Core Remodeling Leads to Long Wavelength Fluoro-Coumarins

Siddharth S. Matikonda, Joseph Ivanic, Miguel Gomez, Gabrielle Hammersley, Martin J. Schnermann

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Section S1: General Materials and Methods

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (passed through activated alumina columns). All commercially obtained reagents were used as received. Dulbecco’s modified Eagle’s Medium (DMEM), fetal bovine serum (FBS), Hank’s balanced salt solution (HBSS), phenol red-free DMEM, and phosphate-buffered saline (PBS) was purchased from Quality Biologicals. Organelle stains, To-Pro™-3 iodide (642/661) and BODIPY 493/503 were purchased from Thermo Fisher and used as advised. MemBrite Fix 488/515 was purchased from Biotium and used according to the protocol provided. Flash column chromatography was performed using reversed phase (100 Å, 20-40-micron particle size, RediSep® Rf Gold® Reversed-phase C18 or C18Aq) and silica on a CombiFlash® Rf 200i (Teledyne Isco, Inc.). High-resolution LC/MS analyses were conducted on a Thermo-Fisher LTQ-Orbitrap-XL hybrid mass spectrometer system with an Ion MAX API electrospray ion source in negative ion mode. Analytical LC/MS was performed using a Shimadzu LC/MS-2020 Single Quadrupole utilizing a Kinetex 2.6 μm C18 100 Å (2.1 × 50 mm) column obtained from Phenomenex, Inc. Runs employed a gradient of 0→90% MeCN/0.1% aqueous formic acid over 4.5 min at a flow rate of 0.2 mL/min. 1H NMR and 13C NMR spectra were recorded on Bruker spectrometers (at 400 or 500 MHz or at 100 or 125 MHz, respectively) and are reported relative to deuterated solvent signals (and CDFCl₂ for 19F NMR). Data for 1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for 13C, 1H and 19F NMR spectra are reported in terms of chemical shift. Absorption curves for quantum yield measurements were performed on a Shimadzu UV-2550 spectrophotometer operated by UVProbe 2.32 software. Fluorescence traces were recorded on a PTI QuantaMaster steady state spectrofluorometer operated by FelixGX 4.2.2 software, with 5 nm excitation and emission slit widths, 0.1 s integration rate, and enabled emission correction. Data analysis and curve fitting were performed using MS Excel 2011 and GraphPad Prism 7. Light intensity measurements were performed with a Thorlabs PM200 optical power and energy meter fitted with an S120VC standard Si photodiode power sensor (200-1100 nm, 50 mW). Cellular imaging was performed using a Zeiss LSM 810 confocal laser-scanning microscope. Cells were plated on CELLview™ slides, advanced TCTM Surface and sterile (VWR). Image processing was conducted using Icy software.
Section S2: Synthesis

Synthesis of \(1,1\)-difluoro-7-hydroxynaphthalen-2(1H)-one (FC1)

\[
\begin{array}{c}
\text{HO} & \text{OH} \\
& & \\
& & \text{Selectfluor, H}_2\text{O} \\
& & \text{r.t., 10 min, 28%}
\end{array}
\]

This compound was prepared through a modified version of the original procedure, which provides more reproducible yields. A solution of naphthalene-2,7-diol (2.0 g, 12.4 mmol) and Selectfluor (8.84 g, 24.9 mmol) dissolved in water (12.5 mL) was allowed to stir at room temperature. The progress of the reaction was monitored using thin-layer chromatography (TLC) and upon completion (10 min), the reaction mixture was quenched using sat. NH\(_4\)Cl (20 mL), neutralized with sat. NaHCO\(_3\) (50 mL) and extracted using DCM (~400 mL). The organic fraction was washed with H\(_2\)O (2 \times 100 mL) and brine (50 mL) then dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (24 g silica; 0 → 20% EtOAc: Hexane) to result in FC1 (687 mg, 28%) as an amorphous yellow powder, which was spectroscopically similar to that previously reported.\(^1\) \(\text{H} NMR (400 MHz, \text{MeOD}) \delta 7.56 (d, J = 10.0 \text{ Hz}, 1\text{H}), 7.35 (d, J = 8.4 \text{ Hz}, 1\text{H}), 7.20 (m, 1\text{H}), 6.95 (m, 1\text{H}), 6.01 (dt, J = 10.0, 2.8 \text{ Hz}, 1\text{H}).

Synthesis of 7-(diethylamino)naphthalen-2-ol (2):

\[
\begin{array}{c}
\text{HO} & \text{OH} \\
& & \\
& & \text{Diethylamine, Na}_2\text{S}_2\text{O}_3 \\
& & \text{H}_2\text{O} \quad 150 \degree \text{C, 15 h, 27%}
\end{array}
\]

In a pressure tube, a solution of naphthalene-2,7-diol 1 (10.0 g, 62.48 mmol) and sodium metabisulfite (23.7 g, 0.124 mol) in water (32 mL) was prepared. To this solution, diethylamine (22.8 g, 0.31 mol) was added and the tube was sealed. The contents in the pressure tube were heated to 150 °C for 15 h. After this time, the cooled reaction mixture was transferred to a separating funnel and basified to a pH = 12 using 1M NaOH. The organics were extracted using EtOAc (300 mL), washed with brine (100 mL), dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (330 g silica; 0 → 25% EtOAc in Hexane) to result in 2 (3.7 g, 27%) as a brown viscous liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.67 (d, J = 9.0 \text{ Hz}, 2\text{H}), 7.62 (d, J = 9.0 \text{ Hz}, 1\text{H}), 7.03 (dd, J = 9.0, 2.5 \text{ Hz}, 1\text{H}), 6.99 (s, 1\text{H}), 6.91 (dd, J = 9.0, 2.0 \text{ Hz}, 1\text{H}), 6.79 (d, J = 2.5 \text{ Hz}, 1\text{H}), 6.54 (s, 1\text{H}) 3.46 (q, J = 7.0 \text{ Hz}, 4\text{H}), 1.25 (t, J = 7.0 \text{ Hz}, 6\text{H}). \(^13\)C \(^1\)H NMR (125 MHz, CDCl\(_3\)) \(\delta 154.0, 146.3, 136.6, 129.3, 128.8, \ldots\)
122.1, 114.1, 113.8, 108.1, 105.3, 44.6, 12.5. HRMS (ESI) m/z: [M+H]+ Calcd. for C_{14}H_{17}NO 216.1310; Found 216.1306.

**Synthesis of 7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (FC2):**

**Acidic conditions:** To a cooled suspension (ice bath) of 7-(diethylamino)naphthalen-2-ol 2 (1.7 g, 7.90 mmol) in H₂O (36 mL) was added TFA (4 mL, 10 vol%) and allowed to stir for 10 min. To this solution, Selectfluor (6.2 g, 17.4 mmol) dissolved in H₂O (15 mL) was added dropwise over 20 min. The reaction mixture was allowed to warm to 0 °C and stirred for 30 min. The progress of the reaction was monitored using LC/MS and TLC (every aliquot collected for analysis was quenched with a sat. NH₄Cl and neutralized with sat. NaHCO₃). Upon completion (1 h), the reaction mixture was quenched using sat. NH₄Cl (50 mL) and transferred to a conical flask and cooled to 0 °C in an ice bath. Sat. NaHCO₃ was slowly added to set the pH of the aqueous mixture between 7 – 8, after which the organics were extracted using EtOAc (2 × 150 mL). The organic fraction was washed with H₂O (2 × 150 mL) and brine (2 × 100 mL) then dried (Na₂SO₄) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (40 g silica; 0→15% EtOAc: Hexane) to result in FC2 (1.63 g, 82%) as a thick viscous dark red liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 10.0 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.10 – 7.03 (m, 1H), 6.71 (dd, J = 8.8, 2.4 Hz, 1H), 5.83 (dt, J = 9.6, 3.2 Hz, 1H), 3.43 (q, J = 7.2 Hz, 4H), 1.14 (t, J = 6.8 Hz, 6H). ¹³C {¹H} NMR (100 MHz, CD₃CN) δ 188.3 (t, Jₐ-C = 24 Hz), 150.8 (t, Jₐ-C = 1 Hz), 148.6, 136.3 (t, Jₐ-C = 22 Hz), 133.4, 117.8 (t, Jₐ-C = 5 Hz), 117.4 (t, Jₐ-C = 2 Hz), 113.8, 111.8 (t, Jₐ-C = 4 Hz), 107.3 (t, Jₐ-C = 243 Hz), 45.3, 12.7. ¹⁹F NMR (376 MHz, CD₃CN) –99.25. HRMS (ESI) m/z: [M+H]+ Calcd. for C_{14}H_{16}F₂NO 252.1194; Found 252.1191.

**Optimal basic conditions:** A solution of 7-(diethylamino)naphthalen-2-ol 2 (696 mg, 2.77 mmol) in THF was cooled to –78 °C. To this solution, LiHMDS (3.81 mL of a 1M solution, 638 mg, 3.81 mmol) was added dropwise over 10 min at –78 °C and allowed to stir for 30 min under argon. In
a separate flask, a solution of Selectfluor (1.38 g, 3.90 mmol) was dissolved in DMF and added to the first mixture dropwise over 20 min at –78 °C under argon. The reaction mixture was allowed to warm to 0 °C and stirred for 1 h. The progress of the reaction was monitored using LC/MS and TLC (every aliquot collected for analysis was quenched with a sat. NH₄Cl). Upon completion (1 h), the reaction mixture was quenched using sat. NH₄Cl (50 mL) and extracted using EtOAc (200 mL). The organic fraction was washed with H₂O (2 × 50 mL) and brine (2 × 30 mL) then dried (Na₂SO₄) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (120 g silica; 0→15% EtOAc: Hexane) to result in FC2 (311 mg, 38%) as a thick viscous dark red liquid.

**Synthesis of 7-(diethylamino)-1,1-difluoro-3-(trifluoromethyl)naphthalen-2(1H)-one (FC3):**

A solution of 7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one FC2 (100 mg, 0.40 mmol), 1-Trifluoromethyl-1,2-benziodoxol-3(1H)-one [Togni-II reagent]¹ (378 mg, 1.19 mmol) and copper iodide (7.6 mg, 10 mol%) in DMF (1 mL, 0.4 M), was heated to 80 °C for 24 h under argon. The progress of the reaction was monitored using LC/MS and TLC. Upon completion (24 h), the reaction was quenched by the addition of water (5 mL) and the organics were extracted using EtOAc (100 mL). The organic fraction was washed with H₂O (2 × 100 mL) and brine (100 mL) then dried (Na₂SO₄) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (24 g silica; 0→10% EtOAc: Hexane) to result in FC3 (92 mg, 72%) as a thick viscous dark red liquid: ¹H NMR (400 MHz, CD₃CN) δ 7.95 (s, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.19 – 7.14 (m, 1H), 6.82 (dd, J = 8.8, 2.8 Hz, 1H), 3.51 (q, J = 6.8 Hz, 4H), 1.19 (t, J = 6.8 Hz, 6H).¹³C {¹H} NMR (125 MHz, CD₃CN) δ 183.8 (t, J_C-F = 26 Hz), 152.9 (t, J_C-F = 1 Hz), 148.9 (q, J_C-F = 10, 5 Hz), 137.7 (t, J_C-F = 22 Hz), 136.5, 123.9 (q, J_C-F = 269, 2 Hz), 116.1 (qt, J_C-F = 61, 31, 3 Hz), 114.6 (t, J_C-F = 5 Hz), 114.1, 112.8 (t, J_C-F = 4 Hz), 107.4 (t, J_C-F = 243 Hz), 46.0, 13.0. ¹⁹F NMR (376 MHz, CD₃CN) –63.13, –98.68. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₅H₁₅F₃NO 320.1062; Found 320.1062.

**Synthesis of 3-bromo-7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (FC4):**

¹ The reaction was higher yielding when Togni-II reagent was used compared to Togni-I reagent.
A solution of 7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one **FC2** (10 mg, 0.04 mmol) and N-bromosuccinamide (8.5 mg, 0.05 mmol) in MeCN (300 µL), was stirred at r.t. for 15 h under argon. The progress of the reaction was monitored using LC/MS and TLC. Upon completion (15 h), the reaction was quenched by the addition of water (5 mL) and the organics were extracted using EtOAc (30 mL). The organic fraction was washed with H₂O (2 × 10 mL) and brine (10 mL) then dried (Na₂SO₄) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (4 g silica; 0→7.5% EtOAc: Hexane) to result in **FC4** (13 mg, 95%) as a thick viscous maroon liquid: ¹H NMR (500 MHz, CDCl₃) δ 7.70 (s, 1H), 7.12 (d, J = 8.5 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.62 (dd, J = 9.0, 2.5 Hz, 1H), 3.45 (q, J = 7.5 Hz, 4H), 1.23 (t, J = 7.0 Hz, 6H). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 181.8 (t, J_C-F = 25 Hz), 150.0, 148.6, 135.4 (t, J_C-F = 23 Hz), 132.1, 116.8 (t, J_C-F = 5 Hz), 112.6 (t, J_C-F = 5 Hz), 111.8 (t, J_C-F = 4 Hz), 110.7 (t, J_C-F = 3 Hz), 106.7 (t, J_C-F = 246 Hz), 44.8, 12.5. ¹⁹F NMR (376 MHz, CDCl₃) –97.53. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₄H₁₅BrF₂NO₃ 332.0380; Found 332.0371.

**Synthesis of 7-(diethylamino)-1,1-difluoro-4-phenynaphthalen-2(1H)-one (FC5):**

7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (**FC2**) (95 mg, 0.38 mmol), phenyl boronic acid (52 mg, 0.43 mmol), palladium acetate (81 mg, 0.36 mmol) and 5-NO₂-1,10-phenanthroline (81 mg, 0.36 mmol) were sealed in a microwave vial. This reaction vessel was purged with O₂, following which DMF (4.5 mL) was added. The solvent was further purged with O₂ for 10 minutes and then the reaction mixture was heated to 80 °C. The progress of the reaction was monitored using LC/MS and TLC. Upon completion (4 h), water (5 mL) was added to the reaction mixture and the organics were extracted using EtOAc (100 mL). The organic fraction was washed with H₂O (2 × 50 mL) and brine (50 mL) then dried (Na₂SO₄) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (24 g silica; 0→7.5% EtOAc: Hexane) to result in **FC5** (86 mg, 69%) as a thick viscous dark red liquid: ¹H NMR (400 MHz,
CDCl$_3$ δ 7.52 – 7.35 (m, 5H), 7.17 (dt, $J = 3.2$, 1.6 Hz, 1H), 7.09 (dt, $J = 8.8$, 1.2 Hz, 1H), 6.56 (dd, $J = 9.2$, 3.2 Hz, 1H), 5.91 (t, $J = 2.8$ Hz, 1H), 3.45 (q, $J = 7.2$ Hz, 4H), 1.22 (t, $J = 6.8$ Hz, 6H). $^{13}$C $^{1}$H NMR (125 MHz, CDCl$_3$) δ 187.4 (t, $J_{C-F} = 24$ Hz), 159.2, 149.5, 137.8, 136.2 (t, $J_{C-F} = 23$ Hz), 131.8, 129.4, 128.7, 128.3, 117.7 (t, $J_{C-F} = 2$ Hz), 117.4 (t, $J_{C-F} = 4$ Hz), 112.0, 111.5 (t, $J_{C-F} = 4$ Hz), 106.6 (t, $J_{C-F} = 243$ Hz), 44.8, 12.7. $^{19}$F NMR (376 MHz, CDCl$_3$) –100.48 (d, $J_{C-F} = 4$ Hz). HRMS (ESI) m/z: [M+H]$^+$ Calcd. for C$_{220}$F$_2$NO 328.1507; Found 328.1503.

6-(diethylamino)-4,4-difluoro-3-oxo-3,4-dihydronaphthalene-1-carbonitrile (FC6):

**Step 1:** 7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (FC2) (165 mg, 0.66 mmol) was reacted with tert-butylammonium cyanide (353 mg, 1.31 mmol) in MeCN (3 mL) for 2.5 h. The progress of the reaction was monitored by LC/MS and after the starting material was consumed resulting in the formation of a peak at m/e = 259.1, the reaction was quenched by the addition of water (5 mL). The organics were extracted into EtOAc (100 mL) and washed with water (2 × 50 mL), brine (50 mL), dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (24 g silica; 0→10% EtOAc: Hexane) to result in 115 mg (yield = 68%) of the intermediate which was subjected to fluorination.

**Step 2:** To a solution of the previous intermediate (115 mg, 0.45 mmol) in MeCN (5 mL), Selectfluor (158 mg, 0.45 mmol) was added in small batches. The reaction was allowed to stir at r.t. for 1 h and the progress of the reaction was monitored using LC/MS. Upon completion (1 h), the reaction was quenched by the addition of sat. NH$_4$Cl (20 mL) and the organics were extracted using EtOAc (50 mL). The organic fraction was washed with H$_2$O (2 × 25 mL) and brine (25 mL) then dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude mixture was purified using normal-phase column chromatography (24 g silica; 0→5 % EtOAc: Hexane) to result in FC6 (63 mg, 35% [two steps]) as a thick viscous purple liquid.$^1$H NMR (400 MHz, CD$_3$CN) δ 7.53 (d, $J = 8.8$ Hz, 1H), 7.21 – 7.16 (m, 1H), 6.85 (dd, $J = 8.8$, 2.8 Hz, 1H), 6.36 (t, $J = 2.8$ Hz, 1H), 3.51 (q, $J = 7.2$ Hz, 4H), 1.19 (t, $J = 7.2$ Hz, 6H). $^{13}$C $^{1}$H NMR (125 MHz, CDCl$_3$) δ 186.2 (t, $J_{C-F} = 25$ Hz), 150.7, 135.4 (t, $J_{C-F} = 23$ Hz), 130.9, 129.1, 122.3 (t, $J_{C-F} = 3$ Hz), 115.2, 113.0 (t, $J_{C-F} = 5$ Hz),
112.6, 112.3 (t, J_{C,F} = 4 Hz), 105.7 (t, J_{C,F} = 245 Hz), 45.2, 12.6. \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)) – 98.31. HRMS (ESI) m/z: [M+H]\(^+\) Calcd. for C\(_{15}\)H\(_7\)F\(_2\)N\(_2\)O\(_2\) 277.1147; Found 277.1144.

(E)-2-(7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-ylidene)acetonitrile (FC7):

7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (FC2) (50 mg, 0.19 mmol) and (Triphenylphosphoranylidene)acetonitrile 3 (90 mg, 0.30 mmol) were added to a 1-dram vial and purged with N\(_2\). This mixture was dissolved in DCM (500 µL) under N\(_2\) and allowed to stir at r.t. for 15 h. The progress of the reaction was monitored by LC/MS and after the starting material was consumed (15 h), the reaction mixture was concentrated to as minimum MeCN as possible. The organics were extracted into EtOAc (10 mL) and washed with water (2 × 10 mL), brine (10 mL), dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (4 g silica; 0→10% EtOAc: Hexane) to result in FC7 (37 mg, 68%) as bright orange solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.12 (dt, J = 8.8, 1.6 Hz, 1H), 7.05 (m, 1H), 6.71 (d, J = 9.6 Hz, 1H), 6.67 (dd, J = 8.8, 2.8 Hz, 1H), 6.52 (dtd, J = 9.2f, 2.4, 0.8 Hz, 1H), 5.89 – 5.85 (m, 1H), 3.43 (q, J = 7.2 Hz, 4H), 1.21 (t, J = 7.2 Hz, 6H). \(^{13}\text{C}\) \(^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.2 (t, J\(_{C,F}\) = 21 Hz), 148.6, 133.6, 132.2 (t, J\(_{C,F}\) = 23 Hz), 130.4, 119.0 (t, J\(_{C,F}\) = 7 Hz), 116.0 (t, J\(_{C,F}\) = 4 Hz), 115.4 (t, J\(_{C,F}\) = 4 Hz), 113.0, 112.4 (d, J\(_{C,F}\) = 238 Hz), 108.9 (t, J\(_{C,F}\) = 4 Hz), 96.7 (t, J\(_{C,F}\) = 21 Hz), 44.6, 12.5. \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)) –78.92. HRMS (ESI) m/z: [M+H]\(^+\) Calcd. for C\(_{16}\)H\(_7\)F\(_2\)N\(_2\)O\(_2\) 275.1354; Found 275.1349.

2-(7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-ylidene)malononitrile (FC8):

7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (FC2) (50 mg, 0.19 mmol) was reacted with malononitrile (53 mg, 0.80 mmol), ammonium acetate (15 mg, 0.20 mmol) and glacial acetic acid (210 µL) in toluene (2.1 mL) under N\(_2\) at 60 °C for 8 h. The progress of the reaction was monitored by LC/MS and after the starting material was consumed (8 h), water (5 mL) was added to the reaction mixture. The organics were extracted into EtOAc (50 mL) and washed with water (2 × 25
mL) and brine (25 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (24 g silica; 0→15% EtOAc: Hexane) to result in FC8 (50 mg, 82%) as navy blue thick viscous liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, J = 8.8 Hz, 1H), 7.12 (s, 1H), 6.96 (d, J = 9.2 Hz, 1H), 6.66 (dd, J = 8.8, 2.8 Hz, 1H), 6.50 (dt, J = 9.2, 2.8 Hz, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.24 (t, J = 6.8 Hz, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 158.6 (t, J = 9.2, 2.8 Hz, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.24 (t, J = 6.8 Hz, 6H). ³⁷F NMR (376 MHz, CDCl₃) δ 79.03. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁7H₁₆F₂N₃ 300.1307; Found 300.1300.

2-(7-(diethylamino)-1,1-difluoro-4-phenylpenthen-2(1H)-ylidene)malononitrile (FC9):

7-(diethylamino)-1,1-difluoro-4-phenylpenthen-2(1H)-one (FC5) (50 mg, 0.15 mmol) was reacted with malononitrile (72 mg, 0.61 mmol), ammonium acetate (12 mg, 0.15 mmol) and glacial acetic acid (210 µL) in toluene (2.1 mL) under N₂ at 60 °C for 8 h. The progress of the reaction was monitored by LC/MS and after the starting material was consumed (8 h), water (5 mL) was added to the reaction mixture. The organics were extracted into EtOAc (100 mL) and washed with water (2 × 50 mL), brine (50 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (24 g silica; 0→15% EtOAc: Hexane) to result in FC9 (48 mg, 84%) as navy blue thick viscous liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.36 (m, 5H), 7.21 (m, 1H), 7.18 (m, 1H), 6.60 (dd, J = 9.2, 2.4 Hz, 1H), 6.50 (t, J = 2.8 Hz, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.24 (t, J = 7.2 Hz, 6H). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 157.6 (t, Jₐ = 21 Hz), 153.9 (t, Jₐ = 3 Hz), 150.0, 137.5, 134.4 (t, Jₐ = 23 Hz), 132.1, 130.0, 128.9, 128.7, 117.3 (t, Jₐ = 5 Hz), 115.4 (t, Jₐ = 4 Hz), 113.1 (t, Jₐ = 4 Hz), 113.0 (t, Jₐ = 3 Hz), 112.5, 112.1 (t, Jₐ = 241 Hz), 111.1 (t, Jₐ = 4 Hz), 78.8 (t, Jₐ = 5 Hz), 45.1, 12.7. ¹⁹F NMR (376 MHz, CDCl₃) -79.13 (d, Jₐ = 4 Hz). HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₂₃H₂ₐF₂N₃ 376.1620; Found 376.1610.
2-(4-cyano-7-(diethylamino)-1,1-difluoronaphthalene-2(1H)-ylidine)malononitrile (FC10):  

![Chemical Structure](image)

6-(diethylamino)-4,4-difluoro-3-oxo-3,4-dihydronaphthalene-1-carbonitrile (FC6) (12.5 mg, 0.045 mmol) was reacted with malononitrile (22 mg, 0.18 mmol), ammonium acetate (3.6 mg, 0.045 mmol) and glacial acetic acid (60 μL) in toluene (600 μL) under N₂ at 60 °C for 8 h. The progress of the reaction was monitored by LC/MS and after the starting material was consumed (8 h), water (5 mL) was added to the reaction mixture. The organics were extracted into EtOAc (20 mL) and washed with water (2 × 10 mL), brine (10 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (4 g silica; 0→15% EtOAc: Hexane) to result in FC10 (8 mg, 46%) as teal colored thick viscous liquid: ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, J = 9.0 Hz, 1H), 7.17 – 7.14 (m, 1H), 6.89 (t, J = 2.5 Hz, 1H), 6.75 (dd, J = 9.0, 3.0 Hz, 1H), 3.53 (q, J = 7.0 Hz, 4H), 1.27 (t, J = 7.0 Hz, 6H).¹⁹F NMR (376 MHz, CDCl₃) –76.66. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₈H₁₅F₂N₄ 325.1259; Found 325.1254.

4-(8-methyl-6-nitroquinolin-3-yl)morpholine (5):

![Chemical Structure](image)

To a microwave vial containing 3-bromo-8-methyl-6-nitroquinoline 4 (2.2 g, 8.22 mmol), synthesized according to a previously reported literature procedure,³ morpholine (2.1 g, 24.7 mmol) and Cs₂CO₃ (5.36 g, 16.4 mmol), was added XPhos-PdG3 (696 mg, 0.82 mmol) (in glove box) and sealed under N₂. To this mixture, THF (10 mL) was added under N₂ and heated at 115 °C for 5 h. The progress of the reaction was monitored by TLC and after the starting material was consumed (5 h), the reaction mixture was filtered and washed with EtOAc (300 mL). The filtrate

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² Characterization for this compound includes ¹H NMR, gCOSY and ¹⁹F NMR and HRMS. Complex C-F splitting in the ¹³C NMR precluded obtaining high quality spectra.
was then transferred to a separating funnel and washed with aq. sat. NaHCO₃ (2 × 200 mL), brine (100 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (120 g silica; 0→30% EtOAc: Hexane) to result in 5 (1.95 g, 87%) as yellow amorphous solid: ¹H NMR (500 MHz, CDCl₃) δ 8.93 (d, J = 3.0 Hz, 1H), 8.45 (d, J = 3.0 Hz, 1H), 8.09 (dd, J = 2.5, 1.0 Hz, 1H), 7.40 (d, J = 3.0 Hz, 1H), 3.97 – 3.92 (m, 4H), 3.36 – 3.32 (m, 4H), 2.82 (s, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 145.8, 145.7, 145.5, 143.7, 139.4, 127.9, 121.1, 119.6, 117.27, 66.5, 48.5, 18.2. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₄H₁₆N₃O₂ 274.1186; Found 274.1181.

8-methyl-3-morpholinoquinolin-6-amine:

![Chemical Structure]

4-(8-methyl-6-nitroquinolin-3-yl)morpholine 5 (203 mg, 0.743 mmol), and iron powder (145 mg, 2.60 mmol) was dissolved in EtOH (6 mL) and 37% HCl (305 µL) was added dropwise. This mixture was heated to 50 ºC for 90 min. The progress of the reaction was monitored by TLC and after the starting material was consumed (90 min), the reaction mixture was quenched with NaHCO₃ to set the pH at 9. The crude was then diluted in EtOAc (100 mL) and washed with aq. sat. NaHCO₃ (2 × 100 mL), brine (50 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (40 g silica; 0→75% EtOAc: Hexane) to result in 100 mg (55%) of the title compound as beige colored solid: ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, J = 3.0 Hz, 1H), 7.09 (d, J = 3.0 Hz, 1H), 6.83 (m, 1H), 6.64 (d, J = 3.0 Hz, 1H), 3.97 – 3.89 (m, 4H), 3.27 – 3.21 (m, 4H), 2.68 (s, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 144.9, 144.8, 139.4, 138.0, 137.6, 130.4, 119.1, 115.3, 104.9, 66.8, 49.4, 18.0. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₄H₁₈N₃O 244.1444; Found 244.1440

5,5-difluoro-8-methyl-3-morpholinoquinolin-6(5H)-one (FC₁1):

![Chemical Structure]
To a cooled (0 °C, ice bath) solution of 8-methyl-3-morpholinoquinolin-6-amine (100 mg, 0.41 mmol) dissolved in THF (2 mL), Selectfluor (146 mg, 0.41 mmol) was added in small batches. The reaction mixture was allowed to warm to r.t. and left to stir for 24 h. The progress of the reaction was monitored by LC/MS and TLC (every aliquot collected for analysis was quenched with a sat. NH₄Cl and washed with sat. NaHCO₃). 24 h were found to be result in an optimum conversion to the desired product and upon completion, the reaction was quenched with aq. sat. NH₄Cl (25 mL) and transferred into a conical flask and cooled to 0 °C. To this cold biphasic mixture, aq. sat. NaHCO₃ (50 mL) was slowly added and the organics were extracted into EtOAc (2 × 100 mL) washed with brine (50 mL), dried (Na₂SO₄) and concentrated in vacuo. The crude concentrate was purified using normal-phase column chromatography (40 g silica; 0→30% EtOAc: Hexane) to result in FC11 (28 mg, 25%) as yellow viscous liquid: ¹H NMR (500 MHz, CDCl₃) δ 8.36 (d, J = 3.0 Hz, 1H), 7.47 (dt, J = 3.5, 1.5 Hz, 1H), 6.19 (m, 1H), 3.94 – 3.85 (m, 4H), 3.40 – 3.32 (m, 4H), 2.43 (d, J = 1.5 Hz, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 186.0(t, J_C-F = 24 Hz), 157.8 (t, J_C-F = 3 Hz), 146.8, 139.7 (t, J_C-F = 5 Hz), 138.0 (t, J_C-F = 1 Hz), 130.1 (t, J_C-F = 24 Hz), 121.7 (t, J_C-F = 3 Hz), 118.2 (t, J_C-F = 3 Hz), 105.6 (t, J_C-F = 245 Hz), 66.3, 47.1, 19.6. ¹⁹F NMR (376 MHz, CDCl₃) –101.65 (d, J_H-F = 4 Hz). HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₁₄H₁₅F₂N₂O₂ 281.1096; Found 281.1093.
To a cooled (0 °C in an ice bath) solution of 3-(dodecylamino) propane-1-sulfonic acid 6 (200 mg, 0.608 mmol), synthesized according to a previously reported literature procedure, and glutaric anhydride (149 mg, 1.31 mmol) in DMF was added NaH (31.36 mg, 1.307 mmol) in ~ 5 batches under N2. The reaction was then sealed under N2 and allowed to stir at r.t. for 15 h. The progress of the reaction was monitored by LC/MS and a clean conversion to the desired product (m/e = 420.2 ([M−H]+)) was seen after 15 h. After this time, the reaction mixture was added to acetone (15 mL) in a centrifuge tube and a solid precipitate crashed out. This was then centrifuged, and supernatant was decanted, following which, the precipitate was washed with acetone (15 mL). This procedure was repeated twice and the solid was dried under high vaccum for at least 2 h to result in 7 (259 mg, 96%) as a beige colored solid: 1H NMR (400 MHz, D2O) δ 3.38 (m, 2H), 3.29 (m,
2H), 2.87 – 2.74 (m, 2H), 2.37 (m, 2H), 2.27 (t, J = 7.6 Hz, 2H), 2.01 – 1.86 (m, 2H), 1.80 (p, J = 7.2 Hz, 2H), 1.48 (d, J = 22.0 Hz, 2H), 1.30 – 1.15 (m, 18H), 0.85 – 0.76 (m, 3H). HRMS (ESI) m/z: [M+H]+ Calcd. for C_{20}H_{39}NO_8S_{42} 422.2571; Found 422.2569.

5-(dodecyl(3-sulfopropyl)amino)-5-oxopentan-succinamidyl ester (8):

To a mixture of 5-(dodecyl(3-sulfopropyl)amino)-5-oxopentanoic acid 7 (65 mg, 0.147 mmol) and TSTU (88 mg, 0.293 mmol) dissolved in DMF (1 mL) was added DIPEA (38 mg, 0.293 mmol). After 1 h at room temperature complete conversion to the NHS ester was observed by LC/MS. The reaction mixture was then added to diethyl ether (2 mL) resulting in a pale brown solid precipitate crashing out. This was then centrifuged, and supernatant was decanted, following which, the precipitate was washed with ether (15 mL). This procedure was repeated twice and the solid was dried under high vacuum for at least 30 min to result in 8 (35 mg, 44%) as a pale brown colored solid that was immediately used without further purification. HRMS (ESI) m/z: [M+H]+ Calcd. for C_{24}H_{43}NO_8S 519.2735; Found 519.2736.

Tert-butyl (4-(6-(diethylamino)-4,4-difluoro-3-oxo-3,4-dihyronaphthalen-1-yl)benzyl)carbamate (9):

A modified literature procedure was followed.² 7-(diethylamino)-1,1-difluoronaphthalen-2(1H)-one (FC2) (48 mg, 0.19 mmol), phenyl boronic acid (26 mg, 0.38 mmol), palladium acetate (41 mg, 0.18 mmol) and 5-NO_2-1,10-phenanthroline (41 mg, 0.18 mmol) were sealed in a microwave vial. This reaction vessel was purged with O_2, following which DMF (2.5 mL) was added. The solvent was further purged with O_2 for 10 minutes and then the reaction mixture was heated to 80
°C. The progress of the reaction was monitored using LC/MS and TLC and upon completion (2 h), water (5 mL) was added to the reaction mixture. The organics were extracted using EtOAc (20 mL). The organic fraction was washed with H₂O (2 × 20 mL) and brine (2 × 20 mL) then dried (Na₂SO₄) and concentrated \textit{in vacuo}. The crude mixture was purified using normal-phase column chromatography (12 g silica; 0→5 – 10% EtOAc: Hexane) to result in 9 (44 mg, 51%) as a thick viscous dark red liquid: HRMS (ESI) m/z: [M+H]^+ Calcd. for C₂₆H₃₀F₂N₂O₄ 457.2297; Found 457.2295.

\textit{Tert-butyl (4-(dicyanomethylene)-6-(diethylamino)-4,4-difluoro-3,4-dihydranthallen-1-yl) benzyl} carbamate (10):

![Reaction Scheme]

To a mixture of tert-butyl (4-(6-(diethylamino)-4,4-difluoro-3-oxo-3,4-dihydranthallen-1-yl)benzyl)carbamate 9 (40 mg, 0.088 mmol) and malononitrile (23 mg, 0.35 mmol) in DMF was added NH₄OAc (7 mg, 0.088 mmol), in one batch, and stirred at r.t. for 15 min. The progress of the reaction was monitored by LC/MS and after the complete consumption of the product, the reaction as quenched with NaHCO₃ (10 mL). The contents were transferred into a separating funnel and the organics were extracted using EtOAc (2 × 20 mL). The organic fraction was washed with H₂O (2 × 20 mL) and brine (2 × 20 mL) then dried (Na₂SO₄) and concentrated \textit{in vacuo}. The crude mixture was purified using normal-phase column chromatography (4 g silica; 0→2% MeOH: DCM) to result in 10 (38 mg, 86%) as a navy-blue amorphous powder: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.41 – 7.38 (m, 4H), 7.20 (m, 1H), 7.20 – 7.16 (m, 1H), 6.59 (dd, \(J = 9.2, 2.8\) Hz, 1H), 6.48 (t, \(J = 3.2\) Hz, 1H), 4.95 (s, 1H), 4.40 (d, \(J = 6.0\) Hz, 2H), 3.48 (q, \(J = 7.2\) Hz, 4H), 1.49 (s, 9H), 1.23 (d, \(J = 7.2\) Hz, 6H). \(^{13}\)C {\(^1\)H} NMR (100 MHz, CDCl₃) \(\delta\) 157.4 (t, \(J_{C:F} = 21\) Hz), 156.0, 153.5, 149.8, 141.2, 134.2 (t, \(J_{C:F} = 23\) Hz), 131.9, 130.1, 128.9, 127.6, 117.0 (m, \(J_{C:F}\)), 115.2 (m, \(J_{C:F}\)), 113.0 (m, \(J_{C:F}\)), 112.9 (m, \(J_{C:F}\)), 112.3, 112.0, 111.0 (m, \(J_{C:F}\)), 78.5 (m, \(J_{C:F}\)), 44.9, 44.3, 29.7, 28.4, 12.5. \(^{19}\)F NMR (376 MHz, CDCl₃) –80.96. HRMS (ESI) m/z: [M+H]^+ Calcd. for C₂₉H₃₀F₂N₄O₂ 505.2410; Found 505.2402.
**Synthesis of FC9-SL:**

![Chemical structures](image.png)

**Step-1 (Boc deprotection):**

To a solution of tert-butyl (4-(3-(dicyanomethylene)-6-(diethylamino)-4,4-difluoro-3,4-dihydrornaphthalen-1-yl)benzyl) carbamate 10 (35 mg, 0.069 mmol) in DCM (1 mL) was added trifluoroacetic acid (100 µL) and allowed to stir at r.t. for 3 h. The progress of the reaction was monitored by LC/MS to find a clean conversion. Upon completion (3 h), the contents were concentrated using N₂ flush and dried *in vacuo* to result in boc-deprotected analog 10 (27 mg, 96%) as a viscous blue liquid, which was taken forward without further purification.

**Step-2 (Conjugating the sulfo lipid 8):**

The boc-deprotected analog (27 mg, 0.067 mmol) from step-1 and 5-(dodecyl(3-sulfopropyl)amino)-5-oxopentan -succinamidyl ester 8 (34 mg, 0.063 mmol) was dissolved in a solution of 1:1 PBS (pH = 7.4):DMF (2 mL). The reaction was allowed to stir at r.t. for 5 h, after which time LC/MS analysis showed a clean conversion to the desired product. The reaction mixture was concentrate down (using N₂ flush) to as minimum solvent as possible, dissolved in DCM (~1 mL), and the crude concentrate was purified using normal-phase column chromatography (4 g silica; 0→20% MeOH: DCM) to result in **FC9-SL** (11 mg, 20%). HRMS confirmed the identify of **FC9-SL**. HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₄₄H₅₉F₂N₅O₅S 808.4278; Found 808.4273.

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\(^c\) NMR spectroscopy was not useful due complexity by the amide rotamers and C-F splitting.
Section S3: Optical Characterization of FC dyes and R1–R3

**Figure S1:** Absorbance of FC1 in pH 4.4, 7.4, 8.5, 10.5 and FBS and the emission of FC1 in FBS, while only negligible emission was seen in other solvents.
S3.1 Hammett Analysis

We hypothesized that introducing electron withdrawing functionalities would lead to red-shifted FC dyes. Surprisingly, a modest red-shift was observed in the case of FC3 (22 nm) in both hydrophilic and hydrophobic solvents. FC4 also showed a small red shift (~32 nm) in its spectra which could be attributed to the relatively weak inductive property of the bromo substituent. While, expectedly, the introduction of a –Ph group (FC5) did not result in any significant changes compared to FC2. FC6 with –CN group at position-4 resulted in a significantly red-shifted absorption (~70 nm) and emission (~70 nm) spectra in all the solvents investigated. Interestingly, our Hammett analysis (Figure S2) shows that this observation was partially correlatable with Hammett constants (except FC3) demonstrating the importance of electron-withdrawing groups at position-4. The anomaly found in the case of FC3 suggests that the modifications at position-3 is not crucial for red-shifting the FC dyes.

Figure S2. Correlation between Hammett constants of substituents at position -3 and -4 on FC2 and the corresponding absorbance maxima in 10% FBS

\[ \text{Hammett Constants} \]

\[ \text{Experimental absorbance (\%)} \]

\[ \text{Ph, Br, CF}_3, \text{CN, H, FC2, FC4, FC5, FC6} \]

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\( ^d \) Drawing similarities of FC dye scaffold with naphthalene core, \( \sigma_p \) and \( \sigma_m \) Hammett constants were used for substituents at 3- and 4-positions respectively.
Table S1: Optical data of the synthesized FC dyes and the reference dyes R1–R3

| Entry | $\lambda_{\text{abs}}^{\text{max}}$ (nm) MeCN | $\lambda_{\text{em}}^{\text{max}}$ (nm) MeCN | $\epsilon$ (M$^{-1}$cm$^{-1}$) MeCN | Stokes shift in Toluene (nm) | Stokes shift in MeCN (nm) | Stokes shift in 10% FBS (nm) |
|-------|--------------------------------|--------------------------------|--------------------------------|--------------------------|--------------------------|--------------------------|
| FC1   | 378                           | 516                          | 7,900                         | 109                      | 138                      | 111                      |
| FC 2  | 476                           | 609                          | 12,500                        | 104                      | 133                      | 84                       |
| FC 3  | 496                           | 607                          | 15,500                        | 84                       | 111                      | 72                       |
| FC 4  | 507                           | 635                          | 13,600                        | 104                      | 128                      | 84                       |
| FC 5  | 481                           | 616                          | 8,900                         | 100                      | 135                      | 92                       |
| FC 6  | 542                           | 683                          | 10,700                        | 106                      | 141                      | 70                       |
| FC 7  | 470                           | 634                          | 14,100                        | 111                      | 164                      | 85                       |
| FC 8  | 611                           | 780                          | 9,800                         | 144                      | 169                      | 110                      |
| FC 9  | 620                           | 779                          | 8,400                         | 135                      | 159                      | 117                      |
| FC 10 | 680                           | 902                          | 10,900                        | 102                      | 222                      | 113                      |
| FC 11 | 416                           | 592                          | 14,500                        | 143                      | 176                      | 109                      |
| R1    | 364                           | 436                          | 25,100                        | 55                       | 72                       | 62                       |
| R2    | 368                           | 433                          | 24,500                        | 48                       | 65                       | 63                       |
| R3    | 475                           | 504                          | 34,000                        | 57                       | 29                       | 35                       |
S3.2 Discussion of optical properties of FC dyes

In the best interest of the reader, we have limited our discussion on the optical properties of FC dyes in the main manuscript to only toluene (mimicking hydrophobic cellular compartments) and 10% FBS (biologically relevant media). Below, we summarize other notable observations that were made.

1. **FC10** exhibited the largest ($\Delta \lambda_{\text{max}}^{\text{abs}} = 205$ nm) bathochromic shift in $\lambda_{\text{max}}^{\text{abs}}$ relative to its reference dye (**R3**), while **FC7** showed the least ($\Delta \lambda_{\text{max}}^{\text{abs}} = -5$ nm) (Figure S3). Only **FC1** had a significant difference in bathochromic shift of $\lambda_{\text{max}}^{\text{abs}}$ (cf. **R1**) within the solvents analyzed. In the case of $\lambda_{\text{max}}^{\text{em}}$, all dyes (except **FC1**) demonstrated higher bathochromic shifts in MeCN with **FC10** being the most striking FC dye with $\Delta \lambda_{\text{max}}^{\text{em}}$ between **FC10** and **R3** 398 nm (Figure S4). This observation signifies the importance of combining the effect of 2-malonodinitrile and 4-nitrile on the FC-scaffold.

2. While the effect of solvent polarity on their $\lambda_{\text{max}}^{\text{abs}}$ with **FC2–FC5** and **FC11** ($\Delta \lambda_{\text{max}}^{\text{abs}} < 10$ nm shift) was insignificant, **FC1**, **FC6–FC10** exhibit positive solvatochromism (toluene $\rightarrow$ MeCN $\rightarrow$ 10% FBS) in their $\lambda_{\text{max}}^{\text{abs}}$ (Figure S5). This is indicative of a large asymmetric push-pull character introduced from the electron-withdrawing groups.

3. In the case of emission, positive solvatochromism was seen for all FC dyes going from toluene $\rightarrow$ MeCN (Figure S6). However, negative solvatochromism between MeCN $\rightarrow$ 10% FBS was recorded in all cases (except **FC1**). This trend has been reported to be significant in the case of Nile red\(^8\) and, less dramatically, the case of COUPY dyes.\(^9\)
Figure S3. Comparison of bathochromic shift in $\lambda_{\text{abs}}^{\max}$ of FC dyes with respect to their corresponding reference dyes R1–R3 in different solvents (shown)

Figure S4. Comparison of bathochromic shift in $\lambda_{\text{em}}^{\max}$ of FC dyes with respect to their corresponding reference dyes R1–R3 in different solvents (shown)
Figure S5. Solvatochromic behavior of the $\lambda_{\text{max}}^{\text{abs}}$ of FC dyes upon indicated solvent transitions

Figure S6. Solvatochromic behavior of the $\lambda_{\text{max}}^{\text{em}}$ of FC dyes upon indicated solvent transitions
Figure S7: Absorption and emission spectra of dyes FC1–FC6 in toluene
Figure S8: Absorption and emission spectra of dyes FC7–FC11 in toluene.
Figure S9: Absorption and emission spectra of dyes FC1–FC6 in 10% FBS
Figure S10: Absorption and emission spectra of dyes FC7–FC11 in 10% FBS
Figure S11: Absorption and emission spectra of dyes FC1–FC6 in MeCN
Figure S12: Absorption and emission spectra of dyes FC7–FC11 in MeCN
Figure S13: Environmental sensitivity of representative fluorocoumarins FC2 and FC8
Table S2: List of selected small molecule fluorophores

| Entry | Structure | Molecular weight | $\lambda_{max}^{abs}$ (nm) (solvent) | $\lambda_{max}^{em}$ (nm) (solvent) |
|-------|-----------|------------------|--------------------------------------|------------------------------------|
| 1$^a$ | ![Structure](image1) | 288.15           | 546 (EtOH)                           | 650 (EtOH)                         |
| 2     | ![Structure](image2) | 510.15           | 638 (MeOH)                           | 657 (MeOH)                         |
| 3     | ![Structure](image3) | 536.16           | 740 (MeOH)                           | 772 (MeOH)                         |
| 4     | ![Structure](image4) | 399.22           | 646 (PBS)                            | 660 (PBS)                          |
| 5     | ![Structure](image5) | 338              | 591 (PBS)                            | 757 (PBS)                          |
| 6$^b$ | (FC8)     | 299.12           | 625 (10% FBS)                        | 735 (10% FBS)                      |
| 7$^b$ | (FC10)    | 324.11           | 694 (10% FBS)                        | 807 (10% FBS)                      |

$^a$The nitrobenzoxadiazole variant reported to be the smallest fluorophore emitting in the 650–900 nm range.$^{10}$

$^b$Smallest dyes with $\lambda_{max}^{abs}$ over 600 nm and $\lambda_{max}^{em}$ above 700 nm.
Section S4: Photostability studies: The photostability of the FC dyes was investigated in toluene and MeCN upon irradiation with an appropriate LED source set to an intensity of 10 mW/cm². The FC dyes were diluted to 25 µM, from a principal stock solution of 10 mM (in DMSO), in a HPLC vial. In general, all the FC dyes (except FC1 and FC7) were photostable in toluene and MeCN (~30 – 50% degradation over 60 min; Figure S14). Dinitrile-substituted dyes (FC8 – FC10) were highly photostable up to 24 h of irradiation. Particularly, FC10 upon irradiation with a 660 nm LED at an intensity of 50 mW/cm² for 8 h was found to be > 80% intact. Dark stability of these dyes was recorded, in parallel, to find that all the FC dyes were stable for the duration of the study in the absence of irradiation.

LEDs used:
- 365 nm: FC1, FC11
- 450 nm: FC5, FC7
- 480 nm: FC2
- 505 nm: FC3, FC4
- 525 nm: FC6
- 590 nm: FC8, FC9
- 660 nm: FC10

Figure S14. Photostability of the FC dyes in toluene and MeCN
**Section S5: Cell Culture**

MCF7 human breast cancer cell line was obtained from ATCC®. They were cultured at 37 °C in an atmosphere of 20% O₂ and 5% CO₂ in DMEM supplemented with 4 mM L-glutamine, 25 mM D-glucose, 44 mM sodium bicarbonate, and 10% heat-inactivated fetal bovine serum. Stock cultures were maintained in a continuous exponential growth by weekly passage of the appropriate number of cells following trypsinization with 0.25% Trypsin-EDTA (0.9 mM) in PBS.

**Section S6: Confocal Cellular Imaging**

**S6.1 General procedure for Passive organelle staining experiments**

Cells were seeded into 6-well plates at a density of $8 \times 10^3$ cells/well and allowed to reach near confluency overnight. The following day, media was replaced with phenol red-free DMEM containing 15 µM of FC dyes (diluted from a 10 mM stock) [and 2 µM BODIPY493/503 or To-Pro™-iodide for co-localization experiments, (see discussion below)], and incubated for 30 min. In the case of FC2–FC10, the media was then removed, and the cells were incubated in DMEM with Hoechst (1 µM) for 20 min, to stain the nuclei. After which time, removed the media and washed with HBSS (1×) and visualized in HBSS. The images were processed using Icy software. The Pearson’s correlation coefficient was measure with the Colocalization Studio plugin using Icy software.

**S6.2 Confocal imaging experiments**

**Lipid droplet stains**: The preliminary study of FC2–FC11 demonstrated FC6 and FC9 showed a selective and intense fluorescence in vesicles in the cellular cytoplasm which apparently looked like lipid droplets. In order to confirm our postulate, a colocalization experiment of FC9, was performed using BODIPY 493/503 as a reference LD marker. The results confirmed a clear colocalization between BODIPY 493/503 and FC9 (Pearson's coefficient = 0.89). Due to an extensive cross talk between FC6 and other commercial lipid droplet stains, BODIPY 493/503, we used FC9 was used in combination with FC6. These colocalization experiments confirmed that the FC6 and FC9 selectively stain the LDs.

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*Note: Red channel (laser: 594 nm, emission filter: 665 – 759 nm), Green Channel (laser: 488 nm, emission filter: 489 – 553 nm), Blue channel (laser: 405 nm, emission filter: 410 – 481 nm).*
Nuclear stain: The hydrophilic nature imparted to FC11 due to the incorporation of the quinoline-like structure prompted us to check its nuclear staining ability. The general procedure was used with FC11 and To-Pro™-iodide co-incubated with live MCF7 cells for 30 minutes. After which time, removed the media and washed with HBSS (1×) and visualized in HBSS. In the case of control experiment, the reference standard (TO-Pro™-iodide) was not added.

![Figure S15: Laser scanning confocal microscopy of live MCF-7 cells incubated for 30 min in phenol red free DMEM in the presence of FC11 (15 µM, blue channel) and the co-stains To-Pro™ 493/503 (red channel). Scale bar is 10 µm. Pearson’s coefficient calculated: 0.88](image)

Note: Blue channel (laser: 405 nm, emission filter: 410 – 481 nm). Red Channel (laser: 594 nm, emission filter: 650 – 759 nm)
S6.3 General procedure for Membrane Staining Experiments

Cells were seeded into 6-well plates at a density of $8 \times 10^3$ cells/well and allowed to reach near confluency overnight. The following day, media was replaced with phenol red–free DMEM containing the pre-stain (provided along with the MemBrite Fix 488/515 plasma membrane labelling kit from Biotium and prepared as directed) and allowed to incubate at 37 °C for 5 min. The media was then removed and phenol red-free DMEM containing 15 µM of FC dyes (diluted from a 10 mM stock) and recommended (undisclosed concentration) amount of MemBrite Fix 488/515 was added for co-localization experiments and incubated for 30 min. The media was then removed, and the cells were incubated in DMEM with Hoechst (1 µM) for 20 min, to stain the nuclei. After which time, removed the media, washed with HBSS (1×) and visualized in HBSS. The images were processed using Icy software.

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8 Red channel (laser: 594 nm, emission filter: 665 – 759 nm), Green Channel (laser: 488 nm, emission filter: 489 – 553 nm), Blue channel; laser: 405 nm, emission filter: 410 – 481 nm.
Section S7: Computational Analysis

Quantum Chemical Analysis: The GAMESS package was utilized for all calculations\textsuperscript{12, 13} and cc-pVTZ basis sets (spherical harmonics) were employed throughout.\textsuperscript{14-16} Density functional theory (DFT)\textsuperscript{17} and time-dependent density functional theory (TDDFT)\textsuperscript{18-21} methods were used together with the B3LYP functional\textsuperscript{22-24} and Euler-MacLaurin radial\textsuperscript{25} and Lebedev angular grids\textsuperscript{26} with respective dimensions (96, 302) and (48, 110). The polarizable continuum model (PCM)\textsuperscript{27-31} approach was used to model water solvent effects and all calculations used a high density of tesserae (NTSALL=960 in $\text{TESCAV}$). Vertical excitation, or absorption, energies and deexcitation, or emission, energies were computed at ground state and singlet excited state optimized geometries, respectively. Mulliken electronic population analysis\textsuperscript{32} was used to examine B3LYP-PCM highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Molecular orbitals were illustrated with MacMolPlt.\textsuperscript{33}

![Figure S16: Correlation between predicted and experimental $\lambda_{\text{abs}}^\text{max}$ using TDDFT-B3LYP-PCM(H$_2$O).](image-url)
**Table S3:** Computed absorbance and emission energies (in eV with oscillator strengths in parentheses) vs. experimentally measured (where available). Calculations included water solvent effects via the Polarizable Continuum Model (PCM). See Methods for full details.

| R-group  | Computed absorbance | Experimental absorbance | Computed emission | Experimental emission |
|----------|---------------------|-------------------------|-------------------|-----------------------|
| N(H)     | 3.624 (0.48)        | 3.522<sup>34</sup>     | 3.250 (0.71)      |                       |
| O        | 3.439 (0.53)        | 3.342<sup>34</sup>     | 3.057 (0.71)      | 2.621<sup>34</sup>   |
| C(Me)<sub>2</sub> | 3.091 (0.43)    | 3.002<sup>35</sup>     | 2.747 (0.61)      | 2.238<sup>35</sup>   |
| Si(Me)<sub>2</sub> | 2.838 (0.39)<sup>a</sup> | 2.649<sup>36</sup>   | 2.469 (0.48)<sup>b</sup> | 1.977<sup>36</sup> |
| S(O)<sub>2</sub>  | 2.622 (0.36)        |                         | 2.058 (0.32)      |                       |
| C(F)<sub>2</sub>  | 2.611 (0.33)        | 2.525<sup>c</sup>     | 2.084 (0.32)      |                       |
| P(OOEt)  | 2.603 (0.32)        |                         | 2.162 (0.37)      |                       |

<sup>a</sup> At the ground state (S0) optimized geometry the S1 state has \( n \rightarrow \pi^* \) character and this S0 → S1\(^*\) transition has a near zero oscillator strength of 0.0016. The S2 state has \( \pi \rightarrow \pi^* \) character and corresponding S0 → S2\(^*\) oscillator strength of 0.39 so this absorption energy is given.

<sup>b</sup> During the geometry optimization of the S2 state (\( \pi \rightarrow \pi^* \), starting from S0 optimized geometry and using small maximum step size of 0.05 Bohr) its energy dropped below the \( n \rightarrow \pi^* \) excited singlet state in the very first step, thus becoming the first excited singlet state S1. Subsequent geometry optimization of this S1 \( \pi \rightarrow \pi^* \) state led to it transforming to \( n \rightarrow \pi^* \) character beginning at step 33, and thus quickly acquiring an essentially zero oscillator strength. Therefore, the S1\(^*\) → S0\(^*\) emission energy given is for step 32 which is the last point that true \( \pi \rightarrow \pi^* \) character is retained and where the oscillator strength of 0.48 is still high. See Figure S18 for more details.

<sup>c</sup> This work.
**Table S4:** Computed absorption energies (eV), solute dipole moments (Debye) and total R-group Mulliken electron populations in the LUMOs. Properties determined at ground state optimized geometries. Calculations included water solvent effects via the Polarizable Continuum Model (PCM). See Methods for full details. Correlation coefficients ($R^2$) for computed absorption vs. property are included in italic font at bottom of columns.

| R-group | Computed absorbance | Solute dipole moment | LUMO Mulliken $e^-$ populations on R-group |
|---------|---------------------|----------------------|-------------------------------------------|
| N(H)    | 3.624               | 10.05                | $-0.056\text{a}$                           |
| O       | 3.439               | 10.35                | $-0.044\text{a}$                           |
| C(Me)$_2$ | 3.091               | 9.76                 | 0.058                                      |
| Si(Me)$_2$ | 2.838               | 11.01                | 0.091                                      |
| S(O)$_2$ | 2.622               | 14.80                | 0.088                                      |
| C(F)$_2$ | 2.611               | 11.90                | 0.085                                      |
| P(OOEt) | 2.603               | 11.95                | 0.105                                      |

$R^2$ | **0.50** | **0.92**

$\text{a}$ These Mulliken populations are penalized to be negative since each R-group introduces a node to the LUMO that passes between the ring-bound R-group atom (not in parentheses) and neighboring carbon atoms, i.e., in these systems the ring-bound R-group atom has a negative bond order with neighboring carbon atoms in the LUMO. For the other molecules, the ring-bound R-group atom has a positive bond order with neighboring carbon atoms in the LUMO. See **Table S5** for further details.
Table S5: Examinations of HOMOs and LUMOs in the coumarin series via Mulliken electronic population analysis and total polar surface area (tPSA). For each orbital, the bond order between C-0 and ring-bound R-group atom is provided along with the total electron population on the R group. Analyses were performed at ground state optimized geometries. tPSA was measured using Chemdraw.

| R-group | HOMO | LUMO | tPSA |
|---------|------|------|------|
|         | C-0–R bond order | e⁻ population | C-0–R bond order | e⁻ population |     |
| (H)N    | 0.000 | 0.000 | −0.038 | 0.056 | 29.54 |
| O       | 0.001 | 0.000 | −0.041 | 0.044 | 32.34 |
| C(Me)₂  | −0.002 | 0.002 | 0.045 | 0.058 | 20.31 |
| Si(Me)₂ | 0.001 | 0.001 | 0.054 | 0.091 | 20.31 |
| S(O)₂   | 0.000 | 0.001 | 0.042 | 0.088 | 54.45 |
| C(F)₂   | 0.000 | 0.001 | 0.048 | 0.085 | 20.31 |
| P(OOEt) | −0.001 | 0.001 | 0.050 | 0.105 | 46.61 |
Figure S17: Illustrations of B3LYP-PCM/cc-pVTZ HOMOs (left) and LUMOs (right) for the coumarin systems studied in this work. All plots show contour value of 0.02 (electron/bohr$^3$)$^{1/2}$. 
Figure S18: Absolute energies (A) and oscillator strengths (B) of R=SiMe₂ excited states S1 and S2 during geometry optimization of the π → π* singlet excited state which starts out as S2 (at S0 minimum geometry) but on the first geometry step becomes S1. Subsequent geometry optimization of this S1 π → π* state led to it transforming to n → π* character beginning at step 33, and thus quickly acquiring an essentially zero oscillator strength. As such, emission data are reported for geometry step 32. Note that the geometry optimization had a small maximum step size of 0.05 Bohr.
Section S8: NMR Spectra

\[ \text{CDCl}_3 \]

\[ \text{CD}_{3}\text{CN} \]

$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of FC2.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of FC2.
$^1$H (400 MHz) and $^{13}$C (125 MHz) NMR spectra of FC3.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of FC3.
$^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra of FC4.
gCOSY (500 MHz) and $^{19}$F (376 MHz) NMR spectra of FC4.
$^1$H (400 MHz) and $^{13}$C (125 MHz) NMR spectra of FC5.
gCOSY (500 MHz) and $^{19}$F (376 MHz) NMR spectra of FC5.
$^1$H (400 MHz) and $^{13}$C (125 MHz) NMR spectra of FC6.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of FC6.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of FC7.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of FC7.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of FC8.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of FC8.
$^1$H (400 MHz) and $^{13}$C (125 MHz) NMR spectra of FC9.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of FC9.
$^{1}$H (500 MHz) and $^{19}$F (376 MHz) NMR spectra of FC10.
gCOSY (500 MHz) NMR spectra of FC10.
$^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra of 5.
gCOSY (500 MHz) NMR spectra of 5.
$^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra of the product obtained after the reduction of 5.
gCOSY (500 MHz) spectra of the product obtained after the reduction of 5.
$^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra of FC11.
gCOSY (500 MHz) and $^{19}$F (376 MHz) NMR spectra of FC11.
$^1$H (400 MHz) and gCOSY (400 MHz) NMR of 7.
$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra of 10.
gCOSY (400 MHz) and $^{19}$F (376 MHz) NMR spectra of 10.
Section S9: Raw Data from Computational Analysis

Energies (hartree), oscillator strengths (S0 → S1*), HOMO & LUMO orbital energies, excitation/de-excitation amplitudes, and ground state optimized structures (Å)

a. C1

![Chemical Structure]

\[ E(S0) = -611.007863 \]
\[ E(S1*) = -610.874667 \]

Oscillator strength = 0.4775

\[ E(HOMO) = -0.1971; E(LUMO) = -0.0498 \]

| OCC | VIR | EXCITATION AMPLITUDE | DE-EXCITATION AMPLITUDE |
|-----|-----|-----------------------|-------------------------|
| I   | A   | X(I→A)               | Y(A→I)                  |
| --- | --- | ---                 | ---                     |
| 50  | 51  | 0.980890             | -0.066118               |
| 49  | 52  | 0.150171             | 0.029857                |
| 50  | 52  | -0.046781            | -0.003400               |
| 47  | 53  | 0.056809             | 0.008881                |
| 49  | 53  | -0.071966            | -0.022543               |
| 50  | 53  | 0.059285             | 0.015921                |

| ATOM | CHARGE | X       | Y       | Z       |
|------|--------|---------|---------|---------|
| C    | 6.0    | -1.2449960515 | 0.6282005680 | 0.0321976523 |
| C    | 6.0    | -2.2802732069 | -0.3340204919 | 0.0185899168 |
| C    | 6.0    | -1.9216424395 | -1.7116836696 | 0.0105406724 |
| C    | 6.0    | -0.6249475033 | -2.1146286891 | 0.0141366278 |
| C    | 6.0    | 0.4557041105 | -1.1538642427 | 0.0263302588 |
| N    | 7.0    | 0.0576772019 | 0.1714342830 | 0.0358166435 |
| H    | 1.0    | -0.3497140216 | -3.1588494054 | 0.0074351239 |
| C    | 6.0    | -2.8503838429 | 2.4537817902 | 0.0334328891 |
| C    | 6.0    | -3.8941706220 | 1.4817529076 | 0.0243404306 |
| C    | 6.0    | -3.6044138346 | 0.1401616169 | 0.0166024423 |
| C    | 6.0    | -1.5216087938 | 1.9926379455 | 0.0429025029 |
| H    | 1.0    | -4.9256926659 | 1.7952413143 | 0.0258724519 |
| H    | 1.0    | -4.4140816102 | -0.5791768699 | 0.0102135751 |
| H    | 1.0    | -0.6954964399 | 2.6868345625 | 0.0569919114 |
| N    | 7.0    | -3.1358206349 | 3.7891629367 | 0.0316837151 |
| O    | 8.0    | 1.6608055477 | -1.4384381482 | 0.0282870148 |
| H    | 1.0    | -2.7157561717 | -2.4494564039 | 0.0010379699 |
### b. C2

![Chemical Structure](image)

\[ E(S0) = -630.865253 \]

\[ E(S1^*) = -630.738857 \]

Oscillator strength = 0.5260

\[ E(HOMO) = -0.2018; E(LUMO) = -0.0631 \]

| OCC | VIR | AMPLITUDE | DE-AMPLITUDE |
|-----|-----|------------|--------------|
| I   | A   | X(I→A)     | Y(A→I)       |
| 49  | 51  | 0.035900   | 0.011138     |
| 50  | 51  | 0.990419   | -0.076881    |
| 49  | 52  | -0.097160  | -0.026838    |
| 48  | 53  | -0.049763  | -0.008599    |
| 49  | 53  | 0.044819   | 0.017033     |
| 50  | 53  | 0.071601   | 0.019173     |

| ATOM | CHARGE | X       | Y       | Z       |
|------|--------|---------|---------|---------|
| C    | 6.0    | -1.2490153828 | 0.6185831626 | -0.0027192434 |
| C    | 6.0    | -2.2723001433 | -0.3441182315 | 0.0073965511 |
| C    | 6.0    | -1.8990672652 | -1.7152616015 | -0.0128725843 |
| C    | 6.0    | -0.5943160860 | -2.0861608428 | -0.0389942488 |
| C    | 6.0    | 0.4555901547  | -1.1025073352 | -0.0482815690 |
| O    | 8.0    | 0.0643368325  | 0.2288908349  | -0.0311645871 |
| H    | 1.0    | -0.2880494335 | -3.1208445953 | -0.0539009285 |
| C    | 6.0    | -2.8331784189 | 2.4438821927  | 0.0514426706 |
| C    | 6.0    | -3.8786394478 | 1.4749916669  | 0.0577230265 |
| C    | 6.0    | -3.5954912754 | 0.1317026805  | 0.0368614329 |
| C    | 6.0    | -1.5016002250 | 1.9759633877  | 0.0151189016 |
| H    | 1.0    | -4.9088615892 | 1.7917875337  | 0.0776181494 |
| H    | 1.0    | -4.4069742713 | -0.5851539161 | 0.0418297065 |
c. C3

\[
E(S0) = -673.518134
E(S1*) = -673.404551
Oscillator strength = 0.4345
E(HOMO) = -0.1948; E(LUMO) = -0.0683
\]

| OCC | VIR | AMPLITUDE | DE-AMPLITUDE |
|-----|-----|------------|--------------|
| I   | A   | X(I->A)    | Y(A->I)      |
| 58  | 59  | -0.993474  | 0.080576     |
| 56  | 60  | -0.058431  | -0.022309    |
| 58  | 60  | -0.076028  | -0.006210    |
| 55  | 61  | -0.036370  | -0.006703    |
| 58  | 61  | 0.060395   | 0.020999     |

| ATOM | CHARGE | X      | Y      | Z      |
|------|--------|--------|--------|--------|
| C    | 6.0    | -1.2427124474 | 0.7026350079 | -0.0124547750 |
| C    | 6.0    | -2.2716661289  | -0.2636390370 | 0.0023146858 |
| C    | 6.0    | -1.9535828152  | -1.6611913768 | -0.0245652284 |
| C    | 6.0    | -0.6878499717  | -2.1388109668 | -0.0636551752 |
| C    | 6.0    | 0.4508682212   | -1.2515495515 | -0.0806314466 |
| C    | 6.0    | 0.2259065977   | 0.2781442943 | -0.0535151905 |
| H    | 1.0    | -0.4834763146  | -3.2011928601 | -0.0826159784 |
| C    | 6.0    | -2.9200520672  | 2.4924067500 | 0.0601258420 |
| C    | 6.0    | -3.9375212464  | 1.5062964307 | 0.0687475244 |
| C    | 6.0    | -3.6058750421  | 0.1710009782 | 0.0413382584 |
| C    | 6.0    | -1.5769760375  | 2.0462559895 | 0.0129744317 |
d. C4

\[
\begin{align*}
E(S0) & = -924.916403 \\
E(S1^*) & = -924.817784 \, (HOMO-1 \rightarrow LUMO; \pi \rightarrow \pi^*) \\
\text{Oscillator strength} & = 0.0016
\end{align*}
\]

| OCC | VIR | AMPLITUDE | DE-AMPLITUDE |
|-----|-----|------------|--------------|
| 61  | 63  | 0.986528   | -0.029890    |
| 62  | 63  | 0.034317   | -0.002589    |
| 61  | 65  | 0.147192   | -0.015452    |

\[
\begin{align*}
E(S2^*) & = -924.812109 \, (HOMO \rightarrow LUMO; \pi \rightarrow \pi^*) \\
\text{Oscillator strength} & = 0.3885 \\
E(HOMO) & = -0.1961; E(LUMO) = -0.0787
\end{align*}
\]
| OCC | VIR | AMPLITUDE | AMPLITUDE |
|-----|-----|-----------|-----------|
| I   | A   | X(I->A)   | Y(A->I)   |
| --- | --- | -------- | -------- |
| 61  | 63  | 0.033824  | -0.001349 |
| 62  | 63  | -0.992352 | 0.083293  |
| 60  | 64  | 0.054671  | 0.024442  |
| 62  | 64  | 0.082603  | 0.008256  |
| 62  | 65  | -0.052652 | -0.022500 |

| ATOM | CHARGE | X       | Y       | Z       |
|------|--------|---------|---------|---------|
| C    | 6.0    | 0.0899882359 | -0.0343066970 | 0.0032042367 |
| C    | 6.0    | 0.1674234951 | -1.4517980368 | 0.0138176881 |
| C    | 6.0    | 1.4083451866 | -2.1954940066 | 0.0119004145 |
| C    | 6.0    | 2.6958924496 | -1.7532080644 | -0.0066656547 |
| C    | 6.0    | 3.0781950685 | -0.3561917454 | -0.0267418862 |
| SI   | 14.0   | 1.6850951126 | 0.972743738     | -0.0022271212 |
| H    | 1.0    | 3.5028311330 | -2.4799108938 | -0.0094766400 |
| C    | 6.0    | -2.3684528839 | -0.1474403758 | 0.0040325620 |
| C    | 6.0    | -2.2707498197 | -1.5586579969 | 0.0183712654 |
| C    | 6.0    | -1.0380665577 | -2.1755932531 | 0.0228324631 |
| C    | 6.0    | -1.1500195248 | 0.5827365526  | -0.0011756935 |
| H    | 1.0    | -3.1603187752 | -2.1689583358 | 0.0253378064 |
| H    | 1.0    | -1.0002808715 | -3.2586469175 | 0.0327354760 |
| H    | 1.0    | -1.1958670383 | 1.6624650114  | -0.0104908800 |
| N    | 7.0    | -3.5764881515 | 0.4839902063  | -0.0049146983 |
| O    | 8.0    | 4.2701280938  | -0.0089177878 | -0.0535354284 |
| H    | 1.0    | 1.2727949290  | -3.2729835108 | 0.0239890975 |
| C    | 6.0    | -4.8089690170 | -0.2909842814 | -0.0106118127 |
| C    | 6.0    | -3.6568470709 | 1.9376147586  | -0.0191614474 |
| H    | 1.0    | -4.8955197188 | -0.9176546205 | 0.8811440097 |
| H    | 1.0    | -4.8731779213 | -0.9379772603 | -0.8895489200 |
| H    | 1.0    | -5.6543818550 | 0.3894951425  | -0.0290404224 |
| H    | 1.0    | -3.1867611324 | 2.3607880978  | -0.911401203 |
| H    | 1.0    | -3.1791980161 | 2.3773356330  | 0.8603913268 |
| H    | 1.0    | -4.7017075966 | 2.2305588822  | -0.0170882911 |
| C    | 6.0    | 1.8571950696  | 2.0007289284  | 1.5617442762 |
| C    | 6.0    | 1.8239624174  | 2.0407619206  | -1.5416616036 |
| H    | 1.0    | 1.7576000308  | 1.3813127305  | 2.4540963610 |
| H    | 1.0    | 1.7234680989  | 1.4410335075  | -2.4473701685 |
| H    | 1.0    | 1.0926116773  | 2.7793798503  | 1.6019704601 |
| H    | 1.0    | 1.0475374902  | 2.8084401564  | -1.5554382410 |
| H    | 1.0    | 2.8342300276  | 2.4868245935  | 1.5884967628 |
| H    | 1.0    | 2.793277638   | 2.5421524494  | -1.5677744791 |
E(S0) = -1104.202520
E(S1*) = -1104.106157
Oscillator strength = 0.3600
E(HOMO) = -0.2143; E(LUMO) = -0.1064

| OCC | VIR | AMPLITUDE | DE-AMPLITUDE |
|-----|-----|-----------|--------------|
| I   | A   | X(I->A)   | Y(A->I)      |
| 59  | 63  | 0.042644  | -0.018469    |
| 60  | 63  | -0.052066 | -0.011152    |
| 62  | 63  | -0.991849 | 0.099316     |
| 60  | 64  | 0.057035  | 0.026658     |
| 62  | 64  | 0.080376  | 0.008465     |
| 59  | 65  | 0.031778  | 0.007060     |
| 62  | 65  | -0.050524 | -0.022992    |
| 61  | 67  | -0.053477 | -0.024489    |
| 61  | 68  | 0.032626  | 0.014960     |

| ATOM | CHARGE | X         | Y         | Z         |
|------|--------|-----------|-----------|-----------|
| C    | 6.0    | -1.2066070859 | 0.7918590702 | 0.0064252052 |
| C    | 6.0    | -2.1746871458 | -0.2327000812 | 0.0029025275 |
| C    | 6.0    | -1.8624197873 | -1.6275186366 | -0.021759629 |
| C    | 6.0    | -0.6373543959 | -2.2263733282 | -0.0532018871 |
| C    | 6.0    | 0.5995272939  | -1.5203829359 | -0.0719658995 |
| S    | 16.0   | 0.5251946674  | 0.3637052042  | -0.0272196225 |
| H    | 1.0    | -0.5621898000 | -3.3059146198 | -0.0710512889 |
| C    | 6.0    | -2.8875544091 | 2.5384589776  | 0.0449563767 |
| C    | 6.0    | -3.8733300812 | 1.5164556021  | 0.0360147885 |
| C    | 6.0    | -3.5187402981 | 0.1894615946  | 0.0183286368 |
| C    | 6.0    | -1.5263365247 | 2.1270850861  | 0.0266631736 |
| H    | 1.0    | -4.9200832078 | 1.7740991703  | 0.0400674414 |
| H    | 1.0    | -4.2965264648 | -0.5632298897 | 0.0116703524 |
| H    | 1.0    | -0.7368710502 | 2.8618716443  | 0.0279888423 |
| N    | 7.0    | -3.2199519042 | 3.8493707546  | 0.068804863 |
| O    | 8.0    | 1.7288056969  | -1.9570635675 | -0.108773966 |
| H    | 1.0    | -2.7222256874 | -2.2877596641 | -0.0163708514 |
| C    | 6.0    | -4.6213211607 | 4.2544973519  | 0.0915448322 |
| C    | 6.0    | -2.1886395434 | 4.8817456635  | 0.0442673805 |
| H    | 1.0    | -5.1410566845 | 3.9562074433  | -0.8224797890 |
H  1.0  -4.6723083243  5.3345798312  0.1766765689
H  1.0  -5.1433712867  3.8193412694  0.9455284865
H  1.0  -1.5306507812  4.8097341451  0.9131877227
H  1.0  -1.5794797273  4.8173358989 -0.8602559071
H  1.0  -2.6670401039  5.8550481802  0.0617532655
O  8.0   1.1427107647  0.7827781524  1.2176078522
O  8.0   1.1018247618  0.8539306425 -1.2651649347

f. C6

\[ E(S0) = -793.411101 \]
\[ E(S1*) = -793.315160 \]

Oscillator strength = 0.3271
\[ E(HOMO) = -0.2048; E(LUMO) = -0.0960 \]

| OCC | VIR | I | A | X(I->A) | Y(A->I) |
|-----|-----|---|---|--------|--------|
| 55  | 59  |  0.036720       | -0.022308 |
| 56  | 59  |  0.045850       |  0.012699 |
| 58  | 59  |  0.994337       | -0.096403 |
| 56  | 60  |  0.048877       |  0.024567 |
| 58  | 60  |  0.087511       |  0.009893 |
| 55  | 61  |  0.033767       |  0.008622 |
| 58  | 61  |  0.045264       |  0.022498 |

| ATOM | CHARGE | X         | Y         | Z         |
|------|--------|-----------|-----------|-----------|
| C    | 6.0    | -1.2150916568 |  0.6937045596 | -0.0081031671 |
| C    | 6.0    | -2.2239859625 | -0.2867169813 |  0.0050298609 |
| C    | 6.0    | -1.8884359040 | -1.6821245745 | -0.0116595011 |
| C    | 6.0    | -0.6185523047 | -2.1636896922 | -0.0392532341 |
| C    | 6.0    |  0.5106647648 | -1.2781227143 | -0.0548267265 |
| C    | 6.0    |  0.2242580056 |  0.2538495078 | -0.0410067613 |
| H    | 1.0    | -0.4157731044 | -3.2256226695 | -0.0497106179 |
| C    | 6.0    | -2.8593970338 |  2.4864175915 |  0.0430127870 |
| C    | 6.0    | -3.8739506866 |  1.4959698498 |  0.0511533519 |
| C    | 6.0    | -3.5544610709 |  0.1556226392 |  0.0337357353 |
| C    | 6.0    | -1.5122629863 |  2.0374024959 |  0.0082751064 |
| H    | 1.0    | -4.9130402455 |  1.7833933123 |  0.0691334492 |
| H    | 1.0    | -4.3514792898 | -0.5772874599 |  0.0405271823 |
| H    | 1.0    | -0.7038200626 |  2.7512695013 | -0.0025454229 |
\[ E(S0) = -1126.653876 \]
\[ E(S1*) = -1126.558203 \]

Oscillator strength = 0.3232

\[ E(HOMO) = -0.2064; E(LUMO) = -0.0979 \]

| EXCITATION | DE-EXCITATION |
|------------|---------------|
| OCC | VIR | AMPLITUDE | AMPLITUDE |
| I | A | X(I->A) | Y(A->I) |
| 67 | 71 | 0.040564 | -0.019068 |
| 68 | 71 | -0.037149 | -0.012360 |
| 69 | 71 | -0.112009 | -0.000241 |
| 70 | 71 | 0.987042 | -0.092378 |
| 68 | 72 | 0.048794 | 0.023050 |
| 70 | 72 | -0.079255 | -0.007694 |
| 67 | 73 | 0.032855 | 0.008294 |
| 70 | 73 | 0.051394 | 0.023597 |

| ATOM | CHARGE | X | Y | Z |
|------|--------|---|---|---|
| C    | 6.0    | -1.1771501626 | 0.7372437687 | 0.025046205 |
| C    | 6.0    | -2.1816112033 | -0.2555507922 | -0.0583540146 |
| C    | 6.0    | -1.9136713503 | -1.6695097560 | -0.0505031983 |
| C    | 6.0    | -0.7177418261 | -2.3091776528 | 0.0678338781 |
| C    | 6.0    | 0.5400898271 | -1.6273688194 | 0.2103456902 |
| P    | 15.0   | 0.5515066732 | 0.2403616768 | 0.1347581899 |
| H    | 1.0    | -0.6835329618 | -3.3921457091 | 0.0763398819 |
Energies (hartree), oscillator strengths (S1 \rightarrow S0*) and excited state (S1) optimized structures (Å).

a. C1

\[ E(S0*) = -611.003722 \]
\[ E(S1) = -610.884291 \]
\[ Oscillator \ strength = 0.7090 \]

| ATOM | CHARGE | X            | Y            | Z            |
|------|--------|--------------|--------------|--------------|
| C    | 6.0    | -1.2459825248| 0.6245145913 | 0.0288934560 |
| C    | 6.0    | -2.2959546852| -0.3491740862| 0.0321316429 |
| C    | 6.0    | -1.9411182239| -1.7299792177| 0.0200474330 |
| C    | 6.0    | -0.5907167614| -2.1106149639| 0.0089062447 |
| C    | 6.0    | 0.4650746421 | -1.1661758758| 0.0030879125 |
| N    | 7.0    | 0.0607670395 | 0.1833903788 | 0.0096068781 |
| H    | 1.0    | -0.3101235114| -3.1548699811| 0.0021421390 |
| C    | 6.0    | -2.8776051520| 2.4425277206 | 0.0553734239 |
| C    | 6.0    | -3.9228875919| 1.4911535497 | 0.0580409688 |
| C    | 6.0    | -3.6273919843| 0.1378148243 | 0.0485869842 |
| C    | 6.0    | -1.5325889660| 1.9774029479 | 0.0427180203 |
| H    | 1.0    | -4.9536087389| 1.8058174707 | 0.0781944345 |
| H    | 1.0    | -4.4370353317| -0.5800340518| 0.0554378365 |
| H    | 1.0    | -0.7131126285| 2.6791884313 | 0.0338015025 |
| N    | 7.0    | -3.1342632484| 3.7913708560 | 0.0614906003 |
| O    | 8.0    | 1.6962525732 | -1.4113366410| -0.0075412663|
| H    | 1.0    | -2.7223995948| -2.4767853126| 0.0231034278 |
| C    | 6.0    | -4.5016819380| 4.2759538486 | 0.0090583797 |
| C    | 6.0    | -2.0579388822| 4.7652430000 | 0.1551536925 |
| H    | 1.0    | -5.0268811279| 3.8559744108 | -0.8513774513|
| H    | 1.0    | -4.4966816527| 5.3567824375 | -0.0746881377|
| H    | 1.0    | -5.0523421208| 3.9961181300 | 0.9130579261 |
| H    | 1.0    | -1.4541362516| 4.5960143218 | 1.049658128 |
| H    | 1.0    | -1.4007831606| 4.7144395236 | -0.7175304583|
| H    | 1.0    | -2.4849717975| 5.7600536953 | 0.2071187802 |
| H    | 1.0    | 0.8077141208 | 0.8614987838 | 0.0077732890 |

b. C2
\[ E(S0^*) = -630.861335 \]

\[ E(S1) = -630.748981 \]

Oscillator strength = 0.7103

| ATOM | CHARGE | X          | Y          | Z          |
|------|--------|------------|------------|------------|
| C    | 6.0    | -1.2479528399 | 0.6107643601 | -0.0002515474 |
| C    | 6.0    | -2.2833776692  | -0.3559480821 | -0.0048925783 |
| C    | 6.0    | -1.9243581681  | -1.7424706529 | -0.0221554577 |
| C    | 6.0    | -0.5698727004  | -2.0760508330 | -0.0302177529 |
| C    | 6.0    | 0.4660066714   | -1.1154882169 | -0.0253190673 |
| O    | 8.0    | 0.0735933133   | 0.2539999637  | -0.0105748124 |
| H    | 1.0    | -0.2527450275  | -3.1096633958 | -0.0415585405 |
| C    | 6.0    | -2.8523675382  | 2.4361165917  | 0.0361932500  |
| C    | 6.0    | -3.9007108573  | 1.4823475972  | 0.0307302744  |
| C    | 6.0    | -3.6110774299  | 0.1339362345  | 0.0093030551  |
| C    | 6.0    | -1.5135479358  | 1.9637225933  | 0.0172152919  |
| H    | 1.0    | -4.9309375328  | 1.7991678894  | 0.0349747747  |
| H    | 1.0    | -4.4232892482  | -0.5810184493 | 0.0017740155  |
| H    | 1.0    | -0.6778625930  | 2.6449057781  | 0.0258478076  |
| N    | 7.0    | -3.1090816740  | 3.7823572149  | 0.0617756327  |
| O    | 8.0    | 1.6863690596   | -1.2952045854 | -0.0328131733 |
| H    | 1.0    | -2.6914545804  | -2.5019442946 | -0.0272605837 |
| C    | 6.0    | -4.4757857779  | 4.2677780333  | 0.1456060461  |
| C    | 6.0    | -2.0293485744  | 4.7533864612  | -0.0164914382 |
| H    | 1.0    | -5.0409703711  | 4.0036139036  | -0.7536098692 |
| H    | 1.0    | -4.4665603106  | 5.3469841250  | 0.2468165014  |
| H    | 1.0    | -4.9864350929  | 3.8350002209  | 1.0082940815  |
| H    | 1.0    | -1.3676997057  | 4.6788189455  | 0.8511477848  |
| H    | 1.0    | -1.4317316965  | 4.5999981893  | -0.9178314162 |
| H    | 1.0    | -2.4523651006  | 5.7509991486  | -0.0438487984 |

c. C3

\[ E(S0^*) = -673.514564 \]
$E(S1) = -673.413615$

Oscillator strength = 0.6095

| ATOM | CHARGE | X               | Y               | Z               |
|------|--------|-----------------|-----------------|-----------------|
| C    | 6.0    | -1.2446883959   | 0.6784301957    | -0.0187991936   |
| C    | 6.0    | -2.2945797941   | -0.2879746841   | -0.0051156443   |
| C    | 6.0    | -2.0072048527   | -1.6958209562   | -0.0310347544   |
| C    | 6.0    | -0.6934967408   | -2.1201539837   | -0.0686792051   |
| C    | 6.0    | 0.4351432125    | -1.2425300706   | -0.0814746502   |
| C    | 6.0    | 0.2319507856    | 0.2823819287    | -0.0510231198   |
| H    | 1.0    | -0.465065653    | -3.1801095824   | -0.0892565536   |
| C    | 6.0    | -2.9196571253   | 2.4787606965    | 0.0478992403    |
| C    | 6.0    | -3.9558029204   | 1.4997913753    | 0.0614045157    |
| C    | 6.0    | -3.6352268310   | 0.1697840728    | 0.0338860249    |
| C    | 6.0    | -1.5807166552   | 2.0248863643    | 0.0043963203    |
| H    | 1.0    | -4.9922134488   | 1.7959247655    | 0.0859030935    |
| H    | 1.0    | -4.4294707208   | -0.565816554    | 0.0404373473    |
| H    | 1.0    | -0.7893852879   | 2.7568192338    | -0.0018651609   |
| N    | 7.0    | -3.2182304093   | 3.8119535096    | 0.0774698031    |
| O    | 8.0    | 1.6142146348    | -1.6887079173   | -0.1128155534   |
| H    | 1.0    | -2.8261406781   | -2.400930564    | -0.0217197953   |
| C    | 6.0    | -4.5984627124   | 4.2657410394    | 0.1766680760    |
| C    | 6.0    | -2.1656793328   | 4.8128405679    | -0.0045656805   |
| H    | 1.0    | -5.1682405164   | 3.9982516700    | -0.7175350550   |
| H    | 1.0    | -4.6092146585   | 5.3446990423    | 0.2826384780    |
| H    | 1.0    | -5.0915462403   | 3.8253818304    | 1.0447530702    |
| H    | 1.0    | -1.4879888424   | 4.7431557259    | 0.8506933344    |
| H    | 1.0    | -1.5790136940   | 4.6889656163    | -0.9178961661   |
| H    | 1.0    | -2.6143129139   | 5.7996821792    | -0.0108254455   |
| C    | 6.0    | 0.9258007552    | 0.8747067379    | -1.3071264177   |
| C    | 6.0    | 0.9629340134    | 0.8273943896    | 1.2064707097    |
| H    | 1.0    | 0.4115639465    | 0.5665226088    | -2.2188081987   |
| H    | 1.0    | 1.9520471142    | 0.5128454867    | -1.3493683561   |
| H    | 1.0    | 0.9460938078    | 1.9643724264    | -1.2769808074   |
| H    | 1.0    | 0.9760564247    | 1.9174888999    | 1.2195083950    |
| H    | 1.0    | 1.9913942109    | 0.4695032267    | 1.2038963644    |
| H    | 1.0    | 0.4778043754    | 0.4803749764    | 2.120283602     |

d. C4 (data at geometry optimization step 32, see Figure S18 for full details)

\[
E(S0^*) = -924.912396
\]
\[ E(S1) = -924.821667 \]

Oscillator strength = 0.4763

| ATOM | CHARGE | X           | Y           | Z           |
|------|--------|-------------|-------------|-------------|
| C    | 6.0    | 0.1206619189| -0.0740814473| 0.0235209207 |
| C    | 6.0    | 0.1655731887| -1.5097884054| 0.0407133178 |
| C    | 6.0    | 1.3859076192| -2.275794184 | 0.0531576603 |
| C    | 6.0    | 2.6662226820| -1.7630333330| -0.0048433116|
| C    | 6.0    | 3.0476089973| -0.3718689026| -0.0914750639|
| SI   | 14.0   | 1.6977106029| 0.9487095031 | -0.0021139089|
| H    | 1.0    | 3.4967693830| -2.4640789712| 0.0461928495 |
| C    | 6.0    | -2.3417197053| -0.1562965355| -0.0279621407|
| C    | 6.0    | -2.2752562882| -1.5825865489| 0.0003094057 |
| C    | 6.0    | -1.0638499813| -2.2167858138| 0.0372989796 |
| C    | 6.0    | -1.1206315655| 0.5557456596 | -0.0188184016|
| H    | 1.0    | -3.1782319624| -2.1722450368| -0.0110810950|
| H    | 1.0    | -1.0402510333| -3.2992513562| 0.0527963917 |
| H    | 1.0    | -1.1544967346| 1.6355482506 | -0.0273719797|
| N    | 7.0    | -3.5470766200| 0.4806262470 | -0.041490529 |
| O    | 8.0    | 4.2694636299 | -0.0356869453| -0.1780508016|
| H    | 1.0    | 1.2740549247 | -3.3514380354| 0.0992936099 |
| C    | 6.0    | -4.7952943861| -0.2718623590| -0.004778905 |
| C    | 6.0    | -3.6150033663| 1.9341865173 | -0.0619775521|
| H    | 1.0    | -4.8612857496| -0.8815686266| 0.9031866599 |
| H    | 1.0    | -4.8879283415| -0.9276596623| -0.8688633933|
| H    | 1.0    | -5.6253829035| 0.4255220578 | -0.0068386614|
| H    | 1.0    | -3.1171215083| 2.3381757293 | -0.9464461693|
| H    | 1.0    | -3.1392004346| 2.3624351420 | 0.8246231425 |
| H    | 1.0    | -4.6549118929| 2.2392918498 | -0.0788575279|
| C    | 6.0    | 1.8641641034 | 2.0103638416 | 1.551930203 |
| C    | 6.0    | 1.7627601800 | 2.1134168070 | -1.4894089280|
| H    | 1.0    | 1.7992724731 | 1.4097326699 | 2.4600635217 |
| H    | 1.0    | 1.6571518696 | 1.565362286 | -2.4269530785|
| H    | 1.0    | 1.0766603110 | 2.7675754640 | 1.5884797954 |
| H    | 1.0    | 0.9727944712 | 2.8660390762 | -1.4427133152|
| H    | 1.0    | 2.8235207732 | 2.5319161620 | 1.5525917546 |
| H    | 1.0    | 2.7200478658 | 2.6389632481 | -1.5084008115 |

**e. C5**

\[ E(S0) = -1104.193043 \]
\( E(S1^*) = -1104.11741 \)

**Oscillator strength = 0.3153**

| ATOM | CHARGE | X              | Y              | Z              |
|------|--------|----------------|----------------|----------------|
| C    | 6.0    | -1.1902784912  | 0.7708510595   | -0.2120932044  |
| C    | 6.0    | -2.1913095265  | -0.2485241854  | -0.2062479289  |
| C    | 6.0    | -1.8756279169  | -1.6566998289  | -0.1295989384  |
| C    | 6.0    | -0.6315617899  | -2.1245310028  | 0.1735632659   |
| C    | 6.0    | 0.5552593746   | -1.3093660689  | 0.3486296677   |
| S    | 16.0   | 0.4892577559   | 0.3089105471   | -0.4656379893  |
| H    | 1.0    | -0.4822658668  | -3.1859868312  | 0.3359143515   |
| C    | 6.0    | -2.8560250028  | 2.5136915678   | 0.0136303779   |
| C    | 6.0    | -3.8659215874  | 1.5048468622   | -0.0661607813  |
| C    | 6.0    | -3.5313053997  | 0.1779431714   | -0.170777178   |
| C    | 6.0    | -1.5067244060  | 2.1112244669   | -0.0746710116  |
| H    | 1.0    | -4.9071455042  | 1.7770863560   | -0.004058322   |
| H    | 1.0    | -4.3152430700  | -0.5669609384  | -0.1830298861  |
| H    | 1.0    | -0.7108387497  | 2.8380528126   | -0.0717385457  |
| N    | 7.0    | -3.2008761593  | 3.8204325576   | 0.1575459020   |
| O    | 8.0    | 1.6027508914   | -1.6430277559  | 0.9138610586   |
| H    | 1.0    | -2.6942131326  | -2.3544576554  | -0.2370465933  |
| C    | 6.0    | -4.5873690267  | 4.2639082789   | 0.0567921455   |
| C    | 6.0    | -2.1819133207  | 4.8287249145   | 0.4095411451   |
| H    | 1.0    | -5.0843565605  | 3.7953972551   | -0.7900554449  |
| H    | 1.0    | -4.5990221631  | 5.3392583194   | -0.0869112718  |
| H    | 1.0    | -5.1422363550  | 4.0304456855   | 0.9698679290   |
| H    | 1.0    | -1.5016240068  | 4.4952150696   | 1.1928612099   |
| H    | 1.0    | -1.6001540089  | 5.0334956845   | -0.4947348416  |
| H    | 1.0    | -2.6642619625  | 5.7468356259   | 0.7269617268   |
| O    | 8.0    | 1.3635914278   | 1.2564094347   | 0.2066380644   |
| O    | 8.0    | 0.7187286979   | 0.1334455572   | -1.8975051875  |

**f. C6**

\[
\begin{array}{ccc}
\text{C} & 6.0 & -1.1975170928 \\
\end{array}
\]

**E(S0*) = -793.403226**

\( E(S1^*) = -793.326623 \)

**Oscillator strength = 0.3242**

| ATOM | CHARGE | X              | Y              | Z              |
|------|--------|----------------|----------------|----------------|
| C    | 6.0    | -1.1975170928  | 0.6708610387   | 0.0065801358   |

---

S81
\[
\begin{align*}
\text{C} & & 6.0 & -2.2398666396 & -0.3045982697 & 0.0161432966 \\
\text{C} & & 6.0 & -1.9385238070 & -1.2183785746 & 0.0416064897 \\
\text{C} & & 6.0 & -0.6424445885 & 0.1506939372 & 0.0420548115 \\
\text{C} & & 6.0 & 0.4900557182 & 3.7954989764 & 0.0481082560 \\
\text{H} & & 1.0 & -0.3964793482 & 3.1805562217 & 0.0981871041 \\
\text{C} & & 6.0 & -2.8396136585 & 2.4701986796 & 0.0416064897 \\
\text{C} & & 6.0 & -3.8783162425 & 1.4860415297 & 0.0551081329 \\
\text{C} & & 6.0 & -3.5725746467 & 0.1506939372 & 0.0420548115 \\
\text{C} & & 6.0 & -1.5036660541 & 3.7954989764 & 0.0481082560 \\
\end{align*}
\]

\[\text{g. C7}\]

\[
\begin{align*}
E(S0^*) & = -1126.647853 \\
E(S1) & = -1126.568391 \\
\text{Oscillator strength} & = 0.3733
\end{align*}
\]
C   6.0  -3.8362995055   1.5418029414  -0.1857008151
C   6.0  -3.4834305906   0.2224067007  -0.2949569824
C   6.0  -1.4969533893   2.1357068442   0.1186329739
H   1.0  -4.8776565788   1.8135787252  -0.2499625702
H   1.0  -4.2561631379  -0.5203857947  -0.4410702844
H   1.0   -0.7189038605   2.8678470248   0.2662030781
N   7.0   -3.2034770641   3.8500956432   0.1811093562
O   8.0    1.6379105452  -1.9904912889   0.7716728178
H   1.0  -2.6896996765  -2.2849221352  -0.3880218140
C   6.0  -4.5796603749   4.2861573728  -0.0304192365
C   6.0  -2.2109753481   4.8547500781   0.5323676916
H   1.0  -4.9637510927   3.9140022316  -0.9796189671
H   1.0  -4.6034876253   5.3700498802  -0.0484906170
H   1.0  -5.2318654423   3.9382646991   0.7749609007
H   1.0  -1.6496177967   4.5494654292   1.4167016937
H   1.0  -1.5033385913   5.0127140796  -0.2871392740
H   1.0  -2.7142700480   5.7917346803   0.7423836575
O   8.0    1.4062420192   1.1794861400   1.0368403830
O   8.0    1.0874440033   0.5648234765  -1.4367610893
C   6.0    2.4749258401   0.3204025245  -1.7933190556
C   6.0    2.6435381755   0.5725955728  -3.2752306232
H   1.0    3.6782217697   0.3771879690  -3.5611991153
H   1.0    2.4071207927   1.6071375877  -3.5254648153
H   1.0    1.9971355136  -0.0844959088  -3.8578527292
H   1.0    3.1075797599   0.9835252323  -1.2027941448
H   1.0    2.7247376472  -0.7116650225  -1.5404530733
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