Highly efficient blue solid emitters and tautomerization-induced ON/OFF fluorescence switching based on structurally simple 3(5)-Phenol-1*H*-pyrazoles

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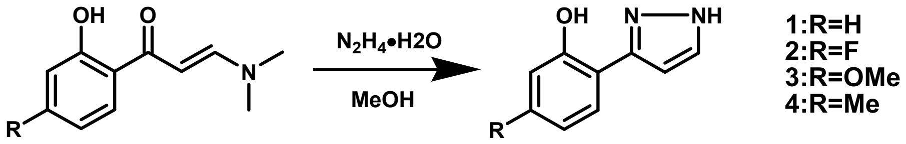
Materials. All chemicals were obtained from Acros, Sigma-Aldrich or TCI Chemical Co. at the highest purity available. Absolute solvents (over molecular sieves) and starting materials obtained from commercial source were used without further purification. Precursor materials (2-hydroxyphenyl)propenone derivatives are synthesized according to literature.[S1]

Instrumentation: NMR spectra were determined on a Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a GC/MS mass spectrometer. Element analyses were performed on a FlashEA1112 spectrometer. UV−vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer with or without an integrating sphere. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer or a Maya2000 Pro CCD spectrometer. The absolute fluorescence quantum yields of crystals were measured on Edinburgh FLS920 by using an integrating sphere. All the measurements were carried out at room temperature under ambient conditions. Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument at a heating rate of 10 °C min^{-1} under nitrogen.

Molecular orbital calculations: The ground-state geometries were fully optimized by the density functional theory (DFT) method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G* (d,p) basis set using the Gaussian 09 software package.

Single crystal structure: Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω-scan mode with graphitemonochromator Mo Kα radiation. The structures were solved with direct methods using the SHELXTL programs and refined with full-matrix leastsquares on F2. Nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The crystallographic information has been deposited with Cambridge Crystallographic Data Centre, and signed to CCDC code 1479795 for **1**, 1479796 for **2**, 1479797 for **3** and 1479798 for **4**.



Scheme S1. Synthetic procedure of compounds **1–4**

General synthetic procedure: In a 100 mL round-bottomed flask, derivatives of (2-hydroxyphenyl)propenone (5 mmol equiv) were dissolved in 30 mL MeOH. Subsequently, Hydrazinium hydroxide (50 mol equiv) was added to the solution and the mixture was heated to reflux for 20 h. After cooling, The solution was evaporated and recrystallized twice from $CHCl_3$/Hexane 1:2 to yield the pure compound as white solid.

5-fluoro-2-(1*H*-pyrazol-3-yl)phenol **2**. Yield: 76 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.44 (s, 2 H), 7.71–7.37 (m, 2 H), 6.84–6.41 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.28 (s), 162.32 (s), 157.49 (d, J = 12.6 Hz), 151.46 (s), 129.17 (s), 127.62 (d, J = 10.5 Hz), 113.10 (s), 106.76 (s), 106.63 (d, J = 22.4 Hz), 104.31 (s), 104.11 (s), 101.88 (s). MS m/z: 178.10 [M]+ (calcd: 178.05). Anal. Calcd (%) for $C_9H_7FN_2O$: C, 60.67; H, 3.96; N, 15.72. (Found: C, 60.52; H, 3.94; N, 15.78).

5-methoxy-2-(1*H*-pyrazol-3-yl)phenol **3**. Yield: 72 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.41 (s, 2 H), 7.58 (d, J = 2.4 Hz, 1 H), 7.48 (d, J = 8.6 Hz, 1 H), 6.60 (dd, J = 5.1, 2.5 Hz, 2 H), 6.51 (dd, J = 8.6, 2.4 Hz, 1 H), 3.81 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.74 (s), 157.24 (s), 151.90 (s), 129.10 (s), 127.43 (s), 109.94 (s), 106.43 (s), 101.70 (s), 101.40 (s), 55.34 (s). MS m/z: 190.14 [M]+ (calcd: 190.20). Anal. Calcd (%) for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. (Found: C, 63.09; H, 5.27; N, 14.78).

5-methyl-2-(1*H*-pyrazol-3-yl)phenol **4**. Yield: 75 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.20 (s, 2 H), 7.59 (d, J = 2.4 Hz, 1 H), 7.47 (d, J = 7.9 Hz, 1 H), 6.87 (s, 1 H), 6.74 (d, J = 7.8 Hz, 1 H), 6.67 (d, J = 2.4 Hz, 1 H), 2.33 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.65 (s), 151.92 (s), 139.69 (s), 129.15 (s), 126.43 (s), 120.42 (s), 117.48 (s), 113.92 (s), 101.79 (s), 21.34 (s). MS m/z: 174.99 [M]+ (calcd: 174.20). Anal. Calcd (%) for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. (Found: C, 68.11; H, 6.85; N, 15.94).

[S1] B. Tang, H. Liu, F. Li, Y. Wang, H. Zhang, *Chem. Commun.* **2016**, *53*, 6577.

Table S1 Photophysical data and thermal stability of compounds **1–4**.

Compd	λ_{abs}/nm^a	λ_{em}/nm(Φ_f)^a	λ_{abs}/nm^b	λ_{em}/nm(Φ_f)^b	τ /ns^b	T_d5/℃
1	294	323 (<0.01)	328	463 (0.52)	3.39	213
2	290	333 (<0.01)	317	454 (0.49)	2.44	183
3	296	333 (<0.01)	324	453 (0.49)	4.37	256
4	303	329 (<0.01)	305	355 (<0.01)	1.97	213

[a)]in DCM solution (1.0×10^{-5} M); [b)] in crystalline state

Table S2 The calculated energies of the investigated compounds in their tautomers and the energy difference between the tautomers in DCM solution at B3LYP/6-31G(d, p) level.

	1	**2**	**3**	**4**
$E_{crystal}$ (a.u.)	−532.3937487	−631.648555	−646.8449707	−571.667395
E_a (a.u)	−532.5142061	−631.7465464	−647.0416303	−571.8350197
E_b (a.u)	−532.5067774	−631.7378702	−647.0336053	−571.8278321
ΔE (a.u)	0.0074287	0.0086762	0.008025	0.071876
ΔE (kcal/mol)	4.66	5.44	5.04	4.51

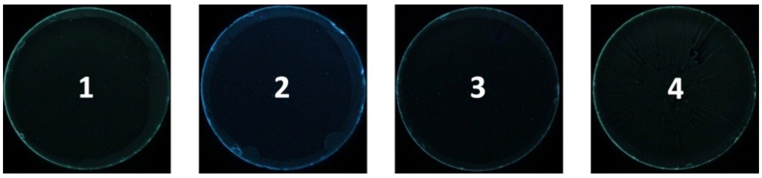


Figure S1. Photographic images of spin-coating thin films under the irradiation of UV light (254 nm).

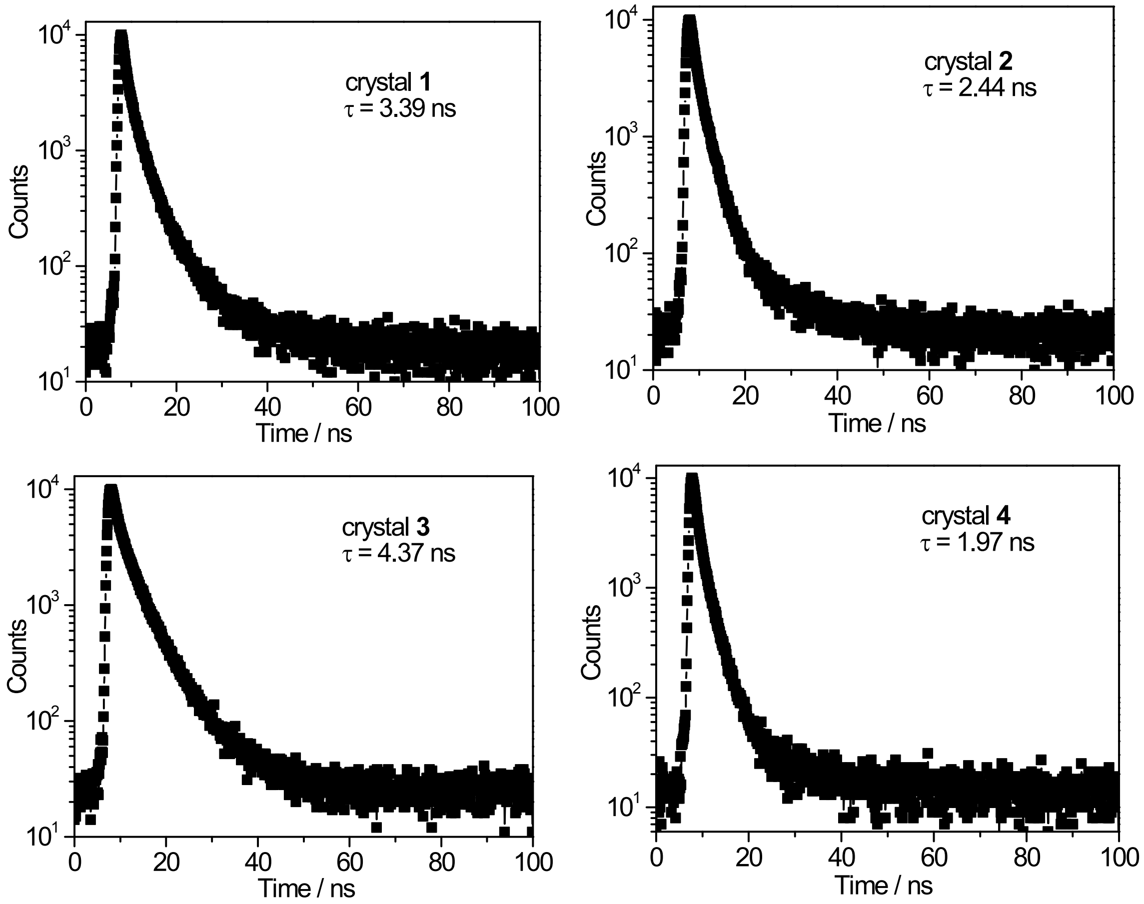


Figure S2 Time-resolved photoluminescent dynamic of crystals **1**–**4**.

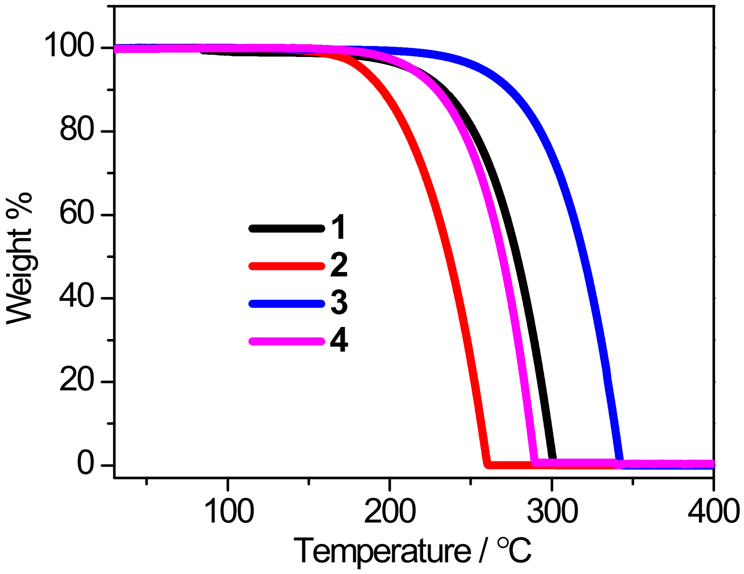


Figure S3. TGA curves of compounds **1**–**4**.

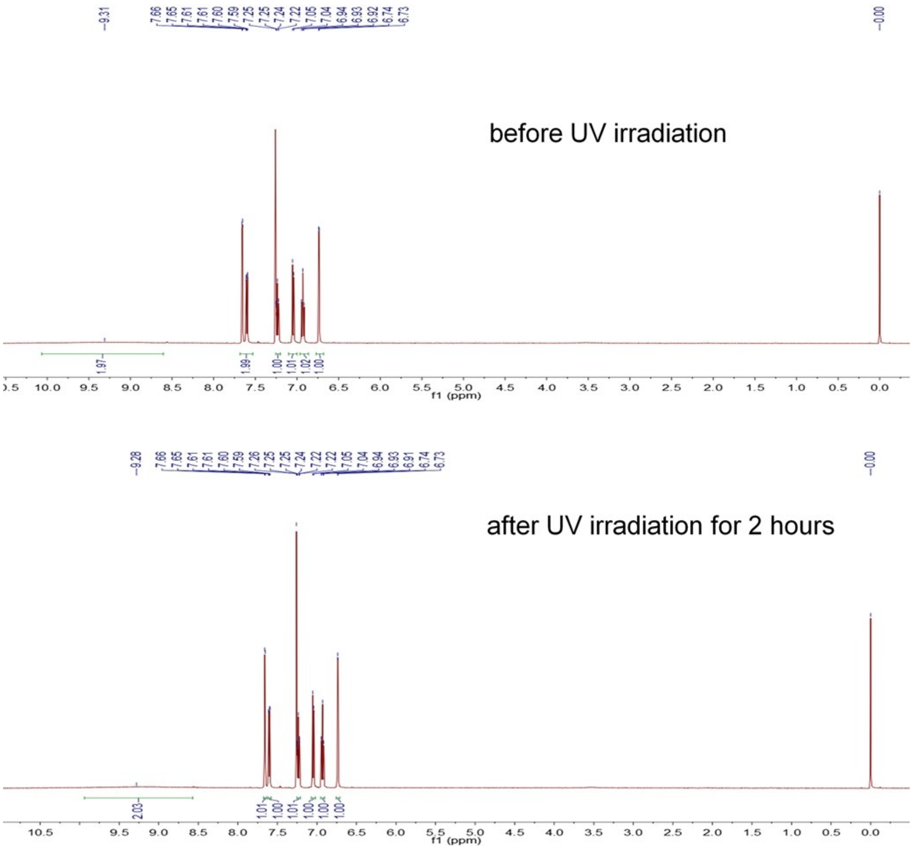


Figure S4. NMR spectra before and after UV irradiation (λ_{ex} = 254 nm) of compound **1** in $CDCl_3$.

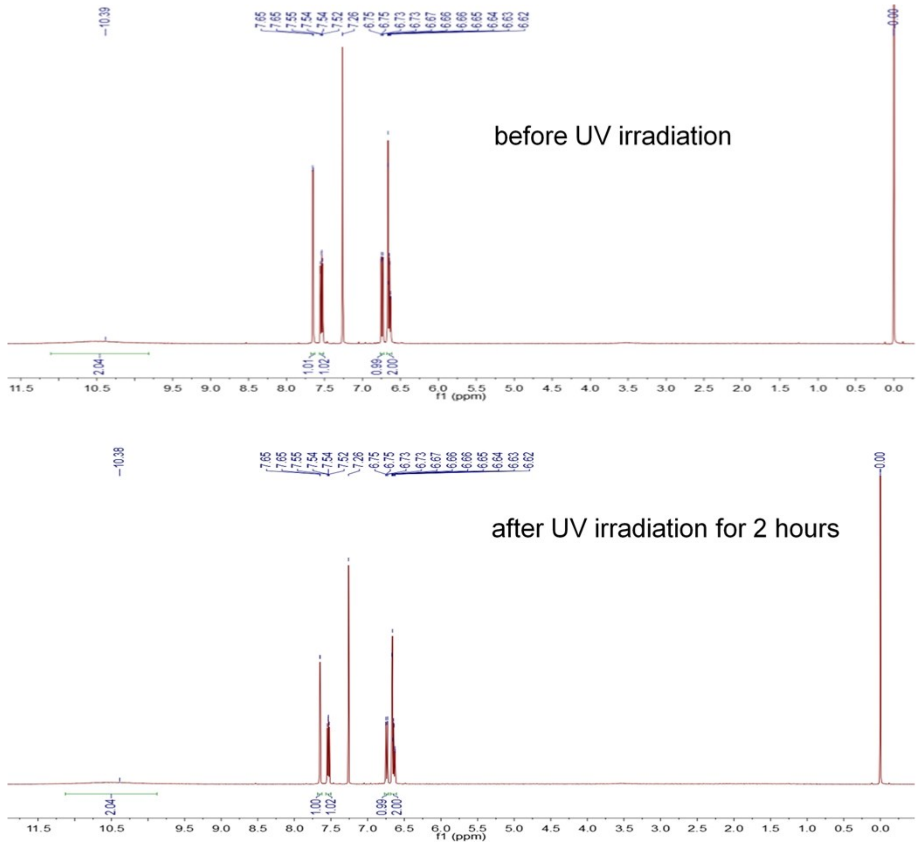


Figure S5. NMR spectra before and after UV irradiation (λ_{ex} = 254 nm) of compound **2** in $CDCl_3$.

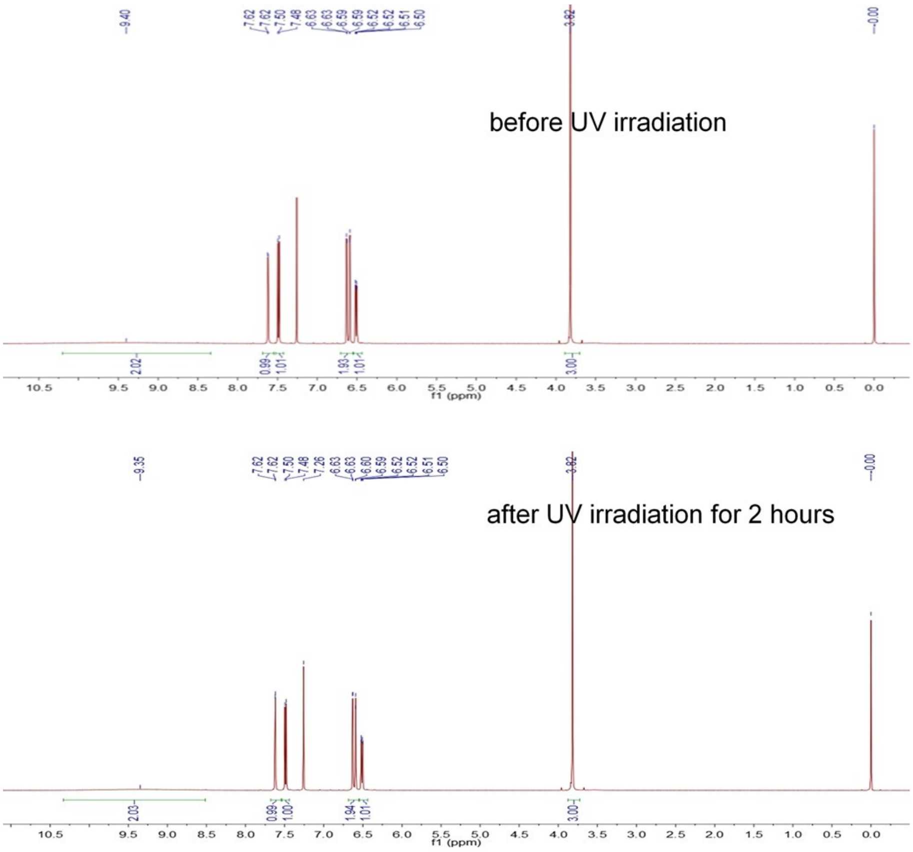


Figure S6. NMR spectra before and after UV irradiation (λ_{ex} = 254 nm) of compound **3** in $CDCl_3$.

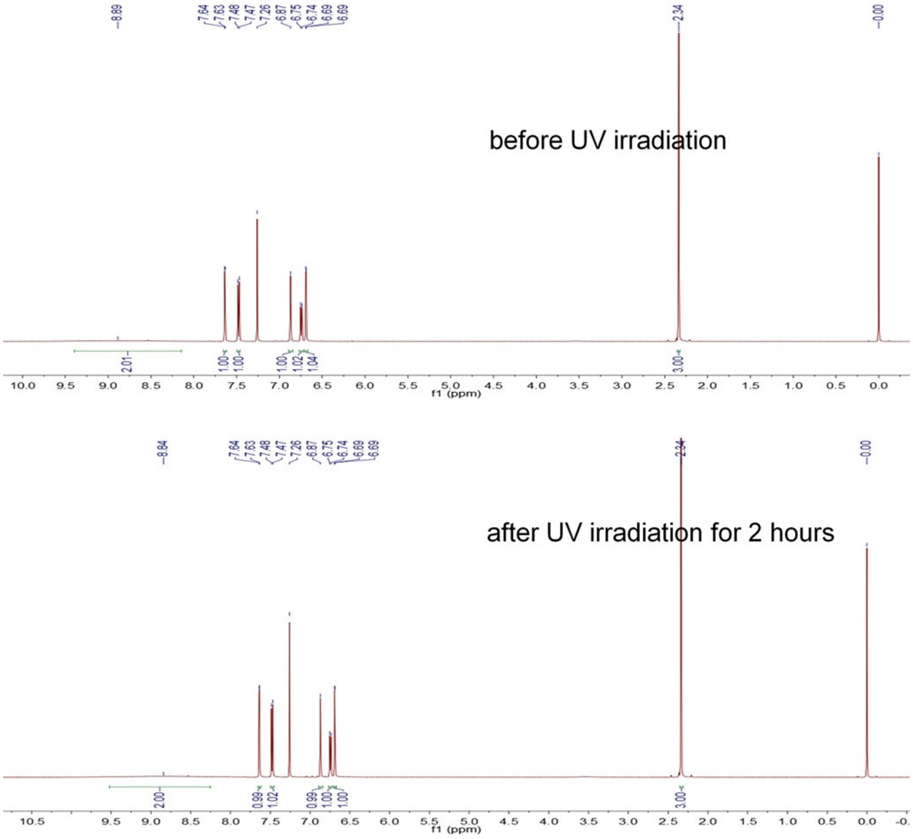


Figure S7. NMR spectra before and after UV irradiation (λ_{ex} = 254 nm) of compound **4** in $CDCl_3$.

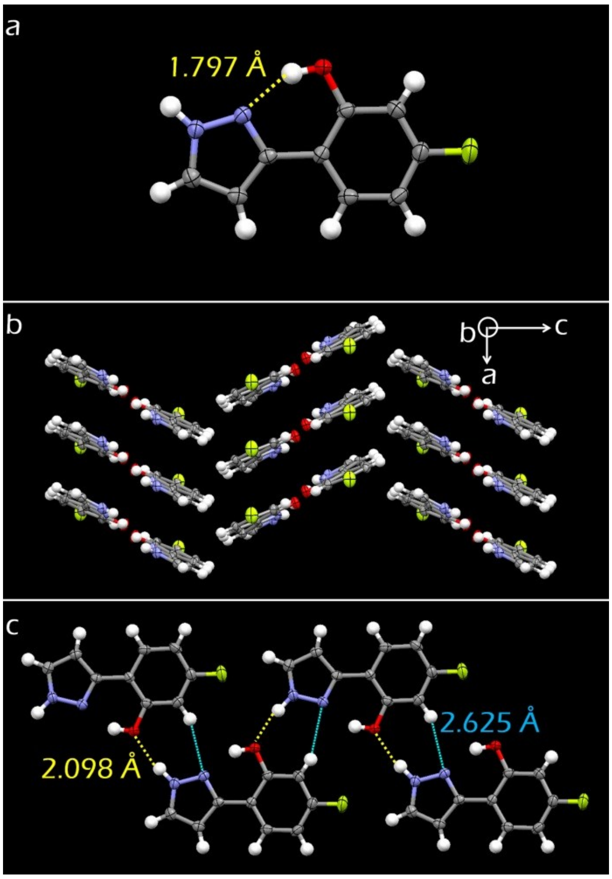


Figure S8. a) Molecular structure, b) packing structure and c) intermolecular hydrogen-bonding interactions of crystal **2**.

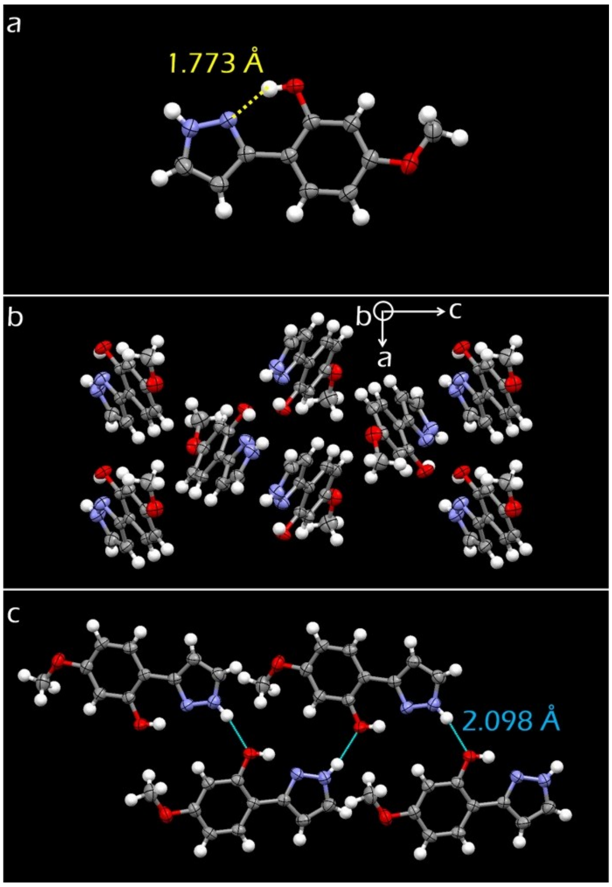


Figure S9. a) Molecular structure, b) packing structure and c) intermolecular hydrogen-bonding interactions of crystal **3**.

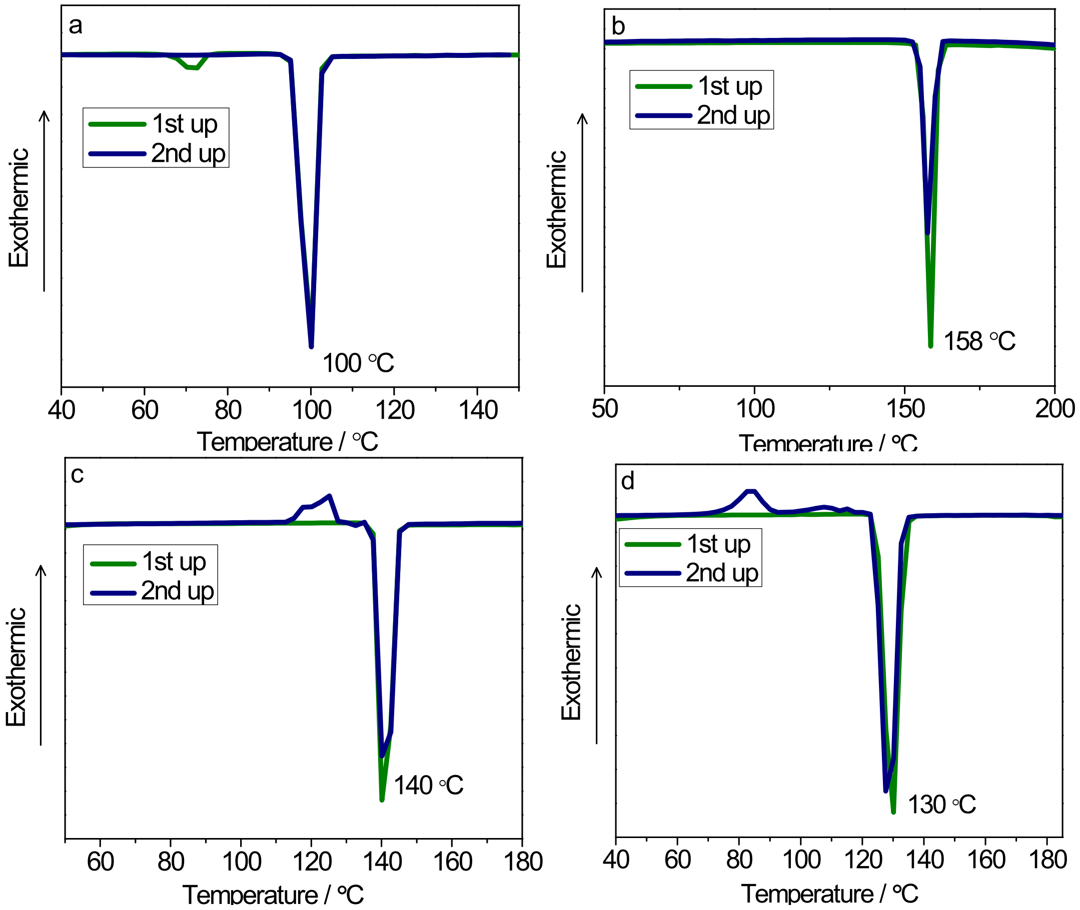


Figure S10. The first (1st) and second (2nd) heating DSC curves of crystals **1** (a), **2** (b), **3** (c) and **4** (d).

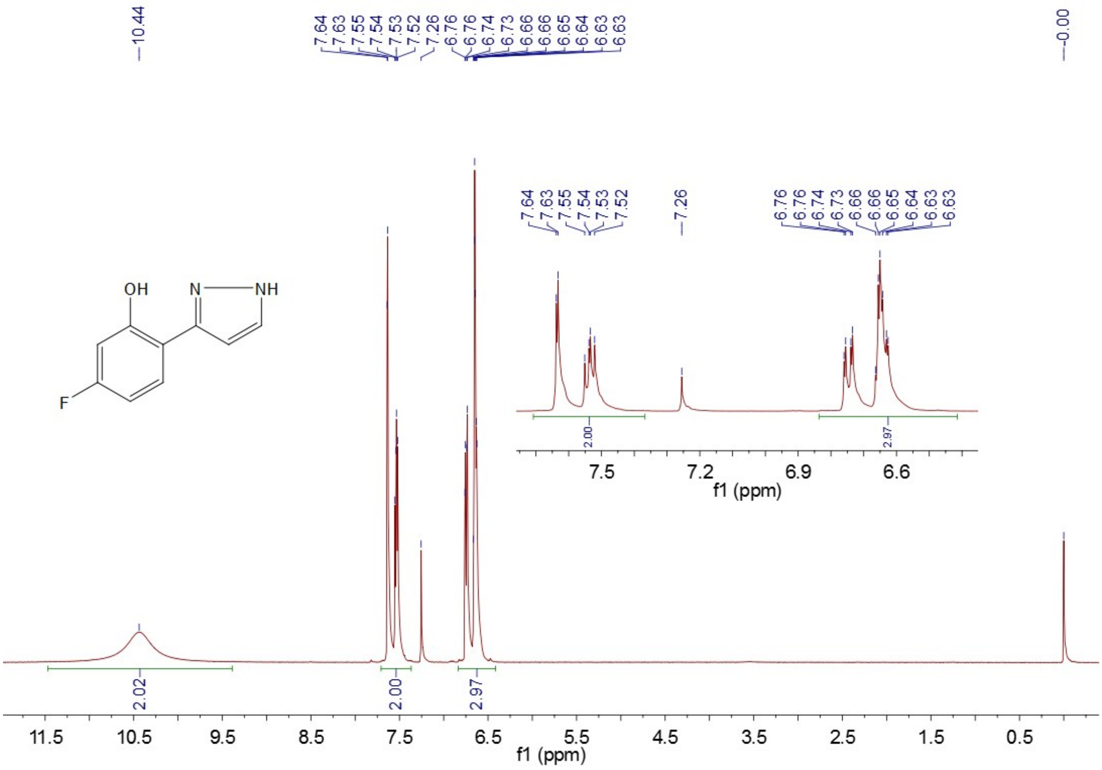


Figure S11. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of compound **2**.

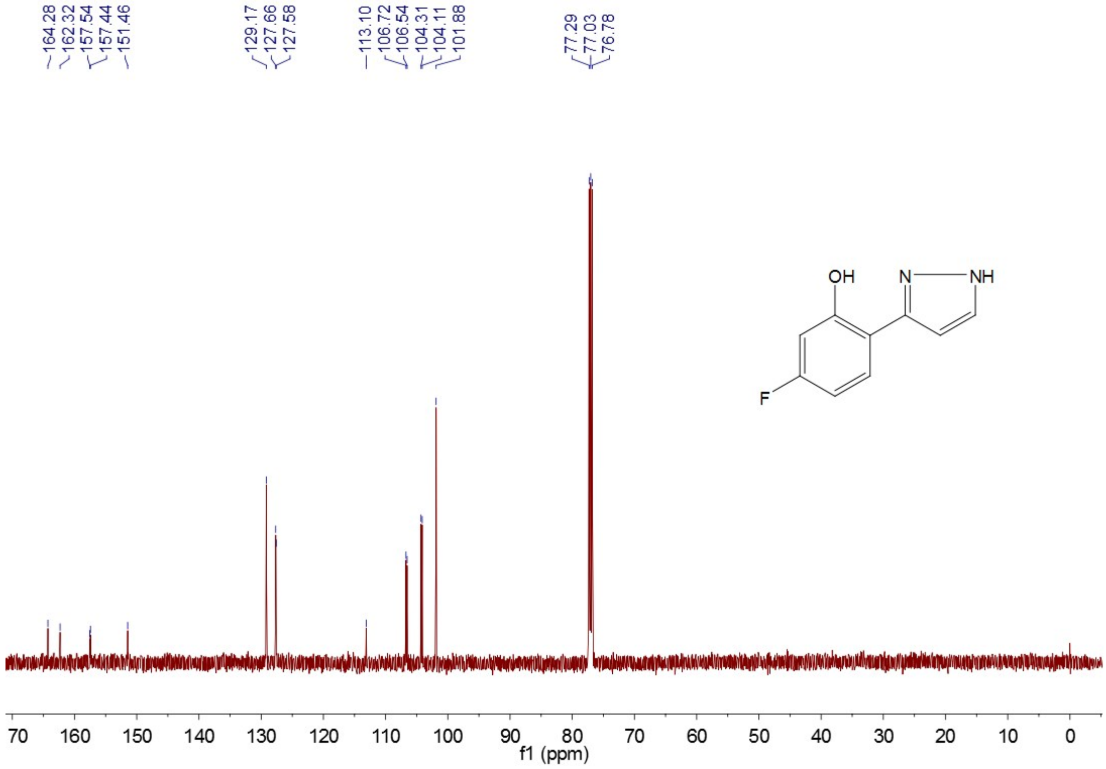


Figure S12. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of compound **2**.

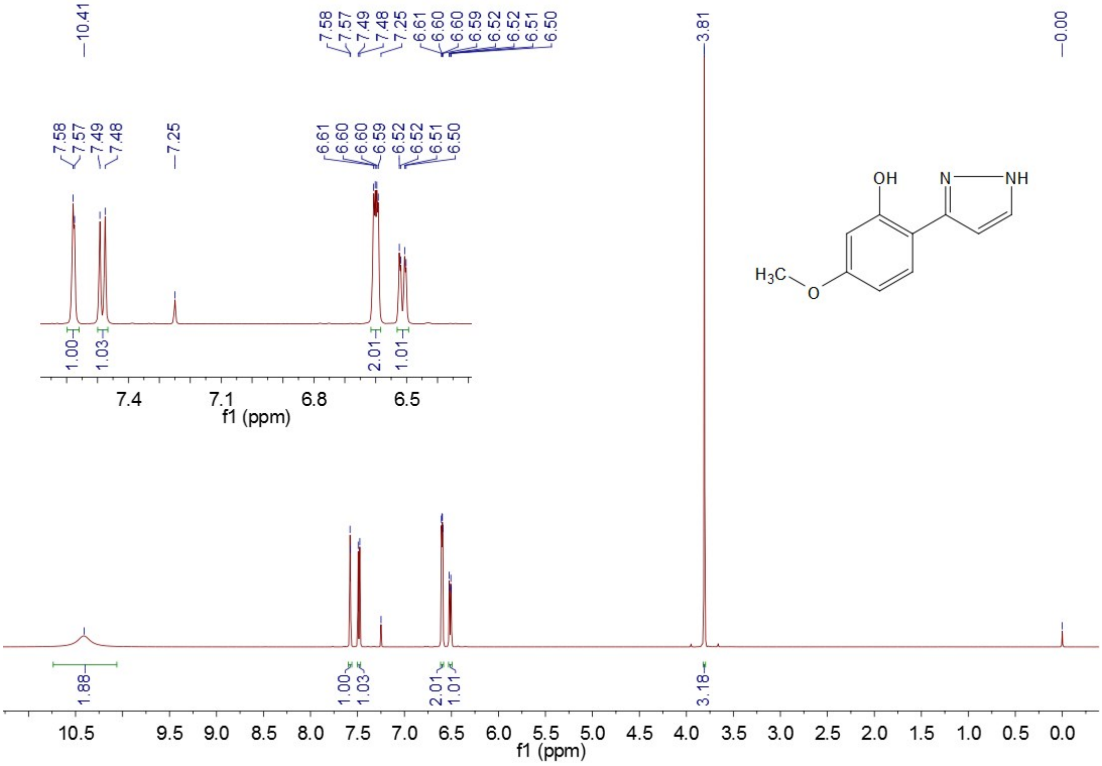


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3**.

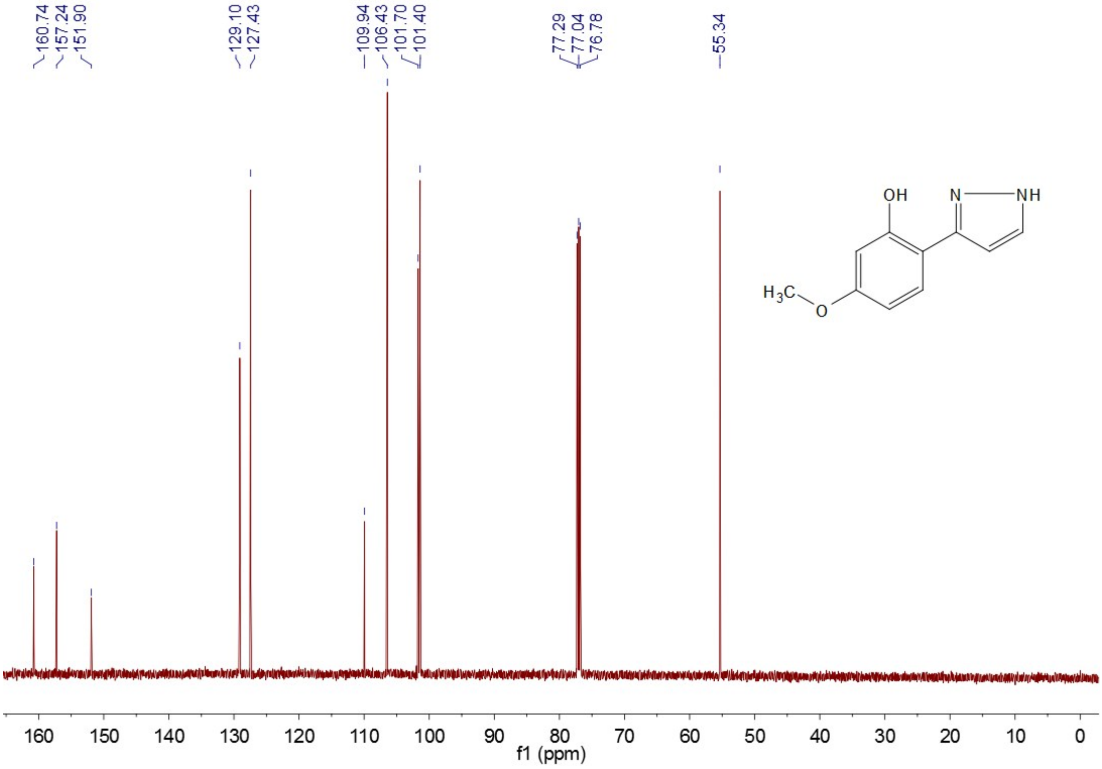


Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3**.

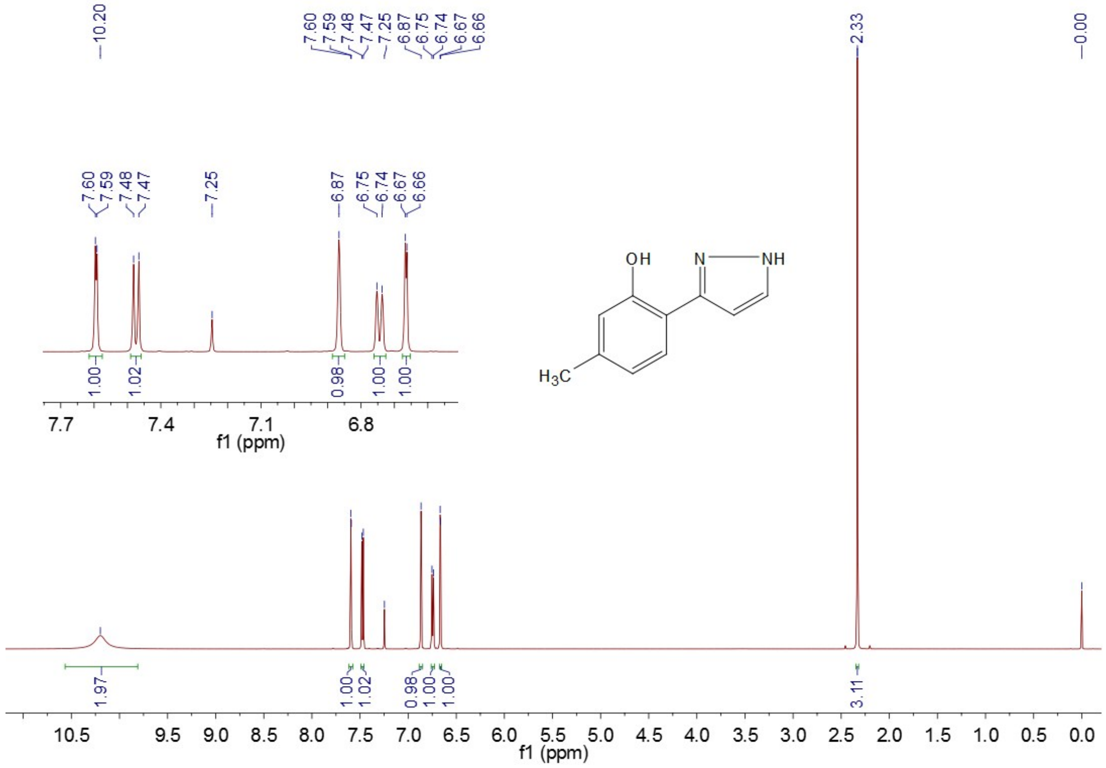


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4**.

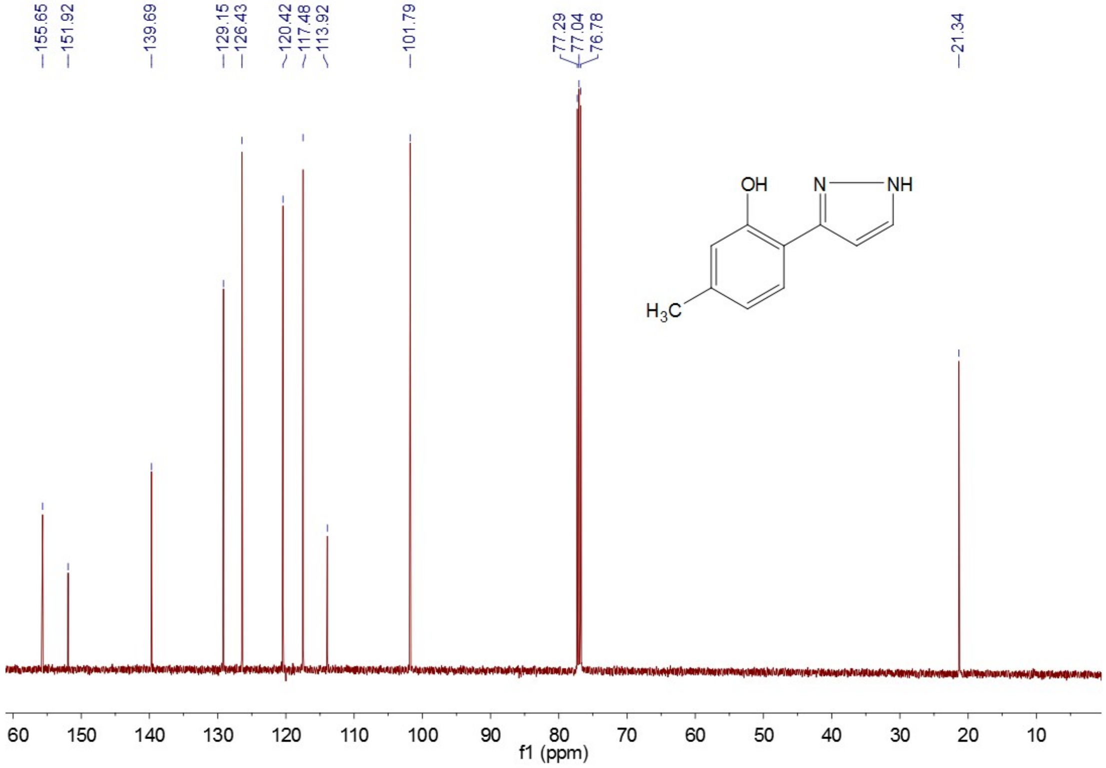


Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **4**.