Supporting information

Organocatalytic Asymmetric Synthesis of Benzazepinoindole Derivatives with Trifluoromethylated Quaternary Stereocenters by Chiral Phosphoric Acid Catalysis

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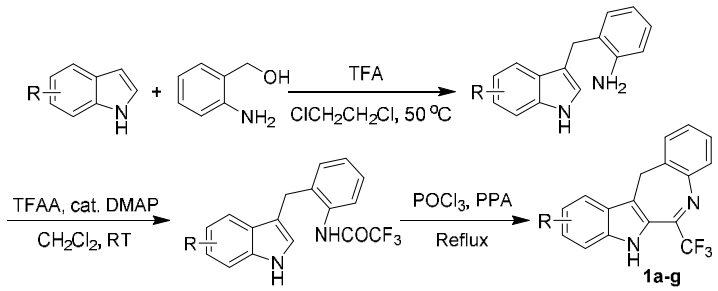
Table of Contents

1. General procedure for synthesis of trifluoromethyl dihydrobenzoazepino-indoles

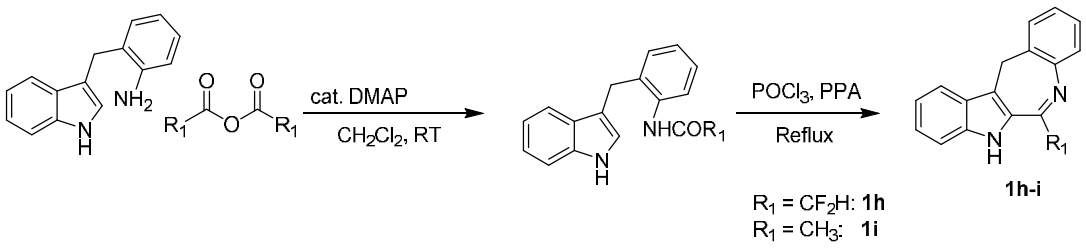


To a solution of indoles (2.8 mmol, 0.4g) and 2-aminobenzyl alcohol (1.4 mmol, 0.17 g) in DCE (4 mL) was added TFA (0.41 mmol, 0.031 mL) at rt. The resulting solution was stirred at 50 ^{o}C overnight. The reaction was quenched with saturated aqueous $NaHCO_3$ (50 mL) and diluted with EtOAc (50 mL). The organic phase was washed with brine (100 mL), and then dried over Na_2SO_4. Solvent was removed using a rotary evaporator, and the residue was purified by silica gel chromatography to give 2-((1-indol-3-yl)methyl)anilines.

To a solution of 2-((1-indol-3-yl)methyl)anilines (15 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 91.5 mg, 0.75 mmol, 0.05 eq.) in dichloromethane (30 mL) was added drop wise trifluoroacetic anhydride (2.5 mL, 18 mmol, 1.2 eq.). The resulting mixture was stirred for 2 h at room temperature in the air. After the reaction was complete, the reaction mixture was washed with saturated brine (30 mL) and extracted with dichloromethane (3x20 mL). The organic layers were dried by anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash column chromatography (petroleum ether/ethyl acetate = 6/1) afforded the desired trifluoroacetamide compound.

trifluoroacetamide compound (10.9 mmol, 1.0 eq.) in PPA (30 mL) was added to a round bottom flask(100 mL), and the flask was heated to 120^{o}C; then phosphorus oxychloride (6.6 mL, 54.5 mmol, 5.0 eq.) was added into it. The resulting mixture was refluxed for 5 h. Upon completion the reaction mixture was allowed to cool to room temperature and quenched with water. Basify the aqueous layer by the addition of saturated solution of $NaHCO_3$. The resulting solution was extracted four times with EtOAc. Organic layer was washed with brine, dried over anhydrous Na_2SO_4, and solvent was removed in vacuo. Purification of the residue by flash column chromatography (petroleum ether/ethyl acetate = 10/1) afforded the corresponding 6-trifluoromethyl-4,12-dihydroindolo[2,3-c][1]benzazepine (**1**).

1.1 General procedure for synthesis of dihydrobenzoazepino-indoles



To a solution of 2-((1-indol-3-yl)methyl)anilines (15 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 91.5 mg, 0.75 mmol, 0.05 eq.) in dichloromethane (30 mL) was added drop wise an

anhydride (18 mmol, 1.2 eq.). The resulting mixture was stirred for 2 h at room temperature in the air. After the reaction was complete, the reaction mixture was washed with saturated brine (30 mL) and extracted with dichloromethane (3x20 mL). The organic layers were dried by anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash column chromatography (petroleum ether/ethyl acetate = 6/1) afforded the desired acetamide compound.

acetamide compound (10.9 mmol, 1.0 eq.) in PPA (30 mL) was added to round bottom flask (100 mL), and the flask was heated to 120^{o}C, then phosphorus oxychloride (54.5 mmol, 5.0 eq.) was added into it. The resulting mixture was refluxed for 5 h. Upon completion the reaction mixture was allowed to cool to room temperature and quenched with water. Basify the aqueous layer by the addition of saturated solution of $NaHCO_3$. The resulting solution was extracted four times with EtOAc. Organic layer was washed with brine, dried over anhydrous Na_2SO_4, and solvent was removed in vacuo. Purification of the residue by flash column chromatography (petroleum ether/ethyl acetate = 10/1) afforded the 6-trifluoromethyl-4,12-dihydroindolo[2,3-c] [1]benzazepine (**1h-i**).

6-trifluoromethyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1a). Yellowish solid, 80% over yield, m.p. 170-171°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.38 (dd, *J* = 6.8, 0.9 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.23 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 3.92 (s, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 144.48, 138.15, 132.11, 129.64, 128.46, 128.25, 126.95, 126.16, 125.64, 124.79, 122.91, 120.81, 119.76, 112.00, 28.87; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.24 (s).

6-trifluoromethyl-4-methyl-5,12-dihydroindolo[2,3 c][1]benzazepine (1b).

Yellowish solid, 85% over yield, m.p. 150-151°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.67 – 7.62 (m, 1H), 7.49 (dd, J = 7.4, 1.5 Hz, 1H), 7.39 – 7.26 (m, 3H), 7.20 – 7.10 (m, 2H), 3.90 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.50, 137.90, 132.16, 129.57, 128.44, 128.15, 126.90, 126.48, 126.31, 124.40, 122.71, 122.30, 121.23, 121.07, 117.42, 29.02, 16.49; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.13 (s).

6-trifluoromethyl-1-methyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1c).

Yellowish solid, 83% over yield, m.p. 140-141°C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.93 (d, *J* = 1.5 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.43 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.32 – 7.30 (d, 1H), 7.30-7.28 (s, 1H), 3.86 (s, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.49, 138.53, 132.82, 132.16, 129.33, 128.00, 127.55, 126.88, 126.29, 126.06, 123.31, 122.99, 122.52, 110.00, 30.33, 21.08; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.07 (s).

6-trifluoromethyl-2-methyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1d).

Yellowish solid, 85% over yield, m.p. 145-146°C**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 7.9, 2.7 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 3.85 (s, 2H), 2.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.55, 136.67, 132.19, 130.22, 129.53, 128.43, 128.21, 128.09, 126.88, 125.22, 125.01, 123.06, 119.05, 111.67, 28.86, 21.52; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.21 (s).

6-trifluoromethyl-3-fluoro-5,12-dihydroindolo[2,3-c][1]benzazepine (1e).

Yellowish solid, 75% over yield**,** m.p. 161-162°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 1H), 7.35 (ddd, *J* = 10.1, 7.7, 1.7 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.19 (dd, *J* = 8.6, 1.7 Hz, 1H), 3.88 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.33,

160.90, 144.43, 138.30, 131.82, 129.73, 128.46, 128.33, 127.07, 125.60, 121.58, 121.15, 121.04, 110.52, 110.26, 98.22, 97.96, 28.88; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.23 (s).

6-trifluoromethyl-3-chloro-5,12-dihydroindolo[2,3-c][1]benzazepine (1f).

Yellowish solid, 78% over yield, m.p. 175-176°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.70 (d, J = Hz, 1H), 7.50 (dd, J = 7.5, 1.4 Hz, 1H), 7.41 (d, J = 1.5 Hz, 1H), 7.34 (pd, J = 7.3, 1.7 Hz, 2H), 7.29 (dd, J 7.1, 1.7 Hz, 1H), 7.19 (dd, J = 8.6, 1.7 Hz, 1H), 3.88 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.37, 138.25, 136.90, 132.03, 131.79, 131.11, 129.83, 129.38, 128.49, 128.38, 127.99, 127.12, 126.95, 125.39, 123.93, 123.40, 121.87, 120.74, 115.21, 111.84, 28.80; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.24.

6-trifluoromethyl-2-bromo-5,12-dihydroindolo[2,3-c][1]benzazepine (1g).

Yellowish solid, 75% over yield, m.p. 225-226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.49 (dd, = 5.7, 3.6 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.21 (dd, *J* = 11.5, 5.1 Hz, 2H), 6.92 (d, *J* = 6.2 Hz, 1H), 4.06 (s, 2H), 2.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.30, 136.54, 131.77, 129.93, 128.99, 128.52, 128.39, 127.14, 126.40, 124.51, 122.33, 121.93, 113.99, 113.50, 28.72; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.25 (d, J = 3.9 Hz).

6-difluoromethyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1h).

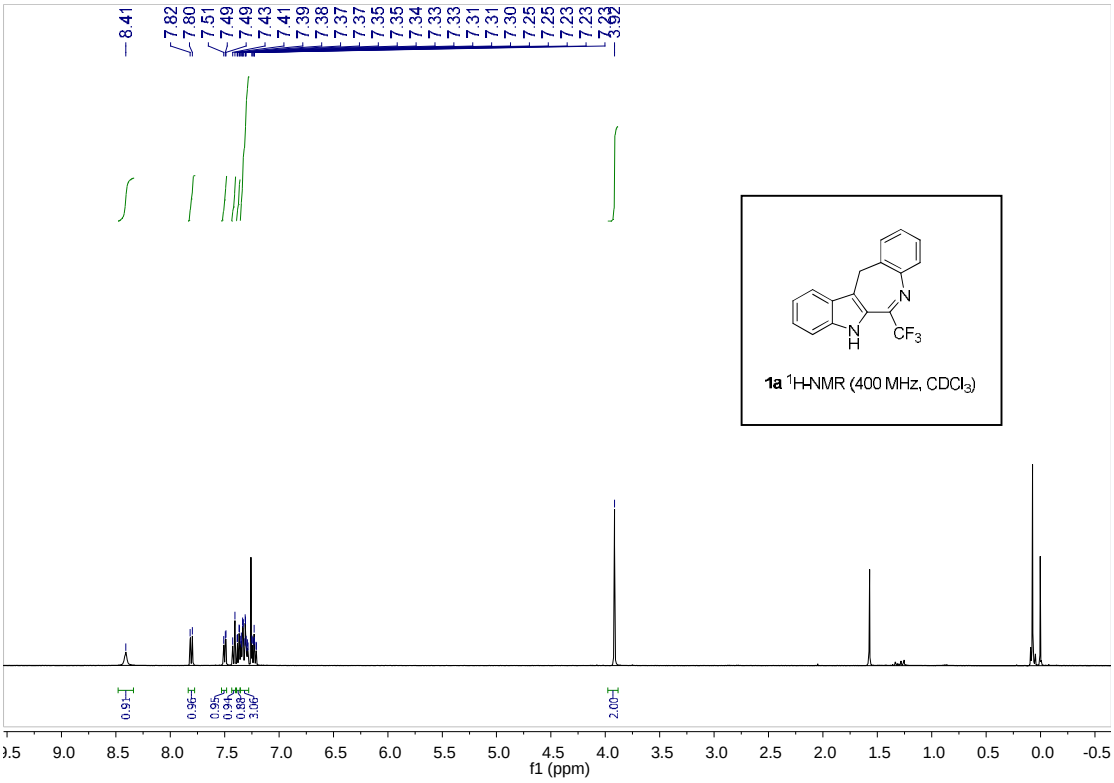
Yellowish solid, 90% over yield, m.p. 151-152°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.73 (dd, *J* = 8.8, 5.3 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.08 (dd, *J* = 9.3, 2.2 Hz, 2H), 7.00 (td, *J* = 9.1, 2.2 Hz, 1H), 3.89 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 138.02, 132.29, 129.18, 128.63, 128.17, 127.90, 126.87, 125.71, 124.84, 124.70, 123.88, 123.28, 120.49, 120.28, 119.64, 117.86, 115.02, 111.98, 29.00; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.46 (d, J = 55.1 Hz).

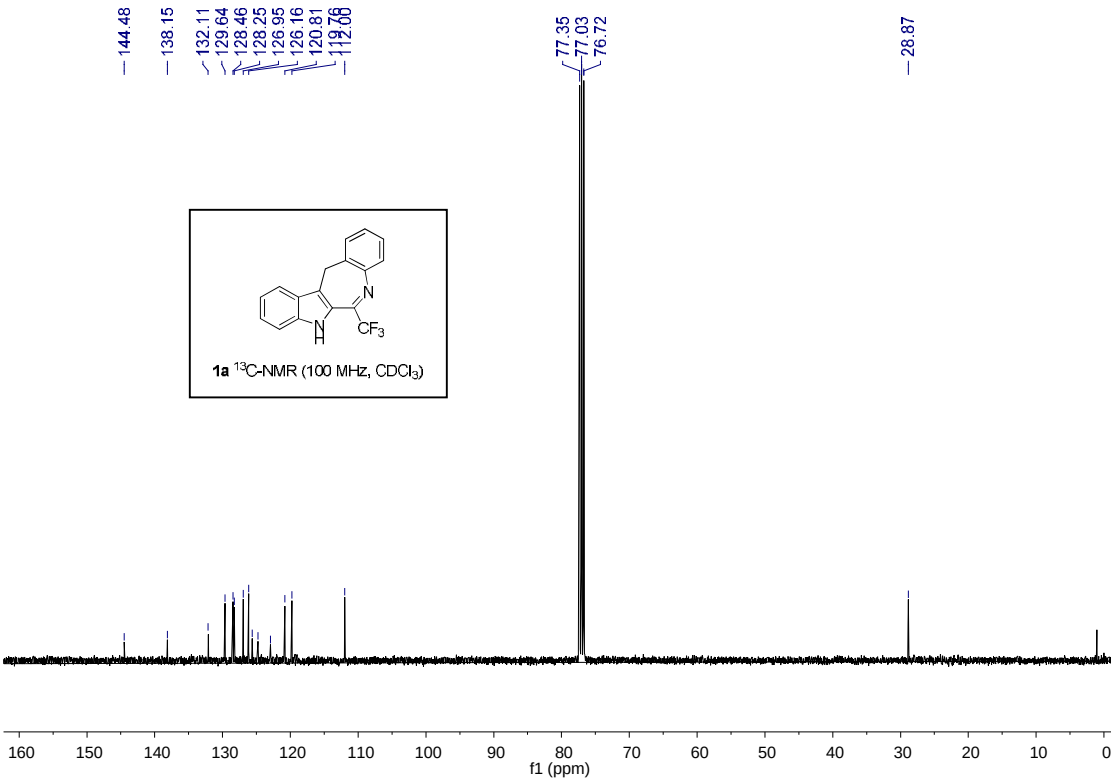
6-methyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1i).

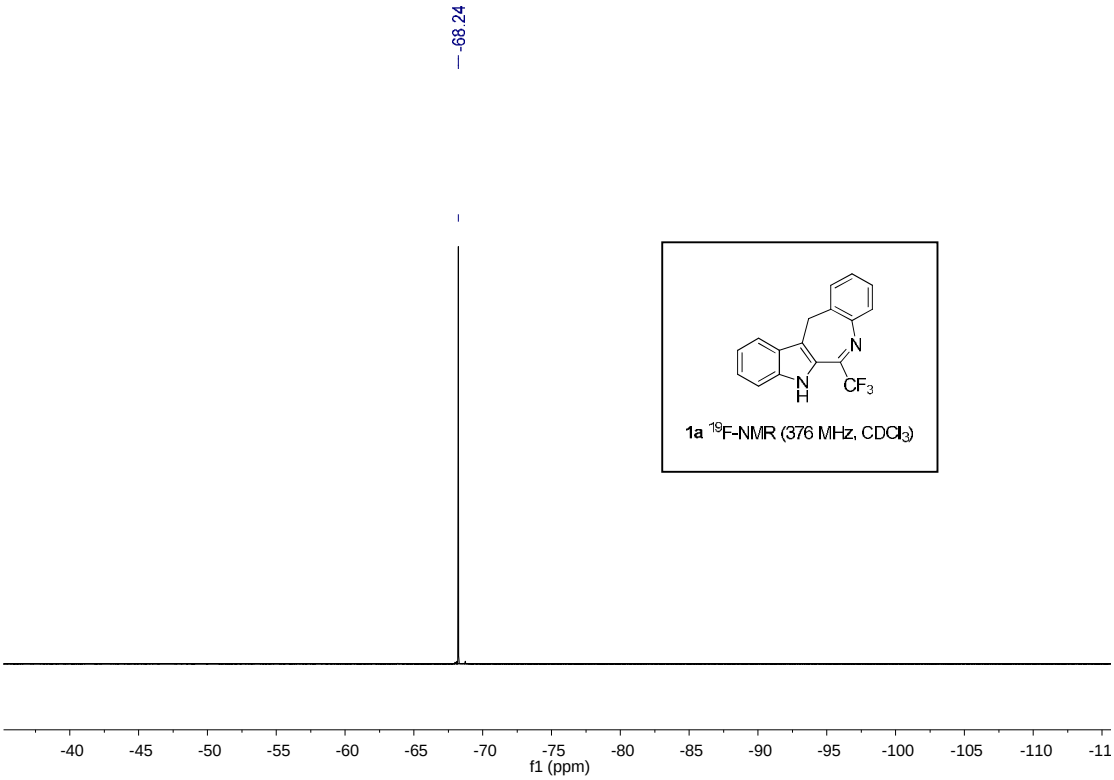
Yellowish soid, 87% over yield, m.p. 172-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.57 (s, 1H), 7.52 – 7.45 (m, 1H), 7.37 – 7.27 (m, 4H), 7.19 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.88 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.49, 146.78, 137.16, 133.38, 132.89, 131.83, 129.08, 128.22, 127.14, 126.81, 126.57, 125.65, 125.33, 125.20, 124.77, 121.75, 120.33, 119.64, 111.61, 28.96, 26.40.

1. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

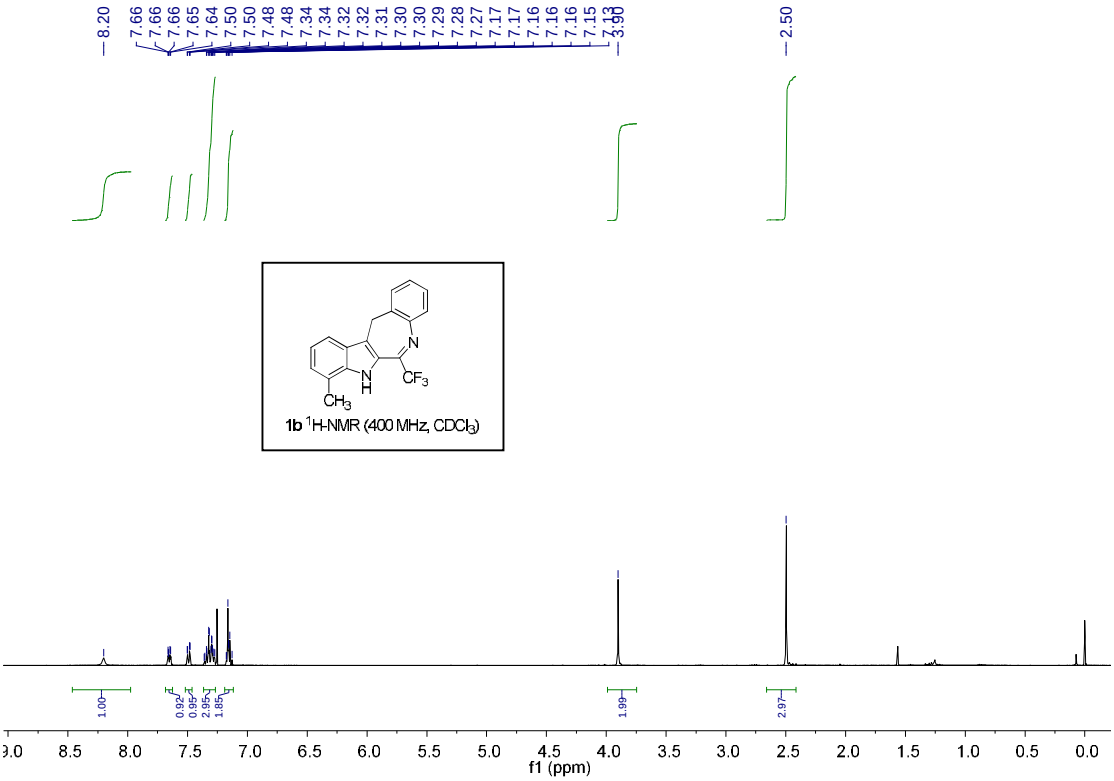
6-trifluoromethyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1a)

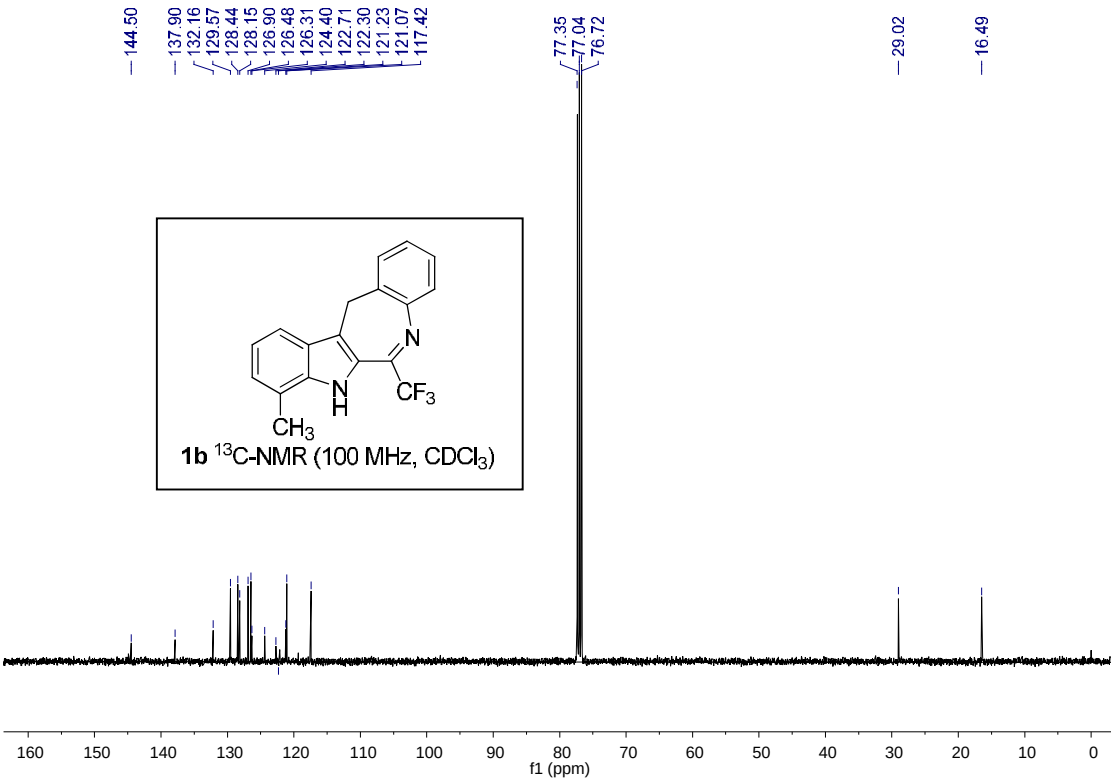






6-trifluoromethyl-4-methyl-5,12-dihydroindolo[2,3-c][1]benzaz- epine (1b)

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121.07
117.42
77.35
77.04
76.72
29.02
16.49
N
N
H
CF3
CH3
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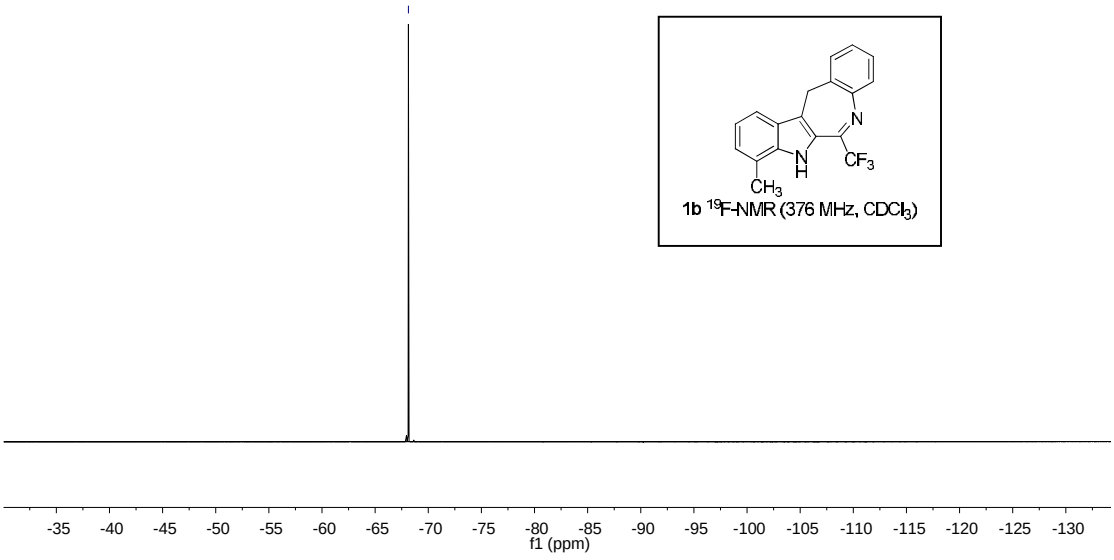
f1 (ppm)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CH3
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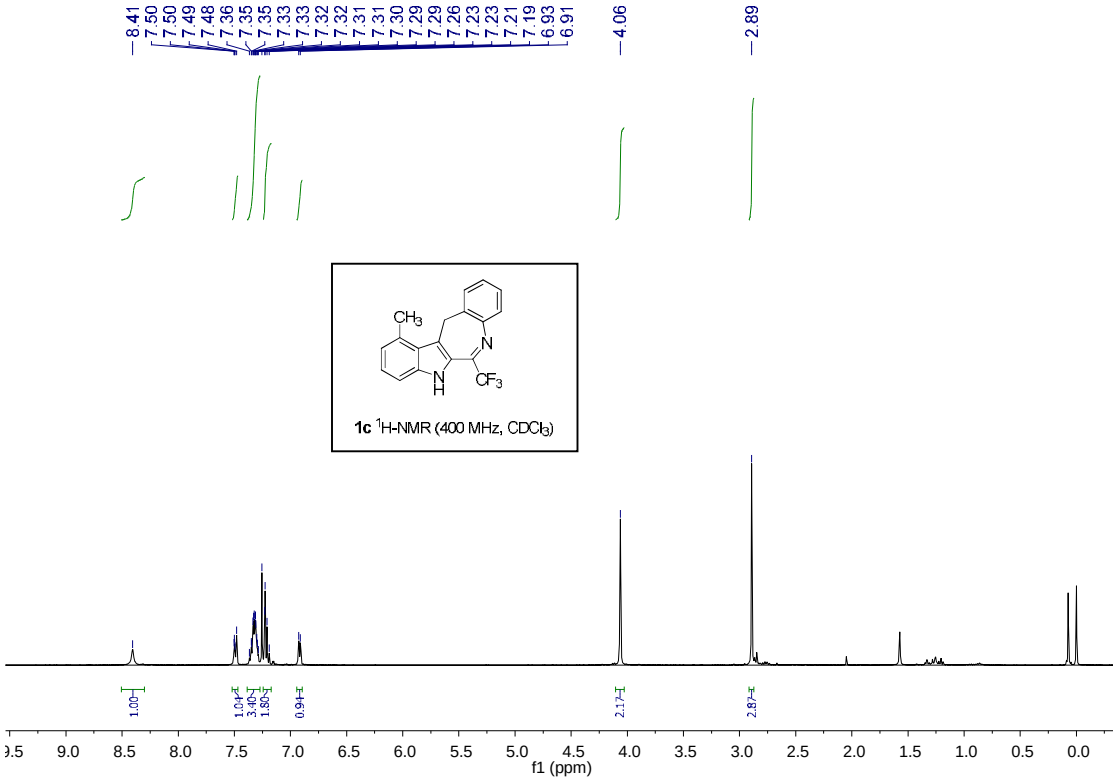
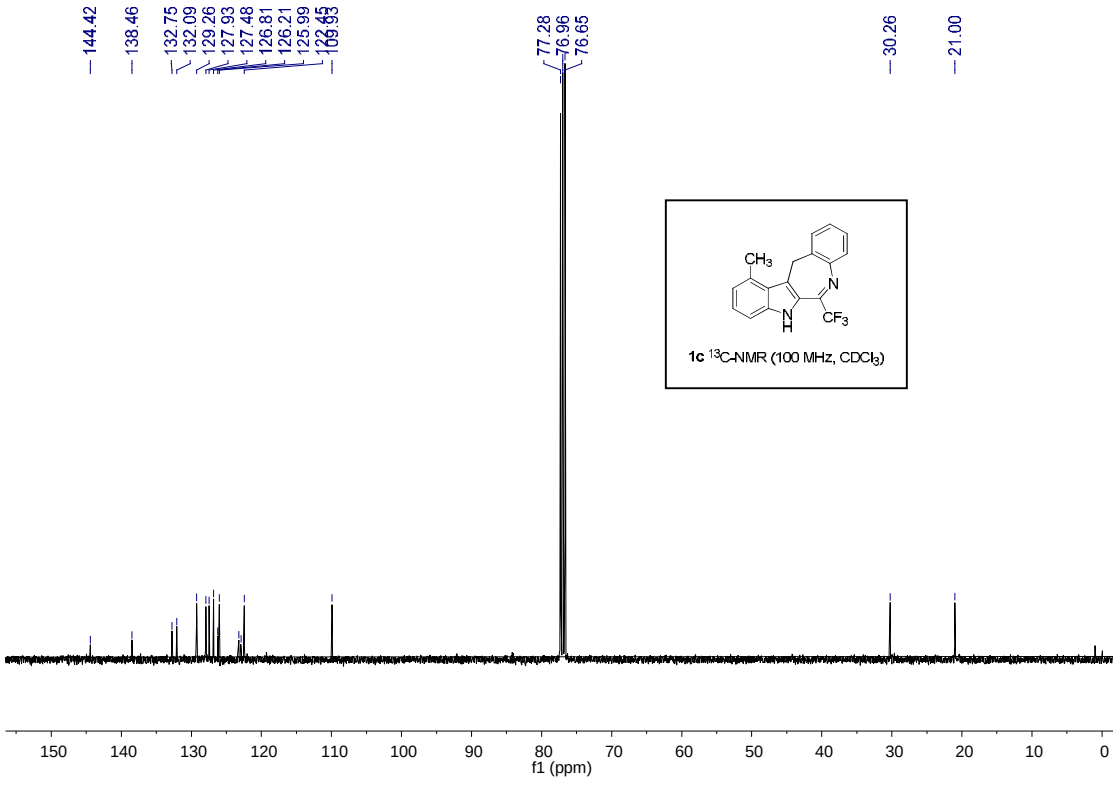
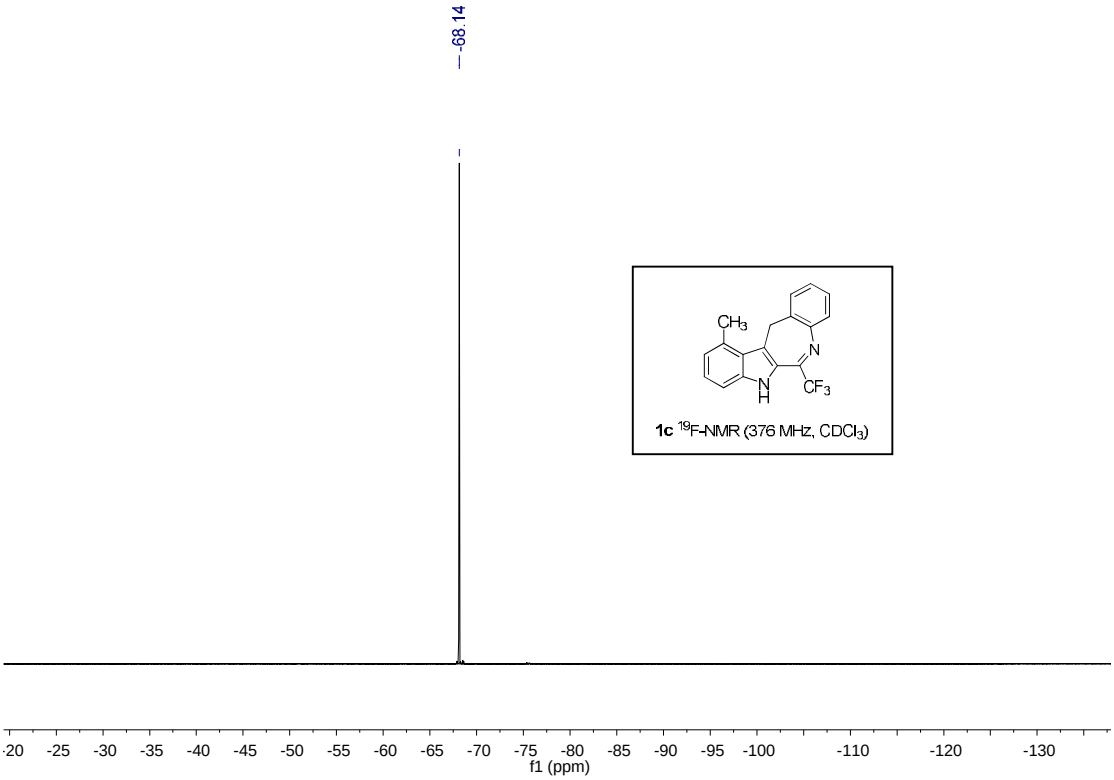
f1 (ppm)

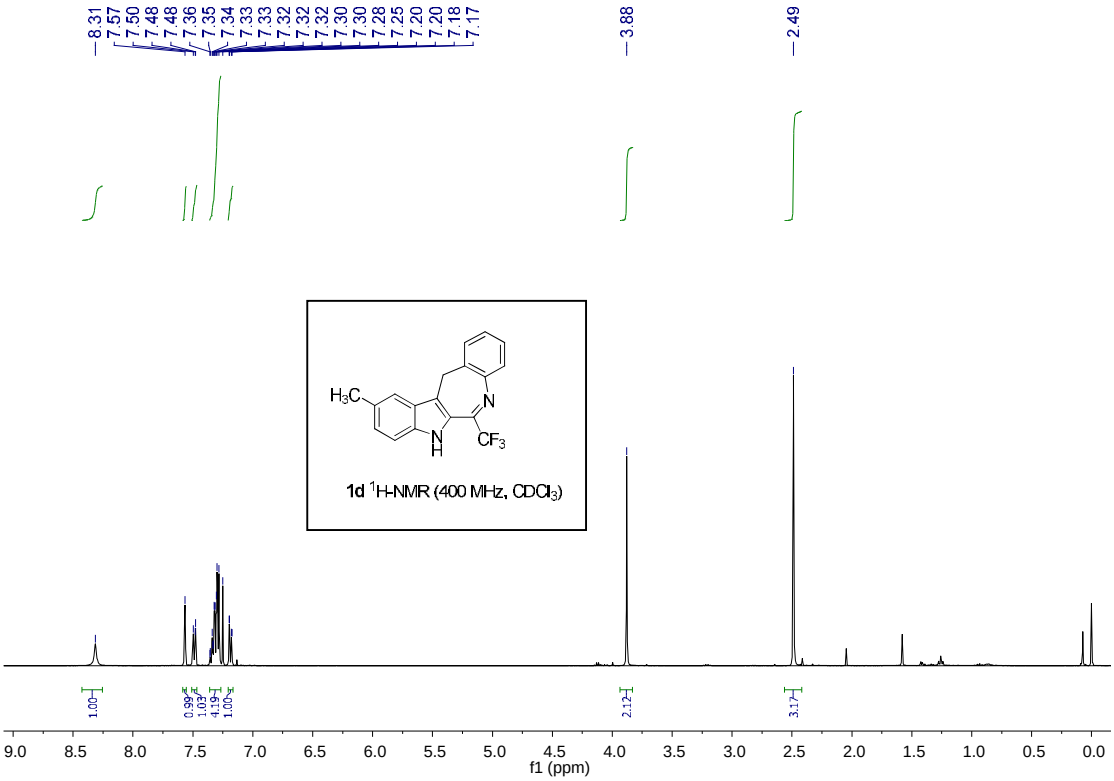
6-trifluoromethyl-1-methyl-5,12-dihydroindolo[2,3-c][1]benzaz- epine (1c)

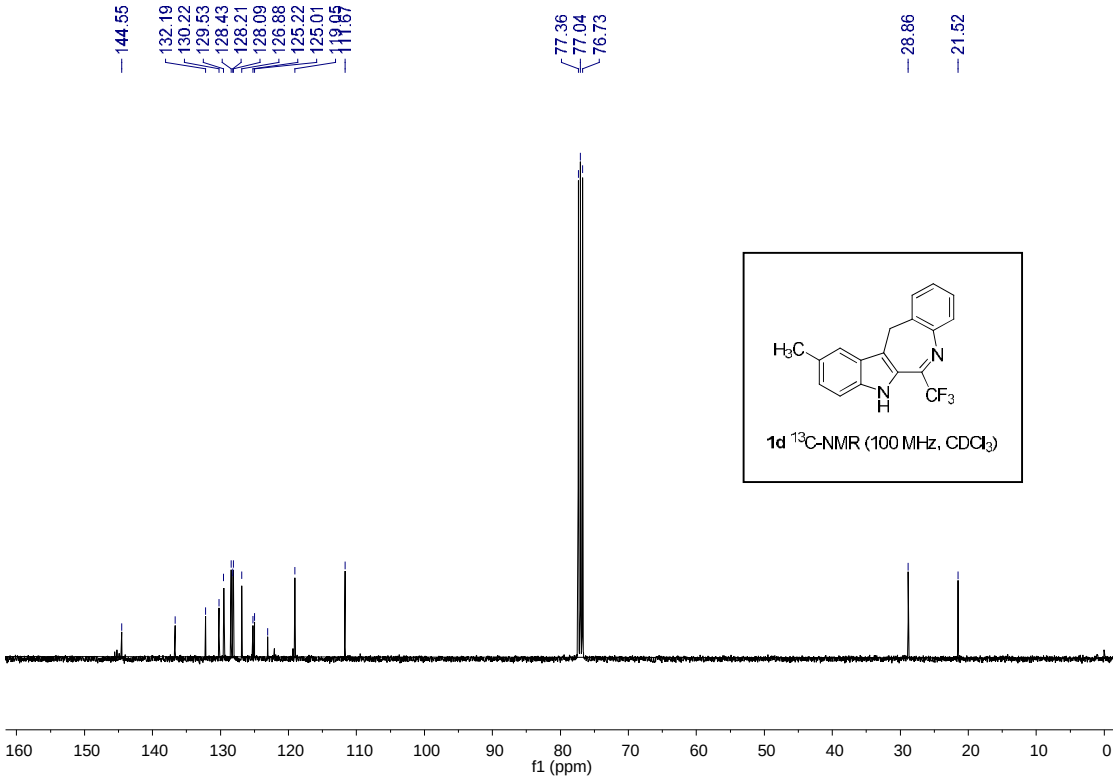






6-trifluoromethyl-2-methyl-5,12-dihydroindolo[2,3-c][1]benzaz- epine (1d)

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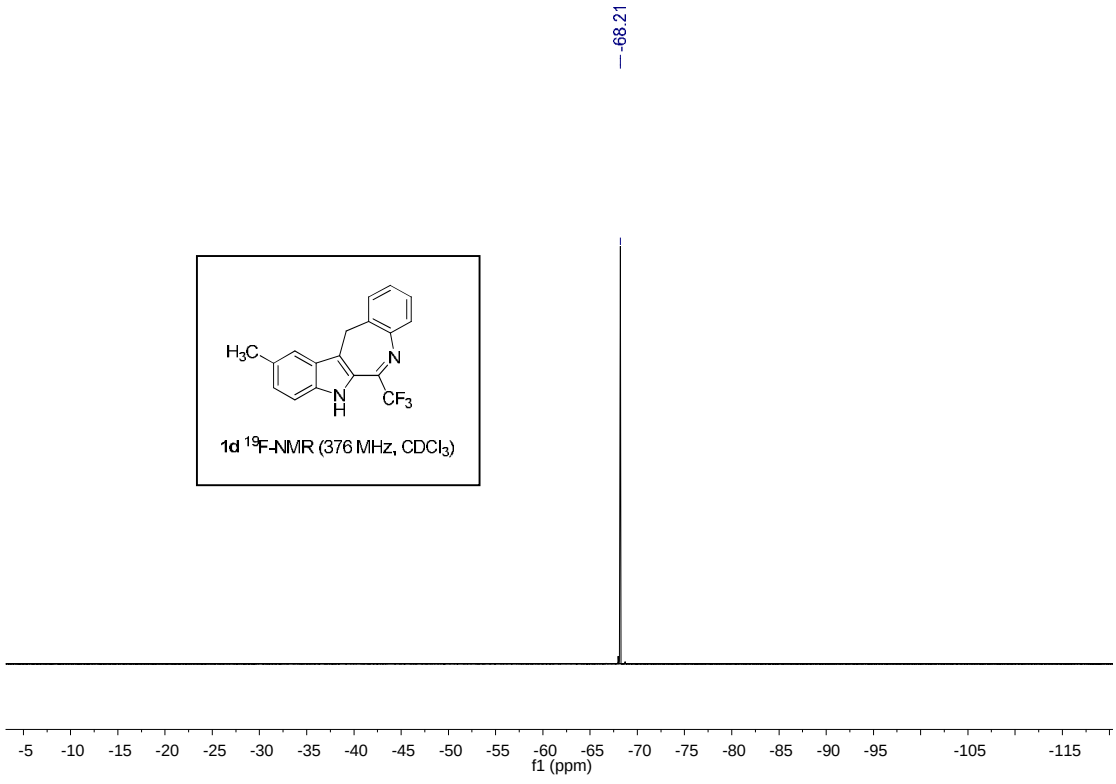
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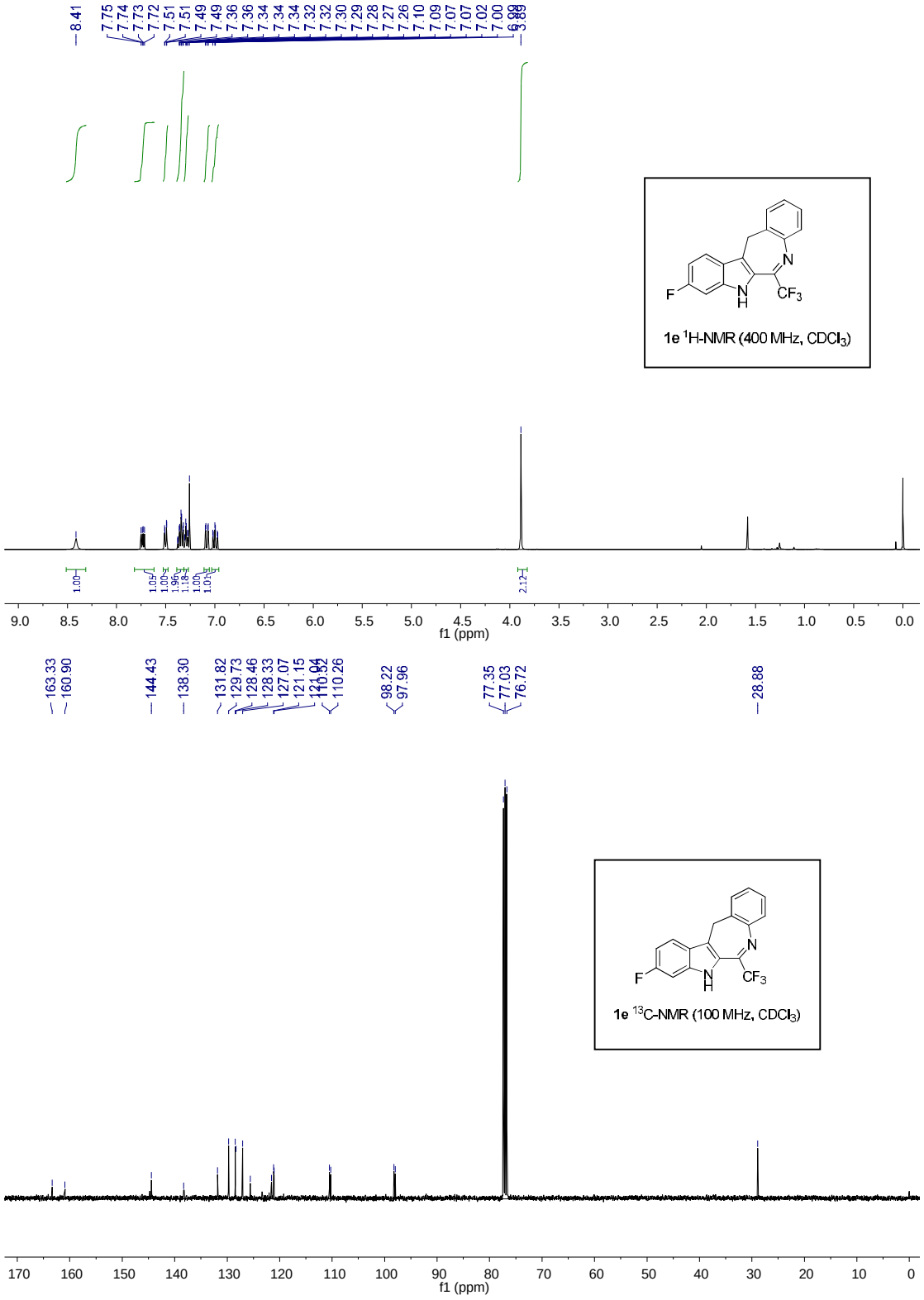
f1 (ppm)

6-trifluoromethyl-3-fluoro-5,12-dihydroindolo[2,3-c][1]benzaze- pine (1e)



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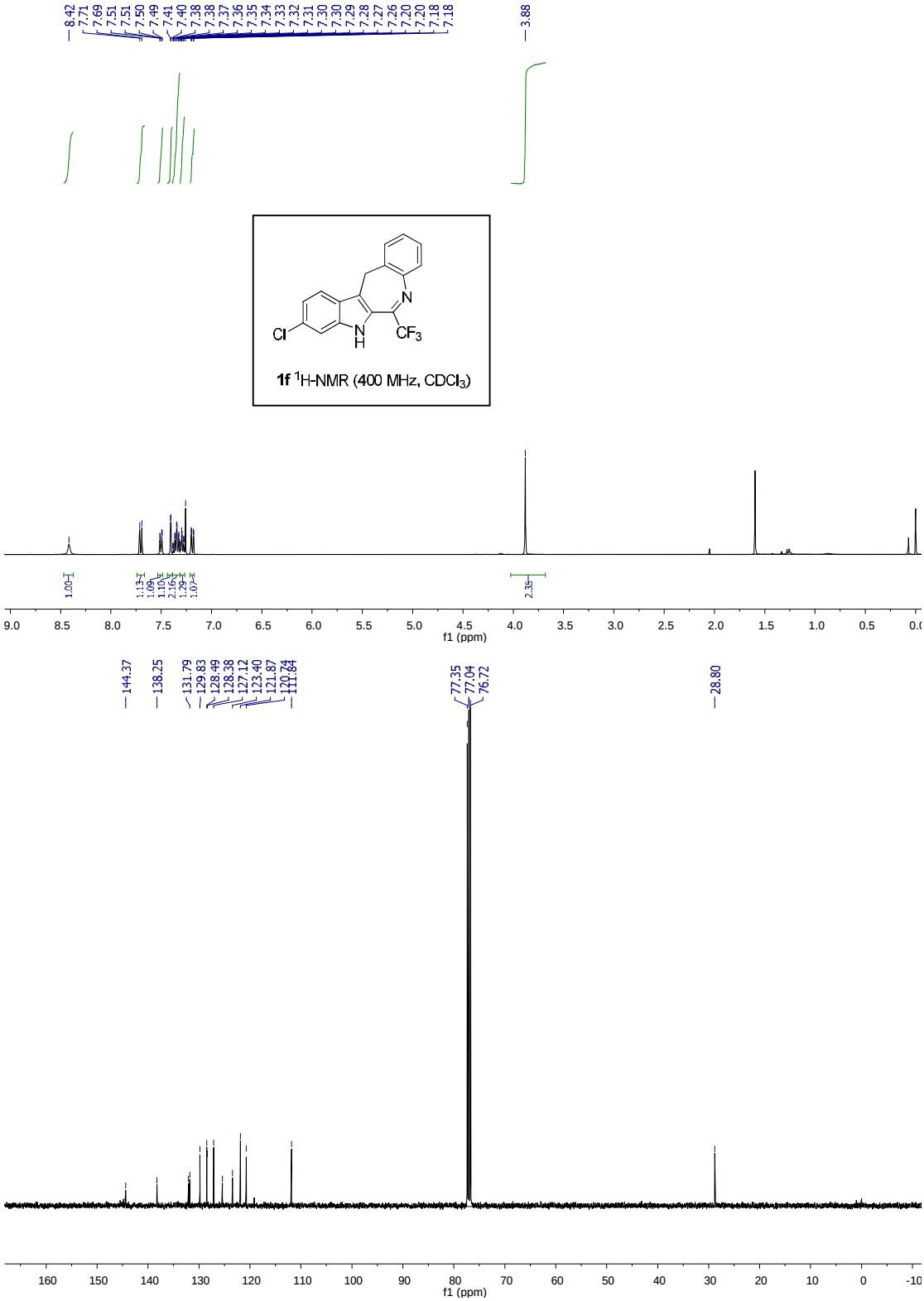
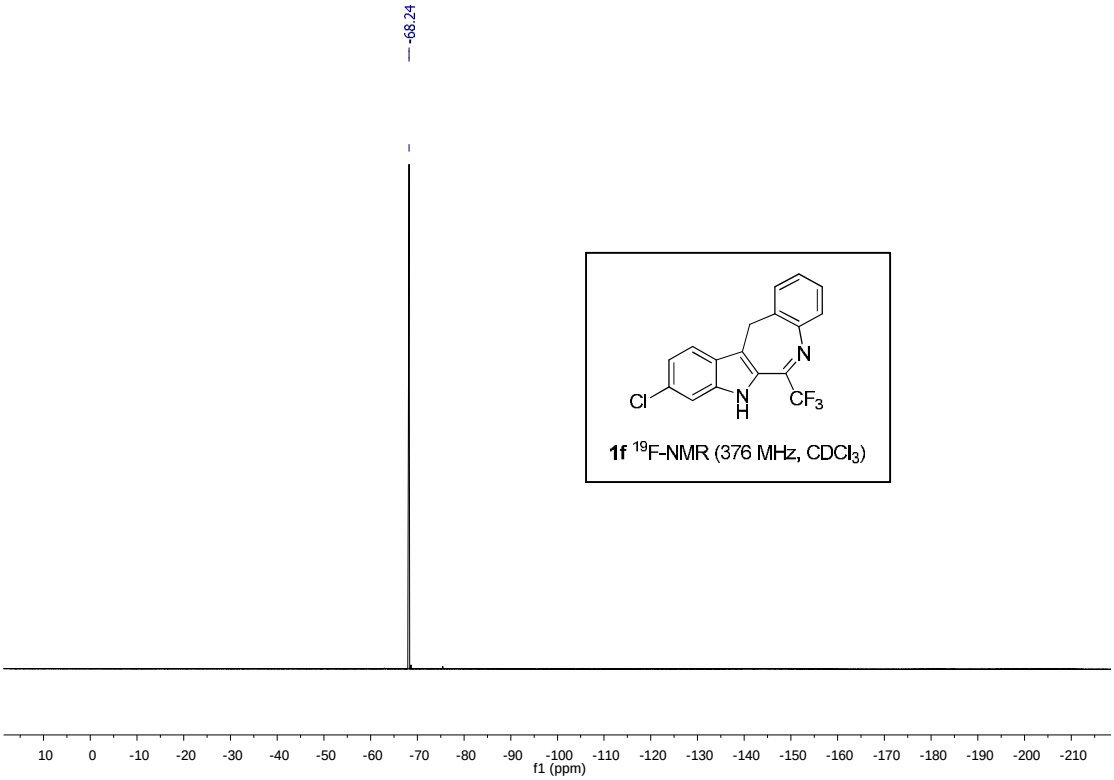
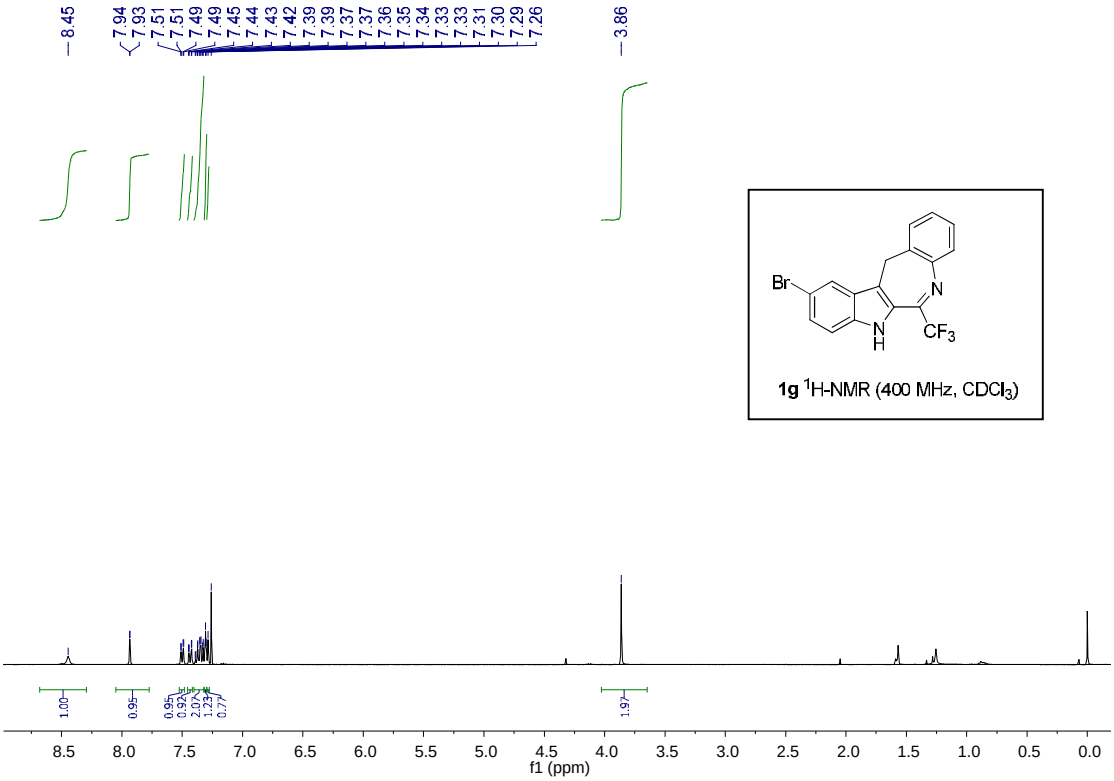




1f ^{19}F-NMR (376 MHz, $CDCl_3$)

6-trifluoromethyl-2-bromo-5,12-dihydroindolo[2,3-c][1]benzaz- epine (1g)



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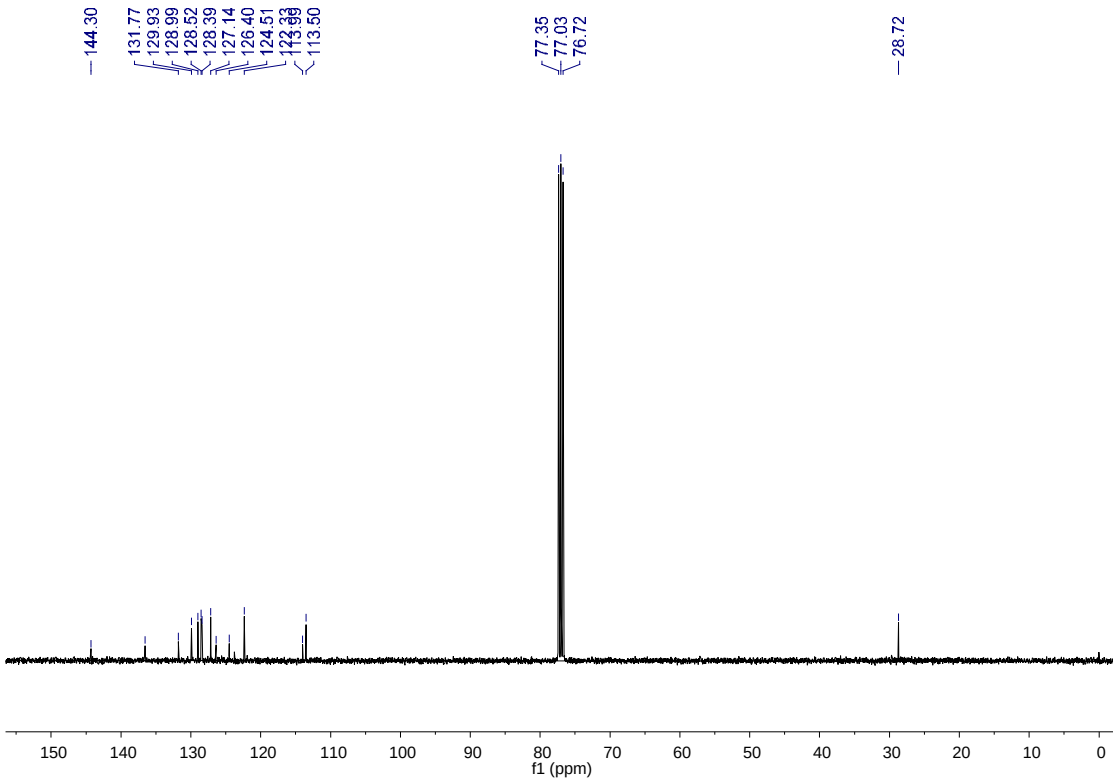
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130
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110
100
90
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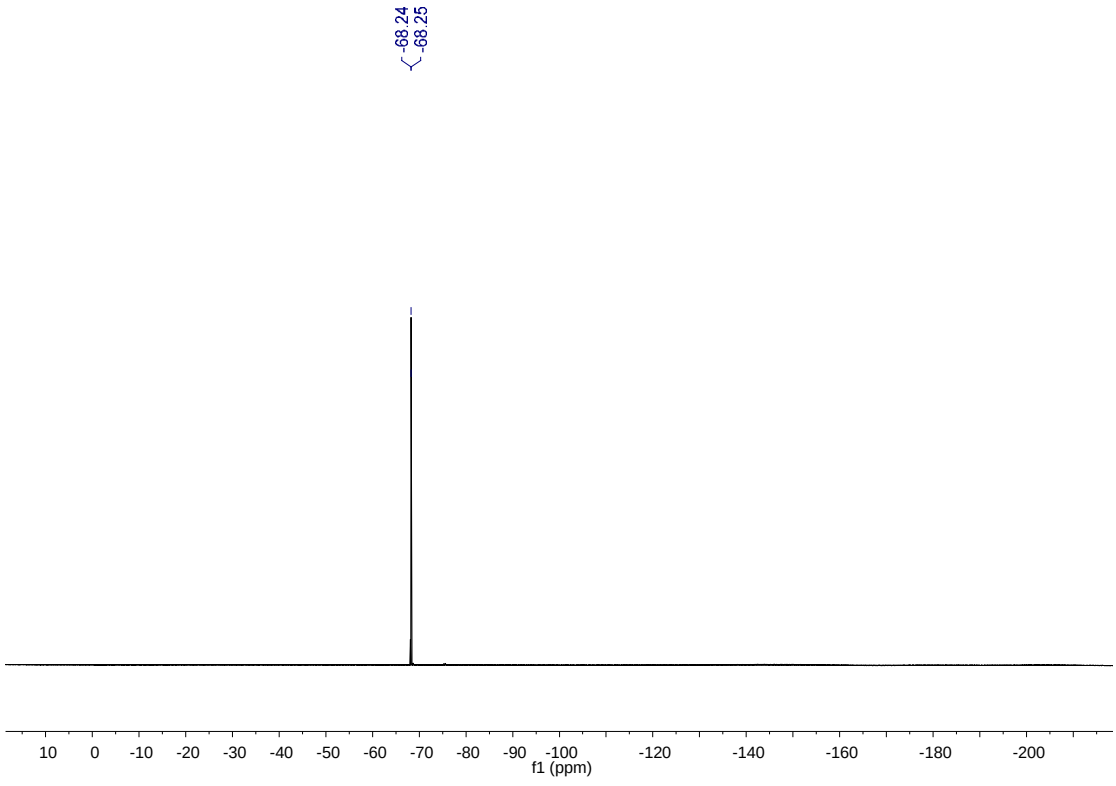
50
40
30
20
10
0
f1 (ppm)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-10
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-80
-90
-100
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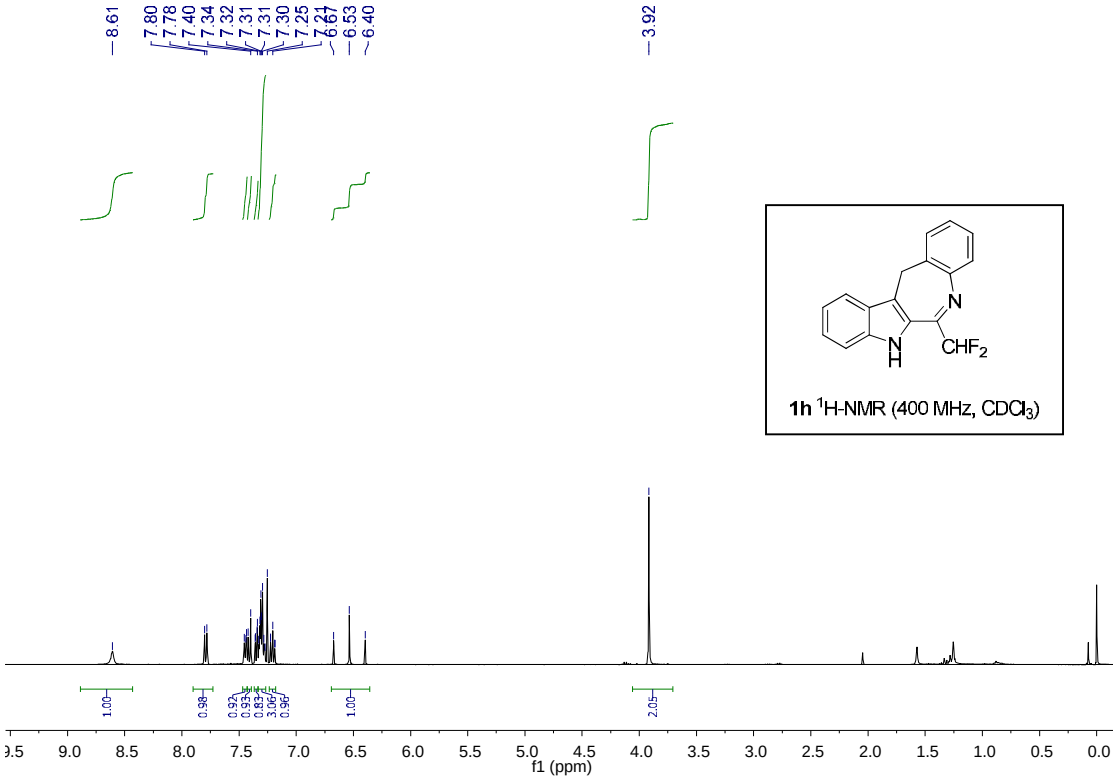
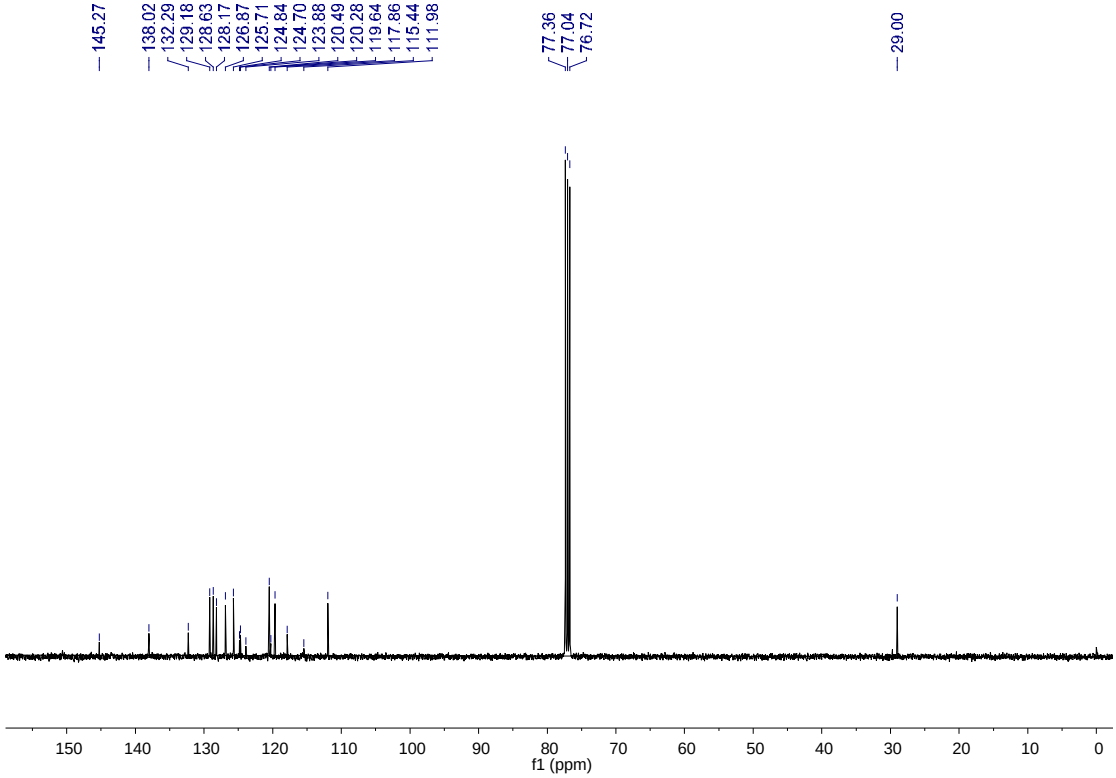
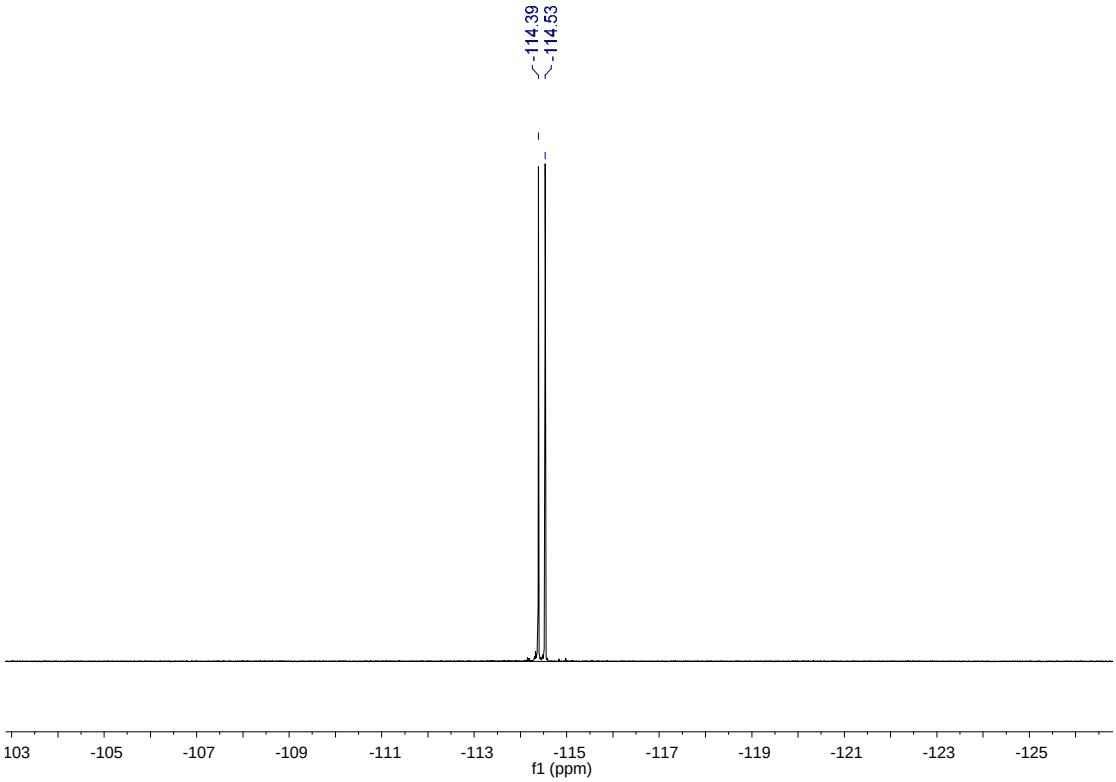
f1 (ppm)

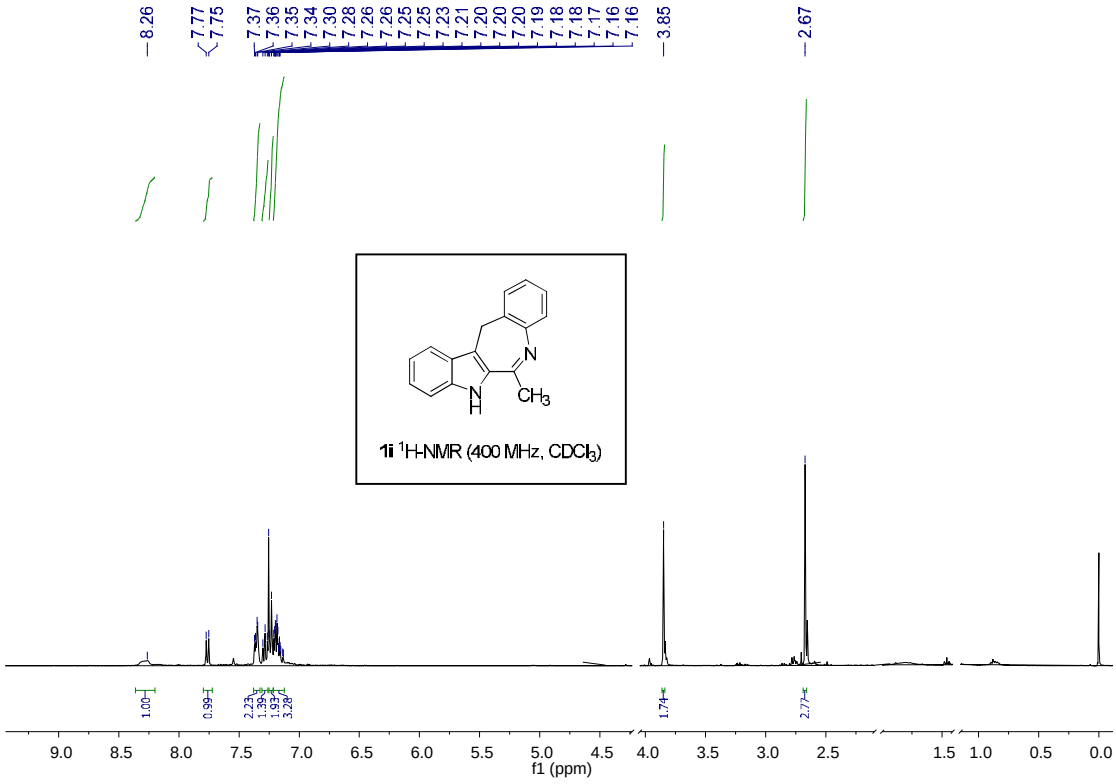
6-difluoromethyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1h)

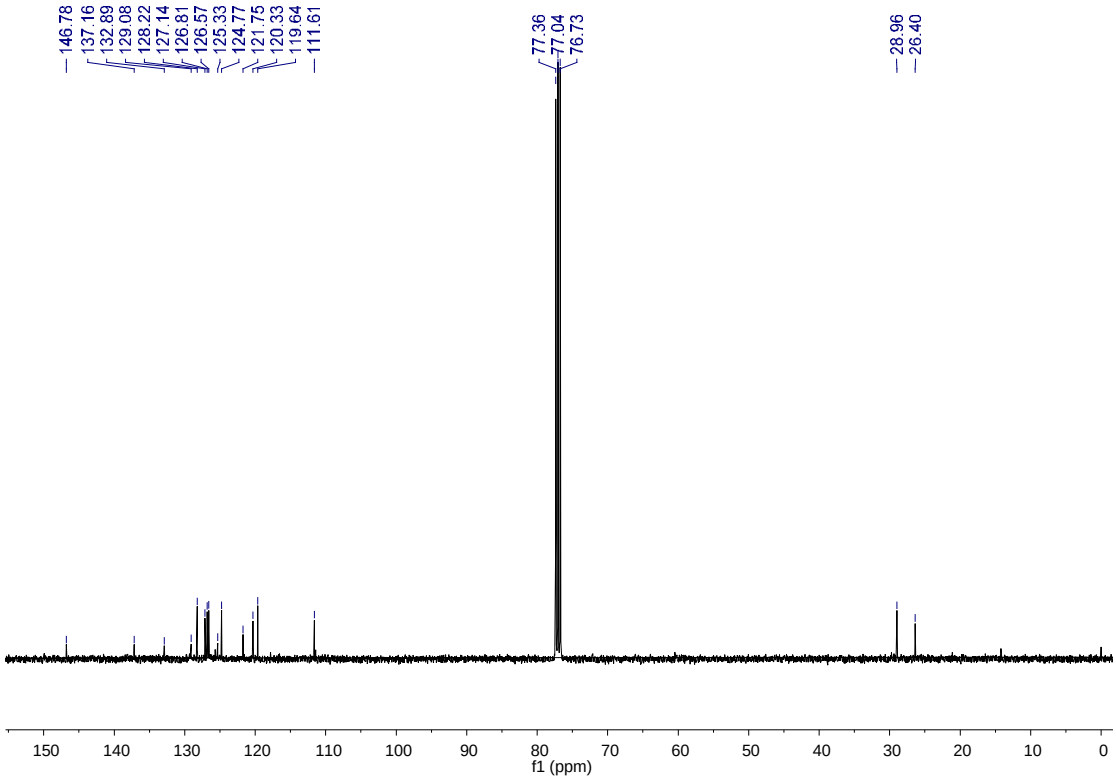




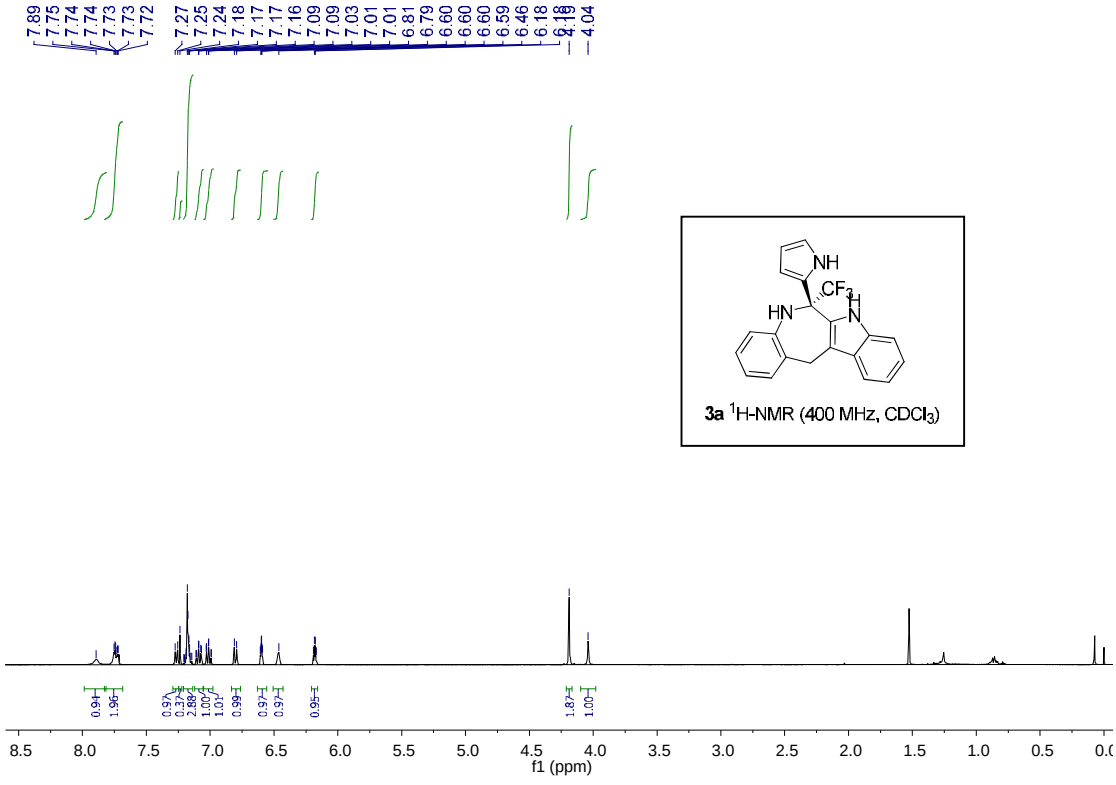


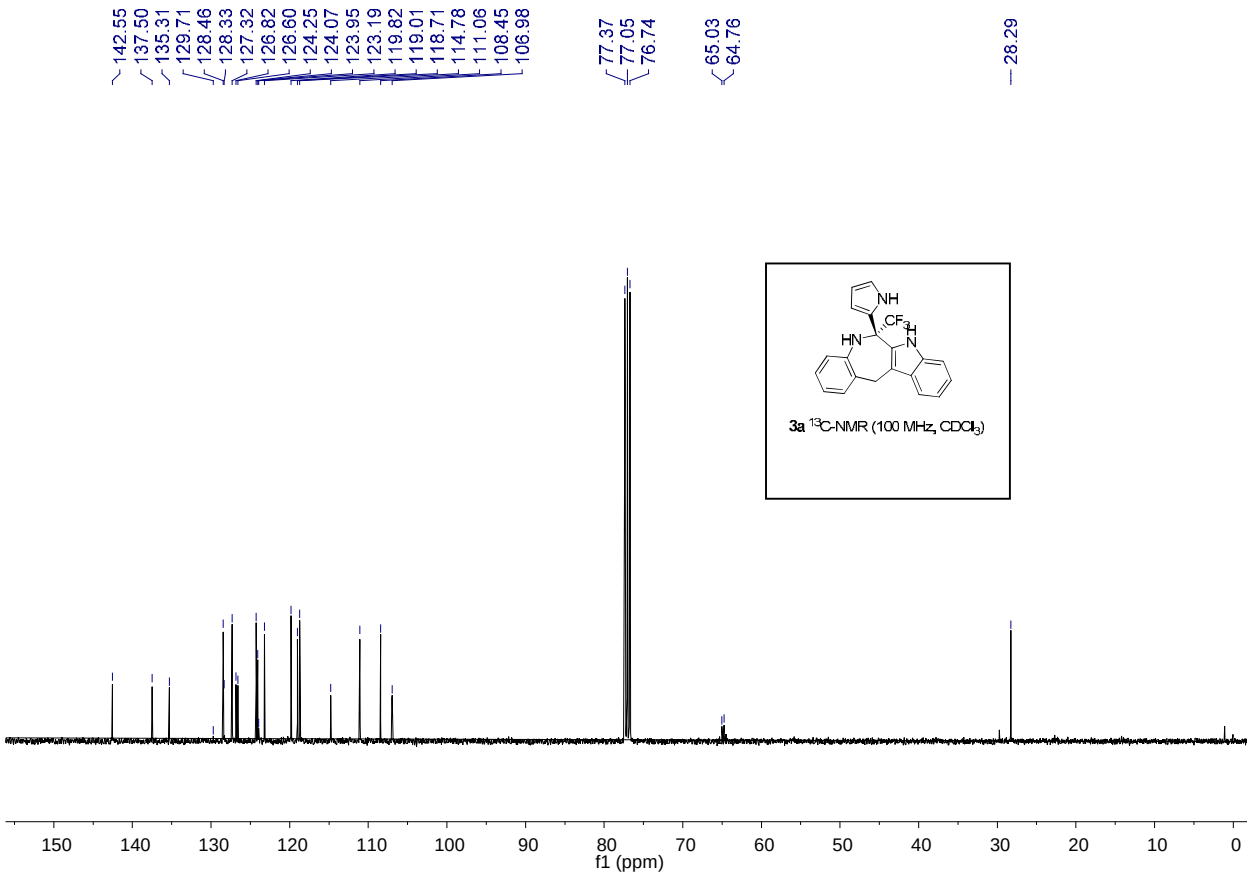
6-methyl-5,12-dihydroindolo[2,3-c][1]benzazepine (1i)





(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3a)

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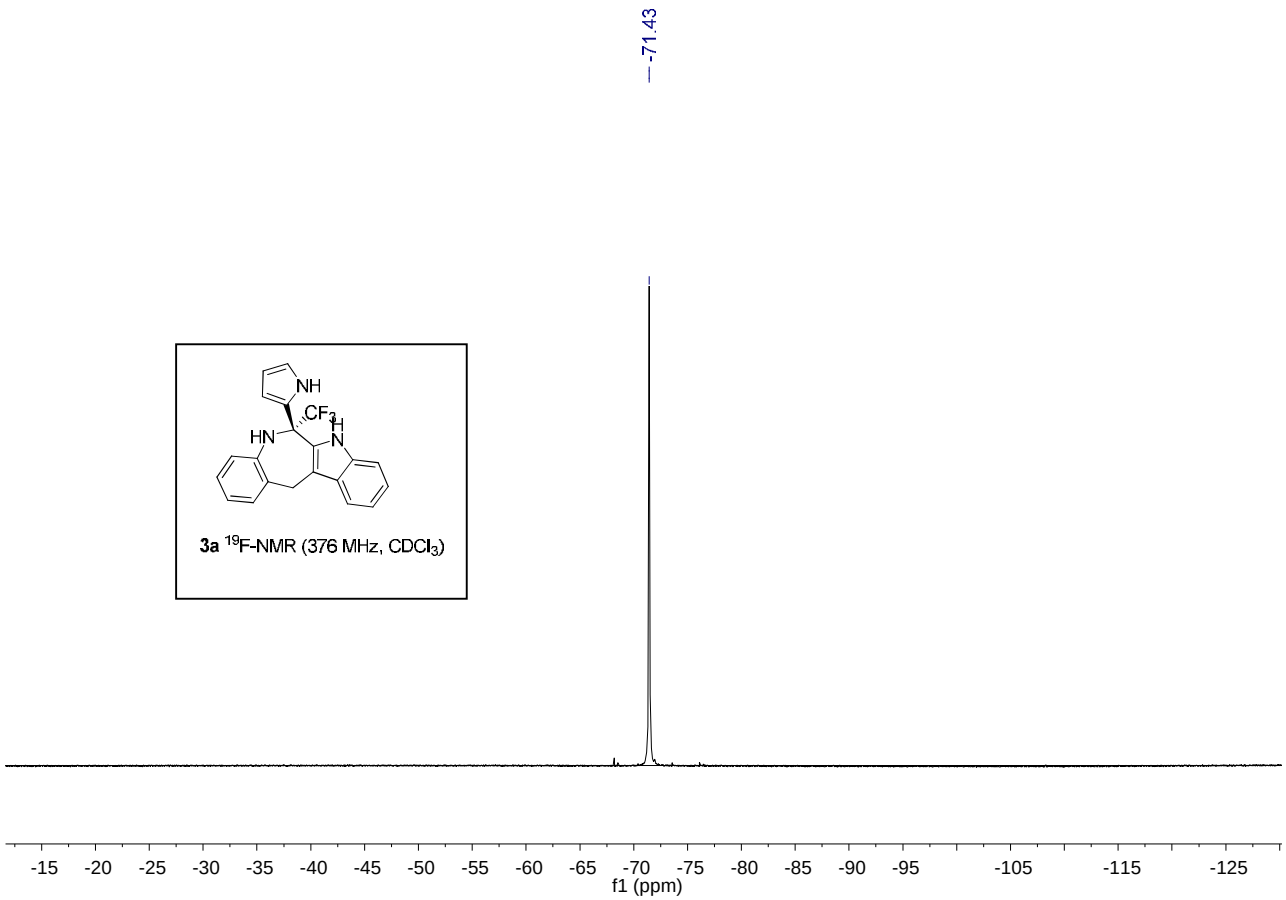
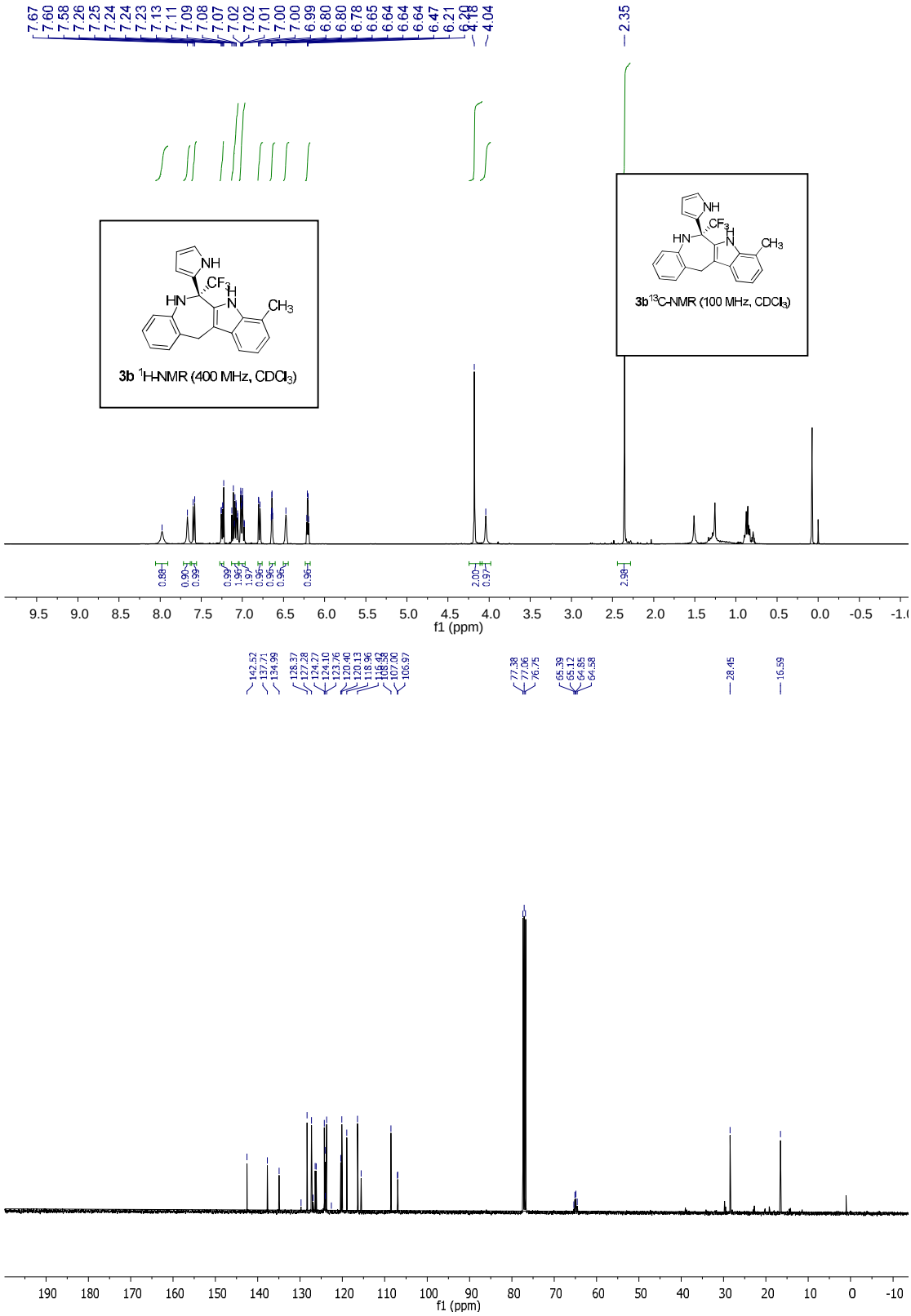
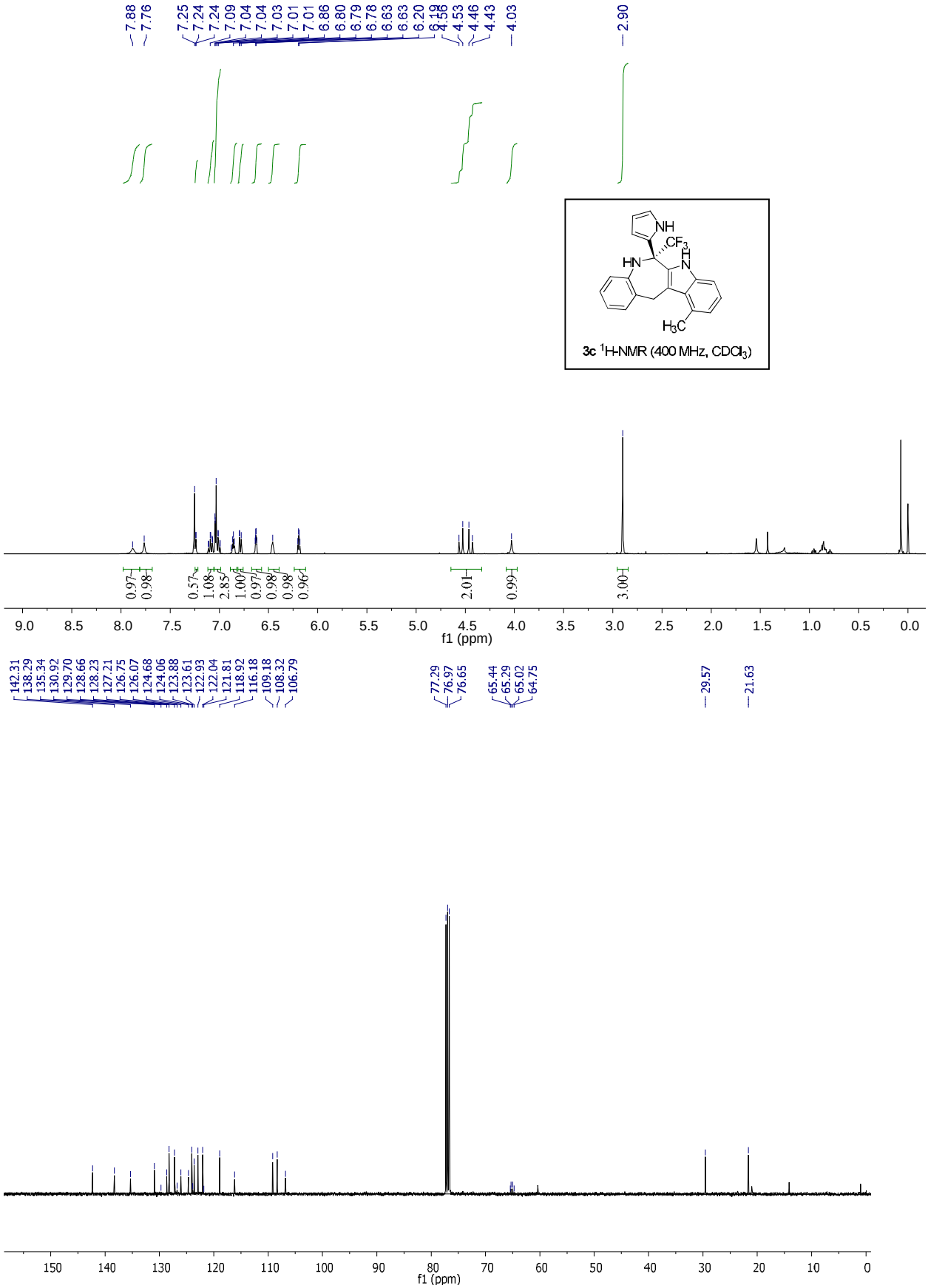
137.50
135.31
129.71
128.46
128.33
127.32
126.82
126.60
124.25
124.07
123.95
123.19
119.82
119.01
118.71
114.78
111.06
108.45
106.98
77.37
77.05
76.74
65.03
64.76
28.29
NH
CF3
HN
H
N
3a 13C-NMR (100 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-71.43
NH
CF3
HN
H
N
3a 19F-NMR (376 MHz, CDCl3)
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-105
-115
-125
f1 (ppm)

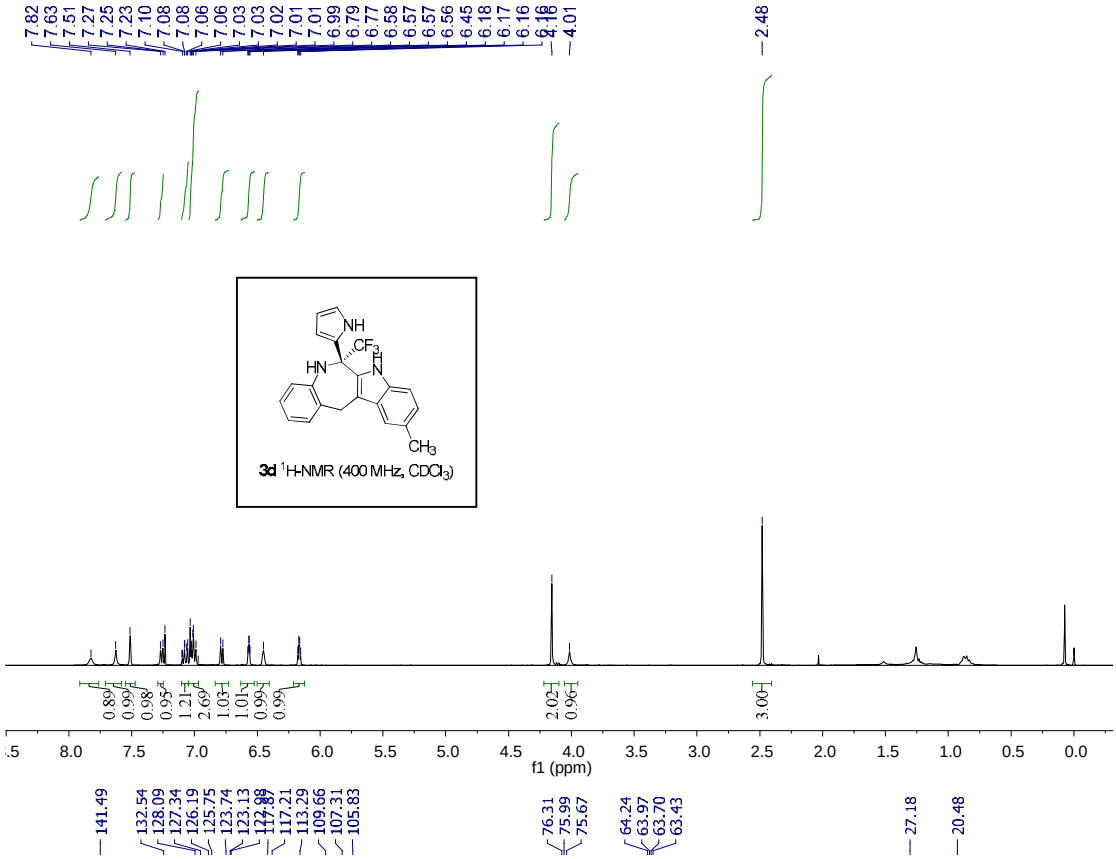
(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-4-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3b)

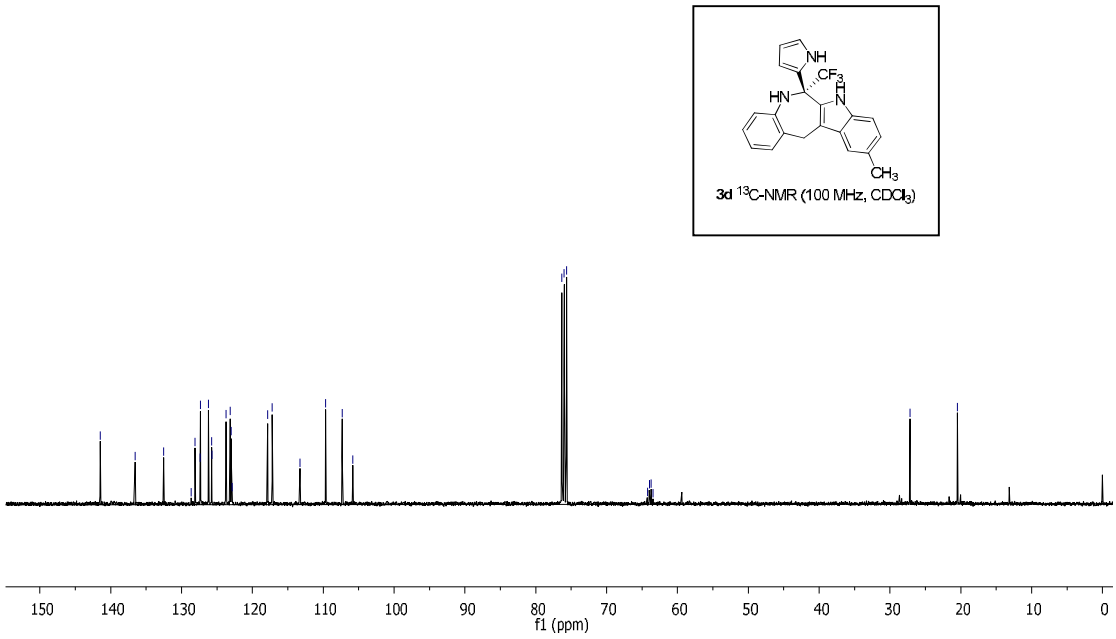


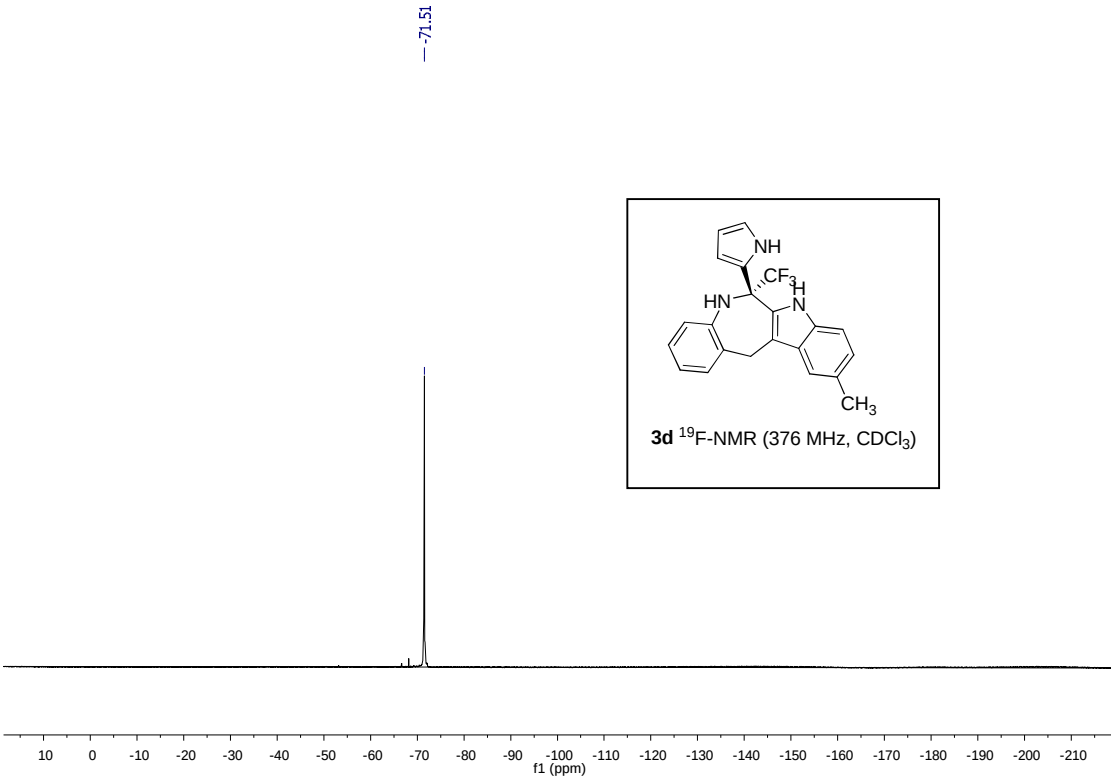
(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-1-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3c)



(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-2-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3d)

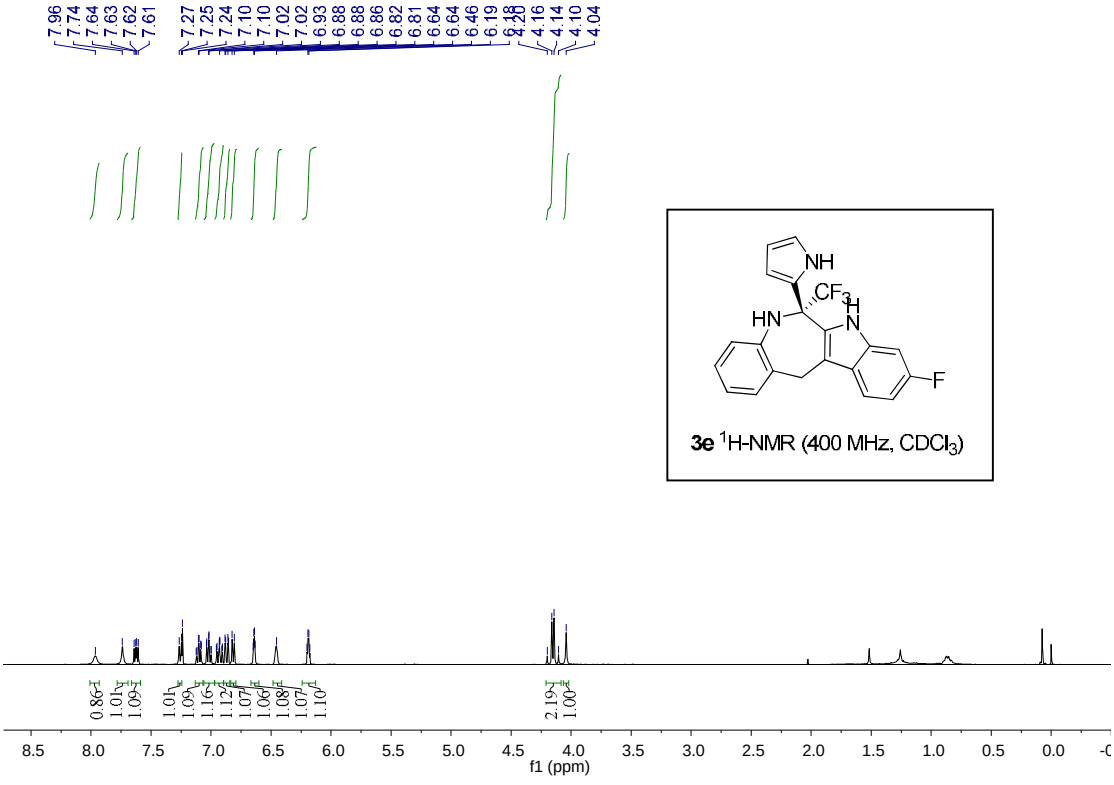




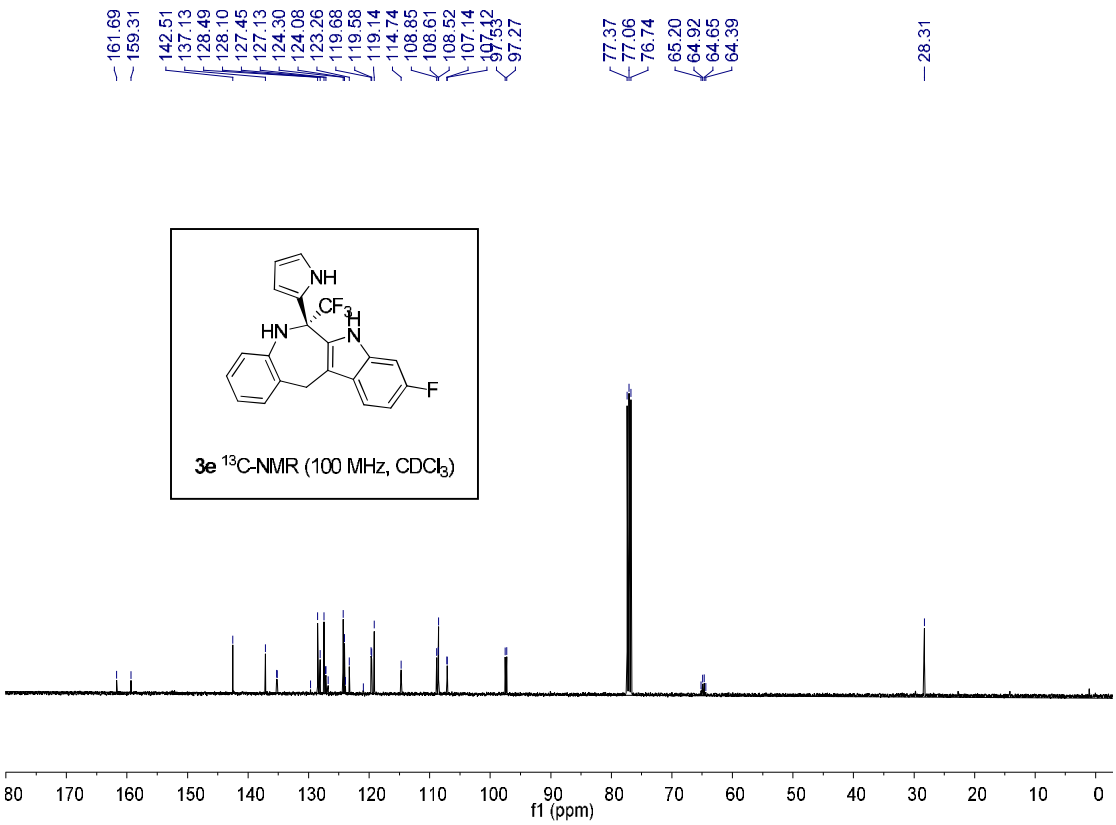


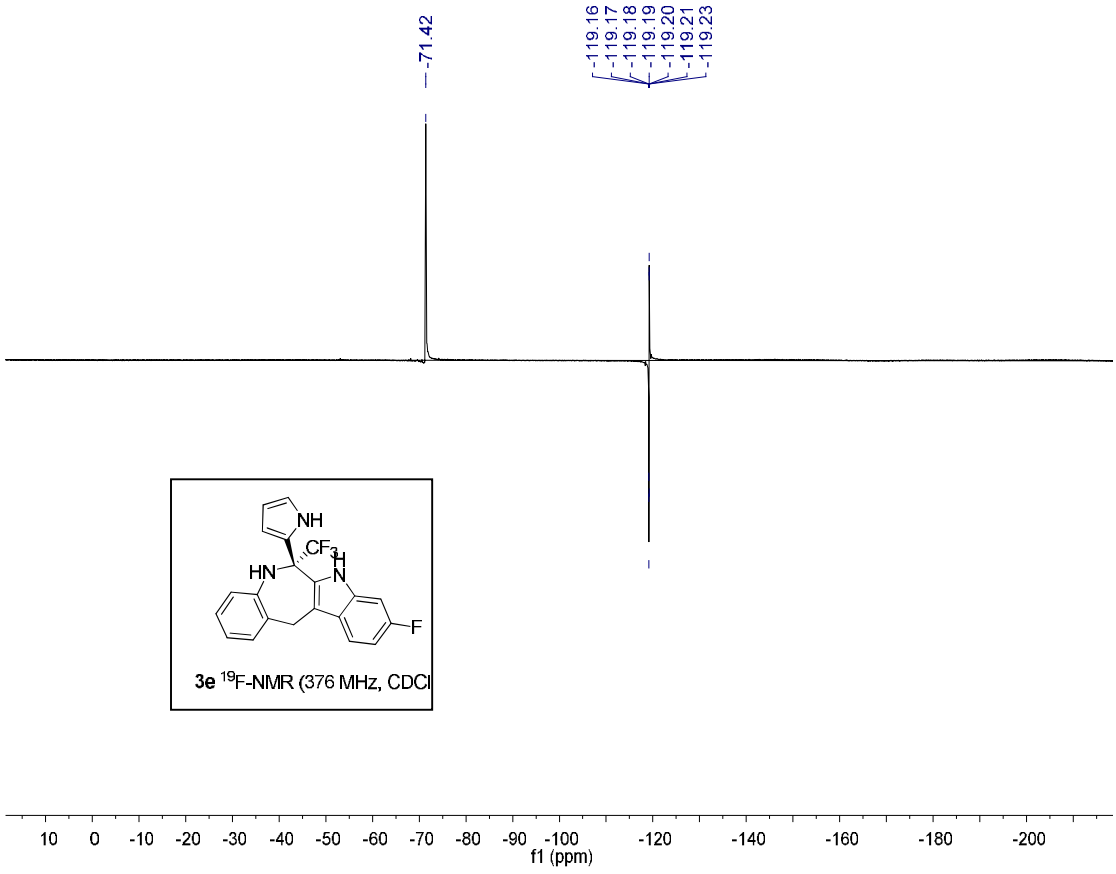
3d ^{19}F-NMR (376 MHz, $CDCl_3$)

(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-3-fluoro-5,6,7,12-tetrahydroind-olo[2,3-c][1]benzazepine (3e)

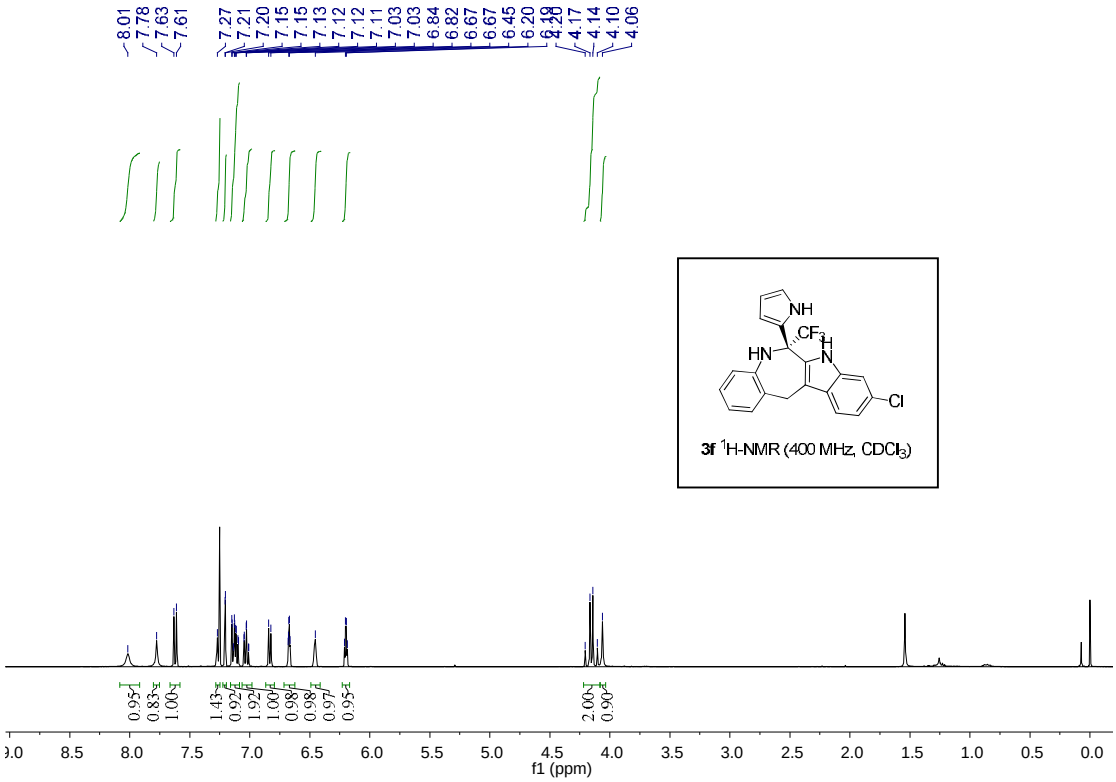


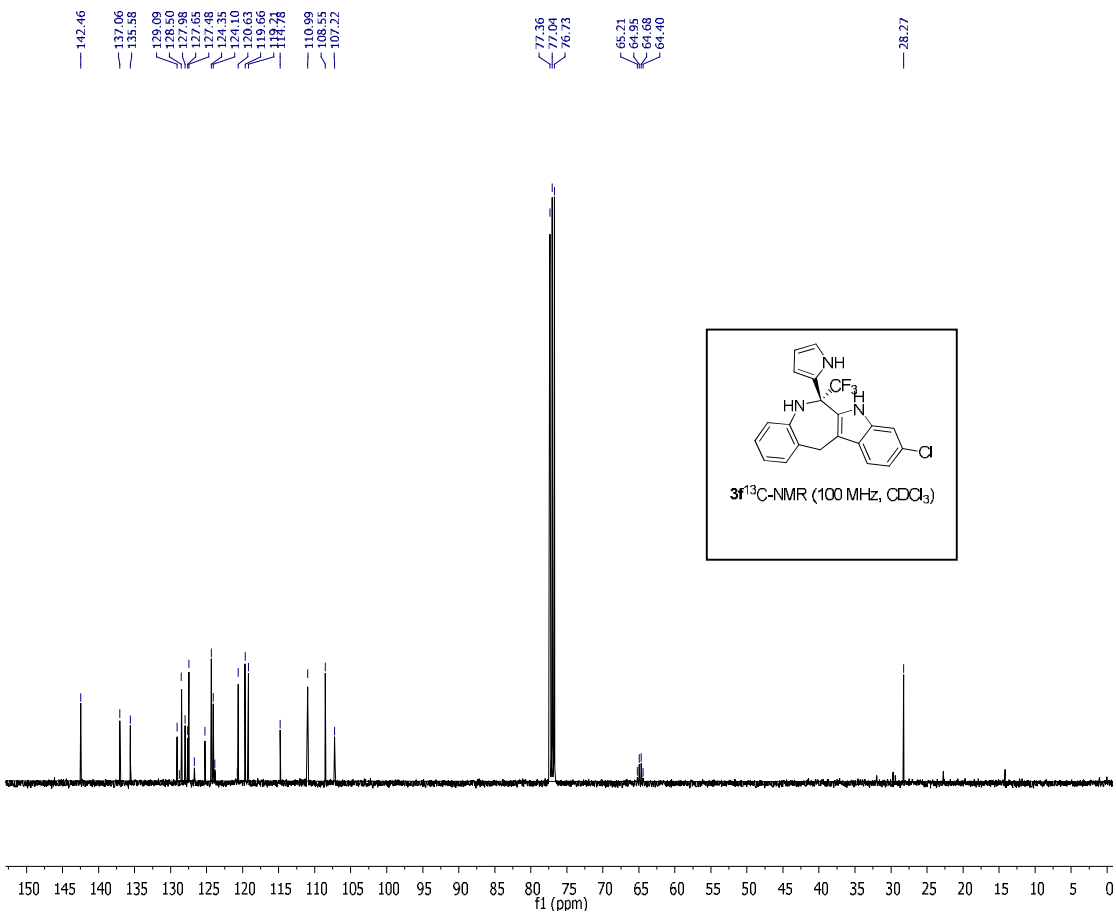
3e ^{1}H-NMR (400 MHz, $CDCl_3$)

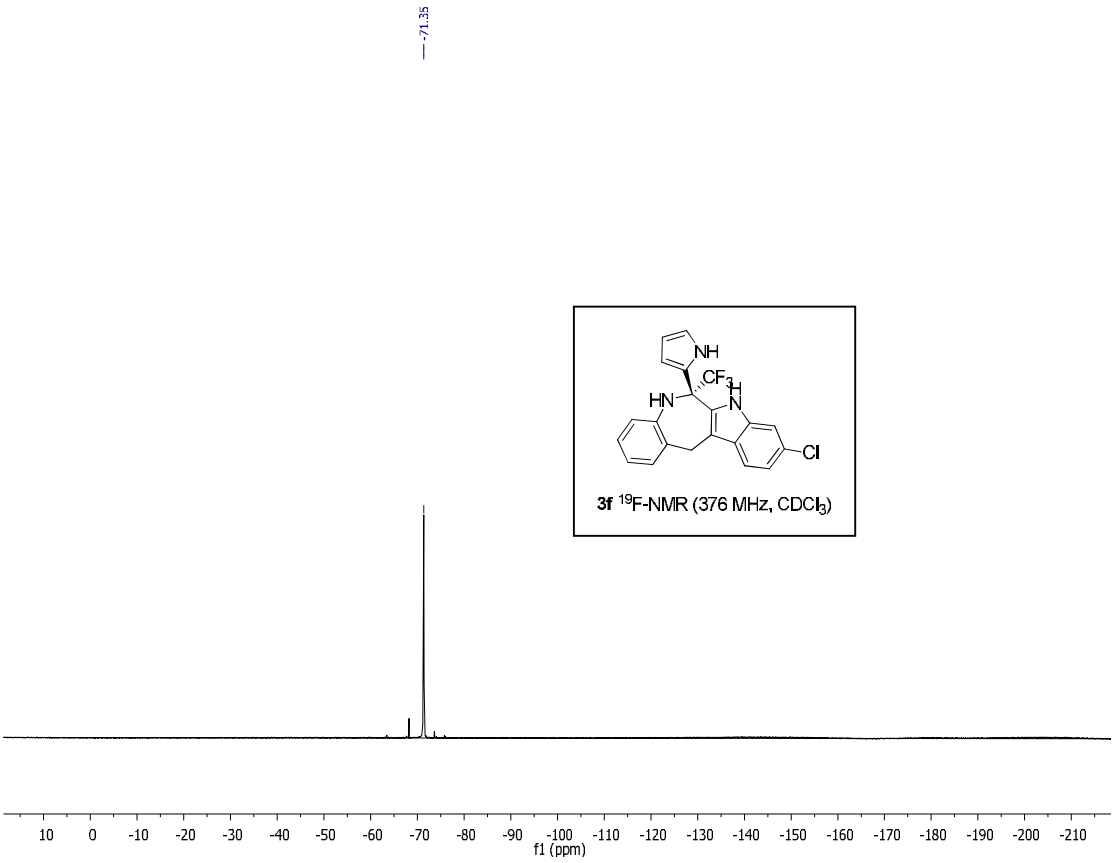

161.69
159.31
142.51
137.13
128.49
128.10
127.45
127.13
124.30
124.08
123.26
119.68
119.58
119.14
114.74
108.85
108.61
108.52
107.14
97.53
97.27
77.37
77.06
76.74
65.20
64.92
64.65
64.39
28.31
NH
CF3
HN
H
N
F
3e 13C-NMR (100 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-71.42
-119.16
-119.17
-119.18
-119.19
-119.20
-119.21
-119.23
NH
CF3
HN
H
N
F
3e 19F-NMR (376 MHz, CDCl
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

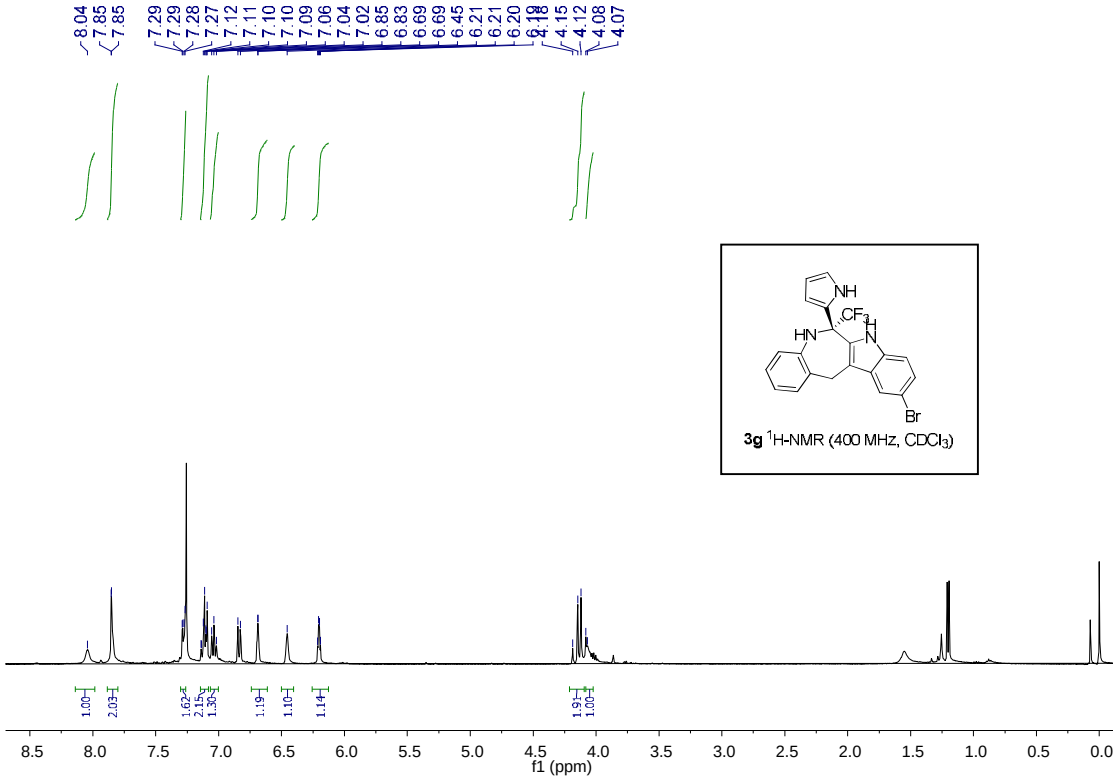
(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3f)

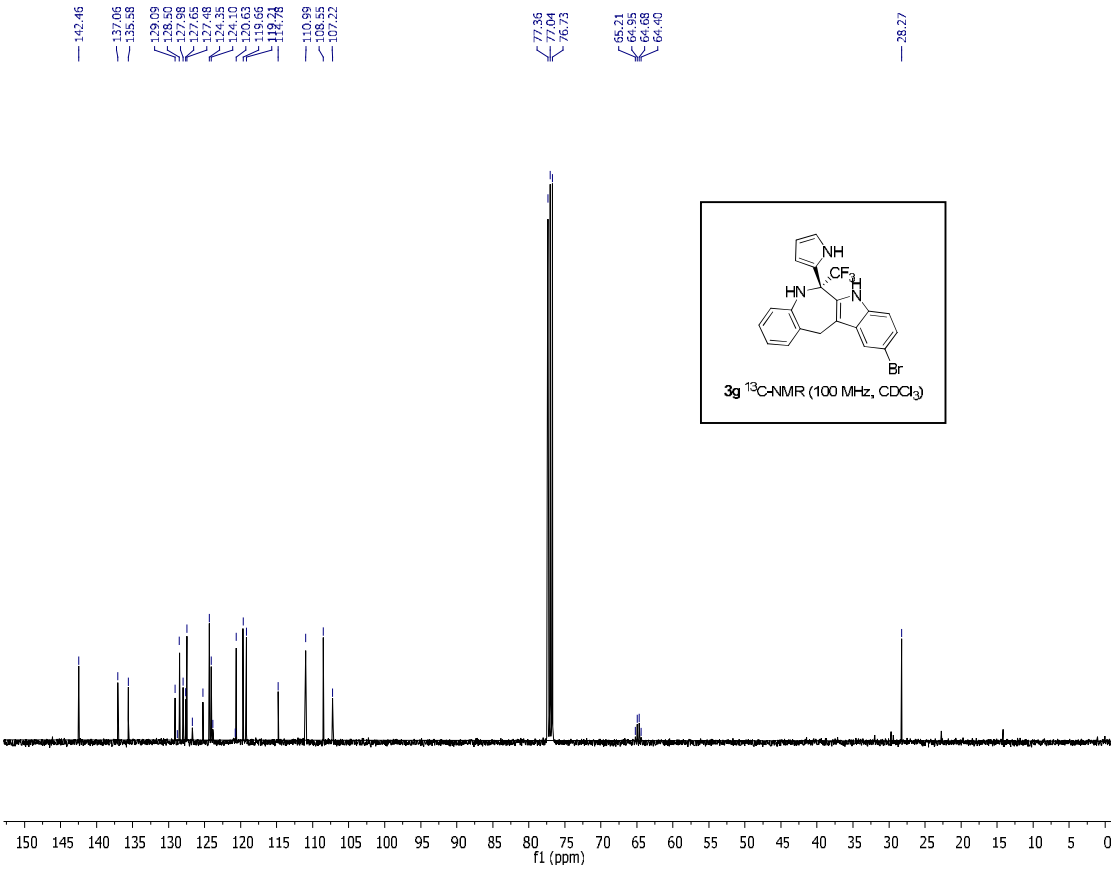


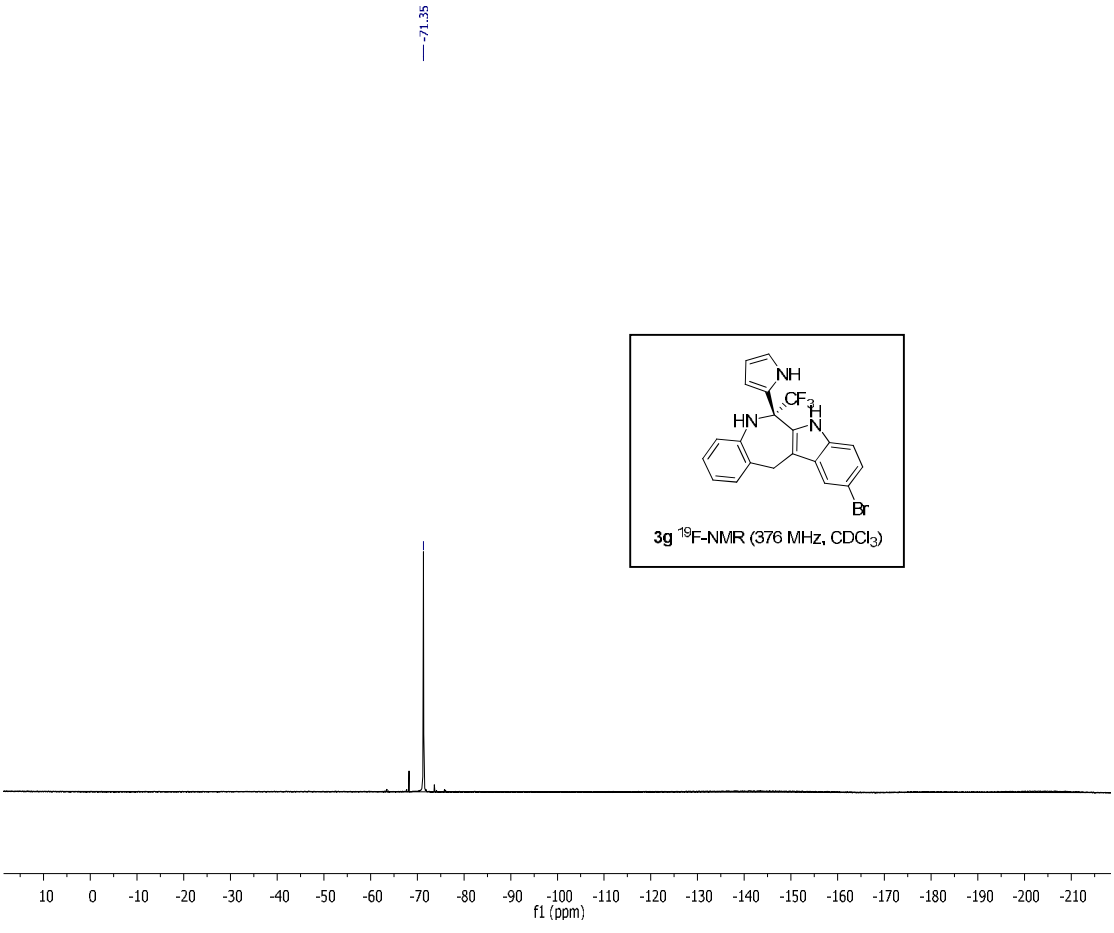




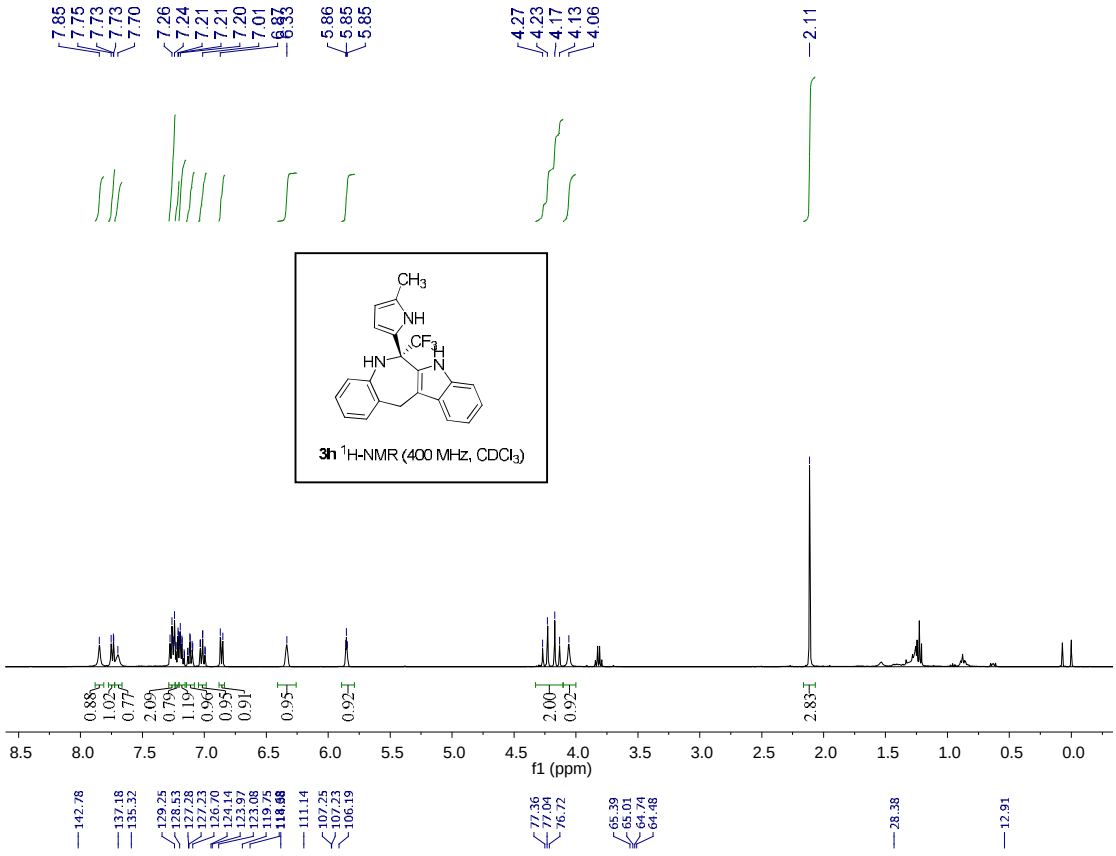
(*S*)-6-(2-pyrrolyl)-6-trifluoromethyl-2-bromo-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3g)

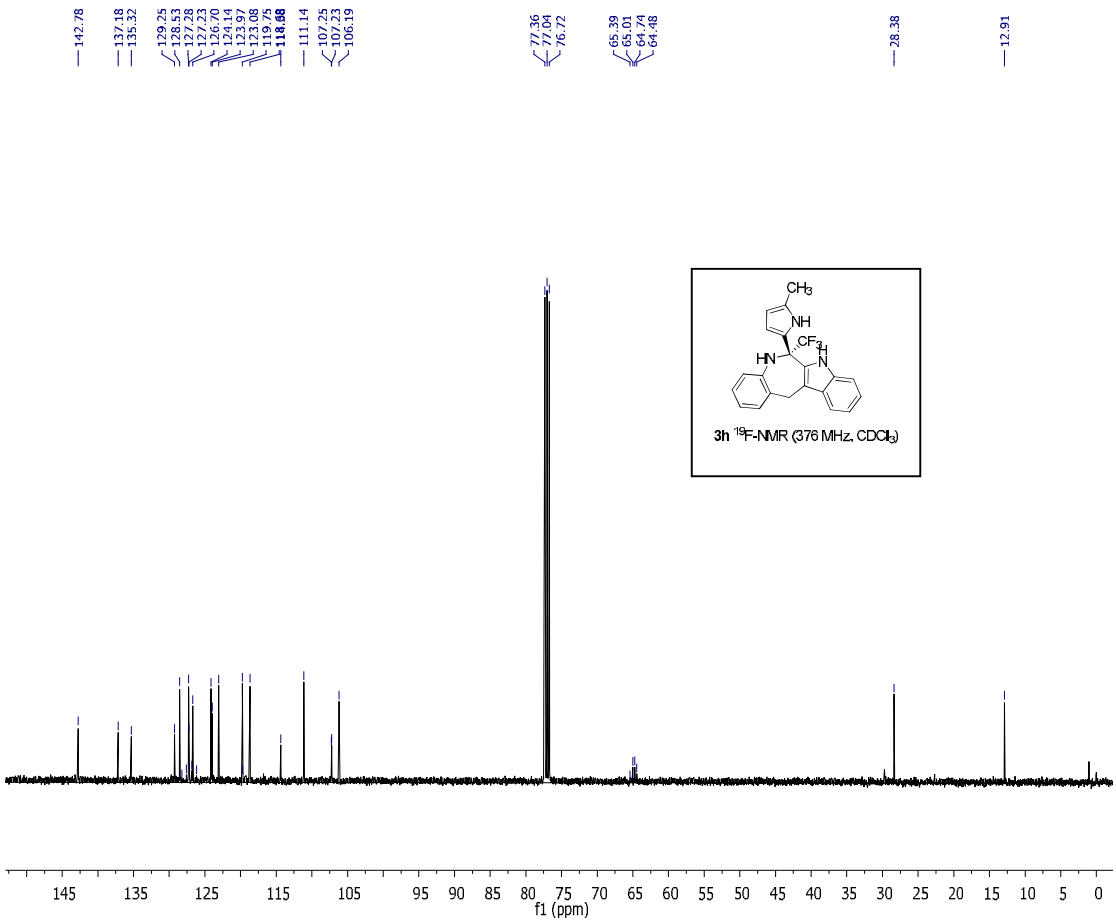


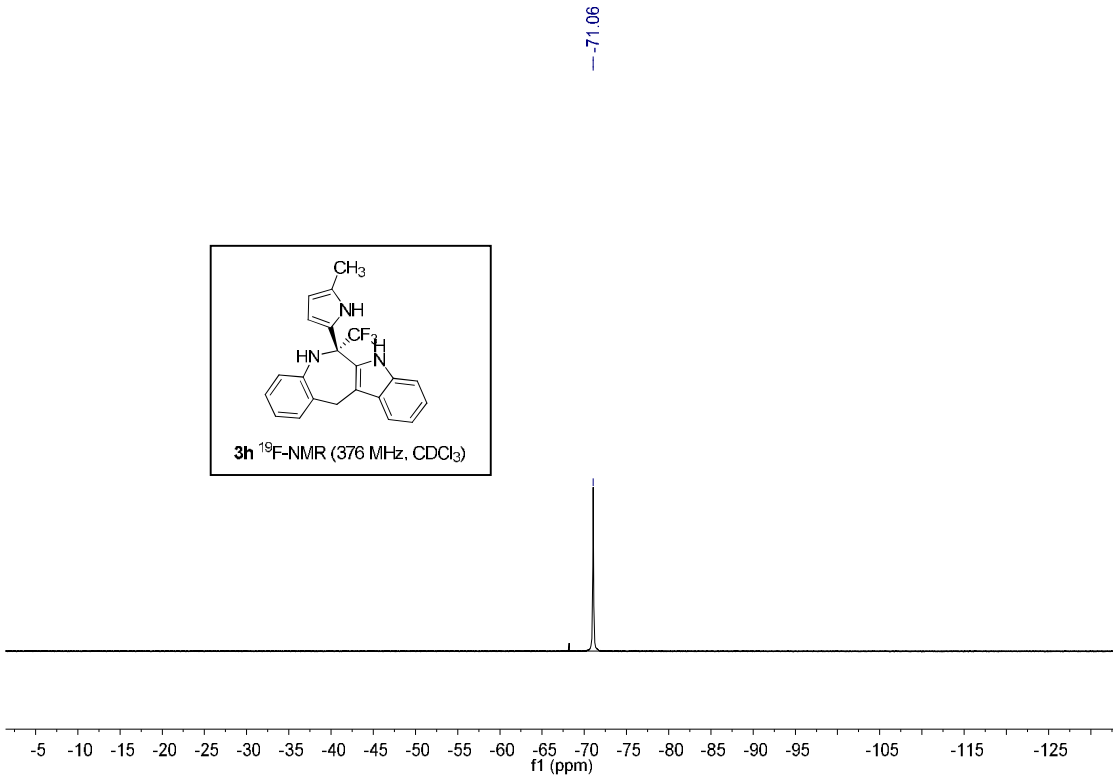

142.46
137.06
135.58
129.09
128.50
127.98
127.65
127.48
124.35
124.10
120.63
119.66
119.21
114.78
110.99
109.55
107.22
77.36
77.04
76.73
65.21
64.95
64.68
64.40
28.27
NH
CF3
H
HN
N
Br
3g 13C-NMR (100 MHz, CDCl3)
f1 (ppm)


-71.35
NH
CF3
H
HN
N
Br
3g 19F-NMR (376 MHz, CDCl3)
f1 (ppm)

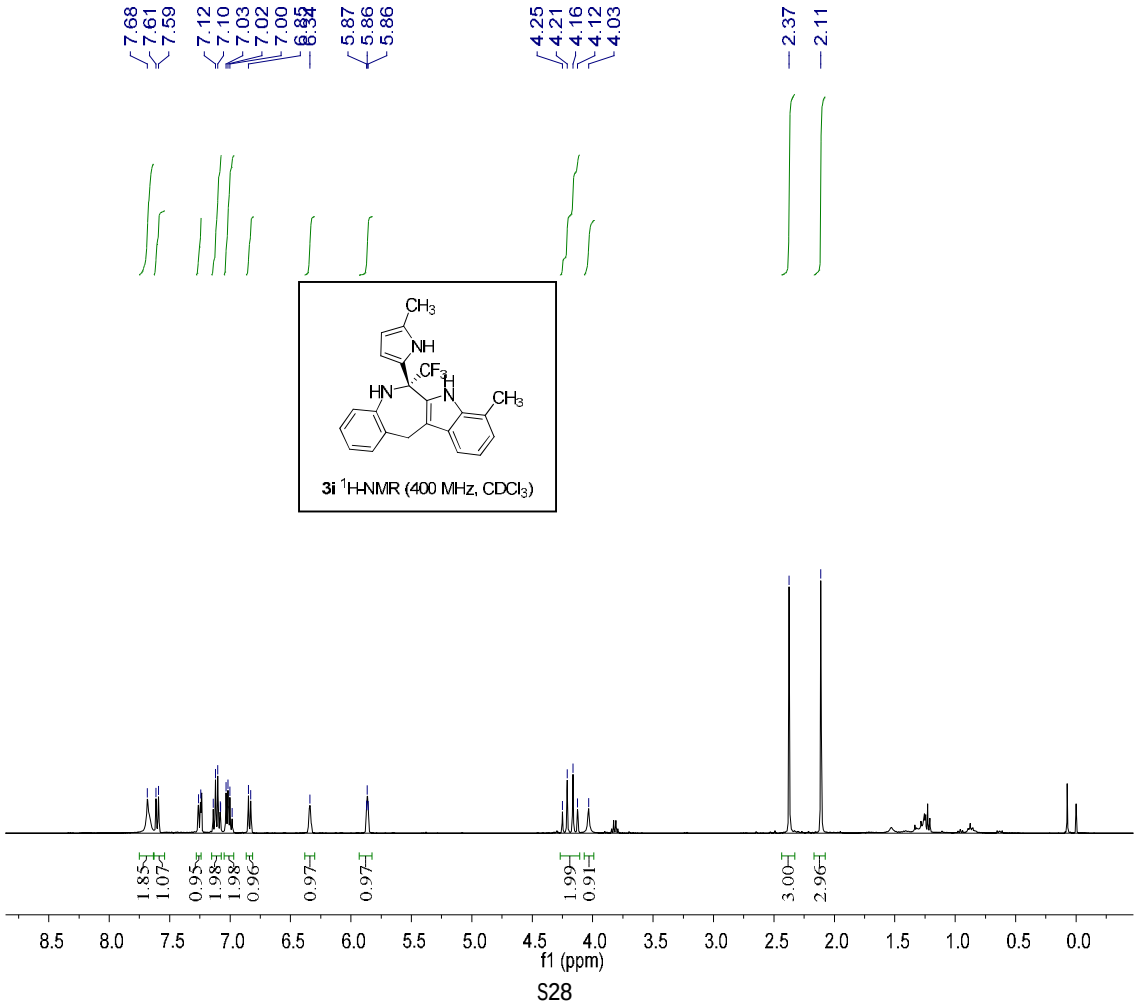
(*S*)-6-(2-pyrrolyl-5'-methyl)-6-trifluoromethyl-5,6,7,12-tetrahydroi-ndolo[2,3-c][1]benzazepine (3h)

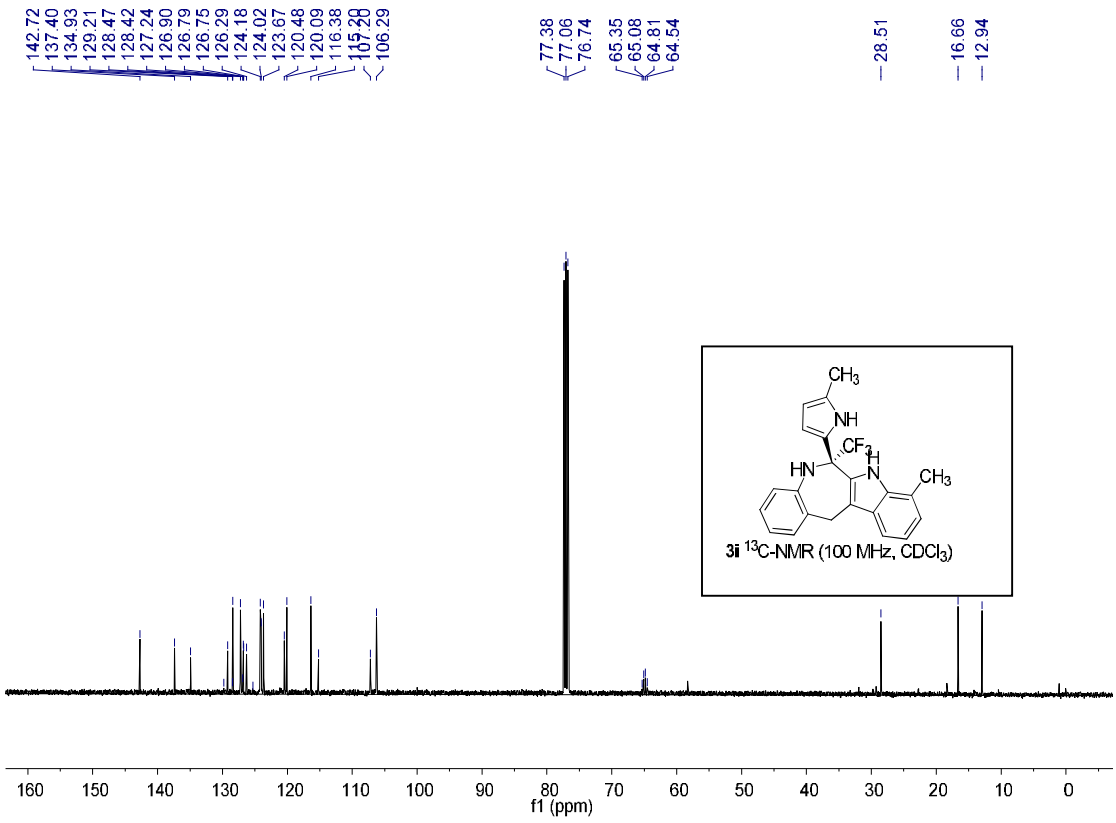






(*S*)-6-(2-pyrrolyl-5'-methyl)-6-trifluoromethyl-4-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3i)




142.72
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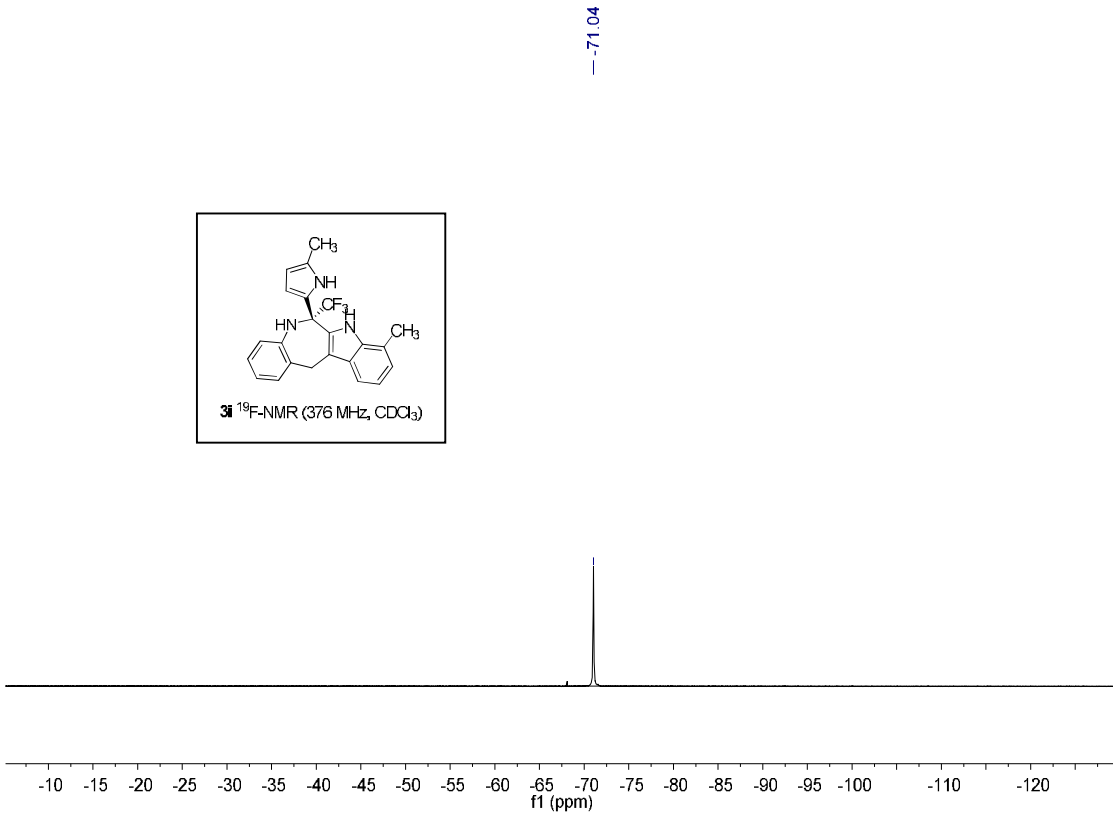
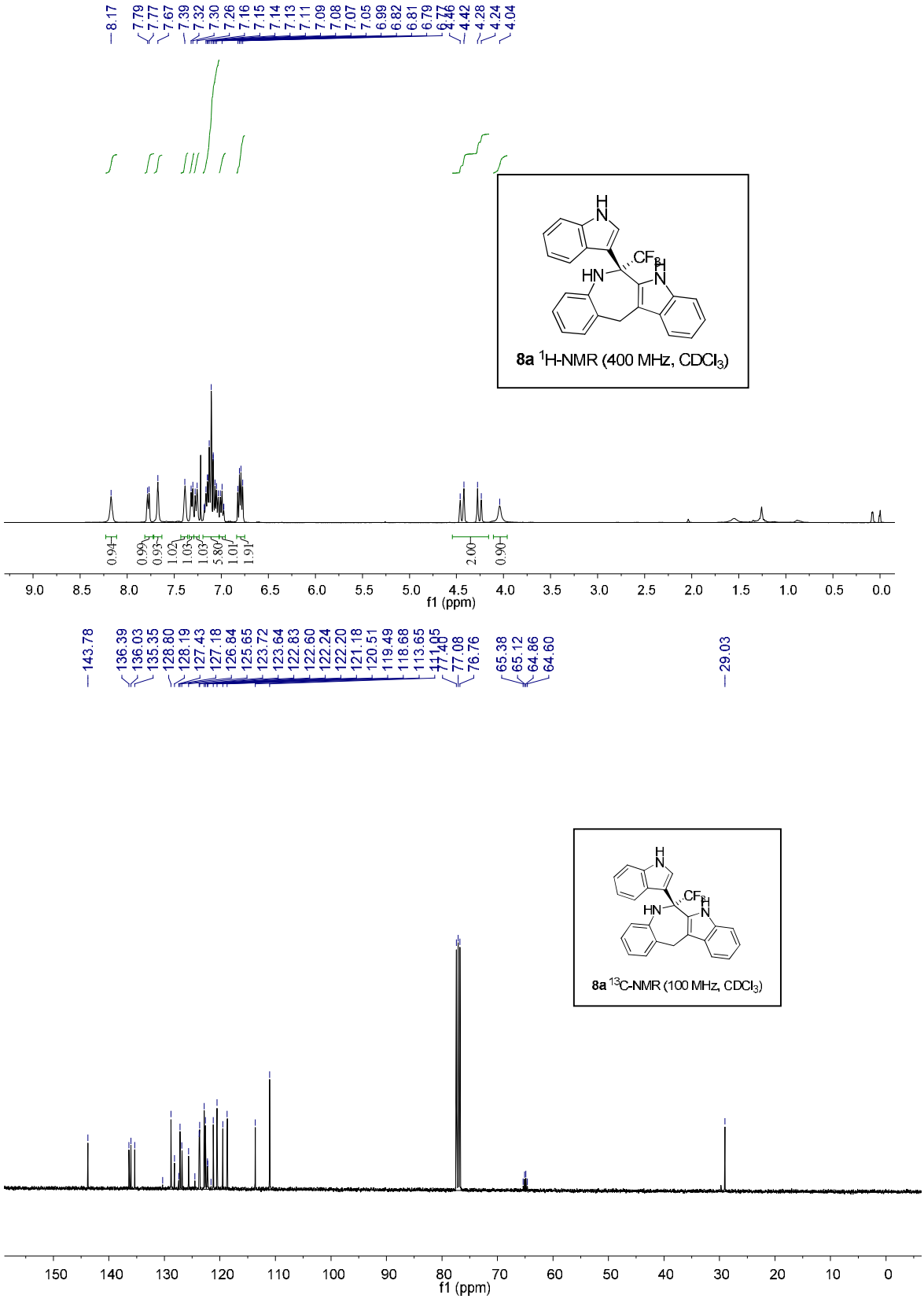
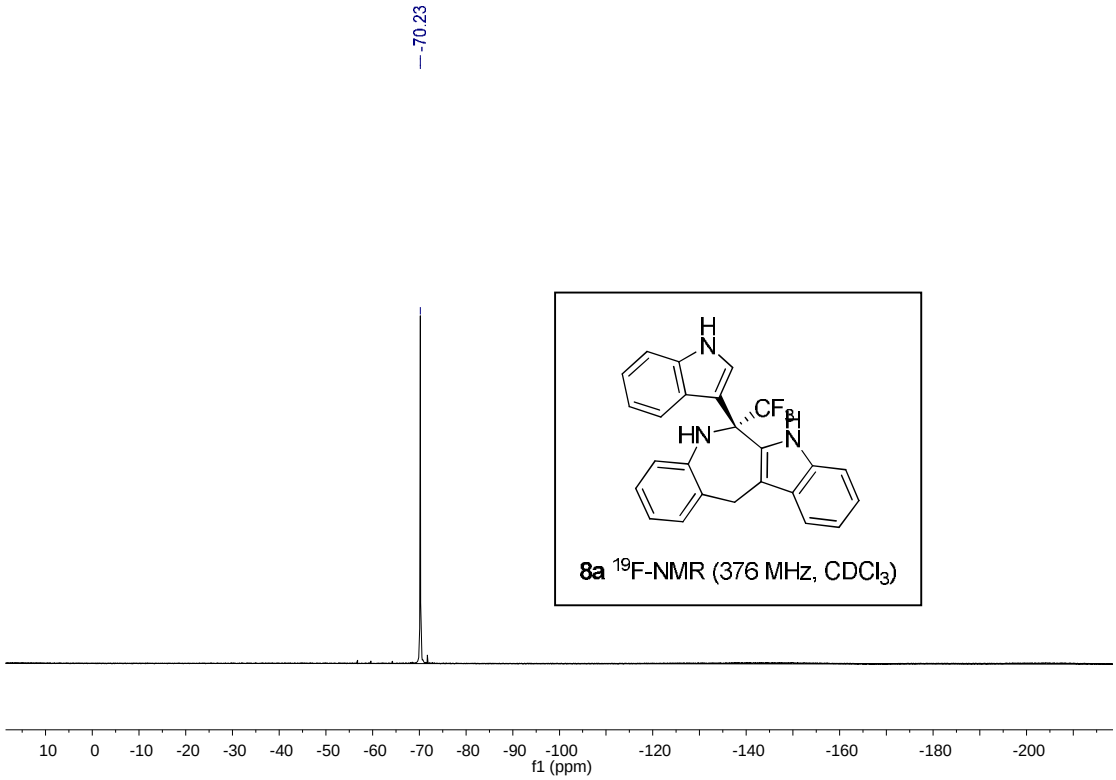
134.93
129.21
128.47
128.42
127.24
126.90
126.79
126.75
126.29
124.18
124.02
123.67
120.48
120.09
116.38
107.20
106.29
77.38
77.06
76.74
65.35
65.08
64.81
64.54
28.51
16.66
12.94
CH3
NH
CF3
H
HN
N
CH3
3i 13C-NMR (100 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

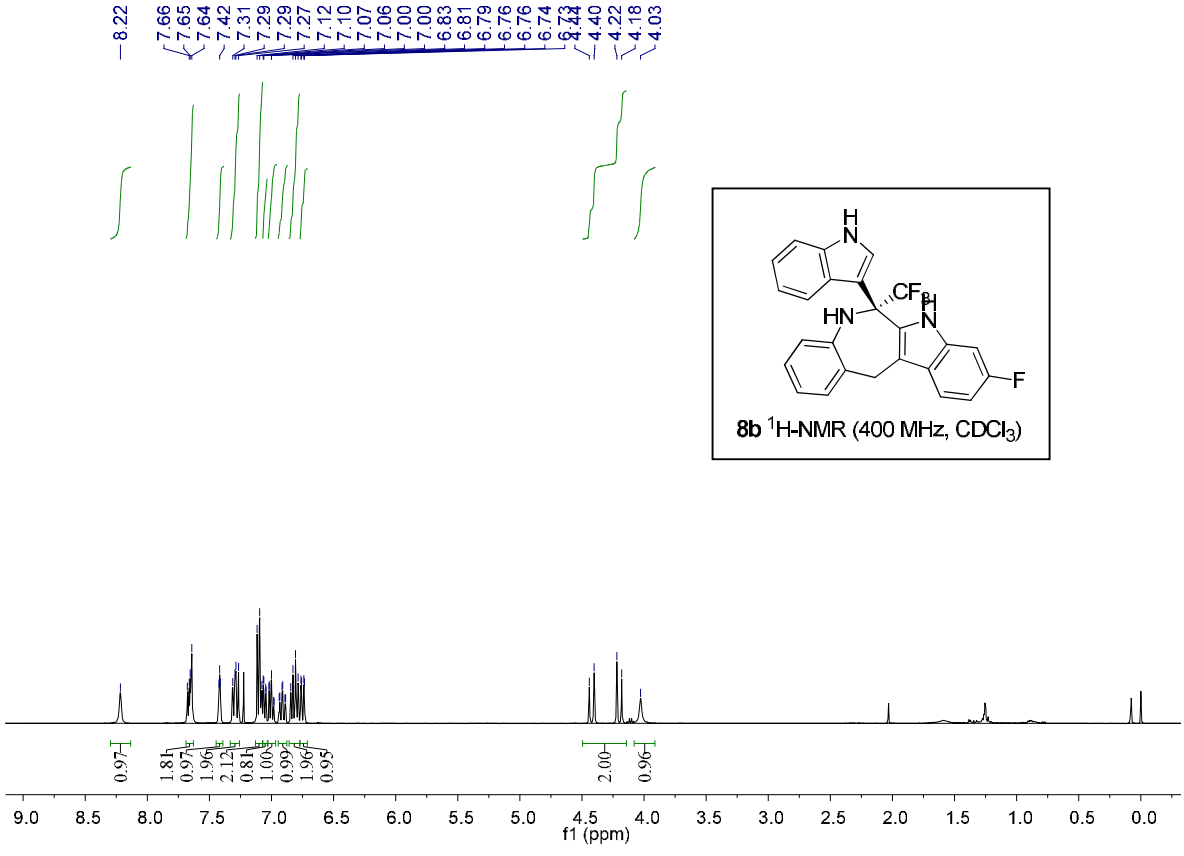

-71.04
CH3
NH
CF3
H
HN
N
CH3
3i 19F-NMR (376 MHz, CDCl3)
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120
f1 (ppm)

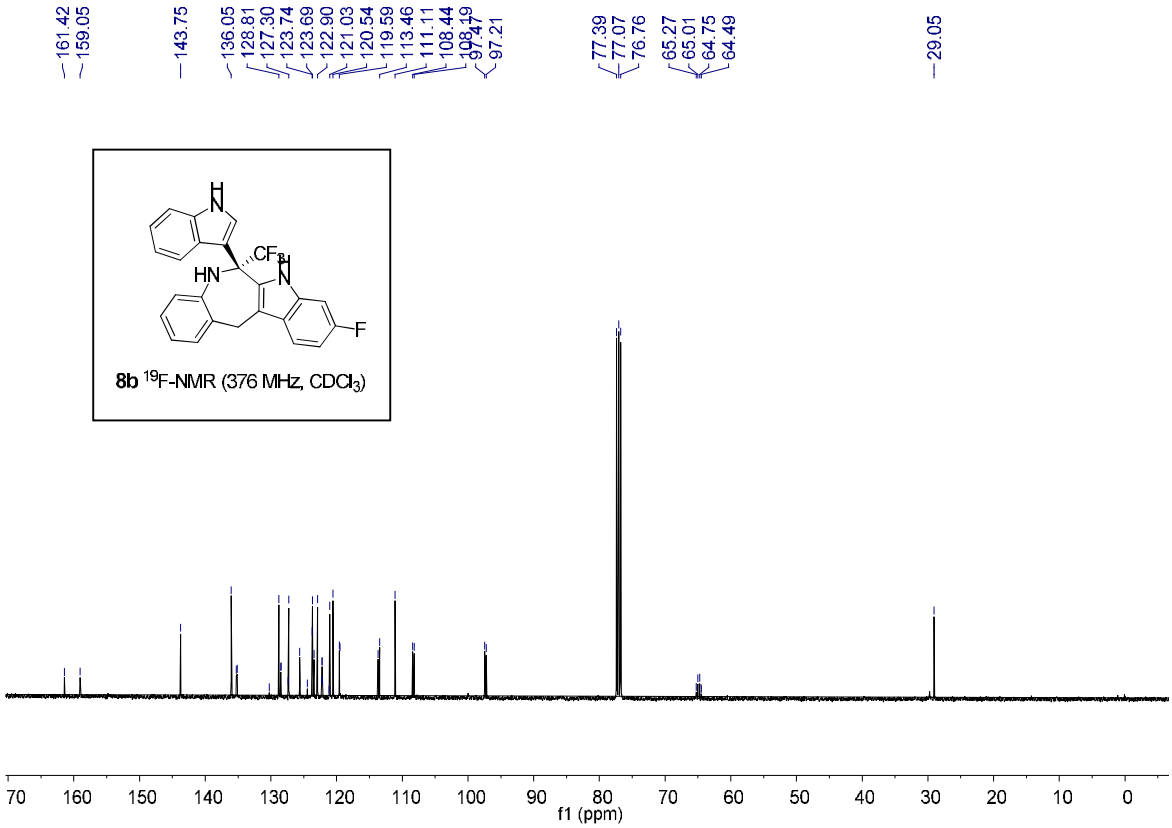
(*S*)-6-(3-indolyl-)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2, 3-c][1]benzazepine (8a)



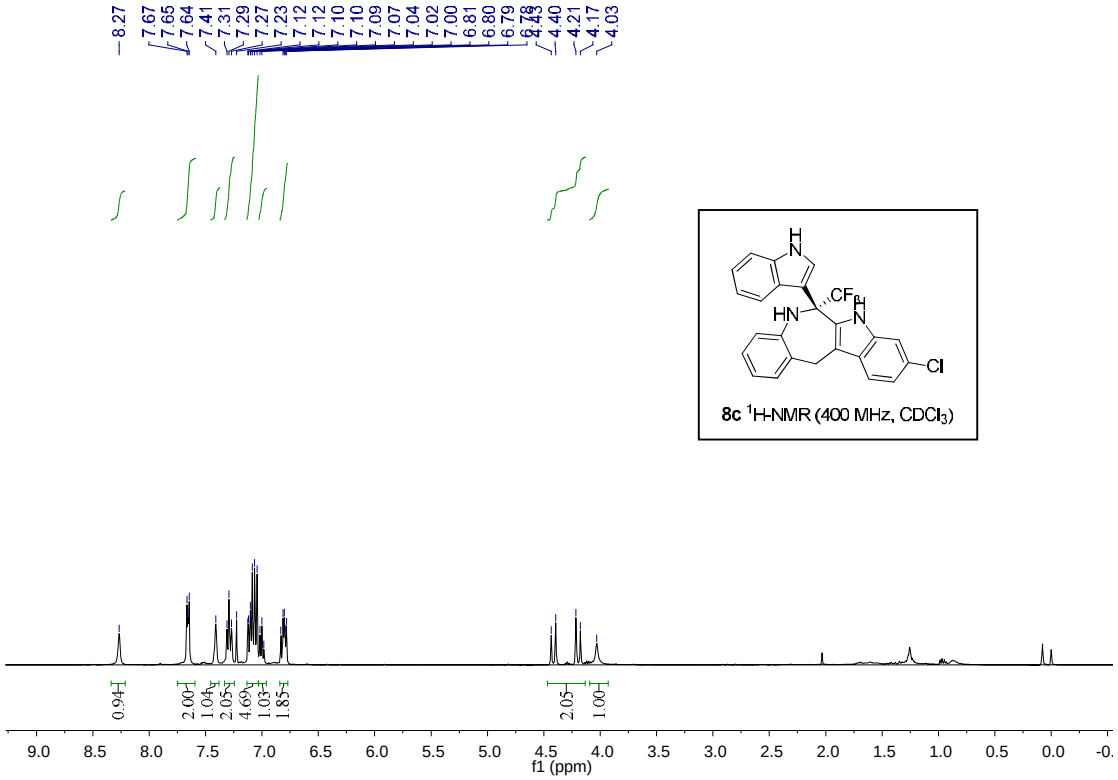


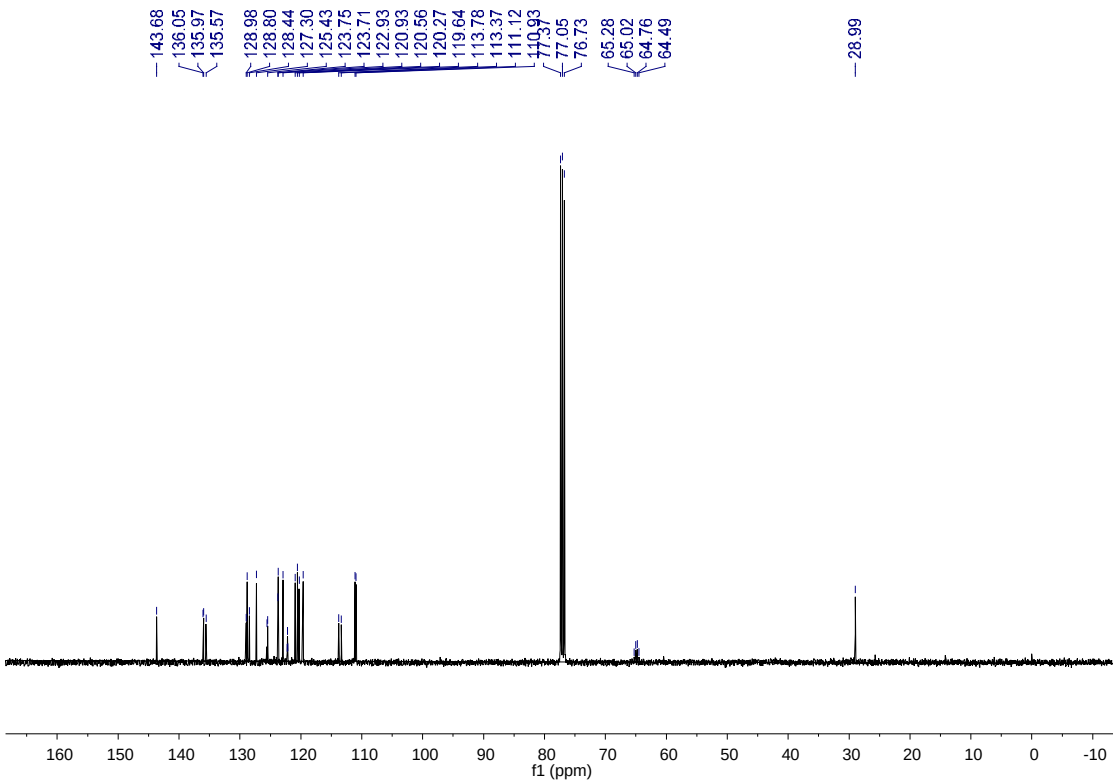
(*S*)-6-(3-indolyl-)-6-trifluoromethyl-3-fluoro-5,6,7,12-tetrahydro- indolo[2,3-c][1]benzazepine (8b)

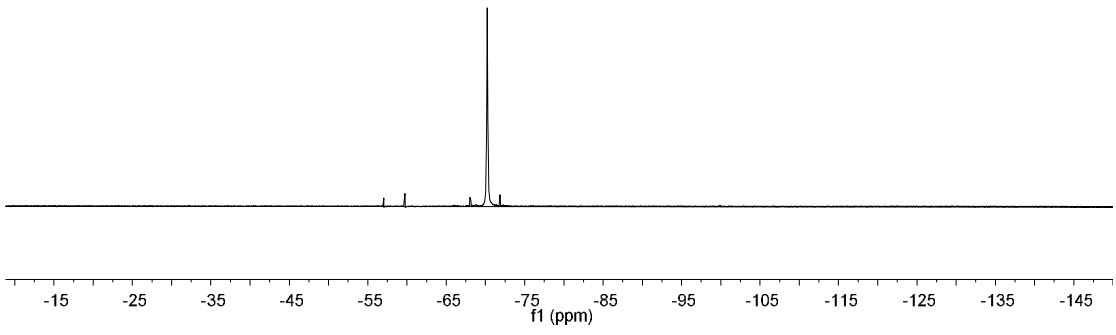




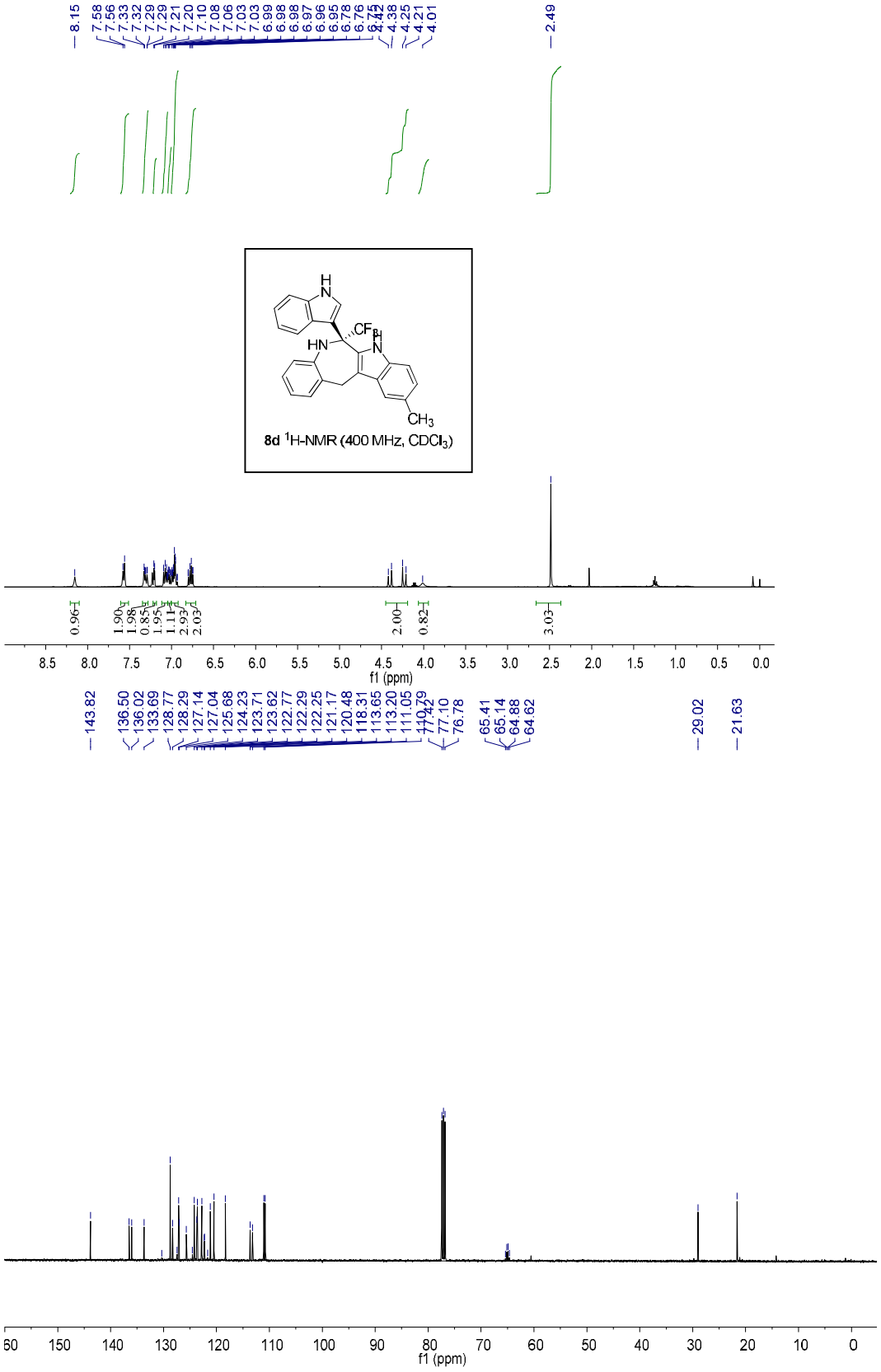
(*S*)-6-(3-indolyl-)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydr-oindolo[2,3-c][1]benzazepine (8c)

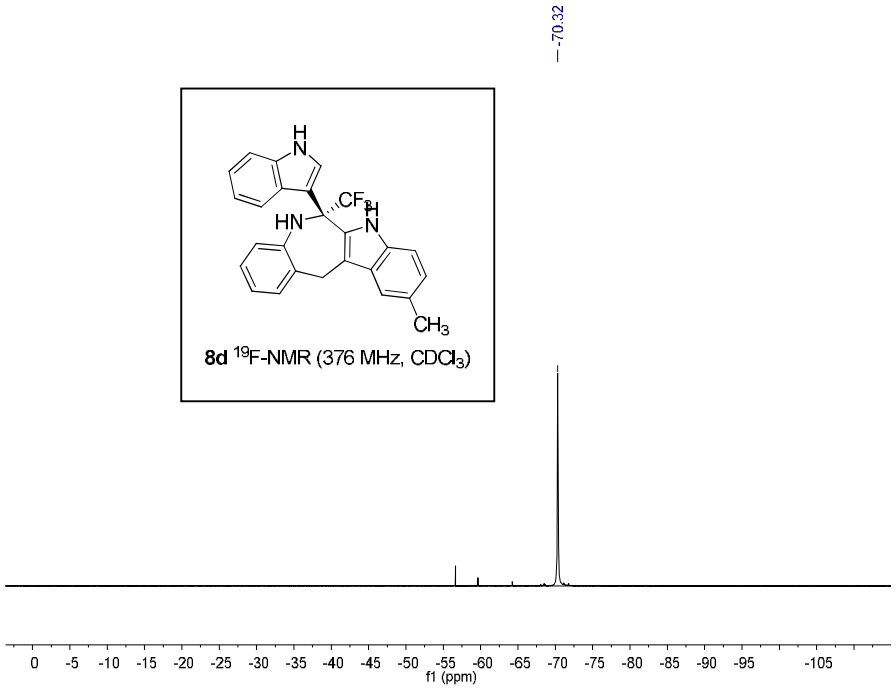



143.68
136.05
135.97
135.57
128.98
128.80
128.44
127.30
125.43
123.75
123.71
122.93
120.93
120.56
120.27
119.64
113.78
113.37
111.12
110.93
77.37
77.05
76.73
65.28
65.02
64.76
64.49
28.99
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

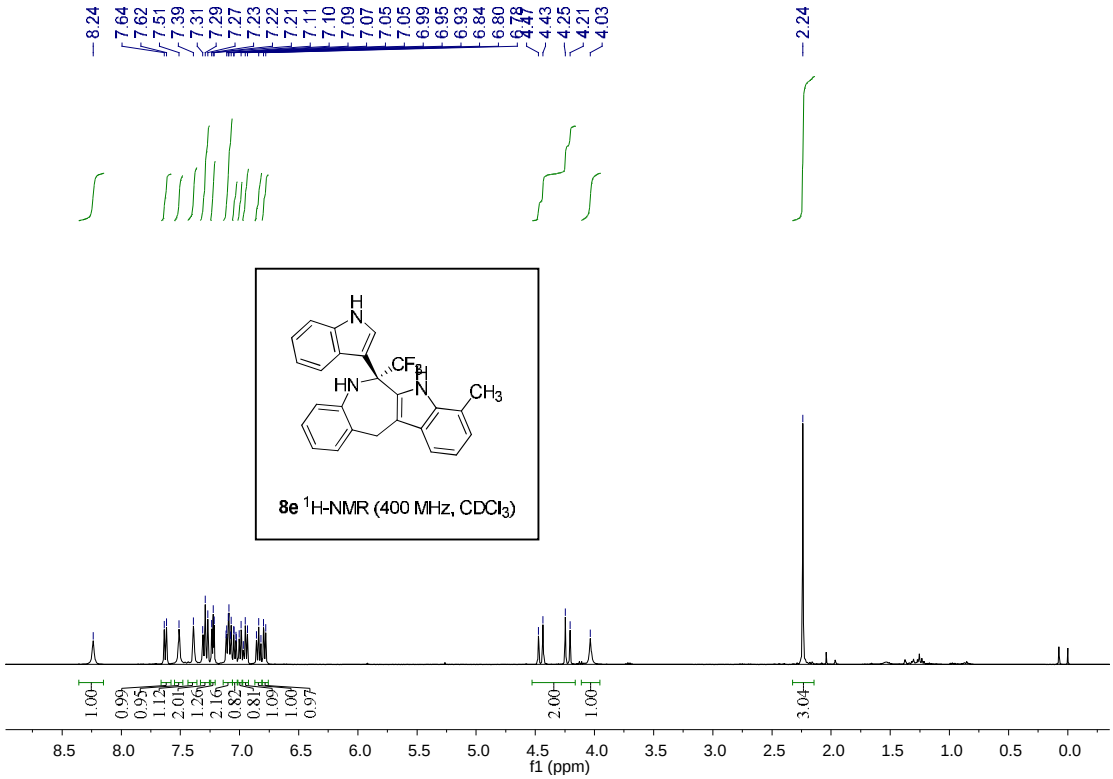

-15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135 -145
f1 (ppm)

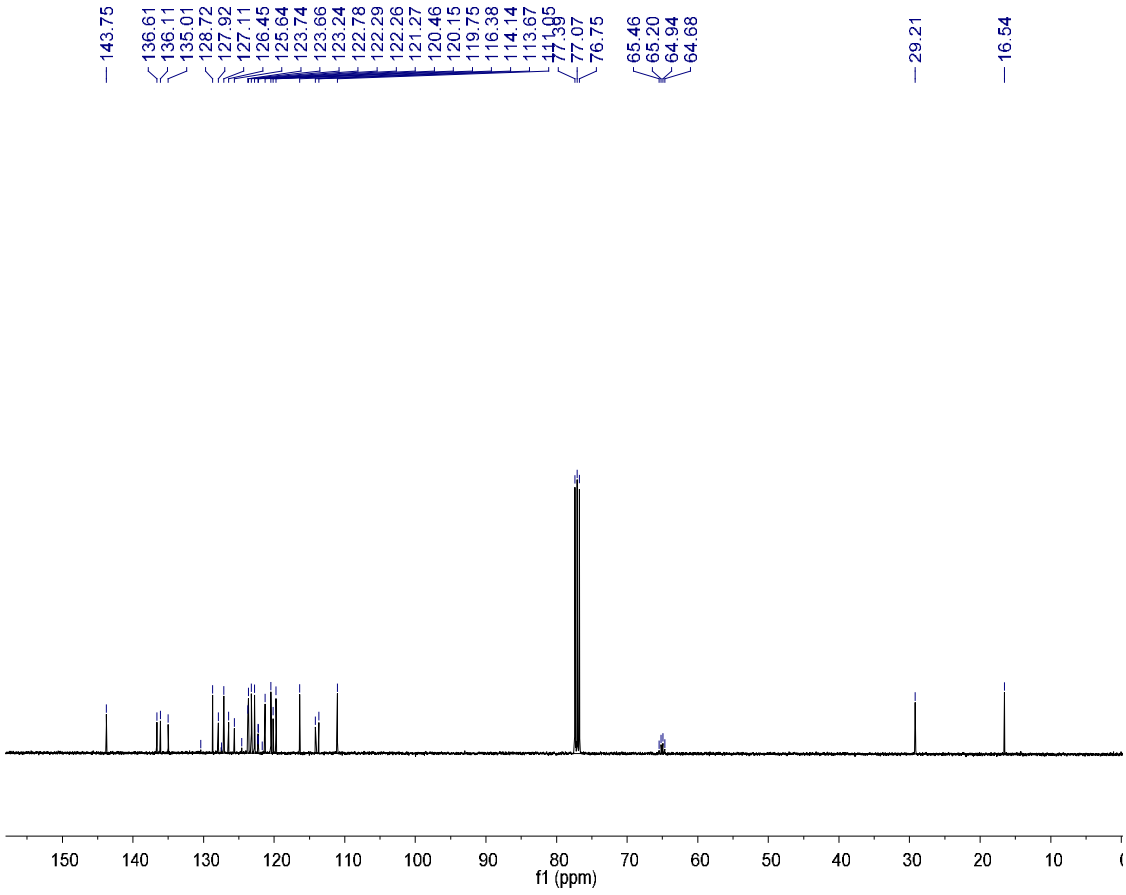
(*S*)-6-(3-indolyl-)-6-trifluoromethyl-2-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8d)

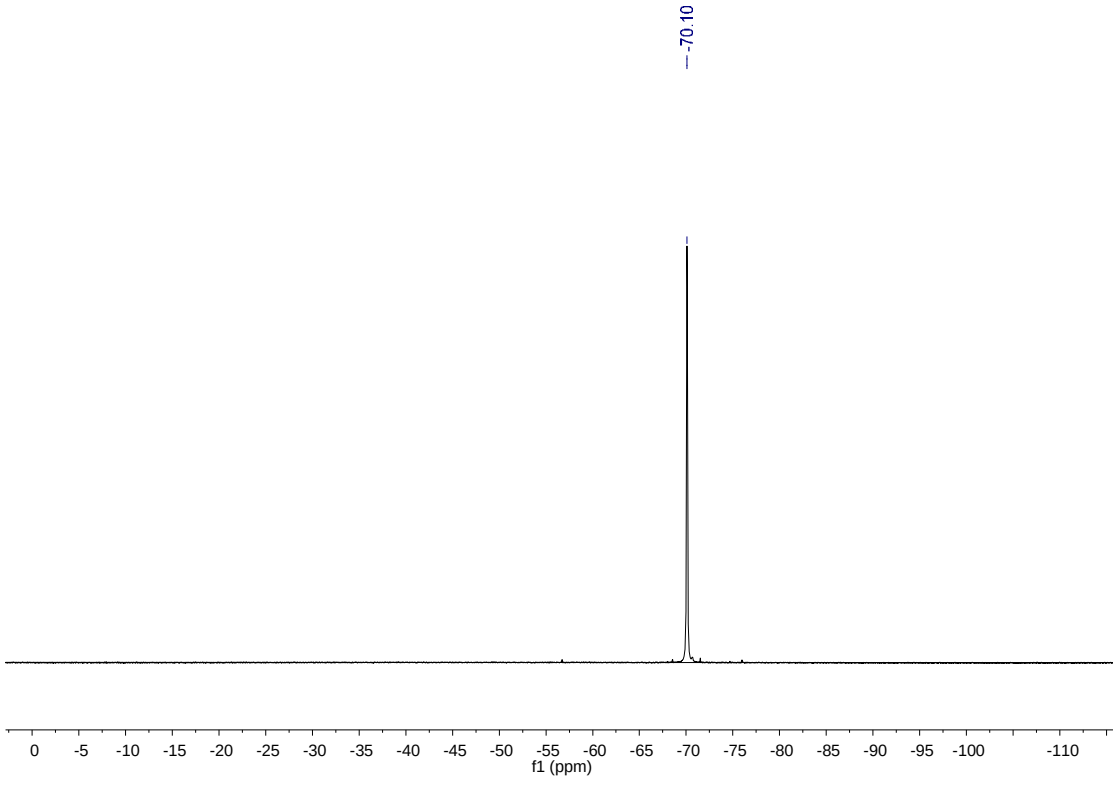




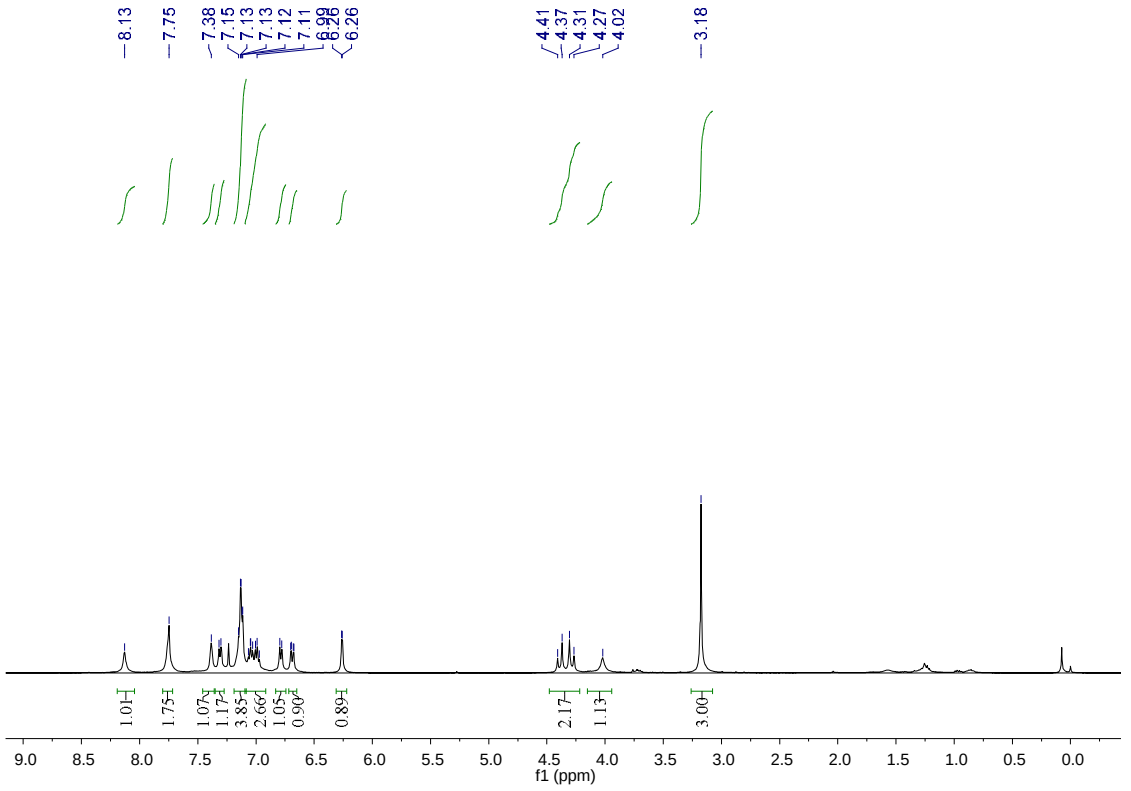
(*S*)-6-(3-indolyl-)-6-trifluoromethyl-4-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8e)

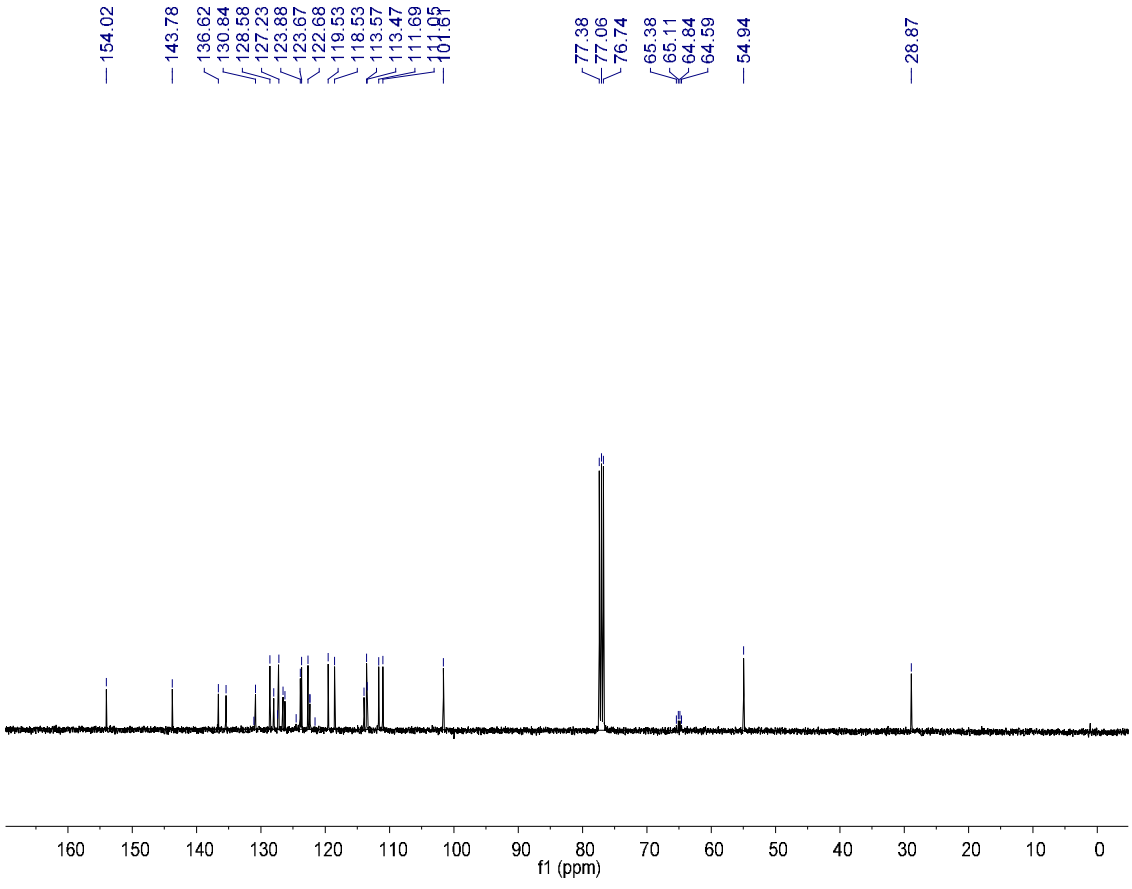


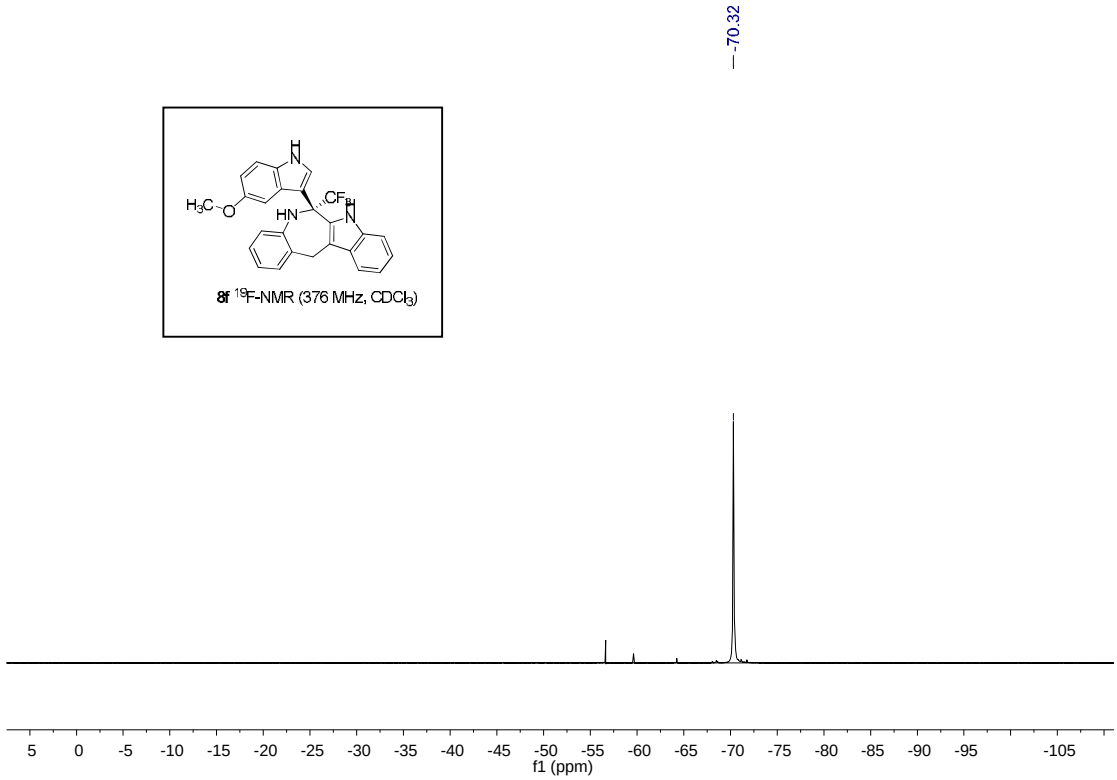

143.75
136.61
136.11
135.01
128.72
127.92
127.11
126.45
125.64
123.74
123.66
123.24
122.78
122.29
122.26
121.27
120.46
120.15
119.75
116.38
114.14
113.67
77.39
77.07
76.75
65.46
65.20
64.94
64.68
29.21
16.54
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-70.10
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
f1 (ppm)

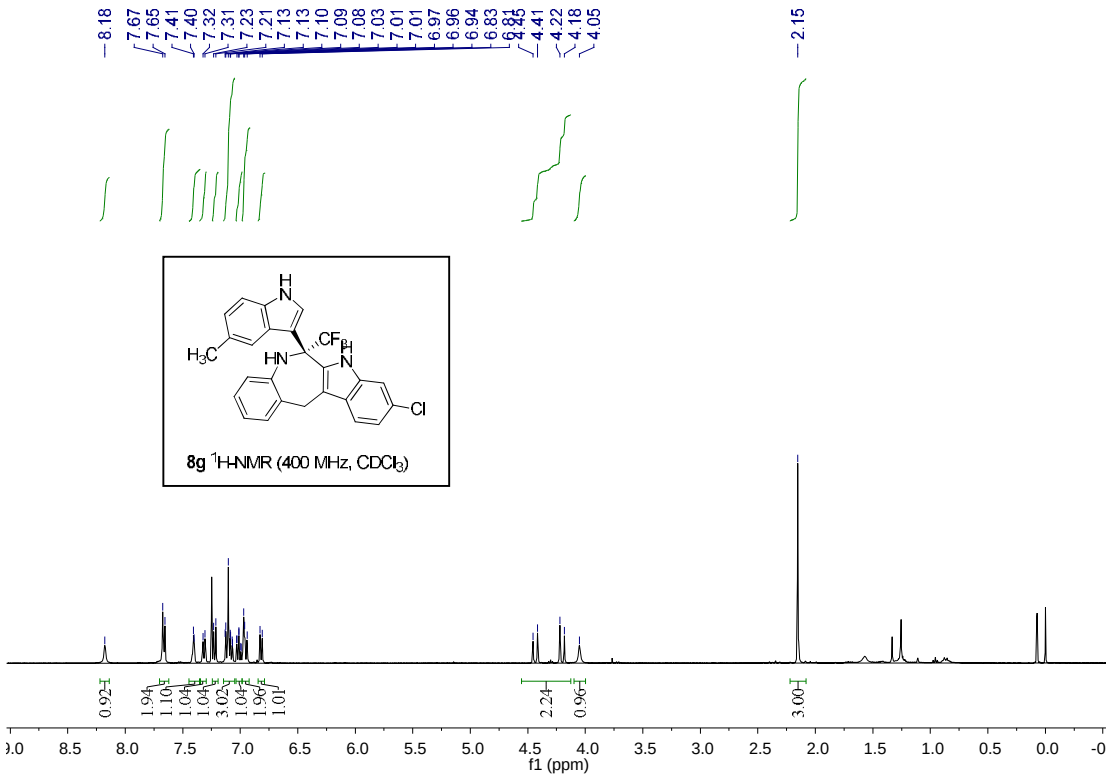
(*S*)-6-(3-indolyl-5'-methoxy)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8f)

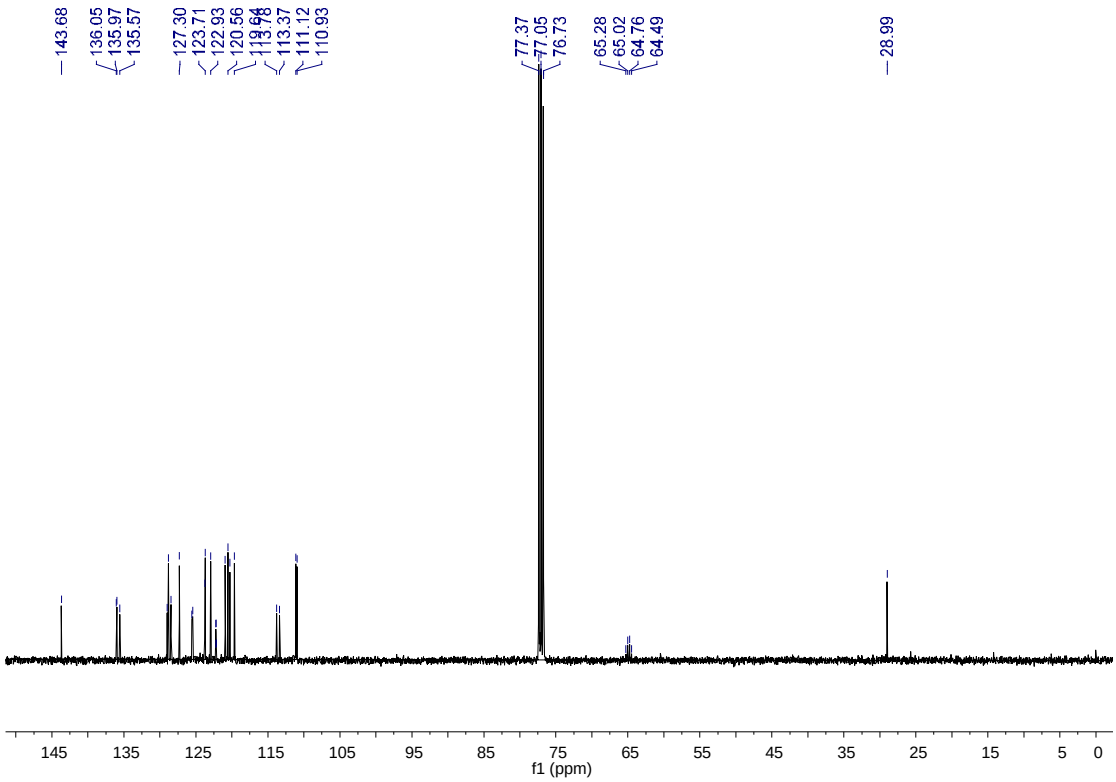


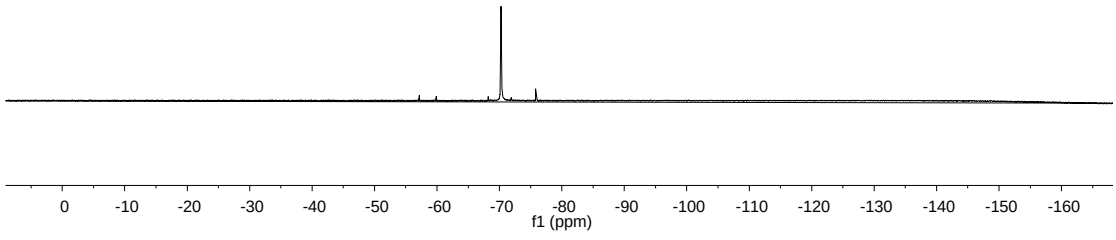




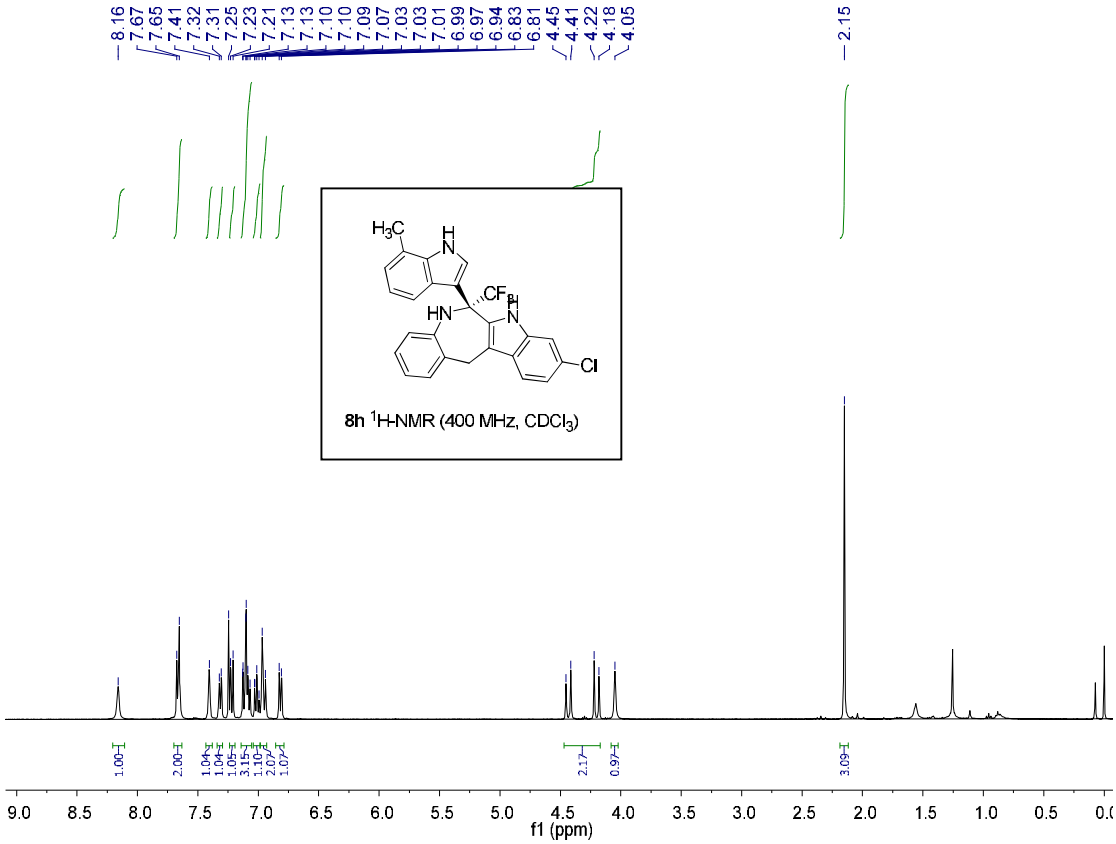
(*S*)-6-(3-indolyl-5'-methyl)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8g)

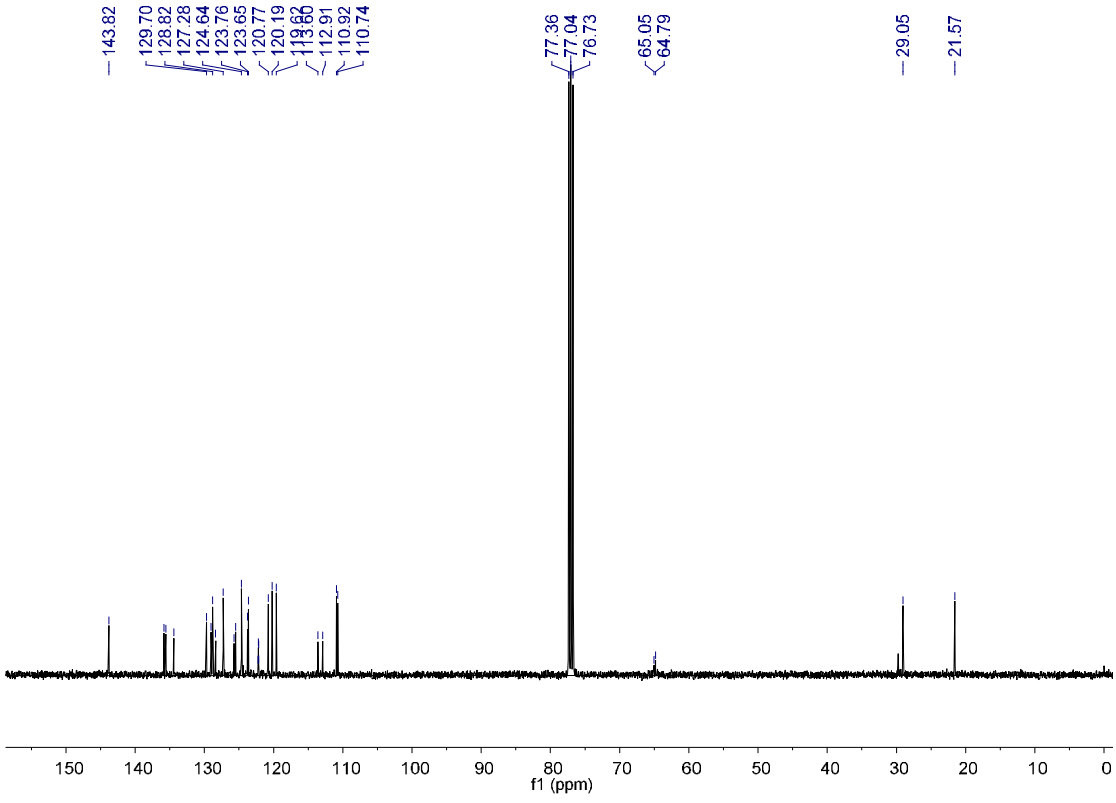


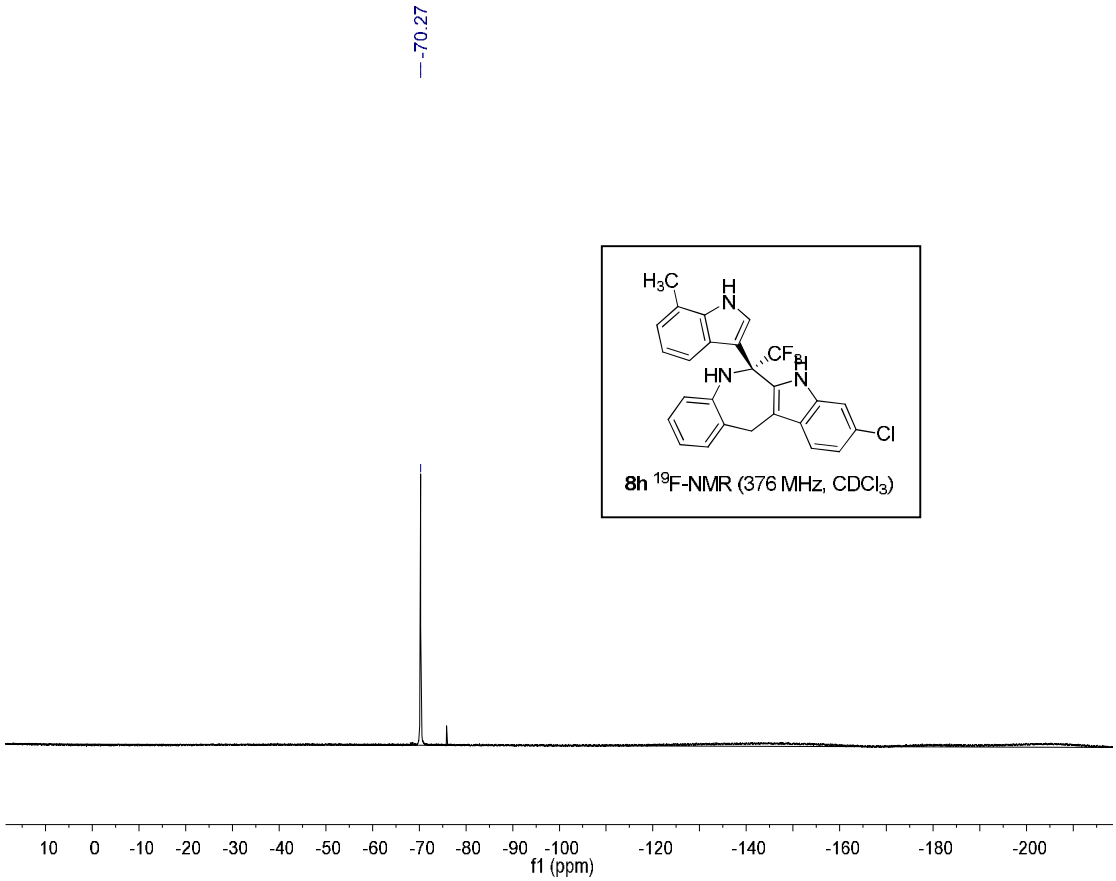

143.68
136.05
135.97
135.57
127.30
123.71
122.93
120.56
113.37
111.12
110.93
77.37
77.05
76.73
65.28
65.02
64.76
64.49
28.99
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5
0
f1 (ppm)


0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

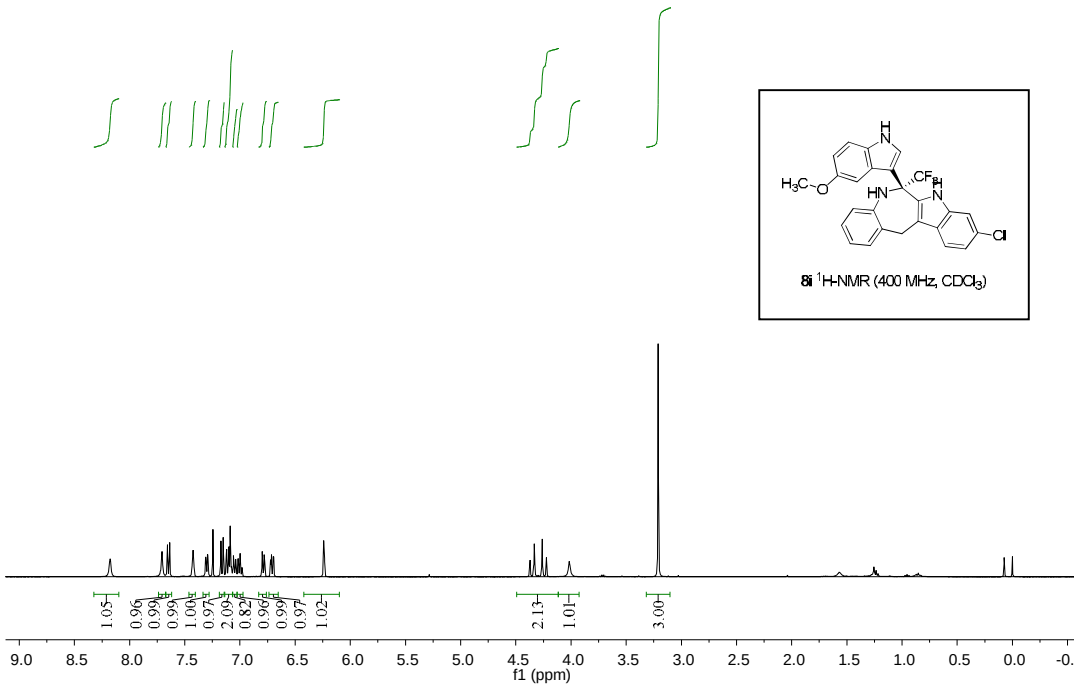
(*S*)-6-(3-indolyl-7'-methyl)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8h)

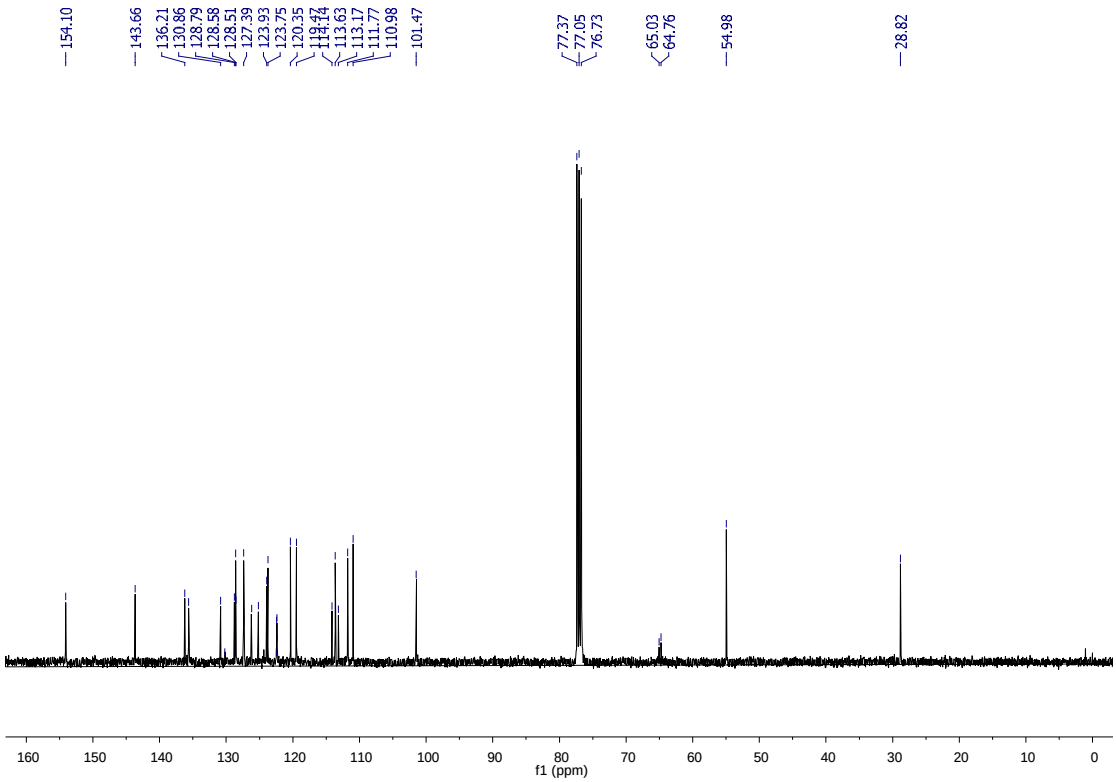


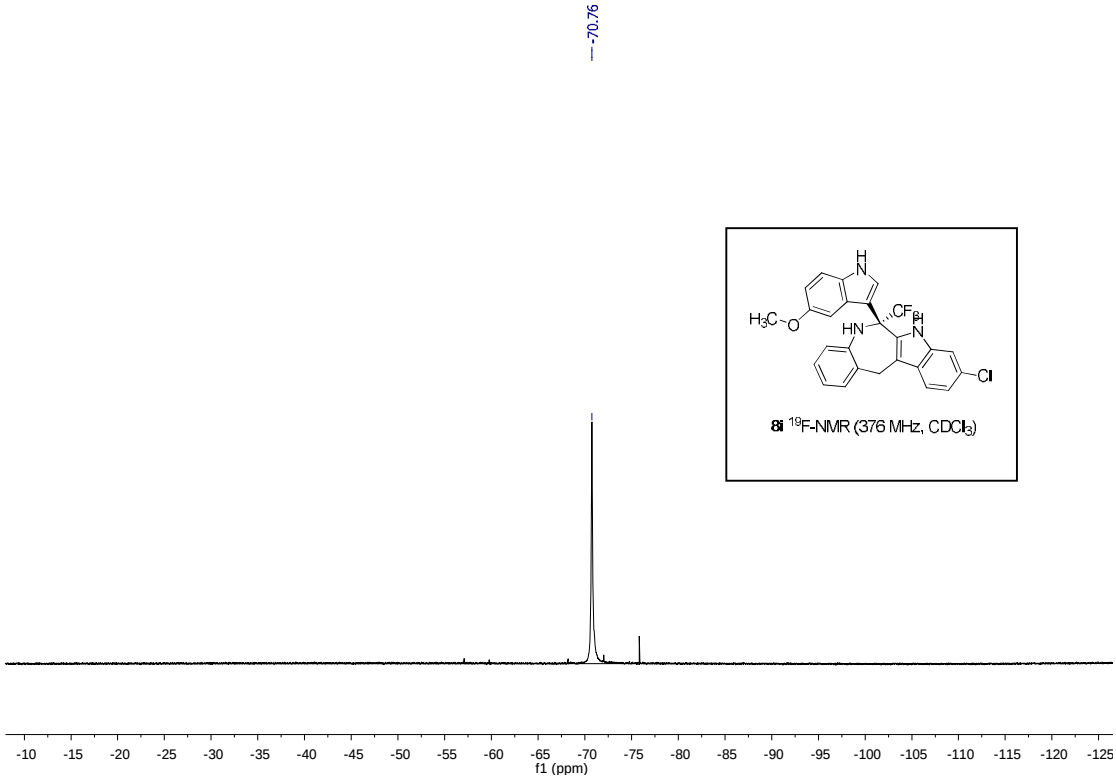




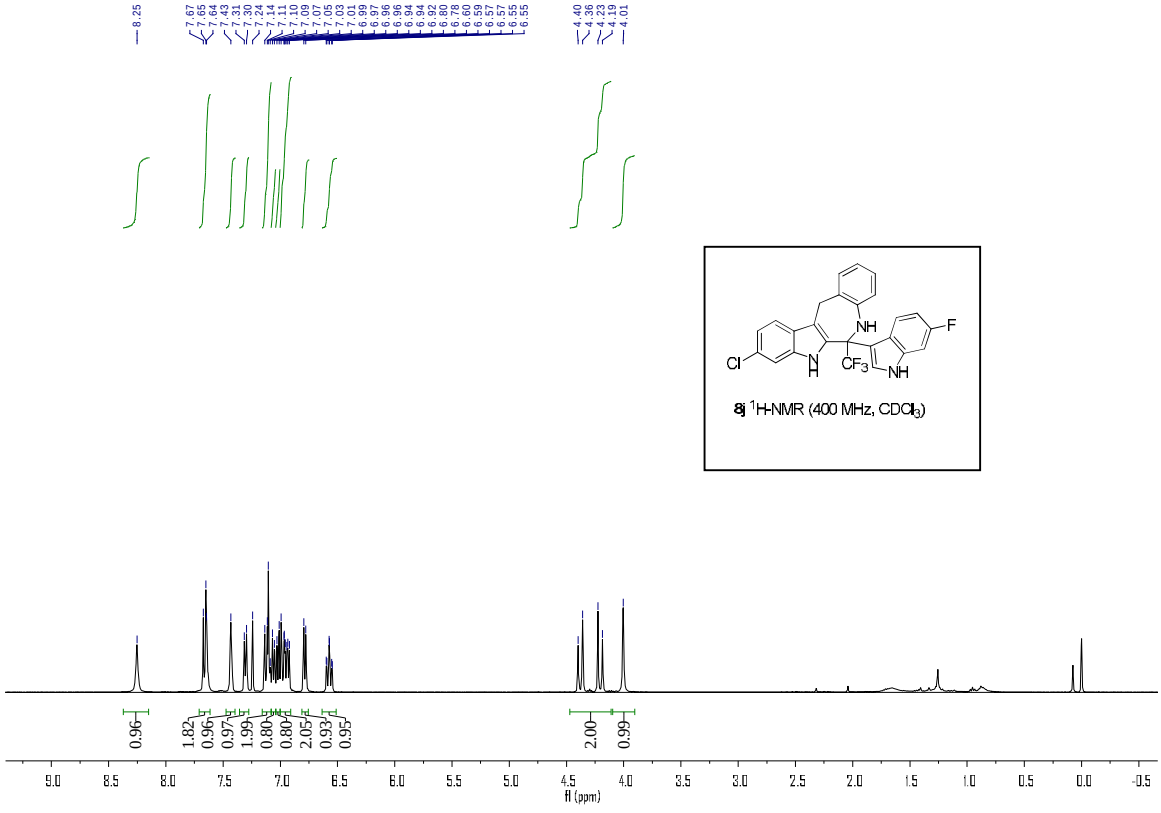
(*S*)-6-(3-indolyl-5'-methoxy)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8i)



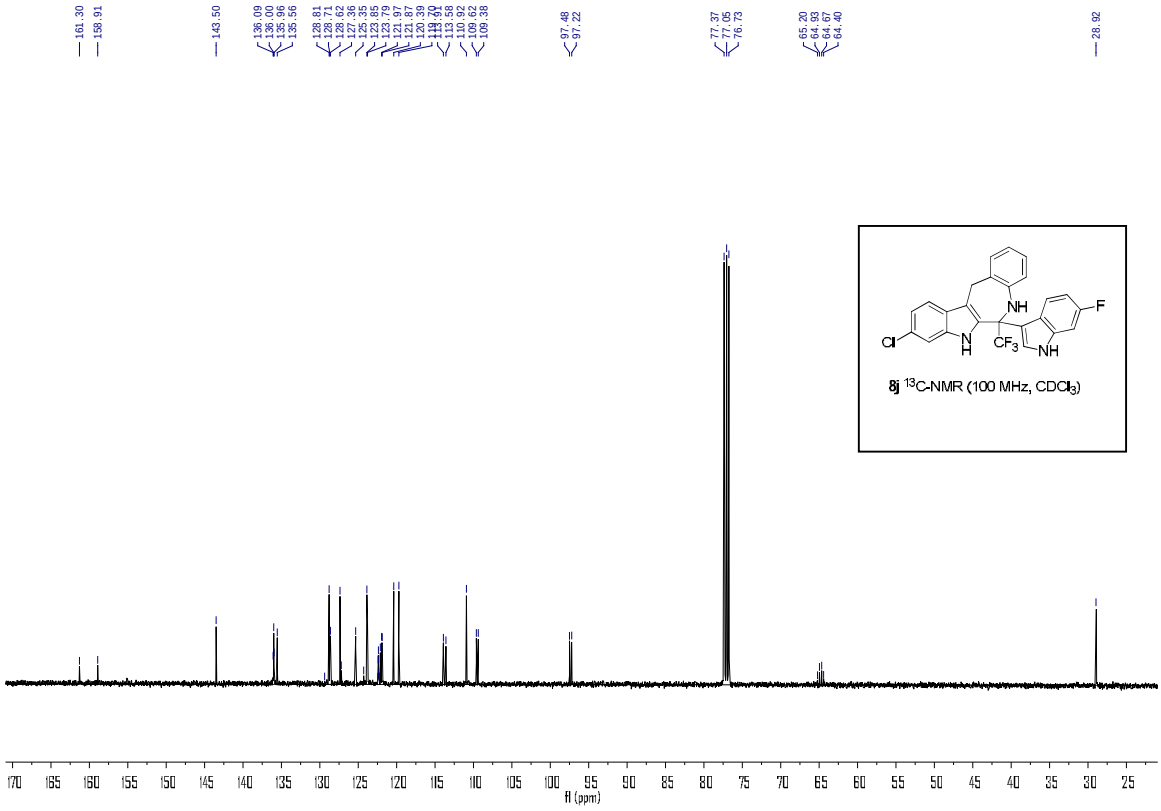




8i ^{19}F-NMR (376 MHz, $CDCl_3$)

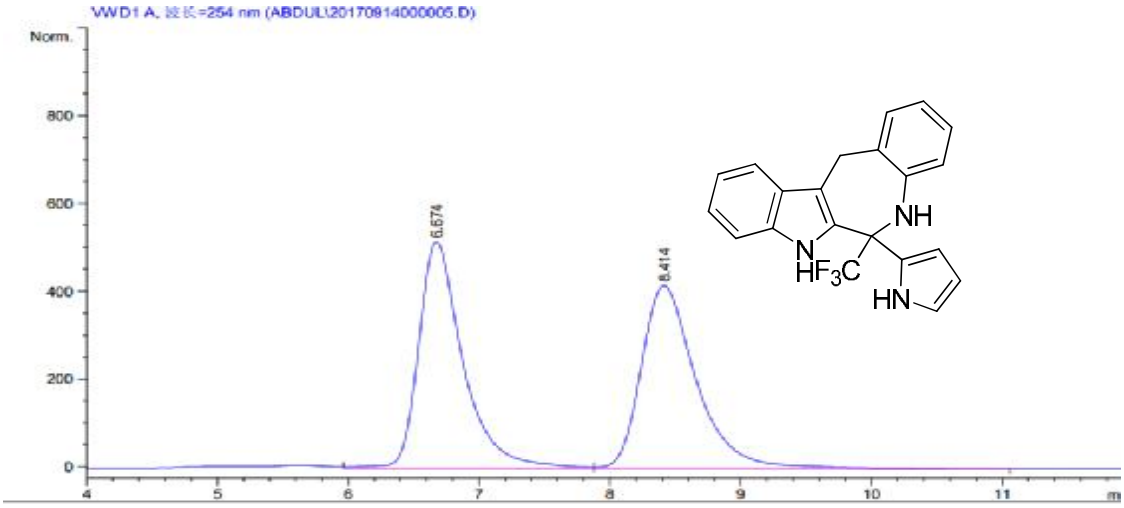


8j ^{1}H-NMR (400 MHz, $CDCl_3$)

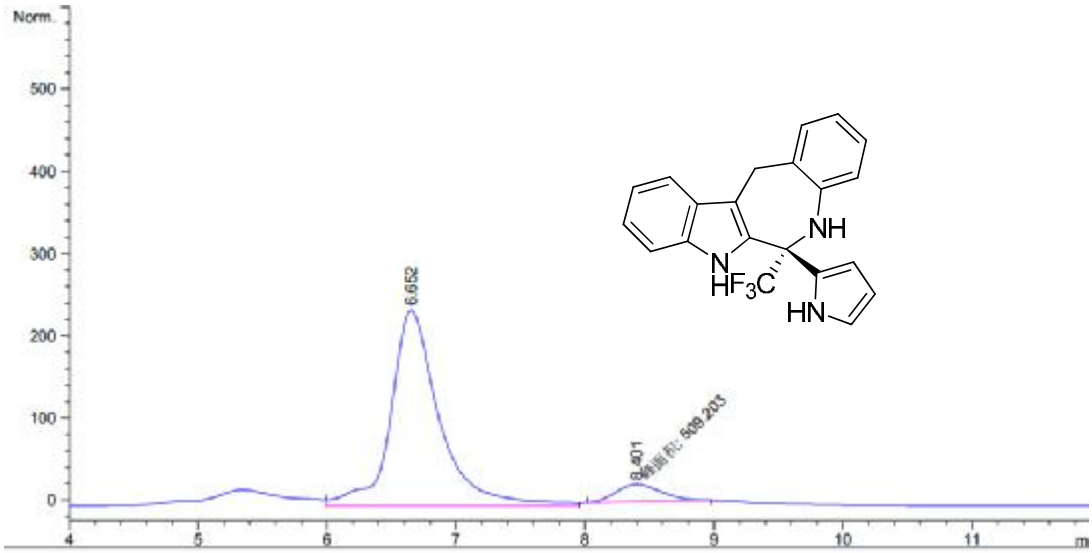


8j ^{13}C-NMR (100 MHz, $CDCl_3$)

6-(2-pyrrolyl)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3a).

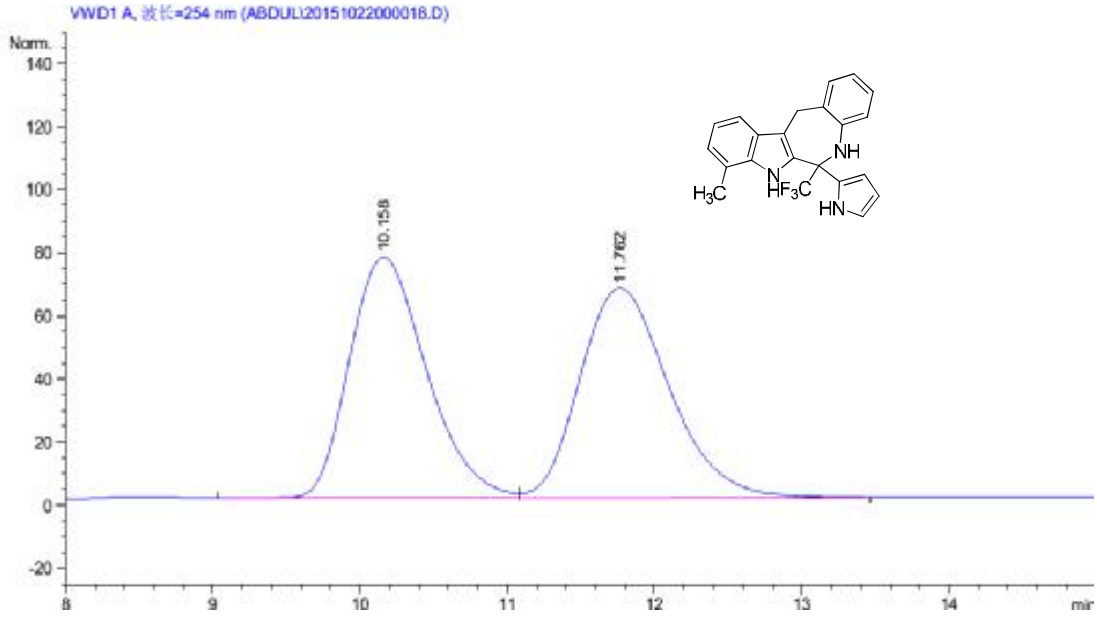


#	[min]		[min]	mAU	*s	[mAU]	%
1	6.674	VV	0.3523	1.22416e4		516.29718	49.9599
2	8.414	VB	0.4391	1.22612e4		417.08533	50.0401

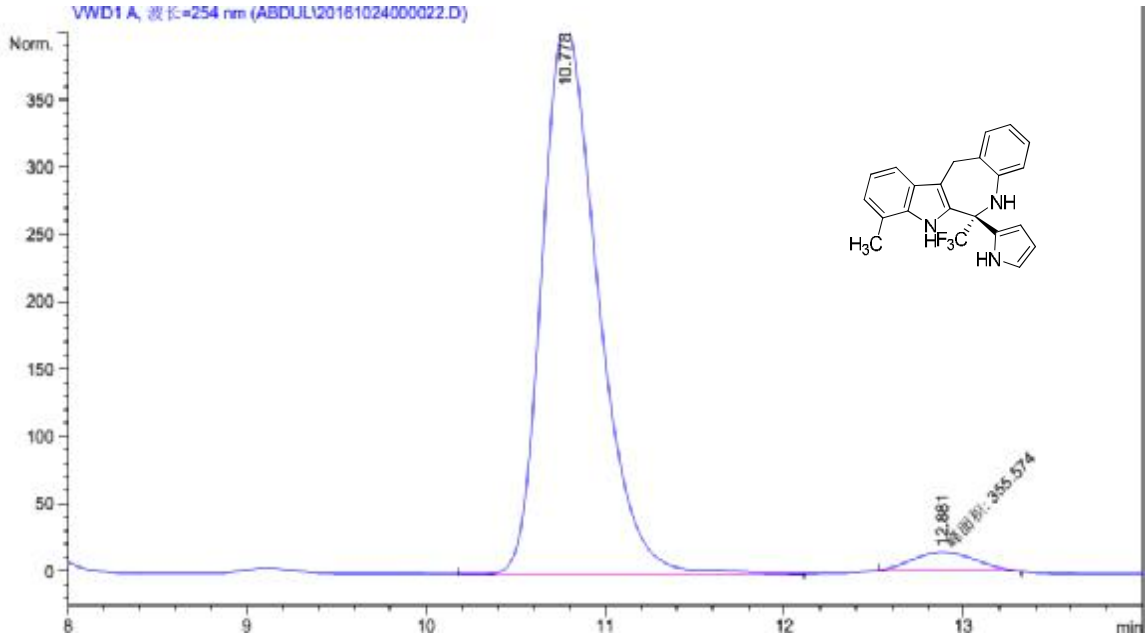


#	[min]		[min]	mAU	*s	[mAU]	%
1	6.652	VV	0.3816	6240.11719		238.02235	92.4555
2	8.401	MM	0.4047	509.20273		20.96988	7.5445

6-(2-pyrrolyl)-6-trifluoromethyl-4-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3b).

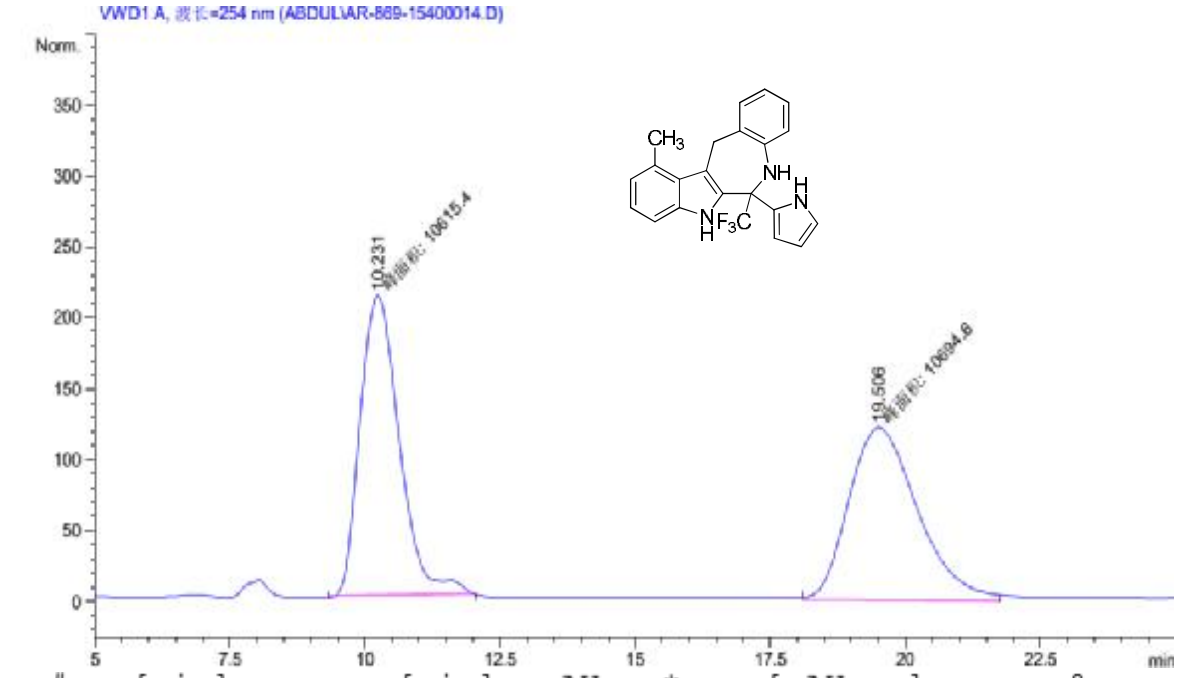


#	[min]		[min]	mAU	*s	[mAU]	%
1	10.158	VV	0.5660	2776.41748		76.52430	49.8100
2	11.762	VB	0.6567	2797.59448		66.51501	50.1900

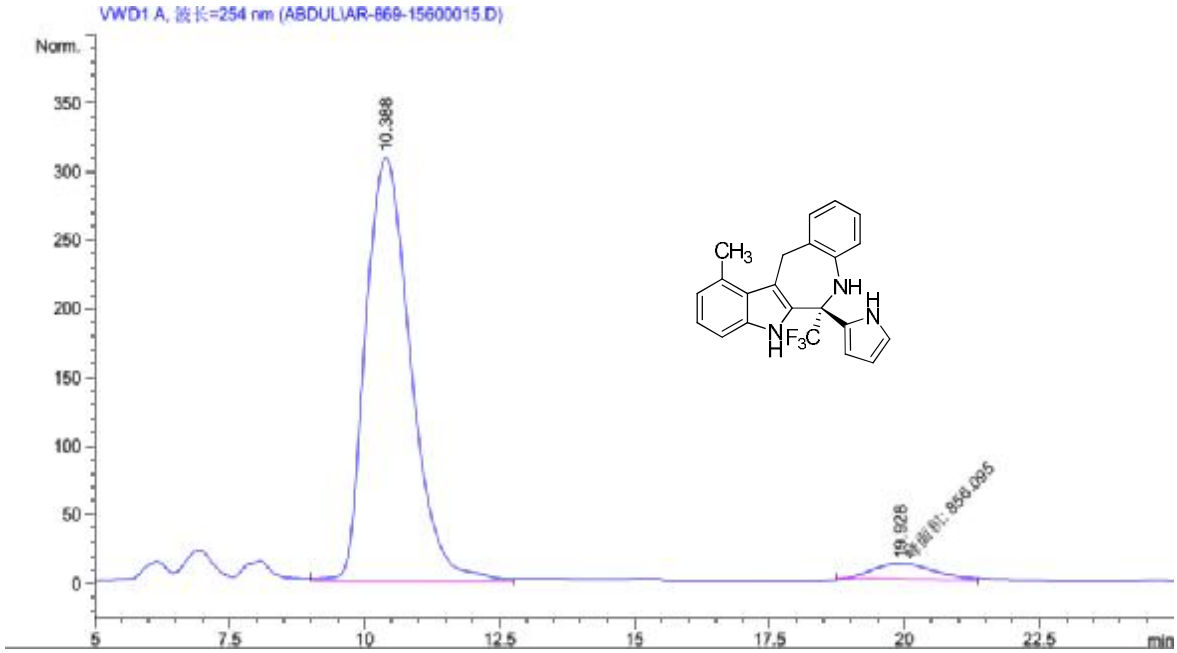


#	[min]		[min]	mAU	*s	[mAU]	%
1	10.778	VV	0.3358	8901.45508		408.49533	96.1589
2	12.881	MM	0.4157	355.57443		14.25768	3.8411

6-(2-pyrrolyl)-6-trifluoromethyl-1-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3c).

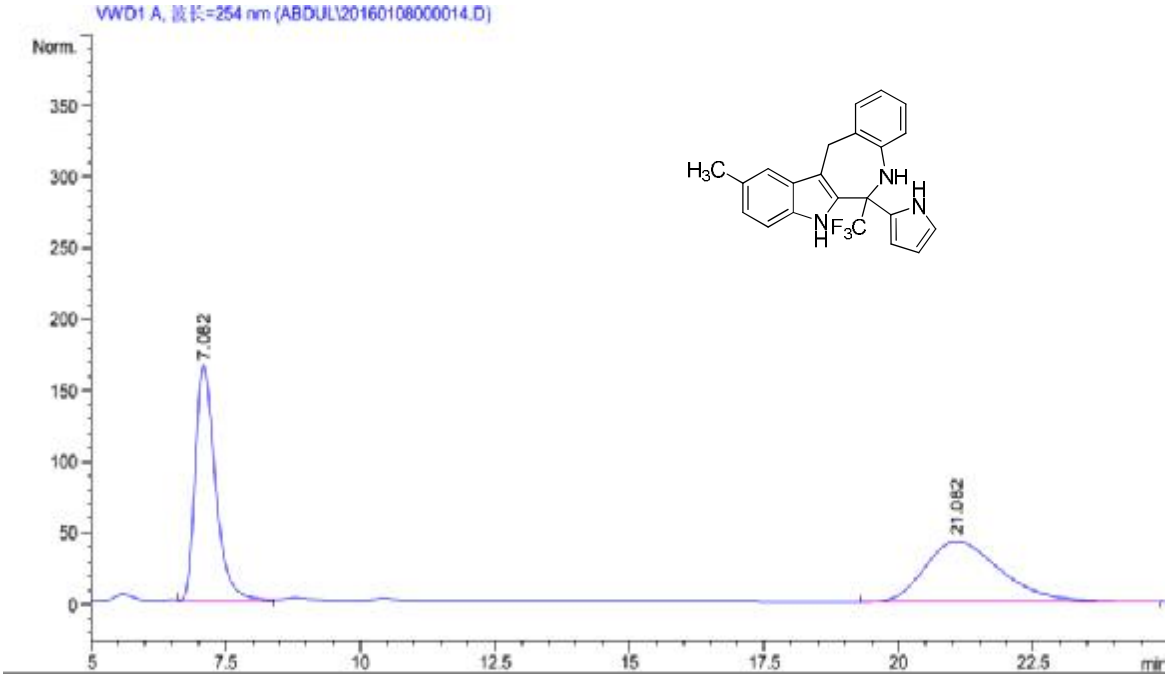


#	[min]		[min]	mAU *s	[mAU]	%
1	10.231	MM	0.8393	1.06154e4	210.78658	49.8142
2	19.506	MM	1.4739	1.06946e4	120.93382	50.1858

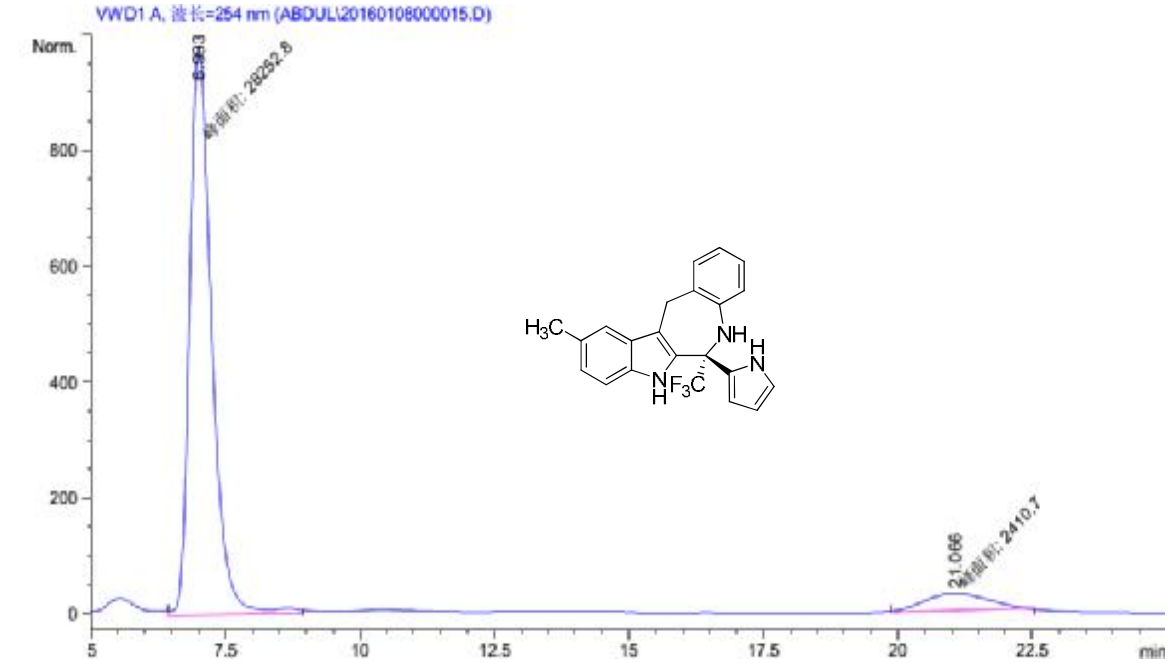


#	[min]		[min]	mAU *s	[mAU]	%
1	10.388	VV	0.9193	1.78246e4	308.21487	95.4172
2	19.928	MM	1.3045	856.09534	10.93736	4.5828

6-(2-pyrrolyl)-6-trifluoromethyl-2-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3d).

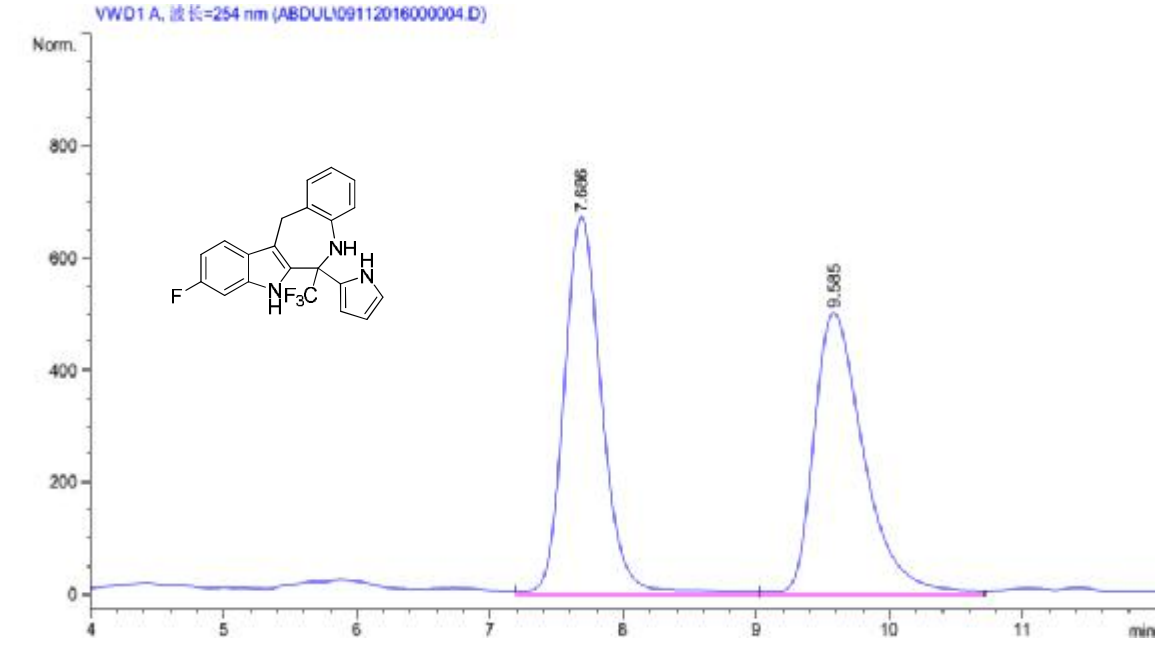


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.082	VV	0.3994	4346.13428	165.57120	50.8805	
2	21.082	BB	1.4783	4195.71045	42.70297	49.1195	

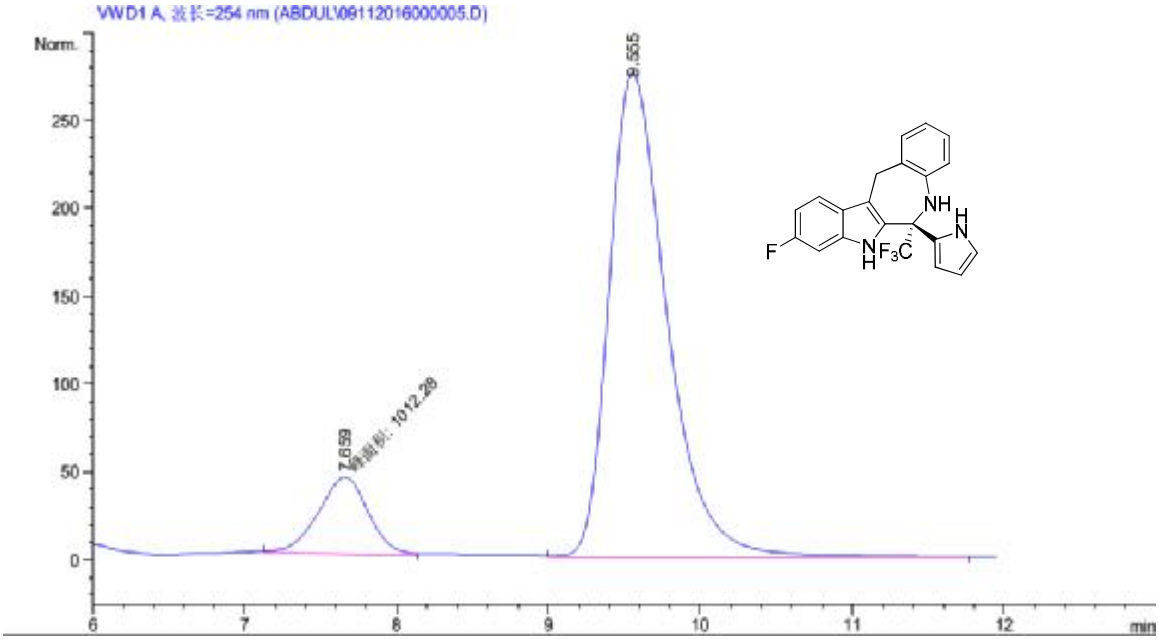


#	[min]		[min]	mAU	*s	[mAU]	%
1	6.993	MM	0.4789	2.82528e4	983.34473	92.1382	
2	21.066	MM	1.3678	2410.70410	29.37412	7.8618	

6-(2-pyrrolyl)-6-trifluoromethyl-3-fluoro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3e).

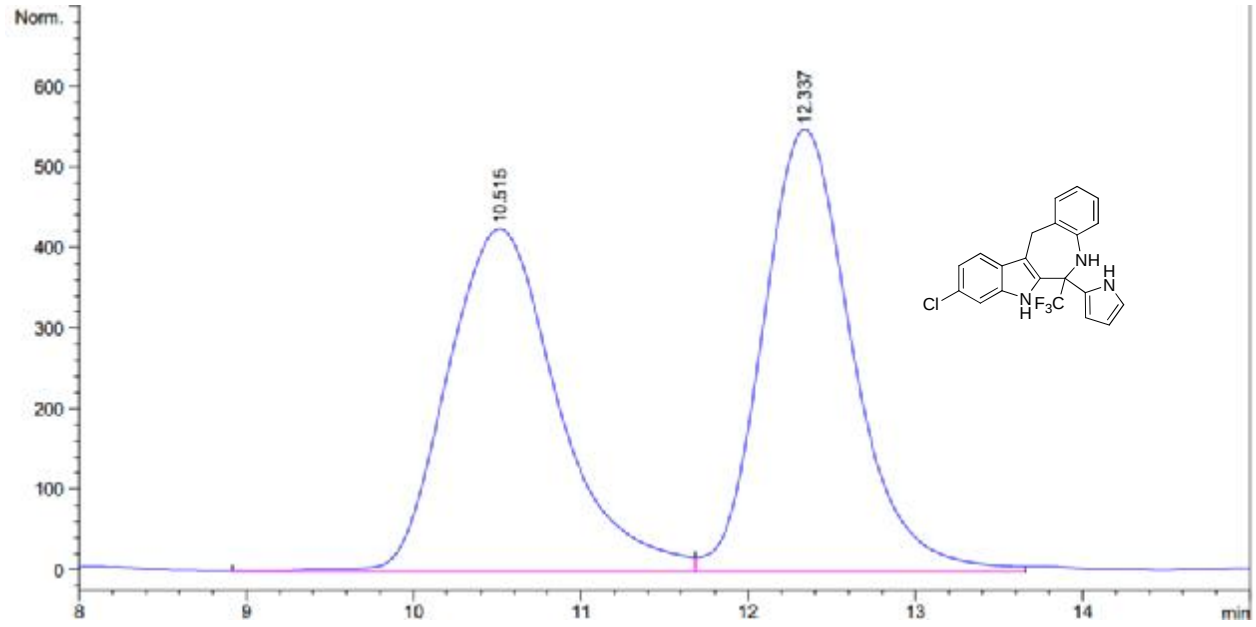


#	[min]		[min]	mAU	*s	[mAU	]	%
1	7.686	VV	0.3038	1.33024e4		671.87836		50.4197
2	9.585	VV	0.3972	1.30809e4		502.06311		49.5803

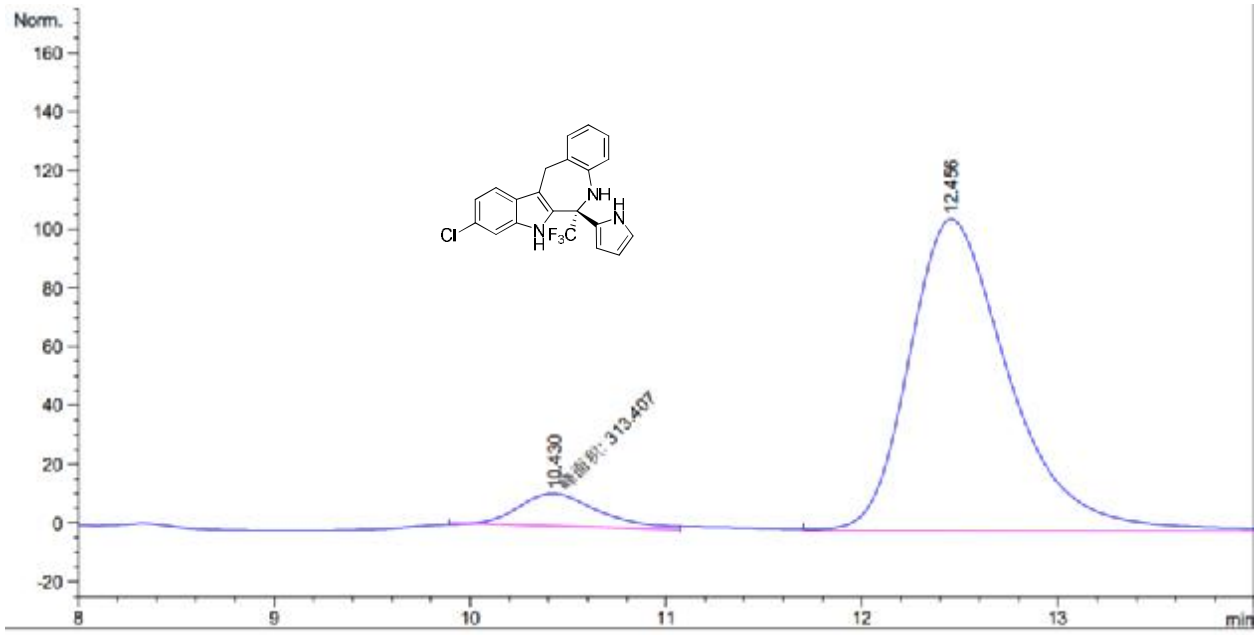


#	[min]		[min]	mAU	*s	[mAU	]	%
1	7.659	MM	0.3844	1012.28229		43.89466		12.2578
2	9.555	VB	0.4031	7245.97217		275.36133		87.7422

6-(2-pyrrolyl)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3f).

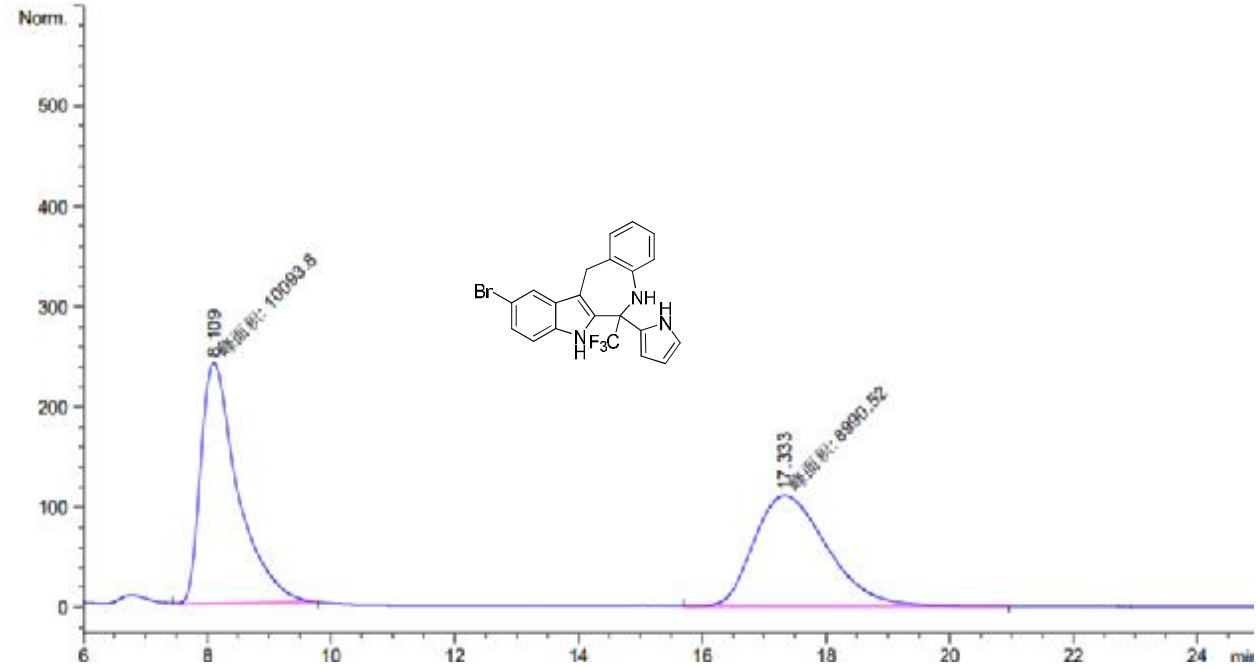


#	[min]		[min]	mAU	*s	[mAU]	%
1	10.515	VV	0.7187	1.95034e4		425.09225	48.9664
2	12.337	VV	0.5718	2.03268e4		548.91077	51.0336

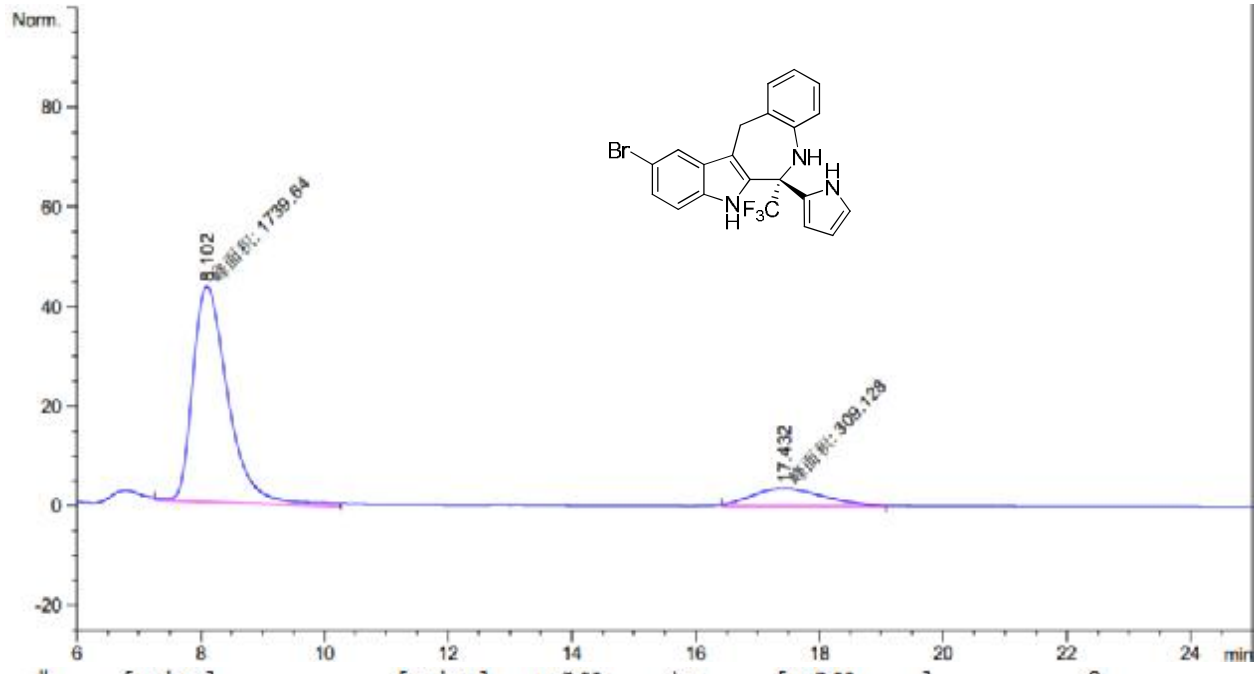


#	[min]		[min]	mAU	*s	[mAU]	%
1	10.430	MM	0.4767	313.40686		10.95790	7.6551
2	12.456	VB	0.5409	3780.69019		106.10232	92.3449

6-(2-pyrrolyl)-6-trifluoromethyl-2-bromo-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3g).

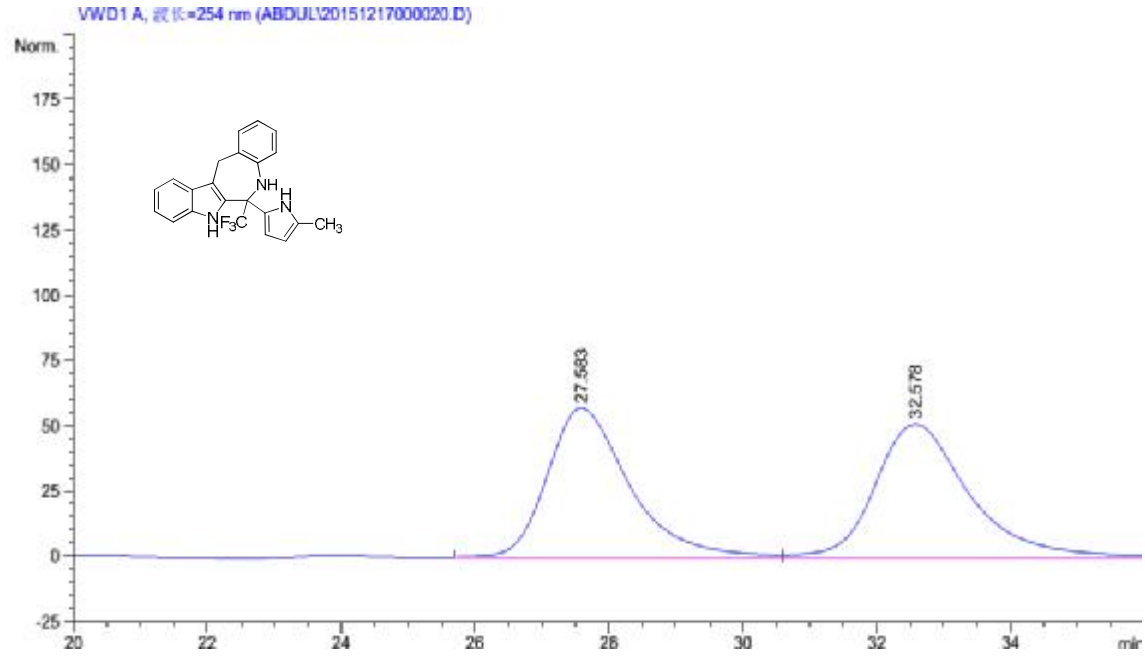


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.109	MM	0.7002	1.00938e4		240.24622	52.8905
2	17.333	MM	1.3617	8990.52441		110.04254	47.1095

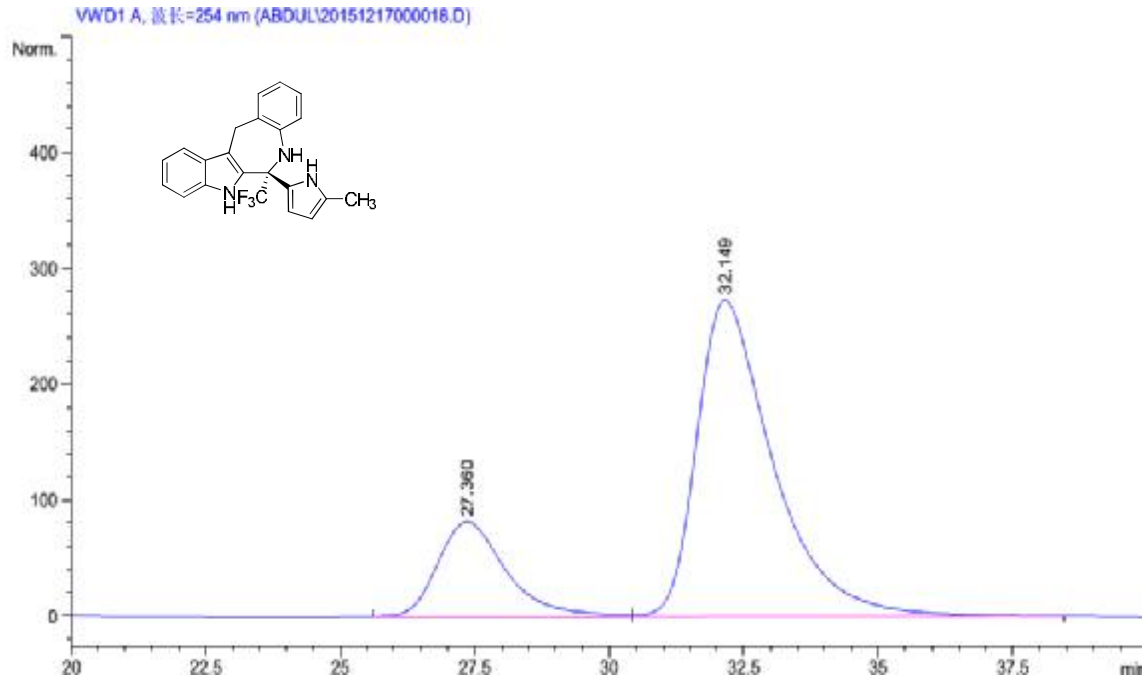


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.102	MM	0.6690	1739.63550		43.33638	84.9115
2	17.432	MM	1.3648	309.12836		3.77490	15.0885

6-(2-pyrrolyl-5`-methyl)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3h).

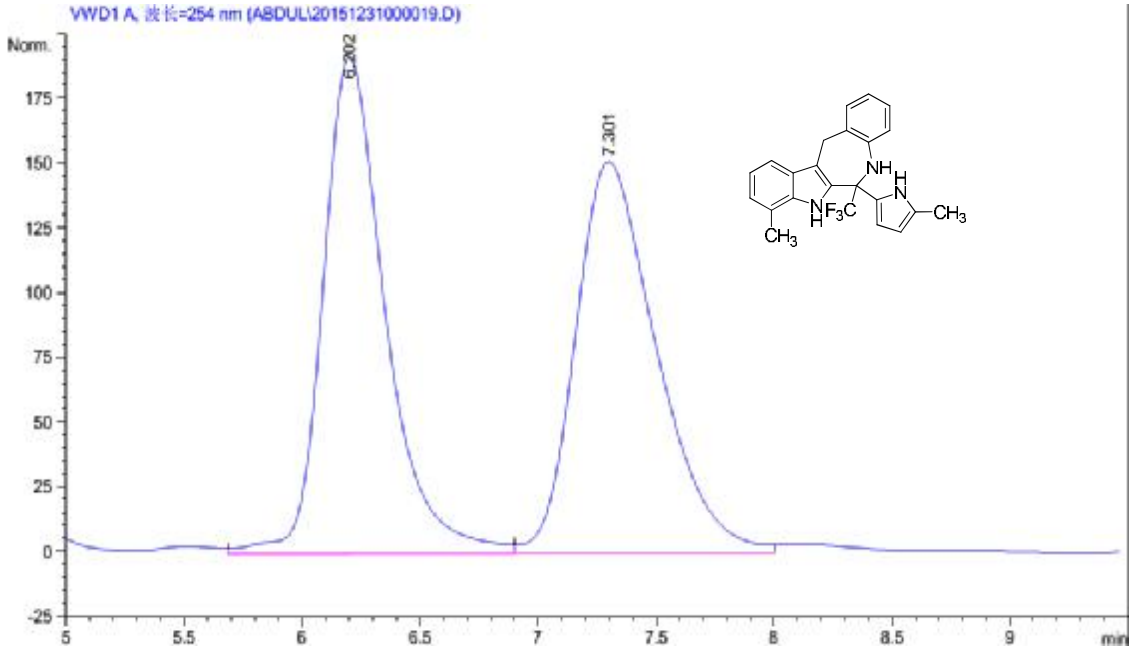


#	[min]		[min]	mAU	*s	[mAU]	%
1	27.583	BV	1.2962	4892.92725		57.29638	49.4370
2	32.578	VBA	1.4824	5004.37598		51.00946	50.5630

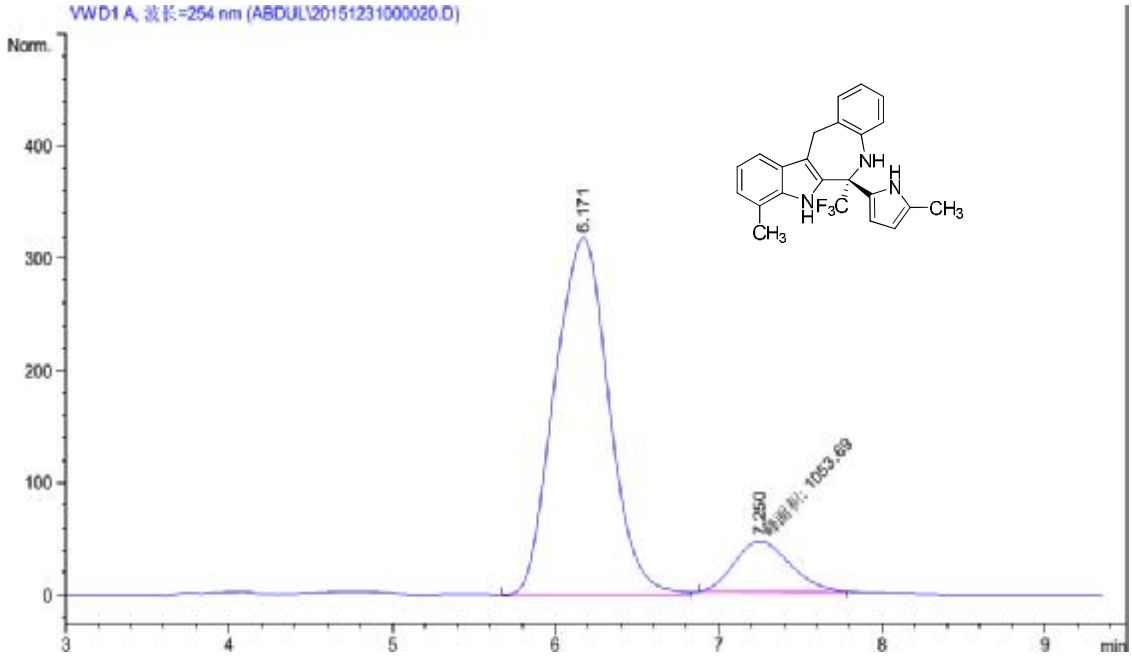


#	[min]		[min]	mAU	*s	[mAU]	%
1	27.360	BV	1.3453	7167.05469		81.57762	20.9524
2	32.149	VB	1.4788	2.70394e4		272.99588	79.0476

6-(2-pyrrolyl-5`-methyl)-6-trifluoromethyl-4-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (3i).

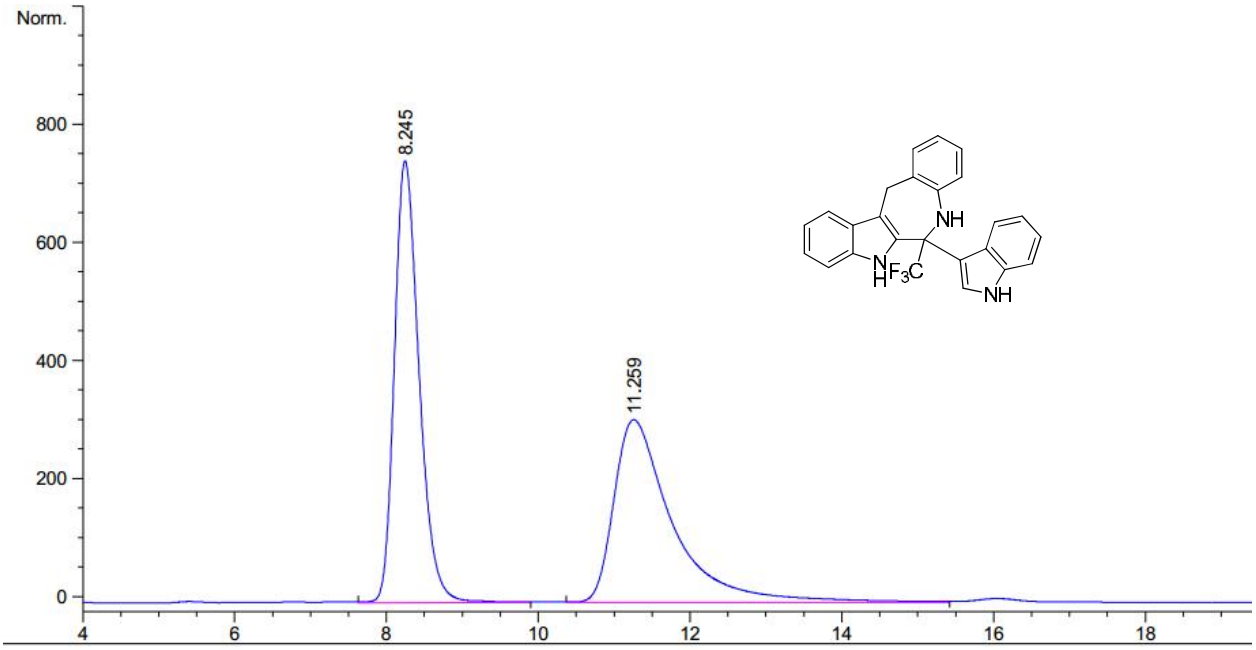


#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.202	VV	0.2785	3524.78223		191.81229		49.4117
2	7.301	VV	0.3600	3608.72217		151.21619		50.5883

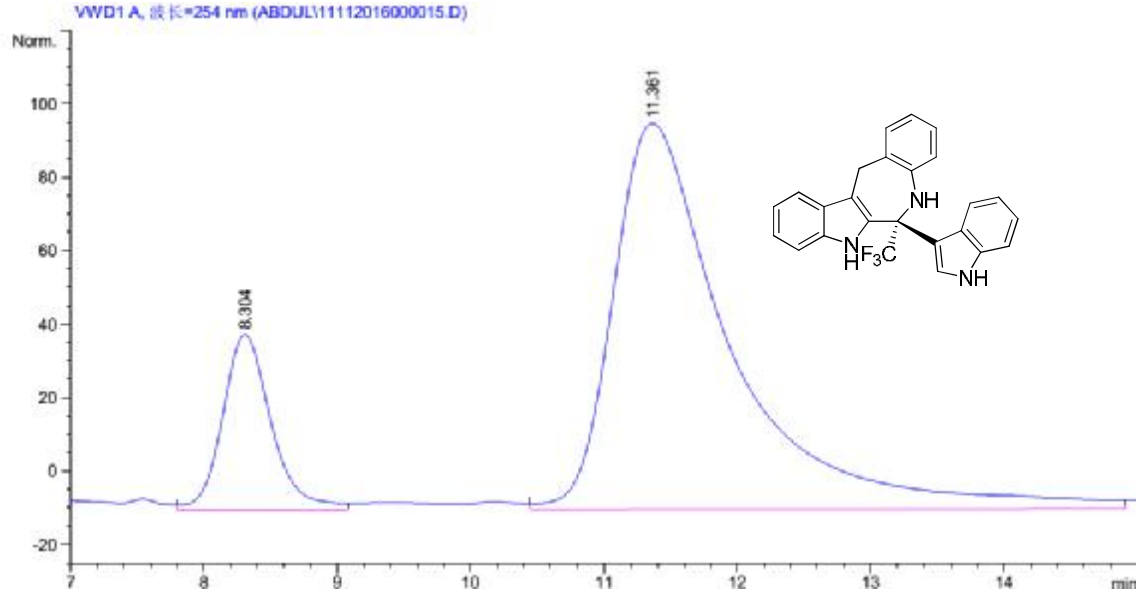


#	[min]		[min]	mAU	*s	[mAU	]	%
1	6.171	VV	0.3753	7385.23535		318.53192		87.5139
2	7.250	MM	0.3934	1053.68848		44.63528		12.4861

6-(3-indolyl-)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8a).

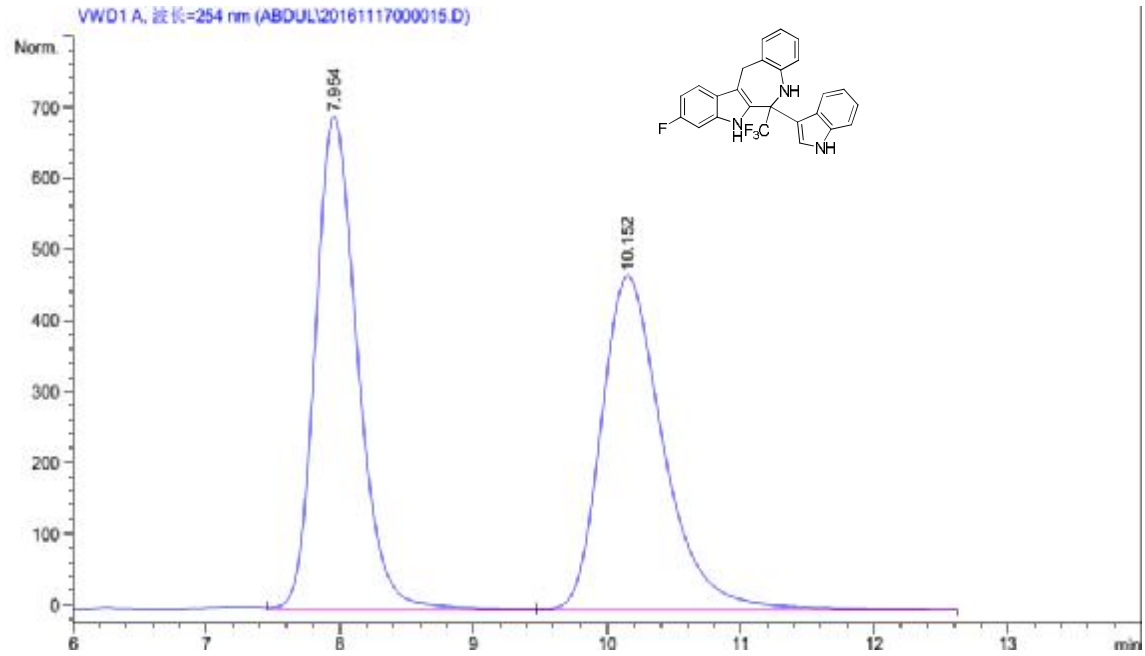


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.245	VV	0.3492	1.69788e4		748.19708	50.3865
2	11.259	VV	0.7870	1.67183e4		309.71814	49.6135

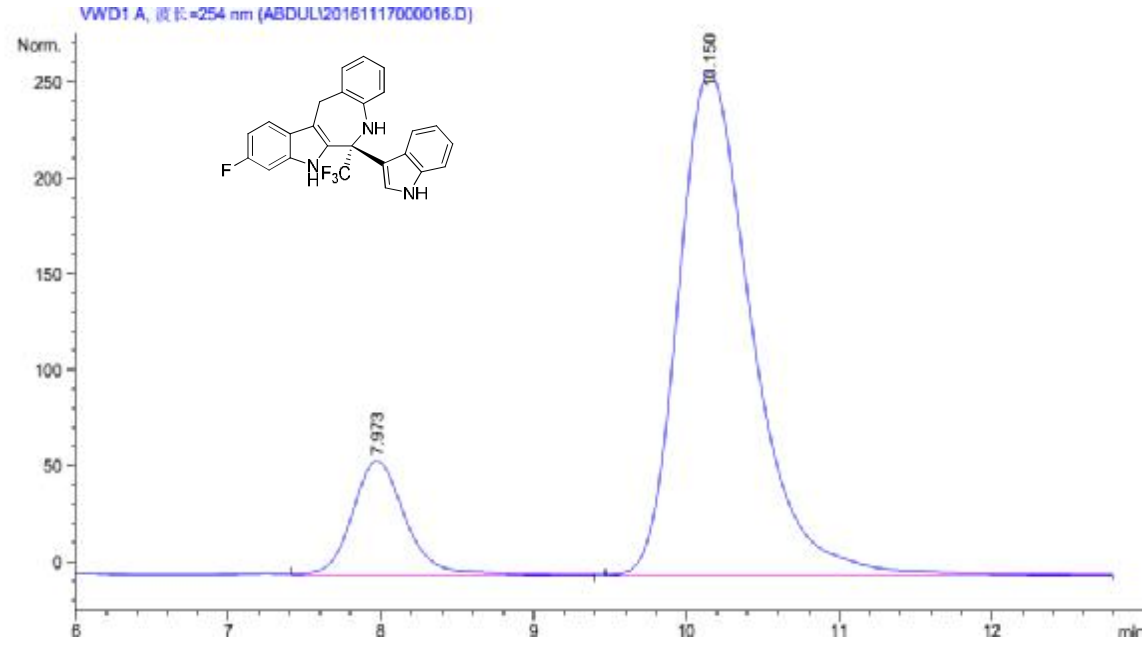


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.304	VV	0.3844	1200.93213		47.62985	15.5954
2	11.361	VV	0.8964	6499.59717		105.07533	84.4046

6-(3-indolyl-)-6-trifluoromethyl-3-fluoro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8b).

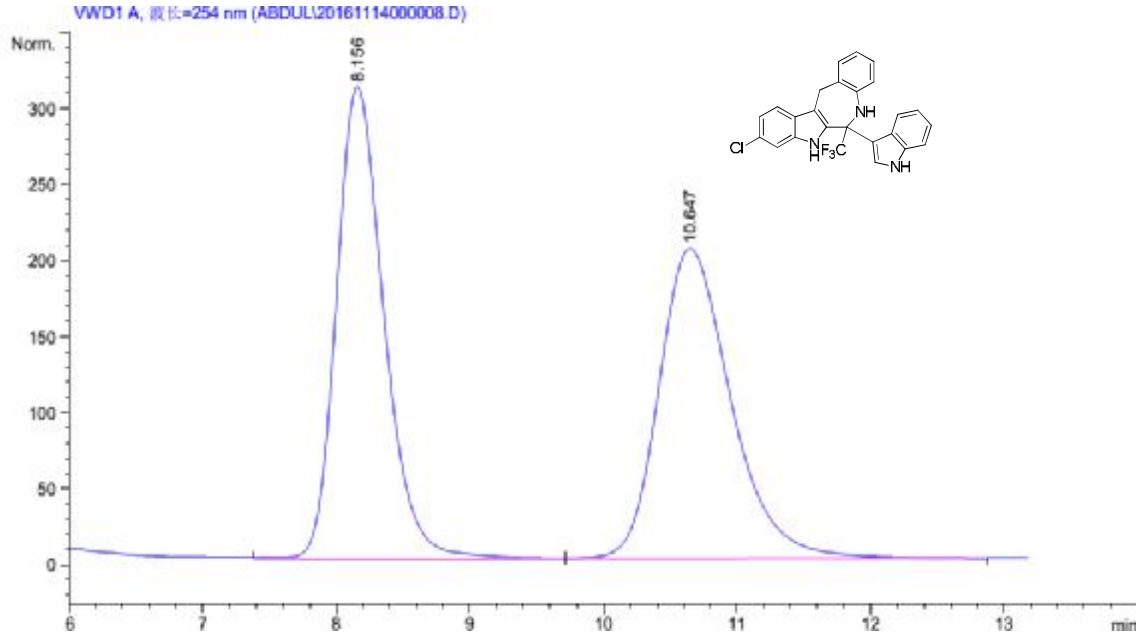


#	[min]		[min]	mAU *s	[mAU]	%
1	7.954	VV	0.3387	1.52779e4	693.07538	50.0700
2	10.152	VBA	0.4954	1.52352e4	469.13000	49.9300

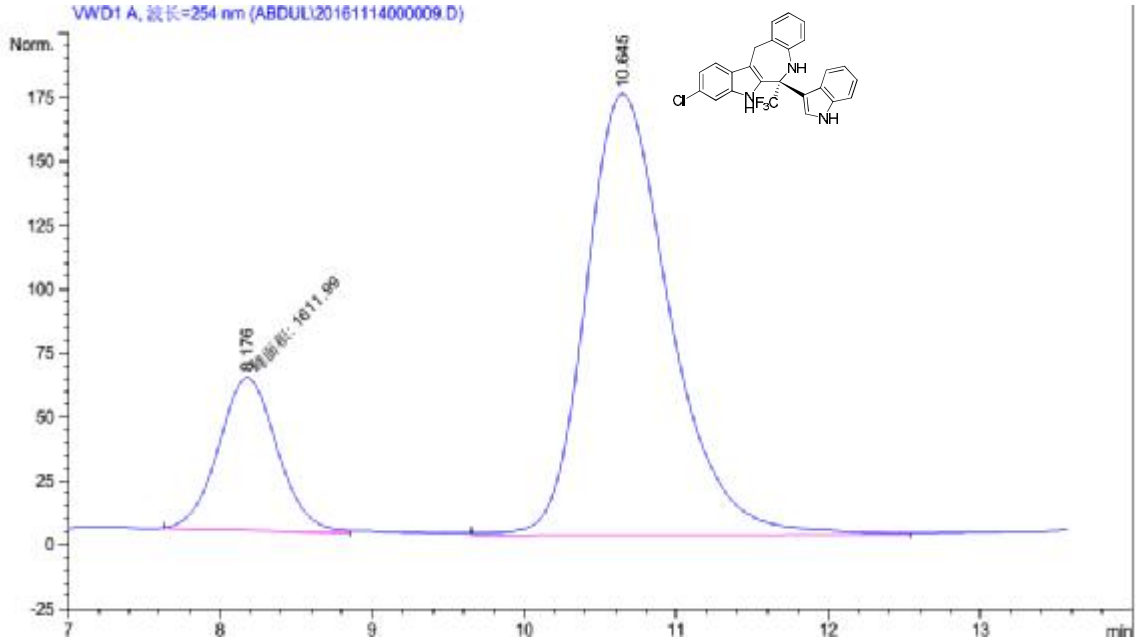


#	[min]		[min]	mAU *s	[mAU]	%
1	7.973	VB	0.3794	1476.45898	59.58084	14.3903
2	10.150	BBA	0.5105	8783.64160	262.01141	85.6097

6-(3-indolyl-)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8c).

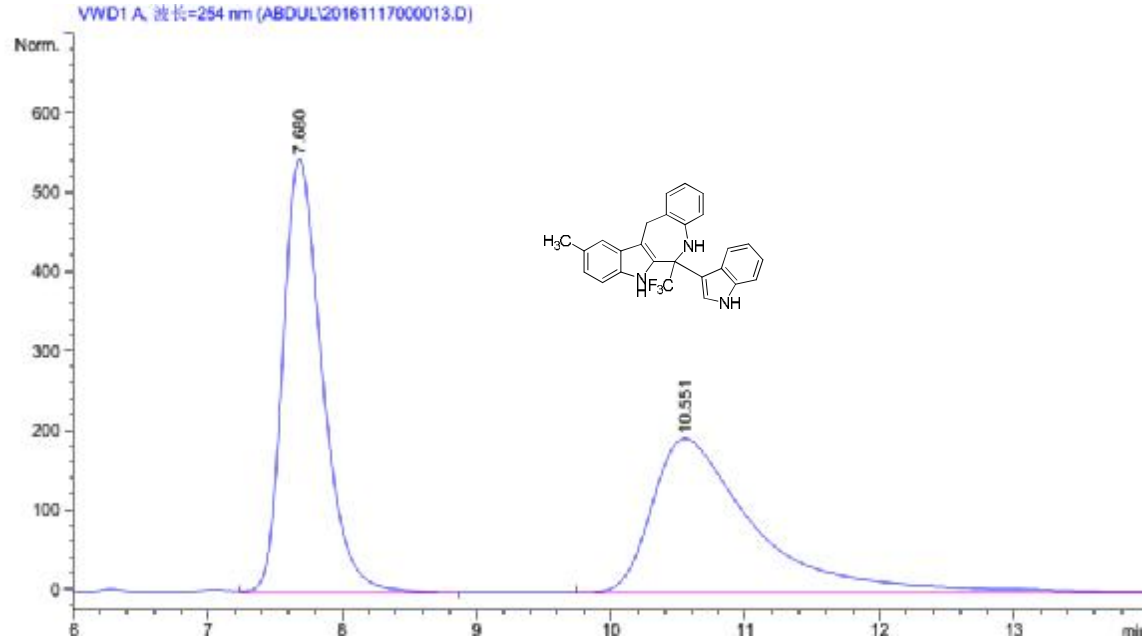


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.156	VV	0.3778	7644.80713	310.16669	50.0485	
2	10.647	VB	0.5765	7629.99023	203.82146	49.9515	

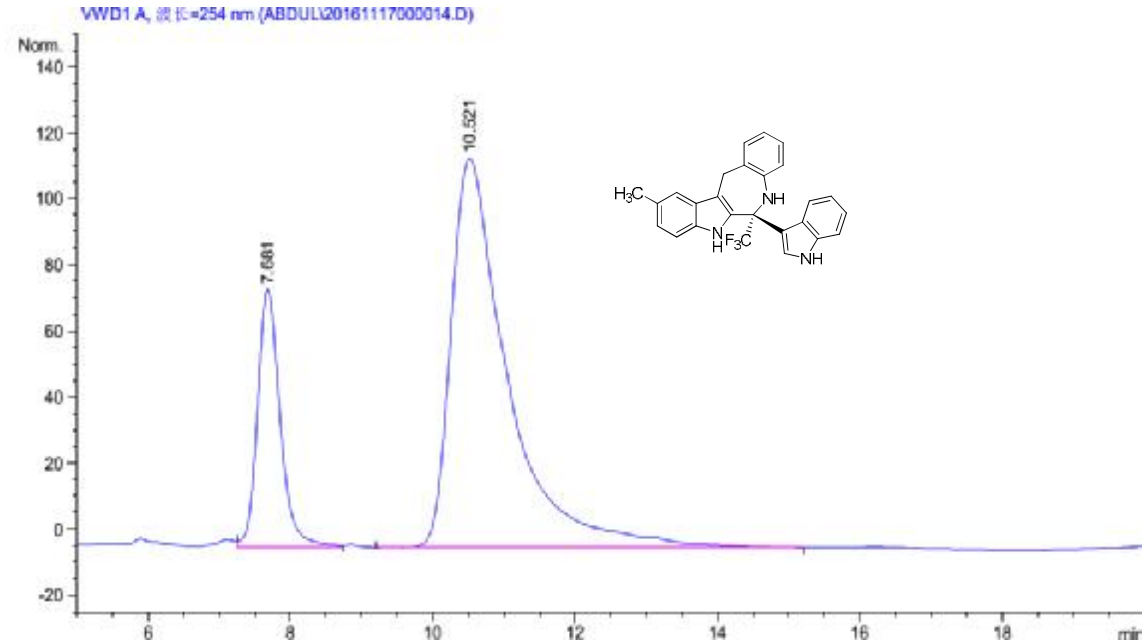


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.176	MM	0.4487	1611.99207	59.88178	19.5047	
2	10.645	VV	0.5864	6652.63965	172.63506	80.4953	

6-(3-indolyl-)-6-trifluoromethyl-2-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8d).

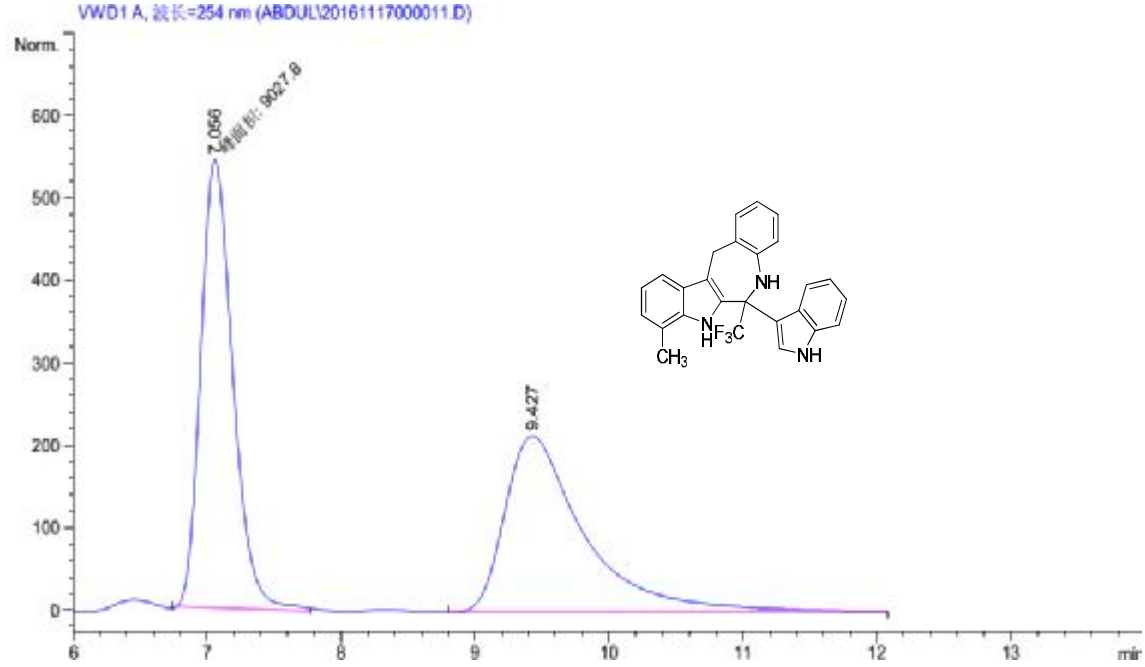


#	[min]		[min]	mAU *s	[mAU]	%
1	7.680	VV	0.3146	1.11968e4	546.76178	51.3961
2	10.551	VBA	0.7823	1.05885e4	194.90926	48.6039

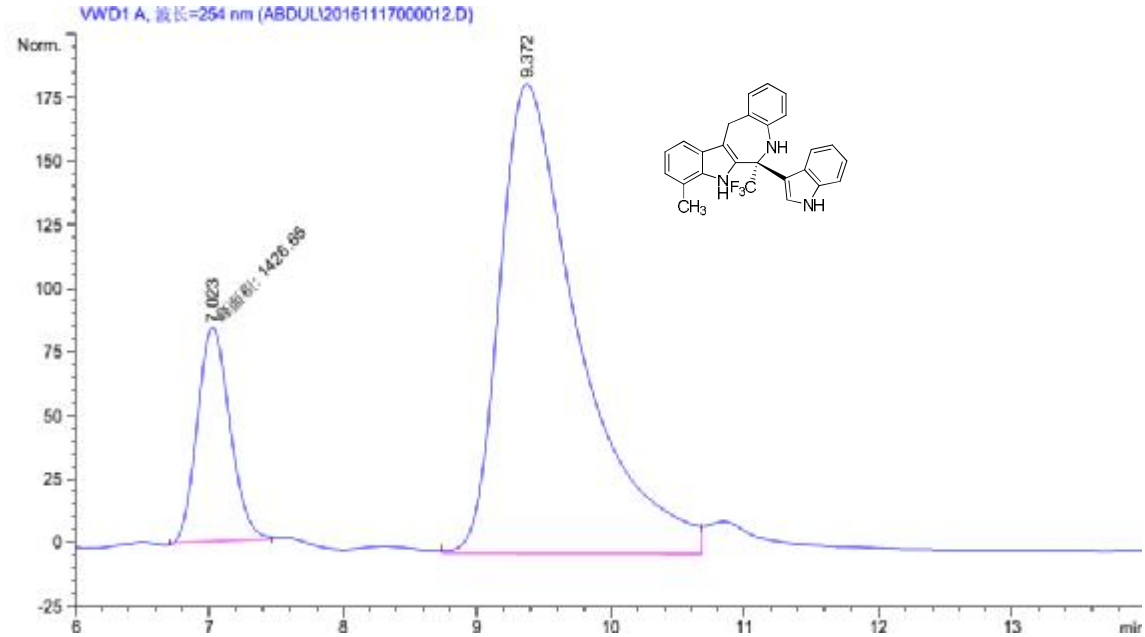


#	[min]		[min]	mAU *s	[mAU]	%
1	7.681	VV	0.3391	1747.95129	78.29907	21.0568
2	10.521	VB	0.7993	6553.16943	117.99763	78.9432

6-(3-indolyl-)-6-trifluoromethyl-4-methyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8e).

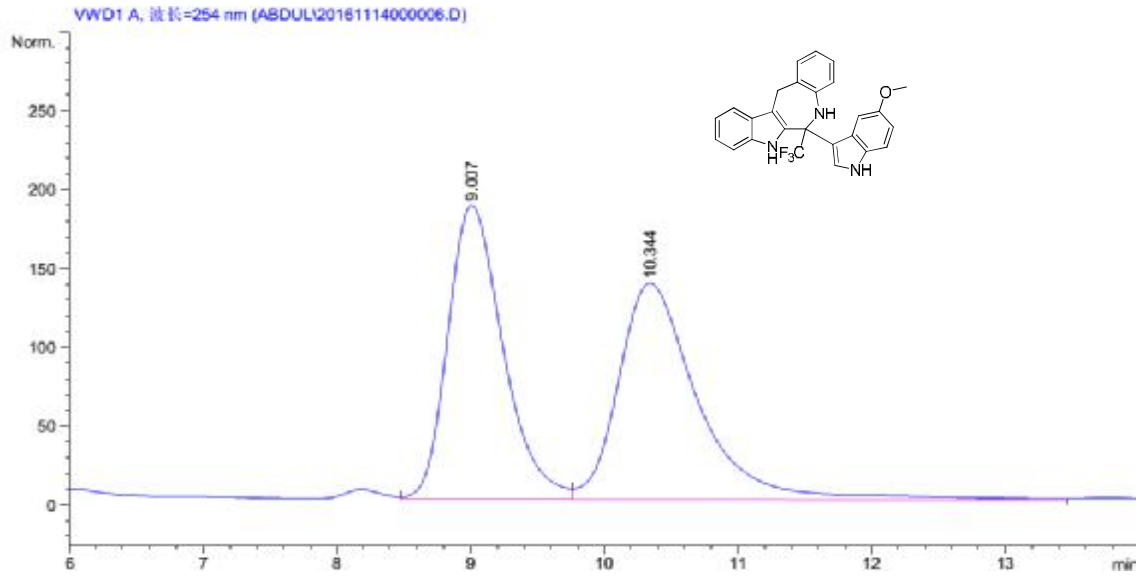


#	[min]		[min]	mAU	*s	[mAU	]	%
1	7.056	MM	0.2769	9027.79785	543.35376			50.5742
2	9.427	VBA	0.6038	8822.79785	213.79129			49.4258

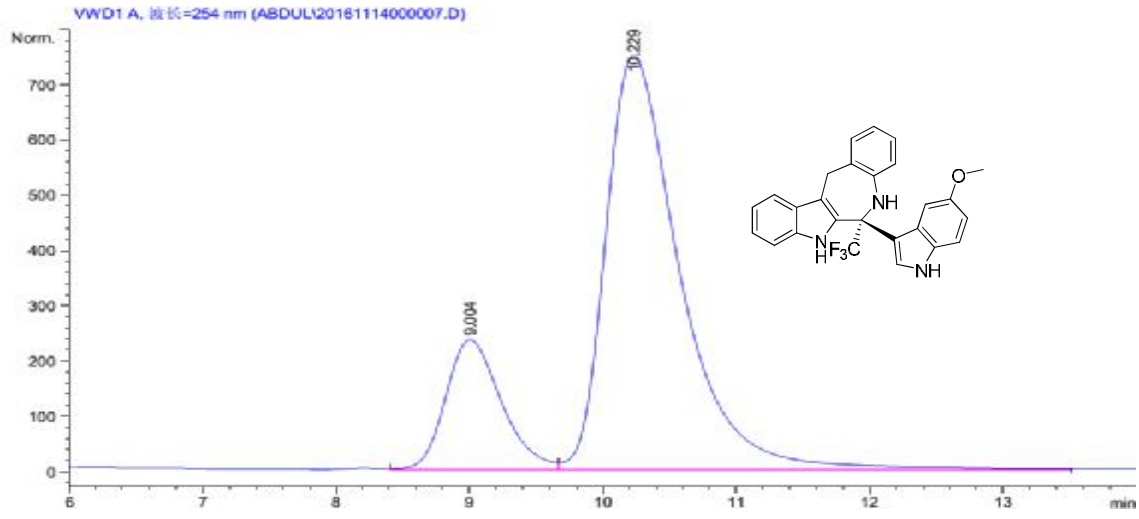


#	[min]		[min]	mAU	*s	[mAU	]	%
1	7.023	MM	0.2823	1426.65295	84.22533			15.8118
2	9.372	VV	0.6049	7596.06689	184.75008			84.1882

6-(3-indolyl-5`-methoxy)-6-trifluoromethyl-5,6,7,12-tetrahydroindolo[2,3-c][1]benzazepine (8f).

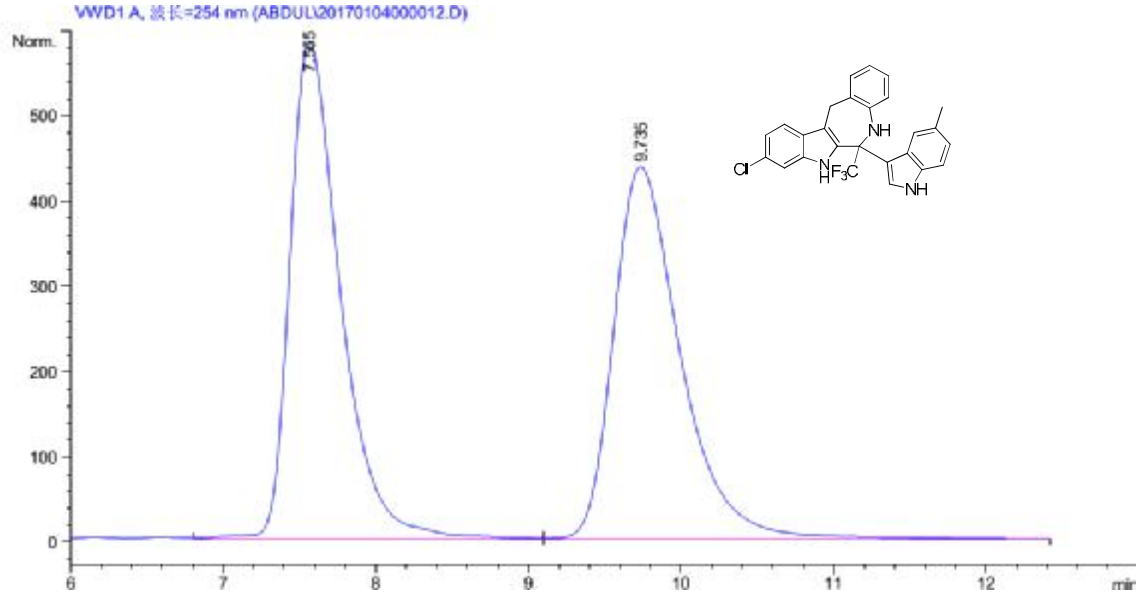


#	[min]		[min]	mAU	*s	[mAU]	%
1	9.007	VV	0.4397	5351.12207		186.40663	48.5065
2	10.344	VV	0.6199	5680.62988		137.19238	51.4935

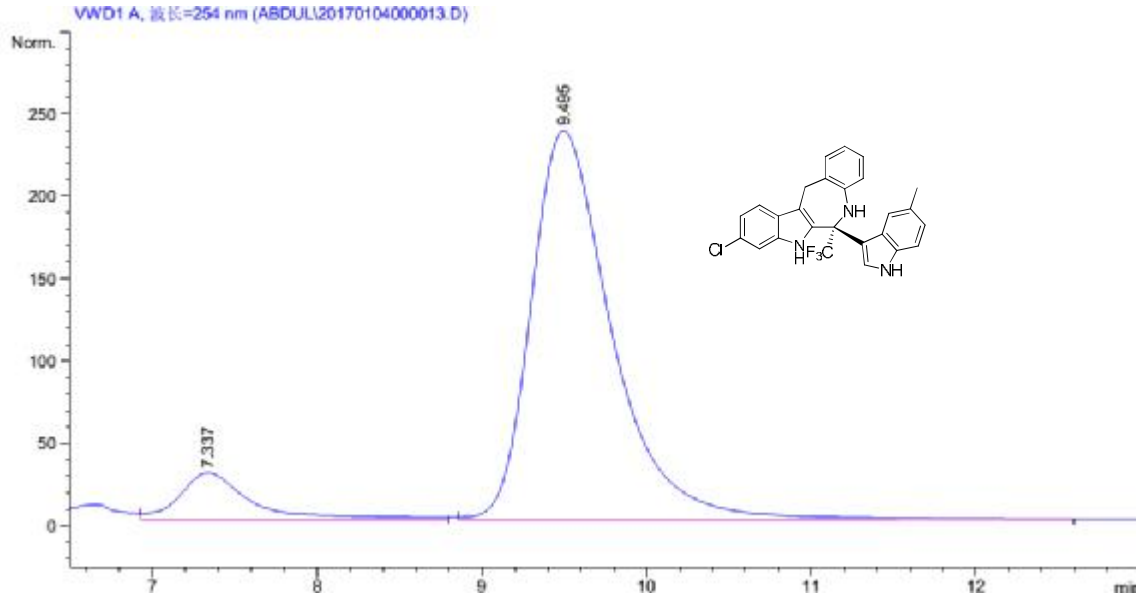


#	[min]		[min]	mAU	*s	[mAU]	%
1	9.004	VV	0.4513	6889.26416		235.97038	19.0990
2	10.229	VB	0.5880	2.91821e4		749.88196	80.9010

6-(3-indolyl-5`-methyl)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1] benzazepine (8g).

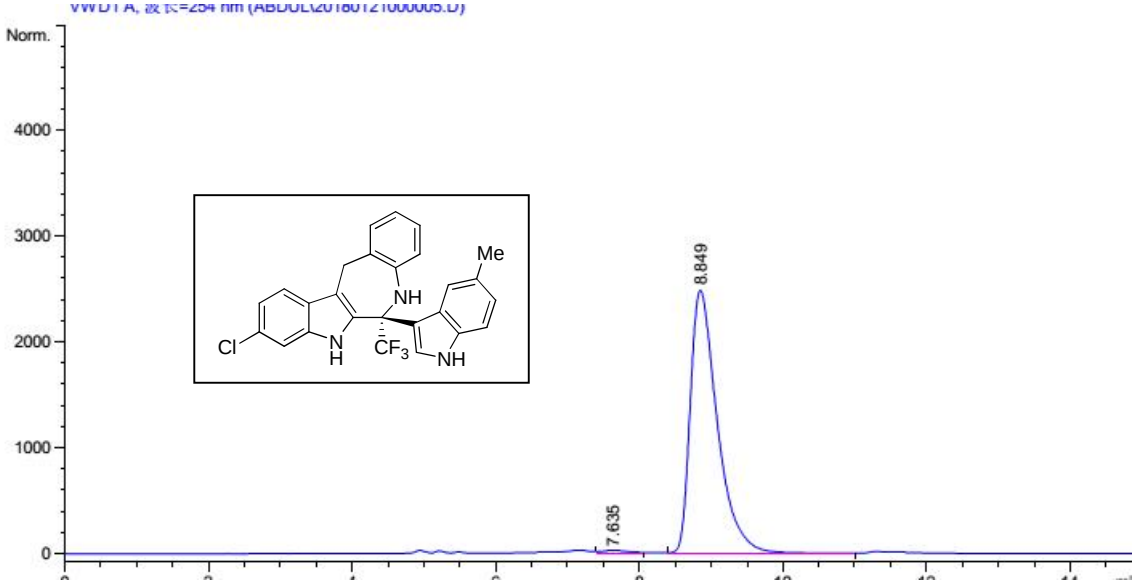


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.565	VV	0.3531	1.36117e4		584.84595	50.0859
2	9.735	VBA	0.4666	1.35650e4		437.49414	49.9141



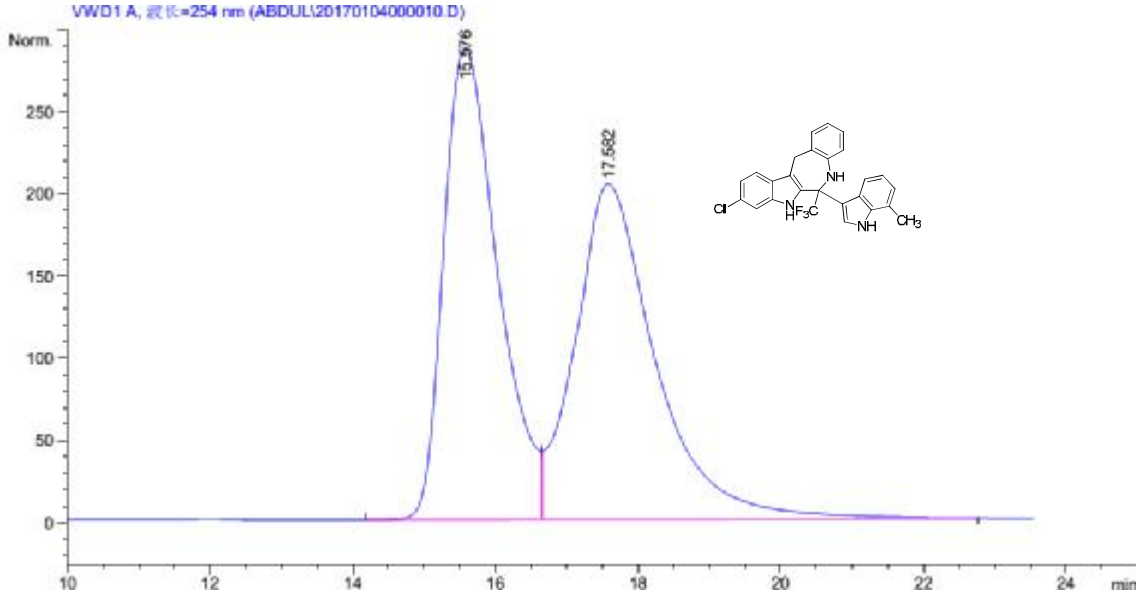
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.337	VB	0.4397	853.87347		28.27629	9.6144
2	9.495	BB	0.5130	8027.27490		236.17618	90.3856

After one single recrystallization

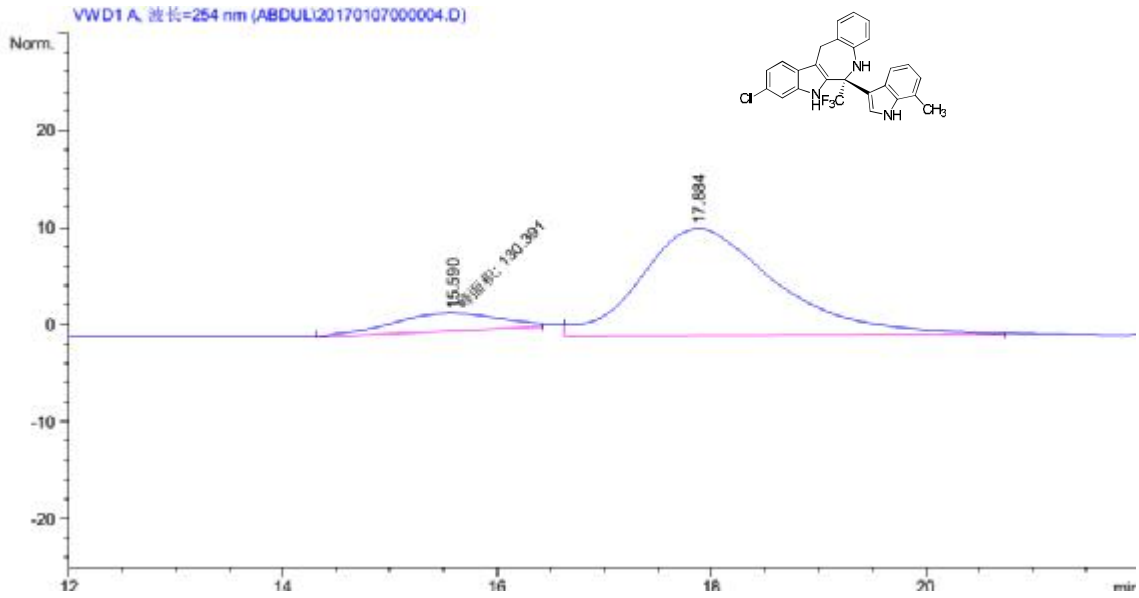


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.635	VV	0.4161	939.14020		32.75224	1.4038
2	8.849	VV	0.3990	6.59620e4		2492.48999	98.5962

6-(3-indolyl-7`-methyl)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1] benzazepine (8h).

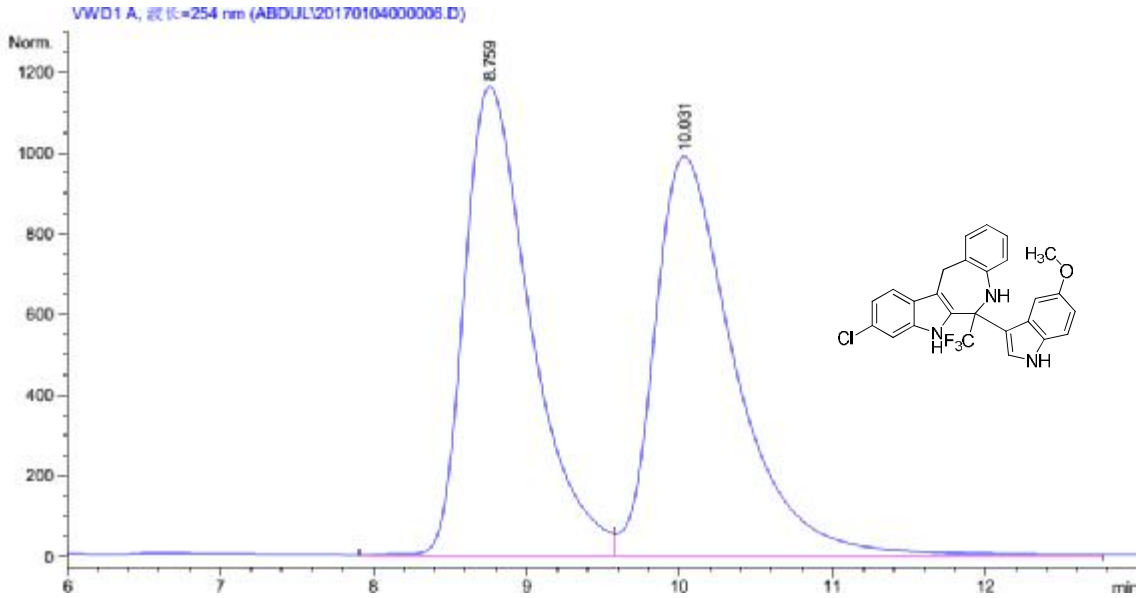


#	[min]		[min]	mAU	*s	[mAU]	%
1	15.576	BV	0.8079	1.51329e4		286.72437	48.5771
2	17.582	VB	1.1375	1.60195e4		203.99461	51.4229

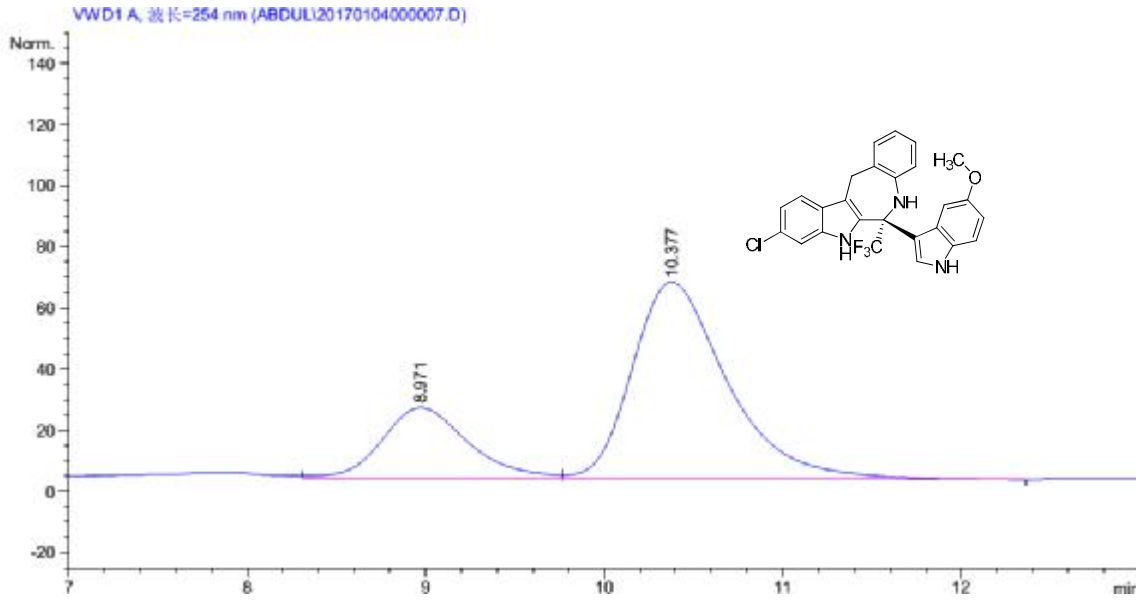


#	[min]		[min]	mAU	*s	[mAU	]	%
1	15.590	MM	0.8544	130.39149		1.82500		11.8520
2	17.884	VB	1.2542	969.76898		11.01620		88.1480

6-(3-indolyl-5`-methoxy)-6-trifluoromethyl-3-chloro-5,6,7,12-tetrahydroindolo[2,3-c][1] benzazepine (8i).

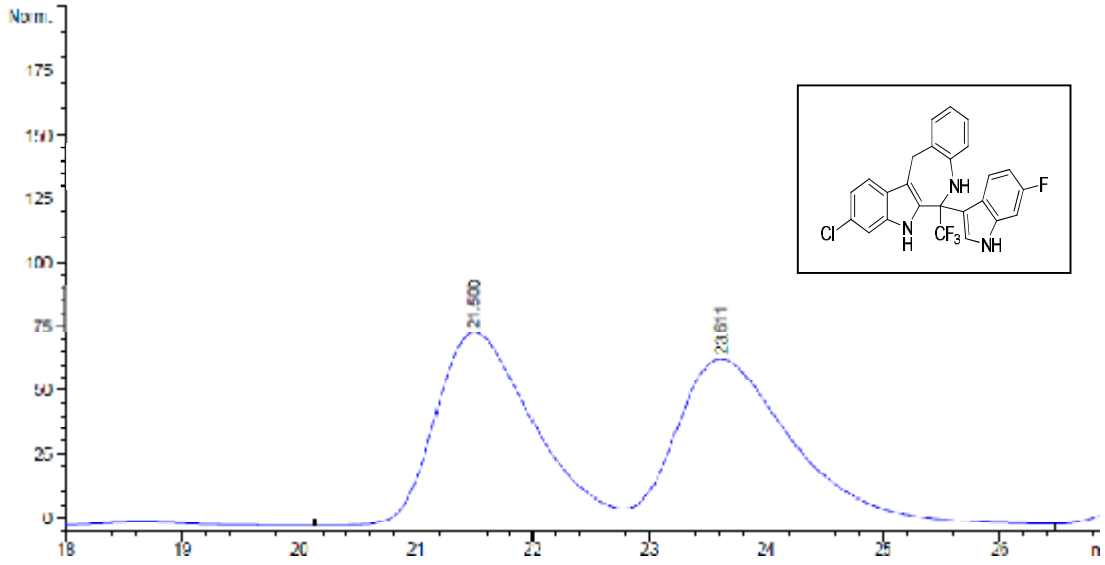


#	[min]		[min]	mAU	*s	[mAU	]	%
1	8.759	VV	0.4521	3.49375e4		1163.83240		49.0757
2	10.031	VV	0.5497	3.62535e4		989.69043		50.9243

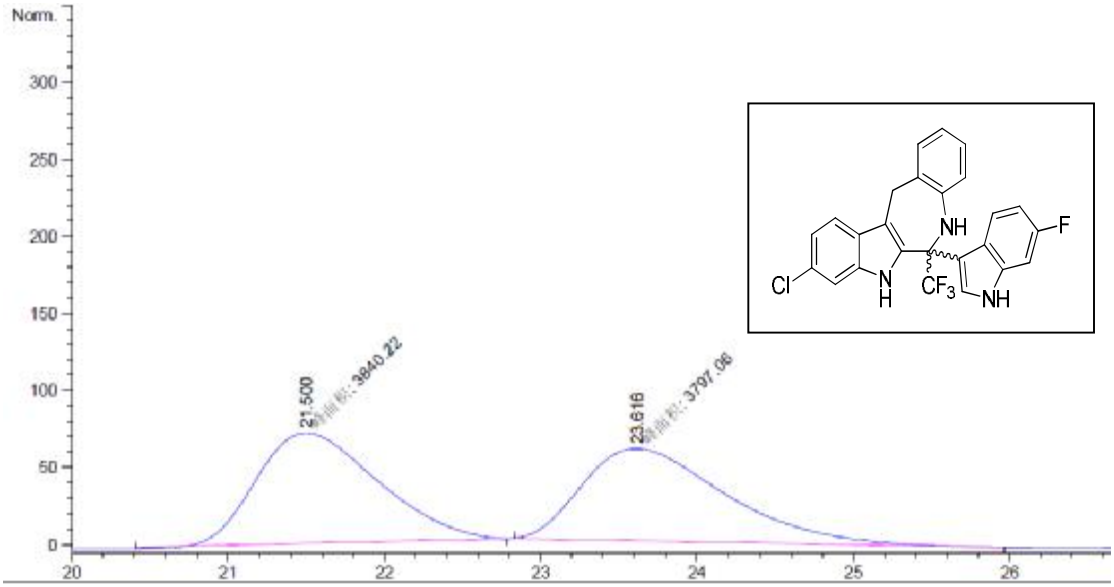


#	[min]		[min]	mAU	*s	[mAU]	%
1	8.971	VV	0.5254	823.75146		23.67321	25.2871
2	10.377	VV	0.5700	2433.84253		64.67993	74.7129

Compound 8j.



#	[min]		[min]	mAU	*s	[mAU]	%
1	21.500	VV	0.8887	4413.32324		75.50684	48.8465
2	23.611	VB	1.0660	4621.75977		65.18178	51.1535



#	[min]		[min]	mAU *s	[mAU]	%
1	21.500	MM	0.8931	3840.21533	71.66099	50.2825
2	23.616	MM	1.0597	3797.06421	59.72063	49.7175