Supplementary Information

3-Perfluoroalkylated fluorescent coumarin dyes: Rational molecular design and photophysical properties

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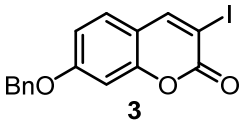
(Contents)

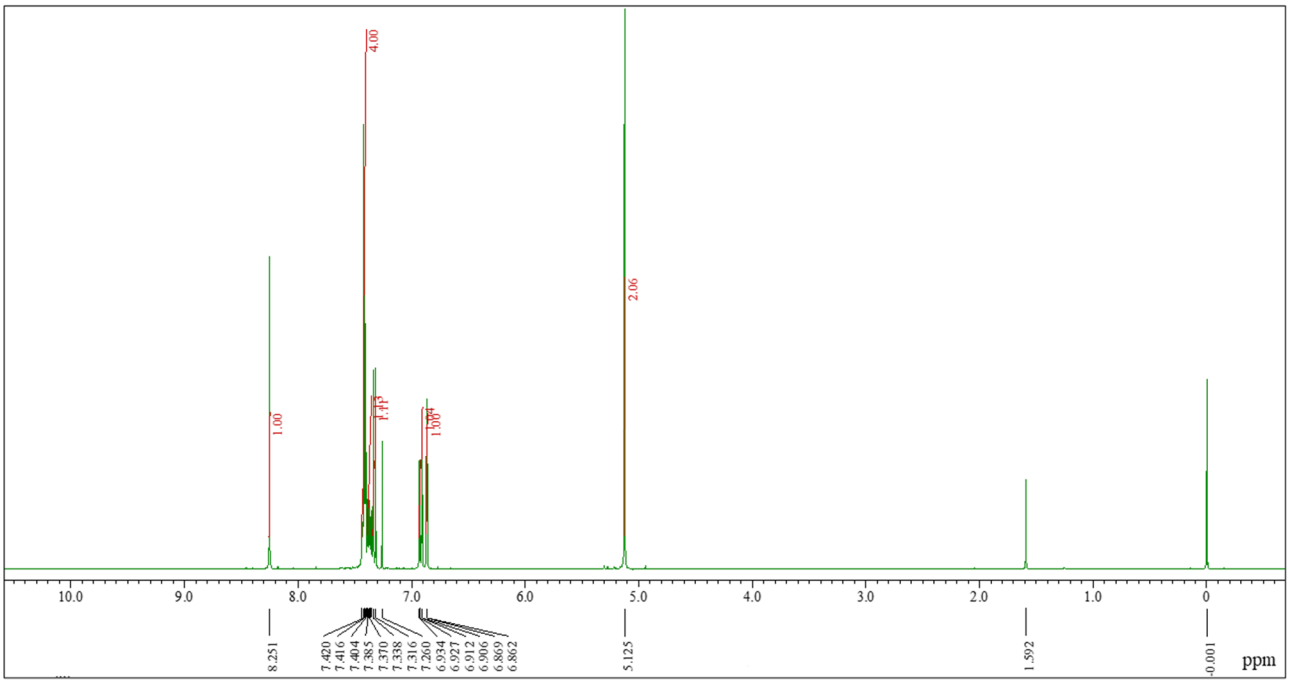
c

7-benzyloxy-3-iodo-2*H*-chromen-2-one (3)

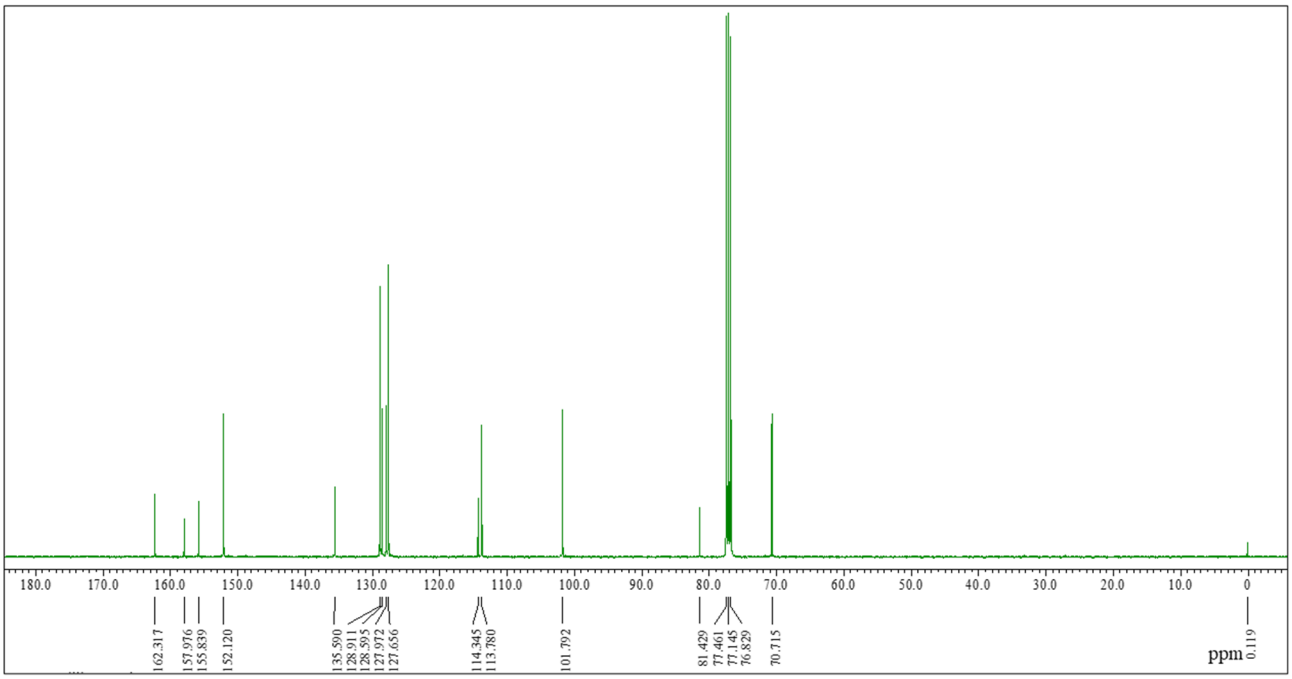


3

^{1}H NMR



^{13}C NMR



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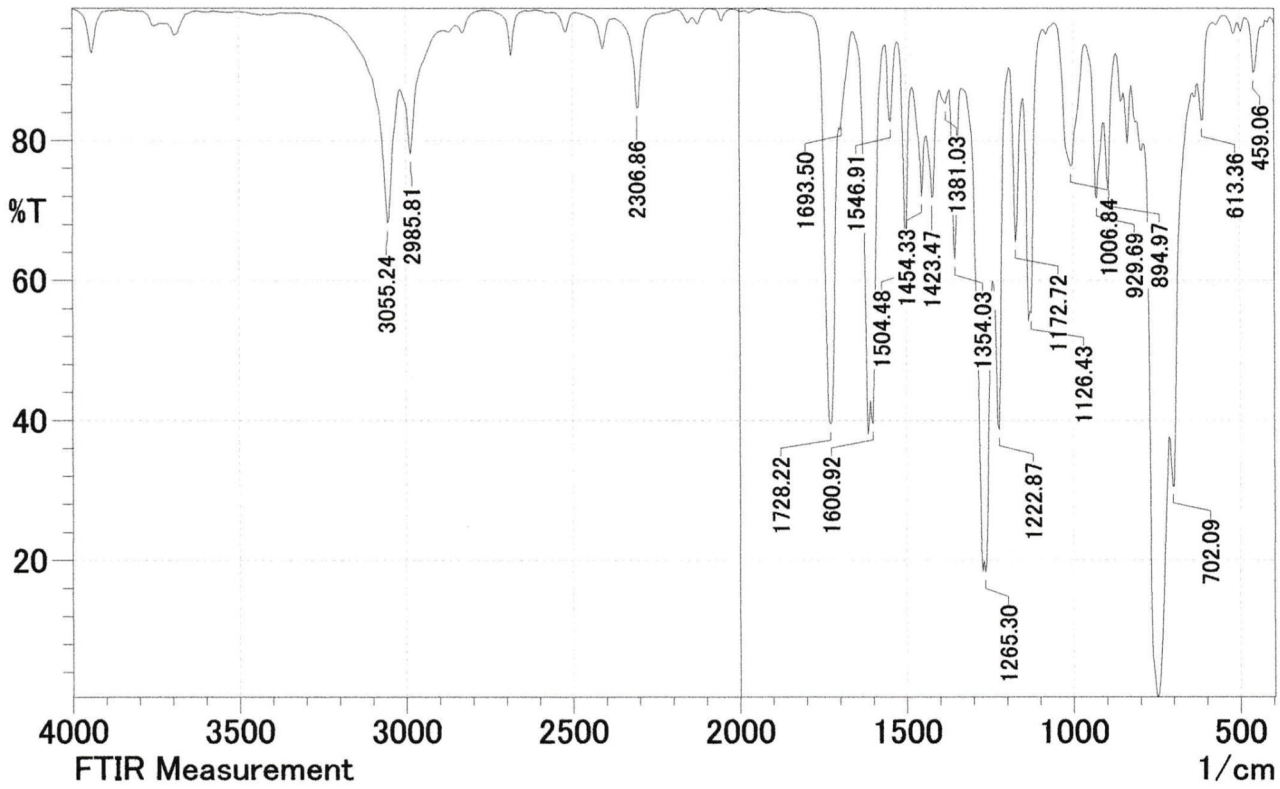
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40
20
3055.24
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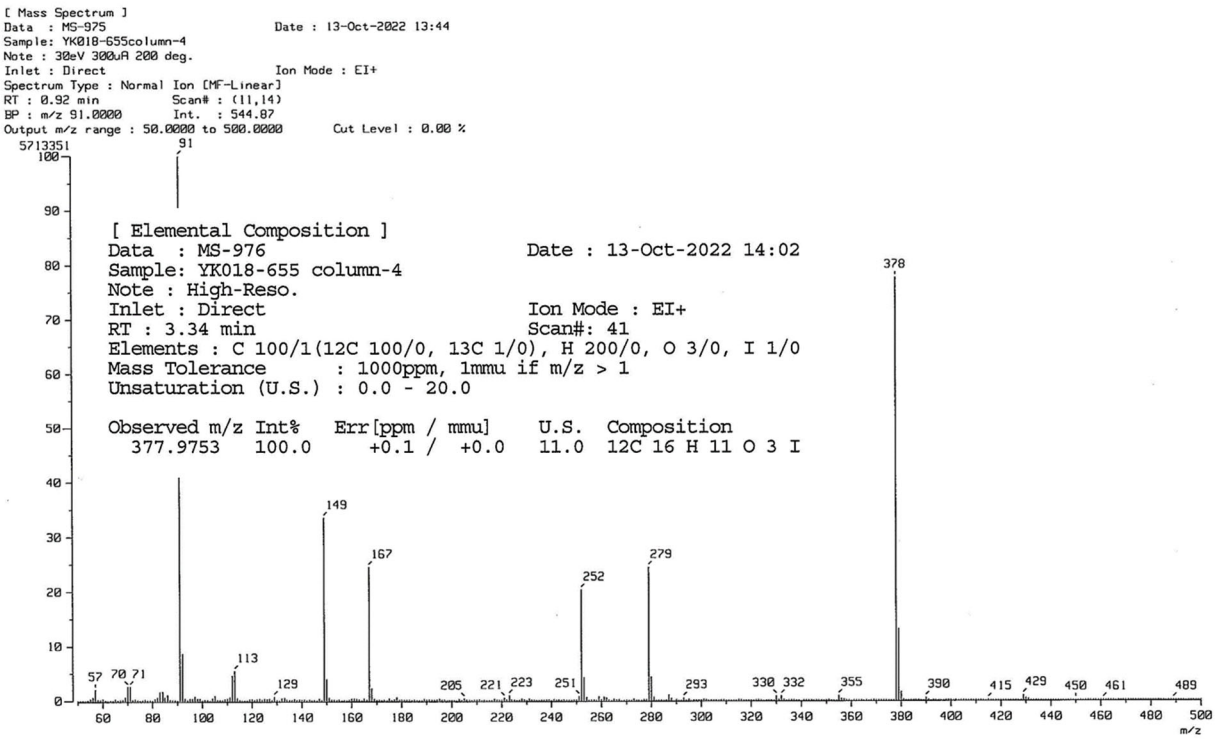
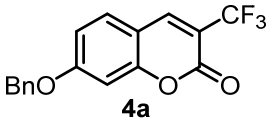
1693.50
1546.91
1504.48
1454.33
1423.47
1381.03
1354.03
1265.30
1222.87
1172.72
1126.43
1006.84
929.69
894.97
1728.22
1600.92
702.09
613.36
459.06
4000
3500
3000
2500
2000
1500
1000
500
FTIR Measurement
1/cm

HRMS

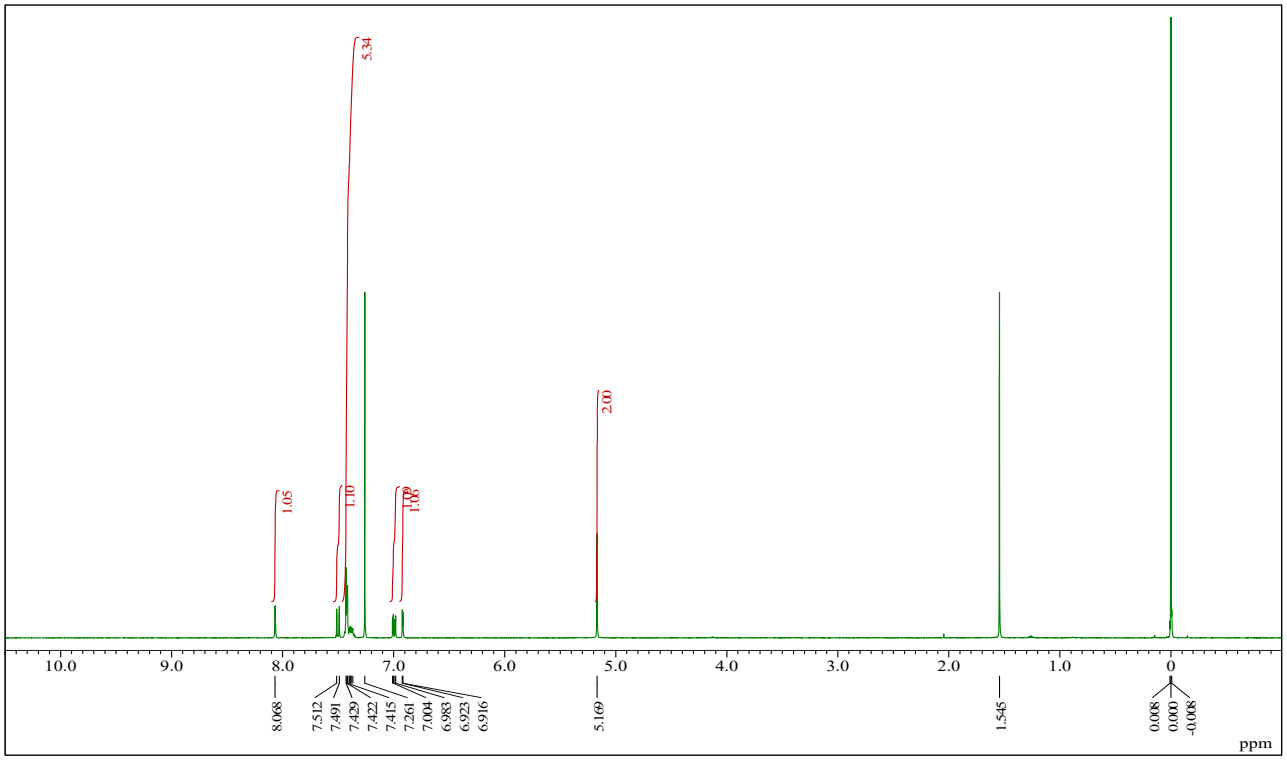

[Mass Spectrum]
Data : MS-975
Date : 13-Oct-2022 13:44
Sample: YK018-655column-4
Note : 30eV 300uA 200 deg.
Inlet : Direct
Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.92 min
Scan# : (11,14)
BP : m/z 91.0000
Int. : 544.87
Output m/z range : 50.0000 to 500.0000
Cut Level : 0.00 %
5713351
91
[Elemental Composition]
Data : MS-976
Date : 13-Oct-2022 14:02
Sample: YK018-655 column-4
Note : High-Reso.
Inlet : Direct
Ion Mode : EI+
RT : 3.34 min
Scan#: 41
Elements : C 100/1(12C 100/0, 13C 1/0), H 200/0, O 3/0, I 1/0
Mass Tolerance : 1000ppm, 1mmu if m/z > 1
Unsaturation (U.S.) : 0.0 - 20.0
Observed m/z Int% Err[ppm / mmu] U.S. Composition
377.9753 100.0 +0.1 / +0.0 11.0 12C 16 H 11 O 3 I
m/z

7-benzyloxy-3-trifluoromethyl-2*H*-chromen-2-one (4a)

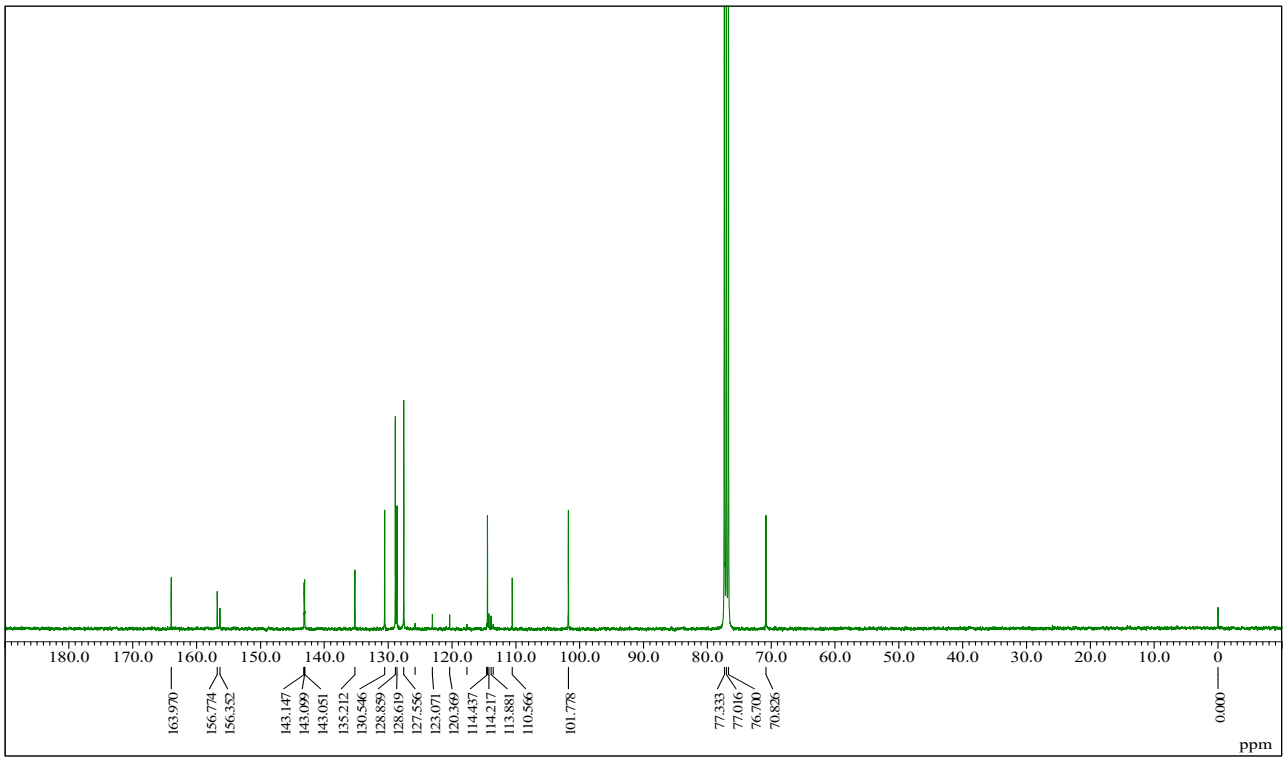


4a

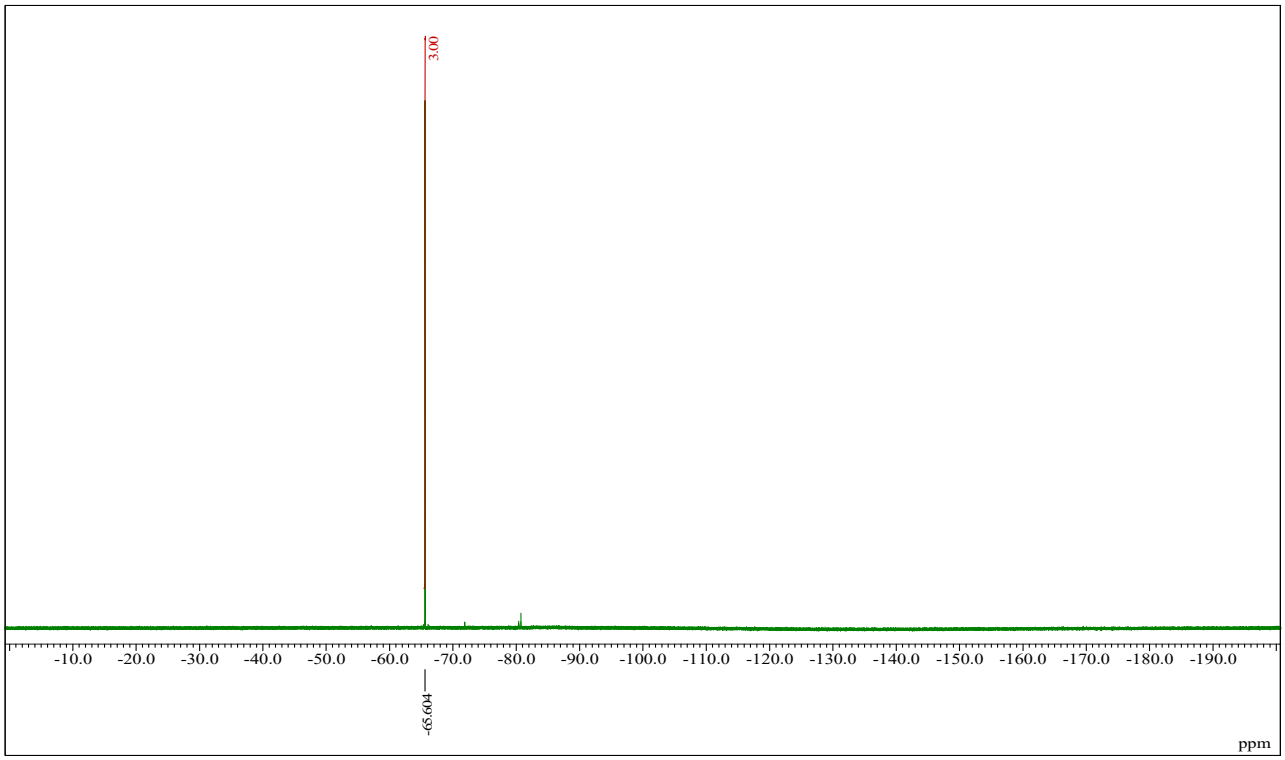
^{1}H NMR



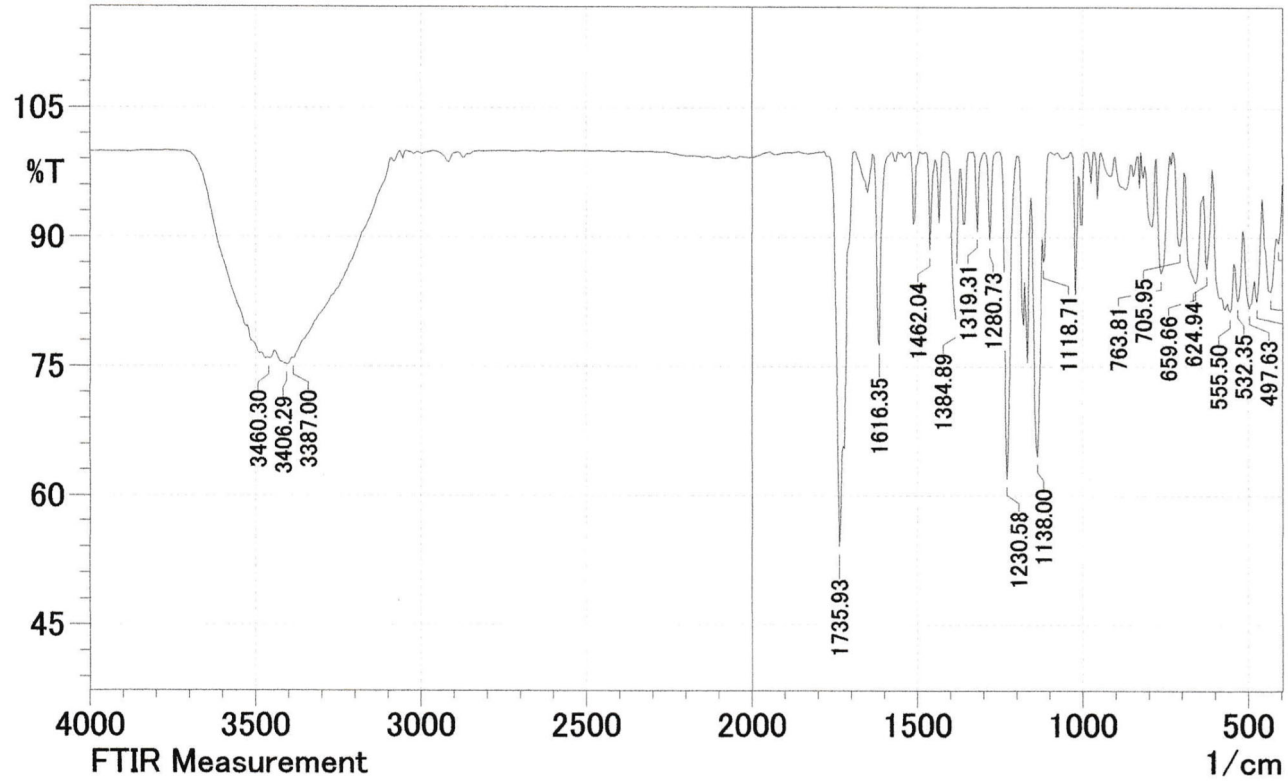
^{13}C NMR



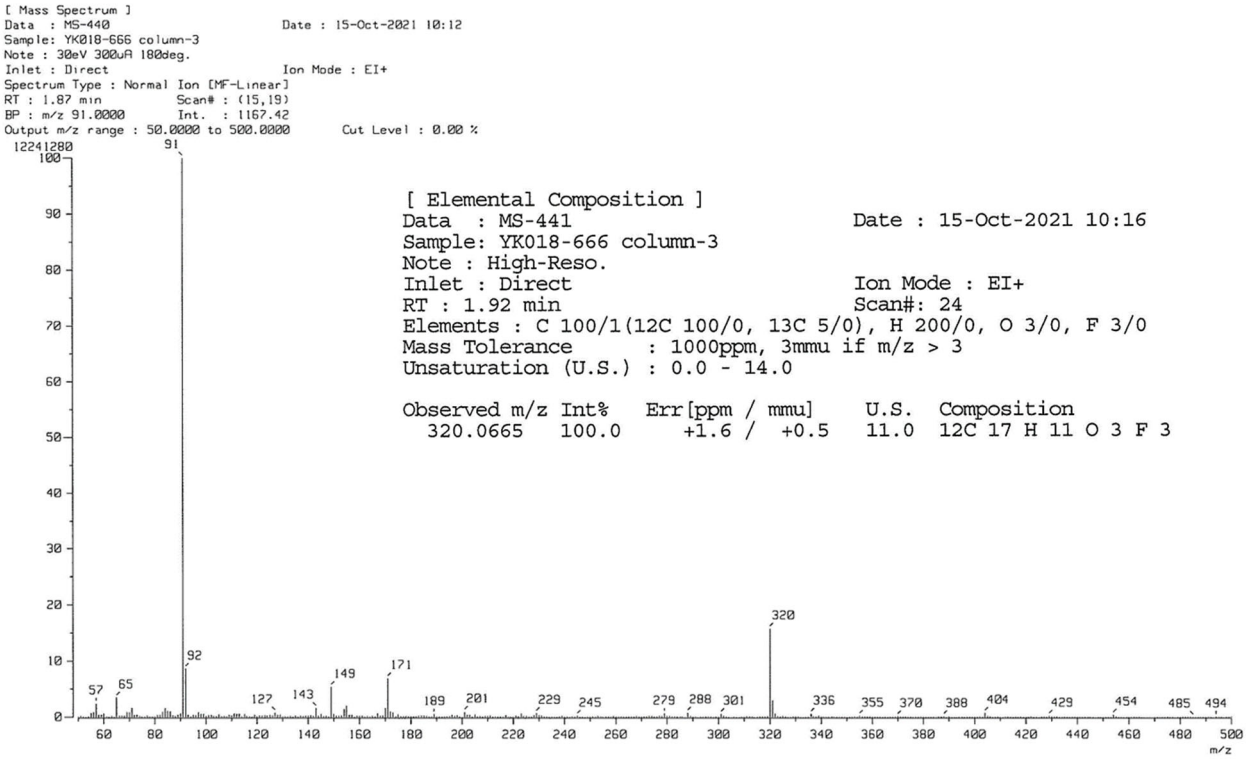
^{19}F NMR


3.00
-10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-65.604
ppm

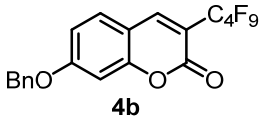
IR


105
%T
90
75
60
45
3460.30
3406.29
3387.00
1735.93
1616.35
1462.04
1384.89
1319.31
1280.73
1230.58
1138.00
1118.71
763.81
705.95
659.66
624.94
555.50
532.35
497.63
4000 3500 3000 2500 2000 1500 1000 500
FTIR Measurement
1/cm

HRMS

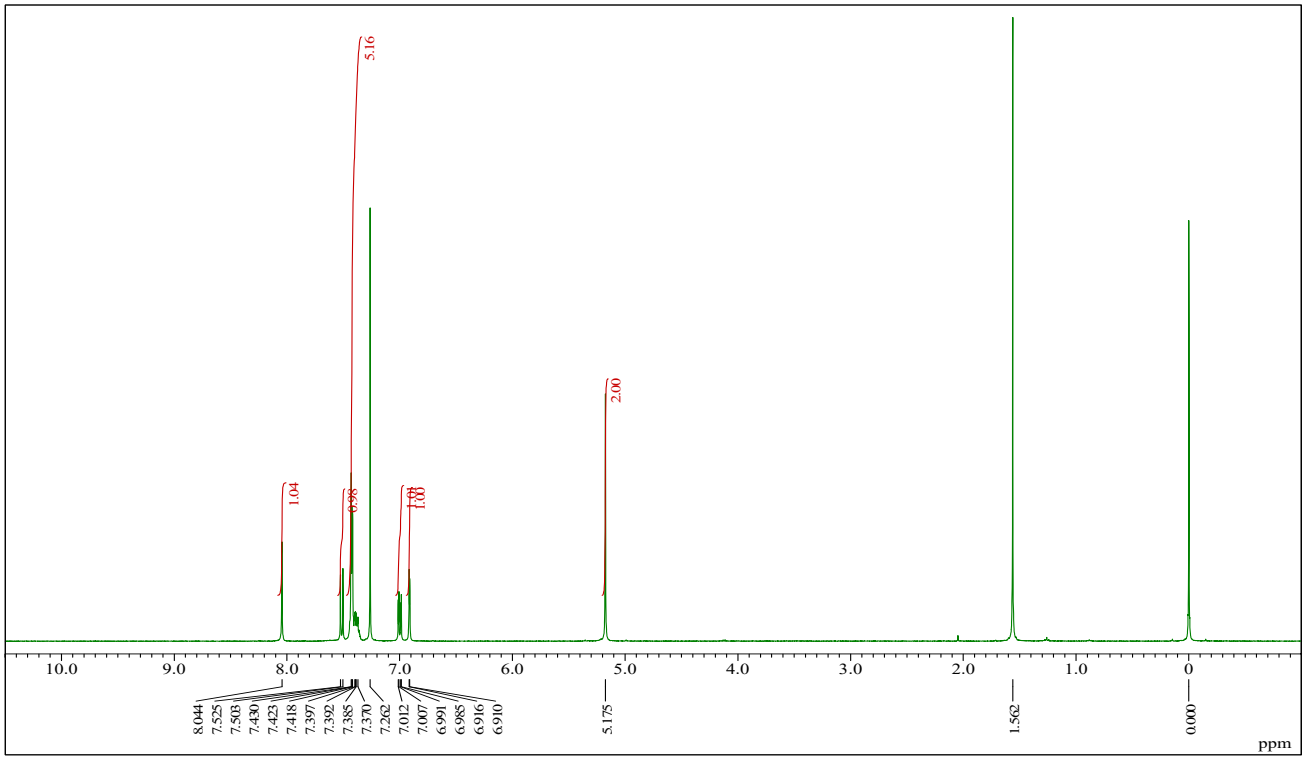

[Mass Spectrum]
Data : MS-440
Date : 15-Oct-2021 10:12
Sample: YK018-666 column-3
Note : 30eV 300uA 180deg.
Inlet : Direct
Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.87 min
Scan# : (15,19)
BP : m/z 91.0000
Int. : 1167.42
Output m/z range : 50.0000 to 500.0000
Cut Level : 0.00 %
[Elemental Composition]
Data : MS-441
Date : 15-Oct-2021 10:16
Sample: YK018-666 column-3
Note : High-Reso.
Inlet : Direct
Ion Mode : EI+
RT : 1.92 min
Scan#: 24
Elements : C 100/1(12C 100/0, 13C 5/0), H 200/0, O 3/0, F 3/0
Mass Tolerance : 1000ppm, 3mmu if m/z > 3
Unsaturation (U.S.) : 0.0 - 14.0
Observed m/z Int% Err[ppm / mmu] U.S. Composition
320.0665 100.0 +1.6 / +0.5 11.0 12C 17 H 11 O 3 F 3
m/z

7-benzyloxy-3-perfluorobutyl-2*H*-chromen-2-one (4b)

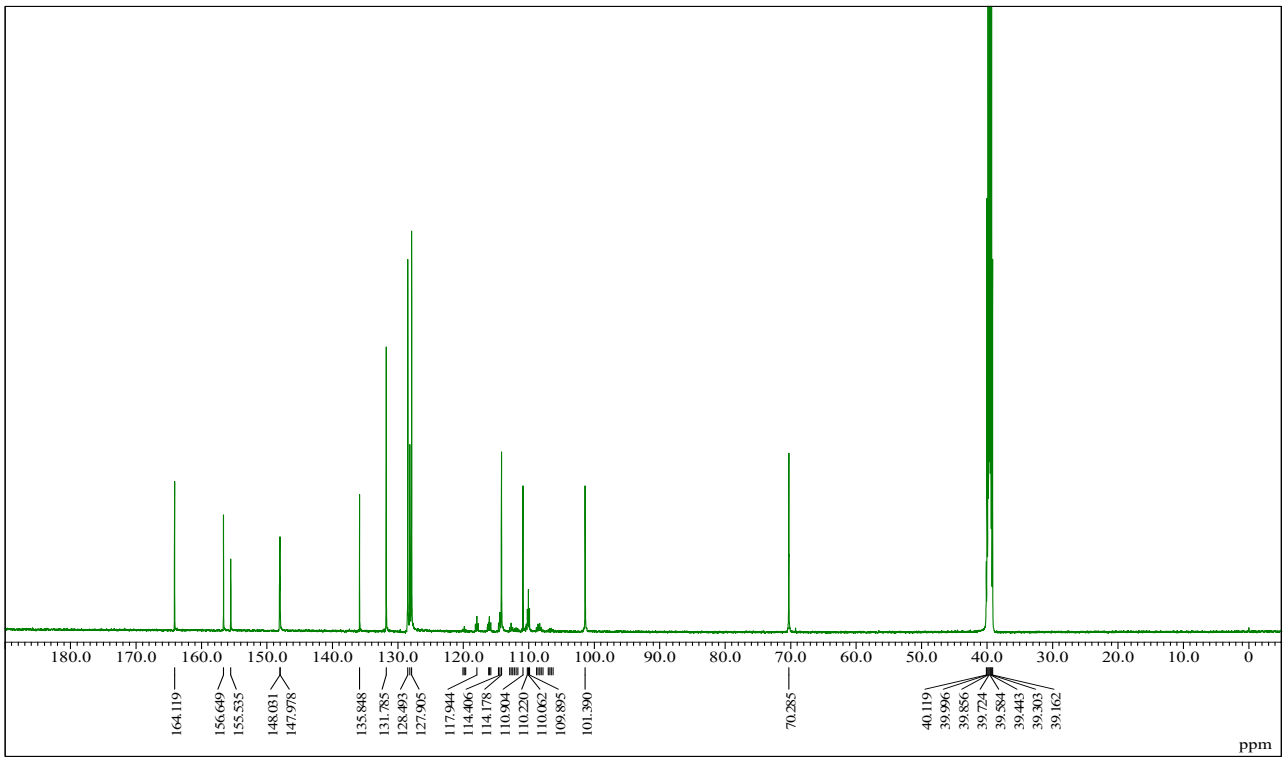


4b

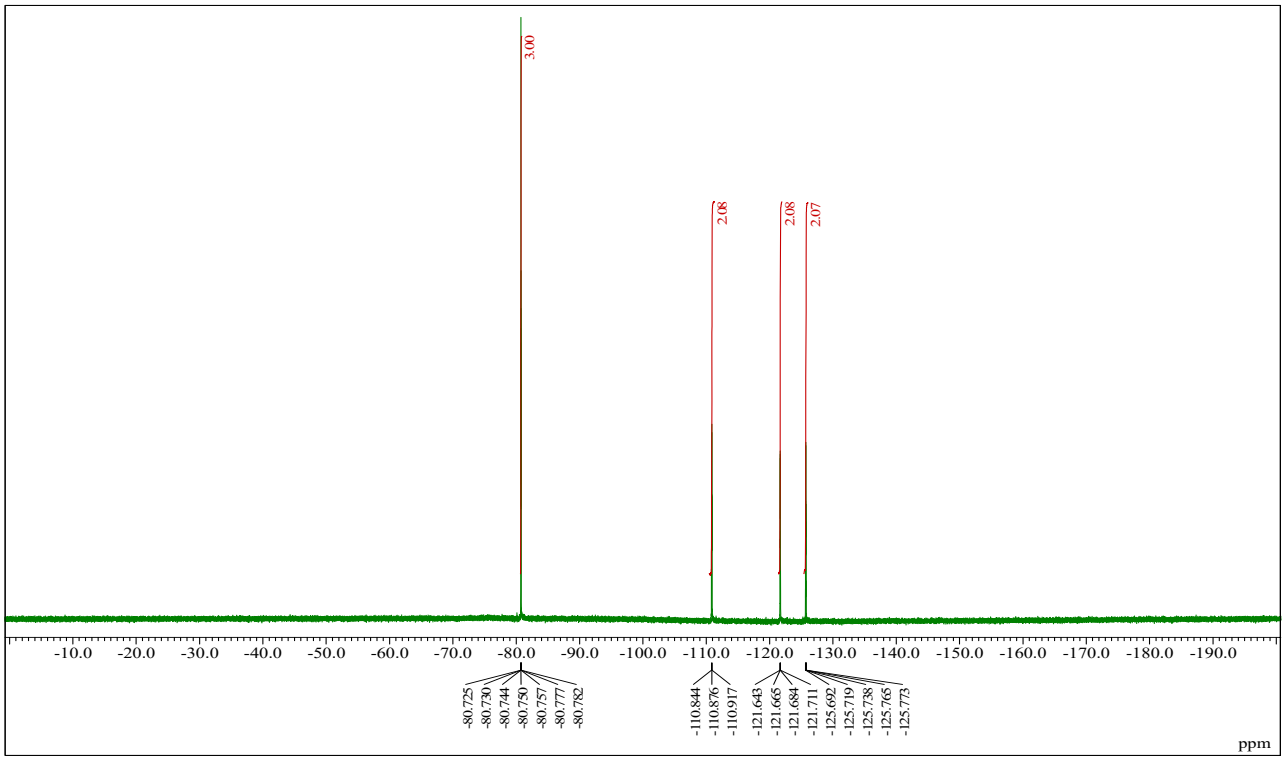
^{1}H NMR



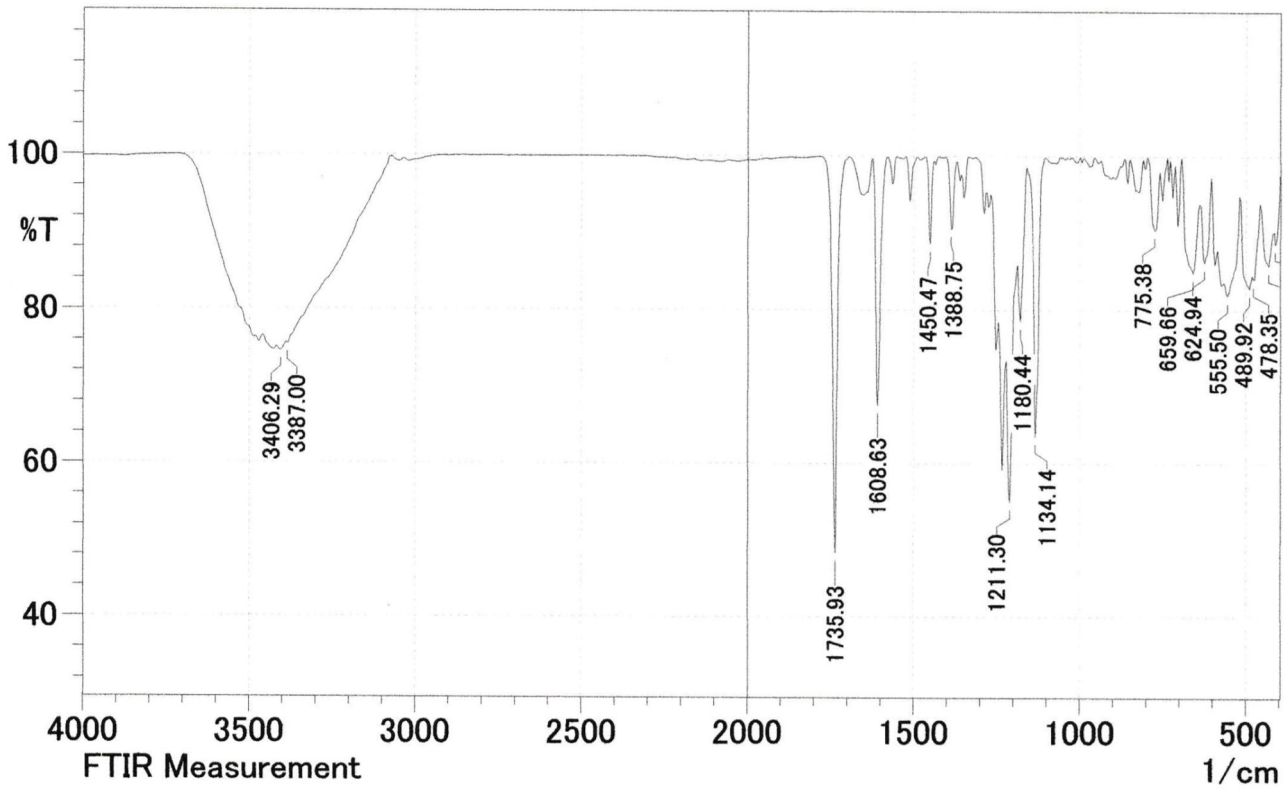
^{13}C NMR



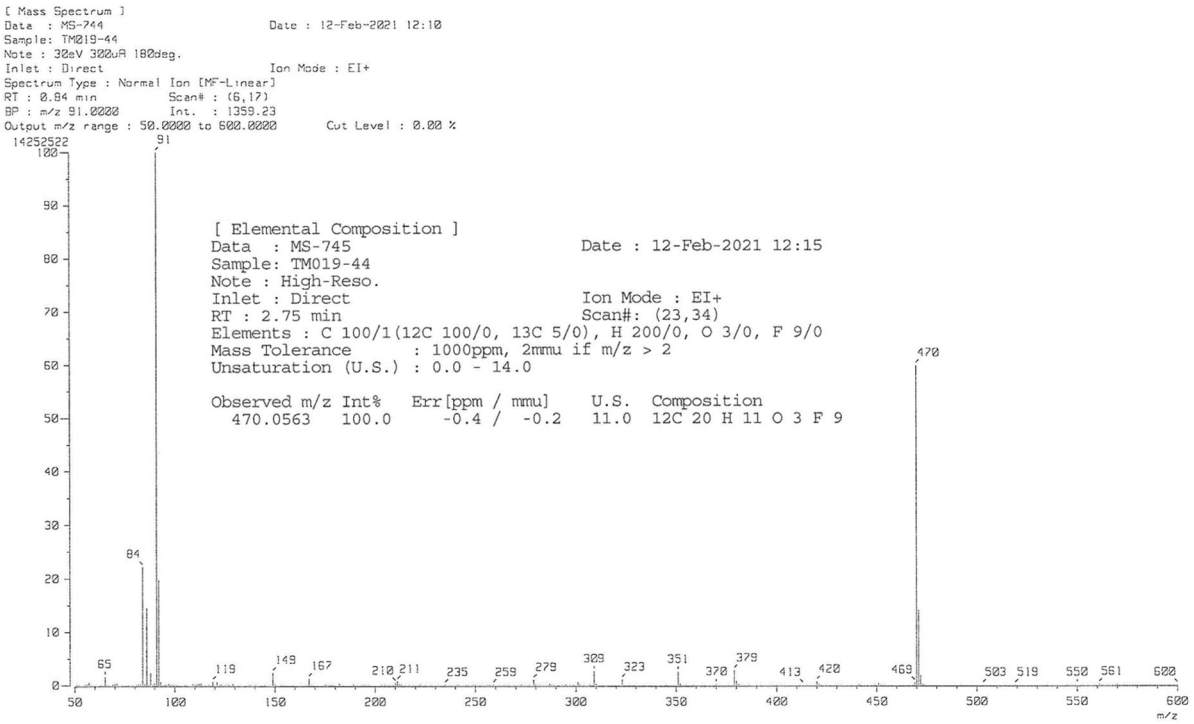
^{19}F NMR


3.00
2.06
2.08
2.07
-10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-80.725
-80.730
-80.744
-80.750
-80.757
-80.777
-80.782
-110.844
-110.876
-110.917
-121.643
-121.665
-121.684
-121.711
-125.692
-125.719
-125.738
-125.765
-125.773
ppm

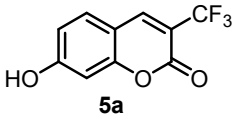
IR


100
%T
80
60
40
3406.29
3387.00
1735.93
1608.63
1450.47
1388.75
1211.30
1180.44
1134.14
775.38
659.66
624.94
555.50
489.92
478.35
4000 3500 3000 2500 2000 1500 1000 500
FTIR Measurement
1/cm

HRMS

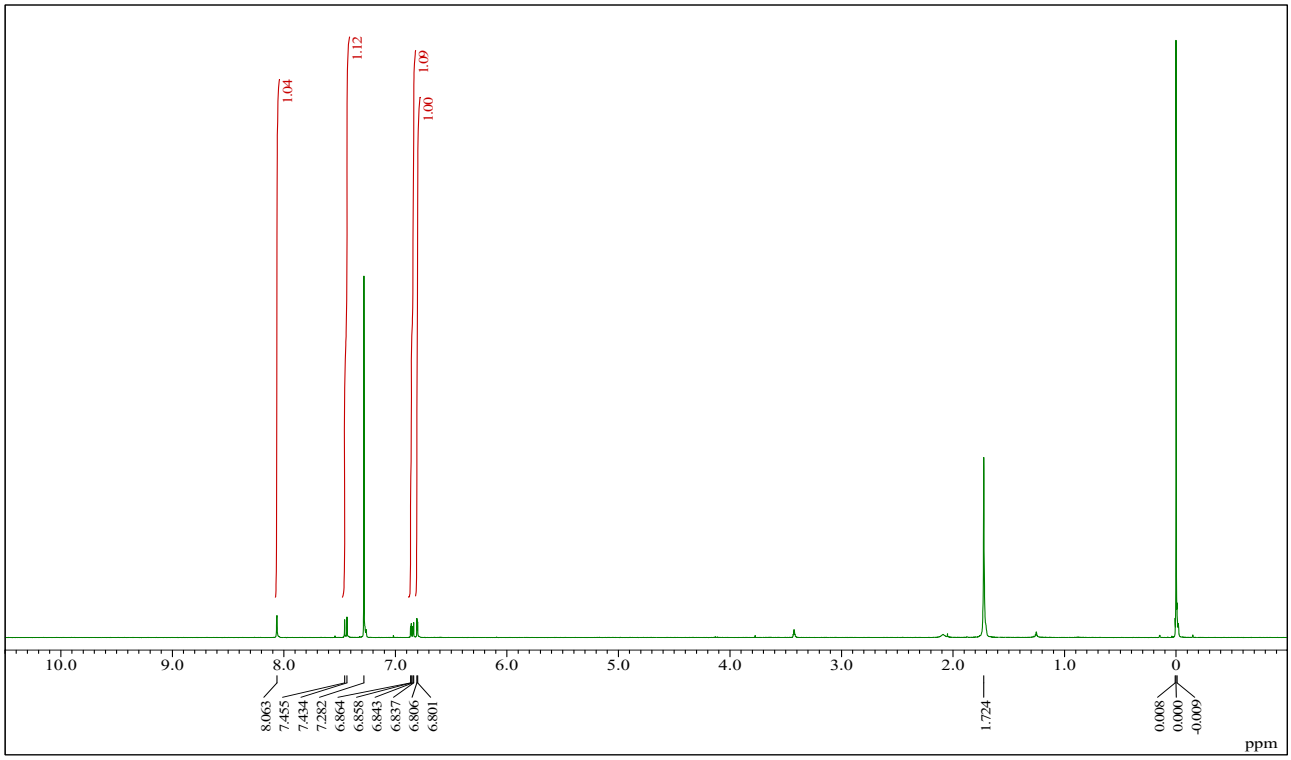

[Mass Spectrum]
Data : MS-744
Date : 12-Feb-2021 12:10
Sample: TM019-44
Note : 30eV 300uA 180deg.
Inlet : Direct
Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.84 min
Scan# : (6,17)
BP : m/z 91.0000
Int. : 1359.23
Output m/z range : 50.0000 to 600.0000
Cut Level : 0.00 %
14252522
[Elemental Composition]
Data : MS-745
Date : 12-Feb-2021 12:15
Sample: TM019-44
Note : High-Reso.
Inlet : Direct
Ion Mode : EI+
RT : 2.75 min
Scan#: (23,34)
Elements : C 100/1(12C 100/0, 13C 5/0), H 200/0, O 3/0, F 9/0
Mass Tolerance : 1000ppm, 2mmu if m/z > 2
Unsaturation (U.S.) : 0.0 - 14.0
Observed m/z Int% Err[ppm / mmu] U.S. Composition
470.0563 100.0 -0.4 / -0.2 11.0 12C 20 H 11 O 3 F 9
m/z

7-hydroxy-3-trifluoromethyl-2*H*-chromen-2-one (5a)

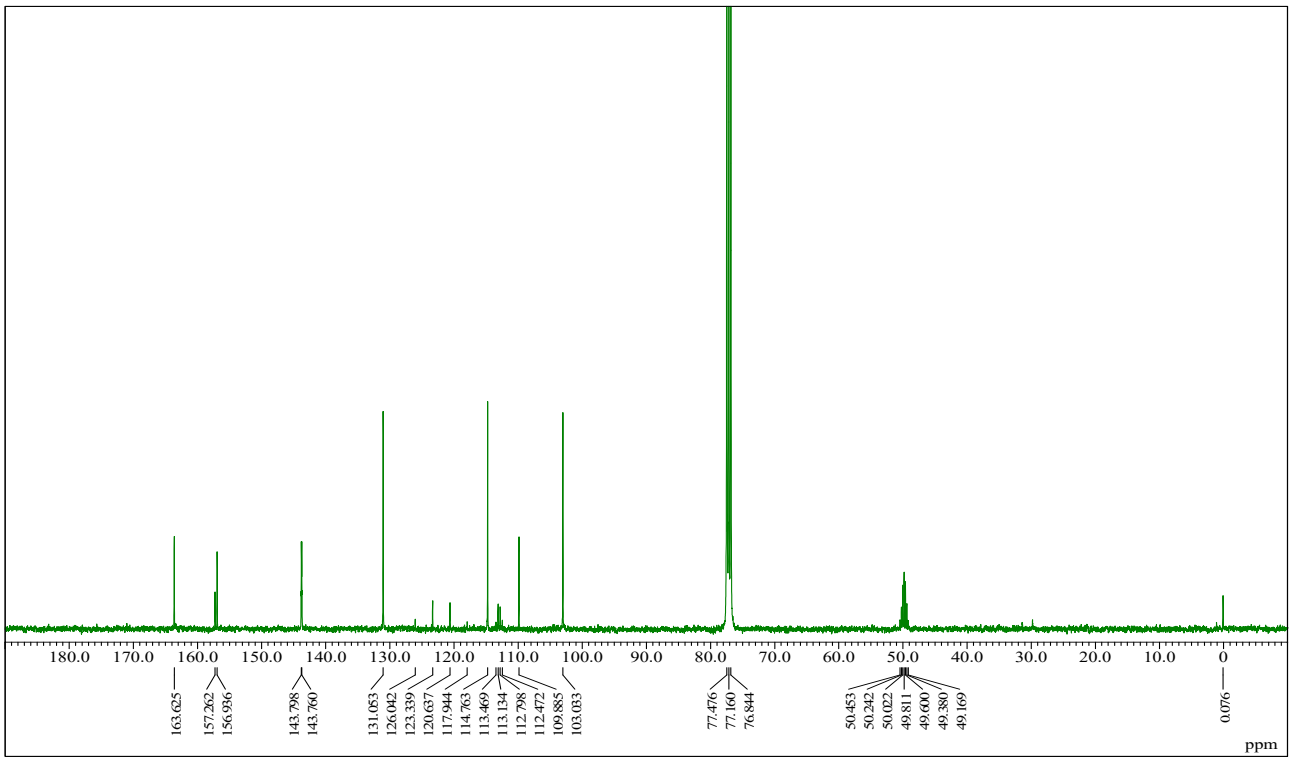


5a

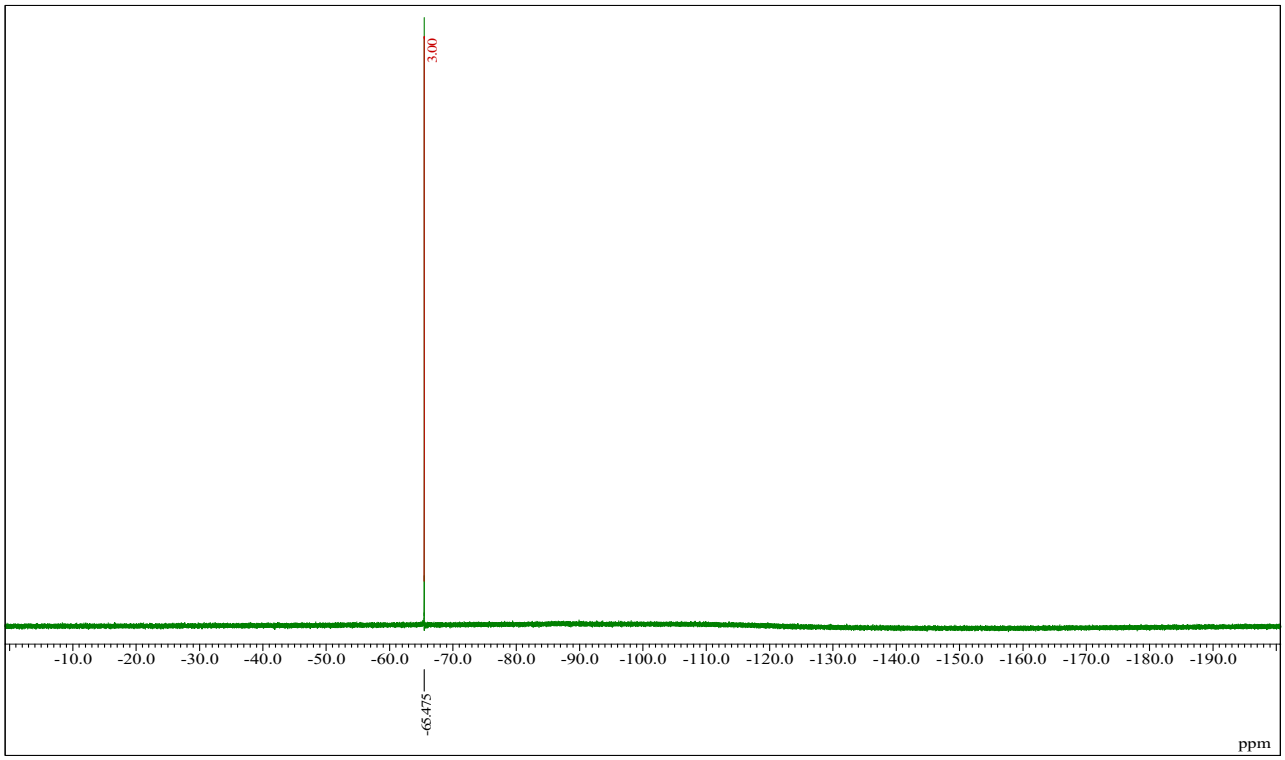
^{1}H NMR



^{13}C NMR



^{19}F NMR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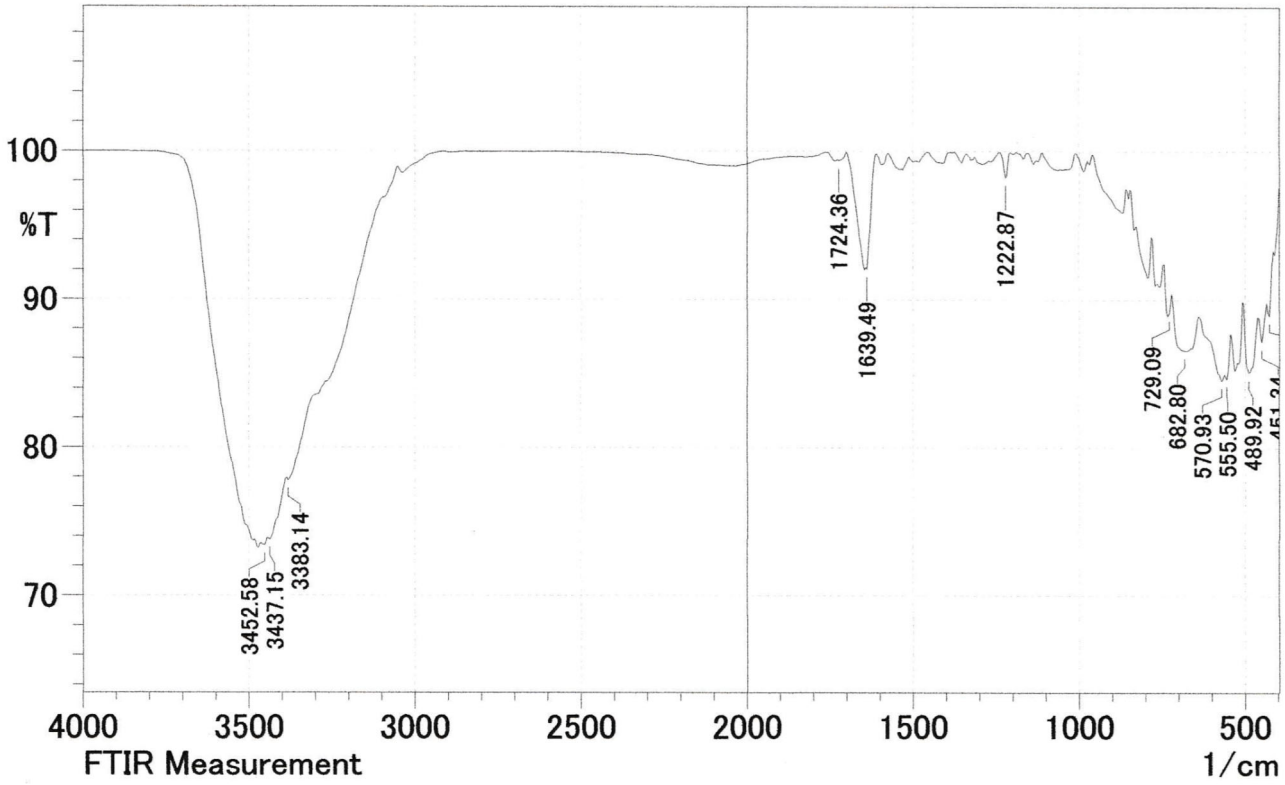
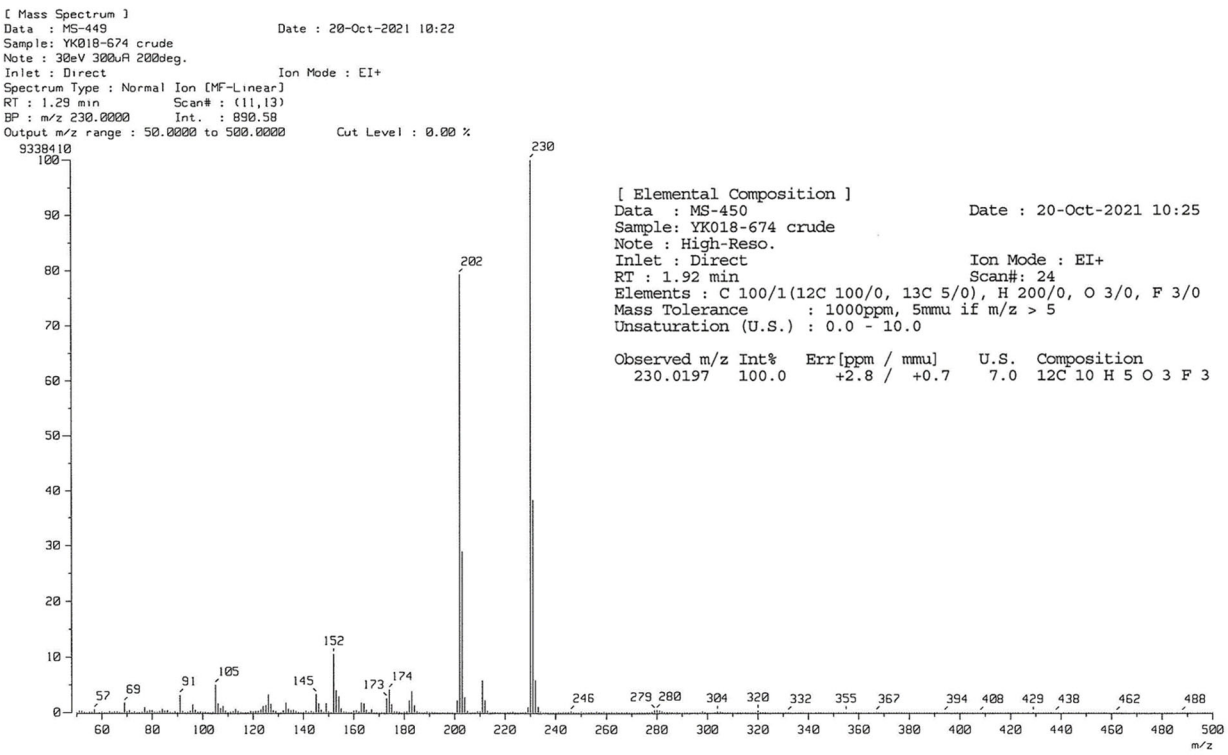
-65.475
ppm

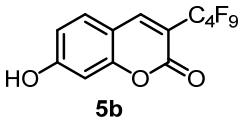
IR


100
%T
90
80
70
3452.58
3437.15
3383.14
1724.36
1639.49
1222.87
729.09
682.80
570.93
555.50
489.92
4000 3500 3000 2500 2000 1500 1000 500
FTIR Measurement
1/cm

HRMS

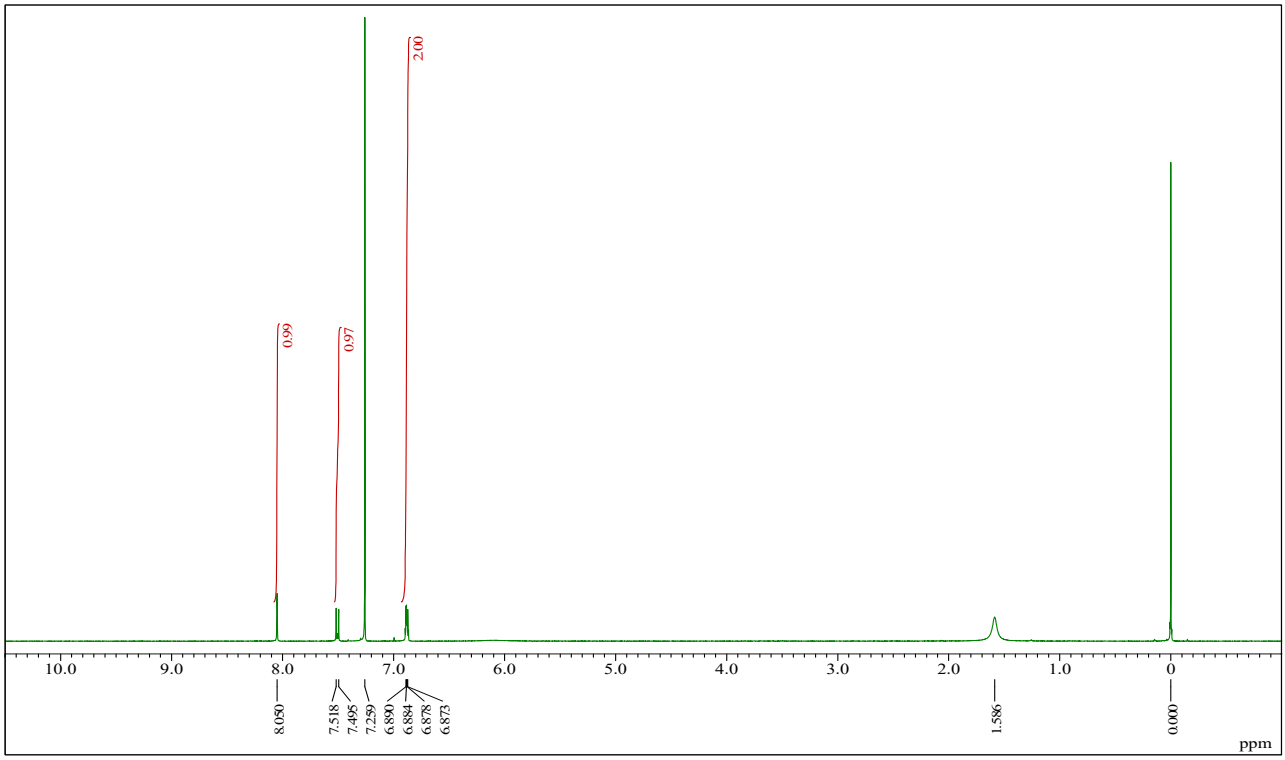

[Mass Spectrum]
Data : MS-449
Date : 20-Oct-2021 10:22
Sample: YK018-674 crude
Note : 30eV 300uA 200deg.
Inlet : Direct
Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.29 min
Scan# : (11,13)
BP : m/z 230.0000
Int. : 890.58
Output m/z range : 50.0000 to 500.0000
Cut Level : 0.00 %
9338410
[Elemental Composition]
Data : MS-450
Date : 20-Oct-2021 10:25
Sample: YK018-674 crude
Note : High-Reso.
Inlet : Direct
Ion Mode : EI+
RT : 1.92 min
Scan#: 24
Elements : C 100/1(12C 100/0, 13C 5/0), H 200/0, O 3/0, F 3/0
Mass Tolerance : 1000ppm, 5mmu if m/z > 5
Unsaturation (U.S.) : 0.0 - 10.0
Observed m/z Int% Err[ppm / mmu] U.S. Composition
230.0197 100.0 +2.8 / +0.7 7.0 12C 10 H 5 O 3 F 3
m/z

7-hydroxy-3-perfluorobutyl-2*H*-chromen-2-one (5b)

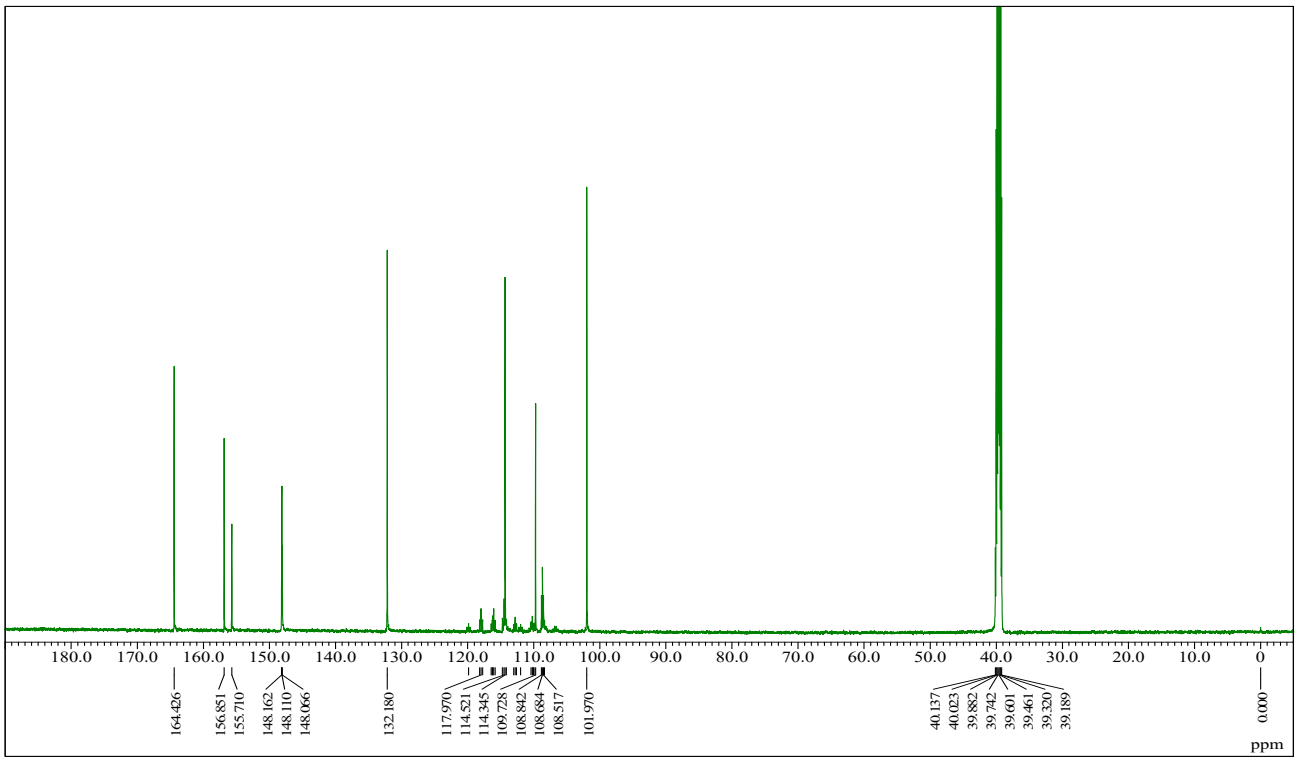


5b

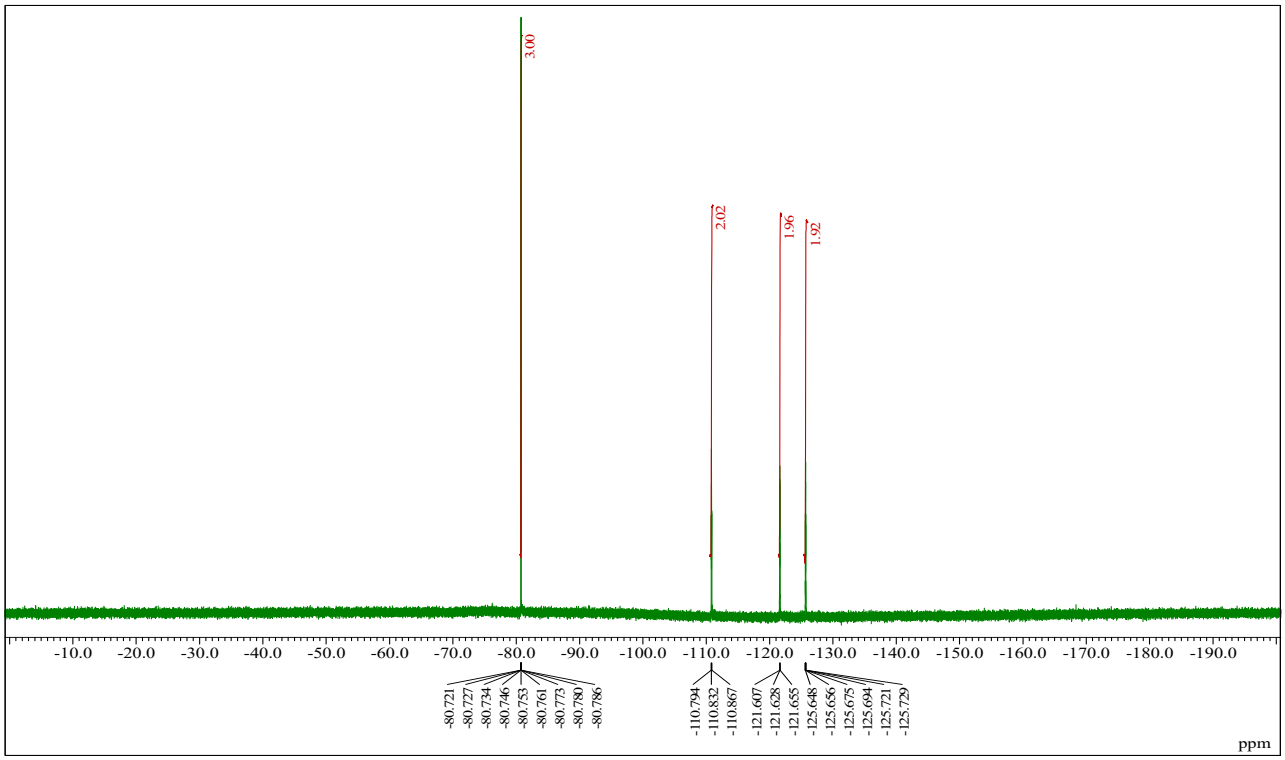
^{1}H NMR



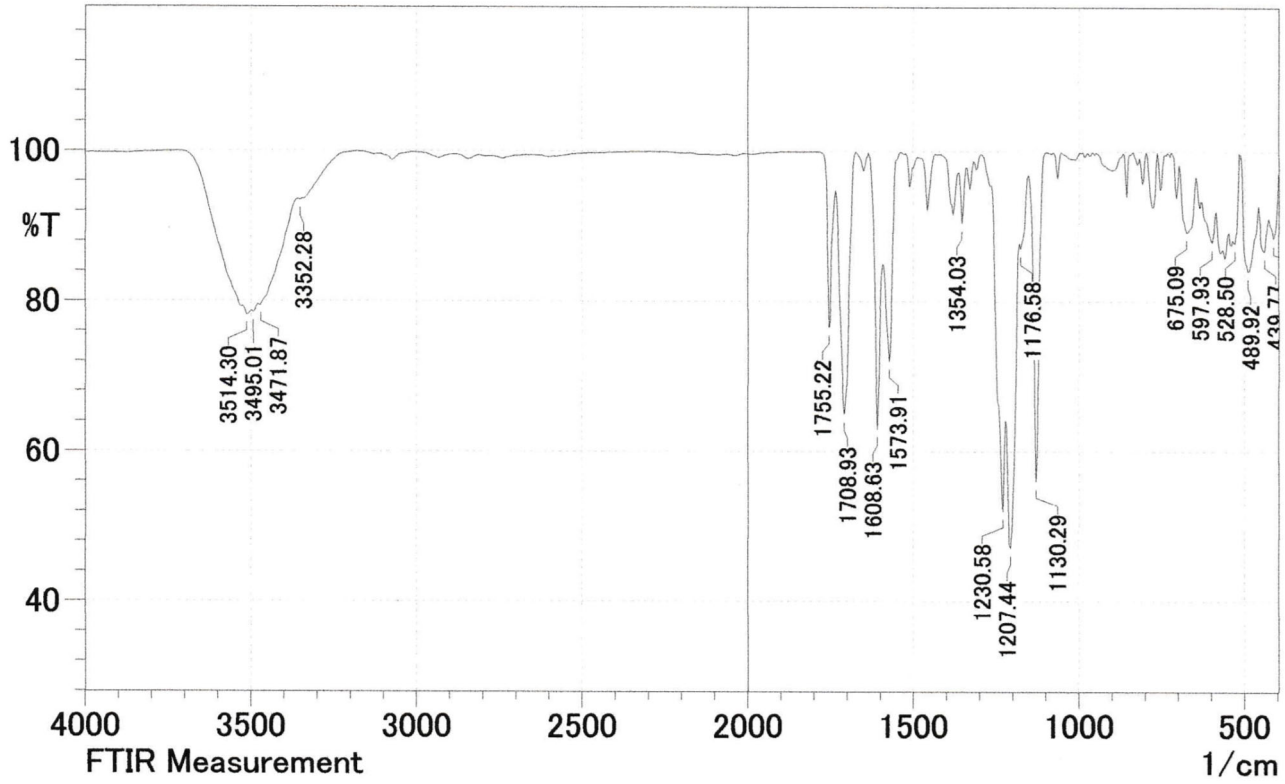
^{13}C NMR



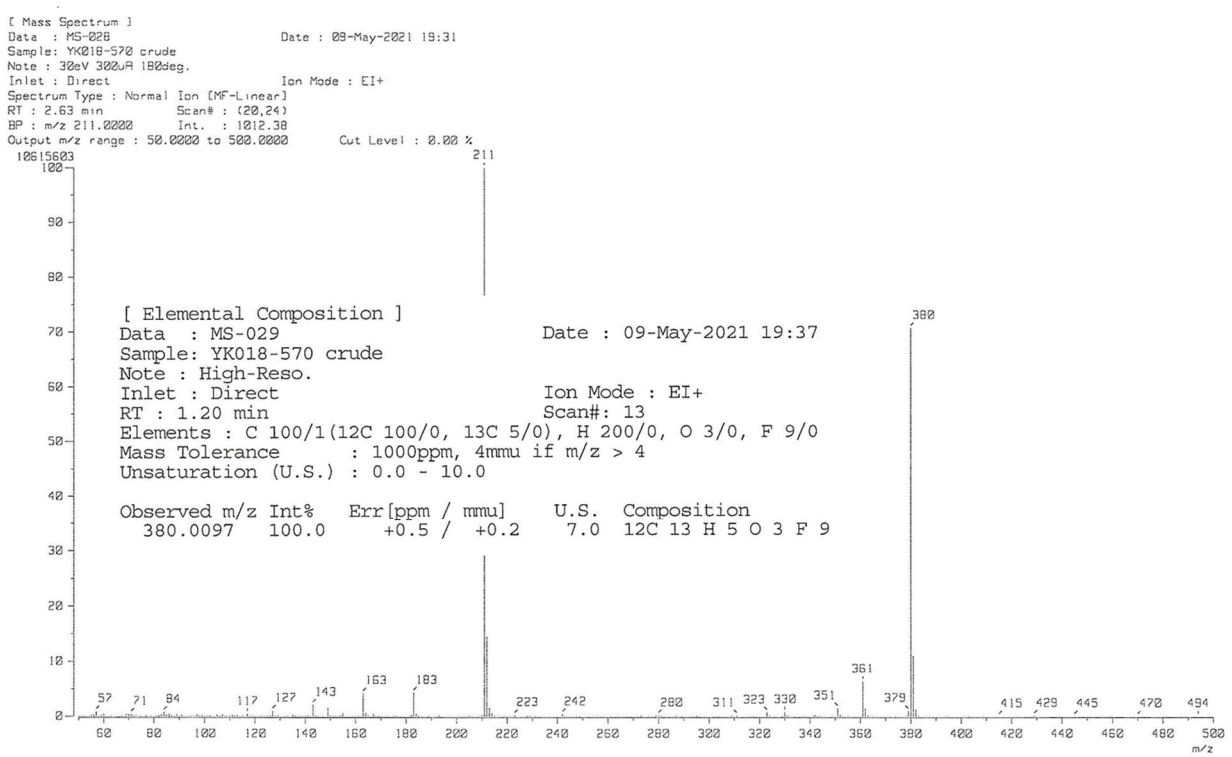
^{19}F NMR


3.00
2.02
1.96
1.92
-10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-80.721 -80.727 -80.734 -80.746 -80.753 -80.761 -80.773 -80.780 -80.786
-110.794 -110.832 -110.867
-121.607 -121.628 -121.655
-125.648 -125.656 -125.675 -125.694 -125.721 -125.729
ppm

IR

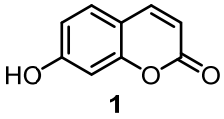

100
%T
80
60
40
3514.30
3495.01
3471.87
3352.28
1755.22
1708.93
1608.63
1573.91
1354.03
1230.58
1207.44
1176.58
1130.29
675.09
597.93
528.50
489.92
4000 3500 3000 2500 2000 1500 1000 500
FTIR Measurement
1/cm

HRMS


[Mass Spectrum]
Data : MS-028 Date : 09-May-2021 19:31
Sample: YK018-570 crude
Note : 30eV 300uA 180deg.
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 2.63 min Scan# : (20,24)
BP : m/z 211.0000 Int. : 1012.38
Output m/z range : 50.0000 to 500.0000 Cut Level : 0.00 %
10615603
[Elemental Composition]
Data : MS-029 Date : 09-May-2021 19:37
Sample: YK018-570 crude
Note : High-Reso.
Inlet : Direct Ion Mode : EI+
RT : 1.20 min Scan#: 13
Elements : C 100/1(12C 100/0, 13C 5/0), H 200/0, O 3/0, F 9/0
Mass Tolerance : 1000ppm, 4mmu if m/z > 4
Unsaturation (U.S.) : 0.0 - 10.0
Observed m/z Int% Err[ppm / mmu] U.S. Composition
380.0097 100.0 +0.5 / +0.2 7.0 12C 13 H 5 O 3 F 9
211
380
361
183
163
143
127
117
84
71
57
223
242
280
311
323
330
351
379
415
429
445
470
494
m/z

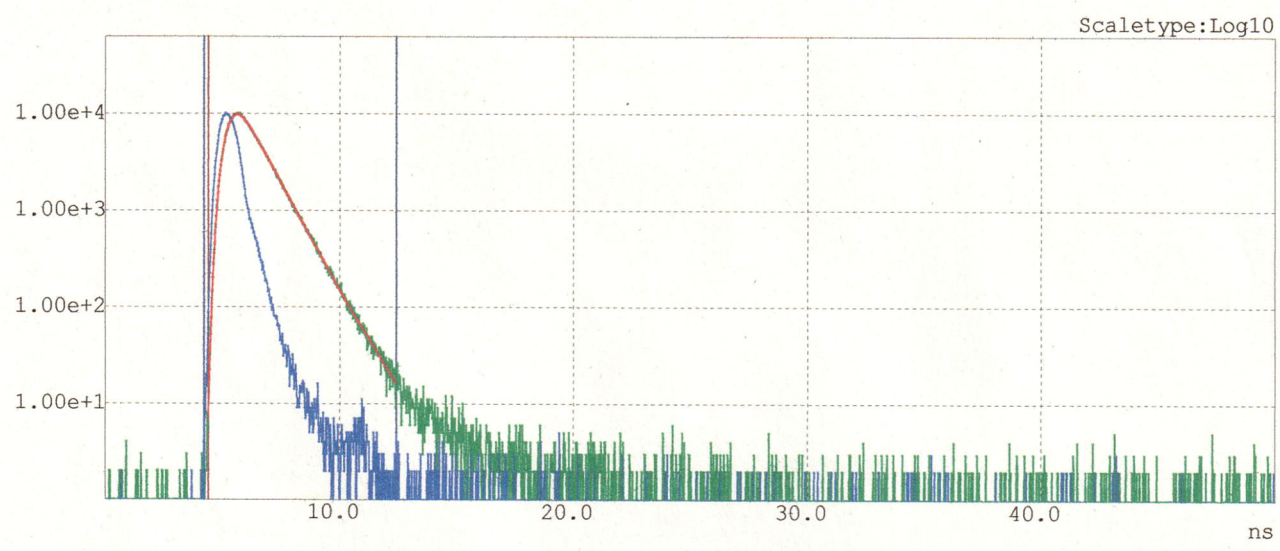
Fluorescence decay curves

7-hydroxy-2*H*-chromen-2-one (1)

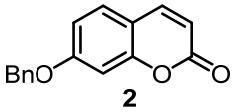


1

MeOH solution (5×10^{-5} M)

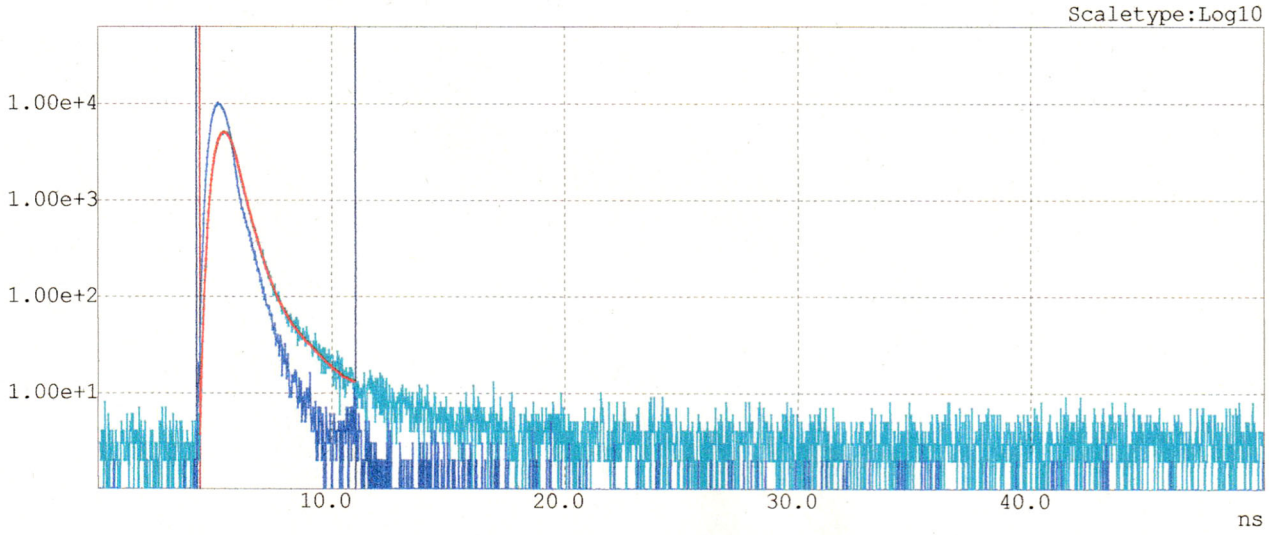


7-benzyloxy-2*H*-chromen-2-one (2)

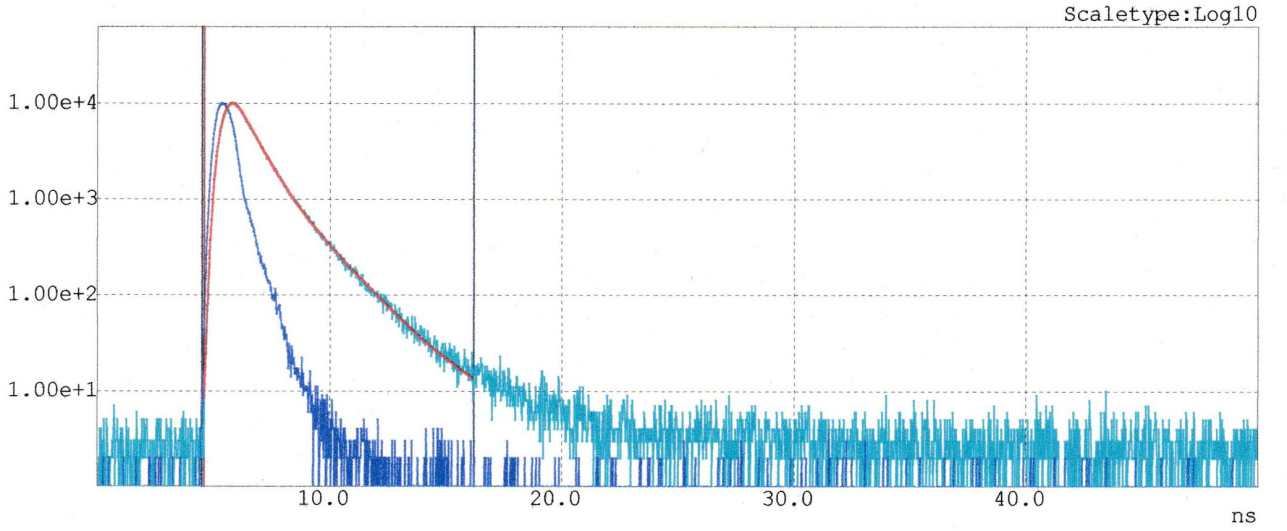


2

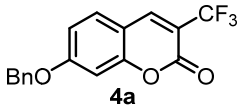
MeOH solution (5×10^{-5} M)



Crystalline state

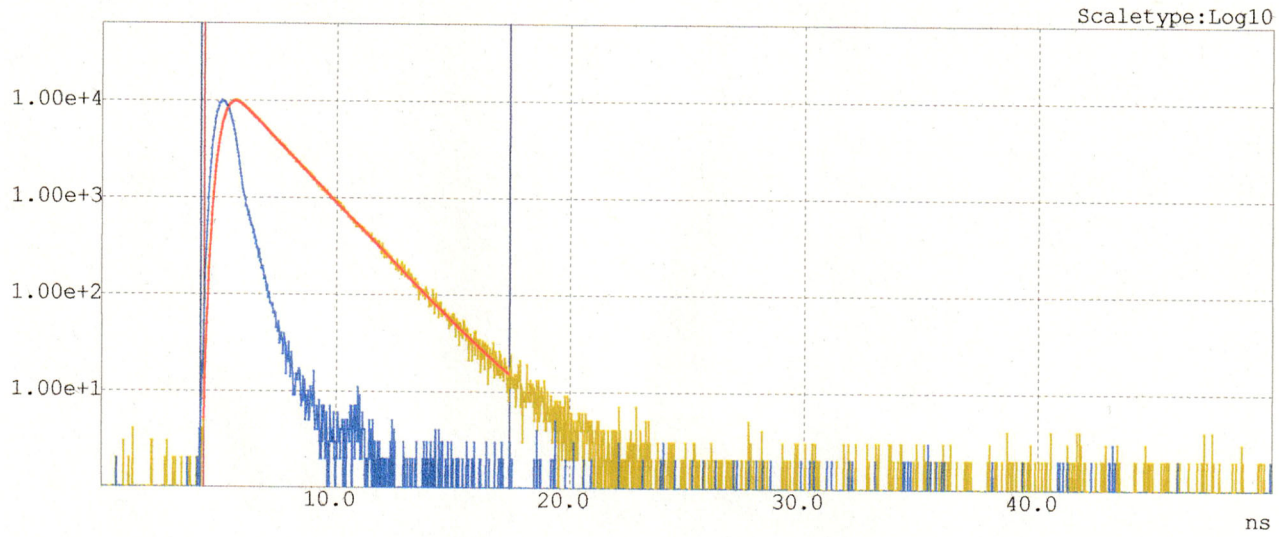


7-benzyloxy-3-trifluoromethyl-2*H*-chromen-2-one (4a)

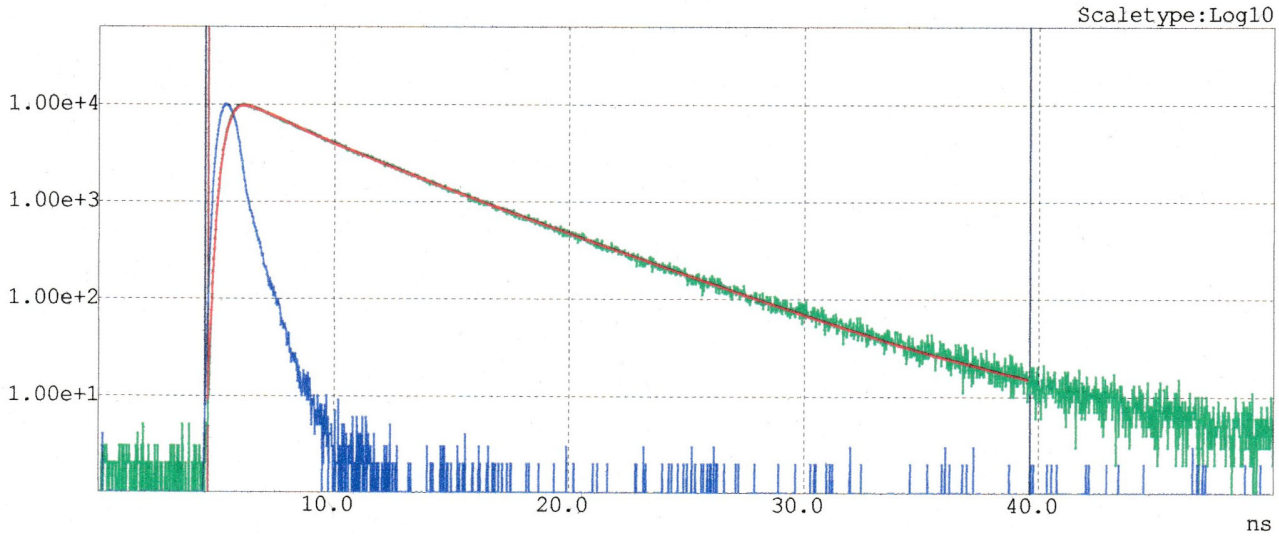


4a

MeOH solution (5×10^{-5} M)



Crystalline state



Name	EMML	CHI	Meas. Time	<τ>	Tau1	Tau2	A1	A2	Background
4 4a	414	1.14316	53.9	4.43105	2.13194	5.01829	128.091	213.049	4

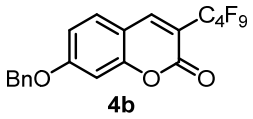
For two-component systems, A_1 and A_2 are constants representing the mixing ratio of each component.
τ is expressed by the following formula
$\langle\boldsymbol{\tau}\rangle = (\text{Tau1} \times A_1) + (\text{Tau2} \times A_2)$
In **4a**, Tau1 is the monomer fluorescence and Tau2 is the dimer fluorescence.
Therefore, the ratio of each component can be calculated as follows.

$$Ratio\ of\ monomers\ present = \frac{A_1}{A_1 + A_2} = \frac{128.091}{128.091 + 213.049} = 38\ \%$$

$$Ratio\ of\ dimer\ present = \frac{A_2}{A_1 + A_2} = \frac{213.049}{128.091 + 213.049} = 62\ \%$$

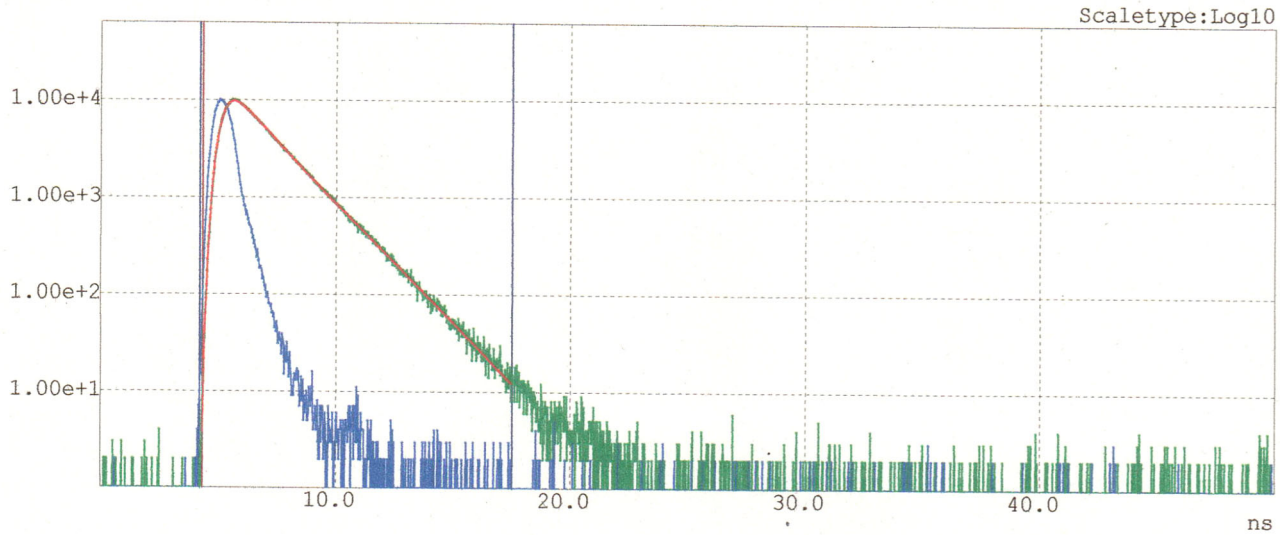
Reference: S. Fukushima, T. Yasui, T. Iwata, T. Araki, *Trans. Jpn. Soc. Med. Biol. Eng.*, **2006**, *44*, 702-706 (https://doi.org/10.11239/jsmbe.44.702).

7-benzyloxy-3-perfluorobutyl-2*H*-chromen-2-one (4b)

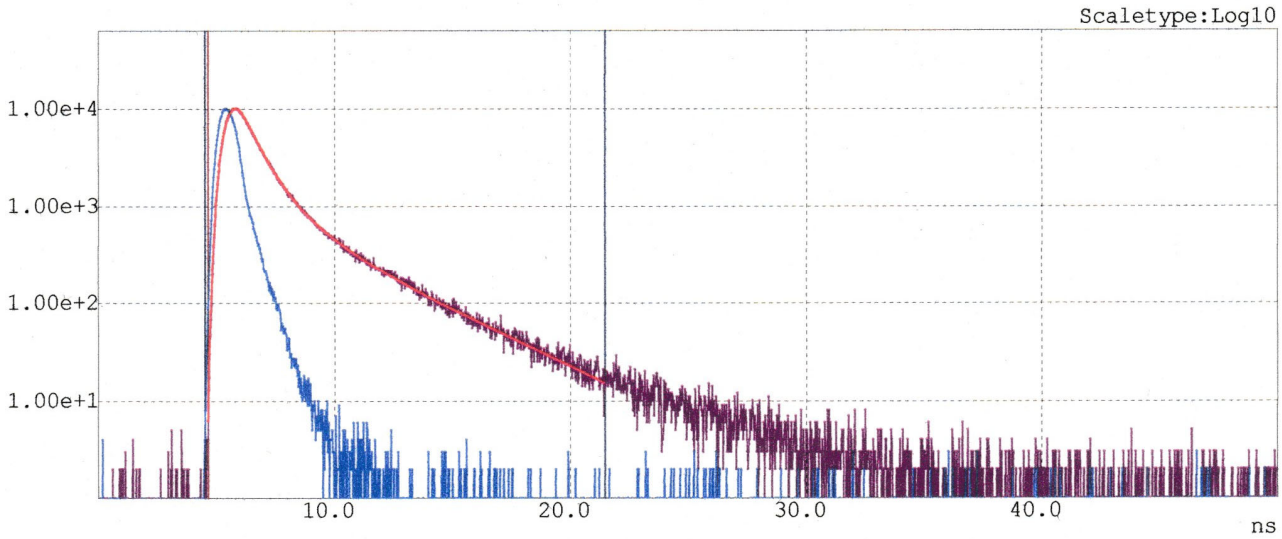


4b

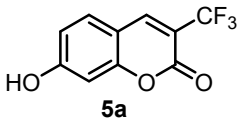
MeOH solution (5×10^{-5} M)



Crystalline state

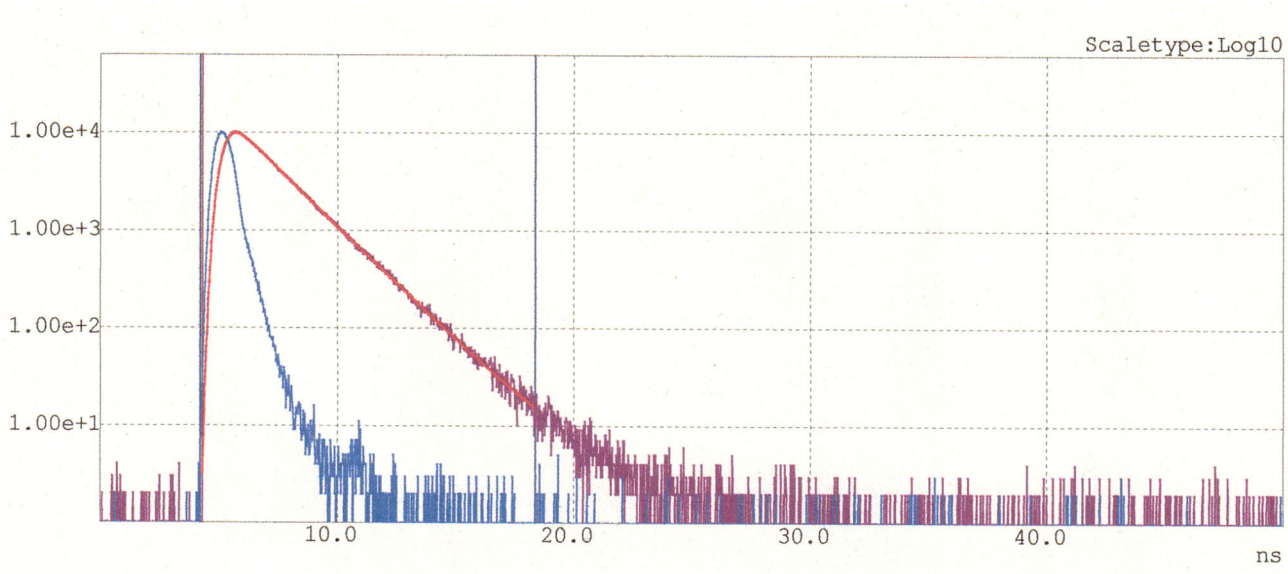


7-hydroxy-3-trifluoromethyl-2*H*-chromen-2-one (5a)

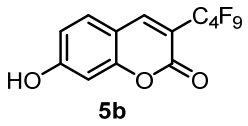


5a

MeOH solution (5×10^{-5} M)

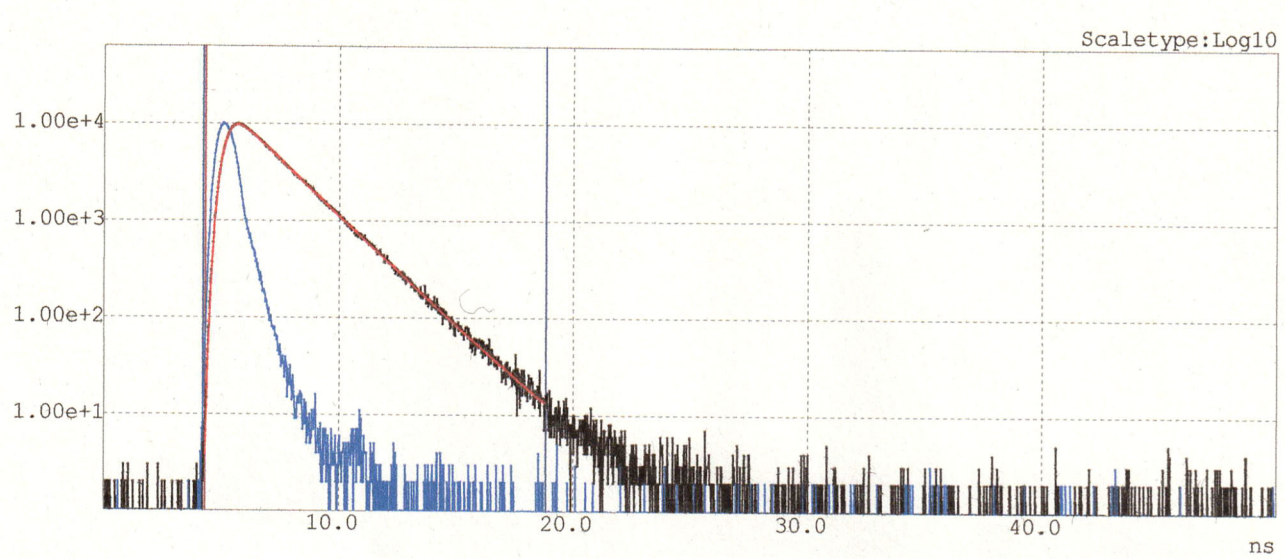


7-hydroxy-3-perfluorobutyl-2*H*-chromen-2-one (5b)

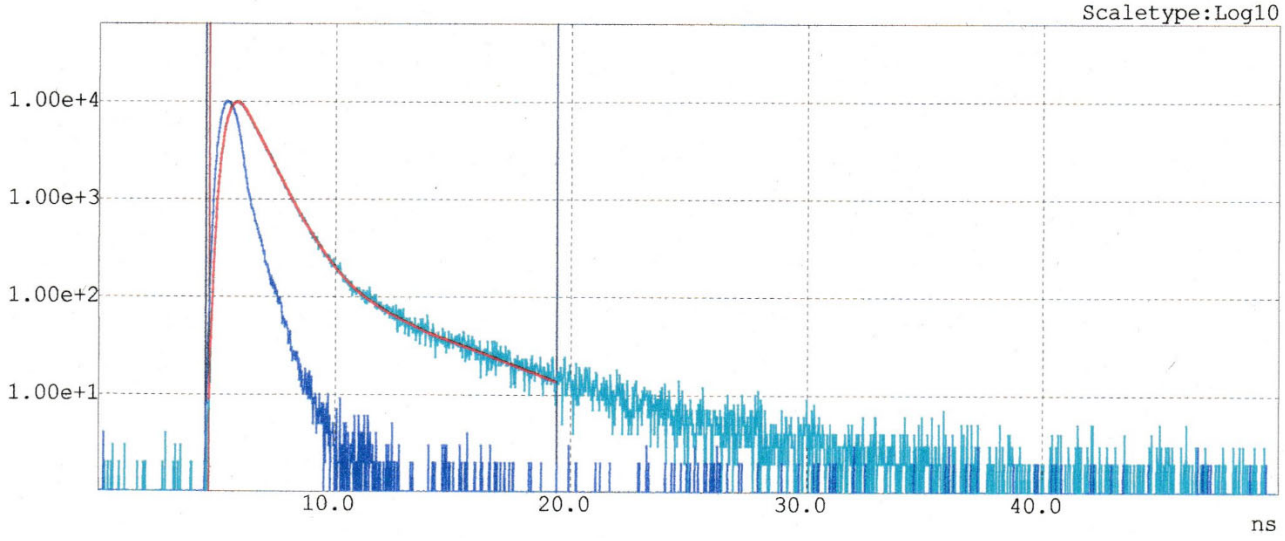


5b

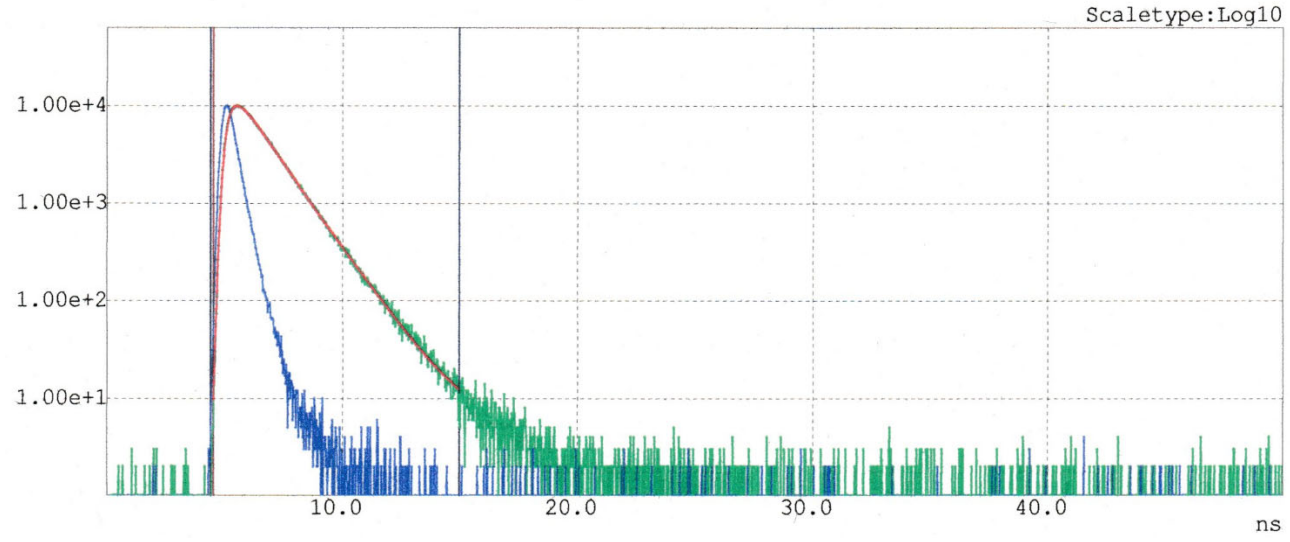
MeOH solution (5×10^{-5} M)



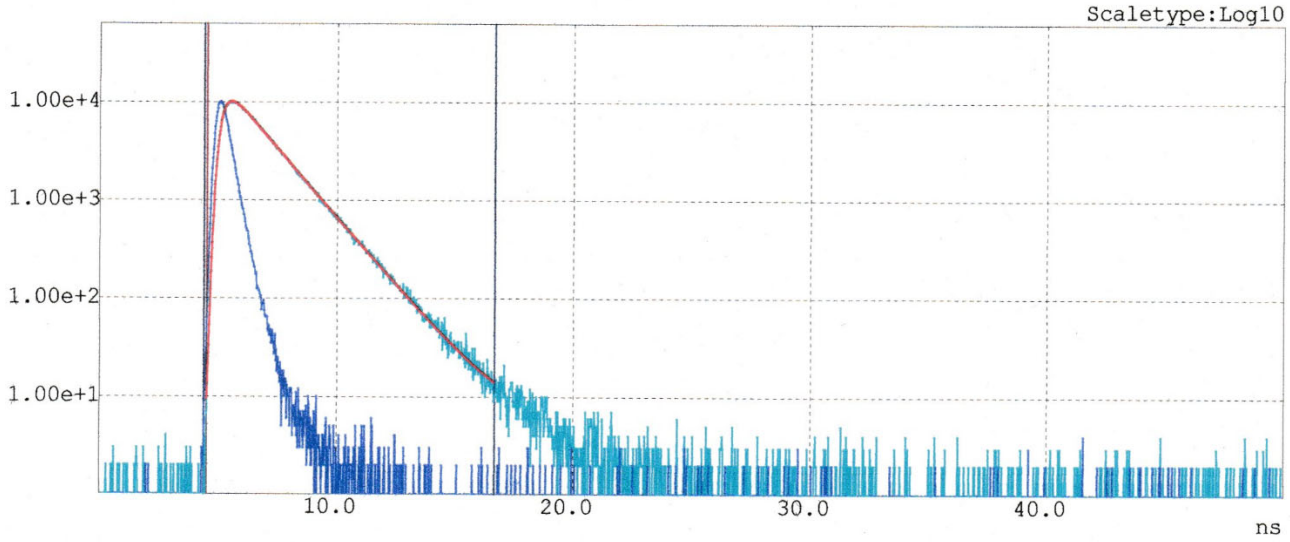
Crystalline state



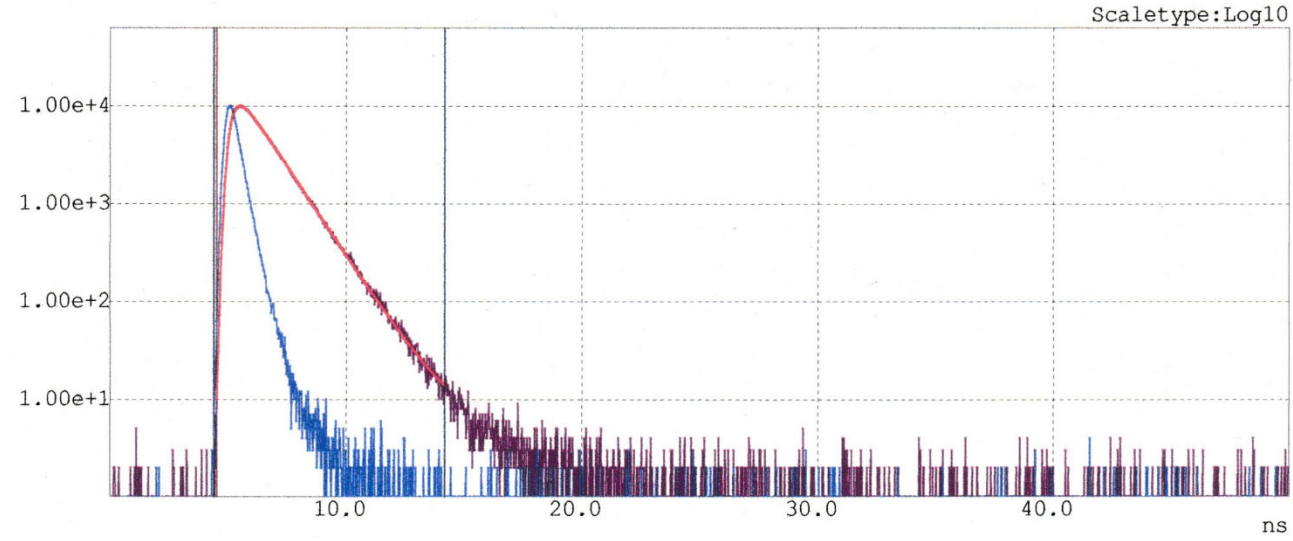
Acetone solution (5×10^{-5} M)



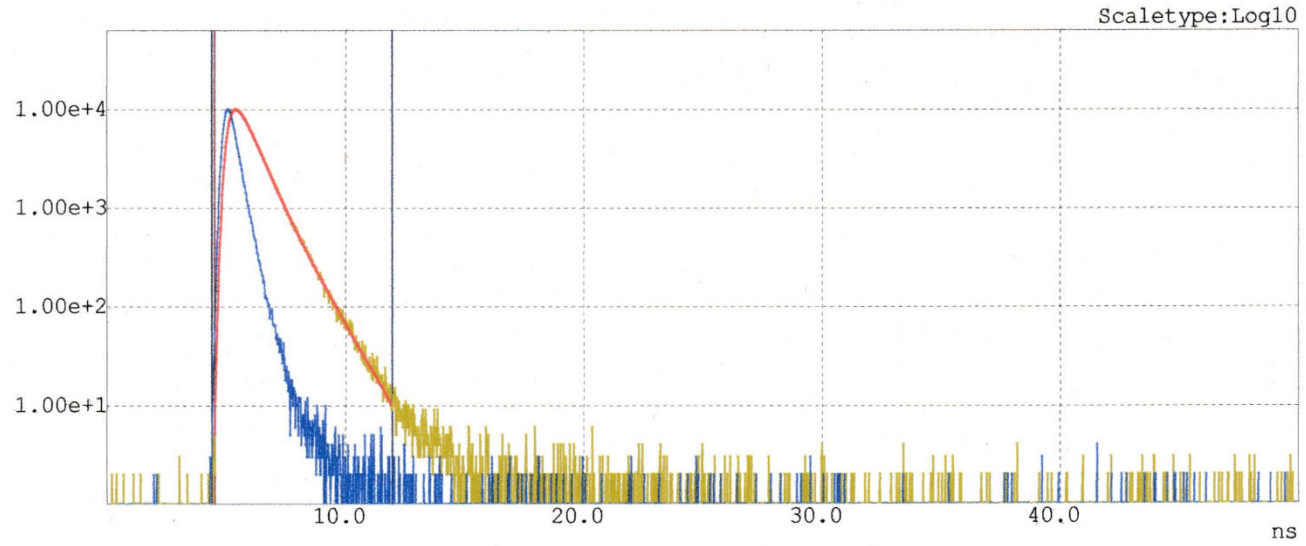
Chloroform solution (5×10^{-5} M)



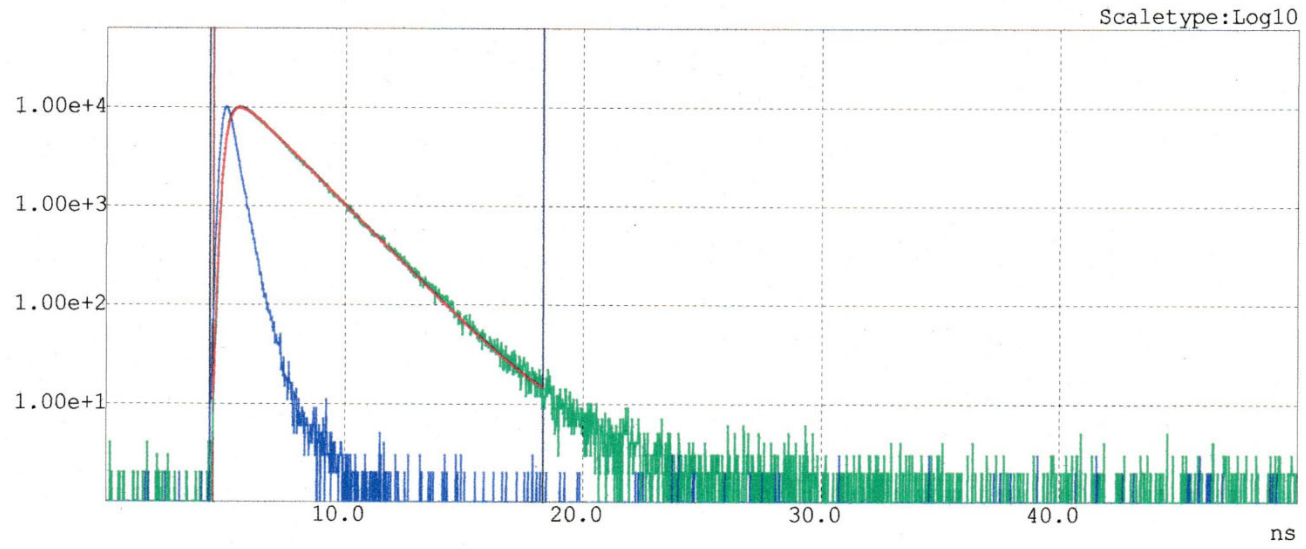
THF (tetrahydrofuran) solution (5×10^{-5} M)



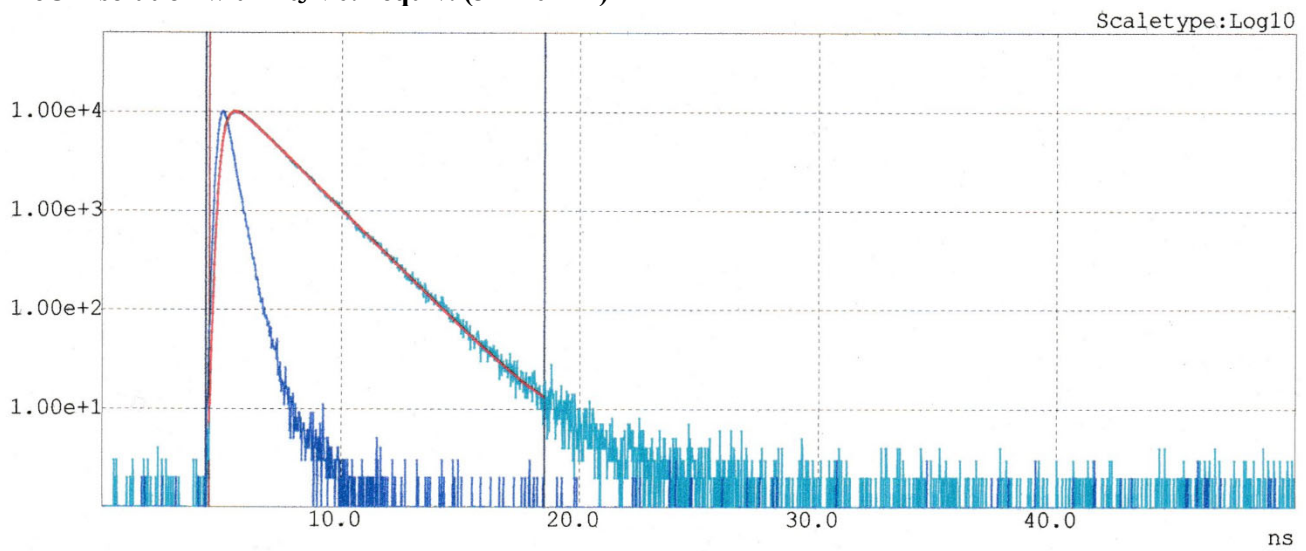
Toluene solution (5×10^{-5} M)



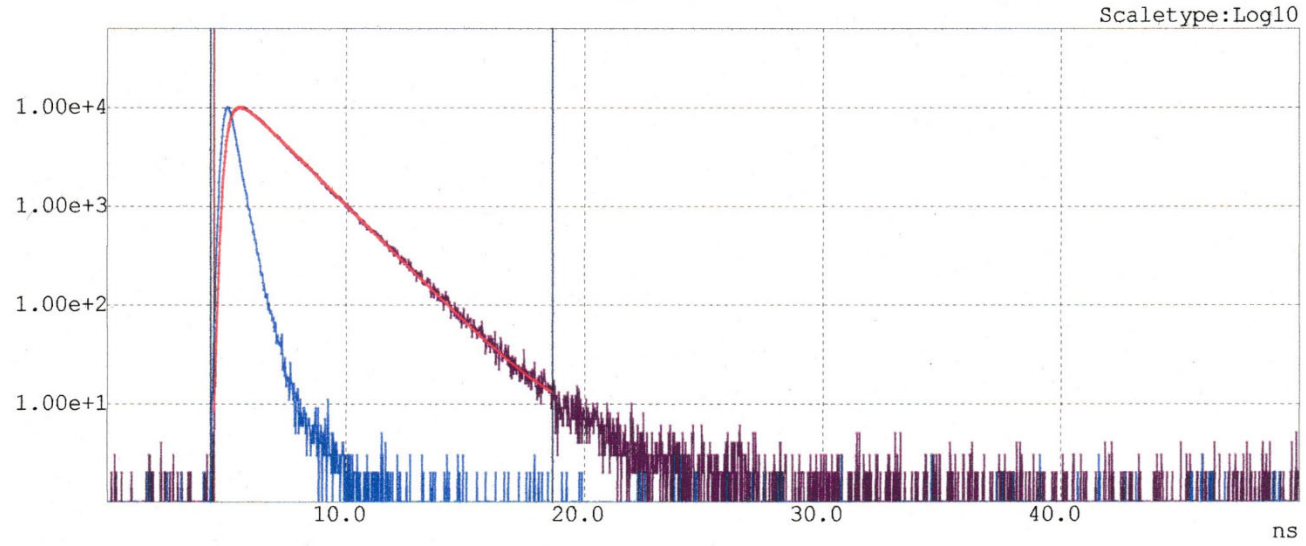
MeOH solution (3×10^{-5} M)



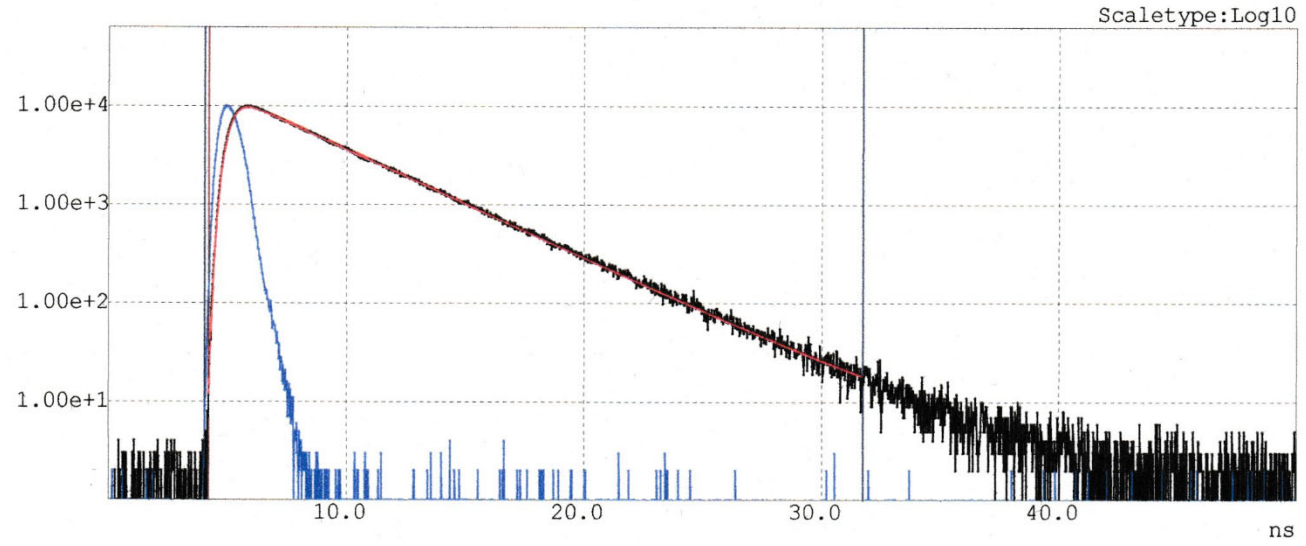
MeOH solution with Et_3N 0.1 equiv. (3×10^{-5} M)



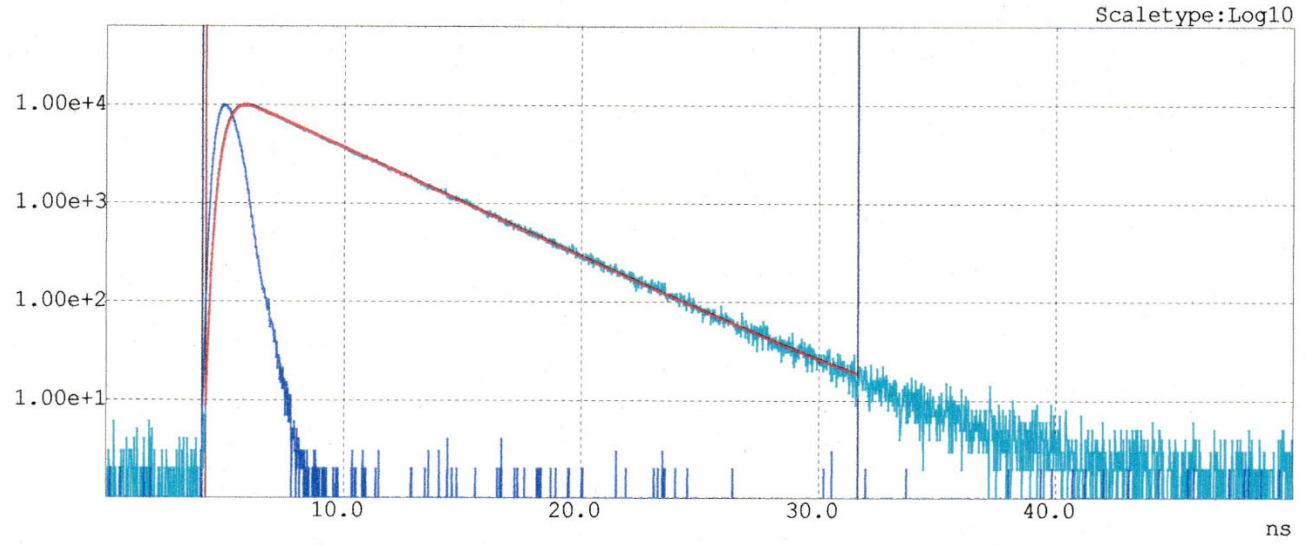
MeOH solution with Et_3N 0.5 equiv. (3×10^{-5} M)



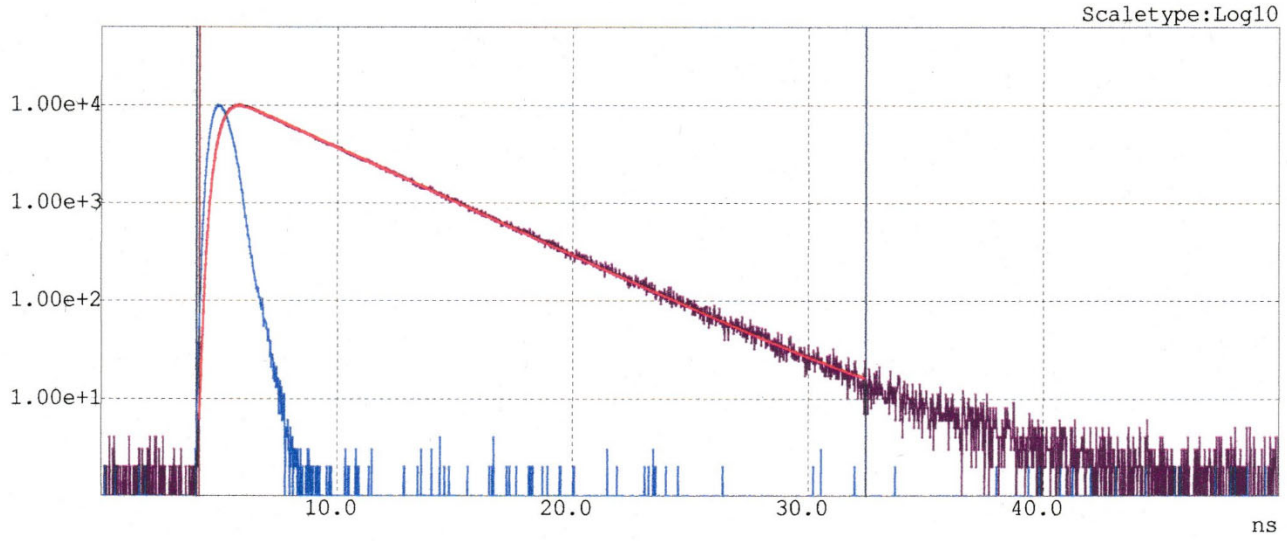
MeOH solution with Et_3N 1.0 equiv. (3×10^{-5} M)



MeOH solution with Et_3N 5.0 equiv. (3×10^{-5} M)



MeOH solution with Et_3N 10 equiv. (3×10^{-5} M)



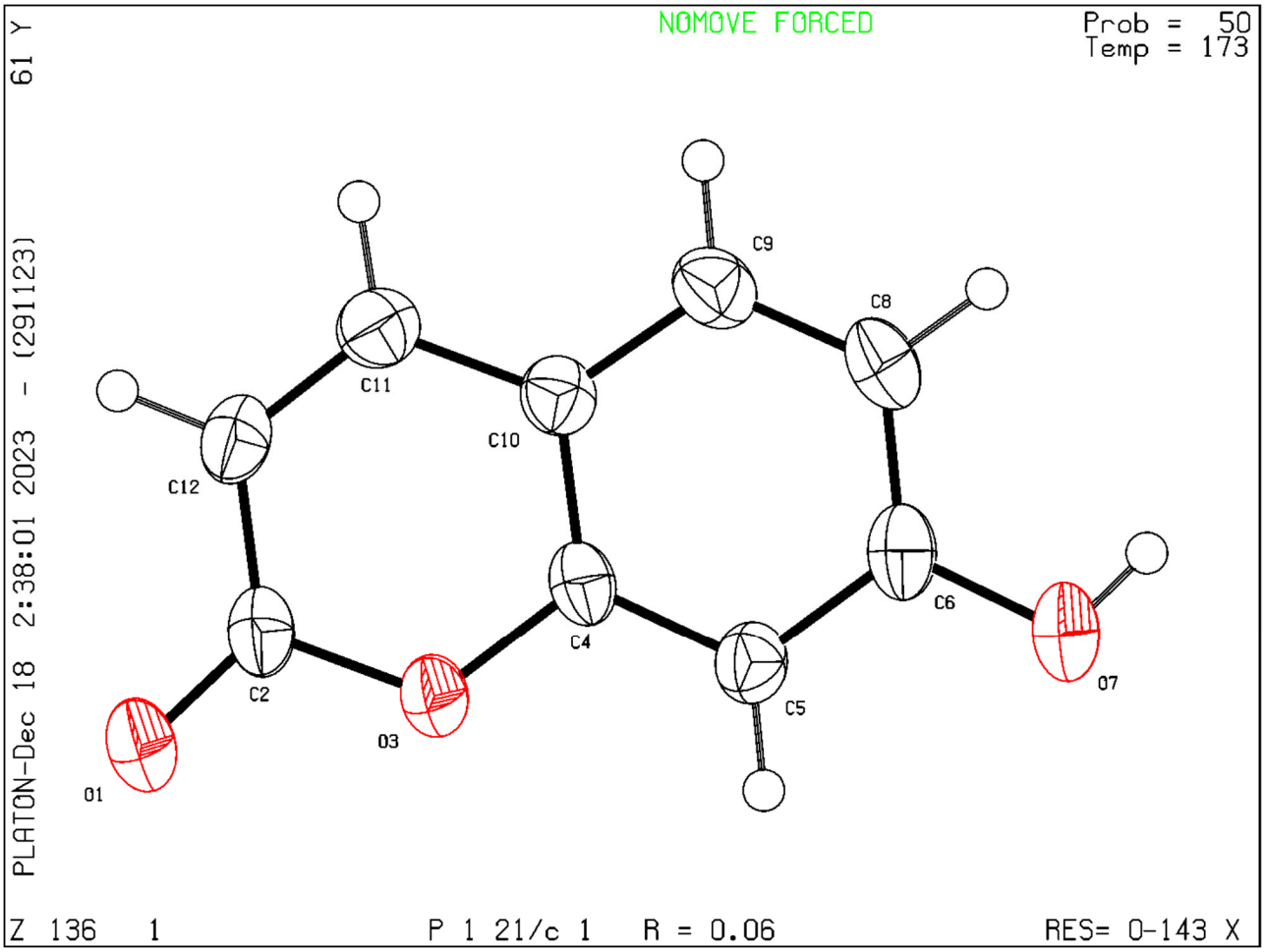


Figure S1. ORTEP diagram of **1**.

A crystal of the **1** was precipitated by using the vapor-diffusion method with hexane and acetone in freezer.

The X-ray Crystal Structure was collected on Rigaku Oxford Diffraction.
The thermal ellipsoids are drawn at the 50 % probability level.

Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	$C_9 H_6 O_3$	
Formula weight	162.14	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3.8515(4) Å	α = 90°.
	b = 11.0399(13) Å	β = 90.489(8)°.
	c = 16.7731(13) Å	γ = 90°.
Volume	713.17(12) $Å^3$	
Z	4	

Density (calculated)	1.510 Mg/m^3
Absorption coefficient	0.115 mm^{-1}
F(000)	336
Crystal size	0.213 x 0.113 x 0.105 mm^3
Theta range for data collection	2.209 to 26.370°.
Index ranges	-4<=h<=4, -13<=k<=13, -20<=l<=20
Reflections collected	6911
Independent reflections	1453 [R(int) = 0.0595]
Completeness to theta = 25.242°	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1453 / 0 / 110
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2sigma(I)]	R_1 = 0.0570, wR_2 = 0.1544
Final R indexes (all data)	R_1 = 0.0751, wR_2 = 0.1696
Extinction coefficient	n/a
Largest diff. peak and hole	0.331 and -0.249 e.$Å^{-3}$

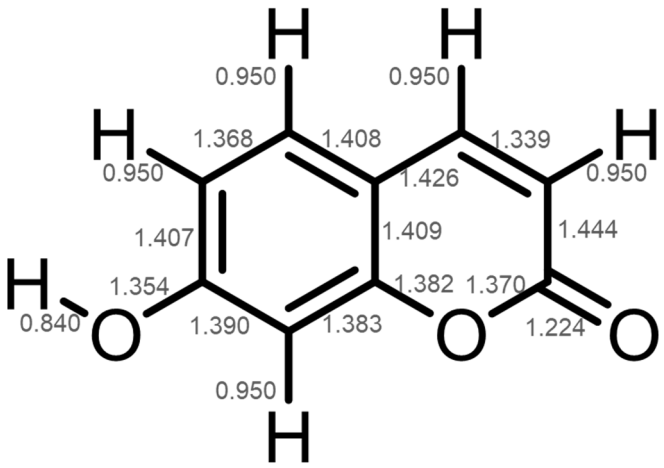


Figure S2. Bond Length of **1**.

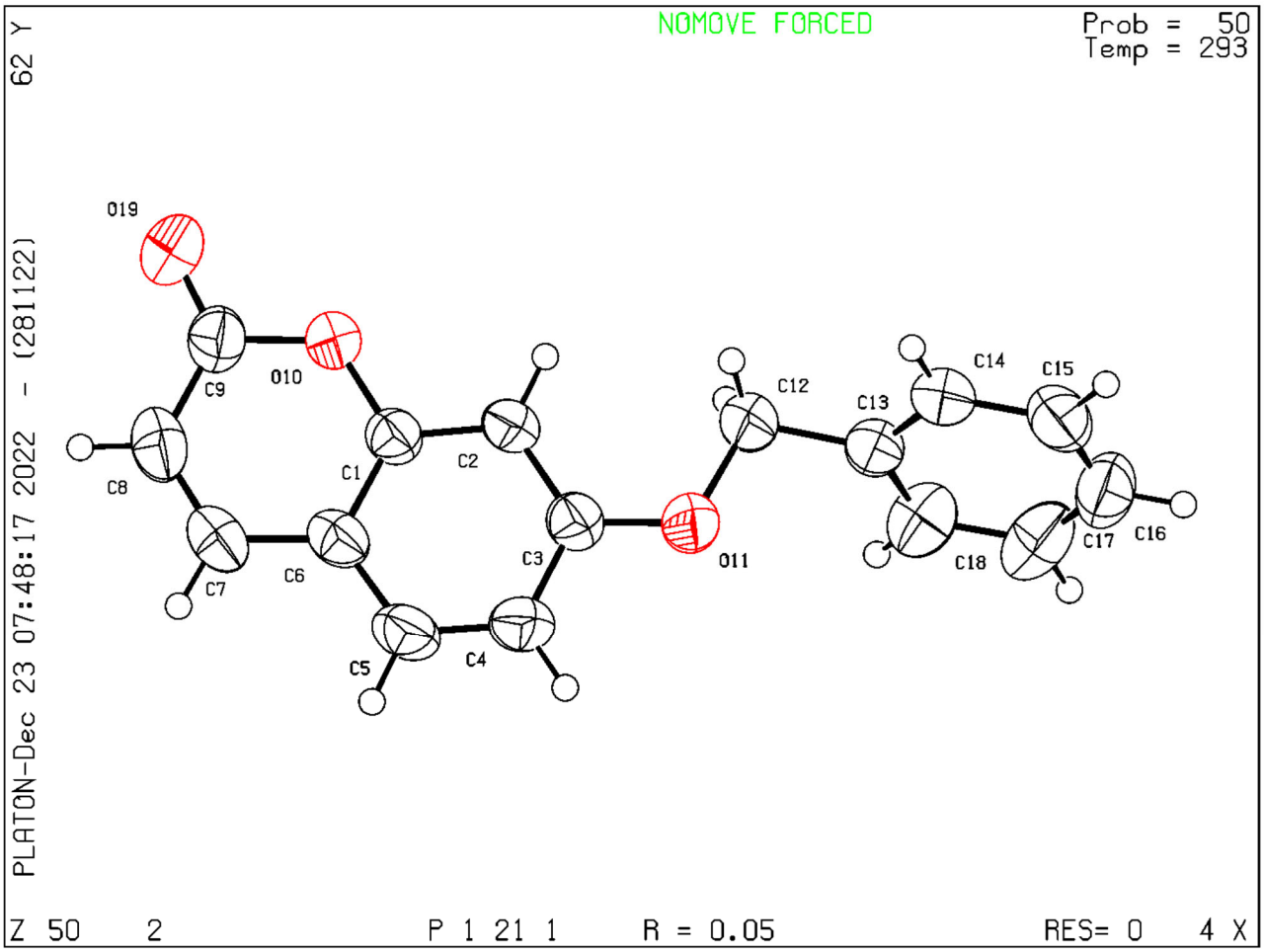


Figure S3. ORTEP diagram of **2**.

A crystal of the **2** was precipitated by using the solvent evaporation method with hexane and chloroform in freezer.

The X-ray Crystal Structure was collected on Rigaku Oxford Diffraction.
The thermal ellipsoids are drawn at the 50 % probability level.

Table S2. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	$C_{16}H_{12}O_3$	
Formula weight	252.26	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 4.4183(2) Å	α = 90°.
	b = 10.1778(4) Å	β = 92.256(4)°.
	c = 13.9165(5) Å	γ = 90°.
Volume	625.32(4) $Å^3$	
Z	2	

Density (calculated)	1.340 Mg/m^3
Absorption coefficient	0.754 mm^{-1}
F(000)	264
Crystal size	0.400 x 0.150 x 0.050 mm^3
Theta range for data collection	3.178 to 69.751°.
Index ranges	-5<=h<=5, -12<=k<=12, -11<=l<=16
Reflections collected	3182
Independent reflections	1957 [R(int) = 0.0311]
Completeness to theta = 25.242°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1957 / 1 / 173
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2sigma(I)]	R_1 = 0.0546, wR_2 = 0.1562
Final R indexes (all data)	R_1 = 0.0567, wR_2 = 0.1599
Extinction coefficient	0.026(5)
Largest diff. peak and hole	0.211 and -0.184 $e.Å^{-3}$

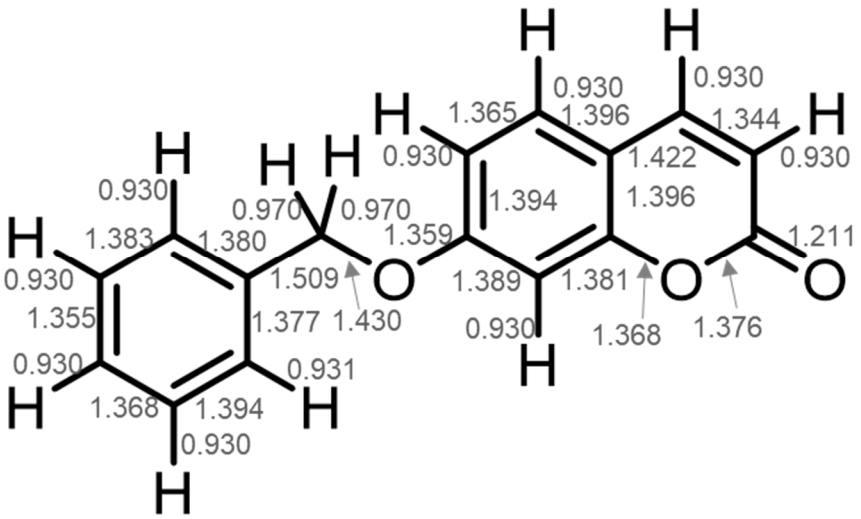


Figure S4. Bond Length of **2**.

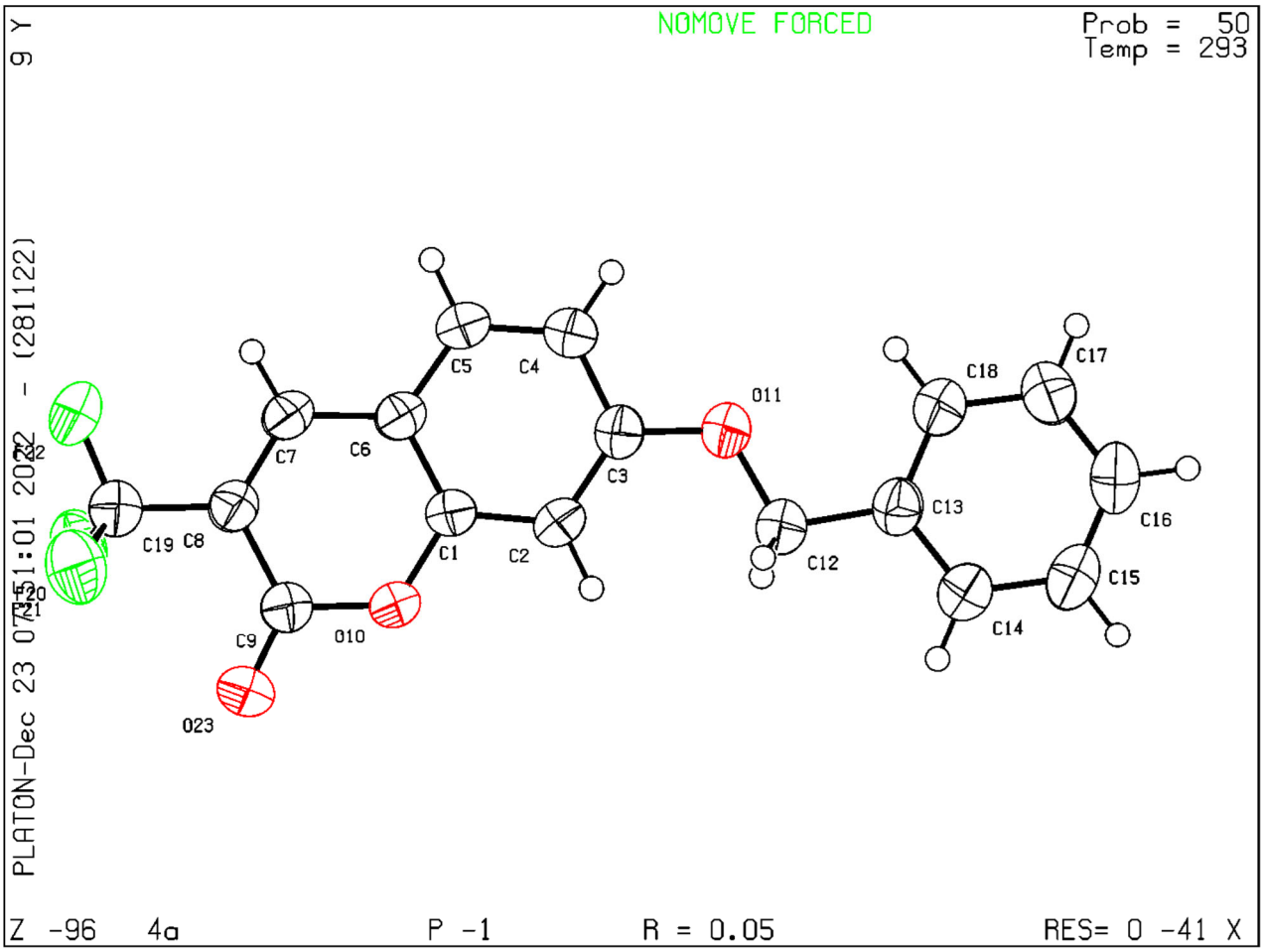


Figure S5. ORTEP diagram of **4a**.

A crystal of the **4a** was precipitated by using the vapor-diffusion method with hexane and chloroform in freezer.

The X-ray Crystal Structure was collected on Rigaku Oxford Diffraction.
The thermal ellipsoids are drawn at the 50 % probability level.

Table S3. Crystal data and structure refinement for **4a**.

Identification code	**4a**	
Empirical formula	$C_{17}H_{11}F_3O_3$	
Formula weight	320.26	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.6324(3) Å	α = 97.289(4)°.
	b = 10.1334(5) Å	β = 91.792(4)°.
	c = 10.8812(5) Å	γ = 104.569(4)°.
Volume	700.56(5) $Å^3$	
Z	2	
Density (calculated)	1.518 Mg/m^3	

Absorption coefficient	1.125 mm^{-1}
F(000)	328
Crystal size	0.300 x 0.080 x 0.040 mm^3
Theta range for data collection	4.105 to 69.676°.
Index ranges	-7<=h<=7, -12<=k<=12, -13<=l<=9
Reflections collected	6299
Independent reflections	2603 [R(int) = 0.0366]
Completeness to theta = 25.242°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2603 / 0 / 209
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2sigma(I)]	R_1 = 0.0453, wR_2 = 0.1338
Final R indexes (all data)	R_1 = 0.0513, wR_2 = 0.1405
Extinction coefficient	0.0077(14)
Largest diff. peak and hole	0.251 and -0.176 e.$Å^{-3}$

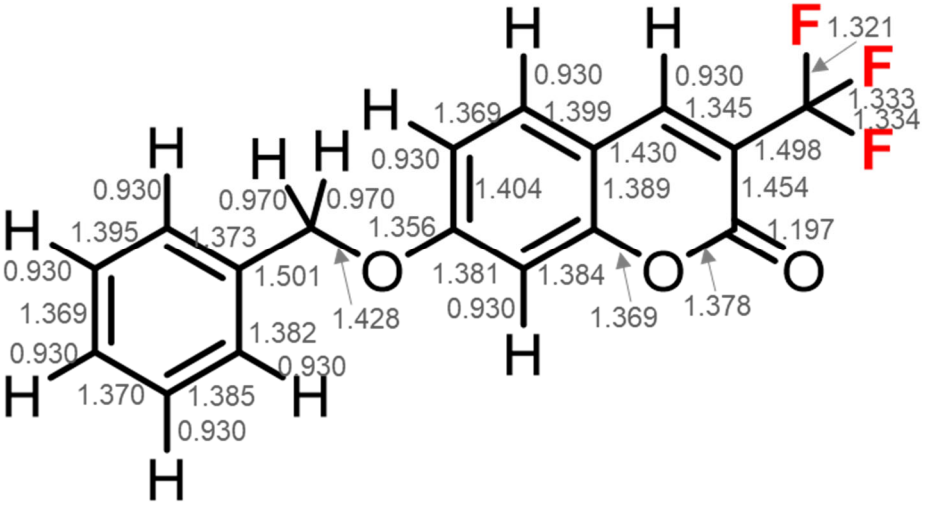


Figure S6. Bond Length of **4a**.

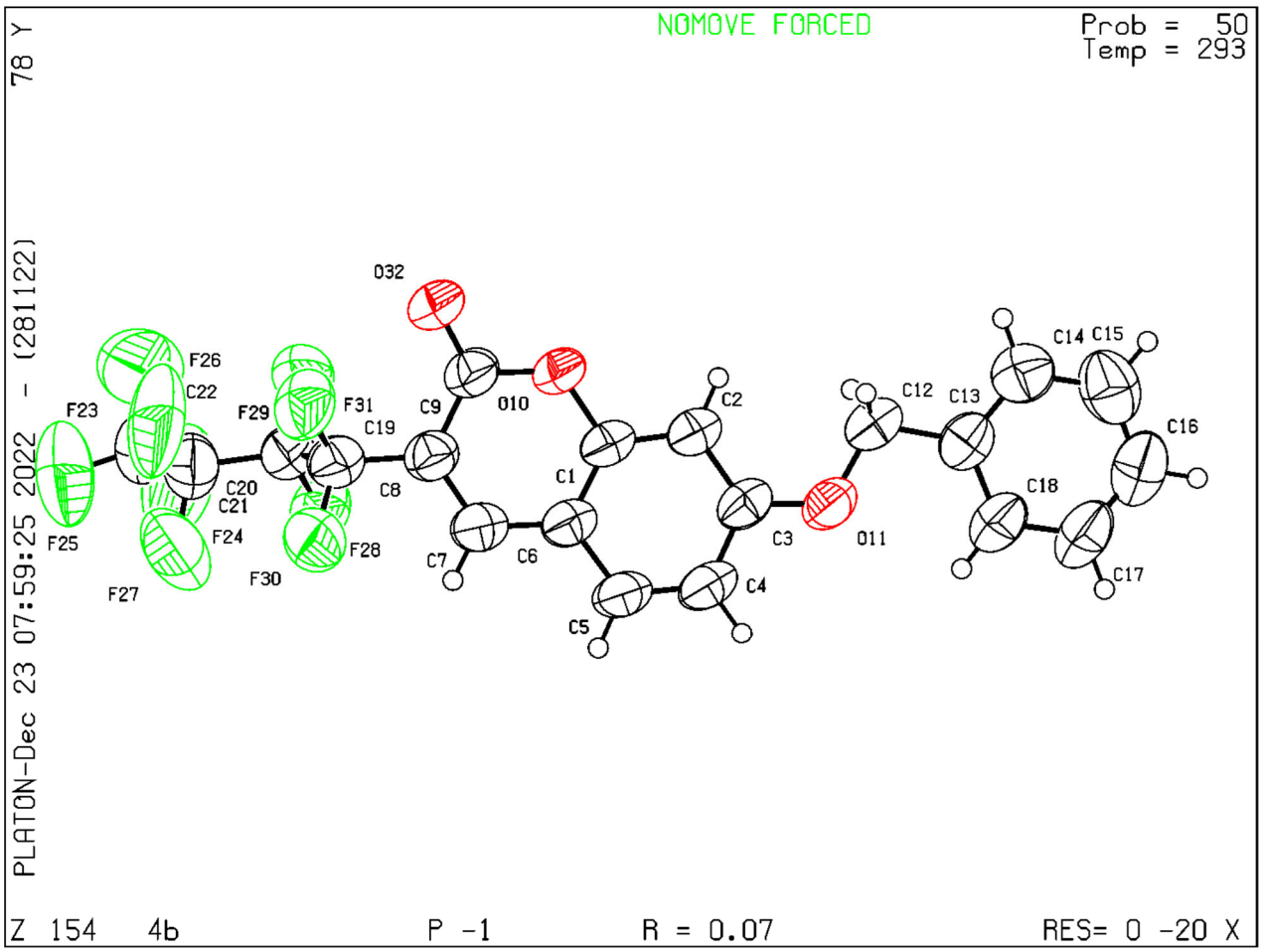


Figure S7. ORTEP diagram of **4b**.

A crystal of the **4b** was precipitated by using the vapor-diffusion method with hexane and chloroform in freezer.

The X-ray Crystal Structure was collected on Rigaku Oxford Diffraction.
The thermal ellipsoids are drawn at the 50 % probability level.

Table S4. Crystal data and structure refinement for **4b**.

Identification code	**4b**	
Empirical formula	$C_{20}H_{11}F_9O_3$	
Formula weight	470.29	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.4736(4) Å	α = 85.931(4)°.
	b = 8.8428(4) Å	β = 88.314(4)°.
	c = 15.7659(7) Å	γ = 69.315(5)°.
Volume	972.29(8) $Å^3$	
Z	2	
Density (calculated)	1.606 Mg/m^3	

Absorption coefficient	1.481 mm^{-1}
F(000)	472
Crystal size	0.400 x 0.200 x 0.050 mm^3
Theta range for data collection	2.810 to 69.918°.
Index ranges	-9<=h<=9, -10<=k<=10, -19<=l<=19
Reflections collected	8997
Independent reflections	3633 [R(int) = 0.0375]
Completeness to theta = 25.242°	100 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3633 / 0 / 290
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2sigma(I)]	R_1 = 0.0660, wR_2 = 0.2043
Final R indexes (all data)	R_1 = 0.0788, wR_2 = 0.2022
Extinction coefficient	0.0077(14)
Largest diff. peak and hole	0.266 and -0.300 e.$Å^{-3}$

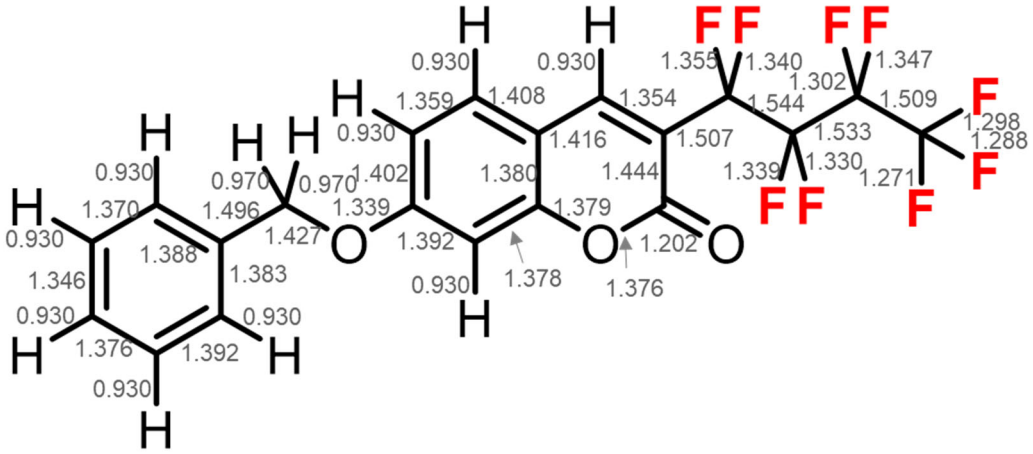


Figure S8. Bond Length of **4b**.

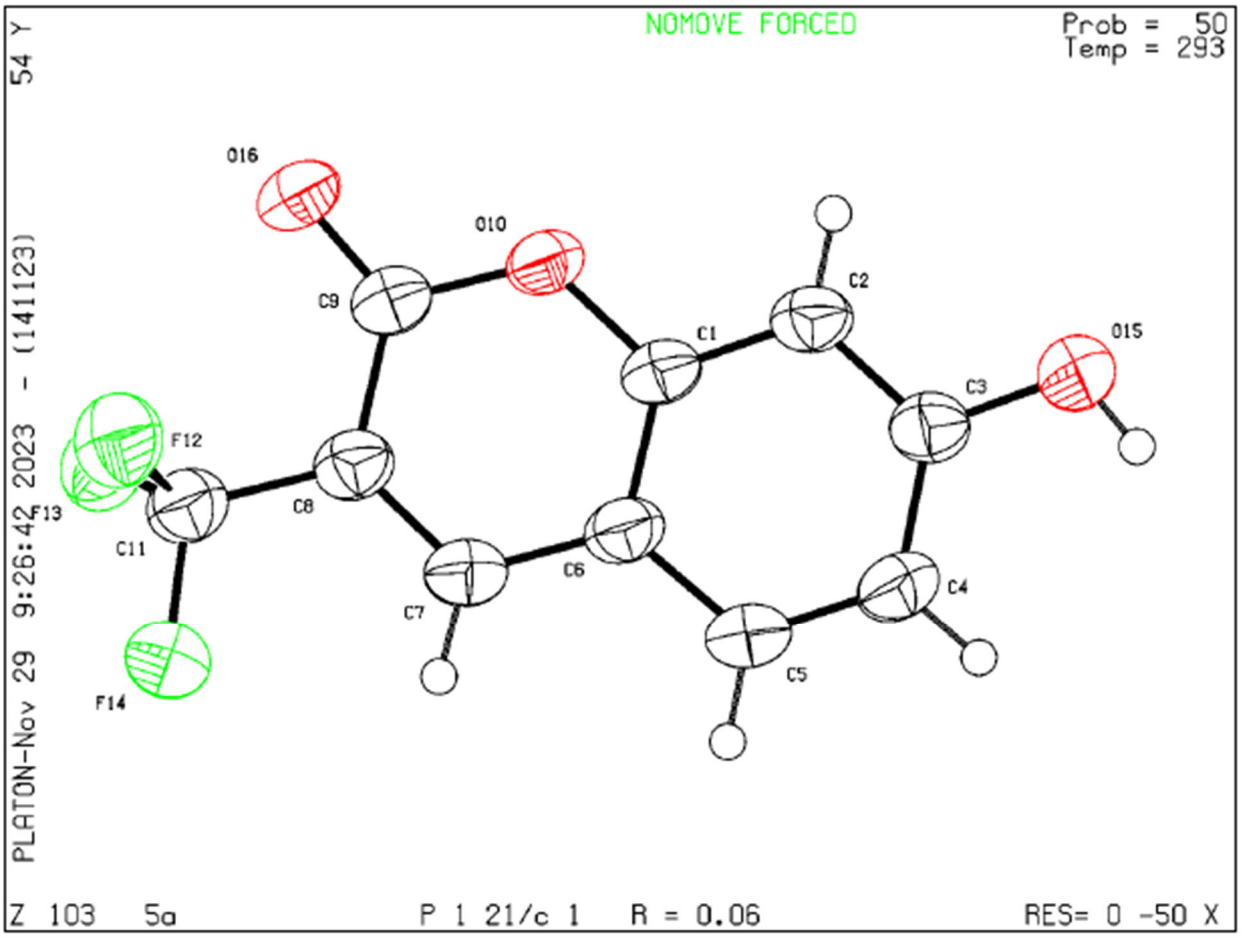


Figure S9. ORTEP diagram of **5a**.

A crystal of the **5a** was precipitated by using the vapor-diffusion method with hexane and chloroform in freezer.

The X-ray Crystal Structure was collected on Rigaku Oxford Diffraction.
The thermal ellipsoids are drawn at the 50 % probability level.

Table S5. Crystal data and structure refinement for **5a**.

Identification code	**5a**	
Empirical formula	$C_{10}H_5F_3O_3$	
Formula weight	230.14	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.6323(4) Å	α = 90°.
	b = 7.1785(3) Å	β = 103.982(5)°.
	c = 14.9074(7) Å	γ = 90°.
Volume	896.40(7) $Å^3$	
Z	4	
Density (calculated)	1.705 Mg/m^3	

Absorption coefficient	1.476 mm^{-1}
F(000)	464
Crystal size	0.300 x 0.200 x 0.020 mm^3
Theta range for data collection	5.281 to 69.492°.
Index ranges	-10<=h<=10, -8<=k<=7, -18<=l<=16
Reflections collected	4316
Independent reflections	1675 [R(int) = 0.0831]
Completeness to theta = 25.242°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1675 / 0 / 147
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2sigma(I)]	R_1 = 0.0574, wR_2 = 0.1647
Final R indexes (all data)	R_1 = 0.0740, wR_2 = 0.1771
Extinction coefficient	0.0021(12)
Largest diff. peak and hole	0.254 and -0.280 e.$Å^{-3}$

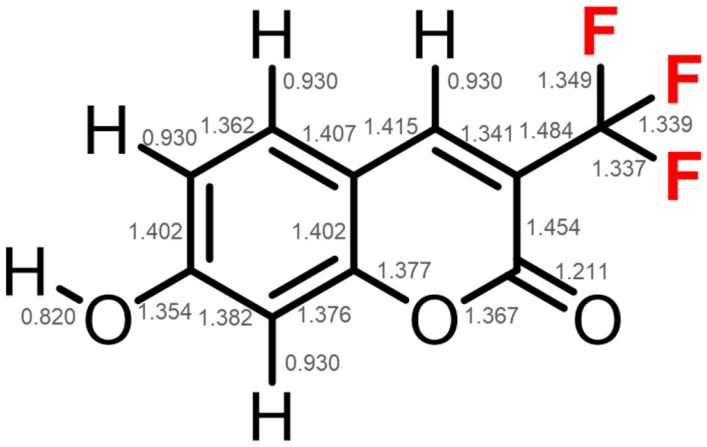


Figure S10. Bond Length of **5a**.

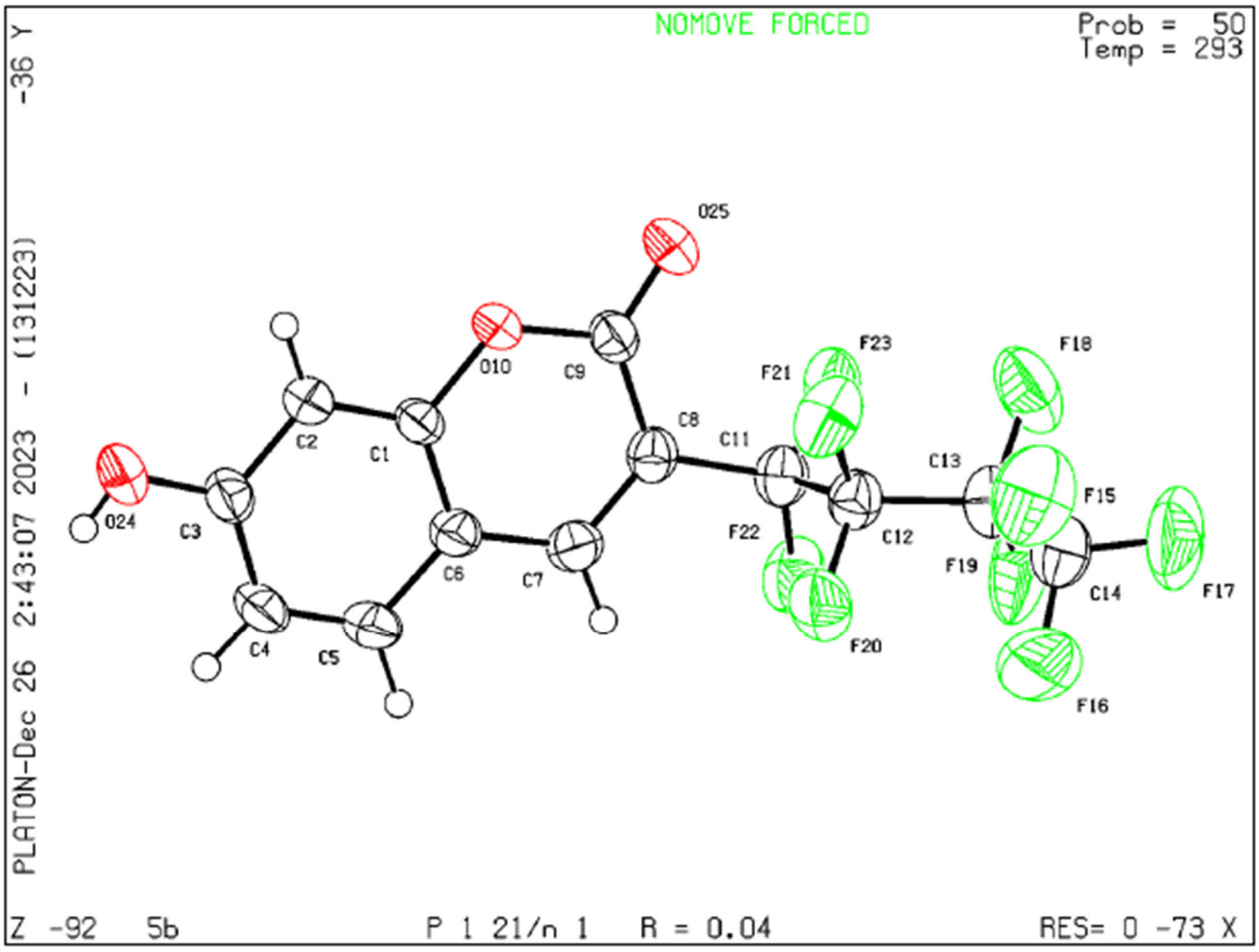


Figure S11. ORTEP diagram of **5b**.

A crystal of the **5b** was precipitated by using the solvent evaporation method with hexane and chloroform in freezer.

The X-ray Crystal Structure was collected on Rigaku Oxford Diffraction.
The thermal ellipsoids are drawn at the 50 % probability level.

Table S6. Crystal data and structure refinement for **5b**.

Identification code	**5b**	
Empirical formula	$C_{13}\,H_5\,F_9\,O_3$	
Formula weight	380.17	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.9448(2) Å	α = 90°.
	b = 5.92150(10) Å	β = 106.068(2)°.
	c = 16.9008(3) Å	γ = 90°.
Volume	1341.05(4) $Å^3$	
Z	4	
Density (calculated)	1.883 Mg/m^3	

Absorption coefficient	1.958 mm^{-1}
F(000)	752
Crystal size	0.200 x 0.100 x 0.050 mm^3
Theta range for data collection	3.649 to 69.679°.
Index ranges	-16<=h<=13, -7<=k<=6, -19<=l<=20
Reflections collected	6943
Independent reflections	2493 [R(int) = 0.0170]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2493 / 0 / 247
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2sigma(I)]	R_1 = 0.0436, wR_2 = 0.1114
Final R indexes (all data)	R_1 = 0.0406, wR_2 = 0.1141
Extinction coefficient	0.0041(4)
Largest diff. peak and hole	0.307 and -0.375 e.$Å^{-3}$

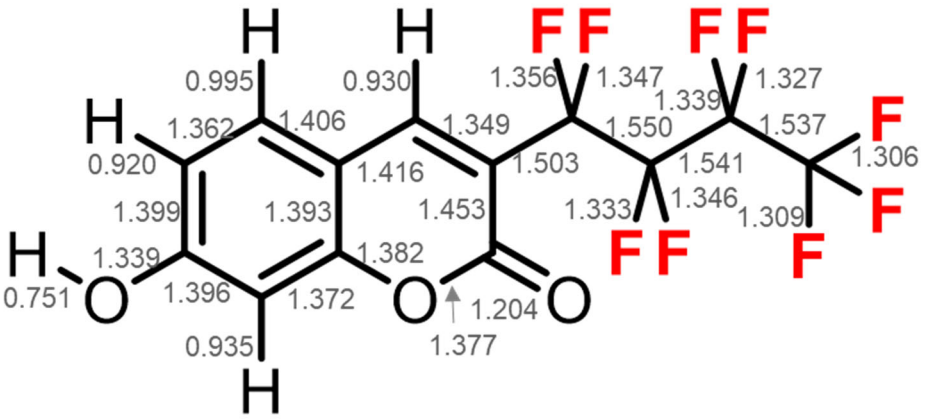


Figure S12. Bond Length of **5b**.

Computational Details

All calculations were performed using the computational chemistry software package Gaussian 16 ver. B.01. Computational resources in the form of super computers were provided by the Institute for Molecular Science.

a) Ground State Details.

Ground state geometries of **1**, **2**, **4a**, **4b**, **5a**, **5b**, **anion of 5b** were computed at RB3LYP/6-31G(d,p) level of theory. At the optimized structures, no imaginary frequency was found through the frequency analysis. All coordinates are reported as XYZ Cartesian coordinates. And computed E (RB3LYP) and sum of zero-point and thermal correction energies of optimized structures are shown.

1

E (RB3LYP) = -572.254342231 a.u.
Sum of electronic and thermal Energies = -572.113830 a.u.
Imaginary Frequency = 0

Table 7. Cartesian coordinates of the optimized **1**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	2.357504	-0.422859	0.000077
C	1.150782	-1.122996	-0.000089
C	-0.041411	-0.405515	-0.000104
C	-0.05903	1.006298	-0.000024
C	1.174114	1.681395	0.000071
C	2.371558	0.985036	0.000095
H	1.140261	-2.206036	-0.000323
C	-1.341832	1.65471	-0.000074
H	1.179863	2.767666	0.00007
H	3.318591	1.518471	0.000213
C	-2.485426	0.930996	-0.000076
C	-2.466721	-0.526283	0.000022
H	-1.377232	2.741495	-0.000081
H	-3.467725	1.386951	-0.000057
O	-1.198917	-1.12447	-0.000242
O	-3.428557	-1.256349	0.000288
O	3.500466	-1.159748	0.000112
H	4.265074	-0.568697	-0.000483

2

E (RB3LYP) = -842.617933605 a.u.
Sum of electronic and thermal Energies = -842.361982 a.u.
Imaginary Frequency = 0

Table 8. Cartesian coordinates of the optimized **2**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.156338	0.400026	0.003709
C	-1.10671	-0.616139	-0.147029
C	-2.456735	-0.299711	-0.07627
C	-2.895858	1.024692	0.144634
C	-1.920354	2.023312	0.290619
C	-0.565141	1.730795	0.222852
H	-0.790062	-1.637899	-0.31747
C	-4.31378	1.253965	0.20275
H	-2.239614	3.048036	0.459373
H	0.160231	2.525947	0.335847
C	-5.188046	0.232244	0.051041
C	-4.734231	-1.134653	-0.175995
H	-4.672402	2.266558	0.371402
H	-6.261742	0.368665	0.089092
O	-3.347115	-1.322025	-0.227655
O	-5.435697	-2.107028	-0.321499
O	1.139108	0.000251	-0.082852
C	2.178521	0.967995	0.104206
H	2.113402	1.746548	-0.666833
H	2.045922	1.452183	1.082824
C	3.51216	0.267012	0.034136
C	4.5586	0.818015	-0.711208
C	3.731839	-0.919144	0.745973
C	5.810953	0.201509	-0.739511
H	4.394245	1.73259	-1.275607
C	4.978421	-1.540802	0.709946
H	2.917975	-1.358355	1.314304
C	6.022661	-0.979994	-0.029739
H	6.615225	0.639716	-1.323021
H	5.136595	-2.463501	1.260541
H	6.994093	-1.464801	-0.055086

4a
E (RB3LYP) = -1179.222409 a.u.
Sum of electronic and thermal Energies = -1179.385708 a.u.
Imaginary Frequency = 0

Table 9. Cartesian coordinates of the optimized **4a**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.225393	-0.358291	0.000051
C	-0.318949	0.709822	-0.000085
C	1.041835	0.441834	-0.000035
C	1.537756	-0.880939	0.000139
C	0.606435	-1.93334	0.00028
C	-0.758201	-1.690405	0.000238
H	-0.680396	1.730788	-0.000221
C	2.957652	-1.058762	0.000173
H	0.970639	-2.956718	0.000419
H	-1.449678	-2.522731	0.000365
C	3.796063	0.007893	0.000005
C	3.283287	1.380438	-0.000274
H	3.366086	-2.064513	0.000337
O	1.892094	1.50774	-0.00015
O	3.940387	2.390848	-0.000547
O	-2.532889	-0.006359	-0.000013
C	-3.536587	-1.040283	0.000133
H	-3.409378	-1.669358	-0.889713
H	-3.409355	-1.669098	0.89016
C	-4.888961	-0.380254	0.000062
C	-5.520413	-0.058468	-1.206735
C	-5.519899	-0.057177	1.206787
C	-6.763391	0.573767	-1.208505
H	-5.035319	-0.304277	-2.147843
C	-6.762866	0.575067	1.208407
H	-5.0344	-0.301981	2.147948
C	-7.386276	0.891013	-0.000087
H	-7.245835	0.816532	-2.150537
H	-7.244909	0.818845	2.150384

H	-8.355637	1.38059	-0.00014
C	5.291402	-0.160501	0.000027
F	5.860147	0.395272	1.086573
F	5.86015	0.394933	-1.08669
F	5.627536	-1.475136	0.000231

4b
E (RB3LYP) = -1892.98988872 a.u.
Sum of electronic and thermal Energies = -1892.680119 a.u.
Imaginary Frequency = 0

Table 10. Cartesian coordinates of the optimized **4b**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	3.588073	0.538135	0.413228
C	2.763783	-0.066329	-0.540125
C	1.396268	0.209217	-0.50996
C	0.827777	1.071783	0.445233
C	1.687823	1.667324	1.395087
C	3.040811	1.409665	1.385286
H	3.138034	-0.738723	-1.300025
C	-0.581894	1.2888	0.382453
H	1.266192	2.336141	2.139728
H	3.712621	1.858663	2.10763
C	-1.352346	0.685908	-0.563205
C	-0.765664	-0.231678	-1.542698
H	-1.044347	1.957187	1.101762
O	0.624198	-0.396658	-1.451465
O	-1.338162	-0.84724	-2.405683
O	4.925087	0.355692	0.493771
C	-2.840585	0.941619	-0.608633
C	-3.688926	-0.172983	0.074279
C	-5.197781	0.152736	0.261499
C	-6.073593	-1.073388	0.63774
F	-3.12242	2.098462	0.076445
F	-3.277543	1.09941	-1.881175
F	-3.167009	-0.386127	1.312767

F	-3.579227	-1.313942	-0.644182
F	-5.703638	0.672409	-0.880939
F	-5.326204	1.061982	1.256047
F	-5.536066	-1.738286	1.670803
F	-7.292871	-0.644114	0.991699
F	-6.197958	-1.90533	-0.401087
C	5.567457	-0.5165	-0.458961
H	5.132691	-1.520344	-0.378172
H	5.382463	-0.139597	-1.472442
C	7.04052	-0.541464	-0.154171
C	7.567737	-1.498339	0.720425
C	7.897559	0.407549	-0.723378
C	8.929703	-1.508843	1.020385
H	6.908123	-2.238093	1.166603
C	9.259665	0.399962	-0.425047
H	7.494976	1.154	-1.403181
C	9.77737	-0.559134	0.447509
H	9.329025	-2.25807	1.697375
H	9.916404	1.138576	-0.874795
H	10.838693	-0.568499	0.677445

5a
E (RB3LYP) = -909.286327 a.u.
Sum of electronic and thermal Energies = -909.137437 a.u.
Imaginary Frequency = 0

Table 11. Cartesian coordinates of the optimized **5a**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-3.636882	0.031212	0.000109
C	-2.639022	1.007173	-0.00016
C	-1.309302	0.601701	-0.000216
C	-0.946907	-0.762726	-0.00018
C	-1.976701	-1.721985	-0.000047
C	-3.306101	-1.339042	0.000117
H	-2.894725	2.059525	-0.000522
C	0.448889	-1.079564	-0.000266

H	-1.715364	-2.776069	-0.000062
H	-4.094348	-2.087109	0.000419
C	1.388532	-0.101155	-0.000254
C	1.013896	1.3148	-0.000365
H	0.756161	-2.12064	-0.000276
O	-0.359457	1.577494	-0.00054
O	1.765648	2.256391	0.00053
O	-4.922444	0.464929	0.00052
H	-5.522372	-0.293016	-0.000779
C	2.860266	-0.41665	0.000061
F	3.064118	-1.757929	0.00035
F	3.480378	0.080094	-1.086601
F	3.480023	0.080525	1.086734

5b
E (RB3LYP) = -1622.62543150 a.u.
Sum of electronic and thermal Energies = -1622.431104 a.u.
Imaginary Frequency = 0

Table 12. Cartesian coordinates of the optimized **5b**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	5.632637	-0.321186	-0.536778
C	4.760888	0.768519	-0.51228
C	3.439333	0.560156	-0.123947
C	2.968357	-0.716267	0.241698
C	3.876341	-1.796021	0.206284
C	5.189422	-1.610823	-0.176213
H	5.082566	1.76834	-0.786463
C	1.598049	-0.826064	0.630432
H	3.526452	-2.785307	0.486111
H	5.895973	-2.431937	-0.207879
C	0.775523	0.256878	0.647336
C	1.258728	1.579921	0.243463
H	1.211091	-1.795858	0.926507
O	2.615306	1.640603	-0.111172

O	0.62884	2.604632	0.186732
O	6.932946	-0.205041	-0.90231
H	7.130192	0.714258	-1.128244
C	-0.667457	0.110065	1.071991
C	-1.664647	0.005817	-0.121037
C	-3.120258	-0.389878	0.256525
C	-4.156471	-0.168779	-0.878978
F	-0.812143	-1.055152	1.784432
F	-1.054107	1.133088	1.871056
F	-1.194336	-0.949583	-0.96801
F	-1.693894	1.189025	-0.775915
F	-3.532657	0.332243	1.324004
F	-3.143973	-1.705035	0.575899
F	-3.727772	-0.722166	-2.022755
F	-5.313727	-0.747131	-0.529701
F	-4.372467	1.135258	-1.077564

Anion of 5b
E (RB3LYP) = -1622.09291922 a.u.
Sum of electronic and thermal Energies = -1621.912401 a.u.
Imaginary Frequency = 0

Table .13 Cartesian coordinates of the optimized **anion of 5b**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	5.757587	-0.338179	-0.569435
C	4.804107	0.760636	-0.551783
C	3.504887	0.569717	-0.164055
C	3.001263	-0.706842	0.2457
C	3.921448	-1.801152	0.235299
C	5.219761	-1.638856	-0.146957
H	5.144948	1.744561	-0.855413
C	1.665724	-0.79264	0.631876
H	3.551883	-2.778303	0.544908

H	5.916491	-2.472894	-0.15393
C	0.822288	0.31269	0.634735
C	1.304737	1.601575	0.188407
H	1.272397	-1.753336	0.95321
O	2.653454	1.654354	-0.172705
O	0.67535	2.640018	0.095052
O	6.949704	-0.200479	-0.916405
C	-0.59996	0.171702	1.0523
C	-1.619751	0.003137	-0.117217
C	-3.075459	-0.371308	0.282625
C	-4.117212	-0.221296	-0.858368
F	-0.766464	-0.971803	1.816522
F	-1.042109	1.220696	1.807637
F	-1.181278	-1.000127	-0.927955
F	-1.675911	1.147735	-0.841285
F	-3.509787	0.407307	1.303788
F	-3.113986	-1.668706	0.676885
F	-3.711819	-0.847257	-1.972867
F	-5.280692	-0.774855	-0.466429
F	-4.345766	1.066313	-1.142415

b) Excited State Calculation

Using the optimized geometry of the ground state (S_0) in the case of **1**, **2**, **4a**, **4b**, **5a**, **5b**, **anion of 5b** single point time dependent density functional theory (TD-DFT) calculations were performed using the UB3LYP/6-31+G(d,p) level of theory. The polarizable continuum model (PCM) was employed to take into account the effect of the polarity of MeOH and methanol for the **1**, **2**, **4a**, **4b**, **5a**, **5b**, **anion of 5b**. The first excited states of **1**, **2**, **4a**, **4b**, **5a**, **5b**, **anion of 5b** are reported below. In calculating 100 kinds of transitions, dominant UV-vis absorption peaks with significant and relevant oscillator strengths (f value) (f≧0.1) are highlighted.

1 (methanol)

Excited State 3: 1.000-A 4.0350 eV 307.27 nm f=0.4276 <S2>=0.000**
42A -> 43A 0.69270 (πHOMO-πLUMO, 96.0% contribution)
42B -> 43B 0.69270 (πHOMO-πLUMO, 96.0% contribution)

Excited State 16: 1.000-A 5.9191 eV 209.46 nm f=0.1903 <S**2>=0.000
37A -> 43A 0.10365
39A -> 43A 0.49412
41A -> 44A -0.44843
41A -> 45A -0.12735
42A -> 45A 0.10574
37B -> 43B 0.10365
39B -> 43B 0.49412
41B -> 44B -0.44843
41B -> 45B -0.12735
42B -> 45B 0.10574

Excited State 23: 1.000-A 6.2600 eV 198.06 nm f=0.6432 <S**2>=0.000
41A -> 44A -0.24963
41A -> 45A 0.58799
42A -> 43A -0.10001
42A -> 44A -0.16968
42A -> 45A -0.14911
41B -> 44B -0.24963
41B -> 45B 0.58799
42B -> 43B -0.10001
42B -> 44B -0.16968
42B -> 45B -0.14911

Excited State 26: 1.000-A 6.4166 eV 193.22 nm f=0.5184 <S**2>=0.000
37A -> 44A -0.10185
39A -> 43A 0.36101
41A -> 44A 0.41476
41A -> 45A 0.26710
42A -> 45A 0.27403
37B -> 44B -0.10185
39B -> 43B 0.36101
41B -> 44B 0.41476
41B -> 45B 0.26710
42B -> 45B 0.27403

Excited State 98: 1.000-A 8.2899 eV 149.56 nm f=0.1534 <S**2>=0.000
37A -> 44A 0.56132
41A -> 53A -0.10262
41A -> 56A 0.24319
42A -> 57A 0.24766

37B -> 44B 0.56132
41B -> 53B -0.10262
41B -> 56B 0.24319
42B -> 57B 0.24766

2 (methanol)

Excited State 4: 1.000-A 3.9599 eV 313.10 nm f=0.5497 <S2>=0.000**
66A -> 67A 0.69517 (πHOMO-πLUMO, 96.7% contribution)
66B -> 67B 0.69517 (πHOMO-πLUMO, 96.7% contribution)

Excited State 31: 1.000-A 5.8380 eV 212.37 nm f=0.1274 <S**2>=0.000
61A -> 67A -0.32916
63A -> 69A 0.11711
63A -> 70A -0.18388
64A -> 68A -0.28316
64A -> 71A -0.10490
65A -> 68A 0.40732
65A -> 69A -0.13368
65A -> 71A -0.12143
66A -> 71A 0.15736
61B -> 67B -0.32916
63B -> 69B 0.11711
63B -> 70B -0.18388
64B -> 68B -0.28316
64B -> 71B -0.10490
65B -> 68B 0.40732
65B -> 69B -0.13368
65B -> 71B -0.12143
66B -> 71B 0.15736

Excited State 40: 1.000-A 6.1103 eV 202.91 nm f=0.1717 <S**2>=0.000
63A -> 69A 0.16755
63A -> 70A -0.13822
64A -> 68A -0.15541
64A -> 69A -0.16292
64A -> 70A 0.44453
65A -> 69A -0.17011
65A -> 70A 0.36529
65A -> 71A 0.12329
63B -> 69B 0.16755
63B -> 70B -0.13822
64B -> 68B -0.15541
64B -> 69B -0.16292
64B -> 70B 0.44453
65B -> 69B -0.17011
65B -> 70B 0.36529
65B -> 71B 0.12329

Excited State 44: 1.000-A 6.1708 eV 200.92 nm f=0.8025 <S**2>=0.000
64A -> 68A -0.20118
64A -> 69A -0.21266
64A -> 70A -0.29417
64A -> 71A 0.21093
65A -> 68A -0.10002

65A -> 69A -0.12780
65A -> 70A -0.17057
65A -> 71A 0.37549
66A -> 71A -0.10223
66A -> 74A 0.10146
64B -> 68B -0.20118
64B -> 69B -0.21266
64B -> 70B -0.29417
64B -> 71B 0.21093
65B -> 68B -0.10002
65B -> 69B -0.12780
65B -> 70B -0.17057
65B -> 71B 0.37549
66B -> 71B -0.10223
66B -> 74B 0.10146

Excited State 47: 1.000-A 6.3076 eV 196.56 nm f=0.5070 <S**2>=0.000
61A -> 67A -0.25930
63A -> 69A -0.11232
64A -> 68A 0.21789
64A -> 69A 0.22238
64A -> 70A 0.16086
64A -> 71A 0.17940
65A -> 68A 0.10540
65A -> 71A 0.37297
66A -> 71A 0.20310
61B -> 67B -0.25930
63B -> 69B -0.11232
64B -> 68B 0.21789
64B -> 69B 0.22238
64B -> 70B 0.16086
64B -> 71B 0.17940
65B -> 68B 0.10540
65B -> 71B 0.37297
66B -> 71B 0.20310

Excited State 66: 1.000-A 6.6202 eV 187.28 nm f=0.4194 <S**2>=0.000
62A -> 68A -0.10531
63A -> 68A -0.13257
63A -> 70A 0.42952
63A -> 77A -0.11251
64A -> 68A -0.13054
64A -> 69A 0.18832
65A -> 69A -0.19417
65A -> 70A 0.16610
65A -> 72A -0.11522
65A -> 73A 0.13287
62B -> 68B -0.10531
63B -> 68B -0.13257
63B -> 70B 0.42952
63B -> 77B -0.11251
64B -> 68B -0.13054
64B -> 69B 0.18832
65B -> 69B -0.19417
65B -> 70B 0.16610

65B -> 72B -0.11522
65B -> 73B 0.13287

Excited State 70: 1.000-A 6.6969 eV 185.14 nm f=0.4269 <S**2>=0.000
63A -> 68A -0.19915
63A -> 69A 0.30511
63A -> 70A -0.17517
63A -> 72A 0.11776
63A -> 73A -0.13516
64A -> 68A 0.11274
64A -> 70A -0.26021
65A -> 69A 0.11518
65A -> 70A 0.26597
65A -> 74A 0.10926
66A -> 76A 0.11246
66A -> 77A -0.16960
63B -> 68B -0.19915
63B -> 69B 0.30511
63B -> 70B -0.17517
63B -> 72B 0.11776
63B -> 73B -0.13516
64B -> 68B 0.11274
64B -> 70B -0.26021
65B -> 69B 0.11518
65B -> 70B 0.26597
65B -> 74B 0.10926
66B -> 76B 0.11246
66B -> 77B -0.16960

4a (methanol)

Excited State 4: 1.000-A 3.8449 eV 322.46 nm f=0.6088 <S2>=0.000**
82A -> 83A 0.69615 (πHOMO-πLUMO, 96.9% contribution)
82B -> 83B 0.69615 (πHOMO-πLUMO, 96.9% contribution)

Excited State 33: 1.000-A 5.9350 eV 208.90 nm f=0.2195 <S**2>=0.000
79A -> 84A 0.19370
79A -> 86A 0.12906
80A -> 86A -0.32353
80A -> 87A 0.16599
81A -> 85A 0.54596
79B -> 84B 0.19370
79B -> 86B 0.12906
80B -> 86B -0.32353
80B -> 87B 0.16599
81B -> 85B 0.54596

Excited State 39: 1.000-A 6.0787 eV 203.96 nm f=0.8544 <S**2>=0.000
79A -> 84A 0.41451
79A -> 86A 0.25638
79A -> 87A 0.19281
80A -> 84A 0.19467
80A -> 86A 0.32919
82A -> 84A -0.15258
82A -> 87A 0.13784
79B -> 84B 0.41451

79B -> 86B 0.25638
79B -> 87B 0.19281
80B -> 84B 0.19467
80B -> 86B 0.32919
82B -> 84B -0.15258
82B -> 87B 0.13784

Excited State 41: 1.000-A 6.2240 eV 199.20 nm f=0.2753 <S**2>=0.000
77A -> 83A 0.15044
79A -> 84A -0.28239
79A -> 86A 0.56872
79A -> 87A -0.10444
80A -> 87A -0.10576
77B -> 83B 0.15044
79B -> 84B -0.28239
79B -> 86B 0.56872
79B -> 87B -0.10444
80B -> 87B -0.10576

Excited State 50: 1.000-A 6.3032 eV 196.70 nm f=0.2001 <S**2>=0.000
77A -> 83A 0.13284
79A -> 84A -0.14145
79A -> 87A 0.60628
80A -> 86A -0.21165
82A -> 84A -0.12562
77B -> 83B 0.13284
79B -> 84B -0.14145
79B -> 87B 0.60628
80B -> 86B -0.21165
82B -> 84B -0.12562

Excited State 64: 1.000-A 6.6822 eV 185.55 nm f=0.3987 <S**2>=0.000
74A -> 83A 0.15003
79A -> 85A -0.14349
80A -> 85A 0.34973
80A -> 90A -0.10718
81A -> 86A -0.30428
81A -> 87A 0.32691
82A -> 91A -0.17058
74B -> 83B 0.15003
79B -> 85B -0.14349
80B -> 85B 0.34973
80B -> 90B -0.10718
81B -> 86B -0.30428
81B -> 87B 0.32691
82B -> 91B -0.17058

Excited State 65: 1.000-A 6.6980 eV 185.11 nm f=0.3882 <S**2>=0.000
75A -> 83A 0.53764
80A -> 86A 0.21020
80A -> 87A -0.24086
81A -> 85A 0.23351
75B -> 83B 0.53764
80B -> 86B 0.21020
80B -> 87B -0.24086

81B -> 85B 0.23351

Excited State 68: 1.000-A 6.7188 eV 184.53 nm f=0.2068 <S**2>=0.000
75A -> 83A 0.40521
79A -> 86A 0.10877
80A -> 86A -0.24881
80A -> 87A 0.24131
81A -> 85A -0.26519
82A -> 92A -0.23374
82A -> 95A -0.14208
75B -> 83B 0.40521
79B -> 86B 0.10877
80B -> 86B -0.24881
80B -> 87B 0.24131
81B -> 85B -0.26519
82B -> 92B -0.23374
82B -> 95B -0.14208

4b (methanol)

Excited State 4: 1.000-A 3.7744 eV 328.48 nm f=0.6301 <S2>=0.000**
118A ->119A 0.69578 (πHOMO-πLUMO, 96.8% contribution)
118B ->119B 0.69578 (πHOMO-πLUMO, 96.8% contribution)

Excited State 35: 1.000-A 5.9305 eV 209.06 nm f=0.4321 <S**2>=0.000
115A ->120A 0.25453
116A ->120A -0.13741
116A ->121A -0.11782
116A ->122A -0.29167
116A ->123A -0.15959
117A ->121A 0.50798
115B ->120B 0.25453
116B ->120B -0.13741
116B ->121B -0.11782
116B ->122B -0.29167
116B ->123B -0.15959
117B ->121B 0.50798

Excited State 37: 1.000-A 6.0165 eV 206.07 nm f=0.6604 <S**2>=0.000
115A ->120A 0.48059
115A ->122A -0.13307
115A ->123A 0.13955
116A ->122A 0.24796
117A ->121A -0.17350
118A ->120A 0.10884
118A ->123A -0.19051
118A ->126A 0.20260
115B ->120B 0.48059
115B ->122B -0.13307
115B ->123B 0.13955
116B ->122B 0.24796
117B ->121B -0.17350
118B ->120B 0.10884
118B ->123B -0.19051
118B ->126B 0.20260

Excited State 56: 1.000-A 6.4004 eV 193.71 nm f=0.3107 <S**2>=0.000
111A ->119A -0.12521
113A ->119A 0.11503
113A ->120A -0.10271
115A ->120A -0.23282
115A ->122A -0.19109
115A ->123A 0.36061
116A ->123A -0.18026
118A ->126A 0.34306
118A ->128A 0.19039
111B ->119B -0.12521
113B ->119B 0.11503
113B ->120B -0.10271
115B ->120B -0.23282
115B ->122B -0.19109
115B ->123B 0.36061
116B ->123B -0.18026
118B ->126B 0.34306
118B ->128B 0.19039

Excited State 71: 1.000-A 6.6624 eV 186.10 nm f=0.2290 <S**2>=0.000
116A ->121A 0.27833
116A ->128A 0.10006
117A ->122A -0.23571
117A ->123A -0.23731
118A ->129A 0.37698
118A ->130A -0.17433
118A ->132A -0.18785
116B ->121B 0.27833
116B ->128B 0.10006
117B ->122B -0.23571
117B ->123B -0.23731
118B ->129B 0.37698
118B ->130B -0.17433
118B ->132B -0.18785

Excited State 72: 1.000-A 6.6674 eV 185.96 nm f=0.1114 <S**2>=0.000
111A ->119A 0.63818
113A ->120A -0.14857
116A ->123A -0.11146
111B ->119B 0.63818
113B ->120B -0.14857
116B ->123B -0.11146

Excited State 73: 1.000-A 6.6969 eV 185.14 nm f=0.2642 <S**2>=0.000
116A ->121A -0.26180
116A ->122A -0.10772
116A ->125A 0.13103
117A ->121A -0.11296
117A ->122A 0.22553
117A ->123A 0.21571
118A ->128A 0.10345
118A ->129A 0.38987
118A ->130A -0.12075

118A ->132A -0.13986
116B ->121B -0.26180
116B ->122B -0.10772
116B ->125B 0.13103
117B ->121B -0.11296
117B ->122B 0.22553
117B ->123B 0.21571
118B ->128B 0.10345
118B ->129B 0.38987
118B ->130B -0.12075
118B ->132B -0.13986

Excited State 75: 1.000-A 6.7168 eV 184.59 nm f=0.4855 <S**2>=0.000
111A ->119A 0.12046
113A ->120A -0.16542
115A ->120A -0.10109
116A ->121A -0.12156
116A ->122A 0.32226
116A ->123A 0.29123
117A ->121A 0.31548
117A ->122A 0.11725
117A ->123A 0.10538
117A ->132A 0.11847
118A ->126A 0.10176
118A ->131A 0.15725
111B ->119B 0.12046
113B ->120B -0.16542
115B ->120B -0.10109
116B ->121B -0.12156
116B ->122B 0.32226
116B ->123B 0.29123
117B ->121B 0.31548
117B ->122B 0.11725
117B ->123B 0.10538
117B ->132B 0.11847
118B ->126B 0.10176
118B ->131B 0.15725

5a (methanol)

Excited State 3: 1.000-A 3.9434 eV 314.41 nm f=0.4544 <S2>=0.000**
58A -> 59A 0.69128 (πHOMO-πLUMO, 95.6% contribution)
58B -> 59B 0.69128 (πHOMO-πLUMO, 95.6% contribution)

Excited State 14: 1.000-A 5.8547 eV 211.77 nm f=0.1475 <S**2>=0.000
53A -> 59A 0.11710
55A -> 59A 0.51332
57A -> 60A -0.37565
57A -> 61A -0.16913
58A -> 60A -0.11492
58A -> 61A 0.17517
53B -> 59B 0.11710
55B -> 59B 0.51332
57B -> 60B -0.37565
57B -> 61B -0.16913

58B -> 60B -0.11492
58B -> 61B 0.17517

Excited State 20: 1.000-A 6.1679 eV 201.01 nm f=0.7273 <S**2>=0.000
57A -> 60A -0.36595
57A -> 61A 0.50968
58A -> 59A -0.10748
58A -> 60A -0.16737
58A -> 61A -0.21476
57B -> 60B -0.36595
57B -> 61B 0.50968
58B -> 59B -0.10748
58B -> 60B -0.16737
58B -> 61B -0.21476

Excited State 23: 1.000-A 6.3976 eV 193.80 nm f=0.4636 <S**2>=0.000
55A -> 59A 0.29252
57A -> 60A 0.39497
57A -> 61A 0.38184
58A -> 60A -0.13612
58A -> 61A 0.21243
58A -> 66A -0.14130
55B -> 59B 0.29252
57B -> 60B 0.39497
57B -> 61B 0.38184
58B -> 60B -0.13612
58B -> 61B 0.21243
58B -> 66B -0.14130

Excited State 100: 1.000-A 8.3368 eV 148.72 nm f=0.1121 <S**2>=0.000
53A -> 60A 0.64380
58A -> 76A -0.11043
53B -> 60B 0.64380
58B -> 76B -0.11043

5b (methanol)
Excited State 3: 1.000-A 3.8681 eV 320.53 nm f=0.4899 <S2>=0.000**
94A -> 95A 0.69054 (πHOMO-πLUMO, 95.4% contribution)
94B -> 95B 0.69054 (πHOMO-πLUMO, 95.4% contribution)

Excited State 14: 1.000-A 5.7908 eV 214.10 nm f=0.1397 <S**2>=0.000
89A -> 95A 0.11733
91A -> 95A 0.52727
93A -> 96A 0.32421
93A -> 97A -0.14171
94A -> 96A 0.16112
94A -> 97A 0.20967
89B -> 95B 0.11733
91B -> 95B 0.52727
93B -> 96B 0.32421
93B -> 97B -0.14171
94B -> 96B 0.16112
94B -> 97B 0.20967

Excited State 21: 1.000-A 6.0778 eV 203.99 nm f=0.6625 <S**2>=0.000
91A -> 95A -0.12170
93A -> 96A 0.46027
93A -> 97A 0.33002
94A -> 96A 0.11650
94A -> 97A -0.20960
94A -> 98A -0.18668
94A ->100A 0.21255
91B -> 95B -0.12170
93B -> 96B 0.46027
93B -> 97B 0.33002
94B -> 96B 0.11650
94B -> 97B -0.20960
94B -> 98B -0.18668
94B ->100B 0.21255

Excited State 23: 1.000-A 6.2189 eV 199.37 nm f=0.1213 <S**2>=0.000
91A -> 95A 0.12209
93A -> 96A -0.13967
93A -> 97A 0.48048
94A -> 96A 0.11172
94A ->100A -0.44410
91B -> 95B 0.12209
93B -> 96B -0.13967
93B -> 97B 0.48048
94B -> 96B 0.11172
94B ->100B -0.44410

Excited State 31: 1.000-A 6.5249 eV 190.02 nm f=0.1291 <S**2>=0.000
91A -> 95A -0.13550
93A -> 96A 0.20640
93A -> 97A -0.18189
94A ->100A -0.31430
94A ->102A 0.48231
94A ->103A 0.19090
91B -> 95B -0.13550
93B -> 96B 0.20640
93B -> 97B -0.18189
94B ->100B -0.31430
94B ->102B 0.48231
94B ->103B 0.19090

Excited State 34: 1.000-A 6.5517 eV 189.24 nm f=0.1498 <S**2>=0.000
91A -> 95A 0.14674
93A -> 96A -0.22398
93A -> 97A 0.18750
94A ->100A 0.35932
94A ->102A 0.43365
94A ->103A 0.17695
91B -> 95B 0.14674
93B -> 96B -0.22398
93B -> 97B 0.18750
94B ->100B 0.35932
94B ->102B 0.43365
94B ->103B 0.17695

Anion of 5b

Excited State 2: 1.000-A 3.3464 eV 370.50 nm f=0.6362 <S2>=0.000**
94A -> 95A 0.69604 (πHOMO-πLUMO, 96.9% contribution)
94B -> 95B 0.69604 (πHOMO-πLUMO, 96.9% contribution)

Excited State 39: 1.000-A 5.9396 eV 208.74 nm f=0.2555 <S**2>=0.000
92A -> 96A 0.56361
92A -> 97A 0.26843
92A ->100A 0.10673
93A -> 99A 0.16272
94A ->104A 0.16283
92B -> 96B 0.56361
92B -> 97B 0.26843
92B ->100B 0.10673
93B -> 99B 0.16272
94B ->104B 0.16283

Excited State 57: 1.000-A 6.3389 eV 195.59 nm f=0.1491 <S**2>=0.000
92A -> 96A -0.14615
92A -> 97A 0.24117
92A -> 98A 0.50296
92A -> 99A 0.23875
93A ->101A -0.12080
94A ->109A -0.15192
92B -> 96B -0.14615
92B -> 97B 0.24117
92B -> 98B 0.50296
92B -> 99B 0.23875
93B ->101B -0.12080
94B ->109B -0.15192

Excited State 55: 1.000-A 6.3058 eV 196.62 nm f=0.1427 <S**2>=0.000
92A -> 96A -0.17198
92A -> 97A 0.40966
92A -> 98A -0.30275
92A -> 99A -0.24092
92A ->100A 0.11406
93A ->101A -0.11625
94A ->108A -0.18768
92B -> 96B -0.17198
92B -> 97B 0.40966
92B -> 98B -0.30275
92B -> 99B -0.24092
92B ->100B 0.11406
93B ->101B -0.11625
94B ->108B -0.18768

Excited State 10: 1.000-A 4.4844 eV 276.48 nm f=0.1406 <S**2>=0.000
92A -> 95A 0.13103
94A -> 96A 0.65050
94A -> 97A -0.20284
92B -> 95B 0.13103
94B -> 96B 0.65050

94B -> 97B -0.20284

Excited State 42: 1.000-A 6.0032 eV 206.53 nm f=0.1350 <S**2>=0.000
92A -> 96A -0.19728
93A -> 98A -0.17568
93A -> 99A 0.49203
93A ->100A -0.18404
93A ->101A -0.23053
93A ->102A -0.18899
93A ->103A -0.20211
92B -> 96B -0.19728
93B -> 98B -0.17568
93B -> 99B 0.49203
93B ->100B -0.18404
93B ->101B -0.23053
93B ->102B -0.18899
93B ->103B -0.20211

Excited State 12: 1.000-A 4.7320 eV 262.01 nm f=0.1146 <S**2>=0.000
94A -> 96A 0.21457
94A -> 97A 0.64996
94A -> 98A 0.12094
94B -> 96B 0.21457
94B -> 97B 0.64996
94B -> 98B 0.12094