Dipolar bent and linear acetylenes substituted by cationic quinolinium and anionic benzoates. Formation of mesomeric betaines.

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1. Frontier orbital profiles

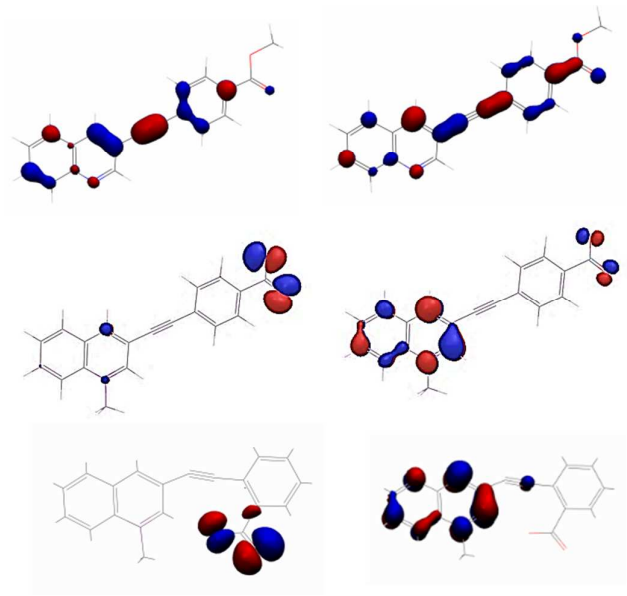


Figure S1. Highest occupied molecular orbitals (HOMOs; left) and lowest unoccupied molecular orbitals (LUMOs; right) of the ester **5a** (above), the mesomeric betaine **8a** (middle), and the instable betaine **8c**$_{bent}$ (below).

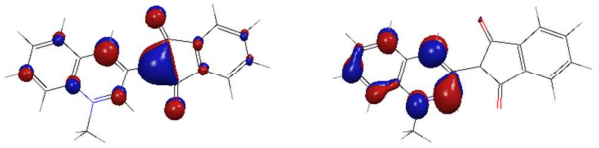


Figure S2. Highest occupied molecular orbital (HOMO, left) and lowest unoccupied molecular orbital (LUMO, right) of mesomeric betaine **10**.

2. Thermal ellipsoid plots

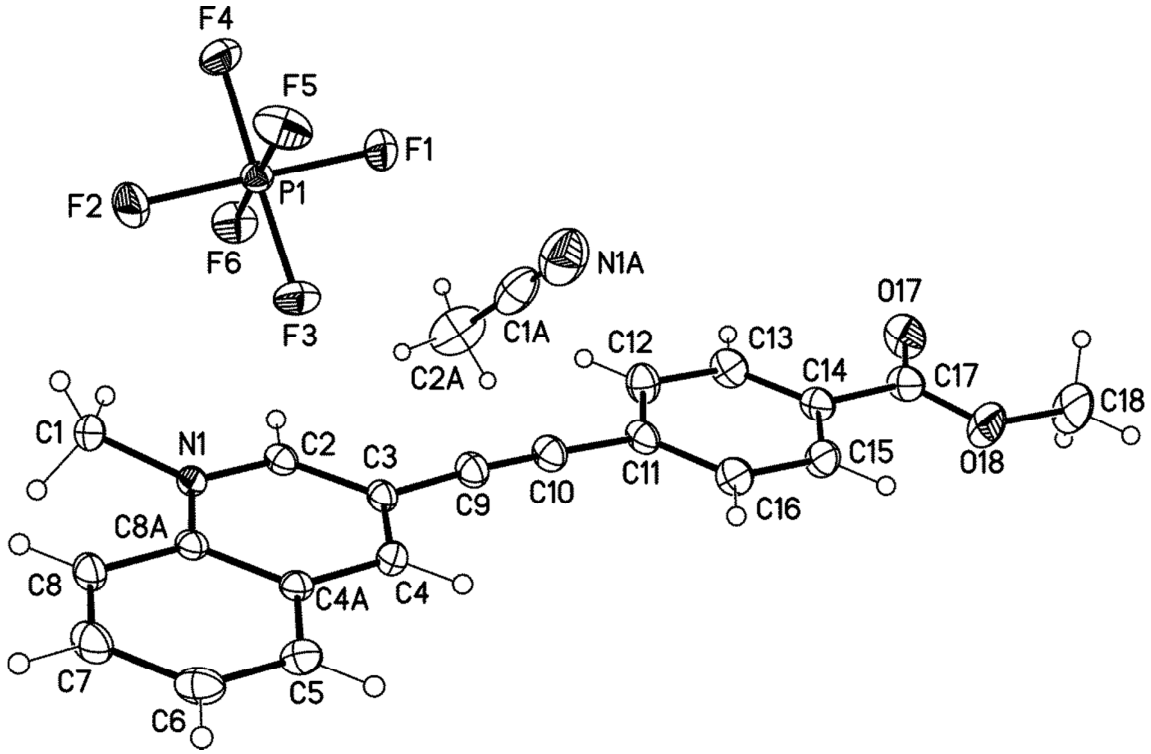


Figure S3. Molecular structure of **6a** (displacement parameters are drawn at 50 % probability level).

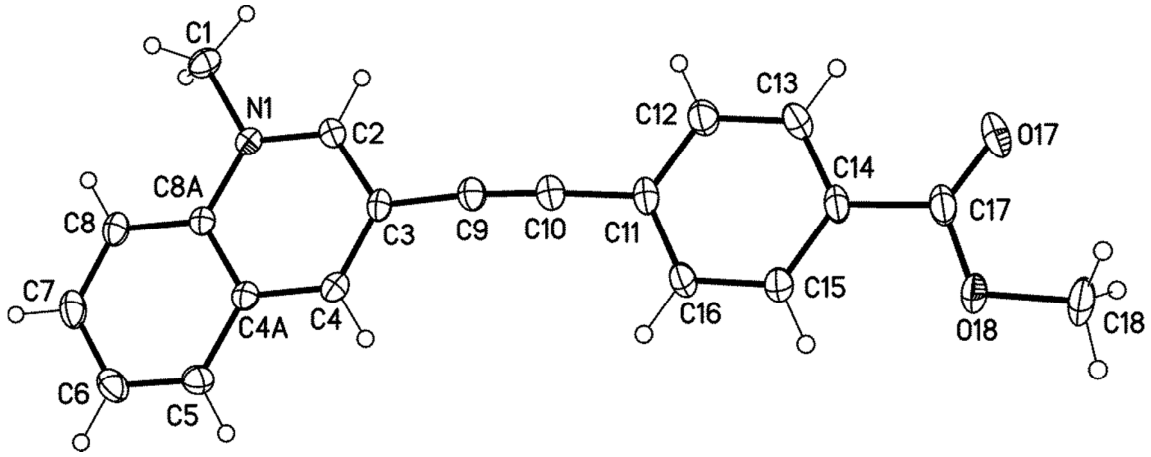


Figure S4. Molecular structure of **6a** (displacement parameters are drawn at 50 % probability level). The anion and MeCN are omitted for clarity.

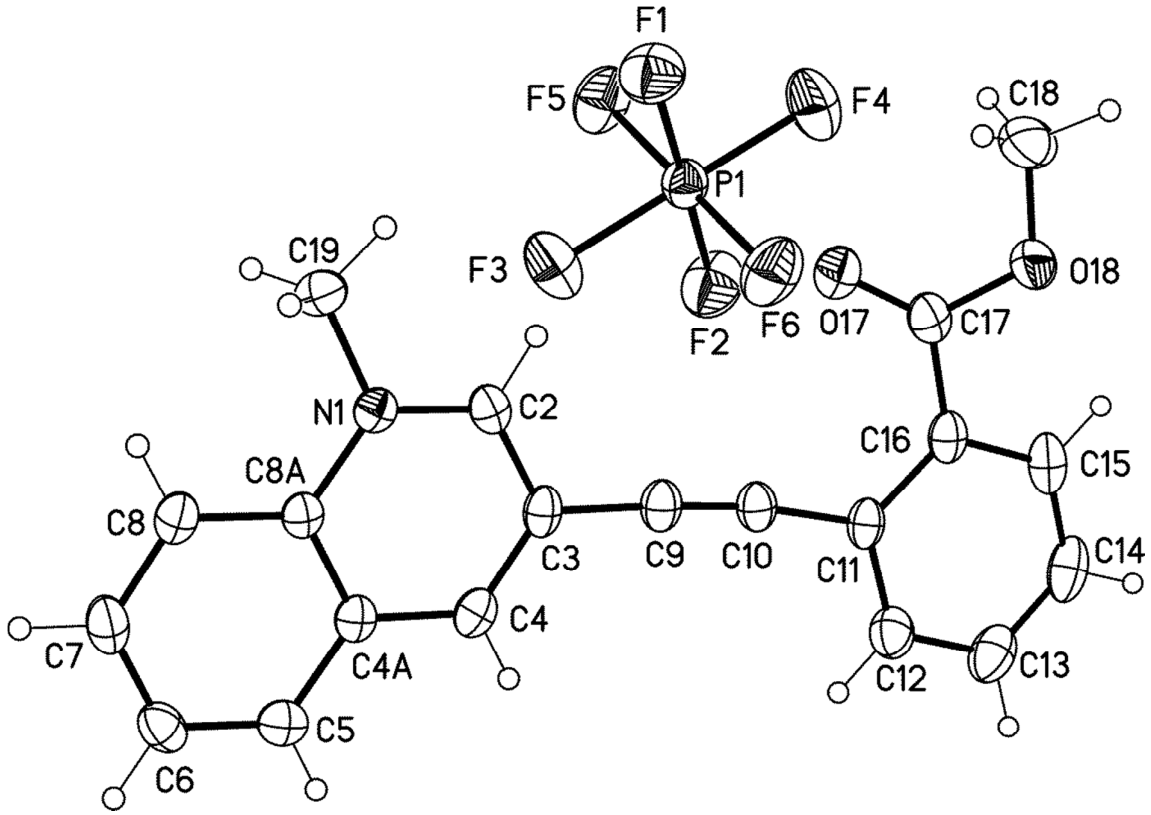


Figure S5. Molecular structure of **6c** (displacement parameters are drawn at 50 % probability level).

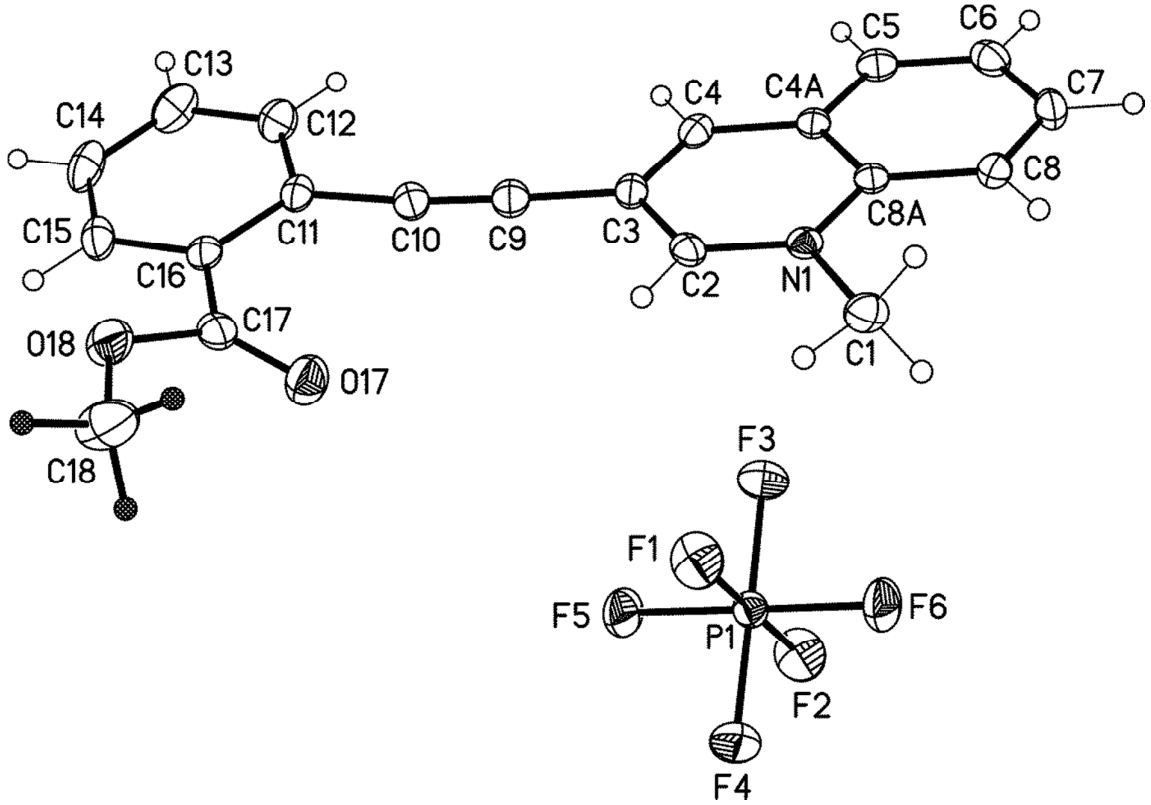


Figure S6. Molecular structure of **6c_D** (displacement parameters are drawn at 50 % probability level).

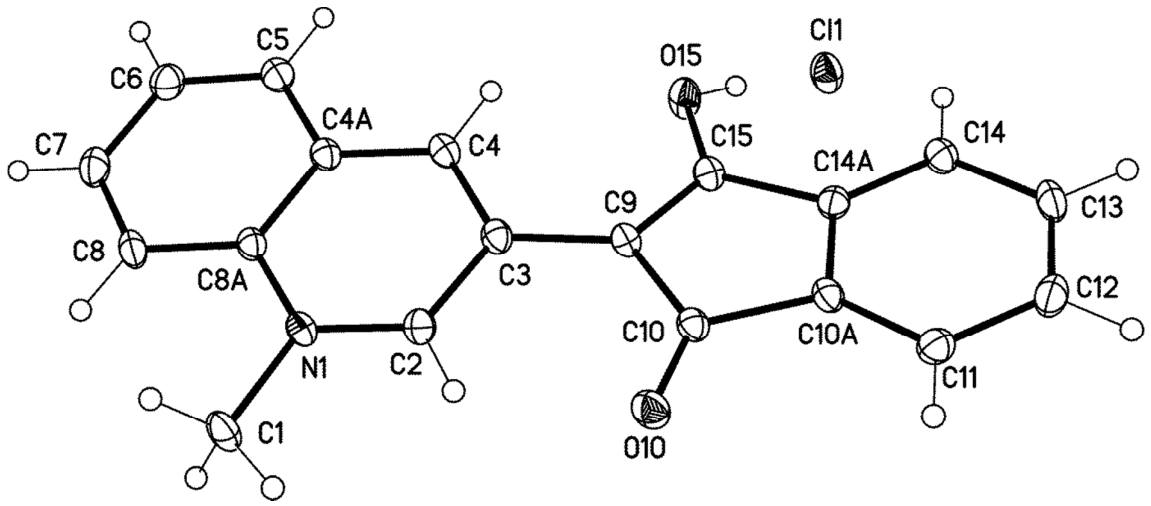
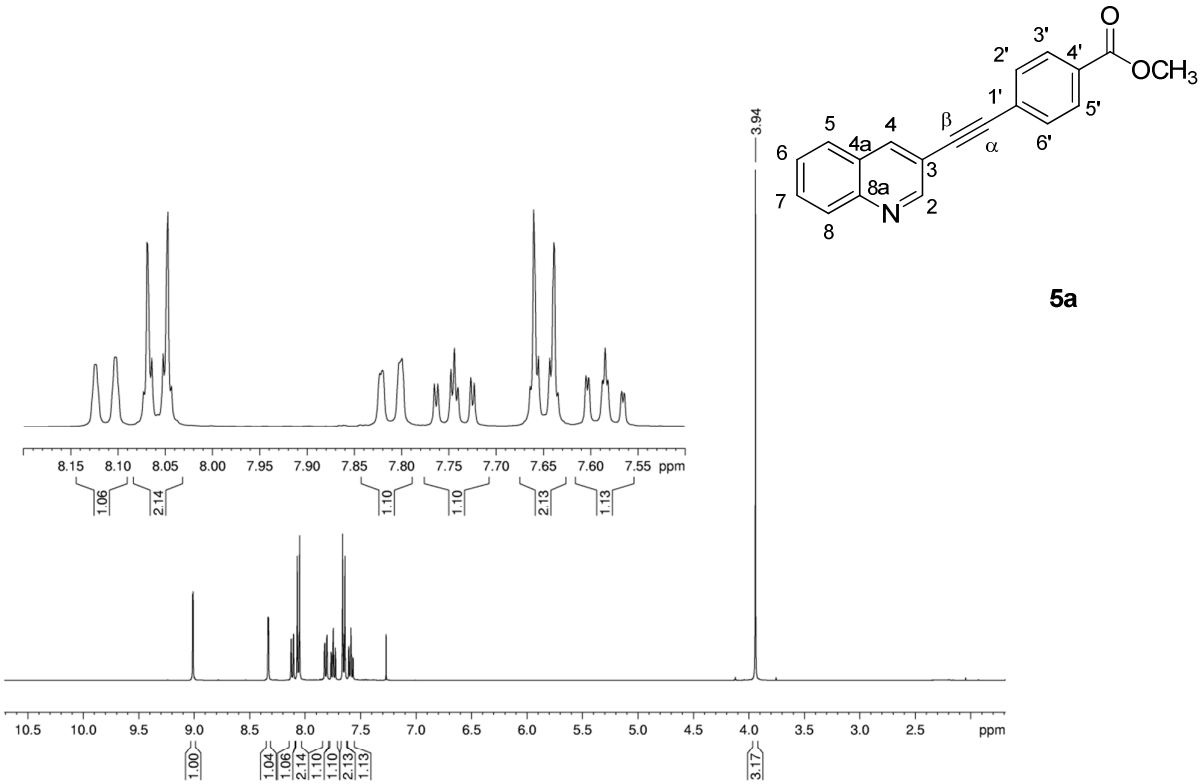
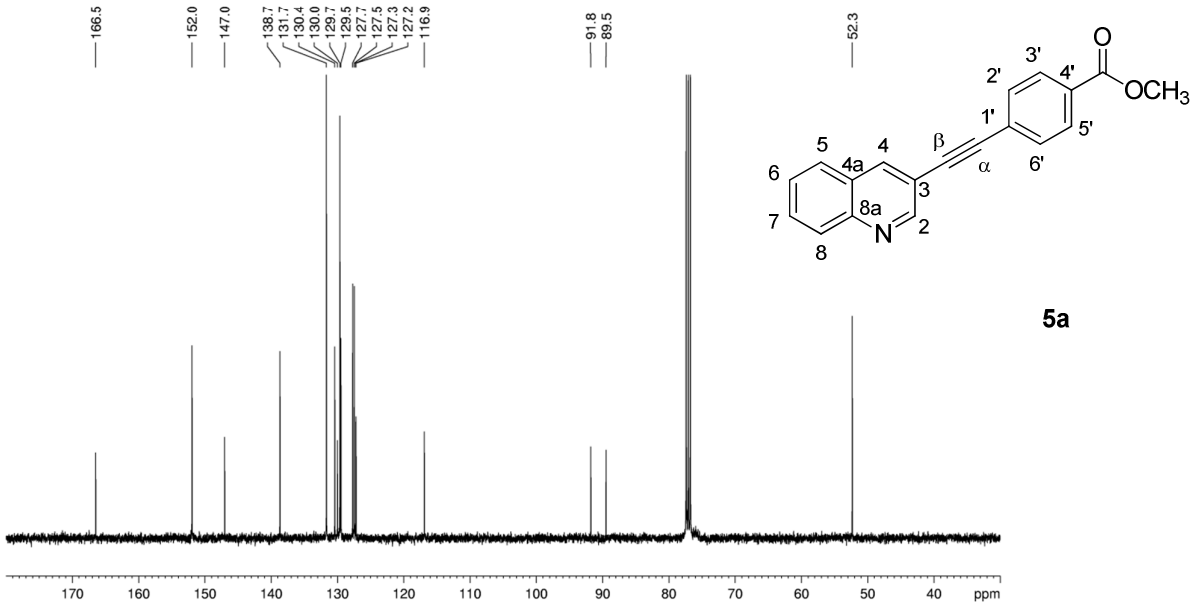
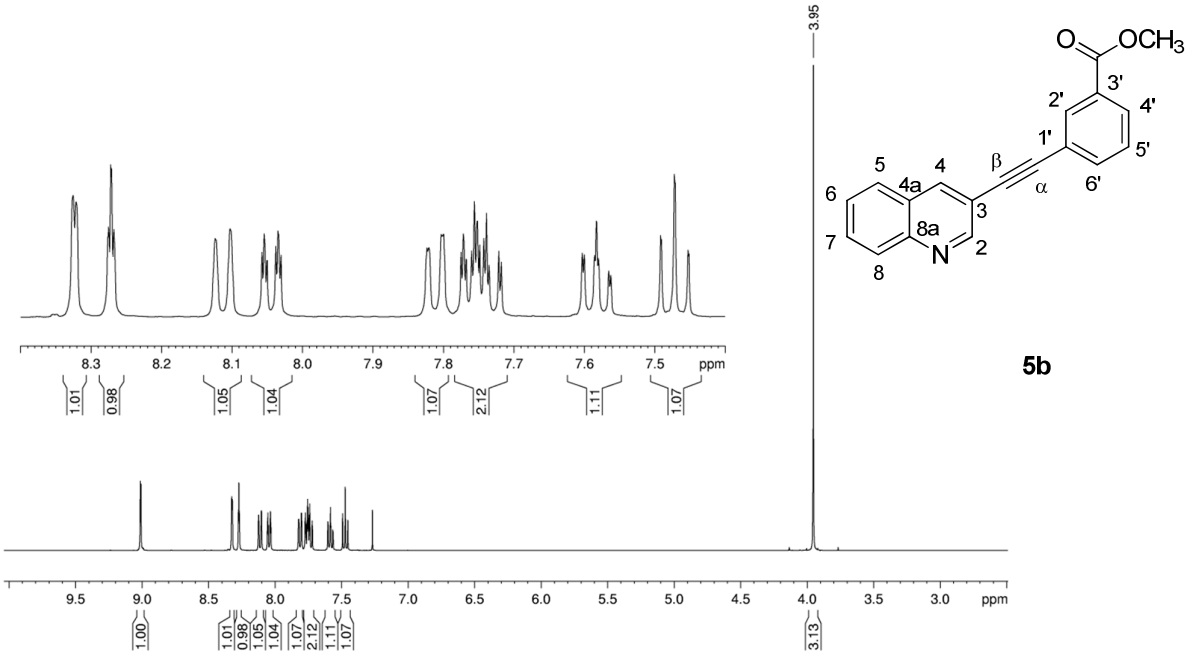


Figure S7. Molecular structure of **10**+H^+ (displacement parameters are drawn at 50 % probability level).

3. NMR spectra






3.95
O
OCH3
3'
2'
4'
1'
5'
6'
β
α
5
4
4a
6
3
8a
7
N
2
8
5b
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
ppm
1.01
0.98
1.05
1.04
1.07
2.12
1.11
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
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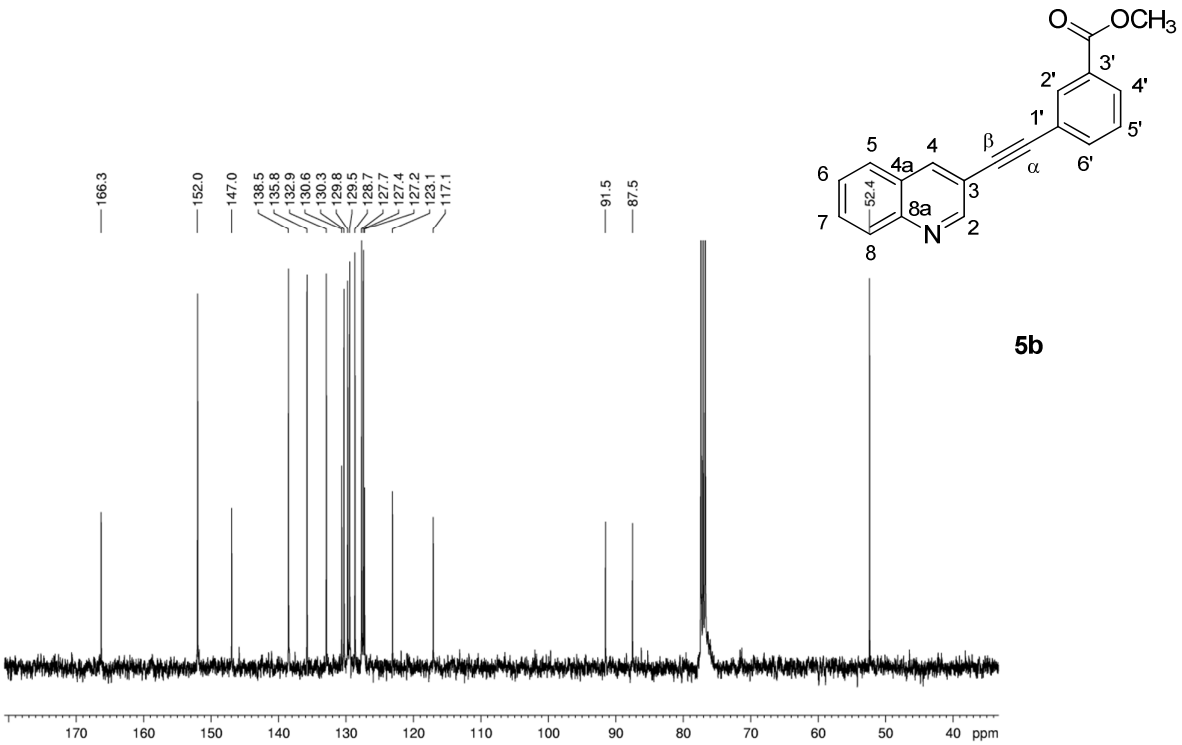
1.05
1.04
1.07
2.12
1.11
1.07
3.13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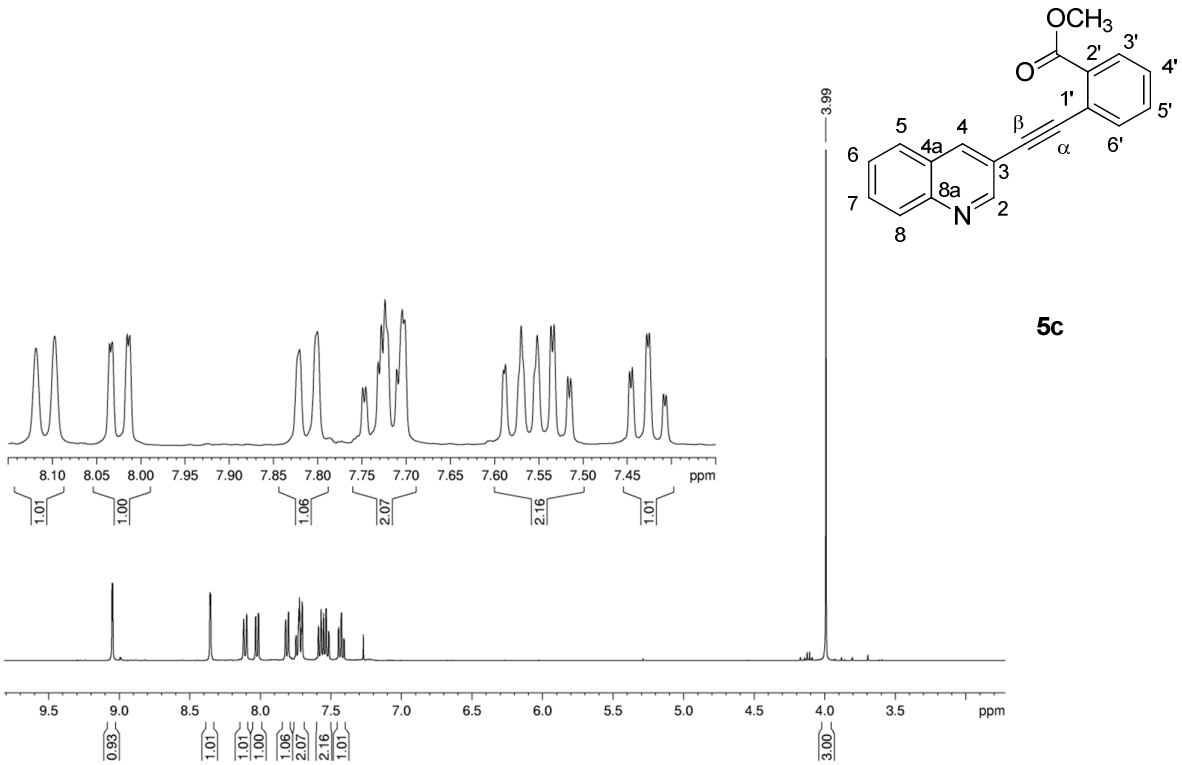
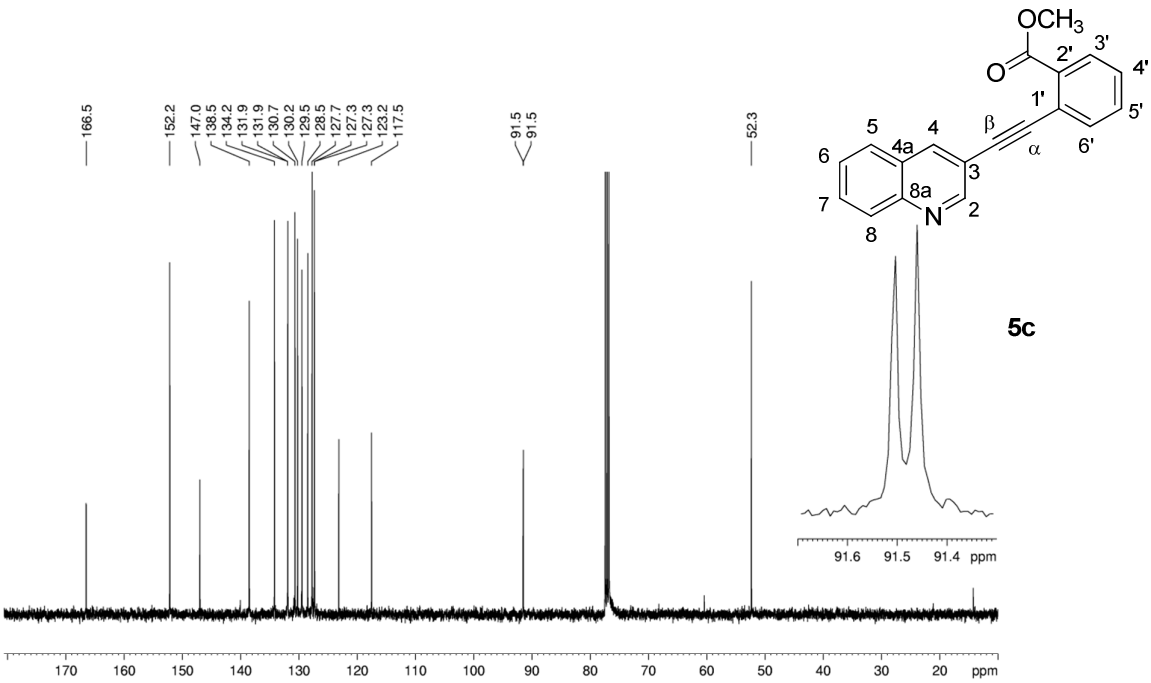
152.0
147.0
138.5
135.8
132.9
130.6
130.3
129.8
129.5
128.7
127.7
127.4
127.2
123.1
117.1
91.5
87.5
52.4
O
OCH3
3'
2'
4'
1'
5'
6'
β
α
5
4
4a
6
3
8a
7
N
2
8
5b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


OCH3
O
2'
3'
4'
1'
5'
6'
β
α
5
4
4a
6
3
8a
7
N
2
8
3.99
5c
8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 ppm
1.01 1.00 1.06 2.07 2.16 1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm
0.93 1.01 1.01 1.00 1.06 2.07 2.16 1.01 3.00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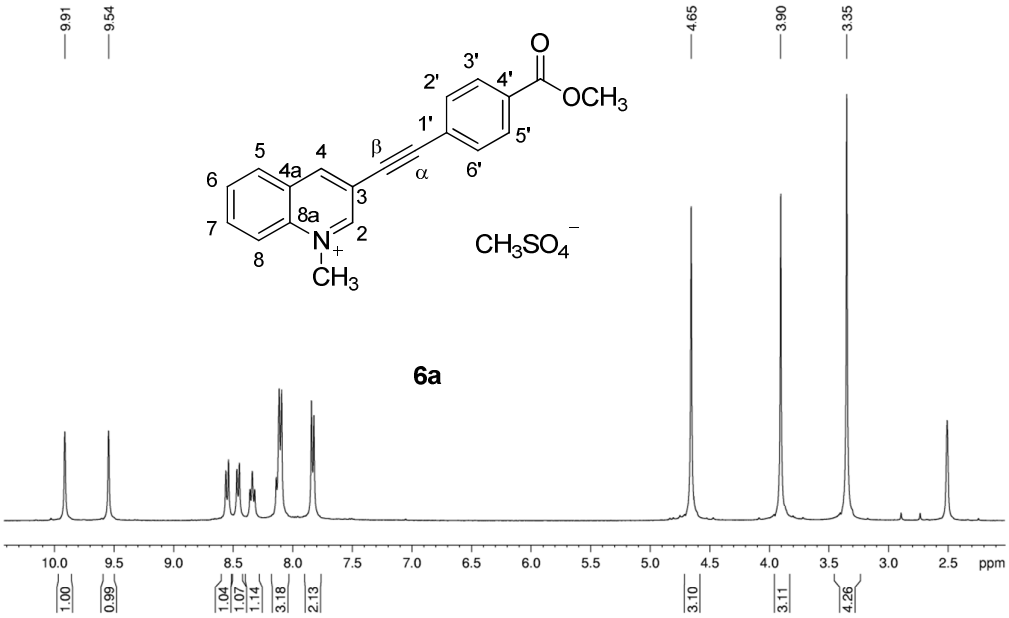
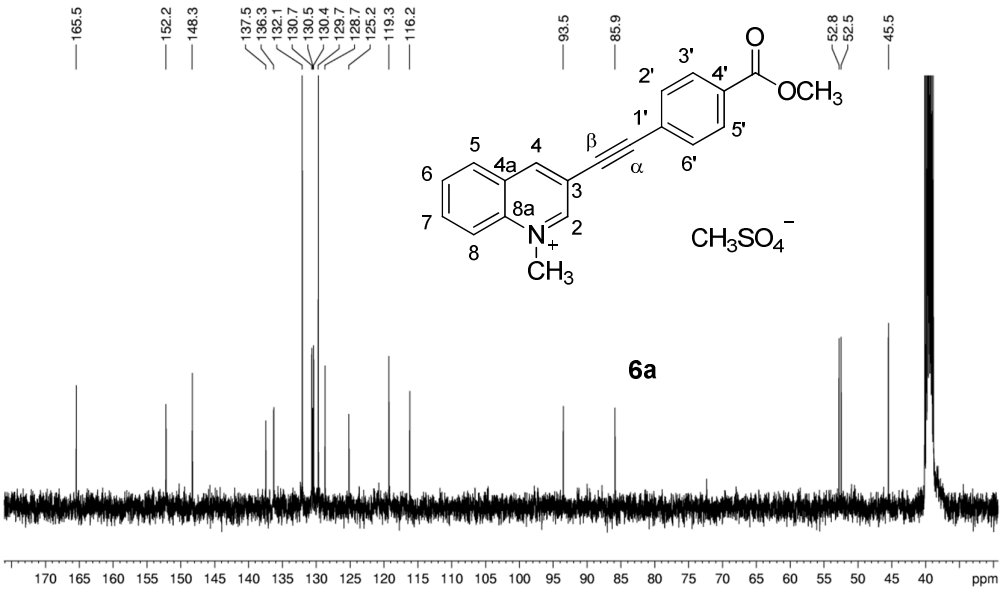
152.2
147.0
138.5
134.2
131.9
131.9
130.7
130.2
129.5
128.5
127.7
127.3
127.3
123.2
117.5
91.5
91.5
52.3
OCH3
O
2'
3'
4'
1'
5'
6'
β
α
5
4
4a
6
3
8a
7
N
2
8
5c
91.6 91.5 91.4 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


9.91
9.54
4.65
3.90
3.35
O
OCH3
CH3SO4−
6a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
0.99
1.04
1.07
1.14
3.18
2.13
3.10
3.11
4.26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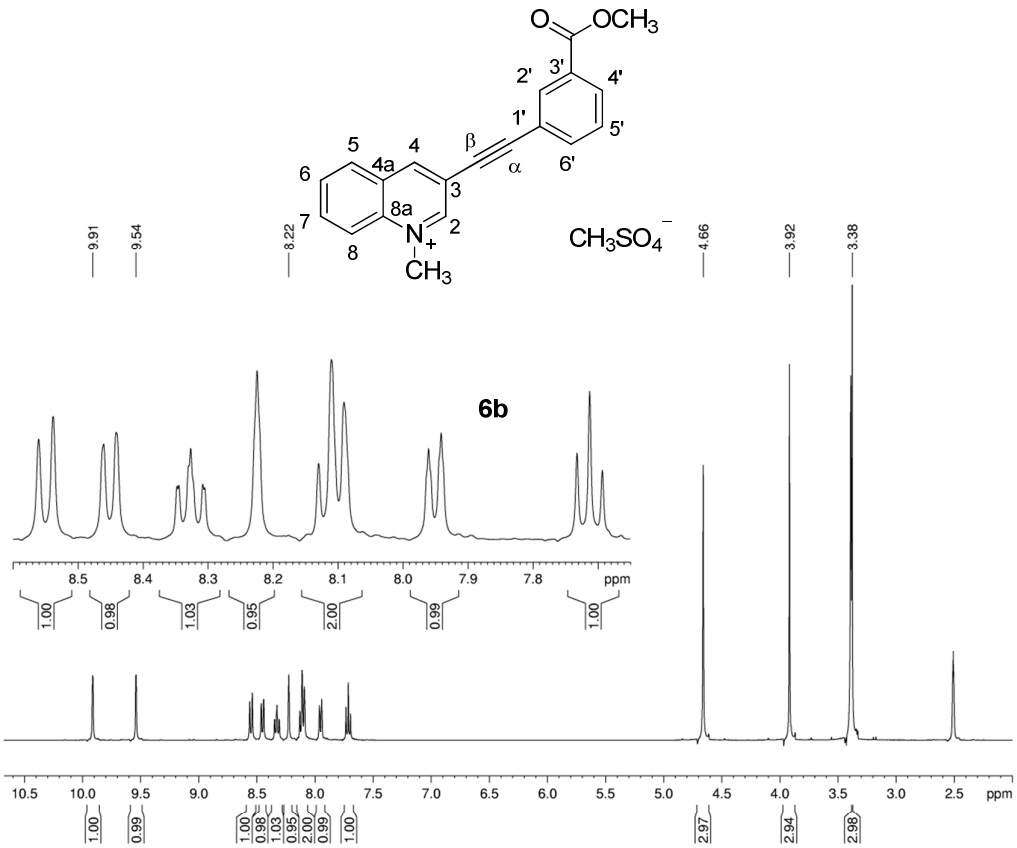
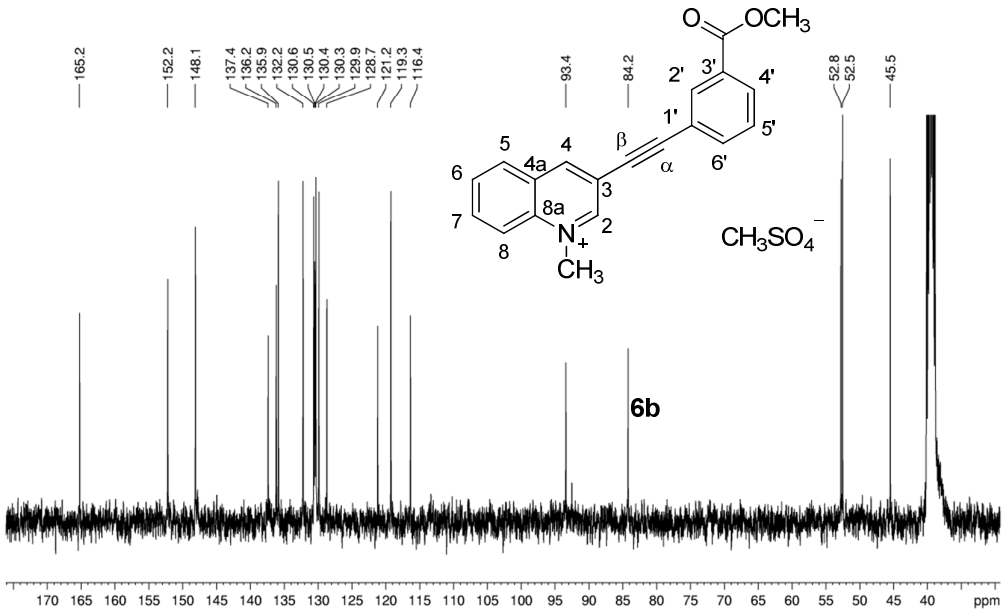
152.2
148.3
137.5
136.3
132.1
130.7
130.5
130.4
129.7
128.7
125.2
119.3
116.2
93.5
85.9
52.8
52.5
45.5
O
OCH3
CH3SO4−
6a
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 ppm


O
OCH3
2'
3'
4'
1'
5'
6'
5
4
4a
β
α
6
3
7
8a
2
8
N+
CH3
CH3SO4−
9.91
9.54
8.22
4.66
3.92
3.38
6b
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
ppm
1.00
0.98
1.03
0.95
2.00
0.99
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.00
0.99
1.00
0.98
1.03
0.95
2.00
0.99
1.00
2.97
2.94
2.98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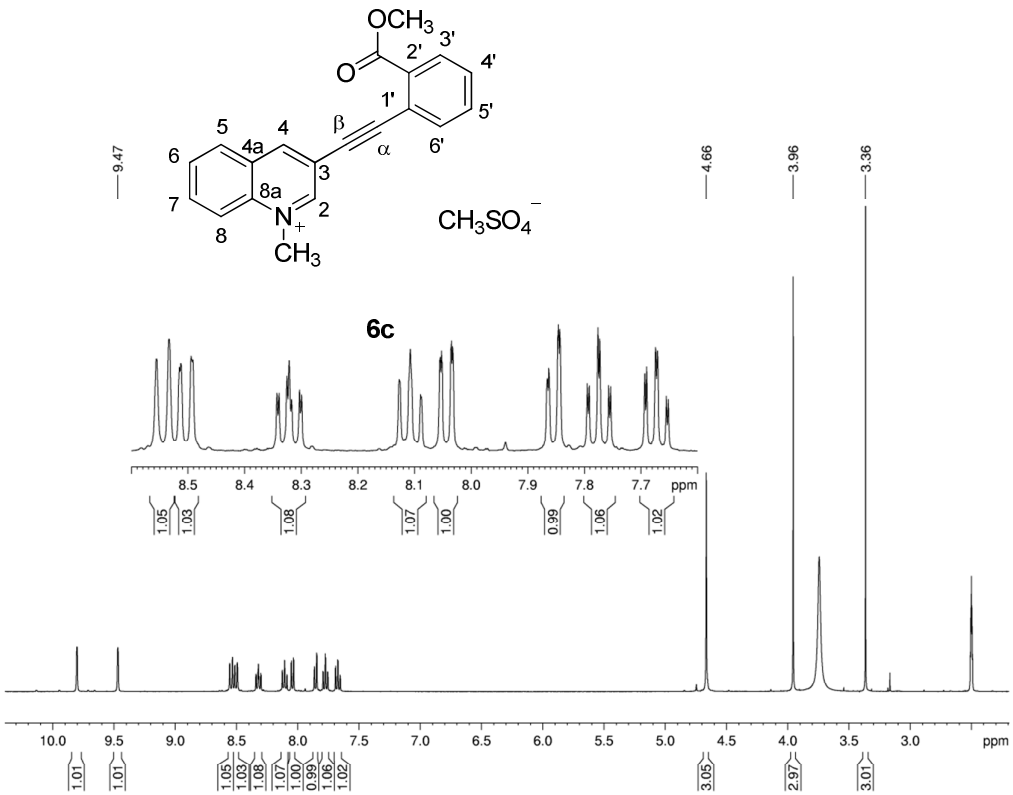
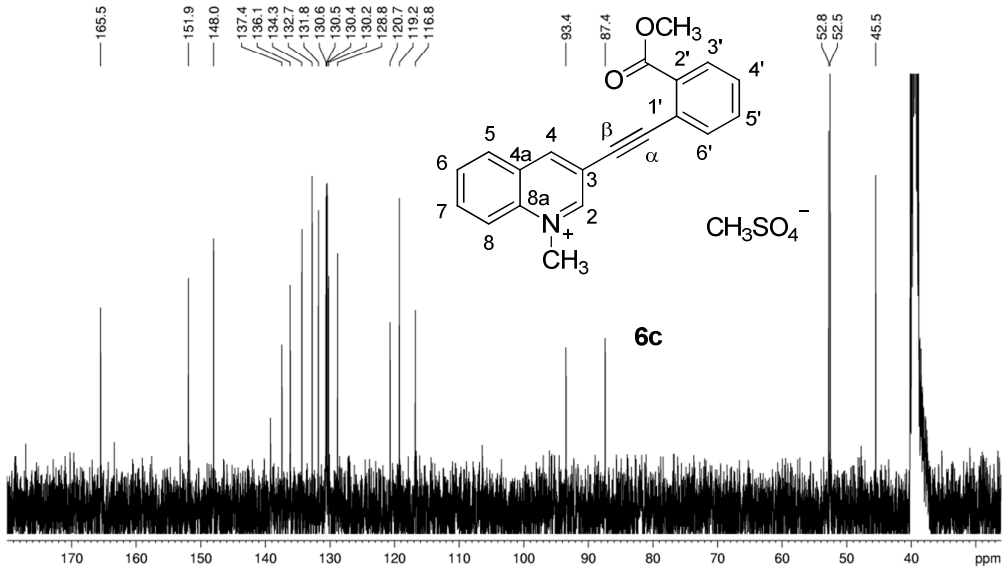
152.2
148.1
137.4
136.2
135.9
132.2
130.6
130.5
130.4
130.3
129.9
128.7
121.2
119.3
116.4
93.4
84.2
52.8
52.5
45.5
O
OCH3
2'
3'
4'
1'
5'
6'
5
4
4a
β
α
6
3
7
8a
2
8
N+
CH3
CH3SO4−
6b
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
ppm


OCH3
O
2'
3'
4'
1'
5'
6'
β
α
5
4
4a
6
3
8a
7
2
N+
8
CH3
CH3SO4−
6c
9.47
4.66
3.96
3.36
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
ppm
1.05
1.03
1.08
1.07
1.00
0.99
1.06
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.01
1.01
1.05
1.03
1.08
1.07
1.00
0.99
1.06
1.02
3.05
2.97
3.01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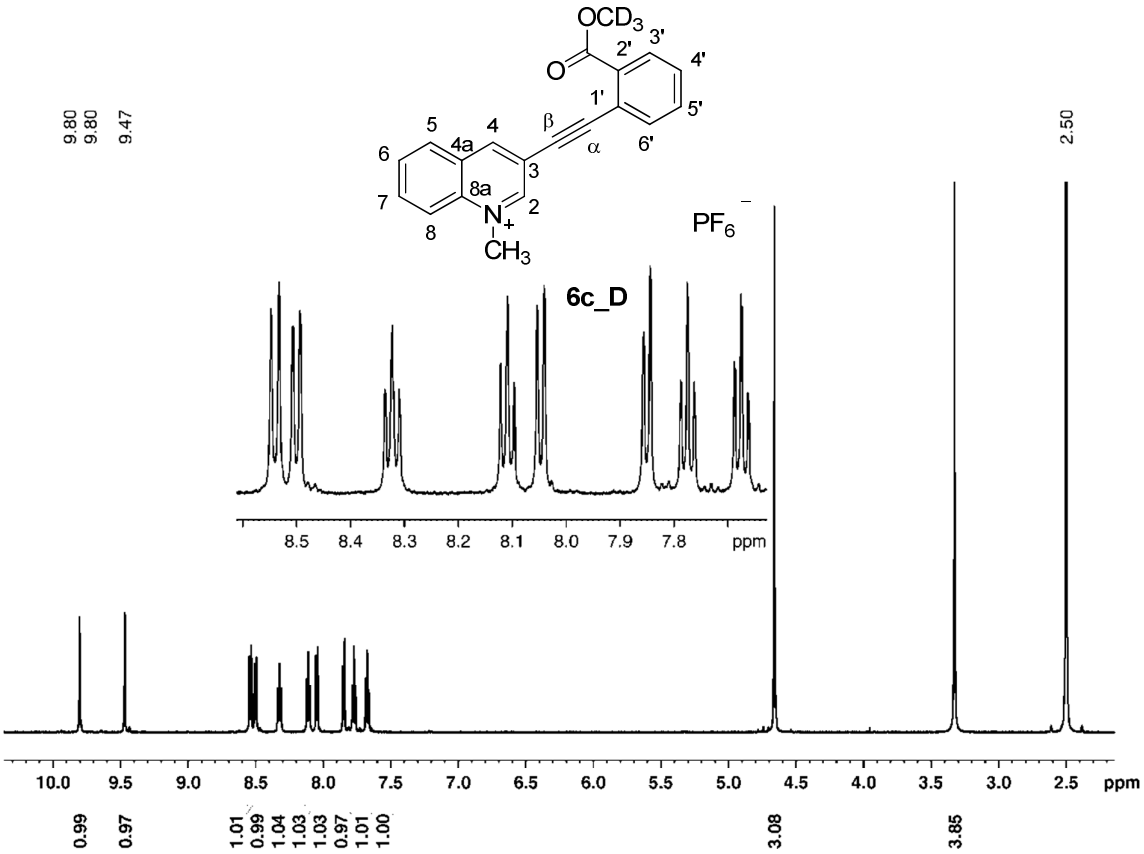
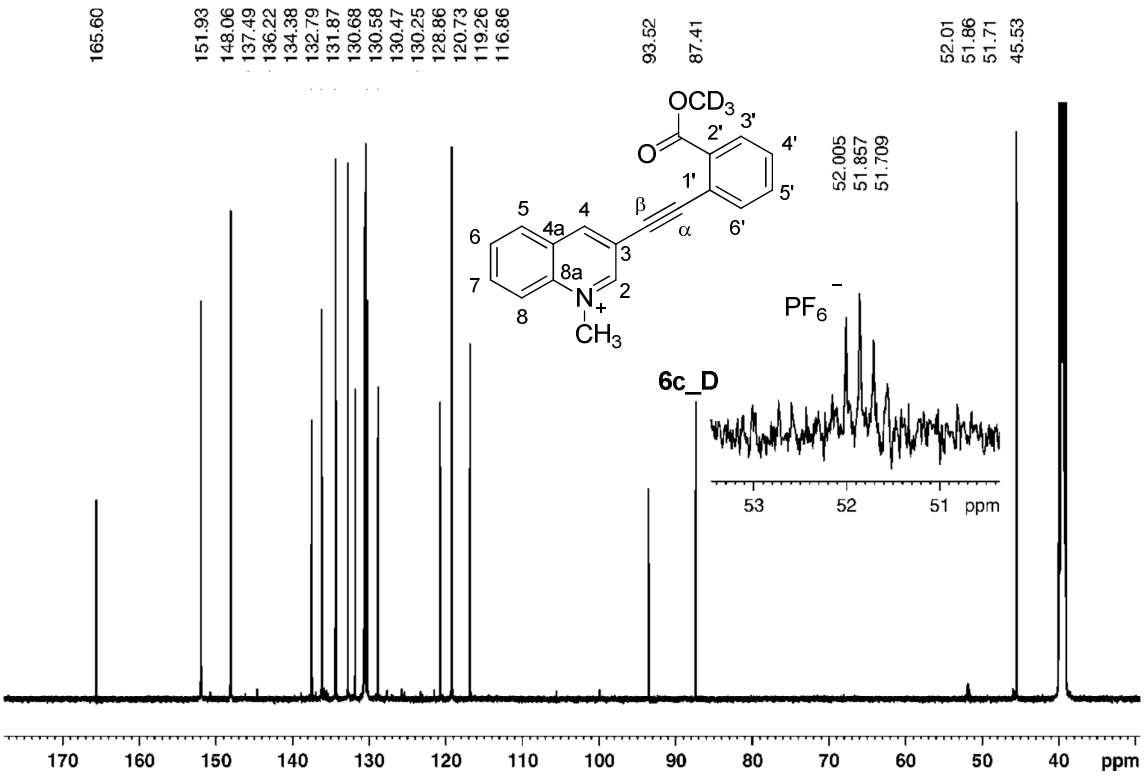
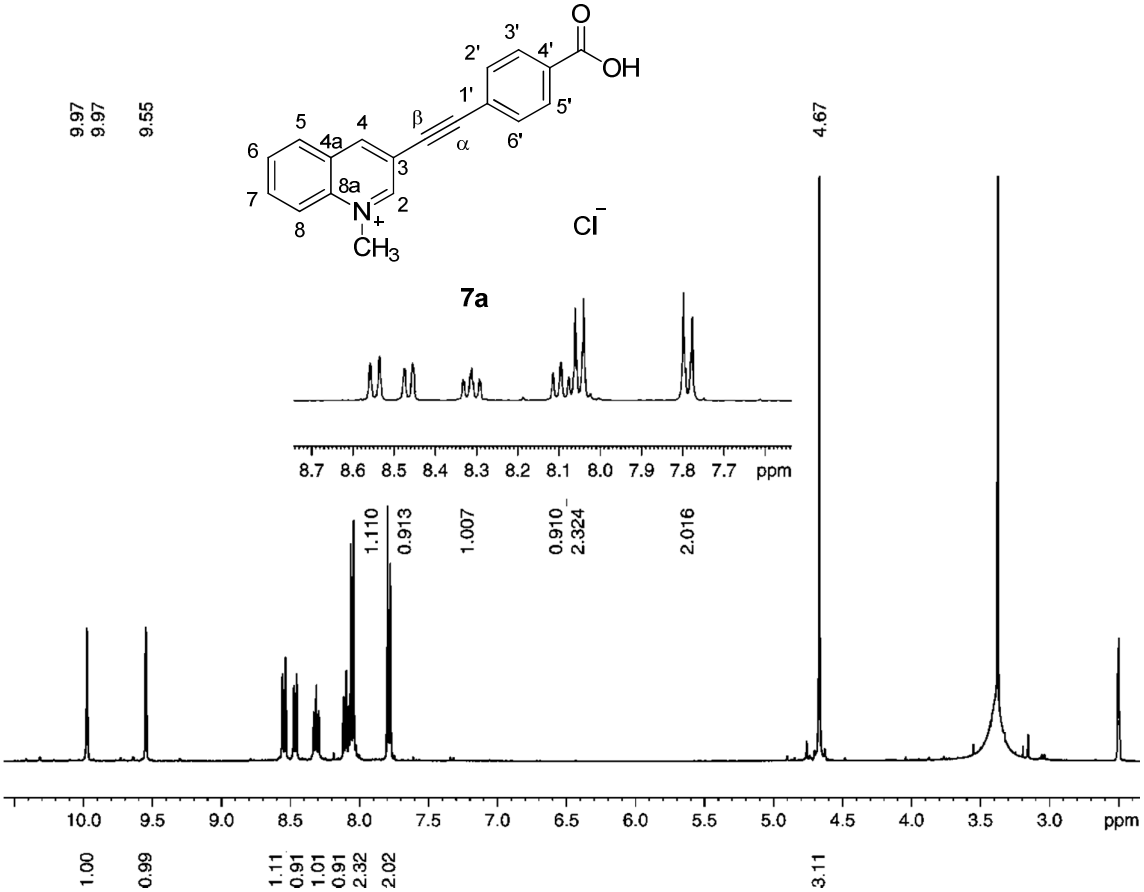
148.0
137.4
136.1
134.3
132.7
131.8
130.6
130.5
130.4
130.2
128.8
120.7
119.2
116.8
93.4
87.4
52.8
52.5
45.5
OCH3
O
2'
3'
4'
1'
5'
6'
β
α
5
4
4a
6
3
8a
7
2
N+
8
CH3
CH3SO4−
6c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


OCD3
O
2'
3'
4'
1'
5'
6'
5
4
4a
β
α
6
3
7
8a
2
8
N+
CH3
PF6 −
6c_D
9.80
9.80
9.47
2.50
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
0.99 0.97 1.01 0.99 1.04 1.03 1.03 0.97 1.01 1.00 3.08 3.85


165.60
151.93
148.06
137.49
136.22
134.38
132.79
131.87
130.68
130.58
130.47
130.25
128.86
120.73
119.26
116.86
93.52
87.41
52.01
51.86
51.71
45.53
52.005
51.857
51.709
OCD3
O
2'
3'
4'
1'
5'
6'
5
4
4a
β
α
6
3
7
8a
2
8
N+
CH3
PF6 −
6c_D
53 52 51 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm


7a
Cl⁻
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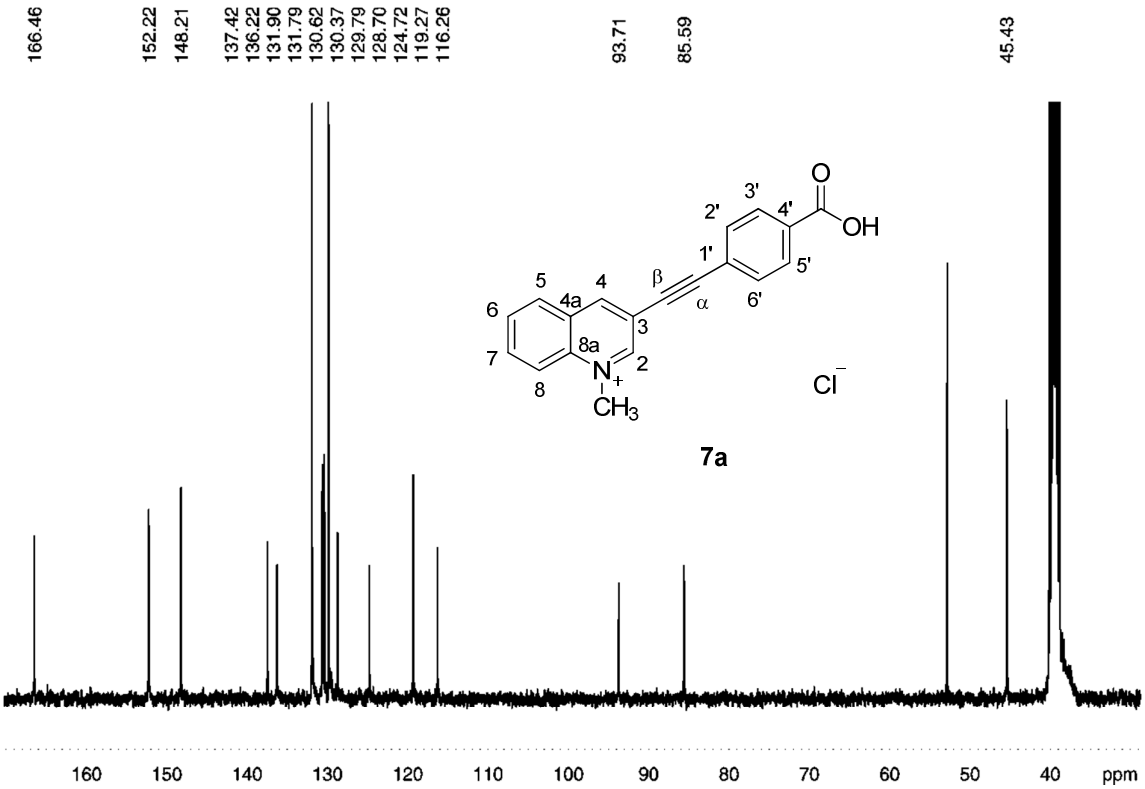
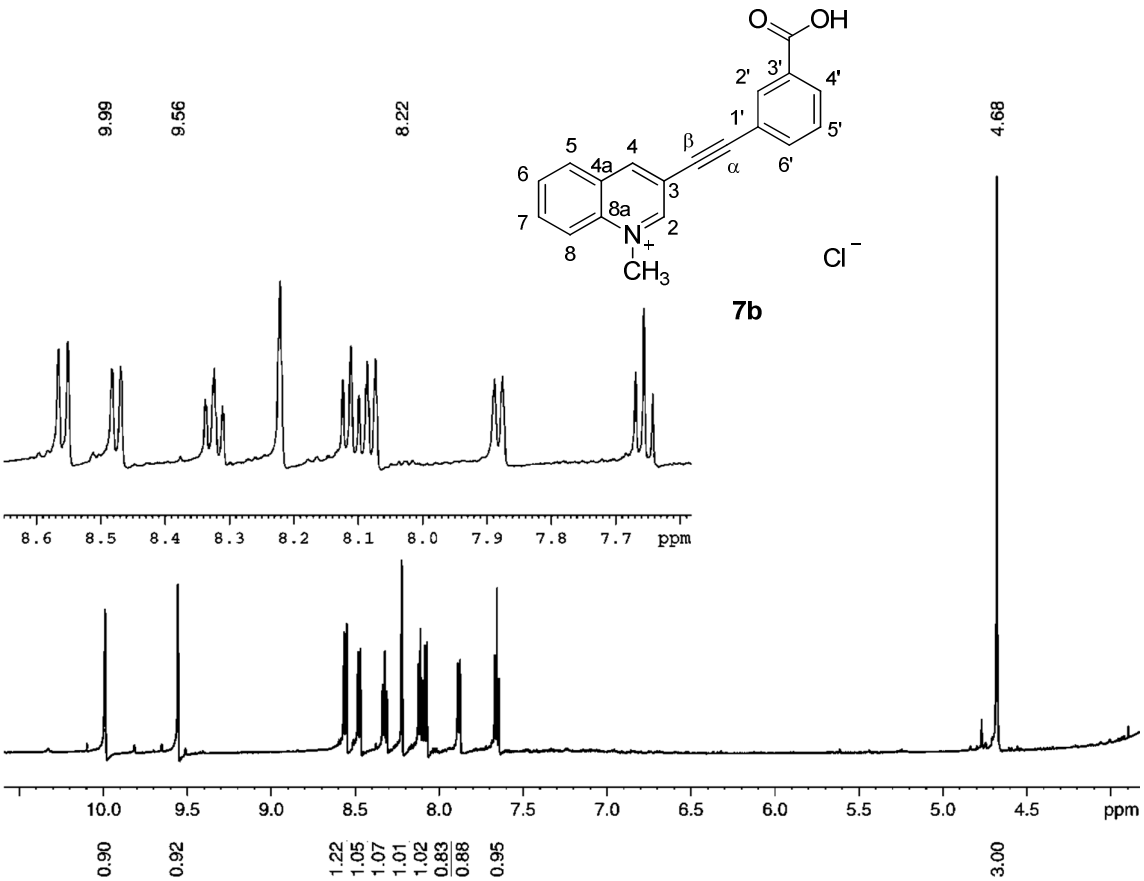
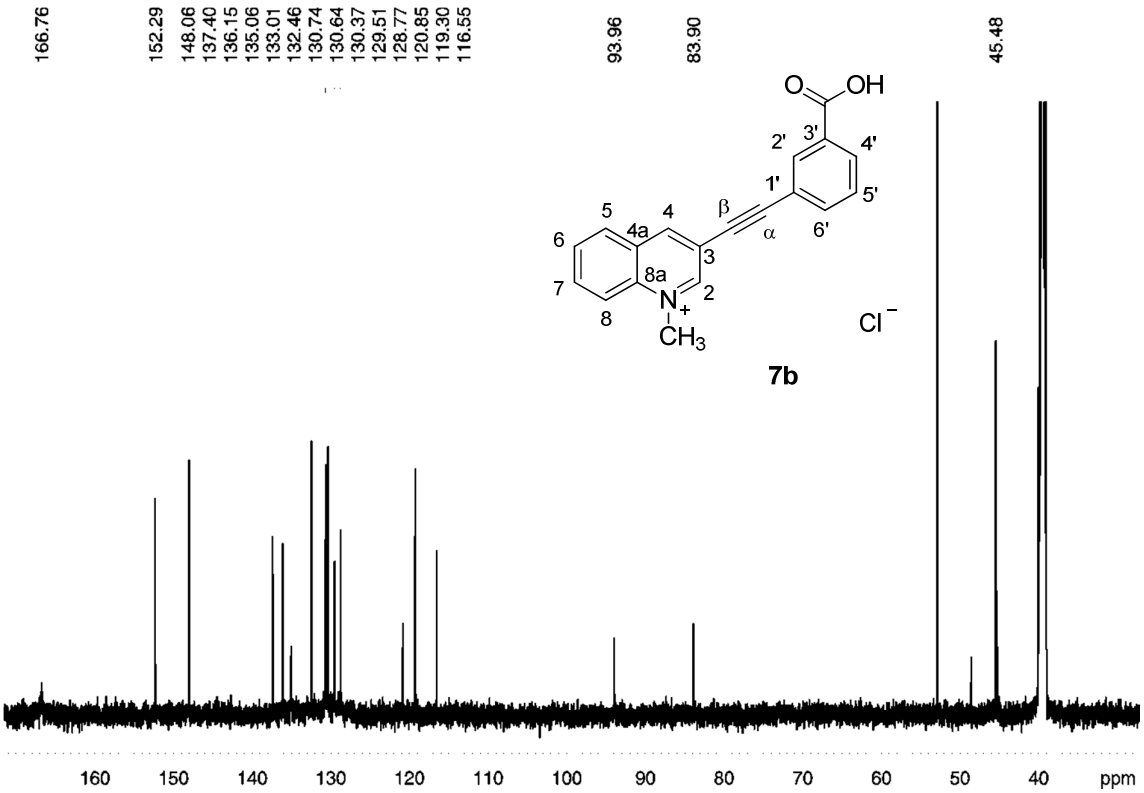
9.97
9.55
4.67
1.110
0.913
1.007
0.910
2.324
2.016
1.00
0.99
1.11
0.91
1.01
0.91
2.32
2.02
3.11
ppm


7a
Cl⁻
166.46
152.22
148.21
137.42
136.22
131.90
131.79
130.62
130.37
129.79
128.70
124.72
119.27
116.26
93.71
85.59
45.43
ppm


9.99
9.56
8.22
4.68
7b
Cl⁻
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 ppm
0.90
0.92
1.22
1.05
1.07
1.01
1.02
0.83
0.88
0.95
3.00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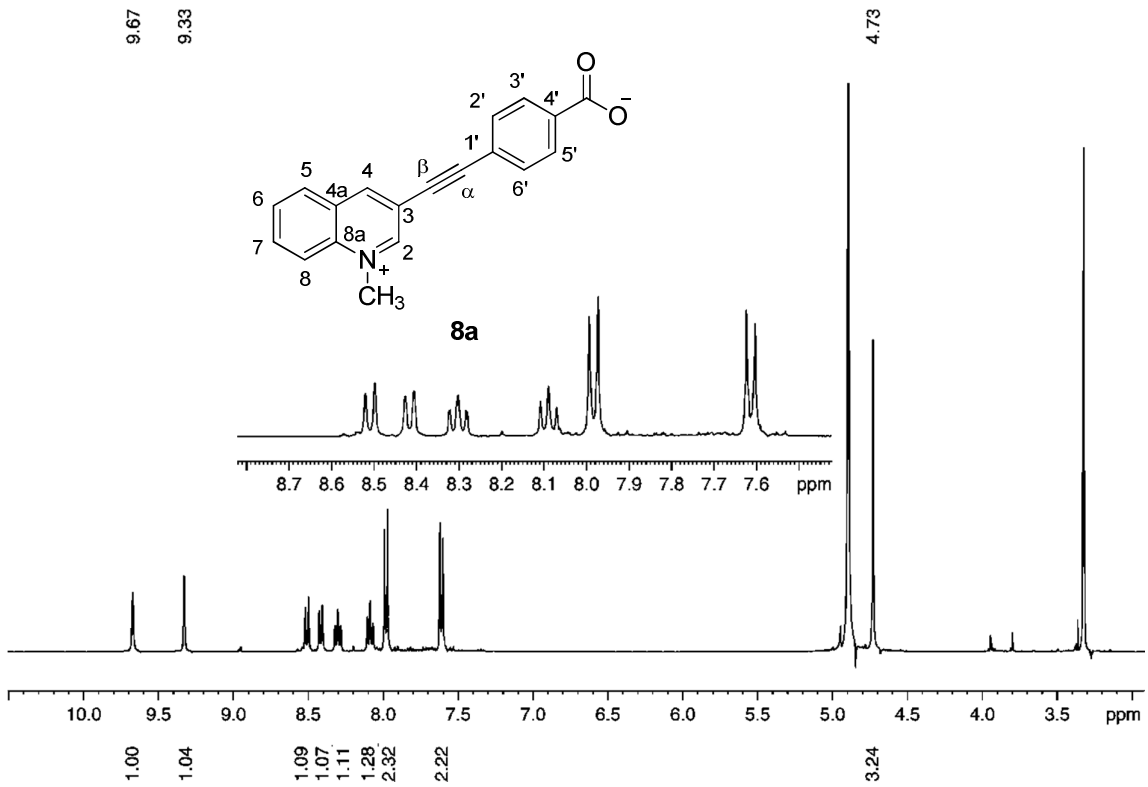
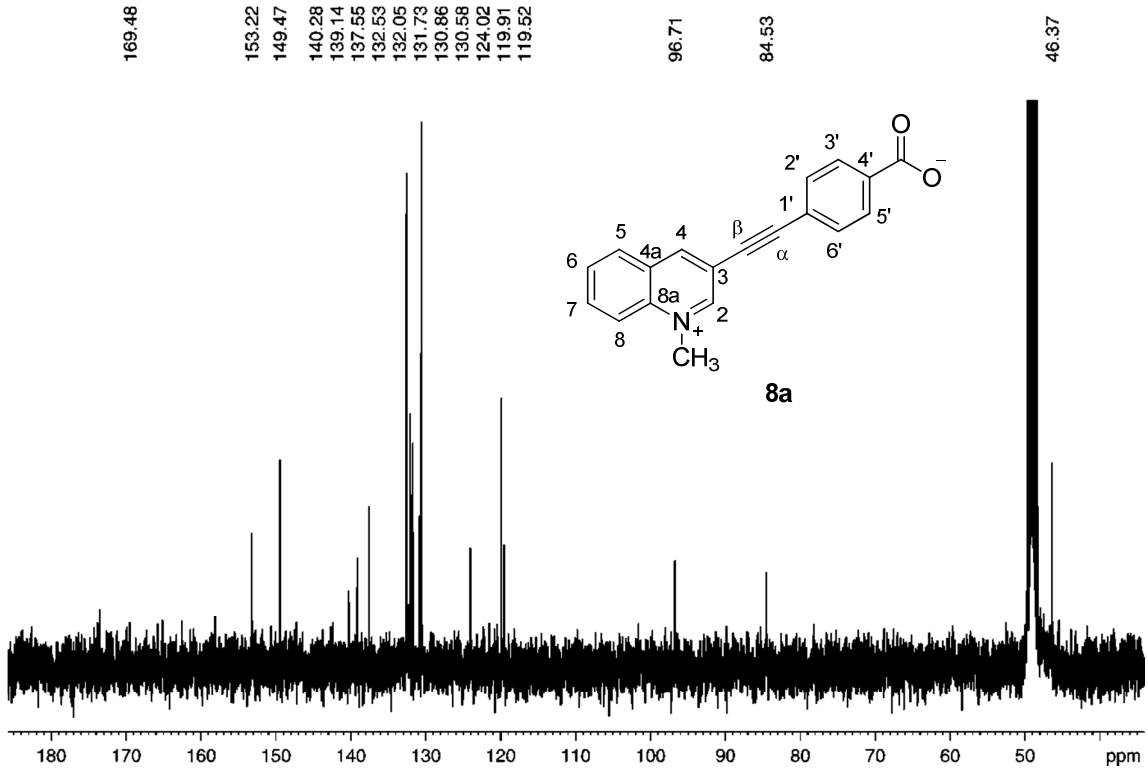
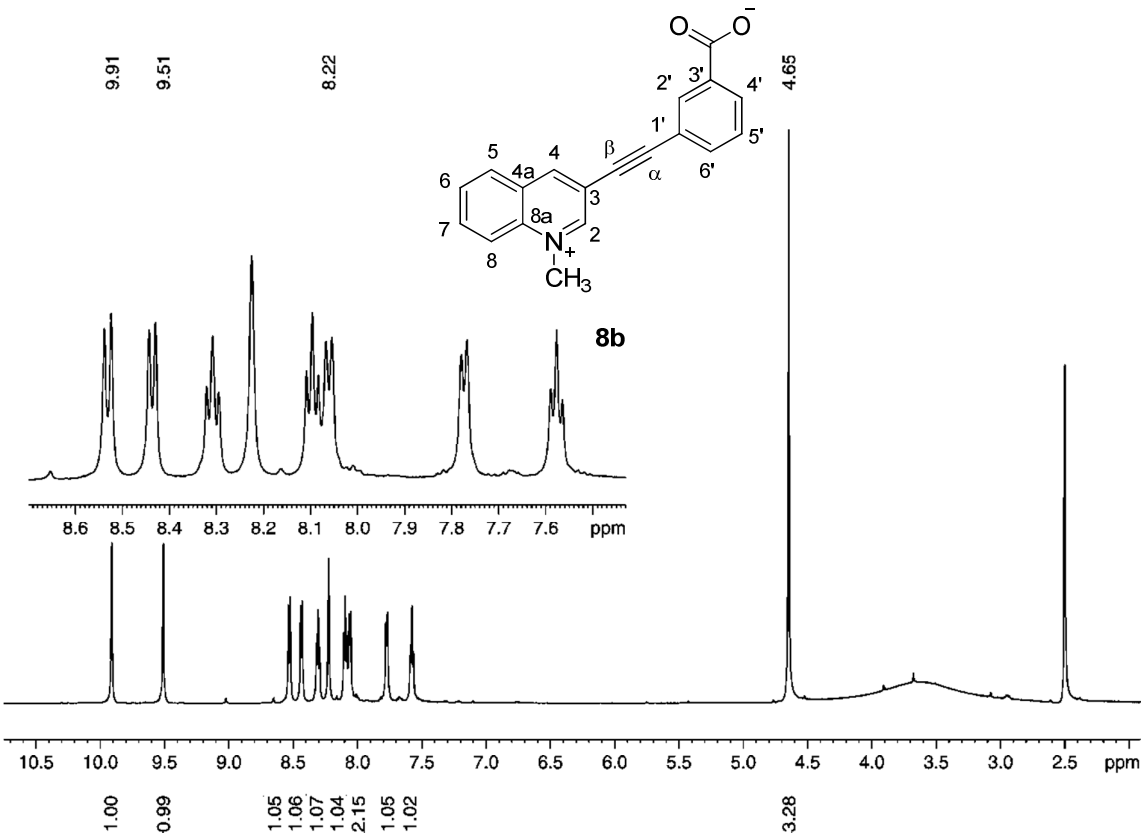
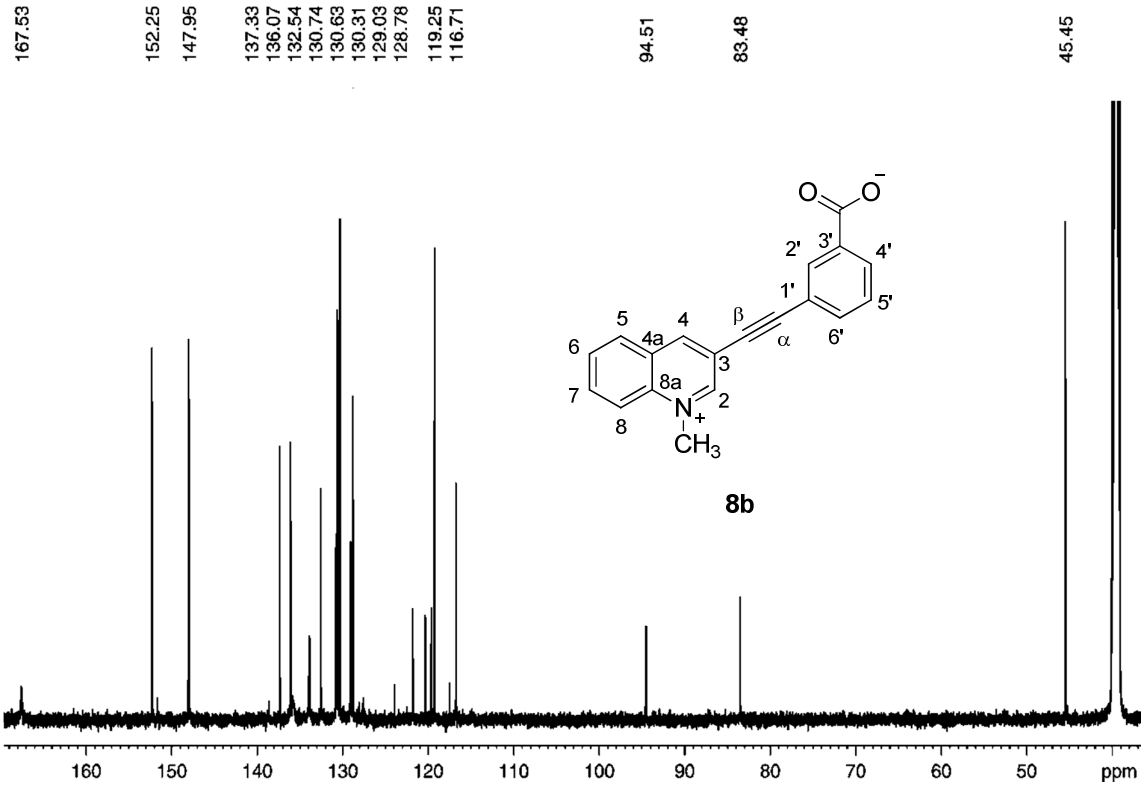
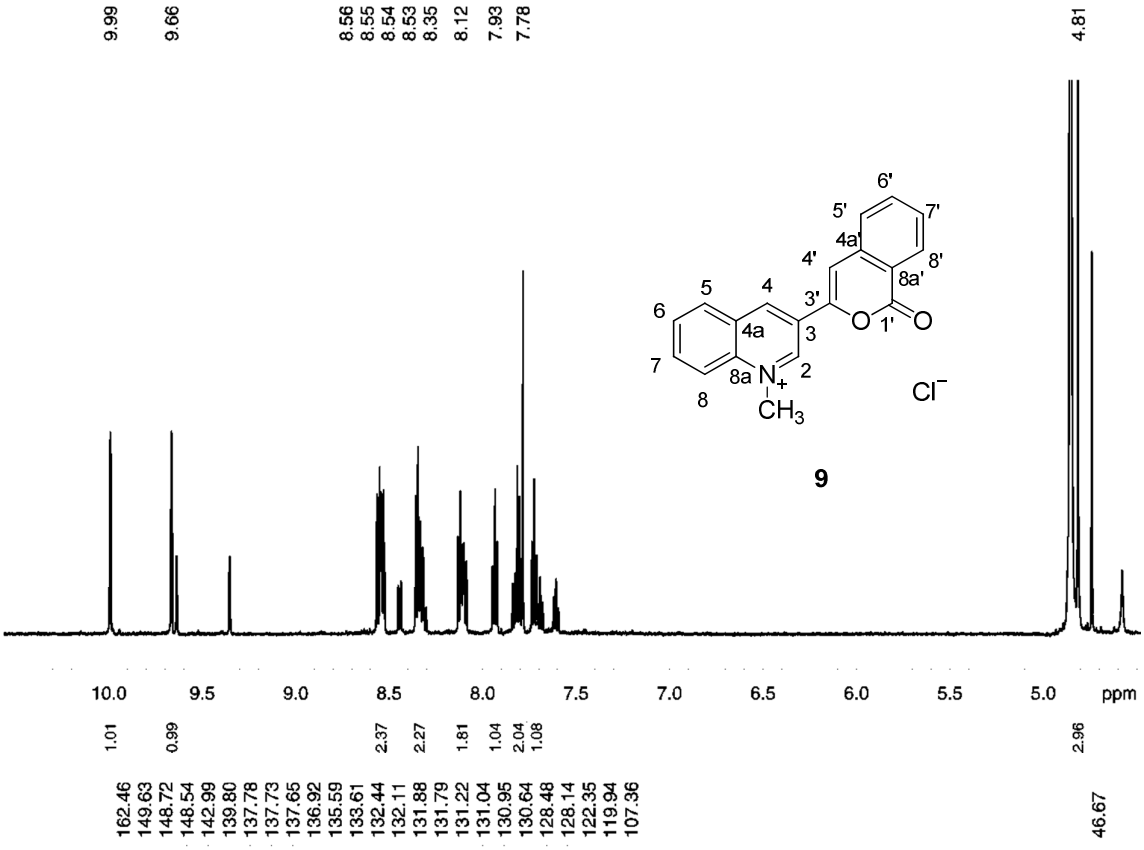
152.29
148.06
137.40
136.15
135.06
133.01
132.46
130.74
130.64
130.37
129.51
128.77
120.85
119.30
116.55
93.96
83.90
45.48
7b
Cl⁻
160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

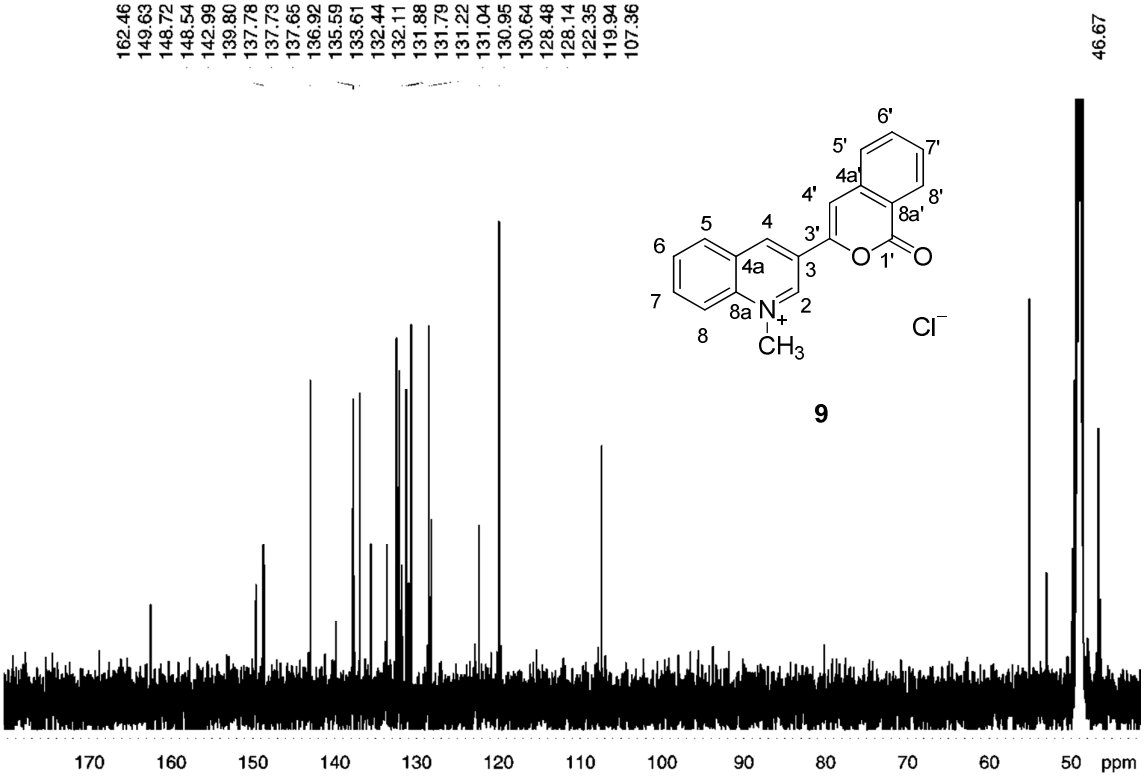

9.67
9.33
4.73
8a
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm
1.00
1.04
1.09
1.07
1.11
1.28
2.32
2.22
3.24

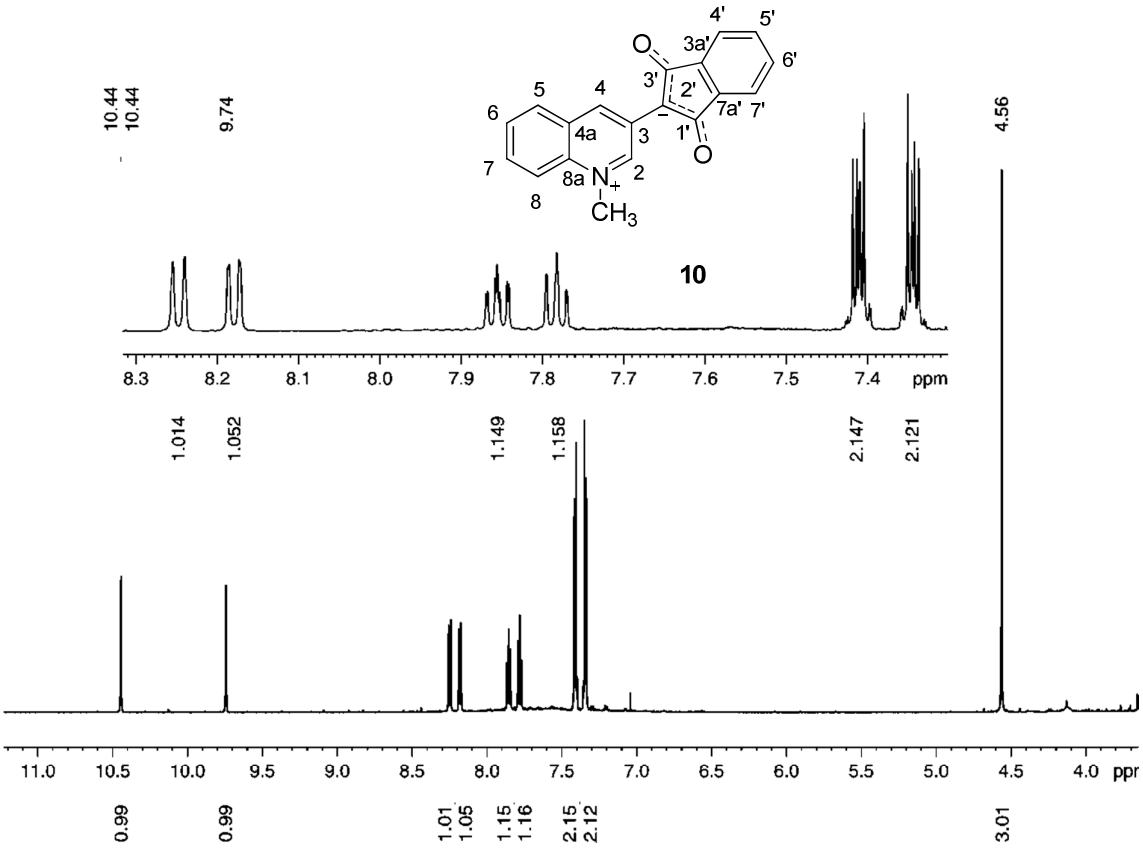

169.48
153.22
149.47
140.28
139.14
137.55
132.53
132.05
131.73
130.86
130.58
124.02
119.91
119.52
96.71
84.53
46.37
8a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm

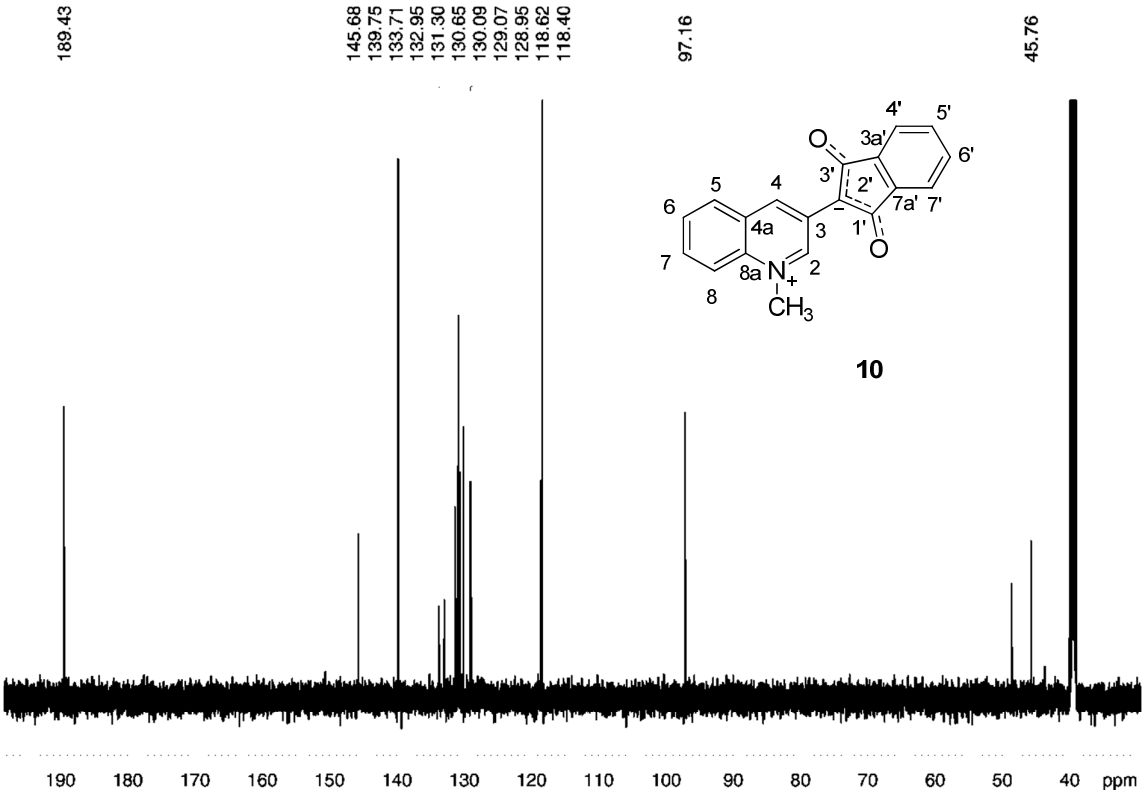

9.91
9.51
8.22
4.65
8b
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 ppm
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.00
0.99
1.05
1.06
1.07
1.04
2.15
1.05
1.02
3.28

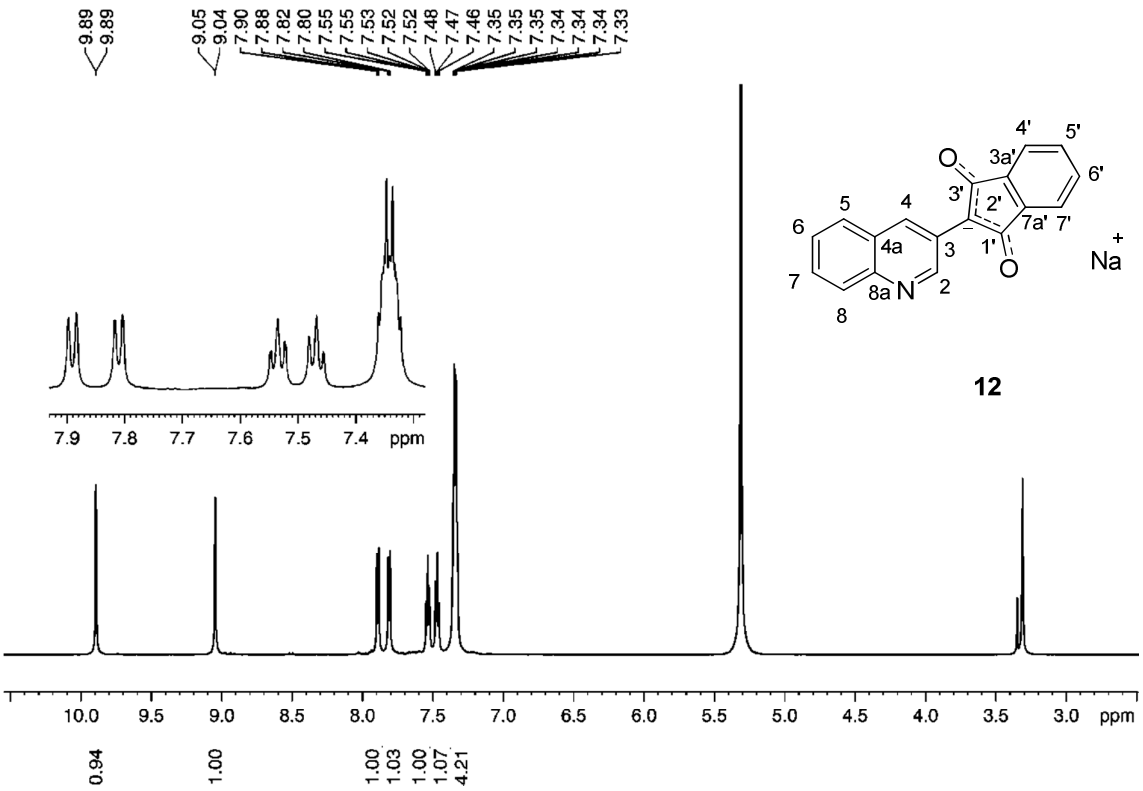

167.53
152.25
147.95
137.33
136.07
132.54
130.74
130.63
130.31
129.03
128.78
119.25
116.71
94.51
83.48
45.45
8b
160 150 140 130 120 110 100 90 80 70 60 50 ppm

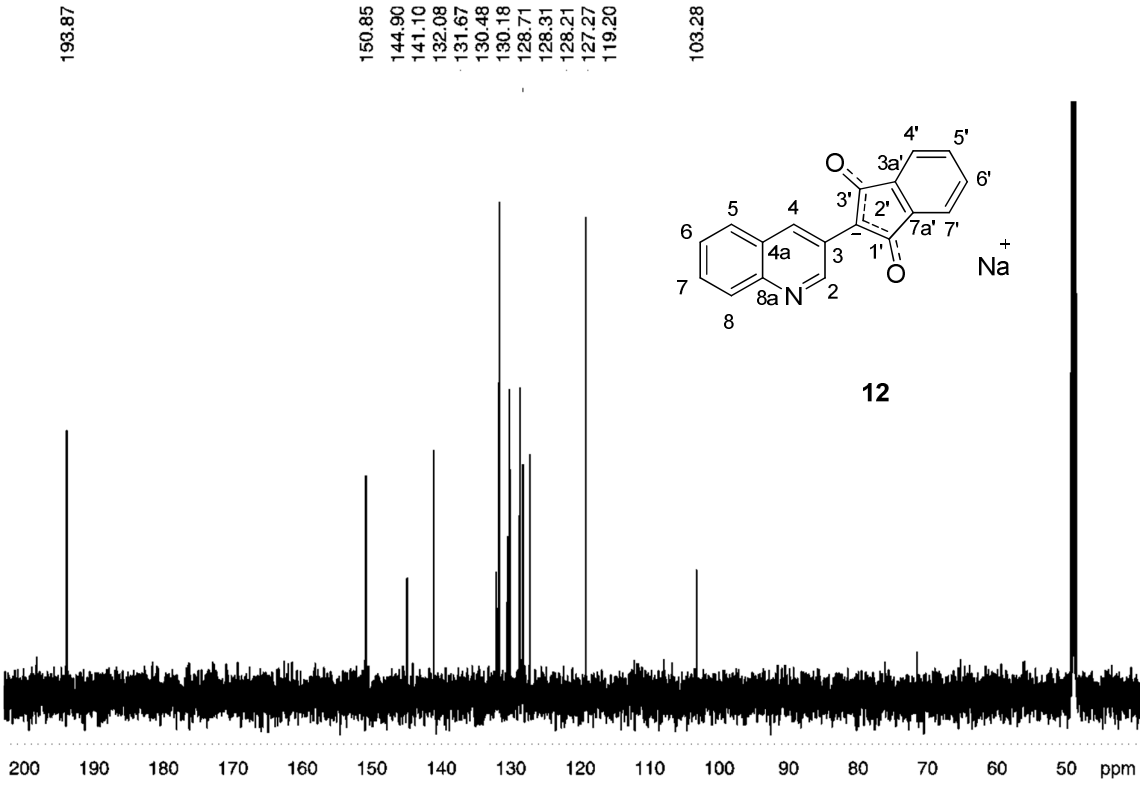

9.99
9.66
8.56
8.55
8.54
8.53
8.35
8.12
7.93
7.78
4.81
9
Cl⁻
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm
1.01
0.99
2.37
2.27
1.81
1.04
2.04
1.08
2.96


162.46
149.63
148.72
148.54
142.99
139.80
137.78
137.73
137.65
136.92
135.59
133.61
132.44
132.11
131.88
131.79
131.22
131.04
130.95
130.64
128.48
128.14
122.35
119.94
107.36
46.67
9
Cl⁻
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm


10.44
10.44
9.74
4.56
1.014
1.052
1.149
1.158
2.147
2.121
0.99
0.99
1.01
1.05
1.15
1.16
2.15
2.12
3.01
10
ppm


189.43
145.68
139.75
133.71
132.95
131.30
130.65
130.09
129.07
128.95
118.62
118.40
97.16
45.76
10
ppm


9.89
9.89
9.05
9.04
7.90
7.88
7.82
7.80
7.55
7.55
7.53
7.52
7.52
7.48
7.47
7.46
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.9 7.8 7.7 7.6 7.5 7.4 ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
0.94
1.00
1.00
1.03
1.00
1.07
4.21
12


193.87
150.85
144.90
141.10
132.08
131.67
130.48
130.18
128.71
128.31
128.21
127.27
119.20
103.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 ppm
12

4. Calculations.

Structure: **8c$_{bent}$**

Number of imaginary frequencies: 0

C1	-6.2225832862	-0.0075230491	0.2250568744
C2	-5.8941340513	-1.3179668501	-0.2384055611
C3	-5.1975077567	0.9498649522	0.4335640097
C4	-3.8736699902	0.6166221388	0.1908660873
C5	-3.5963453422	-0.7004219593	-0.2709330151
N6	-4.5484282523	-1.6036301142	-0.4707382700
C7	-6.9033805120	-2.2763053855	-0.4479096779
C8	-8.2231209694	-1.9437105971	-0.2019967464
C9	-8.5685921128	-0.6554561009	0.2561593246
C10	-7.5892106544	0.2907822624	0.4644898521
H11	-5.4607590099	1.9425225791	0.7855751700
H12	-2.5434044100	-0.9683601943	-0.4726301372
H13	-6.6549027572	-3.2704510873	-0.7992155482
H14	-8.9994024298	-2.6852195796	-0.3644377752
H15	-9.6099000726	-0.4119459753	0.4443003898
H16	-7.8460898100	1.2855644492	0.8174918901
C17	-1.4846618337	1.4817115775	0.2210507783
C18	-2.7033009706	1.3991253860	0.3323941047
C19	2.6729257730	2.1342643749	0.1296221186
C20	2.1657640089	0.8762959879	-0.1905132558
C21	0.7932392978	0.6140563154	-0.1939581354
C22	-0.0809659225	1.6758683037	0.1638615710
C23	0.4376404204	2.9463322700	0.5034469624
C24	1.8061239569	3.1763178470	0.4795844069

H25	2.8171367063	0.0459566062	-0.4435523576
H26	-0.2512476848	3.7378978614	0.7840292827
H27	2.1969289363	4.1573098365	0.7361649414
H28	3.7466609660	2.3062935625	0.1123915174
C29	0.3296744960	-0.8145933494	-0.5776035159
O30	-0.9040472117	-0.9426098906	-0.8615043118
O31	1.2149545021	-1.6828731583	-0.5879941321
C32	-4.1253336582	-2.9353280746	-0.9560848689
H33	-3.0414896044	-2.9151293768	-1.0789196717
H34	-4.4054164458	-3.6994708354	-0.2267243527
H35	-4.6033457913	-3.1448734747	-1.9158890876

Structure: **8cl$_{inear}$**

Number of imaginary frequencies: 1

C1	-6.0121900000	-0.3084330000	-0.0043120000
C2	-5.5617080000	-1.5728280000	-0.5005980000
C3	-5.0852610000	0.7226570000	0.2653410000
C4	-3.7230620000	0.5131680000	0.0486060000
C5	-3.3274500000	-0.7572920000	-0.4517080000
N6	-4.1903390000	-1.7419360000	-0.7020570000
C7	-6.4816450000	-2.6041310000	-0.7686150000
C8	-7.8312480000	-2.3920430000	-0.5520050000
C9	-8.2965050000	-1.1527550000	-0.0638360000
C10	-7.4078500000	-0.1363540000	0.2046020000
H11	-5.4352030000	1.6744220000	0.6508900000
H12	-2.2661940000	-0.9390840000	-0.6138070000

H13	-6.1451930000	-3.5631270000	-1.1429420000
H14	-8.5367330000	-3.1902010000	-0.7607410000
H15	-9.3593500000	-1.0035580000	0.1004940000
H16	-7.7570700000	0.8203720000	0.5821290000
C17	-1.6961960000	2.0994370000	0.4802060000
C18	-2.6406580000	1.3602810000	0.2790930000
C19	1.5663500000	4.6482100000	1.1397170000
C20	1.7804660000	3.3273860000	0.7494480000
C21	0.7155770000	2.4507270000	0.5272950000
C22	-0.6009780000	2.9565780000	0.7134220000
C23	-0.8173920000	4.2905510000	1.1237240000
C24	0.2647940000	5.1329990000	1.3320520000
H25	2.7782590000	2.9216180000	0.6156400000
H26	-1.8346460000	4.6448800000	1.2685930000
H27	0.1021300000	6.1616280000	1.6433660000
H28	2.4147290000	5.3090950000	1.3044990000
C29	1.0262660000	0.9768210000	0.1099880000
O30	0.0459070000	0.2763120000	-0.2604410000
O31	2.2316510000	0.6654710000	0.1920730000
C32	-3.6683330000	-3.0312890000	-1.1922250000
H33	-2.5845340000	-2.9586730000	-1.2706440000
H34	-3.9296710000	-3.8258090000	-0.4894700000
H35	-4.0912420000	-3.2512670000	-2.1753230000

Structure: **8c'**$_{bent}$

Number of imaginary frequencies: 0

C1	-5.5220830000000	0.0388140000000	0.1726190000000
C2	-6.5544710000000	0.9626910000000	0.5294440000000
C3	-4.1775370000000	0.4466000000000	0.1523630000000
C4	-3.8347210000000	1.7719870000000	0.4847330000000
C5	-4.8849100000000	2.6392070000000	0.8231950000000
N6	-6.1769250000000	2.2580950000000	0.8459120000000
C7	-7.9036780000000	0.5464400000000	0.5520410000000
C8	-8.2147320000000	-0.7585560000000	0.2252270000000
C9	-7.2085870000000	-1.6864390000000	-0.1329310000000
C10	-5.8915530000000	-1.2962980000000	-0.1586520000000
H11	-3.3618190000000	-0.2347980000000	-0.1157710000000
H12	-4.6850370000000	3.6706370000000	1.0860180000000
H13	-8.6968590000000	1.2331110000000	0.8215690000000
H14	-9.2533270000000	-1.0754570000000	0.2444730000000
H15	-7.4830420000000	-2.7056860000000	-0.3862040000000
H16	-5.0996830000000	-1.9880770000000	-0.4297640000000
C17	-1.3210620000000	1.8157170000000	0.2664300000000
C18	-2.4802790000000	2.1798220000000	0.4721210000000
C19	2.8402060000000	1.3569920000000	-0.1991760000000
C20	1.9931620000000	0.2685350000000	-0.4041560000000
C21	0.6110140000000	0.3901130000000	-0.2608450000000
C22	0.0804780000000	1.6506250000000	0.1032320000000
C23	0.9391590000000	2.7518490000000	0.3131230000000
C24	2.3121790000000	2.6031800000000	0.1607760000000
H25	2.3698360000000	-0.7113670000000	-0.6812290000000

H26	0.5134650000000	3.7110830000000	0.5938840000000
H27	2.9701770000000	3.4531240000000	0.3221770000000
H28	3.9150700000000	1.2402650000000	-0.3181800000000
C29	-0.3012520000000	-0.8314120000000	-0.4964420000000
O30	-1.5419880000000	-0.5862710000000	-0.3822440000000
O31	0.2662190000000	-1.9025020000000	-0.7676430000000
C32	-7.2029490000000	3.2464200000000	1.2170070000000
H33	-6.7152990000000	4.1972160000000	1.4282280000000
H34	-7.9084730000000	3.3794310000000	0.3930590000000
H35	-7.7387130000000	2.9113260000000	2.1085770000000

Structure: **8c$_{NHC}$**

Number of imaginary frequencies: 0

C1	-6.1834980952	-0.0477229186	0.1922644561
C2	-6.3023095255	-1.4104669965	-0.1921088038
C3	-4.8848211743	0.5219993144	0.2597676068
C4	-3.7756892194	-0.2384416415	-0.0468604361
C5	-3.8518161323	-1.6407178132	-0.4444493315
N6	-5.1226691027	-2.1136917310	-0.4821502366
C7	-7.5822989594	-1.9971893137	-0.2672949086
C8	-8.7089519306	-1.2481088978	0.0311356356
C9	-8.5996493588	0.1021545647	0.4126049711
C10	-7.3536526715	0.6897829678	0.4910266629
H11	-4.7845597945	1.5651041006	0.5544169449
H12	-7.6972143742	-3.0338917785	-0.5580229818
H13	-9.6887718884	-1.7135223969	-0.0315767655
H14	-9.4926556055	0.6757646111	0.6430227536

H15	-7.2485804826	1.7315816631	0.7835388188
C16	-1.3626689813	0.8295996059	0.0621728156
C17	-2.4775188032	0.3465324481	0.0191001874
C18	2.3007617104	2.9357029796	0.4833013325
C19	2.3232279711	1.6392931532	-0.0183314274
C20	1.1449635070	0.9001566731	-0.1908447408
C21	-0.1026752979	1.4815891544	0.1638229378
C22	-0.1007185951	2.7996213984	0.6728359914
C23	1.0780708792	3.5172213671	0.8287765674
H24	3.2588490921	1.1634469311	-0.2917679541
H25	-1.0521596189	3.2446059524	0.9456861398
H26	1.0433567614	4.5297981909	1.2223415040
H27	3.2273988666	3.4894520158	0.6045810192
C28	1.3282556972	-0.4739204641	-0.7466327163
O29	2.4175512276	-0.9858536932	-0.9347981844
C30	-5.2591567964	-3.5279826123	-0.8744692276
H31	-4.2482388869	-3.8881923357	-1.0506568418
H32	-5.7318837925	-4.1081761921	-0.0745568215
H33	-5.8569020188	-3.6213901403	-1.7876645273
O34	0.1780083108	-1.1091622052	-1.0403410265
H35	0.4313418389	-1.9889402428	-1.3771987556