

SUPPORTING INFORMATION

Design and Emissive Features of Ionic White-Light Fluorophore

Illia E. Serdiuk^{†‡§*}

[†] Faculty of Mathematics, Physics and Informatics, University of Gdańsk, Wita Stwosza 57, 80-308 Gdańsk, Poland

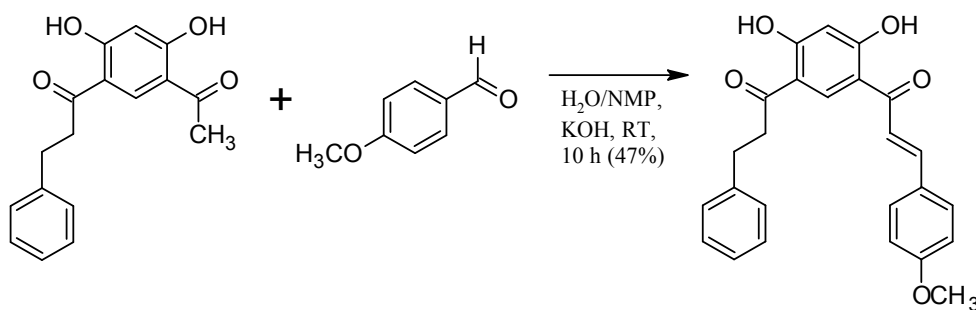
[‡] Center for Supramolecular Optoelectronic Materials, Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea

[§] Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

Synthesis and Identification

The identity of compounds was confirmed by NMR and MALDI TOF MS. Their purity was controlled by TLC and elemental analysis. NMR spectra were recorded on Bruker AVANCE III 500 MHz spectrometer with trimethylsilane as a reference. Mass spectra were obtained on MALDI-TOF MS Bruker Daltonics mass spectrometer. Chromatography was performed on silica gel (230–400 mesh); TLC was conducted on Merck 60 F254 silicagel plates in appropriate eluents. Elemental analysis was performed on an Elementar Vario El Cube CHNS analyzer.

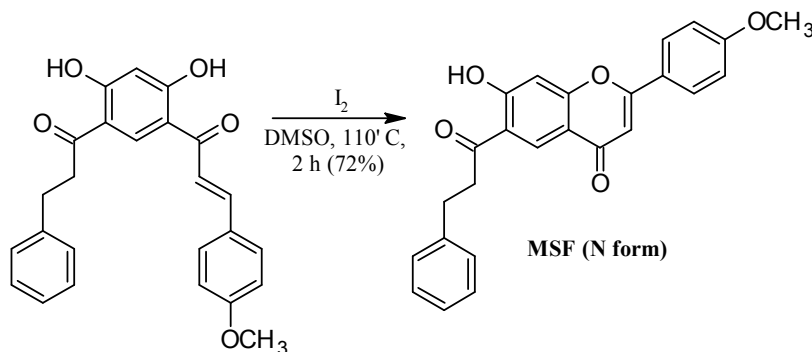
Synthetic procedure for (2*E*)-1-(5-(3-phenylpropanoyl)-2,4-dihydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (chalcone derivative)



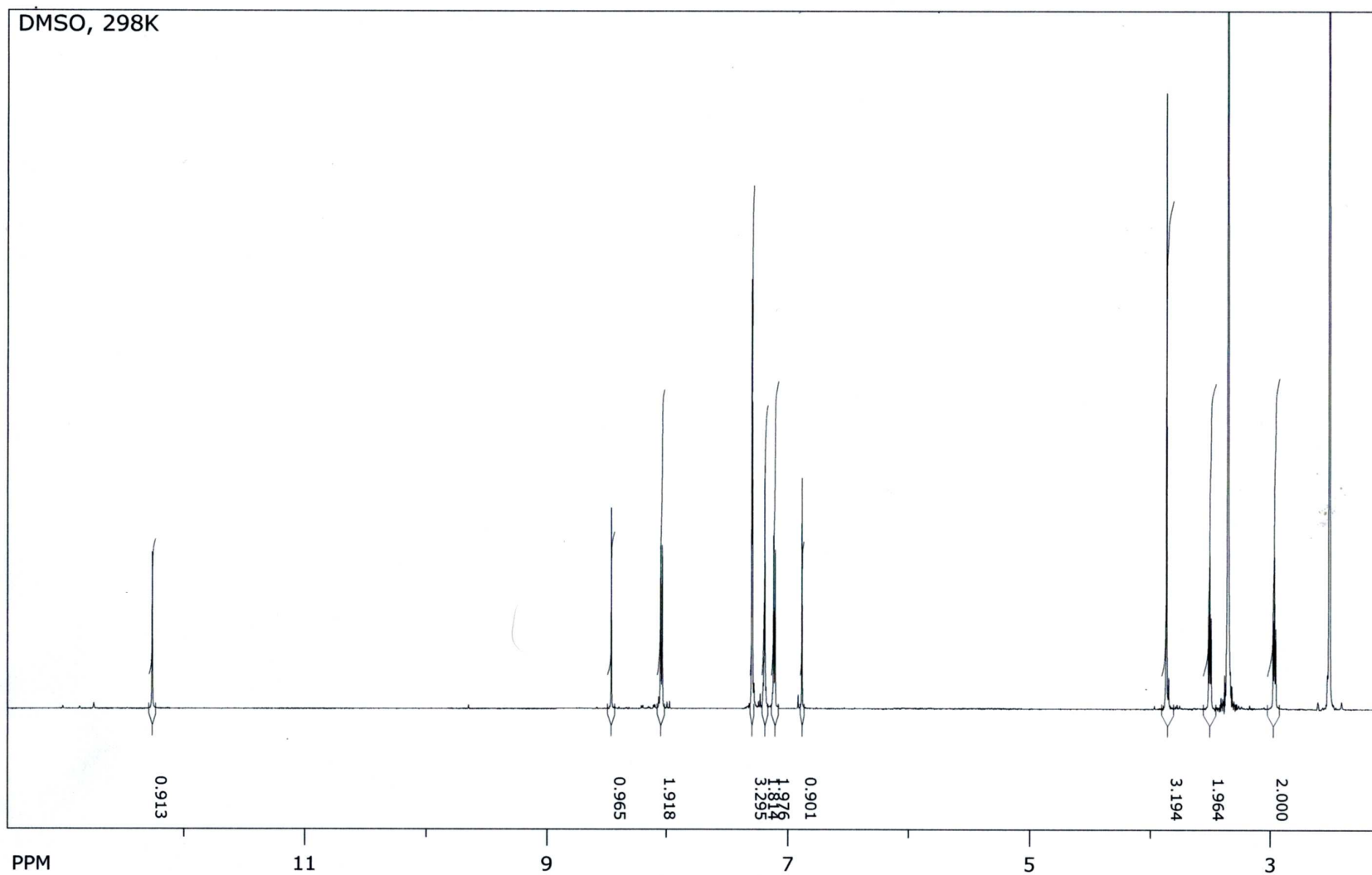
1-(5-Acetyl-2,4-dihydroxyphenyl)-3-phenylpropan-1-one (284 mg, 1 mmol) prepared as described previously^{S1} and 4-methoxybenzaldehyde (0.17 ml, 1.4 mmol) were dissolved in 80% aqueous 1-methyl-2-pyrrolidinone (1.8 ml) and KOH (450 mg, 8 mmol) was added by small portions. The mixture was stirred for 10 h at RT, neutralized by 0.1 M HCl and the resulting precipitate was collected. The crude product was purified by flash chromatography (SiO₂, CHCl₃) followed by recrystallization from MeOH. Yellow powder (190 mg, 47%). ¹H NMR (700 MHz, CDCl₃, δ): 2.99 (t, 2H, *J* = 7.3 Hz), 3.57 (t, 2H, *J* = 7.3 Hz), 3.84 (s, 3H), 6.43 (s, 3H), 7.06 (d, 2H, *J* = 8.7 Hz), 7.18 (t, 1H, *J* = 6.9 Hz), 7.27–7.30 (m, 3H), 7.31 (d, 2H, *J* = 7.3 Hz), 7.85 (d, 1H, *J* = 15.1 Hz), 7.87–7.90 (m, 3H), 8.67 (s, 1H), 12.84 (s, 1H), 13.67 (s, 1H). ¹³C NMR (350 MHz, CDCl₃, δ): 204.4, 192.4, 168.6, 167.4, 145.5, 136.4, 131.8, 129.0, 128.9, 128.8, 128.8, 127.5,

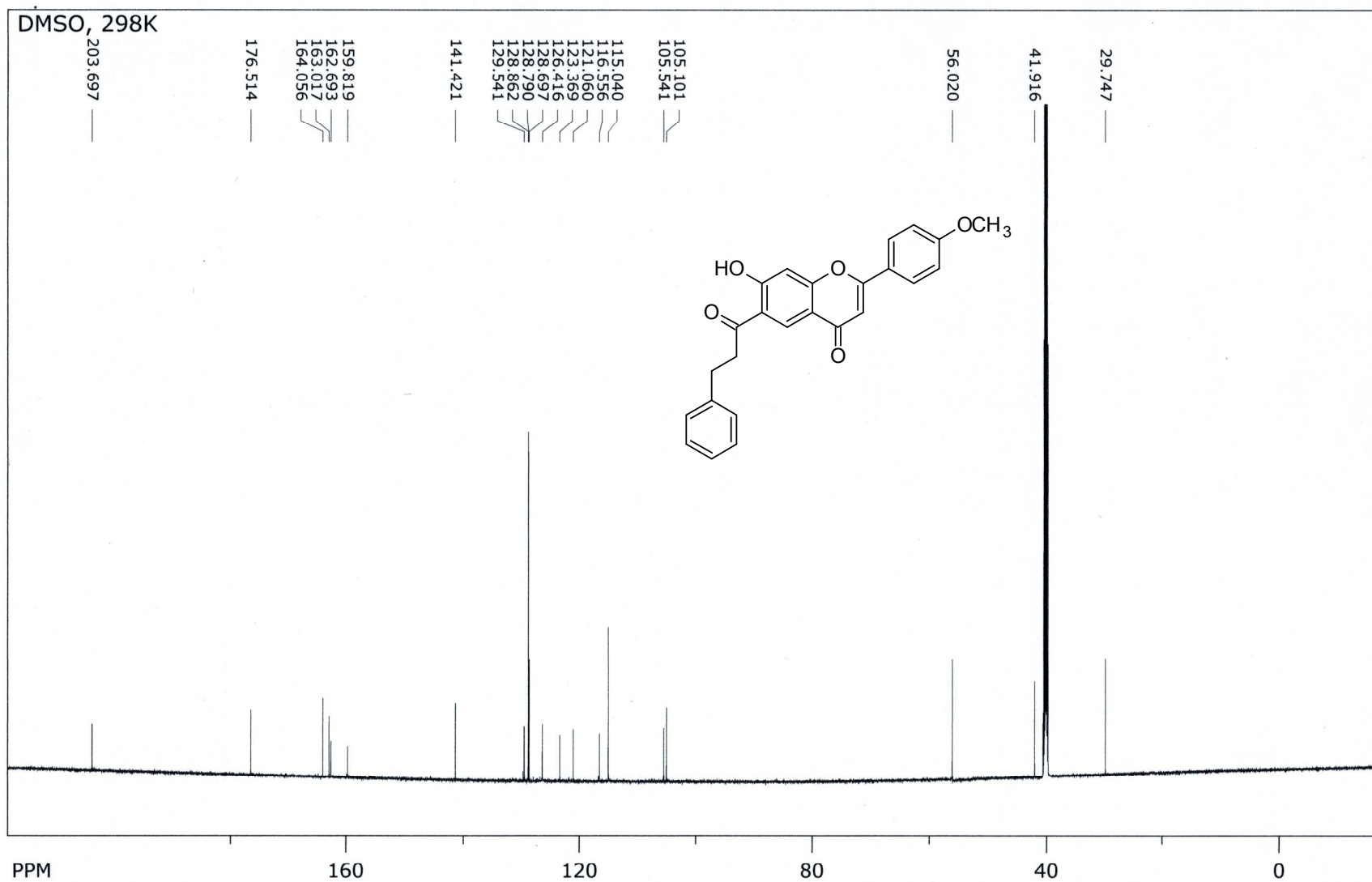
126.4, 119.2, 115.0, 114.7, 114.7, 104.2, 55.9, 40.5, 30.0. Mass spectrum, m/z : 403 $[M+H]^+$. Anal. Calcd. for $C_{25}H_{22}O_5$, %: C 74.61; H 5.51. Found, %: C 74.59; H 5.57.

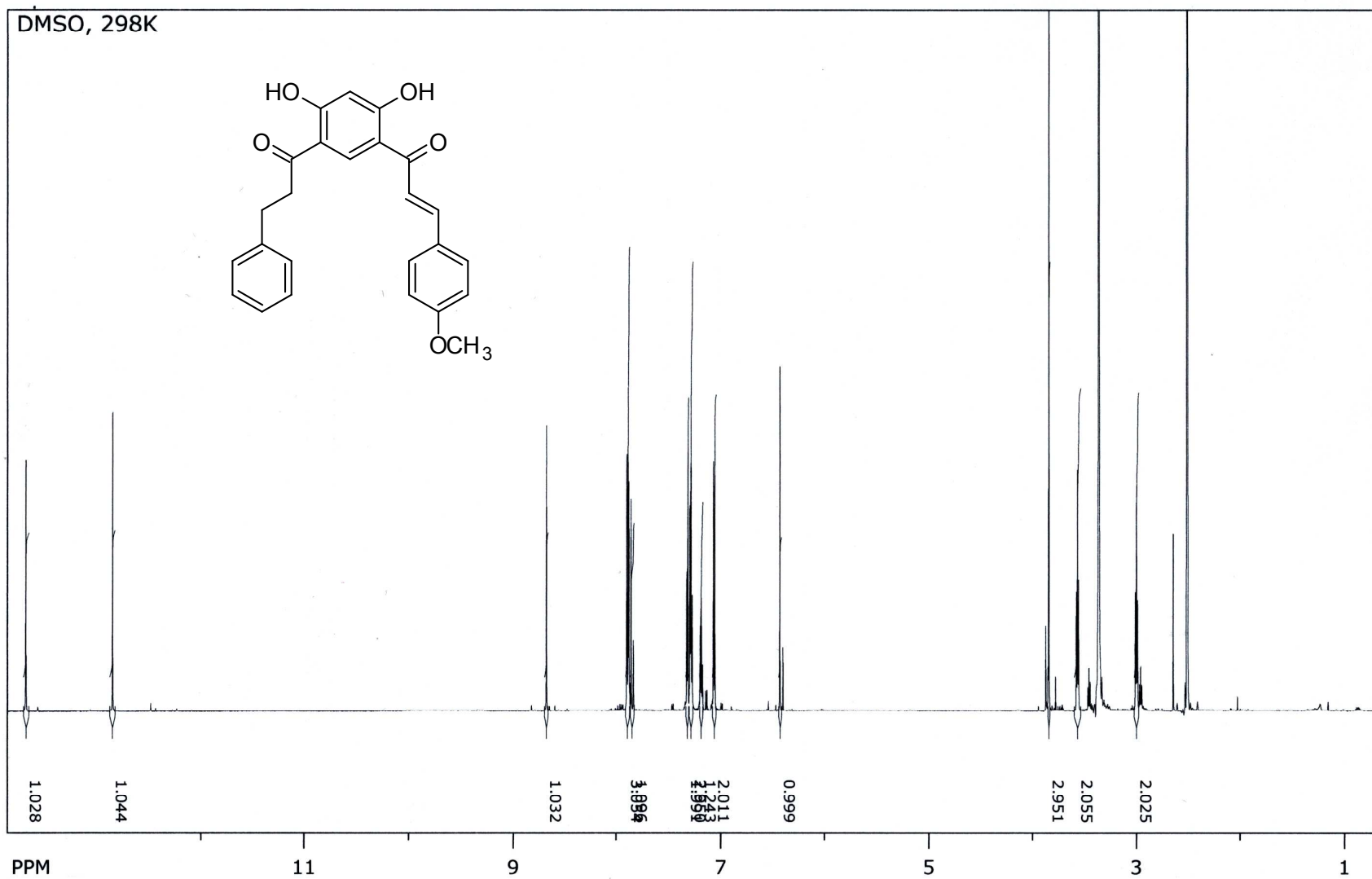
Synthetic procedure for 6-(3-phenylpropanoyl)-7-hydroxy-2-(4-methoxyphenyl)-4*H*-chromen-4-one (MSF)

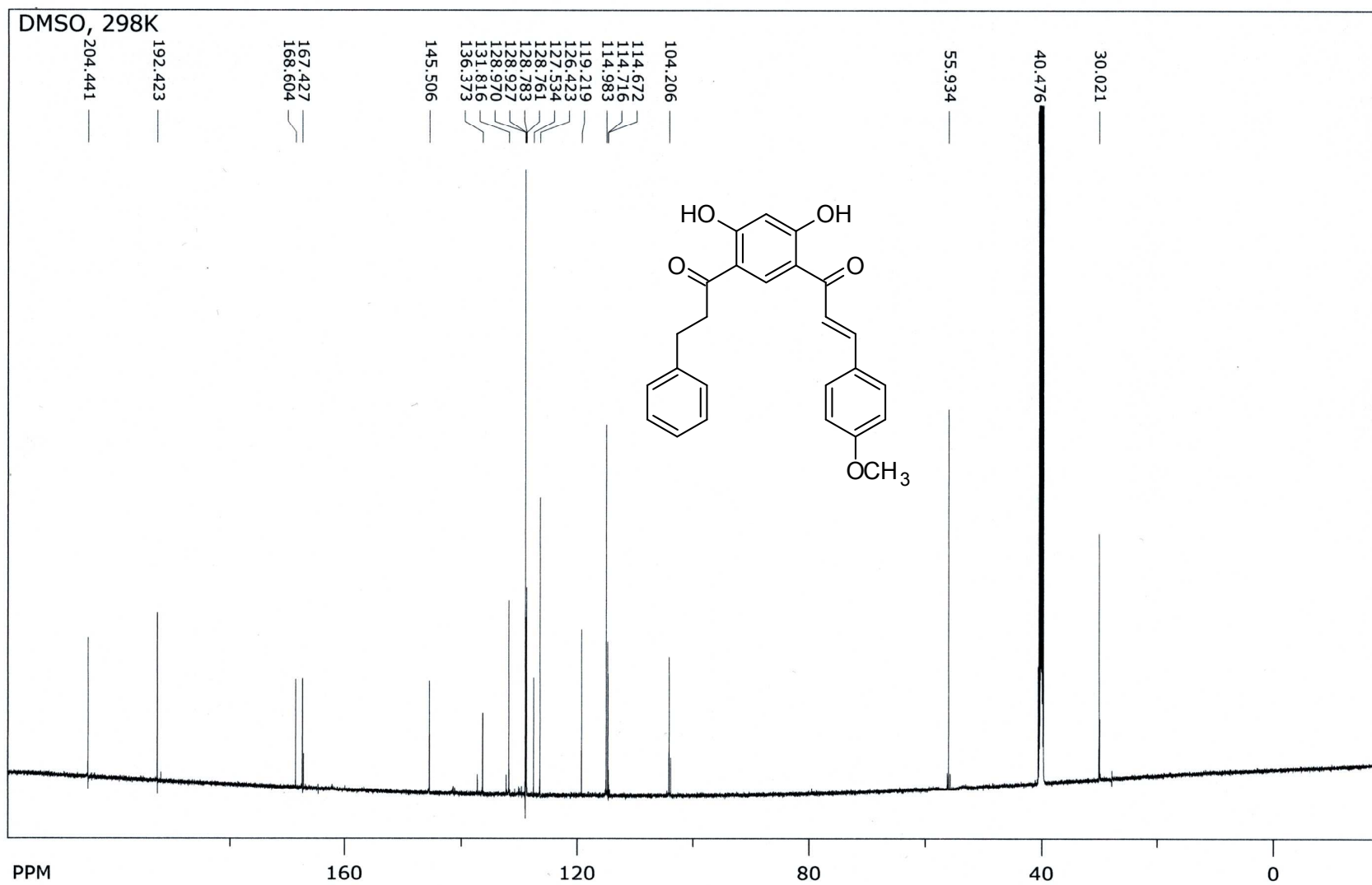


The chalcone derivative (201 mg, 0.5 mmol) from the previous step, iodine (25 mg, 0.2 mmol) and DMSO (3 ml) were stirred at 110°C for 2 h, diluted with thiosulfate aqueous solution, extracted by CHCl_3 , washed 3 times with water and purified by column chromatography (SiO_2 , 1% i-PrOH in CHCl_3). Pale yellow solid (143 mg, 72%), ^1H NMR (700 MHz, CDCl_3 , δ): 2.97 (t, 2H, $J = 7.4$ Hz), 3.51 (t, 2H, $J = 7.4$ Hz), 3.86 (s, 3H), 6.88 (s, 1H), 7.11 (d, 2H, $J = 8.8$ Hz), 7.18–7.21 (m, 2H), 7.27–7.31 (m, 4H), 8.04 (d, 2H, $J = 8.8$ Hz), 8.46 (s, 1H), 12.27 (s, 1H). ^{13}C NMR (350 MHz, CDCl_3 , δ): 203.7, 176.5, 164.1, 163.0, 162.7, 159.8, 141.4, 129.5, 128.9, 128.8, 128.7, 126.4, 123.4, 121.1, 116.6, 115.0, 105.5, 105.1, 56.0, 41.9, 29.7. Mass spectrum, m/z : 401 $[M+H]^+$. Anal. Calcd. for $C_{25}H_{20}O_5$, %: C 74.99; H 5.03. Found, %: C 74.91; H 5.07.



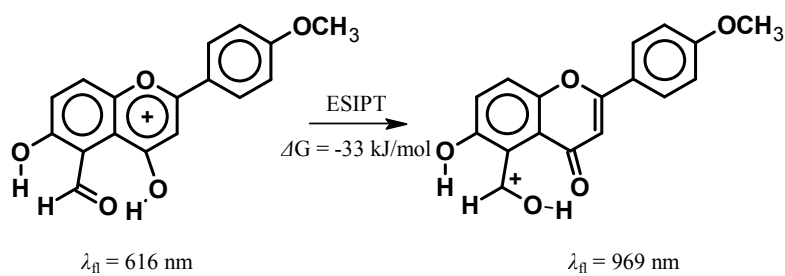




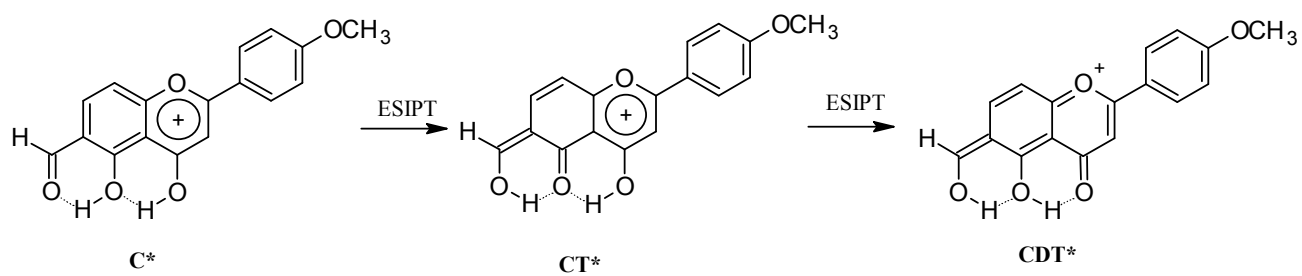


Quantum-chemical calculations on the design stage

Scheme S1. ESIPT in isomeric species of **5**.



Scheme S2. Double ESIPT in **6**.



Spectroscopic investigations

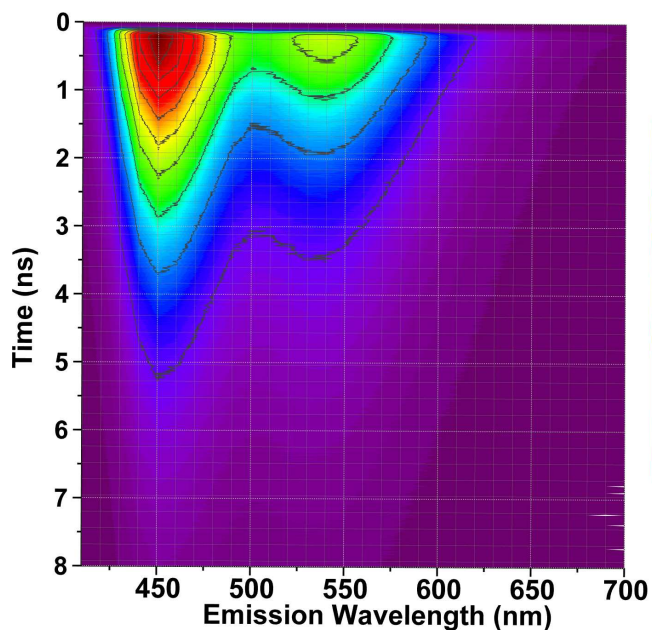


Figure S1. 3D time-resolved emission spectra of **MSF** in a PMMA film with 9% of 4-dodecylbenzenesulfonic acid

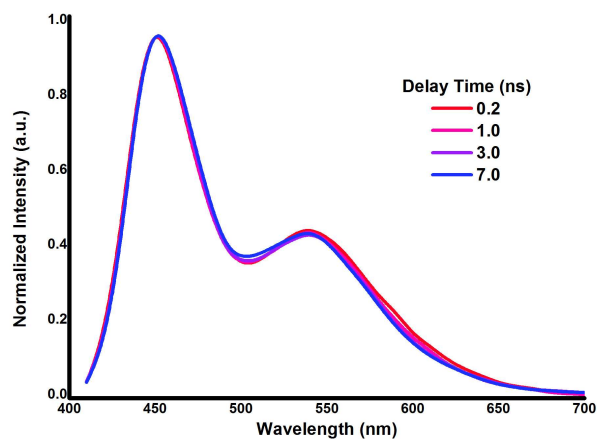


Figure S2. Normalized emission spectra of **MSF** in a PMMA film with 9% of 4-dodecylbenzenesulfonic acid at various delay time after excitation pulse; spectra are not corrected on the instrumental sensitivity.

References

- ^{S1} Serdiuk, I. E.; Roshal, A. D. Single and Double Intramolecular Proton Transfers in the Electronically Excited State of Flavone Derivatives. *RSC Adv.* **2015**, *5*, 102191–102203.