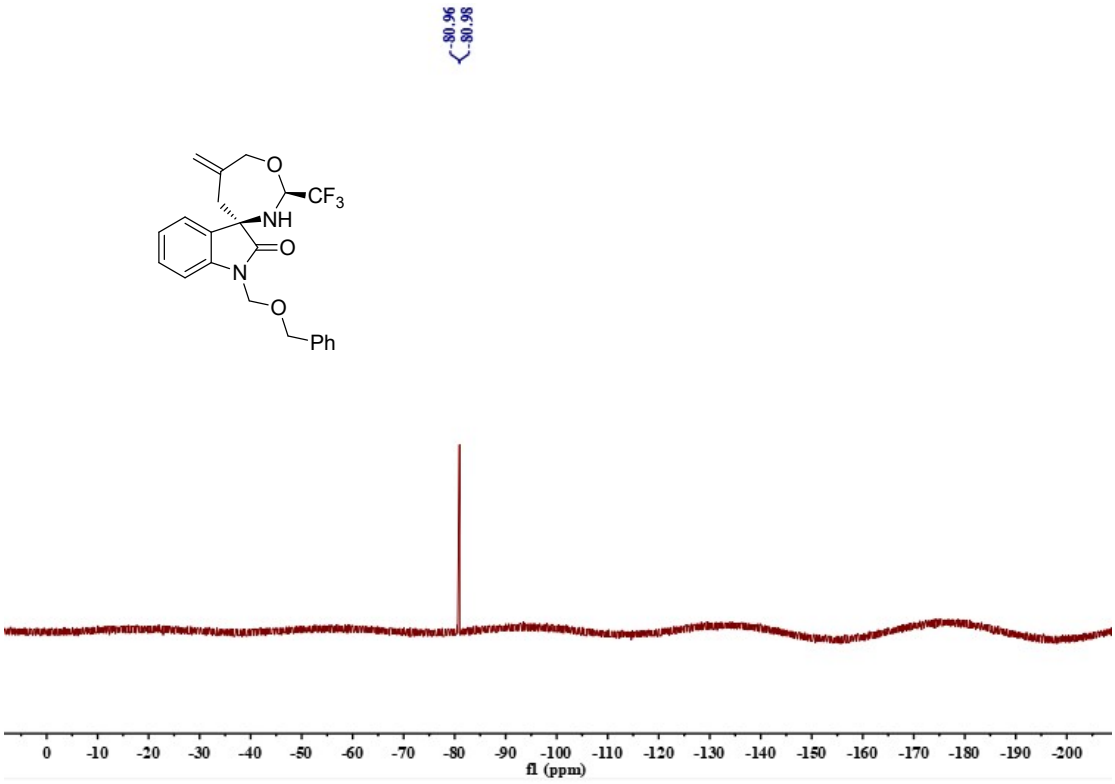
^{19}F NMR (CDCl3, 282 MHz) NMR of **3n**



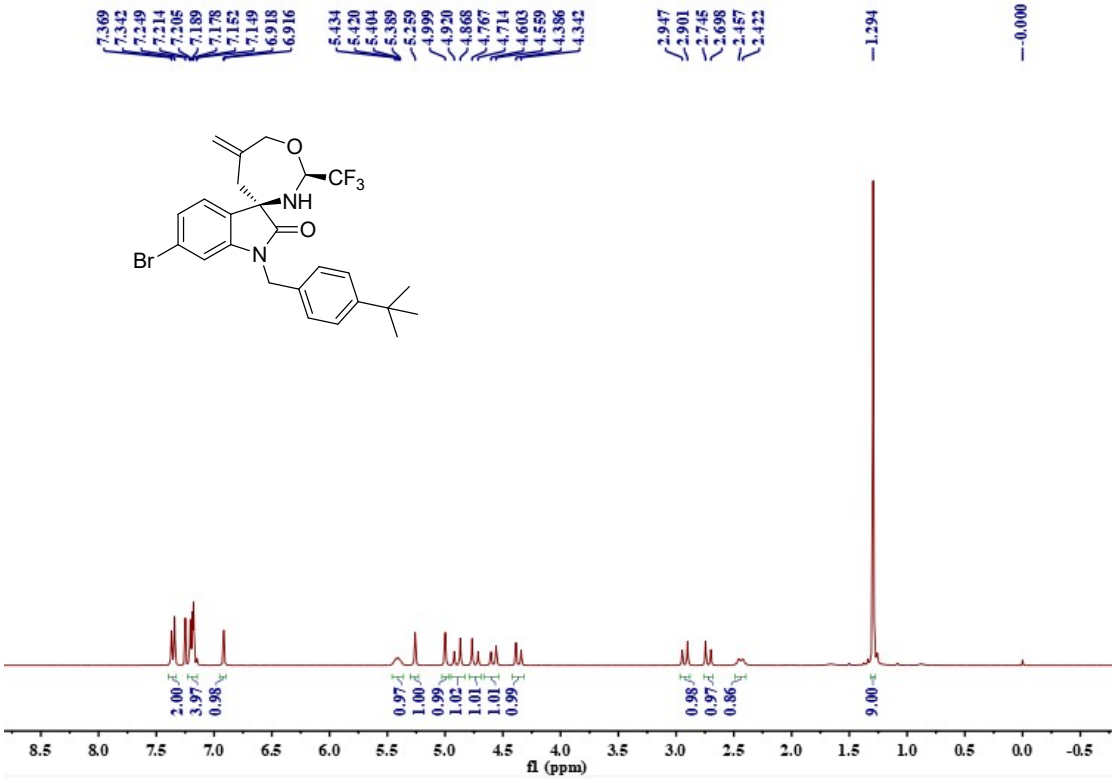
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3o**



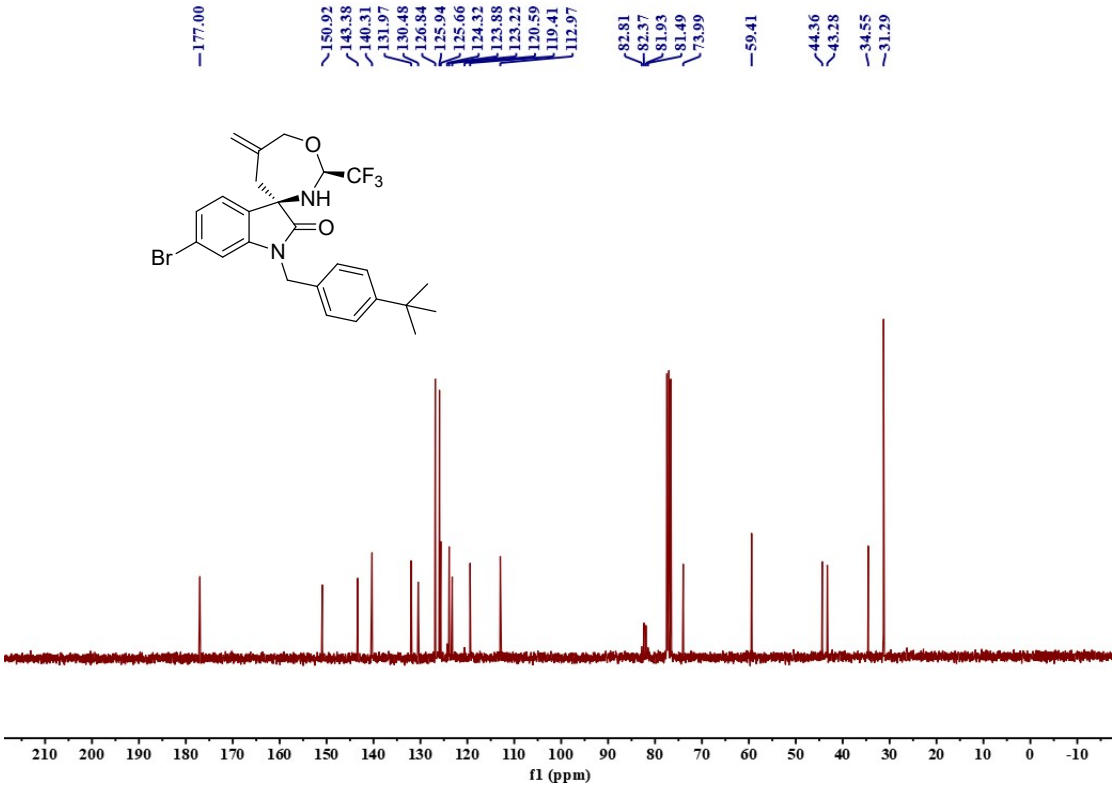
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3o**



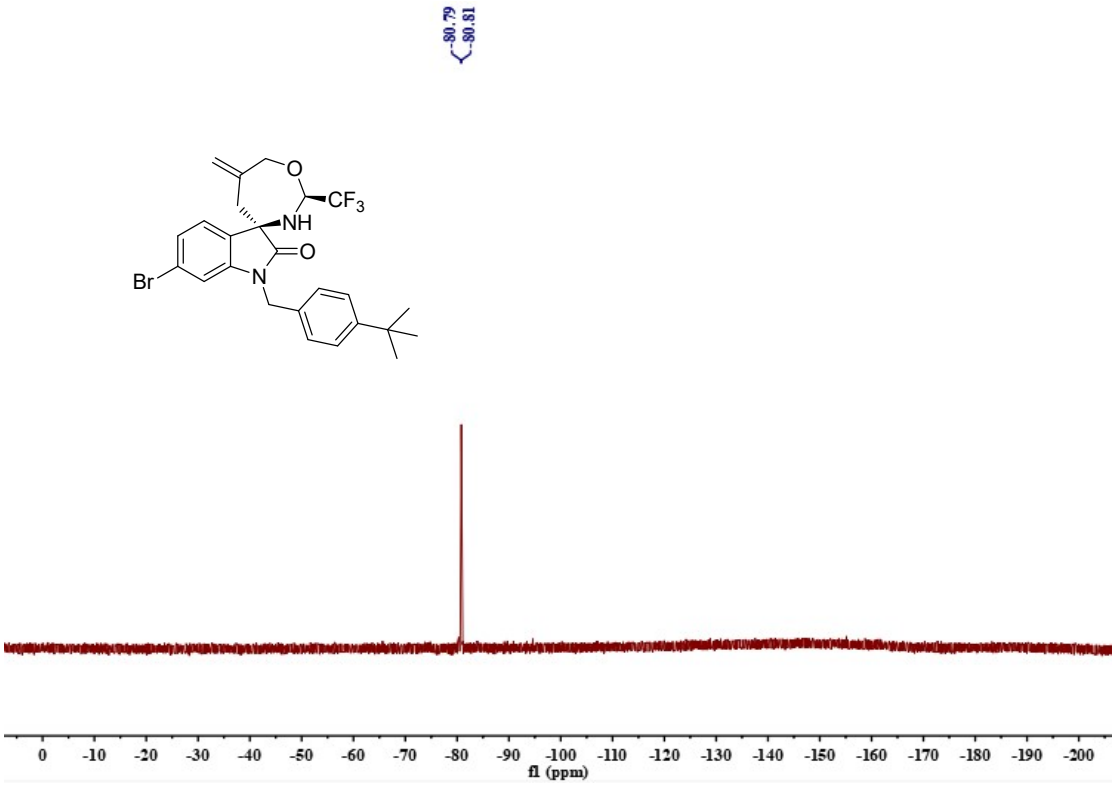
^{19}F NMR (CDCl3, 282 MHz) NMR of **3o**



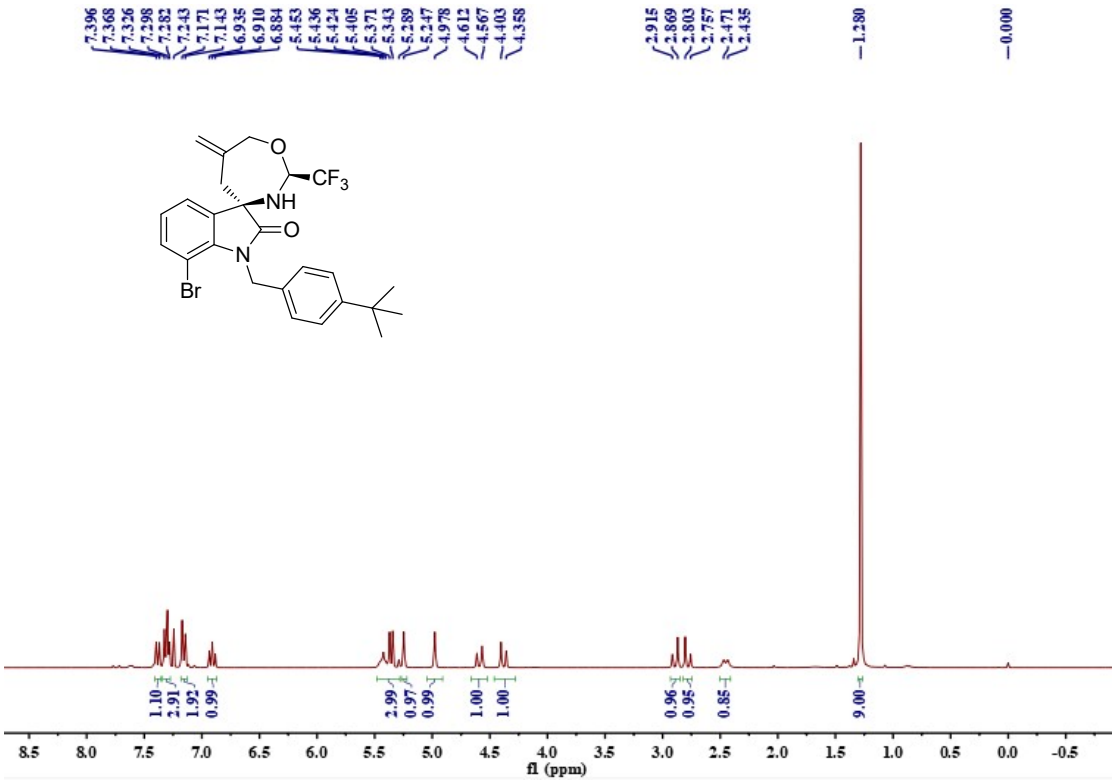
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3p**



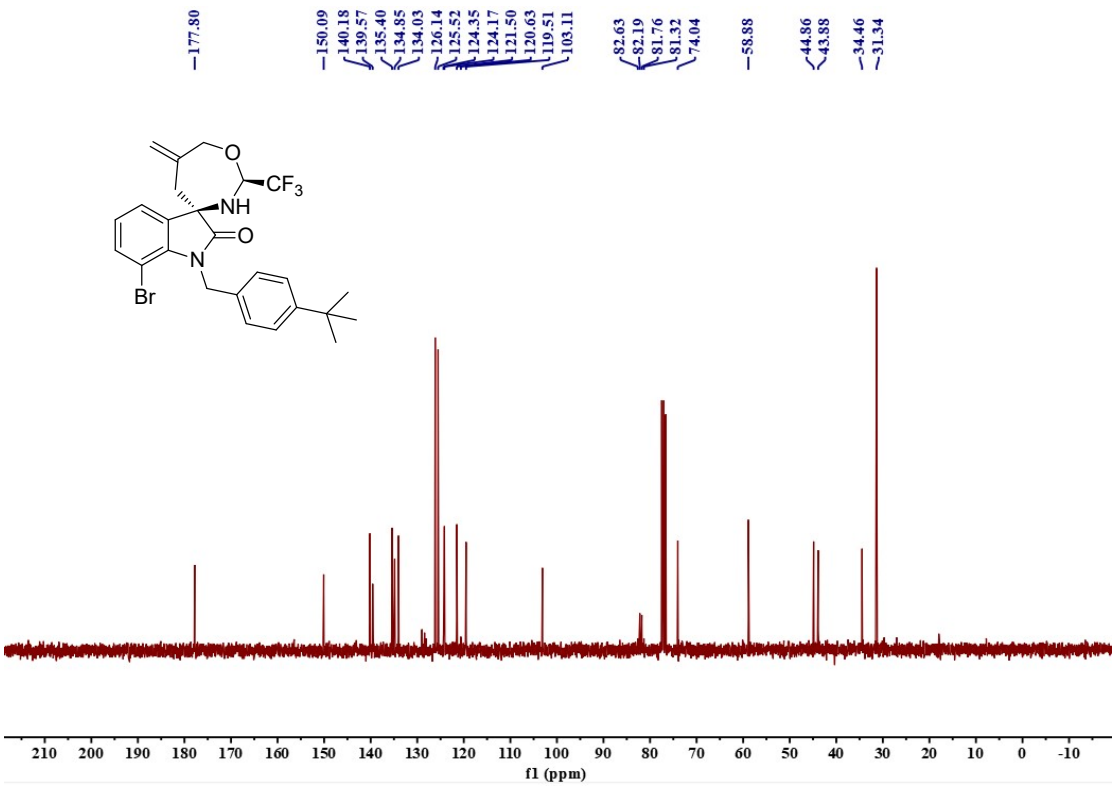
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3p**



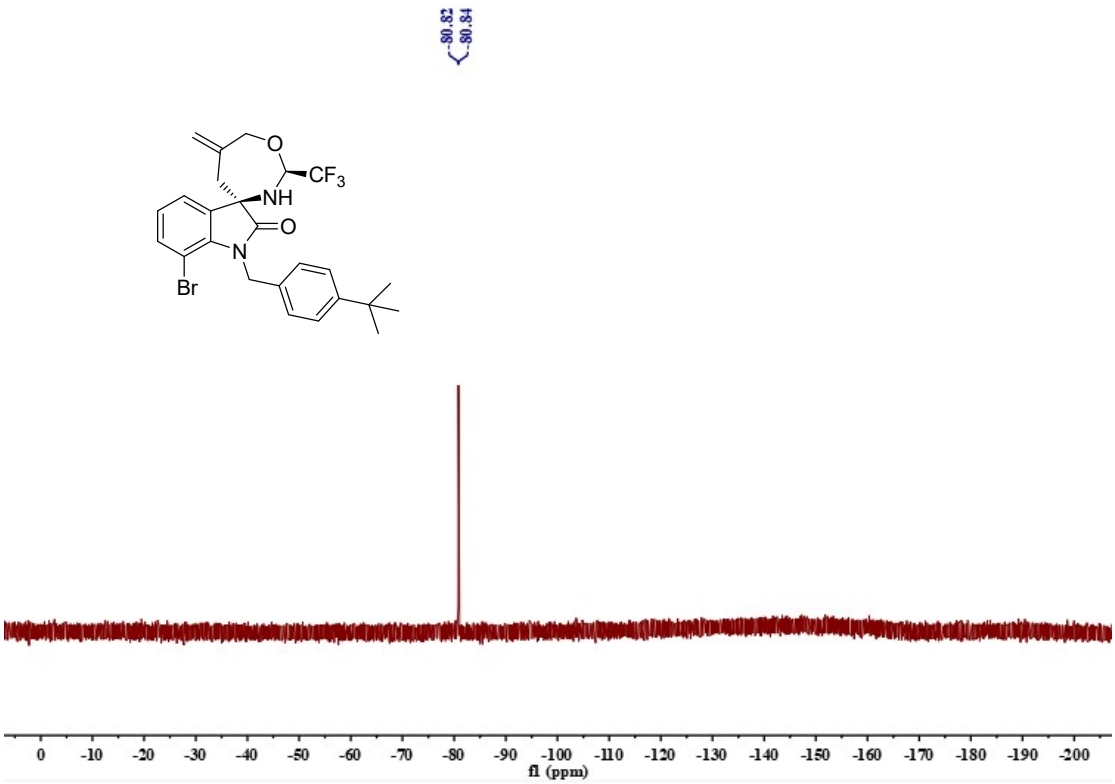
^{19}F NMR (CDCl3, 282 MHz) NMR of **3p**



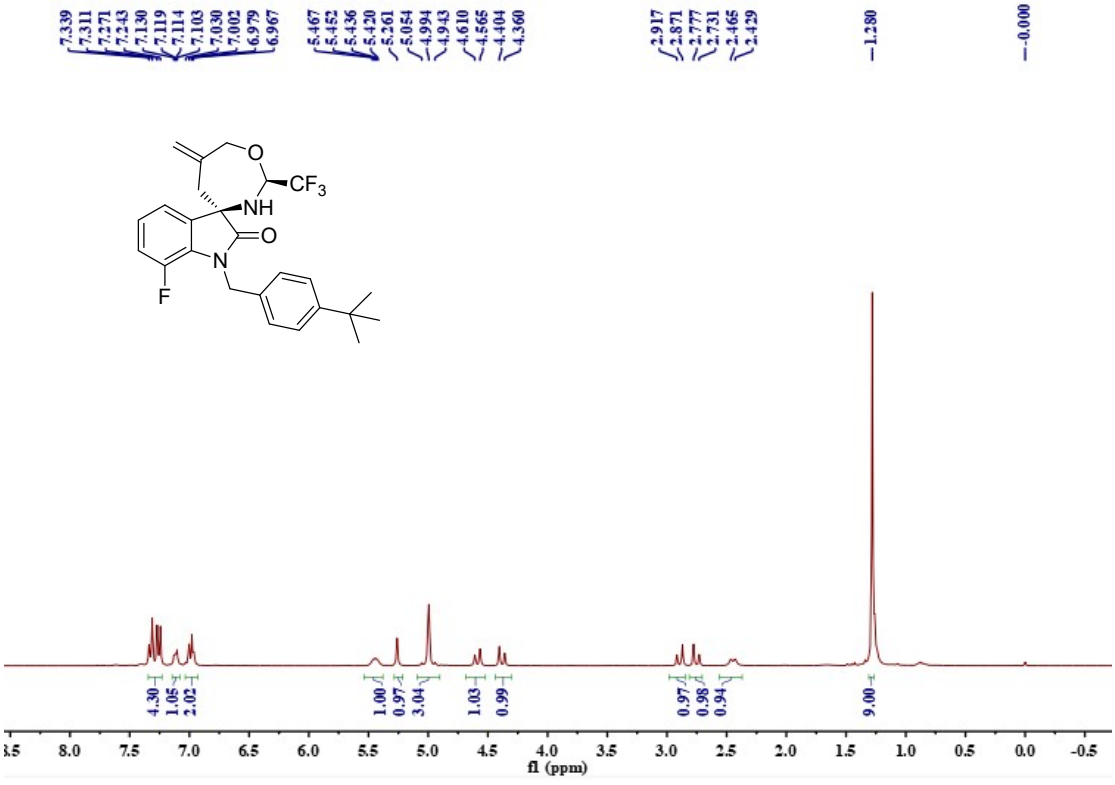
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3q**



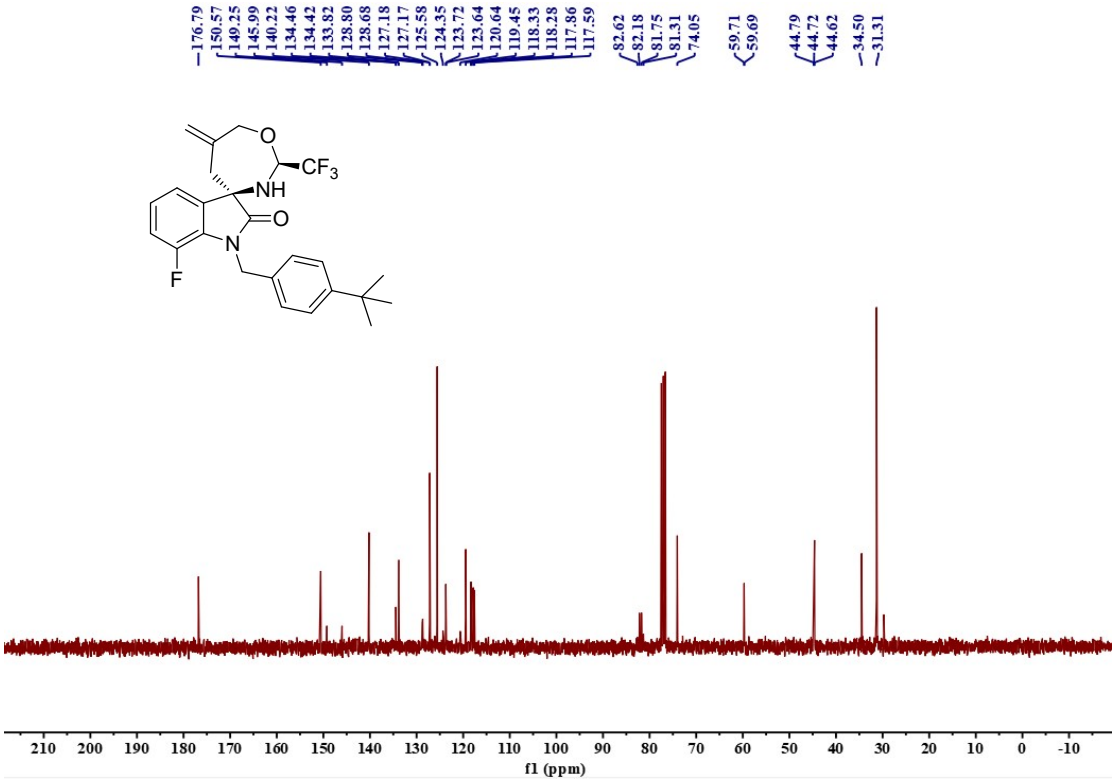
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3q**



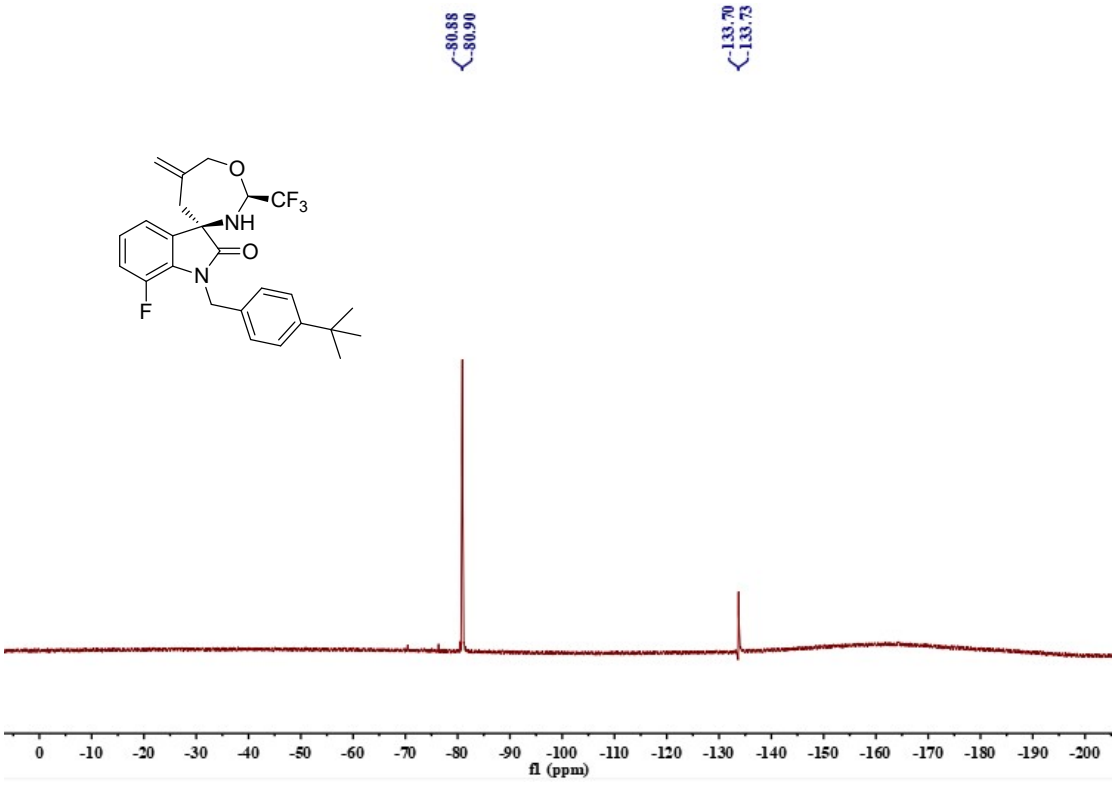
^{19}F NMR (CDCl3, 282 MHz) NMR of **3q**



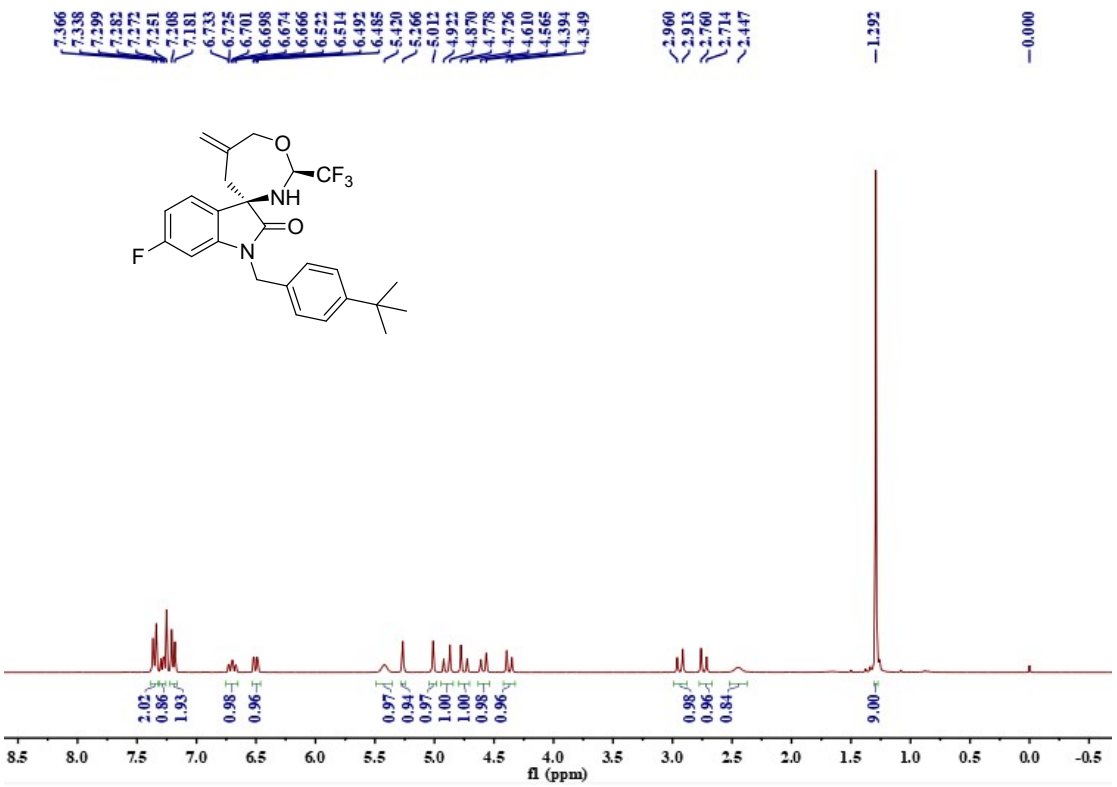
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3r**



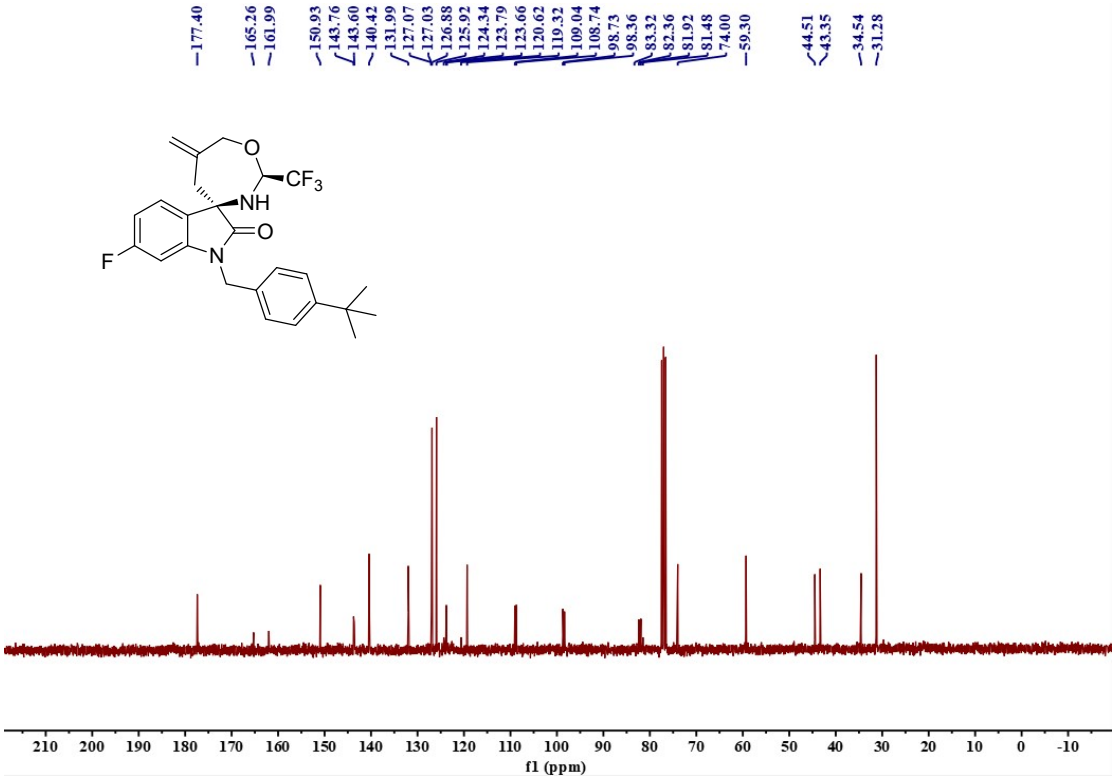
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3r**



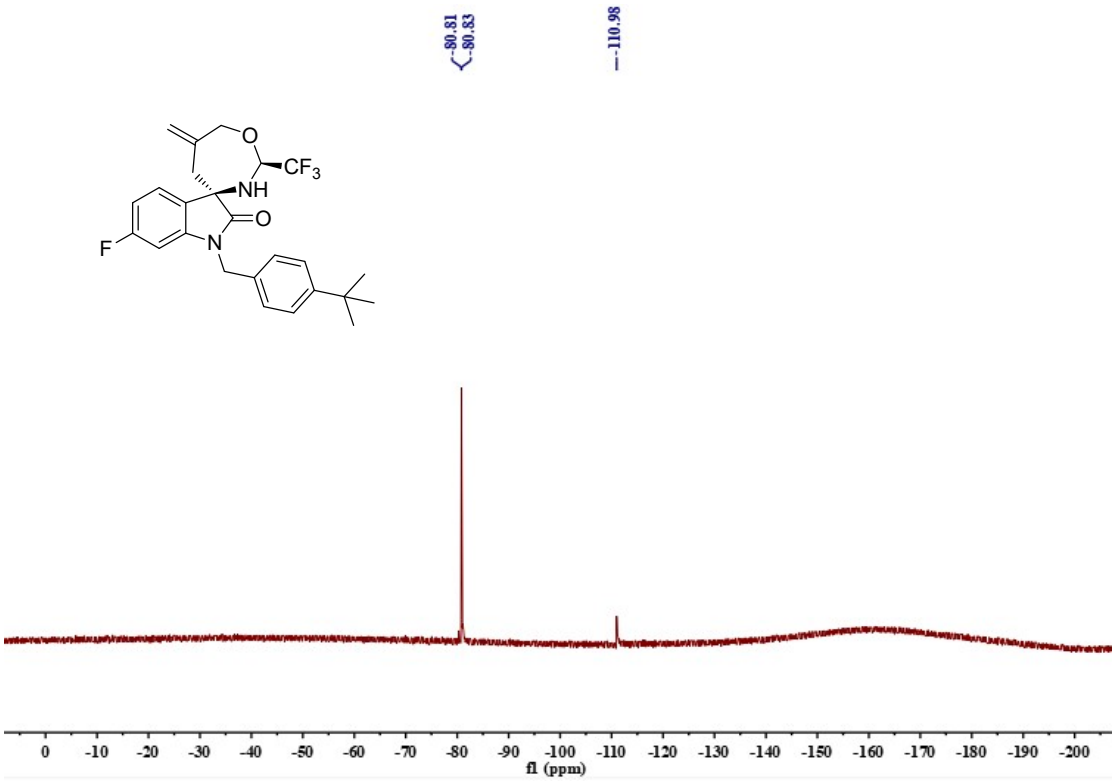
^{19}F NMR (CDCl3, 282 MHz) NMR of **3r**



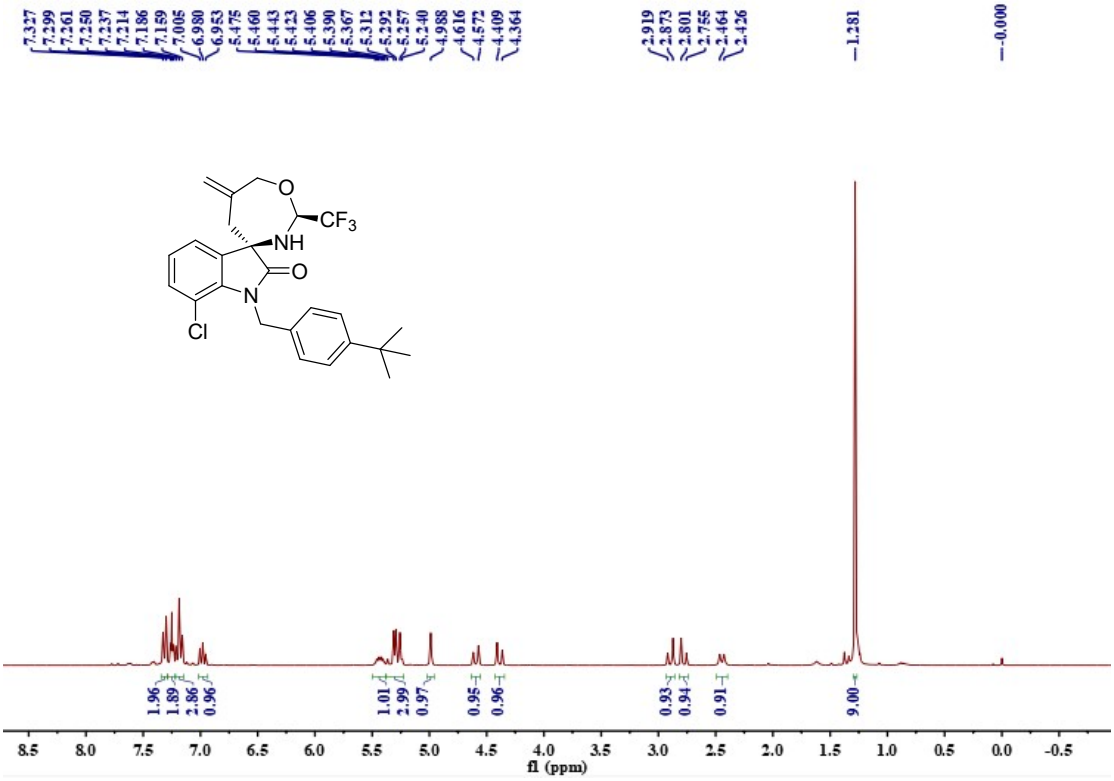
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3s**



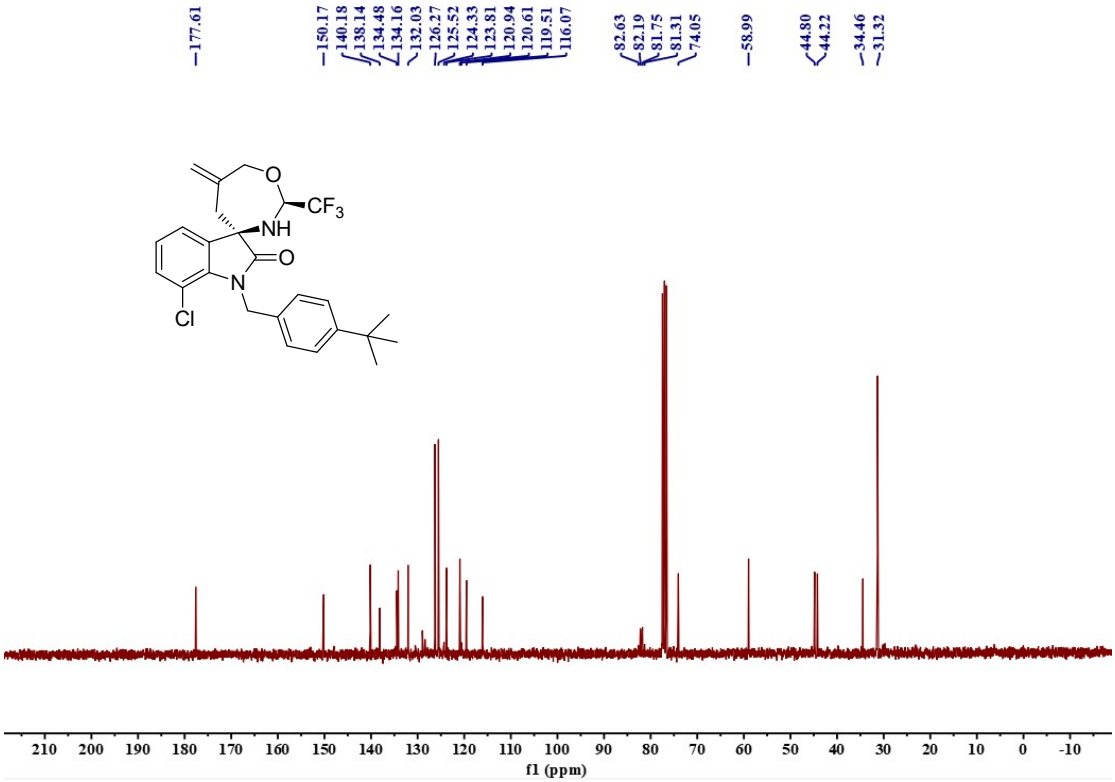
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3s**



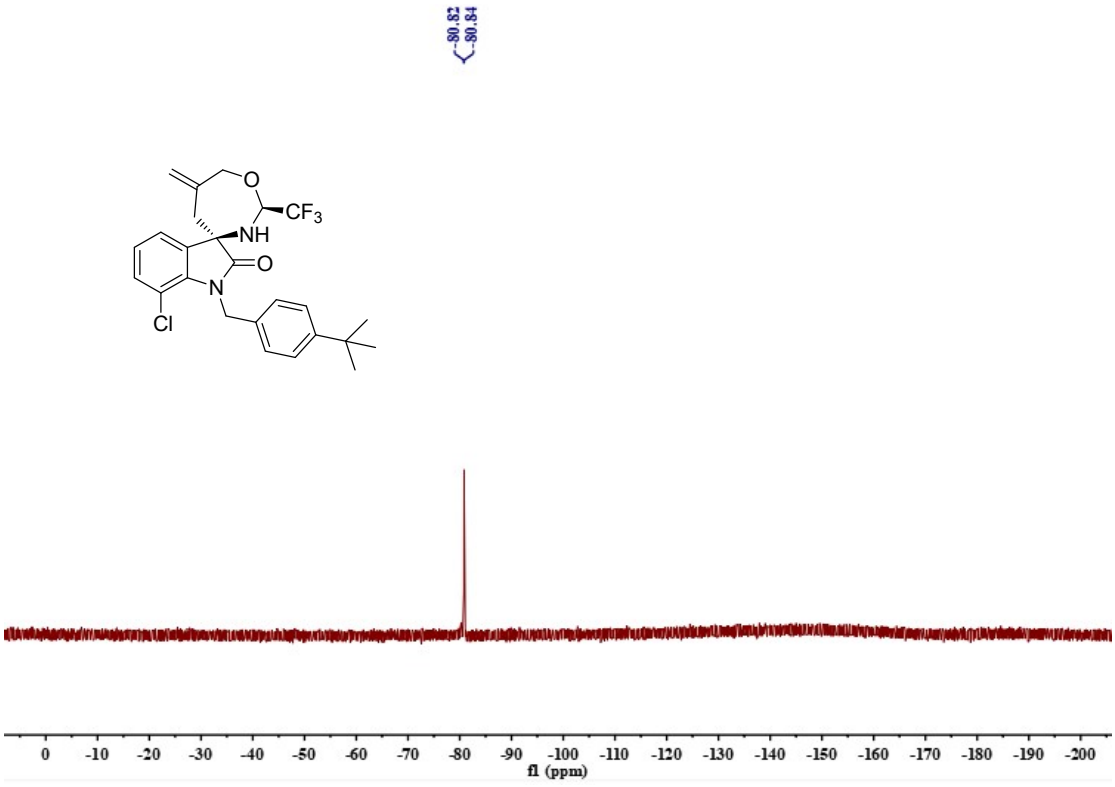
^{19}F NMR (CDCl3, 282 MHz) NMR of **3s**



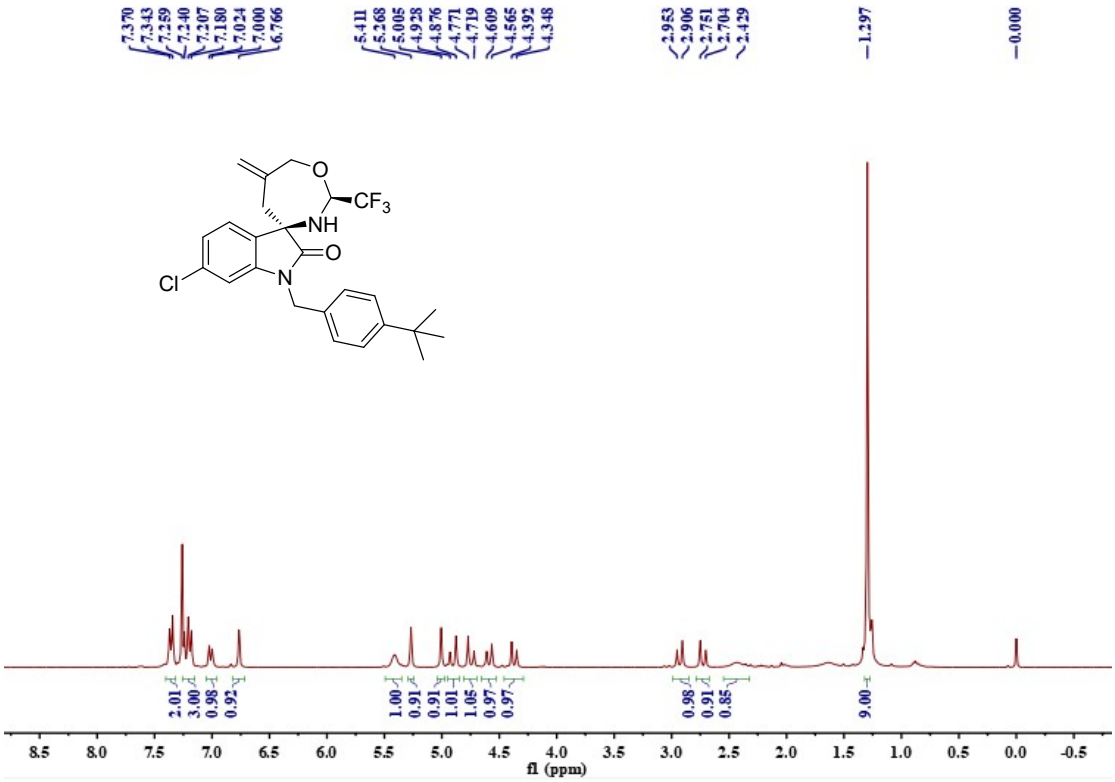
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3t**



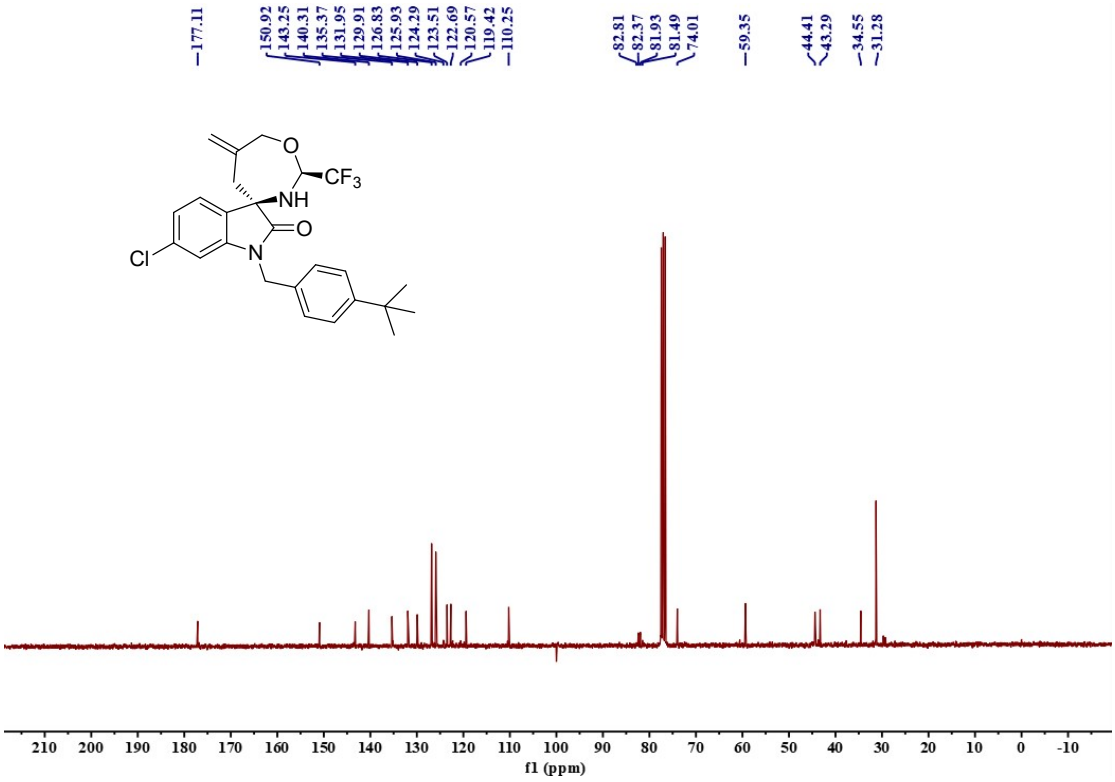
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3t**



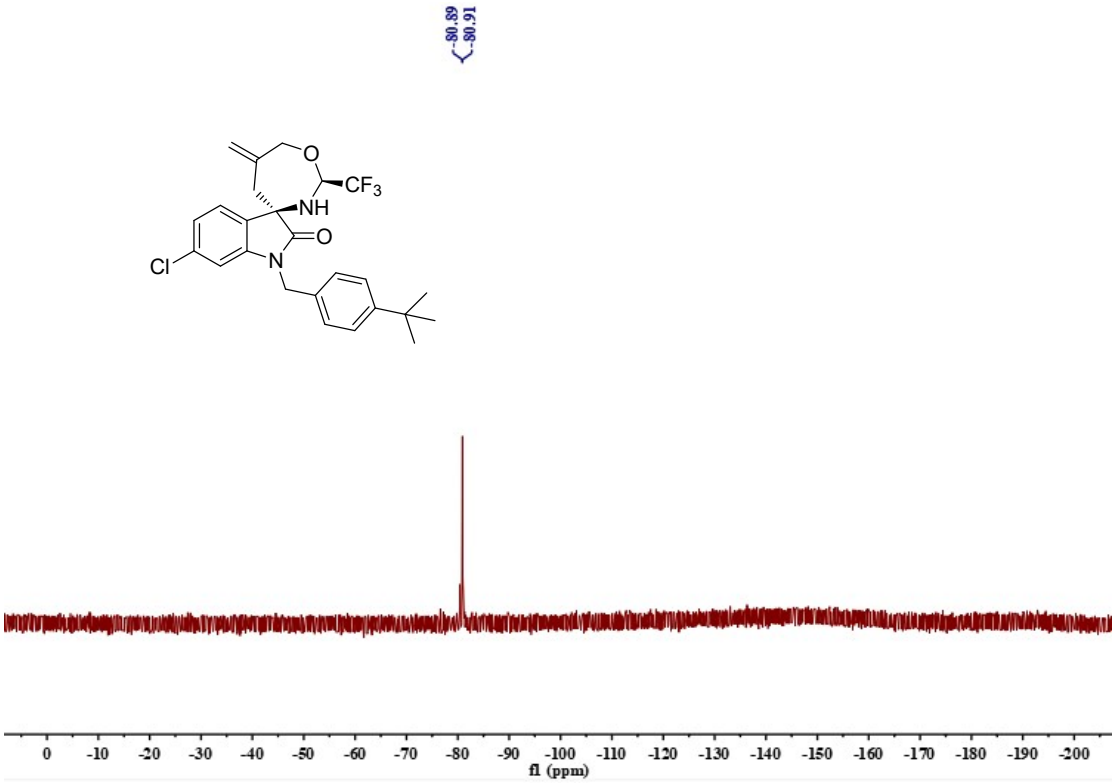
^{19}F NMR (CDCl3, 282 MHz) NMR of **3t**



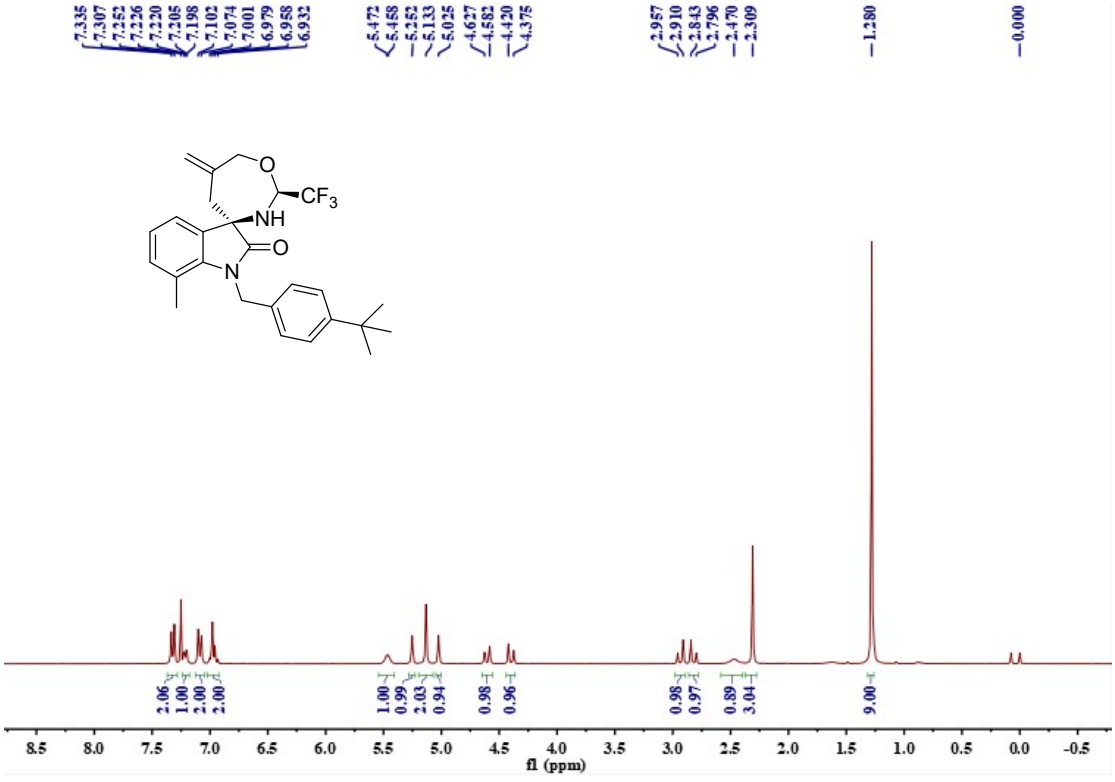
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3u**



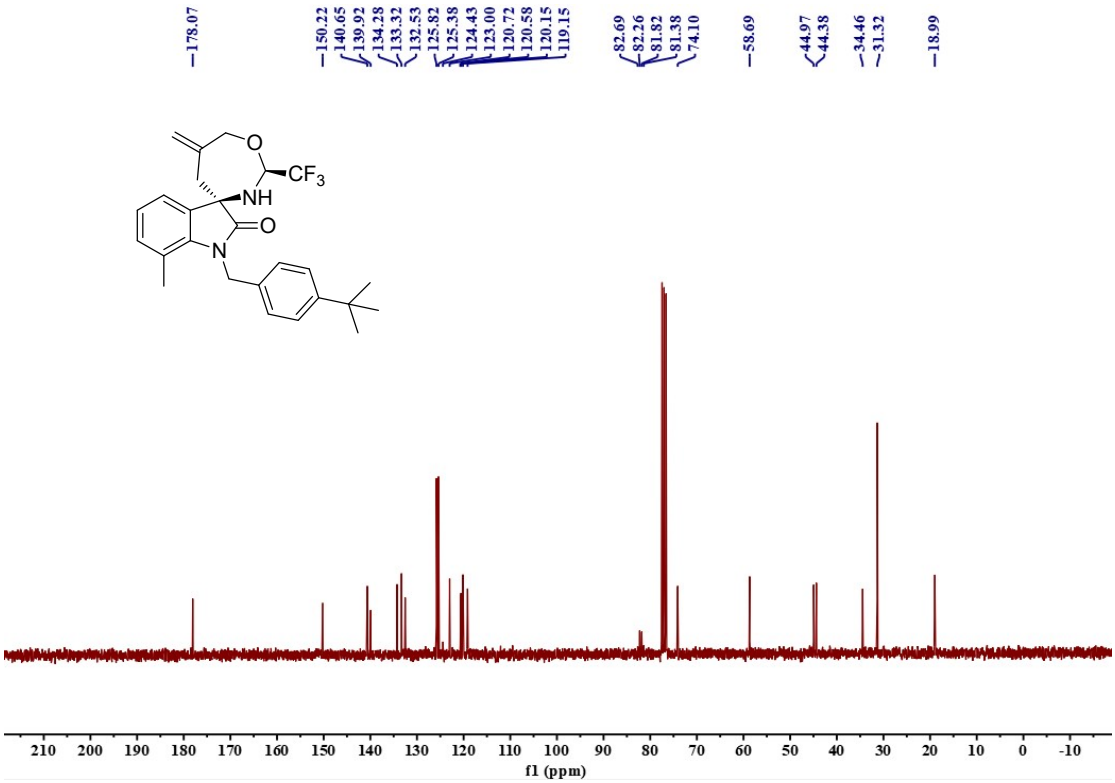
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3u**



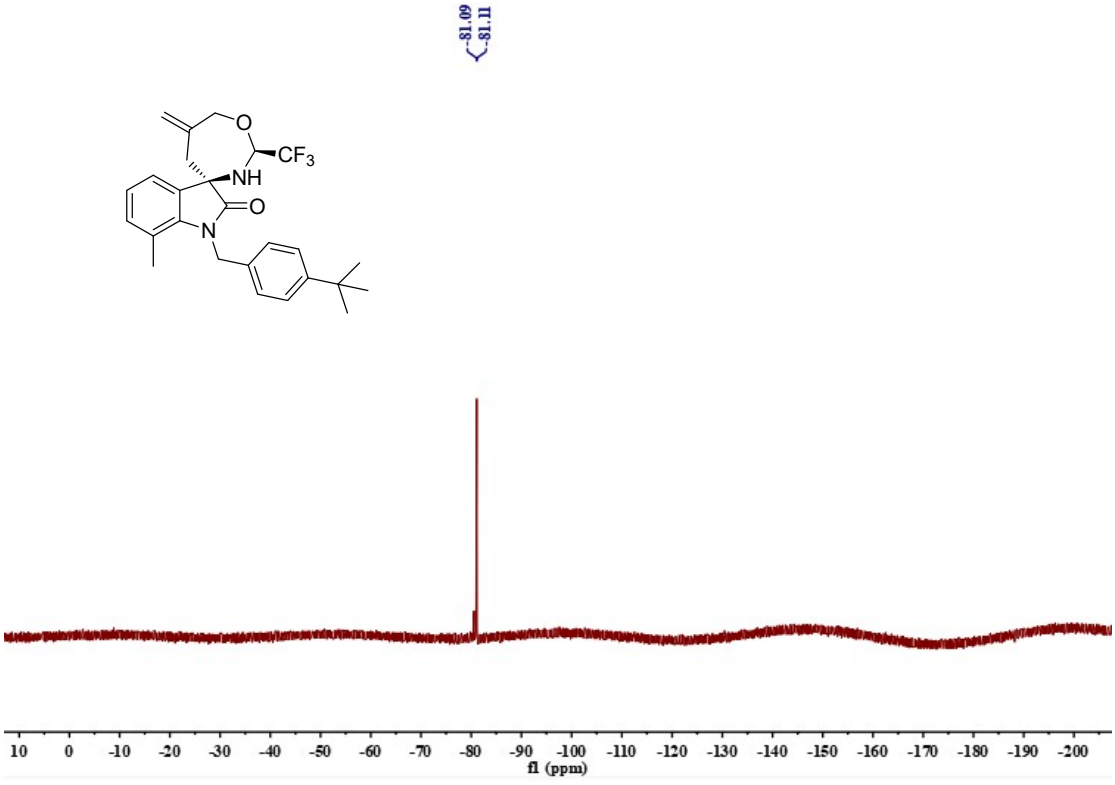
^{19}F NMR (CDCl3, 282 MHz) NMR of **3u**



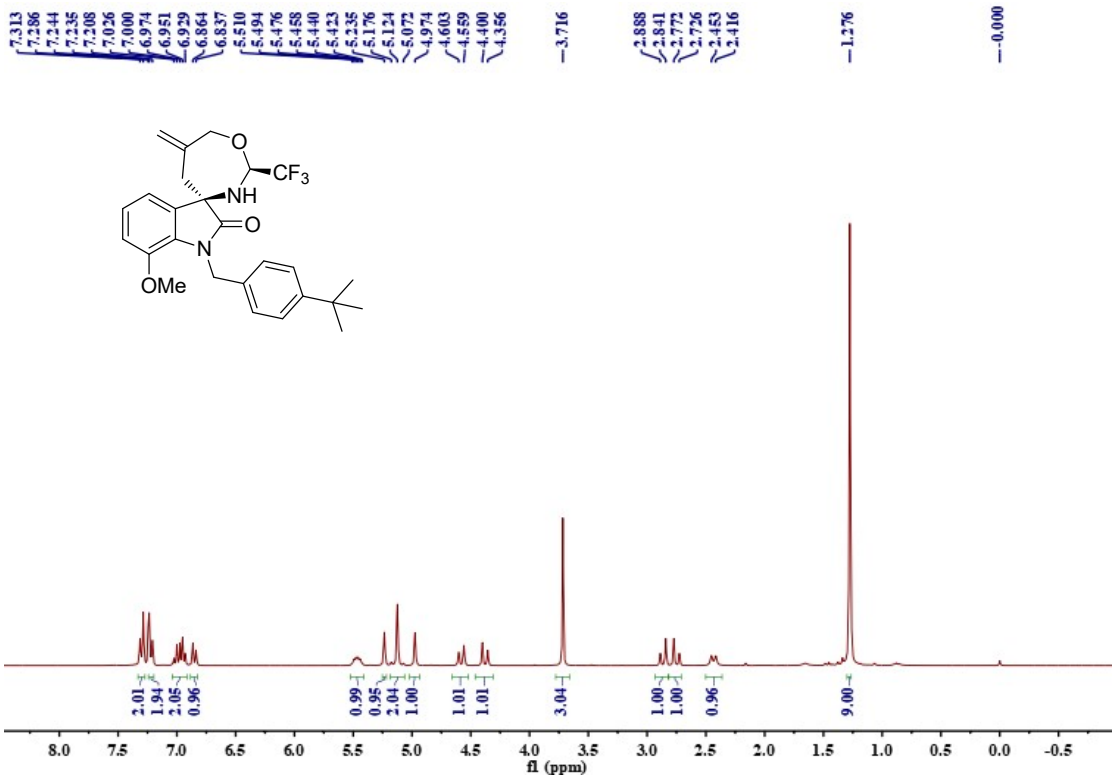
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3v**



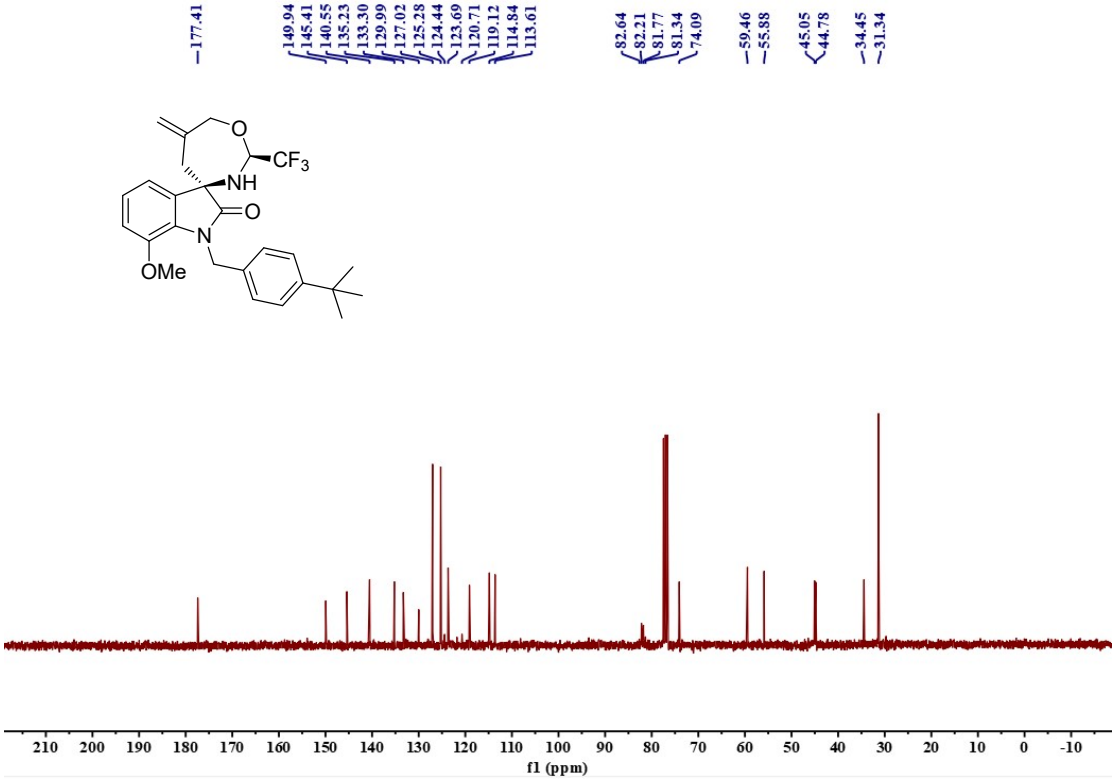
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3v**



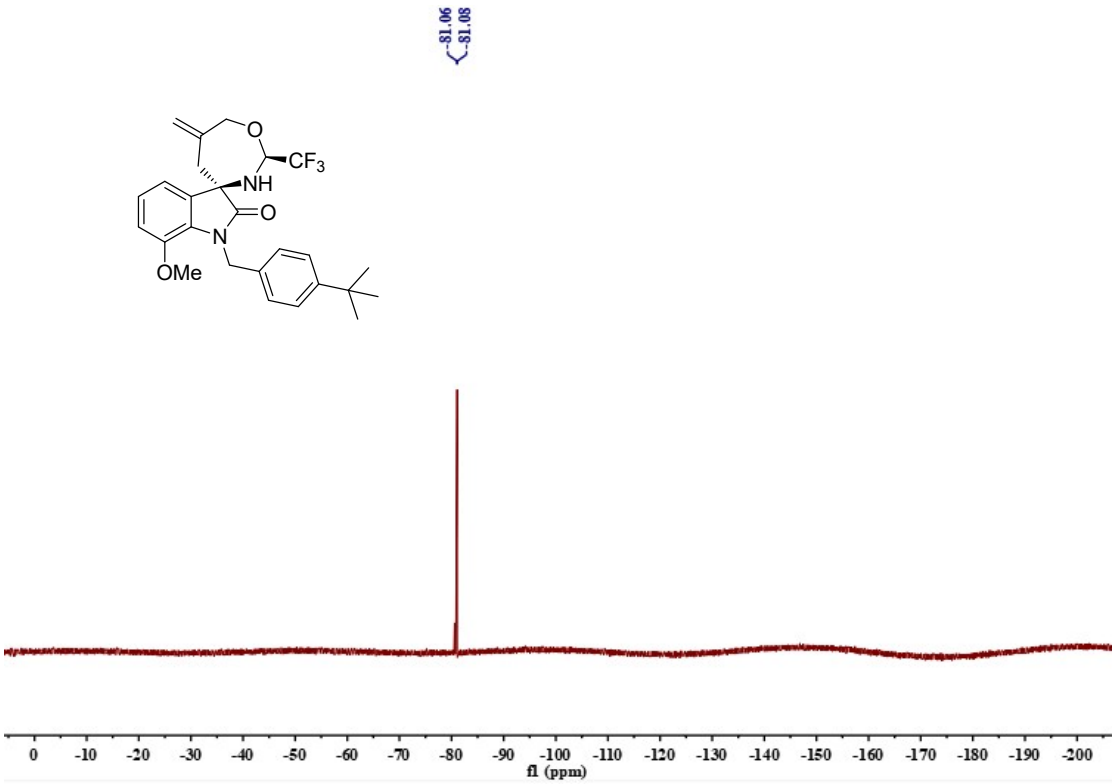
^{19}F NMR (CDCl3, 282 MHz) NMR of **3v**



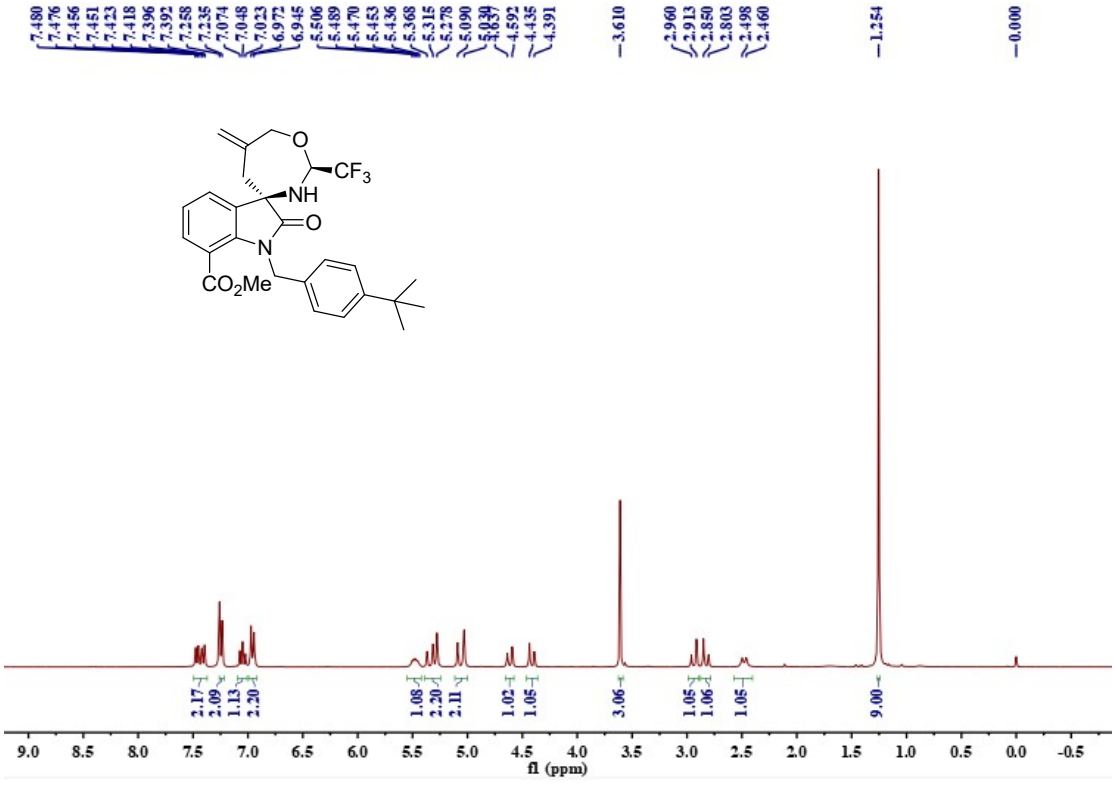
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3w**



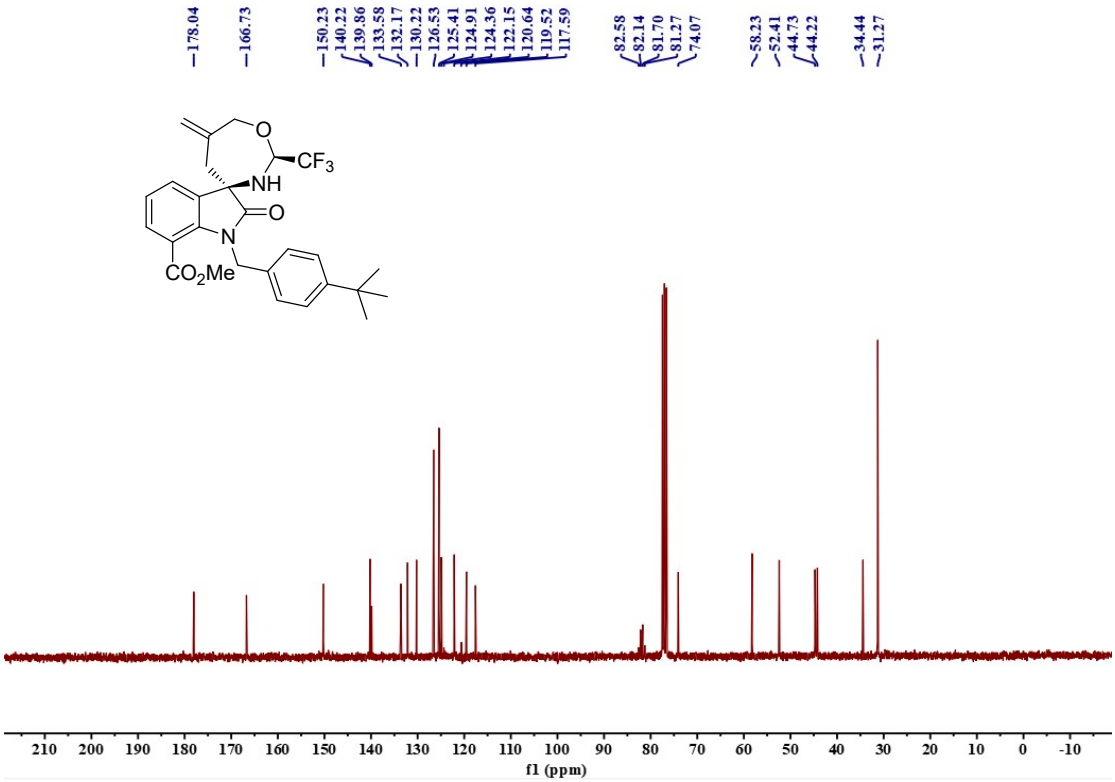
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3w**



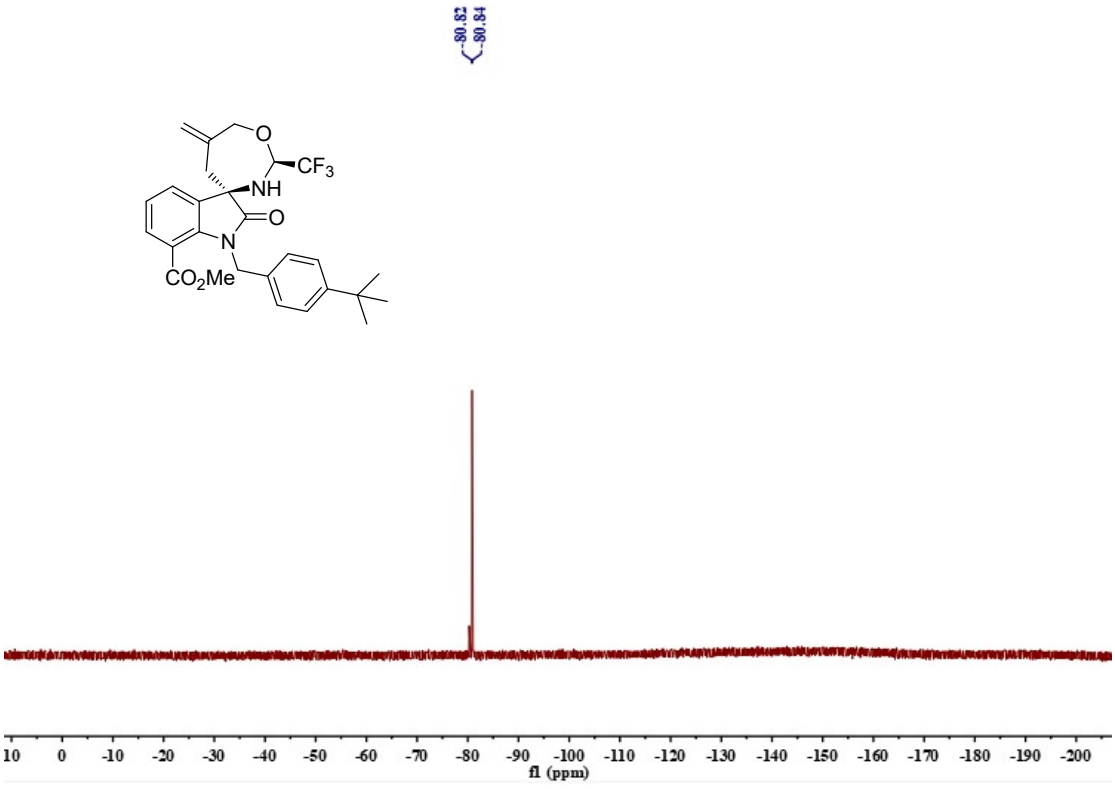
^{19}F NMR (CDCl3, 282 MHz) NMR of **3w**



^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3x**

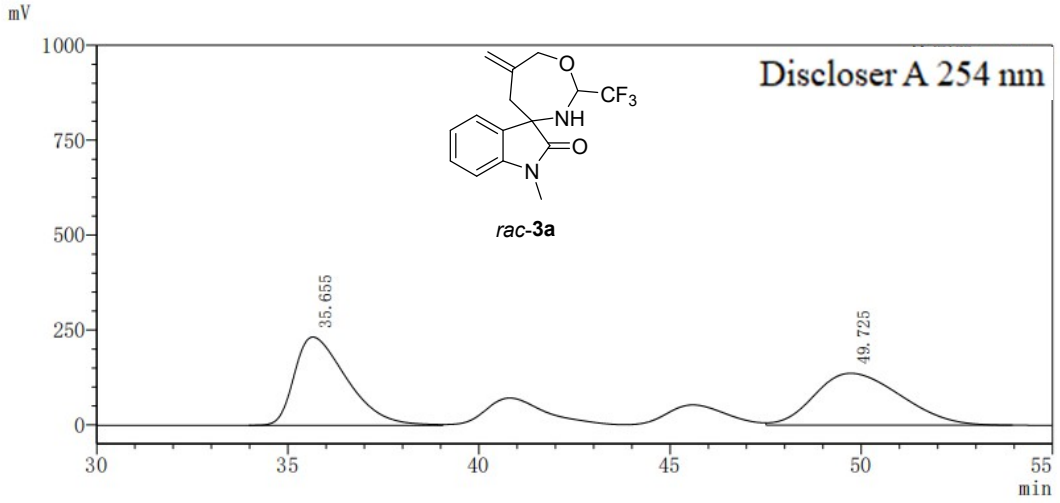


^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3x**



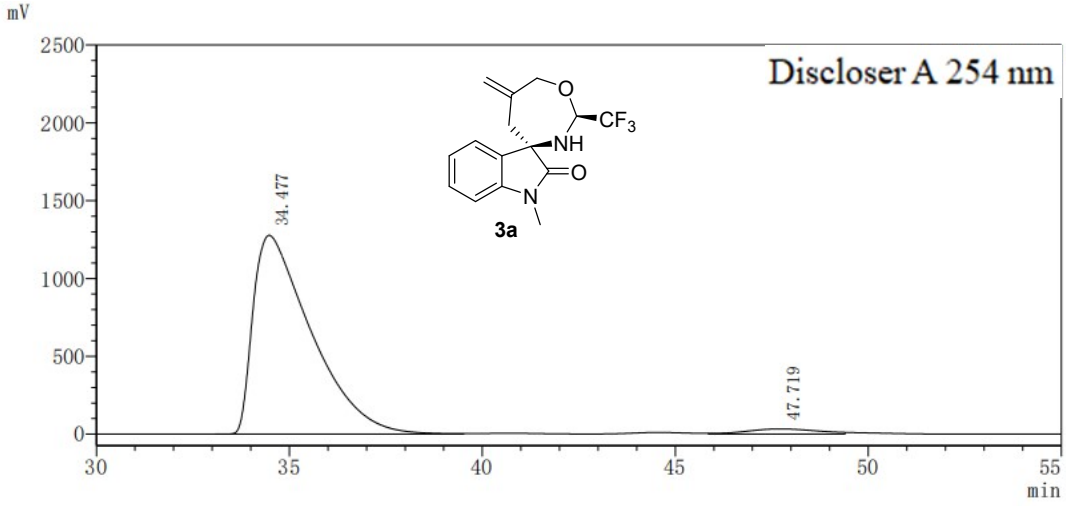
^{19}F NMR (CDCl3, 282 MHz) NMR of **3x**

6. Copies of HPLC Chromatograms



Discloser A 254 nm

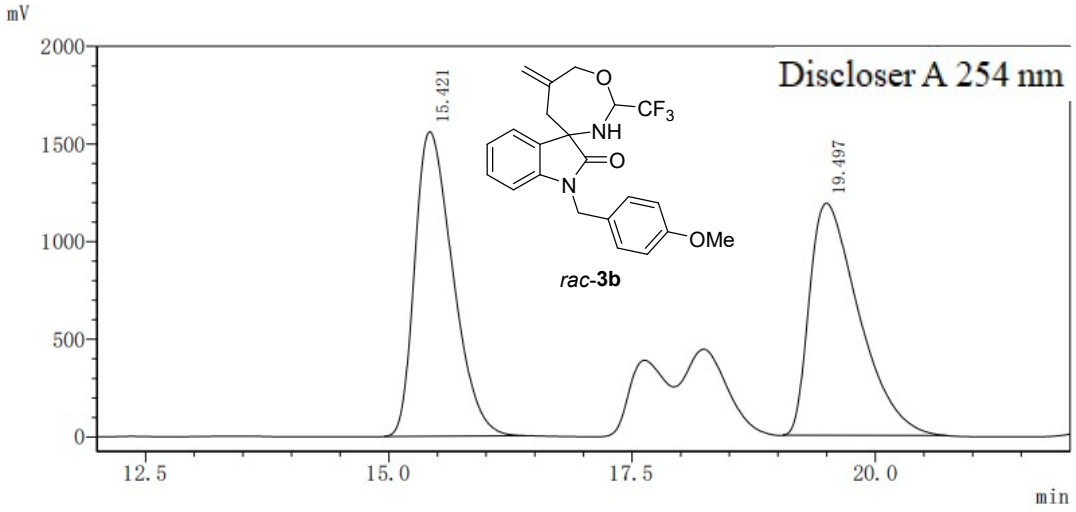
Peak	Reten time (min)	Area (%)
1	35.655	50.692
2	49.725	49.308
total		100



Discloser A 254 nm

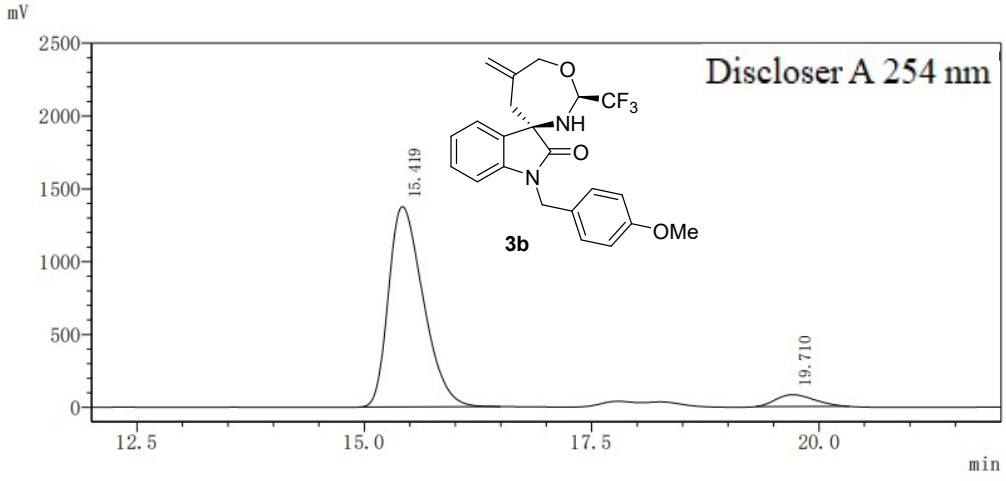
Peak	Reten time (min)	Area (%)
1	34.477	97.016
2	47.719	2.984

total		100



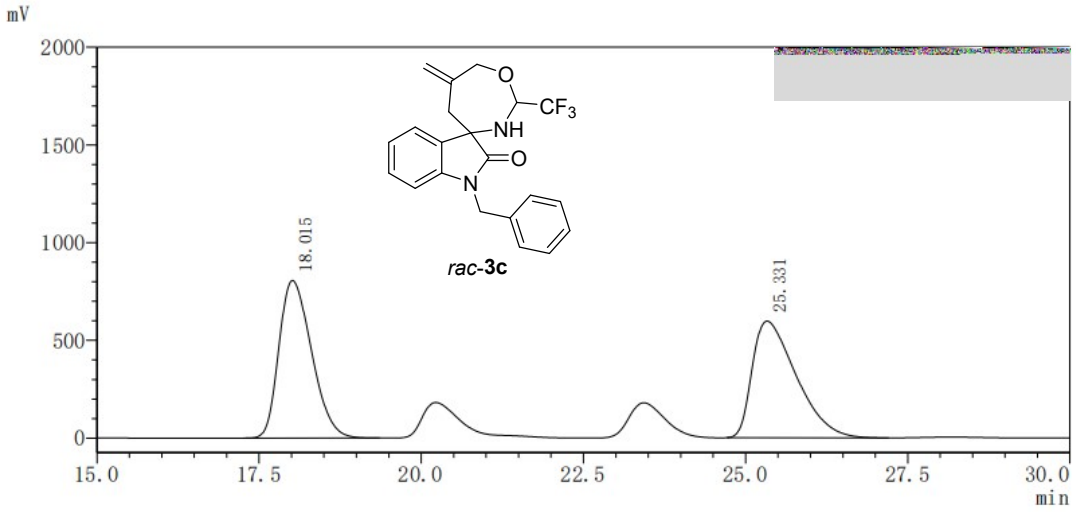
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	15.421	50.120
2	19.497	49.880
total		100



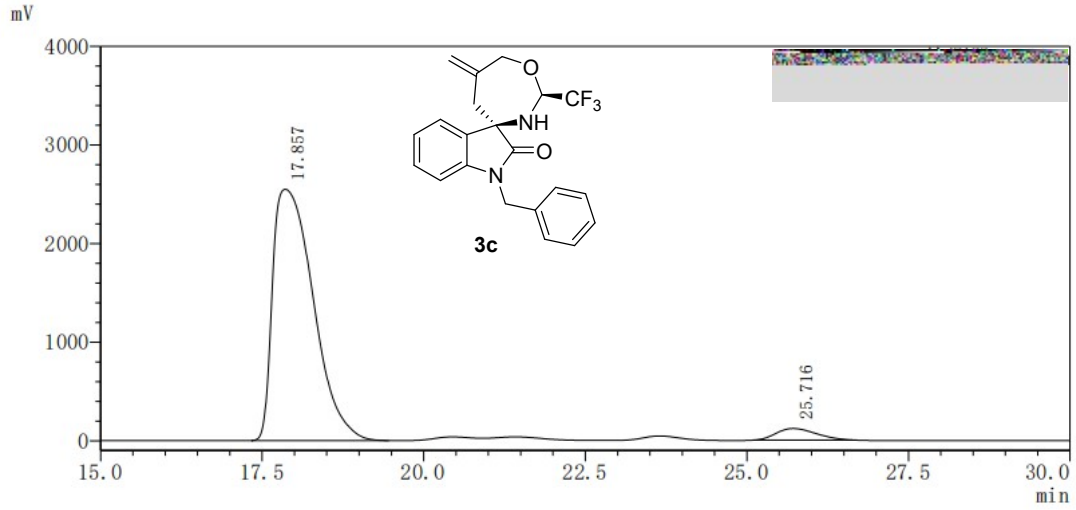
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	15.419	93.919
2	19.710	6.081
total		100



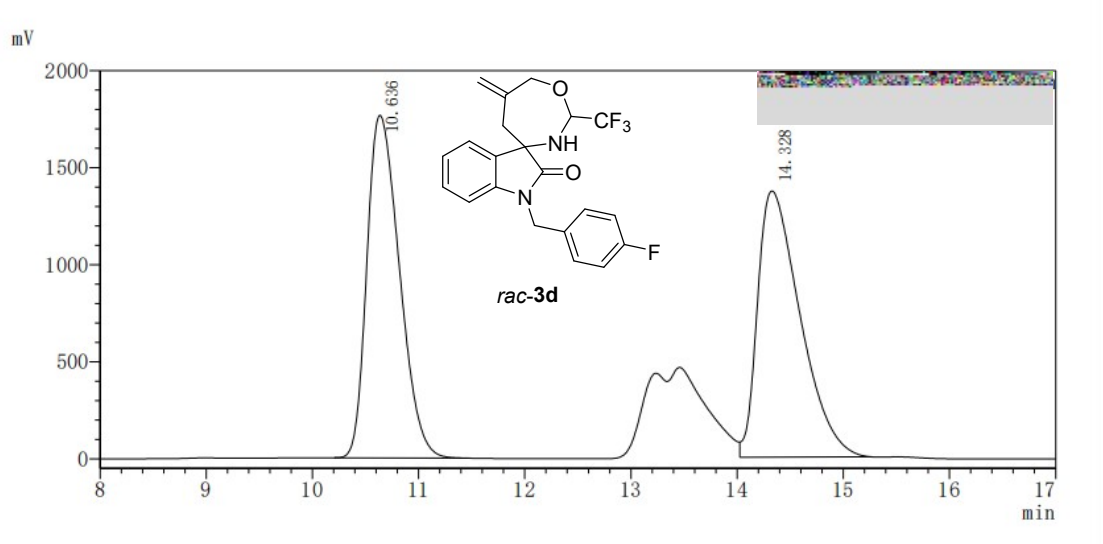
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	18.015	50.107
2	25.331	49.893
total		100



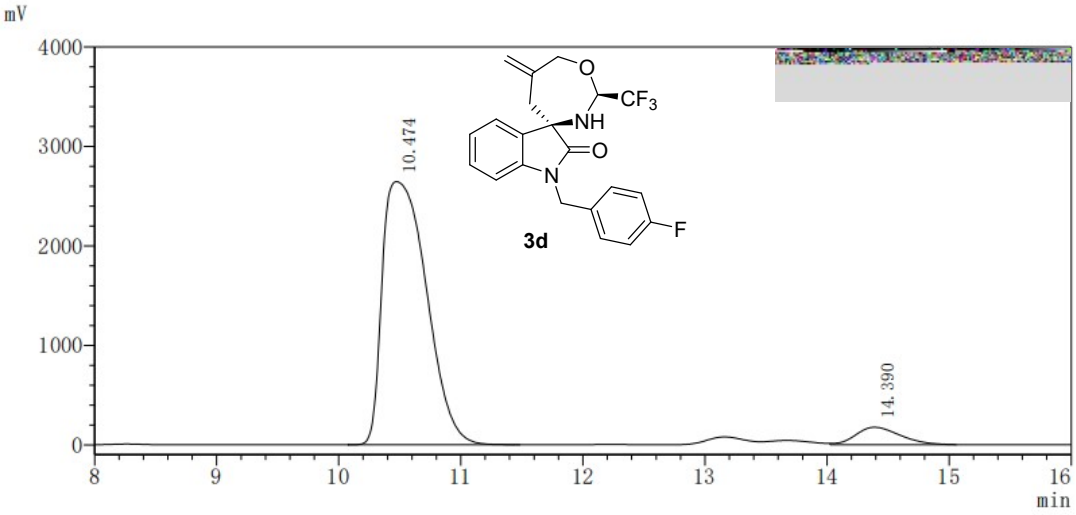
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	17.857	95.623
2	25.716	4.377
total		100



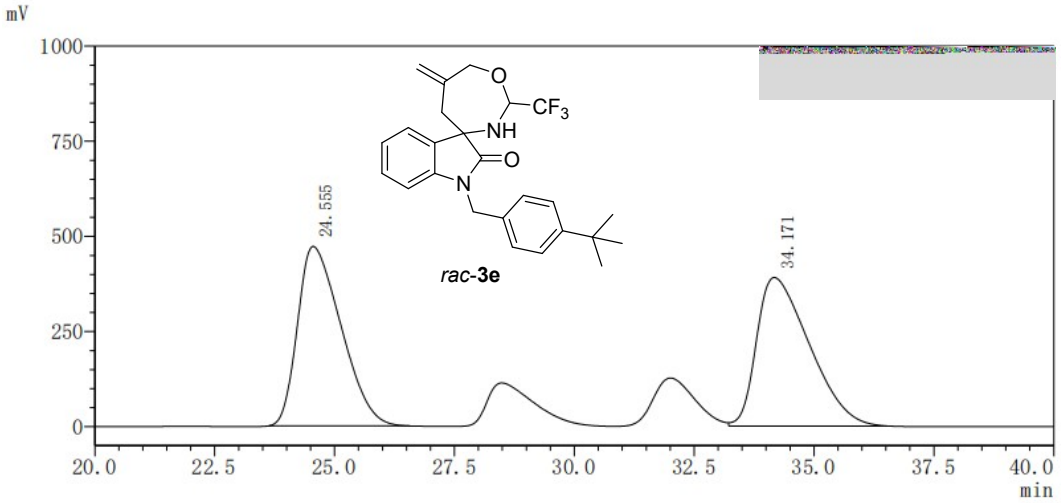
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	10.636	49.618
2	14.328	50.382
total		100



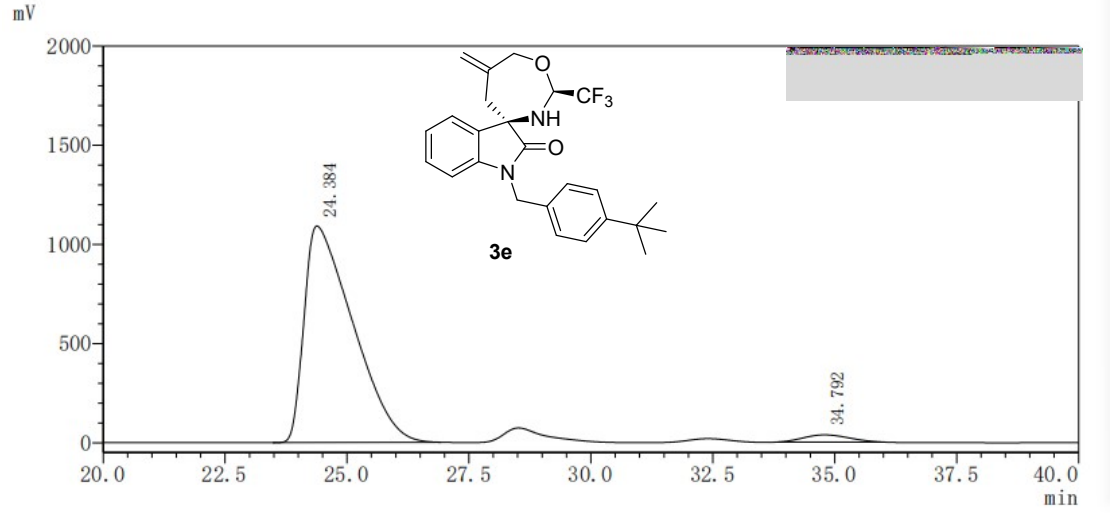
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	10.474	93.821
2	14.390	6.179
total		100



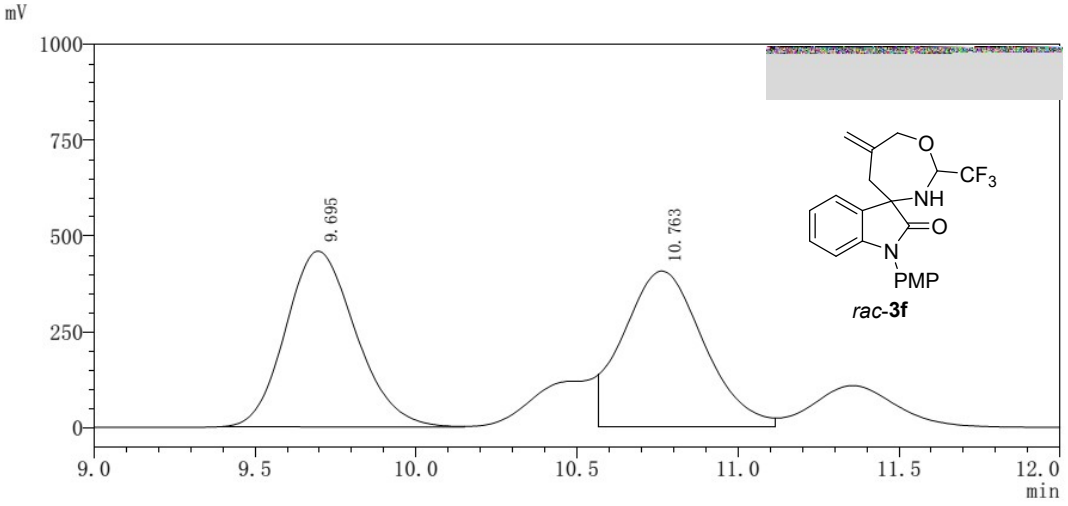
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	24.555	49.892
2	34.171	50.108
total		100



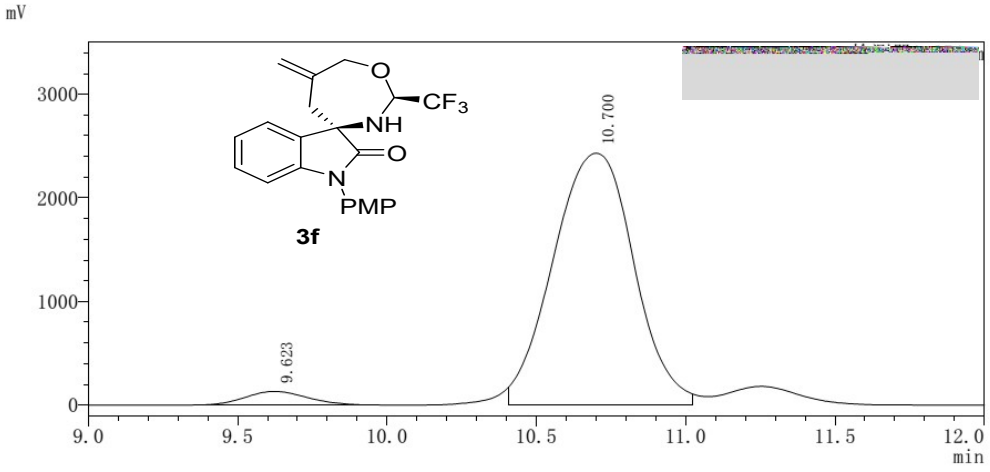
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	24.384	96.996
2	34.792	3.004
total		100



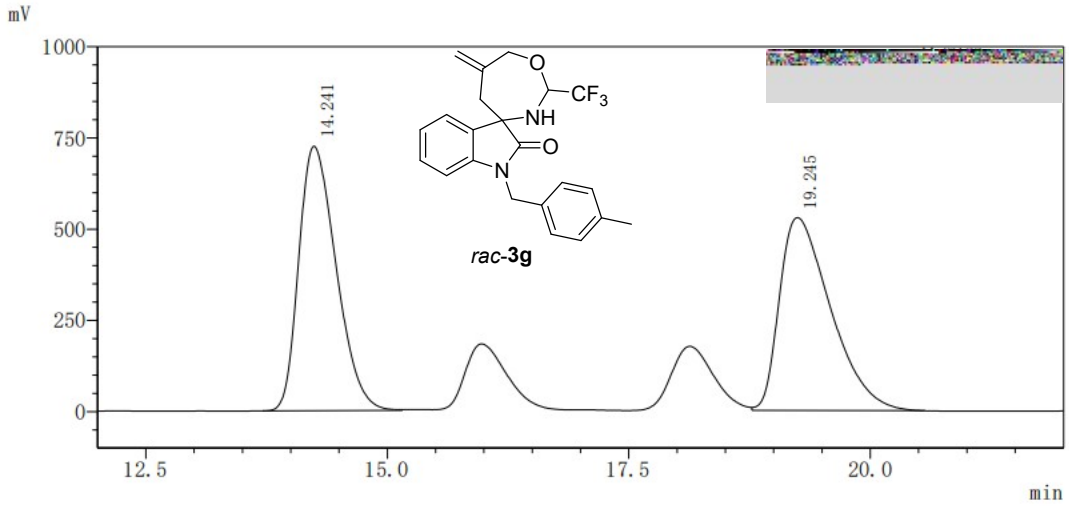
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.695	49.694
2	10.763	50.306
total		100



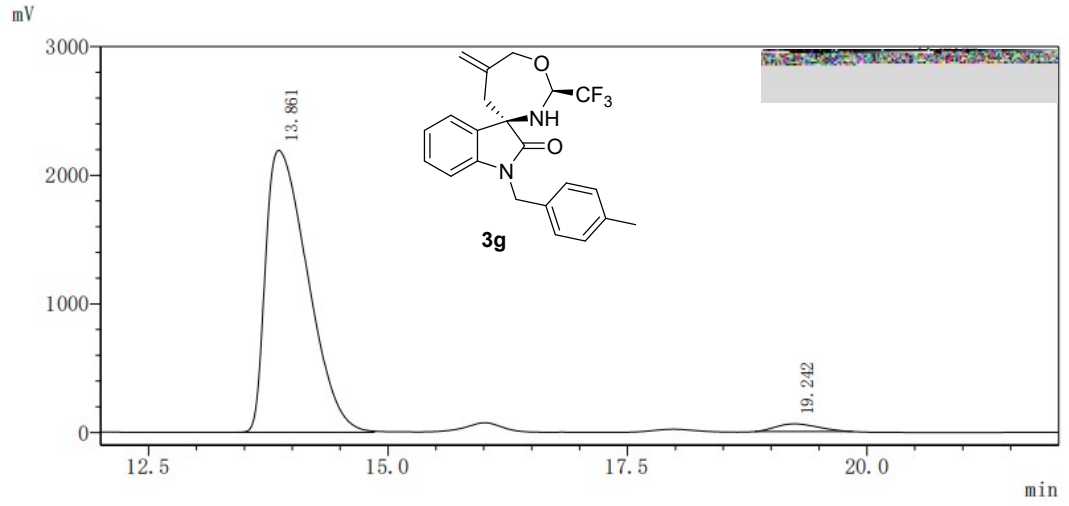
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.623	3.955
2	10.700	96.045
total		100



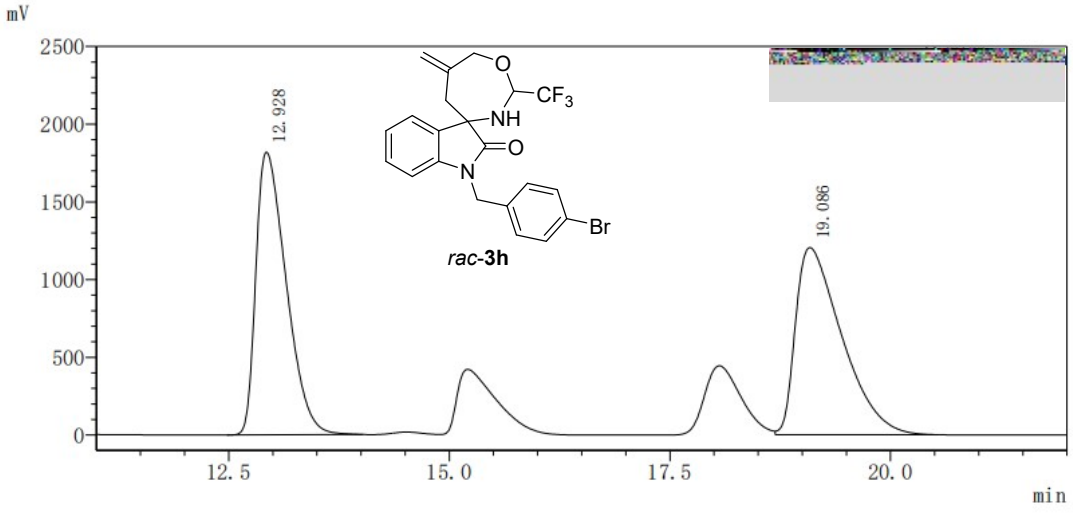
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	14.241	50.051
2	19.245	49.949
total		100



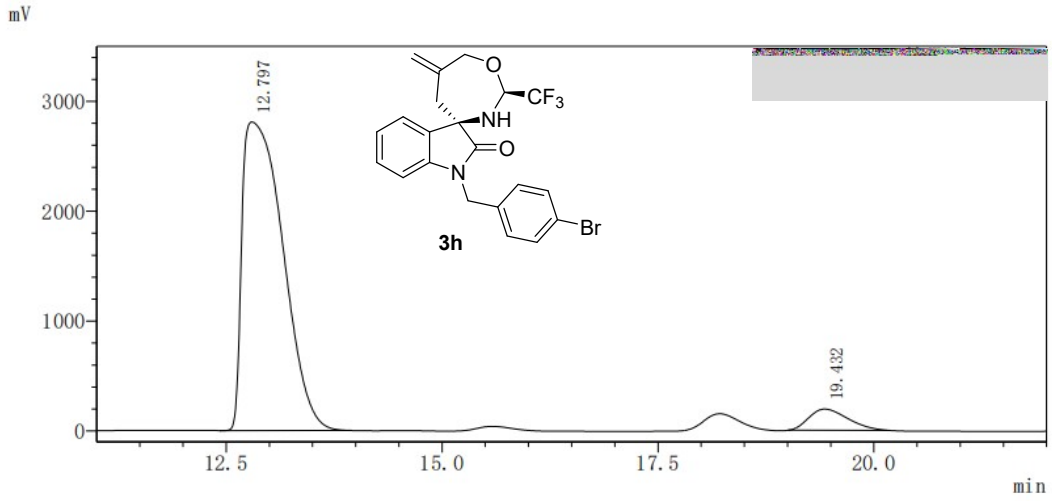
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	13.861	97.344
2	19.242	2.656
total		100



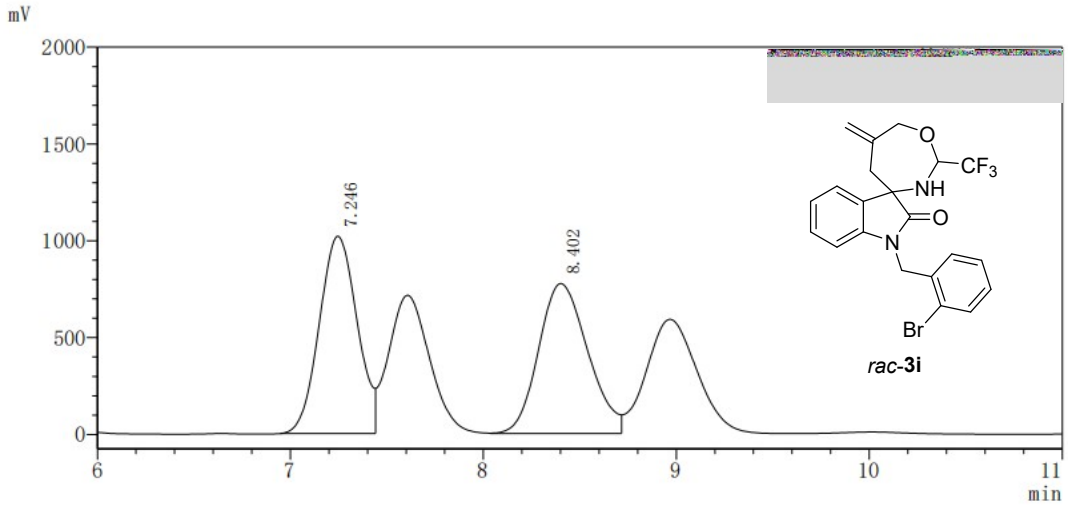
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	12.928	49.732
2	19.096	50.268
total		100



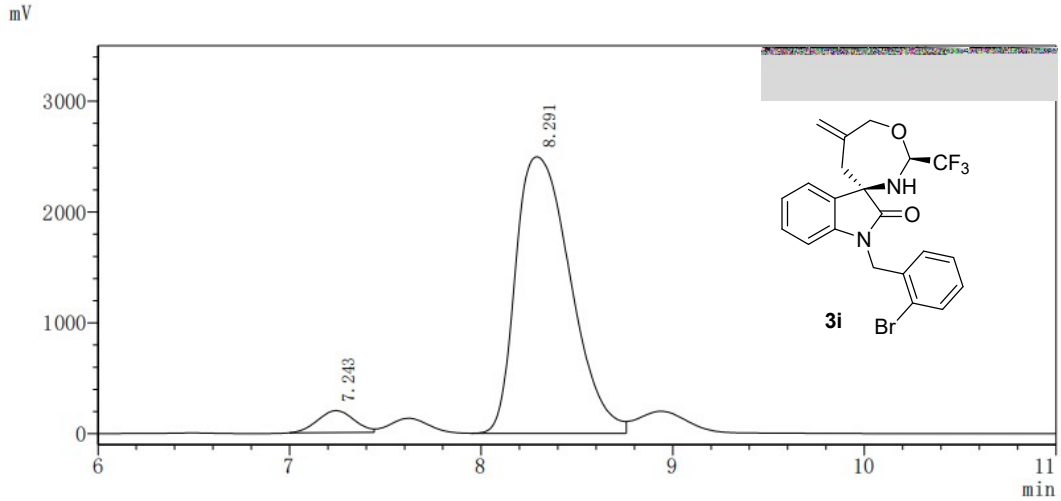
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	12.797	93.855
2	19.432	6.145
total		100



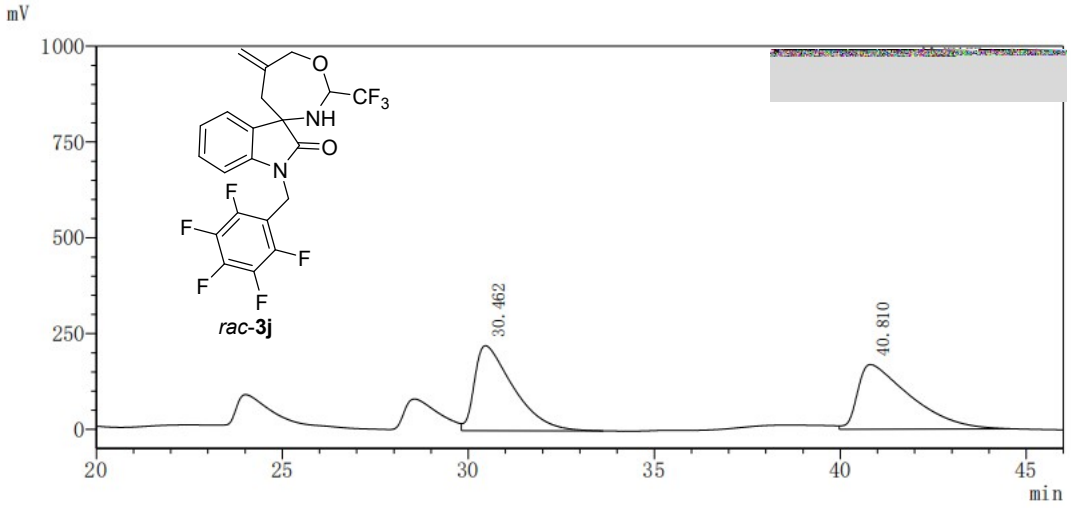
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	7.246	50.377
2	8.402	49.623
total		100



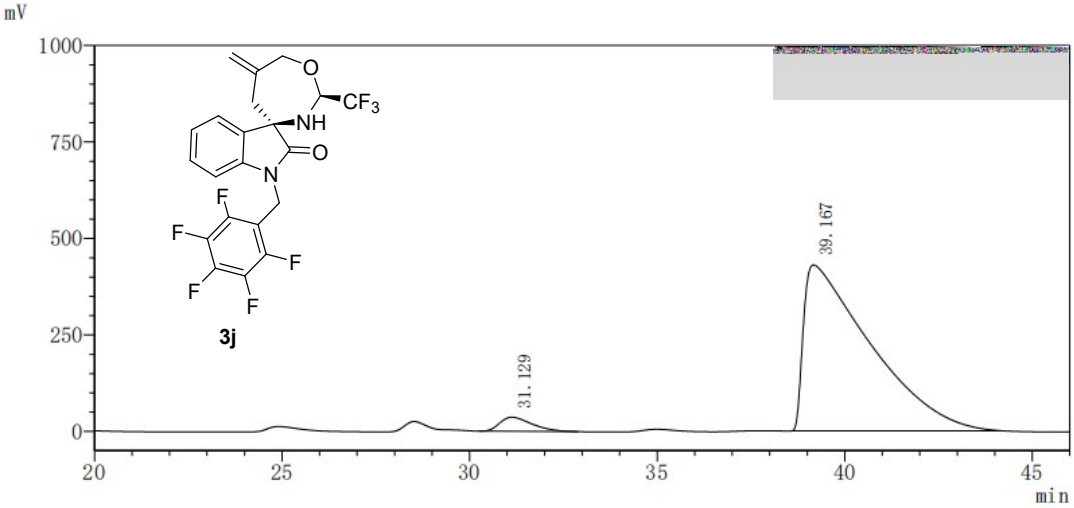
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	7.243	5.025
2	8.291	94.975
total		100



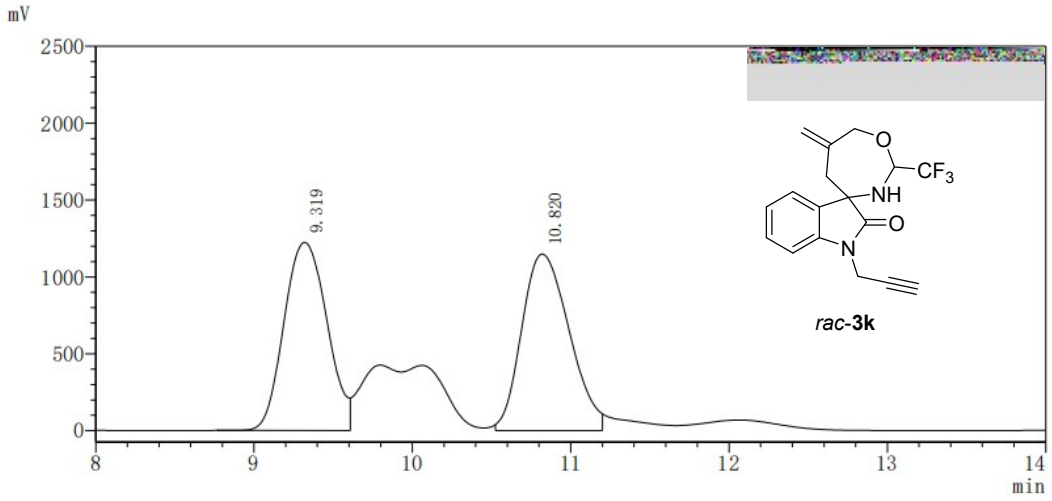
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	30.462	49.285
2	40.810	50.715
total		100



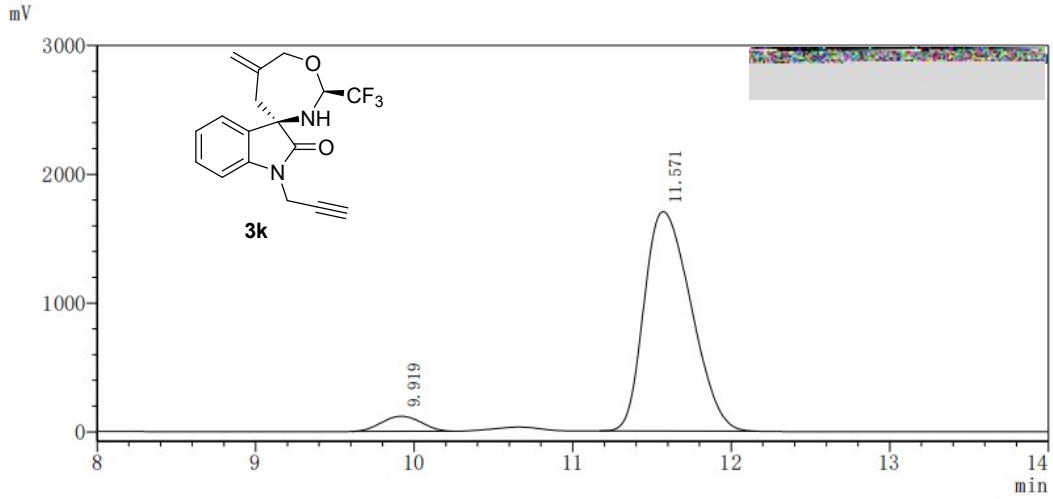
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	31.129	3.927
2	39.167	96.073
total		100



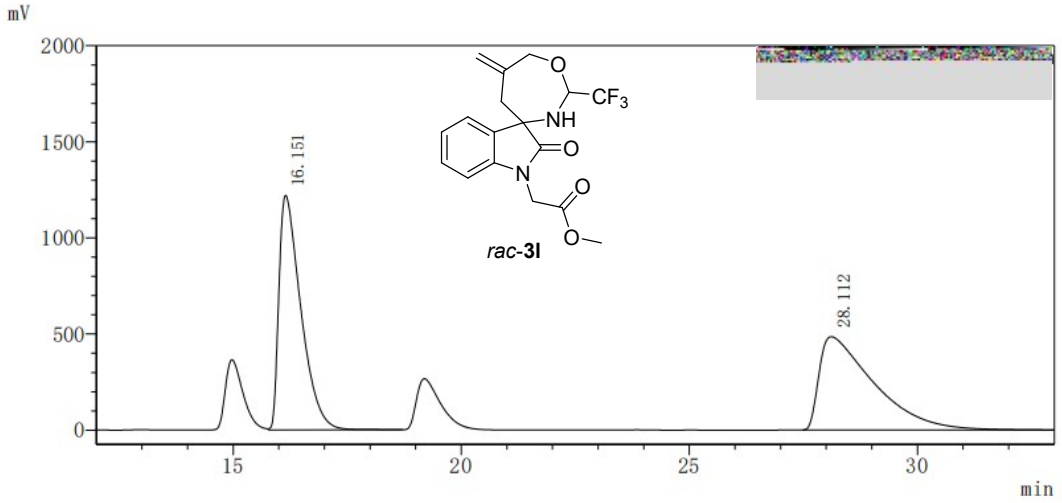
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.319	49.177
2	10.820	50.823
total		100



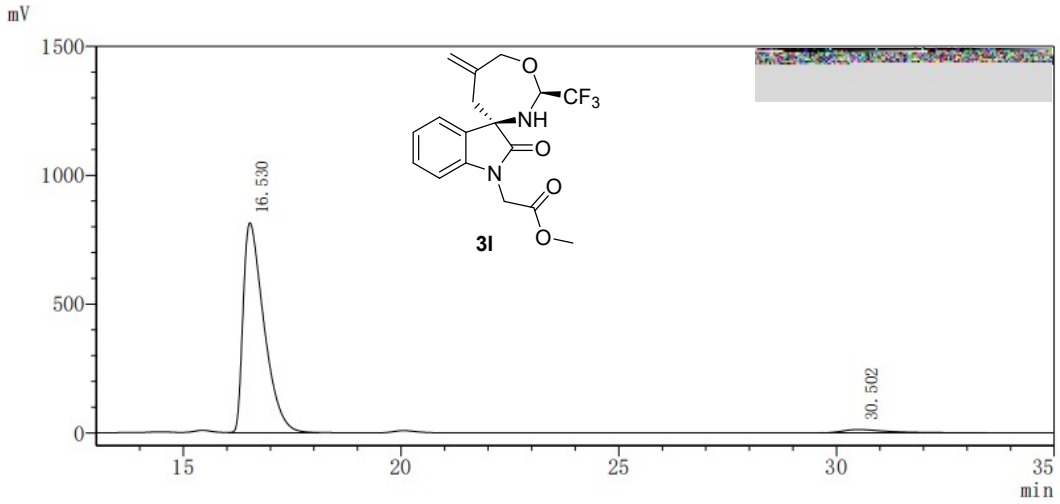
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.919	5.460
2	11.571	94.540
total		100



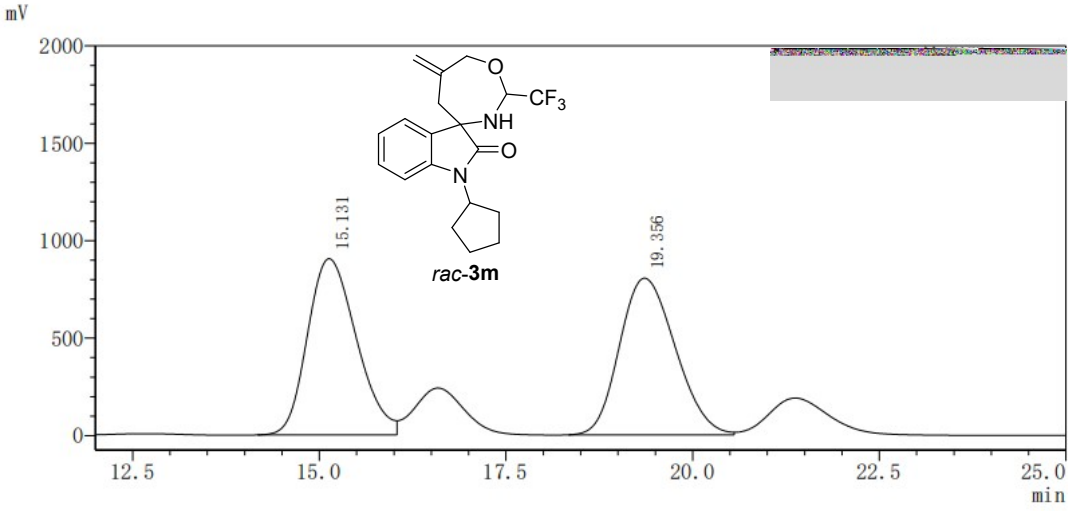
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	16.151	50.207
2	28.112	49.793
total		100



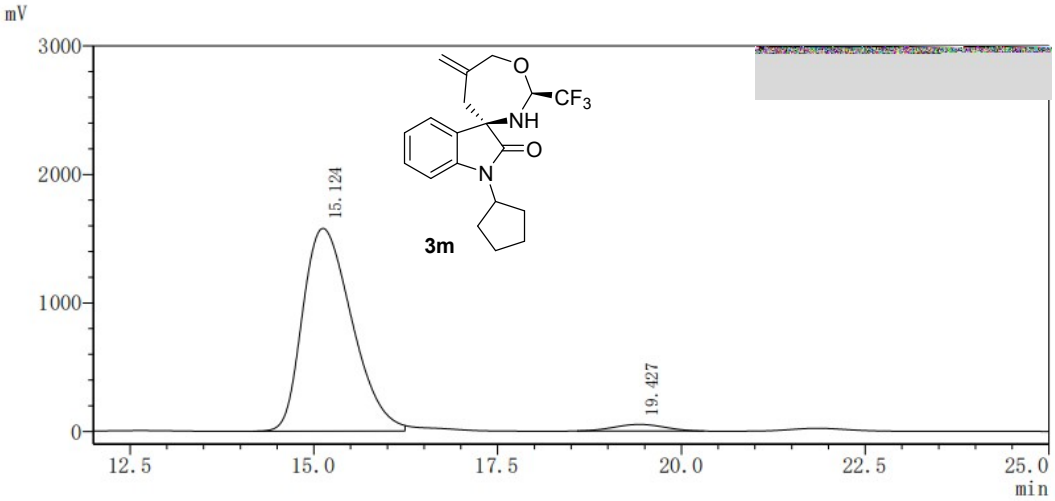
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	16.530	96.711
2	30.502	3.289
total		100



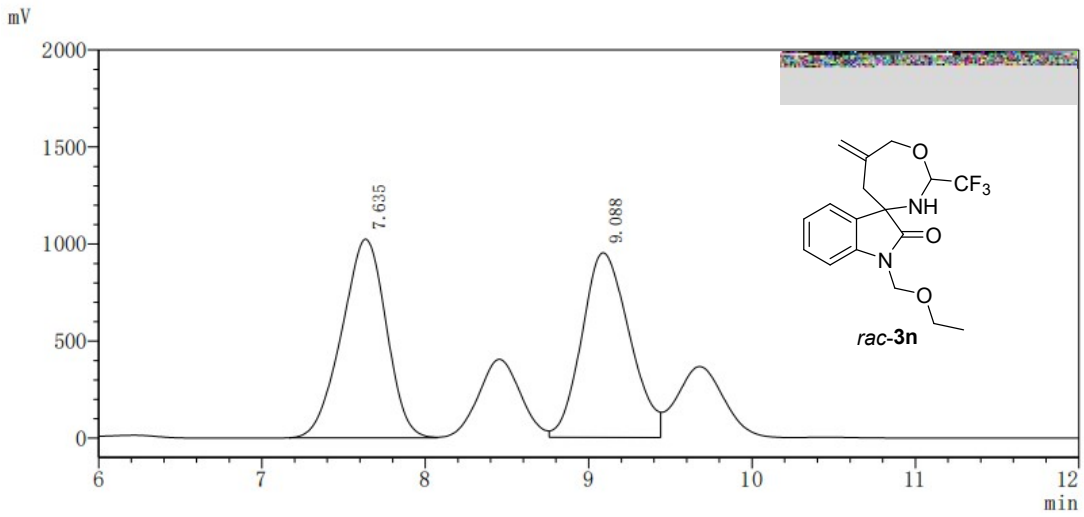
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	15.131	49.686
2	19.356	50.314
total		100



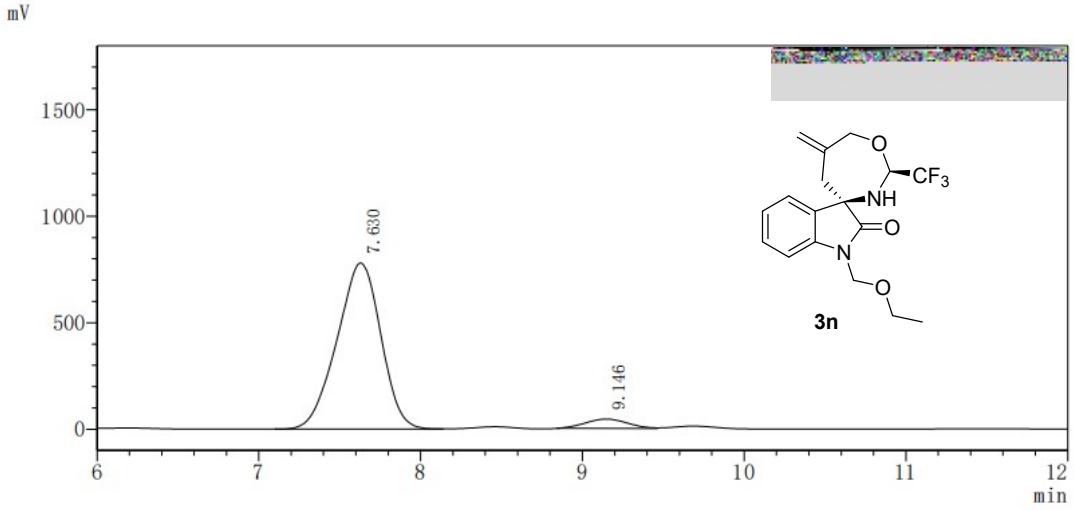
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	15.124	96.775
2	19.427	3.225
total		100



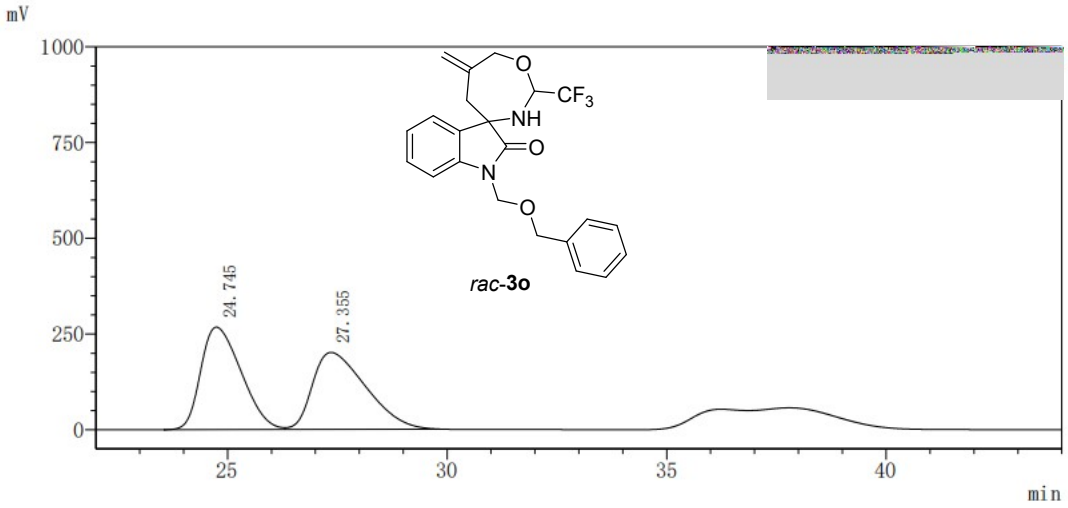
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	7.635	50.053
2	9.088	49.947
total		100



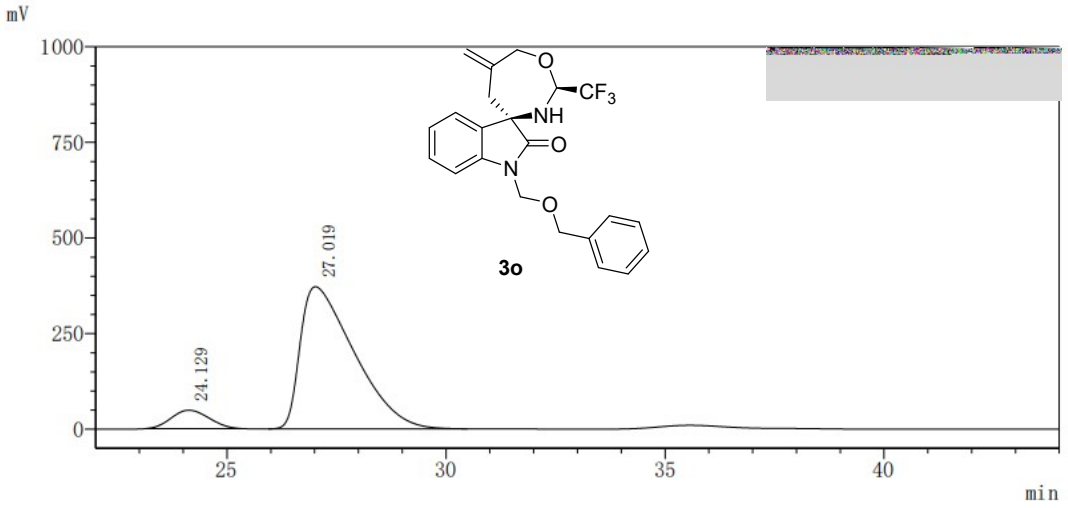
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	7.630	94.807
2	9.146	5.193
total		100



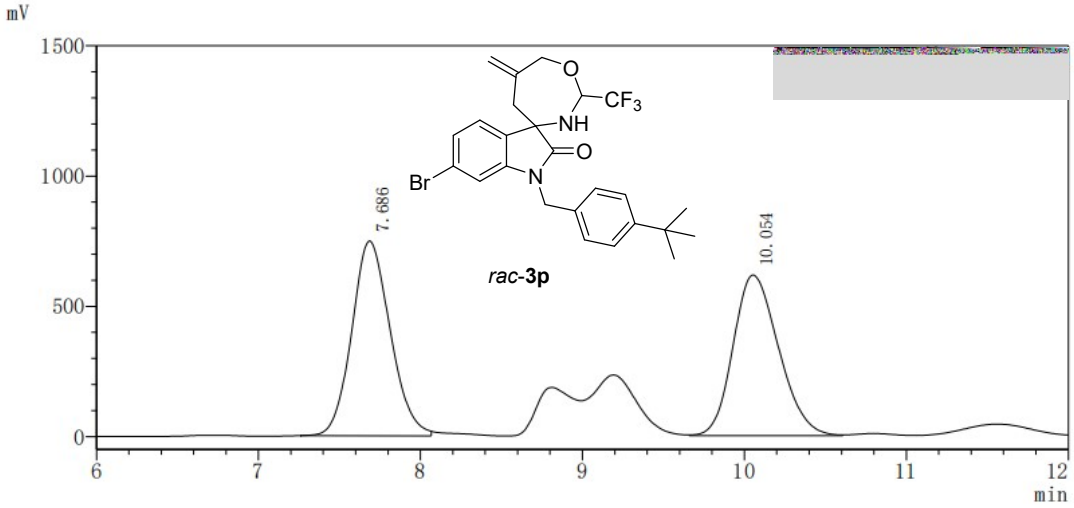
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	24.745	50.177
2	27.355	49.823
total		100



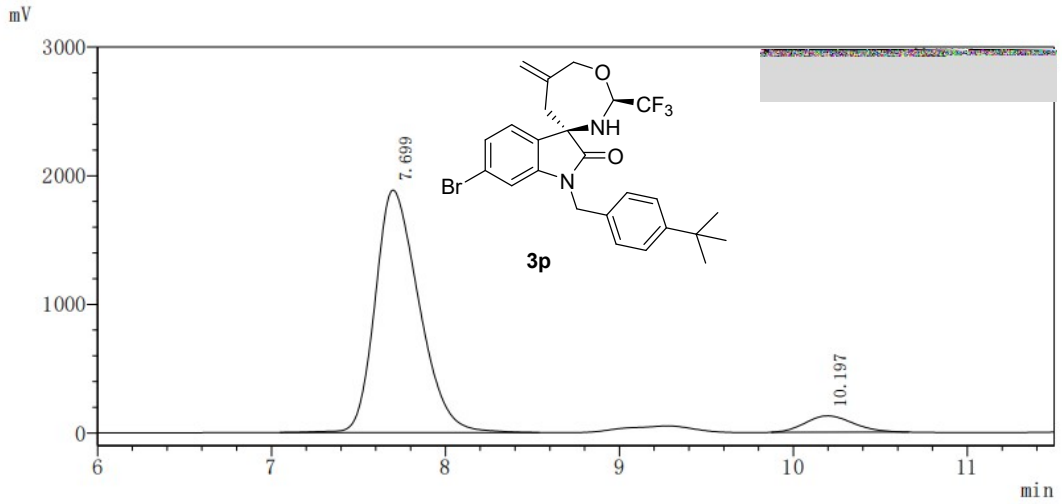
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	24.129	8.342
2	27.019	91.658
total		100



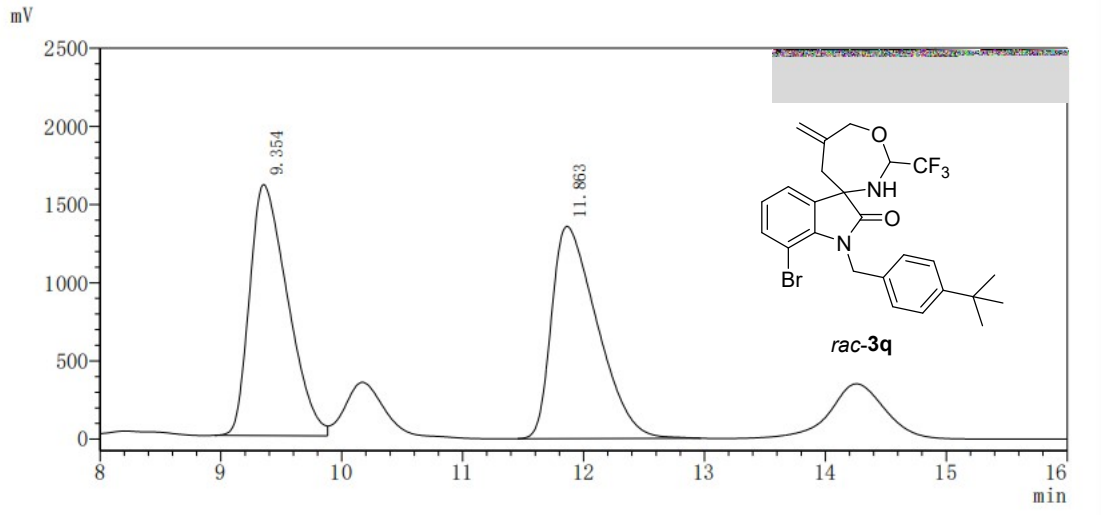
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	7.686	50.565
2	10.054	49.435
total		100



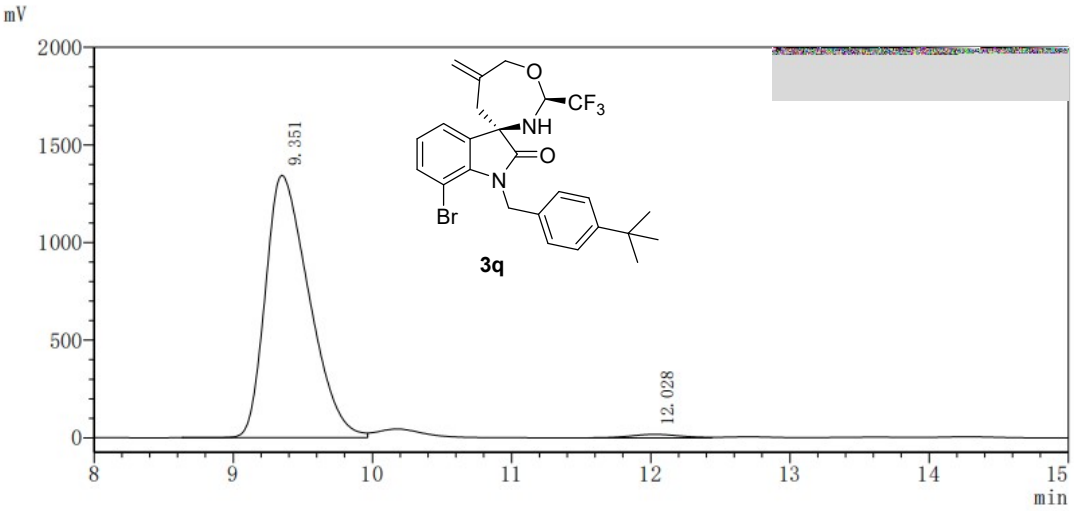
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	7.699	93.115
2	10.197	6.885
total		100



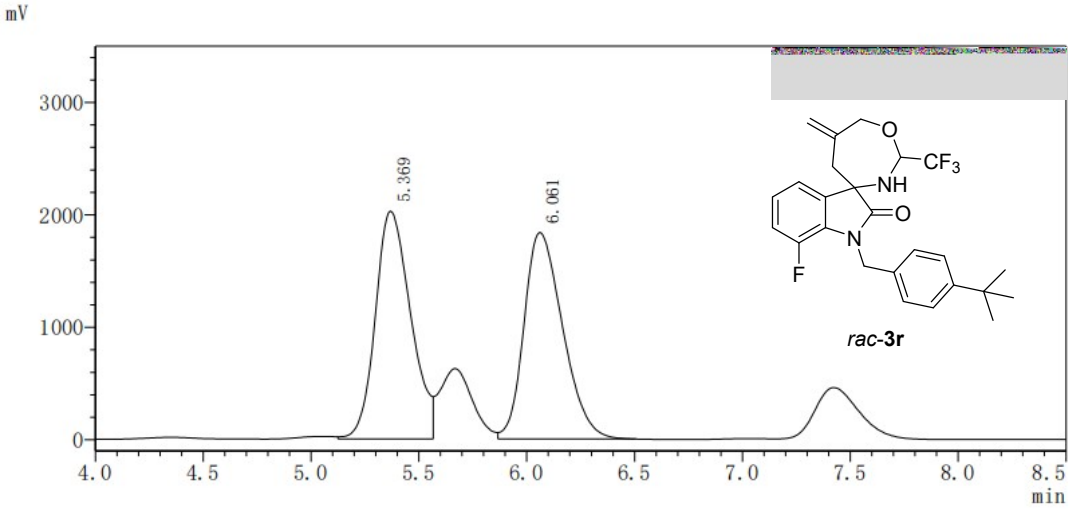
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.354	49.647
2	11.863	50.353
total		100



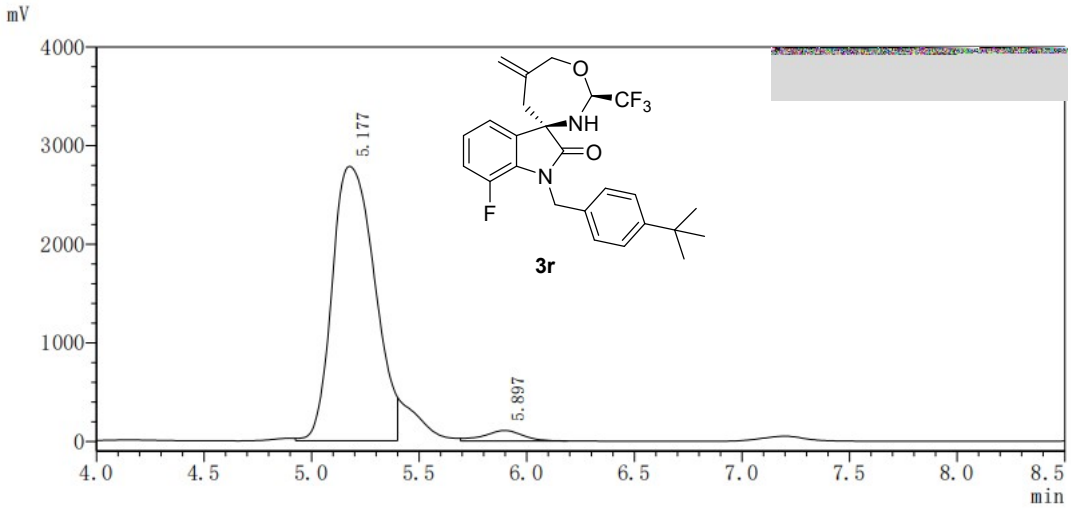
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.351	98.569
2	12.028	1.431
total		100



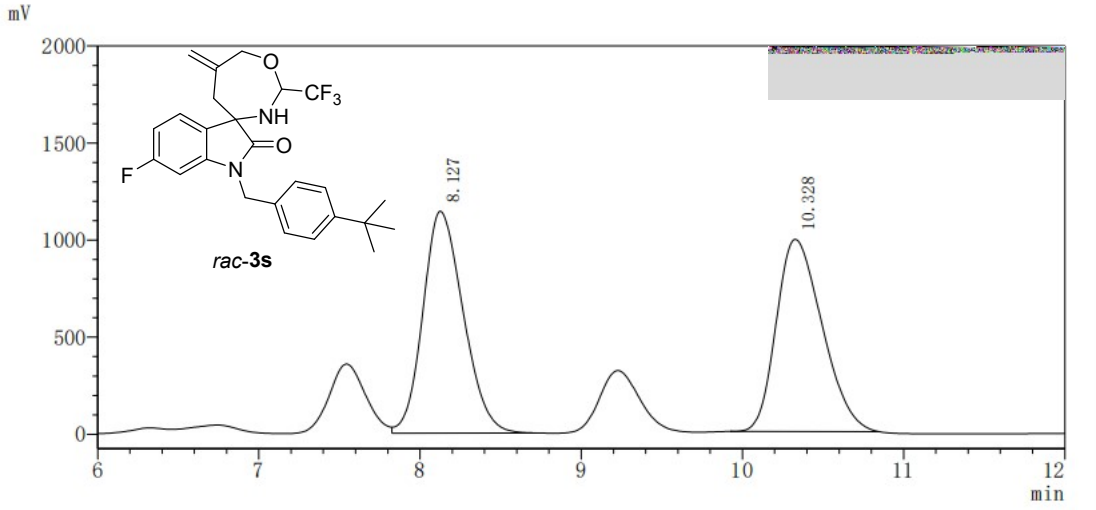
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	5.369	50.345
2	6.061	49.655
total		100



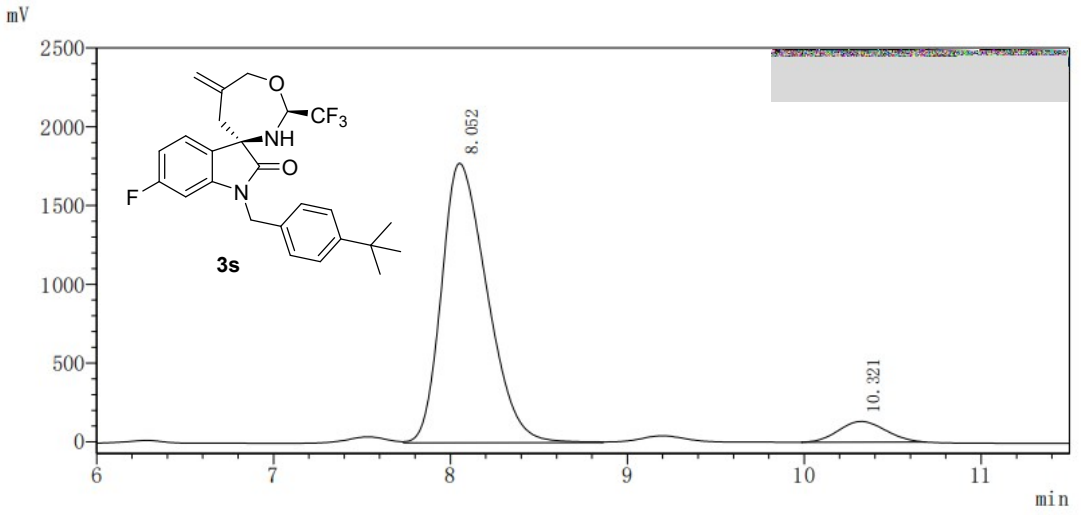
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	5.177	96.373
2	5.897	3.327
total		100



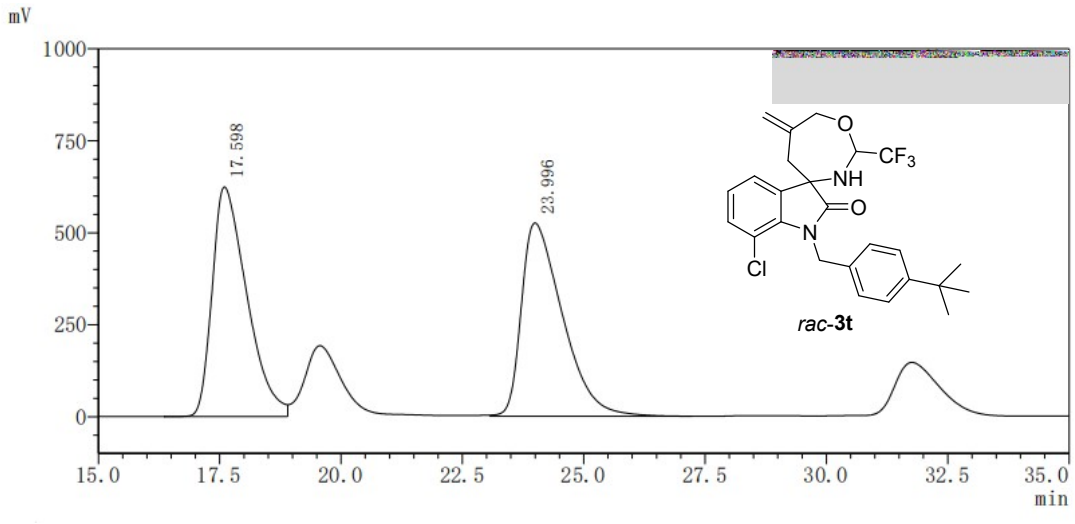
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	8.127	50.331
2	10.328	49.669
total		100



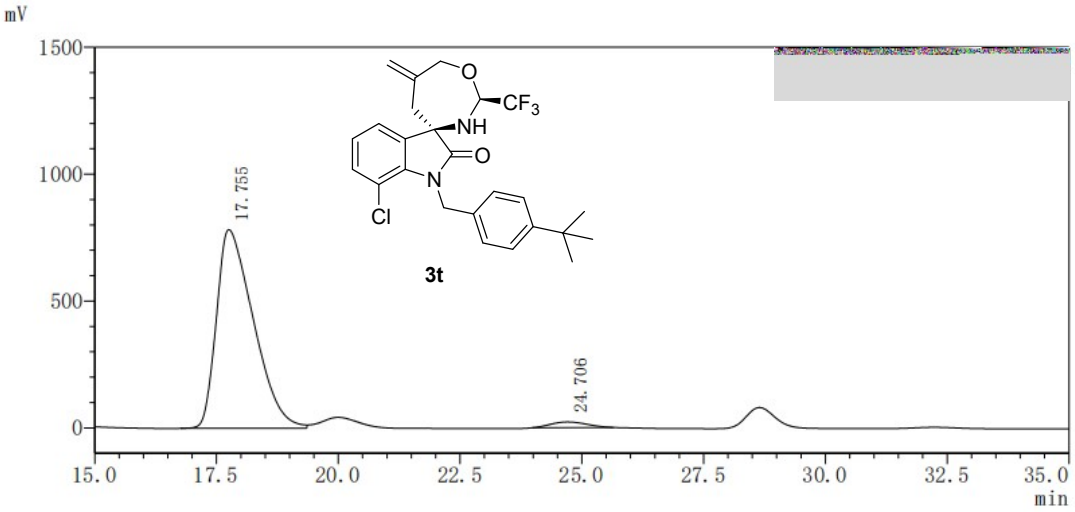
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	8.062	92.943
2	10.321	7.057
total		100



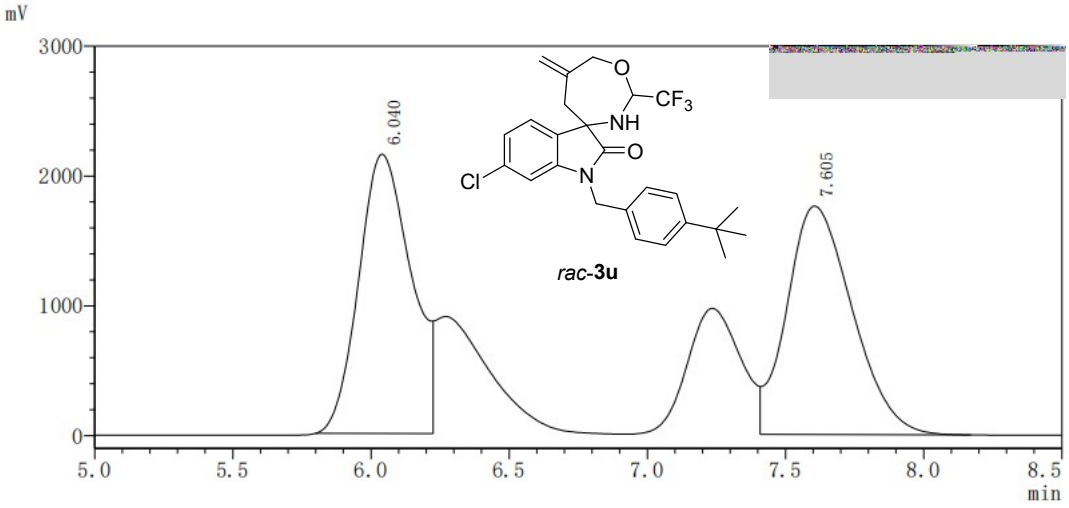
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	17.598	49.970
2	23.996	50.030
total		100



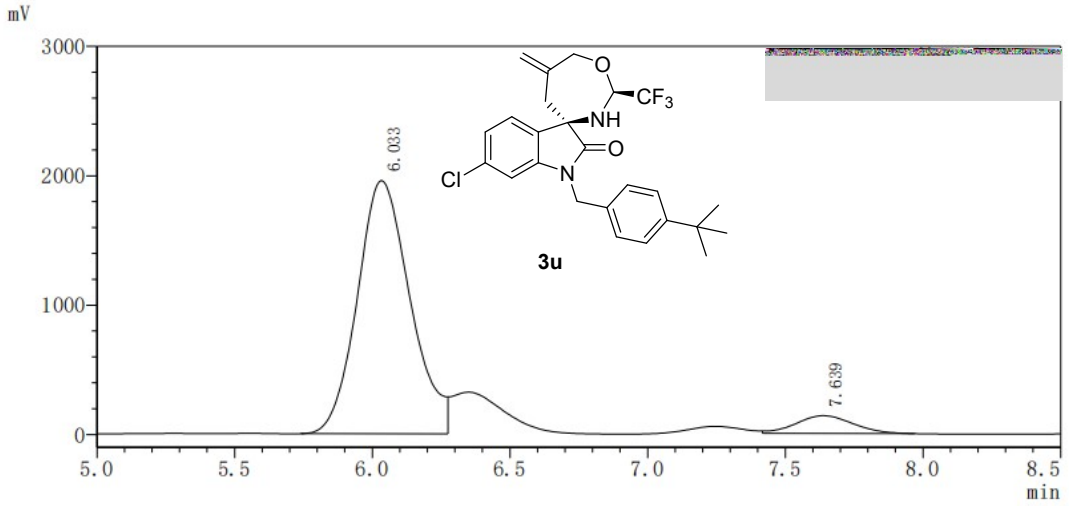
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	17.755	97.304
2	24.706	2.696
total		100



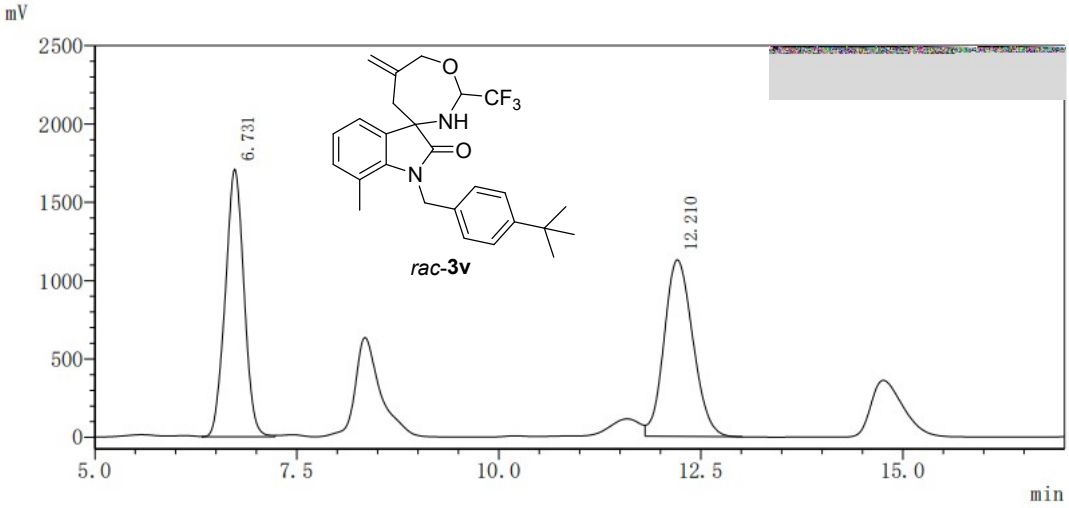
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	6.040	49.650
2	7.605	50.350
total		100



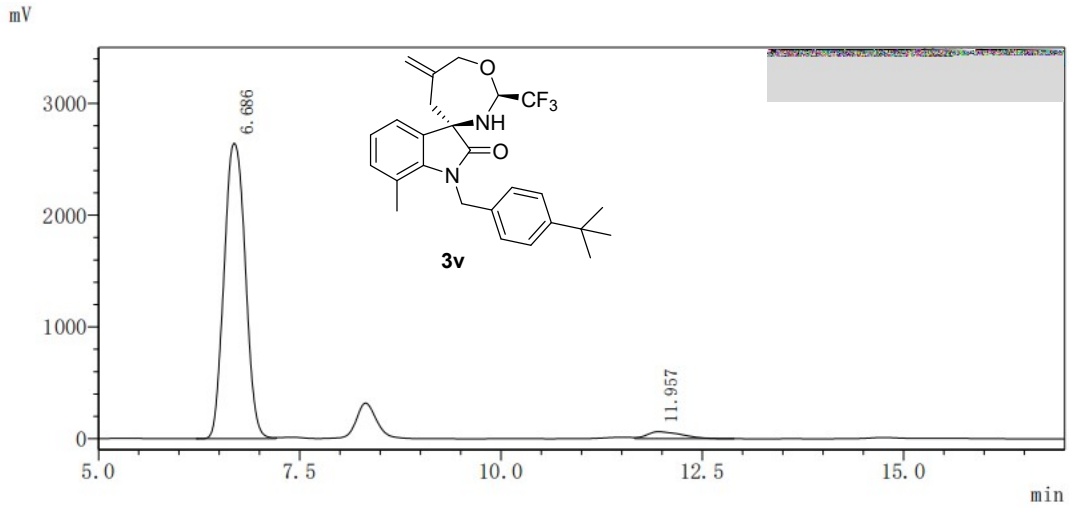
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	6.033	92.928
2	7.639	7.072
total		100



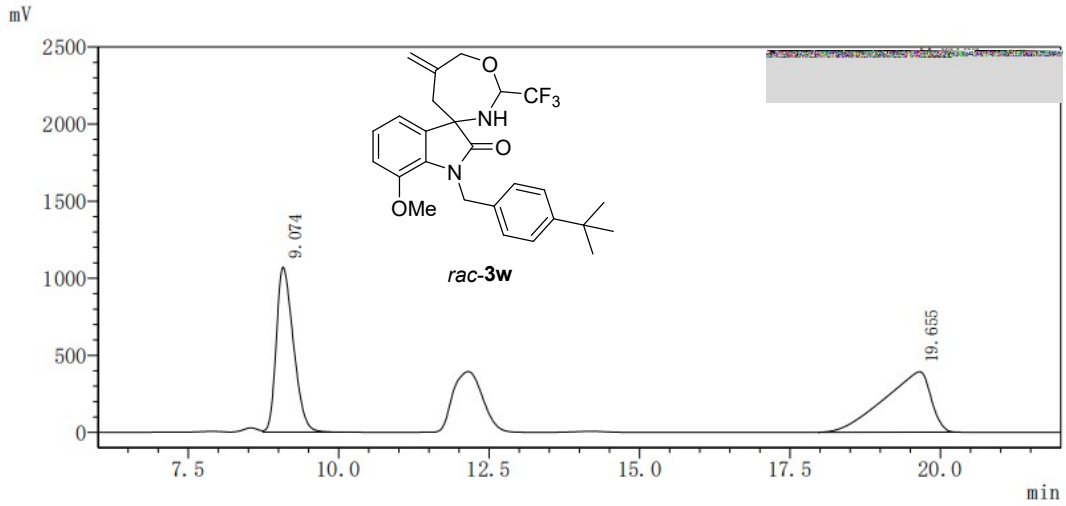
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	6.731	49.556
2	12.210	50.444
total		100



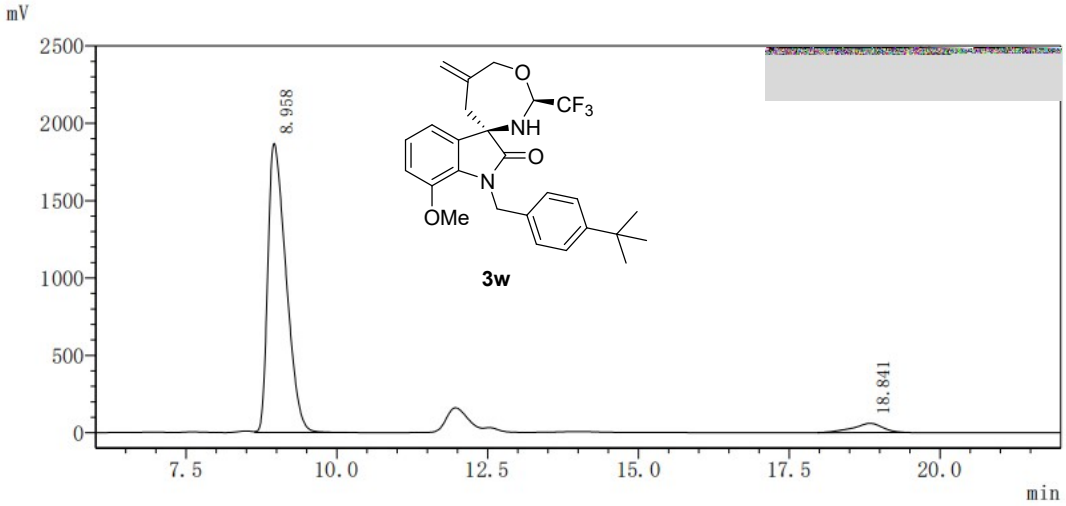
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	6.686	96.227
2	11.957	3.773
total		100



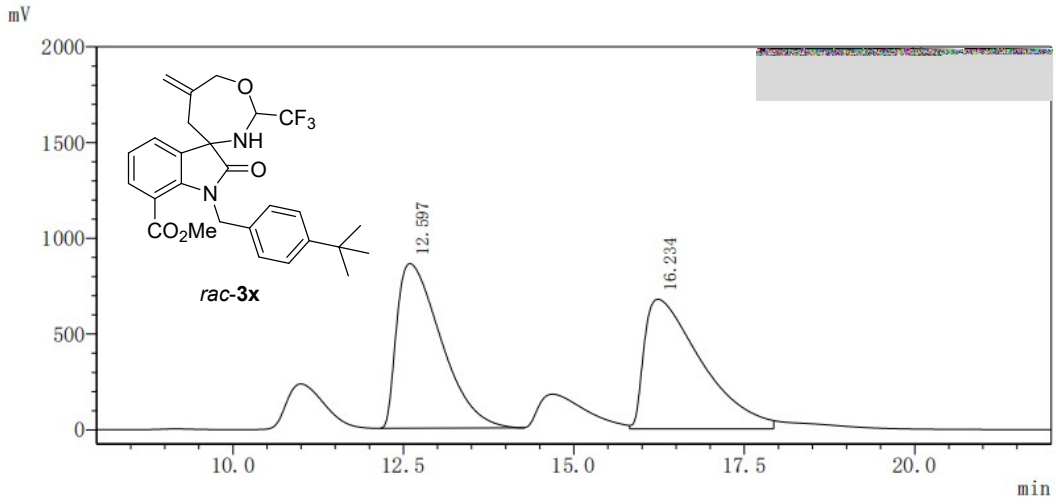
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	9.074	49.972
2	19.655	50.028
total		100



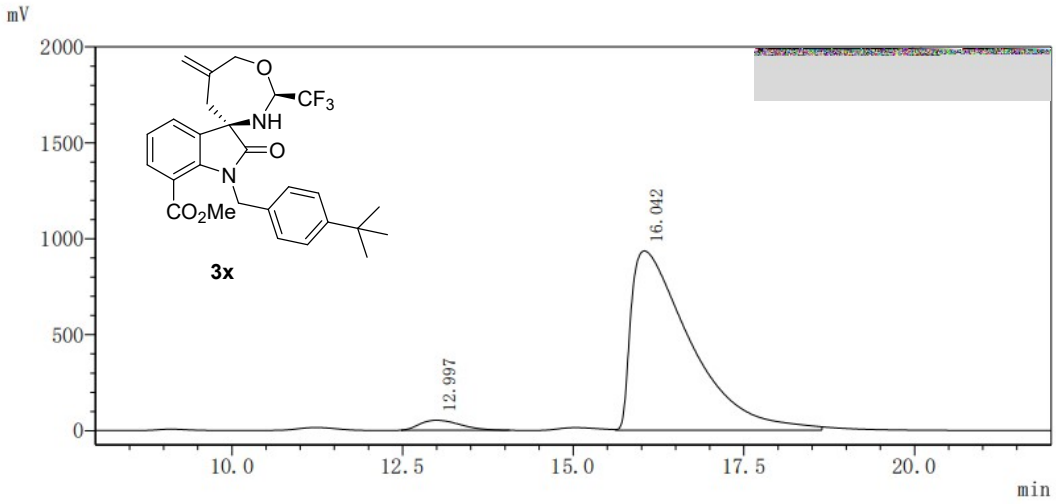
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	8.958	95.002
2	18.841	4.998
total		100



Discloser A 254 nm

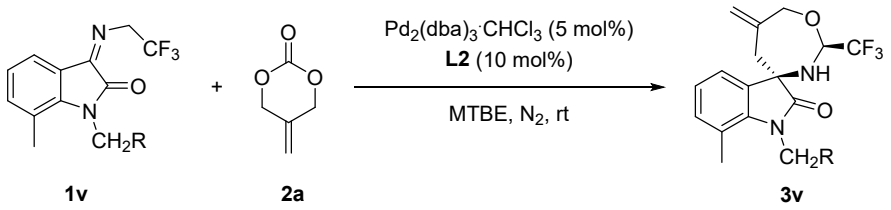
Peak	Reten time (min)	Area (%)
1	12.597	49.562
2	16.234	50.438
total		100



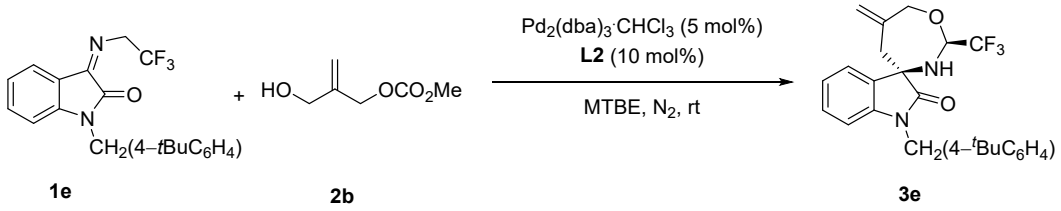
Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	12.997	3.612
2	16.042	96.388
total		100

7. Scale-up Synthesis



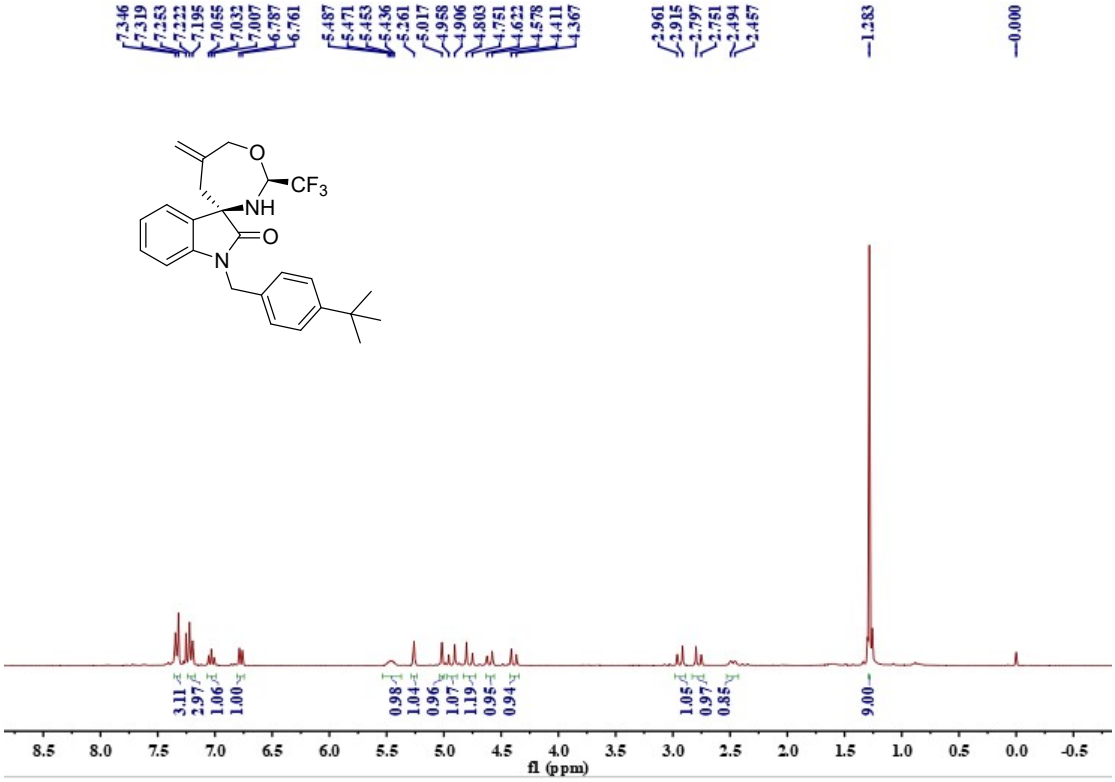
To a flame dried 25 mL sealing tube, $Pd_2(dba)_3 \cdot CHCl_3$(0.005 mmol, 15.6 mg), **L2** (0.01 mmol, 16.2 mg), freshly distilled anhydrous MTBE (10.0 mL) were added. The resulting mixture was allowed to stir for 30 min. Then, compound **1v** (2 mmol) and compound **2a** (3 mmol) were added subsequently. The resulting reaction mixture was stirred at room temperature for 24 h (monitored by TLC). The residue was subjected to column chromatography on silica gel, using a mixture of petroleum ether and ethyl acetate as eluent, to give desired product **3v**.yield 54%, dr > 20 : 1, ee = 86%.



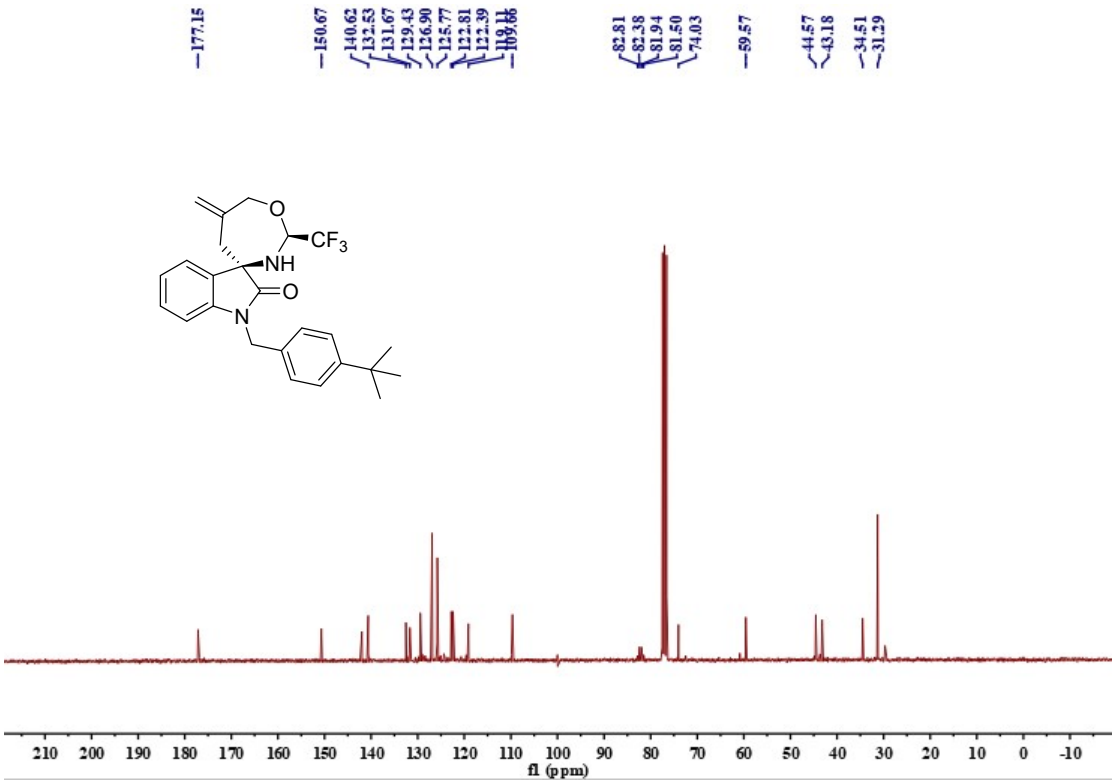
To a flame dried 10ml sealing tube, $Pd_2(dba)_3 \cdot CHCl_3$(0.005 mmol, 5.4 mg), **L2** (0.01 mmol, 4.6 mg), freshly distilled anhydrous MTBE (1.0 mL) were added. The resulting mixture was allowed to stir for 30 min. Then, compound **1e** (0.1 mmol) and compound **2b** (0.15 mmol) were added subsequently. The resulting reaction mixture was stirred at room temperature for 8 h (monitored by TLC). The residue was subjected to column chromatography on silica gel, using a mixture of petroleum ether and ethyl acetate as eluent, to give desired product **3e**.yield 51%, dr=10:1, ee=94%; yellow oil**. ^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.33 (d, J = 8.1 Hz, 3H), 7.21 (d, J = 8.1 Hz, 3H), 7.03 (t, J = 14.4 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.46 (dd, J = 10.2, 4.8 Hz, 1H), 5.26 (s, 1H), 5.02 (s, 1H), 4.93 (d, J = 15.6 Hz, 1H), 4.78 (d, J = 15.6 Hz, 1H), 4.60 (d, J = 13.2 Hz, 1H), 4.39 (d, J = 13.2 Hz, 1H), 2.94 (d, J = 13.8 Hz, 1H), 2.77 (d,

J = 13.8 Hz, 1H), 2.48 (d, *J* = 11.1 Hz, 1H), 1.28 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 177.2, 150.7, 142.0, 140.6, 132.5, 131.7, 129.4, 126.9, 125.8, 122.8, 122.5 (q, *J* = 279.75 Hz), 122.4, 119.1, 109.7, 82.2 (q, *J* = 33.00Hz), 74.1, 59.6, 44.6, 43.2, 34.5, 31.3 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -80.61 (d, *J* = 2.8 Hz,) ppm.

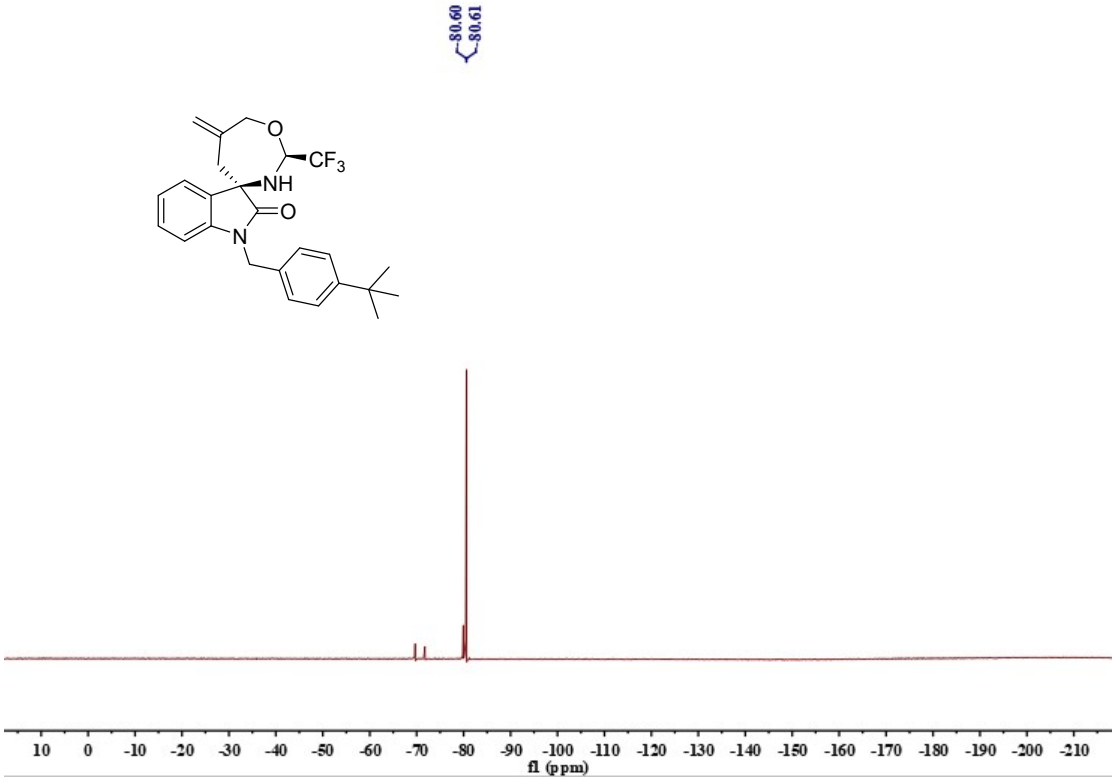
HPLC (Chiralpak AD-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, l = 254 nm) tR =22.49 min (major), 29.42min (minor).



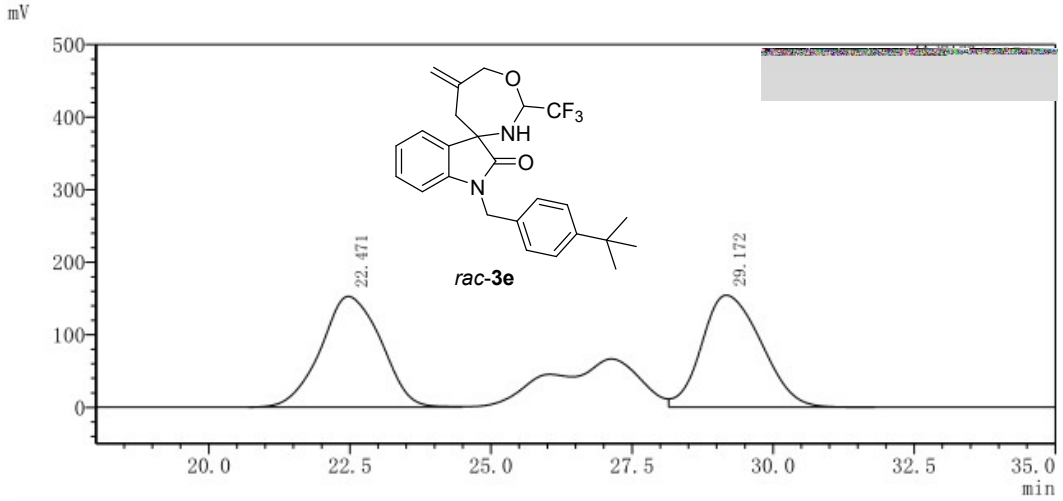
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3e**



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

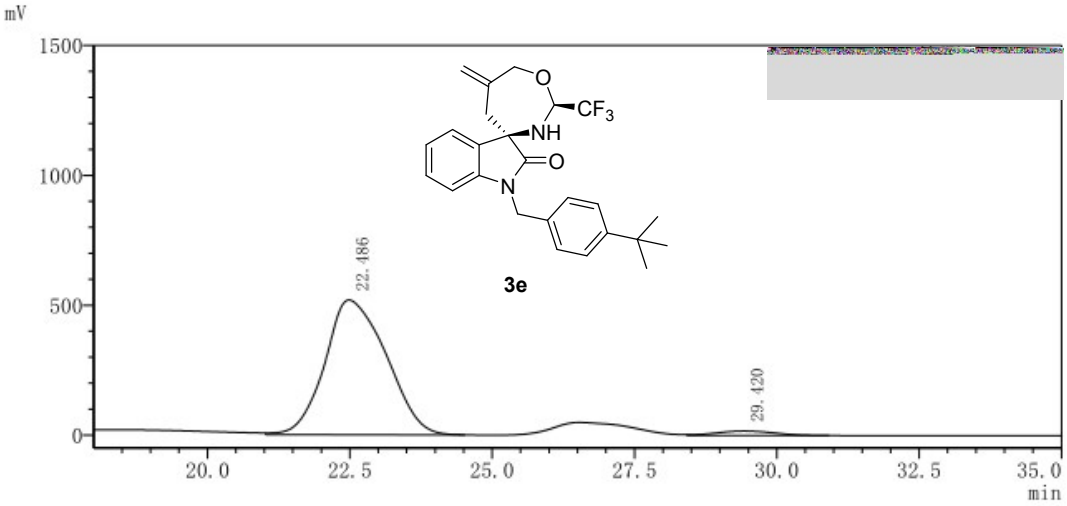


^{19}F NMR (CDCl3, 282 MHz) NMR of **3e**



Discloser A 254 nm

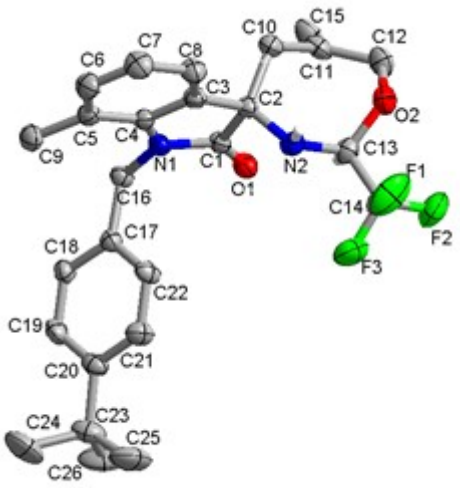
Peak	Reten time (min)	Area (%)
1	22.471	50.018
2	29.172	49.982
total		100

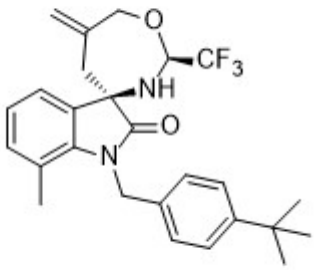


Discloser A 254 nm

Peak	Reten time (min)	Area (%)
1	22.486	97.087
2	29.420	2.913
total		100

8. X-ray crystal structure





Crystal structure of **3v (CCDC: 2132621)**

Table 1 Crystal data and structure refinement for **3v CCDC: 2132621**	
Identification code	2132621
Empirical formula	$C_{26}H_{29}F_3N_2O_2$
Formula weight	458.51
Temperature/K	293(2)
Crystal system	trigonal
Space group	$P3_2$
a/Å	10.6182(3)
b/Å	10.6182(3)
c/Å	18.9438(6)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1849.71(13)
Z	3
ρ_{calc}g/cm^3	1.235

μ/mm^{-1}	0.779
F(000)	726.0
Crystal size/mm^3	0.17 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.618 to 142.158
Index ranges	-12≤h≤10, -11≤k≤12, -22≤l≤23
Reflections collected	11383
Independent reflections	4668 [R_{int} = 0.0302, R_{sigma} = 0.0350]
Data/restraints/parameters	4668/59/319
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1226
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.13
Flack parameter	0.09(11)