Electronic Supplementary Information

BPO promoted direct oxidative C-H functionalization of unactivated alkanes into 6-alkyl 6*H*-benzo[*c*]chromenes under transition-metal-free conditions

Lei Ji, Qinfei Deng, Ping Liu* and Peipei Sun*

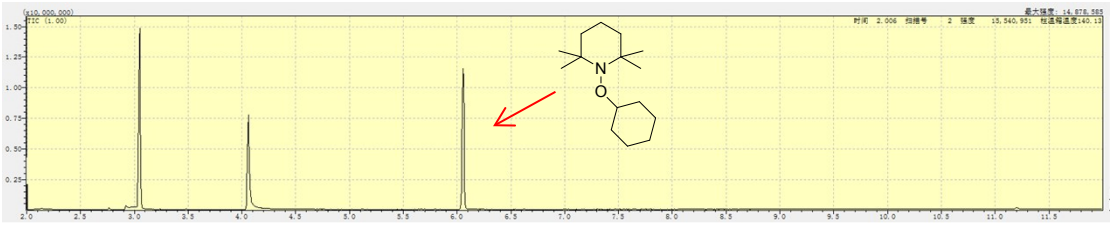
School of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Material Cycle Processes and Pollution Control, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Nanjing Normal University, Nanjing 210023, China

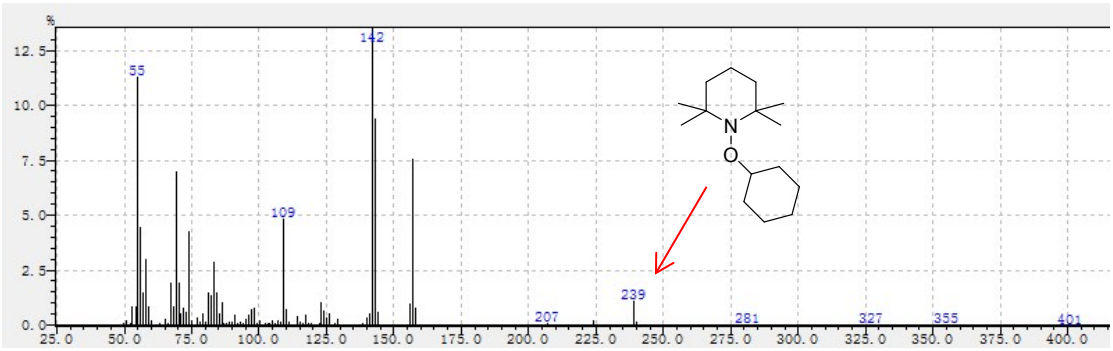
pingliu@njnu.edu.cn; sunpeipei@njnu.edu.cn

Contents

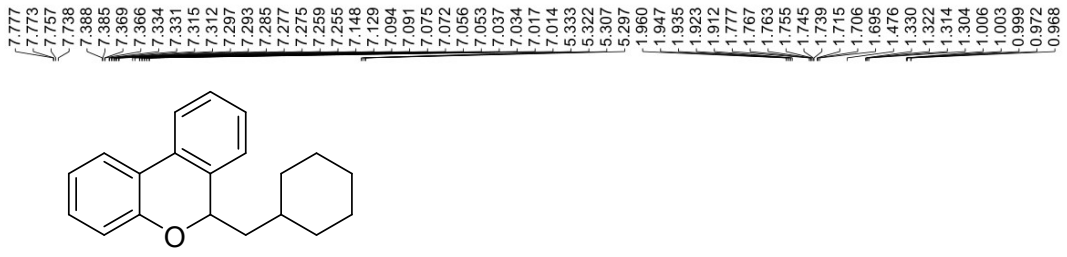
1 Free radical-trapping experiment

An oven-dried Schlenk tube (25 mL) was charged with 2-(vinyloxy)-1,1'-biphenyl (**1a**, 0.2 mmol, 1.0 equiv.), BPO (0.6 mmol, 3.0 equiv.), TEMPO (0.4 mmol, 2.0 equiv.) and cyclohexane (2 mL). The reaction mixture was stirred under Ar atmosphere at 100 °C for 24 h. After that the reaction was stopped and a cyclohexyl radical adduct product was detected by the GC-MS analysis of the reaction solution.

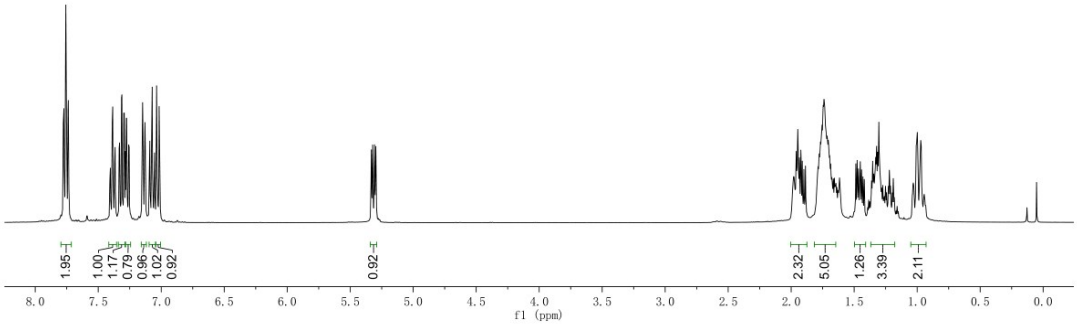


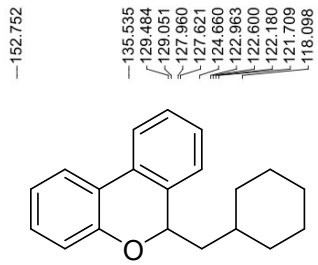


2 NMR spectra of the products 3 and 4



3aa (^{1}H NMR)

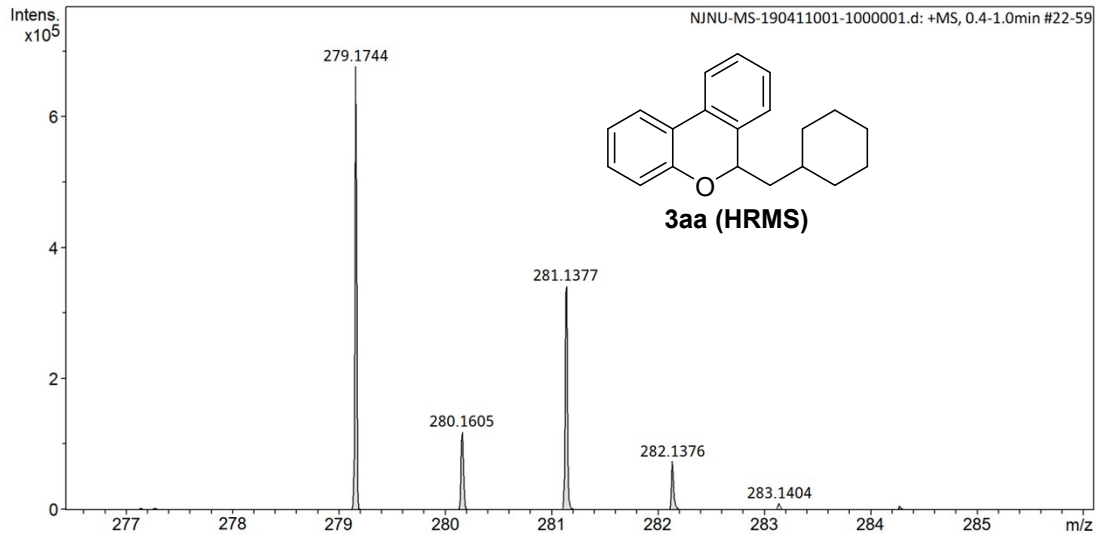




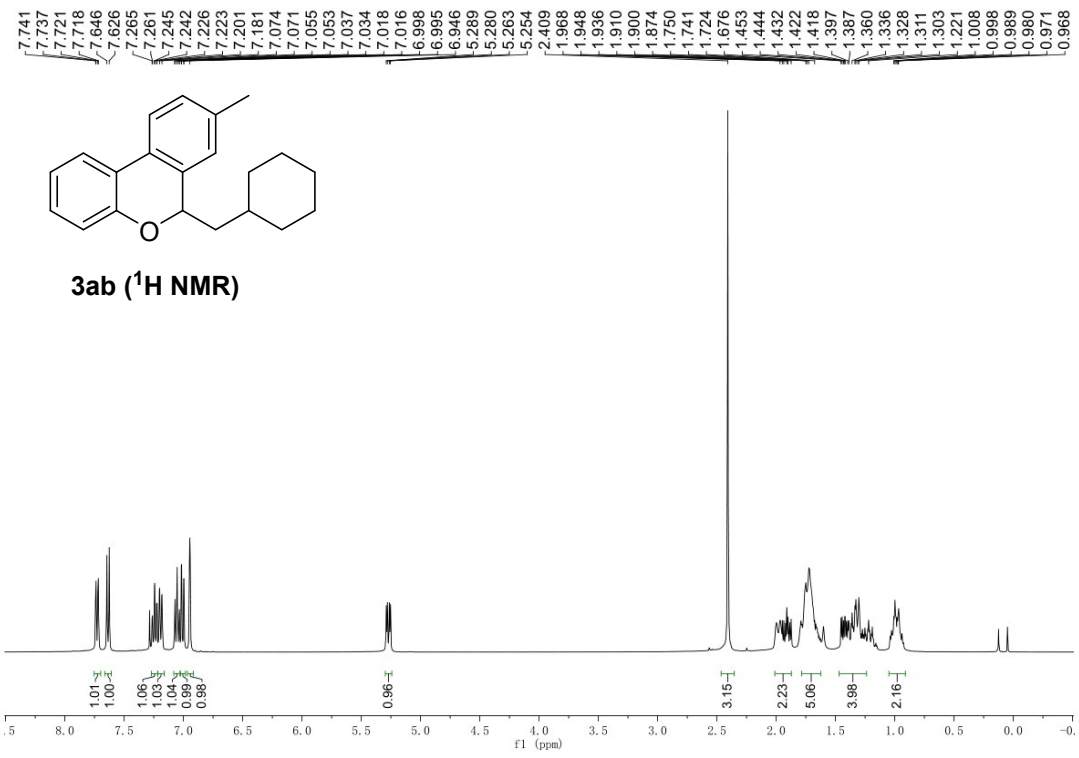
3aa (^{13}C NMR)

Acquisition Parameter

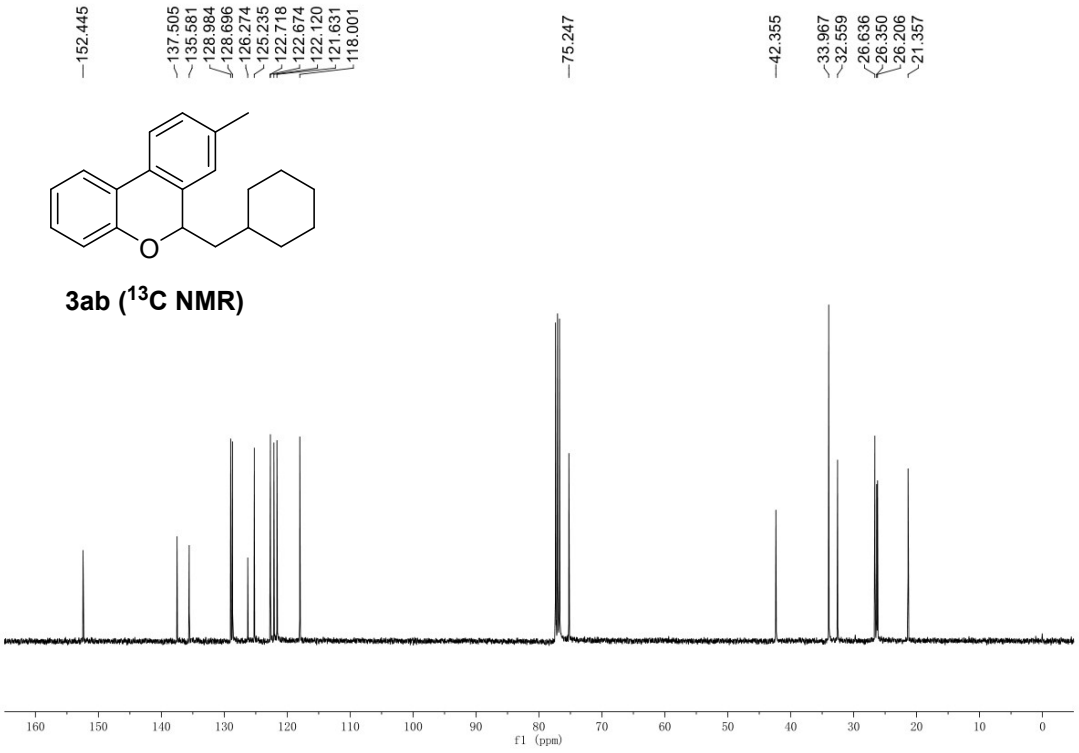
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



3aa (HRMS)



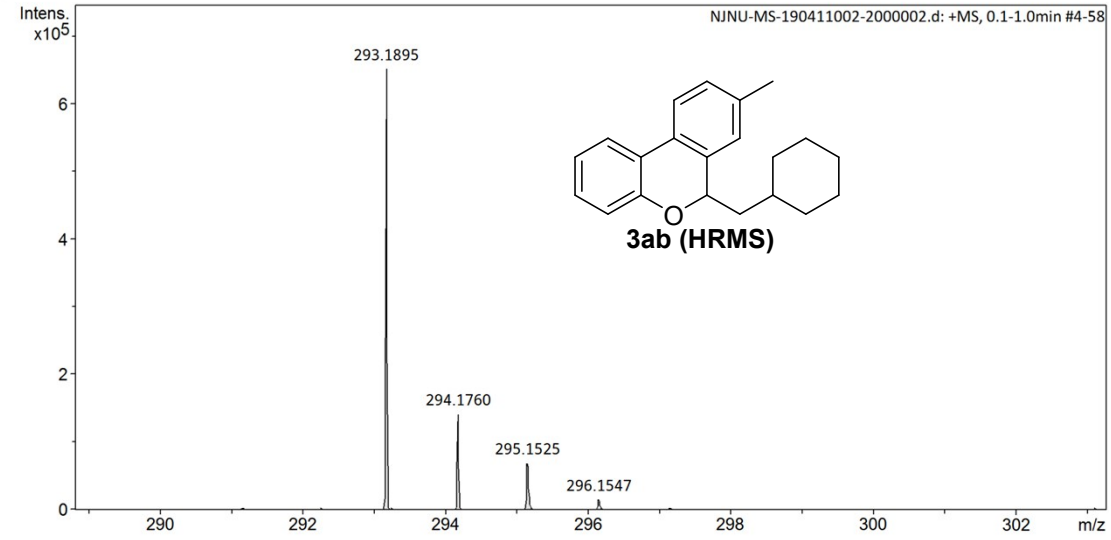
3ab (^{1}H NMR)

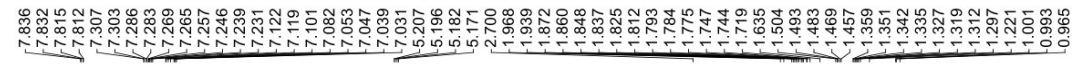


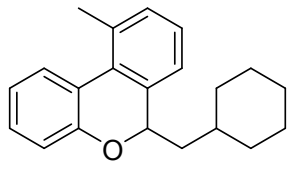
3ab (^{13}C NMR)

Acquisition Parameter

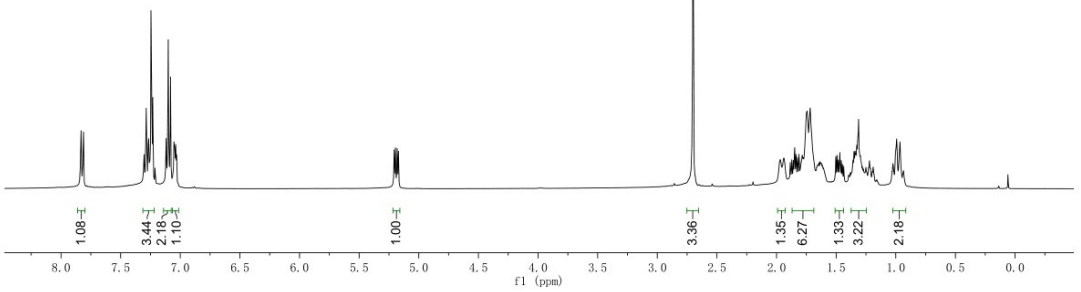
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

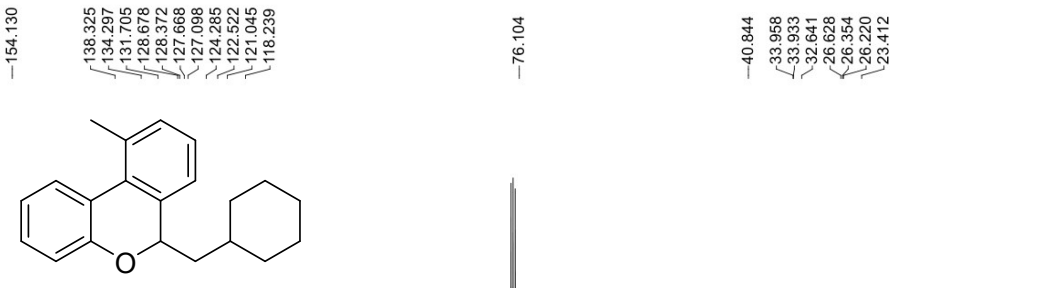




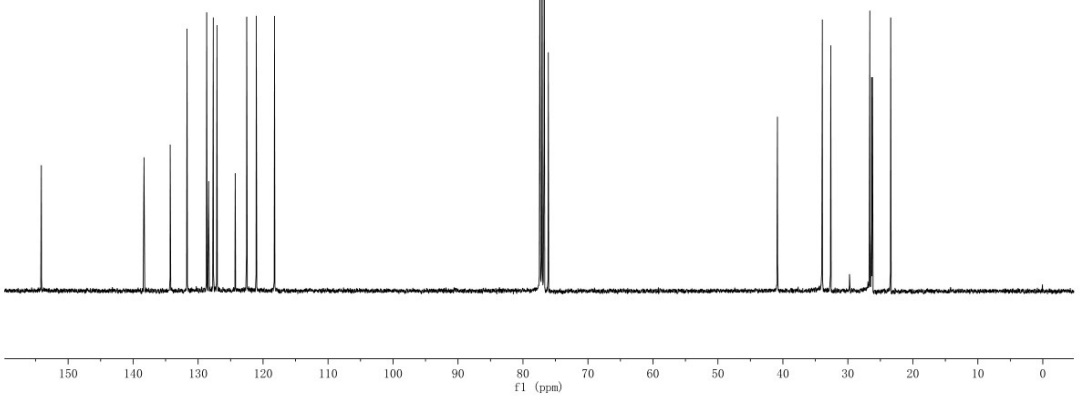


3ac (^{1}H NMR)

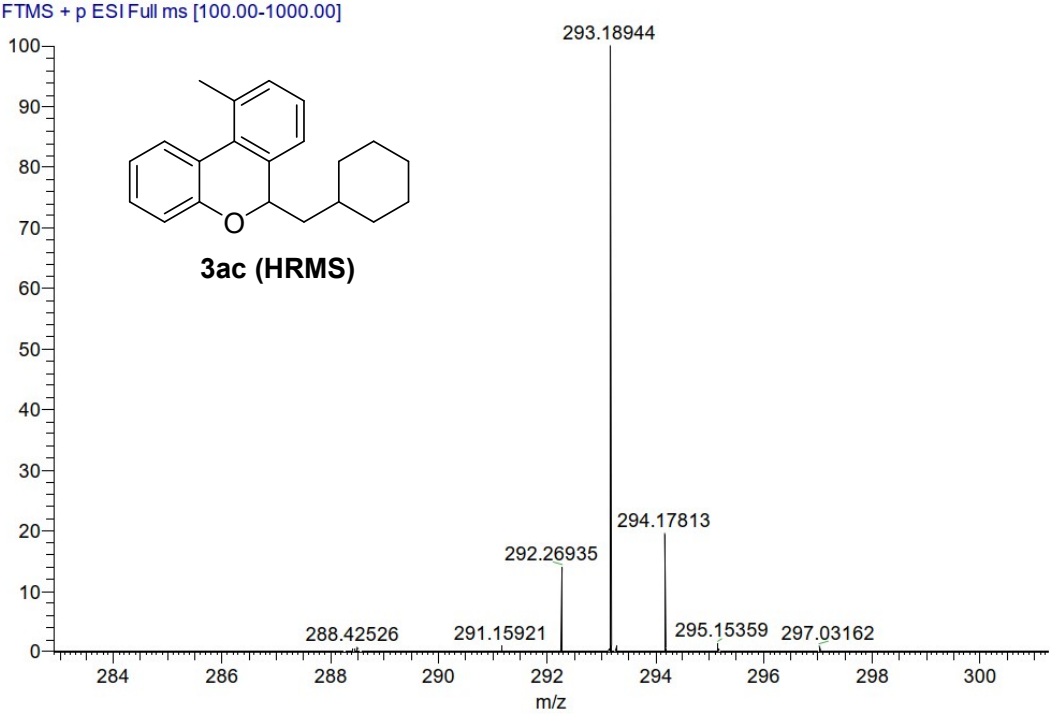




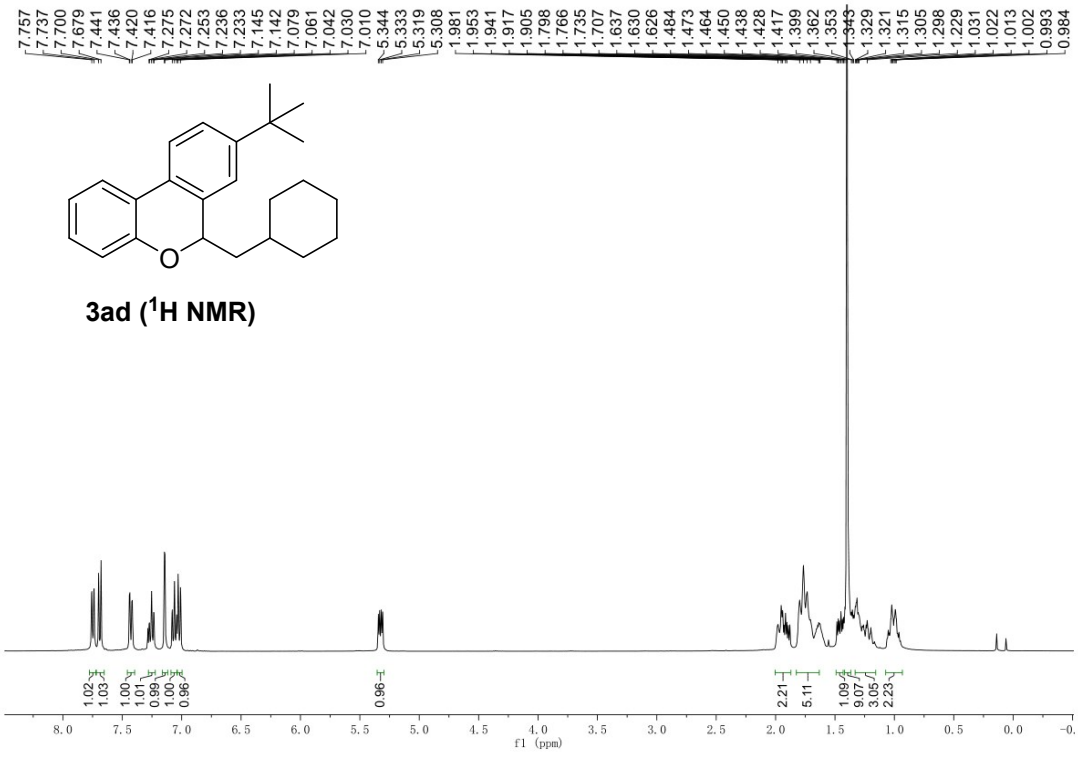
3ac (^{13}C NMR)



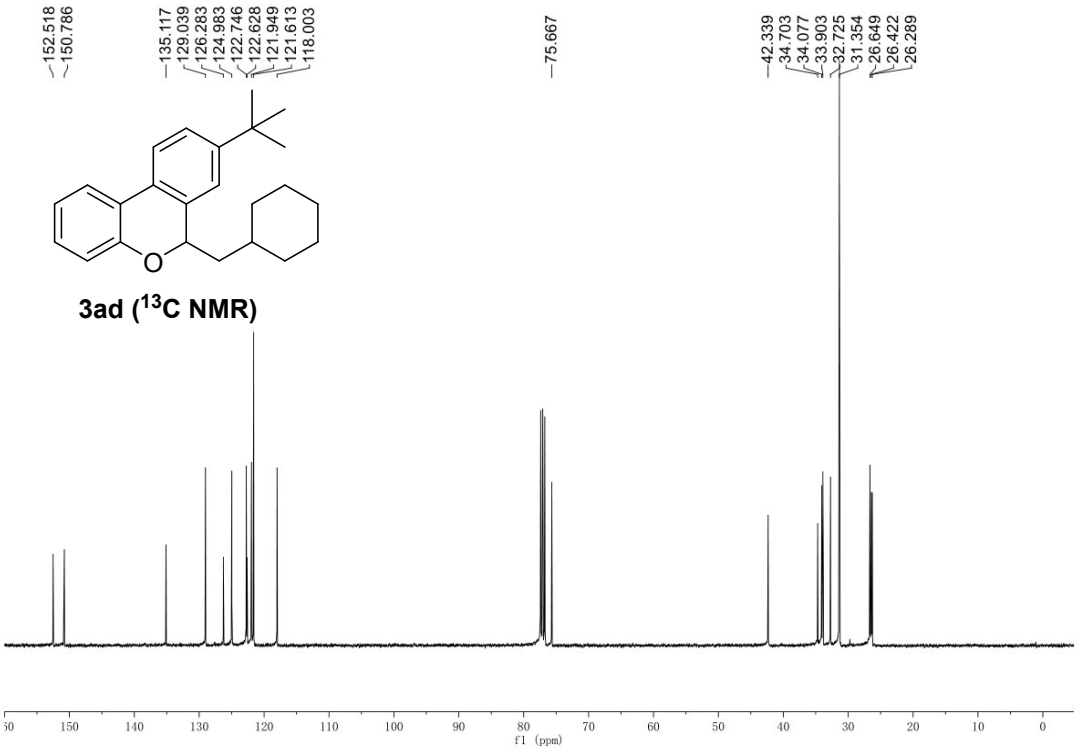
158 #12 RT: 0.15 AV: 1 NL: 3.05E7
T: FTMS + p ESI Full ms [100.00-1000.00]



3ac (HRMS)



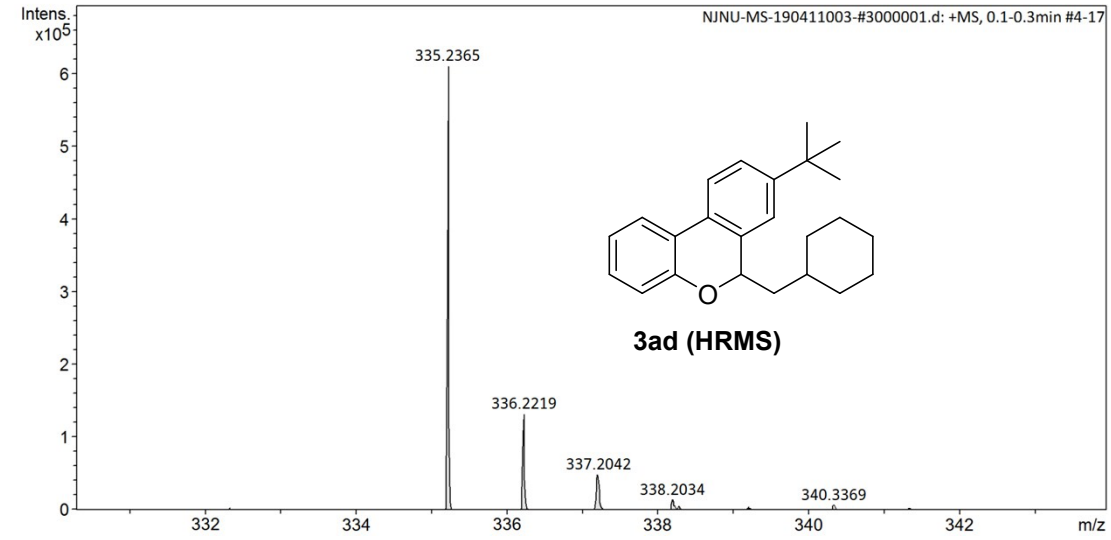
3ad (^{1}H NMR)



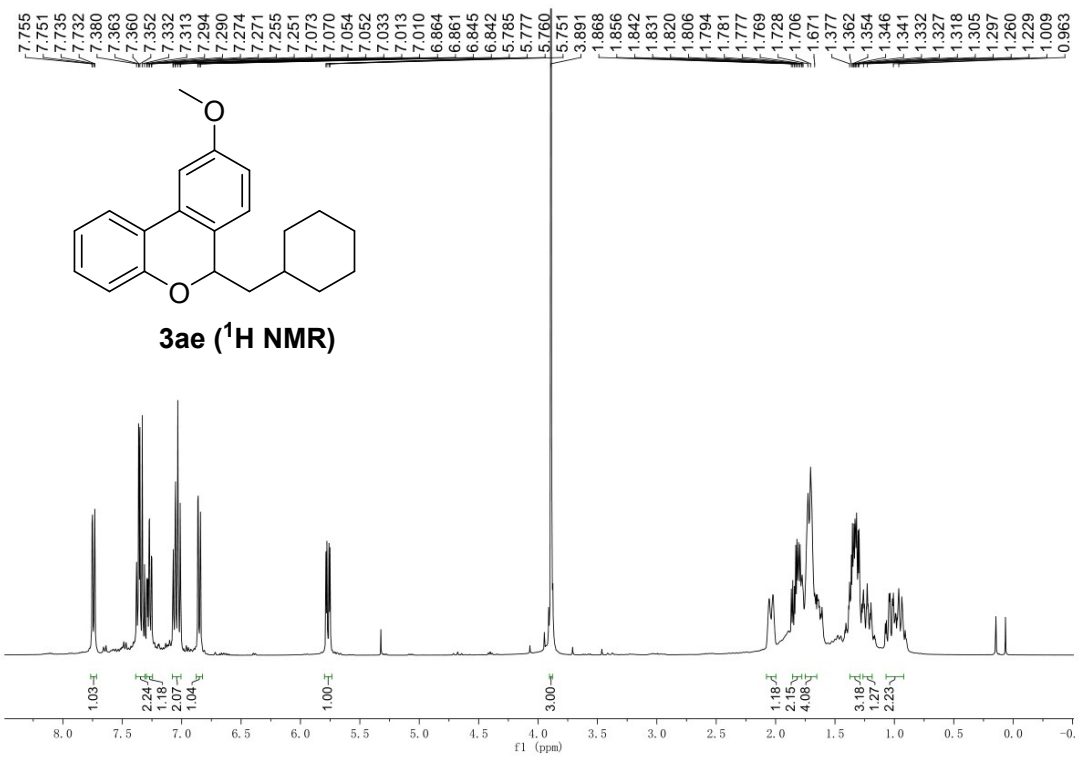
3ad (^{13}C NMR)

Acquisition Parameter

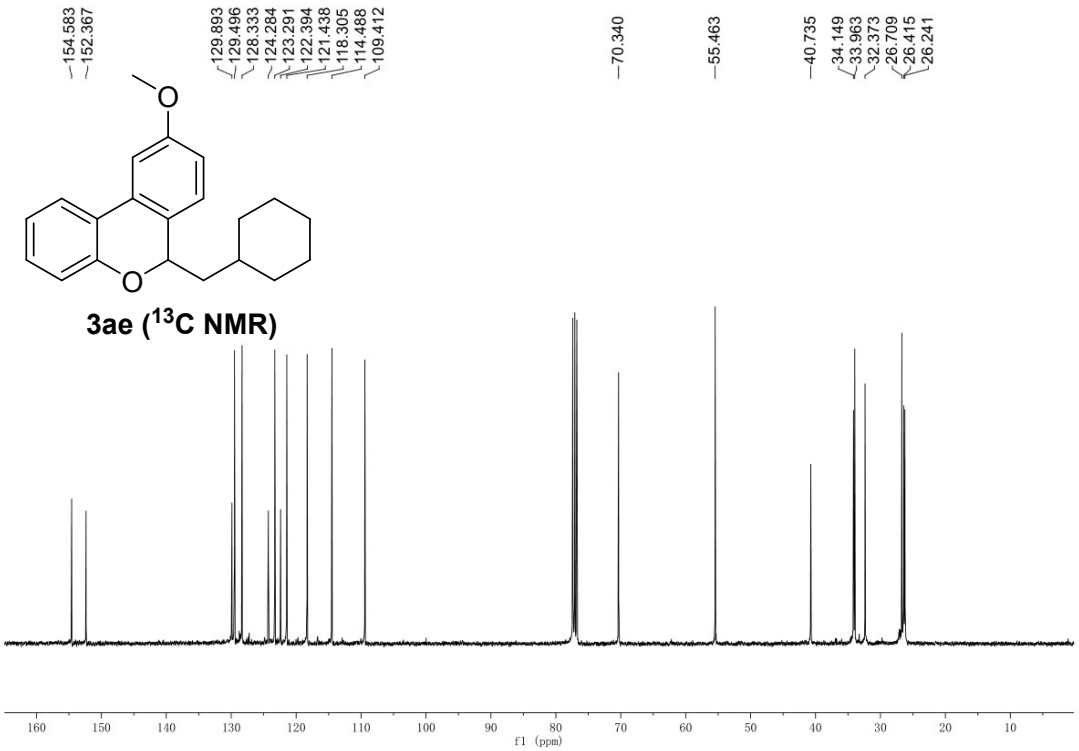
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



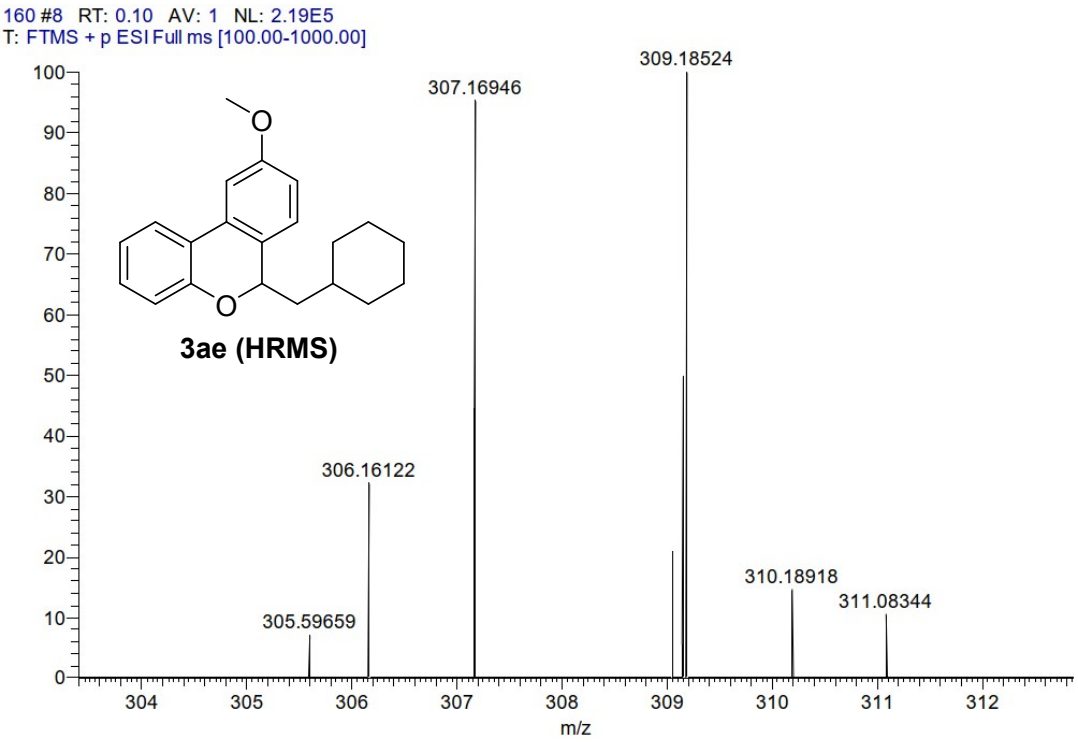
3ad (HRMS)



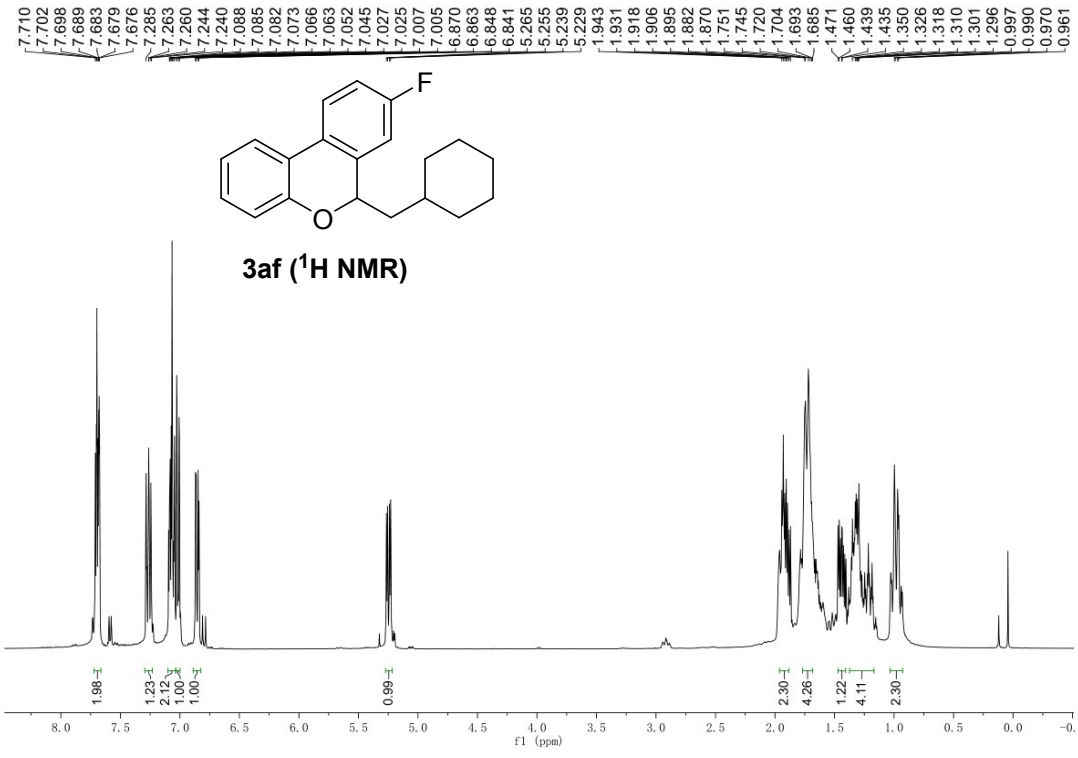
3ae (^{1}H NMR)



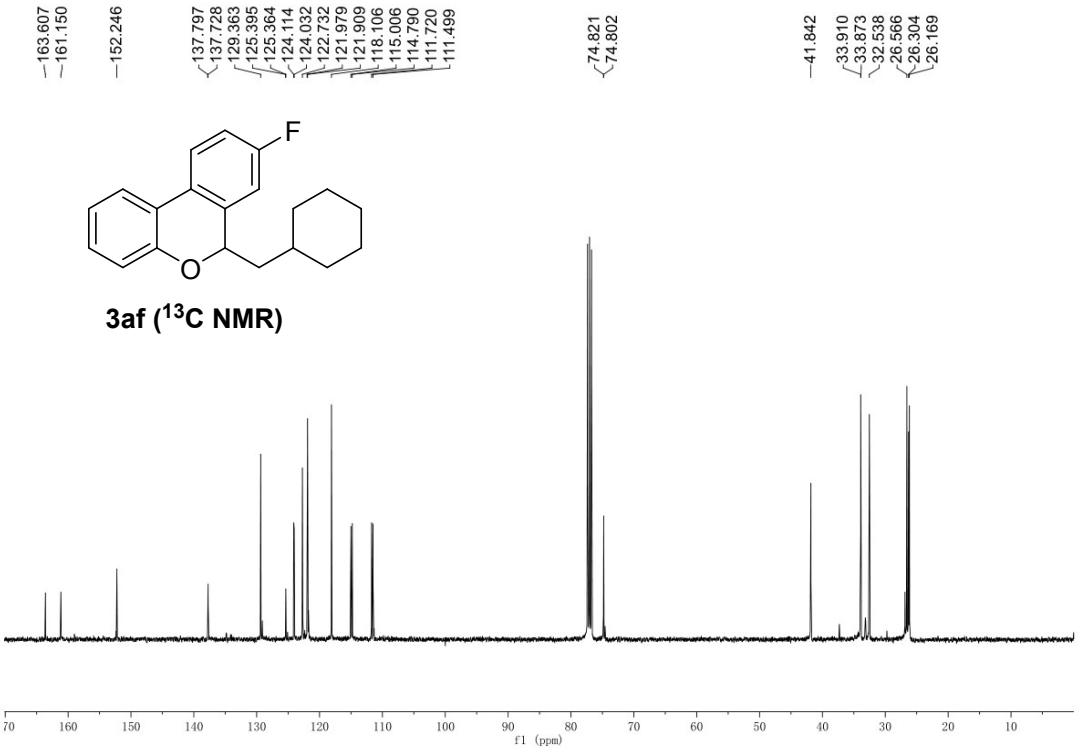
3ae (^{13}C NMR)



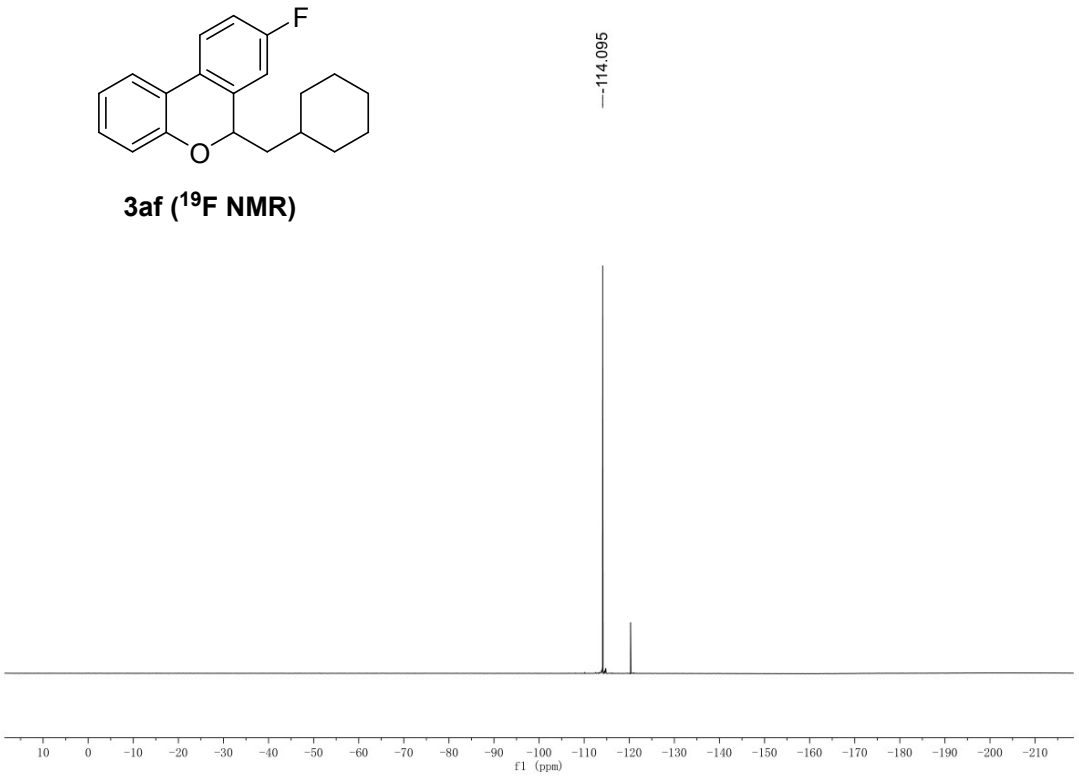
3ae (HRMS)



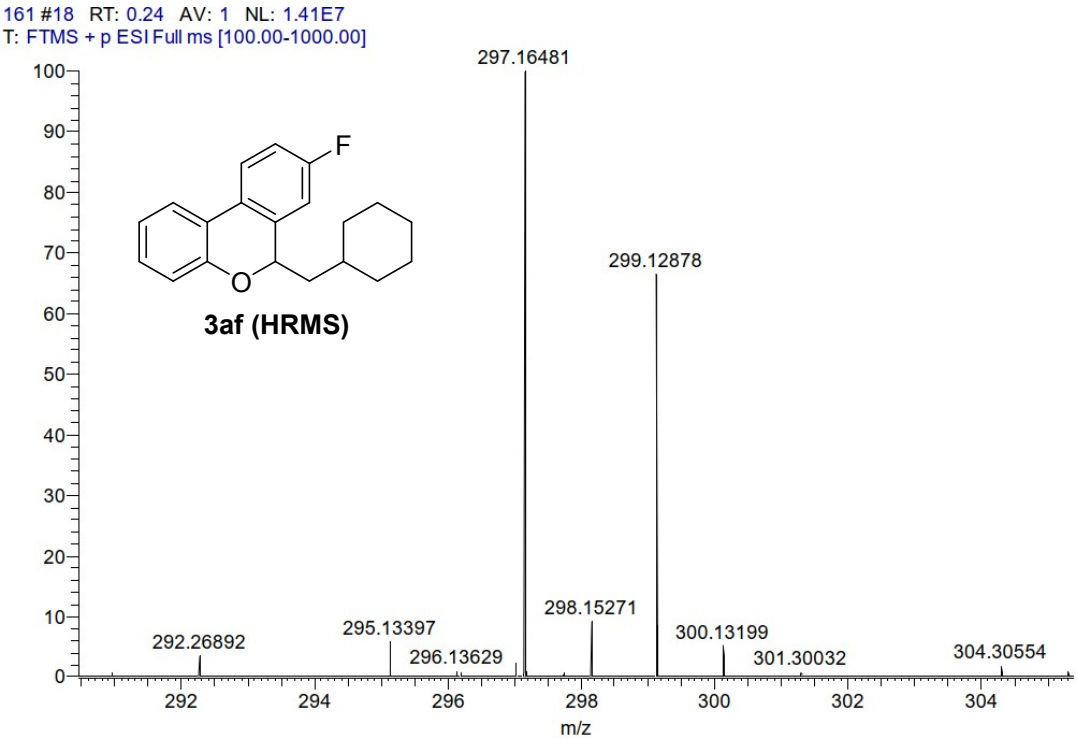
3af (^{1}H NMR)



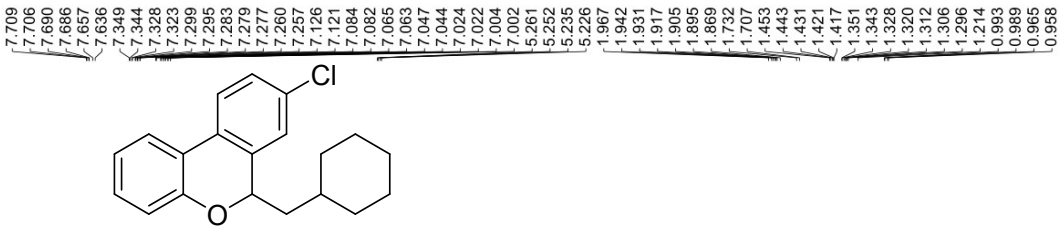
3af (^{13}C NMR)



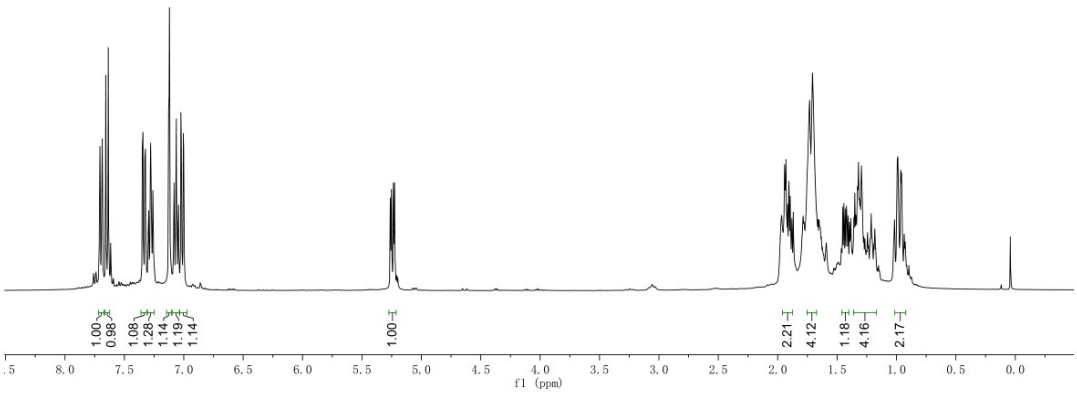
3af (^{19}F NMR)

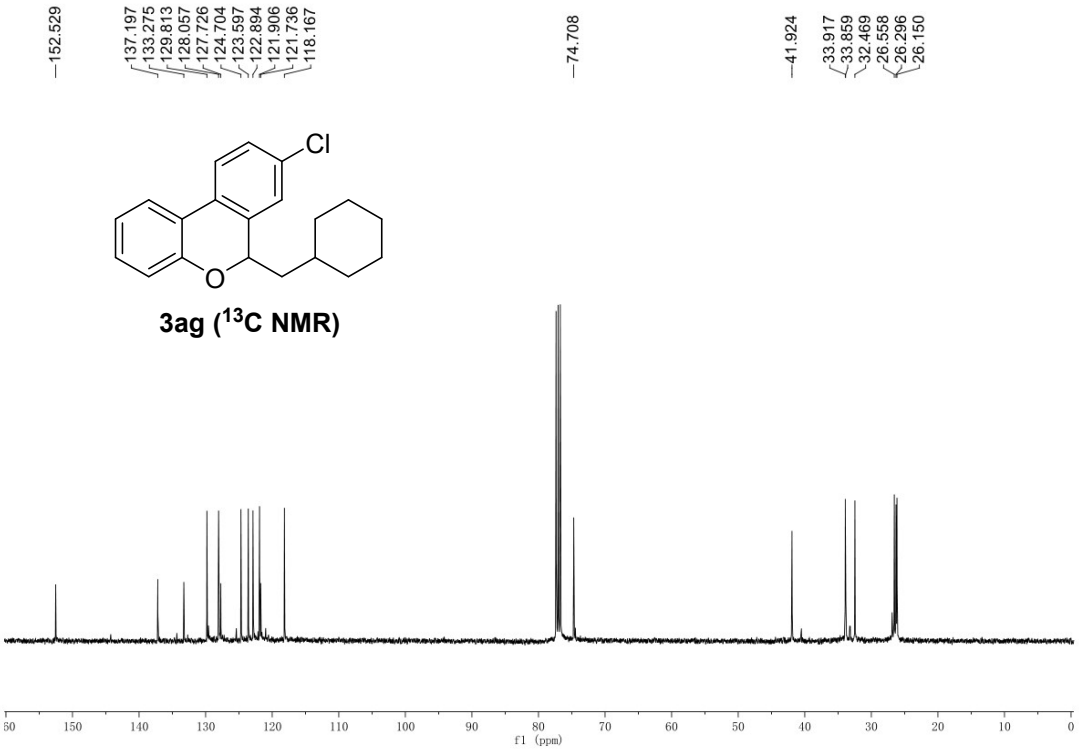


3af (HRMS)

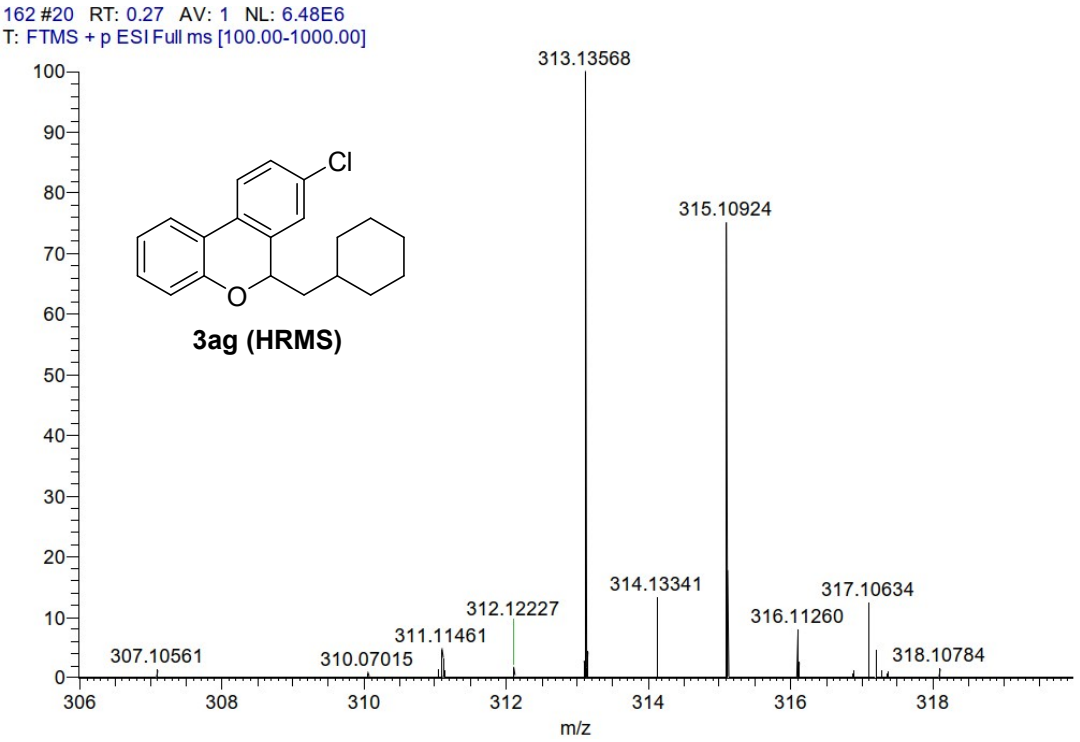


3ag (^{1}H NMR)

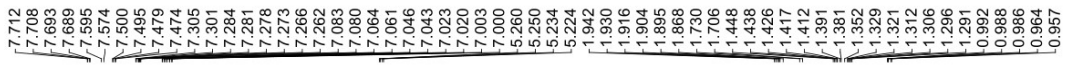


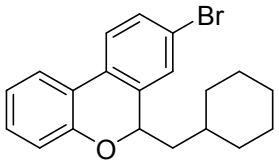


3ag (^{13}C NMR)

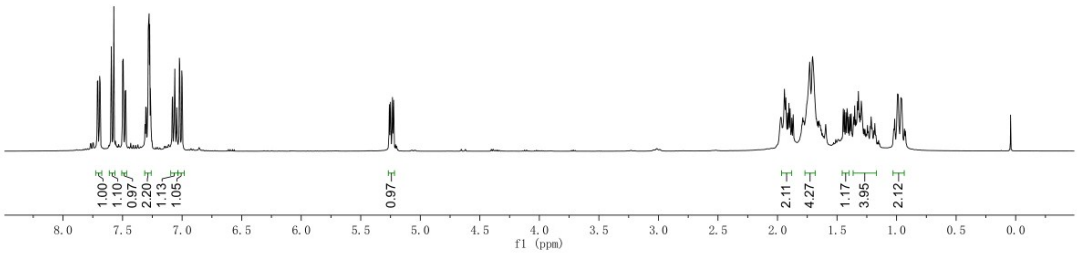


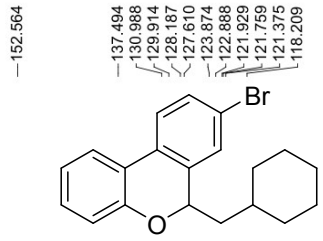
3ag (HRMS)



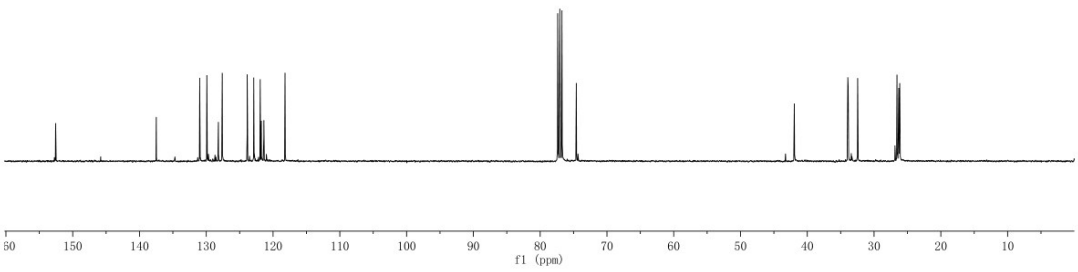


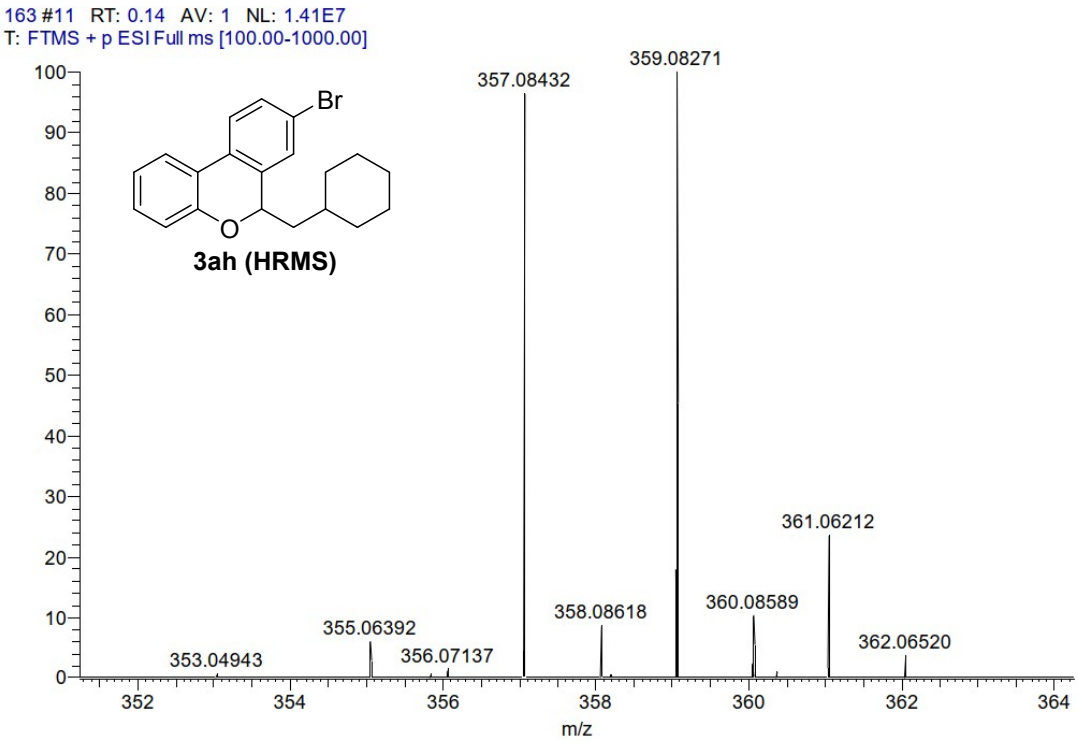
3ah (^{1}H NMR)

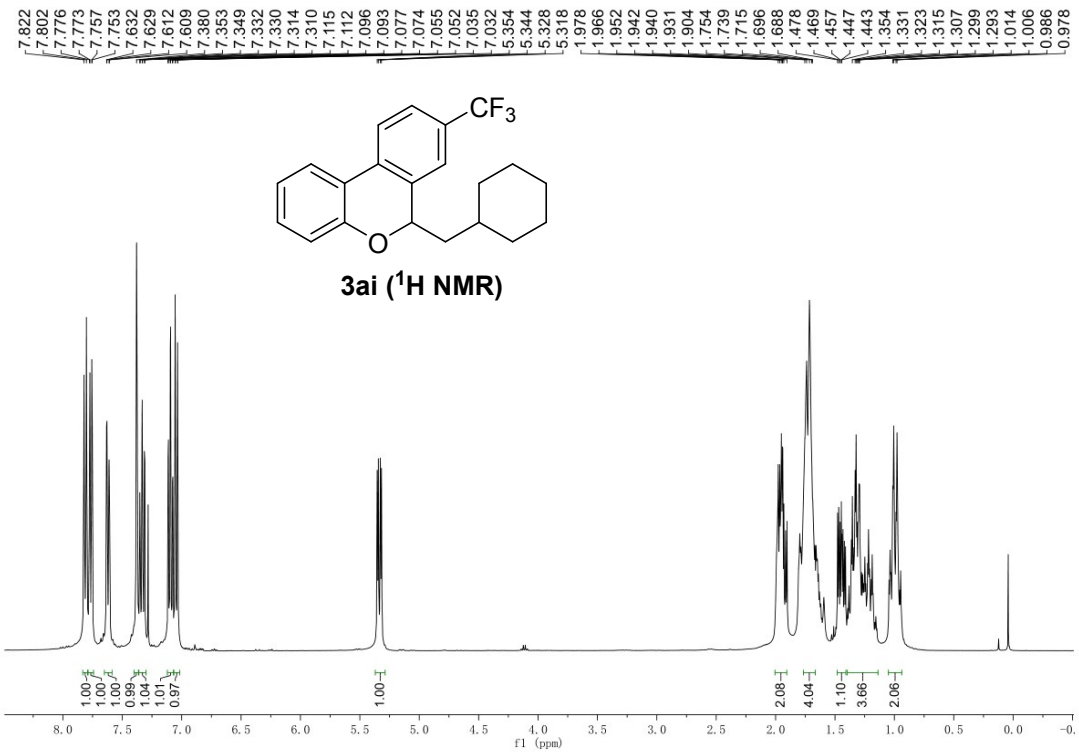


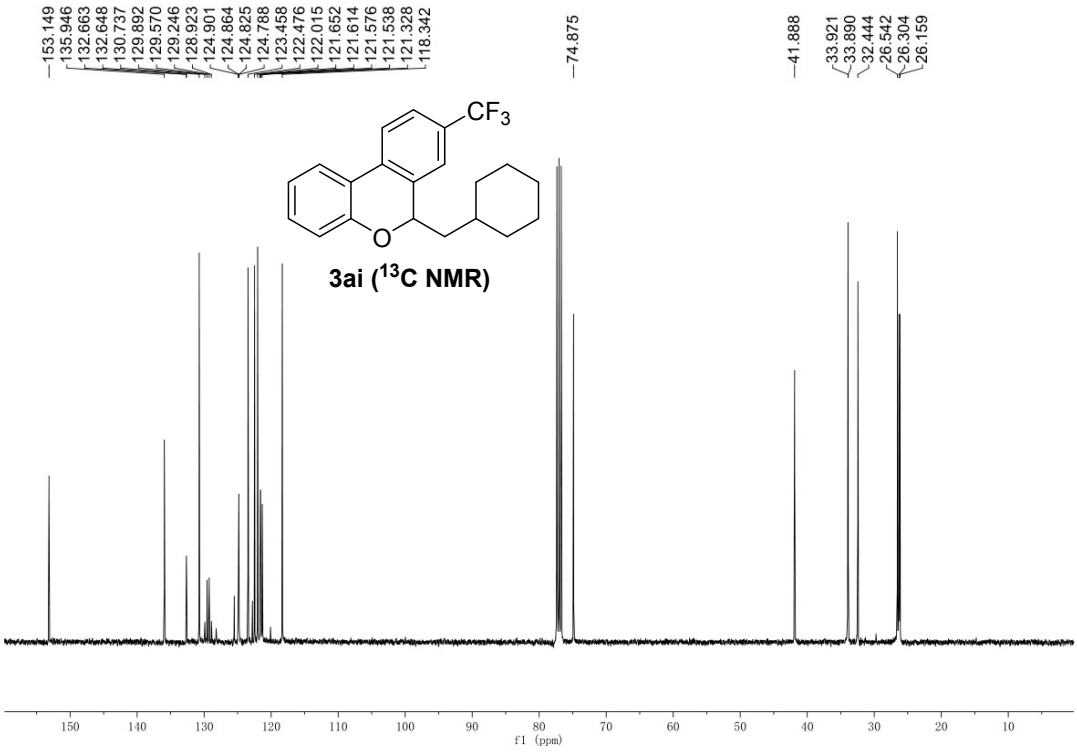


3ah (^{13}C NMR)

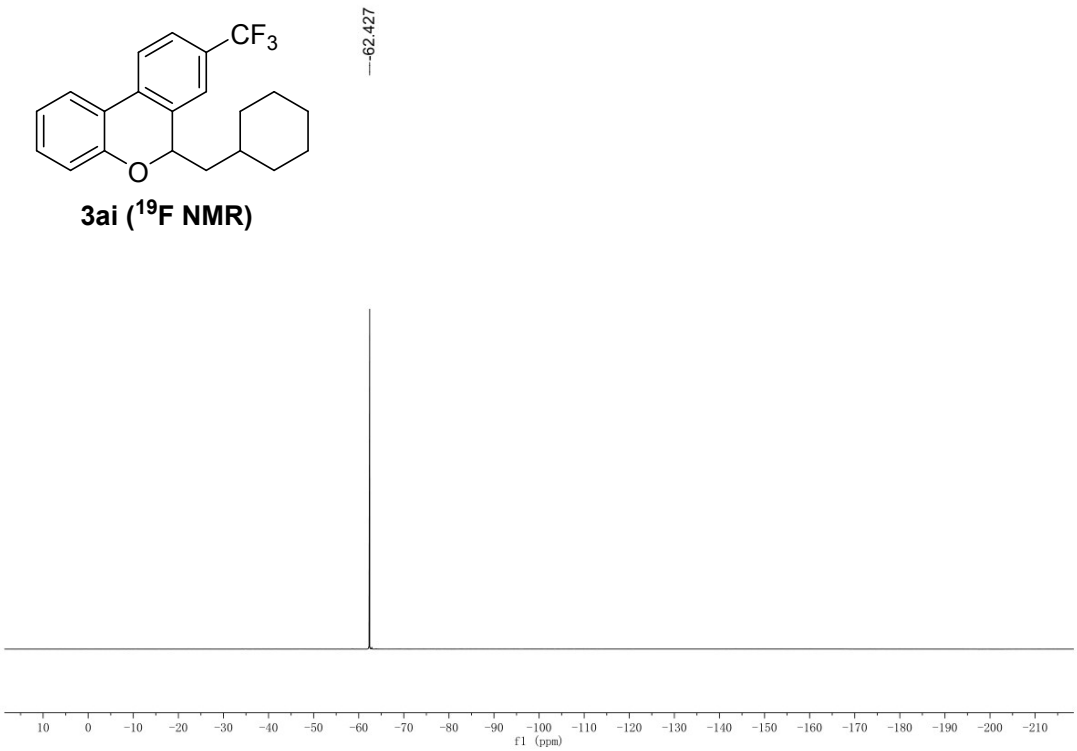



163 #11 RT: 0.14 AV: 1 NL: 1.41E7
T: FTMS + p ESI Full ms [100.00-1000.00]
Br
O
3ah (HRMS)
359.08271
357.08432
361.06212
360.08589
358.08618
362.06520
355.06392
356.07137
353.04943
m/z

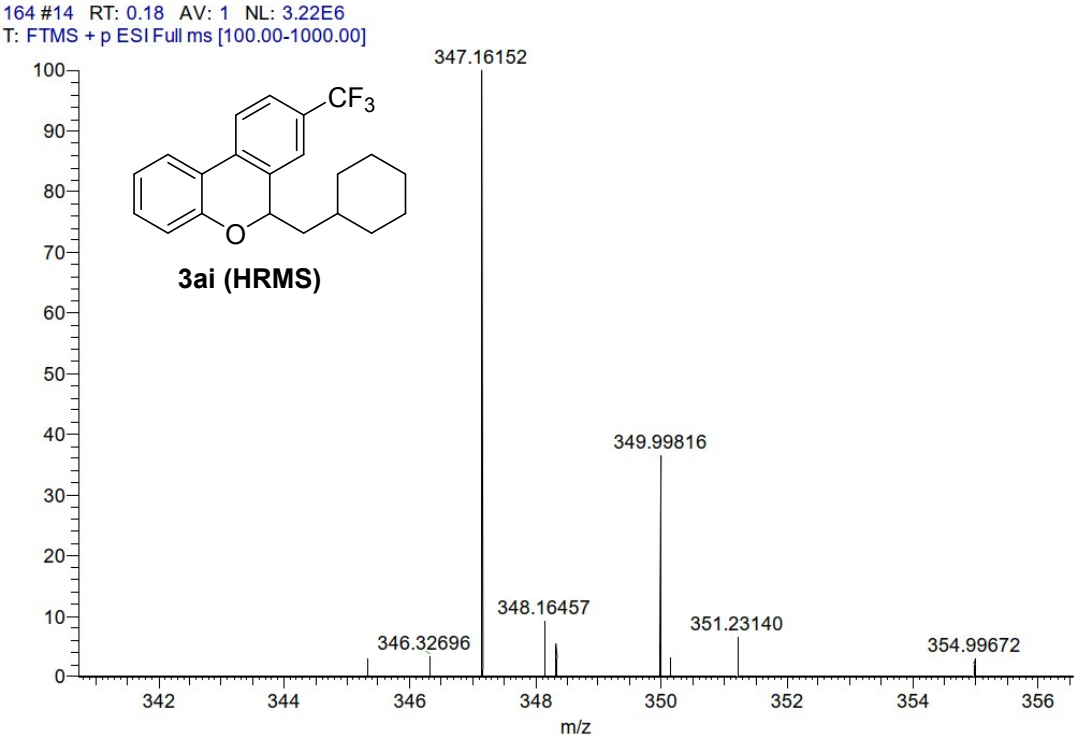

CF3
O
3ai (1H NMR)
f1 (ppm)



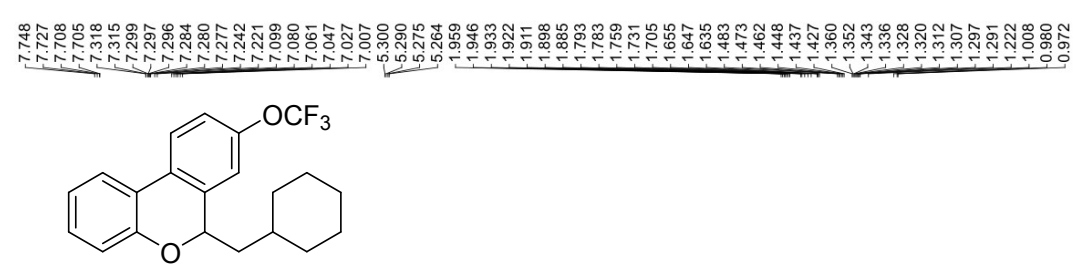
3ai (^{13}C NMR)



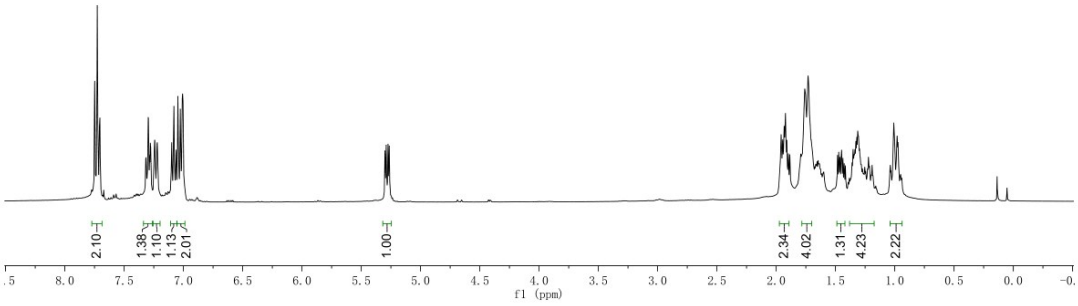
3ai (^{19}F NMR)

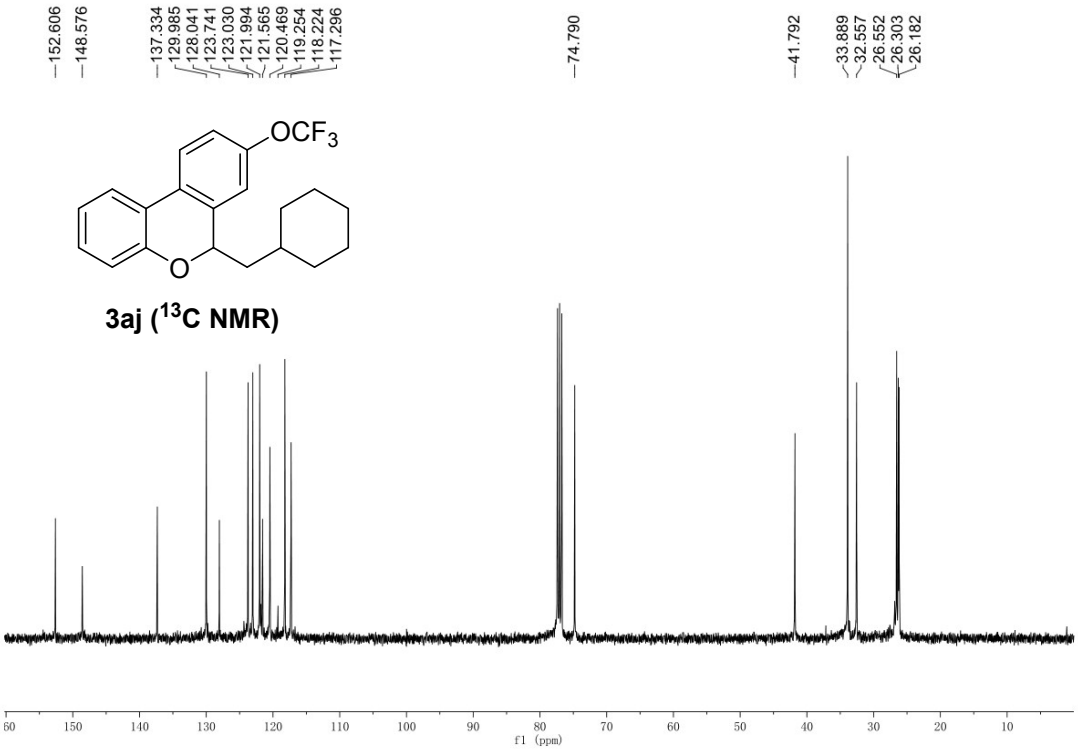


3ai (HRMS)

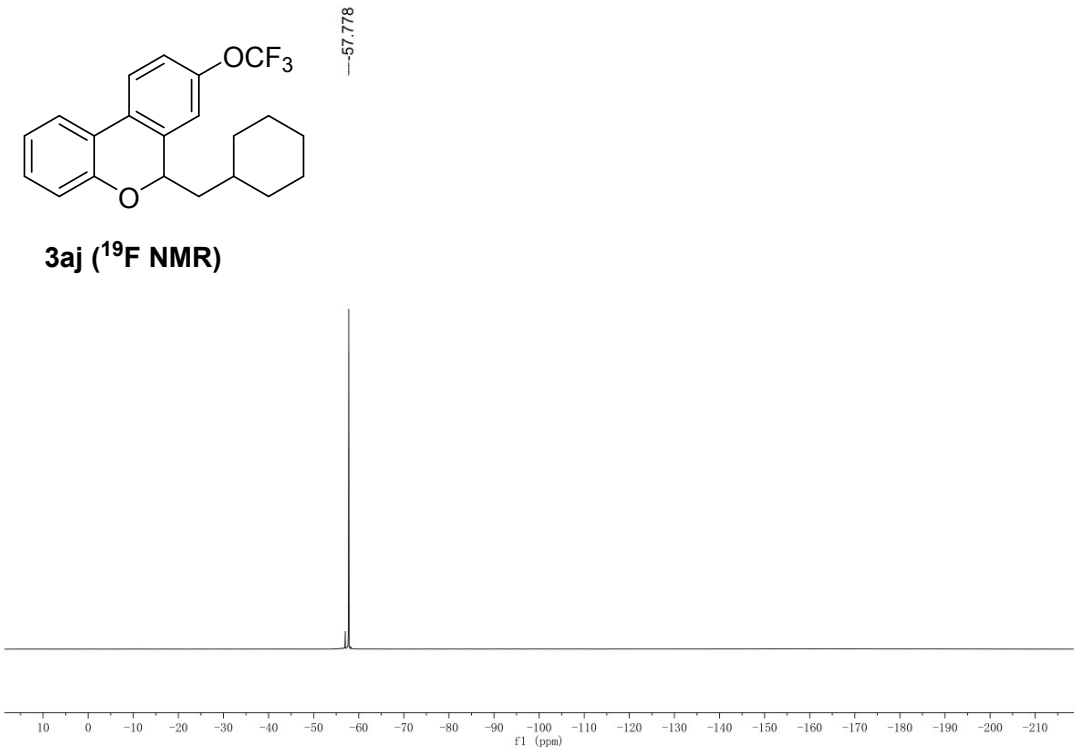


3aj (^{1}H NMR)

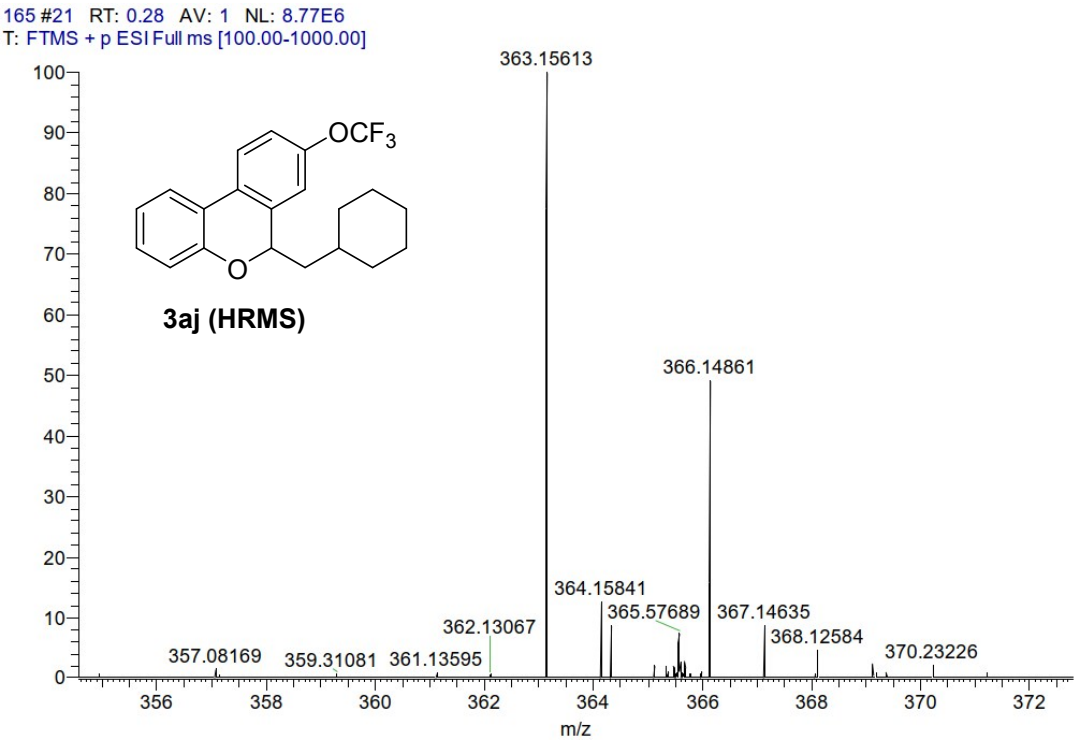


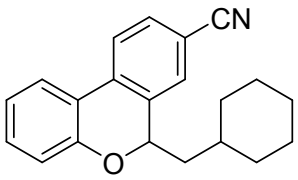


3aj (^{13}C NMR)

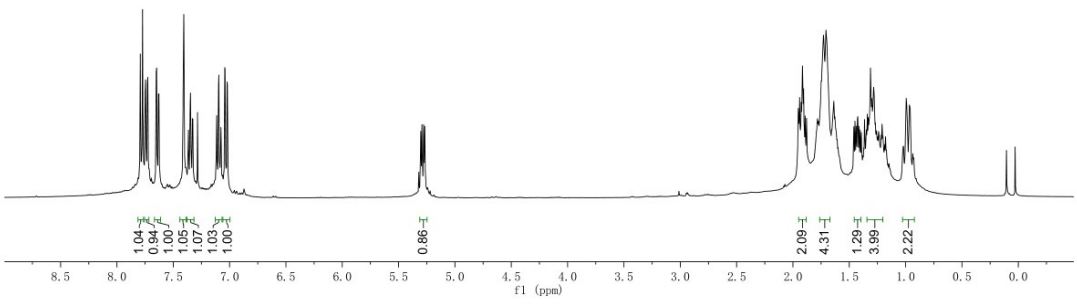


3aj (^{19}F NMR)

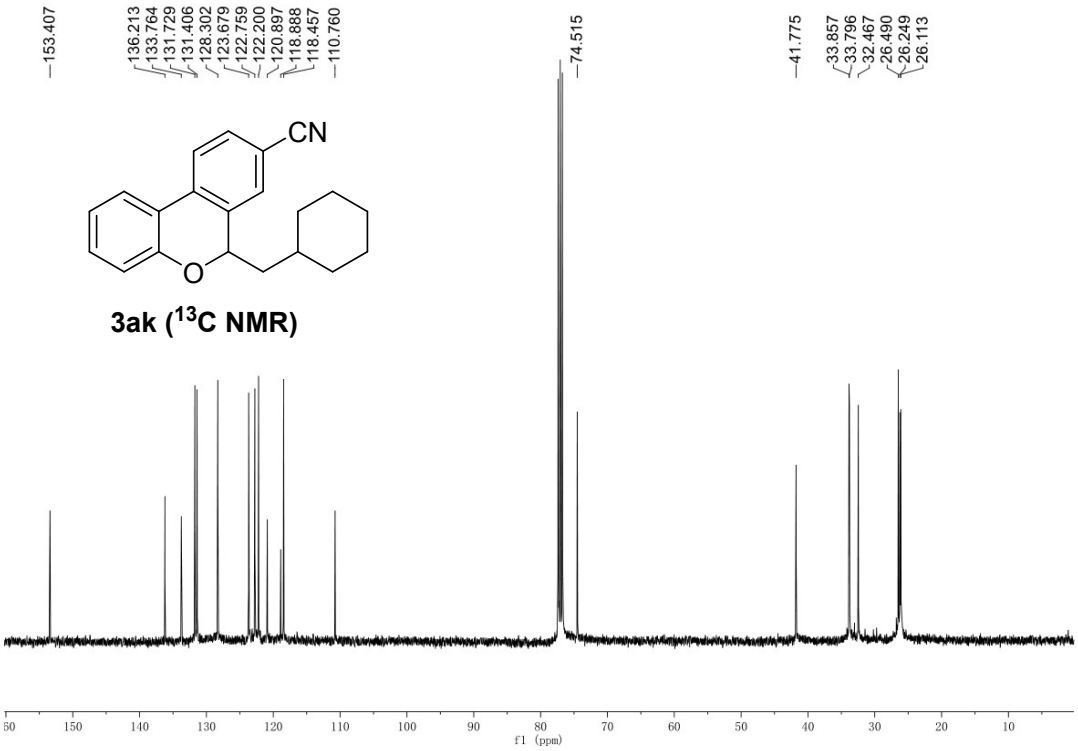




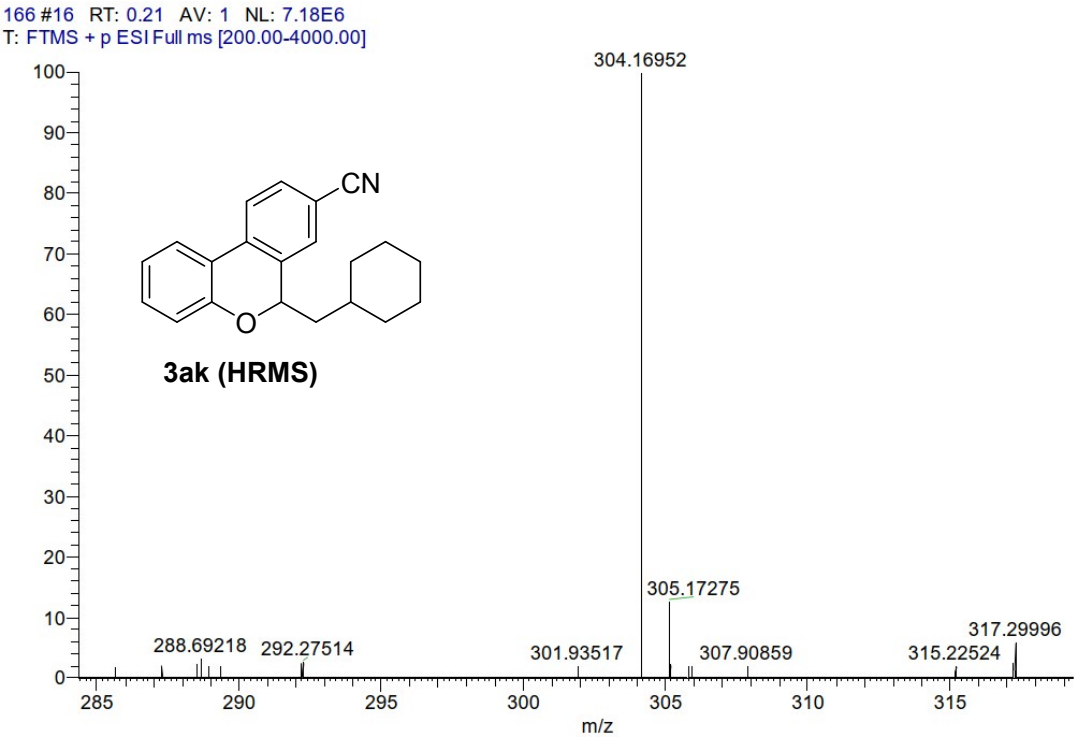
3aj (HRMS)



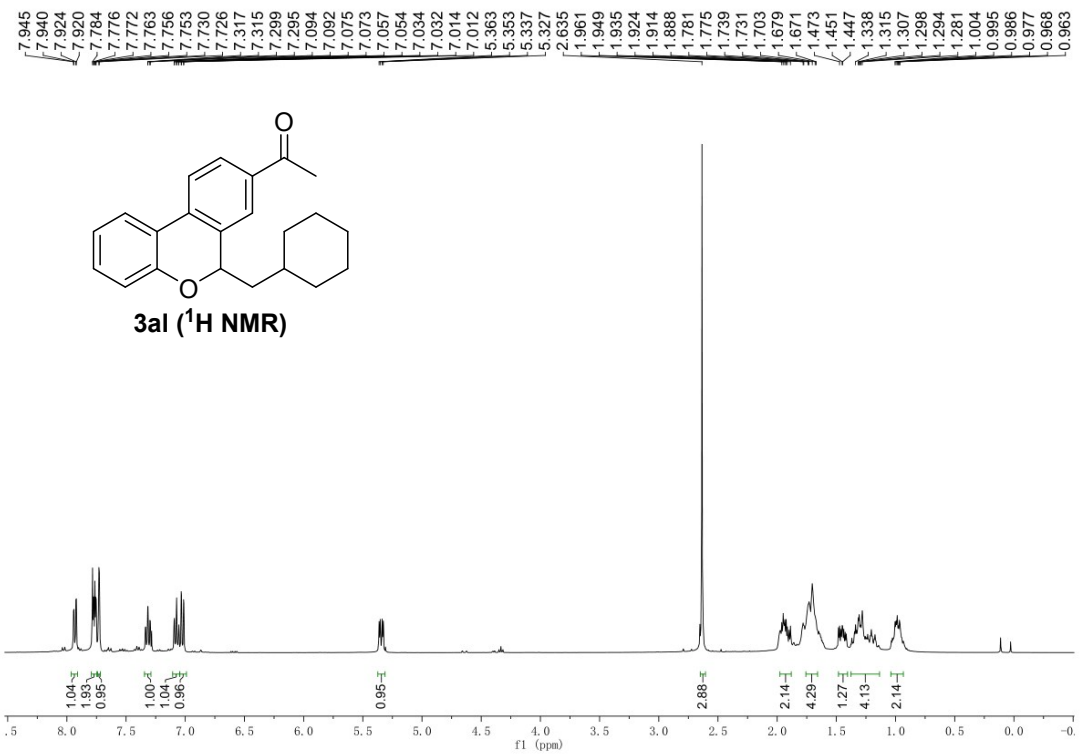
3ak (^{1}H NMR)



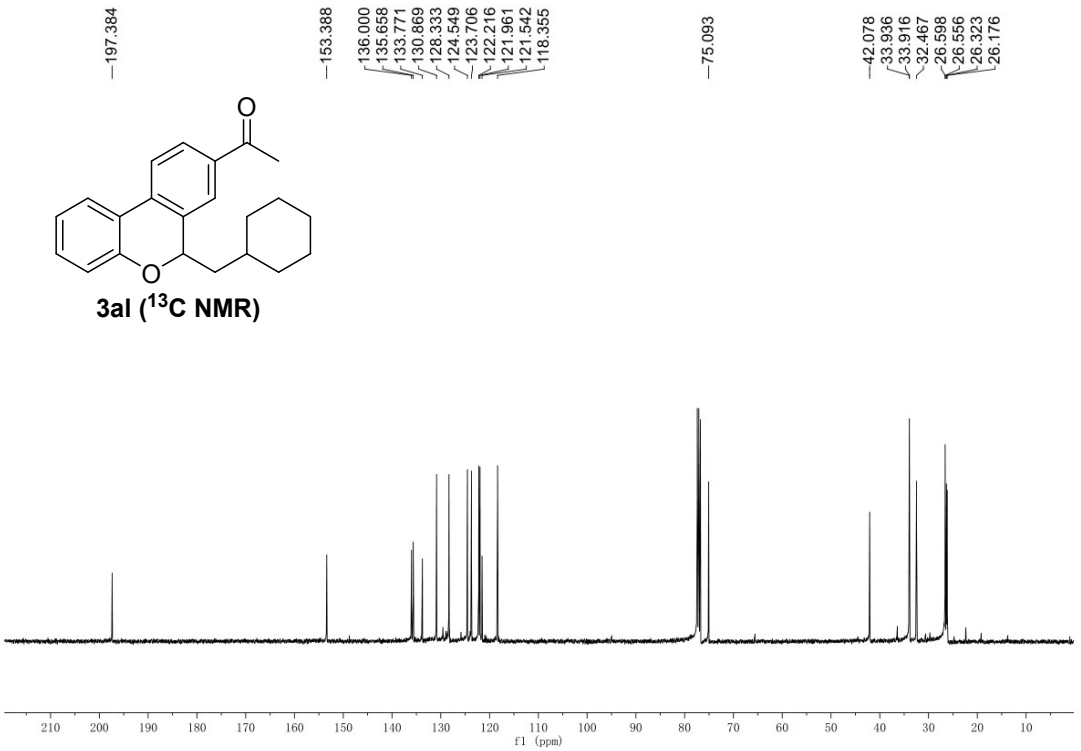
3ak (^{13}C NMR)



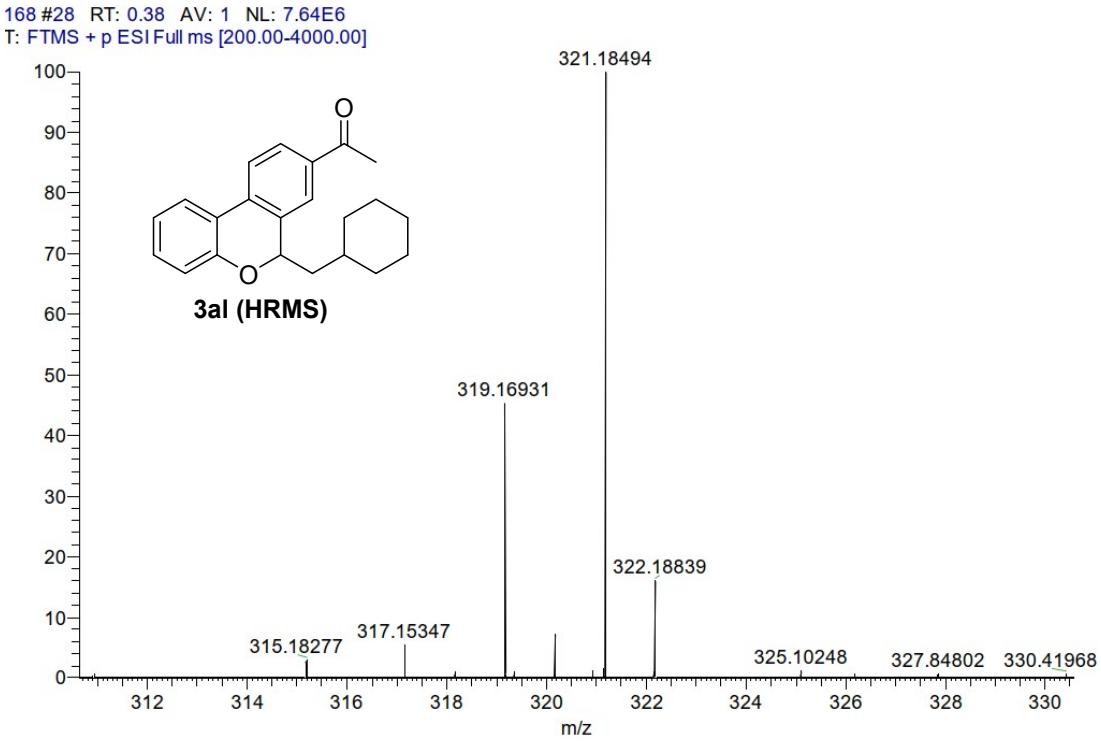
3ak (HRMS)



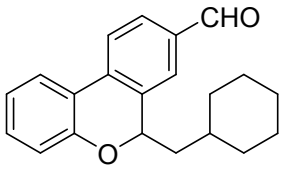
3al (^{1}H NMR)



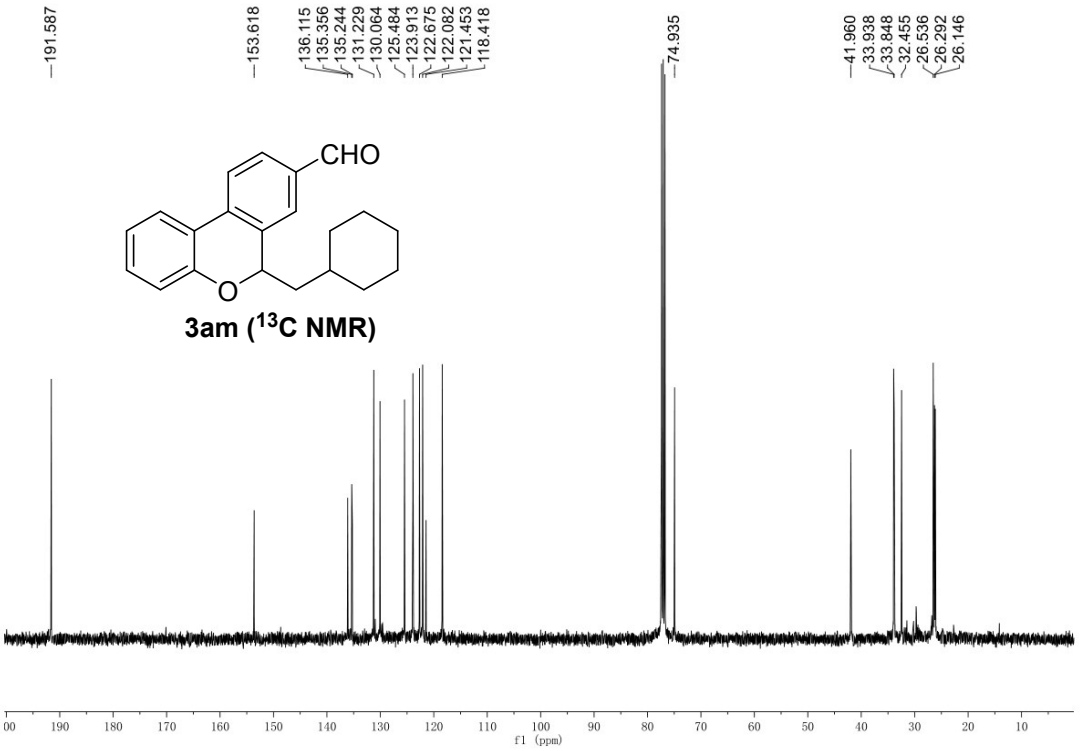
3al (^{13}C NMR)

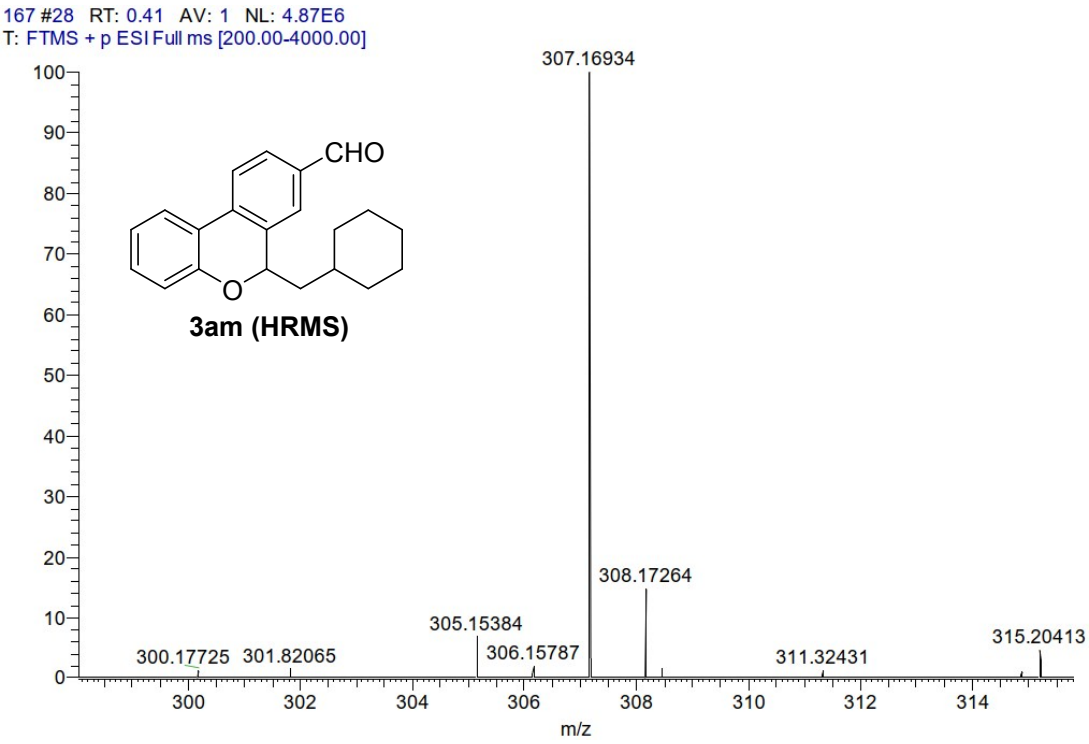


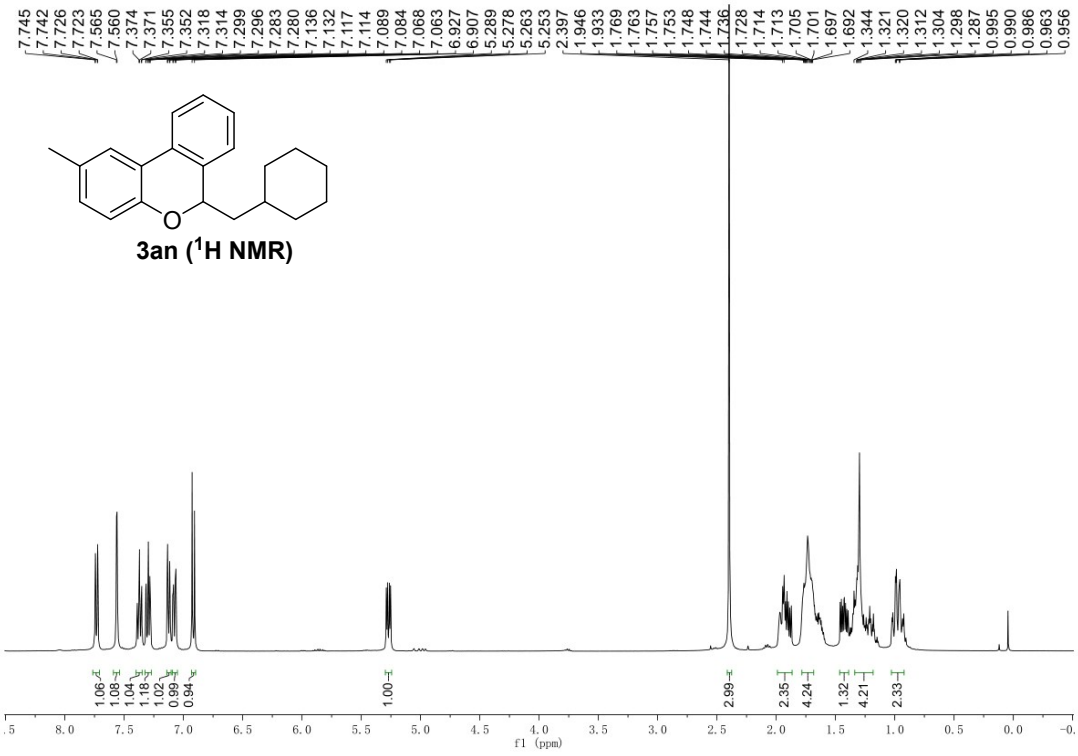
3al (HRMS)



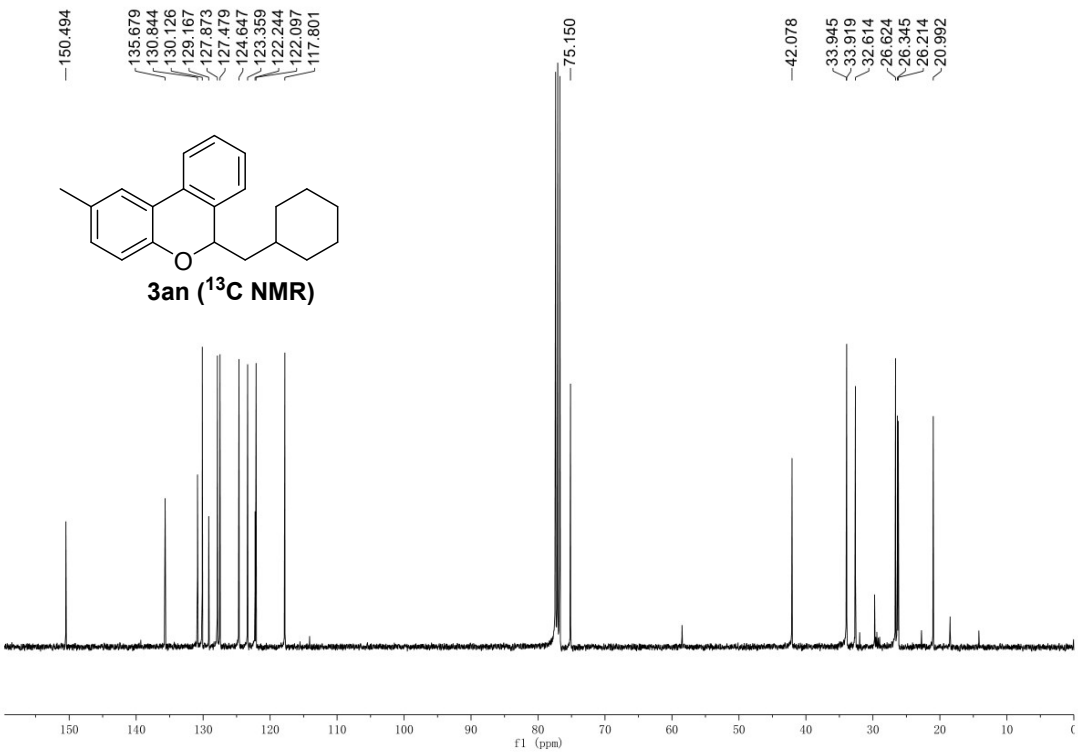
3am (^{1}H NMR)


191.587
153.618
136.115
135.356
135.244
131.229
130.064
125.484
123.913
122.675
122.082
121.453
118.418
74.935
41.960
33.938
33.848
32.455
26.536
26.292
26.146
CHO
O
3am (^{13}C NMR)
f1 (ppm)


167 #28 RT: 0.41 AV: 1 NL: 4.87E6
T: FTMS + p ESI Full ms [200.00-4000.00]
307.16934
308.17264
305.15384
306.15787
300.17725
301.82065
311.32431
315.20413
CHO
O
3am (HRMS)
m/z

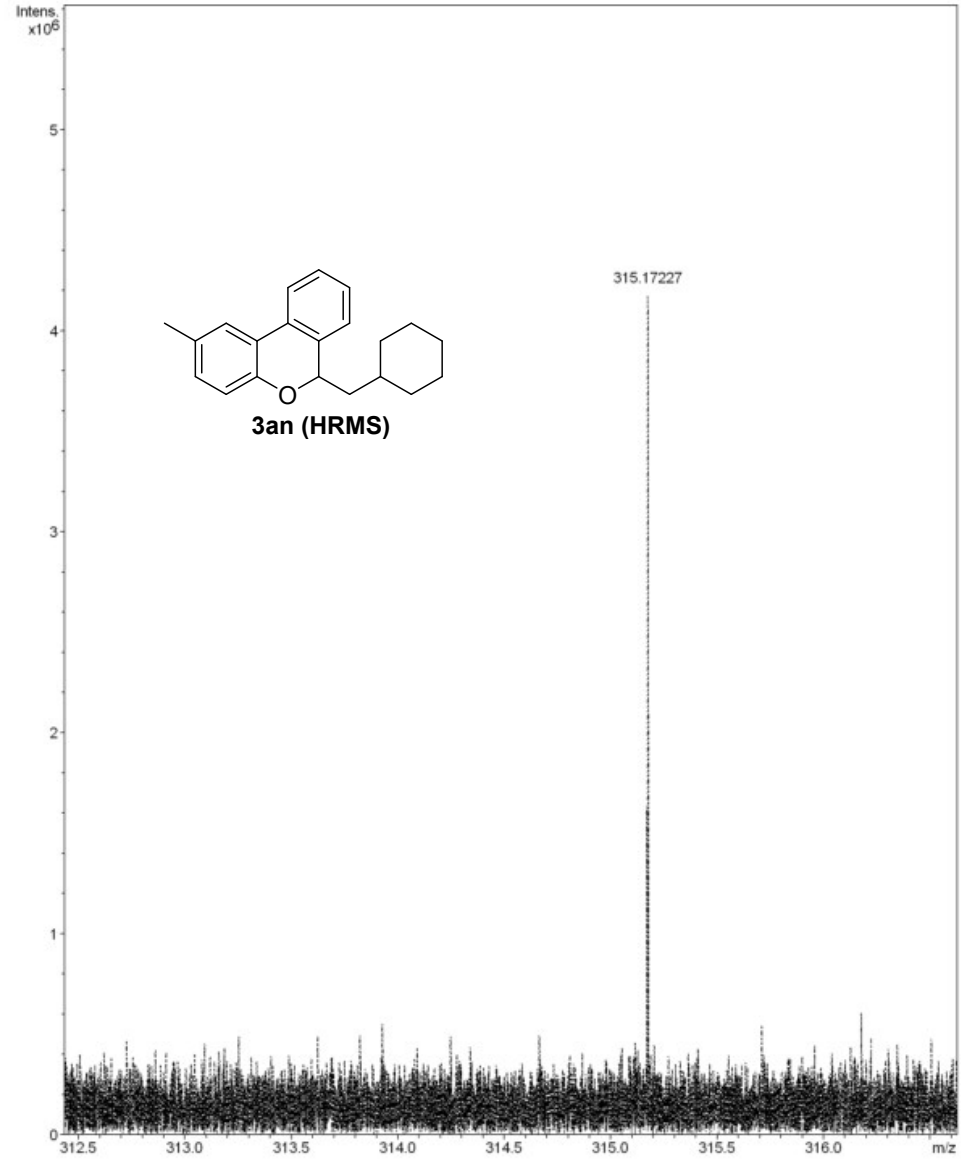


3an (^{1}H NMR)



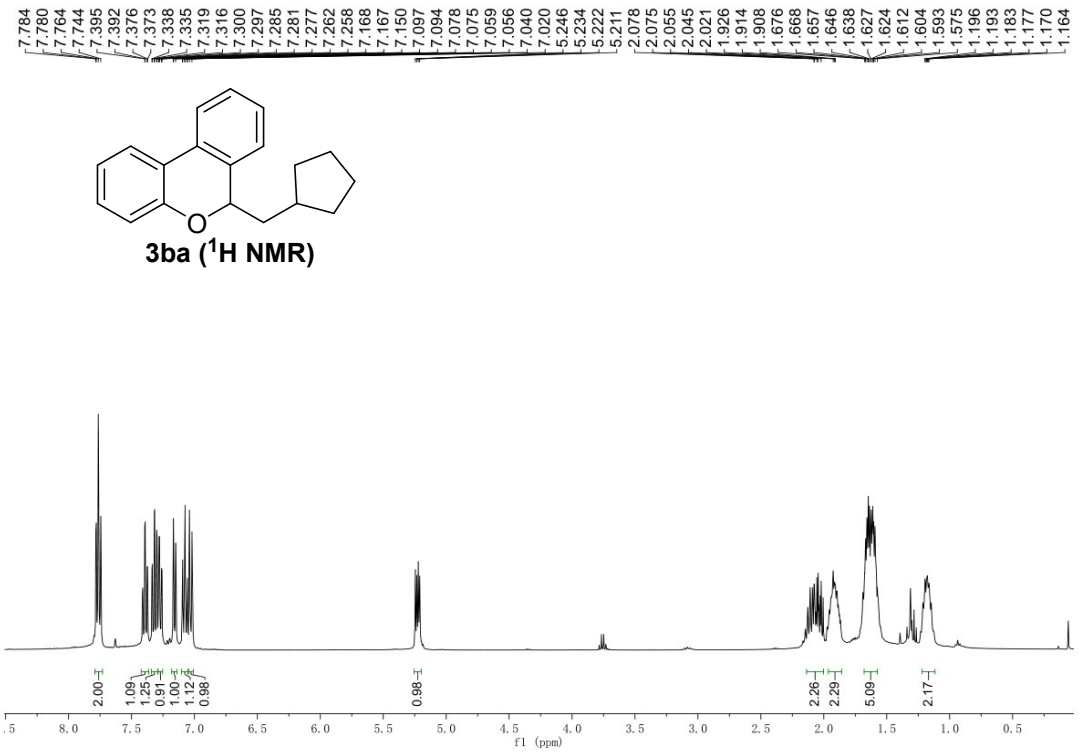
3an (^{13}C NMR)

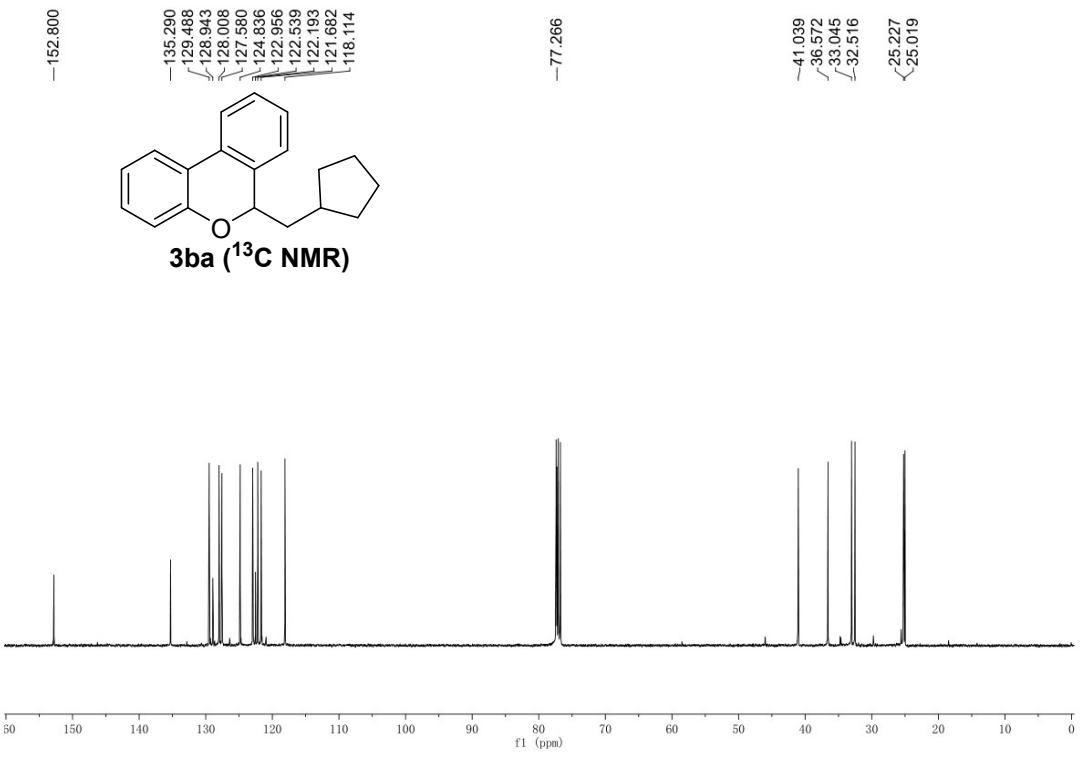
Generic Display Report (all)

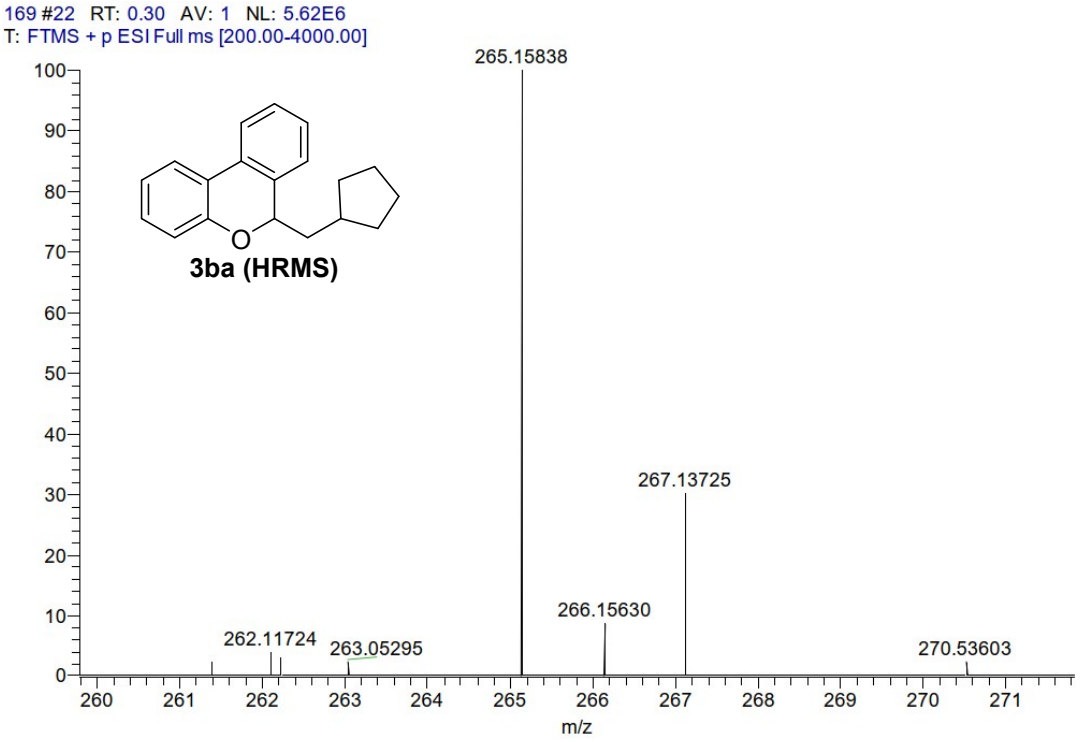


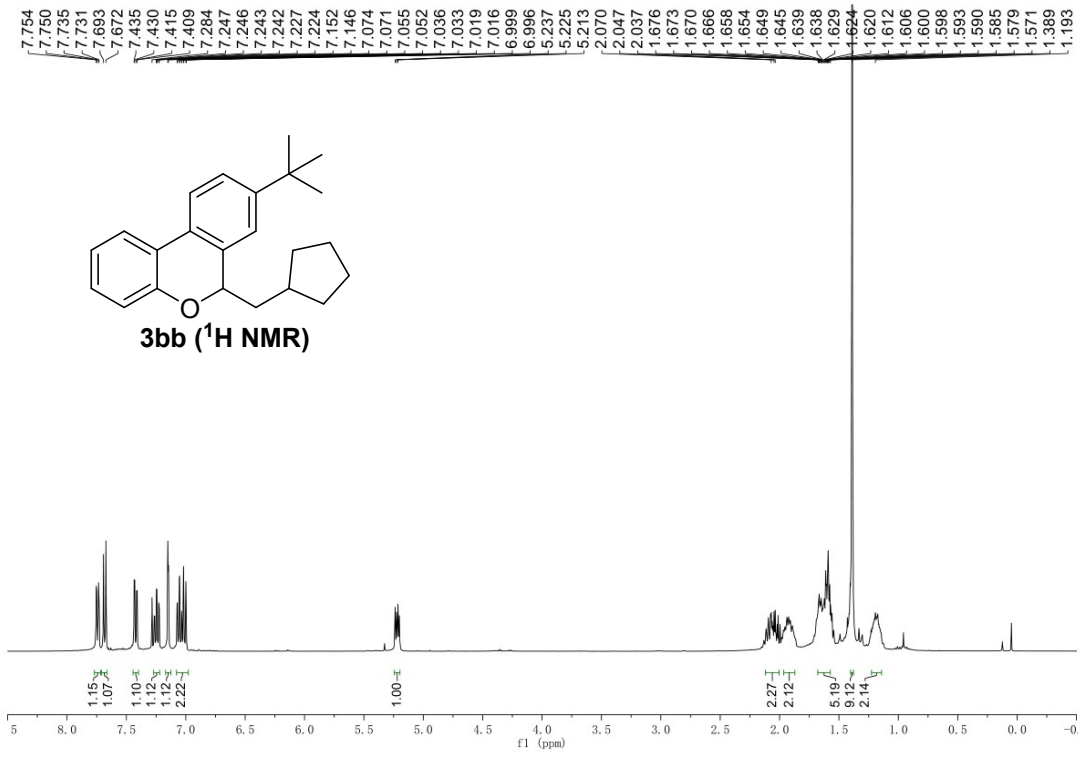
3an (HRMS)

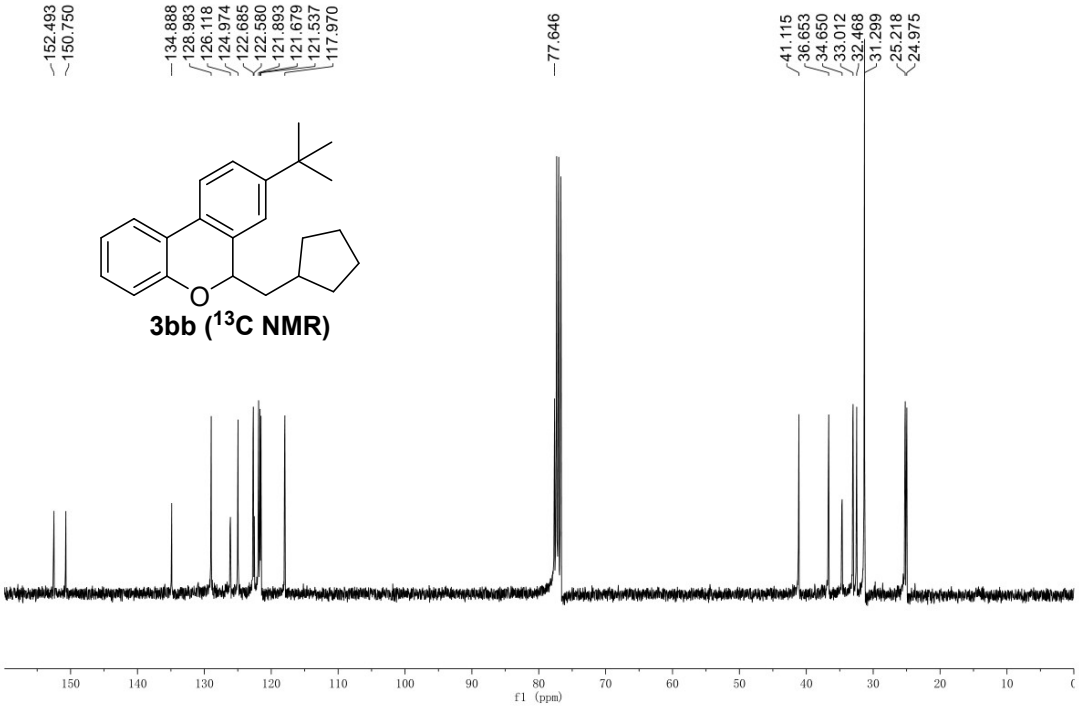
Bruker Compass DataAnalysis 4.0 printed: 4/10/2019 11:07:44 AM Page 1 of 1

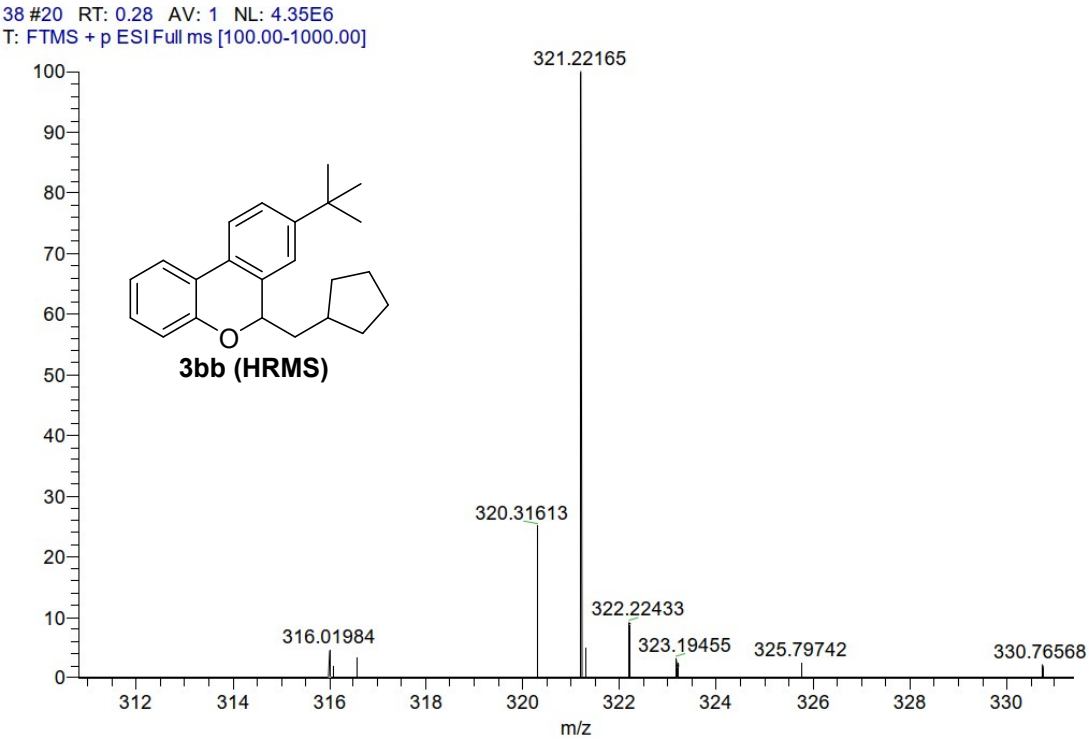

7.784
7.780
7.764
7.744
7.395
7.392
7.376
7.373
7.338
7.335
7.319
7.316
7.300
7.297
7.285
7.281
7.277
7.262
7.258
7.168
7.167
7.150
7.097
7.094
7.078
7.075
7.059
7.056
7.040
7.020
5.246
5.234
5.222
5.211
2.078
2.075
2.055
2.045
2.021
1.926
1.914
1.908
1.676
1.668
1.657
1.646
1.638
1.627
1.624
1.612
1.604
1.593
1.575
1.196
1.193
1.183
1.177
1.170
1.164
O
3ba (^{1}H NMR)
2.00
1.09
1.25
0.91
1.00
1.12
0.98
0.98
2.26
2.29
5.09
2.17
f1 (ppm)

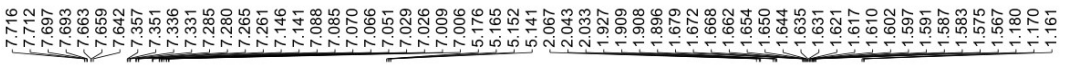

152.800
135.290
129.488
128.943
128.008
127.580
124.836
122.956
122.539
122.193
121.682
118.114
77.266
41.039
36.572
33.045
32.516
25.227
25.019
O
3ba (^{13}C NMR)
f1 (ppm)

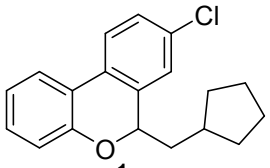

169 #22 RT: 0.30 AV: 1 NL: 5.62E6
T: FTMS + p ESI Full ms [200.00-4000.00]
265.15838
267.13725
266.15630
262.11724
263.05295
270.53603
m/z
3ba (HRMS)


3bb (1H NMR)
f1 (ppm)

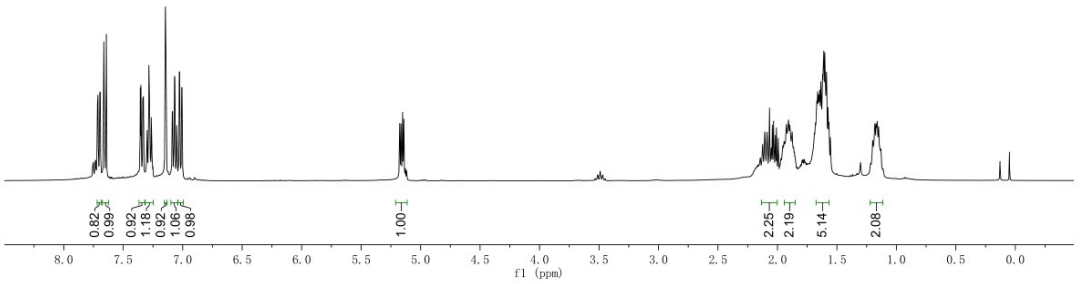

152.493
150.750
134.888
128.983
126.118
124.974
122.685
122.580
121.893
121.679
121.537
117.970
77.646
41.115
36.653
34.650
33.012
32.468
31.299
25.218
24.975
3bb (13C NMR)
f1 (ppm)

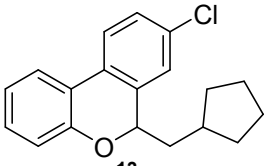

38 #20 RT: 0.28 AV: 1 NL: 4.35E6
T: FTMS + p ESI Full ms [100.00-1000.00]
321.22165
320.31613
322.22433
316.01984
323.19455
325.79742
330.76568
3bb (HRMS)
m/z



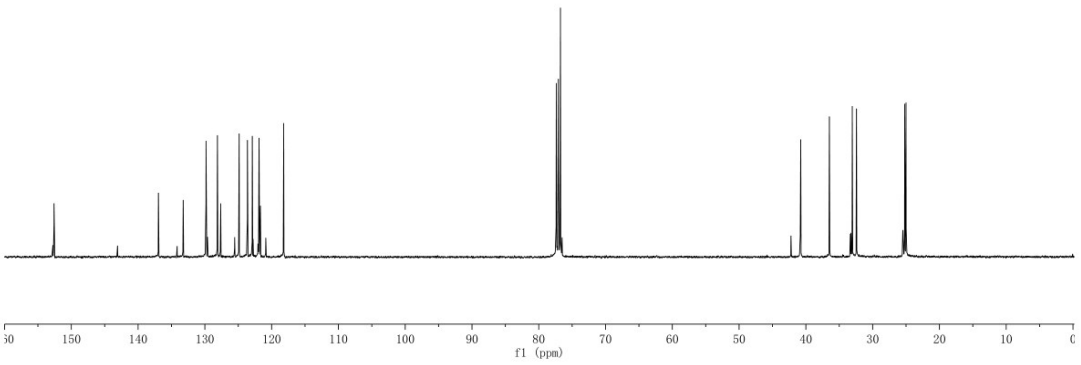


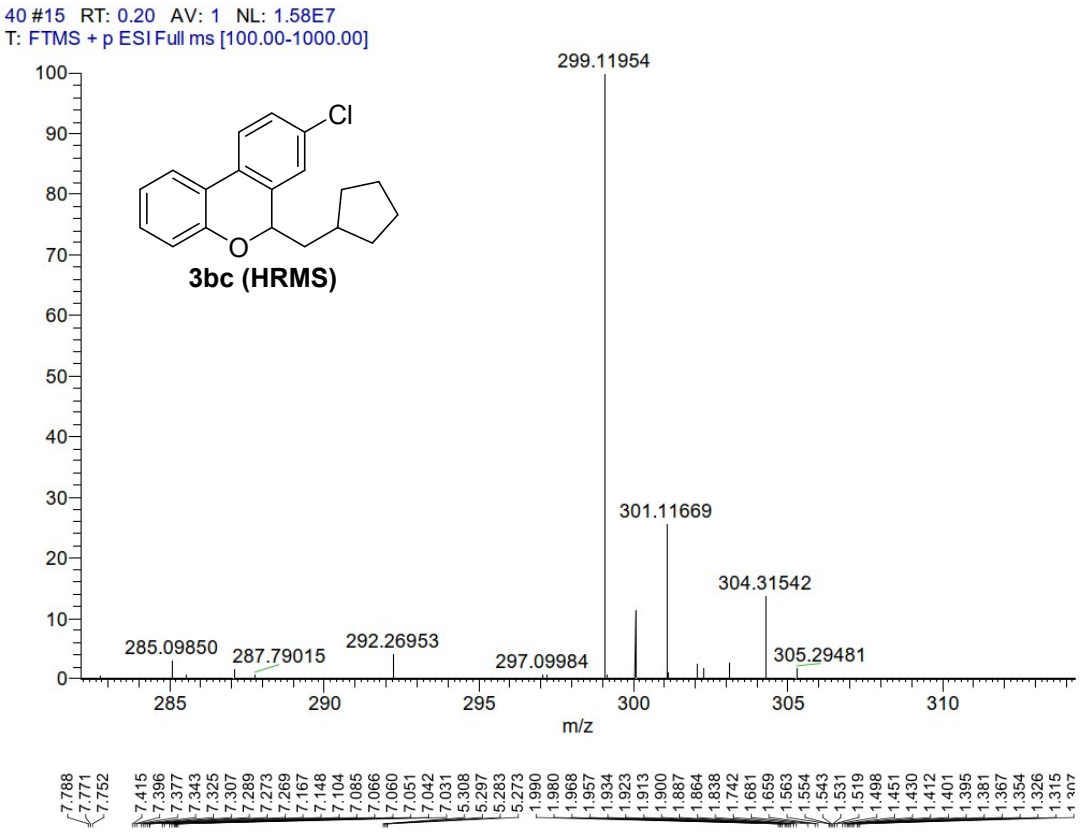
3bc (^{1}H NMR)

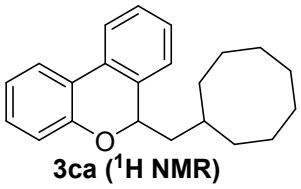


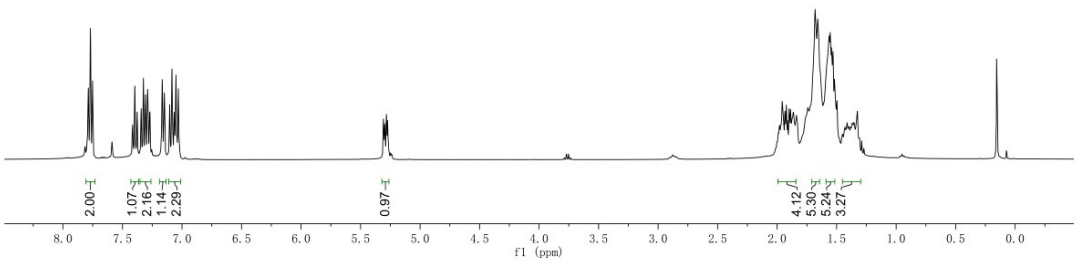


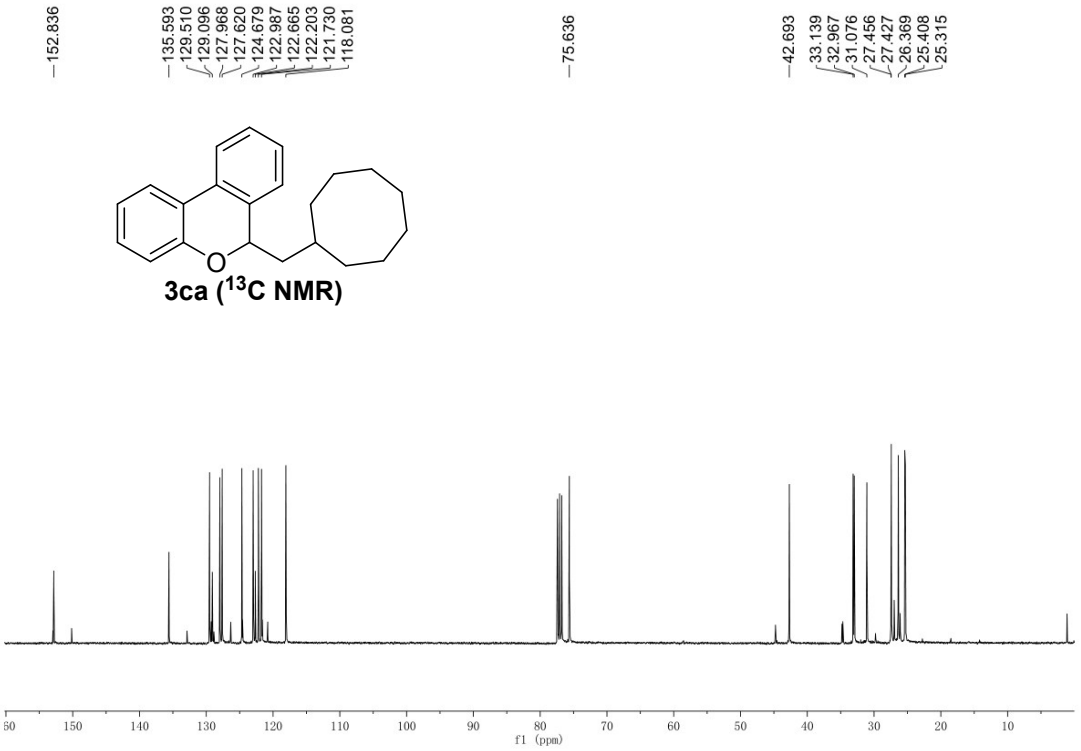
3bc (^{13}C NMR)

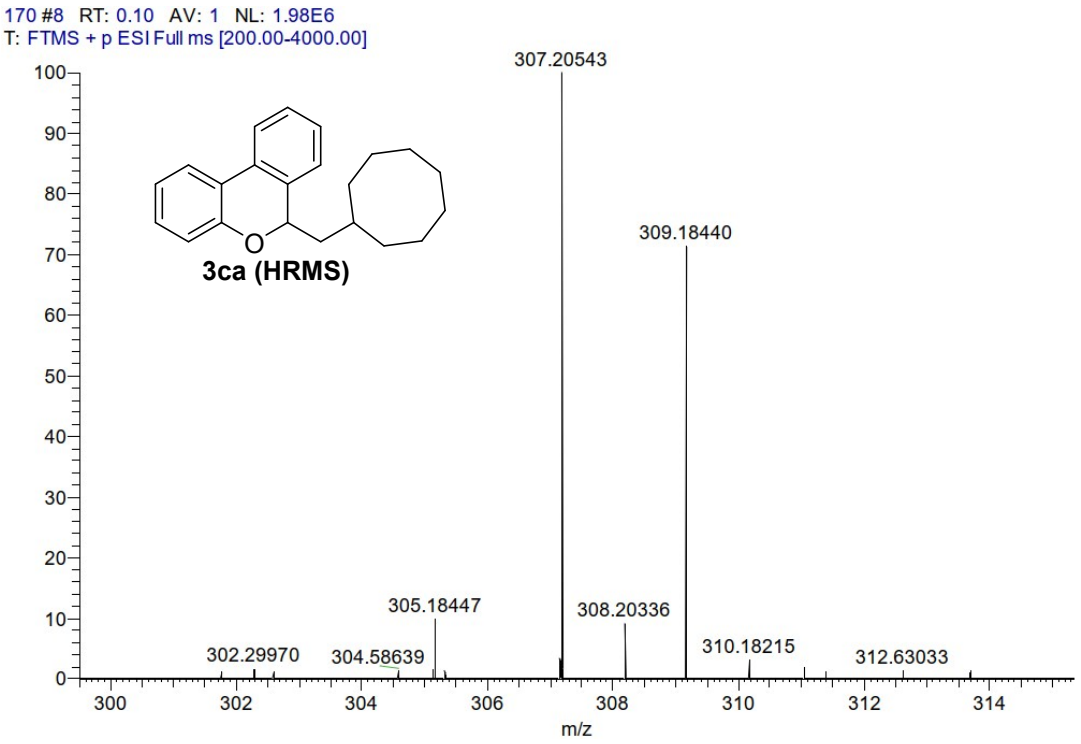


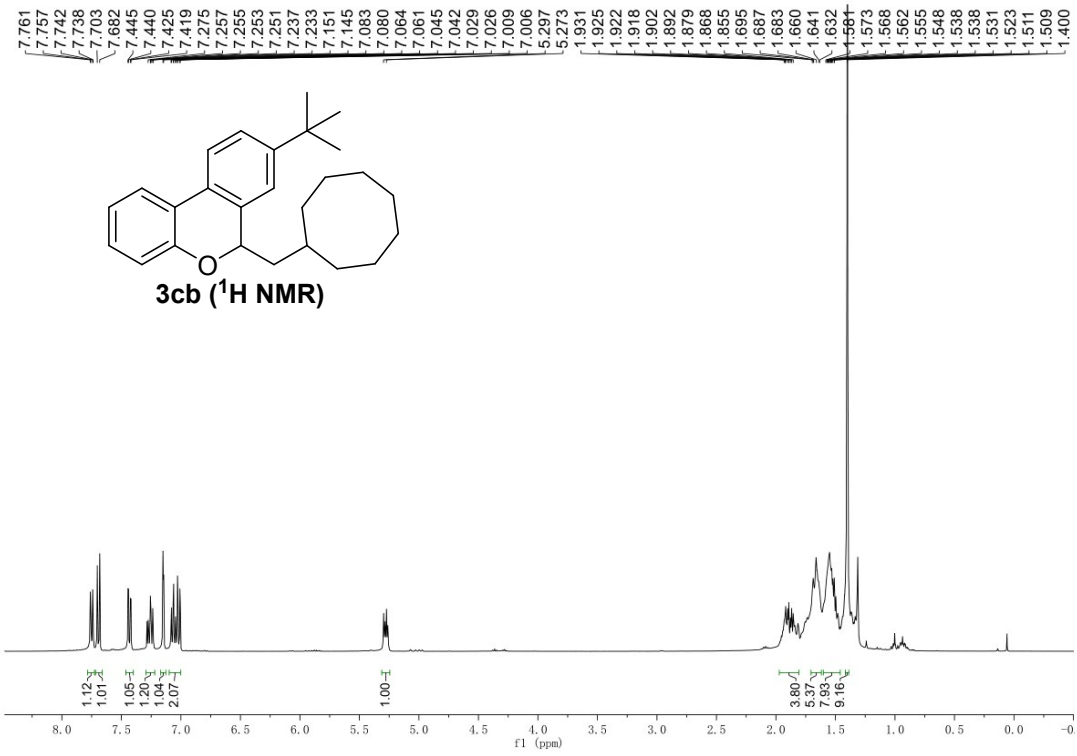

40 #15 RT: 0.20 AV: 1 NL: 1.58E7
T: FTMS + p ESI Full ms [100.00-1000.00]
299.11954
301.11669
304.31542
285.09850
287.79015
292.26953
297.09984
305.29481
m/z
Cl
O
3bc (HRMS)


O
3ca (1H NMR)

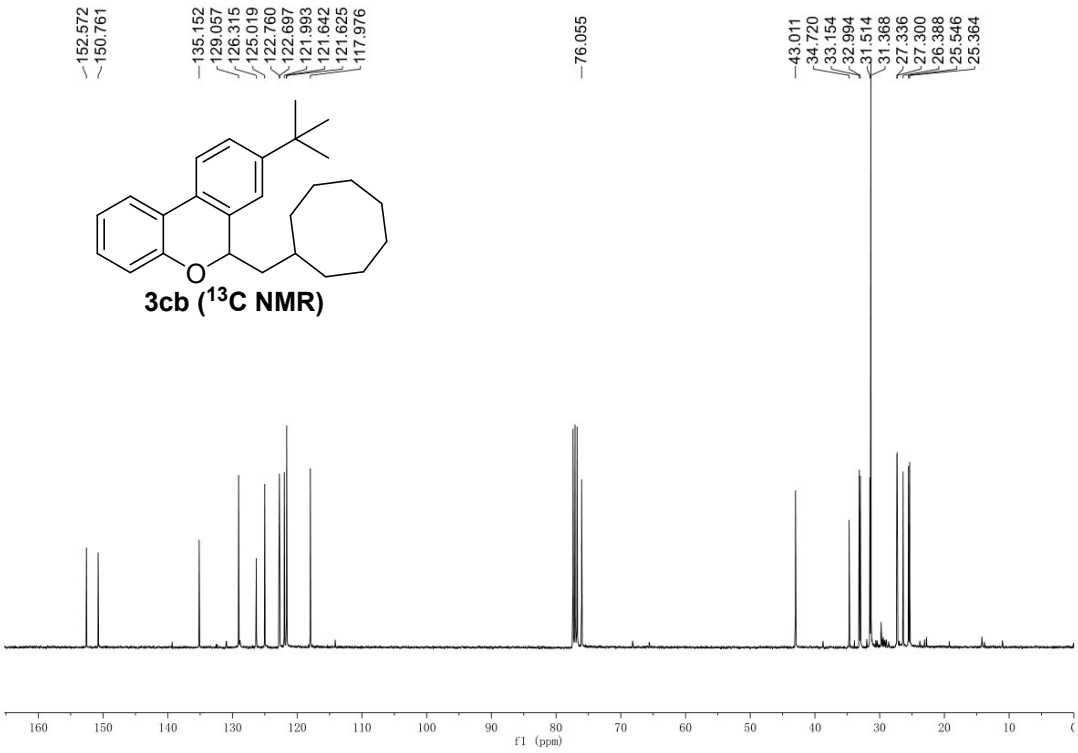

2.00
1.07
2.16
1.14
2.29
0.97
4.12
5.30
5.24
3.27
f1 (ppm)


152.836
135.593
129.510
129.096
127.968
127.620
124.679
122.987
122.665
122.203
121.730
118.081
75.636
42.693
33.139
32.967
31.076
27.456
27.427
26.369
25.408
25.315
O
3ca (13C NMR)
f1 (ppm)

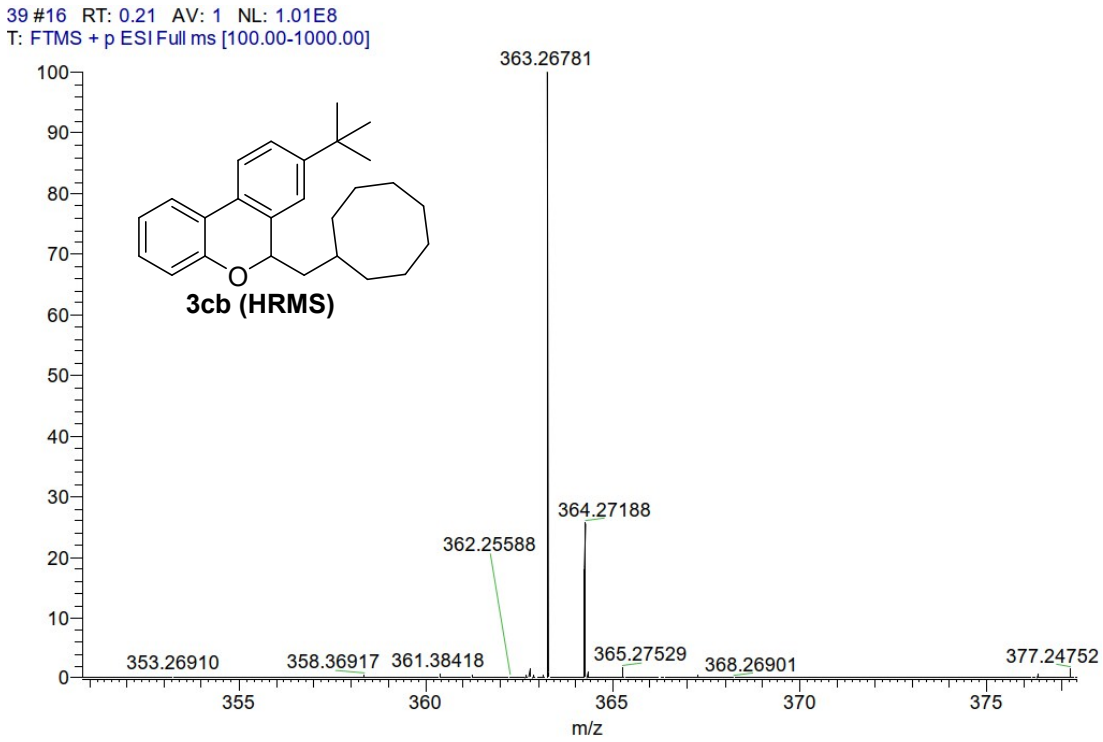

170 #8 RT: 0.10 AV: 1 NL: 1.98E6
T: FTMS + p ESI Full ms [200.00-4000.00]
307.20543
309.18440
305.18447
308.20336
302.29970
304.58639
310.18215
312.63033
O
3ca (HRMS)
m/z



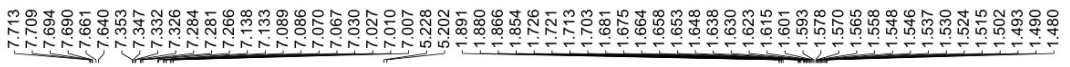
3cb (^{1}H NMR)

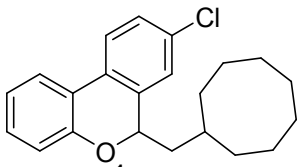


3cb (^{13}C NMR)

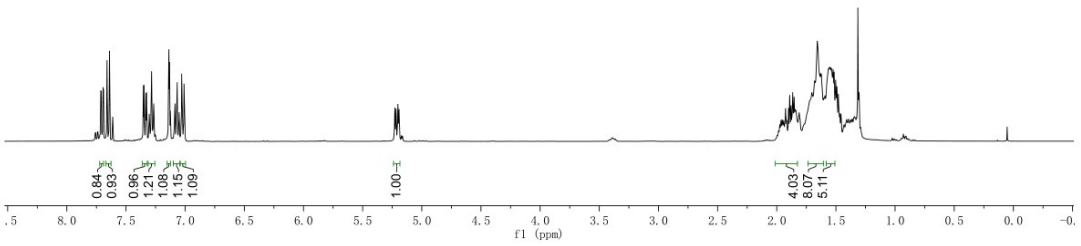


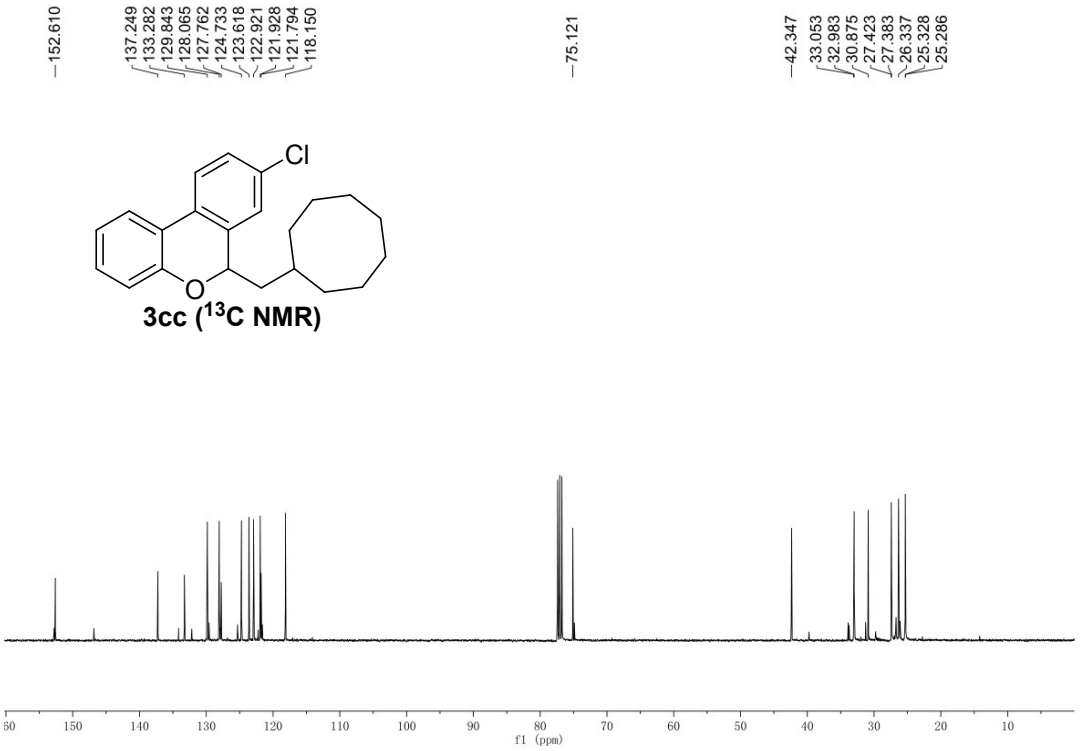
3cb (HRMS)

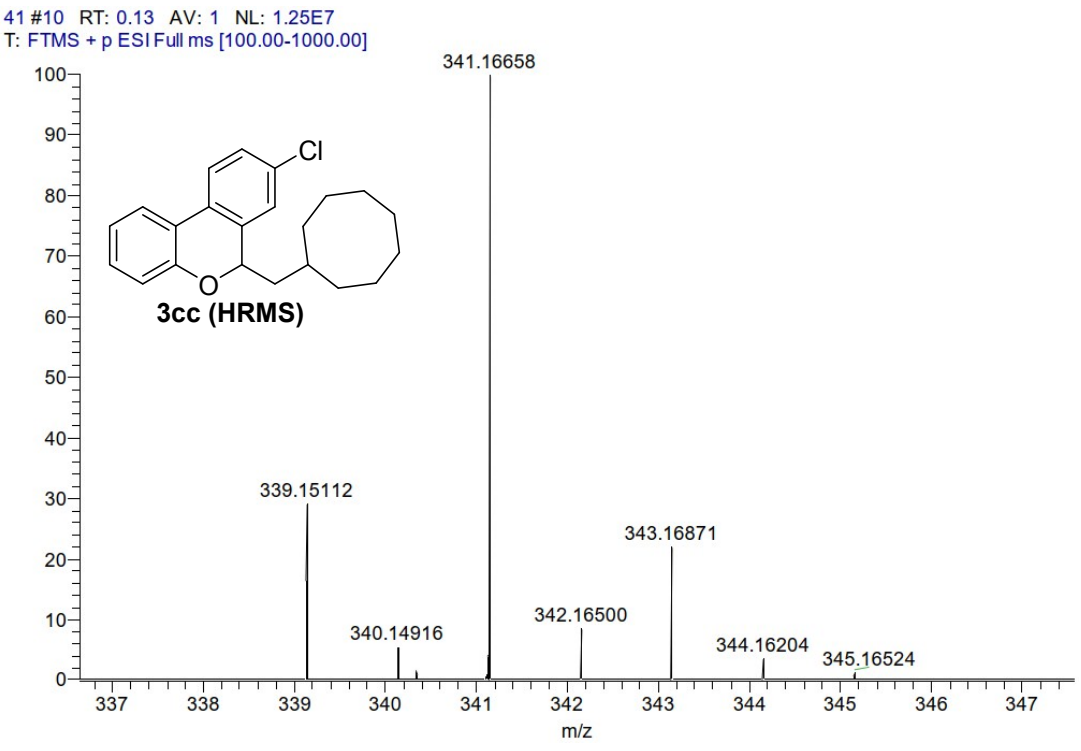


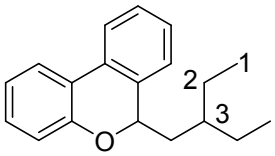


3cc (^{1}H NMR)

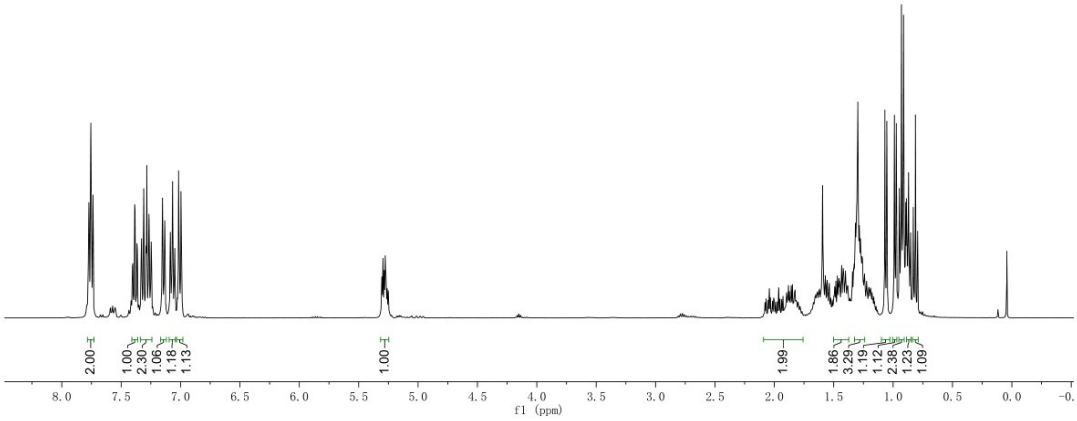


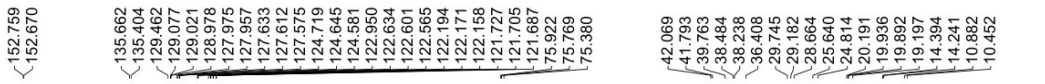

152.610
137.249
133.282
129.843
128.065
127.762
124.733
123.618
122.921
121.928
121.794
118.150
75.121
42.347
33.053
32.983
30.875
27.423
27.383
26.337
25.328
25.286
Cl
O
3cc (13C NMR)
f1 (ppm)

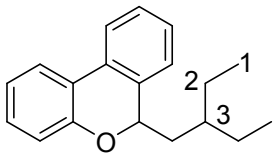

41 #10 RT: 0.13 AV: 1 NL: 1.25E7
T: FTMS + p ESI Full ms [100.00-1000.00]
341.16658
339.15112
343.16871
342.16500
340.14916
344.16204
345.16524
Cl
O
3cc (HRMS)
m/z



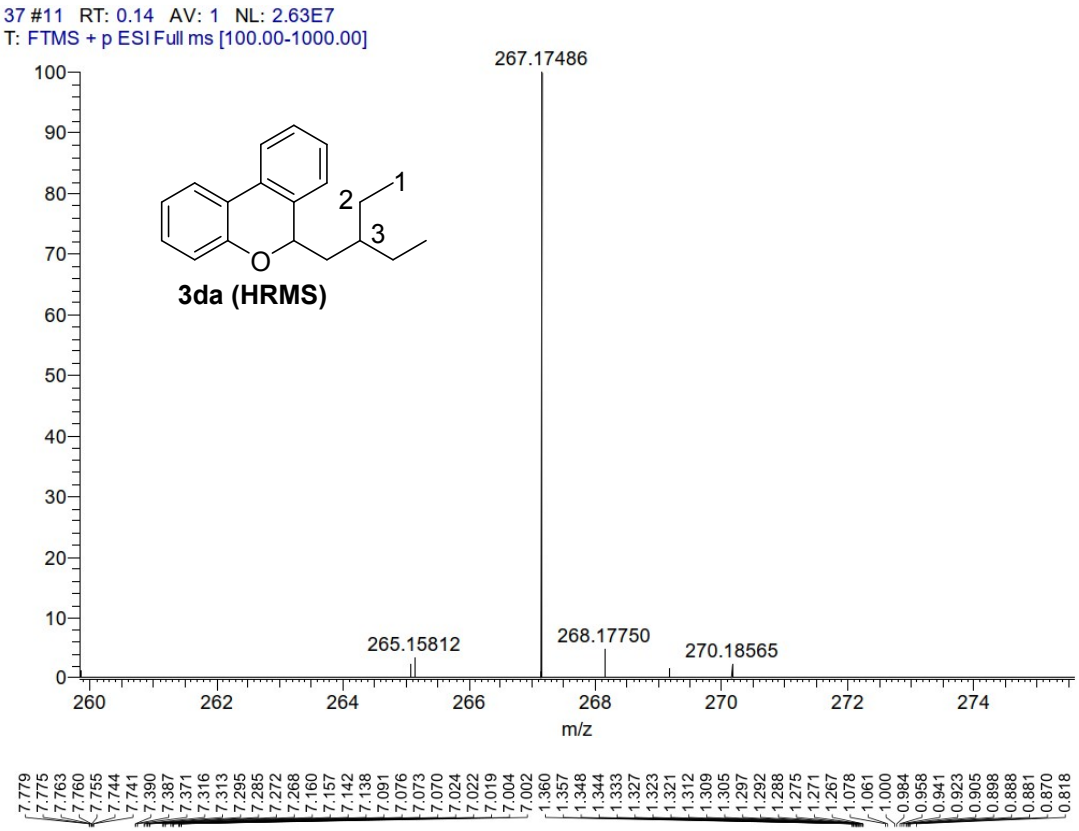
3da (^{13}C NMR)

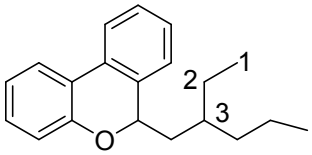


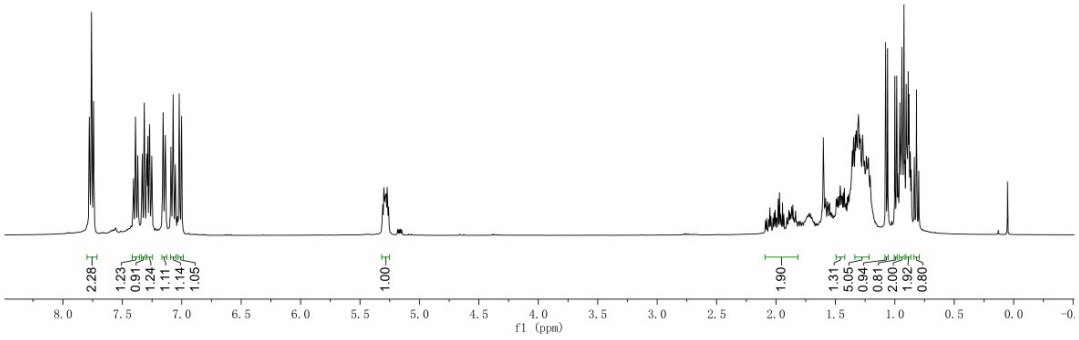


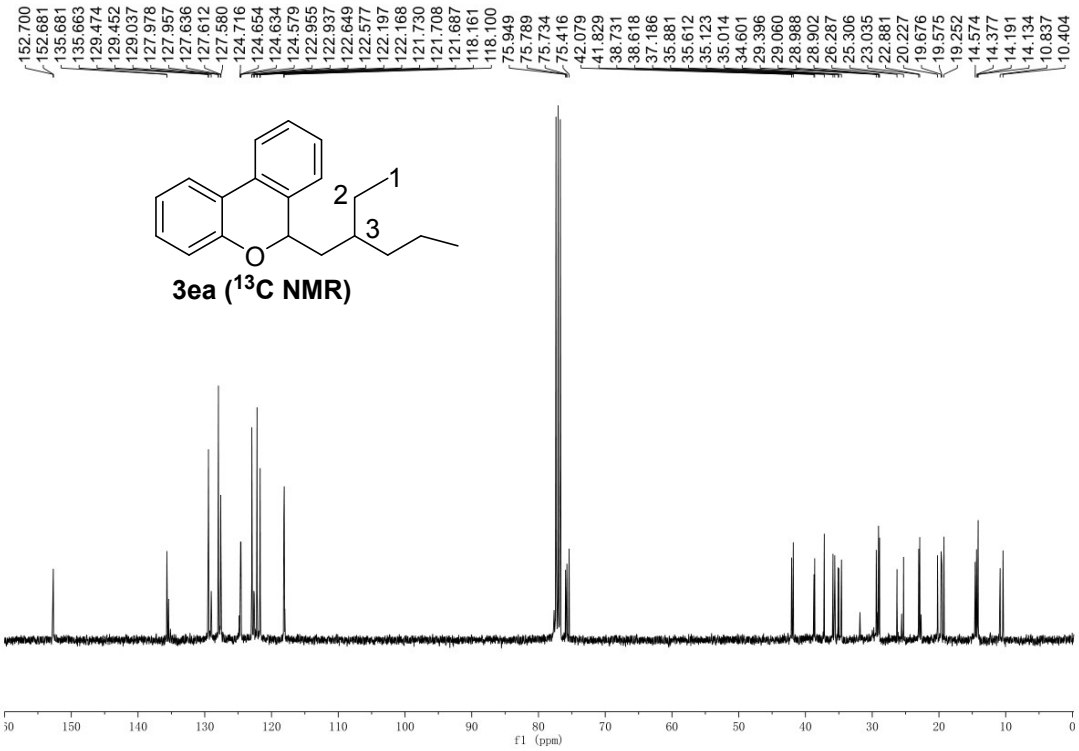


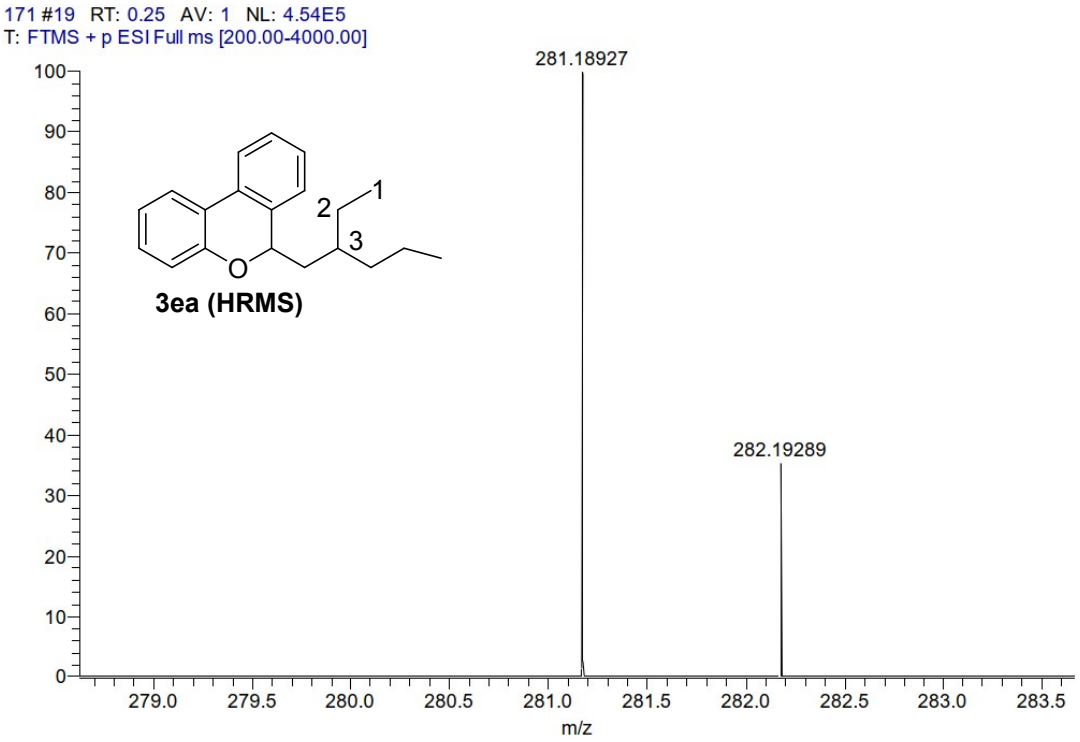
3da (^{1}H NMR)

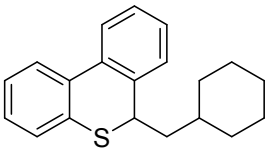

37 #11 RT: 0.14 AV: 1 NL: 2.63E7
T: FTMS + p ESI Full ms [100.00-1000.00]
267.17486
265.15812
268.17750
270.18565
m/z
3da (HRMS)


3ea (1H NMR)

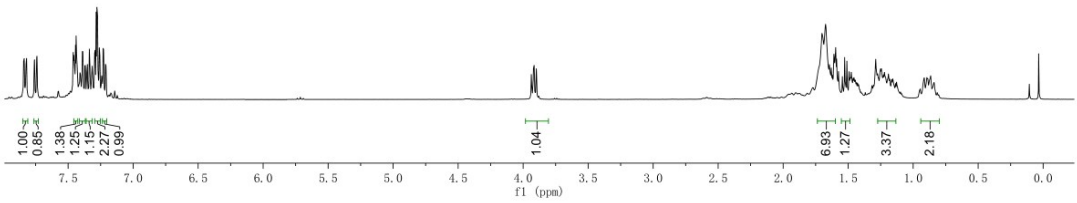

f1 (ppm)

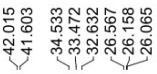

152.700
152.681
135.681
135.663
129.474
129.452
129.037
127.978
127.957
127.636
127.612
127.580
124.716
124.654
124.634
124.579
122.955
122.937
122.649
122.577
122.197
122.168
121.730
121.708
121.687
118.161
118.100
75.949
75.789
75.734
75.416
42.079
41.829
38.731
38.618
37.186
35.881
35.612
35.123
35.014
34.601
29.396
29.060
28.988
28.902
26.287
25.306
23.035
22.881
20.227
19.676
19.575
19.252
14.574
14.377
14.191
14.134
10.837
10.404
1
2
3
O
3ea (^{13}C NMR)
f1 (ppm)

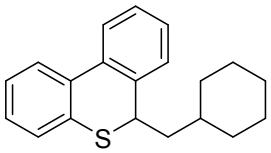

171 #19 RT: 0.25 AV: 1 NL: 4.54E5
T: FTMS + p ESI Full ms [200.00-4000.00]
281.18927
282.19289
1
2
3
O
3ea (HRMS)
m/z



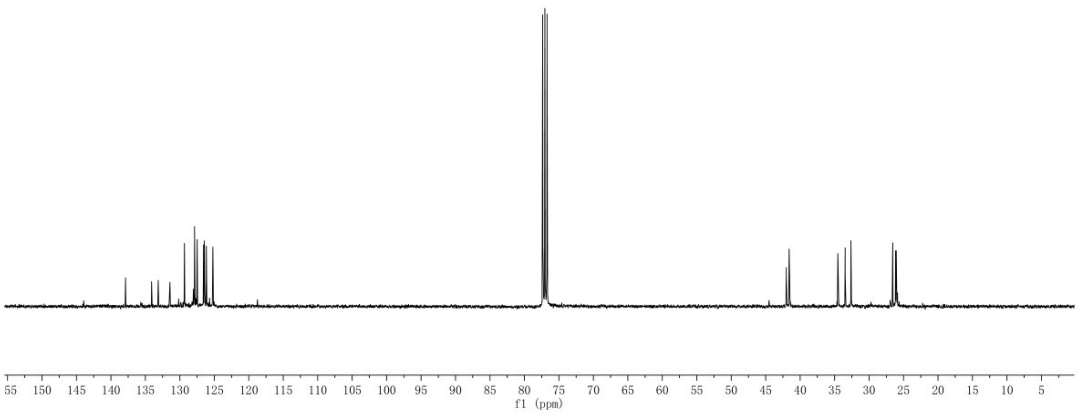
4a (^{1}H NMR)

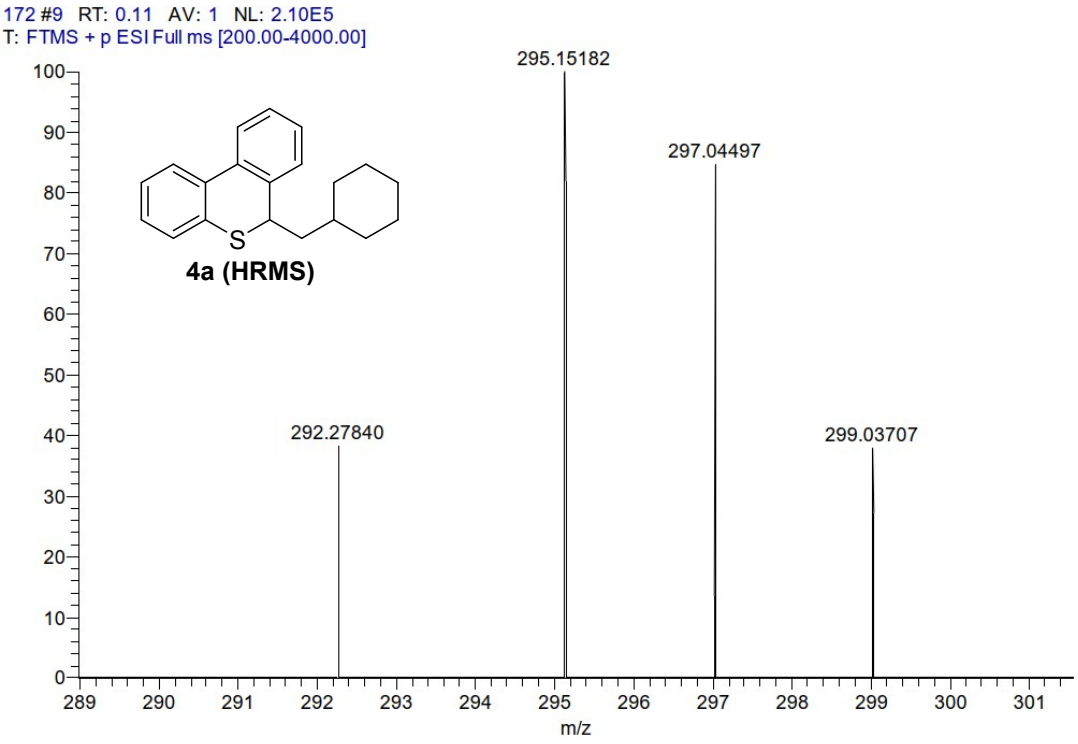




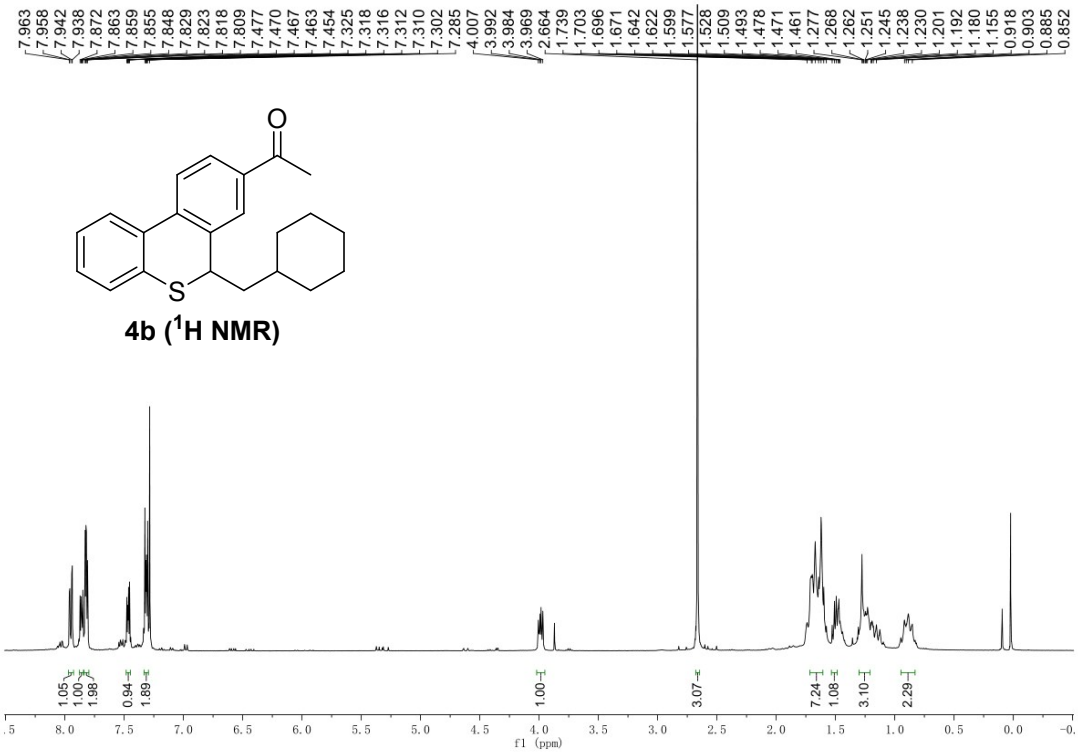


4a (^{13}C NMR)

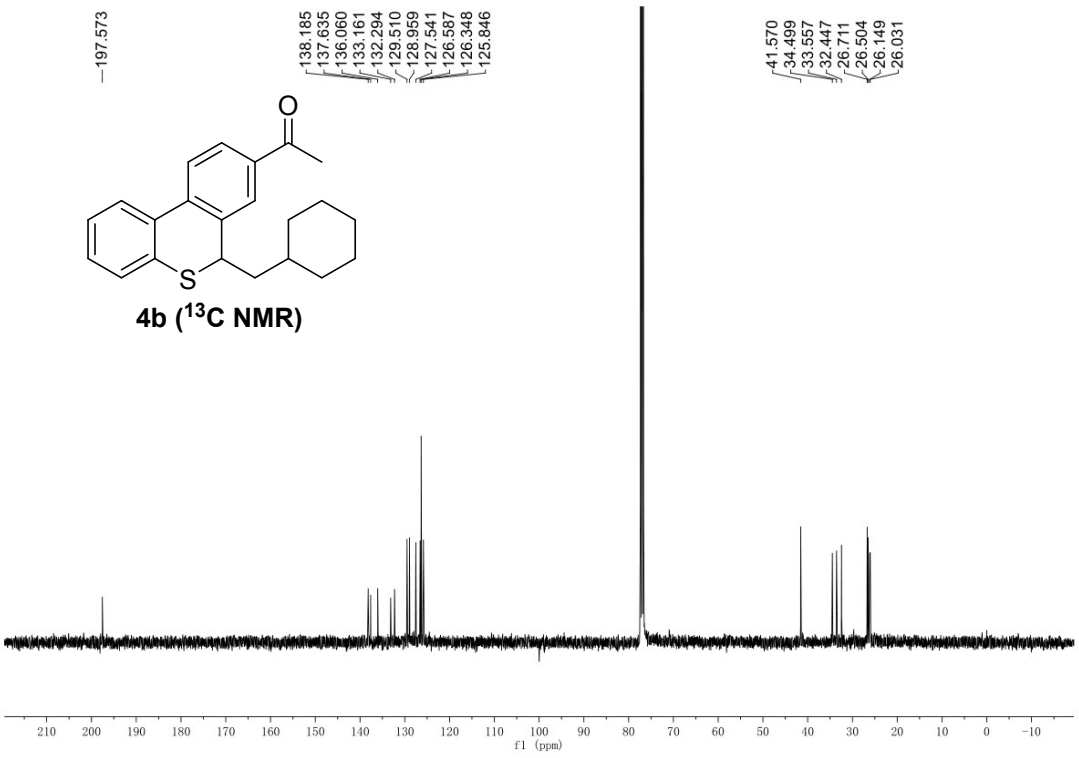




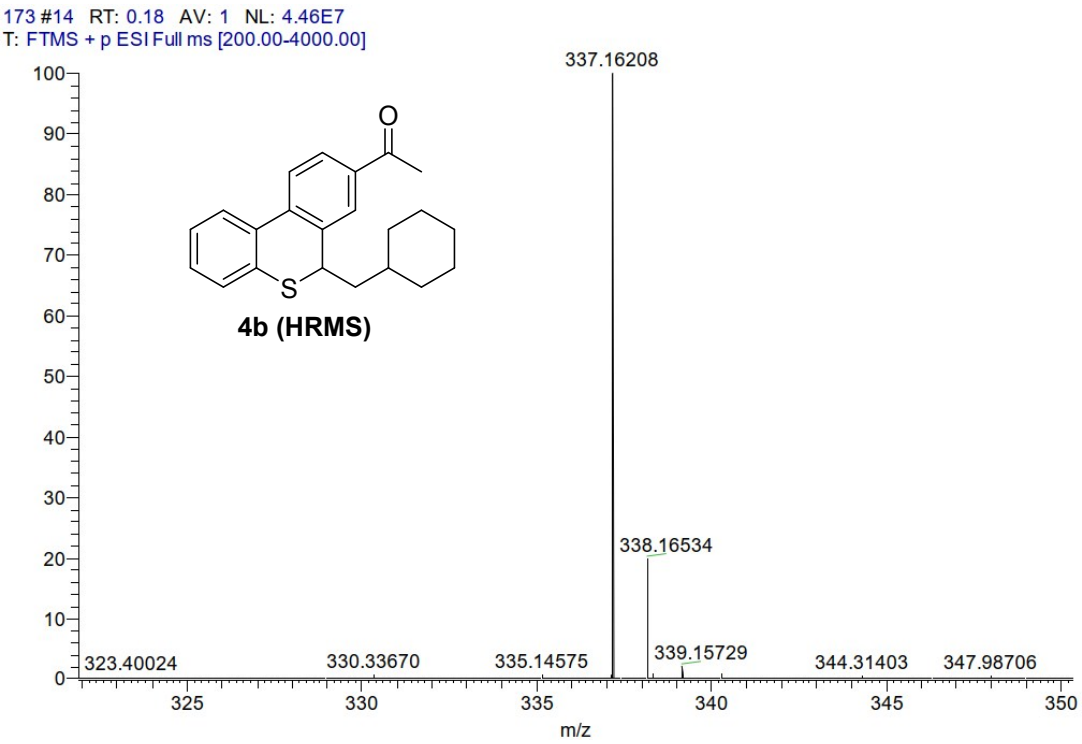
4a (HRMS)



4b (^{1}H NMR)



4b (^{13}C NMR)



4b (HRMS)