Catalytic Enantioselective Synthesis of 3,4-Unsubstituted Thiochromenes through Sulfa-Michael/Julia-Kocienski Olefination Cascade Reaction

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SUPPORTING INFORMATION

Optimization of catalyst and reaction conditions:

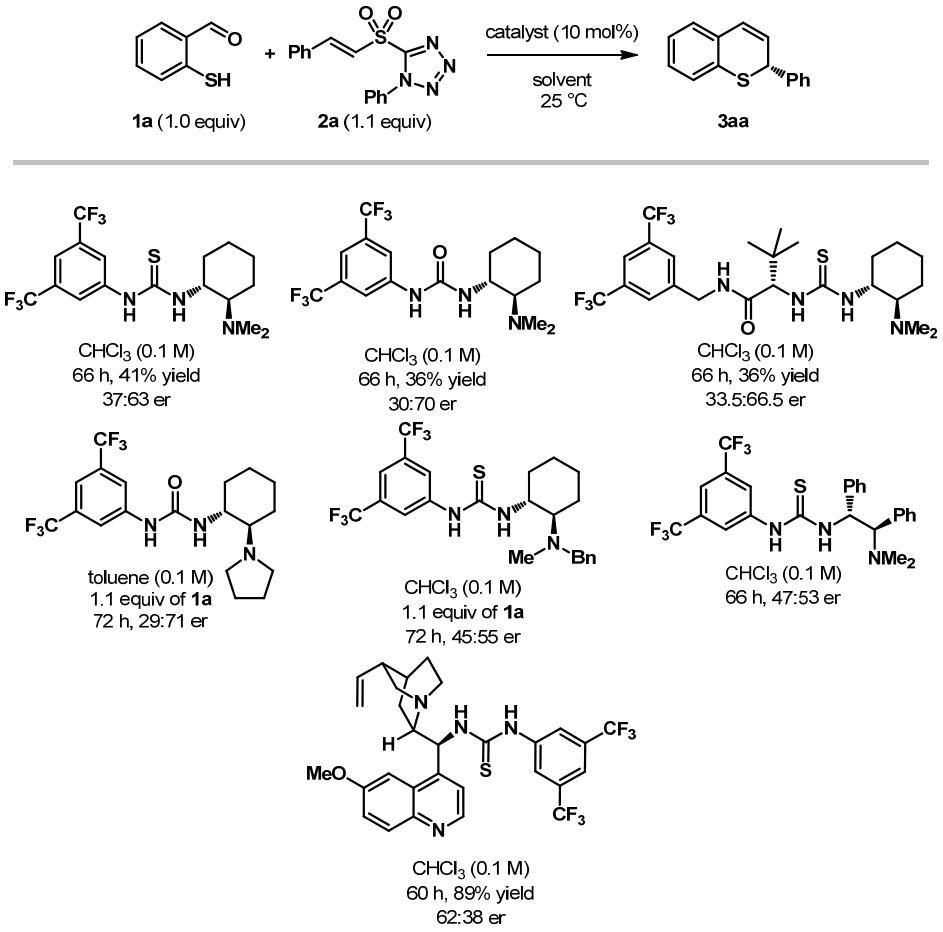


Figure S1. Bifunctional catalyst screening

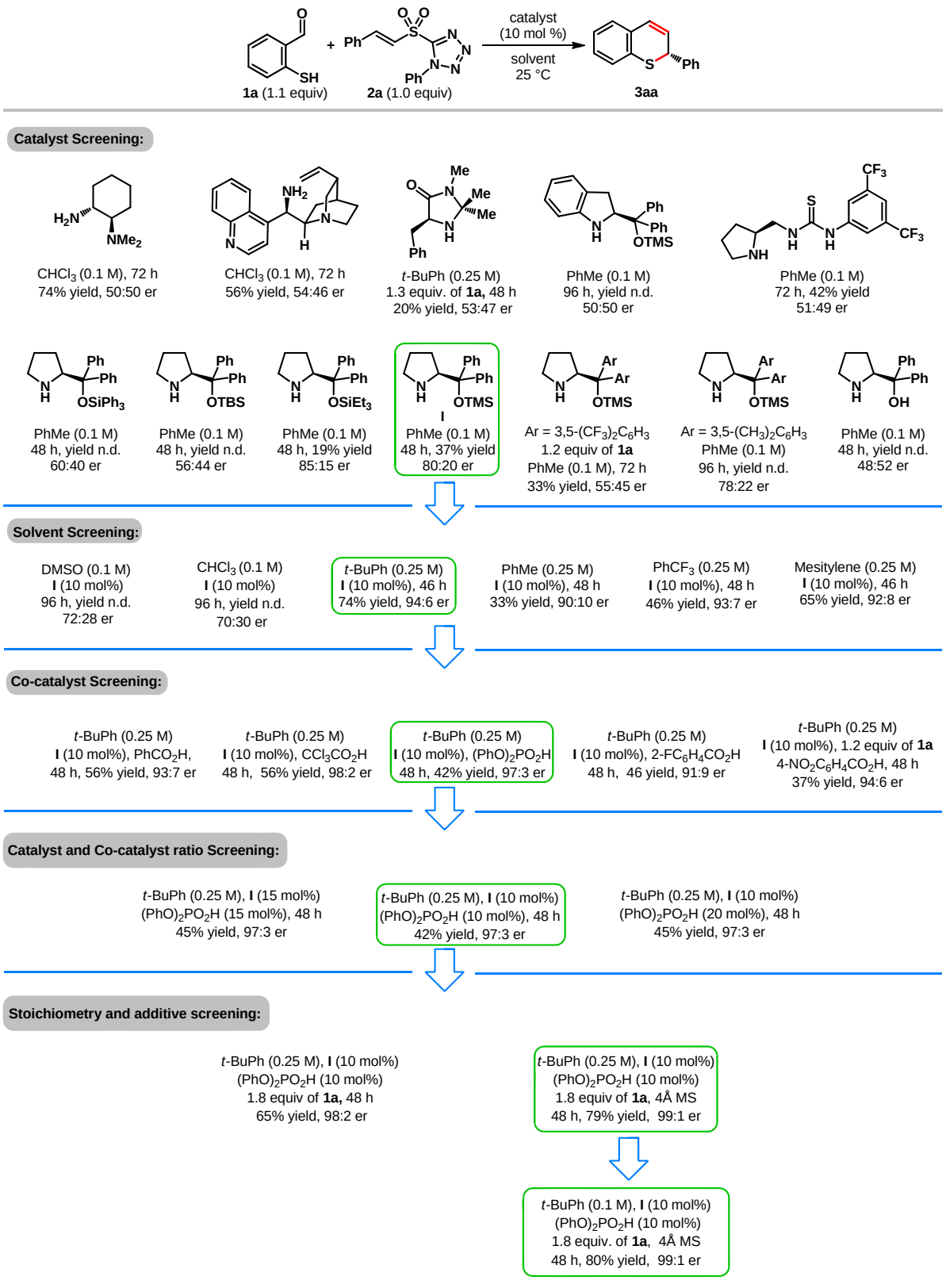
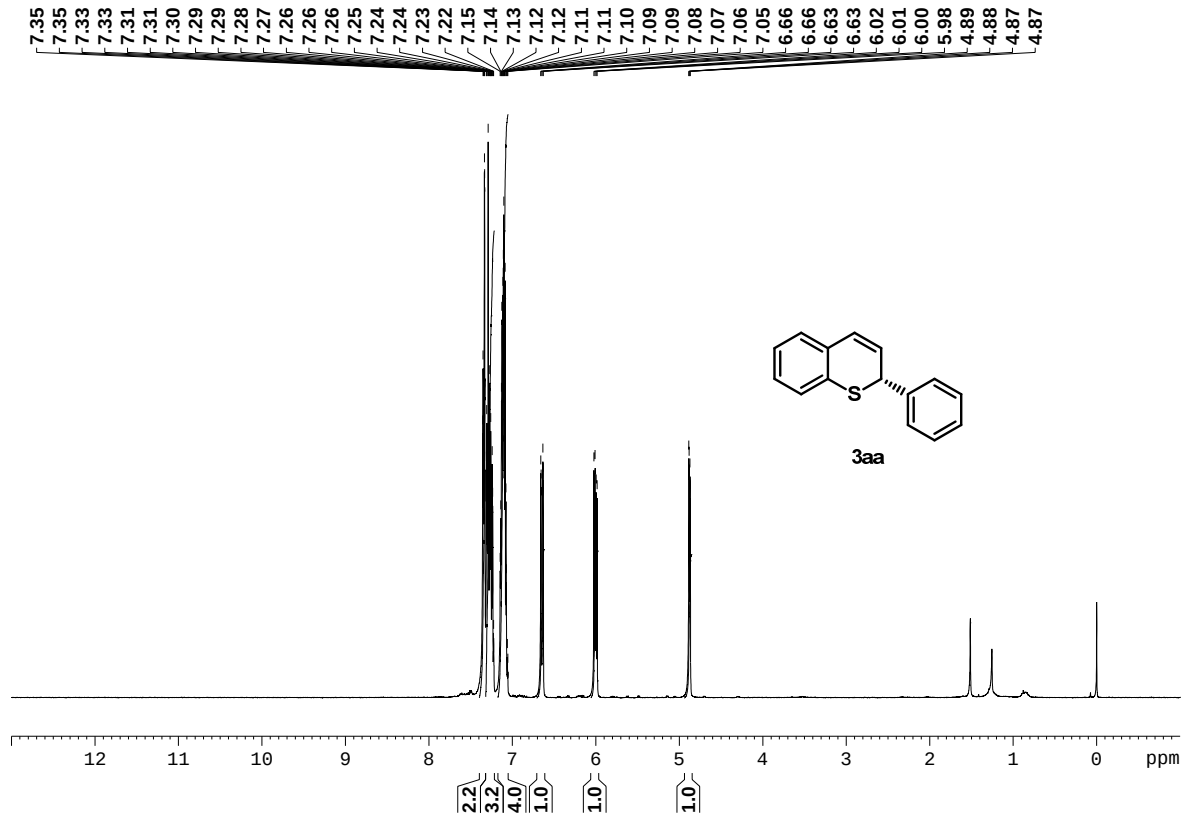
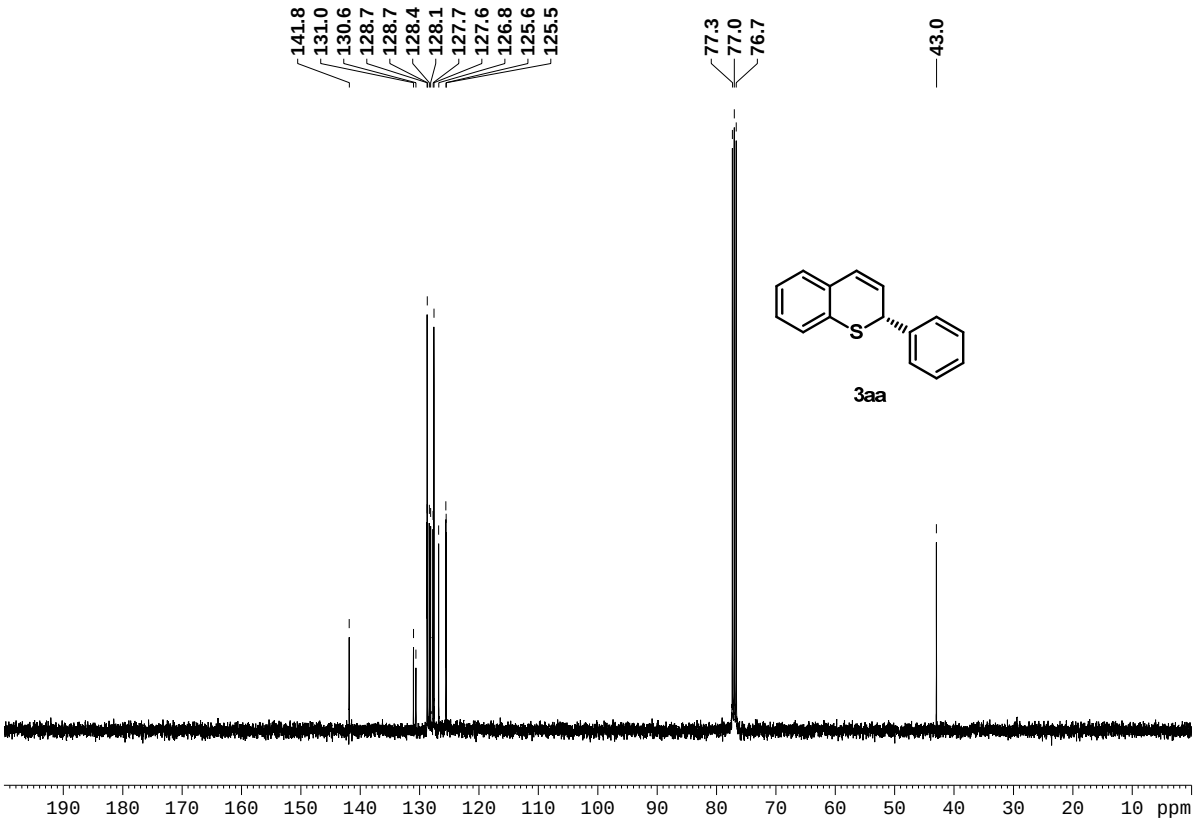
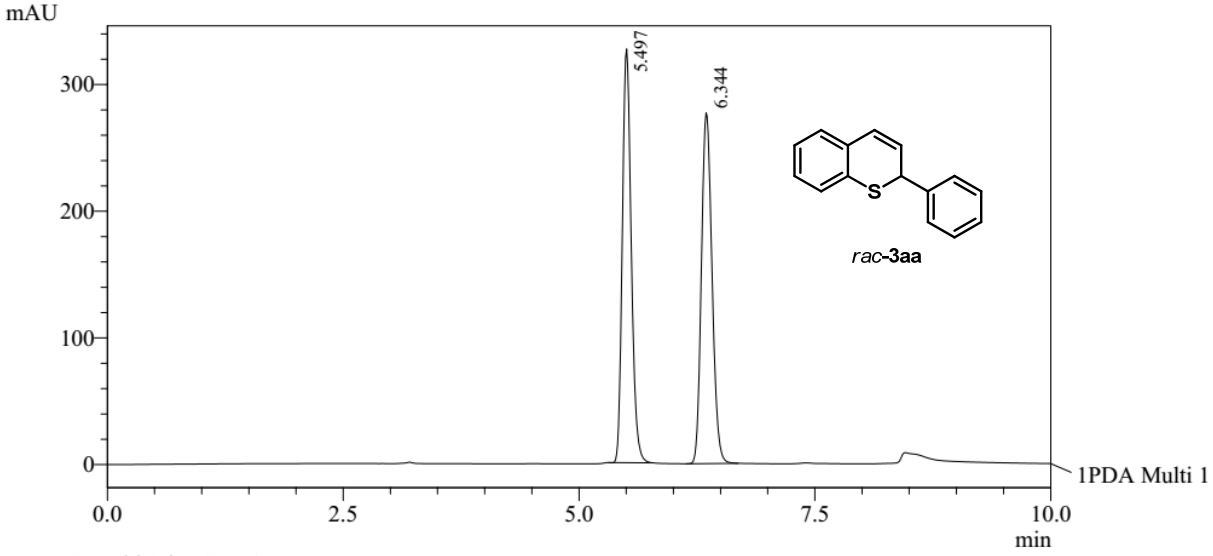


Figure S2. Optimization of reaction conditions with amine catalyst


7.35 7.35 7.33 7.33 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.15 7.14 7.13 7.12 7.12 7.11 7.11 7.10 7.09 7.09 7.08 7.07 7.06 7.05 6.66 6.66 6.63 6.63 6.02 6.01 6.00 5.98 4.89 4.88 4.87 4.87
S
3aa
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.2 3.2 4.0 1.0 1.0 1.0


141.8 131.0 130.6 128.7 128.7 128.4 128.1 127.7 127.6 126.8 125.6 125.5
77.3 77.0 76.7
43.0
S
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



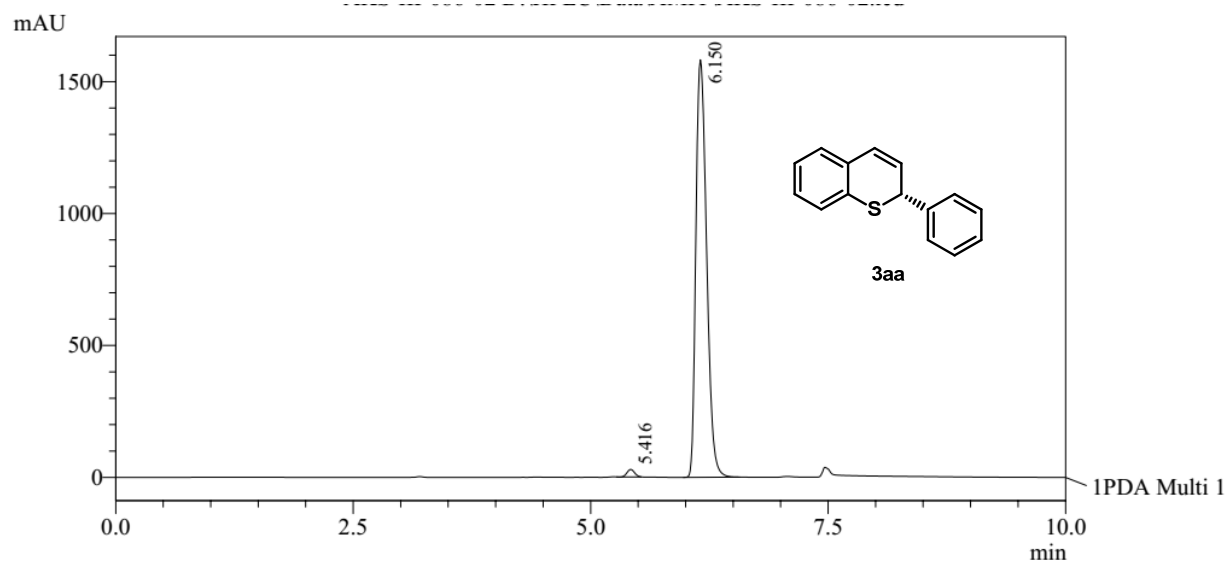
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.497	2145121	49.809
2	6.344	2161532	50.191
Total		4306652	100.000

Daicel Chiralpak IF column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

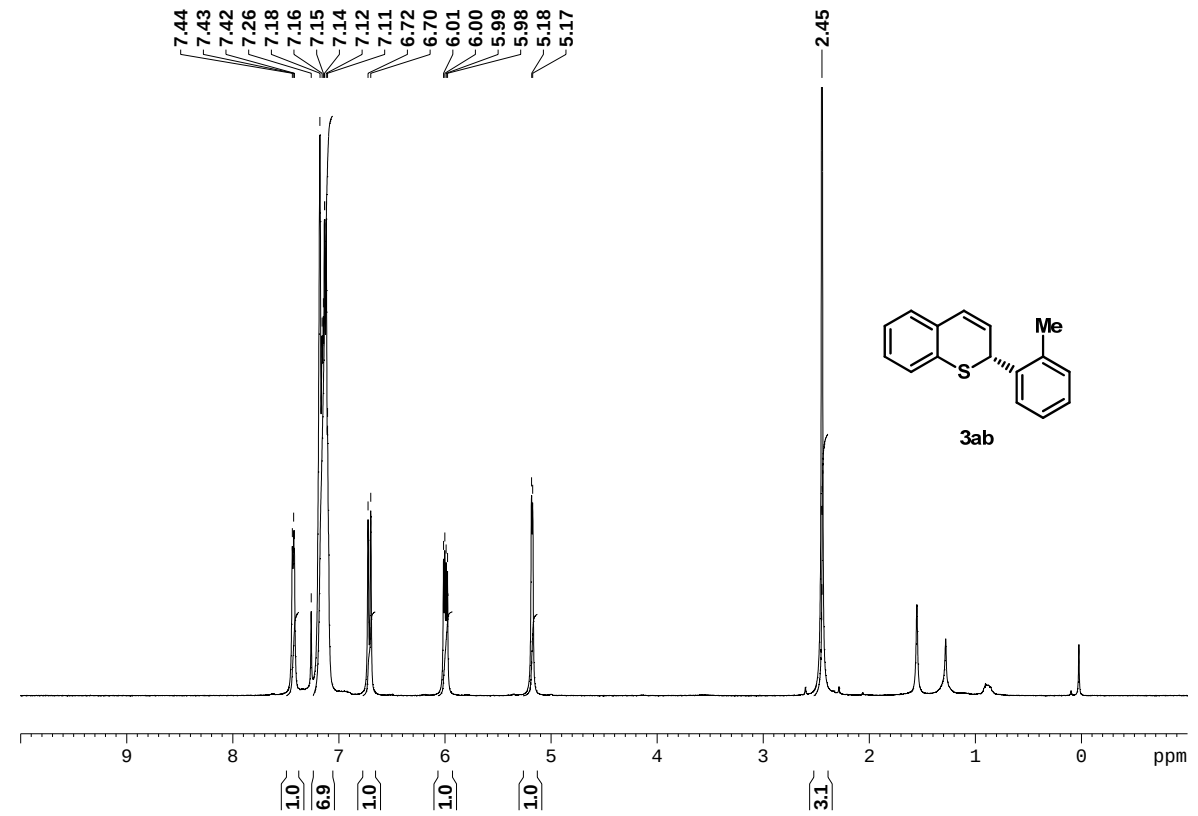


1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.416	155202	1.234
2	6.150	12426083	98.766
Total		12581286	100.000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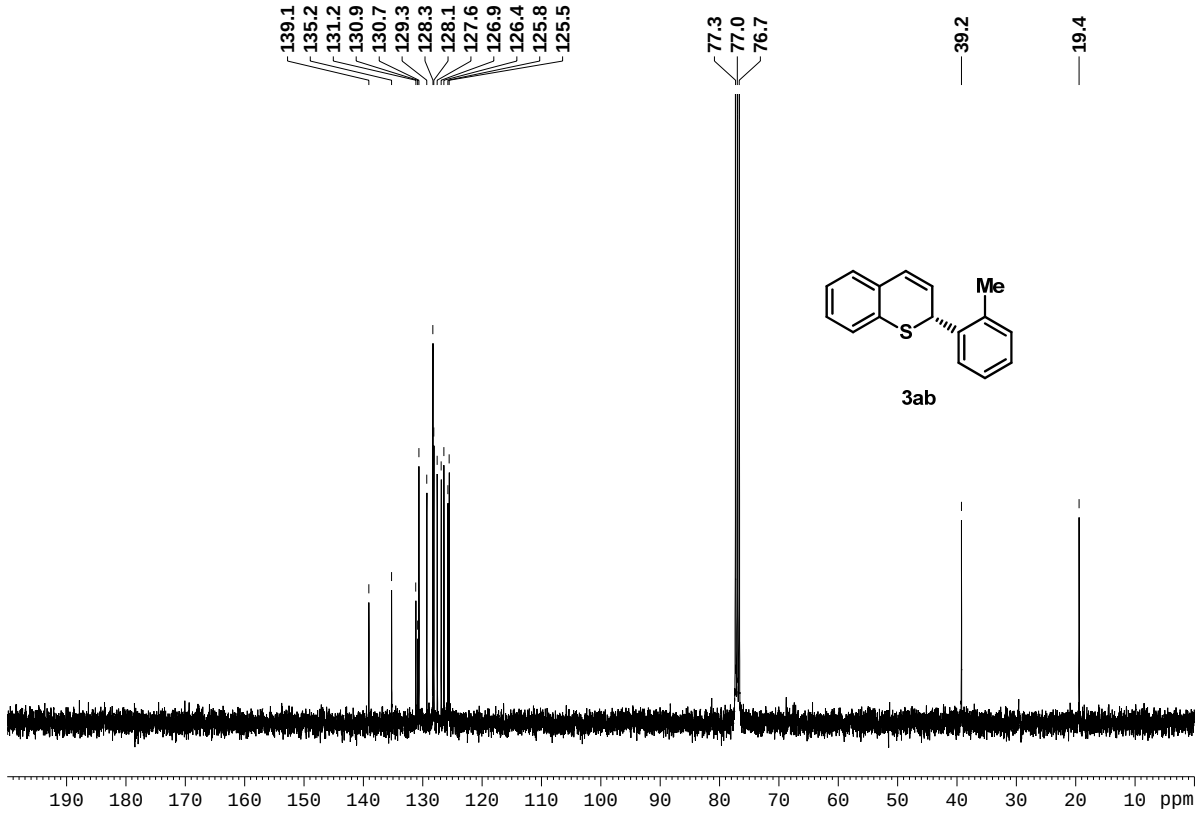
7.43
7.42
7.26
7.18
7.16
7.15
7.14
7.12
7.11
6.72
6.70
6.01
6.00
5.99
5.98
5.18
5.17
2.45
Me
S
3ab
9
8
7
6
5
4
3
2
1
0
ppm
1.0
6.9
1.0
1.0
1.0
3.1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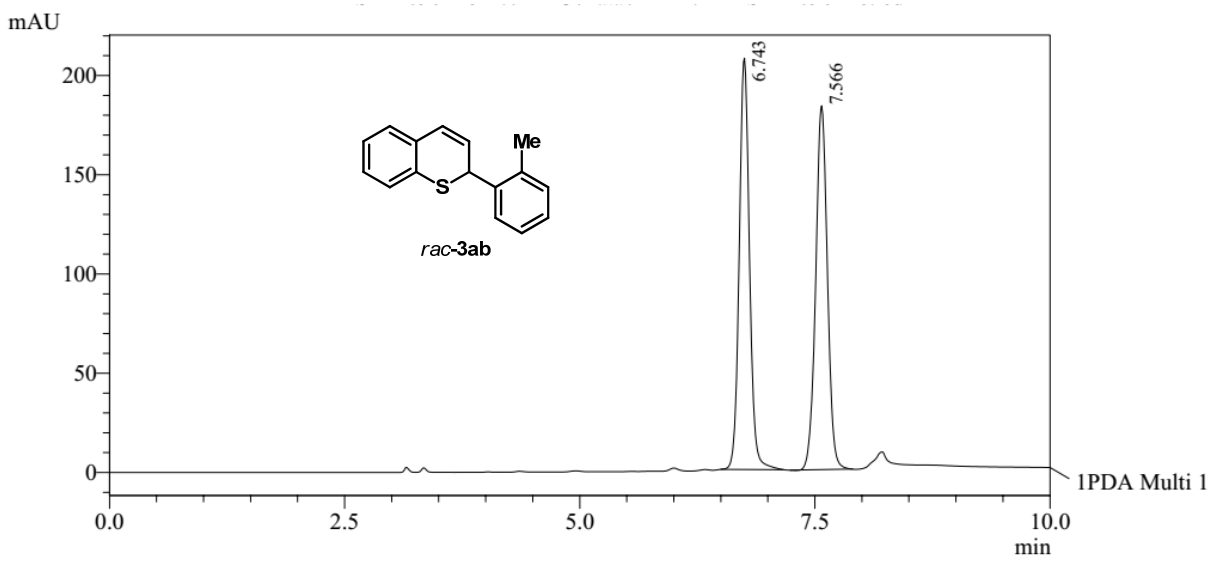
135.2
131.2
130.9
130.7
129.3
128.3
128.1
127.6
126.9
126.4
125.8
125.5
77.3
77.0
76.7
39.2
19.4
Me
S
3ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



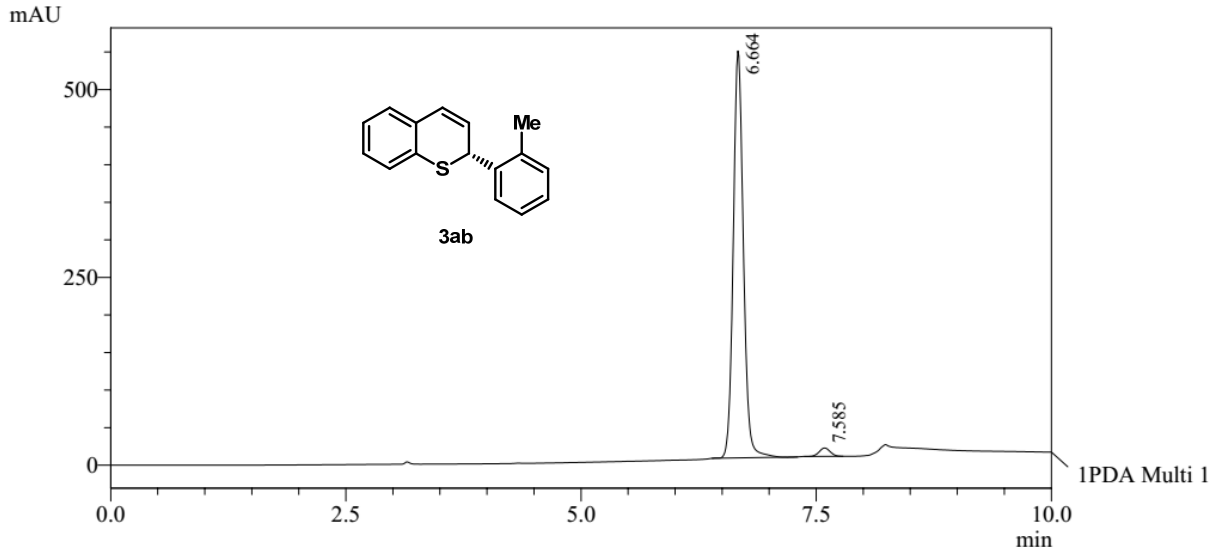
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.743	1573025	49.808
2	7.566	1585129	50.192
Total		3158154	100.000

Daicel Chiralpak IB column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

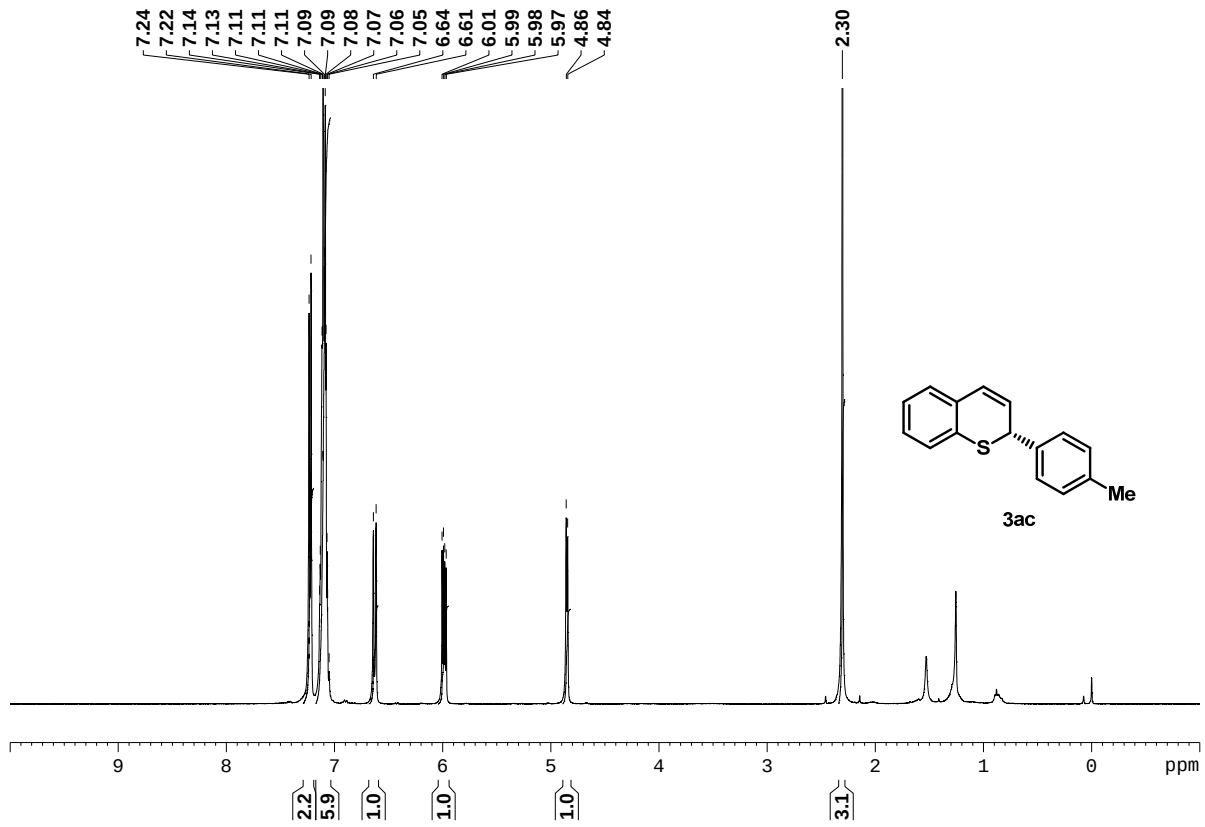


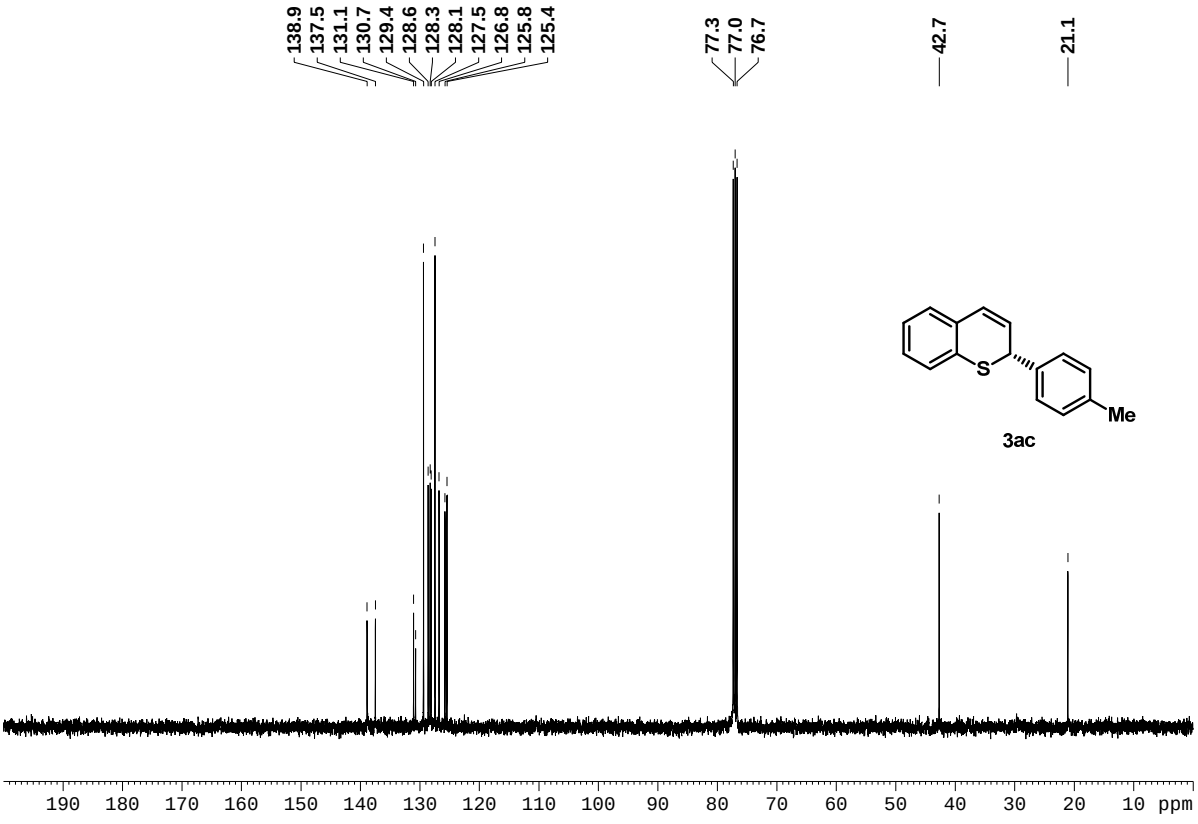
1 PDA Multi 1 / 254nm 4nm

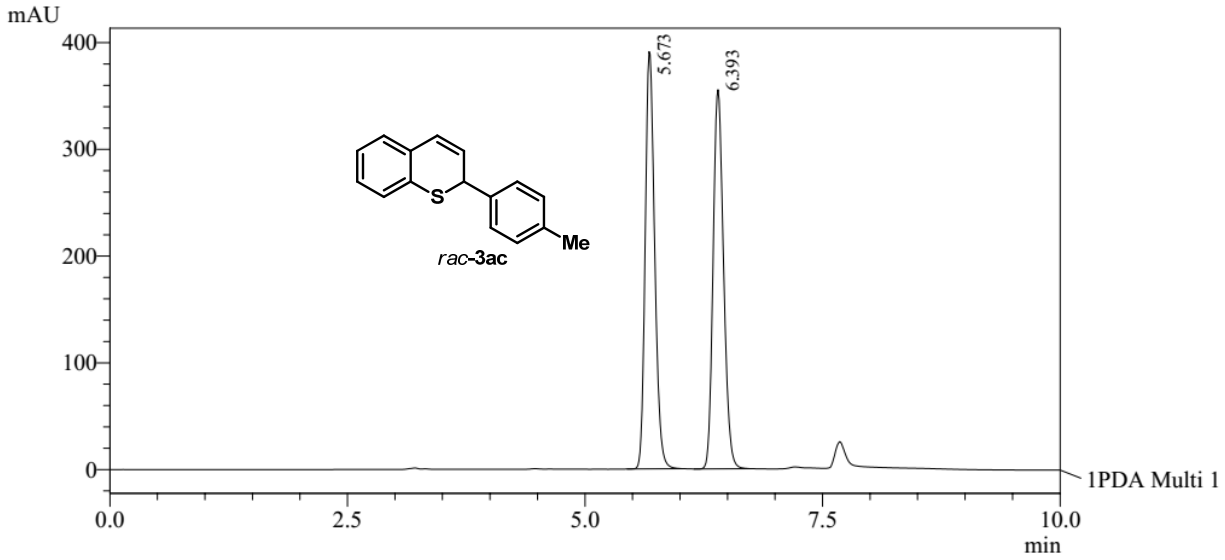
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.664	4060821	97.816
2	7.585	90676	2.184
Total		4151498	100.000


7.24
7.22
7.14
7.13
7.11
7.11
7.11
7.09
7.09
7.08
7.07
7.06
7.05
6.64
6.61
6.01
5.99
5.98
5.97
4.86
4.84
2.30
S
Me
3ac
9
8
7
6
5
4
3
2
1
0
ppm
2.2
5.9
1.0
1.0
1.0
3.1


138.9
137.5
131.1
130.7
129.4
128.6
128.3
128.1
127.5
126.8
125.8
125.4
77.3
77.0
76.7
42.7
21.1
S
Me
3ac
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



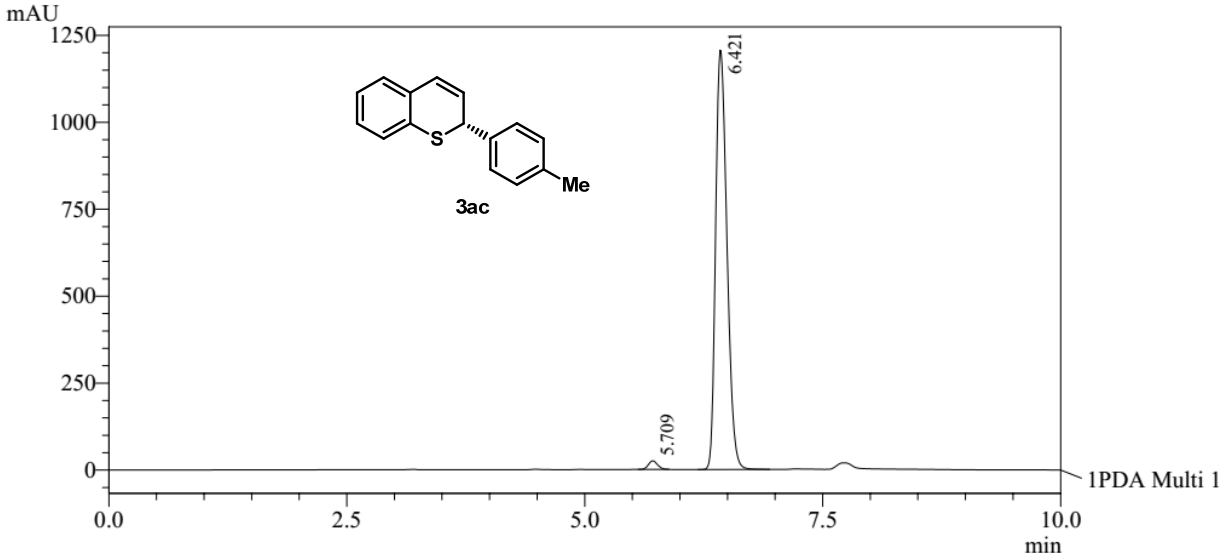
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.673	2714428	49.958
2	6.393	2718979	50.042
Total		5433406	100.000

Daicel Chiralpak IF column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

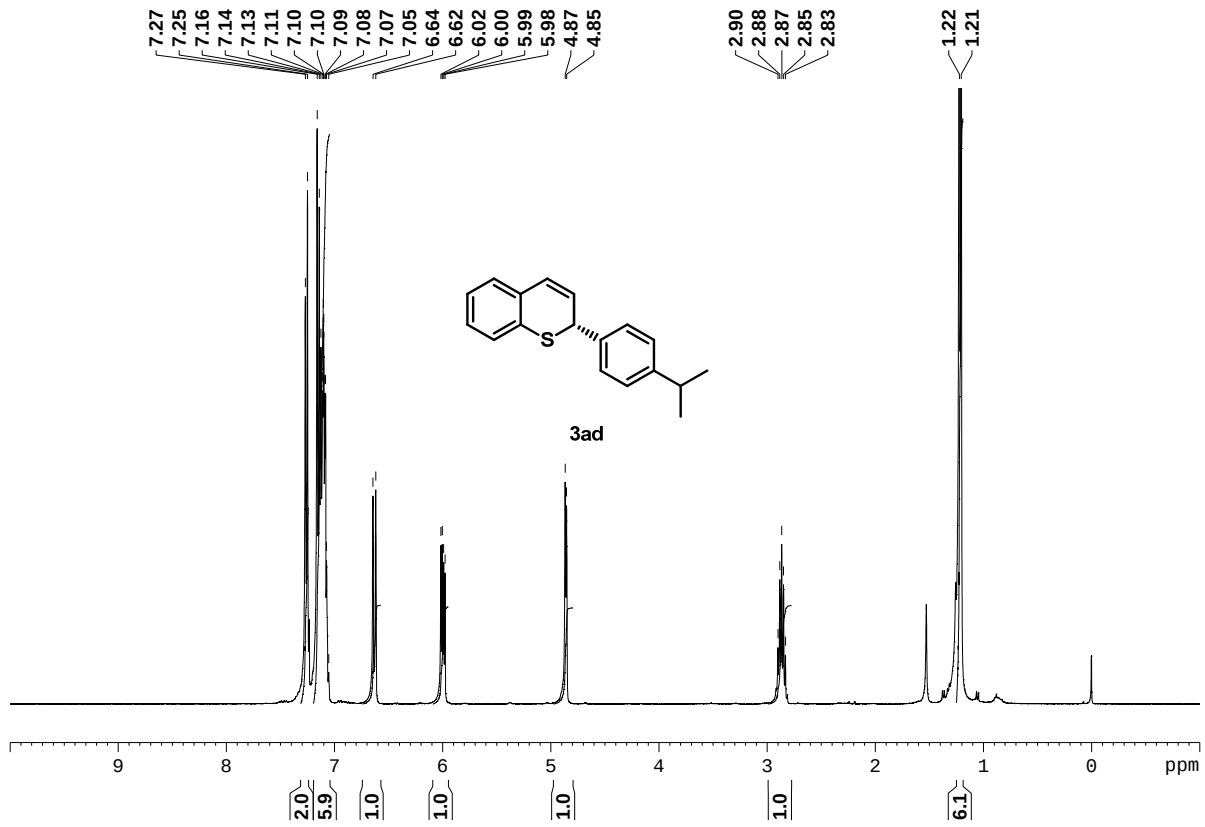


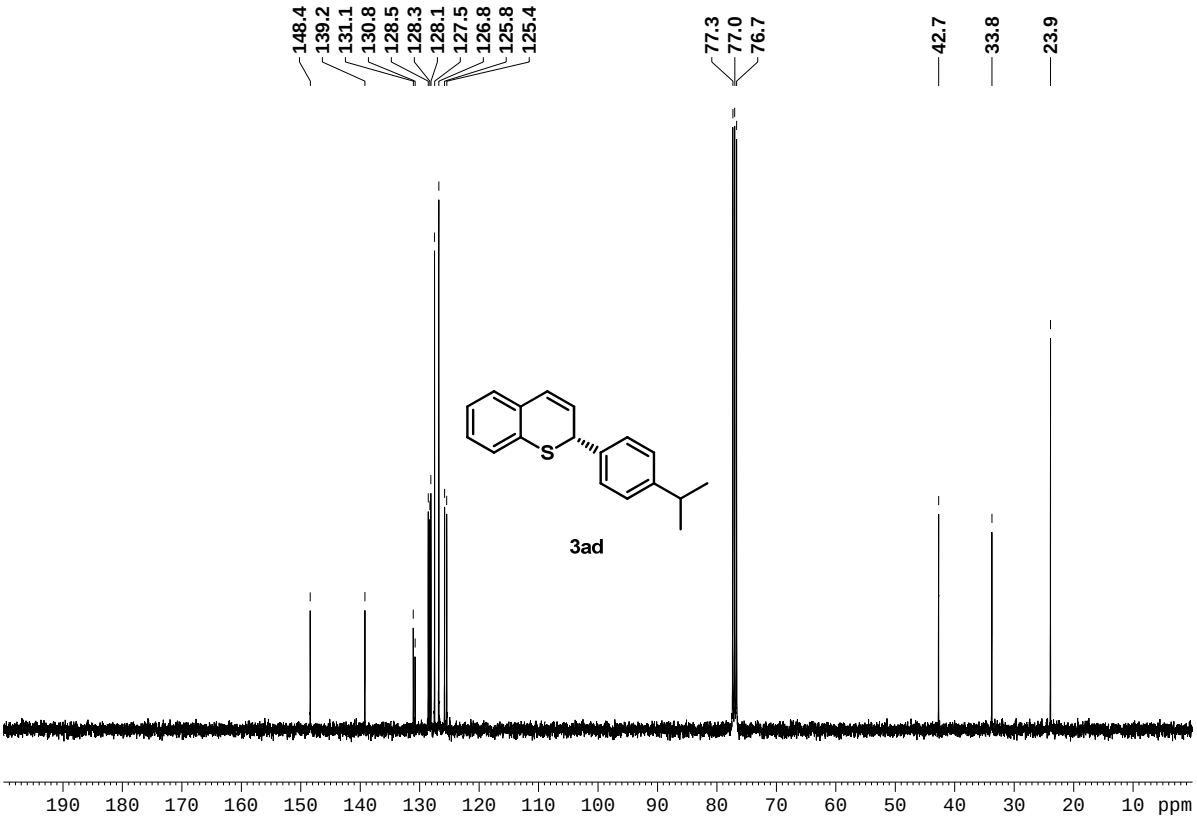
1 PDA Multi 1 / 254nm 4nm

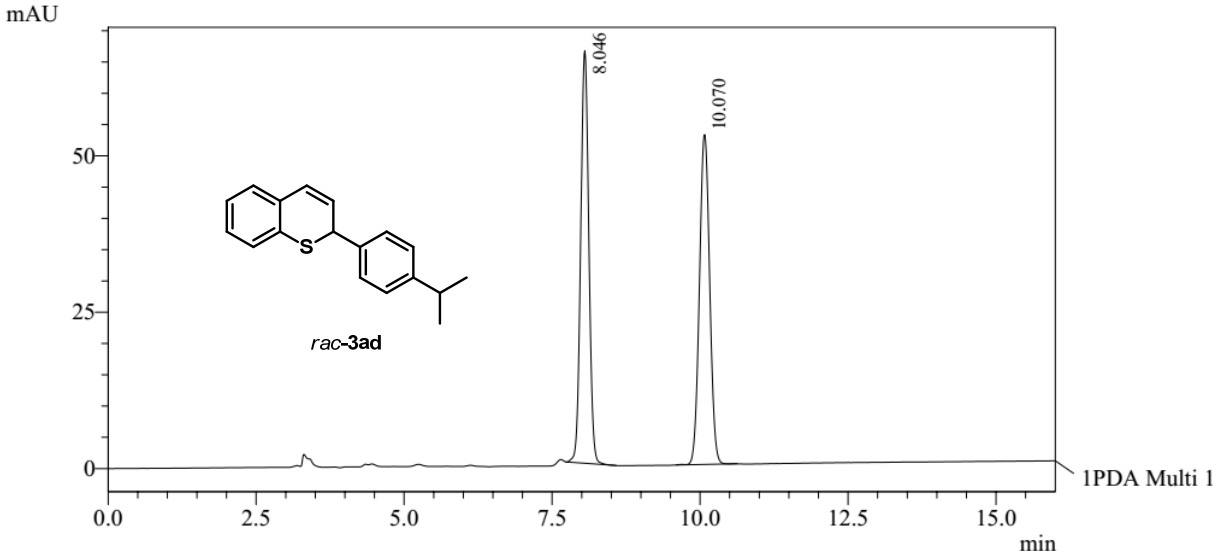
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.709	165267	1.627
2	6.421	9993421	98.373
Total		10158688	100.000


7.27
7.25
7.16
7.14
7.13
7.11
7.10
7.10
7.09
7.08
7.07
7.05
6.64
6.62
6.02
6.00
5.99
5.98
4.87
4.85
2.90
2.88
2.87
2.85
2.83
1.22
1.21
3ad
9
8
7
6
5
4
3
2
1
0
ppm
2.0
5.9
1.0
1.0
1.0
1.0
6.1


148.4
139.2
131.1
130.8
128.5
128.3
128.1
127.5
126.8
125.8
125.4
77.3
77.0
76.7
42.7
33.8
23.9
3ad
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



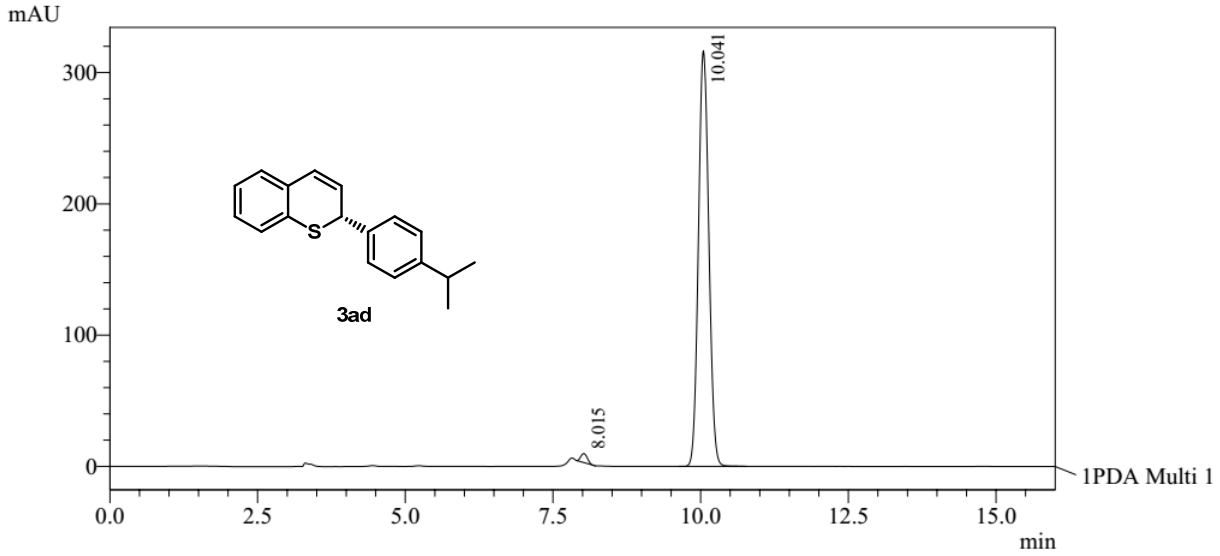
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.046	628147	49.892
2	10.070	630872	50.108
Total		1259019	100.000

Phenomenex Cellulose-3 column (97:3 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

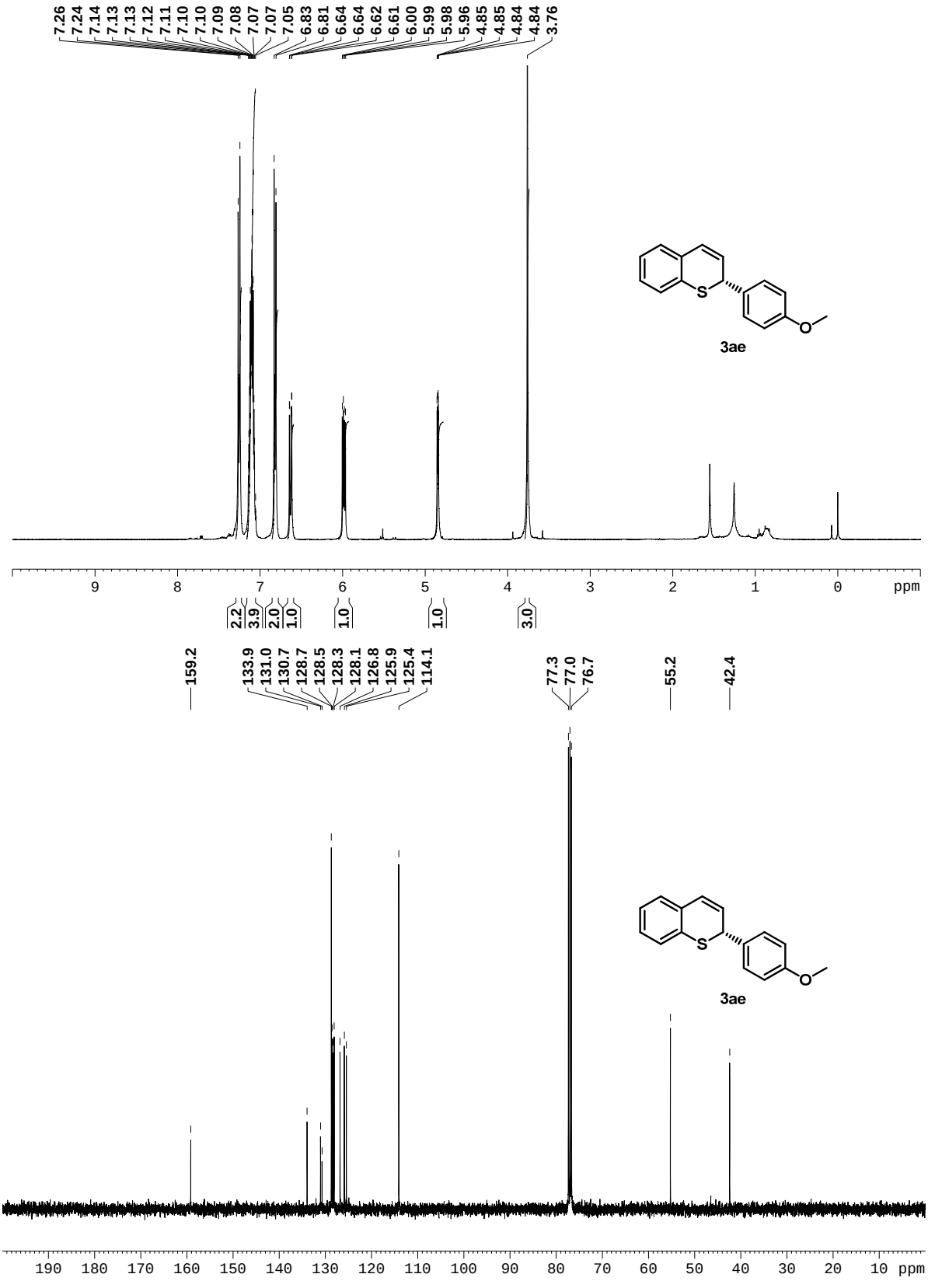


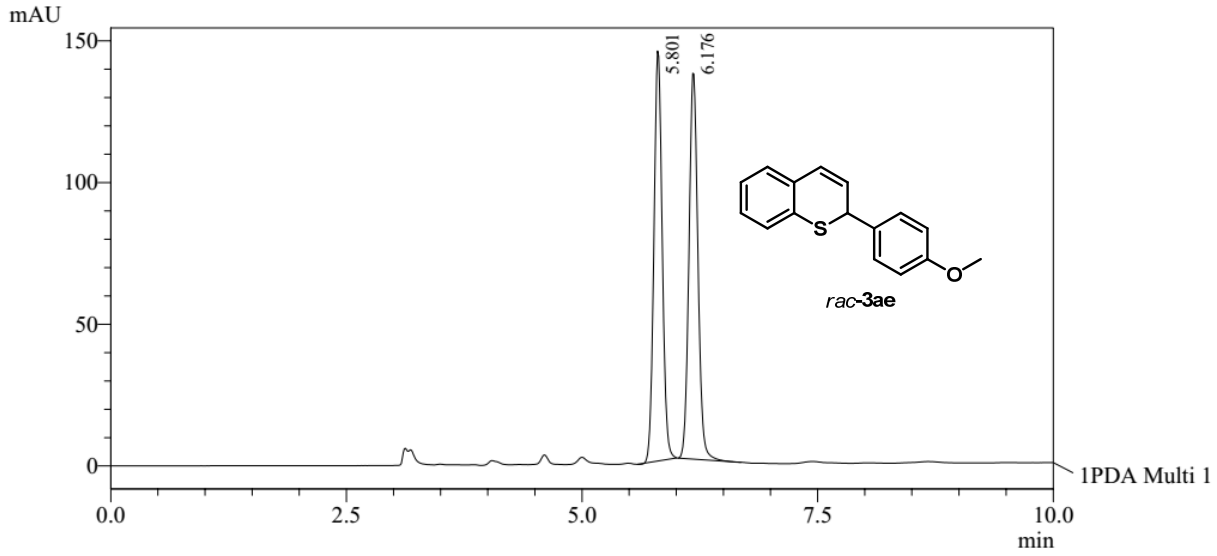
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.015	50141	1.280
2	10.041	3866619	98.720
Total		3916761	100.000


7.26
7.24
7.14
7.13
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.07
7.07
7.05
6.83
6.81
6.64
6.64
6.62
6.61
6.00
5.99
5.98
5.96
4.85
4.85
4.84
4.84
3.76
3ae
9 8 7 6 5 4 3 2 1 0 ppm
2.2
3.9
2.0
1.0
1.0
1.0
3.0
159.2
133.9
131.0
130.7
128.7
128.5
128.3
128.1
126.8
125.9
125.4
114.1
77.3
77.0
76.7
55.2
42.4
3ae
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



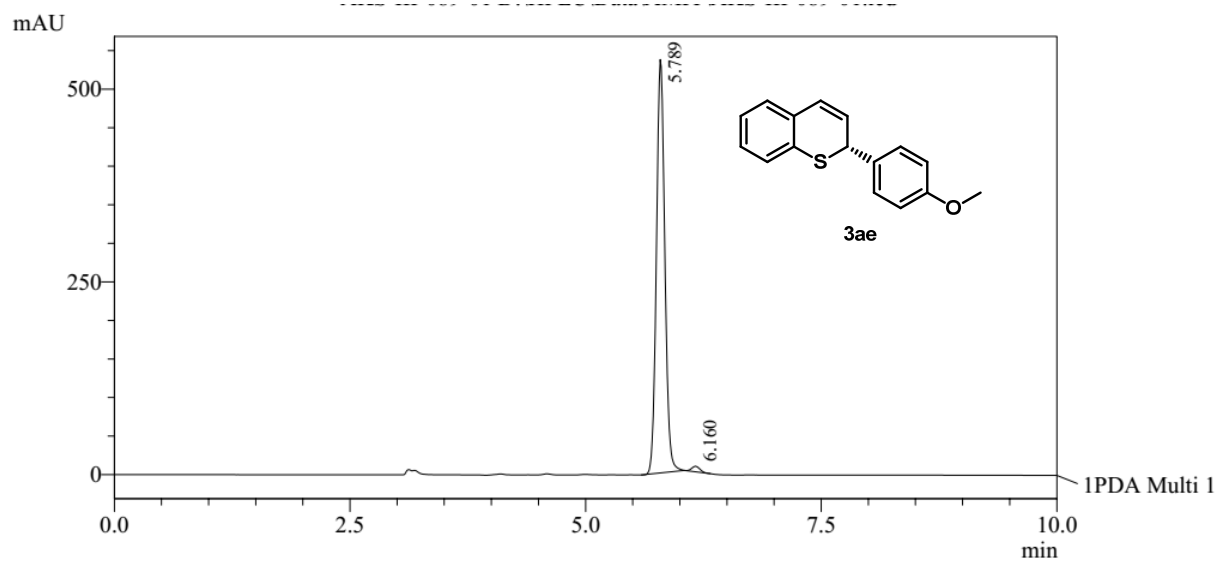
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.801	887248	49.571
2	6.176	902611	50.429
Total		1789858	100.000

Daicel Chiralpak IB column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

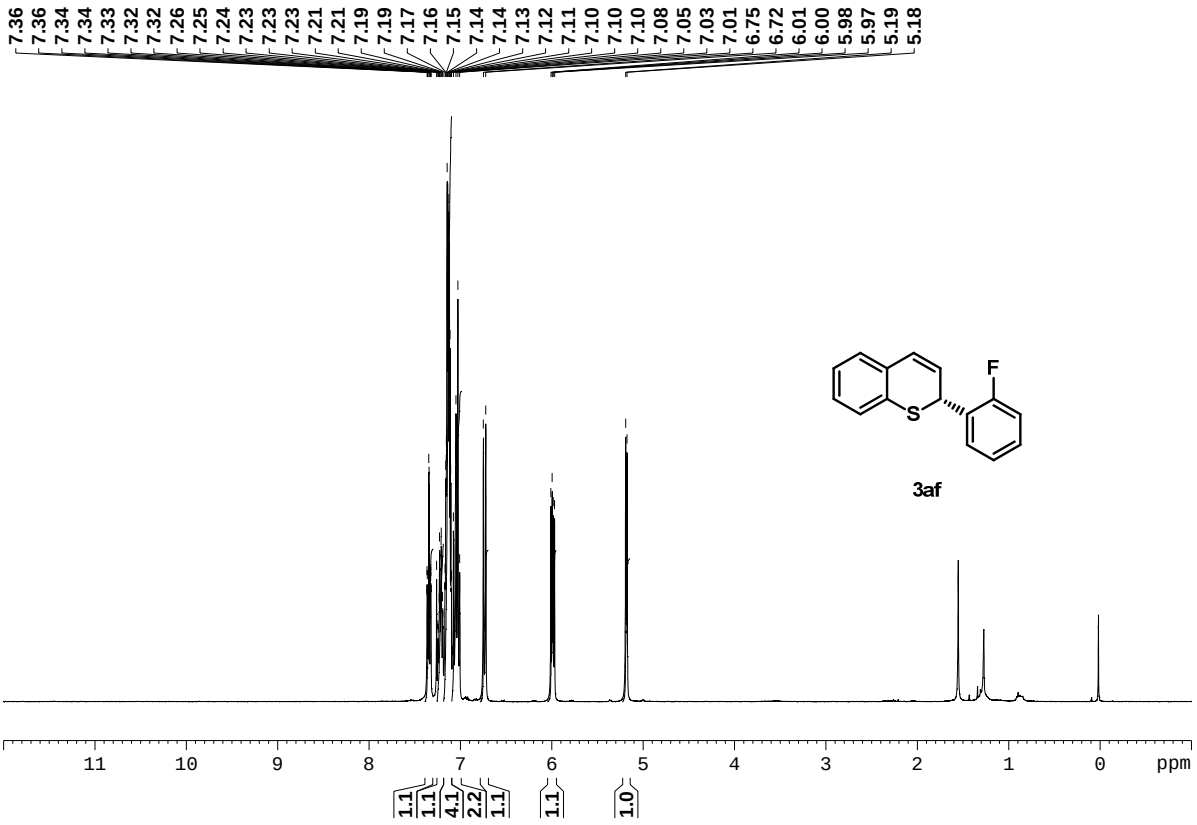


1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.789	3321021	98.744
2	6.160	42228	1.256
Total		3363250	100.000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7.34
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7.32
7.32
7.26
7.25
7.24
7.23
7.23
7.23
7.21
7.21
7.19
7.19
7.17
7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.10
7.10
7.10
7.08
7.05
7.03
7.01
6.75
6.72
6.01
6.00
5.98
5.97
5.19
5.18
F
S
3af
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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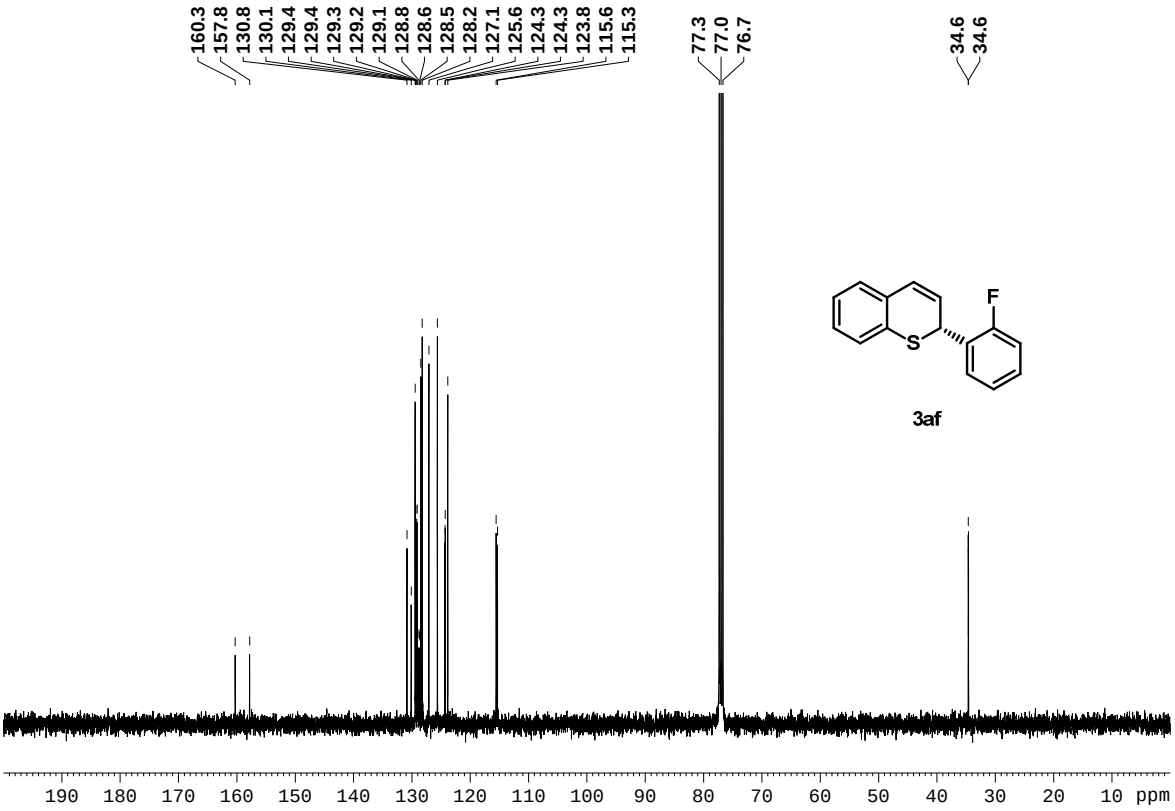
1.1
4.1
2.2
1.1
1.1
1.0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130.1
129.4
129.4
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129.2
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128.8
128.6
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128.2
127.1
125.6
124.3
124.3
123.8
115.6
115.3
77.3
77.0
76.7
34.6
34.6
F
S
3af
190
180
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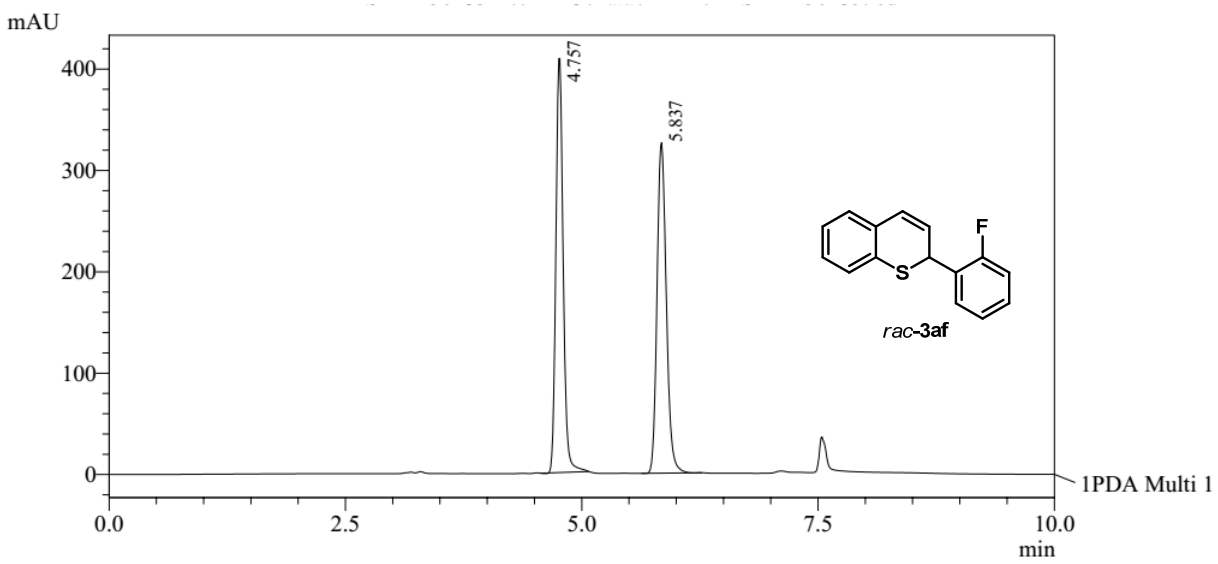
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



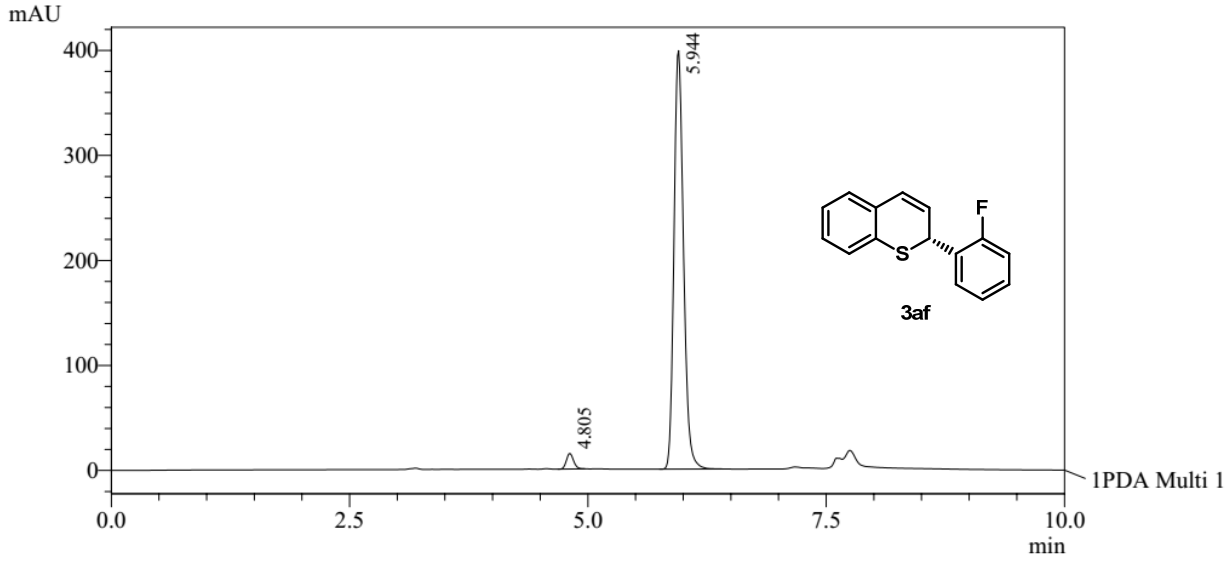
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.757	2190085	49.593
2	5.837	2226006	50.407
Total		4416091	100.000

Daicel Chiralpak IB column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

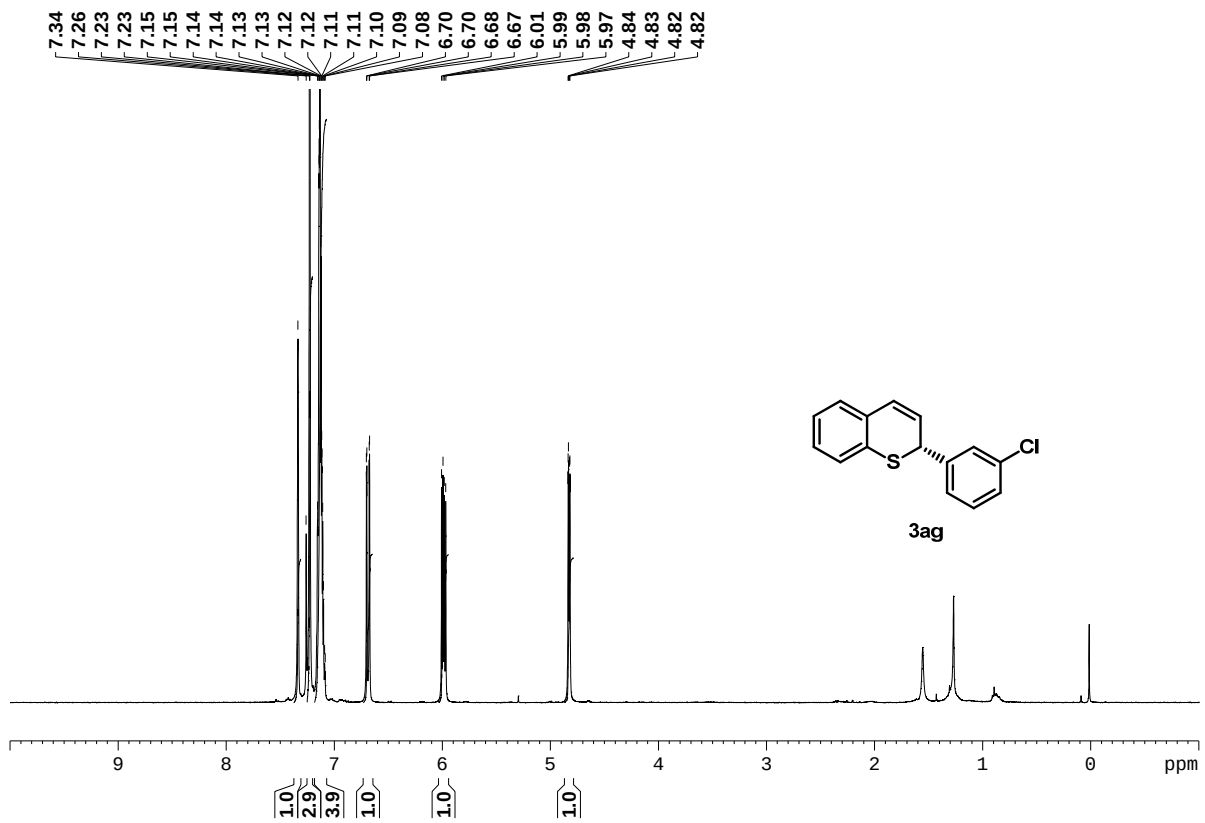


1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.805	77757	2.725
2	5.944	2776051	97.275
Total		2853807	100.000


7.34
7.26
7.23
7.23
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.08
6.70
6.70
6.68
6.67
6.01
5.99
5.98
5.97
4.84
4.83
4.82
4.82
Cl
S
3ag
9
8
7
6
5
4
3
2
1
0
ppm
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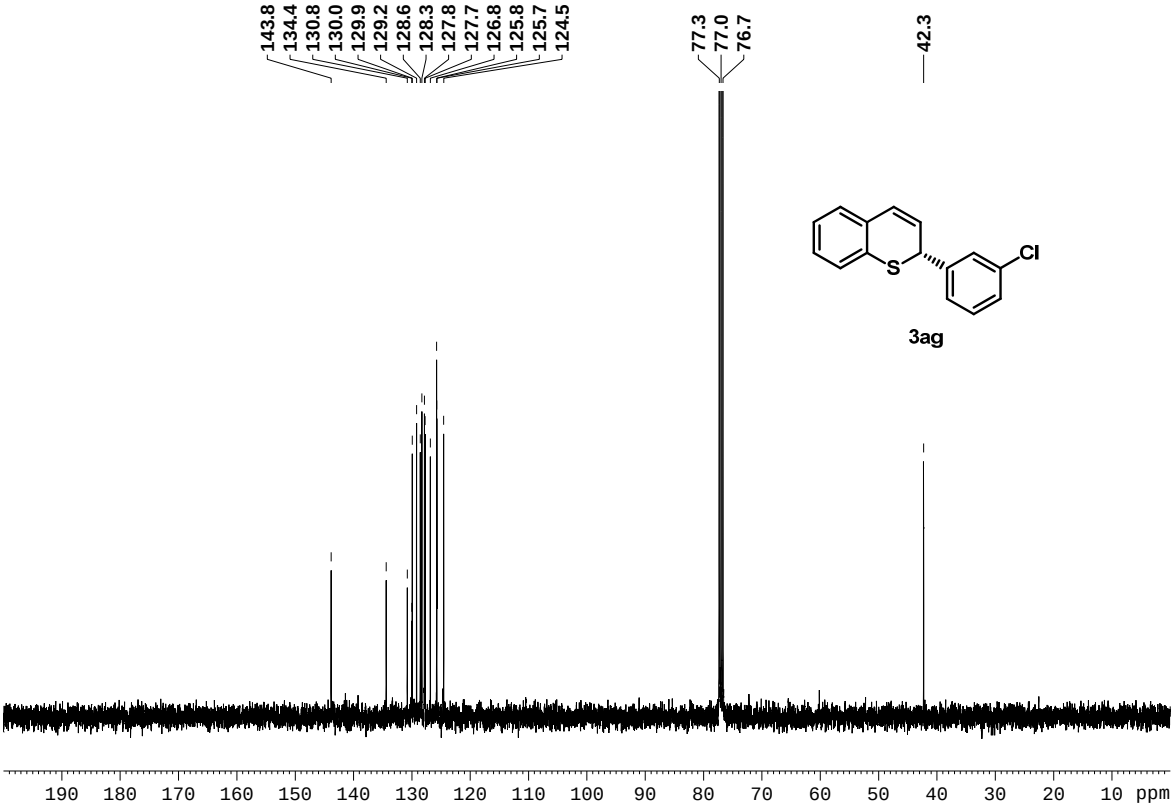
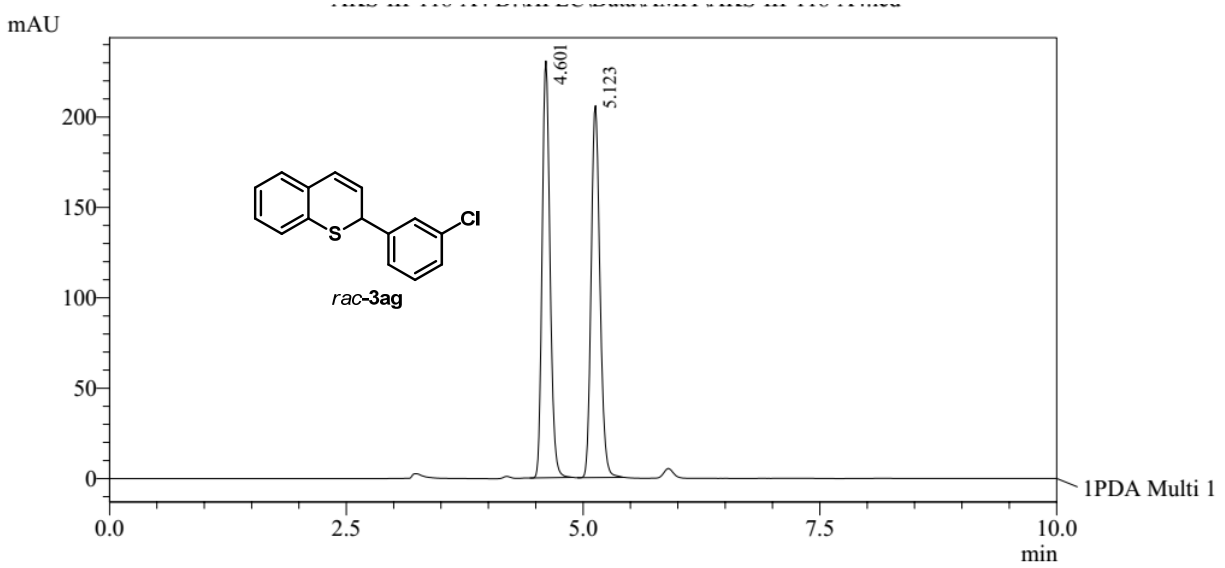
2.9
3.9
1.0
1.0
1.0


143.8
134.4
130.8
130.0
129.9
129.2
128.6
128.3
127.8
127.7
126.8
125.8
125.7
124.5
77.3
77.0
76.7
42.3
Cl
S
3ag
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



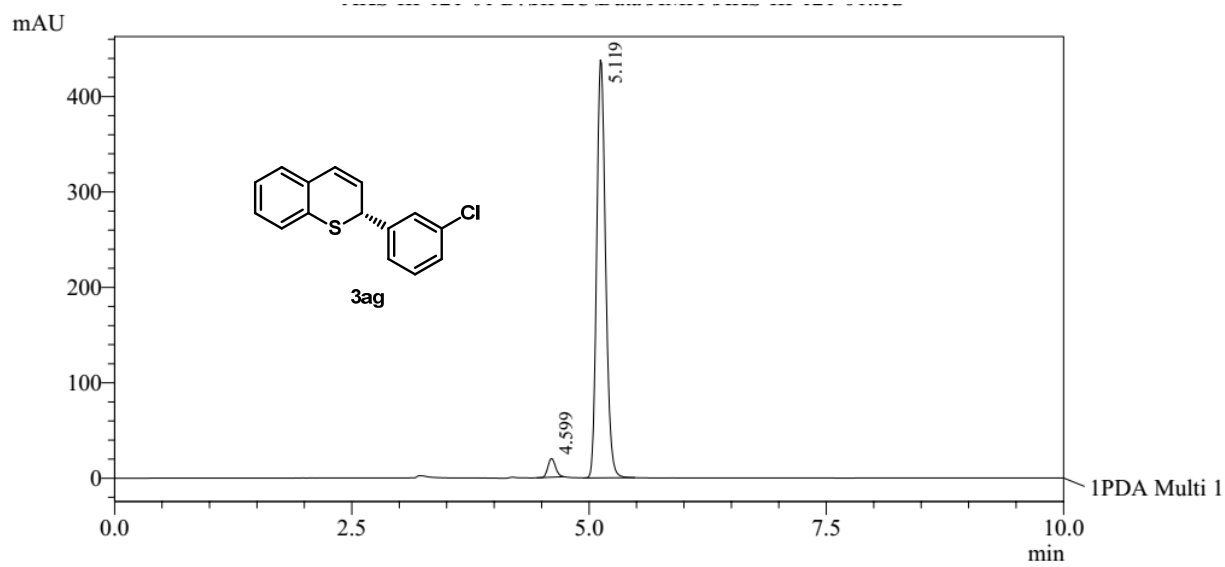
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.601	1329571	50.039
2	5.123	1327523	49.961
Total		2657093	100.000

Daicel Chiralpak IF column (97:3 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

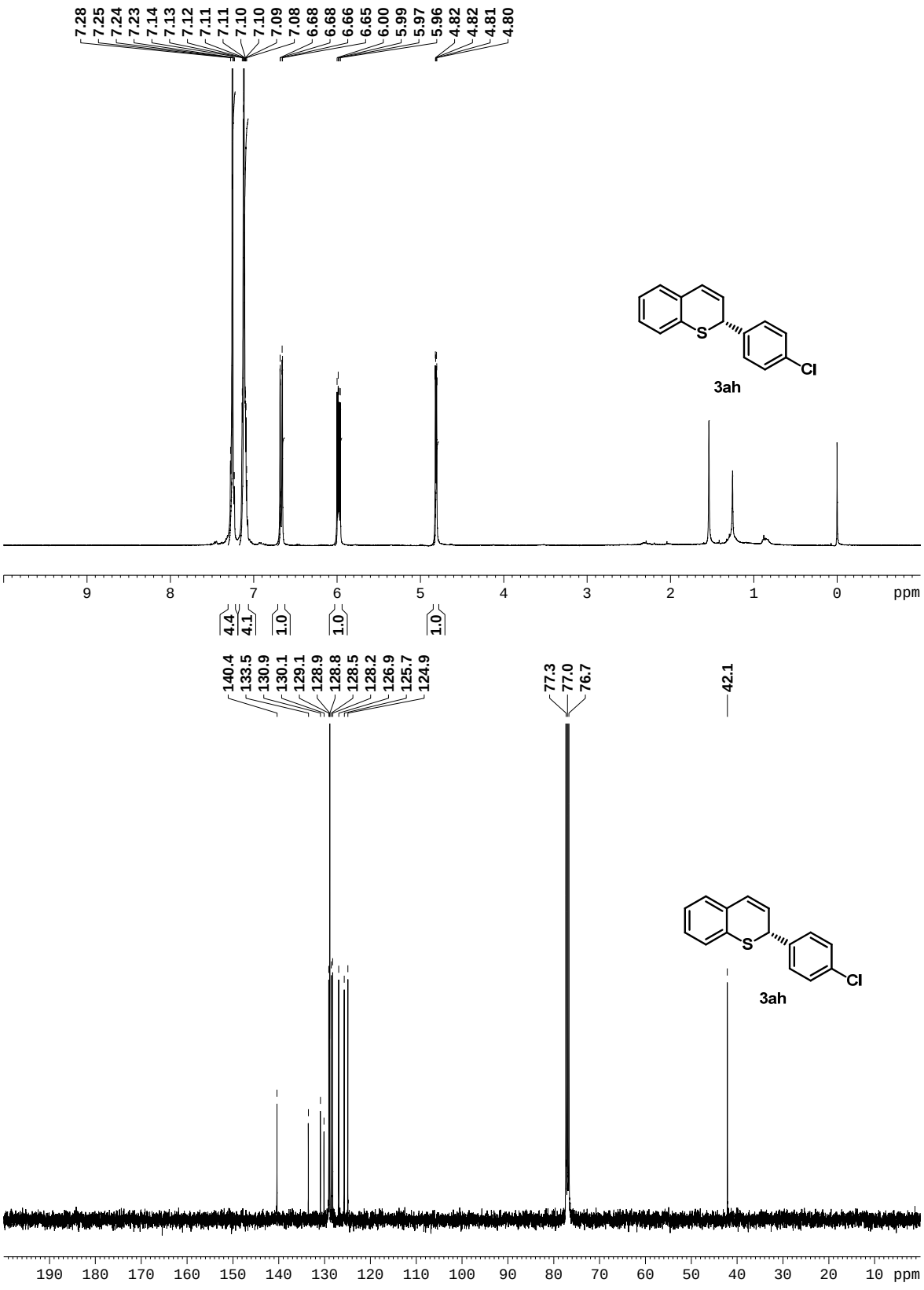


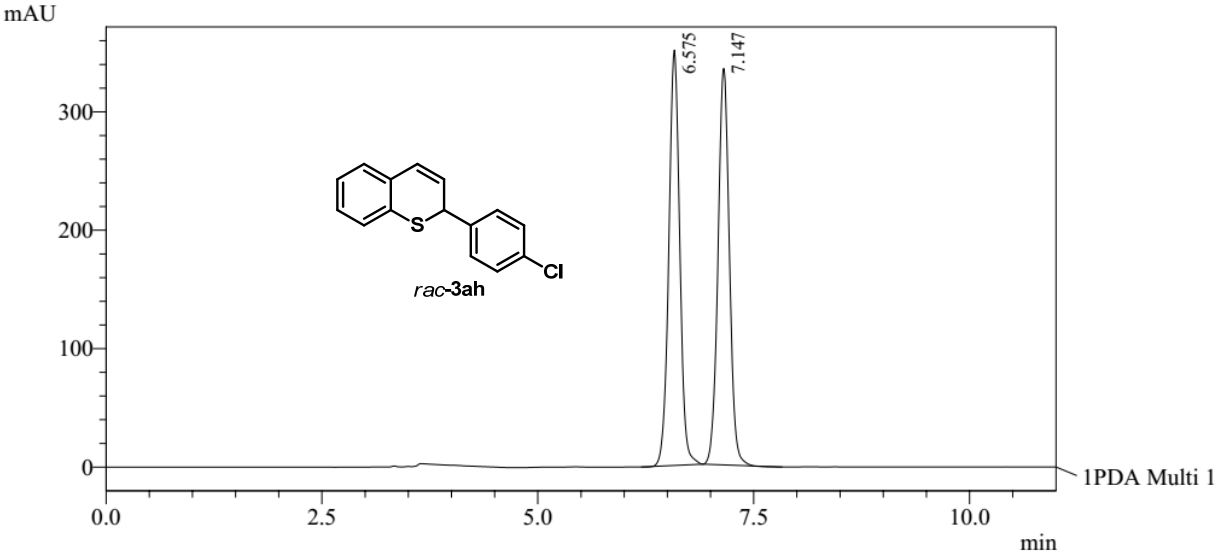
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.599	109244	3.686
2	5.119	2854644	96.314
Total		2963888	100.000


7.28
7.25
7.24
7.23
7.14
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.08
6.68
6.68
6.66
6.65
6.00
5.99
5.97
5.96
4.82
4.82
4.81
4.80
S
Cl
3ah
9
8
7
6
5
4
3
2
1
0
ppm
4.4
4.1
1.0
1.0
1.0
140.4
133.5
130.9
130.1
129.1
128.9
128.8
128.5
128.2
126.9
125.7
124.9
77.3
77.0
76.7
42.1
S
Cl
3ah
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



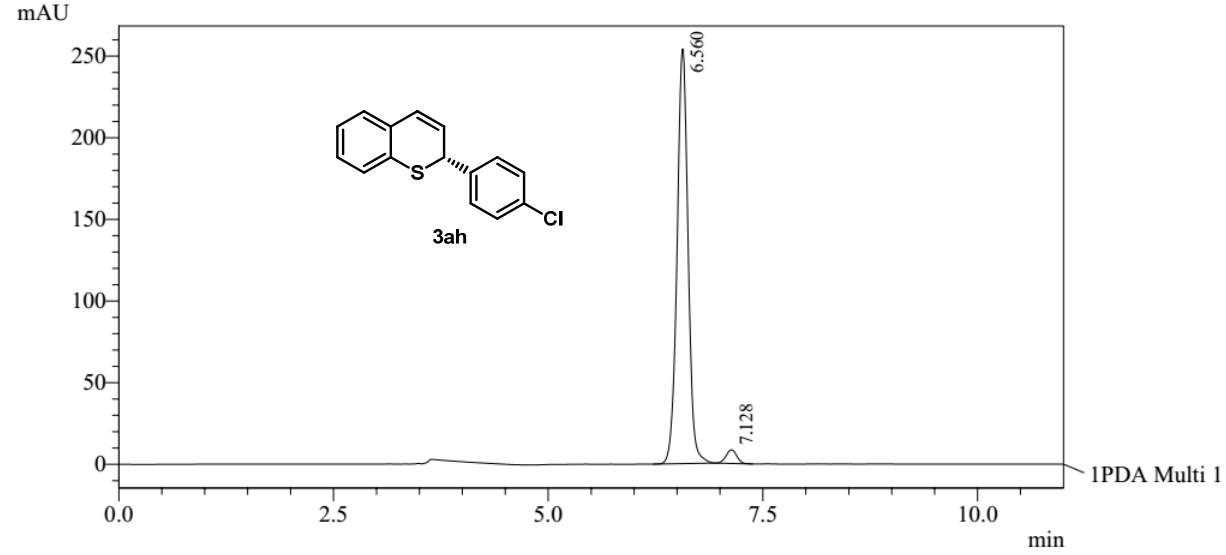
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.575	3089189	50.179
2	7.147	3067186	49.821
Total		6156375	100.000

Daicel Chiralpak IB column (99:1 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

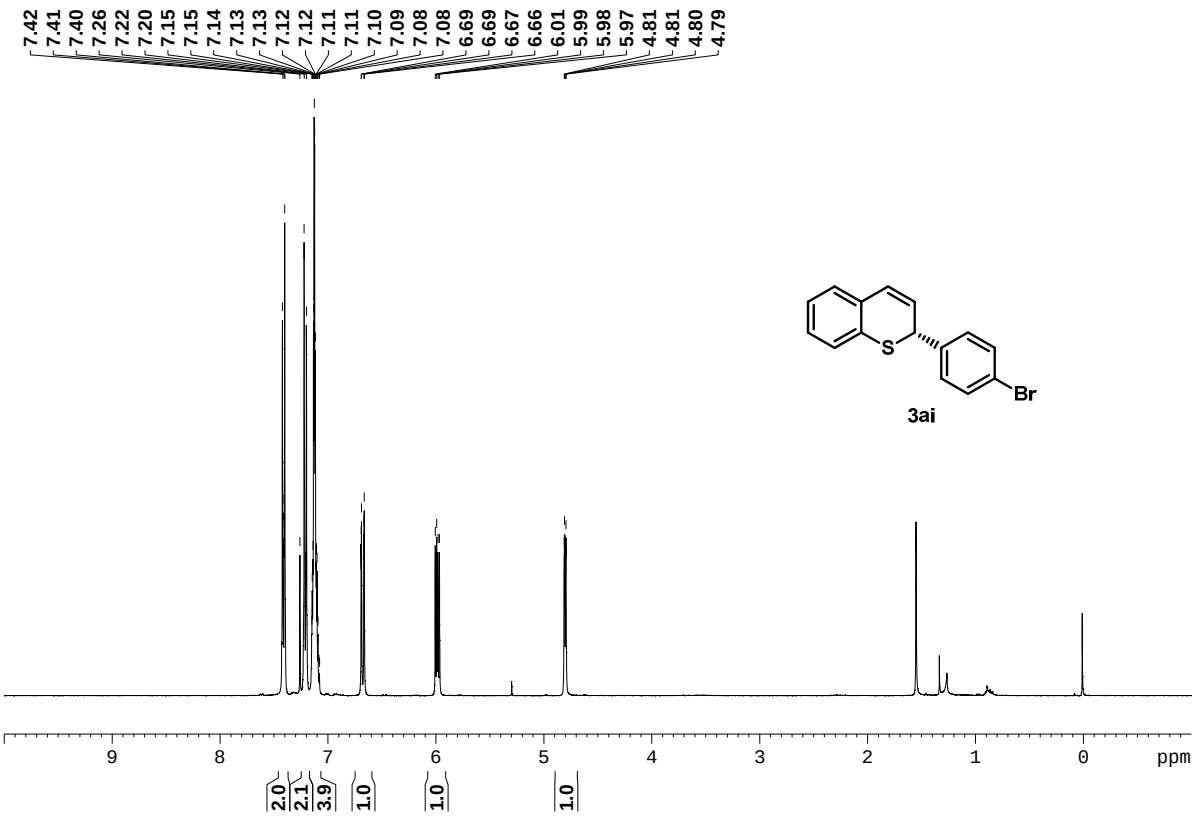


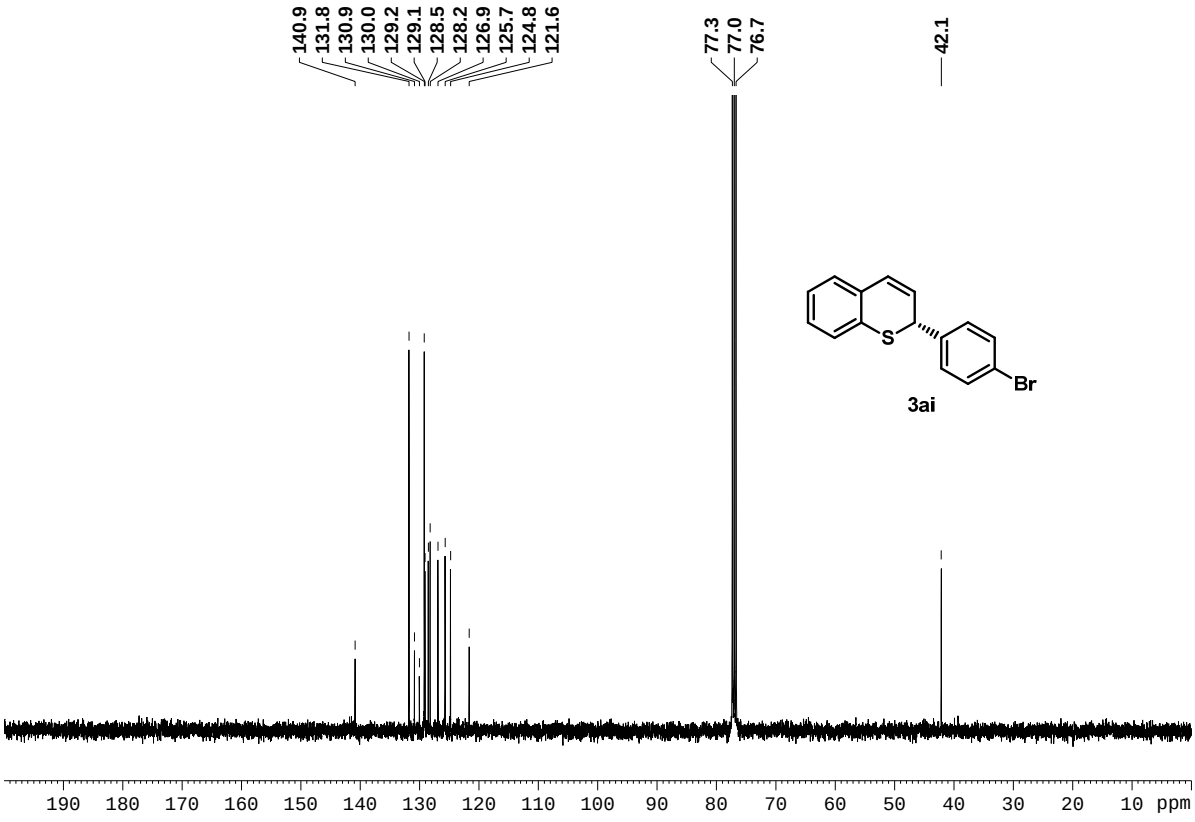
1 PDA Multi 1 / 254nm 4nm

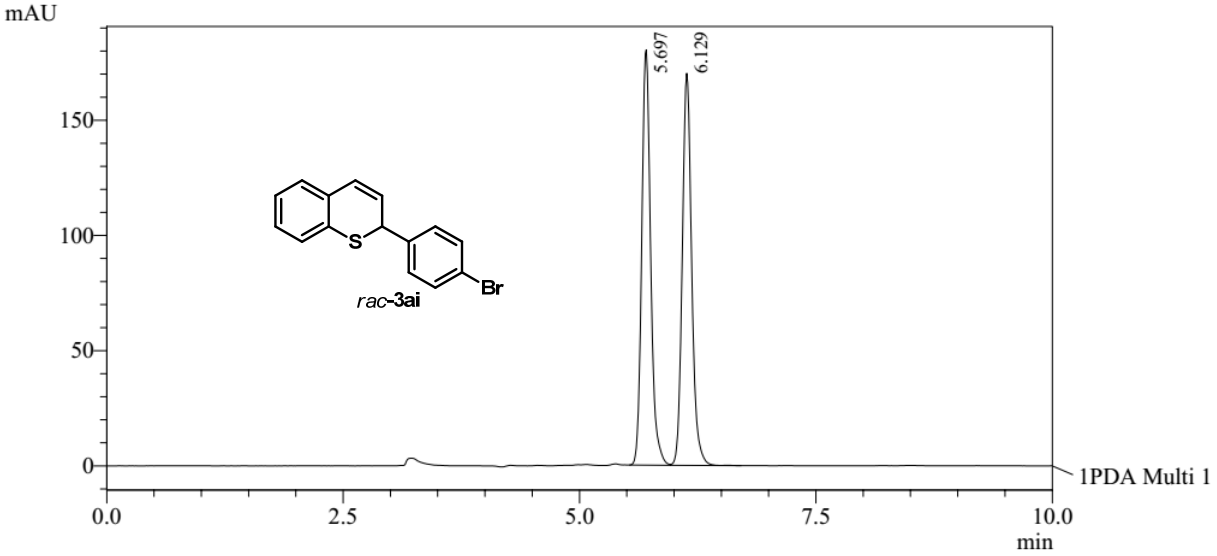
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.560	2262710	96.869
2	7.128	73136	3.131
Total		2335846	100.000


7.42
7.41
7.40
7.26
7.22
7.20
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.08
7.08
6.69
6.69
6.67
6.66
6.01
5.99
5.98
5.97
4.81
4.81
4.80
4.79
S
Br
3ai
9
8
7
6
5
4
3
2
1
0
ppm
2.0
2.1
3.9
1.0
1.0
1.0


140.9
131.8
130.9
130.0
129.2
129.1
128.5
128.2
126.9
125.7
124.8
121.6
77.3
77.0
76.7
42.1
S
Br
3ai
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



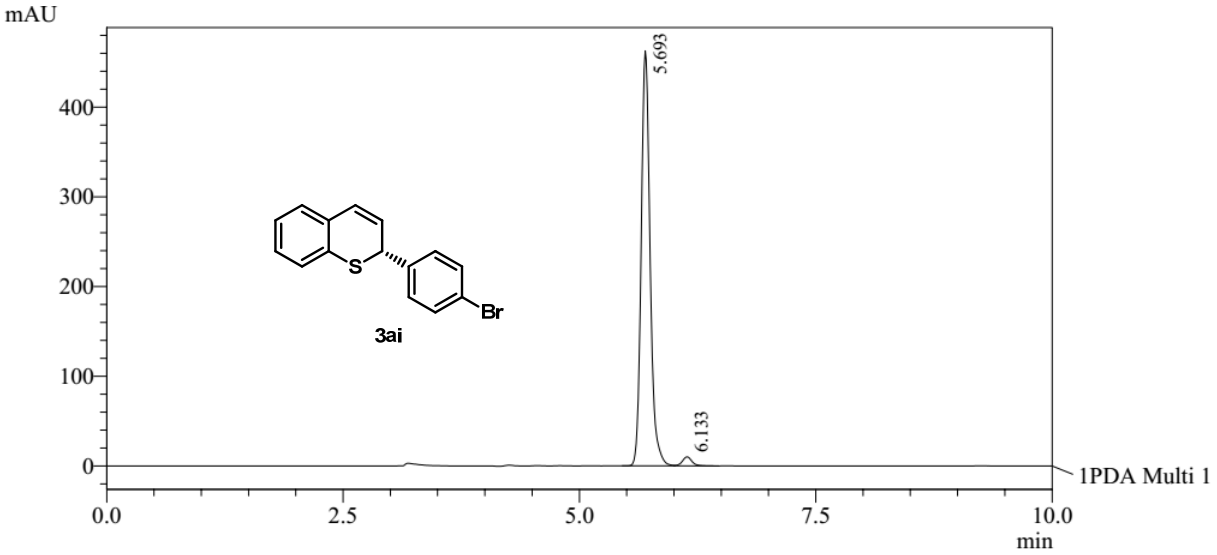
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.697	1183268	50.168
2	6.129	1175337	49.832
Total		2358605	100.000

Daicel Chiralpak IB column (97:3 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

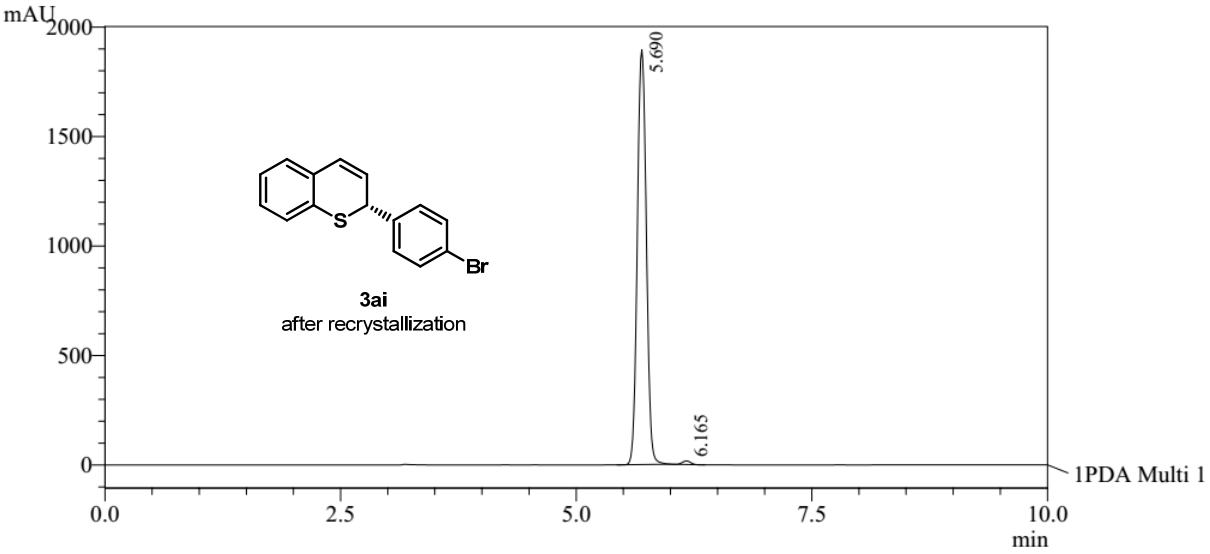


1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.693	3028182	97.713
2	6.133	70887	2.287
Total		3099069	100.000

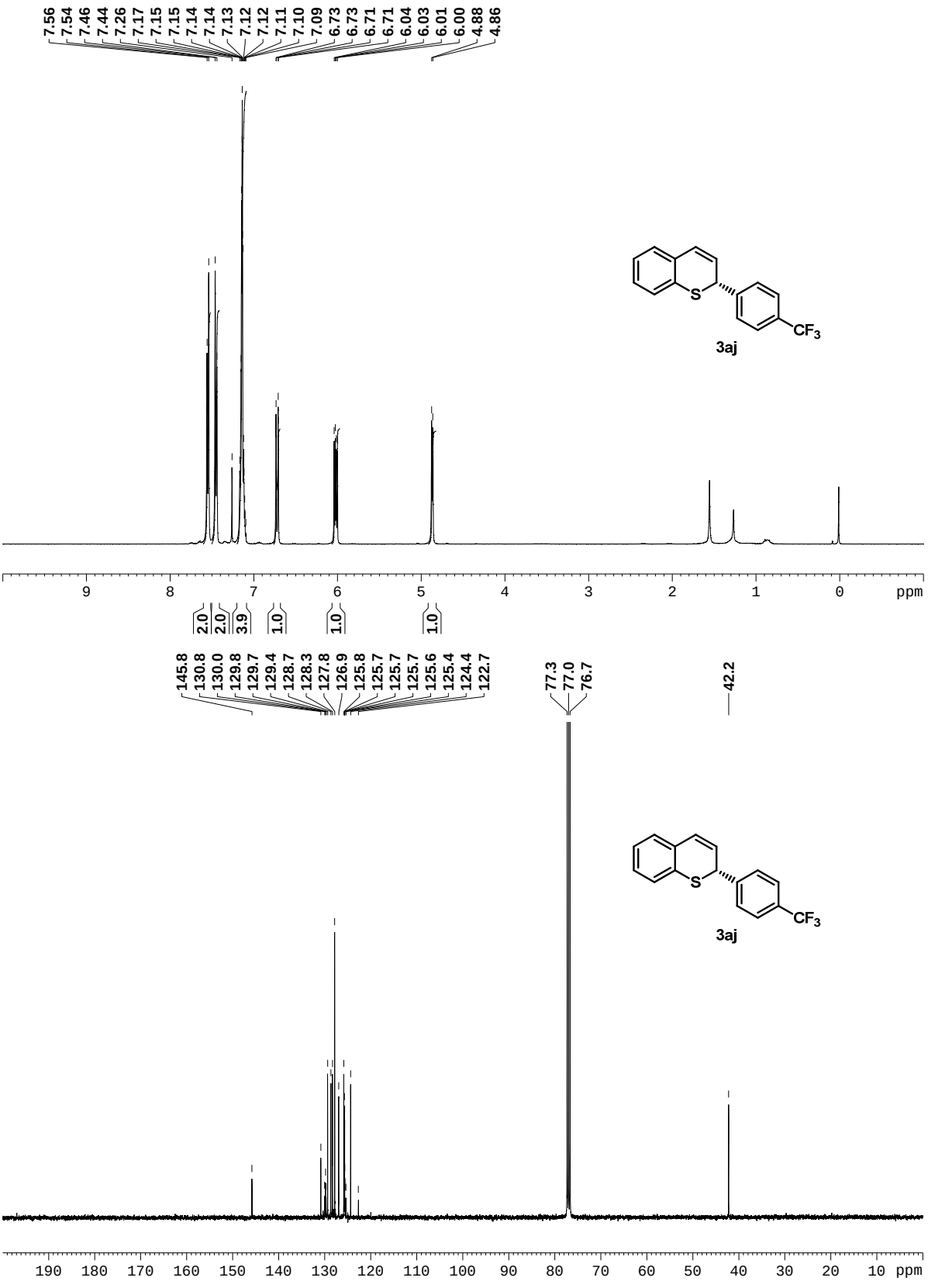


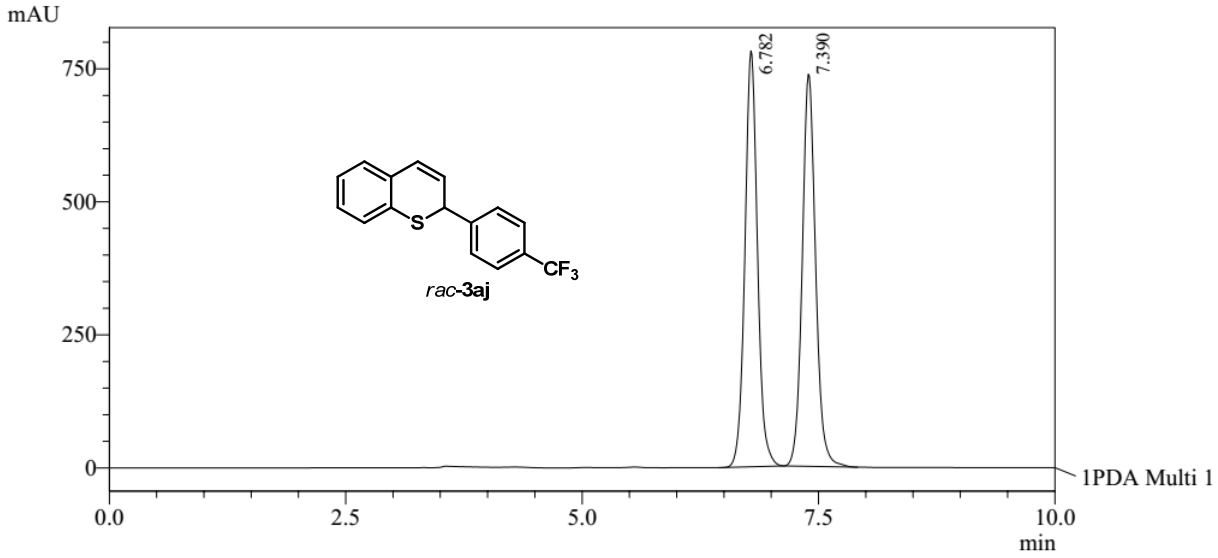
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.690	12595395	99.234
2	6.165	97188	0.766
Total		12692583	100.000


7.56
7.54
7.46
7.44
7.26
7.17
7.15
7.15
7.14
7.14
7.13
7.12
7.12
7.11
7.10
7.09
6.73
6.73
6.71
6.71
6.04
6.03
6.01
6.00
4.88
4.86
S
CF3
3aj
9
8
7
6
5
4
3
2
1
0
ppm
2.0
2.0
3.9
1.0
1.0
1.0
145.8
130.8
130.0
129.8
129.7
129.4
128.7
128.3
127.8
126.9
125.8
125.7
125.7
125.7
125.6
125.4
124.4
122.7
77.3
77.0
76.7
42.2
S
CF3
3aj
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



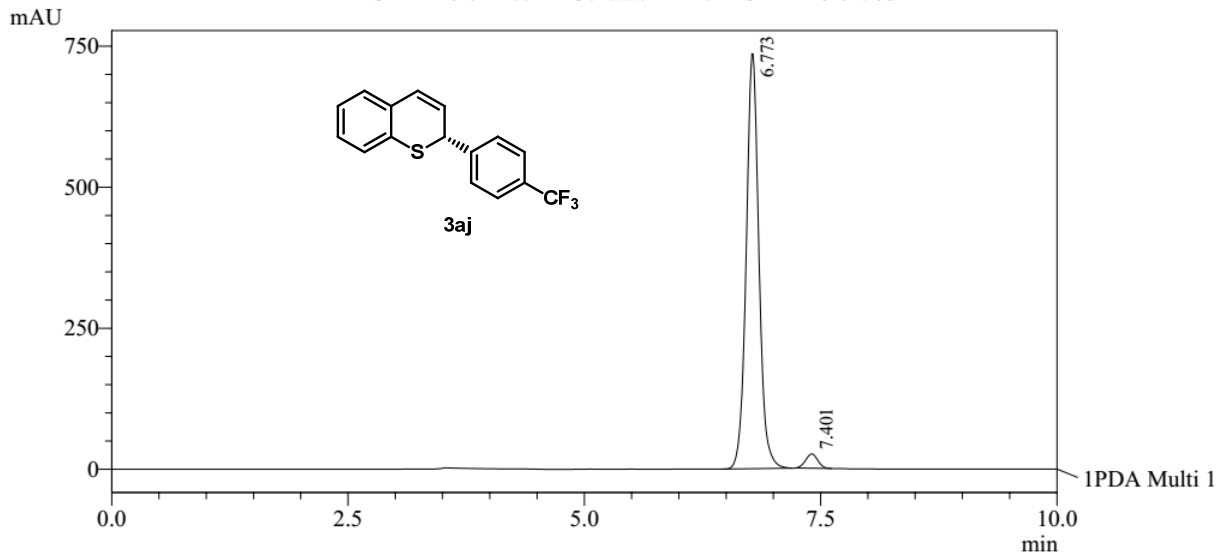
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.782	7206786	49.884
2	7.390	7240318	50.116
Total		14447104	100.000

Daicel Chiralpak IB column (99:1 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

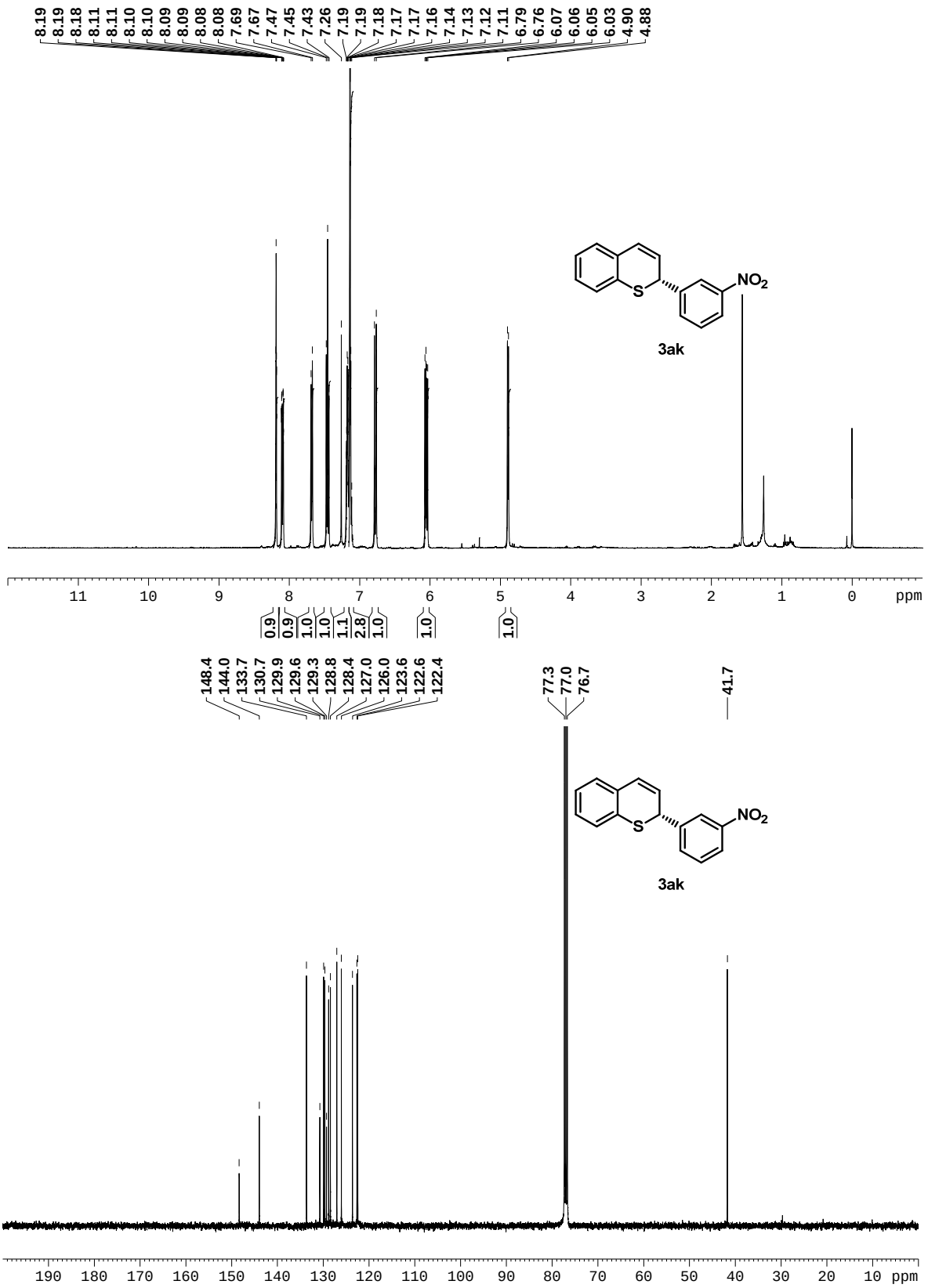


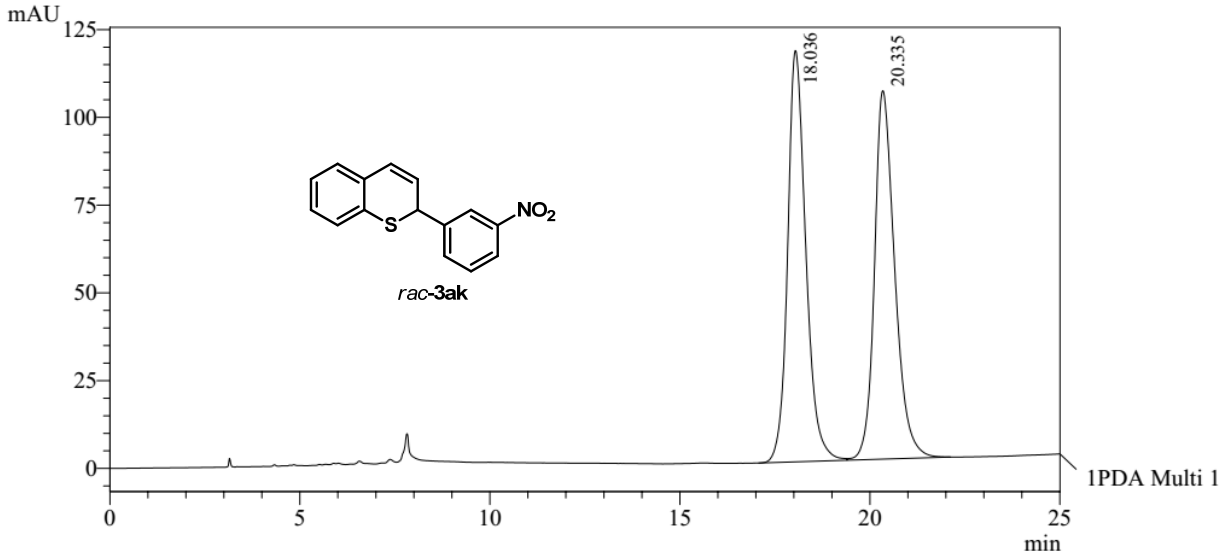
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.773	6880430	96.826
2	7.401	225575	3.174
Total		7106005	100.000


8.19
8.19
8.18
8.11
8.11
8.10
8.10
8.09
8.09
8.08
8.08
7.69
7.67
7.47
7.45
7.43
7.26
7.19
7.19
7.18
7.17
7.17
7.16
7.14
7.13
7.12
7.11
6.79
6.76
6.07
6.06
6.05
6.03
4.90
4.88
NO2
S
3ak
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.9 0.9 1.0 1.0 1.1 2.8 1.0 1.0 1.0
148.4
144.0
133.7
130.7
129.9
129.6
129.3
128.8
128.4
127.0
126.0
123.6
122.6
122.4
77.3
77.0
76.7
41.7
NO2
S
3ak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



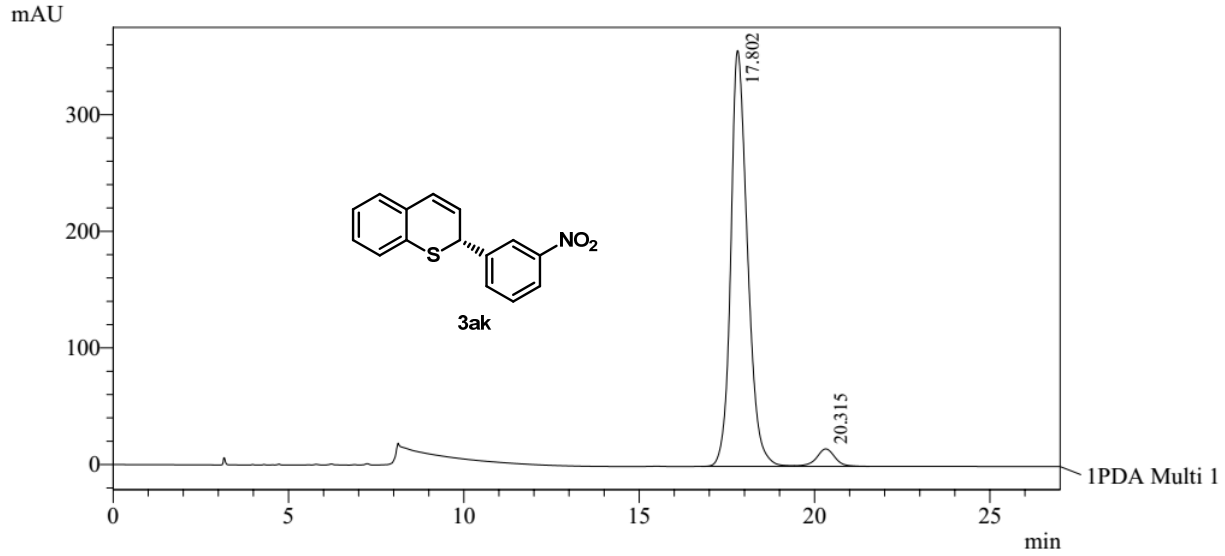
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	18.036	3904147	50.076
2	20.335	3892280	49.924
Total		7796426	100.000

Daicel Chiralpak IB column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

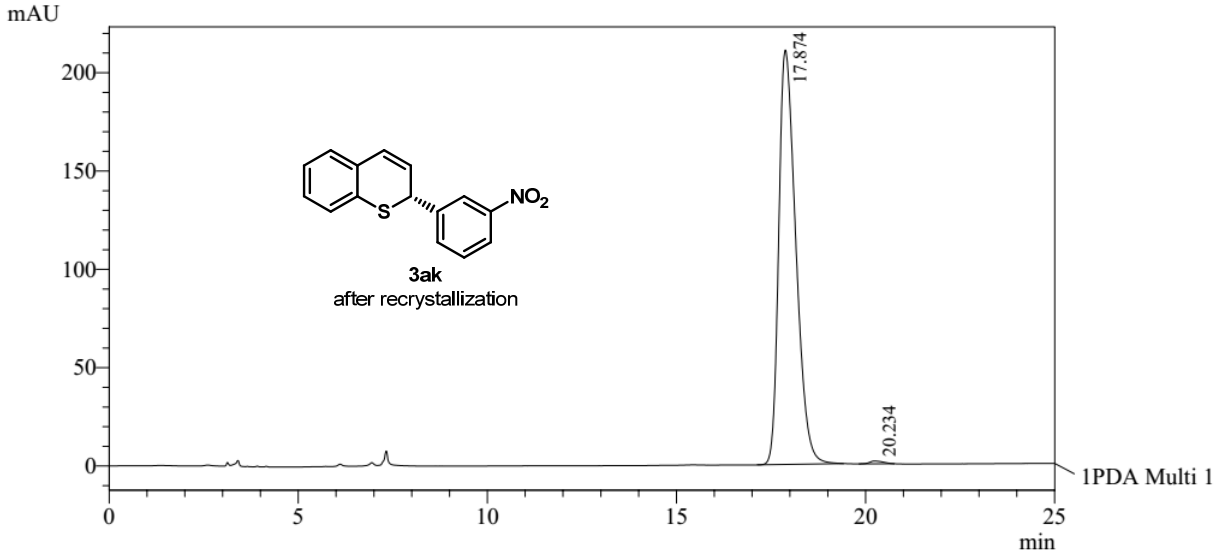


1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.802	11838986	95.565
2	20.315	549399	4.435
Total		12388386	100.000

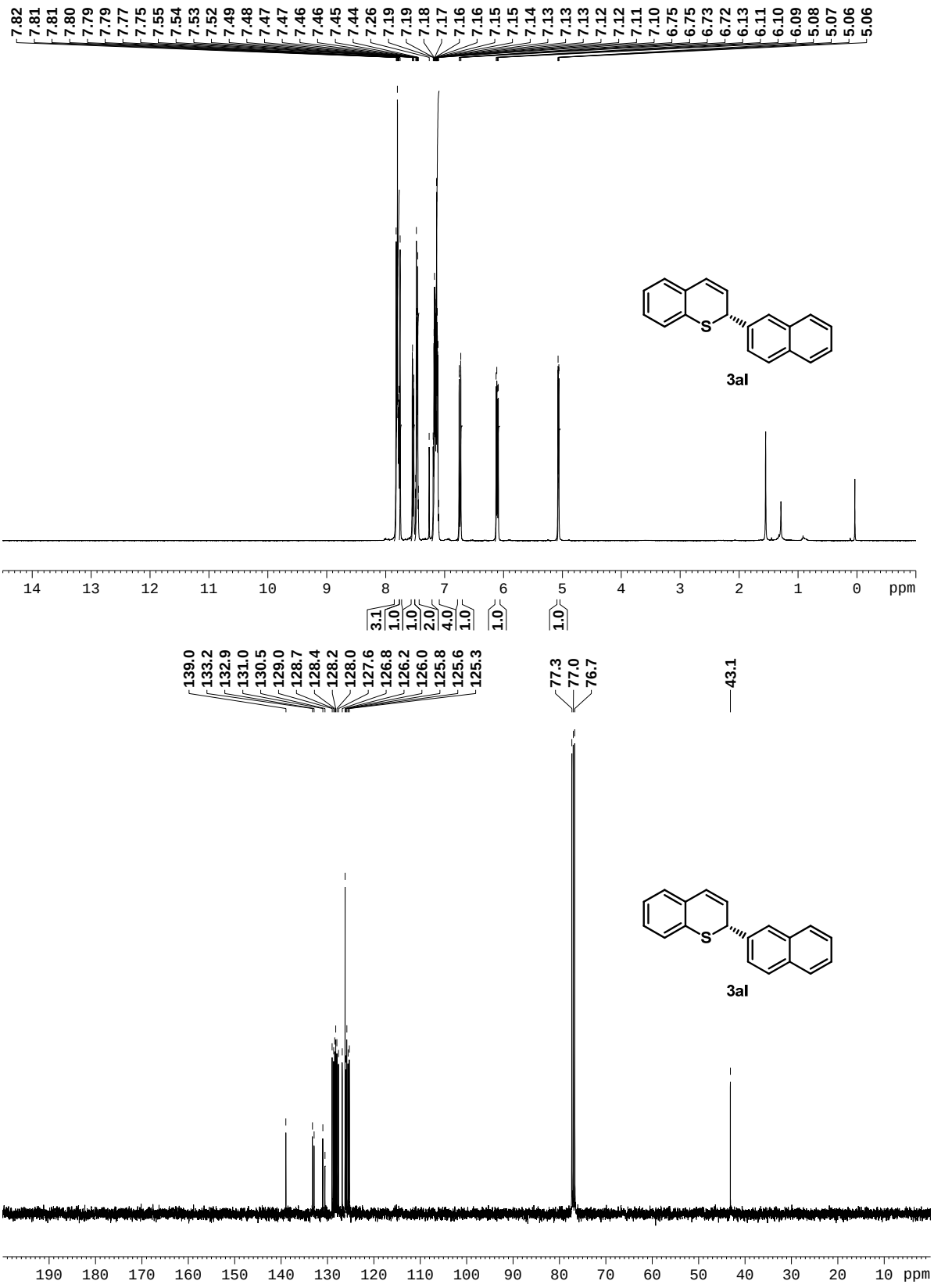


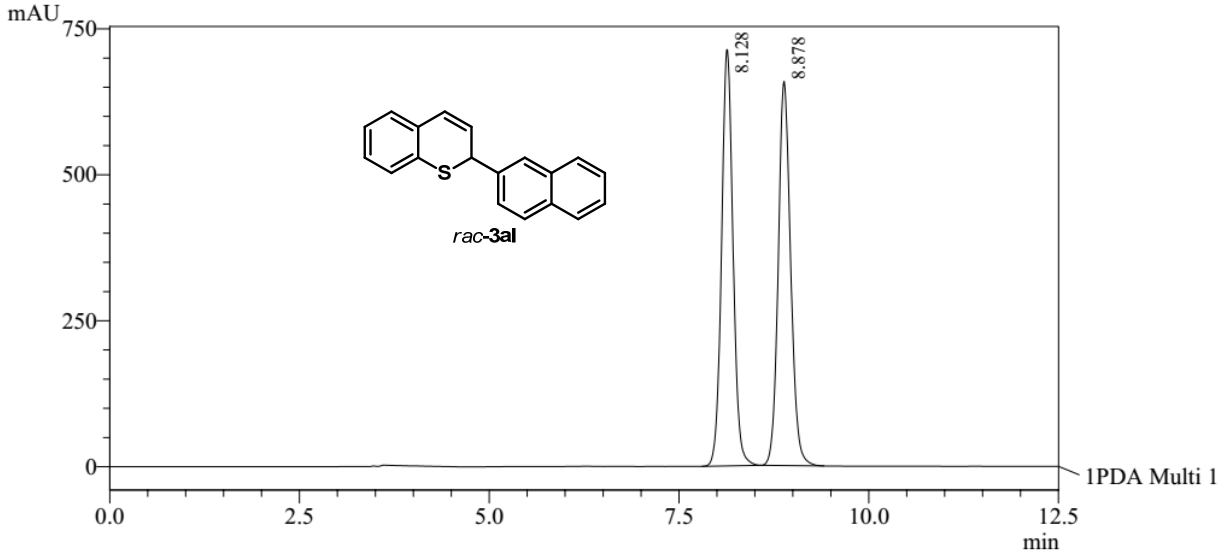
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.874	6614035	99.488
2	20.234	34060	0.512
Total		6648096	100.000


7.82 7.81 7.81 7.80 7.79 7.79 7.77 7.75 7.55 7.54 7.53 7.52 7.49 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.26 7.19 7.19 7.18 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.13 7.13 7.12 7.12 7.11 7.10 6.75 6.75 6.73 6.72 6.13 6.11 6.10 6.09 5.08 5.07 5.06 5.06
S
3al
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.1 1.0 1.0 2.0 4.0 1.0 1.0 1.0
139.0 133.2 132.9 131.0 130.5 129.0 128.7 128.4 128.2 128.0 127.6 126.8 126.2 126.0 125.8 125.6 125.3
77.3 77.0 76.7
43.1
S
3al
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



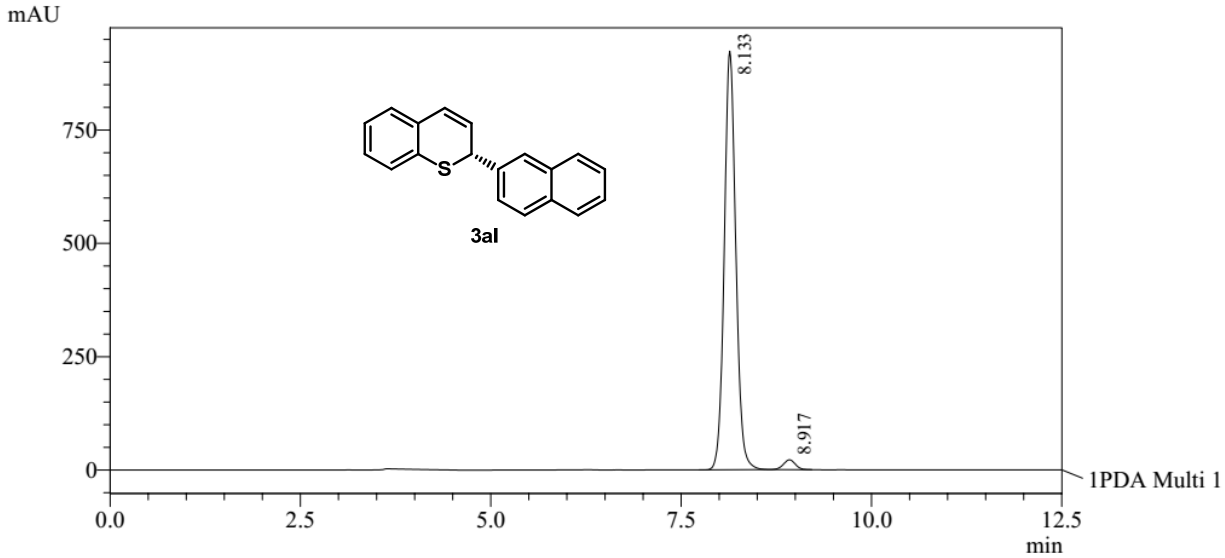
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.128	7490967	50.046
2	8.878	7477099	49.954
Total		14968065	100.000

Daicel Chiralpak IB column (99:1 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

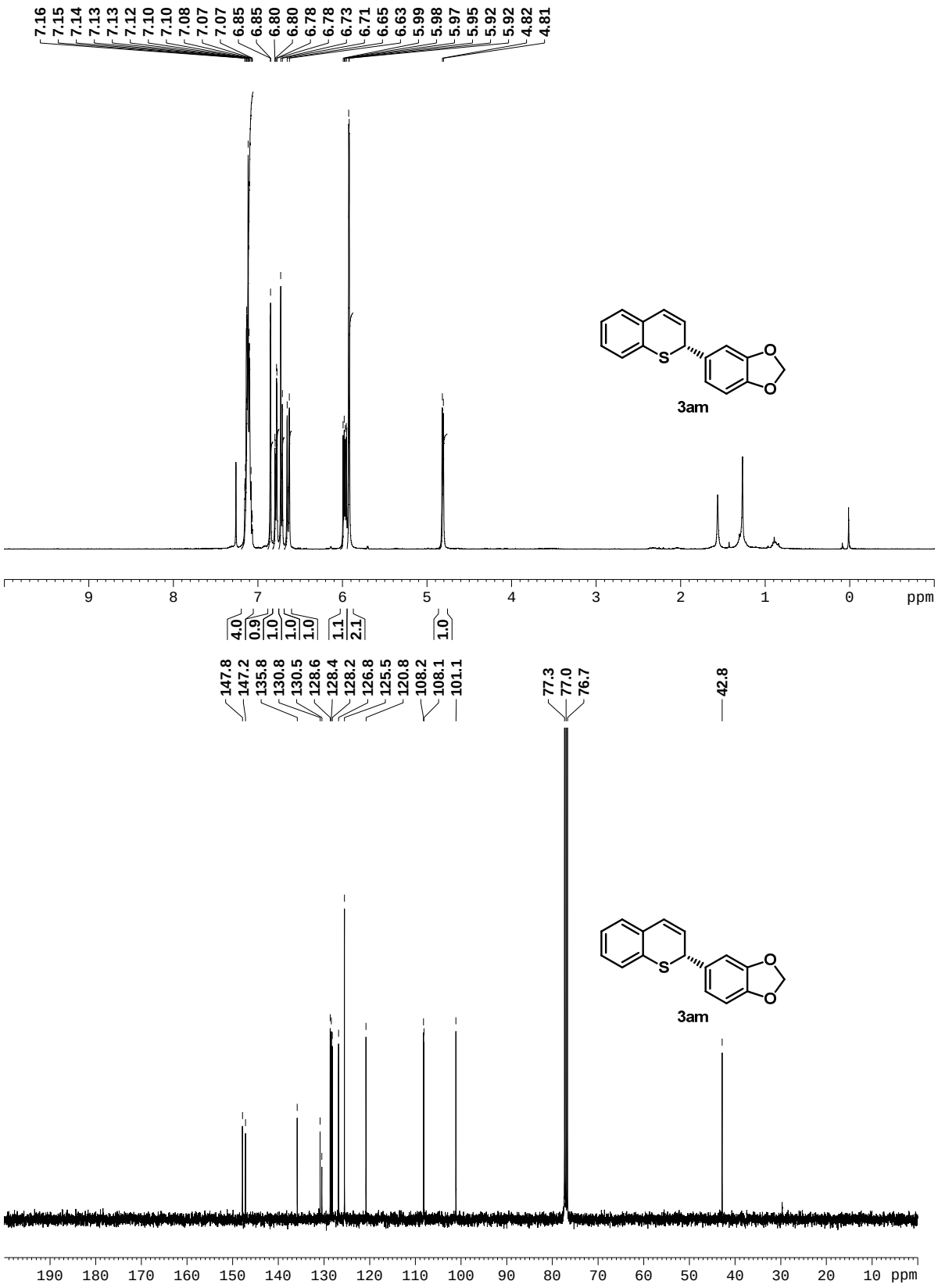


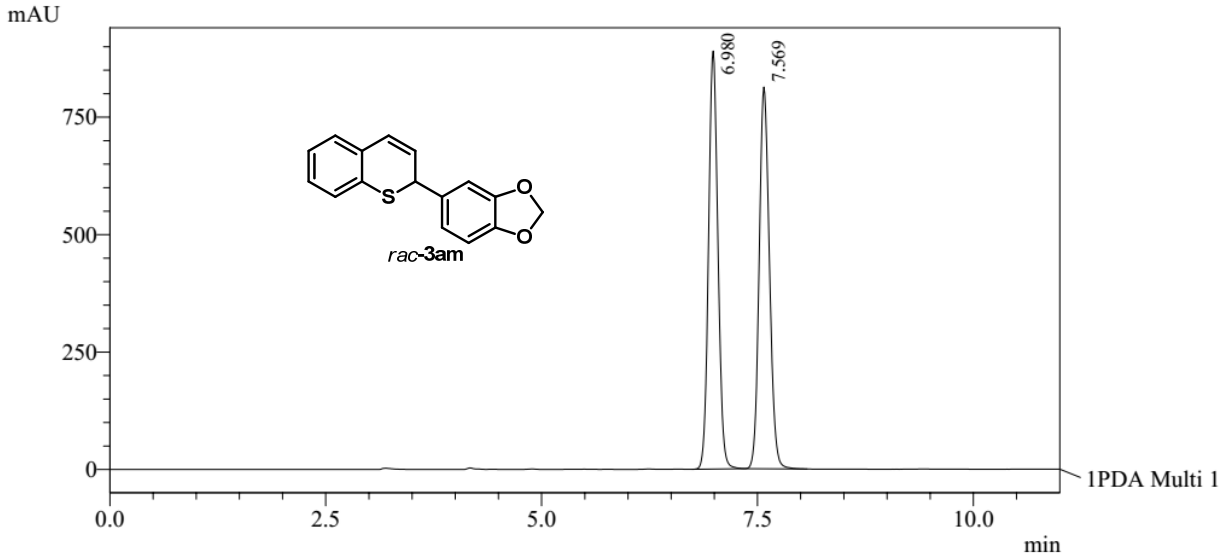
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.133	9744526	97.637
2	8.917	235822	2.363
Total		9980348	100.000


7.16
7.15
7.14
7.13
7.13
7.12
7.10
7.10
7.08
7.07
7.07
6.85
6.85
6.80
6.80
6.78
6.78
6.73
6.71
6.65
6.63
5.99
5.98
5.97
5.95
5.92
5.92
4.82
4.81
3am
9 8 7 6 5 4 3 2 1 0 ppm
4.0
0.9
1.0
1.0
1.0
1.0
1.1
2.1
1.0
147.8
147.2
135.8
130.8
130.5
128.6
128.4
128.2
126.8
125.5
120.8
108.2
108.1
101.1
77.3
77.0
76.7
42.8
3am
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



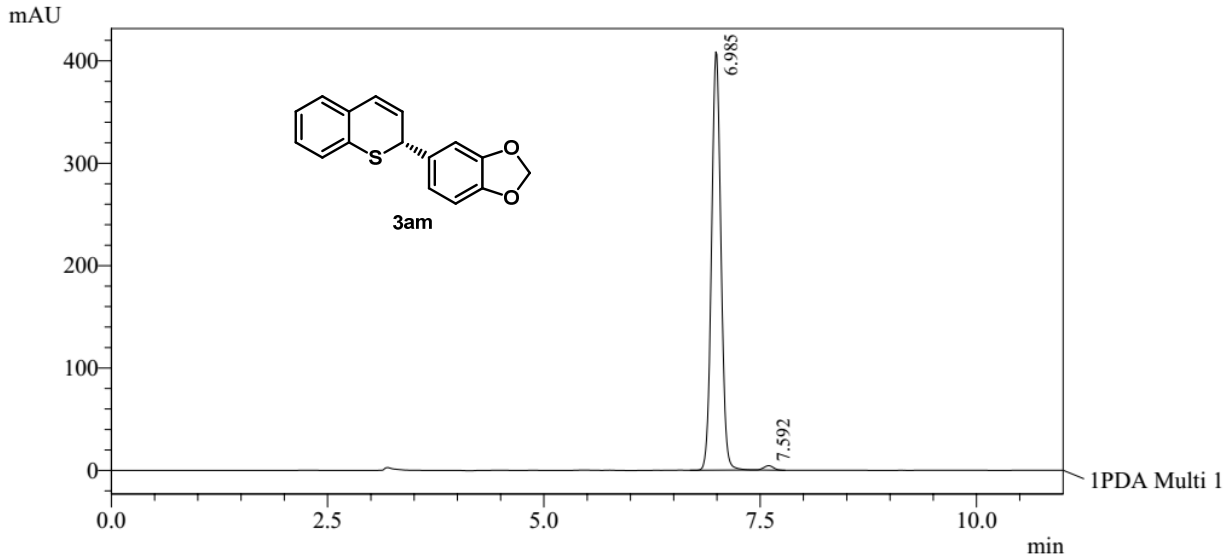
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.980	6719067	50.003
2	7.569	6718310	49.997
Total		13437376	100.000

Daicel Chiralpak IB column (97:3 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

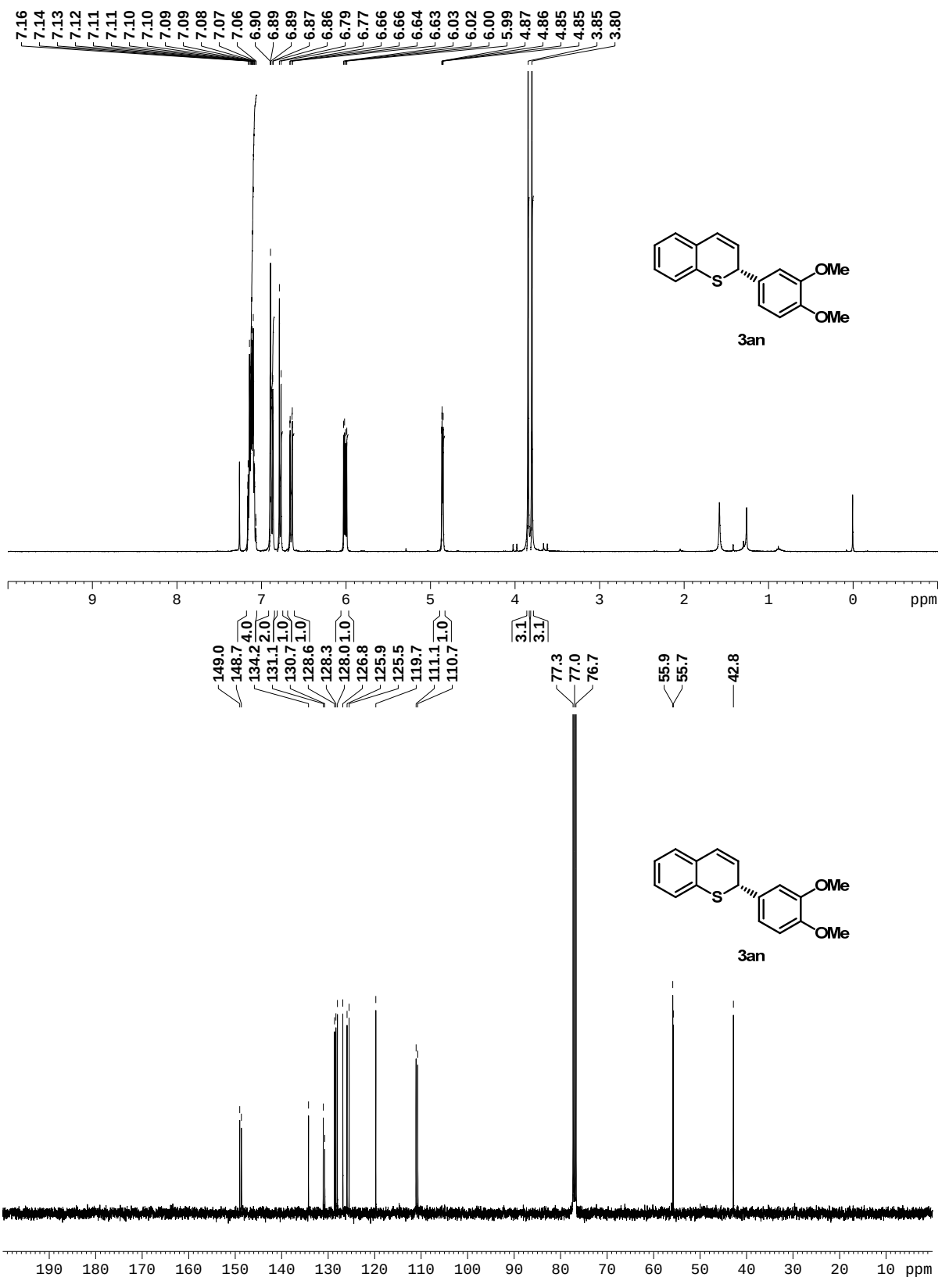


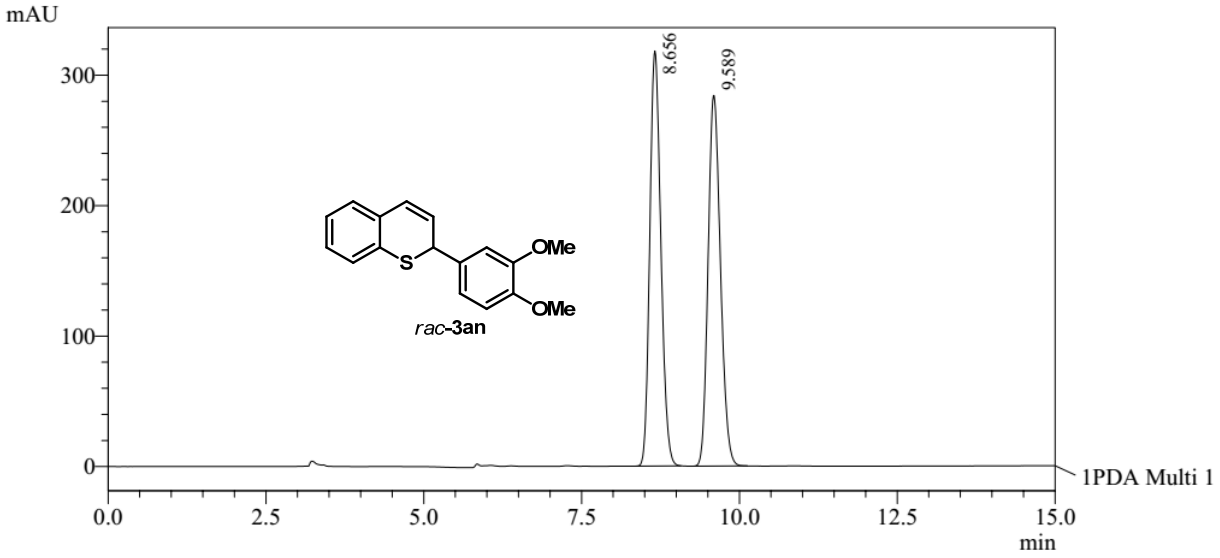
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.985	3086647	98.923
2	7.592	33601	1.077
Total		3120247	100.000


7.16
7.14
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.07
7.06
6.90
6.89
6.89
6.87
6.86
6.79
6.77
6.66
6.66
6.64
6.63
6.03
6.02
6.00
5.99
4.87
4.86
4.85
4.85
3.85
3.80
OMe
OMe
3an
9
8
7
6
5
4
3
2
1
0
ppm
4.0
2.0
1.0
1.0
1.0
1.0
1.0
3.1
3.1
149.0
148.7
134.2
131.1
130.7
128.6
128.3
128.0
126.8
125.9
125.5
119.7
111.1
110.7
77.3
77.0
76.7
55.9
55.7
42.8
OMe
OMe
3an
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



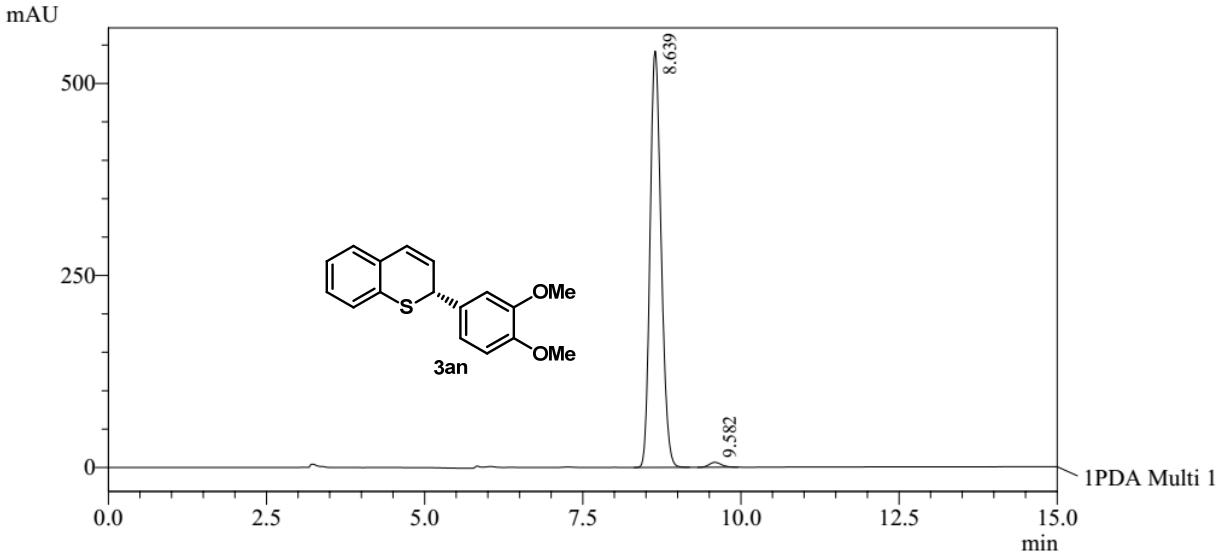
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.656	3877631	50.006
2	9.589	3876675	49.994
Total		7754306	100.000

Daicel Chiralpak AS-H column (97:03 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm)

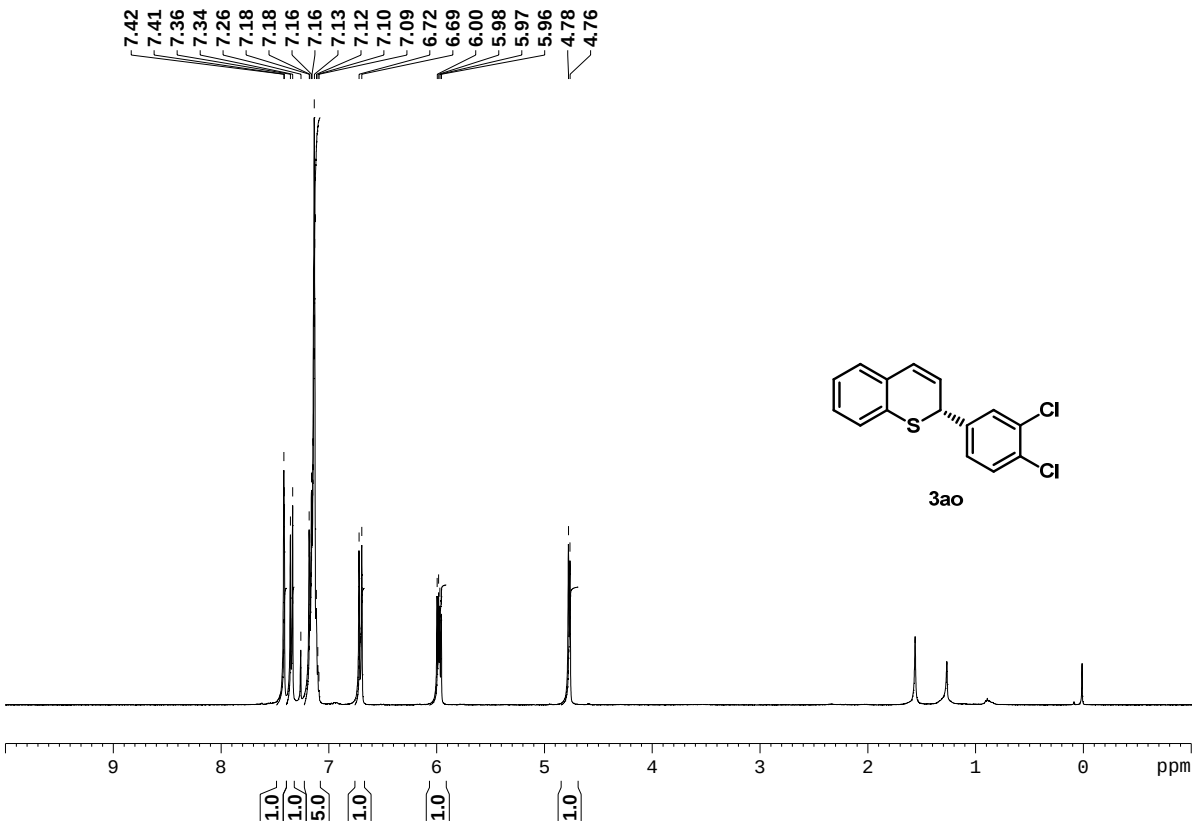


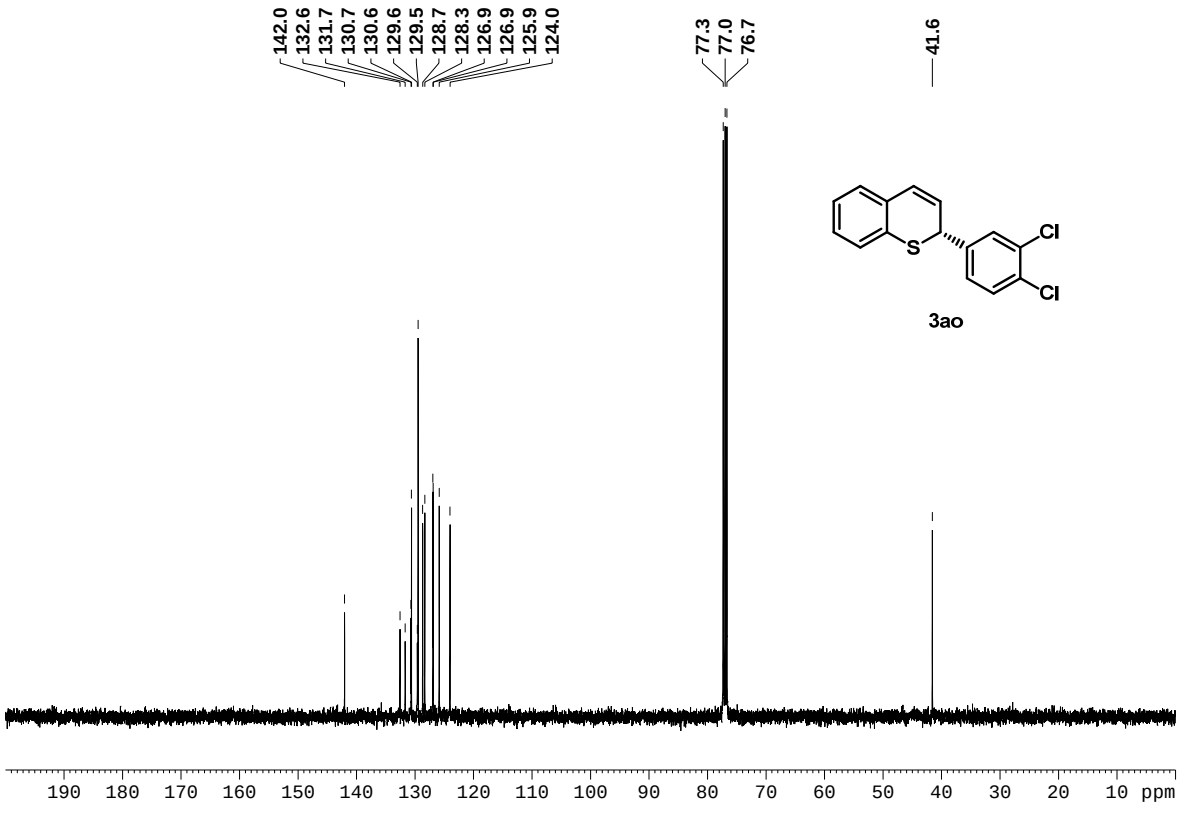
1 PDA Multi 1 / 254nm 4nm

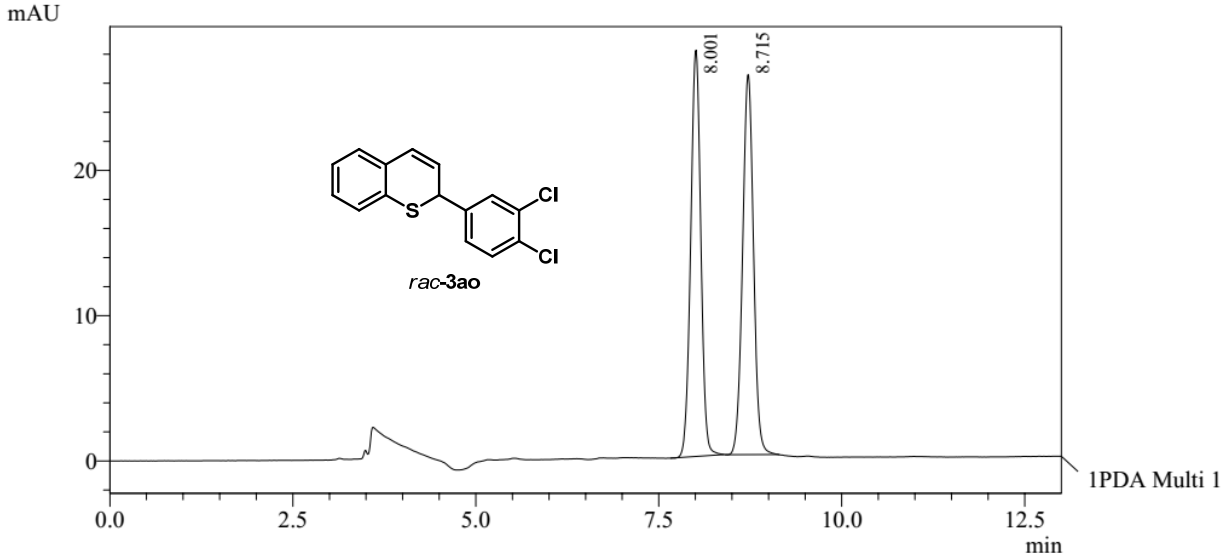
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.639	6624300	98.718
2	9.582	86000	1.282
Total		6710299	100.000


7.42
7.41
7.36
7.34
7.26
7.18
7.18
7.16
7.16
7.13
7.12
7.10
7.09
6.72
6.69
6.00
5.98
5.97
5.96
4.78
4.76
Cl
Cl
S
3ao
9
8
7
6
5
4
3
2
1
0
ppm
1.0
1.0
5.0
1.0
1.0
1.0


142.0
132.6
131.7
130.7
130.6
129.6
129.5
128.7
128.3
126.9
126.9
125.9
124.0
77.3
77.0
76.7
41.6
Cl
Cl
S
3ao
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



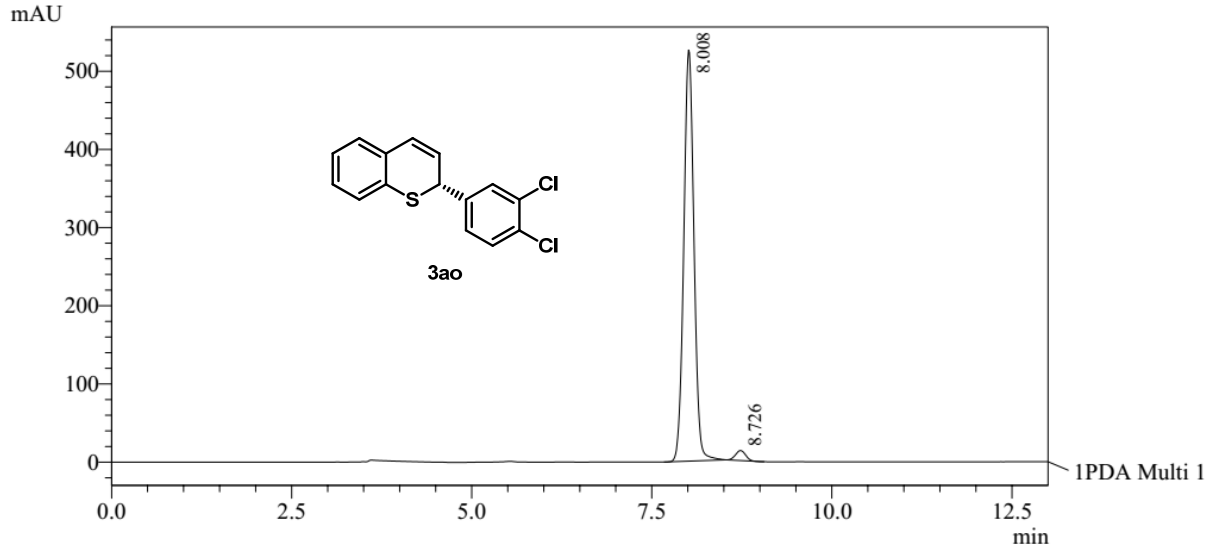
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.001	267922	49.732
2	8.715	270805	50.268
Total		538727	100.000

Daicel Chiralpak IB column (99:1 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

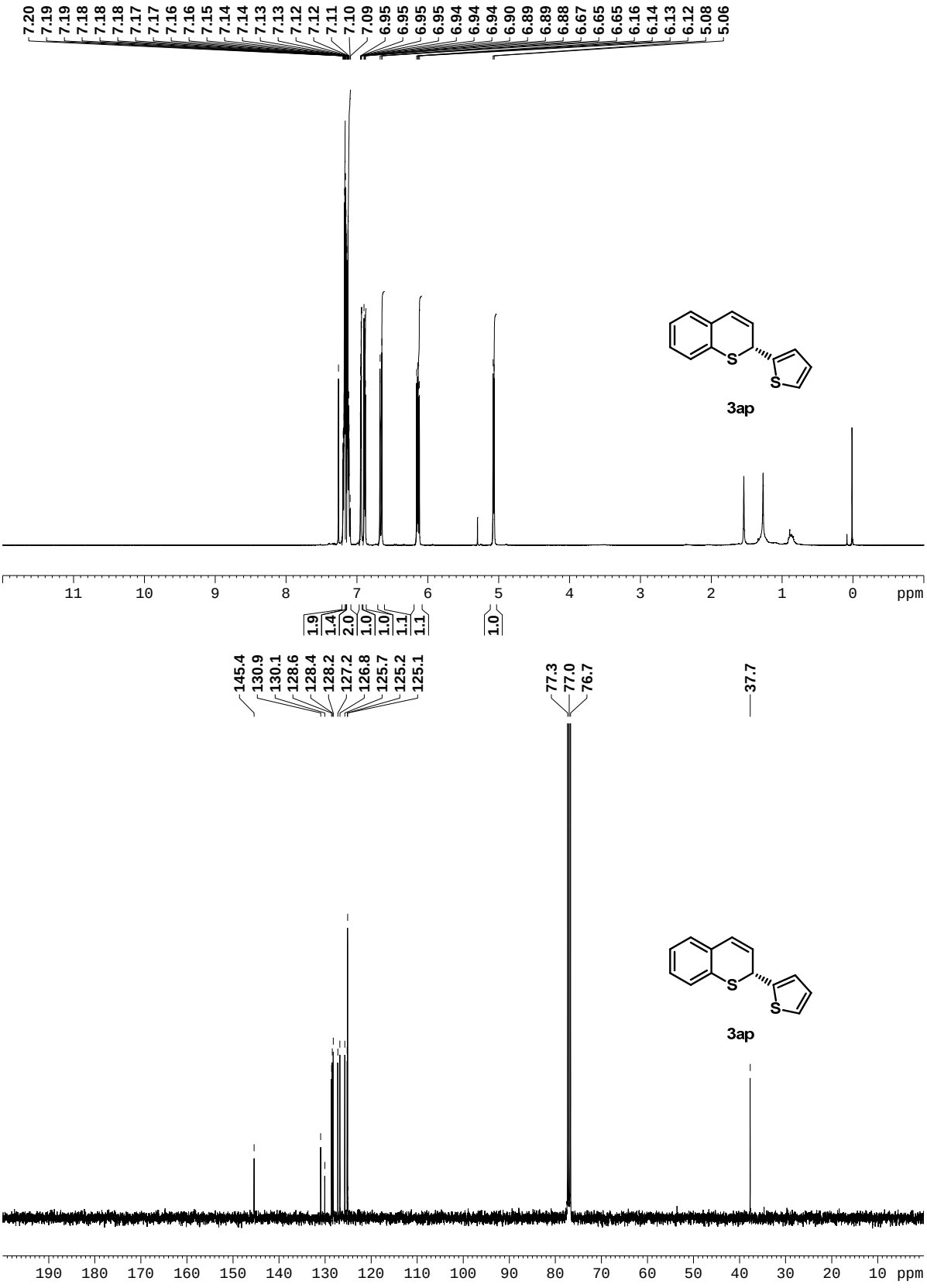


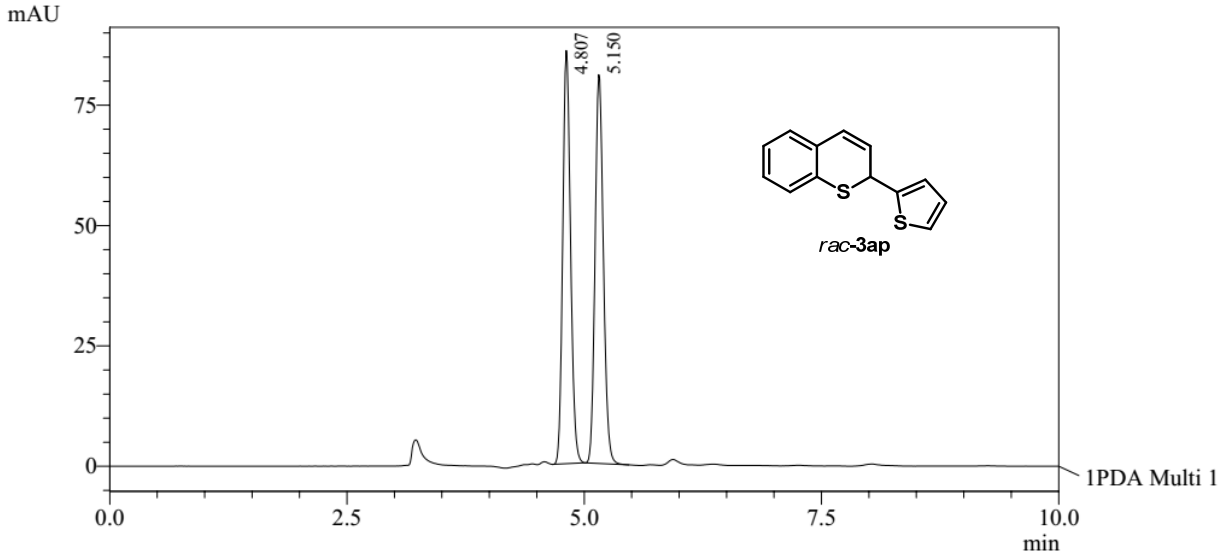
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	8.008	5139749	97.641
2	8.726	124174	2.359
Total		5263923	100.000


7.20 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.13 7.12 7.12 7.11 7.10 7.09 6.95 6.95 6.95 6.94 6.94 6.94 6.90 6.89 6.89 6.88 6.67 6.65 6.65 6.16 6.14 6.13 6.12 5.08 5.06
3ap
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.9 1.4 2.0 1.0 1.0 1.1 1.1 1.0
145.4 130.9 130.1 128.6 128.4 128.2 127.2 126.8 125.7 125.2 125.1
77.3 77.0 76.7
37.7
3ap
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



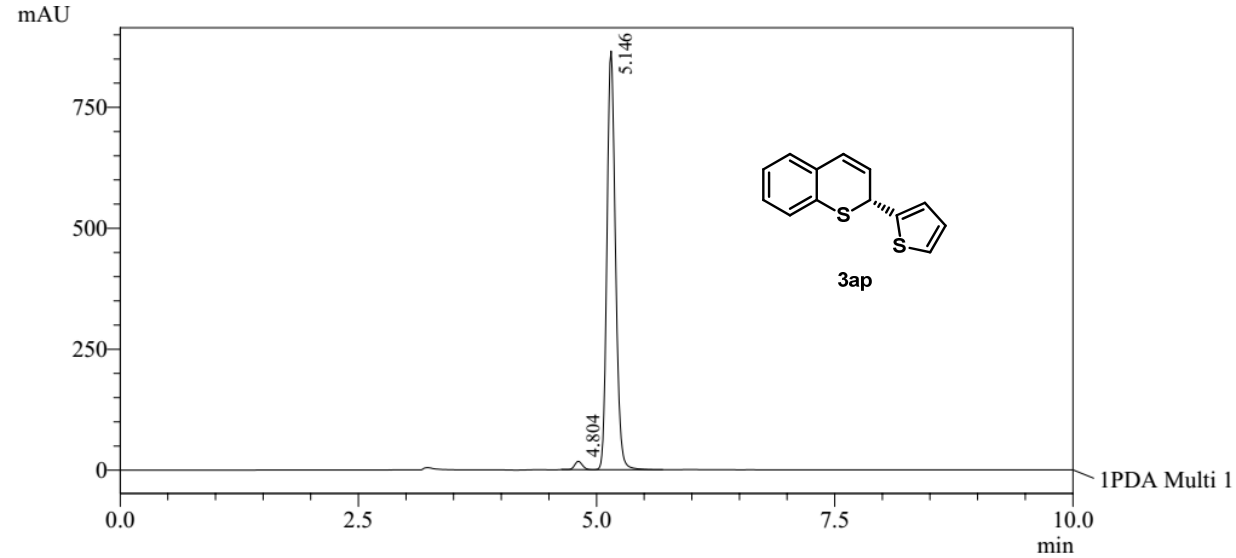
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.807	491875	49.851
2	5.150	494824	50.149
Total		986700	100.000

Daicel Chiralpak IF column (97:3 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

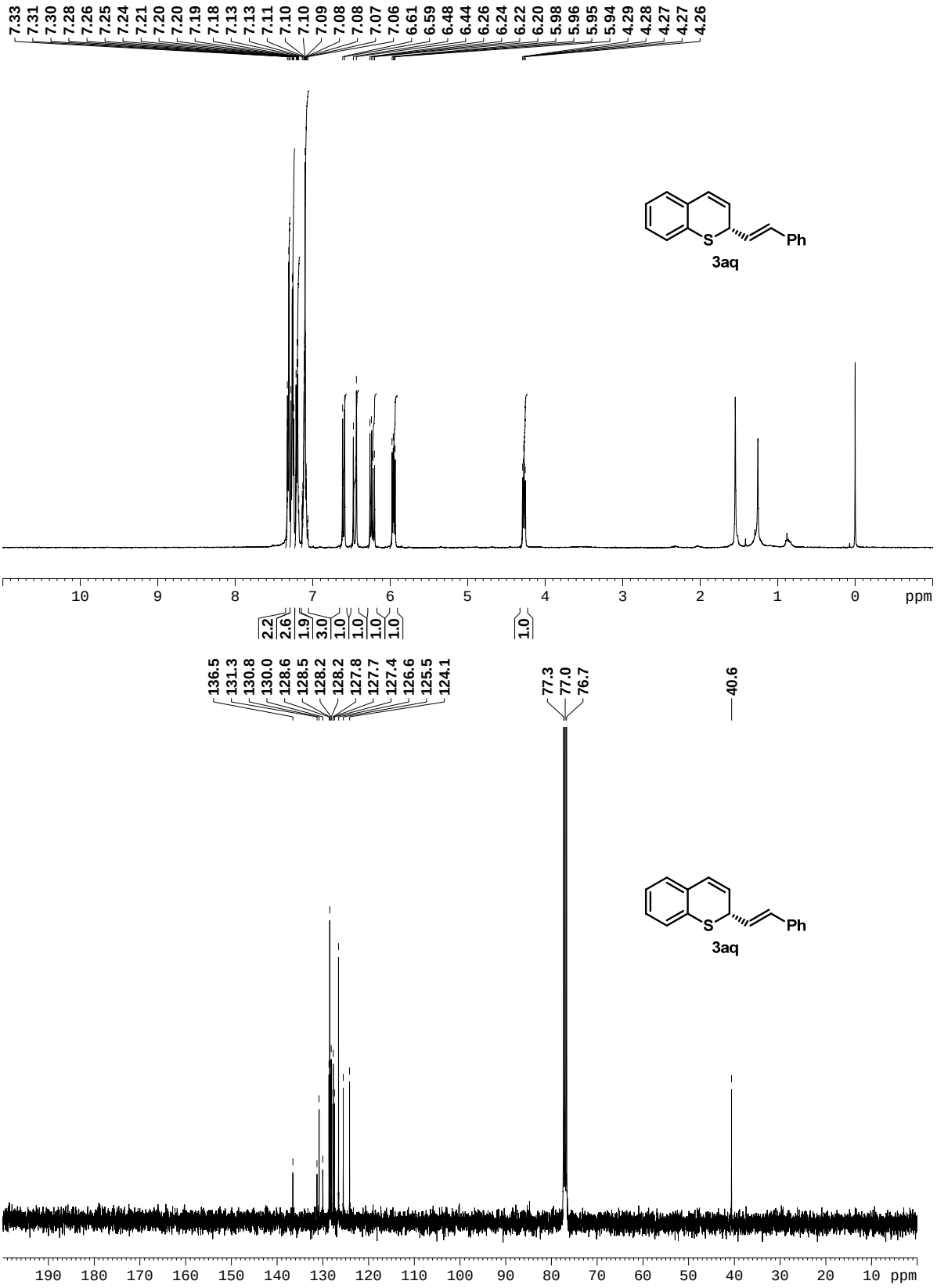


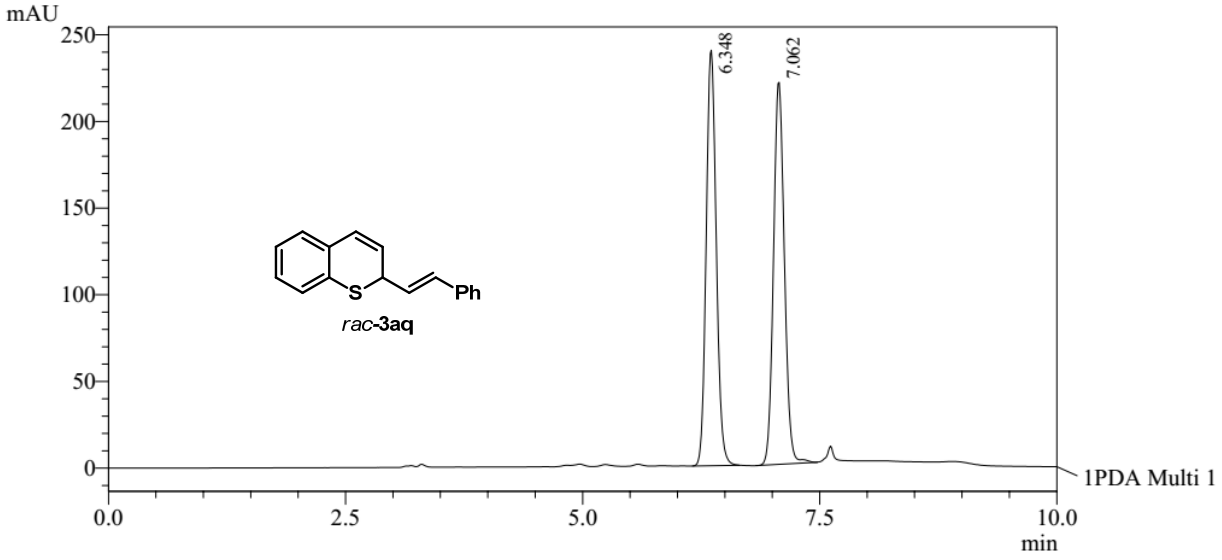
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.804	97052	1.771
2	5.146	5382797	98.229
Total		5479849	100.000


7.33
7.31
7.30
7.28
7.26
7.25
7.24
7.21
7.20
7.20
7.19
7.18
7.13
7.13
7.11
7.10
7.10
7.09
7.08
7.08
7.07
7.06
6.61
6.59
6.48
6.44
6.26
6.24
6.22
6.20
5.98
5.96
5.95
5.94
4.29
4.28
4.27
4.27
4.26
S
Ph
3aq
10 9 8 7 6 5 4 3 2 1 0 ppm
2.2
2.6
1.9
3.0
1.0
1.0
1.0
1.0
1.0
136.5
131.3
130.8
130.0
128.6
128.5
128.2
128.2
127.8
127.7
127.4
126.6
125.5
124.1
77.3
77.0
76.7
40.6
S
Ph
3aq
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



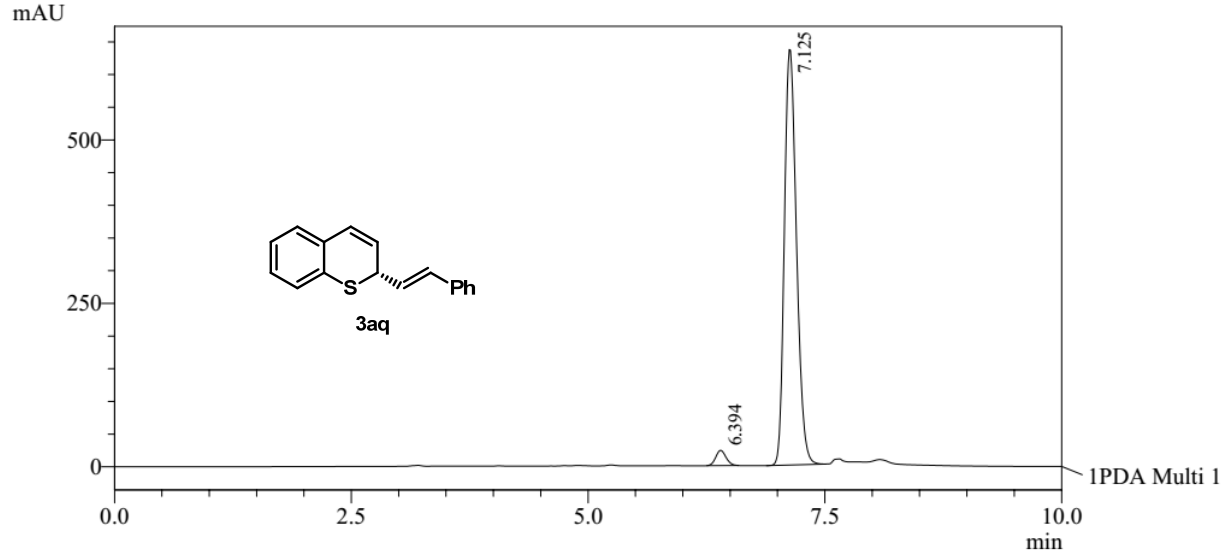
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.348	1766375	50.056
2	7.062	1762432	49.944
Total		3528807	100.000

Daicel Chiralpak IF column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

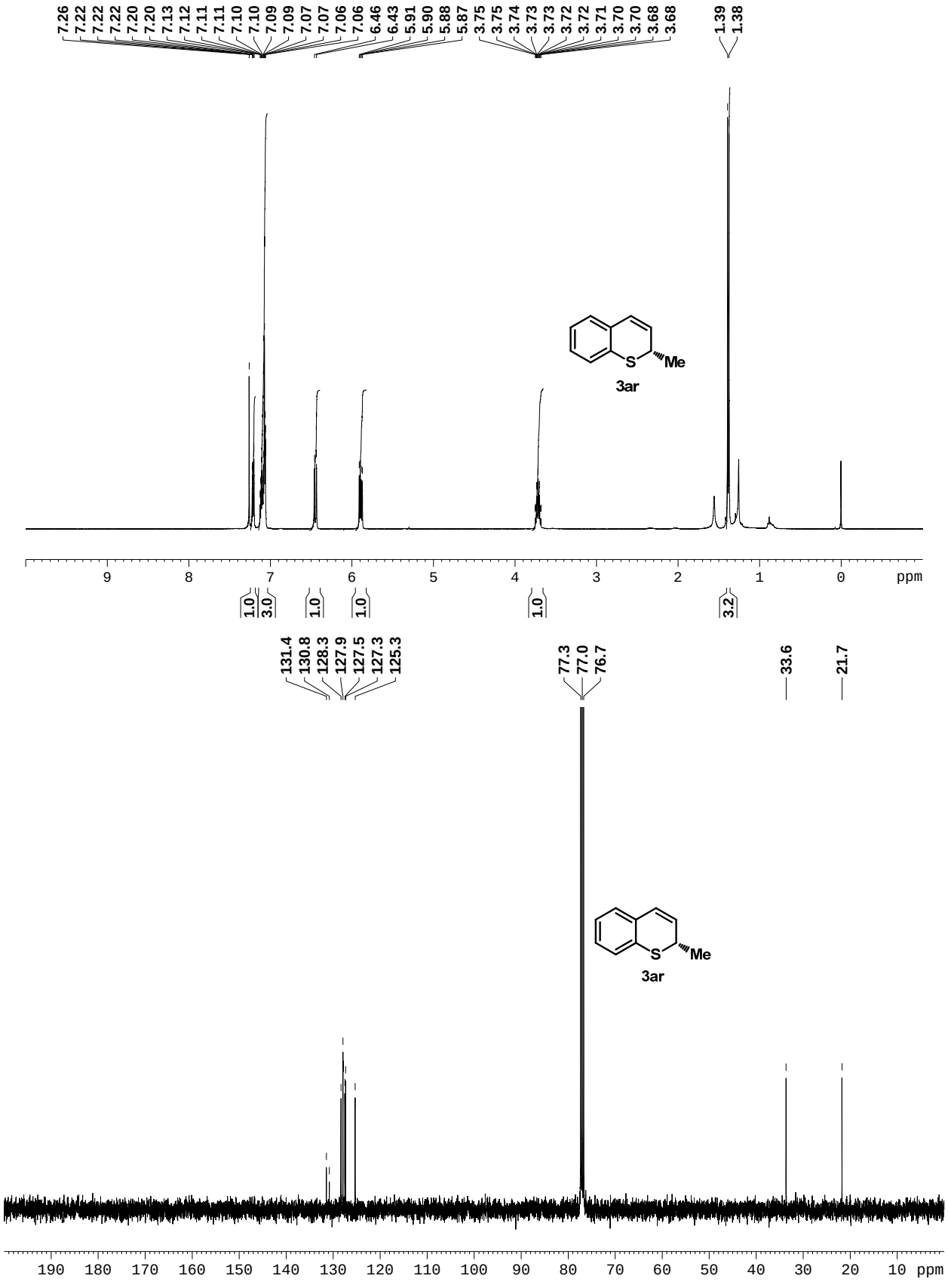


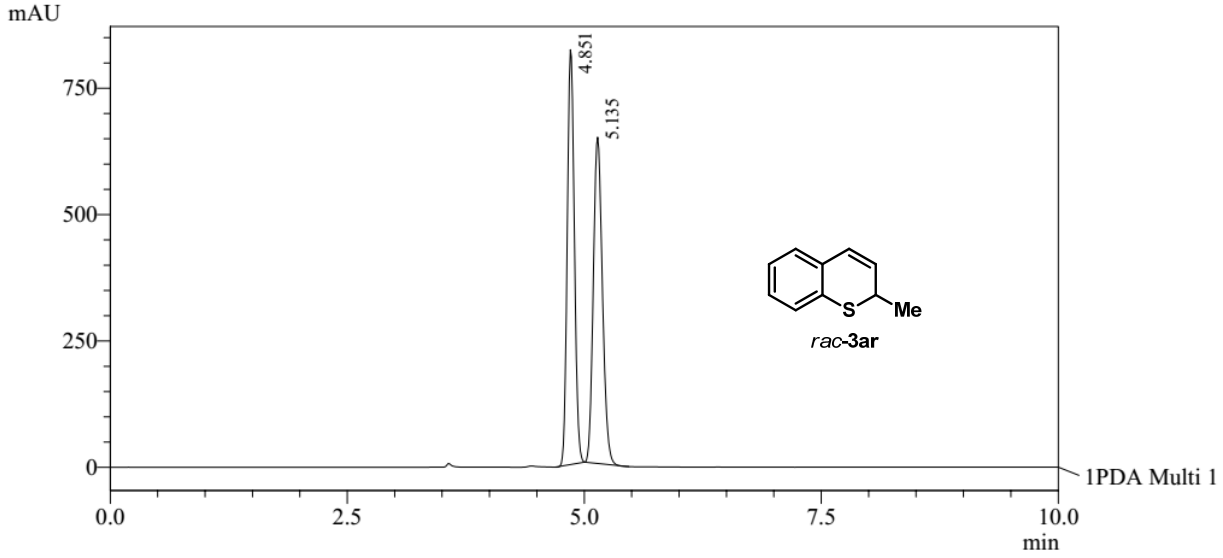
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.394	176644	3.025
2	7.125	5663627	96.975
Total		5840271	100.000


7.26
7.22
7.22
7.22
7.20
7.20
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.07
7.07
7.06
7.06
6.46
6.43
5.91
5.90
5.88
5.87
3.75
3.75
3.74
3.73
3.73
3.72
3.72
3.71
3.70
3.70
3.68
3.68
1.39
1.38
S
Me
3ar
9
8
7
6
5
4
3
2
1
0
ppm
1.0
3.0
1.0
1.0
1.0
3.2
131.4
130.8
128.3
127.9
127.5
127.3
125.3
77.3
77.0
76.7
33.6
21.7
S
Me
3ar
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



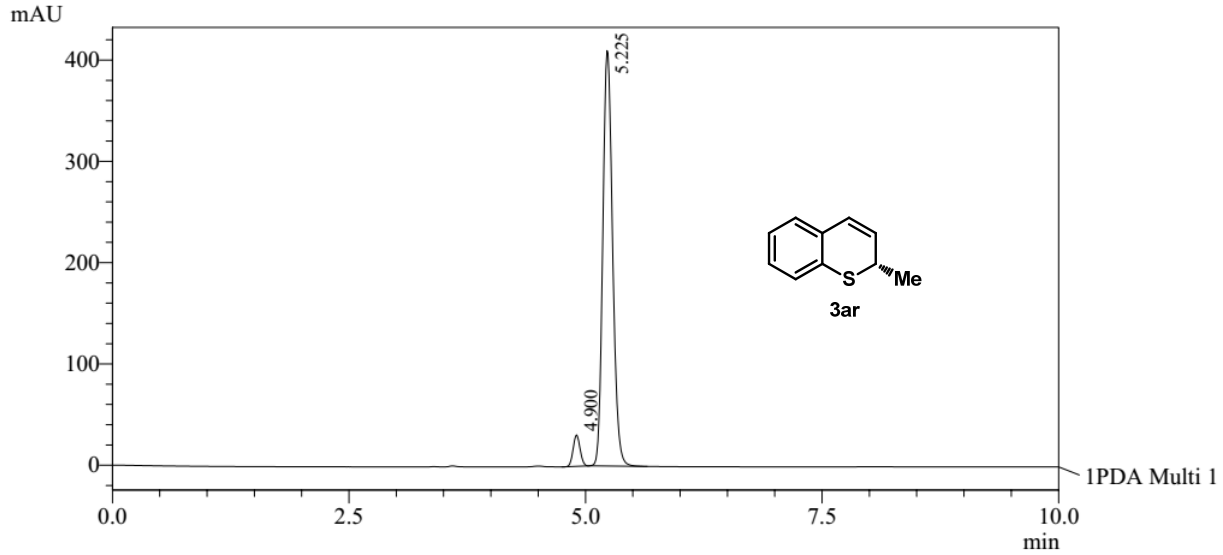
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.851	4282567	49.866
2	5.135	4305588	50.134
Total		8588156	100.000

Daicel Chiralpak ID column (95:5 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

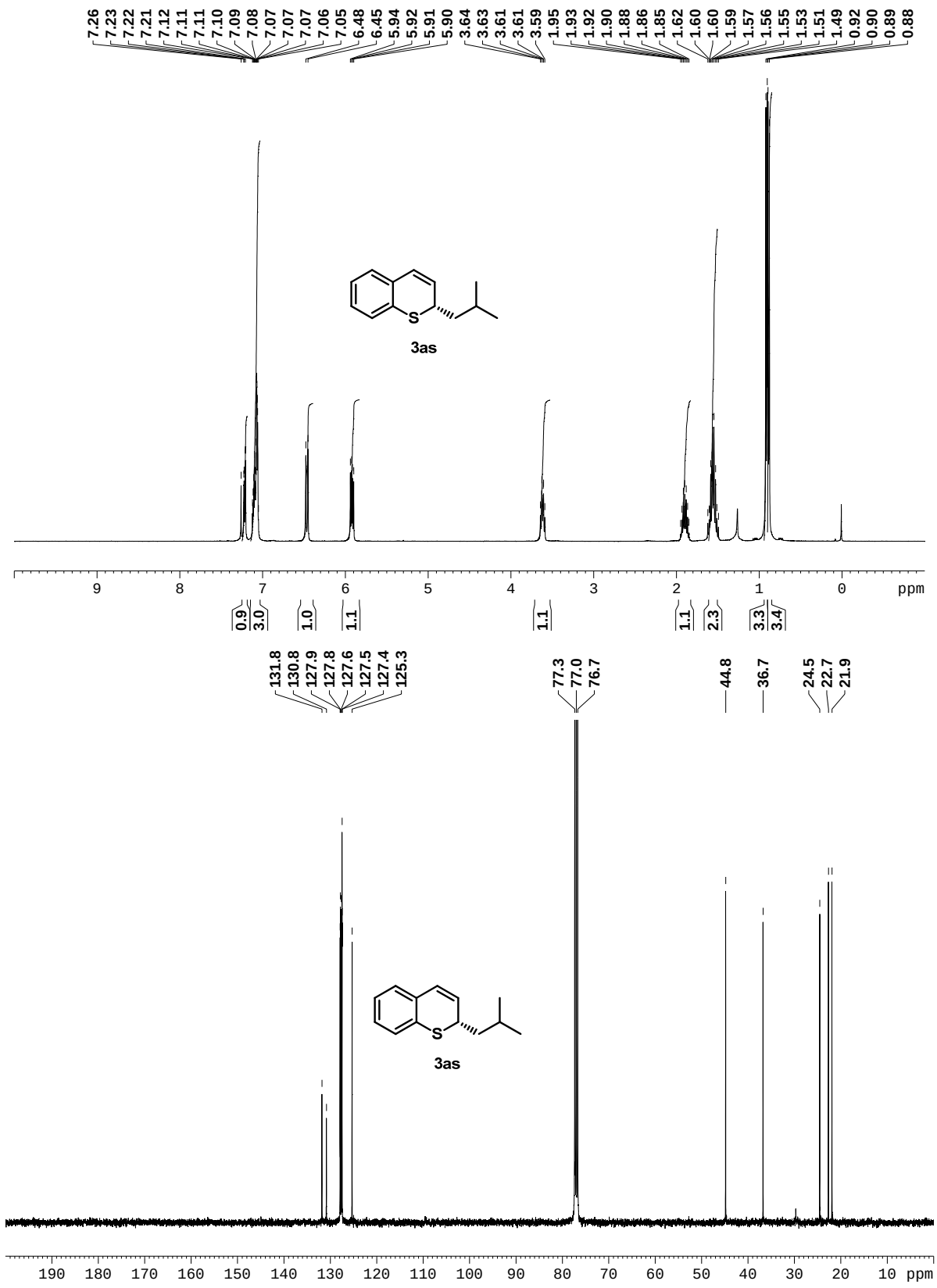


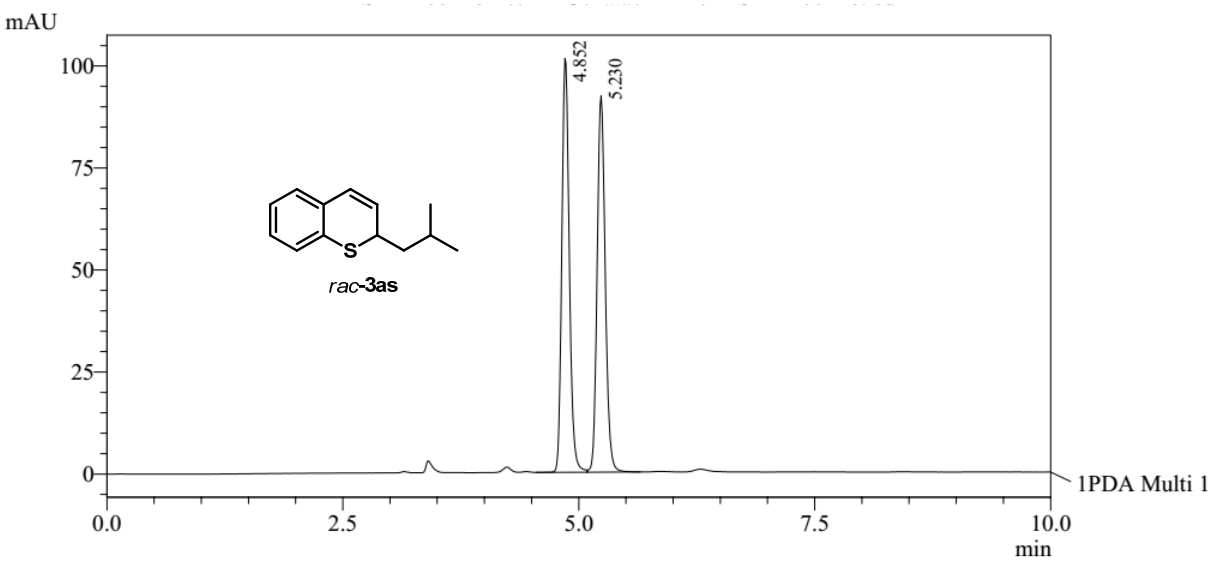
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.900	158577	5.097
2	5.225	2952876	94.903
Total		3111453	100.000


7.26
7.23
7.22
7.21
7.12
7.11
7.11
7.10
7.09
7.08
7.07
7.07
7.07
7.06
7.05
6.48
6.45
5.94
5.92
5.91
5.90
3.64
3.63
3.61
3.61
3.59
1.95
1.93
1.92
1.90
1.88
1.86
1.85
1.62
1.60
1.60
1.59
1.57
1.56
1.55
1.53
1.51
1.49
0.92
0.90
0.89
0.88
S
3as
9
8
7
6
5
4
3
2
1
0
ppm
0.9
3.0
1.0
1.1
1.1
1.1
2.3
3.3
3.4
131.8
130.8
127.9
127.8
127.6
127.5
127.4
125.3
77.3
77.0
76.7
44.8
36.7
24.5
22.7
21.9
S
3as
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



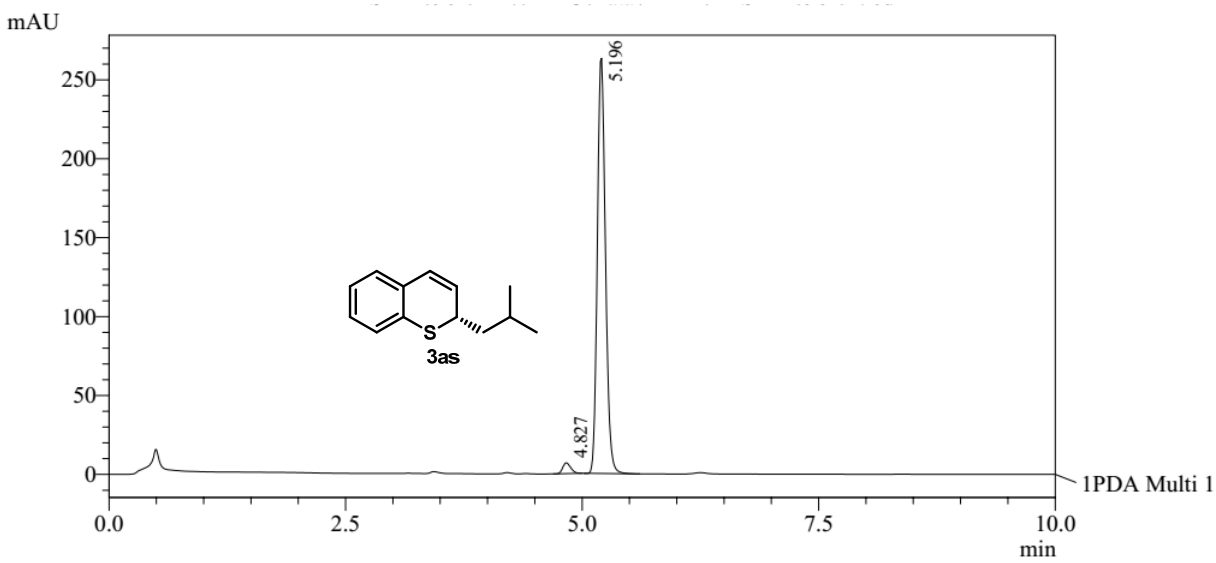
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.852	557905	50.349
2	5.230	550168	49.651
Total		1108073	100.000

Daicel Chiralpak IF column (95:5 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

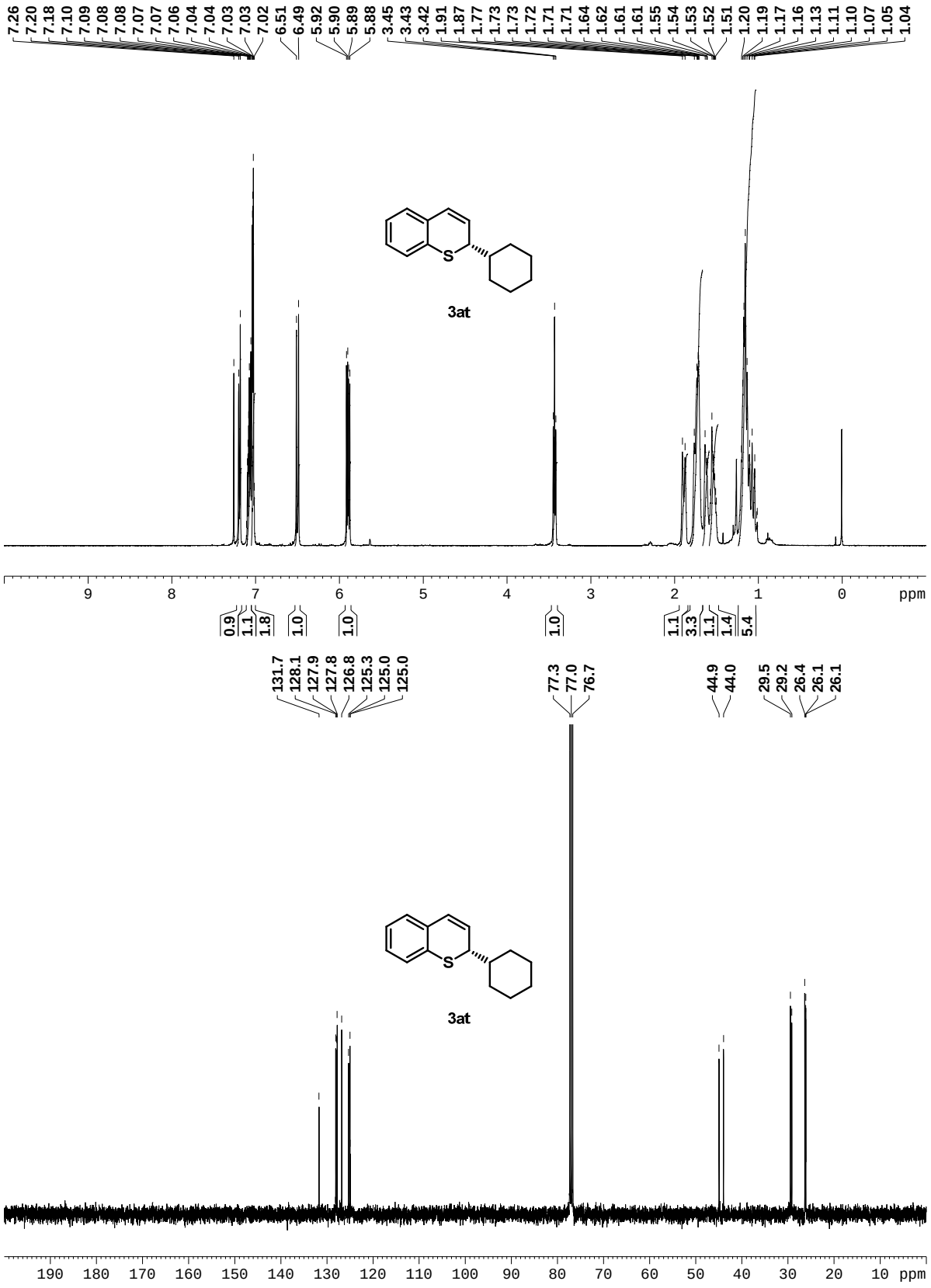


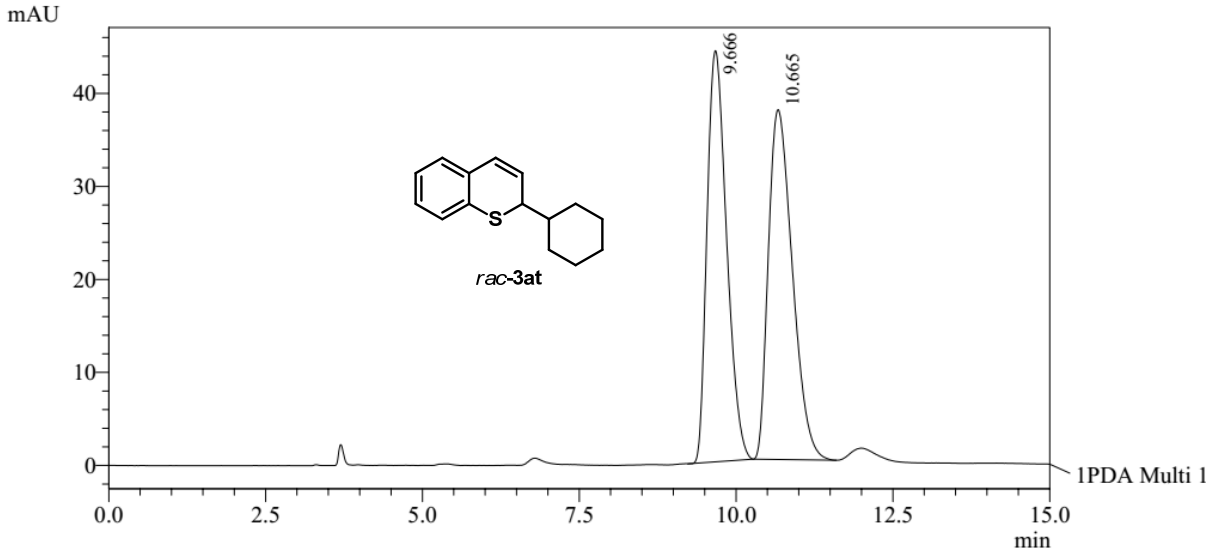
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.827	40408	2.506
2	5.196	1572248	97.494
Total		1612656	100.000


7.26 7.20 7.18 7.10 7.09 7.08 7.08 7.07 7.07 7.06 7.04 7.04 7.03 7.03 7.02 6.51 6.49 5.92 5.90 5.89 5.88 3.45 3.43 3.42 1.91 1.87 1.77 1.73 1.73 1.72 1.71 1.71 1.64 1.62 1.61 1.61 1.55 1.54 1.53 1.52 1.51 1.20 1.19 1.17 1.16 1.13 1.11 1.10 1.07 1.05 1.04
S
3at
9 8 7 6 5 4 3 2 1 0 ppm
0.9 1.1 1.8 1.0 1.0 1.0 1.1 3.3 1.1 1.4 5.4
131.7 128.1 127.9 127.8 126.8 125.3 125.0 125.0
77.3 77.0 76.7
44.9 44.0
29.5 29.2 26.4 26.1 26.1
S
3at
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



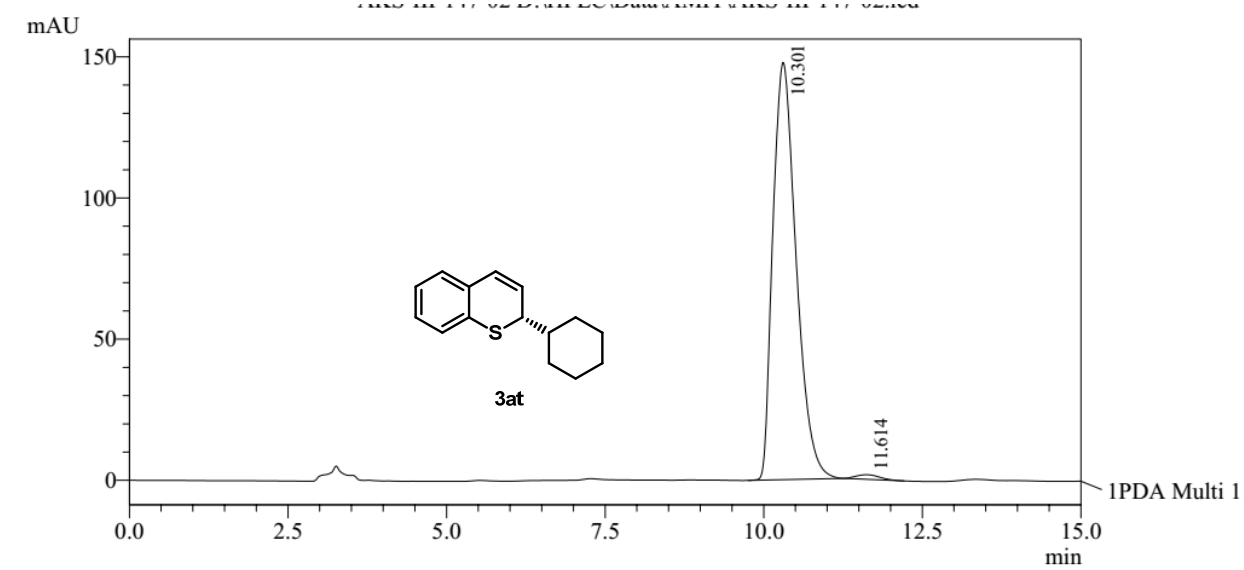
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	9.666	959531	48.921
2	10.665	1001863	51.079
Total		1961394	100.000

Daicel Chiralpak IE column (99:01 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

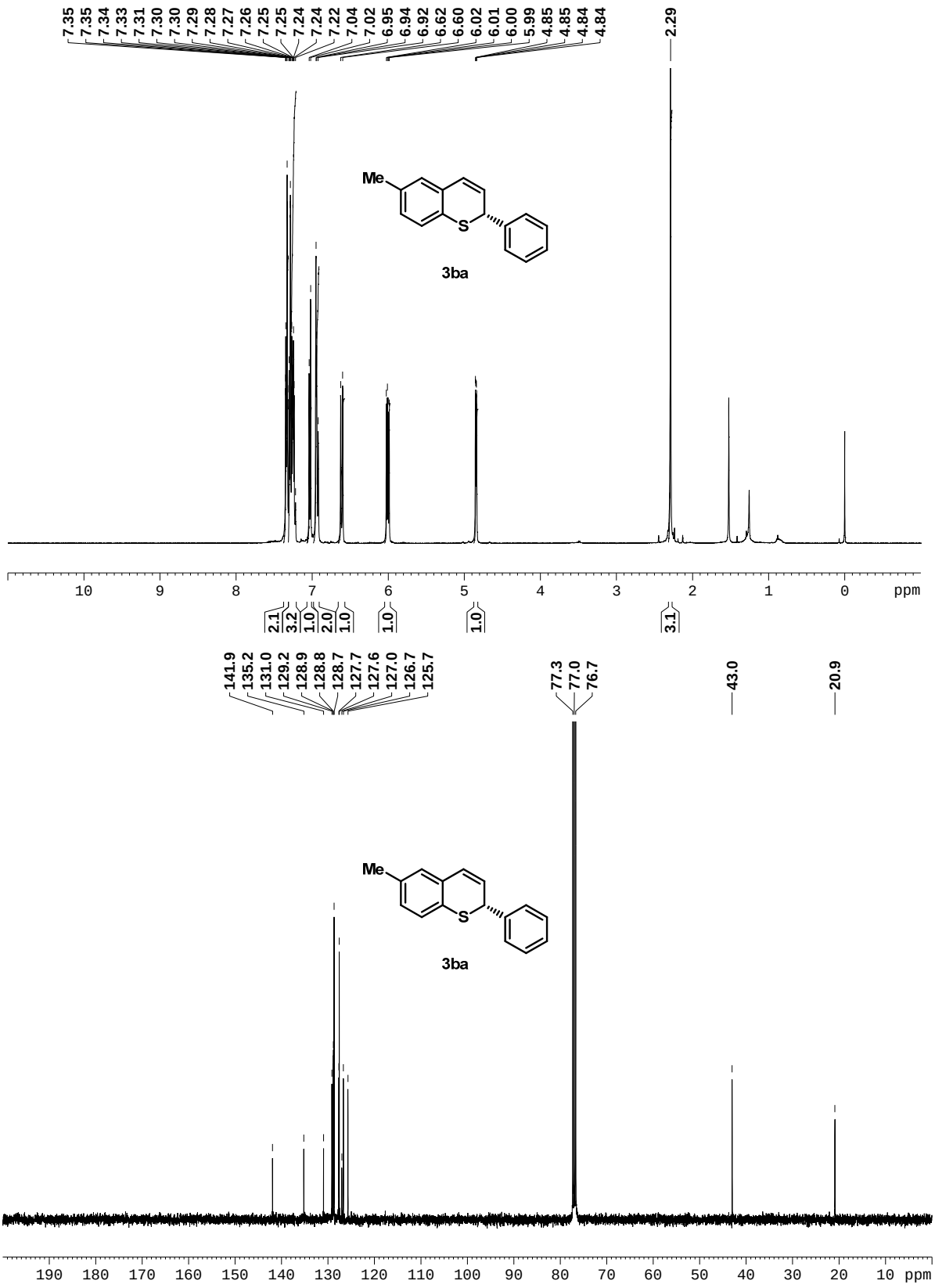


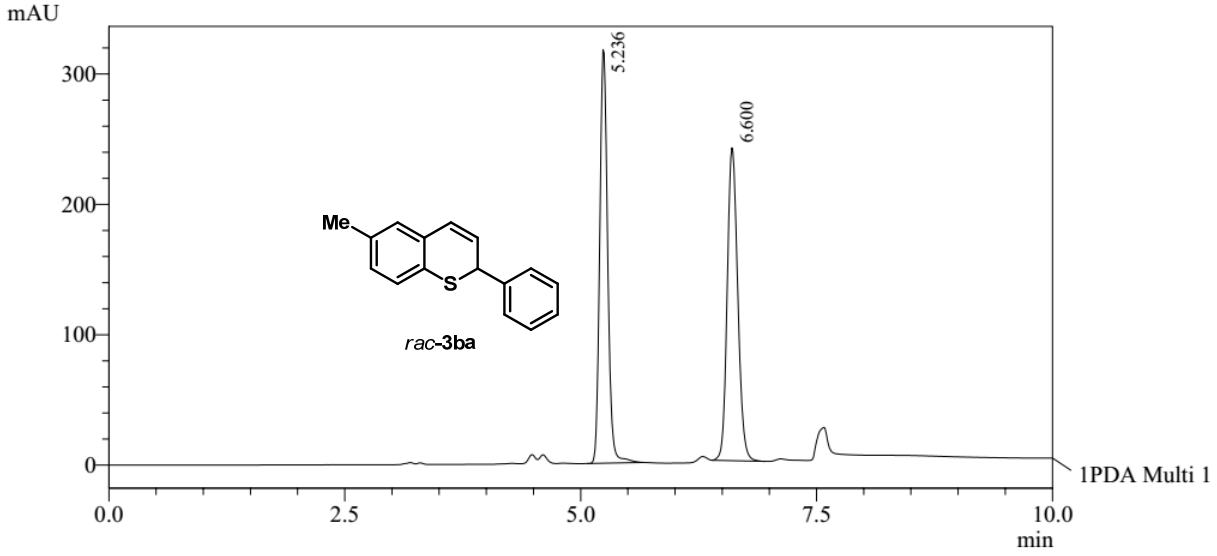
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	10.301	3775753	98.915
2	11.614	41435	1.085
Total		3817188	100.000


7.35
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.22
7.04
7.02
6.95
6.94
6.92
6.62
6.60
6.02
6.01
6.00
5.99
4.85
4.85
4.84
4.84
2.29
Me
S
3ba
10
9
8
7
6
5
4
3
2
1
0
ppm
2.1
3.2
1.0
2.0
1.0
1.0
1.0
3.1
141.9
135.2
131.0
129.2
128.9
128.8
128.7
127.7
127.6
127.0
126.7
125.7
77.3
77.0
76.7
43.0
20.9
Me
S
3ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



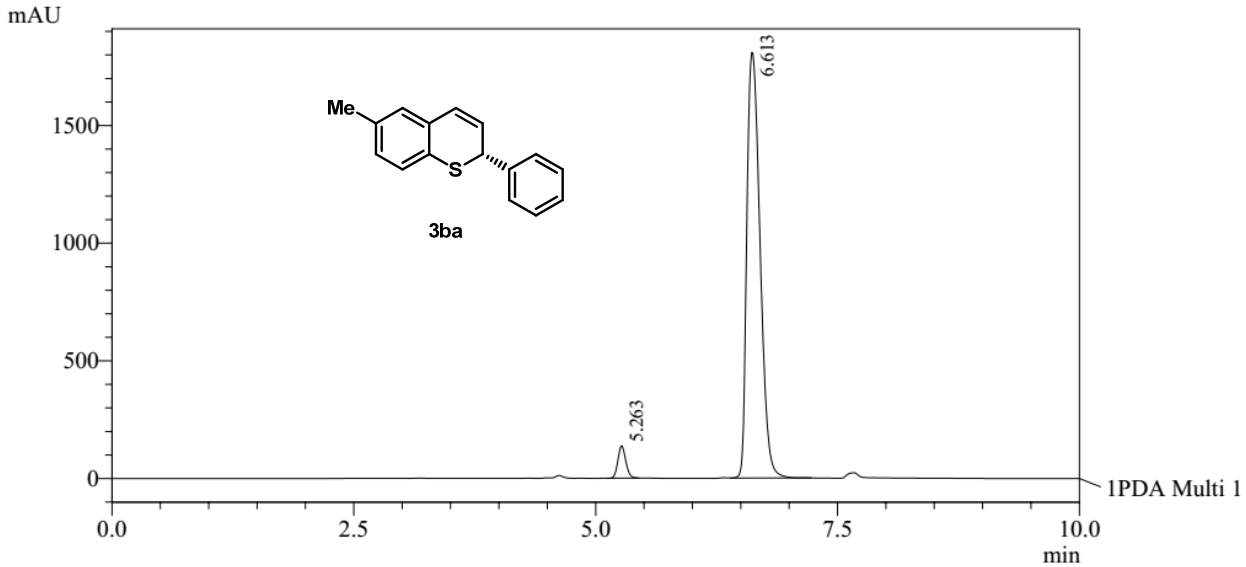
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.236	1854387	49.954
2	6.600	1857812	50.046
Total		3712198	100.000

Daicel Chiralpak IF column (80:20 *n*-Hexane/MTBE, 1.0 mL/min, 20 °C, 254 nm)

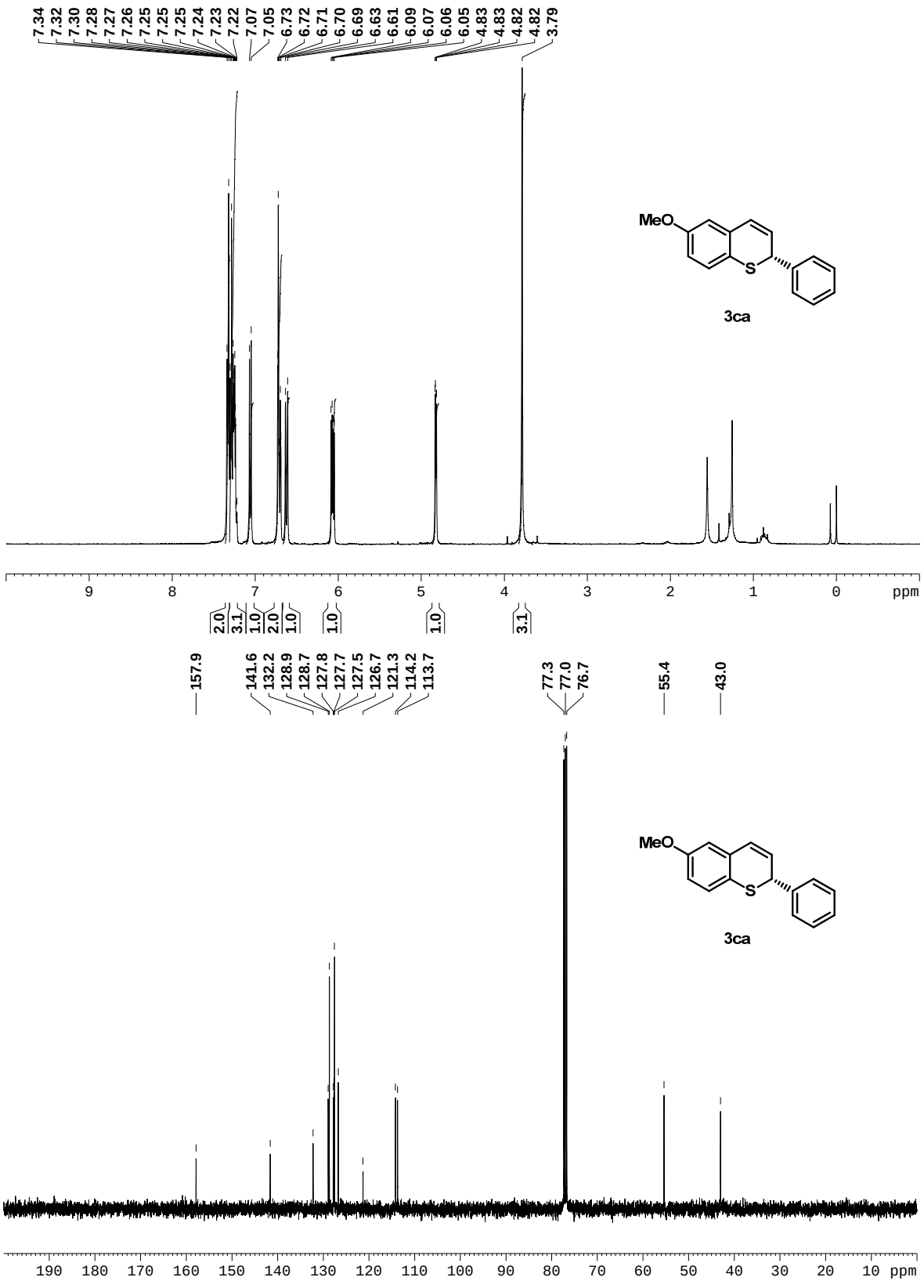


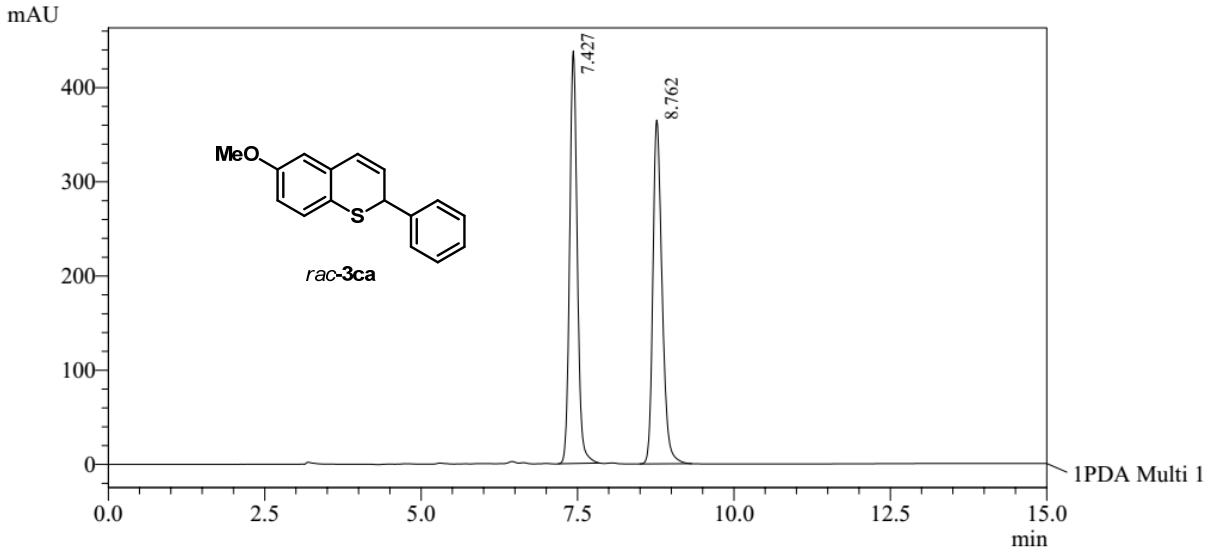
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.263	778269	4.339
2	6.613	17158836	95.661
Total		17937105	100.000


7.34
7.32
7.30
7.28
7.27
7.26
7.25
7.25
7.25
7.24
7.23
7.22
7.07
7.05
6.73
6.72
6.71
6.70
6.69
6.63
6.61
6.09
6.07
6.06
6.05
4.83
4.83
4.82
4.82
3.79
MeO
S
3ca
9
8
7
6
5
4
3
2
1
0
ppm
2.0
3.1
1.0
2.0
1.0
1.0
1.0
3.1
157.9
141.6
132.2
128.9
128.7
127.8
127.7
127.5
126.7
121.3
114.2
113.7
77.3
77.0
76.7
55.4
43.0
MeO
S
3ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



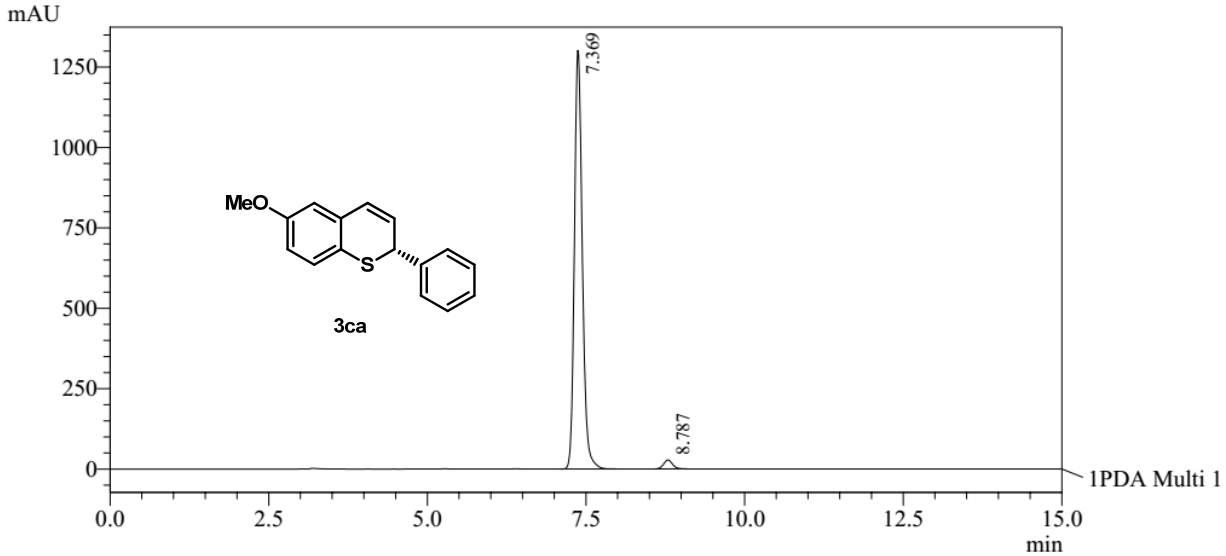
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.427	3719164	49.878
2	8.762	3737392	50.122
Total		7456556	100.000

Daicel Chiralpak IB column (97:03 *n*-Hexane/ *i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

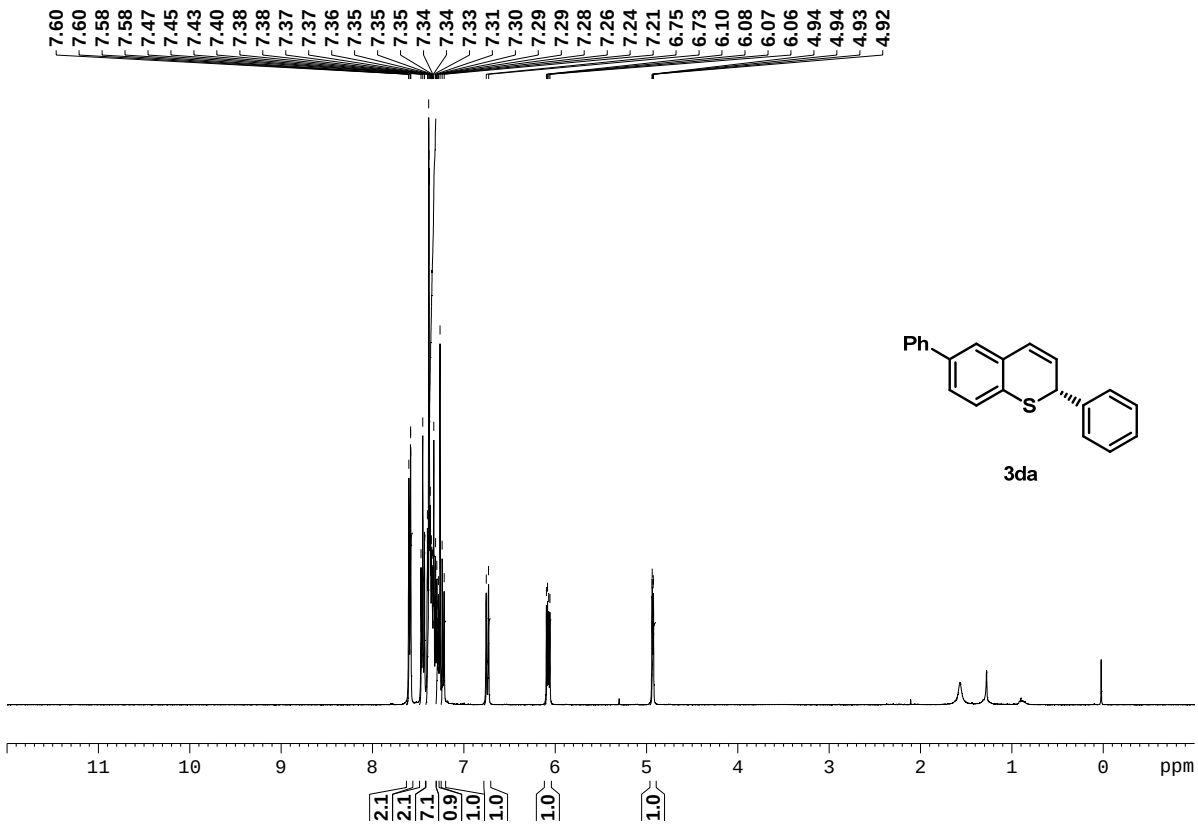


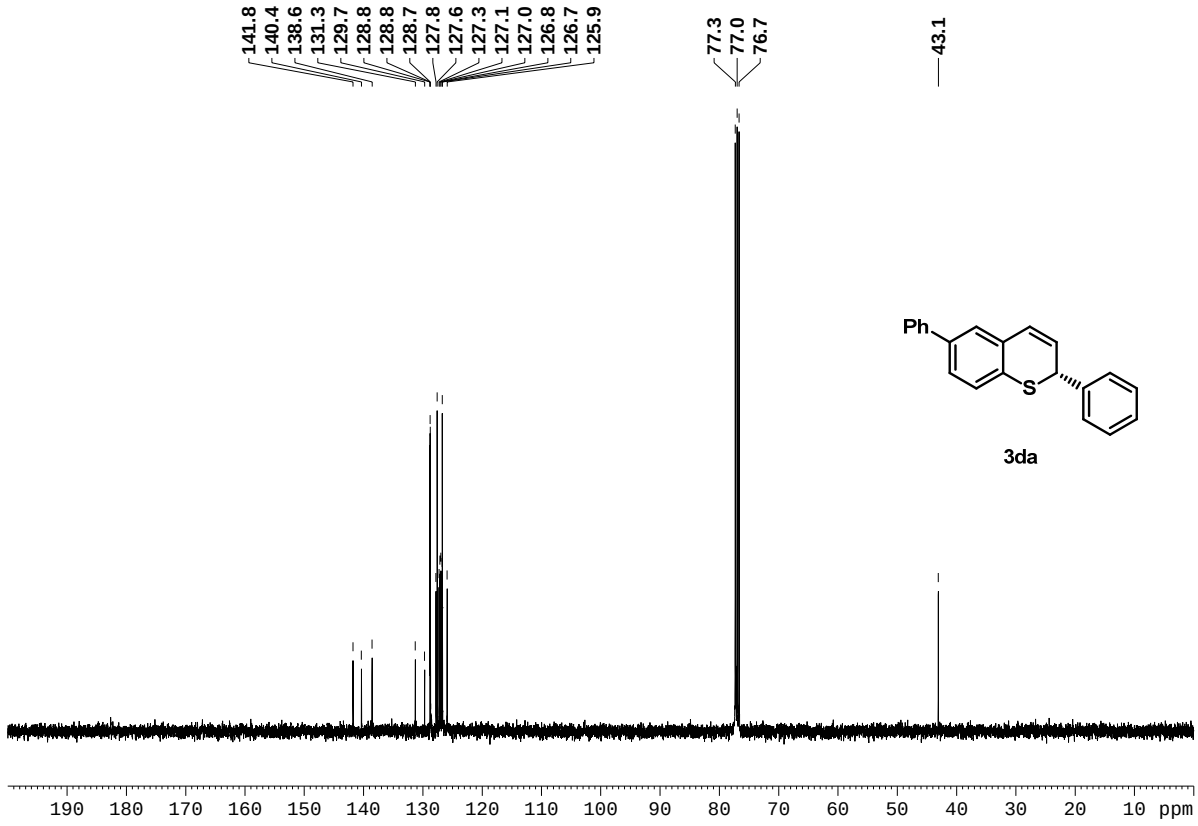
1 PDA Multi 1 / 254nm 4nm

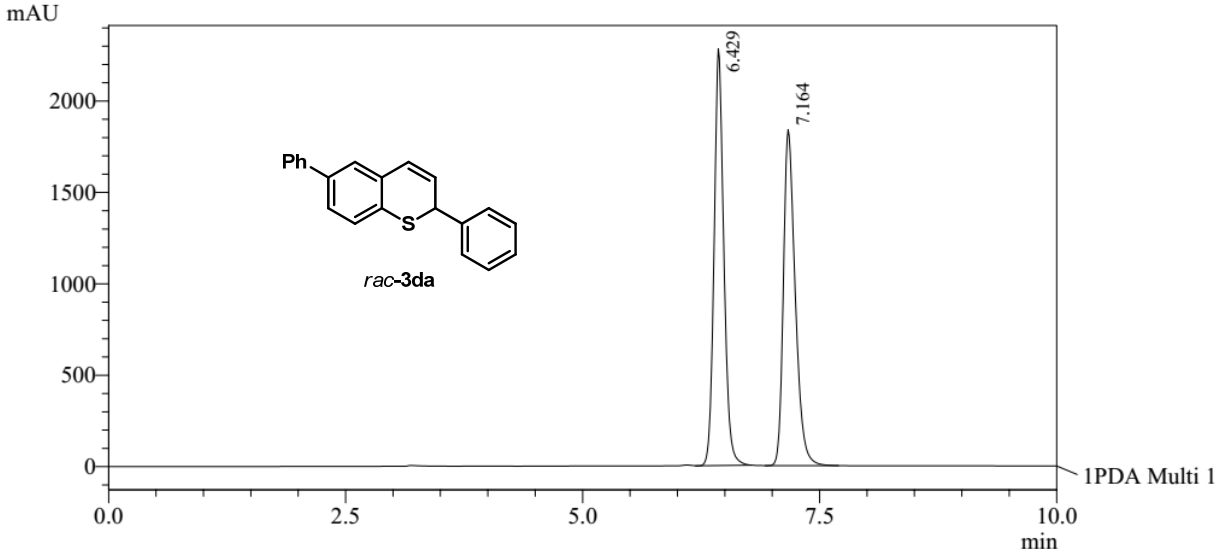
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	7.369	11305147	97.662
2	8.787	270657	2.338
Total		11575804	100.000


7.60
7.60
7.58
7.58
7.47
7.45
7.43
7.40
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.31
7.30
7.29
7.29
7.28
7.26
7.24
7.21
6.75
6.73
6.10
6.08
6.07
6.06
4.94
4.94
4.93
4.92
Ph
S
3da
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.1
2.1
7.1
0.9
1.0
1.0
1.0
1.0


141.8
140.4
138.6
131.3
129.7
128.8
128.8
128.7
127.8
127.6
127.3
127.1
127.0
126.8
126.7
125.9
77.3
77.0
76.7
43.1
Ph
S
3da
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



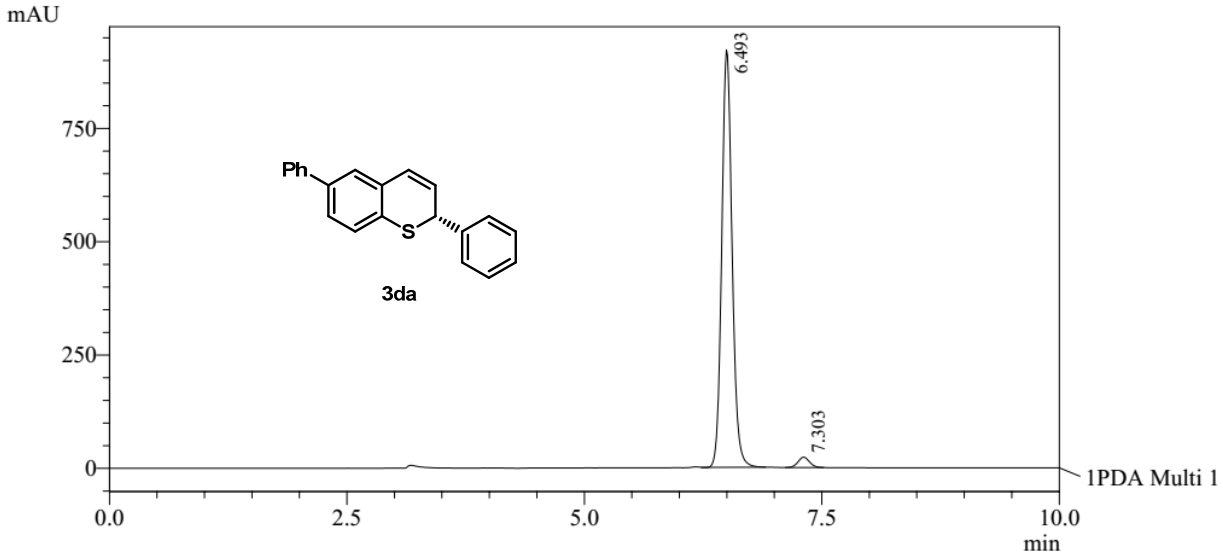
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.429	16278204	50.469
2	7.164	15975850	49.531
Total		32254054	100.000

Daicel Chiralpak IB column (97:03 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

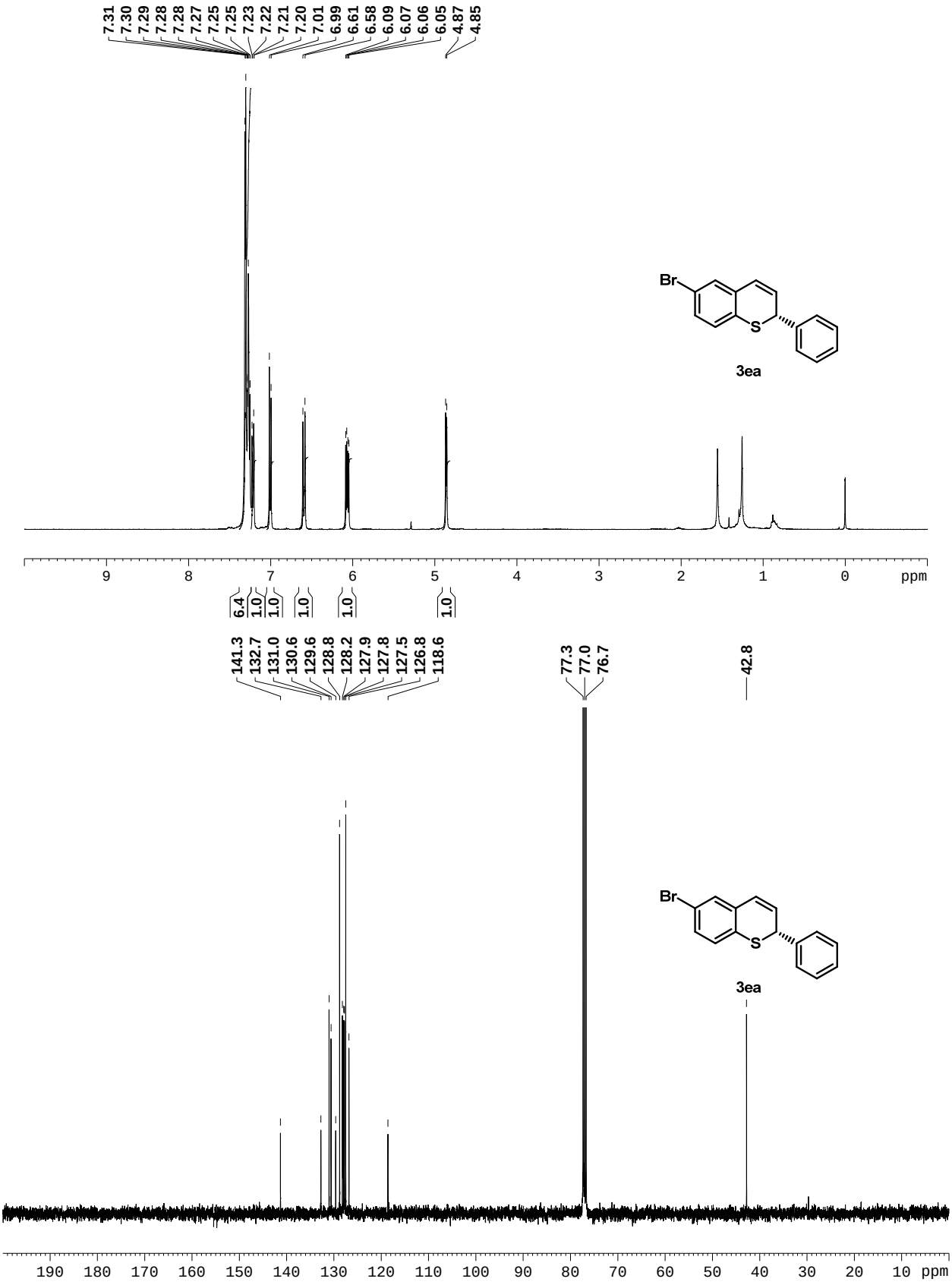


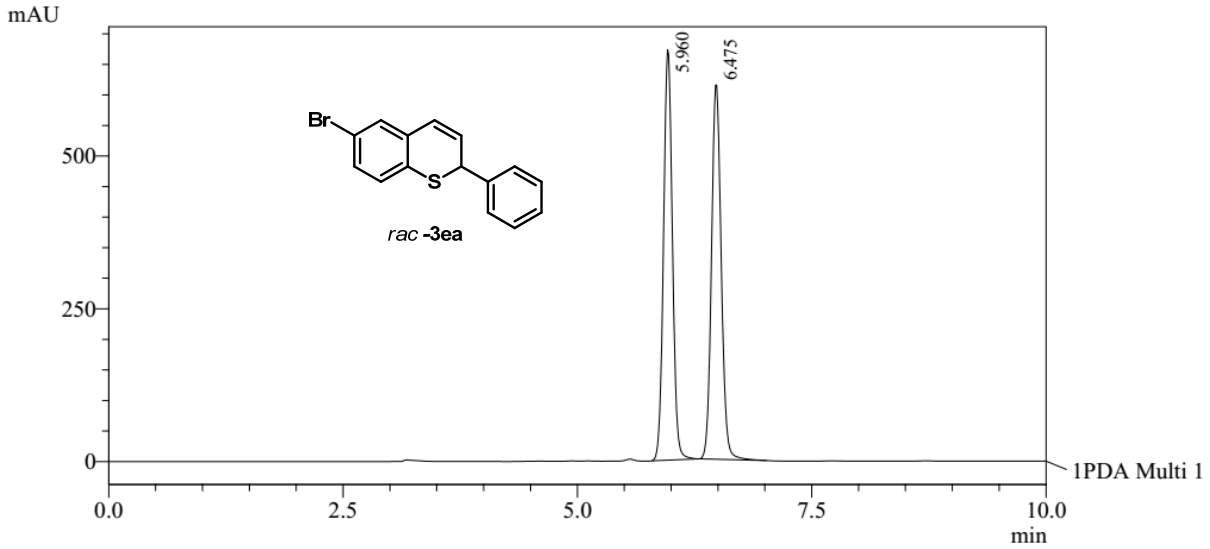
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.493	6977446	97.338
2	7.303	190808	2.662
Total		7168254	100.000


7.31
7.30
7.29
7.28
7.28
7.27
7.25
7.25
7.23
7.22
7.21
7.20
7.01
6.99
6.61
6.58
6.09
6.07
6.06
6.05
4.87
4.85
Br
S
3ea
9
8
7
6
5
4
3
2
1
0
ppm
6.4
1.0
1.0
1.0
1.0
1.0
141.3
132.7
131.0
130.6
129.6
128.8
128.2
127.9
127.8
127.5
126.8
118.6
77.3
77.0
76.7
42.8
Br
S
3ea
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



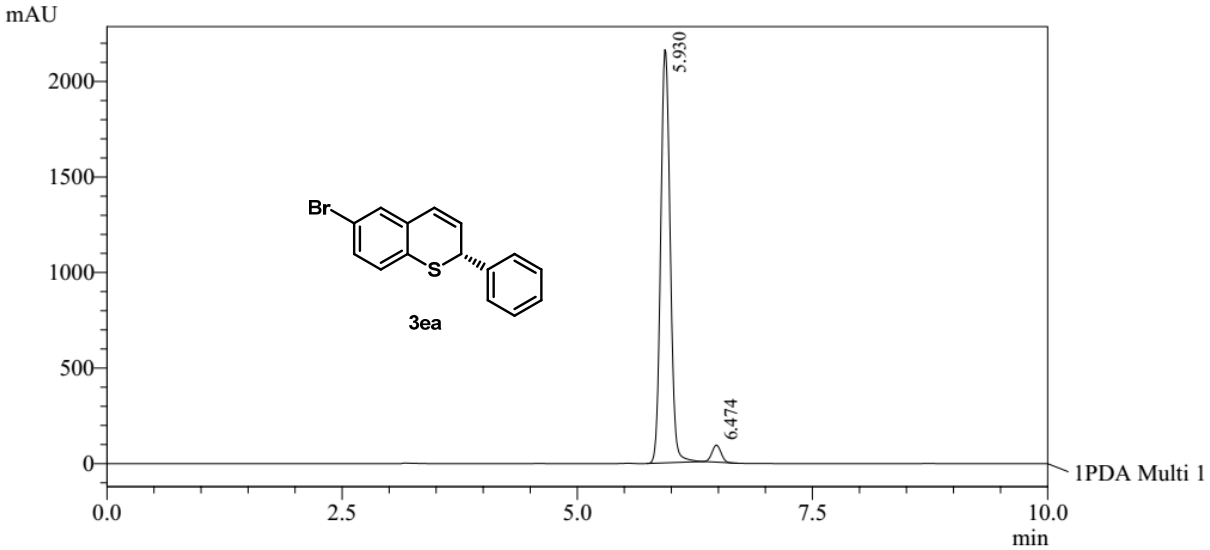
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.960	4419442	50.004
2	6.475	4418701	49.996
Total		8838143	100.000

Daicel Chiralpak IB column (97:03 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

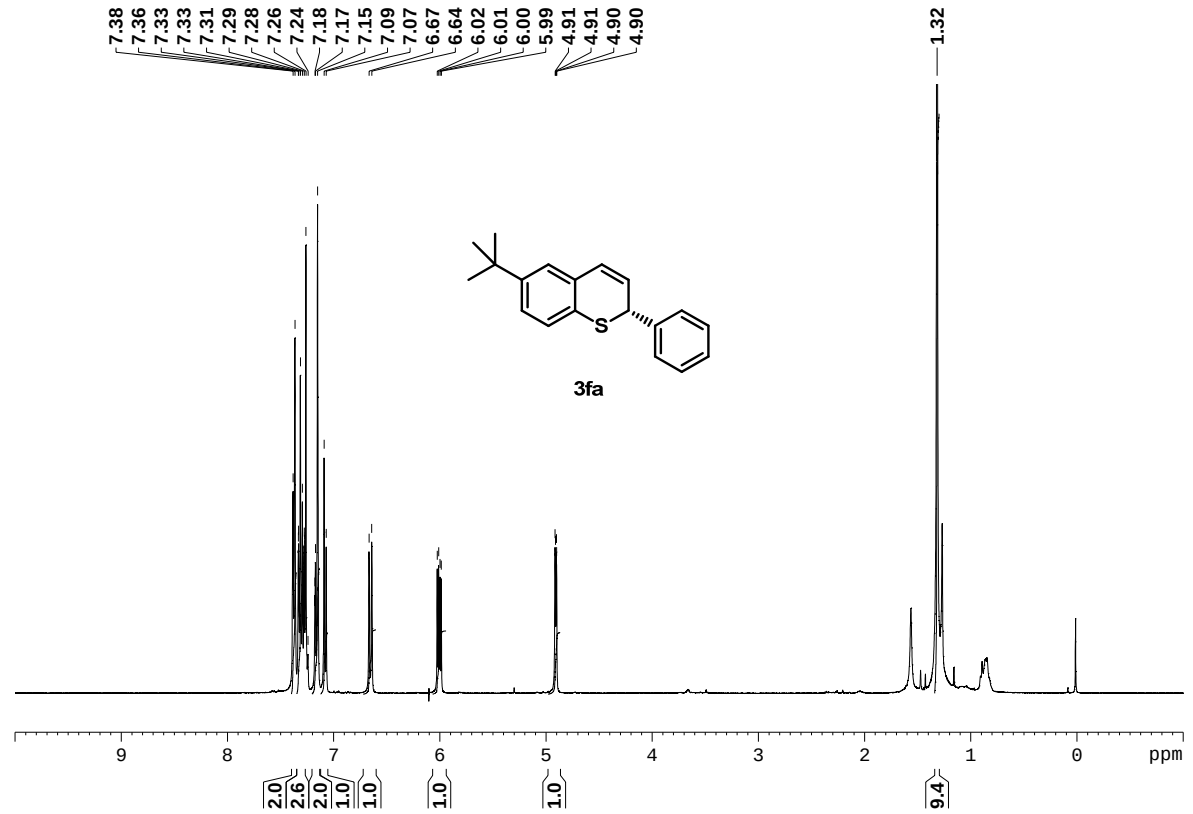


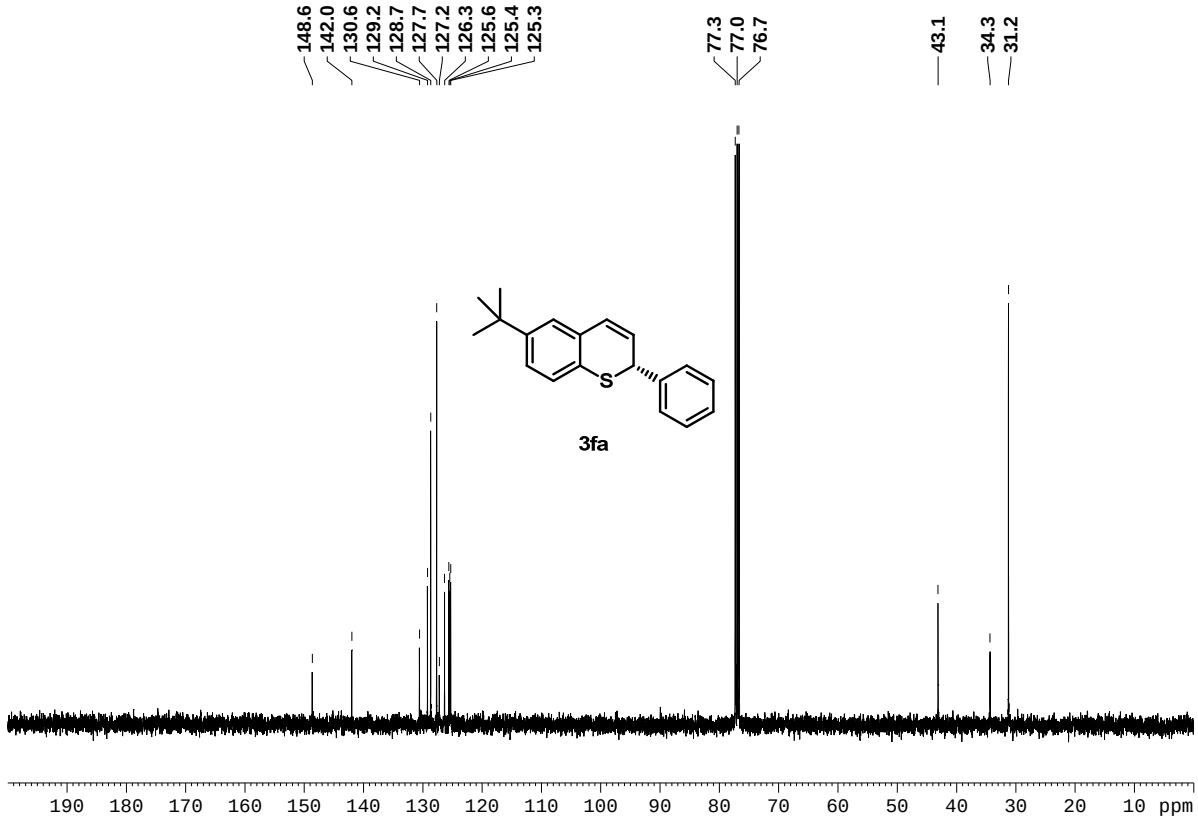
1 PDA Multi 1 / 254nm 4nm

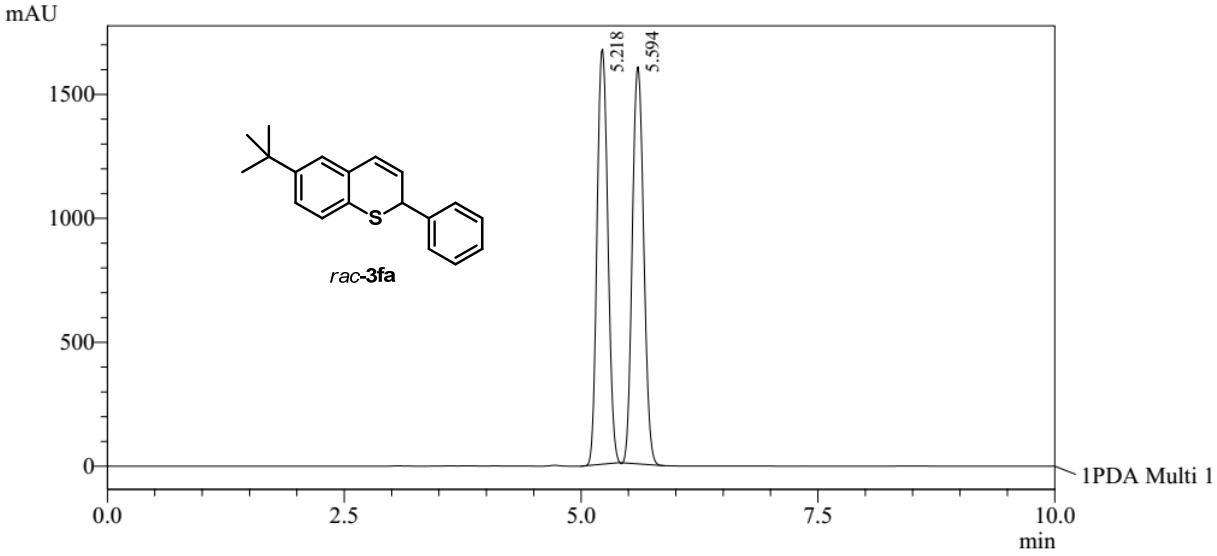
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.930	15174487	96.211
2	6.474	597673	3.789
Total		15772159	100.000


7.38
7.36
7.33
7.33
7.31
7.29
7.28
7.26
7.24
7.18
7.17
7.15
7.09
7.07
6.67
6.64
6.02
6.01
6.00
5.99
4.91
4.91
4.90
4.90
1.32
S
3fa
9
8
7
6
5
4
3
2
1
0
ppm
2.0
2.6
2.0
1.0
1.0
1.0
1.0
9.4


148.6
142.0
130.6
129.2
128.7
127.7
127.2
126.3
125.6
125.4
125.3
77.3
77.0
76.7
43.1
34.3
31.2
S
3fa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



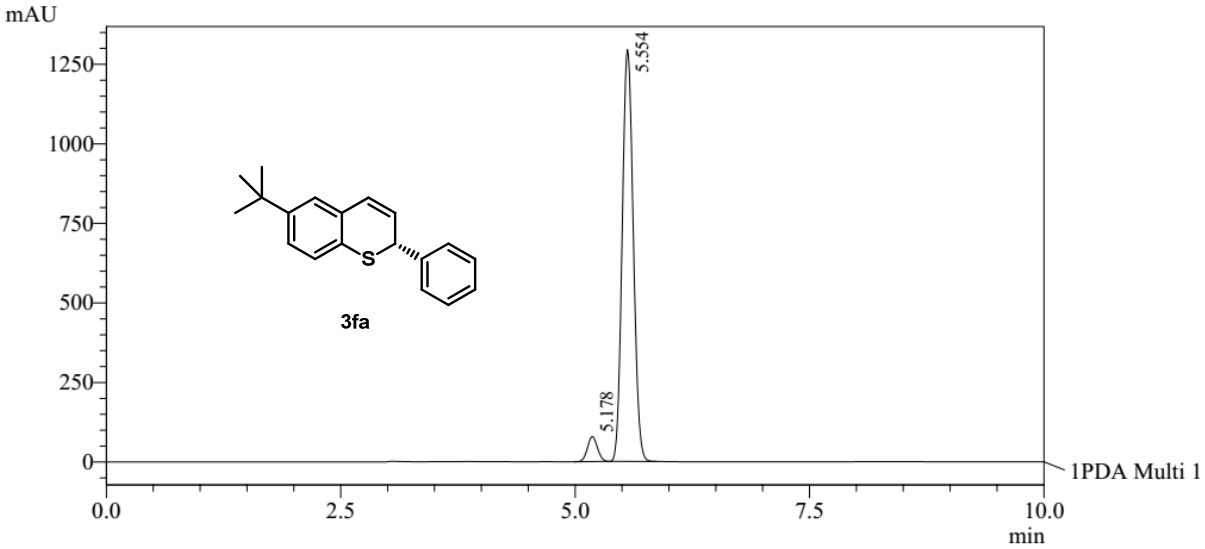
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.218	13254328	49.702
2	5.594	13413074	50.298
Total		26667402	100.000

Phenomenex Cellulose-1 column (97:03 *n*-Hexane/ *i*-PrOH, 1.0 mL/min, 20 °C, 254 nm

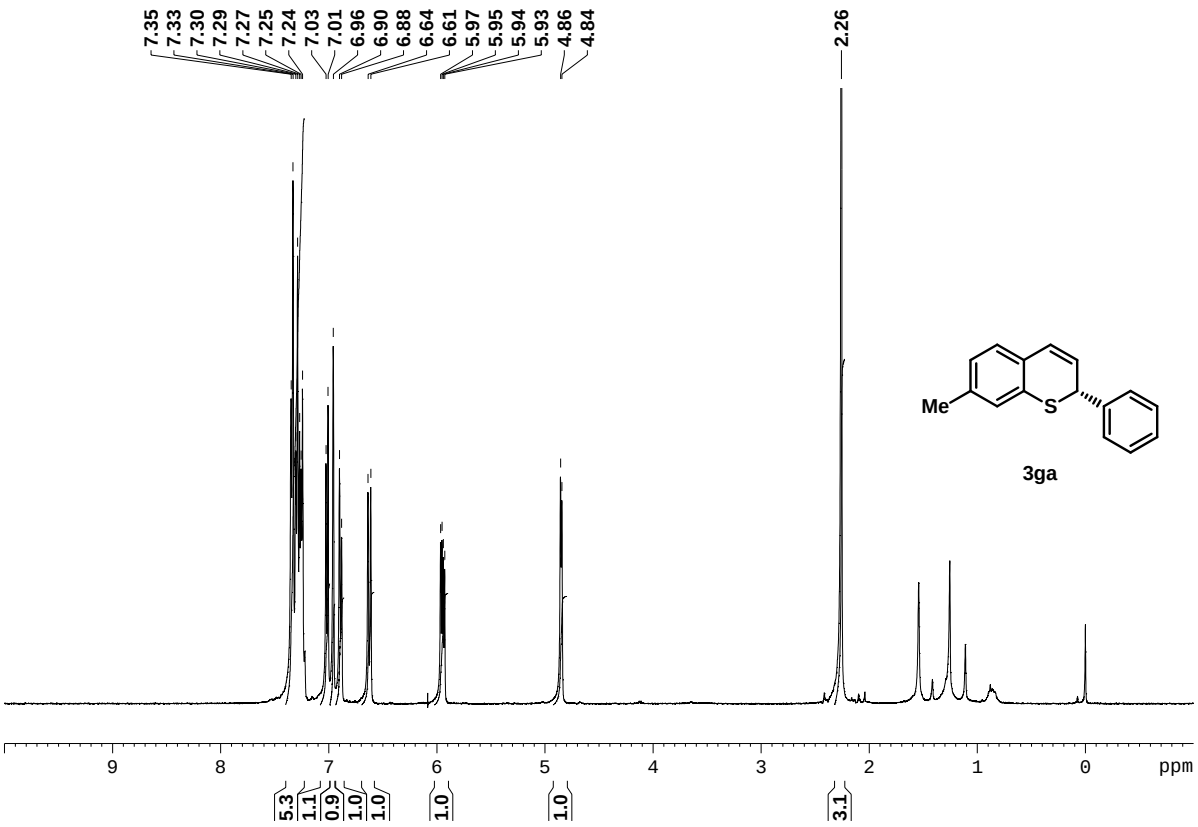


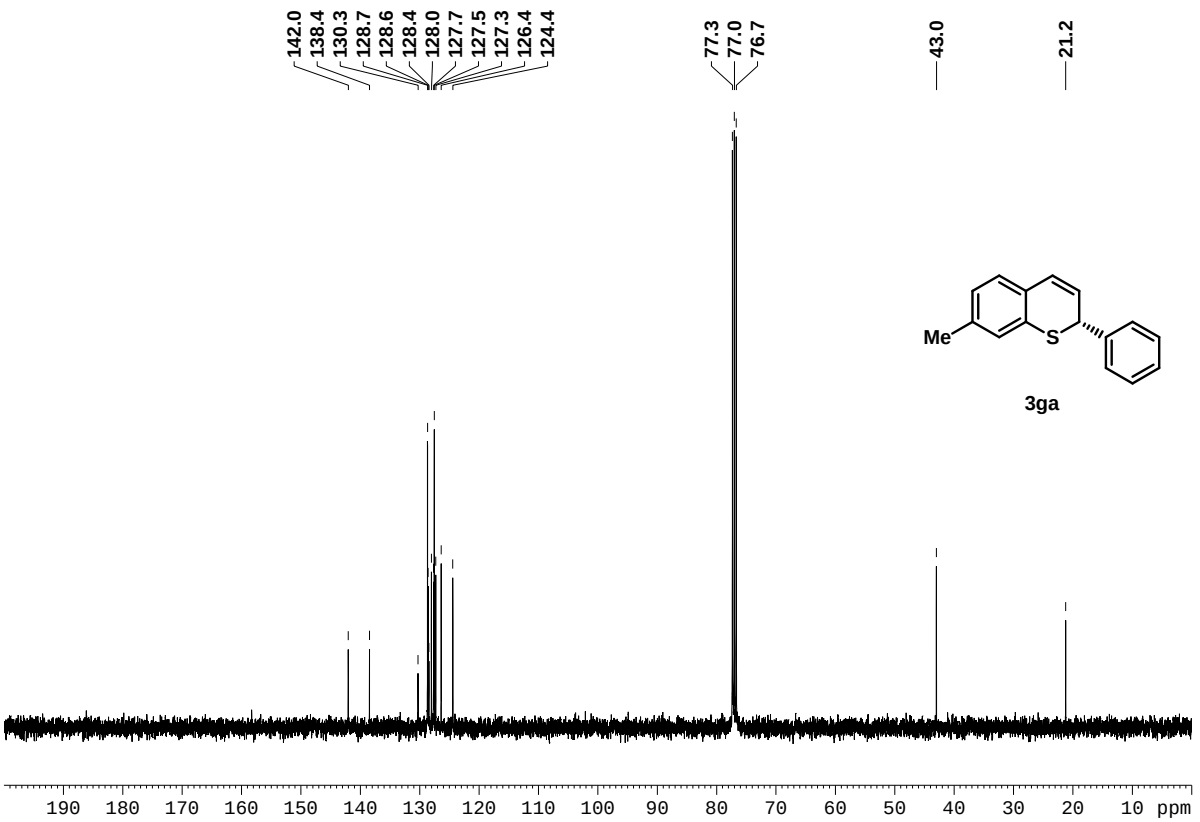
1 PDA Multi 1 / 254nm 4nm

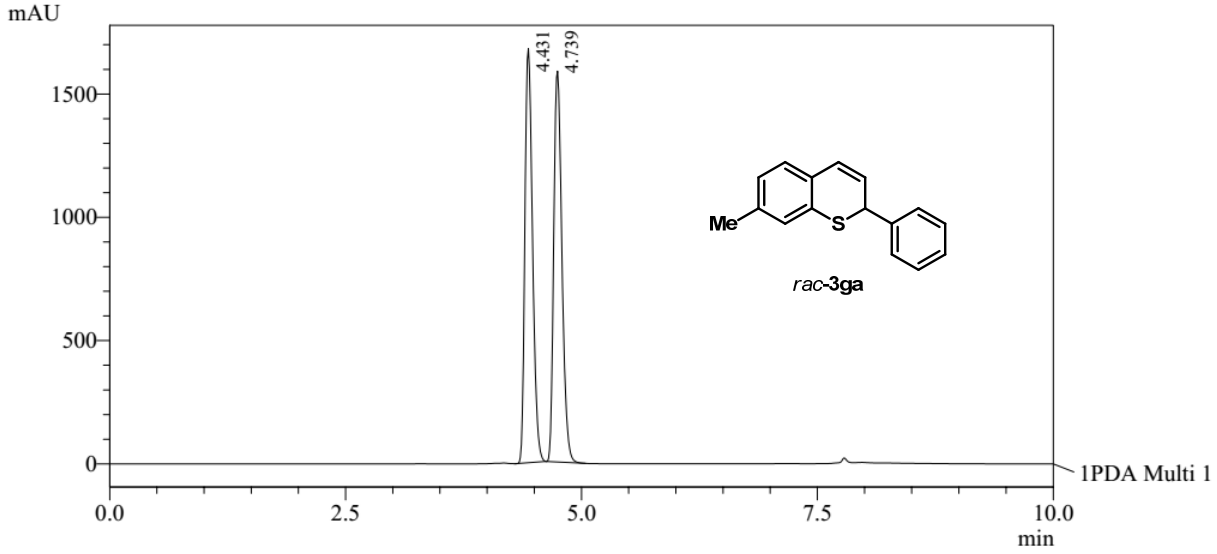
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.178	579865	5.170
2	5.554	10635523	94.830
Total		11215388	100.000


7.35
7.33
7.30
7.29
7.27
7.25
7.24
7.03
7.01
6.96
6.90
6.88
6.64
6.61
5.97
5.95
5.94
5.93
4.86
4.84
2.26
Me
S
3ga
9
8
7
6
5
4
3
2
1
0
ppm
5.3
1.1
0.9
1.0
1.0
1.0
1.0
3.1


142.0
138.4
130.3
128.7
128.6
128.4
128.0
127.7
127.5
127.3
126.4
124.4
77.3
77.0
76.7
43.0
21.2
Me
S
3ga
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



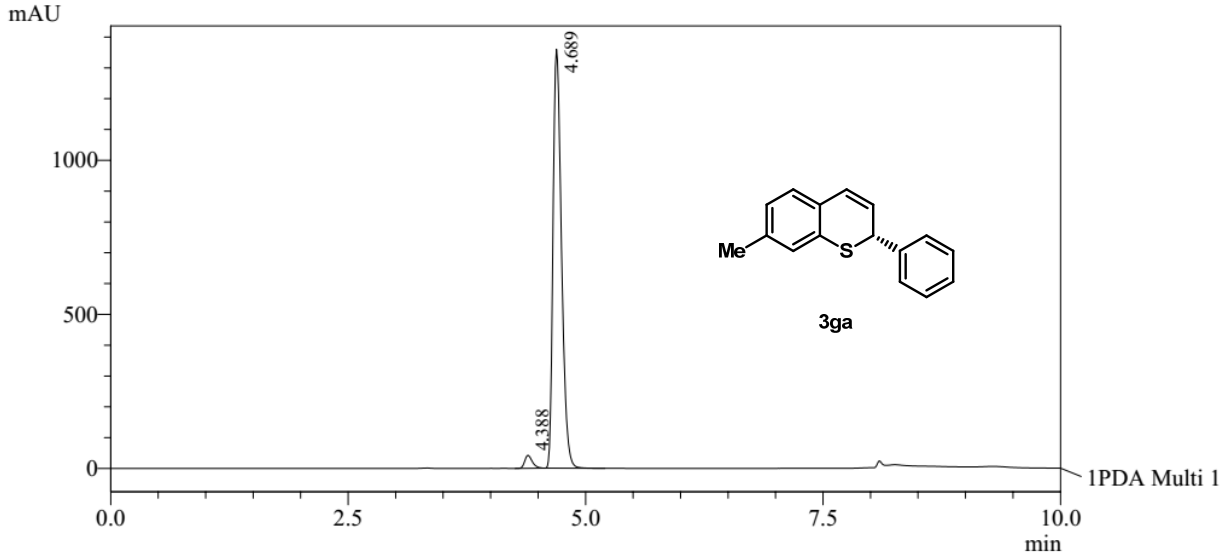
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.431	9456192	49.732
2	4.739	9558207	50.268
Total		19014399	100.000

Daicel Chiralpak IC column (80:20 *n*-Hexane/ MTBE, 1.0 mL/min, 20 °C, 254 nm)

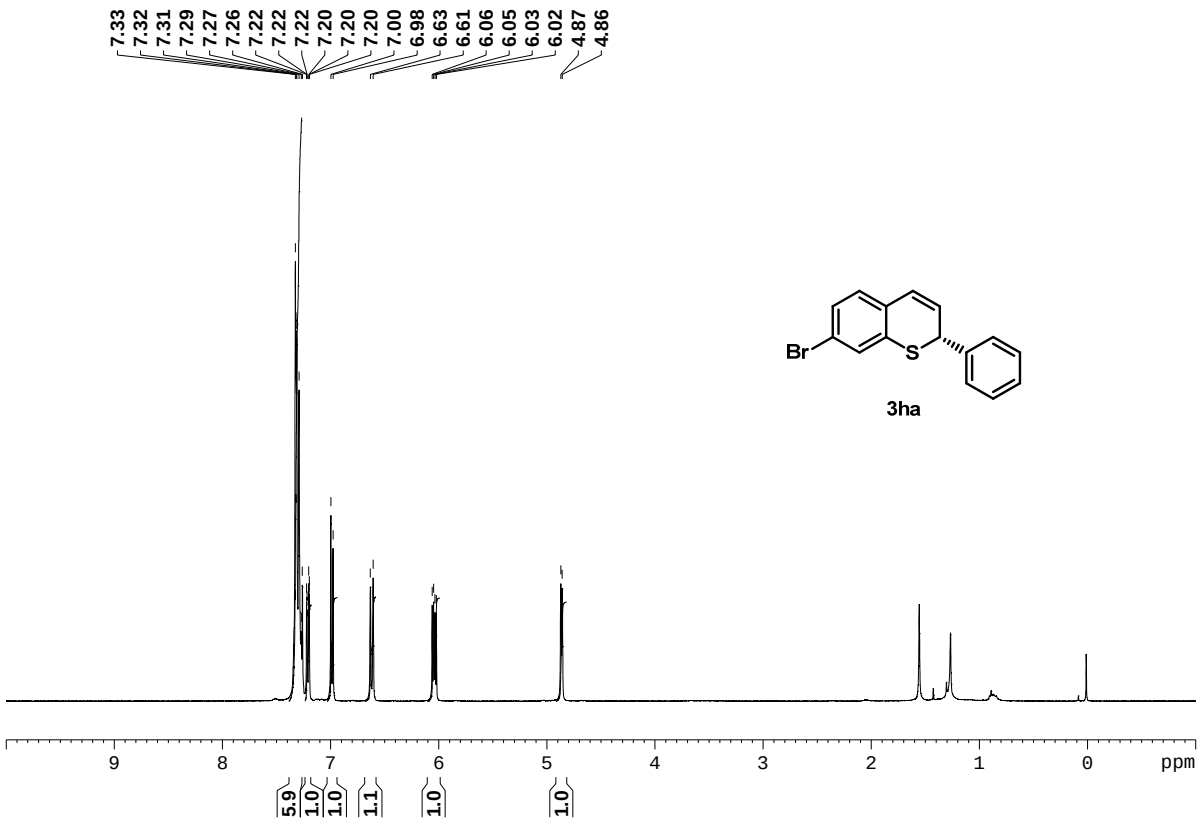


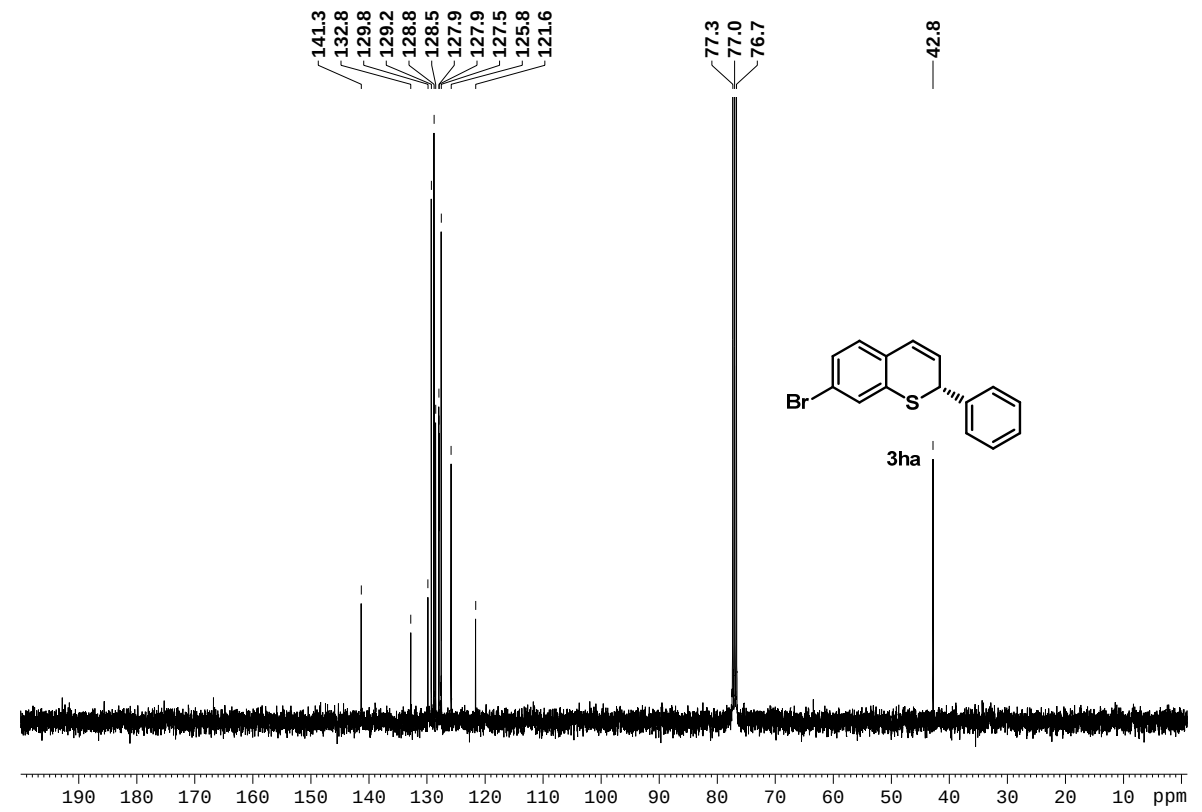
1 PDA Multi 1 / 254nm 4nm

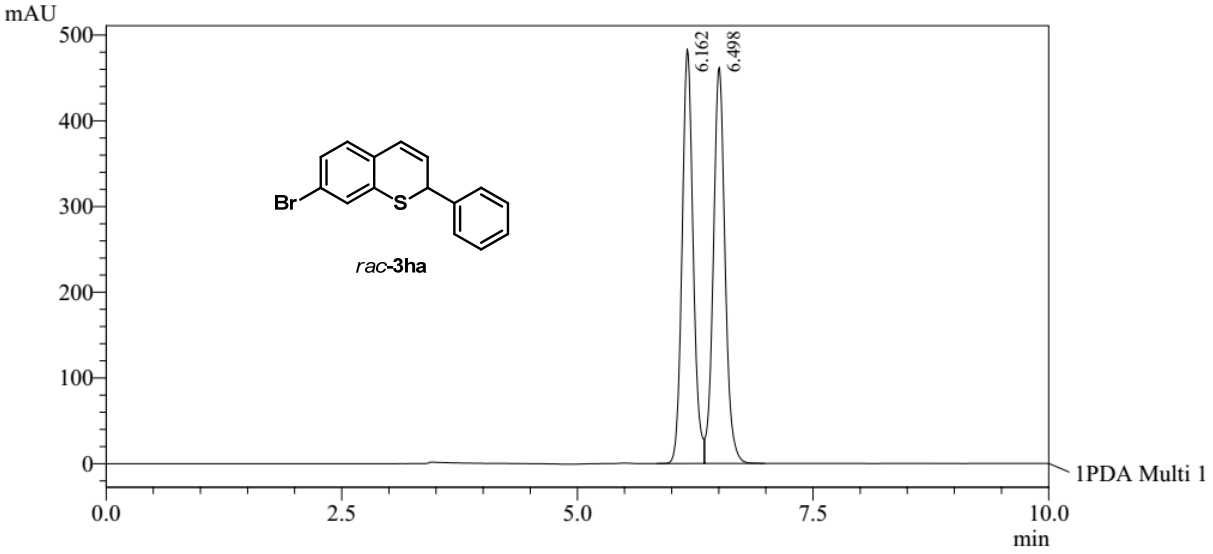
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.388	234268	2.707
2	4.689	8419625	97.293
Total		8653893	100.000


7.33
7.32
7.31
7.29
7.27
7.26
7.22
7.22
7.22
7.20
7.20
7.20
7.00
6.98
6.63
6.61
6.06
6.05
6.03
6.02
4.87
4.86
Br
S
3ha
9
8
7
6
5
4
3
2
1
0
ppm
5.9
1.0
1.0
1.1
1.0
1.0


141.3
132.8
129.8
129.2
128.8
128.5
127.9
127.9
127.5
125.8
121.6
77.3
77.0
76.7
42.8
Br
S
3ha
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



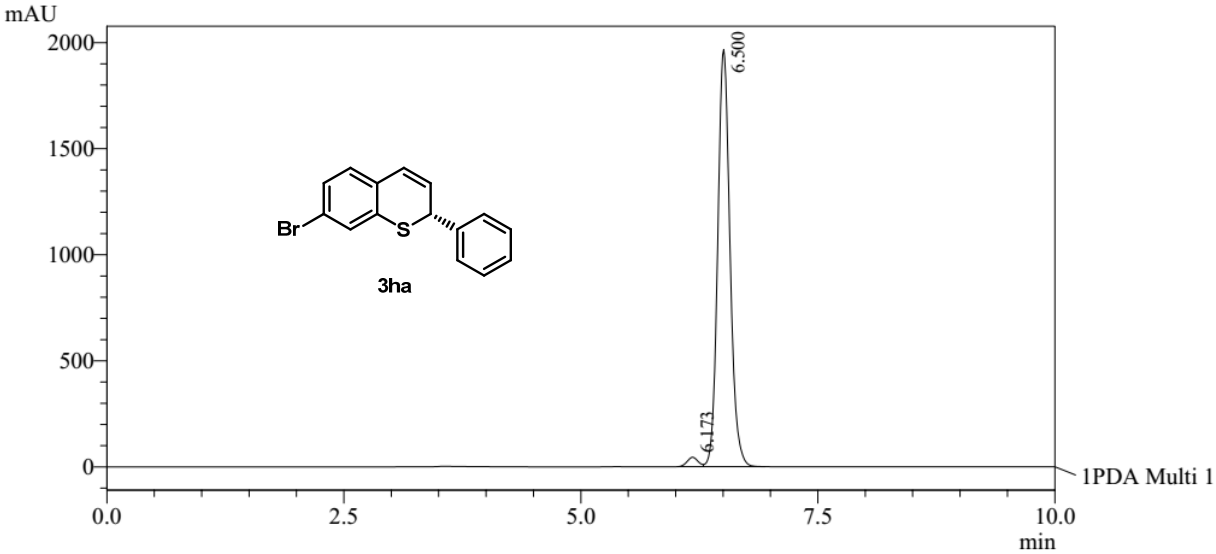
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.162	3950926	49.776
2	6.498	3986467	50.224
Total		7937393	100.000

Daicel Chiralpak IB column (99:01 *n*-Hexane/ *i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

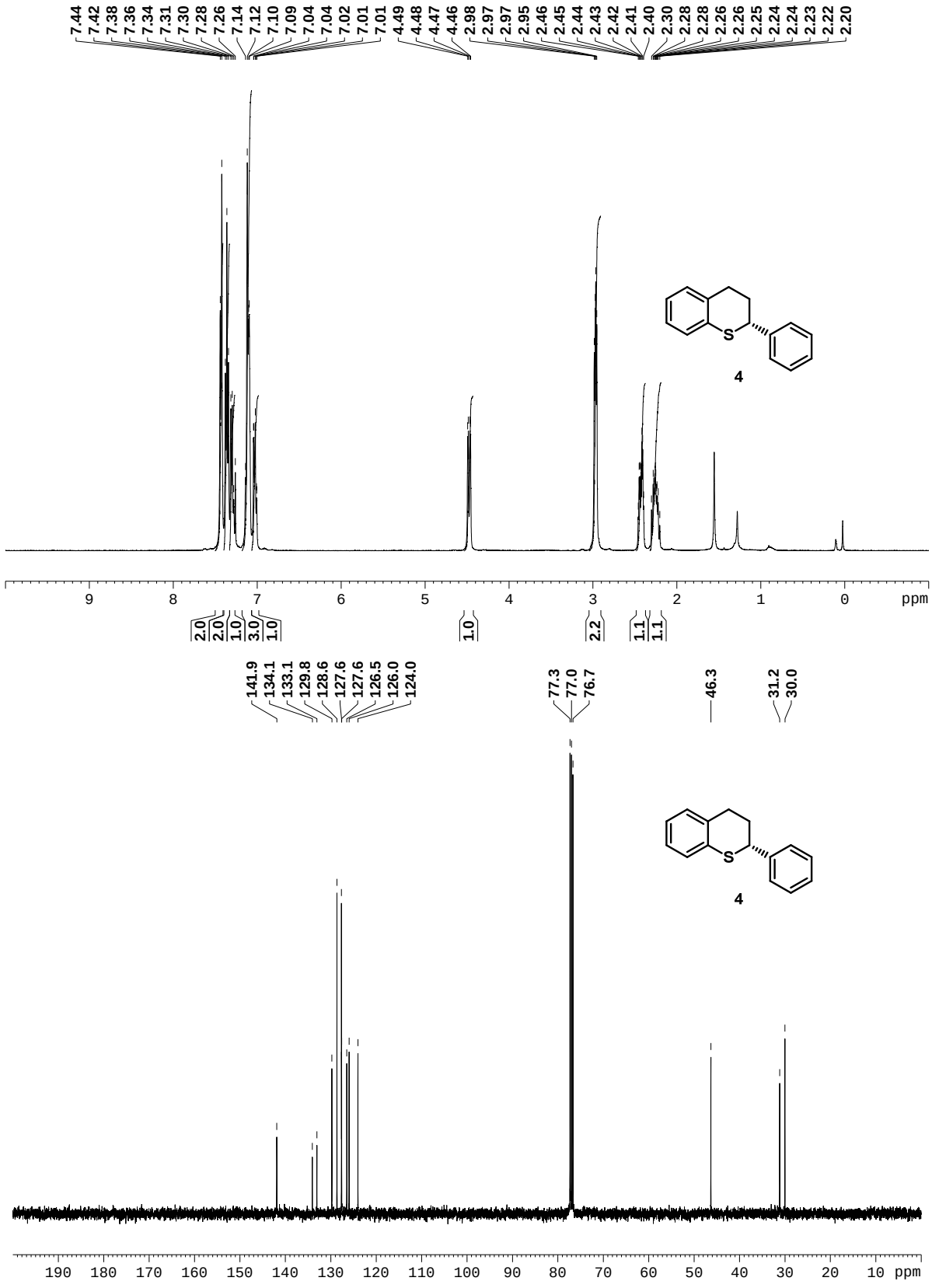


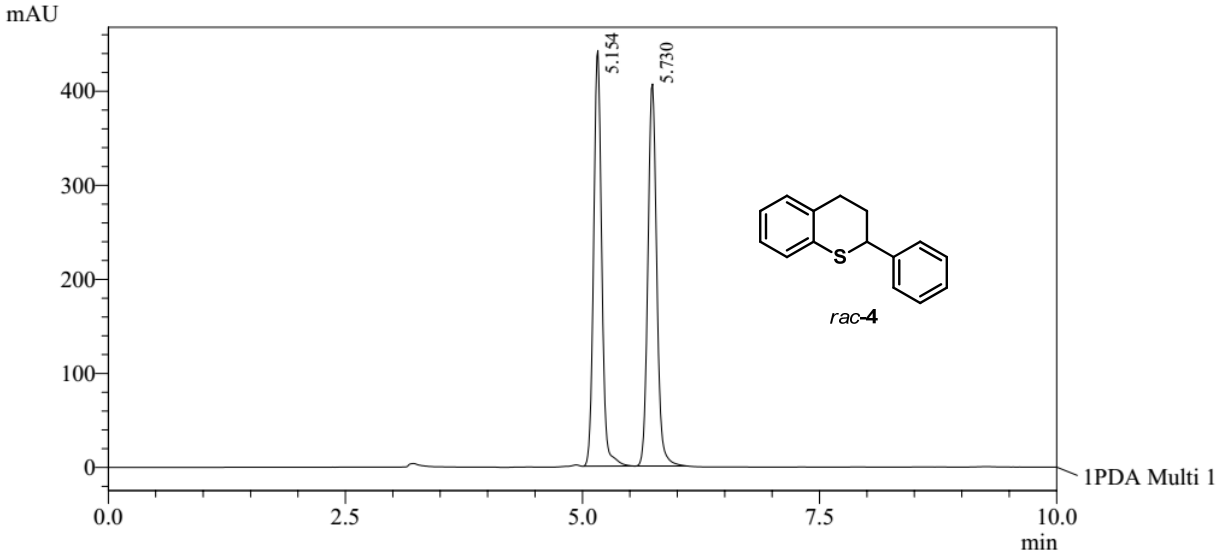
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	6.173	359708	1.992
2	6.500	17696988	98.008
Total		18056695	100.000


7.44 7.42 7.38 7.36 7.34 7.31 7.30 7.28 7.26 7.14 7.12 7.10 7.09 7.04 7.04 7.02 7.01 7.01
4.49 4.48 4.47 4.46
2.98 2.97 2.97 2.95 2.46 2.45 2.44 2.43 2.42 2.41 2.40 2.30 2.28 2.28 2.26 2.26 2.25 2.24 2.24 2.23 2.22 2.20
4
9 8 7 6 5 4 3 2 1 0 ppm
2.0 2.0 1.0 3.0 1.0
1.0
2.2
1.1 1.1
141.9 134.1 133.1 129.8 128.6 127.6 127.6 126.5 126.0 124.0
77.3 77.0 76.7
46.3
31.2 30.0
4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



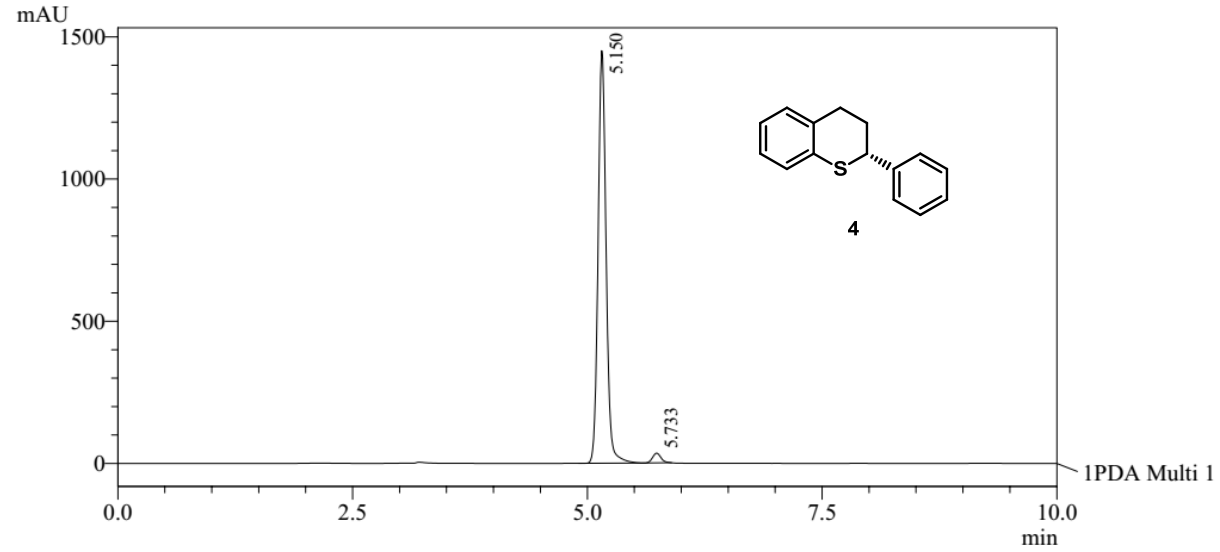
1 PDA Multi 1 / 254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Area %
1	5.154	2624016	49.947
2	5.730	2629538	50.053
Total		5253554	100.000

Daicel Chiralpak IB column (97:3 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm)

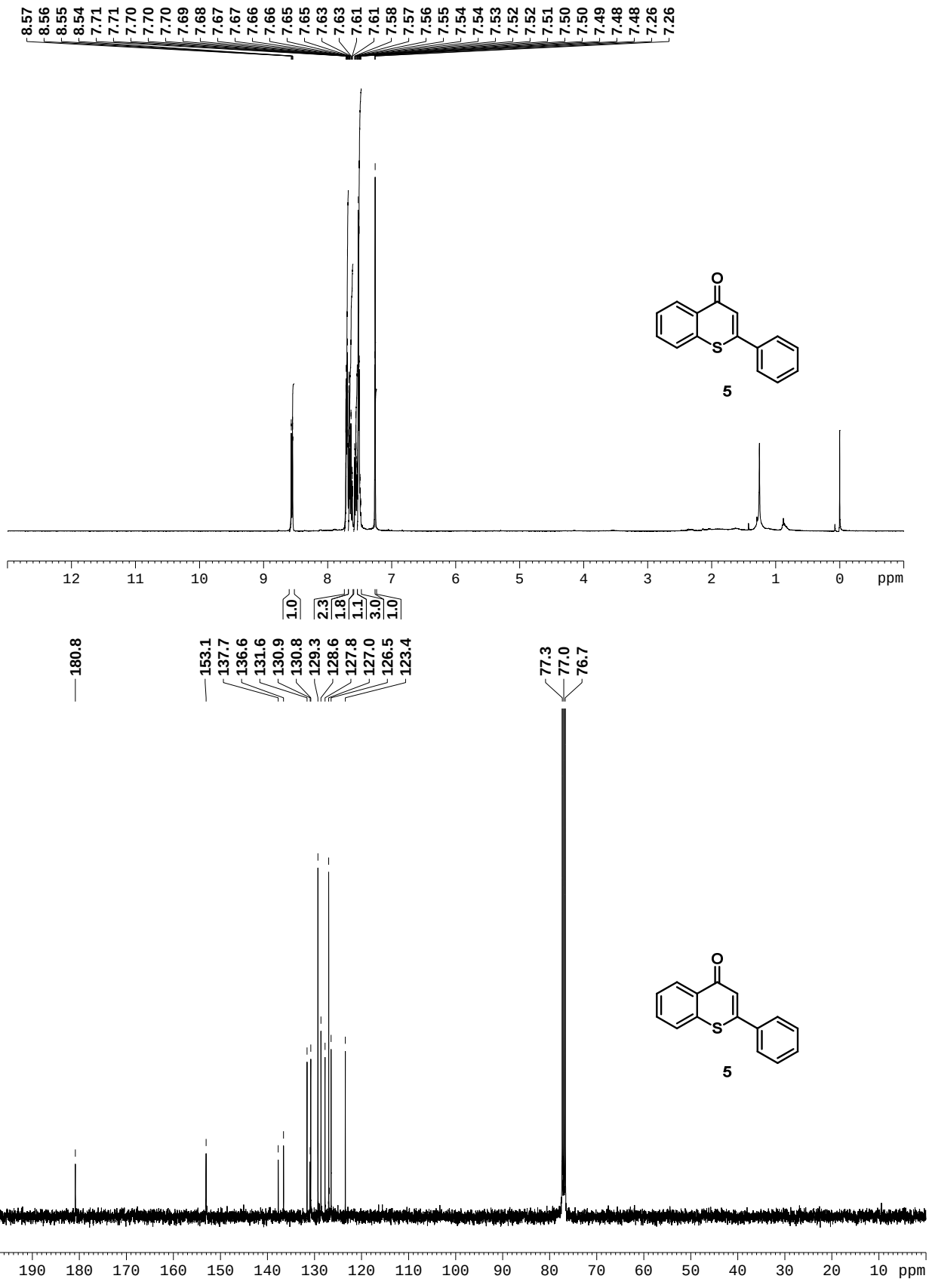


1 PDA Multi 1 / 254nm 4nm

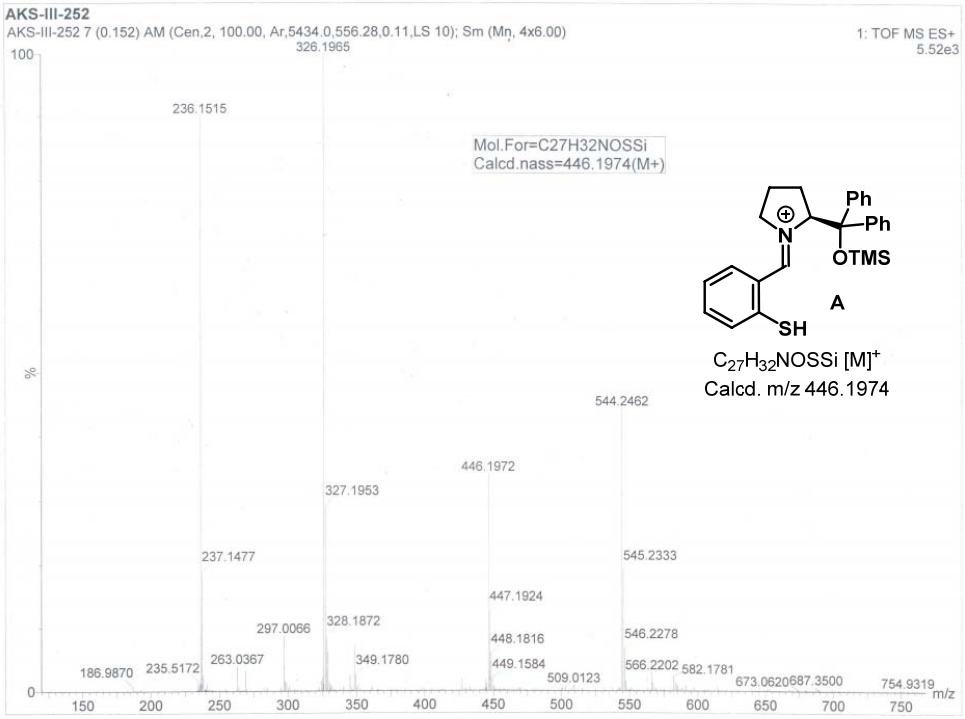
PeakTable

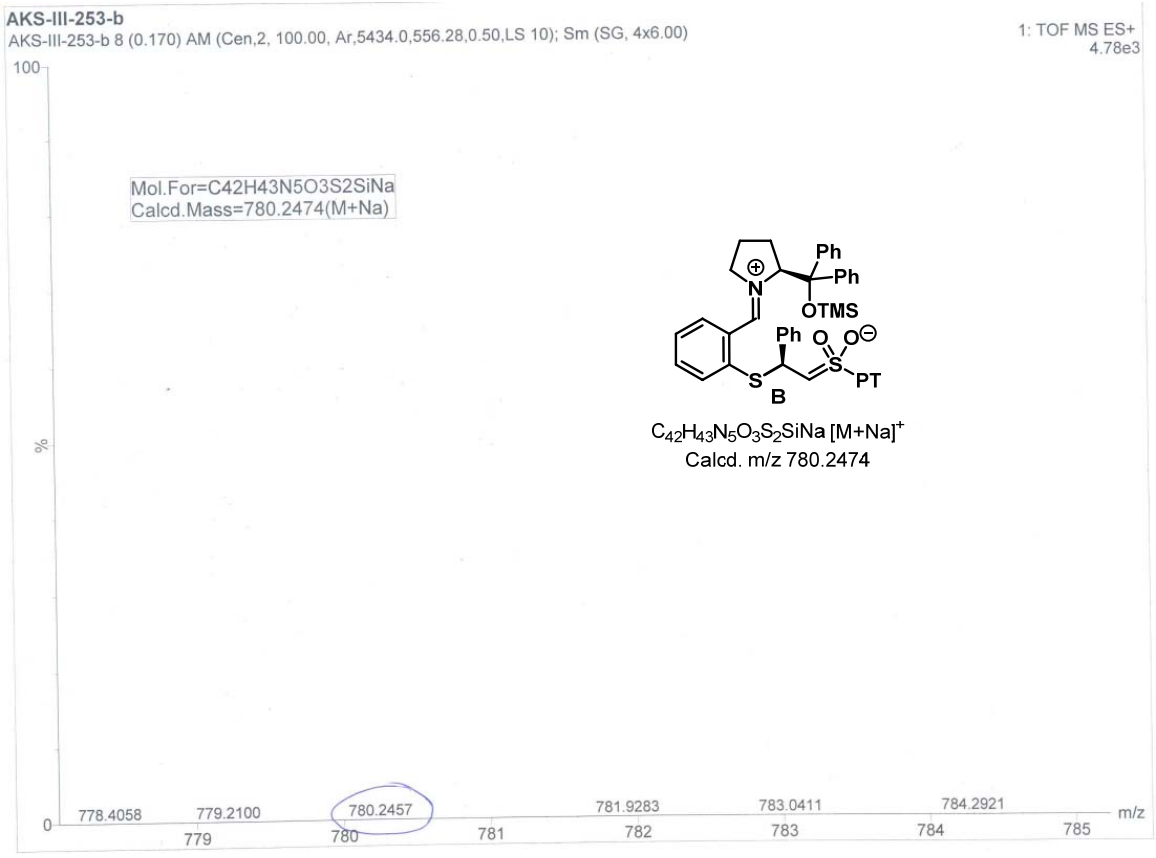
PDA Ch1 254nm 4nm

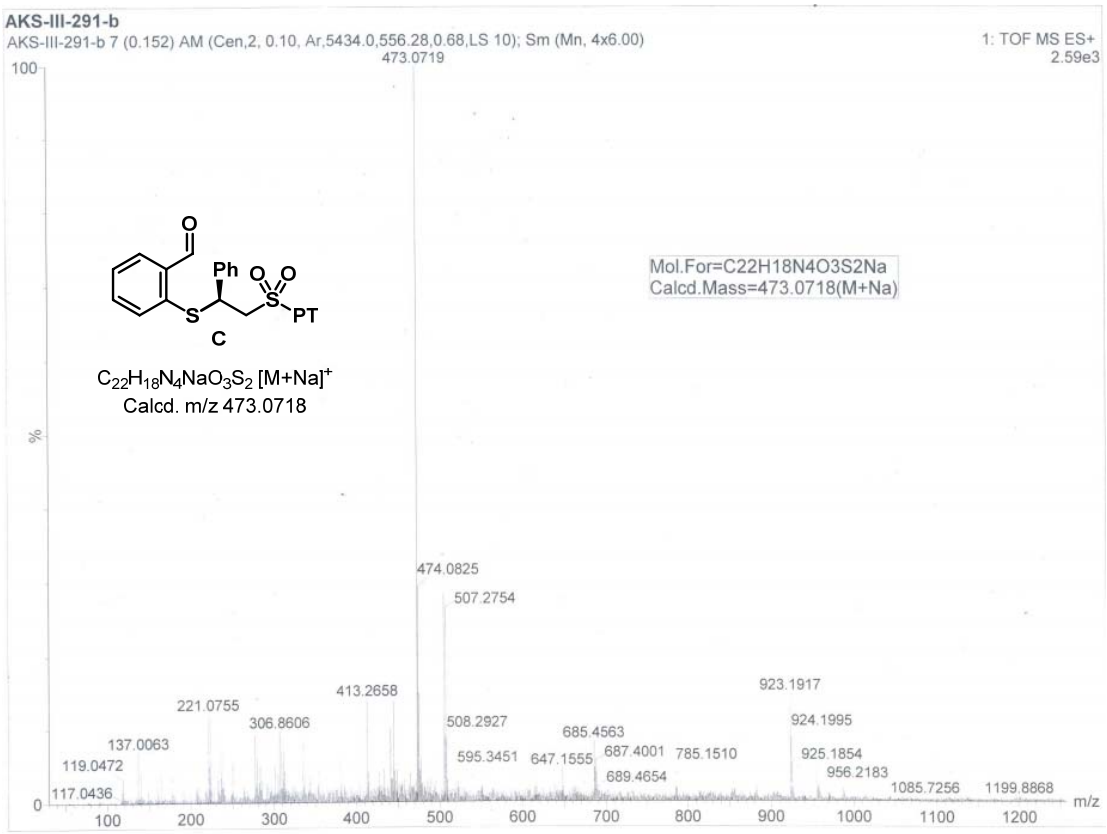
Peak#	Ret. Time	Area	Area %
1	5.150	8637611	97.626
2	5.733	210007	2.374
Total		8847618	100.000


8.57
8.56
8.55
8.54
7.71
7.71
7.70
7.70
7.70
7.69
7.68
7.67
7.67
7.66
7.66
7.65
7.65
7.63
7.63
7.61
7.61
7.58
7.57
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.26
7.26
O
S
5
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.0
2.3
1.8
1.1
3.0
1.0
180.8
153.1
137.7
136.6
131.6
130.9
130.8
129.3
128.6
127.8
127.0
126.5
123.4
77.3
77.0
76.7
O
S
5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Detection of reactive intermediates:






AKS-III-291-b
AKS-III-291-b 7 (0.152) AM (Cen,2, 0.10, Ar,5434.0,556.28,0.68,LS 10); Sm (Mn, 4x6.00)
1: TOF MS ES+
2.59e3
473.0719
100
%
0
O
Ph
O
O
S
S
PT
C
Mol.For=C22H18N4O3S2Na
Calcd.Mass=473.0718(M+Na)
C22H18N4NaO3S2 [M+Na]+
Calcd. m/z 473.0718
474.0825
507.2754
923.1917
413.2658
221.0755
306.8606
924.1995
508.2927
685.4563
137.0063
595.3451
647.1555
687.4001
785.1510
925.1854
119.0472
689.4654
956.2183
117.0436
1085.7256
1199.8868
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200

Single crystal X-ray diffraction analysis of 3ai and 3ak:

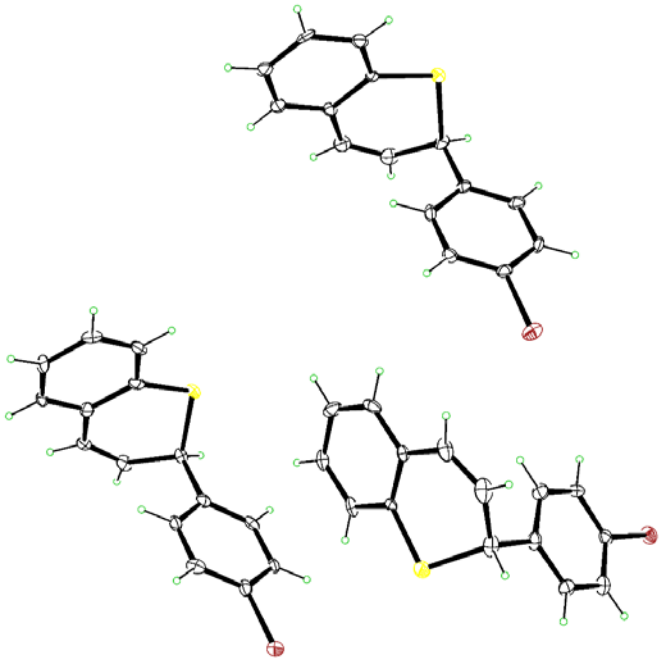
Single crystal X-ray diffraction analysis of 3ai:

Single crystal of **3ai** (recrystallized from $CHCl_3$/*n*-Hexane = 1:10 at 25 °C) was mounted and the diffraction data were collected at 273 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structure was solved by direct method using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table S1. Crystal data and structure refinement for **3ai**

Identification code	**3ai**	
CCDC	1506906	
Empirical formula	$C_{15}H_{11}BrS$	
Formula weight	303.22	
Temperature	102(3) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
	a = 10.9526(7)	α = 90°
	b = 11.6626(10) Å	β = 90°
	c = 29.560(2) Å	γ = 90°
Volume	3775.9(5) $Å^3$	
Z	12	
Density (calculated)	1.600 g/cm^3	
Absorption coefficient	3.404 mm^{-1}	
F(000)	1824.0	
Crystal size	0.171 × 0.124 × 0.047 mm^3	
Theta range for data collection	5.102 to 50°	
Index ranges	$-12 \le h \le 13$, $-9 \le k \le 13$, $-24 \le l \le 35$	
Reflections collected	11268	
Independent reflections	6221 [R_{int} = 0.0506, $R\sigma$ = 0.1039]	

Data/ restraints/ parameters	6221/ 0/ 460
Goodness-of-fit on F^2	0.998
Final R indexes [I> 2σ (I)]	R_1 = 0.0557, ωR_2 = 0.0797
Final R indexes (all data)	R_1 = 0.0842, ωR_2 = 0.0892
Largest diff. peak/hole	0.49/−0.46 e.Å^{-3}
Flack parameter	0.002(11)



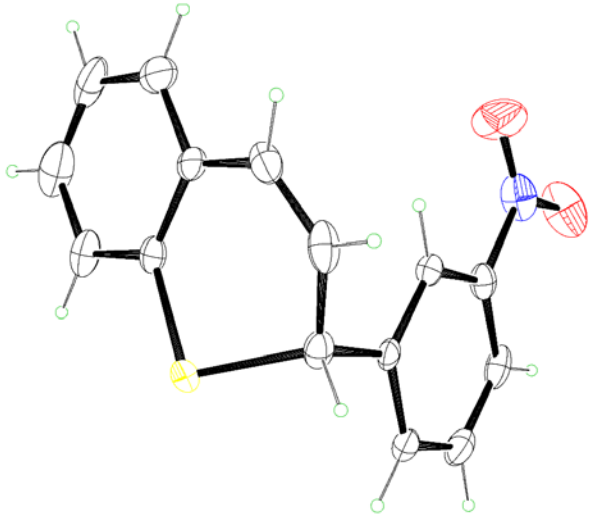
ORTEP representation of the X-ray structure of **3ai** (thermal ellipsoids at 30% probability)

Single crystal X-ray diffraction analysis of 3ak:

Single crystal of **3ak** (recrystallized from 1:4 $CHCl_3$/*n*-Hexane at 25 °C) was mounted and the diffraction data was collected at 273 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structure was solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table S2. Crystal data and structure refinement for **3ak**

Identification code	**3ak**	
CCDC	1506907	
Empirical formula	$C_{15}H_{11}NO_2S$	
Formula weight	269.32	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
	a = 6.9573(7) Å	α = 90°
	b = 13.1585(13) Å	β = 90°
	c = 13.8579(14) Å	γ = 90°
Volume	1268.7(2) $Å^3$	
Z	4	
Density (calculated)	1.410 g/cm^3	
Absorption coefficient	0.251 mm^{-1}	
F(000)	560.0	
Crystal size	0.26 × 0.25 × 0.24 mm^3	
Theta range for data collection	4.268 to 49.954 °	
Index ranges	$-8 \le h \le 8, -15 \le k \le 15, -16 \le l \le 16$	
Reflections collected	21761	
Independent reflections	21761 [R_{int} = 0.0649, $R\sigma$ = 0.0757]	
Data/ restraints/ parameters	21761/ 0/ 173	
Goodness-of-fit on F^2	1.036	
Final R indexes [I>2σ (I)]	R_1 = 0.0488, ωR_2 = 0.1274	
Final R indexes (all data)	R_1 = 0.0554, ωR_2 = 0.1326	
Largest diff. peak/hole	0.67/−0.35 e.$Å^{-3}$	
Flack parameter	0.09(3)	



ORTEP representation of the X-ray structure of **3ak** (thermal ellipsoids at 30% probability)