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A reaction of hexafluoro-1,4-naphthoquinone with 2-aminopyridines

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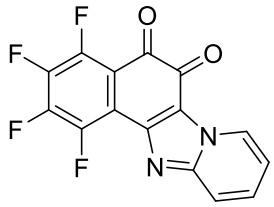
Syntheses of Compounds

General Information. All chemical reagents used were purchased from commercial sources. Solvents were reagent grade and used without further purification unless stated otherwise. ^{1}H, ^{13}C,^{19}F NMR spectra were recorded with Bruker AM 300 (300 MHz) spectrometers in DMSO-d_6. A solvent was employed to achieve a homonuclear lock, and the signals are presented relative to deuterated solvent peaks [DMSO-d_6: 2.50 ppm (^{1}H NMR) and 39.52 ppm (^{13}C NMR)]. C_6F_6 (δ_F = 163.0) served as an external reference for recording the ^{19}F NMR spectra. HRMS was carried out on a Bruker micrOTOF instrument equipped with an electrospray ionization (ESI) source. Melting points were determined on a Kofler hotstage.

Starting compound **1** was prepared in accordance with a procedure described in the literature (G. G. Yakobson, V. D. Shteingarts and N. N. Vorozhtsov, *Zh. Vsesoyuzn. Khim. Ob-va im. D.I. Mendeleeva*, 1964, **9**, 702 (in Russian), [*Chemical Abstracts*, 1965, **62**, 9078b]).

General procedure. A mixture of compound **1** (0.5 mmol, 0.13 g) and the corresponding 2-aminopyridine (0.5 mmol) was refluxed in EtOH (3 mL) for 1 h. Then, the reaction mixture was cooled to ambient, the precipitated product was filtered off and washed with EtOH (3 × 3 mL). The obtained crude product was refluxed in MeCN (2 ml) for 15 min, the precipitate was filtered off from the hot solution and washed with hot MeCN (3 × 3 mL).

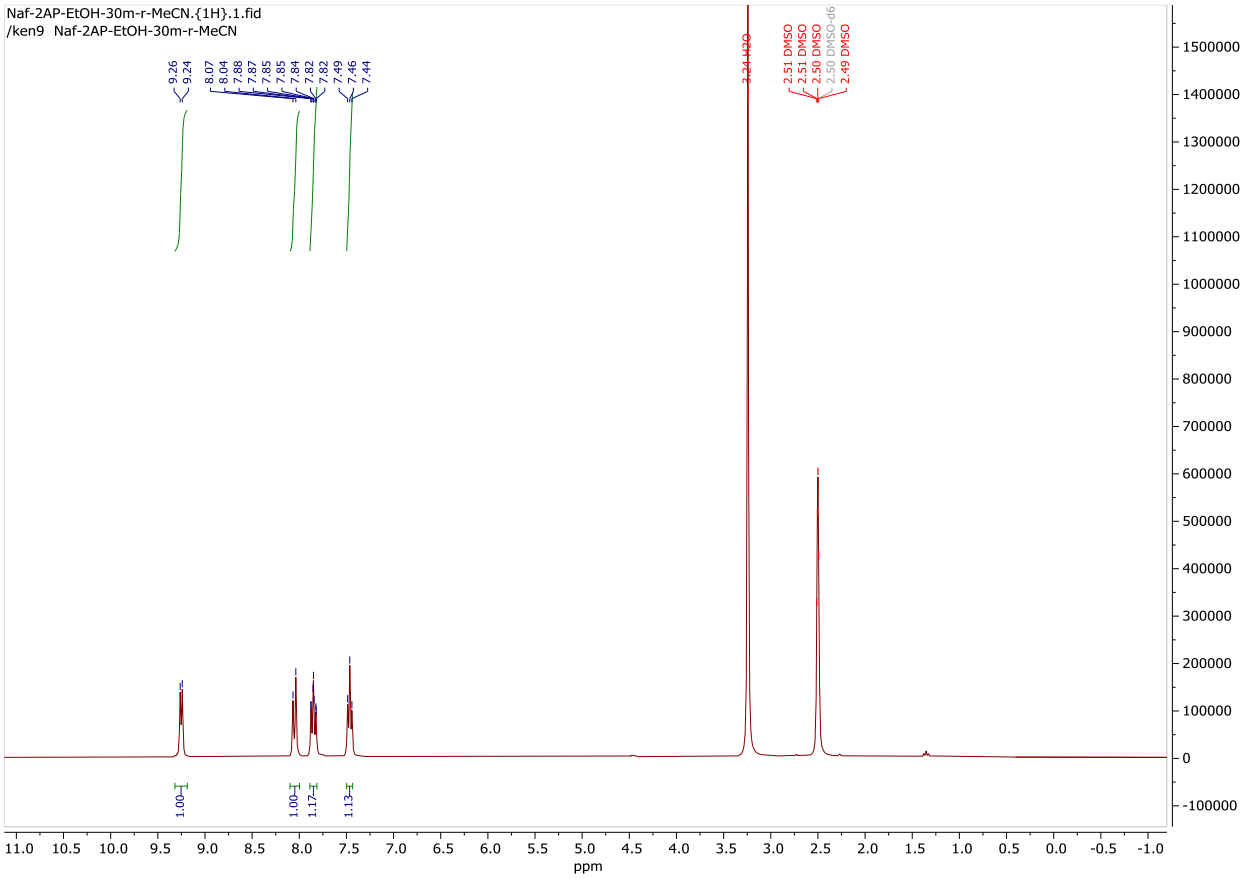
Characterization of Compounds

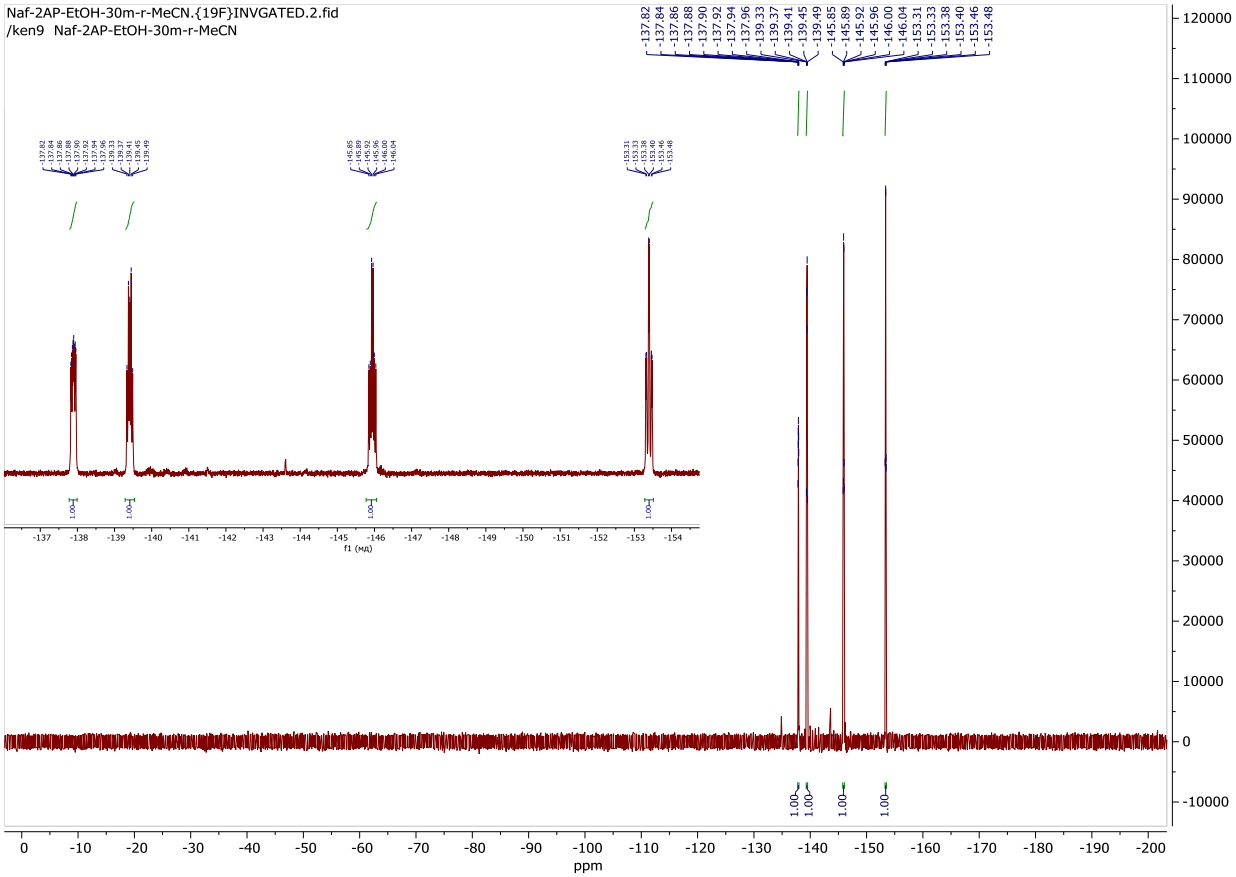


1,2,3,4-Tetrafluoronaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridine-5,6-dione **2a**

Orange powder. Yield 58%, m.p. 292–294 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.25 (d, J = 6.7 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.50 – 7.43 (m, 1H). ^{19}F NMR (282 MHz, DMSO-d_6) δ –137.89 (ddd, J = 21.1, 11.5, 5.0 Hz, 1F), -139.41 (dt, J = 21.8, 11.3 Hz, 1F), –145.94 (td, J = 21.0, 10.9 Hz, 1F), –153.39 (td, J = 20.8, 5.1 Hz, 1F). ^{13}C NMR (126 MHz, DMSO-d_6) δ 177.02, 165.88, 149.10, 132.87, 128.28, 120.33, 118.40, 118.06. HRMS: m/z [M+H]$^{+}$ calcd for $C_{15}H_5F_4N_2O_2$: 321.0282; found 321.0282.

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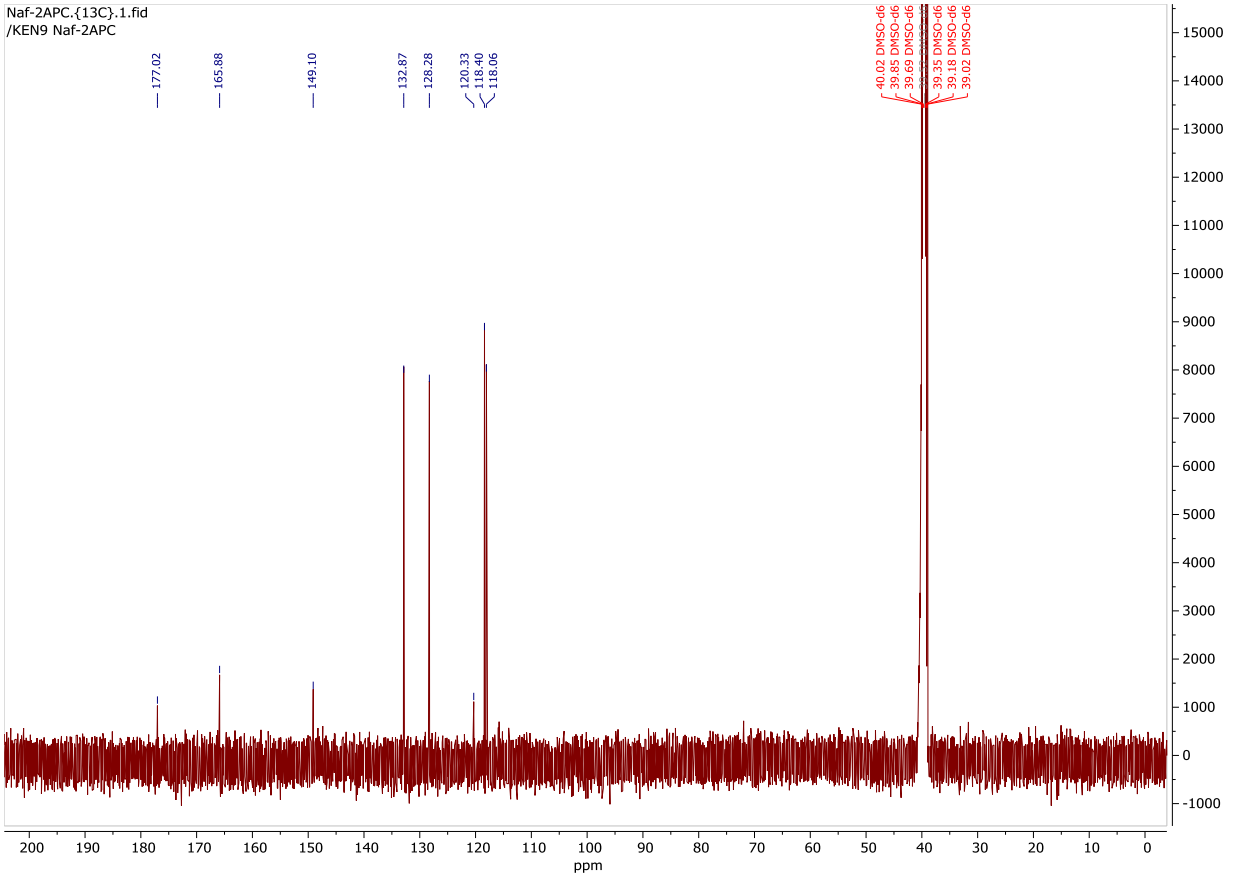
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118.06
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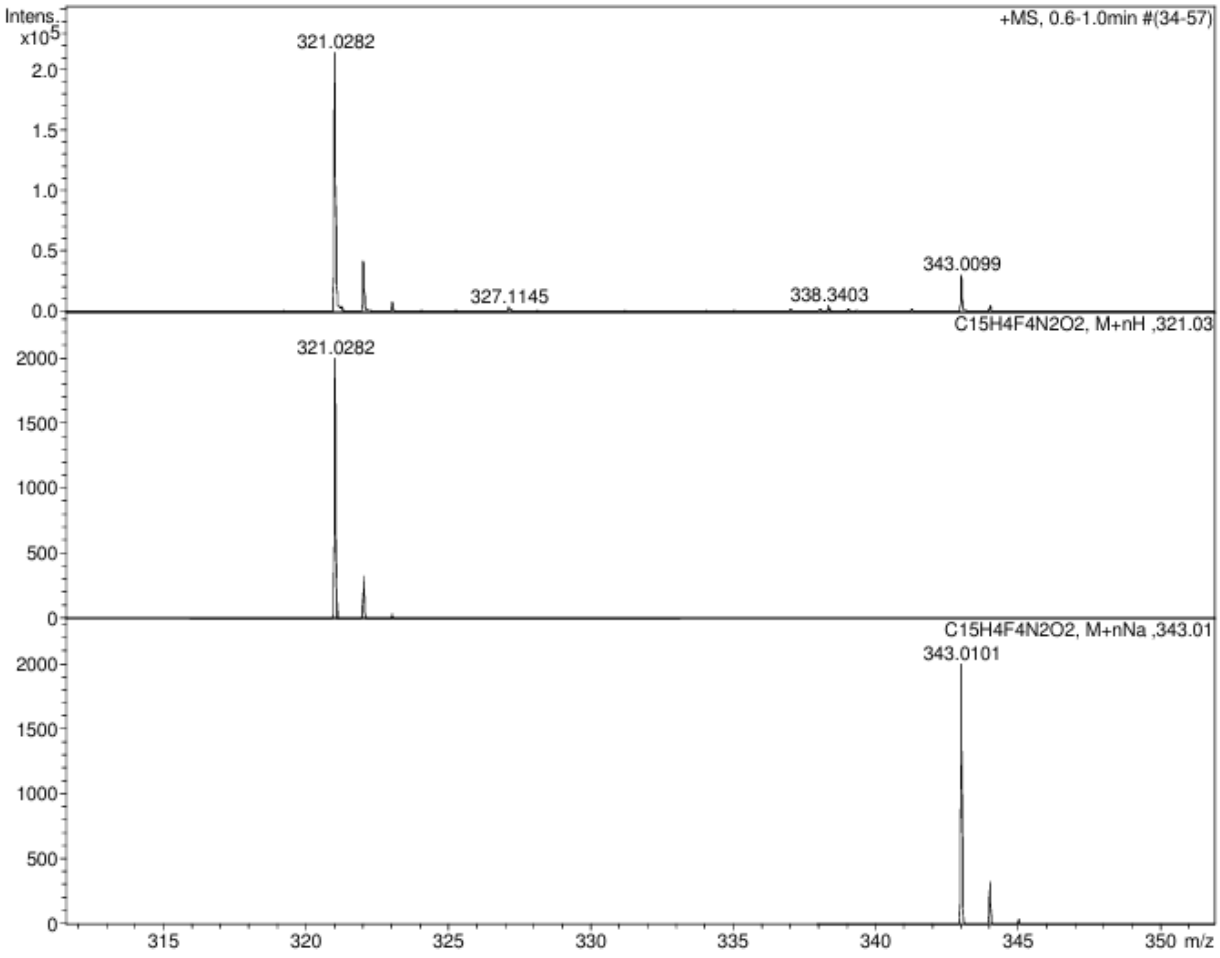
39.02 DMSO-d6
ppm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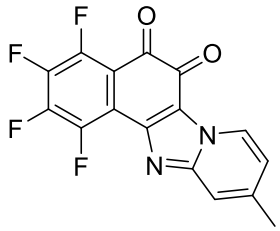
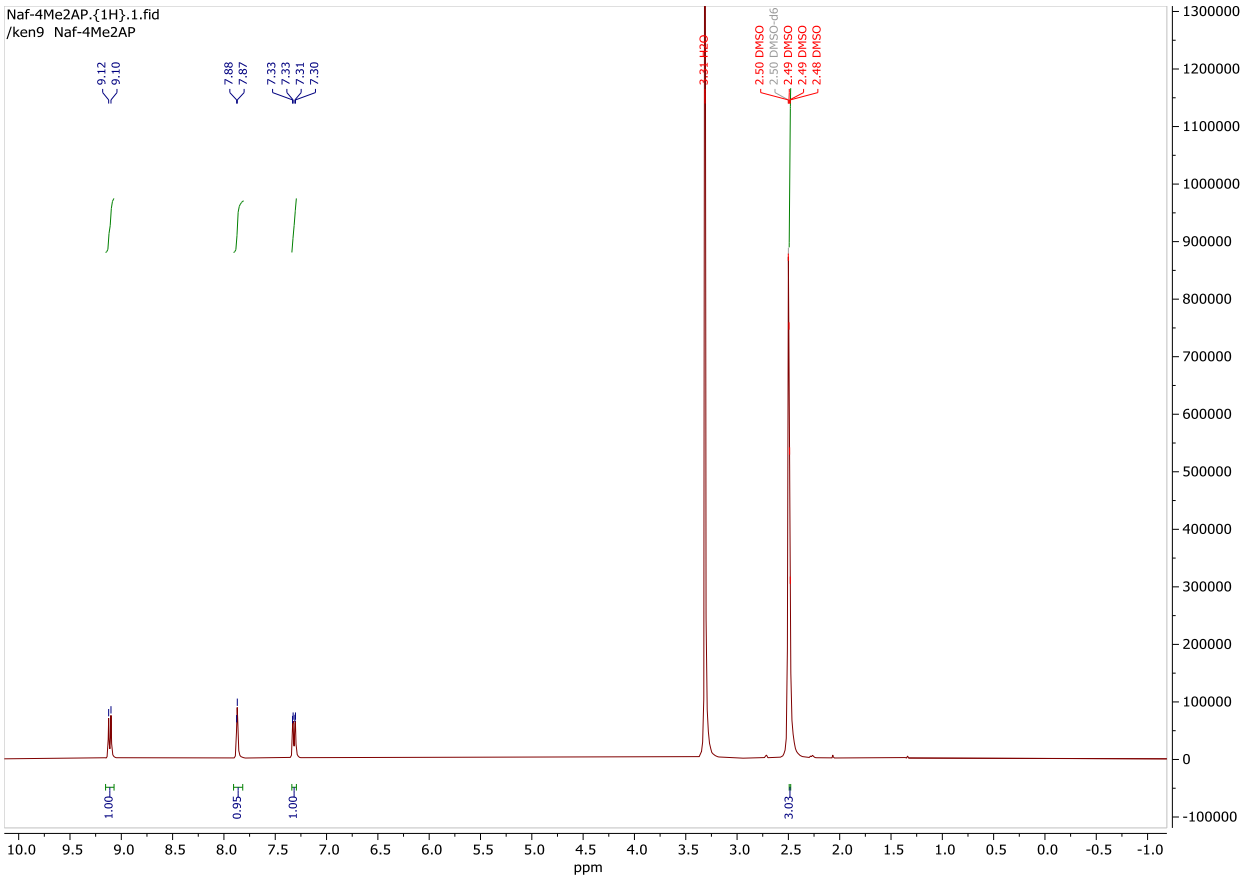
m/z

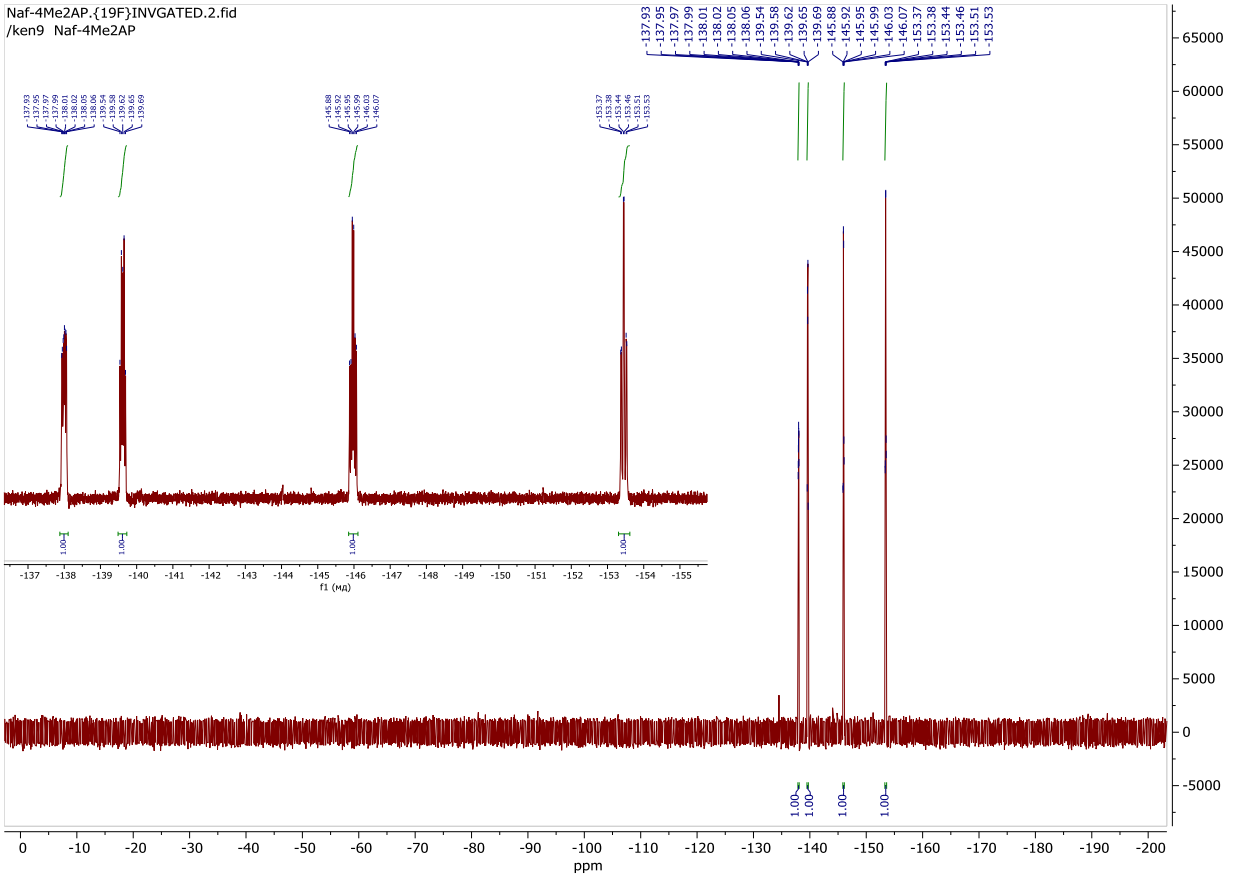


1,2,3,4-Tetrafluoro-10-methylnaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridine-5,6-dione **2b**

Orange powder. Yield 62%, m.p. 283–285 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.11 (d, J = 6.8 Hz, 1H), 7.87 (d, J = 1.9 Hz, 1H), 7.32 (dd, J = 6.8, 1.7 Hz, 1H), 2.48 (s, overlapped with DMSO, 3H). ^{19}F NMR (282 MHz, DMSO-d_6) δ –138.00 (ddd, J = 21.5, 11.5, 5.0 Hz, 1F), –139.62 (dt, J = 21.8, 11.2 Hz, 1F), –145.97 (td, J = 21.2, 10.9 Hz, 1F), –153.45 (td, J = 21.0, 5.1 Hz, 1F). ^{13}C NMR (76 MHz, DMSO-d_6) δ 165.47, 149.59, 144.64, 127.36, 120.12, 117.07, 114.71, 21.24. HRMS: m/z [M+H]$^{+}$ calcd for $C_{16}H_7F_4N_2O_2$: 335.0438; found 335.0443.

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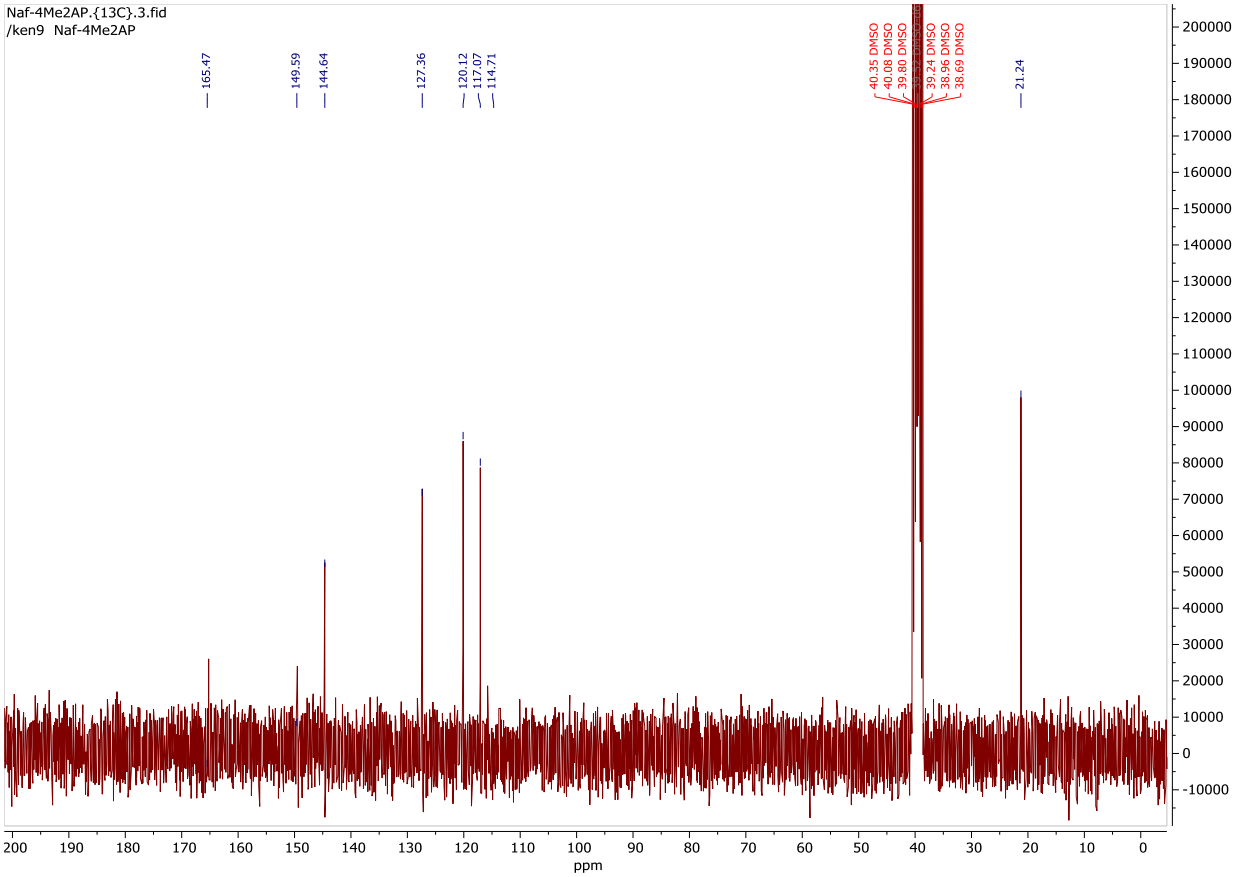
ppm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144.64
127.36
120.12
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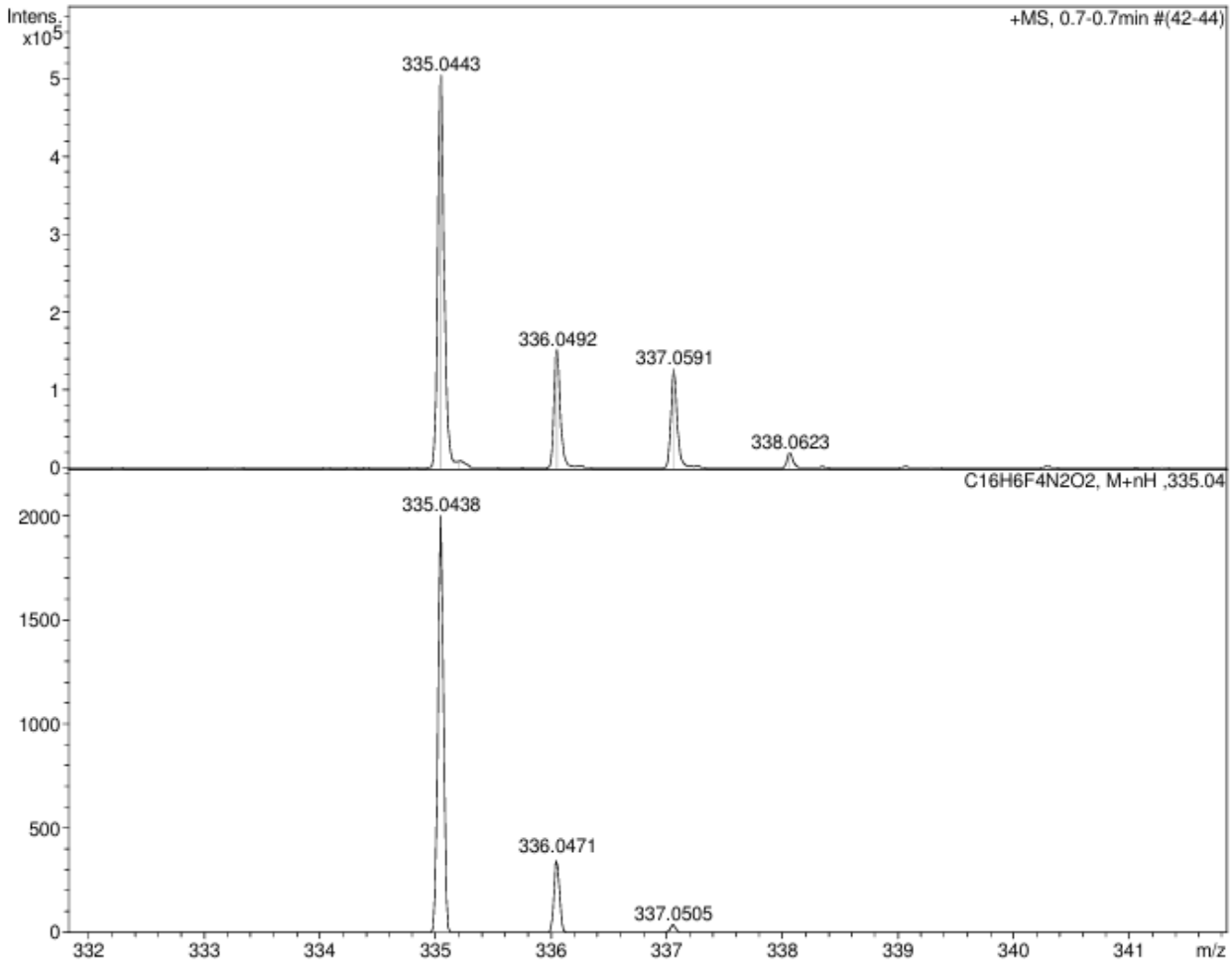
39.80 DMSO
39.24 DMSO
38.96 DMSO
38.69 DMSO
21.24
ppm


Intens.
x10^5
+MS, 0.7-0.7min #(42-44)
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336.0492
337.0591
338.0623
C16H6F4N2O2, M+nH ,335.04
335.0438
336.0471
337.0505
m/z

Table S1. Crystal data and structure refinement for **2b**.

Empirical formula	C16 H6 F4 N2 O2	
Formula weight	334.23	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.4653(2) Å	α= 90°
	b = 5.20120(10) Å	β= 94.9100(10)°
	c = 23.1232(3) Å	γ = 90°
Volume	1254.03(4) $Å^3$	
Z	4	
Density (calculated)	1.770 Mg/m^3	
Absorption coefficient	1.400 mm^{-1}	
F(000)	672	
Crystal size	0.36 × 0.09 × 0.06 mm^3	
Theta range for data collection	3.837 to 79.752°.	
Index ranges	$-13 \le h \le 13$, $-6 \le k \le 5$, $-29 \le l \le 29$	
Reflections collected	14169	
Independent reflections	2720 [R(int) = 0.0447]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.603	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2720 / 0 / 219	
Goodness-of-fit on F^2	1.072	
Final R indices [I > 2sigma(I)]	R_1 = 0.0481, wR_2 = 0.1392	
R indices (all data)	R_1 = 0.0512, wR_2 = 0.1417	
Extinction coefficient	0.0021(5)	
Largest diff. peak and hole	0.351 and –0.282 e·$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **2b**.

F(1)-C(6)	1.345(2)	C(4)-N(1)-C(3)	104.45(14)
F(2)-C(7)	1.339(2)	C(3)-N(2)-C(13)	106.31(14)
F(3)-C(8)	1.335(2)	C(14)-N(2)-C(3)	123.03(15)
F(4)-C(9)	1.341(2)	C(14)-N(2)-C(13)	130.65(15)
O(1)-C(11)	1.212(2)	C(2)-C(1)-C(15)	119.00(16)
O(2)-C(12)	1.229(2)	C(2)-C(1)-C(16)	122.36(16)
N(1)-C(3)	1.355(2)	C(15)-C(1)-C(16)	118.64(16)
N(1)-C(4)	1.346(2)	C(1)-C(2)-H(2)	120.1
N(2)-C(3)	1.387(2)	C(1)-C(2)-C(3)	119.75(16)
N(2)-C(13)	1.391(2)	C(3)-C(2)-H(2)	120.1
N(2)-C(14)	1.364(2)	N(1)-C(3)-N(2)	111.83(15)
C(1)-C(2)	1.382(3)	N(1)-C(3)-C(2)	129.83(16)
C(1)-C(15)	1.419(3)	N(2)-C(3)-C(2)	118.34(16)
C(1)-C(16)	1.501(2)	N(1)-C(4)-C(5)	126.62(16)
C(2)-H(2)	0.9500	N(1)-C(4)-C(13)	112.70(16)
C(2)-C(3)	1.407(2)	C(13)-C(4)-C(5)	120.68(16)
C(4)-C(5)	1.462(3)	C(6)-C(5)-C(4)	122.79(17)
C(4)-C(13)	1.396(2)	C(6)-C(5)-C(10)	118.55(17)
C(5)-C(6)	1.382(2)	C(10)-C(5)-C(4)	118.65(16)
C(5)-C(10)	1.425(2)	F(1)-C(6)-C(5)	121.58(16)
C(6)-C(7)	1.385(3)	F(1)-C(6)-C(7)	116.60(16)
C(7)-C(8)	1.377(3)	C(5)-C(6)-C(7)	121.82(17)
C(8)-C(9)	1.386(3)	F(2)-C(7)-C(6)	119.71(17)
C(9)-C(10)	1.389(3)	F(2)-C(7)-C(8)	120.29(16)
C(10)-C(11)	1.495(2)	C(8)-C(7)-C(6)	119.99(17)
C(11)-C(12)	1.551(2)	F(3)-C(8)-C(7)	120.23(17)
C(12)-C(13)	1.414(2)	F(3)-C(8)-C(9)	120.52(17)
C(14)-H(14)	0.9500	C(7)-C(8)-C(9)	119.25(16)
C(14)-C(15)	1.362(3)	F(4)-C(9)-C(8)	116.07(16)
C(15)-H(15)	0.9500	F(4)-C(9)-C(10)	121.97(16)
C(16)-H(16A)	0.9800	C(8)-C(9)-C(10)	121.93(17)
C(16)-H(16B)	0.9800	C(5)-C(10)-C(11)	120.71(16)
C(16)-H(16C)	0.9800	C(9)-C(10)-C(5)	118.44(17)
		C(9)-C(10)-C(11)	120.85(16)
		O(1)-C(11)-C(10)	122.70(17)
		O(1)-C(11)-C(12)	117.92(16)
		C(10)-C(11)-C(12)	119.38(15)
		O(2)-C(12)-C(11)	119.12(16)
		O(2)-C(12)-C(13)	126.97(17)
		C(13)-C(12)-C(11)	113.90(15)
		N(2)-C(13)-C(4)	104.70(15)
		N(2)-C(13)-C(12)	128.70(16)
		C(4)-C(13)-C(12)	126.59(16)
		N(2)-C(14)-H(14)	120.8

	C(15)-C(14)-N(2)	118.45(16)
	C(15)-C(14)-H(14)	120.8
	C(1)-C(15)-H(15)	119.3
	C(14)-C(15)-C(1)	121.41(17)
	C(14)-C(15)-H(15)	119.3
	C(1)-C(16)-H(16A)	109.5
	C(1)-C(16)-H(16B)	109.5
	C(1)-C(16)-H(16C)	109.5
	H(16A)-C(16)-H(16B)	109.5
	H(16A)-C(16)-H(16C)	109.5
	H(16B)-C(16)-H(16C)	109.5