Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

New 2-Pyridone-Based Donor-Acceptor Dyes: The Effect of Donor Group Position, Type of π-linker and Acid-Base Characteristics of a Medium on the Photophysical Properties

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**Corresponding author. E-mail address: ssp_9999@mail.ru (S.P. Sorokin)*

Contents:

1. (Fluoro)solvatochromism of compound 4 in different solvents.

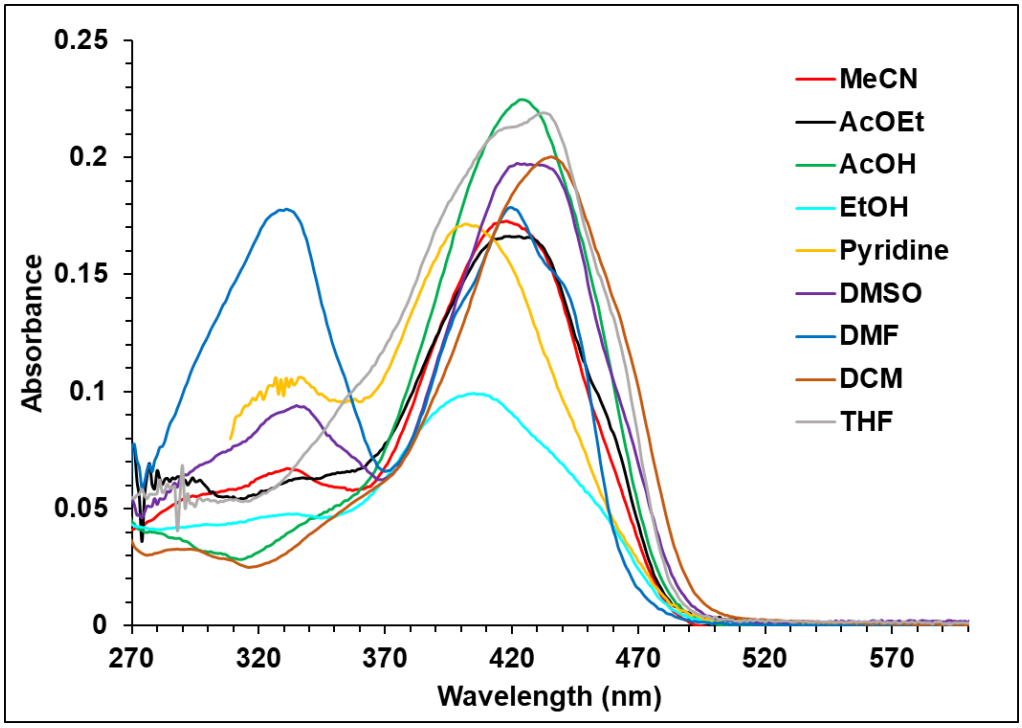

Figure S1. Absorption spectra of compound **4** in various solvents (10^{-5} M).

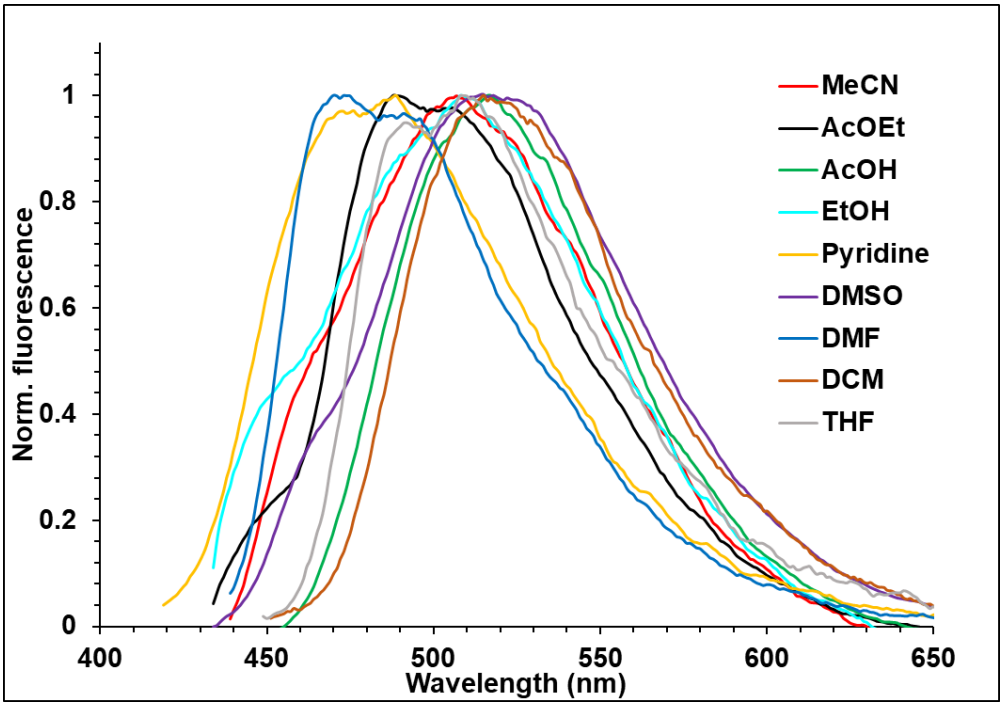

Figure S2. Emission spectra of compounds **4** in various solvents (10^{-5} M), long-wavelength absorption maxima were used for excitation.

Table S1. Photophysical properties of compound **4** in various solvents.

Solvent	$\lambda_{abs(max)}$, nm[a]	$\varepsilon_{(max)}$, M^{-1} cm^{-1}	$\lambda_{em\ (max)}$, nm[b]	$FWHM_{em}$, nm (cm^{-1})	Stokes shift		Φ_{em}[c], %
					nm	cm^{-1}	
Acetonitrile	331, 418	6700, 17300	507	94 (3650)	89	4200	1.2
Ethylacetate	419	16600	488	80 (3150)	69	3350	2.4
Acetic acid	424	22500	517	78 (2900)	93	4250	2.4
Ethanol	405	9900	508	97 (3800)	103	5000	2.2
Pyridine	403	17200	489	89 (3750)	86	4350	5.0
DMSO	336, 424	9400, 19800	515	92 (3400)	92	4200	4.3
DMF	331, 420	17800, 17850	470	78 (3250)	50	2550	3.5
THF	432	21900	509	80 (3050)	77	3500	2.7
DCM	435	-	515	79 (2900)	80	3550	1.1

[a] Absorption spectra of solutions were registered at 10^{-5} M.

[b] Emission spectra of solutions were registered at 10^{-5} M, long-wavelength absorption maxima were used for excitation.

[c] Relative quantum yield was estimated using fluorescein in 0.05 M KOH in ethanol at 425 nm excitation wavelength (Φ_{em}=0.97) [1].

2. Quantum-chemical calculations details for compounds 4, 6 and 7.

Calculations were performed in Gaussian 09, rev. D.01 [2] at PBE0/6-311G (d,p) theory level

Table S2. Optimized geometry for compound **6**

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%mem=11000MB
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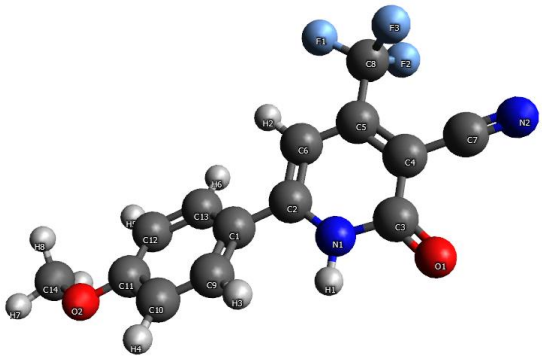
0 1



Energy: -688643.1158598

C	1.63651	0.30972	0.03085
C	0.17725	0.42600	-0.01547
N	-0.35753	1.66428	-0.14808
C	-1.71752	1.99797	-0.18931
C	-2.59751	0.83867	-0.08933
C	-2.06470	-0.42762	0.03656
C	-0.67892	-0.64686	0.08305
O	-2.05703	3.15477	-0.31172
C	-3.99105	1.10172	-0.14084
C	-2.98613	-1.62727	0.14180
N	-5.12216	1.32871	-0.18370
F	-2.29239	-2.76714	0.27910
F	-3.74217	-1.75373	-0.95215
F	-3.79825	-1.52870	1.19681
C	2.42792	1.30770	0.61984
C	3.80114	1.19056	0.66407
C	4.43014	0.06848	0.11346
C	3.65673	-0.93350	-0.47649
C	2.27601	-0.80599	-0.51077
O	5.77167	0.04495	0.19996
C	6.46309	-1.06896	-0.32976
H	0.25569	2.45800	-0.28419
H	-0.28677	-1.64054	0.23593
H	1.96355	2.17057	1.08825
H	4.41490	1.95124	1.13265
H	4.11842	-1.80629	-0.92035
H	1.68938	-1.57903	-0.99582
H	7.51926	-0.87844	-0.14668
H	6.16946	-1.99589	0.17485
H	6.29446	-1.16588	-1.40783

Table S3. Calculated vertical excitations for compound **6**

%nprocshared=4 %mem=11000MB # td=(nstates=6) pbe1pbe /6-311+g(d,p) guess=read geom=check				
No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	**359.0518**	**0.5721**	**HOMO->LUMO (99%)**	
2	298.6491	0.0156	H-2->LUMO (50%), H-1->LUMO (48%)	
3	289.5542	0.0468	H-2->LUMO (48%), H-1->LUMO (49%)	
4	271.3477	0.006	H-3->LUMO (33%), HOMO->L+1 (58%)	HOMO->L+2 (4%)
5	253.8423	0.0116	H-3->LUMO (48%), HOMO->L+1 (38%)	H-1->L+1 (2%), HOMO->L+2 (8%)
6	246.7298	0.0901	H-3->LUMO (12%), HOMO->L+2 (77%)	H-4->LUMO (6%)

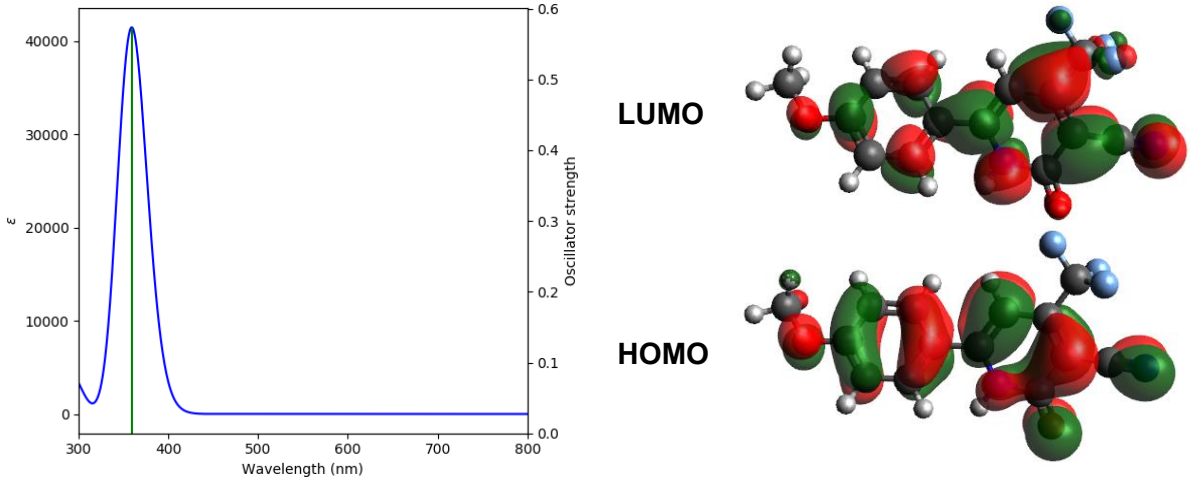


Figure S3. Calculated absorption spectrum of compound **6** and frontier orbital distributions (HOMO, LUMO) involved in the first excitation

Table S4. Optimized geometry for compound **4**

%nprocshared=4
%mem=11000MB
#opt freq=noraman pbe1pbe /6-311+g(d,p)

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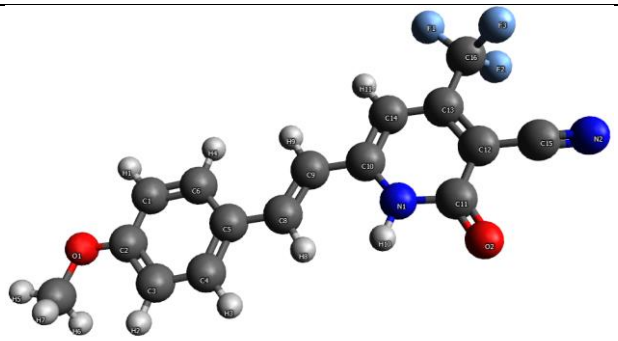


Energy: -737169.5883826

C	4.83614	-1.43870	-0.00060
C	5.78613	-0.40699	-0.00028
C	5.35888	0.92061	-0.00004
C	3.99907	1.19790	-0.00004
C	3.03540	0.18446	-0.00030
C	3.49202	-1.14671	-0.00060
O	7.07347	-0.79668	-0.00037
C	8.07806	0.19756	0.00167
C	1.63285	0.54922	-0.00027
C	0.57366	-0.28532	-0.00053
C	-0.81712	0.10217	-0.00043
N	-1.17774	1.41095	-0.00042
C	-2.47707	1.92815	-0.00022
C	-3.51302	0.89969	0.00001
C	-3.16280	-0.43563	-0.00008
C	-1.82231	-0.84458	-0.00031
O	-2.65512	3.12719	-0.00022
C	-4.85458	1.35954	0.00036
C	-4.24312	-1.49892	0.00024
N	-5.94257	1.74629	0.00040
F	-3.71759	-2.73266	-0.00044
F	-5.02244	-1.40006	-1.08000
F	-5.02107	-1.40066	1.08153
H	5.18947	-2.46367	-0.00078
H	6.06936	1.73754	0.00008
H	3.67654	2.23530	0.00014
H	2.78308	-1.96761	-0.00080
H	9.02681	-0.33665	0.00289
H	8.01737	0.82606	-0.89362
H	8.01455	0.82520	0.89736
H	1.46318	1.62557	0.00003
H	0.72908	-1.35906	-0.00077
H	-0.46995	2.13249	-0.00059
H	-1.56742	-1.89409	-0.00034

Table S5. Calculated vertical excitations for compound **4**

%nprocshared=4 %mem=11000MB # td=(nstates=6) pbe1pbe /6-311+g(d,p) guess=read geom=check				
No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	**408.5954**	**1.0808**	**HOMO->LUMO (99%)**	
2	334.3695	0.0467	H-1->LUMO (95%)	
3	314.5849	0	H-2->LUMO (97%)	H-2->L+1 (2%)
4	288.4561	0.0006	H-3->LUMO (77%), HOMO->L+2 (16%)	H-1->L+2 (2%), HOMO->L+1 (3%)
5	273.2856	0.1418	HOMO->L+1 (86%)	H-5->LUMO (3%), H-3->LUMO (5%)
6	257.1966	0.1065	H-3->LUMO (17%), HOMO->L+2 (73%)	H-3->L+1 (2%)

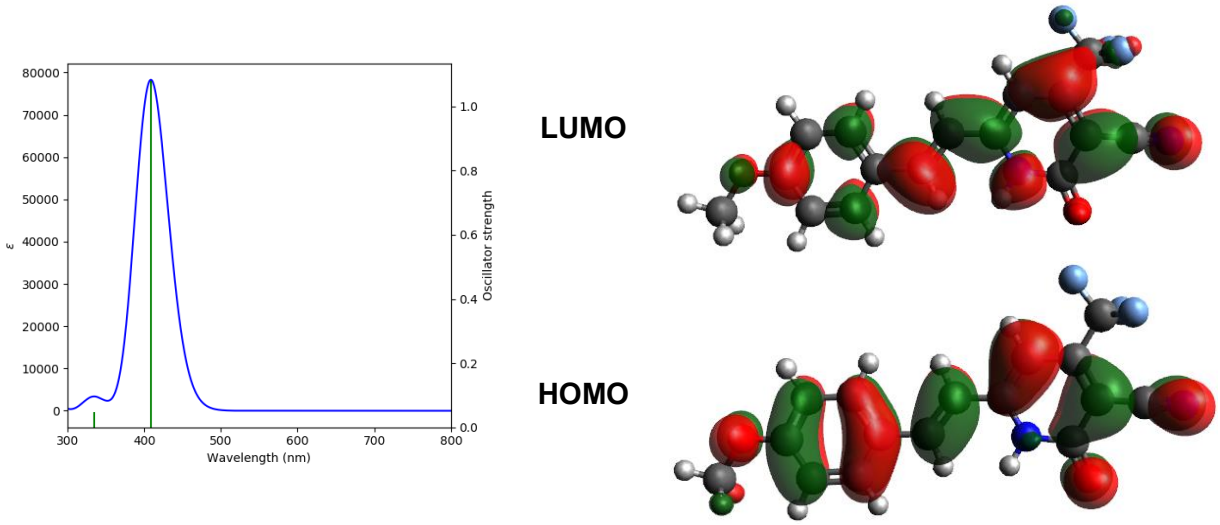
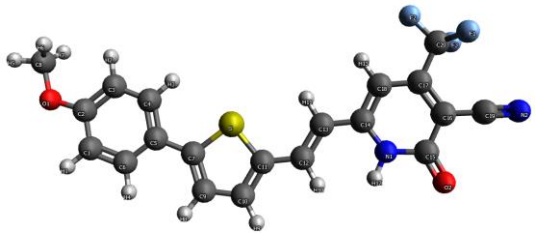


Figure S4. Calculated absorption spectrum of compound **4** and frontier orbital distributions (HOMO, LUMO) involved in the first excitation

Table S6. Optimized geometry for compound **7**

%nprocshared=4
%mem=11000MB
#opt freq=noraman pbe1pbe /6-311+g(d,p)

0 1



Energy: -1083195.0268180

C	7.23727	-0.65557	0.00034
C	7.35328	0.73863	0.00021
C	6.19741	1.51880	-0.00002
C	4.95297	0.90427	-0.00014
C	4.81588	-0.48587	-0.00003
C	5.99498	-1.25139	0.00023
C	3.50945	-1.13057	-0.00017
O	8.60945	1.22807	0.00035
C	8.78208	2.62953	-0.00006
C	3.21281	-2.47827	-0.00062
C	1.83516	-2.75086	-0.00066
C	1.04611	-1.61856	-0.00025
S	2.04569	-0.19659	0.00022
C	-0.38164	-1.57993	-0.00023
C	-1.15985	-0.47339	0.00005
C	-2.59958	-0.44332	0.00007
N	-3.32311	-1.59282	0.00021
C	-4.71695	-1.71273	0.00022
C	-5.41193	-0.42887	0.00001
C	-4.69043	0.74895	-0.00010
C	-3.28972	0.75396	-0.00008
O	-5.23310	-2.80945	0.00036
C	-6.82890	-0.48190	0.00002
N	-7.98233	-0.53800	0.00052
C	-5.41735	2.07905	-0.00016
F	-6.19169	2.21036	-1.08045
F	-4.55759	3.10865	-0.00058
F	-6.19104	2.21070	1.08059
H	8.14380	-1.25030	0.00054
H	6.25223	2.60018	-0.00010
H	4.06975	1.53601	-0.00036
H	5.93967	-2.33407	0.00037
H	9.85786	2.79873	-0.00017
H	8.34452	3.08525	-0.89546
H	8.34461	3.08577	0.89511
H	3.96942	-3.25165	-0.00095
H	1.41652	-3.75068	-0.00101
H	-0.83533	-2.57021	-0.00051
H	-0.69292	0.50709	0.00023
H	-2.85461	-2.48828	0.00046
H	-2.74280	1.68526	-0.00023

Table S7. Calculated vertical excitations for compound **7**

%nprocshared=4 %mem=11000MB # td=(nstates=6) pbe1pbe /6-311+g(d,p) guess=read geom=check				
No.	Wavelength (nm)	Osc. Strength	Major contribs	Minor contribs
1	**473.2402**	**1.3707**	**HOMO->LUMO (100%)**	
2	375.3684	0.0496	H-1->LUMO (93%)	HOMO->L+1 (4%)
3	322.6067	0.075	HOMO->L+1 (92%)	H-1->LUMO (4%)
4	319.8437	0	H-4->LUMO (95%)	H-4->L+1 (4%)
5	311.7139	0.0329	H-2->LUMO (87%)	H-5->LUMO (5%), H-3->LUMO (4%)
6	294.5273	0.0582	H-3->LUMO (78%)	H-2->LUMO (5%), HOMO->L+2 (9%)

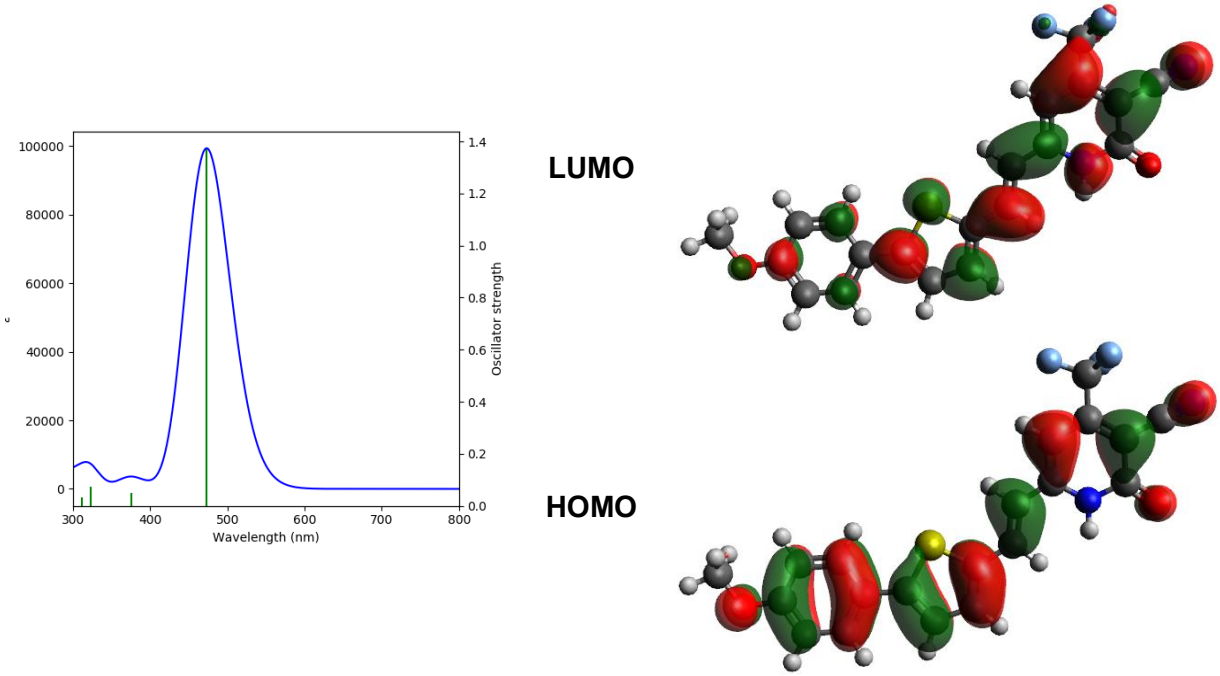


Figure S5. Calculated absorption spectrum of compound **7** and frontier orbital distributions (HOMO, LUMO) involved in the first excitation

3. Absorption spectra and emission spectra of compounds 1-5, 7 in THF and DCM

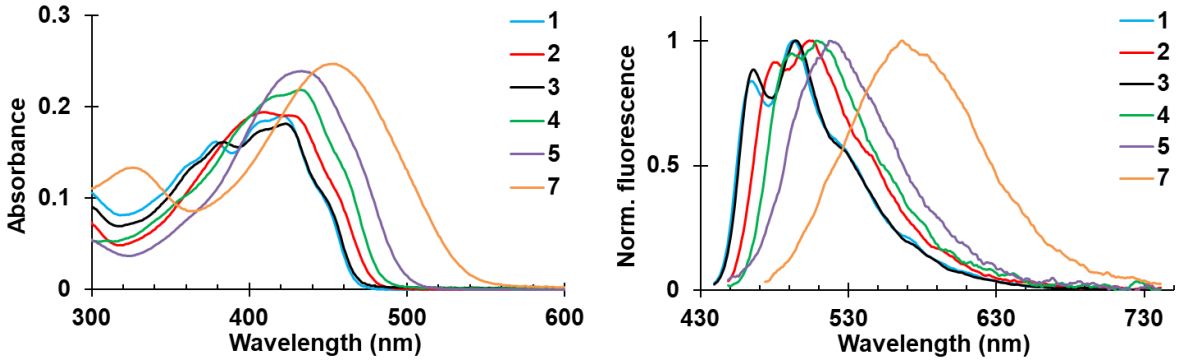


Figure S6. Absorption and emission spectra of compounds **1-5, 7** in THF (10^{-5} M).

Table S8. Photophysical properties of compounds **1-5, 7** in THF.

Compound	$\lambda_{abs(max)}$, nm[a]	$\varepsilon_{(max)}$, M^{-1} cm^{-1}	$\lambda_{em\ (max)}$, nm[b]	$FWHM_{em}$, nm (cm^{-1})	Stokes shift		Φ_{em}[c], %
					nm	cm^{-1}	
1	422	18950	464, 493	80 (3300)	71	3400	7.8
2	409	19450	482, 504	83 (3250)	95	4600	4.2
3	423	18150	465, 494	79 (3250)	71	3400	9.6
4	432	21900	494, 509	80 (3050)	77	3500	2.7
5	433	23950	518	80 (2900)	85	3800	1.6
7	455	24750	566	106 (3250)	111	4300	1.4

[a] Absorption spectra of solutions were registered at 10^{-5} M.

[b] Emission spectra of solutions were registered at 10^{-5} M, long-wavelength absorption maxima were used for excitation.

[c] Relative quantum yield was estimated using fluorescein in 0.05 M KOH in ethanol at 425 nm and 450 nm excitation wavelengths (Φ_{em}=0.97) [1].

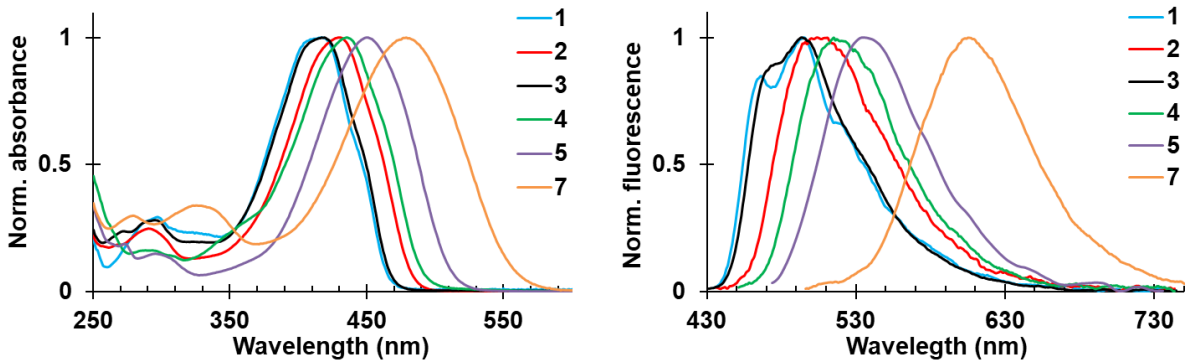


Figure S7. Absorption and emission spectra of compounds **1-5, 7** in DCM.

Table S9. Photophysical properties of compounds **1-5, 7** in DCM.

Compound	$\lambda_{abs(max)}$, nm	$\varepsilon_{(max)}$, M^{-1} cm^{-1}	$\lambda_{em\ (max)}$, nm[a]	$FWHM_{em}$, nm (cm^{-1})	Stokes shift		Φ_{em}[b], %
					nm	cm^{-1}	
1	417	-	466, 495	81 (3350)	78	3800	5.3
2	430	-	504	84 (3200)	74	3400	1.0
3	417	-	494	79 (3200)	77	3750	6.4
4	435	-	515	79 (2900)	80	3550	1.1
5	450	-	534	80 (2700)	84	3500	1.0
7	479	-	605	87 (2350)	126	4350	1.6

[a] Emission spectra of solutions were registered using long-wavelength absorption maxima for excitation.

[b] Relative quantum yield was estimated using fluorescein in 0.05 M KOH in ethanol at 425 nm and 450 nm excitation wavelengths (Φ_{em}=0.97) [1].

4. Absorption spectra and emission spectra of compounds 1-7 in DMSO (10^{-5} M) in the presence of TFA and DBN.

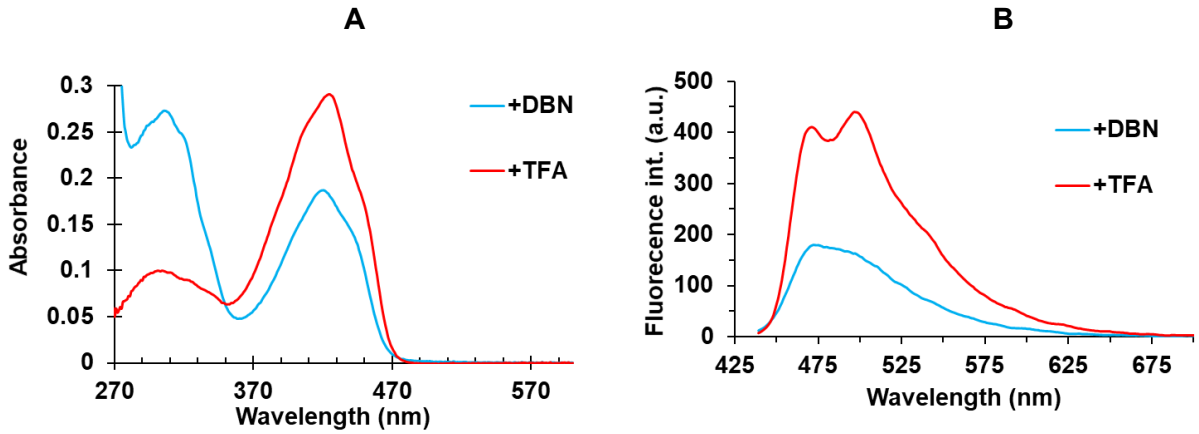


Figure S8. Absorption spectra (A) and emission spectra (B) of **1** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

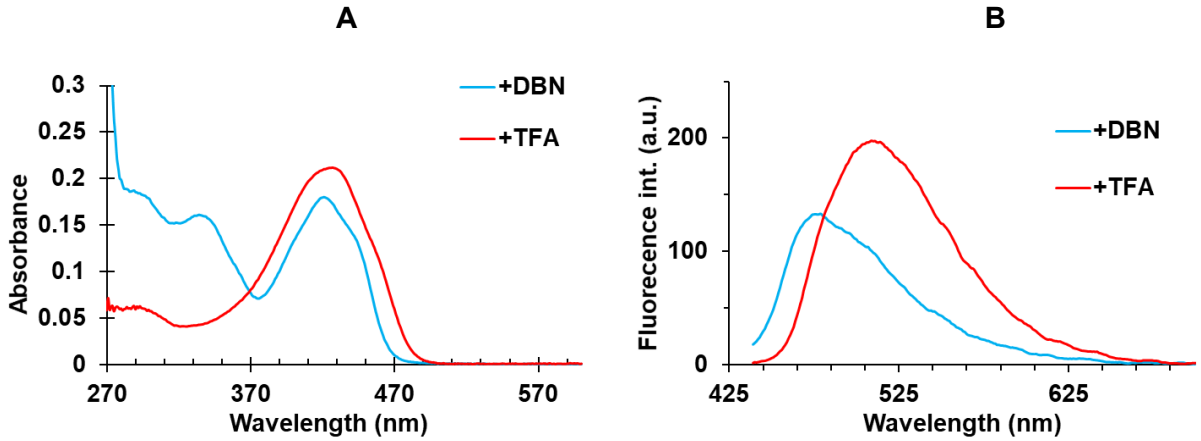


Figure S9. Absorption spectra (A) and emission spectra (B) of **2** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

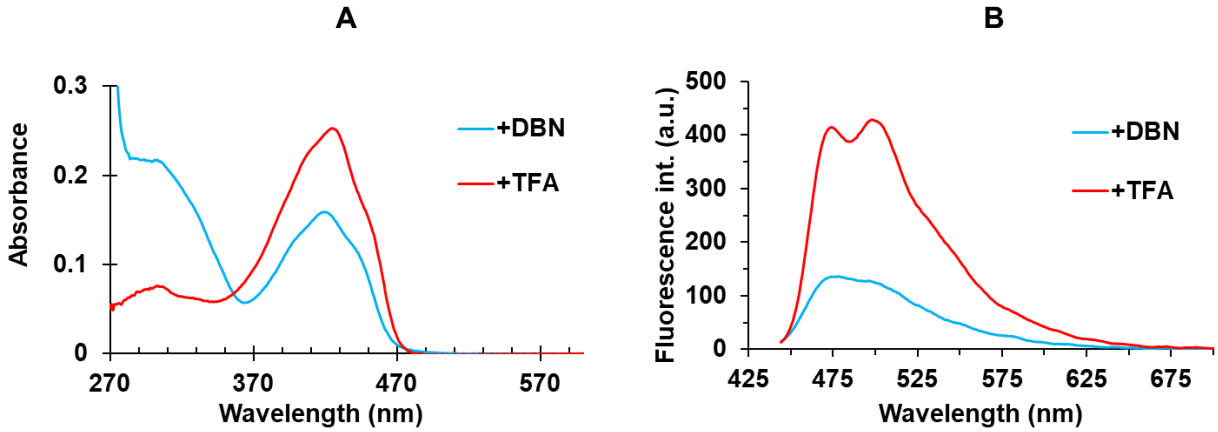


Figure S10. Absorption spectra (A) and emission spectra (B) of **3** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

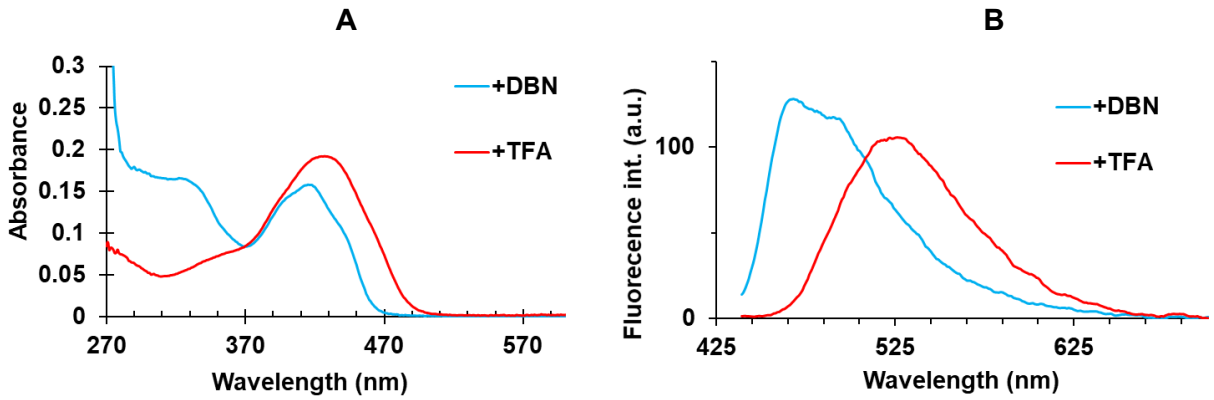


Figure S11. Absorption spectra (A) and emission spectra (B) of **4** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

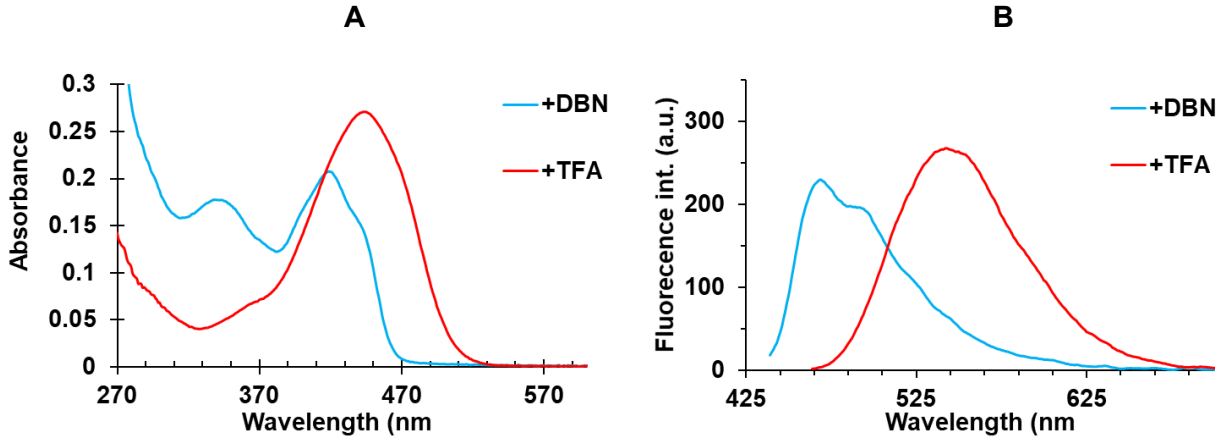


Figure S12. Absorption spectra (A) and emission spectra (B) of **5** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

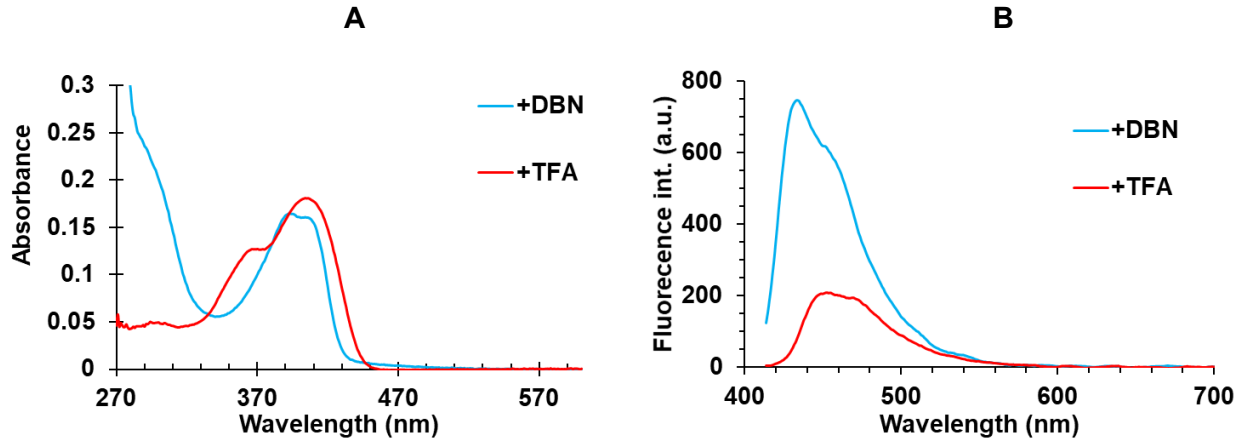


Figure S13. Absorption spectra (A) and emission spectra (B) of **6** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

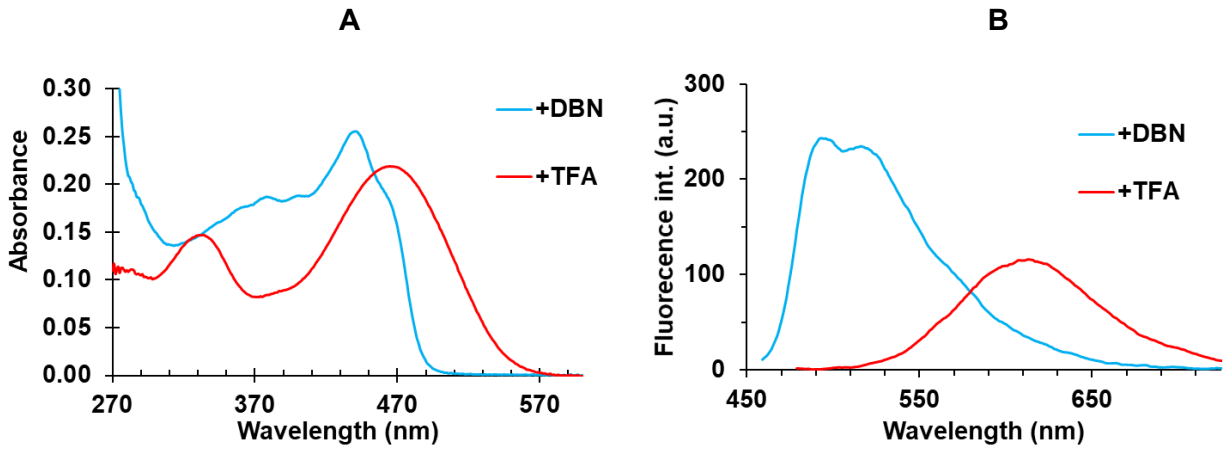


Figure S14. Absorption spectra (A) and emission spectra (B) of **7** solution in DMSO (C = 10^{-5} M) with the addition of DBN (blue line), with the addition of TFA (red line).

5. NMR-spectra of compounds 1-7.

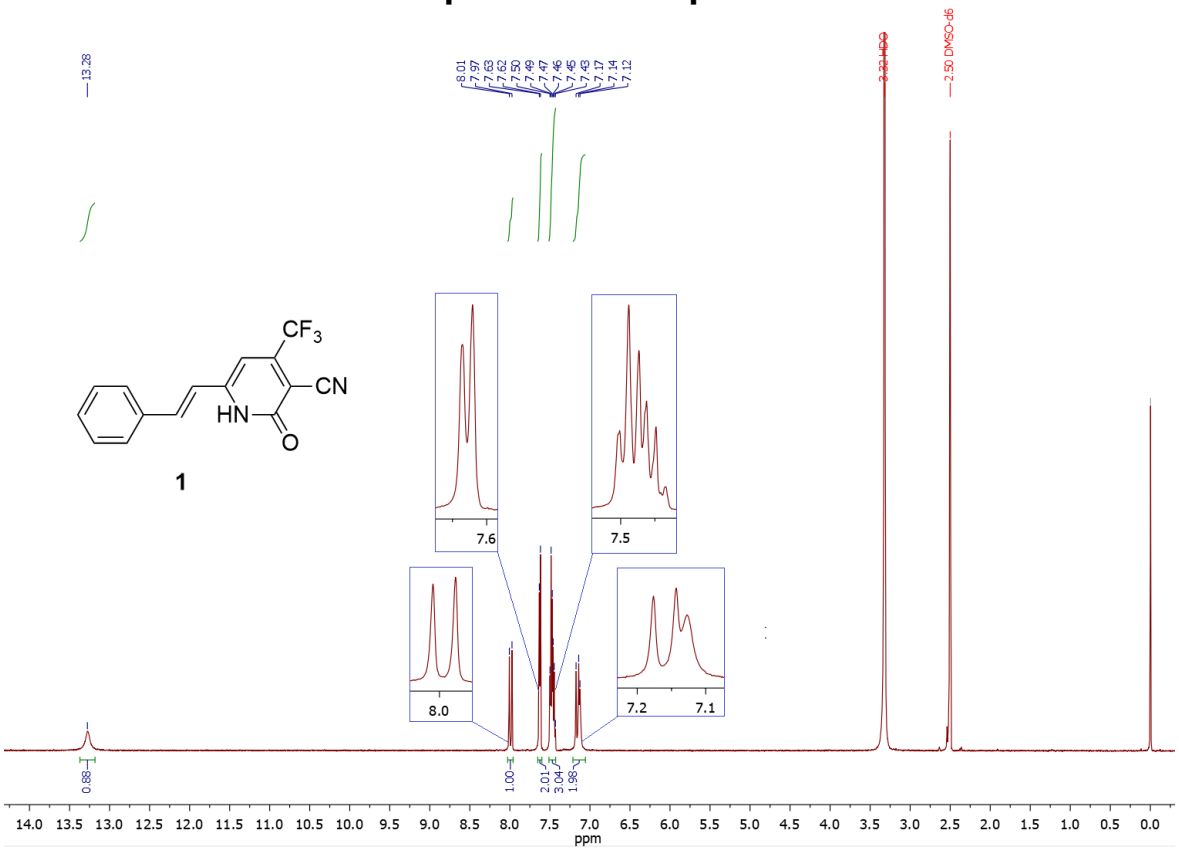


Figure S15. ^{1}H NMR spectrum of **1** in DMSO-d_6

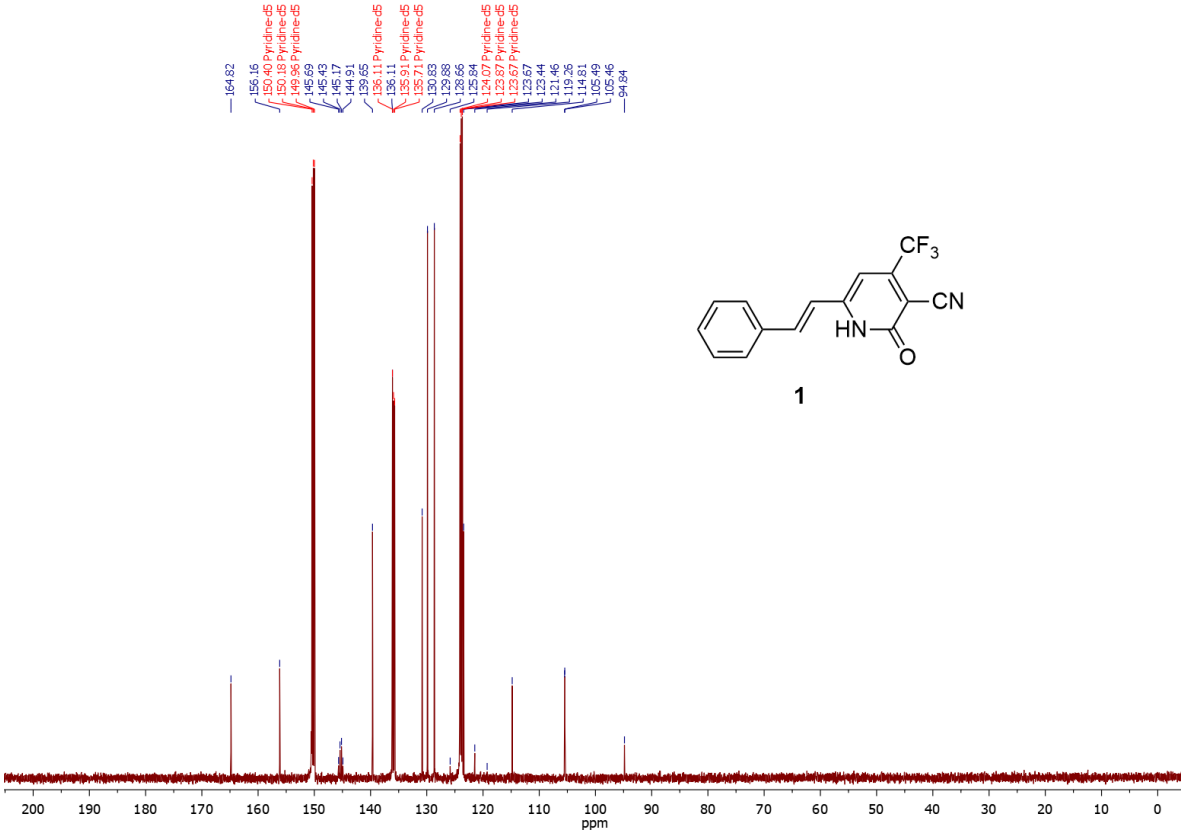


Figure S16. ^{13}C NMR spectrum of **1** in Pyridine-*d*5

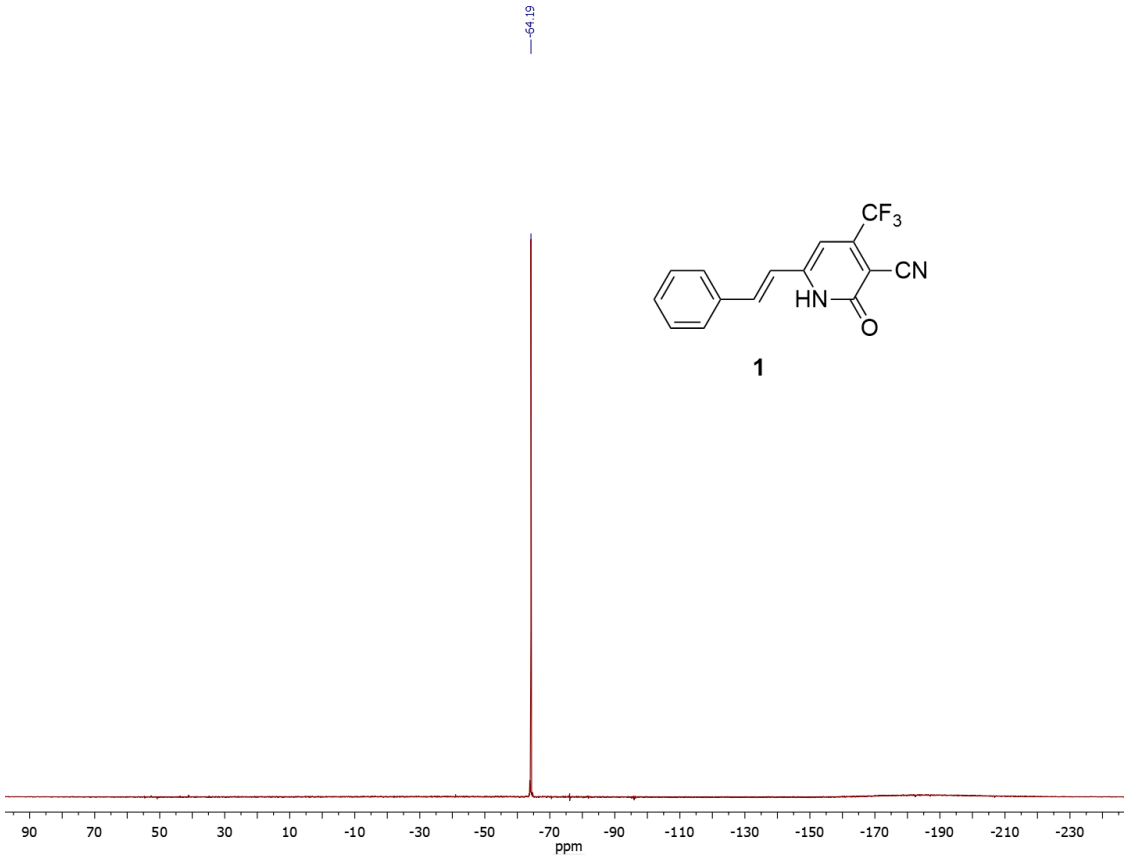


Figure S17. ^{19}F NMR spectrum of **1** in DMSO-*d*6

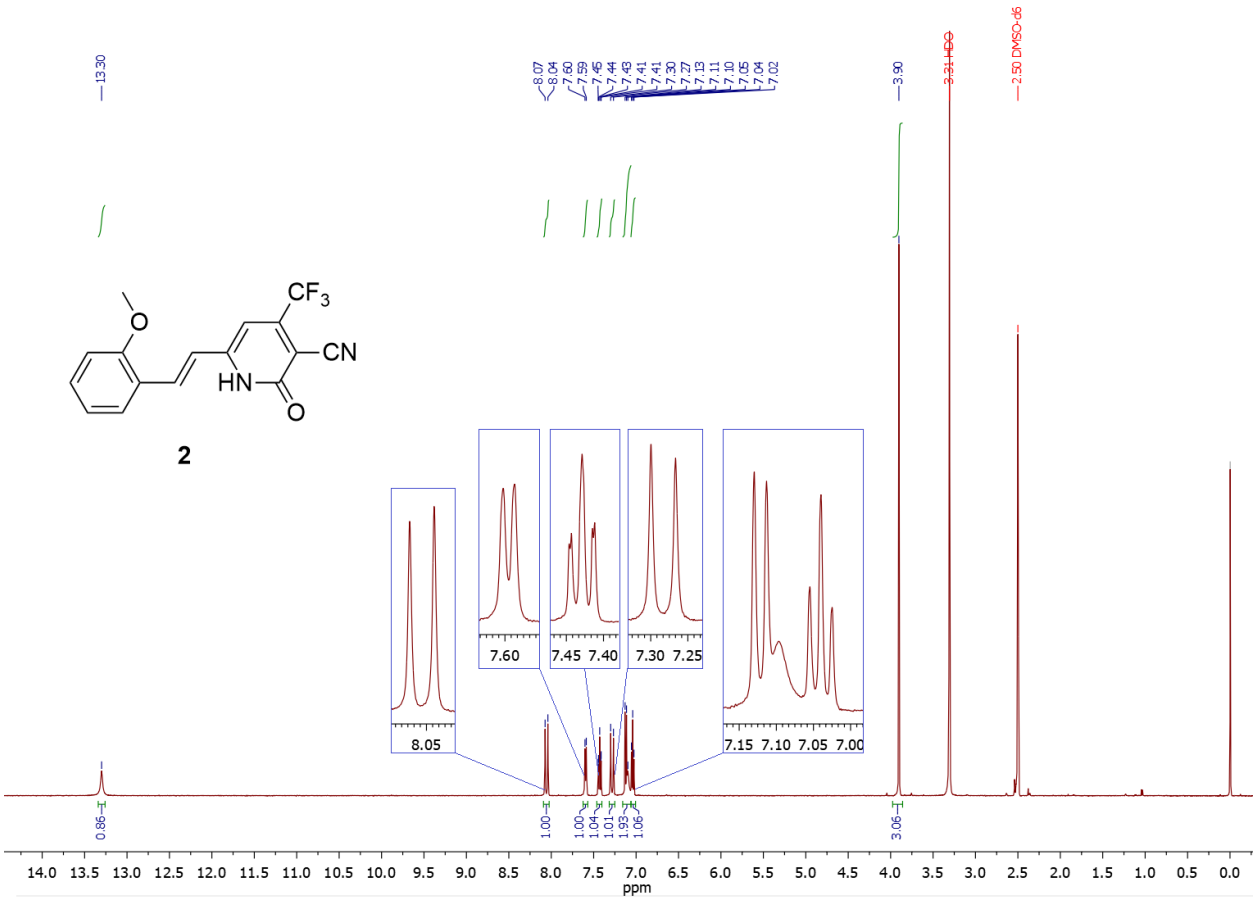


Figure S18. ^{1}H NMR spectrum of **2** in DMSO-d_6

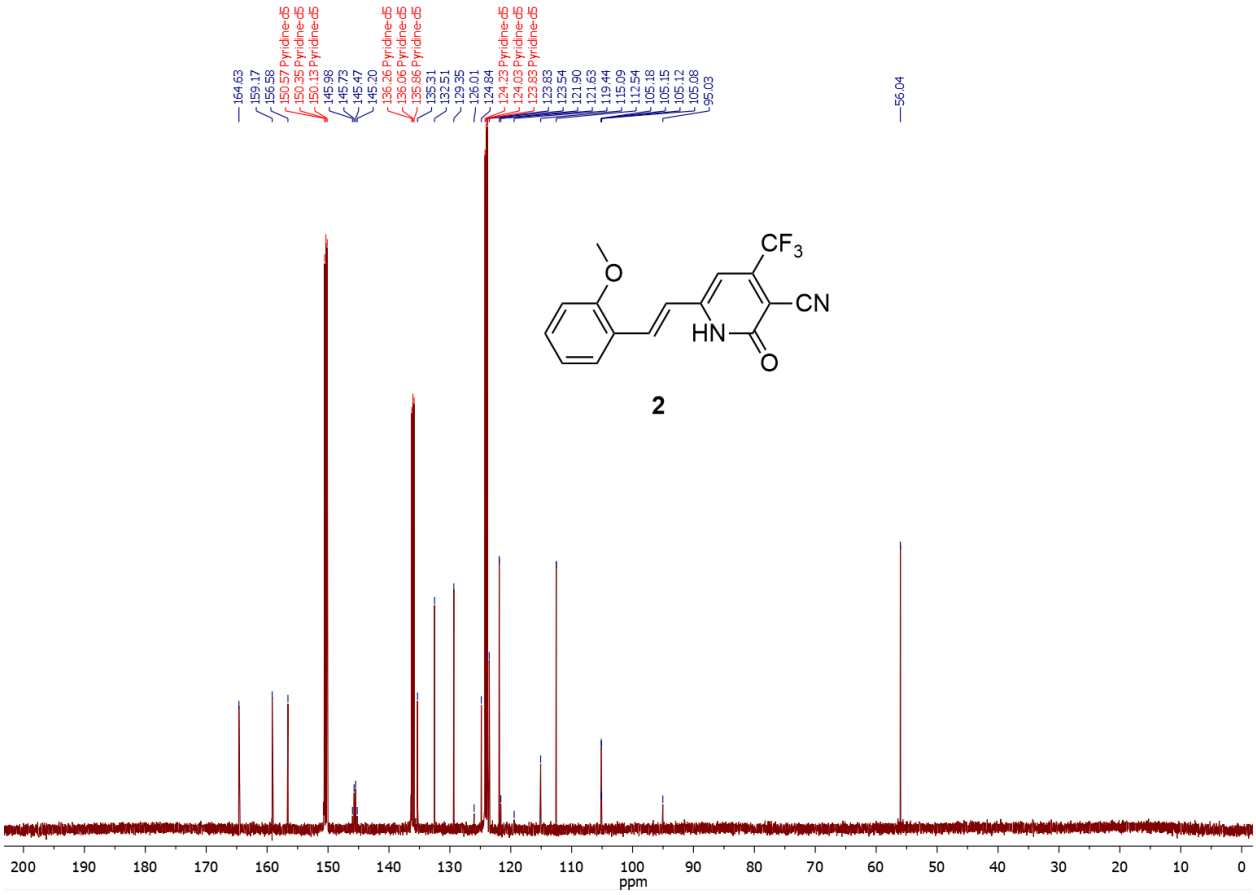


Figure S19. ^{13}C NMR spectrum of **2** in Pyridine-*d*5

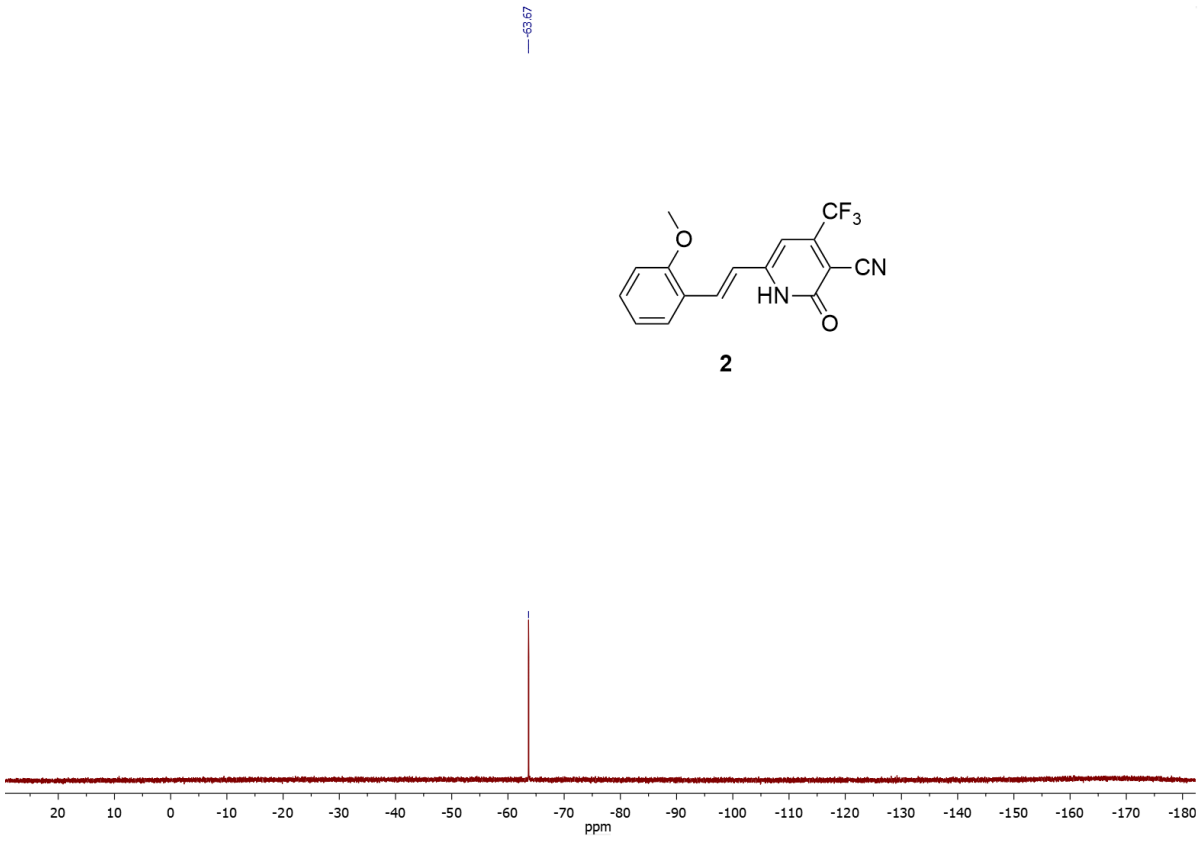


Figure S20. ^{19}F NMR spectrum of **2** in DMSO-d_6

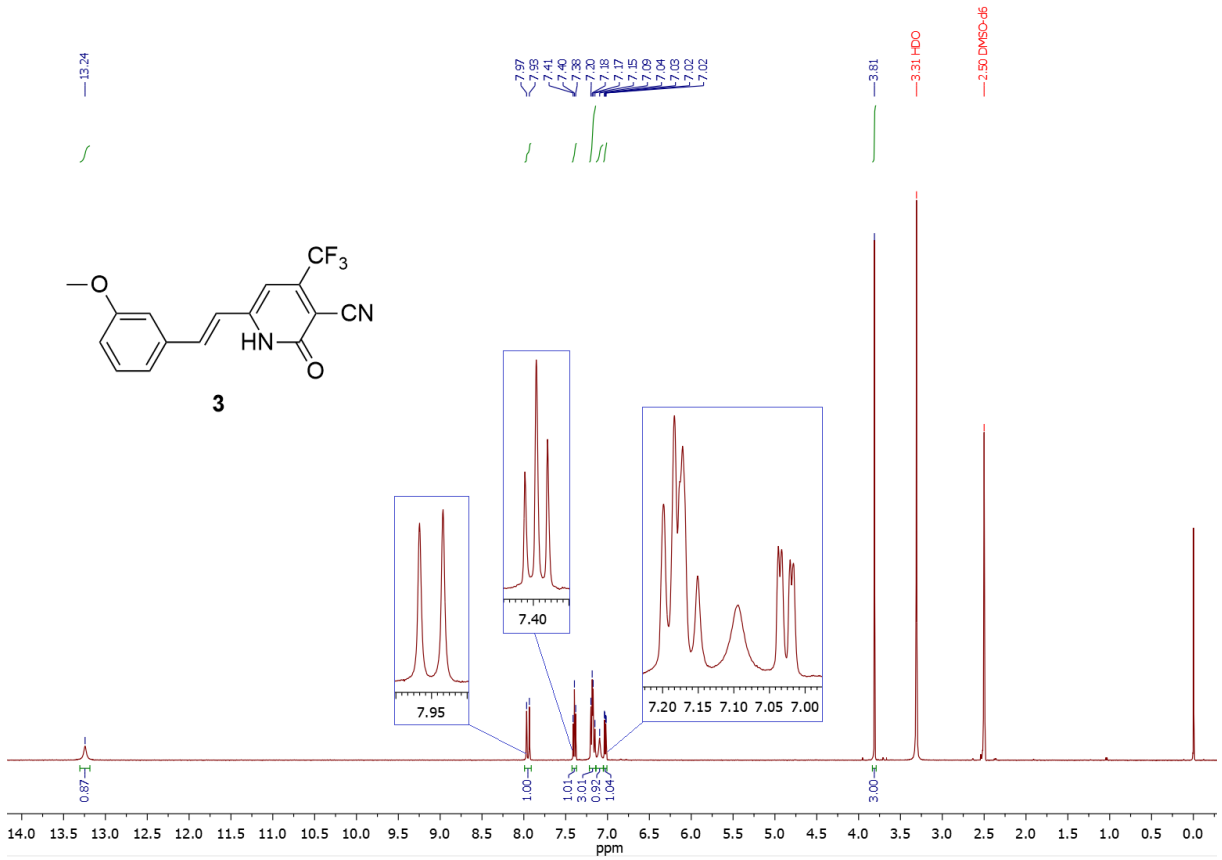


Figure S21. ^{1}H NMR spectrum of **3** in DMSO-d_6

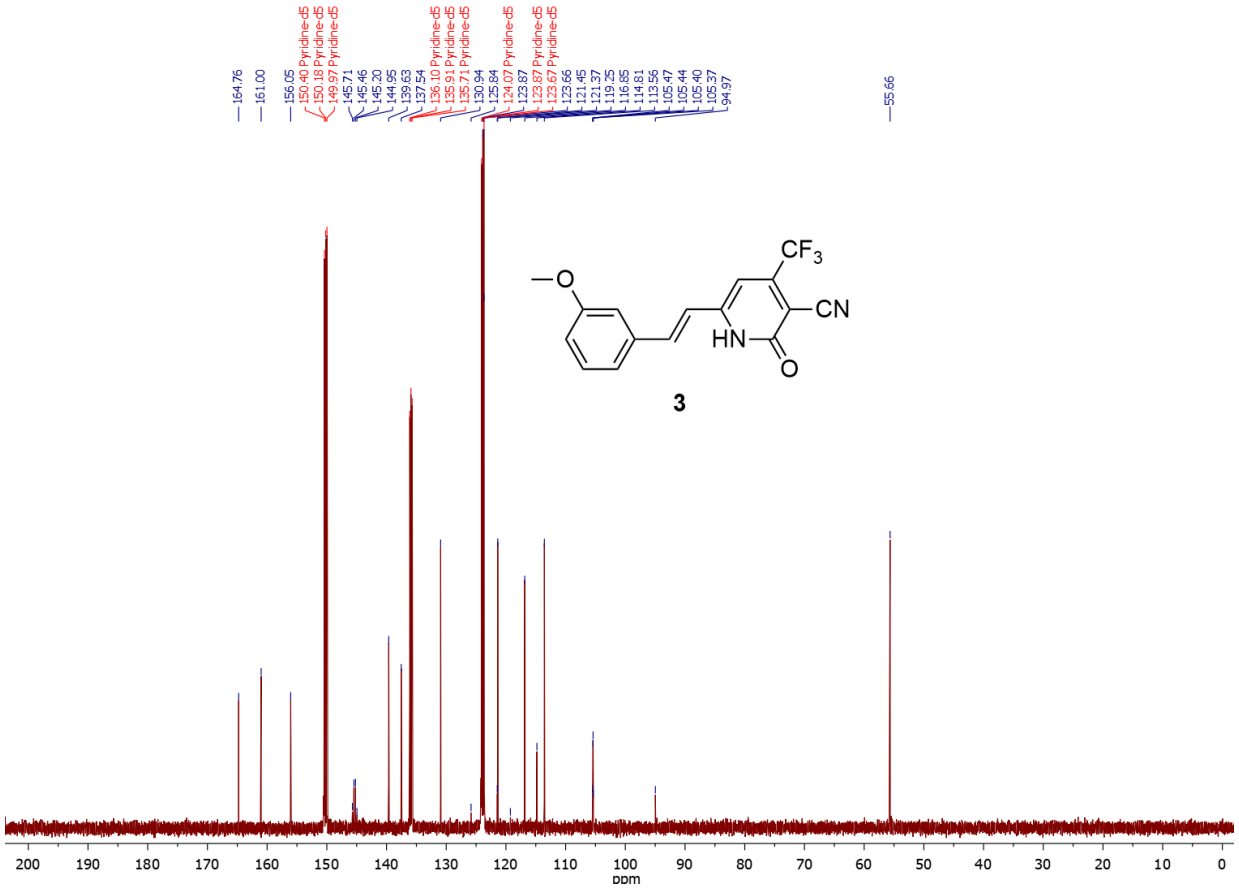


Figure S22. ^{13}C NMR spectrum of **3** in Pyridine-*d*5

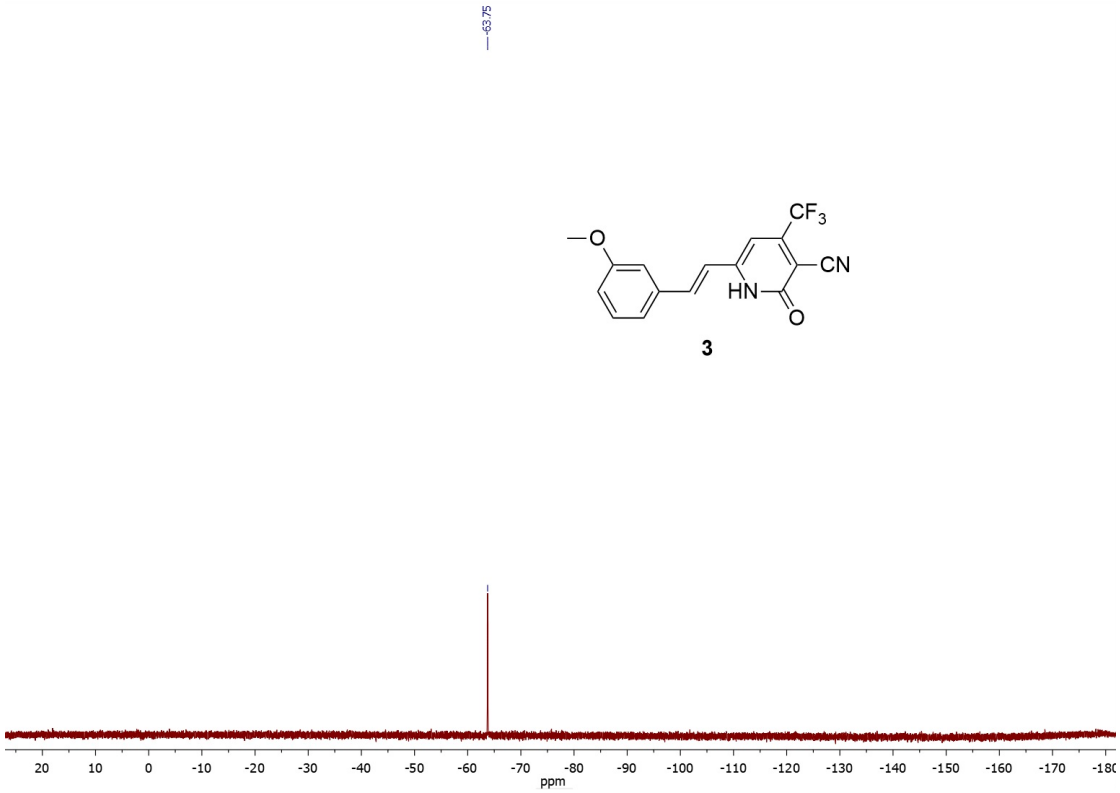


Figure S23. ^{19}F NMR spectrum of **3** in DMSO-d_6

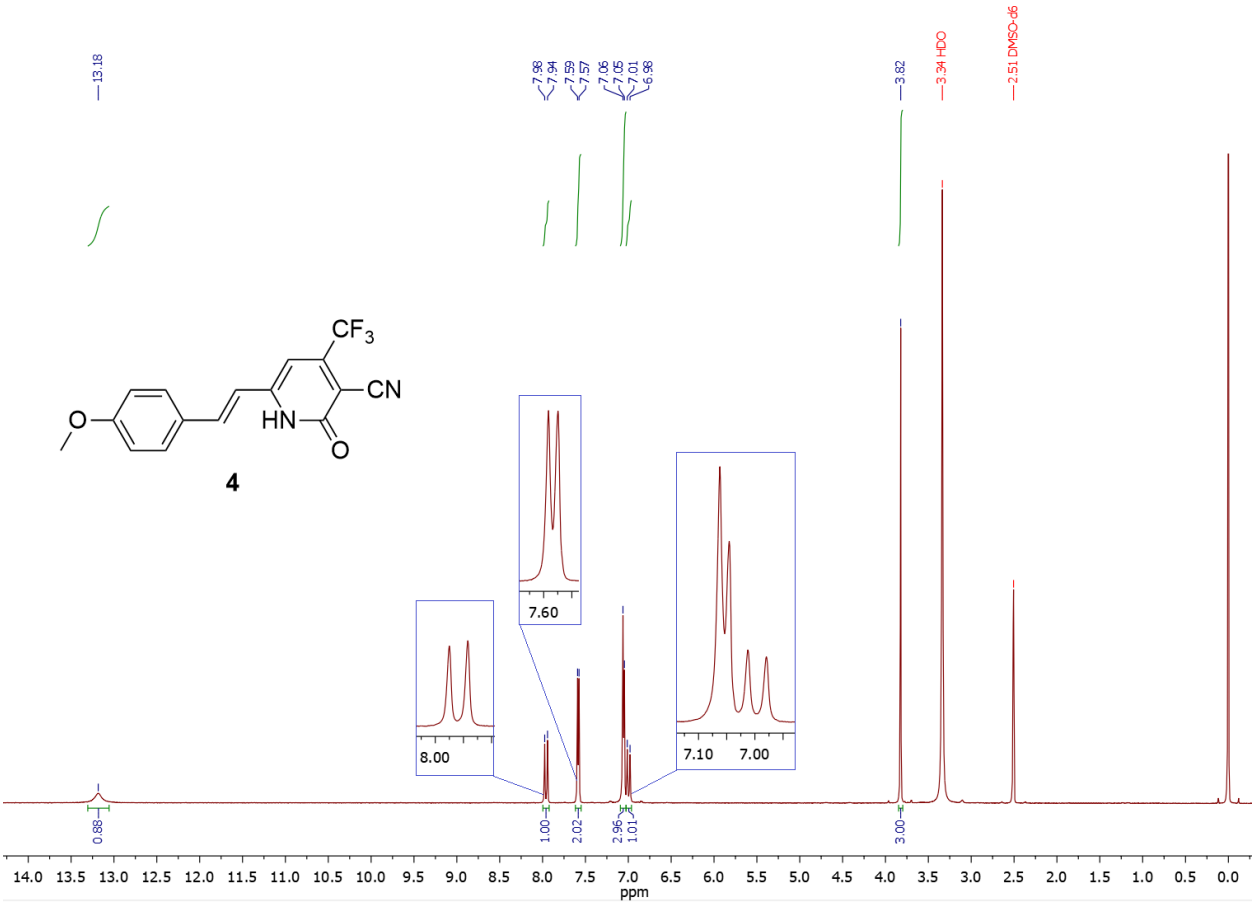


Figure S24. ^{1}H NMR spectrum of **4** in DMSO-d_6

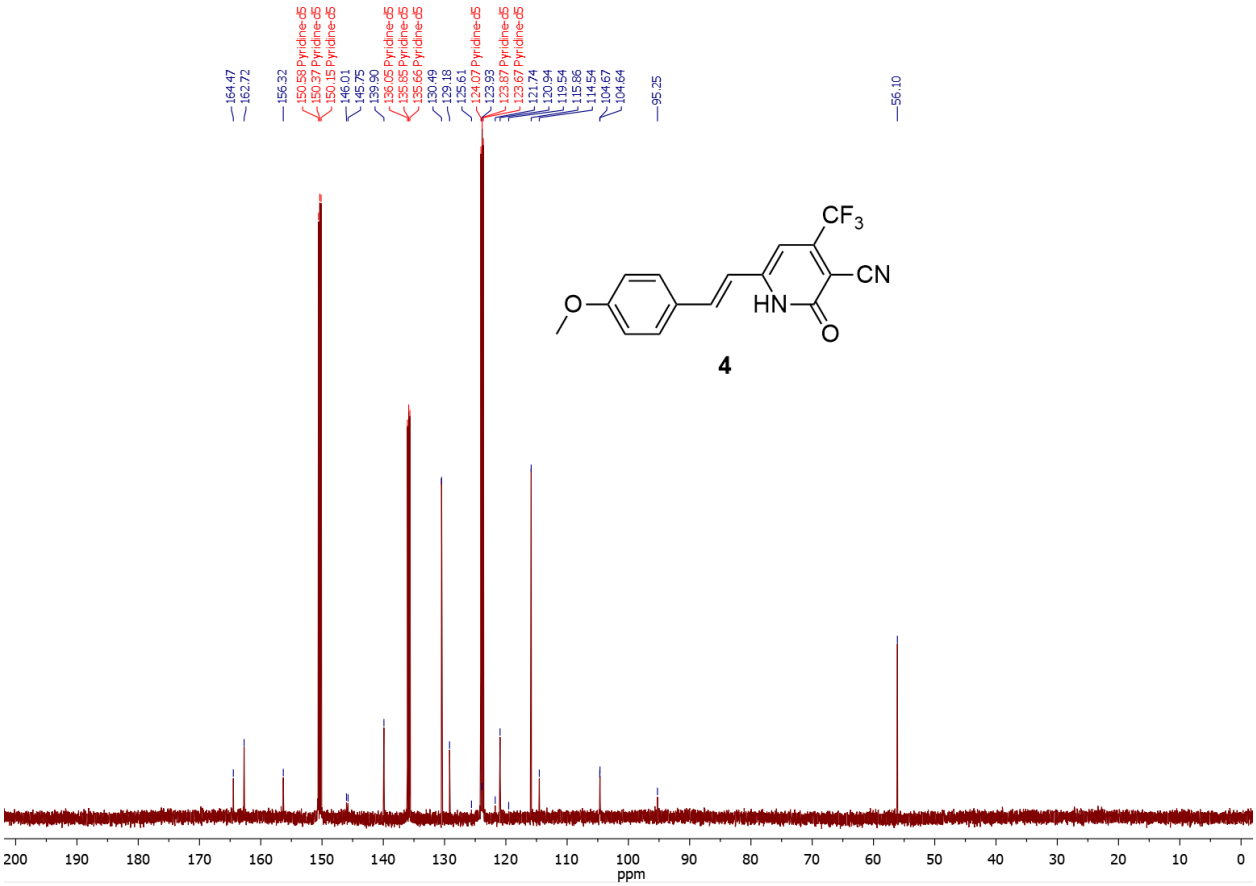


Figure S25. ^{13}C NMR spectrum of **4** in Pyridine-*d*5

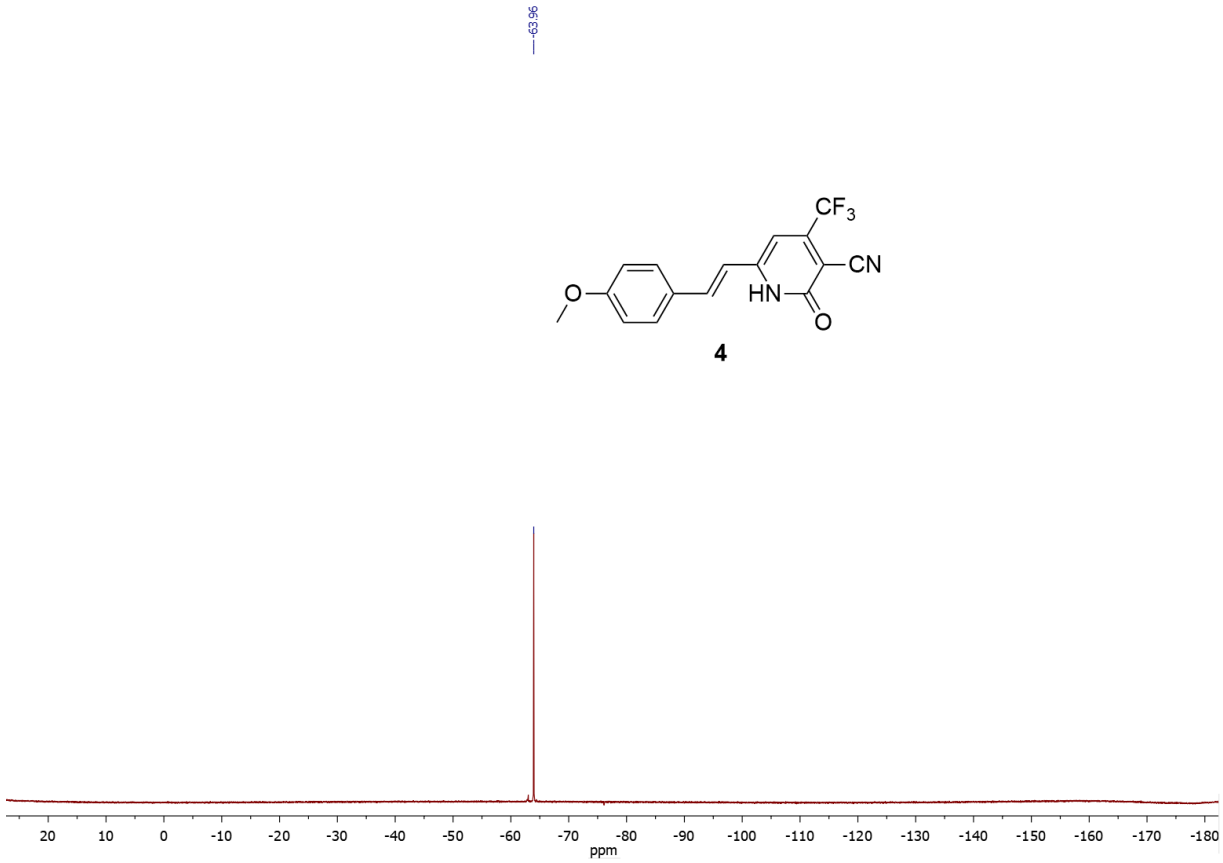


Figure S26. ^{19}F NMR spectrum of **4** in DMSO-d_6

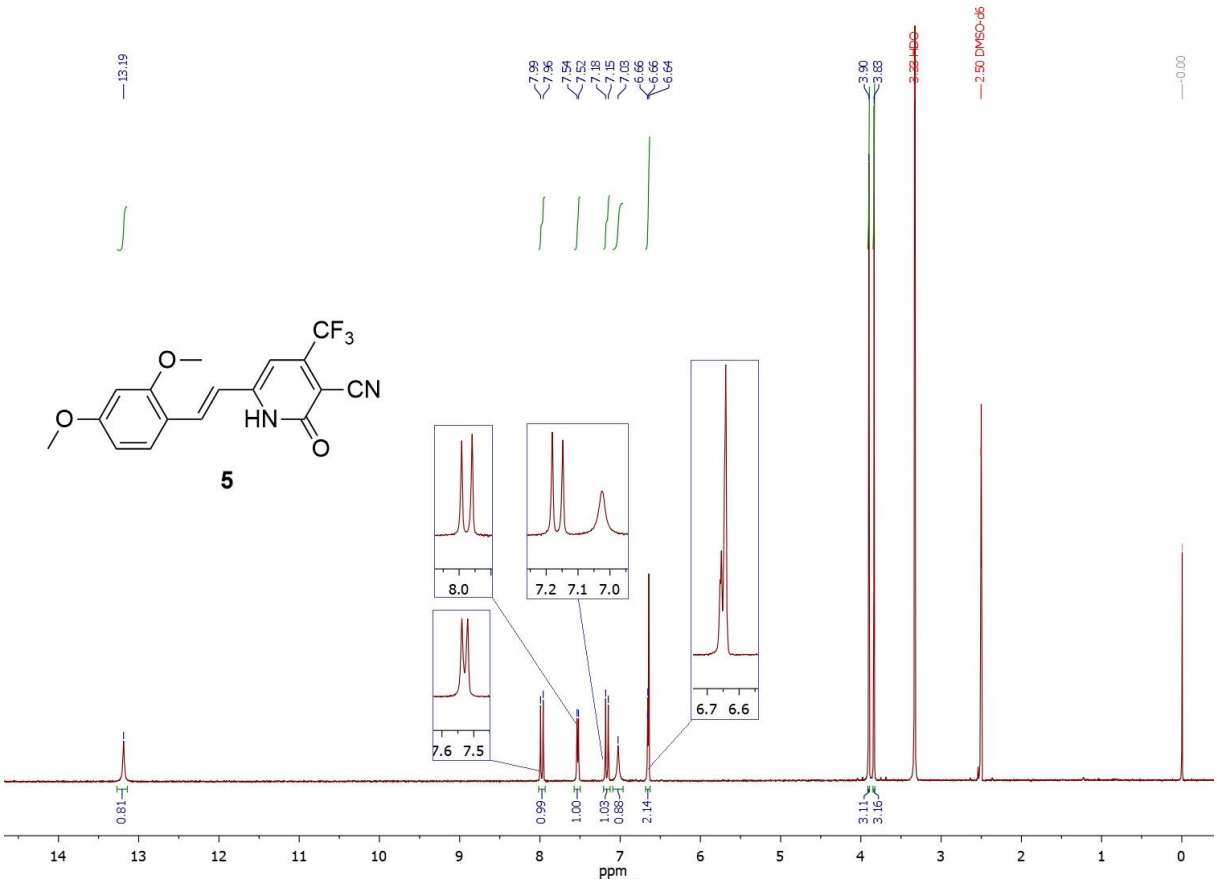


Figure S27. ^{1}H NMR spectrum of **5** in DMSO-d_6

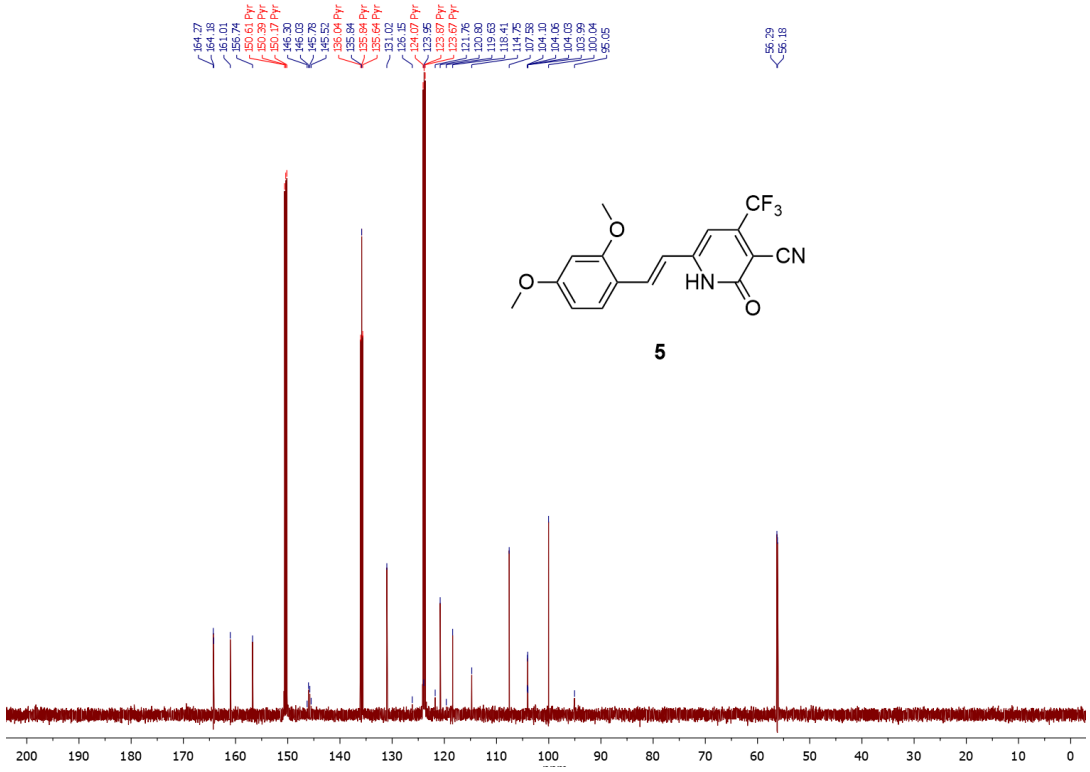


Figure S28. ^{13}C NMR spectrum of **5** in Pyridine-*d*5

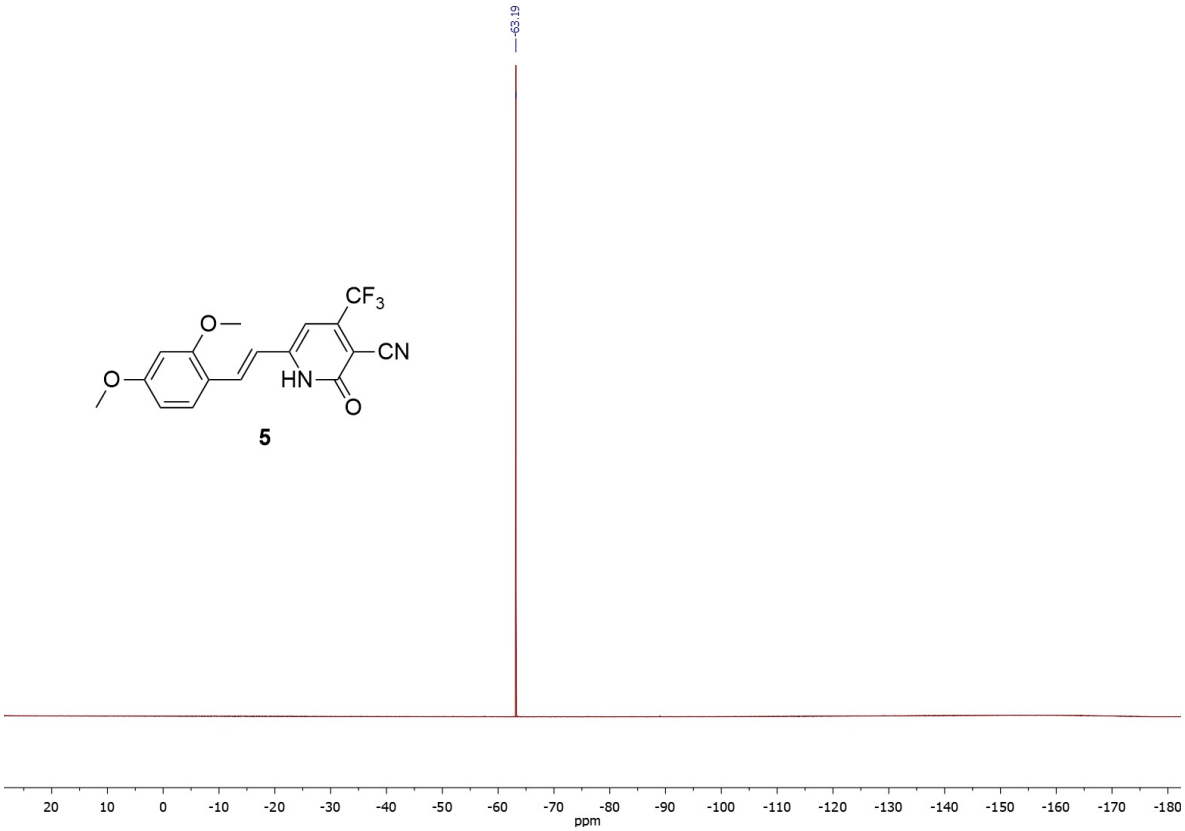


Figure S29. ^{19}F NMR spectrum of **5** in DMSO-d_6

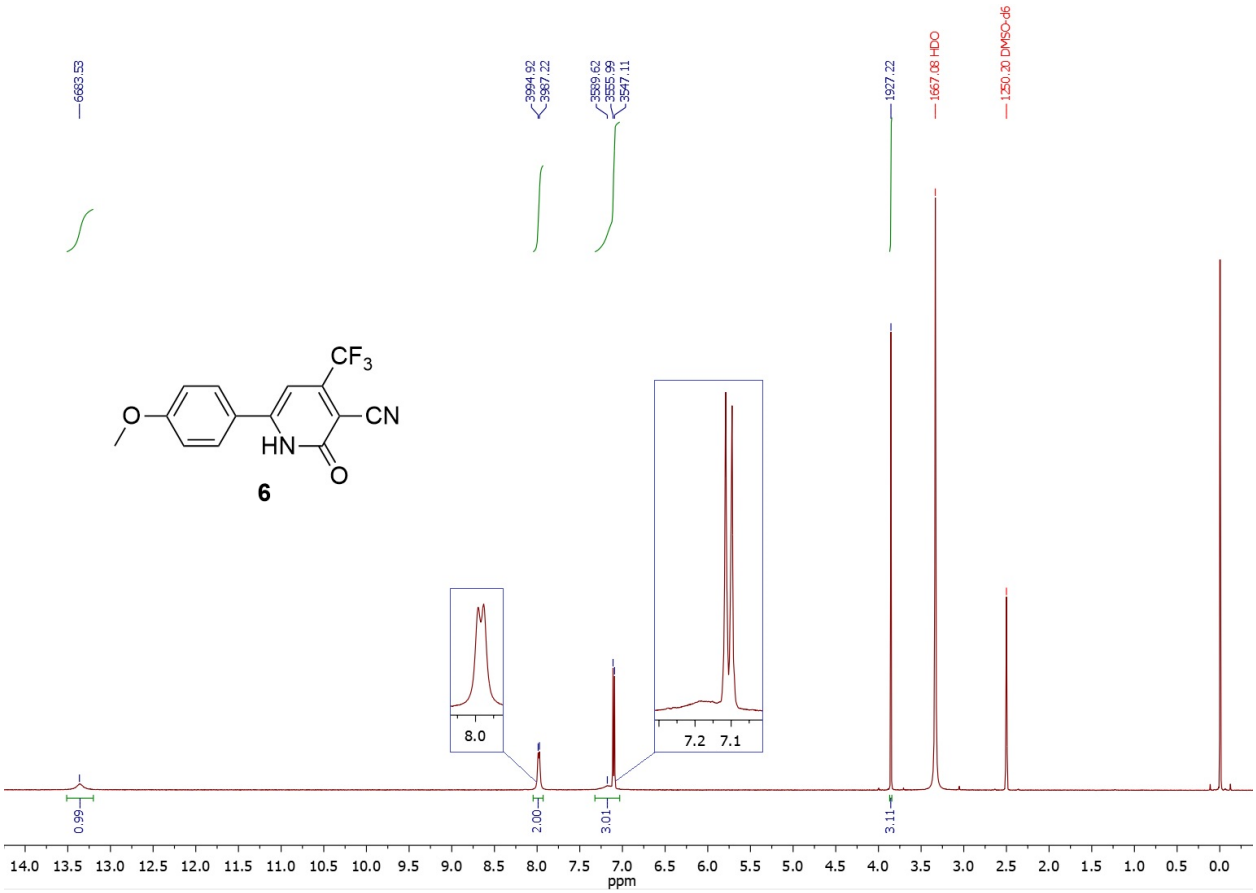


Figure S30. ^{1}H NMR spectrum of **6** in DMSO-d_6

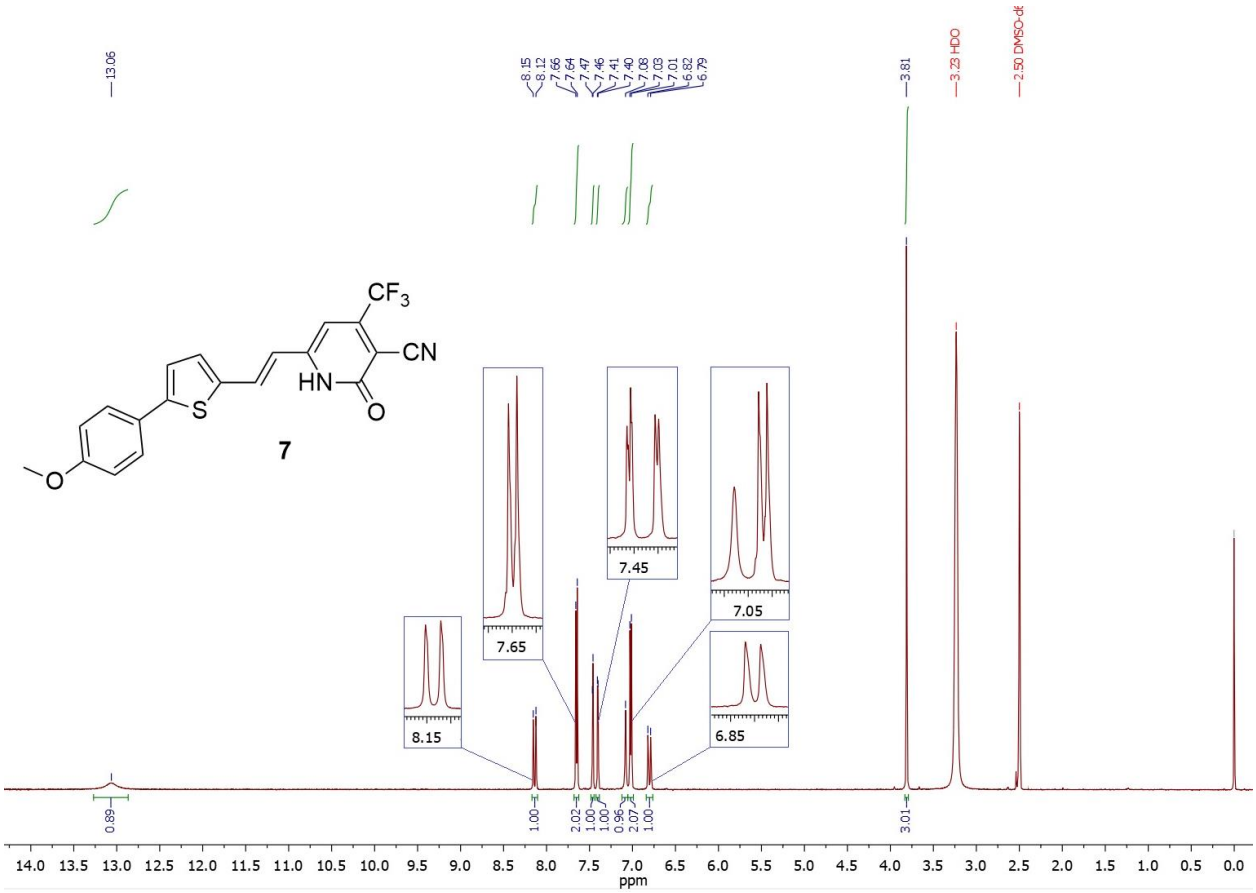


Figure S31. ^{1}H NMR spectrum of **7** in DMSO-d_6

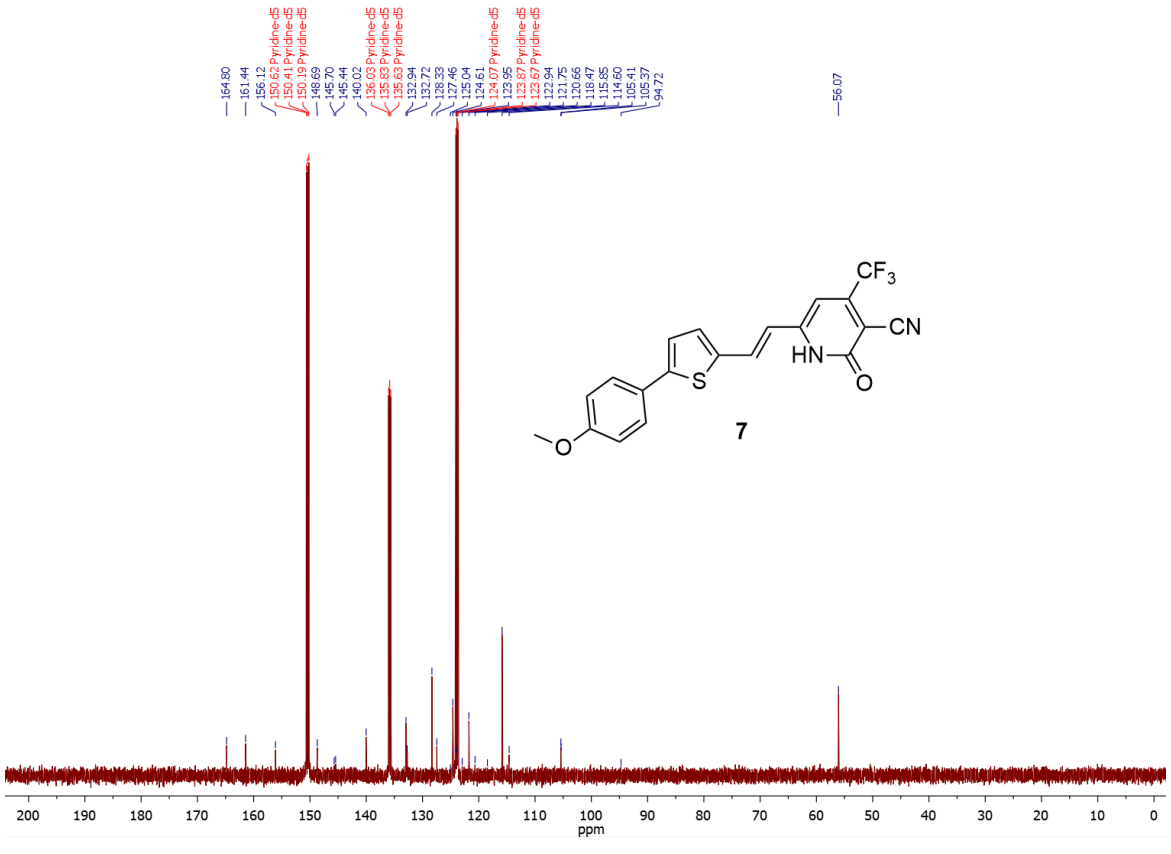


Figure S32. ^{13}C NMR spectrum of **7** in Pyridine-d_5

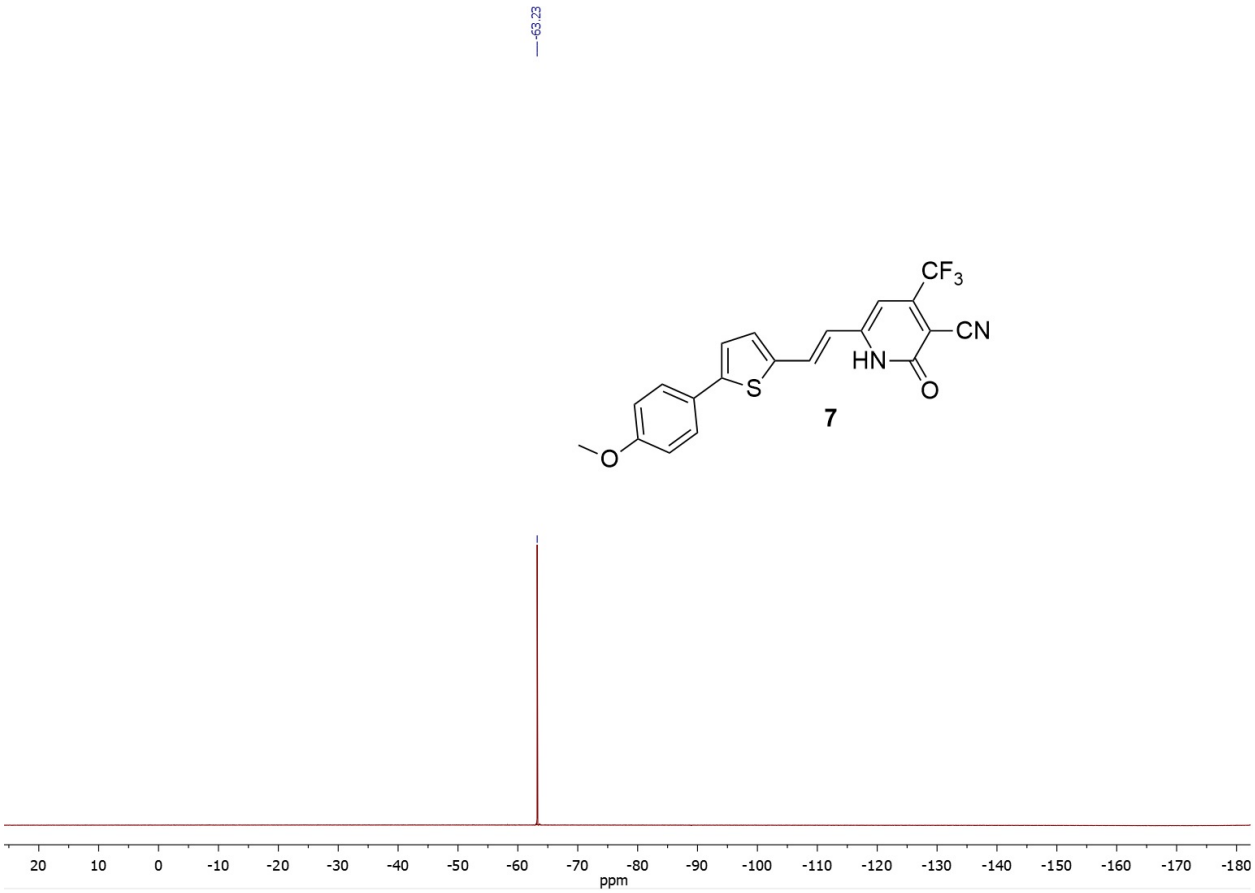


Figure S33. ^{19}F NMR spectrum of **7** in DMSO-d_6

6. Mass spectra of compounds 1-7.

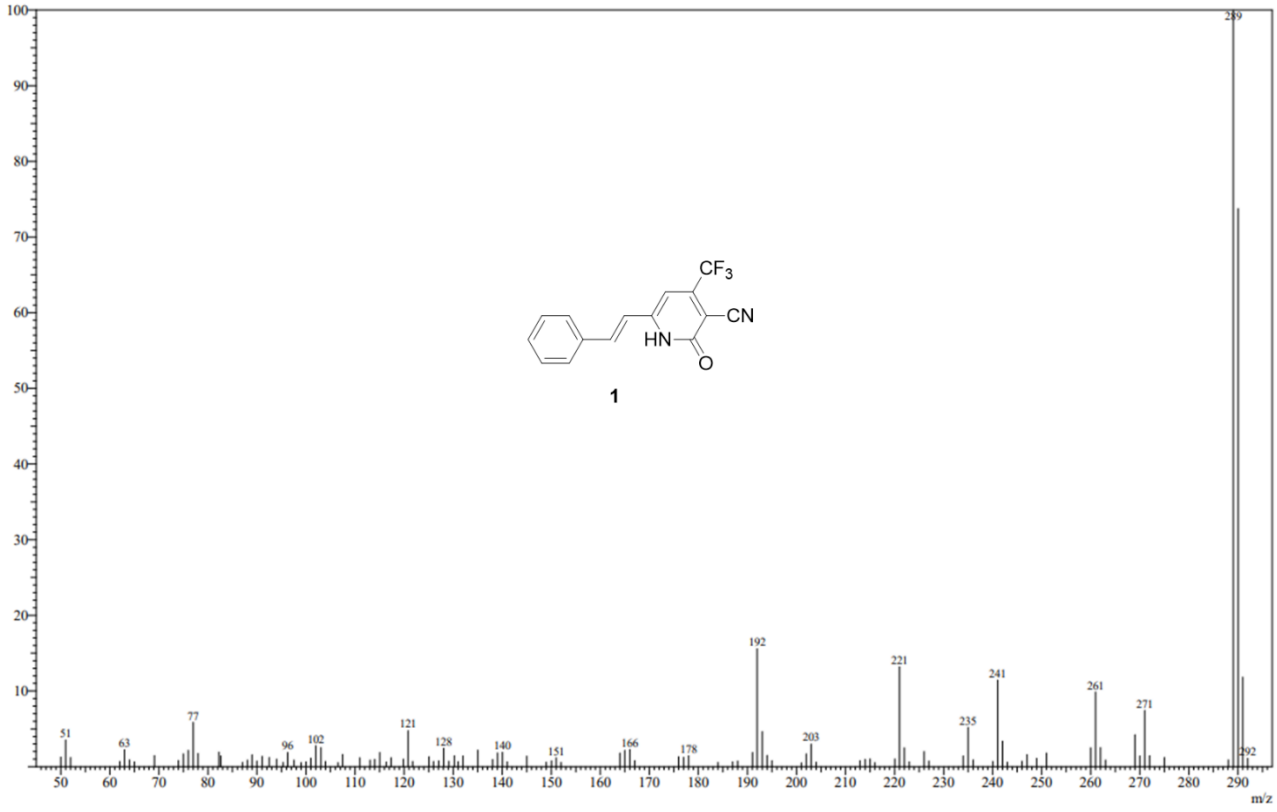


Figure S34. Mass-spectrum of compound **1**.

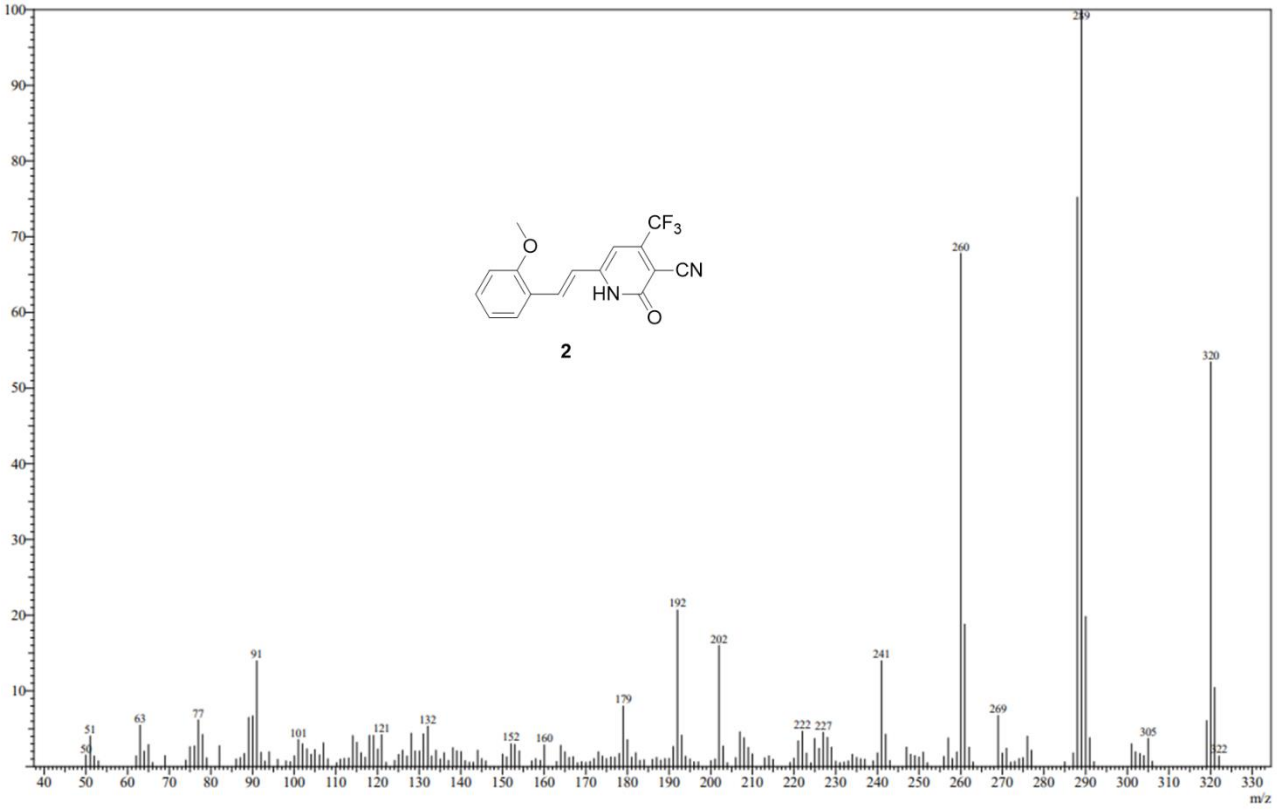


Figure S35. Mass-spectrum of compound **2**.

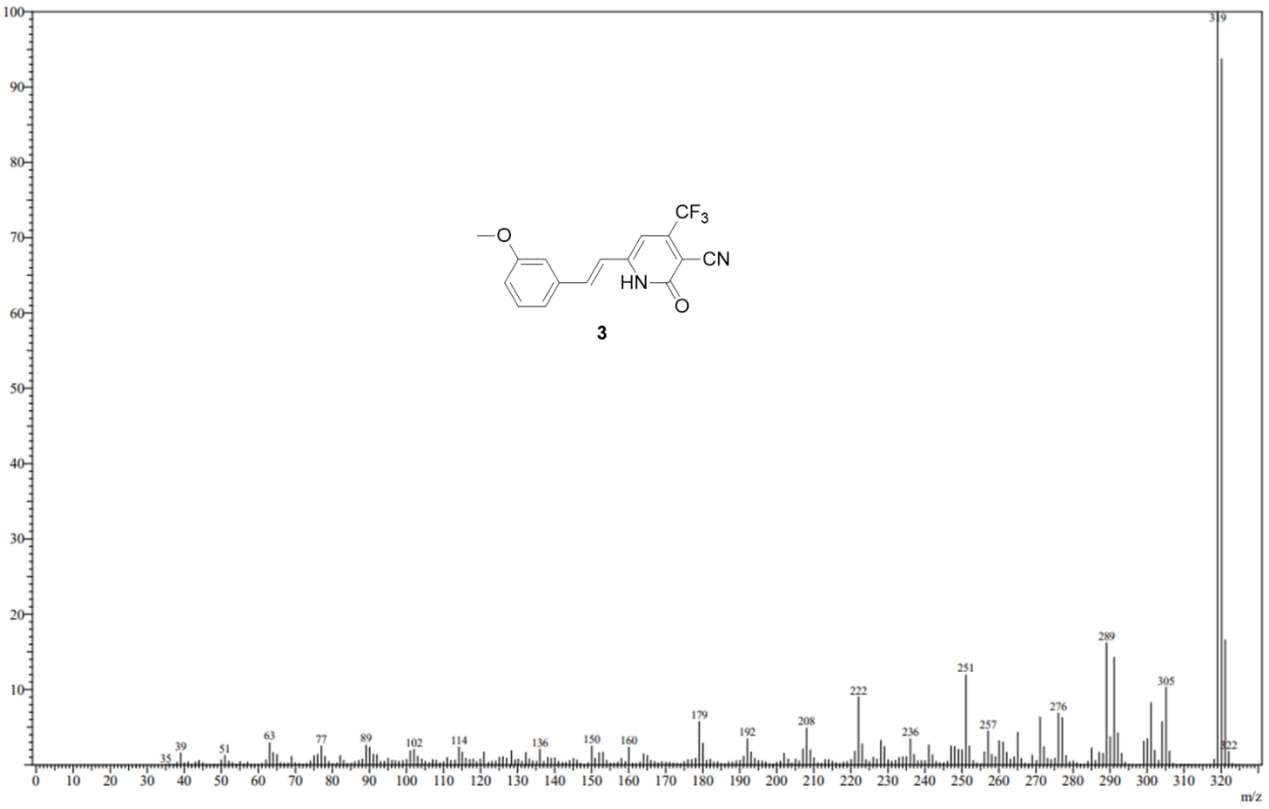


Figure S36. Mass-spectrum of compound **3**.

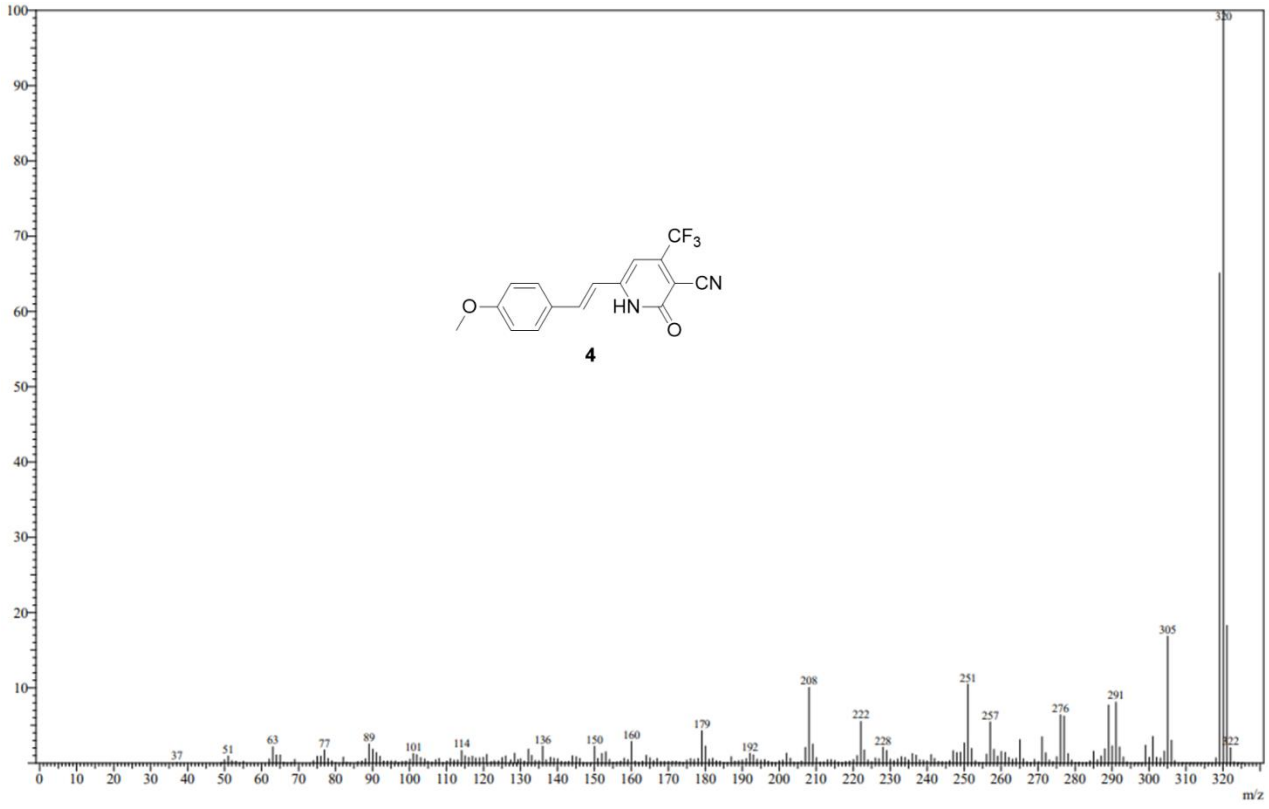


Figure S37. Mass-spectrum of compound **4**.

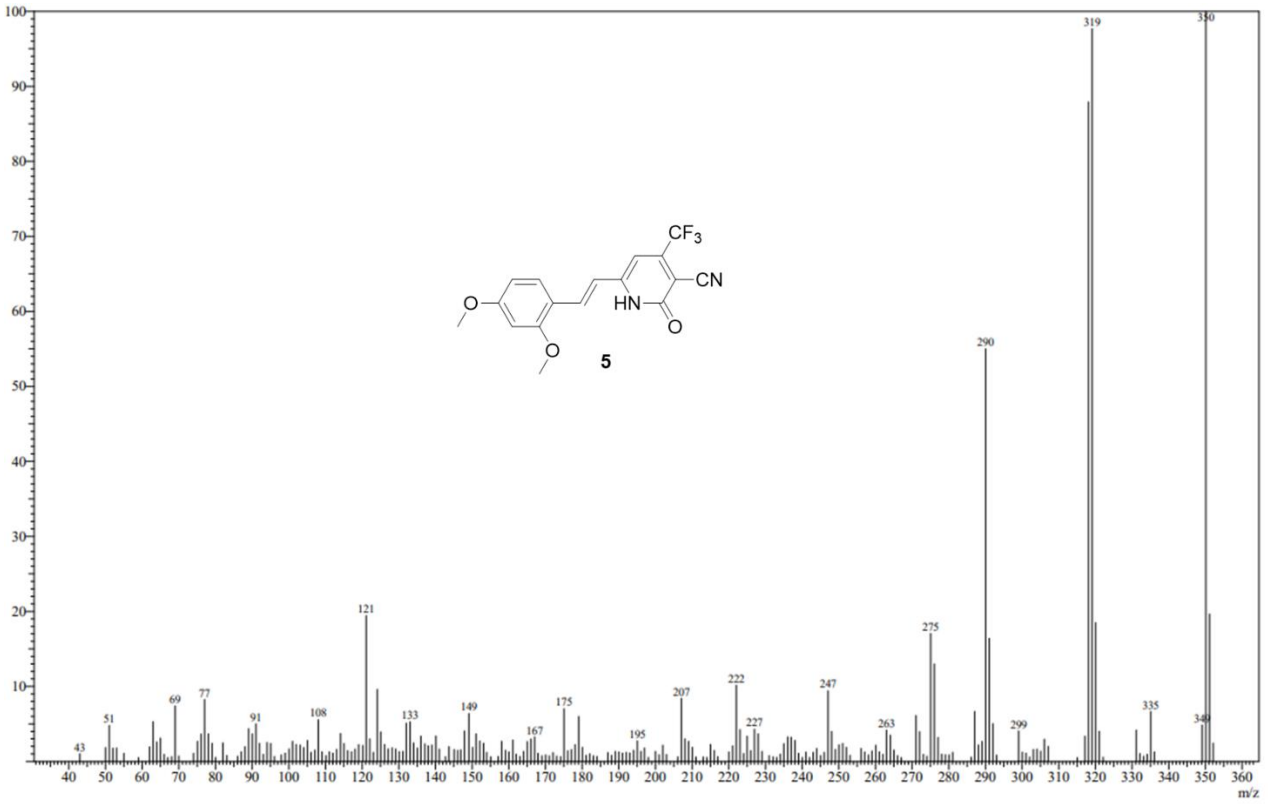


Figure S38. Mass-spectrum of compound **5**.

Figure S39. Mass-spectrum of compound **6**.

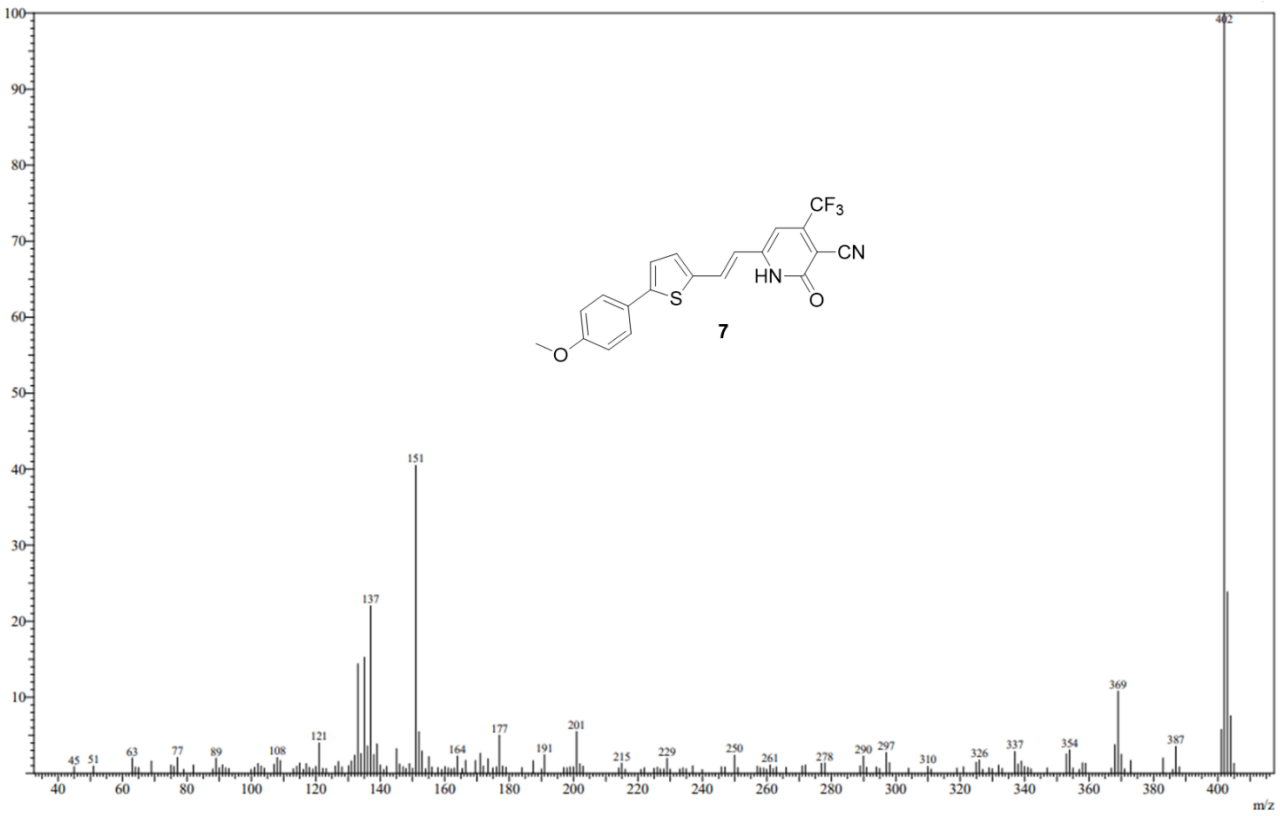


Figure S40. Mass-spectrum of compound **7**.

7. References.

[1] P. G. Seybold, M. Gouterman and J. Callis, *Photochem. Photobiol.*, 1969, **9**, 229–242.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, revision D.01, Gaussian*, Inc., Wallingford, CT, 2009.