

Photo-Induced Tandem Cyclizations of 3-Iodofalvones with Electron Rich Five-member Heteroarenes

Qian Yang^{a,b}, Rui Wang^a, Jie Han^a, Chenchen Li^a, Tao Wang,^a Yong Liang,[†] Zunting Zhang^{a,*}

^a*Key Laboratory of the Ministry of Education for Medicinal Resources and Natural Pharmaceutical Chemistry, National Engineering Laboratory for Resource Development of Endangered Crude Drugs in Northwest of China, and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, People's Republic of China.*

^b*School of Sciences, Xi'an University of Technology, Xi'an 710054, China.*

E-mail: zhangzunting@sina.com; Fax: (+86)-29-81530727; Tel: (+86) -29-85303940.

[†]*Department of Molecular Medicine, Beckman Research Institute, Hope Duarte, CA 91010*

SUPPORTING INFORMATION

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1. Spectroscopic Data of 1, 3, 5, 1aa and 1ab

3-Iodo-2-(4-methoxyphenyl)-6-methyl-4H-chromen-4-one (1b)¹

Yield: 76%. Characteristic: a white powder. m.p. 151.4-152.0. IR(KBr):3452, 2388, 1616, 1348, 1254, 1074, 1020, 937, 802. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.81 – 7.79 (m, 1H), 7.79 – 7.77 (m, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.49 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.05 – 7.02 (m, 1H), 7.00 (d, J = 2.8 Hz, 1H), 3.90 (s, 3H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.8, 164.3, 161.7, 154.3, 135.9, 135.5, 131.5, 127.5, 126.1, 119.8, 117.43, 113.7, 87.6, 55.6, 21.1. HRMS (ESI): calc. for C₁₇H₁₃IO₃ [M + Na]⁺ 414.9807, found 414.9801.

6-Fluoro-3-iodo-2-(4-methoxyphenyl)-4H-chromen-4-one (1d)¹

Yield: 63%. Characteristic: a brown powder. m.p. 299.4-302.0. IR(KBr):3452, 2641, 2359, 1932, 1638, 1385, 1277, 1211, 1026, 854, 822, 698. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 5.8 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.50 (dd, J = 8.5, 3.7 Hz, 1H), 7.42 (t, J = 6.7 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.1, 164.5, 161.8, 160.9, 158.5, 152.1, 131.4, 126.9, 122.5, 122.3, 121.0, 120.9, 119.8, 119.7, 113.6, 111.6, 111.4, 86.8, 55.6. HRMS (ESI) calc. for C₁₆H₁₀FIO₃ [M + Na]⁺ 418.9556, found 418.9558.

3-Iodo-6-methyl-2-p-tolyl-4H-chromen-4-one (1f)¹

Yield: 37%. Characteristic: a white powder. m.p. 179.1-180.2. IR(KBr):3740, 3450, 2356, 1643, 1567, 1453, 1330, 1226, 1057, 967, 824, 754. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 8.6, 2.0 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 2.48 (s, 3H), 2.46 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.7, 164.7, 154.3, 141.6, 135.9, 135.5, 132.5, 129.6, 129.0, 126.1, 119.8, 117.5, 88.0, 77.5, 77.2, 76.8, 21.7, 21.1. HRMS (ESI) calc. for C₁₇H₁₃IO₂ [M + Na]⁺ 398.9852, found 398.9851.

3-Iodo-7-methoxy-2-p-tolyl-4H-chromen-4-one (1g).¹

Yield: 33%. Characteristic: a white powder. m.p. 193.3-194.1. IR(KBr):2941, 2357, 1796, 1693, 1560, 1500, 1442, 1364, 1329, 1057, 976, 860, 824. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 8.8, 2.3 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 164.4, 164.2, 157.6, 141.4, 132.3, 129.4, 128.9, 128.1, 115.2, 113.9, 99.7, 88.3, 55.9, 21.6. HRMS (ESI) calc. for C₁₇H₁₃IO₃ [M + Na]⁺ 414.9807, found 414.9809.

6-Fluoro-3-iodo-2-p-tolyl-4H-chromen-4-one (1h)¹

Yield: 32%. Characteristic: a white powder. m.p. 192.4-193.4. IR(KBr):3740, 3506, 3074, 2918, 2357, 1649, 1557, 1474, 1319, 1180, 1089, 1049, 823, 756. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, J = 8.1, 3.0 Hz, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.50 (dd, J = 9.1, 4.2 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.1, 174.1, 165.1, 161.14, 158.7, 152.3, 141.9, 132.1, 129.5, 129.1, 122.7, 122.4, 121.2, 121.1, 120.0, 119.9, 111.7, 111.5, 87.3, 21.74. HRMS (ESI) calc. for C₁₆H₁₀FIO₂ [M + Na]⁺ 402.9602, found 402.9594.

2-(4-Fluorophenyl)-3-iodo-4H-chromen-4-one (1m)¹

Yield: 16%. Characteristic: a white powder. m.p. 166.2-128.1. IR(KBr):3506,

(3H-Benz[e]indol-4-yl)(phenyl)methanone (5b)

Yield: 42%. Characteristic: a yellow powder. m.p. 172.3-174.5 IR(KBr): 3347, 3053, 2922, 2356, 1699, 1622, 1446, 1298, 1095, 966, 881, 741. ¹H NMR (600 MHz, CDCl₃) δ 10.52 (s, 1H), 8.29 (d, J = 8.2 Hz, 1H), 8.04 (s, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.3 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 2.7 Hz, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.15 (t, J = 2.6 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 198.2, 139.0, 131.8, 131.1, 130.9, 130.8, 130.5, 129.6, 128.9, 128.4, 127.8, 124.3, 124.0, 123.5, 123.1, 121.1, 101.4. HRMS (ESI) calc. for C₁₉H₁₃NO [M + Na]⁺ 294.0889, found 294.0900.

1-(3-Methyl-3H-benzo[e]indol-4-yl)ethan-1-one (5c)

Yield: 47%. Characteristic: a white crystal. m.p. 98.1-99.3 IR(KBr): 3445, 3130, 2357, 1674, 1441, 1356, 1244, 1155, 1085, 949, 851, 743. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 7.8 Hz, 2H), 7.66 – 7.58 (m, 1H), 7.45 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.14 (d, J = 3.0 Hz, 1H), 7.06 (d, J = 3.1 Hz, 1H), 3.85 (s, 3H), 2.84 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 195.3, 125.0, 124.8, 124.0, 123.5, 122.6, 122.2, 122.0, 121.1, 119.9, 118.7, 117.6, 95.1, 32.91, 24.22. HRMS (ESI) calc. for C₁₅H₁₃NO [M + Na]⁺ 246.0889, found 246.0895.

1-(3H-Benz[e]indol-4-yl)ethan-1-one (5d)

Yield: 38%. Characteristic: a silver powder. m.p. 143.4-144.5 IR(KBr): 3742, 3371, 2922, 2359, 1751, 1647, 1366, 1292, 1213, 1082, 972, 889, 745. ¹H NMR (600 MHz, CDCl₃) δ 10.61 (s, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.22 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 2.7 Hz, 1H), 7.09 (t, J = 2.7 Hz, 1H), 2.82 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 200.5, 131.1, 130.3, 130.0, 128.8, 128.0, 127.9, 124.2, 124.0, 123.5, 123.1, 121.9, 101.1, 26.48. HRMS (ESI) calc. for C₁₄H₁₁NO [M + Na]⁺ 232.0733, found 232.0737.

2-(4-Methoxyphenyl)-3-(1-methyl-1H-pyrrol-2-yl)-4H-chromen-4-one (1aa)

Yield: 25%. Characteristic: a white powder. m.p. 155.6-159.2. IR(KBr): 3447, 3118, 2922, 2356, 1638, 1462, 1369, 1253, 1175, 1028, 928, 878, 718. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (dd, J = 7.9, 1.4 Hz, 1H), 7.70 (ddd, J = 8.7, 7.2, 1.6 Hz, 1H), 7.54 (d, J = 8.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.32 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 6.86 – 6.84 (m, 1H), 6.83 – 6.81 (m, 1H), 6.78 – 6.69 (m, 1H), 6.20 – 6.13 (m, 1H), 5.98 (dd, J = 3.6, 1.7 Hz, 1H), 3.82 (s, 3H), 3.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 177.8, 162.7, 161.23, 155.9, 133.6, 130.3, 126.3, 125.4, 125.1, 124.6, 123.2, 122.7, 117.8, 113.7, 110.8, 108.4, 55.32, 34.20. HRMS (ESI) calc. for C₂₁H₁₇NO₃ [M + Na]⁺ 354.1101, found 354.1107.

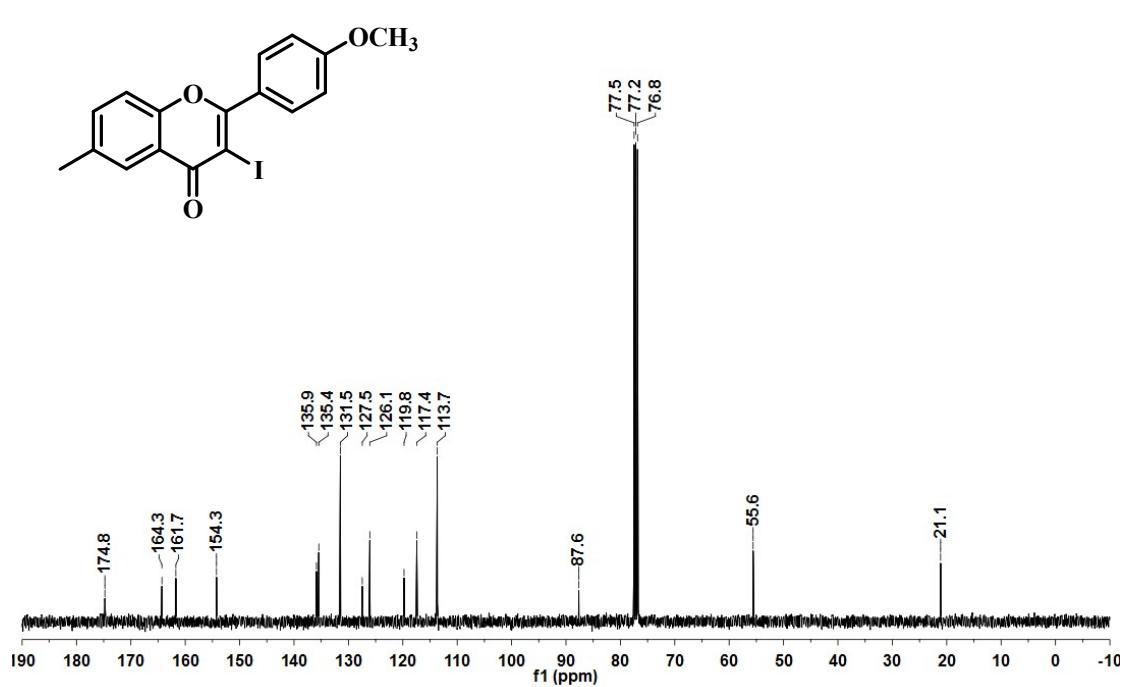
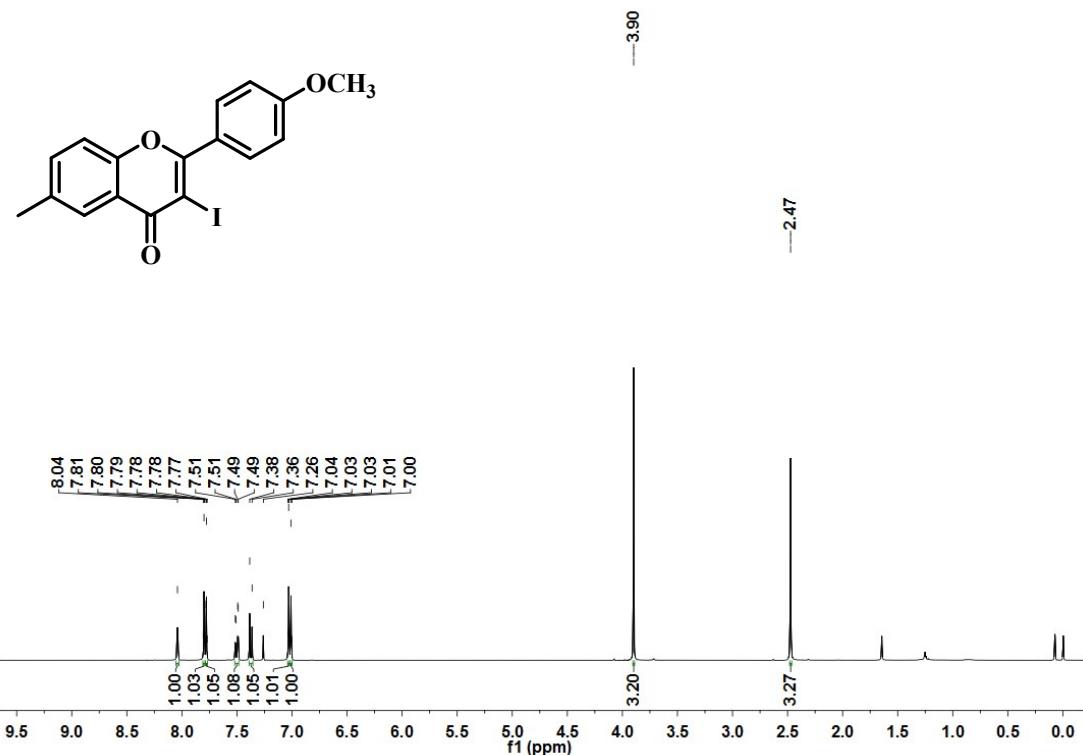
2-(2-(4-Methoxyphenyl)-4H-chromen-3-yl)-1-methyl-1H-pyrrole (1ab)^{2,3}

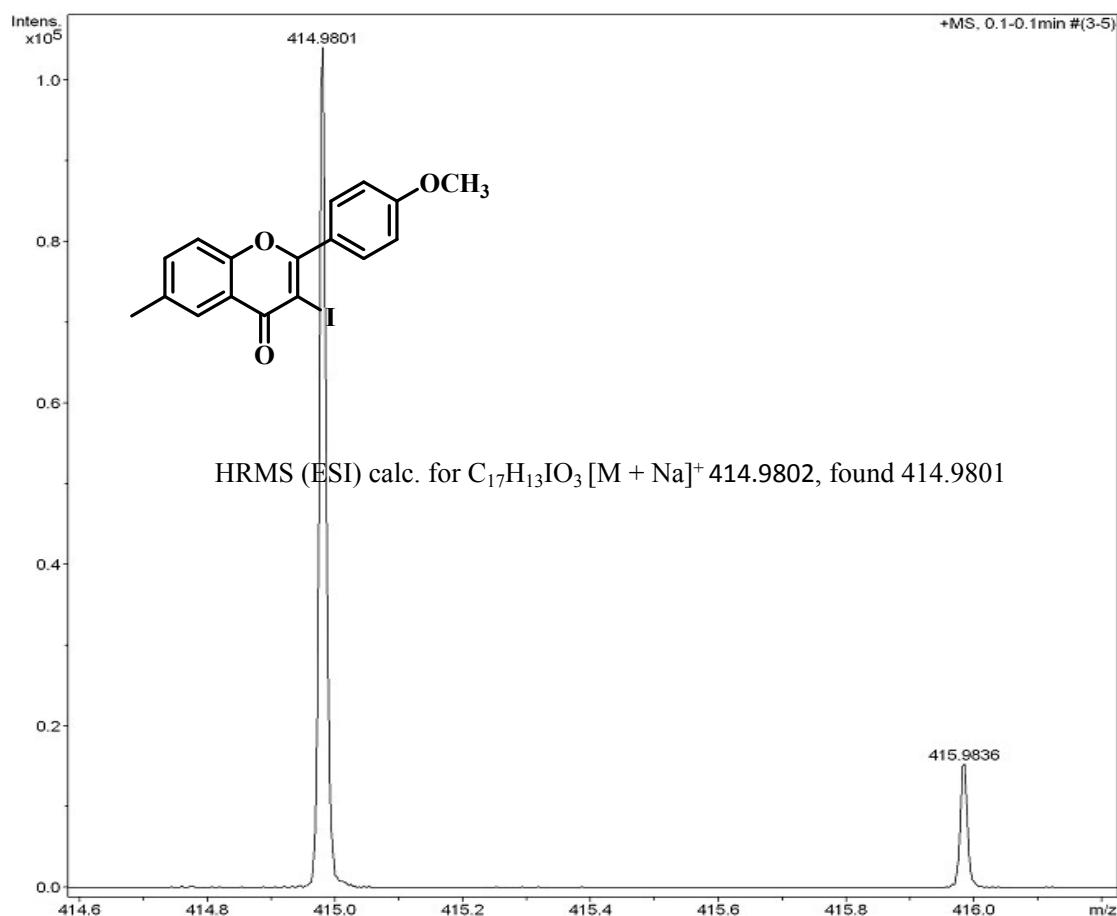
Yield: 60%. Characteristic: a pale yellow liquid. IR(KBr): 3690, 3443, 3123, 2384, 1719, 1578, 1506, 1246, 1121, 920, 843, 611. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 4.1 Hz, 1H), 7.04 (t, J = 5.3 Hz, 1H), 6.78 (d, J = 8.8 Hz, 2H), 6.49 (s, 1H), 6.18 (t, J = 3.0 Hz, 1H), 6.16 – 6.12 (m, 1H), 3.79 (s, 3H), 3.75 (s, 2H), 3.07 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 151.6, 147.1, 131.7, 129.0, 128.4, 127.7, 127.4, 123.3, 121.2, 120.5, 116.1, 113.3, 107.9, 107.8, 100.6, 55.13, 33.82, 31.67. HRMS (ESI) calc. for C₂₁H₁₉NO₂ [M + Na]⁺ 340.1308, found 340.1306.

2. References:

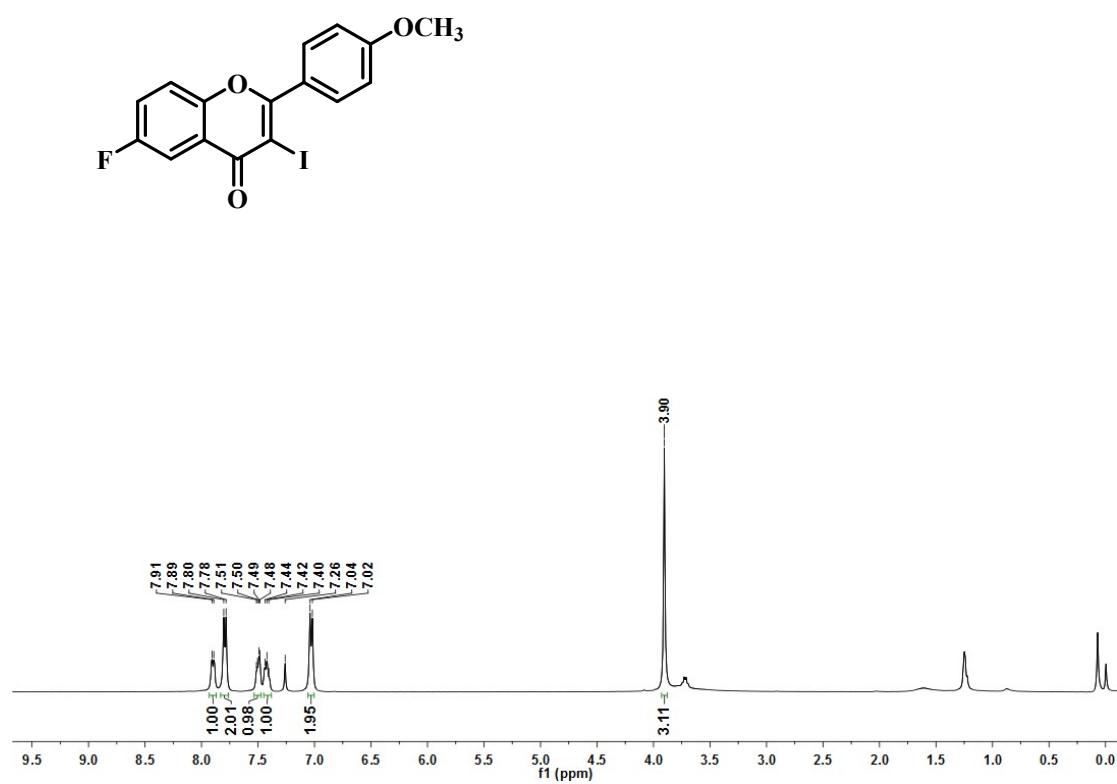
1. F. J. Zhang and Y. L. Li, *Synthesis*, 1993, **1993**, 565-567.
2. C. Valla, A. Baeza, F. Menges and A. Pfaltz, *Synlett*, 2008, **2008**, 3167-3171.
3. T. G. C. Bird, B. R. Brown, I. A. Stuart and A. W. R. Tyrrell, *Journal of the Chemical Society, Perkin Transactions 1*, 1983, 1831-1846.

3. ^1H NMR, ^{13}C NMR and HRMS Spectra of 1, 3, 5, 1aa and 1ab

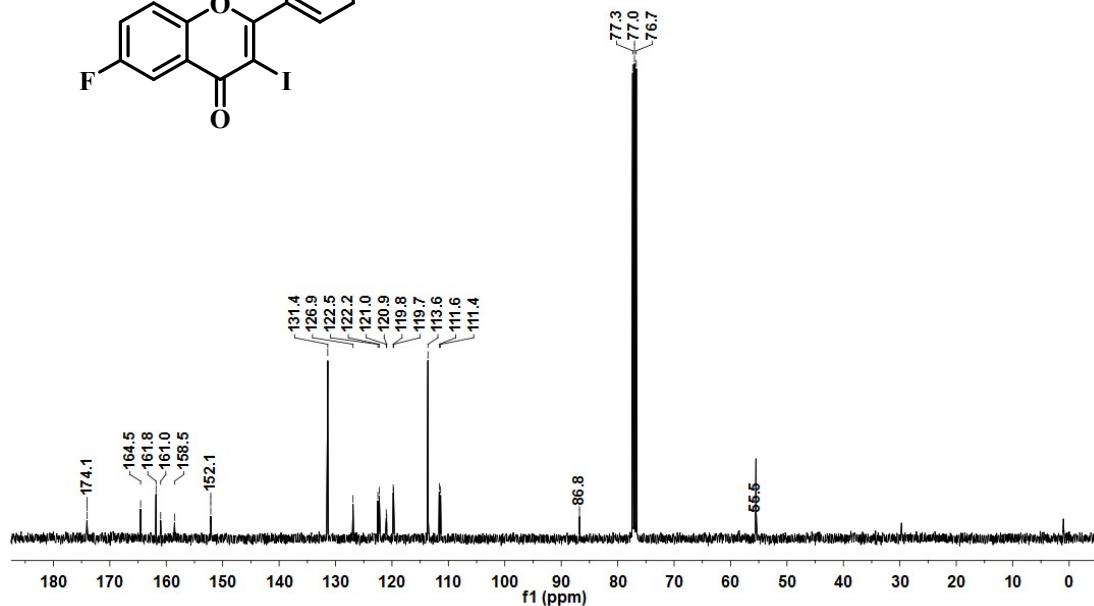
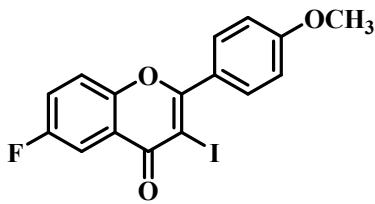




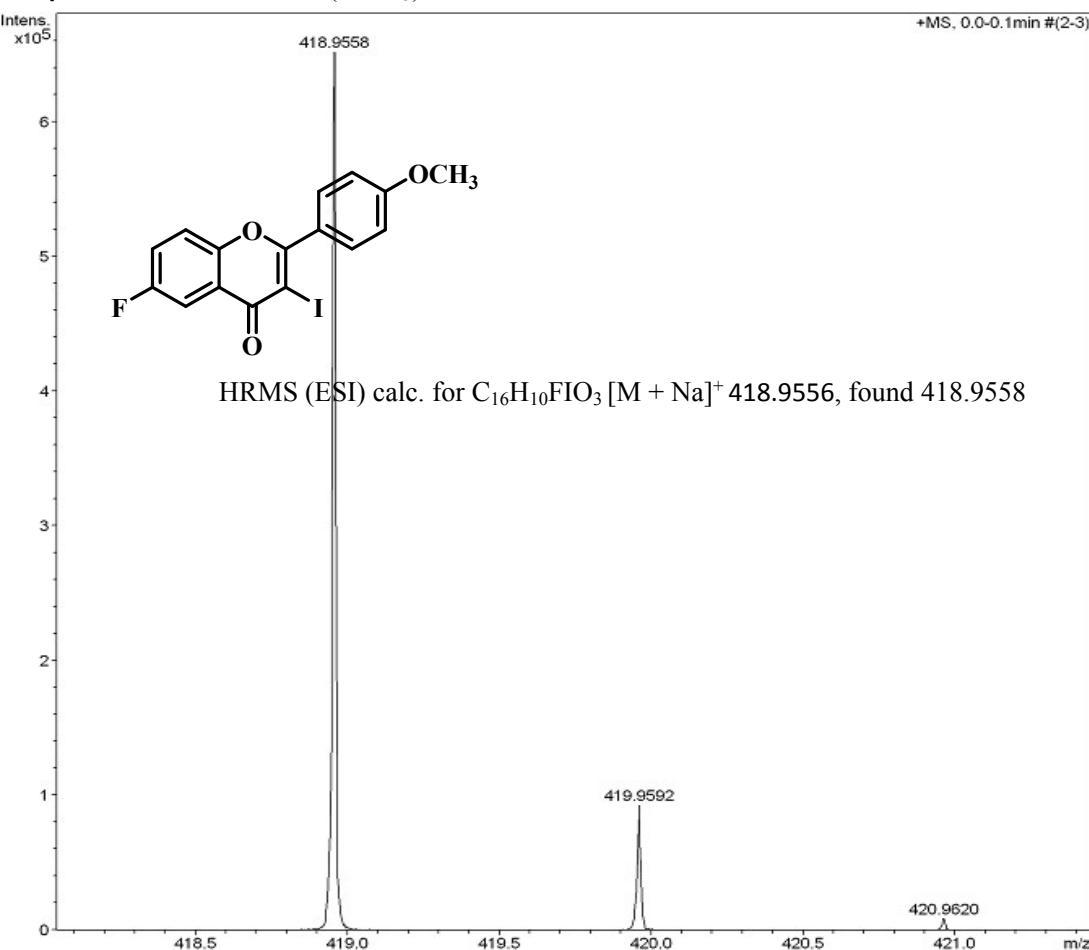
Compound 1b HRMS(MeOH)



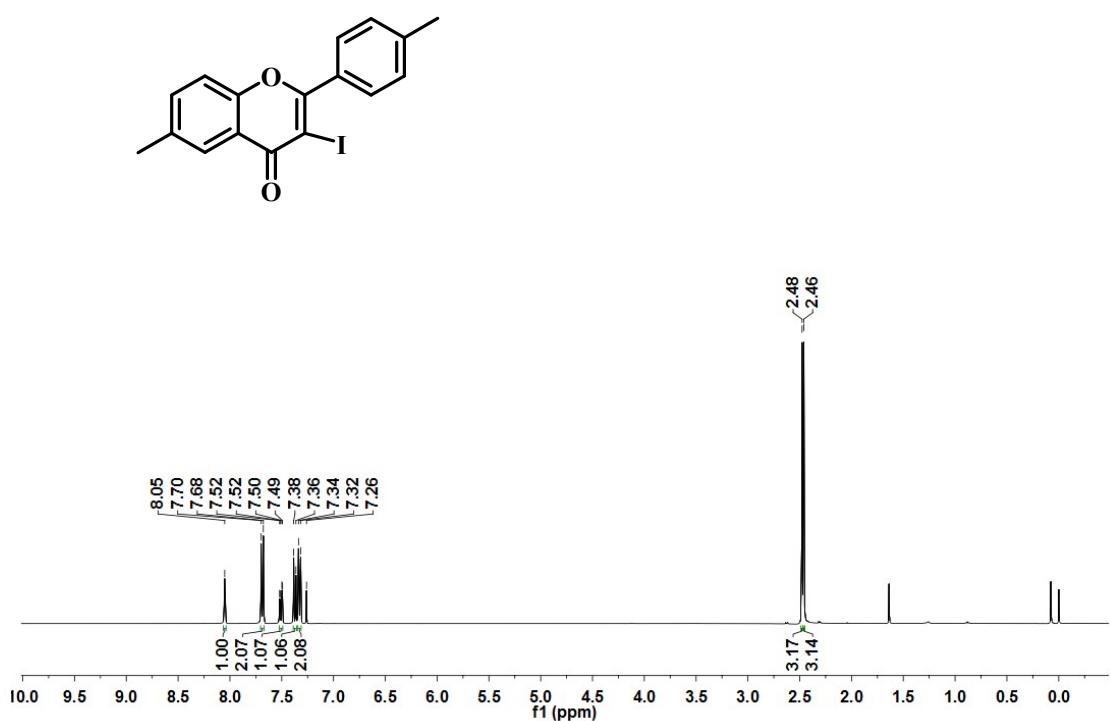
Compound 1d ^1H NMR(CDCl_3)



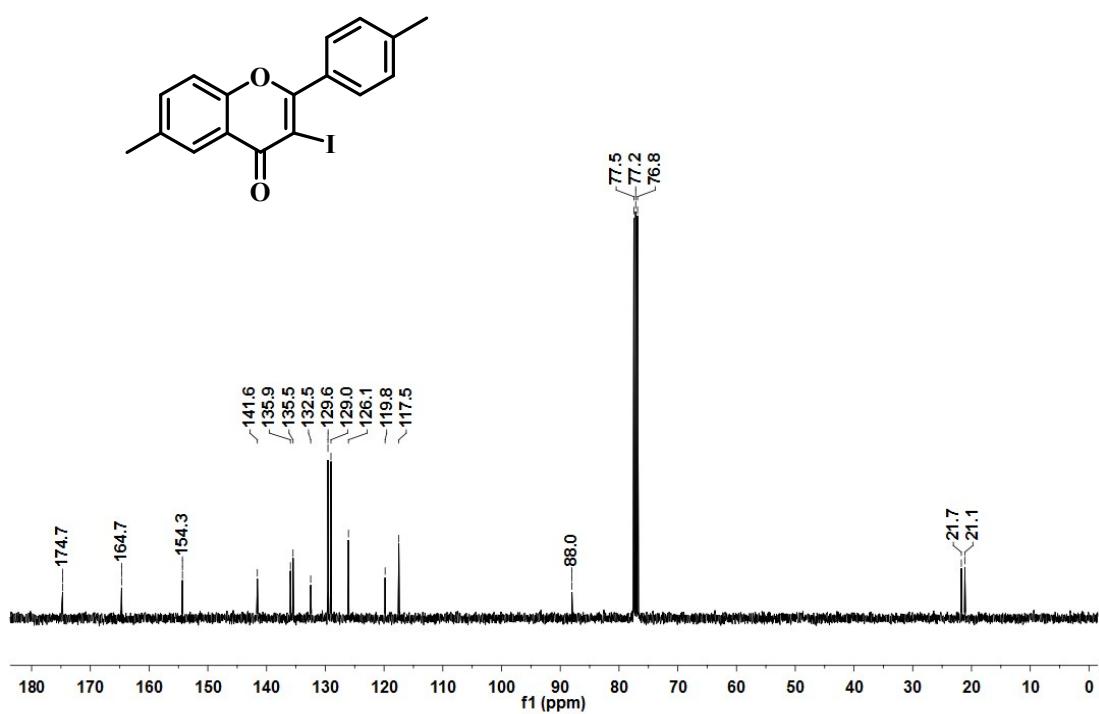
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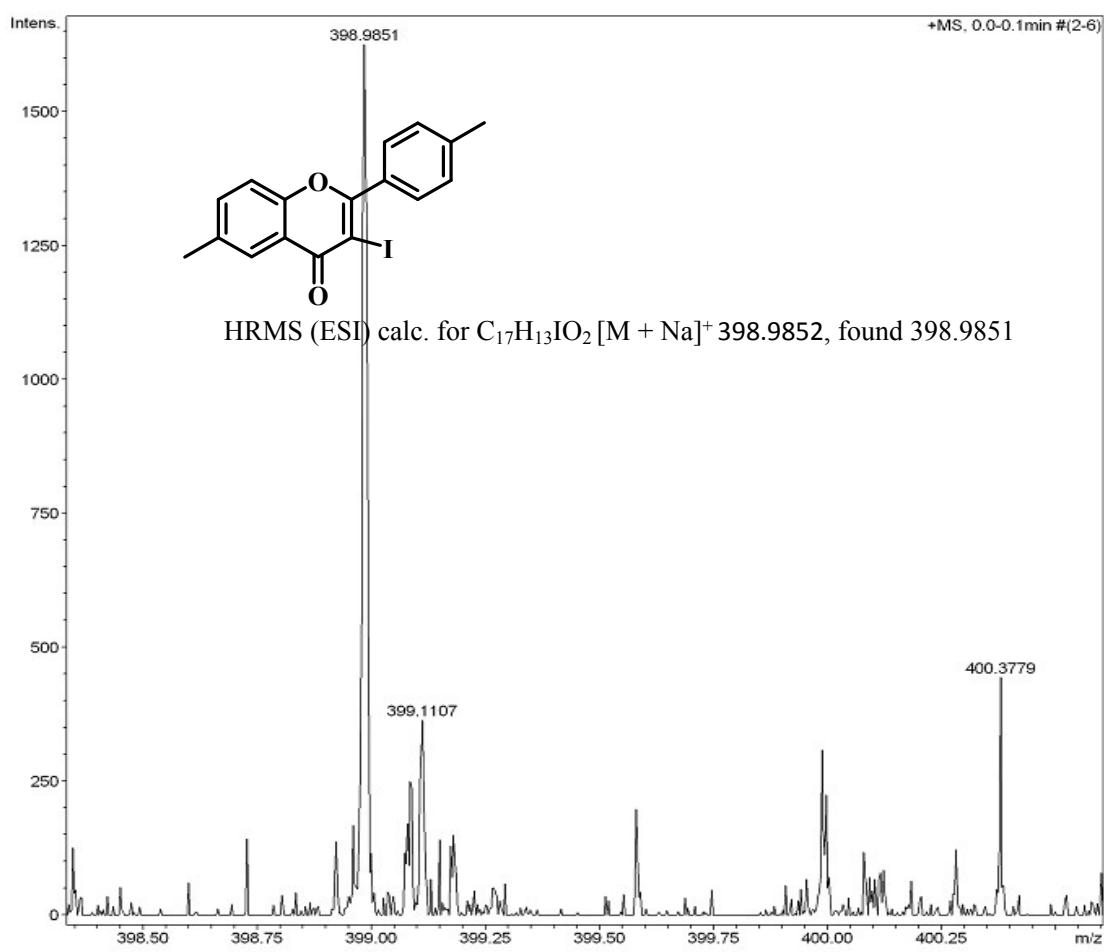
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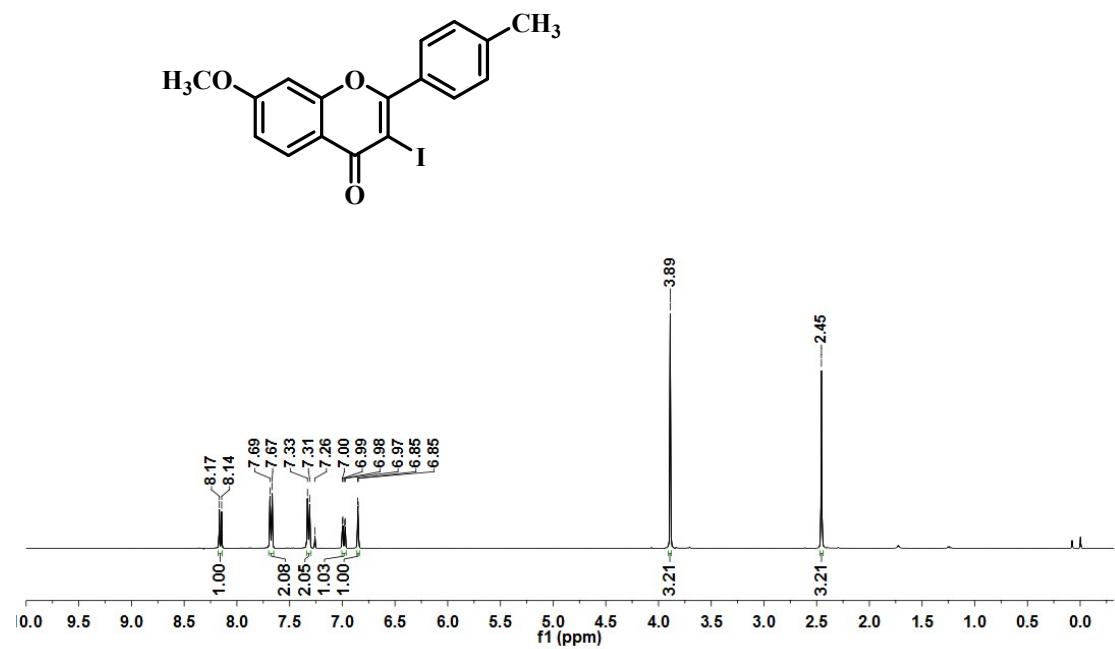
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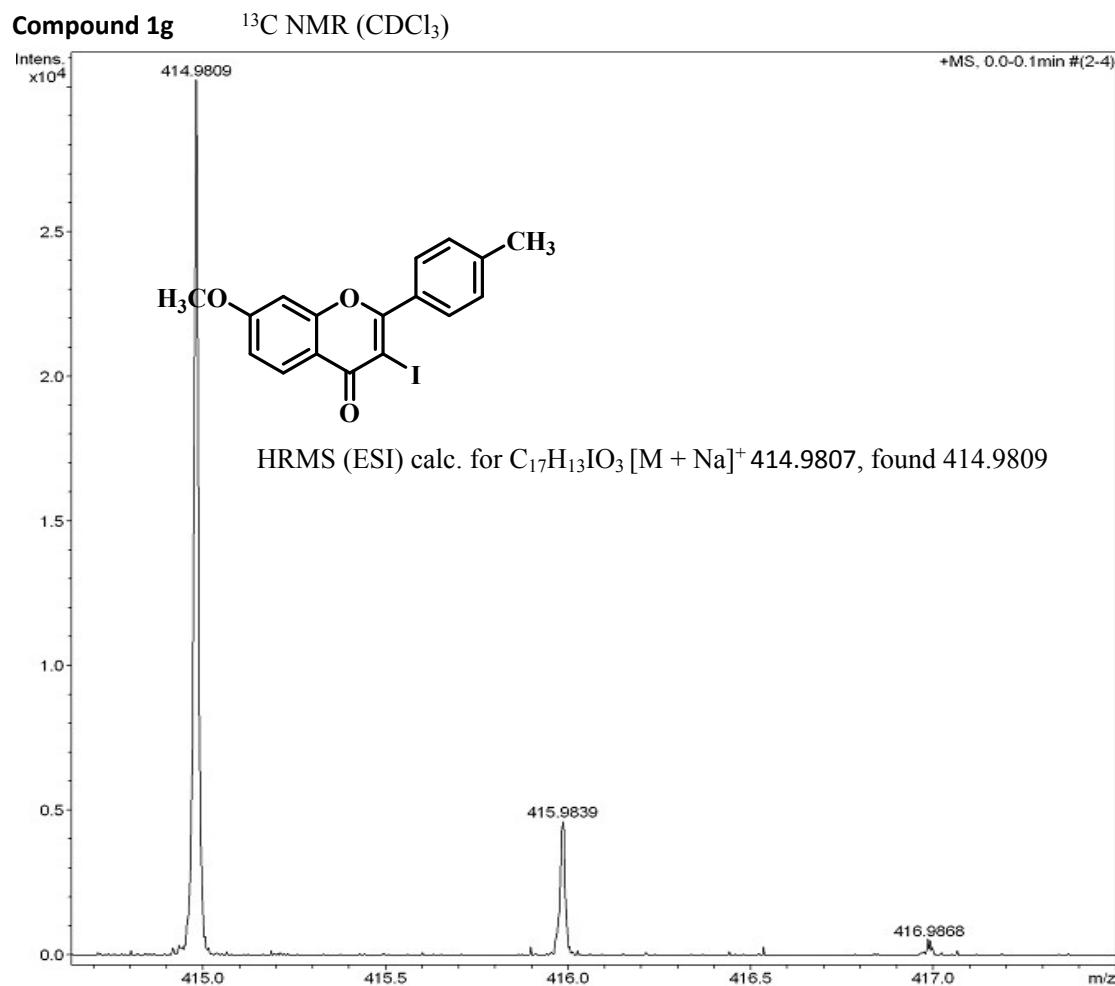
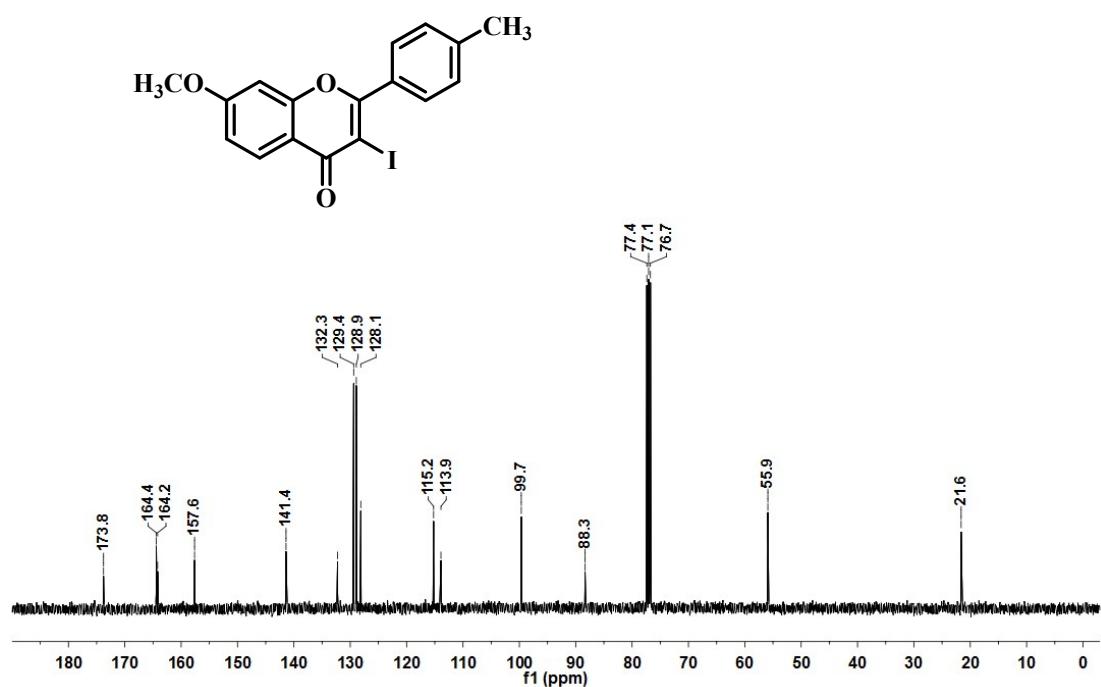
Compound 1f ^{13}C NMR (CDCl_3)



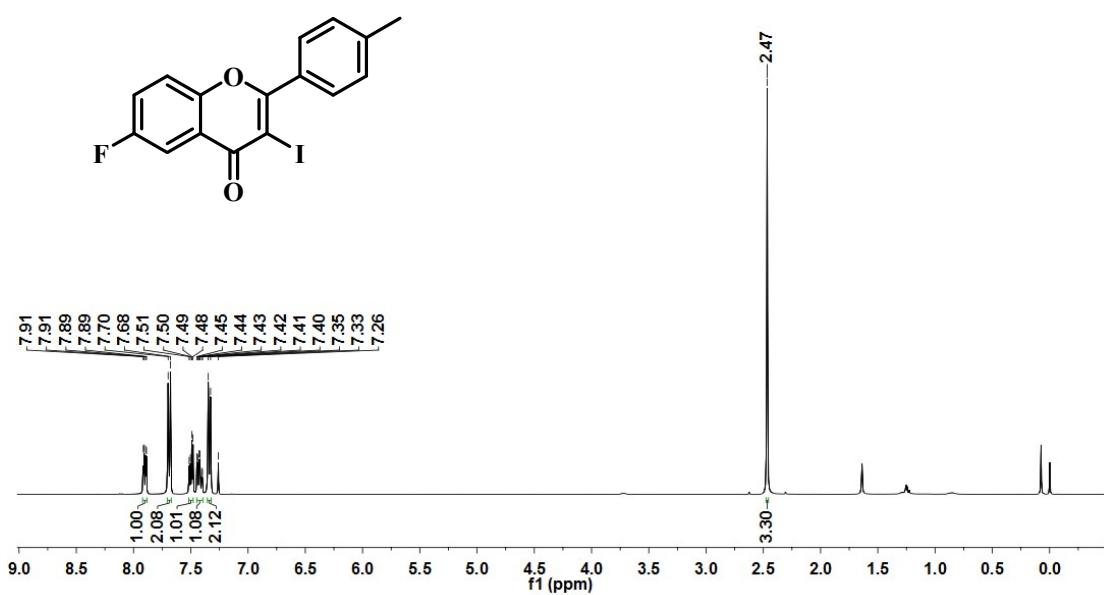
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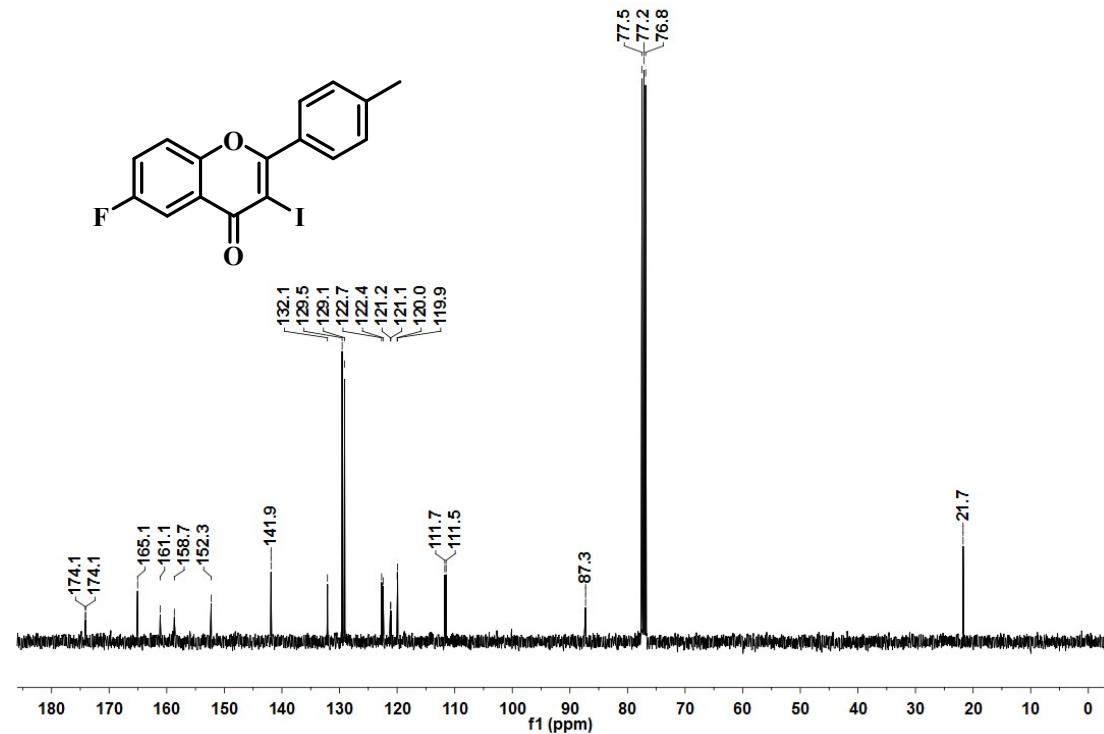
Compound 1g ^1H NMR(CDCl_3)



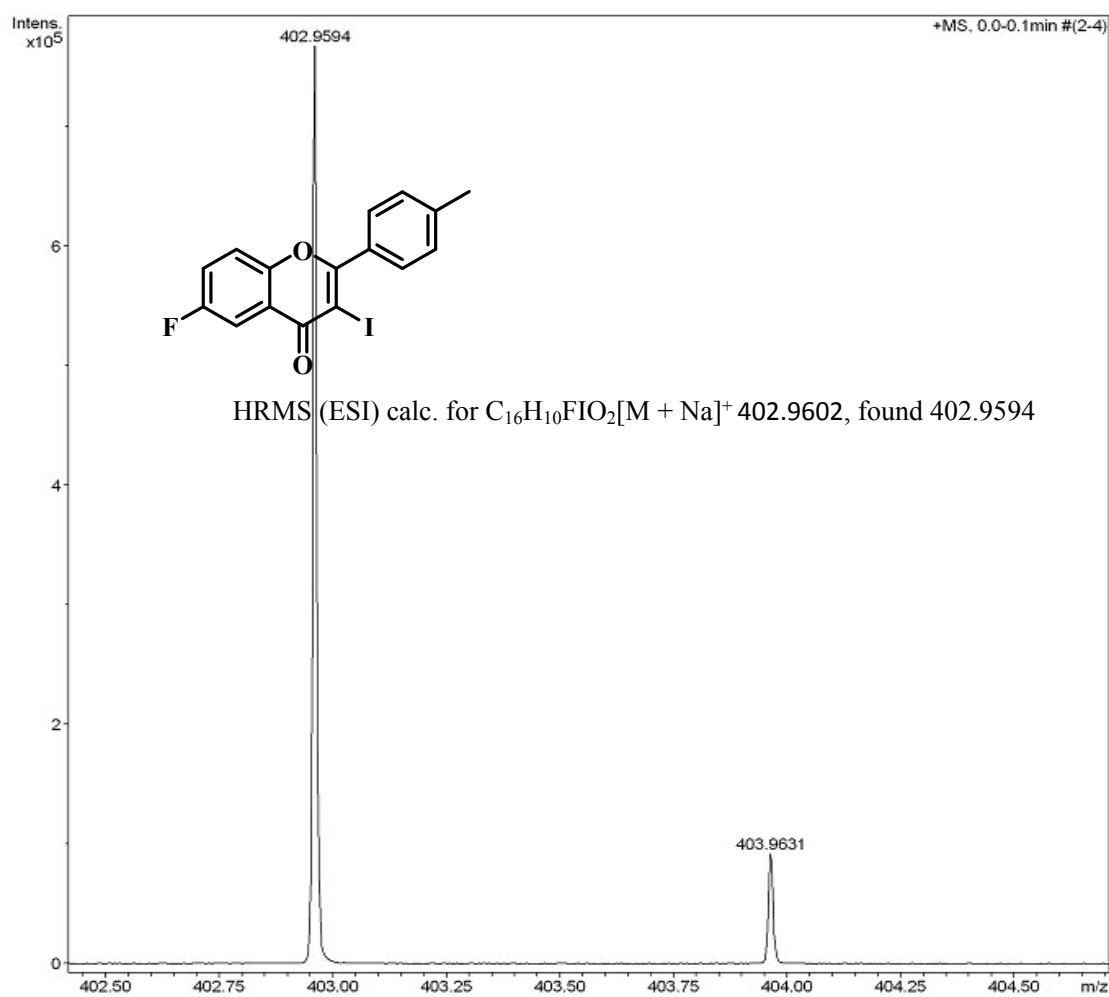
Compound 1g HRMS(MeOH)



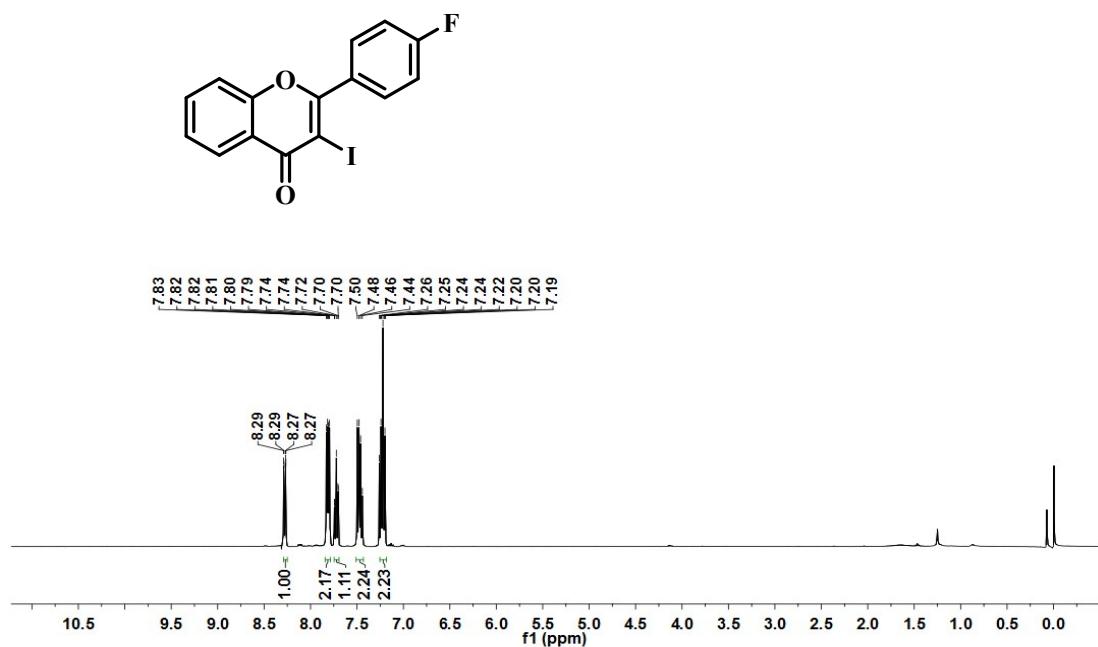
Compound 1h ^1H NMR(CDCl_3)



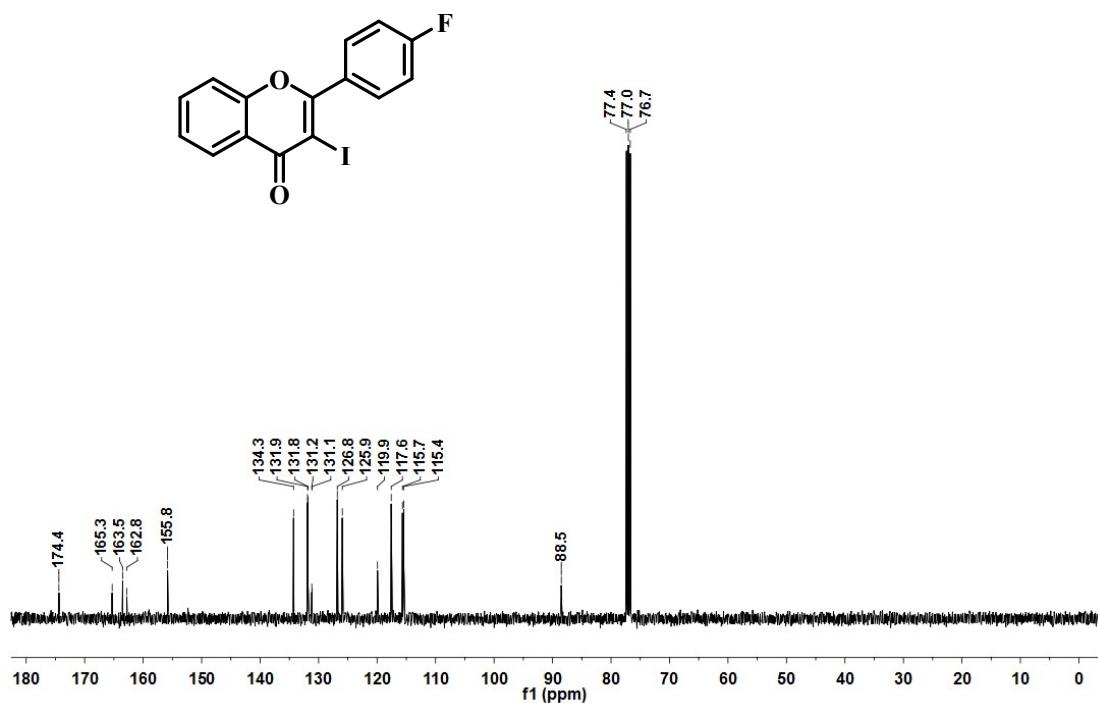
Compound 1h ^{13}C NMR (CDCl_3)



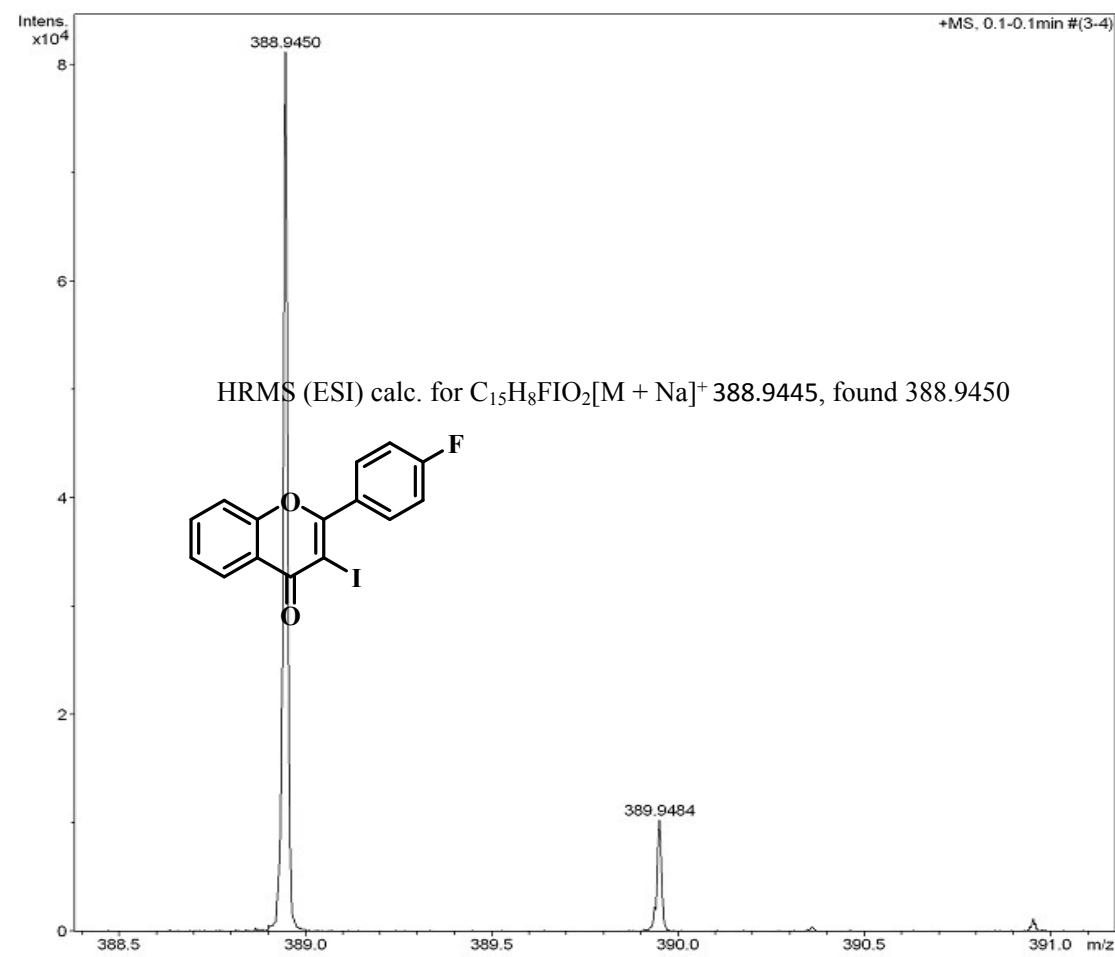
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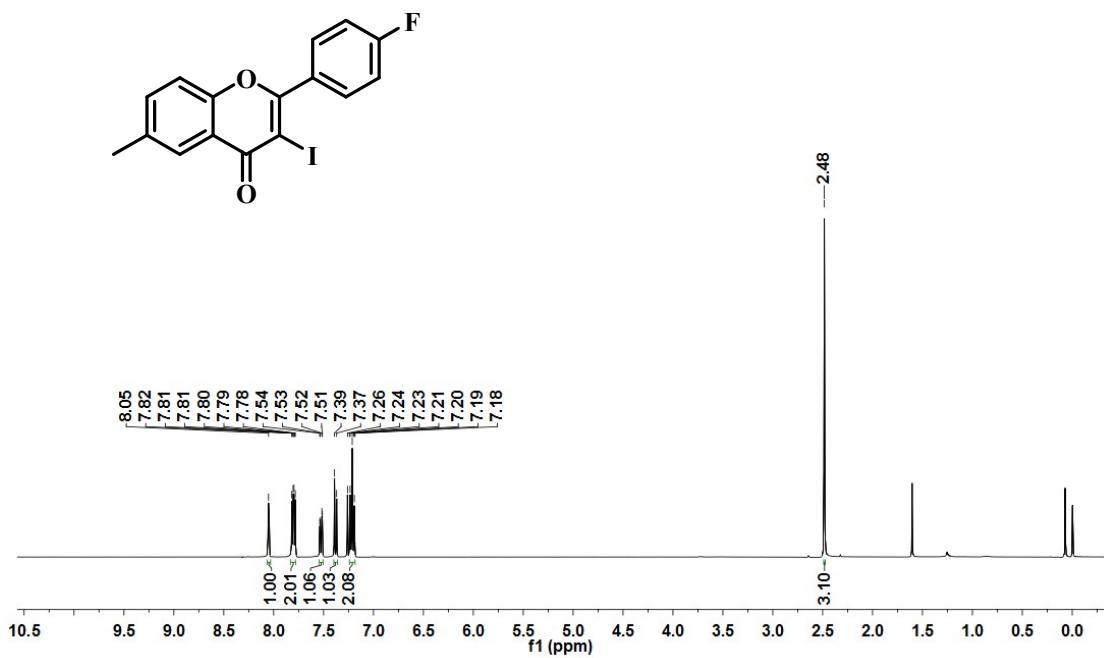
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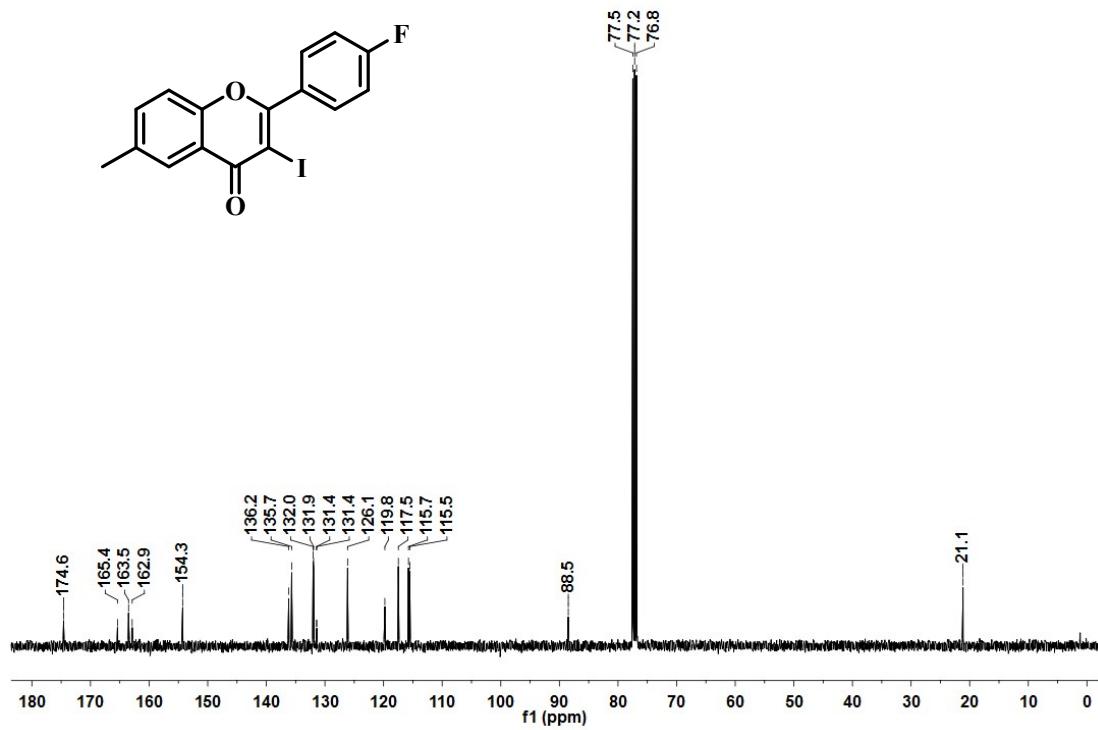
Compound 1m ^{13}C NMR (CDCl_3)



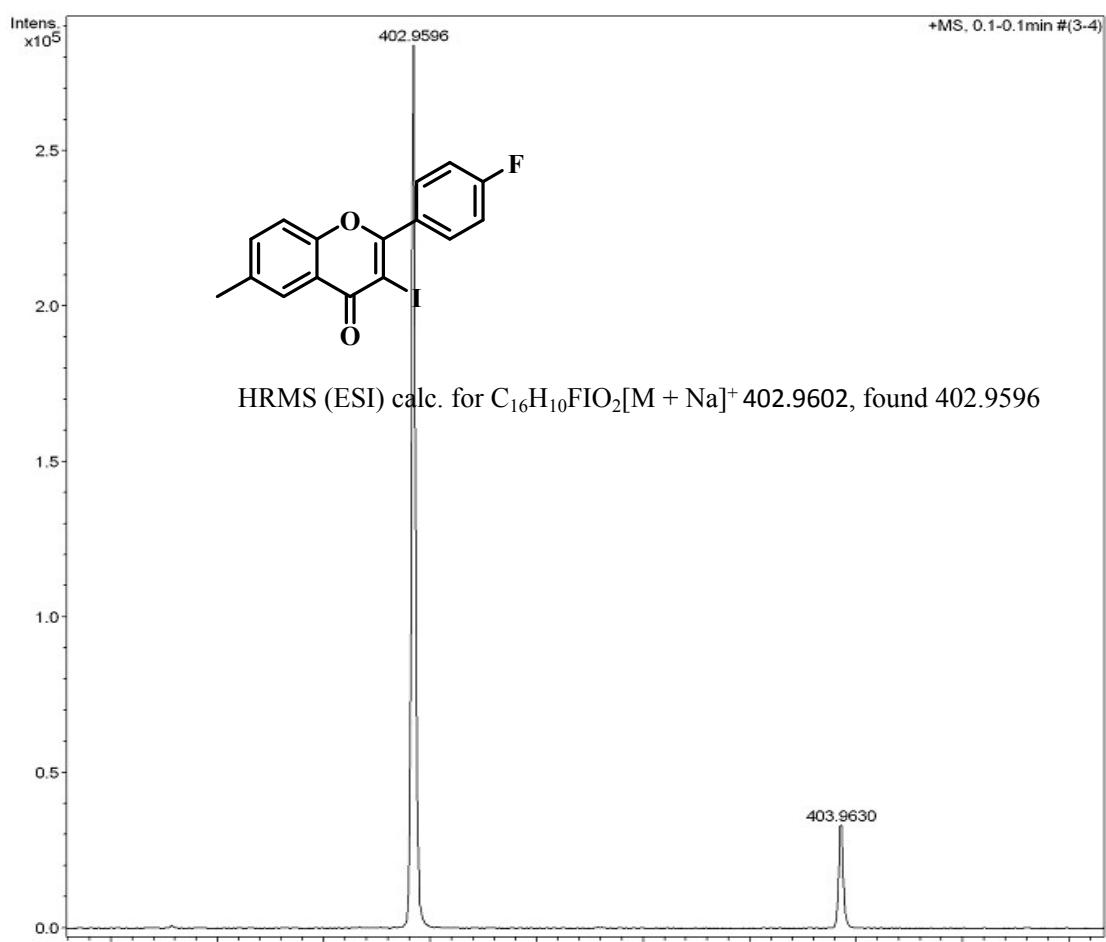
Compound 1m HRMS(MeOH)



Compound 1n ^1H NMR(CDCl_3)

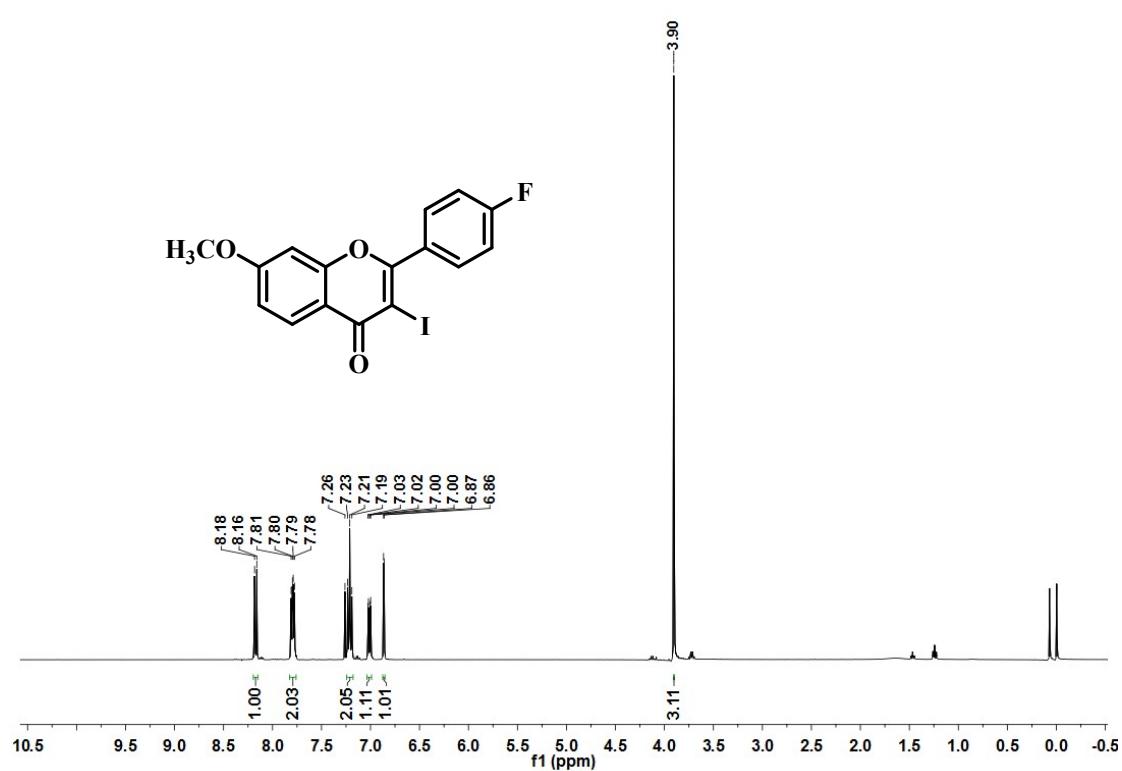


Compound 1n ^{13}C NMR (CDCl_3)



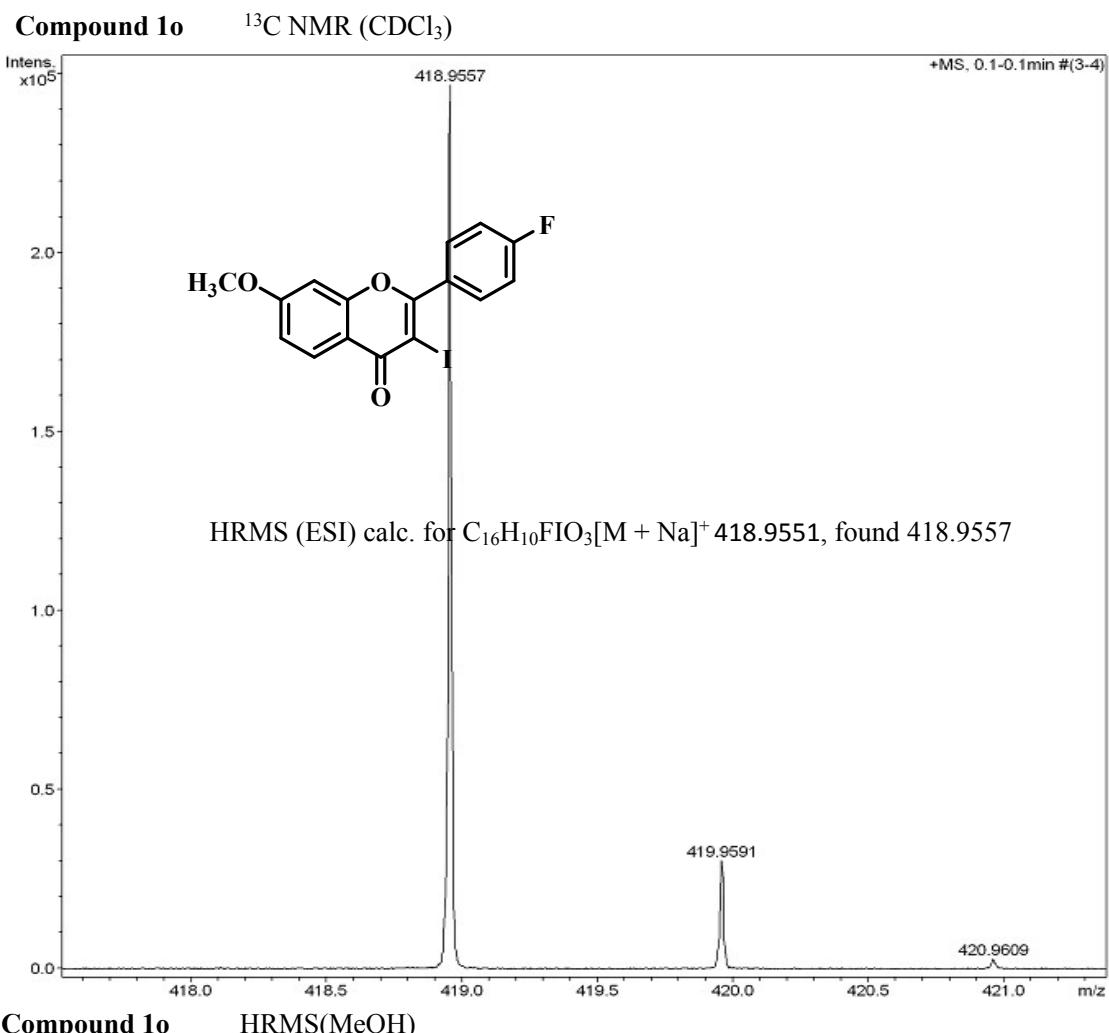
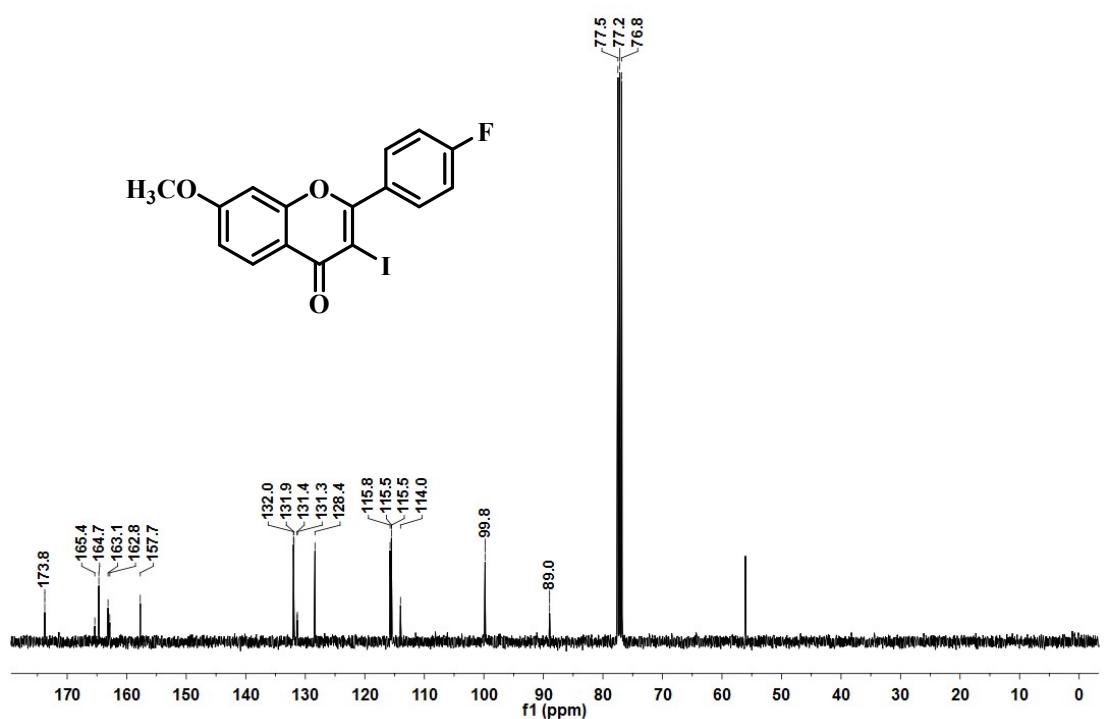
Compound 1n

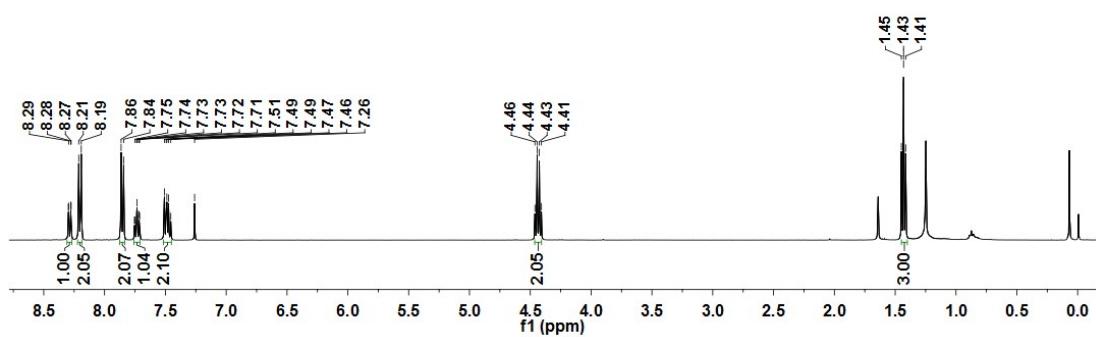
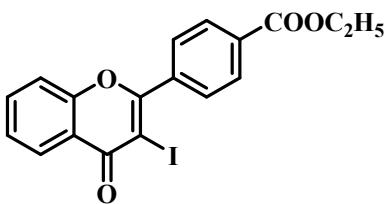
HRMS(MeOH)



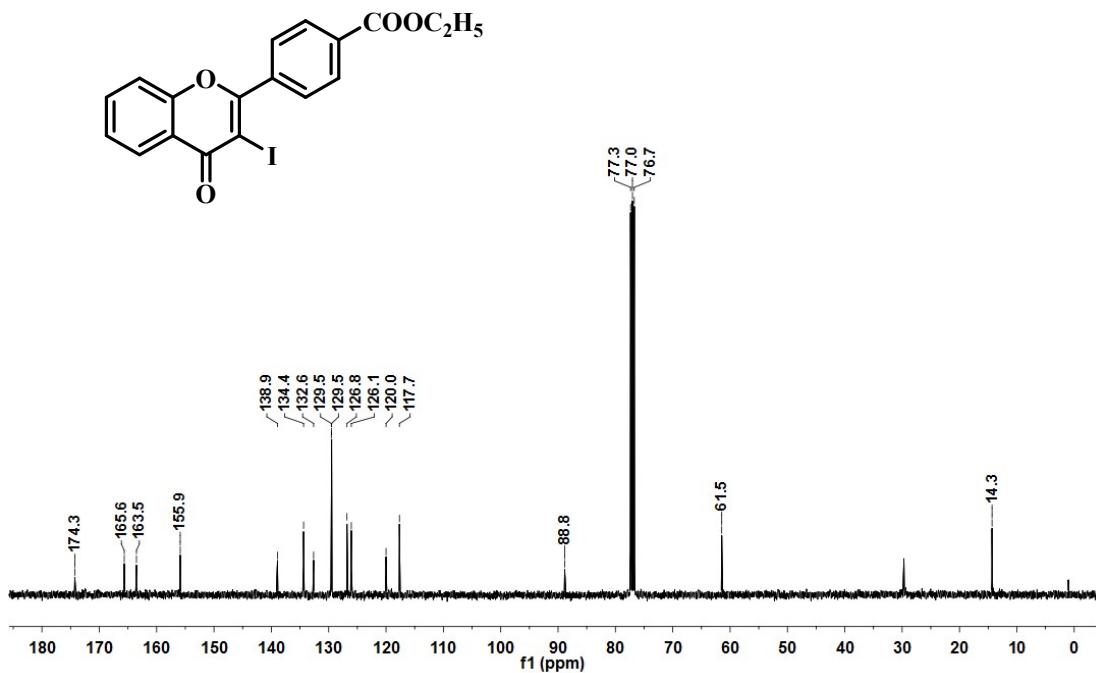
Compound 1o

^1H NMR(CDCl_3)

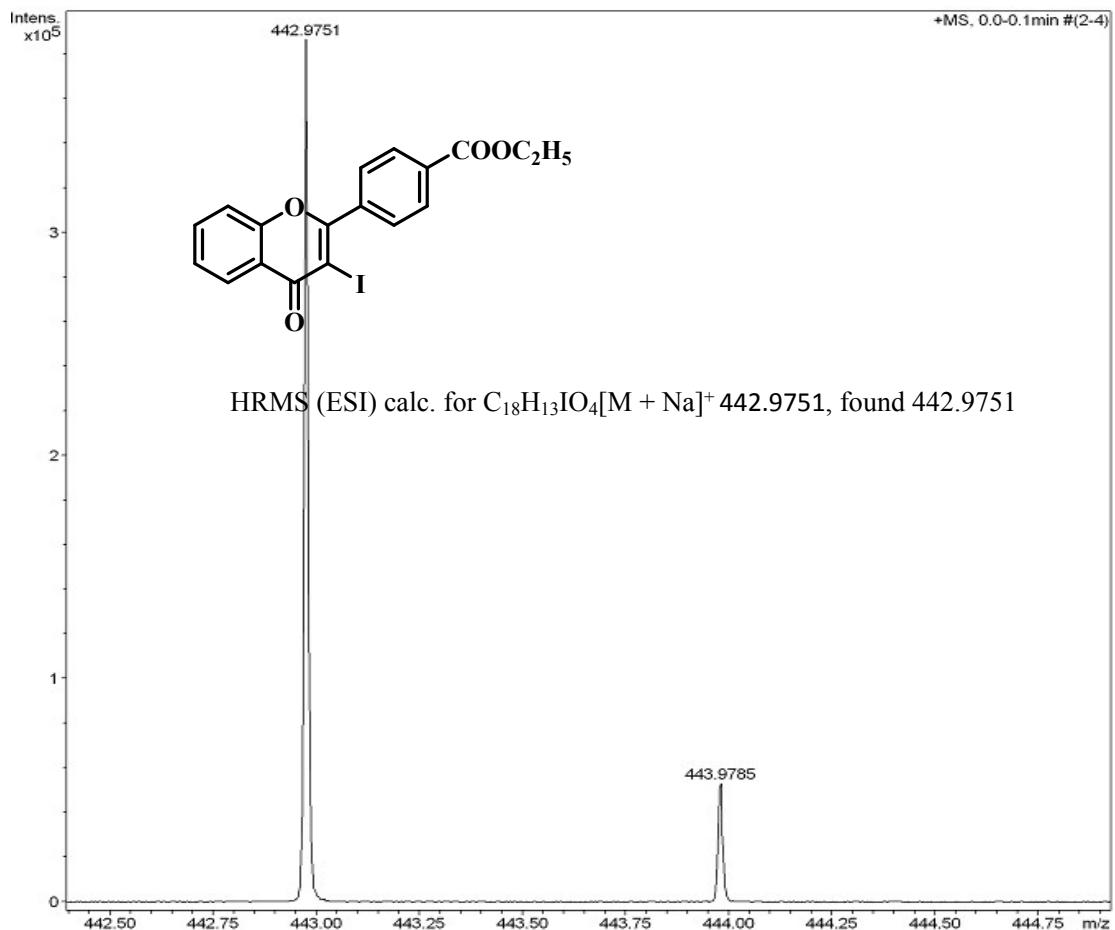




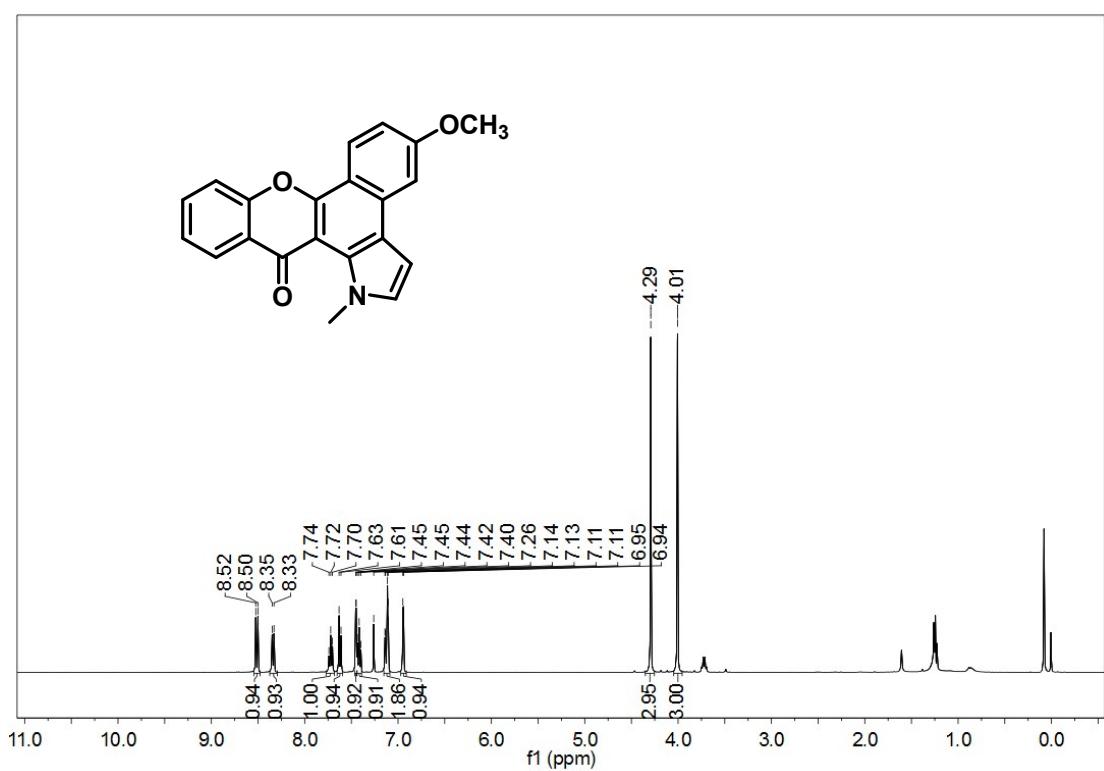
Compound 1p ¹H NMR(CDCl_3)



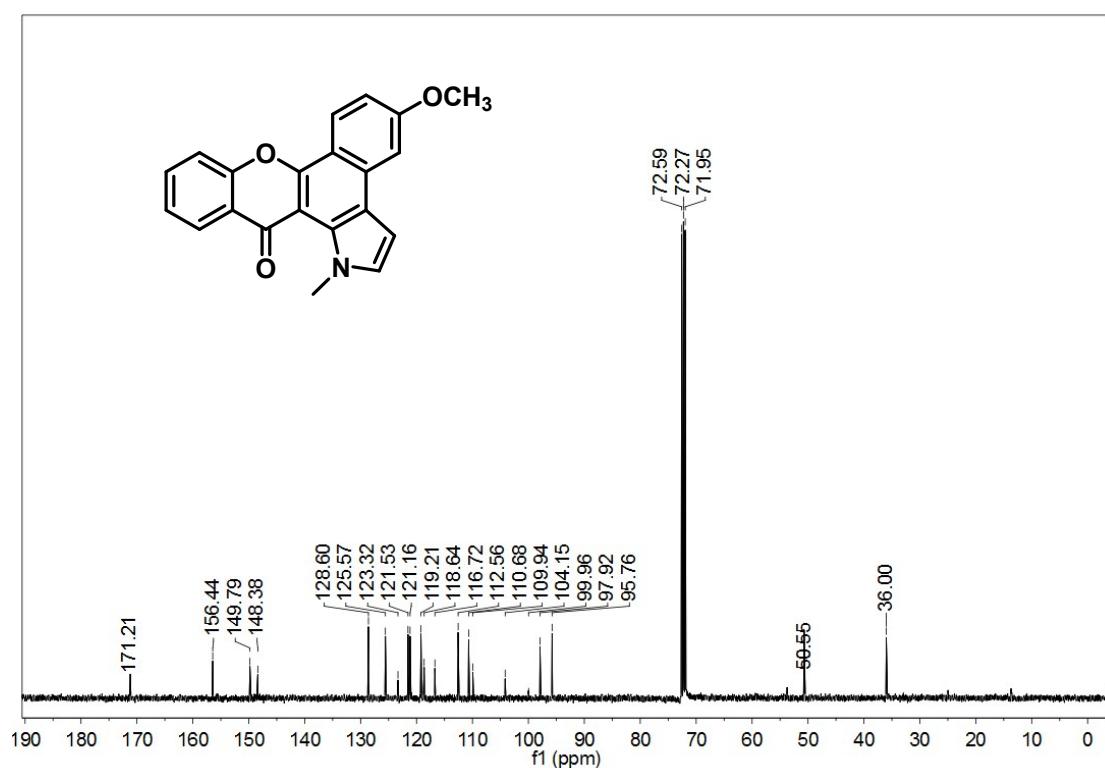
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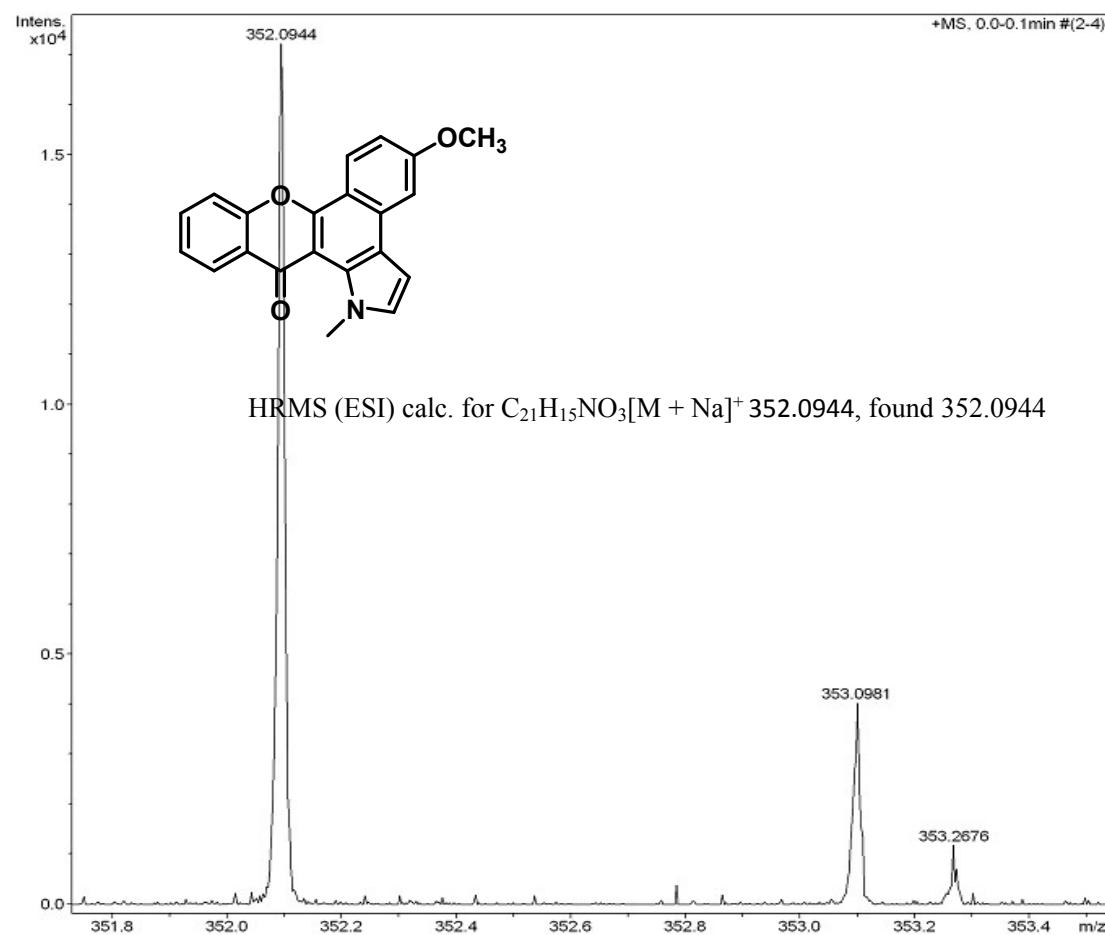
Compound 1p HRMS(MeOH)



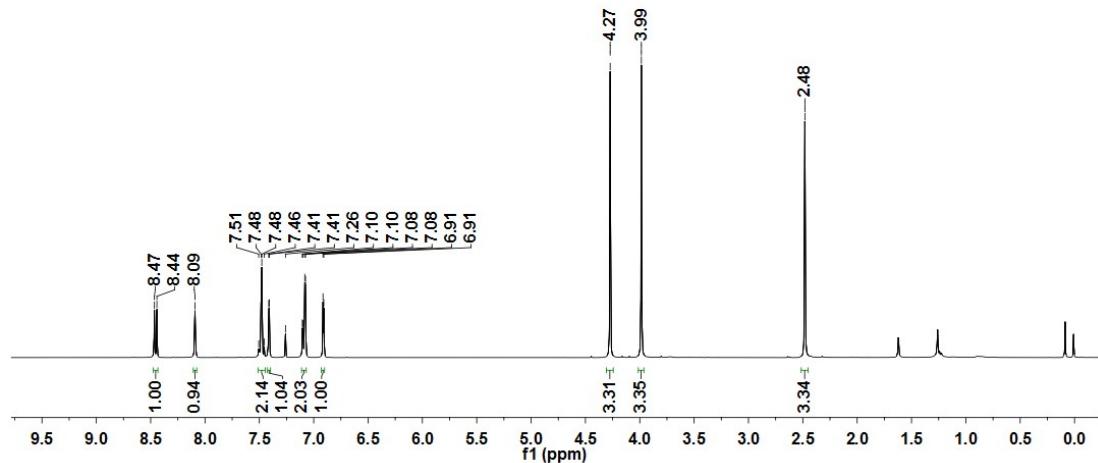
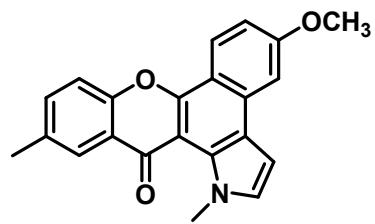
Compound 3a ^1H NMR(CDCl_3)



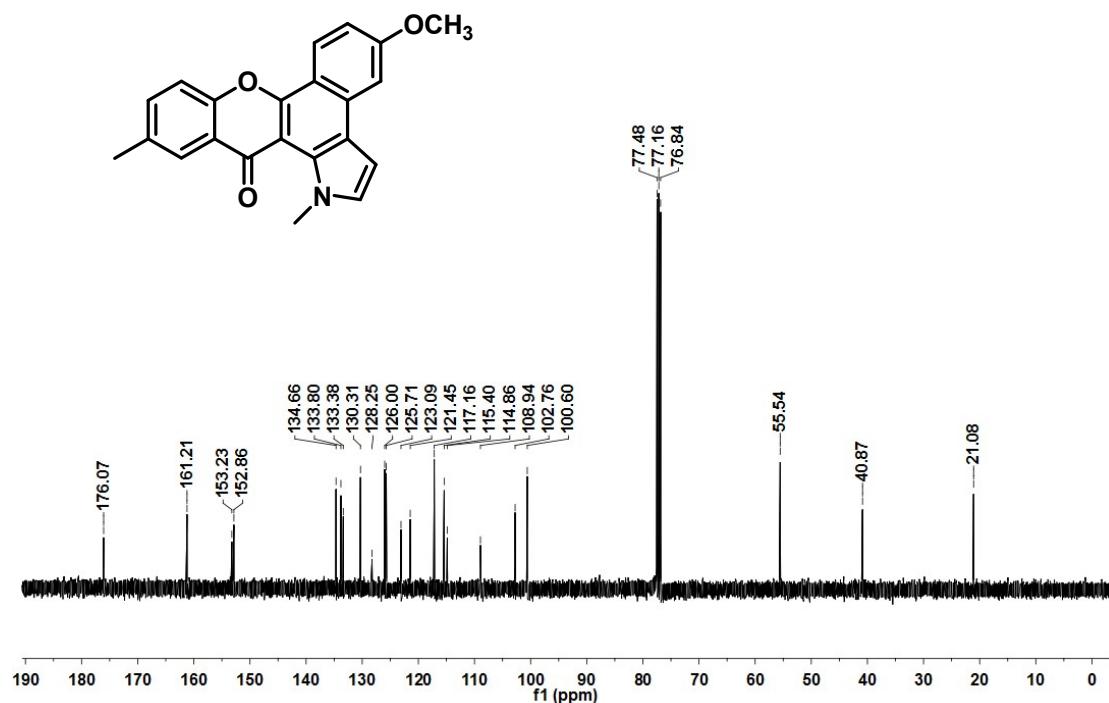
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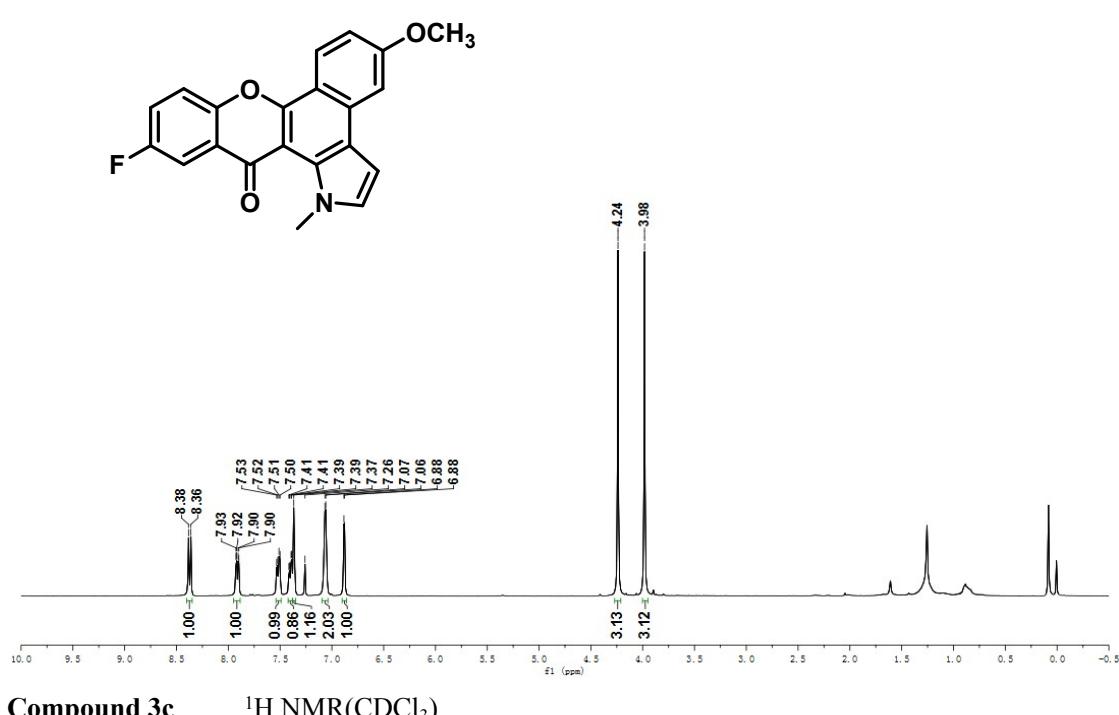
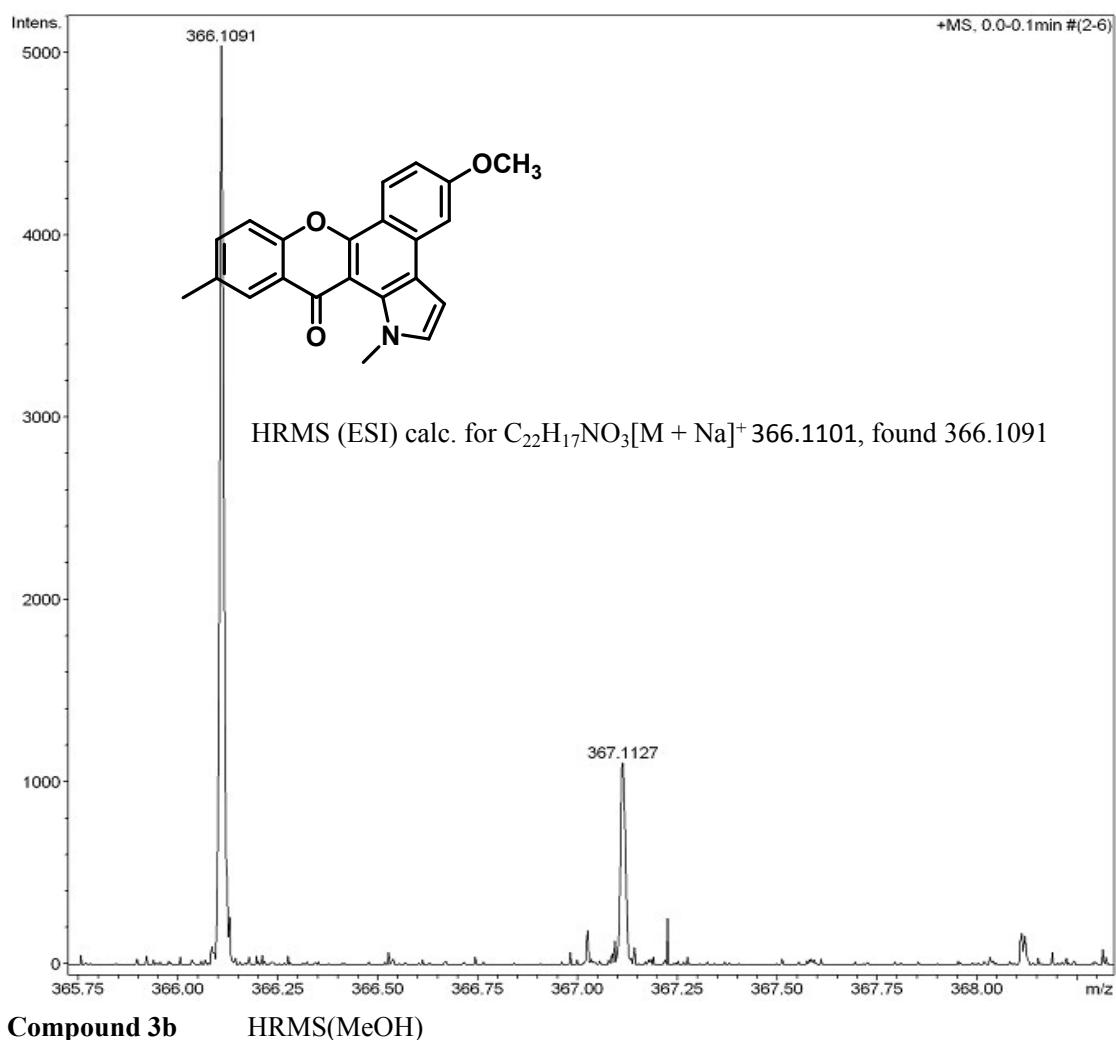
Compound 3a HRMS(MeOH)

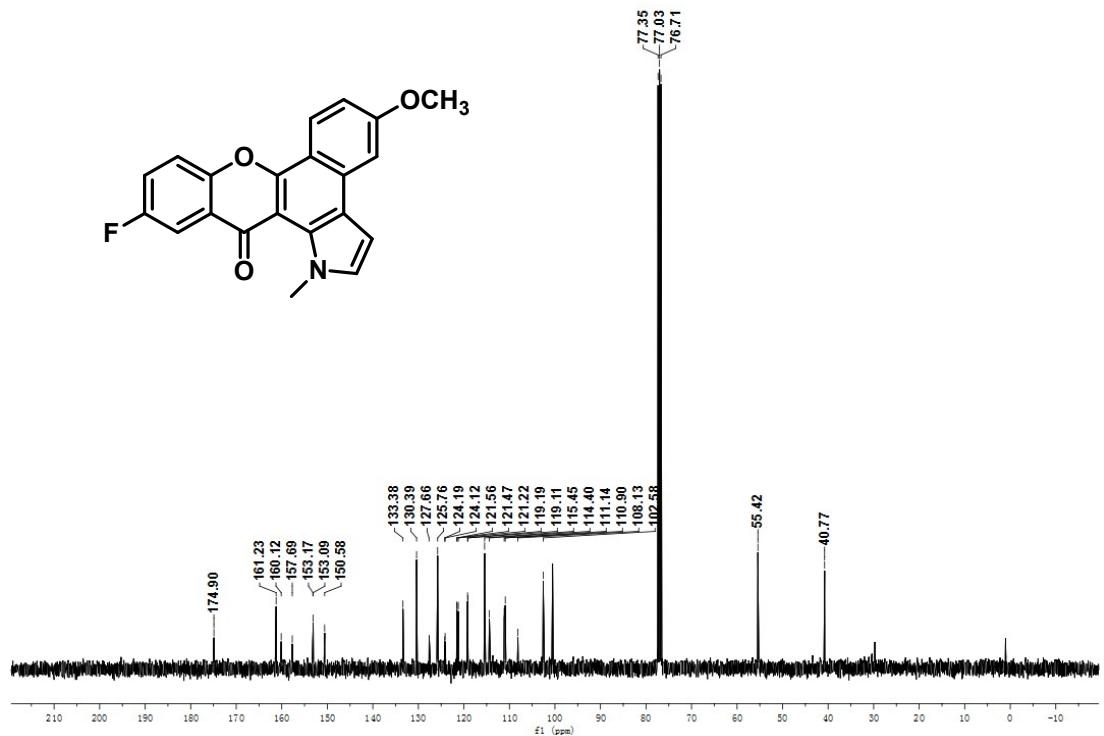


Compound 3b ¹H NMR(CDCl_3)

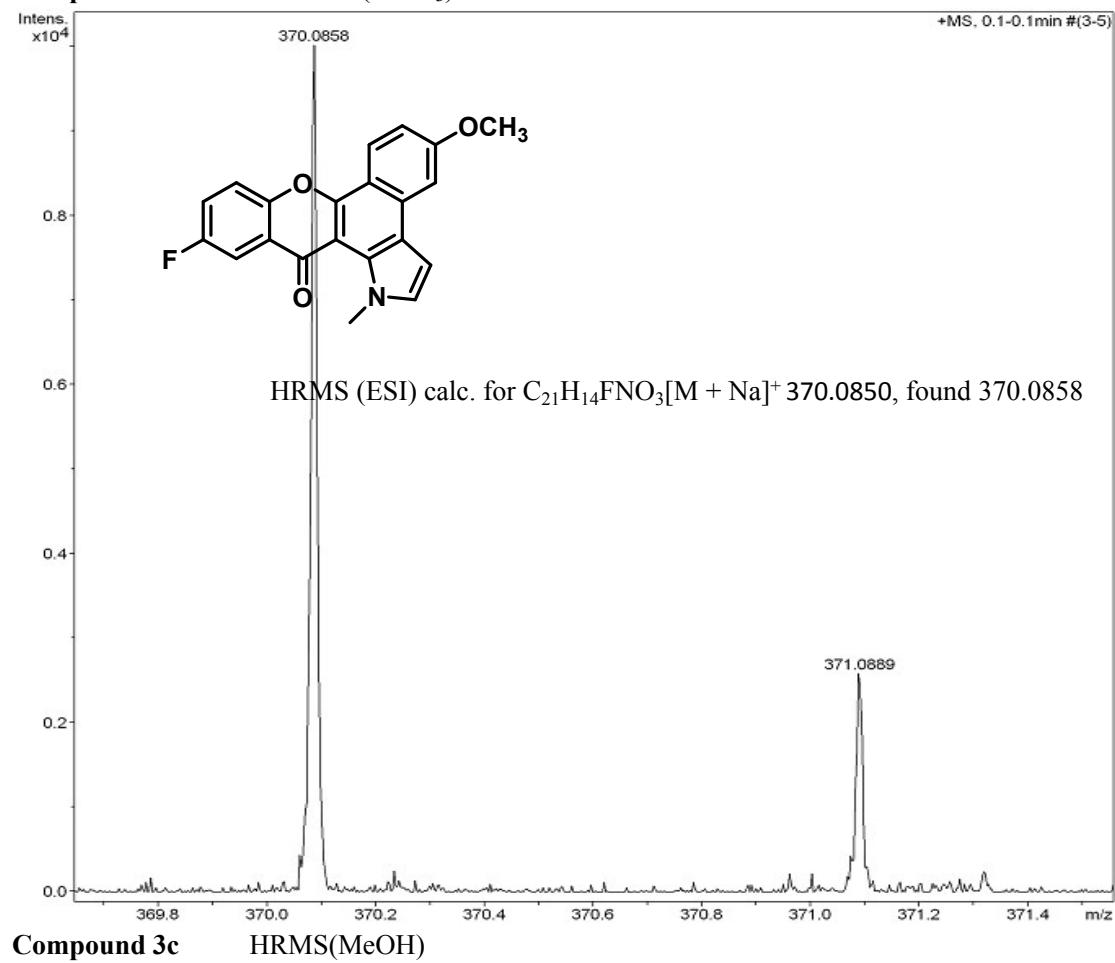


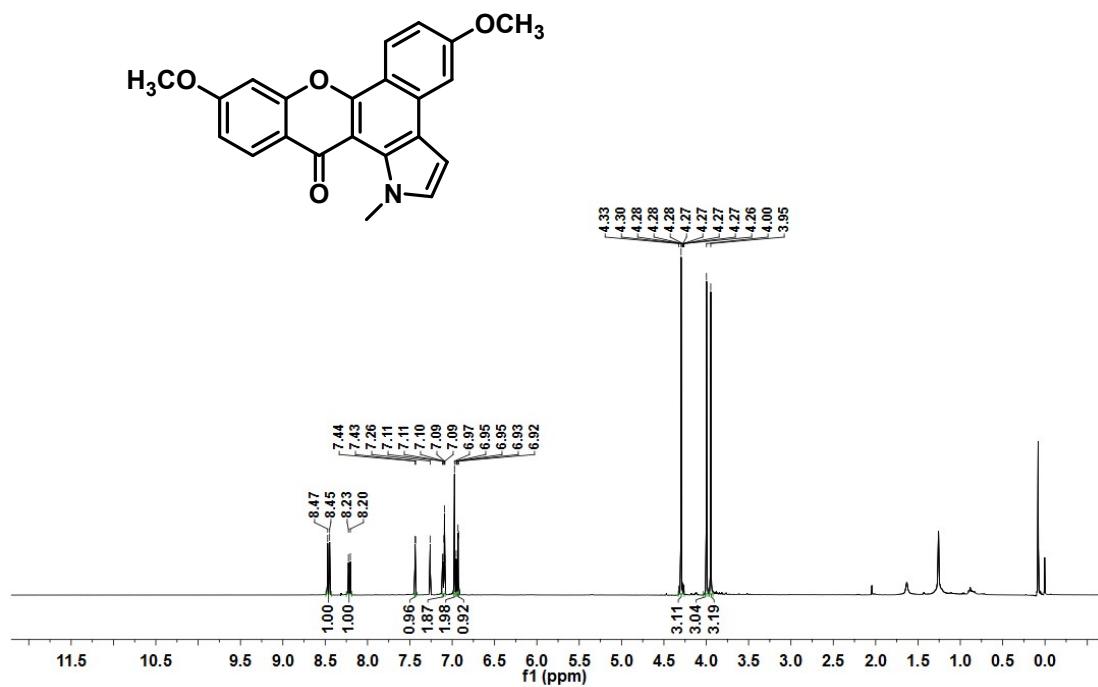
Compound 3b ¹³C NMR (CDCl_3)



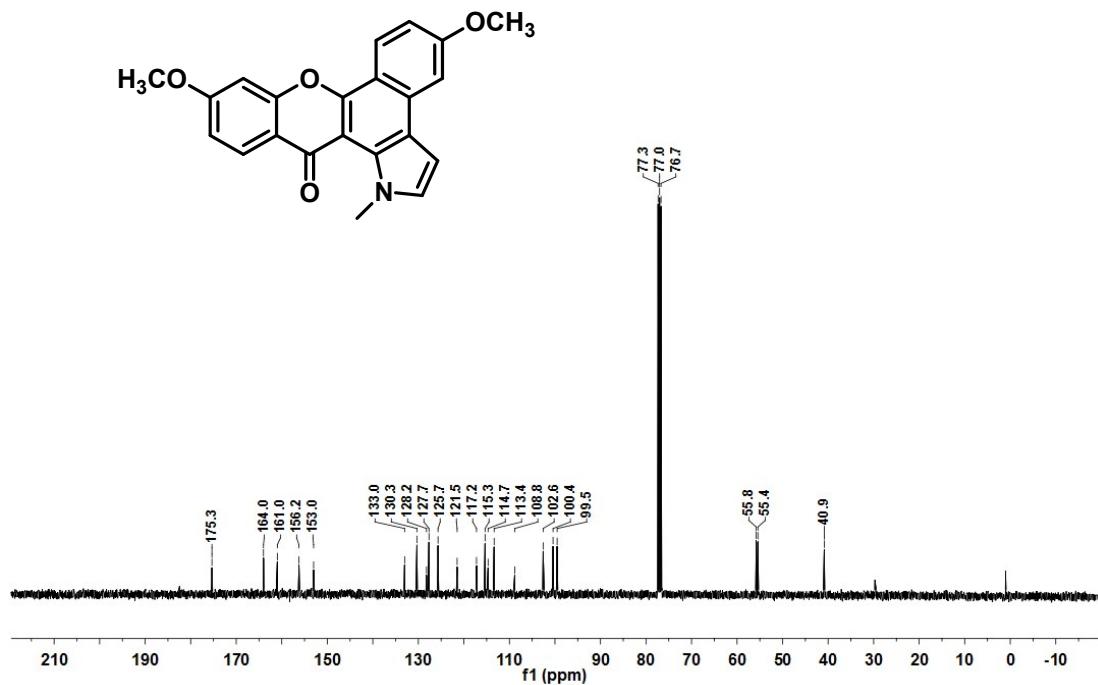


Compound 3c ^{13}C NMR (CDCl_3)

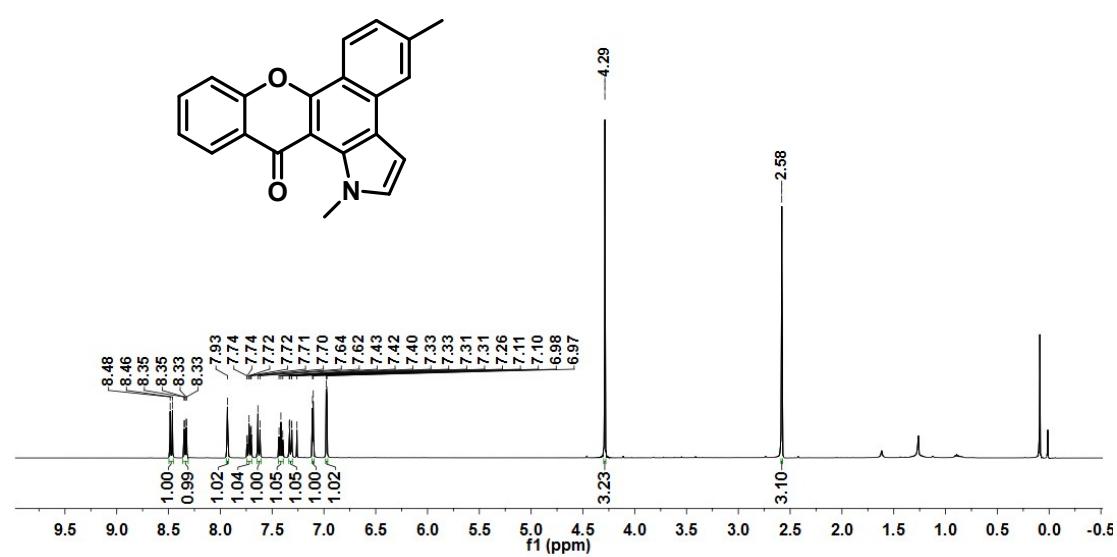
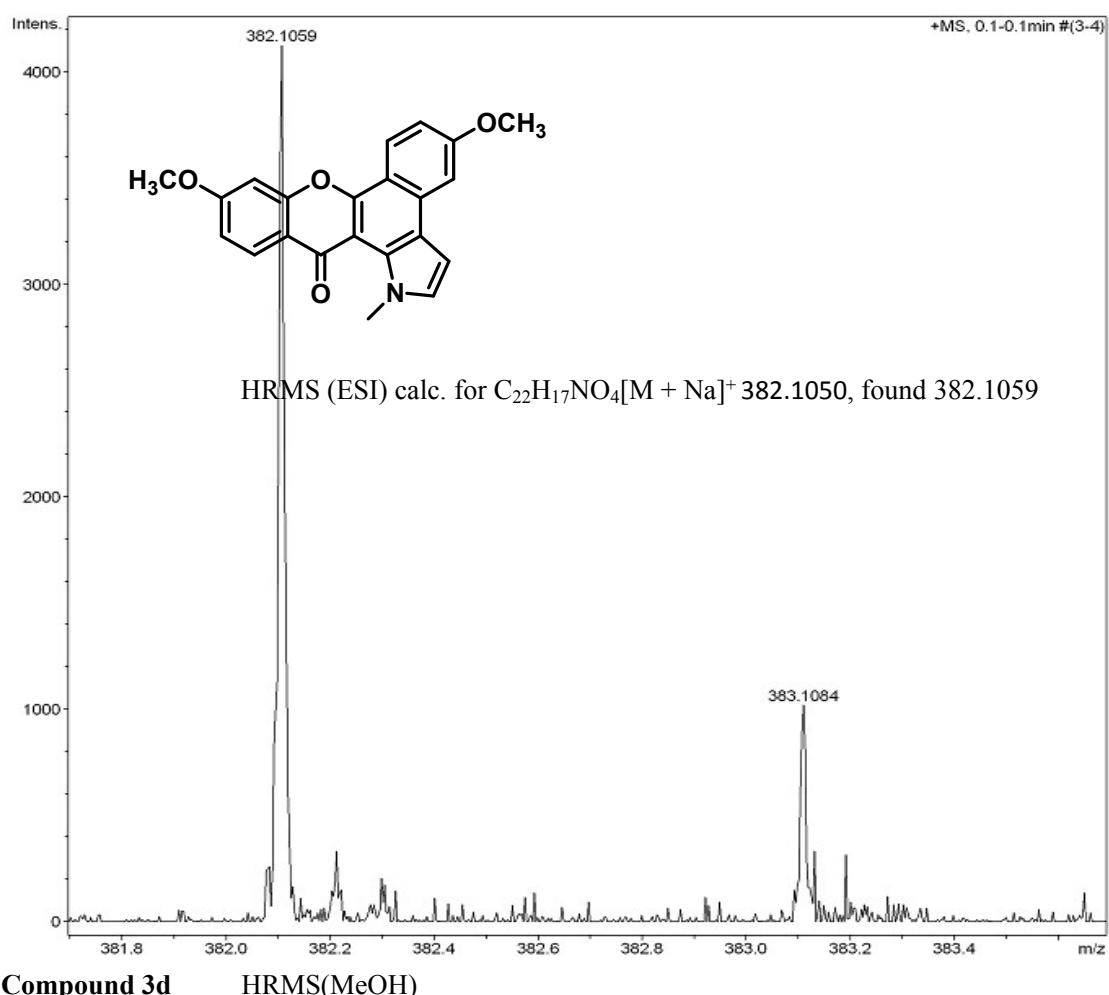


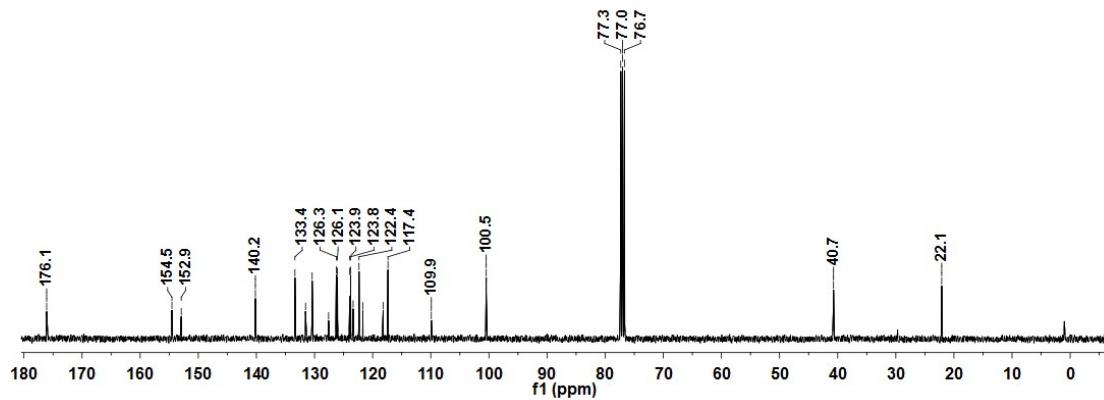
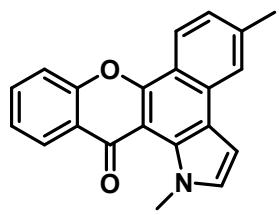


Compound 3d ^1H NMR(CDCl_3)

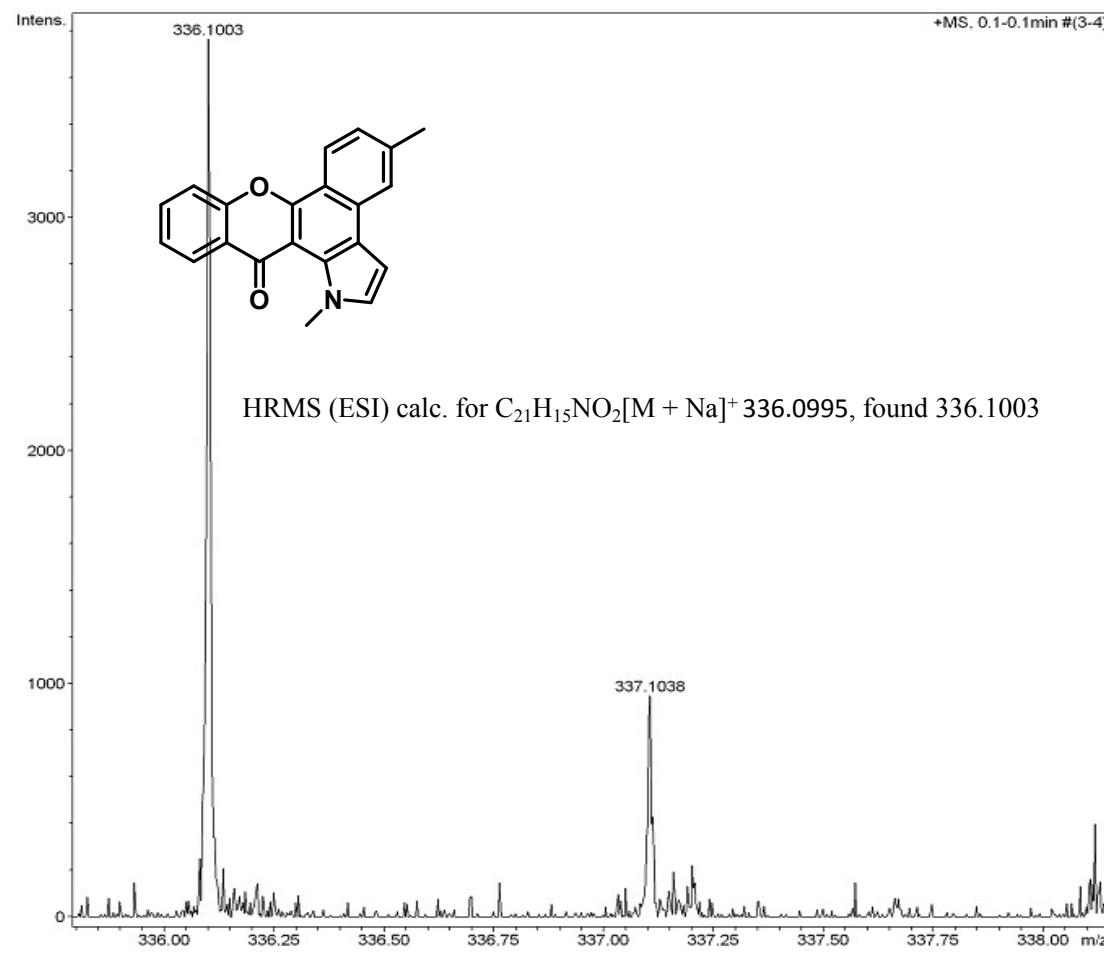


Compound 3d ^{13}C NMR (CDCl_3)

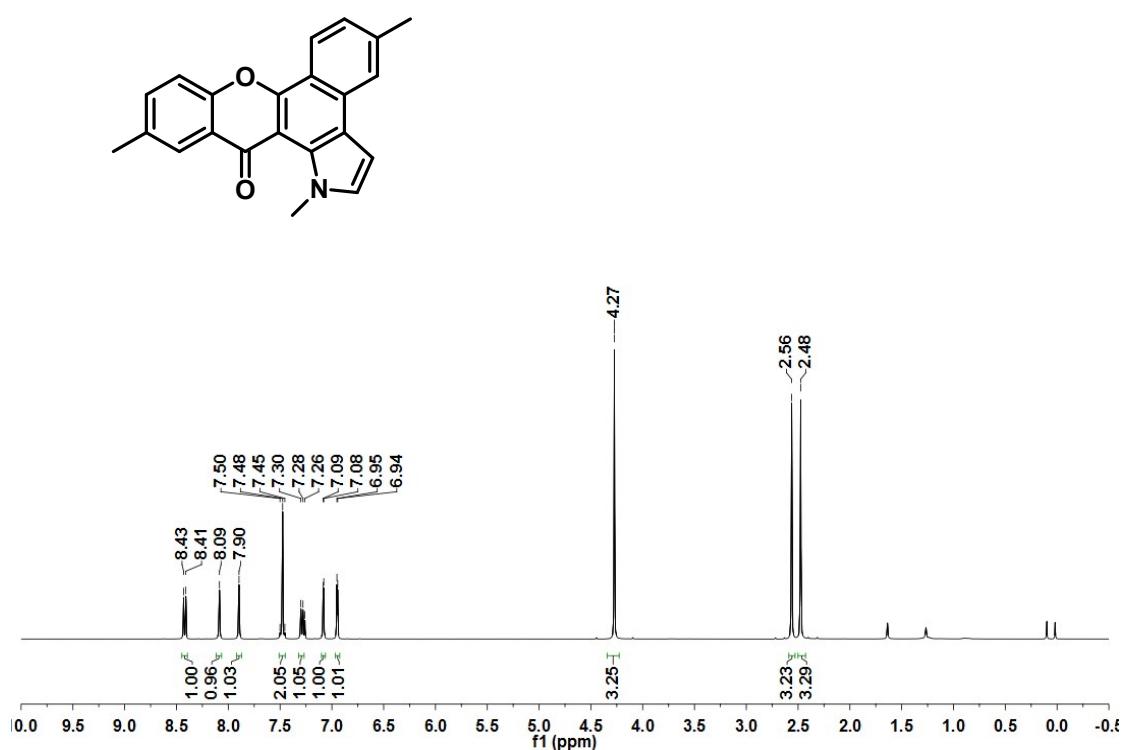




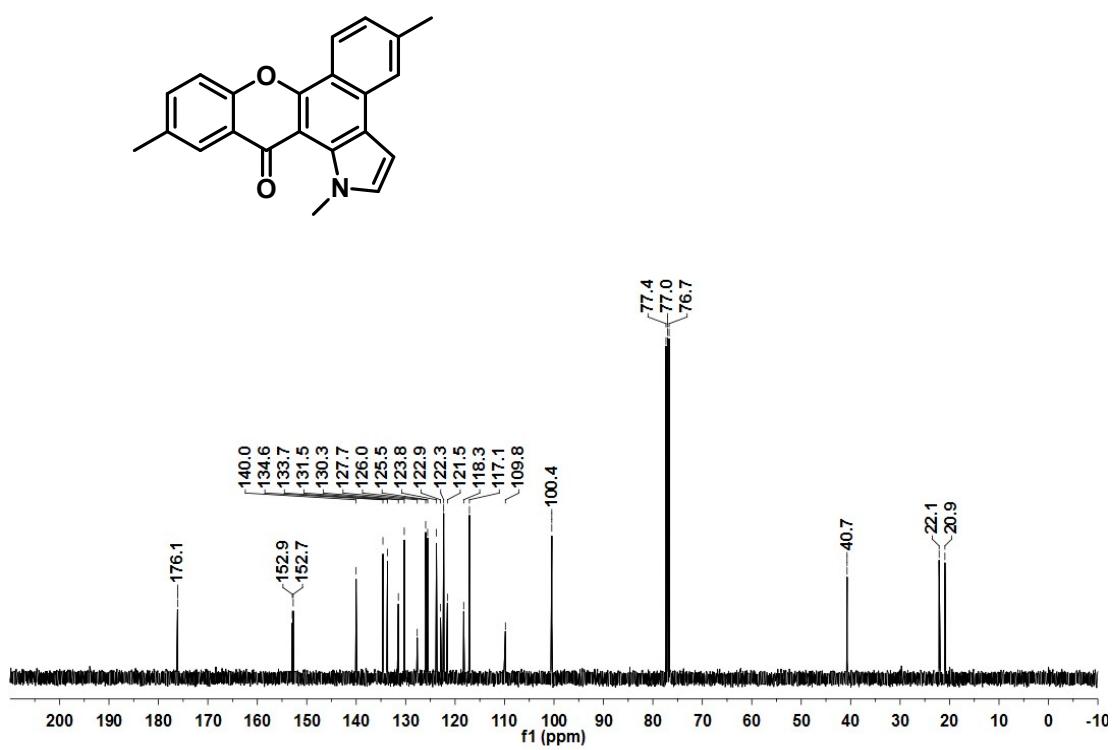
Compound 3e ^{13}C NMR (CDCl_3)



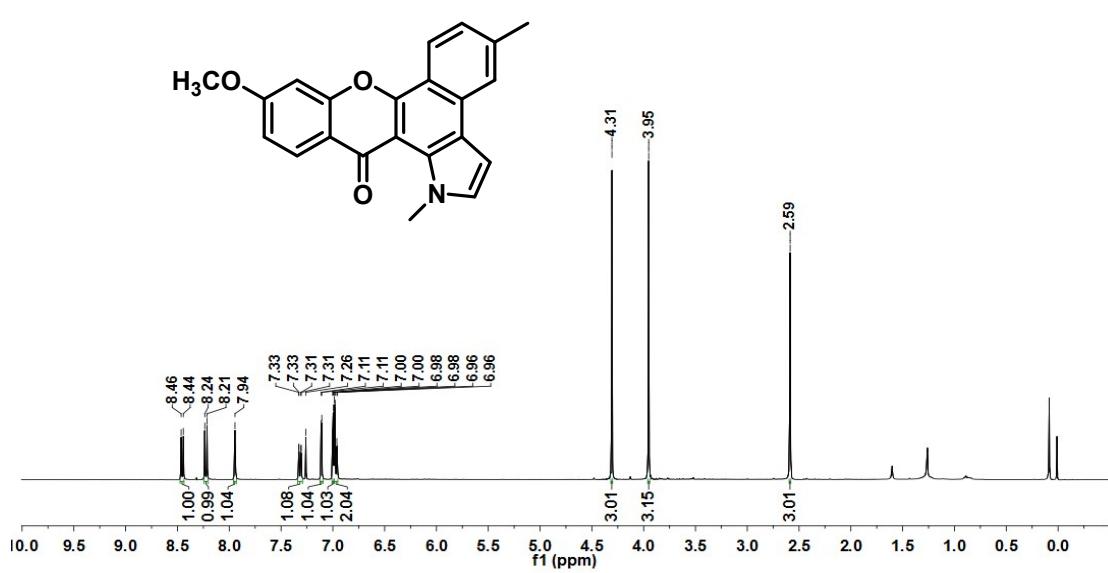
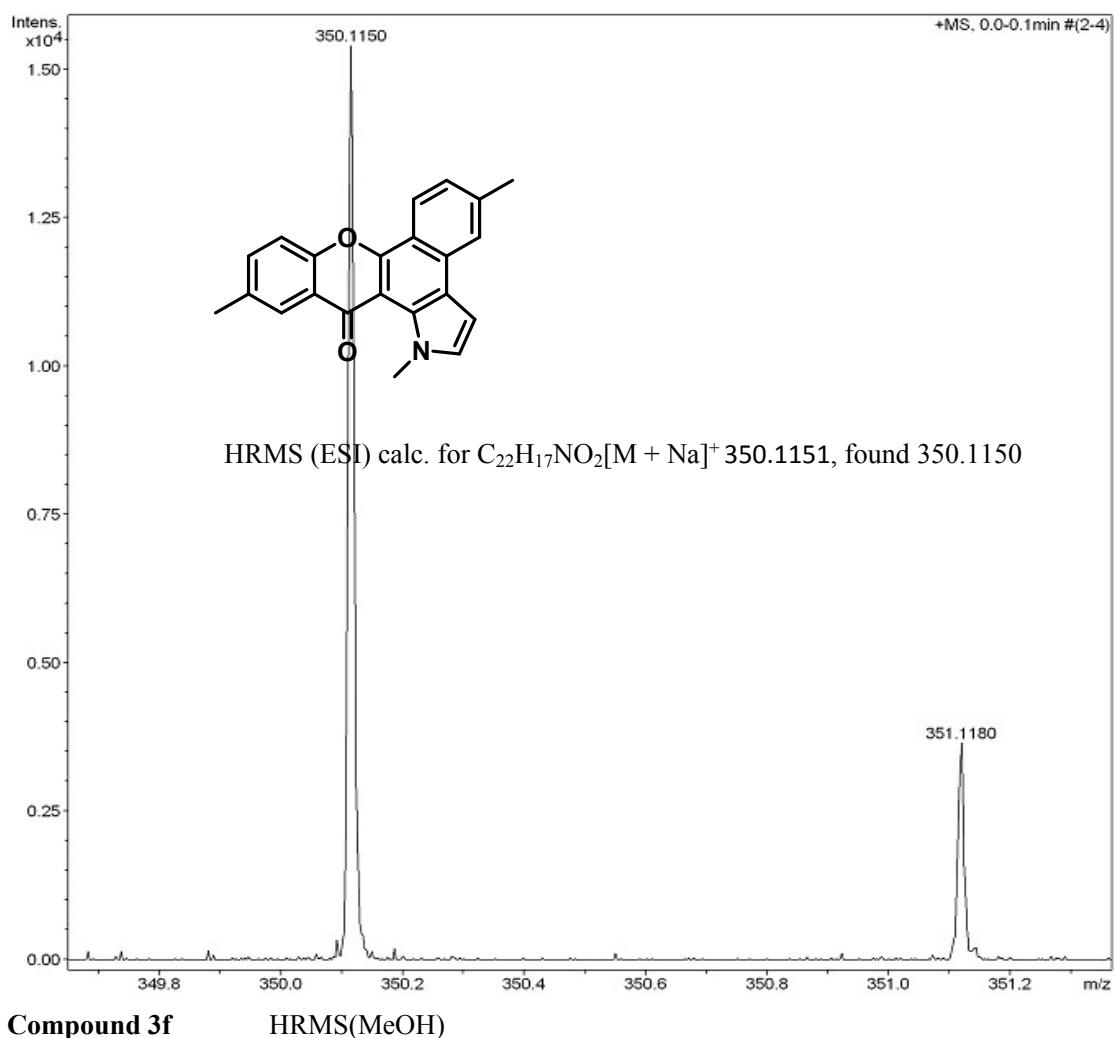
Compound 3e HRMS(MeOH)

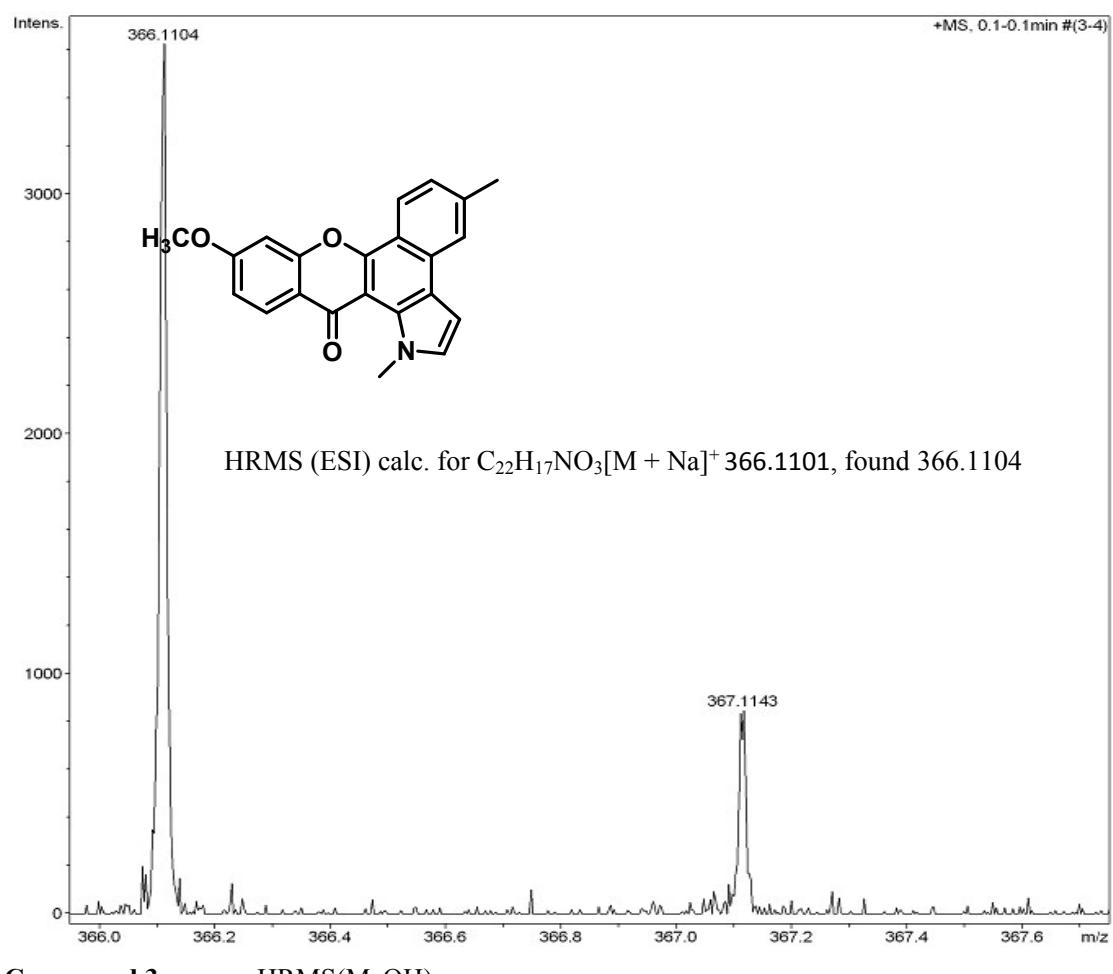
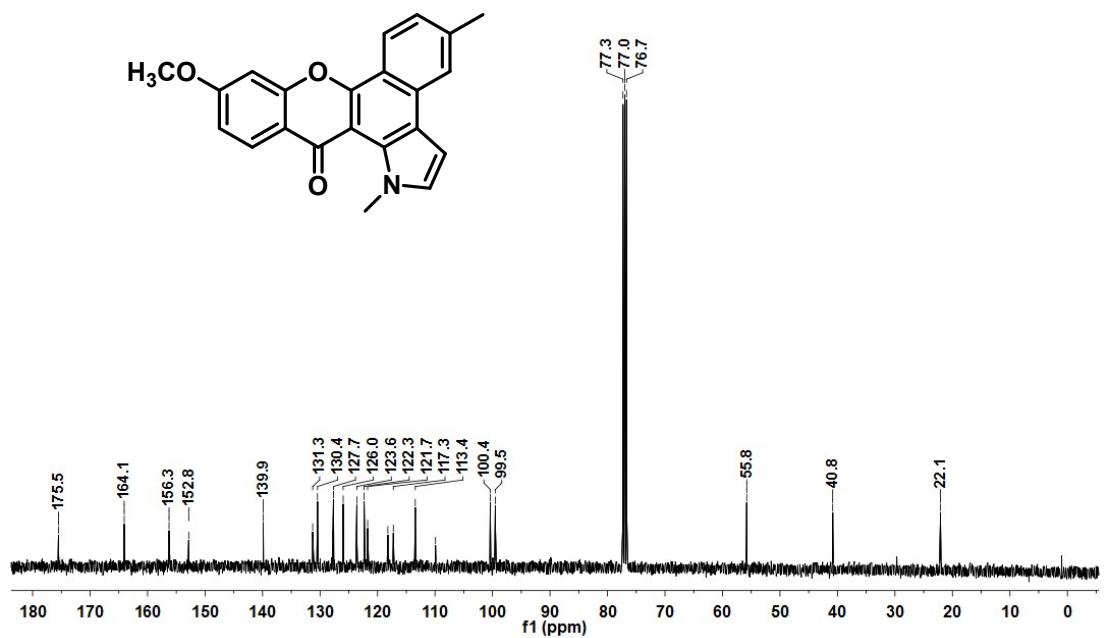


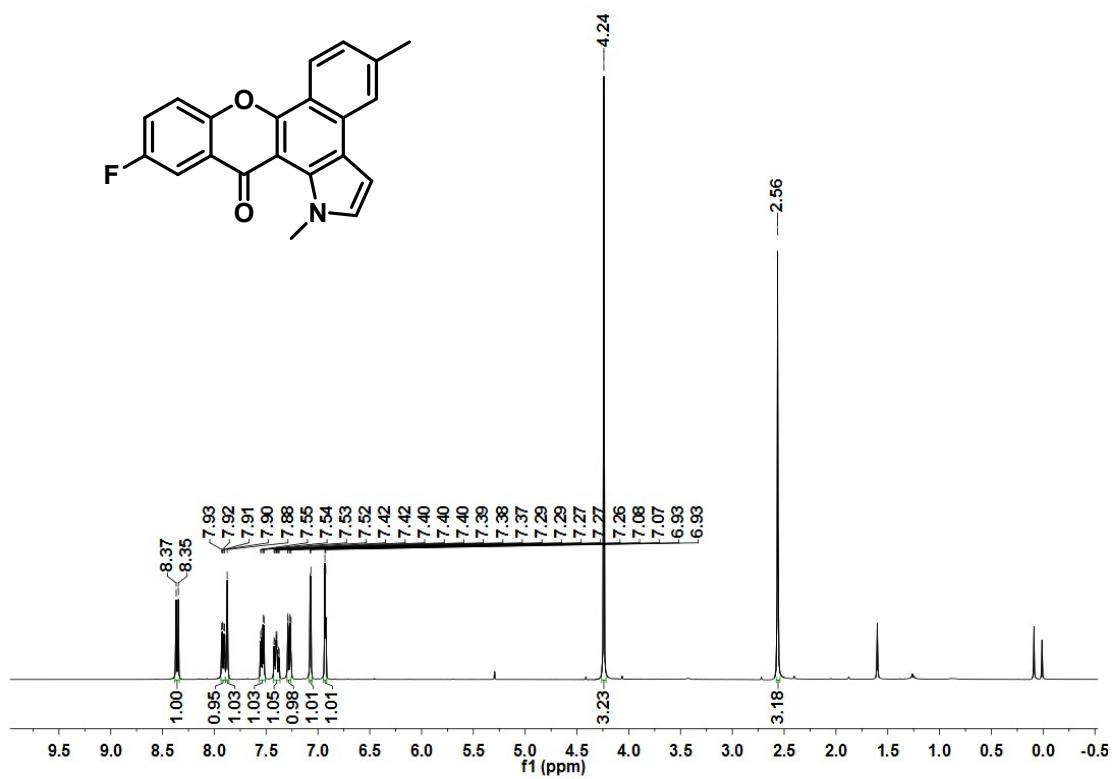
Compound 3f ^1H NMR(CDCl_3)



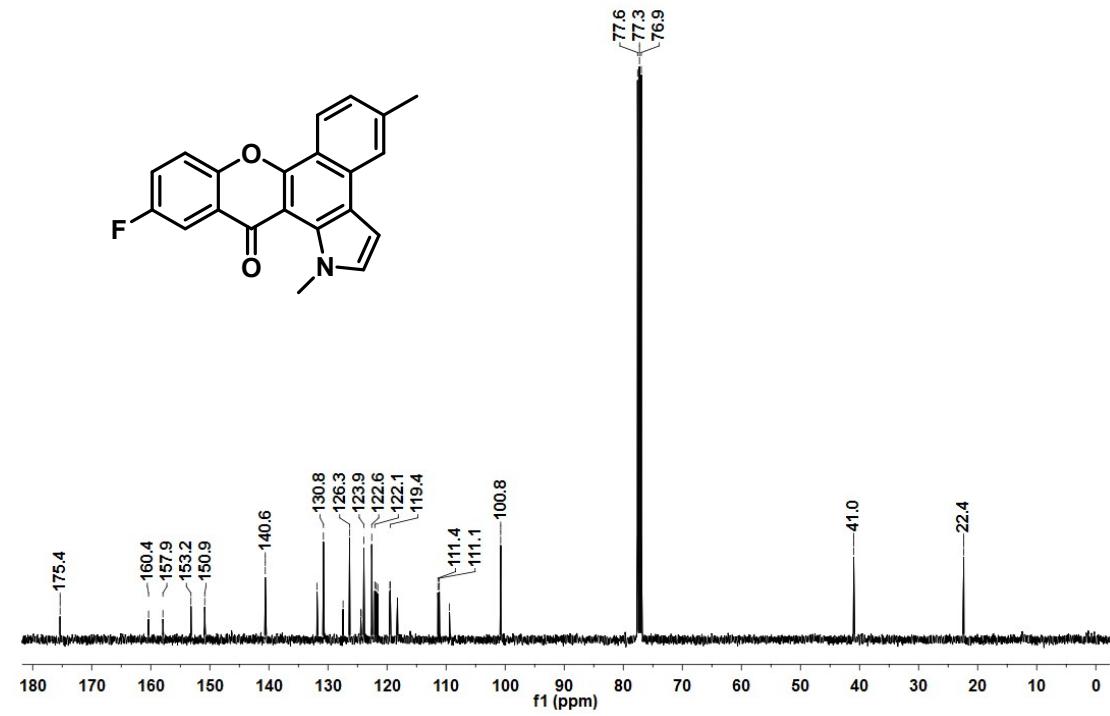
Compound 3f ^{13}C NMR (CDCl_3)



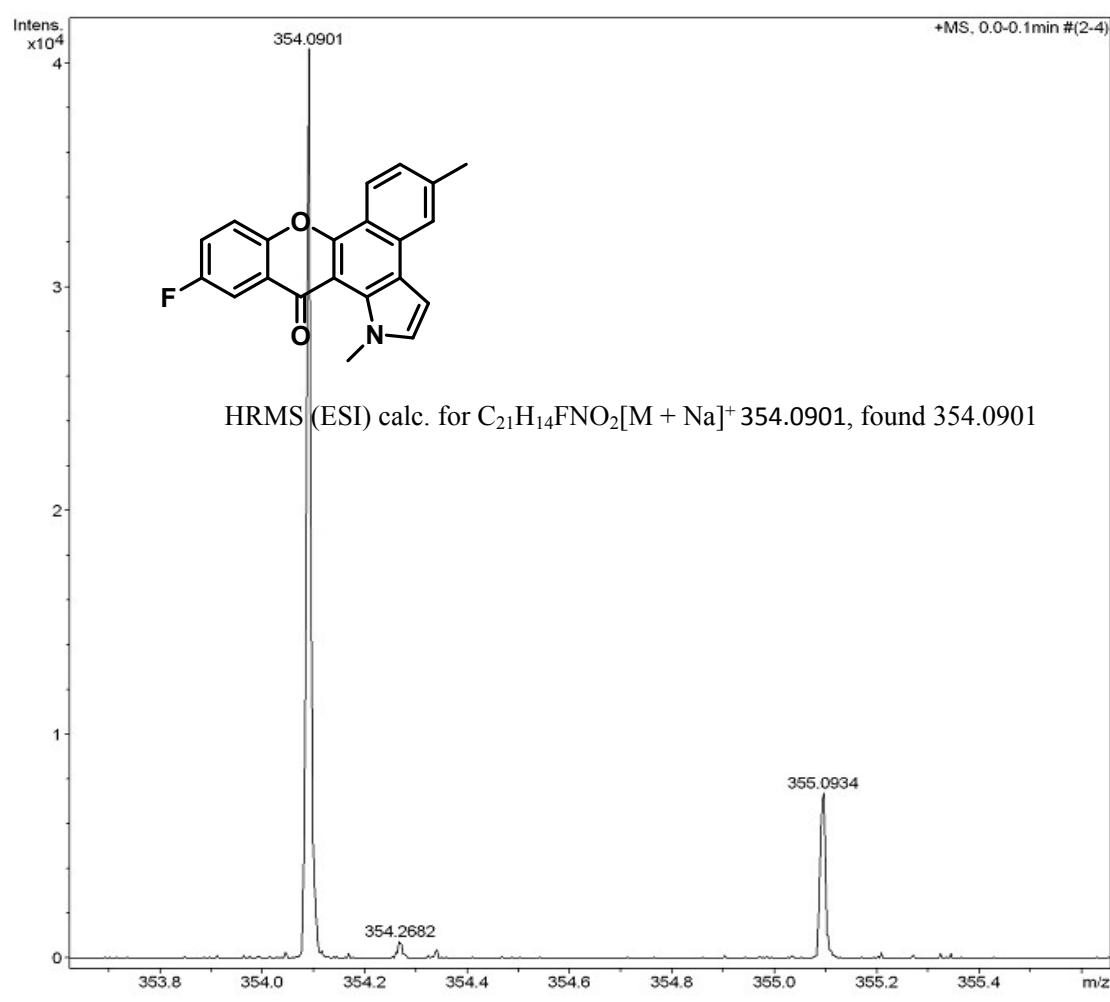




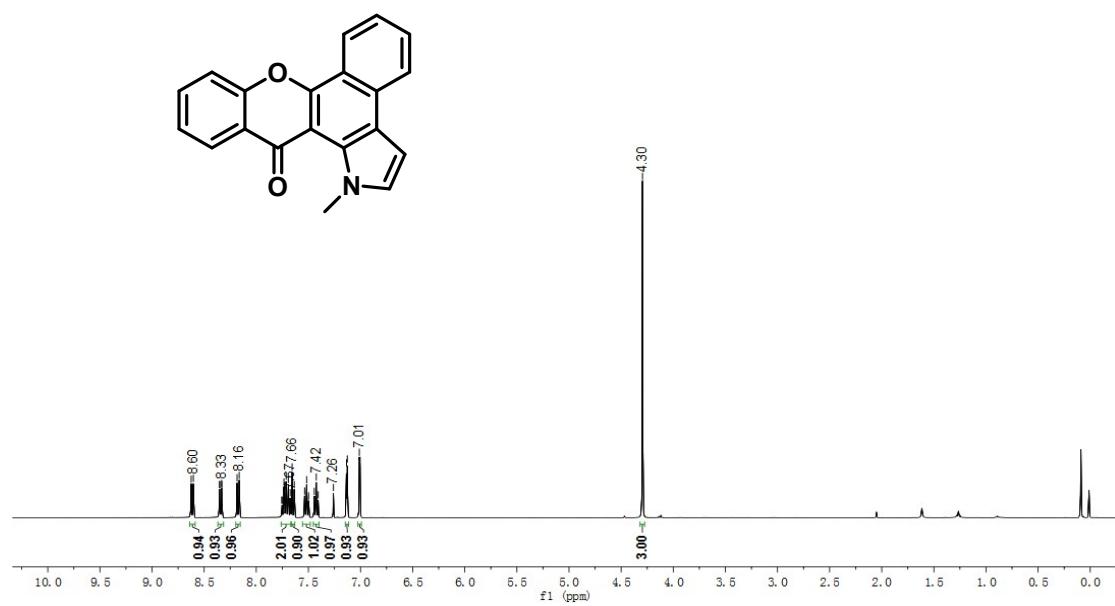
Compound 3h ¹H NMR (CDCl_3)



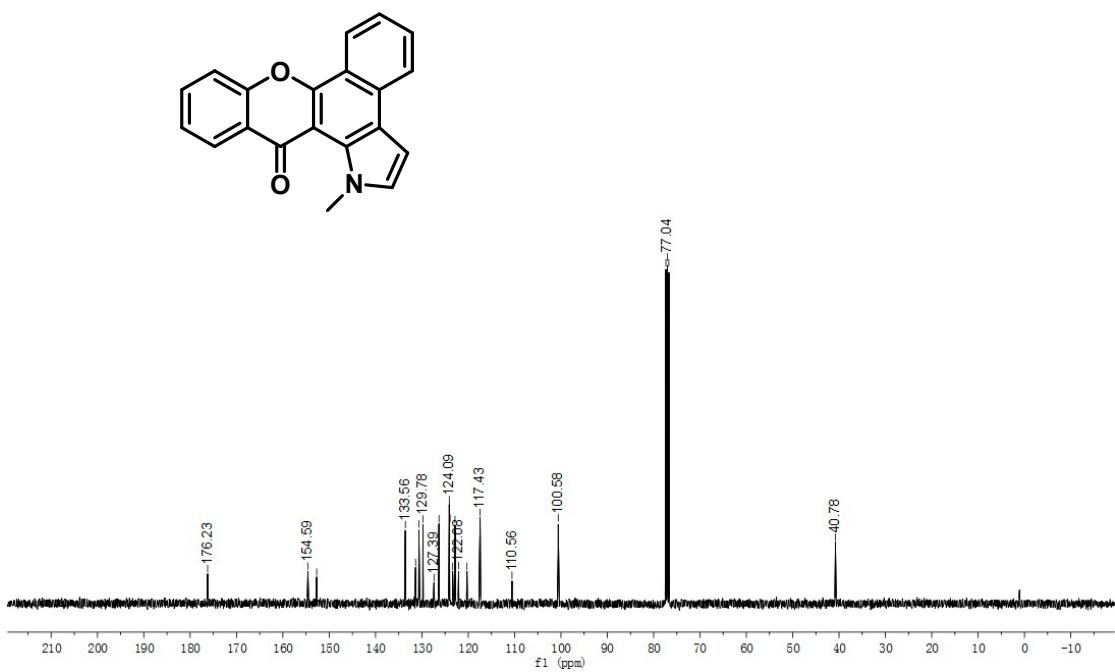
Compound 3h ¹³C NMR (CDCl_3)



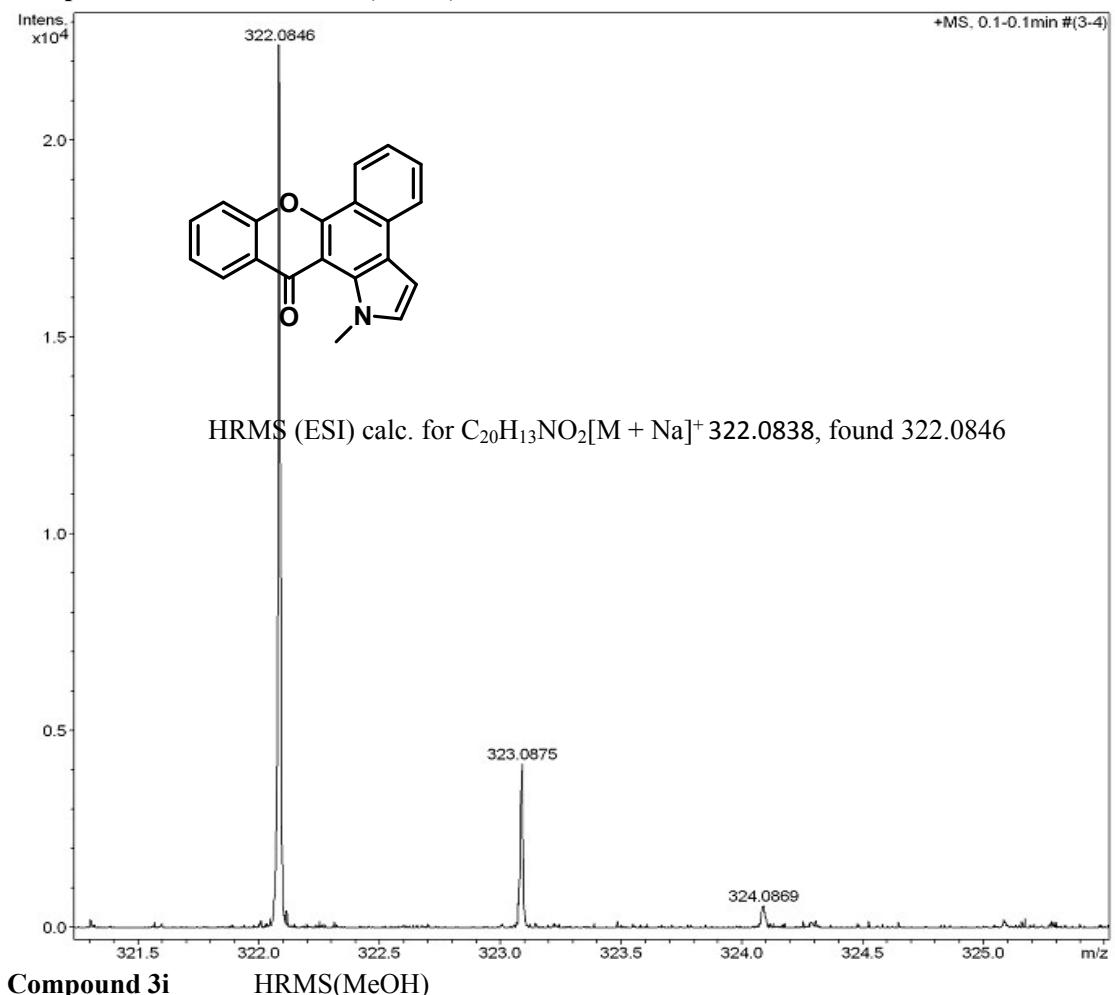
Compound 3h HRMS(MeOH)



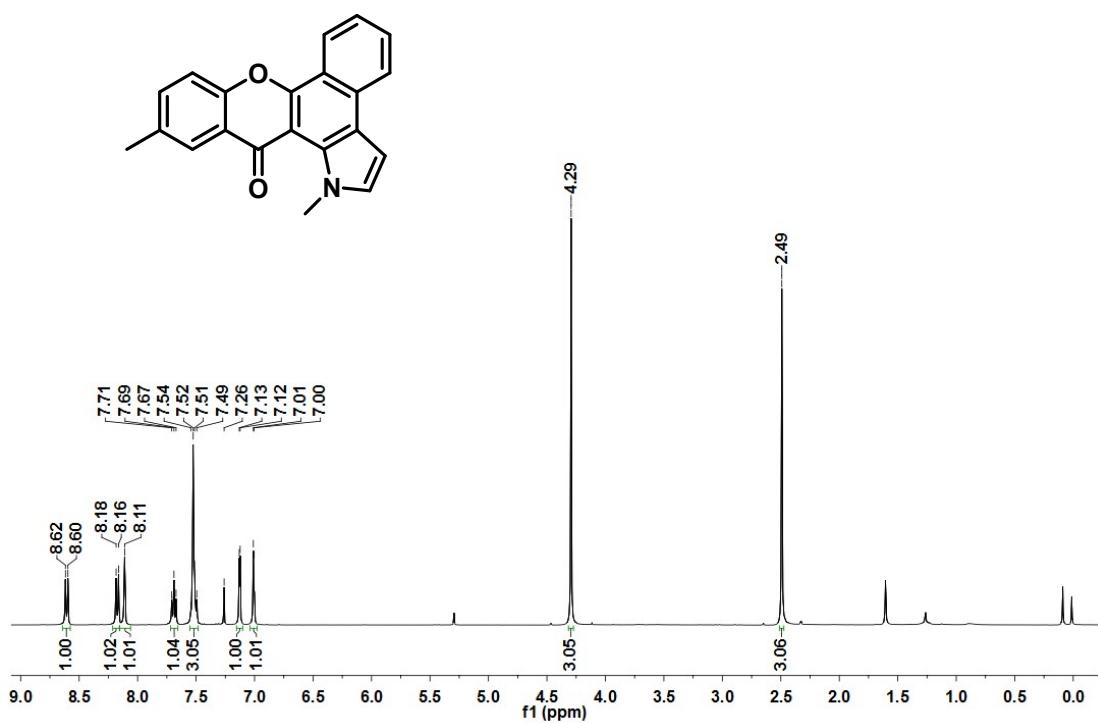
Compound 3i ^1H NMR(CDCl_3)



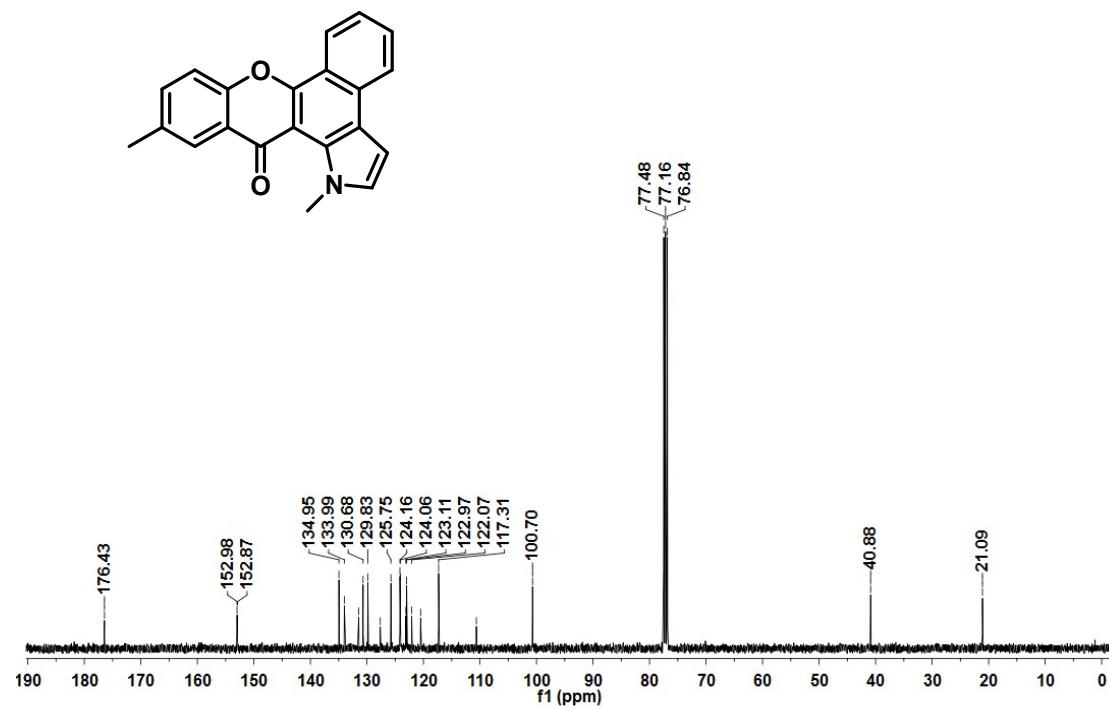
Compound 3i ^{13}C NMR (CDCl_3)



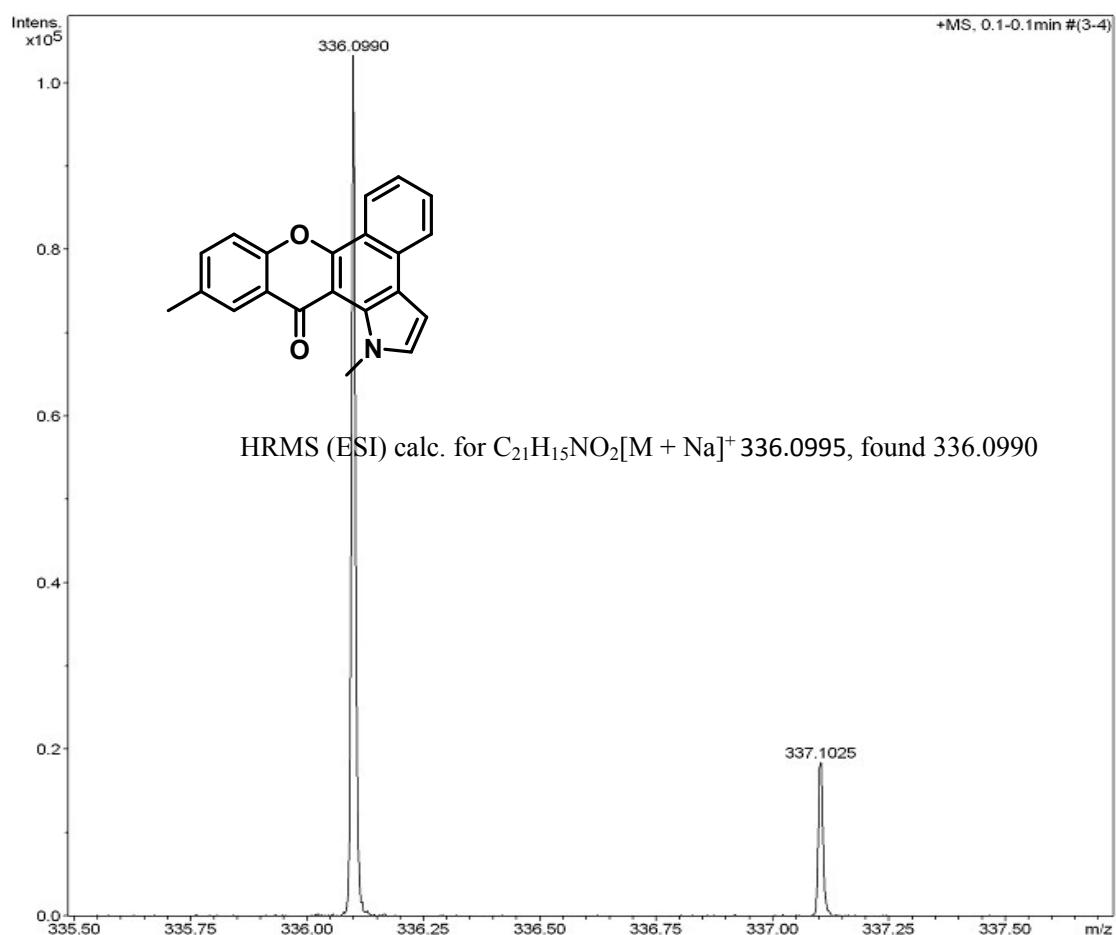
Compound 3i HRMS(MeOH)



Compound 3j ^1H NMR(CDCl_3)

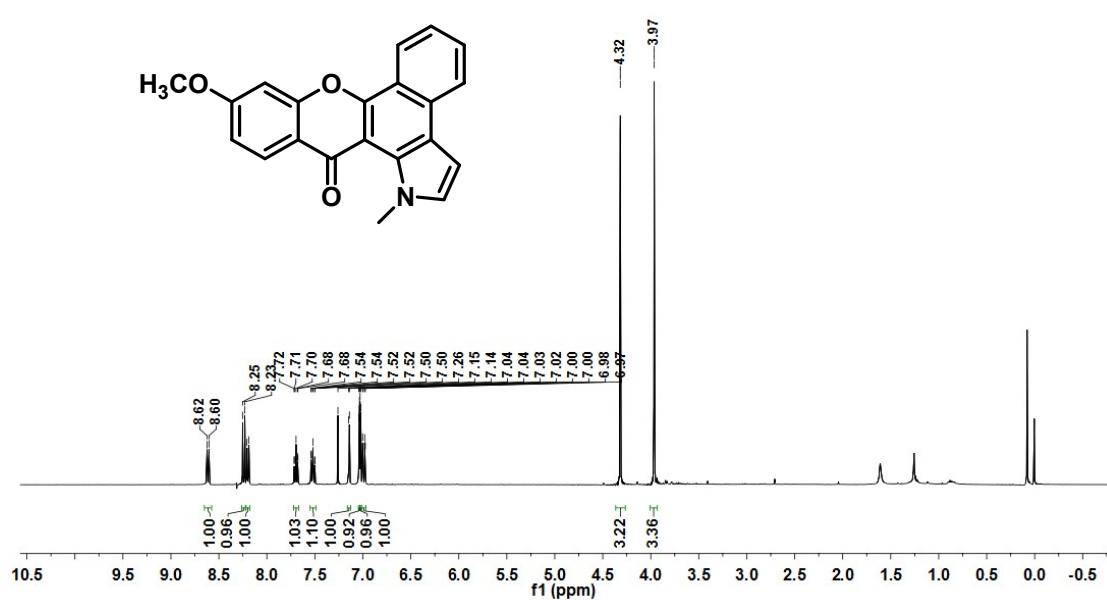


Compound 3j ^{13}C NMR (CDCl_3)



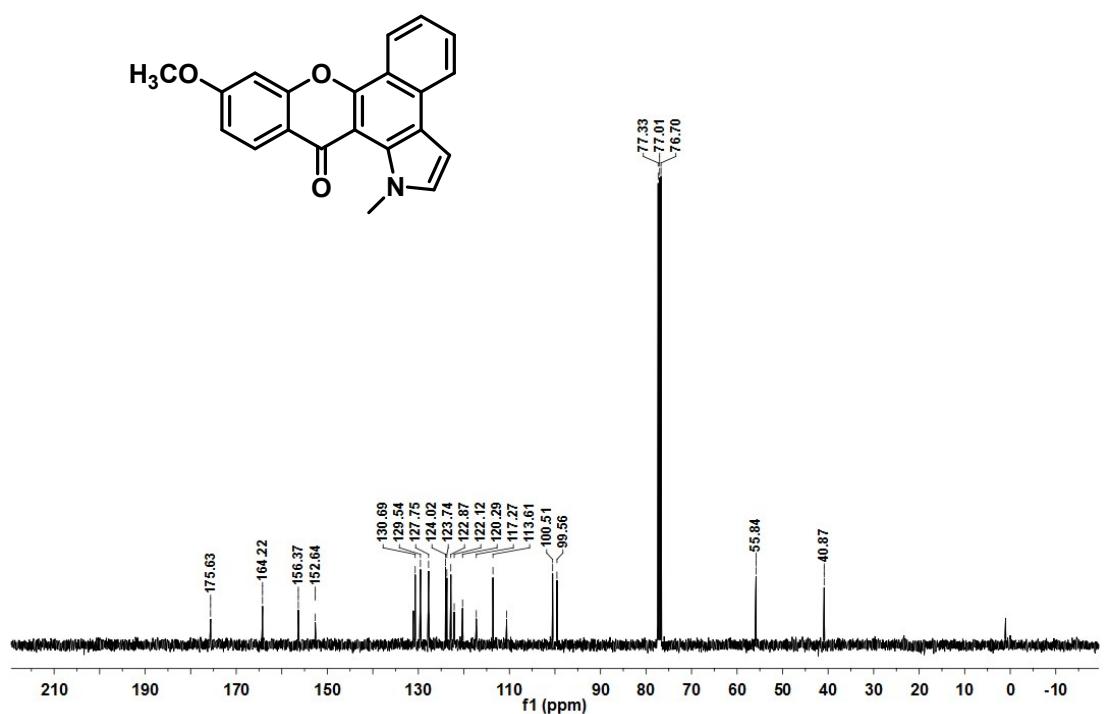
Compound 3j

HRMS(MeOH)

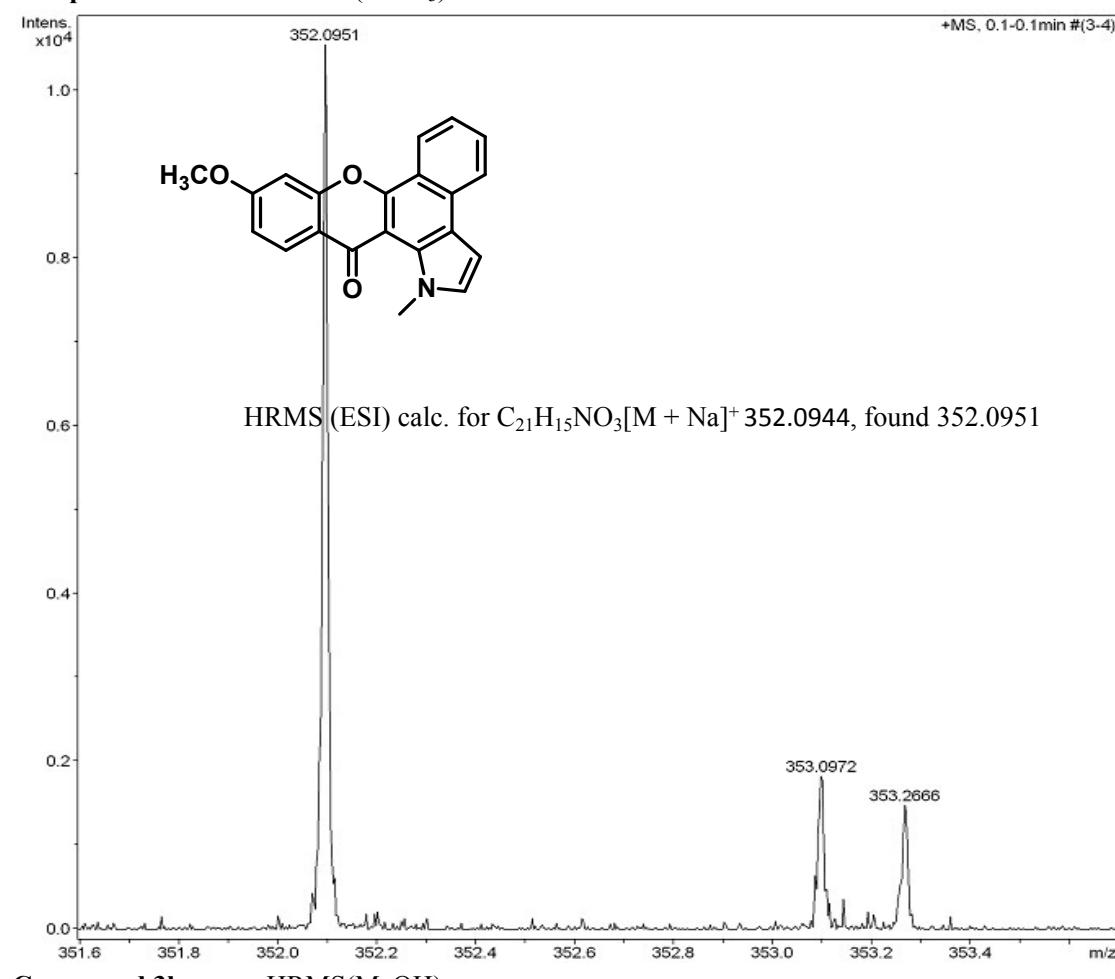


Compound 3k

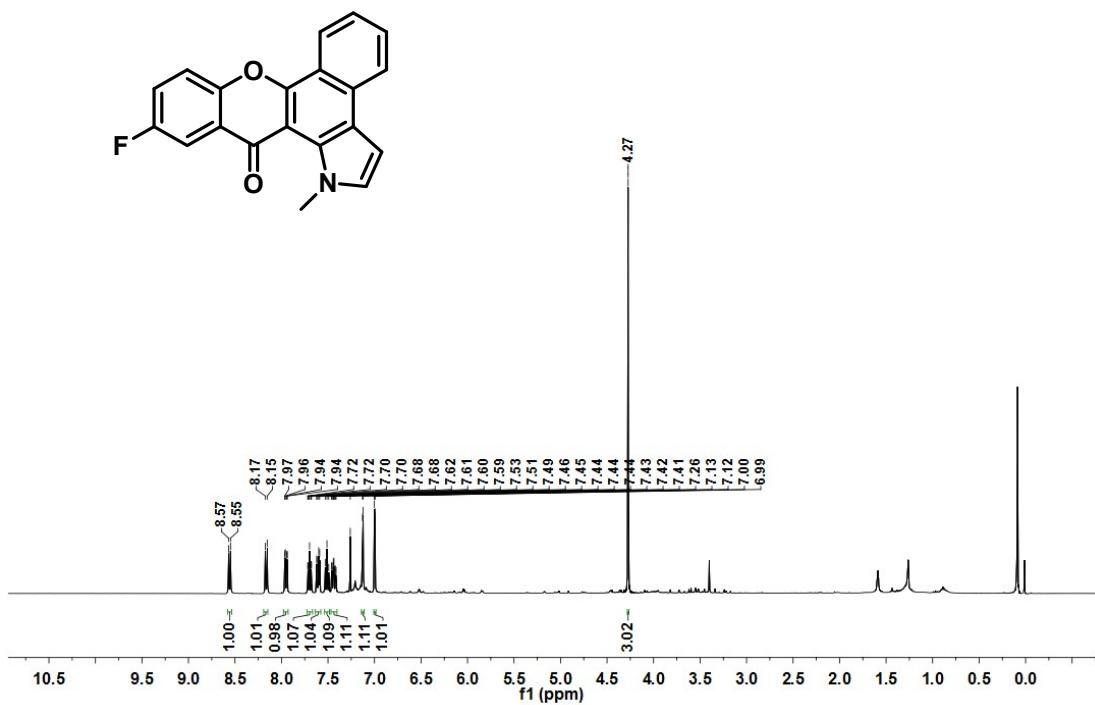
^1H NMR(CDCl_3)



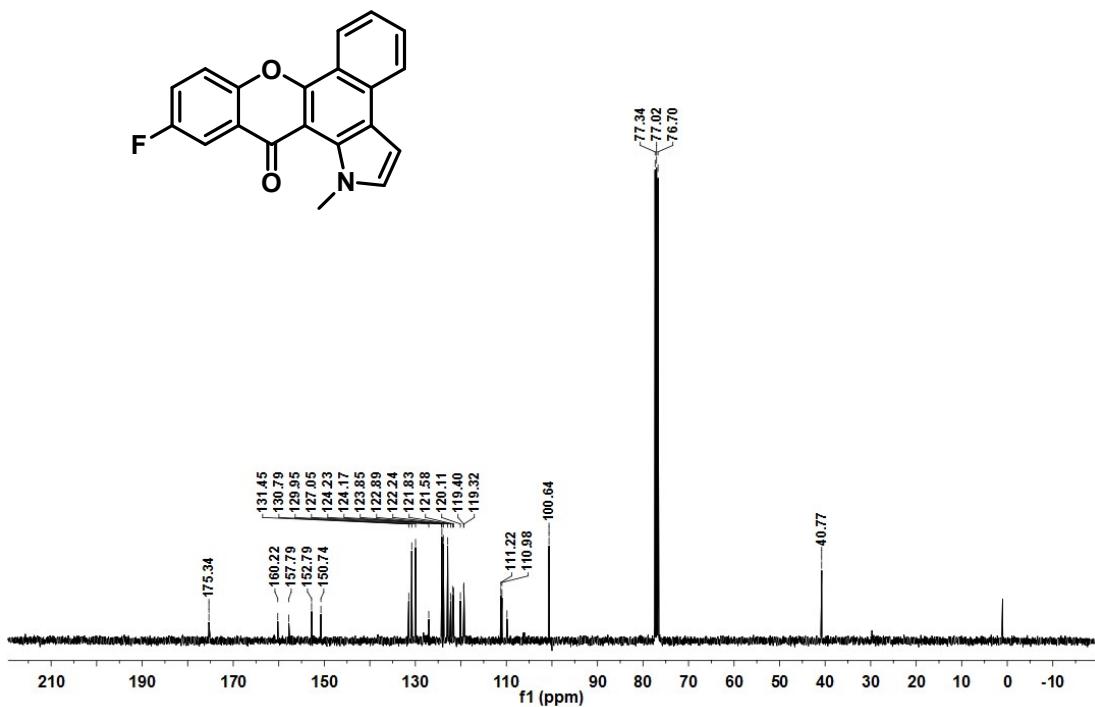
Compound 3k ¹³C NMR (CDCl₃)



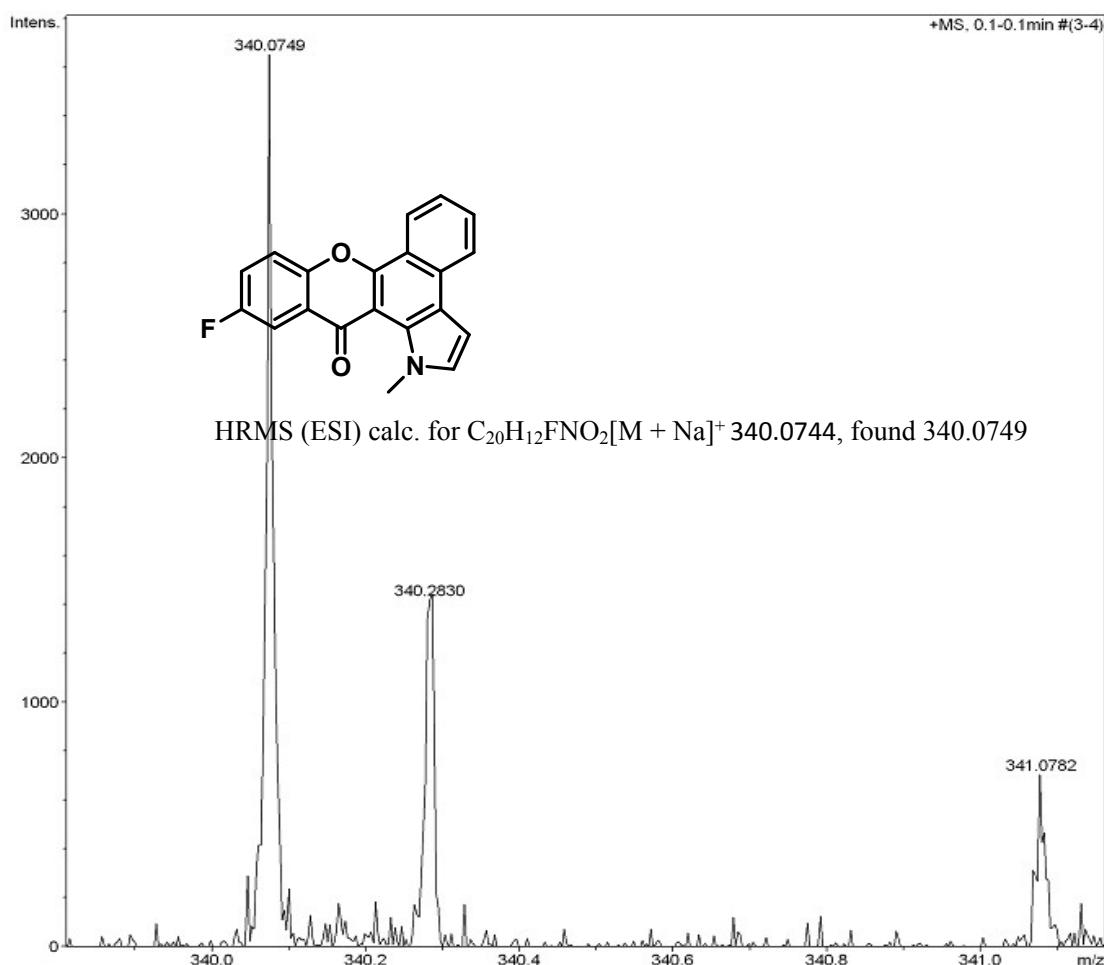
Compound 3k HRMS(MeOH)



Compound 3l ¹H NMR(CDCl_3)

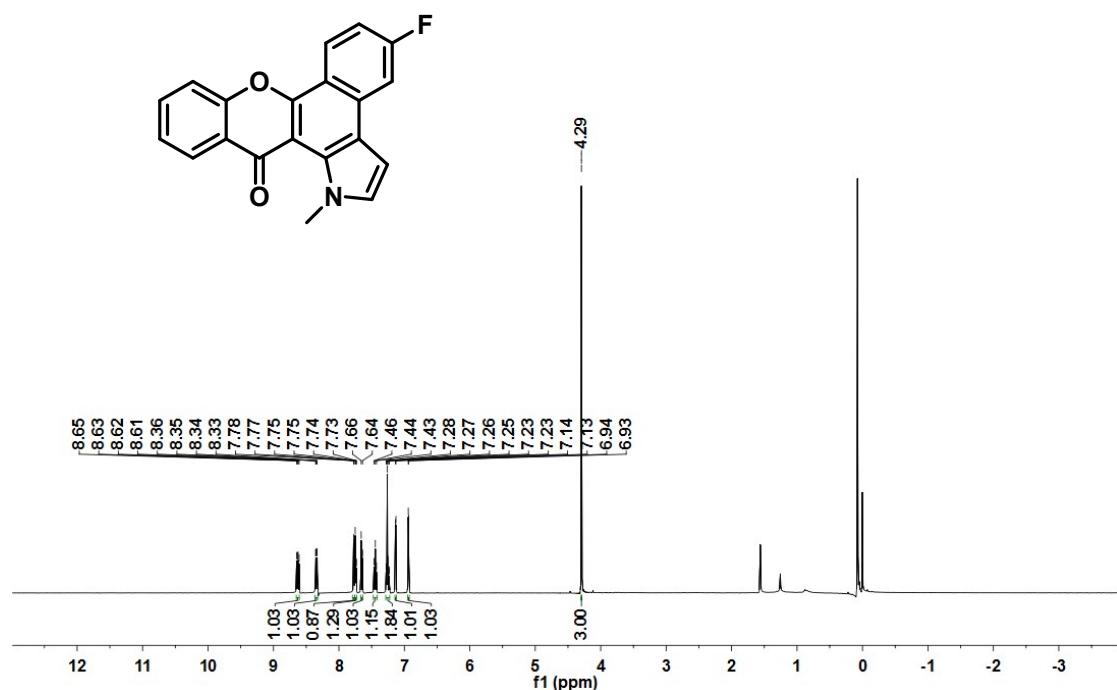


Compound 3l ¹³C NMR (CDCl_3)

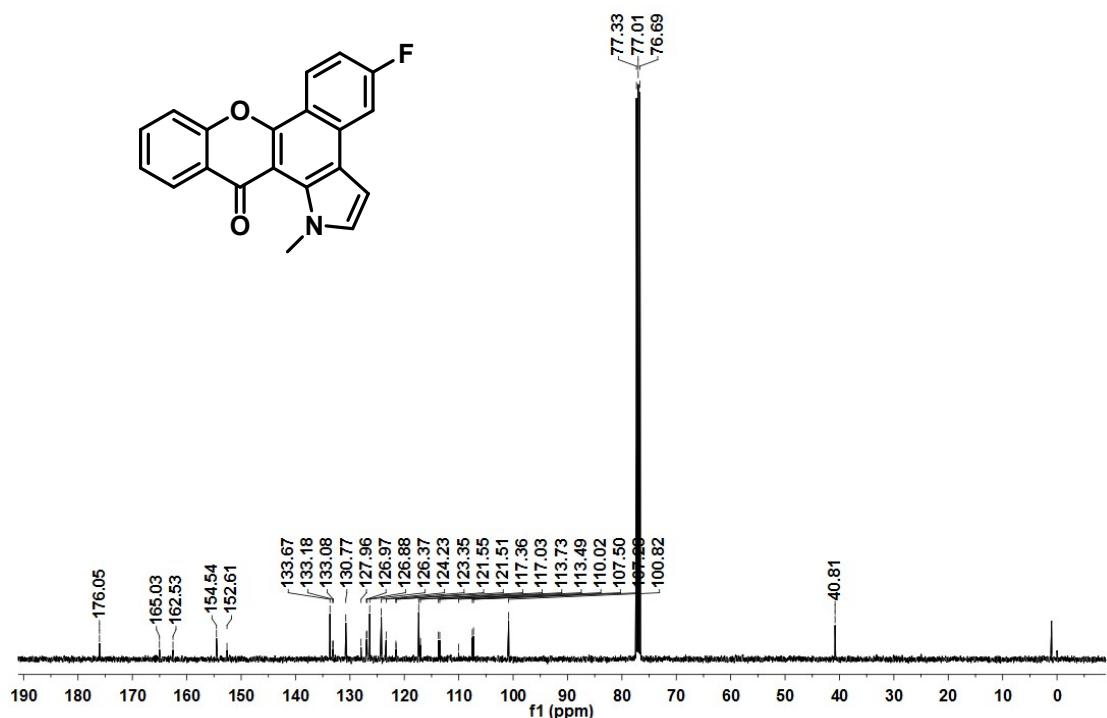


Compound 3l

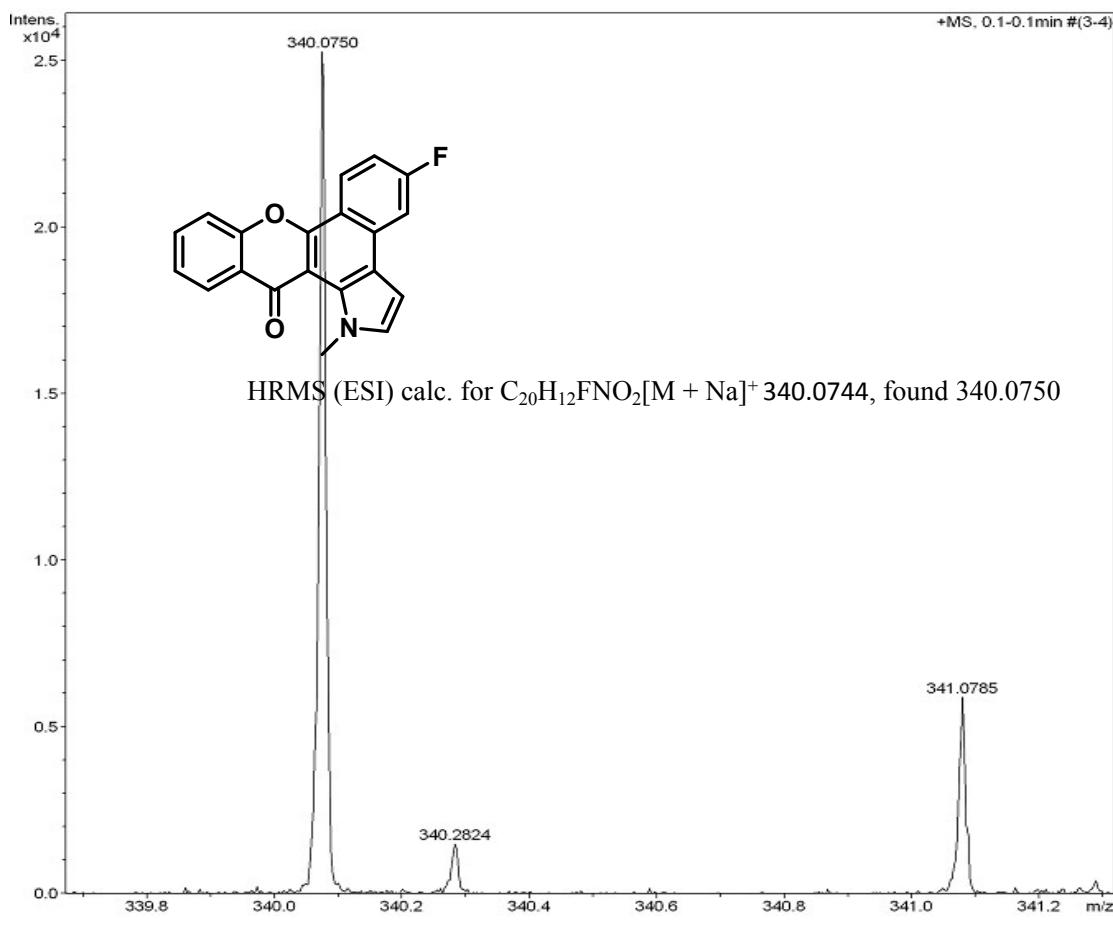
HRMS(MeOH)



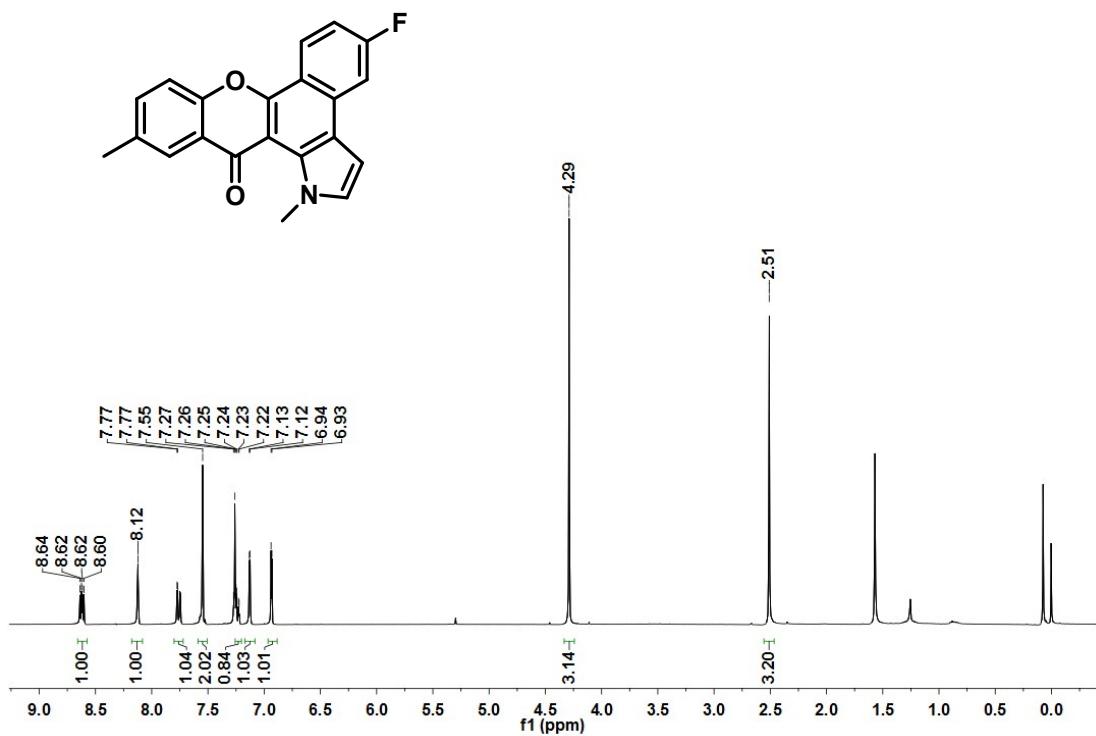
Compound 3m ^1H NMR(CDCl_3)



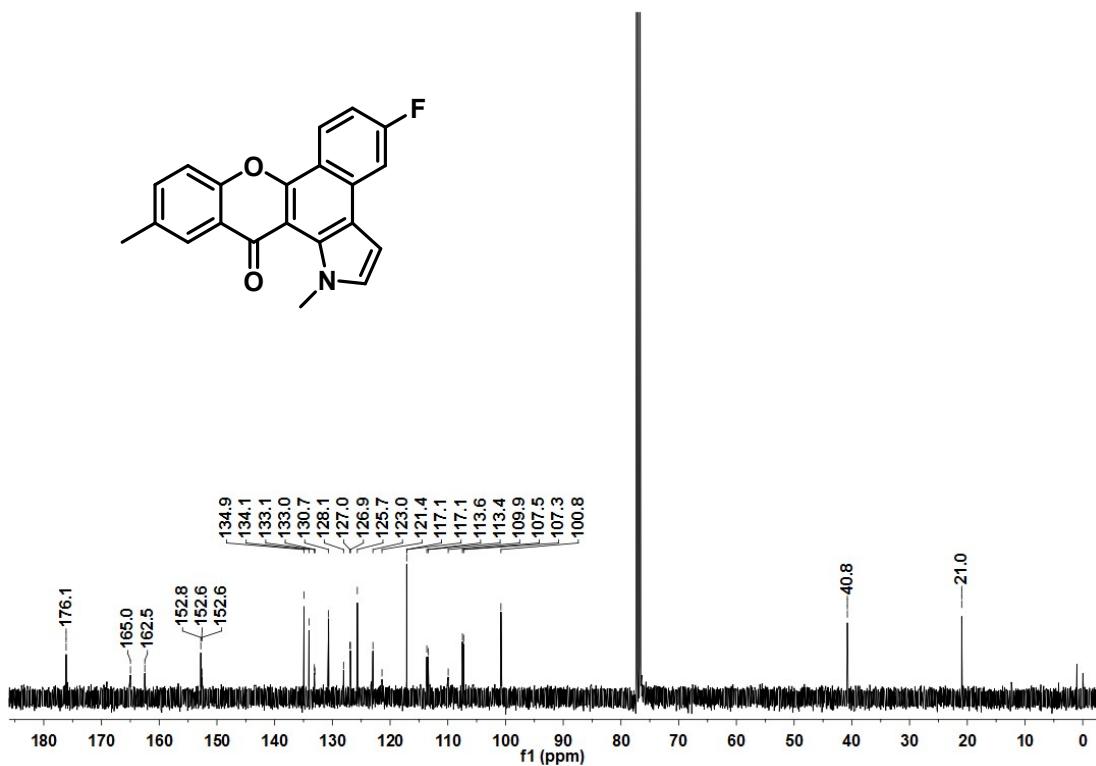
Compound 3m ^{13}C NMR (CDCl_3)



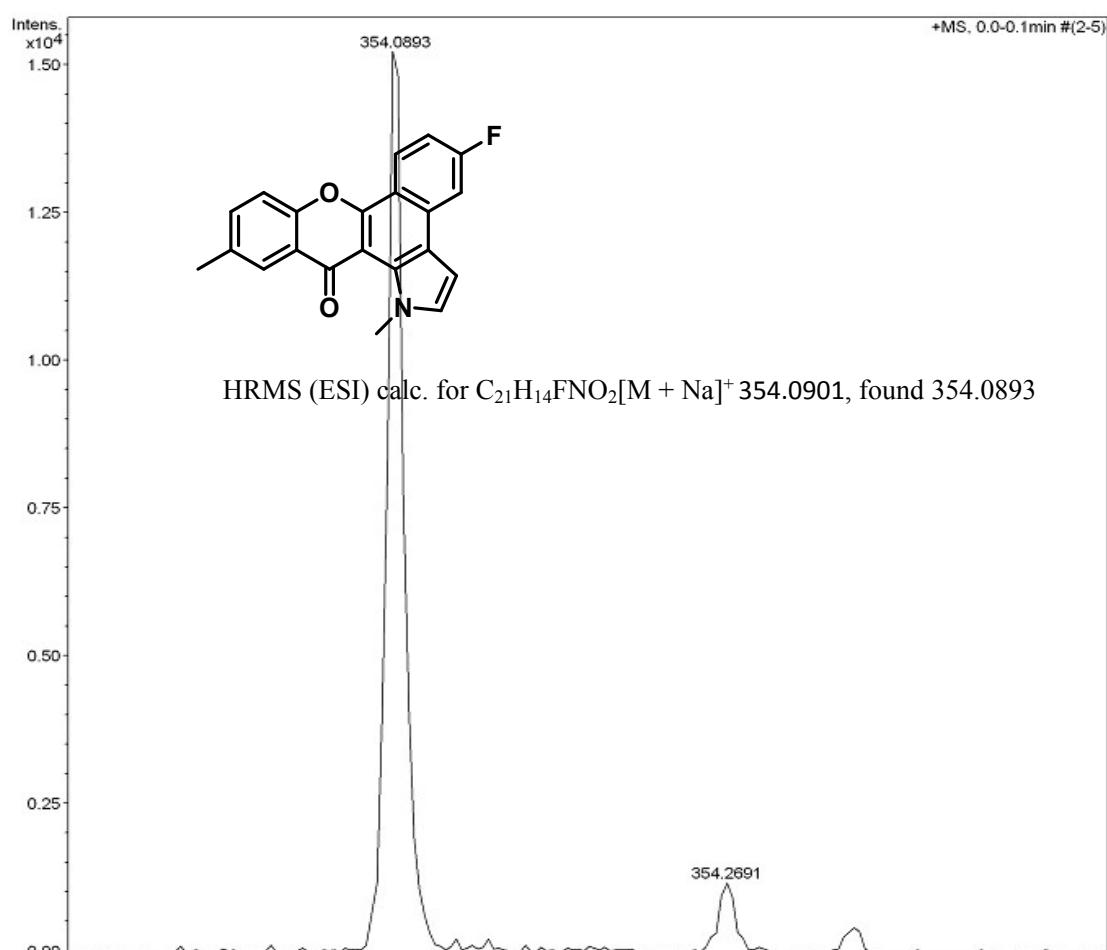
Compound 3m HRMS(MeOH)



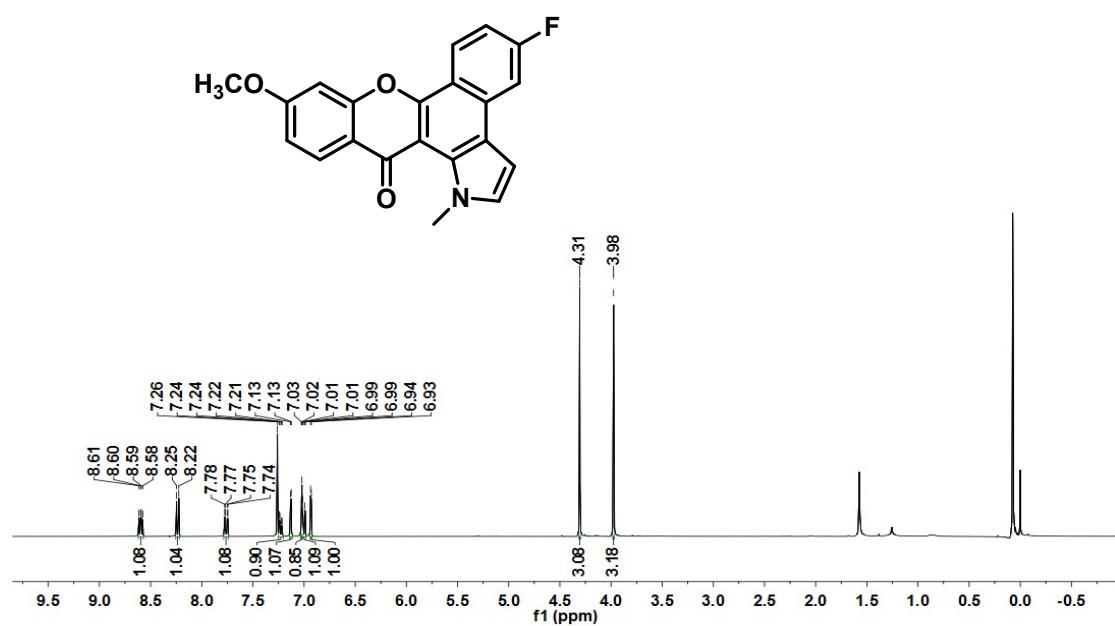
Compound 3n ^1H NMR(CDCl_3)



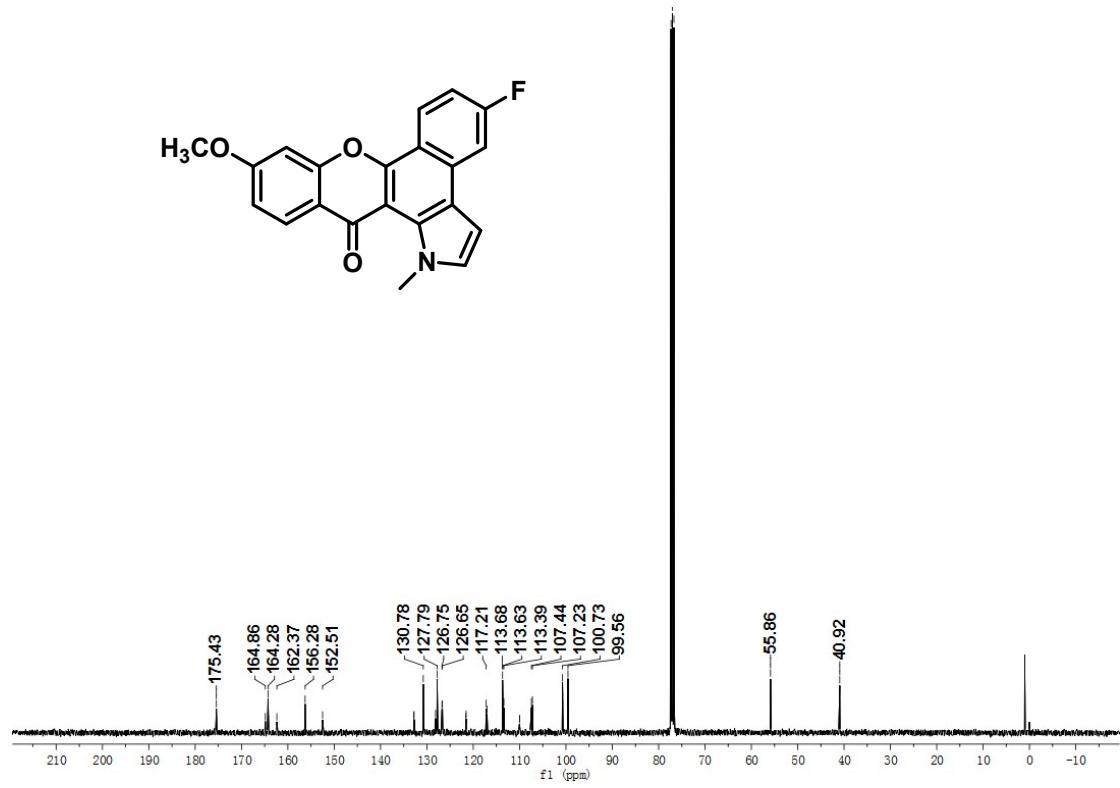
Compound 3n ^{13}C NMR (CDCl_3)



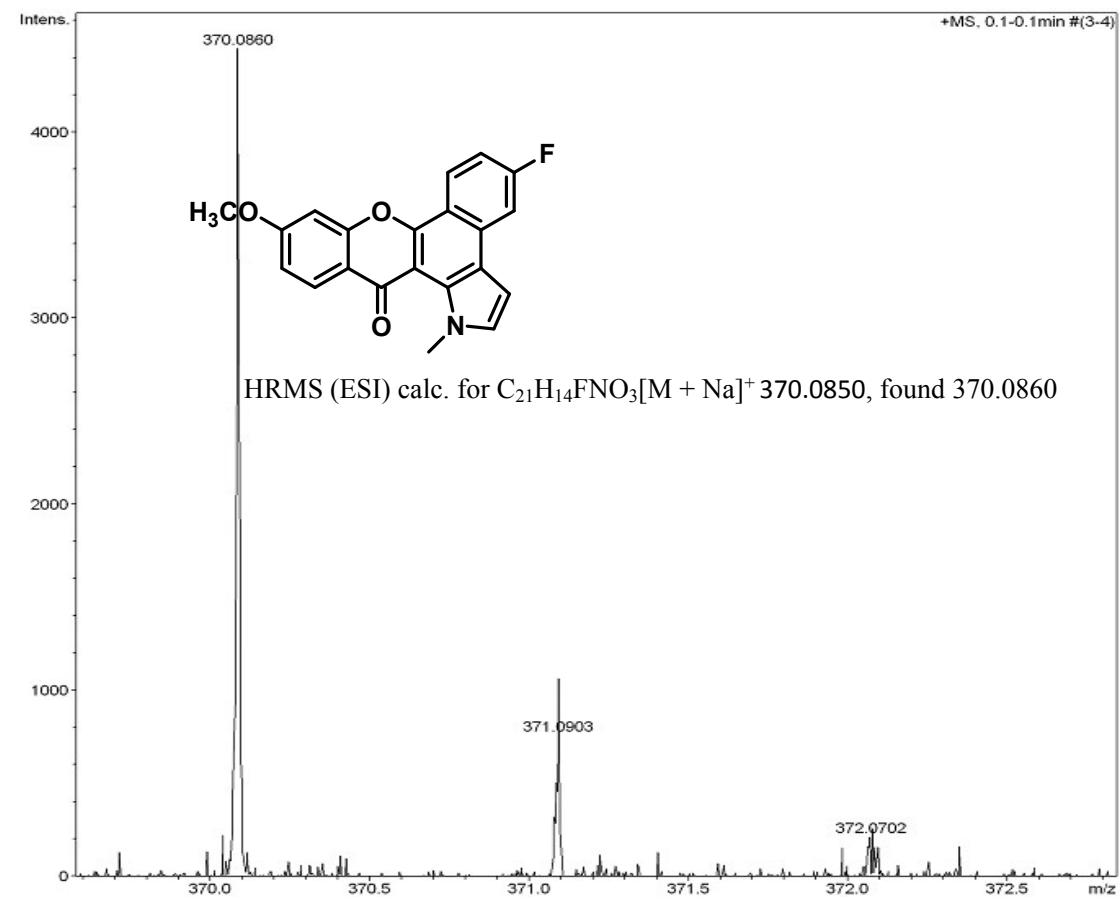
Compound 3n HRMS(MeOH)



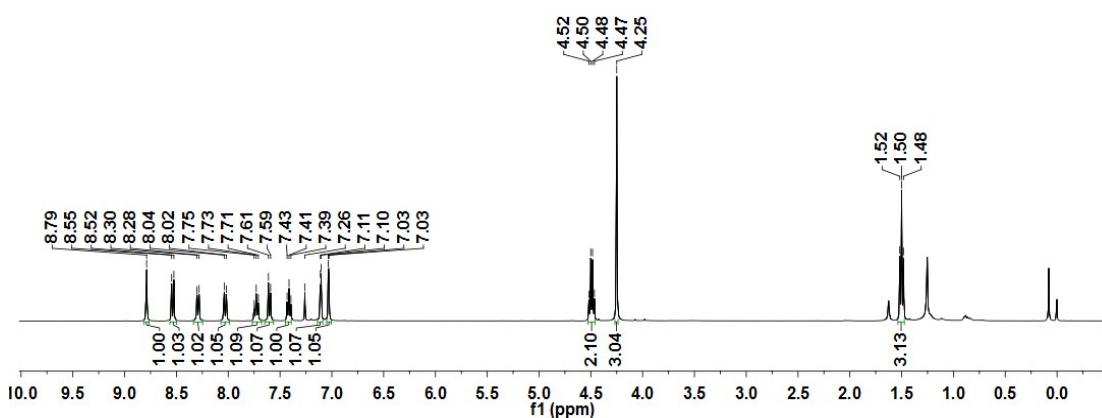
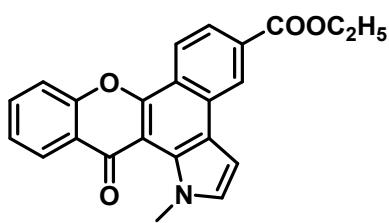
Compound 3o ¹H NMR(CDCl₃)



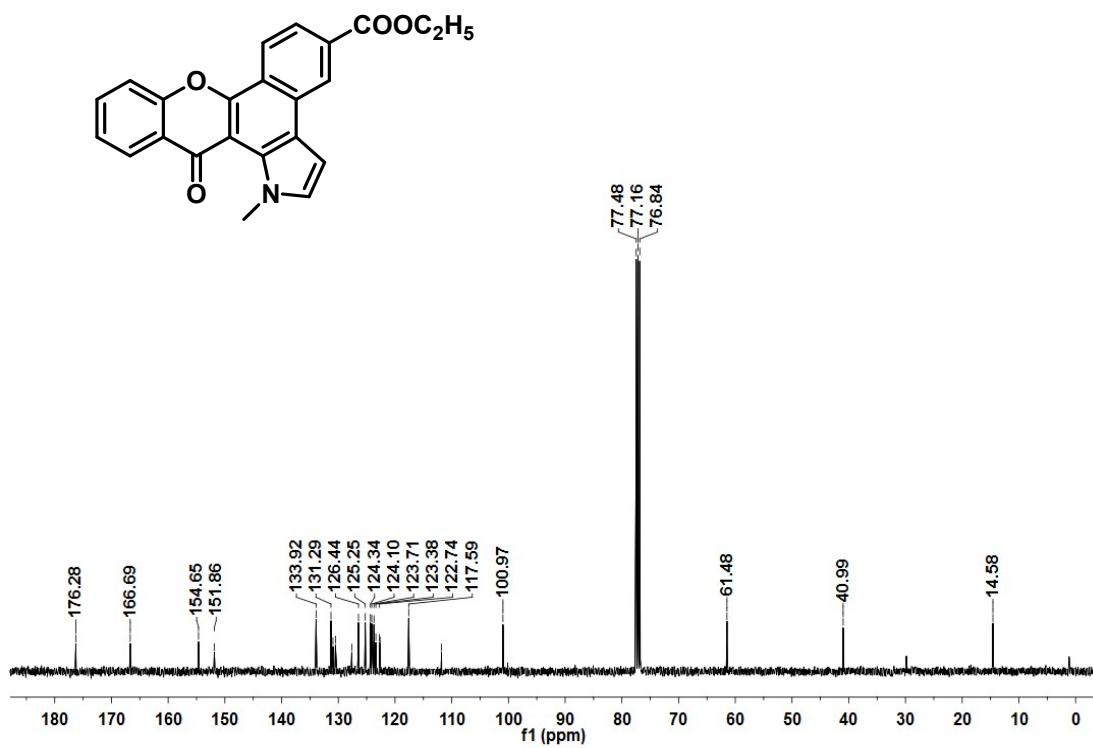
Compound 3o ^{13}C NMR (CDCl_3)



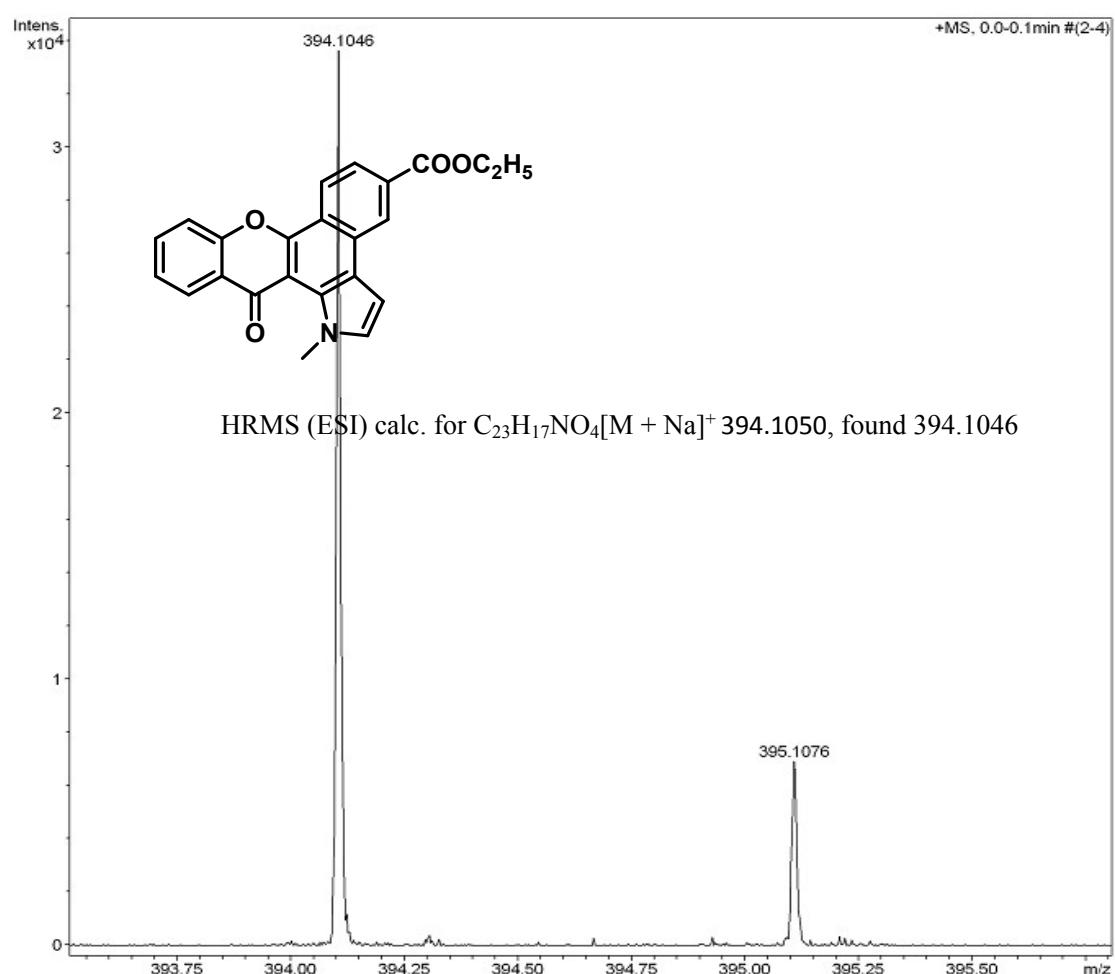
Compound 3o HRMS(MeOH)



Compound 3p ^1H NMR(CDCl_3)

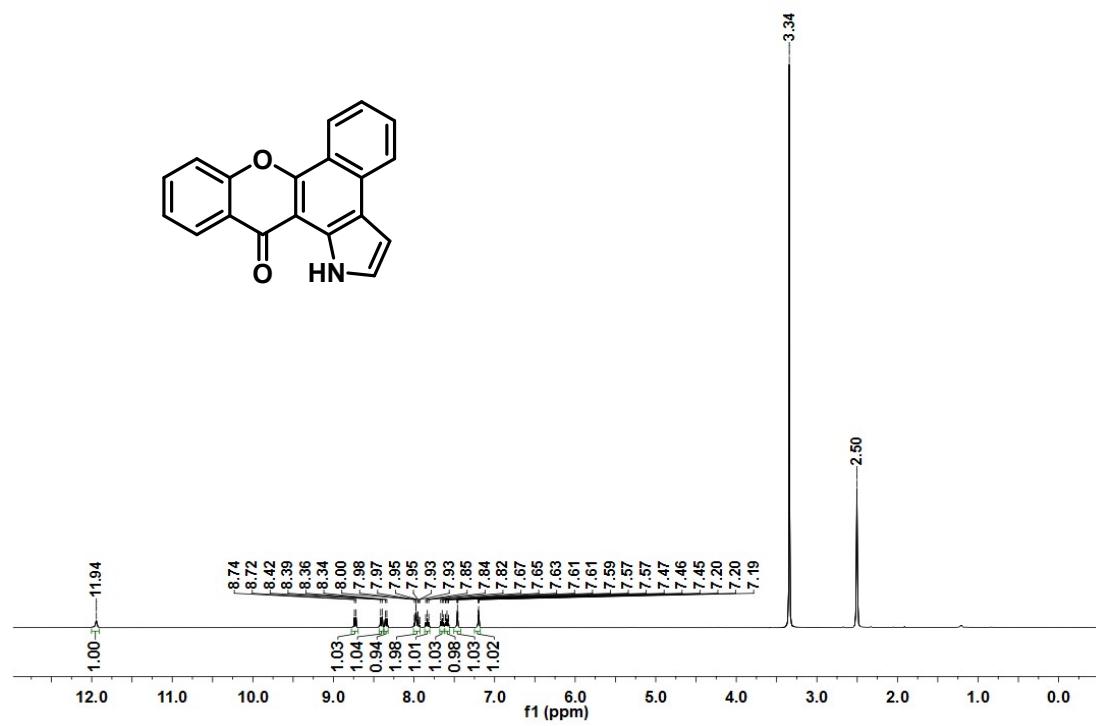


Compound 3p ^{13}C NMR (CDCl_3)



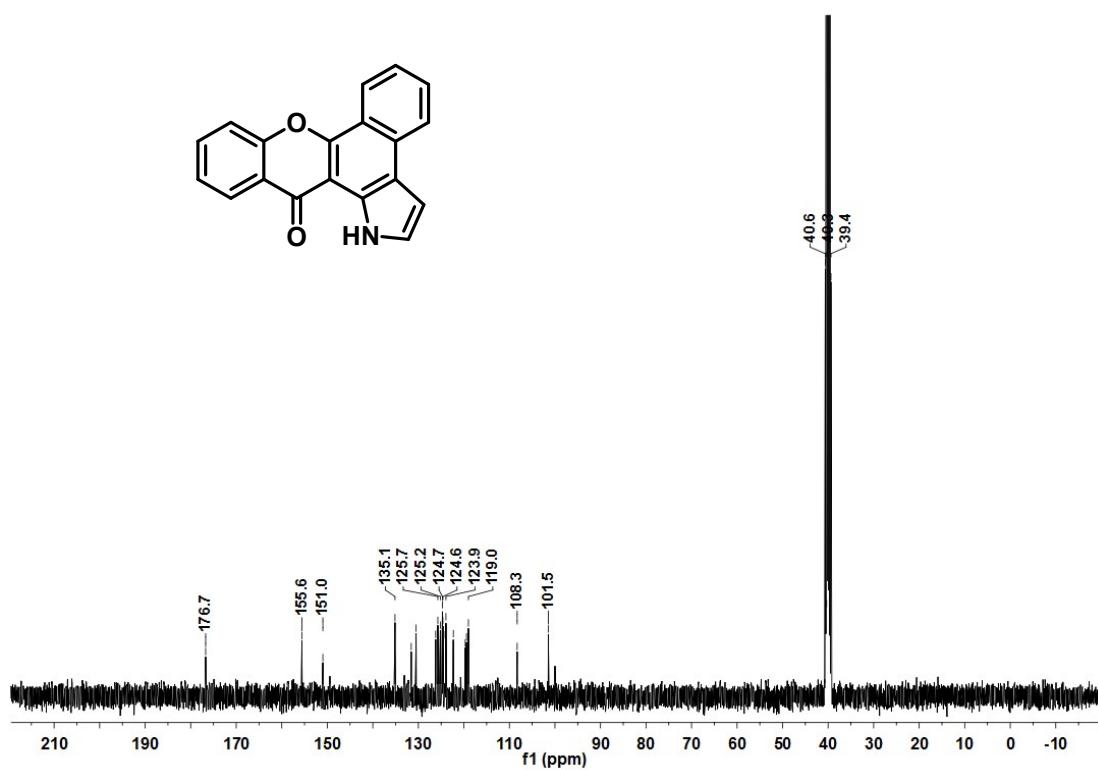
Compound 3p

HRMS(MeOH)

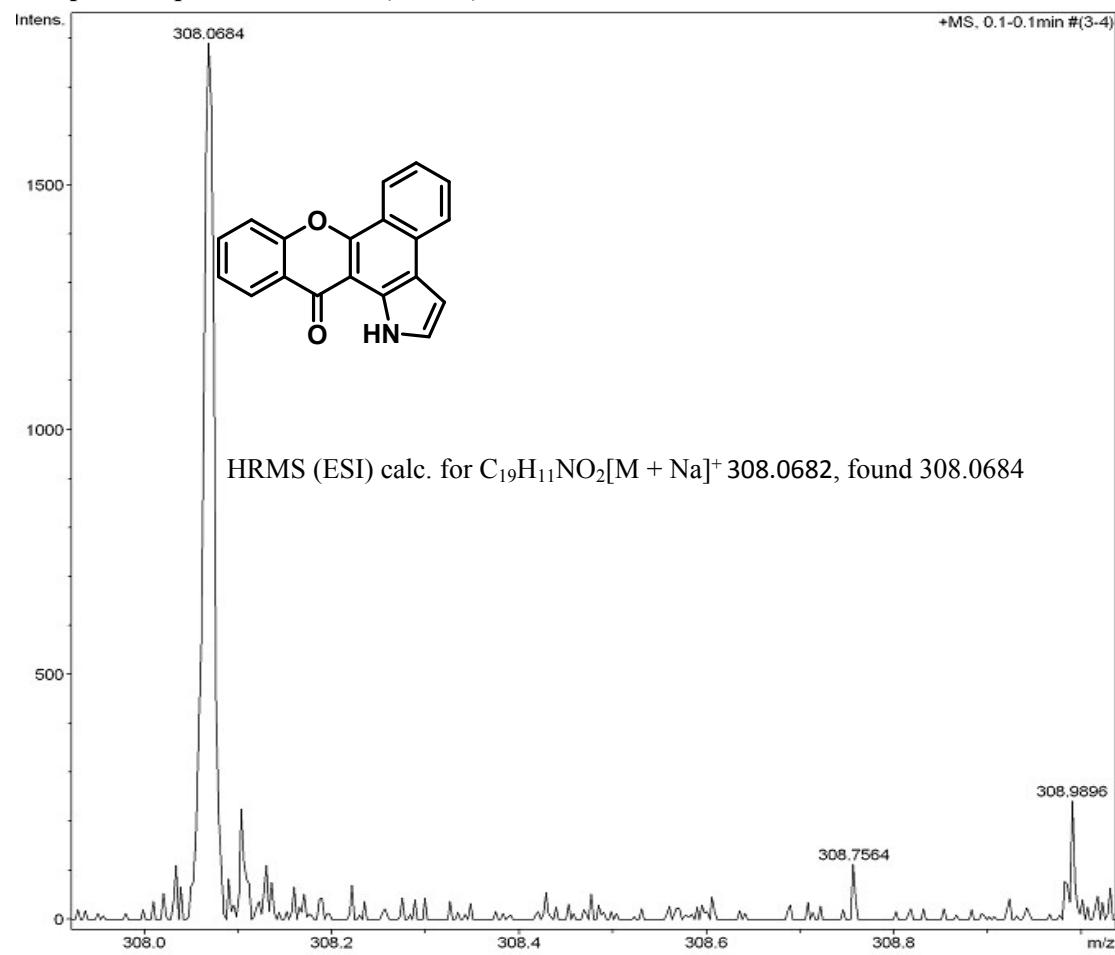


Compound 3q

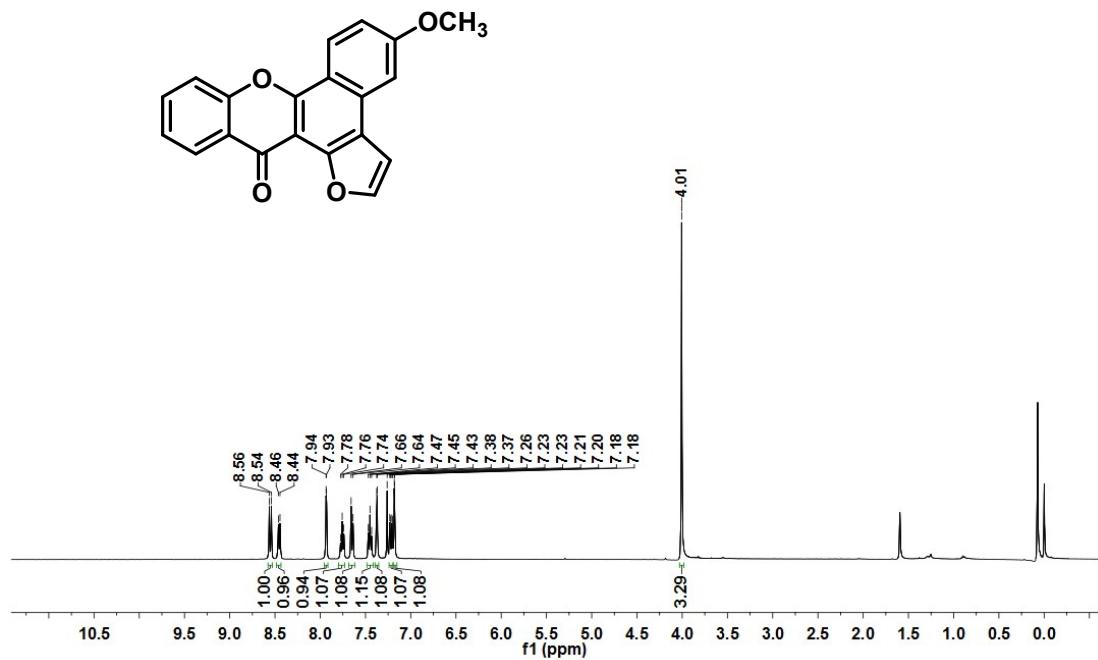
^1H NMR(DMSO)



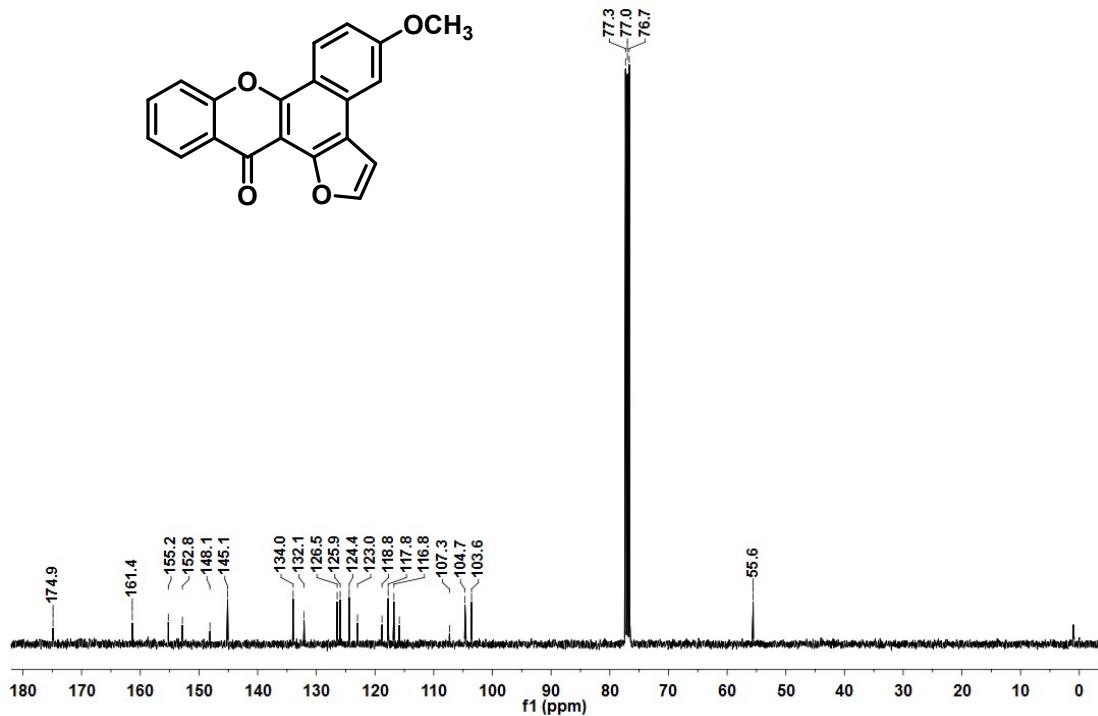
Compound 3q ^{13}C NMR (DMSO)



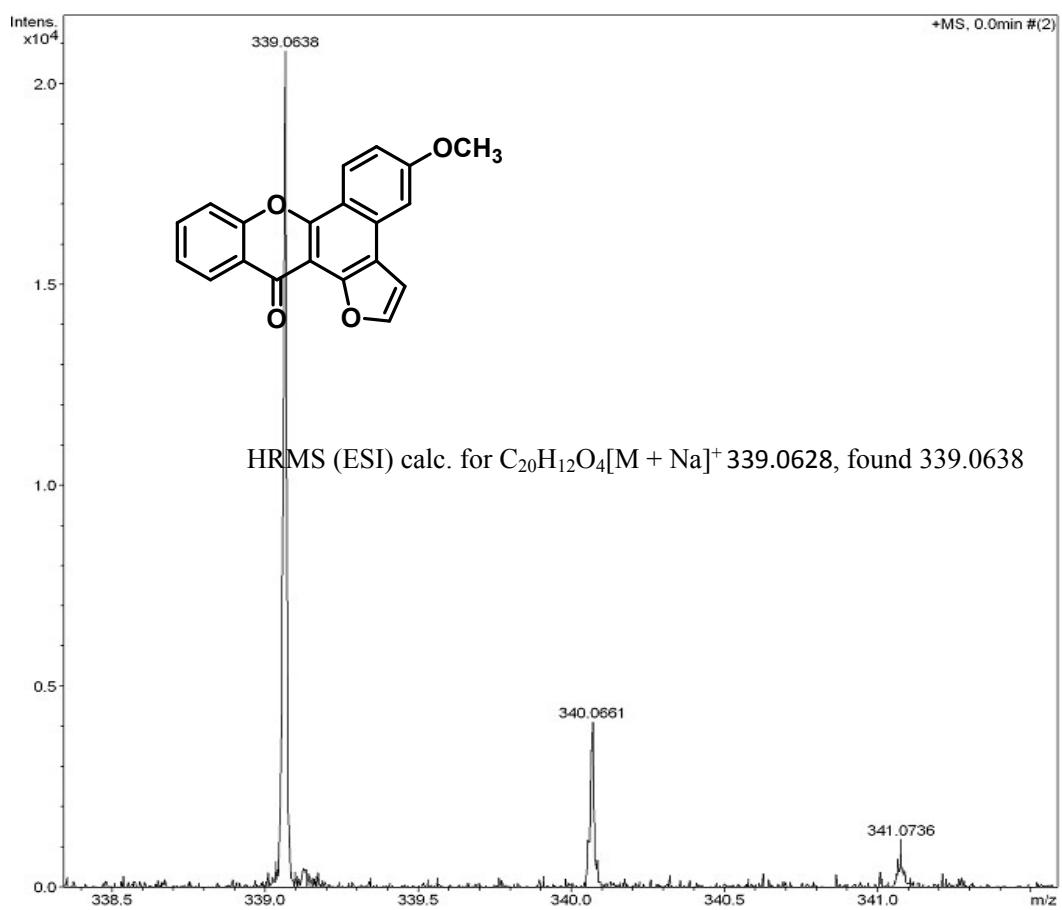
Compound 3q HRMS(MeOH)



Compound 3r ^1H NMR(CDCl_3)

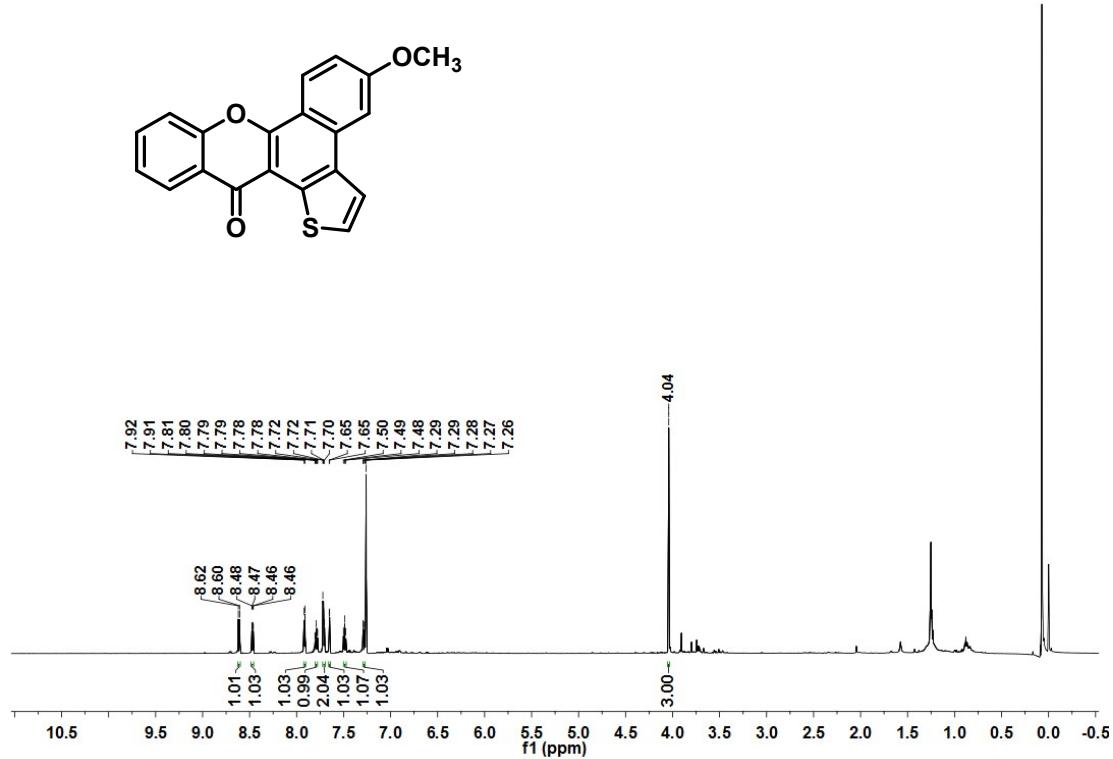


Compound 3r ^{13}C NMR (CDCl_3)



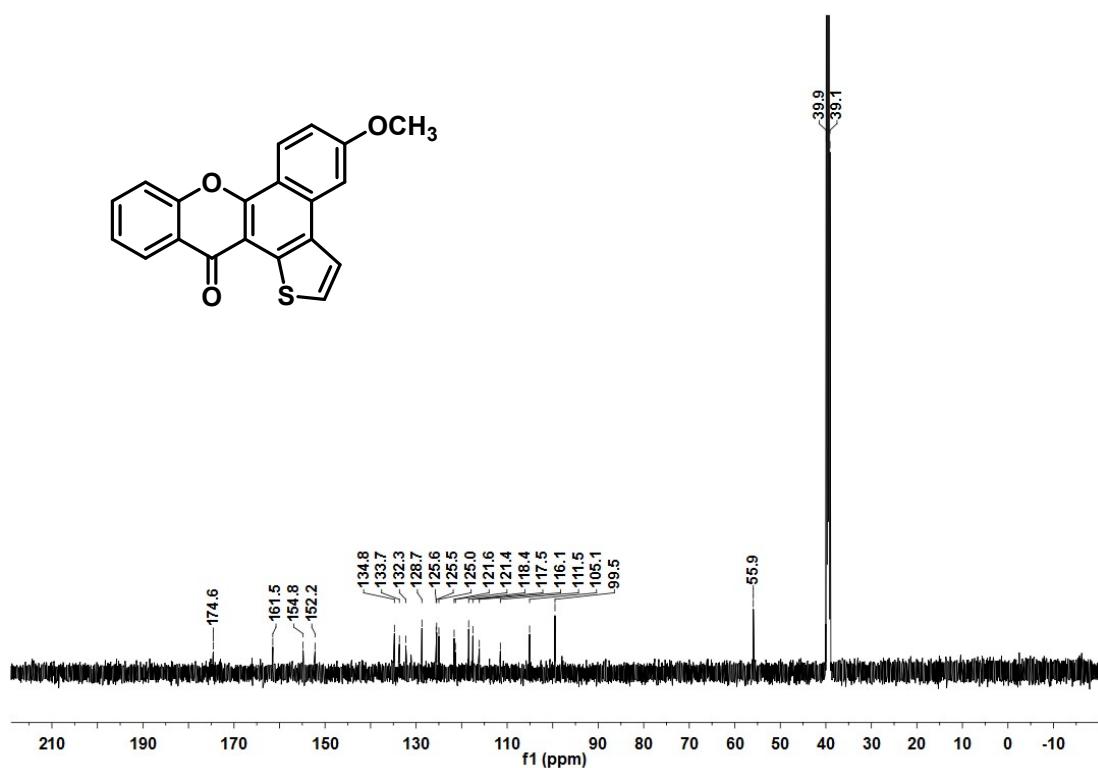
Compound 3r

HRMS(MeOH)

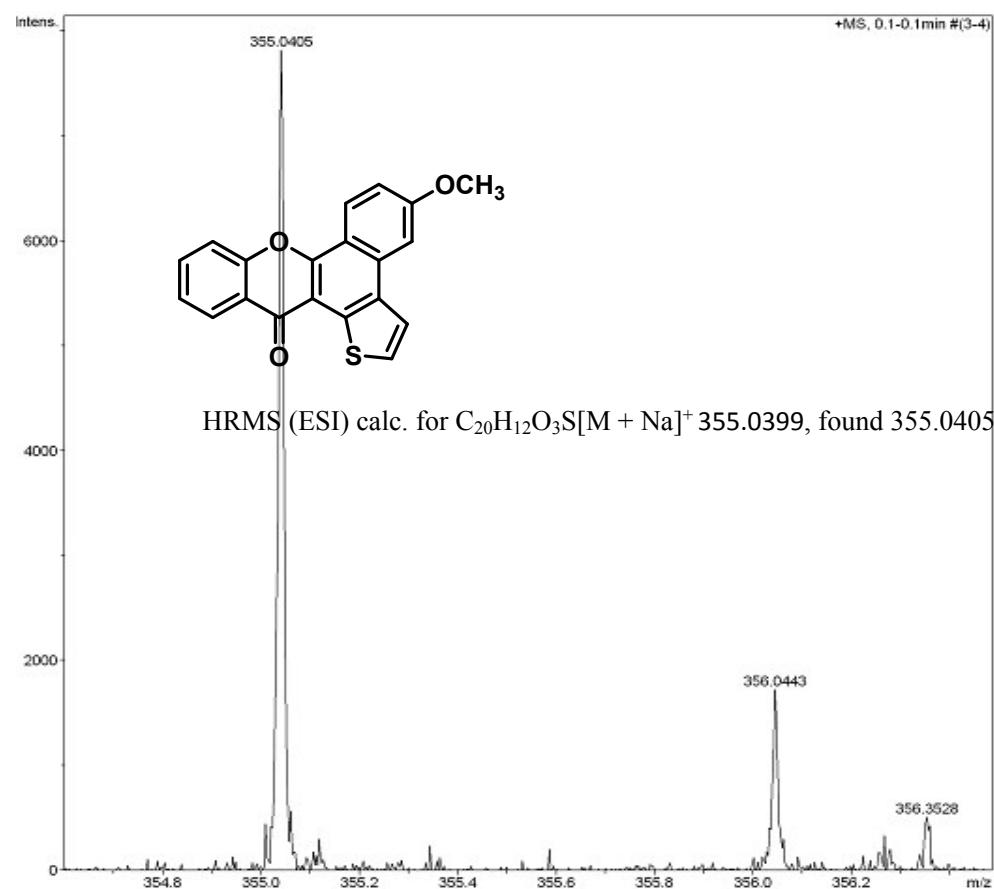


Compound 3s

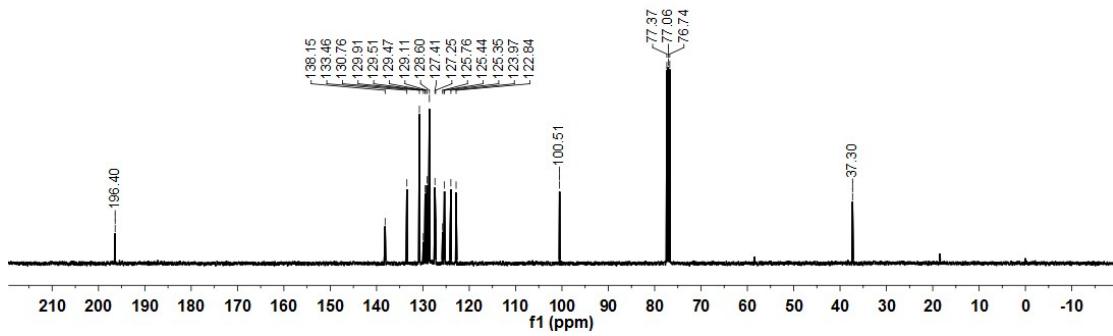
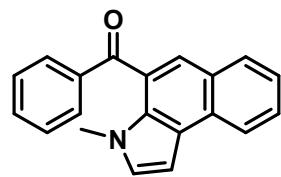
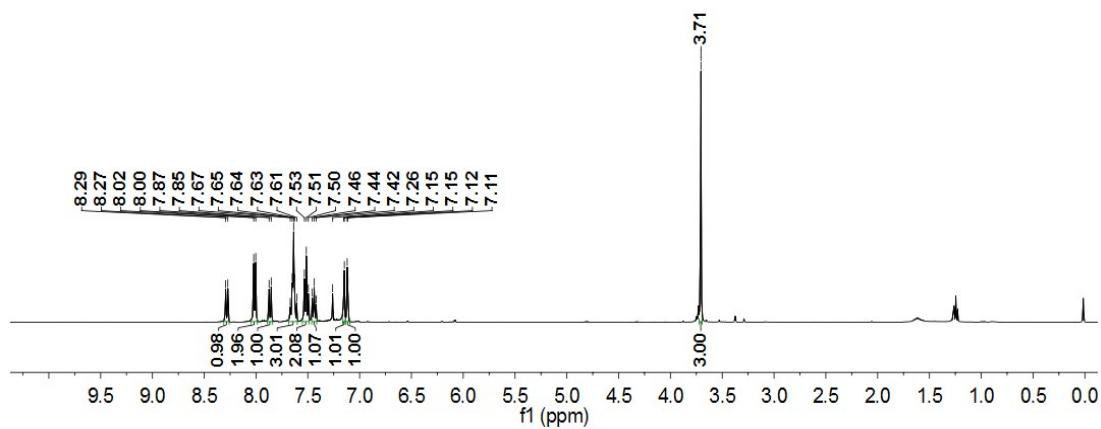
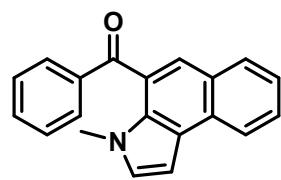
^1H NMR(CDCl_3)



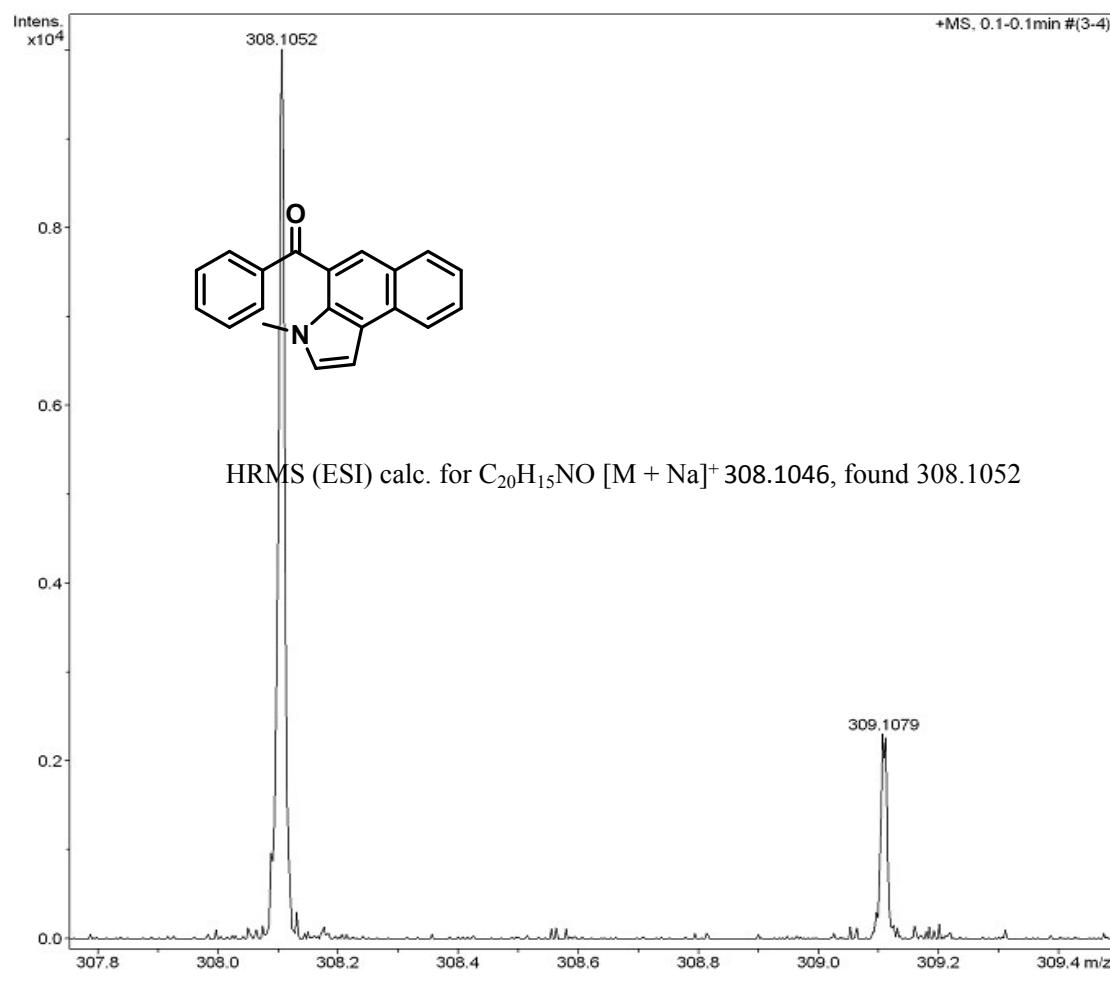
Compound 3s ^{13}C NMR (DMSO)



Compound 3s HRMS(MeOH)

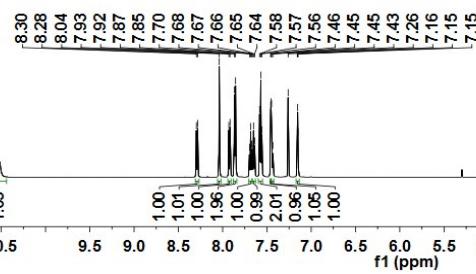
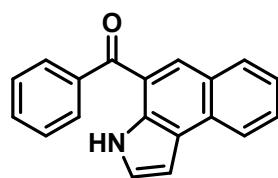


Compound 5a ^{13}C NMR (CDCl_3)



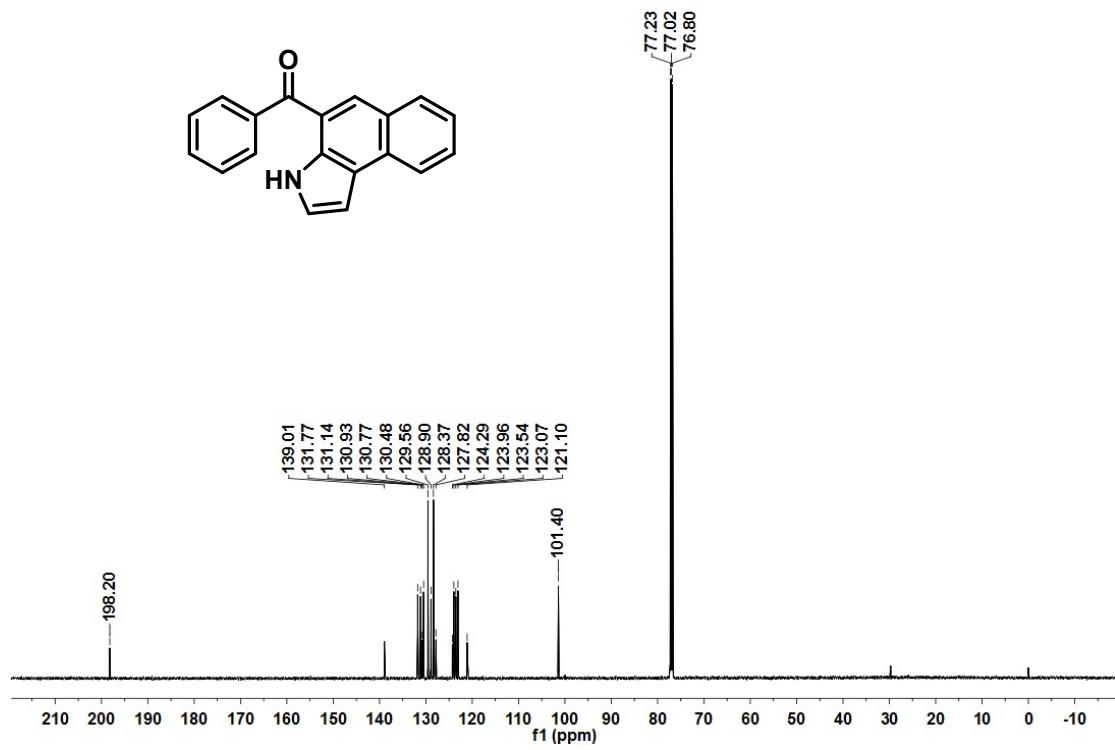
Compound 5a

HRMS(MeOH)

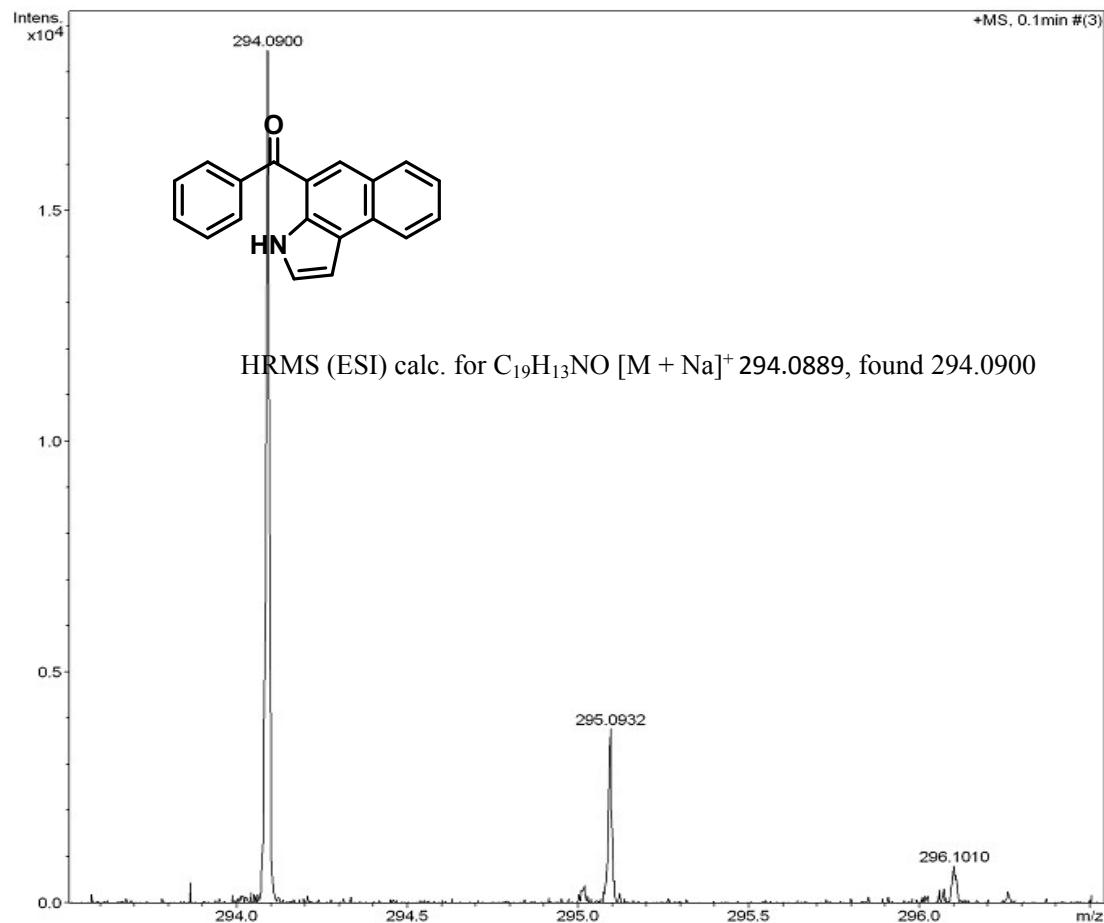


Compound 5b

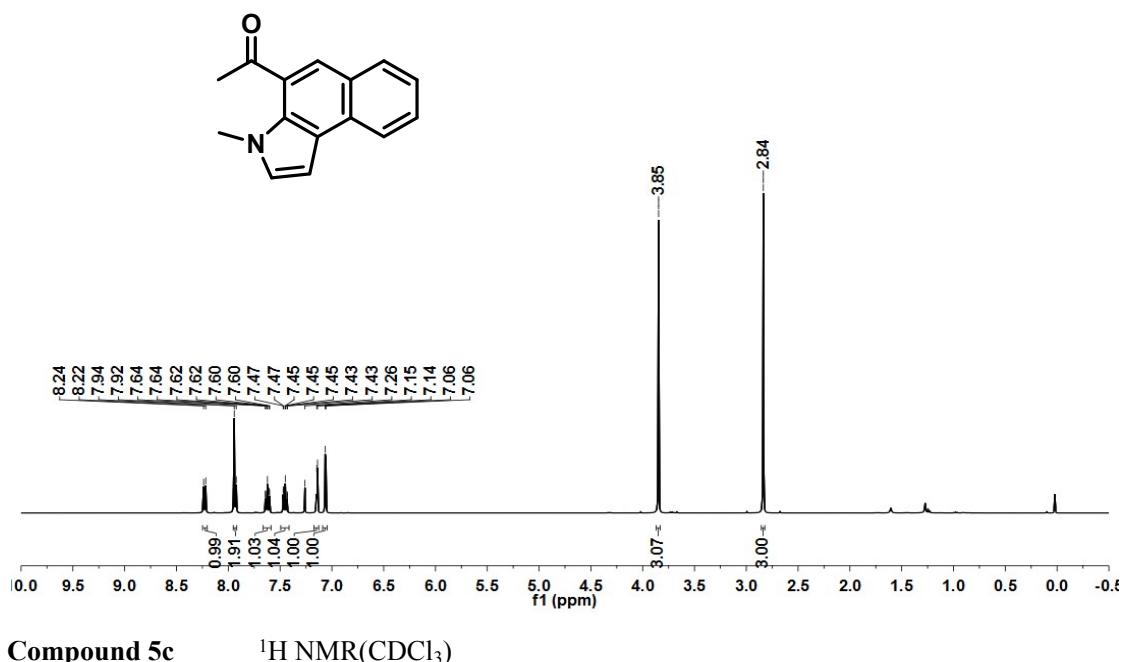
1H NMR($CDCl_3$)



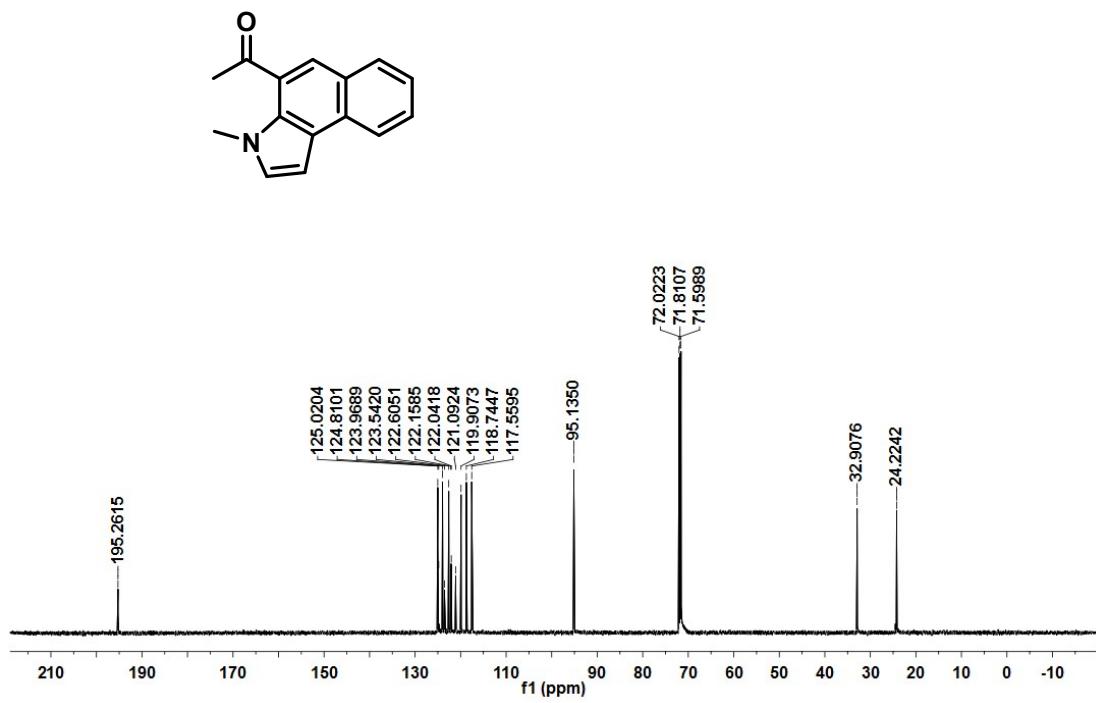
Compound 5b ^{13}C NMR (CDCl_3)



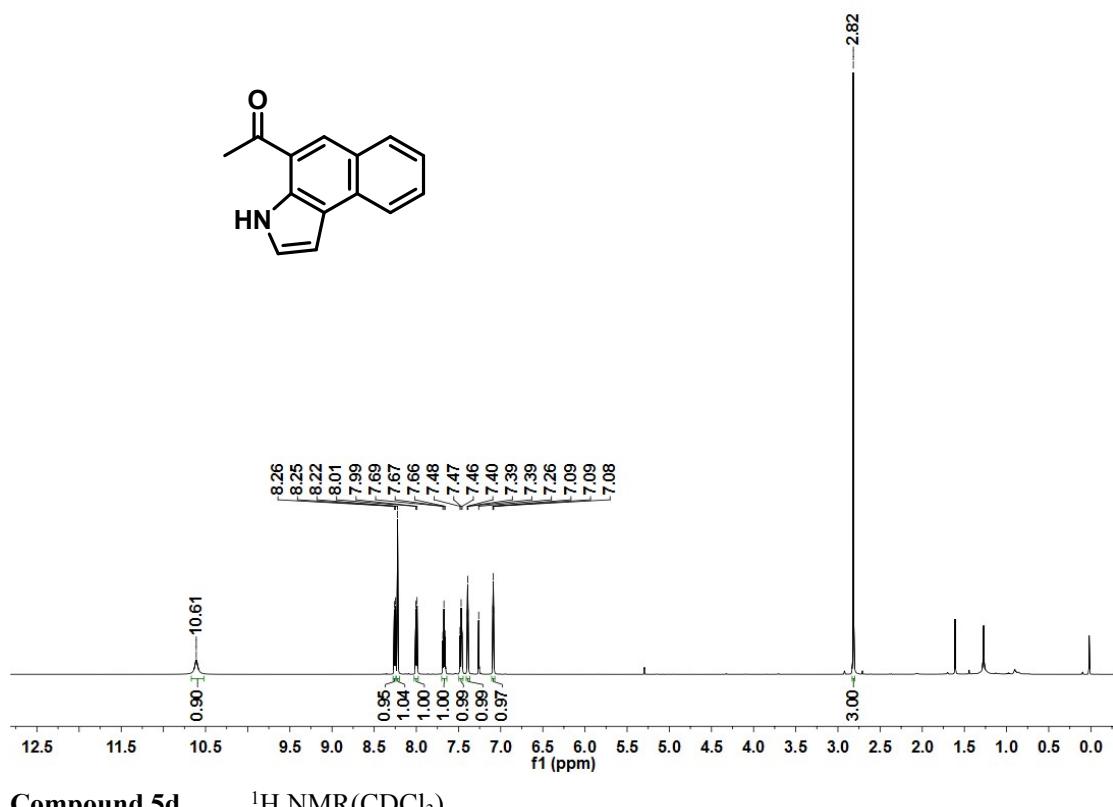
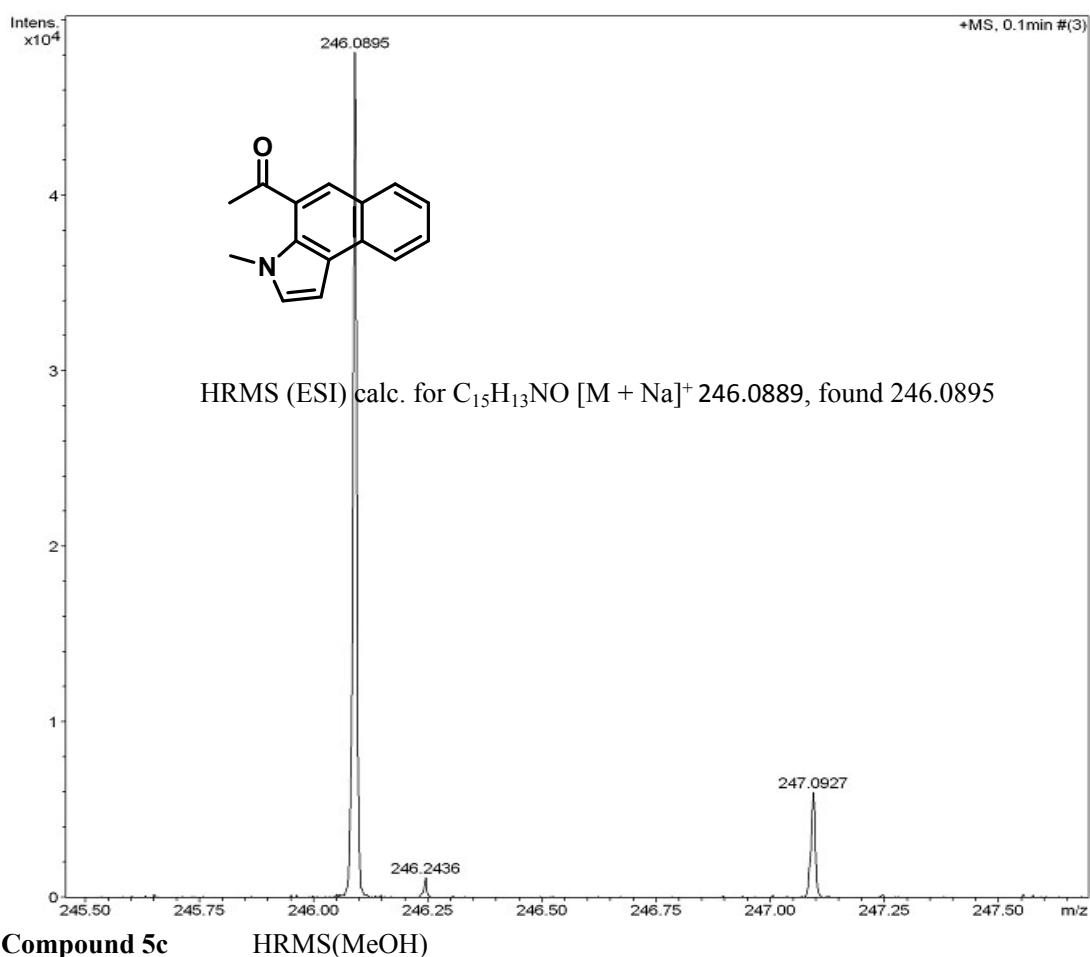
Compound 5b HRMS(MeOH)

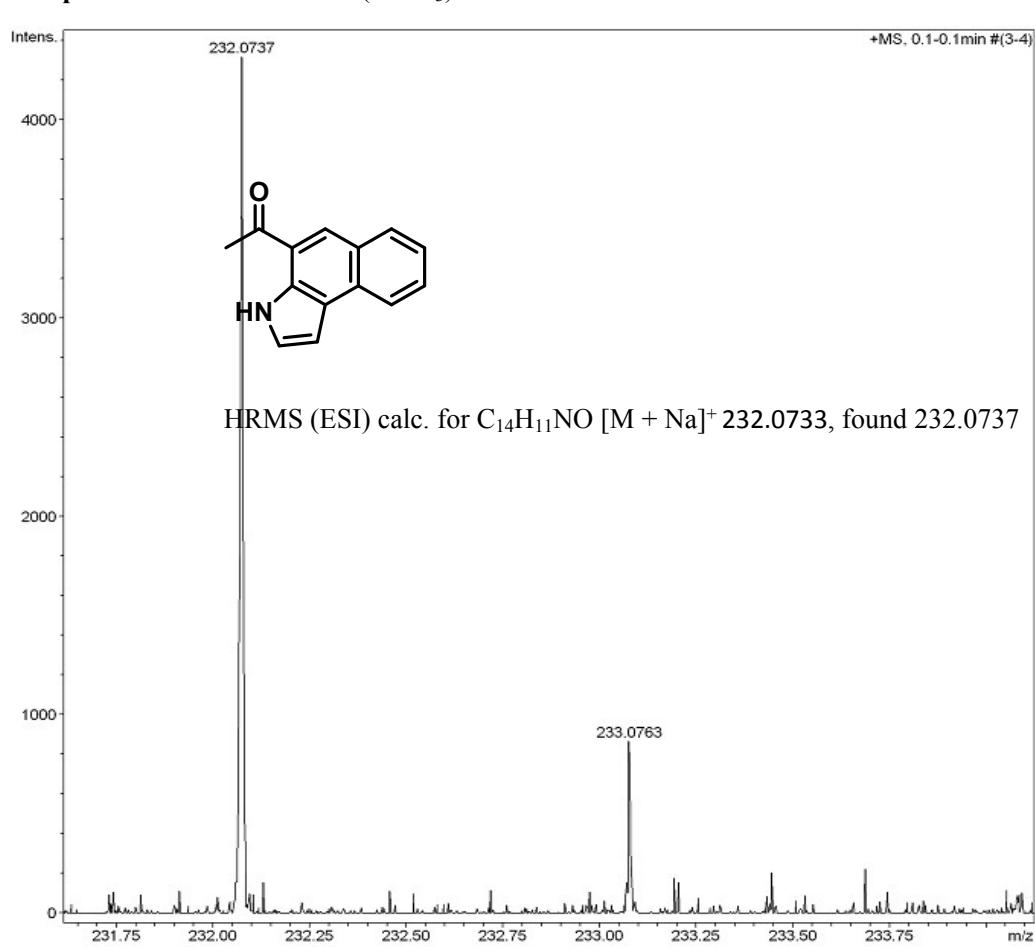
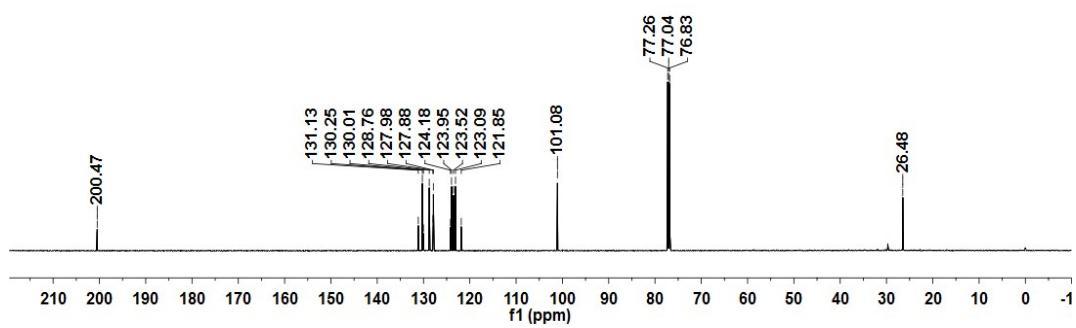
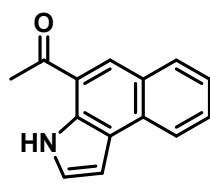


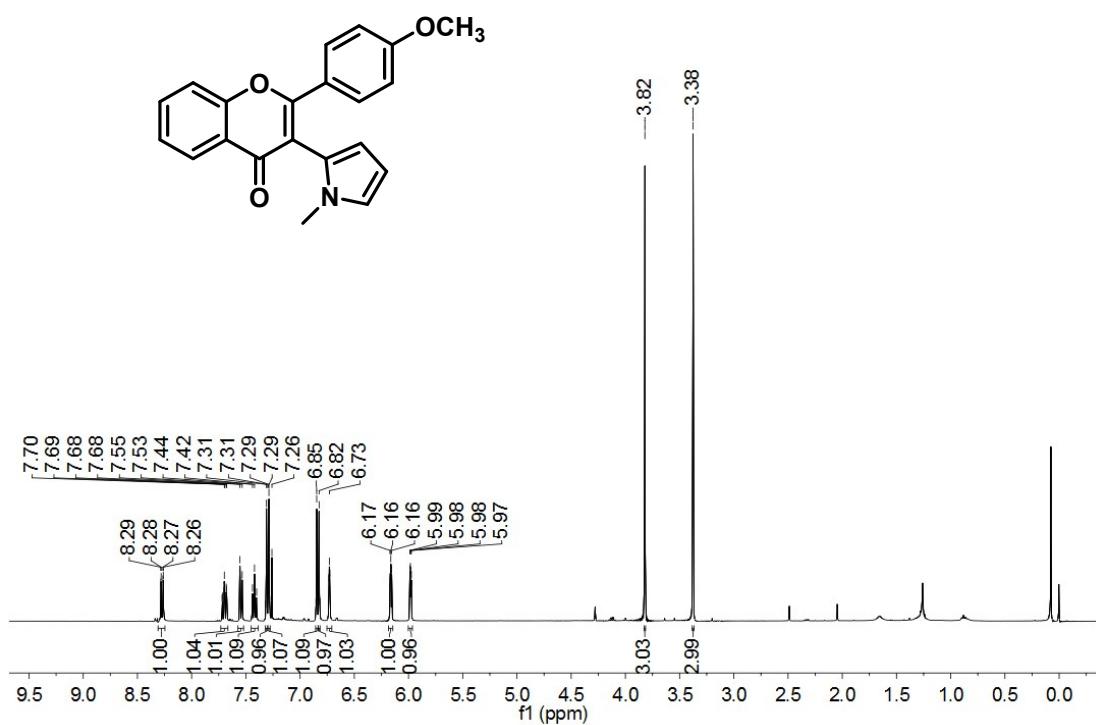
Compound 5c ¹H NMR (CDCl_3)



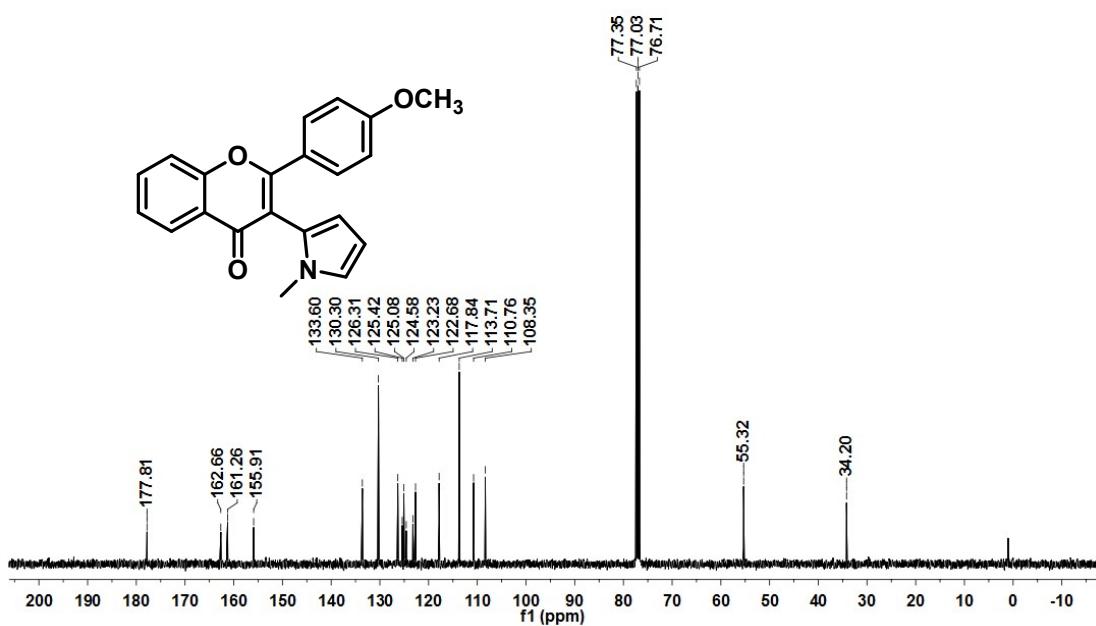
Compound 5c ¹³C NMR (CDCl_3)



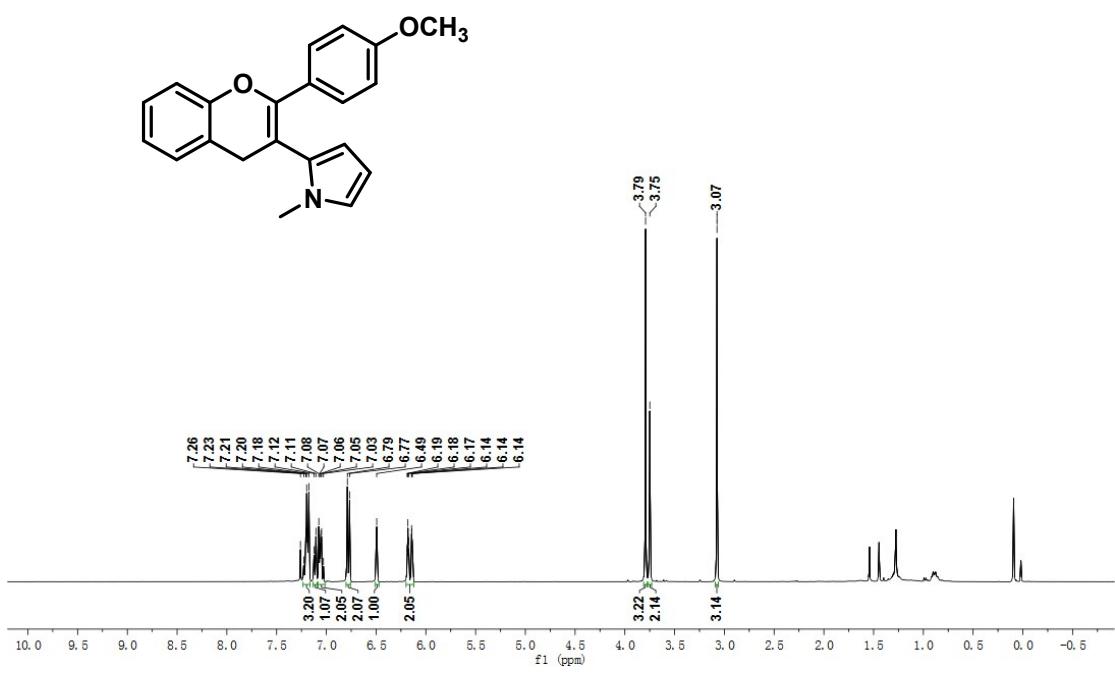
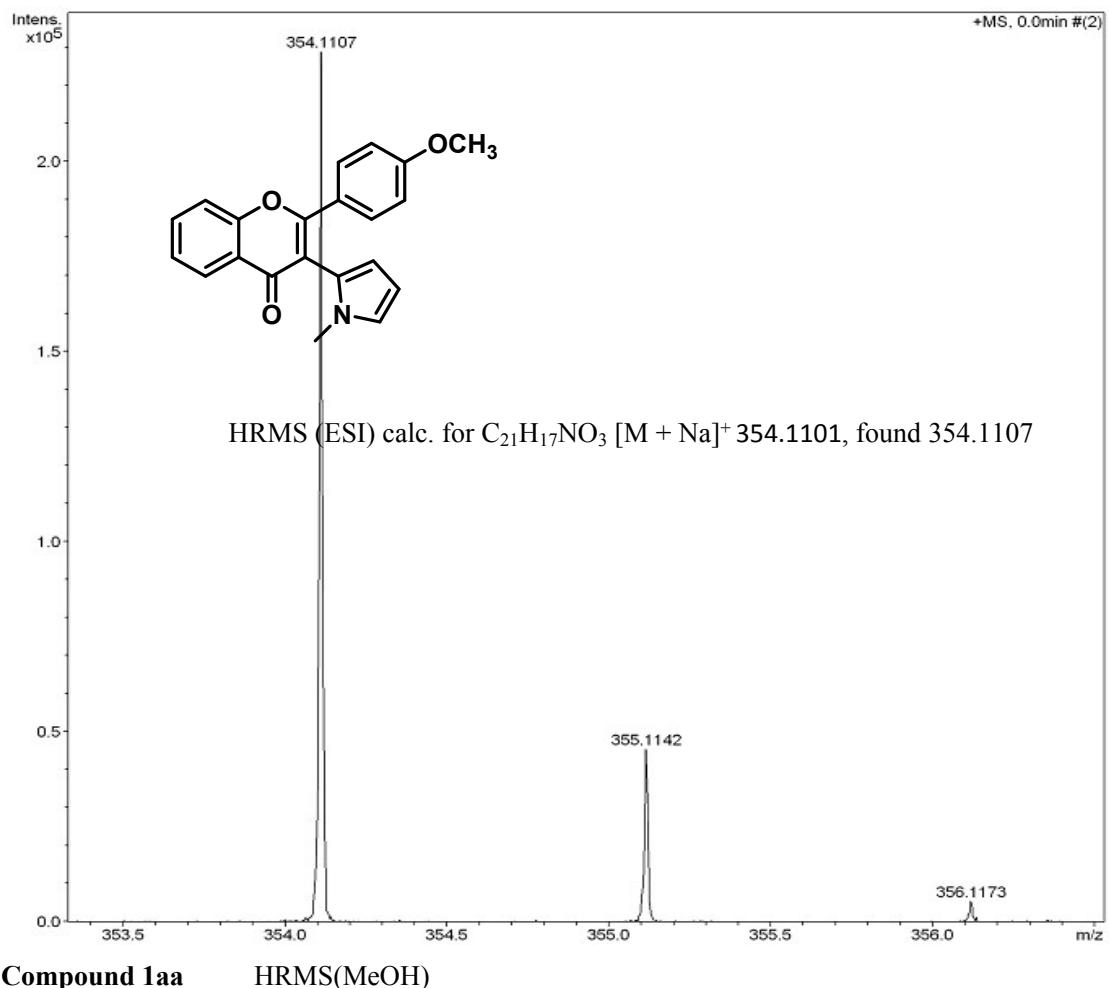


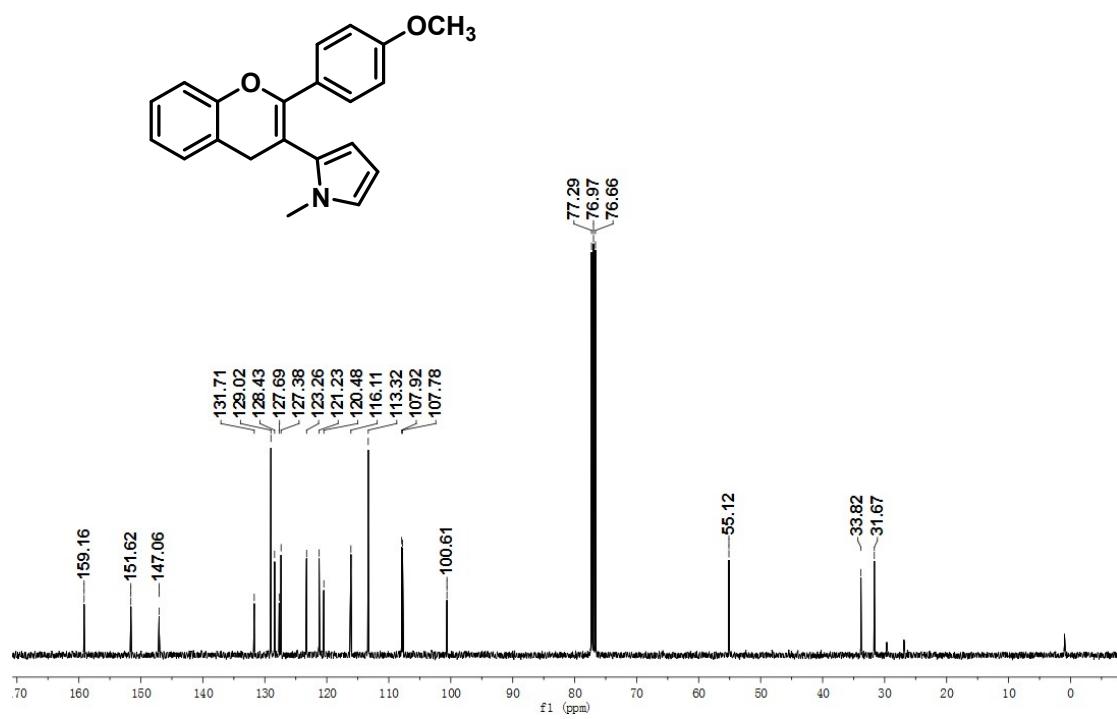


Compound 1aa ^1H NMR(CDCl_3)

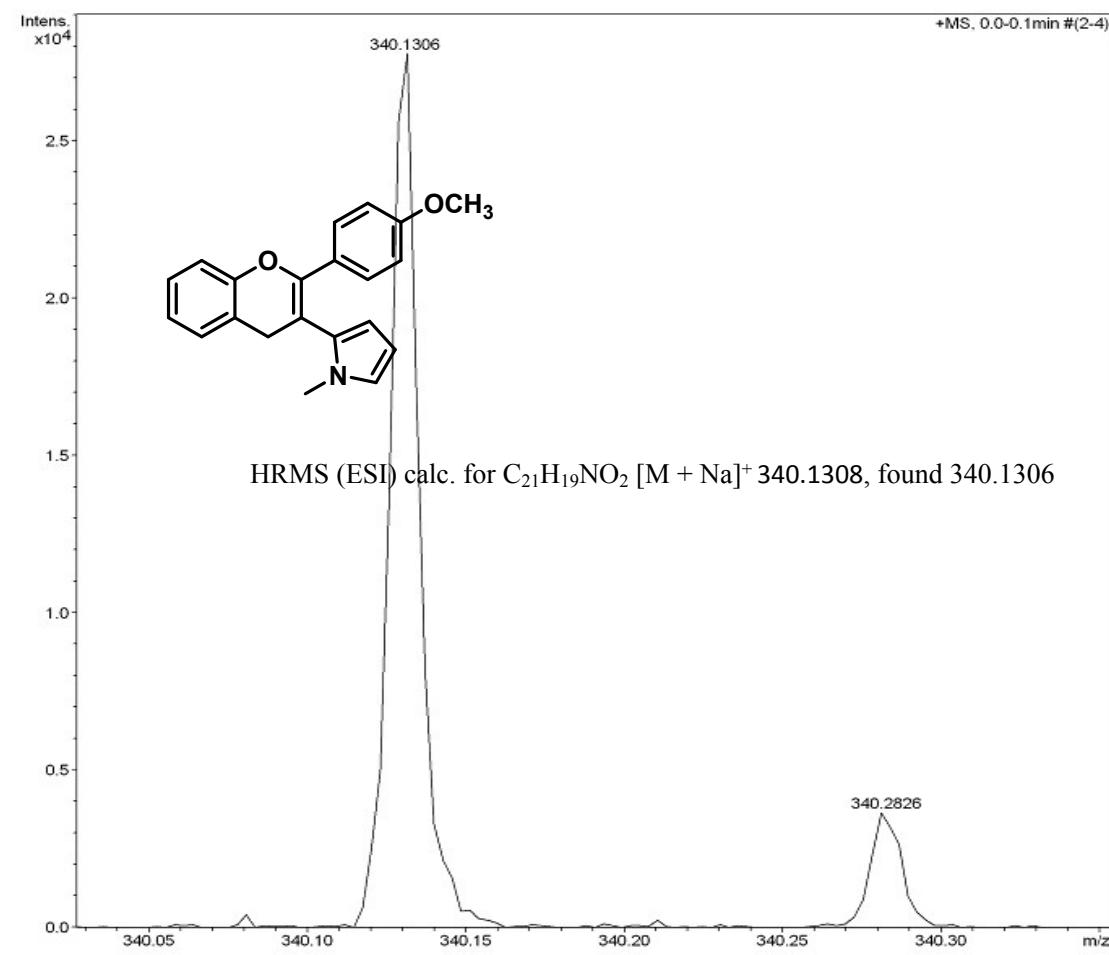


Compound 1aa ^{13}C NMR (CDCl_3)





Compound 1ab ^{13}C NMR (CDCl_3)



Compound 1ab HRMS(MeOH)