SUPPORTING INFORMATION

Gold nanoparticles supported on TiO_2 catalyse the cycloisomerisation/oxidative dimerisation of aryl propargyl ethers

Christina Efe, Ioannis N. Lykakis, and Manolis Stratakis*

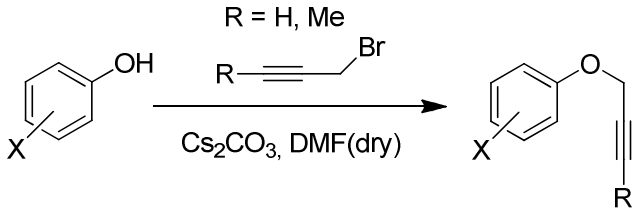
Department of Chemistry, University of Crete, Voutes 71003, Iraklion, Greece.
E-mail: stratakis@chemistry.uoc.gr

Table of Contents

Experimental Section

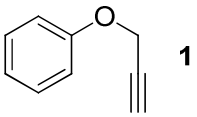
Nuclear magnetic resonance spectra were obtained on 300 and 500 MHz instruments. Isomeric purities were determined by ^{1}H NMR and by GC analysis on a 60 meters HP-5 capillary column. All spectra reported herein were recorded in $CDCl_3$.

Synthesis of propargyl aryl ethers 1-9



Propargyl aryl ethers **1-9** were prepared in yields ranging from 85-97% by alkylation of the corresponding phenols with propargyl bromide or 1-bromo-2-butyne. In a typical example, 1 equivalent of phenol was dissolved in dry DMF (1 mL of solvent per 1 mmol of phenol), and then 1.2 equivalents of Cs_2CO_3 were added. After 15 minutes 1.3 equivalents of propargyl bromide (substrates **1**-**6**) or 1-bromo-2-butyne (substrates **7**-**9**) were added at ambient temperature. The reaction was monitored by TLC and after completion (1-3 h), the mixture was diluted with ether and washed at least 3 times with brine, to completely remove DMF. The ethers **1**-**9** were isolated after solvent evaporation without requiring further purification.

(Prop-2-yn-1-yloxy)benzene (1)[1]

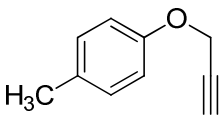


1

^{1}H NMR: 7.36 (dt, J_1=8.0 Hz, J_2=1.0 Hz, 2H), 7.06 (t, J=7.0 Hz, 3H), 4.72 (d, J=2.5 Hz, 2H), 2.60 (t, J=2.5 Hz, 1H).

^{13}C NMR: 157.4, 129.4, 121.5, 114.8, 78.6, 75.4, 55.6.

1-Methyl-4-(prop-2-yn-1-yloxy)benzene (2)[1]

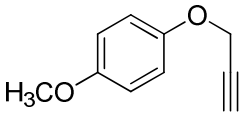


2

^{1}H NMR: 7.10 (d, J=8.5 Hz, 2H), 6.86 (d, J=8.5 Hz, 2H), 4.66 (d, J=2.5 Hz, 2H), 2.50 (t, J=2.5 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR: 155.4, 130.9, 129.9, 114.8, 78.8, 75.3, 55.9, 20.5.

1-Methoxy-4-(prop-2-yn-1-yloxy)benzene (3)[1]

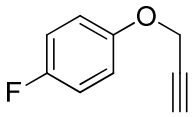


3

^{1}H NMR: 6.93 (d, *J*=9.0 Hz, 2H), 6.85 (d, *J*=9.0 Hz, 2H), 4.64 (d, *J*=2.5 Hz, 2H), 3.78 (s, 3H), 2.51 (t, *J*=2.5 Hz, 1H).

^{13}C NMR: 154.5, 151.6, 116.1, 114.6, 78.9, 75.3, 56.6, 55.7.

1-Fluoro-4-(prop-2-yn-1-yloxy)benzene (4)[2]

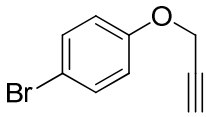


4

^{1}H NMR: 6.97 (m, 4H), 4.66 (d, *J*=2.5 Hz, 2H), 2.52 (t, *J*=2.5 Hz, 1H).

^{13}C NMR: 157.8 (d, *J*=238.0 Hz), 153.6 (d, *J*=2.0 Hz), 116.2 (d, *J*=8.0 Hz), 115.9 (d, *J*=23.0 Hz), 78.2, 75.6, 56.5.

1-Bromo-4-(prop-2-yn-1-yloxy)benzene (5)[3]

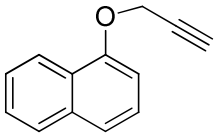


5

^{1}H NMR: 7.38 (d, *J*=7.0 Hz, 2H), 6.85 (d, *J*=7.0 Hz, 2H), 4.65 (d, *J*=2.5 Hz, 2H), 2.51 (t, *J*=2.5 Hz, 1H).

^{13}C NMR: 156.6, 132.3, 116.7, 113.9, 78.1, 75.9, 56.0.

1-(Prop-2-yn-1-yloxy)naphthalene (6)[2]

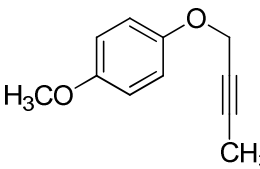


6

^{1}H NMR: 8.29 (m, 1H), 7.82 (m, 1H), 7.48-7.55 (m, 3H), 7.40 (t, *J*=8.0 Hz, 1H), 4.91 (d, *J*=2.5 Hz, 2H), 2.57 (q, *J*=2.5 Hz, 1H).

^{13}C NMR: 153.3, 134.5, 127.4, 126.5, 125.6, 125.5, 125.4, 122.0, 121.2, 105.5, 78.6, 75.5, 56.1.

1-(But-2-yn-1-yloxy)-4-methoxybenzene (7)[3]

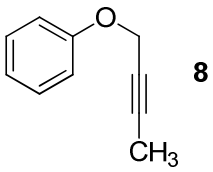


7

^{1}H NMR: 6.91 (d, *J*=8.5 Hz, 2H), 6.84 (d, J_1=8.5 Hz, 2H), 4.59 (q, *J*=2.5 Hz, 2H), 3.77 (s, 3H), 1.86 (t, *J*=2.5 Hz, 3H).

^{13}C NMR: 154.2, 151.9, 115.9, 114.5, 83.4, 74.3, 57.1, 55.6, 3.7.

(But-2-yn-1-yloxy)benzene (8)[4]

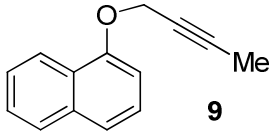


8

^{1}H NMR: 7.30 (m, 2H), 6.99 (t, *J*=7.0 Hz, 3H), 4.66 (d, *J*=2.0 Hz, 2H), 1.88 (t, *J*=2.0 Hz, 3H).

^{13}C NMR: 157.8, 129.4, 121.2, 114.8, 83.6, 74.0, 56.3, 3.7.

1-(But-2-yn-1-yloxy)naphthalene (9)[5]

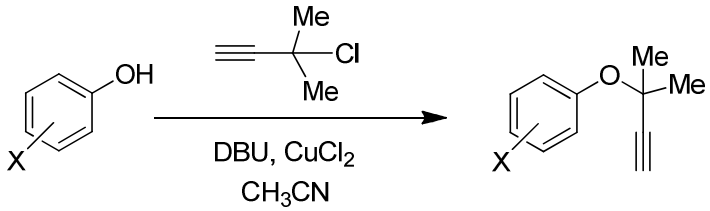


9

^{1}H NMR: 8.29 (m, 1H), 7.81 (m, 1H), 7.37-7.50 (m, 4H), 6.94 (d, *J*=7.5 Hz, 1H), 4.86 (d, *J*=2.0 Hz, 2H), 1.89 (d, *J*=2.0 Hz, 3H).

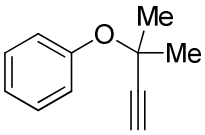
^{13}C NMR: 153.6, 134.5, 127.4, 126.4, 125.7, 125.6, 125.2, 122.1, 120.8, 105.4, 83.7, 74.1, 56.7, 3.7.

Synthesis of aryl propargyl ethers 10-12[6]



In flame dried flask were placed 1 mmol of phenol and 1 mL of anhydrous CH_3CN. At 0 ^{o}C were subsequently added 1.1 mmol of DBU, a catalytic amount (1%) of $CuCl_2 \cdot 2H_2O$ and 0.9 mmol of 3-chloro-3-methyl-1-butyne. The reaction progress was monitored by TLC and was completed after approximately 20 h at room temperature. Diethyl ether was added and the organic layer was washed with dilute HCl and brine. The ethers **10**-**12** were isolated in pure form after chromatographic purification (isolated yields: 69% for **10**, 71% for **11**, and 52% for **12**).

((2-Methylbut-3-yn-2-yl)oxy)benzene (10)[7]

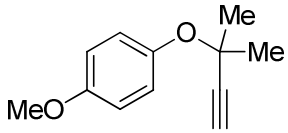


10

^{1}H NMR: 7.24 (m, 4H), 7.07 (m, 1H), 2.57 (s, 1H), 1.66 (s, 6H).

^{13}C NMR: 155.5, 128.9, 122.9, 121.5, 86.1, 73.8, 72.3, 29.6.

1-Methoxy-4-((2-methylbut-3-yn-2-yl)oxy)benzene (11)[8]

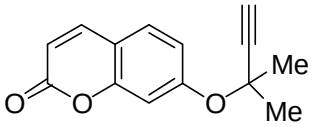


11

^{1}H NMR: 7.13 (d, *J*=8.0 Hz, 2H), 6.81 (d, *J*=8.0 Hz, 2H), 3.78 (s, 3H), 2.52 (s, 1H), 1.60 (s, 6H).

^{13}C NMR: 155.8, 148.9, 123.8, 123.7, 113.8, 113.7, 86.4, 73.5, 73.0, 55.5, 29.5.

7-((2-Methylbut-3-yn-2-yl)oxy)-2*H*-chromen-2-one (12)[9]



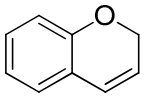
12

^{1}H NMR: 7.64 (d, *J*=9.0 Hz, 1H), 7.36 (d, *J*=8.5 Hz, 1H), 7.31 (d, *J*=2.0 Hz, 1H), 7.04 (dd, J_1=8.5 Hz, J_2=2.0 Hz, 1H), 6.27 (d, *J*=9.0 Hz, 1H), 2.66 (s, 1H). 1.71 (s, 6H).

^{13}C NMR: 161.2, 159.1, 155.0, 143.3, 128.2, 117.0, 113.7, 113.5, 107.0, 84.7, 75.2, 72.8, 29.5.

Characterization of the Au/TiO_2-catalyzed cyclization products

2*H*-Chromene (1a)[1]

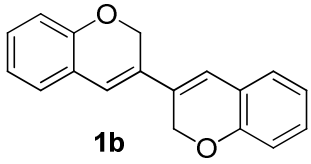


1a

^{1}H NMR: 7.11 (t, *J*=7.5 Hz, 1H), 6.96 (d, *J*=7.5 Hz, 1H), 6.87 (t, *J*=7.5 Hz, 1H), 6.78 (d, *J*=8.0 Hz, 1H), 6.43 (d, *J*=9.5 Hz, 1H), 5.77 (dt, J_1=9.5 Hz, J_2=3.5 Hz, 1H), 4.83 (m, 1H).

^{13}C NMR: 154.0, 129.1, 126.5, 124.5, 122.4, 121.9, 121.3, 115.7, 65.5.

2*H*,2'*H*-3,3'-Bichromene (1b)



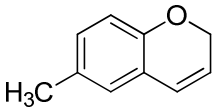
1b

^{1}H NMR: 7.13 (dt, J_1=8.0 Hz, J_2=1.5 Hz, 2H), 7.05 (dd, J_1=8.0 Hz, J_2=1.5 Hz, 2H), 6.90 (dt, J_1=7.0 Hz, J_2=0.5 Hz, 2H), 6.84 (d, *J*=8.0 Hz, 2H), 6.38 (s, 2H), 5.06 (s, 4H).

^{13}C NMR: 153.6, 129.5, 127.6, 127.3, 122.3, 121.7, 119.5, 115.6, 65.2.

MS (EI): 262 (M^+, 100%), 247 (55%), 245 (47%), 233 (12%), 215 (18%), 130 (27%), 115 (22%), 77 (20%).

6-Methyl-2*H*-chromene (2a)[1]

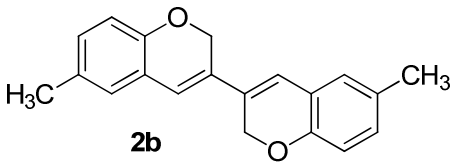


2a

^{1}H NMR: 6.90 (dd, J_1=8.0 Hz, J_2=2.0 Hz, 1H), 6.78 (s, 1H), 6.68 (d, J=8.0 Hz, 1H), 6.39 (br d, J=9.5 Hz, 1H), 5.76 (dt, J_1=9.5 Hz, J_2=3.5 Hz, 1H), 4.78 (m, 2H), 2.25 (s, 3H).

^{13}C NMR: 151.9, 130.5, 129.5, 127.1, 124.7, 122.2, 122.0, 115.4, 65.5, 20.5.

6,6'-Dimethyl-2*H*,2'*H*-3,3'-bichromene (2b)



2b

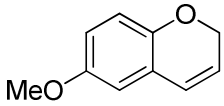
^{1}H NMR: 6.93 (d, J=8.0 Hz, 2H), 6.87 (s, 2H), 6.74 (d, J=8.0 Hz, 2H), 6.35 (s, 2H), 5.01 (s, 4H), 2.26 (s, 6H).

^{13}C NMR: 151.5, 130.9, 129.9, 127.8, 127.7, 122.1, 119.5, 115.3, 65.3, 20.5.

MS (EI): 290 (M^+, 72%), 275 (100%), 245 (10%), 232 (11%), 202 (12%), 144 (30%), 115 (31%).

HRMS: calcd for $C_{20}H_{18}O_2$+H, 291.1385; found 291.1387.

6-Methoxy-2*H*-chromene (3a)[1]

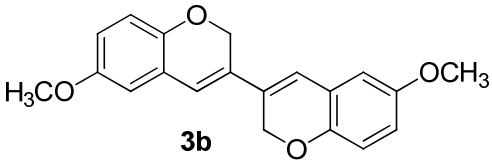


3a

^{1}H NMR: 6.71 (d, J=8.5 Hz, 1H), 6.66 (dd, J_1=8.5 Hz, J_2=3.0 Hz, 1H), 6.54 (d, J= 3.0 Hz, 1H), 6.39 (d, J=9.5 Hz, 1H), 5.81 (td, J_1=9.5 Hz, J_2=3.5 Hz, 1H), 4.75 (m, 2H), 3.75 (s, 3H).

^{13}C NMR: 154.1, 147.9, 124.7, 123.1, 123.0, 116.2, 114.1, 111.8, 65.4, 55.7.

6,6'-Dimethoxy-2*H*,2'*H*-3,3'-bichromene (3b)



3b

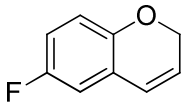
^{1}H NMR: 6.79 (d, J=8.0 Hz, 2H), 6.71 (dd, J_1=8.0 Hz, J_2=1.5 Hz, 2H), 6.63 (d, J=1.5 Hz, 2H), 6.39 (s, 2H), 5.04 (s, 4H), 3.78 (s, 6H).

^{13}C NMR: 154.4, 147.7, 128.6, 123.0, 119.8, 116.1, 115.1, 111.9, 65.3, 55.8.

MS (EI): 322 (M^+, 100%), 307 (73%), 291 (36%), 279 (10%), 161 (18%).

HRMS: calcd for $C_{20}H_{18}O_4$+Na, 345.1097; found 345.1097.

6-Fluoro-2*H*-chromene (3a)[10]

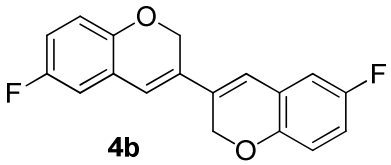


4a

^{1}H NMR: 6.65-6.80 (m, 3H), 6.37 (td, J_1=10.0 Hz, J_2=1.5 Hz, 1H), 5.84 (td, J_1=9.5 Hz, J_2=3.5 Hz, 1H), 4.78 (m, 2H).

^{13}C NMR: 157.4 (d, J=237.0 Hz), 149.9 (d, J=2.5 Hz), 124.0 (d, J=2.0 Hz), 123.4 (d, J=6.0 Hz), 116.5, 116.4, 115.0 (d, J=23.0 Hz), 112.7 (d, J=23.5 Hz), 65.5.

6,6'-Difluoro-2*H*,2'*H*-3,3'-bichromene (4b)



4b

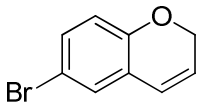
^{1}H NMR: 6.75-6.86 (m, 6H), 6.36 (s, 2H), 5.01 (s, 4H).

^{13}C NMR: 157.8 (d, J=237.5 Hz), 149.8, 128.8, 123.3, 119.7, 116.7 (d, J=5.0 Hz), 115.9 (d, J=14.0 Hz), 113.4 (d, J=14.0 Hz), 65.4.

MS (EI): 298 (M^+, 97%), 283(100%), 278 (17%), 251 (18%), 220 (21%), 162 (23%), 149 (73%), 133 (32%), 101 (46%), 75 (47%).

HRMS: calcd for $C_{18}H_{12}O_2F_2$, 298.0805; found 298.0803.

6-Bromo-2*H*-chromene (3a)[11]

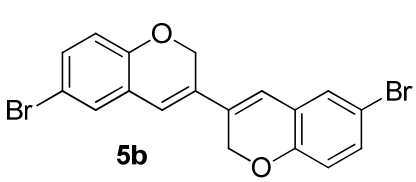


5a

^{1}H NMR: 7.17 (dd, J_1=8.5 Hz, J_2=2.0 Hz, 1H) 7.06 (d, J=2.0 Hz, 1H), 6.64 (d, J=8.5 Hz, 1H), 6.34 (br d, J=9.5 Hz, 1H), 5.80 (td, J_1=9.5 Hz, J_2=3.5 Hz, 1H), 4.82 (m, 2H).

^{13}C NMR: 153.1, 131.6, 129.0, 124.1, 123.5, 123.2, 117.4, 113.2, 65.6.

6,6'-Dibromo-2*H*,2'*H*-3,3'-bichromene (4b)



5b

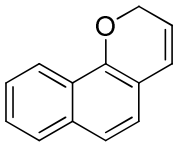
^{1}H NMR: 7.22 (dd, J_1=8.5 Hz, J_2=2.0 Hz, 2H), 7.17 (d, J=2.0 Hz, 2H), 6.73 (d, J=8.5 Hz, 2H), 6.32 (s, 2H), 5.03 (s, 4H).

^{13}C NMR: 152.7, 132.2, 129.7, 128.2, 123.9, 119.0, 117.4, 113.7, 65.2.

MS (EI): 420 (M^+, 88%), 407 (48%), 339 (64%), 202 (83%), 101 (100%).

HRMS: calcd for $C_{18}H_{12}O_2Br_2$, 417.9204; found 417.9208.

2*H*-Benzo[h]chromene (6a)[12]

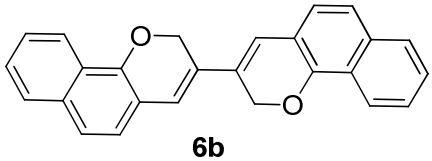


6a

^{1}H NMR: 8.18 (m, 1H), 7.61 (m, 1H), 7.43 (m, 3H), 7.16 (d, *J*=8.5 Hz, 1H), 6.56 (dd, J_1=9.5 Hz, J_2=1.5 Hz, 1H), 5.82 (td, J_1=9.5 Hz, J_2=3.5 Hz, 1H), 5.03 (m, 2H).

^{13}C NMR: 149.6, 134.4, 127.6, 126.2, 125.4, 125.2, 124.6, 124.4, 121.8, 120.4, 120.3, 116.8, 65.9.

2*H*,2'*H*-3,3'-Dibenzo[h]chromene (6b)



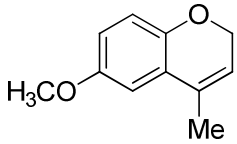
6b

This compound was formed in ~2% relative yield and could be isolated.

^{1}H NMR (characteristic absorptions from the crude reaction mixture): 6.58 (s, 2H), 5.31 (s, 4H).

MS (EI): 362 (M^+, 18%), 281 (7%), 263 (5%), 207 (4%), 181 (100%), 166 (10%), 152 (19%), 127 (3%).

6-Methoxy-4-methyl-2*H*-chromene (7a)[13]

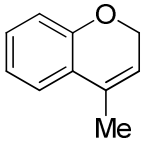


7a

^{1}H NMR: 6.65-6.75 (m, 3H), 5.61 (m, 1H), 4.66 (m, 2H), 3.77 (s, 3H), 2.00 (q, *J*=2.0 Hz, 3H).

^{13}C NMR: 154.0, 148.0, 130.2, 125.2, 119.4, 116.0, 113.3, 109.6, 65.3, 55.7, 17.9.

4-Methyl-2*H*-chromene (8a)[14]

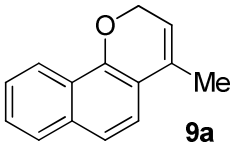


8a

^{1}H NMR: 7.13 (m, 2H), 6.91 (dt, J_1=7.5 Hz, J_2=1.0 Hz, 1H), 6.80 (d, *J*=7.5 Hz, 1H), 5.58 (br s, 1H), 4.75 (m, 2H), 2.02 (q, *J*=1.5 Hz, 3H).

^{13}C NMR: 154.1, 130.2, 128.9, 124.3, 123.5, 121.1, 118.4, 115.7, 65.4, 17.9.

4-Methyl-2*H*-benzo[h]chromene (9a)[13]

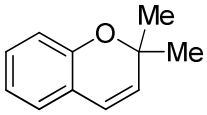


9a

^{1}H NMR: 8.20 (m, 1H), 7.76 (m, 1H), 7.35-7.47 (m, 4H), 5.62 (br s, 1H), 4.94 (br s, 2H), 2.14 (s, 3H).

^{13}C NMR: 149.7, 134.1, 131.1, 127.5, 126.2, 125.3, 124.4, 122.1, 121.5, 120.1, 118.7, 116.5, 65.8, 18.3.

2,2-Dimethyl-2*H*-chromene (10a)[15]

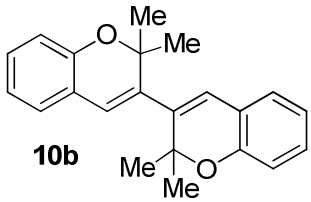


10a

^{1}H NMR: 7.10 (dt, J_1=8.0 Hz, J_2=2.0 Hz, 1H), 6.98 (dd, J_1=7.0 Hz, J_2=1.5 Hz, 1H), 6.84 (dt, J_1=7.5 Hz, J_2=1.0 Hz, 1H), 6.78 (d, J=8.0 Hz, 1H), 6.33 (d, J=10.0 Hz, 1H), 5.61 (d, J=10.0 Hz, 1H), 1.44 (s, 6H).

^{13}C NMR: 152.9, 130.7, 129.0, 126.3, 122.3, 121.2, 120.7, 116.3, 76.1, 28.0.

2,2,2',2'-Tetramethyl-2*H*,2'*H*-3,3'-bichromene (10b)



10b

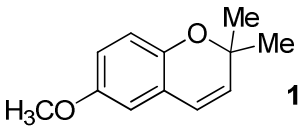
^{1}H NMR: 7.14 (dt, J_1=7.5 Hz, J_2=1.5 Hz, 2H), 7.02 (dd, J_1=7.5 Hz, J_2=1.5 Hz, 2H), 6.82-6.92 (m, 4H), 6.30 (s, 2H), 1.56 (s, 12H).

^{13}C NMR: 152.3, 138.2, 129.3, 126.4, 123.1, 122.5, 121.1, 116.5, 78.8, 27.1.

MS (EI): 318 (M^+, 36%), 303 (100%), 261 (12%), 215 (9%), 144 (71%), 107 (22%).

HRMS: calcd for $C_{22}H_{22}O_2$+H, 319.1698; found 319.1695.

6-Methoxy-2,2-dimethyl-2*H*-chromene (11a)[16]

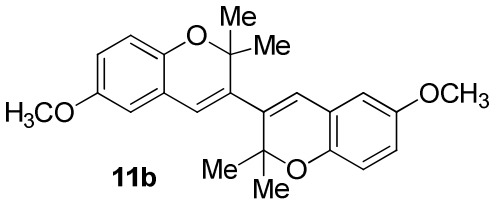


11a

^{1}H NMR: 6.71 (d, J=8.5 Hz, 1H), 6.66 (br d, J=8.5 Hz, 1H), 6.55 (br s, 1H), 6.28 (d, J=9.5 Hz, 1H), 5.64 (d, J=9.5 Hz, 1H), 3.75 (s, 3H), 1.41 (s, 6H).

^{13}C NMR: 153.7, 146.7, 131.7, 122.4, 121.9, 116.8, 114.1, 111.4, 75.8, 55.7, 27.6.

6,6'-Dimethoxy-2,2,2',2'-tetramethyl-2*H*,2'*H*-3,3'-bichromene (11b)



11b

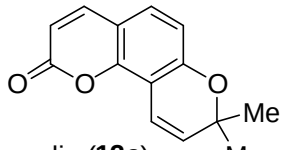
^{1}H NMR: 6.77 (d, *J*=8.5 Hz, 2H), 6.71 (br d, *J*=8.5 Hz, 2H), 6.60 (br s, 2H), 6.26 (s, 2H), 3.77 (s, 6H), 1.53 (s, 12H).

^{13}C NMR: 154.0, 146.7, 139.2, 123.0, 122.9, 117.0, 114.6, 111.2, 78.5, 55.7, 26.9.

MS (EI): 378 (M^{+}, 38%), 363 (100%), 321 (18%), 239 (8%), 189 (11%), 174 (32%).

HRMS: calcd for $C_{24}H_{26}O_4$+H, 379.1909; found 379.1902.

8,8-Dimethylpyrano[2,3-f]chromen-2(8*H*)-one (seselin, 12a)[17]

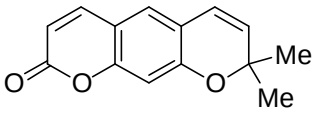


seselin (**12a**)

^{1}H NMR: 7.61 (d, *J*=9.5 Hz, 1H), 7.21 (d, *J*=8.5 Hz, 1H), 6.87 (d, *J*=10.0 Hz, 1H), 6.72 (d, *J*=8.5 Hz, 1H), 6.23 (d, *J*=9.5 Hz, 1H), 5.72 (d, *J*=10.0 Hz, 1H), 1.47 (s, 6H).

^{13}C NMR: 161.4, 156.4, 150.0, 144.1, 130.8, 127.8, 114.9, 113.6, 112.6, 112.5, 109.3, 77.6, 28.1.

8,8-Dimethylpyrano[3,2-g]chromen-2(8*H*)-one (xanthyletin, 12b)[17]

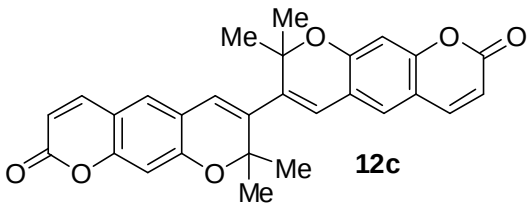


xanthyletin (**12b**)

^{1}H NMR: 7.57 (d, *J*=9.5 Hz, 1H), 7.04 (s, 1H), 6.72 (s, 1H), 6.33 (d, *J*=10.0 Hz, 1H), 6.21 (d, *J*=9.5 Hz, 1H), 5.68 (d, *J*=10.0 Hz, 1H), 1.46 (s, 6H).

^{13}C NMR: 161.2, 156.8, 155.4, 143.3, 131.2, 124.7, 120.8, 118.5, 113.0, 112.7, 104.4, 77.7, 28.3.

2,2,2',2'-Tetramethyl-[3,3'-bipyrano[3,2-g]chromene]-8,8'(2*H*,2'*H*)-dione (12c)



12c

^{1}H NMR: 7.61 (d, *J*=9.5 Hz, 2H), 7.13 (s, 2H), 6.82 (s, 2H), 6.35 (s, 2H), 6.27 (d, *J*=9.5 Hz, 2H), 1.59 (s, 12H).

^{13}C NMR: 160.9, 156.0, 155.6, 143.1, 138.3, 125.1, 122.2, 119.4, 113.6, 113.3, 104.8, 80.1, 27.4.

HRMS: calcd for $C_{28}H_{22}O_6$+H, 455.1494; found 455.1488.

References

1. Menon, R. S.; Findlay, A. D.; Bissember, A. C.; Banwell, M. G. *J. Org. Chem.* **2009**, *74*, 8901-8903.

2. Chaudhary, P. M.; Chavan, S. R. Shirazi, F.; Razdan, M.; Nimkar, P.; Maybhate, S. P.; Likhite, A. P.; Gonnade, R.; Hazara, B. G.; Deshpande, M. V.; Deshpande, S. R. *Bioorg. Med. Chem.* **2009**, *17*, 2433-2440.

3. Punna, S.; Meunier, S.; Finn, M. G. *Org. Lett.* **2004**, *6*, 2777-2779.

4. Worlikar, S. A.; Kesharwani, T.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 1347-1353.

5. Savitha, G.; Felix, K.; Perumal, P. T. *Synlett* **2009**, 2079-2082.

6. Godfrey, J. D.; Mueller, R. H.; Sedergran, T. C.; Soundararajan, N.; Colandrea, V. J. *Tetrahedron Lett.* **1994**, *35*, 6405-6408.

7. Wegner, H. A.; Ahles, S.; Neuburger, M. *Chem. Eur. J.* **2008**, *14*, 11310-11313.

8. Bell, D.; Davies, M. R.; Geen, G. R.; Mann, I. S. *Synthesis* **1995**, 707-712.

9. Pillai, S. P.; Menon, S. R.; Mitscher, L. A.; Pillai, C. A.; Shankel, D. M. *J. Nat. Prod.* **1999**, *62*, 1358-1362.

10. Antonov, D.; Sund, C.; Lindstroem, S.; Sahlberg, C. PCT Int. Appl. (**2004**), WO 2004021969 A2 20040318.

11. Furstner, A.; Guth, O.; Duffels, A.; Seidel, G.; Liebl, M.; Gabor, B. Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811-4820.

12. Chang S.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 864-866.

13. Balasubramanian, T.; Balasubramanian, K. K. *J. Chem. Soc., Chem. Commun.* **1992**, 1760-1761.

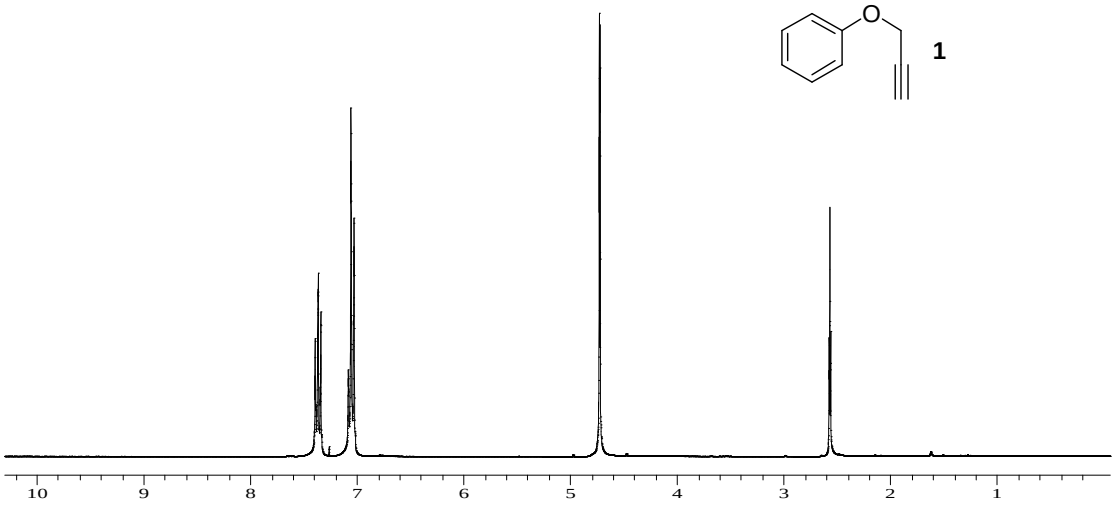
14. Pastine, S. J.; Youn, S. W.; Sames, D. *Tetrahedron* **2003**, *59*, 8859-8868.

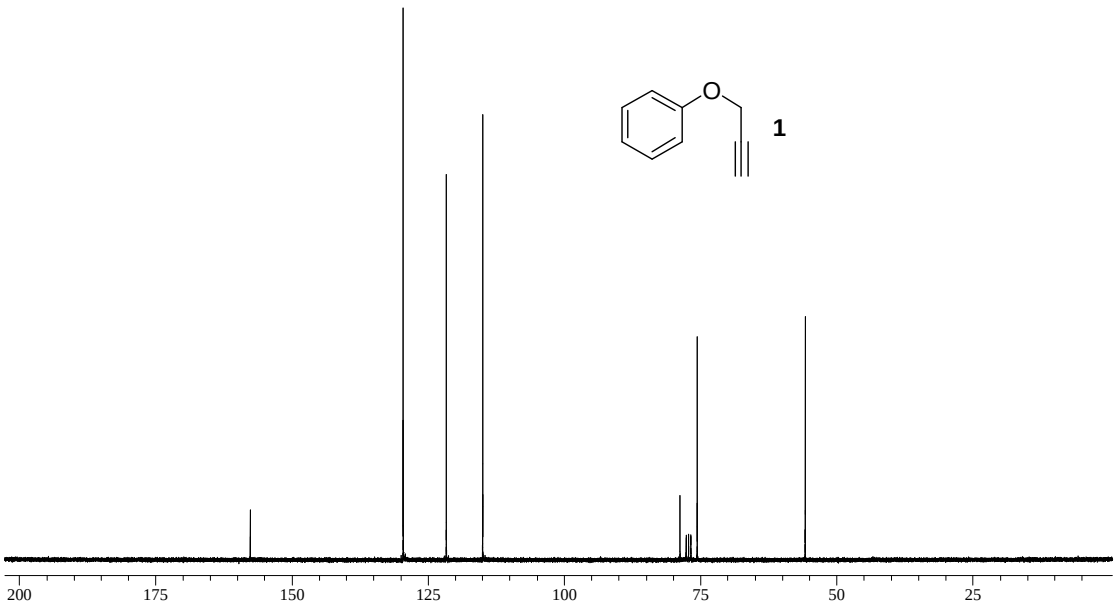
15. Yamazaki S. *Org. Biomol. Chem.* **2010**, *8*, 2377-2385.

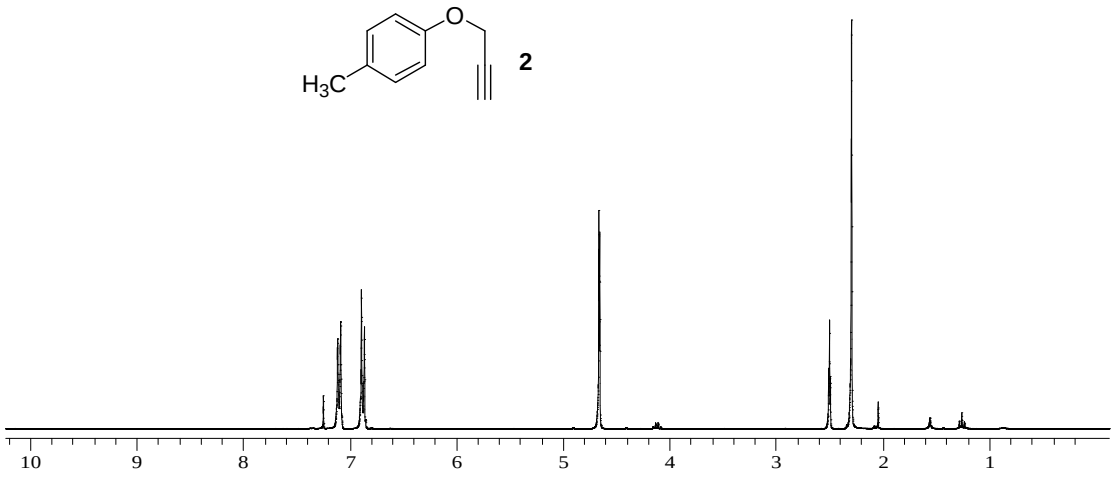
16. Aniol, M.; Wawrzenczyk, C. *Heterocycles* **1994**, *38*, 2655-2662.

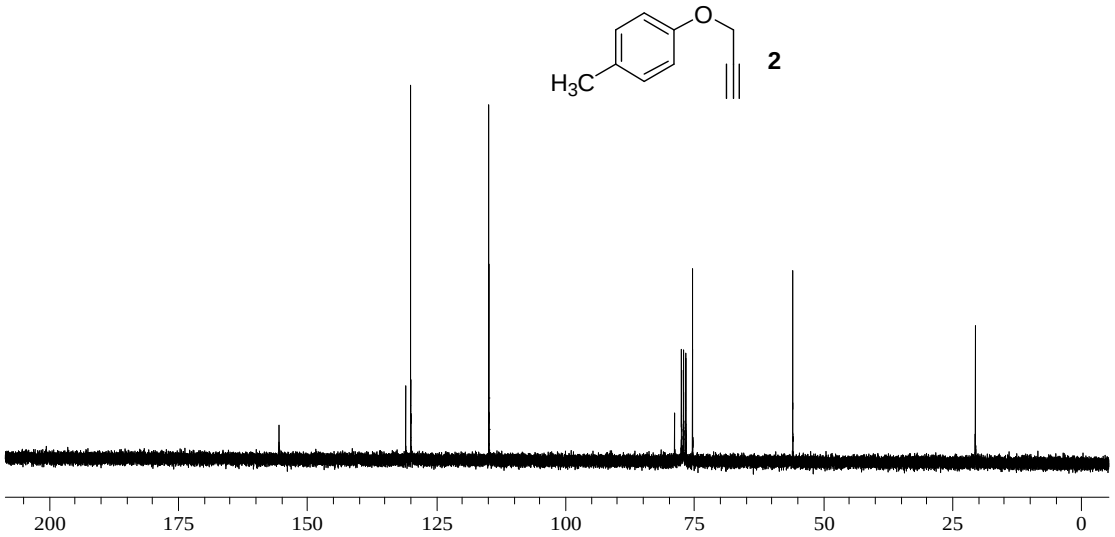
17. Nicolaou, K. C.; Pfefferkorn, J. A.; Cao, G.-Q. *Angew. Chem. Int. Ed.* **2000**, *39*, 734-739.

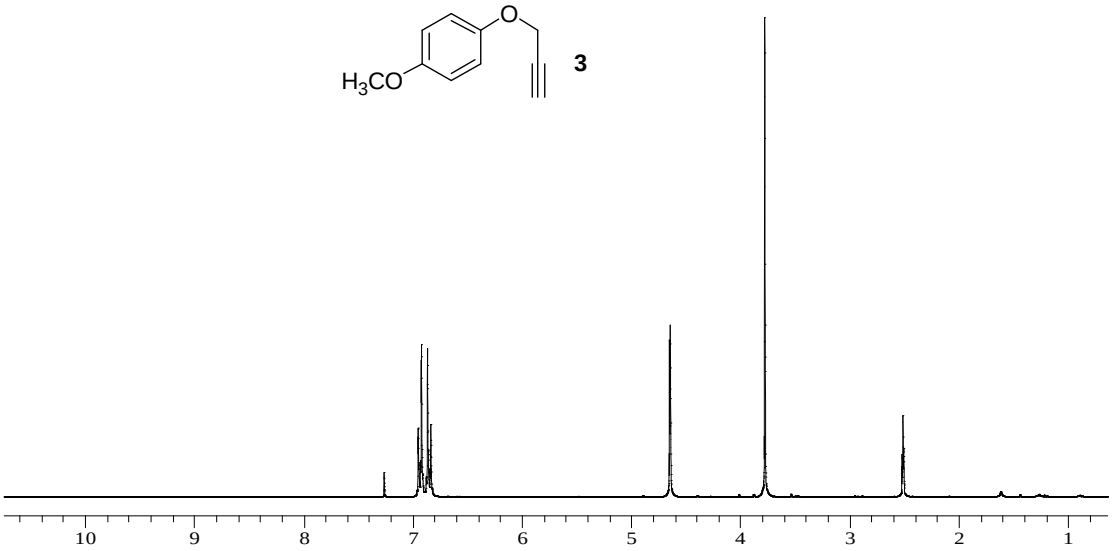
^{1}H, ^{13}C-NMR and MS/HRMS spectra of key compounds and reactions

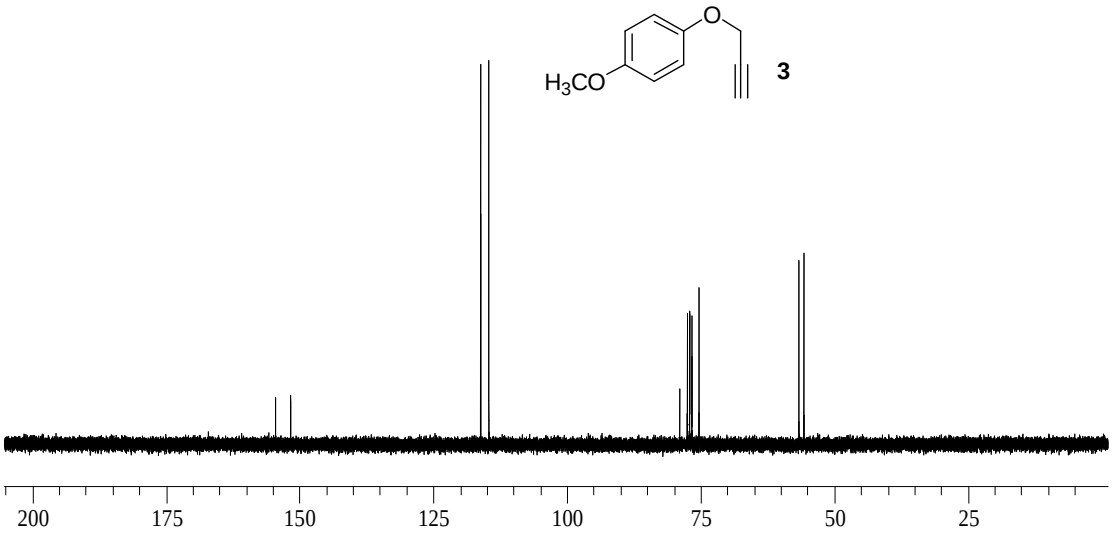


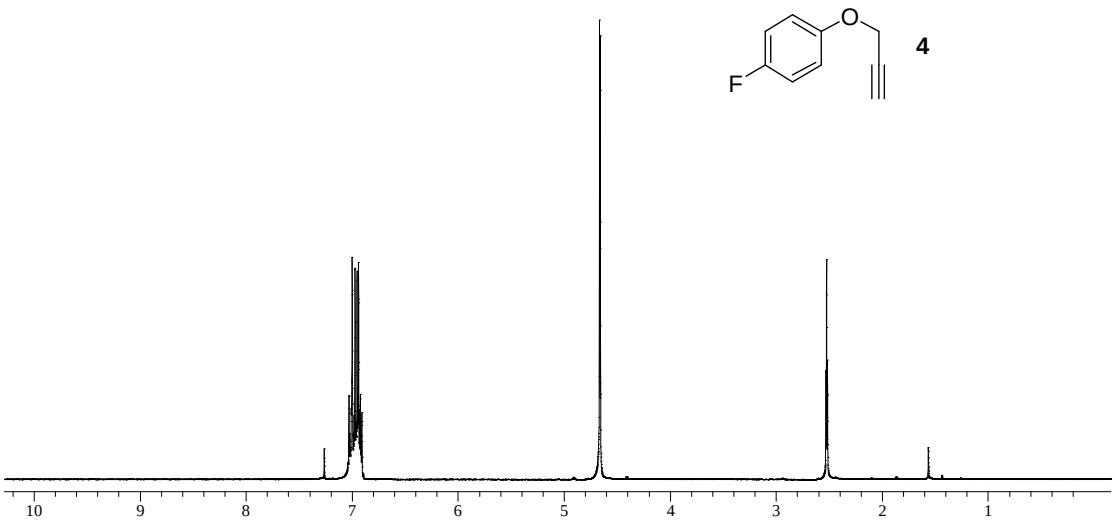


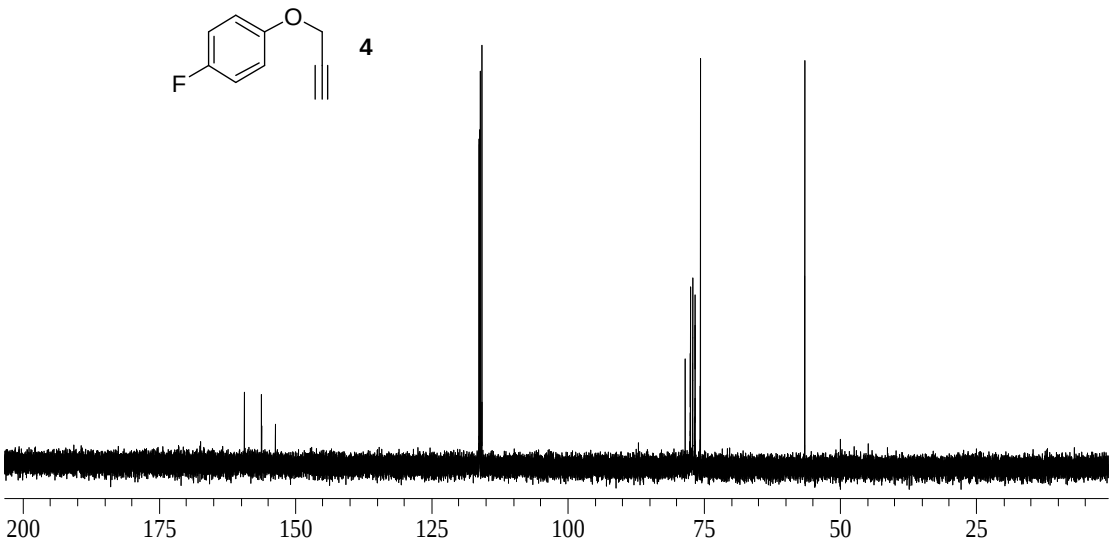

O
H3C
2
10
9
8
7
6
5
4
3
2
1

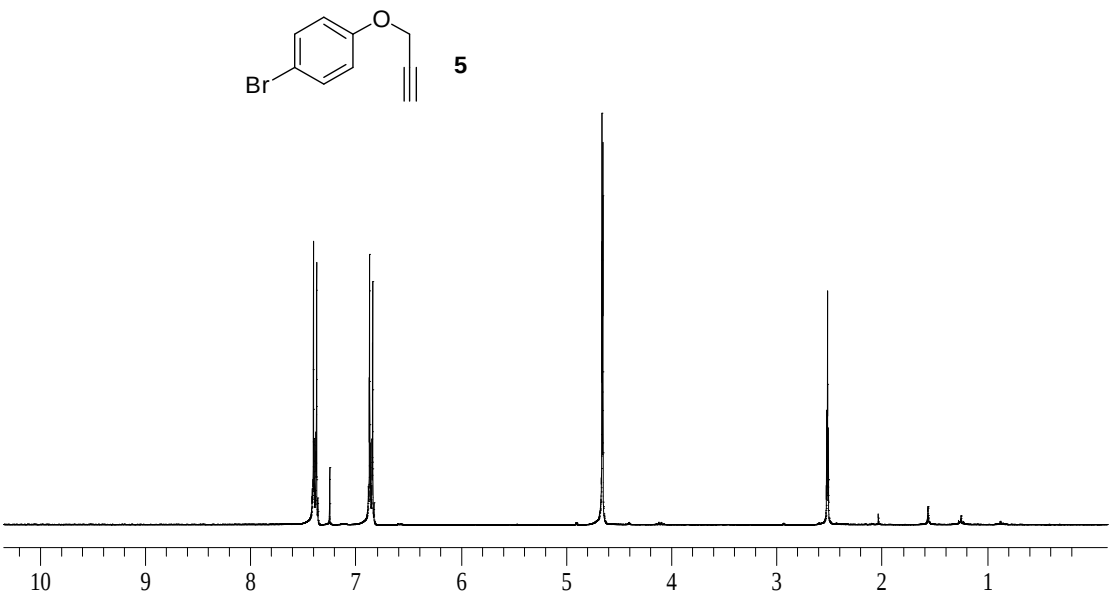

O
H3C
2
200
175
150
125
100
75
50
25
0

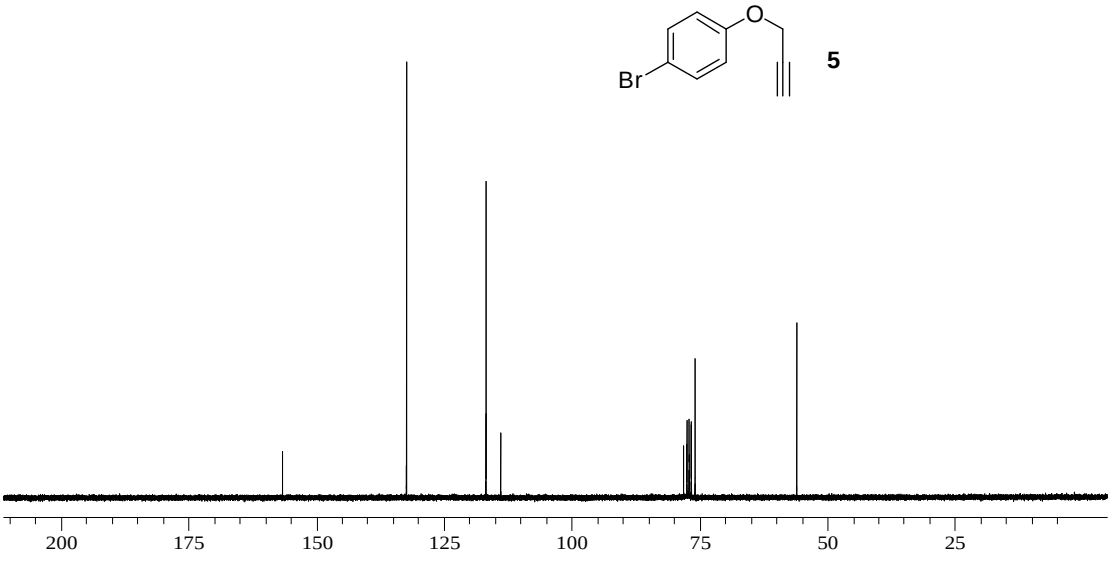

O
H3CO
3
10
9
8
7
6
5
4
3
2
1

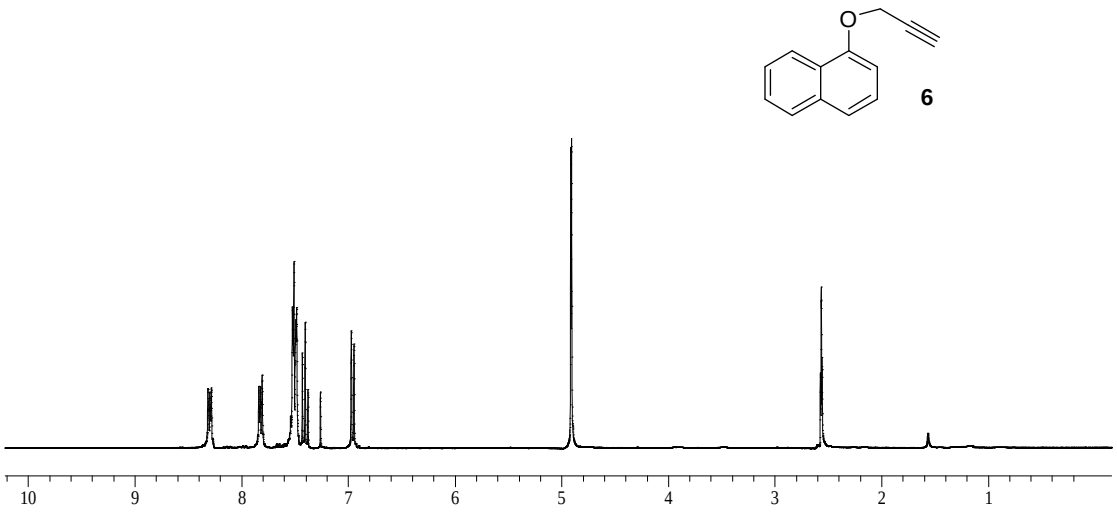

O
H3CO
3
200
175
150
125
100
75
50
25

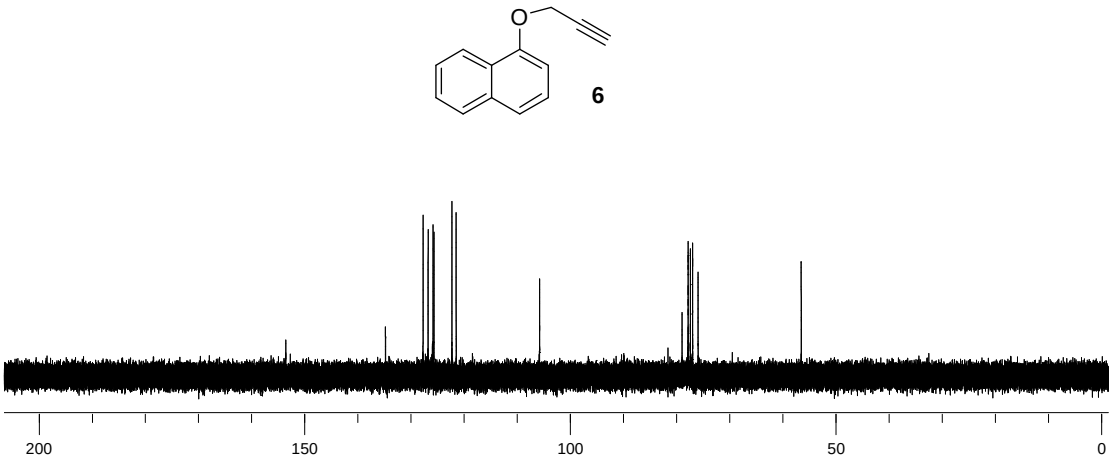

O
F
4
10
9
8
7
6
5
4
3
2
1

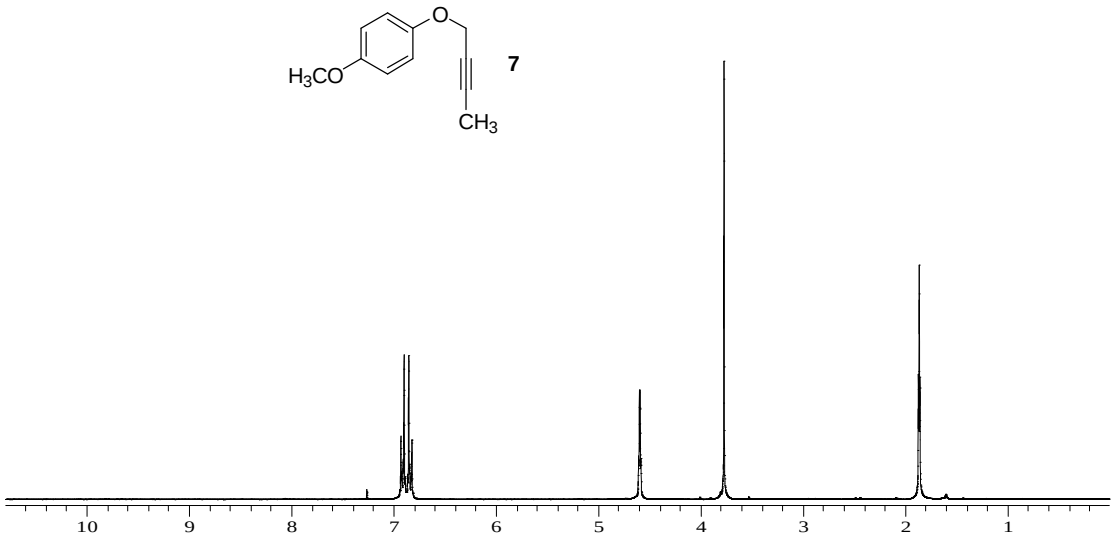

O
F
4
200
175
150
125
100
75
50
25

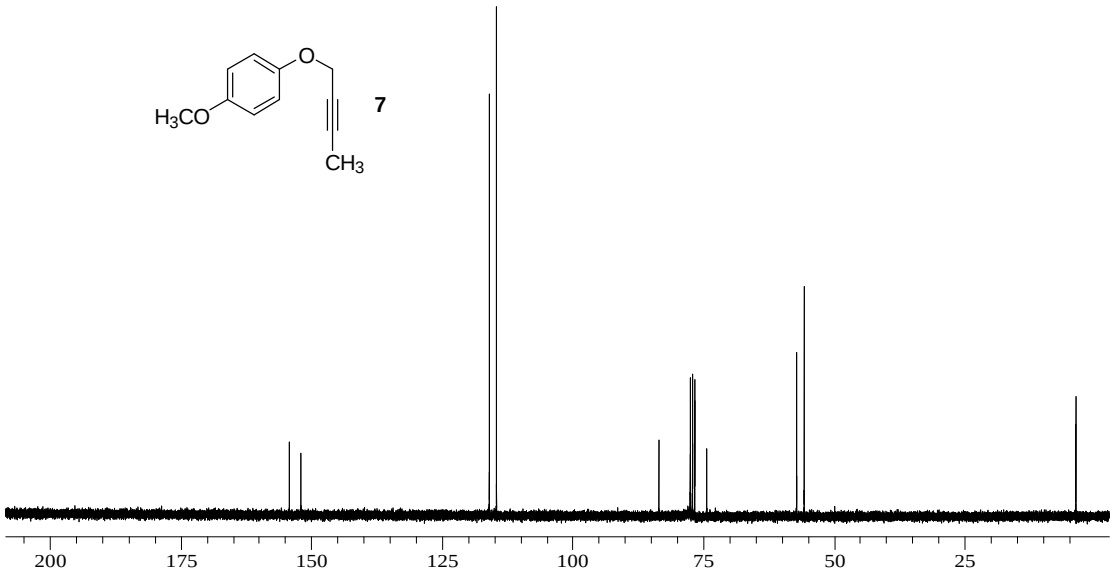

O
Br
5
10
9
8
7
6
5
4
3
2
1

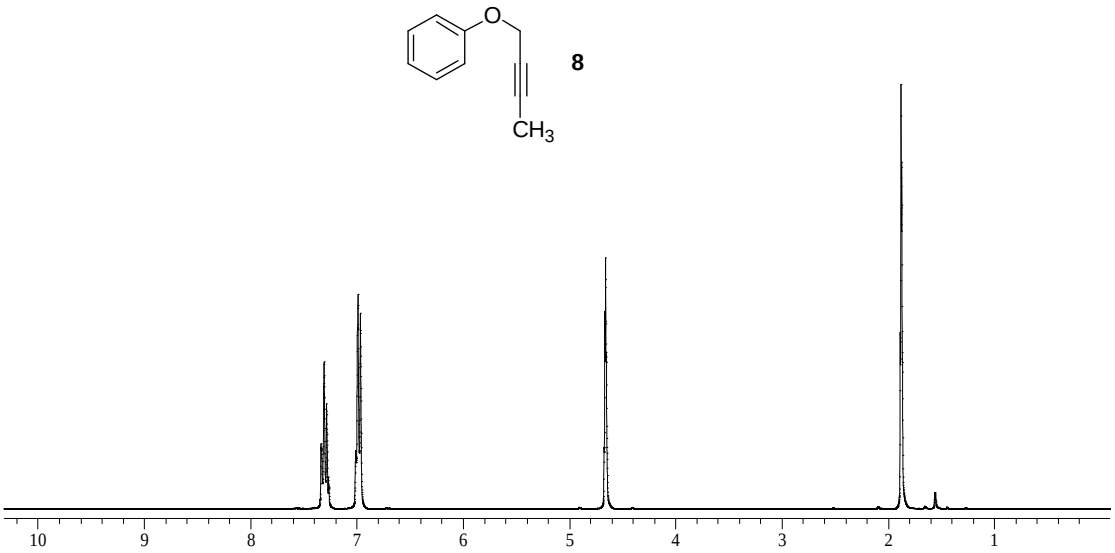

O
Br
5
200
175
150
125
100
75
50
25

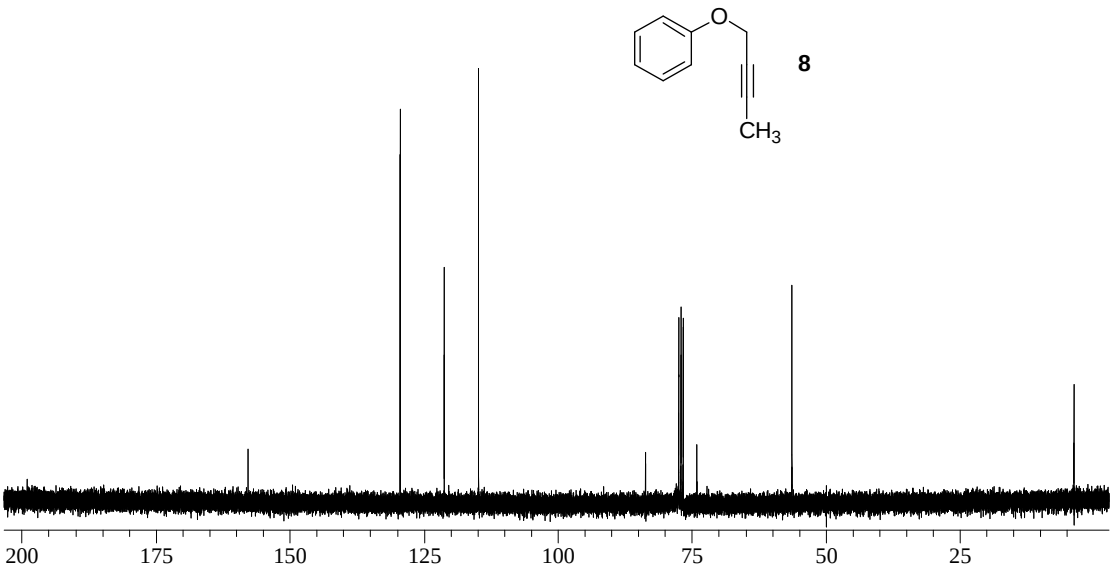

O
6
10
9
8
7
6
5
4
3
2
1

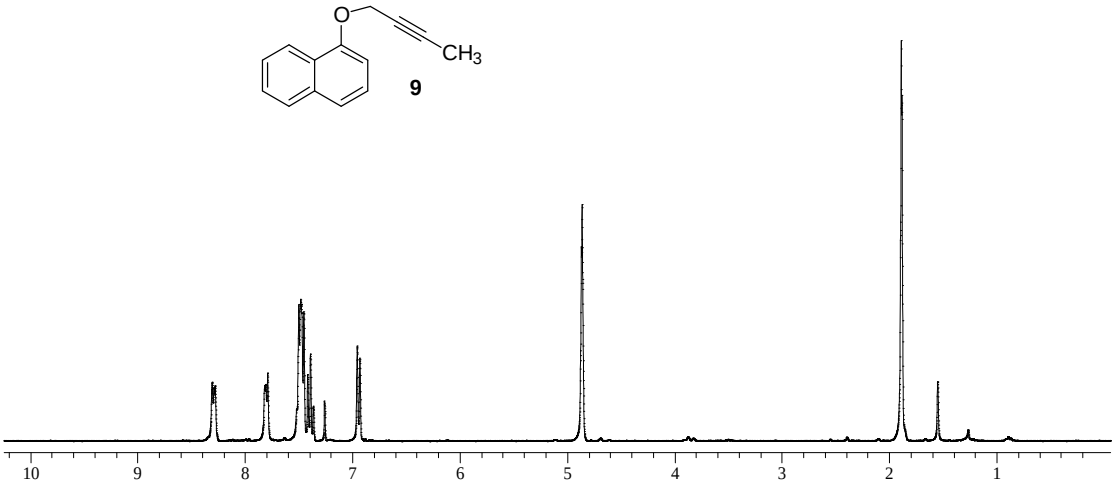

O
6
200
150
100
50
0

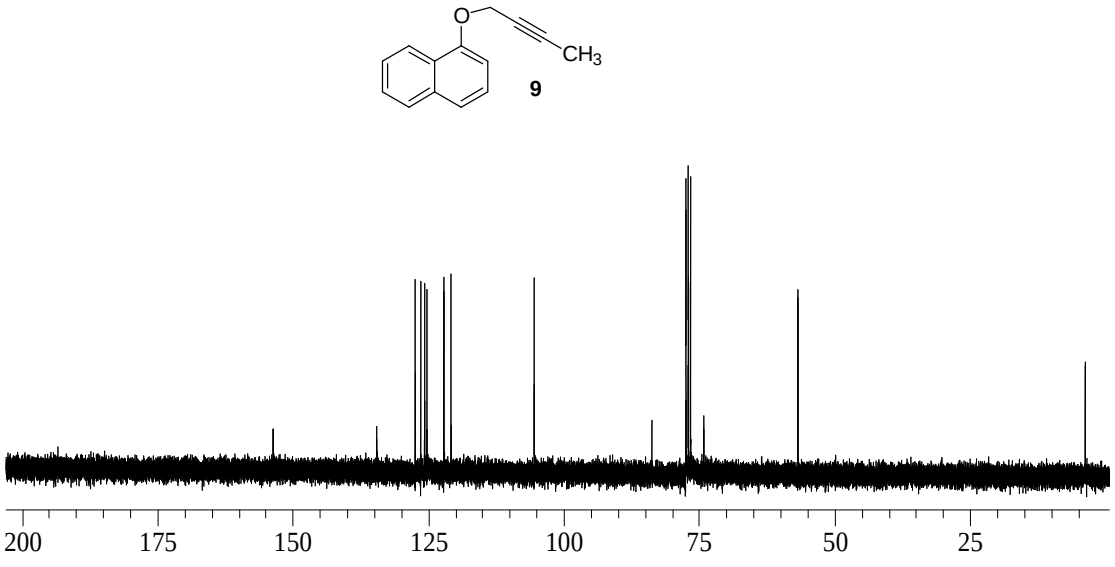

O
H3CO
7
CH3
10
9
8
7
6
5
4
3
2
1

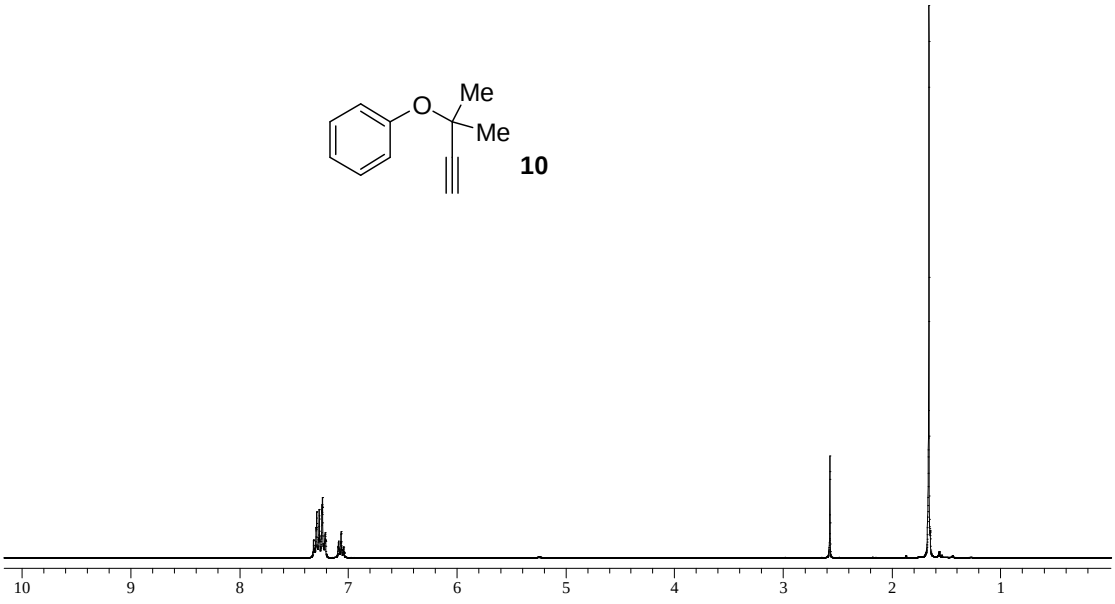

O
H3CO
7
CH3
200
175
150
125
100
75
50
25

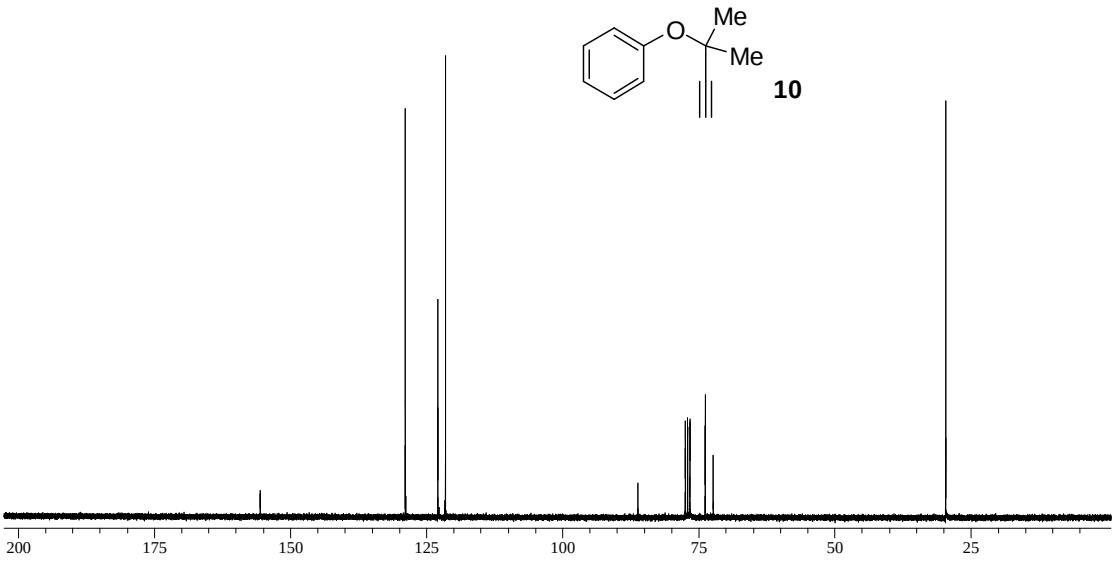

O
CH3
8
10
9
8
7
6
5
4
3
2
1

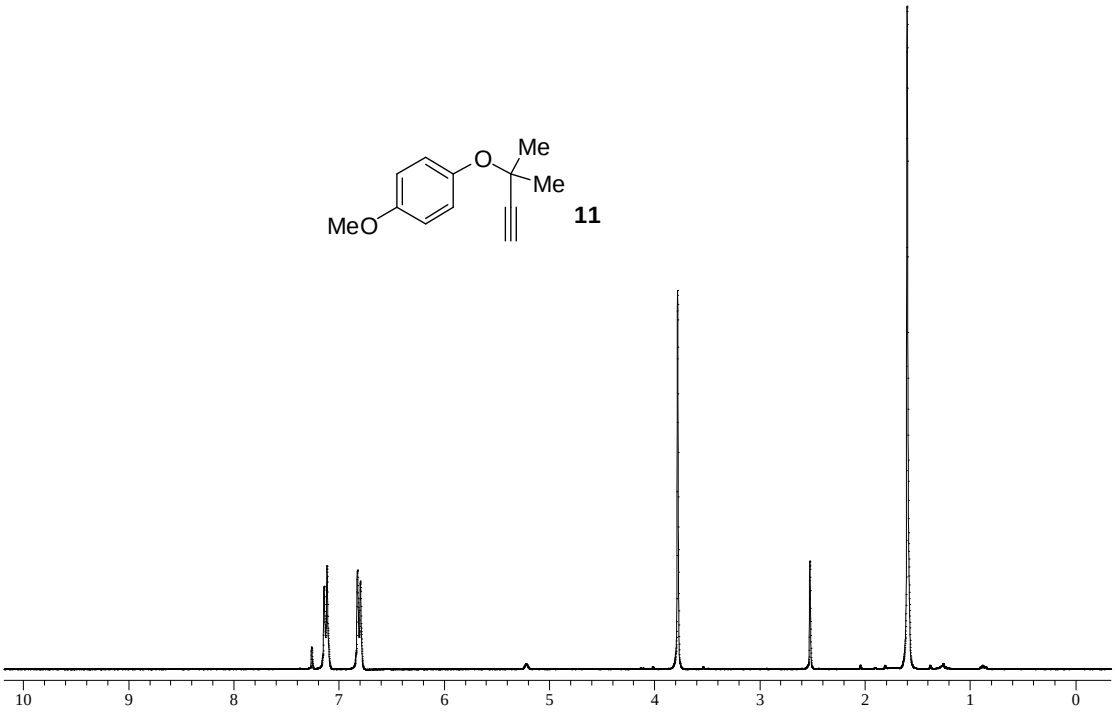

O
CH3
8
200
175
150
125
100
75
50
25

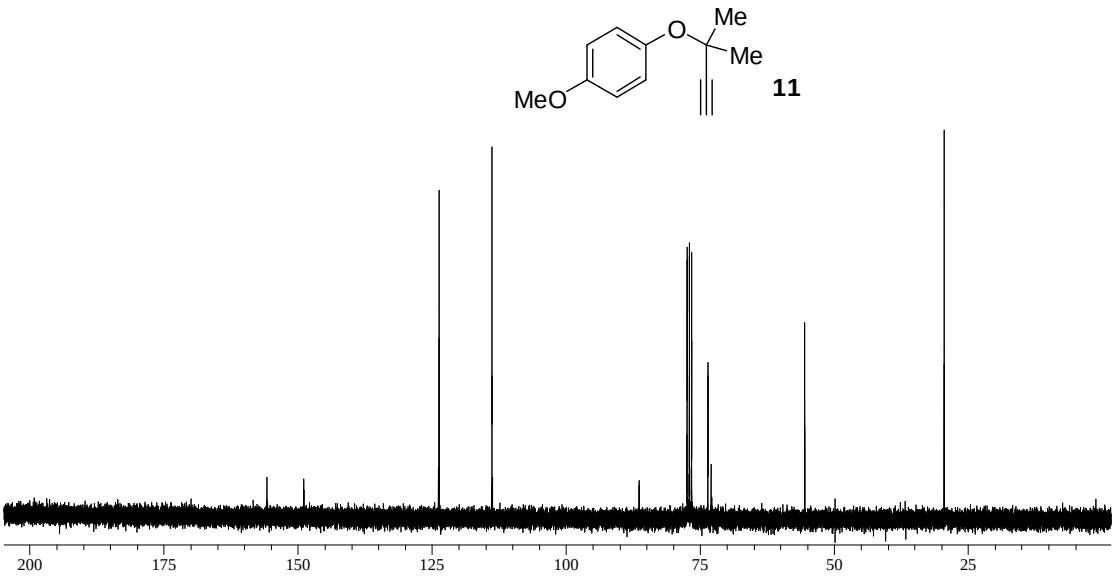

O
CH3
9
10
9
8
7
6
5
4
3
2
1

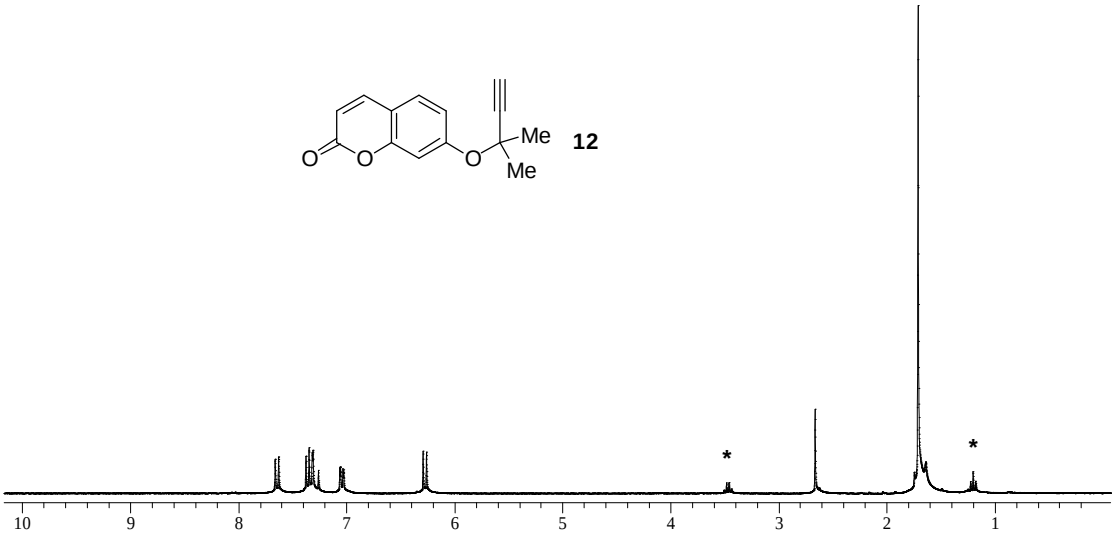

O
CH3
9
200
175
150
125
100
75
50
25


O
Me
Me
10
10
9
8
7
6
5
4
3
2
1

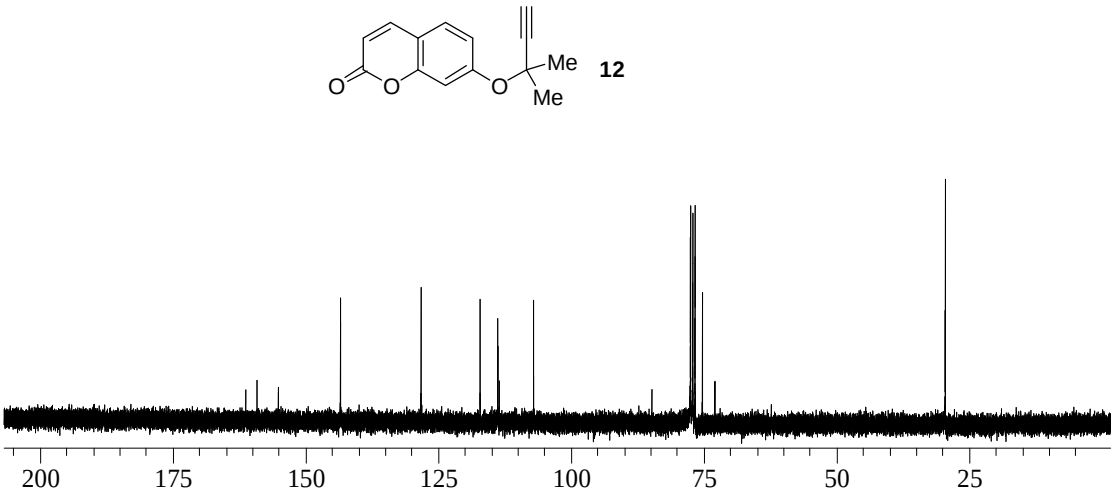

O
Me
Me
10
200
175
150
125
100
75
50
25

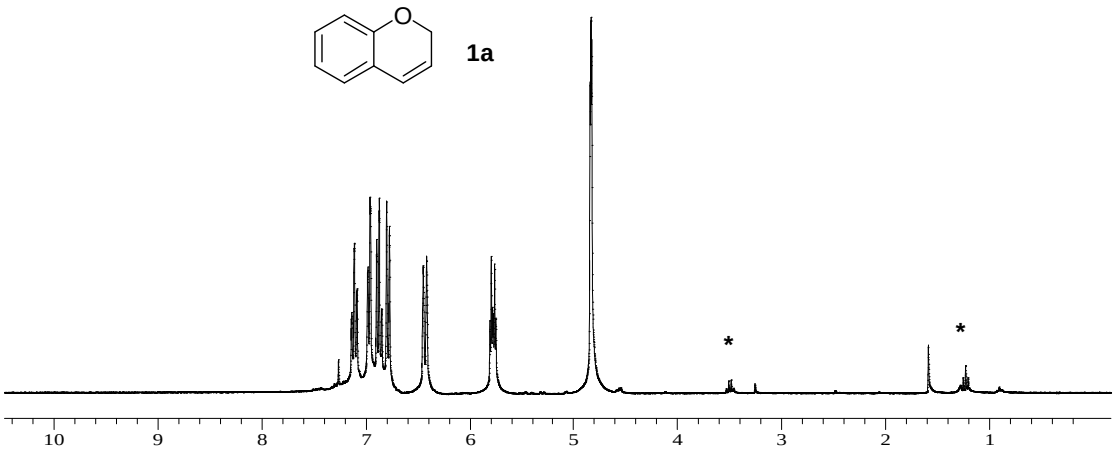

Me
O
Me
MeO
11
10
9
8
7
6
5
4
3
2
1
0


Me
O
Me
MeO
11
200
175
150
125
100
75
50
25

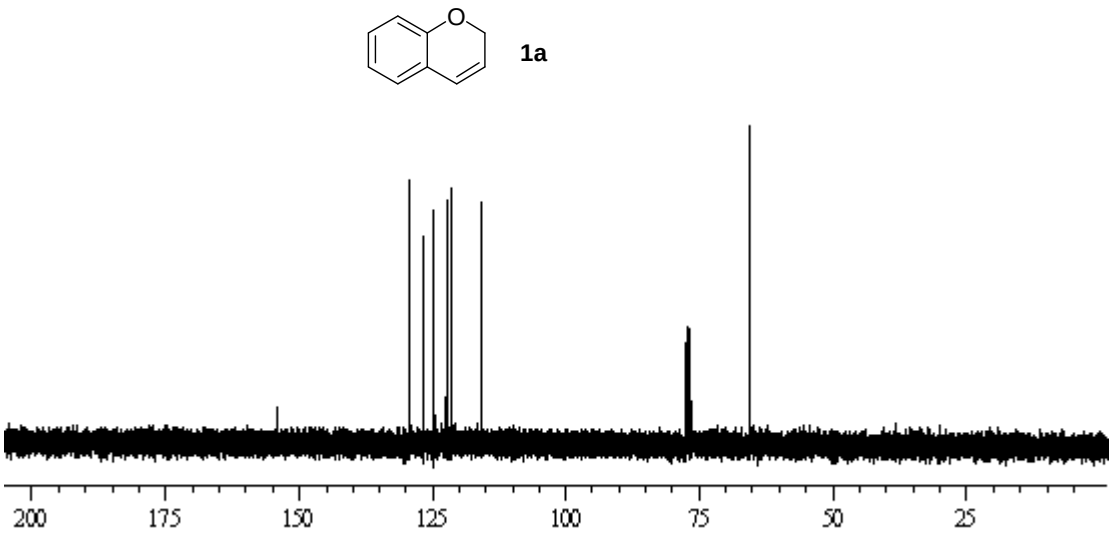


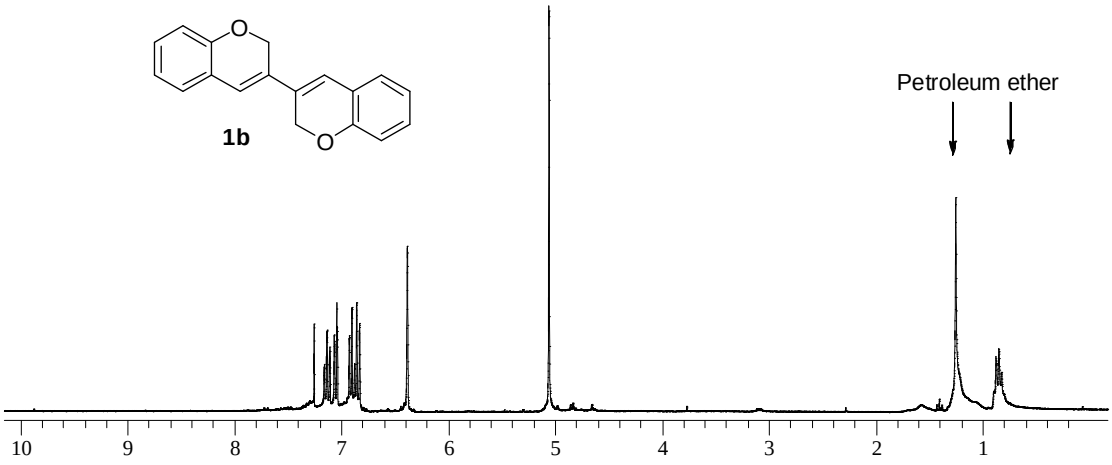
* = Diethyl ether

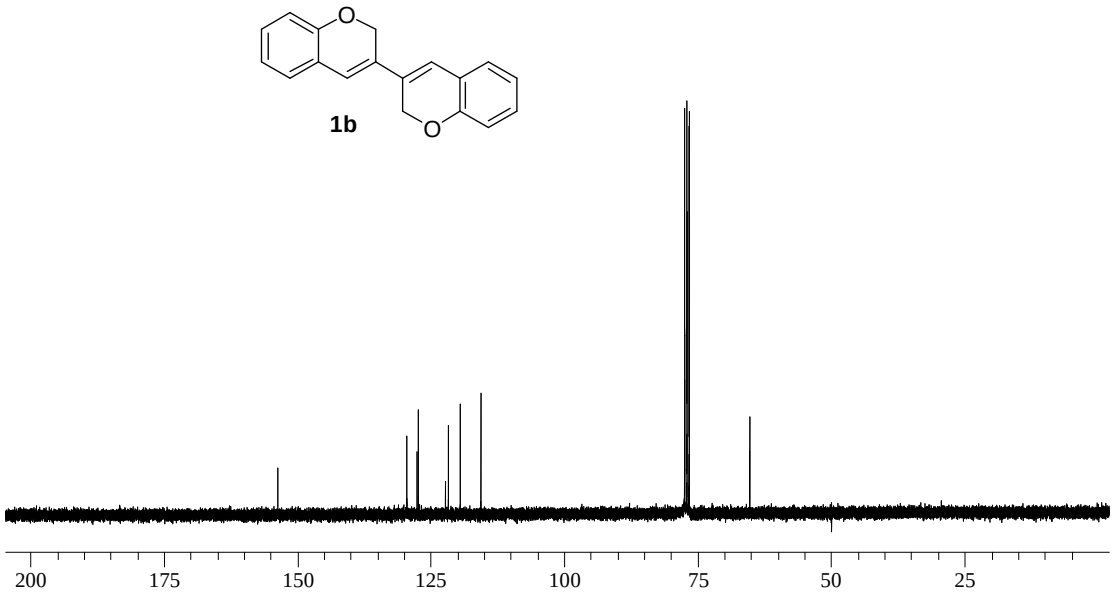


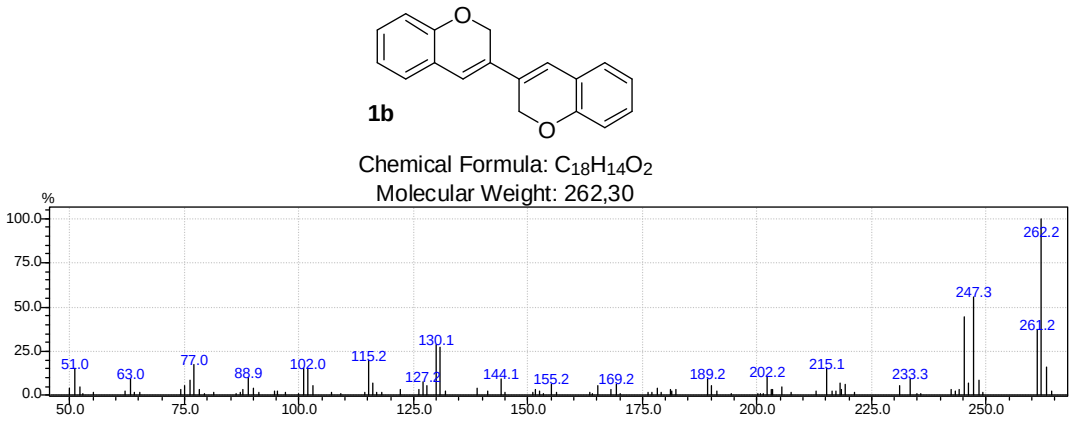


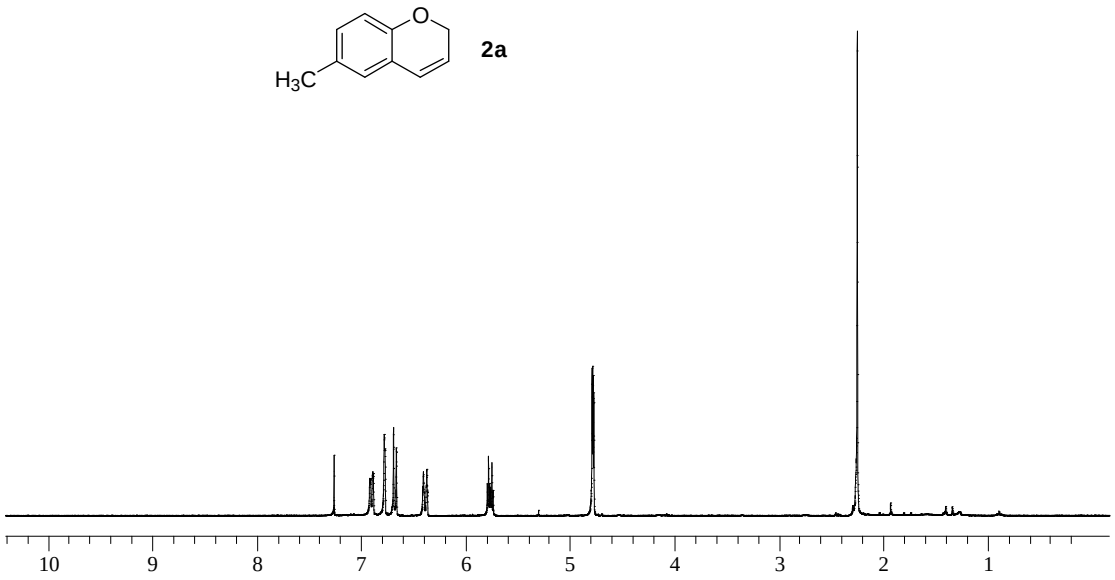
* = Diethyl ether

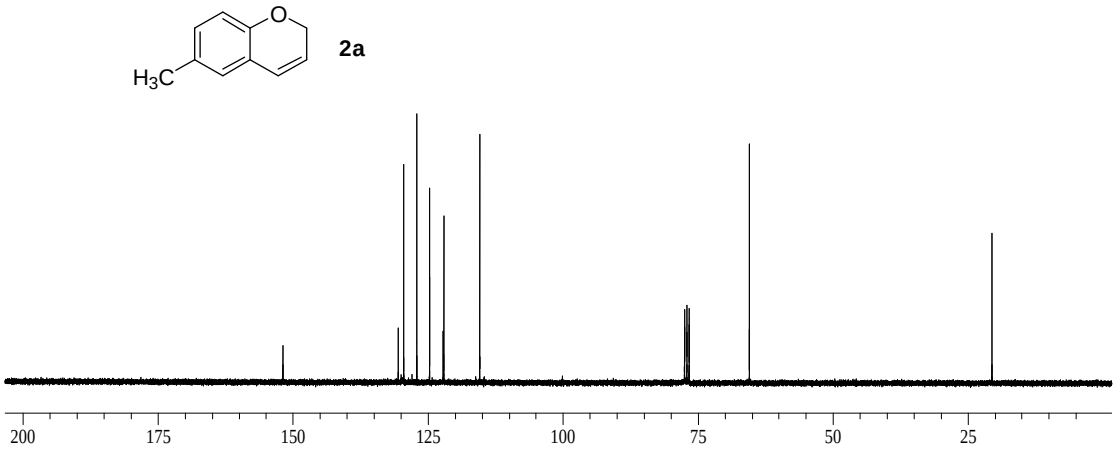


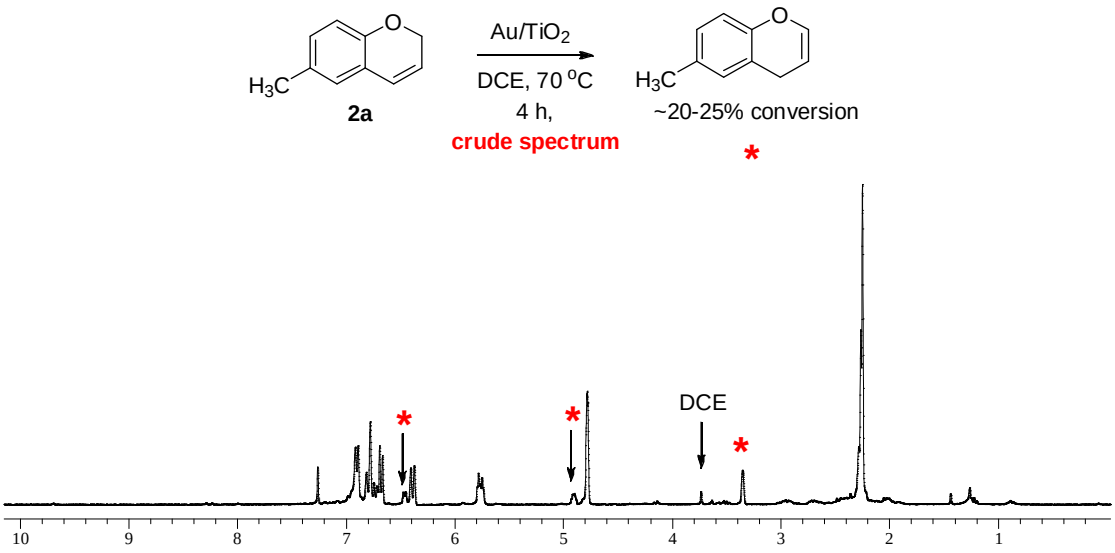

1b
Petroleum ether
10
9
8
7
6
5
4
3
2
1

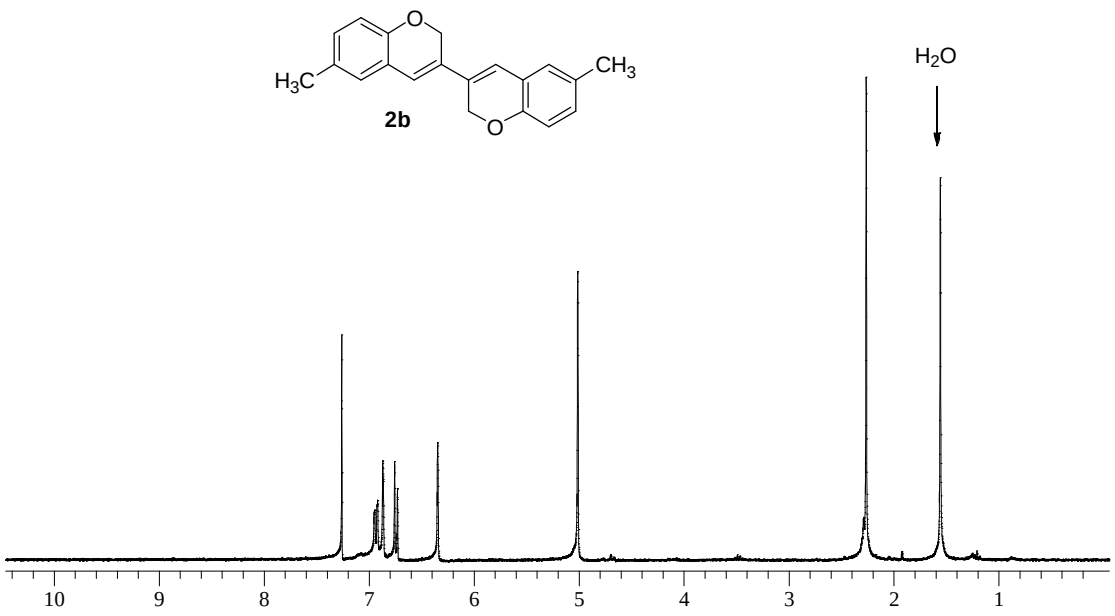

1b
200
175
150
125
100
75
50
25

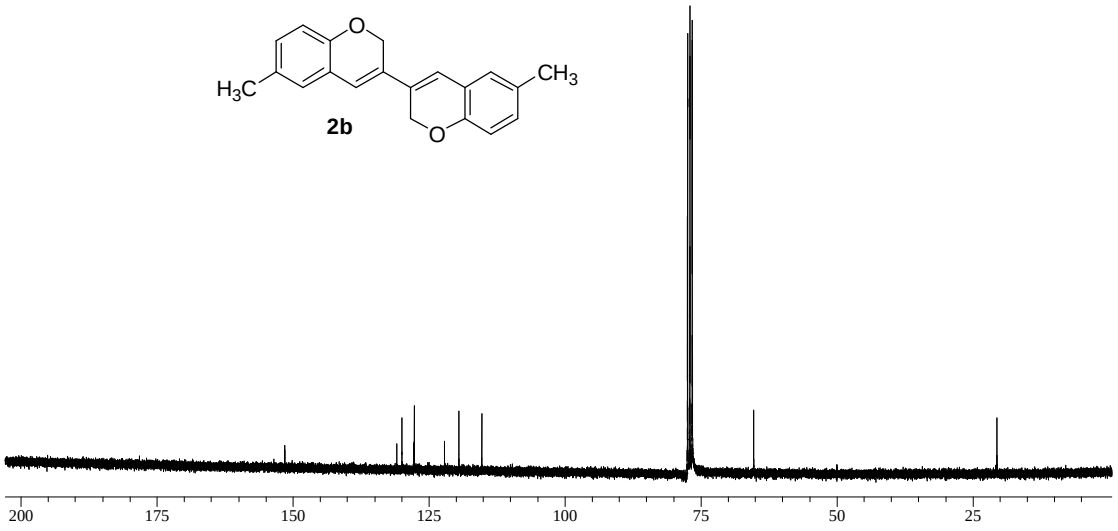

1b
Chemical Formula: C18H14O2
Molecular Weight: 262,30
%
100.0
75.0
50.0
25.0
0.0
51.0
63.0
77.0
88.9
102.0
115.2
127.2
130.1
144.1
155.2
169.2
189.2
202.2
215.1
233.3
247.3
261.2
262.2
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0

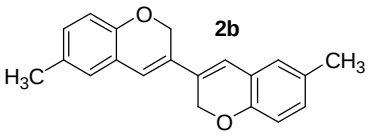

O
H3C
2a
10
9
8
7
6
5
4
3
2
1


O
H3C
2a
200
175
150
125
100
75
50
25

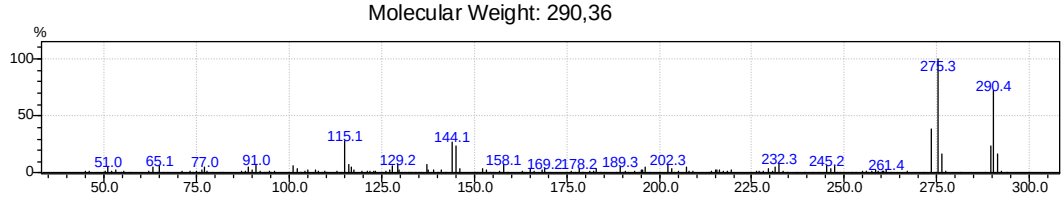

Au/TiO2
DCE, 70 °C
4 h,
crude spectrum
H3C
2a
H3C
~20-25% conversion
*
*
*
*
DCE
10
9
8
7
6
5
4
3
2
1


O
H3C
CH3
O
2b
H2O
10
9
8
7
6
5
4
3
2
1

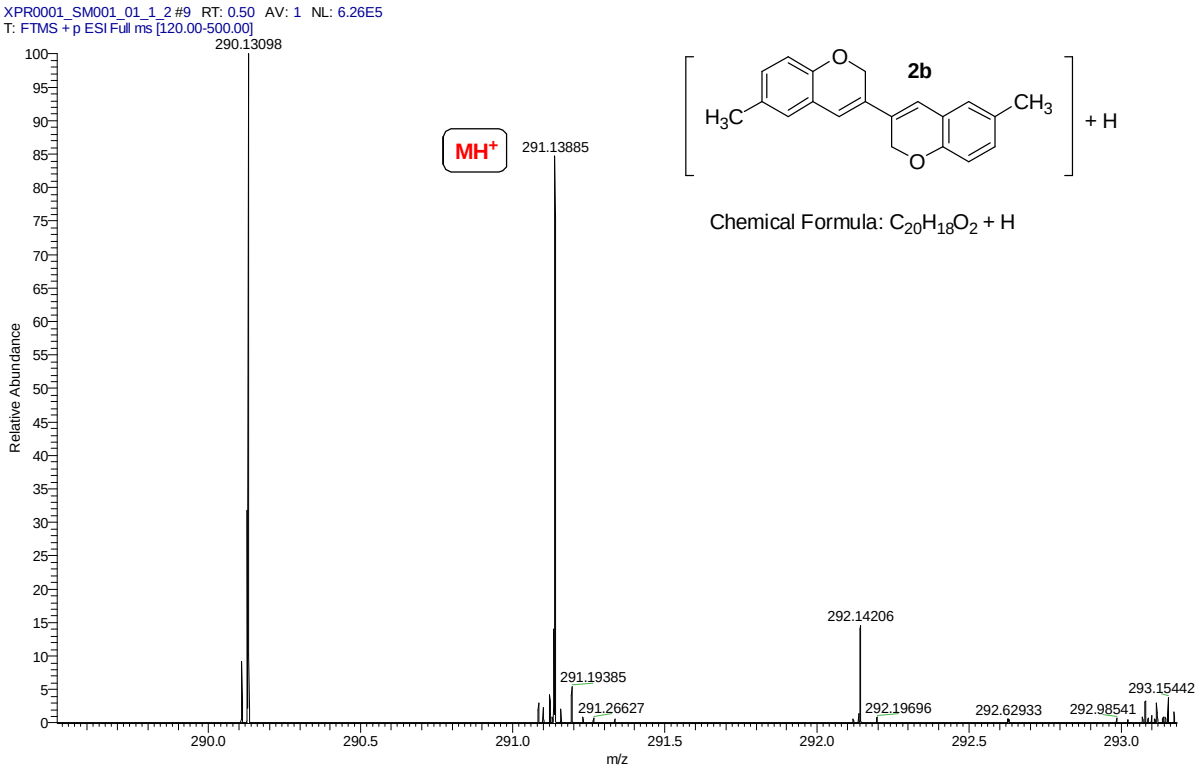

O
H3C
CH3
O
2b
200
175
150
125
100
75
50
25



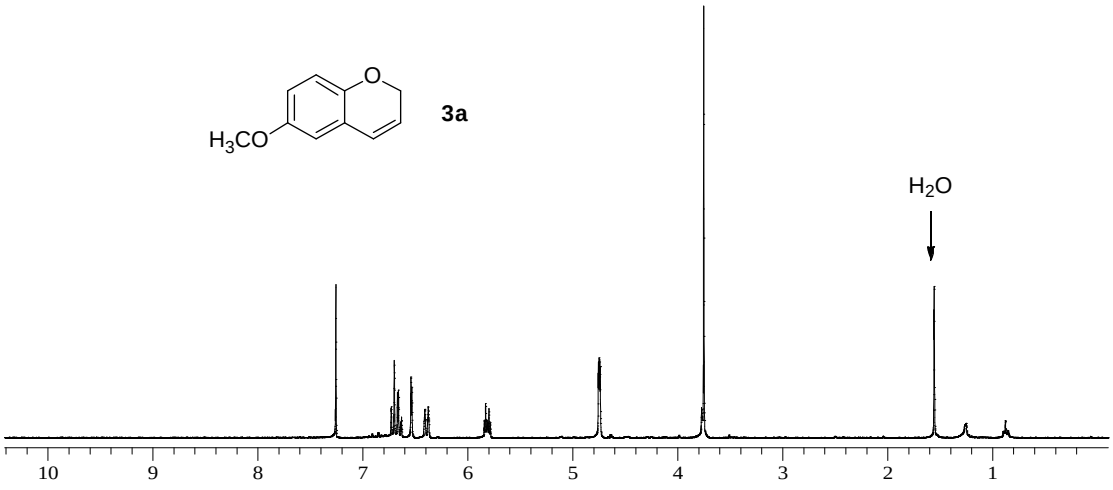
Chemical Formula: $C_{20}H_{18}O_2$
Molecular Weight: 290,36

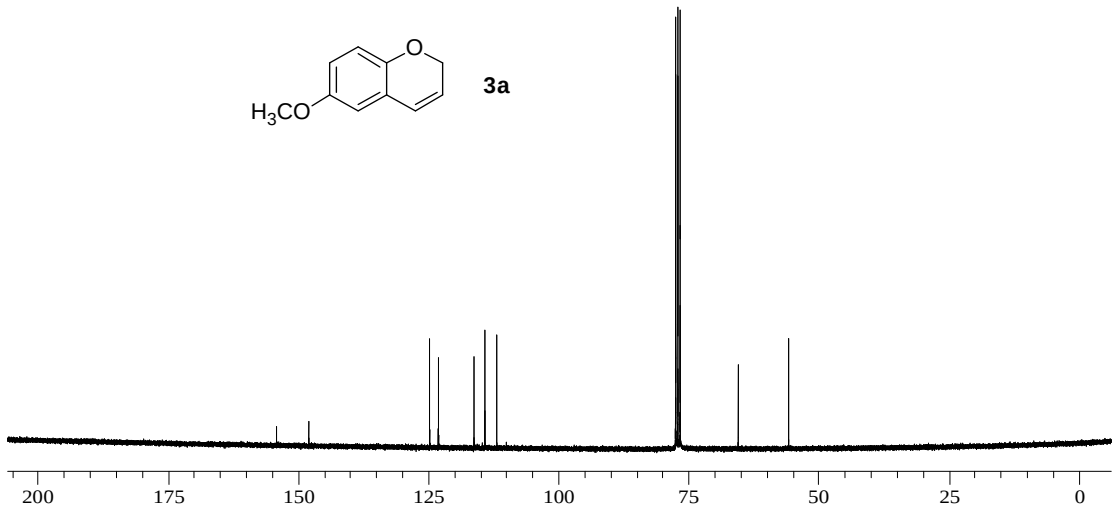


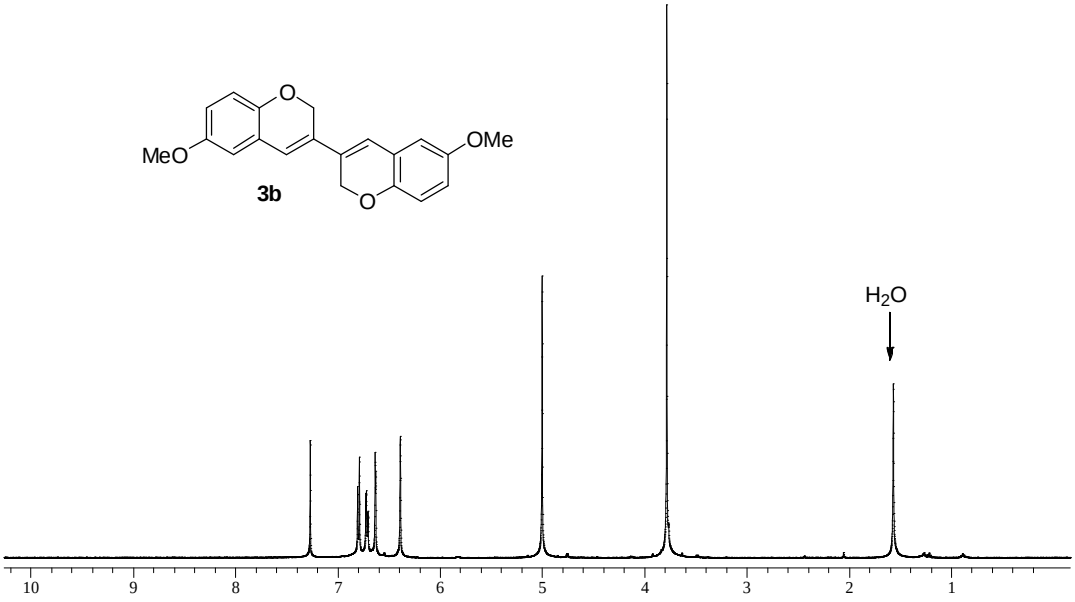
HRMS

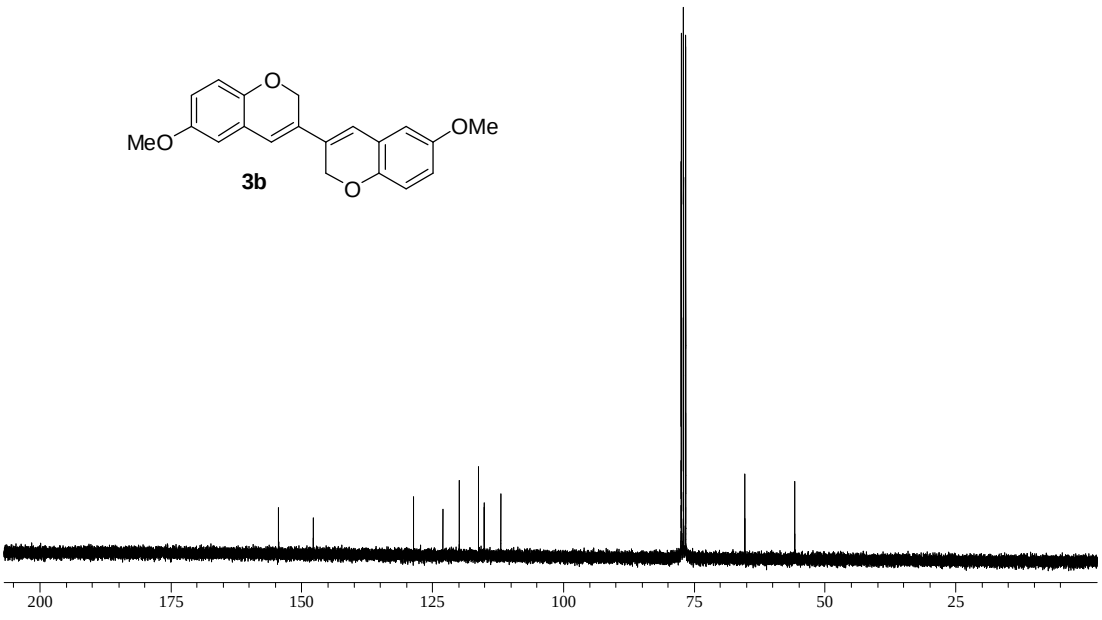


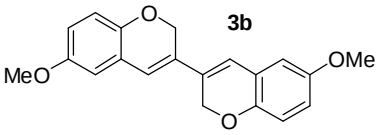
Chemical Formula: $C_{20}H_{18}O_2 + H$


O
H3CO
3a
H2O
10
9
8
7
6
5
4
3
2
1

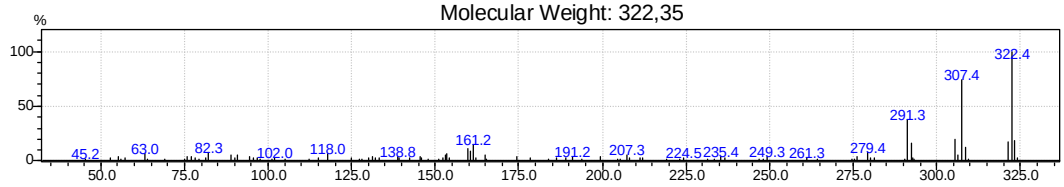

O
H3CO
3a
200
175
150
125
100
75
50
25
0


MeO
OMe
O
O
3b
H2O
10
9
8
7
6
5
4
3
2
1


MeO
OMe
O
O
3b
200
175
150
125
100
75
50
25



Chemical Formula: $C_{20}H_{18}O_4$
Molecular Weight: 322,35



HRMS

Mass to be matched (m/z): 345.109743 Charge: 1

Mass Tolerance: ±0.030000
Restriction of atom numbers:
C H O Na
1-100 1-100 1-10 1-1
Number of calculated Formulas: 6

Formula	Diff.(ppm)	theor. m/z
C20 H18 O4 Na1	-0.04	345.109728
C13 H22 O9 Na1	16.98	345.115602
C24 H18 O1 Na1	44.17	345.124987
C16 H18 O7 Na1	-44.24	345.094477
C17 H22 O6 Na1	61.19	345.130861
C23 H14 O2 Na1	-61.26	345.088602

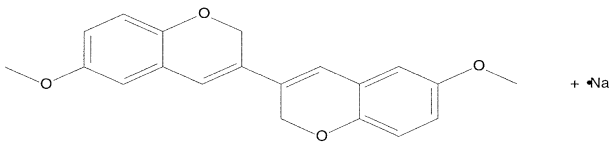
1.07.2010
File: 90860

Analyse: RPS-RC-014-11
LIS: Rampalakos,Konstantinos

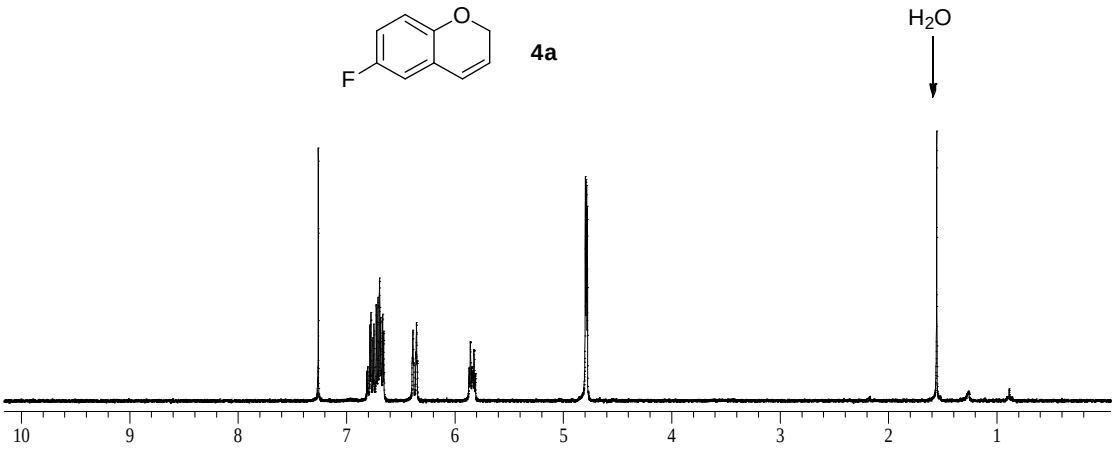
Messung:Massenfeinbestimmung
Ionis. :ESIpos
Lsgsm. :CH2Cl2+CH3OH
Spectr.:ICR

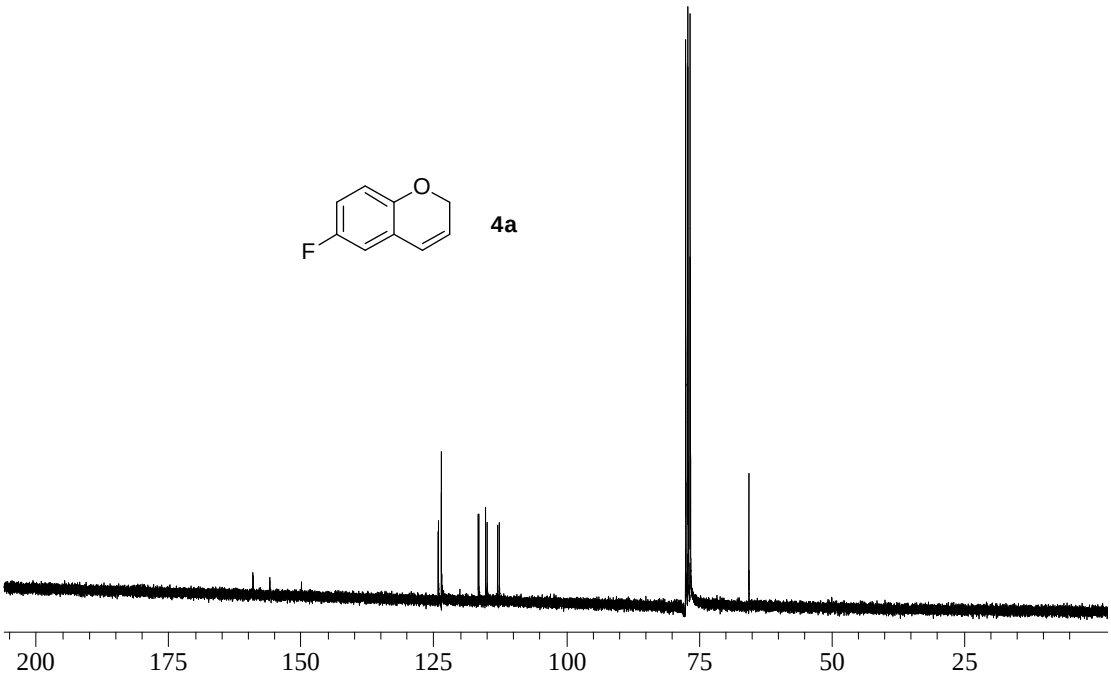
Blumenthal, Tel. 2235

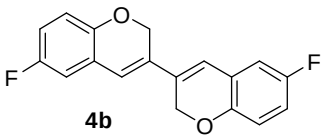
Vorschlag:



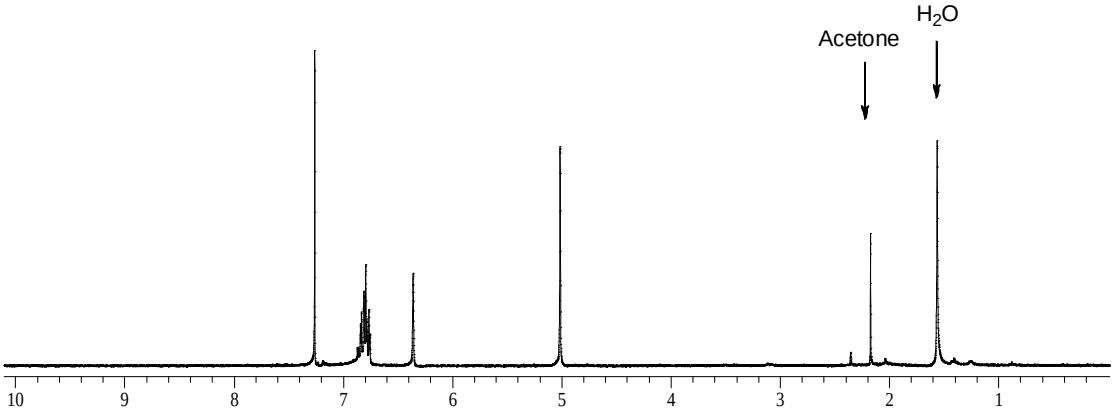
C20H18Na1O4


O
F
4a
H2O
10
9
8
7
6
5
4
3
2
1


O
F
4a
200
175
150
125
100
75
50
25

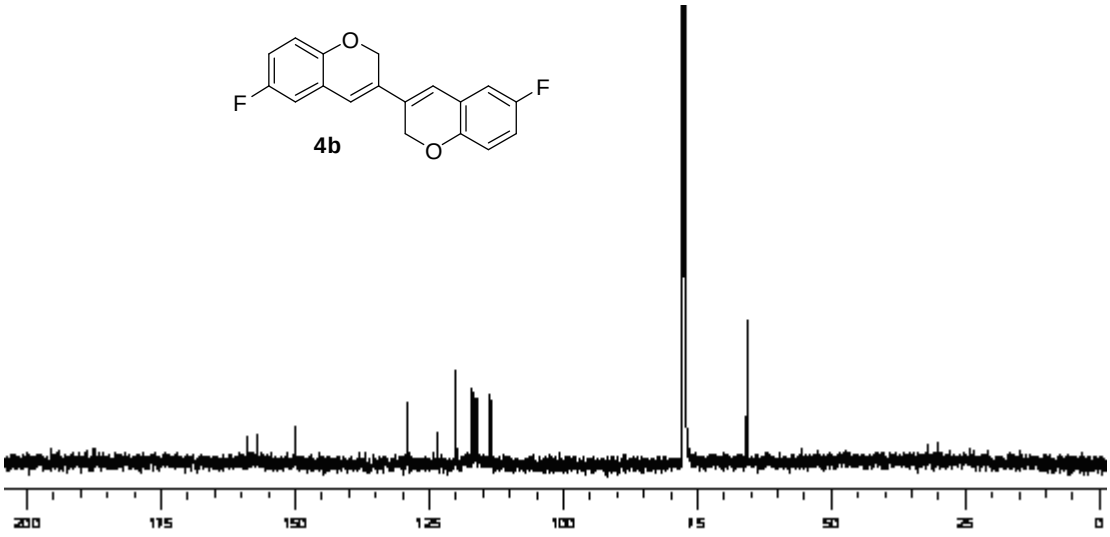

O
F
F
O

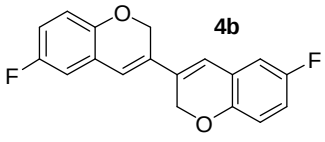
4b


Acetone
H2O
10
9
8
7
6
5
4
3
2
1

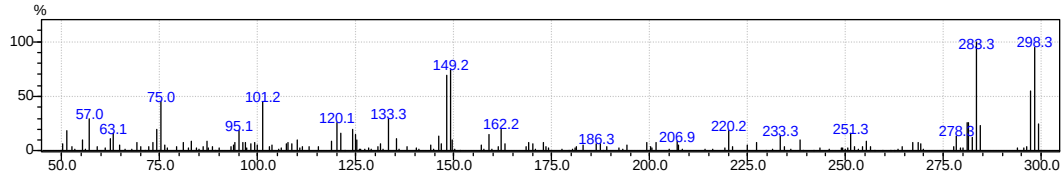
O
F
F
O

4b


200
175
150
125
100
75
50
25
0



Chemical Formula: $C_{18}H_{12}F_2O_2$
Molecular Weight: 298,28



HRMS

Mass to be matched (m/z): 298.080274 Charge: 0

Mass Tolerance: ±0.030000
Restriction of atom numbers:
C H O F
1-100 1-100 1-10 2-2
Number of calculated Formulas: 6

Formula	Diff.(ppm)	theor. m/z
C18 H12 O2 F2	0.87	298.080534
C11 H16 O7 F2	20.58	298.086408
C7 H16 O10 F2	-30.59	298.071157
C14 H12 O5 F2	-50.29	298.065282
C15 H16 O4 F2	71.77	298.101667
C8 H20 O9 F2	91.48	298.107542

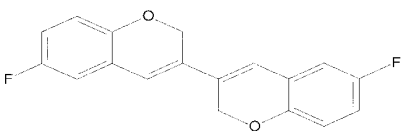
2.07.2010
File: 90866.mcu

Analyse:RPS-RC-014-09
LIS: Rampalakos,Konstantinos

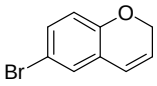
Messung:Massenfeinbestimmung
Ionis. :EI(DE)
Refer. :PFK
Spectr.:MAT95

M.Blumenthal,Tel.:2235

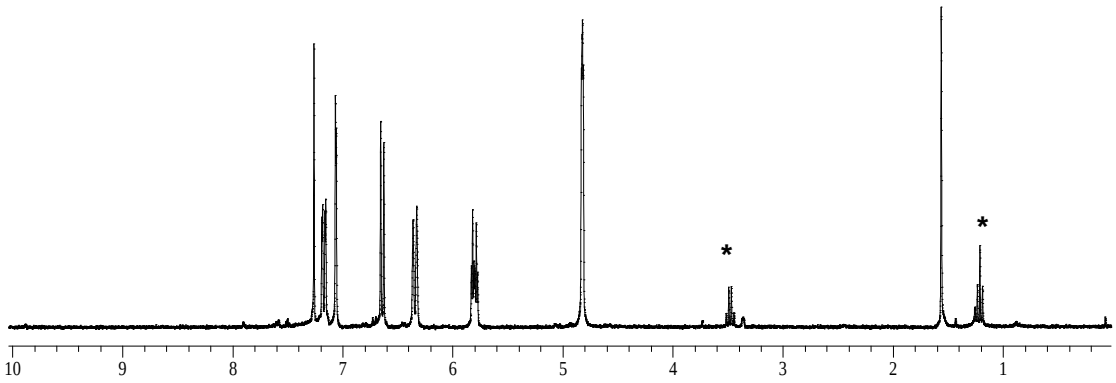
Vorschlag:



C18H12F2O2

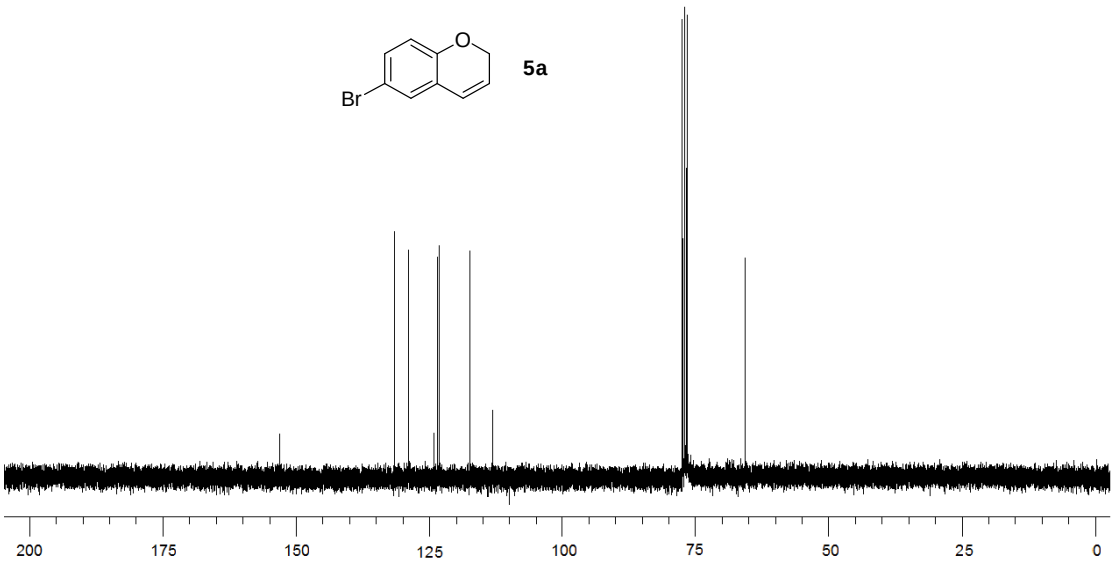


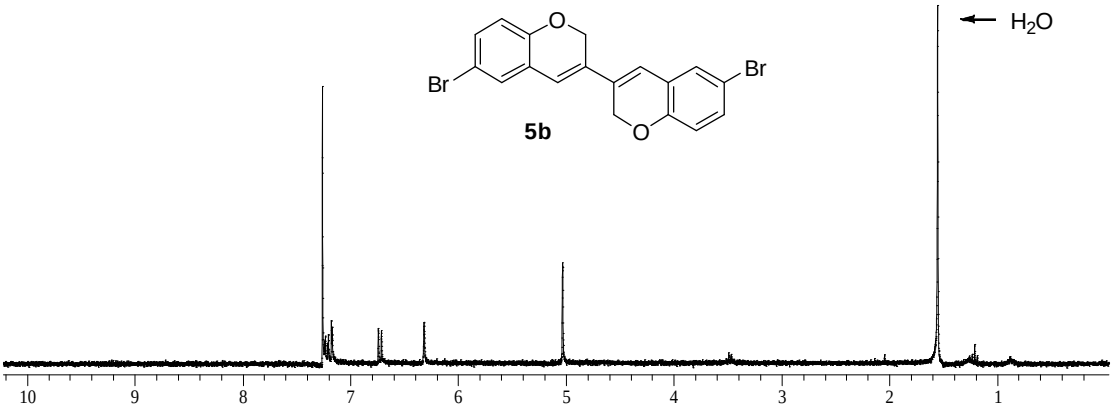
5a

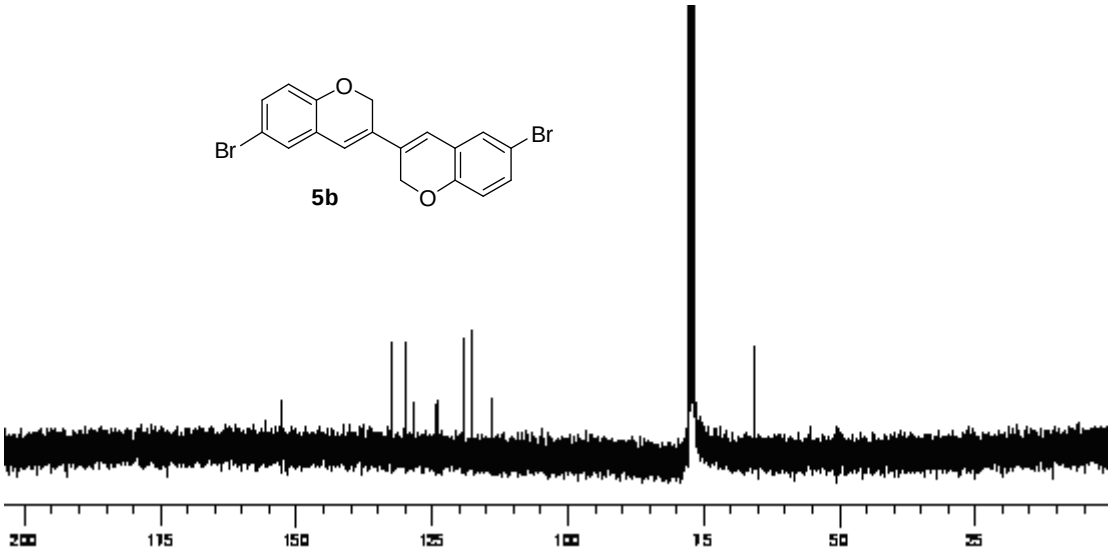


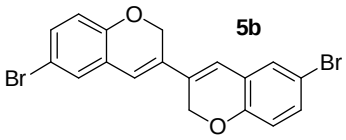
***** = Diethyl ether

5a

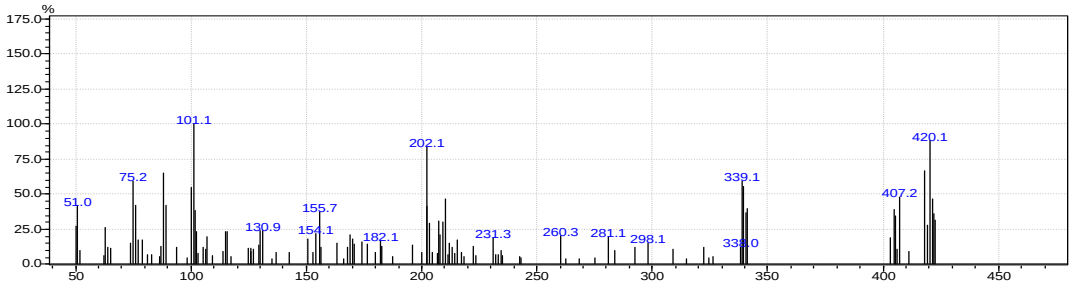



O
Br
Br
O
5b
H2O
10
9
8
7
6
5
4
3
2
1


O
Br
Br
O
5b
200
175
150
125
100
75
50
25



Chemical Formula: $C_{18}H_{12}Br_2O_2$
Molecular Weight: 420,09



HRMS

Mass to be matched (m/z): 417.920817 Charge: 0

Mass Tolerance: ±0.030000
Restriction of atom numbers:

C	H	O	Br
1-100	1-100	1-10	2-2

Number of calculated Formulas: 6

Formula	Diff.(ppm)	theor. m/z
C18 H12 O2 Br2	-0.93	417.920428
C11 H16 O7 Br2	13.13	417.926302
C7 H16 O10 Br2	-23.37	417.911051
C14 H12 O5 Br2	-37.42	417.905176
C15 H16 O4 Br2	49.64	417.941561
C8 H20 O9 Br2	63.69	417.947436

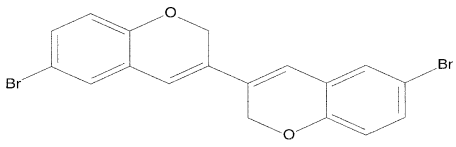
2.07.2010
File: 90867.mcu

Analyse:RPS-RC-014-10
LIS: Rampalakos,Konstantinos

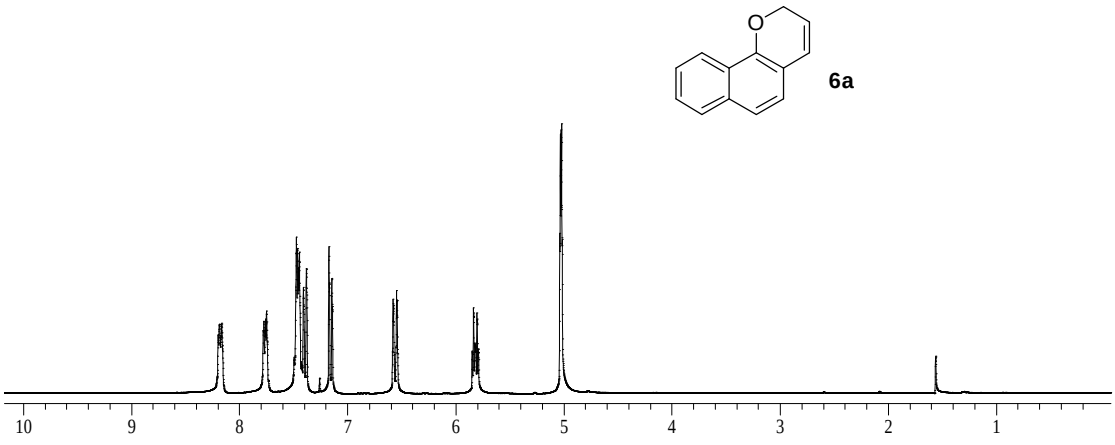
Messung:Massenfeinbestimmung
Ionis. :EI(DE)
Refer. :PFK
Spectr.:MAT95

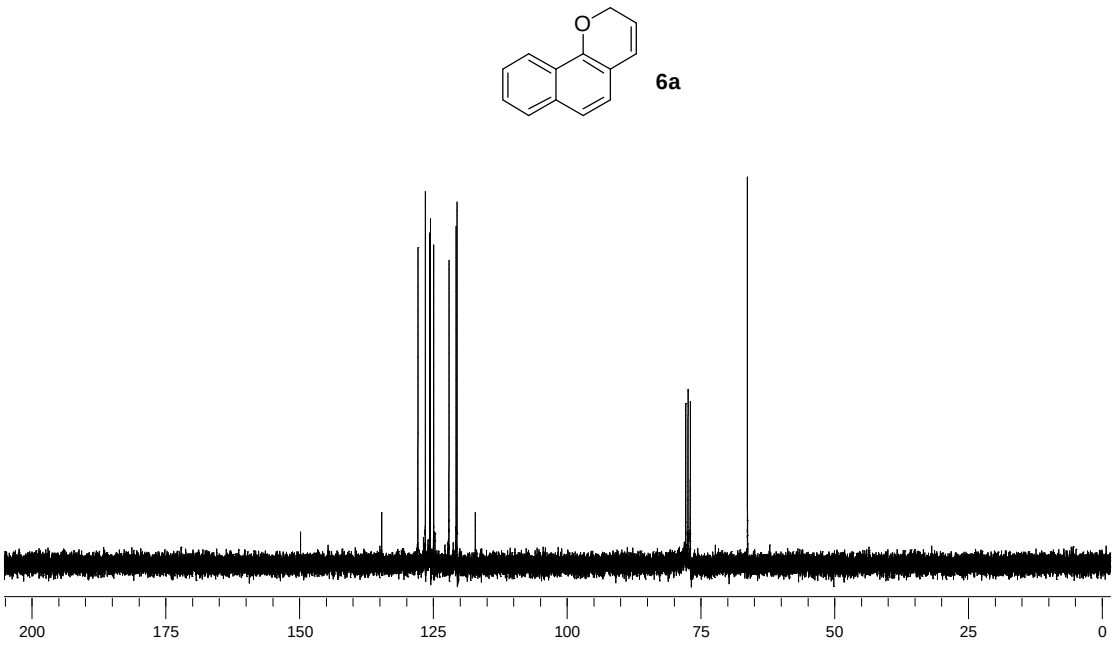
M.Blumenthal,Tel.:2235

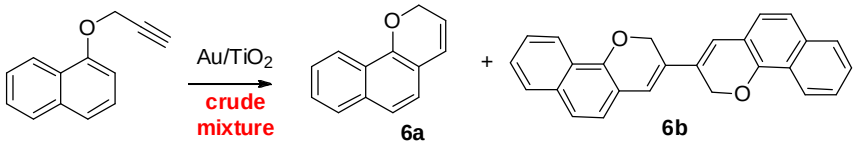
Vorschlag:

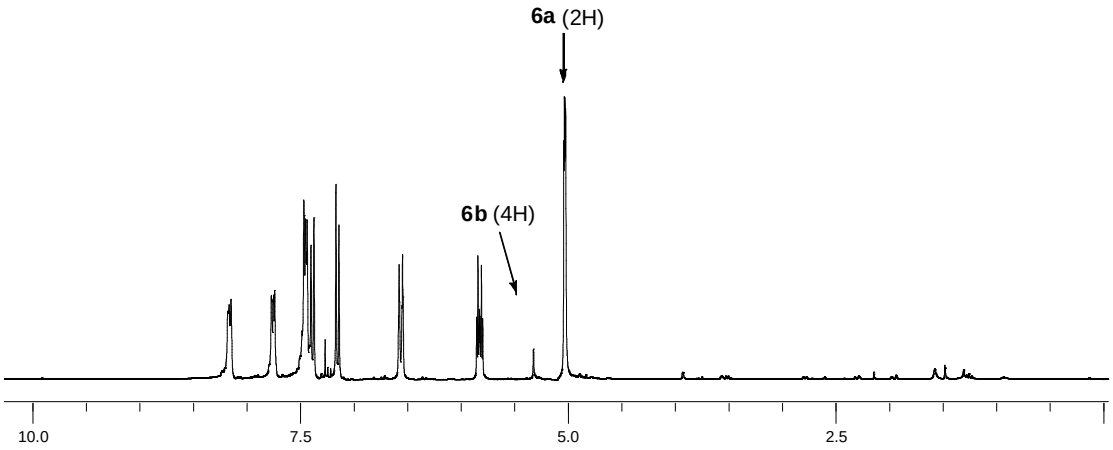


C18H12Br2O2

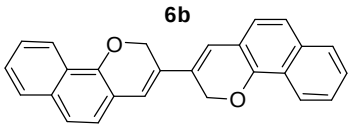

O
6a
10
9
8
7
6
5
4
3
2
1


O
6a
200
175
150
125
100
75
50
25
0

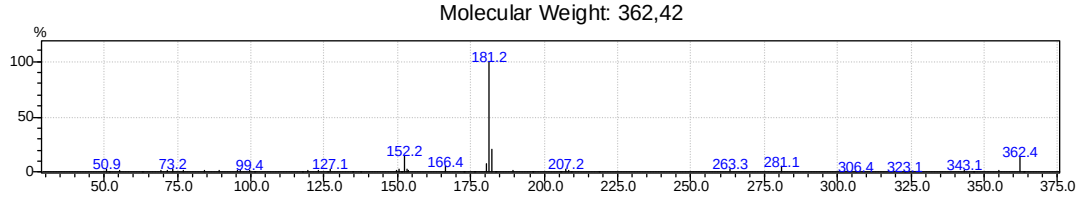


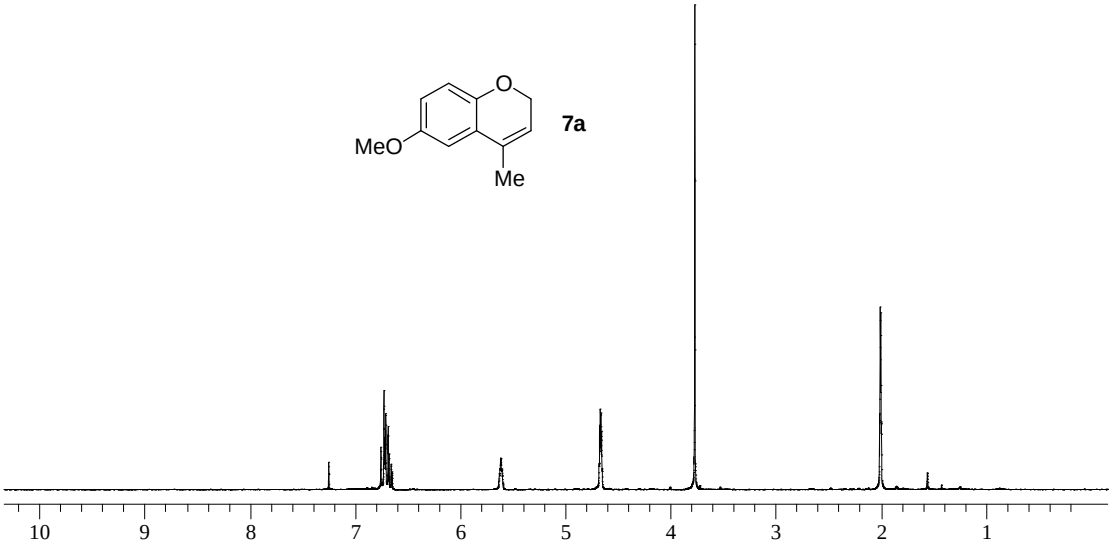


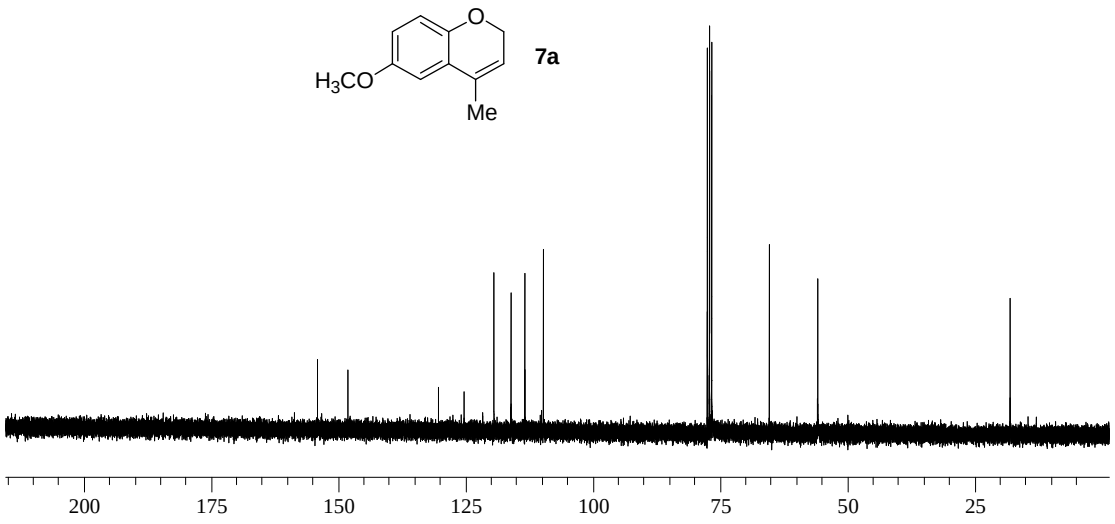
Identification of dimer 6b by analysis of the crude reaction mixture by GC-MS

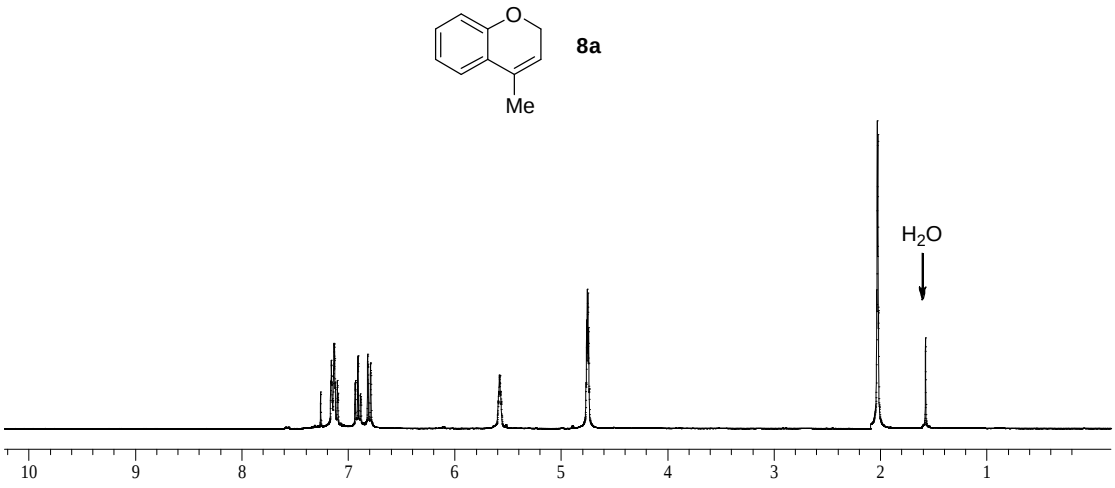


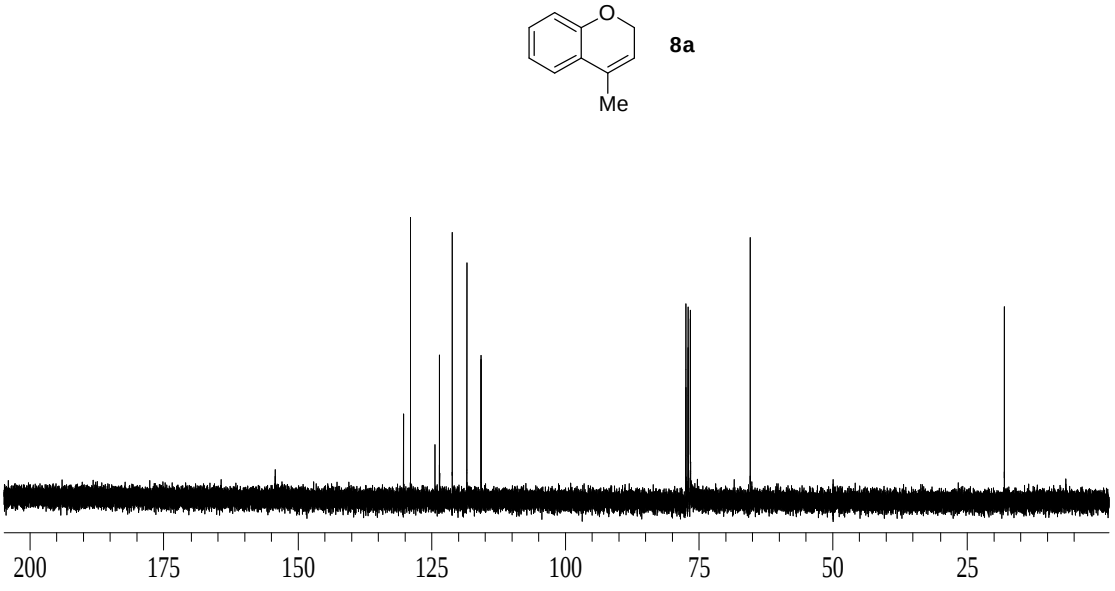
Chemical Formula: $C_{26}H_{18}O_2$
Molecular Weight: 362,42

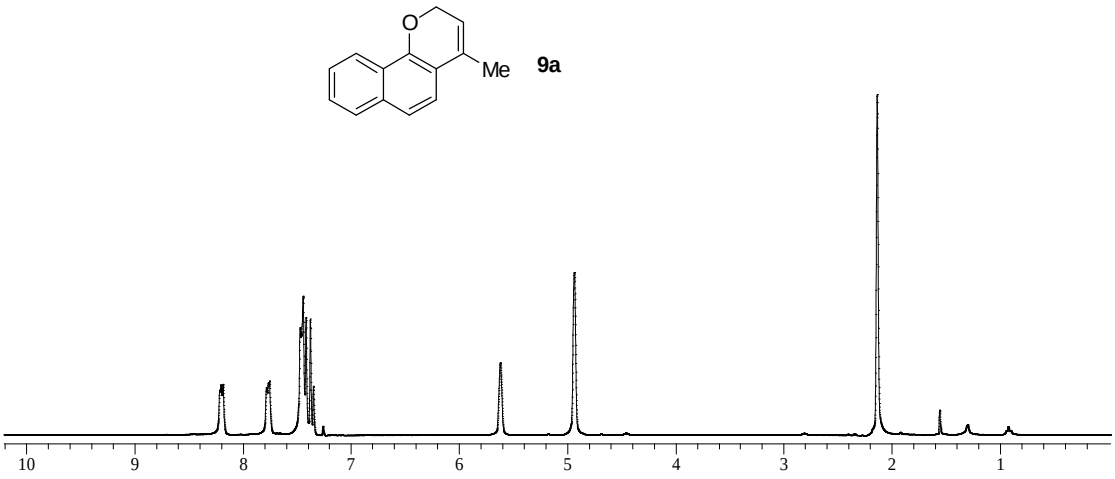


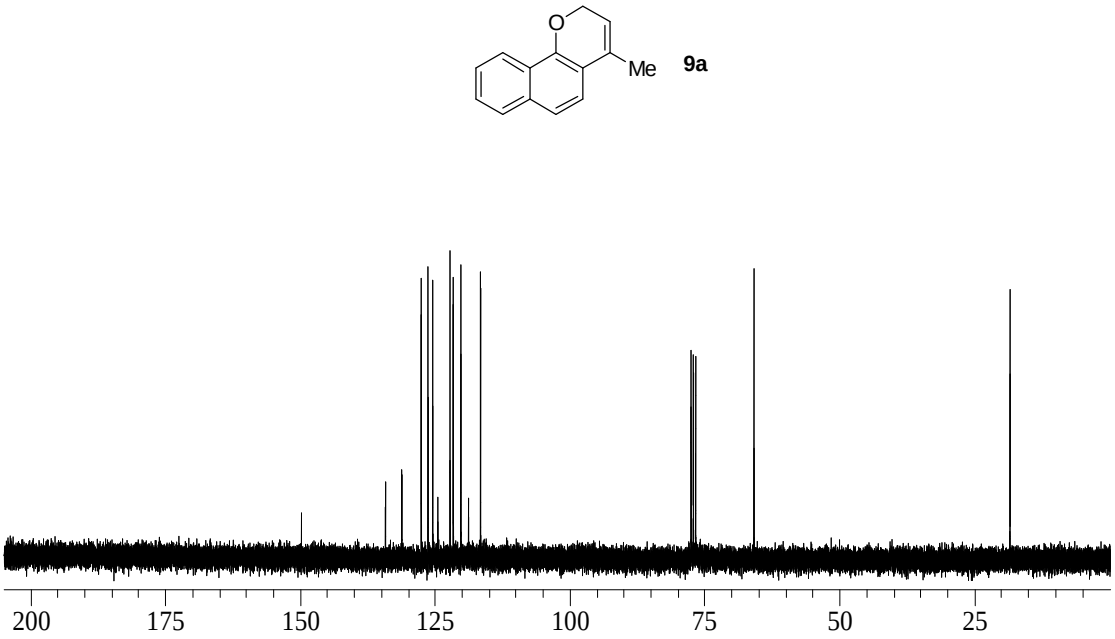

O
MeO
Me
7a
10
9
8
7
6
5
4
3
2
1

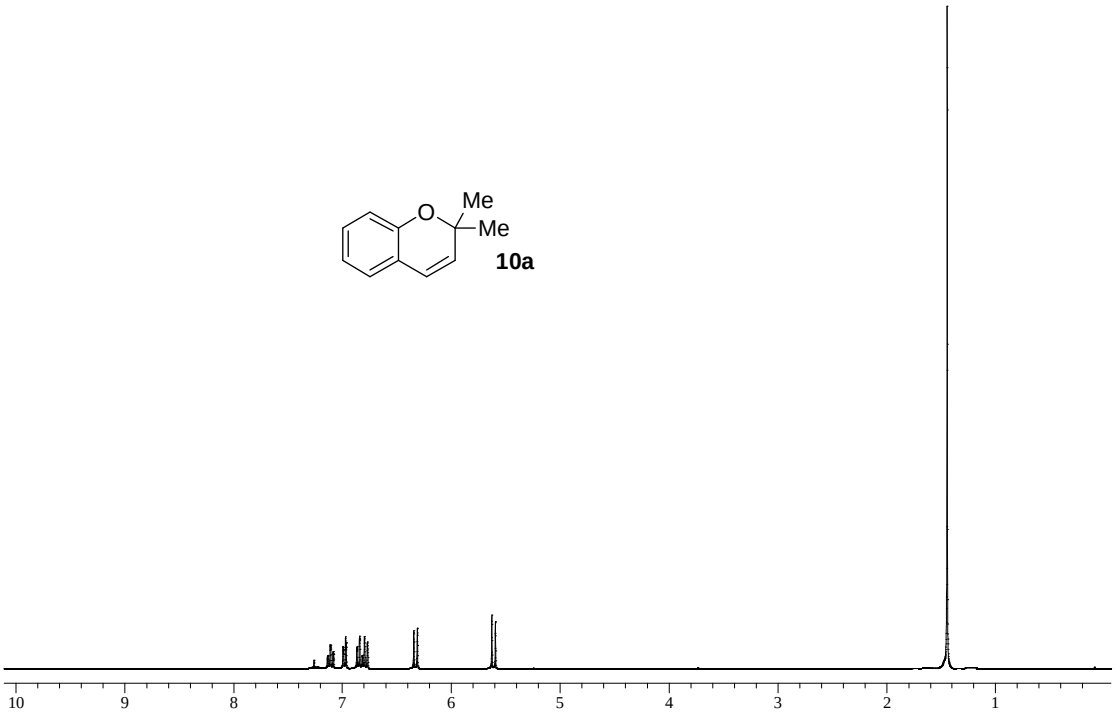

O
H3CO
Me
7a
200
175
150
125
100
75
50
25

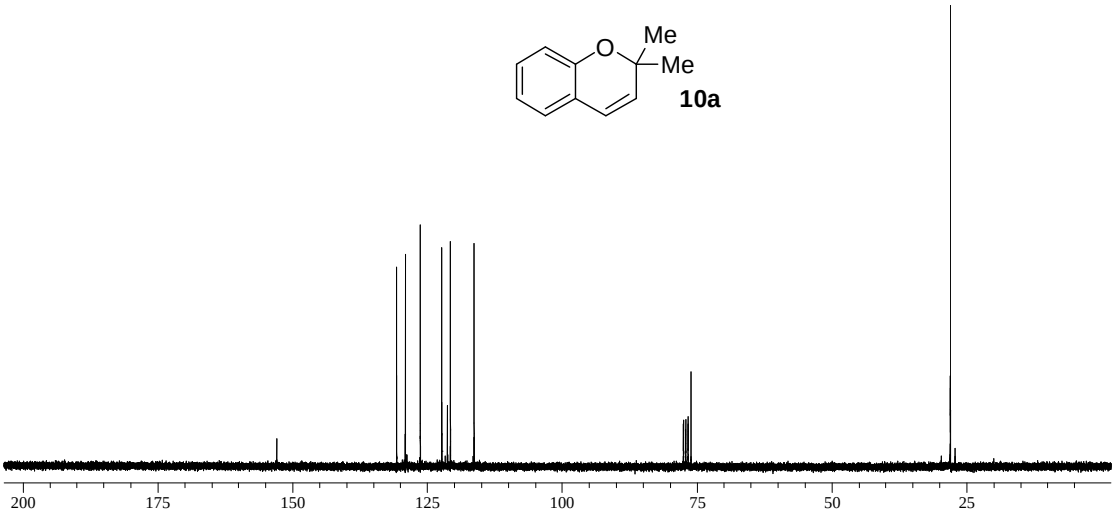

O
Me
8a
H2O
10
9
8
7
6
5
4
3
2
1

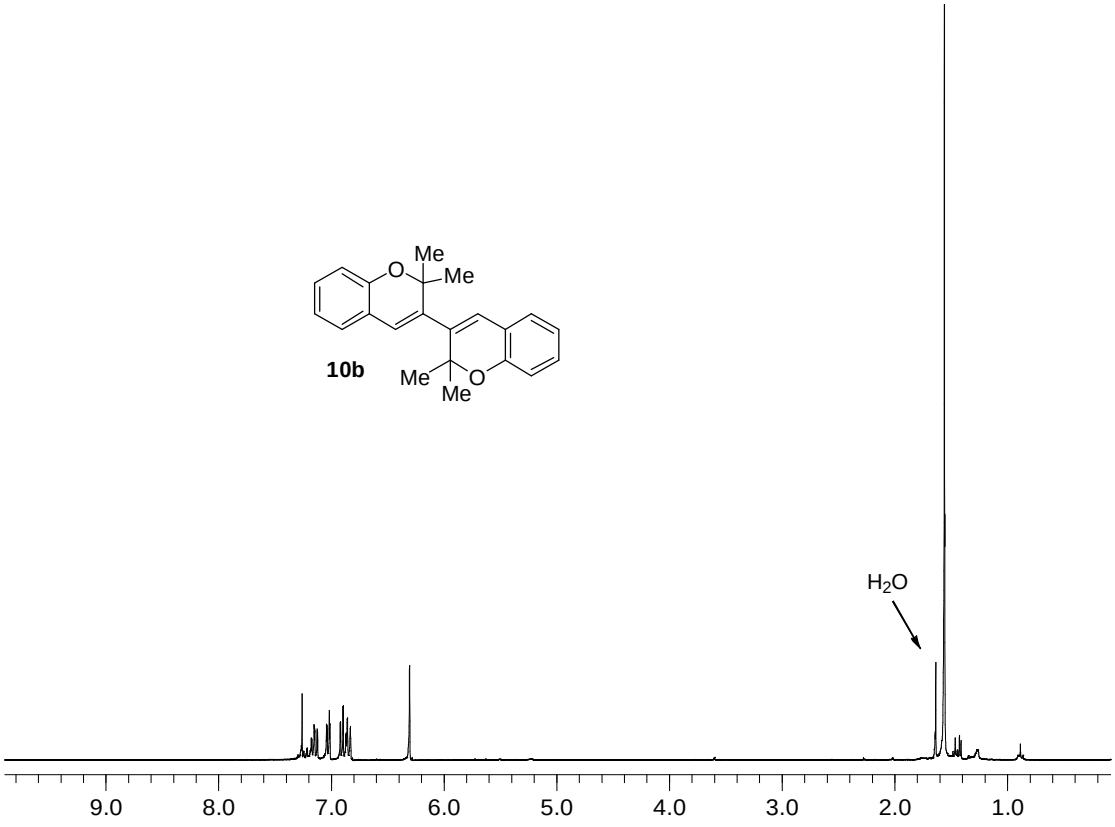

O
Me
8a
200
175
150
125
100
75
50
25

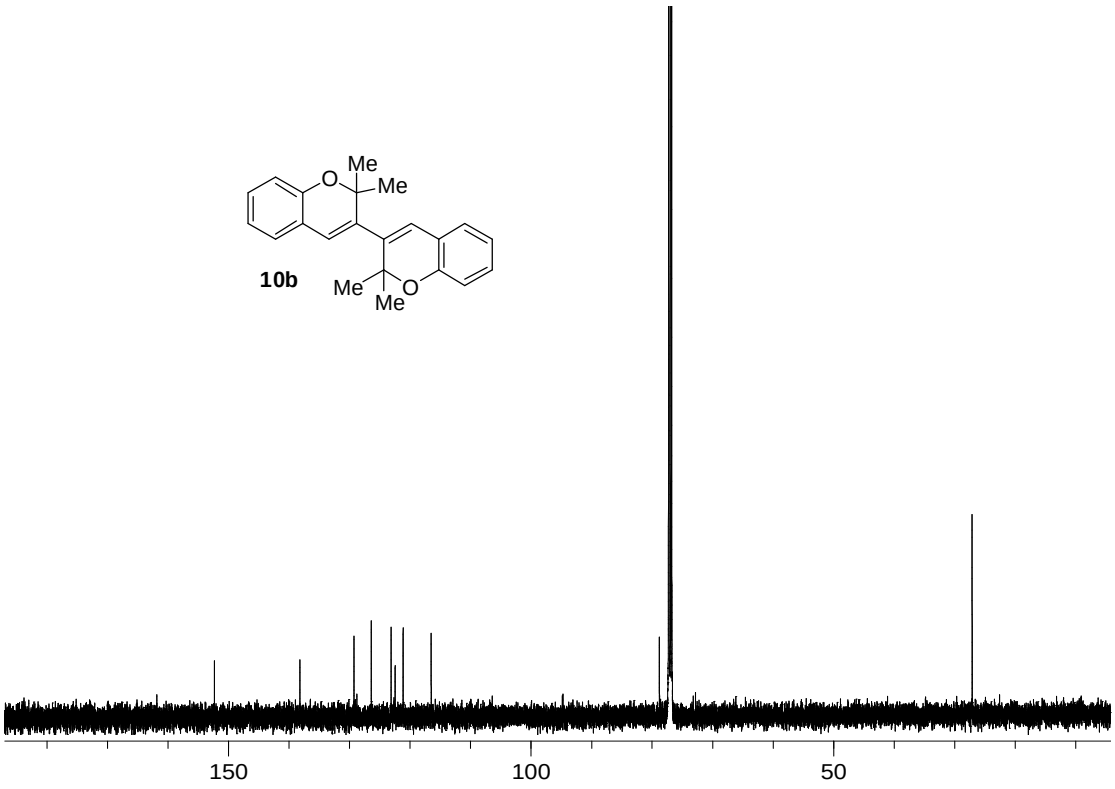

O
Me
9a
10
9
8
7
6
5
4
3
2
1

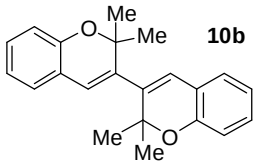

O
Me
9a
200
175
150
125
100
75
50
25


Me
Me
10a
10
9
8
7
6
5
4
3
2
1


Me
Me
10a
200
175
150
125
100
75
50
25

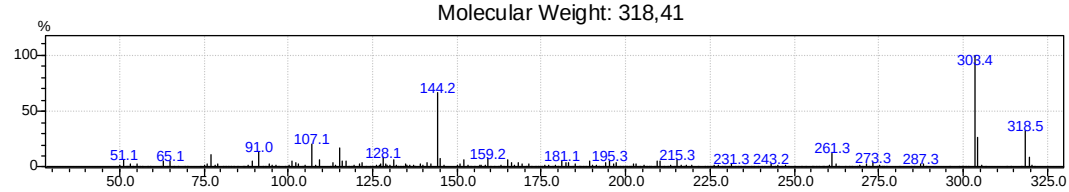

Me
O
Me
Me
O
Me
10b
H2O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


Me
O
Me
Me
O
Me
10b
150
100
50

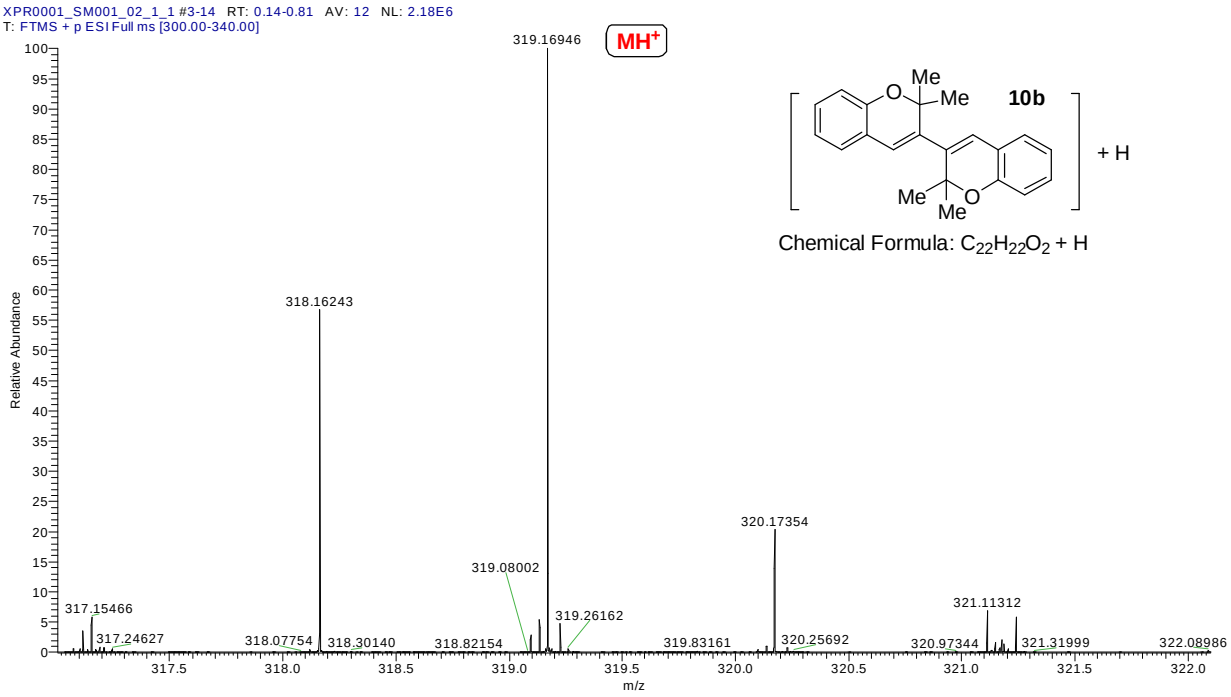


10b

Chemical Formula: $C_{22}H_{22}O_2$
Molecular Weight: 318,41

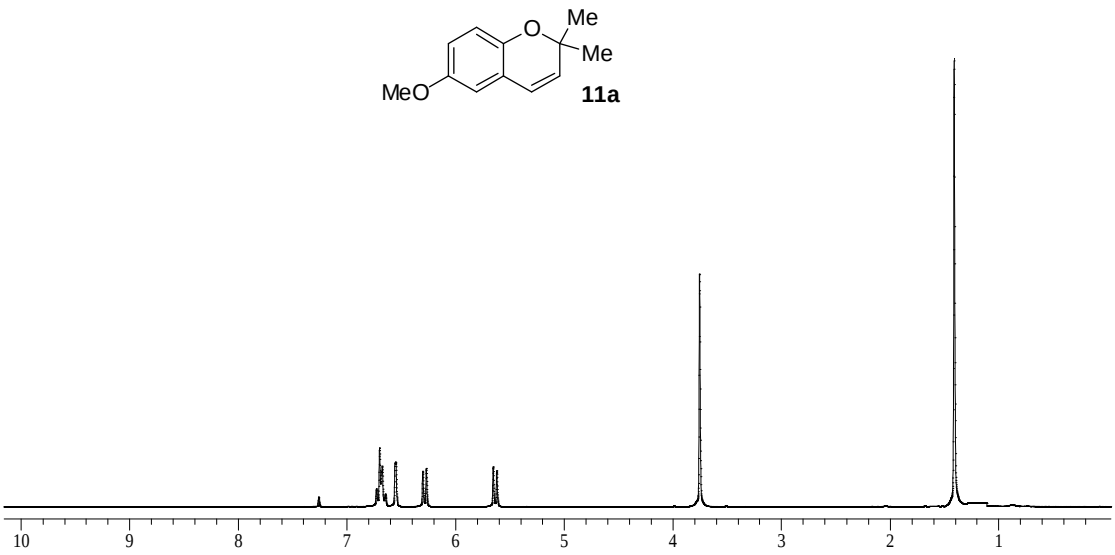


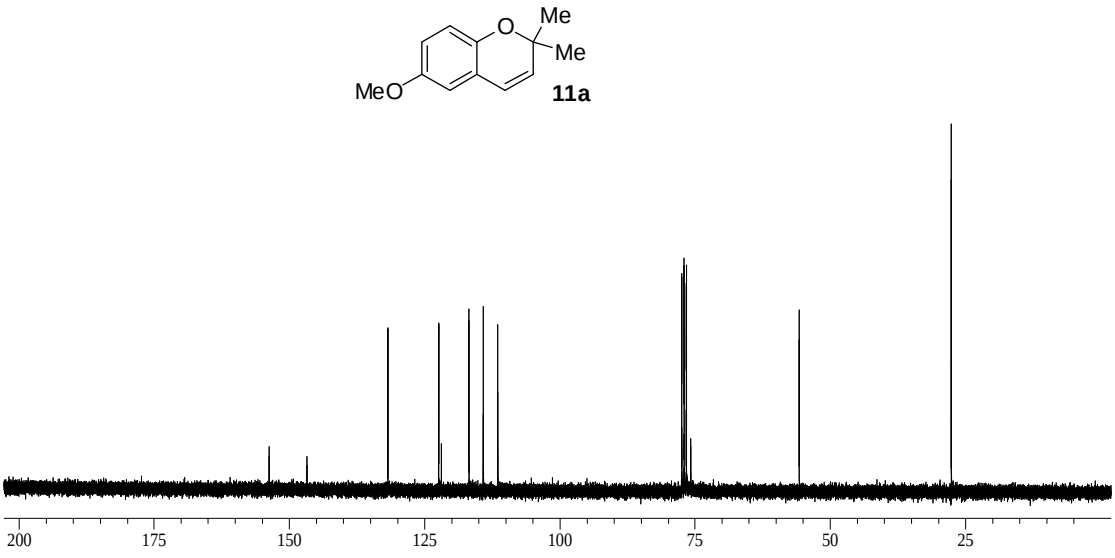
HRMS

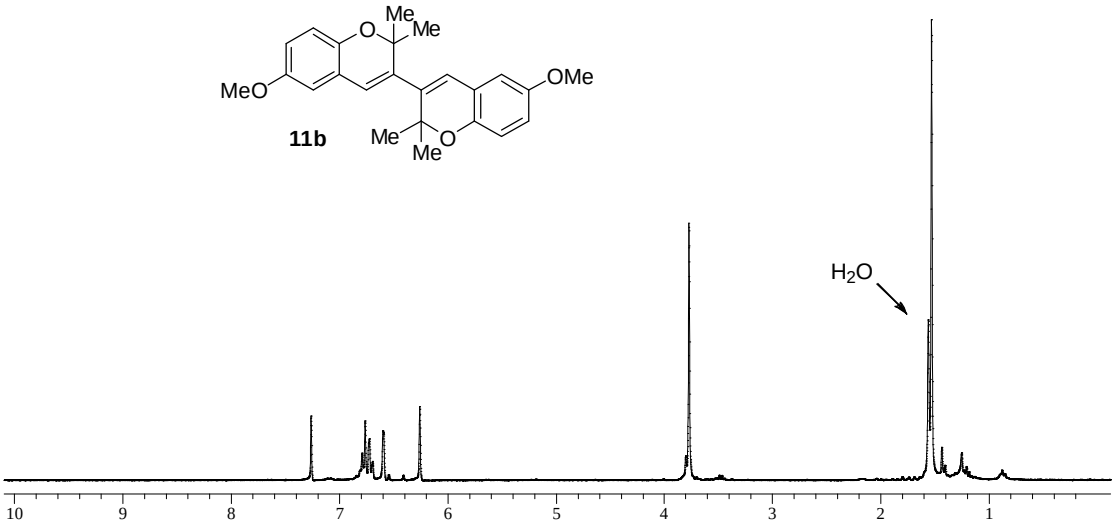


10b

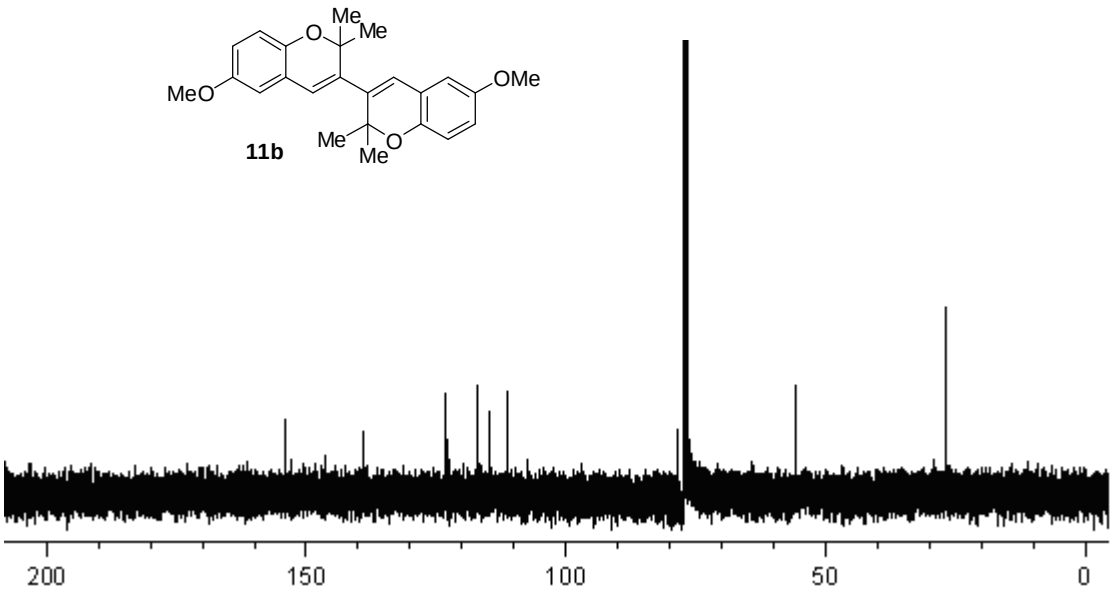
Chemical Formula: $C_{22}H_{22}O_2$ + H


Me
O
Me
MeO
11a
10
9
8
7
6
5
4
3
2
1

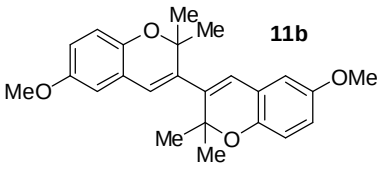

Me
O
Me
MeO
11a
200
175
150
125
100
75
50
25


Me
Me
O
MeO
OMe
Me
O
Me
H2O
10
9
8
7
6
5
4
3
2
1

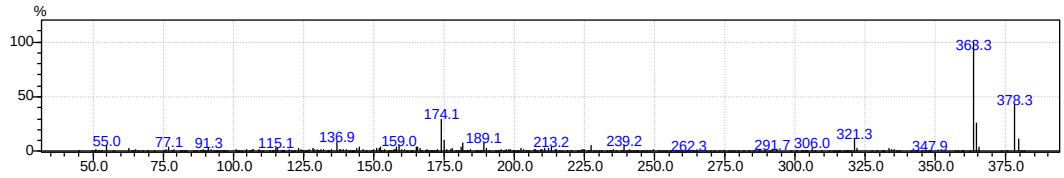
11b


Me
Me
O
MeO
OMe
Me
O
Me
200
150
100
50
0

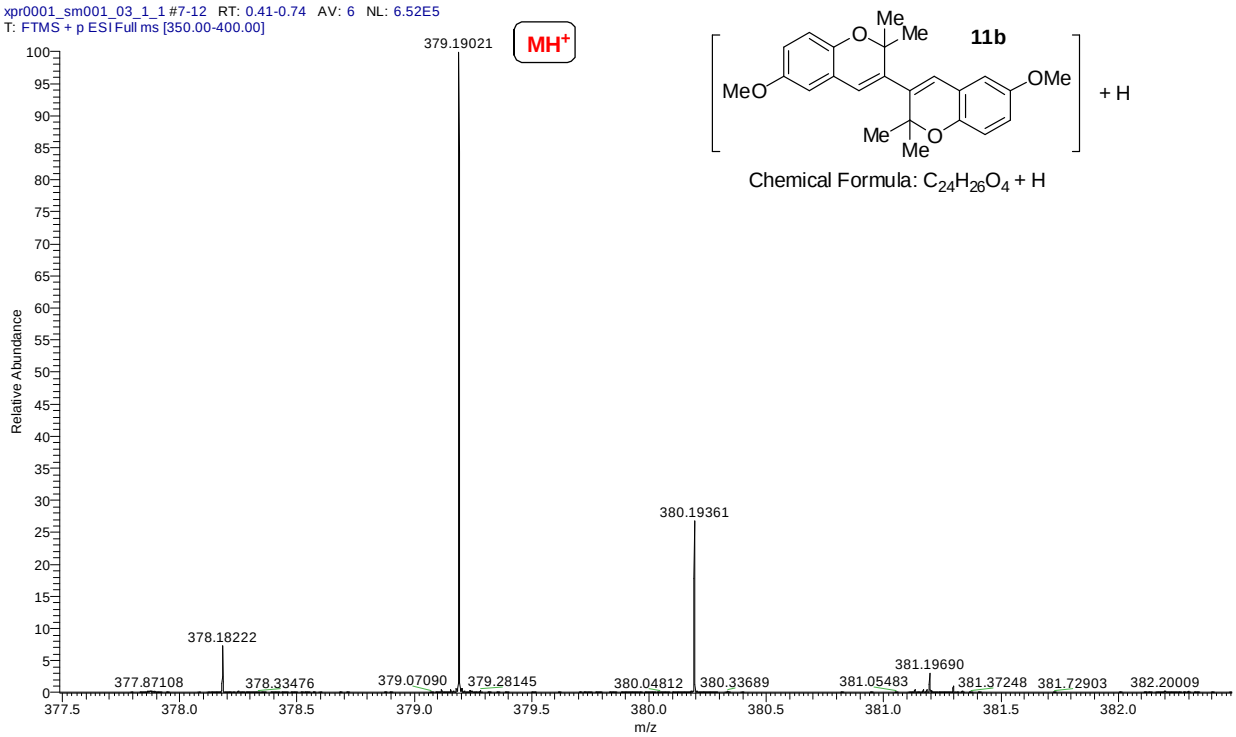
11b



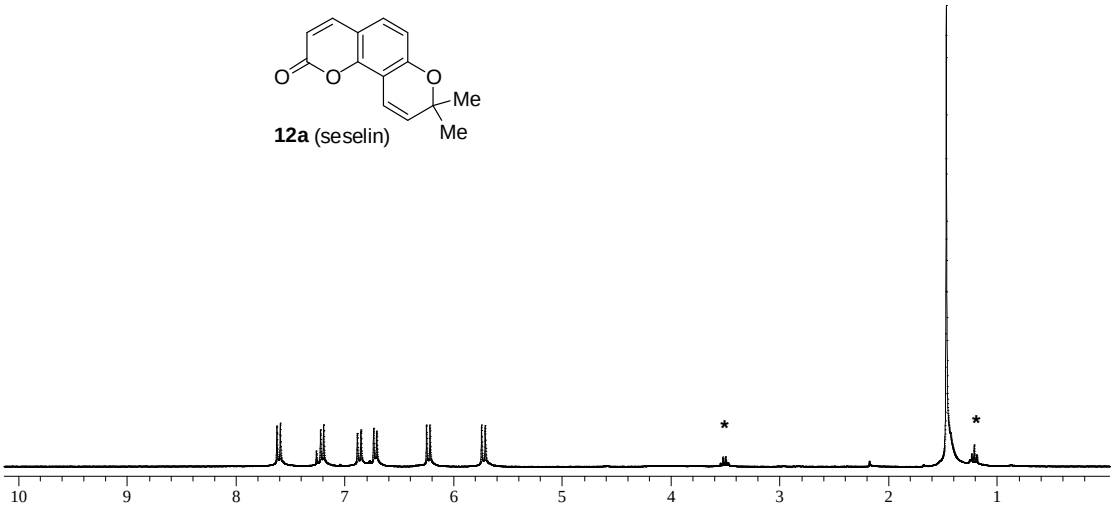
Chemical Formula: $C_{24}H_{26}O_4$
Molecular Weight: 378,46



HRMS

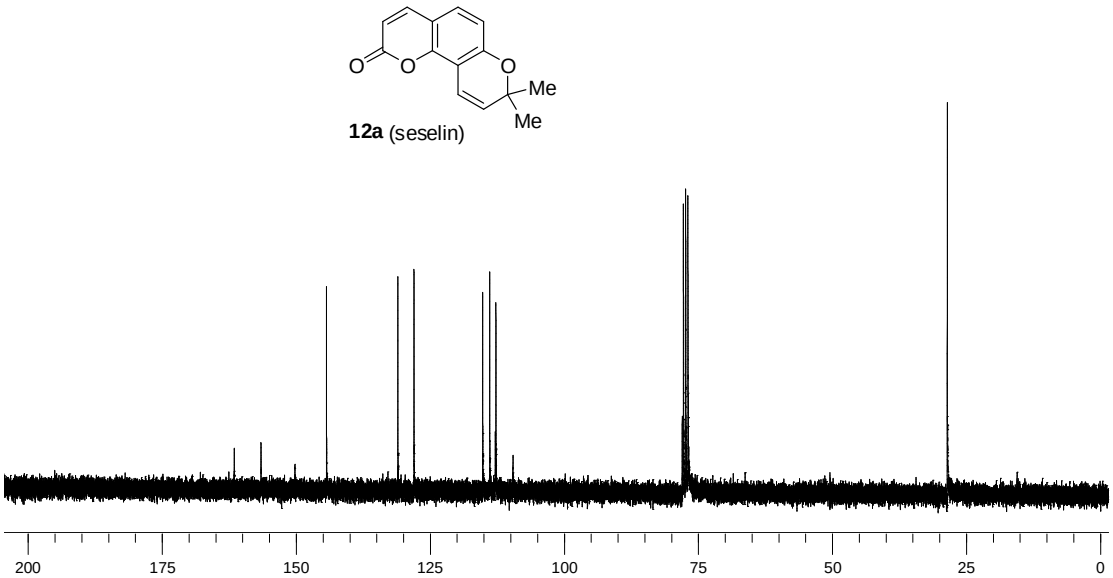


Chemical Formula: $C_{24}H_{26}O_4$ + H



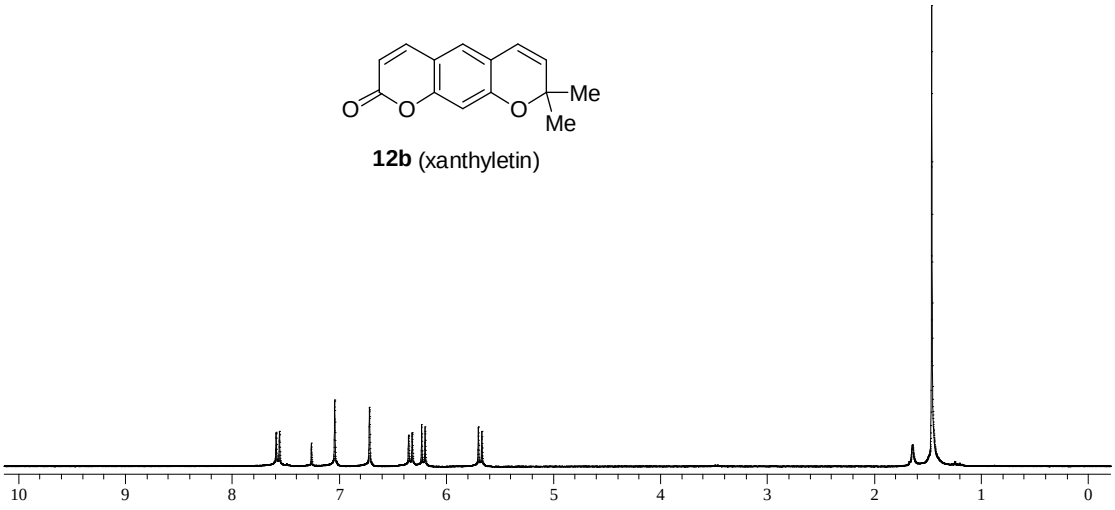
12a (seselin)

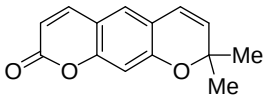
* = Diethyl ether



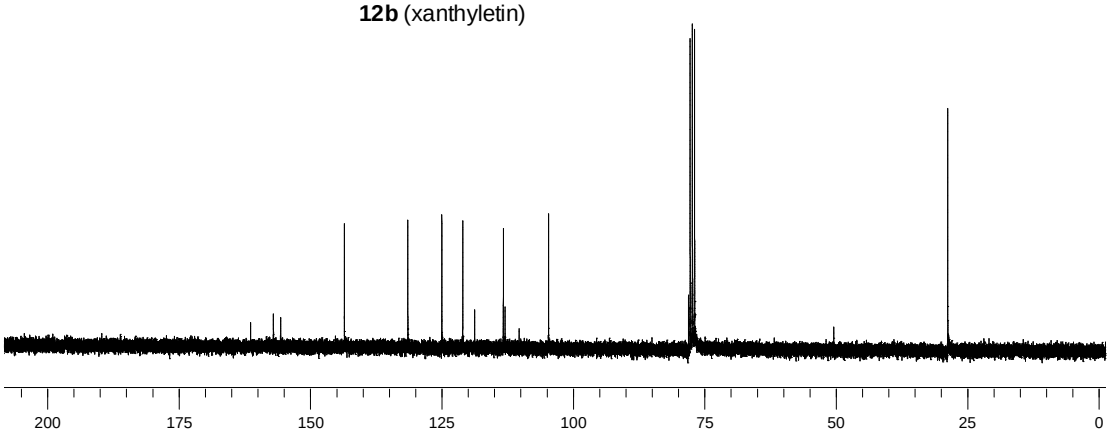
12a (seselin)

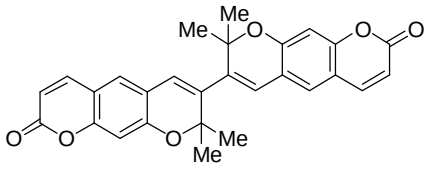
12b (xanthyletin)



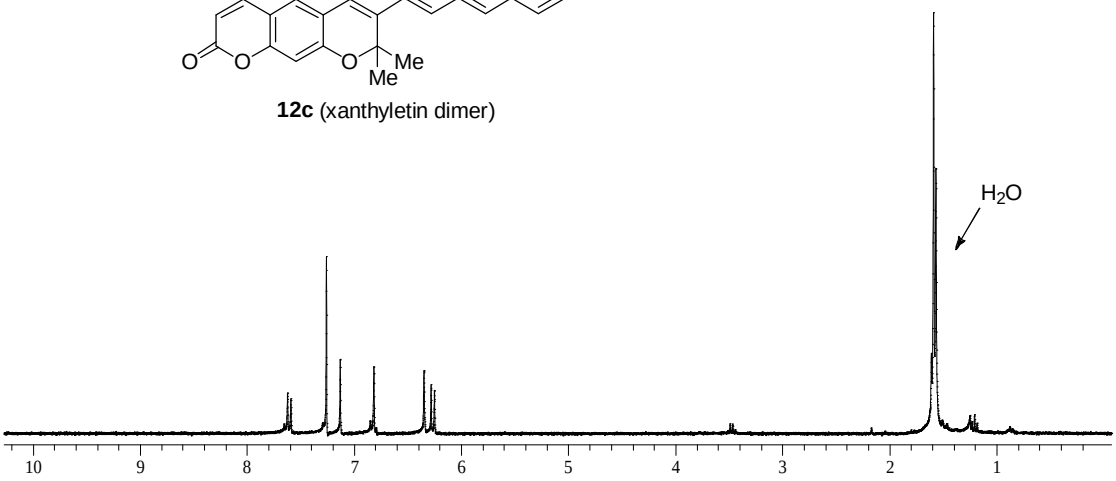


12b (xanthyletin)

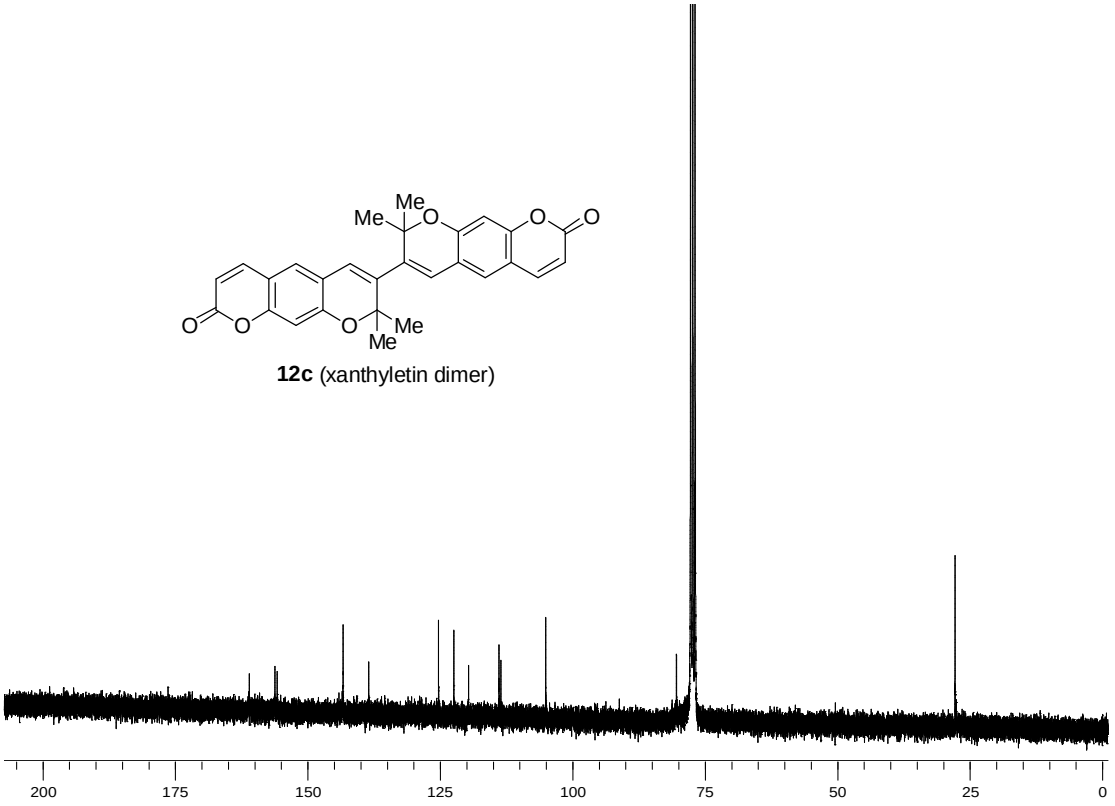




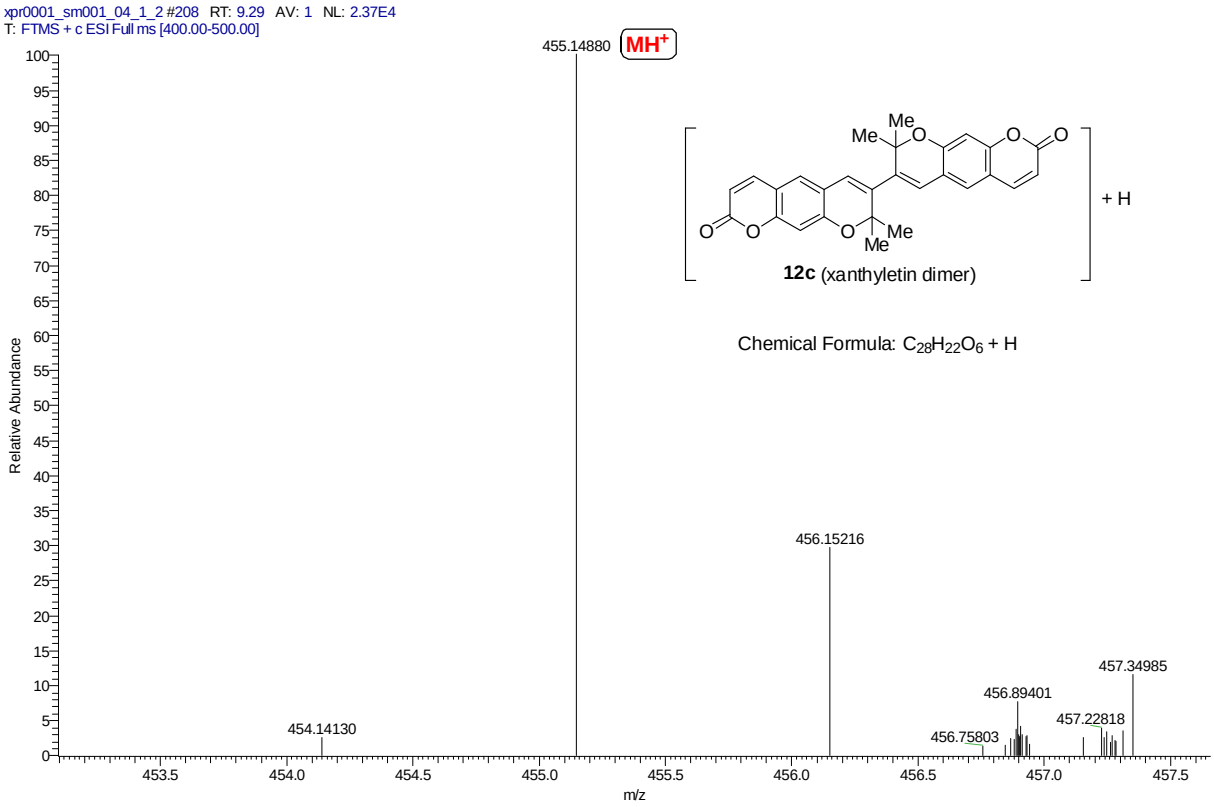
12c (xanthyletin dimer)



12c (xanthyletin dimer)



HRMS


xpr0001_sm001_04_1_2 #208 RT: 9.29 AV: 1 NL: 2.37E4
T: FTMS + c ESI Full ms [400.00-500.00]
455.14880
MH+
456.15216
457.34985
456.89401
457.22818
456.75803
454.14130
Relative Abundance
m/z
Me
Me
O
O
O
O
O
O
Me
Me
+ H
12c (xanthyletin dimer)
Chemical Formula: C28H22O6 + H