Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Tuning the organic microcrystals laser wavelength of ESIPT compound via controlling the excited enol* and keto* emission

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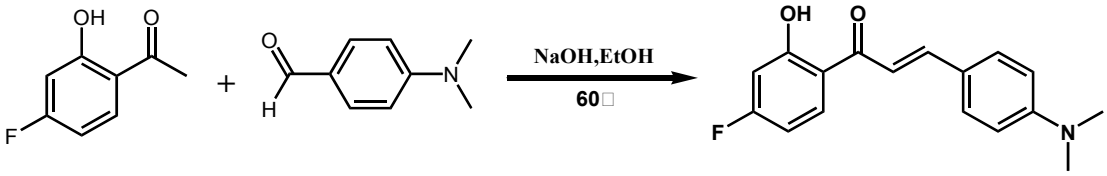
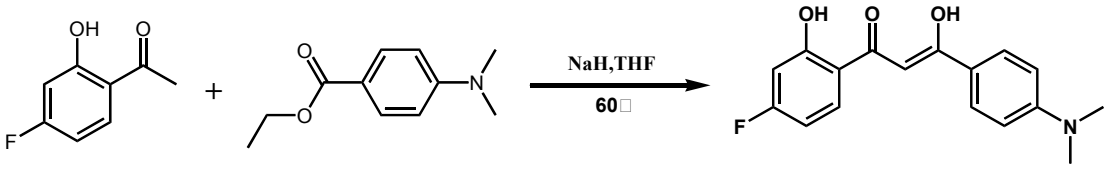
Experimental Section

Materials: 1-(4-fluoro-2-hydroxyphenyl)ethanone, 4-(dimethylamino)benzaldehyde, ethyl 4-(dimethylamino)benzoate, NaH, NaOH were purchased from Aldrich Chemical Co. and used without further purification. THF, EhOH were common commercial grade and were used as received.



Fug. S1a. Synthetic route of M1.



Fug. S1b. Synthetic route of M2.

(*E*)-3-(4'-Dimethylaminophenyl)-1-(4'-fluoro-2'-hydroxyphenyl)-2-propen-1-one (M**1**): Yield was 38%.1H NMR (400 MHz, $CDCl_3$， 400MHz,δ):13.60 (d, J = 1.2 Hz, 1H), 13.60 (d, J = 1.2 Hz, 2H), 7.97 – 7.87 (m, 2H), 7.58 (d, J = 8.9 Hz, 2H), 7.37 (d, J = 15.2 Hz, 1H), 6.77 – 6.58 (m, 4H), 3.07 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 192.48, 166.17, 152.75, 146.81, 131.87, 131.03, 122.17, 117.60, 113.99, 111.91, 106.79, 106.57, 104.90, 104.67, 40.02. MS m/z: [M]+ calcd for C17H16FNO3: 301.18; found: 301.11.

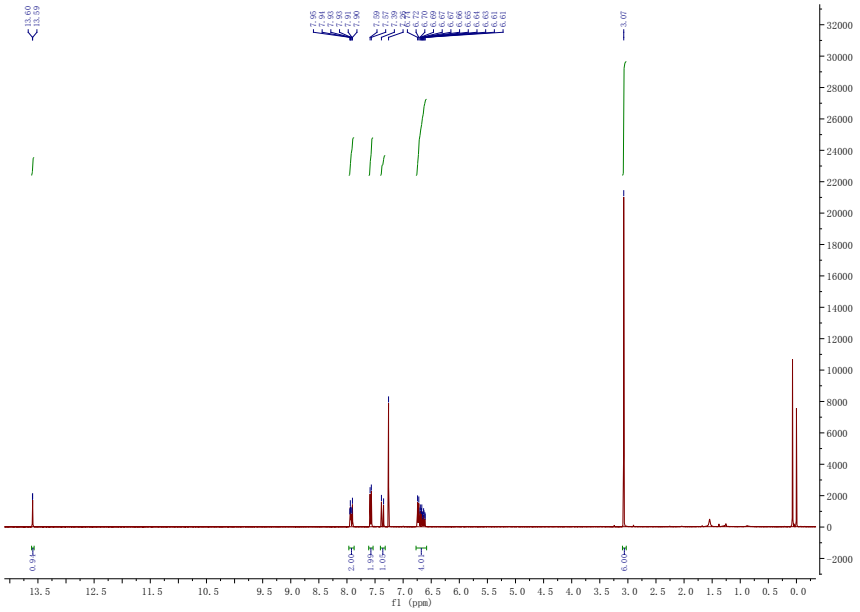


Fig. S2a. ^1H NMR spectra of M1 recorded in $CDCl_3$(400 MHz).

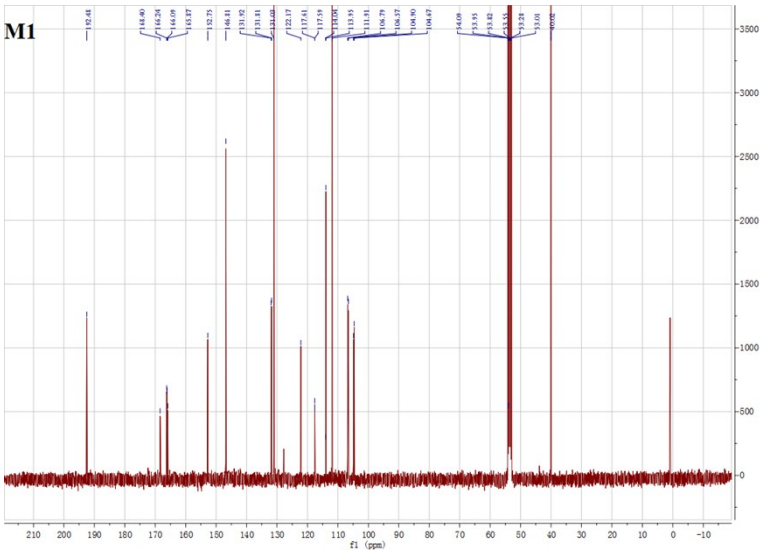


Fig. S2b. ^{13}C NMR spectra of M1 recorded in CD_2Cl_2(400 MHz).

(Z)-3-(4-(dimethylamino)phenyl)-1-(4-fluoro-2-hydroxyphenyl)-3-hydroxyprop-2-en-1-one(M2):Yield was 42%.1H NMR (400 MHz, CD_2Cl_2, 400MHz,δ):enol tautomer（73%）：15.74 (1H),12.57 (1H), 7.86 (3H), 6.85(2H),6.71(1H),6.63 (2H), 3.06 (6H); diketone tautomer（27%）：12.35 (1H), 7.79(3H), 6.63 (4H), 4.49 (2H), 3.06 (6H). 13C NMR (100 MHz, CD_2Cl_2, δ): 200.64, 192.55, 190.64, 179.07, 168.10, 165.59, 164.61, 164.48, 154.18, 153.75, 134.15, 134.03, 131.06, 130.57, 130.45, 128.94, 119.49, 116.35, 111.34, 110.84, 107.58, 107.35, 107.07, 106.85, 105.85, 105.09, 104.86, 89.47, 49.92, 39.99, 39.95. MS m/z: [M]+ calcd for C17H16FNO2, 285.12; found, 284.98.

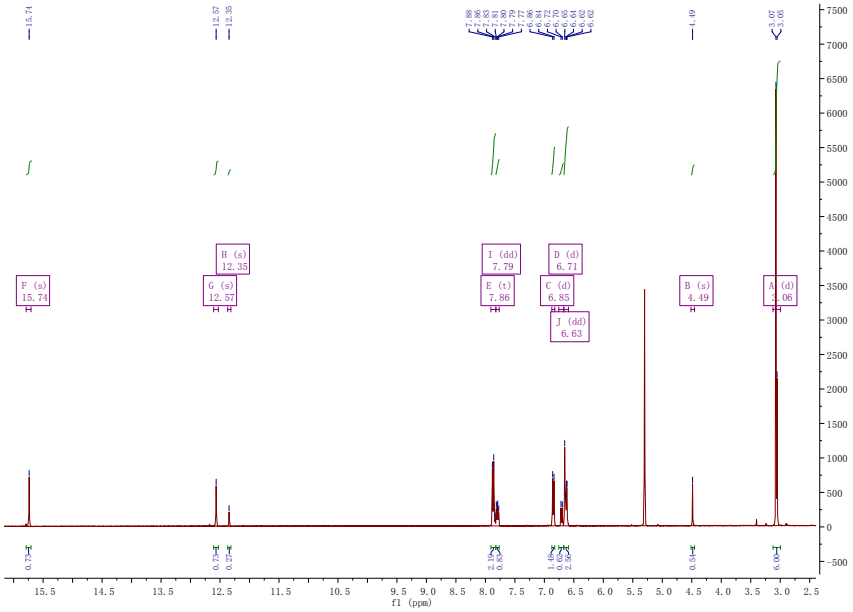


Fig. S2c. ^{1}H NMR spectra of M2 recorded in CD_2Cl_2(400 MHz).

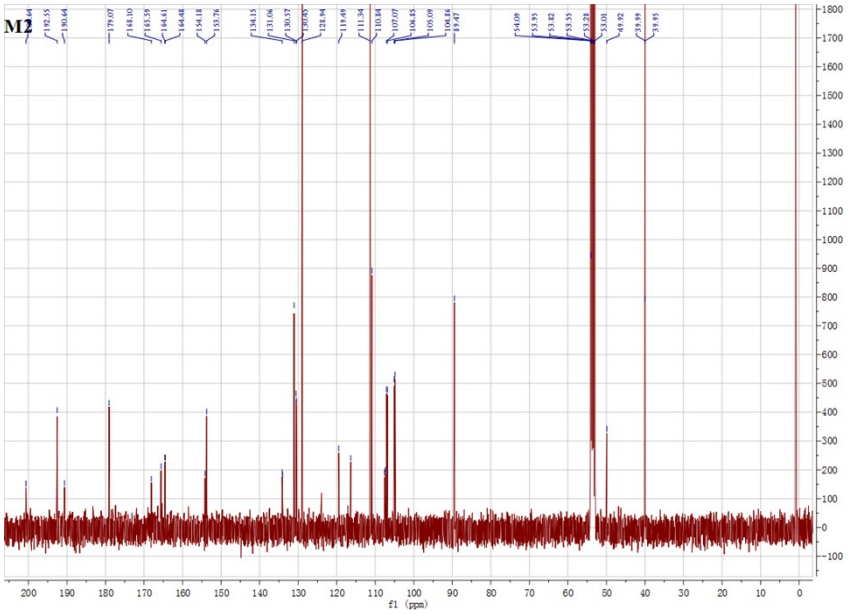


Fig. S2d. ^{13}C NMR spectra of M2 recorded in CD_2Cl_2(400 MHz).

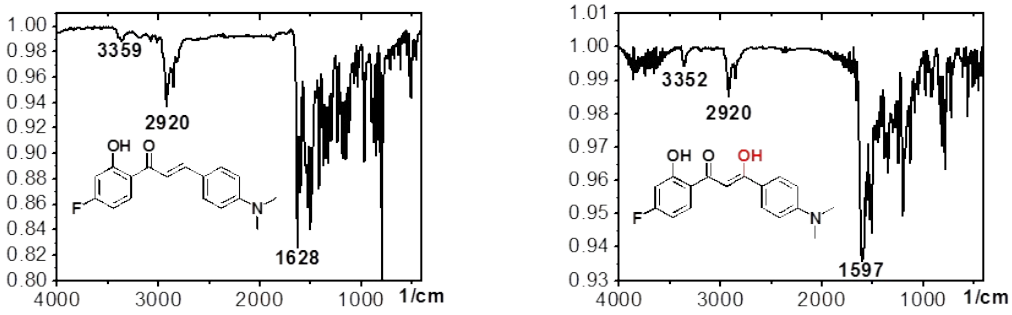


Fig.S3. FT-IR spectrum of the M1 and M2 solid form.

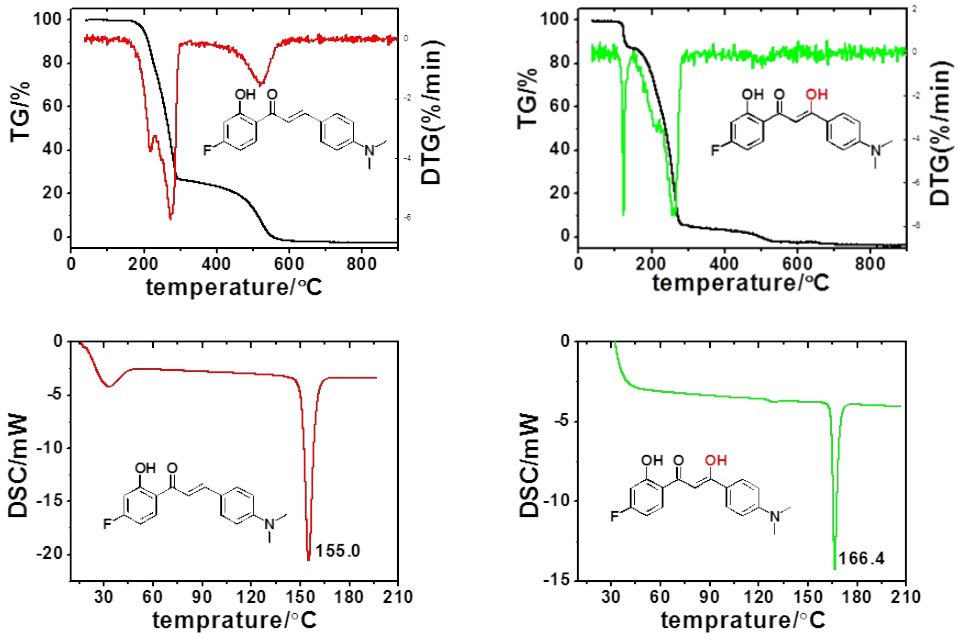


Fig.S4. Thermal gravity（TG）and differential scanning calorimetry(DSC) analysis spectrum of the M1 and M2 crystal.

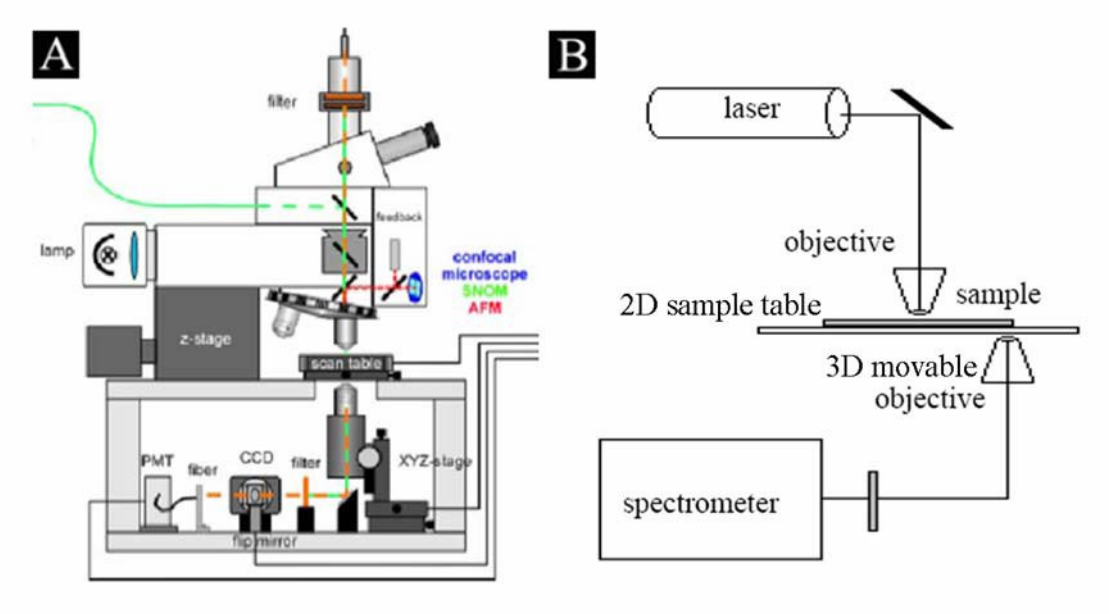


Fig S5. Schematic illustration of (a) the near-field scanning optical microscopy, and (b) the transmittance optical path for the waveguide measurements.

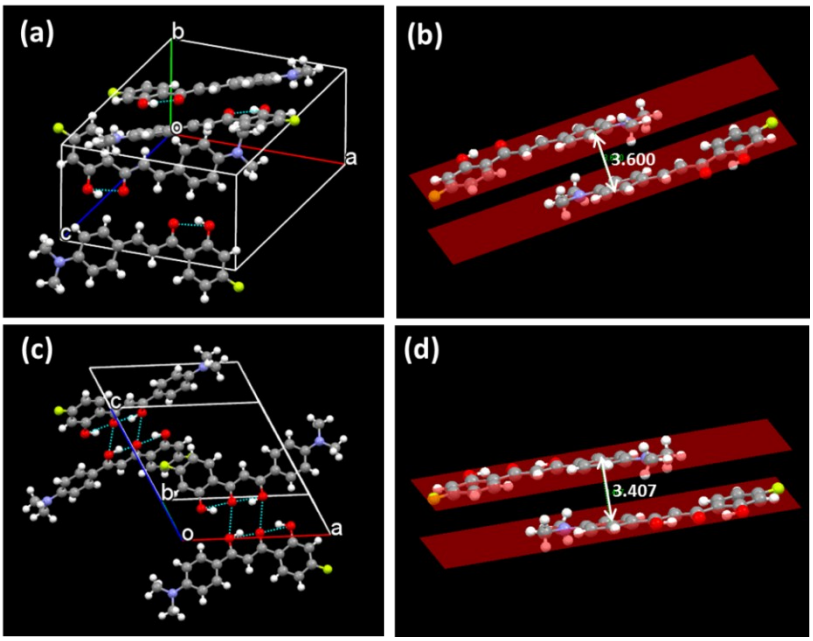


Fig.S6. a) The packing arrangement of M1 molecules in crystals. b) View of the crystal structure of M1 parallel to molecular plan. c) The packing arrangement of M2 molecules in crystals. d) View of the crystal structure of M2 parallel to molecular plan.

We calculated the electric field distribution of our single-crystalline hexagonal-plate microcrystals (HPMCs) microresonator of M1 and M2 by using a finite element (FE) method (COMSOL). The microstructures are on the quartz substrate (nquatz = 1.45). And the refractive index (n_{HPMC}) of HPMC microcrystal is regarded as 1.8.

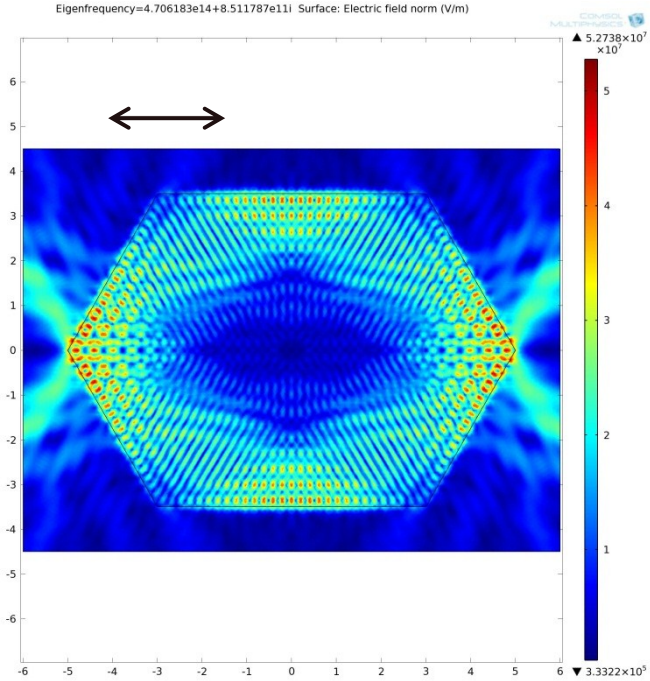


Fig.S7a. Simulated 2D normalized electric field (λ= 637nm, n= 1.80) of microdisk of M1 (W1 = 6μm, W2 = 4μm.

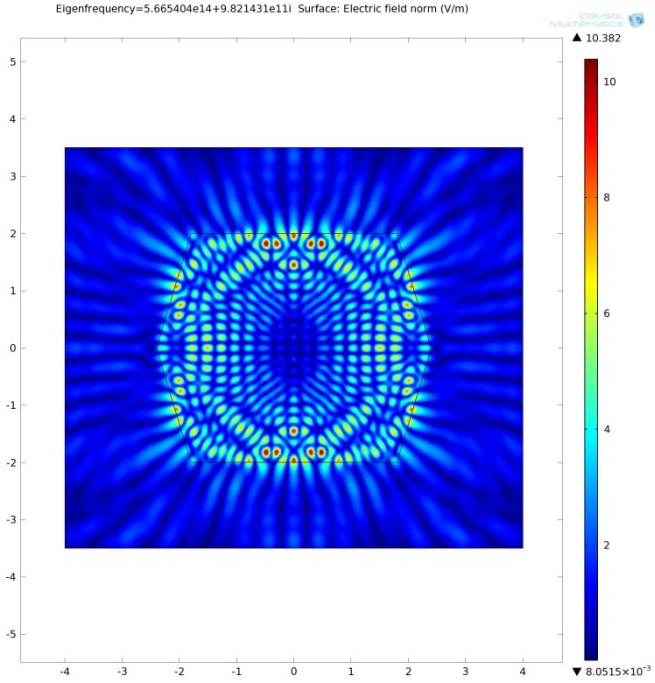


Fig.S7b. Simulated 2D normalized electric field (V/m, λ= 530nm, n= 1.80) of microdisk of M2 (W1 = 4 μm, W2 = 2.1 μm).

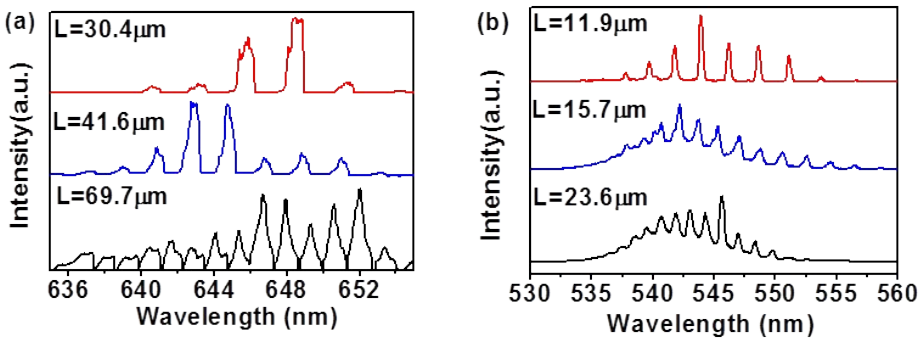


Figure S8. High-resolution PL spectra of laser emission recorded above threshold for three microdisks of a). M1 and b) M2 with different size.

Table S1. Crystal data and structure refinement for M1 (CCDC no. 1494892)

Name	M2	
Identification code	b	
Empirical formula	C17 H16 F N O2	
Formula weight	285.31	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.394(3) Å	α= 90°.
	b = 10.203(3) Å	β= 115.798(2)°.
	c = 12.264(3) Å	γ= 90°.
Volume	1396.4(6) $Å^3$	
Z	4	
Density (calculated)	1.357 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	600	
Crystal size	0.53 x 0.35 x 0.34 mm^3	
Theta range for data collection	2.71 to 27.49°.	
Index ranges	-14<=h<=16, -13<=k<=12, -15<=l<=15	
Reflections collected	10199	
Independent reflections	3164 [R(int) = 0.0223]	
Completeness to theta = 26.000°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8123	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3164 / 0 / 193	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2 sigma(I)]	R1 = 0.0443, wR2 = 0.1053	
R indices (all data)	R1 = 0.0463, wR2 = 0.1065	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.246 and -0.173 e.$Å^{-3}$	

Hydrogen bonds for M2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O2	0.82	1.77	2.4980(14)	147.6

Table S2. Crystal data and structure refinement for M2 (CCDC no. 1494891)

Name	M2	
Empirical formula	C17 H16 F N O3	
Formula weight	301.31	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.931(4) Å	α= 90°.
	b = 10.515(3) Å	β= 117.644(4)°.
	c = 12.710(5) Å	γ= 90°.
Volume	1412.5(8) $Å^3$	
Z	4	
Density (calculated)	1.417 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	632	
Crystal size	0.35 x 0.3 x 0.015 mm^3	
Theta range for data collection	2.74 to 27.47°.	
Index ranges	-15<=h<=15, -13<=k<=13, -16<=l<=16	
Reflections collected	9391	
Independent reflections	3230 [R(int) = 0.0289]	
Completeness to theta = 26.000°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8194	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3230 / 0 / 209	
Goodness-of-fit on F^2	1.176	
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1207	
R indices (all data)	R1 = 0.0568, wR2 = 0.1233	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.235 and -0.191 e.$Å^{-3}$	

Hydrogen bonds for M2 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O2	0.98(3)	1.64(3)	2.5250(18)	147(2)
O1-H1...O3#1	0.98(3)	2.55(3)	3.2280(18)	126.1(19)
O3-H3...O2	0.94(3)	1.62(3)	2.5012(18)	153(2)