Supporting Information

Catalytic Asymmetric Ring-Opening/Cyclopropanation of Cyclic Sulfur Ylides: Construction of Sulfur-containing Spirocyclopropyloxindoles with Three Vicinal Stereocenters

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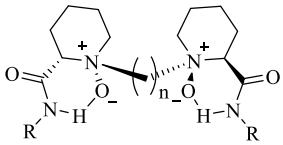
(A) General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.262 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.160 ppm). Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel ADH, IA, IB, IE at 23 ^{o}C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in CH_2Cl_2). HRMS were recorded on a commercial apparatus (ESI source). All the reactions were carried out under air condition. All the solvents were purified by usual methods before use. Molecular sieves were activated at 500 ^{o}C for 5 h before use. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

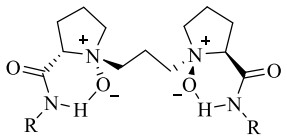
(B) General procedure for the synthesis of chiral *N,N'*-dioxides

The *N,N'*-dioxide ligands were prepared by the similar procedure in the literatures[1].

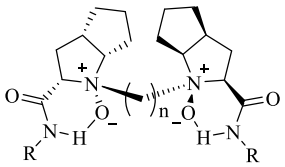
L-PiPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 3,
L-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 3,
L-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 3,
L-PiEt$_3$: R = 2,4,6-Et$_3$C$_6$H$_2$, n = 3,
L-PiEt$_2$Me: R = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 3,
L-PiMe$_3$: R = 2,4,6-Me$_3$C$_6$H$_2$, n = 3,
L-PiMe$_2$^{t}Bu: R = 2,6-Me$_2$-4-tBuC$_6$H$_2$, n = 3,
L-PiBn: R = C$_6$H$_5$CH$_2$, n = 3,
L-Pi*m*^{t}Bu$_2$: R = 3,5-^{i}Bu$_2$C$_6$H$_3$, n = 3,



L-Pi*p*MeO: R = 4-MeOC$_6$H$_4$, n = 3,
L-Pi*c*H: R = cyclohexyl, n = 3,
L-PiAd: R = Adamyl n = 3,
L$_2$-PiPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 2,
L$_2$-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2,
L$_2$-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 2,
L$_2$-PiEt$_2$Me: R = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 2,
L$_2$-PiPh: R = C$_6$H$_5$, n = 2,
L$_4$-PiPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 4,



L-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$



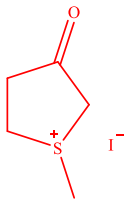
L-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 3,
L-RaEt$_2$Me: R = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 3,
L-RaPh: R = C$_6$H$_5$, n = 3,
L-Ra*c*P: R = cyclopentyl, n = 3,
L$_2$-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2,
L$_4$-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 4,

(C) General procedure for the synthesis of cyclic sulfur salts 9.

9a and **9d** were prepared by the similar procedure as following: dihydrothiophen-3(2*H*)-one (1.0 equiv) or 2-methyldihydrothiophen-3(2*H*)-one (1.0 equiv) was added dropwise to CH_3I (2.0 equiv) with continuous stirring in the dark. When solid was precipitated, it was filtered, washed with petroleum ether, dried under vacuum and stored in nitrogen atmosphere at 0 °C.

9b and **9c** were prepared by the similar procedure as following: C_2H_5I (2.0 equiv) or (2-iodoethyl)benzene (2.0 equiv) was added dropwise to the dihydrothiophen-3(2*H*)-one (1.0 equiv) and AgOTf (1.2 equiv) solution of CH_3CN with continuous stirring in the dark for 2 h at 0 °C. When solid was precipitated, it was filtered, washed with petroleum ether, dried under vacuum and stored in nitrogen atmosphere at 0 °C.

(D) The analytical and spectral characterization data of cyclic sulfur salts 9

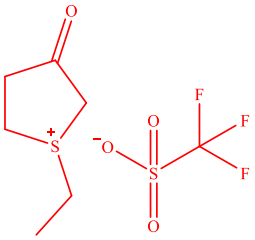


1-Methyl-3-oxotetrahydro-1*H*-thiophen-1-ium iodide (9a), C_5H_9IOS. White solid, ^{1}H NMR (400 MHz, d^6-DMSO) δ 3.97 (dd, *J* = 23.2, 17.8 Hz, 2H), 3.82 – 3.73 (m, 1H), 3.64 – 3.58 (m, 1H), 3.17 – 3.06 (m, 1H), 2.97 (s, 3H), 2.88 – 2.81 (m, 1H).

^{13}C NMR (101 MHz, d^6-DMSO) δ 205.9, 46.3, 36.3, 33.8, 24.2.

HRMS (ESI-FT) calcd for $C_5H_9OS^+$ ([M-I$^-$]) = 117.0369, Found 117.0371.

1-ethyl-3-oxotetrahydro-1*H*-thiophen-1-ium trifluoromethane- sulfonate



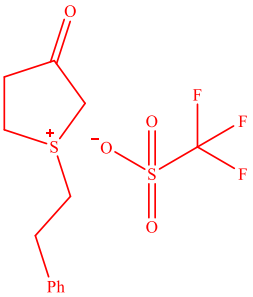
(**9b**), $C_7H_{11}F_3O_4S_2$. White solid, 1H NMR (400 MHz, d^6-DMSO) δ 4.01 (q, *J* = 18.0 Hz, 2H), 3.82 – 3.62 (m, 2H), 3.44 – 3.38 (m, 1H), 3.10 – 2.95 (m, 1H), 2.88 – 2.80 (m, 1H), 1.37 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, d^6-DMSO) δ 205.8, 43.8, 35.5, 34.4, 34.1, 9.4.

^{19}F NMR (376 MHz, d^6-DMSO) δ -77.8.

HRMS (ESI-FT) calcd for $C_6H_{11}OS^+$ ([M-OTf$^-$]) = 131.0525, Found 131.0525.

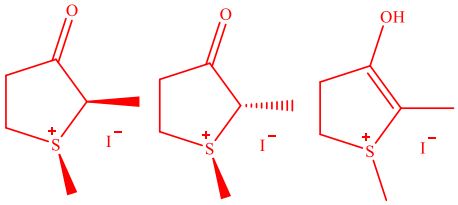
3-oxo-1-phenethyltetrahydro-1*H*-thiophen-1-ium trifluoromethane-sulfonate (9c), $C_{13}H_{15}F_3O_4S_2$. White solid, ^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ 7.91 – 6.93 (m, 5H), 4.06 (dd, *J* = 46.0, 18.0 Hz, 2H), 3.90 – 3.52 (m, 4H), 3.23 – 2.96 (m, 3H), 2.89 – 2.81 (m, 1H).



^{13}C NMR (101 MHz, *d*^{6}-DMSO) δ 205.7, 137.4, 128.8, 128.7, 127.2, 44.0, 41.7, 35.1, 34.1, 29.9.

^{19}F NMR (376 MHz, *d*^{6}-DMSO) δ -77.8.

HRMS (ESI-FT) calcd for $C_{12}H_{15}OS^+$ ([M-OTf$^-$]) = 207.0838, Found 207.0842.

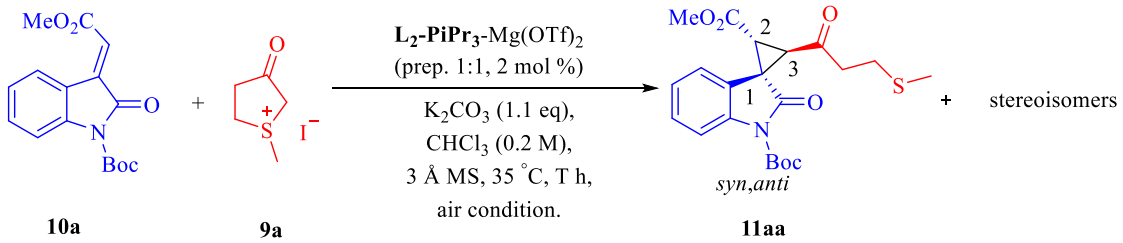


Sulfur salt **9d** include three isomers, they are ***syn*-1,2-dimethyl-3-oxotetrahydro-1*H*-thio phen-1-ium, *anti*-1,2-dimethyl-3-oxotetrahydro-1*H*-thio phen-1-ium** and **4-hydroxy-1,5-dimethyl-2,3-dihydro-1*H*-thiophen-1-ium iodide,** (*syn*: *anti*: enolate = 1:1.34: 0.66), $C_6H_{11}IOS$. ^{1}H NMR (400 MHz, *d*^{6}-DMSO) δ 11.22 (s, 0.66H, enolate), 4.48 (q, *J* = 7.2 Hz, 0.44H, *anti*), 4.20 (q, *J* = 7.4 Hz, 0.33H, *syn*), 3.95 – 3.62 (m, 1.54H), 3.59 – 3.42 (m, 0.77H), 3.29 – 3.14 (m, 0.66H), 3.11 (s, 1H), 3.09 – 2.98 (m, 1H), 2.97 – 2.90 (m, 0.66H), 2.88 (s, 0.66H), 2.80 (s, 1.34H), 1.85 (s, 0.66H, enolate), 1.54 (d, *J* = 7.6 Hz, 1H, *syn*), 1.42 (d, *J* = 7.2 Hz, 1.34H, *anti*).

^{13}C NMR (101 MHz, *d*^{6}-DMSO) δ 207.1, 163.0, 92.4, 56.3, 53.4, 34.4, 34.0, 33.8, 32.4, 31.1, 27.4, 25.5, 17.3, 13.2, 9.0, 8.7.

HRMS (ESI-FT) calcd for $C_6H_{11}OS^+$ ([M-I$^-$]) = 131.0525, Found 131.0529.

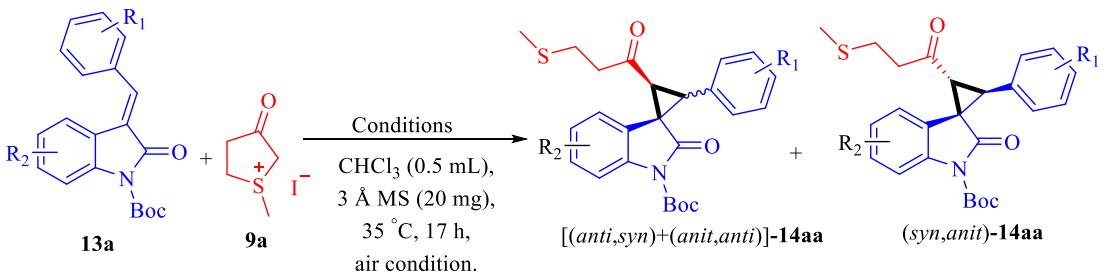
(E) General procedure for the catalytic asymmetric reaction of 10a with 9a.



Preparation of the catalyst: A dry reaction tube was charged with **L_2-PiPr$_3$** (0.1 mmol, 71.9 mg) and Mg(OTf)$_2$ (0.1 mmol, 32.2 mg) under N_2 atmosphere. Then, $CHCl_3$ (3.0 mL) was added and the resulting solution was stirred at 35 °C for 2 h. Then, removing the solvent under vacuo obtained colorless powder, which was keeped under N_2 atmosphere. Other catalysts were prepared by the similar procedure.

General procedure: To an oven-dried tube was charged with **L_2-PiPr$_3$**/Mg(OTf)$_2$ (prep., 1:1, 2 mol %), **10a** (0.1 mmol, 30.3 mg), **9a** (0.11 mmol, 24.4 mg), 3 Å MS 20.0 mg, K_2CO_3 (0.11 mmol, 15.2 mg) and $CHCl_3$ (0.5 mL), the reaction mixture was stirred at 35 °C for 4 h under air atmosphere. The reaction mixture was then purified directly by flash column chromatography (ethyl acetate/petroleum ether = 1:9 – 1:4) to afford the corresponding product **11aa** (96% yield).

(F) General procedure for the catalytic asymmetric reaction of 13a with 9a.



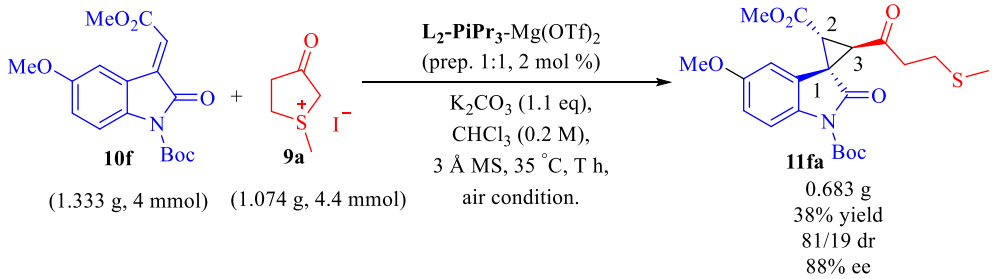
Condition A: **13a/9a** = 1/1.2, **L_4-PiPr$_3$**/Mg(OTf)$_2$ (2 mol %, prep.), K_2CO_3 (0.12 mmol)
Condition B: **13a/9a** = 1/1.1, **L_2-PiEt$_2$**/Mg(OTf)$_2$ (2 mol %, prep.), K_2CO_3 (0.11 mmol)
Condition C: **13a/9a** = 1/1.5, **L_4-RaPr$_2$**/Mg(OTf)$_2$ (2 mol %, prep.), K_2CO_3 (0.15 mmol)

General procedure for condition A: To an oven-dried tube was charged with **L4-PiPr3**/Mg(OTf)2 (prep. 1:1, 2 mol %), **13a** (0.1 mmol, 32.1 mg), **9a** (0.12 mmol, 26.9 mg), 3 Å MS 20.0 mg, K_2CO_3 (0.12 mmol, 16.6 mg) and $CHCl_3$ (0.5 mL), the reaction mixture was stirred at 35 °C for 17 h under air condition. The reaction mixture was then purified directly by flash column chromatography (ethyl acetate/petroleum ether = 1:9) to afford the major product (*syn*,*anti*)-**14aa**.

General procedure for condition B: To an oven-dried tube was charged with **L2-PiEt2**/Mg(OTf)2 (prep. 1:1, 2 mol %), **13a** (0.1 mmol), **9a** (0.11 mmol, 24.4 mg), 3 Å MS 20.0 mg, K_2CO_3 (0.11 mmol, 15.2 mg) and $CHCl_3$ (0.5 mL), the reaction mixture was stirred at 35 °C for 17 h under air condition. The reaction mixture was then purified directly by flash column chromatography (ethyl acetate/petroleum ether = 1:9) to afford the major product (*anti*,*anti*)-**14aa**.

General procedure for condition C: To an oven-dried tube was charged with **L4-RaPr2**/Mg(OTf)2 (prep. 1:1, 2 mol %), **15a** (0.1 mmol), **9a** (0.15 mmol, 33.6 mg), 3 Å MS 20.0 mg, K_2CO_3 (0.15 mmol, 20.7 mg) and $CHCl_3$ (0.5 mL), the reaction mixture was stirred at 35 °C for 17 h under air condition. The reaction mixture was then purified directly by flash column chromatography (ethyl acetate/petroleum ether = 1:9) to afford the major product (*anti*,*syn*)-**14aa**.

(G) Experimental procedure for the scale-up reaction

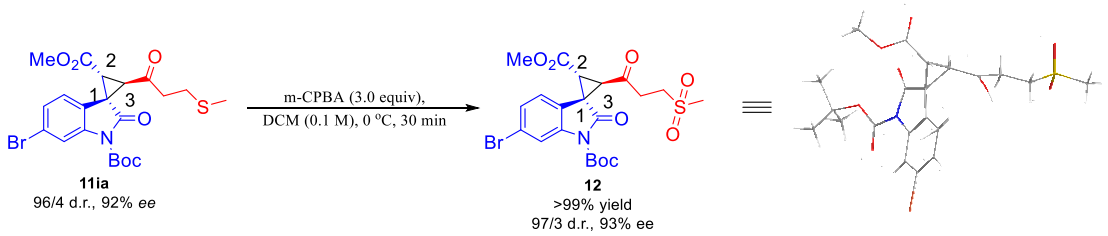


General procedure: To an oven-dried flask was charged with **L2-PiPr3**/Mg(OTf)2 (prep., 1:1, 2 mol %, 83.4 mg), **10f** (4 mmol, 1.333 g), **9a** (4.4 mmol, 1.074 mg), 3Å MS (800 mg), K_2CO_3 (4.4 mmol, 669 mg) and $CHCl_3$ (20.0 mL), the reaction mixture was stirred at 35 °C for 23 h under air atmosphere. The reaction mixture was then purified directly by flash column chromatography (ethyl acetate/petroleum ether = 1:9 – 1:4) to afford the corresponding product

11fa (38% yield, 81/19 dr, 88% ee) and recycled starting material **10f** (37% yield).

Note: We assumed that the bad results for the scale-up reaction mainly resulted from the low solubility of substrate **9a**, 3Å MS, and K_2CO_3 in chloroform, which caused a heterogeneous system under reaction conditions. As you shown above, the yield did not improve although we extended the reaction time from 4 h to 23 h.

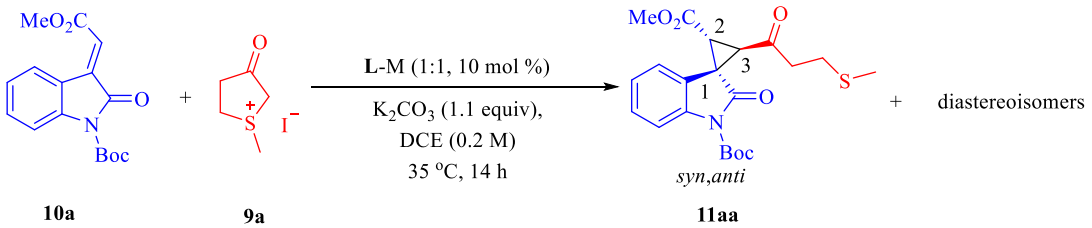
(H) Experimental procedure for the transformation of 11ia.



To an oven-dried reaction tube was added **11ia** (99.6 mg, 0.20 mmol) and CH_2Cl_2 (2.0 mL). The mixture was cool to 0 °C, then *m*-CPBA (3.0 equiv, 0.6 mmol, 103.6 mg) was added. The reaction mixture was stirred at 0 °C for 30 min, and purified directly by flash column chromatography (ethyl acetate/dichloromethane = 1:1) to afford the desired product (106.0 mg, 99% yield, 97/3 dr, 93% ee). The absolute configuration of **12** was determined to be (1*S*,2*R*,3*R*) by X-ray crystallographic analysis (CCDC 1841132). The supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(I) Optimization of reaction conditions

Table 1: Screening of ligand and metal salt.[a]

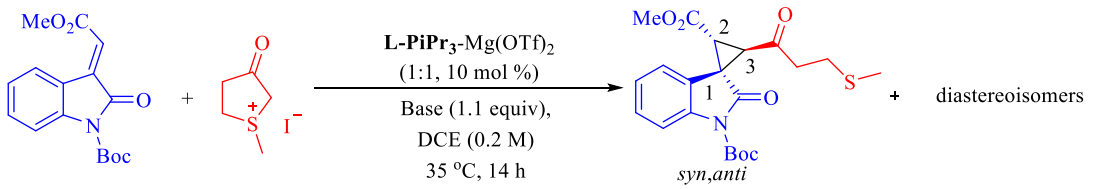


Entry	Ligand	Metal	Yield (%)[b]	d.r. (%)[c]	ee (%)[d]
1	**L-PiPr$_2$**	$Mg(OTf)_2$	87	71/29	90

2	**L-RaPr$_2$**	Mg(OTf)$_2$	97	50/50	70
3	**L-PrPr$_2$**	Mg(OTf)$_2$	85	76/24	75
4	**L-PiPr$_3$**	Mg(OTf)$_2$	85	78/22	95
5	**L-PiEt$_2$**	Mg(OTf)$_2$	88	65/35	90
6	**L-PiBn**	Mg(OTf)$_2$	85	92/8	66
7	**L-Pi*c*H**	Mg(OTf)$_2$	90	94/6	64
8	**L-PiAd**	Mg(OTf)$_2$	84	93/7	40
9	**L-Pi*m*^{t}Bu$_2$**	Mg(OTf)$_2$	77	88/12	-32
12	**L-Pi*p*MeO**	Mg(OTf)$_2$	81	94/6	35
13	**L$_2$-PiPr$_3$**	Mg(OTf)$_2$	79	93/7	88
14	**L$_2$-PiPr$_2$**	Mg(OTf)$_2$	78	94/6	86
15	**L$_2$-PiPr$_3$**	Ni(OTf)$_2$	89	84/16	88
16	**L$_2$-PiPr$_3$**	Mg(NTf$_2$)$_2$	87	91/9	80

[a] Unless otherwise noted, all reactions were performed with **L**-M (1:1, 10 mol %), **10a** (0.1 mmol, 30.3 mg) **9a** (0.1 mmol, 22.4 mg), K_2CO_3 (0.11 mmol, 15.2 mg) in DCE (0.5 mL) under N_2 at 35 °C for 14 h. [b]Total yield, the *syn,anti* isomer couldn't be isolated with other diastereoisomers. [c] d.r. is the ratio of *syn,anti*/other diastereoisomers, determined by chiral HPLC analysis. [d] ee for *syn,anti* isomer, determined by chiral HPLC analysis.

Table 2: Screening of base.[a]



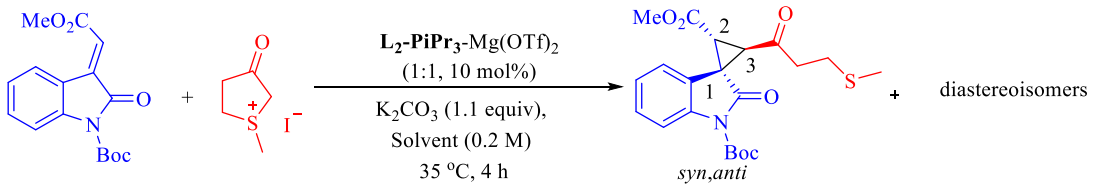
10a **9a** **11aa**

Entry	Base	Yield (%)[b]	d.r. (%)[c]	ee (%)[d]
1	Na_2CO_3	18	52/48	60
2	Cs_2CO_3	79	93/8	72
3	DABCO	Mess	nd	nd
4	DMAP	Mess	nd	nd
5	$K_3PO_4 \cdot 7H_2O$	Mess	nd	nd
6	$Na_3PO_4 \cdot 12H_2O$	Mess	nd	nd

[a] Unless otherwise noted, all reactions were performed with **L$_2$-PiP$_3$**-Mg(OTf)$_2$ (1:1, 10 mol %), **10a** (0.1 mmol, 30.3 mg) **9a** (0.1 mmol, 22.4 mg), Base (0.11 mmol) in DCE (0.5 mL) under N_2 at 35 °C for 14 h. [b] Total

yield，the *syn,anti* isomer couldn't be isolated with other diastereoisomers. [c] d.r. is the ratio of *syn,anti*/diastereoisomers, determined by chiral HPLC analysis. [d] ee for *syn,anti* isomer, determined by chiral HPLC analysis.

Table 3: Screening of solvent.[a]

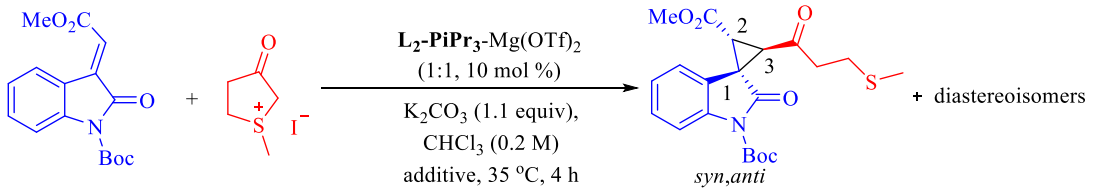


10a **9a** **11aa**

Entry	Solvent	Yield (%)[b]	d.r. (%)[c]	ee (%)[d]
1[e]	DCE	82	85/15	88
2	$CHCl_3$	90	90/10	90
3	TCE	90	90/10	90
4	THF	85	93/7	11
5	EA	77	93/7	35
6	DCM	79	96/4	81

[a] Unless otherwise noted, all reactions were performed with **L_2-PiP$_3$**-Mg(OTf)$_2$ (1:1, 10 mol %), **10a** (0.1 mmol, 30.3 mg) **9a** (0.1 mmol, 22.4 mg), K_2CO_3 (0.11 mmol, 15.2 mg) in solvent (0.5 mL) under N_2 at 35 °C for 14 h. [b] Total yield，the *syn,anti* isomer couldn't be isolated with other diastereoisomers. [c] d.r. is the ratio of *syn,anti*/diastereoisomers, determined by chiral HPLC analysis. [d] ee for *syn,anti* isomer, determined by chiral HPLC analysis. [e] 1.0 mL of DCE was used.

Table 4: Screening of additive.[a]



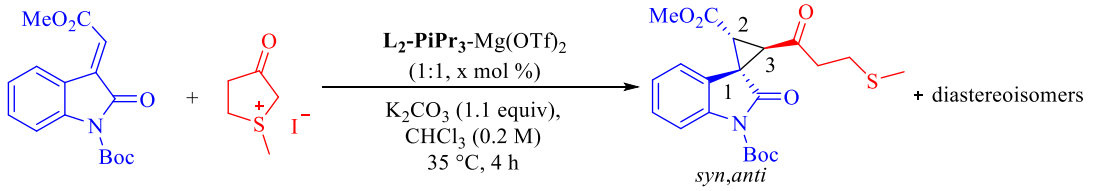
10a **9a** **11aa**

Entry	Additive	Yield (%)[b]	d.r. (%)[c]	ee (%)[d]
1	none	85	91/9	91
2	3 Å MS (20.0 mg)	77	91/9	92
3	4 Å MS (20.0 mg)	58	89/11	86
4	5 Å MS (20.0 mg)	42	91/9	83
5	$NaBAr^F{}_4$ (8.9 mg)	93	90/10	88

[a] Unless otherwise noted, all reactions were performed with **L_2-PiP$_3$**-Mg(OTf)$_2$ (1:1, 10 mol %), **10a** (0.1

mmol, 30.3 mg), **9a** (0.11 mmol, 26.8 mg), additive and K_2CO_3 (0.11 mmol, 15.2 mg) in $CHCl_3$ (0.5 mL) under N_2 at 35 °C for 4 h. [b]Total yield, the *syn-anti* isomer couldn't be isolated with other diastereoisomers. [c] d.r. is the ratio of *syn,anti*/diastereoisomers, determined by chiral HPLC analysis. [d] ee for *Syn,anti* isomer, determined by chiral HPLC analysis.

Table 5: The screen of catalyst loading. [a]

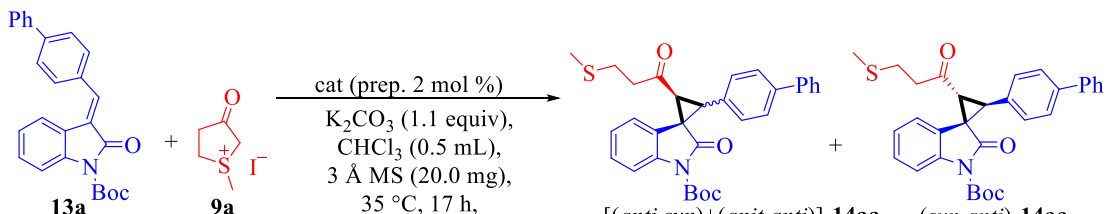


10a **9a** **11aa**

Entry	x	Additive	Yield (%)[b]	d.r. (%)[c]	ee (%)[d]
1	10	none	85	90/10	91
2	5	none	93	93/7	92
3	2	none	80	95/5	75
4	1	none	76	95/5	60
5[e]	5	none	88	91/9	92
6[e]	5	3 Å MS (20 mg)	99	90/10	92
7[e]	2	3 Å MS (20 mg)	96	93/7	92
8[e]	1	3 Å MS (20 mg)	84	92/8	86
9[e,f]	1	3 Å MS (20 mg)	97	88/12	93
10[e,g]	2	3 Å MS (20 mg)	96	93/7	92

[a] Unless otherwise noted, all reactions were performed with **L_2-PiP$_3$**-Mg(OTf)$_2$ (1:1, x mol %), **10a** (0.1 mmol, 30.3 mg), **9a** (0.11 mmol, 26.8 mg), additive and K_2CO_3 (0.11 mmol, 15.2 mg) in $CHCl_3$ (0.5 mL) under N_2 at 35 °C for 4 h. [b] Total yield, the *syn-anti* isomer couldn't be isolated with other diastereoisomers. [c] d.r. is the ratio of *syn,anti*/diastereoisomers, determined by chiral HPLC analysis. [d] ee for *syn,anti* isomer, determined by chiral HPLC analysis. [e] the catalyst was prepared in $CHCl_3$ before used, and catalyst, **10a**, **9a**, additive and K_2CO_3 were weighed to reactor, then $CHCl_3$ was added. [f] at 45 °C for 7 h. [g] air condition.

Table 6: Optimization of reaction conditions for **13a** reacting with **9a**.[a]



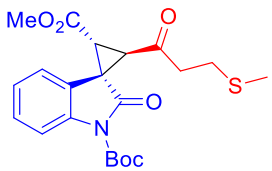
13a (0.1 mmol) **9a** (0.11 mmol) [(*anti,syn*)+(*anit,anti*)]-**14aa** (*syn,anti*)-**14aa**

entry	cat (prep.)	[(*anti,syn*)+(*anti,anti*)]-**14aa**			(*syn,anti*)-**14aa**	
		yield (%)[b]	d.r. (%)[c]	*ee* (%)[c]	yield (%)[e]	*ee* (%)[c]
1	**L$_2$-PiPr$_2$**/Mg(OTf)$_2$	52	74/26	-47	34	97
2	**L$_2$-PiEt$_2$**/Mg(OTf)$_2$	67	9/91	67	19	90
3	**L$_2$-PiMe$_2$**/Mg(OTf)$_2$	64	4/96	60	11	88
4	**L$_2$-PiPh**/Mg(OTf)$_2$	66	3/97	<5	6	61
5	**L-PiEt$_3$**/Mg(OTf)$_2$	27	23/77	-54	36	99
6	**L-PiEt$_2$Me**/Mg(OTf)$_2$	32	26/74	-57	49	98
7	**L-PiMe$_3$**/Mg(OTf)$_2$	56	11/89	-29	14	96
8	**L-PiMe$_2$^{t}Bu**/Mg(OTf)$_2$	58	10/90	<5	15	95
9	**L-PiBu$_2$**/Mg(OTf)$_2$	23	7/93	<5	<5	Nd
10	**L-PiPr$_3$**/Mg(OTf)$_2$	37	53/47	99	51	98
11	**L$_4$-PiPr$_3$**/Mg(OTf)$_2$	47	83/17	98	48	99
12	**L-RaEt$_2$Me**/Mg(OTf)$_2$	49	80/20	98	34	99
13	**L-RaPr$_2$**/Mg(OTf)$_2$	46	81/9	98	33	98
14	**L-RaPh**/Mg(OTf)$_2$	21	14/86	47	6	93
15	**L-Rac*P***/Mg(OTf)$_2$	12	6/94	43	8	90
16	**L$_2$-RaPr$_3$**/Mg(OTf)$_2$	26	6/94	18	6	94
17	**L$_3$-RaPr$_3$**/Mg(OTf)$_2$	51	81/19	98	42	99
18	**L$_4$-RaPr$_2$**/Mg(OTf)$_2$	77	90/10	99	19	99

[a] Unless otherwise noted, all reactions were performed with cat. (prep. 1:1, 2 mol %), **13a** (0.10 mmol), **9a** (0.11 mmol), 1.1 equiv of K_2CO_3 in $CHCl_3$ (0.5 mL) under air condition at 35 °C for 17 h. [b] The isolated total yield of *anti,anti* and *anti,syn* isomers. [c] Ratio of (*anti,anti*)/(*anti,syn*). [d] Isolated yield of *syn,anti* isomer.

(J) The analytical and spectral characterization data of products

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-3-[3-(methylthio)-propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11aa)



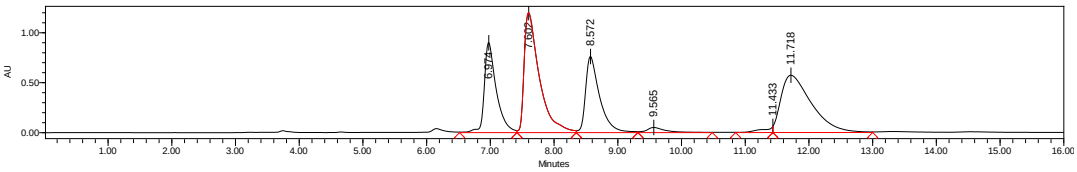
White solid, m.p. 30 – 34 °C, 40.2 mg, 96% yield, 92/8 d.r. (determined by ^{1}H NMR), 92% ee. $[\alpha]^{27}_D$ = -214.0 (*c* = 0.60 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 7.61 min, t_R (major) = 12.09 min.

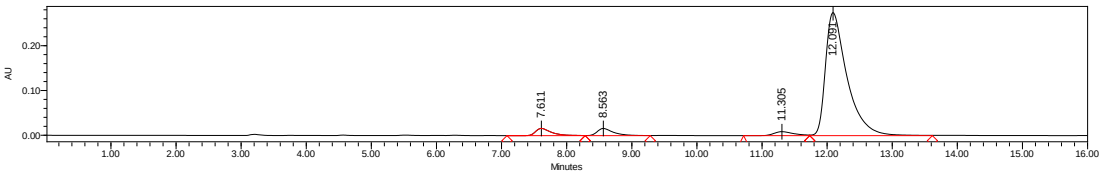
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 1H), 7.34 – 7.28 (m, 1H), 7.16 – 7.05 (m, 2H), 3.75 (s, 2.76H), 3.72 (s, 0.12H), 3.68 (s, 0.12H), 3.51 (d, *J* = 8.0 Hz, 1H), 3.39 (d, *J* = 8.0 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.71 – 2.52 (m, 3H), 2.07 (s, 0.12H), 2.05 (s, 0.12H), 1.99 (s, 2.76H), 1.68 (s, 0.72H), 1.64 (s, 8.28H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 170.5, 166.1, 148.9, 140.3, 129.0, 124.6, 122.8, 122.4, 115.1, 85.1, 52.9, 44.4, 43.1, 39.7, 35.5, 28.2, 27.4, 15.8.

HRMS (ESI-FT) calcd for $C_{21}H_{25}NaNO_6S^+$ ([M+Na$^+$]) = 442.1295, Found 442.1295.

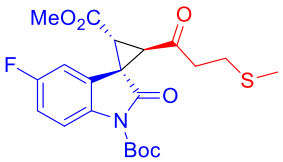


	Retention Time	Area	% Area
1	6.974	11771643	18.38
2	7.602	19778325	30.88
3	8.572	11680706	18.24
4	9.565	1086097	1.70
5	11.433	660200	1.03
6	11.718	19076032	29.78



	Retention Time	Area	% Area
1	7.611	271570	3.86
2	8.563	281668	4.00
3	11.305	187642	2.67
4	12.091	6296847	89.47

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-5'-fluoro-3-[3-(methylthio)-propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ba)



White solid, m.p. 72 – 76 °C, 35.1 mg, 80% yield, 98/2 d.r. (determined by ^{1}H NMR), 92% ee. $[\alpha]^{25}_{D}$ = -195.6 (*c* = 0.59 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0

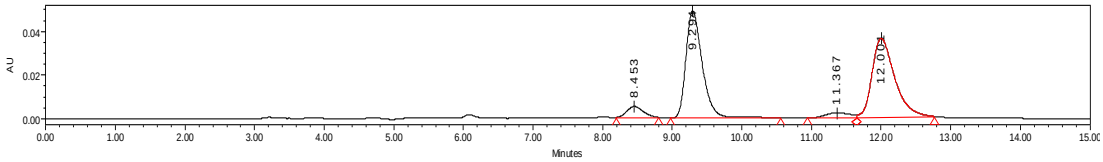
mL/min, λ = 254 nm, t_R (major) = 9.49 min, t_R (minor) = 12.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 1H), 7.03 – 6.98 (m, 1H), 6.95 – 6.92 (m, 1H), 3.75 (s, 2.91H), 3.71 (s, 0.09), 3.51 (d, *J* = 8.0 Hz, 1H), 3.35 (d, *J* = 7.6 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.76 – 2.56 (m, 3H), 2.06 (s, 0.09), 2.01 (s, 2.91H), 1.62 (s, 9H).

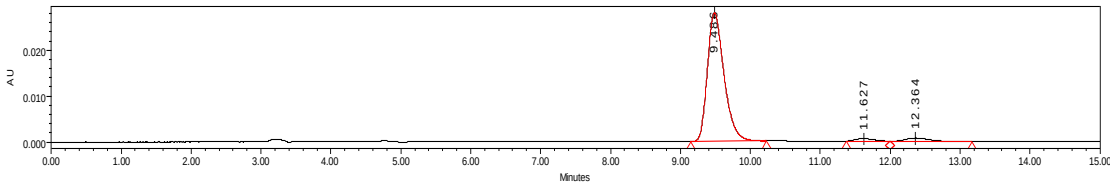
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 170.1, 165.8, 161.0, 158.5, 148.8, 136.3 (d, *J* = 2.0 Hz), 124.7 (d, *J* = 9.1 Hz), 116.4 (d, *J* = 8.1 Hz), 115.6, 115.4, 110.6, 110.3, 85.3, 53.0, 44.5, 43.1, 39.7, 35.9, 28.2, 27.5, 15.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9.

HRMS (ESI-FT) calcd for $C_{21}H_{24}FKNO_6S^+$ ([M+K$^+$]) = 476.0940, Found 476.0939.

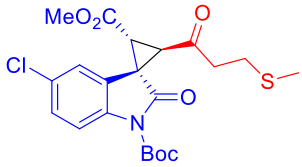


	Retention Time	Area	% Area
1	8.453	81522	4.64
2	9.294	807873	46.02
3	11.367	54866	3.13
4	12.001	811394	46.22



	Retention Time	Area	% Area
1	9.486	463850	94.08
2	11.627	10941	2.22
3	12.364	18228	3.70

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-5'-chloro-3-[3-(methylthio)-propanoyl]-2'-oxospiro(cyclopropane-1,3'- indoline)- 1',2-dicarboxylate (11ca)



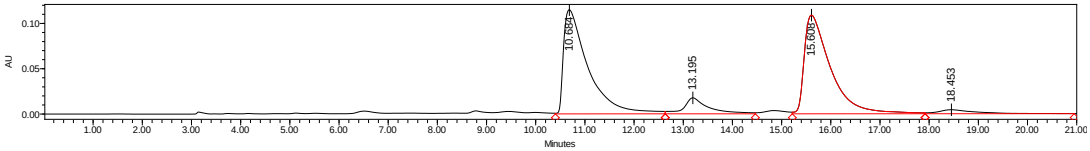
White solid, m.p. 90 – 92 °C, 42.8 mg, 94% yield, 95/5 d.r. (determined by ^{1}H NMR), 88% ee. $[\alpha]^{27}_D$ = -150.1 (*c* = 0.73 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 11.17 min, t_R (major) = 15.77 min.

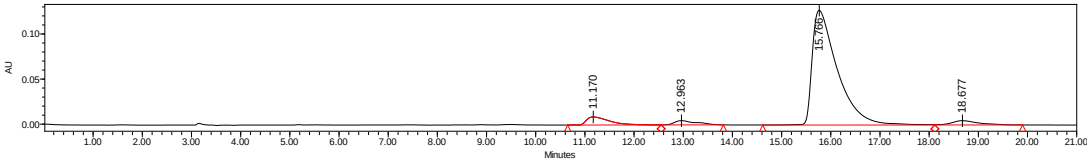
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.81(m, 1H), 7.30 – 7.26 (m, 1H), 7.19 – 7.16 (m, 1H), 3.74 (s, 3H), 3.51 (d, *J* = 8.0 Hz, 3H), 3.36 (d, *J* = 8.0 Hz, 3H), 2.98 – 2.88 (m, 1H), 2.76 – 2.57 (m, 3H), 2.01 (s, 3H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 169.8, 165.8, 148.7, 138.8, 130.2, 128.9, 124.6, 122.9, 116.3, 85.4, 53.0, 44.5, 43.1, 39.5, 35.9, 28.2, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{21}H_{24}{}^{35}ClNaNO_6S^+$ ([M+Na$^+$]) = 476.0905, Found 476.0905. $C_{21}H_{24}{}^{37}ClNaNO_6S^+$ ([M+Na$^+$]) = 478.0876, Found 478.0878.

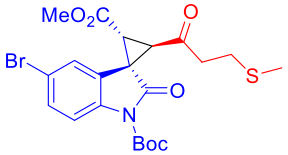


	Retention Time	Area	% Area
1	10.684	3985642	44.98
2	13.195	614071	6.93
3	15.608	4030159	45.48
4	18.453	230916	2.61



	Retention Time	Area	% Area
1	11.170	286582	5.59
2	12.963	147587	2.88
3	15.766	4515607	88.04
4	18.677	179430	3.50

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-5'-bromo-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11da)



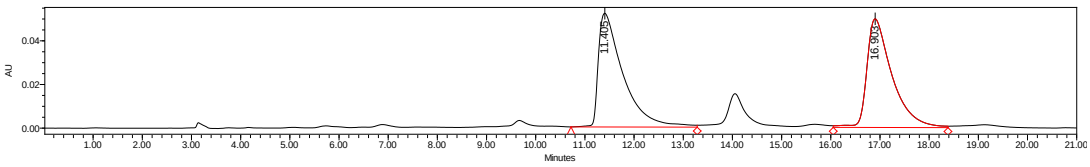
White solid, m.p. 60 – 64 °C, 45.5 mg, 91% yield, 94/6 d.r. (determined by ^{1}H NMR), 91% ee. $[\alpha]^{27}_D$ = -132.5 (*c* = 0.83 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 11.67 min, t_R (major) = 16.88 min.

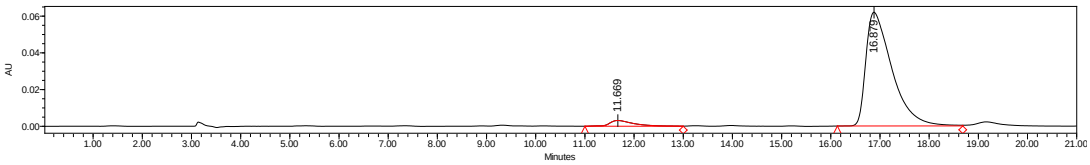
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.81 (m, 0.06H), 7.79 – 7.75 (m, 0.94H), 7.51 – 7.50 (m, 0.06H), 7.45 – 7.42 (m, 0.94H), 7.38 – 7.37 (m, 0.06H), 7.35 – 7.30 (m, 0.94H), 3.74 (s, 0.94H), 3.72 (s, 0.06H), 3.56 (d, *J* = 7.2 Hz, 0.06H), 3.50 (d, *J* = 8.0 Hz, 0.94H), 3.36 (d, *J* = 8.0 Hz, 0.94H), 3.31 (d, *J* = 3.2 Hz, 0.06H), 2.99 – 2.88 (m, 1H), 2.76 – 2.57 (m, 3H), 2.06 (s, 0.18H), 2.01 (s, 2.82H), 1.68 (s, 0.54H), 1.62 (s, 8.46H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 169.7, 165.8, 148.7, 139.3, 131.9, 125.7, 124.9, 117.7, 116.7, 85.4, 53.0, 44.5, 43.2, 39.4, 35.9, 28.2, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{21}H_{24}{}^{79}BrKNO_6S^+$ ([M+K$^+$]) = 536.0139, Found 536.0136. $C_{21}H_{24}{}^{81}BrKNO_6S^+$ ([M+K$^+$]) = 538.0119, Found 538.0115.

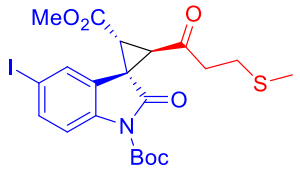


	Retention Time	Area	% Area
1	11.405	1818463	50.68
2	16.903	1769961	49.32



	Retention Time	Area	% Area
1	11.669	106266	4.45
2	16.879	2280686	95.55

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-5'-iodo-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ea)



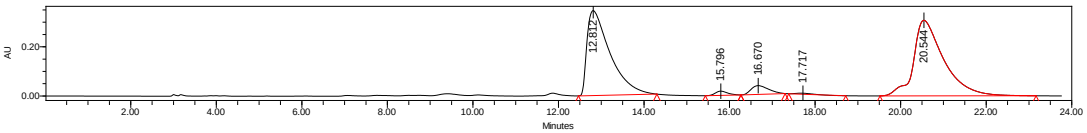
White solid, m.p. 84 – 88 °C, 51.8 mg, 95% yield, >99/1 d.r. (determined by ^{1}H NMR), 90% ee. $[\alpha]^{27}_D$ = -92.4 (*c* =1.07 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 13.12 min, t_R (major) = 20.64 min.

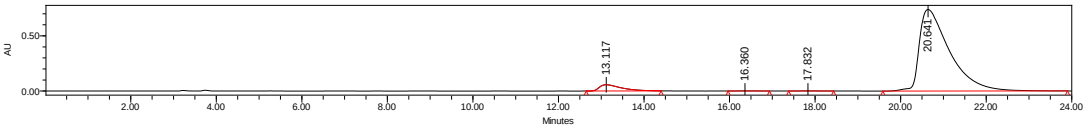
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 1H), 7.49 – 7.41 (s, 1H), 3.74 (s, 3H), 3.49 (d, *J* = 7.6 Hz, 1H), 3.35 (d, *J* = 7.6 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.75 – 2.58 (m, 3H), 2.01 (s, 3H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 169.6, 165.8, 148.6, 140.0, 137.9, 131.3, 125.1, 117.0, 88.0, 85.4, 53.0, 44.4, 43.2, 39.1, 35.8, 28.2, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{21}H_{24}INaNO_6S^+$ ([M+Na$^+$]) = 568.0261, Found 568.0264.

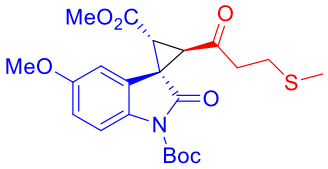


	Retention Time	Area	% Area
1	12.812	12933729	43.92
2	15.796	339139	1.15
3	16.670	1012734	3.44
4	17.717	115938	0.39
5	20.544	15045693	51.09



	Retention Time	Area	% Area
1	13.117	2017163	5.24
2	16.360	35665	0.09
3	17.832	26434	0.07
4	20.641	36406774	94.60

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-5'-methoxy-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11fa)



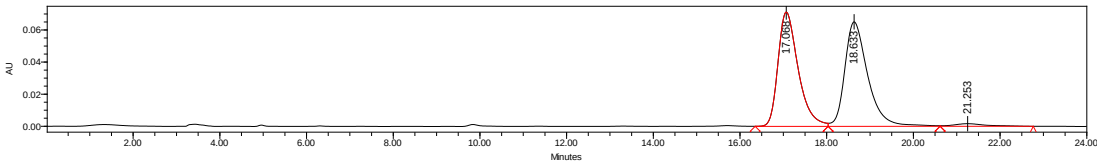
White solid, m.p. 82 – 86 °C, 43.2 mg, 96% yield, 96/4 d.r. (determined by ^{1}H NMR), 92% ee. $[\alpha]^{27}_D$ = -195.1 (*c* = 0.69 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 16.61 min, t_R (minor) = 18.35 min.

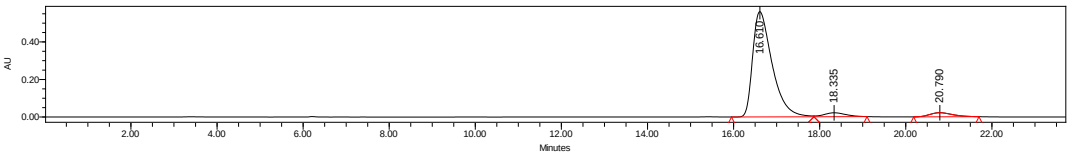
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 1H), 6.95 – 6.93 (m, 0.04H), 6.88 – 6.80 (m, 1H), 6.77 – 6.60 (m, 0.96H), 3.77 (s, 3H), 3.74 (s, 2.88H), 3.69 (s, 0.12H), 3.56 (s, 0.04H), 3.50 (d, *J* = 8.0 Hz, 0.96H), 3.41 (s, 1H), 3.36 (d, *J* = 8.0 Hz, 0.96H), 2.96 – 2.87 (m, 1H), 2.72 – 2.55 (m, 3H), 2.04 (s, 0.12H), 1.99 (s, 2.88H), 1.71 (s, 0.36H), 1.62 (s, 8.64H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 170.6, 166.1, 156.8, 148.9, 133.6, 124.0, 116.1, 114.4, 108.1, 84.8, 55.8, 52.9, 44.3, 43.1, 39.9, 35.5, 28.2, 27.4, 15.7.

HRMS (ESI-FT) calcd for $C_{22}H_{27}NNaO_7S^+$ ([M+Na$^+$]) = 472.1400, Found 472.1402.

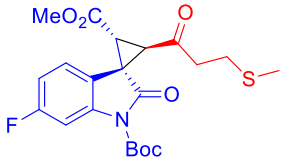


	Retention Time	Area	% Area
1	17.068	2295540	48.11
2	18.633	2391510	50.12
3	21.253	84245	1.77



	Retention Time	Area	% Area
1	16.610	17604806	91.87
2	18.335	748159	3.90
3	20.790	809613	4.22

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-6'-fluoro-3-(3-(methylthio)propanoyl)-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ga)



Pale yellow solid, m.p. 36 – 40 °C, 39.8 mg, 91% yield, 93/7 d.r. (determined by ^{1}H NMR), 93% ee. $[\alpha]^{27}_D$ = -194.9 (*c* = 0.64 in CH_2Cl_2).

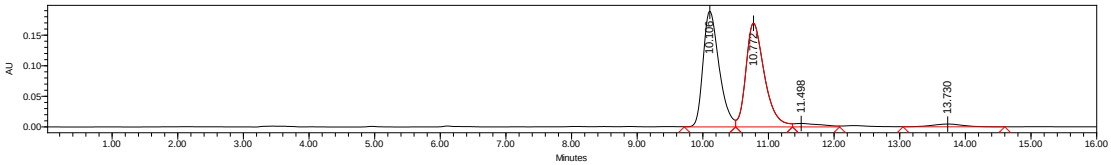
HPLC DAICEL CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 9.92 min, t_R (minor) = 10.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.14 – 7.10 (m, 1H), 6.83 – 6.77 (m, 1H), 3.75 (s, 3H), 3.49 (d, *J* = 8.0 Hz, 1H), 3.36 (d, *J* = 7.6 Hz, 1H), 2.96 – 2.88 (m, 1H), 2.73 – 2.53 (m, 3H), 2.00 (s, 3H), 1.63 (s, 9H).

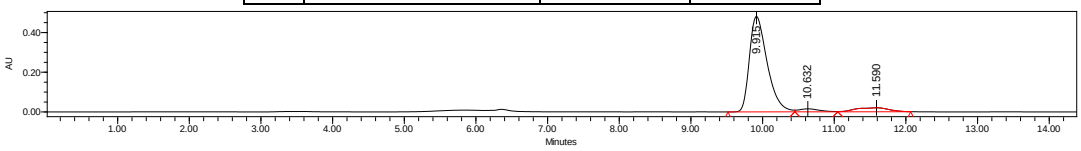
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 170.4, 166.0, 164.3, 161.8, 148.6, 141.38 (d, *J* = 12.1 Hz), 123.79 (d, *J* = 10.1 Hz), 118.27 (d, *J* = 2.0 Hz), 111.3, 111.1, 104.2, 103.9, 85.6, 53.0, 44.4, 43.0, 39.6, 35.5, 28.1, 27.5, 15.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9.

HRMS (ESI-FT) calcd for $C_{21}H_{24}FNaNO_6S^+$ ([M+Na$^+$]) = 460.1201, Found 460.1210.

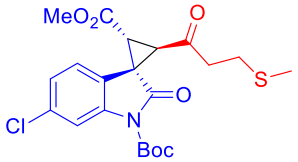


	Retention Time	Area	% Area
1	10.106	3207414	46.98
2	10.772	3310092	48.48
3	11.498	159871	2.34
4	13.730	150362	2.20



	Retention Time	Area	% Area
1	9.915	8271256	89.87
2	10.632	297827	3.24
3	11.590	634286	6.89

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-6'-chloro-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ha)



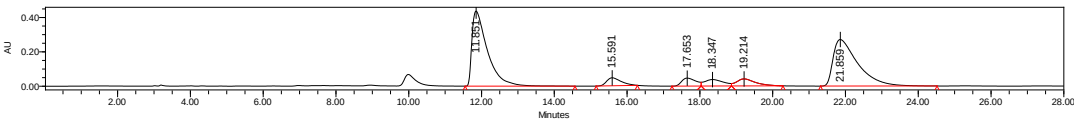
Pale yellow solid, m.p. 38 – 42 °C, 45.0 mg, 99% yield, 95/5 d.r. (determined by ^{1}H NMR), 88% ee. $[\alpha]^{27}_D$ = -173.9 (c = 0.88 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 12.11 min, t_R (major) = 21.79 min.

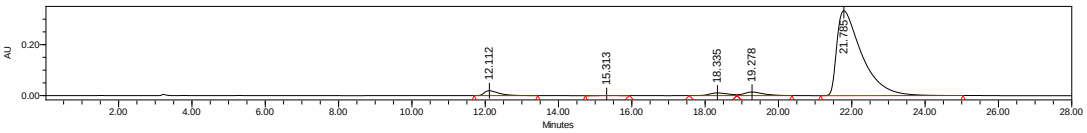
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.87 (m, 1H), 7.15 – 7.03 (m, 2H), 3.75 (s, 2.85H), 3.72 (s, 0.09H), 3.69 (s, 0.06H), 3.56 (s, 0.05H), 3.50 (d, J = 7.6 Hz, 0.95H), 3.37 (d, J = 8.0 Hz, 0.95H), 3.32 (s, 0.05H), 2.97 – 2.87 (m, 1H), 2.74 – 2.54 (m, 3H), 2.06 (s, 0.06H), 2.05 (s, 0.09H), 2.00 (s, 2.85H), 1.66 (s, 0.45H), 1.63 (s, 8.55H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 1701, 165.9, 148.6, 141.1, 134.9, 124.6, 123.5, 121.2, 115.9, 85.6, 53.0, 44.4, 43.1, 39.6, 35.7, 28.1, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{21}H_{24}{}^{35}ClNaNO_6S^+$ ([M+Na$^+$]) = 476.0905, Found 476.0901. $C_{21}H_{24}{}^{37}ClNaNO_6S^+$ ([M+Na$^+$]) = 478.0876, Found 478.0870.

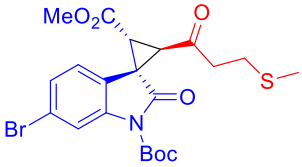


	Retention Time	Area	% Area
1	11.851	12909858	41.58
2	15.591	1286711	4.14
3	17.653	1266840	4.08
4	18.347	1363631	4.39
5	19.214	1480931	4.77
6	21.859	12738156	41.03



	Retention Time	Area	% Area
1	12.112	533816	3.11
2	15.313	22881	0.13
3	18.335	377999	2.20
4	19.278	514131	2.99
5	21.785	15717555	91.56

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-6'-bromo-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ia)



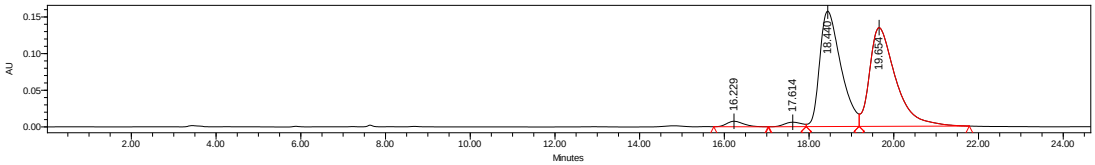
White solid, m.p. 44 – 46 °C, 48.4 mg, 97% yield, 96/4 d.r. (determined by ^{1}H NMR), 92% ee. $[\alpha]^{27}_D$ = -177.1 (*c* = 0.80 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 18.36 min, t_R (minor) = 19.74 min.

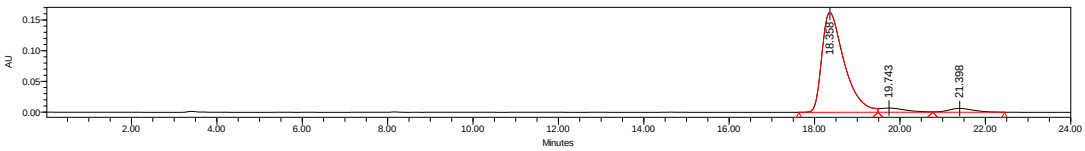
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.03 (m, 1H), 7.32 – 7.20 (m, 1H), 7.13 – 7.10 (m, 0.04H), 7.10 – 6.89 (m, 0.96H), 3.76 (s, 2.88H), 3.70 (s, 0.12H), 3.57 (d, *J* = 1.2 Hz, 0.04H), 3.52 (d, *J* = 8.0 Hz, 0.96H), 3.45 (d, *J* = 1.2 Hz, 2H), 3.38 (d, *J* = 8.0 Hz, 0.96H), 2.99 – 2.88 (m, 1H), 2.76 – 2.54 (m, 3H), 2.07 (s, 0.12H), 2.02 (s, 2.88H), 1.68 (s, 0.36H), 1.64 (s, 8.64H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 169.9, 165.8, 148.6, 141.2, 127.5, 123.8, 122.8, 121.8, 118.6, 85.6, 53.0, 44.4, 43.1, 39.6, 35.6, 28.1, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{21}H_{24}{}^{79}BrKNO_6S^+$ ([M+K$^+$]) = 536.0139, Found 536.0131. $C_{21}H_{24}{}^{81}BrKNO_6S^+$ ([M+K$^+$]) = 538.0119, Found 538.0106.

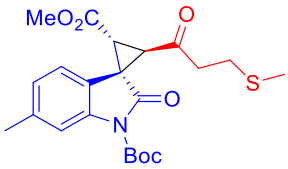


	Retention Time	Area	% Area
1	16.229	204377	1.77
2	17.614	172996	1.50
3	18.440	5440151	47.02
4	19.654	5751772	49.72



	Retention Time	Area	% Area
1	18.358	5898302	91.61
2	19.743	287831	4.47
3	21.398	252171	3.92

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-6'-methyl-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ja)



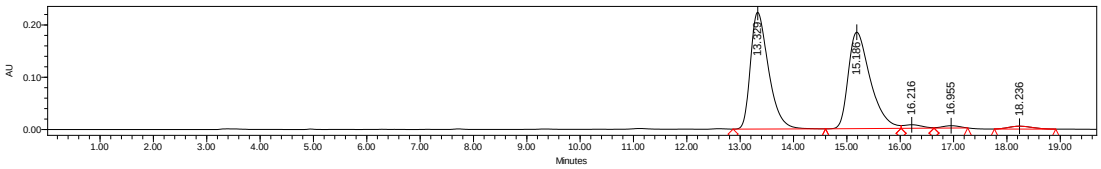
White solid, m.p. 34 – 38 °C, 41.9 mg, 97% yield, 96/4 d.r. (determined by ^{1}H NMR), 88% ee. $[\alpha]^{27}_D$ = -209.7 (*c* = 0.65 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 13.17 min, t_R (minor) = 15.37 min.

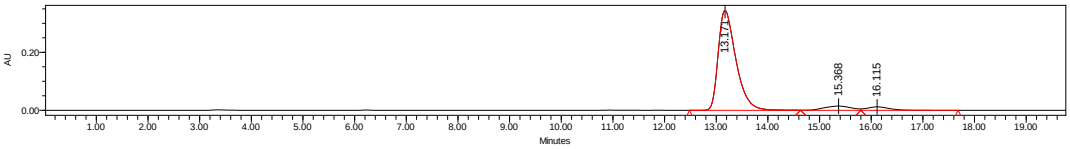
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 1H), 7.22 – 7.19 (m, 0.04H), 7.12 – 7.09 (m, 0.04H), 7.02 – 6.97 (m, 0.96H), 6.93 – 6.87 (m, 0.96H), 3.74 (s, 2.88H), 3.68 (s, 0.12H), 3.55 (s, 0.04H), 3.48 (d, *J* = 7.6 Hz, 0.96H), 3.40 (s, 0.04H), 3.35 (d, *J* = 7.6 Hz, 0.96H), 2.97 – 2.86 (m, 1H), 2.69 – 2.52 (m, 3H), 2.39 (s, 0.12H), 2.36 (s, 2.88H), 2.05 (s, 0.12H), 2.00 (s, 2.88H), 1.67 (s, 0.36H), 1.63 (s, 8.64H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 170.8, 166.2, 149.1, 140.3, 139.3, 125.2, 122.1, 119.8, 115.9, 85.0, 52.9, 52.8, 44.4, 43.0, 39.8, 35.3, 28.2, 27.4, 22.1, 15.8.

HRMS (ESI-FT) calcd for $C_{22}H_{27}NNaO_6S^+$([M+Na$^+$]) = 456.1451, Found 456.1459.

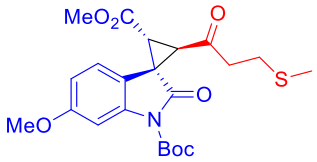


	Retention Time	Area	% Area
1	13.329	5248741	47.89
2	15.186	5282494	48.20
3	16.216	163382	1.49
4	16.955	98707	0.90
5	18.236	166212	1.52



	Retention Time	Area	% Area
1	13.171	8197408	90.08
2	15.368	539087	5.92
3	16.115	363795	4.00

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-6'-methoxy-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ka)



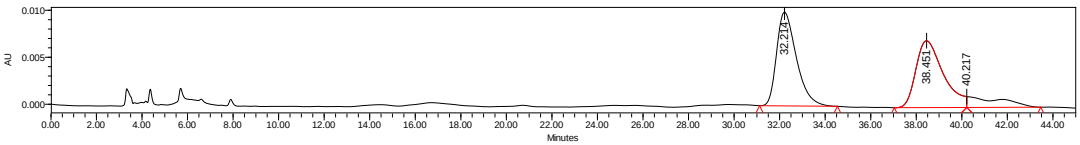
Pale yellow oil, 40.0 mg, 89% yield, 97/3 d.r. (determined by ^{1}H NMR), 97% ee. $[\alpha]^{26}_D$ = -193.8 (*c* = 0.64 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 30.89 min, t_R (minor) = 38.01 min.

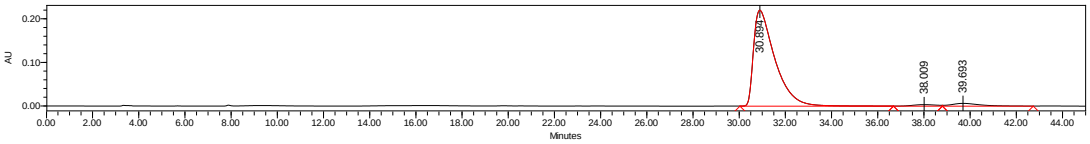
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 1H), 7.08 – 7.00 (m, 1H), 6.65 – 6.56 (m, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.55 (s, 0.03H), 3.46 (d, *J* = 8.0 Hz, 0.97H), 3.42 (s, 0.03H), 3.32 (d, *J* = 8.0 Hz, 0.97H), 2.95 – 2.84 (m, 1H), 2.71 – 2.52 (m, 3H), 2.06 (s, 0.12H), 2.00 (s, 2.88H), 1.63 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 171.0, 166.3, 160.5, 148.8, 141.4, 123.2, 114.5, 110.0, 102.2, 85.0, 55.7, 52.9, 44.4, 42.8, 39.8, 35.2, 28.2, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{22}H_{27}NNaO_7S^+$ ([M+Na$^+$]) = 472.1400, Found 472.1401.

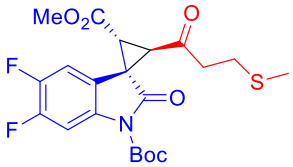


	Retention Time	Area	% Area
1	32.214	602652	45.69
2	38.451	595410	45.14
3	40.217	120936	9.17



	Retention Time	Area	% Area
1	30.894	14108111	94.99
2	38.009	229388	1.54
3	39.693	515050	3.47

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-5',6'-difluoro-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11la)



White solid, m.p. 34 – 38 °C, 41.8 mg, 92% yield, 97/3 d.r. (determined by ^{1}H NMR), 90% ee. $[\alpha]^{27}_D$ = -188.0 (*c* = 0.65 in CH_2Cl_2).

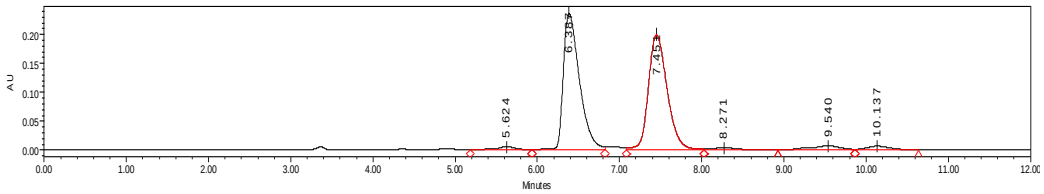
HPLC DAICEL CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 6.38 min, t_R (minor) = 7.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.12 – 7.07 (m, 1H), 3.75 (s, 2.91H), 3.72 (s, 0.09H), 3.56 (s, 0.03H), 3.49 (d, *J* = 8.0 Hz, 0.97H), 3.46 (s, 0.03H), 3.33 (d, *J* = 7.6 Hz, 0.97H), 3.00 – 2.88 (m, 1H), 2.79 – 2.57 (m, 3H), 2.07 (s, 0.09H), 2.02 (s, 2.91H), 1.62 (s, 9H).

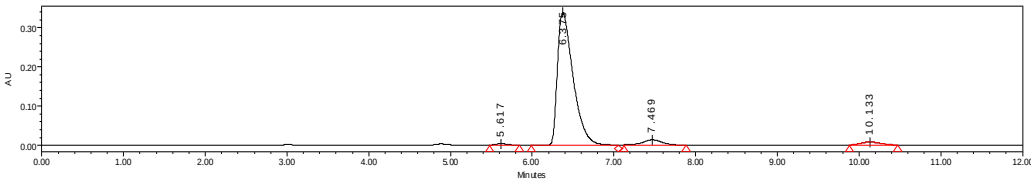
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 169.8, 165.7, 151.7 (d, *J* = 13.1 Hz), 149.2 (d, *J* = 13.1 Hz), 148.7 (d, *J* = 13.1 Hz), 148.5, 146.3 (d, *J* = 13.1 Hz), 136.4 (d, *J* = 3.0 Hz), 136.3 (d, *J* = 3.0 Hz), 118.7, 112.4, 112.2, 106.0, 105.8, 85.7, 53.0, 44.5, 42.9, 39.5, 36.0, 28.1, 27.5, 15.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.6, -141.5.

HRMS (ESI-FT) calcd for $C_{21}H_{23}F_2NaNO_6S^+$ ([M+Na$^+$]) = 478.1106, Found 478.1107.

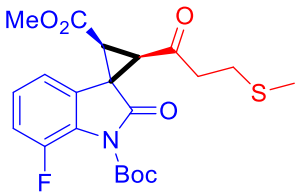


	Retention Time	Area	% Area
1	5.624	97781	1.42
2	6.387	3229937	46.94
3	7.451	3167092	46.03
4	8.271	78801	1.15
5	9.540	181541	2.64
6	10.137	126043	1.83



	Retention Time	Area	% Area
1	5.617	34827	0.71
2	6.375	4531847	92.21
3	7.469	216913	4.41
4	10.133	131120	2.67

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-7'-fluoro-3-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ma)



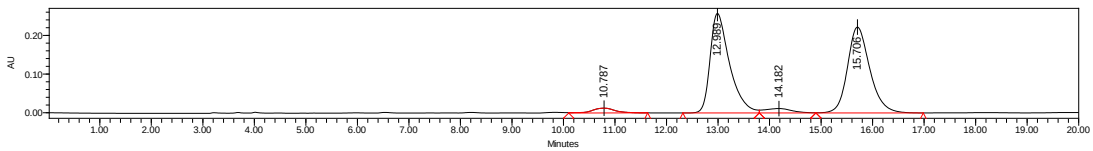
Pale yellow oil, 41.5 mg, 95% yield, 90/10 d.r. (determined by ^{1}H NMR), 89% ee. $[\alpha]^{25}_D$ = -185.0 (c = 0.67 in CH_2Cl_2). HPLC DAICEL CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 11.56 min, t_R (major) = 13.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 0.10H), 7.18 – 7.15 (m, 0.10H), 7.12 – 7.10 (m, 0.10H), 7.10 – 7.03 (m, 1.80H), 6.99 – 6.90 (m, 0.90H), 3.74 (s, 2.70H), 3.70 (s, 0.30H), 3.53 (d, J = 8.0 Hz, 0.90H), 3.39 (d, J = 8.0 Hz, 0.90H), 3.34 (d, J = 2.4 Hz, 0.10H), 3.00 – 2.85 (m, 1.10H), 2.78 – 2.54 (m, 3H), 2.06 (s, 0.30H), 2.00 (s, 2.70H), 1.60 (s, 9H).

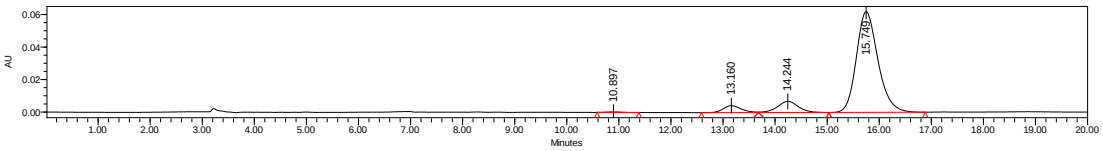
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 167.0, 165.7, 149.9, 147.4, 147.2, 127.1 (d, J = 10.1 Hz), 126.1 (d, J = 2.0 Hz), 125.6 (d, J = 7.1 Hz), 118.6 (d, J = 4.0 Hz), 117.4, 117.2, 85.7, 53.0, 44.4, 43.1, 39.9, 35.9, 27.8, 27.5, 15.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.86.

HRMS (ESI-FT) calcd for $C_{21}H_{24}FKNO_6S^+$ ([M+K$^+$]) = 476.0940, Found 476.0949.

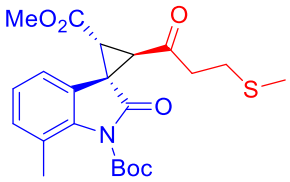


	Retention Time	Area	% Area
1	10.787	384420	2.70
2	12.989	6746008	47.43
3	14.182	419806	2.95
4	15.706	6671824	46.91



	Retention Time	Area	% Area
1	10.897	4413	0.21
2	13.160	103516	4.97
3	14.244	191738	9.21
4	15.749	1782321	85.61

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-7'-methyl-3-(3-(methylthio)propanoyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (11na)

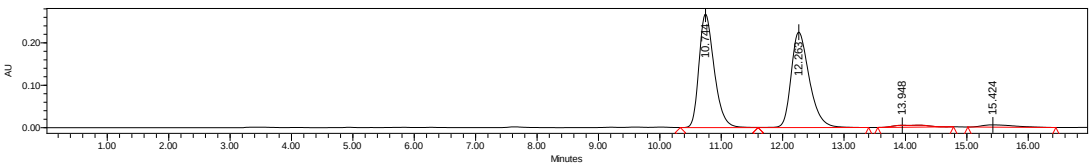


Pale yellow oil, 37.6 mg, 87% yield, 97/3 d.r. (determined by ^{1}H NMR), 94% ee. $[\alpha]^{19}_D$ = -233.9 (c = 0.65 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 10.38 min, t_R (minor) = 11.91 min.

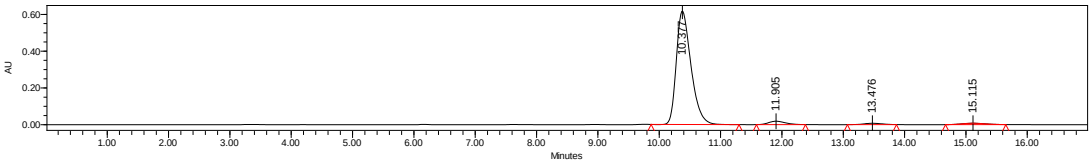
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 1H), 7.04 – 6.89 (m, 2H), 3.73 (s, 2.91H), 3.69 (s, 0.09H), 3.55 (s, 0.03H), 3.51 (d, J = 8.0 Hz, 0.97H), 3.42 (s, 0.03H), 3.36 (d, J = 8.0 Hz, 0.97H), 2.95 – 2.86 (m, 1H), 2.74 – 2.63 (m, 2H), 2.61 – 2.52 (m, 1H), 2.24 (s, 3H), 2.05 (s, 0.09H), 2.00 (s, 2.91H), 1.67 (s, 0.27H), 1.62 (s, 8.73H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 171.2, 166.2, 149.0, 138.7, 132.0, 124.4, 124.0, 123.6, 120.0, 85.4, 52.9, 44.3, 42.9, 39.9, 35.5, 27.9, 27.5, 19.6, 15.8.

HRMS (ESI-FT) calcd for $C_{22}H_{27}NKO_6S^+$([M+K$^+$]) = 472.1191, Found 472.1195.

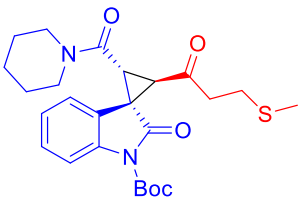


	Retention Time	Area	% Area
1	10.744	4595934	47.94
2	12.263	4613251	48.12
3	13.948	176721	1.84
4	15.424	200908	2.10



	Retention Time	Area	% Area
1	10.377	10268781	93.60
2	11.905	349627	3.19
3	13.476	149537	1.36
4	15.115	202934	1.85

***Tert*-butyl (1*S*,2*R*,3*R*)-2-[3-(methylthio)propanoyl]-2'-oxo-3-(piperidine-1-carbonyl)spiro(cyclopropane-1,3'-indoline)-1'-carboxylate (11oa)**



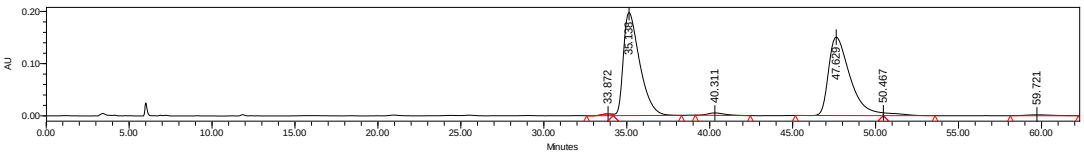
Pale yellow oil, 16.0 mg, 34% yield, 99/1 d.r. (determined by ^{1}H NMR), 96% ee. $[\alpha]^{27}_D$ = -151.0 (*c* = 0.51 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 33.60 min, t_R (minor) = 48.31 min.

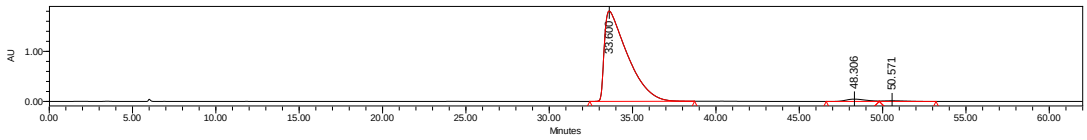
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1 – 7.86 (m, 1H), 7.35 – 7.30 (m, 1H), 7.14 – 7.09 (m, 2H), 3.74 – 3.65 (m, 1H), 3.51 – 3.45 (m, 2H), 3.33 – 3.17 (m, 3H), 2.98 – 2.88 (m, 1H), 2.81 – 2.70 (m, 3H), 2.06 (s, 3H), 1.63 (s, 9H), 1.55 – 1.32 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 170.4, 162.6, 149.0, 140.0, 128.8, 124.7, 124.0, 121.2, 115.1, 85.1, 46.8, 43.5, 43.2, 43.1, 38.3, 36.9, 28.2, 27.8, 26.2, 25.7, 24.3, 15.8.

HRMS (ESI-FT) calcd for $C_{25}H_{32}N_2NaO_5S^+$([M+Na$^+$]) = 495.1924, Found 495.1921.

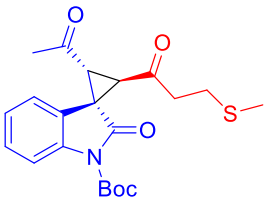


	Retention Time	Area	% Area
1	33.872	145736	0.52
2	35.138	13459443	48.19
3	40.311	331125	1.19
4	47.629	13436633	48.11
5	50.467	379822	1.36
6	59.721	177798	0.64



	Retention Time	Area	% Area
1	33.600	173412278	97.08
2	48.306	3872808	2.17
3	50.571	1351325	0.76

***Tert*-butyl (1*R*,2*R*,3*R*)-2-acetyl-3-[3-(methylthio)propanoyl]-2'-oxospiro-(cyclopropane-1,3'-indoline)-1'-carboxylate (11pa)**



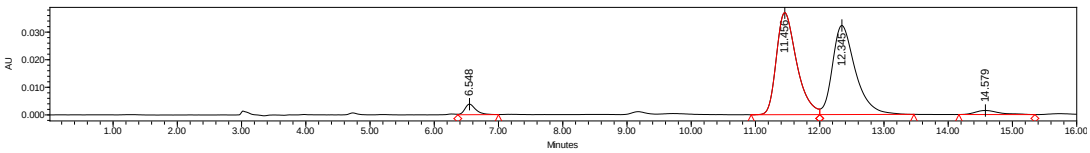
Pale yellow oil, 37.9 mg, 94% yield, 99/1 d.r. (determined by ^{1}H NMR), 92% ee. $[\alpha]^{27}_D$ = -270.2 (c = 0.58 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 11.50 min, t_R (minor) = 12.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 1H), 7.36 – 7.29 (m, 1H), 7.19 – 7.05 (m, 2H), 3.54 (d, J = 8.4 Hz, 1H), 3.41 (d, J = 8.4 Hz, 1H), 2.97 – 2.85 (m, 1H), 2.71 – 2.52 (m, 3H), 2.26 (s, 3H), 1.99 (s, 3H), 1.63 (s, 9H).

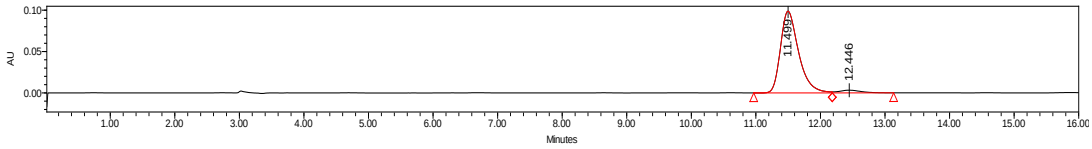
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 198.5, 170.3, 148.9, 140.2, 129.0, 124.6, 123.0, 122.3, 115.1, 85.2, 44.3, 43.3, 42.7, 40.8, 30.4, 28.2, 27.5, 15.7.

HRMS (ESI-FT) calcd for $C_{21}H_{25}NNaO_5S^+$([M+Na$^+$]) = 426.1346, Found 426.1343.



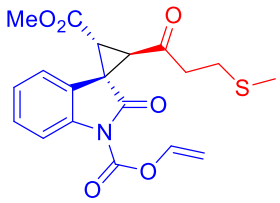
	Retention Time	Area	% Area
1	6.548	45302	2.68
2	11.456	809293	47.84

3	12.345	798013	47.18
4	14.579	38970	2.30



	Retention Time	Area	% Area
1	11.499	1919401	96.22
2	12.446	75347	3.78

2-Methyl 1'-vinyl (1*S*,2*R*,3*R*)-3-[3-(methylthio)propanoyl]-2'-oxospiro-(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11qa)



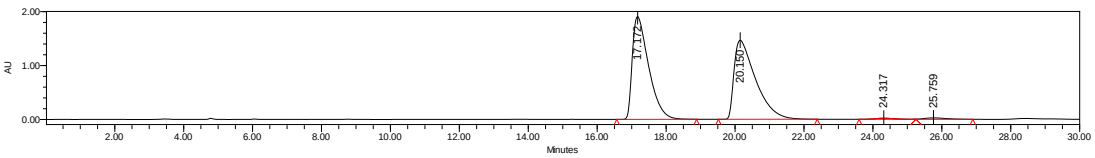
Pale yellow oil, 33.3 mg, 85% yield, 91/9 d.r. (determined by ^{1}H NMR), 88% ee. $[\alpha]^{27}_D$ = -206.4 (*c* = 0.56 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 17.30 min, t_R (minor) = 20.80min.

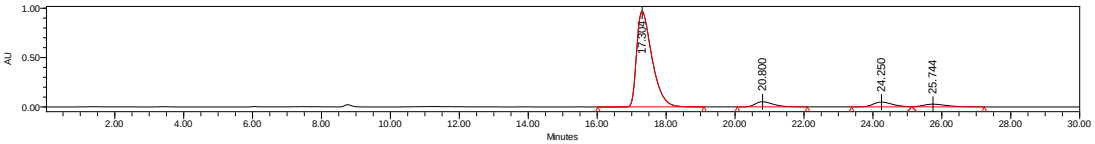
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 1H), 7.38 – 7.29 (m, 1H), 7.25 – 7.08 (m, 2H), 6.12 – 5.92 (m, 1H), 5.51 (d, *J* = 17.2 Hz, 1H), 5.34 (d, *J* = 10.4 Hz, 1H), 4.96 – 4.84 (m, 2H), 3.75 (s, 2.73H), 3.69 (s, 0.27H), 3.53 (d, *J* = 8.0 Hz, 0.91H), 3.42 (d, *J* = 8.0 Hz, 0.91H), 3.35 (s, 0.09H), 3.05 (d, *J* = 8.4 Hz, 0.09H), 2.96 – 2.85 (m, 1H), 2.74 – 2.52 (m, 3H), 2.06 (s, 0.27H), 1.98 (s, 2.73H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 170.4, 166.0, 150.4, 139.8, 131.0, 129.1, 125.0, 122.9, 122.5, 119.9, 115.3, 68.0, 53.0, 44.4, 43.3, 39.7, 35.7, 27.5, 15.8.

HRMS (ESI-FT) calcd for $C_{19}H_{19}NNaO_6S^+$([M+Na$^+$]) = 412.0821, Found 412.0825.

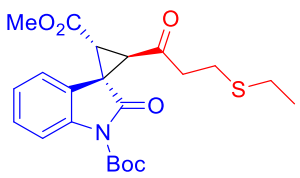


	Retention Time	Area	% Area
1	17.172	62806029	48.98
2	20.150	63517958	49.54
3	24.317	751018	0.59
4	25.759	1147535	0.89



	Retention Time	Area	% Area
1	17.304	29852942	85.39
2	20.800	1891385	5.41
3	24.250	1923162	5.50
4	25.744	1291787	3.70

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-3-(3-(ethylthio)propanoyl)-2'-oxospiro-[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (11ab)

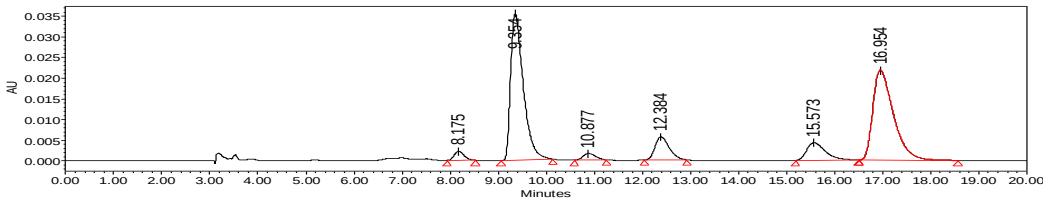


Pale yellow oil, 37.8 mg, 87% yield, 93/7 d.r. (determined by ^{1}H NMR), 96% ee. $[\alpha]^{25}_D$ = -142.9 (c = 0.72 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 9.45 min, t_R (major) = 16.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 1H), 7.34 – 7.28 (m, 1H), 7.18 – 7.02 (m, 2H), 3.75 (s, 2.79H), 3.68 (s, 0.21H), 3.51 (d, J = 7.6 Hz, 0.93H), 3.45 (d, J = 6.8 Hz, 0.07H), 3.39 (d, J = 7.6 Hz, 0.93H), 3.03 (d, J = 9.3 Hz, 0.07H), 2.95 – 2.85 (m, 1H), 2.73 – 2.55 (m, 3H), 2.51 – 2.48 (m, 0.14H), 2.41 (q, J = 7.6 Hz, 1.86H), 1.68 (s, 0.63H), 1.64 (s, 8.37H), 1.22 – 1.20 (m, 0.21H), 1.15 (t, J = 7.2 Hz, 2.79H).

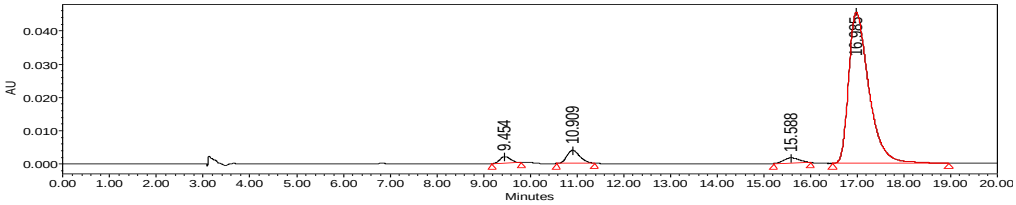
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 170.5, 166.1, 148.9, 140.3, 128.9, 124.6, 122.8, 122.4, 115.1, 85.1, 52.9, 44.7, 43.2, 39.8, 35.4, 28.2, 26.2, 24.9, 14.6.

HRMS (ESI-FT) calcd for $C_{22}H_{27}NNaO_6S^+$([M+Na$^+$]) = 456.1451, Found 456.1451.



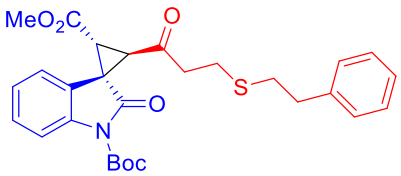
	Retention Time	Area	% Area
1	8.175	31269	1.96
2	9.354	652963	40.88

3	10.877	28717	1.80
4	12.384	114963	7.20
5	15.573	118906	7.44
6	16.954	650376	40.72



	Retention Time	Area	% Area
1	9.454	32141	2.14
2	10.909	75001	4.99
3	15.588	35546	2.37
4	16.985	1360125	90.51

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-2'-oxo-3-[3-(phenethylthio)propanoyl] spiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (11ac)



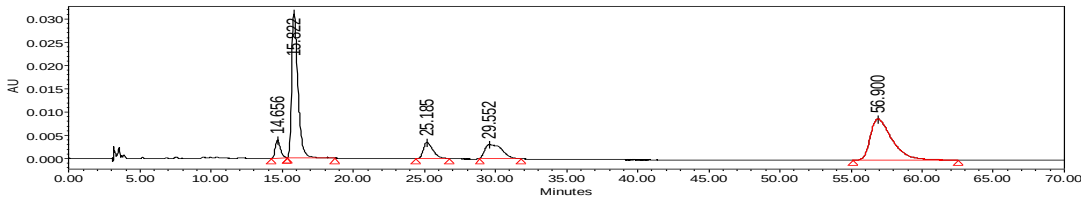
Pale yellow oil, 43.2 mg, 85% yield, 90/10 d.r. (determined by ^{1}H NMR), 94% ee. $[\alpha]^{25}_D$ = -186.9 (c = 0.79 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IB, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 15.52 min, t_R (major) = 52.95 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 1H), 7.37 – 7.23 (m, 3H), 7.21 – 7.06 (m, 5H), 3.74 (s, 2.73H), 3.68 (s, 0.27H), 3.49 (d, J = 7.6 Hz, 0.90H), 3.45 (d, J = 8.0 Hz, 0.10H), 3.38 (d, J = 7.6 Hz, 0.90H), 3.01 (d, J = 3.2 Hz, 0.10H), 2.90 – 2.83 (m, 1H), 2.83 – 2.70 (m, 3H), 2.68 – 2.58 (m, 4H), 1.66 (s, 0.90H), 1.63 (s, 8.10H).

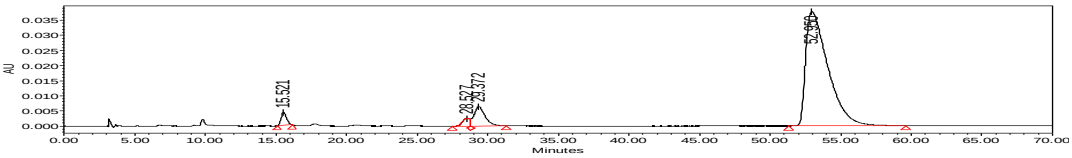
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 170.5, 166.1, 148.9, 140.3, 140.2, 129.0, 128.6, 126.5, 124.6, 122.8, 122.4, 115.1, 85.1, 52.9, 44.7, 43.1, 39.7, 36.2, 35.4, 34.0, 28.2, 25.5.

HRMS (ESI-FT) calcd for $C_{28}H_{31}NNaO_6S^+$([M+Na$^+$]) = 532.1764, Found 532.1766.



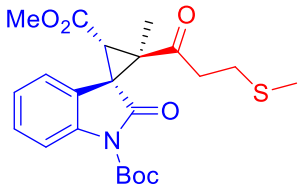
	Retention Time	Area	% Area

1	14.656	96986	4.06
2	15.822	934883	39.17
3	25.185	164973	6.91
4	29.552	251348	10.53
5	56.900	938327	39.32



	Retention Time	Area	% Area
1	15.521	115541	2.46
2	28.527	90396	1.92
3	29.372	348620	7.41
4	52.950	4148735	88.21

1'-(*Tert*-butyl) 3-methyl (1*S*,2*R*,3*R*)-2-methyl-2-[3-(methylthio)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',3-dicarboxylate (11ad)

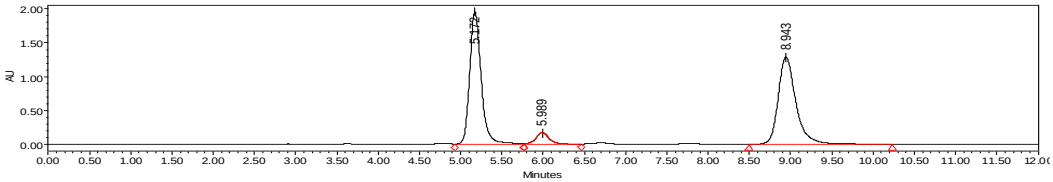


Pale yellow oil, 19.9 mg, 55% yield, >95/5 d.r. (determined by ^{1}H NMR), 68% ee. $[\alpha]^{19}_D$ = -102.9 (*c* = 0.24 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.17 min, t_R (minor) = 9.03 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 1H), 7.57 – 7.54 (m, 1H), 7.40 – 7.34 (m, 1H), 7.19 – 7.15 (m, 1H), 3.70 (s, 3H), 3.29 (s, 1H), 3.02 – 2.91 (m, 1H), 2.86 – 2.61 (m, 3H), 2.11 (s, 2.88H), 2.10 (s, 0.12H), 1.79 (s, 0.12H), 1.75 (s, 2.88H), 1.61 (s, 9H).

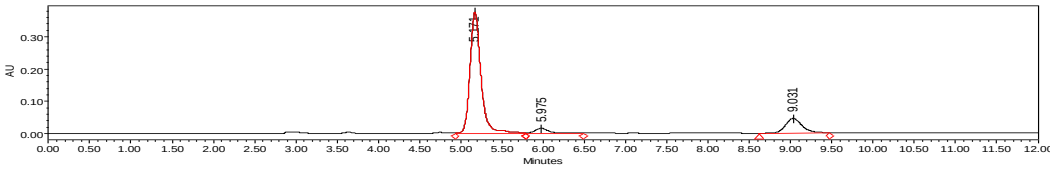
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 171.6, 167.5, 148.8, 141.0, 128.6, 125.1, 124.2, 121.7, 115.1, 85.0, 52.3, 48.2, 42.0, 40.3, 37.9, 28.2, 28.1, 15.9, 10.7.

HRMS (ESI-FT) calcd for $C_{22}H_{27}KNO_6S^+$ ([M+K$^+$]) = 472.1191, Found 472.1195.



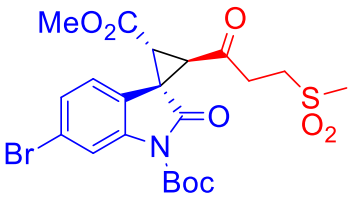
	Retention	Area	% Area

	Time		
1	5.172	19145098	47.52
2	5.989	2006372	4.98
3	8.943	19135110	47.50



	Retention Time	Area	% Area
1	5.171	3473116	80.58
2	5.975	176375	4.09
3	9.031	660398	15.32

1'-(*Tert*-butyl) 2-methyl (1*S*,2*R*,3*R*)-6'-bromo-3-[3-(methylsulfonyl)propanoyl]-2'-oxospiro(cyclopropane-1,3'-indoline)-1',2-dicarboxylate (12)



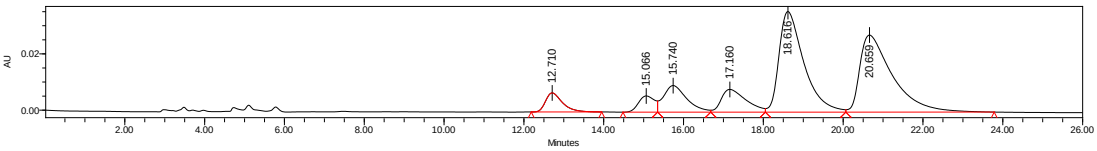
White solid, m.p. 90 – 96 °C, 106.0 mg, 99% yield, 97/3 d.r. (determined by ^{1}H NMR), 93% ee, $[\alpha]^{27}_D$ = -168.4 (c = 0.82 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 18.85 min, t_R (major) = 20.43 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 1H), 7.26 – 7.22 (m, 1H), 7.03 – 6.94 (m, 1H), 3.75 (s, 2.91H), 3.70 (s, 0.09H), 3.55 (d, J = 8.0 Hz, 1H), 3.38 (d, J = 7.6 Hz, 1H), 3.34 – 3.15 (m, 3H), 3.01 – 2.90 (m, 1H), 2.86 (s, 3H), 1.63 (s, 9H).

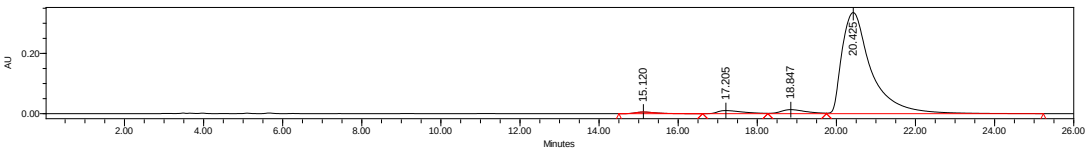
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 169.6, 165.5, 148.5, 141.4, 127.5 123.6, 123.1, 121.3, 118.9, 85.7, 53.1, 48.4, 42.9, 41.5, 39.9, 36.9, 35.7, 28.1.

HRMS (ESI-FT) calcd for $C_{21}H_{24}{}^{79}BrNaNO_8S^+$ ([M+Na$^+$]) = 552.0298, Found 552.0308. $C_{21}H_{24}{}^{81}BrNaNO_8S^+$ ([M+Na$^+$]) = 554.0278, Found 554.0290.



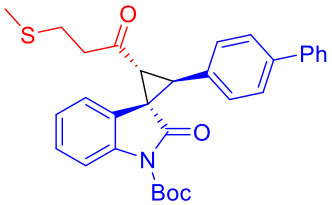
	Retention Time	Area	% Area
1	12.710	199024	4.75

2	15.066	160311	3.83
3	15.740	382466	9.13
4	17.160	347908	8.31
5	18.616	1546396	36.92
6	20.659	1552080	37.06



	Retention Time	Area	% Area
1	15.120	196295	1.06
2	17.205	458848	2.49
3	18.847	589995	3.20
4	20.425	17195921	93.25

Tert-butyl-2-[(1,1'-biphenyl)-4-yl]-3-[3-(methylthio)propanoyl]-2'-oxospiro (cyclopropane-1,3'-indoline)-1'-carboxylate (14aa)

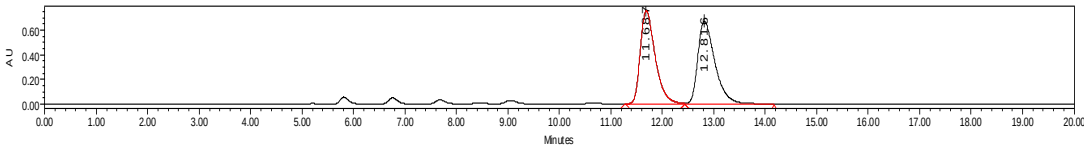


Condition A: [(*anti-syn*)+(*anti-anti*)]/*syn-anti* = 1/1, isolated *syn-anti* isomer, white solid, m.p. 48 – 50 °C, 24.5 mg, 48% yield, 99% ee, $[\alpha]^{19}_{D}$ = -227.3 (*c* = 0.34 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 11.84 min, t_R (major) = 12.93 min.

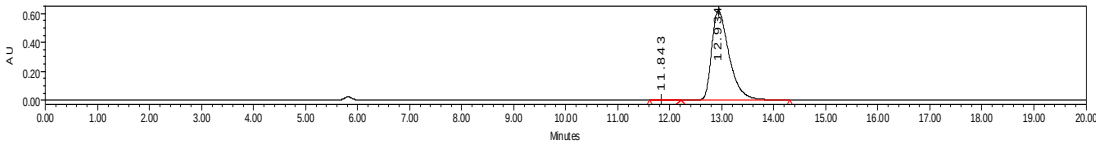
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 1H), 7.64 – 7.51 (m, 4H), 7.46 – 7.42 (m, 2H), 7.37 – 7.33 (m, 1H), 7.27 – 7.19 (m, 3H), 6.88 – 6.75 (m, 1H), 6.16 – 5.98 (m, 1H), 4.02 (d, *J* = 8.8 Hz, 1H), 3.16 (d, *J* = 8.8 Hz, 1H), 3.13 – 3.02 (m, 1H), 2.94 – 2.74 (m, 3H), 2.12 (s, 3H), 1.66 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 171.7, 149.2, 141.0, 140.3, 140.0, 131.7, 130.3, 129.0, 128.0, 127.7, 127.4, 127.1, 124.6, 124.0, 120.9, 115.1, 84.8, 45.0, 42.9, 39.9, 28.3, 28.0, 15.9.

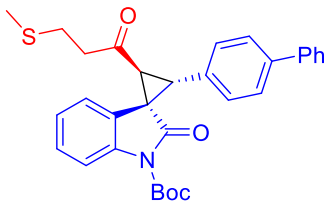
HRMS (ESI-FT) calcd for $C_{31}H_{31}NaNO_4S^+$([M+Na$^+$]) = 536.1866, Found 536.1863.



	Retention Time	Area	% Area
1	11.687	15275738	49.68
2	12.816	15470604	50.32



	Retention Time	Area	% Area
1	11.843	9407	0.07
2	12.934	14435636	99.93

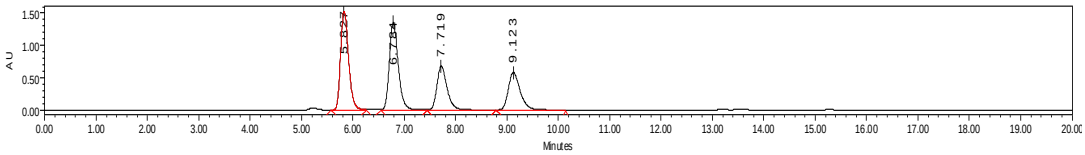


Condition B: [(*anti,syn*)+(*anti,anti*)]/*syn,anti* = 3.7/1, isolated (*anti,syn*)+(*anti,anti*) isomers, White solid, m.p. 54 – 58 °C, 34.4 mg, 67% yield, 91/9 dr (*anti-anti*/*anti-syn*, determined by ^{1}H NMR), 67% ee, $[\alpha]^{19}_D$ = +174.5 (*c* = 0.47 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 7.55 min, t_R (major) = 8.81 min.

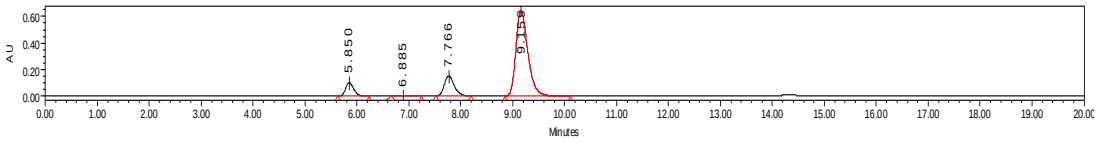
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 0.09H), 7.91 – 7.85 (m, 0.91H), 7.71 – 7.69 (m, 0.18H), 7.62 – 7.49 (m, 4.55H), 7.39 – 7.33 (m, 4H), 7.20 – 7.14 (m, 0.91H), 7.06 – 7.01 (m, 0.18H), 6.97 – 6.93 (m, 0.09H), 6.84 – 6.80 (m, 0.09H), 3.94 (d, *J* = 8.4 Hz, 0.91H), 3.75 (d, *J* = 9.6 Hz, 0.09H), 3.71 (d, *J* = 8.4 Hz, 0.91H), 3.32 (d, *J* = 9.6 Hz, 0.09H), 3.00 (m, 1H), 2.77 (m, 2H), 2.71 – 2.62 (m, 1H), 2.07 (s, 0.27H), 2.06 (s, 2.73H), 1.71 (s, 0.81H), 1.61 (s, 8.19H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 170.2, 149.1, 140.8, 140.6, 139.9, 131.3, 129.7, 128.9, 128.1, 127.4, 127.2, 127.0, 124.9, 124.5, 122.1, 114.9, 84.8, 45.3, 44.6, 42.0, 41.1, 28.2, 27.7, 15.8.

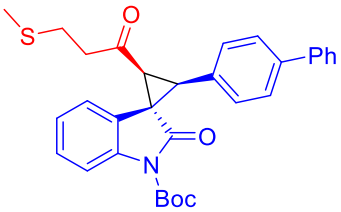
HRMS (ESI-FT) calcd for $C_{31}H_{31}NaNO_4S^+$([M+Na$^+$]) =536.1866, Found 536.1867.



	Retention Time	Area	% Area
1	5.827	16499770	32.02
2	6.784	16377361	31.79
3	7.719	9354567	18.16
4	9.123	9292834	18.04



	Retention Time	Area	% Area
1	5.850	1099047	8.19
2	6.885	43432	0.32
3	7.766	2057380	15.34
4	9.159	10213446	76.14



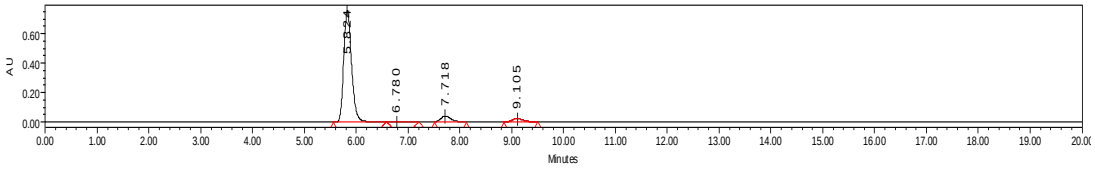
Condition C: [(*anti,syn*)+(*anti,anti*)]/*syn,anti* = 5.1/1, isolated (*anti,syn*)+(*anti,anti*) isomers, White solid, m.p. 65 – 68 °C, 39.6 mg, 77% yield, 90/10 dr (*anti,syn*/*anti,anti*, determined by ^{1}H NMR), 98% ee, $[\alpha]^{19}_D$ = +99.6 (*c* = 0.78 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 5.82 min, t_R (minor) = 6.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 0.90H), 7.89 – 7.86 (m, 0.10H), 7.62 – 7.56 (m, 2.10H), 7.52 – 7.47 (m, 1.90H), 7.46 – 7.39 (m, 2.10H), 7.38 – 7.26 (m, 2.30H), 7.06 – 7.00 (m, 1.80H), 6.98 – 6.92 (m, 0.90H), 6.85 – 6.78 (m, 0.90H), 3.93 (d, *J* = 8.4 Hz, 0.10H), 3.75 (d, *J* = 9.6 Hz, 0.90H), 3.71 (d, *J* = 8.8 Hz, 0.10H), 3.31 (d, *J* = 9.6 Hz, 0.90H), 3.11 – 3.01 (m, 1H), 2.87 – 2.71 (m, 2H), 2.66 – 2.55 (m, 1H), 2.07 (s, 2.70H), 2.06 (s, 0.30H), 1.70 (s, 8.10H), 1.61 (s, 0.90H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 174.0, 149.1, 140.7, 140.4, 140.2, 131.5, 129.1, 128.9, 128.1, 127.5, 127.2, 127.1, 126.7, 123.7, 121.8, 114.6, 85.0, 45.8,

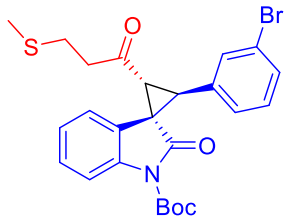
42.6, 40.6, 38.8, 28.2, 27.7, 15.9.

HRMS (ESI-FT) calcd for $C_{31}H_{31}NaNO_4S^+$ ([M+Na$^+$]) =536.1866, Found 536.1864.



	Retention Time	Area	% Area
1	5.824	7950583	89.46
2	6.780	50909	0.57
3	7.718	532002	5.99
4	9.105	353746	3.98

***Tert*-butyl-2-(3-bromophenyl)-3-(3-(methylthio)propanoyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1'-carboxylate (14ba)**



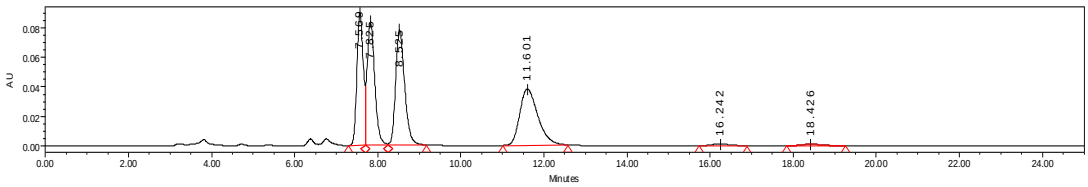
Condition A, [(*anti*,*syn*)+(*anti*,*anti*)]/*syn*,*anti* = 1.2/1, isolated *syn*,*anti* isomer. White solid, m.p. 135 – 140 °C, 21.2 mg, 70% yield, 86/14 dr (*anti*,*syn*/*anti*,*anti*, determined by ^{1}H NMR), 99% ee, $[\alpha]^{19}_D$ = -200.8 (*c* = 0.37 in CH_2Cl_2).

HPLC DAICEL CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (minor) = 15.95 min, t_R (major) = 17.92 min.

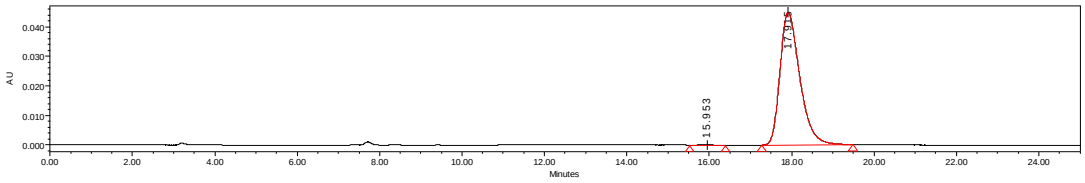
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 1H), 7.47 – 7.40 (m, 1H), 7.37 – 7.31 (m, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 1H), 7.09 – 7.00 (m, 1H), 6.92 – 6.78 (m, 1H), 6.09 – 5.94 (m, 1H), 3.93 (d, *J* = 8.8 Hz, 1H), 3.71 (d, *J* = 7.6 Hz, 1H), 3.09 (d, *J* = 8.8 Hz, 1H), 3.06 – 2.97 (m, 1H), 2.89 – 2.71 (m, 3H), 2.10 (s, 3H), 1.65 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 171.3, 149.1, 140.1, 135.1, 132.8, 131.5, 130.3, 128.7, 128.3, 124.1, 124.0, 122.8, 120.8, 115.2, 85.0, 58.6, 44.7, 42.9, 39.7, 39.1, 28.2, 28.0, 18.6, 15.9.

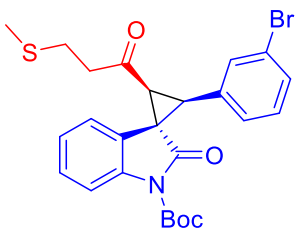
HRMS (ESI-FT) calcd for $C_{25}H_{26}{}^{79}BrNNaO_4S^+$ ([M+Na$^+$]) = 538.0658, Found 538.0663. $C_{25}H_{26}{}^{81}BrNNaO_4S^+$ ([M+Na$^+$]) = 540.0638, Found 540.0641.



	Retention Time	Area	% Area
1	7.569	953332	21.46
2	7.825	1080447	24.32
3	8.525	1179673	26.56
4	11.601	1157090	26.05
5	16.242	34597	0.78
6	18.426	36926	0.83



	Retention Time	Area	% Area
1	15.953	1563	0.10
2	17.915	1495992	99.90



Condition C, [(*anti,syn*)+(*anti,anti*)]/*syn,anti* = 4.6/1, isolated (*anti,syn*)+(*anti,anti*) isomers. White solid, m.p. 50 – 54 °C, 36.2 mg, 70% yield, 86/14 dr (*anti,syn*/*anti,anti*, determined by ^{1}H NMR), 82% ee, $[\alpha]^{19}_D$ = +117.7 (*c* = 0.64 in CH_2Cl_2).

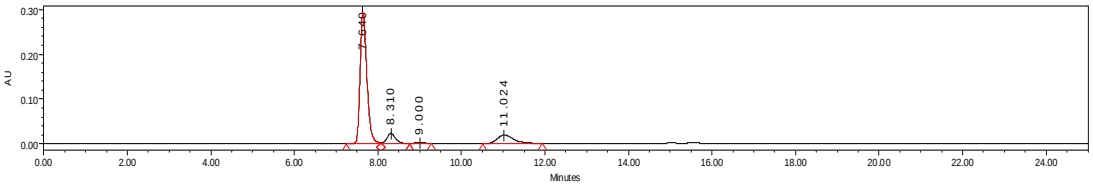
HPLC DAICEL CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, t_R (major) = 7.64 min, t_R (minor) = 8.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.89 (m, 0.86H), 7.89 – 7.84 (m, 0.14H), 7.44 – 7.36 (m, 1.14H), 7.33 – 7.27 (m, 1H), 7.23 – 7.07 (m, 2.28H), 7.00 – 6.92 (m, 0.86H), 6.91 – 6.83 (m, 0.86H), 6.80 – 6.69 (m, 0.86H), 3.84 (d, *J* = 8.8 Hz, 0.14H), 3.64 (d, *J* = 9.6 Hz, 0.86H), 3.61 (d, *J* = 8.8 Hz, 0.14H), 3.26 (d, *J* = 9.6 Hz, 0.86H), 3.04 – 2.94 (m, 1H), 2.81 – 2.67 (m, 2H), 2.66 – 2.54 (m, 1H), 2.05 (s, 2.48H), 2.04 (s, 0.52H), 1.69 (s, 7.74H), 1.61 (s, 1.26H).

^{13}C NMR (101 MHz, $CDCl_3$) (for major) δ 201.4, 173.8, 149.0, 140.3, 134.0, 132.4, 130.8, 129.8, 129.5, 128.3, 126.8, 123.8, 121.9, 121.4, 114.7, 85.1, 45.7, 42.3, 40.2,

37.9, 28.2, 27.7, 15.9.

HRMS (ESI-FT) calcd for $C_{25}H_{26}{}^{79}BrNNaO_4S^+$ ([M+Na$^+$]) = 538.0658, Found 538.0660. $C_{25}H_{26}{}^{81}BrNNaO_4S^+$ ([M+Na$^+$]) = 540.0638, Found 540.0638.



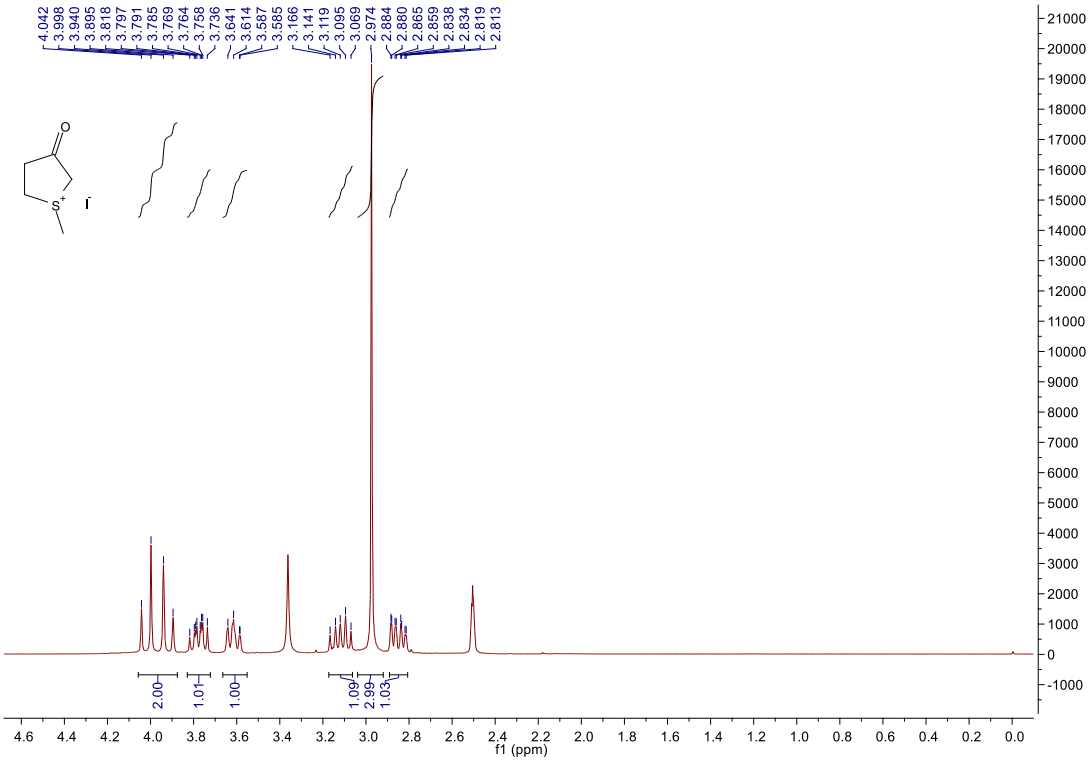
	Retention Time	Area	% Area
1	7.640	3302151	78.54
2	8.310	321928	7.66
3	9.000	33349	0.79
4	11.024	546927	13.01

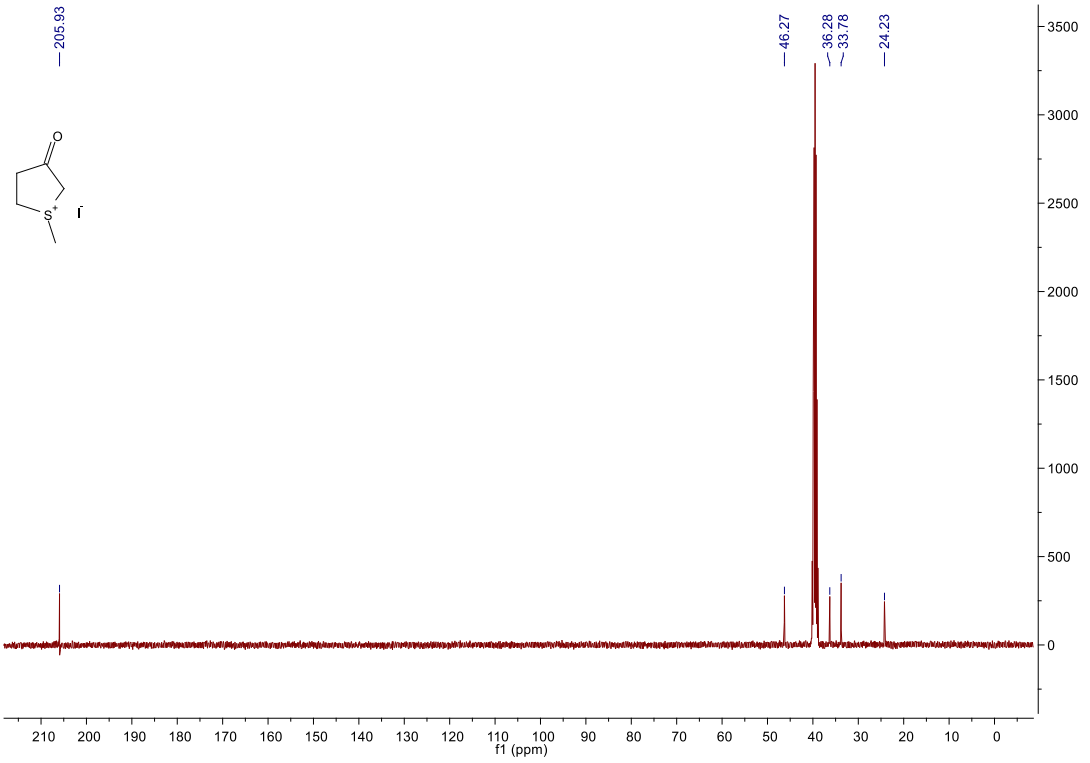
(K) References

1. (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett.*, **2005**, *16*, 2445; (b) X. Li, X. H. Liu, Y. Z. Fu, L. J. Wang, L. Zhou, X. M. Feng, *Chem. Eur. J.* **2008**, *14*, 4796.

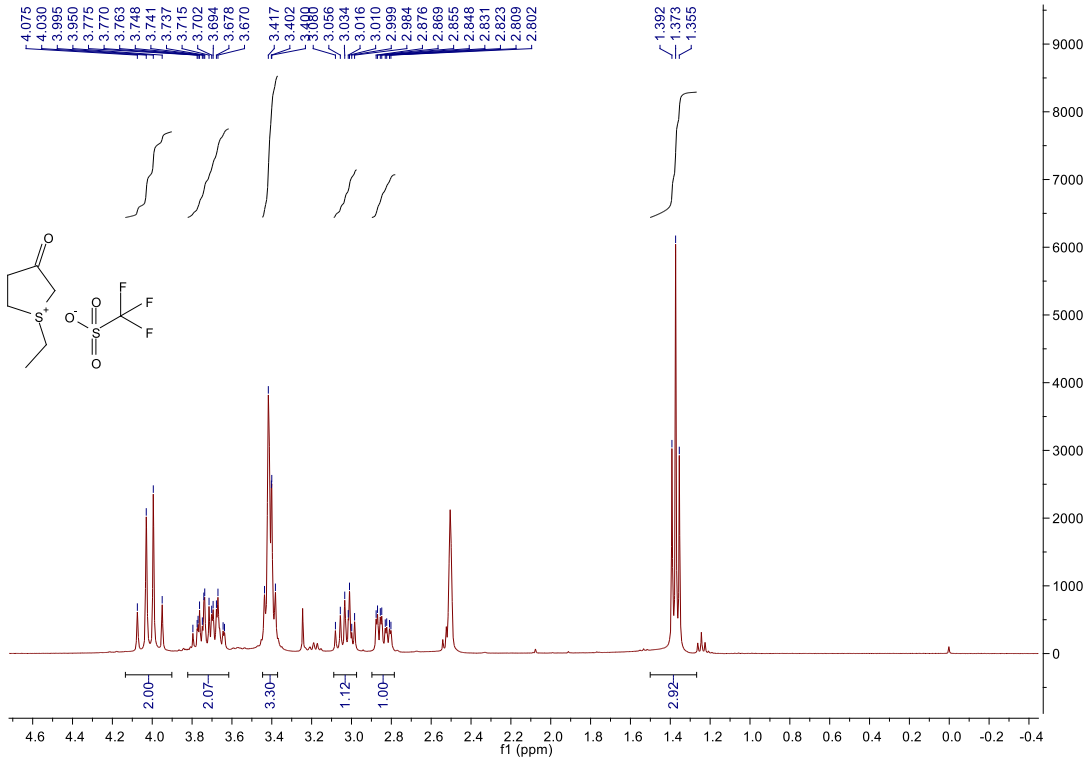
(L) Copies of NMR spectra.

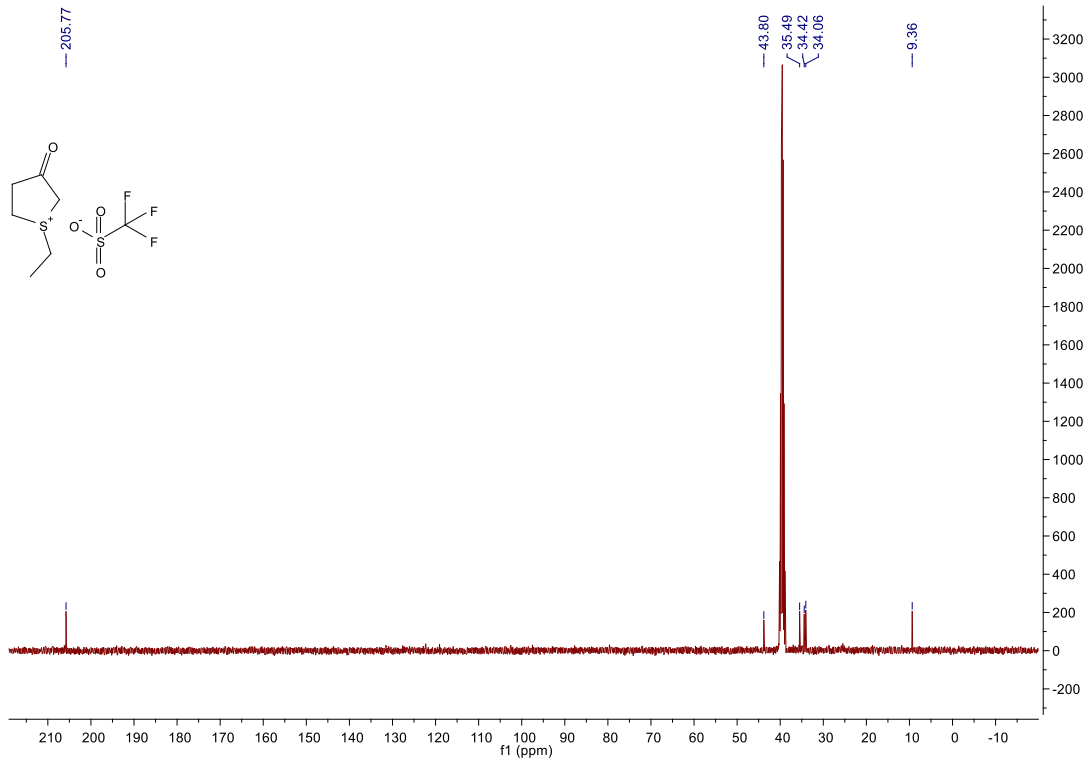
9a

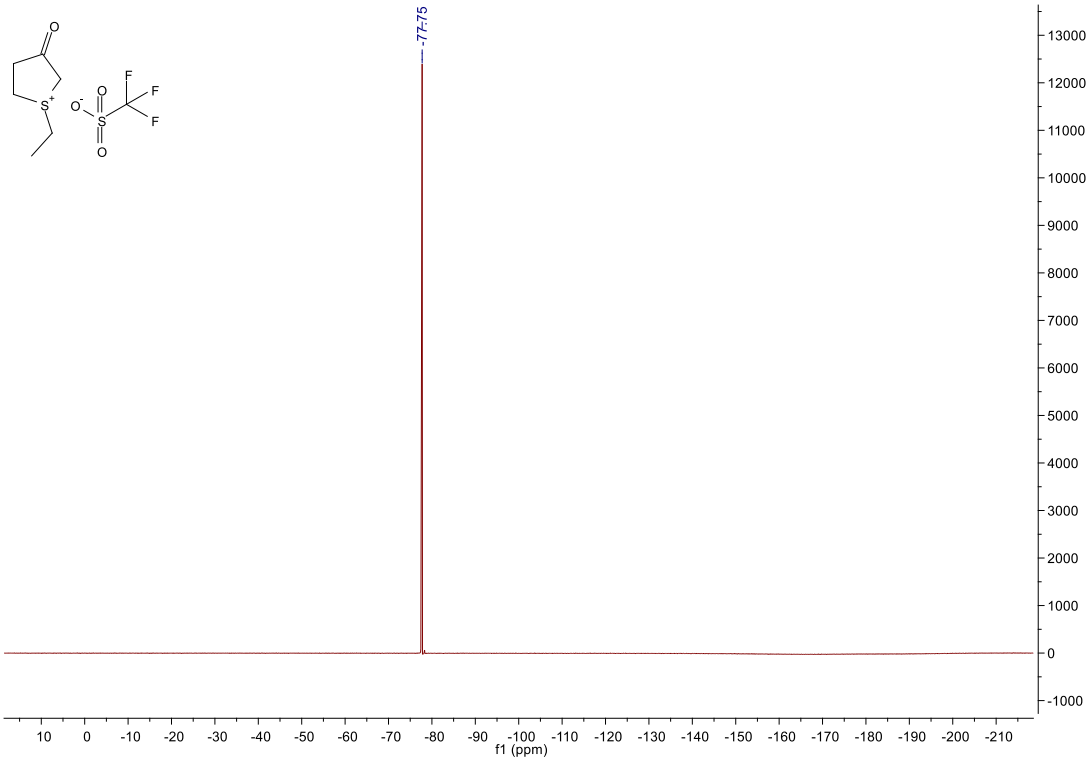




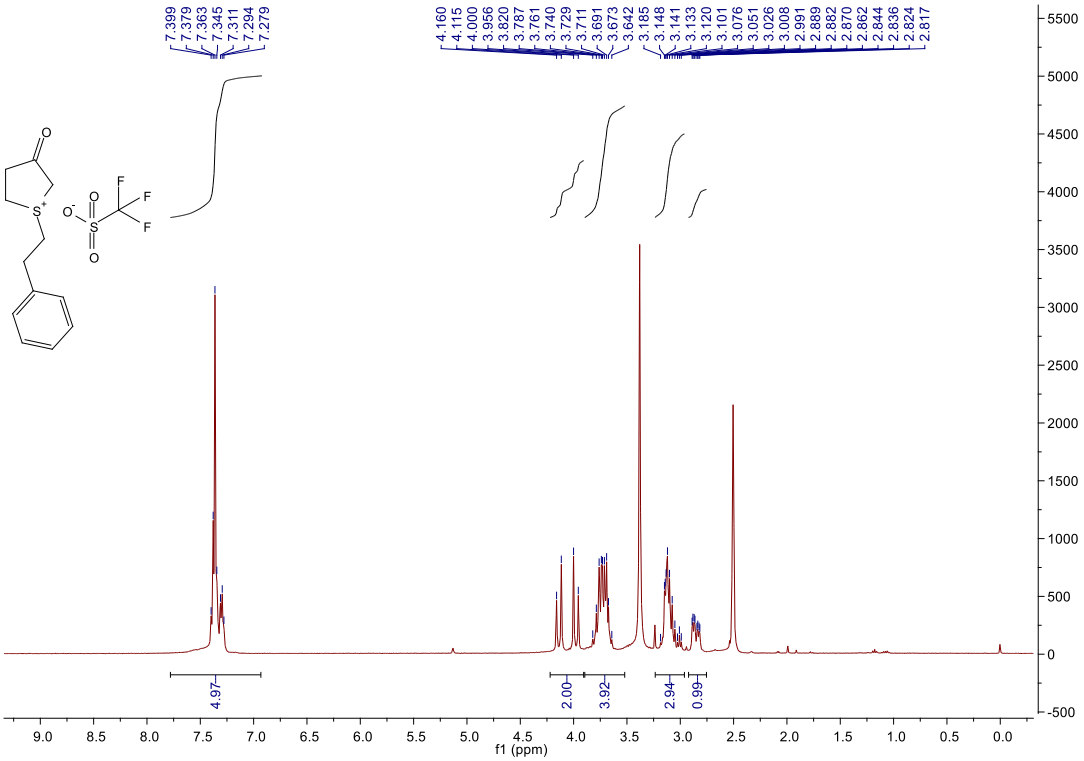
9b

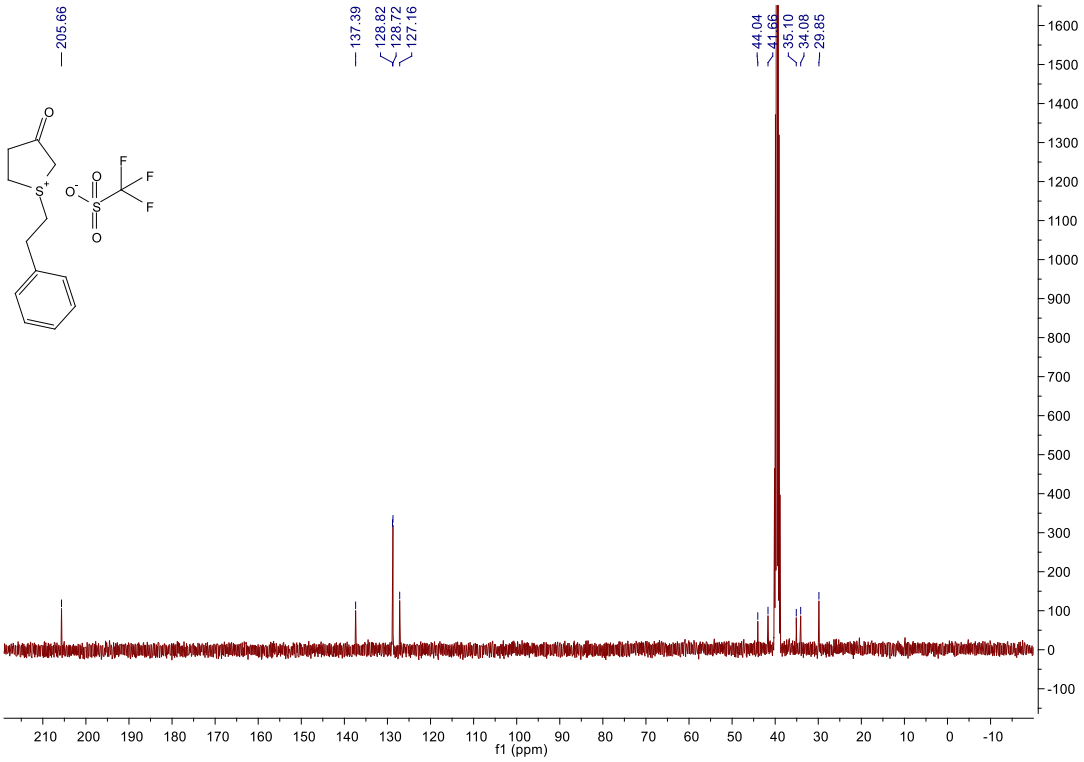

4.075
4.030
3.995
3.950
3.775
3.770
3.763
3.748
3.741
3.737
3.715
3.702
3.694
3.678
3.670
3.417
3.402
3.056
3.034
3.016
3.010
2.999
2.984
2.876
2.869
2.855
2.848
2.831
2.823
2.809
2.802
1.392
1.373
1.355
2.00
2.07
3.30
1.12
1.00
2.92
f1 (ppm)

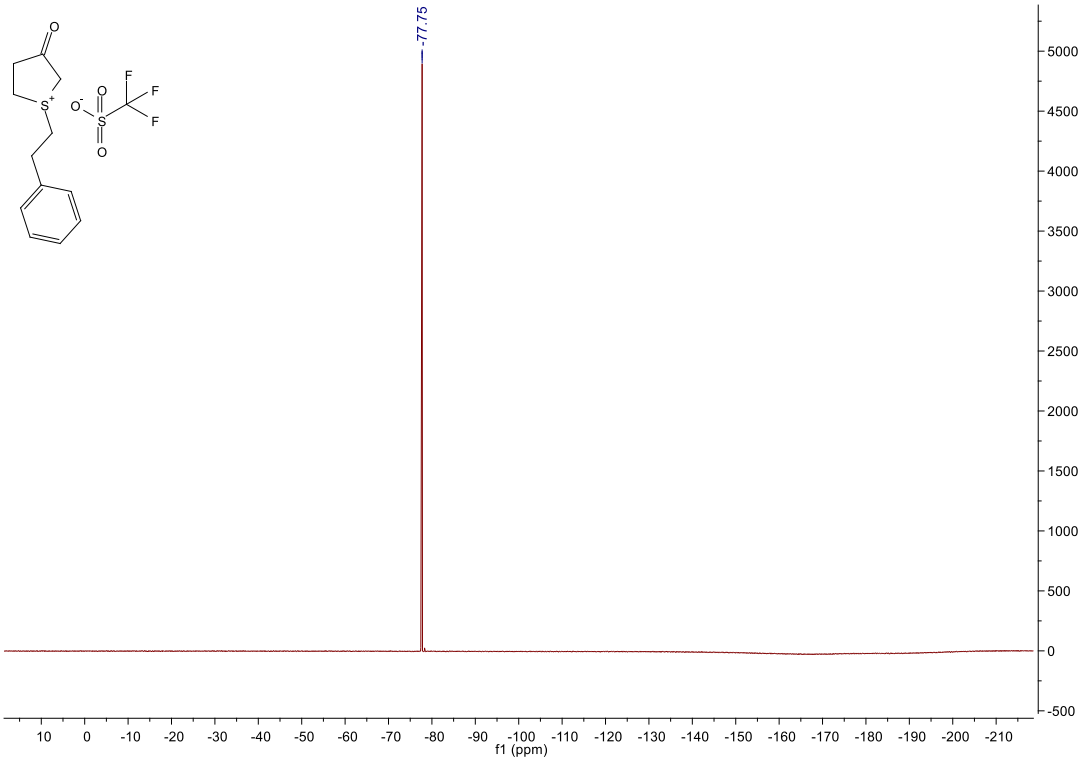

205.77
43.80
35.49
34.42
34.06
9.36
f1 (ppm)


-77.75
f1 (ppm)

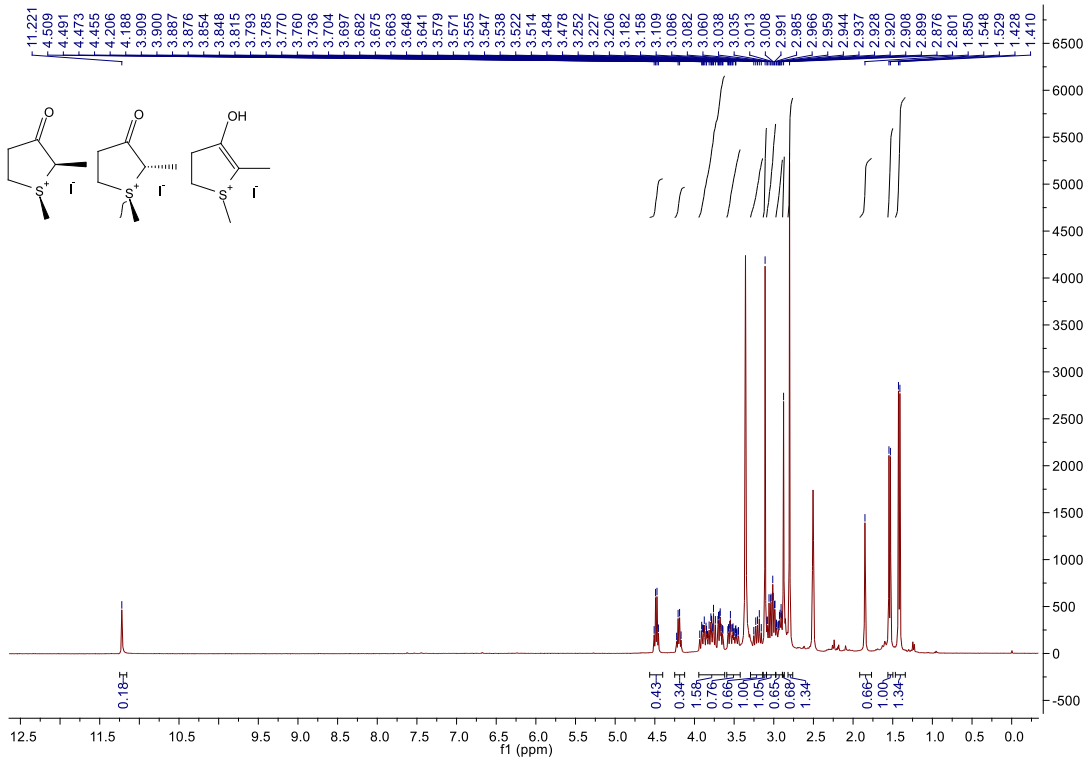
9c

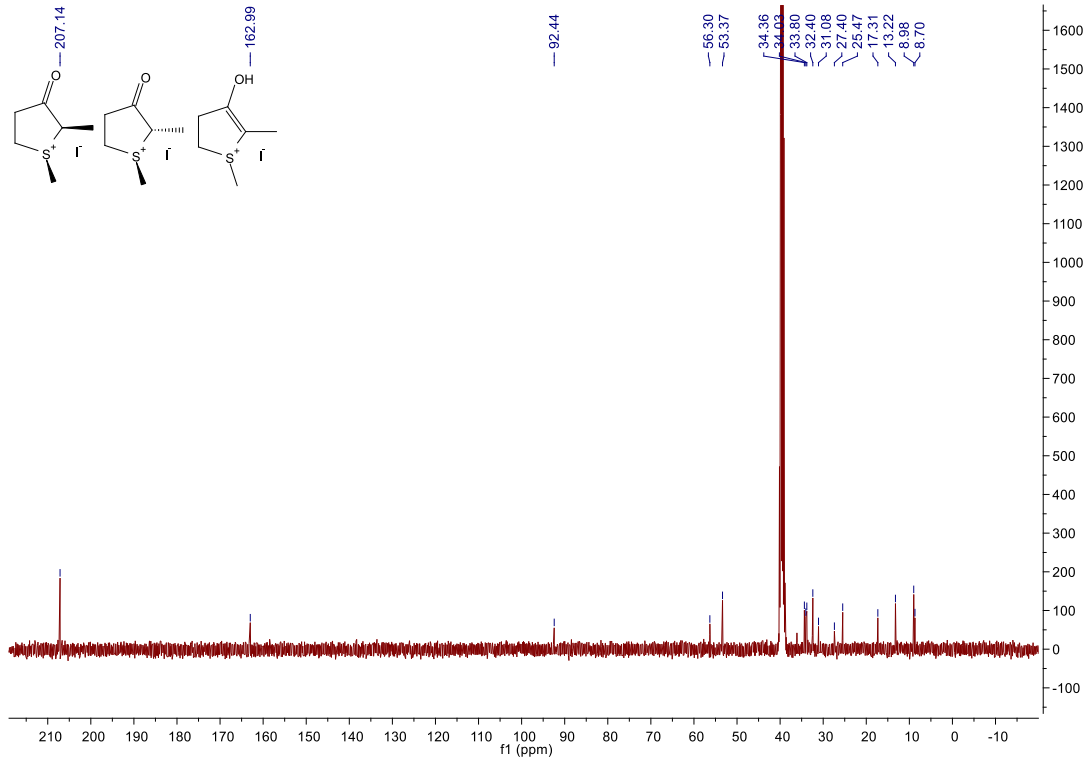

7.399
7.379
7.363
7.345
7.311
7.294
7.279
4.160
4.115
4.000
3.956
3.820
3.787
3.761
3.740
3.729
3.711
3.691
3.673
3.642
3.185
3.148
3.141
3.133
3.120
3.101
3.076
3.051
3.026
3.008
2.991
2.889
2.882
2.870
2.862
2.844
2.836
2.824
2.817
4.97
2.00
3.92
2.94
0.99
f1 (ppm)


205.66
137.39
128.82
128.72
127.16
44.04
41.66
35.10
34.08
29.85
f1 (ppm)

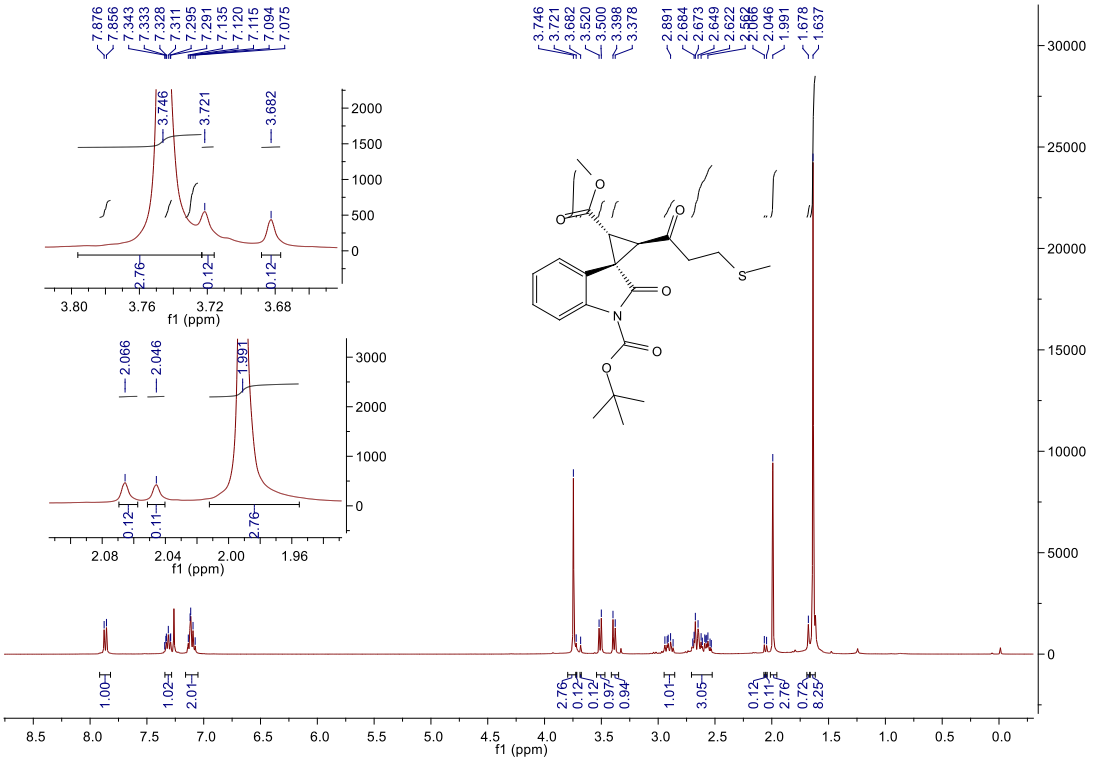

-77.75
f1 (ppm)

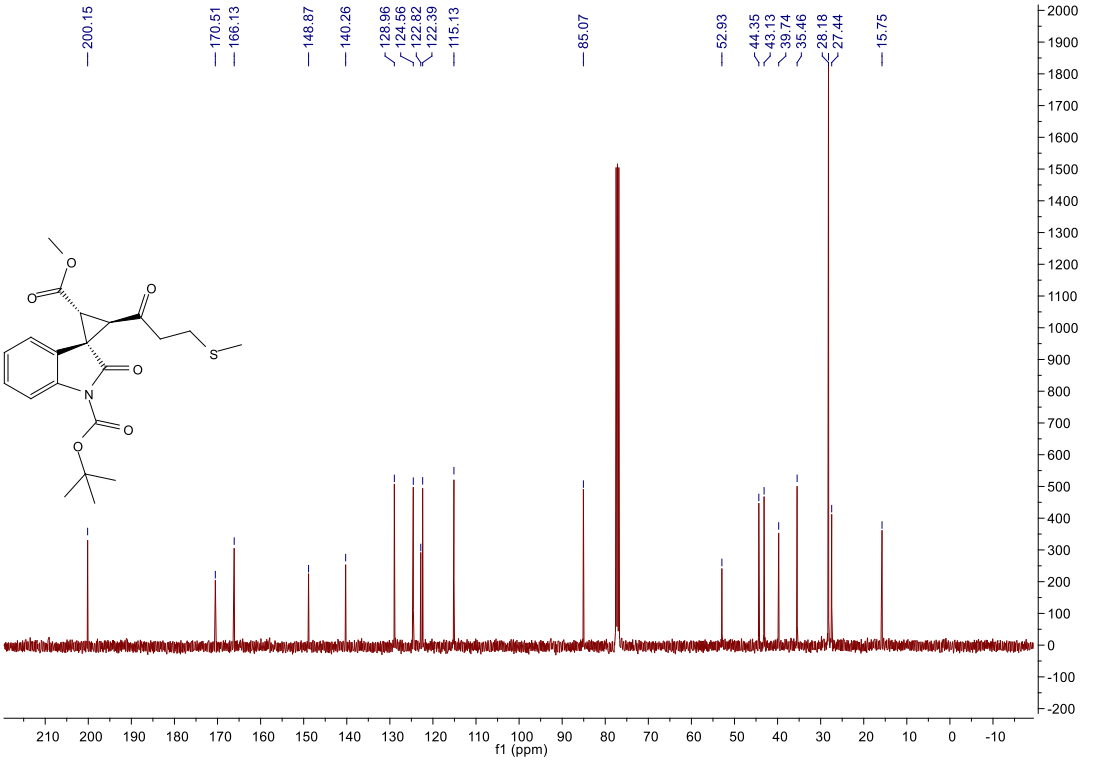
9d


11.221
4.509
4.491
4.473
4.455
4.206
4.188
3.909
3.900
3.887
3.876
3.854
3.848
3.815
3.793
3.785
3.770
3.760
3.736
3.704
3.697
3.682
3.675
3.663
3.648
3.641
3.579
3.571
3.555
3.547
3.538
3.522
3.514
3.484
3.478
3.252
3.227
3.206
3.182
3.158
3.109
3.086
3.082
3.060
3.038
3.035
3.013
3.008
2.991
2.985
2.966
2.959
2.944
2.937
2.928
2.920
2.908
2.899
2.876
2.801
1.850
1.548
1.529
1.428
1.410
0.18
0.43
0.34
1.58
0.76
0.66
1.00
1.05
0.65
0.68
1.34
0.66
1.00
1.34
f1 (ppm)

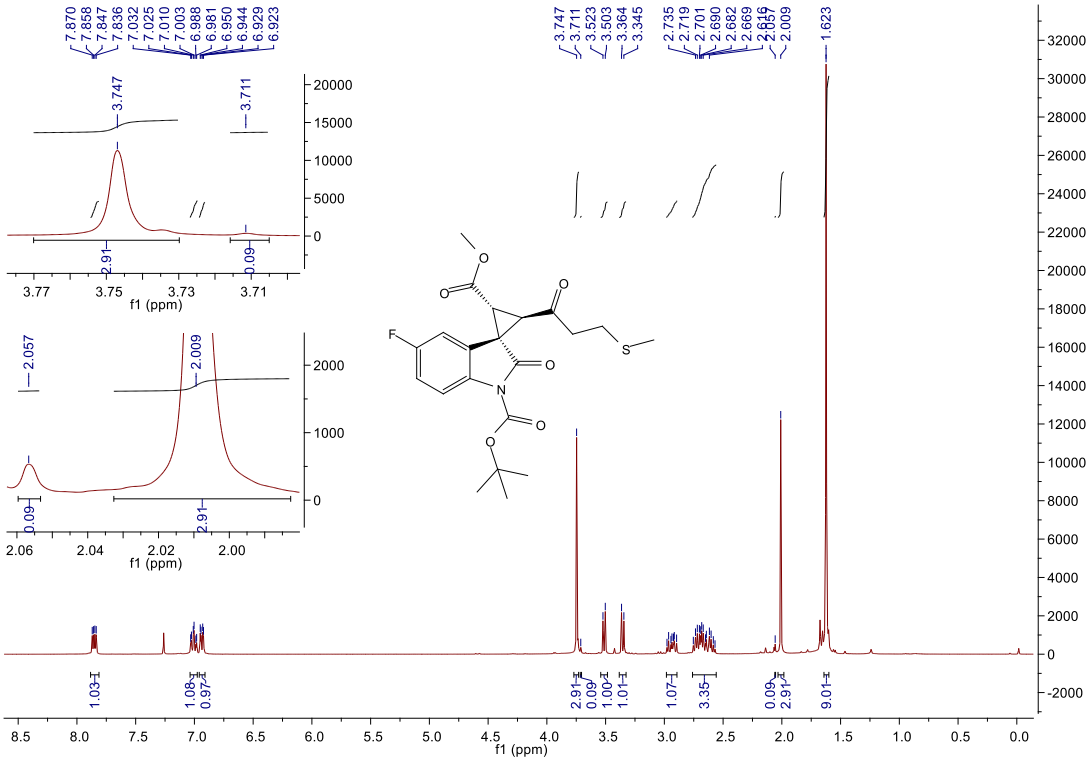

207.14
162.99
92.44
56.30
53.37
34.36
34.03
33.80
32.40
31.08
27.40
25.47
17.31
13.22
8.98
8.70
f1 (ppm)

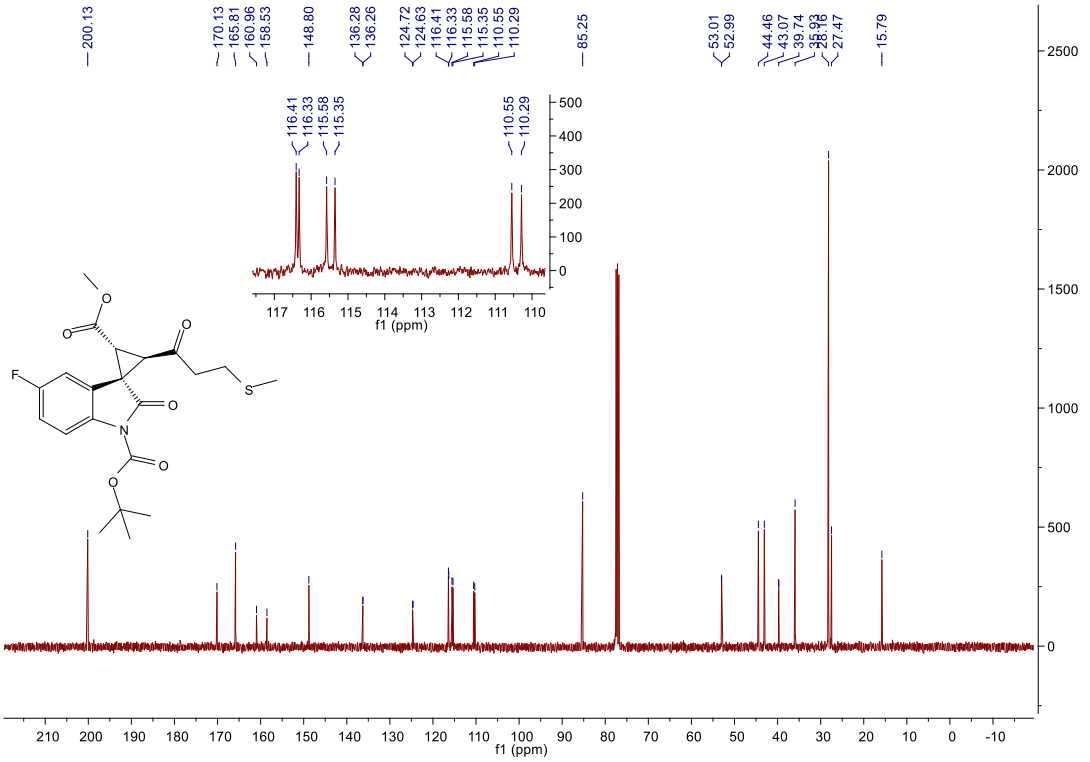
11aa


7.876
7.856
7.343
7.333
7.328
7.311
7.295
7.291
7.135
7.120
7.115
7.094
7.075
3.746
3.721
3.682
3.520
3.500
3.398
3.378
2.891
2.684
2.673
2.649
2.622
2.066
2.046
1.991
1.678
1.637
f1 (ppm)

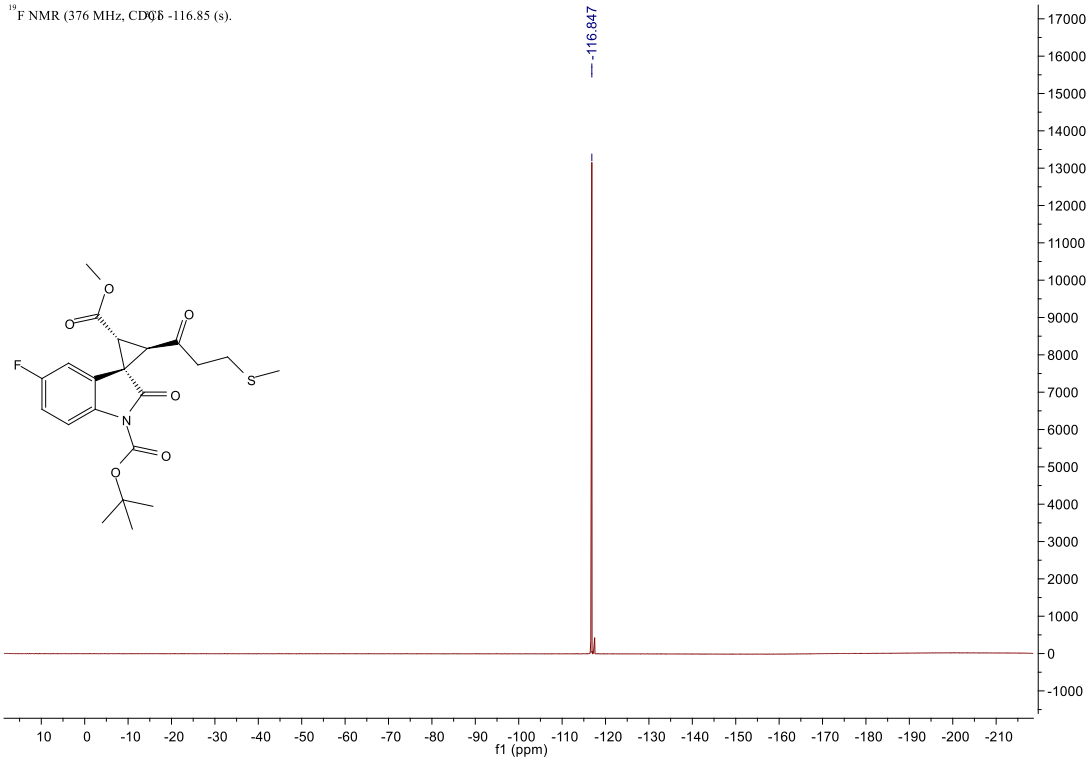

200.15
170.51
166.13
148.87
140.26
128.96
124.56
122.82
122.39
115.13
85.07
52.93
44.35
43.13
39.74
35.46
28.18
27.44
15.75
f1 (ppm)

11ba

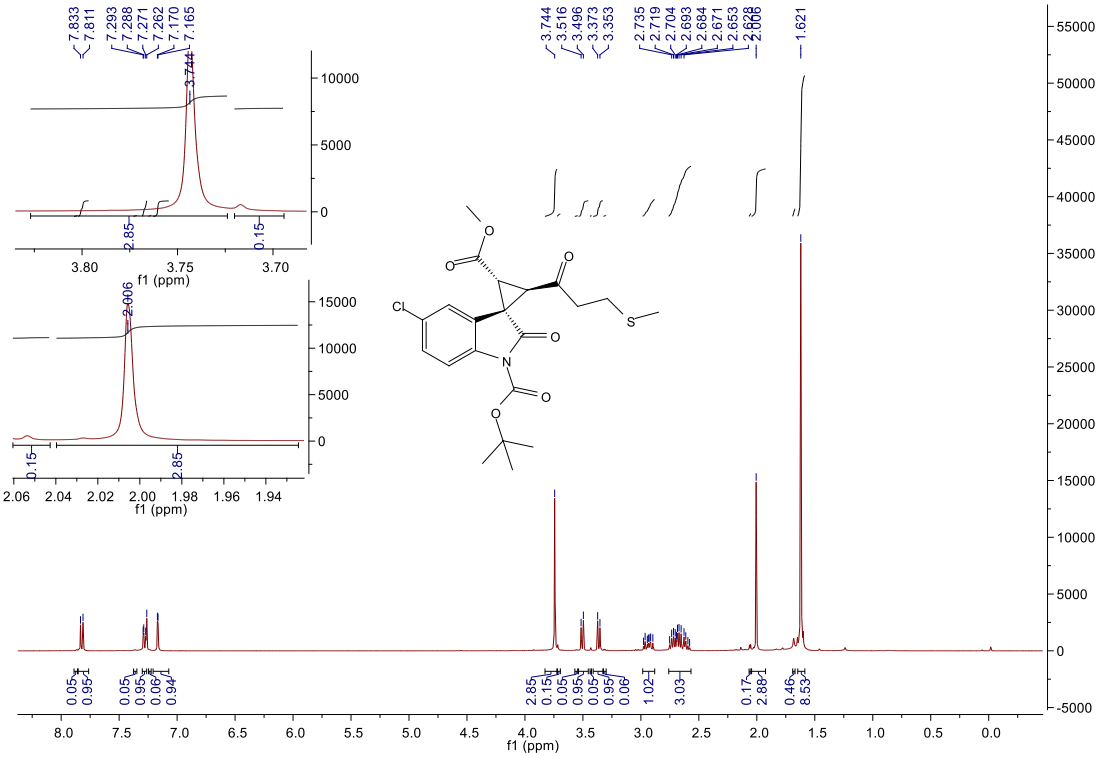


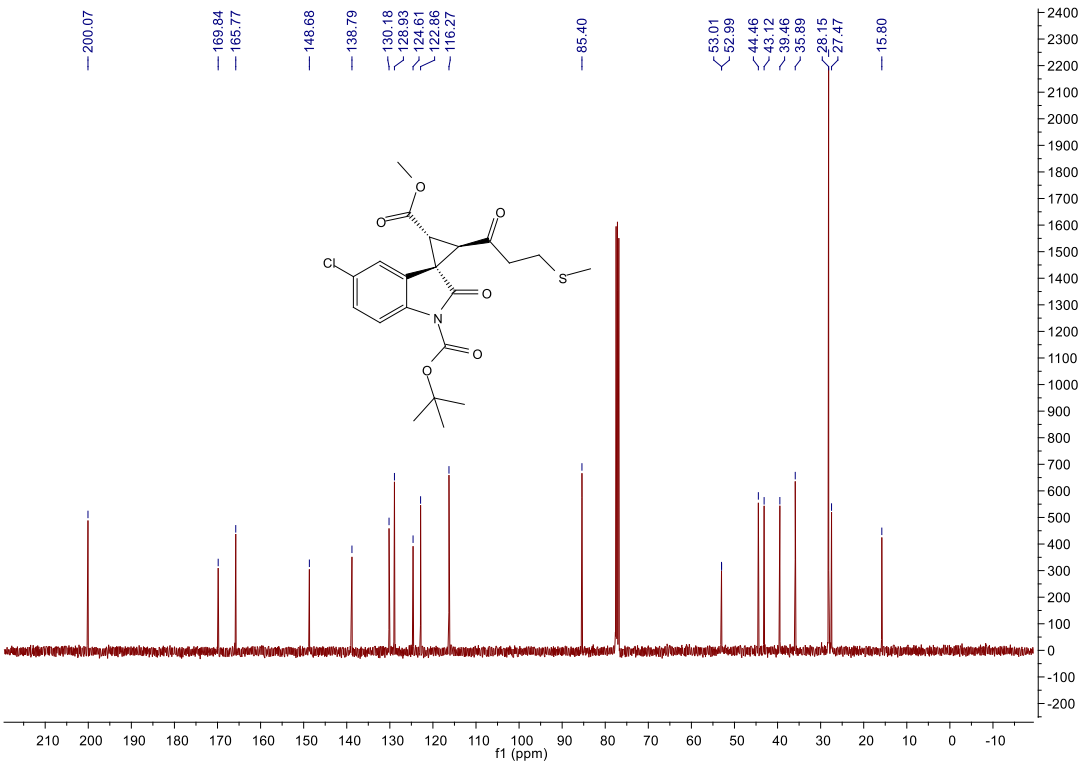


^{19}F NMR (376 MHz, $CDCl_3$) δ -116.85 (s).

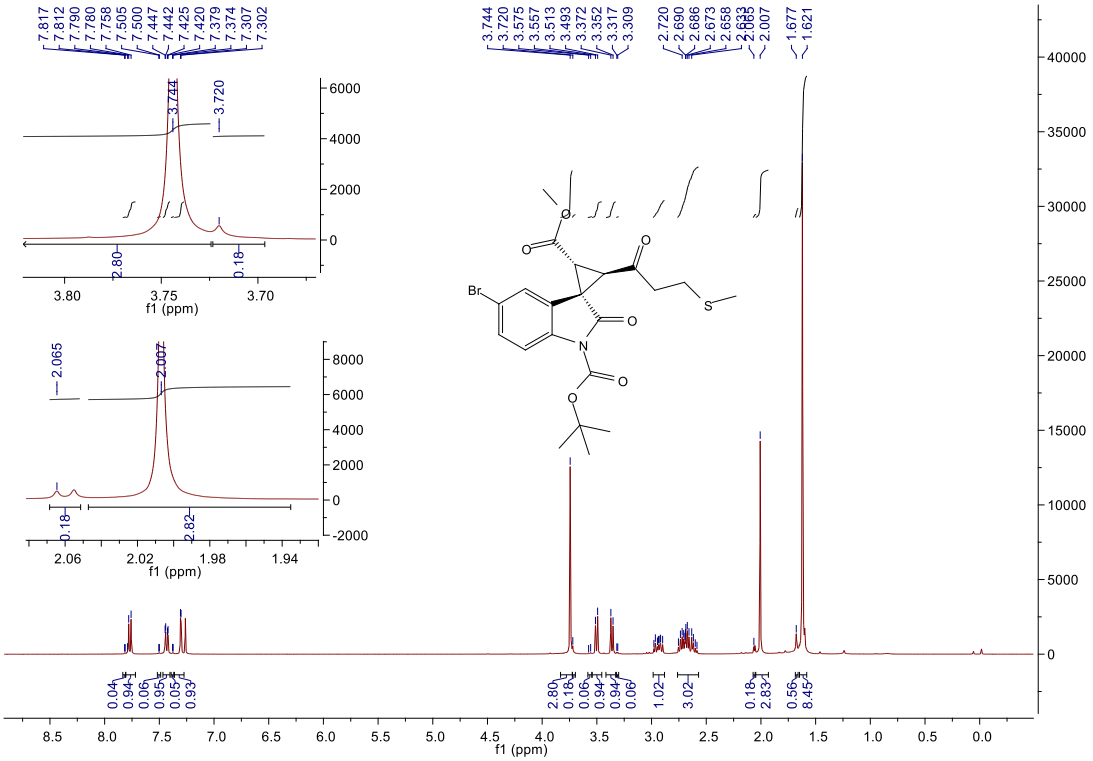


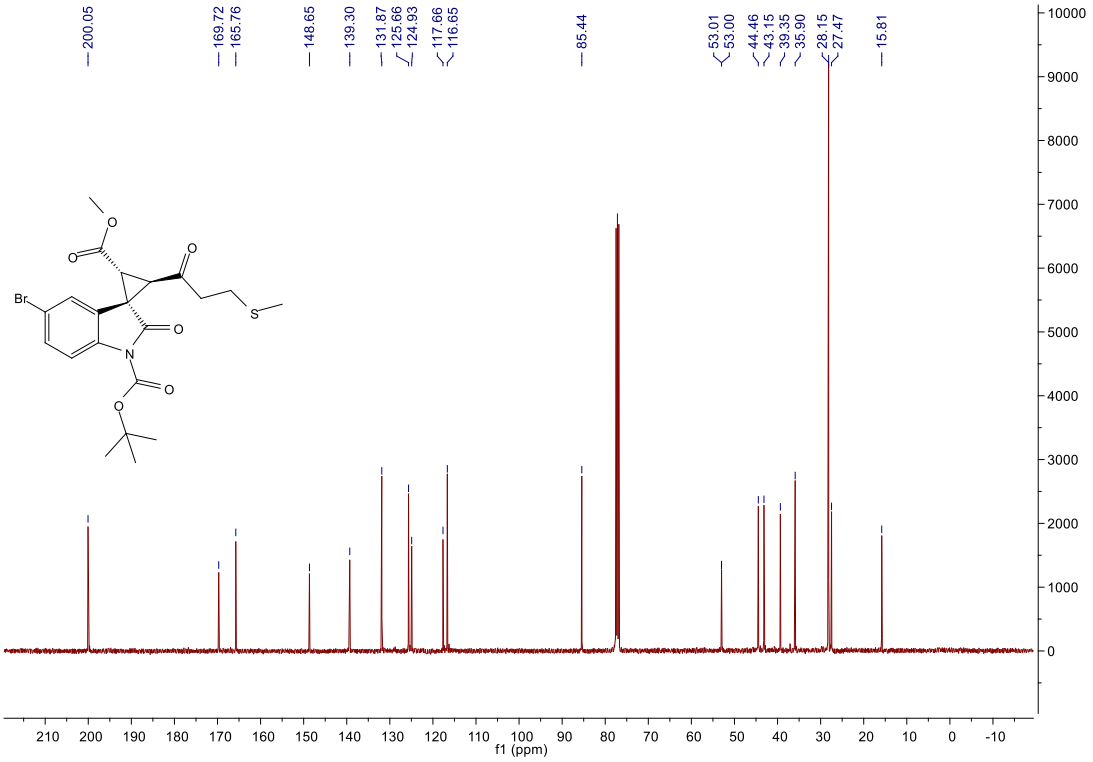
11ca


7.833
7.811
7.293
7.288
7.271
7.262
7.170
7.165
3.744
3.516
3.496
3.373
3.353
2.735
2.719
2.704
2.693
2.684
2.671
2.653
2.006
1.621
2.906
f1 (ppm)

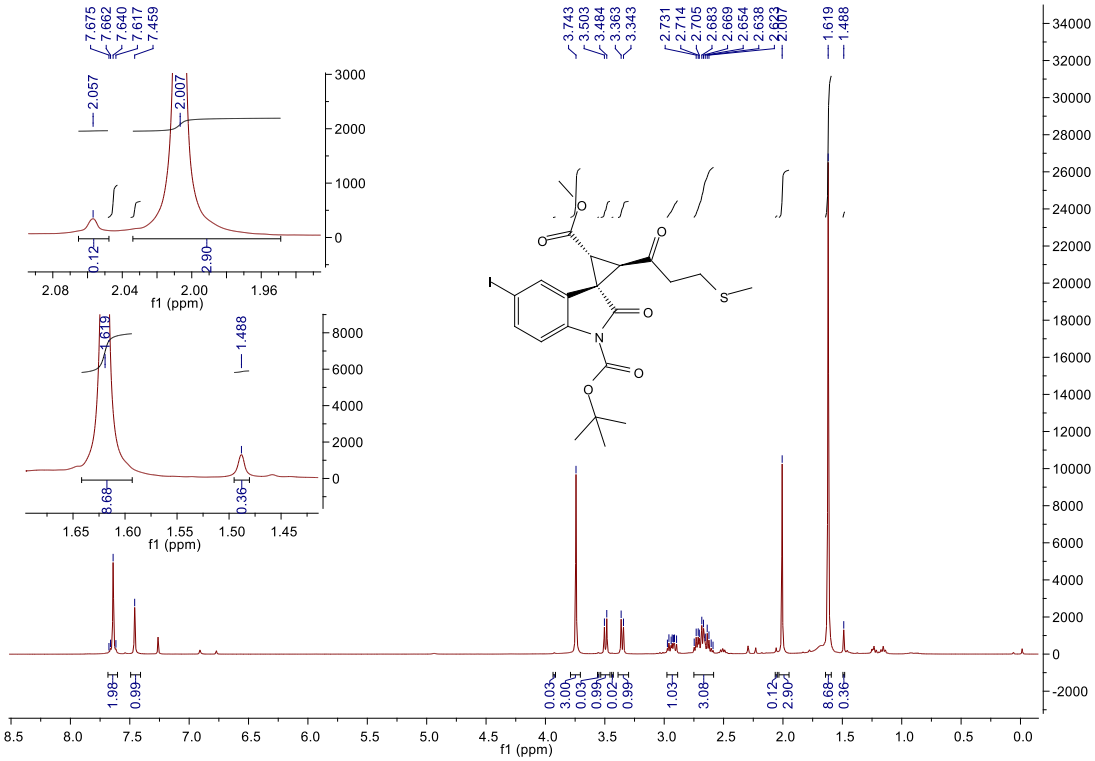

200.07
169.84
165.77
148.68
138.79
130.18
128.93
124.61
122.86
116.27
85.40
53.01
52.99
44.46
43.12
39.46
35.89
28.15
27.47
15.80
f1 (ppm)

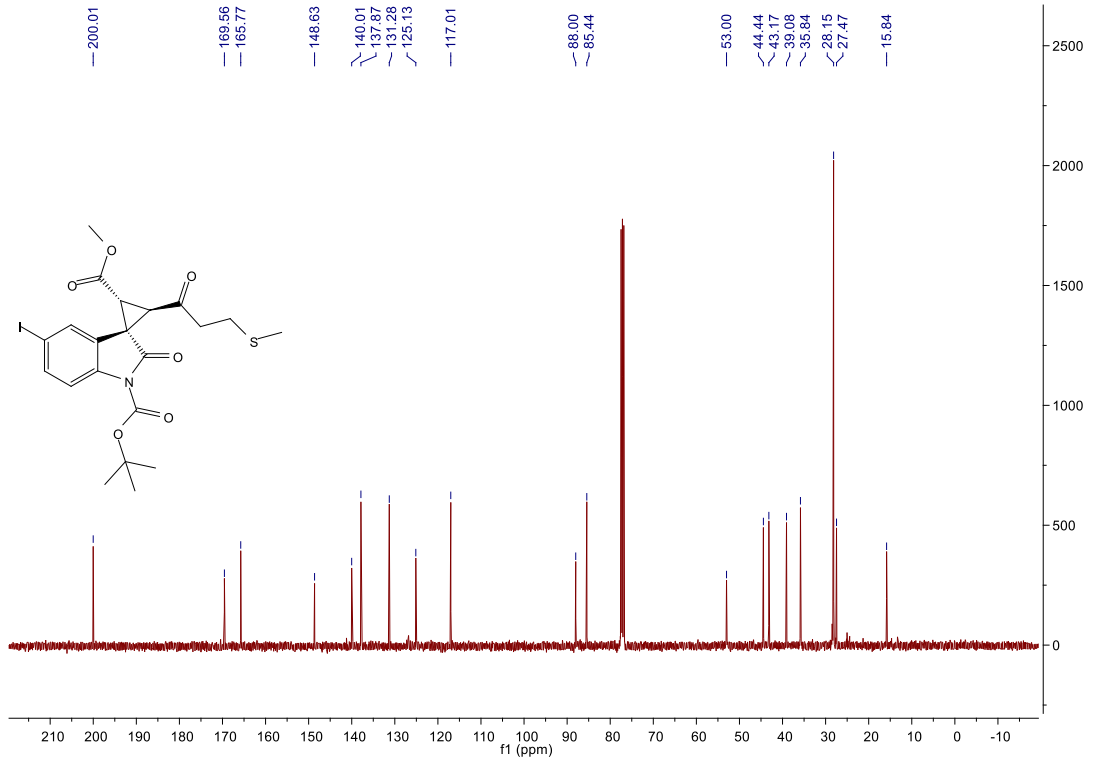
11da


7.817
7.812
7.790
7.780
7.758
7.505
7.500
7.447
7.442
7.425
7.420
7.379
7.374
7.307
7.302
3.744
3.720
3.575
3.557
3.513
3.493
3.372
3.352
3.317
3.309
2.720
2.690
2.686
2.673
2.658
2.007
1.677
1.621
2.065
2.007
f1 (ppm)

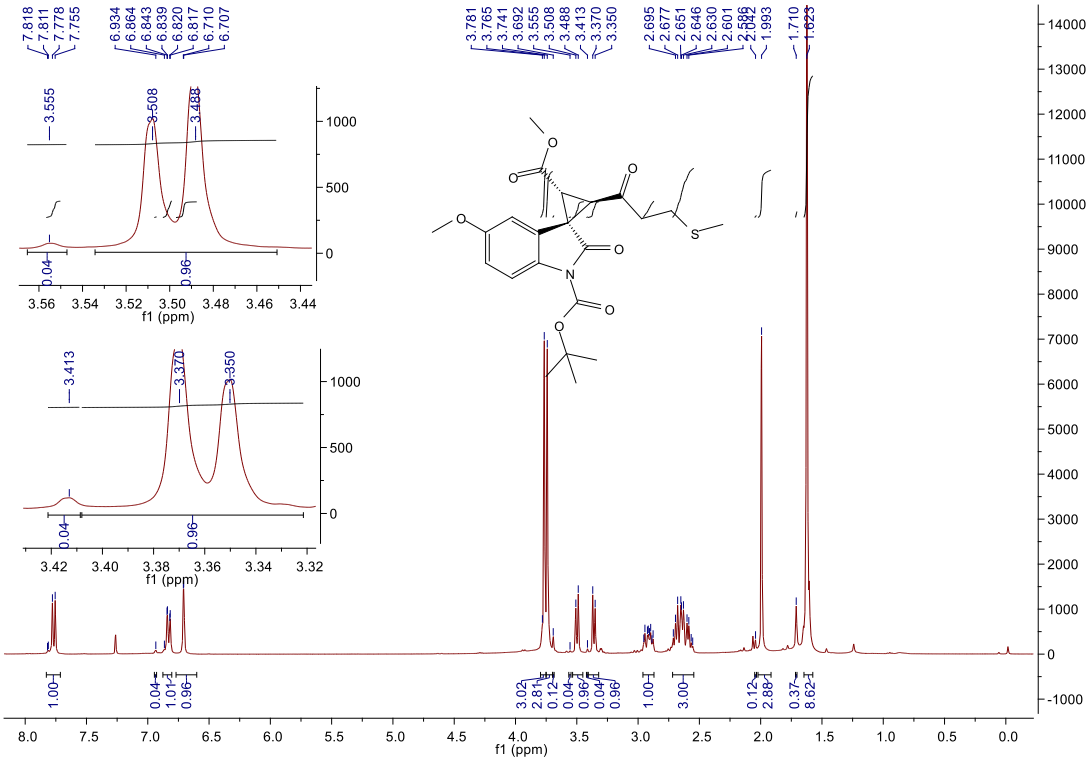

200.05
169.72
165.76
148.65
139.30
131.87
125.66
124.93
117.66
116.65
85.44
53.01
53.00
44.46
43.15
39.35
35.90
28.15
27.47
15.81
f1 (ppm)

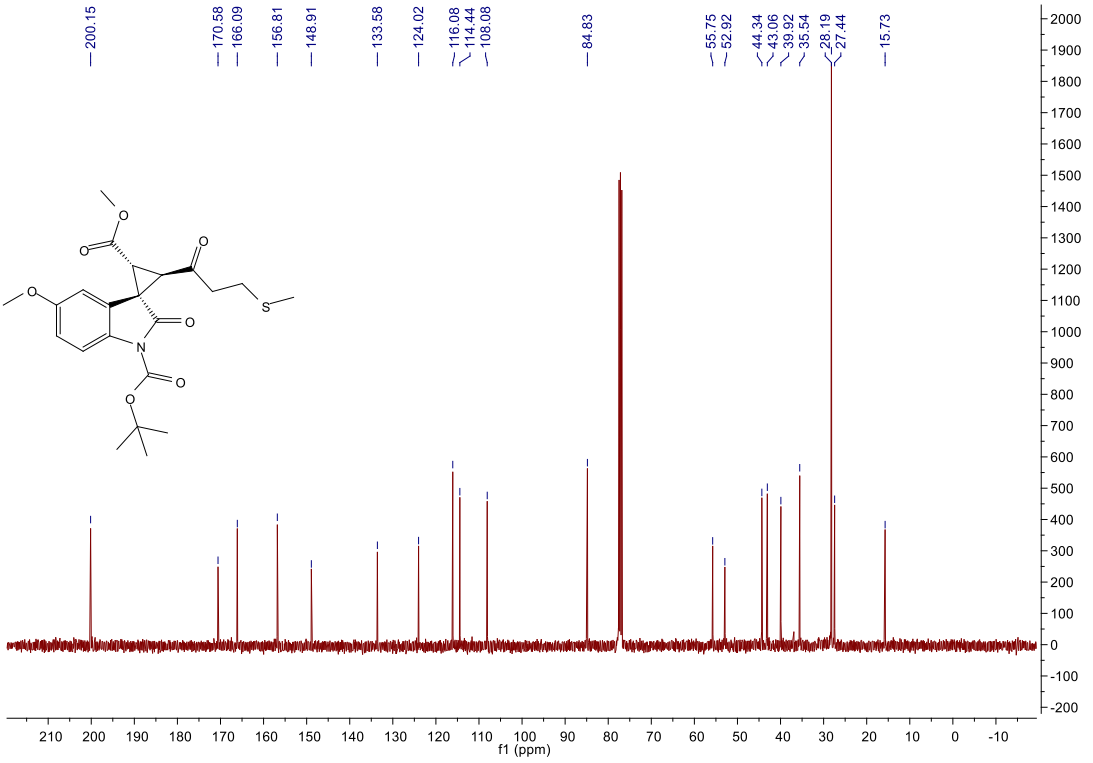
11ea


7.675
7.662
7.640
7.617
7.459
2.057
2.007
0.12
2.90
f1 (ppm)
1.619
1.488
8.68
0.36
3.743
3.503
3.484
3.363
3.343
2.731
2.714
2.705
2.683
2.669
2.654
2.638
2.623
2.007
1.98
0.99
0.03
3.00
0.03
0.99
0.02
0.99
1.03
3.08
0.12
2.90
8.68
0.36
f1 (ppm)

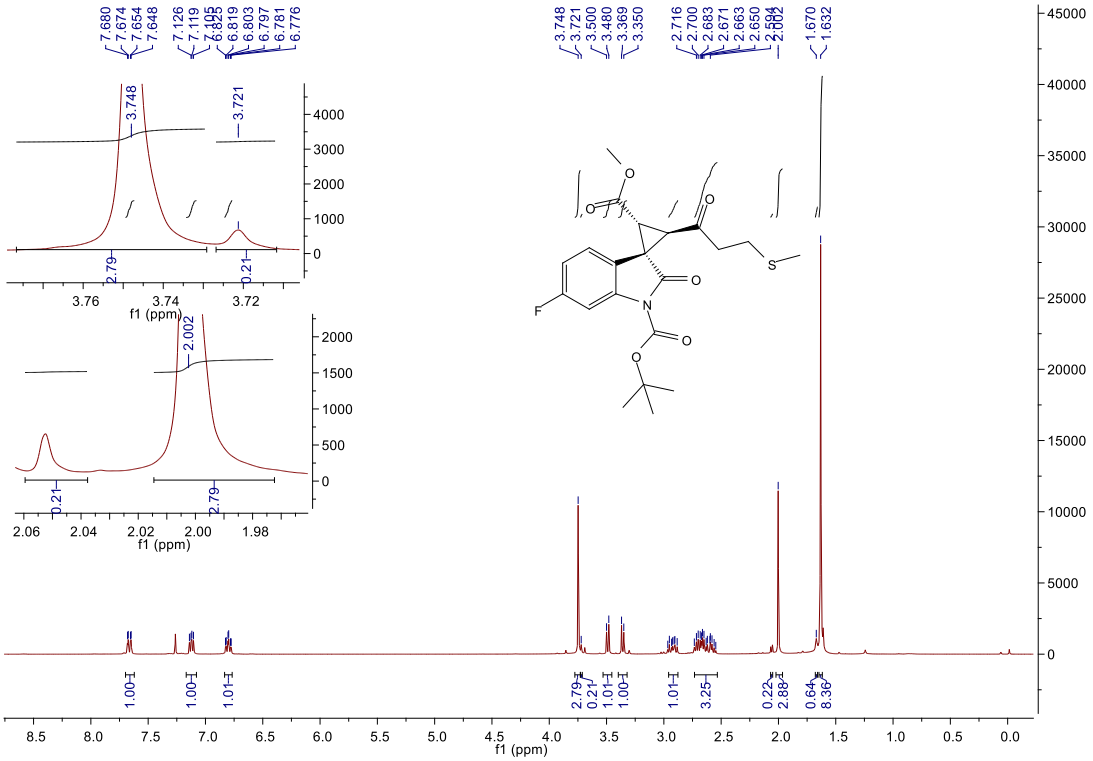

200.01
169.56
165.77
148.63
140.01
137.87
131.28
125.13
117.01
88.00
85.44
53.00
44.44
43.17
39.08
35.84
28.15
27.47
15.84
f1 (ppm)

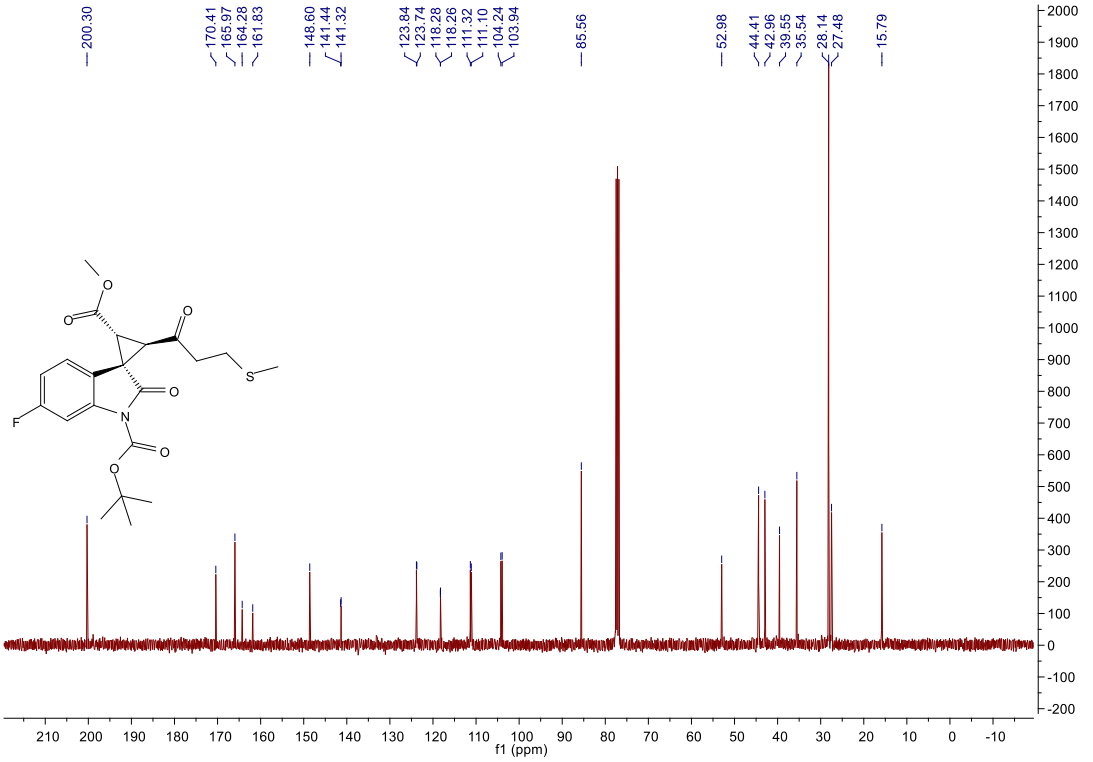
11fa

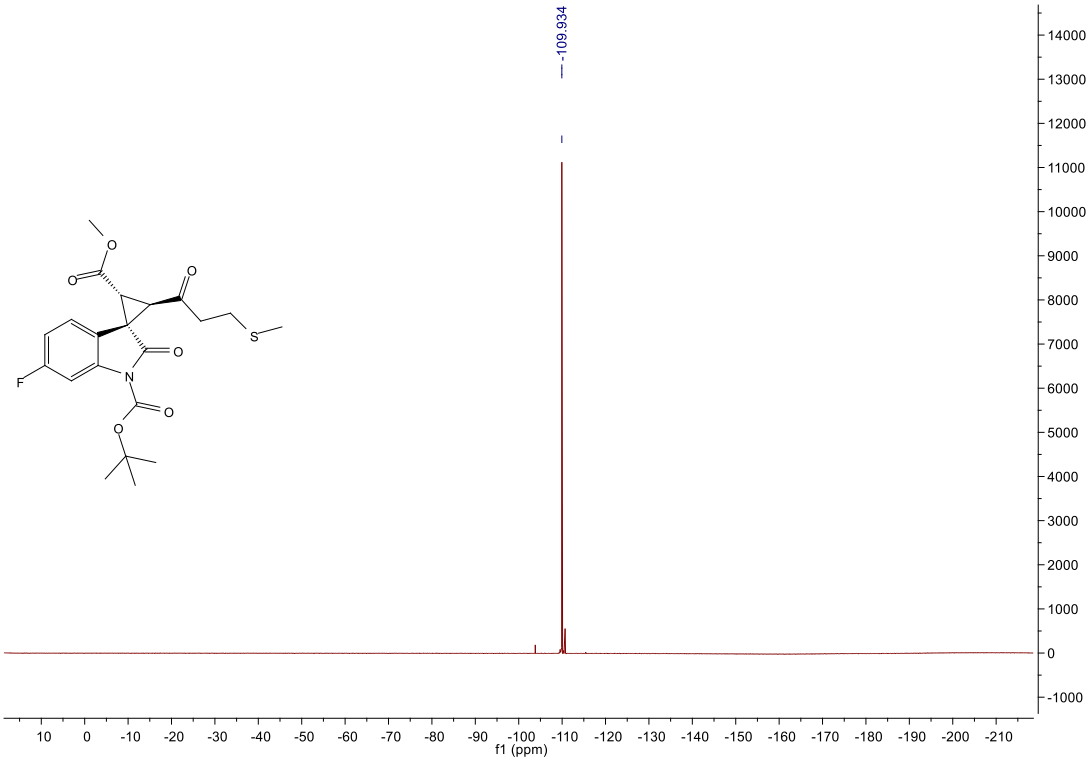

7.818
7.811
7.778
7.755
6.934
6.864
6.843
6.839
6.820
6.817
6.710
6.707
3.781
3.765
3.741
3.692
3.555
3.508
3.488
3.413
3.370
3.350
2.695
2.677
2.651
2.646
2.630
2.601
2.586
2.042
1.993
1.710
1.623
3.555
3.508
3.488
3.413
3.370
3.350
f1 (ppm)


200.15
170.58
166.09
156.81
148.91
133.58
124.02
116.08
114.44
108.08
84.83
55.75
52.92
44.34
43.06
39.92
35.54
28.19
27.44
15.73
f1 (ppm)

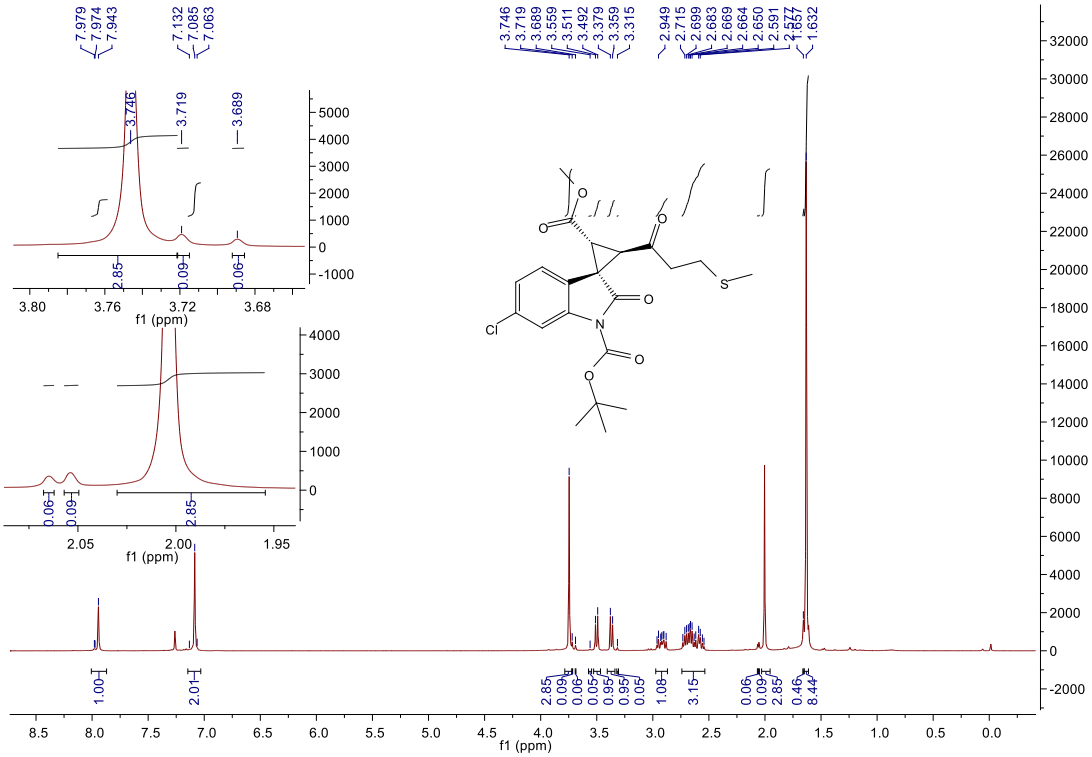
11ga

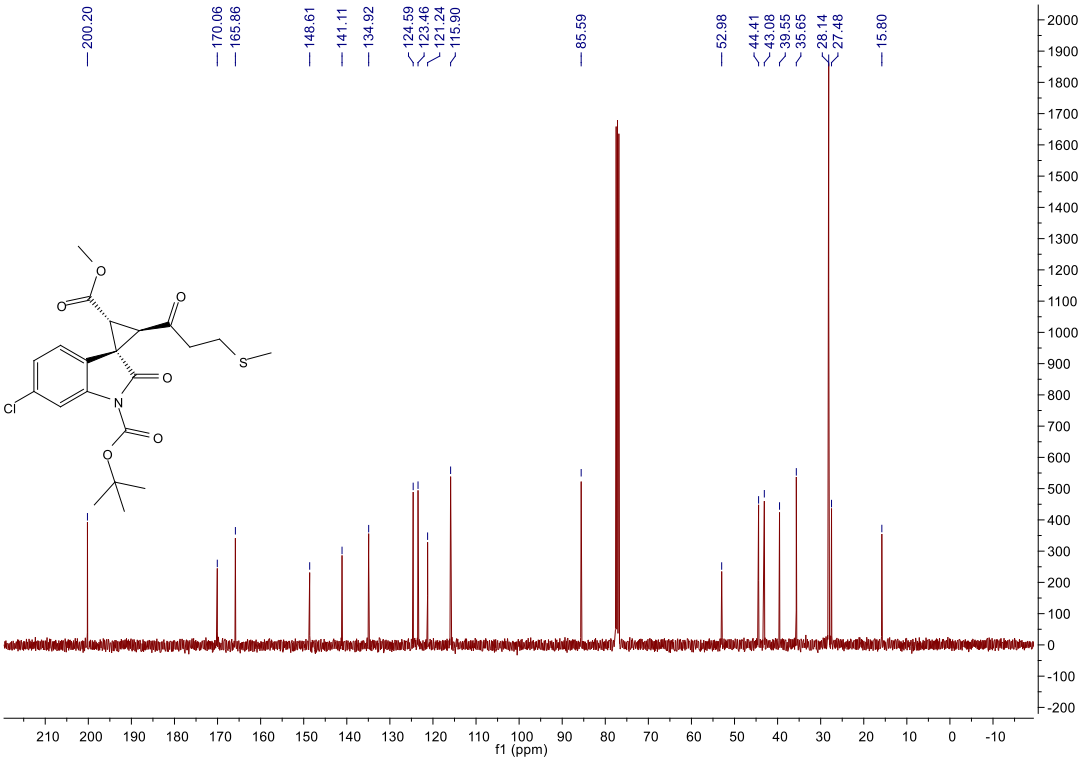




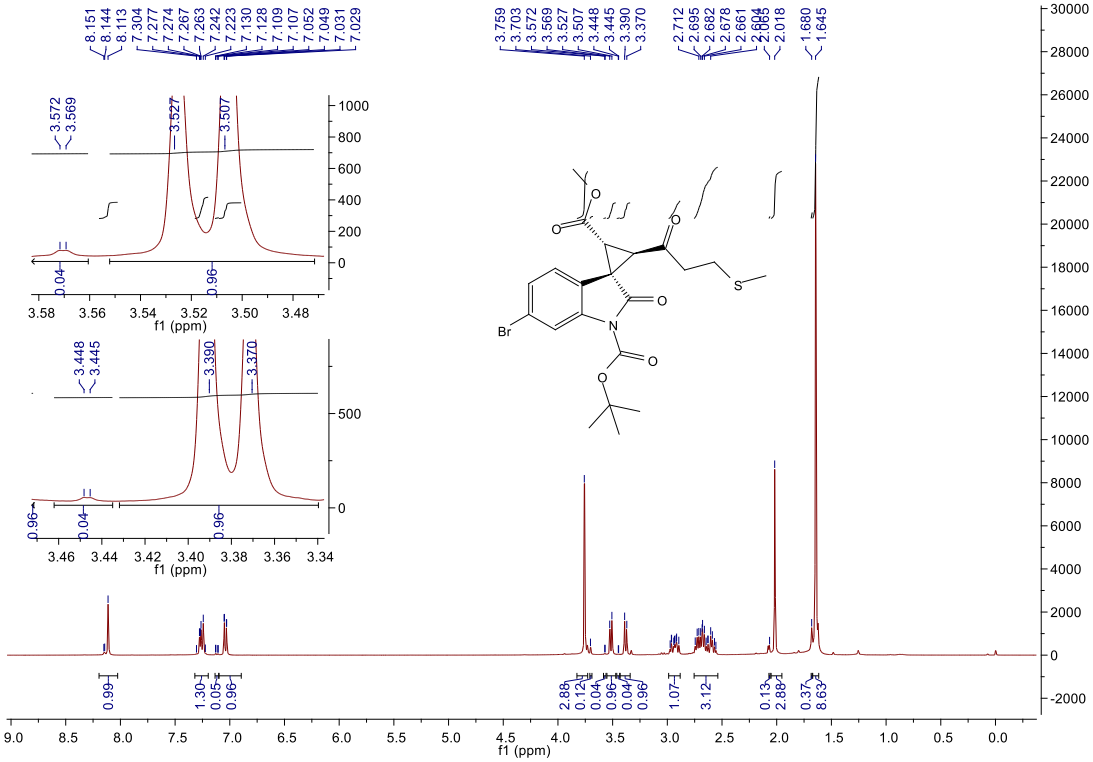

-109.934
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
O
O
O
S
O
N
F
O
O

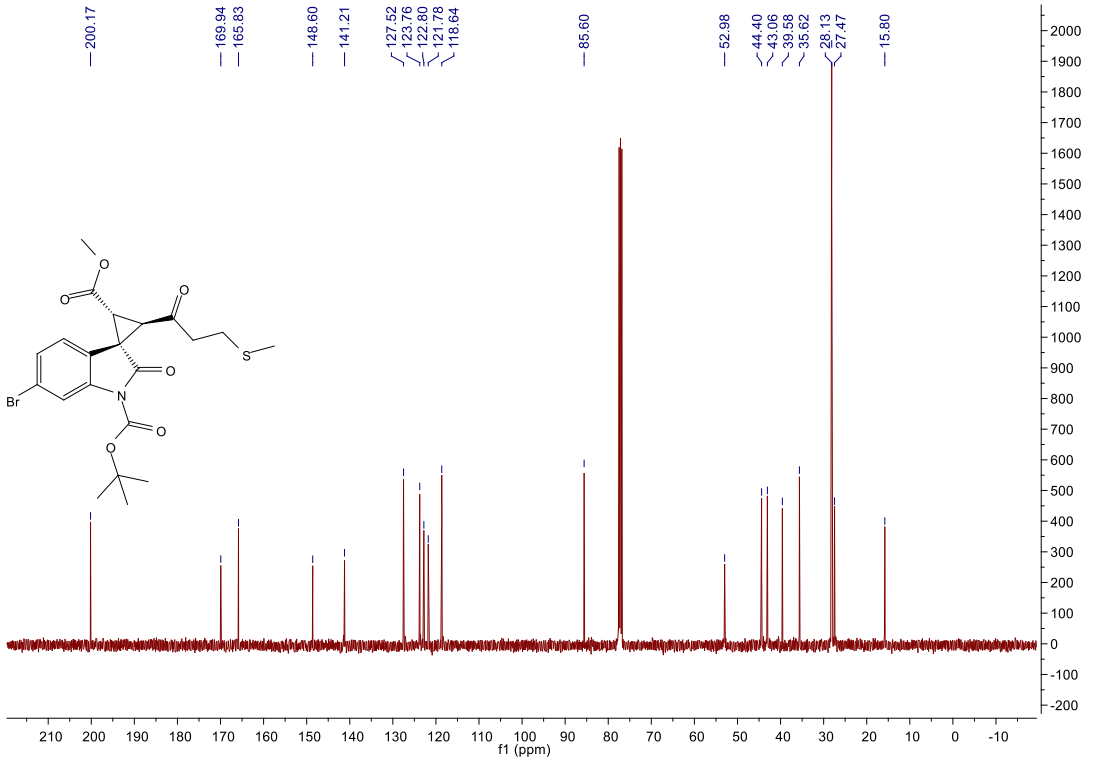
11ha


7.979
7.974
7.943
7.132
7.085
7.063
3.746
3.719
3.689
3.746
3.719
3.689
2.85
0.09
0.06
f1 (ppm)
0.06
0.09
2.85
f1 (ppm)
3.746
3.719
3.689
3.559
3.511
3.492
3.379
3.359
3.315
2.949
2.715
2.699
2.683
2.669
2.664
2.650
2.591
1.632
1.00
2.01
2.85
0.09
0.06
0.05
0.95
0.05
1.08
3.15
0.06
0.09
2.85
0.46
8.44
f1 (ppm)

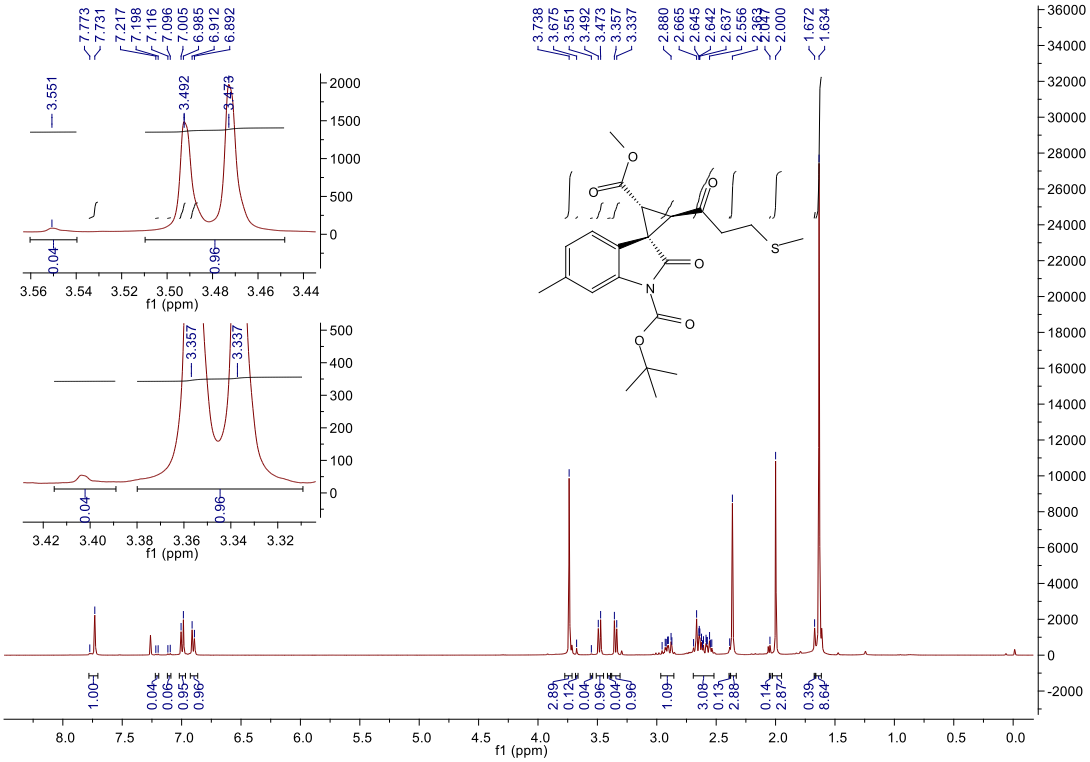

200.20
170.06
165.86
148.61
141.11
134.92
124.59
123.46
121.24
115.90
85.59
52.98
44.41
43.08
39.55
35.65
28.14
27.48
15.80
f1 (ppm)

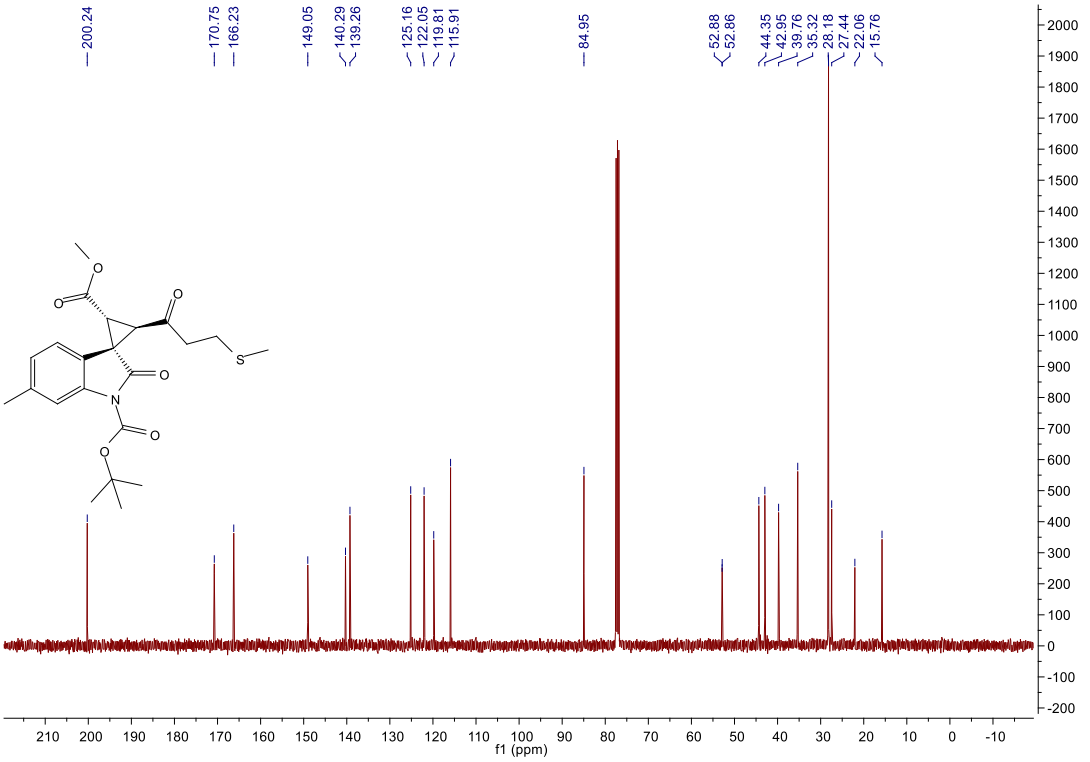
11ia



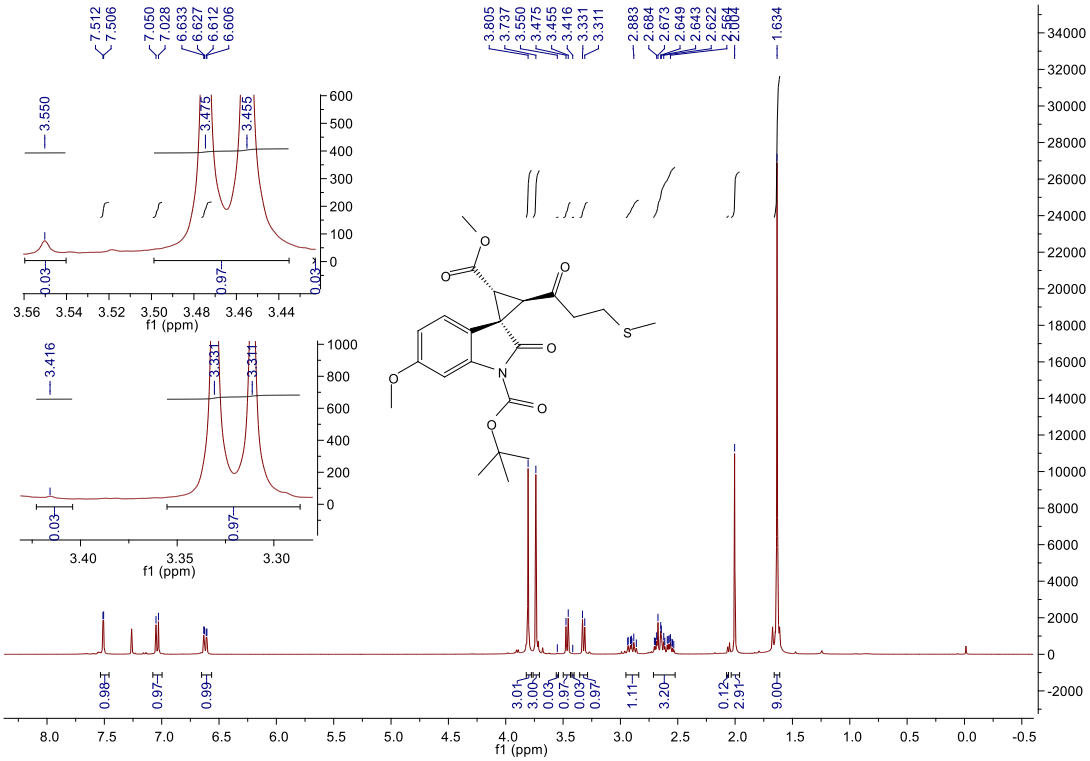


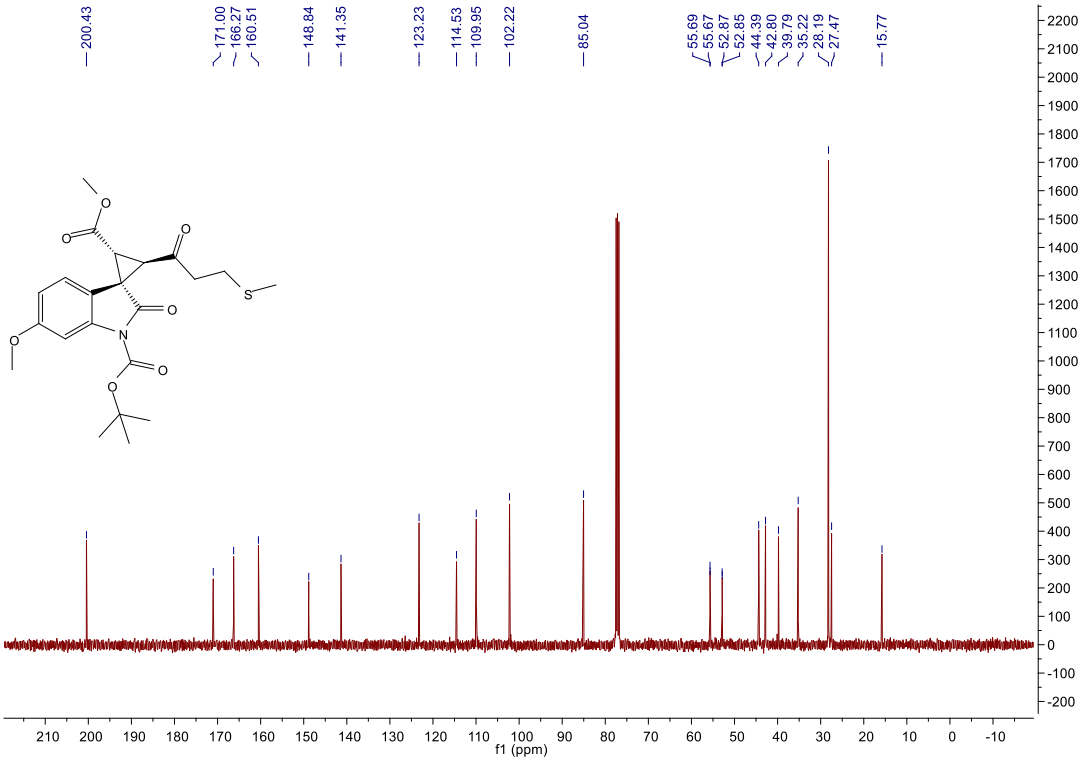
11ja


7.773
7.731
7.217
7.198
7.116
7.096
7.005
6.985
6.912
6.892
3.738
3.675
3.551
3.492
3.473
3.357
3.337
2.880
2.665
2.645
2.642
2.637
2.556
2.363
2.047
2.000
1.672
1.634
3.551
3.492
3.473
3.357
3.337
0.04
0.96
f1 (ppm)
1.00
0.04
0.06
0.95
0.96
2.89
0.12
0.04
0.96
0.04
0.96
1.09
3.08
0.13
2.88
0.14
2.87
0.39
8.64

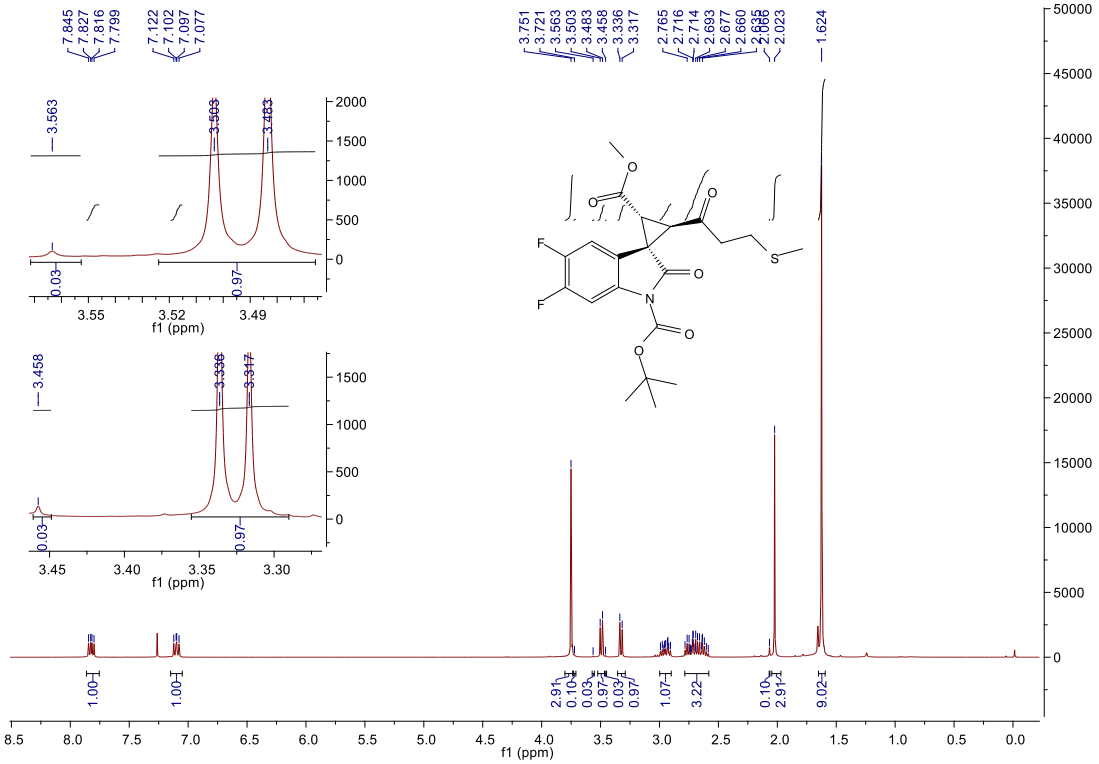

200.24
170.75
166.23
149.05
140.29
139.26
125.16
122.05
119.81
115.91
84.95
52.88
52.86
44.35
42.95
39.76
35.32
28.18
27.44
22.06
15.76
f1 (ppm)

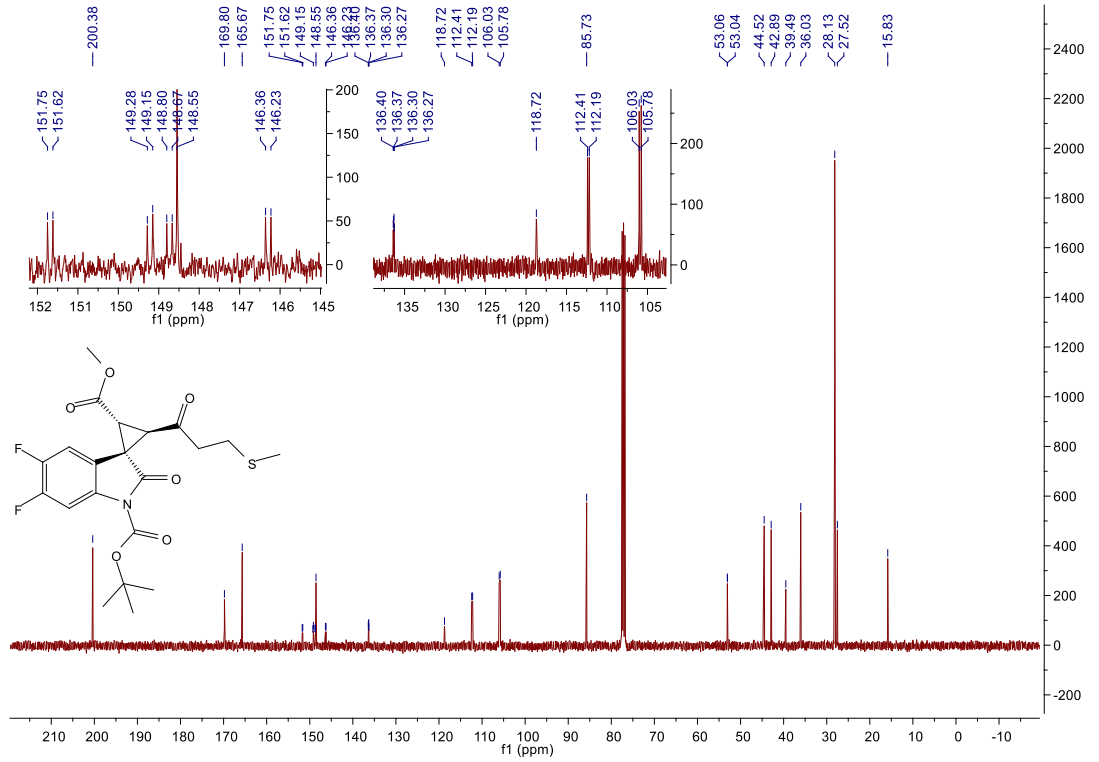
11ka

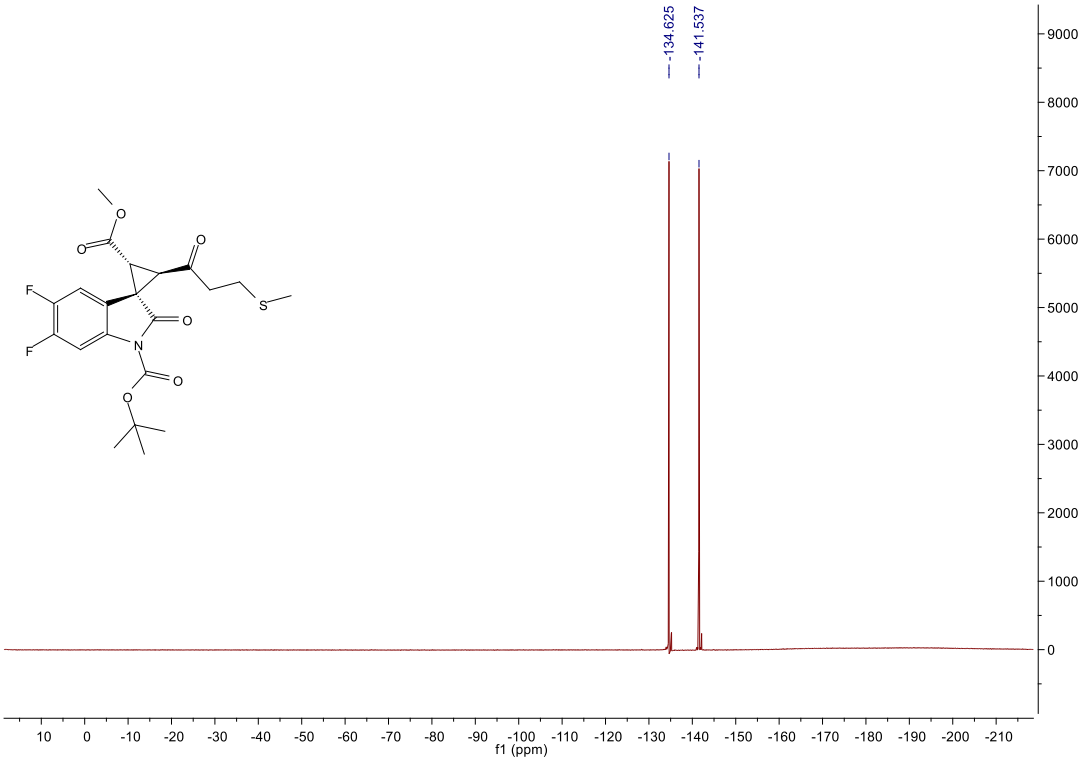

7.512
7.506
7.050
7.028
6.633
6.627
6.612
6.606
3.805
3.737
3.550
3.475
3.455
3.416
3.331
3.311
2.883
2.684
2.673
2.649
2.643
2.622
2.564
2.004
1.634
3.550
3.475
3.455
3.416
3.331
3.311
f1 (ppm)
0.98
0.97
0.99
3.01
3.00
0.03
0.97
0.03
0.97
1.11
3.20
0.12
2.91
9.00


200.43
171.00
166.27
160.51
148.84
141.35
123.23
114.53
109.95
102.22
85.04
55.69
55.67
52.87
52.85
44.39
42.80
39.79
35.22
28.19
27.47
15.77
f1 (ppm)

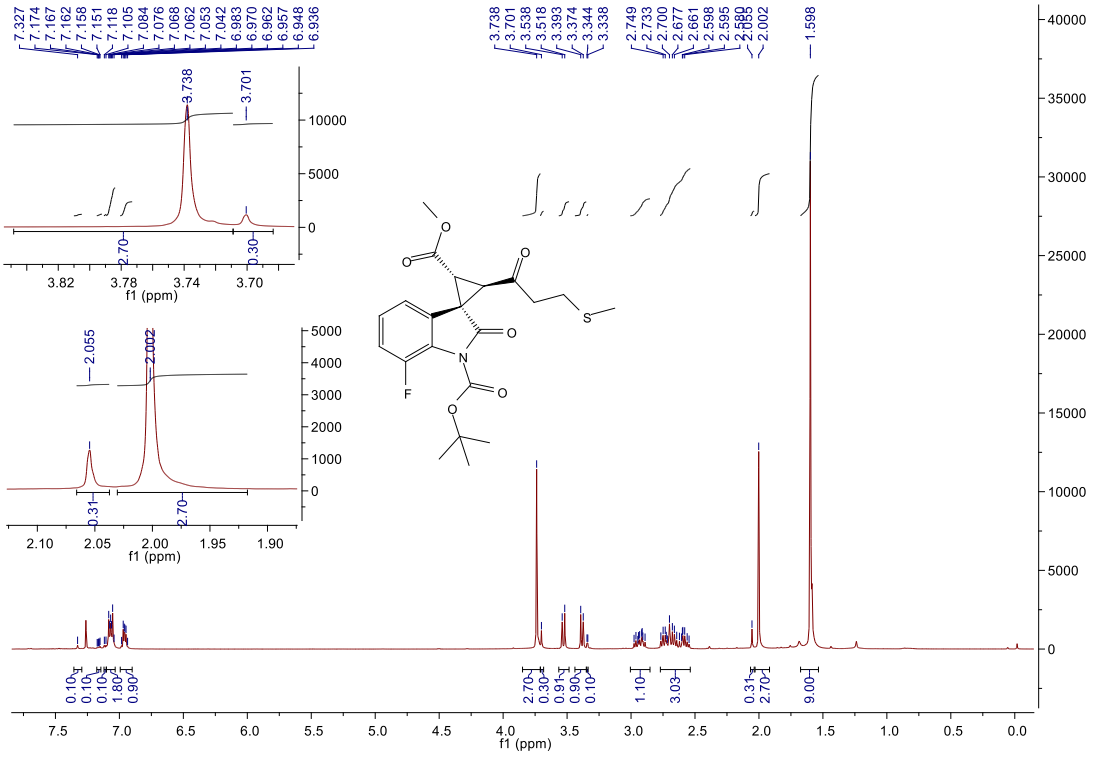
11la

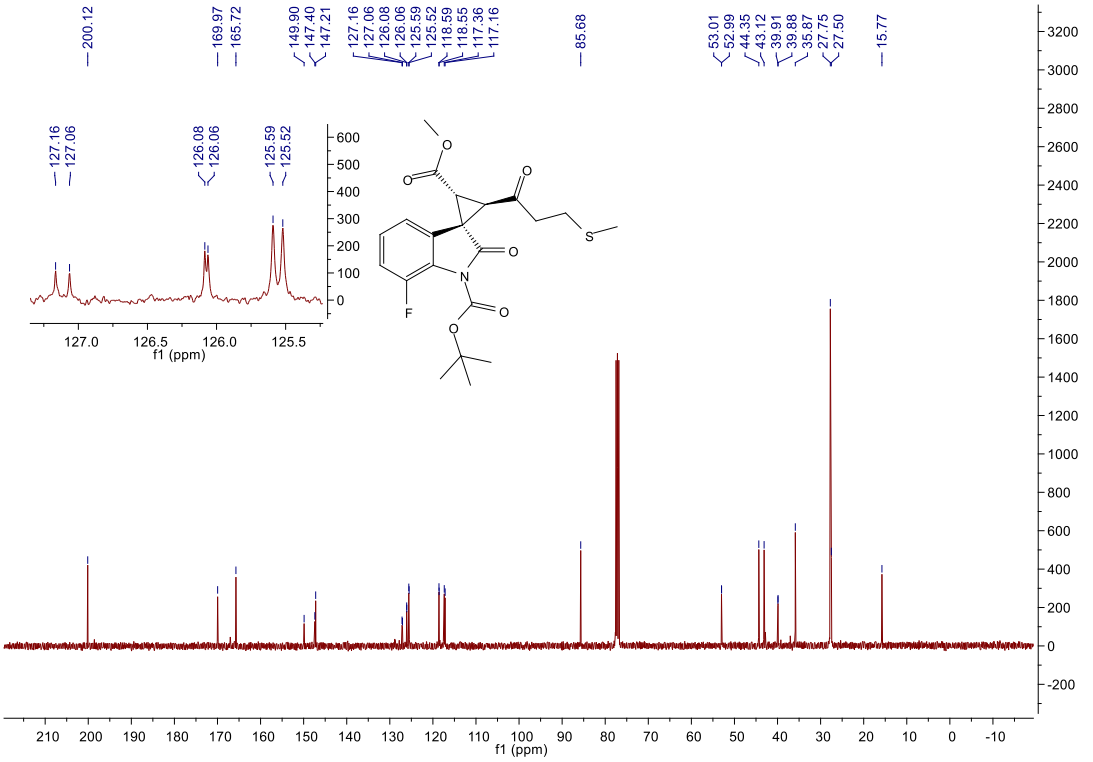


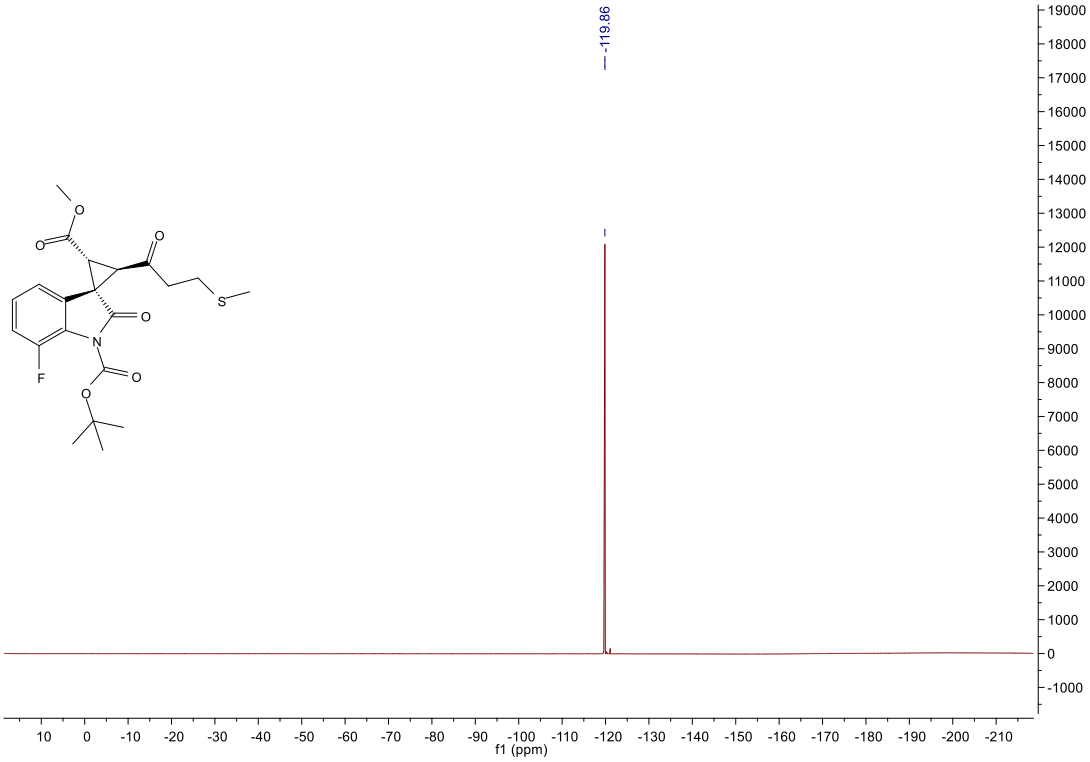



-134.625
-141.537
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
O
O
O
F
F
O
N
O
O
O
S

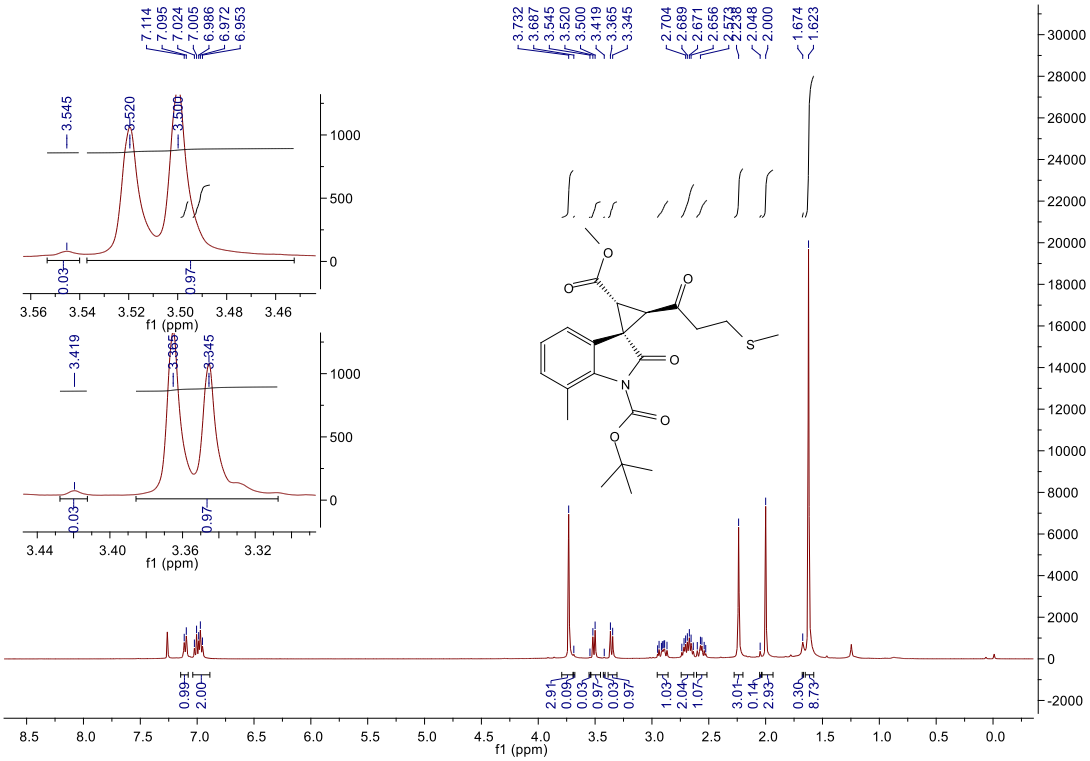
11ma

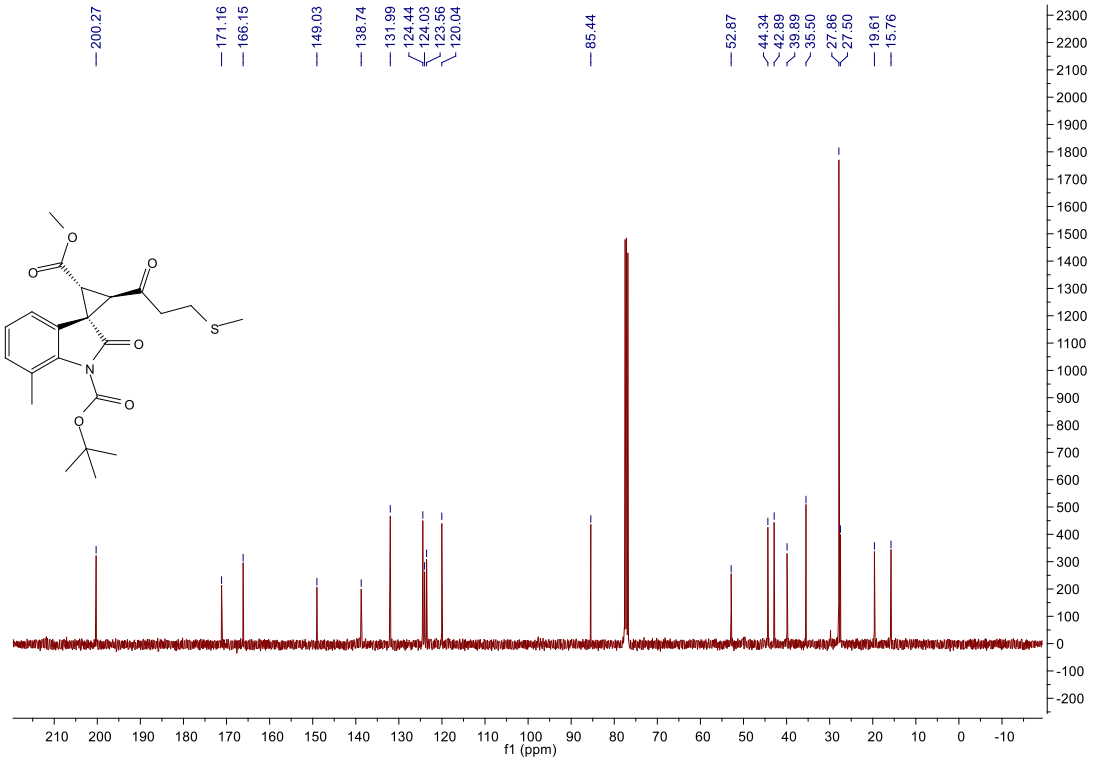




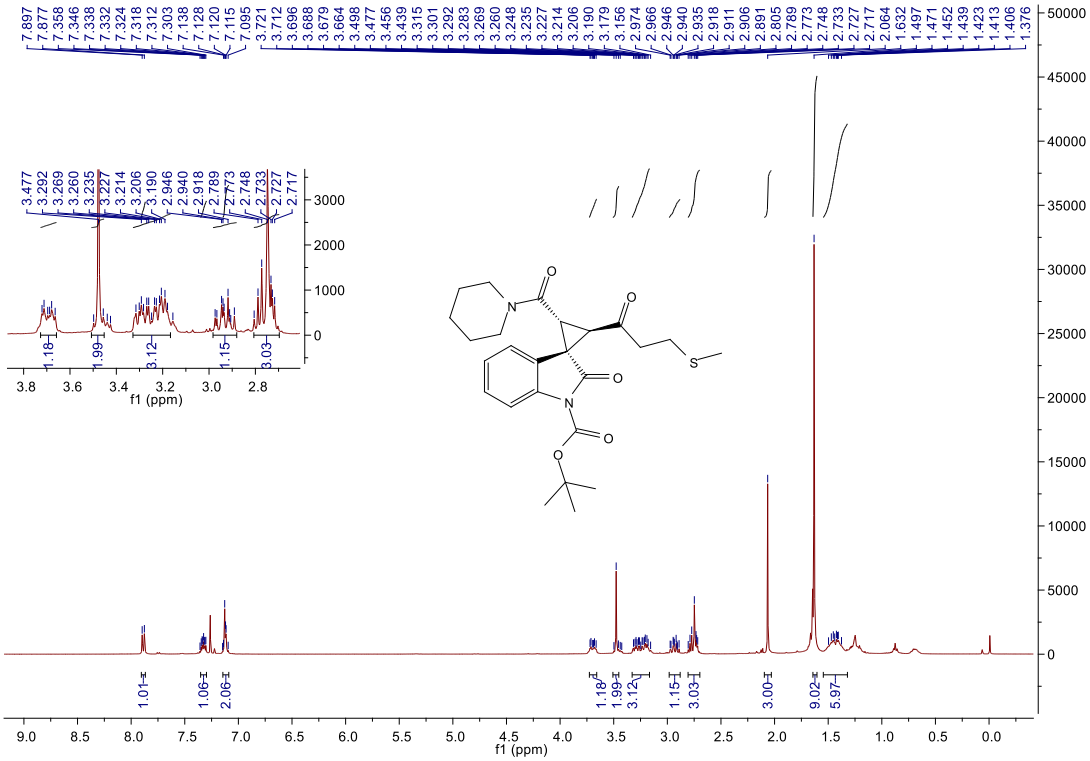

-119.86
f1 (ppm)

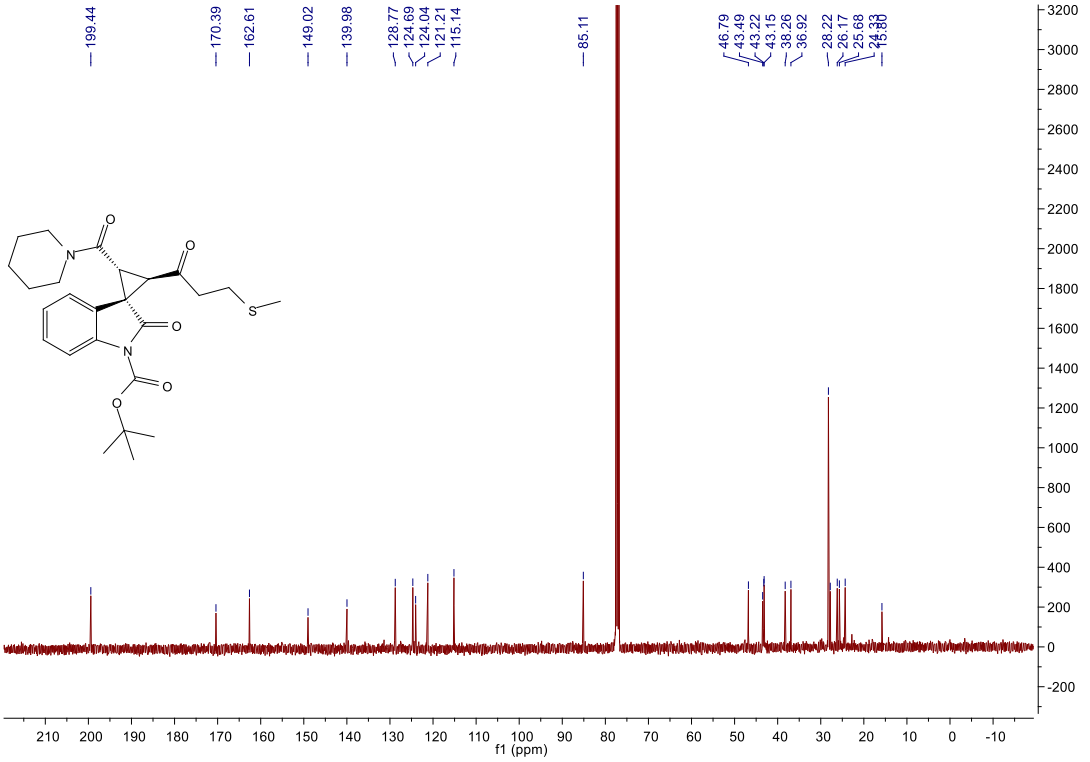
11na


7.114
7.095
7.024
7.005
6.986
6.972
6.953
3.732
3.687
3.545
3.520
3.500
3.419
3.365
3.345
2.704
2.689
2.671
2.656
2.573
2.238
2.048
2.000
1.674
1.623
3.545
3.520
3.500
3.419
3.365
3.345
0.03
0.97
0.99
2.00
2.91
0.09
0.03
0.97
0.03
0.97
1.03
2.04
1.07
3.01
0.14
2.93
0.30
8.73
f1 (ppm)

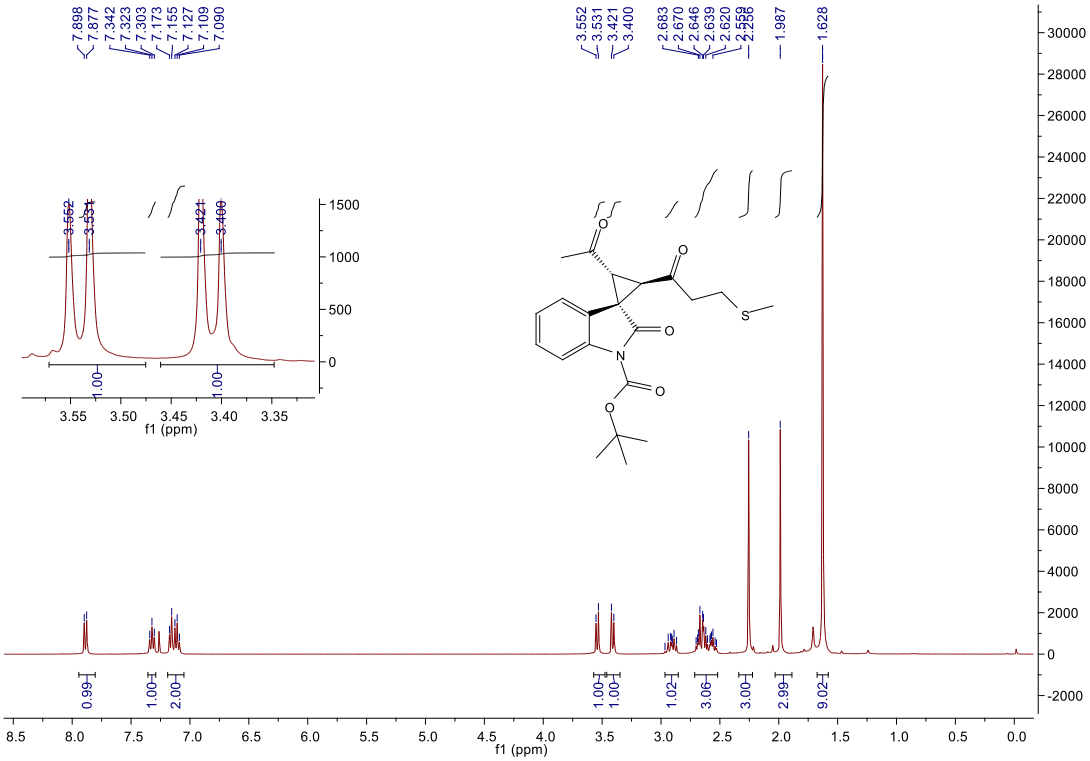

200.27
171.16
166.15
149.03
138.74
131.99
124.44
124.03
123.56
120.04
85.44
52.87
44.34
42.89
39.89
35.50
27.86
27.50
19.61
15.76
f1 (ppm)

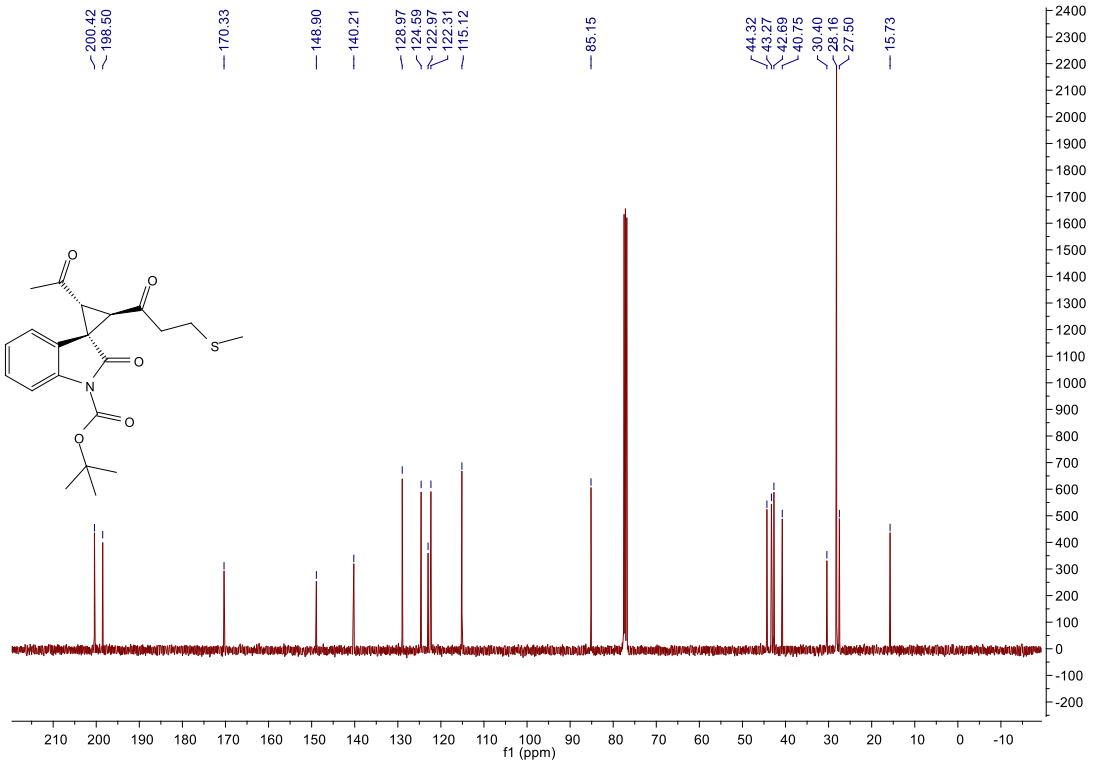
11oa



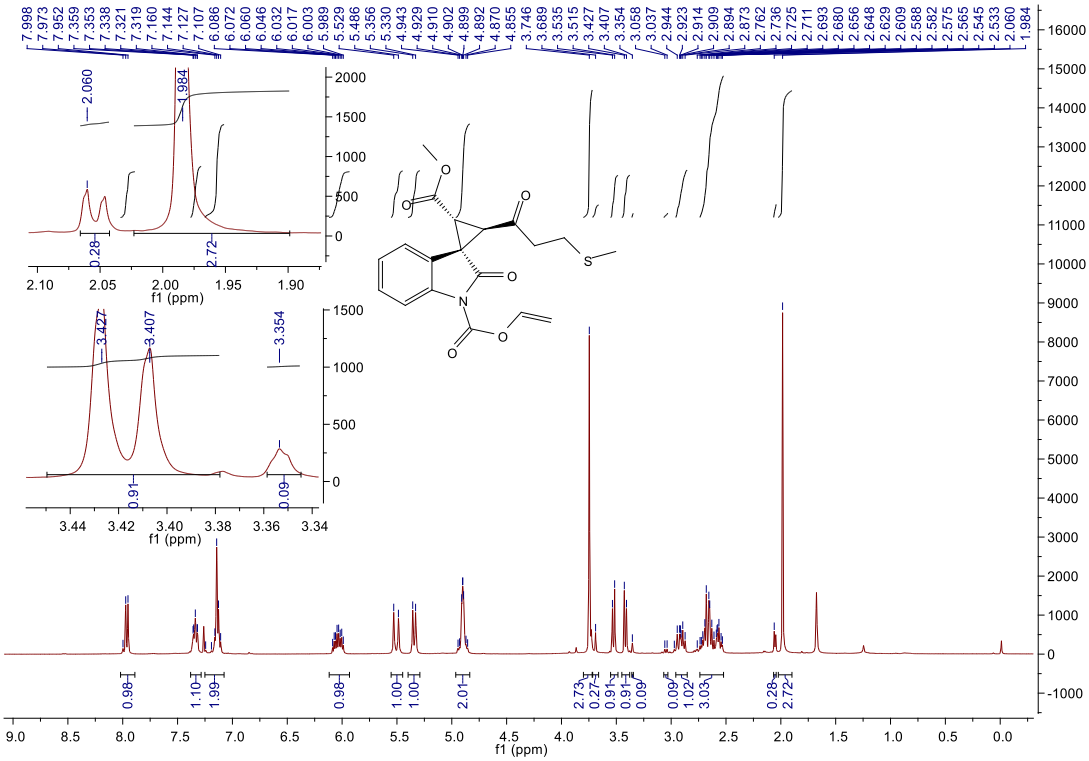


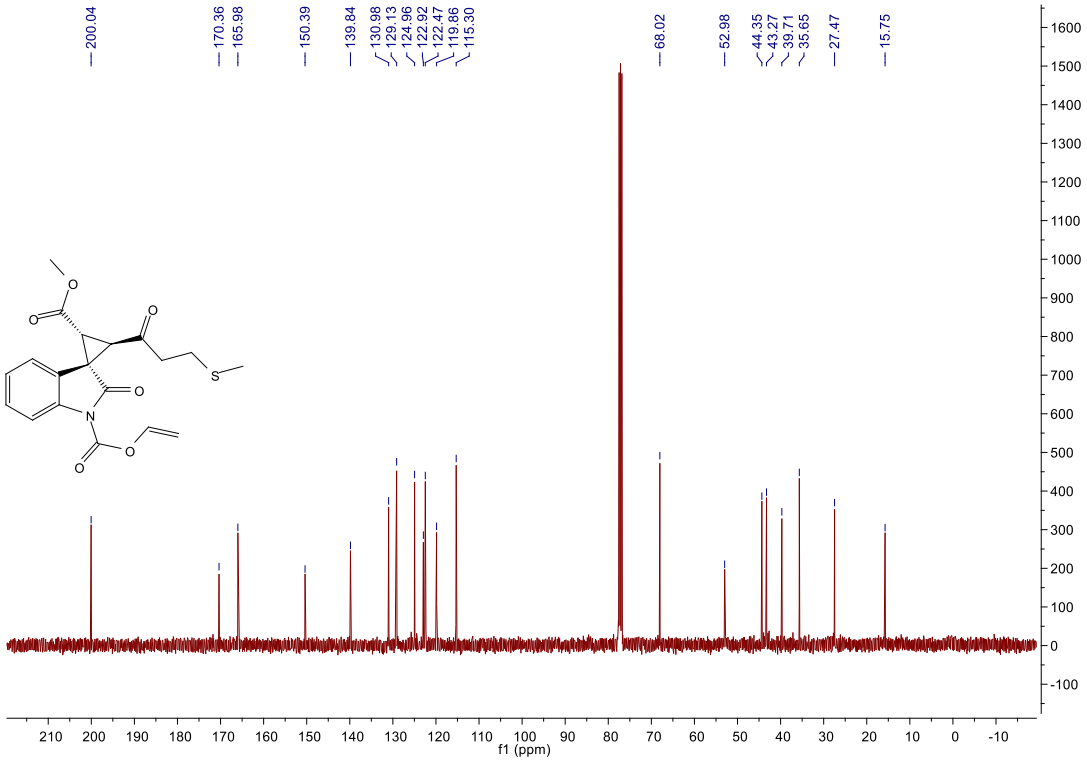
11pa


7.898
7.877
7.342
7.323
7.303
7.173
7.155
7.127
7.109
7.090
3.552
3.531
3.421
3.400
2.683
2.670
2.646
2.639
2.620
2.559
2.556
1.987
1.628
f1 (ppm)

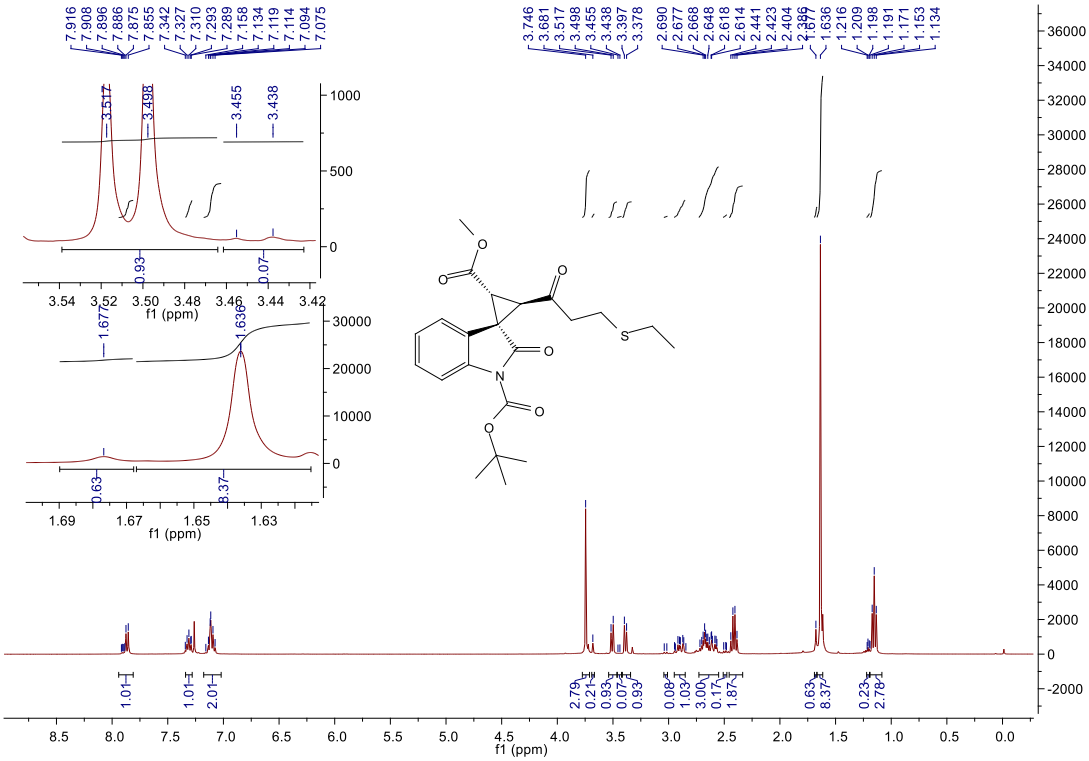

200.42
198.50
170.33
148.90
140.21
128.97
124.59
122.97
122.31
115.12
85.15
44.32
43.27
42.69
40.75
30.40
28.16
27.50
15.73
f1 (ppm)

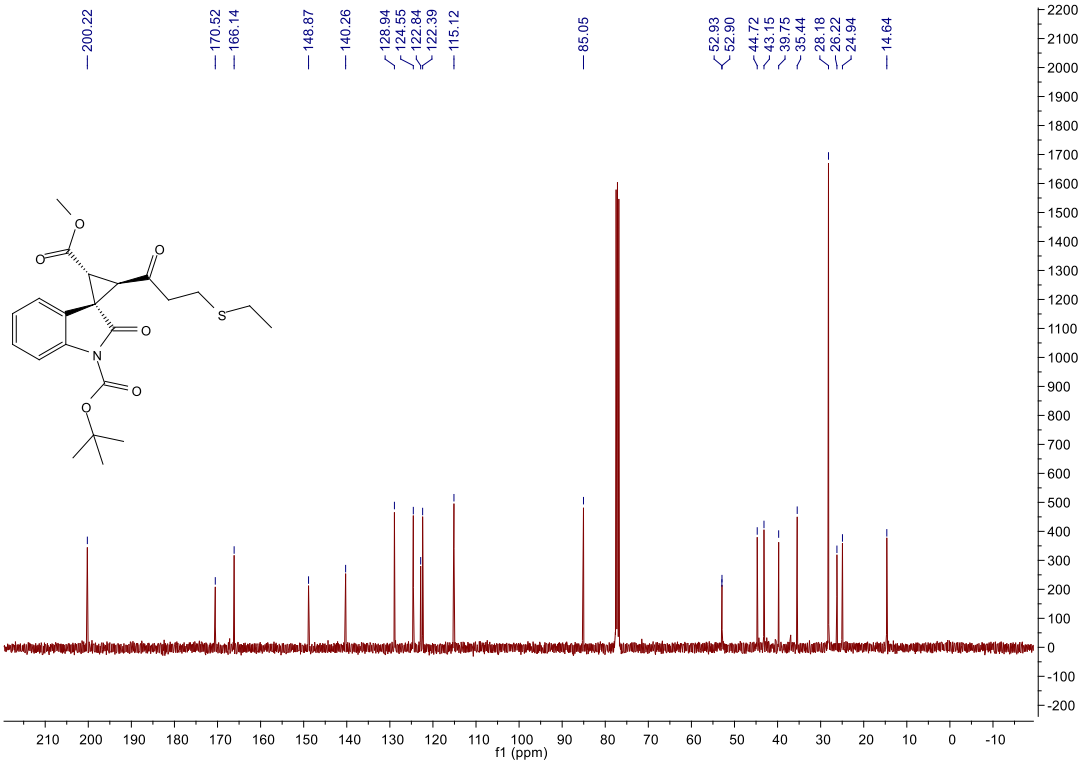
11qa



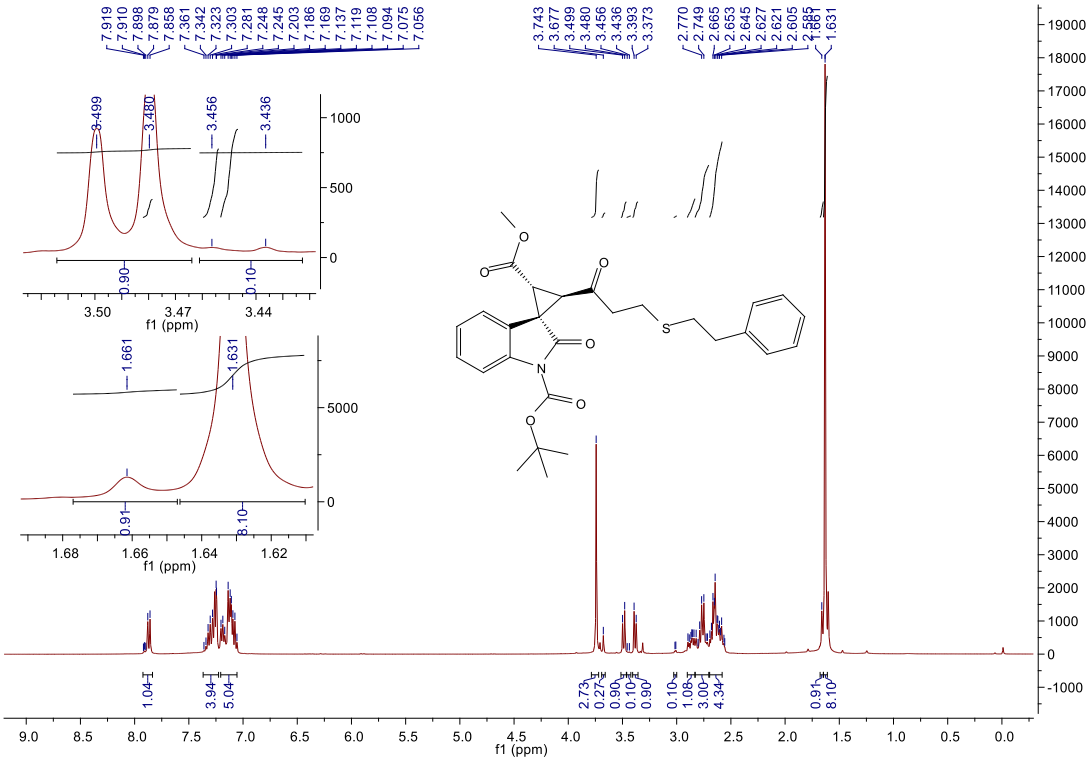


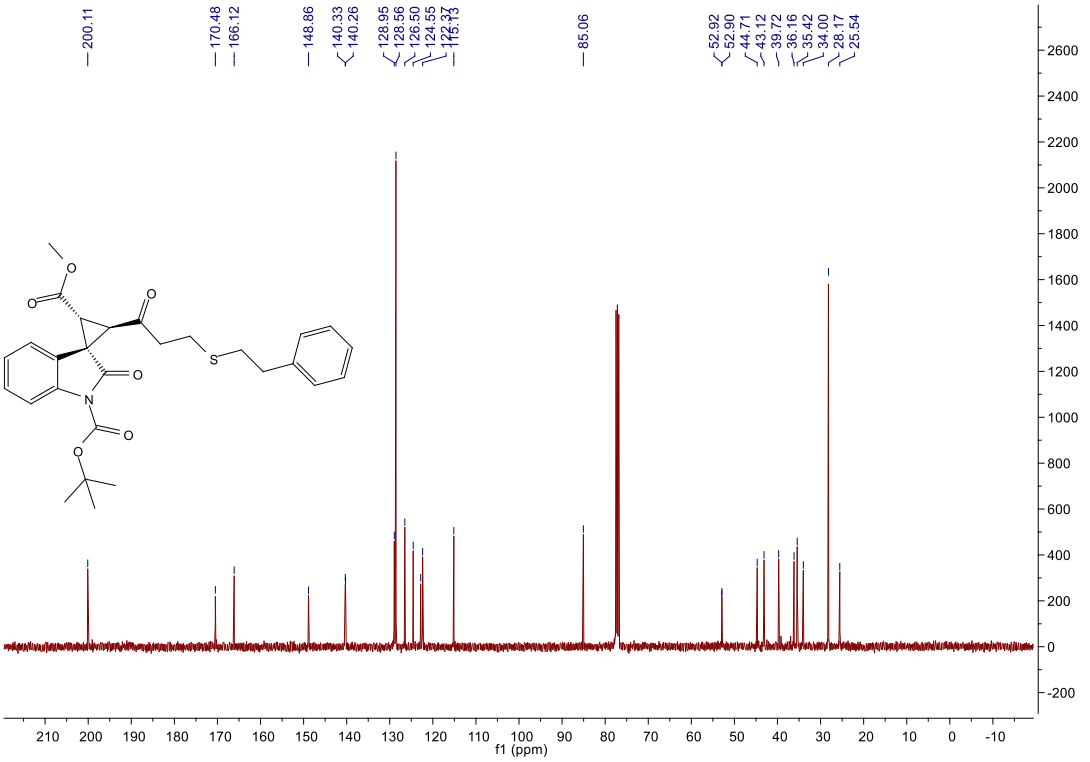
11ab



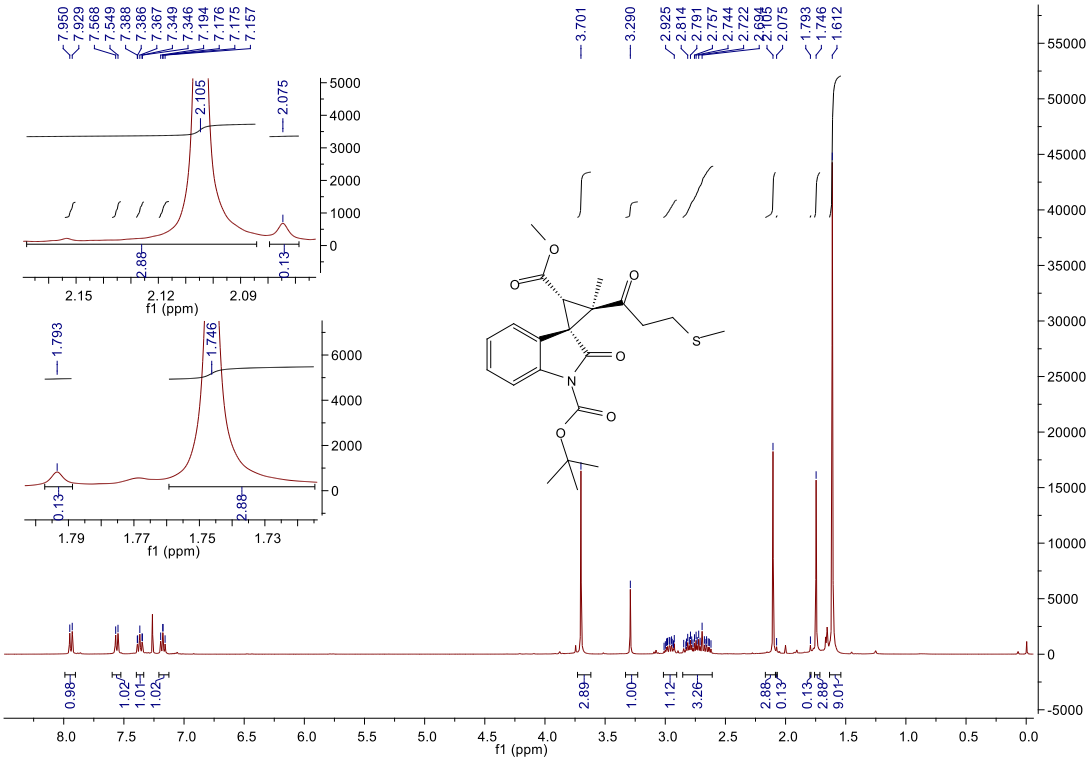


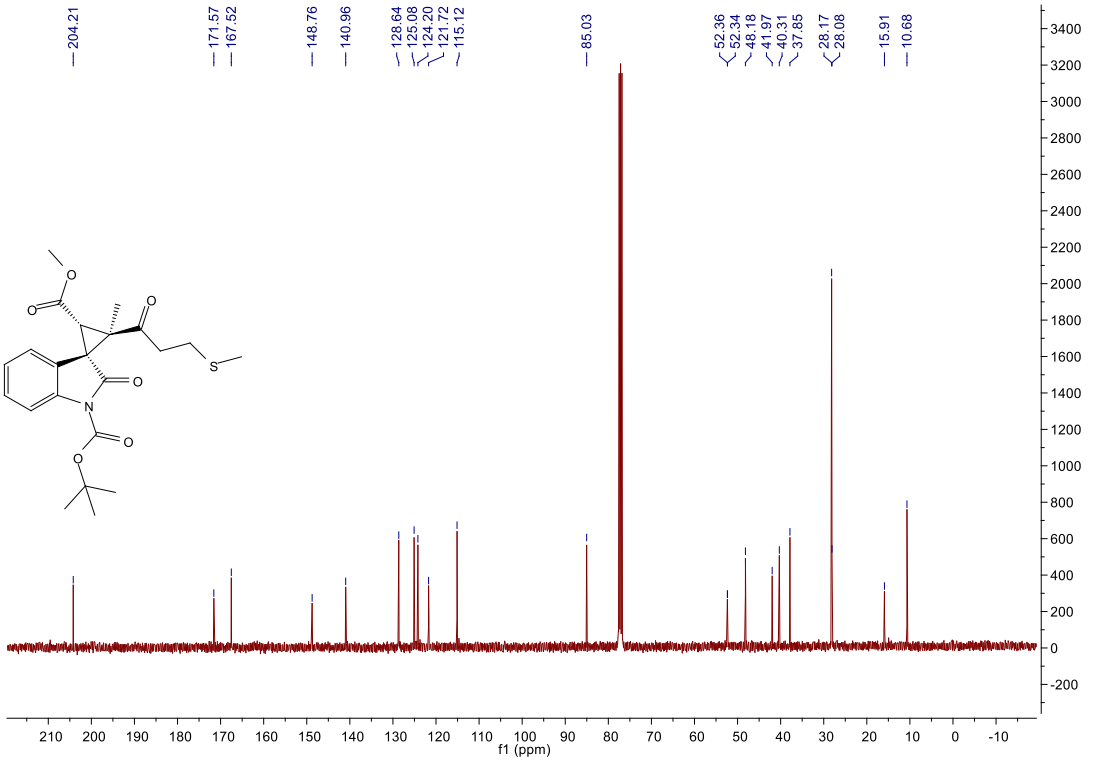
11ac



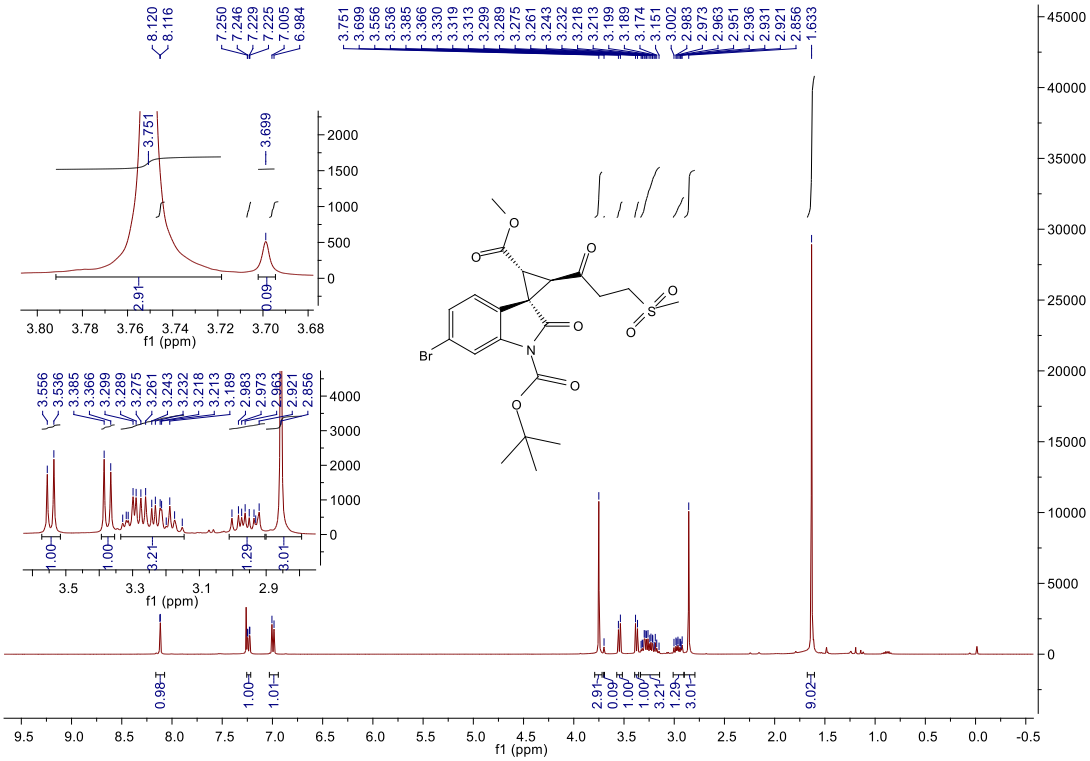


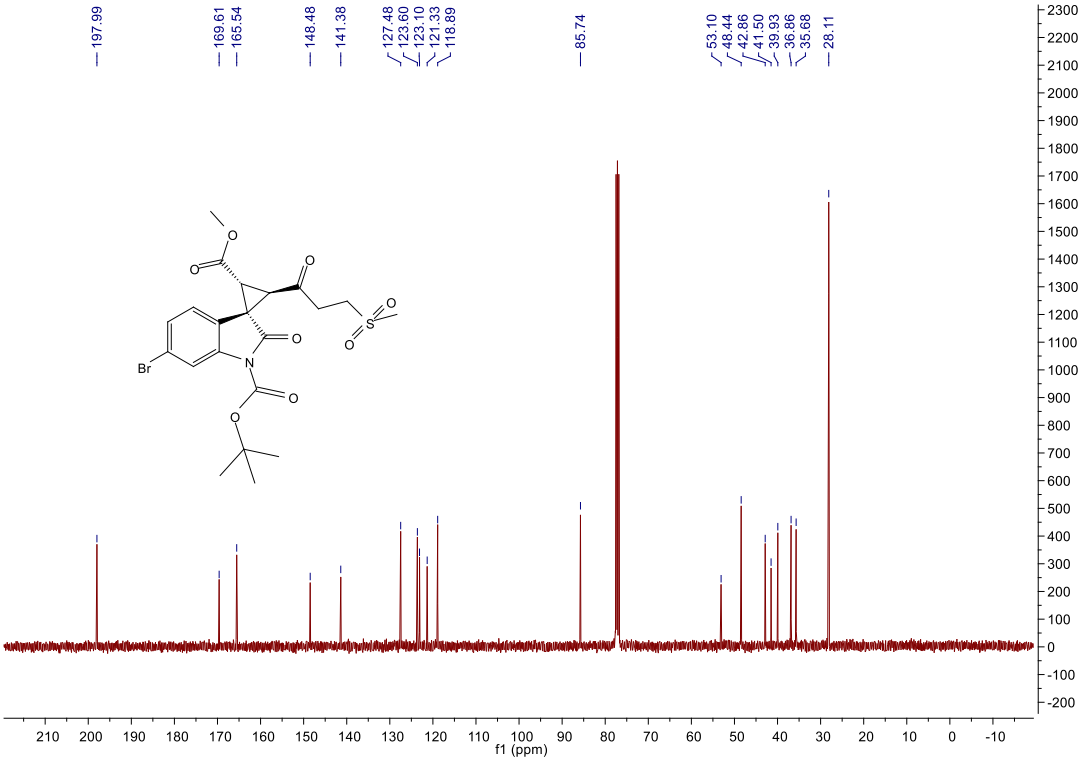
11ad



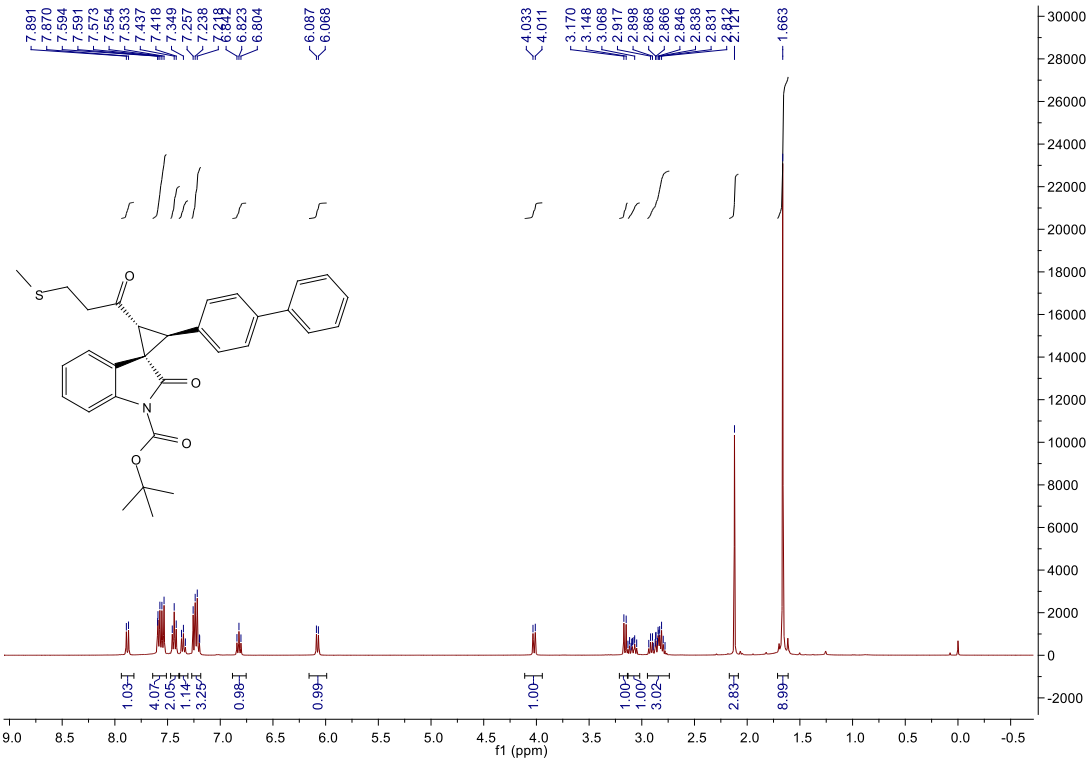


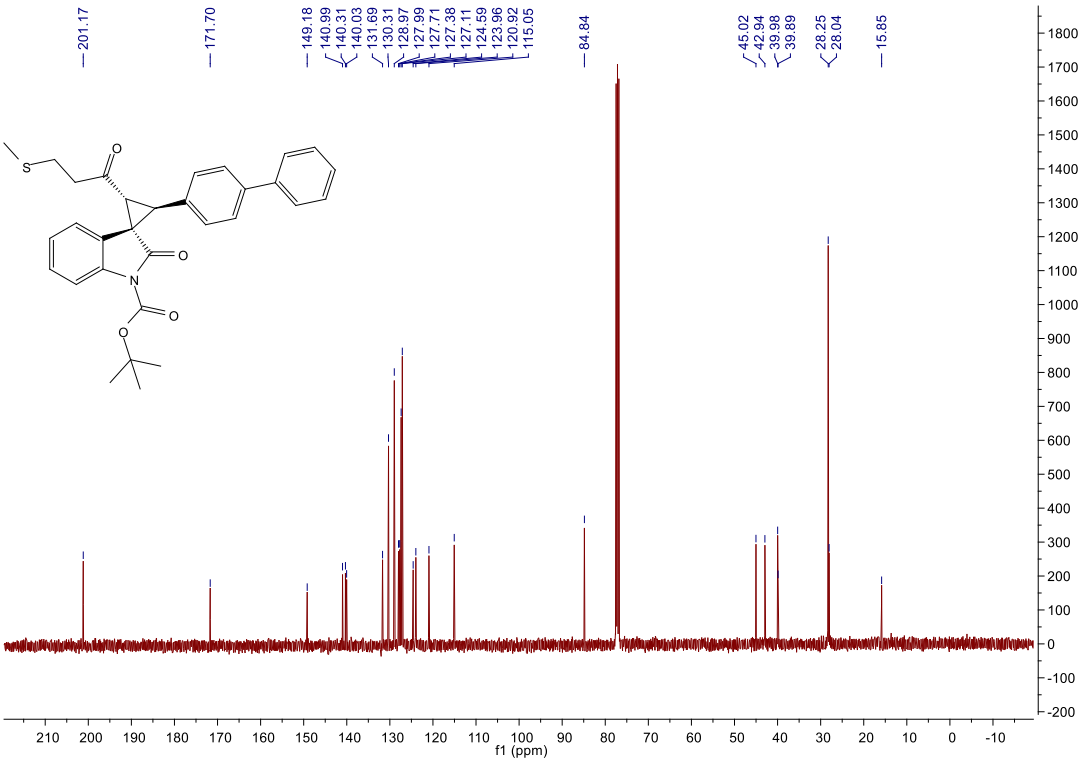
12


8.120
8.116
7.250
7.246
7.229
7.225
7.005
6.984
3.751
3.699
3.556
3.536
3.385
3.366
3.330
3.319
3.313
3.299
3.289
3.275
3.261
3.243
3.232
3.218
3.213
3.199
3.189
3.174
3.151
3.002
2.983
2.973
2.963
2.951
2.936
2.931
2.921
2.856
1.633
0.98
1.00
1.01
2.91
0.09
1.00
3.21
1.29
3.01
9.02
f1 (ppm)

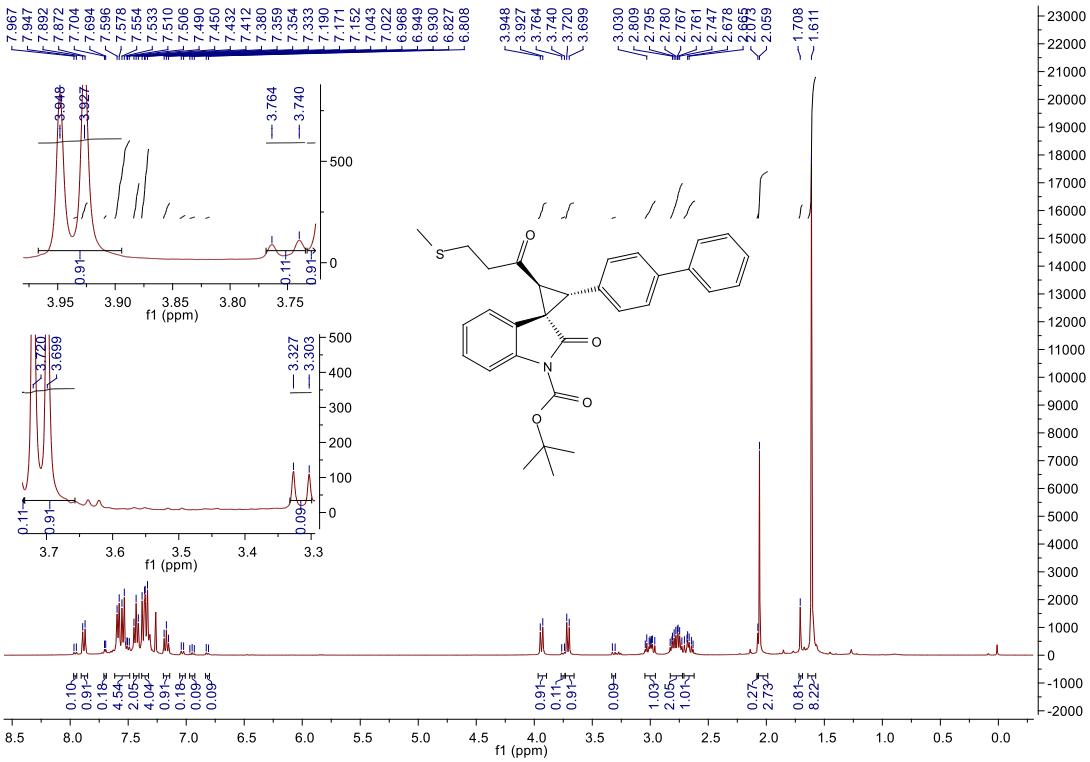

197.99
169.61
165.54
148.48
141.38
127.48
123.60
123.10
121.33
118.89
85.74
53.10
48.44
42.86
41.50
39.93
36.86
35.68
28.11
f1 (ppm)

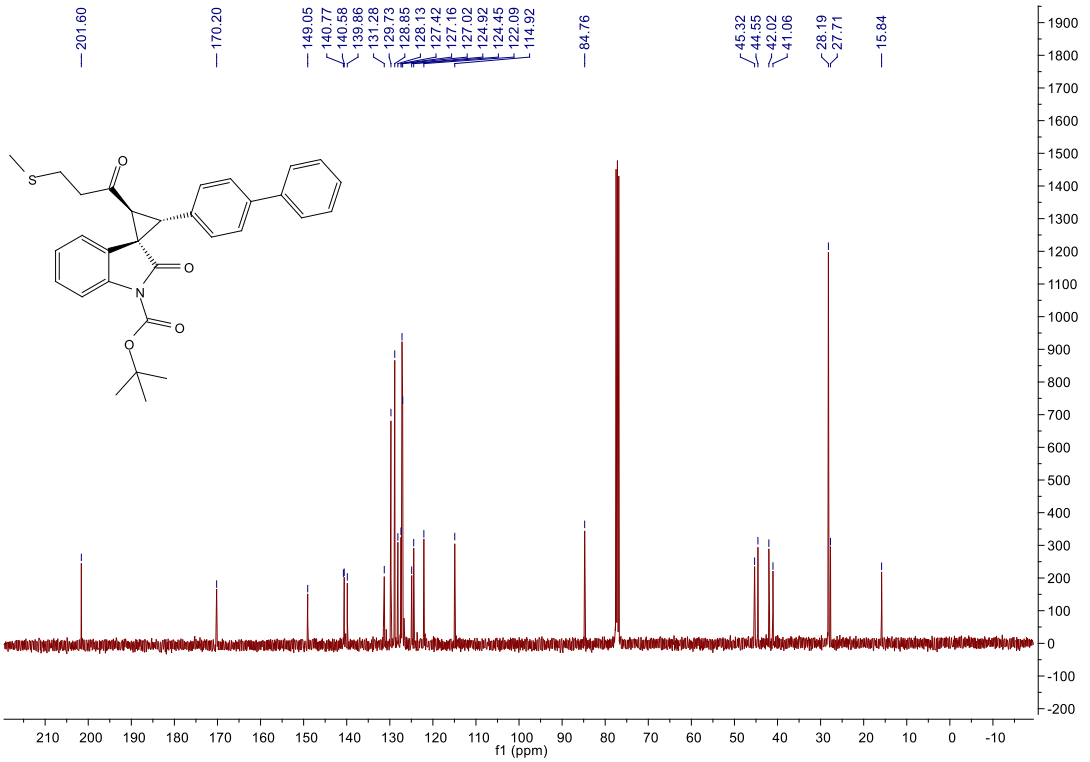
Syn,anti-**14aa** (Condition A)



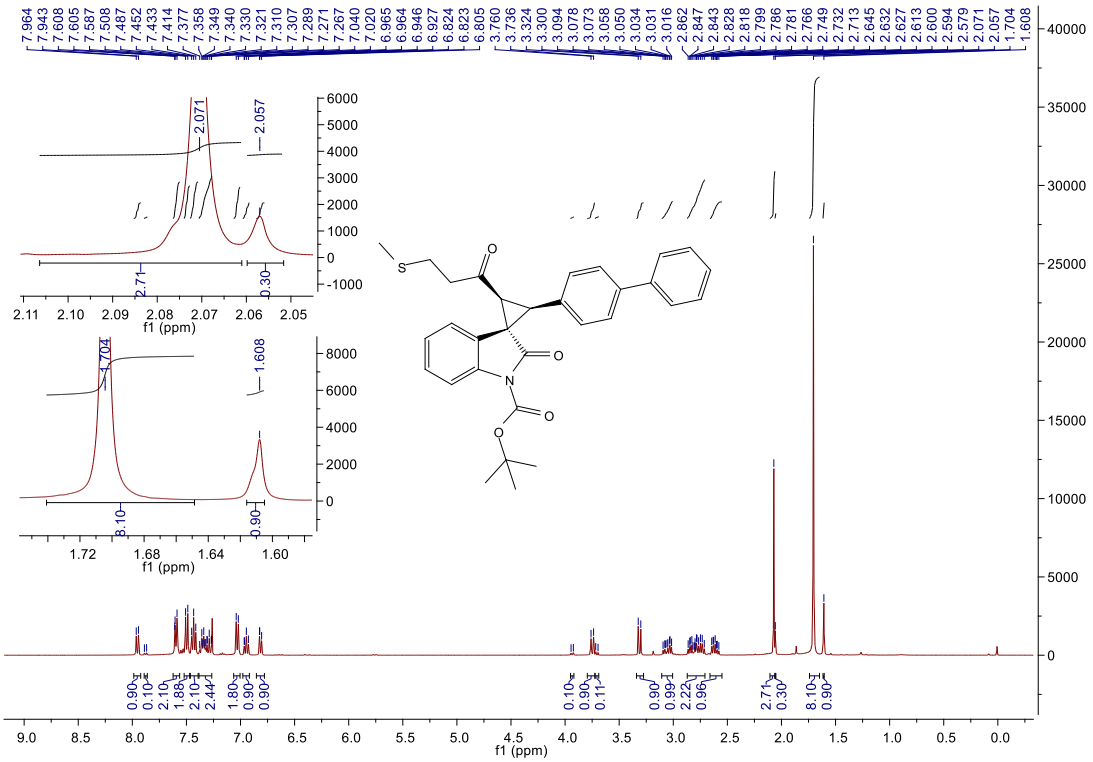


anti,anti-**14aa** (Condition B)

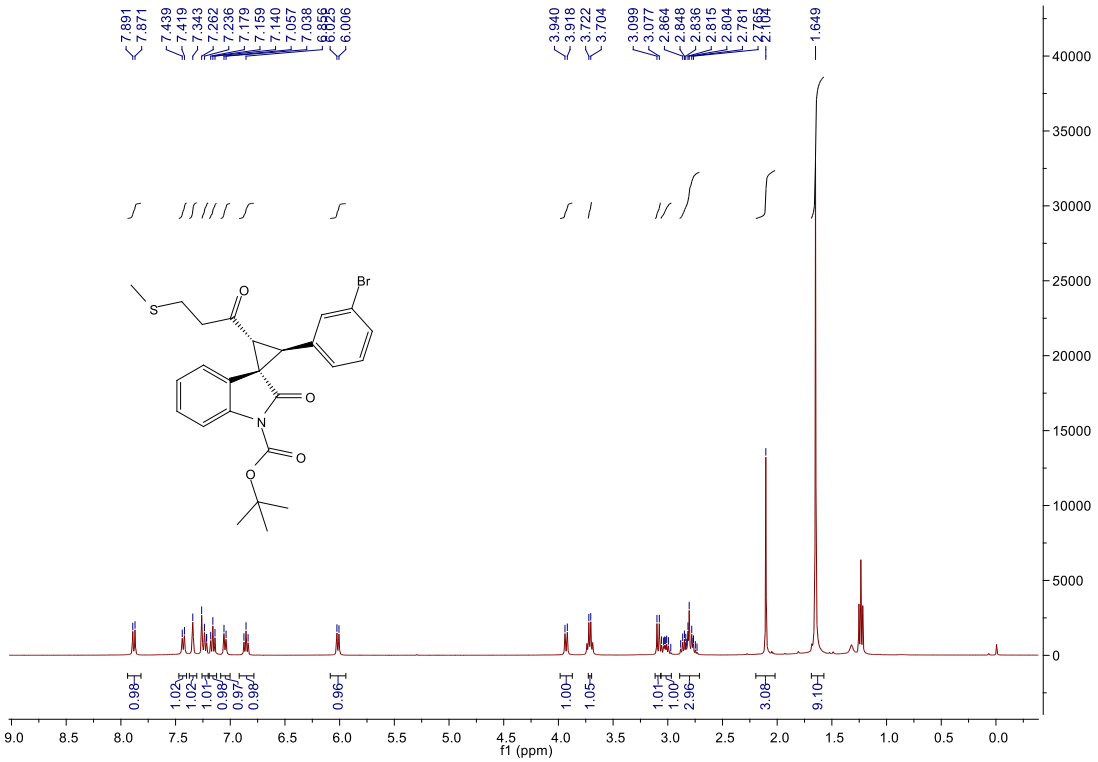


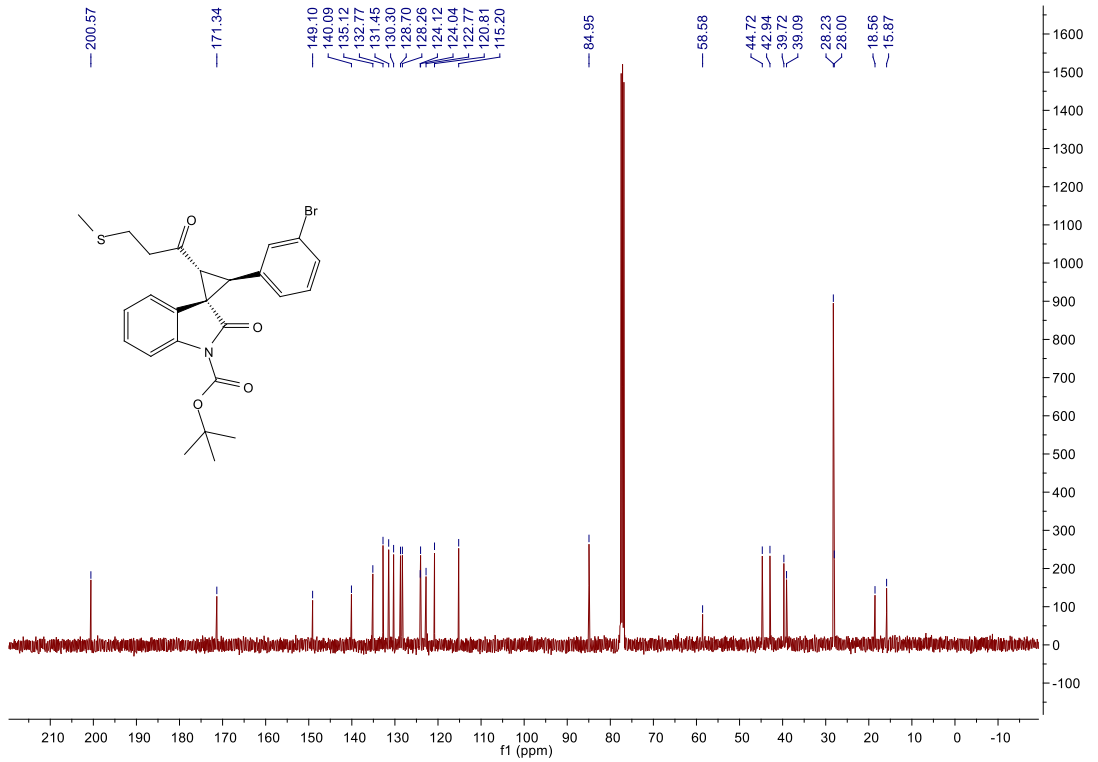
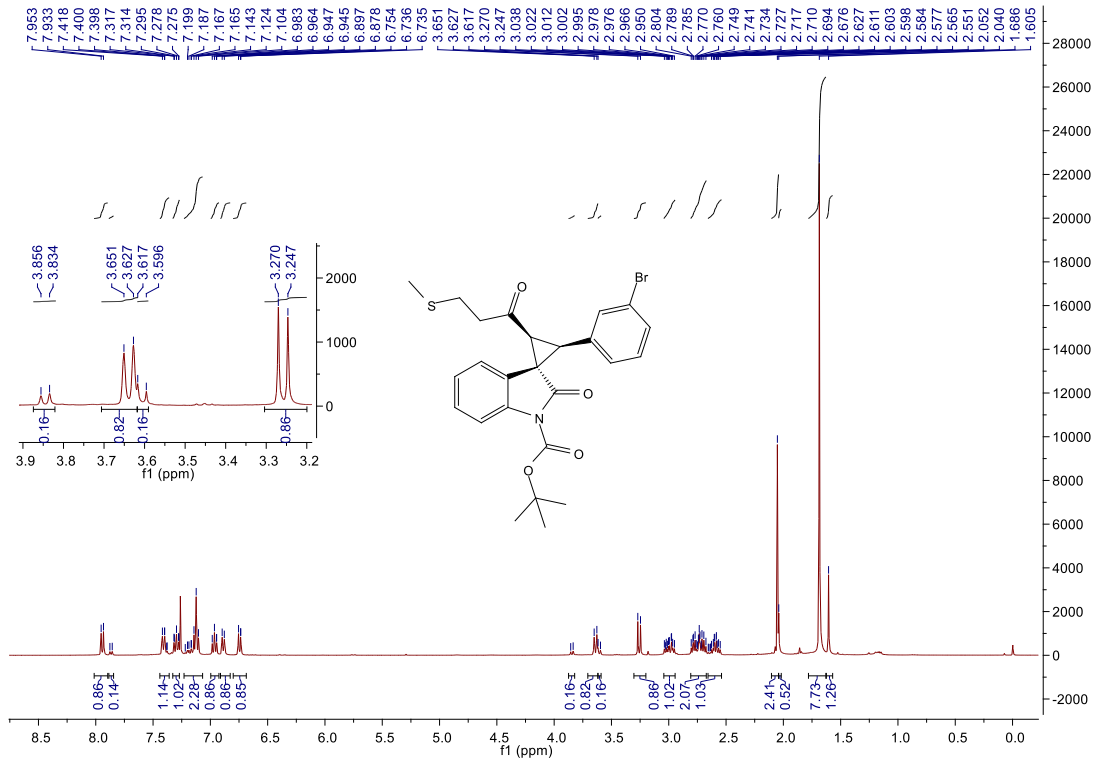
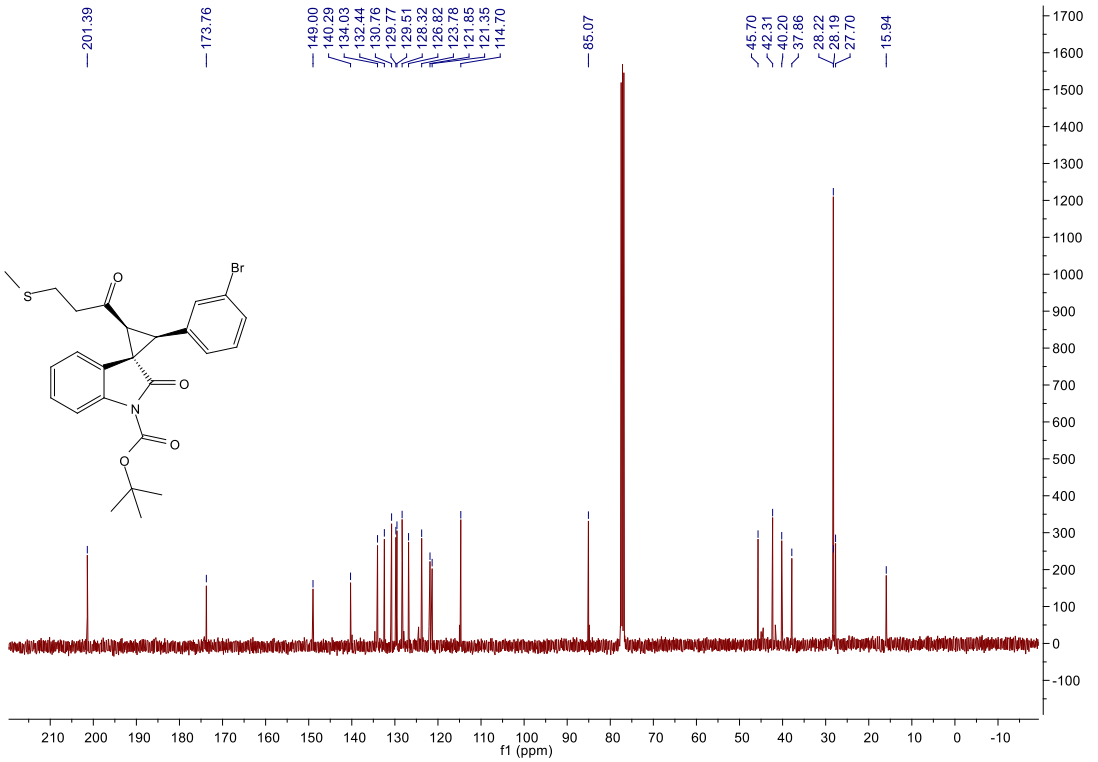


anti,syn-**14aa** (Condition C)



Syn-anti-**14ba** (Condition A)





Anti-syn-**14ba** (Condition C)