Supplementary Information

Synthesis and Characterization of Acridinium Dyes for Photoredox Catalysis

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I. Materials and Methods

All chemical reactions were carried out in oven-dried or flame-dried glassware under an atmosphere of dry argon with magnetic stirring unless otherwise noted. Dry dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), diethyl ether (Et₂O), and dimethylformamide (DMF) were obtained by passing through a column packed with activated alumina under a positive pressure of nitrogen. Anhydrous n-hexane was purchased from Alfa Aesar and used directly from the bottle. Reactions that were performed open to air utilized solvent dispensed from a wash bottle or solvent bottle, and no precautions were taken to exclude water. Column chromatography was performed using SiliaFlash P60 (0.040 – 0.063 mm) mesh silica gel (SiO₂) from Silicycle. Analytical thin-layer chromatography (TLC) was performed on SiliaPlate 250 μm TLC plates. Visualization was accomplished with UV (210 nm), and potassium permanganate (KMnO₄) or p-anisaldehyde staining solutions.

¹H NMR and ¹³C NMR were recorded at 298 K on a Bruker Avance III 600 (¹H NMR at 600 MHz and ¹³C NMR at 151 MHz) spectrometer equipped with a cryoprobe or a Bruker Avance III 500 (¹H NMR at 500 MHz and ¹³C NMR at 126 MHz) spectrometer. ¹⁹F NMR spectra were recorded at 298 K on a Bruker DRX 400 (¹⁹F NMR at 376 MHz). ¹H and ¹³C spectra were referenced to residual chloroform (7.26 ppm, ¹H; 77.00 ppm, ¹³C). Chemical shifts are reported in ppm and multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), hept (heptet), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet of doublets (td), m (multiplet), and br s (broad singlet). Coupling constants, J, are reported in Hertz. The raw fid files were processed into the included NMR spectra using MestReNova 11.0, (Mestrelab Research S. L.). High-resolution mass spectra (HRMS) were obtained using a ThermoFisher Q-Exactive HF-X Quadrupole-Orbitrap mass spectrometer and data are reported in the form of (m/z).

Cyclic Voltammetry was performed using a Pine Instruments Wavenow potentiostat with a standard three electrode setup (working: glassy carbon, reference: Ag/AgCl in 3 M NaCl, counter: platinum) at a scan rate of 100 mV/s. The glassy carbon electrode was polished between scans. All measurements were taken at a substrate concentration of 5.0 mM in degassed MeCN with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The voltammograms have been corrected by subtracting the background current of the electrolyte solution. Ground state reduction potentials [E₁/₂(C/C⁻)] were identified as half of the absolute maximum current value during the reduction event. The values for E₁/₂(C/C⁻) were referenced to SCE (Saturated Calomel Electrode) by subtracting 30 mV from the potential measured against Ag/AgCl (3 M NaCl).

Samples for photophysical measurements were prepared using spectrophotometric grade 1,2-dichloroethane (DCE). Solutions of the acridinium salts were prepared at a concentration of 16 μM, transferred to a 4 mL quartz cell, and sealed with a PTFE-lined screw cap. Absorbance spectra were recorded on a Varian Cary 50 Bio UV-Visible spectrophotometer. The solvent absorbance background was subtracted from the reported spectra. Steady state emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Time-resolved emission
experiments were performed using an Edinburgh FLS920 spectrophotometer. Excited state lifetimes were determined by time-correlated single photon counting (TCSPC) with pulsed excitation light (444.2 nm, pulse width = 95 ps) generated by a Edinburgh EPL-445 ps pulsed laser diode operating at a repetition rate of 5 MHz. The lifetime of fluorescence was determined by reconvolution fit with the instrument response function using the Edinburgh FS900 software. Fluorescence decay fit satisfactorily according to the function $I_t = A_0 e^{-t/\tau}$ (or $I_t = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ when two $\tau$-values are reported.)

Excited state reduction potentials $[E_{1/2}(C^*/C^-)]$ were calculated by subtracting the ground-state reduction potential $[E_{1/2}(C/C^-)]$, obtained by cyclic voltammetry, from the excitation energy $E_{0,0}$; $E_{0,0}$ is the energy corresponding to the wavelength at which the normalized absorption and emission spectra intersect.

II. Preparation of Biaryl Ethers

**General Procedure A:** Preparation of biaryl ethers was accomplished using a modified version of a published procedure.\(^1\)

![Chemical Reaction]

3,3'-oxybis(tert-butylbenzene) (4): To a 100 mL round bottom flask equipped with a stir bar were added 1-bromo-3-(tert-butyl)benzene (10.0 g, 46.9 mmol, 1 equiv), 3-(tert-butyl)phenol (10.6 g, 70.4 mmol, 1.5 equiv), Cs\(_2\)CO\(_3\) (30.6 g, 93.8 mmol, 2 equiv), copper(I)iodide (894 mg, 4.69 mmol, 10 mol%), 2,2,6,6-tetramethylheptane-3,5-dione (979 \(\mu\)L, 4.69 mmol, 10 mol%) and DMF (9 mL). No measures were taken to exclude air or moisture. The flask was sealed and heated to 110 °C for 24 h. The reaction was cooled to room temperature and DMF was removed by rotary evaporation. The residue was suspended in Et\(_2\)O (200 mL) and filtered through celite. The filter cake was washed with Et\(_2\)O until the washings became colorless. The filtrate was extracted with water (2 x 100 mL) followed by brine (1 x 100 mL). The organic layer was dried over MgSO\(_4\), filtered, and concentrated to dryness. The residue was purified by column chromatography (SiO\(_2\), 100% hexanes to 2% EtOAc in hexanes) to give ether 4 (11.6 g, 41.2 mmol, 88% yield) as a colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 7.25 (t, $J = 7.9$ Hz, 2H), 7.13 (ddd, $J = 7.9, 1.9, 1.0$ Hz, 2H), 7.10 (t, $J = 2.1$ Hz, 2H), 6.79 (ddd, $J = 8.1, 2.3, 1.0$ Hz, 2H), 6.31 (s, 18 H).
\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 157.0, 153.3, 129.1, 120.0, 116.2, 115.4, 34.8, 31.3.

\(\text{HRMS (ESI+)}\) \(m/z\) calculated for C\(_{20}\)H\(_{27}\)O [M+H]\(^+\): 283.2062; found 283.2061.

4,4’-oxybis(tert-butylbenzene) (S1) was prepared from 1-bromo-4-(tert-butyl)benzene (2.10 g, 10.0 mmol, 1 equiv) and 4-(tert-butyl)phenol (2.30 g, 15.0 mmol, 1.5 equiv) according to General Procedure A. The crude product was purified by column chromatography (SiO\(_2\), 100% hexanes to 5% EtOAc in hexanes) to give ether S1 (2.60 g, 9.20 mmol, 92% yield) as a colorless oil. Spectral data are in agreement with those previously published.\(^2\)

\(^1\text{H NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) 7.33 (d, \(J = 8.7\) Hz, 4H), 6.94 (d, \(J = 8.7\) Hz, 4H), 1.32 (s, 18H).

\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 157.25, 153.55, 153.46, 134.83, 129.20, 127.67, 126.66, 126.54, 125.80, 125.77, 122.82, 122.10, 120.40, 116.50, 115.64, 112.50, 34.82, 31.28.

\(\text{HRMS (ESI+)}\) \(m/z\) calculated for C\(_{20}\)H\(_{27}\)O [M+H]\(^+\): 283.2062; found 283.2061.

\(^1\text{H NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) 7.33 (d, \(J = 8.7\) Hz, 4H), 6.94 (d, \(J = 8.7\) Hz, 4H), 1.32 (s, 18H).

\(^1\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 157.0, 153.3, 129.1, 120.0, 116.2, 115.4, 34.8, 31.3.

\(\text{HRMS (ESI+)}\) \(m/z\) calculated for C\(_{20}\)H\(_{27}\)O [M+H]\(^+\): 283.2062; found 283.2061.

\(^1\text{H NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) 7.33 (d, \(J = 8.7\) Hz, 4H), 6.94 (d, \(J = 8.7\) Hz, 4H), 1.32 (s, 18H).

\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 157.0, 153.3, 129.1, 120.0, 116.2, 115.4, 34.8, 31.3.

\(\text{HRMS (ESI+)}\) \(m/z\) calculated for C\(_{20}\)H\(_{27}\)O [M+H]\(^+\): 283.2062; found 283.2061.
1-(4-(tert-butyl)phenoxy)naphthalene (S3) was prepared from 1-bromo-4-(tert-butyl)benzene (1.71 g, 8.00 mmol, 1 equiv) and naphthalen-1-ol (1.73 g, 12.0 mmol, 1.5 equiv) according to General Procedure A. The crude product was purified by column chromatography (SiO₂, 100% hexanes) to give ether S3 (1.42 g, 5.14 mmol, 64% yield) as a white solid.

\[^{1}H \text{NMR}\] (600 MHz, CDCl₃) δ 8.26 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.41 – 7.35 (m, 3H), 7.03 – 6.98 (m, 2H), 6.96 – 6.92 (m, 1H), 1.34 (s, 9H).

\[^{13}C \text{NMR}\] (151 MHz, CDCl₃) δ 155.23, 153.43, 146.05, 134.84, 127.67, 126.75, 126.58, 126.52, 125.80, 125.77, 122.92, 122.11, 118.21, 112.84, 34.30, 31.50.

HRMS (ESI+) m/z calculated for C₂₀H₂₁O [M+H]⁺: 277.1592; found 277.1592.

III. Preparation of Benzoate Ester Derivatives

**General Procedure B**: Preparation of benzoate ester derivatives was accomplished using a modified version of a published procedure:³

methyl 2,4,6-trimethylbenzoate (S₄) To a 250 mL round bottom flask equipped with a stir bar were added 2,4,6-trimethylbenzoic acid (6.57 g, 40.0 mmol, 1 equiv), potassium carbonate (8.29 g, 60.0 mmol, 1.5 equiv) and DMF (50 mL). Iodomethane (3.00 mL, 48.0 mmol, 1.2 equiv) was slowly added to the reaction vessel and the resulting suspension was stirred vigorously at room temperature for 24 h. The reaction was poured onto 300 mL of H₂O and extracted with 3 x 300 mL portions of Et₂O. The combined organic extracts were washed with 3 x 150 mL portions of H₂O and 2 x 150 mL portions of brine. The organic layer was dried over MgSO₄, filtered, and concentrated to dryness. The residue was purified by passing through a pad of silica eluting with 1:1 EtOAc/hexanes to give methyl ester S₄ (6.28 g, 35.2 mmol, 88% yield) as a pale yellow oil. Spectral data are in agreement with those previously published.⁴

\[^{1}H \text{NMR}\] (600 MHz, CDCl₃) δ 6.85 (s, 2H), 3.89 (s, 3H), 2.28 (s, 6H), 2.28 (s, 3H).

[^3]: References for S3 and S4.
**methyl 2,6-dimethylbenzoate (S5)** was prepared from 2,6-dimethylbenzoic acid (6.50 g, 43.3 mmol, 1 equiv) using *General Procedure B* to give methyl ester S5 (6.89 g, 42.0 mmol, 97% yield) as a colorless oil. Spectral data are in agreement with those previously published.3

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.19 (t, $J$ = 7.6 Hz, 1H), 7.03 (d, $J$ = 7.6 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 6H).

**4-fluoro-2,6-dimethylbenzoic acid (S6)** was prepared using a modified version of a published procedure.5 To an oven‐dried 25 mL round bottom flask under argon atmosphere were added 2-bromo-5-fluoro-1,3-dimethylbenzene (3.07 g, 15.1 mmol, 1 equiv) and dry Et$_2$O (18.0 mL). The resulting solution was cooled to 0 °C and $n$-butyllithium (1.6 M solution in hexanes, 10.4 mL, 16.6 mmol, 1.1 equiv) was added dropwise. The solution was stirred at 0 °C for 1 h. The ice bath was removed and the reaction vessel was fitted with a balloon of CO$_2$ (equipped with a calcium sulfate drying tube) and a vent needle. Dry CO$_2$ was then bubbled through the reaction for 1 h. The reaction was quenched with 2 M HCl. The biphasic mixture was diluted with water and extracted with 3 x 50 mL portions of Et$_2$O. The combined organic layers were dried over MgSO$_4$, filtered, and concentrated. The resulting residue was purified by trituration with hexanes to give 4-fluoro-2,6-dimethylbenzoic acid (437 mg, 2.60 mmol, 17% yield) as a white solid. The product was used in the next step without any further purification.

**methyl 4-fluoro-2,6-dimethylbenzoate (S7)** was prepared from 4-fluoro-2,6-dimethylbenzoic acid (345 mg, 2.05 mmol, 1 equiv) using *General Procedure B* to give methyl ester S7 (341 mg, 1.87 mmol, 91% yield) as a colorless oil that crystallized on hi-vac.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.74 (d, $J$ = 9.4 Hz, 2H), 3.90 (s, 3H), 2.31 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 169.74, 163.49, 161.85, 138.16, 129.80, 114.46, 51.96, 19.95.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.37.

HRMS (ESI+) $m/z$ calculated for C$_{10}$H$_{12}$FO$_2$ [M+H]$^+$: 183.0821; found 183.0826.
2,6-dichlorobenzoic acid (S8) was prepared according to literature precedent.\(^6\) To an oven-dried 50 mL round bottom flask under argon atmosphere was added dry THF (12 mL). The flask was cooled to \(-78^\circ C\) and \(n\)-butyllithium (1.6 M solution in hexanes, 6.3 mL, 10 mmol, 1 equiv) was added. To the resulting cold solution was slowly added 1,3-dichlorobenzene (1.1 mL, 10 mmol, 1 equiv) and was allowed to stir at this temperature for 45 min. The reaction vessel was fitted with a balloon of CO\(_2\) (equipped with a calcium sulfate drying tube) and a vent needle. Dry CO\(_2\) was then bubbled through the reaction for 10 min at \(-78^\circ C\). The cooling bath was removed and CO\(_2\) was continuously bubbled through the solution until it reached room temperature. Formation a white precipitate was observed. The reaction was quenched with sat. NaHCO\(_3\) (aq) and the resulting biphasic mixture was diluted with H\(_2\)O and partitioned with Et\(_2\)O. The layers were separated and the organic layer was washed twice more with H\(_2\)O. The combined aqueous layers were acidified to pH 2 with conc. HCl and extracted three times with CH\(_2\)Cl\(_2\). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered, and concentrated to give crude 2,6-dichlorobenzoic acid as a viscous yellow oil. This material was used in the next step without purification.

methyl 2,6-dichlorobenzoate (S9) was prepared from 2,6-dichlorobenzoic acid (1.91 g, 10.0 mmol, 1 equiv) using General Procedure B to give methyl ester S9 (1.56 g, 7.61 mmol, 76% yield over two steps) as a colorless oil. Spectral data are in agreement with those previously published.\(^7\)

\(^{1}H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.26 (m, 3H), 3.98 (s, 3H).

ethyl 2-acetyl-3-methoxybut-2-enoate (S10) was prepared according to literature precedent.\(^8\) To an oven-dried 50 mL round bottom flask under argon atmosphere were added Cs\(_2\)CO\(_3\) (3.4 g, 11 mmol, 1.05 equiv), ethyl diacetoacetate (1.6 mL, 10 mmol, 1.01 equiv), and acetonitrile (10.5 mL). The resulting suspension was cooled in an ice water bath. With vigorous stirring, methyl trifluoromethanesulfonate (1.1 mL, 10 mmol, 1 equiv) was added to the reaction dropwise. The ice water bath was removed and the reaction was stirred vigorously at room temperature for 2
The reaction was filtered and the remaining solids were washed with Et₂O. The filtrate was diluted with Et₂O until no more precipitate formed. The suspension was filtered again to give a clear solution. The filtrate was washed twice with H₂O and once with brine. The organic layer was dried over MgSO₄, filtered, and concentrated to dryness. The residue was purified by column chromatography (SiO₂, 20% to 50% EtOAc in hexanes) to give S10 as a mixture of alkene isomers (1.16 g, 6.2 mmol, 62% yield) as a pale yellow oil.

1H NMR (Major Isomer) (600 MHz, CDCl₃) δ 4.17 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

1H NMR (Minor Isomer) (600 MHz, CDCl₃) δ 4.27 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H), 2.17 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H).

13C NMR (151 MHz, CDCl₃) δ 200.15, 194.37, 171.26, 168.52, 168.27, 166.00, 115.69, 61.08, 60.39, 55.34, 31.60, 29.83, 14.47, 14.46, 14.13, 14.06.

HRMS (ESI+) m/z calculated for C₉H₁₄O₄Na [M+Na]⁺: 209.0790; found 209.0789.

ethyl 2,4,6-trimethylpyrimidine-5-carboxylate (S11) was prepared according to literature precedent. Sodium ethoxide (6.44 mmol, 1.2 equiv) was freshly prepared in an oven-dried 25 mL round bottom flask under argon atmosphere by slowly adding sodium metal (148 mg, 6.44 mmol, 1.2 equiv) portion wise to dry EtOH (5.0 mL) at 0 °C. Upon complete consumption of the sodium metal, acetamidine hydrochloride (558 mg, 5.91 mmol, 1.1 equiv) and S10 (1.00 g, 5.37 mmol, 1 equiv) were added to the solution. The reaction flask was equipped with a condenser and the reaction mixture was refluxed for 12 h. The reaction mixture was cooled to room temperature and the resulting precipitate was filtered off and ethanol was removed under reduced pressure. The resulting residue was partitioned between H₂O and CH₂Cl₂ and the layers were separated. The aqueous layer was washed two more times with CH₂Cl₂ and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated to dryness. The residue was purified by column chromatography (SiO₂, 20% EtOAc in hexanes) to give S11 (930 mg, 4.79 mmol, 89% yield) as a pale yellow oil.

1H NMR (600 MHz, CDCl₃) δ 4.42 (q, J = 7.1 Hz, 2H), 2.67 (s, 3H), 2.51 (s, 6H), 1.40 (t, J = 7.1 Hz, 3H).

13C NMR (151 MHz, CDCl₃) δ 167.75, 167.50, 164.22, 123.62, 61.72, 26.02, 22.80, 14.16.

HRMS (ESI+) m/z calculated for C₁₀H₁₅N₂O₂ [M+H]⁺: 195.1134; found 195.1132.
IV. Preparation of Xanthylium Salts

*General Procedure C:*

\[
\begin{align*}
1. \text{sec-BuLi, TMEDA} \\
2. \text{MesCO}_2\text{Me} \\
3. \text{HCl}
\end{align*}
\]

3,6-di-tert-butyl-9-mesitylxanthylium tetrafluoroborate (3): To a flame-dried 250 mL round bottom flask under argon were added 4 (8.02 g, 28.4 mmol, 1 equiv), TMEDA (8.71 mL, 58.2 mmol, 2.05 equiv), and anhydrous n-hexane (28 mL). The resulting solution was cooled in an ice bath and sec-butyllithium (1.4 M solution in cyclohexane, 42.0 mL, 58.2 mmol, 2.05 equiv) was added dropwise. The ice bath was removed and the reaction mixture was stirred at room temperature for 4 h. The reaction was cooled to –78 °C and a solution of methyl 2,4,6-trimethylbenzoate (5.11 g, 28.7 mmol, 1.01 equiv) in anhydrous n-hexane (28 mL) was added slowly via cannula. After the addition, the reaction was allowed to slowly warm to room temperature and stirred for 12 h. The reaction was quenched with water (25 mL) and the biphasic mixture was stirred vigorously for 30 min. The mixture was diluted with 100 mL of Et₂O and the layers were separated. The organic layer was washed with water (2 x 150 mL) and brine (1 x 150 mL). The organic layer was transferred to a 250 mL round bottom flask equipped with a stir bar. To the vigorously stirred solution was added conc. HCl (12 mL) resulting in a bright yellow precipitate that slowly turned brown over the course of addition. The brown suspension was stirred vigorously for 30 min then diluted with water (150 mL). The layers were separated, and the organic layer was extracted with water (3 x 150 mL or until the washings become colorless). To the combined aqueous layers was added solid NaBF₄ (9.35 g, 85.2 mmol, 3 equiv) resulting in a bright yellow precipitate. The resulting suspension was extracted with dichloromethane (3 x 150 mL or until the washings become colorless). To the combined organic layers was added HBF₄·Et₂O complex (3.46 mL, 28.4 mmol, 1 equiv). The solution was swirled to achieve homogeneity then washed with water (1 x 100 mL) and aq. NaBF₄ (1 M, 1 x 100 mL). The organic layer was dried over solid NaBF₄, filtered, and concentrated to dryness. The residue was purified by trituration with hexanes and filtered. The solid was rinsed with n-pentane and dried in vacuo to give xanthylium 3 (10.6 g, 21.3 mmol, 75% yield) as a yellow-orange solid.

\(^1\text{H NMR}\) (600 MHz, CDCl₃) δ 8.50 (s, 2H), 7.97 – 7.88 (m, 2H), 7.76 (d, J = 8.9 Hz, 2H), 7.17 (s, 2H), 2.49 (s, 3H), 1.87 (s, 6H), 1.54 (s, 18H).

\(^13\text{C NMR}\) (151 MHz, CDCl₃) δ 174.2, 171.0, 158.4, 141.3, 135.3, 129.2, 129.1, 128.5, 127.4, 122.0, 116.7, 37.5, 30.4, 21.3, 20.1.

\(^19\text{F NMR}\) (376 MHz, CDCl₃) δ -153.90, -153.96.
3,6-di-tert-butyl-9-(2,6-dimethylphenyl)xanthylum tetrafluoroborate (5) was prepared from 3,3’-oxybis(tert-butylbenzene) (4) (305 mg, 1.08 mmol, 1 equiv) and methyl 2,6-dimethylbenzoate (S5) (179 mg, 1.09 mmol, 1.01 equiv) using General Procedure C to give xanthylum 5 (400 mg, 826 μmol, 77% yield) as a yellow solid.

1H NMR (600 MHz, CDCl3) δ 8.49 (d, J = 1.7 Hz, 2H), 7.90 (dd, J = 8.9, 1.8 Hz, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.52 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 1.89 (s, 6H), 1.52 (s, 18H).

13C NMR (151 MHz, CDCl3) δ 173.39, 171.13, 158.58, 135.46, 131.06, 130.27, 128.99, 128.59, 128.31, 121.73, 116.79, 37.56, 30.39, 20.22.

19F NMR (376 MHz, CDCl3) δ -154.00, -154.05.

HRMS (ESI+) m/z calculated for C29H33O [M]+: 397.2531; found 397.2532.

3,6-di-tert-butyl-9-(4-fluoro-2,6-dimethylphenyl)xanthylum tetrafluoroborate (6) was prepared from 3,3’-oxybis(tert-butylbenzene) (4) (500 mg, 1.77 mmol, 1 equiv) and methyl 4-fluoro-2,6-dimethylbenzoate (S6) (326 mg, 1.79 mmol, 1.01 equiv) using General Procedure C to give xanthylum 6 (493 mg, 981 μmol, 77% yield) as a yellow solid.

1H NMR (600 MHz, CDCl3) δ 8.48 (d, J = 1.2 Hz, 2H), 7.90 (dd, J = 8.9, 1.4 Hz, 2H), 7.70 (d, J = 8.9 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 1.90 (s, 6H), 1.52 (s, 18H).

13C NMR (151 MHz, CDCl3) δ 171.98, 171.12, 164.67, 163.00, 158.72, 138.62, 138.56, 128.68, 126.17, 121.97, 116.91, 115.50, 115.35, 37.57, 30.38, 20.38.
$^{19}$F NMR (376 MHz, CDCl$_3$) δ -110.39, -154.21, -154.26.

HRMS (ESI+) $m/z$ calculated for C$_{29}$H$_{32}$OF [M]$^+$: 415.2437; found 415.2437.

3,6-di-tert-butyl-9-(2,4,6-trimethylpyrimidin-5-yl)xanthylium tetrafluoroborate (7) was prepared from 3,3’-oxybis(tert-butylbenzene) (4) (500 mg, 1.77 mmol, 1 equiv) and ethyl 2,4,6-trimethylpyrimidine-5-carboxylate (S11) (322 mg, 1.79 mmol, 1.01 equiv) using General Procedure C to give xanthylium 7 (390 mg, 779 µmol, 28% yield) as a yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.47 (d, $J$ = 1.7 Hz, 2H), 7.93 (dd, $J$ = 9.0, 1.7 Hz, 2H), 7.67 (d, $J$ = 8.9 Hz, 2H), 2.89 (s, 3H), 2.17 (s, 6H), 1.53 (s, 18H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.39, 169.94, 168.08, 163.92, 158.58, 128.92, 127.74, 121.54, 121.27, 117.14, 37.63, 30.37, 26.10, 23.34.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -153.43, -153.49.

HRMS (ESI+) $m/z$ calculated for C$_{28}$H$_{33}$N$_2$O [M]$^+$: 413.2593; found 413.2594.

3,6-di-tert-butyl-9-(2,6-dichlorophenyl)xanthylium tetrafluoroborate (8) was prepared from 3,3’-oxybis(tert-butylbenzene) (4) (500 mg, 1.77 mmol, 1 equiv) and methyl 2,6-dichlorobenzoate (S9) (367 mg, 1.79 mmol, 1.01 equiv) using General Procedure C to give xanthylium 8 (426 mg, 811 µmol, 46% yield) as a yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.60 (s, 2H), 8.00 (d, $J$ = 8.9 Hz, 2H), 7.79 – 7.70 (m, 5H), 1.54 (s, 18H).
\[ ^{13}\text{C NMR} (151 \text{ MHz, CDCl}_3) \delta 172.05, 165.92, 158.97, 133.74, 133.63, 129.19, 129.15, 128.74, 128.59, 121.27, 116.94, 37.81, 30.39. \]

\[ ^{19}\text{F NMR} (376 \text{ MHz, CDCl}_3) \delta -153.40, -153.45. \]

HRMS (ESI+) \( m/z \) calculated for C\(_{27}\)H\(_{27}\)Cl\(_2\)O [M\(^+\)]: 437.1439; found 437.1440.

2,7-di-tert-butyl-9-(2,6-dimethylphenyl)xanthylium tetrafluoroborate (9) was prepared from 4,4'-oxybis(tert-butylbenzene) (S1) (1.13 g, 4.00 mmol, 1 equiv) and methyl 2,6-dimethylbenzoate (S5) (663 mg, 4.04 mmol, 1.01 equiv) using a modified version of General Procedure C (n-butyllithium was used instead of sec-butyllithium) to give xanthylium 9 (1.05 g, 2.16 mmol, 54% yield) as a yellow solid.

\[ ^{1}\text{H NMR} (600 \text{ MHz, CDCl}_3) \delta 8.65 (d, J = 9.3 \text{ Hz}, 2\text{H}), 8.61 – 8.56 (m, 2\text{H}), 7.61 (d, J = 2.1 \text{ Hz}, 2\text{H}), 7.57 (t, J = 7.8 \text{ Hz}, 1\text{H}), 7.39 (d, J = 7.8 \text{ Hz}, 2\text{H}), 1.87 (s, 6\text{H}), 1.34 (s, 18\text{H}). \]

\[ ^{13}\text{C NMR} (151 \text{ MHz, CDCl}_3) \delta 174.41, 157.12, 153.79, 143.87, 135.30, 131.31, 130.28, 128.39, 123.49, 123.43, 120.94, 35.55, 30.65, 20.26. \]

\[ ^{19}\text{F NMR} (376 \text{ MHz, CDCl}_3) \delta -152.90, -152.96. \]

HRMS (ESI+) \( m/z \) calculated for C\(_{29}\)H\(_{33}\)O [M\(^+\)]: 397.2531; found 397.2534.

10-(tert-butyl)-7-(2,6-dimethylphenyl)benzo[c]xanthen-12-ium tetrafluoroborate (10) was prepared from 1-(3-(tert-butyl)phenoxy)naphthalene (S2) (1.1 g, 4.0 mmol, 1 equiv) and methyl
2,6-dimethylbenzoate (S5) (0.66 g, 4.0 mmol, 1 equiv) using General Procedure C to give xanthylium 10 (1.2 g, 2.5 mmol, 63% yield) as an orange solid.

^1H NMR (600 MHz, CDCl₃) δ 9.58 – 9.48 (m, 1H), 8.87 – 8.74 (m, 1H), 8.18 – 8.03 (m, 4H), 7.99 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 9.1 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 1.90 (s, 6H), 1.56 (s, 9H).

^13C NMR (151 MHz, CDCl₃) δ 171.18, 169.66, 159.56, 156.93, 146.51, 138.96, 136.43, 135.25, 131.35, 131.08, 130.51, 130.40, 129.32, 129.27, 128.42, 127.30, 122.87, 122.03, 121.84, 121.37, 117.04, 37.49, 30.50, 20.22.

^19F NMR (376 MHz, CDCl₃) δ -153.65, -153.70.

HRMS (ESI+) m/z calculated for C₂₉H₂₇O [M]+: 391.2062; found 391.2060.

9-({tert-butyl}-7-(2,6-dimethylphenyl)benzo[c]xanthen-12-ium tetrafluoroborate (11) was prepared from 1-({4-({tert-butyl}phenoxy)naphthalene (S3) (553 mg, 2.00 mmol, 1 equiv) and methyl 2,6-dimethylbenzoate (S5) (332 mg, 2.02 mmol, 1.01 equiv) using General Procedure C to give xanthylium 11 (957 mg, 1.17 mmol, 58% yield) as an orange solid.

^1H NMR (600 MHz, CDCl₃) δ 9.52 – 9.45 (m, 1H), 8.92 – 8.88 (m, 1H), 8.67 (d, J = 9.0 Hz, 1H), 8.19 – 8.04 (m, 4H), 7.64 (s, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 9.1 Hz, 1H), 7.39 (d, J = 7.8 Hz, 2H), 1.89 (s, 6H), 1.35 (s, 9H).

^13C NMR (151 MHz, CDCl₃) δ 171.34, 159.81, 155.42, 154.49, 142.18, 138.82, 136.60, 135.26, 131.49, 131.17, 130.58, 130.56, 129.32, 128.46, 127.73, 123.48, 122.94, 122.32, 121.39, 121.15, 35.62, 30.78, 20.27.

^19F NMR (376 MHz, CDCl₃) δ -153.68, -153.73.

HRMS (ESI+) m/z calculated for C₂₉H₂₇O [M]+: 391.2062; found 391.2062.
V. Preparation of Acridinium Salts

General Procedure D:

3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-i um tetrafluoroborate (2): To an oven-dried 250 mL round bottom flask under argon were added 3,6-di-tert-butyl-9-mesitylxanthylum tetrafluoroborate 3 (10.0 g, 20.1 mmol, 1 equiv) and dry, degassed dichloromethane (40 mL). To the resulting solution were added acetic acid (3.40 mL, 60.2 mmol, 3 equiv) followed by NEt₃ (4.20 mL, 30.1 mmol, 1.5 equiv). Aniline (2.20 mL, 24.1 mmol, 1.2 equiv) was then added dropwise. The flask was covered with aluminum foil and stirred at room temperature for 12 h. The reaction was transferred to a separatory funnel and washed with water (1 x 50 mL) followed by sat. aq. NaHCO₃ (1 x 50 mL). To the organic layer was added HBF₄·Et₂O complex (2.44 mL, 20.1 mmol, 1 equiv). The solution was swirled to achieve homogeneity then washed with water (1 x 100 mL) and aq. NaBF₄ (1 M, 1 x 100 mL). The organic layer was dried over solid NaBF₄, filtered, and concentrated to dryness. The residue was purified by trituration with 1:2 Et₂O/hexanes and filtered. The solid was rinsed with n-pentane and dried in vacuo to give acridinium 2 (10.5 g, 18.3 mmol, 91% yield) as a bright yellow solid. Spectral data are in agreement with those previously published by our group.⁹

¹H NMR (500 MHz, CDCl₃) δ 7.96 (t, J = 7.6 Hz, 2H), 7.90 (t, J = 7.5 Hz, 1H), 7.83 – 7.75 (m, 4H), 7.72 (d, J = 7.7 Hz, 2H), 7.40 (s, 2H), 7.16 (s, 2H), 2.48 (s, 3H), 1.85 (s, 6H), 1.28 (s, 18H).

¹³C NMR (151 MHz, CDCl₃) δ 163.6, 162.3, 142.1, 140.2, 136.8, 136.1, 131.8, 131.6, 129.2, 128.9, 128.3, 128.0, 127.5, 124.0, 115.0, 36.6, 30.2, 21.3, 20.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -154.39, -154.44.

HRMS (ESI+) m/z calculated for C₃₆H₄₀N [M]+: 486.3161; found 486.3157.
3,6-di-tert-butyl-9-(2,6-dimethylphenyl)-10-phenylacridin-10-ium tetrafluoroborate (12) was prepared from xanthylum 5 (205 mg, 423 µmol, 1 equiv) and aniline (58.0 µL, 635 µmol, 1.5 equiv) using General Procedure D to give acridinium 12 (214 mg, 382 µmol, 90% yield) as a bright yellow solid.

\[ \text{1H NMR} \quad (600 \text{ MHz, CDCl}_3) \delta 7.96 (t, J = 7.7 \text{ Hz}, 2H), 7.90 (t, J = 7.5 \text{ Hz}, 1H), 7.81 - 7.73 (m, 6H), 7.50 (t, J = 7.7 \text{ Hz}, 1H), 7.42 (d, J = 1.2 \text{ Hz}, 3H), 7.35 (d, J = 7.7 \text{ Hz}, 2H), 1.90 (s, 6H), 1.29 (s, 18H). \]

\[ \text{13C NMR} \quad (151 \text{ MHz, CDCl}_3) \delta 163.58, 161.62, 142.16, 136.80, 136.30, 132.21, 131.79, 131.56, 130.17, 128.15, 128.07, 127.99, 127.55, 123.77, 115.09, 36.65, 30.17, 20.29. \]

\[ \text{19F NMR} \quad (376 \text{ MHz, CDCl}_3) \delta -154.42, -154.48. \]

\[ \text{HRMS (ESI+)} \quad m/z \text{ calculated for C}_{35}\text{H}_{38}\text{N} [\text{M}]^+: 472.3004; \text{ found 472.3003.} \]

3,6-di-tert-butyl-9-(4-fluoro-2,6-dimethylphenyl)-10-phenylacridin-10-ium tetrafluoroborate (13) was prepared from xanthylum 6 (200 mg, 398 µmol, 1 equiv) and aniline (55.0 µL, 597 µmol, 1.5 equiv) using General Procedure D to give acridinium 13 (223 mg, 386 µmol, 97% yield) as a bright yellow solid.

\[ \text{1H NMR} \quad (600 \text{ MHz, CDCl}_3) \delta 7.94 (t, J = 7.5 \text{ Hz}, 2H), 7.88 (tt, J = 7.5, 1.2 \text{ Hz}, 1H), 7.82 - 7.72 (m, 6H), 7.42 (d, J = 1.6 \text{ Hz}, 2H), 7.08 (d, J = 9.1 \text{ Hz}, 2H), 1.91 (s, 6H), 1.29 (s, 18H). \]

\[ \text{13C NMR} \quad (151 \text{ MHz, CDCl}_3) \delta 163.49, 160.31, 142.28, 139.30, 139.25, 136.91, 131.70, 131.46, 128.07, 127.74, 127.65, 124.05, 115.25, 115.16, 115.02, 36.65, 30.16, 20.42. \]
\( ^{19}F \text{NMR} \) (376 MHz, CDCl\(_3\)) \( \delta -112.10, -154.50, -154.56. \)

HRMS (ESI+) \( m/z \) calculated for C\(_{35}\)H\(_{37}\)FN [M]\(^{+}\): 490.2910; found 490.2906.

3,6-di-tert-butyl-10-phenyl-9-(2,4,6-trimethylpyrimidin-5-yl)acridin-10-ium tetrafluoroborate (14) was prepared from xanthylum 7 (91 mg, 180 \( \mu \)mol, 1 equiv) and aniline (20.0 \( \mu \)L, 220 \( \mu \)mol, 1.2 equiv) using General Procedure D to give acridinium 14 (70 mg, 120 \( \mu \)mol, 67 % yield) as a bright yellow solid.

\( ^{1}H \text{NMR} \) (500 MHz, CDCl\(_3\)) \( \delta 7.96 – 7.79 \) (m, 7H), 7.69 (d, \( J = 9.1 \) Hz, 2H), 7.45 (s, 2H), 2.90 (s, 3H), 2.18 (s, 6H), 1.30 (s, 18H).

\( ^{13}C \text{NMR} \) (151 MHz, CDCl3) \( \delta 169.07, 164.98, 163.45, 156.12, 142.35, 137.02, 131.63, 131.32, 128.18, 127.92, 126.85, 123.73, 122.92, 115.65, 36.67, 26.16, 23.17.

\( ^{19}F \text{NMR} \) (376 MHz, CDCl\(_3\)) \( \delta -154.41, -154.47. \)

HRMS (ESI+) \( m/z \) calculated for C\(_{34}\)H\(_{38}\)N\(_3\) [M]\(^{+}\): 488.3066; found 488.3064.

3,6-di-tert-butyl-9-(2,6-dichlorophenyl)-10-phenylacridin-10-ium tetrafluoroborate (15) was prepared from xanthylum 8 (208 mg, 396 \( \mu \)mol, 1 equiv) and aniline (43.0 \( \mu \)L, 597 \( \mu \)mol, 1.2 equiv) using General Procedure D to give acridinium 15 (215 mg, 358 \( \mu \)mol, 90 % yield) as a bright yellow solid.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.01 (t, $J$ = 7.5 Hz, 2H), 7.95 (t, $J$ = 7.1 Hz, 1H), 7.90 (dd, $J$ = 9.1, 1.7 Hz, 2H), 7.78 (d, $J$ = 9.1 Hz, 2H), 7.73 (s, 3H), 7.68 (d, $J$ = 7.2 Hz, 2H), 7.45 (d, $J$ = 1.6 Hz, 2H), 1.31 (s, 18H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 164.35, 155.36, 142.23, 136.47, 134.58, 132.94, 132.27, 131.85, 130.68, 129.01, 128.34, 127.62, 123.48, 115.01, 36.84, 30.14.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -154.15, -154.20.

HRMS (ESI+) m/z calculated for C$_{33}$H$_{32}$Cl$_2$N [M]+: 512.1912; found 512.1914.

2,7-di-tert-butyl-9-(2,6-diethylphenyl)-10-phenylacridin-10-ium tetrafluoroborate (16) was prepared from xanthylum 9 (200 mg, 413 $\mu$mol, 1 equiv) and aniline (57.0 $\mu$L, 619 $\mu$mol, 1.5 equiv) using General Procedure D to give acridinium 16 (215 mg, 384 $\mu$mol, 93 % yield) as a bright yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J$ = 9.5, 2.2 Hz, 2H), 7.92 (t, $J$ = 7.5, 0.8 Hz, 1H), 7.72 (d, $J$ = 7.9 Hz, 2H), 7.68 (d, $J$ = 2.0 Hz, 2H), 7.57 (d, $J$ = 9.2 Hz, 2H), 7.54 (t, $J$ = 7.7 Hz, 1H), 7.39 (d, $J$ = 7.7 Hz, 2H), 1.89 (s, 6H), 1.29 (s, 18H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 161.92, 151.95, 140.16, 137.88, 136.76, 136.08, 132.19, 131.86, 131.57, 130.33, 128.17, 127.92, 125.59, 119.96, 35.25, 30.53, 20.25.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -154.46, -154.51.

HRMS (ESI+) m/z calculated for C$_{35}$H$_{38}$N [M]+: 472.3004; found 472.3000.
9-(tert-buty1)-7-(2,6-dimethylphenyl)-12-phenylbenzo[c]acridin-12-ium tetrafluoroborate (17) was prepared from xanthylum 11 (200 mg, 418 µmol, 1 equiv) and aniline (57.3 µL, 627 µmol, 1.5 equiv) using General Procedure D to give acridinium 17 (208 mg, 376 µmol, 90 % yield) as a bright yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.18 (dd, $J = 9.6$, 2.2 Hz, 1H), 8.01 (d, $J = 7.9$ Hz, 1H), 7.98 – 7.93 (m, 3H), 7.91 (d, $J = 9.2$ Hz, 1H), 7.80 – 7.74 (m, 3H), 7.72 (dd, $J = 9.5$, 2.1 Hz, 1H), 7.67 (d, $J = 2.2$ Hz, 1H), 7.57 – 7.51 (m, 2H), 7.41 – 7.36 (m, 3H), 7.32 (tt, $J = 8.4$, 1.4 Hz, 1H), 1.89 (s, 6H), 1.29 (s, 9H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 159.92, 153.05, 142.61, 140.85, 140.17, 138.16, 136.69, 136.03, 132.95, 132.50, 132.21, 131.65, 131.58, 130.29, 130.26, 129.32, 128.30, 128.25, 127.84, 126.21, 126.07, 123.37, 122.67, 122.25, 120.63, 35.23, 30.57, 20.23.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -154.44, -154.50.

HRMS (ESI+) m/z calculated for C$_{35}$H$_{32}$N [M]$^+$: 466.2535; found 466.2531.

10-(tert-buty1)-7-(2,6-dimethylphenyl)-12-phenylbenzo[c]acridin-12-ium tetrafluoroborate (18) was prepared from xanthylum 10 (200 mg, 418 µmol, 1 equiv) and aniline (57.3 µL, 627 µmol, 1.5 equiv) using General Procedure D to give acridinium 18 (225 mg, 418 µmol, 97 % yield) as a bright yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.01 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.99 – 7.94 (m, 3H), 7.91 (d, $J = 9.1$ Hz, 1H), 7.86 (dd, $J = 8.9$, 1.6 Hz, 1H), 7.81 – 7.74 (m, 4H), 7.63 (d, $J = 1.5$ Hz, 1H), 7.55 (d, $J = 9.1$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 8.9$ Hz, 1H), 7.37 (d, $J = 7.7$ Hz, 2H), 7.32 (ddd, $J = 8.8$, 7.0, 1.5 Hz, 1H), 1.90 (s, 6H), 1.29 (s, 9H).
\textbf{13C NMR} (151 MHz, CDCl$_3$) \(\delta\) 162.26, 159.83, 142.97, 141.88, 140.90, 138.29, 136.14, 132.96, 132.43, 132.18, 132.09, 131.43, 130.18, 130.13, 129.29, 128.43, 128.37, 128.28, 127.80, 127.59, 125.74, 124.56, 123.38, 122.61, 115.93, 36.66, 30.28, 20.27.

\textbf{19F NMR} (376 MHz, CDCl$_3$) \(\delta\) -154.35, -154.40.

HRMS (ESI+) \(m/z\) calculated for C$_{35}$H$_{32}$N [M]$^+$: 466.2535; found 466.2535.

\textbf{3,6-di-tert-butyl-9-(2,6-dimethylphenyl)-10-(4-methoxyphenyl)acridin-10-ium tetrafluoroborate (19) was prepared from xanthylum 5 (97.0 mg, 200 \(\mu\)mol, 1 equiv) and 4-methoxyaniline (37.0 mg, 300 \(\mu\)mol, 1.5 equiv) using General Procedure D to give acridinium 19 (113 mg, 192 \(\mu\)mol, 96 % yield) as a green/yellow solid.}

\textbf{1H NMR} (600 MHz, CDCl$_3$) \(\delta\) 7.78 (dd, \(J = 9.0, 1.6\) Hz, 2H), 7.74 (d, \(J = 9.0\) Hz, 2H), 7.64 (d, \(J = 8.8\) Hz, 2H), 7.53 – 7.47 (m, 3H), 7.45 (d, \(J = 8.6\) Hz, 2H), 7.34 (d, \(J = 7.7\) Hz, 2H), 4.06 (s, 3H), 1.89 (s, 6H), 1.31 (s, 18H).


\textbf{19F NMR} (376 MHz, CDCl$_3$) \(\delta\) -154.48, -154.54.

HRMS (ESI+) \(m/z\) calculated for C$_{36}$H$_{40}$NO [M]$^+$: 502.3110; found 502.3106.
3,6-di-tert-butyl-9-(2,6-dimethylphenyl)-10-(4-fluorophenyl)acridin-10-ium tetrafluoroborate (20) was prepared from xanthylum 5 (100 mg, 206 μmol, 1 equiv) and 4-fluoroaniline (29.0 μL, 310 μmol, 1.5 equiv) using General Procedure D to give acridinium 20 (102 mg, 177 μmol, 86 % yield) as a bright yellow solid.

\( ^1H \text{NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.83 (dd, \( J = 8.7, 4.4 \text{ Hz}, 2H \)), 7.80 – 7.73 (m, 4H), 7.64 (t, \( J = 8.3 \text{ Hz}, 2H \)), 7.49 (t, \( J = 7.7 \text{ Hz}, 1H \)), 7.41 (s, 2H), 7.34 (d, \( J = 7.7 \text{ Hz}, 2H \)), 1.90 (s, 6H), 1.31 (s, 18H).

\( ^13C \text{NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) 163.68, 161.89, 142.44, 136.42, 132.81, 132.28, 130.56, 130.50, 130.12, 128.16, 127.48, 123.86, 118.77, 118.61, 114.96, 36.68, 30.20, 20.26.

\( ^19F \text{NMR} \) (376 MHz, CDCl\(_3\)) \( \delta \) -106.81, -154.23, -154.28.

HRMS (ESI+) \( m/z \) calculated for C\(_{35}\)H\(_{37}\)FN [M]+: 490.2910; found 490.2908.

10-benzyl-3,6-di-tert-butyl-9-(2,6-dimethylphenyl)acridin-10-ium tetrafluoroborate (26) was prepared from xanthylum 5 (500 mg, 1.03 mmol, 1 equiv) and benzylamine (169 μL, 1.55 mmol, 1.5 equiv) using General Procedure D to give acridinium 26 (548 mg, 955 μmol, 93 % yield) as a bright yellow solid.

\( ^1H \text{NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 8.31 (s, 2H), 7.79 (d, \( J = 9.0 \text{ Hz}, 2H \)), 7.73 (d, \( J = 9.0 \text{ Hz}, 2H \)), 7.50 (t, \( J = 7.7 \text{ Hz}, 1H \)), 7.43 – 7.29 (m, 7H), 6.77 (s, 2H), 1.83 (s, 6H), 1.41 (s, 18H).

\( ^13C \text{NMR} \) (151 MHz, CDCl\(_3\)) \( \delta \) 164.33, 160.97, 141.70, 135.99, 133.93, 132.27, 130.18, 129.55, 128.61, 128.45, 128.16, 127.40, 125.95, 123.95, 114.32, 54.19, 37.00, 30.37, 20.20.

\( ^19F \text{NMR} \) (376 MHz, CDCl\(_3\)) \( \delta \) -153.07, -153.12.
HRMS (ESI+) m/z calculated for C_{36}H_{40}N [M]^+: 486.3161; found 486.3157.

Preparation of acridinium salts possessing electron deficient or sterically hindered N-aryl substitution: an aminomethyl polystyrene resin was used to scavenge unreacted xanthylium from the reaction mixture and removed by filtration.

*General Procedure E*: (for reactions with solid anilines)

3,6-di-tert-butyl-9-(2,6-dimethylphenyl)-10-(4-(ethoxycarbonyl)phenyl)acridin-10-ium tetrafluoroborate (21): 3,6-di-tert-butyl-9-mesitylxanthylium tetrafluoroborate 5 (100 mg, 206 μmol, 1 equiv) and ethyl 4-aminobenzoate (51.2 mg, 310 μmol, 1.5 equiv) were added to a 1-dram vial equipped with a stir bar. The vial was evacuated and backfilled with Argon 3 times. To the vial were added dry, degassed dichloromethane (0.50 mL), acetic acid (35.0 μL, 620 μmol, 3 equiv), and NEt₃ (43.0 μL, 310 μmol, 1.5 equiv). The vial was sealed, covered with aluminum foil, and stirred at 40 °C for 24 h. The reaction mixture was cooled to room temperature and aminomethyl polystyrene resin (1.15 mmol/g loading, 270 mg, 1 equiv) was added. The resulting suspension was stirred vigorously for an additional 1 h. The reaction was then filtered and washed with CH₂Cl₂ until the washings became colorless. The filtrate was transferred to a separatory funnel and washed with water followed by sat. aq. NaHCO₃. To the organic layer was added HBF₄·Et₂O complex (28.0 μL, 206 mmol, 1 equiv). The solution was swirled to achieve homogeneity then washed with water and aq. NaBF₄ (1 M). The organic layer was dried over solid NaBF₄, filtered, and concentrated to dryness. The residue was purified by trituration with 1:1 Et₂O/hexanes and filtered. The solid was rinsed with n-pentane and dried in vacuo to give acridinium 21 (61.0 mg, 97.0 μmol, 47% yield) as a yellow solid.

**¹H NMR** (600 MHz, CDCl₃) δ 8.60 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.82 – 7.73 (m, 4H), 7.49 (t, J = 7.7 Hz, 1H), 7.36 (s, 2H), 7.34 (d, J = 7.7 Hz, 2H), 4.54 (q, J = 7.2 Hz, 2H), 1.91 (s, 6H), 1.52 (t, J = 7.2 Hz, 3H), 1.29 (s, 17H).

**¹³C NMR** (151 MHz, CDCl₃) δ 165.23, 163.71, 162.02, 141.95, 140.55, 136.46, 133.44, 132.54, 132.26, 130.11, 128.66, 128.21, 128.07, 127.49, 123.83, 114.85, 62.07, 36.67, 30.20, 20.25, 14.29.
$^{19}$F NMR (376 MHz, CDCl$_3$) δ -154.31, -154.37.

HRMS (ESI+) m/z calculated for C$_{38}$H$_{42}$NO$_2$ [M]$^+$: 544.3216; found 544.3216.

3,6-di-tert-butyl-9-(2,6-dimethylphenyl)-10-(pyridin-2-yl)acridin-10-ium tetrafluoroborate (24) was prepared from xanthylum 5 (100 mg, 206 μmol, 1 equiv) and pyridine-2-amine (29.1 mg, 310 μmol, 1.5 equiv) using General Procedure E to give acridinium 24 (44.0 mg, 79.0 μmol, 38% yield) as a brown/yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.95 (dd, J = 4.5, 1.0 Hz, 1H), 8.60 (td, J = 7.8, 1.7 Hz, 1H), 8.35 (d, J = 7.9 Hz, 1H), 7.92 (dd, J = 7.4, 5.0 Hz, 1H), 7.82 – 7.72 (m, 4H), 7.50 (t, J = 7.7 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.22 (s, 2H), 1.95 (s, 3H), 1.83 (s, 3H), 1.30 (s, 18H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.75, 162.19, 150.88, 149.95, 142.48, 141.45, 137.14, 135.49, 132.21, 130.17, 128.43, 128.06, 127.61, 127.14, 125.59, 123.73, 114.42, 36.65, 30.10, 20.34, 20.25.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -153.91, -153.97.

HRMS (ESI+) m/z calculated for C$_{34}$H$_{37}$N$_2$ [M]$^+$: 473.2957; found 473.2955.

General Procedure F: (for reactions with liquid anilines)

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -153.91, -153.97.

HRMS (ESI+) m/z calculated for C$_{33}$H$_{37}$N$_2$ [M]$^+$: 473.2957; found 473.2955.

General Procedure F: (for reactions with liquid anilines)

3,6-di-tert-butyl-9-(2,6-dimethylphenyl)-10-(4-(trifluoromethyl)phenyl)acridin-10-ium tetrafluoroborate (22): 3,6-di-tert-butyl-9-mesitylxanthylum tetrafluoroborate 5 (306 mg, 632
μmol, 1 equiv) was added to a 1-dram vial equipped with a stir bar. The vial was evacuated and backfilled with Argon 3 times. To the vial were added dry, degassed dichloromethane (0.50 mL), acetic acid (35.0 μL, 620 μmol, 3 equiv), NEt₃ (43.0 μL, 310 μmol, 1.5 equiv), and 4-(trifluoromethyl)aniline (95.0 μL, 758 μmol, 1.2 equiv). The vial was sealed, covered with aluminum foil, and stirred at 40 °C for 24 h. The reaction mixture was cooled to room temperature and aminomethyl polystyrene resin (1.15 mmol/g loading, 550 mg, 1 equiv) was added. The resulting suspension was stirred vigorously for an additional 1 h. The reaction was then filtered and washed with CH₂Cl₂ until the washings became colorless. The filtrate was transferred to a separatory funnel and washed with water followed by sat. aq. NaHCO₃. To the organic layer was added HBF₄·Et₂O complex (86.0 μL, 632 mmol, 1 equiv). The solution was swirled to achieve homogeneity then washed with water and aq. NaBF₄ (1 M). The organic layer was dried over solid NaBF₄, filtered, and concentrated to dryness. The residue was purified by trituration with 1:2 Et₂O/hexanes and filtered. The solid was rinsed with n-pentane and dried in vacuo to give acridinium 22 (188 mg, 300 μmol, 47% yield) as a yellow solid.

**1H NMR** (600 MHz, CDCl₃) δ 8.22 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H), 7.81 – 7.74 (m, 4H), 7.49 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.7 Hz, 2H), 7.31 (s, 2H), 1.91 (s, 6H), 1.29 (s, 18H).

**13C NMR** (151 MHz, CDCl₃) δ 163.89, 162.30, 141.99, 140.03, 136.47, 134.03, 133.81, 133.59, 133.37, 132.23, 130.13, 129.42, 128.58, 128.29, 128.08, 127.51, 124.17, 123.86, 122.36, 114.67, 36.68, 30.15, 20.26.

**19F NMR** (376 MHz, CDCl₃) δ -62.70, -154.20, -154.26.

**HRMS** (ESI+) m/z calculated for C₃₆H₃₇F₃N [M]+: 540.2878; found 540.2879.

10-(3,5-bis(trifluoromethyl)phenyl)-3,6-di-tert-butyl-9-(2,6-dimethylphenyl)acridin-10-ium tetrafluoroborate (23) was prepared from xanthylum 5 (300 mg, 619 μmol, 1 equiv) and 3,5-bis(trifluoromethyl)aniline (116 μL, 743 μmol, 1.2 equiv) using General Procedure F to give acridinium 23 (82.0 mg, 120 μmol, 19 % yield) as a brown/yellow solid.

**1H NMR** (600 MHz, CDCl₃) δ 8.51 (s, 2H), 8.40 (s, 1H), 7.82 – 7.76 (m, 4H), 7.49 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.7 Hz, 2H), 7.23 (s, 2H), 1.90 (s, 6H), 1.30 (s, 18H)
\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 164.41, 163.36, 142.06, 138.68, 136.57, 135.34, 135.11, 134.88, 134.64, 132.16, 130.18, 128.71, 128.07, 127.58, 125.25, 124.09, 123.18, 121.37, 114.21, 36.73, 30.10, 20.15.

\(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)) \(\delta\) -62.72, -153.84, -153.89.

\(\text{HRMS (ESI\(^+\)) m/z calculated for C}\(_{37}\)H\(_{36}\)F\(_6\)N [M]\(^+\): 608.2752; found 608.2747.

3,6-di-tert-butyl-9,10-bis(2,6-dimethylphenyl)acridin-10-ium tetrafluoroborate (25) was prepared from xanthylium 5 (183 mg, 378 \(\mu\)mol, 1 equiv) and 2,6-dimethylaniline (56.0 \(\mu\)L, 453 \(\mu\)mol, 1.2 equiv) using General Procedure F to give acridinium 25 (125 mg, 213 \(\mu\)mol, 56 % yield) as a light orange solid.

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 7.90 (dd, \(J = 9.1, 1.7 \text{ Hz}, 2\text{H}\)), 7.85 (d, \(J = 9.0 \text{ Hz}, 2\text{H}\)), 7.73 (t, \(J = 7.7 \text{ Hz}, 1\text{H}\)), 7.61 (d, \(J = 7.7 \text{ Hz}, 2\text{H}\)), 7.54 (t, \(J = 7.7 \text{ Hz}, 1\text{H}\)), 7.39 (d, \(J = 7.7 \text{ Hz}, 2\text{H}\)), 7.35 (d, \(J = 1.6 \text{ Hz}, 2\text{H}\)), 1.88 (s, 6\text{H}), 1.81 (s, 6\text{H}), 1.31 (s, 18\text{H}).

\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 165.63, 162.33, 140.67, 135.72, 134.64, 134.45, 132.19, 131.73, 130.54, 128.88, 128.38, 128.18, 123.87, 112.98, 36.79, 30.33, 20.17, 16.93.

\(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)) \(\delta\) -154.30, -154.36.

\(\text{HRMS (ESI\(^+\)) m/z calculated for C}\(_{37}\)H\(_{42}\)N [M]\(^+\): 500.3317; found 500.3317.

*Synthesis of Acridinium 27:*

2,7-di-tert-butyl-9-(2,6-dichlorophenyl)xanthylium tetrafluoroboratetetrafluoroborate (S12) was prepared from 4,4'-oxybis(tert-butylbenzene) (S1) (293 mg, 1.04 mmol, 1 equiv) and methyl
2,6-dichlorobenzoate (S9) (215 mg, 1.05 mmol, 1.01 equiv) using General Procedure C to give xanthylum S12 (167 mg, 318 μmol, 31% yield) as an orange-brown solid.

$^1$H NMR (600 MHz, Chloroform-δ) δ 8.74 (dd, J = 9.2, 2.1 Hz, 2H), 8.69 (d, J = 9.2 Hz, 2H), 7.84 – 7.76 (m, 3H), 7.59 (d, J = 2.0 Hz, 2H), 1.38 (s, 18H).

$^{13}$C NMR (151 MHz, CDCl₃) δ 166.57, 157.54, 154.45, 144.74, 133.93, 133.60, 129.20, 128.75, 122.99, 122.75, 121.12, 35.71, 30.56.

$^{19}$F NMR (376 MHz, CDCl₃) δ -152.70, -152.76.

HRMS (ESI+) m/z calculated for C₂₇H₂₇Cl₂O [M]+: 437.1439; found 437.1416.

10-benzyl-2,7-di-tert-butyl-9-(2,6-dichlorophenyl)acridin-10-ium tetrafluoroborate (27) was prepared from xanthylum S12 (100 mg, 190 μmol, 1 equiv) and benzylamine (22.9 μL, 1.55 mmol, 1.1 equiv) using General Procedure D to give acridinium 27 (94 mg, 150 μmol, 80 % yield) as a bright yellow solid.

$^1$H NMR (600 MHz, CDCl₃) δ 8.52 (d, J = 9.6 Hz, 2H), 8.38 (dd, J = 9.6, 2.1 Hz, 2H), 7.77 – 7.68 (m, 3H), 7.58 (d, J = 2.0 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.20 (d, J = 7.1 Hz, 2H), 6.88 (s, 2H), 1.33 (s, 18H).

$^{13}$C NMR (151 MHz, CDCl₃) δ 154.46, 152.41, 139.88, 139.08, 134.59, 133.23, 132.65, 131.22, 129.50, 128.85, 128.68, 125.82, 125.55, 122.13, 119.16, 54.43, 35.31, 30.43.

$^{19}$F NMR (376 MHz, CDCl₃) δ -152.72, -152.77.

HRMS (ESI+) m/z calculated for C₃₄H₃₄Cl₂N [M]+: 526.2068; found 526.2037.
VI. Spectrophotometric and Electrochemical Data

![Chemical Structure]

![Absorbance and Emission Spectra](300,350,700)

![Cyclic Voltammetry](400,500,700)

$E_{\text{H0}} =$ 2.66 eV

$E_{\text{red}} =$ -0.53 V vs. Ag/AgCl (-0.66 vs. SCE)
\[ E_{0,0} = 2.66 \text{ eV} \]
\[ E_{1/2}(C/C^-) = -0.56 \text{ V vs. SCE} \]
\[ E_{1/2}(C^*/C^-) = 2.66 + (-0.56) = 2.10 \text{ V vs. SCE} \]
\[ \tau = 13.8 \text{ ns} \]
$E_{0,0} = 2.67 \text{ eV}$

$E_{\text{re}} = -0.83 \text{ V vs. Ag/AgCl} (-0.56 \text{ vs. SCE})$

$E_{0,0} = 2.67 \text{ eV}$
\[ E_{1/2}(C^*/C^-) = 2.67 + (-0.56) = 2.11 \text{ V vs. SCE} \]

\[ \tau = 16.4 \text{ ns} \]
\[ E_{0,0} = 2.67 \text{ eV} \]

\[ E_{1/2}(C/C^-) = -0.54 \text{ V vs. SCE} \]

\[ E_{1/2}(C^*/C^-) = 2.67 + (-0.54) = 2.13 \text{ V vs. SCE} \]

\[ \tau = 16.8 \text{ ns} \]
$E_{0,0} = 2.63$ eV

$E_{1/2}(C/C^-) = -0.47$ V vs. SCE

$E_{1/2}(C*/C^-) = 2.63 + (-0.47) = 2.16$ V vs. SCE

$\tau = 16.1$ ns
$E_{00} = 2.64 \text{ eV}$
\[ E_{1/2}(C^-/C^-) = -0.43 \text{ V vs. SCE} \]

\[ E_{1/2}(C^*/C^-) = 2.64 + (-0.43) = 2.21 \text{ V vs. SCE} \]

\[ \tau = 17.1 \text{ ns} \]
$E_{0,0} = 2.62$ eV

$E_{1/2}^{\text{C/C}} = -0.53$ V vs. SCE

$E_{1/2}^{\text{C*/C}} = 2.62 + (-0.53) = 2.09$ V vs. SCE

$\tau = 19.0$ ns
$E_{0,0} = 2.60 \text{ eV}$

$E_{1/2}(C/C^-) = -0.53 \text{ V vs. SCE}$

$E_{1/2}(C^*/C^-) = 2.60 + (-0.53) = 2.07 \text{ V vs. SCE}$

$\tau_1 = 0.3 \text{ ns}, \tau_2 = 16.8 \text{ ns}$
$E_{0,0} = 2.60 \text{ eV}$

$E_{1/2}(C/\text{C}^-) = -0.54 \text{ V vs. SCE}$

$E_{1/2}(\text{C}^*/\text{C}^-) = 2.60 + (-0.54) = 2.06 \text{ V vs. SCE}$

$\tau_1 = 0.3 \text{ ns}, \tau_2 = 16.6 \text{ ns}$
$E_{0,0} = 2.63$ eV

$E_{1/2}(C/C^-) = -0.58$ V vs. SCE

$E_{1/2}(C^*/C^-) = 2.63 + (-0.58) = 2.05$ V vs. SCE

$\tau_1 = 1.1$ ns, $\tau_2 = 18.8$ ns
$E_{00} = 2.66 \text{ eV}$

![Graph showing absorbance and emission spectra with normalized intensity vs. wavelength (nm).]

![Graph showing current vs. potential (V) with E_{00} = -0.52 \text{ V vs. Ag/AgCl} (4.05 \text{ vs. SCE}).]

![Graph showing count rate vs. time (ns) with residuals and fit results.]

$E_{0,0} = 2.66 \text{ eV}$
$E_{1/2}(C/\text{C}^-) = -0.55 \text{ V vs. SCE}$

$E_{1/2}(\text{C}*/\text{C}^-) = 2.66 + (-0.55) = 2.11 \text{ V vs. SCE}$

$\tau = 17.6 \text{ ns}$
$E_{0,0} = 2.66$ eV

$E_{1/2}(C/C^-) = -0.54$ V vs. SCE

$E_{1/2}(C^*/C^-) = 2.66 + (-0.54) = 2.12$ V vs. SCE

$\tau = 18.4$ ns
$E_{0,0} = 2.65 \text{ eV}$

$E_{1/2}(C/C^-) = -0.51 \text{ V vs. SCE}$

$E_{1/2}(C^*/C^-) = 2.65 + (-0.51) = 2.14 \text{ V vs. SCE}$

$\tau = 20.7 \text{ ns}$

![Chemical Structure](image)
$E_{0,0} = 2.64 \text{ eV}$

Counts Residuals

$\tau_1 = 20.75 \text{ ns}$

$\chi^2 = 1.380$
$E_{0,0} = 2.64 \text{ eV}$

$E_{1/2}(C/C^-) = -0.45 \text{ V vs. SCE}$

$E_{1/2}(C^*/C^-) = 2.64 + (-0.45) = 2.19 \text{ V vs. SCE}$

$\tau = 20.7 \text{ ns}$
\[ E_{0,0} = 2.67 \, \text{eV} \]

\[ E_{1/2}(C/C^-) = -0.50 \, \text{V vs. SCE} \]

\[ E_{1/2}(C^*/C^-) = 2.67 + (-0.50) = 2.17 \, \text{V vs. SCE} \]

\[ \tau_1 = 2.7 \, \text{ns}, \tau_2 = 19.1 \, \text{ns} \]
$E_{0,0} = 2.67 \text{ eV}$

Normalized Intensity

Wavelength (nm)

$E_{ab} = 0.30 \text{ V vs. Ag/AgCl (0.03 vs. SCE)}$

Current / A

Potential / V
$E_{0,0} = 2.67 \text{ eV}$

$E_{1/2}(C/C^-) = -0.53 \text{ V vs. SCE}$

$E_{1/2}(C^*/C^-) = 2.67 + (-0.53) = 2.14 \text{ V vs. SCE}$

$\tau = 22.8 \text{ ns}$
$E_{0,0} = 2.67 \text{ eV}$

$E_{1/2}(C/C^-) = -0.54 \text{ V vs. SCE}$

$E_{1/2}(C^*/C^-) = 2.67 + (-0.54) = 2.13 \text{ V vs. SCE}$

$\tau = 23.7 \text{ ns}$
$E_{0,0} = 2.59 \text{ eV}$

$E_{1/2}(\text{C}/\text{C}^-) = -0.39 \text{V vs. SCE}$

$E_{1/2}(\text{C}^*/\text{C}^-) = 2.59 + (-0.39) = 2.20 \text{ V vs. SCE}$

$\tau = 25.7 \text{ ns}$
VII. References


VIII. NMR Spectra

![NMR Spectra Diagram](image)

4

S55
11

2
S83
S93