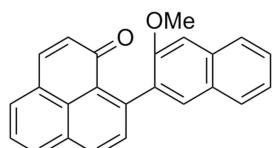


An Electronically-Stabilized Non-Planar Phenalenyl Radical and Its Planar Isomer

*Ommid Ananimoghadam, Mark D. Symes, De-Liang Long, Stephen Sproules, Leroy Cronin, Götz Bucher**

General procedure for the synthesis of 9-(methoxynaphthalenyl)-1*H*-phenalen-1-ones. In a two-neck round bottom flask, Mg in 5 ml of THF was activated with 0.1 mL 1,2-dibromoethane under argon atmosphere. Then the brominated aryl compound was added to the reaction mixture dropwise in THF by means of a syringe. With slow stirring and heating, the Grignard-reagent began to form. After 45 min, 1.00 g (5.5 mmol, 1 eq) of 1*H*-phenalen-1-one dissolved in 10 mL of dry THF was gradually added to the grey solution. The mixture was then refluxed for 4 h. After cooling down to room temperature, the reaction was quenched with 5 mL sat. NH₄Cl solution. Then 20 mL H₂O was added and the product was extracted with EtOAc (3 x 30 mL) and washed with 20 mL brine and dried over MgSO₄. When the solvent was evaporated to dryness, the crude product and 1.30 g DDQ (5.6 mmol; 1 eq) were mixed in CH₂Cl₂ and refluxed overnight at 55-60 °C. The next day, the solvent was evaporated by rotary evaporator inside a fumehood. By flash column chromatography using silica and CH₂Cl₂ as the eluent, the desired product was obtained.

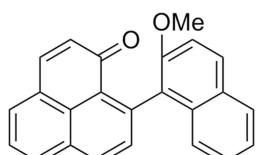
Synthesis of 9-(3-methoxynaphthalenyl)-1*H*-phenalen-1-one (6). Following the general procedure, the Grignard reagent was generated from 0.23 g (9.4 mmol; 1.7 eq) Mg and 1.97 g (8.32 mmol; 1.5 eq) 2-bromo-3-methoxynaphthalene dissolved in 5 mL THF at 40-50 °C. After reflux with 1*H*-phenalen-1-one (1 eq) and subsequent oxidation with DDQ, 9-(3-methoxynaphthalenyl)- 1*H*-phenalen-1-one was obtained as a yellow powder in a yield of 36% (0.68 g; 2 mmol).



Chemical Formula: C₂₄H₁₆O₂
Molecular Weight: 336.38

¹H-NMR (400 MHz; CDCl₃) δ 3.79 (s, OMe), 6.58 (d, J = 9.7 Hz, 1H), 7.22 (s, 1H), 7.33 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.44 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 9.8 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.80 (dd, J = 8.2, 0.5 Hz, 1H), 8.06 (dd, J = 8.2, 1.0 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H). ¹³C-NMR (100 MHz; CDCl₃) δ 55.78 (OMe), 105.49 (Cq), 123.73 (CH), 126.28 (CH), 126.24 (CH), 126.84 (CH), 127.47 (CH), 127.87 (2CH), 128.36 (Cq), 128.86 (Cq), 129.54 (Cq), 130.35 (CH), 131.20 (2CH), 131.73 (CH), 131.84 (CH), 132.28 (Cq), 133.94 (CH), 134.64 (Cq), 134.85 (Cq), 140.35 (Cq), 155.79 (Cq), 185.49 (C=O). UV (in MeCN) – λ_{max} [nm] (log ε): 305 (3.73), 320 (3.75), 360 (3.97). IR (ATIR) ν_{max} [cm⁻¹] 3010-2827 (CH_{aromatic}, weak), 1636 (C=O, sharp & intense), 1622, 1598, 1579, 1555, 1503, 1497, 1476, 1458, 1427, 1390, 1385, 1352, 1327, 1248, 1244, 1241 (C-O, sharp), 1198, 1171, 1123, 1107, 1076, 1040. MS (EI+) m/z (rel. intensity): 336 (M⁺, 23), 320 (7), 306 (80), 305 (100), 292 (14), 276 (27), 263 (30), 237 (7), 160 (18), 153 (23), 146 (15), 132 (11), 86 (12), 84 (18), 49 (12), 44 (8). HRMS calcd for C₂₄H₁₆O: 336.1150, found: 336.1146. Melting point: 194-196 °C; crystals from CH₂Cl₂.

Synthesis of 9-(2-methoxynaphthalenyl)-1*H*-phenalen-1-one (7). Following the general procedure, the Grignard reagent was generated from 0.23 g (9.4 mmol; 1.7 eq) Mg and 1.97 g (8.32 mmol; 1.5 eq) 1-bromo-2-methoxynaphthalene dissolved in 5 mL THF at 40-50 °C. After reflux with 1*H*-phenalen-1-one (1 eq) and subsequent oxidation with DDQ 9-(2-methoxynaphthalenyl)-1*H*-phenalen-1-one was obtained as an orange powder in a yield of 70% (1.30 g; 3.86 mmol).



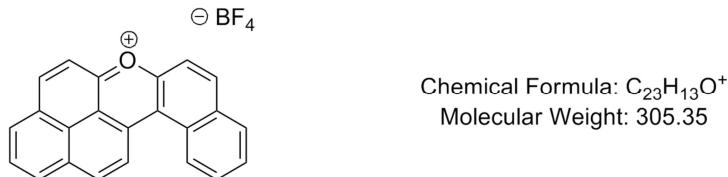
Chemical Formula: C₂₄H₁₆O₂
Molecular Weight: 336.38

¹H-NMR (400 MHz; CDCl₃) δ 3.79 (s, OMe), 6.50 (d, J = 9.7 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 7.20 (ddd, J = 8.1, 6.7, 1.3 Hz, 1H), 7.30 (ddd, J = 8.1, 6.7, 1.2 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.66 (dd, J = 8.2, 7.1 Hz, 1H), 7.70 (d, J = 9.7 Hz, 1H), 7.80 (d, J = 6.3 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H). ¹³C-NMR (100 MHz; CDCl₃) δ 56.85 (OMe), 113.95 (CH), 123.58 (CH), 124.16 (CH), 126.23 (Cq), 126.35 (CH), 126.54 (CH), 127.97 (Cq), 128.29 (CH), 128.66 (Cq), 128.70 (Cq), 128.94 (CH), 129.44 (Cq), 130.33 (CH), 131.15 (CH), 131.84 (CH), 132.20 (Cq), 132.56 (2CH), 134.21 (CH), 153.06 (Cq), 185.39 (C=O).

UV (in MeCN) – λ_{max} [nm] (log ϵ): 312 (3.75), 341 (3.91), 358 (4.03). IR (ATIR) ν_{max} [cm^{-1}] 3032-2830 ($\text{CH}_{\text{aromatic}}$, weak), 1630 (C=O, sharp & intense), 1609, 1591, 1545, 1510, 1447, 1380, 1384, 1329, 1253 (C-O, sharp & intense), 1236, 1183, 1176, 1145, 1120, 1084, 1065, 1064. MS (EI+) m/z (rel. intensity): 336 (M^+ , 9), 305 (93), 263 (7), 153 (8), 86 (65), 84 (100), 51 (22), 49 (68), 47 (18). HRMS calcd for $C_{24}H_{16}O$: 336.1150, found: 336.1145. Melting point: 203-205 °C; crystals from CH_2Cl_2 .

General procedure for the synthesis of benzonaphthoxanthenium cations. 0.100 g 9-(2-Methoxyaryl)-1*H*-phenalen-1-one (0.35 mmol) was dissolved in 40 mL CH_2Cl_2 in a round bottom flask placed in a NaCl/ice bath. Argon was purged through for 5 minutes and the flask was sealed with a septum and supplied with an argon-filled balloon. While stirring, 1.2 mL BBr_3 in heptane (1 M) was slowly added by syringe. The colour of the solution changed from orange to dark brown. After 10 minutes, the NaCl/ice-bath was removed and the solution was stirred for 4 hours. After this time, adding 30 mL of H_2O quenched the reaction and dissolved the precipitate giving an orange solution. The aqueous layer was separated and the organic salt in the organic layer was extracted with distilled H_2O (2 x 10 mL). When the aqueous layers were combined and filtered, 5 mL HBF_4 solution was added, yielding a precipitate which was separated by vacuum filtration.

Synthesis of benzo[*j*]naphtho[2,1,8-mna]xanthenium tetrafluoroborate (8 $^+$). Following the general procedure, 8 $^+$ was obtained as a brown powder in a yield of 64%.



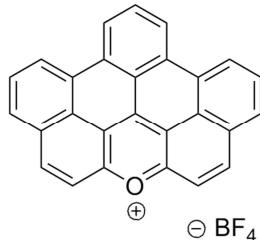
$^1\text{H-NMR}$ (400 MHz; CD_3CN) δ 7.71 (t, J = 7.5 Hz, 1H), 7.79 (t, J = 7.1 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.39 (d, J = 9.1 Hz, 1H), 8.43 (t, J = 7.7 Hz, 1H), 8.61 (s, 1H), 9.05 (m, 2H), 9.20 (d, J = 8.7 Hz, 1H), 9.29 (d, J = 9.1 Hz, 1H), 9.36 (d, J = 8.7 Hz, 1H), 9.49 (s, 1H). $^{13}\text{C-NMR}$ (100 MHz; CD_3CN) δ 115.63 (Cq), 116.82 (CH), 118.66 (Cq), 120.92 (CH), 122.33 (Cq), 123.45 (CH), 128.40 (CH), 128.48 (CH), 128.63 (Cq), 128.96 (CH), 130.21 (CH), 131.20 (Cq), 131.45 (CH), 131.86 (CH), 132.33 (Cq), 137.30 (Cq), 141.83 (CH), 142.75 (CH), 145.96 (Cq), 148.40 (CH), 149.11 (Cq), 150.36 (CH), 166.07 (C=O^+). UV (in MeCN) – λ_{max} [nm] (log ϵ): 322 (4.15), 363 (3.82), 469 (4.68). IR (ATIR) ν_{max} [cm^{-1}] 3074 ($\text{CH}_{\text{aromatic}}$, weak), 1603, 1597, 1566 (C=O+, sharp & intense), 1507, 1472, 1445, 1421, 1360, 1334, 1288, 1239, 1211, 1199, 1163, 1144, 1136, 1027 (B-F, sharp & intense). MS(EI+) m/z (rel. intensity): 305 (100), 276 (21), 274 (9), 231 (5), 219 (5), 187 (8), 181 (7), 169 (8), 153 (13), 131 (10), 119 (8), 85 (6), 69 (16), 44 (83), 40 (15), 36 (22). HRMS calcd for $C_{23}H_{13}O^+$: 305.0966, found: 336.0967. Melting point: 276-280 °C, crystals from acetone.

Synthesis of benzo[a]naphtho[8,1,2-jk]xanthenium tetrafluoroborate (9 $^+$). Following the general procedure, 9 $^+$ was obtained as a brown powder in a yield of 67%.



$^1\text{H-NMR}$ (400 MHz; CD^3CN) δ 7.95 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 8.07 (ddd, J = 8.5, 7.1, 1.4 Hz, 1H), 8.26 (d, J = 9.1 Hz, 1H), 8.33 (dd, J = 8.0, 1.2 Hz, 1H), 8.58 (t, J = 7.7 Hz, 1H), 8.60 (d, J = 9.1 Hz, 1H), 8.69 (d, J = 9.1 Hz, 1H), 9.18 – 9.10 (m, 2H), 9.28 (d, J = 8.5 Hz, 1H), 9.34 (d, J = 9.1 Hz, 1H), 9.39 (d, J = 9.1 Hz, 1H), 9.61 (d, J = 9.1 Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz; CD_3CN) δ 117.00 (Cq), 117.64 (Cq), 118.65 (CH), 120.11 (CH), 121.84 (Cq), 126.27 (CH), 128.26 (CH), 129.20 (Cq), 129.24 (Cq), 129.97 (CH), 130.57 (Cq), 131.39 (CH), 131.43 (CH), 131.45 (CH), 133.17 (Cq), 139.27 (CH), 140.42 (CH), 140.95 (CH), 144.32 (Cq), 146.73 (CH), 146.88 (CH), 155.76 (Cq), 161.38 (C=O^+). UV (in MeCN) – λ_{max} [nm] (log ϵ): 311 (4.91), 505 (5.12). IR (ATIR) ν_{max} [cm^{-1}] 3061, 1617, 1602, 1577, 1564, 1545, 1518, 1495, 1472, 1431, 1412, 1382, 1350, 1324, 1279, 1246, 1236, 1224, 1192, 1176, 1147, 1137, 1115, 1091, 1032, 983. MS(EI+) m/z (rel. intensity): 305 (100), 276 (28), 274 (10), 153 (9), 152 (8), 137 (7), 69 (3), 44 (4), 40 (3). HRMS calcd for $C_{23}H_{13}O^+$: 305.0966, found: 305.0972. Melting point: 273-275 °C; crystals from acetone.

Synthesis of benzo[5,6]naphthaceno[1,12,11,10-*jklmna*]xanthylium tetrafluoroborate (5⁺**).** In a two-neck round bottom flask, 300 mg (0.8 mmol; 1 eq) of 14-phenyl-14*H*-dibenzo[a,j]xanthene was dissolved in 25 mL of glacial acetic acid under reflux at 100 °C. Then 0.05 mL (1 mmol; 1.2 eq) of Br₂ mixed with 5 mL acetic acid were added dropwise to the solution and the reaction was refluxed for 30 minutes. After cooling down the red solution, the precipitate was separated by vacuum filtration. The crude product was recrystallized from acetic acid resulting in 14-phenyldibenzo[a,j]xanthenium bromide as red-orange crystals with a golden lustre in a yield of 59% (216 mg; 0.5 mmol; lit.: 83%). Without further purification, the batch of 14-phenyldibenzo[a,j]xanthenium bromide was dissolved in 60 mL of MeCN and 5 mL of HBF₄ solution (48 wt. % in H₂O). After UV irradiation overnight, black needles indicating **5⁺** were obtained in a yield of 30% over two steps (112 mg; 0.3 mmol). This compound analyzed as per the analogous bromide salt previously reported.¹ IR (ATIR) ν_{max} [cm⁻¹] 3055 (CH_{aromatics}, weak), 1617, 1605, 1582 (C=O⁺, intense), 1464, 1431, 1395, 1353, 1335, 1314, 1264, 1251, 1241, 1210, 1199, 1144, 1077, 1022 (B-F, intense). MS (FAB+) m/z (rel. intensity): 353 (36), 121 (30), 91 (10), 77 (10), 44 (100). Melting Point: > 360 °C; crystals from acetonitrile. HRMS calcd for C₂₇H₁₃O: 353.0966, found: 353.0968.



Chemical Formula: C₂₇H₁₃BF₄O
Molecular Weight: 440.20

General Electrochemistry: Electrochemical measurements were performed on a CH Instruments 760D Electrochemical Workstation using CHI Version 10.03 software. Electrochemical experiments for obtaining the cyclic voltammograms (CVs) in the main text were conducted at 295 K using a CH Instruments glassy carbon button working electrode (area = 0.071 cm²), BASi Ag/AgNO₃ reference electrode, and Pt mesh counter electrode. All electrode potentials were referenced to the ferrocene/ferrocenium couple by doping in samples of ferrocene to the electrolyte. Electrochemical experiments were conducted in electrolyte solutions prepared using HPLC grade CH₃CN (for compounds **8⁺** and **9⁺**) or DMF (for compound **5⁺**), and were thoroughly degassed with argon. Compounds **8⁺** and **9⁺** were present at a concentration of 5 mM; compound **5⁺** was significantly less soluble than this in all solvents tested. The supporting electrolyte in all cases was tetrabutylammonium tetrafluoroborate (TBABF₄) at a concentration of 0.1 mol dm⁻³. Cyclic voltammograms were conducted at a scan rate of 0.1 V/s unless otherwise stated. Bulk electrolysis experiments were conducted under an argon atmosphere at room temperature with stirring in a two-compartment cell, and using a CH Instruments glassy carbon button working electrode (area = 0.071 cm²), BASi Ag/AgNO₃ reference electrode, and Pt mesh counter electrode in HPLC grade CH₃CN with 0.1 M TBABF₄ as the supporting electrolyte.

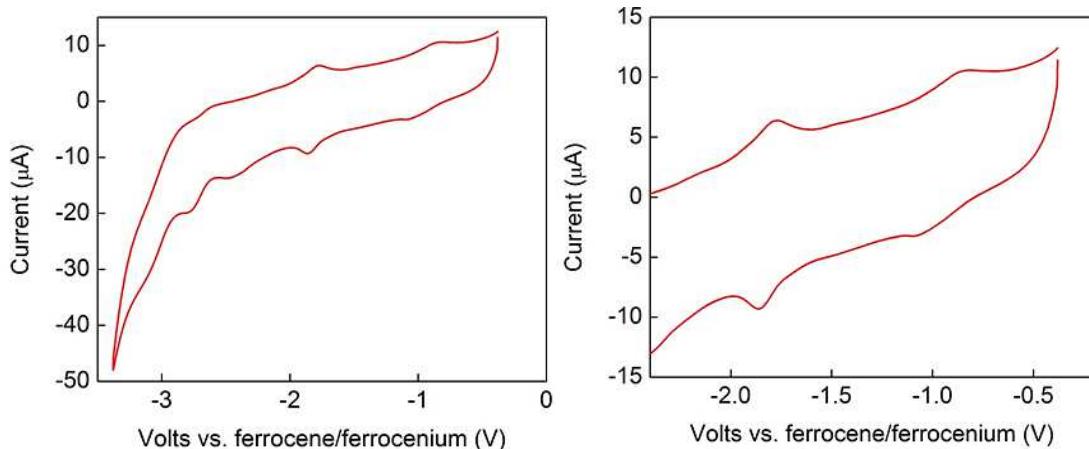


Figure S1. Full scan range cyclic voltammogram of Compound **5⁺** and expansion showing the two redox waves corresponding to the cation/radical couple and the radical/anion couple.

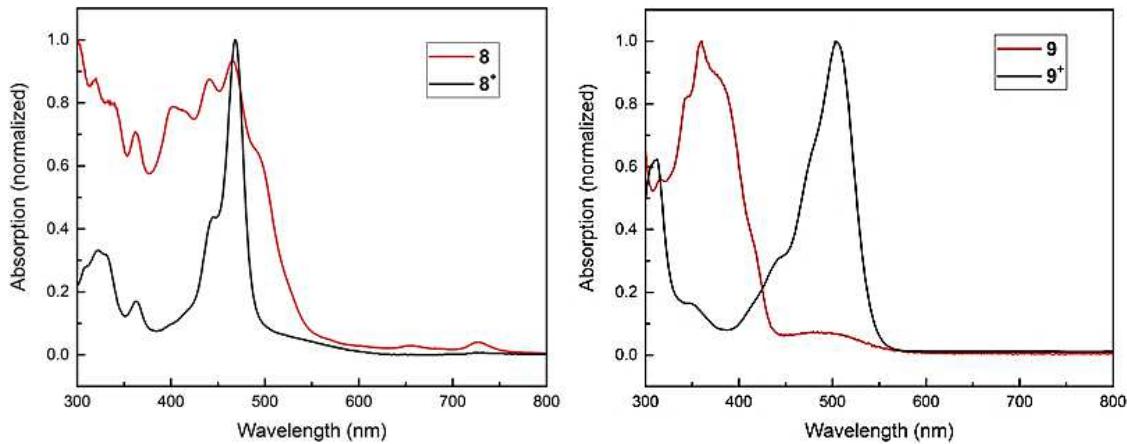


Figure S2. Absorption spectra of compound **8⁺** (black) and **8** (red), left spectrum, and compound **9⁺** (black) and **9** (red), right spectrum, before and after bulk electrolysis, respectively.

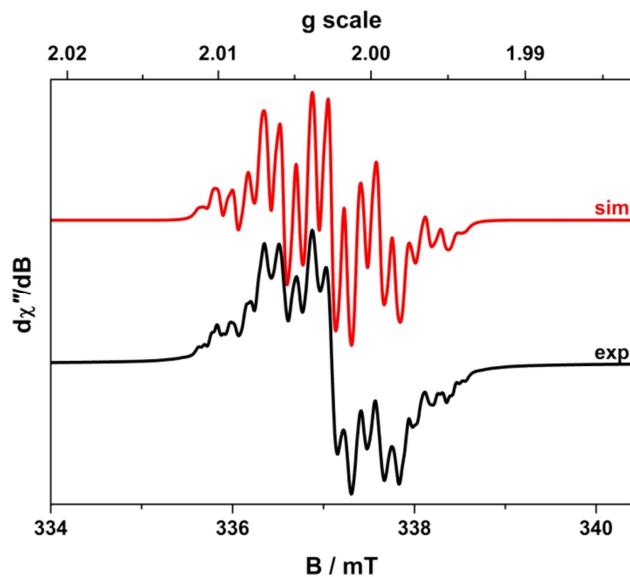


Figure S1. X-band EPR spectrum of **8** in DMSO at 293 K (experimental conditions: frequency, 9.4481 GHz; power, 0.63 mW; modulation, 0.02 mT). Experimental data are shown by the black line and simulation as the red trace using parameters: $g_{\text{iso}} = 2.00258$; $a_{\text{H(1)}} = 5.1 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H(3)}} = 4.9 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H(1)}} = 1.6 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H(3)}} = 1.5 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H(2)}} = 0.55 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H(3)}} = 0.18 \times 10^{-4} \text{ cm}^{-1}$ (value in parenthesis represents number of coupling nuclei).

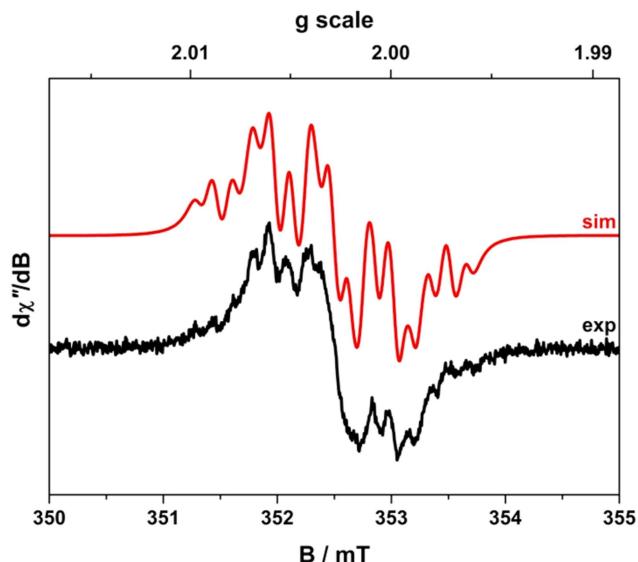


Figure S4. X-band EPR spectrum of **9** in DMSO at 293 K (experimental conditions: frequency, 9.8812 GHz; power, 0.63 mW; modulation, 0.02 mT). Experimental data are shown by the black line and simulation as the red trace using parameters: $g_{\text{iso}} = 2.0028$; $a_{\text{H}(1)} = 4.8 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H}(2)} = 4.55 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H}(1)} = 3.7 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H}(1)} = 1.7 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H}(2)} = 1.4 \times 10^{-4} \text{ cm}^{-1}$ (value in parenthesis represents number of coupling nuclei).

Table S1. HOMA and NICS indices calculated benzenoid rings and pyrilium rings of **8⁺**, **9⁺** and **5⁺**. HOMA indices were calculated using bond lengths from X-ray data. NICS indices were computed based on the B3LYP level of theory using a basis set of 6-31+G*.

	Compound 8⁺		Compound 9⁺			Compound 5⁺	
	HOMA	NICS	HOMA	NICS Top	NICS Down	HOMA	NICS
A	0.91	-10.72	0.88	-11.05	-11.43	0.91	-11.24
B	0.81	-7.12	0.83	-6.21	-7.63.	0.91	-11.24
C	0.79	-7.25	0.77	-8.09	-8.60	0.52	-2.39
D	0.84	-12.66	0.71	-8.83	-8.52	0.84	-8.15
E	0.76	-11.04	0.88	-12.02	-10.44	0.91	-11.23
F	#	#	#	#	#	0.51	-2.37
G	#	#	#	#	#	0.86	-11.01
P	0.27	-4.67	0.52	-5.93	-7.22	0.42	-4.21

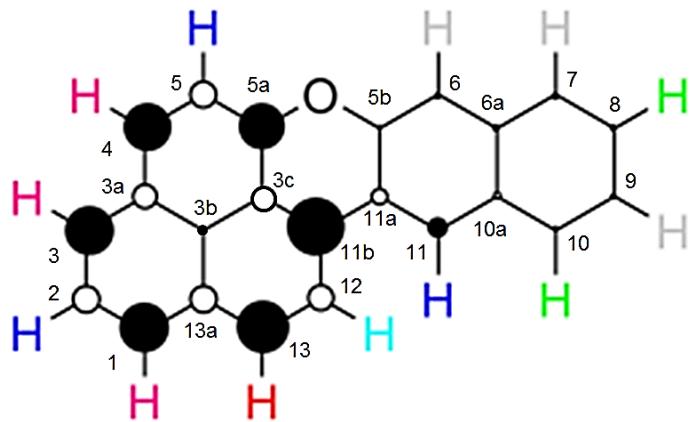


Table S2. Mulliken spin densities of **8**. (Spin density at oxygen is 0.054628).

Carbon	Mull. Spin Dens.	Proton	Mull. Spin. Dens.
C1	0.281396	H1	-0.011531
C2	-0.14994	H2	0.004959
C3	0.277682	H3	-0.011415
C3a	-0.13522	#	
C3b	0.080042	#	
C3c	-0.14307	#	
C4	0.273096	H4	-0.011158
C5	-0.14729	H5	0.004782
C5a	0.262173	#	
C5b	0.033918	#	
C6	-0.02487	H6	0.000827
C6a	0.044855	#	
C7	-0.02791	H7	0.000999
C8	0.04388	H8	-0.001894
C9	-0.02298	H9	0.000779
C10	0.038967	H10	-0.001599
C10a	-0.03457	#	
C11	0.118484	H11	-0.004929
C11a	-0.08869	#	
C11b	0.328069	#	
C12	-0.17611	H12	0.005930
C13	0.299087	H13	-0.012075
C13a	-0.14931	#	

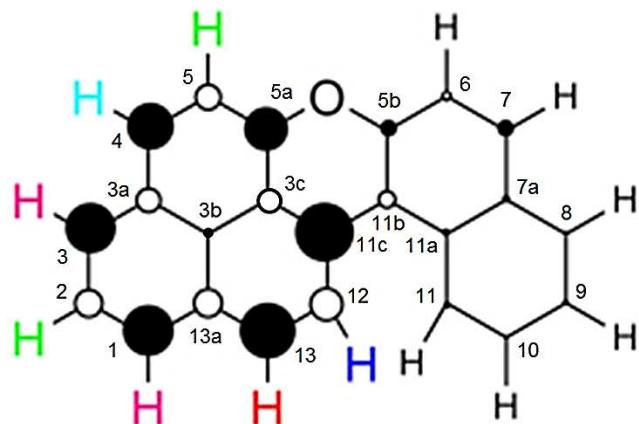


Table S3. Mulliken spin densities of **9**. (Spin density at oxygen is 0.073637).

Carbon	Mull. Spin. Dens.	Protons	Mull. Spin. Dens.
C1	0.279437	H1	-0.011497
C2	-0.147881	H2	0.004891
C3	0.275120	H3	-0.011379
C3a	-0.128704	#	
C3b	0.077799	#	
C3c	-0.137662	#	
C4	0.256547	H4	-0.010555
C5	-0.136024	H5	0.004476
C5a	0.241949	#	
C5b	0.092985	#	
C6	-0.044777	H6	0.001356
C7	0.093666	H7	-0.003944
C7a	-0.028882	#	
C8	0.024878	H8	-0.001055
C9	-0.019014	H9	0.000681
C10	0.030139	H10	-0.001284
C11	-0.025556	H11	0.001280
C11a	0.045098	#	
C11b	-0.090897	#	
C11c	0.321035	#	
C12	-0.173935	H12	0.005788
C13	0.304573	H13	-0.012428
C13a	-0.149861	#	

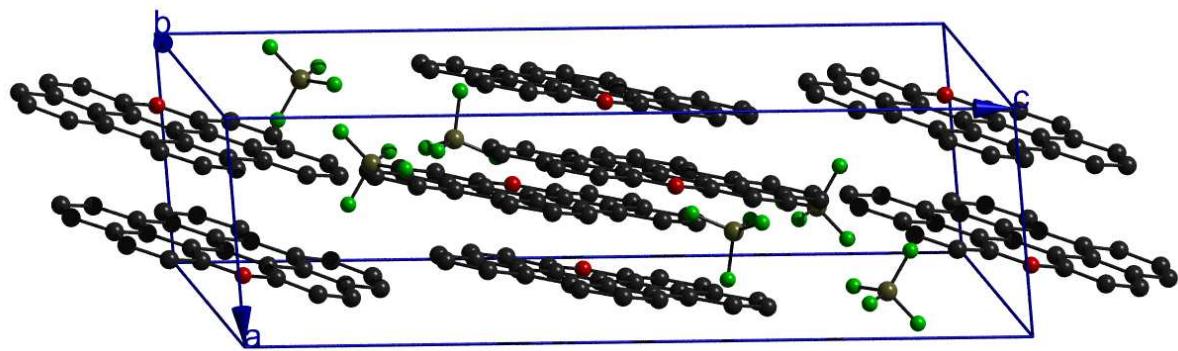


Figure S5. Unit cell content compound 5^+ illustration π -stacking arrangement.

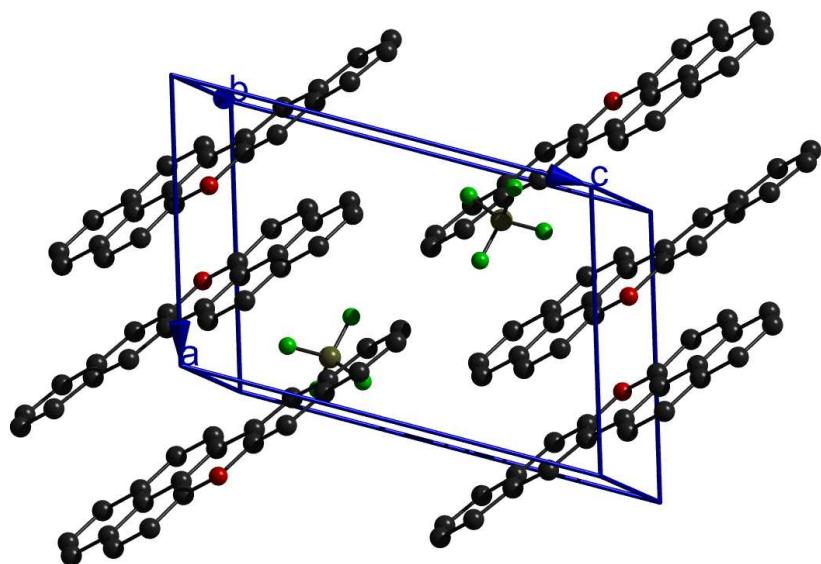


Figure S6. Unit cell content compound 8^+ illustration π -stacking arrangement.

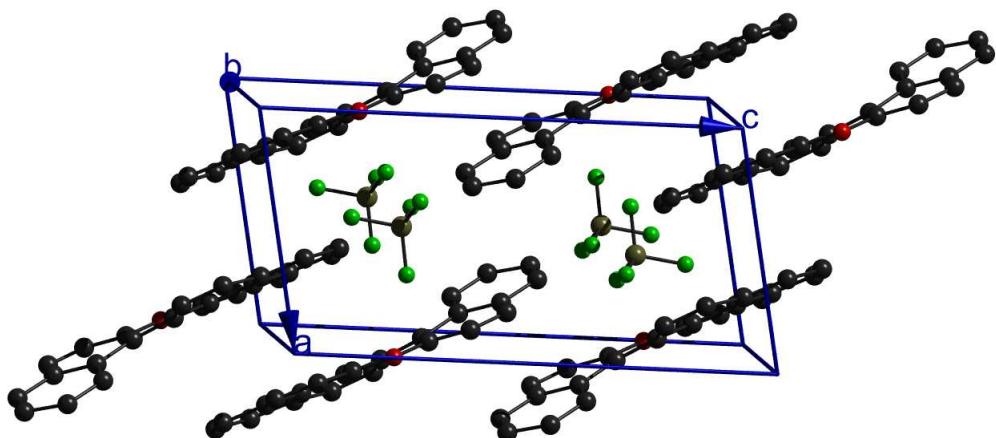
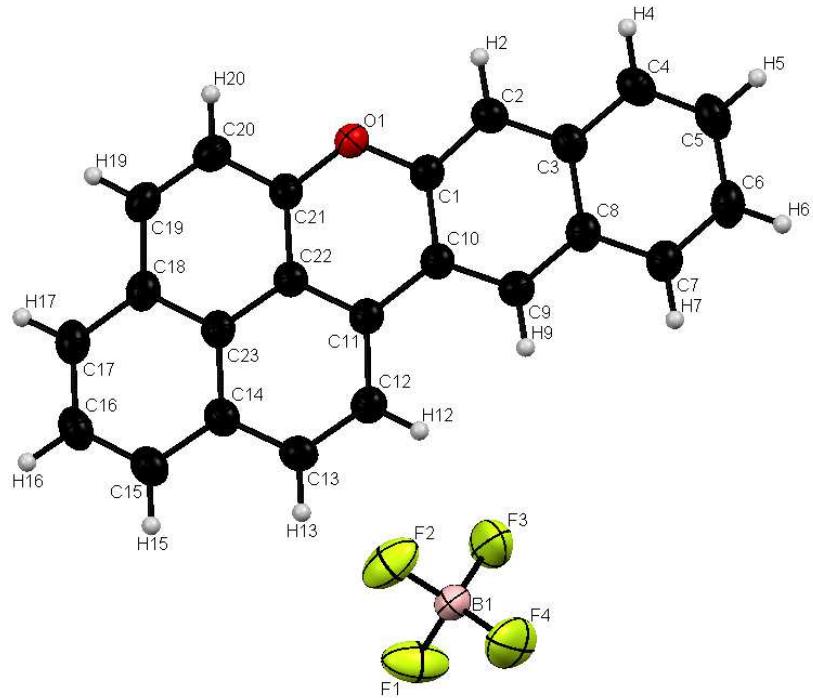


Figure S7. Unit cell content compound 9^+ illustration π -stacking arrangement.

Table S4. Bond lengths and bond angles of benzo[*i*]naphtho[2,1,8-*mna*]xanthinium tetrafluoroborate **8⁺**.

Crystal data and structure refinement for benzo[<i>i</i>]naphtho[2,1,8-<i>mna</i>]xanthinium tetrafluoroborate		
Empirical formula	$C_{23}H_{13}BF_4O$	
Formula weight	392.14	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	$a = 8.0816(7)$ Å	$\alpha = 67.764(7)$ deg. $b = 10.1745(8)$ Å
		$\beta = 71.133(8)$ deg =
		$\gamma = 71.903(8)$ deg.
Volume	842.32(12) Å ³	
Z, Calculated density	2, 1.546 Mg/m ³	
Absorption coefficient	1.048 mm ⁻¹	
F(000)	400	
Crystal size	0.38 x 0.20 x 0.04 mm	
Theta range for data collection	4.10 to 67.49 deg.	
Limiting indices	-9<=h<=9, -12<=k<=12, -14<=l<=14	
Reflections collected / unique	11968 / 3002 [R(int) = 0.0344]	
Completeness to theta = 67.49	99.1 %	
Absorption correction	Analytical	
Max. and min. Transmission	0.9593 and 0.6915	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3002 / 64 / 283	
Goodness-of-fit on F ²	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1591	
R indices (all data)	R1 = 0.0727, wR2 = 0.1768	
Extinction coefficient	none	
Largest diff. peak and hole	0.73 and -0.45 e.Å ⁻³	



Bond lengths			Bond angles			
Atom 1	Atom 2	Length	Atom 1	Atom 2	Atom 3	
C1	C2	1.366(3)	C2	C1	C10	122.8(2)
C1	C10	1.425(3)	C2	C1	O1	116.3(2)
C1	O1	1.381(2)	C10	C1	O1	120.9(2)
C2	H2	0.950(2)	C1	C2	H2	120.1(2)
C2	C3	1.407(3)	C1	C2	C3	119.8(2)
C3	C4	1.422(3)	H2	C2	C3	120.1(2)
C3	C8	1.432(3)	C2	C3	C4	122.2(2)
C4	H4	0.950(3)	C2	C3	C8	118.9(2)
C4	C5	1.359(3)	C4	C3	C8	118.8(2)
C5	H5	0.950(2)	C3	C4	H4	119.8(2)
C5	C6	1.418(4)	C3	C4	C5	120.4(2)
C6	H6	0.950(2)	H4	C4	C5	119.8(3)
C6	C7	1.367(3)	C4	C5	H5	119.4(3)
C7	H7	0.950(3)	C4	C5	C6	121.1(2)
C7	C8	1.421(3)	H5	C5	C6	119.5(3)
C8	C9	1.400(3)	C5	C6	H6	119.9(3)
C9	H9	0.951(2)	C5	C6	C7	120.2(2)
C9	C10	1.391(3)	H6	C6	C7	119.9(3)
C10	C11	1.443(3)	C6	C7	H7	119.8(3)
C11	C12	1.415(3)	C6	C7	C8	120.4(2)
C11	C22	1.414(3)	H7	C7	C8	119.8(2)
C12	H12	0.950(2)	C3	C8	C7	119.0(2)
C12	C13	1.373(3)	C3	C8	C9	119.5(2)
C13	H13	0.950(2)	C7	C8	C9	121.5(2)
C13	C14	1.424(3)	C8	C9	H9	119.2(2)
C14	C15	1.408(3)	C8	C9	C10	121.7(2)
C14	C23	1.412(3)	H9	C9	C10	119.1(2)
C15	H15	0.950(3)	C1	C10	C9	117.2(2)
C15	C16	1.383(3)	C1	C10	C11	118.8(2)
C16	H16	0.950(2)	C9	C10	C11	124.0(2)
C16	C17	1.390(4)	C10	C11	C12	123.9(2)
C17	H17	0.950(2)	C10	C11	C22	117.4(2)
C17	C18	1.401(3)	C12	C11	C22	118.7(2)

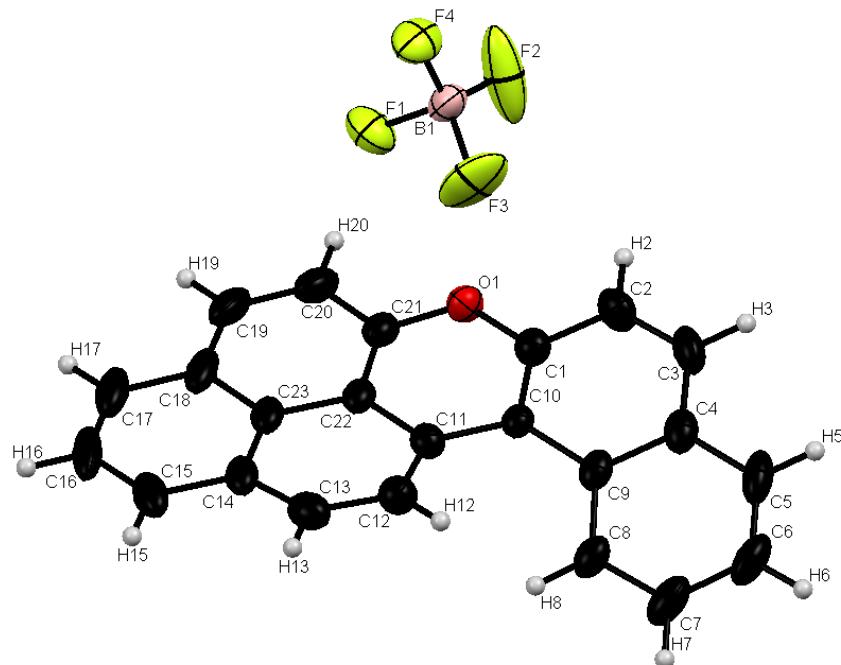
C18	C19	1.428(3)	C11	C12	H12	119.7(2)
C18	C23	1.419(3)	C11	C12	C13	120.6(2)
C19	H19	0.950(2)	H12	C12	C13	119.7(2)
C19	C20	1.362(3)	C12	C13	H13	119.2(2)
C20	H20	0.950(2)	C12	C13	C14	121.7(2)
C20	C21	1.404(3)	H13	C13	C14	119.2(2)
C21	C22	1.409(3)	C13	C14	C15	122.5(2)
C21	O1	1.337(2)	C13	C14	C23	118.7(2)
C22	C23	1.420(3)	C15	C14	C23	118.8(2)
B1	F1	1.371(6)	C14	C15	H15	119.7(2)
B1	F2	1.375(6)	C14	C15	C16	120.7(2)
B1	F3	1.385(4)	H15	C15	C16	119.7(3)
B1	F4	1.361(5)	C15	C16	H16	119.8(3)
			C15	C16	C17	120.5(2)
			H16	C16	C17	119.7(3)
			C16	C17	H17	119.6(3)
			C16	C17	C18	120.9(2)
			H17	C17	C18	119.5(2)
			C17	C18	C19	122.9(2)
			C17	C18	C23	118.6(2)
			C19	C18	C23	118.5(2)
			C18	C19	H19	119.1(2)
			C18	C19	C20	121.8(2)
			H19	C19	C20	119.1(3)
			C19	C20	H20	120.3(2)
			C19	C20	C21	119.5(2)
			H20	C20	C21	120.2(2)
			C20	C21	C22	121.6(2)
			C20	C21	O1	116.8(2)
			C22	C21	O1	121.6(2)
			C11	C22	C21	120.6(2)
			C11	C22	C23	120.9(2)
			C21	C22	C23	118.5(2)
			C14	C23	C18	120.5(2)
			C14	C23	C22	119.4(2)
			C18	C23	C22	120.1(2)
			C1	O1	C21	120.7(2)
			F1	B1	F2	108.3(3)
			F1	B1	F3	107.5(3)
			F1	B1	F4	107.7(3)
			F2	B1	F3	109.2(3)
			F2	B1	F4	112.8(3)
			F3	B1	F4	111.2(3)

Table S5. Bond lengths and bond angles of **9⁺**.

Crystal data and structure refinement for **benzo[*a*]naphtho[8,1,2-*jk*l]xanthenium tetrafluoroborate**

Empirical formula	C ₂₃ H ₁₃ BF ₄ O
Formula weight	392.14
Temperature	150(2) K

Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	$a = 7.1692(8)$ Å $\alpha = 86.021(6)$ deg. $b = 8.6347(11)$ Å $\beta = 77.850(6)$ deg. $c = 13.9776(15)$ Å $\gamma = 86.143(6)$ deg.
Volume	842.616 Å ³
Z, Calculated density	2, 1.546 Mg/m ³
Absorption coefficient	0.123 mm ⁻¹
F(000)	400
Crystal size	0.3 x 0.2 x 0.1 mm
Theta range for data collection	2.37 to 26.00 deg.
Limiting indices	-8<=h<=8, -10<=k<=10, -17<=l<=16
Reflections collected / unique	12126 / 3291 [R(int) = 0.0265]
Completeness to theta = 26.00	99.3 %
Absorption correction	Empirical
Max. and min. Transmission	0.980 and 0.843
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3291 / 31 / 296
Goodness-of-fit on F ²	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.1666
R indices (all data)	R1 = 0.0850, wR2 = 0.1816
Extinction coefficient	none
Largest diff. peak and hole	0.70 and -0.30 e.Å ⁻³



Bond lengths			Bond angles		
Atom 1	Atom 2	Length	Atom 1	Atom 2	Atom 3
C1	C2	1.401(4)	C2	C1	C10
C1	C10	1.395(4)	C2	C1	O1
C1	O1	1.359(4)	C10	C1	O1
C2	H2	0.950(3)	C1	C2	H2

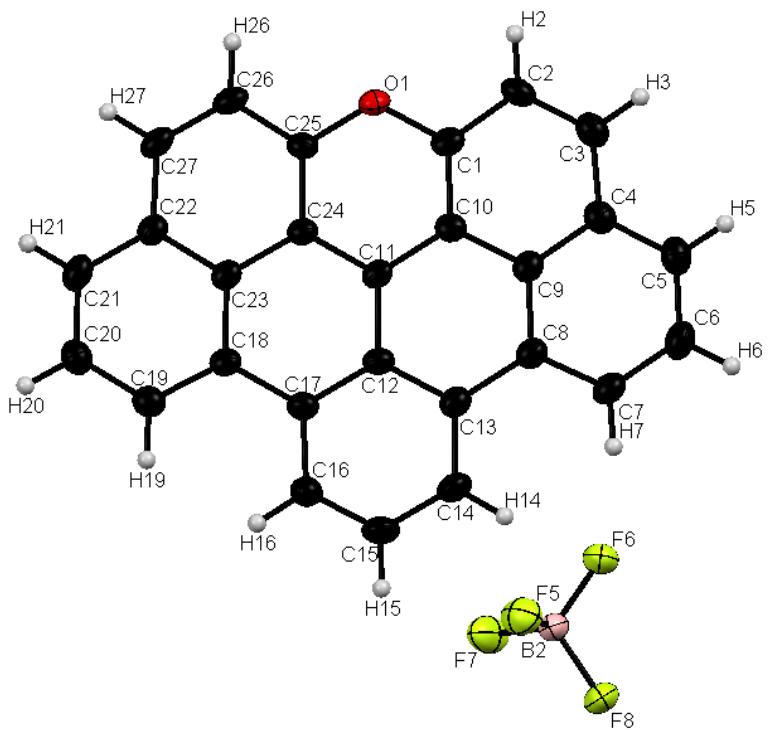
C2	C3	1.358(4)	C1	C2	C3	118.3(3)
C3	H3	0.950(3)	H2	C2	C3	120.8(3)
C3	C4	1.415(5)	C2	C3	H3	119.2(3)
C4	C5	1.417(4)	C2	C3	C4	121.6(3)
C4	C9	1.418(4)	H3	C3	C4	119.2(3)
C5	H5	0.950(3)	C3	C4	C5	120.7(3)
C5	C6	1.366(6)	C3	C4	C9	120.1(3)
C6	H6	0.950(3)	C5	C4	C9	119.0(3)
C6	C7	1.386(5)	C4	C5	H5	119.5(3)
C7	H7	0.950(4)	C4	C5	C6	121.0(3)
C7	C8	1.385(5)	H5	C5	C6	119.6(4)
C8	H8	0.951(3)	C5	C6	H6	119.9(4)
C8	C9	1.411(5)	C5	C6	C7	120.1(3)
C9	C10	1.452(4)	H6	C6	C7	119.9(4)
C10	C11	1.430(4)	C6	C7	H7	119.7(4)
C11	C12	1.418(4)	C6	C7	C8	120.6(3)
C11	C22	1.423(4)	H7	C7	C8	119.6(4)
C12	H12	0.951(3)	C7	C8	H8	119.7(3)
C12	C13	1.367(4)	C7	C8	C9	120.6(3)
C13	H13	0.950(4)	H8	C8	C9	119.6(3)
C13	C14	1.401(4)	C4	C9	C8	118.4(3)
C14	C15	1.411(5)	C4	C9	C10	118.4(3)
C14	C23	1.405(5)	C8	C9	C10	123.1(3)
C15	H15	0.950(4)	C1	C10	C9	116.7(3)
C15	C16	1.395(6)	C1	C10	C11	117.5(3)
C16	H16	0.949(3)	C9	C10	C11	125.8(3)
C16	C17	1.381(7)	C10	C11	C12	127.1(3)
C17	H17	0.950(4)	C10	C11	C22	117.6(3)
C17	C18	1.398(4)	C12	C11	C22	115.0(3)
C18	C19	1.413(6)	C11	C12	H12	119.2(3)
C18	C23	1.431(5)	C11	C12	C13	121.5(3)
C19	H19	0.950(3)	H12	C12	C13	119.3(3)
C19	C20	1.352(4)	C12	C13	H13	118.4(3)
C20	H20	0.950(3)	C12	C13	C14	123.2(3)
C20	C21	1.412(4)	H13	C13	C14	118.3(3)
C21	C22	1.396(5)	C13	C14	C15	123.5(3)
C21	O1	1.332(3)	C13	C14	C23	117.4(3)
C22	C23	1.419(4)	C15	C14	C23	119.0(3)
B1	F1	1.450(5)	C14	C15	H15	120.1(4)
B1	F2	1.36(1)	C14	C15	C16	119.6(3)
B1	F3	1.343(7)	H15	C15	C16	120.2(4)
B1	F4	1.377(6)	C15	C16	H16	119.3(4)
			C15	C16	C17	121.4(4)
			H16	C16	C17	119.3(4)
			C16	C17	H17	119.6(4)
			C16	C17	C18	120.9(3)
			H17	C17	C18	119.5(4)
			C17	C18	C19	122.4(3)
			C17	C18	C23	118.1(3)
			C19	C18	C23	119.5(3)
			C18	C19	H19	119.5(3)
			C18	C19	C20	121.1(3)
			H19	C19	C20	119.5(3)
			C19	C20	H20	120.4(3)
			C19	C20	C21	119.3(3)
			H20	C20	C21	120.3(3)
			C20	C21	C22	123.0(3)
			C20	C21	O1	116.5(3)
			C22	C21	O1	120.5(3)

C11	C22	C21	120.0(3)
C11	C22	C23	122.7(3)
C21	C22	C23	117.3(3)
C14	C23	C18	120.9(3)
C14	C23	C22	119.2(3)
C18	C23	C22	119.9(3)
C1	O1	C21	121.1(2)
F1	B1	F2	101.6(5)
F1	B1	F3	102.4(4)
F1	B1	F4	106.4(4)
F2	B1	F3	112.8(6)
F2	B1	F4	117.6(5)
F3	B1	F4	113.8(5)

Table S6. Bond lengths and bond angles of Benzo[5,6]naphthaceno[1,12,11,10-jklmna]xanthylum tetrafluoroborate 5^+

Crystal data and structure refinement for **Benzo[5,6]naphthaceno[1,12,11,10-jklmna]xanthylum tetrafluoroborate**

Empirical formula	$\text{C}_{27}\text{H}_{13}\text{BF}_4\text{O}$	
Formula weight	440.18	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P -1	
Unit cell dimensions	$a = 7.0623(5)$ Å	$\alpha = 89.162(4)$ deg.
	$b = 10.8007(9)$ Å	$\beta = 83.187(4)$ deg.
	$c = 24.0268(18)$ Å	$\gamma = 89.936(4)$ deg.
Volume	1819.57 Å ³	
Z, Calculated density	4, 1.607 Mg/m ³	
Absorption coefficient	0.124 mm ⁻¹	
F(000)	896	
Crystal size	0.11 x 0.06 x 0.03 mm	
Theta range for data collection	1.89 to 25.75 deg.	
Limiting indices	-8<=h<=8, -13<=k<=13, -29<=l<=29	
Reflections collected / unique	24852 / 6922 [R(int) = 0.0360]	
Completeness to theta = 25.75	99.3 %	
Absorption correction	Empirical	
Max. and min. Transmission	0.9963 and 0.9865	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6922 / 42 / 612	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1015	
R indices (all data)	R1 = 0.0969, wR2 = 0.1248	
Extinction coefficient	none	
Largest diff. peak and hole	0.30 and -0.26 e.Å ⁻³	



Bond lengths			Bond angles			
Atom 1	Atom 2	Length	Atom 1	Atom 2	Atom 3	Angle
C1	C2	1.401(4)	C2	C1	C12	121.8(4)
C1	C10	1.395(4)	C2	C1	I1	114.3(3)
C1	O1	1.359(4)	C12	C1	I1	123.8(3)
C2	H2	0.950(3)	C1	C2	H2	119.4(4)
C2	C3	1.358(4)	C1	C2	C3	121.1(4)
C3	H3	0.950(3)	H2	C2	C3	119.5(5)
C3	C4	1.415(5)	C2	C3	H3	119.7(5)
C4	C5	1.417(4)	C2	C3	C4	120.6(4)
C4	C9	1.418(4)	H3	C3	C4	119.7(5)
C5	H5	0.950(3)	C3	C4	C5	122.2(4)
C5	C6	1.366(6)	C3	C4	C13	118.9(4)
C6	H6	0.950(3)	C5	C4	C13	118.9(4)
C6	C7	1.386(5)	C4	C5	H5	119.4(5)
C7	H7	0.950(4)	C4	C5	C6	121.2(5)
C7	C8	1.385(5)	H5	C5	C6	119.4(5)
C8	H8	0.951(3)	C5	C6	H6	120.2(5)
C8	C9	1.411(5)	C5	C6	C7	119.8(5)
C9	C10	1.452(4)	H6	C6	C7	120.1(5)
C10	C11	1.430(4)	C6	C7	H7	119.4(5)
C11	C12	1.418(4)	C6	C7	C8	121.1(4)
C11	C22	1.423(4)	H7	C7	C8	119.4(4)
C12	H12	0.951(3)	C7	C8	C9	120.6(4)
C12	C13	1.367(4)	C7	C8	C13	120.0(4)
C13	H13	0.950(4)	C9	C8	C13	119.4(4)
C13	C14	1.401(4)	C8	C9	H9	119.5(5)
C14	C15	1.411(5)	C8	C9	C10	121.0(4)
C14	C23	1.405(5)	H9	C9	C10	119.5(5)
C15	H15	0.950(4)	C9	C10	H10	118.4(5)
C15	C16	1.395(6)	C9	C10	C11	123.4(4)
C16	H16	0.949(3)	H10	C10	C11	118.2(4)
C16	C17	1.381(7)	C10	C11	C12	117.0(4)
C17	H17	0.950(4)	C10	C11	O1	120.9(4)

C17	C18	1.398(4)	C12	C11	O1	122.1(4)
C18	C19	1.413(6)	C1	C12	C11	124.5(4)
C18	C23	1.431(5)	C1	C12	C13	117.1(4)
C19	H19	0.950(3)	C11	C12	C13	118.4(4)
C19	C20	1.352(4)	C4	C13	C8	119.0(4)
C20	H20	0.950(3)	C4	C13	C12	120.5(4)
C20	C21	1.412(4)	C8	C13	C12	120.5(4)
C21	C22	1.396(5)				
C21	O1	1.332(3)				
C22	C23	1.419(4)				
B1	F1	1.450(5)				
B1	F2	1.36(1)				
B1	F3	1.343(7)				
B1	F4	1.377(6)				

9-(3-Methoxynaphthalenyl)-1*H*-phenalen-1-one (6**)**

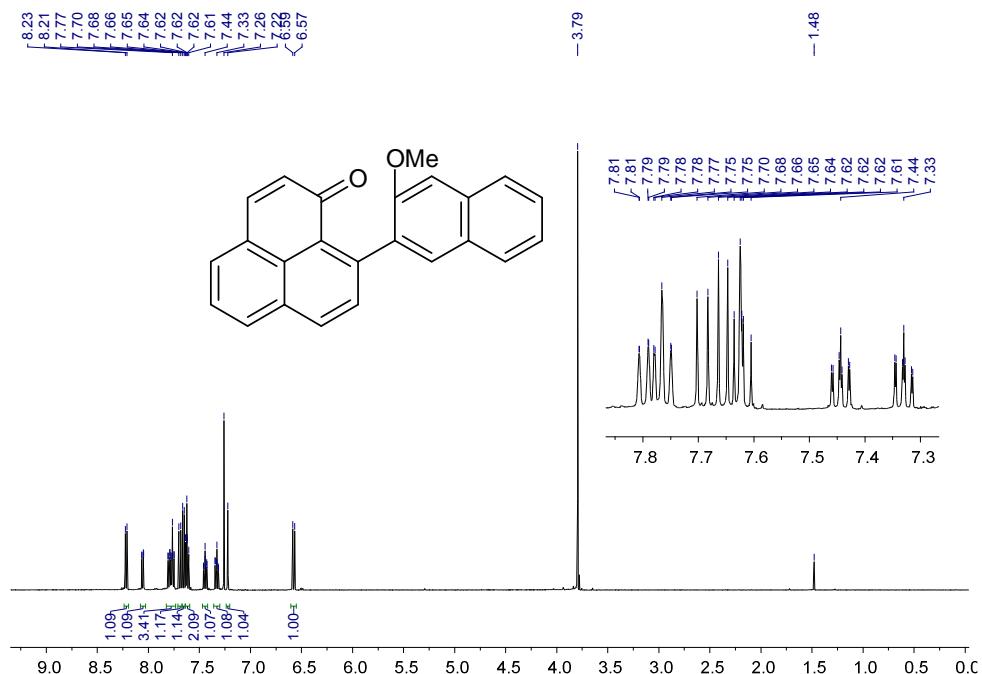
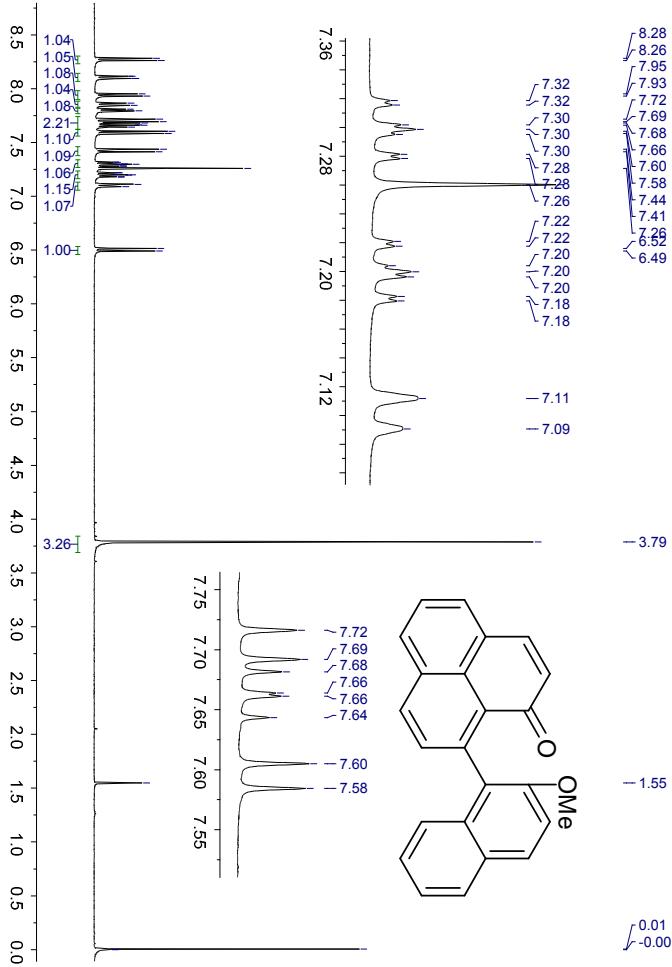


Figure S8. ^1H -NMR spectrum (400 MHz; CDCl_3) of 9-(3-methoxynaphthalenyl)-1*H*-phenalen-1-one (**6**).



9-(2-Methoxynaphthalenyl)-1*H*-phenalen-1-one (7)

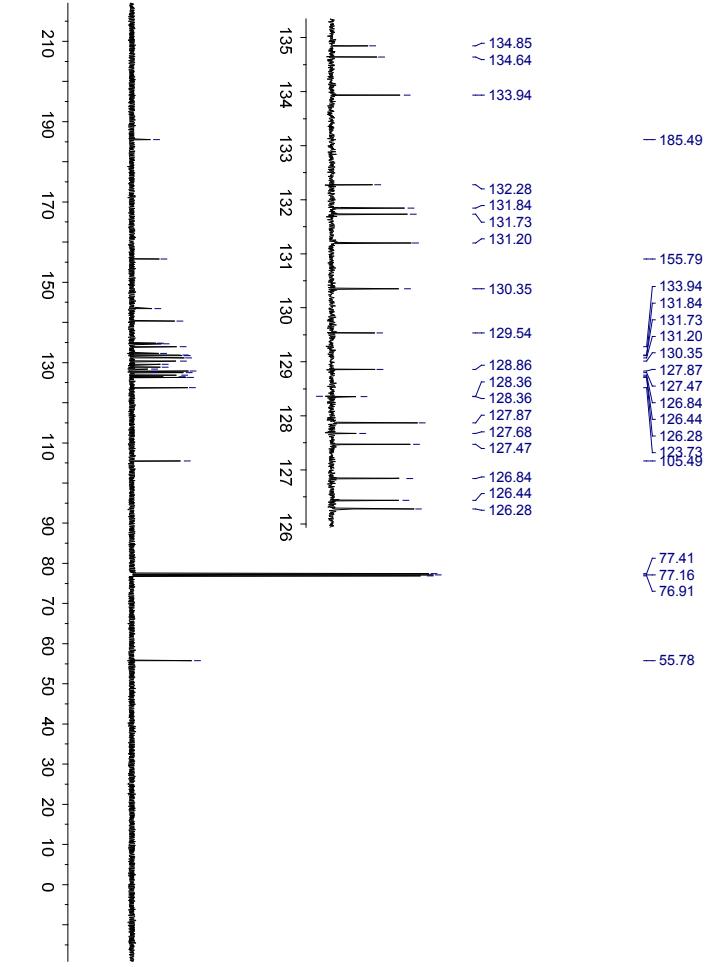


Figure S9. $^{13}\text{C-NMR}$ spectrum (100 MHz; CDCl_3) of 9-(3-methoxynaphthalenyl)-1*H*-phenalen-1-one (6).

Figure S10. $^1\text{H-NMR}$ spectrum (400 MHz; CDCl_3) of 9-(2-methoxynaphthalenyl)-1*H*-phenalen-1-one (7).

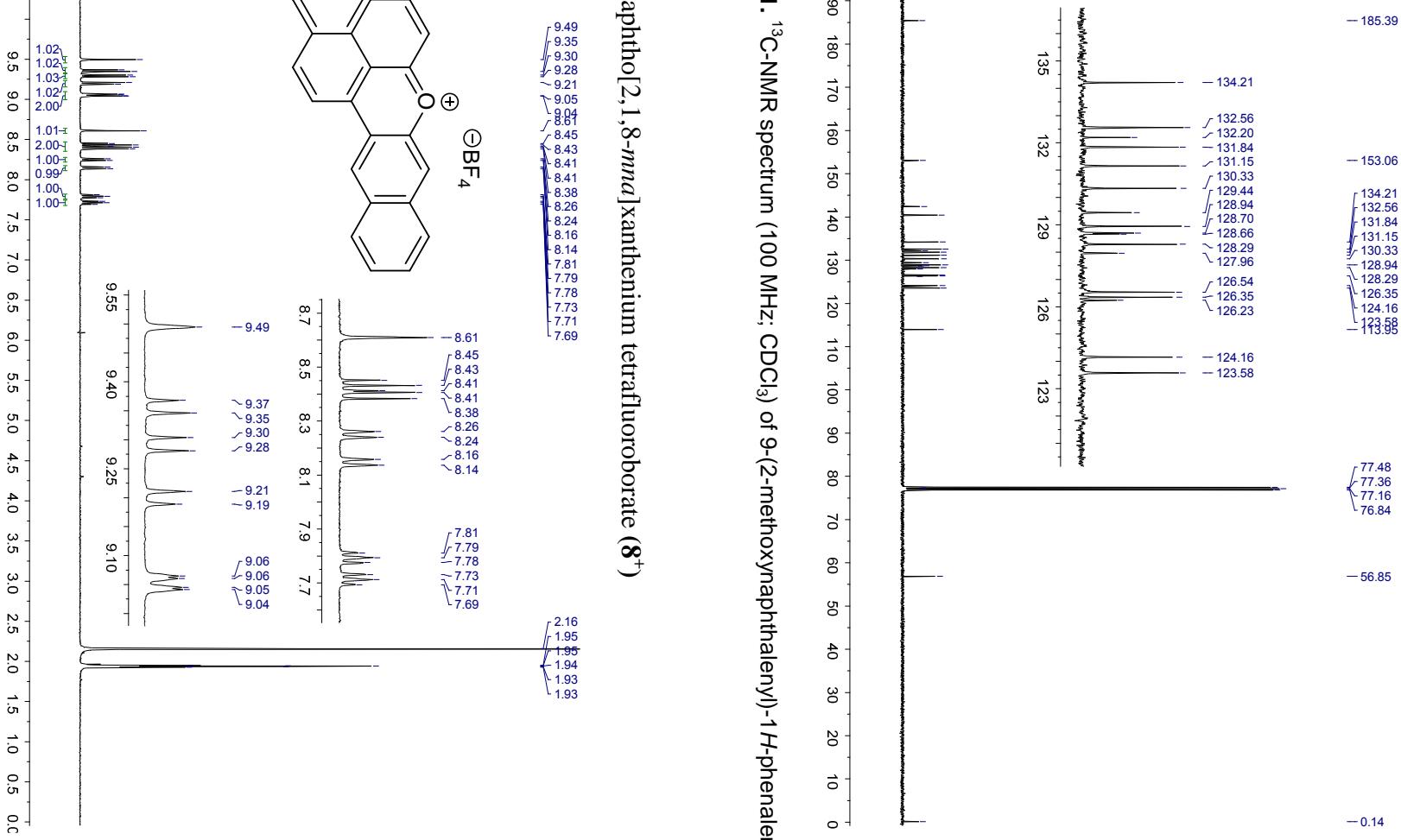


Figure S11. ^{13}C -NMR spectrum (100 MHz; CDCl_3) of 9-(2-methoxynaphthalenyl)-1*H*-phenalen-1-one (7).

Benzo[*i*]naphtho[2,1,8-*mna*]xanthenium tetrafluoroborate (**8⁺**)

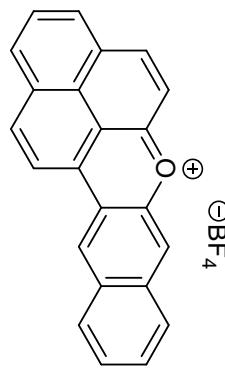


Figure S12. $^1\text{H-NMR}$ spectrum (400 MHz; CD_3CN) of benzo[*j*]aphtho[2,1-*m*]xanthenium tetrafluoroborate (**8^t**).

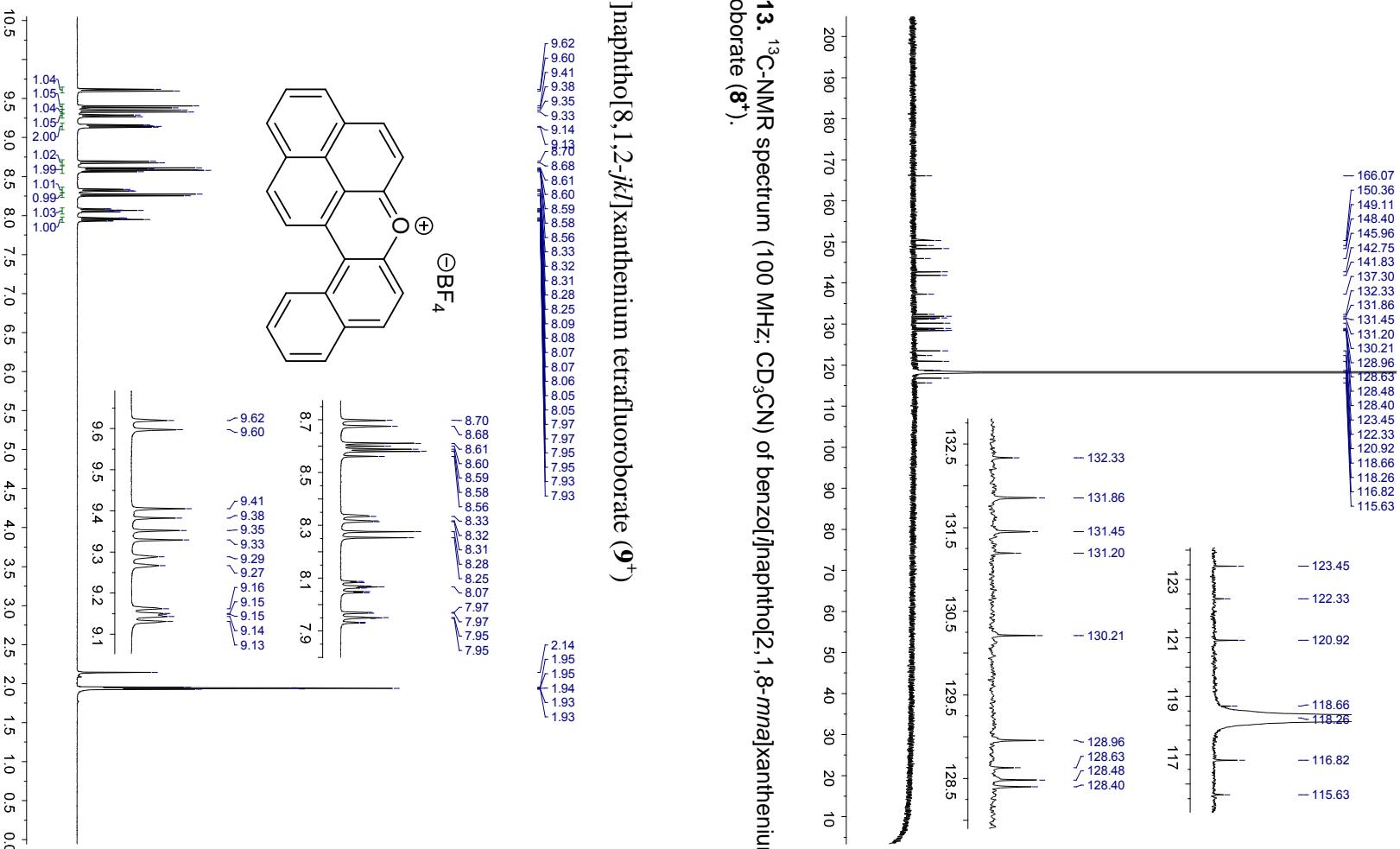


Figure S13. ^{13}C -NMR spectrum (100 MHz; CD_3CN) of benzo[*j*]aphtho[2,1,-*mna*]xanthenium tetrafluoroborate (**8⁺**).

Benzo[*a*]naphtho[8,1,2-*jk**l*]xanthenium tetrafluoroborate (**9**⁺)

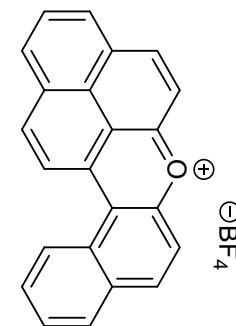


Figure S14. ^1H -NMR spectrum (400 MHz; CD_3CN) of benzo[a]naphtho[8,1,2-*jk*]xanthenium tetrafluoroborate (**9⁺**).

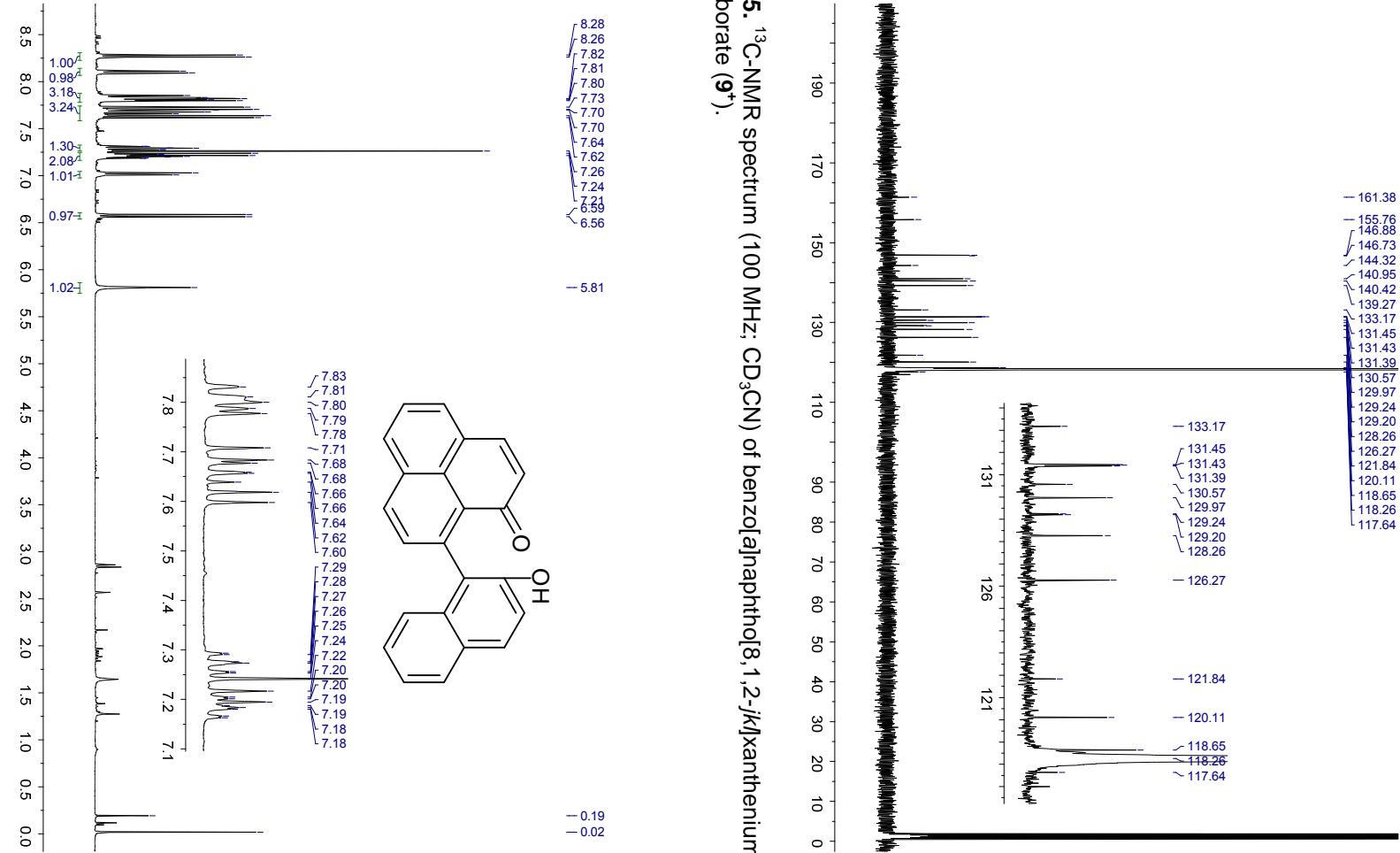


Figure S15. ^{13}C -NMR spectrum (100 MHz; CD_3CN) of benzo[*a*]naphtho[8,1,2-*jk*]xanthenium tetrafluoroborate (**9⁺**).

Figure S16. $^1\text{H-NMR}$ spectrum (400 MHz; CDCl_3) of 9-(2-hydroxynaphthalenyl)-1*H*-phenalen-1-one.

(1) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, 100(24), 7629.

Calculated geometries

Benzo[*a*]naphtho[8,1,2-*jk*l]xanthenium (B3LYP/6-31+G*). The atoms labelled "0" indicate the position of dummy atoms for calculation of NICS values.

1	0.859860	-3.372284	1.106598
6	1.401379	-2.430193	1.084708
6	2.773922	-2.433418	1.133459
1	3.348073	-3.350167	1.202783
6	3.498670	-1.223635	1.101511
6	2.831779	0.010718	1.000915
6	1.410065	0.000000	1.003599
6	0.702048	-1.234826	1.032099
0	2.117061	-1.226635	1.060569
0	2.146595	-1.261284	0.061606
0	2.087527	-1.191986	2.059533
6	-0.706961	-1.208613	1.018697
1	-1.255077	-2.145752	1.028245
6	-1.399574	0.001971	0.999999
1	-2.484561	0.000963	0.994401
6	-0.706173	1.210966	1.000000
1	-1.251885	2.150510	1.004606
6	0.700594	1.230704	1.000001
0	0.000000	0.000000	1.000000
0	0.000000	0.000000	0.000000
0	0.000000	0.000000	2.000000
6	1.458808	2.437021	1.051755
1	0.927578	3.381476	1.129429
6	2.832912	2.441649	1.024962
1	3.350351	3.384322	1.121014
6	3.579140	1.229657	0.931211
0	2.134083	1.227345	0.959555
0	2.114411	1.292406	-0.038134
0	2.153755	1.162284	1.957241
6	5.014797	1.136491	0.836687
6	5.587395	-0.126446	1.101305
8	4.833271	-1.255628	1.215447
0	4.229340	-0.049073	0.957141
0	4.324323	-0.211782	-0.024951
0	4.134356	0.113635	1.939232
6	5.938578	2.224556	0.550038
6	7.336209	2.020601	0.801496
6	7.809817	0.737043	1.202558
6	6.965632	-0.335233	1.301985
1	8.872265	0.607778	1.384006
1	7.313332	-1.332207	1.545509
0	6.453221	0.927829	0.898518
0	6.634842	0.696224	-0.057188
0	6.271601	1.159434	1.854223
6	5.559546	3.454703	-0.040438
1	4.547403	3.607649	-0.384906
6	6.486214	4.457133	-0.269885
1	6.162748	5.382329	-0.737010
6	7.837828	4.285131	0.073918
1	8.550998	5.084627	-0.097767
6	8.255385	3.072794	0.584395
1	9.305384	2.899871	0.802243
0	6.909834	3.238570	0.244037
0	7.104321	2.915564	-0.682161
0	6.715346	3.561577	1.170234

benzo[*i*]naphtho[2,1,8-*mna*]xanthenium (B3LYP/6-31+G*). The atoms labelled "0" indicate the position of dummy atoms for calculation of NICS values.

1	-0.063000	-2.940000	0.000000
6	-0.802000	-2.149000	0.000000
1	-2.427000	-3.528000	0.000000
6	-2.137000	-2.481000	0.000000

6	-1.396000	0.214000	0.000000
6	-3.162000	-1.490000	0.000000
6	-0.389000	-0.791000	0.000000
6	-2.777000	-0.122000	0.000000
6	-4.534000	-1.814000	0.000000
6	-5.502000	-0.812000	0.000000
1	-4.834000	-2.857000	0.000000
1	-6.554000	-1.077000	0.000000
6	-5.124000	0.531000	0.000000
1	-5.885000	1.307000	0.000000
6	-3.766000	0.901000	0.000000
6	-3.342000	2.265000	0.000000
1	-4.096000	3.047000	0.000000
6	-2.011000	2.607000	0.000000
1	-1.682000	3.639000	0.000000
6	-1.039000	1.584000	0.000000
8	0.240000	1.965000	0.000000
6	1.264000	1.044000	0.000000
6	0.988000	-0.362000	0.000000
6	2.541000	1.553000	0.000000
1	2.686000	2.628000	0.000000
6	3.645000	0.675000	0.000000
6	3.407000	-0.749000	0.000000
6	2.087000	-1.226000	0.000000
1	1.931000	-2.299000	0.000000
6	4.986000	1.147000	0.000000
1	5.166000	2.218000	0.000000
6	6.035000	0.260000	0.000000
1	7.055000	0.630000	0.000000
6	5.803000	-1.144000	0.000000
1	6.649000	-1.823000	0.000000
6	4.524000	-1.636000	0.000000
1	4.343000	-2.707000	0.000000
0	4.733333	-0.241167	0.000000
0	2.322000	0.155833	0.000000
0	-0.055333	0.609000	0.000000
0	-1.777167	-1.136500	0.000000
0	-2.388500	1.241500	0.000000
0	-4.144167	-0.467667	0.000000
0	4.733333	-0.241167	1.000000
0	2.322000	0.155833	1.000000
0	-0.055333	0.609000	1.000000
0	-1.777167	-1.136500	1.000000
0	-2.388500	1.241500	1.000000
0	-4.144167	-0.467667	1.000000

Benzo[5,6]naphthaceno[1,12,11,10-*jklmma*]xanthylidium (B3LYP/6-31+G*). The atoms labelled "0" indicate the position of dummy atoms for calculation of NICS values.

6	4.948000	1.043000	0.000000
1	5.904000	1.556000	0.000000
6	3.770000	1.796000	0.000000
1	3.856000	2.876000	0.000000
6	2.509000	1.186000	0.000000
6	2.469000	-0.236000	0.000000
6	3.666000	-1.008000	0.000000
6	4.907000	-0.342000	0.000000
1	5.826000	-0.919000	0.000000
6	1.250000	1.942000	0.000000
6	3.570000	-2.434000	0.000000
1	4.488000	-3.013000	0.000000
6	0.000000	1.241000	0.000000
6	1.213000	3.340000	0.000000
1	2.129000	3.918000	0.000000
6	0.000000	4.020000	0.000000
1	0.000000	5.105000	0.000000
6	-1.214000	3.340000	0.000000
1	-2.129000	3.918000	0.000000
6	-1.250000	1.942000	0.000000
6	1.216000	-0.908000	0.000000
6	0.000000	-0.181000	0.000000

6	2.361000	-3.084000	0.000000
1	2.288000	-4.165000	0.000000
6	1.184000	-2.312000	0.000000
8	0.000000	-2.983000	0.000000
6	-1.184000	-2.312000	0.000000
6	-1.215000	-0.909000	0.000000
6	-2.469000	-0.236000	0.000000
6	-2.361000	-3.084000	0.000000
1	-2.288000	-4.165000	0.000000
6	-3.570000	-2.434000	0.000000
1	-4.487000	-3.014000	0.000000
6	-3.666000	-1.008000	0.000000
6	-2.509000	1.186000	0.000000
6	-3.770000	1.796000	0.000000
1	-3.856000	2.875000	0.000000
6	-4.948000	1.043000	0.000000
1	-5.904000	1.555000	0.000000
6	-4.907000	-0.342000	0.000000
1	-5.826000	-0.919000	0.000000
0	-2.410833	-1.663833	0.000000
0	-3.711500	0.406500	0.000000
0	-1.240500	0.507167	0.000000
0	0.000167	-1.600833	0.000000
0	2.411000	-1.663667	0.000000
0	1.240667	0.507333	0.000000
0	3.711500	0.406500	0.000000
0	-0.000167	2.637500	0.000000
0	-2.410833	-1.663833	1.000000
0	-3.711500	0.406500	1.000000
0	-1.240500	0.507167	1.000000
0	0.000167	-1.600833	1.000000
0	2.411000	-1.663667	1.000000
0	1.240667	0.507333	1.000000
0	3.711500	0.406500	1.000000
0	-0.000167	2.637500	1.000000

Benzo[a]naphtho[8,1,2-jkl]xanthenyl (M05-2X/6-31G**), optimised geometry.

6	-1.255230	1.651902	-0.154968
6	-1.268451	0.264715	-0.094903
6	1.094225	1.762249	0.057081
6	0.013466	-0.429265	-0.199034
8	-0.105041	2.390010	-0.121627
6	1.184421	0.366378	-0.032522
6	0.195973	-1.786618	-0.516733
6	1.448555	-2.365654	-0.518429
1	-0.652613	-2.389734	-0.800877
1	1.554245	-3.414259	-0.767415
6	2.617087	-1.617894	-0.213100
6	3.900449	-2.190230	-0.164516
6	2.478692	-0.218785	0.003440
6	5.018936	-1.399051	0.085475
1	4.008991	-3.254892	-0.330641
1	5.999159	-1.857703	0.122937
6	4.895944	-0.032005	0.274384
1	5.772521	0.578409	0.453688
6	3.627675	0.589807	0.225616
6	3.459136	1.989190	0.370045
1	4.331399	2.607682	0.540534
6	2.210765	2.568641	0.267441
1	2.070400	3.639047	0.336092
6	-2.424092	2.429773	-0.282826
1	-2.310962	3.501330	-0.377578
6	-3.640899	1.814923	-0.308800
6	-3.740050	0.413092	-0.106547
6	-2.558564	-0.364077	0.059880
1	-4.548185	2.392080	-0.438816
6	-2.723490	-1.716856	0.456529
1	-1.858576	-2.298161	0.734955
6	-3.969831	-2.282818	0.571296
1	-4.058962	-3.312609	0.893740
6	-5.131466	-1.532009	0.300545
1	-6.107777	-1.992920	0.377553

6	-5.011213	-0.203287	-0.012626
1	-5.891555	0.408926	-0.171522

HF=-959.4758312

benzo[*i*]naphtho[2,1,8-*mna*]xanthenium (M05-2X/6-31G**). Optimised geometry.

6	0.560821	-1.503492	0.000000
6	1.046700	-0.129227	0.000000
6	-1.643538	-0.940950	0.000000
6	0.000000	0.886164	0.000000
8	-0.657096	-1.880622	0.000000
6	-1.344890	0.432722	0.000000
6	0.240012	2.268726	0.000000
6	-0.797626	3.175399	0.000000
1	1.256010	2.639330	0.000000
1	-0.587318	4.237733	0.000000
6	-2.154464	2.750407	0.000000
6	-3.232025	3.654805	0.000000
6	-2.427050	1.354586	0.000000
6	-4.544798	3.192259	0.000000
1	-3.026033	4.718055	0.000000
1	-5.361615	3.902993	0.000000
6	-4.818771	1.833146	0.000000
1	-5.842651	1.479882	0.000000
6	-3.770028	0.887583	0.000000
6	-4.004517	-0.510415	0.000000
1	-5.025470	-0.870840	0.000000
6	-2.956542	-1.408585	0.000000
1	-3.122542	-2.477401	0.000000
6	1.577338	-2.519154	0.000000
1	1.223344	-3.542096	0.000000
6	2.961475	-2.231909	0.000000
6	3.377961	-0.872016	0.000000
6	2.400580	0.146843	0.000000
1	2.742112	1.174057	0.000000
6	3.944290	-3.253443	0.000000
1	3.621000	-4.287778	0.000000
6	5.277974	-2.937575	0.000000
1	6.020750	-3.725394	0.000000
6	5.695119	-1.584417	0.000000
1	6.752031	-1.350163	0.000000
6	4.766711	-0.577191	0.000000
1	5.078747	0.460997	0.000000

HF=-959.4845041