SUPPORTING INFORMATION

Freezing out the Vavilov's rule: temperature-dependent fluorescence of a rhodanine dye

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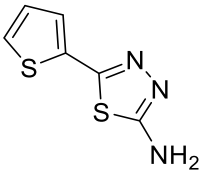
Synthesis of rhodanine-based monomer

5-(thiophen-2-yl)-1,3,4-thiadiazol-2-amine ***(2)***



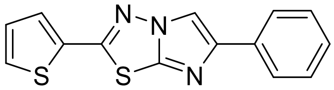
In a three-neck flask equipped with a condenser and maintained under nitrogen atmosphere, thiophene-2-carboxylic acid and thiosemicarbazide in equivalent ratio were placed. Subsequently, 1.85 equivalents of phosphorus oxychloride ($POCl_3$) were added through the addition funnel. The mixture was heated to reflux with stirring for 30 minutes with the formation of a green solution. The mixture was cooled to room temperature and water was slowly added until a yellowish coloration was obtained. The mixture was then refluxed for 4 hours and basified with a 5M NaOH solution until reaching pH = 8. The suspended white solid was filtered and dried.

^{1}H-NMR (600 MHz in DMSO): δ 7.63 (1H, dd, J = 1.3, 5.1 Hz, thiophene-**H**), 7.48 (2H, s, N**H₂**), 7.42 (1H, dd, J = 1.2, 3.7 Hz, thiophene-**H**), 7.13 (1H, dd, J = 3.5, 5.1 Hz, thiophene-**H**)

IR ν (cm^{-1}): 3277; 3089; 1618; 1510

Yield: 92%

6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazole ***(3)***



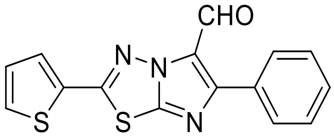
In a flask, one equivalent of the first intermediate (**2**) and 1.3 equivalents of phenacyl bromide were dissolved in ethanol. The mixture was refluxed under nitrogen for 24 hours. Subsequently, the excess of ethanol was removed using a rotary evaporator. The obtained solid was suspended in water and refluxed for 4 hours. The mixture was then neutralized with a 10% Na_2CO_3 solution. After filtration, a yellow solid was obtained. The product was purified by column chromatography on silica using a petroleum ether: ethyl acetate (8:2) mixture as the eluent.

^{1}H-NMR (600 MHz in DMSO): δ 8.71 (1H, s, imidazole-**H**), 7.93 (1H, dd, *J* = 1.2, 5.0 Hz, thiophene-**H**), 7.89 – 7.87 (2H, dd, phenyl-**H**), 7.86 (1H, dd, *J* = 1.2, 3.7 Hz, thiophene-**H**), 7.42 (2H, dd, phenyl-**H**), 7.30 (1H, dd, phenyl-**H**), 7.27 (1H, dd, J = 3.7, 5.0 Hz, thiophene-**H**).

IR ν (cm^{-1}): 3064; 1602; 1490

Yield: 78%

6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazole-5-carbaldehyde ***(4)***



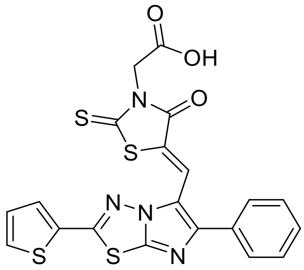
In a three-neck flask, 5 equivalents of DMF, previously dehydrated using molecular sieves, were placed and cooled in an ice bath. Using a syringe, 5 equivalents of phosphorus oxychloride ($POCl_3$) were added dropwise. The solution was stirred for 45 minutes until a dense yellow liquid containing a precipitate formed, indicating the production of the Vilsmeier salt. The second (**3**) intermediate was dissolved in DMF and then placed in the addition funnel. This solution was added dropwise to the suspension containing the Vilsmeier salt at room temperature. The mixture was then heated to reflux for 6 hours. After this step, the mixture was poured in flask in the presence of ice, followed by neutralization with a 5M NaOH solution. The orange precipitate was filtered and dried.

^{1}H-NMR (600 MHz in DMSO): δ 10.01 (1H, s, Ar-C**H**O), 8.01-7.96 (4H, m, Ar-**H**), 7.57 –7.51 (3H, m, Ar-**H**), 7.35 – 7.29 (1H, m, Ar-**H**).

IR ν (cm^{-1}): 3079; 1668; 1542; 1505

Yield: 82%

*(Z)-2-(4-oxo-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetic acid **(5)***



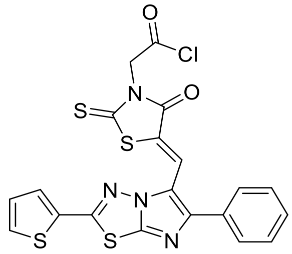
The Knoevenagel condensation was carried out by dissolving one equivalent of the third intermediate (**4**), 1.3 equivalents of rhodanine-3-acetic acid, and 2 equivalents of ammonium acetate in glacial acetic acid inside a flask. The flask was connected to a condenser under an inert nitrogen atmosphere. The mixture was heated to reflux for 4 hours. As the reaction progressed, a yellow suspended solid formed. At the end of the reaction, the solid was filtered and dried.

^{1}H-NMR (600 MHz in DMSO): δ 11.97 (1H, bs, -COO**H**), 8.06 (1H, dd, thiophene-**H**), 8.00 (1H, dd, thiophene-**H**), 7.80 (1H, s, -C**H**=rhodanine), 7.72 (2H, dd, phenyl-**H**), 7.58 (3H, m, phenyl-**H**), 7.33 (1H, dd, thiophene-**H**), 4.70 (2H, s, -C**H₂**COOH).

IR ν (cm^{-1}): 1736; 1705; 1585; 1312

Yield: 76%

*(Z)-2-(4-oxo-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetyl chloride **(6)***



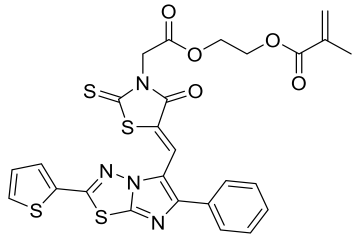
The carboxylic acid previously prepared (**5**) was placed in a flask, and a catalytic amount of N,N-dimethylformamide (DMF) was added. The flask was connected to a dropping funnel containing oxalyl chloride dissolved in dichloromethane, with an excess of oxalyl chloride with respect to the carboxylic acid. The reaction was conducted at room temperature for 1 hour under an inert nitrogen atmosphere. The mixture was dried with sodium sulfate and filtered. The excess of dichloromethane was removed using a rotary evaporator.

^{1}H-NMR (600 MHz, DMSO): δ 8.07 (1H, dd, *J* = 1.2, 5.0 Hz, thiophene-**H**), 8.01 (1H, dd, *J* = 1.2, 3.7 Hz, thiophene-**H**), 7.81 (1H, s, -C**H**=rhodanine), 7.74 – 7.70 (2H, m, phenyl--**H**), 7.63 – 7.52 (3H, m, phenyl--**H**), 7.34 (1H, dd, *J* = 3.8, 5.1 Hz, thiophene-**H**), 4.74 (2H, s, -C**H₂**COOH).

IR ν (cm^{-1}): 1791; 1703; 1585; 1312

Yield: >95%

(Z)-2-(2-(4-oxo-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetoxy)ethyl methacrylate **(7)**



In a flask, equimolar amounts of 2-hydroxyethyl methacrylate (HEMA) and triethylamine were dissolved in dichloromethane. The flask was placed in an ice bath, and an equimolar amount of acyl chloride (**6**) dissolved in dichloromethane was added dropwise at 0°C. The reaction mixture was then maintained at room temperature for 6 hours under an inert nitrogen atmosphere. The mixture was washed with a 1% NaOH solution, resulting in the formation of a precipitate. The suspended solid was separated by filtration, and the organic phase was further washed with the 1% NaOH solution, 1% HCl solution and brine. The solution was then dried and filtered. The excess of dichloromethane was removed using a rotary evaporator.

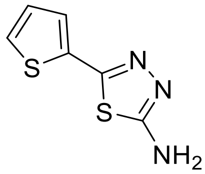
^{1}H-NMR (600 MHz in DMSO): δ 8.07 (1H, dd, *J* = 1.2, 5.0 Hz, thiophene-**H**), 8.01 (1H, dd, *J* = 1.2, 3.8 Hz, thiophene-**H**), 7.81 (1H, s, -C**H**=rhodanine), 7.73 – 7.70 (2H, m, phenyl--**H**), 7.63 – 7.56 (3H, m, phenyl--**H**), 7.34 (1H, dd, *J* = 3.8, 5.0 Hz, thiophene-**H**), 6.01 (1H, s, -C=C**H₂**), 5.63 (1H, s, -C=C**H**2), 4.87 (2H, s, -C**H2**COO-), 4.40 (2H, t, -OC**H₂**CH₂O-CO), 4.30 (2H, t, -OCH₂C**H₂**O-CO), 1.84 (3H, s, -C**H₃**)

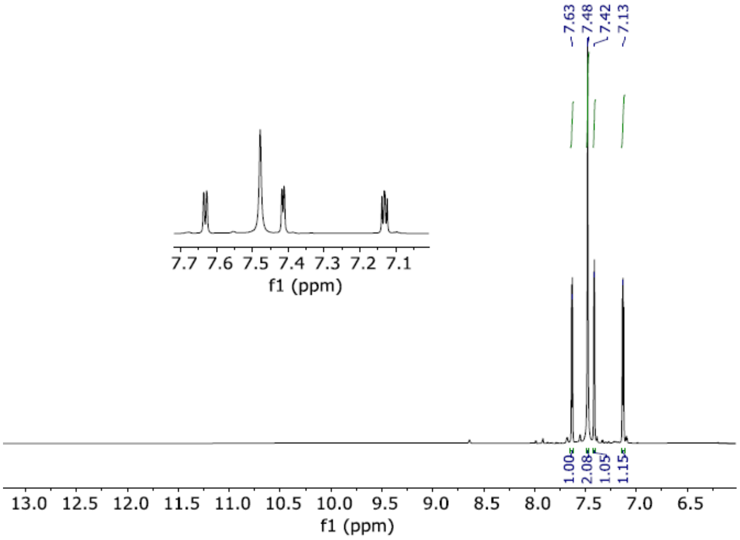
IR ν (cm^{-1}): 2932; 1738; 1706; 1635; 1585; 1317

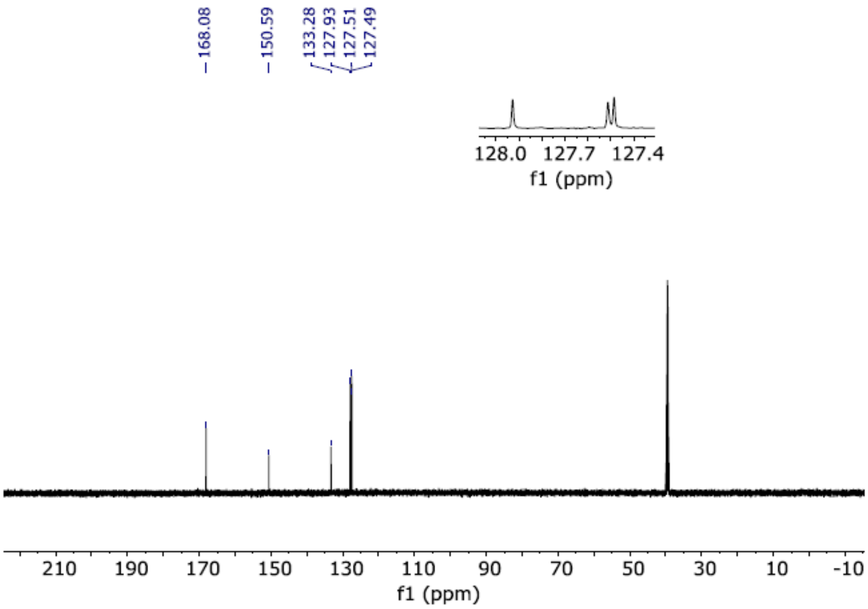
Yield: 78%

NMR and FT-IR Characterization

5-(thiophen-2-yl)-1,3,4-thiadiazol-2-amine ***(2)***







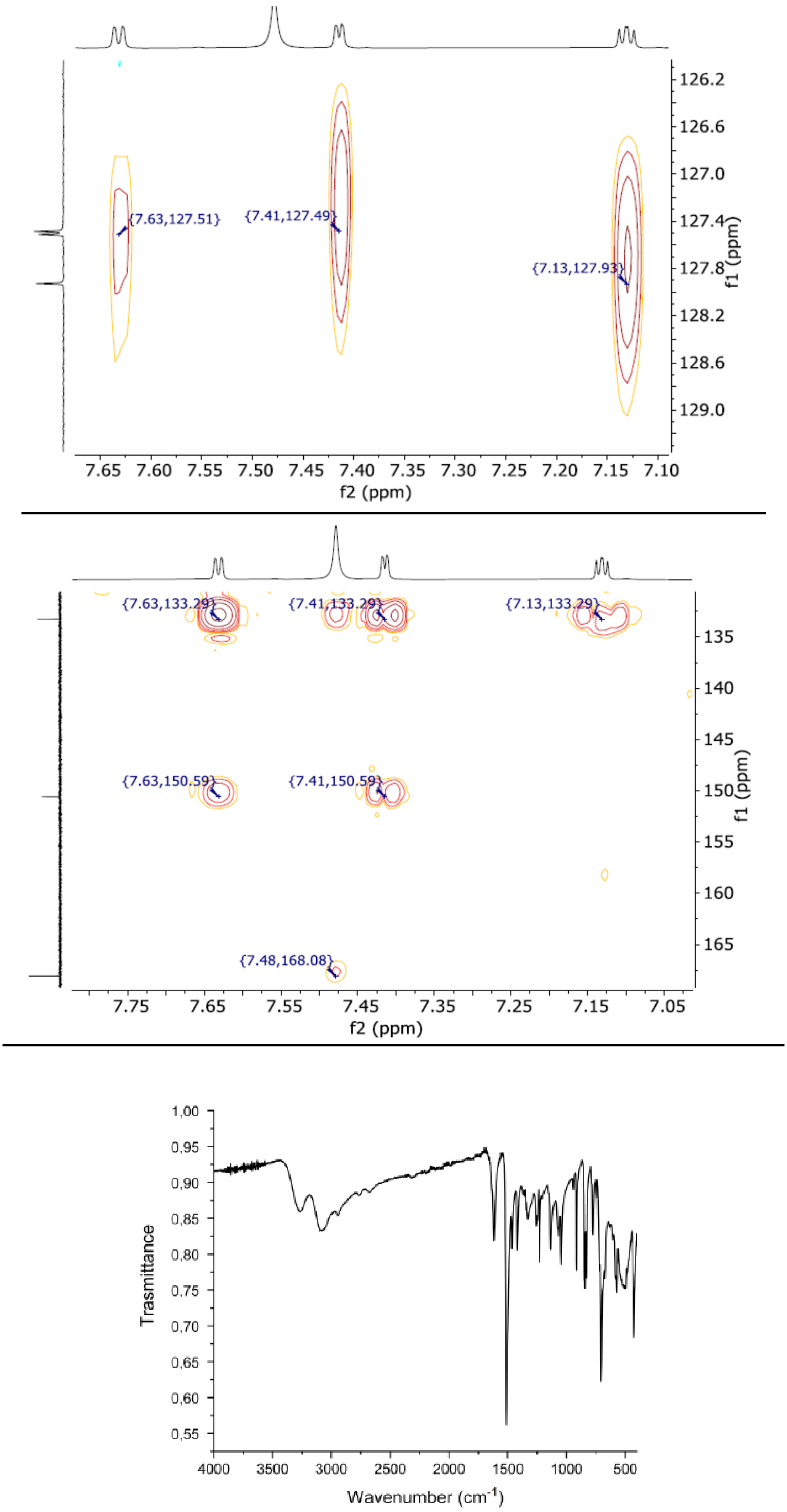
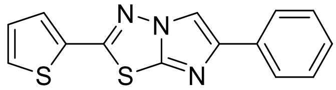
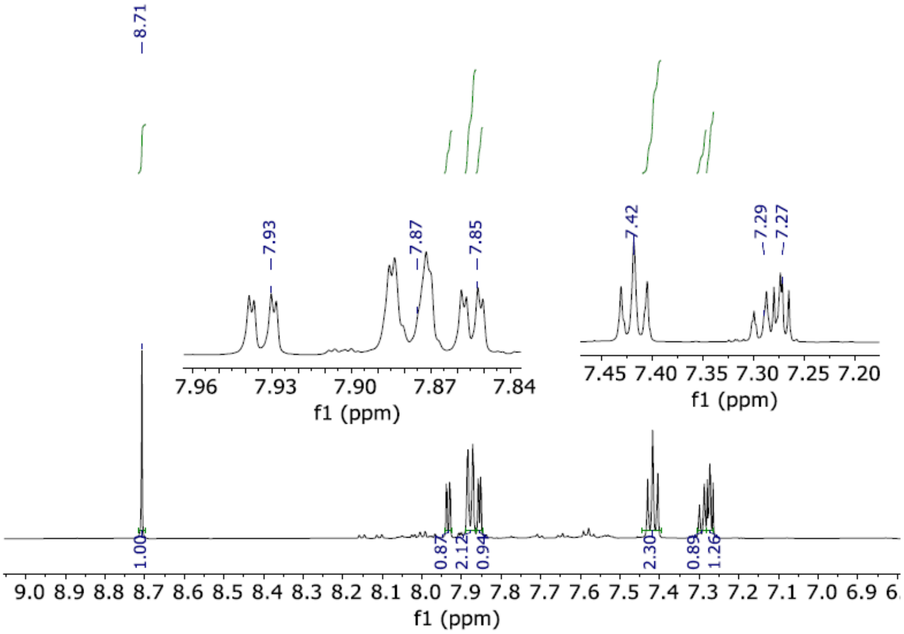
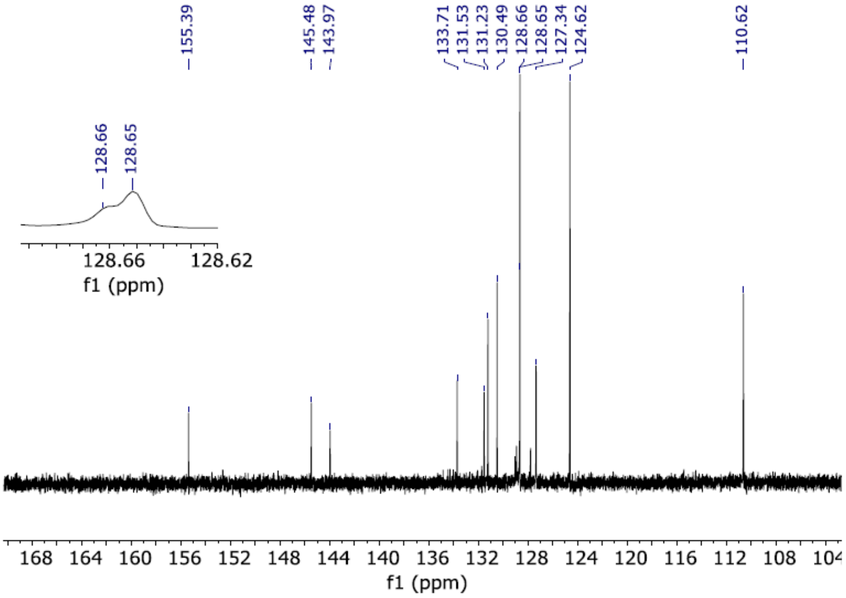


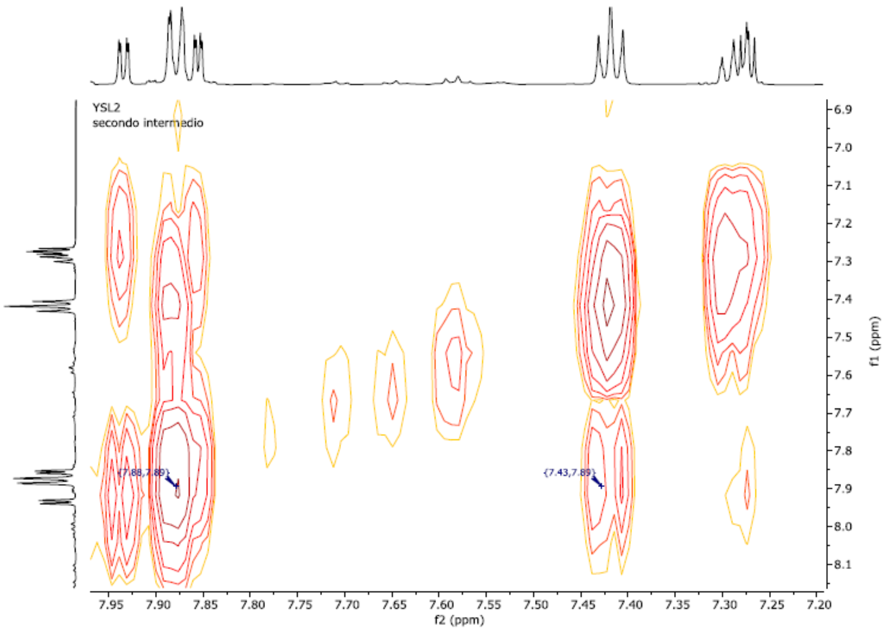
Figure S1: ^{1}H-NMR, ^{13}C-NMR, HSQC, HMBC and FT-IR spectra of **2**

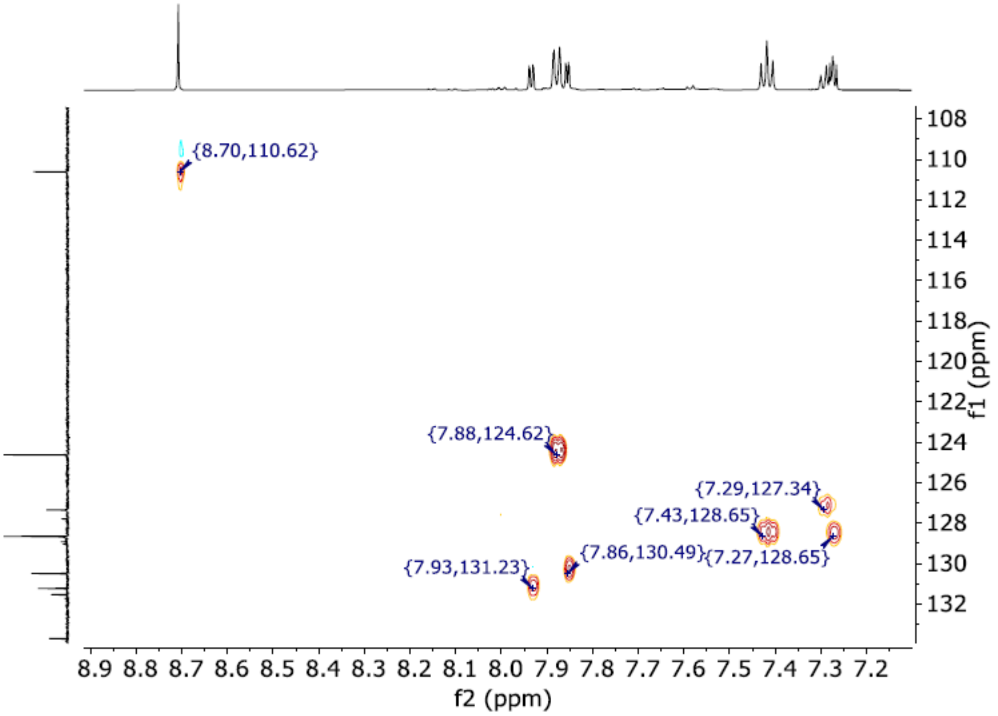
*6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazole **(3)***








YSL2
secondo intermedio
{7.88,7.89}
{7.43,7.89}
7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f2 (ppm)
6.9 7.0 7.1 7.2 7.3 7.4 7.5 7.6 7.7 7.8 7.9 8.0 8.1
f1 (ppm)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{7.88,124.62}
{7.29,127.34}
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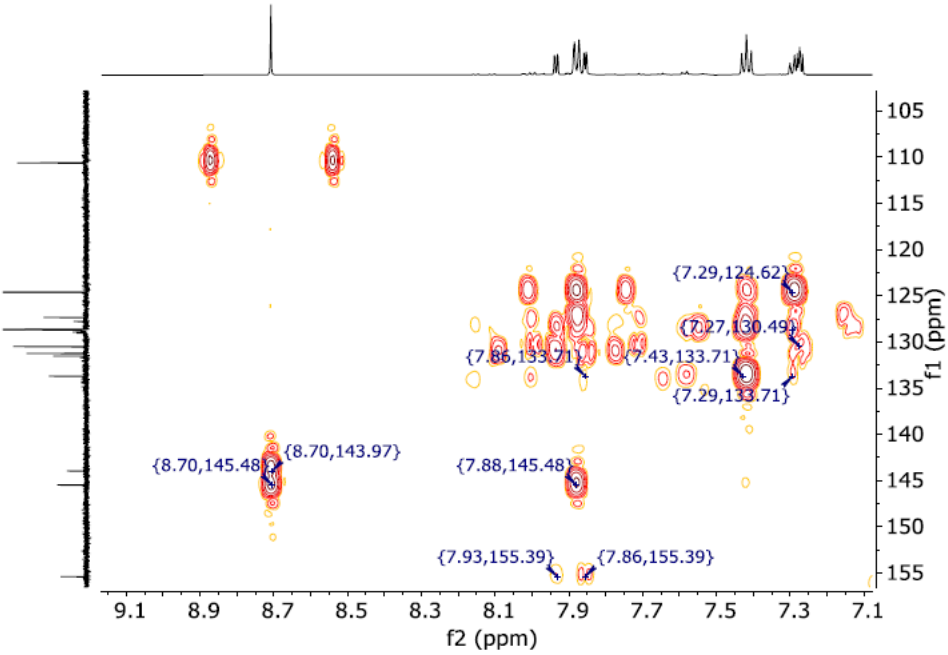
{7.27,128.65}
{7.93,131.23}
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f2 (ppm)
108 110 112 114 116 118 120 122 124 126 128 130 132
f1 (ppm)



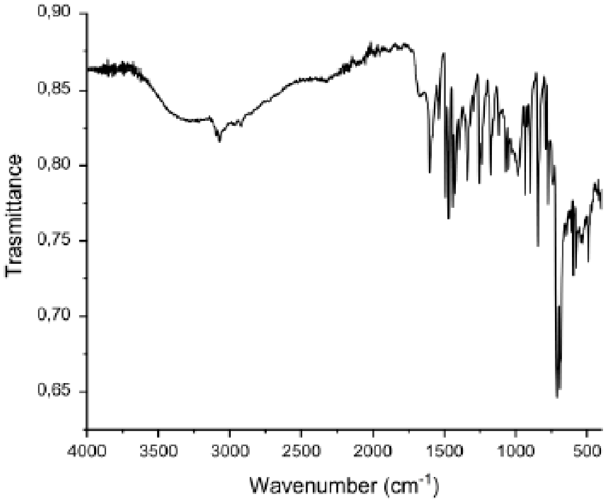
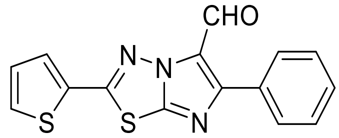


Figure S2: ^{1}H-NMR, ^{13}C-NMR, COSY, HSQC, HMBC, and FT-IR spectra of **3**

6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazole-5-carbaldehyde ***(4)***



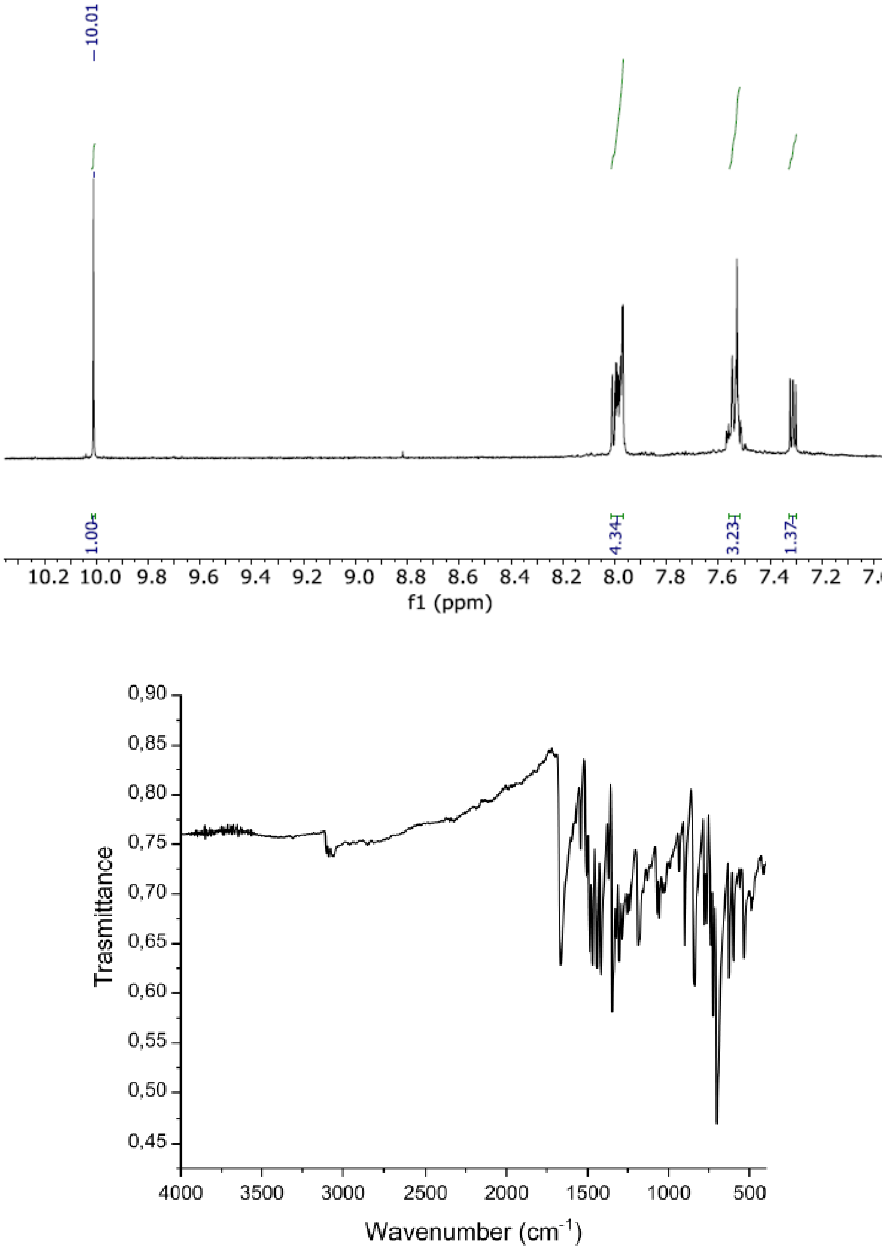
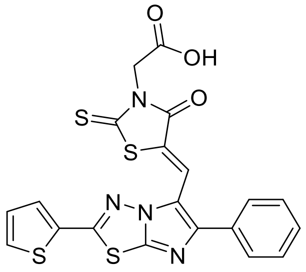


Figure S3: ^{1}H-NMR and FT-IR spectra of **4**

(Z)-2-(4-oxo-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetic acid ***(5)***



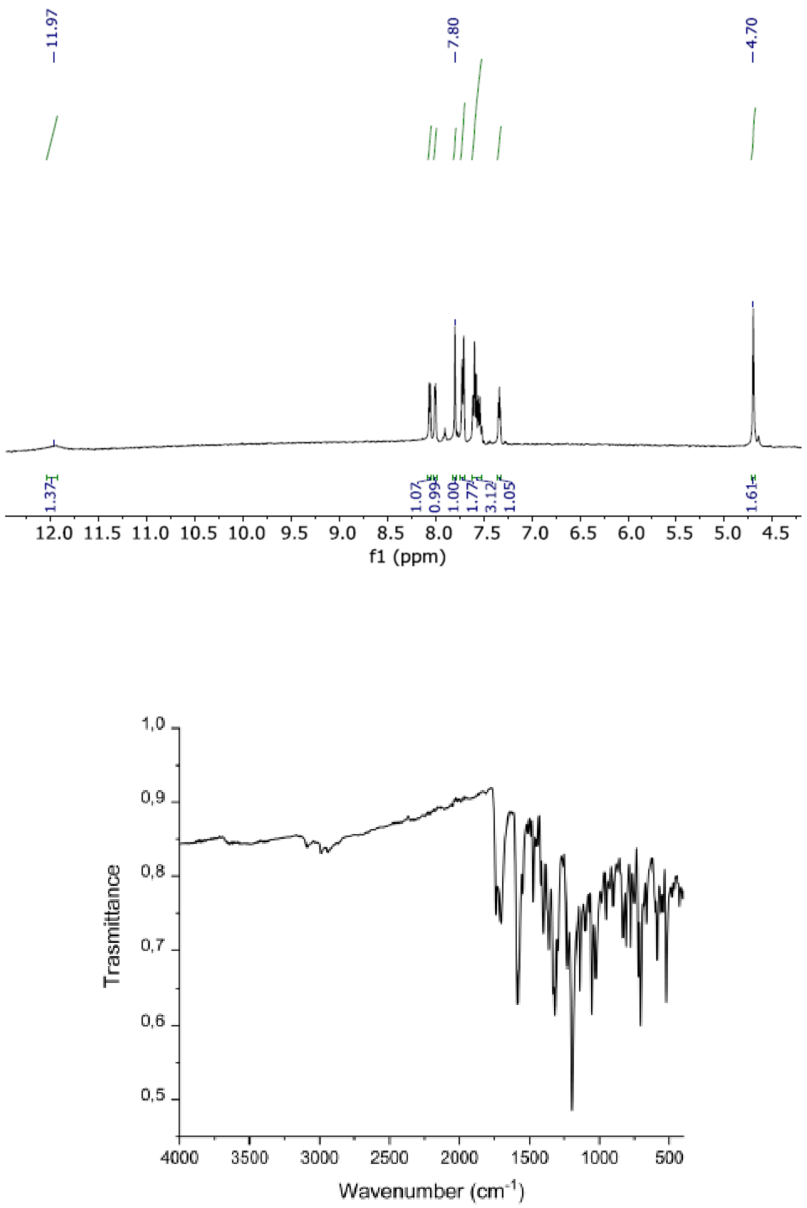
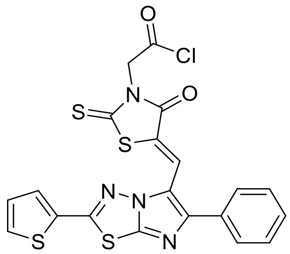


Figure S4: ^{1}H-NMR and FT-IR spectra of **5**

(Z)-2-(4-oxo-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetyl chloride ***(6)***



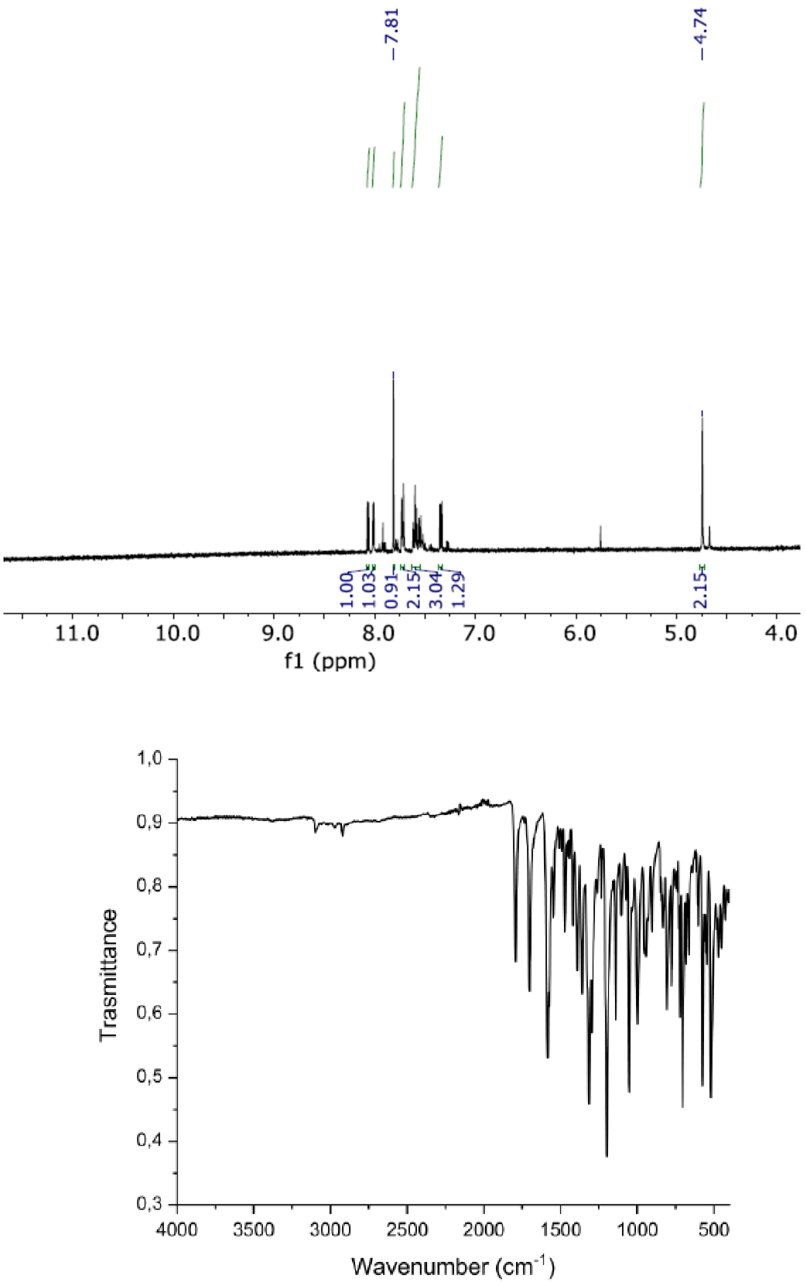
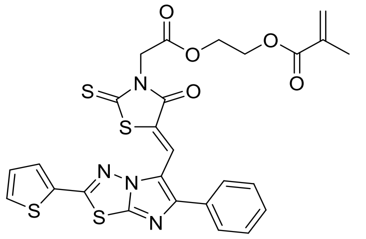


Figure S5: ^{1}H-NMR and FT-IR spectra of **6**

(Z)-2-(2-(4-oxo-5-((6-phenyl-2-(thiophen-2-yl)imidazo[2,1-b][1,3,4]thiadiazol-5-yl)methylene)-2-thioxothiazolidin-3-yl)acetoxy)ethyl methacrylate **(7)**



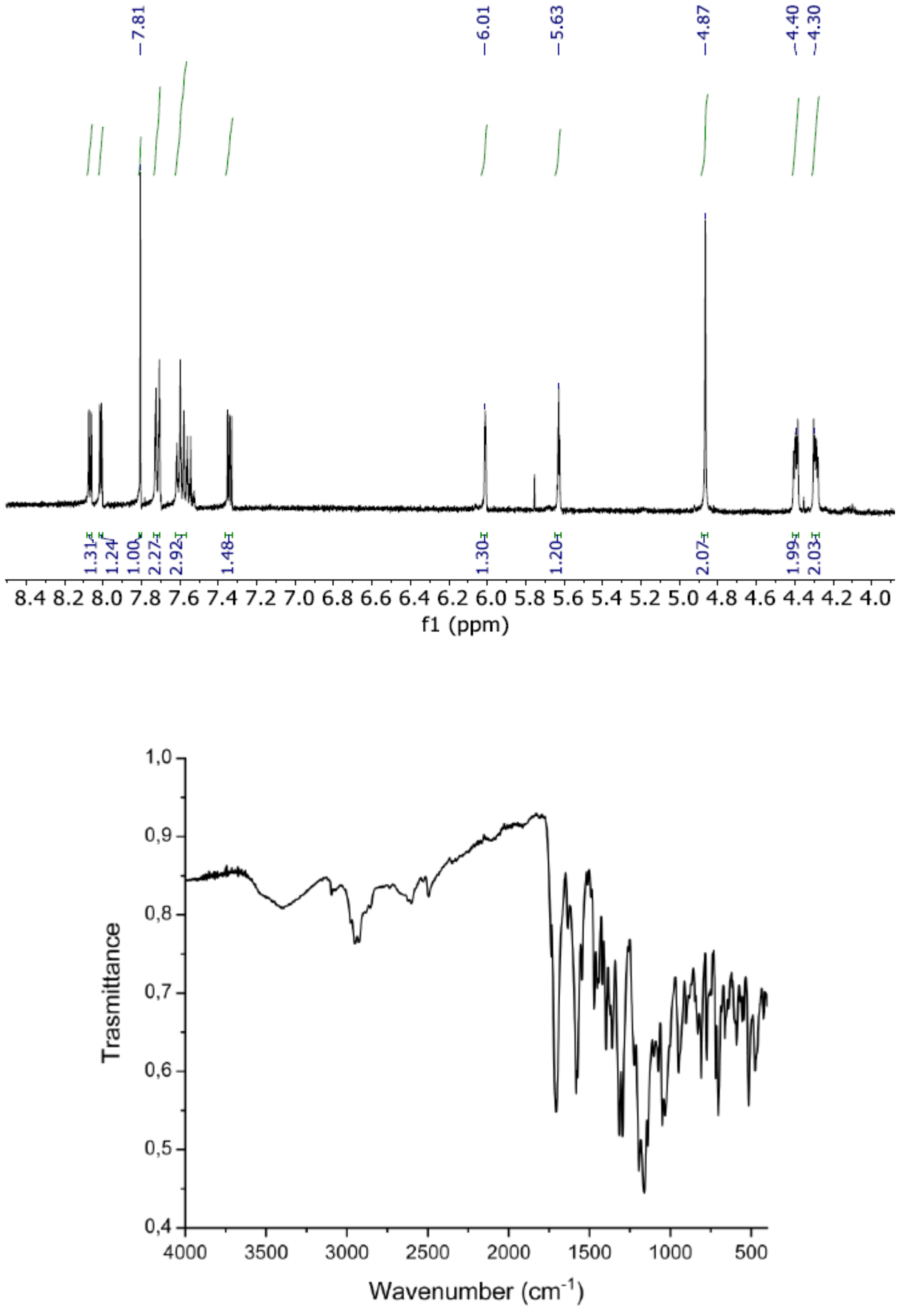


Figure S6: ^{1}H-NMR and FT-IR spectra of **7**

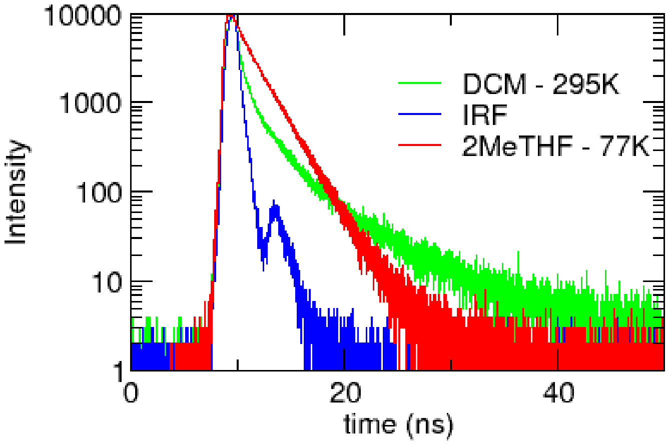


Figure S7. Fluorescence decays and Instrument response function (IRF) in DCM at r.T. and 2MeTHF at 77K.

Table S1. In DCM, the lifetimes were obtained from a reconvolution fit of the fluorescence decays shown in Figure S7, taking into account the instrument response function (IRF). The first ~2 nanoseconds of the decay were excluded from the fitting procedure, as this portion overlaps significantly with the IRF. Including it would result in artificially short lifetimes, below the time resolution of the instrument. At 77 K, the IRF was not measured under the same experimental conditions as the sample. Nevertheless, a reasonable estimation of the lifetime can still be obtained by excluding the initial nanoseconds of the decay, where the IRF contribution is most significant. As in the case of DCM at room temperature, the first ~2 nanoseconds were omitted from the fitting.

Solvent	**T1 (ns)**	**%**	**T2 (ns)**	**%**
DCM -295K	0.82	71	3.26	29
2Me-THF-77K	2.05	100		

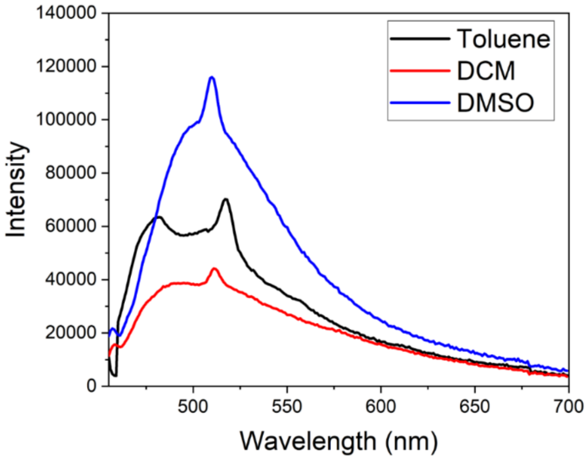


Figure S8: Raw emission spectra of **7**

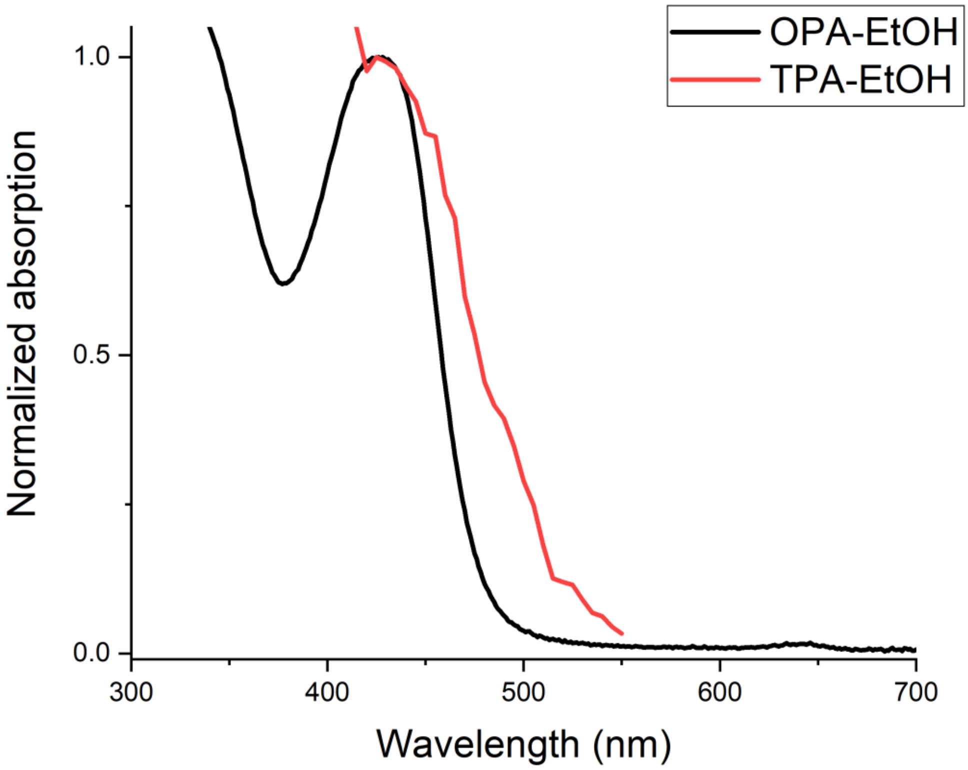


Figure S9: One photon absorption and two photon absorption spectra of **7** in ethanol

Table S2. Gas-phase energies obtained from geometry optimization of the ground state minimum (CAM-B3LYP/6-31g(d); B3LYP/6-31g(d)).

Functional	**Ground State Energy of the lowest minimum (Hartree) and geometry**

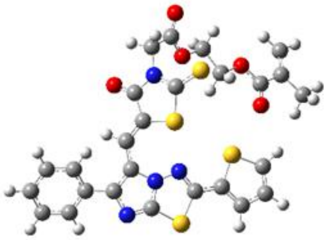
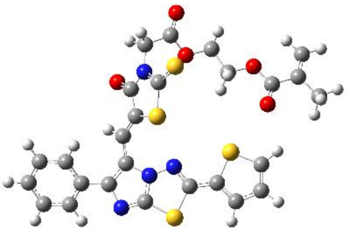
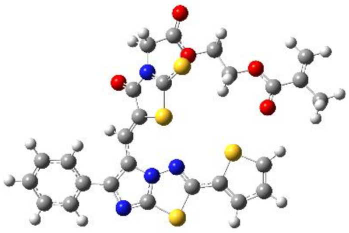
CAM-B3LYP	-3189.875403 
B3LYP	-3190.67660 
M062X	-3189.9213 

Table S3: Computational results obtained from TD-DFT/B3LYP/6-31g(d) and TD-DFT/M062X/6-31g(d) calculations in gas phase.

	Excited state	**Energy (eV)**	**Oscillator strength**
CAM-B3LYP	1	3.2600	0.0013
	2	3.4009	0.6625
	3	3.9947	0.4583

	4	4.2131	0.0364
B3LYP	1	2.8637	0.0378
	2	2.9008	0.4789
	3	3.1061	0.0345
	4	3.2968	0.2056
M062X	1	3.1400	0.0001
	2	3.3696	0.6486
	3	3.9885	0.4138
	4	4.1513	0.0427

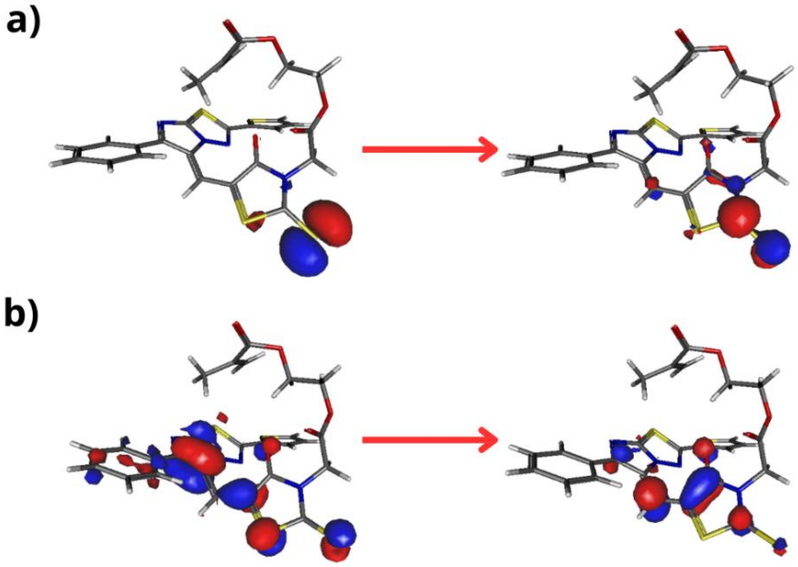


Figure S10: a) Dominant NTO of the dark optimized S_1(nπ*) **b)** Dominant NTO of the bright optimized S_1(ππ*)

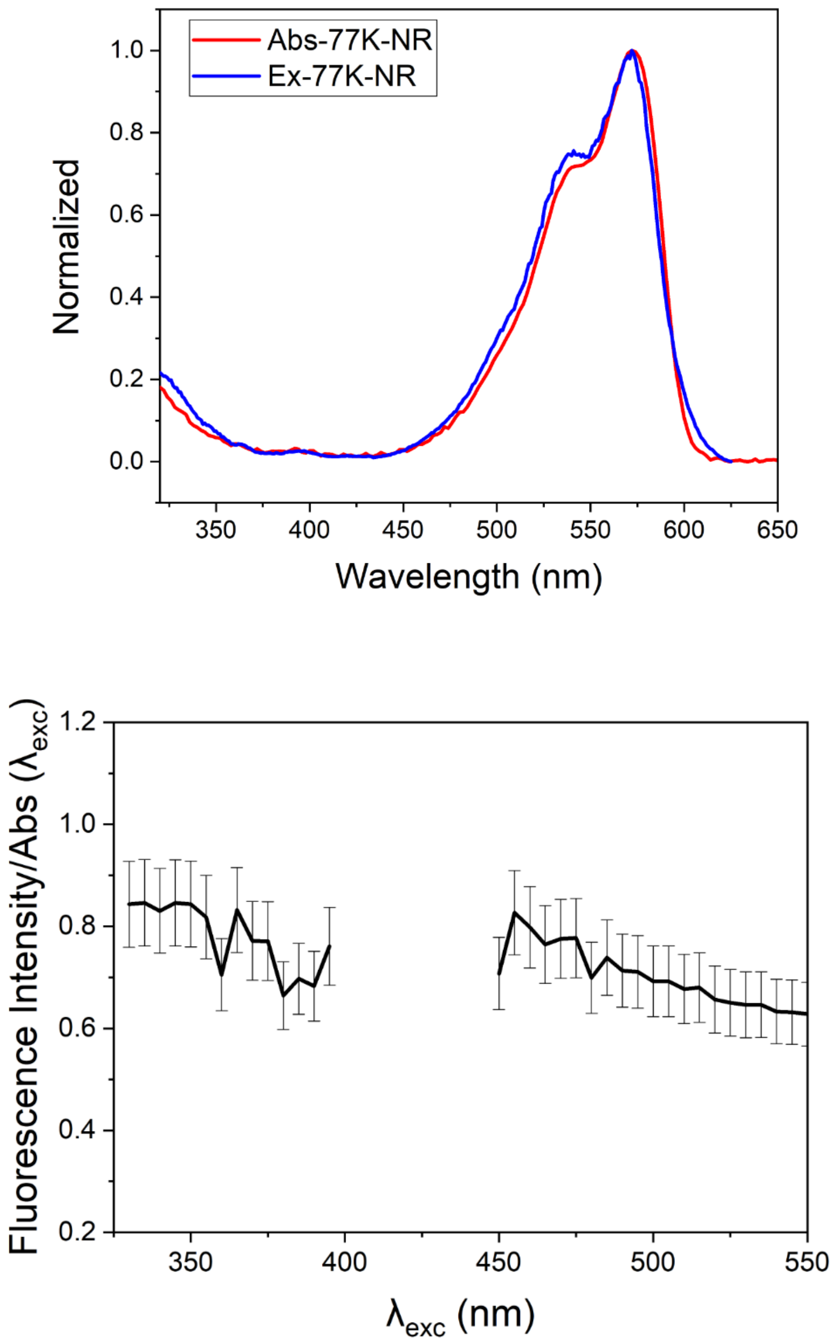


Figure S11: Top: comparison between the excitation and absorbance spectra of **7** measured in 2Me-THF at 77K; Bottom: excitation wavelength dependence of a quantity proportional to the fluorescence quantum yield (ratio between the integrated fluorescence intensity and the absorbance at the excitation wavelength). The ratio has been calculated from experimental data collected at 77K. Error bar: ± 10%. Results are not shown in the 400-450nm region because the absorbance signal is too low.

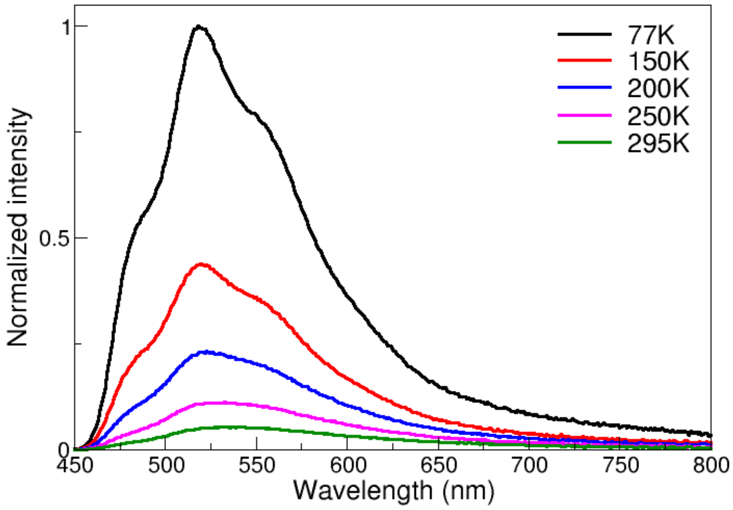


Figure S12: Emission spectra collected from **7** dispersed in a polystyrene thin film at different temperatures. All spectra were collected opening the slits at 2 nm.

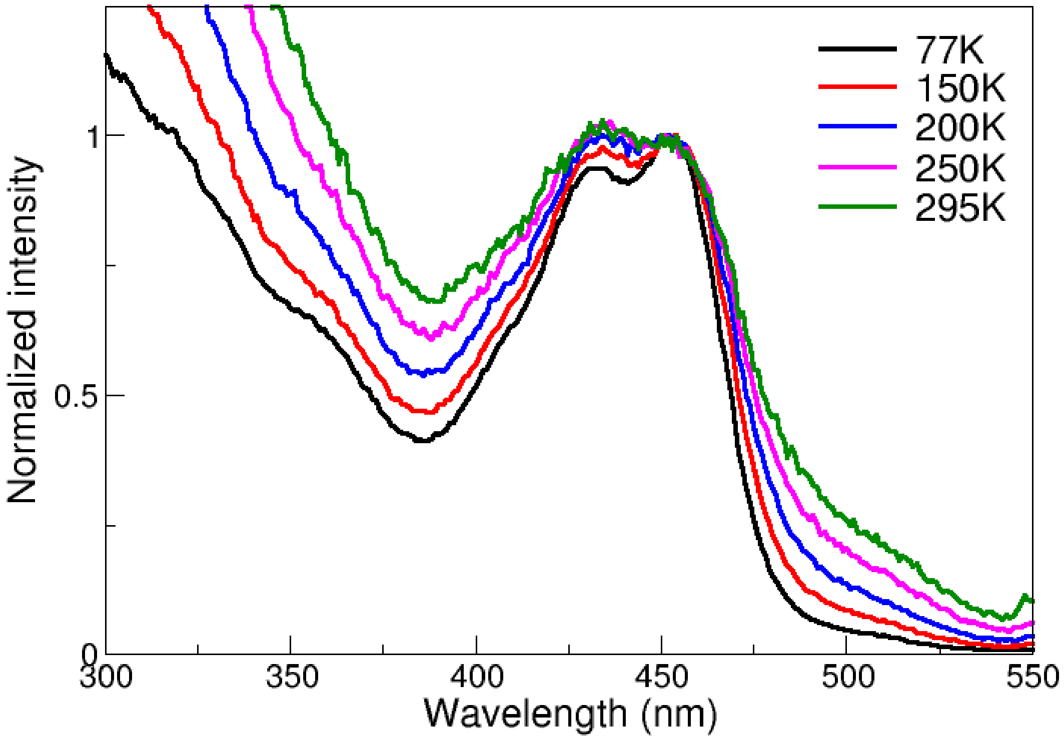


Figure S13: Excitation spectra collected from **7** dispersed in polystyrene with a concentration of 1 mg ml^{-1} collected at different temperatures. The opening of the slits for the measurements carried out was 2 nm.

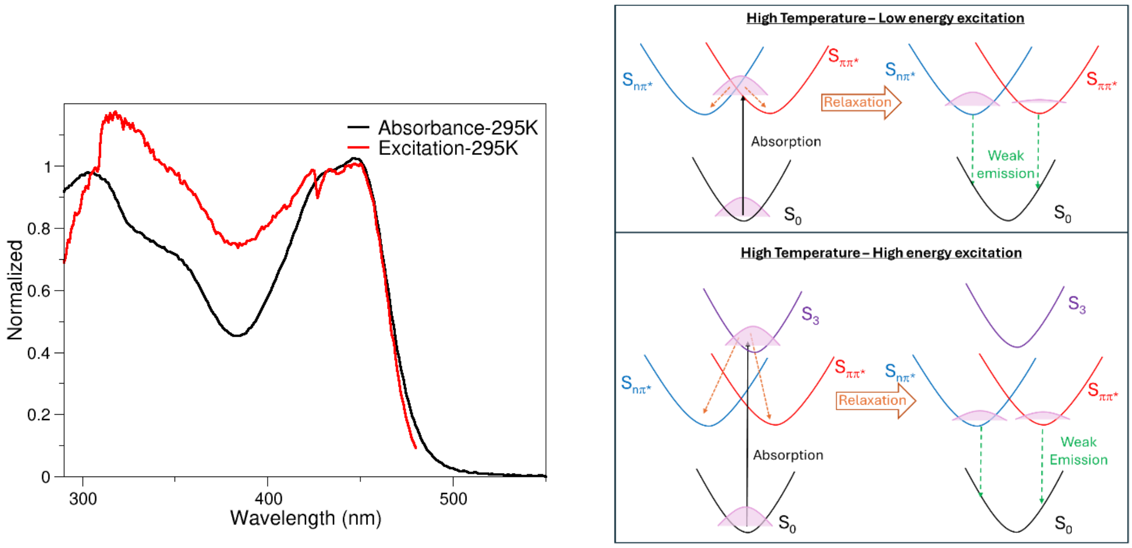


Figure S14: Left panel: comparison between the excitation and absorbance spectra of **7** measured in toluene at 295K. Right panel: qualitative description of the effect of the branching of population. Exciting at high energy, we observe an increment of emission intensity, which is the result of the branching of population, but possibly with different ratios compared to that occurring when exciting at low energy.

Cartesian coordinates of the minimum optimized using MP2/cc-pVDZ

S	0.9334103	-5.8520837	-0.3270933
C	0.5605547	-4.2106593	-0.7531710
C	-0.0279213	-4.1307912	-2.0182624
C	-0.1726283	-5.4047039	-2.6255025
C	0.2964050	-6.4371837	-1.8201194

C	0.8555469	-3.0871095	0.1184292
N	1.0658547	-1.8739900	-0.3805808
N	1.1953273	-1.0214716	0.6600378
C	1.1883308	-1.5270400	1.9515050
S	0.8545542	-3.2311002	1.8825914
N	1.4373595	-0.6047289	2.8780804
C	1.6186783	0.5531723	2.1427321
C	1.4722206	0.3313277	0.7423181
C	1.9212022	1.8249549	2.8067980
C	2.5446255	1.8051463	4.0766337
C	2.8601794	3.0048865	4.7283631
C	2.5617849	4.2419514	4.1264593
C	1.9302615	4.2697562	2.8716179
C	1.6027747	3.0716720	2.2159955
C	1.6749670	1.2250945	-0.3685909
C	0.9843557	1.2205747	-1.5537426
C	-0.2873489	0.5038091	-1.8088013
N	-0.7818478	0.8692419	-3.0732789
C	-0.0758064	1.8067043	-3.8085113
S	1.3860126	2.2697428	-2.9172418
C	-2.0793872	0.3521850	-3.4662550
S	-0.4679723	2.4166565	-5.2826372
O	-0.8944668	-0.2565065	-1.0633347
C	-3.0983207	0.7031188	-2.3896412

O	-3.0366635	1.6850678	-1.6801466
O	-4.0672937	-0.2383027	-2.3523112
C	-4.9468256	-0.1085591	-1.2100100
C	-4.2652473	-0.7749437	-0.0107965
O	-4.8481501	-0.2754269	1.1986821
C	-4.2330651	0.8481642	1.7214628
O	-4.8973815	1.7986296	2.0724901
C	-2.7460693	0.7776009	1.9267916
C	-2.1858503	-0.3671324	2.3836482
C	-1.9934548	2.0664277	1.7423197
H	-0.3437406	-3.1755680	-2.4445198
H	-0.6141879	-5.5742223	-3.6106450
H	0.3033365	-7.5080349	-2.0300384
H	2.7729725	0.8375175	4.5333267
H	3.3452895	2.9773207	5.7099142
H	2.8093472	5.1776366	4.6383720
H	1.6721290	5.2274151	2.4073994
H	1.0624117	3.1056898	1.2646476
H	2.4683754	1.9732078	-0.2325557
H	-2.3519747	0.8268403	-4.4220665
H	-2.0378533	-0.7400284	-3.5934813
H	-5.1329834	0.9537994	-0.9941773
H	-5.8849413	-0.6028062	-1.4957567
H	-4.4160262	-1.8658523	-0.0181780

H	-3.1836147	-0.5706965	-0.0508911
H	-1.1269227	-0.4015847	2.6607711
H	-2.7886187	-1.2715846	2.5176433
H	-2.4589054	2.8647164	2.3433074
H	-0.9419658	1.9466195	2.0433136
H	-2.0365692	2.3763073	0.6830925

Cartesian coordinates of the S1 minima with nπ* character optimized using ADC(2)/cc-pVDZ

S	0.8771681	-5.6176053	-0.3381235
C	0.4005967	-3.9721270	-0.6130831
C	-0.4400061	-3.8576844	-1.7235809
C	-0.6903847	-5.1123746	-2.3372910
C	-0.0485231	-6.1624095	-1.6891642
C	0.8338246	-2.8665511	0.2236453
N	0.9934279	-1.6547488	-0.2938330
N	1.2098521	-0.7976137	0.7272005
C	1.3192412	-1.3000044	2.0200110
S	1.0115996	-3.0127100	1.9796391
N	1.6456928	-0.3739023	2.9163722
C	1.7416475	0.7833622	2.1620370
C	1.4855712	0.5564547	0.7793998
C	2.0302146	2.0757643	2.7885597
C	2.8245094	2.1279007	3.9573833
C	3.1088518	3.3601750	4.5623820
C	2.6059625	4.5555362	4.0146237

C	1.8004463	4.5086151	2.8639496
C	1.5057216	3.2777149	2.2558602
C	1.6482125	1.4445660	-0.3414902
C	0.9852369	1.3978066	-1.5465570
C	-0.2595213	0.6495677	-1.8445256
N	-0.6325596	0.8809127	-3.1691230
C	0.0494449	1.8806301	-3.8597722
S	1.4230908	2.4537231	-2.8943523
C	-1.9024331	0.3361536	-3.6157661
S	0.2739164	1.7797422	-5.6287837
O	-0.9406695	-0.0357131	-1.0748841
C	-3.0150564	0.8330465	-2.6943844
O	-2.9978756	1.8965115	-2.1175426
O	-3.9979728	-0.0955814	-2.6255917
C	-4.9124303	0.1193642	-1.5223541
C	-4.2546717	-0.5069047	-0.2969533
O	-4.9583813	-0.0507519	0.8652992
C	-4.2030956	0.4720620	1.8889529
O	-4.6848045	1.3042145	2.6253659
C	-2.8172387	-0.0836438	2.0890148
C	-2.6406551	-1.4234060	2.1505597
C	-1.7217586	0.9191444	2.3305515
H	-0.8534073	-2.8918267	-2.0257254
H	-1.3287341	-5.2585182	-3.2121258

H	-0.0692214	-7.2243179	-1.9393194
H	3.2102149	1.1921081	4.3738121
H	3.7282114	3.3914985	5.4651076
H	2.8310543	5.5162842	4.4893977
H	1.3828325	5.4316235	2.4479839
H	0.8351749	3.2401275	1.3906892
H	2.4168428	2.2178801	-0.2033568
H	-2.0930762	0.6739650	-4.6476263
H	-1.8766207	-0.7635643	-3.5958912
H	-5.0747140	1.1941880	-1.3606660
H	-5.8538095	-0.3703892	-1.8045252
H	-4.2896730	-1.6084377	-0.3539759
H	-3.1979028	-0.2020807	-0.2710847
H	-1.6606786	-1.8470454	2.3920753
H	-3.4708946	-2.1152279	1.9735453
H	-2.0770564	1.7109442	3.0098332
H	-0.8358706	0.4353702	2.7693425
H	-1.4245999	1.3890267	1.3752637

Cartesian coordinates of the S1 minima with ππ* character optimized using ADC(2)/cc-pVDZ

S	0.9301642	0.2875720	0.8189334
C	0.4451479	0.3150513	2.4852511
C	1.5418629	0.4376704	3.3458635
C	2.7676401	0.5087072	2.6362382
C	2.5917438	0.4473238	1.2566499

C	-0.9291102	0.2059607	2.9269751
N	-1.2282976	-0.3948801	4.0676225
N	-2.5350408	-0.1631454	4.3200264
C	-3.2994034	0.5201100	3.3734395
S	-2.2734266	1.0211288	2.0754849
N	-4.5819046	0.6442744	3.7231681
C	-4.6433785	0.0477939	4.9586223
C	-3.3494289	-0.5119569	5.3680906
C	-5.8616752	0.0409203	5.7415930
C	-7.0993243	0.3396164	5.1082971
C	-8.2826859	0.3573236	5.8526405
C	-8.2569281	0.0970539	7.2384810
C	-7.0332843	-0.1768576	7.8781453
C	-5.8433347	-0.2103820	7.1422640
C	-2.9906217	-1.3690301	6.4585370
C	-1.7578431	-1.2863033	7.1531226
C	-0.8000671	-0.2041767	7.0859885
N	0.2626090	-0.4658601	7.9872332
C	0.2024628	-1.5894625	8.7655177
S	-1.2909746	-2.4562233	8.3551626
C	1.3595593	0.4806973	8.0534816
S	1.3037497	-2.1497128	9.8885177
O	-0.8152650	0.8252647	6.3638409
C	0.8079338	1.8870742	8.2298519

O	-0.1124454	2.1880622	8.9573677
O	1.5378627	2.7521244	7.4767713
C	0.9659511	4.0702652	7.3756210
C	-0.0307538	4.0311982	6.2266262
O	-0.6310157	5.3389940	6.1733068
C	-1.9034760	5.3961330	5.6681446
O	-2.7048545	6.1866523	6.1125822
C	-2.2214417	4.5155498	4.4877531
C	-1.3720431	4.5079818	3.4343117
C	-3.5643088	3.8357704	4.5030735
H	1.4063953	0.5028706	4.4295052
H	3.7496260	0.6162761	3.1034651
H	3.3554160	0.4798015	0.4777866
H	-7.1023785	0.5463607	4.0338354
H	-9.2343964	0.5759179	5.3570692
H	-9.1855042	0.1154570	7.8187732
H	-7.0047089	-0.3572357	8.9579553
H	-4.8899365	-0.3882094	7.6483361
H	-3.7574403	-2.0751811	6.7971706
H	1.9778577	0.2039388	8.9225470
H	1.9664346	0.4298189	7.1367923
H	0.4685213	4.3559994	8.3131588
H	1.7998539	4.7548438	7.1645686
H	0.4875554	3.7821736	5.2855753

H	-0.7857114	3.2514120	6.4200928
H	-1.6281249	3.9856903	2.5070616
H	-0.4225462	5.0514608	3.4716860
H	-4.3388755	4.5548707	4.8157168
H	-3.8225553	3.4332754	3.5116302
H	-3.5706866	3.0019269	5.2291316