Supporting Information

Naphthalimide trifluoroacetyl acetonate: A hydrazine-selective chemodosimetric sensor

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Contents

1. Synthetic materials and methods

All reagents, including amines, metal ions, and other chemicals for synthesis, were purchased from Aldrich, TCI and used as received. All solvents were HPLC reagent grade, and triple-deionized water was used throughout the analytical experiments. Silica gel 60 (Sorbent, 40–63 mm) was used for column chromatography. Analytical thin layer chromatography was performed using Silicycle 60 F254 silica gel (precoated sheets, 0.25 mm thick). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (Cambridge Isotope Laboratories, Cambridge, MA) on Varian 400 MHz spectrometers.

2. UV/Vis absorption and fluorescence spectroscopy

Stock solutions of compounds **1**, **6**, and amines were prepared in CH_3CN. The chloride salts of the test metal ions Cs^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, and Ba^{2+} were prepared in triple-distilled water. The fluorescence quantum yields (Φ_f) were measured relative to quinine sulfate ($\Phi_f = 0.54$ in 0.5 M H_2SO_4).[20] Absorption spectra were recorded on Varian-5000 UV/Vis-NIR spectrophotometer, and fluorescence spectra were recorded using a FL3-11T spectrofluorometer (Nanolog) equipped with a xenon lamp (FL 1039). Samples for absorption and emission measurements were contained in quartz cuvettes (3 mL volume). Excitation was provided at 348 nm with excitation and emission slit widths both set at 5 nm.

3. Cell culture and imaging

A human cervical cancer cell line (HeLa) was cultured in Dulbecco's Modified Eagle’s Medium (DMEM) supplemented with 10% FBS (WelGene), penicillin (100 units/mL), and streptomycin (100 μg/mL). Two days before imaging, the cells were passed and plated on glass-bottomed dishes (MatTek). All the cells were maintained in a humidified atmosphere of 5/95 (v/v) of CO_2/air at 37 ℃. For labelling, the growth medium was removed and replaced with DMEM without FBS. The cells were treated and incubated with 10 μM of **1** at 37 ℃ under 5% CO_2 for 2 h. The cells were washed three times with phosphate buffered saline (PBS, Gibco) and then cell images were obtained using a confocal microscope from Leica (Leica TCS SP2 model). Other information is available in the Fig. captions.

4. Two-photon fluorescence microscopy

Two-photon fluorescence microscopy images of HeLa cells incubated with **1** were obtained using spectral confocal and multiphoton microscopes (Leica TCS SP2 model) with a ×10 (NA = 0.30 DRY) and ×100 (NA = 1.30 OIL) objective lens. The two-photon fluorescence microscopic images were obtained using a DM IRE2 Microscope (Leica) by exciting probe **1** with a mode-locked titanium sapphire laser source (Coherent Chameleon, 90 MHz, 200 fs) set at wavelength 740 nm and using an output power of 1580 mW, which corresponded to approximately 10 mW average power in the focal plane. To obtain images, internal photomultiplier tubes (PMTs) were used to collect the signals in an 8 bit unsigned 512 × 512 pixels at 400 Hz scan speed.

5. Synthesis

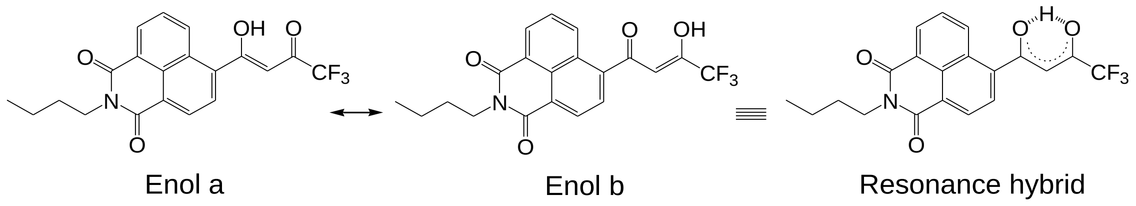
Compounds 4 and 5 were prepared by adapting published procedures.[1]

Synthesis of 6. Compound **5** (2.0 g, 8.3 mmol) and *n*-butylamine (1.2 mL, 16.6 mmol) were dissolved in ethanol (100 mL). The reaction mixture was then stirred and heated at reflux for

3 h. After removal of solvent under reduced pressure, the crude product was purified over silica gel using ethyl acetate/hexanes (v/v, 1:2) as the eluent to yield **6** as a white solid (2.0 g, 81%). HRESI-MS *m/z* (M+Na$^+$) calc 318.11006, obs 318.11015. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.91 (d, 1 H, *J* = 8.8 Hz); 8.59 (d, 2 H, *J* = 8.6 Hz); 8.08 (d, 1 H, *J* = 8.1 Hz); 7.78 (t, 1 H, *J* = 7.8 Hz); 4.12 (t, 2 H, *J* = 4.2 Hz); 2.76 (s, 3 H); 1.70–1.63 (m, 2 H); 1.42–1.37 (m, 2 H); 0.92 (t, 3 H, *J* = 0.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): 200.6, 163.8, 163.3, 139.7, 132.3, 131.5, 129.6, 128.8, 128.3, 125.6, 122.3, 40.4, 30.3, 20.4, 14.2 ppm.

Synthesis of 1. To a solution of **6** (1.3 g, 4.4 mmol) in dichloromethane was added ethyl trifluoroacetate (10 mL). The mixture was stirred for 5 min before an ethanolic 21% NaOEt solution (20 mL) was added. The reaction mixture was then heated at reflux for 2 h under a nitrogen atmosphere in the dark. After allowing the vessel to cool to room temperature, the reaction was quenched by adding dilute $HCl_{(aq.)}$. The solution was then extracted with dichloromethane several times. The combined organic phases were dried over Na_2SO_4, and filtered. After removal of solvent under reduced pressure, the crude product was purified over silica gel using ethyl acetate/hexanes (v/v, 4:1) as the eluent to yield **1** as a brownish solid (1.2 g, 88%). HRESI-MS *m/z* (M+Na$^+$) calc 414.09236, obs 414.09219. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 14.8 (s, 1 H); 8.79 (d, 1 H, *J* = 8.8 Hz); 8.70–8.65 (m, 2 H); 8.06 (d, 1 H, *J* = 8.1 Hz); 7.88 (t, 1 H, *J* = 7.8 Hz); 6.54 (s, 1 H); 4.19 (t, 2 H, *J* = 4.2 Hz); 1.77–1.71 (m, 2 H); 1.50–1.41 (m, 2 H); 0.99 (t, 3 H, *J* = 0.9 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): 188.5, 163.4, 163.0, 136.6, 131.7, 131.2, 129.7, 128.5, 128.1, 125.7, 122.8, 97.7, 41.0, 30.5, 20.1, 13.1 ppm.

6. Additional data



Scheme S1 The structure of enols a/b and resonance hybrid of compound **1**.

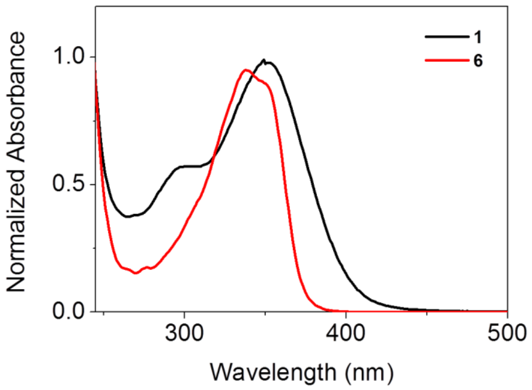


Fig. S1 Absorption spectra of **1** and **6** in CH_3CN.

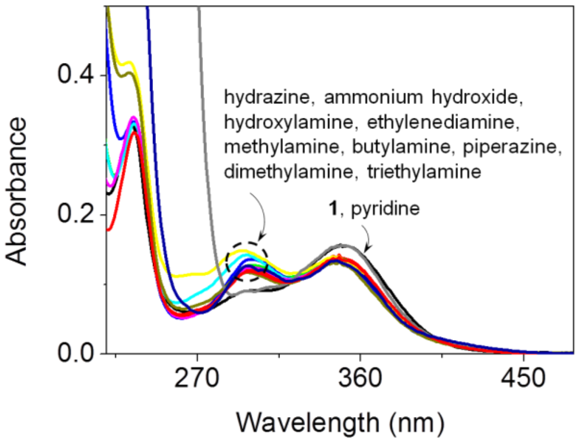


Fig. S2 Absorption spectra of **1** (10.0 μM) recorded after exposure to various amines, including hydrazine, ammonium hydroxide, hydroxylamine, ethylenediamine, methylamine, butylamine, piperazine, dimethylamine, triethylamine, and pyridine (1.0 mM, respectively) in CH_3CN.

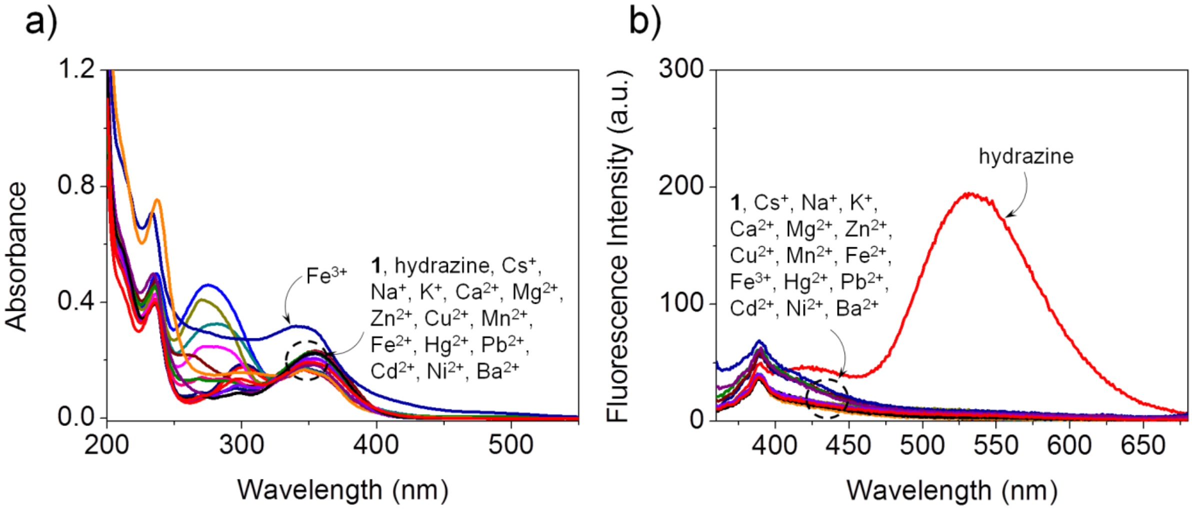


Fig. S3 Absorption (a) and fluorescence spectra (b) of **1** (10.0 μM) observed after exposure to hydrazine and the chloride salts of carious metal ions, including Cs^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, and Ba^{2+} (0.1 mM, respectively), in $CH_3CN:H_2O$ (v/v, 9:1) with λ_{ex} = 348 nm.

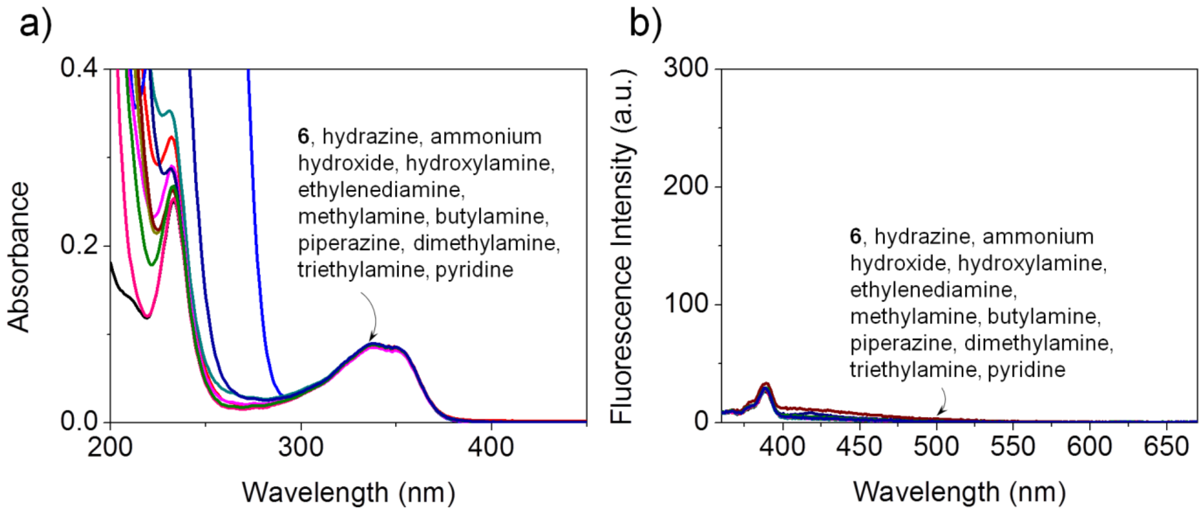


Fig. S4 Absorption (a) and fluorescence spectra (b) of **6** (10.0 μM) recorded in the presence of various amines, including hydrazine, ammonium hydroxide, hydroxylamine, ethylenediamine, methylamine, butylamine, piperazine, dimethylamine, triethylamine, and pyridine (1.0 mM, respectively), in CH_3CN with λ_{ex} = 348 nm.

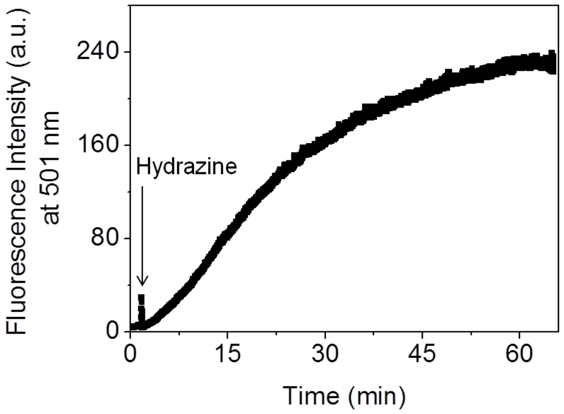


Fig. S5 Time-dependent fluorescence intensity changes at 501 nm observed when probe **1** (1.0 μM) was treated with hydrazine (1.0 mM) in CH_3CN with λ_{ex} = 348 nm.

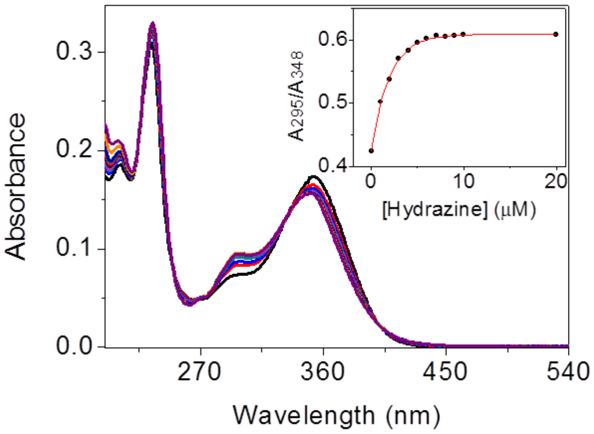


Fig. S6 UV/Vis absorption changes observed for **1** (10.0 μM in CH_3CN) upon exposure to increasing concentrations of hydrazine (0–20.0 μM). All spectra were acquired 1 h after the addition of hydrazine. Inset: Change in the absorbance ratio (A_{295}/A_{348}) as a function of hydrazine concentration.

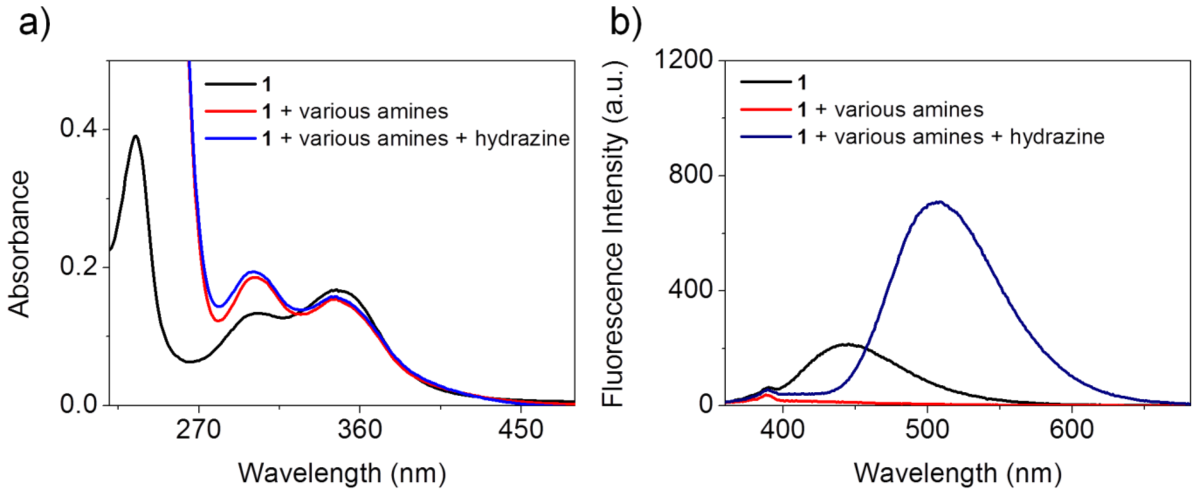


Fig. S7 Absorption (a) and fluorescence spectra (b) of **1** (10.0 μM) recorded upon exposure to hydrazine (0.3 mM) in the presence of various potentially competitive amines, including ammonium hydroxide, hydroxylamine, ethylenediamine, methylamine, butylamine, piperazine, dimethylamine, triethylamine, and pyridine (0.3 mM, respectively), in CH_3CN with λ_{ex} = 348 nm.

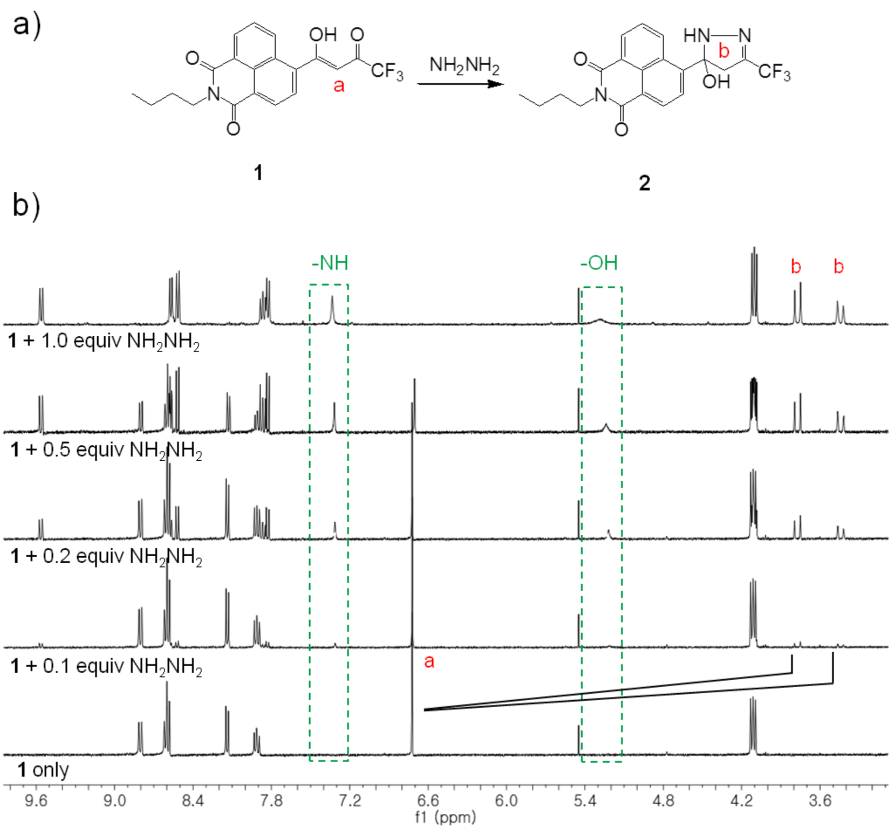


Fig. S8 (a) Proposed reaction mechanism for the hydrazine-induced cyclization of **1**. (b) Partial ^{1}H-NMR spectra of **1** recorded upon subjecting to increasing concentrations of hydrazine (0.1–1.0 equiv) in CD_3CN.

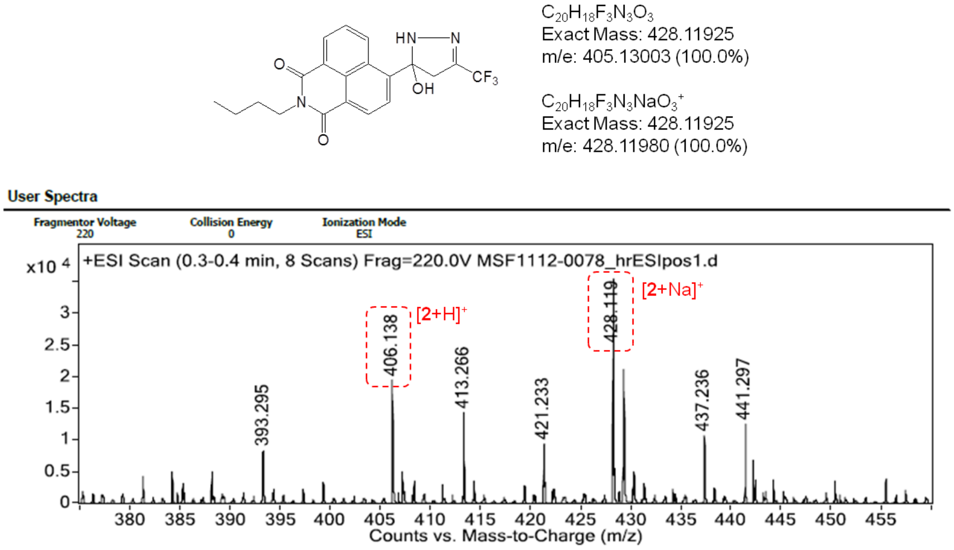


Fig. S9 HRESI-MS spectrum of **1** recorded after the addition of 1.0 equiv of hydrazine.

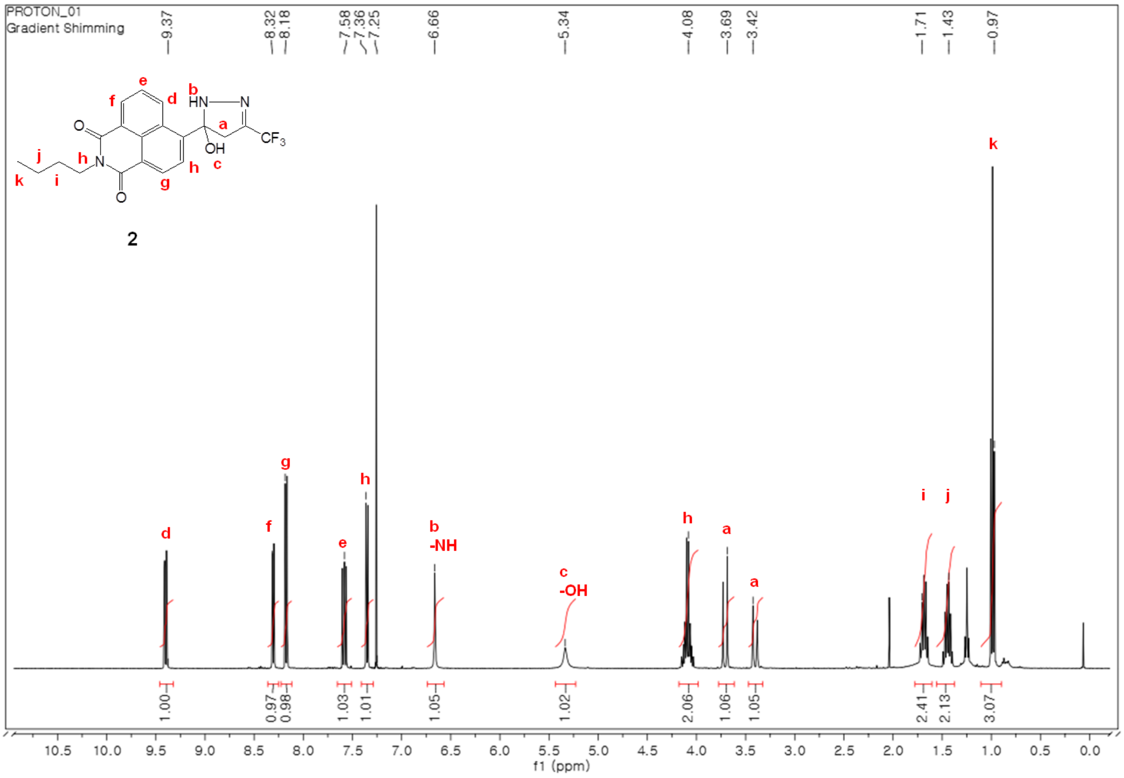


Fig. S10 ^{1}H NMR spectrum of **2** after purification by silica gel column chromatography (ethyl acetate:hexanes = 1:3) in CD_3CN.

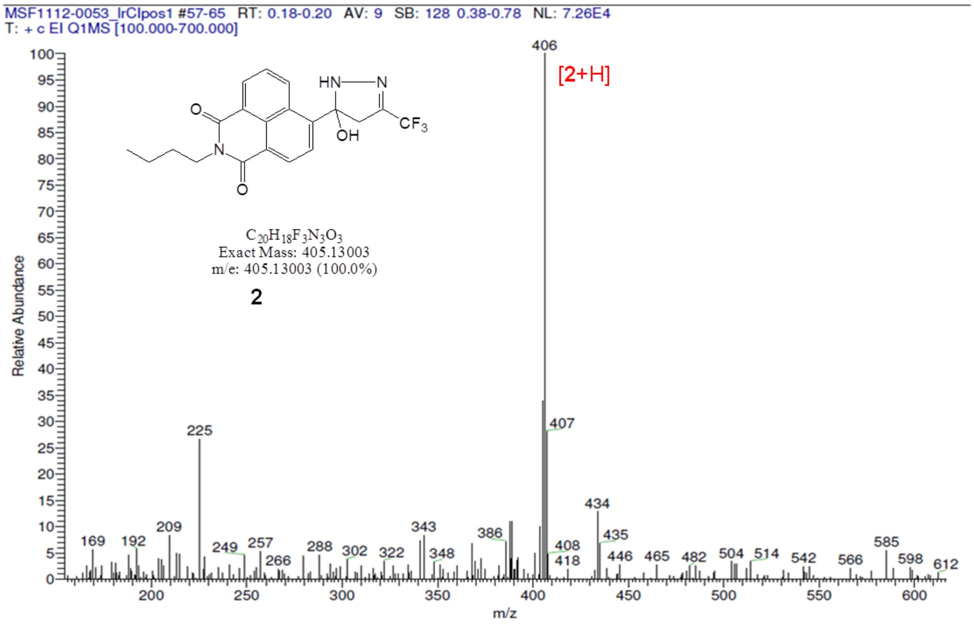


Fig. S11 ESI-MS spectrum of **2** recorded after purification by silica gel column chromatography (ethyl acetate:hexanes = 1:3).

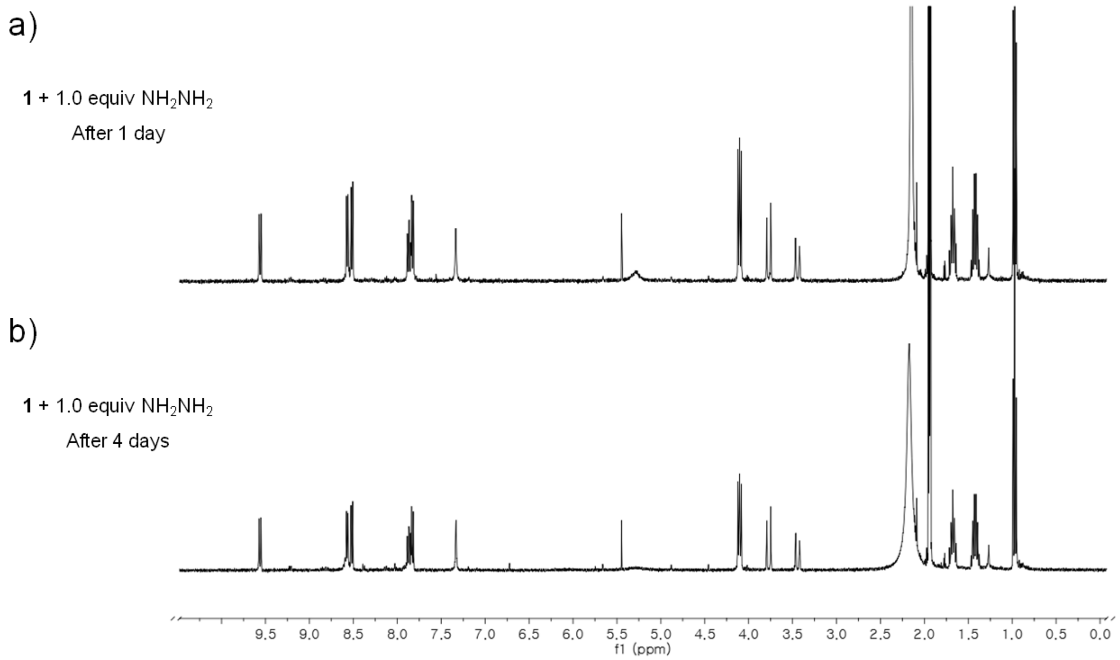


Fig. S12 ^{1}H-NMR spectra of **1** recorded at 1 (a) and 4 days (b) after the addition of 1.0 equiv of hydrazine in CD_3CN.

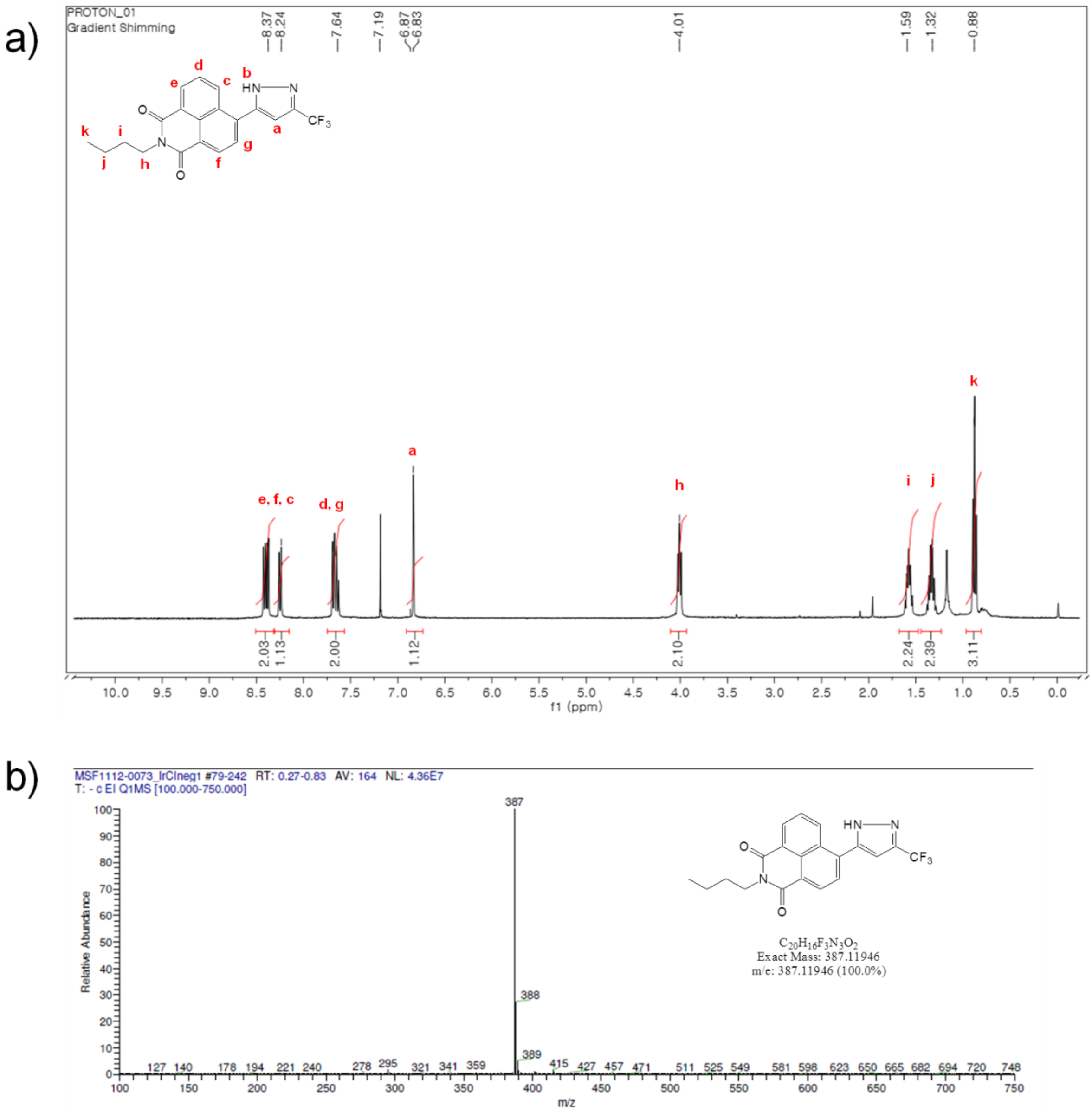


Fig. S13 ^{1}H-NMR (a) and ESI-MS spectra (b) of **3**, a product resulting from the dehydration of **2** in $CDCl_3$.

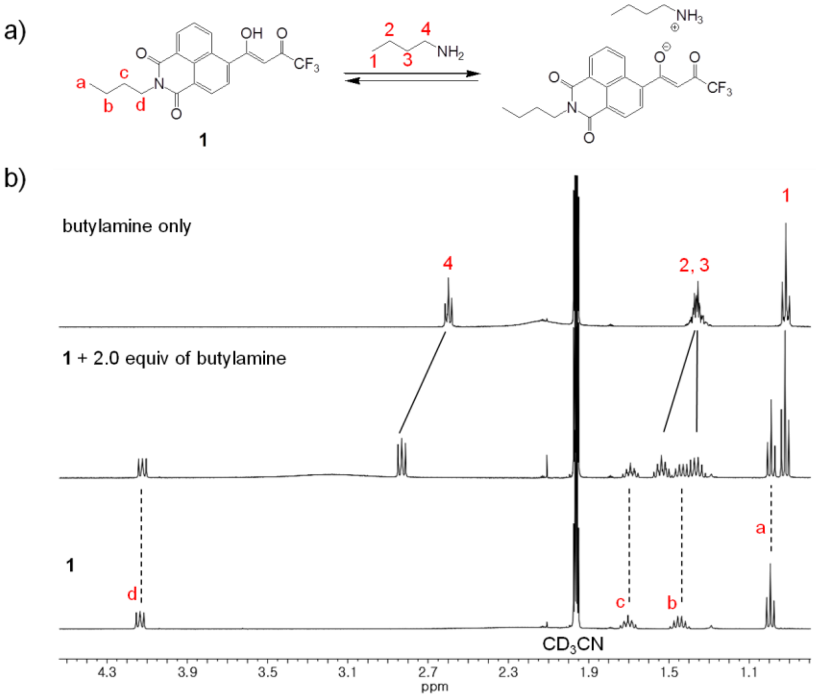


Fig. S14 (a) Proposed reactions of **1** with butylamine. (b) Partial ^1H NMR spectra of **1** recorded in the absence and presence of butylamine, respectively, in CD_3CN.

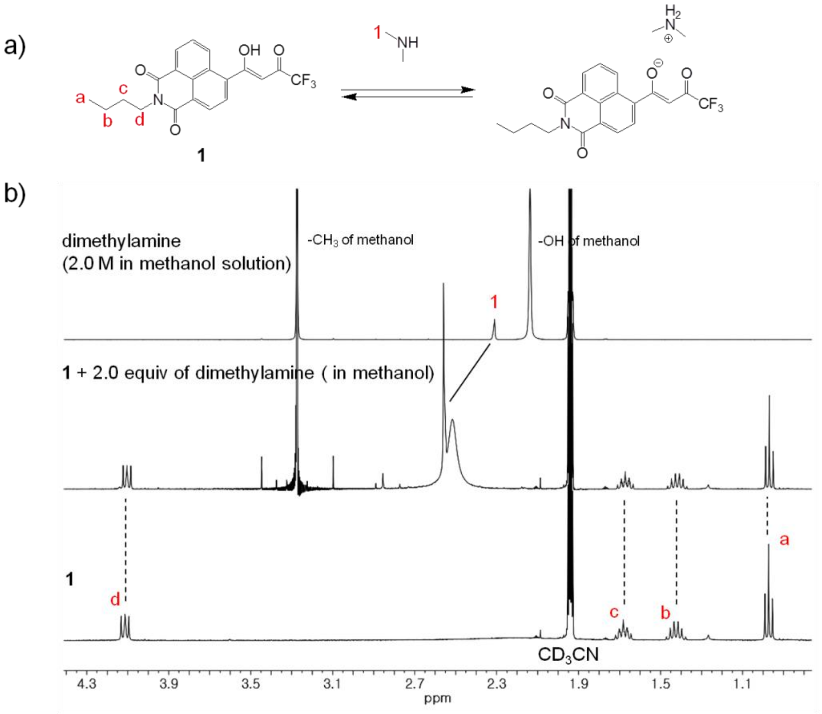


Fig. S15 (a) Proposed reaction of **1** with dimethylamine (2.0 M in methanol solution). (b) Partial ^1H NMR spectra of **1** recorded in the absence and presence of the dimethylamine, respectively, in CD_3CN.

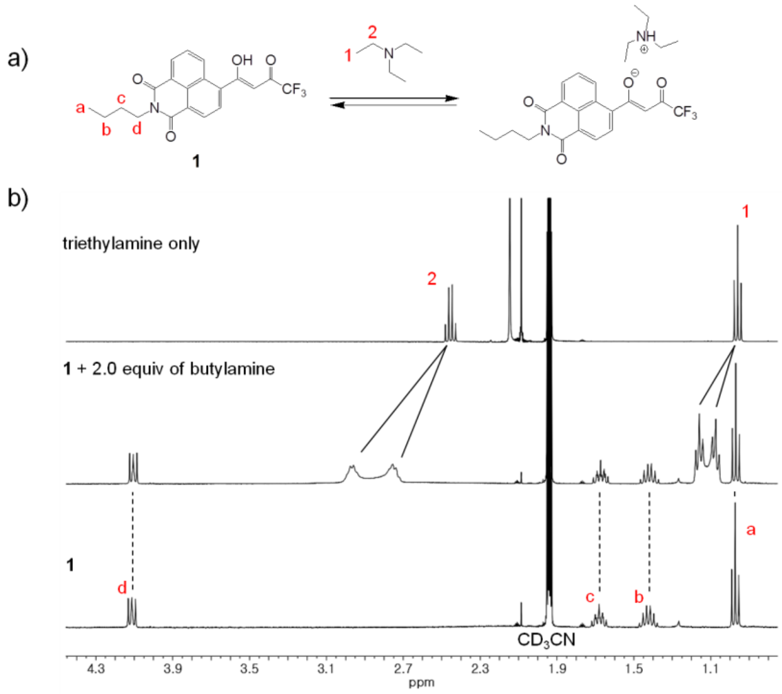


Fig. S16 (a) Proposed reaction of **1** of **1** with triethylamine. (b) Partial ^{1}H NMR spectra of **1** recorded in the absence and presence of triethylamine, respectively, in CD$_3$CN.

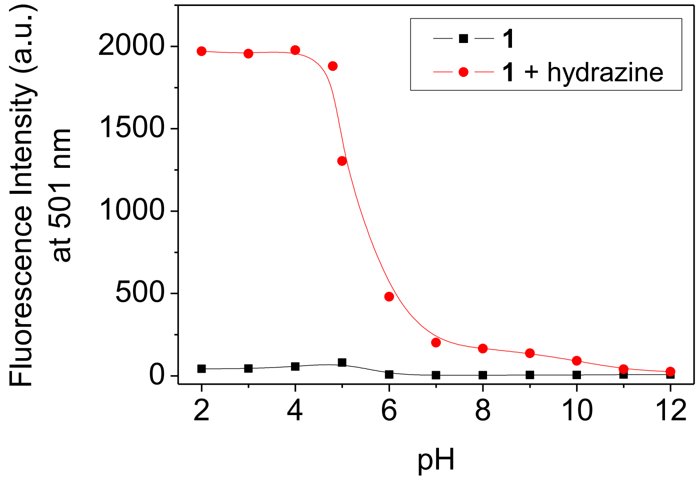


Fig. S17 Changes in the fluorescence intensity at 501 nm of **1** (10.0 μM) with and without hydrazine (1.0 mM) as a function of pH (2, 3, 4, 4.8, 5, 6, 7, 8, 9, 10, 11, and 12). Each point was acquired 1 h after hydrazine addition and obtained using excitation at 348 nm.

7. ^{1}H NMR, ^{13}C NMR and ESI-MS analyses

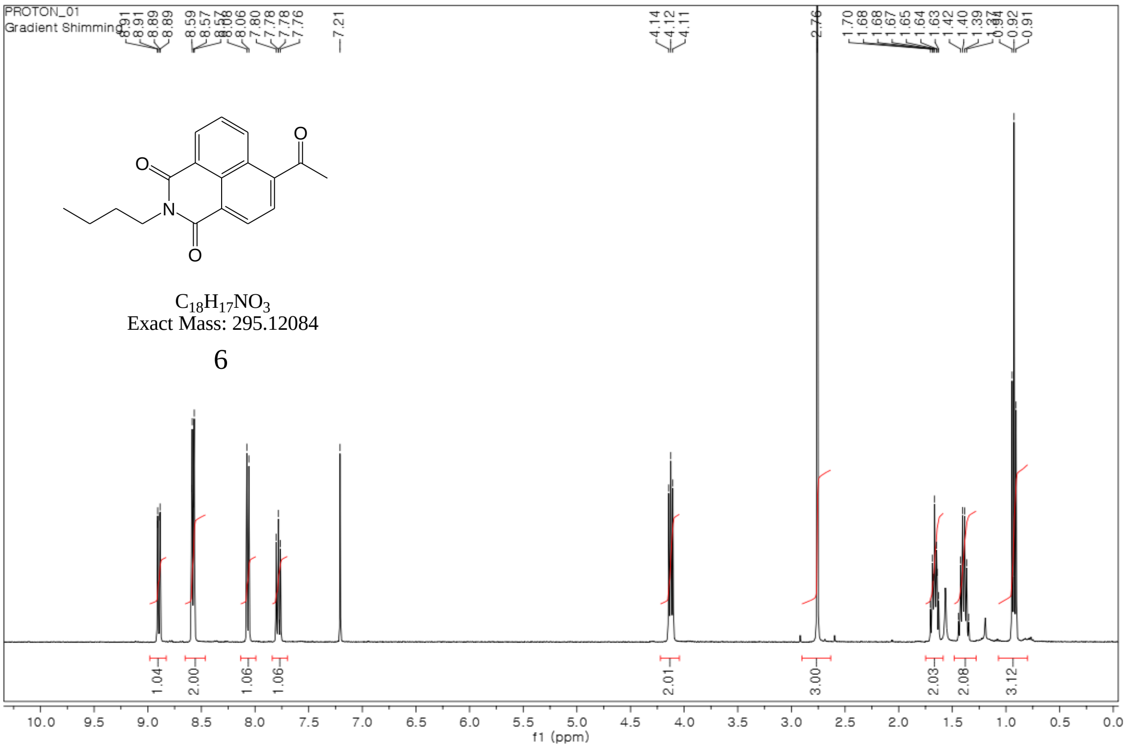


Fig. S18 ^{1}H NMR spectrum of **6** recorded in $CDCl_3$.

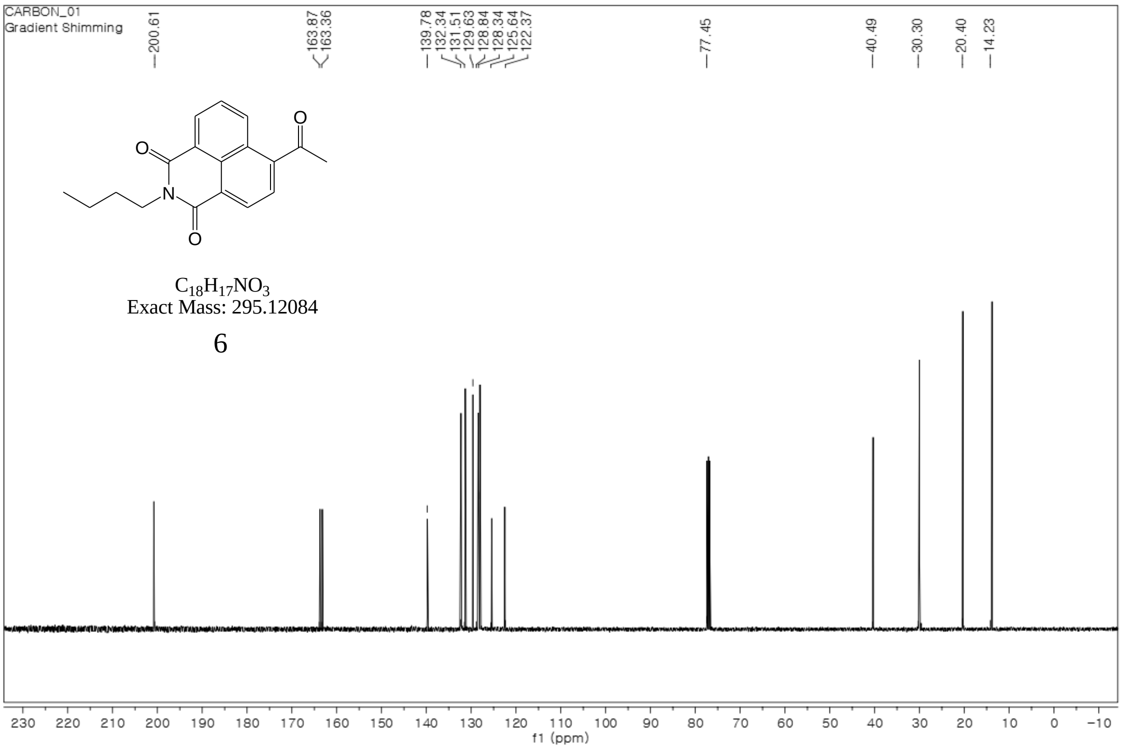
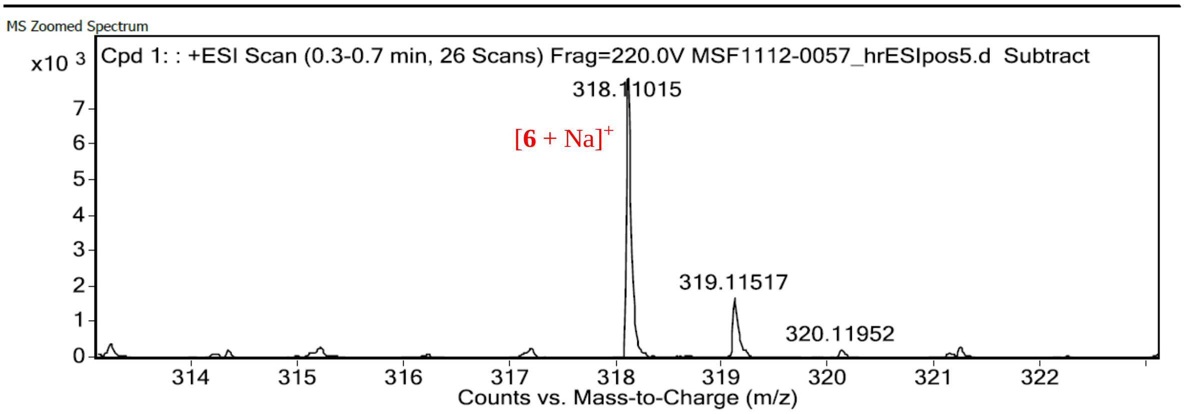


Fig. S19 ^{13}C NMR spectrum of **6** recorded in $CDCl_3$.



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
318.11015	318.11006	1	8073.2	C18H17NNaO3	(M+Na)+	0.26
319.11517	319.11334	1	1707.6	C18H17NNaO3	(M+Na)+	5.75
320.11952	320.11605	1	249.9	C18H17NNaO3	(M+Na)+	10.84
360.32353			14432.7			

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Fig. S20 HR-ESI-MS spectrum of **6**.

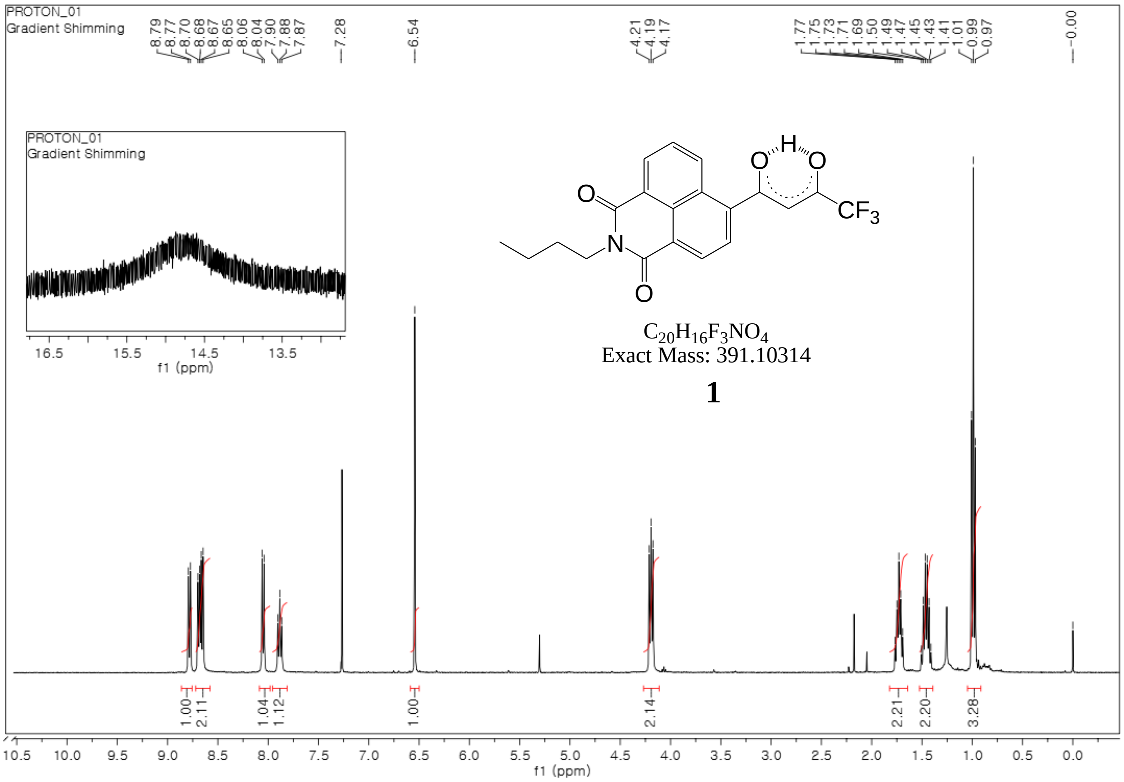


Fig. S21 ^{1}H NMR spectrum of **1** recorded in $CDCl_3$.

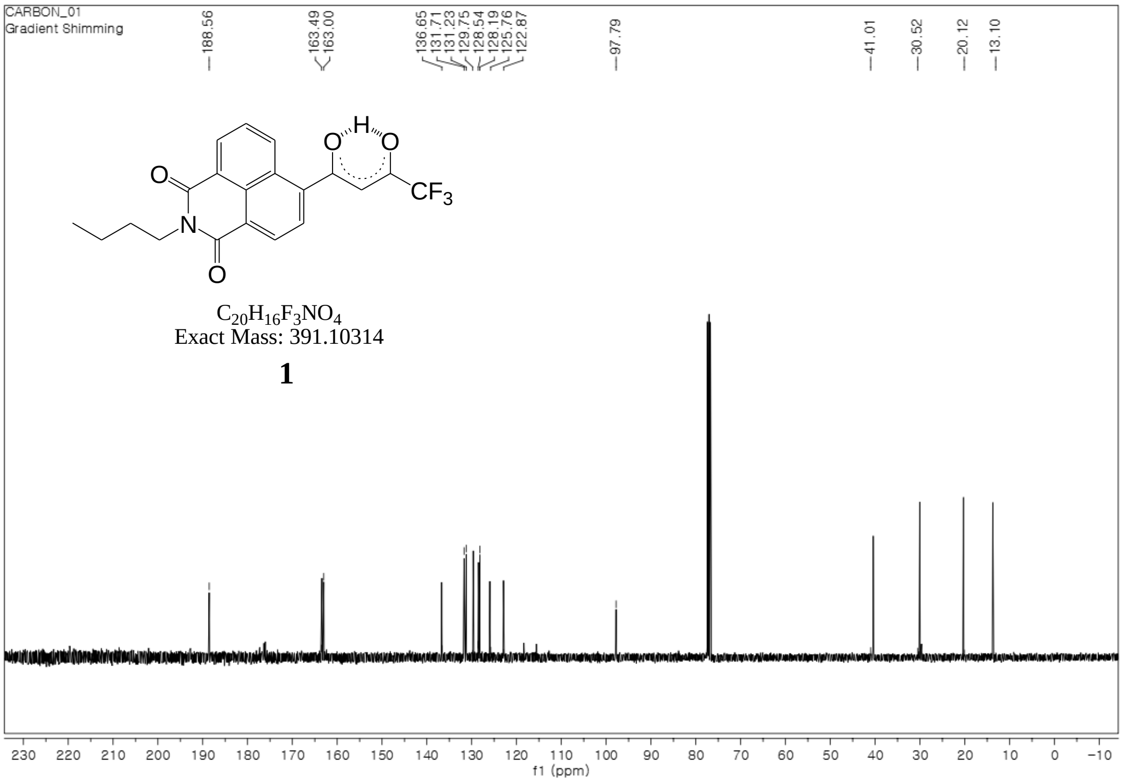
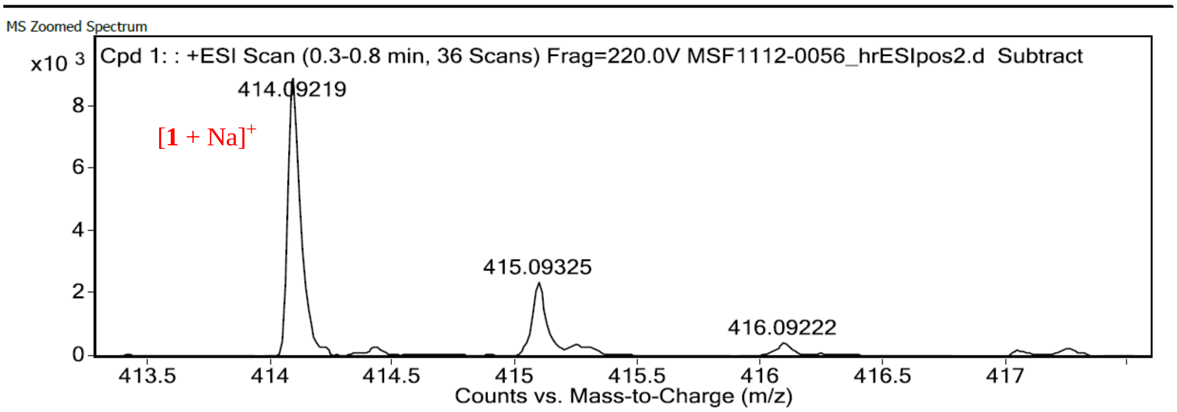


Fig. S22 ^{13}C NMR spectrum of **1** recorded in $CDCl_3$.



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abund	Formula	Ion/Isotope	Tgt Mass Error (ppm)
414.09219	414.09236	1	9086.8	C20H16F3NNaO4	(M+Na)+	-0.43
415.09325	415.09565	1	2380.6	C20H16F3NNaO4	(M+Na)+	-5.77
416.09222	416.09833	1	438.9	C20H16F3NNaO4	(M+Na)+	-14.68
685.43698			75544.5			

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Fig. S23 HRESI-MS spectrum of **1**.

8. X-ray crystallography for 3

Crystals were grown as yellow prisms by slow evaporation from chloroform-*d*$_3$ (CCDC number: 942177). The data were collected at -120 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71075 Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 2194 frames of data were collected using ω-scans with a scan range of 0.9° and a counting time of 62 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using SAINT V8.27B.[2] The structure was solved by direct methods using SIR97[3] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[4] Structure analysis was aided by use of the programs PLATON98[5] and WinGX.[6] The hydrogen atoms on carbon were observed in a ΔF map and refined with isotropic displacement parameters. The hydrogen atoms bound to O1W were observed in a ΔF map and refined with an isotropic displacement parameter. The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0117*P)^2]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.0670, with R(F) equal to 0.0421 and a goodness of fit, S, = 0.967. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[7] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kFc/[1 + (1.02(9) \times 10^{-6})* Fc^2\lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[8] All Fig.s were generated using SHELXTL/PC.[9] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and Fig.s may be obtained from the Cambridge Crystallographic Data Centre by referencing the CCDC number given above.

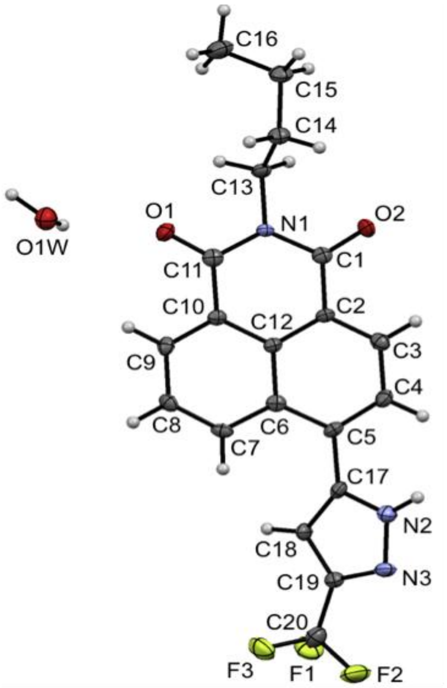

Fig. S24 View of **3** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level (CCDC number: 942177).

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	C20 H18 F3 N3 O3	
Formula weight	405.37	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 27.371(2) Å	= 90°.
	b = 7.0453(6) Å	= 99.010(7)°.
	c = 18.8951(14) Å	= 90°.
Volume	3598.8(5) Å^{3}	
Z	8	
Density (calculated)	1.496 Mg/m^{3}	
Absorption coefficient	0.123 mm^{-1}	
F(000)	1680	
Theta range for data collection	2.18 to 24.97°.	
Index ranges	-32<=h<=32, -8<=k<=8, -22<=l<=22	
Reflections collected	32499	
Independent reflections	3159 [R(int) = 0.1522]	
Completeness to theta = 24.97°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.865	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	3159 / 0 / 276	
Goodness-of-fit on F^{2}	0.967	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.0595	
R indices (all data)	R1 = 0.1192, wR2 = 0.0670	
Extinction coefficient	1.02(9)x10^{-6}	
Largest diff. peak and hole	0.227 and -0.244 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3092(1)	5279(4)	4258(2)	18(1)
C(2)	2730(1)	5141(4)	4758(1)	14(1)
C(3)	2882(1)	5523(4)	5468(1)	17(1)
C(4)	2546(1)	5398(4)	5955(1)	18(1)
C(5)	2064(1)	4923(4)	5726(1)	17(1)
C(6)	1886(1)	4540(4)	4996(1)	15(1)
C(7)	1388(1)	4028(4)	4718(2)	16(1)
C(8)	1262(1)	3569(4)	4005(2)	20(1)
C(9)	1606(1)	3696(4)	3530(2)	19(1)
C(10)	2084(1)	4237(4)	3775(1)	14(1)
C(11)	2437(1)	4404(4)	3257(2)	18(1)
C(12)	2235(1)	4638(4)	4506(1)	14(1)
C(13)	3272(1)	5149(4)	3019(1)	19(1)
C(14)	3507(1)	3282(4)	2861(1)	22(1)
C(15)	3832(1)	3478(4)	2272(1)	26(1)
C(16)	4292(1)	4670(4)	2490(2)	37(1)
C(17)	1003(1)	4052(4)	5187(1)	18(1)
C(18)	893(1)	5320(4)	5688(1)	18(1)
C(19)	471(1)	4604(4)	5915(1)	18(1)
C(20)	204(1)	5376(5)	6469(2)	26(1)
N(1)	2922(1)	4943(3)	3534(1)	14(1)
N(2)	650(1)	2671(4)	5136(1)	22(1)
N(3)	317(1)	2979(3)	5586(1)	23(1)
O(1)	3526(1)	5698(3)	4453(1)	23(1)
O(2)	2320(1)	4088(3)	2616(1)	23(1)
O(1W)	4406(1)	5758(4)	5561(1)	30(1)
F(1)	42(1)	7159(3)	6325(1)	37(1)
F(2)	-191(1)	4340(3)	6558(1)	47(1)
F(3)	495(1)	5474(3)	7112(1)	39(1)

Table S3. Bond lengths [Å] and angles [°] for **3**.

C(1)-O(1)	1.226(3)	C(13)-H(13A)	0.99
C(1)-N(1)	1.394(3)	C(13)-H(13B)	0.99
C(1)-C(2)	1.474(3)	C(14)-C(15)	1.537(3)
C(2)-C(3)	1.369(3)	C(14)-H(14A)	0.99
C(2)-C(12)	1.410(3)	C(14)-H(14B)	0.99
C(3)-C(4)	1.402(3)	C(15)-C(16)	1.516(3)
C(3)-H(3)	0.95	C(15)-H(15A)	0.99
C(4)-C(5)	1.365(3)	C(15)-H(15B)	0.99
C(4)-H(4)	0.95	C(16)-H(16A)	0.98
C(5)-C(6)	1.414(3)	C(16)-H(16B)	0.98
C(5)-H(5)	0.95	C(16)-H(16C)	0.98
C(6)-C(7)	1.428(3)	C(17)-N(2)	1.363(3)
C(6)-C(12)	1.432(3)	C(17)-C(18)	1.369(3)
C(7)-C(8)	1.375(3)	C(18)-C(19)	1.388(3)
C(7)-C(17)	1.480(3)	C(18)-H(18)	0.95
C(8)-C(9)	1.403(3)	C(19)-N(3)	1.339(3)
C(8)-H(8)	0.95	C(19)-C(20)	1.472(3)
C(9)-C(10)	1.371(3)	C(20)-F(2)	1.337(3)
C(9)-H(9)	0.95	C(20)-F(1)	1.346(3)
C(10)-C(12)	1.407(3)	C(20)-F(3)	1.347(3)
C(10)-C(11)	1.484(3)	N(2)-N(3)	1.358(3)
C(11)-O(2)	1.224(3)	N(2)-H(2N)	0.93(3)
C(11)-N(1)	1.401(3)	O(1W)-H(1WA)	0.98(4)
C(13)-N(1)	1.475(3)	O(1W)-H(1WB)	0.76(4)
C(13)-C(14)	1.515(3)		

O(1)-C(1)-N(1)	119.7(2)	C(5)-C(4)-H(4)	119.7
O(1)-C(1)-C(2)	122.7(3)	C(3)-C(4)-H(4)	119.7
N(1)-C(1)-C(2)	117.6(3)	C(4)-C(5)-C(6)	121.6(2)
C(3)-C(2)-C(12)	120.6(2)	C(4)-C(5)-H(5)	119.2
C(3)-C(2)-C(1)	119.0(3)	C(6)-C(5)-H(5)	119.2
C(12)-C(2)-C(1)	120.5(3)	C(5)-C(6)-C(7)	124.7(2)
C(2)-C(3)-C(4)	120.1(3)	C(5)-C(6)-C(12)	117.3(2)
C(2)-C(3)-H(3)	119.9	C(7)-C(6)-C(12)	117.9(2)
C(4)-C(3)-H(3)	119.9	C(8)-C(7)-C(6)	119.9(2)
C(5)-C(4)-C(3)	120.5(3)	C(8)-C(7)-C(17)	119.8(2)

C(6)-C(7)-C(17)	120.3(2)
C(7)-C(8)-C(9)	121.5(3)
C(7)-C(8)-H(8)	119.3
C(9)-C(8)-H(8)	119.3
C(10)-C(9)-C(8)	120.1(3)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(12)	120.4(2)
C(9)-C(10)-C(11)	118.9(3)
C(12)-C(10)-C(11)	120.7(2)
O(2)-C(11)-N(1)	120.4(2)
O(2)-C(11)-C(10)	122.8(3)
N(1)-C(11)-C(10)	116.8(2)
C(10)-C(12)-C(2)	120.0(2)
C(10)-C(12)-C(6)	120.2(2)
C(2)-C(12)-C(6)	119.8(3)
N(1)-C(13)-C(14)	112.6(2)
N(1)-C(13)-H(13A)	109.1
C(14)-C(13)-H(13A)	109.1
N(1)-C(13)-H(13B)	109.1
C(14)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.8
C(13)-C(14)-C(15)	112.2(2)
C(13)-C(14)-H(14A)	109.2
C(15)-C(14)-H(14A)	109.2
C(13)-C(14)-H(14B)	109.2
C(15)-C(14)-H(14B)	109.2
H(14A)-C(14)-H(14B)	107.9
C(16)-C(15)-C(14)	113.8(2)
C(16)-C(15)-H(15A)	108.8
C(14)-C(15)-H(15A)	108.8
C(16)-C(15)-H(15B)	108.8
C(14)-C(15)-H(15B)	108.8
H(15A)-C(15)-H(15B)	107.7
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(2)-C(17)-C(18)	106.6(2)
N(2)-C(17)-C(7)	120.8(3)
C(18)-C(17)-C(7)	132.5(3)
C(17)-C(18)-C(19)	105.1(2)
C(17)-C(18)-H(18)	127.5
C(19)-C(18)-H(18)	127.5
N(3)-C(19)-C(18)	112.6(2)
N(3)-C(19)-C(20)	119.4(2)
C(18)-C(19)-C(20)	128.0(3)
F(2)-C(20)-F(1)	106.7(2)
F(2)-C(20)-F(3)	106.8(2)
F(1)-C(20)-F(3)	105.3(3)
F(2)-C(20)-C(19)	113.0(3)
F(1)-C(20)-C(19)	112.7(2)
F(3)-C(20)-C(19)	111.8(2)
C(1)-N(1)-C(11)	124.3(2)
C(1)-N(1)-C(13)	118.6(2)
C(11)-N(1)-C(13)	117.1(2)
N(3)-N(2)-C(17)	112.2(2)
N(3)-N(2)-H(2N)	118.8(16)
C(17)-N(2)-H(2N)	128.7(16)
C(19)-N(3)-N(2)	103.5(2)
H(1WA)-O(1W)-H(1WB)	108(4)

Table S4. Anisotropic displacement parameters (Å ^{2} x 10^3) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(2)	13(2)	21(2)	2(2)	4(2)	2(2)
C(2)	17(2)	10(2)	16(2)	3(1)	5(2)	0(1)
C(3)	15(2)	16(2)	19(2)	0(2)	-1(2)	1(1)
C(4)	21(2)	20(2)	13(2)	0(2)	1(2)	2(2)
C(5)	20(2)	18(2)	14(2)	4(2)	7(1)	5(2)
C(6)	19(2)	10(2)	17(2)	4(2)	4(2)	2(2)
C(7)	11(2)	17(2)	21(2)	2(2)	5(2)	0(1)
C(8)	13(2)	21(2)	24(2)	-1(2)	1(2)	-1(1)
C(9)	21(2)	19(2)	18(2)	-1(2)	3(2)	3(2)
C(10)	13(2)	14(2)	17(2)	2(2)	6(2)	0(2)
C(11)	18(2)	14(2)	21(2)	0(2)	4(2)	2(2)
C(12)	14(2)	11(2)	17(2)	1(2)	5(2)	0(1)
C(13)	16(2)	23(2)	18(2)	2(2)	7(1)	-2(2)
C(14)	21(2)	23(2)	24(2)	0(2)	7(2)	2(2)
C(15)	23(2)	29(2)	27(2)	-3(2)	9(2)	5(2)
C(16)	25(2)	50(3)	39(2)	2(2)	14(2)	-4(2)
C(17)	12(2)	20(2)	20(2)	1(2)	2(2)	-3(2)
C(18)	18(2)	14(2)	21(2)	-5(2)	5(1)	-5(2)
C(19)	16(2)	19(2)	19(2)	-1(2)	4(2)	1(2)
C(20)	23(2)	27(2)	30(2)	0(2)	6(2)	-5(2)
N(1)	13(1)	18(2)	13(1)	0(1)	5(1)	-1(1)
N(2)	21(2)	23(2)	24(2)	-6(2)	8(1)	-3(1)
N(3)	18(1)	34(2)	18(2)	1(1)	9(1)	0(1)
O(1)	14(1)	31(1)	22(1)	0(1)	1(1)	-2(1)
O(2)	21(1)	34(1)	13(1)	-2(1)	0(1)	-4(1)
O(1W)	29(2)	28(2)	32(2)	-3(1)	5(1)	-4(1)
F(1)	38(1)	35(1)	37(1)	-4(1)	6(1)	13(1)
F(2)	41(1)	51(1)	58(1)	-19(1)	33(1)	-18(1)
F(3)	40(1)	56(1)	19(1)	-2(1)	2(1)	8(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2} x 10^3) for **3**.

	x	y	z	U(eq)
H(3)	3216	5874	5632	21
H(4)	2655	5645	6449	22
H(5)	1842	4848	6064	20
H(8)	935	3157	3831	24
H(9)	1508	3406	3037	23
H(13A)	3535	6056	3215	22
H(13B)	3095	5686	2566	22
H(14A)	3244	2337	2709	27
H(14B)	3711	2806	3304	27
H(15A)	3933	2196	2137	31
H(15B)	3633	4055	1843	31
H(16A)	4196	5956	2610	56
H(16B)	4483	4728	2092	56
H(16C)	4495	4098	2909	56
H(18)	1068	6446	5846	21
H(1WA)	4721(15)	6430(60)	5590(20)	125(18)
H(2N)	632(10)	1540(40)	4873(15)	48(11)
H(1WB)	4208(15)	6360(60)	5340(20)	110(20)

Table S6. Torsion angles [°] for **3**

O(1)-C(1)-C(2)-C(3)	1.0(4)	C(5)-C(6)-C(12)-C(2)	-1.3(4)
N(1)-C(1)-C(2)-C(3)	-177.9(2)	C(7)-C(6)-C(12)-C(2)	179.9(2)
O(1)-C(1)-C(2)-C(12)	-179.5(3)	N(1)-C(13)-C(14)-C(15)	174.6(2)
N(1)-C(1)-C(2)-C(12)	1.6(4)	C(13)-C(14)-C(15)-C(16)	67.3(3)
C(12)-C(2)-C(3)-C(4)	0.7(4)	C(8)-C(7)-C(17)-N(2)	41.6(4)
C(1)-C(2)-C(3)-C(4)	-179.8(2)	C(6)-C(7)-C(17)-N(2)	-140.5(3)
C(2)-C(3)-C(4)-C(5)	-1.0(4)	C(8)-C(7)-C(17)-C(18)	-134.2(3)
C(3)-C(4)-C(5)-C(6)	0.1(4)	C(6)-C(7)-C(17)-C(18)	43.6(5)
C(4)-C(5)-C(6)-C(7)	179.7(3)	N(2)-C(17)-C(18)-C(19)	0.2(3)
C(4)-C(5)-C(6)-C(12)	1.0(4)	C(7)-C(17)-C(18)-C(19)	176.4(3)
C(5)-C(6)-C(7)-C(8)	-175.9(3)	C(17)-C(18)-C(19)-N(3)	0.1(3)
C(12)-C(6)-C(7)-C(8)	2.8(4)	C(17)-C(18)-C(19)-C(20)	177.7(3)
C(5)-C(6)-C(7)-C(17)	6.2(4)	N(3)-C(19)-C(20)-F(2)	-2.6(4)
C(12)-C(6)-C(7)-C(17)	-175.1(2)	C(18)-C(19)-C(20)-F(2)	180.0(3)
C(6)-C(7)-C(8)-C(9)	-3.7(4)	N(3)-C(19)-C(20)-F(1)	-123.6(3)
C(17)-C(7)-C(8)-C(9)	174.2(2)	C(18)-C(19)-C(20)-F(1)	58.9(4)
C(7)-C(8)-C(9)-C(10)	1.8(4)	N(3)-C(19)-C(20)-F(3)	118.0(3)
C(8)-C(9)-C(10)-C(12)	1.1(4)	C(18)-C(19)-C(20)-F(3)	-59.5(4)
C(8)-C(9)-C(10)-C(11)	-178.5(2)	O(1)-C(1)-N(1)-C(11)	178.1(2)
C(9)-C(10)-C(11)-O(2)	0.4(4)	C(2)-C(1)-N(1)-C(11)	-2.9(4)
C(12)-C(10)-C(11)-O(2)	-179.2(3)	O(1)-C(1)-N(1)-C(13)	-1.4(4)
C(9)-C(10)-C(11)-N(1)	-179.4(2)	C(2)-C(1)-N(1)-C(13)	177.5(2)
C(12)-C(10)-C(11)-N(1)	1.0(4)	O(2)-C(11)-N(1)-C(1)	-178.1(3)
C(9)-C(10)-C(12)-C(2)	178.1(2)	C(10)-C(11)-N(1)-C(1)	1.7(4)
C(11)-C(10)-C(12)-C(2)	-2.2(4)	O(2)-C(11)-N(1)-C(13)	1.4(4)
C(9)-C(10)-C(12)-C(6)	-1.9(4)	C(10)-C(11)-N(1)-C(13)	-178.8(2)
C(11)-C(10)-C(12)-C(6)	177.7(3)	C(14)-C(13)-N(1)-C(1)	95.0(3)
C(3)-C(2)-C(12)-C(10)	-179.6(3)	C(14)-C(13)-N(1)-C(11)	-84.6(3)
C(1)-C(2)-C(12)-C(10)	0.9(4)	C(18)-C(17)-N(2)-N(3)	-0.4(3)
C(3)-C(2)-C(12)-C(6)	0.5(4)	C(7)-C(17)-N(2)-N(3)	-177.2(2)
C(1)-C(2)-C(12)-C(6)	-179.0(2)	C(18)-C(19)-N(3)-N(2)	-0.4(3)
C(5)-C(6)-C(12)-C(10)	178.8(3)	C(20)-C(19)-N(3)-N(2)	-178.2(2)
C(7)-C(6)-C(12)-C(10)	0.0(4)	C(17)-N(2)-N(3)-C(19)	0.5(3)

Table S7. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WB)...O(1)	0.76(4)	2.35(4)	2.932(3)	134(4)
O(1W)-H(1WA)...N(3)#1	0.98(4)	1.96(4)	2.939(3)	174(3)
N(2)-H(2N)...O(1W)#2	0.93(3)	1.81(3)	2.744(3)	175(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,y+1/2,z #2 -x+1/2,-y+1/2,-z+1

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7) $Rw(F^2) = \{\Sigma w(|Fo|^2 - |Fc|^2)^2/\Sigma w(|Fo|)^4\}^{1/2}$ where w is the weight given each reflection. $R(F) = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|\}$ for reflections with $Fo > 4(\sigma(Fo))$. $S = [\Sigma w(|Fo|^2 - |Fc|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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