Supporting Information

A Novel Visible Light Catalyzed Radical Cyclization of Enol Lactone: A General Method for Fluorinated Sesquiterpene Lactones Analogues

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General Information

$^1$H NMR and $^{13}$C NMR spectra were measured on 400 MHz spectrometer, using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz. LRMS and HRMS were obtained in the EI, ESI mode. All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Difluoroacyl arenes$^{[1]}$ 2a-2k and butenolides$^{[2]}$ 1b-1f were prepared according to the literature. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. The 33W LEDs were directly got from the supermarket.

General procedure for radical cyclizations of butenolides

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1a-g (0.2 mmol), fac-Ir(ppy)$_3$ (0.01 equiv, 0.002mmol ), difluoroacyl arenes 2a-k (1.5 equiv, 0.3mmol ), 2, 6-lutidine (2.0 equiv, 0.4mmol). The flask was evacuated and backfilled with Ar for 3 times. 0.5 mL dry DMA and 0.5 mL dry DCE was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 33W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the reaction was finished, The mixture was then diluted with MTBE (2 x 20 mL) and water. The combined organic layers were dried over sodium sulfate and the solvent concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the 3aa-ak.

Optimization of the Reaction Conditions Of Radical Annulation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Additive</th>
<th>Yield$^b$(%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Ir(ppy)$_3$</td>
<td>DCM</td>
<td>/</td>
<td>2$^c$</td>
</tr>
<tr>
<td>2</td>
<td>Ir(ppy)$_3$</td>
<td>DCM</td>
<td>/</td>
<td>9$^d$</td>
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<tr>
<td>3</td>
<td>Ir(ppy)(dtbbpy)PF$_6$</td>
<td>DCM</td>
<td>/</td>
<td>N.R</td>
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<tr>
<td>4</td>
<td>[Ir$_2$(CF$_3$)$_2$(ppy)$_2$(dtbbpy)]PF$_6$</td>
<td>DCM</td>
<td>/</td>
<td>N.R</td>
</tr>
<tr>
<td>5</td>
<td>[Ru(bpy)$_3$]PF$_6$</td>
<td>DCM</td>
<td>/</td>
<td>N.R</td>
</tr>
<tr>
<td>6</td>
<td>9-mesityl-10-methylacridinium perchlorate</td>
<td>DCM</td>
<td>/</td>
<td>N.R</td>
</tr>
<tr>
<td>7</td>
<td>Eosin Y</td>
<td>DCM</td>
<td>/</td>
<td>N.R</td>
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<td>Ru(bpy)$_3$Cl$_2$</td>
<td>DCM</td>
<td>/</td>
<td>N.R</td>
</tr>
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</table>
Ir(ppy)$_3$ CHCl$_3$ / N.R
Ir(ppy)$_3$ DCE / 24
Ir(ppy)$_3$ DMSO / trace
Ir(ppy)$_3$ MeOH / trace
Ir(ppy)$_3$ NMP / 30
Ir(ppy)$_3$ DMF / 32
Ir(ppy)$_3$ DMA / 40
Ir(ppy)$_3$ DMA/DCE=1/1 / 29
Ir(ppy)$_3$ DMA PhCOOH 20
Ir(ppy)$_3$ DMA Et$_3$N 36
Ir(ppy)$_3$ DMA Na$_2$HPO$_4$ trace
Ir(ppy)$_3$ DMA NaOAc trace
Ir(ppy)$_3$ DMA 2,6-lutidine 68
Ir(ppy)$_3$ DMA 2,6-lutidine 54$^c$
Ir(ppy)$_3$ DMA/DCE=1/1 2,6-lutidine 73
Ir(ppy)$_3$ DMA/DCE=1/1 2,6-lutidine N.R
Ir(ppy)$_3$ DMA/DCE=1/1 2,6-lutidine N.R

$^a$Reaction conditions: 1a (0.2 mmol), 2a (0.3 mmol), additive (0.4 mmol), photocatalyst (1 mol%), solvent (1 mL), 33W fluorescent light bulb, 15 h, rt. $^b$ Isolated yield. $^c$ Irradiated by 5W Blue LED light. $^d$ Determined by $^1$H-NMR analysis 1,1,2,2-tetrachloroethane as an internal standard. $^e$ for 34h. $^f$ In the dark.

Characterization data of compounds
4,4-difluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3aa)

15h, 73% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.04-8.01 (m, 1H), 7.77-7.72 (m, 1H), 7.65-7.63 (m, 1H), 7.53-7.49 (m, 1H), 3.46-3.40 (m, 1H), 2.85-2.78 (m, 1H), 2.45-2.38 (m, 1H), 1.89 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 182.0 (t, $J$ = 25.2 Hz), 170.8, 140.9, 135.7, 129.1, 126.8, 126.2, 111.3 (dd, $J$ = 241.0 Hz, $J$ = 253.0 Hz), 81.8 (d, $J$ = 7.8 Hz), 48.0 (dd, $J$ = 22.5 Hz, $J$ = 25.3 Hz), 29.7 (d, $J$ = 6.9 Hz), 28.4 (d, $J$ = 1.7 Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -99.4 (d, $J$ = 284.6 Hz), -113.1 (d, $J$ = 284.6 Hz) ppm; m/z (EI): 252.1 [M]$^+$, HRMS (EI): exact mass calculated for [M]$^+$ (C$_{13}$H$_{10}$F$_2$O$_3$)$^+$ requires m/z 252.0589, found m/z 252.0605.
9b-ethyl-4,4-difluoro-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ba)

15h, 66% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.05-8.03 (m, 1H), 7.76-7.72 (m, 1H), 7.62 (d, $J =$ 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 3.58-3.50 (m, 1H), 2.83 (dd, $J =$ 8.8 Hz, $J =$ 17.6 Hz, 1H), 2.52-2.45 (m, 1H), 2.24-2.18 (m, 1H), 2.07-1.97 (m, 1H), 1.00 (t, $J =$ 7.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 183.1 (t, $J =$ 24.8 Hz), 172.0, 141.9, 136.6, 130.1, 128.7, 127.8, 112.1 (dd, $J =$ 243.0 Hz, $J =$ 250.0 Hz), 85.3 (d, $J =$ 7.0 Hz), 44.1 (dd, $J =$ 23.6 Hz, $J =$ 25.0 Hz), 33.7, 30.6-30.5 (m, 8.0 ppm); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta =$ -101.2 (d, $J =$ 284.3 Hz), -111.7 (d, $J =$ 284.3 Hz) ppm; m/z (EI): 266.1 [M]$^+$, 237.1 [M-CH$_2$CH$_3$]$^+$, 217.1 [M-CH$_2$CH$_3$-HF]$^+$.

4,4-difluoro-9b-propyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ca)

15h, 43% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.05-8.02 (m, 1H), 7.76-7.72 (m, 1H), 7.63 (d, $J =$ 8.0 Hz, 1H), 7.53-7.50 (m, 1H), 3.59-3.53 (m, 1H), 2.85-2.78 (m, 1H), 2.51-2.44 (m, 1H), 2.10-1.98 (m, 2H), 1.51-1.34 (m, 2H), 0.92 (t, $J =$ 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 183.1 (t, $J =$ 26.0 Hz), 172.0, 142.0, 136.5, 130.0, 128.7, 127.8, 112.1 (dd, $J =$ 243.0 Hz, $J =$ 250.0 Hz), 85.1 (d, $J =$ 7.1 Hz), 44.7 (dd, $J =$ 22.8 Hz, $J =$ 24.9 Hz), 42.9 (d, $J =$ 1.6 Hz), 30.5 (d, $J =$ 6.4 Hz), 17.9, 13.9 ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta =$ -101.2 (d, $J =$ 284.3 Hz), -111.7 (d, $J =$ 284.3 Hz) ppm; m/z (EI): 280.1 [M]$^+$, 237.1 [M-CH$_2$CH$_3$CH$_3$]$^+$, 217.1 [M-CH$_2$CH$_2$CH$_3$-HF]$^+$.

9b-butyl-4,4-difluoro-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3da)

15h, 60% yield, $^1$HNMR (400 MHz, CDCl$_3$): $\delta =$ 8.03 (d, $J =$ 8.0 Hz, 1H), 7.74 (t, $J =$ 7.2 Hz, 1H), 7.63 (d, $J =$ 8.0 Hz, 1H), 7.51 (t, $J =$ 7.2 Hz, 1H), 3.60-3.54 (m, 1H),
2.82 (dd, J = 8.8 Hz, J = 18.0 Hz, 1H), 2.47 (dd, J = 10.8 Hz, J = 18.0 Hz, 1H), 2.12-2.00 (m, 2H), 1.46-1.25 (m, 8H), 0.85 (t, J = 7.2 Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ = 183.1 (t, J = 25.5 Hz), 173.0, 142.1, 136.9, 129.6, 128.4 (d, J = 6.0 Hz), 126.9, 126.8 (d, J = 3.5 Hz), 113.2 (dd, J = 246.3 Hz, J = 253.3 Hz), 81.7 (dd, J = 2.0 Hz, J = 8.1 Hz), 46.4 (dd, J = 20.3 Hz, J = 22.1 Hz), 33.3 (d, J = 5.6 Hz), 27.9, 18.7 ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ = -96.0 (d, J = 285.4 Hz), 15h, 50% yield, \(^{1}\)HNMR (400 MHz, CDCl\(_3\)): δ = 8.03 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz), 7.51 (t, J = 7.6 Hz, 1H), 3.60-3.54 (m, 1H), 2.81 (dd, J = 9.2 Hz, J = 18.0 Hz, 1H), 2.47 (dd, J = 10.8 Hz, J = 18.0 Hz, 1H), 2.13-1.97 (m, 2H), 1.45-1.21 (m, 8H), 0.80-0.79 (m, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ = 183.1 (t, J = 25.5 Hz), 172.0, 142.1, 136.5, 130.0, 128.7, 127.8, 112.2 (dd, J = 243.8 Hz, J = 252.1 Hz), 85.1 (d, J = 7.3 Hz), 44.9-44.4 (m), 40.8, 35.7, 31.5, 30.5 (d, J = 22.0 Hz), 29.1 (d, J = 15.4 Hz), 23.5, 22.5, 14.0 ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ = -101.3 (d, J = 284.6 Hz), -111.7 (d, J = 284.6 Hz) ppm; m/z (EI): 322.1 [M]\(^{+}\), 237.0 [M-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)]\(^{+}\), 217.1 [M-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)-HF]\(^{+}\).

5,5-difluoro-10b-methyl-3,4,4a,5-tetrahydro-2H-benzo[h]chromene-2,6(10bH)-dione (3fa)

16h, 31% yield, \(^{1}\)HNMR (400 MHz, CDCl\(_3\)): δ = 8.07 (d, J = 8.0 Hz, 1H), 7.74-7.70 (m, 2H), 7.50-7.46 (m, 1H), 3.02-2.94 (m, 1H), 2.50-2.41 (m, 1H), 2.32-2.25 (m, 1H), 2.17-2.09 (m, 1H), 1.83 (d, J = 2. Hz, 3H), 1.70-1.59 (m, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ = 183.3 (t, J = 25.0 Hz), 168.8 (d, J = 3.9 Hz), 144.9, 136.9, 129.6, 128.4 (d, J = 6.0 Hz), 126.9, 126.8 (d, J = 3.5 Hz), 113.2 (dd, J = 246.3 Hz, J = 253.3 Hz), 81.7 (dd, J = 2.0 Hz, J = 8.1 Hz), 46.4 (dd, J = 20.3 Hz, J = 22.1 Hz), 33.3 (d, J = 5.6 Hz), 27.9, 18.7 ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ = -96.0 (d, J = 285.4 Hz),
-113.9 (d, J = 285.4 Hz) ppm; m/z (EI): 266.1 [M]+, HRMS (EI): exact mass calculated for [M]+ (C_{14}H_{12}F_{2}O_{3}) requires m/z 266.0755, found m/z 266.0752.

3,3-difluoro-1-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (3ga)

15h, 59% yield, ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.44-7.39 (m, 1H), 2.92-2.83 (m, 1H), 1.98 (s, 3H), 1.79 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 184.3 (t, J = 25.8 Hz), 169.7, 146.3, 135.7, 128.8 (d, J = 6.9 Hz), 128.6 (d, J = 1.9 Hz), 127.8 (d, J = 3.4 Hz), 125.4, 112.1 (d, J = 242.6 Hz, J = 249.9 Hz), 77.5 (d, J = 10.9 Hz), 41.8 (t, J = 22.2 Hz), 30.1 (d, J = 4.9 Hz), 22.1 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -99.3 (d, J = 282.7 Hz), -106.2 (d, J = 282.7 Hz) ppm; m/z (EI): 254.1 [M]+, 212.1 [M-COCH₃]+, 195.1 [M-OOCCH₃]+, 175.1 [M-OOCCH₃-HF]⁺.

4,4-difluoro-8-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ab)

15h, 77% yield, ¹H NMR (400 MHz, CDCl₃): δ = 8.02 (d, J = 9.2 Hz), 7.01-6.99 (m, 2H), 3.87 (s, 3H), 3.46-3.36 (m, 1H), 2.79 (dd, J = 8.8 Hz, J = 18.0 Hz, 1H), 2.47-2.39 (m, 1H), 1.89 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 181.1 (t, J = 25.7 Hz), 171.9, 166.4, 144.7, 130.5 (d, J = 2.2 Hz), 120.5 (d, J = 3.6 Hz), 117.3, 112.4, 112.1 (d, J = 242.3 Hz, J = 251.8 Hz), 82.8 (d, J = 8.4 Hz), 56.0, 49.3 (d, J = 23.4 Hz, J = 26.3 Hz), 30.9 (d, J = 6.9 Hz), 29.4 (d, J = 1.7 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -97.7 (d, J = 286.5 Hz), -112.7 (d, J = 286.5 Hz) ppm; m/z (EI):282.1 [M]+, HRMS (EI): exact mass calculated for [M]+ (C_{14}H_{11}F_{2}O_{4}) requires m/z 282.0704, found m/z 282.0692.

4,4-difluoro-6-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ac)
15h, 90% yield, $^1$HNMR (400 MHz, CDCl$_3$): $\delta = 7.63$ (t, $J = 8.4$ Hz, 1H), 7.20-7.17 (m, 1H), 6.99 (d, $J = 8.4$ Hz, 1H), 3.89 (s, 3H), 3.34-3.29 (m, 1H), 2.84 (dd, $J = 8.8$ Hz, $J = 18.0$ Hz, 1H), 2.59-2.52 (m, 1H), 1.84 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 181.5$ (t, $J = 25.8$ Hz), 172.1, 160.4, 144.0, 137.2, 120.3, 117.0, 112.5, 112.3 (dd, $J = 246.2$ Hz, $J = 249.9$ Hz), 82.9 (d, $J = 5.5$ Hz), 56.4, 48.3-47.8 (m), 30.4 (d, $J = 2.0$ Hz), 30.2 (dd, $J = 1.7$ Hz, $J = 5.2$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -104.7$ (d, $J = 269.2$ Hz), -113.0 (d, $J = 269.2$ Hz) ppm; m/z (EI): 282.1 $[M]^+$, HRMS (EI): exact mass calculated for $[M]^+$ (C$_{14}$H$_{12}$F$_2$O$_4$) requires m/z 282.0704, found m/z 282.0696.

4,4-difluoro-7-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad)

4,4-difluoro-9-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad')

15h, 91% yield, 3ad/3ad' = 2/1, $^1$HNMR (400 MHz, CDCl$_3$): $\delta = 7.65$ (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 0.53H), 7.47 (t, $J = 8.4$ Hz, 1H), 7.42 (d, $J = 2.8$ Hz, 0.51H), 7.29 (d, $J = 2.8$ Hz, 0.34H), 7.27-7.25 (m, 1H), 3.88 (s, 3H), 3.82 (s, 1.6H), 3.44-3.31 (m, 1.5H), 2.82-2.75 (m, 1.51H), 2.46-2.39 (m, 1.8H), 2.02 (s, 3H), 1.87 (s, 1.6H) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -98.8$ (d, $J = 284.3$ Hz), -112.9 (d, $J = 280.1$ Hz), -114.0 (d, $J = 280.1$ Hz) ppm; m/z (EI): 282.1 $[M]^+$, HRMS (EI): exact mass calculated for $[M]^+$ (C$_{14}$H$_{12}$F$_2$O$_4$) requires m/z 282.0704, found m/z 282.0694.

4,4,8-trifluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ae)

15h, 76% yield, $^1$HNMR (400 MHz, CDCl$_3$): $\delta = 8.09$ (dd, $J = 5.6$ Hz, $J = 8.8$ Hz, 1H), 7.30 (dd, $J = 2.4$ Hz, $J = 8.8$ Hz, 1H), 7.23-7.19 (m, 1H), 3.50-3.40 (m, 1H), 2.86-2.79 (m, 1H), 2.45-2.38 (m, 1H), 1.89 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 181.5$ (t, $J = 25.6$ Hz), 171.3, 167.8 (d, $J = 260.1$ Hz), 145.3 (d, $J = 9.0$ Hz), 131.3 (dd, $J = 2.0$ Hz, $J = 9.9$ Hz), 123.9 (t, $J = 2.4$ Hz), 118.5 (d, $J = 22.7$ Hz), 115.6 (d, $J = 23.4$ Hz), 112.0 (dd, $J = 241.5$ Hz, $J = 252.5$ Hz), 82.2 (d, $J = 7.2$ Hz), 49.0 (dd, $J = 22.8$ Hz, $J = 25.2$ Hz), 30.6 (d, $J = 6.4$ Hz), 29.3 (d, $J = 2.3$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -98.9$ (d, $J = 284.3$ Hz), -100.0 (d, $J = 280.1$ Hz), -112.9 (d, $J = 280.1$ Hz), -114.0 (d, $J = 280.1$ Hz) ppm; m/z (EI): 282.1 $[M]^+$, HRMS (EI): exact mass calculated for $[M]^+$ (C$_{14}$H$_{12}$F$_2$O$_4$) requires m/z 282.0704, found m/z 282.0694.
8-chloro-4,4-difluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3af)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{F} & \quad \text{F} \\
\text{Cl} & \quad \text{Me}
\end{align*}
\]

15h, 94% yield, \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta = 7.98 \, (d, \, J = 8.4 \, Hz, \, 1H),\) 7.62 (d, \(J = 1.6 \, Hz, \, 1H),\) 7.49 (dd, \(J = 2.0 \, Hz, \, J = 8.4 \, Hz, \, 1H),\) 3.47-3.39 (m, 1H), 2.86-2.79 (m, 1H), 2.44-2.37 (m, 1H), 1.90 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 182.0 \, (t, \, J = 26.1 \, Hz),\) 171.3, 143.8, 143.5, 130.9, 129.5, 128.9, 125.6 (d, \(J = 3.5 \, Hz),\) 112.0 (dd, \(J = 242.4 \, Hz, \, J = 253.3 \, Hz),\) 82.2 (d, \(J = 8.9 \, Hz),\) 49.3-48.8 (m), 30.6 (d, \(J = 6.1 \, Hz),\) 29.4 (d, \(J = 1.5 \, Hz)\) ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta = -99.0 \, (d, \, J = 285.8 \, Hz),\) -113.3 (d, \(J = 285.8 \, Hz)\) ppm; \(m/z\) (EI): 286.0 \([M]^+\), HRMS (EI): exact mass calculated for \([M]^+\) (\(C_{13}H_9F_3O_3^+\)) requires \(m/z\) 286.0208, found \(m/z\) 286.0210.

4,4-difluoro-8,9b-dimethyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ag)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{F} & \quad \text{F} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

15h, 76% yield, \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta = 7.93 \, (d, \, J = 8.0 \, Hz, \, 1H),\) 7.41 (s, 1H), 7.31 (d, \(J = 8.0 \, Hz, \, 1H),\) 3.47-3.37 (m, 1H), 2.80 (dd, \(J = 8.8 \, Hz, \, J = 17.6 \, Hz, \, 1H),\) 2.44-2.35 (m, 1H), 2.42 (s, 3H), 1.89 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 182.5 \, (t, \, J = 25.7 \, Hz),\) 171.9, 148.5, 141.9, 131.3, 129.0, 127.9 (d, \(J = 1.9 \, Hz),\) 124.9 (d, \(J = 3.3 \, Hz),\) 112.3 (dd, \(J = 241.9 \, Hz, \, J = 252.4 \, Hz),\) 82.9 (d, \(J = 8.8 \, Hz),\) 49.2 (dd, \(J = 23.1 \, Hz, \, J = 25.5 \, Hz),\) 30.9 (d, \(J = 6.7 \, Hz),\) 29.4-29.3 (m), 22.2 ppm; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta = -98.6 \, (d, \, J = 285.0 \, Hz),\) -113.0 (d, \(J = 285.0 \, Hz)\) ppm; \(m/z\) (EI): 266.1 \([M]^+\), HRMS (EI): exact mass calculated for \([M]^+\) (\(C_{14}H_{12}F_3O_3^+\)) requires \(m/z\) 266.0755, found \(m/z\) 266.0765.

4,4-difluoro-10b-methyl-3a,4-dihydrofuro[2',3':5,6]naphtho[2,3-d][1,3]dioxole-2,5(3H,10bH)-dione (3ah)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{F} & \quad \text{F} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

7,7-difluoro-10a-methyl-7a,8-dihydrofuro[3',2':7,8]naphtho[1,2-d][1,3]dioxole-6,9(7H,10aH)-dione (3ah')
15h, 76% yield, 3ah/3ah' = 5/1, ¹H NMR (400 MHz, CDCl₃): δ = 7.72 (d, J = 8.4 Hz, 0.41H), 7.37 (s, 1H), 6.97 (s, 1H), 6.95 (d, J = 8.4 Hz, 0.41H), 6.15 (d, J = 4.0 Hz, 0.65H), 6.06 (s, 2H), 3.43-3.34 (m, 1.2H), 2.86-2.75 (m, 1.3H), 2.51-2.38 (m, 1.6H), 1.97 (s, 1.1H), 1.85 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 184.7 (t, J = 180.0 Hz), 171.9, 143.6, 137.6, 133.6, 130.4, 129.9, 128.7, 128.2, 126.4, 124.4, 123.0 (d, J = 18.0 Hz), 112.6 (dd, J = 8.8 Hz, J = 12.0 Hz, J = 177.6 Hz, 1H), 1.87 (s, 3H) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -271.3 (d, J = 286.5 Hz), -112.0 (d, J = 286.1 Hz), -113.4 (d, J = 290.0 Hz) ppm; HRMS (ES⁺): exact mass calculated for [M-H]⁺ (C₁₄H₉F₂O₅⁻) requires m/z 295.0423, found m/z 295.0424.

11,11-difluoro-3a-methyl-11,11a-dihydrophenanthro[1,2-b]furan-2,10(1H,3aH)-dione (3ai)

15h, 84% yield, ¹H NMR (400 MHz, CDCl₃): δ = 9.09 (d, J = 8.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.68-7.54 (m, 3H), 3.47-3.42 (m, 1H), 2.88 (dd, J = 9.2 Hz, J = 18.0 Hz, 1H), 2.62-2.55 (m, 1H), 1.91 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 184.7 (t, J = 264.4 Hz), 171.9, 143.6, 137.6, 133.6, 130.4, 129.9, 128.7, 128.2, 126.4, 124.4, 123.0 (d, J = 18.0 Hz), 112.6 (dd, J = 244.3 Hz, J = 251.1 Hz), 83.2 (d, J = 7.4 Hz), 48.3 (dd, J = 23.7 Hz, J = 25.7 Hz), 30.4 (d, J = 5.3 Hz), 30.0 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -271.3 (d, J = 286.5 Hz), -112.0 (d, J = 290.0 Hz) ppm; m/z (EI): 302.1 [M⁺], HRMS (EI): exact mass calculated for [M⁺]⁺ (C₁₇H₁₂F₂O₃⁺) requires m/z 302.0755, found m/z 302.0749.

4,4-difluoro-8b-methyl-3a,4-dihydrothieno[2,3-g]benzofuran-2,5(3H,8bH)-dione (3aj)

15h, 63% yield, ¹H NMR (400 MHz, CDCl₃): δ = 7.90 (d, J = 5.2 Hz, 1H), 7.24 (d, J = 5.2 Hz, 1H), 3.45-3.39 (m, 1H), 2.83 (dd, J = 8.8 Hz, J = 17.6 Hz, 1H), 2.49 (dd, J = 12.0 Hz, J = 17.6 Hz, 1H), 1.87 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 176.1 (t, J = 264.4 Hz), 171.5, 150.7, 139.7, 132.7 (d, J = 4.4 Hz), 127.8, 113.3 (dd, J = 244.6 Hz, J = 254.7 Hz), 81.2 (d, J = 8.2 Hz), 50.2 (dd, J = 21.9 Hz, J = 26.0 Hz), 30.8 (d, J = 5.9 Hz), 27.8 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -95.5 (d, J = 286.5 Hz), -
112.9 (d, J = 286.5 Hz) ppm; HRMS (ES⁻): exact mass calculated for [M-H]⁻ (C₁₁H₂ₘF₂S⁻) requires m/z 257.0089, found m/z 257.0100.

4,4-difluoro-7,8-dimethoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ak)
4,4-difluoro-8,9-dimethoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ak’)

15h, 36% yield, ¹H NMR (400 MHz, CDCl₃): δ = 7.41 (s, 1H), 6.95 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.92- 3.80 (m, 1.49H), 3.46-3.38 (m, 1H), 2.83-2.67 (m, 1H), 2.48-2.40 (m, 1H), 1.89 (s, 3H) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -96.9 (d, J = 287.0 Hz), -105.5 (d, J = 267.7 Hz), -112.2 (d, J = 287.0 Hz), -113.8 (d, J = 267.7 Hz) ppm; m/z (EI): 312.1 [M]⁺, HRMS (EI): exact mass calculated for [M]⁺ (C₁₅H₁₄F₂O₅⁺) requires m/z 312.0809, found m/z 312.0801.

References:
Copies $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR

4,4-difluoro-9b-methyl-3a,4-dihydropaptho[1,2-b]furan-2,5(3H,9bH)-dione (3aa)
9b-ethyl-4,4-difluoro-3a,4-dihyronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ba)
4,4-difluoro-9b-propyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ca)
9b-butyl-4,4-difluoro-3a,4-dihydonaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3da)
4,4-difluoro-9b-hexyl-3a,4-dihydronaph[1,2-b]furan-2,5(3H,9bH)-dione (3ea)
5,5-difluoro-10b-methyl-3,4,4a,5-tetrahydro-2H-benzo[h]chromene-2,6(10bH)-dione (3fa)
3,3-difluoro-1-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (3ga)
4,4-difluoro-8-methoxy-9b-methyl-3a,4-dihydropthalto[1,2-b]furan-2,5(3H,9bH)-dione (3ab)
4,4-difluoro-6-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ac)
4,4-difluoro-9-methoxy-9b-methyl-3a,4-dihyronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad)
4,4-difluoro-7-methoxy-9b-methyl-3a,4-dihyronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad’
4,4,8-trifluoro-9b-methyl-3a,4-dihydropaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ae)
8-chloro-4,4-difluoro-9-b-methyl-3a,4-dihyronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3af)
4,4-difluoro-8,9b-dimethyl-3a,4-dihyronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ag)
4,4-difluoro-10b-methyl-3a,4-dihydrofuro[2',3':5,6]naphtho[2,3-d][1,3]dioxole-2,5(3H,10bH)-dione (3ah)
7,7-difluoro-10a-methyl-7a,8-dihydrofuro[3',2':7,8]naphtho[1,2-d][1,3]dioxole-6,9(7H,10aH)-dione (3ah')
11,11-difluoro-3a-methyl-11,11a-dihydrophenanthro[1,2-b]furan-2,10(1H,3aH)-dione (3ai)
4,4-difluoro-8b-methyl-3a,4-dihydrothieno[2,3-g]benzofuran-2,5(3H,8bH)-dione (3aj)
4,4-difluoro-7,8-dimethoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ak)
4,4-difluoro-8,9-dimethoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ak')