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Guaiazulene-4-carbaldehyde: Synthesis and Derivatisation

Georgia E. Williams, Gabriele Kociok-Köhn, Tony D. James and Simon E. Lewis

ELECTRONIC SUPPORTING INFORMATION

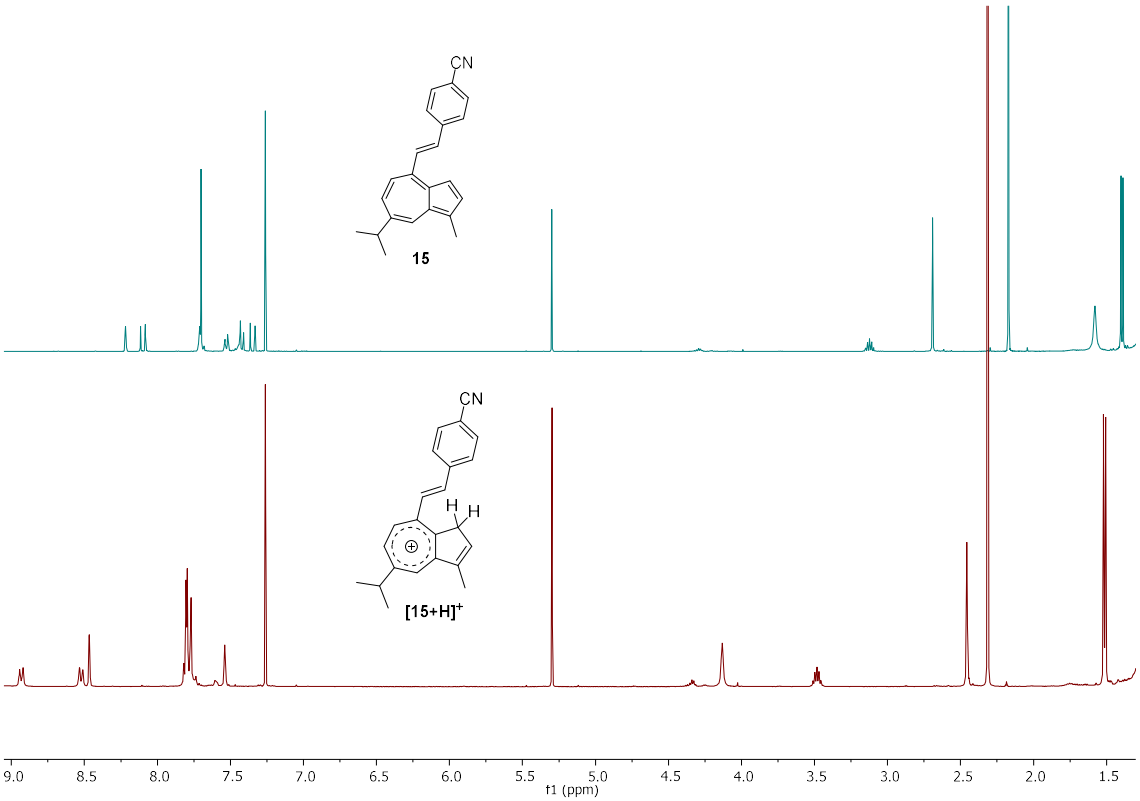


Figure S1: *Top*: ^{1}H-NMR spectrum of **15** in $CDCl_3$. *Bottom*: ^{1}H-NMR spectrum of **15** in TFA/$CDCl_3$ 1:9.

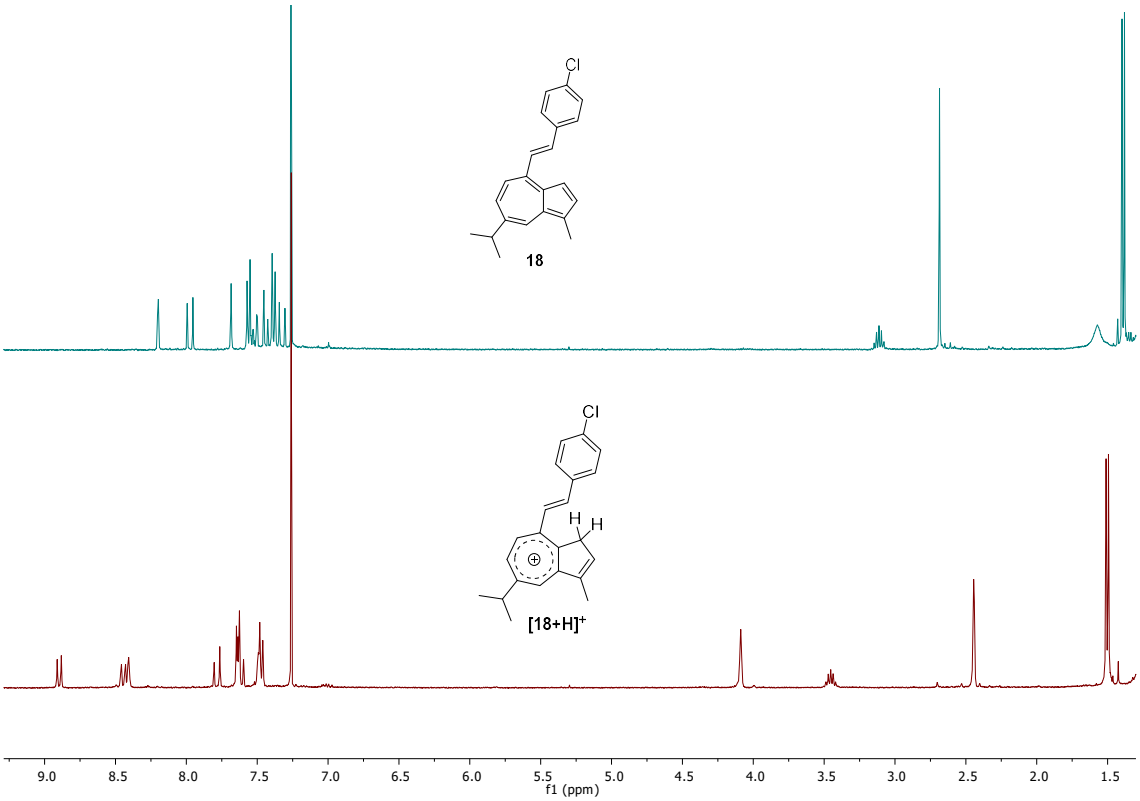
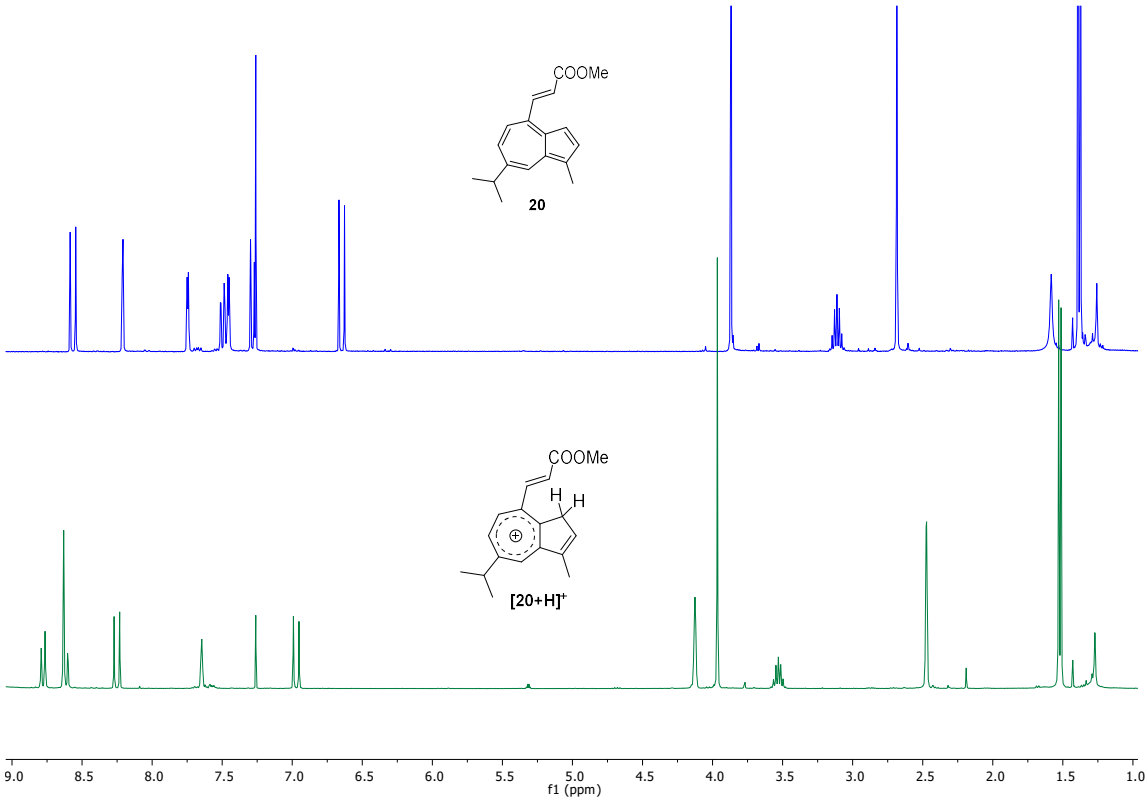


Figure S2: *Top*: ^{1}H-NMR spectrum of **18** in $CDCl_3$. *Middle*: ^{1}H-NMR spectrum of **18** in TFA/$CDCl_3$ 1:9. *Bottom*: NMR tubes containing **18** in $CDCl_3$ (left) and **1** in TFA/$CDCl_3$ (right).



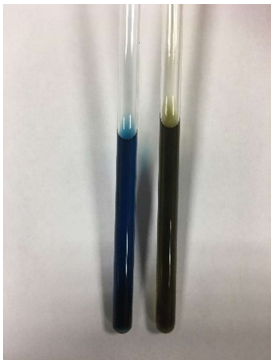


Figure S3: *Top*: ^{1}H-NMR spectrum of **20** in $CDCl_3$. *Middle*: ^{1}H-NMR spectrum of **20** in TFA/$CDCl_3$ 1:9. *Bottom*: NMR tubes containing **20** in $CDCl_3$ (left) and **1** in TFA/$CDCl_3$ (right).

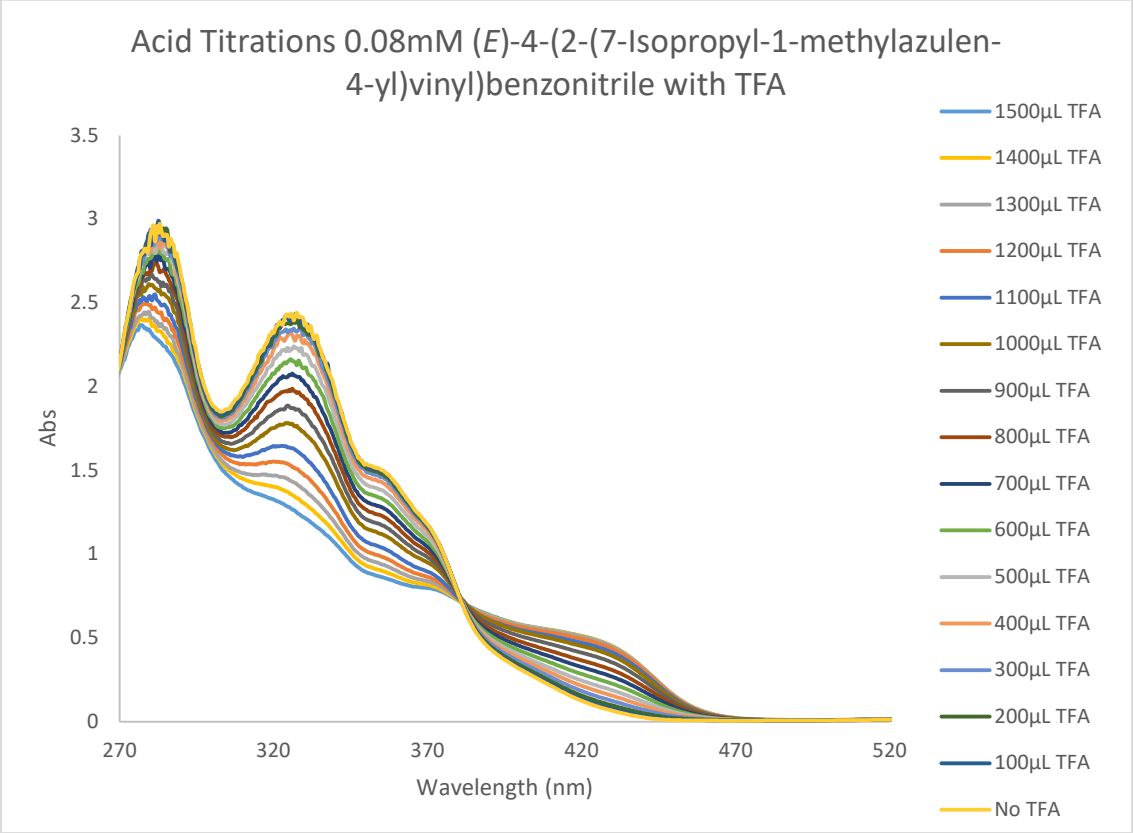


Figure S4: Titration of **15** with TFA in CH_2Cl_2.

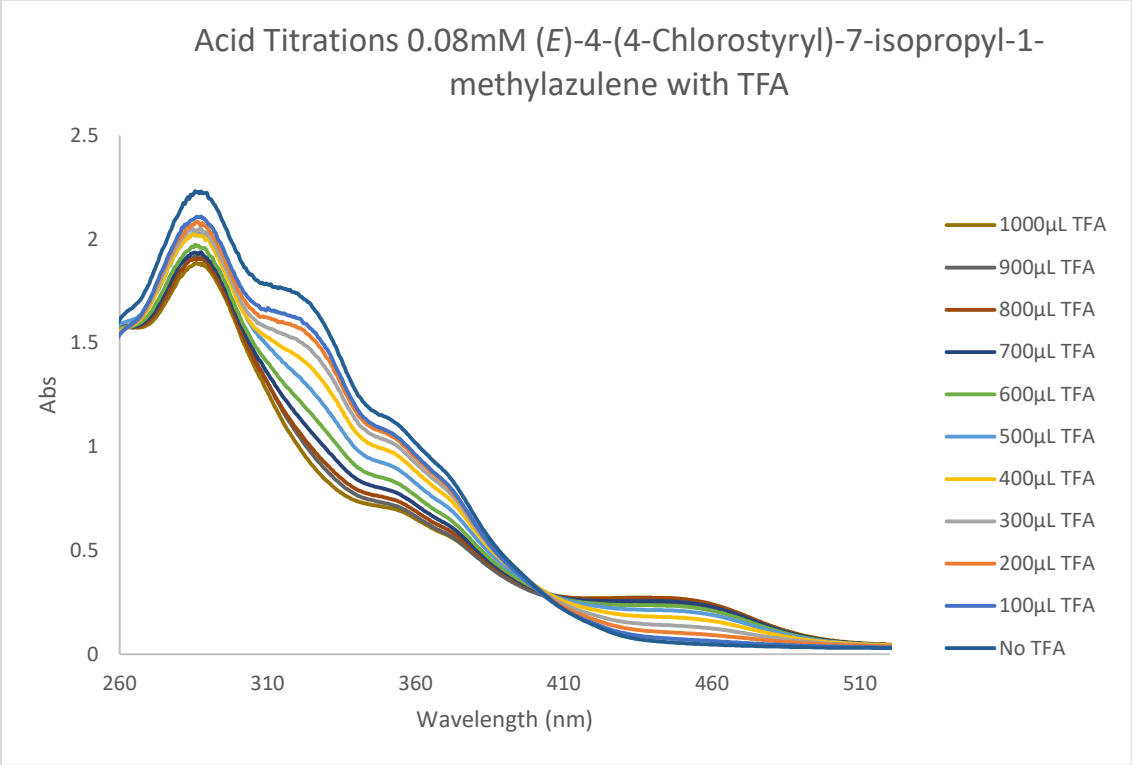


Figure S5: Titration of **18** with TFA in CH_2Cl_2.

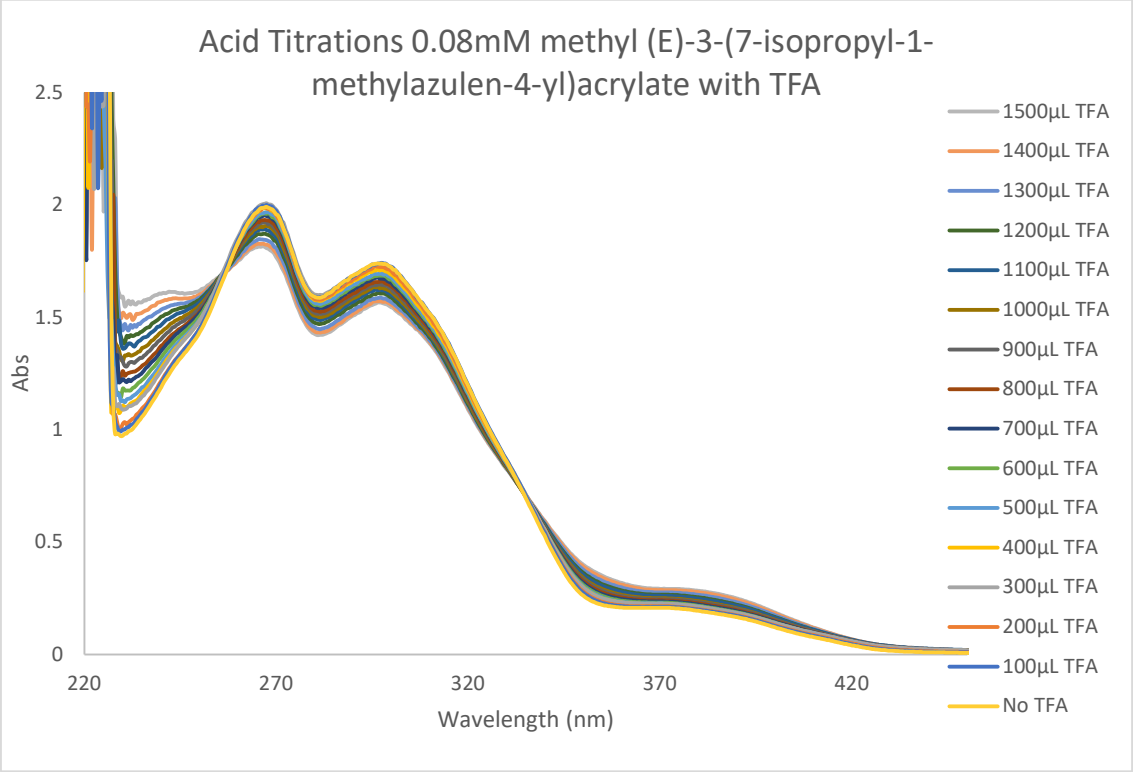


Figure S6: Titration of **20** with TFA in CH_2Cl_2.

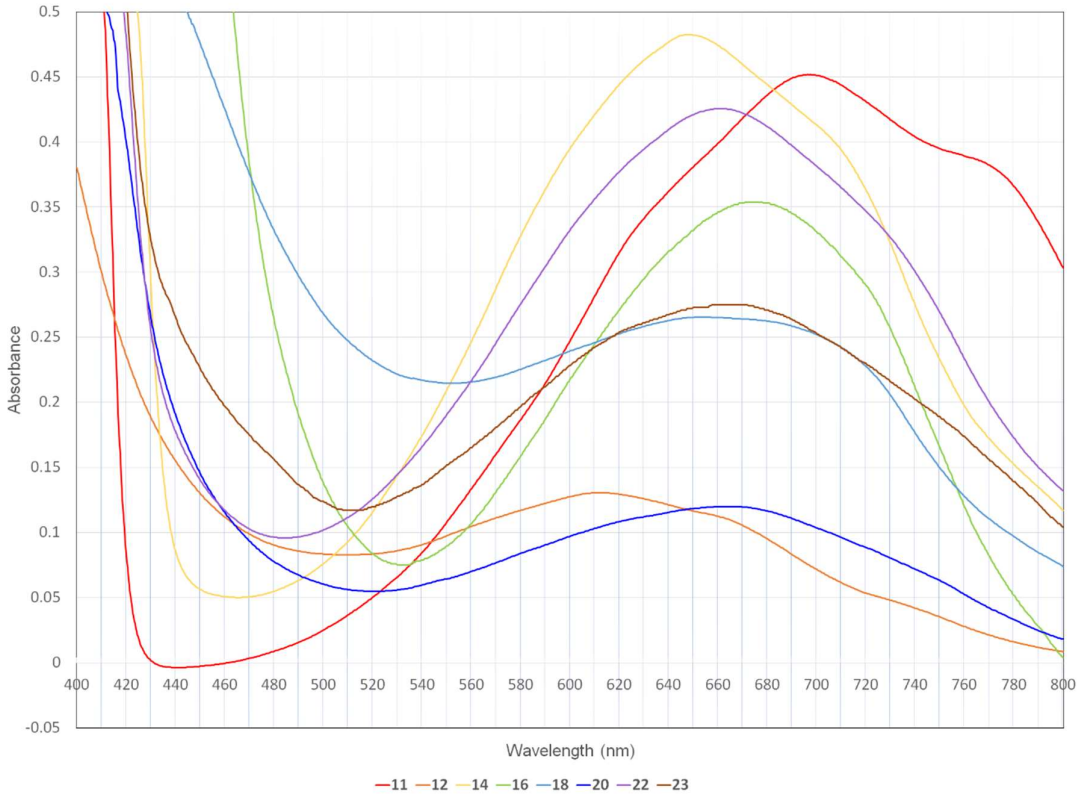


Figure S7: Visible region absorption spectra of selected azulenes in CH_2Cl_2 (normalised to 0.1 mM)

Table S1: Absorption maxima of selected azulenes in CH_2Cl_2.

Azulene	λ_{max} [nm] (log ε)
11	697 (2.65)
12	612 (2.12)
14	648 (2.68)
16	675 (2.55)
18	654 (2.42)
20	664 (2.08)
22	661 (2.63)
23	665 (2.44)

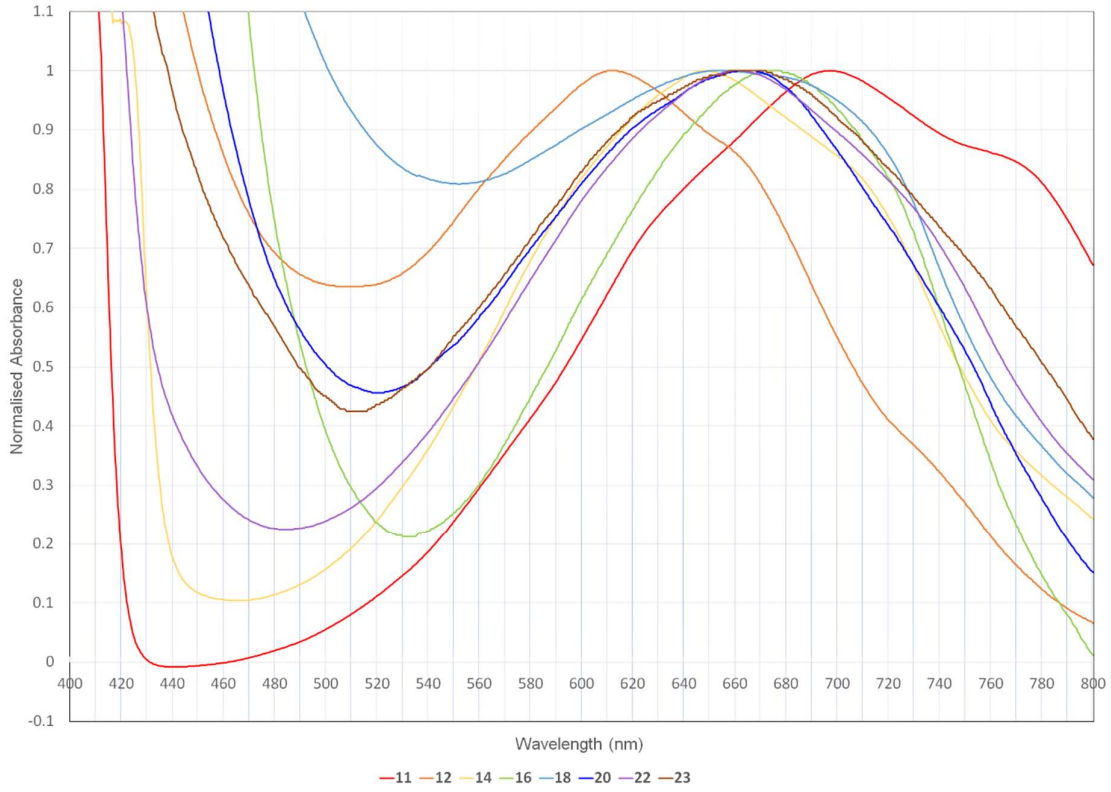
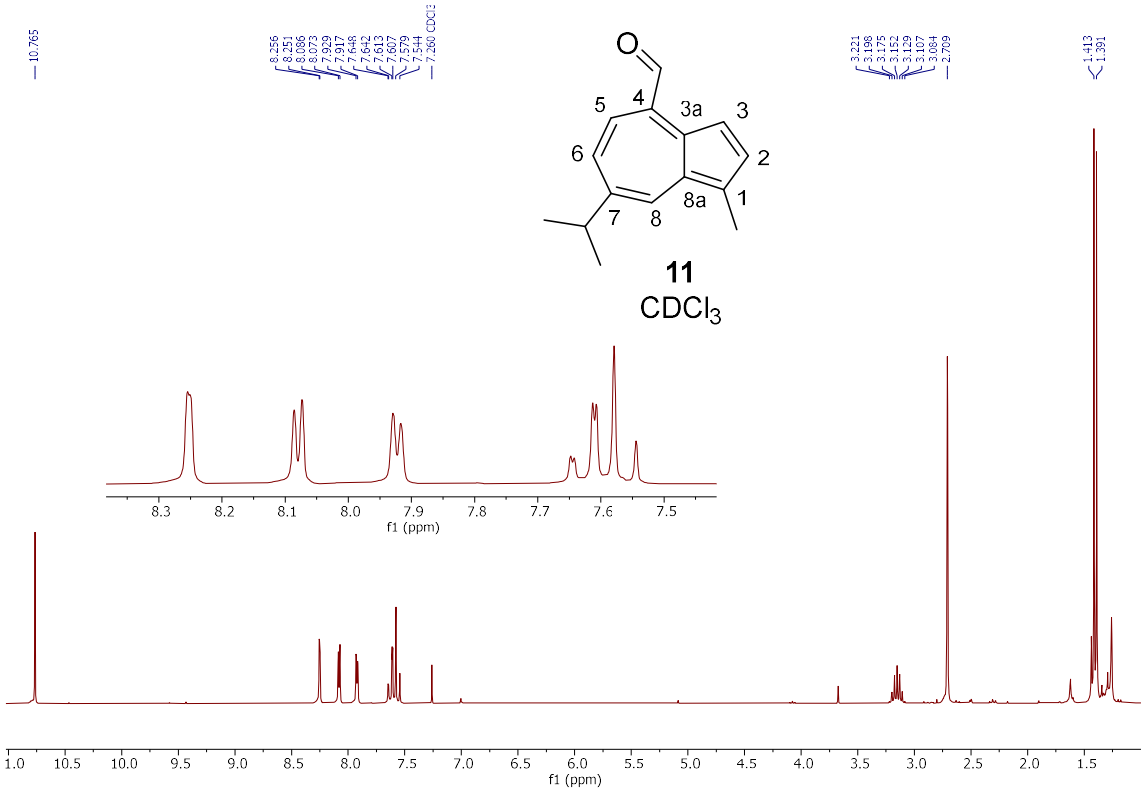
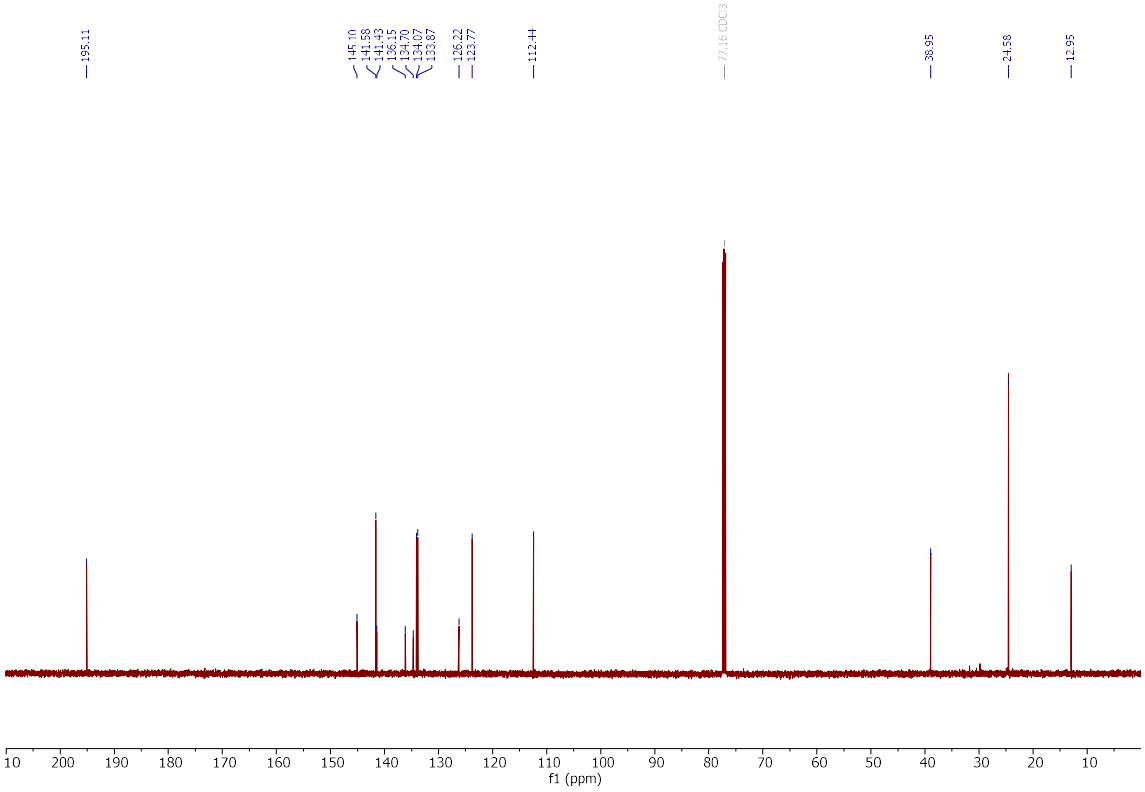
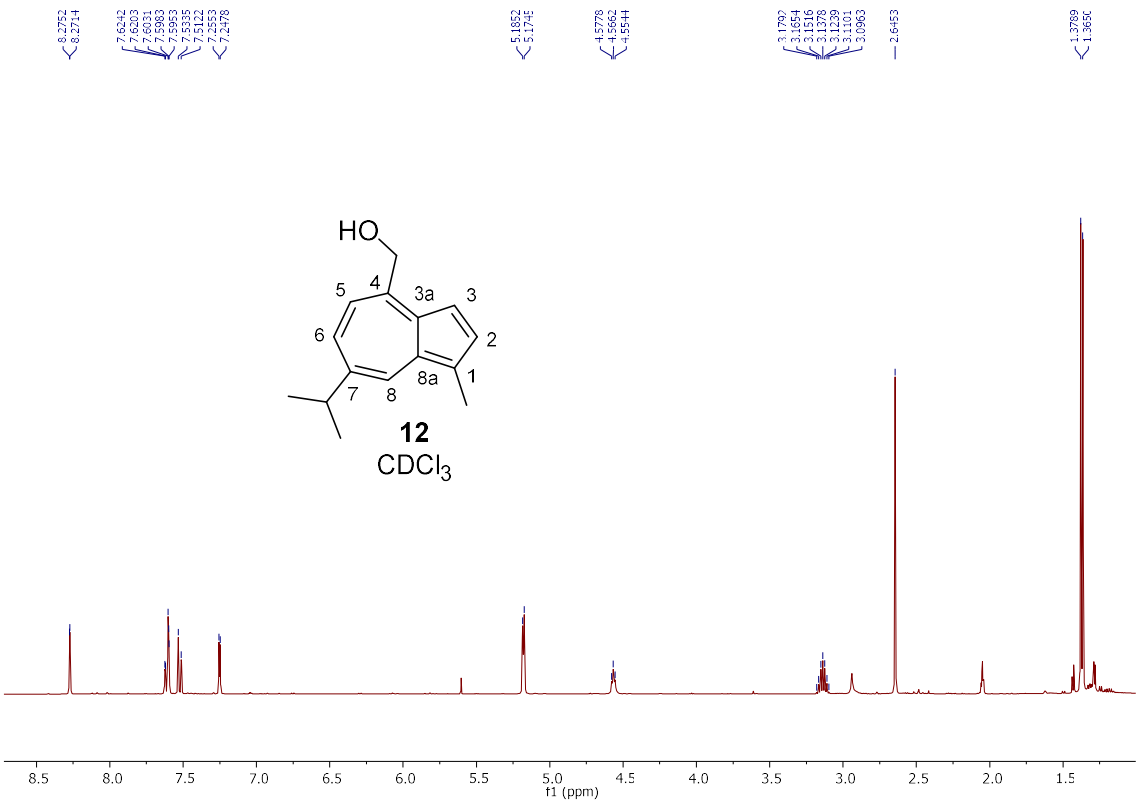


Figure S8: Visible region absorption spectra of selected azulenes in CH_2Cl_2 (normalised Abs = 1)


10.765
8.256
8.251
8.086
8.073
7.929
7.917
7.648
7.642
7.613
7.607
7.579
7.544
7.260 CDCl3
3.221
3.198
3.175
3.152
3.129
3.107
3.084
2.709
1.413
1.391
O
4
5
3a
3
6
2
8a
1
7
8
11
CDCl3
f1 (ppm)
f1 (ppm)


195.11
146.10
141.58
141.43
136.15
134.70
134.07
133.87
126.22
123.77
112.44
77.16 CDCl3
38.95
24.58
12.95
f1 (ppm)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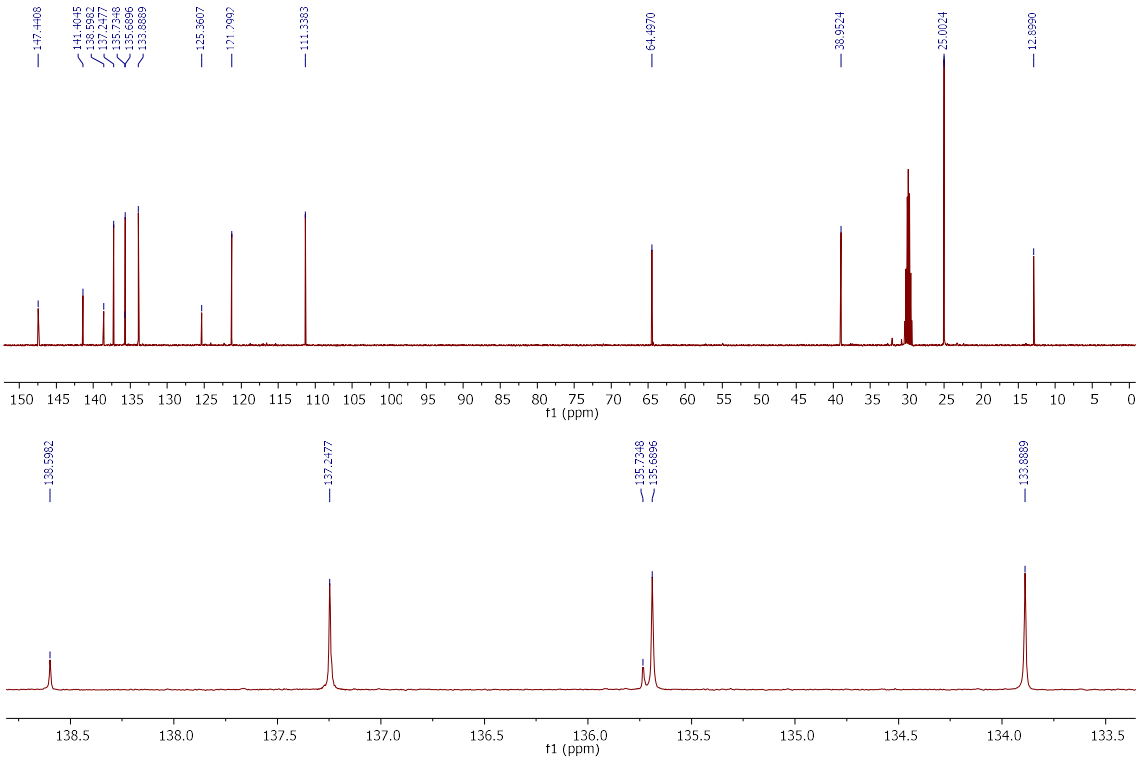
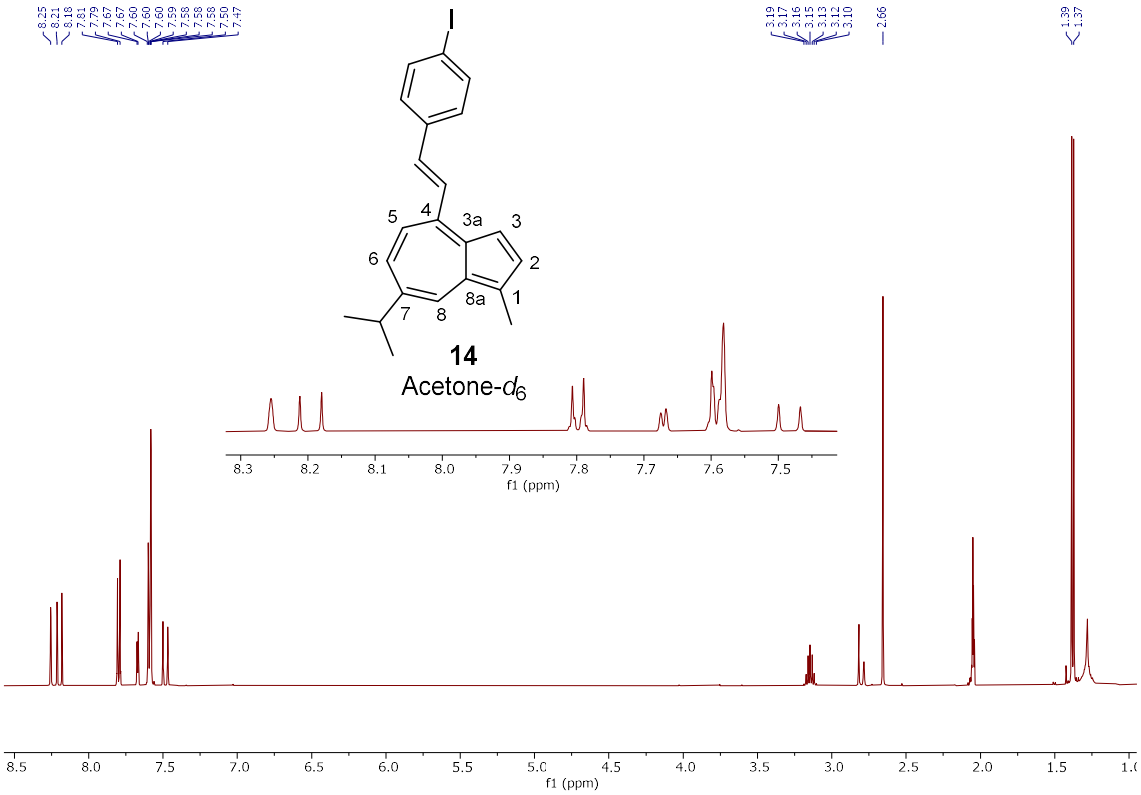
8.2714
7.6242
7.6203
7.6031
7.5983
7.5963
7.5335
7.5122
7.2553
7.2478
5.1852
5.1745
4.5778
4.5662
4.5544
3.1797
3.1654
3.1516
3.1378
3.1239
3.1101
3.0963
2.6453
1.3789
1.3650
HO
5
4
3a
3
6
2
8a
1
7
8
12
CDCl3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


147.4408
141.4045
138.5982
137.2477
135.7348
135.6896
133.8889
125.3607
121.7997
111.3383
64.4970
38.9524
25.0024
12.8990
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)
138.5982
137.2477
135.7348
135.6896
133.8889
138.5
138.0
137.5
137.0
136.5
136.0
135.5
135.0
134.5
134.0
133.5
f1 (ppm)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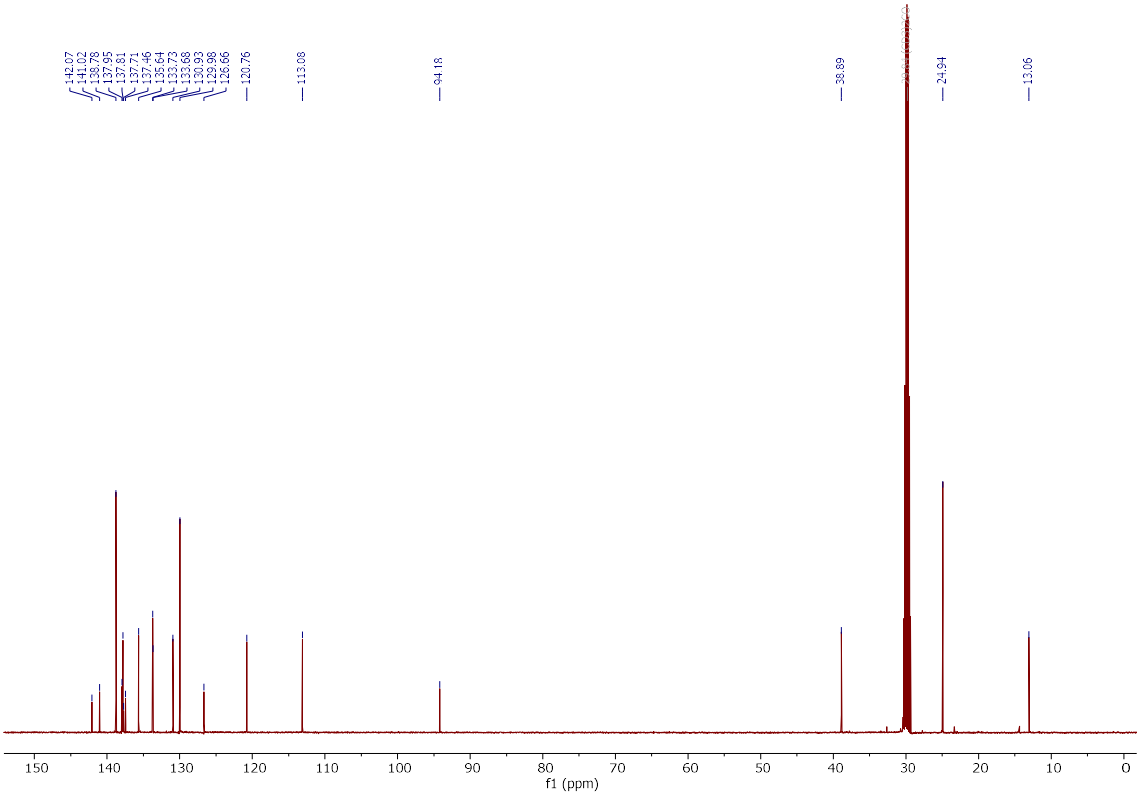
8.21
8.18
7.81
7.79
7.67
7.67
7.60
7.60
7.59
7.58
7.58
7.58
7.50
7.47
3.19
3.17
3.16
3.15
3.13
3.12
3.10
2.66
1.39
1.37
I
4
5
3a
3
6
2
8a
1
7
8
14
Acetone-d_6
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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141.02
138.78
137.95
137.81
137.71
137.46
137.44
133.73
133.68
130.93
129.98
126.66
120.76
113.08
94.16
38.89
24.94
13.06
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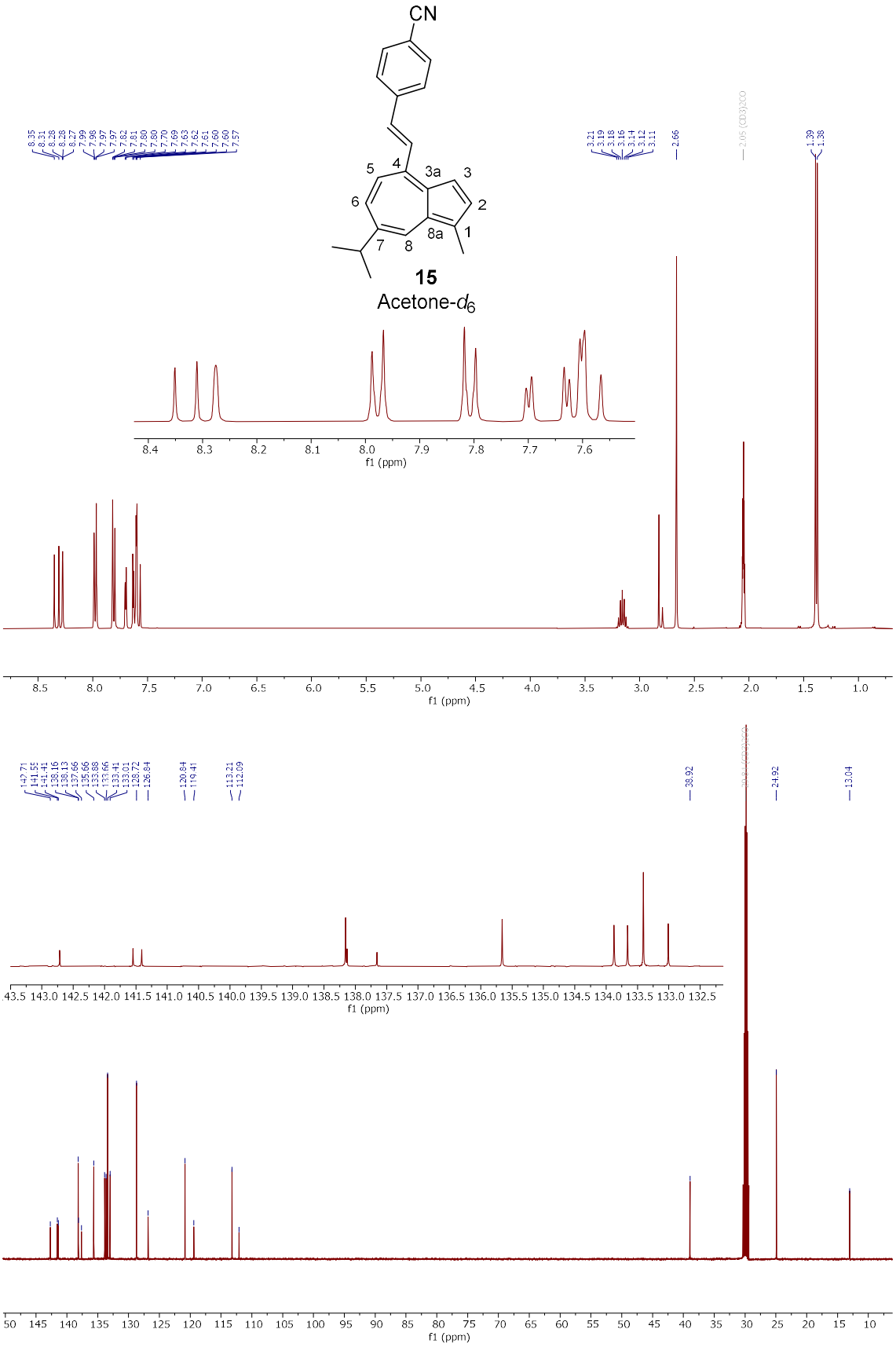
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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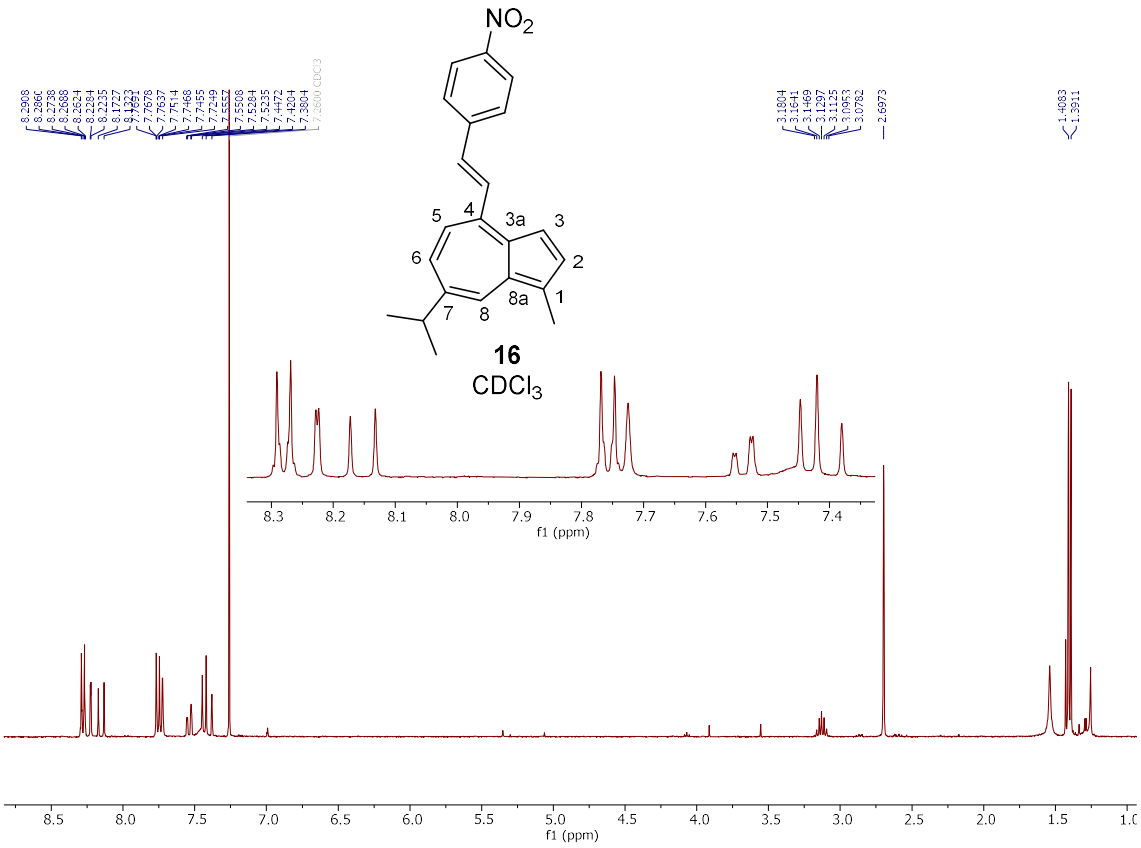
4
3a
3
6
2
8a
1
7
8
15
Acetone-d6
f1 (ppm)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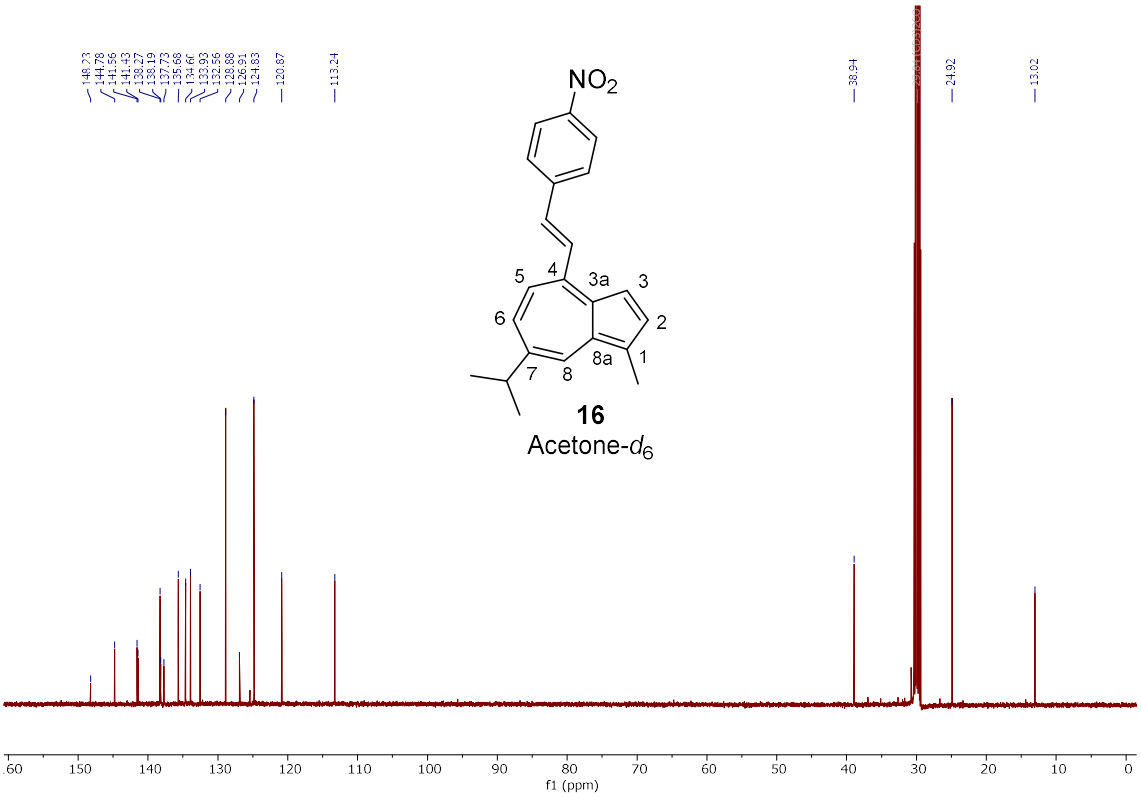
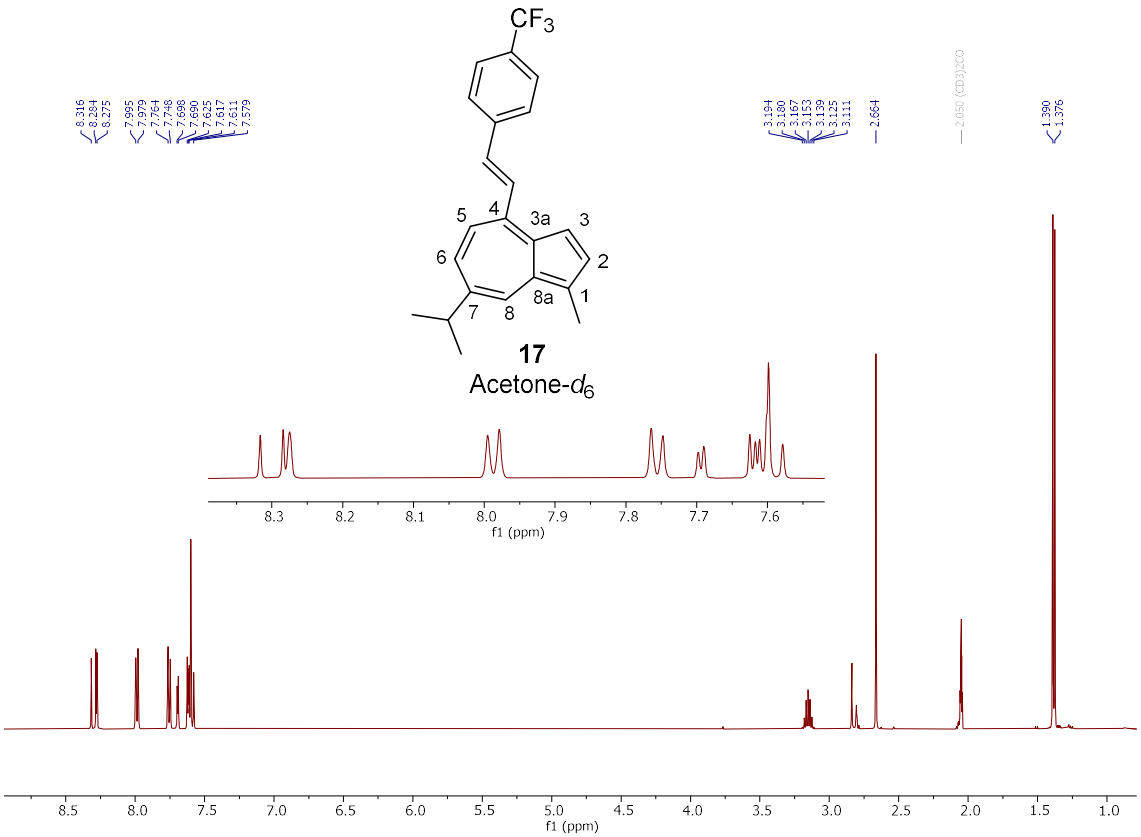
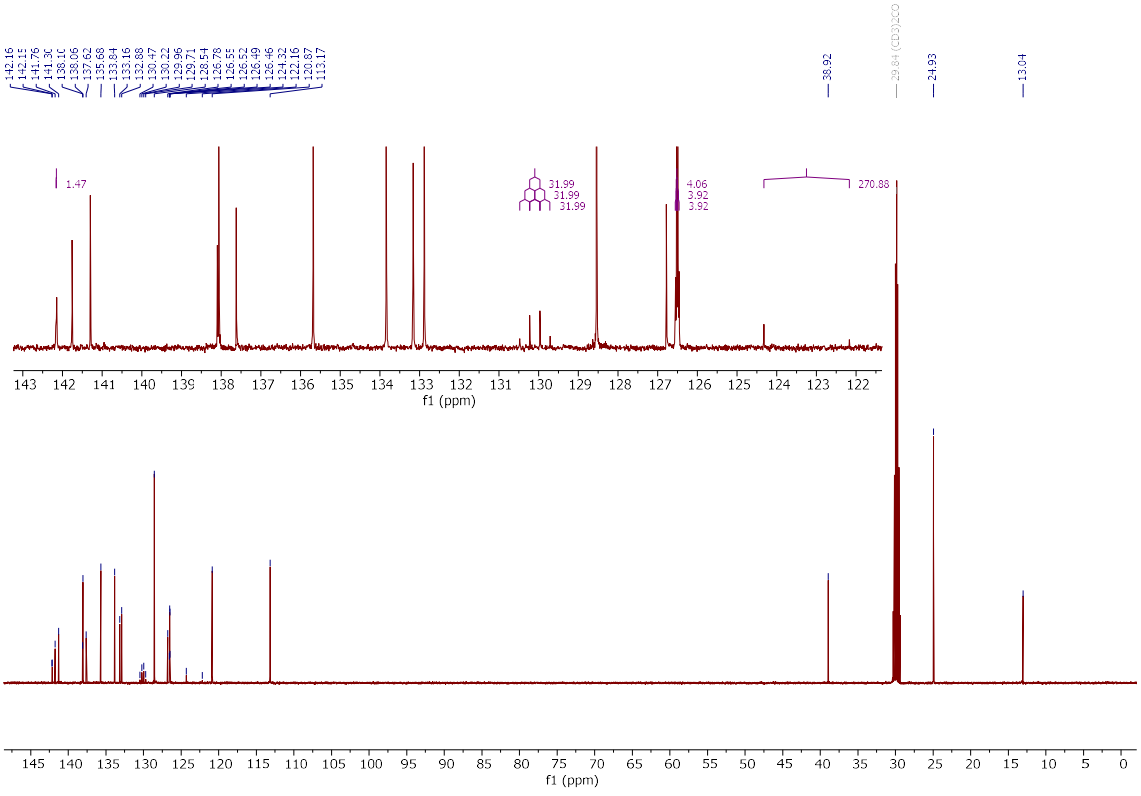
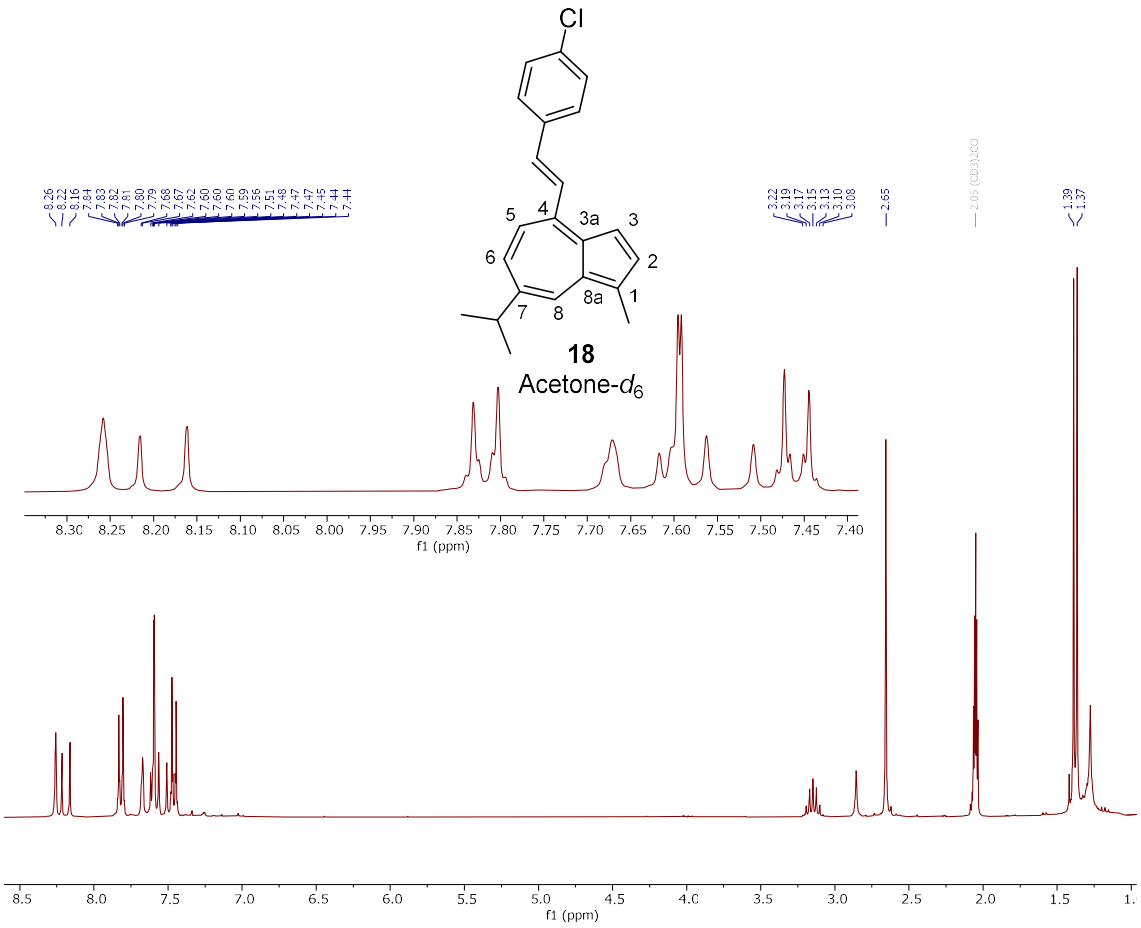
3
6
2
8a
1
7
8
16
CDCl3
f1 (ppm)


NO2
5
4
3a
3
6
2
8a
1
7
8
16
Acetone-d6
f1 (ppm)





S15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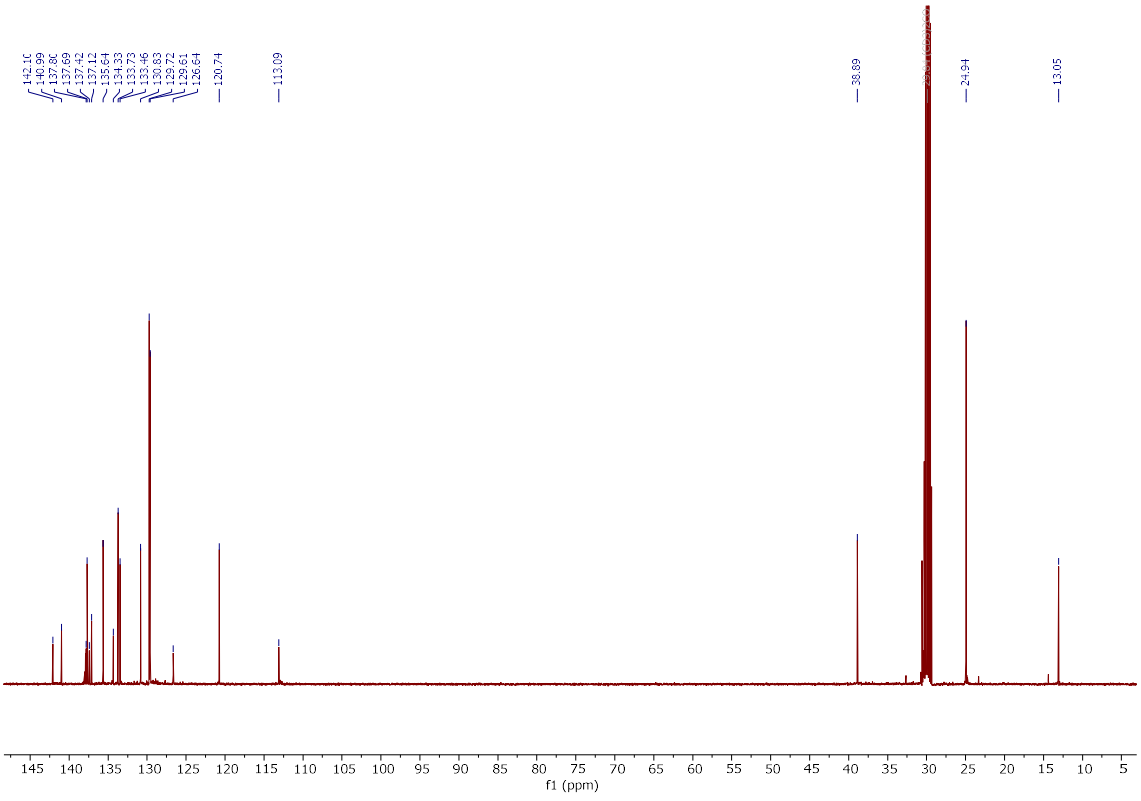
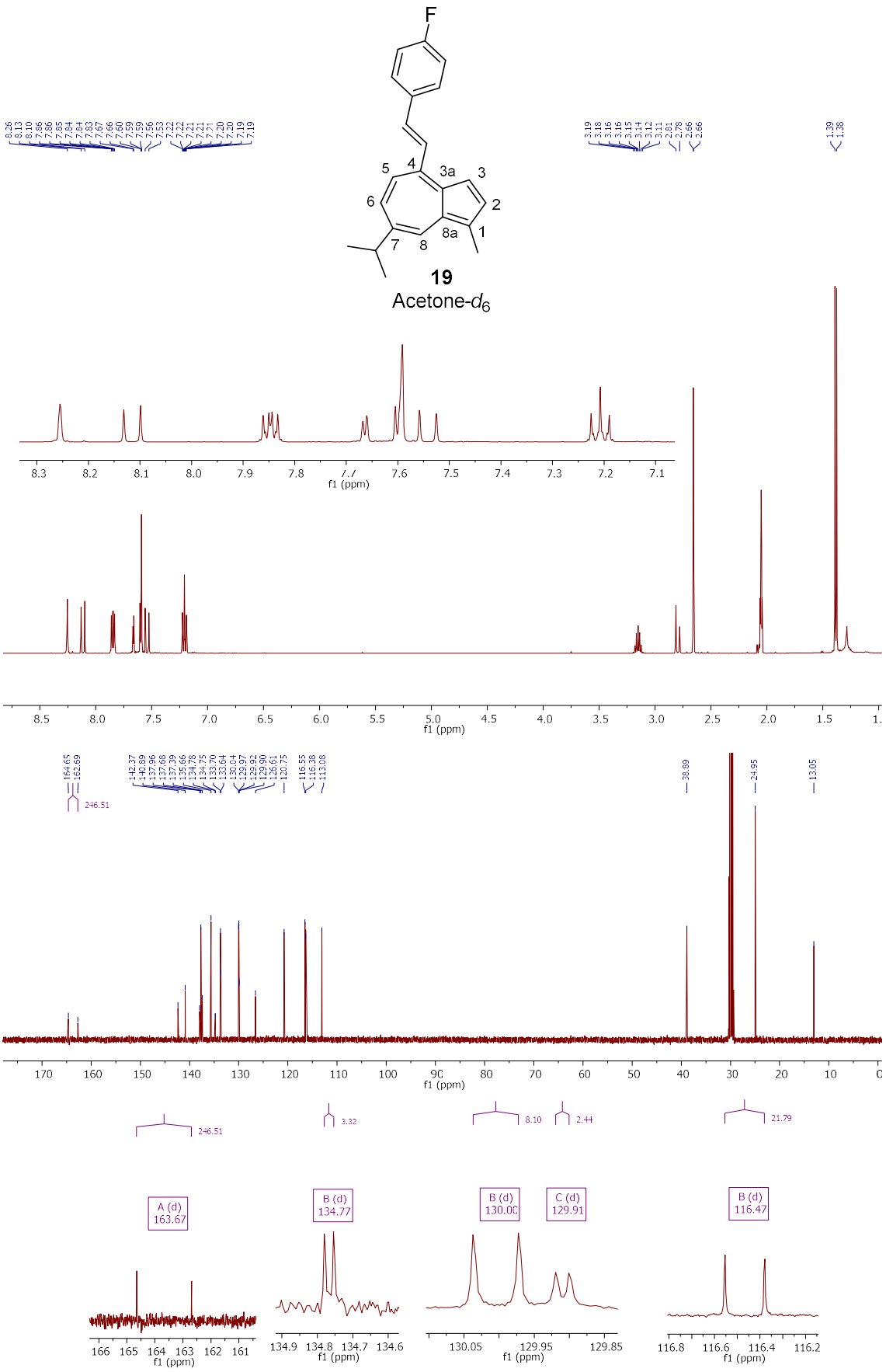
4
3a
3
6
2
8a
1
7
8
18
Acetone-d_6
f1 (ppm)


f1 (ppm)


F
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4
3a
3
6
2
8a
1
7
8
19
Acetone-d_6
f1 (ppm)
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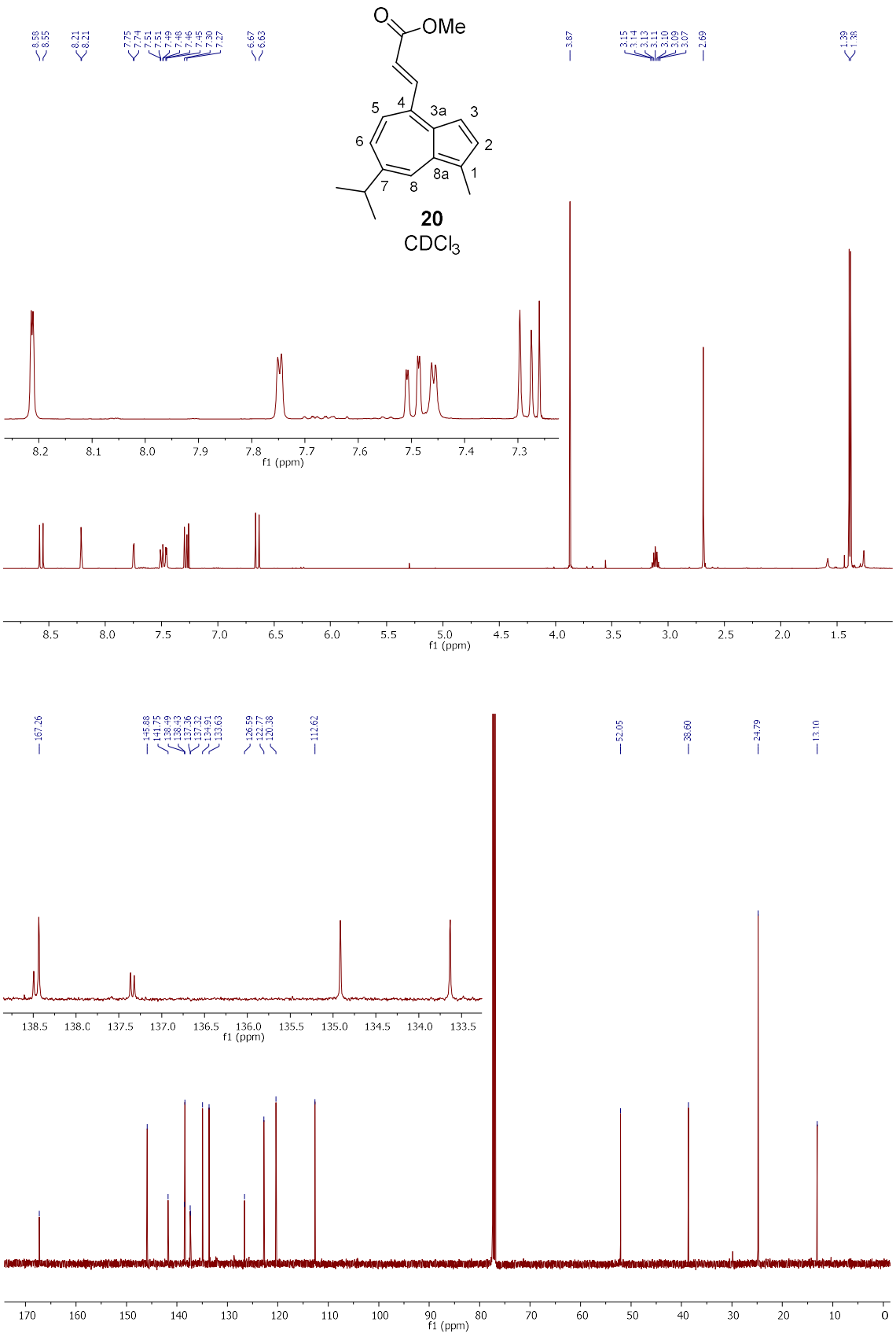
3.32
8.10
2.44
21.79
A (d)
163.67
B (d)
134.77
B (d)
130.00
C (d)
129.91
B (d)
116.47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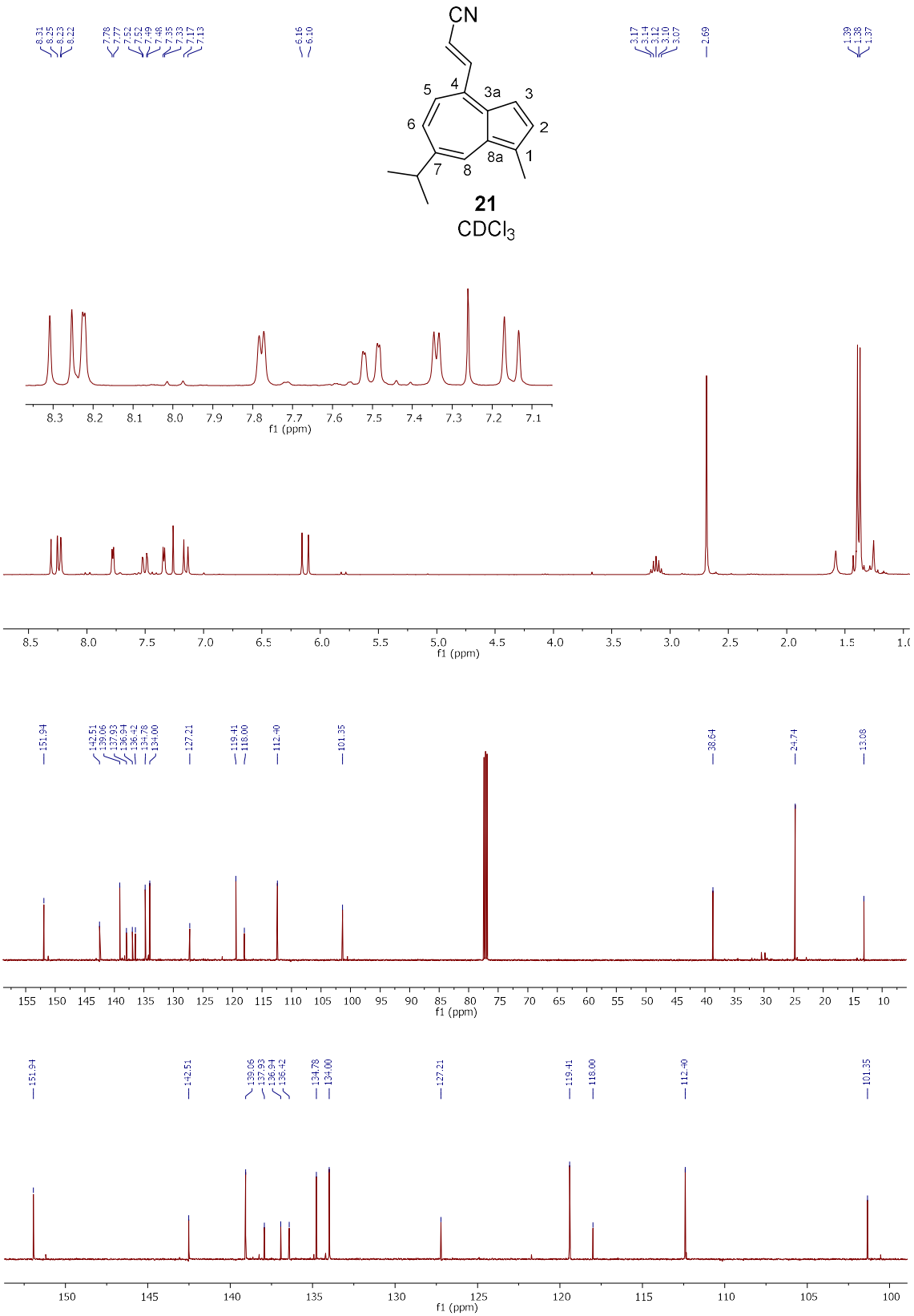
8.21
7.75
7.74
7.51
7.51
7.49
7.48
7.46
7.45
7.30
7.27
6.67
6.63
3.87
3.15
3.14
3.13
3.11
3.10
3.09
3.07
2.69
1.39
1.38
O
OMe
4
5
3a
3
6
2
8a
1
7
8
20
CDCl3
f1 (ppm)
167.26
145.88
141.75
138.49
138.43
137.36
137.32
134.91
133.63
126.59
122.77
120.38
112.62
52.05
38.60
24.79
13.10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7.77
7.77
7.52
7.49
7.48
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7.33
7.17
7.13
6.16
6.10
3.17
3.14
3.12
3.10
3.07
2.69
1.39
1.38
1.37
CN
5
4
3a
3
6
2
8a
1
7
8
21
CDCl3
f1 (ppm)
151.94
142.51
139.06
137.93
136.94
136.42
134.78
134.00
127.21
119.41
118.00
112.40
101.35
38.64
24.74
13.08
f1 (ppm)
151.94
142.51
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136.94
136.42
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134.00
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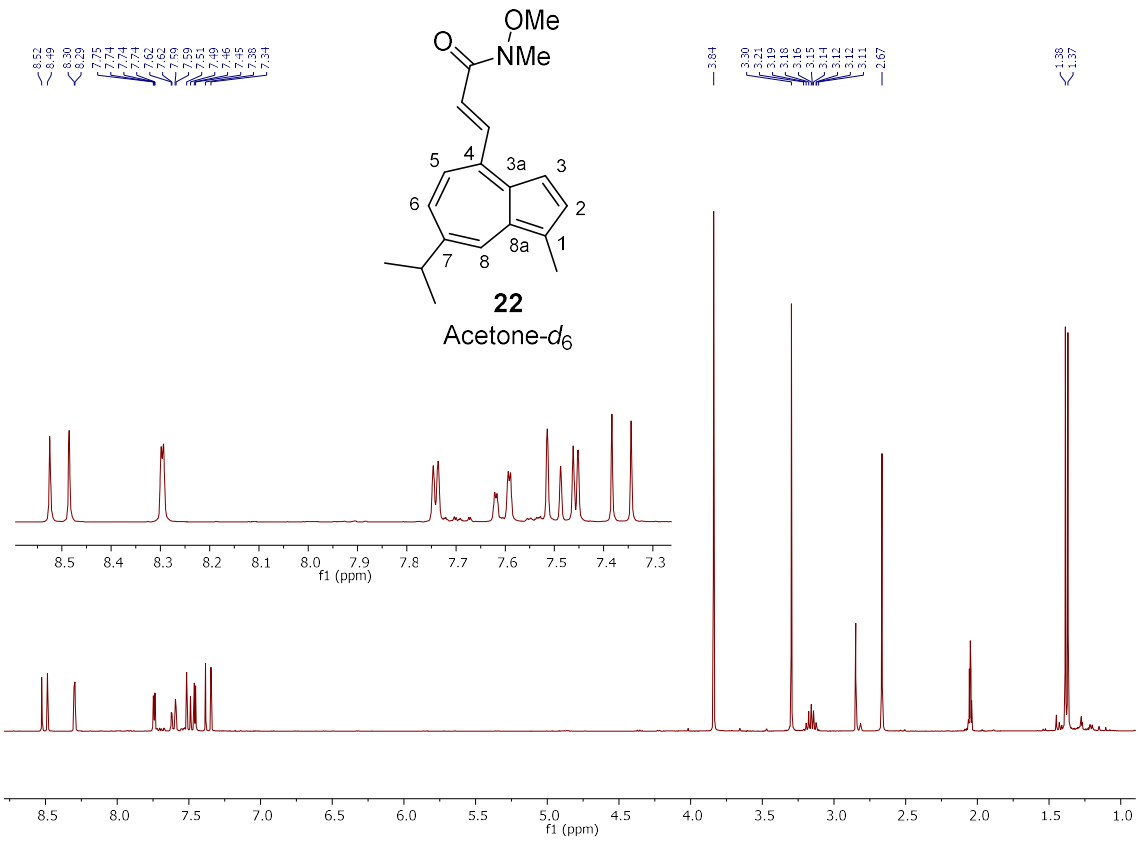
119.41
118.00
112.40
101.35
f1 (ppm)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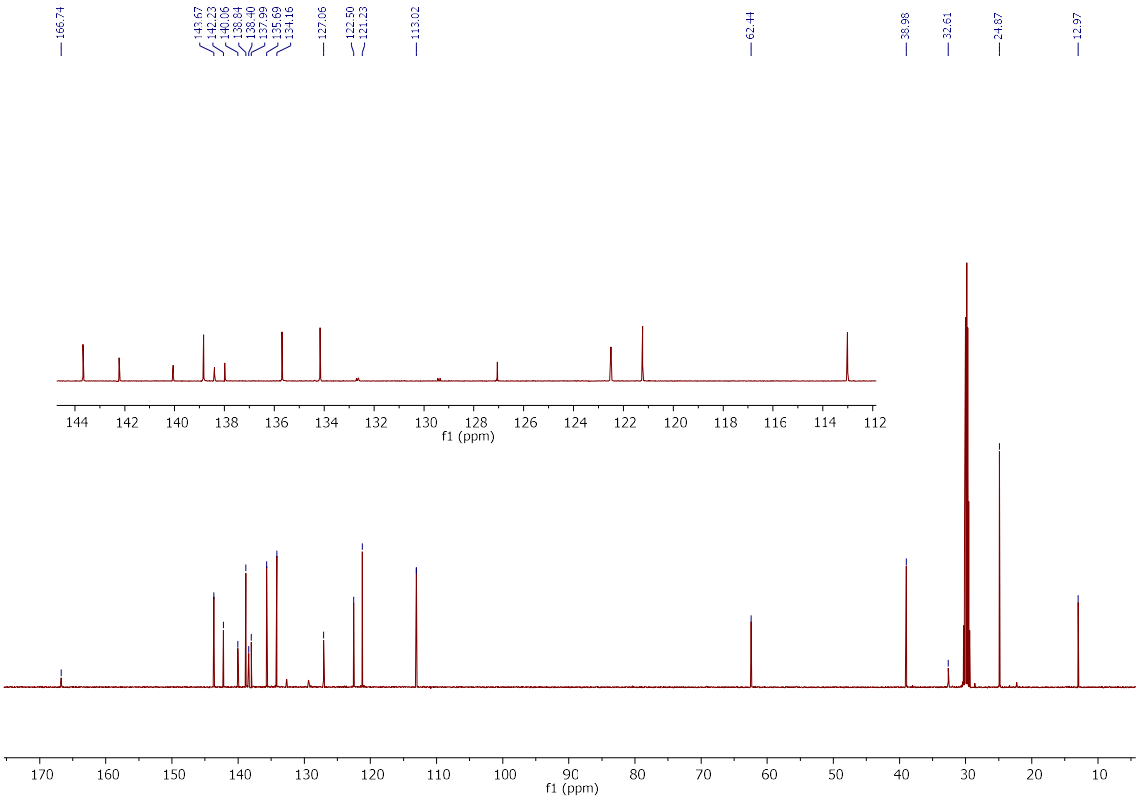
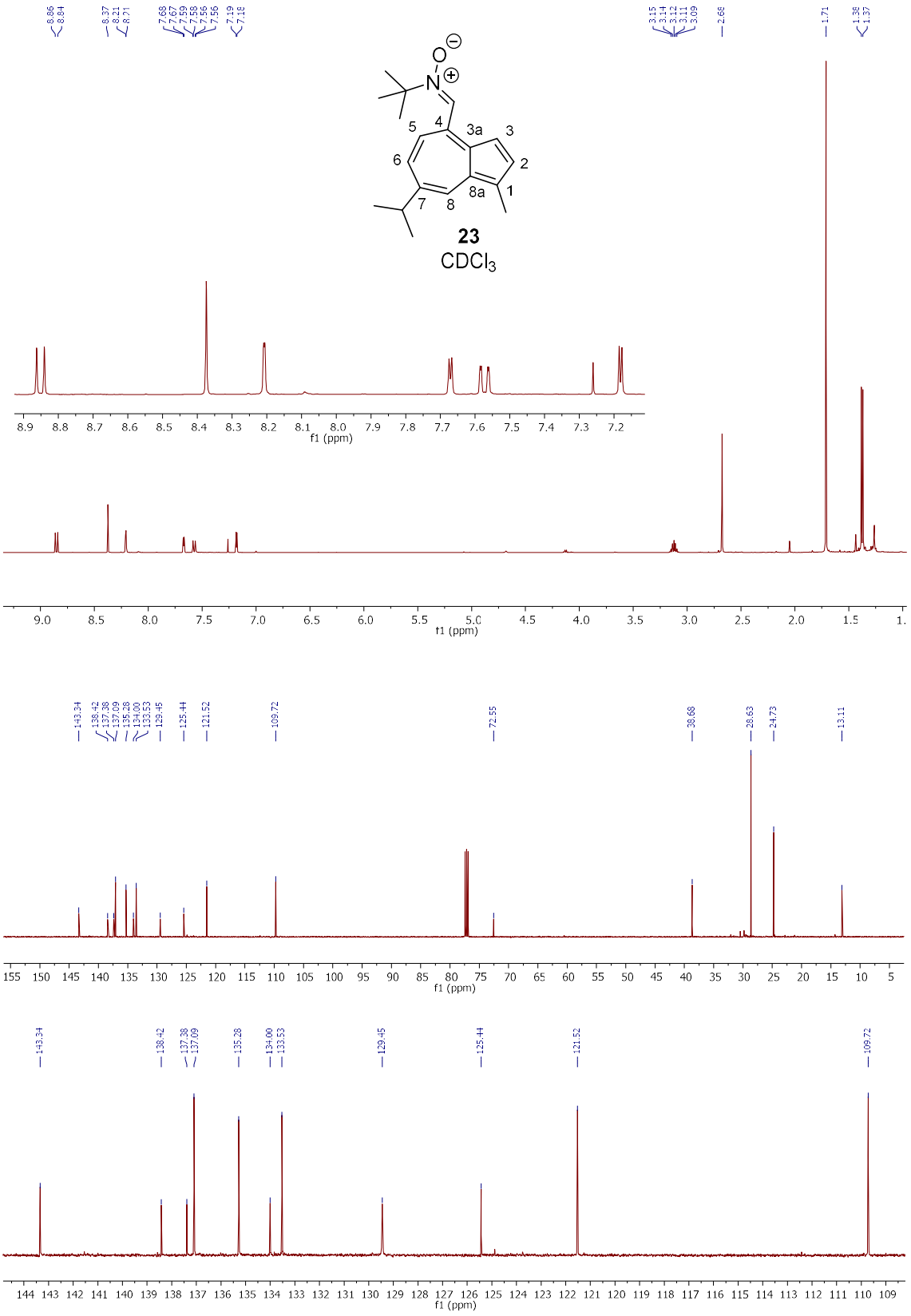
NMe
5
4
3a
3
6
2
8a
1
7
8
22
Acetone-d_6
f1 (ppm)


f1 (ppm)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8.11
7.68
7.67
7.59
7.58
7.56
7.56
7.19
7.18
3.15
3.14
3.12
3.11
3.09
2.68
1.71
1.38
1.37
O
N
4
5
3a
3
6
2
8a
1
7
8
23
CDCl3
f1 (ppm)
143.34
138.42
137.38
137.09
135.28
134.00
133.53
129.45
125.44
121.52
109.72
72.55
38.68
28.63
24.73
13.11

Table S2. Crystal data and structure refinement for **11**.

Identification code	CCDC **2047319**	
Empirical formula	$C_{15}H_{16}O$	
Formula weight	212.28	
Temperature	150.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 10.37310(10) Å	α= 90°.
	b = 6.72170(10) Å	β= 90°.
	c = 16.6660(2) Å	γ = 90°.
Volume	1162.03(2) $Å^3$	
Z	4	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	0.572 mm^{-1}	
F(000)	456	
Crystal size	0.493 x 0.145 x 0.080 mm^3	
Theta range for data collection	5.022 to 73.439°.	
Index ranges	-12<=h<=11, -8<=k<=7, -20<=l<=20	
Reflections collected	11287	
Independent reflections	1277 [R(int) = 0.0371]	
Completeness to θ = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.559	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1277 / 0 / 97	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2σ(I)]	R1 = 0.0431, wR2 = 0.1183	
R indices (all data)	R1 = 0.0442, wR2 = 0.1197	
Extinction coefficient	0.0034(7)	
Largest diff. peak and hole	0.369 and -0.202 e.$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O	6959(1)	2500	6716(1)	35(1)
C(1)	6615(2)	2500	6024(1)	29(1)
C(2)	5245(1)	2500	5752(1)	23(1)
C(3)	4328(2)	2500	6366(1)	26(1)
C(4)	2992(1)	2500	6334(1)	25(1)
C(5)	2147(1)	2500	5674(1)	23(1)
C(6)	702(1)	2500	5854(1)	28(1)
C(7)	290(1)	4359(2)	6309(1)	38(1)
C(8)	2512(1)	2500	4872(1)	23(1)
C(9)	3734(1)	2500	4522(1)	21(1)
C(10)	3957(2)	2500	3692(1)	25(1)
C(11)	2967(2)	2500	3039(1)	29(1)
C(12)	5304(2)	2500	3576(1)	28(1)
C(13)	5949(1)	2500	4303(1)	27(1)
C(14)	5031(1)	2500	4926(1)	22(1)

Table S4. Bond lengths [Å] for **11**.

O-C(1)	1.208(2)	C(8)-C(9)	1.395(2)
C(1)-C(2)	1.491(2)	C(8)-H(8)	0.9500
C(1)-H(1)	0.9500	C(9)-C(10)	1.4025(19)
C(2)-C(14)	1.394(2)	C(9)-C(14)	1.5044(19)
C(2)-C(3)	1.397(2)	C(10)-C(12)	1.410(2)
C(3)-C(4)	1.387(2)	C(10)-C(11)	1.497(2)
C(3)-H(3)	0.9500	C(11)-H(11A)	0.9800
C(4)-C(5)	1.406(2)	C(11)-H(11B)	0.9800
C(4)-H(4)	0.9500	C(11)-H(11C)	0.9800
C(5)-C(8)	1.389(2)	C(11)-H(11A)#1	0.980(13)
C(5)-C(6)	1.5288(19)	C(11)-H(11B)#1	0.980(9)
C(6)-C(7)	1.5231(15)	C(11)-H(11C)#1	0.980(4)
C(6)-C(7)#1	1.5232(15)	C(12)-C(13)	1.384(2)
C(6)-H(6)	1.0000	C(12)-H(12)	0.9500
C(7)-H(7A)	0.9800	C(13)-C(14)	1.409(2)
C(7)-H(7B)	0.9800	C(13)-H(13)	0.9500
C(7)-H(7C)	0.9800		

Table S5. Bond angles [°] for **11**.

O-C(1)-C(2)	124.90(15)	C(9)-C(10)-C(12)	107.38(13)
O-C(1)-H(1)	117.5	C(9)-C(10)-C(11)	127.16(14)
C(2)-C(1)-H(1)	117.5	C(12)-C(10)-C(11)	125.46(14)
C(14)-C(2)-C(3)	127.91(13)	C(10)-C(11)-H(11A)	109.5
C(14)-C(2)-C(1)	116.90(13)	C(10)-C(11)-H(11B)	109.5
C(3)-C(2)-C(1)	115.19(13)	H(11A)-C(11)-H(11B)	109.5
C(4)-C(3)-C(2)	130.66(13)	C(10)-C(11)-H(11C)	109.5
C(4)-C(3)-H(3)	114.7	H(11A)-C(11)-H(11C)	109.5
C(2)-C(3)-H(3)	114.7	H(11B)-C(11)-H(11C)	109.5
C(3)-C(4)-C(5)	130.78(13)	C(10)-C(11)-H(11A)#1	109.5(3)
C(3)-C(4)-H(4)	114.6	H(11A)-C(11)-H(11A)#1	71.7
C(5)-C(4)-H(4)	114.6	H(11B)-C(11)-H(11A)#1	137.7
C(8)-C(5)-C(4)	125.62(13)	H(11C)-C(11)-H(11A)#1	40.6
C(8)-C(5)-C(6)	117.16(13)	C(10)-C(11)-H(11B)#1	109.5(2)
C(4)-C(5)-C(6)	117.21(12)	H(11A)-C(11)-H(11B)#1	137.7
C(7)-C(6)-C(7)#1	110.27(13)	H(11B)-C(11)-H(11B)#1	40.6
C(7)-C(6)-C(5)	111.89(8)	H(11C)-C(11)-H(11B)#1	71.7
C(7)#1-C(6)-C(5)	111.89(8)	H(11A)#1-C(11)-H(11B)#1	109.5
C(7)-C(6)-H(6)	107.5	C(10)-C(11)-H(11C)#1	109.47(8)
C(7)#1-C(6)-H(6)	107.5	H(11A)-C(11)-H(11C)#1	40.6
C(5)-C(6)-H(6)	107.5	H(11B)-C(11)-H(11C)#1	71.7
C(6)-C(7)-H(7A)	109.5	H(11C)-C(11)-H(11C)#1	137.7
C(6)-C(7)-H(7B)	109.5	H(11A)#1-C(11)-H(11C)#1	109.5
H(7A)-C(7)-H(7B)	109.5	H(11B)#1-C(11)-H(11C)#1	109.5
C(6)-C(7)-H(7C)	109.5	C(13)-C(12)-C(10)	111.05(13)
H(7A)-C(7)-H(7C)	109.5	C(13)-C(12)-H(12)	124.5
H(7B)-C(7)-H(7C)	109.5	C(10)-C(12)-H(12)	124.5
C(5)-C(8)-C(9)	130.56(14)	C(12)-C(13)-C(14)	108.57(13)
C(5)-C(8)-H(8)	114.7	C(12)-C(13)-H(13)	125.7
C(9)-C(8)-H(8)	114.7	C(14)-C(13)-H(13)	125.7
C(8)-C(9)-C(10)	124.22(14)	C(2)-C(14)-C(13)	128.30(14)
C(8)-C(9)-C(14)	128.68(13)	C(2)-C(14)-C(9)	125.78(13)
C(10)-C(9)-C(14)	107.09(12)	C(13)-C(14)-C(9)	105.91(13)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O	29(1)	40(1)	37(1)	0	-12(1)	0
C(1)	22(1)	32(1)	34(1)	0	-5(1)	0
C(2)	20(1)	20(1)	28(1)	0	-4(1)	0
C(3)	26(1)	27(1)	23(1)	0	-5(1)	0
C(4)	24(1)	29(1)	22(1)	0	1(1)	0
C(5)	20(1)	24(1)	26(1)	0	0(1)	0
C(6)	20(1)	37(1)	27(1)	0	0(1)	0
C(7)	27(1)	33(1)	55(1)	1(1)	5(1)	6(1)
C(8)	21(1)	23(1)	24(1)	0	-4(1)	0
C(9)	21(1)	20(1)	23(1)	0	-2(1)	0
C(10)	27(1)	23(1)	24(1)	0	0(1)	0
C(11)	33(1)	31(1)	22(1)	0	-1(1)	0
C(12)	29(1)	29(1)	28(1)	0	7(1)	0
C(13)	20(1)	28(1)	33(1)	0	3(1)	0
C(14)	20(1)	19(1)	29(1)	0	-1(1)	0

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **11**.

	x	y	z	U(eq)
H(1)	7265	2500	5623	35
H(3)	4678	2500	6893	31
H(4)	2578	2500	6842	30
H(6)	237	2500	5328	33
H(7A)	547	5544	6006	57
H(7B)	707	4377	6837	57
H(7C)	-648	4353	6378	57
H(8)	1817	2500	4501	27
H(11A)	2243	1646	3194	43
H(11B)	3353	1994	2542	43
H(11C)	2656	3860	2952	43
H(12)	5714	2500	3066	34
H(13)	6858	2500	4370	32

Table S8. Torsion angles [°] for **11**.

O-C(1)-C(2)-C(14)	180.000(1)	C(14)-C(9)-C(10)-C(12)	0.000(1)
O-C(1)-C(2)-C(3)	0.000(1)	C(8)-C(9)-C(10)-C(11)	0.000(1)
C(14)-C(2)-C(3)-C(4)	0.000(1)	C(14)-C(9)-C(10)-C(11)	180.000(1)
C(1)-C(2)-C(3)-C(4)	180.000(1)	C(9)-C(10)-C(12)-C(13)	0.000(1)
C(2)-C(3)-C(4)-C(5)	0.000(1)	C(11)-C(10)-C(12)-C(13)	180.000(1)
C(3)-C(4)-C(5)-C(8)	0.000(1)	C(10)-C(12)-C(13)-C(14)	0.000(1)
C(3)-C(4)-C(5)-C(6)	180.000(1)	C(3)-C(2)-C(14)-C(13)	180.000(1)
C(8)-C(5)-C(6)-C(7)	-117.84(9)	C(1)-C(2)-C(14)-C(13)	0.000(1)
C(4)-C(5)-C(6)-C(7)	62.16(9)	C(3)-C(2)-C(14)-C(9)	0.000(1)
C(8)-C(5)-C(6)-C(7)#1	117.84(9)	C(1)-C(2)-C(14)-C(9)	180.000(1)
C(4)-C(5)-C(6)-C(7)#1	-62.16(9)	C(12)-C(13)-C(14)-C(2)	180.000(1)
C(4)-C(5)-C(8)-C(9)	0.000(1)	C(12)-C(13)-C(14)-C(9)	0.000(1)
C(6)-C(5)-C(8)-C(9)	180.000(1)	C(8)-C(9)-C(14)-C(2)	0.000(1)
C(5)-C(8)-C(9)-C(10)	180.000(1)	C(10)-C(9)-C(14)-C(2)	180.000(1)
C(5)-C(8)-C(9)-C(14)	0.000(1)	C(8)-C(9)-C(14)-C(13)	180.000(1)
C(8)-C(9)-C(10)-C(12)	180.000(1)	C(10)-C(9)-C(14)-C(13)	0.000(1)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z