Reaction of 2-polyfluoroalkylchromones with 1,3,3-trimethyl-3,4-dihydroisoquinolines and methylketimines as a direct route to zwitter-ionic axially chiral 6,7-dihydrobenzo[*a*]quinolizinium derivatives and 2,6-diaryl-4-polyfluoroalkylpyridines

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Crystallographic data for 3d ($\text{C}_{22}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_3 \cdot \text{C}_4\text{H}_8\text{O} \cdot 0.5\text{H}_2\text{O}$). CCDC 213183. The crystal system is triclinic at 110 K: $a = 10.032(3)$, $b = 10.206(3)$, $c = 12.847(3)$ Å, $\alpha = 74.002(6)$, $\beta = 85.066(6)$, $\gamma = 65.669(5)^\circ$, $V = 1151.6(5)$ Å³, $d_{\text{calc}} = 1.377$ g cm⁻³, $\mu = 0.105$ mm⁻¹, space group P-1, $Z = 2$. The intensities of 4012 independent reflections ($R_{\text{int}} = 0.04$) were measured on a Bruker SMART 1K CCD diffractometer, ($\text{MoK}\alpha$) = 0.71073 Å, graphite monochromator, 1800 scans (scan step in 2θ 0.3°, exposition time of the frame 20 s), $2\theta_{\text{max}} = 50^\circ$, data completeness 99%. The intensities of all reflections were obtained by the use of the SAINT Plus and SADABS program packages (max./min. transmission coefficients ratio 0.492) (*SMART* and *SAINT*, Release 5.0, Area detector control and integration software; Bruker AXS, Analytical X-Ray Instruments: Madison, WI, 1998; Sheldrick, G. M. *SADABS*, Program for exploiting the redundancy of area-detector X-ray data; University of Göttingen: Göttingen, Germany, 1999). The structure was solved by the direct method using the *SHELXTL-97* program package (Sheldrick, G. M. *SHELXTL-97*, Program for Solution and Refinement of Crystal Structure; Bruker AXS Inc.: Madison, WI, 1997). Non-hydrogen atoms were refined by the full-matrix least-squares procedure on F^2 in an anisotropic approximation. The positions of hydrogen atoms were found by a difference Fourier synthesis and refined isotropically. The hydrogen atoms of THF molecule were refined using the riding model with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, where $U_{\text{eq}}(\text{C})$ were equivalent isotropic displacement parameters of corresponding C atoms. The final discrepancy factors were as follows: $R_1 = 0.085$ (based on F for 2190 reflections with $I > 2\sigma(I)$), $wR_2 = 0.288$ (calculated based on F^2 for all 4000 reflections, used at the final stage of the refinement); the total number of the parameters in the refinement was 392, GOOF = 0.945.

Table 1. Comparison of the geometric parameters (bond lengths in Å, angles in deg) of the phenoxide fragment in structure **3d**, *p*-nitrophenoxide anions of salts (CCDC, codes FEDQUA, FEDQUA01, FEDWEQ, FITZEN, KATBOW, KATBOW01, NUZKAU), and neutral *p*-benzoquinone molecule (CCDC, code BNZQUI03)

	3d	[<i>p</i> -nitrophenoxides] ^{−1}	<i>p</i> -benzoquinone
O(3)–C(22)	1.264(6)	1.289–1.312 1.302	1.222
C(17)–C(22)	1.438(7)	1.405–1.427	1.469
C(21)–C(22)	1.426(6)	1.416	1.479
C(17)–C(18)	1.374(6)	1.365–1.396	1.330
C(20)–C(21)	1.364(7)	1.373	
C(18)–C(19)	1.396(6)	1.375–1.400	
C(19)–C(20)	1.392(7)	1.387	
N(2)–C(19)	1.430(6)	1.417–1.452 1.431	
N(2)–O(1)	1.232(5)	1.220–1.247	
N(2)–O(2)	1.245(5)	1.236	
C(21)–C(22)–C(17)	115.6(4)	117.0–117.5 117.2	117.8
C(20)–C(19)–C(18)	121.0(4)	120.5–121.3 120.9	

Table 2. Crystal data and structure refinement for $C_{22}H_{18}F_2N_2O_3 \cdot C_4H_8O \cdot 0.5H_2O$.

Identification code	vs10	
Empirical formula	C ₂₆ H ₂₇ F ₂ N ₂ O _{4.50}	
Formula weight	477.50	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.032(3) Å	= 74.002(6)°.
	b = 10.206(3) Å	= 85.066(6)°.
	c = 12.847(3) Å	= 65.669(5)°.
Volume	1151.6(5) Å ³	
Z	2	
Density (calculated)	1.377 Mg/m ³	
Absorption coefficient	0.105 mm ⁻¹	
F(000)	502	
Crystal size	0.08 x 0.08 x 0.12 mm ³	
Theta range for data collection	1.65 to 25.03°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 15	
Reflections collected	6638	
Independent reflections	4012 [R(int) = 0.0427]	
Absorption correction	SADABS	
Max. and min. transmission	1.000000 and 0.492105	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4000 / 3 / 392	
Goodness-of-fit on F ²	0.945	
Final R indices [for 2190 rfl. with I > 2σ(I)]		R1 = 0.0853, wR2 = 0.2276
R indices (all data)		R1 = 0.1267, wR2 = 0.2877
Largest diff. peak and hole		0.644 and -0.444 e.Å ⁻³

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_3 \cdot \text{C}_4\text{H}_8\text{O} \cdot 0.5\text{H}_2\text{O}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	-32(3)	-2705(3)	890(3)	69(1)
F(2)	-1790(4)	-2582(4)	2012(3)	74(1)
N(1)	-1085(4)	1917(4)	1914(3)	29(1)
N(2)	2747(4)	-371(4)	5440(3)	41(1)
O(1)	1560(4)	85(4)	5875(3)	53(1)
O(2)	3925(4)	-919(4)	5965(3)	58(1)
O(3)	2817(4)	-90(5)	1090(3)	62(1)
C(2)	111(4)	586(5)	2088(3)	30(1)
C(3)	34(5)	-594(5)	1801(3)	34(1)
C(4)	-1252(5)	-483(5)	1424(3)	34(1)
C(5)	-2494(5)	801(5)	1363(3)	30(1)
C(6)	-2415(4)	2006(4)	1625(3)	28(1)
C(7)	-1007(5)	3375(5)	1981(3)	32(1)
C(8)	487(5)	3393(6)	1712(4)	40(1)
C(9)	-1471(6)	3601(6)	3103(4)	38(1)
C(10)	-2092(5)	4637(5)	1099(3)	34(1)
C(11)	-3608(5)	4729(5)	1258(3)	32(1)
C(12)	-4851(5)	6048(5)	1127(3)	35(1)
C(13)	-6200(5)	6007(6)	1310(4)	42(1)
C(14)	-6343(5)	4665(5)	1637(3)	36(1)
C(15)	-5113(5)	3337(5)	1756(3)	32(1)
C(16)	-3752(4)	3367(4)	1561(3)	29(1)
C(17)	1482(5)	273(5)	2660(3)	34(1)
C(18)	1464(5)	180(5)	3748(4)	34(1)
C(19)	2782(5)	-285(5)	4308(3)	36(1)
C(20)	4109(5)	-694(5)	3788(4)	43(1)
C(21)	4126(5)	-628(6)	2713(4)	48(1)
C(22)	2824(5)	-157(6)	2087(4)	48(1)
C(23)	-1349(6)	-1777(5)	1136(4)	41(1)
O(1S)	8659(5)	-4685(5)	6208(3)	76(1)
C(2S)	8913(7)	-5970(7)	5900(5)	69(2)
C(3S)	7437(7)	-6053(7)	5862(5)	70(2)
C(4S)	6435(7)	-4390(7)	5457(5)	67(2)
C(5S)	7363(7)	-3606(7)	5568(6)	76(2)
O(1W)	5204(8)	-715(8)	-94(6)	61(2)

Table 4. Bond lengths [Å] and angles [°] for C₂₂H₁₈F₂N₂O₃·C₄H₈O·0.5H₂O.

F(1)-C(23)	1.344(5)	C(10)-H(10A)	1.02(4)
F(2)-C(23)	1.357(6)	C(10)-H(10B)	0.97(5)
N(1)-C(2)	1.368(5)	C(11)-C(12)	1.387(6)
N(1)-C(6)	1.376(5)	C(11)-C(16)	1.400(6)
N(1)-C(7)	1.547(5)	C(12)-C(13)	1.369(7)
N(2)-O(1)	1.232(5)	C(12)-H(12)	0.96(5)
N(2)-O(2)	1.245(5)	C(13)-C(14)	1.382(7)
N(2)-C(19)	1.430(6)	C(13)-H(13)	0.97(5)
O(3)-C(22)	1.264(6)	C(14)-C(15)	1.386(6)
C(2)-C(3)	1.385(6)	C(14)-H(14)	0.91(4)
C(2)-C(17)	1.488(6)	C(15)-C(16)	1.379(6)
C(3)-C(4)	1.367(6)	C(15)-H(15)	0.92(4)
C(3)-H(3)	0.92(5)	C(17)-C(18)	1.374(6)
C(4)-C(5)	1.375(6)	C(17)-C(22)	1.438(7)
C(4)-C(23)	1.507(6)	C(18)-C(19)	1.396(6)
C(5)-C(6)	1.394(6)	C(18)-H(18)	0.93(4)
C(5)-H(5)	0.90(4)	C(19)-C(20)	1.392(7)
C(6)-C(16)	1.468(5)	C(20)-C(21)	1.364(7)
C(7)-C(8)	1.516(6)	C(20)-H(20)	0.95(5)
C(7)-C(9)	1.526(6)	C(21)-C(22)	1.426(6)
C(7)-C(10)	1.543(6)	C(21)-H(21)	1.13(5)
C(8)-H(8A)	0.95(5)	C(23)-H(23)	0.94(5)
C(8)-H(8B)	0.93(5)	O(1S)-C(2S)	1.390(7)
C(8)-H(8C)	0.98(5)	O(1S)-C(5S)	1.443(7)
C(9)-H(9A)	1.07(5)	C(2S)-C(3S)	1.524(8)
C(9)-H(9B)	0.99(4)	C(3S)-C(4S)	1.536(8)
C(9)-H(9C)	0.91(5)	C(4S)-C(5S)	1.493(8)
C(10)-C(11)	1.484(6)	O(1W)-H(1WA)	1.136(9)
C(2)-N(1)-C(6)	119.8(3)	C(4)-C(3)-C(2)	120.9(4)
C(2)-N(1)-C(7)	122.8(3)	C(4)-C(3)-H(3)	120.0(25)
C(6)-N(1)-C(7)	117.4(3)	C(2)-C(3)-H(3)	119.0(25)
O(1)-N(2)-O(2)	121.5(4)	C(3)-C(4)-C(5)	119.4(4)
O(1)-N(2)-C(19)	119.7(4)	C(3)-C(4)-C(23)	121.0(4)
O(2)-N(2)-C(19)	118.8(4)	C(5)-C(4)-C(23)	119.5(4)
N(1)-C(2)-C(3)	119.5(4)	C(4)-C(5)-C(6)	119.9(4)
N(1)-C(2)-C(17)	123.6(4)	C(4)-C(5)-H(5)	124.2(27)
C(3)-C(2)-C(17)	116.7(4)	C(6)-C(5)-H(5)	115.8(27)

N(1)-C(6)-C(5)	119.7(4)	C(14)-C(15)-H(15)	124.3(26)
N(1)-C(6)-C(16)	121.0(3)	C(15)-C(16)-C(11)	120.3(4)
C(5)-C(6)-C(16)	119.3(4)	C(15)-C(16)-C(6)	122.3(4)
C(8)-C(7)-C(9)	112.0(4)	C(11)-C(16)-C(6)	117.4(4)
C(8)-C(7)-C(10)	106.7(4)	C(18)-C(17)-C(22)	122.0(4)
C(9)-C(7)-C(10)	110.6(4)	C(18)-C(17)-C(2)	119.4(4)
C(8)-C(7)-N(1)	112.6(4)	C(22)-C(17)-C(2)	117.8(4)
C(9)-C(7)-N(1)	108.7(3)	C(17)-C(18)-C(19)	119.2(4)
C(10)-C(7)-N(1)	106.0(3)	C(17)-C(18)-H(18)	122.5(21)
C(7)-C(8)-H(8A)	112.6(26)	C(19)-C(18)-H(18)	118.1(21)
C(7)-C(8)-H(8B)	107.7(29)	C(20)-C(19)-C(18)	121.0(4)
H(8A)-C(8)-H(8B)	115.1(43)	C(20)-C(19)-N(2)	120.3(4)
C(7)-C(8)-H(8C)	110.5(29)	C(18)-C(19)-N(2)	118.6(4)
H(8A)-C(8)-H(8C)	109.2(39)	C(21)-C(20)-C(19)	119.7(4)
H(8B)-C(8)-H(8C)	101.2(39)	C(21)-C(20)-H(20)	125.7(28)
C(7)-C(9)-H(9A)	115.6(22)	C(19)-C(20)-H(20)	114.6(27)
C(7)-C(9)-H(9B)	111.6(23)	C(20)-C(21)-C(22)	122.5(5)
H(9A)-C(9)-H(9B)	104.3(32)	C(20)-C(21)-H(21)	115.4(23)
C(7)-C(9)-H(9C)	111.0(30)	C(22)-C(21)-H(21)	122.1(23)
H(9A)-C(9)-H(9C)	108.9(39)	O(3)-C(22)-C(21)	123.4(5)
H(9B)-C(9)-H(9C)	104.6(37)	O(3)-C(22)-C(17)	121.0(4)
C(11)-C(10)-C(7)	112.3(3)	C(21)-C(22)-C(17)	115.6(4)
C(11)-C(10)-H(10A)	113.2(22)	F(1)-C(23)-F(2)	106.5(4)
C(7)-C(10)-H(10A)	107.6(23)	F(1)-C(23)-C(4)	111.2(4)
C(11)-C(10)-H(10B)	113.0(28)	F(2)-C(23)-C(4)	109.0(4)
C(7)-C(10)-H(10B)	109.3(28)	F(1)-C(23)-H(23)	107.8(27)
H(10A)-C(10)-H(10B)	100.8(33)	F(2)-C(23)-H(23)	106.6(26)
C(12)-C(11)-C(16)	119.4(4)	C(4)-C(23)-H(23)	115.3(27)
C(12)-C(11)-C(10)	124.5(4)	C(2S)-O(1S)-C(5S)	102.3(5)
C(16)-C(11)-C(10)	116.1(4)	O(1S)-C(2S)-C(3S)	107.1(5)
C(13)-C(12)-C(11)	119.9(4)	C(2S)-C(3S)-C(4S)	100.6(5)
C(13)-C(12)-H(12)	126.9(27)	C(5S)-C(4S)-C(3S)	104.3(5)
C(11)-C(12)-H(12)	112.9(27)	O(1S)-C(5S)-C(4S)	108.2(5)
C(12)-C(13)-C(14)	120.9(4)		
C(12)-C(13)-H(13)	115.6(26)		
C(14)-C(13)-H(13)	123.3(27)		
C(13)-C(14)-C(15)	119.9(4)		
C(13)-C(14)-H(14)	123.7(28)		
C(15)-C(14)-H(14)	116.3(28)		
C(16)-C(15)-C(14)	119.6(4)		
C(16)-C(15)-H(15)	115.8(26)		

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_3 \cdot \text{C}_4\text{H}_8\text{O} \cdot 0.5\text{H}_2\text{O}$. The anisotropic displacement factor exponent takes the form: $-2 \text{ [h}^2 \text{ a}^*{}^2 \text{U}^{11} + \dots + 2 \text{ h k a}^* \text{ b}^* \text{U}^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	52(2)	49(2)	106(3)	-50(2)	-8(2)	2(2)
F(2)	119(3)	54(2)	68(2)	-21(2)	4(2)	-51(2)
N(1)	28(2)	25(2)	30(2)	-8(1)	-3(1)	-7(2)
N(2)	43(3)	42(2)	41(2)	-4(2)	-8(2)	-23(2)
O(1)	48(2)	80(3)	39(2)	-13(2)	2(2)	-35(2)
O(2)	52(2)	67(3)	47(2)	3(2)	-23(2)	-24(2)
O(3)	32(2)	92(3)	42(2)	-17(2)	5(2)	-5(2)
C(2)	23(2)	31(2)	26(2)	-6(2)	-1(2)	-1(2)
C(3)	29(2)	27(2)	35(2)	-8(2)	-3(2)	0(2)
C(4)	41(3)	26(2)	29(2)	-8(2)	-3(2)	-7(2)
C(5)	25(2)	28(2)	32(2)	-8(2)	-4(2)	-5(2)
C(6)	27(2)	23(2)	31(2)	-8(2)	-3(2)	-6(2)
C(7)	35(2)	24(2)	38(2)	-10(2)	-5(2)	-10(2)
C(8)	40(3)	37(3)	44(3)	-10(2)	-1(2)	-16(2)
C(9)	43(3)	35(3)	35(3)	-13(2)	-6(2)	-12(2)
C(10)	40(3)	25(2)	33(3)	-5(2)	1(2)	-10(2)
C(11)	35(2)	30(2)	30(2)	-9(2)	-4(2)	-11(2)
C(12)	37(3)	24(2)	35(2)	-8(2)	-3(2)	-3(2)
C(13)	36(3)	36(3)	37(3)	-11(2)	-4(2)	3(2)
C(14)	28(3)	39(3)	33(2)	-7(2)	-1(2)	-7(2)
C(15)	33(3)	31(3)	30(2)	-8(2)	-2(2)	-11(2)
C(16)	29(2)	24(2)	28(2)	-9(2)	-5(2)	-3(2)
C(17)	27(2)	30(2)	37(2)	-5(2)	-5(2)	-5(2)
C(18)	28(3)	32(3)	38(3)	-6(2)	-3(2)	-10(2)
C(19)	40(3)	36(3)	31(2)	0(2)	-9(2)	-19(2)
C(20)	36(3)	35(3)	47(3)	2(2)	-12(2)	-10(2)
C(21)	30(3)	55(3)	44(3)	1(2)	-7(2)	-9(2)
C(22)	31(3)	53(3)	45(3)	-5(2)	-4(2)	-6(2)
C(23)	49(3)	25(2)	41(3)	-13(2)	-8(2)	-2(2)
O(1S)	75(3)	82(3)	77(3)	-25(2)	1(2)	-34(3)
C(2S)	70(4)	70(4)	60(4)	-18(3)	-8(3)	-20(4)
C(3S)	87(5)	55(4)	69(4)	-20(3)	12(3)	-29(4)
C(4S)	67(4)	58(4)	73(4)	-15(3)	-4(3)	-22(3)
C(5S)	62(4)	58(4)	91(5)	-5(3)	-11(3)	-15(3)
O(1W)	63(5)	66(5)	67(5)	-26(4)	26(4)	-38(5)

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_3 \cdot \text{C}_4\text{H}_8\text{O} \cdot 0.5\text{H}_2\text{O}$.

	x	y	z	U(eq)
H(3)	852(49)	-1481(51)	1904(33)	32(11)
H(5)	-3397(48)	917(46)	1188(33)	29(11)
H(8A)	900(48)	2990(50)	1119(37)	33(12)
H(8B)	1063(56)	2940(57)	2351(43)	48(14)
H(8C)	429(53)	4409(64)	1552(38)	50(14)
H(9A)	-2518(53)	3587(49)	3345(34)	39(12)
H(9B)	-779(44)	2809(45)	3677(32)	22(10)
H(9C)	-1455(53)	4457(60)	3166(37)	49(14)
H(10A)	-1696(43)	4478(43)	365(33)	26(10)
H(10B)	-2021(50)	5567(57)	1064(36)	45(13)
H(12)	-4646(47)	6919(54)	846(35)	36(12)
H(13)	-7015(52)	6964(56)	1246(36)	42(13)
H(14)	-7213(49)	4585(49)	1820(34)	33(12)
H(15)	-5122(43)	2404(49)	2024(30)	26(11)
H(18)	600(42)	494(40)	4117(28)	13(9)
H(20)	4943(52)	-957(51)	4234(37)	42(12)
H(21)	5244(55)	-988(53)	2352(37)	48(13)
H(23)	-2010(50)	-1517(50)	561(38)	40(12)
H(2SA)	9589(7)	-6860(7)	6431(5)	82
H(2SB)	9357(7)	-5925(7)	5180(5)	82
H(3SA)	7164(7)	-6507(7)	6587(5)	84
H(3SB)	7426(7)	-6617(7)	5349(5)	84
H(4SA)	6116(7)	-4137(7)	4693(5)	80
H(4SB)	5559(7)	-4121(7)	5905(5)	80
H(5SA)	7638(7)	-3151(7)	4844(6)	91
H(5SB)	6815(7)	-2804(7)	5928(6)	91
H(1WA)	4306(72)	-134(50)	429(65)	191(44)

Table 7. Torsion angles [°] for C₂₂H₁₈F₂N₂O₃·C₄H₈O·0.5H₂O.

C(6)-N(1)-C(2)-C(3)	10.6(6)	N(1)-C(6)-C(16)-C(15)	-150.4(4)
C(7)-N(1)-C(2)-C(3)	-166.8(4)	C(5)-C(6)-C(16)-C(15)	31.2(6)
C(6)-N(1)-C(2)-C(17)	-164.1(4)	N(1)-C(6)-C(16)-C(11)	31.5(5)
C(7)-N(1)-C(2)-C(17)	18.5(6)	C(5)-C(6)-C(16)-C(11)	-146.9(4)
N(1)-C(2)-C(3)-C(4)	-5.0(6)	N(1)-C(2)-C(17)-C(18)	67.8(5)
C(17)-C(2)-C(3)-C(4)	170.0(4)	C(3)-C(2)-C(17)-C(18)	-107.0(5)
C(2)-C(3)-C(4)-C(5)	-2.1(6)	N(1)-C(2)-C(17)-C(22)	-122.0(5)
C(2)-C(3)-C(4)-C(23)	-178.5(4)	C(3)-C(2)-C(17)-C(22)	63.2(5)
C(3)-C(4)-C(5)-C(6)	3.7(6)	C(22)-C(17)-C(18)-C(19)	2.8(7)
C(23)-C(4)-C(5)-C(6)	-179.9(4)	C(2)-C(17)-C(18)-C(19)	172.5(4)
C(2)-N(1)-C(6)-C(5)	-9.0(6)	C(17)-C(18)-C(19)-C(20)	-1.8(7)
C(7)-N(1)-C(6)-C(5)	168.5(3)	C(17)-C(18)-C(19)-N(2)	179.8(4)
C(2)-N(1)-C(6)-C(16)	172.6(3)	O(1)-N(2)-C(19)-C(20)	175.3(4)
C(7)-N(1)-C(6)-C(16)	-9.9(5)	O(2)-N(2)-C(19)-C(20)	-5.2(6)
C(4)-C(5)-C(6)-N(1)	1.8(6)	O(1)-N(2)-C(19)-C(18)	-6.2(6)
C(4)-C(5)-C(6)-C(16)	-179.8(4)	O(2)-N(2)-C(19)-C(18)	173.2(4)
C(2)-N(1)-C(7)-C(8)	27.9(5)	C(18)-C(19)-C(20)-C(21)	0.6(7)
C(6)-N(1)-C(7)-C(8)	-149.6(4)	N(2)-C(19)-C(20)-C(21)	179.0(4)
C(2)-N(1)-C(7)-C(9)	-96.9(4)	C(19)-C(20)-C(21)-C(22)	-0.3(8)
C(6)-N(1)-C(7)-C(9)	85.7(4)	C(20)-C(21)-C(22)-O(3)	-179.9(5)
C(2)-N(1)-C(7)-C(10)	144.1(4)	C(20)-C(21)-C(22)-C(17)	1.2(7)
C(6)-N(1)-C(7)-C(10)	-33.3(4)	C(18)-C(17)-C(22)-O(3)	178.6(5)
C(8)-C(7)-C(10)-C(11)	179.1(4)	C(2)-C(17)-C(22)-O(3)	8.7(7)
C(9)-C(7)-C(10)-C(11)	-58.8(5)	C(18)-C(17)-C(22)-C(21)	-2.4(7)
N(1)-C(7)-C(10)-C(11)	58.9(4)	C(2)-C(17)-C(22)-C(21)	-172.3(4)
C(7)-C(10)-C(11)-C(12)	138.1(4)	C(3)-C(4)-C(23)-F(1)	-24.2(6)
C(7)-C(10)-C(11)-C(16)	-41.8(5)	C(5)-C(4)-C(23)-F(1)	159.4(4)
C(16)-C(11)-C(12)-C(13)	0.9(6)	C(3)-C(4)-C(23)-F(2)	92.9(5)
C(10)-C(11)-C(12)-C(13)	-179.0(4)	C(5)-C(4)-C(23)-F(2)	-83.5(5)
C(11)-C(12)-C(13)-C(14)	0.8(6)	C(5S)-O(1S)-C(2S)-C(3S)	-43.1(6)
C(12)-C(13)-C(14)-C(15)	-1.7(6)	O(1S)-C(2S)-C(3S)-C(4S)	35.0(6)
C(13)-C(14)-C(15)-C(16)	0.9(6)	C(2S)-C(3S)-C(4S)-C(5S)	-12.6(6)
C(14)-C(15)-C(16)-C(11)	0.8(6)	C(2S)-O(1S)-C(5S)-C(4S)	34.2(7)
C(14)-C(15)-C(16)-C(6)	-177.2(4)	C(3S)-C(4S)-C(5S)-O(1S)	-12.1(7)
C(12)-C(11)-C(16)-C(15)	-1.7(6)		
C(10)-C(11)-C(16)-C(15)	178.2(4)		
C(12)-C(11)-C(16)-C(6)	176.4(4)		
C(10)-C(11)-C(16)-C(6)	-3.7(5)		

Table 8. Hydrogen bonds for $C_{22}H_{18}F_2N_2O_3 \cdot C_4H_8O \cdot 0.5H_2O$ [$\text{\AA}$ and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(3)	1.14	1.64(2)	2.665(8)	146(3)
O(1W)#1-H(1WA)...O(3)	1.13	1.64(2)	2.565(7)	134(2)
C(12)-H(12)...O(1W)#2	0.96(5)	2.33(5)	3.264(8)	164(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z; #2 x-1,y+1,z.

Spectral and Analytical Data of Compounds 3b–i,4a

4-Nitro-2-[6,6,9,10-tetramethyl-2-(trifluoromethyl)-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]phenolate (3b). Yield 80%, mp 165–167°C (decomp.); (Found: C, 64.88; H, 4.83; N, 6.27. C₂₄H₂₁F₃N₂O₃ requires C, 65.15; H, 4.78; N, 6.33%); $\nu_{\max}$ 1645, 1595, 1565, 1510 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 1.65 (3H, s, Me), 1.83 (3H, s, Me), 2.41 (3H, s, Me), 2.43 (3H, s, Me), 2.87 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, CHH), 3.36 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, CHH), 6.59 (1H, d, $^oJ=9.6$ Hz, H^{6'}), 7.14 (1H, s, H⁸), 7.57 (1H, s, H¹¹), 7.91 (1H, d, $^mJ=3.0$ Hz, H^{3'}), 7.94 (1H, d, $^mJ=2.1$ Hz, H¹ or H³), 8.07 (1H, d, $^mJ=2.1$ Hz, H³ or H¹), 8.14 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.0$ Hz, H^{5'}); δ_{H} (400 MHz, DMSO-*d*₆) 1.52 (3H, s, Me), 1.60 (3H, s, Me), 2.35 (3H, s, Me), 2.37 (3H, s, Me), 3.05 (1H, d, $^2J_{\text{AX}}=16.3$ Hz, CHH), 3.35 (1H, d, $^2J_{\text{AX}}=16.3$ Hz, CHH), 6.21 (1H, d, $^oJ=9.6$ Hz, H^{6'}), 7.20 (1H, s, H⁸), 7.94 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.1$ Hz, H^{5'}), 7.97 (1H, d, $^mJ=2.1$ Hz, H¹ or H³), 8.03 (1H, s, H¹¹), 8.07 (1H, d, $^mJ=3.1$ Hz, H^{3'}), 8.67 (1H, d, $^mJ=2.1$ Hz, H³ or H¹).

2-[9,10-Dimethoxy-6,6-dimethyl-2-(trifluoromethyl)-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]-4-nitrophenolate (3c). Yield 49%, mp 184–186°C (decomp.); (Found: C, 57.42; H, 4.98; N, 5.53. C₂₄H₂₁F₃N₂O₅·1.5H₂O requires C, 57.49; H, 4.82; N, 5.59%); $\nu_{\max}$ 3400, 3210 (H₂O), 1640, 1600, 1560, 1510 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 1.64 (3H, s, Me), 1.82 (3H, s, Me), 2.85 (1H, d, $^2J_{\text{AX}}=16.5$ Hz, CHH), 3.37 (1H, d, $^2J_{\text{AX}}=16.5$ Hz, CHH), 4.01 (3H, s, MeO), 4.05 (3H, s, MeO), 6.56 (1H, d, $^oJ=9.6$ Hz, H^{6'}), 6.80 (1H, s, H⁸), 7.23 (1H, s, H¹¹), 7.86 (1H, d, $^mJ=2.1$ Hz, H¹ or H³), 7.92 (1H, d, $^mJ=3.1$ Hz, H^{3'}), 7.97 (1H, d, $^mJ=2.1$ Hz, H³ or H¹), 8.10 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.1$ Hz, H^{5'}).

2-[2-(Difluoromethyl)-6,6-dimethyl-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]-4-nitrophenolate (3d). Yield 65%, mp 138–140°C (decomp.); (Found: C, 64.19; H, 5.36; N, 5.94. C₂₂H₁₈F₂N₂O₃·C₄H₈O·H₂O requires C, 64.19; H, 5.80; N, 5.76%); $\nu_{\max}$ 1640, 1600, 1570, 1510 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 1.64 (3H, s, Me), 1.83 (3H, s, Me), 2.95 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, CHH), 3.41 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, CHH), 6.58 (1H, d, $^oJ=9.6$ Hz, H^{6'}), 6.80 (1H, t, $^2J_{\text{H,F}}=54.5$ Hz, CHF₂), 7.38 (1H, d, $^oJ=7.3$ Hz, H⁸), 7.61 (1H, t, $^oJ=7.5$ Hz, H⁹ or H¹⁰), 7.67 (1H, td, $^oJ=7.5$ Hz, $^mJ=1.2$ Hz, H¹⁰ or H⁹), 7.86 (1H, d, $^oJ=7.6$ Hz, H¹¹), 7.88 (1H, d, $^mJ=1.9$ Hz, H¹ or H³), 7.92 (1H, d, $^mJ=3.0$ Hz, H^{3'}), 8.09 (1H, d, $^mJ=1.9$ Hz, H³ or H¹), 8.12 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.0$ Hz, H^{5'}).

2-[2-(Difluoromethyl)-6,6,9,10-tetramethyl-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]-4-nitrophenolate (3e). Yield 80%, mp 152–153°C; (Found: C, 65.40; H, 5.49; N, 6.15. C₂₄H₂₂F₂N₂O₃·H₂O requires C, 65.15; H, 5.47; N, 6.33%); $\nu_{\max}$ 3440 (H₂O), 1640, 1595, 1560, 1540, 1515 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 1.63 (3H, s, Me), 1.81 (3H, s, Me), 2.40 (3H, s, Me), 2.43

(3H, s, Me), 2.85 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, $\underline{\text{CHH}}$), 3.33 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, $\underline{\text{CHH}}$), 6.58 (1H, d, $^oJ=9.6$ Hz, H^6), 6.78 (1H, t, $^2J_{\text{H,F}}=54.6$ Hz, CHF_2), 7.12 (1H, s, H^8), 7.57 (1H, s, H^{11}), 7.81 (1H, s, H^1 or H^3), 7.90 (1H, d, $^mJ=3.0$ Hz, $\text{H}^{3'}$), 8.05 (1H, s, H^3 or H^1), 8.13 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.0$ Hz, $\text{H}^{5'}$); ^1H (400 MHz, $\text{CDCl}_3+\text{CD}_3\text{CO}_2\text{D}$) 1.57 (3H, s, Me), 1.88 (3H, s, Me), 2.40 (3H, s, Me), 2.43 (3H, s, Me), 2.85 (1H, d, $^2J_{\text{AX}}=16.6$ Hz, $\underline{\text{CHH}}$), 3.51 (1H, d, $^2J_{\text{AX}}=16.6$ Hz, $\underline{\text{CHH}}$), 6.96 (1H, t, $^2J_{\text{H,F}}=54.4$ Hz, CHF_2), 7.05 (1H, d, $^oJ=9.4$ Hz, H^6), 7.14 (1H, s, H^8), 7.64 (1H, s, H^{11}), 7.88 (1H, s, H^1 or H^3), 8.00 (1H, d, $^mJ=2.8$ Hz, $\text{H}^{3'}$), 8.23 (1H, s, H^3 or H^1), 8.24 (1H, dd, $^oJ=9.4$ Hz, $^mJ=2.8$ Hz, $\text{H}^{5'}$).

2-[2-(Difluoromethyl)-9,10-dimethoxy-6,6-dimethyl-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]-4-nitrophenolate (3f). Yield 73%, mp 144–145°C (decomp.); (Found: C, 61.95; H, 5.82; N, 5.15. $\text{C}_{24}\text{H}_{22}\text{F}_2\text{N}_2\text{O}_5\cdot\text{C}_4\text{H}_8\text{O}\cdot\text{H}_2\text{O}$ requires C, 61.53; H, 5.90; N, 5.13%); ν_{max} 1645, 1600, 1570 cm^{-1} ; ^1H (400 MHz, CDCl_3) 1.64 (3H, s, Me), 1.81 (3H, s, Me), 2.85 (1H, d, $^2J_{\text{AX}}=16.5$ Hz, $\underline{\text{CHH}}$), 3.35 (1H, d, $^2J_{\text{AX}}=16.5$ Hz, $\underline{\text{CHH}}$), 4.01 (3H, s, MeO), 4.04 (3H, s, MeO), 6.56 (1H, d, $^oJ=9.6$ Hz, H^6), 6.78 (1H, t, $^2J_{\text{H,F}}=54.6$ Hz, CHF_2), 6.80 (1H, s, H^8), 7.23 (1H, s, H^{11}), 7.74 (1H, d, $^mJ=1.8$ Hz, H^1 or H^3), 7.91 (1H, d, $^mJ=3.1$ Hz, $\text{H}^{3'}$), 7.96 (1H, d, $^mJ=1.8$ Hz, H^3 or H^1), 8.11 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.1$ Hz, $\text{H}^{5'}$).

2-[6,6-Dimethyl-2-(1,1,2,2-tetrafluoroethyl)-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]-4-nitrophenolate (3g). Yield 52%, mp 140–142°C (decomp.); (Found: C, 60.47; H, 4.23; N, 6.00. $\text{C}_{23}\text{H}_{18}\text{F}_4\text{N}_2\text{O}_3\cdot 0.5\text{C}_2\text{H}_6\text{O}\cdot 0.5\text{H}_2\text{O}$ requires C, 60.25; H, 4.63; N, 5.86%); ν_{max} 3210 (H_2O), 1640, 1600, 1570, 1515 cm^{-1} ; ^1H (400 MHz, CDCl_3) 1.64 (3H, s, Me), 1.83 (3H, s, Me), 2.97 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, $\underline{\text{CHH}}$), 3.44 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, $\underline{\text{CHH}}$), 6.12 (1H, tt, $^2J_{\text{H,F}}=53.3$ Hz, $^3J_{\text{H,F}}=2.2$ Hz, CHF_2CF_2), 6.57 (1H, d, $^oJ=9.6$ Hz, H^6), 7.39 (1H, d, $^oJ=7.5$ Hz, H^8), 7.62 (1H, t, $^oJ=7.5$ Hz, H^9 or H^{10}), 7.66 (1H, t, $^oJ=7.5$ Hz, H^{10} or H^9), 7.85 (1H, d, $^oJ=7.6$ Hz, H^{11}), 7.94 (1H, d, $^mJ=3.0$ Hz, $\text{H}^{3'}$), 7.94 (1H, mask., H^1 or H^3), 8.07 (1H, d, $^mJ=2.0$ Hz, H^3 or H^1), 8.11 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.0$ Hz, $\text{H}^{5'}$).

4-Nitro-2-[2-(1,1,2,2-tetrafluoroethyl)-6,6,9,10-tetramethyl-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]phenolate (3h). Yield 94%, mp 208–209°C (decomp.); (Found: C, 62.96; H, 4.83; N, 5.55. $\text{C}_{25}\text{H}_{22}\text{F}_4\text{N}_2\text{O}_3$ requires C, 63.29; H, 4.67; N, 5.90%); ν_{max} 1635, 1595, 1550, 1515 cm^{-1} ; ^1H (400 MHz, CDCl_3) 1.65 (3H, s, Me), 1.82 (3H, s, Me), 2.40 (3H, s, Me), 2.43 (3H, s, Me), 2.88 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, $\underline{\text{CHH}}$), 3.36 (1H, d, $^2J_{\text{AX}}=16.4$ Hz, $\underline{\text{CHH}}$), 6.11 (1H, br t, $^2J_{\text{H,F}}=53.3$ Hz, CHF_2CF_2), 6.58 (1H, d, $^oJ=9.6$ Hz, H^6), 7.13 (1H, s, H^8), 7.53 (1H, s, H^{11}), 7.88 (1H, d, $^mJ=2.0$ Hz, H^1 or H^3), 7.92 (1H, d, $^mJ=3.0$ Hz, $\text{H}^{3'}$), 8.02 (1H, d, $^mJ=2.0$ Hz, H^3 or H^1), 8.14 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.0$ Hz, $\text{H}^{5'}$).

2-[9,10-Dimethoxy-6,6-dimethyl-2-(1,1,2,2-tetrafluoroethyl)-6*H*,7*H*-pyrido[2,1-*a*]isoquinolinium-4-yl]-4-nitrophenolate (3i). Yield 35%, mp 203–205°C (decomp.); (Found: C, 59.20; H, 4.28; N, 5.53. C₂₅H₂₂F₄N₂O₅ requires C, 59.29; H, 4.38; N, 5.53%); $\nu_{\max}$ 1645, 1600, 1555, 1525 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 1.65 (3H, s, Me), 1.82 (3H, s, Me), 2.85 (1H, d, $^2J_{\text{AX}}=16.5$ Hz, CHH), 3.37 (1H, d, $^2J_{\text{AX}}=16.5$ Hz, CHH), 4.01 (3H, s, MeO), 4.04 (3H, s, MeO), 6.09 (1H, tt, $^2J_{\text{H,F}}=53.4$ Hz, $^3J_{\text{H,F}}=1.8$ Hz, CHF₂CF₂), 6.55 (1H, d, $^oJ=9.6$ Hz, H^{6'}), 6.80 (1H, s, H⁸), 7.19 (1H, s, H¹¹), 7.81 (1H, d, $^mJ=2.1$ Hz, H¹ or H³), 7.91 (1H, d, $^mJ=2.1$ Hz, H³ or H¹), 7.92 (1H, d, $^mJ=3.1$ Hz, H^{3'}), 8.11 (1H, dd, $^oJ=9.6$ Hz, $^mJ=3.1$ Hz, H⁵).

2-{6-[2-(2-Methylallyl)phenyl]-4-(trifluoromethyl)pyridin-2-yl}-4-nitrophenol (4a) and 2-{6-[2-(2-methylprop-1-enyl)phenyl]-4-(trifluoromethyl)pyridin-2-yl}-4-nitrophenol (4b). Yield 80%; (Found: C, 63.59; H, 4.13; N, 6.67. C₂₂H₁₇F₃N₂O₃ requires C, 63.77; H, 4.14; N, 6.76%); $\nu_{\max}$ 1620, 1590, 1570, 1530 cm⁻¹; δ_{H} (400 MHz, CDCl₃) **4a** (77%) 1.62 (3H, s, Me), 3.38 (2H, s, CH₂), 4.41 (1H, m, =CHH), 4.79 (1H, sept, $J=1.3$ Hz, =CHH), 7.10 (1H, d, $^oJ=9.1$ Hz, H^{6'}), 7.37–7.50 (4H, m, benzene ring), 7.72 (1H, s, H³ or H⁵), 8.17 (1H, s, H⁵ or H³), 8.26 (1H, dd, $^oJ=9.1$ Hz, $^mJ=2.7$ Hz, H^{5'}), 8.87 (1H, d, $^mJ=2.7$ Hz, H^{3'}), 14.91 (1H, s, OH); **4b** (23%) 1.70 (3H, d, $^4J=1.2$ Hz, Me), 1.80 (3H, d, $^4J=1.3$ Hz, Me), 6.13 (1H, br s, =CH), 7.10 (1H, d, $^oJ=9.1$ Hz, H^{6'}), 7.37–7.50 (3H, m, benzene ring), 7.62 (1H, dd, $^oJ=7.7$ Hz, $^mJ=1.2$ Hz, benzene ring), 7.75 (1H, s, H¹ or H³), 8.13 (1H, s, H³ or H¹), 8.25 (1H, dd, $^oJ=9.1$ Hz, $^mJ=2.7$ Hz, H^{5'}), 8.85 (1H, d, $^mJ=2.7$ Hz, H^{3'}).

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2000 年 12 月 31 日
 1999 年 12 月 31 日

61741 : —
79227 : —
9519 : —

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Spectrum No B* 3326