Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Organocatalytic synthesis of chiral CF_3-containing oxazolidines and 1,2-amino alcohols: asymmetric *oxa*-1,3-dipolar cycloaddition of trifluoroethylamine-derived azomethine ylide

Wen-Run Zhu,[a,b] Qiong Su,[a] Ning Lin,*[,b] Qing Chen,*[,b] Zhen-Wei Zhang,[b] Jiang Weng,[a] and Gui Lu*[,a]

[a] Guangdong Provincial Key Laboratory of Chiral Molecule and Drug Discovery, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, P. R. China.

[b] College of Pharmacy, Guangxi Zhuang Yao Medicine Center of Engineering and Technology, Guangxi University of Chinese Medicine, Nanning, Guangxi, 530200, P. R. China.

E-mail for N.L.: linninginnanning@163.com. E-mail for Q.C.: qing0082@163.com. E-mail for G.L.: lugui@mail.sysu.edu.cn.

Table of Contents

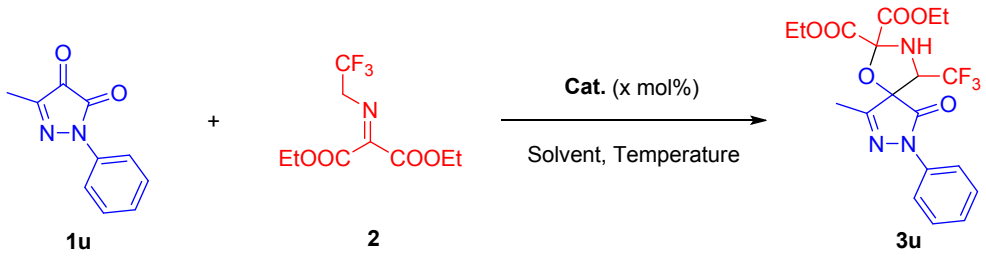
1. General Information

All reactions were carried out in oven-dried reaction vessel unless otherwise noted and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC). Purification of reaction product was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200-300 mesh). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0 ppm). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.0 ppm). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant in Hertz (Hz). HPLC analyses were conducted on an Agilent instrument using a Daicel Chiralpak IA, IB, IC and AD-H column. High resolution mass spectra were obtained with a Shimadzu LCMS-IT-TOF mass spectrometer. The single crystal X-ray diffraction studies were carried out on a Xcalibur Onyx Nova diffractometer equipped with CuK/α radiation.

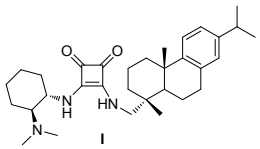
Substrates **2**,[1a] **5**,[1b] and **7**[1b] were synthesized according to the literature method.

2. Screening of Catalysts and Condition Optimization

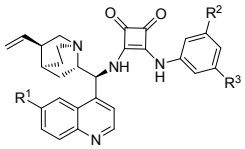
Table S1. Screening of catalysts and optimization of reaction conditions[a]



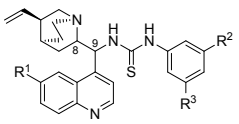
1u + **2** → **3u**



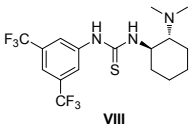
I



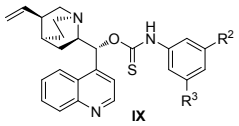
II R^1=H, R^2=H R^3=H
III R^1=H, R^2=CF_3 R^3=CF_3
IV R^1=OMe, R^2=CF_3 R^3=CF_3



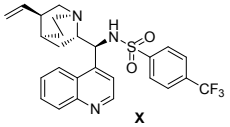
V (8*R*,9*R*), R^1=H, R^2=CF_3 R^3=CF_3
VI (8*S*,9*S*), R^1=H, R^2=CF_3 R^3=CF_3
VII (8*S*,9*S*), R^1=OMe, R^2=CF_3 R^3=CF_3



VIII



IX



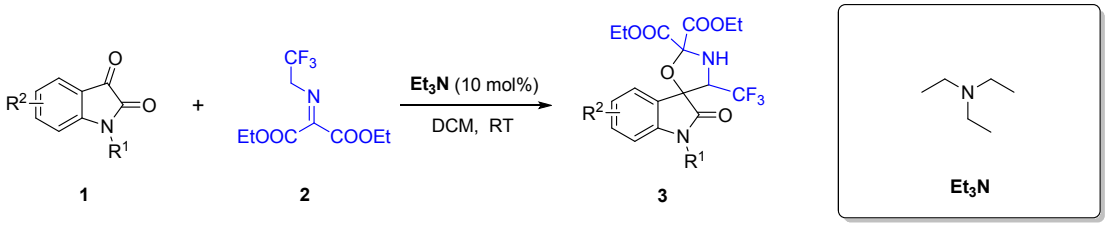
X

Entry	Catalyst (x mol%)	Solvent (x mL)	Temperature [°C]	Time	Yield[b] [%]	*dr*[c]	*ee*[d]
1	**I** (10)	DCM (1)	35	1h	99	>20:1	15
2	**II** (10)	DCM (1)	35	<5min	96	>20:1	5
3	**III** (10)	DCM (1)	35	1.5h	96	>20:1	18
4	**IV** (10)	DCM (1)	35	2h	96	>20:1	19
5	**V** (10)	DCM (1)	35	<30min	96	>20:1	82
6	**VI** (10)	DCM (1)	35	40min	96	>20:1	-75
7	**VII** (10)	DCM (1)	35	<30min	96	>20:1	-55
8	**VIII** (10)	DCM (1)	35	40min	92	>20:1	60
9	**IX** (10)	DCM (1)	35	2h	96	>20:1	76
10	**X** (10)	DCM (1)	35	24h	90	>20:1	84
11	**V** (10)	DCE (1)	35	<30min	96	>20:1	72
12	**V** (10)	$CHCl_3$ (1)	35	<30min	96	>20:1	70
13	**V** (10)	THF (1)	35	<30min	96	>20:1	78
14	**V** (10)	Toluene (1)	35	<30min	96	>20:1	45
15	**V** (10)	MeOH (1)	35	<30min	90	1:8	0
16	**V** (10)	MeCN (1)	35	<30min	90	>20:1	70
17	**V** (10)	MTBE (1)	35	<30min	96	>20:1	75
18	**V** (10)	DCM (1)	-20	72h	68	>20:1	63
19	**V** (10)	DCM (1)	0	72h	82	>20:1	81
20	**V** (10)	DCM (1)	10	36h	92	>20:1	82
21	**V** (10)	DCM (1)	25	30min	98	>20:1	84
22	**V** (5)	DCM (1)	25	30min	98	>20:1	68
23	**V** (20)	DCM (1)	25	<30min	98	>20:1	82
24	**V** (10)	DCM (3)	25	1h	98	>20:1	88
25	**V (10)**	**DCM (5)**	**25**	**1h**	**98**	>20:1	**90**
26[e]	**V** (10)	DCM (5)	25	4h	98	>20:1	46

[a]Unless otherwise specified, all reactions were carried out with catalyst (x mol%), **1u** (0.10 mmol) and **2** (0.15 mmol) in the indicated solvent (x mL) at 35 °C. [b] Isolated yield of **3u**. [c] Determined by ^{1}H NMR analysis of the crude product. [d] Determined by chiral-phase HPLC analysis. [e] 50 mg 4Å was used.

3. Experimental Procedure and Characterization of Products

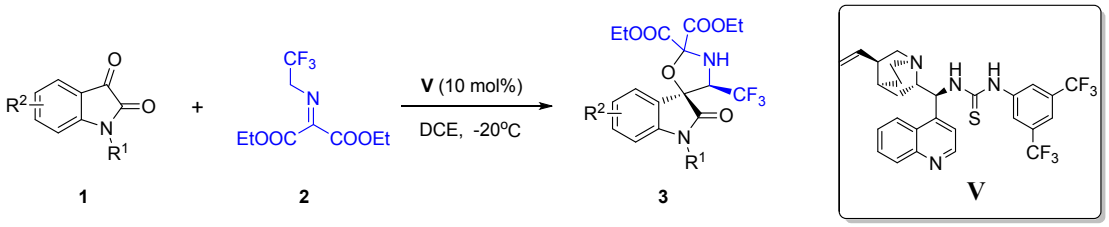
a. General Procedure to Prepare Racemic Products 3a-3t, 3aa



1 2 3

To a solution of diethyl 2-((2,2,2-trifluoroethyl)imino)malonate **2** (0.15 mmol, 1.5 equiv.), and catalyst Et_3N (0.01 mmol, 10 mol%) in DCM (1 mL) was added isatin **1** (0.10 mmol, 1.0 equiv.). The mixture was stirred at room temperature until the reaction was completed (monitored by TLC analysis). The crude product was purified directly by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1~3:1) to give the desired racemic products **3a-3t**, **3aa**.

b. General Procedure to Prepare Chiral Products 3a-3t, 3aa

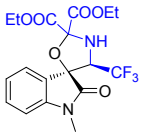


1 2 3

To a solution of diethyl 2-((2,2,2-trifluoroethyl)imino)malonate **2** (0.15 mmol, 1.5 equiv.) and catalyst **V** (0.01 mmol, 10 mol%) in DCE (1 mL) was added isatin **1** (0.10 mmol, 1.0 equiv.). The mixture was stirred at -20 °C until the reaction was completed (monitored by TLC analysis). The crude product was purified directly by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1~3:1) to give the desired chiral products **3a-3t**, **3aa**.

c. Analytical Data for Products 3a-3t, 3aa

(*3S,4'R*)-diethyl 1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3a**): petroleum ether/ ethyl acetate = 3:1, Rf=0.6.



White solid, 95% yield, >20:1 *dr,* 96% *ee*, $[a]_D^{20}$ = +40.12 (c = 0.42, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.38 (td, *J* = 7.8, 1.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.67 (d, *J* = 13.6 Hz, 1H), 4.51-4.38 (m, 2H), 4.37-4.26 (m, 3H), 3.15 (s, 3H), 1.34 (dt, *J* = 8.8, 7.1 Hz, 6H);

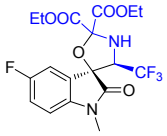
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.82, 167.43, 165.26, 144.64, 131.33, 124.84, 123.70, 123.68, 122.51 (q, *J* = 279.6 Hz), 108.87, 94.32, 81.25, 67.66 (q, *J* = 31.3 Hz), 63.28, 63.07, 26.43, 14.07, 14.04;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.09.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{20}N_2O_6F_3$ $[M+H]^+$: 417.1268; found: 417.1264.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL·min^{-1}, λ = 254 nm): t_{major} = 6.4 min, t_{minor} = 7.5 min.

(*3S,4'R*)-diethyl 5-fluoro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3b**): petroleum ether/ ethyl acetate = 3:1, Rf=0.6.



Light yellow oil, 97% yield, >20:1 *dr*, 94% *ee*, $[\alpha]_D^{20}$ = +52.38 (c = 0.37, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (dd, *J* = 7.4, 2.6 Hz, 1H), 7.08 (td, *J* = 8.8, 2.6 Hz, 1H), 6.76 (dd, *J* = 8.5, 3.9 Hz, 1H), 4.66 (d, *J* = 13.7 Hz, 1H), 4.51-4.37 (m, 2H), 4.36-4.24 (m, 3H), 3.14 (s, 3H), 1.34 (dt, *J* = 9.8, 7.1 Hz, 6H);

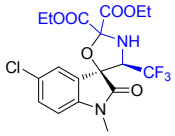
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.61, 167.28, 165.01, 159.70 (d, *J* = 243.0 Hz), 140.57 (d, *J* = 2.1 Hz), 125.46 (d, *J* = 8.2 Hz), 122.40 (q, *J* = 279.5 Hz), 117.63 (d, *J* = 23.7 Hz), 113.18 (d, *J* = 25.5 Hz), 109.61 (d, *J* = 7.9 Hz), 94.51, 81.09, 67.91 (q, *J* = 31.6 Hz), 63.38, 63.20, 26.59, 14.06, 14.04;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.09, -118.71.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}N_2O_6F_4$ $[M+H]^+$: 435.1174; found: 435.1169.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 8.2 min, t_{minor} = 10.9 min.

(*3S,4'R*)-diethyl 5-chloro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3c**): petroleum ether/ ethyl acetate = 3:1, Rf=0.6.



Colorless oil, 92% yield, >20:1 *dr*, 95% *ee*, $[\alpha]_D^{20}$ = +70.02 (c = 0.40, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 4.65 (d, *J* = 13.7 Hz, 1H), 4.50-4.37 (m, 2H), 4.36-4.24 (m, 3H), 3.13 (s, 3H), 1.34 (dt, *J* = 13.9, 7.1 Hz, 6H);

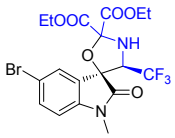
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.42, 167.23, 164.98, 143.16, 131.24, 129.15, 125.51, 125.43, 122.38 (q, *J* = 279.6 Hz), 109.91, 94.50, 80.91, 67.87 (q, *J* = 31.6 Hz), 63.38, 63.23, 26.57, 14.05, 14.02;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.04.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}ClN_2O_6F_3$ $[M+H]^+$: 451.0878; found: 451.0873.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 8.4 min, t_{minor} = 10.3 min.

(*3S,4'R*)-diethyl 5-bromo-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3d**): petroleum ether/ ethyl acetate = 3:1, Rf=0.6.



Yellow solid, 95% yield, >20:1 *dr*, 95% *ee*, $[\alpha]_D^{20}$ = +77.26 (c = 0.28, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 4.65 (d, *J* = 13.6

Hz, 1H), 4.50-4.38 (m, 2H), 4.37-4.25 (m, 3H), 3.14 (s, 3H), 1.40-1.29 (m, 6H);

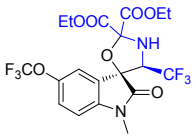
^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.33, 167.24, 164.99, 143.70, 134.17, 128.19, 125.86, 122.40 (q, *J* = 279.6 Hz), 116.30, 110.35, 94.53, 80.88, 67.92 (q, *J* = 31.5 Hz), 63.39, 63.24, 26.57, 14.08, 14.04;

^{19}F NMR (471 MHz, $CDCl_3$) δ: -69.01.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}BrN_2O_6F_3$ $[M+H]^+$: 495.0373; found: 495.0363.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 90/10, 0.8 mL·min^{-1}, λ = 254 nm): t_{major} = 8.1 min, t_{minor} = 9.3 min.

(*3S,4'R*)-diethyl 1-methyl-2-oxo-5-(trifluoromethoxy)-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3e**): petroleum ether/ ethyl acetate = 3:1, Rf=0.3.



colourless foam, 98% yield, >20:1 *dr*, 93% *ee*, $[a]_D^{20}$ = +44.49 (c = 0.45, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 1.7 Hz, 1H), 7.26 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.66 (d, *J* = 13.7 Hz, 1H), 4.52-4.37 (m, 2H), 4.32 (tdd, *J* = 10.2, 6.9, 3.3 Hz, 3H), 3.16 (s, 3H), 1.34 (dt, *J* = 9.4, 7.1 Hz, 6H);

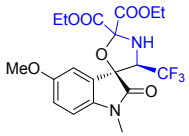
^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.69, 167.17, 165.01, 145.45, 143.24, 125.47, 124.38, 122.37 (q, *J* = 279.4 Hz), 120.59 (q, *J* = 257.1 Hz), 118.98, 109.52, 94.59, 80.94, 67.98 (q, *J* = 31.7 Hz), 63.45, 63.26, 26.64, 14.04;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -58.35, -69.10.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{19}N_2O_7F_6$ $[M+H]^+$: 501.1092; found: 501.1096.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 7.0 min, t_{minor} = 13.8 min.

(*3S,4'R*)-diethyl 5-methoxy-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3f**): petroleum ether/ ethyl acetate = 8:1, Rf=0.3.



colourless foam, 92% yield, >20:1 *dr*, 97% *ee*, $[a]_D^{20}$ = +75.65 (c = 0.37, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 2.6 Hz, 1H), 6.89 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 4.67 (d, *J* = 13.7 Hz, 1H), 4.51-4.38 (m, 2H), 4.35-4.23 (m, 3H), 3.81 (s, 3H), 3.12 (s, 3H), 1.34 (dt, *J* = 10.1, 7.1 Hz, 6H);

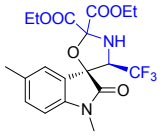
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.59, 167.41, 165.21, 156.76, 137.92, 124.89, 122.50 (q, *J* = 279.5 Hz), 115.95, 111.70, 109.46, 94.38, 81.47, 67.84 (q, *J* = 31.4 Hz), 63.27, 63.06, 55.97, 26.51, 14.09, 14.04;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.08.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{22}N_2O_7F_3$ $[M+H]^+$: 447.1374; found: 447.1368.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 11.2 min, t_{minor} = 21.0 min.

(*3S,4'R*)-diethyl 1,5-dimethyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3g**): petroleum ether/ ethyl acetate = 3:1, Rf=0.5.



colourless foam, 90% yield, >20:1 *dr*, 96% *ee*, $[a]_D^{20}$ = +67.31 (c = 0.35, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (s, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.68 (d, *J* = 13.7 Hz, 1H), 4.49-4.38 (m, 2H), 4.37-4.24 (m, 3H), 3.12 (s, 3H), 2.35 (s, 3H), 1.33 (dt, *J* = 14.1, 7.1 Hz, 6H);

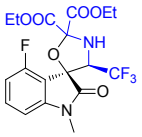
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.77, 167.53, 165.25, 142.26, 133.41, 131.56, 125.49, 123.59, 122.53 (q, *J* = 279.6 Hz), 108.65, 94.25, 81.36, 67.61 (q, *J* = 31.3 Hz), 63.22, 63.05, 26.43, 21.16, 14.06, 14.03;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.07.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{22}N_2O_6F_3$ $[M+H]^+$: 431.1424; found: 431.1423.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 90/10, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 5.7 min, t_{minor} = 6.6 min.

(*3S,4'R*)-diethyl 4-fluoro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3h**): petroleum ether/ ethyl acetate = 8:1, Rf=0.5.



colourless foam, 95% yield, >20:1 *dr*, 95% *ee*, $[a]_D^{20}$ = +56.36 (c = 0.28, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (td, *J* = 8.2, 5.5 Hz, 1H), 6.79 (t, *J* = 8.8 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.74-4.62 (m, 2H), 4.47-4.39 (m, 1H), 4.38-4.26 (m, 3H), 3.13 (s, 3H), 1.33 (td, *J* = 7.1, 2.4 Hz, 6H);

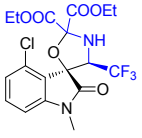
^{13}C NMR (126 MHz, $CDCl_3$) δ: 171.95, 166.78, 165.54, 159.80 (d, *J* = 253.7 Hz), 146.65 (d, *J* = 7.6 Hz), 133.64 (d, *J* = 9.0 Hz), 122.46 (q, *J* = 279.5 Hz), 111.47 (d, *J* = 20.3 Hz), 108.45 (d, *J* = 18.2 Hz), 105.16 (d, *J* = 3.2 Hz), 94.66, 80.77, 64.50 (qd, *J* = 31.5, 1.1 Hz), 63.26, 63.03, 26.79, 14.02, 13.94;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.13, -116.81.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}N_2O_6F_4$ $[M+H]^+$: 435.1174; found: 435.1180.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 11.8 min, t_{minor} = 22.3 min.

(*3S,4'R*)-diethyl 4-chloro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3i**): petroleum ether/ ethyl acetate = 8:1, Rf=0.6.



colourless foam, 88% yield, >20:1 *dr*, 95% *ee*, $[a]_D^{20}$ = +40.36 (c = 0.45, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (t, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.00 (dq, *J* = 13.8, 6.9 Hz, 1H), 4.60 (d, *J* = 12.9 Hz, 1H), 4.45-4.27 (m, 4H), 3.13 (s, 3H), 1.32 (td, *J* = 7.1, 5.1 Hz, 6H);

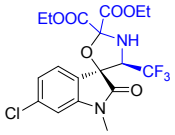
^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.90, 166.36, 165.74, 146.60, 132.66, 132.24, 124.86, 122.46 (q, *J* = 279.5 Hz), 118.66, 107.54, 94.88, 81.79, 63.22, 63.01, 63.00 (q, *J* = 31.5 Hz), 26.60, 14.07;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.16.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}ClN_2O_6F_3$ $[M+H]^+$: 451.0878; found: 451.0870.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 99/1, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 28.4 min, t_{minor} = 55.2 min.

(*3S,4'R*)-diethyl 6-chloro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3j**): petroleum ether/ ethyl acetate = 3:1, Rf=0.4.



colourless foam, 93% yield, >20:1 *dr*, 95% *ee*, $[\alpha]_D^{20}$ = +43.76 (c = 0.38, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.83 (d, *J* = 1.7 Hz, 1H), 4.64 (d, *J* = 13.7 Hz, 1H), 4.51-4.37 (m, 2H), 4.36-4.23 (m, 3H), 3.13 (s, 3H), 1.33 (dd, *J* = 13.5, 7.1 Hz, 6H);

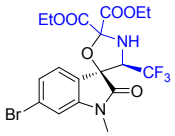
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.77, 167.31, 165.05, 145.79, 137.32, 125.93, 123.58, 122.42 (q, *J* = 279.4 Hz), 122.21, 109.75, 94.39, 80.81, 67.71 (q, *J* = 31.5 Hz), 63.37, 63.15, 26.57, 14.06, 14.04;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.06.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}ClN_2O_6F_3$ $[M+H]^+$: 451.0878; found: 451.0873.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 99/1, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 15.0 min, t_{minor} = 43.8 min.

(*3S,4'R*)-diethyl 6-bromo-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3k**): petroleum ether/ ethyl acetate = 3:1, Rf=0.5.



colourless oil, 98% yield, >20:1 *dr,* 94% *ee*, $[\alpha]_D^{20}$ = +32.65 (c = 0.37, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 7.9 Hz, 1H), 7.28 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 4.65 (d, *J* = 13.7 Hz, 1H), 4.51-4.37 (m, 2H), 4.37-4.23 (m, 3H), 3.13 (s, 3H), 1.34 (dd, *J* = 13.2, 7.1 Hz, 6H);

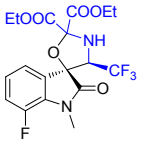
^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.67, 167.32, 165.05, 145.85, 126.57, 126.22, 125.25, 122.79, 122.43 (q, *J* = 281.0 Hz), 112.54, 94.42, 80.87, 67.70 (q, *J* = 31.4 Hz), 63.39, 63.18, 26.59, 14.07, 14.06;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.04.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}BrN_2O_6F_3$ $[M+H]^+$: 495.0373; found: 495.0366.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 280 nm): t_{major} = 9.5 min, t_{minor} = 20.5 min.

(*3S,4'R*)-diethyl 7-fluoro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3l**): petroleum ether/ ethyl acetate = 8:1, Rf=0.3.



colourless oil, 93% yield, >20:1 *dr*, 96% *ee*, $[\alpha]_D^{20}$ = +49.03 (c = 0.32, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.15-7.04 (m, 2H), 4.67 (d, *J* = 13.7 Hz, 1H), 4.51-4.38 (m, 2H), 4.38-4.24 (m, 3H), 3.36 (d, *J* = 2.6 Hz, 3H), 1.34 (dd, *J* = 13.5, 7.0 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.54, 167.32, 165.09, 147.78 (d, *J* = 244.9 Hz), 131.12 (d, *J* = 9.1 Hz), 126.62 (d, *J* = 3.2 Hz), 124.42 (d, *J* = 6.3 Hz), 122.42 (q, *J* = 280.5 Hz), 120.82 (d, *J* = 3.2 Hz), 119.40 (d, *J* =

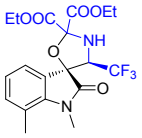
19.2 Hz), 94.46, 81.00, 68.03 (q, *J* = 31.6 Hz), 63.37, 63.15, 29.03 (d, *J* = 5.5 Hz), 14.07;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.08, -135.67.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{19}N_2O_6F_4$ $[M+H]^+$: 435.1174; found: 435.1172.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 220 nm): t_{major} = 6.2 min, t_{minor} = 11.1 min.

(*3S,4'R*)-diethyl 1,7-dimethyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3m**): petroleum ether/ ethyl acetate = 8:1, Rf=0.3.



colourless foam, 98% yield, >20:1 *dr,* 95% *ee*, $[a]_D^{20}$ = +37.33 (c = 0.15, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 4.68 (d, *J* = 13.6 Hz, 1H), 4.49-4.36 (m, 2H), 4.36-4.21 (m, 3H), 3.40 (s, 3H), 2.52 (s, 3H), 1.33 (dd, *J* = 15.4, 7.2 Hz, 6H);

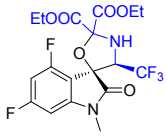
^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.60, 167.48, 165.36, 142.24, 135.03, 124.28, 123.60, 122.74, 122.53 (q, *J* = 279.6 Hz), 120.56, 94.16, 80.81, 67.85 (q, *J* = 31.3 Hz), 63.20, 63.00, 29.79, 18.88, 14.05, 14.03;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.11.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{22}N_2O_6F_3$ $[M+H]^+$: 431.1424; found: 431.1422.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 9.4 min, t_{minor} = 20.7 min.

(*3S,4'R*)-diethyl 4,6-difluoro-1-methyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3n**): petroleum ether/ ethyl acetate = 3:1, Rf=0.5.



colourless oil, 93% yield, >20:1 *dr*, 93% *ee*, $[a]_D^{20}$ = +30.94 (c = 0.35, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.53 (td, *J* = 9.5, 2.0 Hz, 1H), 6.42 (dd, *J* = 8.1, 1.8 Hz, 1H), 4.67-4.60 (m, 2H), 4.47-4.40 (m, 1H), 4.36-4.25 (m, 3H), 3.12 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H);

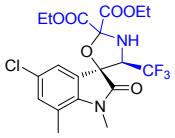
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.18, 166.70, 165.73 (dd, *J* = 252.4, 12.8 Hz), 165.46, 160.06 (dd, *J* = 255.4, 14.6 Hz), 147.72 (dd, *J* = 14.0, 10.0 Hz), 122.41 (q, *J* = 279.3 Hz), 104.18 (dd, *J* = 18.4, 3.6 Hz), 99.20 (dd, *J* = 26.0, 24.8 Hz), 94.67 (dd, *J* = 27.8, 3.6 Hz), 94.59, 80.46, 64.47 (q, *J* = 31.5 Hz), 63.37, 63.11, 26.92, 14.04, 13.96;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.11, -102.27 (d, *J* = 9.9 Hz), -112.76 (d, *J* = 9.9 Hz).

HRMS (ESI): *m/z* calcd. for $C_{18}H_{18}N_2O_6F_5$ $[M+H]^+$: 453.1080; found: 453.1083.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 8.8 min, t_{minor} = 16.9 min.

(*3S,4'R*)-diethyl 5-chloro-1,7-dimethyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3o**): petroleum ether/ ethyl acetate = 3:1, Rf=0.4.



colourless oil, 97% yield, >20:1 *dr*, 96% *ee*, $[a]_D^{20}$ = +56.19 (c = 0.37, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 2.1 Hz, 1H), 7.10 (d, *J* = 1.8 Hz, 1H), 4.66 (d, *J* = 13.7 Hz, 1H), 4.49-4.38 (m, 2H), 4.36-4.20 (m, 3H), 3.39 (s, 3H), 2.50 (s, 3H), 1.34 (dt, *J* = 13.5, 7.1 Hz, 6H);

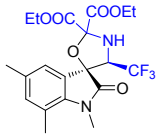
^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.27, 167.29, 165.11, 140.88, 134.51, 128.74, 126.09, 123.11, 122.39 (q, *J* = 279.6 Hz), 122.21, 94.33, 80.52, 68.05 (q, *J* = 31.4 Hz), 63.33, 63.20, 29.81, 18.70, 14.06, 14.03;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.05.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{21}ClN_2O_6F_3$ $[M+H]^+$: 465.1035; found: 465.1039.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 8.3 min, t_{minor} = 20.9 min.

(*3S,4'R*)-diethyl 1,5,7-trimethyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3p**): petroleum ether/ ethyl acetate = 8:1, Rf=0.3.



colourless oil, 91% yield, >20:1 *dr*, 98% *ee*, $[a]_D^{20}$ = +49.82 (c = 0.38, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (s, 1H), 6.90 (s, 1H), 4.68 (d, *J* = 13.7 Hz, 1H), 4.52-4.40 (m, 2H), 4.34-4.21 (m, 3H), 3.38 (s, 3H), 2.47 (s, 3H), 2.29 (s, 3H), 1.36-1.29 (m, 6H);

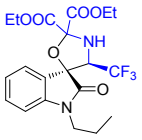
^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.56, 167.59, 165.37, 139.80, 135.47, 133.25, 124.23, 123.29, 122.55 (q, *J* = 279.6 Hz), 120.28, 94.09, 80.95, 67.80 (q, *J* = 31.2 Hz), 63.17, 63.02, 29.74, 20.85, 18.73, 14.06, 14.03;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.07.

HRMS (ESI): *m/z* calcd. for $C_{20}H_{24}N_2O_6F_3$ $[M+H]^+$: 445.1581; found: 445.1576.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 7.4 min, t_{minor} = 13.9 min.

(*3S,4'R*)-diethyl 2-oxo-1-propyl-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3q**): petroleum ether/ ethyl acetate = 8:1, Rf=0.3.



colourless oil, 98% yield, >20:1 *dr*, 97% *ee*, $[a]_D^{20}$ = +54.91 (c = 0.11, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.4 Hz, 1H), 7.35 (td, *J* = 7.8, 1.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 4.68 (d, *J* = 13.7 Hz, 1H), 4.50-4.38 (m, 2H), 4.38-4.24 (m, 3H), 3.73 (dt, *J* = 14.4, 7.4 Hz, 1H), 3.43 (dt, *J* = 14.1, 7.1 Hz, 1H), 1.71-1.60 (m, 2H), 1.33 (dt, *J* = 11.6, 7.1 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 3H);

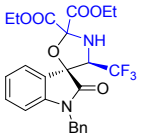
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.82, 167.45, 165.31, 144.27, 131.24, 124.95, 123.78, 123.41, 122.55 (q, *J* = 279.5 Hz), 109.10, 94.28, 81.18, 67.67 (q, *J* = 31.3 Hz), 63.24, 63.05, 41.97, 20.70, 14.07, 14.04, 11.28;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.99.

HRMS (ESI): *m/z* calcd. for $C_{20}H_{24}N_2O_6F_3$ $[M+H]^+$: 445.1581; found: 445.1578.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 6.2 min, t_{minor} = 9.2 min.

(*3S,4'R*)-diethyl 1-benzyl-2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3r**): petroleum ether/ ethyl acetate = 8:1, Rf=0.4.



colourless foam, 92% yield, >20:1 *dr*, 96% *ee*, $[a]_D^{20}$ = +41.71 (c = 0.43, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.61 (d, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 6.0 Hz, 2H), 7.26 (s, 4H), 7.10 (t, *J* = 6.6 Hz, 1H), 6.68 (d, *J* = 7.3 Hz, 1H), 5.05 (d, *J* = 15.7 Hz, 1H), 4.73 (d, *J* = 13.6 Hz, 1H), 4.61 (d, *J* = 15.6 Hz, 1H), 4.52-4.28 (m, 5H), 1.35 (dd, *J* = 14.5, 7.1 Hz, 6H);

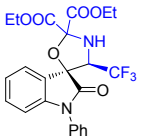
^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.99, 167.43, 165.30, 143.90, 135.10, 131.26, 128.93, 127.92, 127.37, 124.92, 123.71, 122.40 (q, *J* = 330.4 Hz), 110.02, 94.38, 81.28, 67.69 (q, *J* = 31.4 Hz), 63.31, 63.10, 44.23, 14.09, 14.07;

^{19}F NMR (471 MHz, $CDCl_3$) δ: -68.75.

HRMS (ESI): *m/z* calcd. for $C_{24}H_{24}N_2O_6F_3$ $[M+H]^+$: 493.1581; found: 493.1572.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 220 nm): t_{major} = 8.6 min, t_{minor} = 10.5 min.

(*3S,4'R*)-diethyl 2-oxo-1-phenyl-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3s**): petroleum ether/ ethyl acetate = 8:1, Rf=0.3.



colourless foam, 90% yield, >20:1 *dr*, 94% *ee*, $[a]_D^{20}$ = +22.52 (c = 0.16, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.31 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 4.73 (d, *J* = 13.7 Hz, 1H), 4.50-4.37 (m, 3H), 4.36-4.28 (m, 2H), 1.35 (dt, *J* = 19.8, 7.1 Hz, 6H);

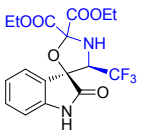
^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.30, 167.44, 165.13, 144.56, 133.53, 131.23, 129.84, 128.59, 126.28, 125.19, 124.18, 123.57, 122.67 (q, *J* = 279.4 Hz), 110.21, 94.54, 81.46, 68.32 (q, *J* = 31.3 Hz), 63.35, 63.14, 14.11, 14.06;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.77.

HRMS (ESI): *m/z* calcd. for $C_{23}H_{22}N_2O_6F_3$ $[M+H]^+$: 479.1424; found: 479.1422.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 99/1, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 16.0 min, t_{minor} = 32.5 min.

(*3S,4'R*)-diethyl 2-oxo-4'-(trifluoromethyl)spiro[indoline-3,5'-oxazolidine]-2',2'-dicarboxylate (**3t**): petroleum ether/ ethyl acetate = 3:1, Rf=0.4.



Yellow oil, 58% yield, >20:1 *dr*, 96% *ee*, $[a]_D^{20}$ = +22.37 (c = 0.35, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.32 (td, *J* = 7.8, 1.2 Hz, 1H), 7.12 (td, *J* = 7.7, 0.7 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.64 (d, *J* = 13.7 Hz, 1H), 4.49-4.39 (m, 2H), 4.38-4.26 (m, 3H), 1.34 (dt, *J* = 14.5, 7.1 Hz, 6H);

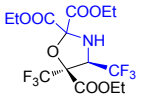
^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.85, 167.39, 165.34, 141.68, 131.36, 125.27, 124.14, 123.76, 122.52 (q, *J* = 279.6 Hz), 110.80, 94.38, 81.52, 67.88 (q, *J* = 31.4 Hz), 63.34, 63.15, 14.10, 14.06;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.12.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{18}N_2O_6F_3$ $[M+H]^+$: 403.1111; found: 403.1105.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IB column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 220 nm): t_{major} = 9.1 min, t_{minor} = 14.8 min.

(4R,5S)-triethyl 4,5-bis(trifluoromethyl)oxazolidine-2,2,5-tricarboxylate (**3aa**): petroleum ether/ ethyl acetate = 8:1, Rf=0.6.



Colorless oil, 86% yield, >20:1 *dr*, 80% *ee*, $[\alpha]_D^{20}$ = +16.32 (c = 0.28, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.51 – 4.19 (m, 8H), 1.37 – 1.29 (m, 9H);

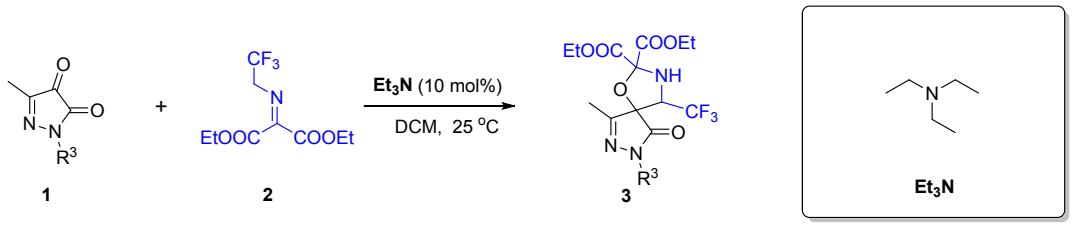
^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.94, 165.41, 163.07, 122.26 (q, *J* = 280.1 Hz), 122.03 (q, *J* = 284.8 Hz), 95.86, 84.00 (q, *J* = 31.1 Hz), 64.43 (q, *J* = 33.2 Hz), 63.77, 63.46, 63.41, 14.03, 13.93, 13.71;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -70.09 (dq, *J* = 7.8, 3.9 Hz), -73.87 (q, *J* = 3.9 Hz).

HRMS (ESI): *m/z* calcd. for $C_{14}H_{18}NO_7F_6$ $[M+H]^+$: 426.0982; found: 426.0984.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IA column (hexane/*i*-PrOH = 98/2, 1 mL·min^{-1}, λ = 220 nm): t_{major} = 7.2 min, t_{minor} = 22.8 min.

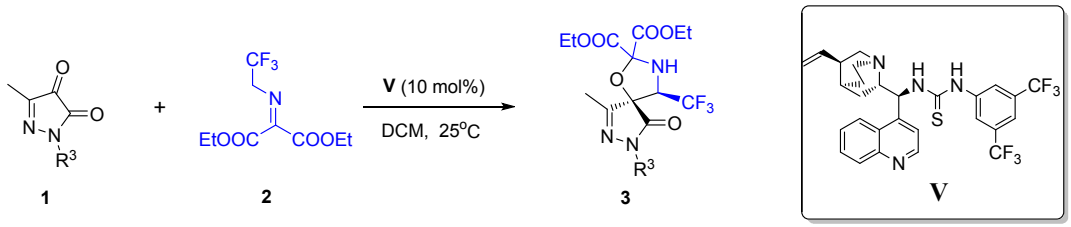
d. General Procedure to Prepare Racemic Products 3u-3z



1 2 3

To a solution of diethyl 2-((2,2,2-trifluoroethyl)imino)malonate **2** (0.15 mmol, 1.5 equiv.), and catalyst Et_3N (0.01 mmol, 10 mol%) in DCM (1 mL) was added pyrazolone **1** (0.10 mmol, 1.0 equiv.). The mixture was stirred at room temperature until the reaction was completed (monitored by TLC analysis). The crude product was purified directly by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 20:1~10:1) to give the desired racemic products **3u-3z**.

e. General Procedure to Prepare Chiral Products 3u-3z

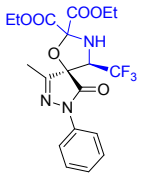


1 2 3

To a solution of diethyl 2-((2,2,2-trifluoroethyl)imino)malonate **2** (0.15 mmol, 1.5 equiv.) and catalyst **V** (0.01 mmol, 10 mol%) in DCE (1 mL) was added pyrazolone **1** (0.10 mmol, 1.0 equiv.). The mixture was stirred at 25 °C until the reaction was completed (monitored by TLC analysis). The crude product was purified directly by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 20:1~10:1) to give the desired chiral products **3u-3z**.

f. Analytical Data for Products 3u-3z

(4R,5R)-diethyl-6-methyl-9-oxo-8-phenyl-4-(trifluoromethyl)-1-oxa-3,7,8-triazaspiro[4.4]non-6-ene-2,2-dicarboxylate (**3u**): petroleum ether/ ethyl acetate = 10:1, Rf=0.5.



Colorless oil, 98% yield, >20:1 *dr*, 90% *ee*, $[a]_D^{20}$ = +28.31 (c = 0.38, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.68 (d, *J* = 13.6 Hz, 1H), 4.51 – 4.43 (m, 1H), 4.42 – 4.33 (m, 2H), 4.33 – 4.21 (m, 2H), 2.32 (s, 3H), 1.34 (td, *J* = 7.1, 4.1 Hz, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.22, 166.64, 164.73, 155.72, 137.29, 129.06, 125.83, 122.05 (q, *J* = 279.2 Hz), 118.88, 95.05, 82.32, 65.05 (q, *J* = 32.6 Hz), 63.68, 63.32, 14.04, 13.05;

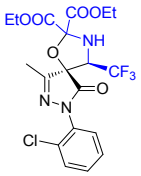
^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.94.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{21}N_3O_6F_3$ $[M+H]^+$: 444.1377; found: 444.1375.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak AD-H column (hexane/*i*-

PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 7.9 min, t_{minor} = 7.3 min.

(4R,5R)-diethyl-8-(2-chlorophenyl)-6-methyl-9-oxo-4-(trifluoromethyl)-1-oxa-3,7,8-triazaspiro[4.4]non-6-ene-2,2-dicarboxylate (**3v**): petroleum ether/ ethyl acetate = 10:1, Rf=0.5.



Colorless oil, 96% yield, >20:1 *dr*, 85% *ee*, $[a]_D^{20}$ = +22.33 (c = 0.30, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 1H), 7.39 – 7.27 (m, 3H), 4.63 (d, *J* = 13.6 Hz, 1H), 4.49 – 4.41 (m, 1H), 4.41 – 4.33 (m, 2H), 4.32 – 4.21 (m, 2H), 2.30 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H);

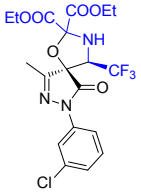
^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.91, 166.62, 164.57, 155.65, 133.83, 131.67, 130.76, 130.11, 128.13, 127.56, 122.05 (q, *J* = 279.4 Hz), 95.07, 81.23, 64.91 (q, *J* = 32.7 Hz), 63.67, 63.34, 14.03, 13.08;

^{19}F NMR (376 MHz, $CDCl_3$) δ -68.72.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}N_3O_6F_3Cl$ $[M+H]^+$: 478.0987; found: 478.0989.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 95/5, 0.8 mL·min^{-1}, λ = 254 nm): t_{major} = 9.5 min, t_{minor} = 8.5 min.

(4R,5R)-diethyl-8-(3-chlorophenyl)-6-methyl-9-oxo-4-(trifluoromethyl)-1-oxa-3,7,8-triazaspiro[4.4]non-6-ene-2,2-dicarboxylate (**3w**): petroleum ether/ ethyl acetate = 10:1, Rf=0.4.



Colorless oil, 96% yield, >20:1 *dr*, 80% *ee*, $[a]_D^{20}$ = +6.40 (c = 0.25, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (t, *J* = 2.0 Hz, 1H), 7.79 – 7.66 (m, 1H), 7.30 (t, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.66 (d, *J* = 13.6 Hz, 1H), 4.53 – 4.43 (m, 1H), 4.42 – 4.33 (m, 2H), 4.31 – 4.21 (m, 2H), 2.32 (s, 3H), 1.38 – 1.32 (m, 6H);

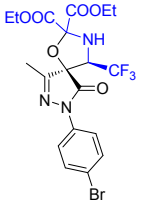
^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.16, 166.42, 164.55, 156.10, 138.20, 134.76, 130.02, 125.61, 121.87 (q, *J* = 279.4 Hz), 118.56, 116.39, 94.98, 82.22, 65.01 (q, *J* = 32.6 Hz), 63.63, 63.25, 13.92, 12.95;

^{19}F NMR (376 MHz, $CDCl_3$) δ: -68.91

HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}N_3O_6F_3Cl$ $[M+H]^+$: 478.0987; found: 478.0988.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 95/5, 0.8 mL·min^{-1}, λ = 254 nm): t_{major} = 6.1 min, t_{minor} = 7.8 min.

(4R,5R)-diethyl-8-(4-bromophenyl)-6-methyl-9-oxo-4-(trifluoromethyl)-1-oxa-3,7,8-triazaspiro[4.4]non-6-ene-2,2-dicarboxylate (**3x**): petroleum ether/ ethyl acetate = 10:1, Rf=0.4.



Colorless oil, 98% yield, >20:1 *dr*, 77% *ee*, $[a]_D^{20}$ = +14.33 (c = 0.31, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 4.65 (d, *J* = 13.6 Hz, 1H), 4.52

– 4.42 (m, 1H), 4.41 – 4.32 (m, 2H), 4.31 – 4.19 (m, 2H), 2.32 (s, 3H), 1.34 (td, *J* = 7.1, 3.7 Hz, 6H);

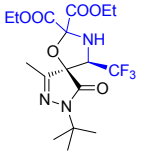
^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.18, 166.57, 164.68, 156.18, 136.39, 132.10, 122.00 (q, *J* = 279.4 Hz), 120.19, 118.74, 95.10, 82.32, 65.13 (q, *J* = 32.5 Hz), 63.75, 63.38, 14.06, 13.09;

^{19}F NMR (376 MHz, $CDCl_3$) δ: 68.93.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{20}N_3O_6F_3Br$ $[M+H]^+$: 522.0482; found: 522.0483.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 95/5, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 5.0 min, t_{minor} = 6.5 min.

(4R,5R)-diethyl-8-(tert-butyl)-6-methyl-9-oxo-4-(trifluoromethyl)-1-oxa-3,7,8-triazaspiro[4.4]non-6-ene-2,2-dicarboxylate (**3y**): petroleum ether/ ethyl acetate = 10:1, Rf=0.3.



Colorless oil, 98% yield, >20:1 *dr*, 82% *ee*, $[\alpha]_D^{20}$ = +39.67 (c = 0.30, MeOH).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.54 (d, *J* = 13.6 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.40 – 4.31 (m, 2H), 4.29 – 4.21 (m, 1H), 4.08 (dq, *J* = 13.5, 6.7 Hz, 1H), 2.14 (s, 3H), 1.42 (s, 9H), 1.35 – 1.29 (m, 6H);

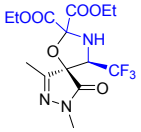
^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.93, 166.82, 164.87, 152.95, 122.15 (q, *J* = 279.3 Hz), 94.80, 82.50, 64.57 (q, *J* = 32.2 Hz), 63.52, 63.15, 58.01, 27.90, 14.03, 12.87;

^{19}F NMR (471 MHz, $CDCl_3$) δ: -69.19.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{25}N_3O_6F_3$ $[M+H]^+$: 424.1690; found: 424.1688.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 98/2, 1 mL·min^{-1}, λ = 254 nm): t_{major} = 8.4 min, t_{minor} = 7.7 min.

(4R,5R)-diethyl 6,8-dimethyl-9-oxo-4-(trifluoromethyl)-1-oxa-3,7,8-triazaspiro[4.4]non-6-ene-2,2-dicarboxylate (**3z**): petroleum ether/ ethyl acetate = 10:1, Rf=0.3.



Colorless oil, 98% yield, >20:1 *dr*, 83% *ee*, $[\alpha]_D^{20}$ = +46.67 (c = 0.24, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.56 (d, *J* = 13.5 Hz, 1H), 4.50 – 4.41 (m, 1H), 4.39 – 4.29 (m, 2H), 4.28 – 4.21 (m, 1H), 4.14 (td, *J* = 13.4, 6.6 Hz, 1H), 3.22 (s, 3H), 2.18 (s, 3H), 1.32 (dt, *J* = 9.6, 7.1 Hz, 6H);

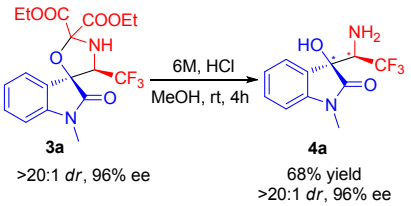
^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.91, 166.69, 164.71, 154.72, 122.02 (q, *J* = 279.3 Hz), 94.87, 81.17, 64.59 (q, *J* = 32.5 Hz), 63.59, 63.24, 31.61, 14.02, 12.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -69.24.

HRMS (ESI): *m/z* calcd. for $C_{14}H_{19}N_3O_6F_3$ $[M+H]^+$: 382.1220; found: 382.1202.

HPLC analysis: The enantiomeric excess was determined by HPLC with Chiralpak IC column (hexane/*i*-PrOH = 95/5, 0.8 mL·min^{-1}, λ = 254 nm): t_{major} = 10.3 min, t_{minor} = 17.1 min.

g. Transformation of 3a to 4a

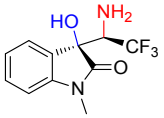


3a
>20:1 *dr*, 96% ee

4a
68% yield
>20:1 *dr*, 96% ee

To a solution of spirooxindole-oxazoline **3a** (0.30 mmol) in MeOH (5 mL) was added 6M HCl (3 mL). The mixture was stirred at room temperature until the reaction was completed (monitored by TLC analysis). Remove the solvent under vacuum. Then 5 mL water was added and extract three times with 10 mL of DCM. The water phase uses ammonia to adjust pH to alkaline. Then extract with DCM (10 mL x 3). The organic phase was dried with Na_2SO_4 and the solution was removed to obtain the desired product **4a** as a colourless oil.

(*S*)-3-((*R*)-1-amino-2,2,2-trifluoroethyl)-3-hydroxy-1-methylindolin-2-one (**4a**): petroleum ether/ ethyl acetate = 3:1, Rf=0.2.



colourless oil, 68% yield, >20:1 *dr*, 96% *ee*, $[\alpha]_D^{20}$ = +42.17 (c=0.29, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.85 (s, 1H), 3.78 – 3.61 (m, 1H), 3.18 (s, 3H), 2.11 (s, 2H).

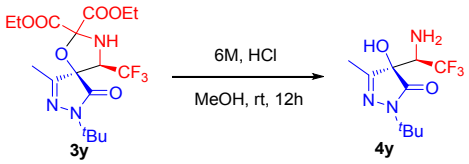
^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.77, 144.24, 130.61, 126.44, 124.84 (q, *J* = 284.5 Hz), 124.45, 123.22, 108.68, 72.61, 59.98 (q, *J* = 28.5 Hz), 26.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -71.94.

HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{11}H_{12}N_2F_3O_2]^+$: 261.0846, found: 261.0853;

HPLC analysis: The enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/*i*-PrOH = 95/5, 1.0 mL·min^{-1}, λ = 245 nm): t_{major} = 57.5 min, t_{minor} = 39.0 min.

h. Transformation of 3y to 4y

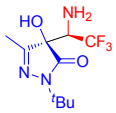


3y
>20:1 *dr*, 82% *ee*

4y
90% yield
>20:1 *dr*, 80% ee

To a solution of spiropyrazolones-oxazolidine **3y** (0.30 mmol) in MeOH (5 mL) was added 6M HCl (3 mL). The mixture was stirred at room temperature until the reaction was completed (monitored by TLC analysis). Remove the solvent under vacuum. Then 5 mL water was added and extract three times with 10 mL of DCM. The water phase uses ammonia to adjust pH to alkaline. Then extract with DCM (10 mL x 3). The organic phase was dried with Na_2SO_4 and the solution was removed to obtain the desired product **4y** as a colourless oil.

(R)-4-((R)-1-amino-2,2,2-trifluoroethyl)-1-(tert-butyl)-4-hydroxy-3-methyl-1H-pyrazol-5(4H)-one (**4y**): petroleum ether/ ethyl acetate = 3:1, Rf=0.4.



colourless oil, 90% yield, >20:1 *dr*, 80% *ee*, $[a]_D^{20}$ = +21.16 (c=0.23, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41 (q, *J* = 7.4 Hz, 1H), 2.03 (s, 3H), 1.46 (s, 9H).

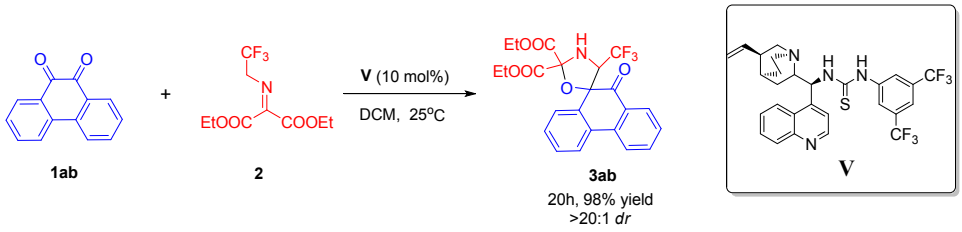
^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.58, 156.26, 124.52 (q, *J* = 282.4 Hz), 74.25, 58.31 (q, *J* = 29.6 Hz), 57.83, 27.98, 12.99.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -73.28.

HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{10}H_{17}N_3F_3O_2]^+$: 268.1267, found: 268.1262;

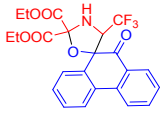
HPLC analysis: The enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexane/*i*-PrOH = 90/10, 1.0 mL·min^{-1}, λ = 254 nm): t_{major} = 6.4 min, t_{minor} = 7.3 min.

i. Application of *oxa*-1,3-DC in desymmetrization



To a solution of diethyl 2-((2,2,2-trifluoroethyl)imino)malonate **2** (0.15 mmol, 1.5 equiv.) and catalyst **V** (0.01 mmol, 10 mol%) in DCE (1 mL) was added phenanthrenequinone **1ab** (0.10 mmol, 1.0 equiv.). The mixture was stirred at 25 °C until the reaction was completed (monitored by TLC analysis). The crude product was purified directly by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 20:1~10:1) to give the desired chiral products **3ab**.

Diethyl 10'-oxo-4-(trifluoromethyl)-10'H-spiro[oxazolidine-5,9'-phenanthrene]-2,2-dicarboxylate (**3ab**): petroleum ether/ ethyl acetate = 20:1, Rf=0.4.



colourless oil, 98% yield, >20:1 *dr*.

^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.70 – 7.54 (m, 4H), 4.49 (d, *J* = 8.0 Hz, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 4.25 – 4.15 (m, 2H), 4.14 – 4.05 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 167.43, 137.14, 127.69, 127.42, 125.61, 123.55, 120.35, 120.30, 120.03 (q, *J* = 288.1 Hz), 116.45 (q, *J* = 35.7 Hz), 62.68, 56.59, 13.84.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -85.37.

HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $[C_{23}H_{21}NF_3O_6]^+$: 464.1315, found: 464.1313;

4. Proposed Reaction Mechanism

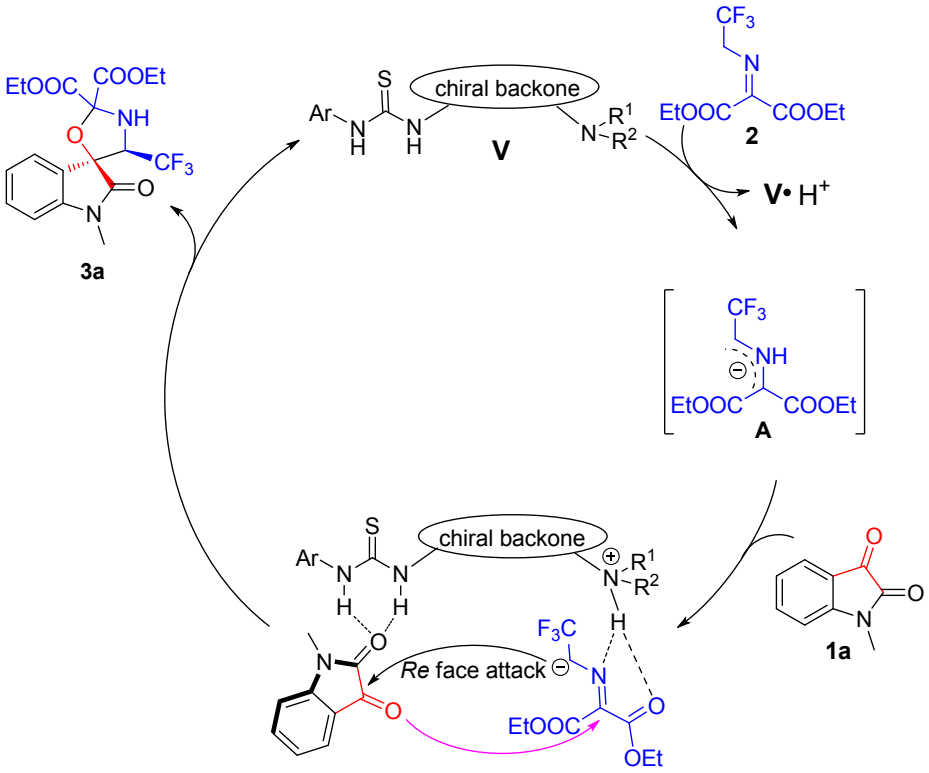


Figure S1. Proposed reaction mechanism

According to the absolute configuration of **3a** and literature reports,[1a,2] we proposed a possible reaction mechanism for the catalytic asymmetric *oxa*-1,3-dipolar cycloaddition as shown in **Figure S1**. Catalyst **V** initially promoted the formation of an intermediate **A** through the deprotonation of the precursor **2**. Both the intermediate **A** and **1a** are simultaneously activated *via* hydrogen-bonding interactions. The thiourea moiety of catalyst **V** formed two hydrogen bonds with the carbonyl group of the isatin **1a**. The tertiary amine moiety deprotonated and activated the diethyl 2-(2,2,2-trifluoroethylimino)malonate **2** *via* double hydrogen bonds. In this *oxa*-1,3-dipolar cycloaddition step, the trifluoromethyl ortho carbon position of activated diethyl 2-(2,2,2-trifluoroethylimino)malonate **2** attacks the 3-position of isatin **1a** (*Re*-face), Subsequently, an intramolecular cycloaddition generates the product **3a** (Figure S1).

5. References

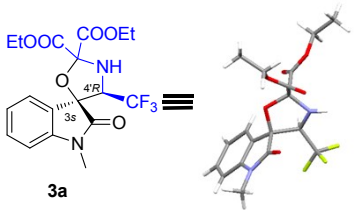
[1] a) Su, J.; Ma, Z.; Li, X.; Lin, L.; Shen, Z.; Yang, P.; Li, Y.; Wang, H.; Yan, W.; Wang, K.; Wang, R. *Adv. Synth. Catal.* **2016**, *358*, 3777. b) Ponce, A.; Alonso, I.; Adrio, J.; Carretero, J. C. *Chem. Eur. J.* **2016** , *22* , 4952.

[2] a) Huang, W. J.; Chen, Q.; Lin, N.; Long, X. W.; Pan, W. G.; Xiong, Y. S.; Weng, J.; Lu, G. *Org. Chem. Front.* **2017**, *4*, 472. b) N. Lin, X. W. Long, Q. Chen, W. R. Zhu, B. C. Wang, K. B. Chen, C. W. Jiang, J. Weng, G. Lu, *Tetrahedron* **2018**, *74*, 3734; c) W. R. Zhu, Q. Chen, N. Lin, K. B. Chen, Z. W. Zhang, G. Fang, J. Weng, G. Lu, *Org. Chem. Front.* **2018**, *5*, 1375; d) Zhu, W. R.; Zhang, Z. W.; Huang, W. H.; Lin, N.; Chen, Q.; Chen, K. B.; Wang, B. C.; Weng, J.; Lu, G. *Synthesis* **2019**, *51*, 1969.

6. Data for X-Ray Crystal Structure of 3a

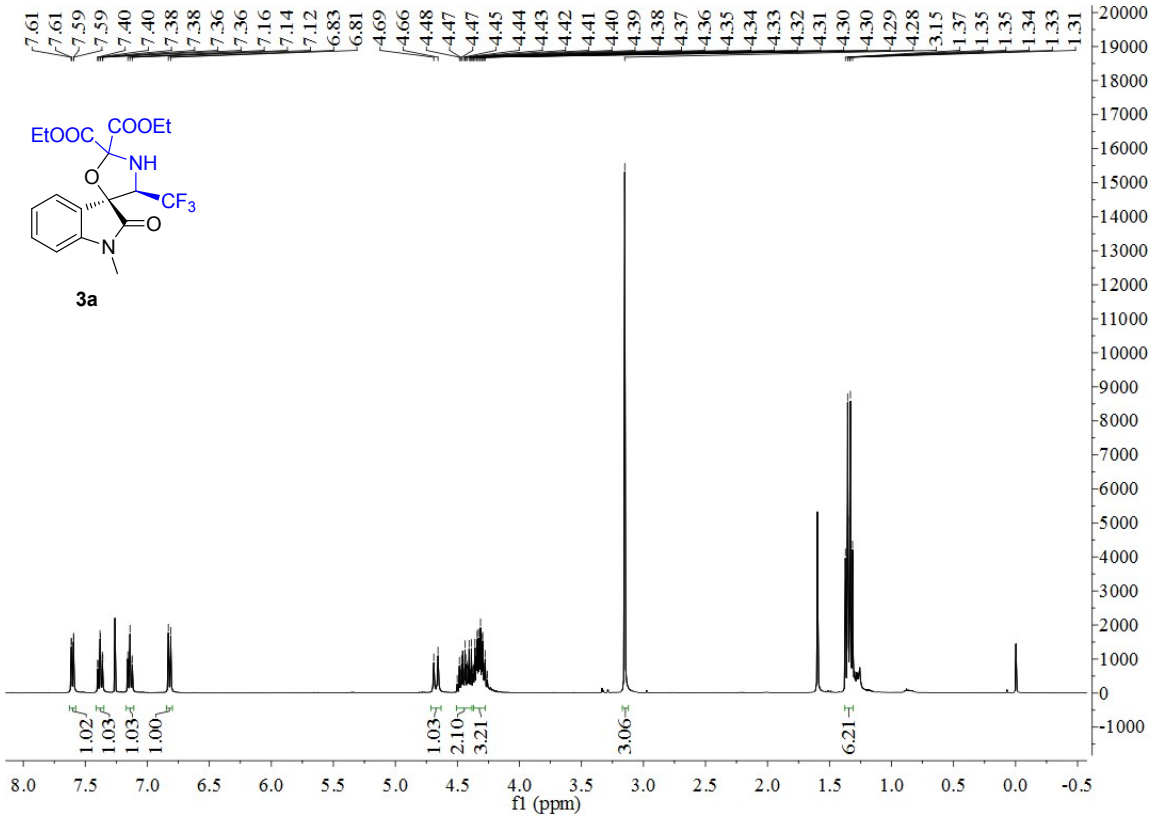
Procedure for the recrystallization of 3a: To a 10 mL vial containing **3a** (35 mg), was added a 1:9 mixture of isopropanol and n-hexane until it formed a clear solution. The mixture was kept aside 3 days at room temperature to obtain crystals by slow evaporation. These crystals were subjected for single crystal XRD to determine the absolute configuration of **3a**.

Table 1 Crystal data and structure refinement

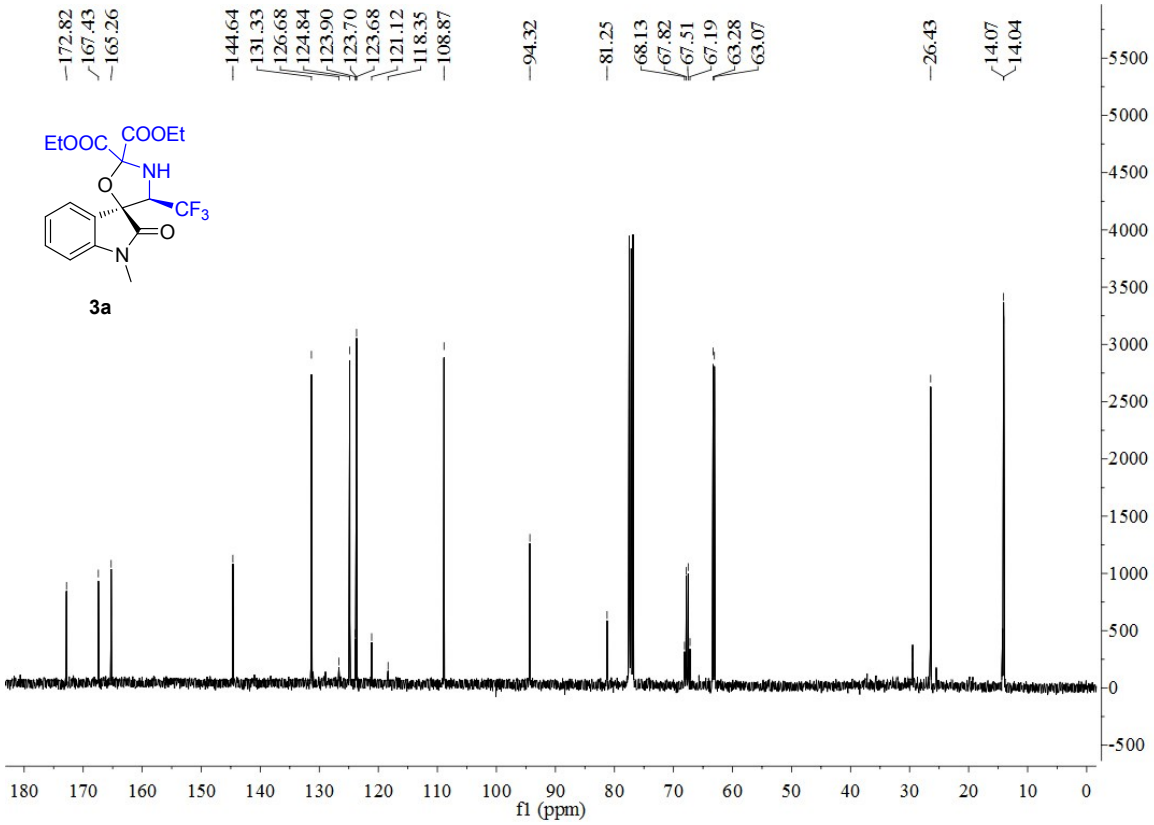
Compound	 **3a**
Empirical formula	$C_{18}H_{19}F_3N_2O_6$
Formula weight	416.35
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.80560(10)
b/Å	8.83160(10)
c/Å	24.7208(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1922.48(4)
Z	4
ρ_{calc}g/cm^3	1.438
μ/mm^{-1}	1.102
F(000)	864.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	14.202 to 151.914
Index ranges	-10 ≤ h ≤ 10,
Reflections collected	19227
Independent reflections	3936 [Rint = 0.0335,
Data/restraints/parameters	3936/8/317
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1109
Final R indexes [all data]	R_1 = 0.0404, wR_2 = 0.1114
Largest diff. peak/hole/e Å^{-3}	0.42/-0.43

7. Copies of NMR Spectra of Compounds

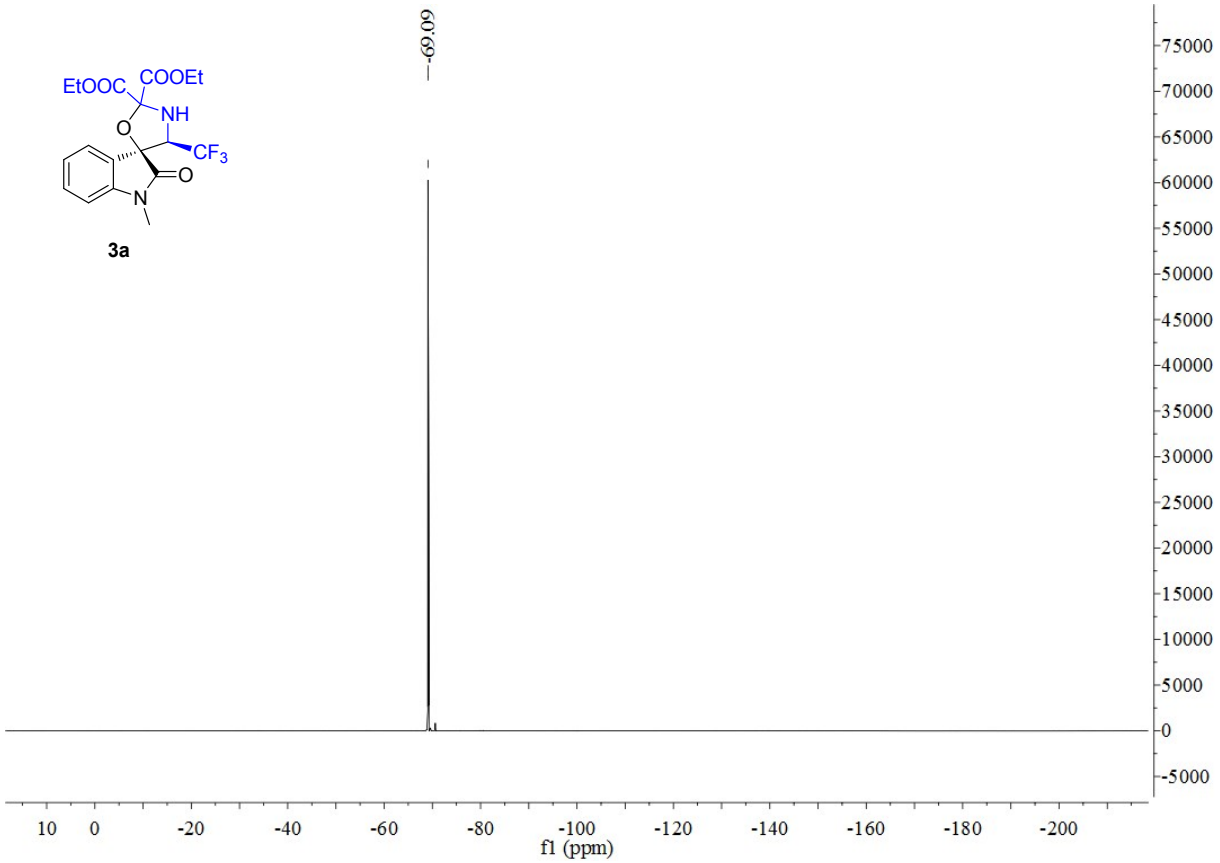
^{1}H NMR of compound 3a (in $CDCl_3$)



^{13}C NMR of compound 3a (in $CDCl_3$)

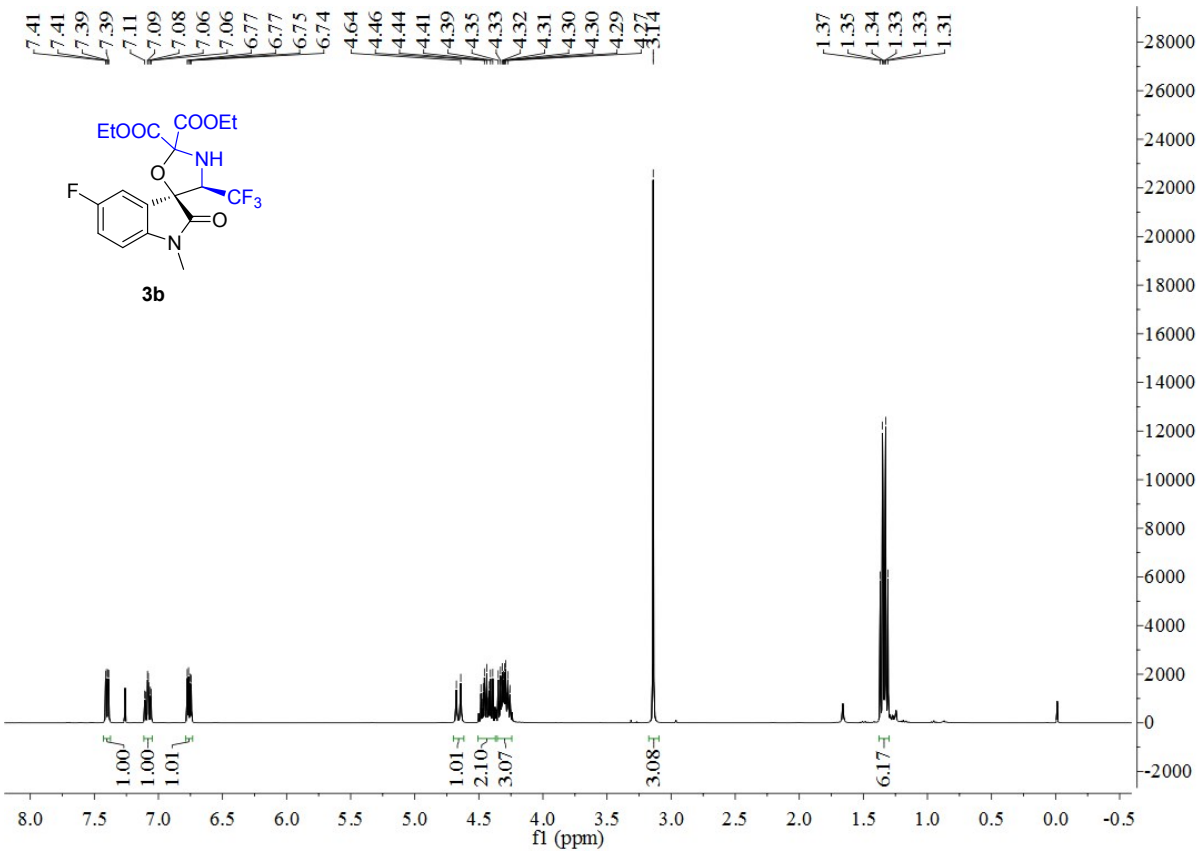


^{19}F NMR of compound 3a (in $CDCl_3$)



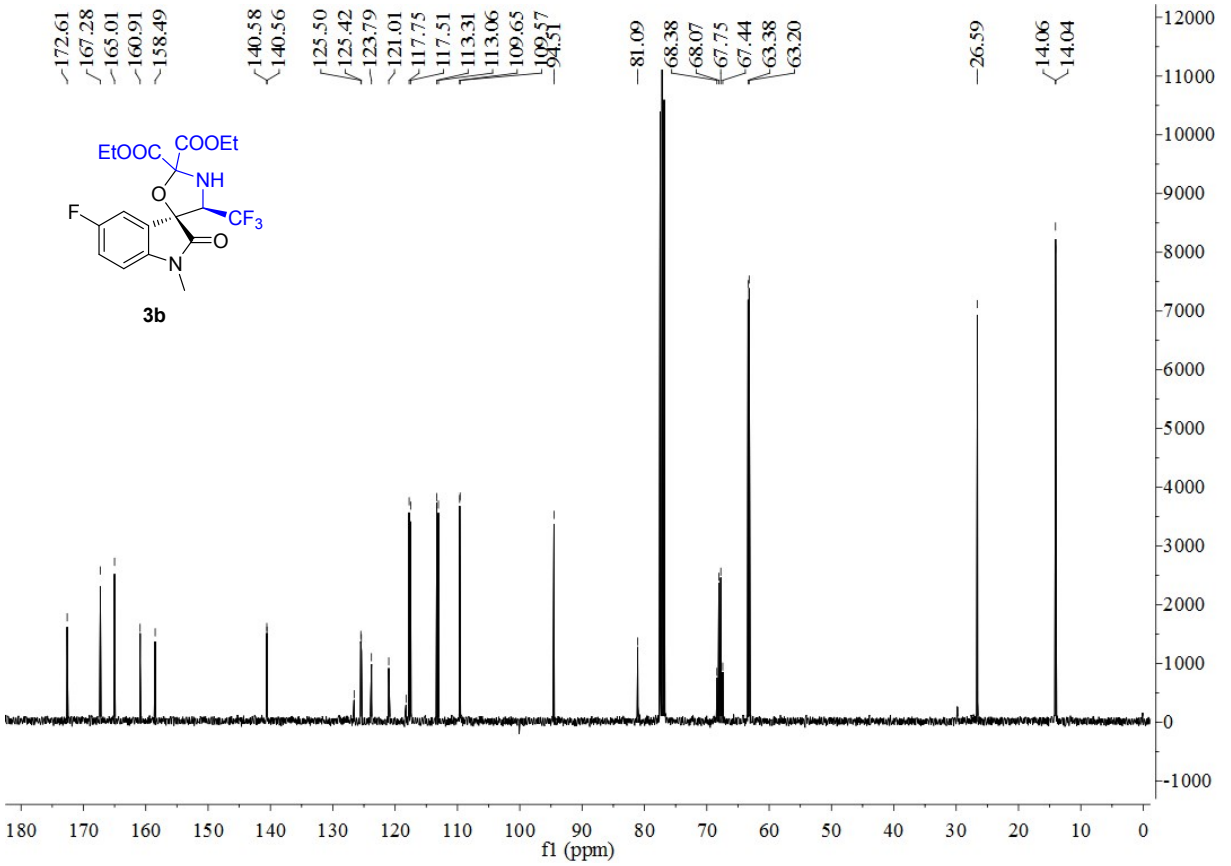
3a

^{1}H NMR of compound 3b (in $CDCl_3$)

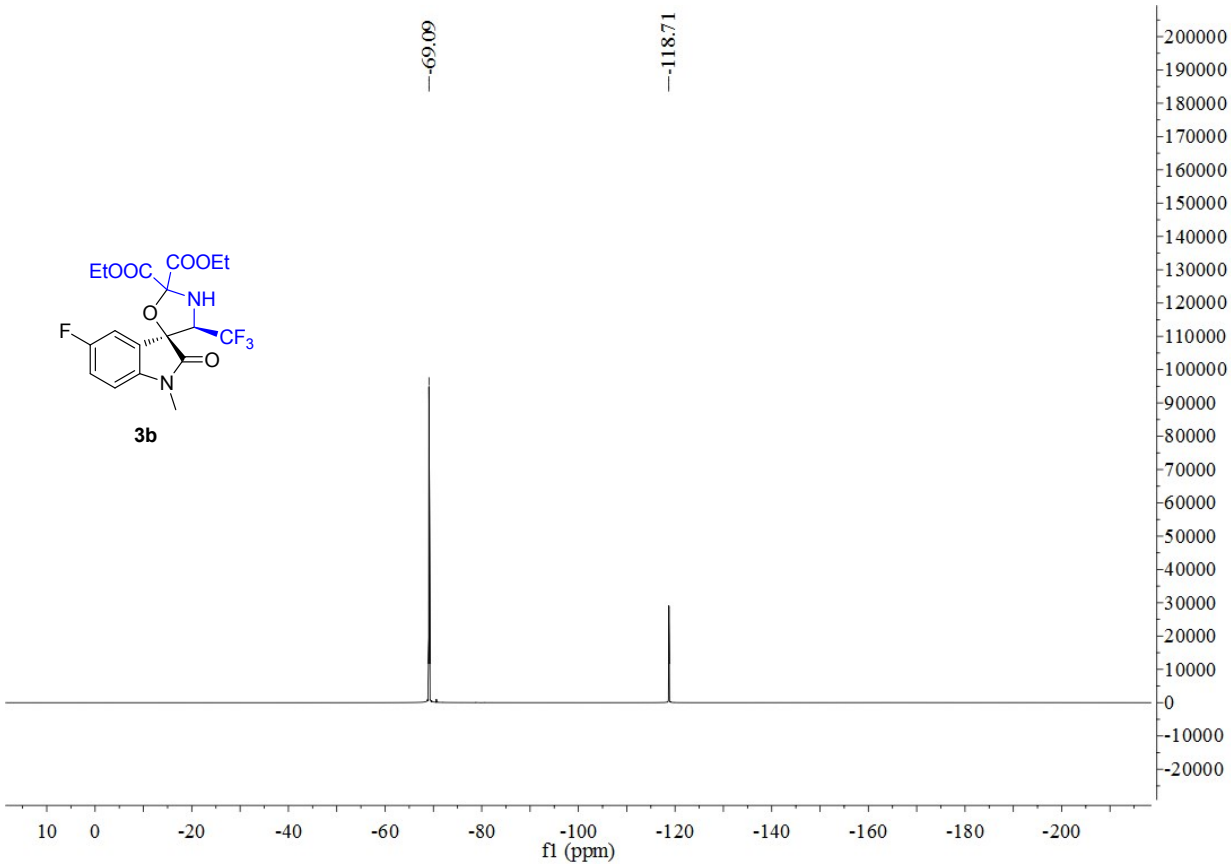


3b

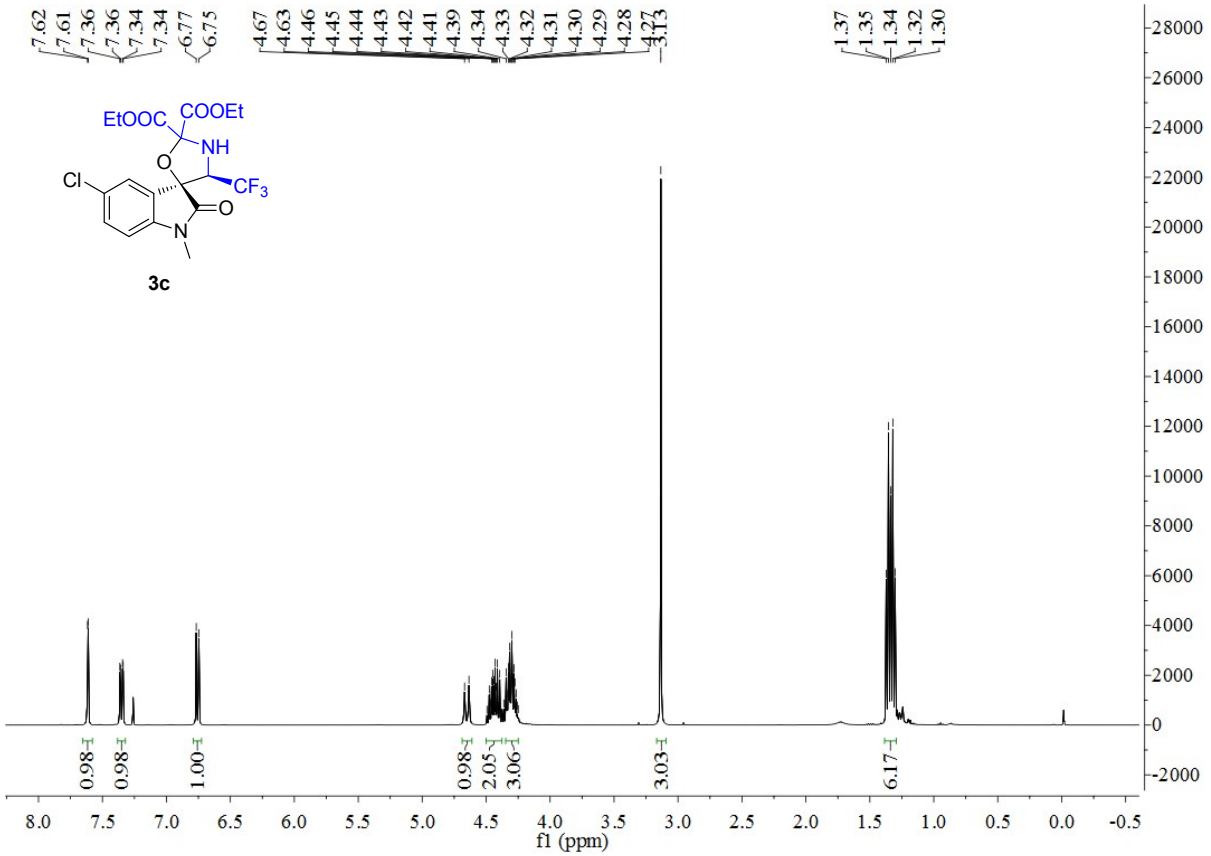
^{13}C NMR of compound 3b (in $CDCl_3$)



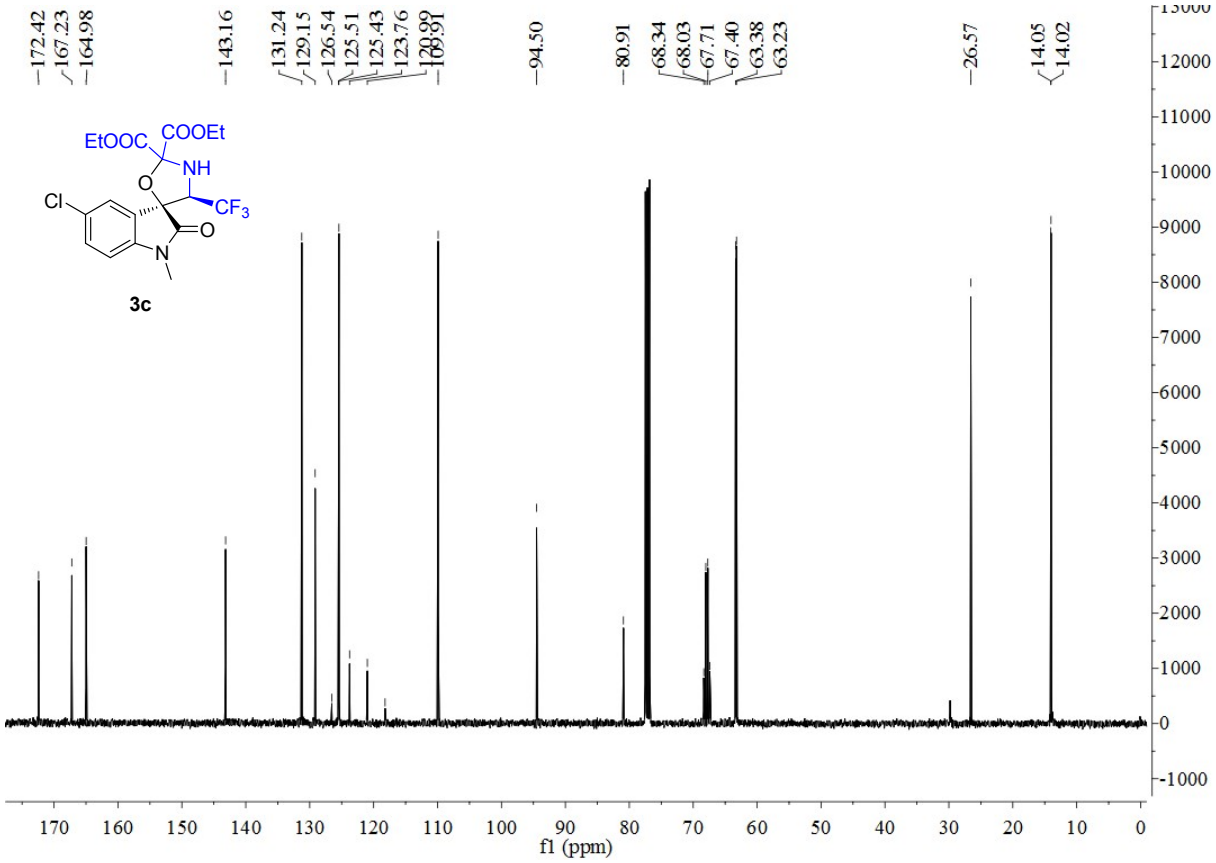
^{19}F NMR of compound 3b (in $CDCl_3$)



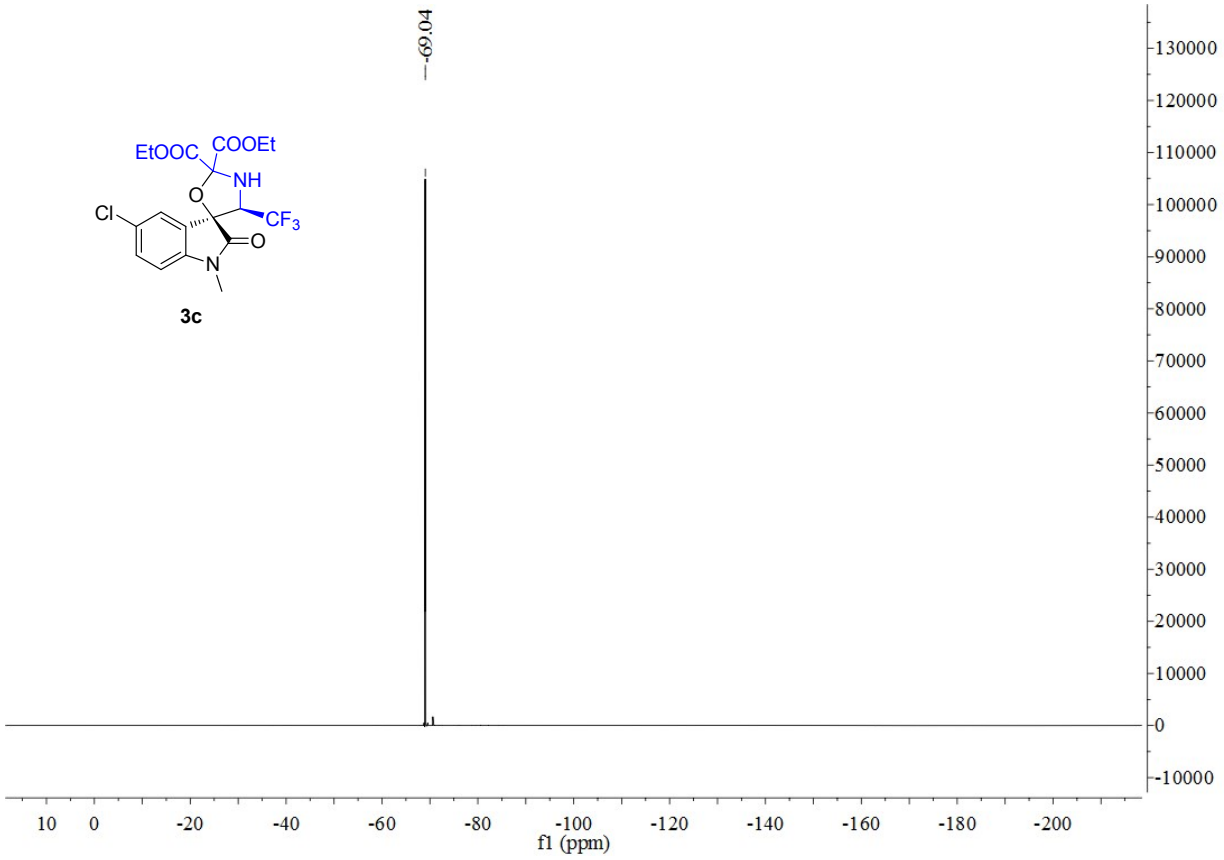
^{1}H NMR of compound 3c (in $CDCl_3$)



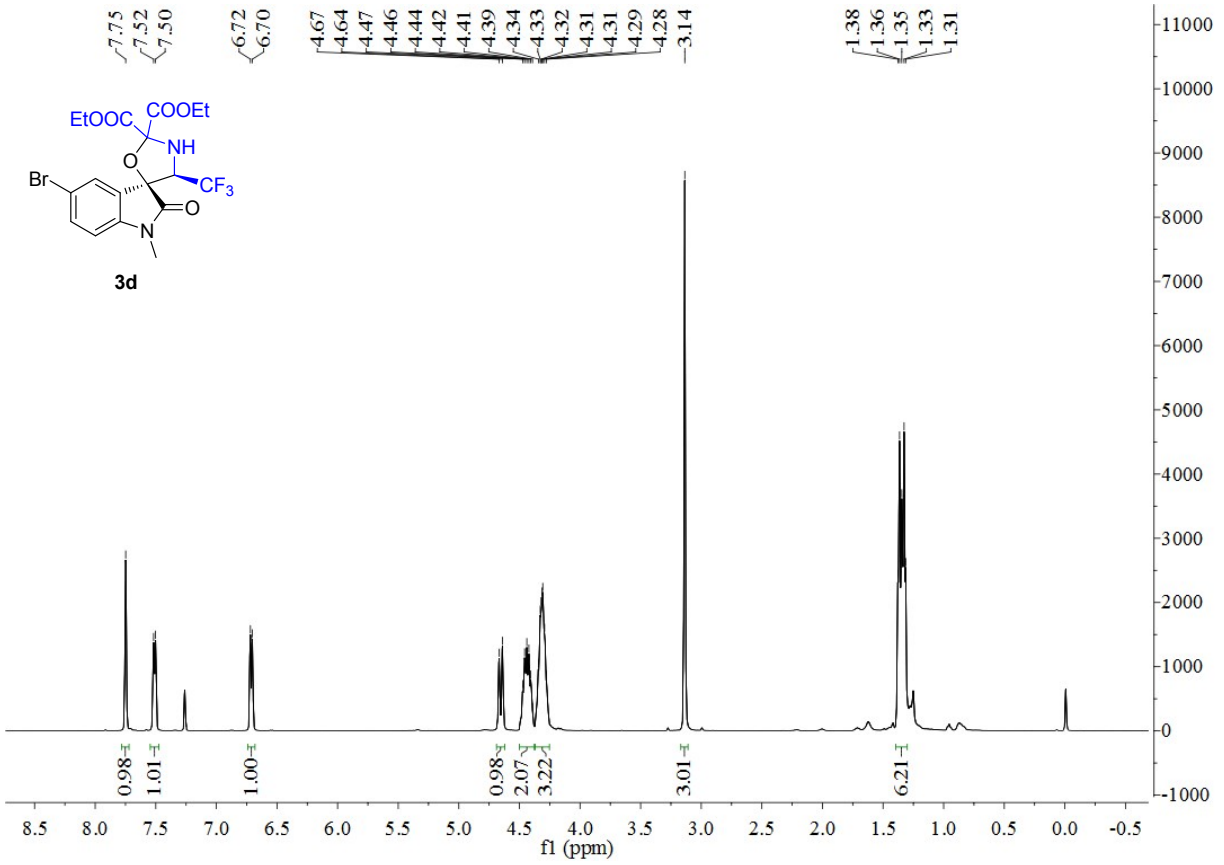
^{13}C NMR of compound 3c (in $CDCl_3$)



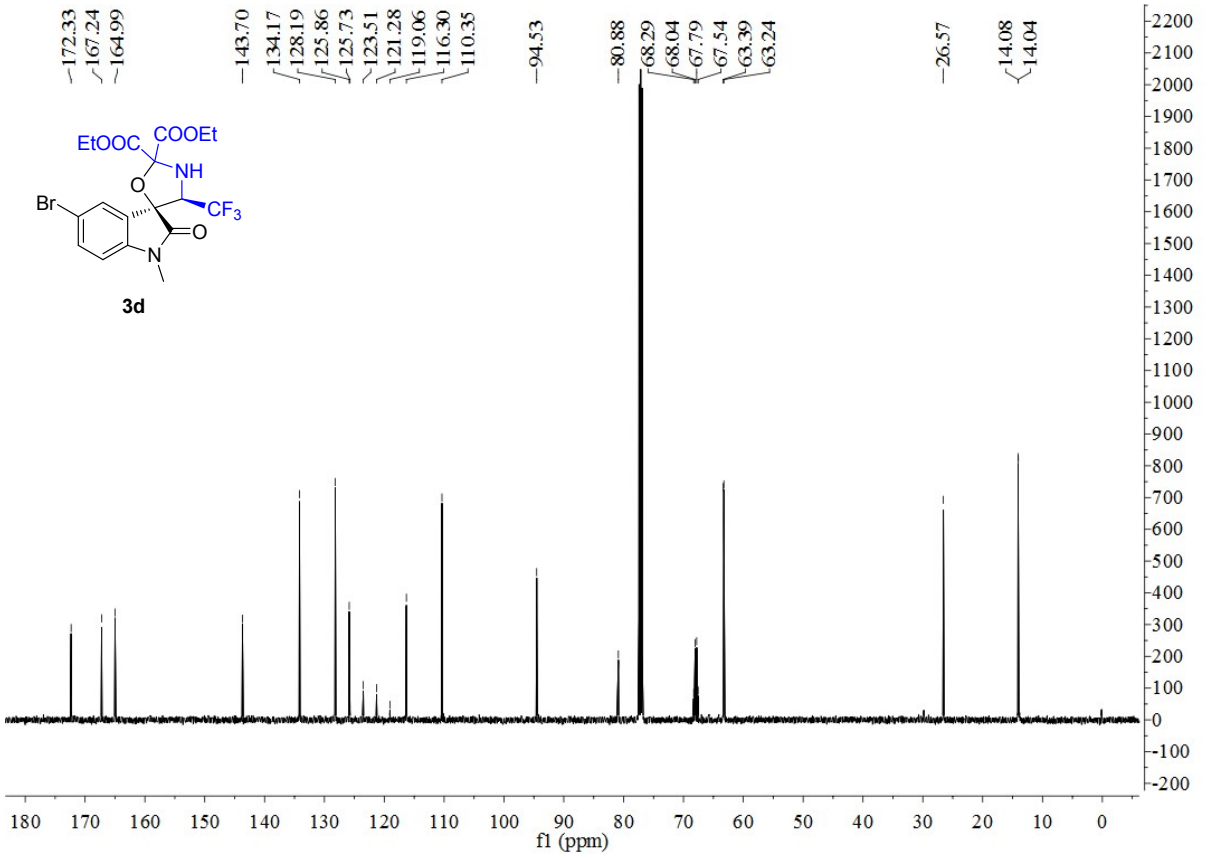
^{19}F NMR of compound 3c (in $CDCl_3$)



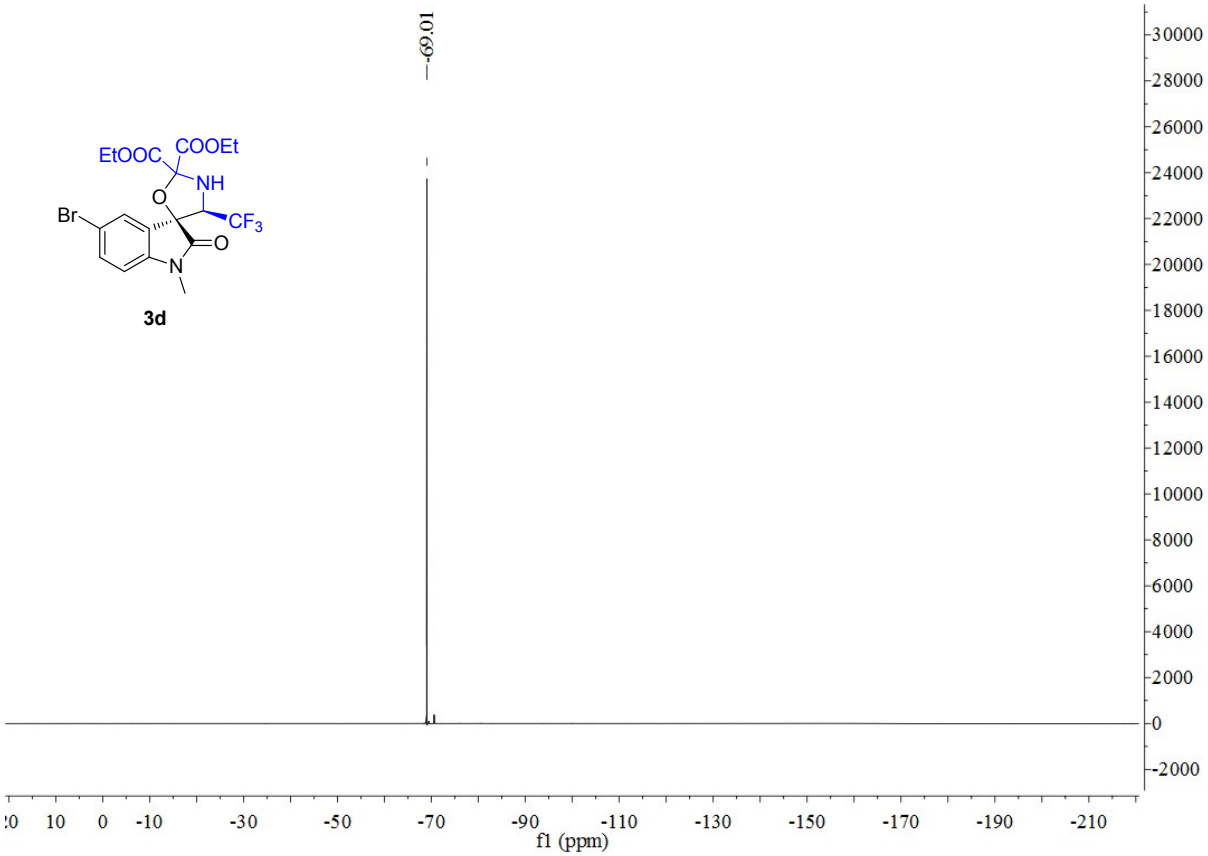
^{1}H NMR of compound 3d (in $CDCl_3$)



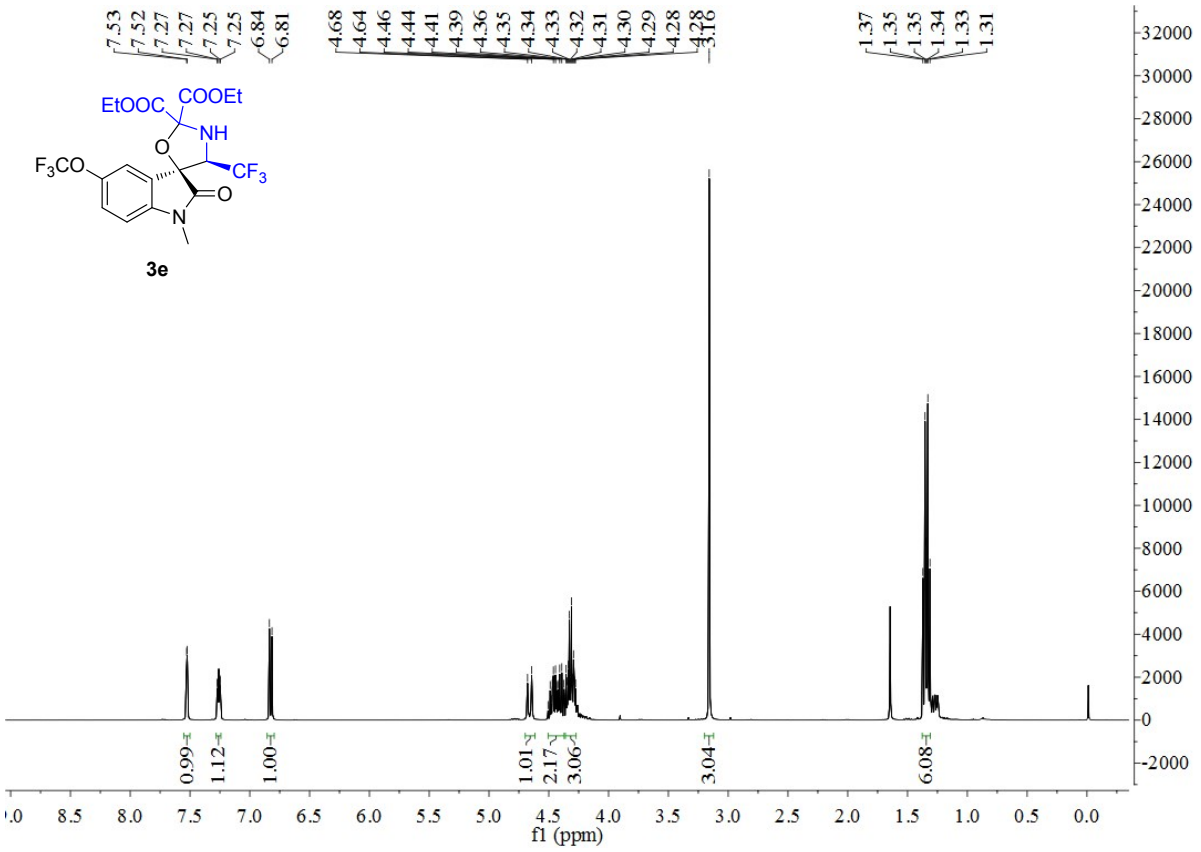
^{13}C NMR of compound 3d (in $CDCl_3$)



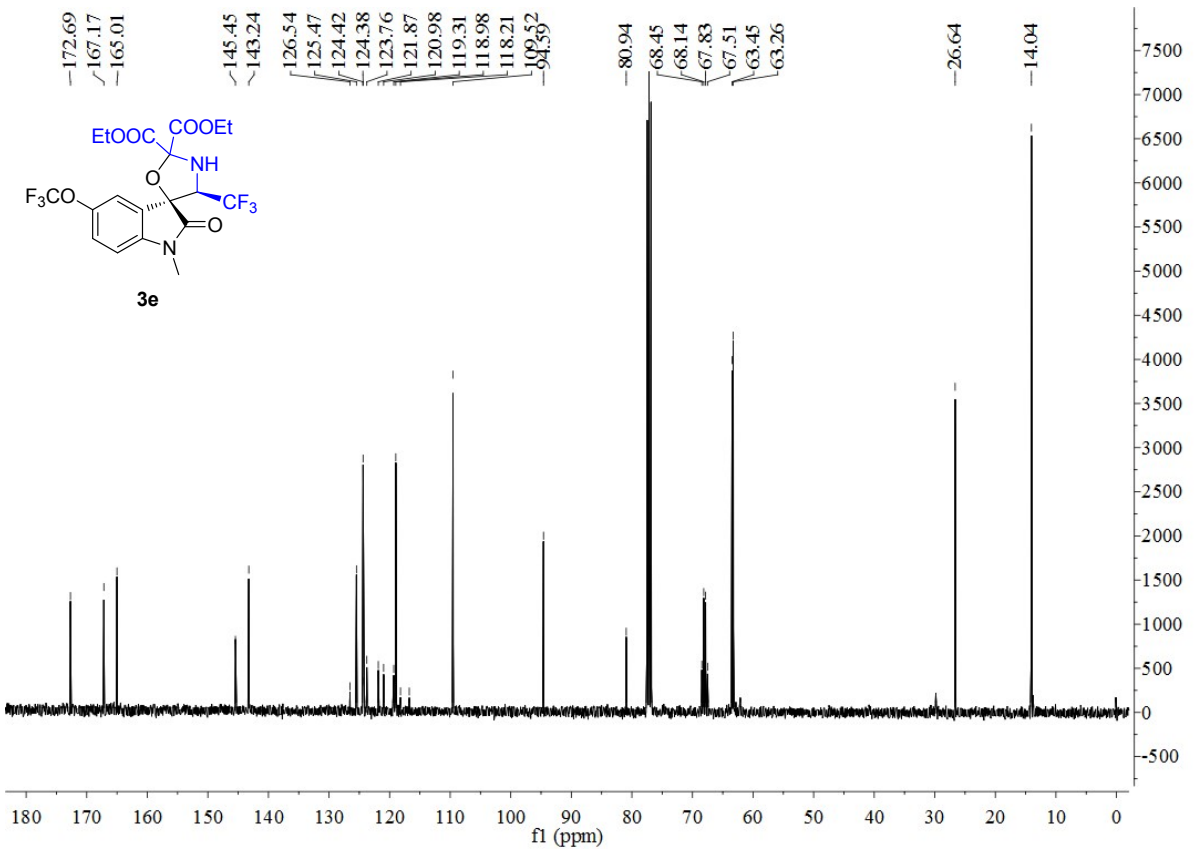
^{19}F NMR of compound 3d (in $CDCl_3$)



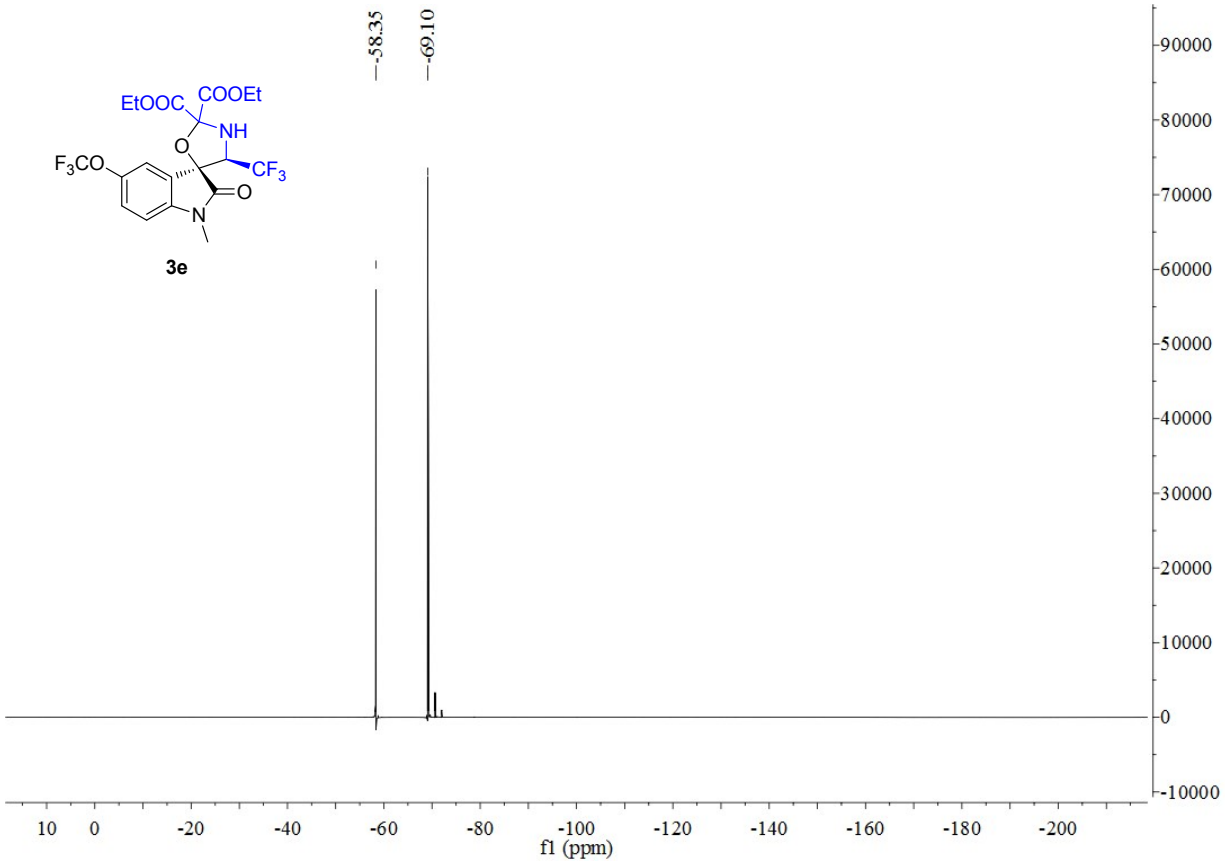
^{1}H NMR of compound 3e (in $CDCl_3$)



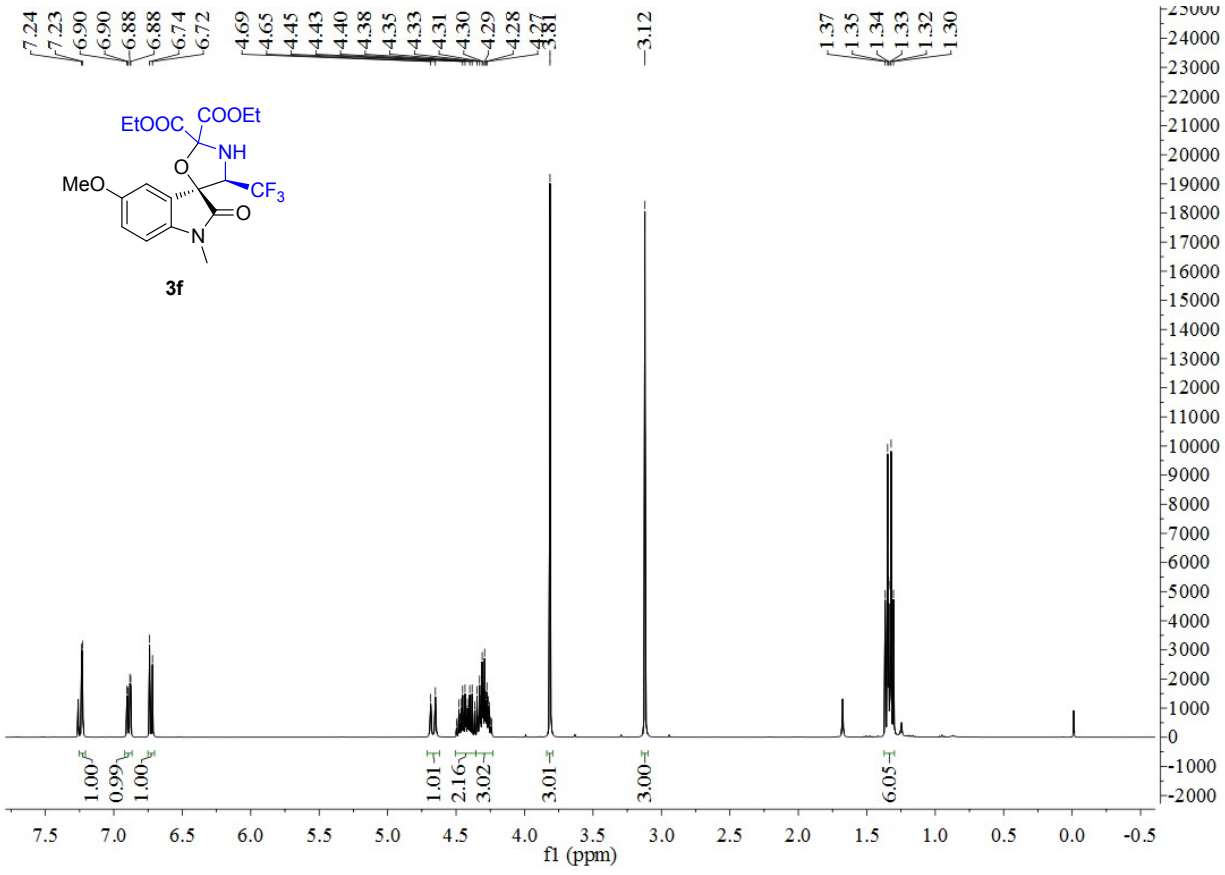
^{13}C NMR of compound 3e (in $CDCl_3$)



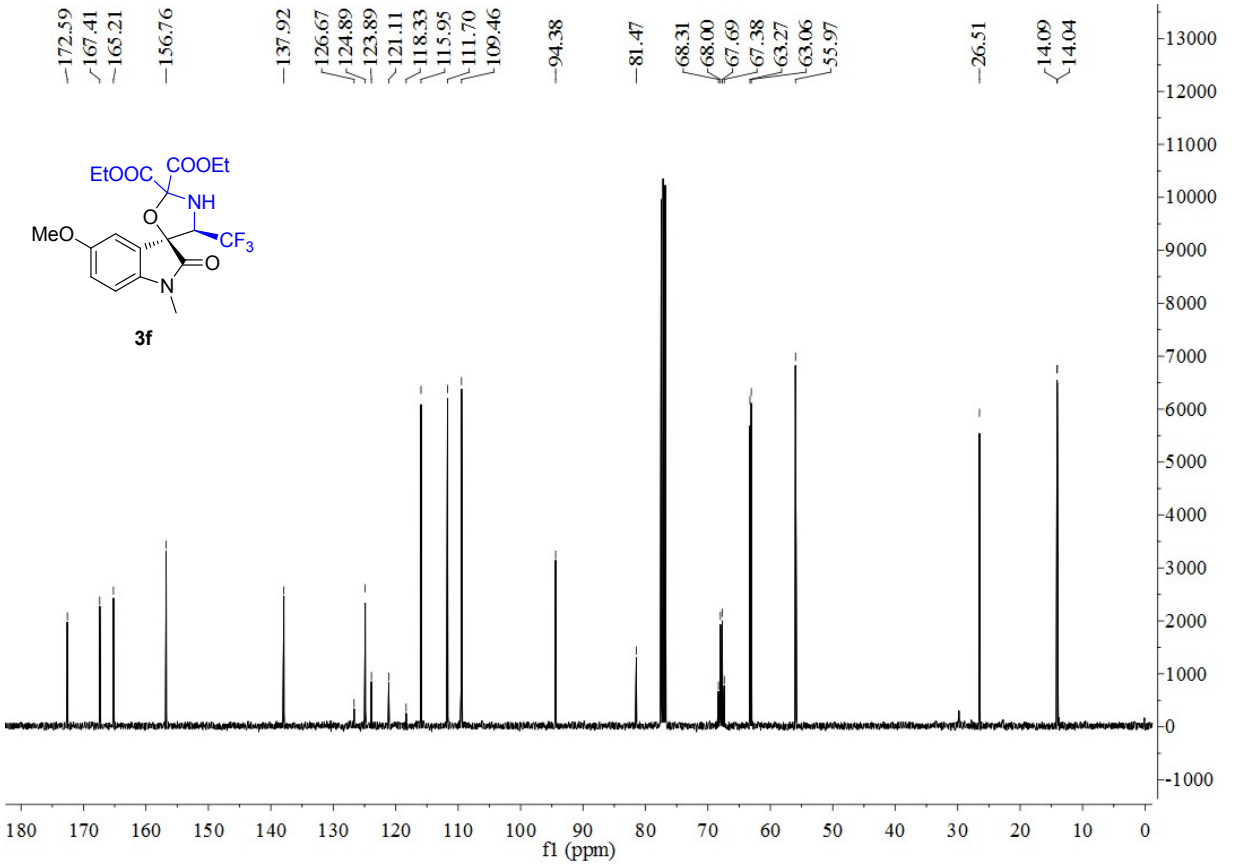
^{19}F NMR of compound 3e (in $CDCl_3$)



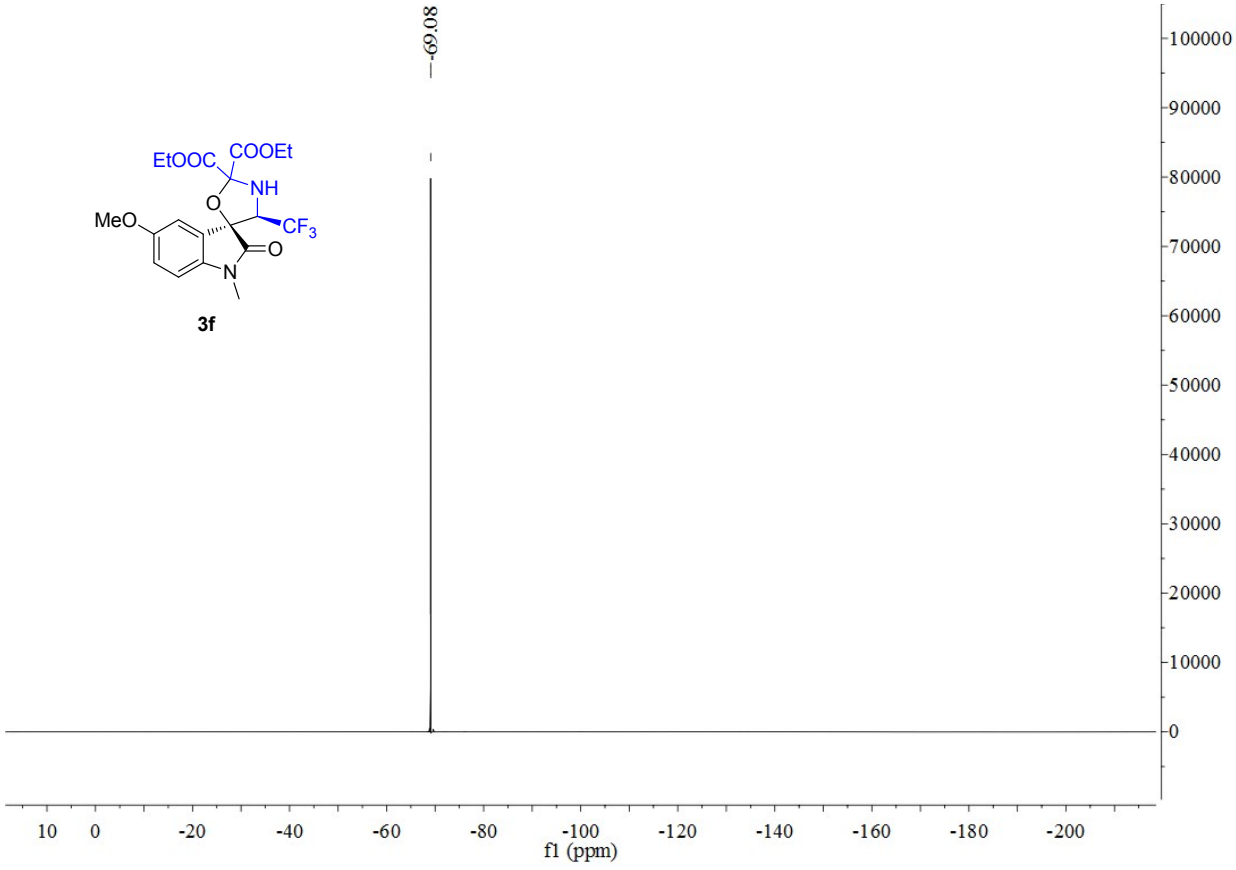
^{1}H NMR of compound 3f (in $CDCl_3$)



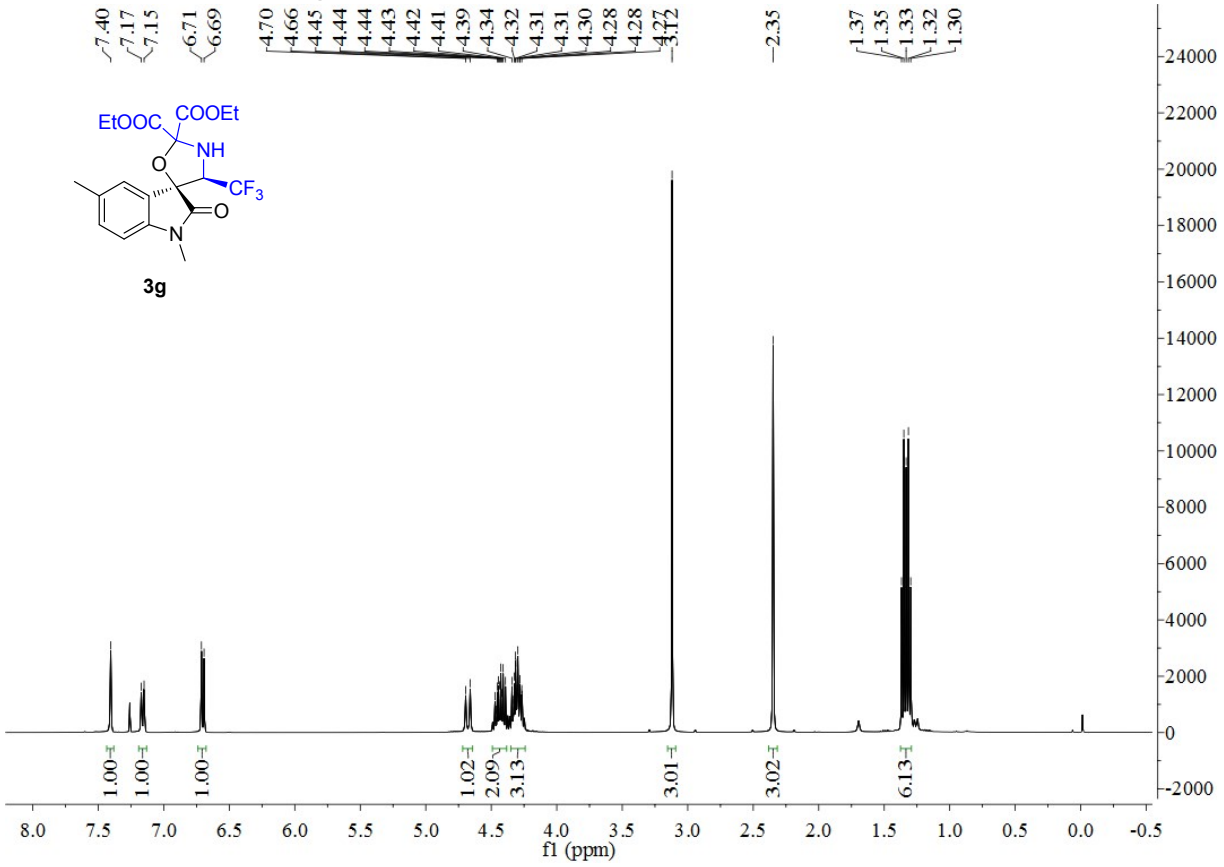
^{13}C NMR of compound 3f (in $CDCl_3$)



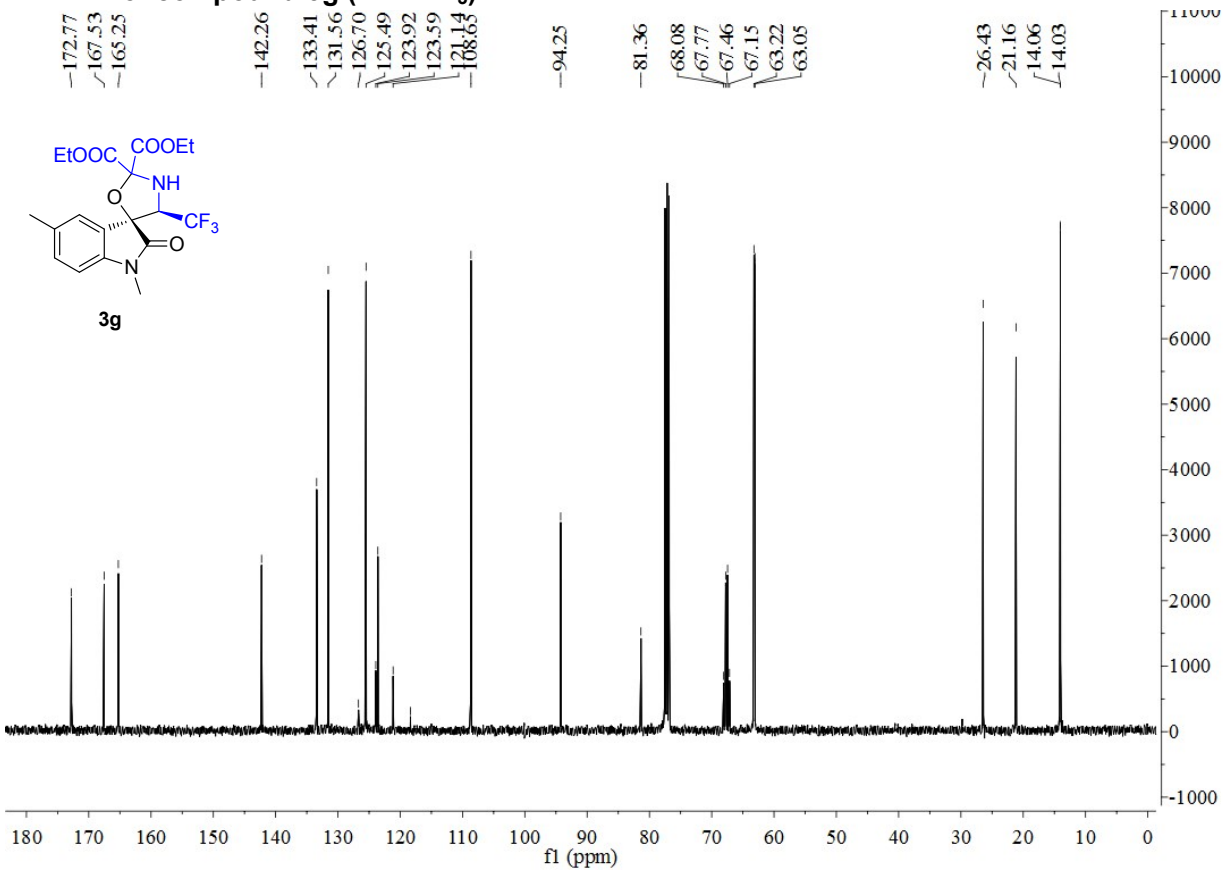
^{19}F NMR of compound 3f (in $CDCl_3$)



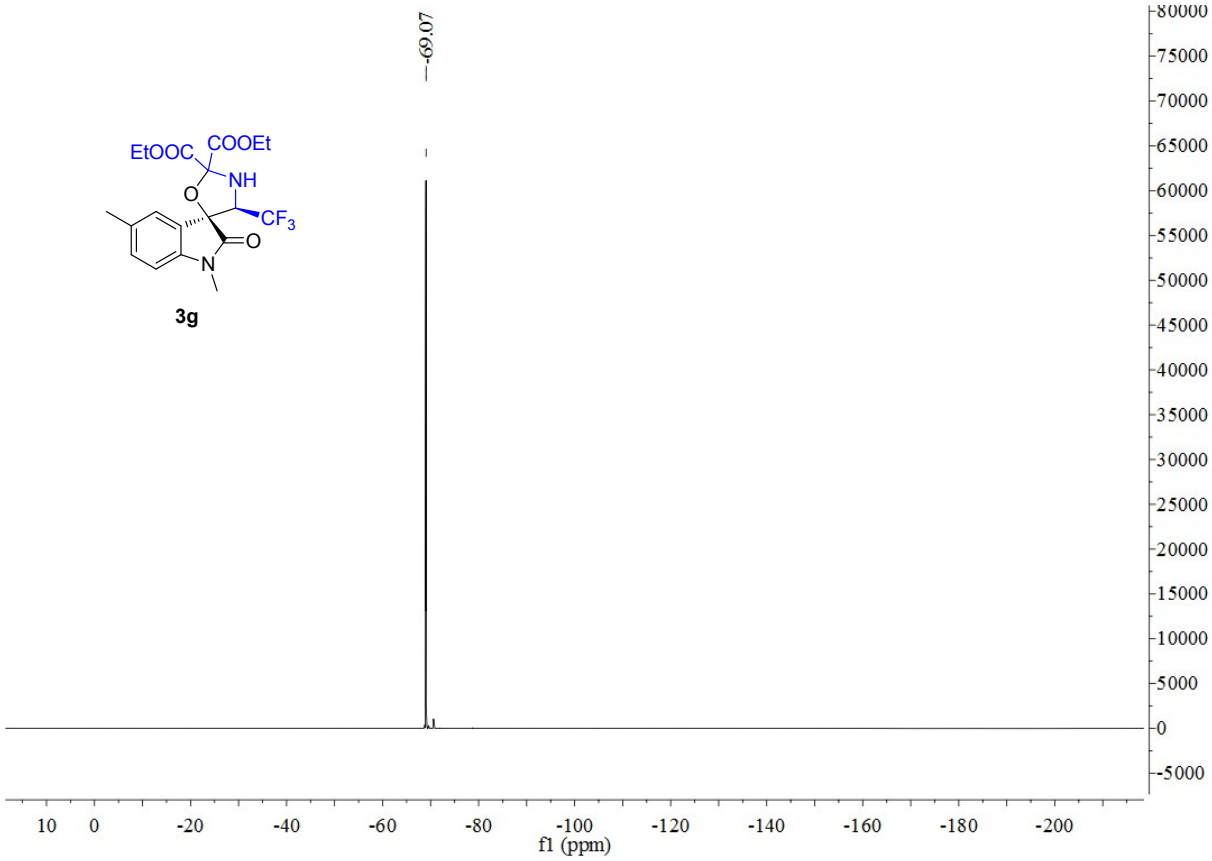
^{1}H NMR of compound 3g (in $CDCl_3$)



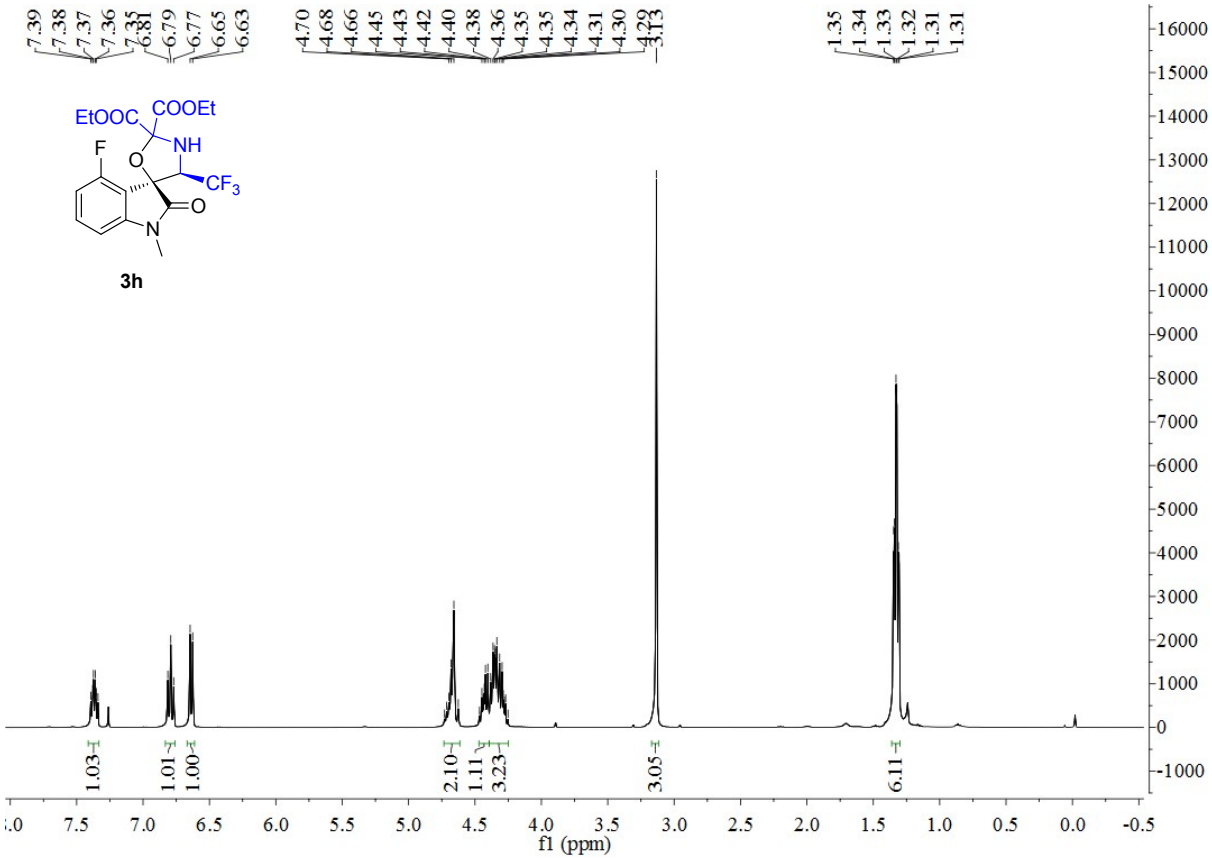
^{13}C NMR of compound 3g (in $CDCl_3$)



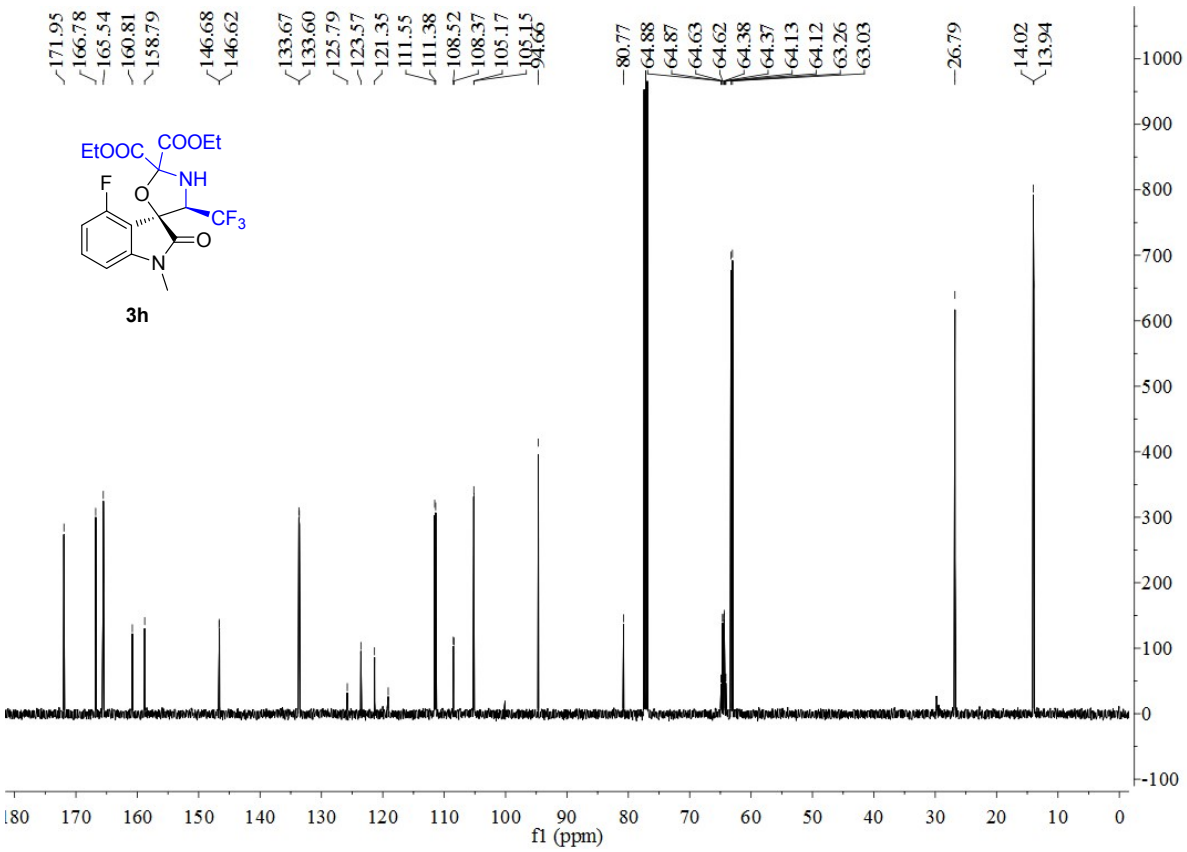
^{19}F NMR of compound 3g (in $CDCl_3$)



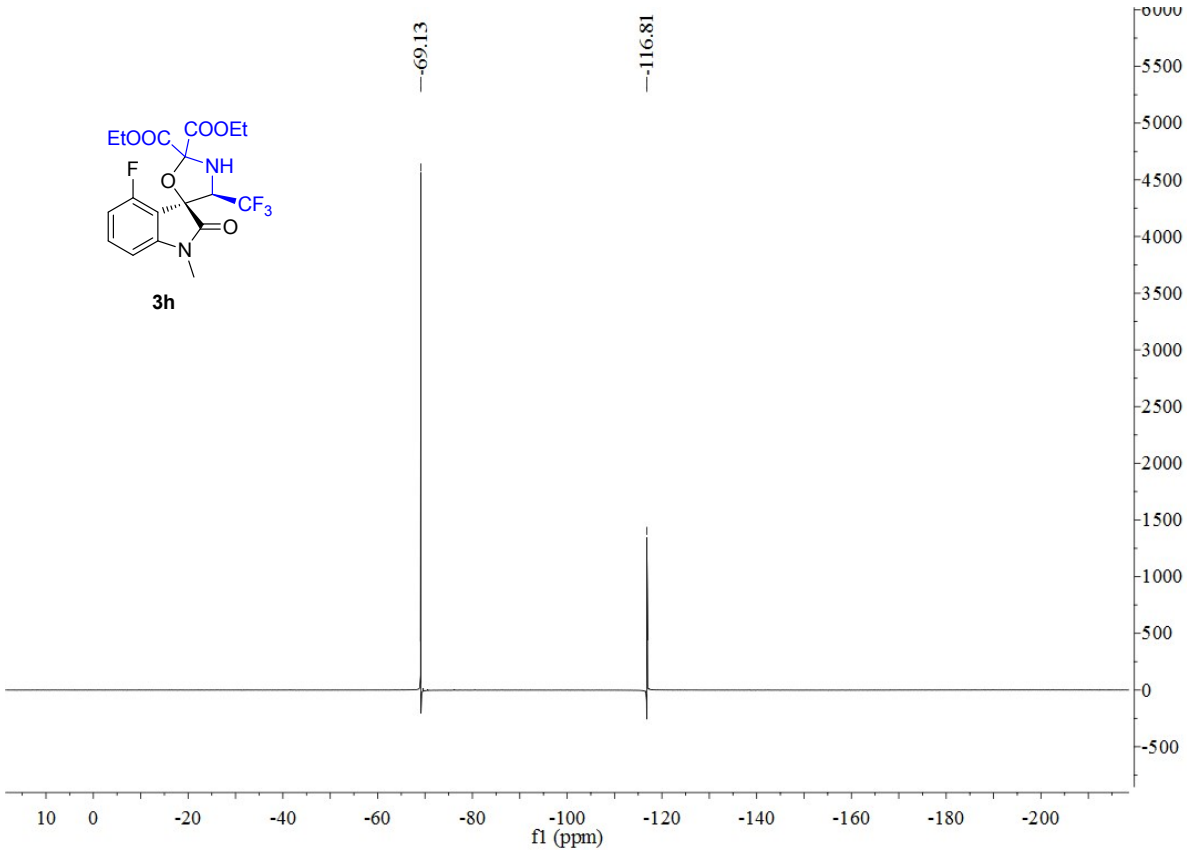
^{1}H NMR of compound 3h (in $CDCl_3$)



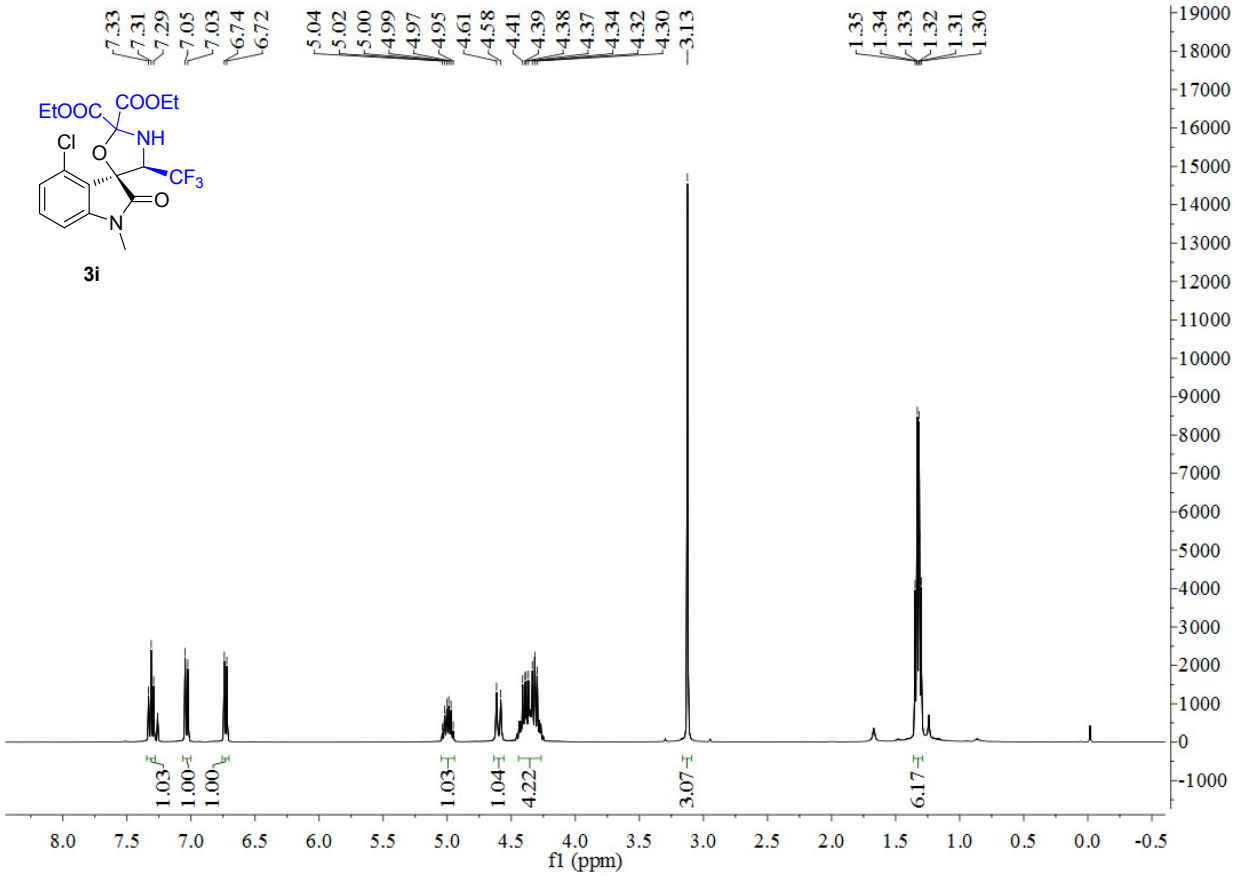
^{13}C NMR of compound 3h (in $CDCl_3$)



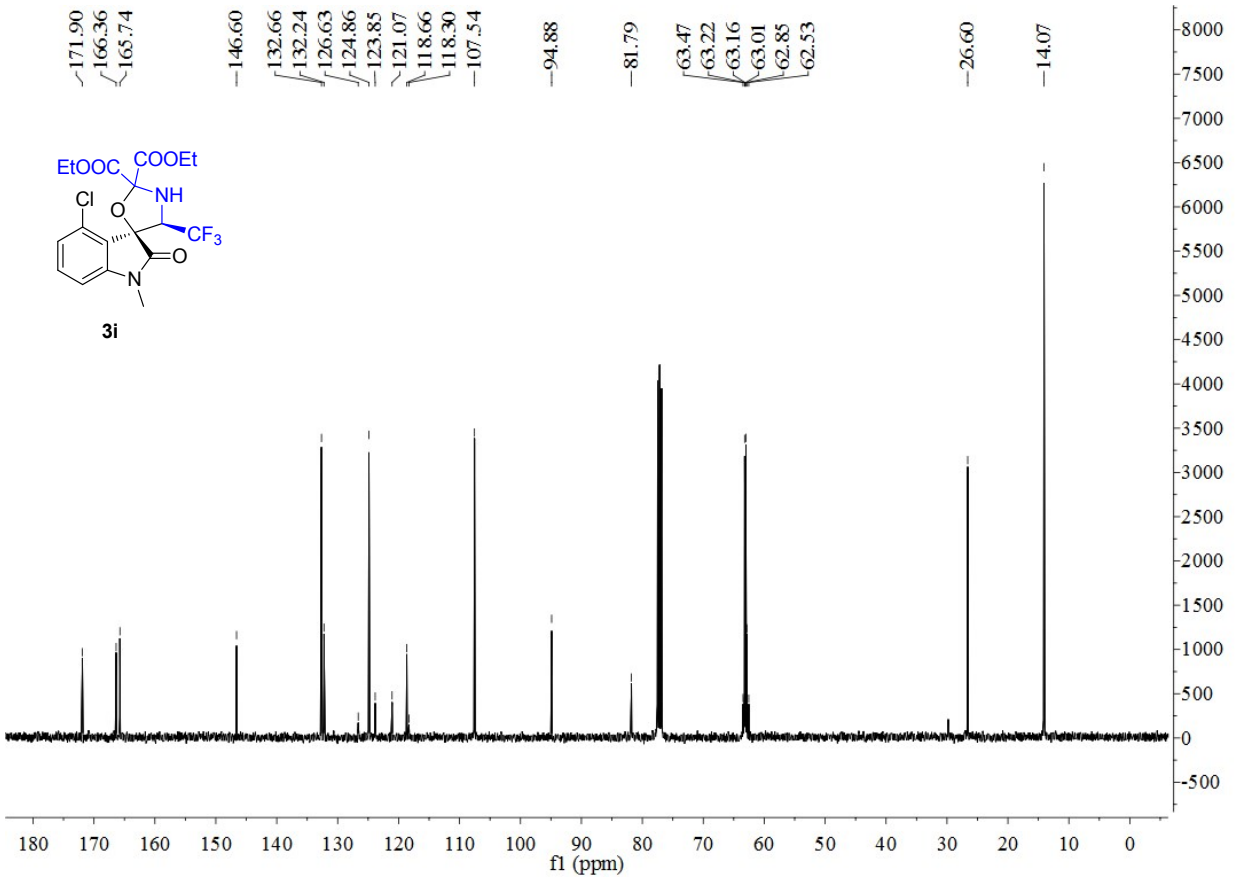
^{19}F NMR of compound 3h (in $CDCl_3$)



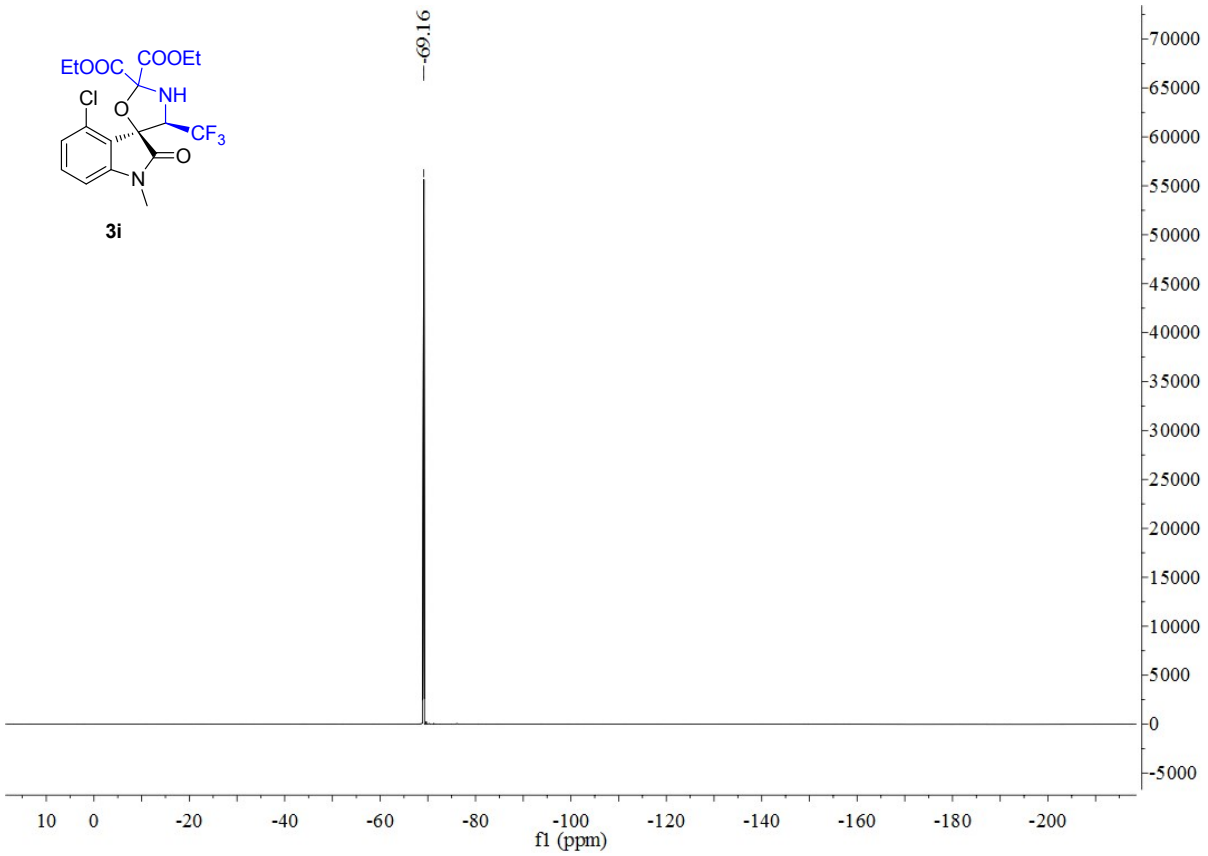
^{1}H NMR of compound 3i (in $CDCl_3$)



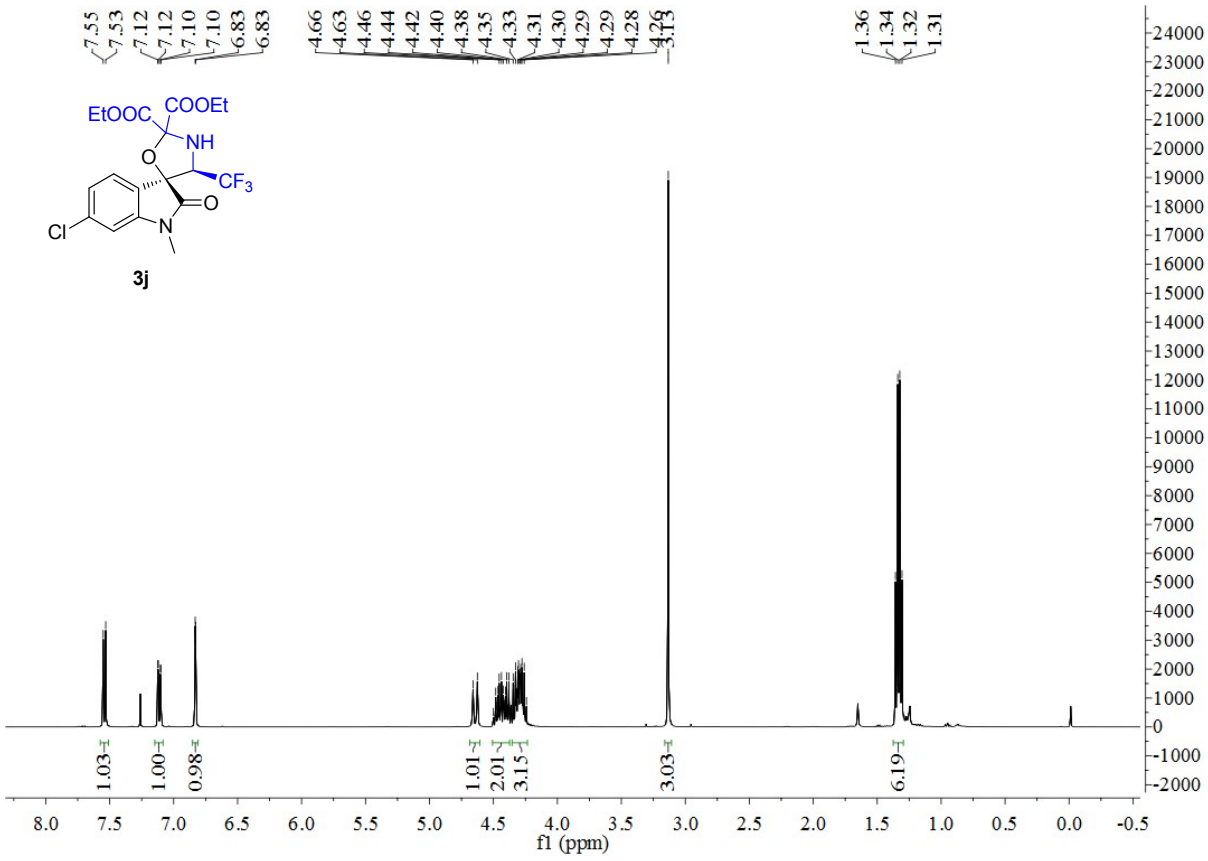
^{13}C NMR of compound 3i (in $CDCl_3$)



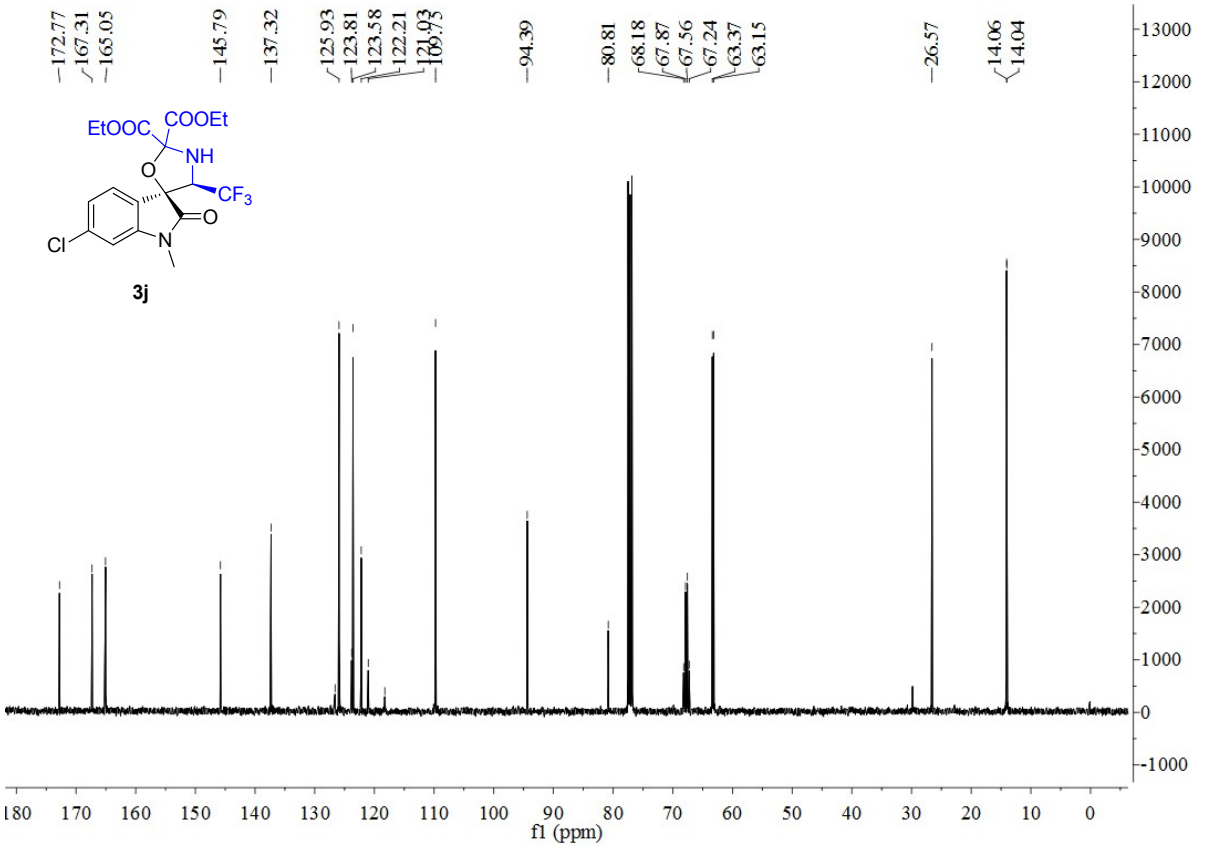
^{19}F NMR of compound 3i (in $CDCl_3$)



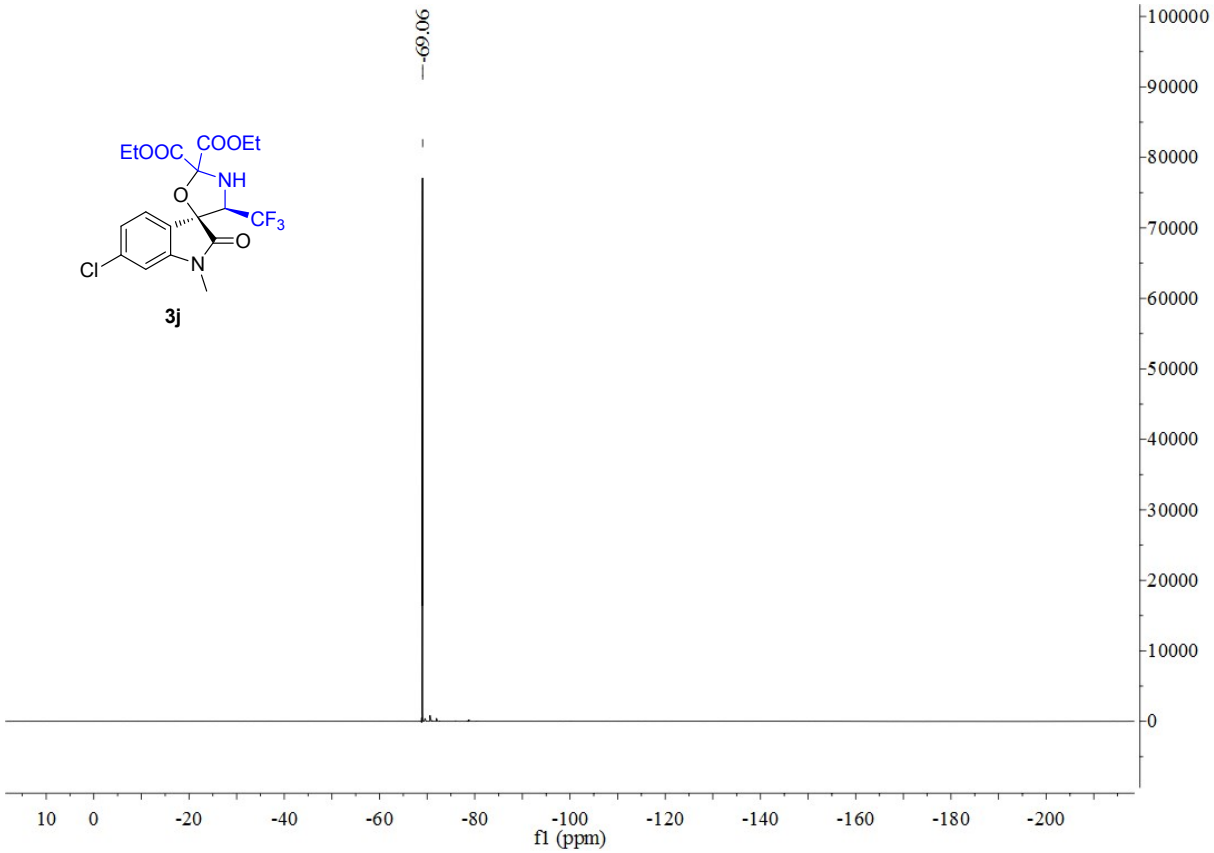
^{1}H NMR of compound 3j (in $CDCl_3$)



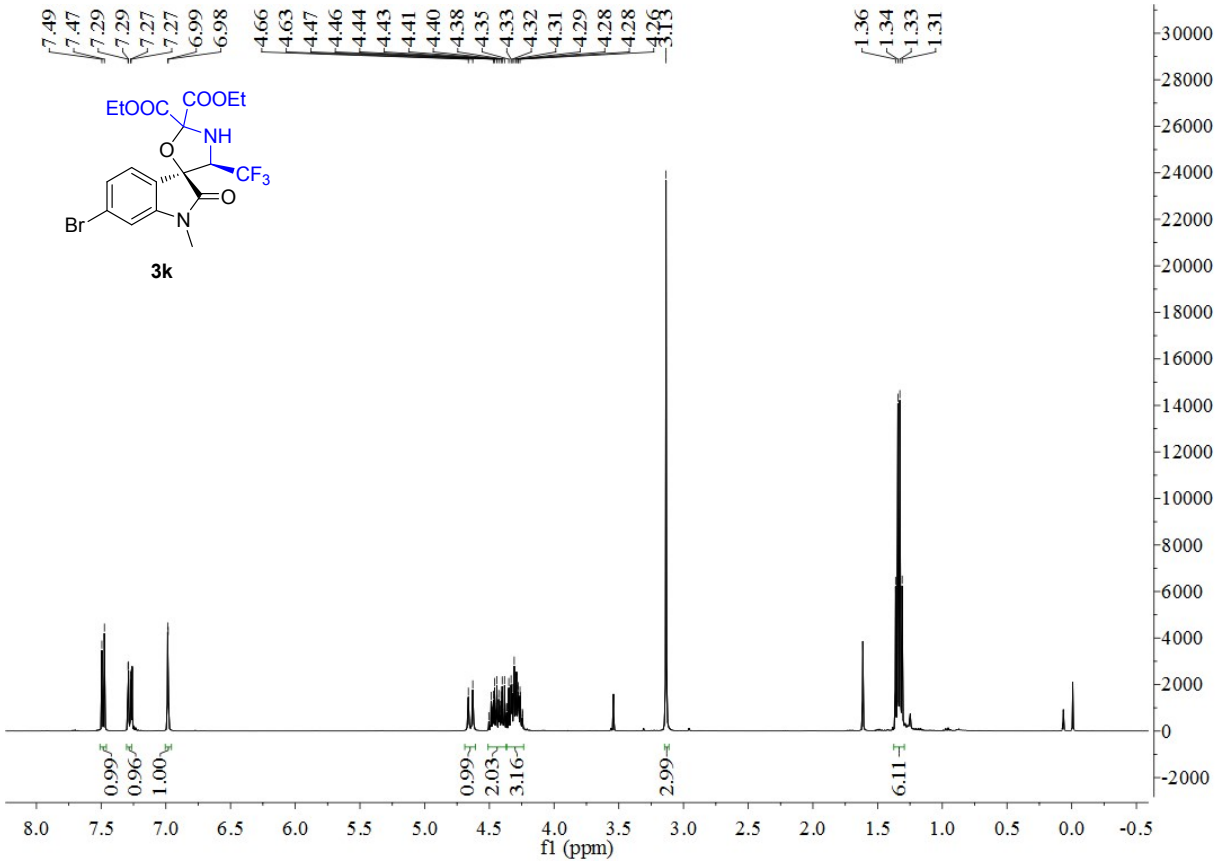
^{13}C NMR of compound 3j (in $CDCl_3$)



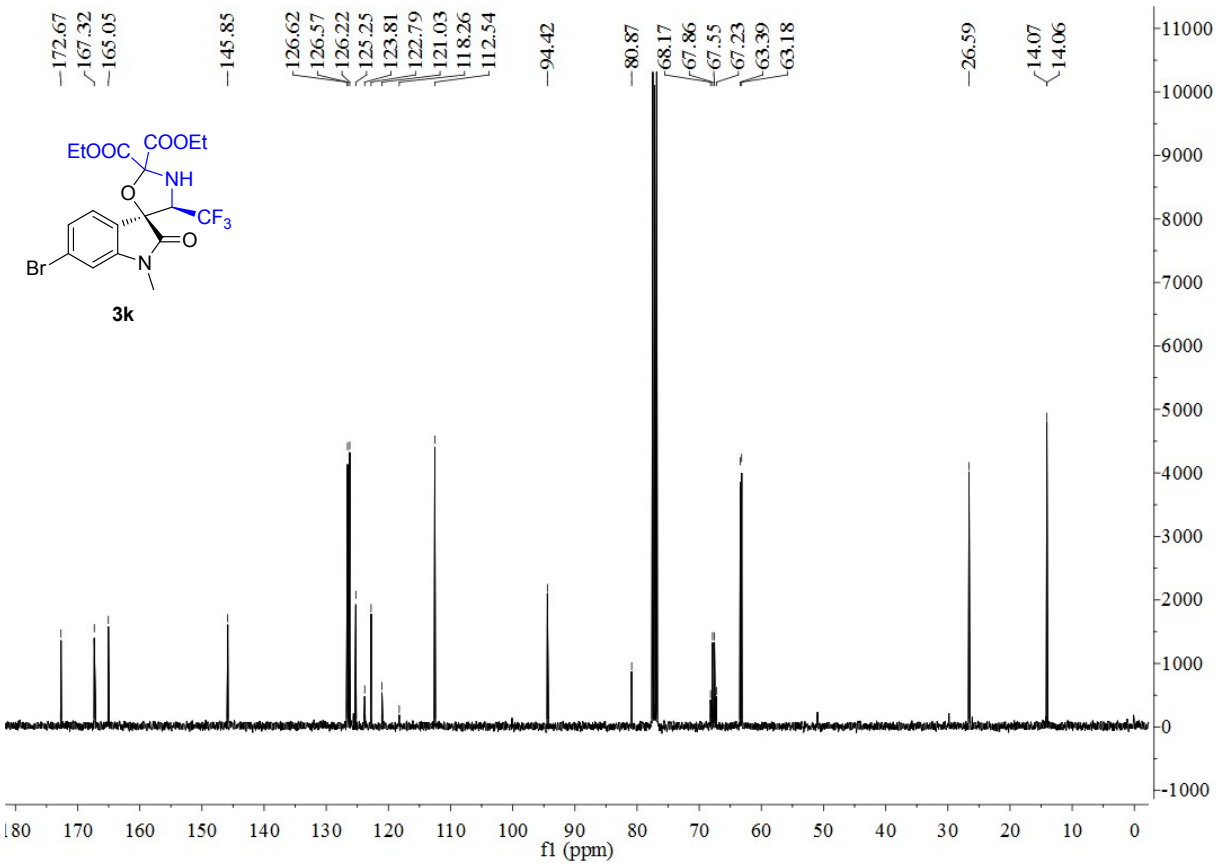
^{19}F NMR of compound 3j (in $CDCl_3$)



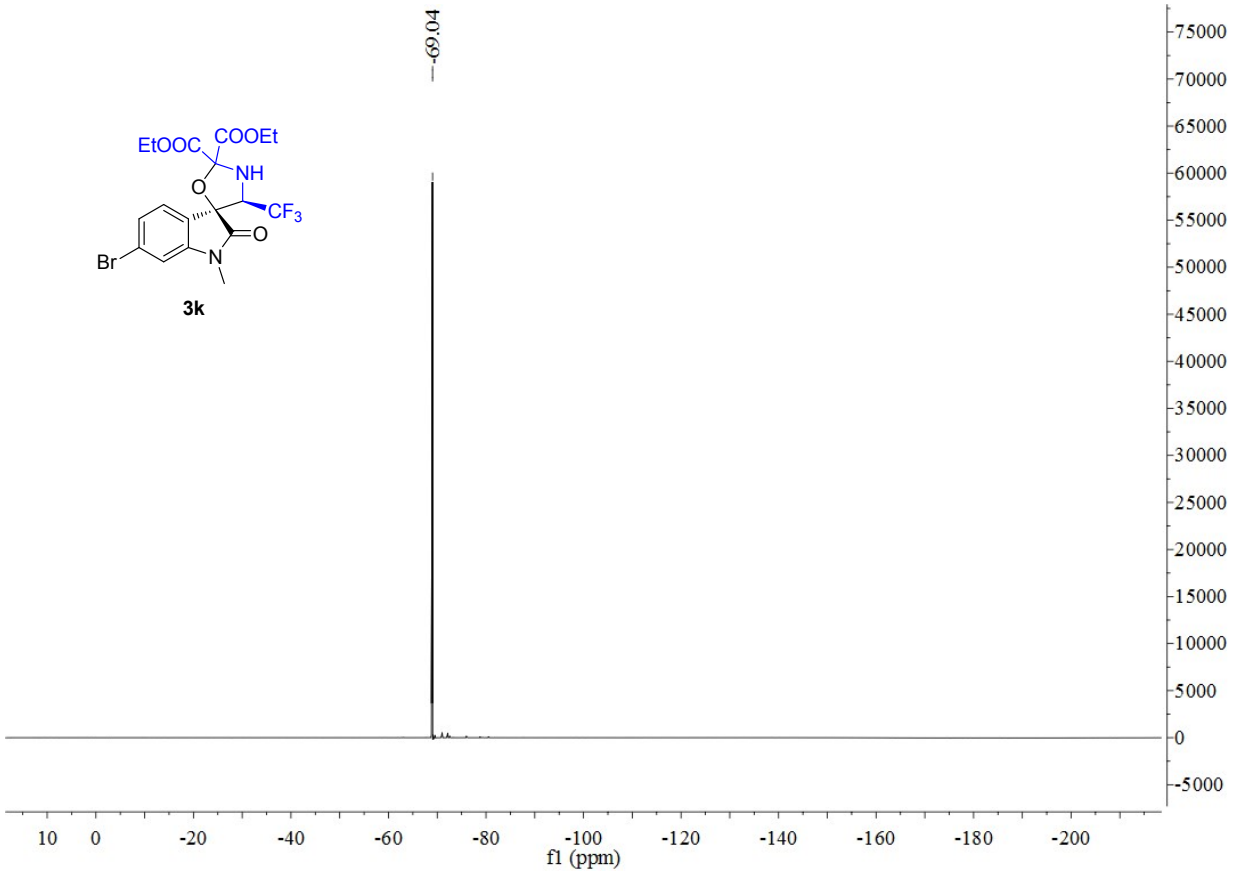
^{1}H NMR of compound 3k (in $CDCl_3$)



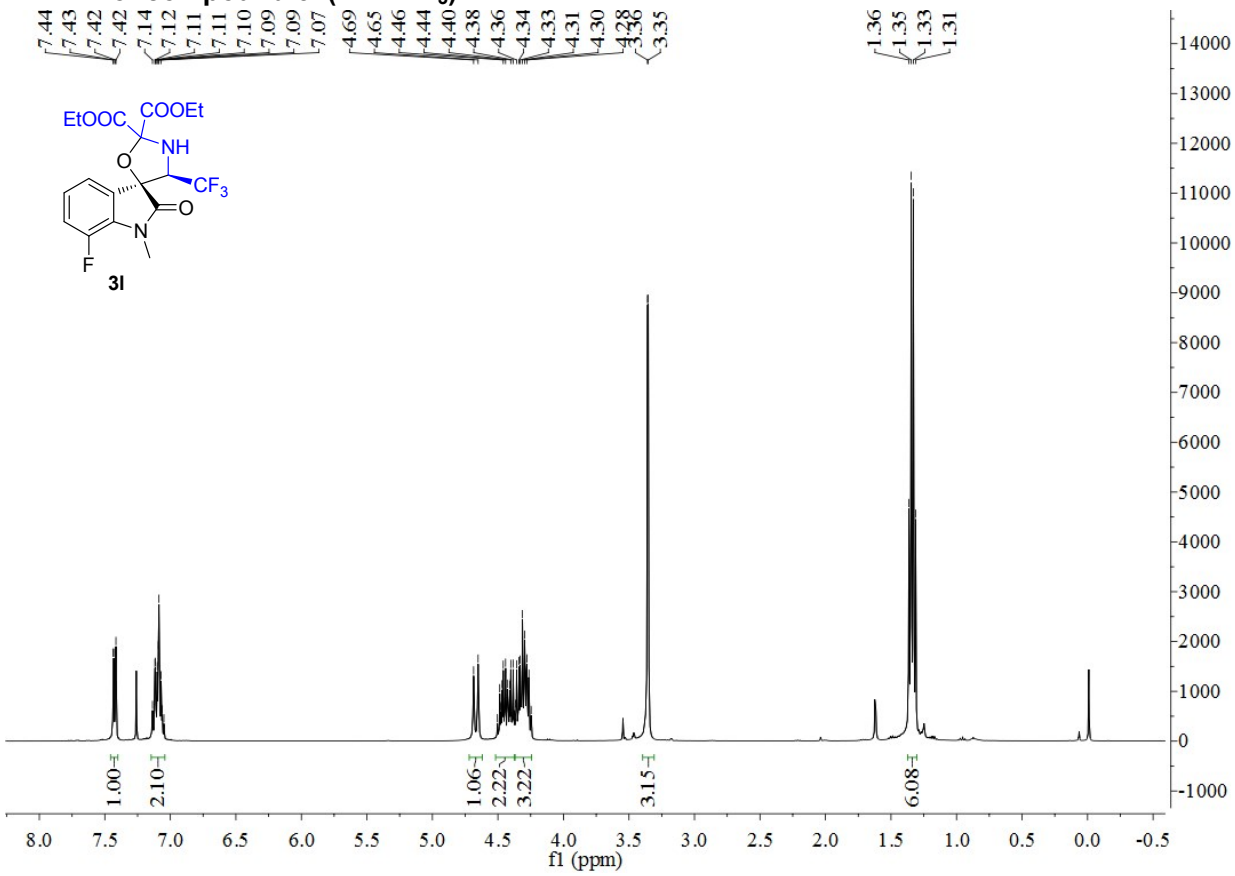
^{13}C NMR of compound 3k (in $CDCl_3$)



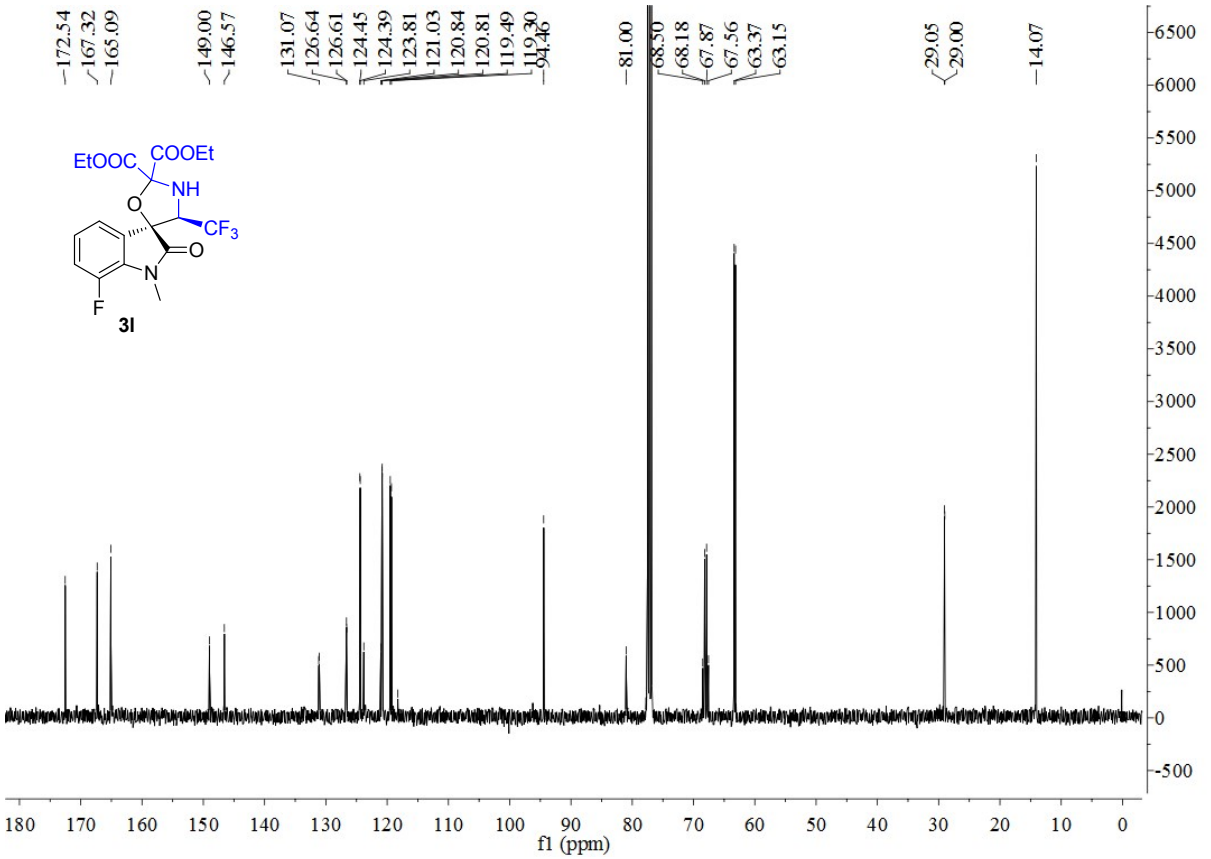
^{19}F NMR of compound 3k (in $CDCl_3$)



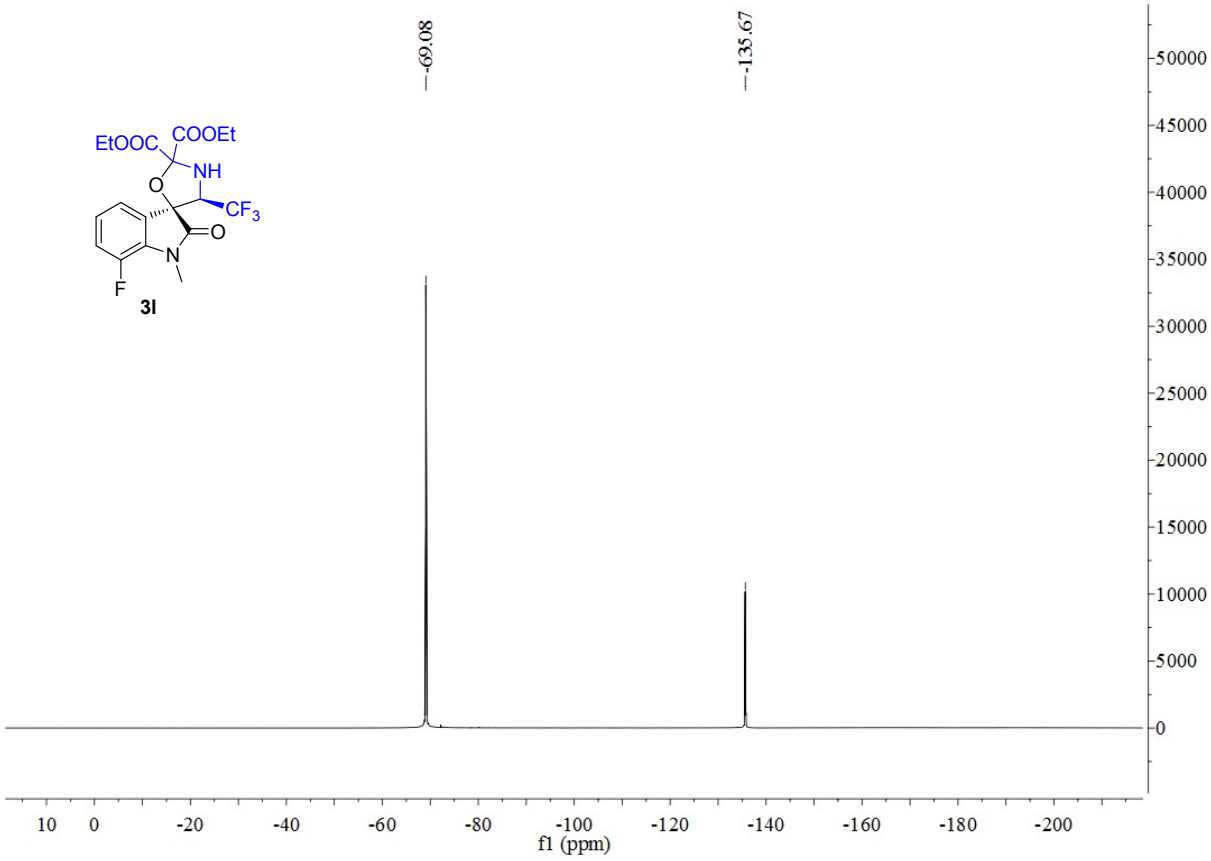
^{1}H NMR of compound 3l (in $CDCl_3$)



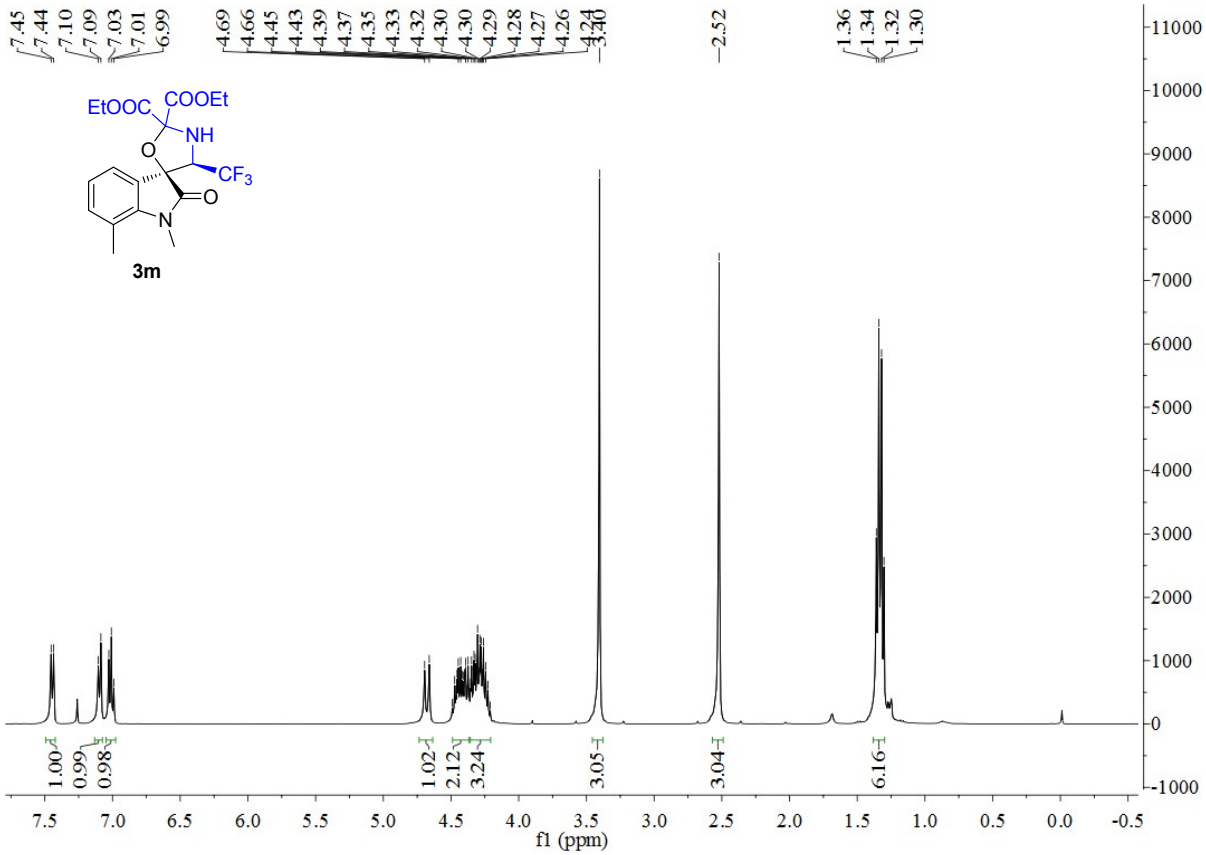
^{13}C NMR of compound 3l (in $CDCl_3$)



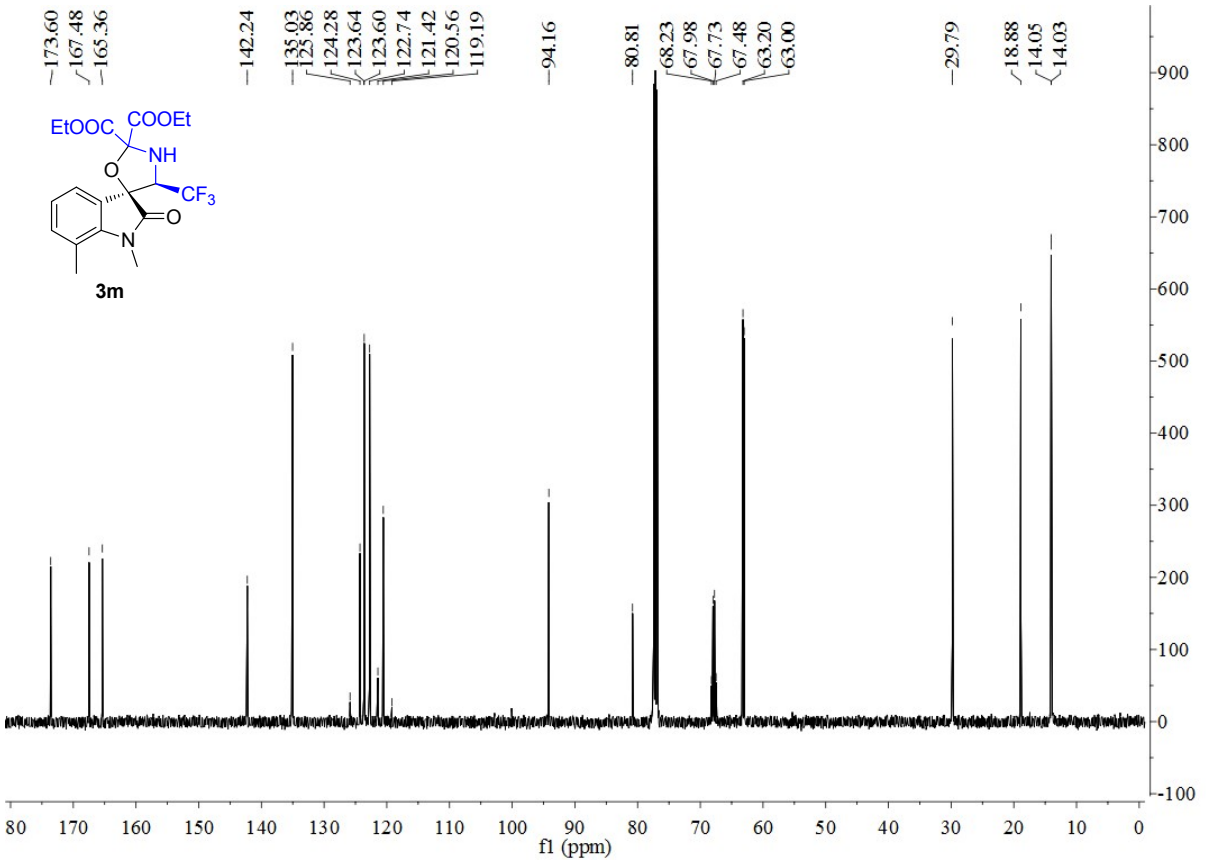
^{19}F NMR of compound 3l (in $CDCl_3$)



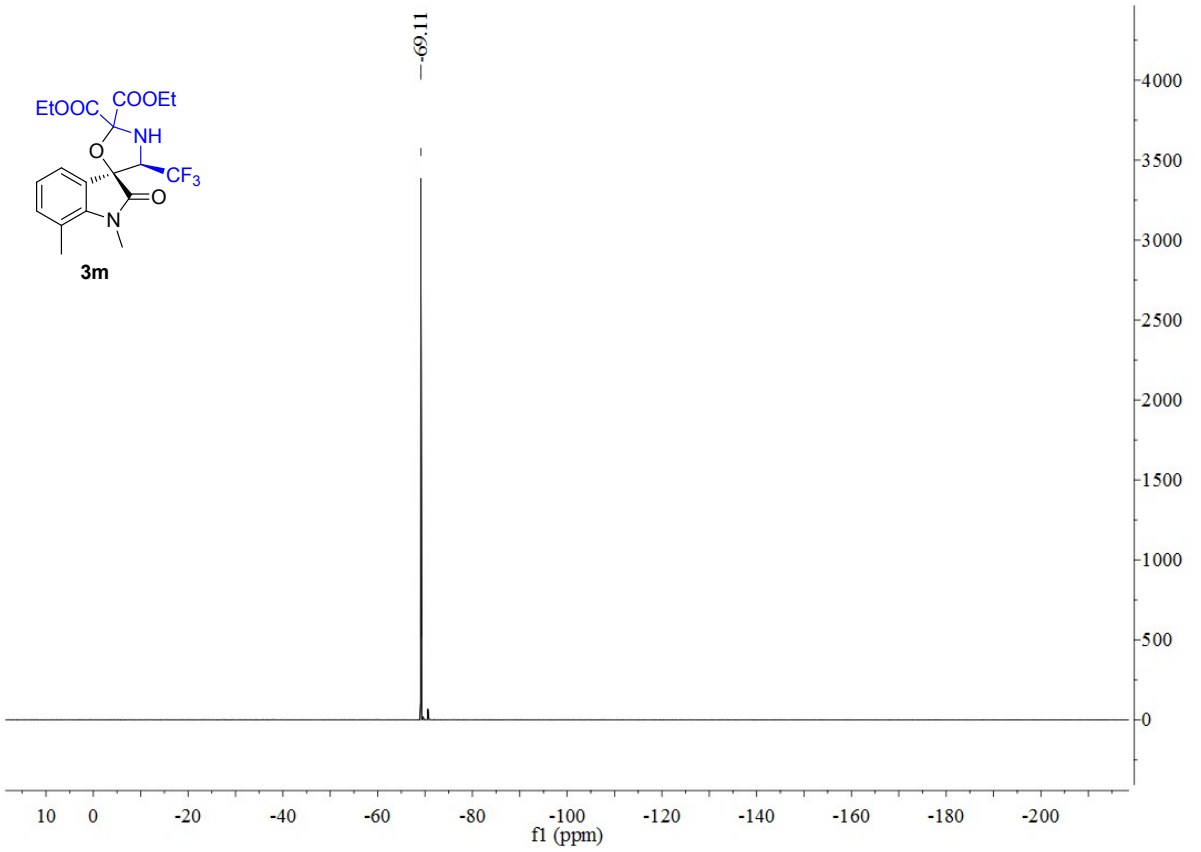
^{1}H NMR of compound 3m (in $CDCl_3$)



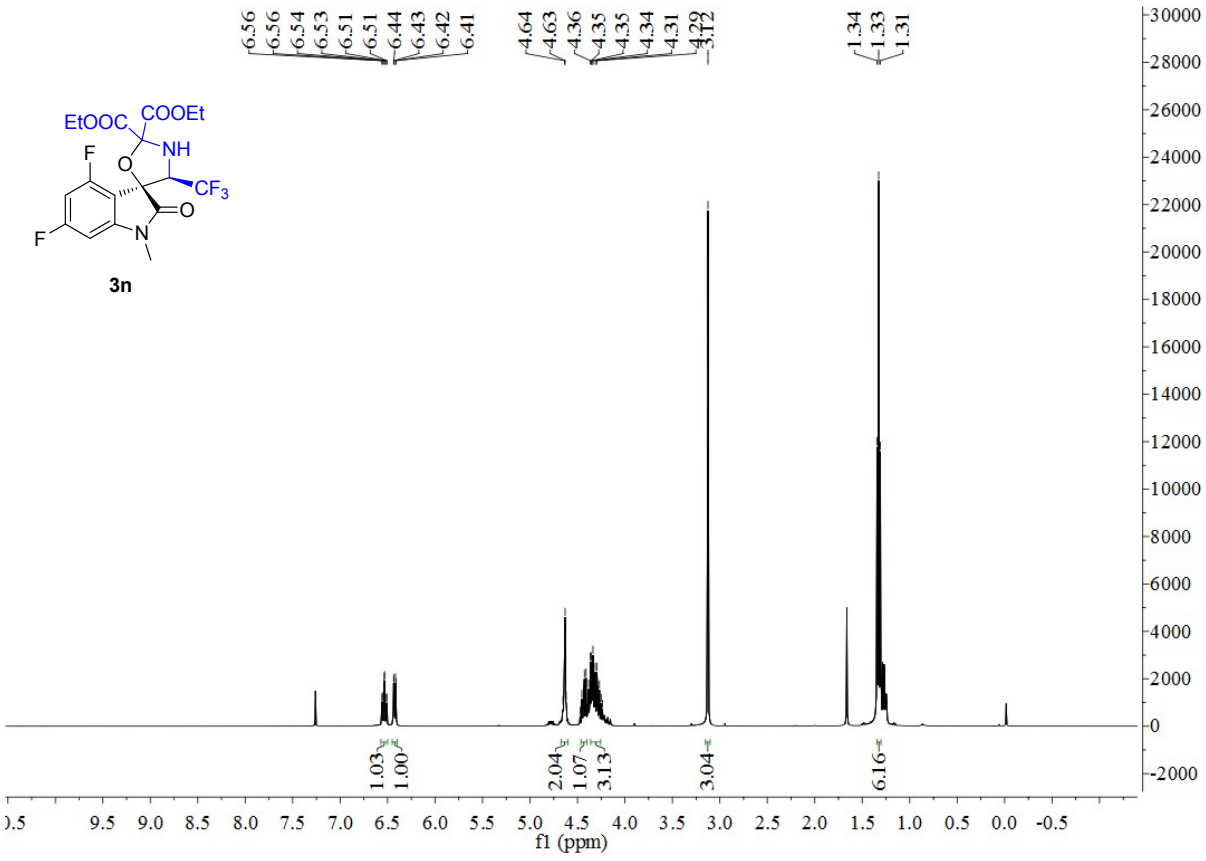
^{13}C NMR of compound 3m (in $CDCl_3$)



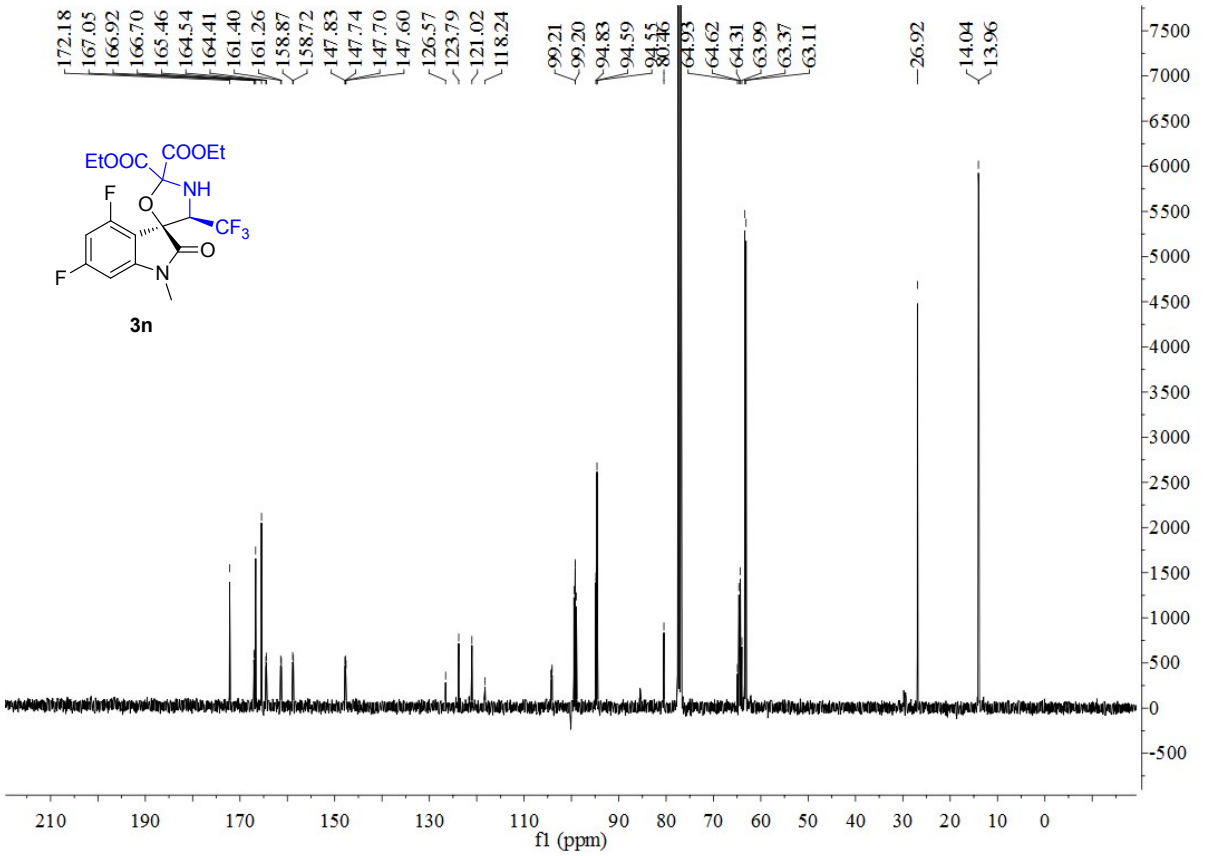
^{19}F NMR of compound 3m (in $CDCl_3$)



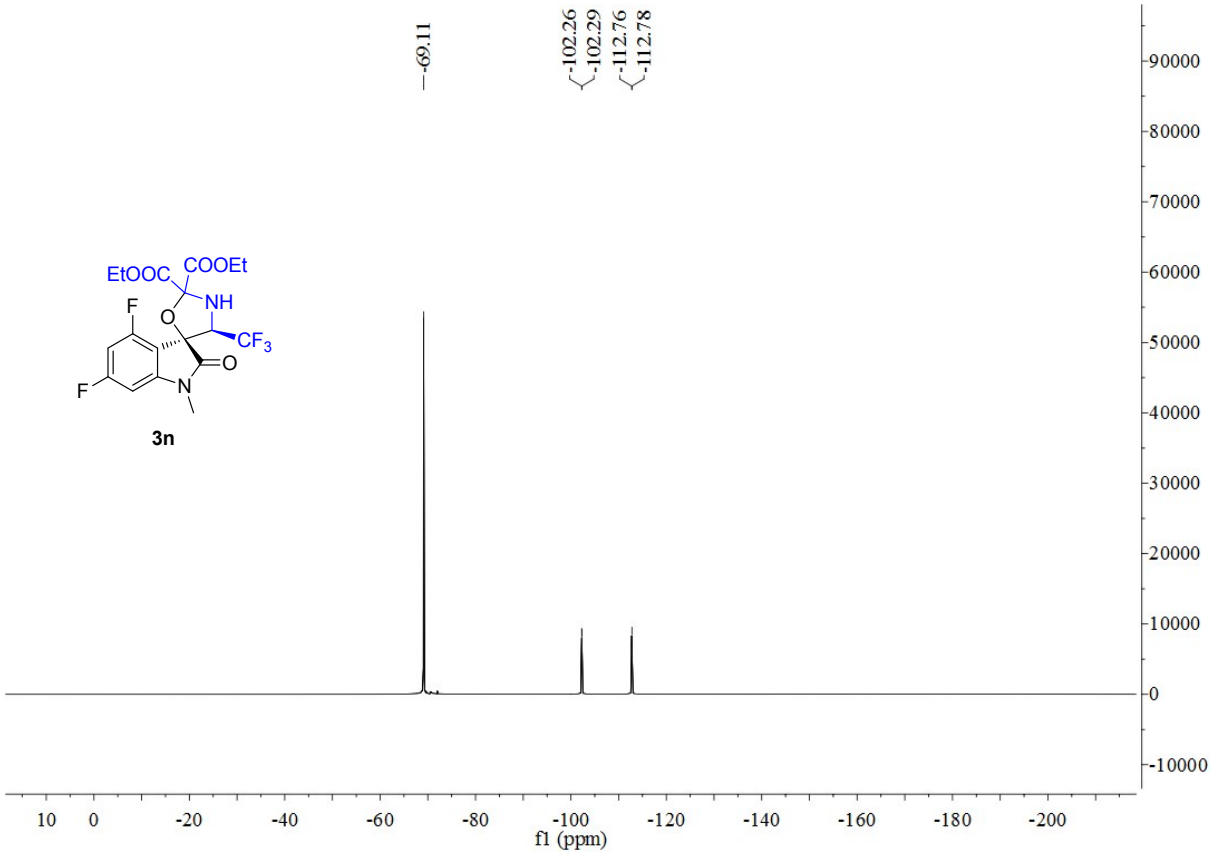
^{1}H NMR of compound 3n (in $CDCl_3$)



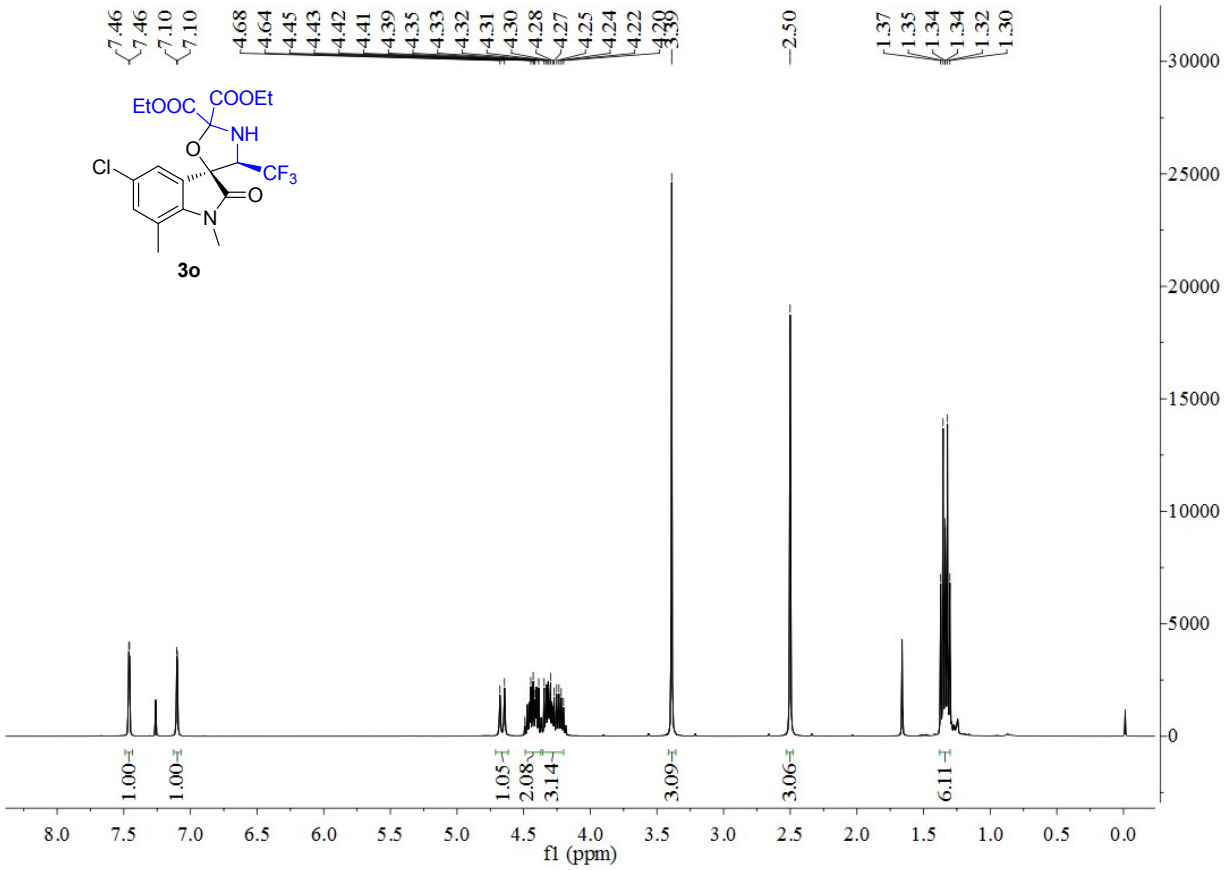
^{13}C NMR of compound 3n (in $CDCl_3$)



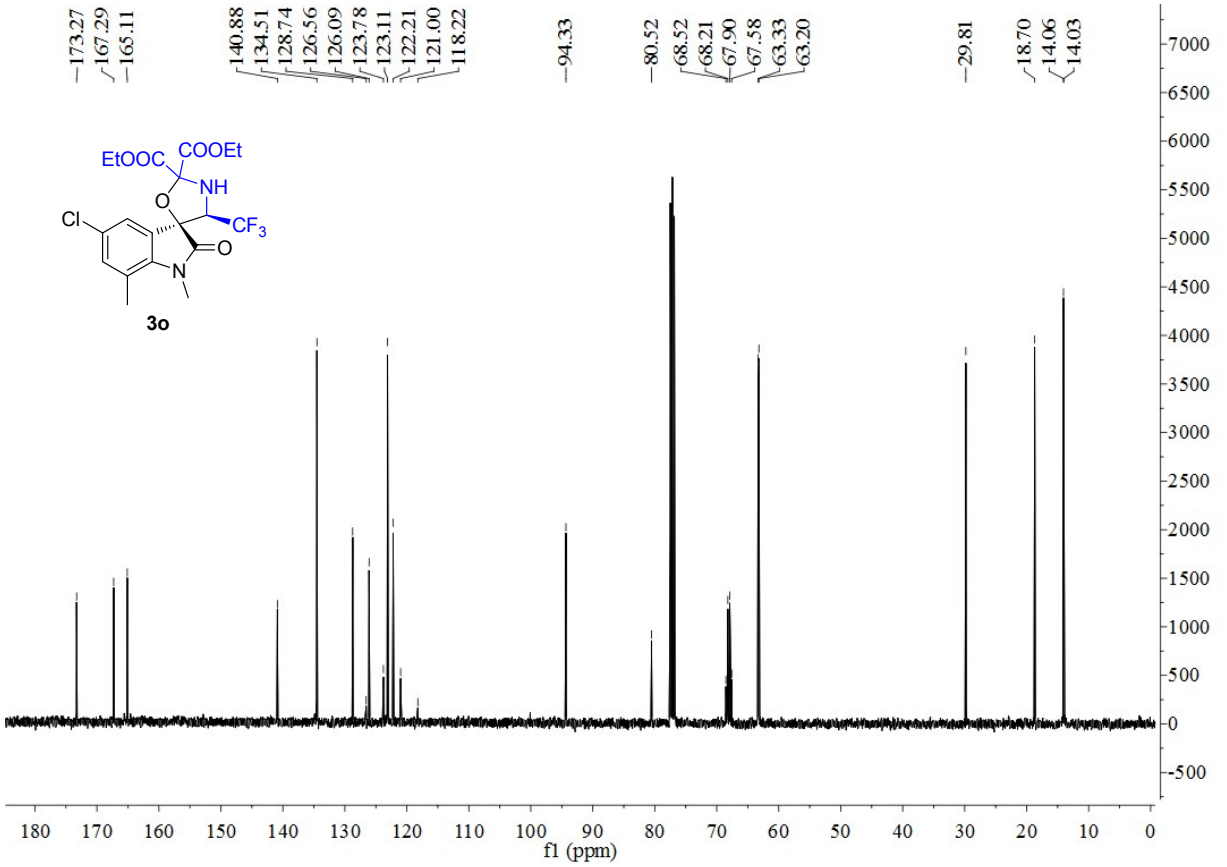
^{19}F NMR of compound 3n (in $CDCl_3$)



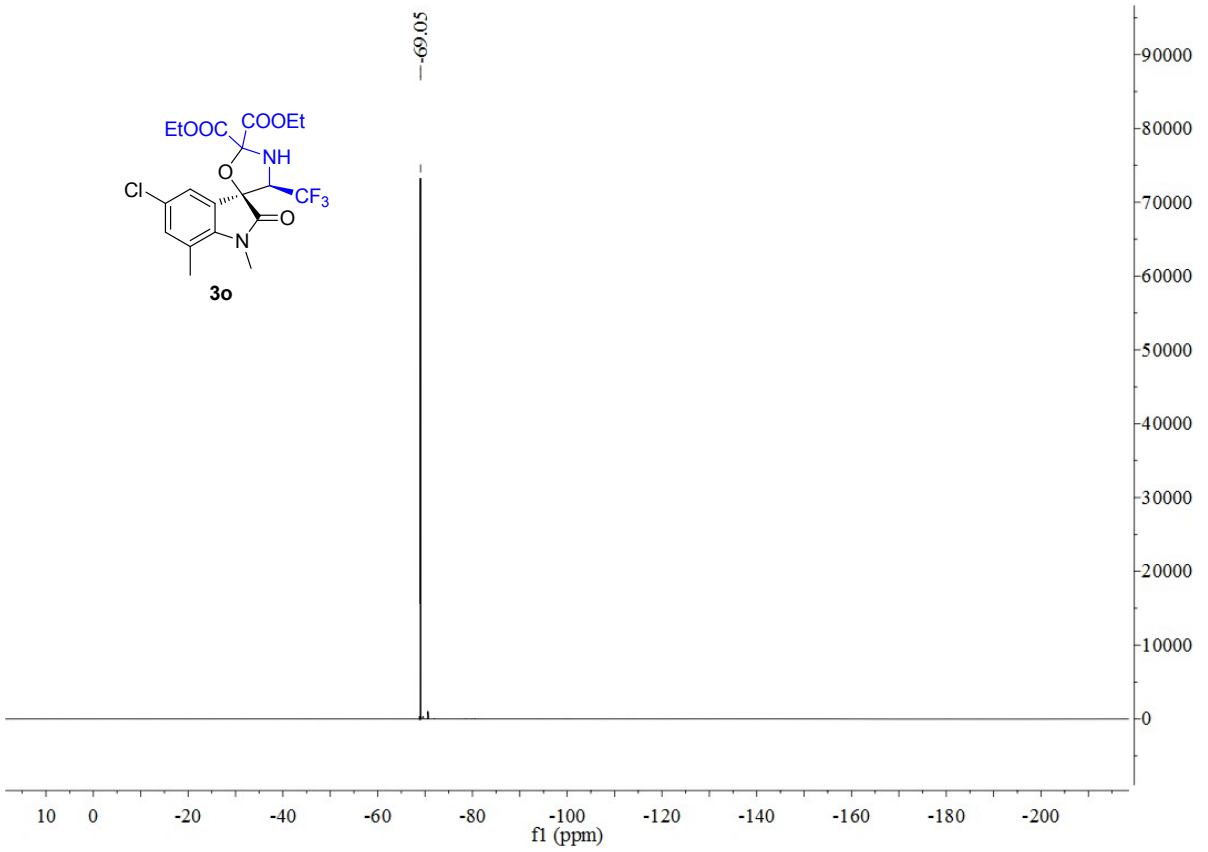
^{1}H NMR of compound 3o (in $CDCl_3$)



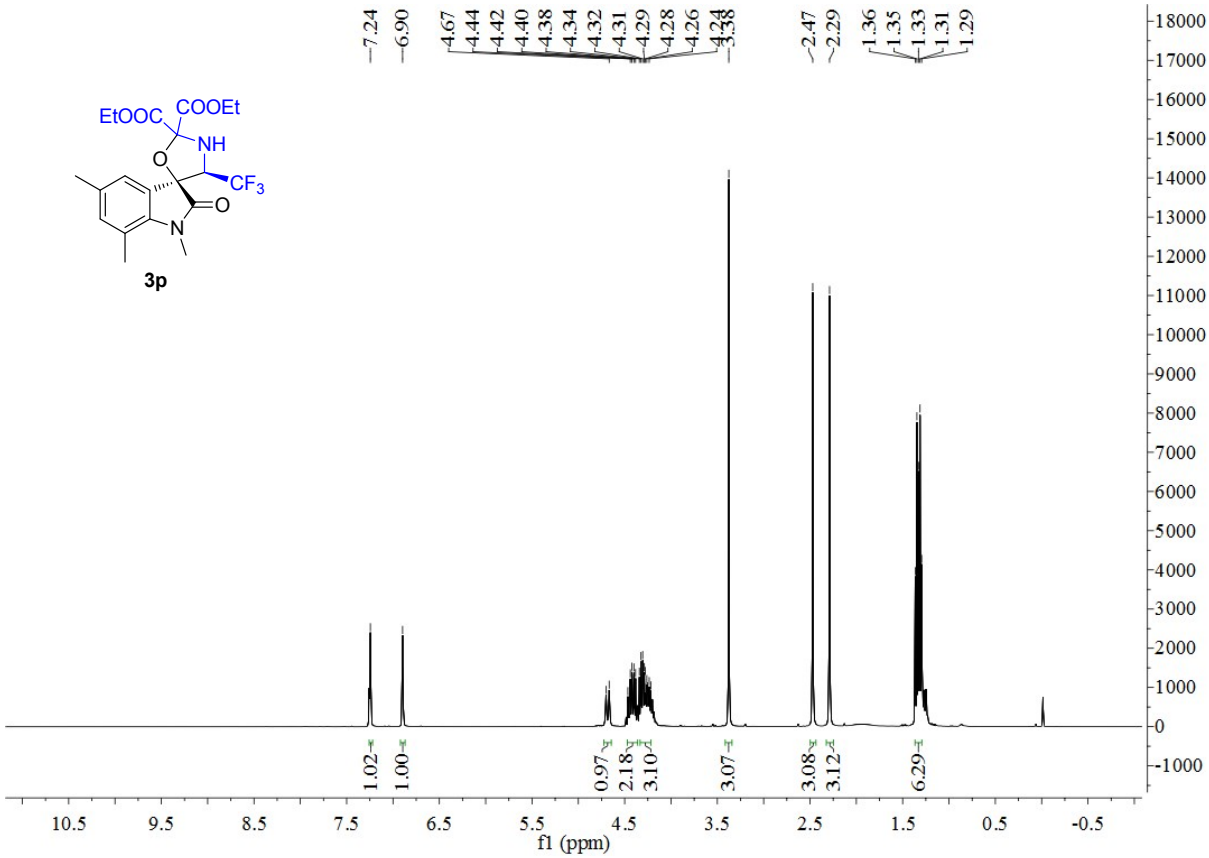
^{13}C NMR of compound 3o (in $CDCl_3$)



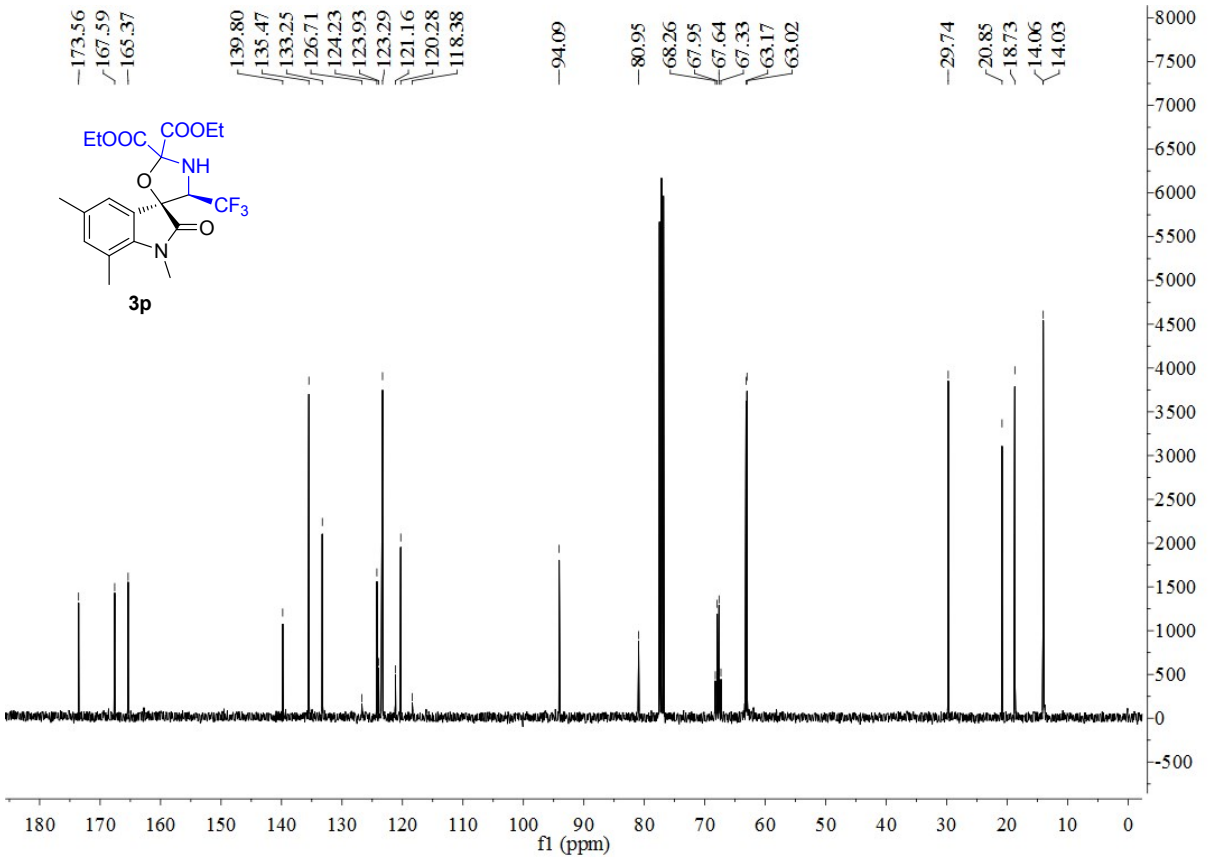
^{19}F NMR of compound 3o (in $CDCl_3$)



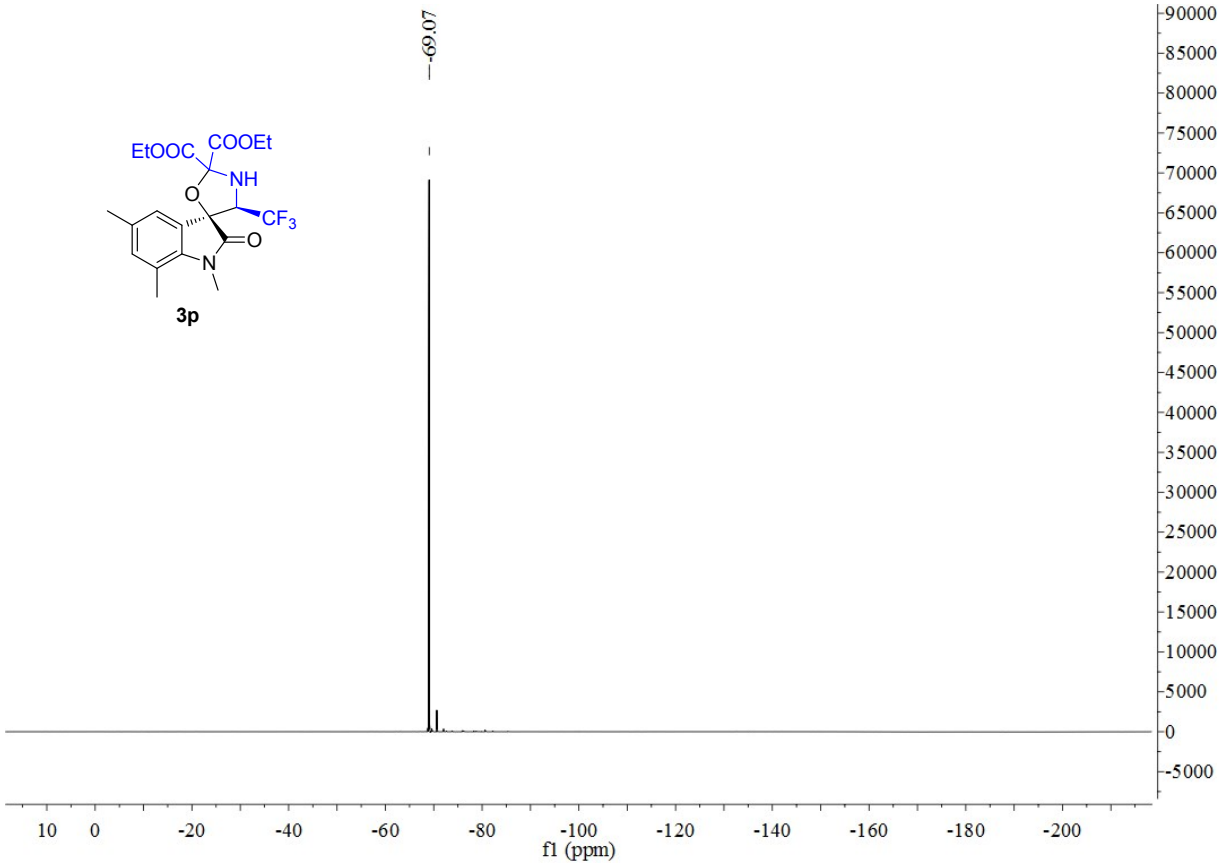
^{1}H NMR of compound 3p (in $CDCl_3$)



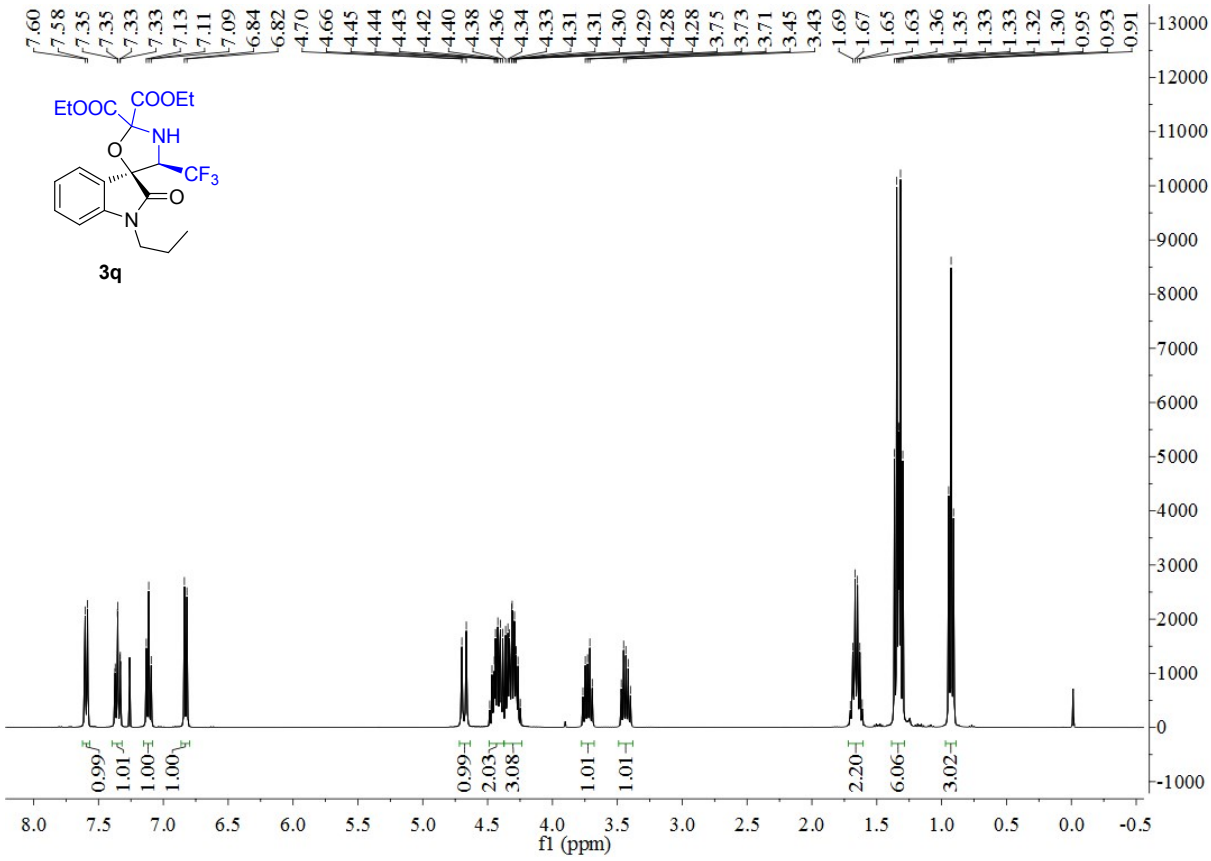
^{13}C NMR of compound 3p (in $CDCl_3$)



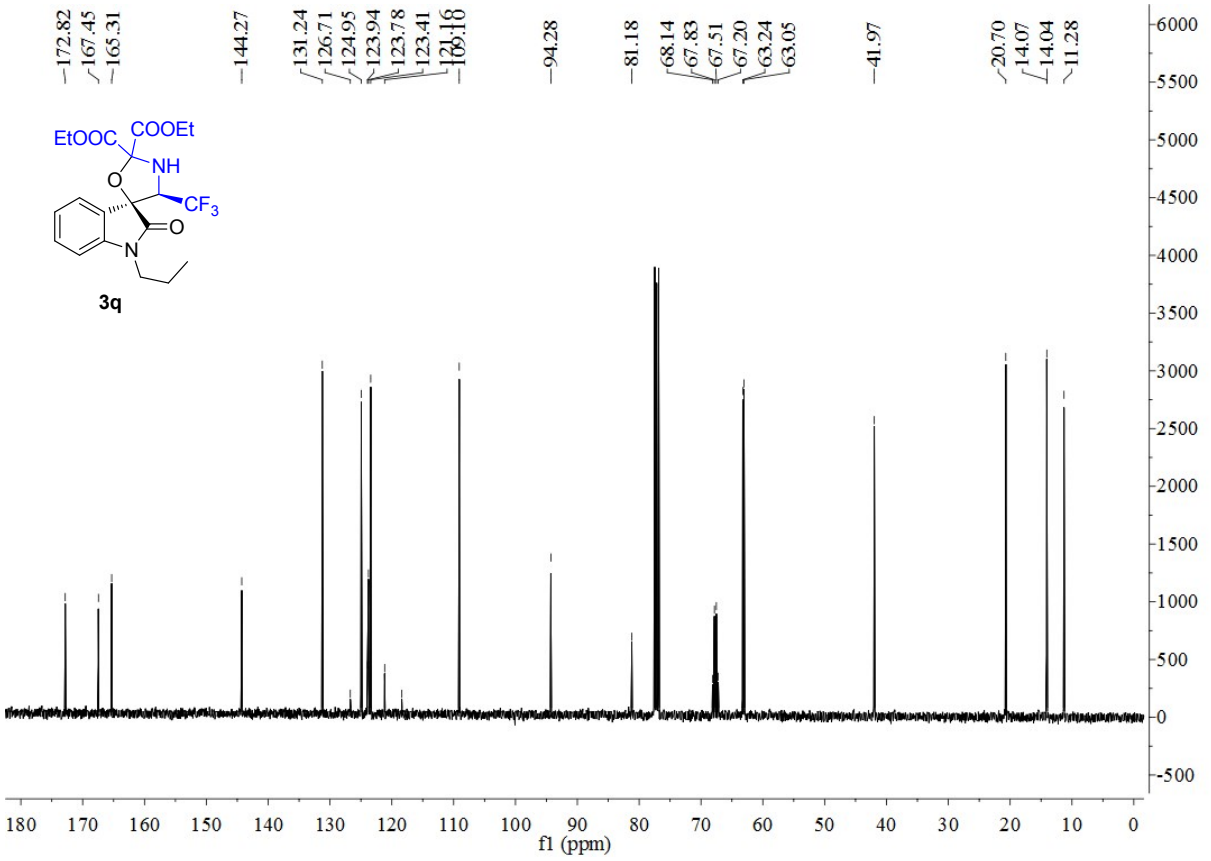
^{19}F NMR of compound 3p (in $CDCl_3$)



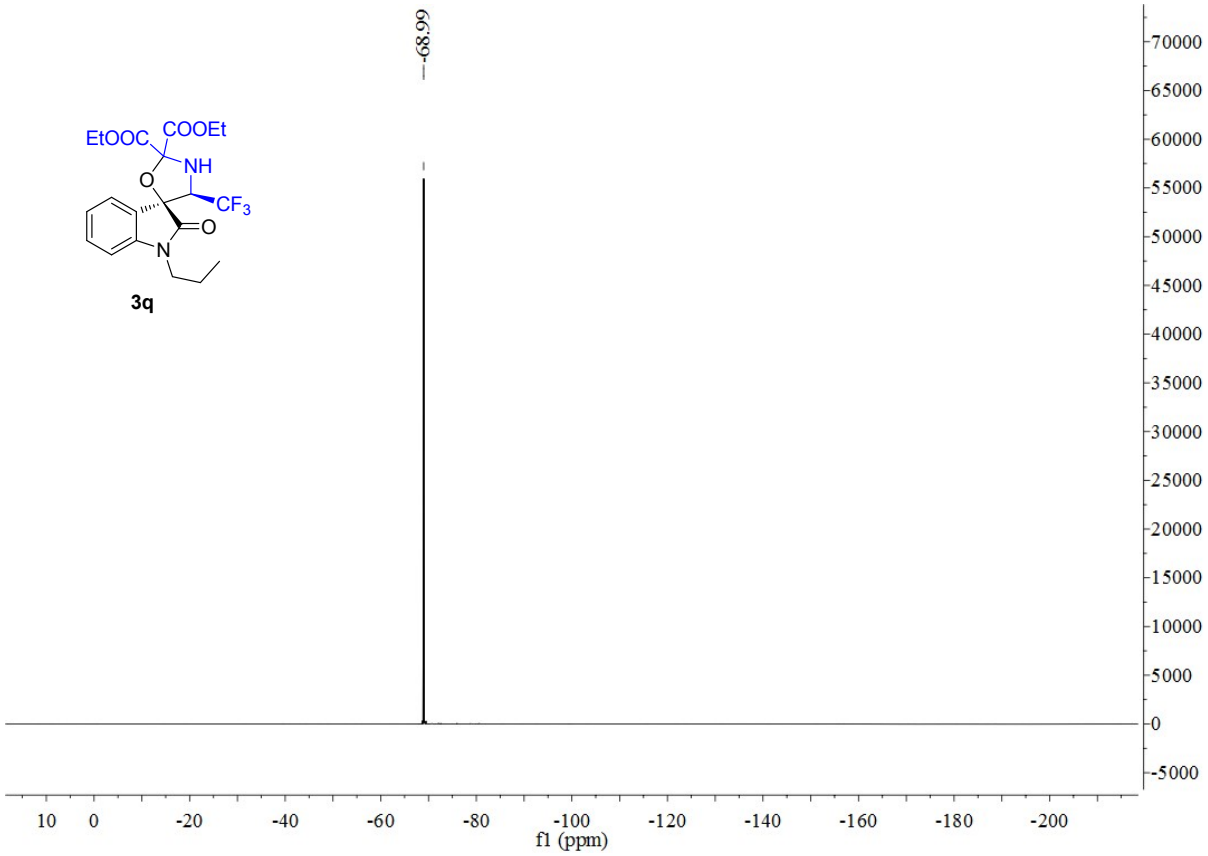
^{1}H NMR of compound 3q (in $CDCl_3$)



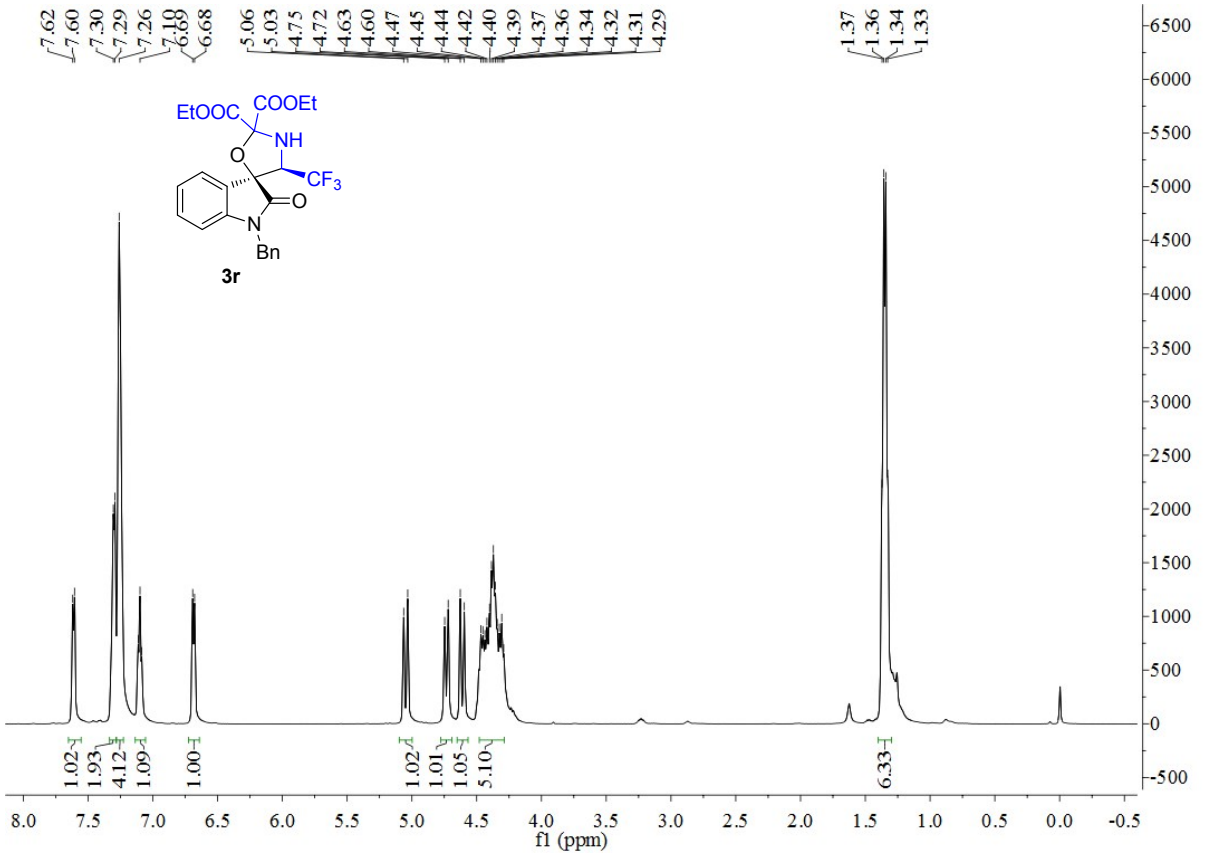
^{13}C NMR of compound 3q (in $CDCl_3$)



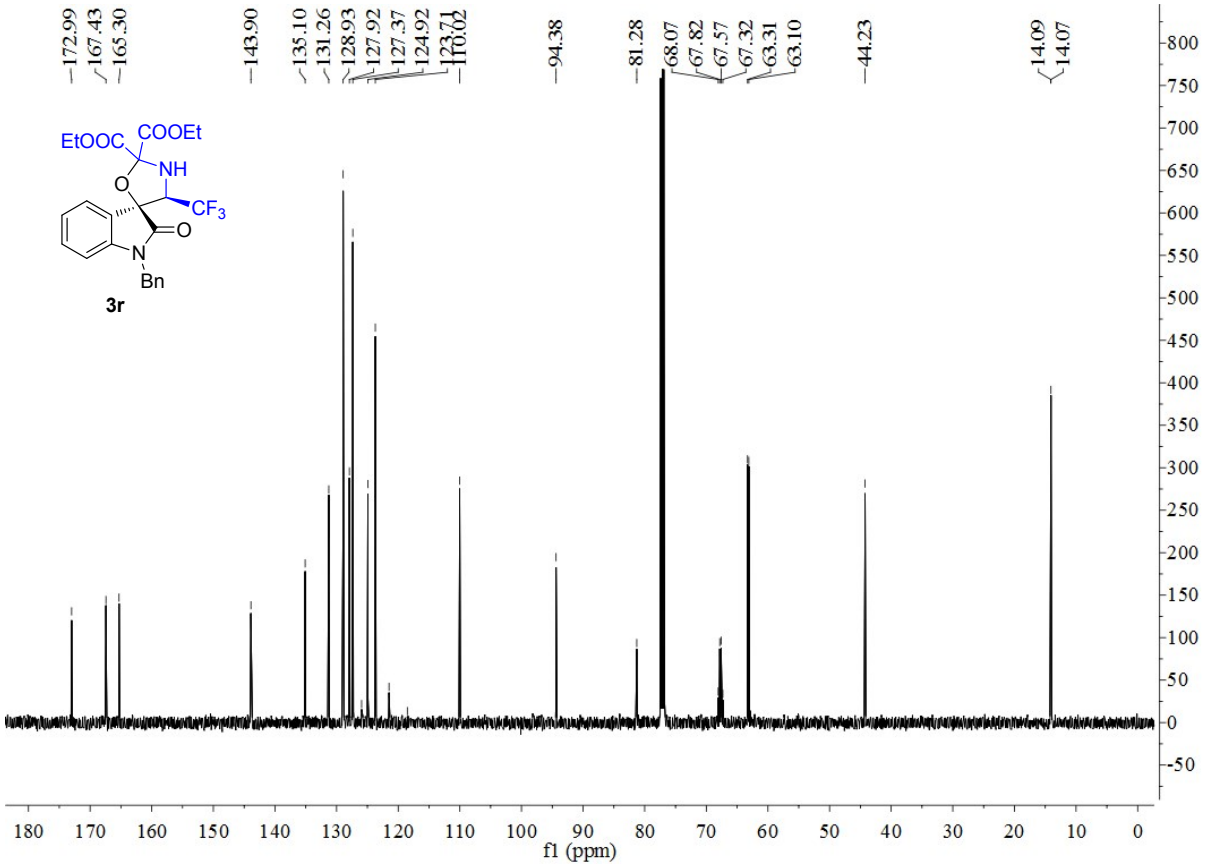
^{19}F NMR of compound 3q (in $CDCl_3$)



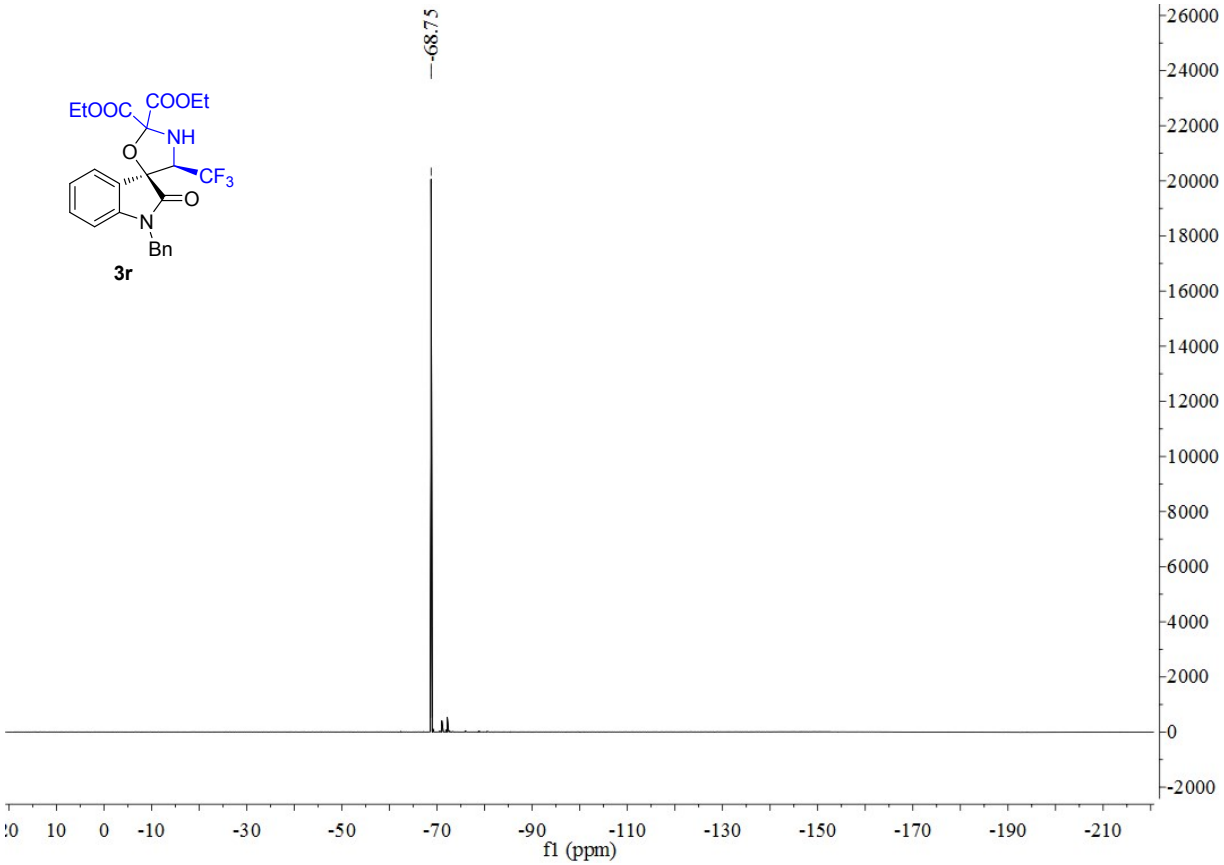
^{1}H NMR of compound 3r (in $CDCl_3$)



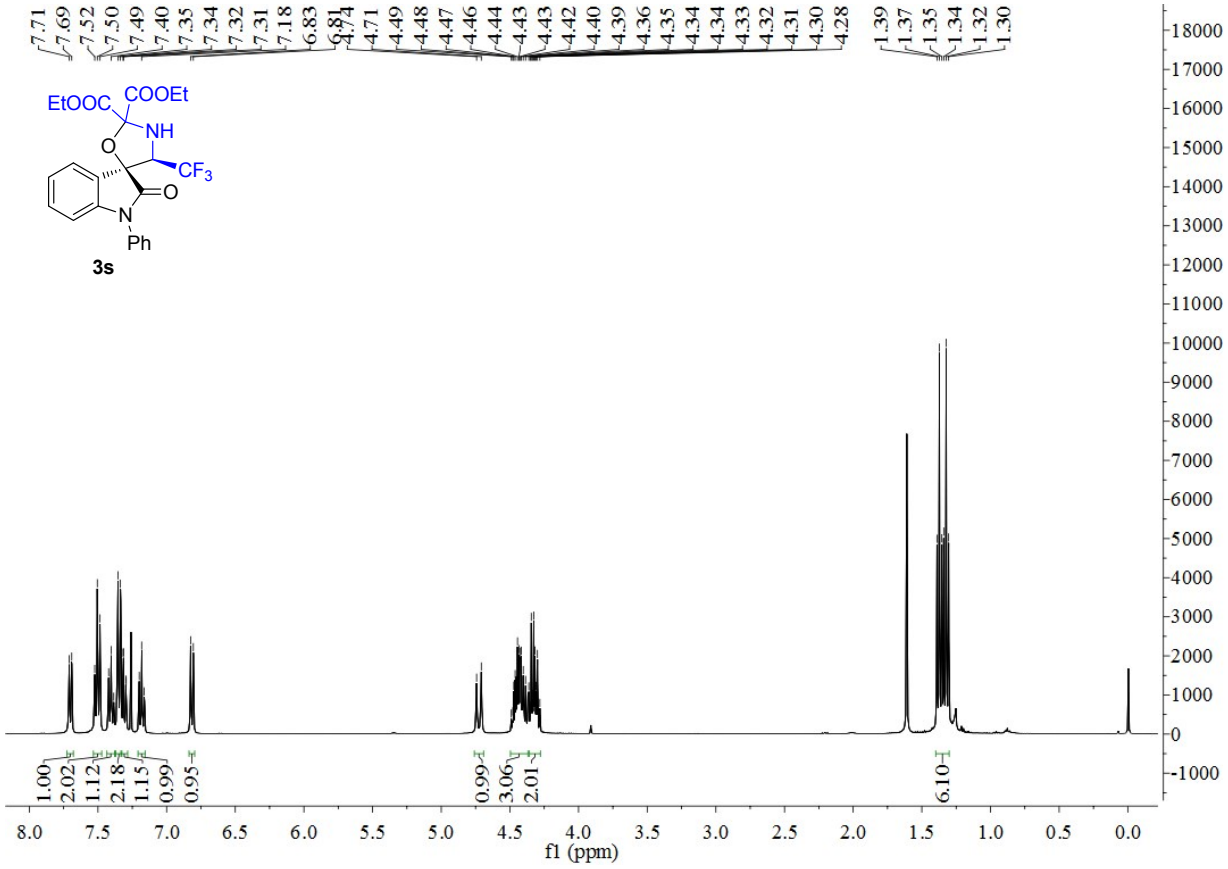
^{13}C NMR of compound 3r (in $CDCl_3$)



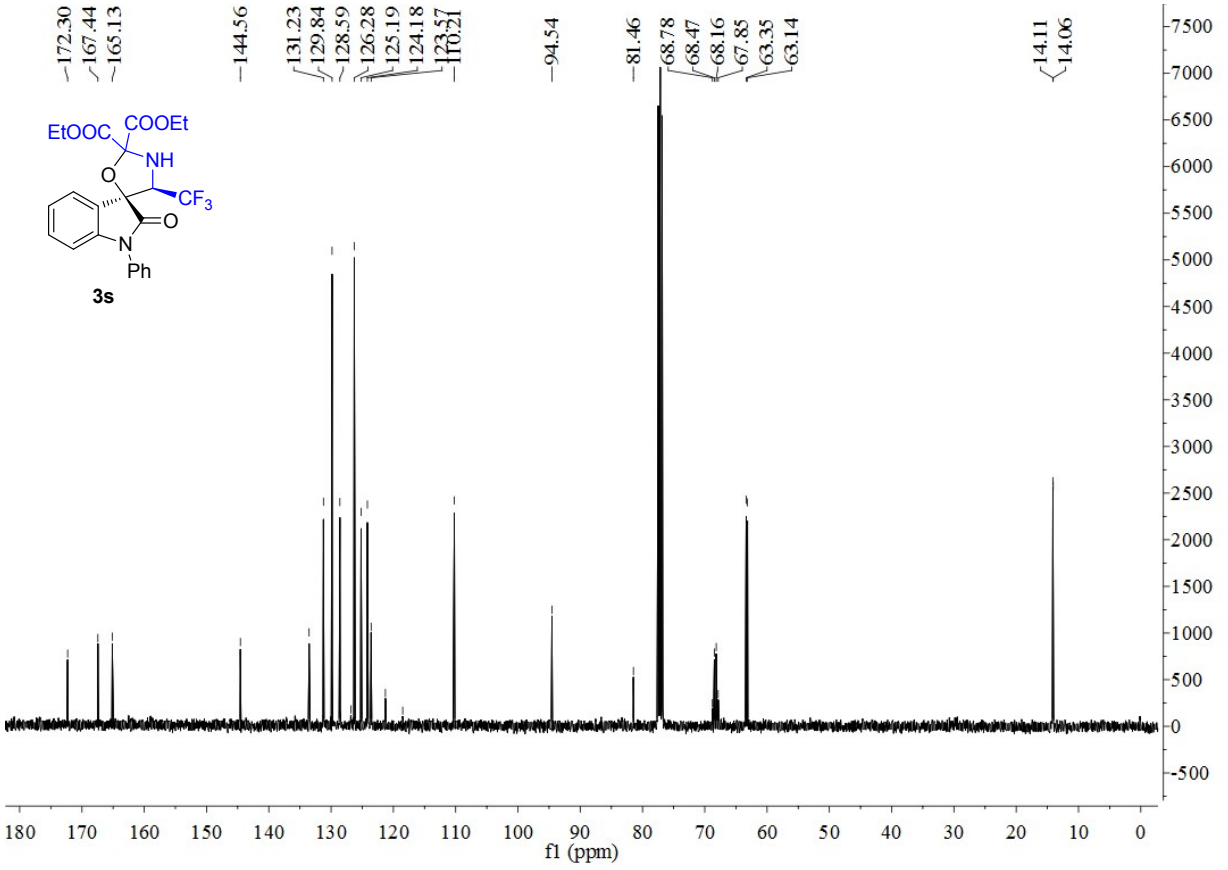
^{19}F NMR of compound 3r (in $CDCl_3$)



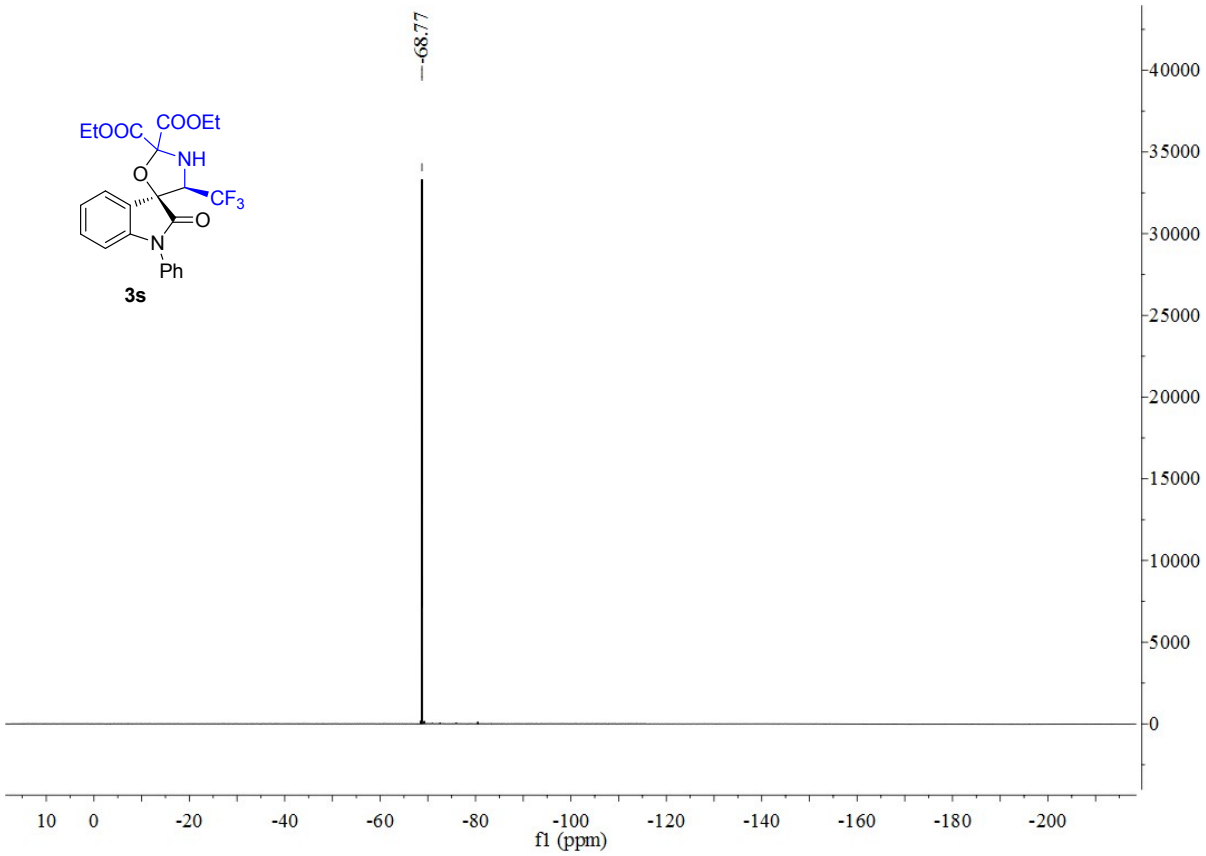
^{1}H NMR of compound 3s (in $CDCl_3$)



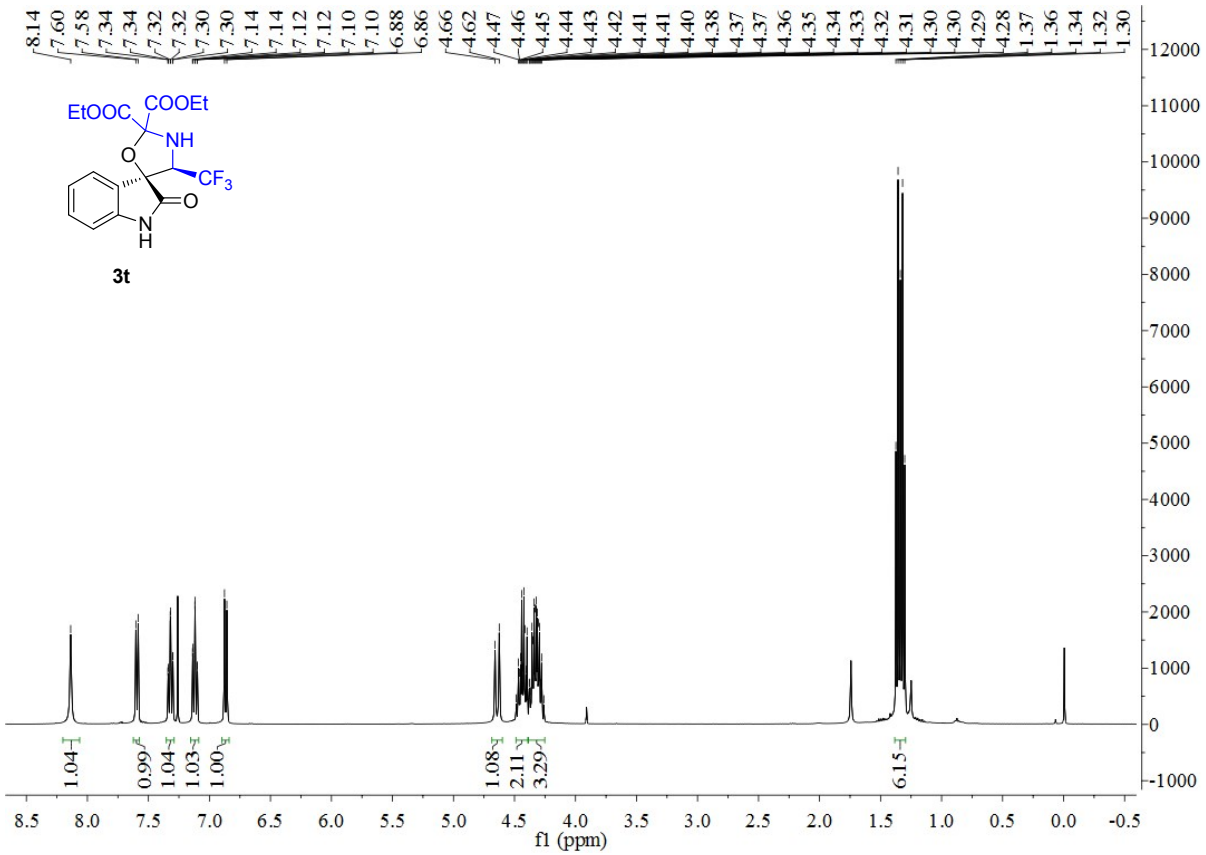
^{13}C NMR of compound 3s (in $CDCl_3$)



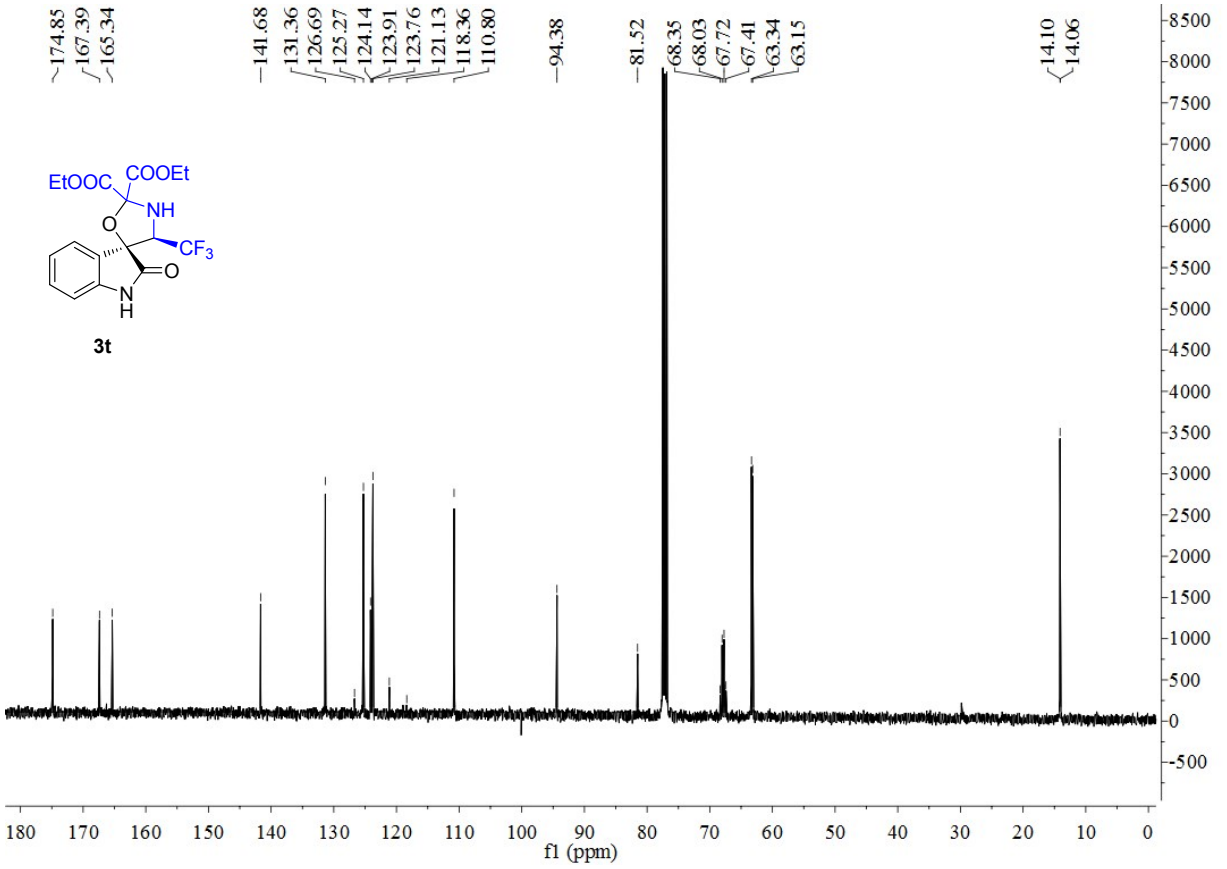
^{19}F NMR of compound 3s (in $CDCl_3$)



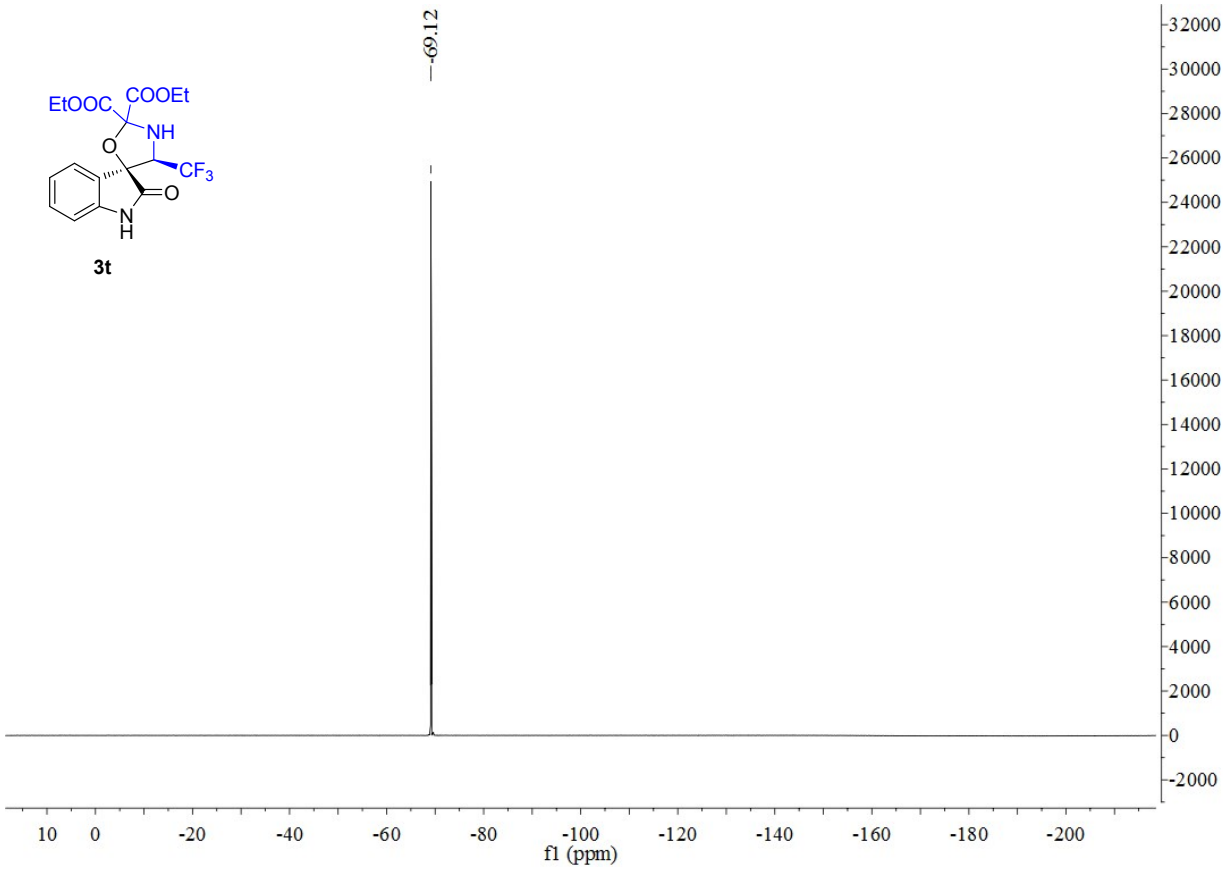
^{1}H NMR of compound 3t (in $CDCl_3$)



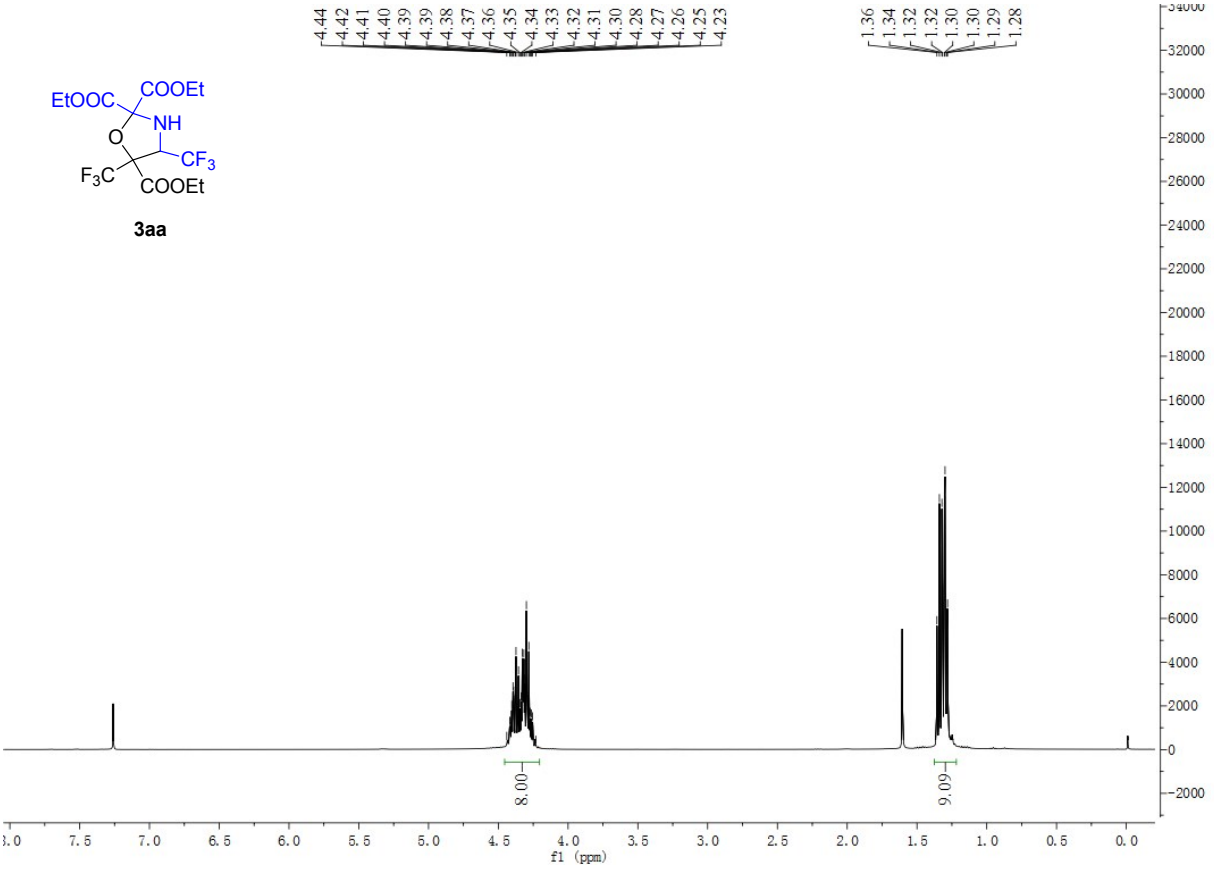
^{13}C NMR of compound 3t (in $CDCl_3$)



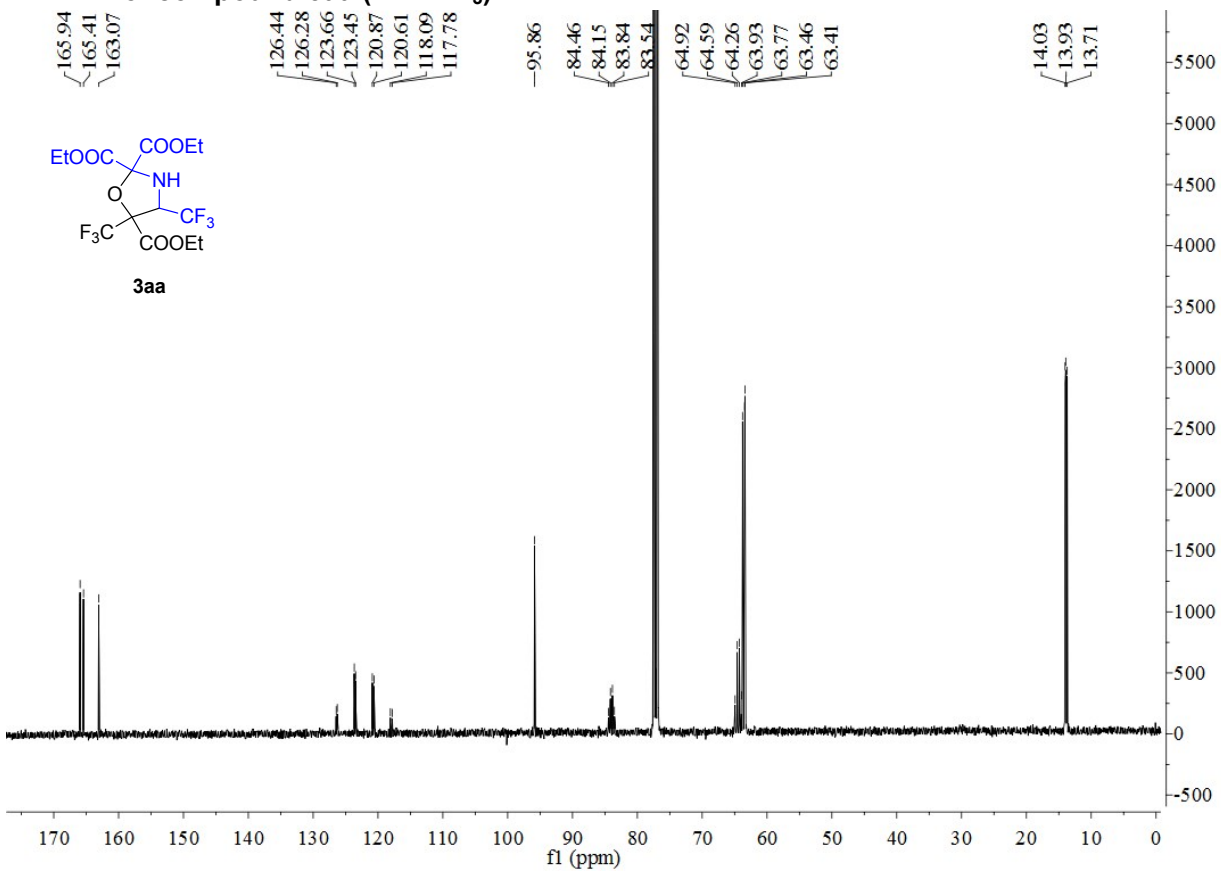
^{19}F NMR of compound 3t (in $CDCl_3$)



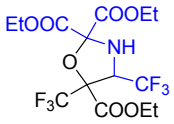
^{1}H NMR of compound 3aa (in $CDCl_3$)



^{13}C NMR of compound 3aa (in $CDCl_3$)

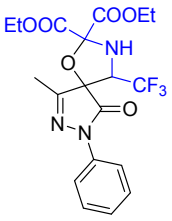


^{19}F NMR of compound 3aa (in $CDCl_3$)



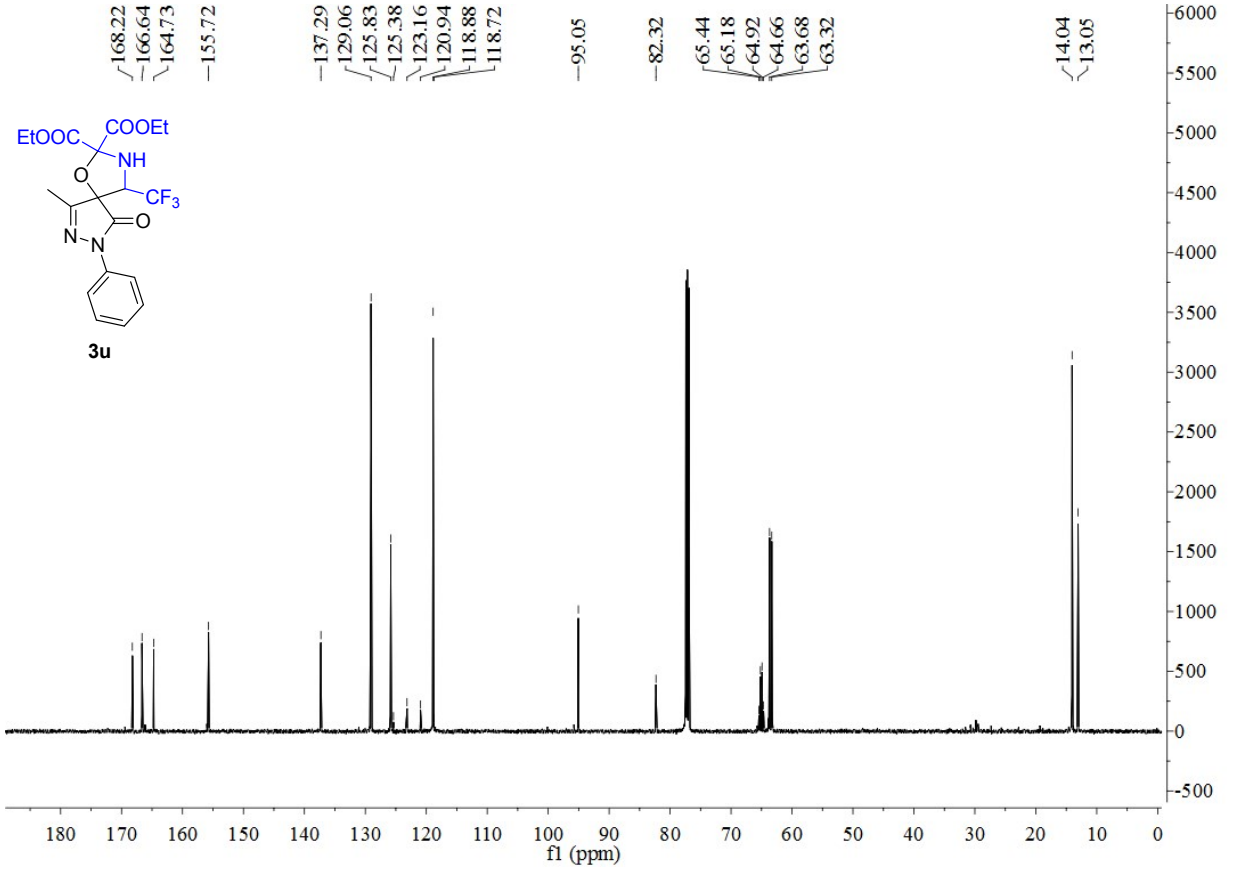
3aa

^{1}H NMR of compound 3u (in $CDCl_3$)

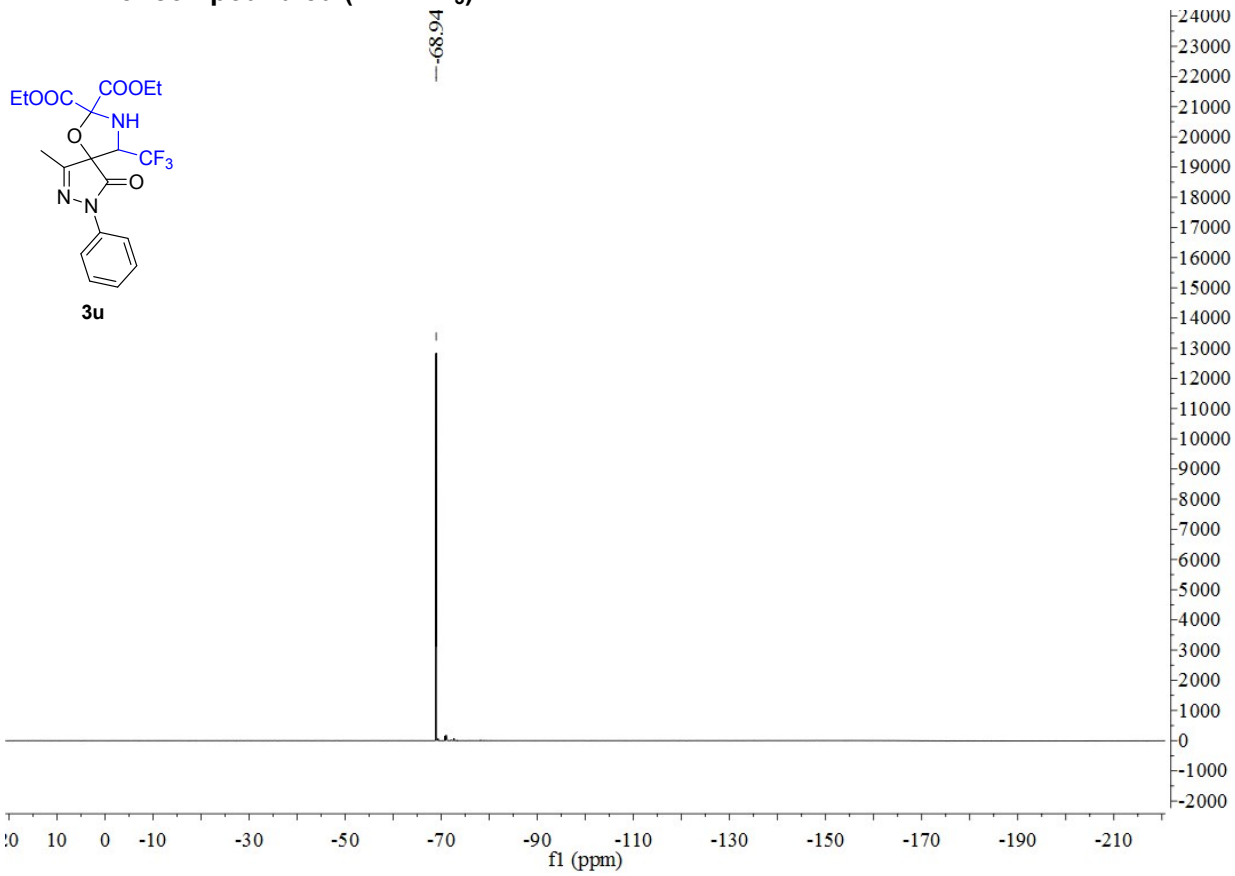


3u

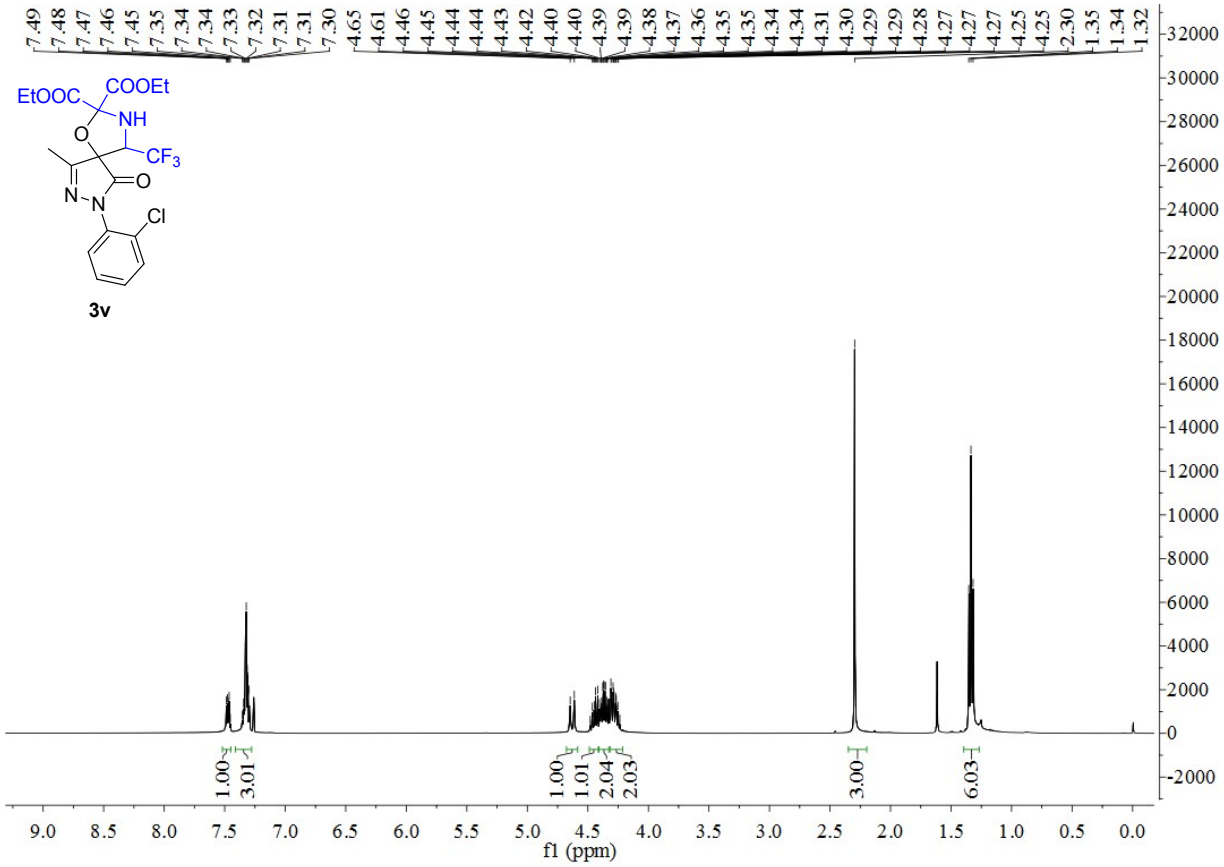
^{13}C NMR of compound 3u (in $CDCl_3$)



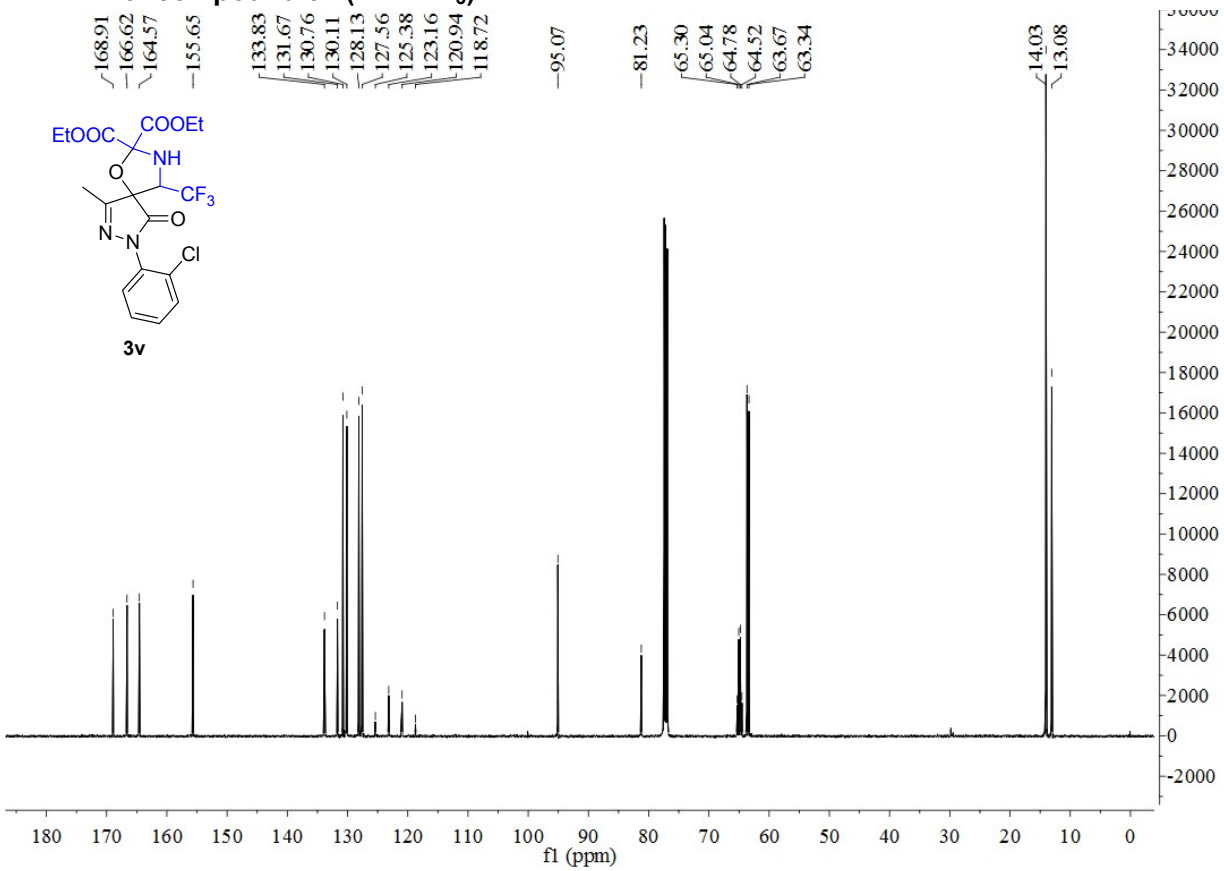
^{19}F NMR of compound 3u (in $CDCl_3$)



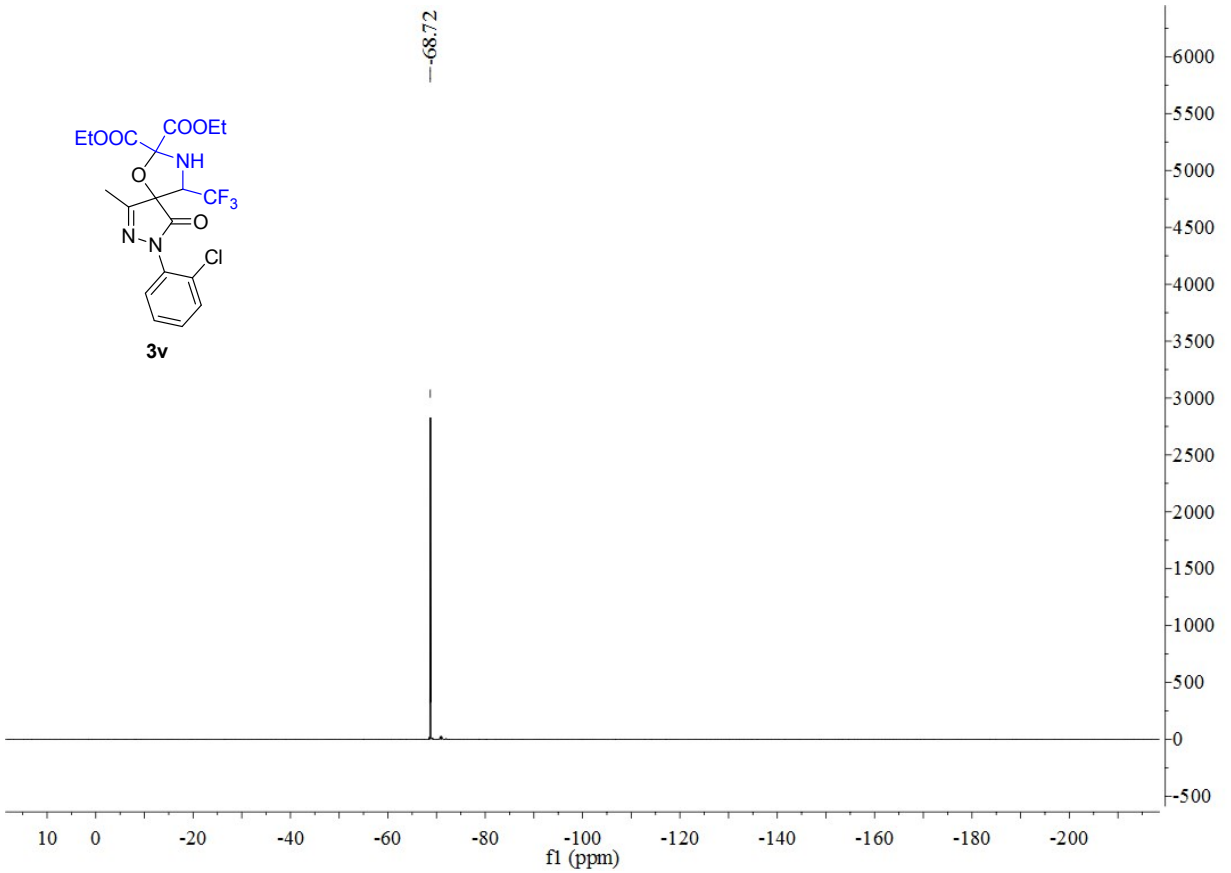
^{1}H NMR of compound 3v (in $CDCl_3$)



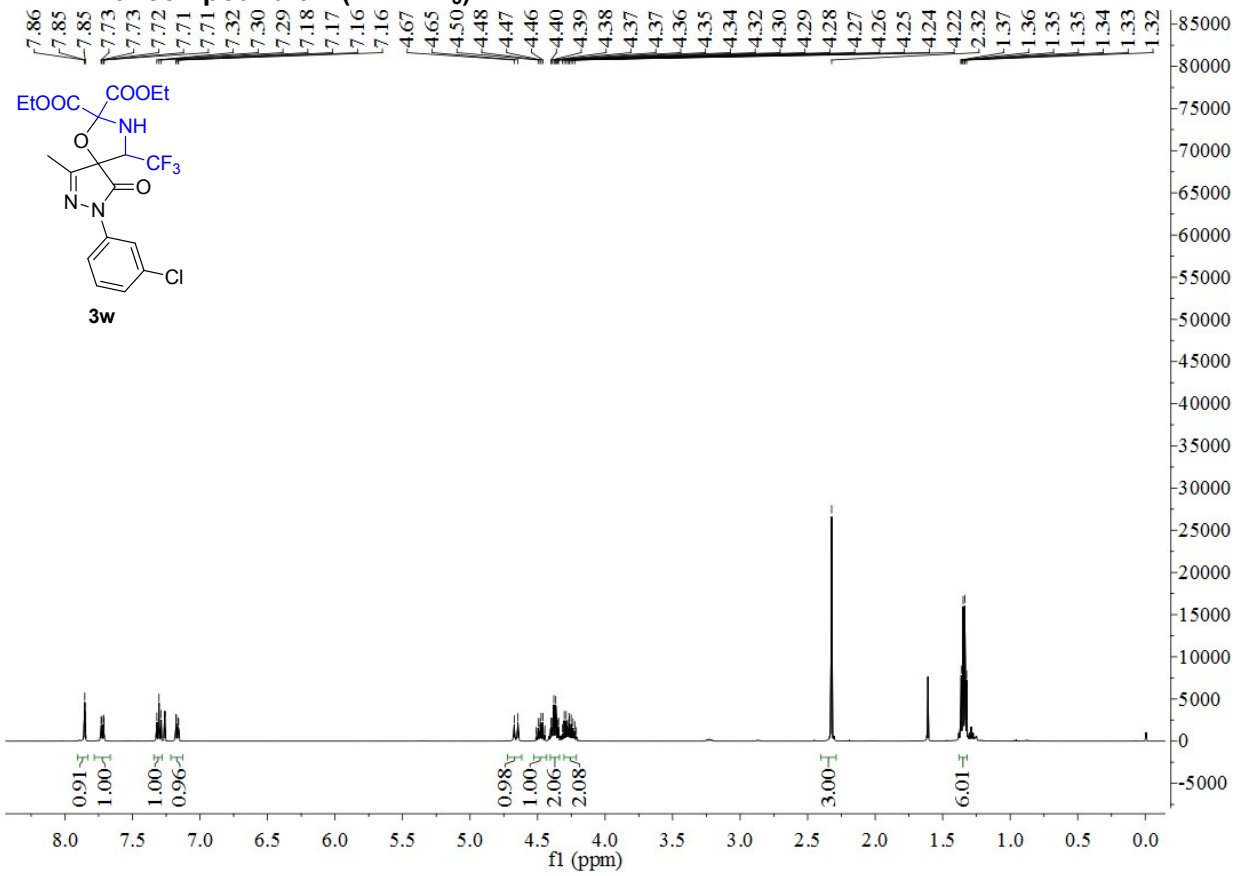
^{13}C NMR of compound 3v (in $CDCl_3$)



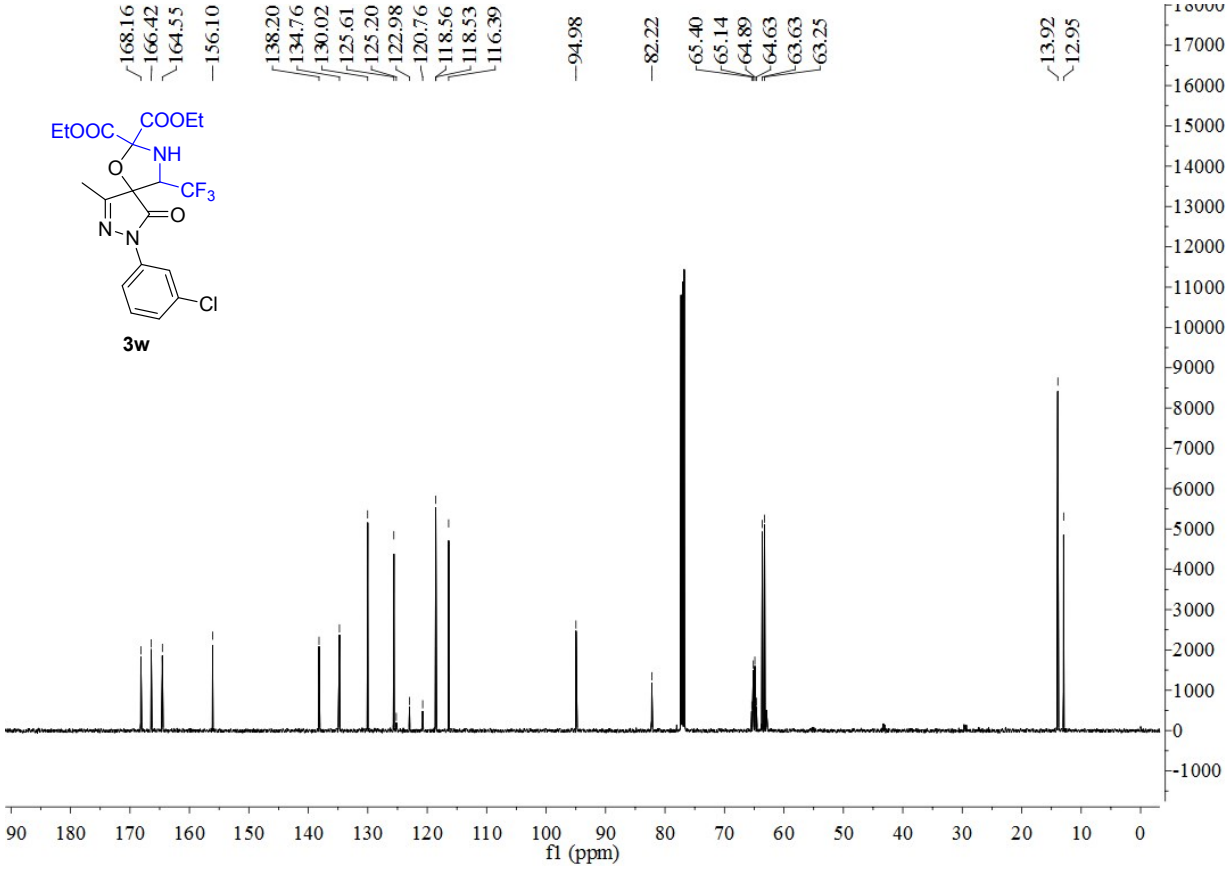
^{19}F NMR of compound 3v (in $CDCl_3$)



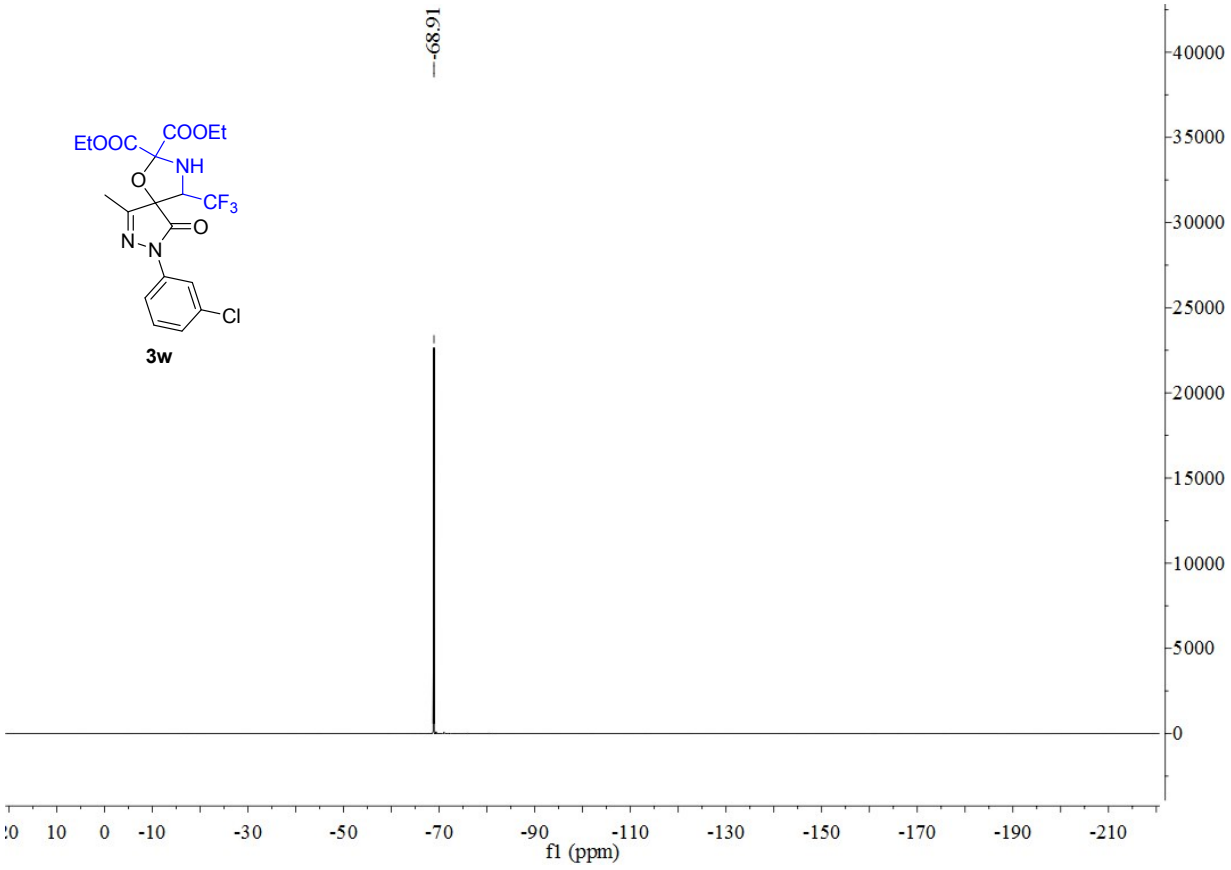
^{1}H NMR of compound 3w (in $CDCl_3$)



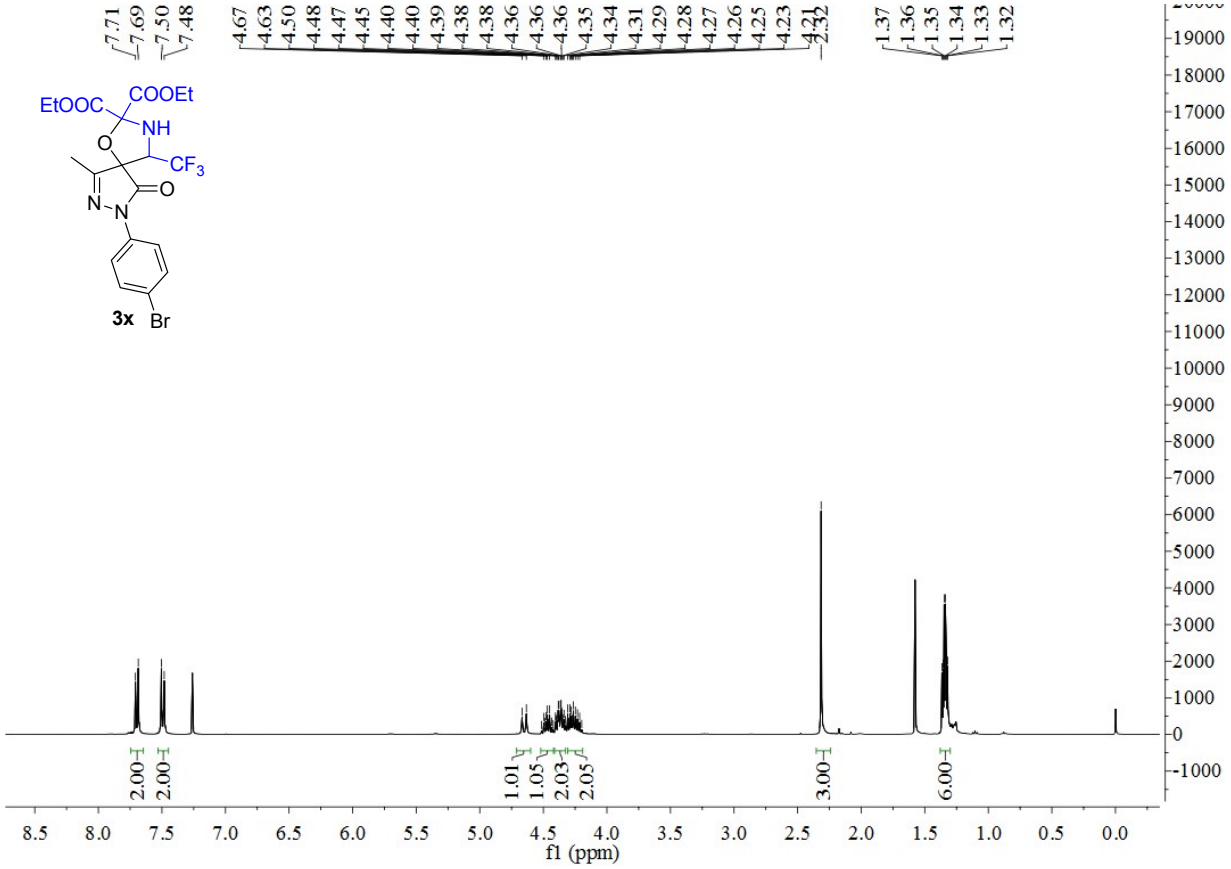
^{13}C NMR of compound 3w (in $CDCl_3$)



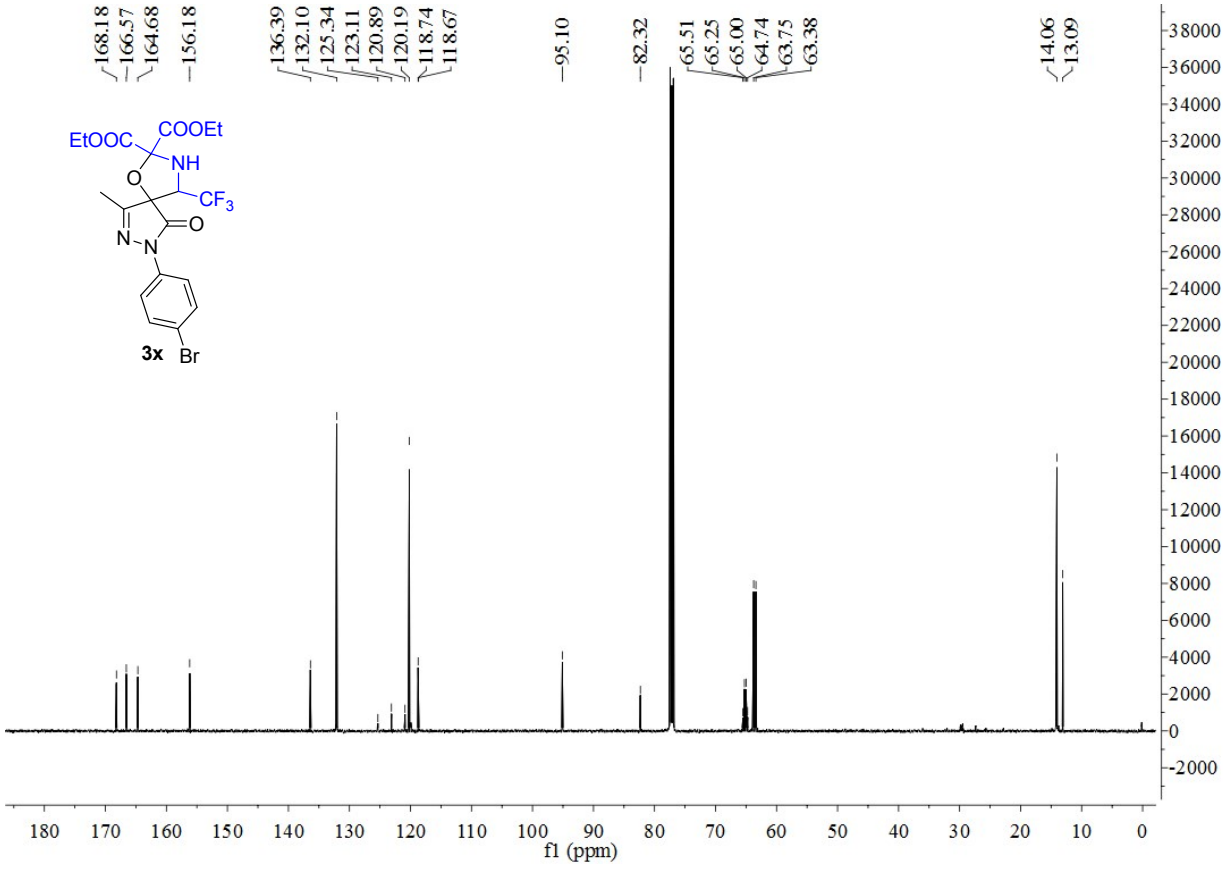
^{19}F NMR of compound 3w (in $CDCl_3$)



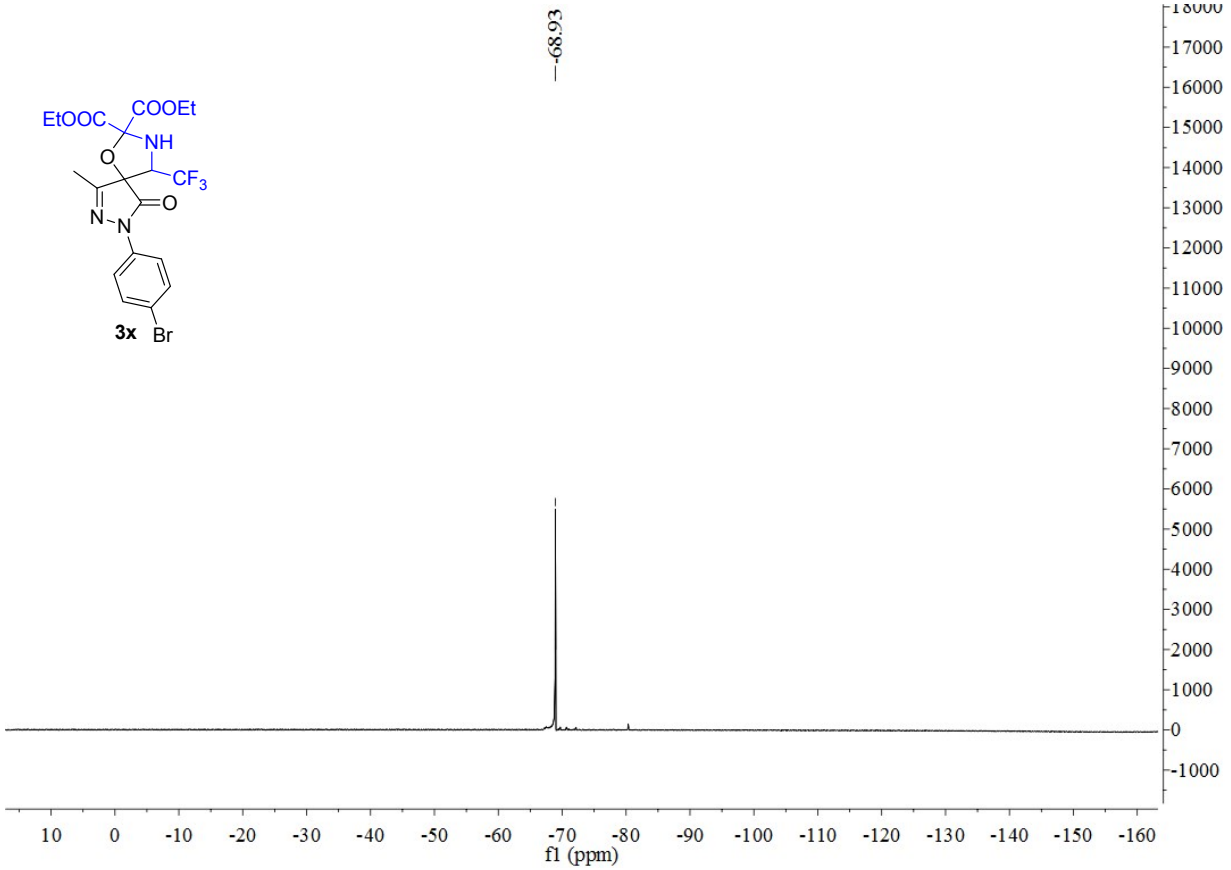
^{1}H NMR of compound 3x (in $CDCl_3$)



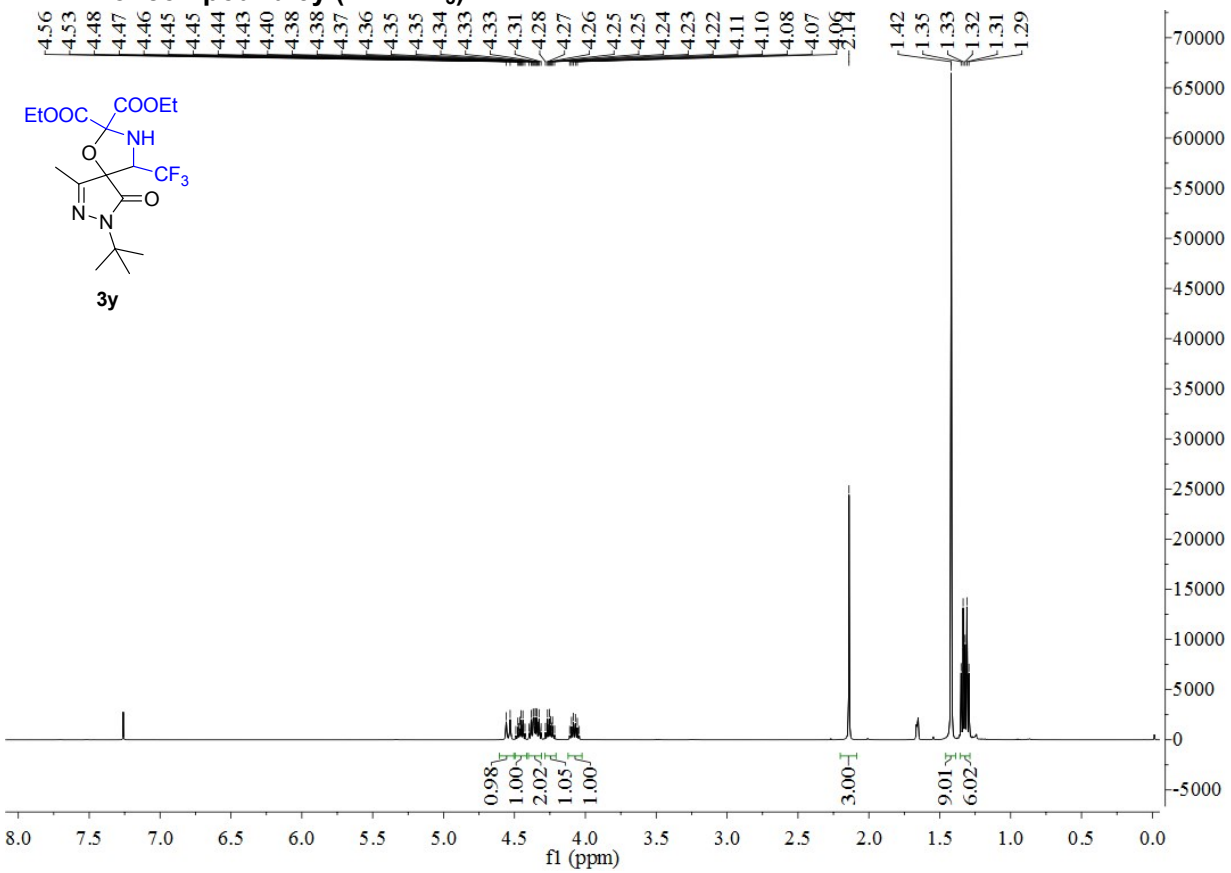
^{13}C NMR of compound 3x (in $CDCl_3$)



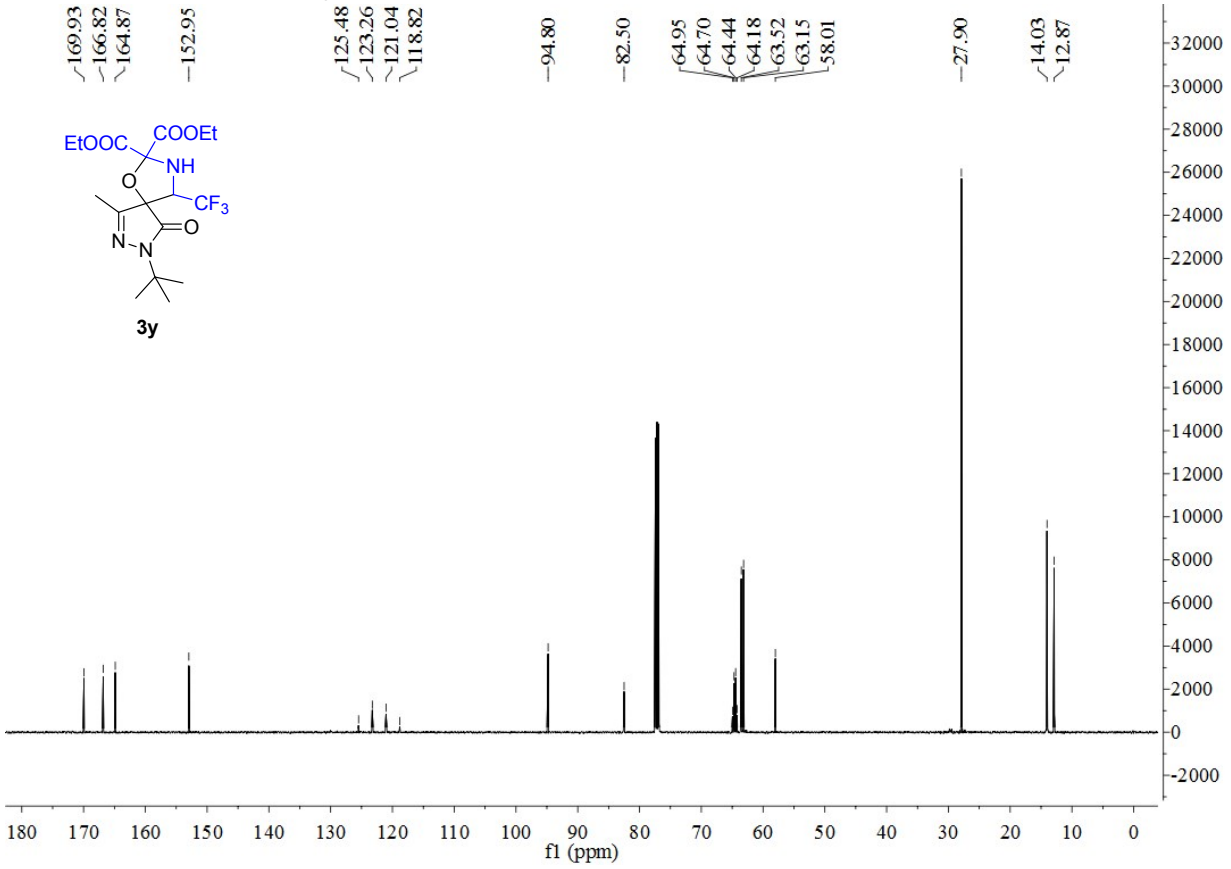
^{19}F NMR of compound 3x (in $CDCl_3$)



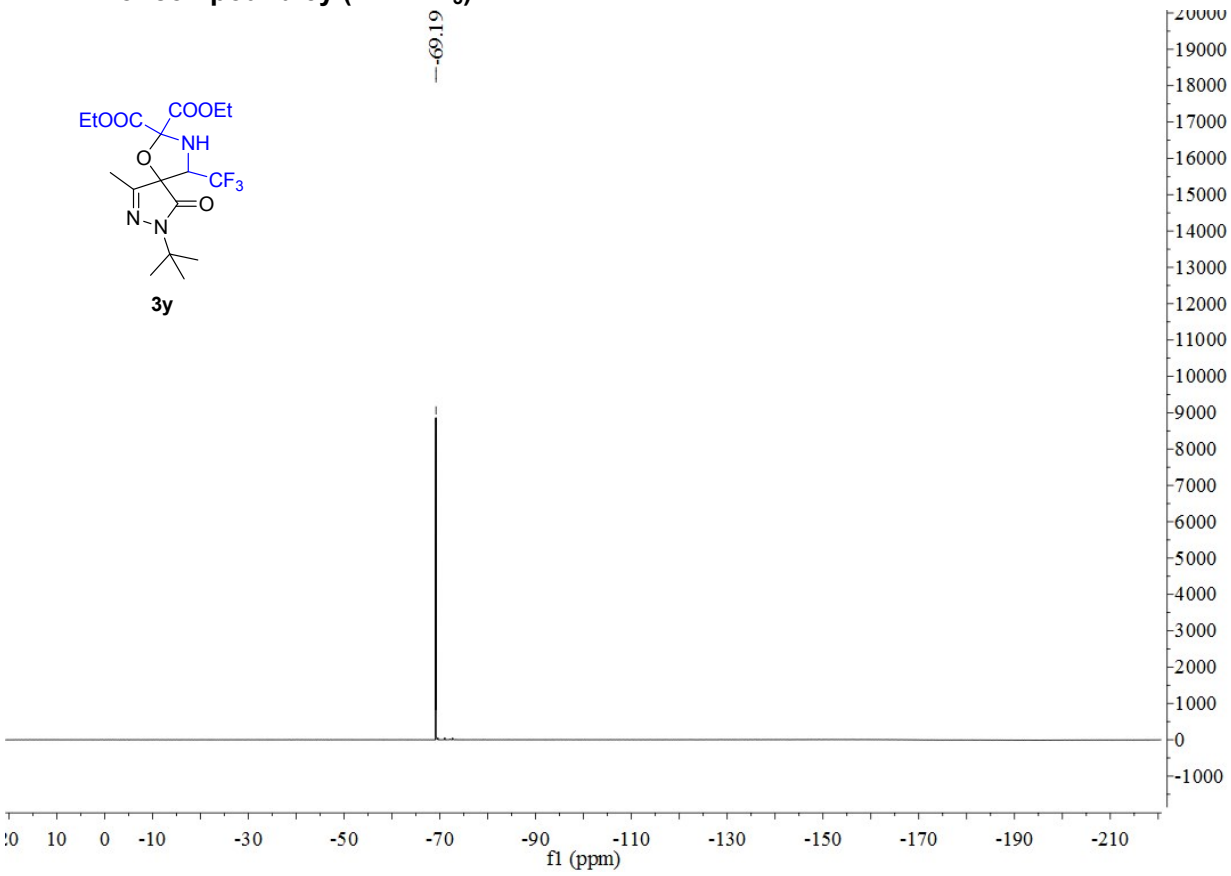
^{1}H NMR of compound 3y (in $CDCl_3$)



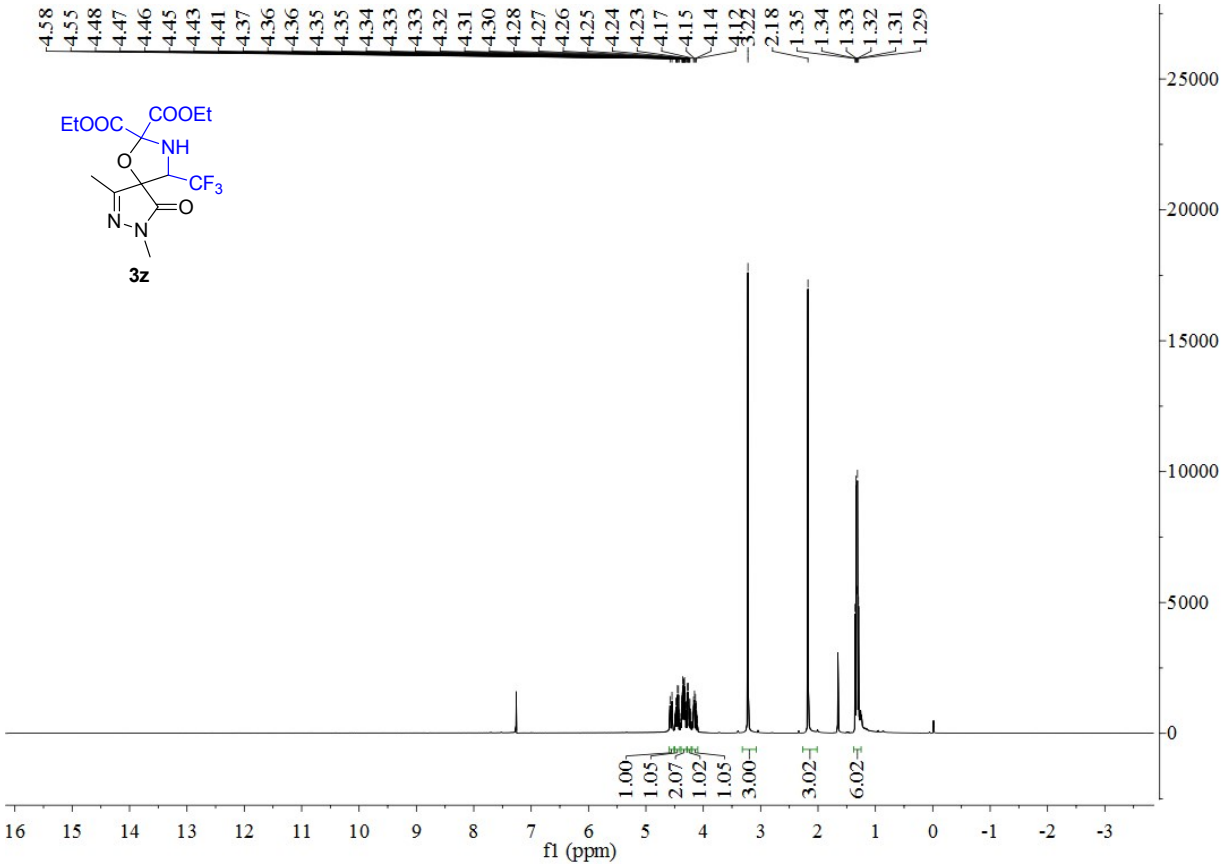
^{13}C NMR of compound 3y (in $CDCl_3$)



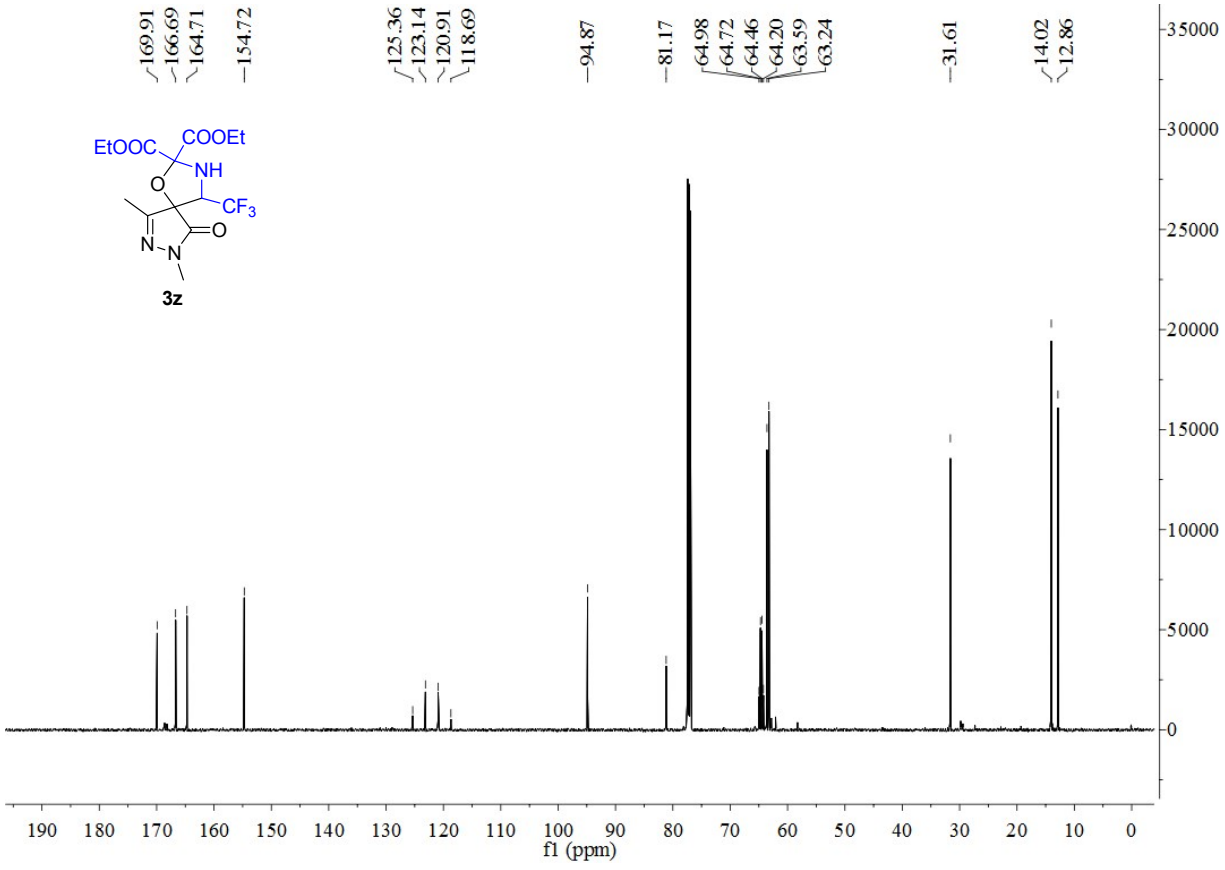
^{19}F NMR of compound 3y (in $CDCl_3$)



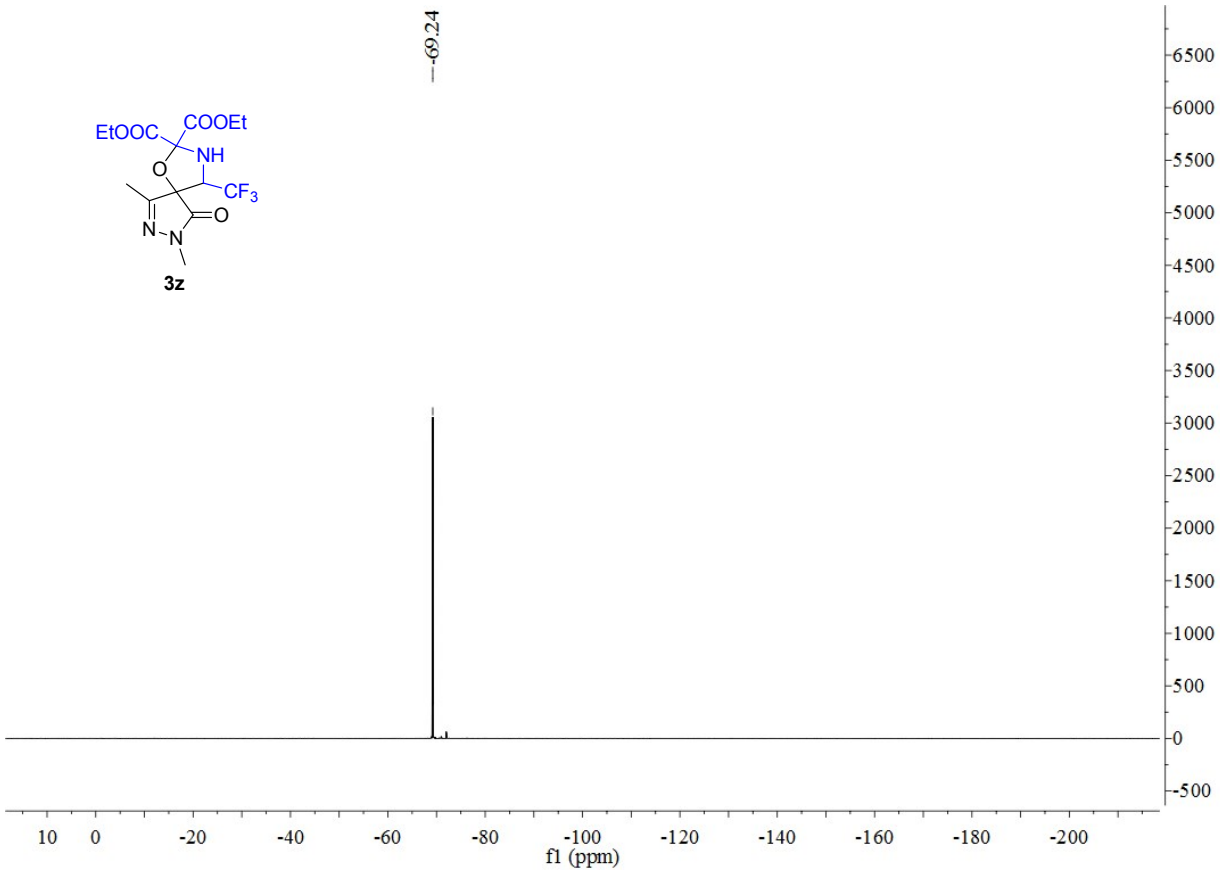
^{1}H NMR of compound 3z (in $CDCl_3$)



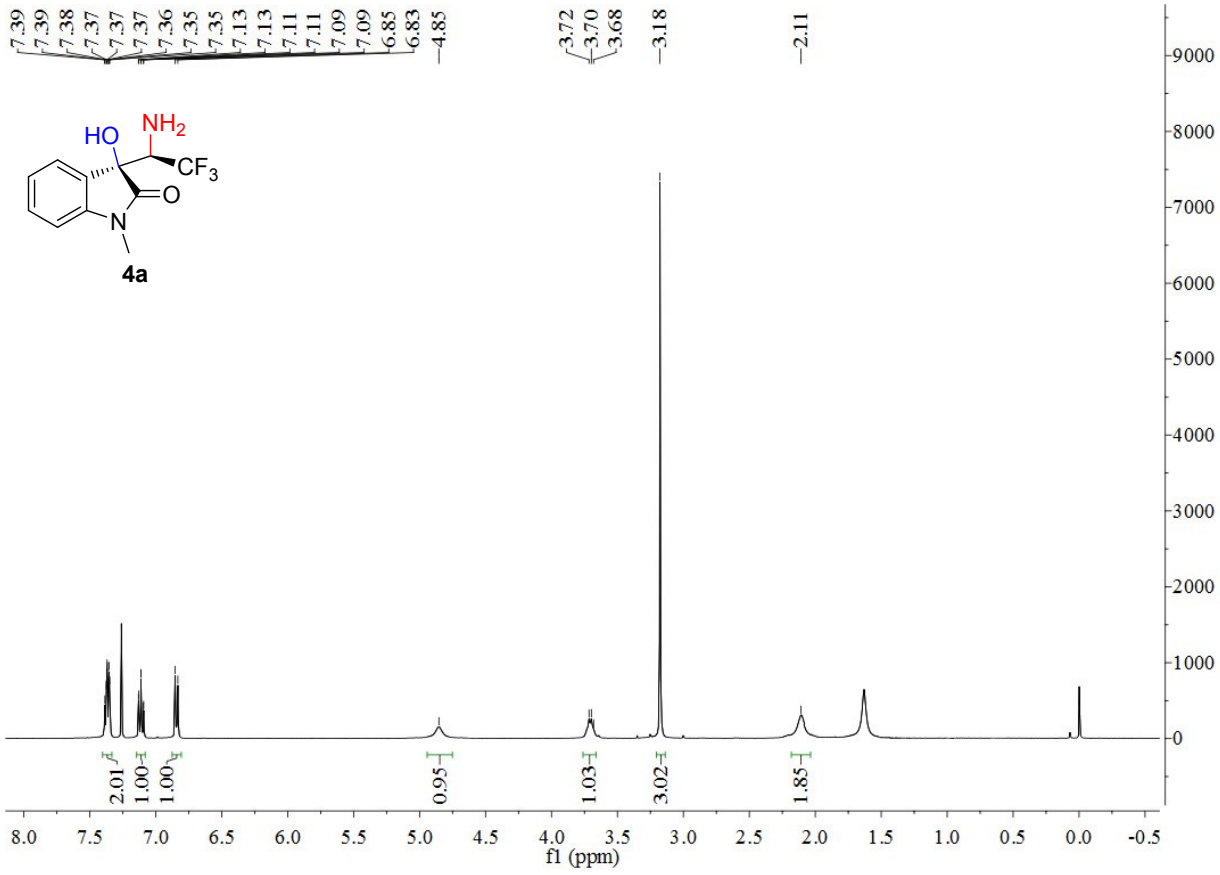
^{13}C NMR of compound 3z (in $CDCl_3$)



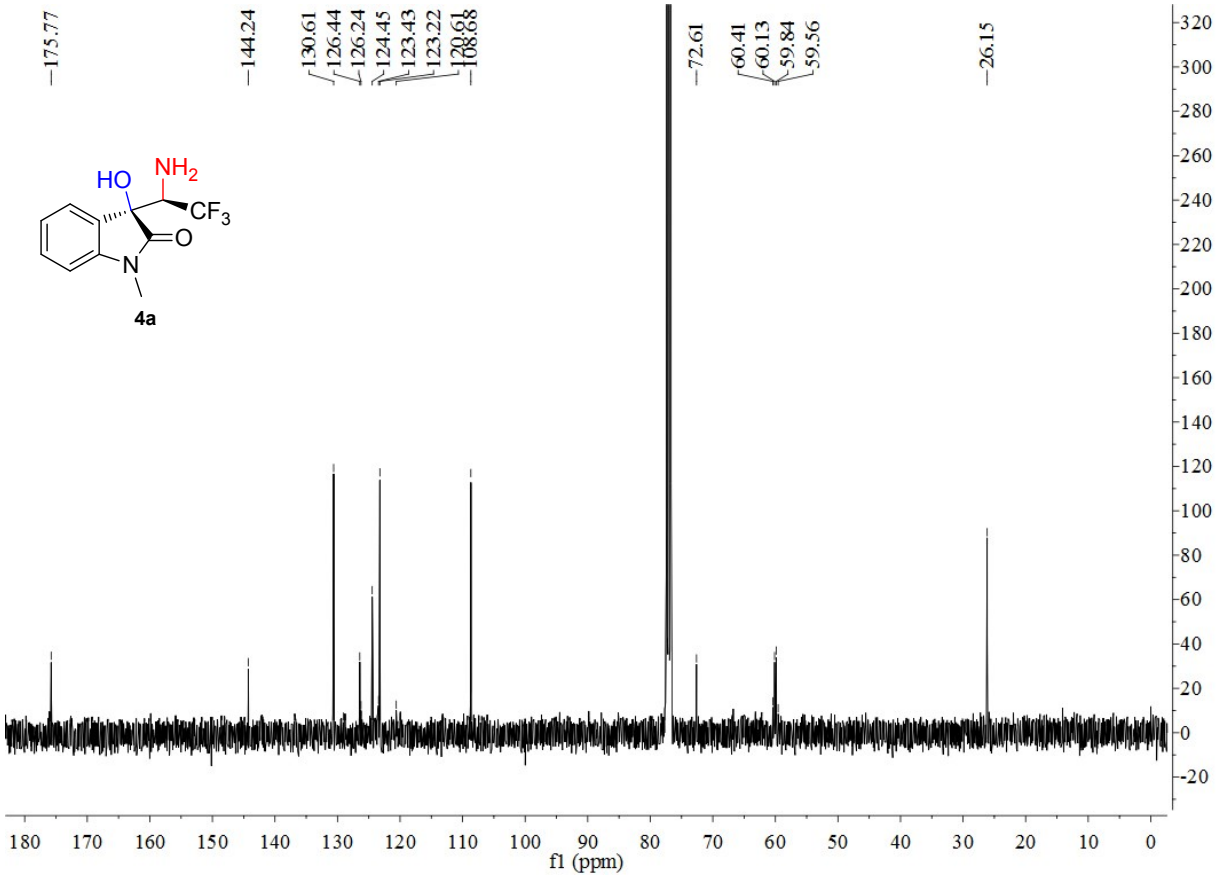
^{19}F NMR of compound 3z (in $CDCl_3$)



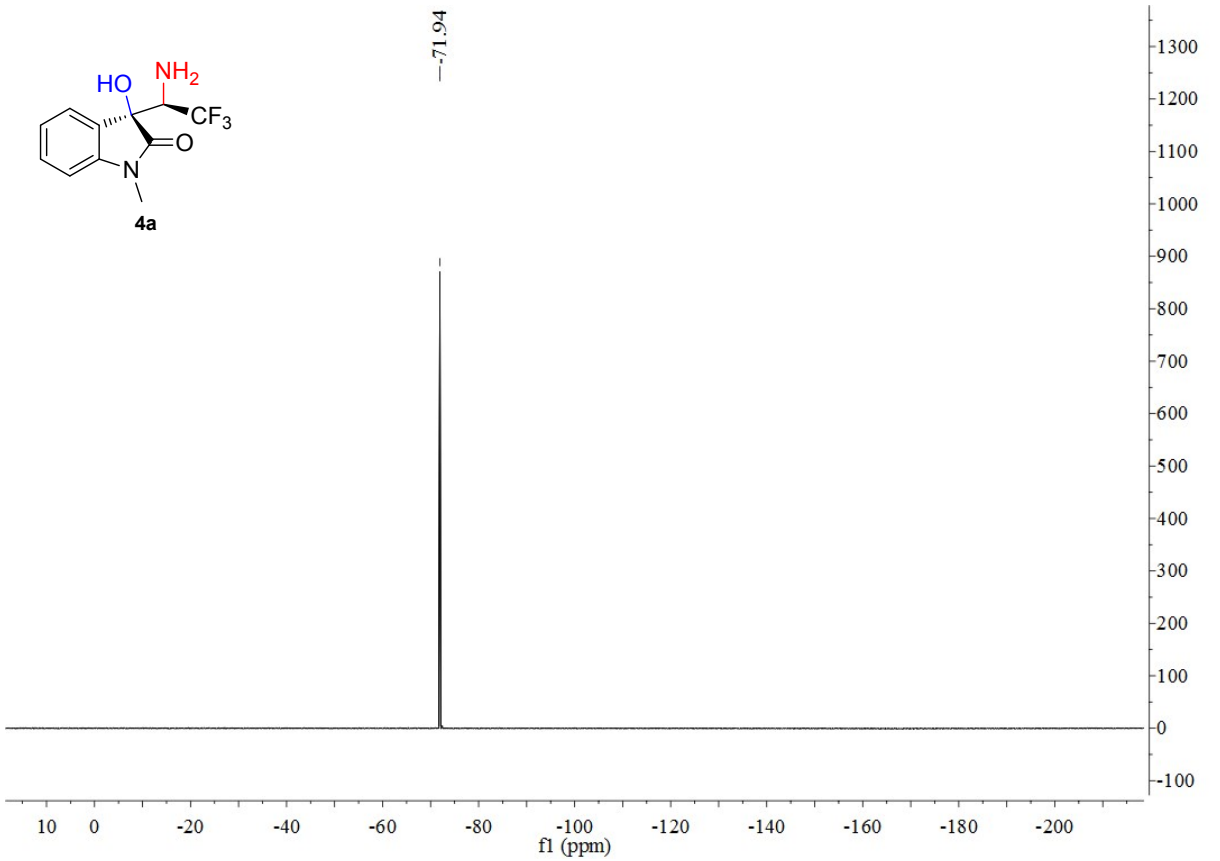
^{1}H NMR of compound 4a (in $CDCl_3$)



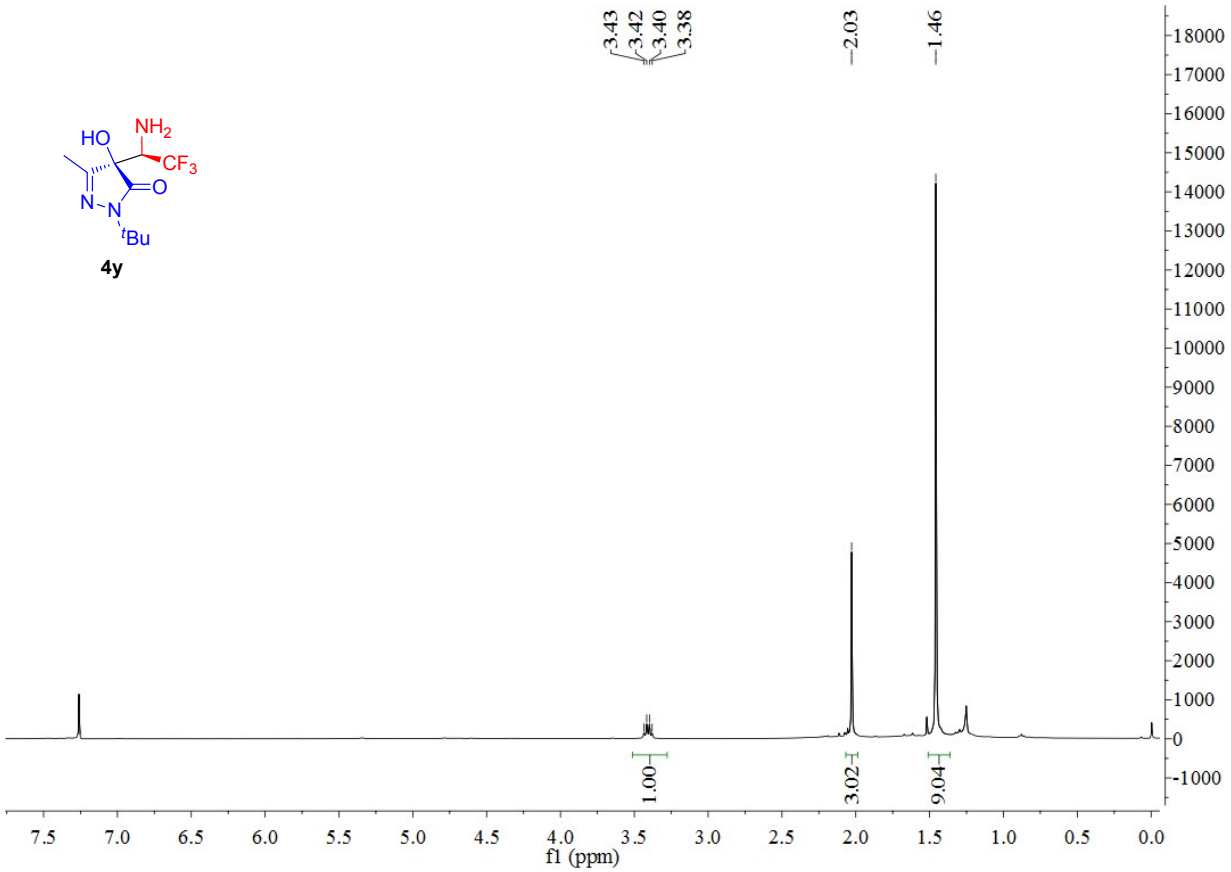
^{13}C NMR of compound 4a (in $CDCl_3$)



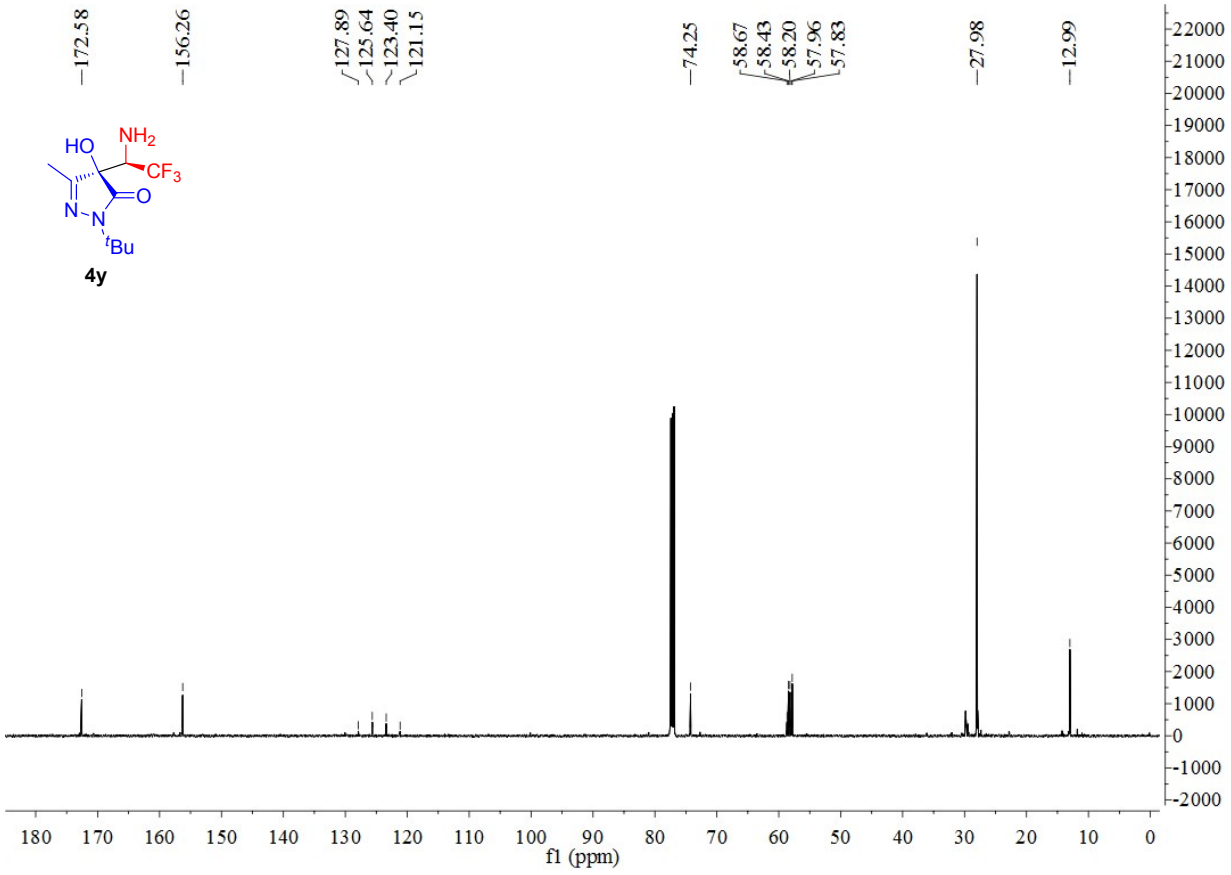
^{19}F NMR of compound 4a (in $CDCl_3$)



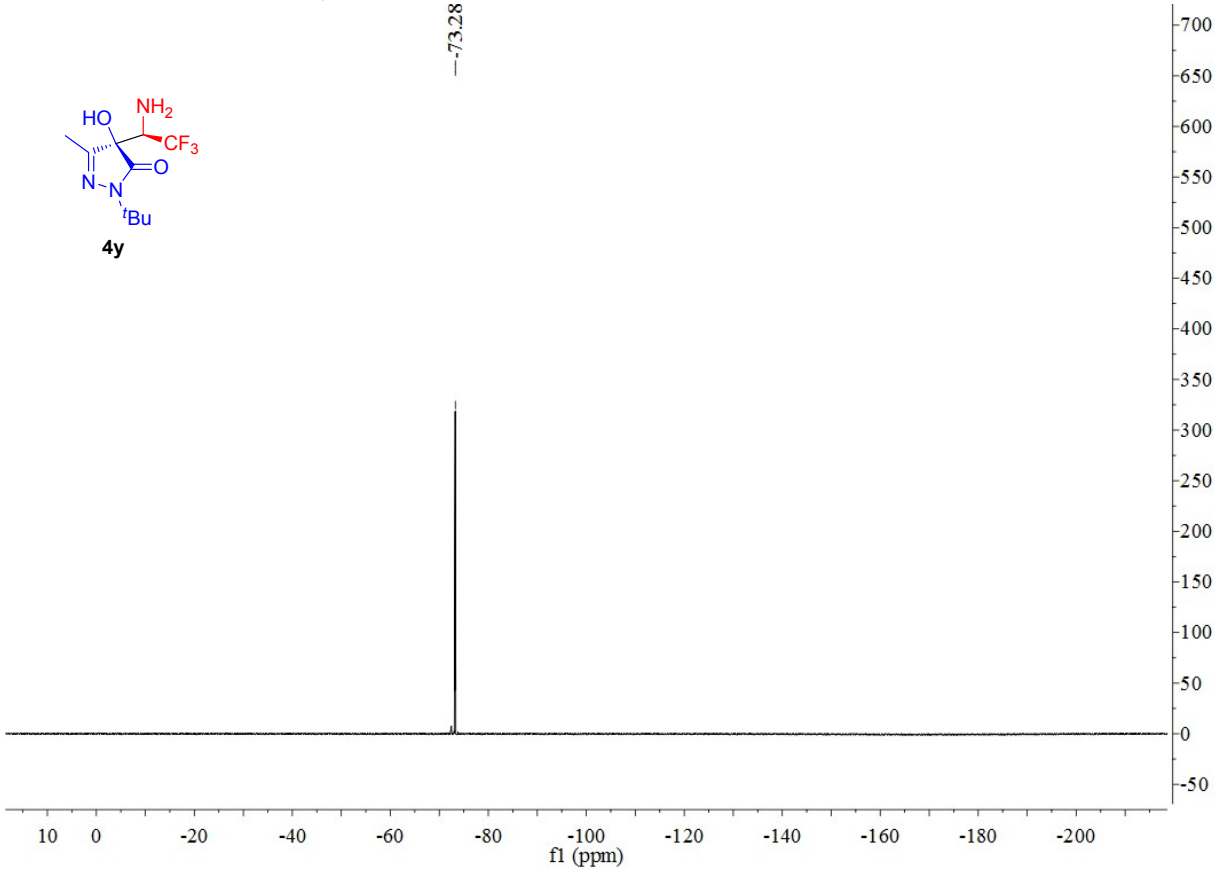
^{1}H NMR of compound 4y (in $CDCl_3$)



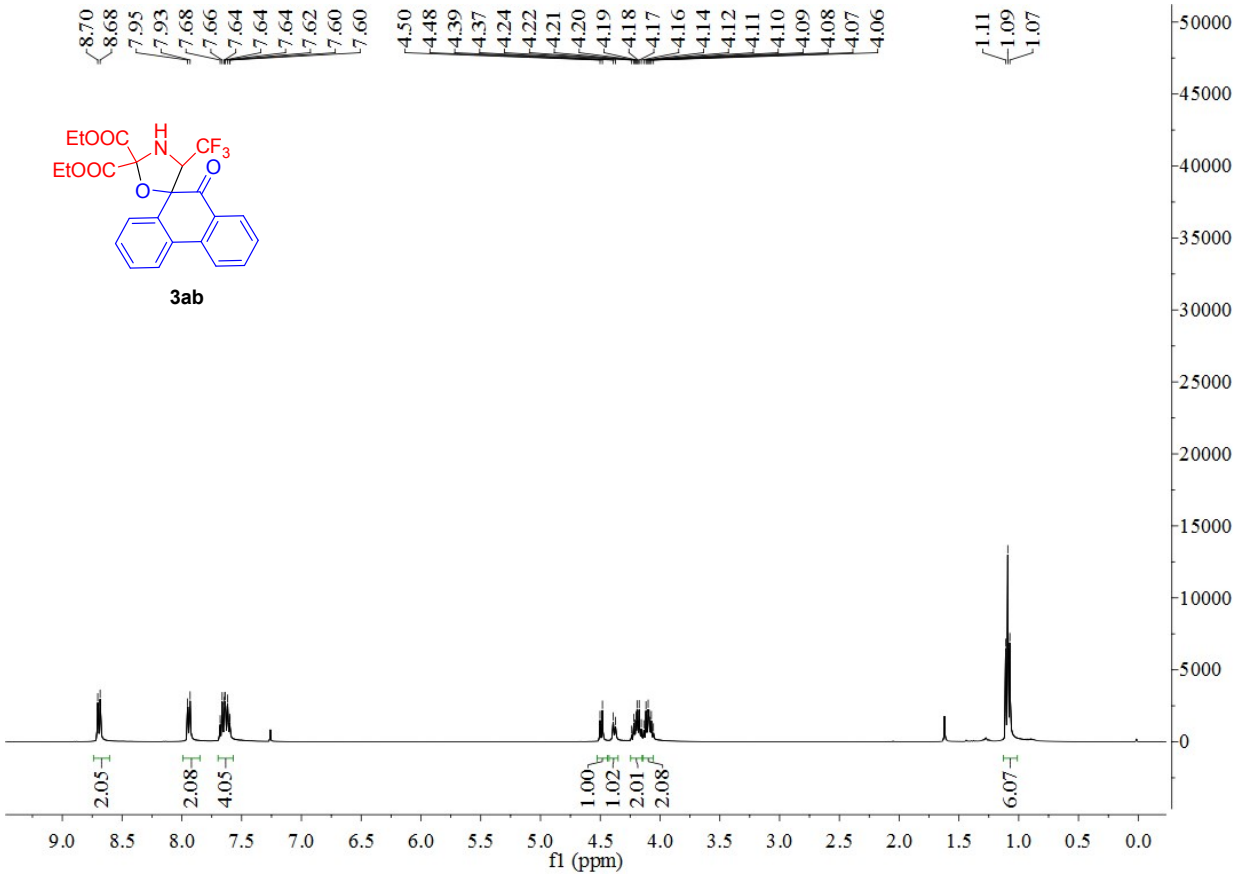
^{13}C NMR of compound 4y (in $CDCl_3$)



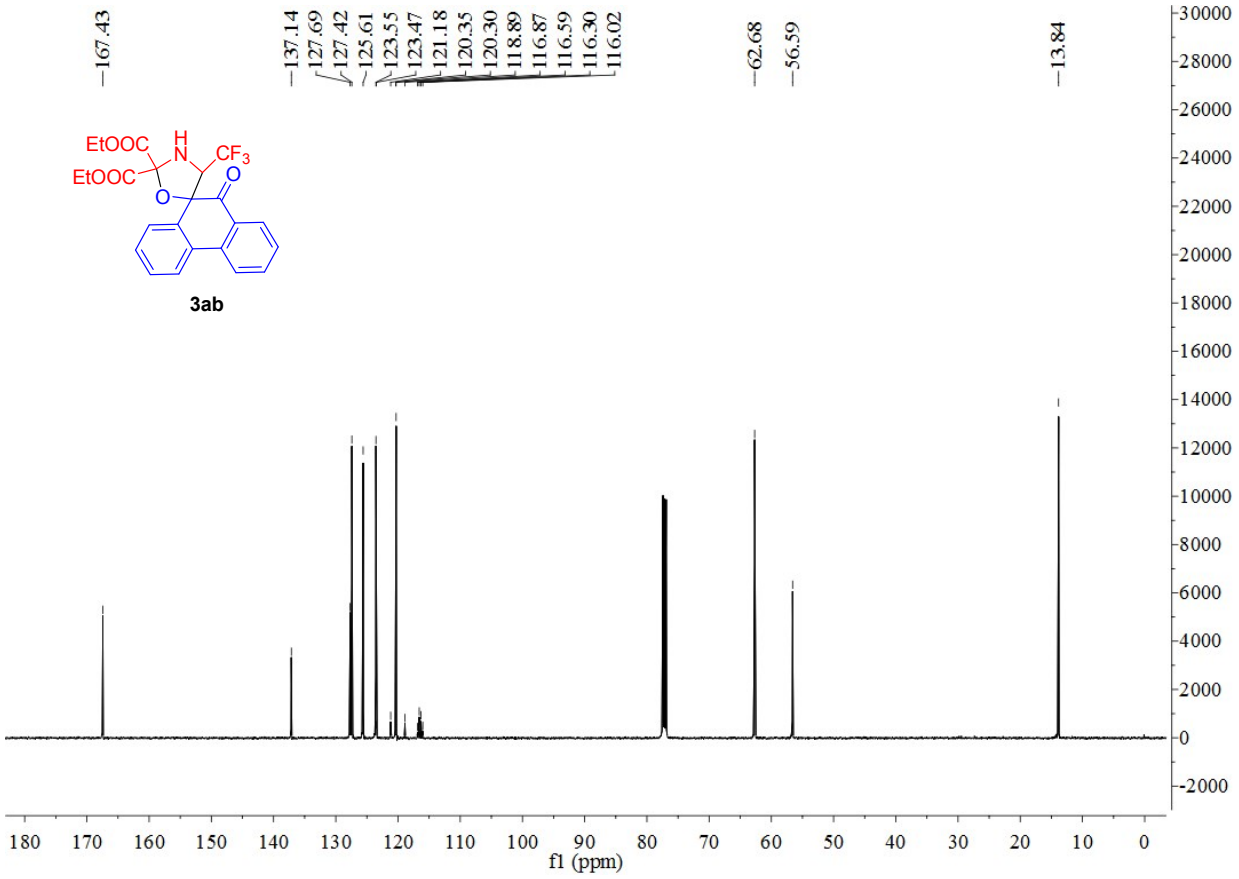
^{19}F NMR of compound 4y (in $CDCl_3$)



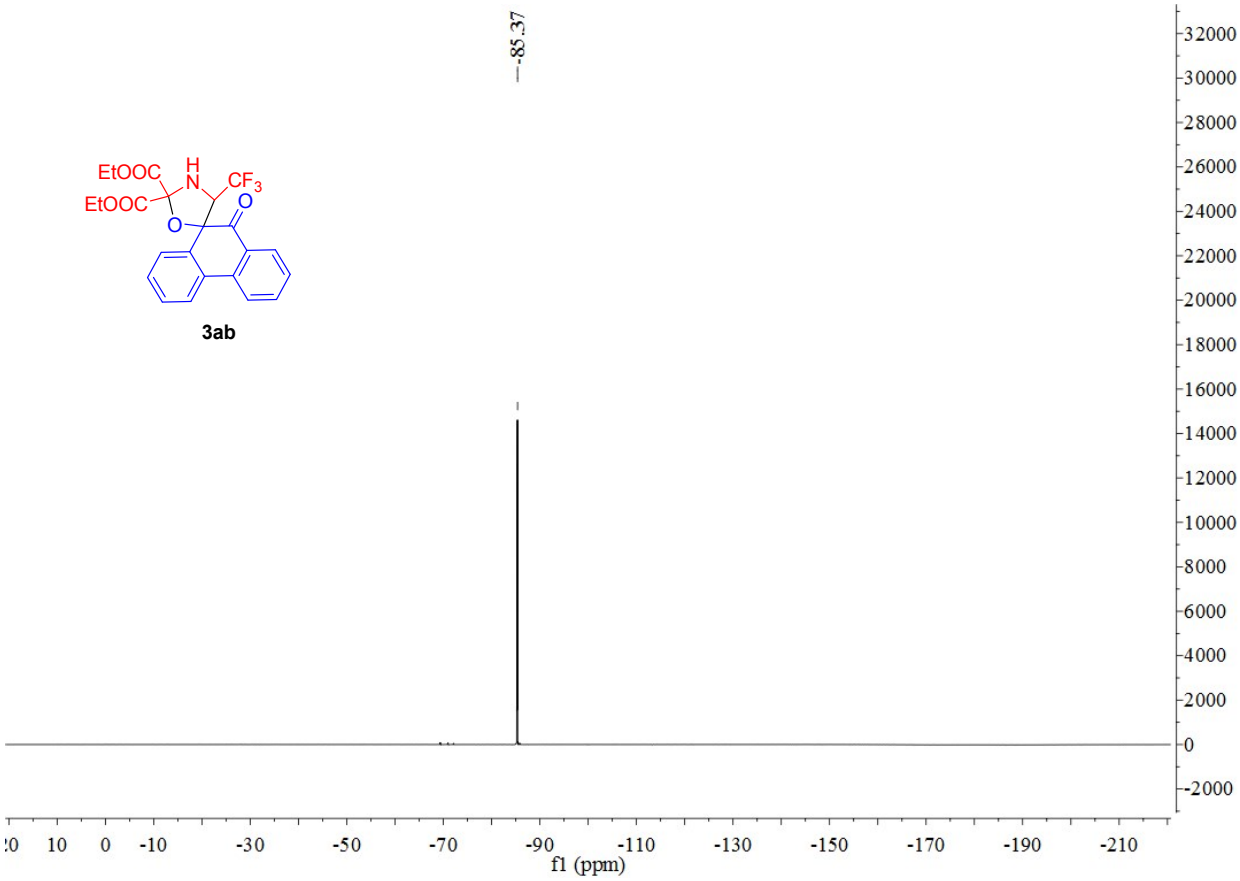
^{1}H NMR of compound 3ab (in $CDCl_3$)



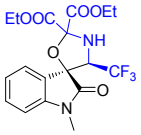
^{13}C NMR of compound 3ab (in $CDCl_3$)



^{19}F NMR of compound 3ab (in $CDCl_3$)

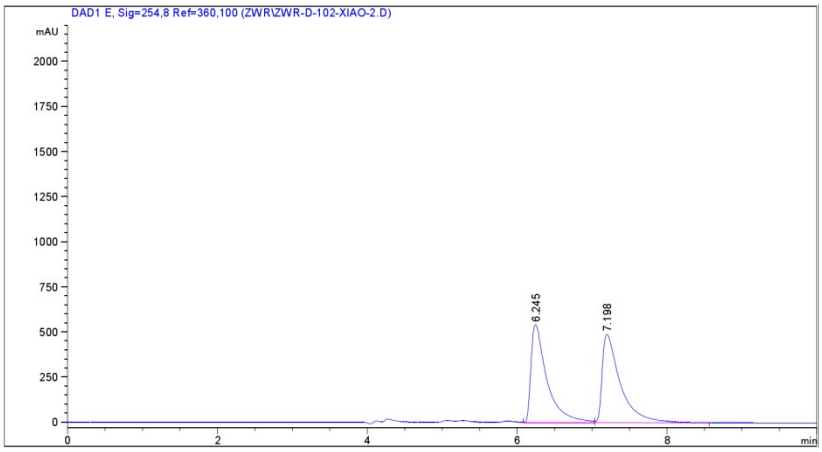


8. Copies of HPLC Spectra of Compounds



3a

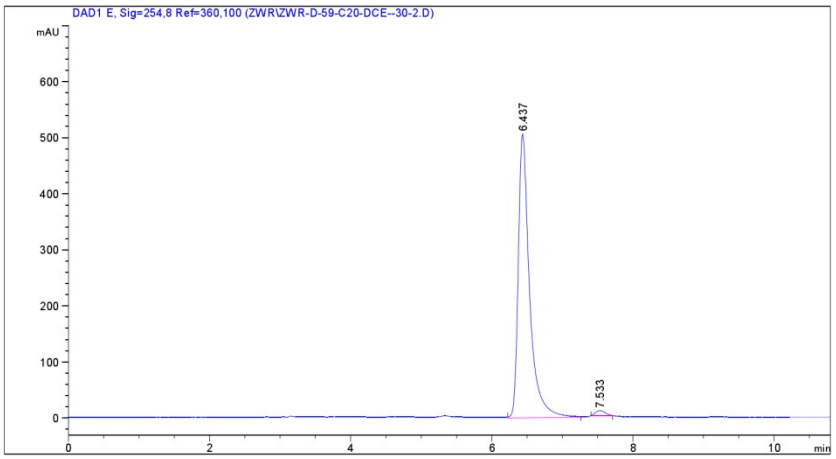
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

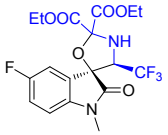
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.245	VV	0.2154	8071.95508	542.94879	49.4232
2	7.198	VB	0.2424	8260.35254	490.63766	50.5768

HPLC spectrum of the chiral compound



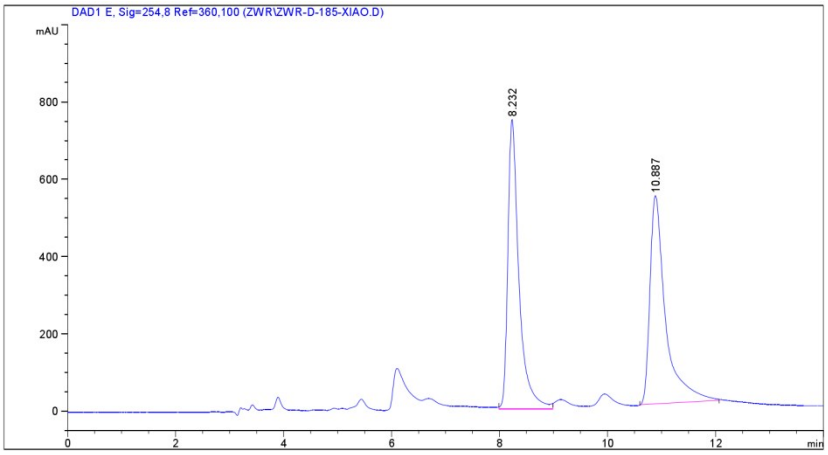
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.437	MM R	0.1851	5626.01758	506.70685	98.4868
2	7.533	MM R	0.1602	86.44145	8.99090	1.5132



3b

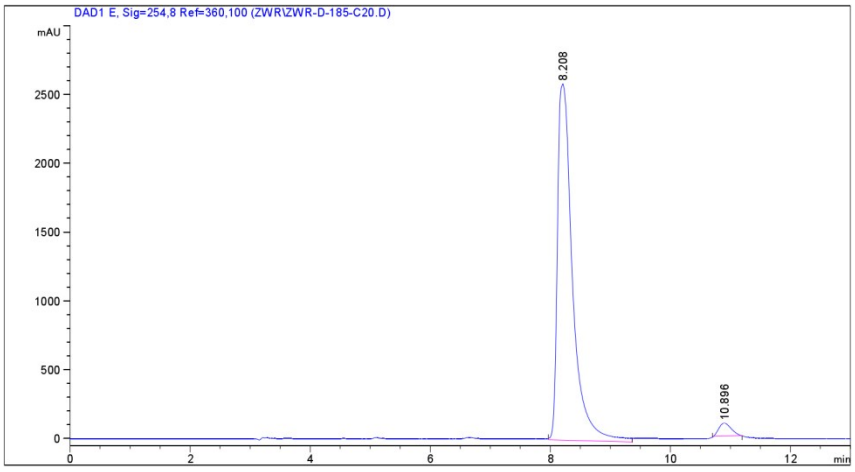
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

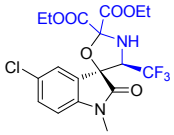
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.232	MM R	0.2386	1.07375e4	749.95599	49.7674
2	10.887	MM R	0.3350	1.08379e4	539.11768	50.2326

HPLC spectrum of the chiral compound



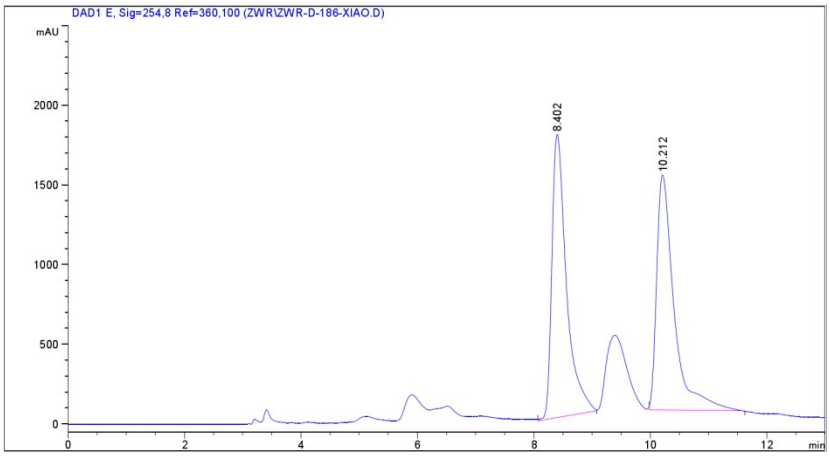
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.208	MM R	0.2897	4.50090e4	2589.83960	97.1046
2	10.896	MM R	0.2357	1342.06641	94.91537	2.8954



3c

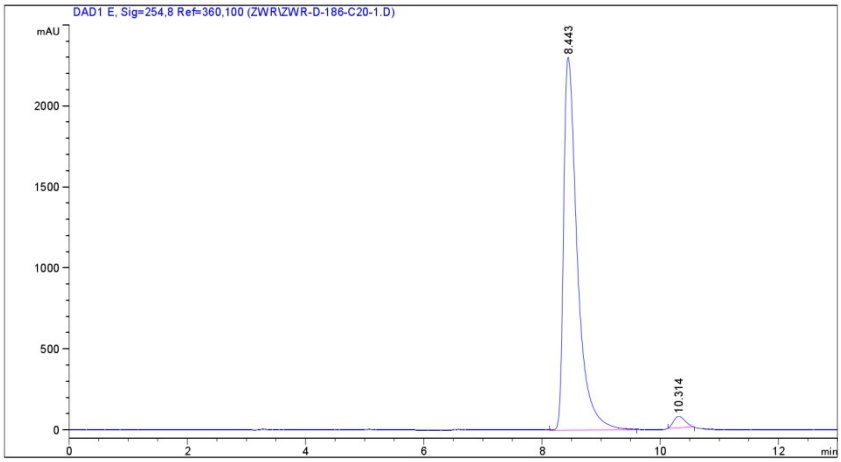
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

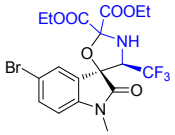
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.402	MM R	0.2893	3.08358e4	1776.74500	50.2900
2	10.212	MM R	0.3444	3.04802e4	1475.09961	49.7100

HPLC spectrum of the chiral compound



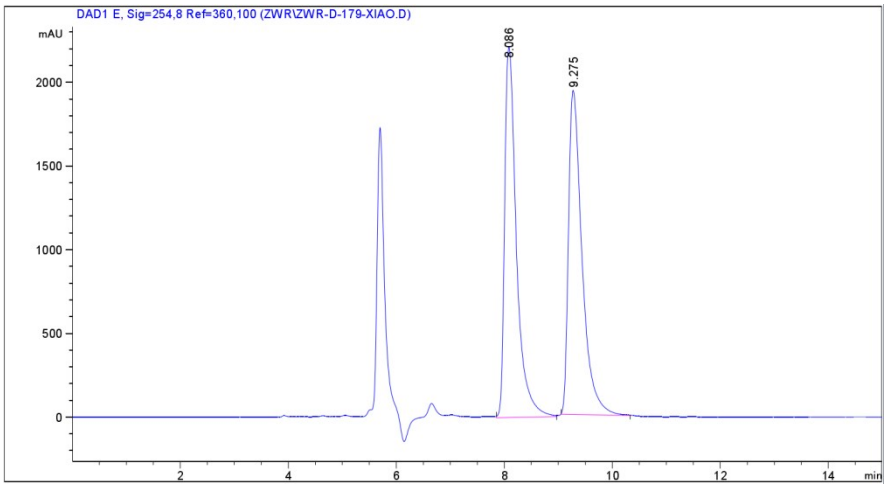
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.443	MM R	0.2686	3.71184e4	2303.38599	97.5124
2	10.314	MM R	0.2216	946.91833	71.20676	2.4876



3d

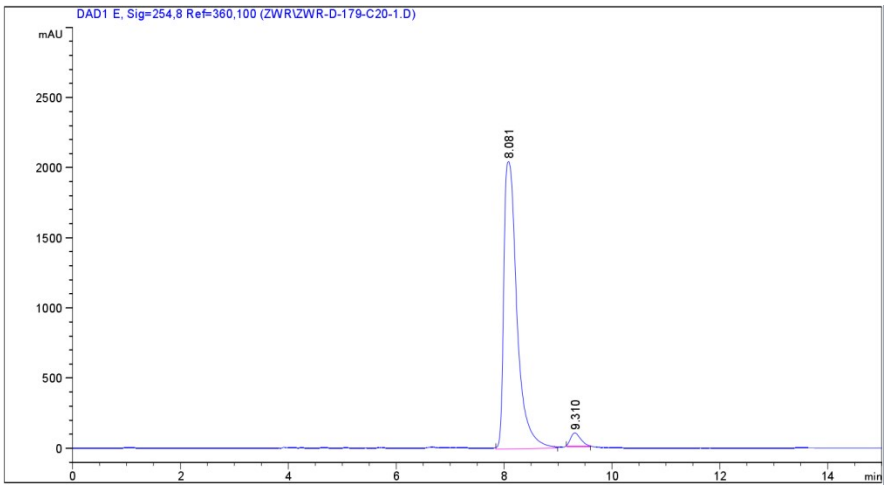
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

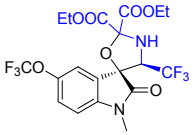
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.086	MM R	0.2521	3.35187e4	2216.31592	49.9384
2	9.275	MM R	0.2892	3.36014e4	1936.74280	50.0616

HPLC spectrum of the chiral compound



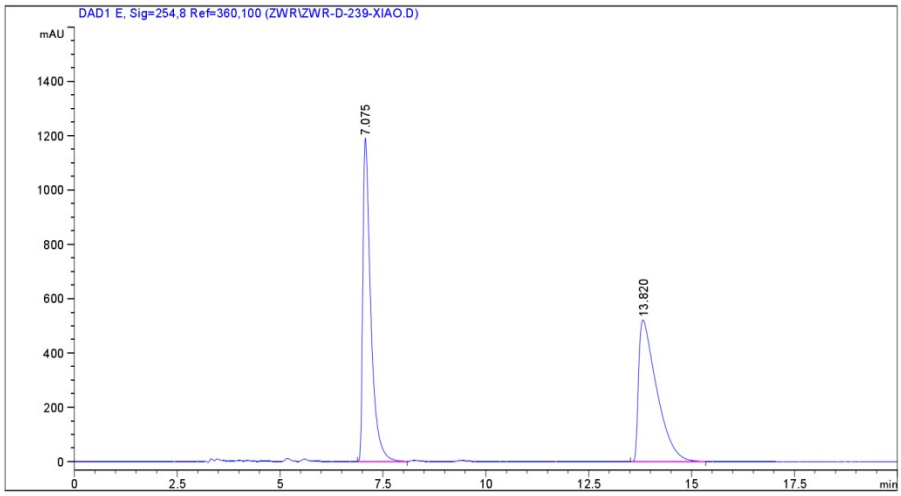
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.081	MM R	0.2821	3.46698e4	2048.64160	96.5048
2	9.310	MM R	0.2188	1255.65295	95.63361	3.4952



3e

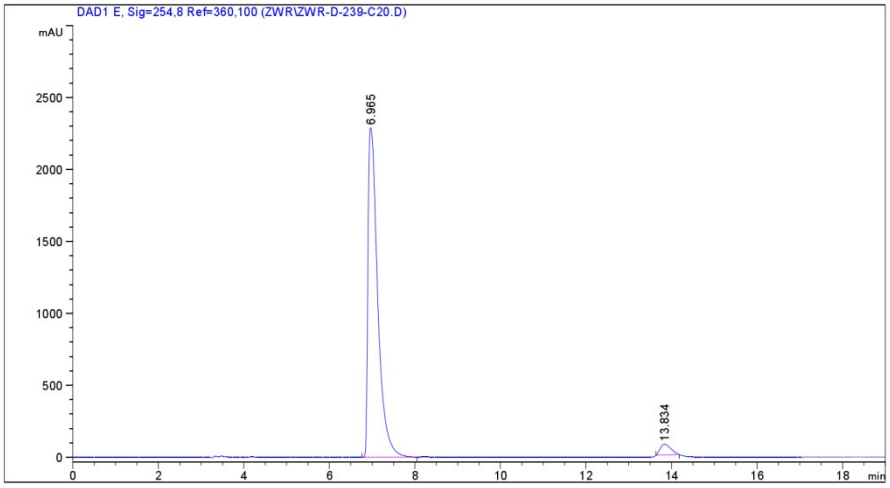
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

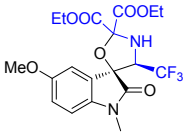
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.075	BV	0.1985	1.59620e4	1190.16321	49.9877
2	13.820	BB	0.4449	1.59698e4	521.99591	50.0123

HPLC spectrum of the chiral compound



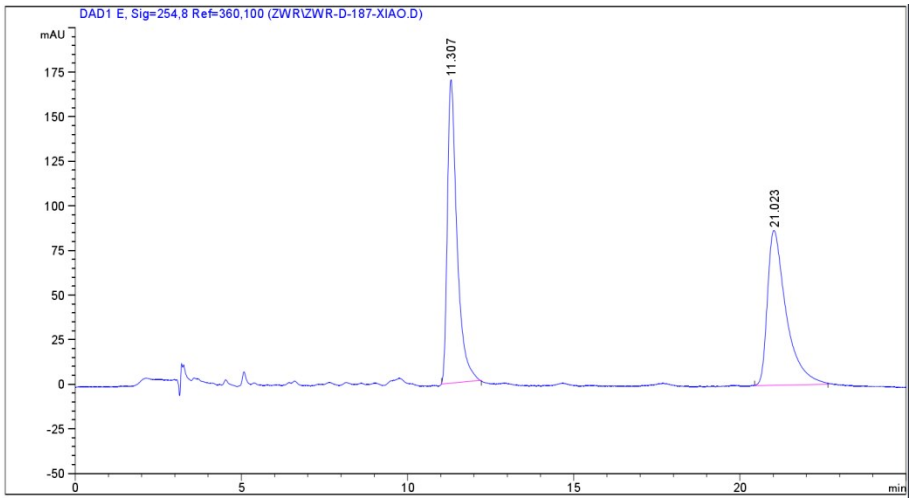
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.965	BV	0.2402	3.61492e4	2289.11157	96.6393
2	13.834	MM R	0.2819	1257.12305	74.33344	3.3607



3f

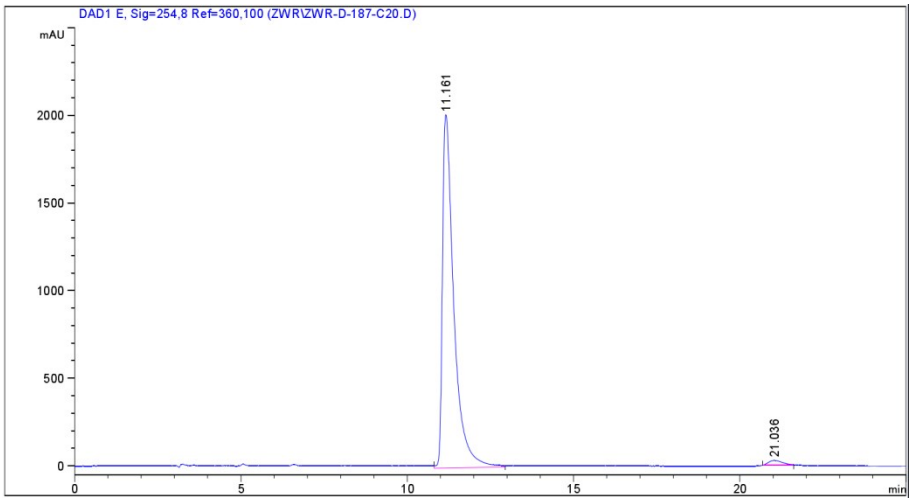
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

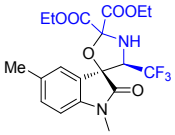
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.307	MM R	0.3362	3433.17090	170.20604	50.1833
2	21.023	BB	0.5698	3408.08813	86.85492	49.8167

HPLC spectrum of the chiral compound



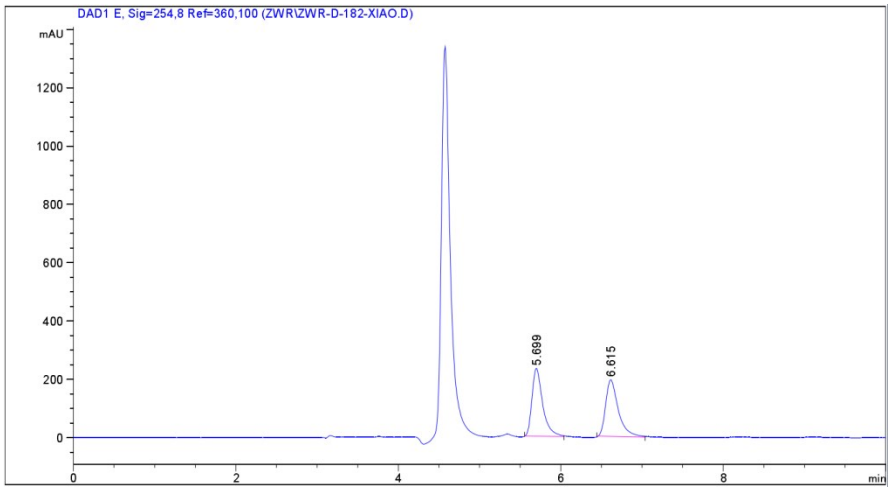
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.161	MM R	0.3966	4.79681e4	2015.66321	98.5663
2	21.036	MM R	0.4639	697.73688	25.06953	1.4337



3g

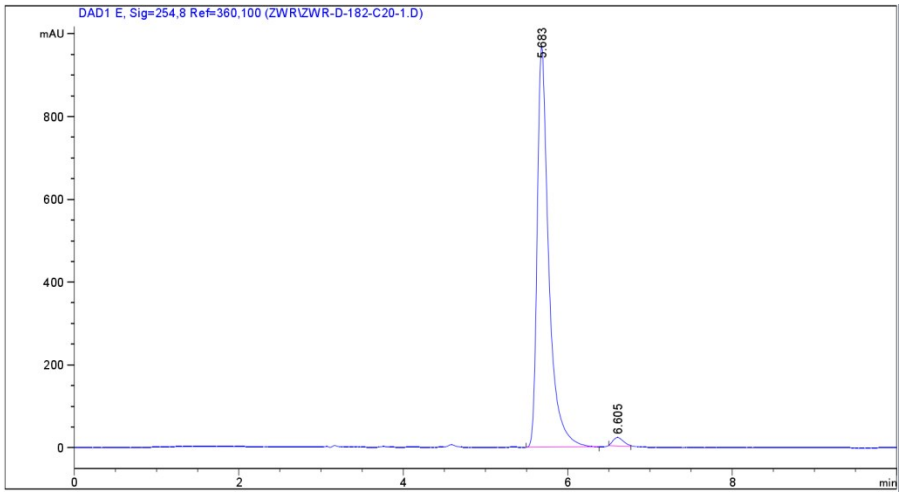
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

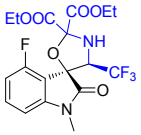
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.699	MM R	0.1526	2133.52319	233.02663	50.4447
2	6.615	MM R	0.1800	2095.90356	194.08434	49.5553

HPLC spectrum of the chiral compound



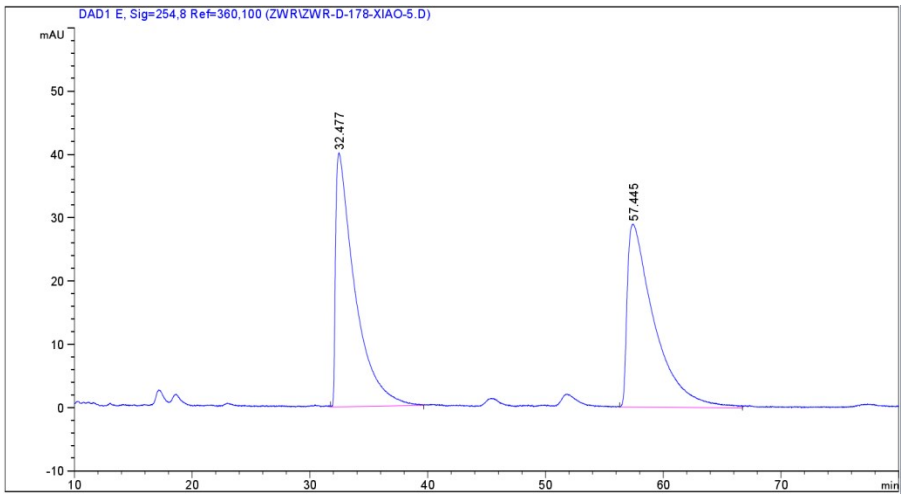
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.683	MM R	0.1622	9418.52637	967.80298	98.1174
2	6.605	MM R	0.1475	180.71445	20.42197	1.8826



3h

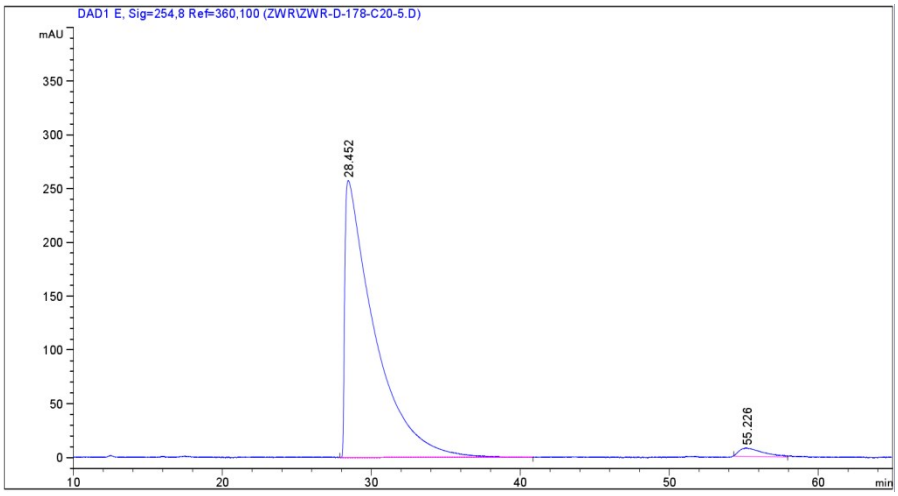
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

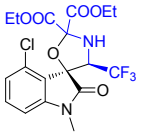
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	32.477	MM R	1.8912	4549.71289	40.09584	49.6162
2	57.445	MM R	2.6625	4620.09131	28.92040	50.3838

HPLC spectrum of the chiral compound



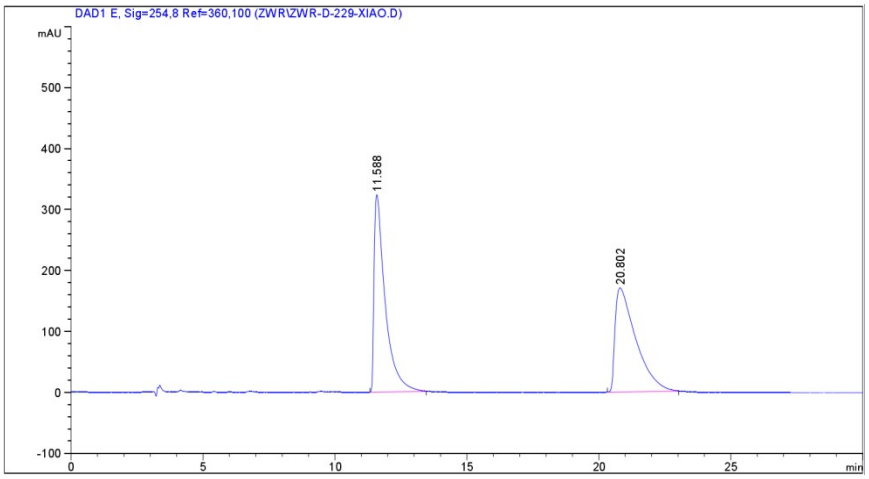
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.452	MM R	2.2854	3.53003e4	257.43811	97.5789
2	55.226	MM R	1.9014	875.87122	7.67730	2.4211



3i

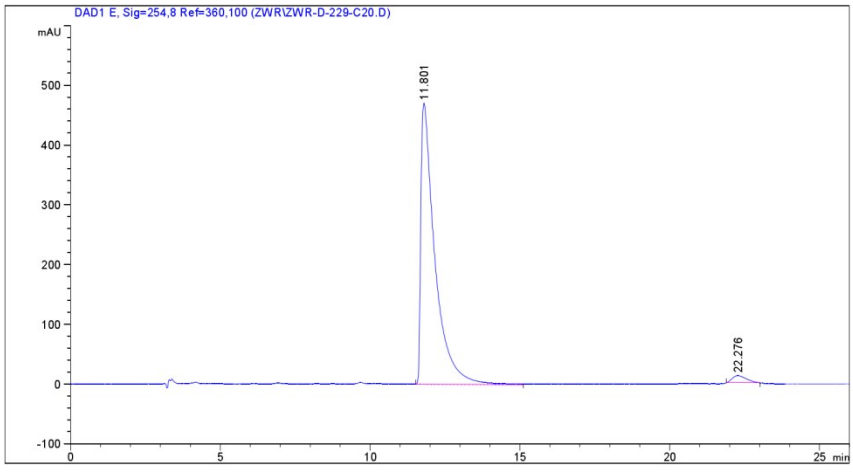
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

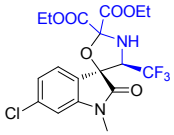
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.588	BB	0.4209	9465.59375	323.95599	50.3167
2	20.802	BB	0.7903	9346.42480	170.82303	49.6833

HPLC spectrum of the chiral compound



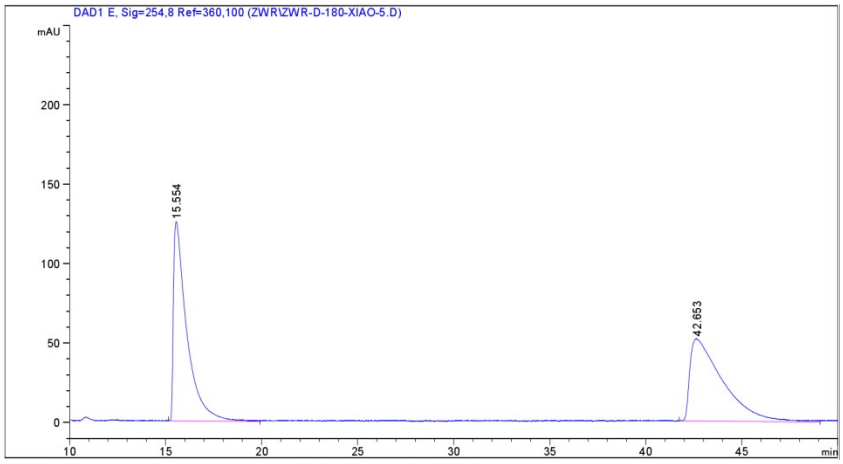
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.801	MM R	0.5435	1.53492e4	470.71323	97.6325
2	22.276	MM R	0.5403	372.20627	11.48090	2.3675



3j

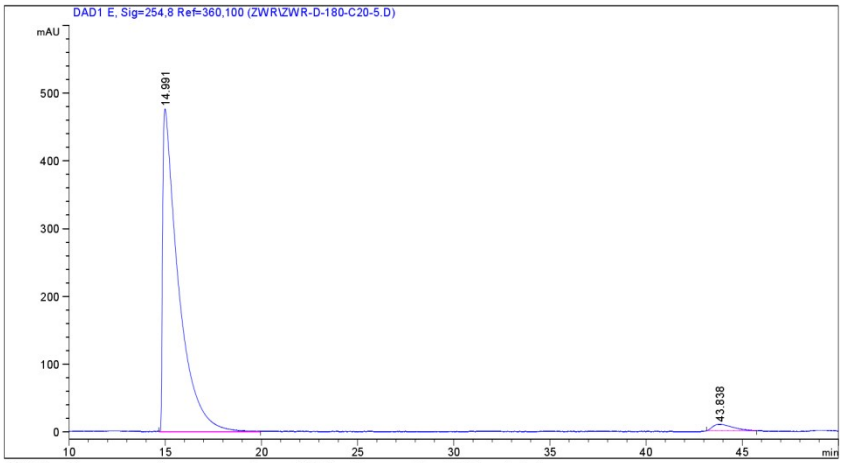
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

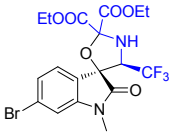
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.554	MM R	0.8107	6100.55566	125.41557	49.6984
2	42.653	MM R	1.9952	6174.60400	51.57790	50.3016

HPLC spectrum of the chiral compound



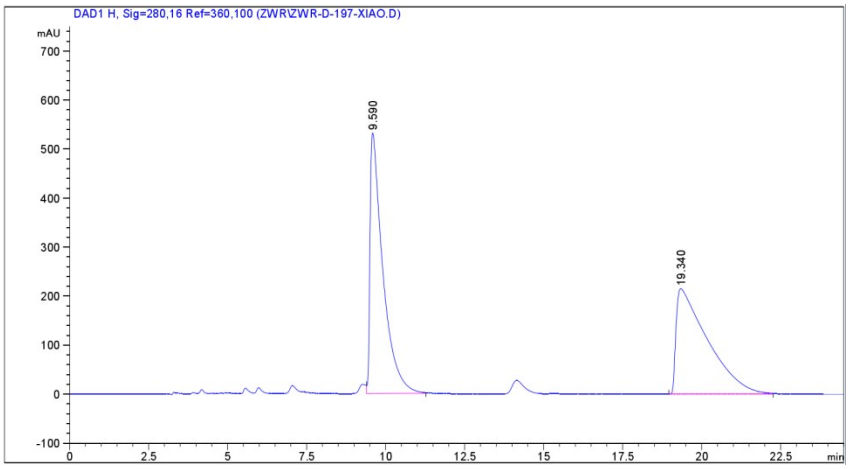
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.991	MM R	0.9488	2.71094e4	476.22778	97.5234
2	43.838	MM R	1.2126	688.44714	9.46276	2.4766



3k

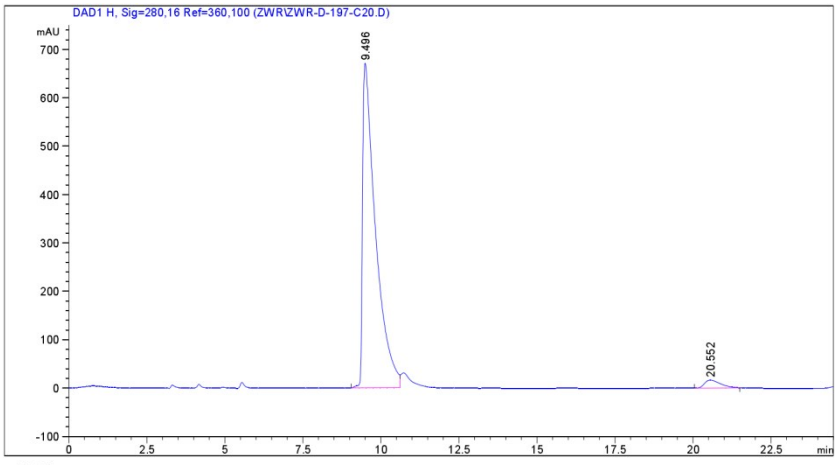
HPLC spectrum of the racemate



信号 1: DAD1 H, Sig=280,16 Ref=360,100

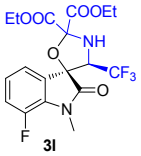
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.590	VB	0.3968	1.49935e4	532.07349	50.3271
2	19.340	BB	0.9614	1.47986e4	214.89743	49.6729

HPLC spectrum of the chiral compound



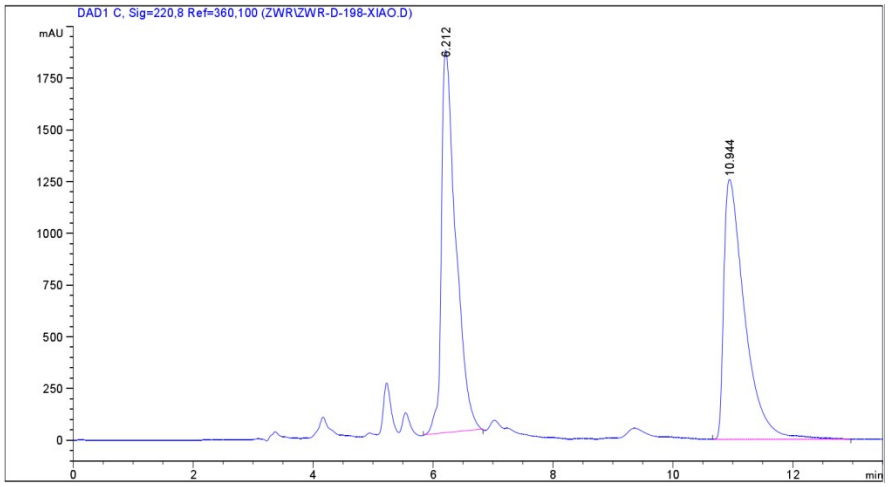
信号 1: DAD1 H, Sig=280,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.496	BV	0.4057	1.94314e4	671.24786	97.0382
2	20.552	BB	0.5411	593.07715	16.58925	2.9618



3l

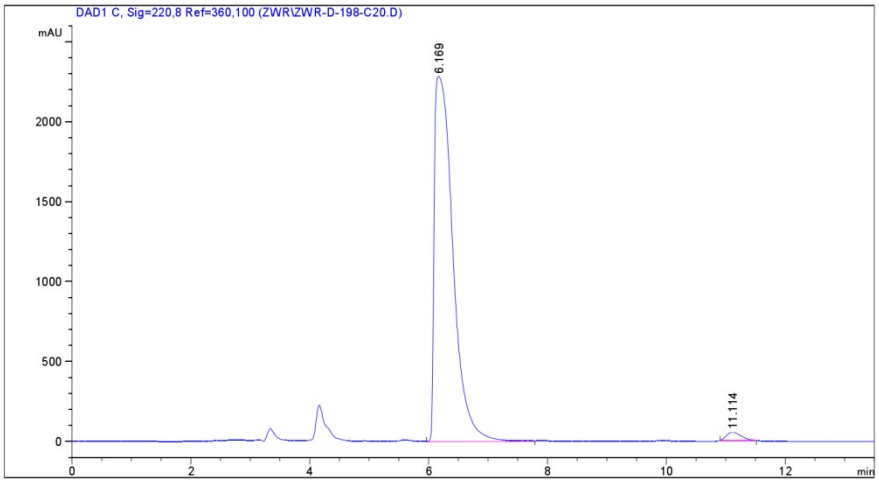
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=220,8 Ref=360,100

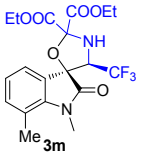
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.212	MM R	0.2769	3.07272e4	1849.41077	50.2942
2	10.944	VB	0.3597	3.03678e4	1257.90369	49.7058

HPLC spectrum of the chiral compound



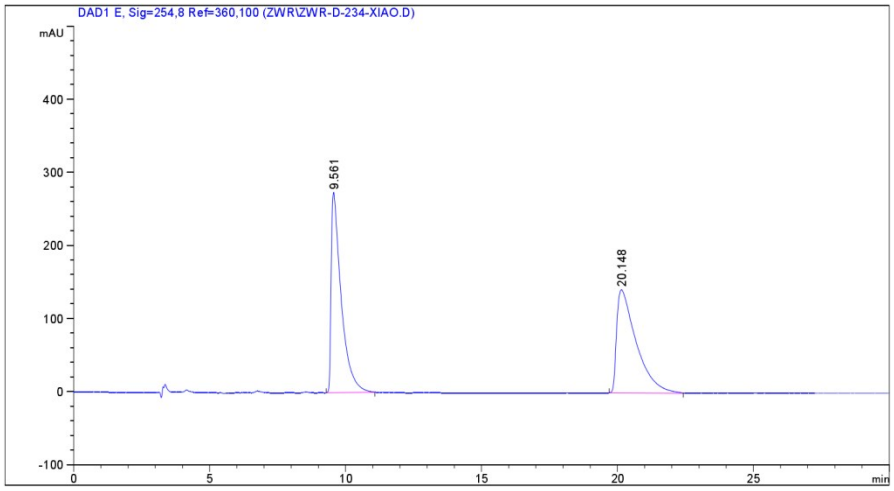
信号 1: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.169	MM R	0.3627	4.97712e4	2287.07739	98.3224
2	11.114	MM R	0.2766	849.21753	51.16344	1.6776



3m

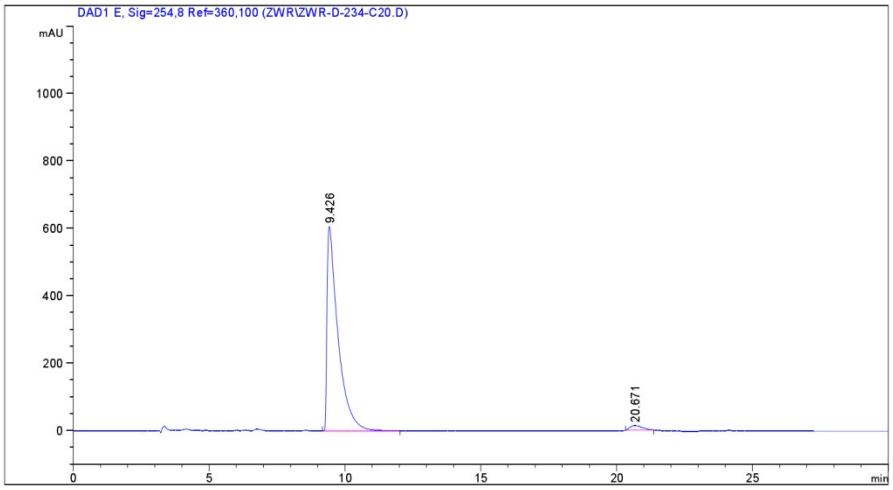
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

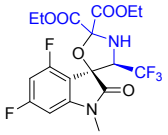
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.561	BB	0.3661	7005.50391	274.20383	49.7717
2	20.148	BB	0.7218	7069.77979	141.28125	50.2283

HPLC spectrum of the chiral compound



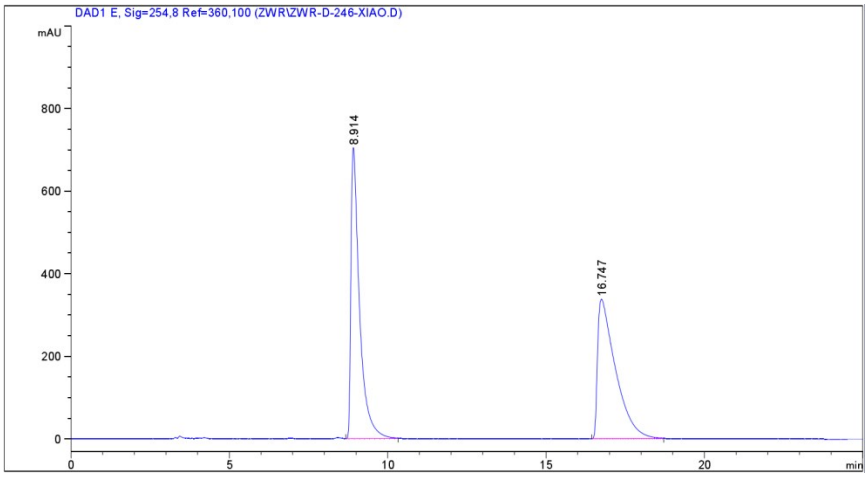
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.426	MM R	0.4688	1.70727e4	606.96600	97.5528
2	20.671	MM R	0.5205	428.29263	13.71483	2.4472



3n

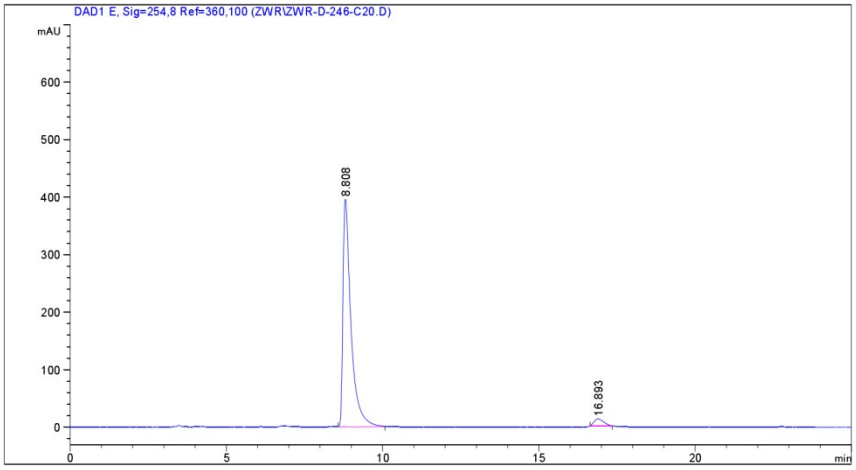
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

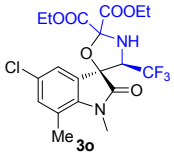
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.914	VB	0.2735	1.32555e4	704.56580	49.9670
2	16.747	BB	0.5641	1.32730e4	338.02145	50.0330

HPLC spectrum of the chiral compound

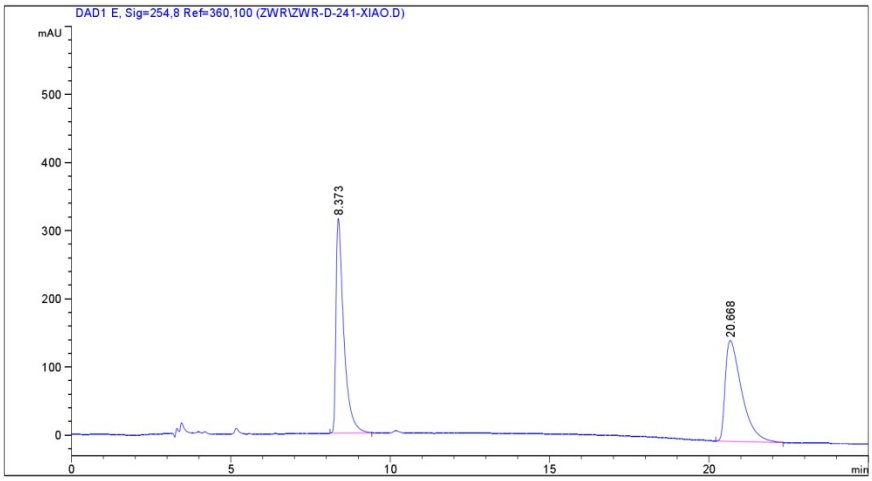


信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.808	BB	0.2593	7024.94336	395.31964	96.5529
2	16.893	MM R	0.3516	250.80075	11.88923	3.4471



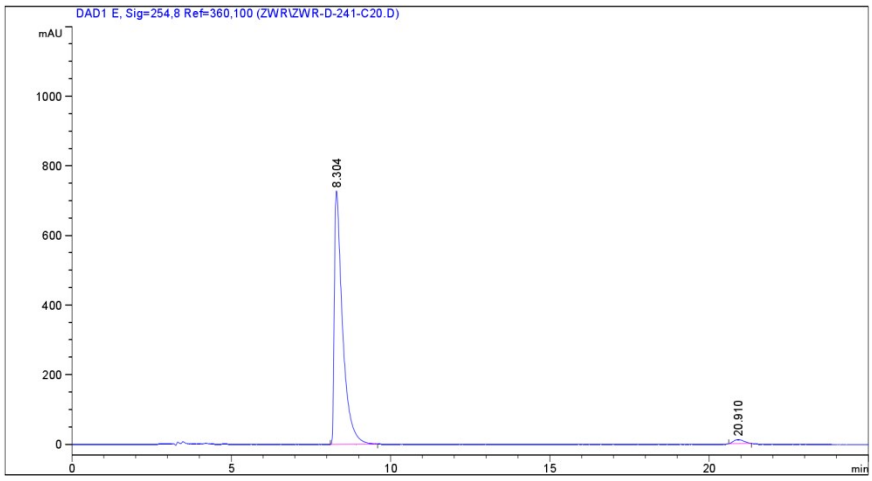
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

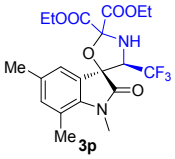
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.373	BB	0.2489	5375.18066	315.21082	50.2738
2	20.668	BB	0.5452	5316.62646	147.96509	49.7262

HPLC spectrum of the chiral compound



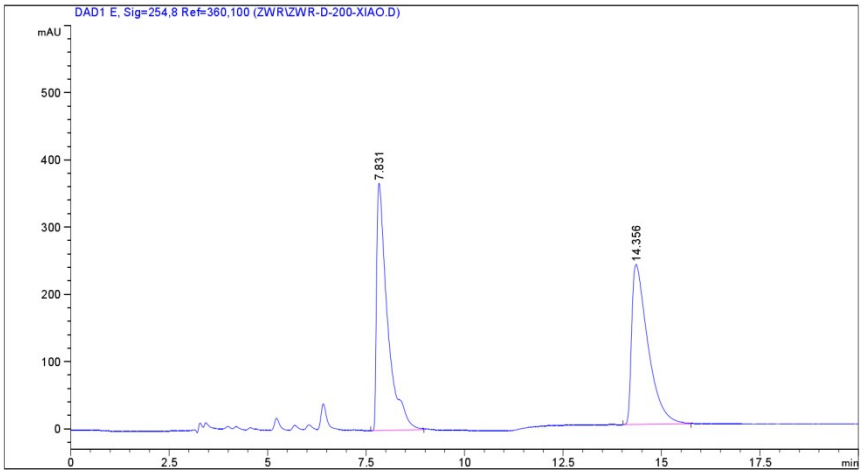
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.304	BB	0.2587	1.30323e4	728.46429	98.0617
2	20.910	MM R	0.3743	257.59369	11.47105	1.9383



3p

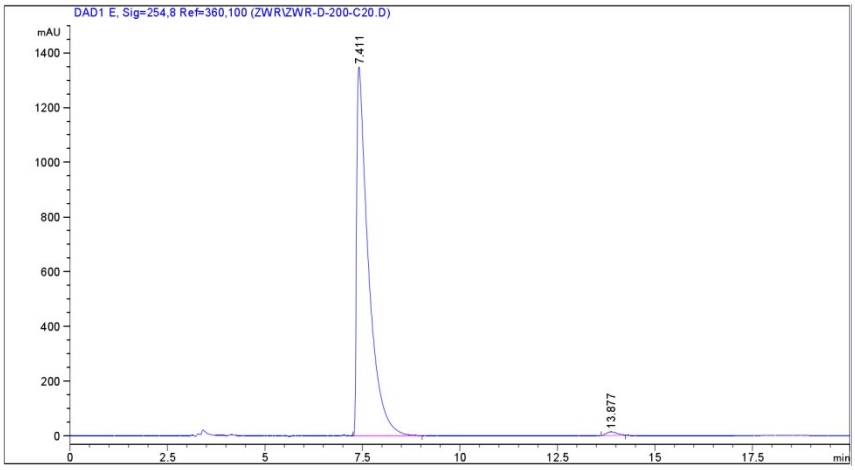
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

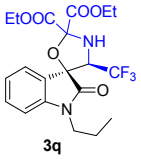
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.831	BB	0.2756	7113.29248	367.81454	50.9964
2	14.356	BB	0.4229	6835.33350	238.09776	49.0036

HPLC spectrum of the chiral compound



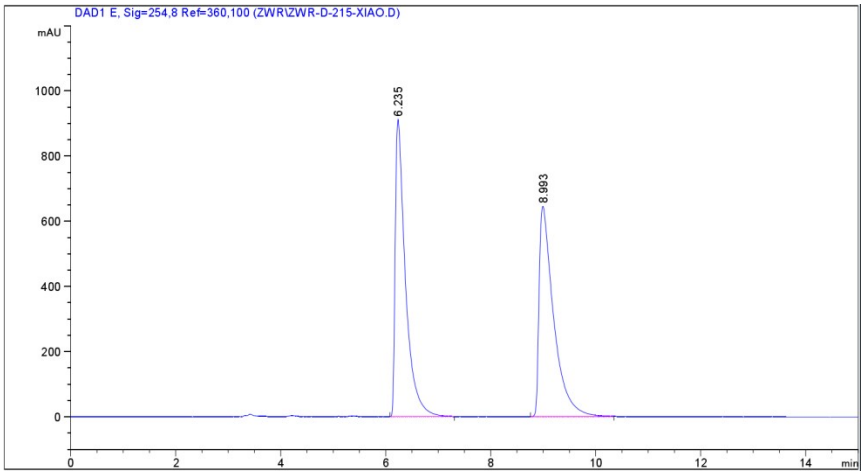
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.411	VB	0.2934	2.81178e4	1347.86340	99.1188
2	13.877	MM R	0.3172	249.97513	13.13626	0.8812



3q

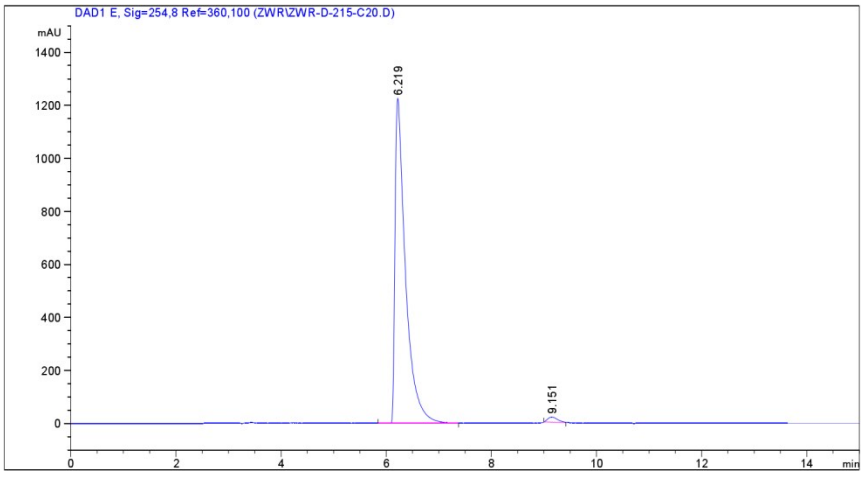
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

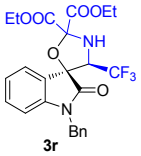
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.235	BB	0.1954	1.23049e4	912.26514	49.8460
2	8.993	BB	0.2798	1.23810e4	645.49097	50.1540

HPLC spectrum of the chiral compound



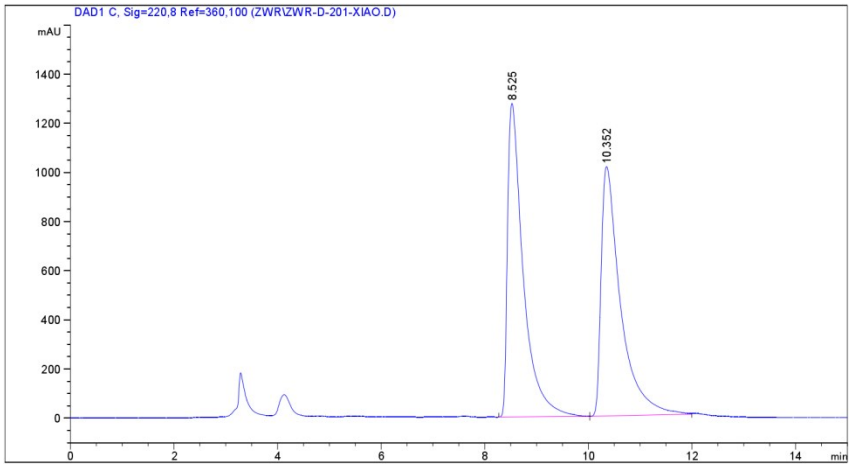
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.219	BB	0.1995	1.69634e4	1225.15601	98.5500
2	9.151	MM R	0.2155	249.59605	19.30588	1.4500



3r

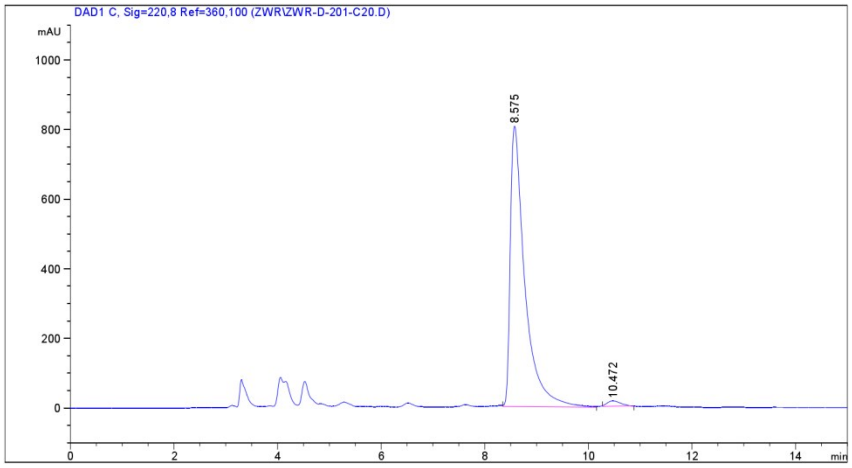
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=220,8 Ref=360,100

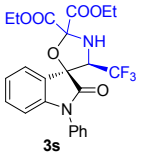
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.525	BV	0.3074	2.68487e4	1276.58691	50.4776
2	10.352	VB	0.3768	2.63406e4	1014.90851	49.5224

HPLC spectrum of the chiral compound



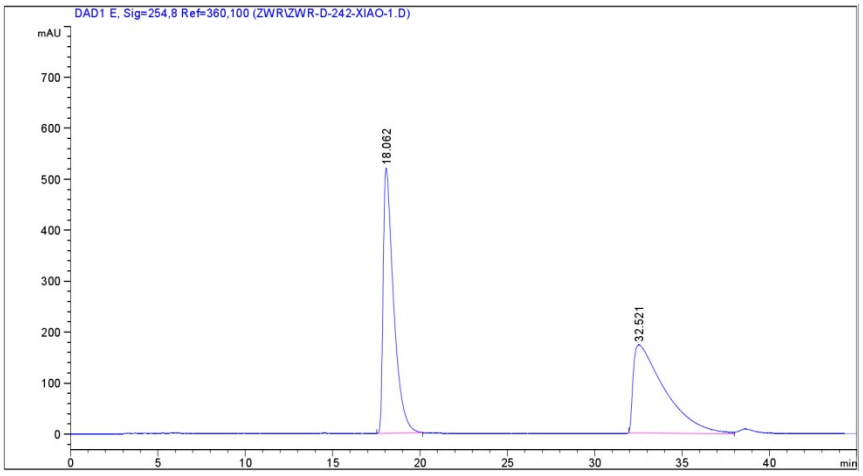
信号 1: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.575	MM R	0.3258	1.57537e4	805.85107	98.3383
2	10.472	MM R	0.2899	266.20459	15.30641	1.6617



3s

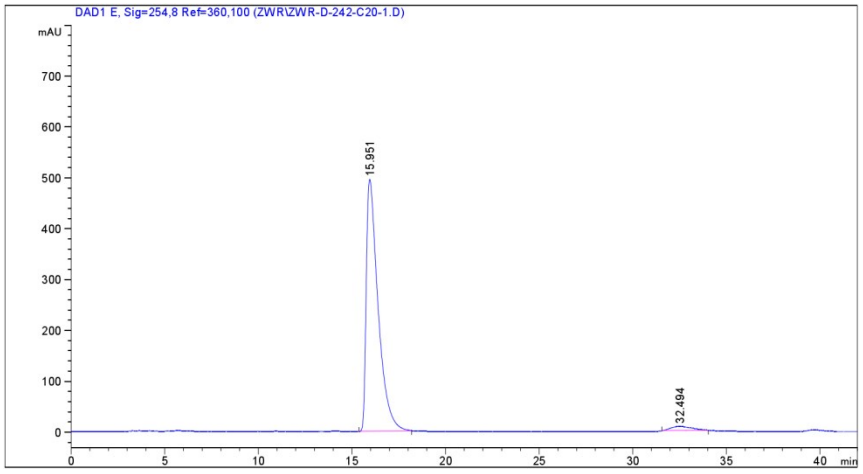
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

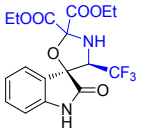
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.062	BB	0.6081	2.16007e4	520.61768	49.8783
2	32.521	MM R	2.0904	2.17062e4	173.06105	50.1217

HPLC spectrum of the chiral compound



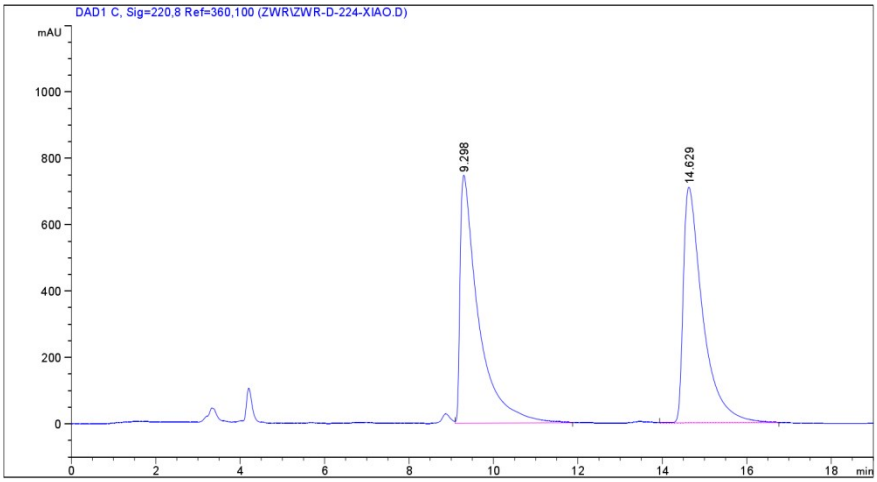
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.951	BB	0.6499	2.17413e4	495.51501	97.2864
2	32.494	MM R	1.3283	606.43573	7.60925	2.7136



3t

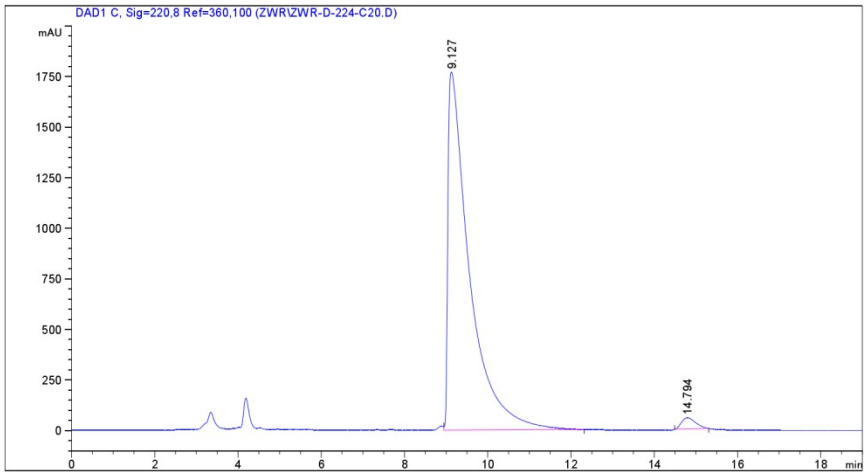
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=220,8 Ref=360,100

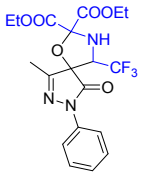
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.298	VB	0.4238	2.25330e4	747.27838	49.8165
2	14.629	VB	0.4708	2.26990e4	710.37402	50.1835

HPLC spectrum of the chiral compound



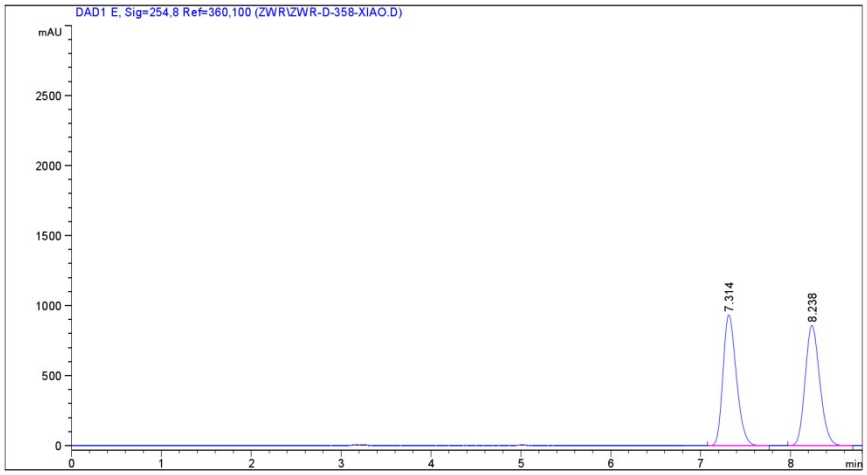
信号 1: DAD1 C, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.127	VB	0.5066	6.32087e4	1770.06873	98.0464
2	14.794	MM R	0.3839	1259.43494	54.67139	1.9536



3u

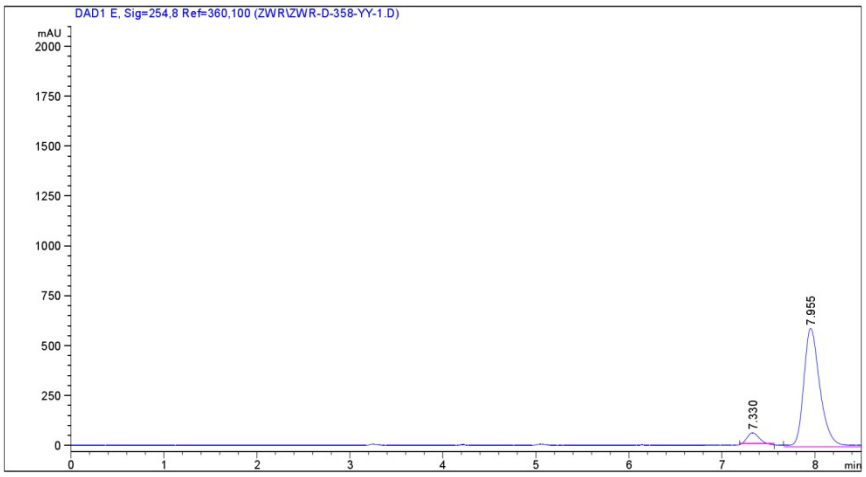
HPLC spectrum of the racemate



信号 1: DAD1 E, Sig=254,8 Ref=360,100

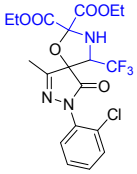
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.314	BB	0.1605	9657.23828	935.30853	49.8554
2	8.238	BB	0.1740	9713.27539	858.48425	50.1446

HPLC spectrum of the chiral compound



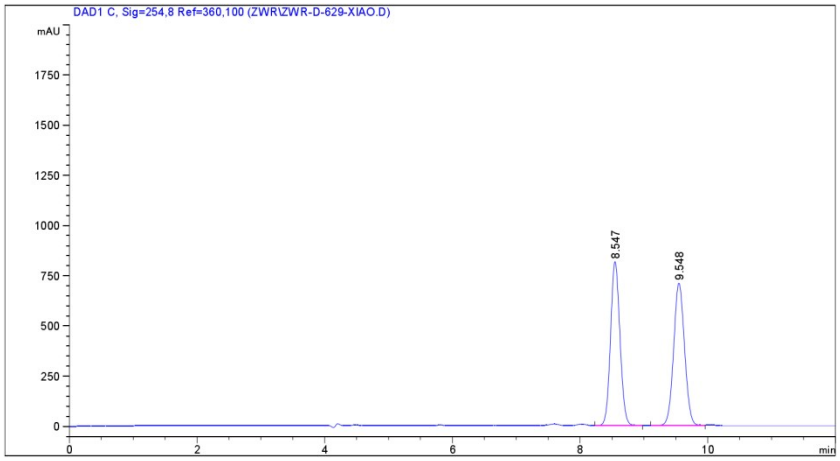
信号 1: DAD1 E, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.330	MM R	0.1362	424.31387	51.93313	4.9522
2	7.955	MM R	0.2277	8143.83301	596.21027	95.0478



3v

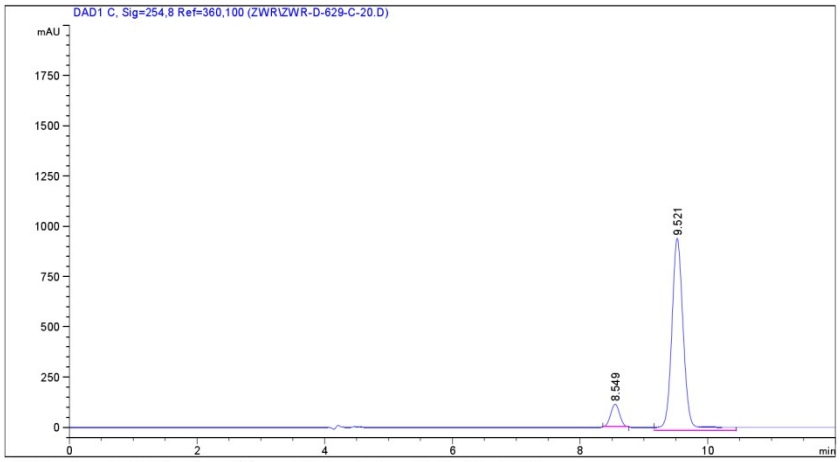
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=254,8 Ref=360,100

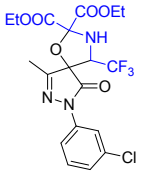
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.547	VB	0.1594	8348.12402	815.76562	49.7739
2	9.548	BB	0.1826	8423.97754	709.18329	50.2261

HPLC spectrum of the chiral compound



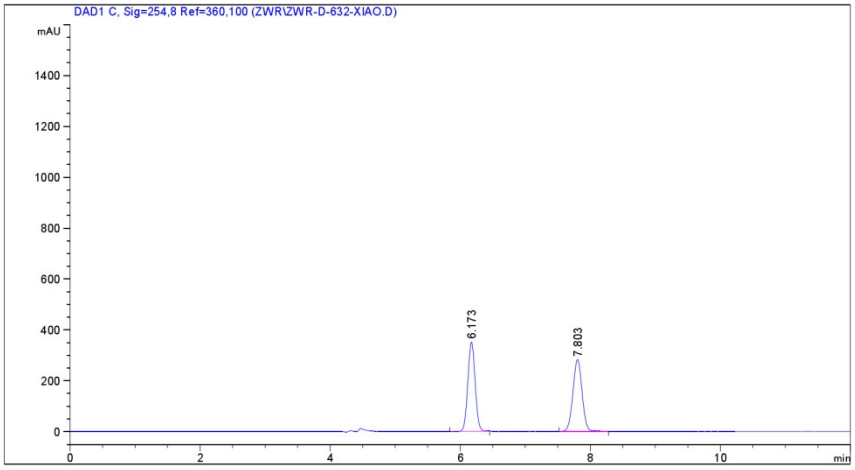
信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.549	MM R	0.1558	1026.55884	109.82549	7.6213
2	9.521	MM R	0.2168	1.24431e4	956.64935	92.3787



3w

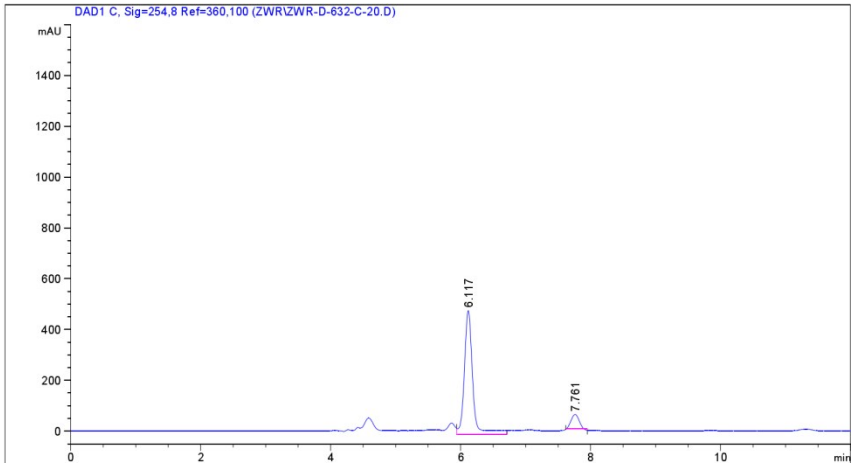
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=254,8 Ref=360,100

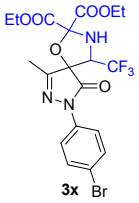
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.173	BB	0.1213	2748.66260	351.37128	49.7521
2	7.803	BB	0.1526	2776.05127	282.67242	50.2479

HPLC spectrum of the chiral compound



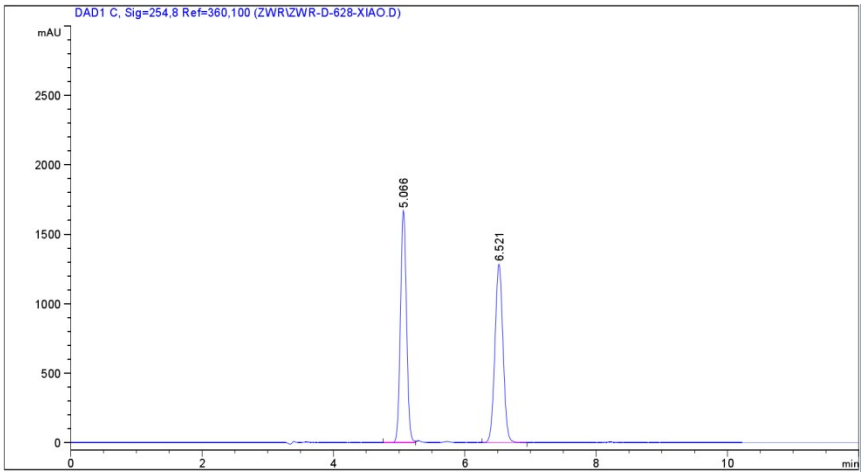
信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.117	MM R	0.1524	4474.48877	489.22321	90.0975
2	7.761	MM R	0.1424	491.78622	57.54036	9.9025



3x

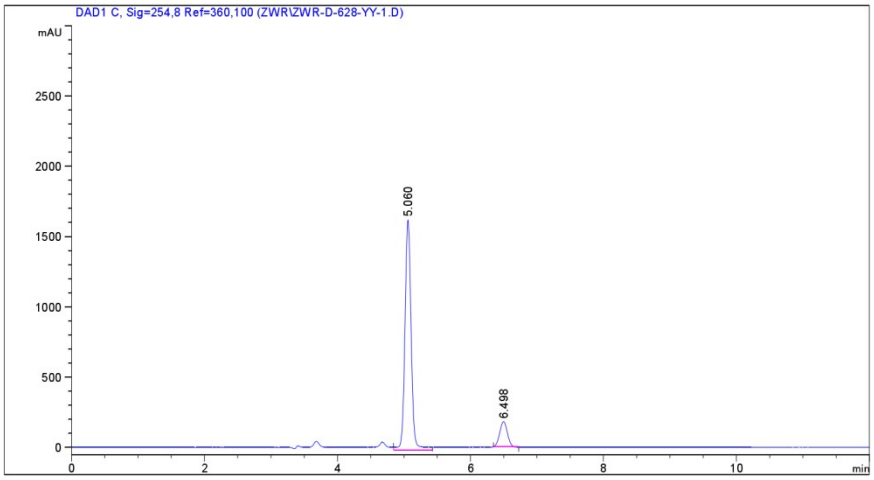
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=254,8 Ref=360,100

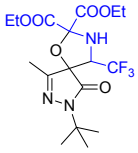
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.066	VV	0.1010	1.07297e4	1669.82471	49.3265
2	6.521	VB	0.1341	1.10227e4	1284.40063	50.6735

HPLC spectrum of the chiral compound



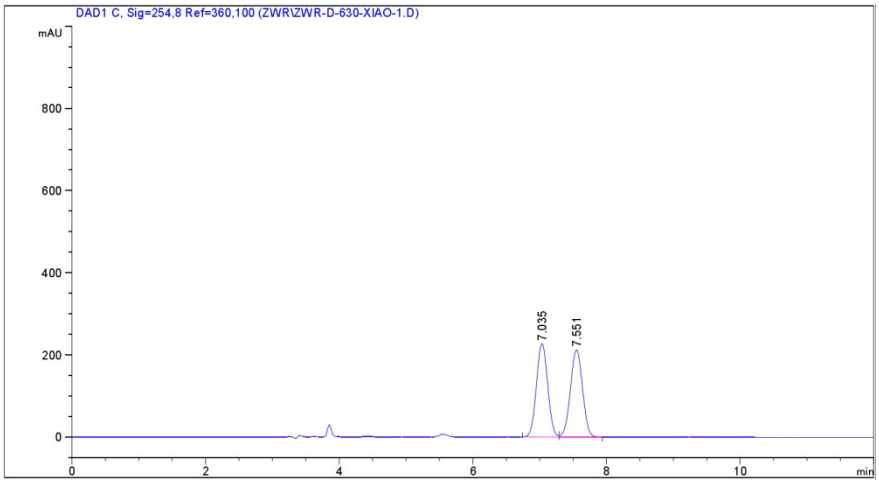
信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.060	MM R	0.1081	1.06276e4	1638.56396	88.5926
2	6.498	MM R	0.1295	1368.43567	176.05740	11.4074



3y

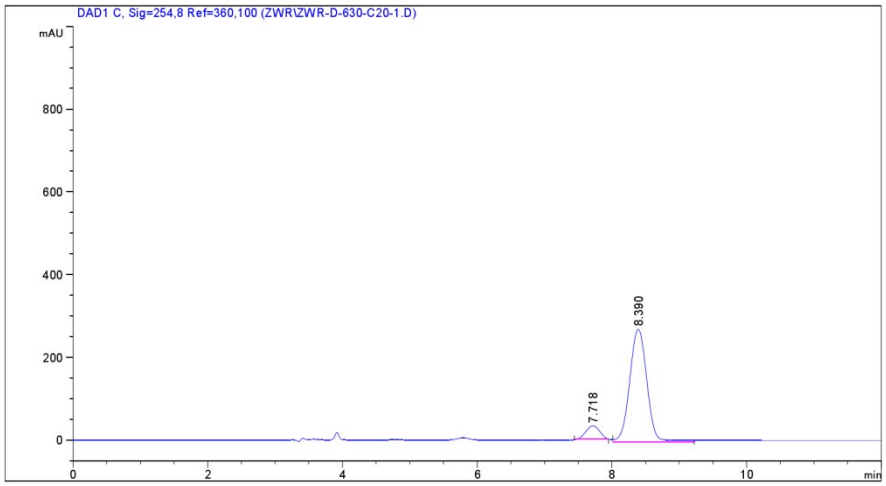
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=254,8 Ref=360,100

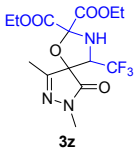
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.035	BV	0.1851	2673.10693	227.48076	49.9695
2	7.551	VB	0.1991	2676.37085	212.26019	50.0305

HPLC spectrum of the chiral compound



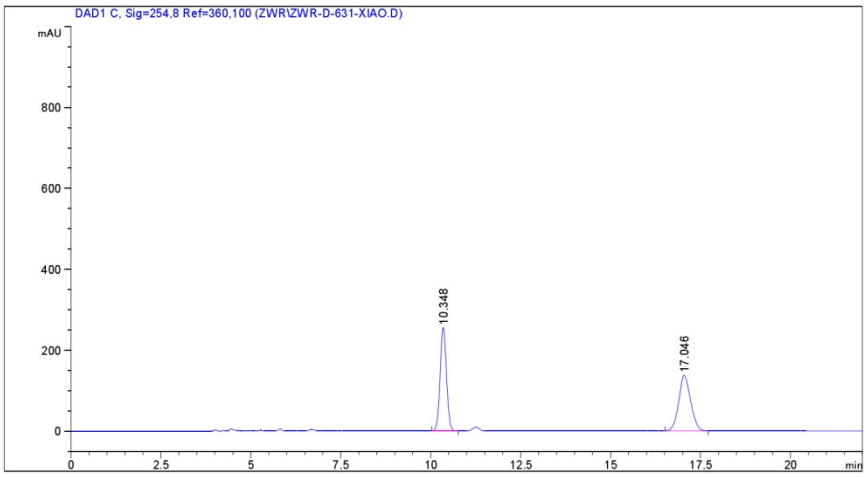
信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.718	MM R	0.2390	468.76962	32.68374	8.8518
2	8.390	MM R	0.2959	4826.97900	271.85806	91.1482



3z

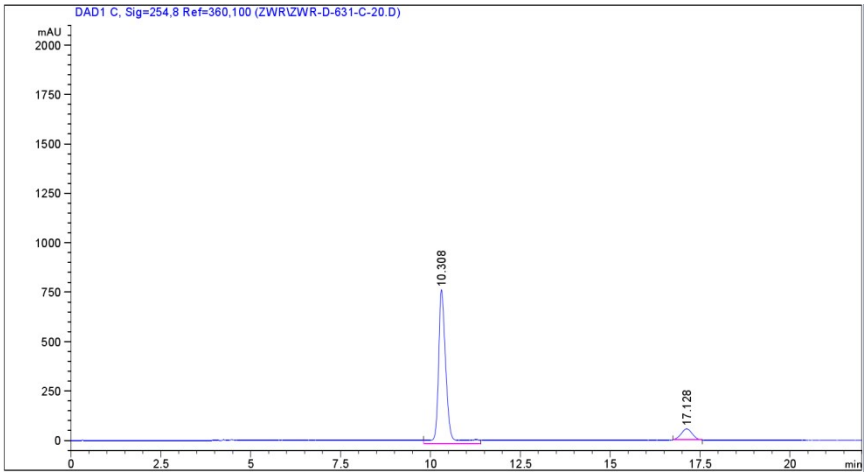
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=254,8 Ref=360,100

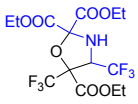
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.348	BB	0.1895	3144.93726	255.71109	49.9660
2	17.046	BB	0.3476	3149.22119	137.30154	50.0340

HPLC spectrum of the chiral compound



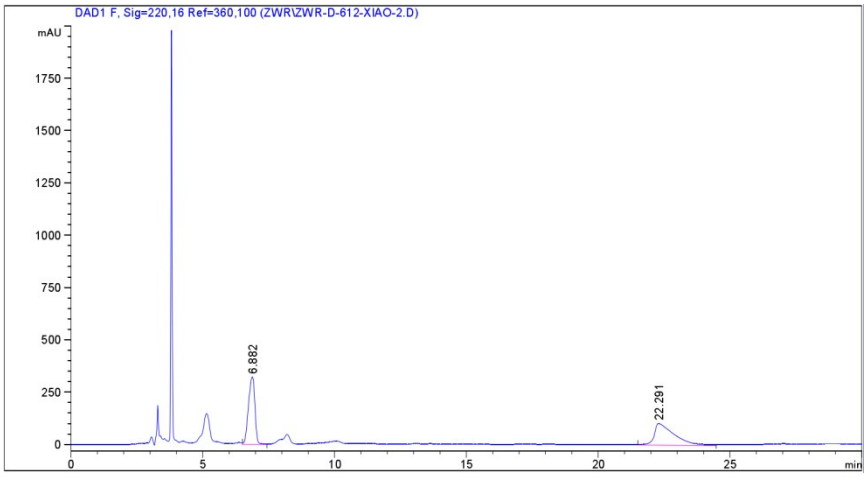
信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.308	MM R	0.2476	1.15707e4	778.83331	91.6262
2	17.128	MM R	0.3338	1057.45215	52.79362	8.3738



3aa

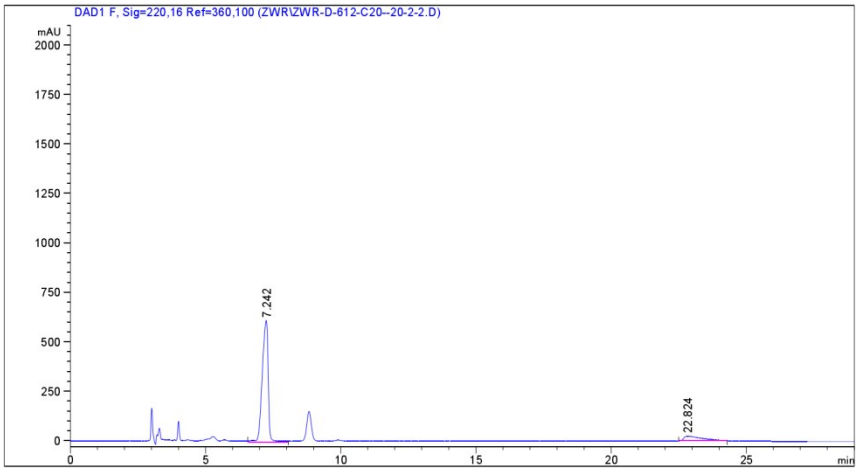
HPLC spectrum of the racemate



信号 1: DAD1 F, Sig=220,16 Ref=360,100

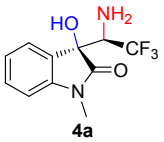
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.882	VB	0.2808	5505.06934	323.07227	49.8763
2	22.291	MM R	0.8889	5532.37598	103.73302	50.1237

HPLC spectrum of the chiral compound



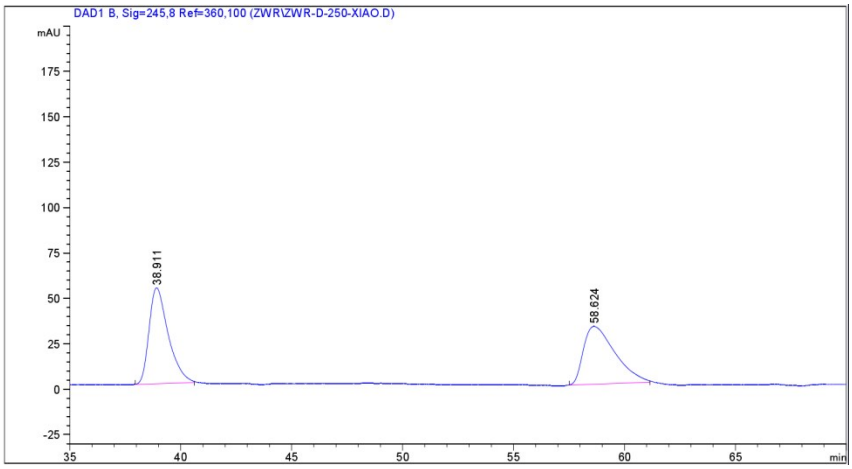
信号 1: DAD1 F, Sig=220,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.242	MM R	0.2558	9466.18164	616.73773	90.0572
2	22.824	MM R	0.7582	1045.11938	22.97465	9.9428



4a

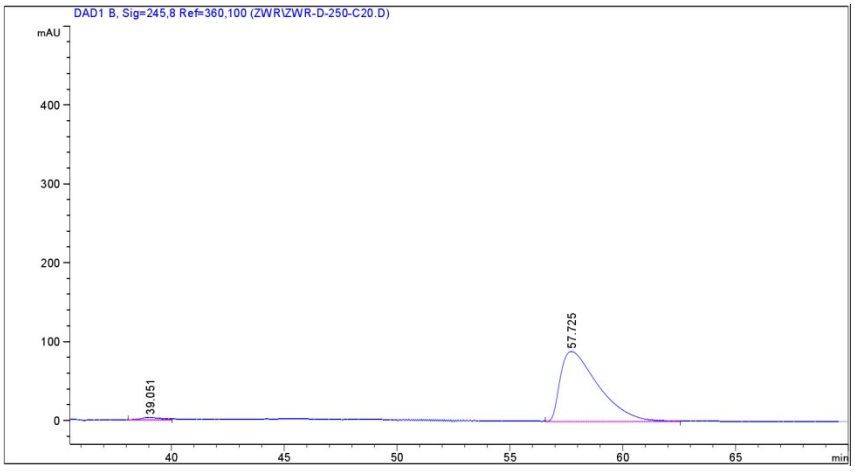
HPLC spectrum of the racemate



信号 1: DAD1 B, Sig=245,8 Ref=360,100

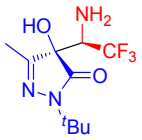
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	38.911	BB	0.8958	3177.13989	52.81759	50.2385
2	58.624	BB	1.3358	3146.97388	31.87579	49.7615

HPLC spectrum of the chiral compound



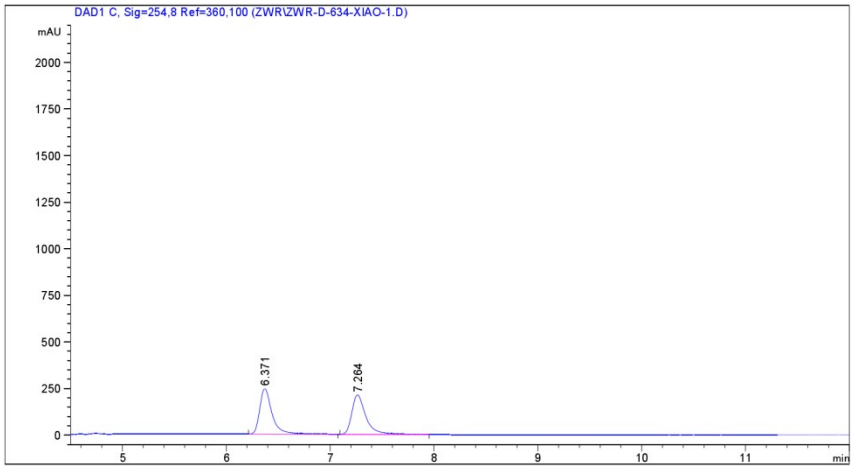
信号 1: DAD1 B, Sig=245,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	39.051	MM R	1.0838	183.21825	2.81752	1.7304
2	57.725	MM R	1.9515	1.04049e4	88.86322	98.2696



4y

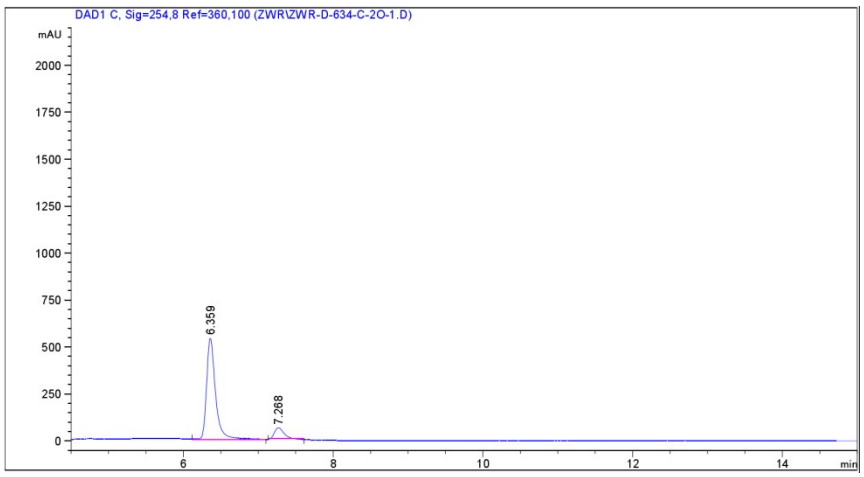
HPLC spectrum of the racemate



信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.371	BB	0.1248	2023.93164	243.85034	50.4573
2	7.264	BB	0.1417	1987.24854	211.37042	49.5427

HPLC spectrum of the chiral compound



信号 1: DAD1 C, Sig=254,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.359	MM R	0.1412	4592.78516	542.20740	90.1742
2	7.268	MM R	0.1411	500.44873	59.10970	9.8258