Electronic Supplementary Material (ESI) for New Journal of Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Small heterocycles as highly luminescent building blocks in the solid state for organic synthesis

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Summary

1. Spectroscopic characterization

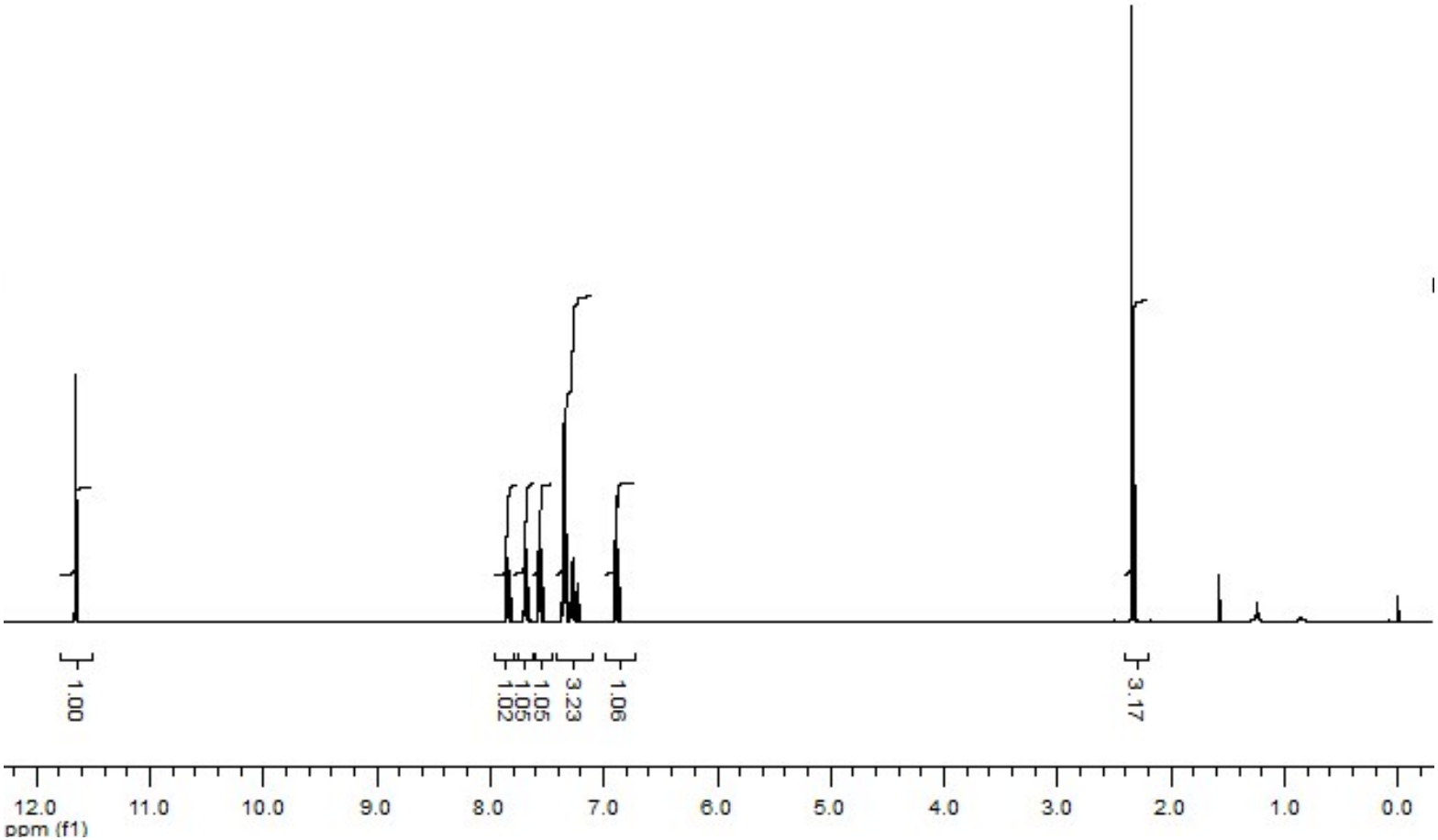


Fig. ESI1. ^{1}H NMR spectra of **16** in $CDCl_3$.

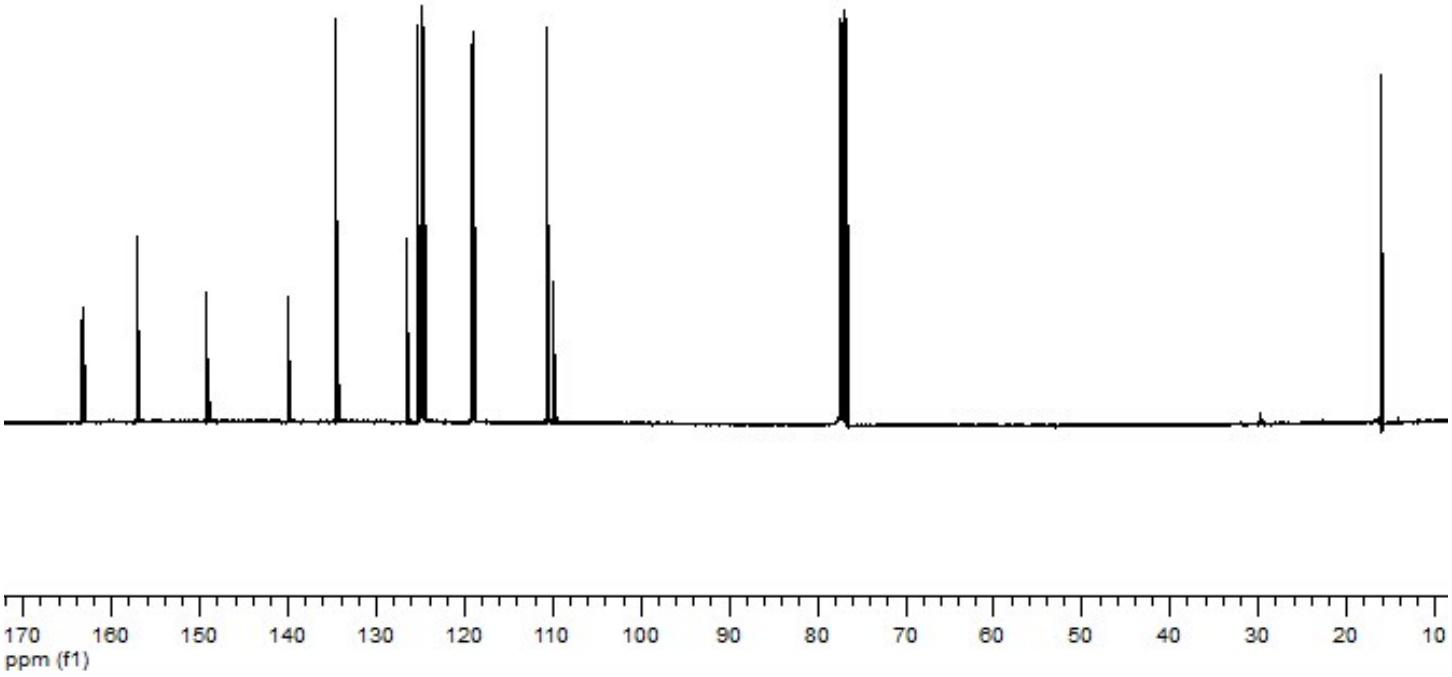


Fig. ESI2. ^{13}C NMR spectra of **16** in $CDCl_3$.

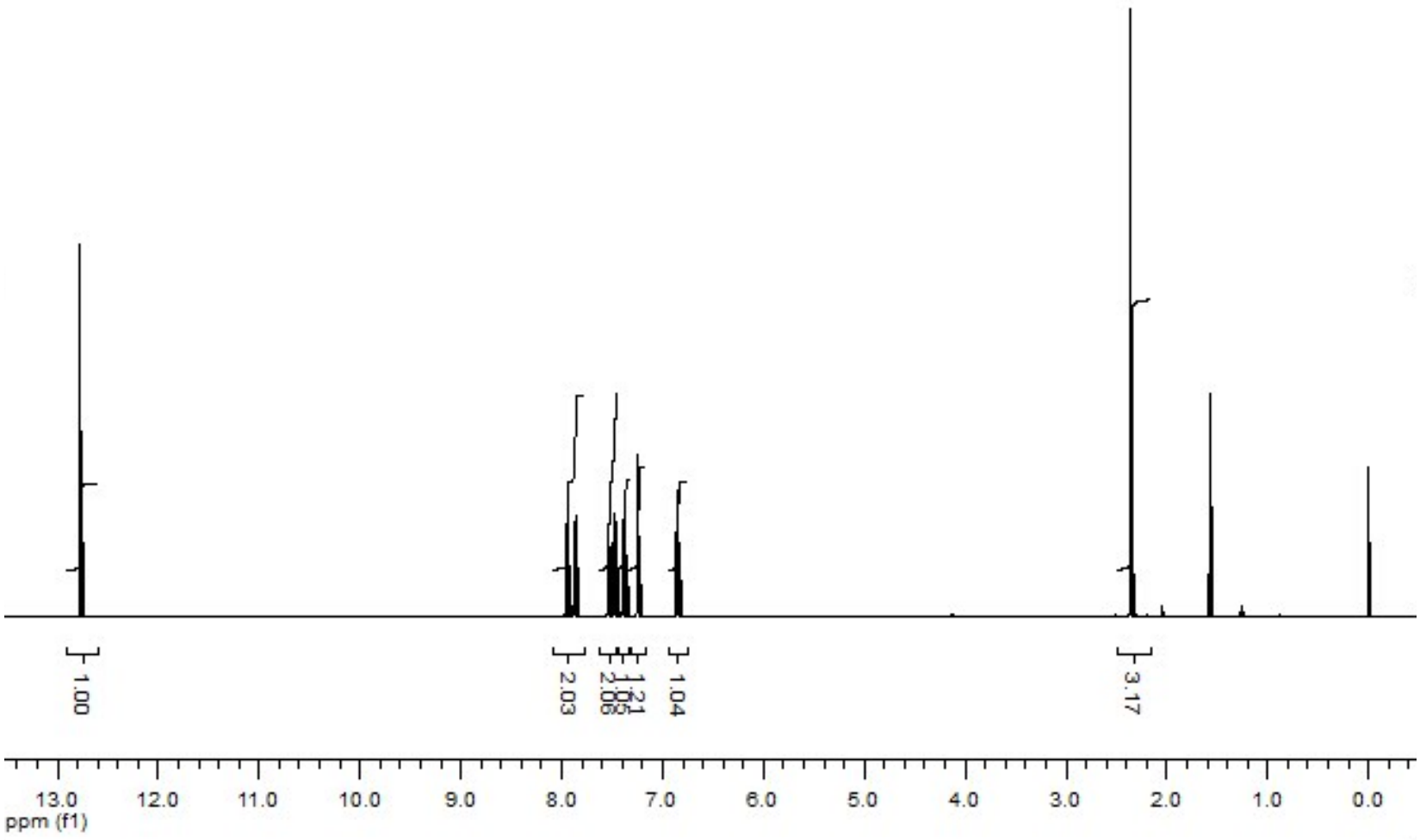


Fig. ESI3. ^{1}H NMR spectra of **17** in $CDCl_3$.

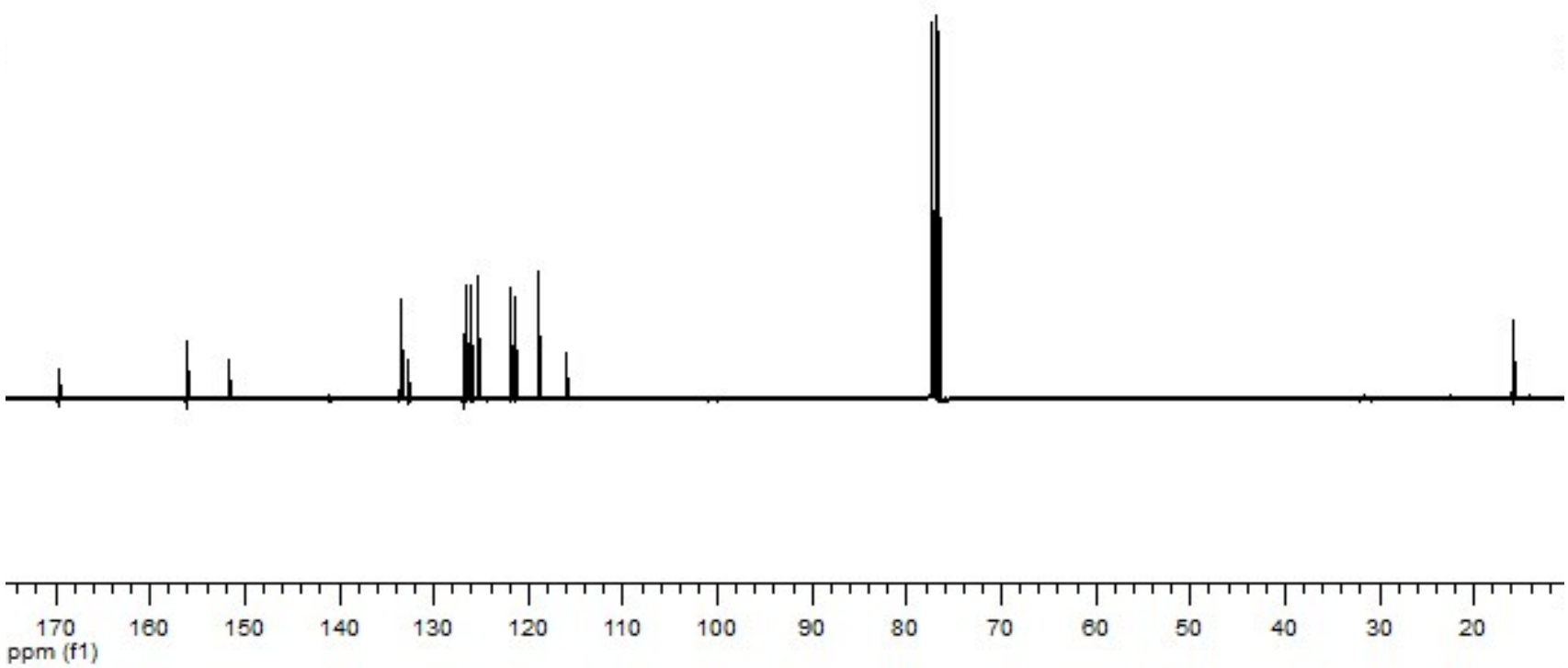


Fig. ESI4. ^{13}C NMR spectra of **17** in $CDCl_3$.

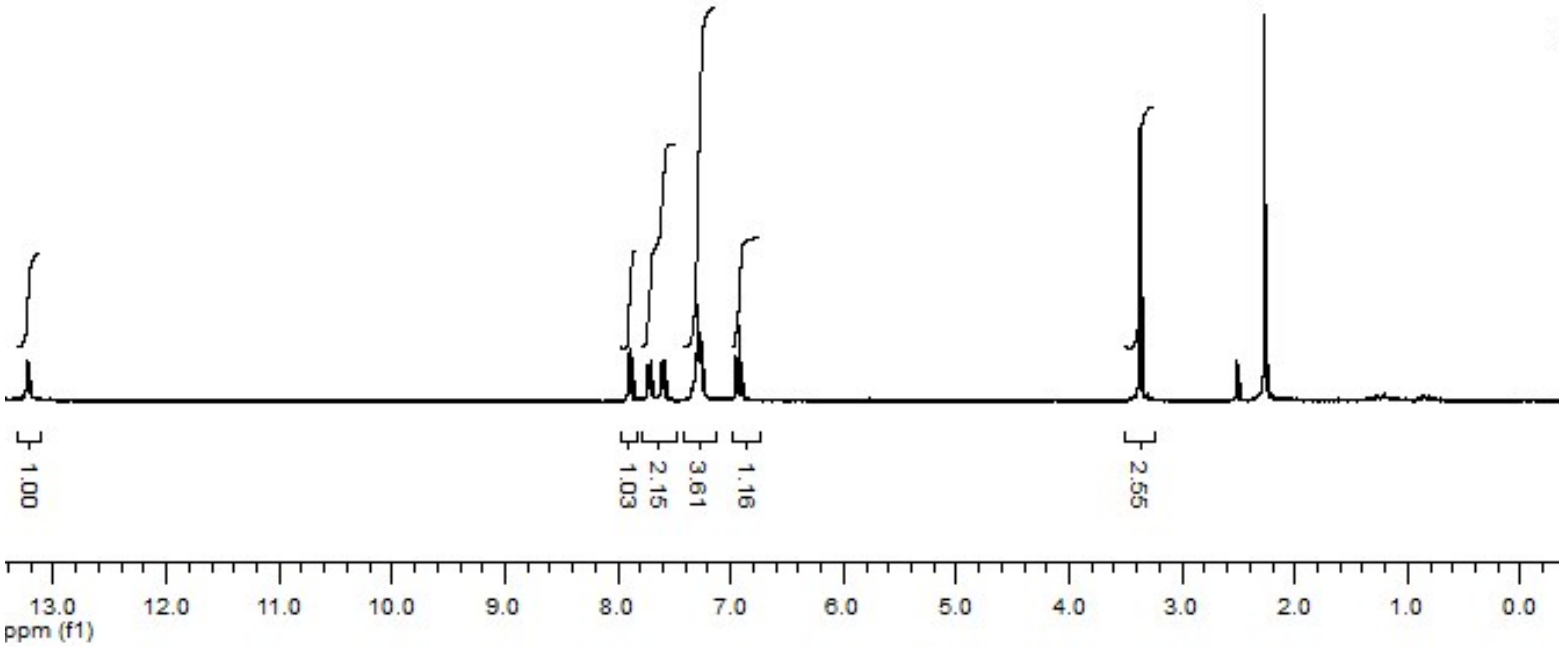


Fig. ESI5. ^{1}H NMR spectra of **18** in dmso-*d6*.

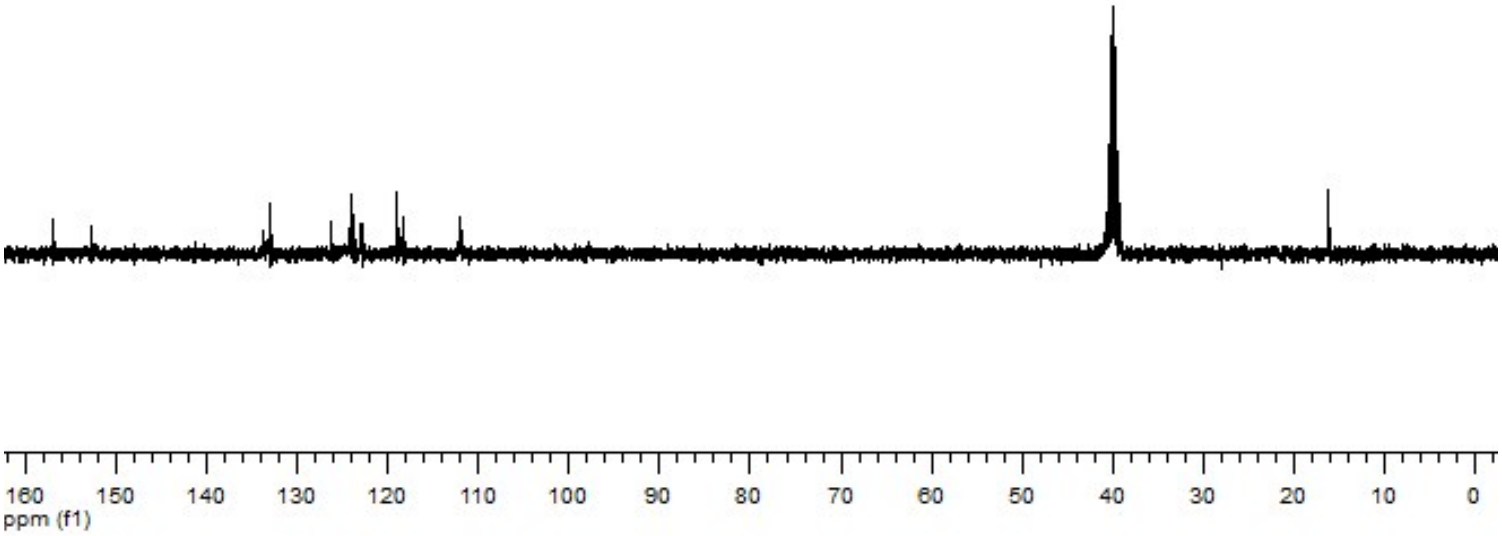


Fig. ESI6. ^{13}C NMR spectra of **18** in dmso-*d6*.

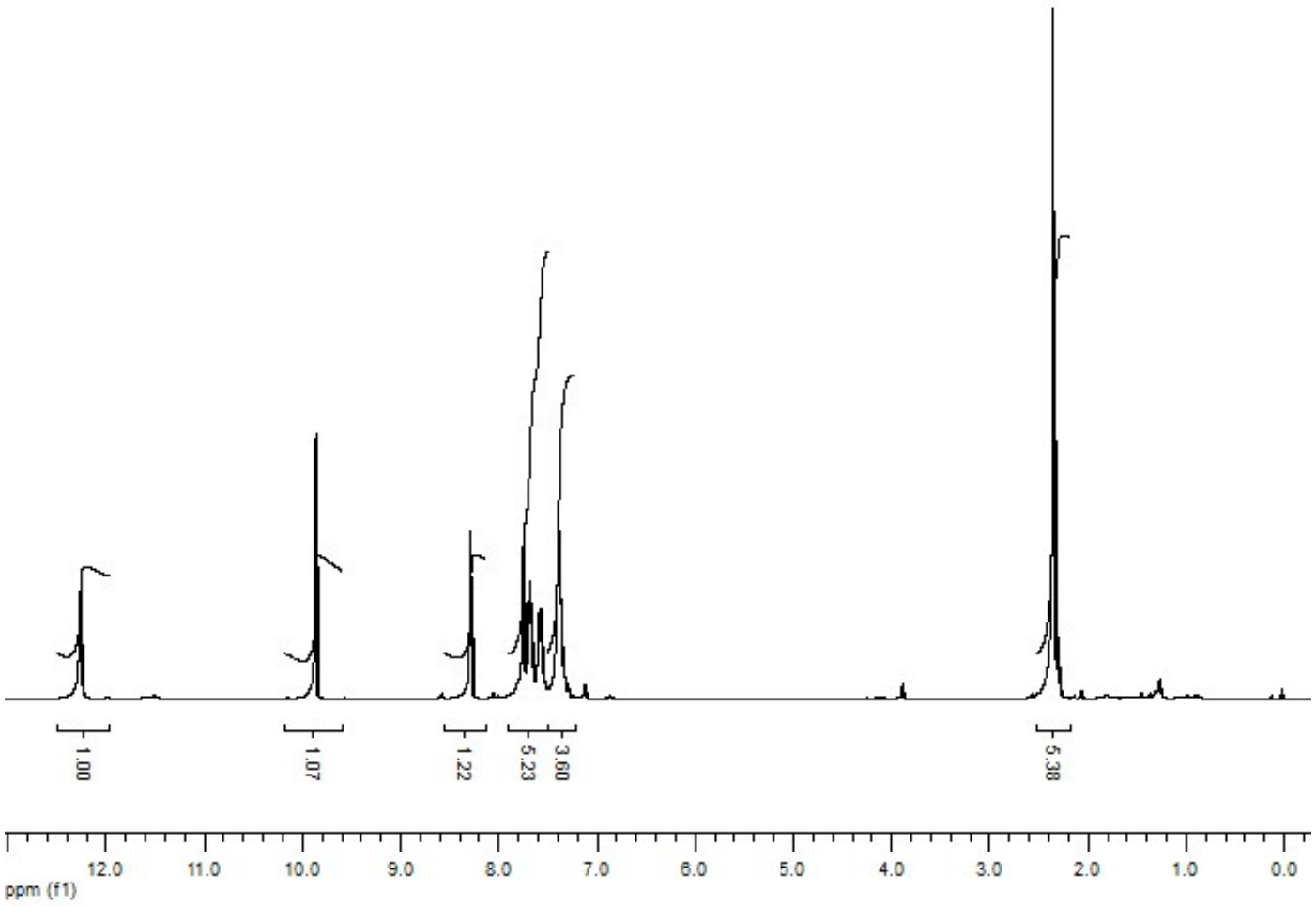


Fig. ESI7. ^{1}H NMR spectra of **19** in $CDCl_3$.

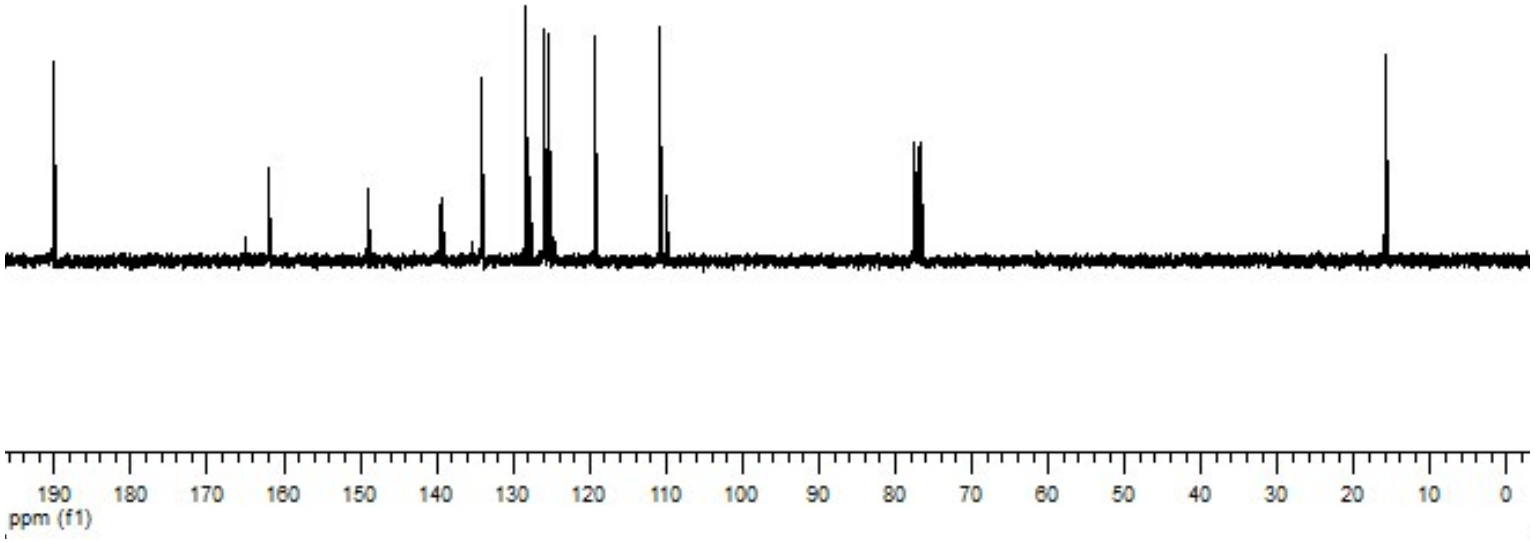


Fig. ESI8. ^{13}C NMR spectra of **19** in $CDCl_3$.

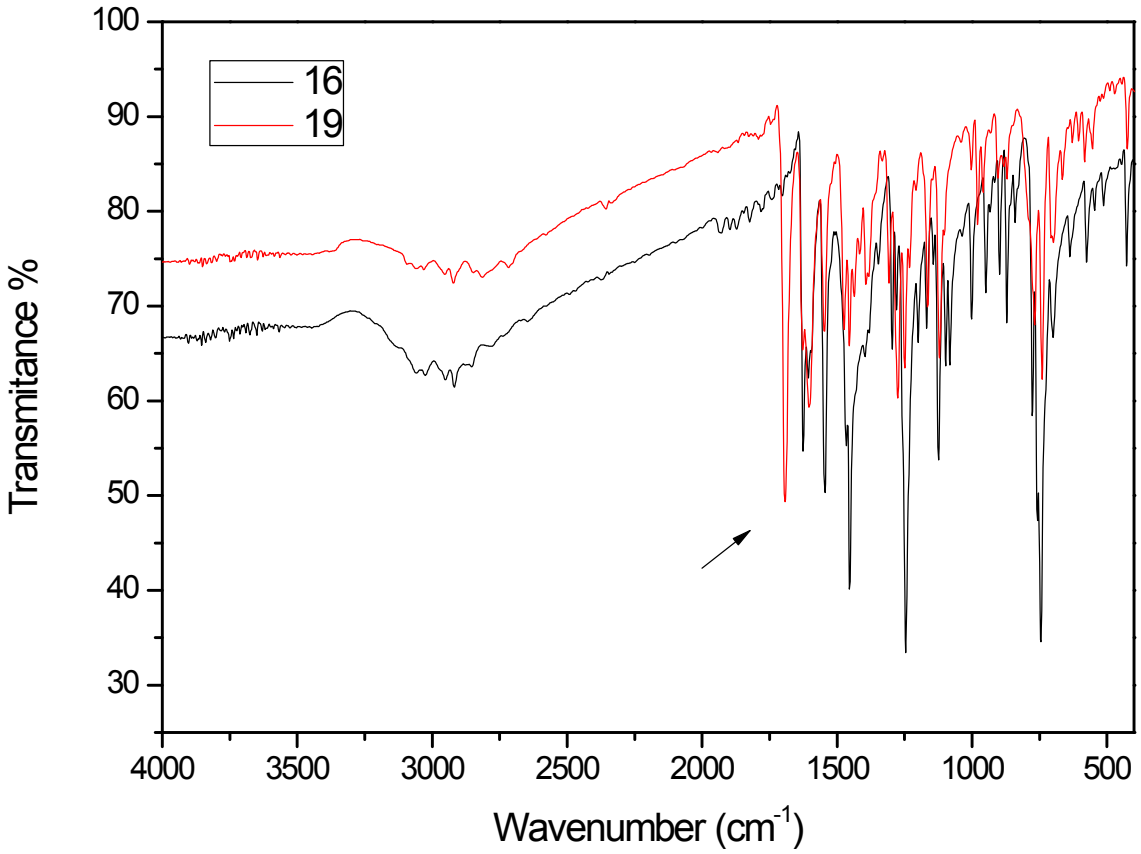


Fig. ESI9. FTIR spectra of **16** and **19**.

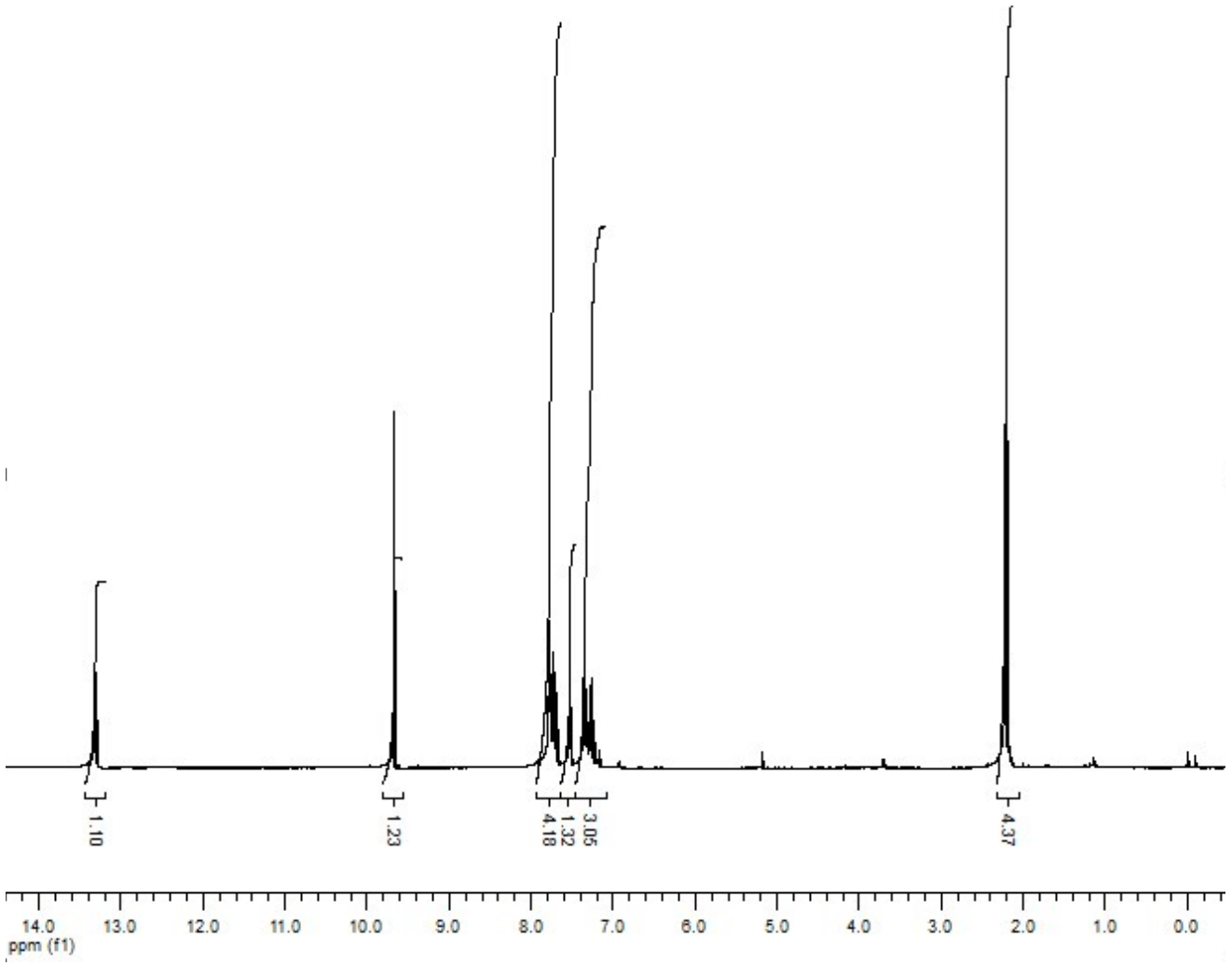


Fig. ESI10. ^{1}H NMR spectra of **20** in $CDCl_3$.

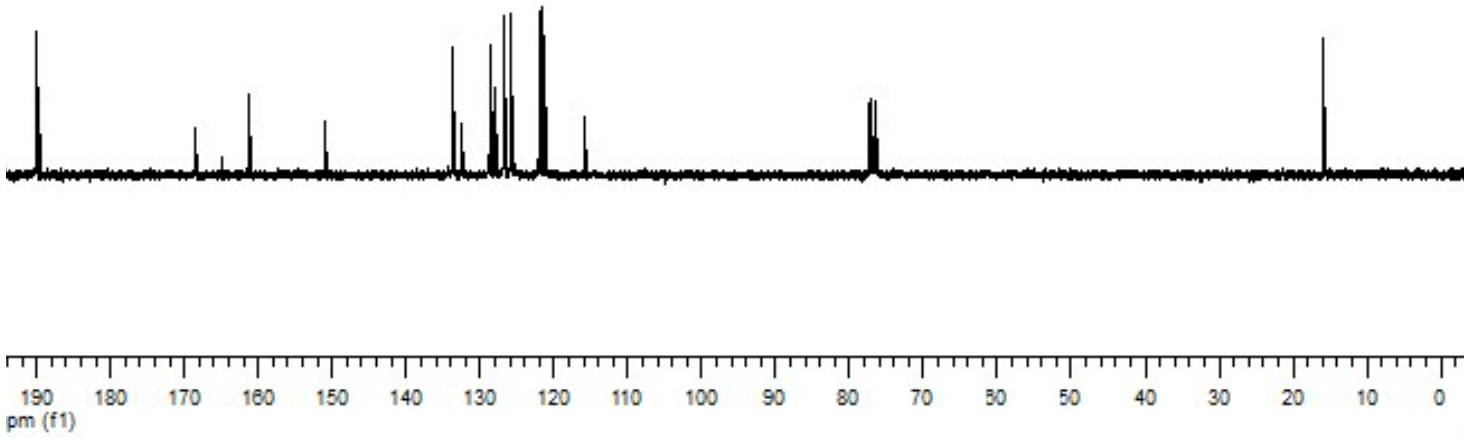


Fig. ESI11. ^{13}C NMR spectra of **20** in $CDCl_3$.

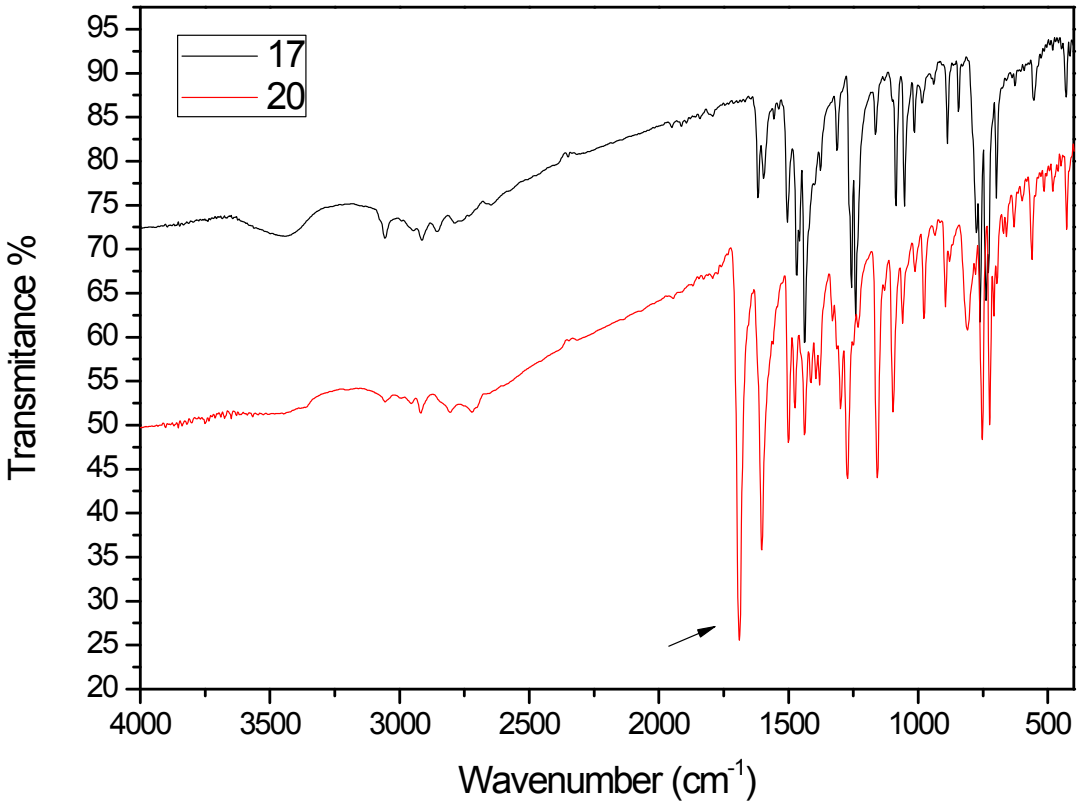


Fig. ESI12. FTIR spectra of **17** and **20**.

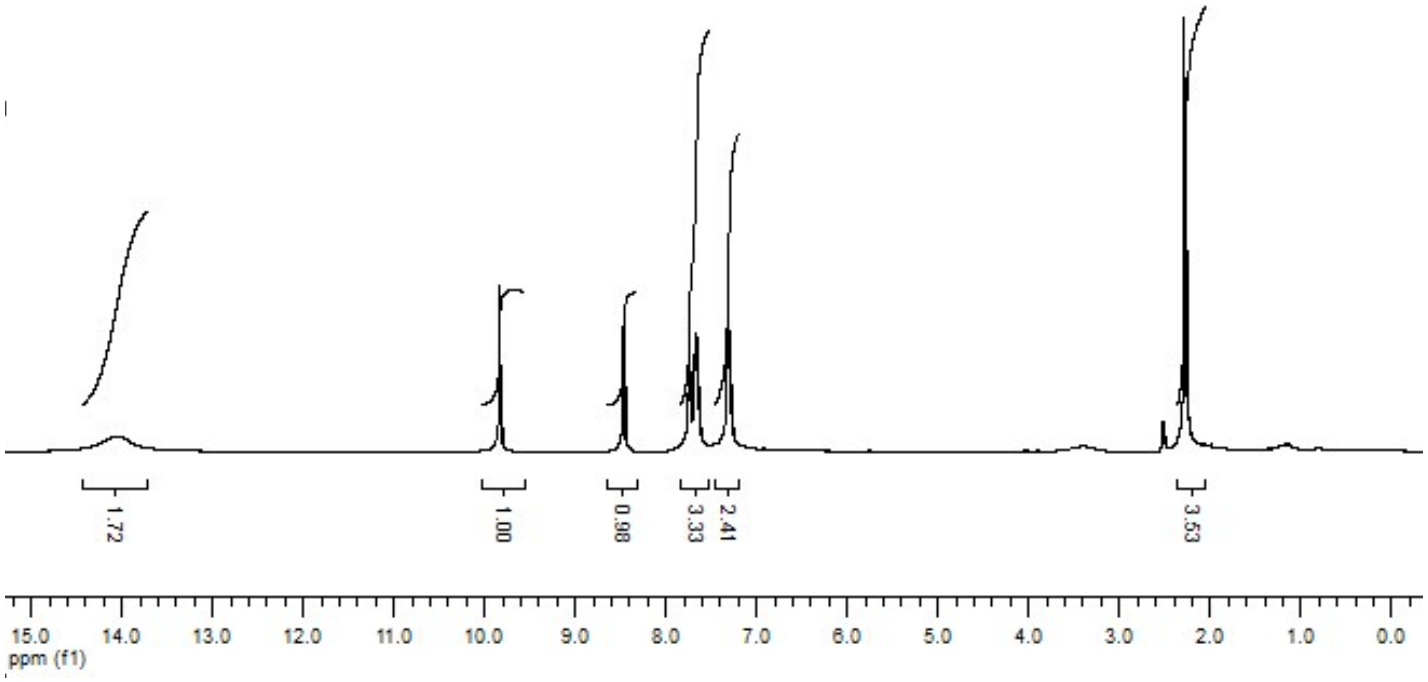


Fig. ESI13. ^{1}H NMR spectra of **21** in DMSO-d_6.

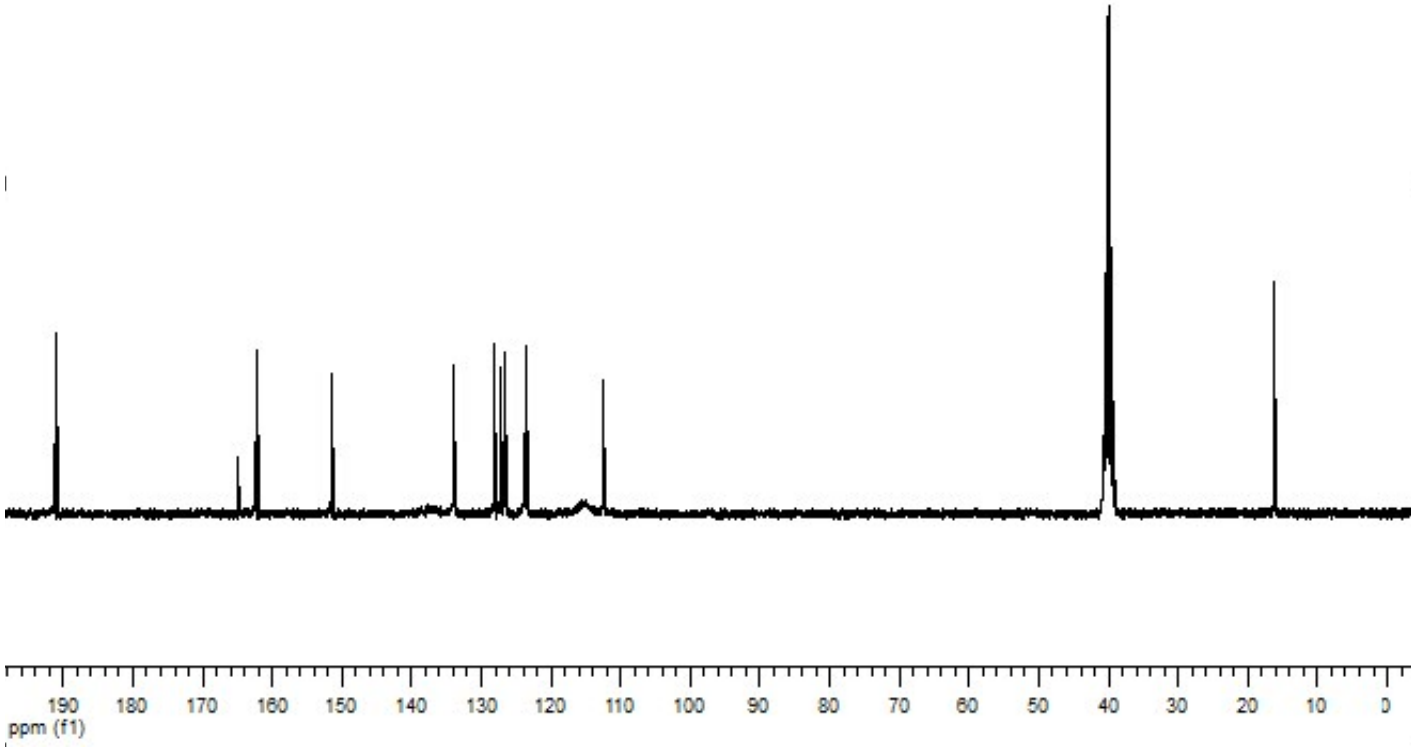


Fig. ESI14. ^{13}C NMR spectra of **21** in DMSO-d_6.

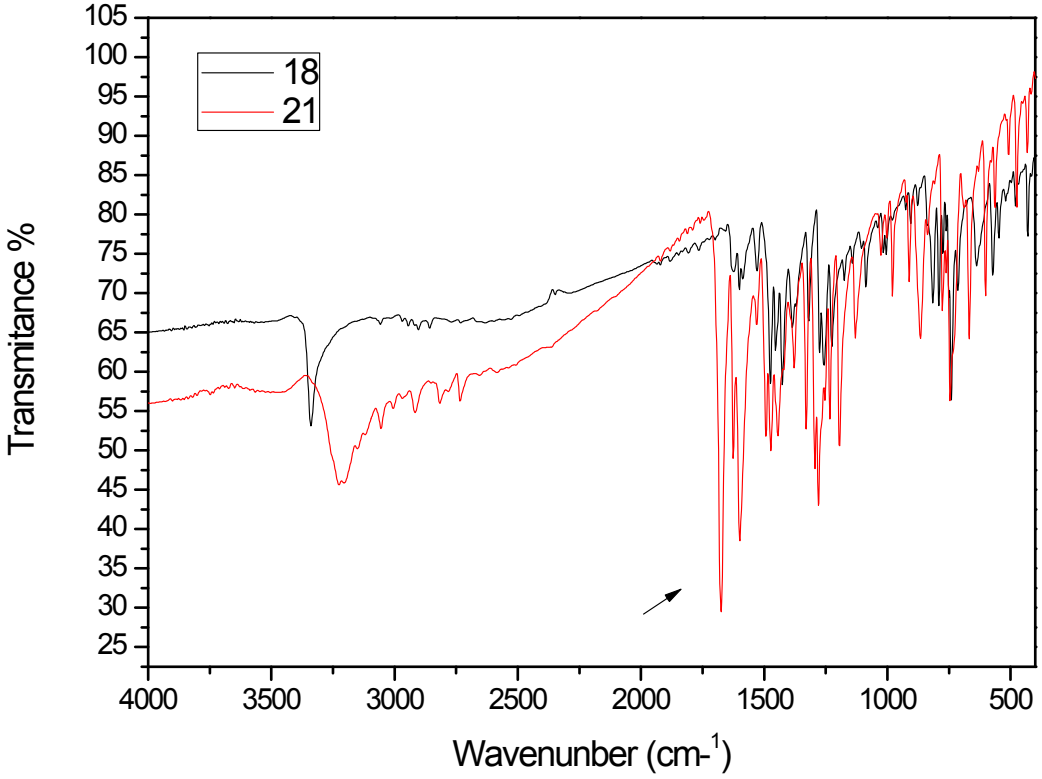


Fig. ESI15. FTIR spectra of **18** and **21**.

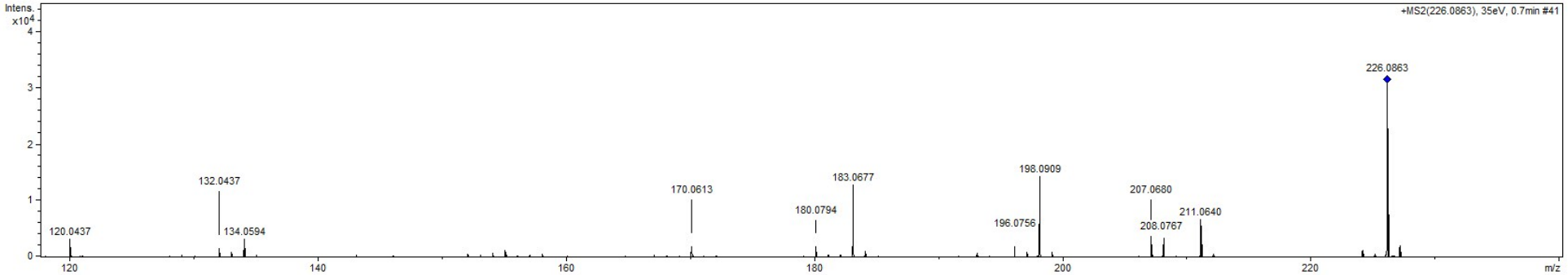


Fig. ESI16. HRMS spectra of **16**.

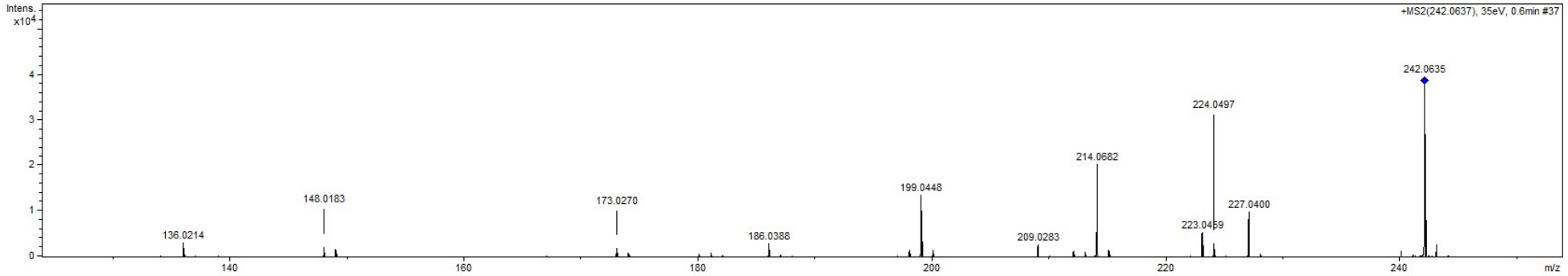


Fig. ESI17. HRMS spectra of **17**.

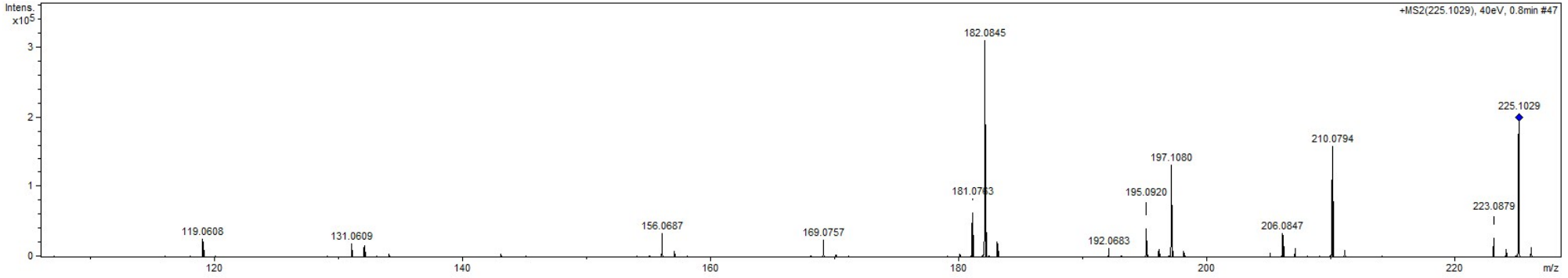


Fig. ESI18. HRMS spectra of **18**.

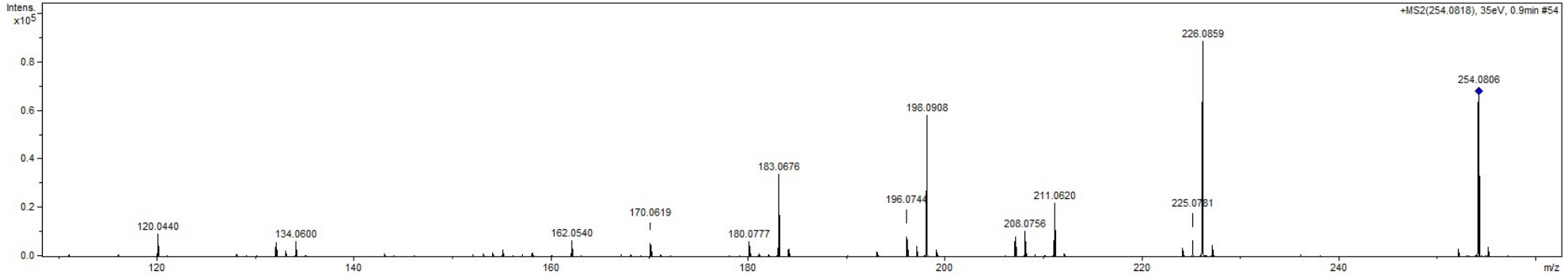


Fig. ESI19. HRMS spectra of **19**.

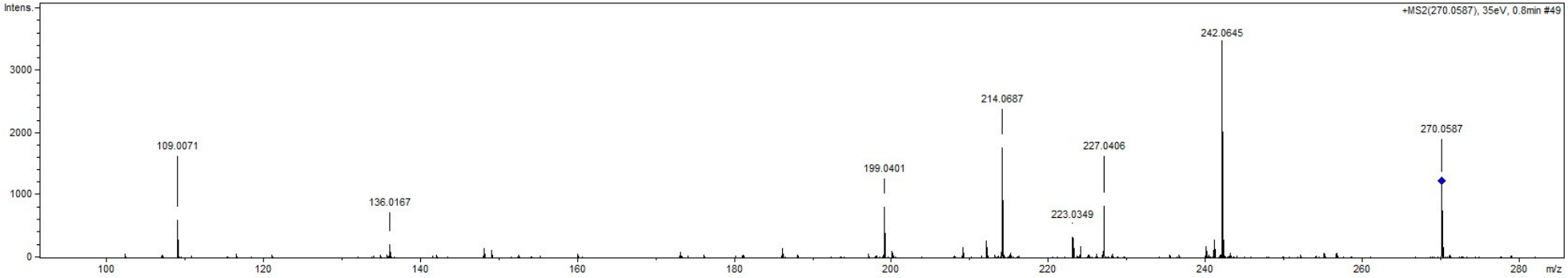


Fig. ESI20. HRMS spectra of **20**.

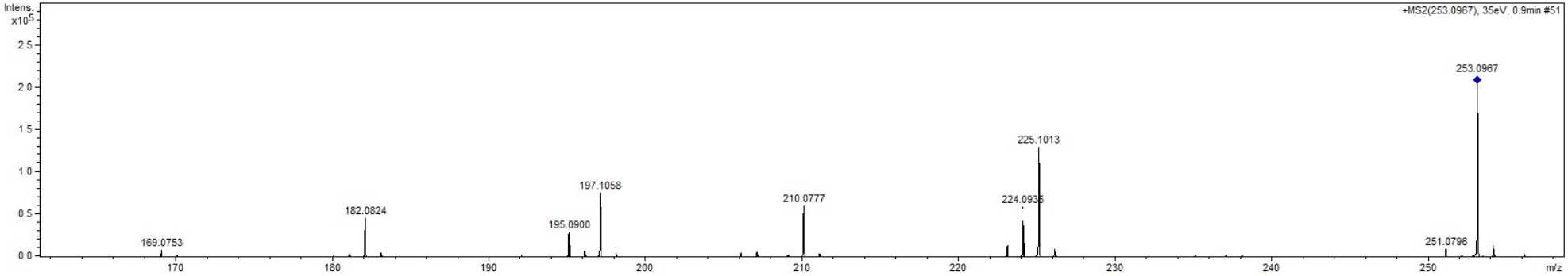


Fig. ESI21. HRMS spectra of **21**.

2. Photophysical data

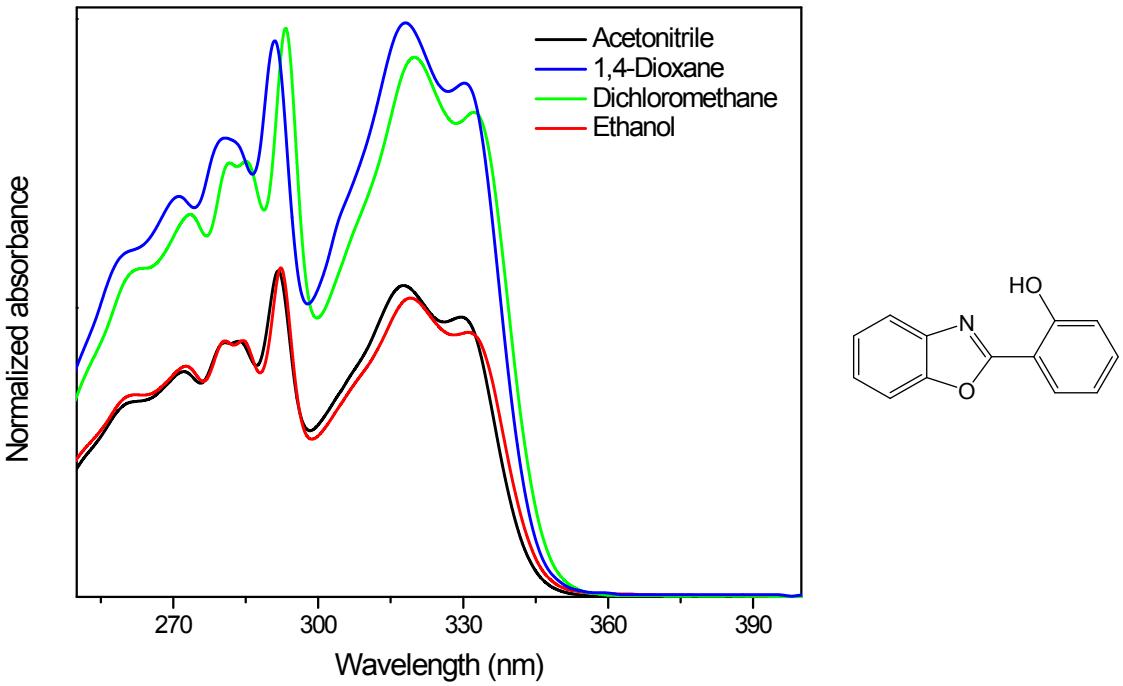


Fig. ESI22. Normalized UV-Vis absorption spectra of non-methylated HBO.

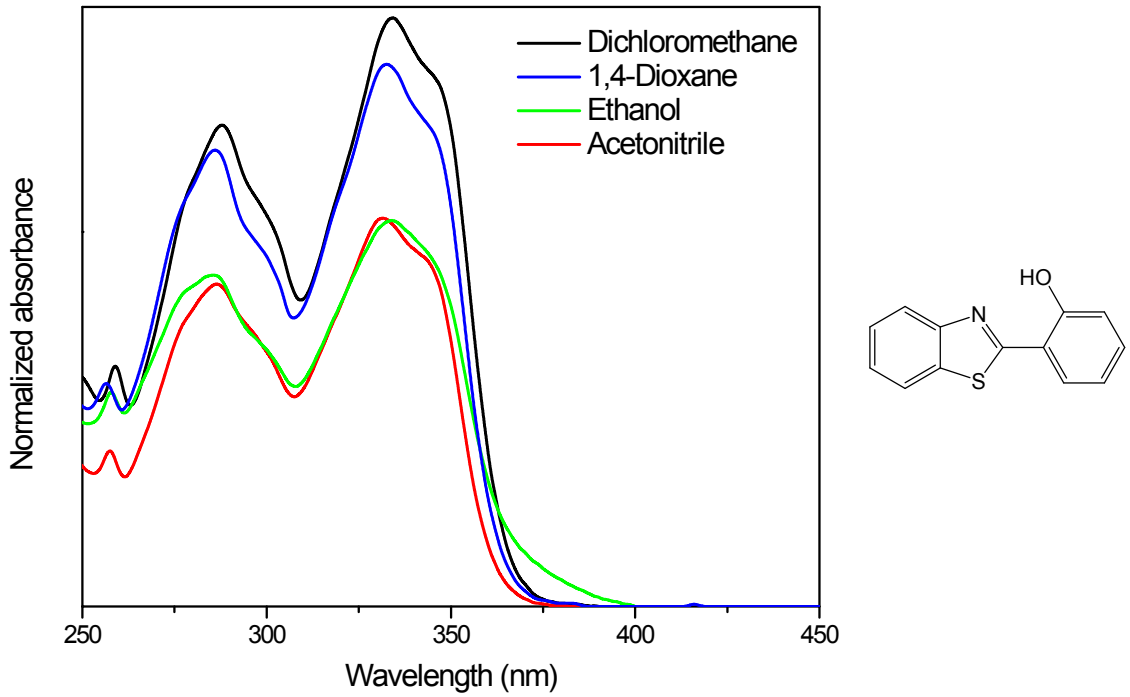


Fig. ESI23. Normalized UV-Vis absorption spectra of non-methylated HBT.

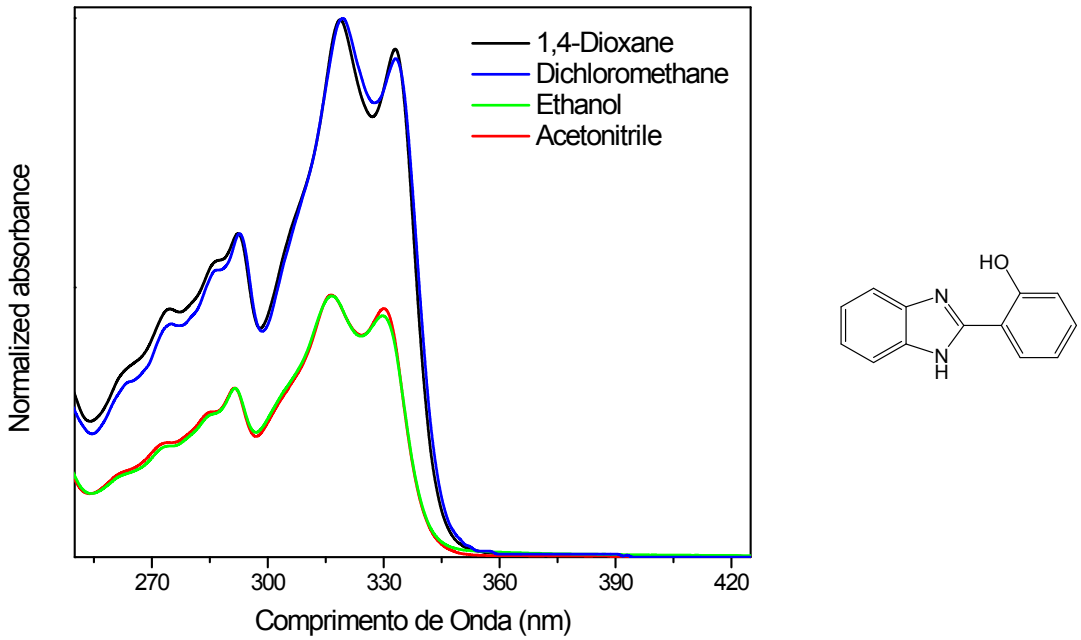


Fig. ESI24. Normalized UV-Vis absorption spectra of non-methylated HBI.

Table ESI1. Photophysical data of the non-methylated HBO, HBT and HBI, where λ_{abs} and λ_{em} are the absorption and emission maxima (nm), respectively, ε is the molar extinction coefficient (10^4 $M^{-1} \cdot cm^{-1}$) and $\Delta\lambda_{ST}$ is the Stokes' shift (cm^{-1}).

#	Solvent	λ_{abs}	ε	Enol		Keto	
				λ_{em}	$\Delta\lambda_{ST}$	λ_{em}	$\Delta\lambda_{ST}$
HBO	1,4-Dioxane	330	1.03	367	3055	490	9895
HBT		342	0.95	369	2139	511	9670
HBI		330	2.15	-	-	464	8751
HBO	Dichloromethane	332	1.34	360	2343	482	9374
HBT		344	0.42	381	2823	511	9500
HBI		333	1.67	-	-	463	8432
HBO	Ethanol	331	1.55	364	2739	479	9335
HBT		335	1.20	375	3184	-	-
HBI		330	2.10	355	2134	451	8130
HBO	Acetonitrile	330	1.12	359	2448	482	9556
HBT		342	1.58	372	2358	512	9709
HBI		330	2.00	-	-	460	8564

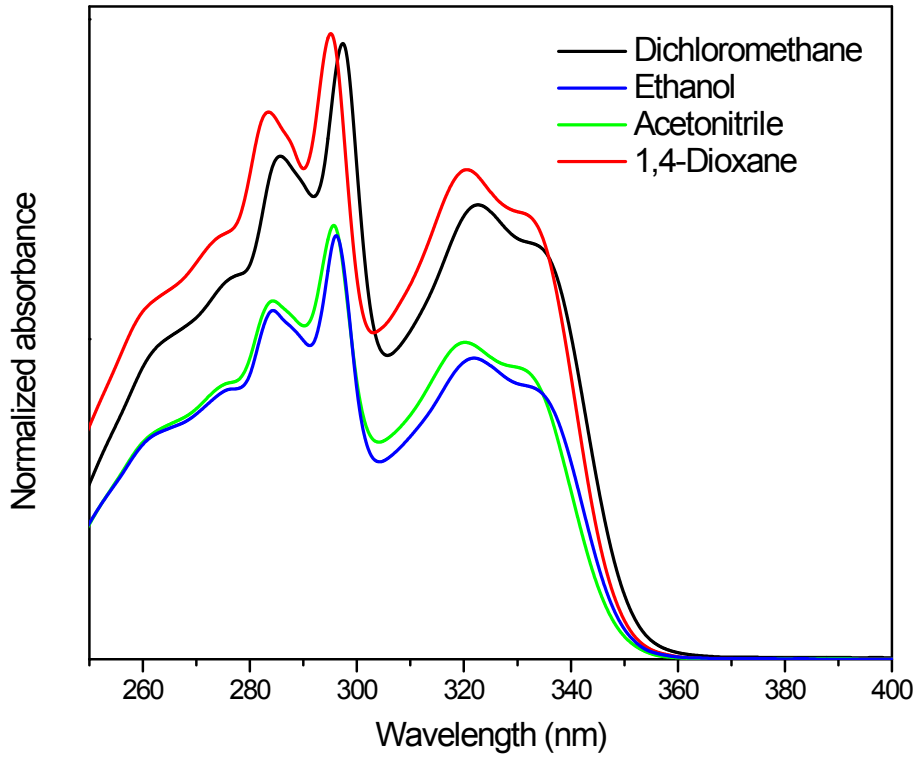


Fig. ESI25. Normalized UV-Vis absorption spectra of **16**.

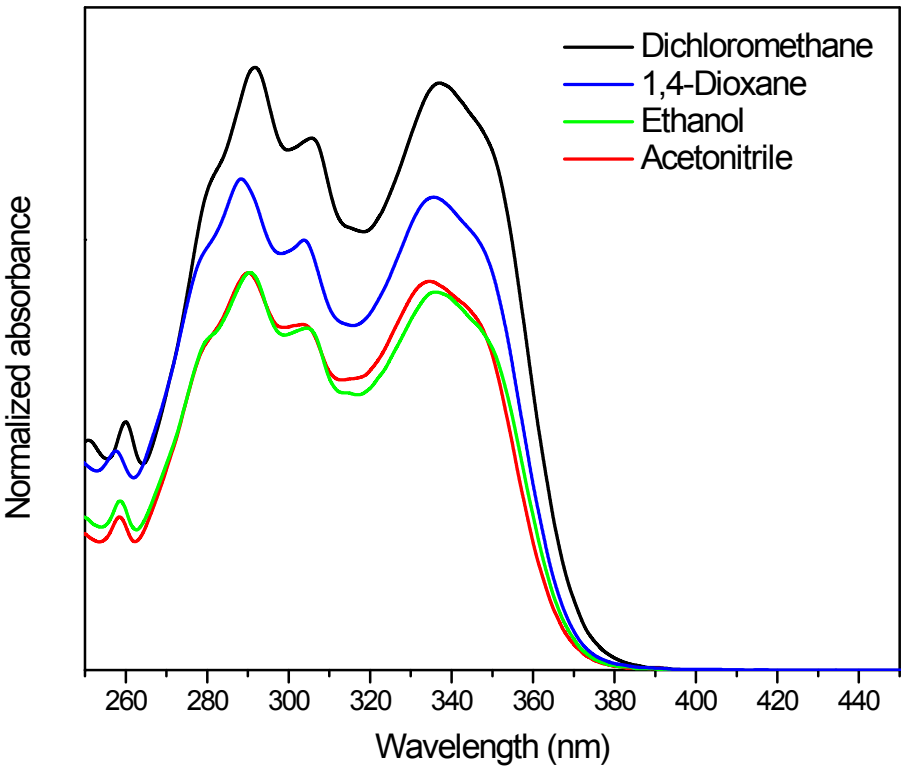


Fig. ESI26. Normalized UV-Vis absorption spectra of **17**.

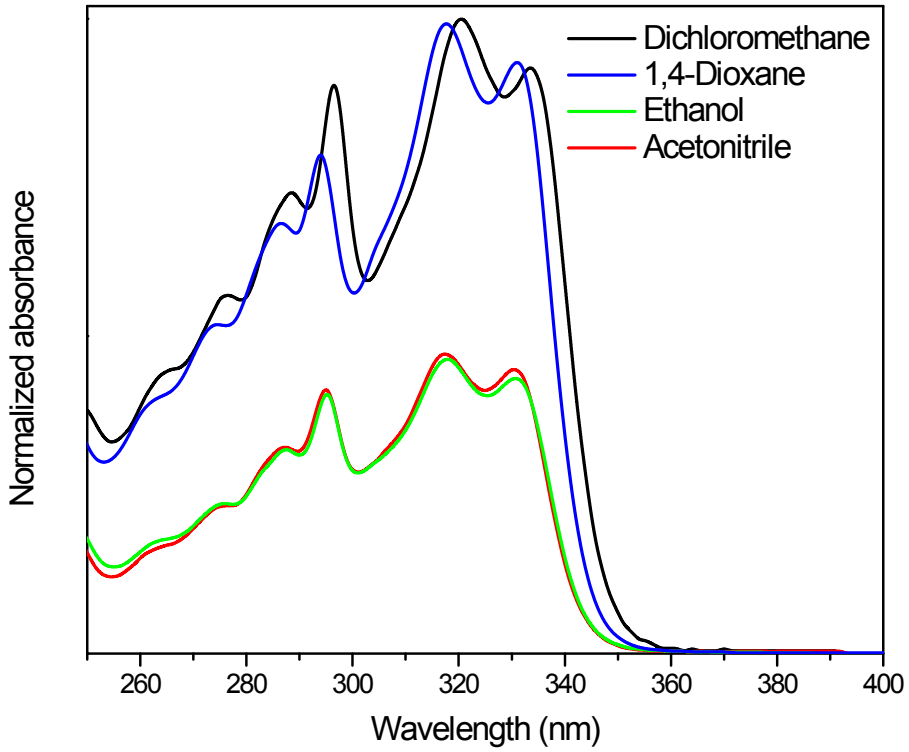


Fig. ESI27. Normalized UV-Vis absorption spectra of **18**.

Table ESI2. Photophysical data of **16-18**, where λ_{abs} and λ_{em} are the absorption and emission maxima (nm), respectively, ε is the molar extinction coefficient (10^4 $M^{-1}\cdot cm^{-1}$), $\Delta\lambda_{ST}$ is the Stokes' shift (cm^{-1}) and QY is the total quantum yield.

#	Solvent	λ_{abs}	e	Enol		Keto		QY
				λ_{em}	$\Delta\lambda_{ST}$	λ_{em}	$\Delta\lambda_{ST}$	
16		331	1.15	368	3038	498	10131	0.008
17	1,4-Dioxane	341	2.73	390	3684	529	10422	0.014
18		331	4.59	-	-	473	9070	0.368
16		335	1.10	382	3673	493	9567	0.057
17	Dichloromethane	346	1.21	384	2860	530	10034	0.024
18		336	1.21	-	-	466	8303	0.490
16		333	1.33	372	3148	490	9622	0.001
17	Ethanol	338	0.52	382	3408	510	9978	0.010
18		331	2.56	-	-	460	8472	0.469
16		331	1.19	-	-	497	10091	0.006
17	Acetonitrile	342	1.19	369	2139	470	7963	0.006
18		330	0.73	-	-	469	8981	0.313

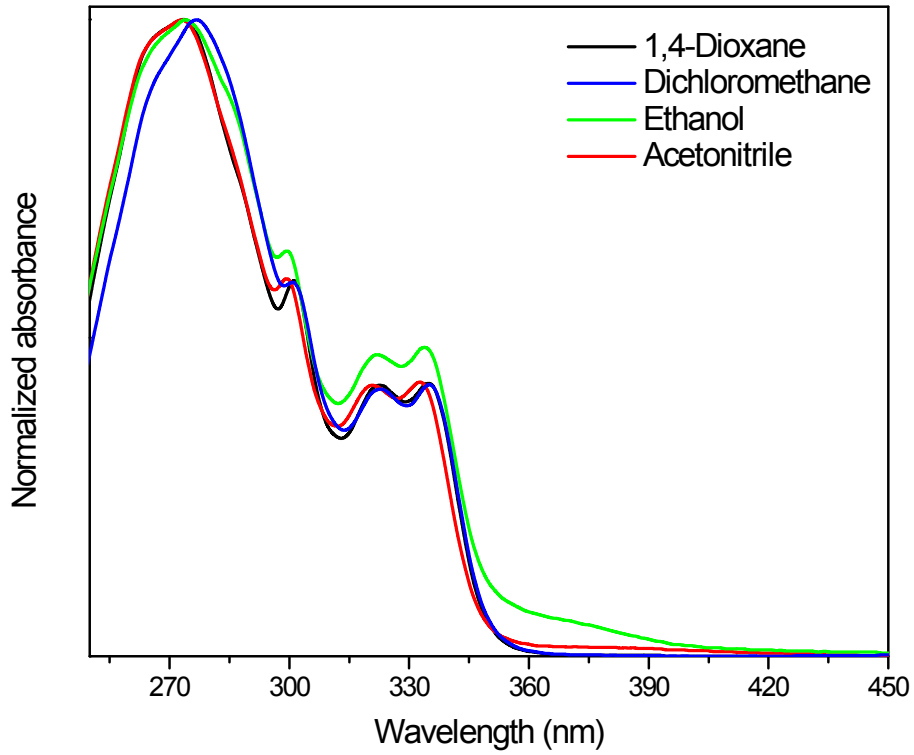


Fig. ESI28. Normalized UV-Vis absorption spectra of **19**.

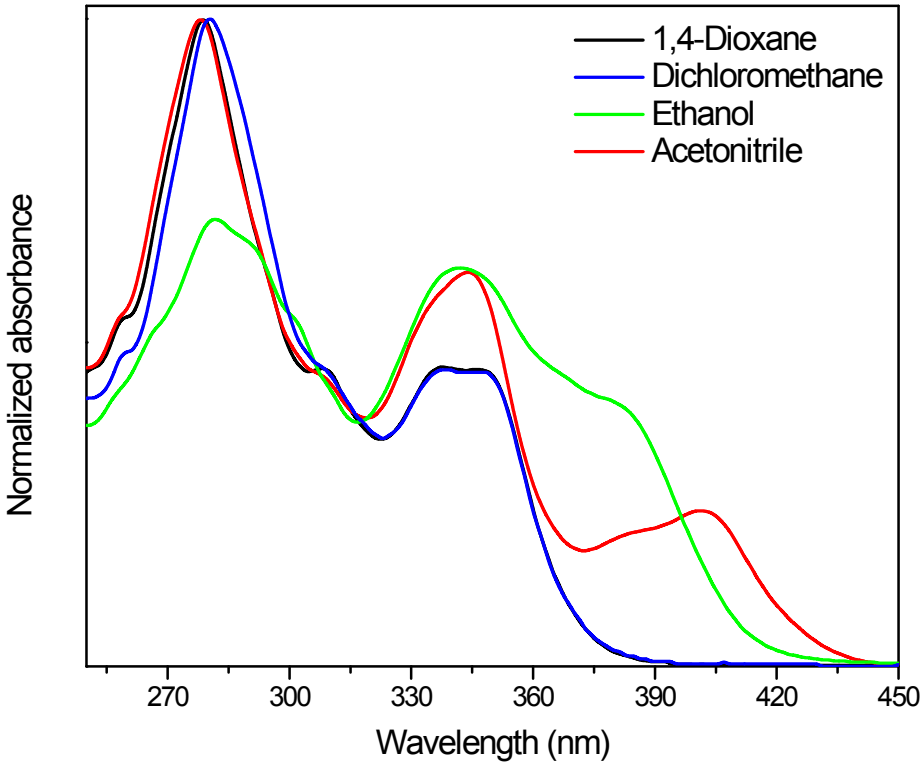


Fig. ESI29. Normalized UV-Vis absorption spectra of **20**.

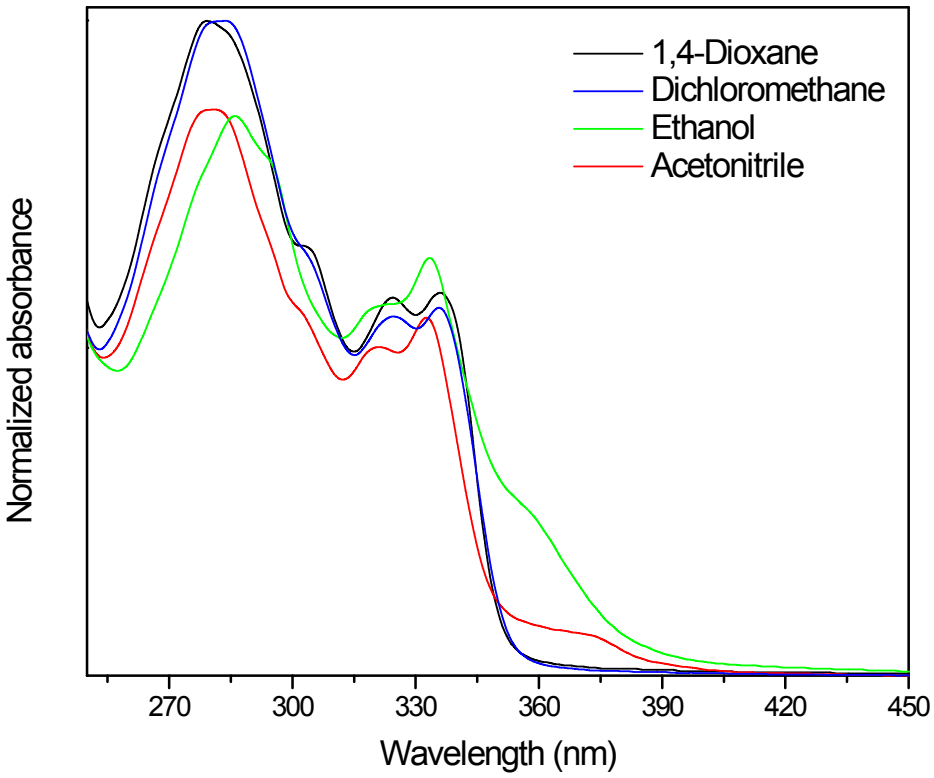


Fig. ESI30. Normalized UV-Vis absorption spectra of **21**.

Table ESI3. Photophysical data of **19-21**, where λ_{abs} and λ_{em} are the absorption and emission maxima (nm), respectively, ε is the molar extinction coefficient (10^4 $M^{-1}\cdot cm^{-1}$), $\Delta\lambda_{ST}$ is the Stokes' shift (cm^{-1}) and QY is the total quantum yield.

#	Solvent	λ_{abs}	ε	Enol		Keto		QY
				λ_{em}	$\Delta\lambda_{ST}$	λ_{em}	$\Delta\lambda_{ST}$	
19	1,4-Dioxane	335	1.10	382	3673	493	9567	0.057
20		346	1.21	384	2860	530	10034	0.024
21		336	1.21	-	-	466	8303	0.490
19	Dichloromethane	335	1.58	-	-	486	9275	0.097
20		347	0.91	-	-	520	9588	0.051
21		336	1.04	-	-	463	8164	0.535
19	Ethanol	334	1.37	422	6243	487	9406	0.076
20		343	1.52	445	6683	-	-	0.173
21		333	1.59	397	4841	457	8148	0.241
19	Acetonitrile	333	1.15	-	-	486	9454	0.152
20		345	1.35	448	6664	-	-	0.260
21		332	2.05	-	-	461	8429	0.062

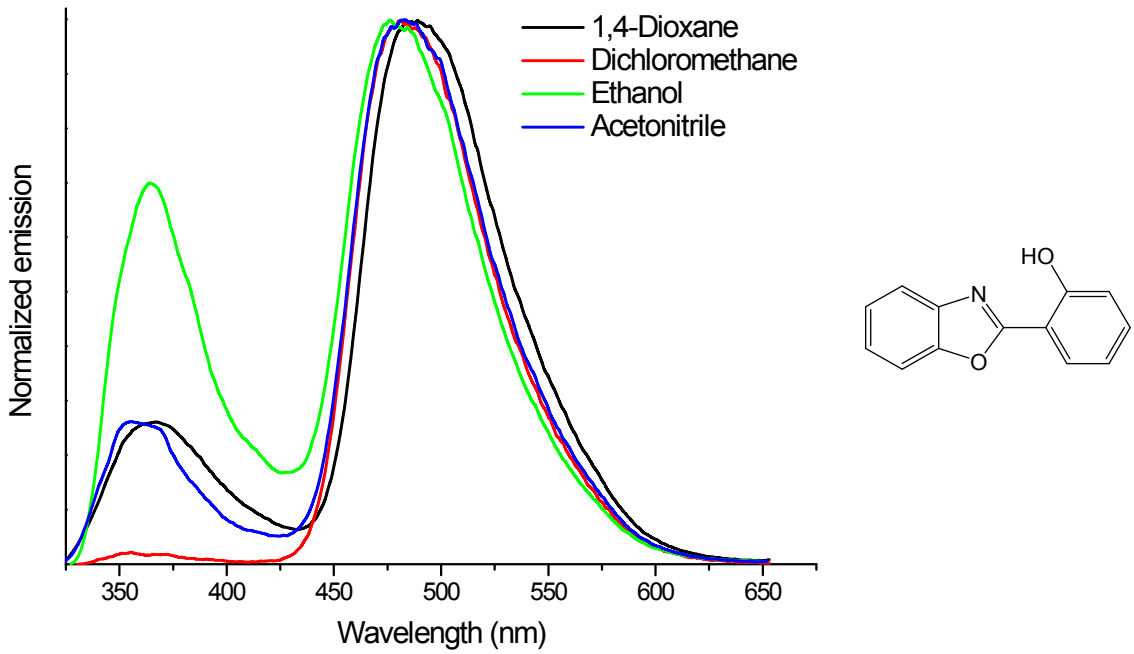


Fig. ESI31. Normalized fluorescence emission spectra of non-methylated HBO.

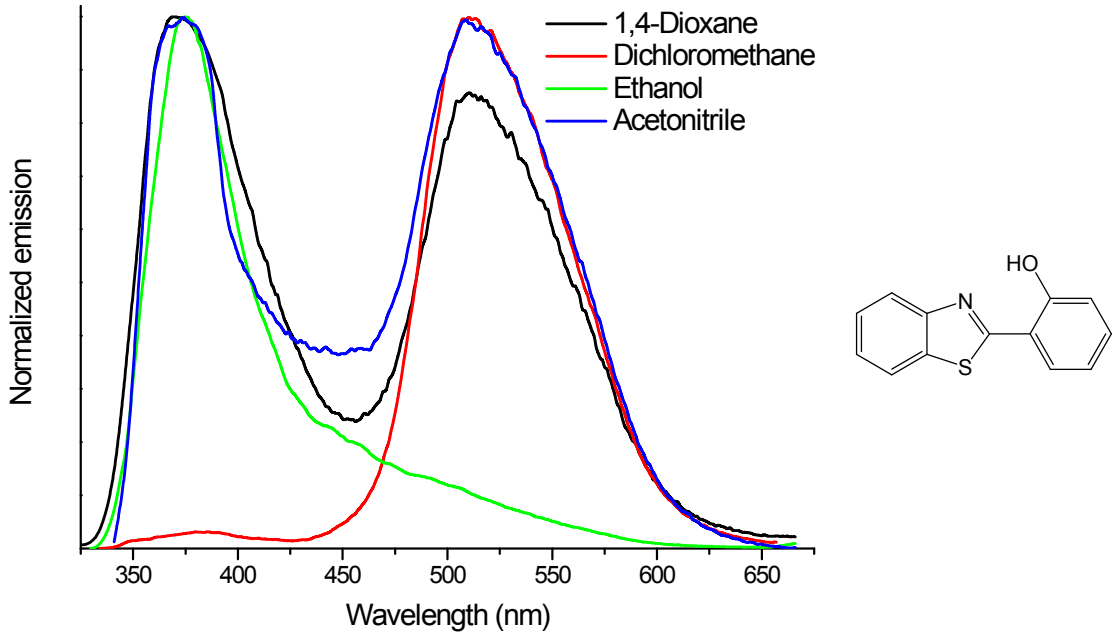


Fig. ESI32. Normalized fluorescence emission spectra of non-methylated HBT.

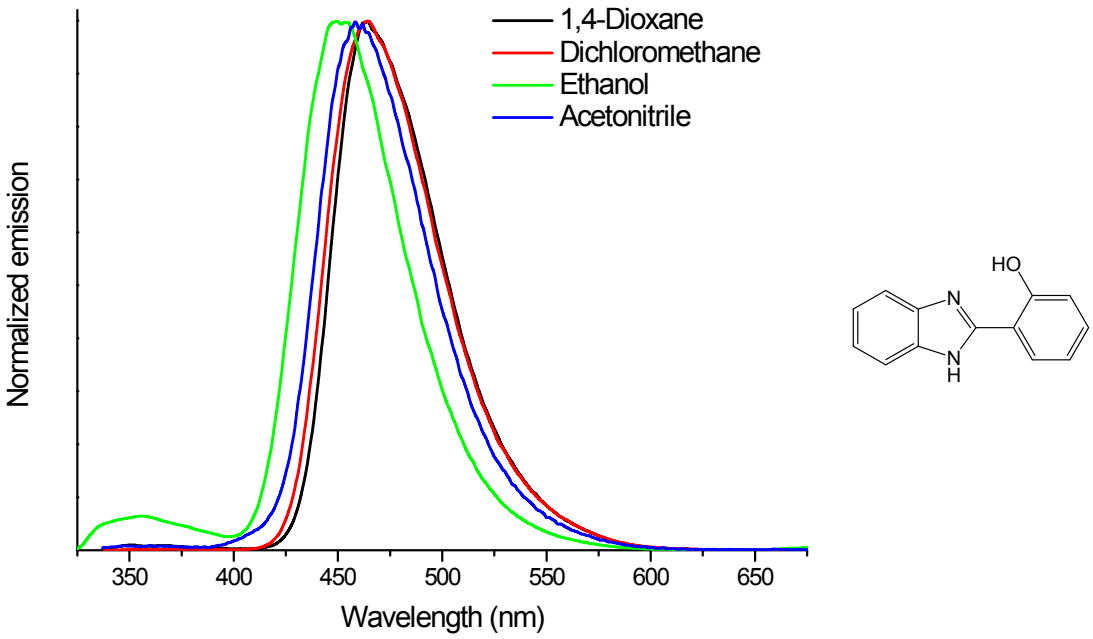


Fig. ESI33. Normalized fluorescence emission spectra of non-methylated HBI.

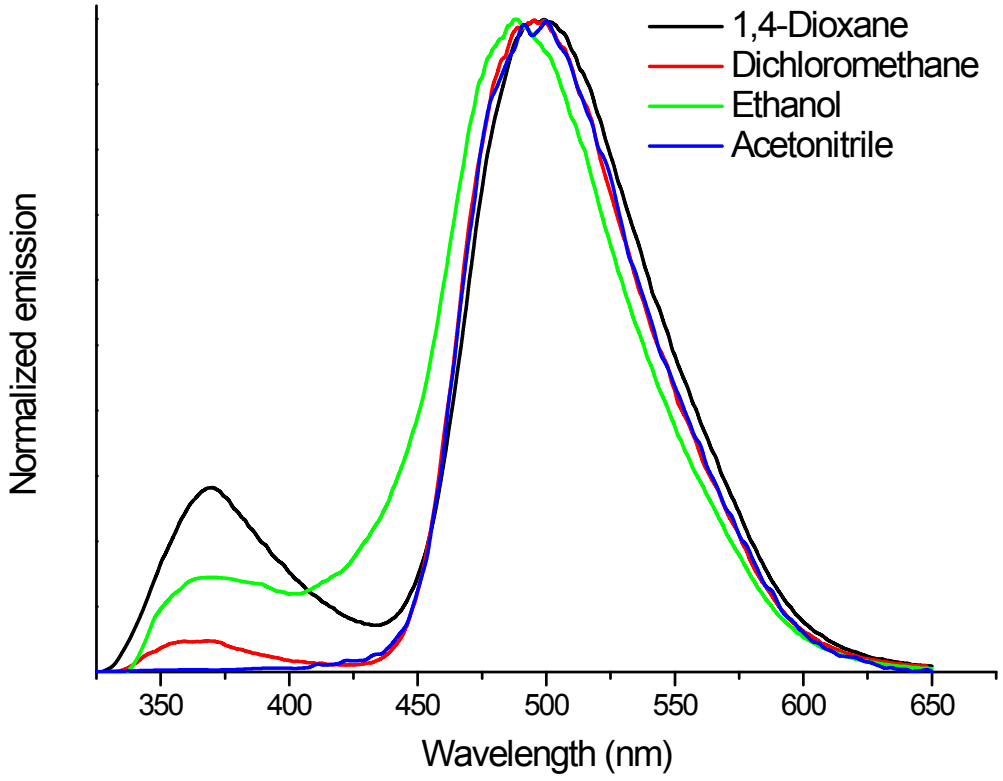


Fig. ESI34. Normalized fluorescence emission spectra of **16**.

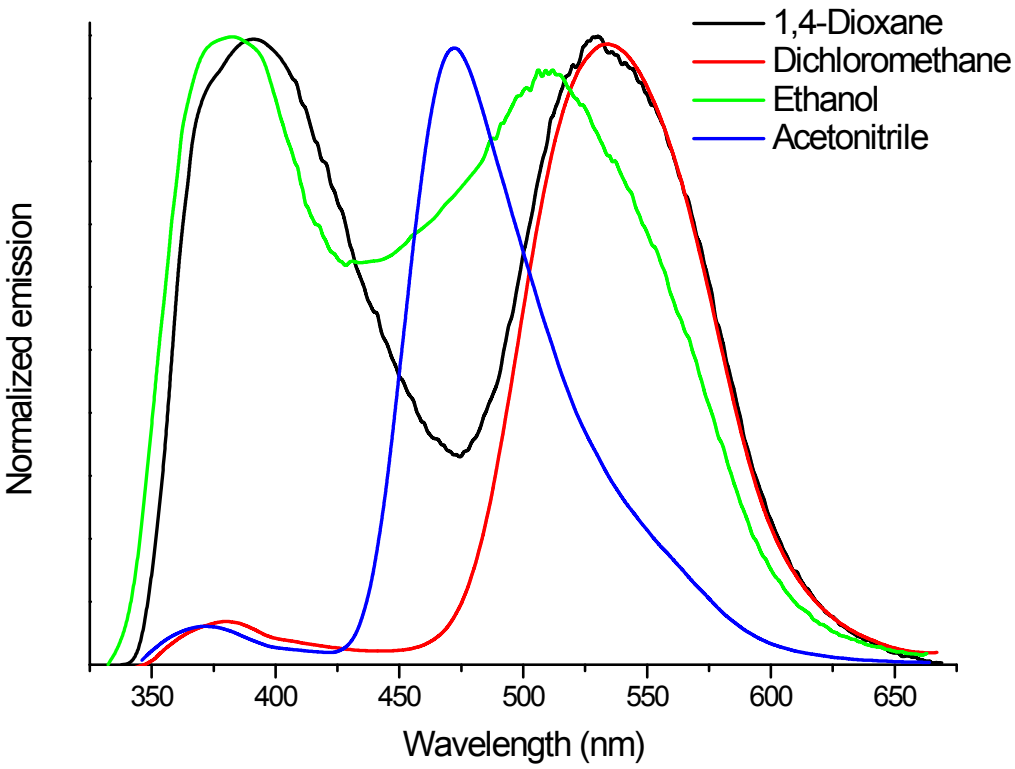


Fig. ESI35. Normalized fluorescence emission spectra of **17**.

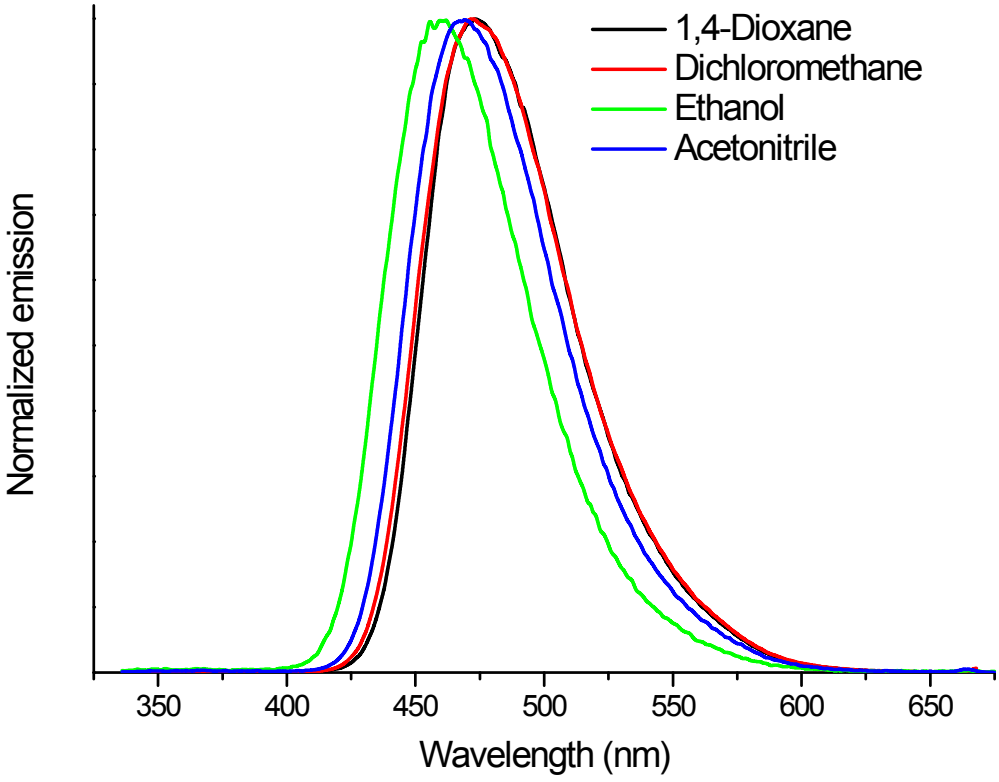


Fig. ESI36. Normalized fluorescence emission spectra of **18**.

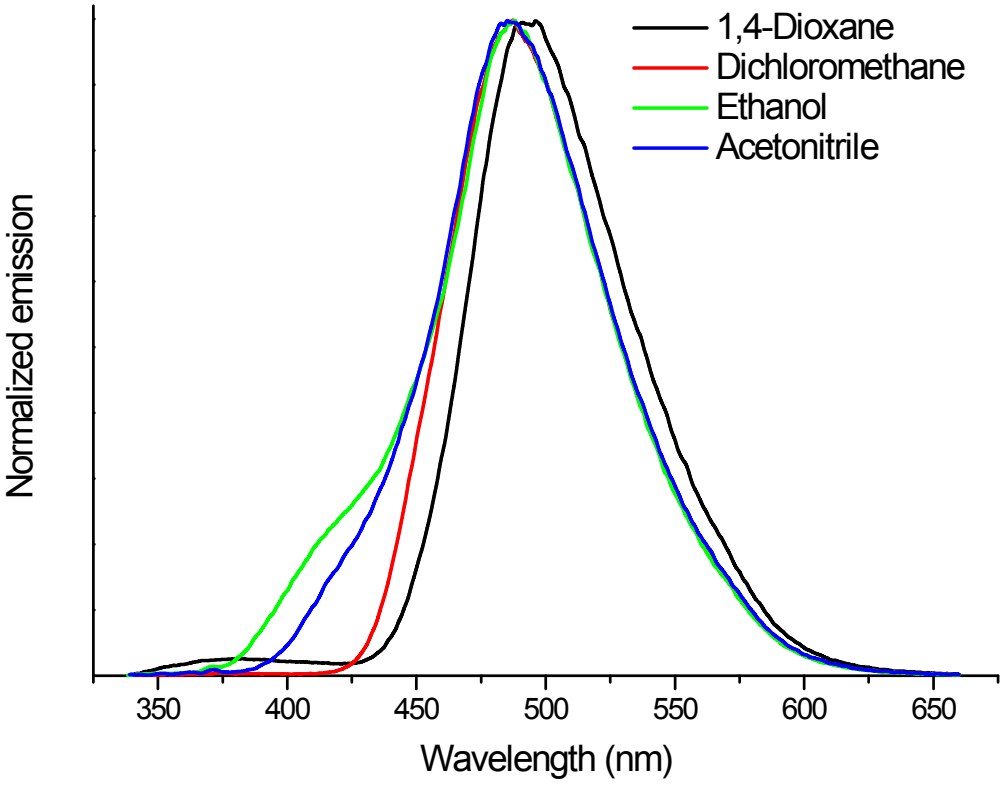


Fig. ESI37. Normalized fluorescence emission spectra of **19**.

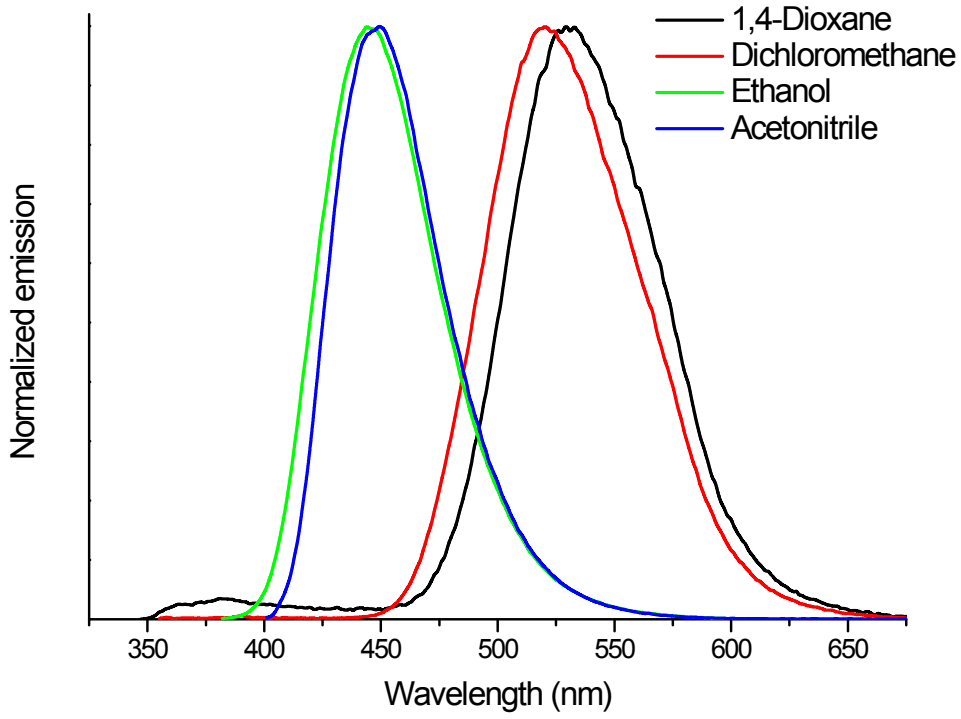


Fig. ESI38. Normalized fluorescence emission spectra of **20**.

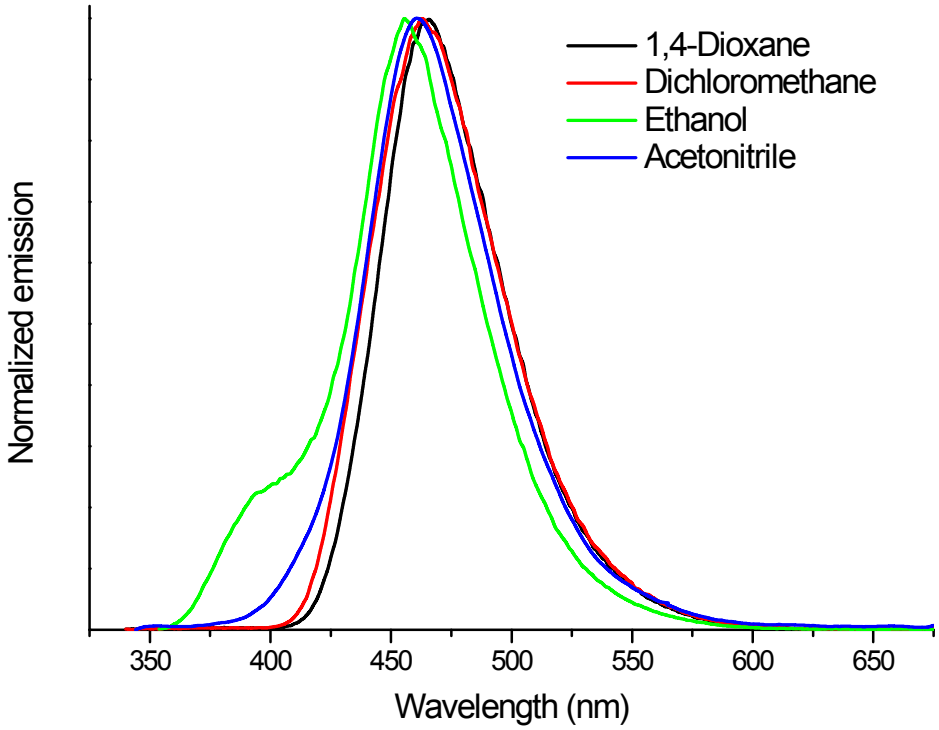


Fig. ESI39. Normalized fluorescence emission spectra of **21**.

Table ESI4. Relevant data from the time resolved fluorescence spectroscopy from non-methylated derivatives (HBO, HBT and HBI), methylated **16-18** and formyled **20-21**.

#	Solvent	χ^2	Pre-exp. 1	τ_1 ns (%)	Pre-exp. 2	τ_2 ns (%)
16		1.176	5.531	0.098 (100)	-	-
19	MeCN	1.048	0.955	0.429 (56)	0.743	1.642 (44)
HBO		1.099	4.423	0.209 (100)	-	-
16		1.148	6.976	0.164 (100)	-	-
19	DCM	1.135	0.630	2.393 (35)	1.166	0.826 (65)
HBO		1.137	4.469	0.332 (100)	-	-
17		1.049	0.315	1.688 (26)	0.896	0.256 (74)
20	MeCN	1.114	1.681	1.493 (100)	-	-
HBT		1.181	1.080	0.214 (100)	-	-
17		1.054	1.945	0.240 (100)	-	-
20	DCM	1.194	1.168	0.422 (59)	0.812	1.972 (41)
HBT		1.192	3.496	0.225 (100)	-	-
18		1.195	0.430	2.573 (100)	-	-
21	MeCN	1.162	0.393	4.740 (43)	0.525	1.621 (57)
HBI		1.176	0.610	3.482 (100)	-	-
18		1.145	0.892	2.307 (100)	-	-
21	DCM	1.039	1.117	3.456 (100)	-	-
HBI		1.161	0.839	3.626 (100)	-	-

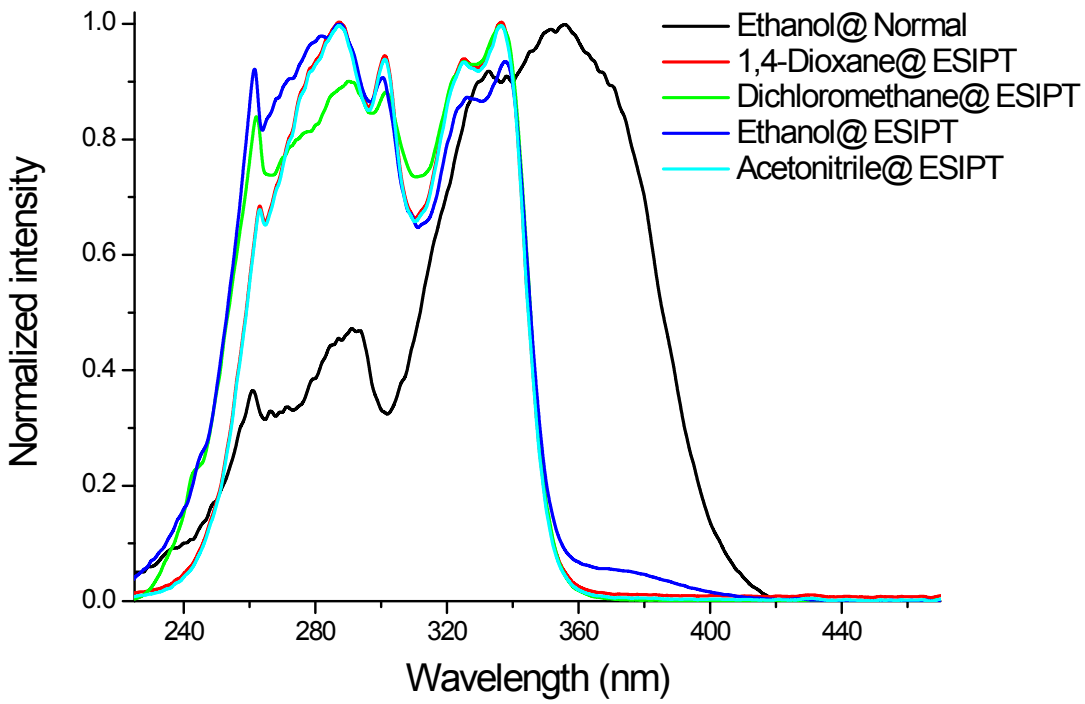


Fig. ESI40. Normalized excitation spectra of **19**, where Normal and ESIPT is ascribed to the observation at shorter and longer wavelengths, respectively.

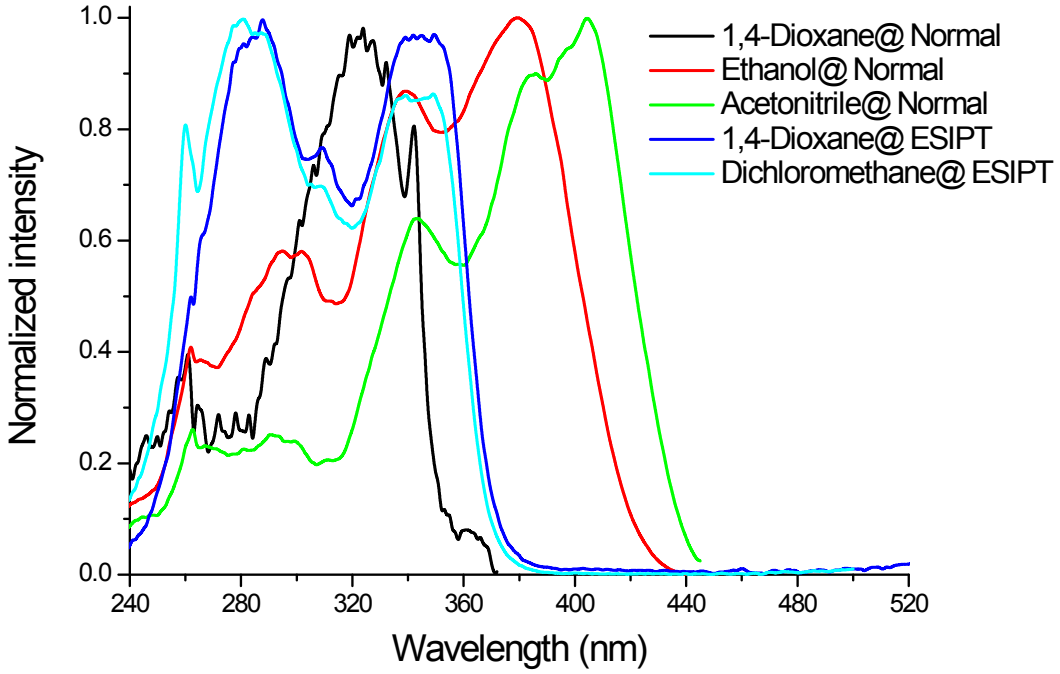


Fig. ESI41. Normalized excitation spectra of **20**, where Normal and ESIPT is ascribed to the observation at shorter and longer wavelengths, respectively.

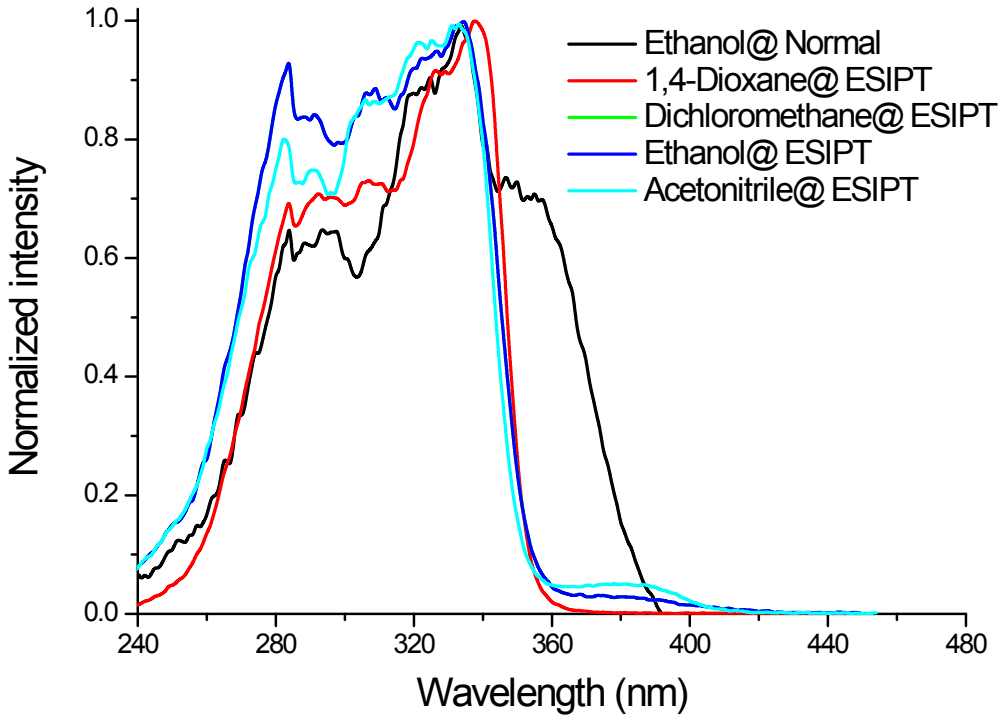


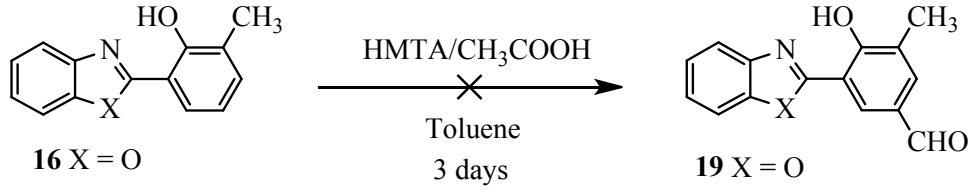
Fig. ESI42. Normalized excitation spectra of **21**, where Normal and ESIPT is ascribed to the observation at shorter and longer wavelengths, respectively.

3. Attempts to obtain the formyl derivatives

#1. Formylation using urotropine/acetic acid

(Chen, W. H.; Xing, Y.; Pang, Y., A highly selective pyrophosphate sensor based on ESIPT turn-on in water. Org. Lett. 2011, 13, 1362)

In a Schlenk vessel was added 0.178 mmol of previously synthesized compound **16**, 3 mL of toluene and 0.4 mmol of hexamethylenetetramine (2.4 equivalent) followed by 3 mL of acetic acid. The mixture was heated at reflux for 3 days. After 3 days, water was added and the mixture was refluxed for 10 min. The progress of a chemical reaction was monitored by TLC. It was not observed the formation of the product **19**, as well as the consumption of the reagents. Since it was not observed progress in this approach, the additional precursors (**17**-**18**) were not tested.



16 X = O

19 X = O

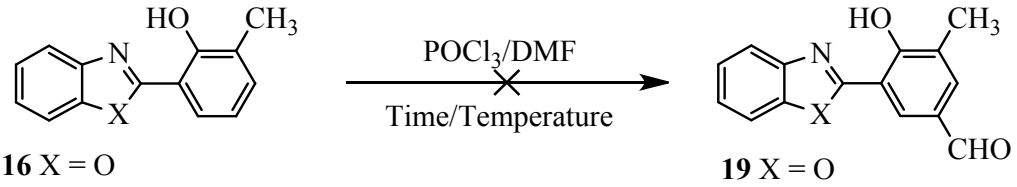
#	Benzazole	HMTA	Toluene (mL)	Ácido acético (mL)	Reflux (days)
1	40 mg (0.178 mmol)	60 mg (0.427 mmol)	3.0	3.0	3

#2. Formylation using $POCl_3$

(Togo, H.; Ushijima, S., Metal-Free One-Pot Conversion of Electron-Rich Aromatics into Aromatic Nitriles. Synlett. 2010, 2010, 1067-1070. Liu, K.; Zhao, X.; Liu, Q.; Huo, J.; Fu, H.; Wang, Y., Turn on ESPT: novel salicylaldehyde based sensor for biological important fluoride sensing. J. Photochem. Photobiol. B Biol. 2014, 138, 75)

In a first step, in an ice bath the $POCl_3$ was added in DMF under stirring during 30 minutes at 0^{o}C (see Time Step 1). In a second step, the precursor benzoxazole **16** was added and the mixture was stirred from 1.5-48h at 50-100^{o}C (see Time Step 2). The progress of a chemical reaction was monitored by TLC.

To this mixture water was added. It was not observed the formation of the product **19**, as well as the consumption of the reagents. Since it was not observed progress in this approach, the additional precursors (**17**-**18**) were not tested.



16 X = O

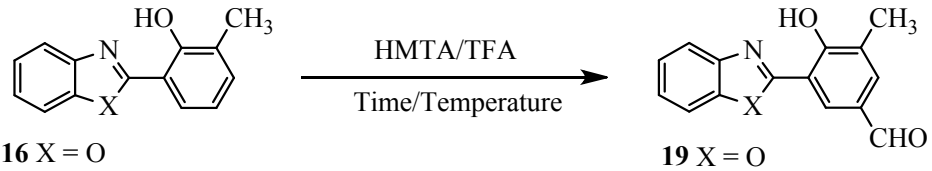
19 X = O

#	Benzazole (mmol)	$POCl_3$ (mmol)	DMF (mmol)	Time Step 1 (h)	Temp. (°C)	Time Step 2 (h)	Temp. (°C)
1	1.132	1.26	8.27	0.5	0	1.5	50
2	1.132	1.26	8.27	0.5	0	4.0	70
3	1.200	1.32	4.48	0.5	0	4.0	90
4	0.222	1.11	9.29	0.5	0	48	100

#3. Formylation using Trifluoroacetic acid

(Wang, J.; Li, Y.; Patel, N. G.; Zhang, G.; Zhou, D.; Pang, Y., A single molecular probe for multi-analyte (Cr(3)(+), Al(3)(+) and Fe(3)(+)) detection in aqueous medium and its biological application. Chem. Commun. 2014, 50, 12258.)

In a Schlenk vessel was added the previously synthesized compound **16**-**18** and hexamethylenetetramine (~10 equivalent) followed by 2.5 mL of trifluoroacetic acid. The mixture was heated at reflux for 3-5 h depending on the precursor (see Step 1). The progress of a chemical reaction was monitored by TLC. Water (2.5 mL) was added and the mixture was refluxed for 10-60 min (see Step 2). The reaction mixture was kept overnight at 5°C. The obtained precipitate was filtered in silica, washed with water, extracted in ethyl acetate. No additional purification procedure was needed. The products **19**-**21** were obtained in 91, 84 and 93% yields respectively.



16 X = O
17 X = S
18 X = NH

19 X = O
20 X = S
21 X = NH

#	Precursor (mmol)	HMTA	Time Step 1 (h)	Time Step 2 (min)	Mass (mg)	Yield (%)
1	16 (0.218 mmol)	1.85 mmol	3	10	50.4	91
2	17 (0.166 mmol)	1.83 mmol	4	20	37.4	84
3	18 (0.174 mmol)	1.89 mmol	5	60	40.8	93