# Supporting Information

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

Chuanhua Qu,[a] Pan Xu,[a] Wujiang Ma,[a] Yixiang Cheng,[a] and Chengjian Zhu*[a,b]
(*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,*
*Nanjing University Nanjing 210093 E-mail:* cjzhu@nju.edu.cn)

### Table of Contents

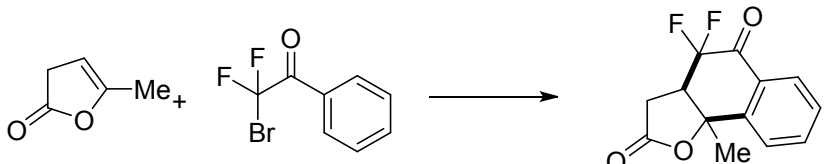
## General Information

$^{1}H$ 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




**1a** **2a** **3aa**

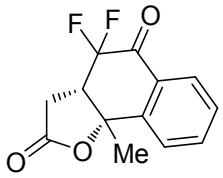
| Entry | Catalyst | Solvent | Additive | Yield[b](%) |
|---|---|---|---|---|
| 1 | Ir(ppy)$_3$ | DCM | / | 2[c] |
| 2 | Ir(ppy)$_3$ | DCM | / | 9[d] |
| 3 | Ir(ppy)(dtbpy)$PF_6$ | DCM | / | N.R |
| 4 | [IrdF($CF_3$)(ppy)$_2$(dtbbpy)]$PF_6$ | DCM | / | N.R |
| 5 | [Ru(bpy)$_3$]$PF_6$ | DCM | / | N.R |
| 6 | 9-mesityl-10-methylacridinium perchlorate | DCM | / | N.R |
| 7 | Eosin Y | DCM | / | N.R |
| 7 | Ru(bpy)$_3Cl_2$ | DCM | / | N.R |

| | | | | |
|---|---|---|---|---|
| 8 | $Ir(ppy)_3$ | $CHCl_3$ | / | N.R |
| 9 | $Ir(ppy)_3$ | DCE | / | 24 |
| 10 | $Ir(ppy)_3$ | DMSO | / | trace |
| 11 | $Ir(ppy)_3$ | MeOH | / | trace |
| 12 | $Ir(ppy)_3$ | NMP | / | 30 |
| 13 | $Ir(ppy)_3$ | DMF | / | 32 |
| 14 | $Ir(ppy)_3$ | DMA | / | 40 |
| 15 | $Ir(ppy)_3$ | DMA/DCE=1/1 | / | 29 |
| 16 | $Ir(ppy)_3$ | DMA | PhCOOH | 20 |
| 17 | $Ir(ppy)_3$ | DMA | $Et_3N$ | 36 |
| 18 | $Ir(ppy)_3$ | DMA | $Na_2HPO_4$ | trace |
| 19 | $Ir(ppy)_3$ | DMA | NaOAc | trace |
| 20 | $Ir(ppy)_3$ | DMA | 2,6-lutdine | 68 |
| 21 | $Ir(ppy)_3$ | DMA | 2,6-lutdine | 54[e] |
| 22 | $Ir(ppy)_3$ | DMA/DCE=1/1 | 2,6-lutidine | 73 |
| 23 | | DMA/DCE=1/1 | 2,6-lutidine | N.R |
| 24[f] | $Ir(ppy)_3$ | 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.

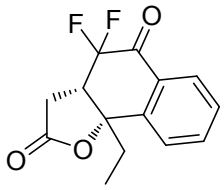
## Characterization data of compounds

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



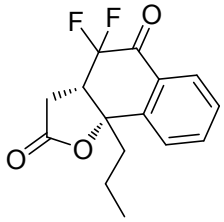

15h, 73% yield; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.04-8.01 (m, 1H), 7.77-7.72 (m, 1H), 7.65-7.63 (m, 1H), 7.53-7.49 (m, 1H), 3.46-3.40 (m, 1H), 2.85-2.78 (m, 1H), 2.45-2.38 (m, 1H), 1.89 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 182.0 (t, $J$ = 25.2 Hz), 170.8, 140.9, 135.7, 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 $[M]^+$ ($C_{13}H_{10}F_2O_3^+$) 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)**



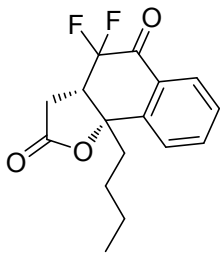
15h, 66% yield; $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.05-8.03 (m, 1H), 7.76-7.72 (m, 1H), 7.62 (d, $J$ = 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 3.58-3.50 (m, 1H), 2.83 (dd, $J$ = 8.8 Hz, $J$ = 17.6 Hz, 1H), 2.52-2.45 (m, 1H), 2.24-2.18 (m, 1H), 2.07-1.97 (m, 1H), 1.00 (t, $J$ = 7.4 Hz, 3H) ppm; $^{13}$C 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, $J$ = 284.3Hz), -111.8 (d, $J$ = 284.3 Hz) ppm; *m/z* (EI): 266.1 $[M]^+$, 237.1 $[M\text{-}CH_2CH_3]^+$, 217.1 $[M\text{-}CH_2CH_3\text{-}HF]^+$.

**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, $J$ = 7.2Hz, 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, 127.7, 112.1 (dd, $J$ = 243.0 Hz, $J$ = 250.0 Hz), 85.1 (d, $J$ = 7.1Hz), 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 $[M\text{-}CH_2CH_2CH_3]^+$, 217.1 $[M\text{-}CH_2CH_2CH_3\text{-}HF]^+$.

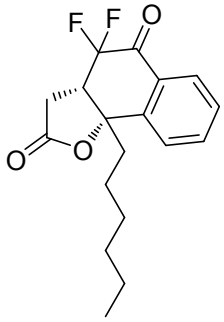
**9b-butyl-4,4-difluoro-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3da)**



15h, 60% yield, $^{1}$HNMR (400 MHz, $CDCl_3$): $\delta$ = 8.03 (d, $J$ = 8.0Hz, 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),

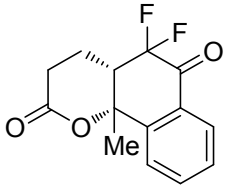
2.82 (dd, $J$ = 8.8 Hz, $J$ = 18.0 Hz, 1H), 2.47 (dd, $J$ = 10.8 Hz, $J$ = 18.0 Hz, 1H), 2.12-2.00 (m, 2H), 1.46-1.25 (m, 4H), 0.85 (t, $J$ = 7.2Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 183. (t, $J$ = 25.7 Hz), 172.0, 142.0, 136.5, 130.0, 128.7, 127.8, 127.7, 112.1 (dd, $J$ = 243.4 Hz, $J$ = 251.4 Hz), 85.1 (d, $J$ = 7.3 Hz), 44.6 (d, $J$ = 22.9 Hz, $J$ = 25.6 Hz), 40.6, 30.5 (d, $J$ = 3.1 Hz), 25.6, 22.4, 13.8 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -101.3 (d, $J$ = 285.0 Hz), -111.7 (d, $J$ = 285.0 Hz) ppm; HRMS (ES$^-$): exact mass calculated for $[M-H]^-$ ($C_{16}H_{15}F_2O_3^-$) requires m/z 293.0995, found m/z 293.1009.

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




15h, 50% yield, $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = -101.3 (d, $J$ = 284.6 Hz), -111.7 (d, $J$ = 284.6 Hz) ppm; *m/z* (EI): 322.1 $[M]^+$, 237.0 $[M-CH_2CH_2CH_2CH_3]^+$, 217.1 $[M-CH_2CH_2CH_2CH_3-HF]^+$.

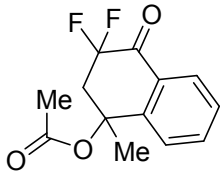
**5,5-difluoro-10b-methyl-3,4,4a,5-tetrahydro-2H-benzo[h]chromene-2,6(10bH)-dione (3fa)**




16h, 31% yield, $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = 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, $CDCl_3$): $\delta$ = -96.0 (d, $J$ = 285.4 Hz),

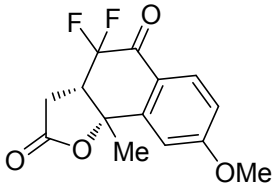
-113.9 (d, $J$ = 285.4 Hz) ppm; *m/z* (EI): 266.1 $[M]^+$, HRMS (EI): exact mass calculated for $[M]^+$ ($C_{14}H_{12}F_2O_3^+$) requires *m/z* 266.0755, found *m/z* 266.0752.

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



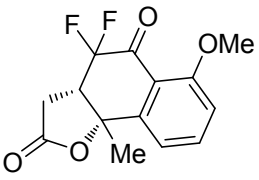

15h, 59% yield, $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 8.04(d, $J$ = 8.0Hz, 1H), 7.64-7.60 (m, 1H), 7.44-7.39 (m, 2H), 3.45-3.33 (m, 1H), 2.92-2.83 (m, 1H), 1.98 (s, 3H), 1.79 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 184.3 (t, $J$ = 25.8 Hz), 169.7, 146.3, 135.7, 128.8 (d, $J$ = 6.9 Hz), 128.6 (d, $J$ = 1.9Hz), 127.8 (d, $J$ = 3.4 Hz), 125.4, 112.1 (dd, $J$ = 242.6 Hz, $J$ = 249.9 Hz), 77.5 (d, $J$ = 10.9 Hz), 41.8 (t, $J$ = 22.2Hz), 30.1 (d, $J$ = 4.9 Hz), 22.1 ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -99.3 (d, $J$ = 282.7 Hz), -106.2 (d, $J$ = 282.7 Hz) ppm; *m/z* (EI): 254.1 $[M]^+$, 212.1 $[M\text{-}COCH_3]^+$, 195.1 $[M\text{-}OCOCH_3]^+$, 175.1 $[M\text{-}OCOCH_3\text{-}HF]^+$.

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




15h, 77% yield, $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 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; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 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 (dd, $J$ = 242.3 Hz, $J$ = 251.8 Hz), 82.8 (d, $J$ = 8.4 Hz), 56.0, 49.3 (dd, $J$ = 23.4 Hz, $J$ = 26.3 Hz), 30.9 (d, $J$ = 6.9 Hz), 29.4 (d, $J$ = 1.7 Hz) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -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 $[M]^+$ ($C_{14}H_{11}F_2O_4^+$) requires *m/z* 282.0704, found *m/z* 282.0692.

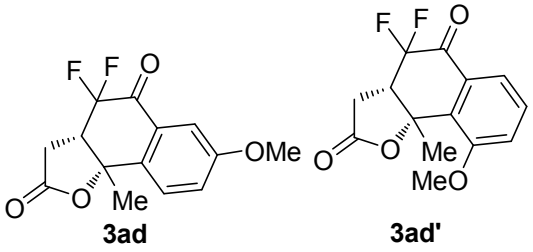
**4,4-difluoro-6-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ac)**



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, $J$ = 249.9Hz), 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 $[M]^+$ ($C_{14}H_{12}F_2O_4^+$) requires *m/z* 282.0704, found *m/z* 282.0696.

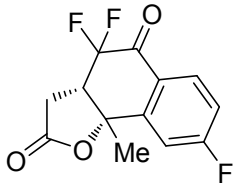
**4,4-difluoro-7-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad)**

**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), -102.7 (d, $J$ = 280.1 Hz), -112.9 (d, $J$ = 284.3 Hz), -114.0 (d, $J$ = 280.1 Hz) ppm; *m/z* (EI): 282.1 $[M]^+$, HRMS (EI): exact mass calculated for $[M]^+$ ($C_{14}H_{12}F_2O_4^+$) requires *m/z* 282.0704, found *m/z* 282.0694.

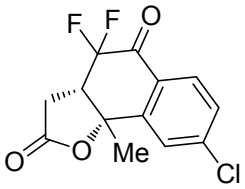
**4,4,8-trifluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ae)**




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

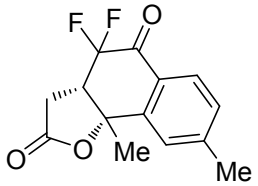
MHz, $CDCl_3$): $\delta$ = -96.9 (s), -98.9 (d, $J$ = 286.1 Hz), -113.2 (d, $J$ = 286.1 Hz) ppm; HRMS ($ES^-$): exact mass calculated for $[M-H]^-$ ($C_{13}H_9F_3O_3^-$) requires m/z 269.0431, found m/z 269.0424.

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




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 $[M]^+$ ($C_{13}H_9ClF_2O_3^+$) requires *m/z* 286.0208, found *m/z* 286.0210.

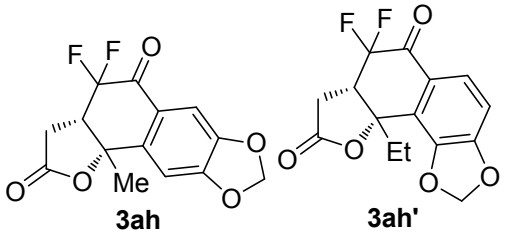
**4,4-difluoro-8,9b-dimethyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ag)**




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 $[M]^+$ ($C_{14}H_{12}F_2O_3^+$) requires *m/z* 266.0755, found *m/z* 266.0765.

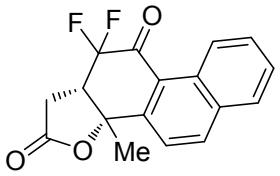
**4,4-difluoro-10b-methyl-3a,4-dihydrofuro[2',3':5,6]naphtho[2,3-d][1,3]dioxole-2,5(3H,10bH)-dione (3ah)**

**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')**



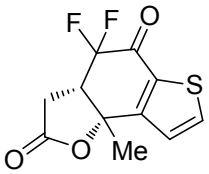

15h, 76% yield, **3ah/3ah'** = 5/1, $^{1}$HNMR (400 MHz, $CDCl_3$): $\delta$ = 7.72 (d, $J$ = 8.4 Hz, 0.41H), 7.37 (s, 1H), 6.97 (s, 1H), 6.95 (d, $J$ = 8.4 Hz, 0.41H), 6.15 (d, $J$ = 4.0 Hz, 0.65H), 6.06 (s, 2H), 3.43-3.34 (m, 1.2H), 2.86-2.75 (m, 1.3H), 2.51-2.38 (m, 1.6H), 1.97 (s, 1.1H), 1.85 (s, 3H) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -97.3 (d, $J$ = 285.4 Hz), -100.0 (d, $J$ = 285.4 Hz), -112.4 (d, $J$ = 286.1 Hz), -113.4 (d, $J$ = 282.0 Hz) ppm; HRMS ($ES^-$): exact mass calculated for $[M-H]^-$ ($C_{14}H_9F_2O_5^-$) 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, $^{1}$HNMR (400 MHz, $CDCl_3$): $\delta$ = 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; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 184.7 (t, $J$ = 26.4 Hz), 171.9, 143.6, 137.6, 133.6, 130.4, 129.9, 128.7, 128.2, 126.4, 124.4, 123.0 (d, $J$ = 1.8 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; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -103.3 (d, $J$ = 269.2 Hz), -112.0 (d, $J$ = 269.2 Hz) ppm; *m/z* (EI): 302.1 $[M]^+$, HRMS (EI): exact mass calculated for $[M]^+$ ($C_{17}H_{12}F_2O_3^+$) requires *m/z* 302.0755, found *m/z* 302.0749.

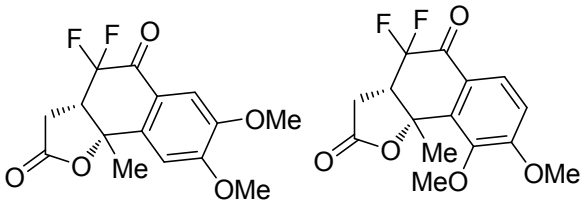
**4,4-difluoro-8b-methyl-3a,4-dihydrothieno[2,3-g]benzofuran-2,5(3H,8bH)-dione (3aj)**




15h, 63% yield, $^{1}$HNMR (400 MHz, $CDCl_3$): $\delta$ = 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; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 176.1 (t, $J$ = 26.9 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; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -95.5 (d, $J$ = 286.5 Hz), -

112.9 (d, $J$ = 286.5 Hz) ppm; HRMS ($ES^-$): exact mass calculated for $[M-H]^-$ ($C_{11}H_7F_2O_3S^-$) 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')**




**3ak** **3ak'**

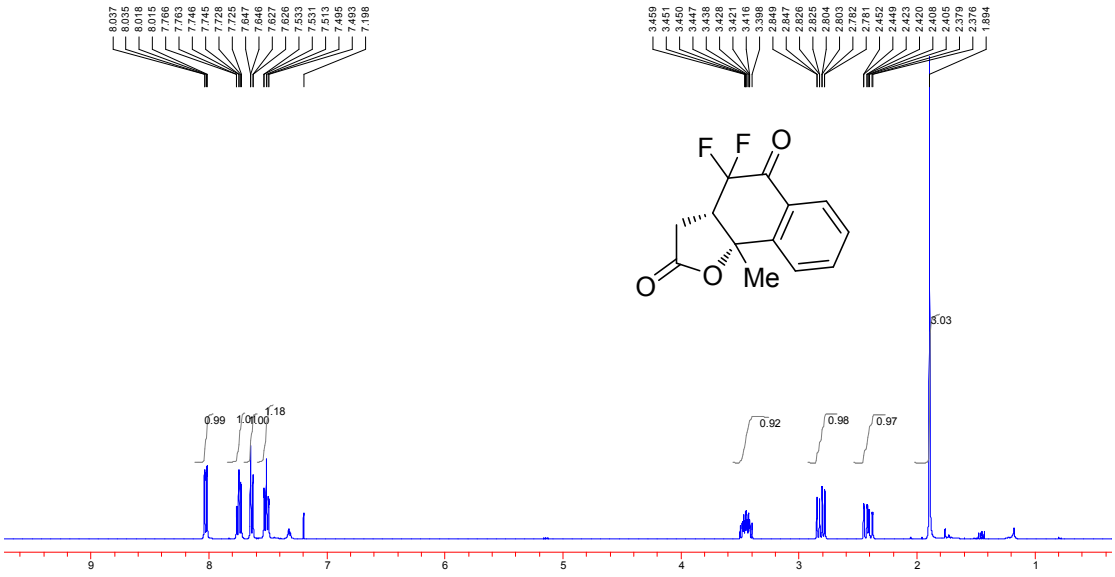
15h, 36% yield, $^1$HNMR (400 MHz, $CDCl_3$): $\delta$ = 7.41 (s, 1H), 6.95 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.92- 3.80 (m, 1.49H), 3.46-3.38 (m, 1H), 2.83-2.67 (m, 1H), 2.48-2.40 (m, 1H), 1.89 (s, 3H) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = -96.9 (d, $J$ = 287.0 Hz), -105.5 (d, $J$ = 267.7 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 $[M]^+$ ($C_{15}H_{14}F_2O_5^+$) requires *m/z* 312.0809, found *m/z* 312.0801.

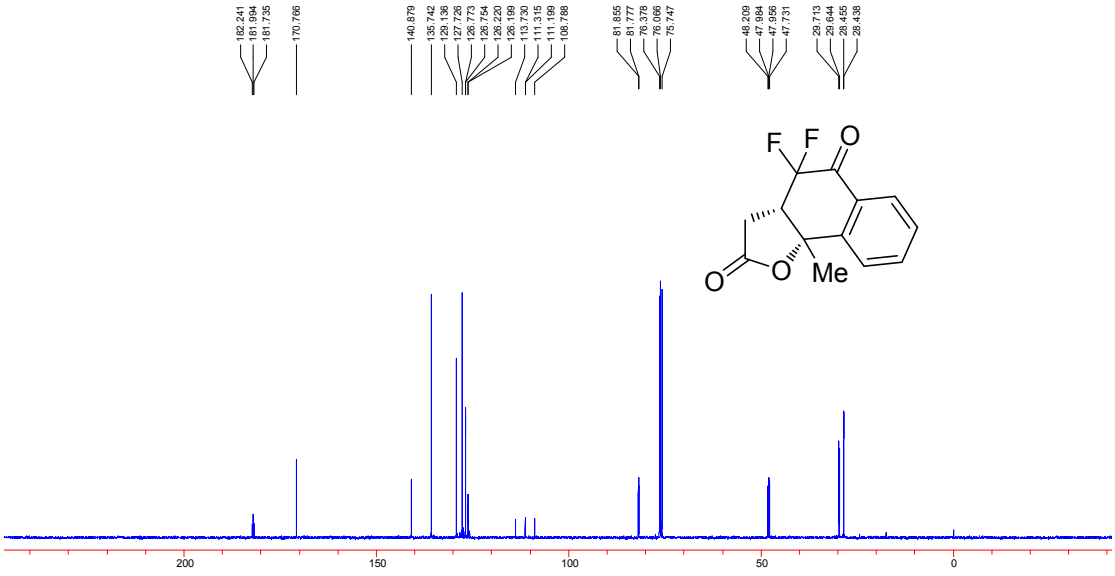
## References:

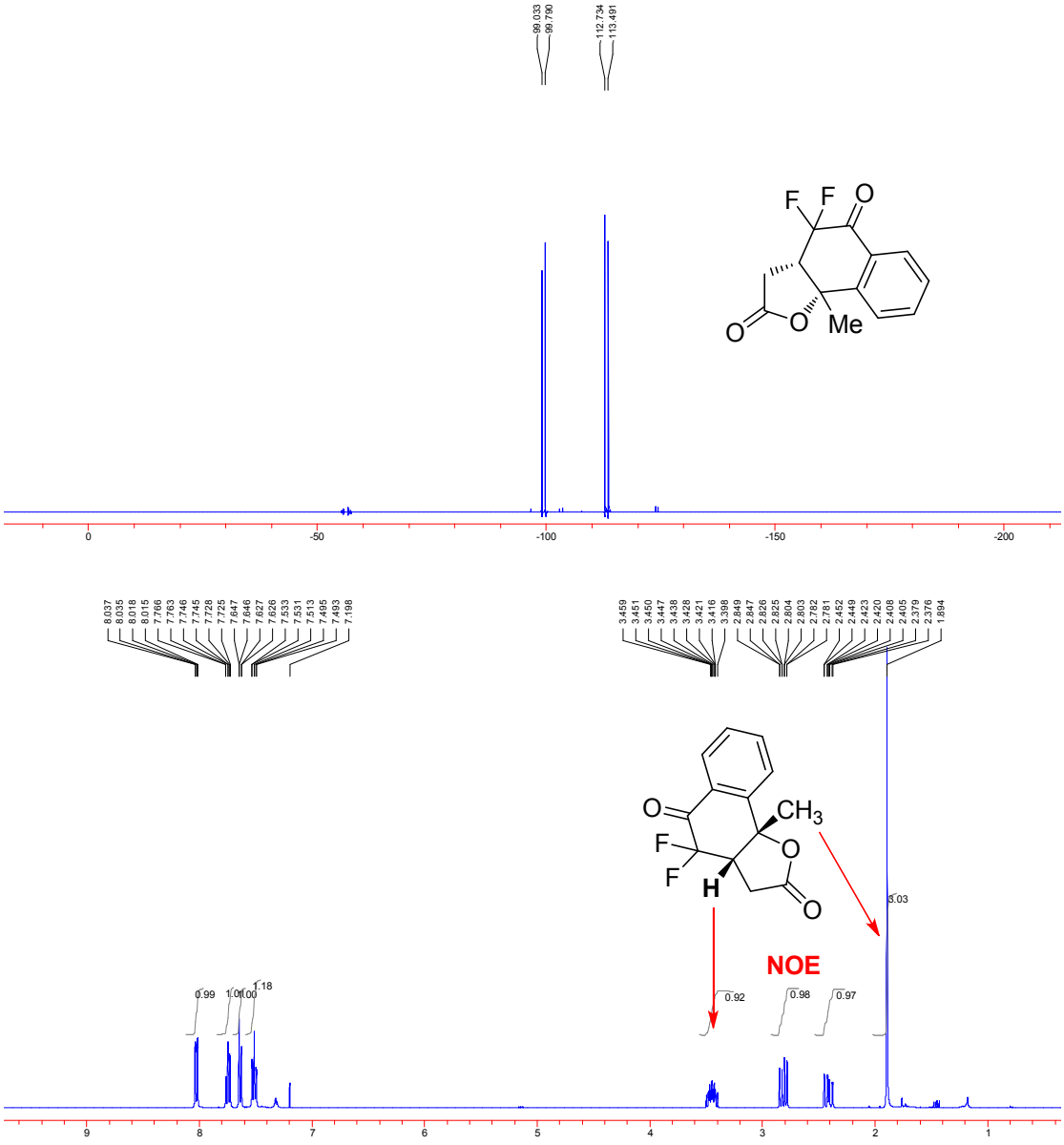
[1]T. Nihei, N. Iwai, T. Matsuda and T. Kitazume, *J. Org. Chem.*, **2005**, *70*, 5912-5915.
[2]M. E. Muratore, C. A. Holloway, A. W. Piling, R. L. Storer, G. Trevitt and D. J. Dixon, *J. Am. Chem. Soc*., **2009**, *131*, 10796-10797.

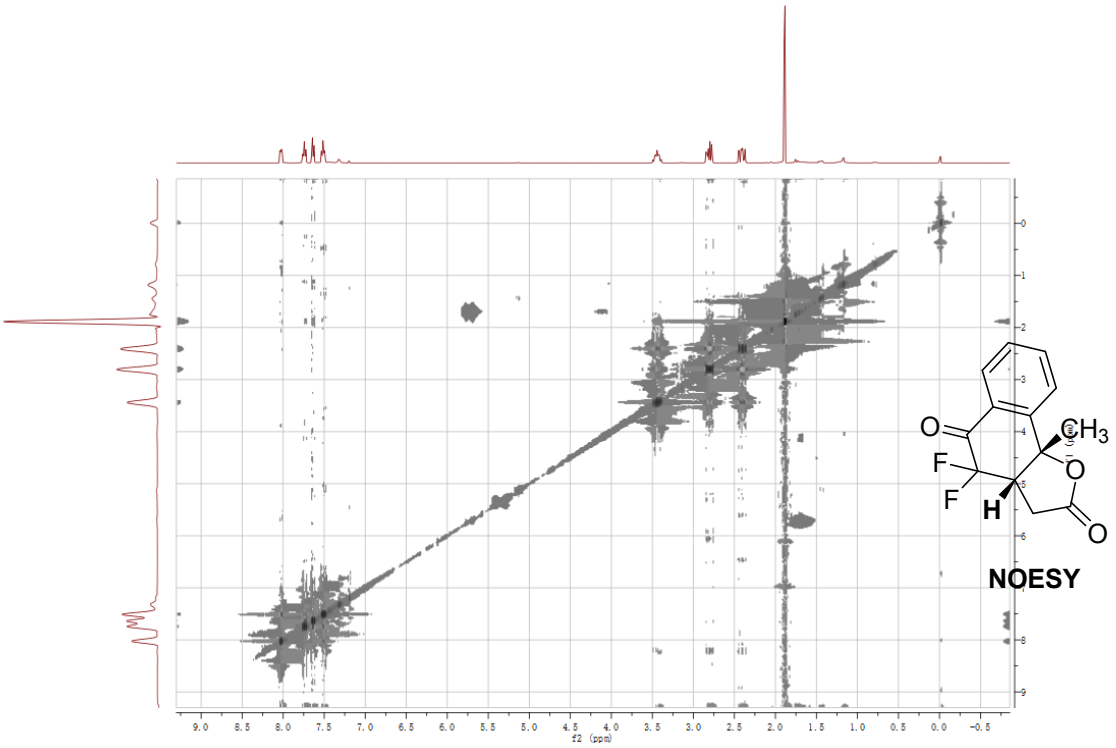
## Copies $^{1}H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR

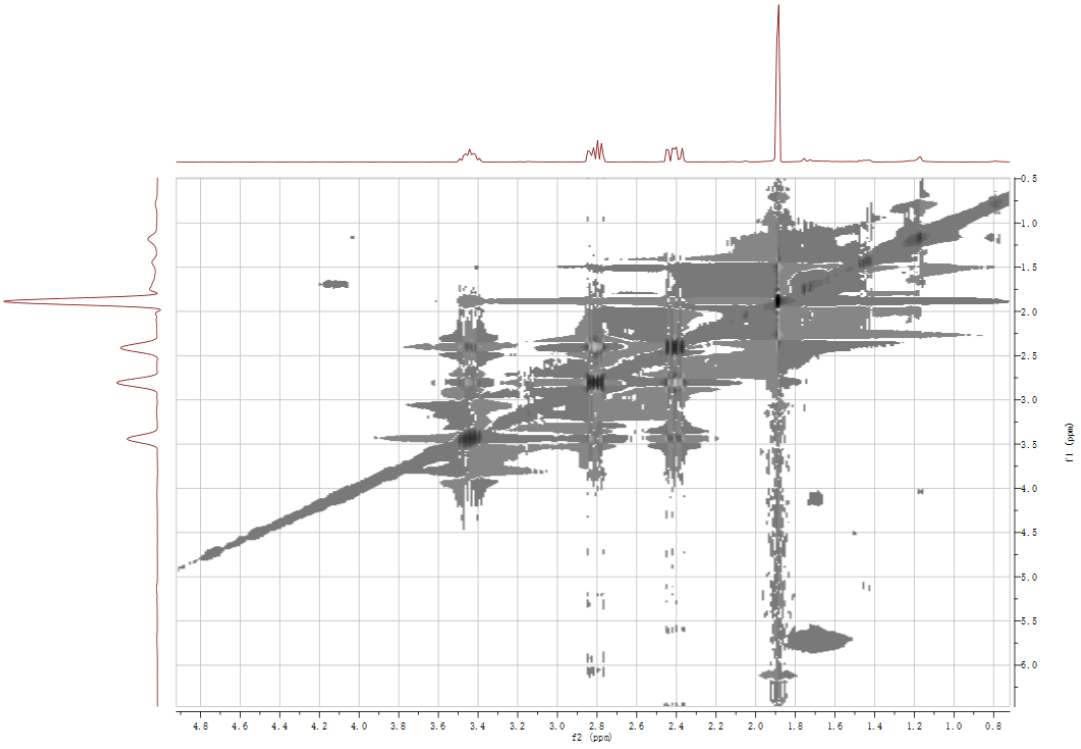
**4,4-difluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3aa)**



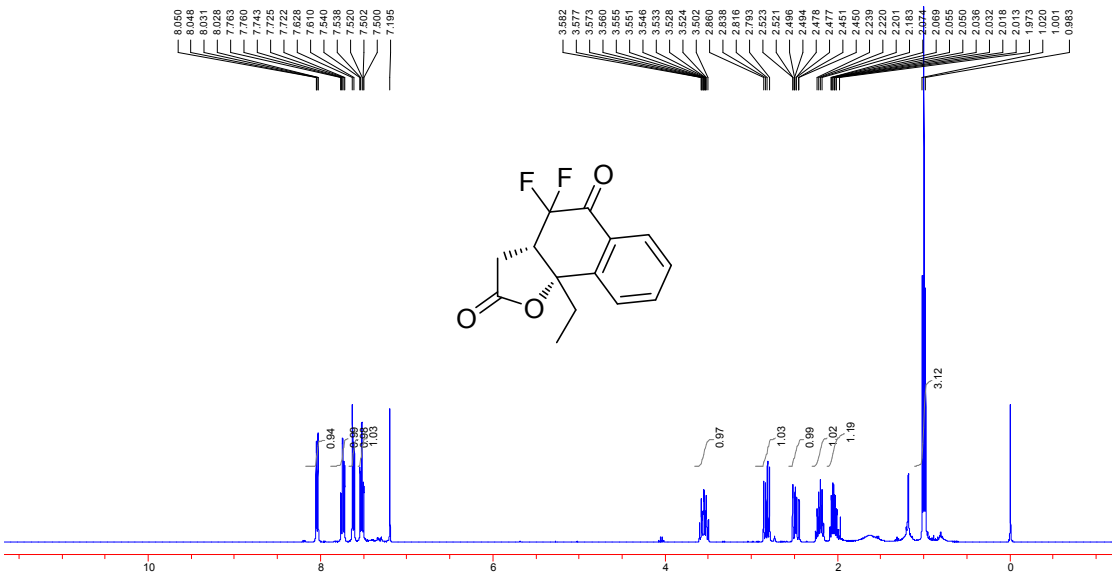



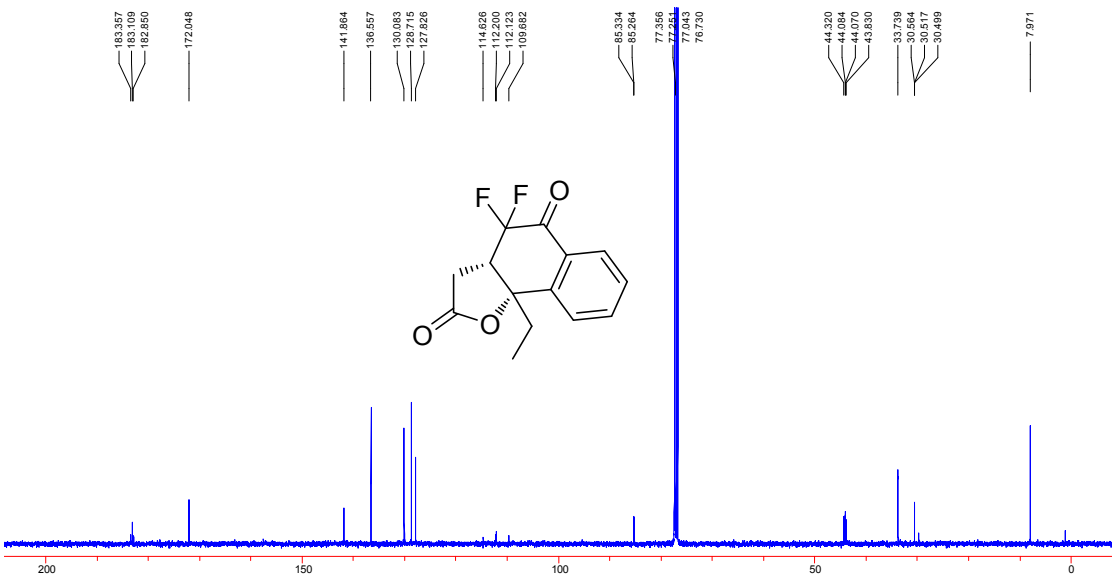

99.033
99.190
112.734
113.491
F F O
O O Me
0 -50 -100 -150 -200
8.037 8.035 8.018 8.015 7.766 7.763 7.746 7.745 7.728 7.725 7.647 7.646 7.627 7.626 7.533 7.531 7.513 7.495 7.493 7.198
3.459 3.451 3.450 3.447 3.438 3.428 3.421 3.416 3.398 2.849 2.847 2.826 2.825 2.804 2.803 2.782 2.781 2.452 2.449 2.423 2.420 2.408 2.405 2.379 2.376 1.894
O CH3 F O F H O
NOE
0.99 1.00 1.00 1.18
0.92 0.98 0.97
3.03
9 8 7 6 5 4 3 2 1

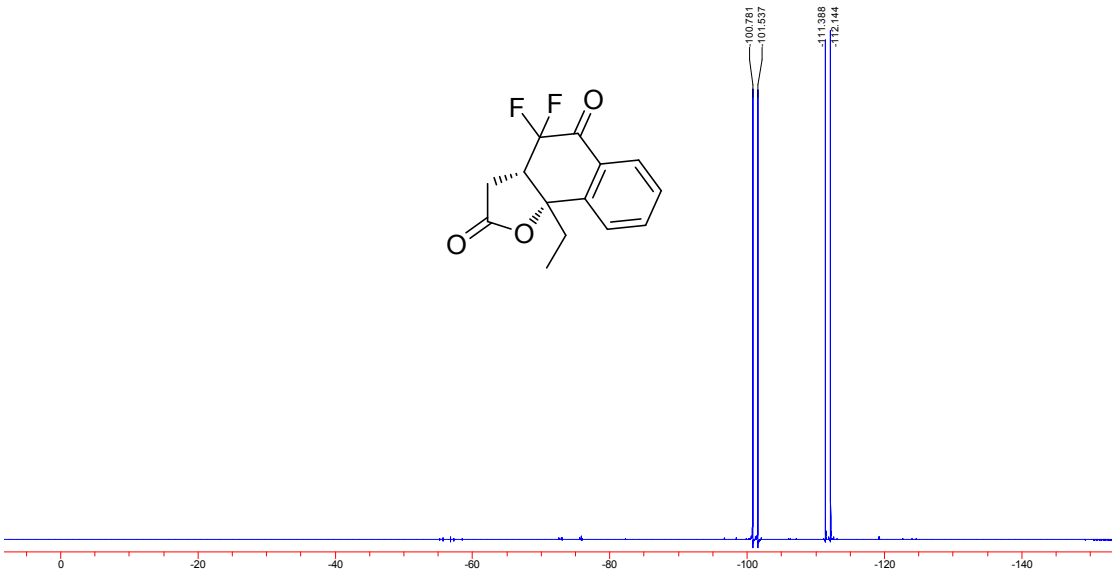


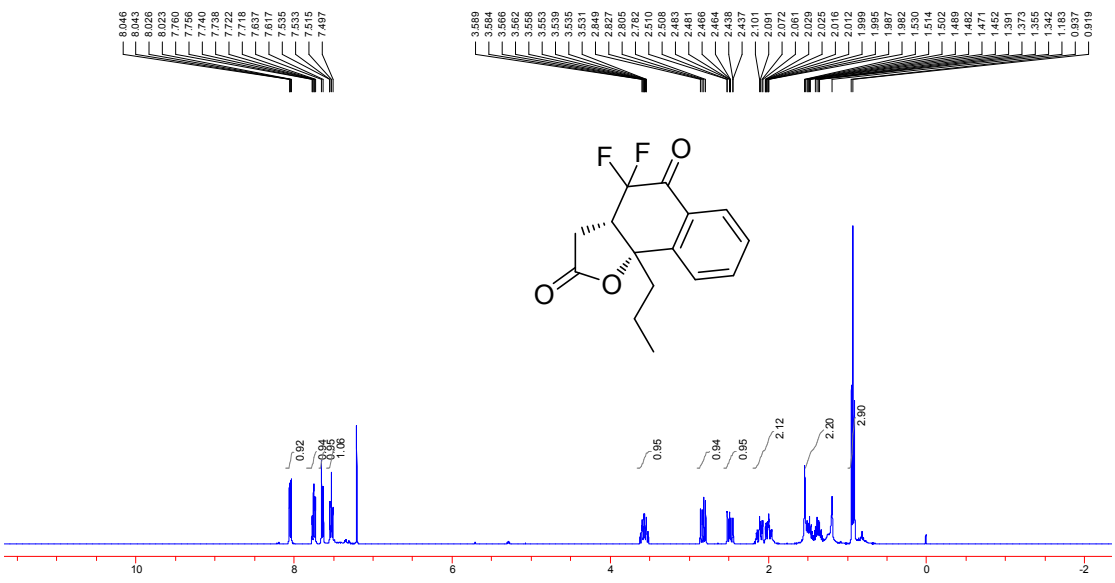

**9b-ethyl-4,4-difluoro-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione（3ba）**

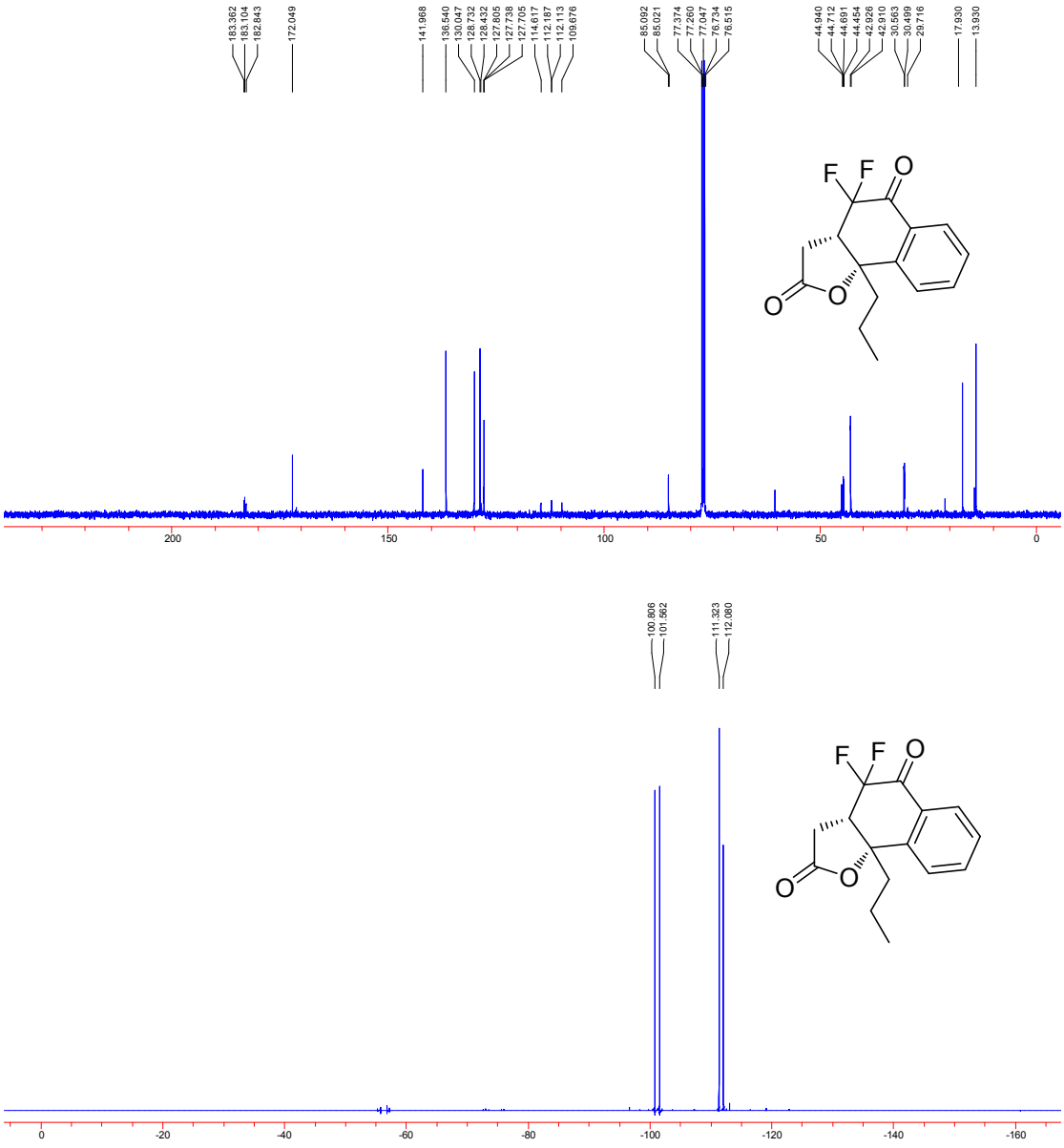

8.050
8.048
8.031
8.028
7.763
7.760
7.743
7.725
7.722
7.628
7.610
7.540
7.538
7.520
7.502
7.500
7.195
3.582
3.577
3.573
3.560
3.555
3.551
3.546
3.533
3.528
3.524
3.502
2.860
2.838
2.816
2.793
2.523
2.521
2.496
2.494
2.478
2.477
2.461
2.439
2.238
2.220
2.201
2.183
2.074
2.069
2.055
2.050
2.036
2.032
2.018
2.013
1.973
1.020
1.001
0.983
F
F
O
O
O
0.94
0.98
0.98
1.03
0.97
1.03
0.99
1.02
1.19
3.12
10
8
6
4
2
0


183.357
183.109
182.850
172.048
141.864
136.557
130.083
128.715
127.826
114.626
112.200
112.123
109.682
85.334
85.264
77.356
77.251
77.043
76.730
44.320
44.084
44.070
43.830
33.739
30.564
30.517
30.499
7.971
F
F
O
O
O
200
150
100
50
0

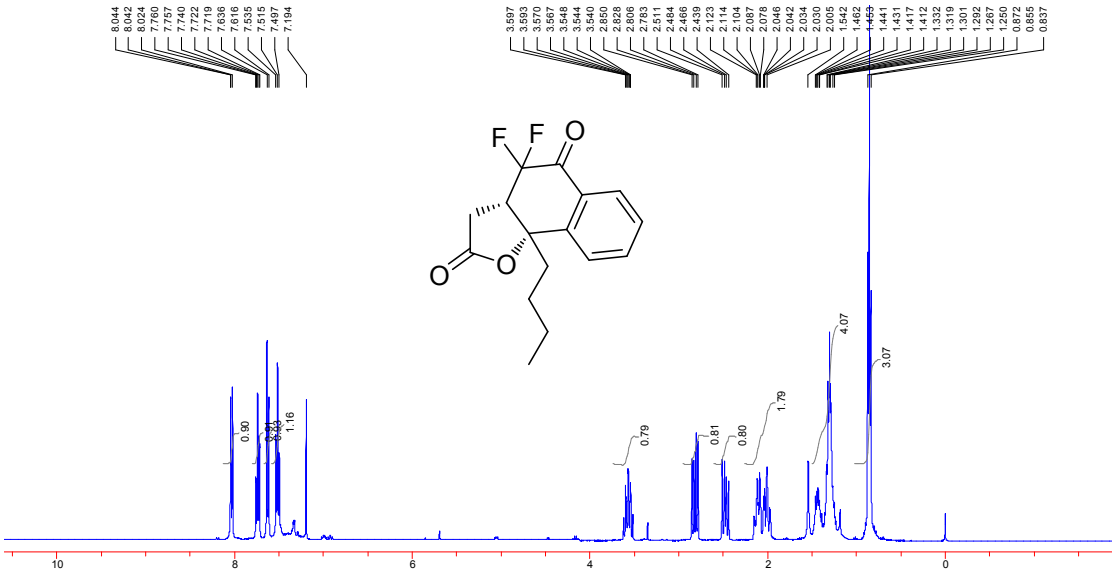


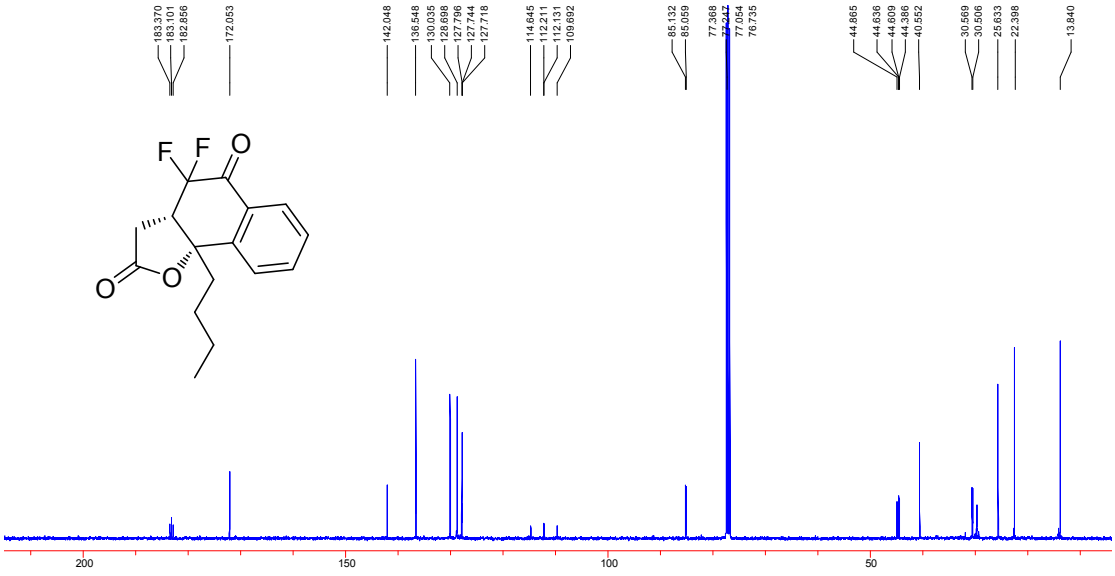

**4,4-difluoro-9b-propyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ca)**

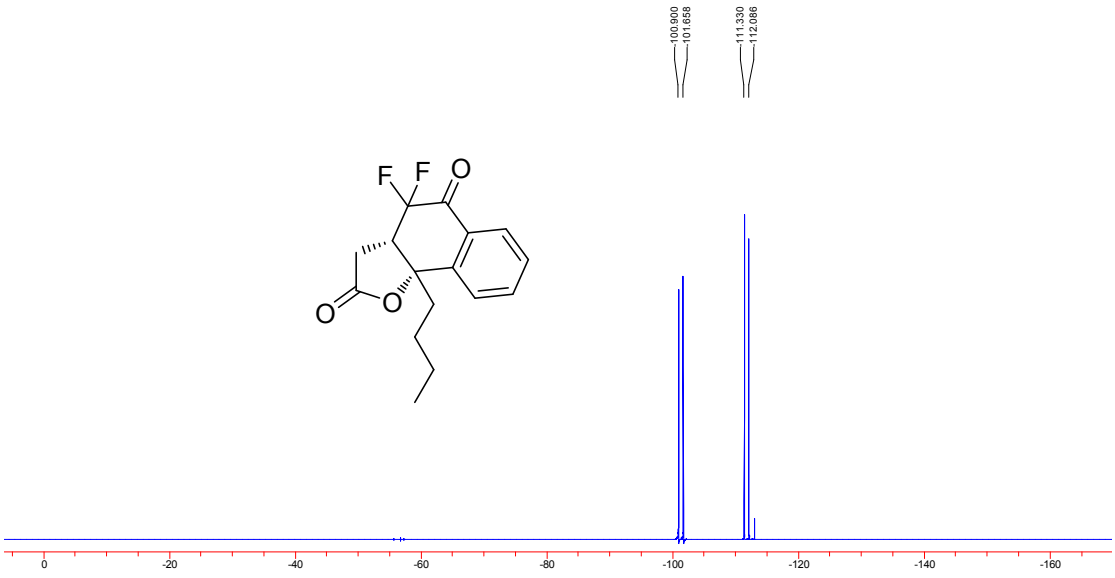




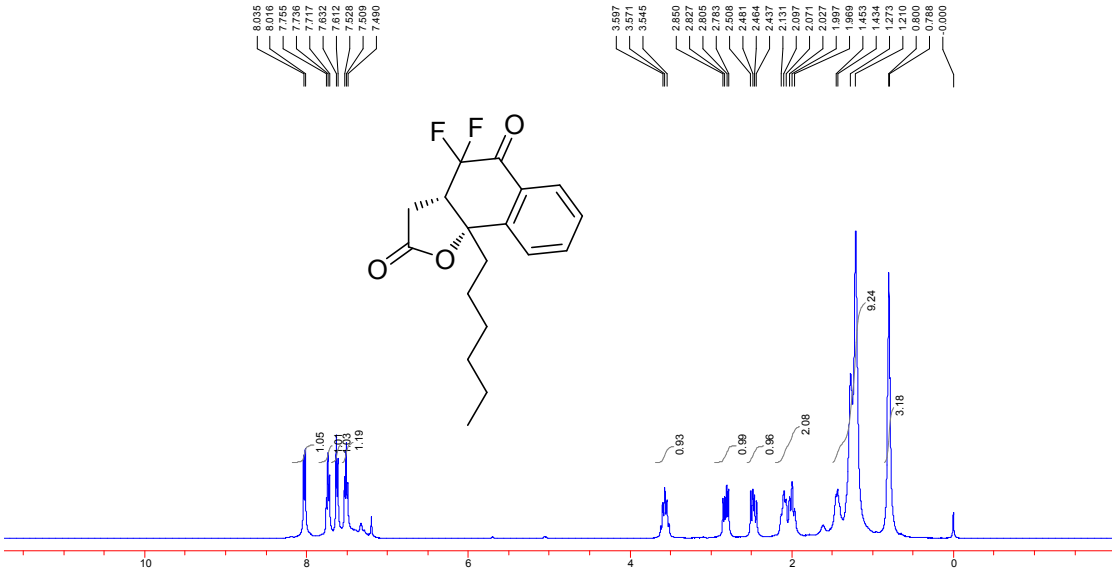

**9b-butyl-4,4-difluoro-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3da)**

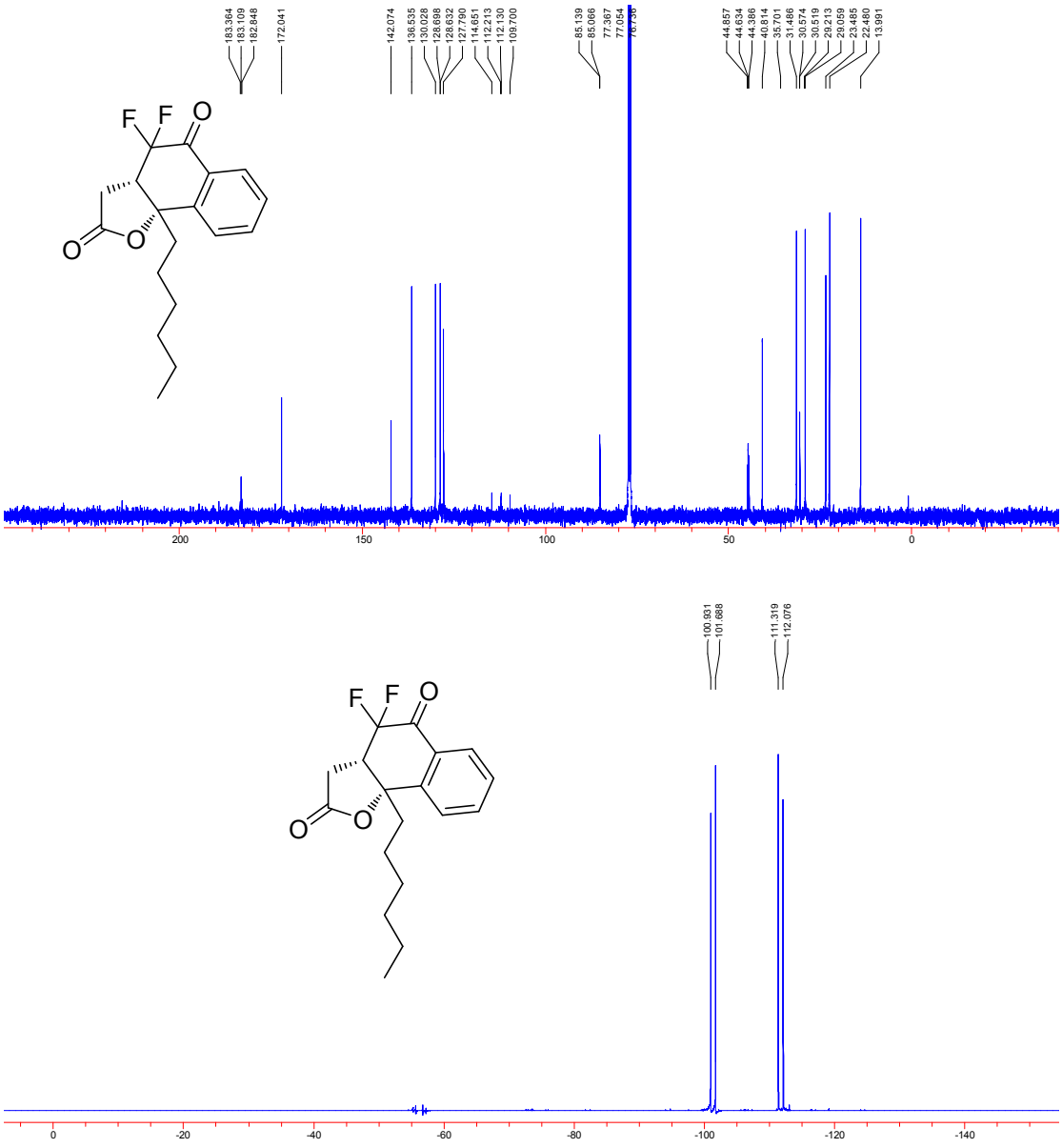

8.044
8.042
8.024
7.760
7.757
7.740
7.722
7.719
7.638
7.616
7.535
7.515
7.497
7.194
3.597
3.593
3.570
3.567
3.548
3.544
3.540
3.465
2.828
2.806
2.783
2.511
2.484
2.466
2.439
2.123
2.114
2.104
2.087
2.078
2.046
2.042
2.034
2.030
2.005
1.542
1.462
1.441
1.431
1.417
1.412
1.332
1.319
1.301
1.292
1.267
1.250
0.872
0.855
0.837
F
F
O
O
O
0.90
1.16
0.79
0.81
0.80
1.79
4.07
3.07
10
8
6
4
2
0


183.370
183.071
182.856
172.053
142.048
136.548
130.035
128.698
127.796
127.744
127.718
114.645
112.211
112.131
109.692
85.132
85.059
77.368
77.247
77.054
76.735
44.865
44.636
44.609
44.386
40.552
30.569
30.506
25.633
22.398
13.840
F
F
O
O
O
200
150
100
50

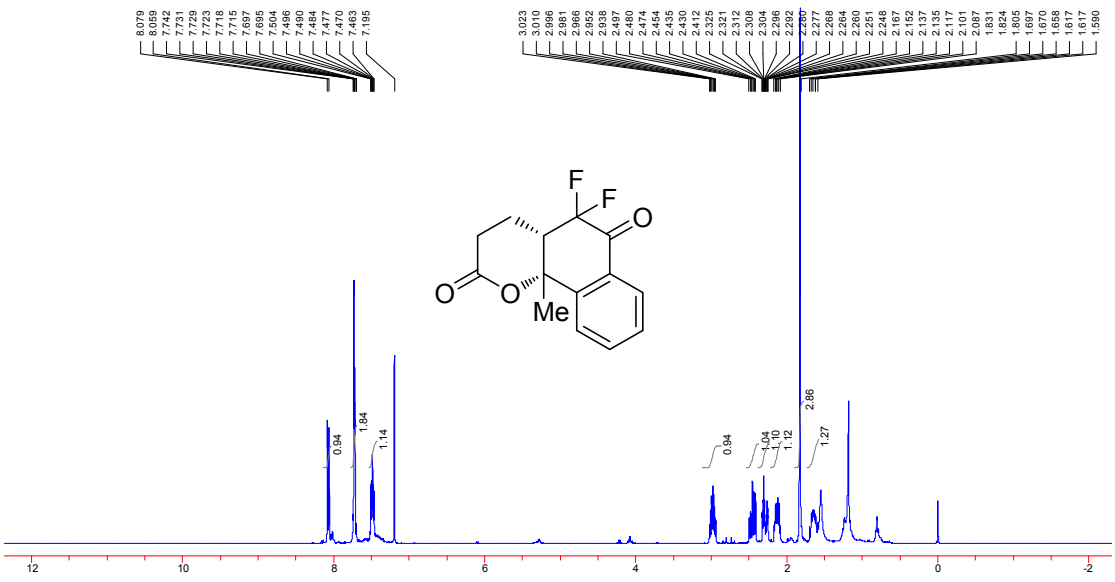


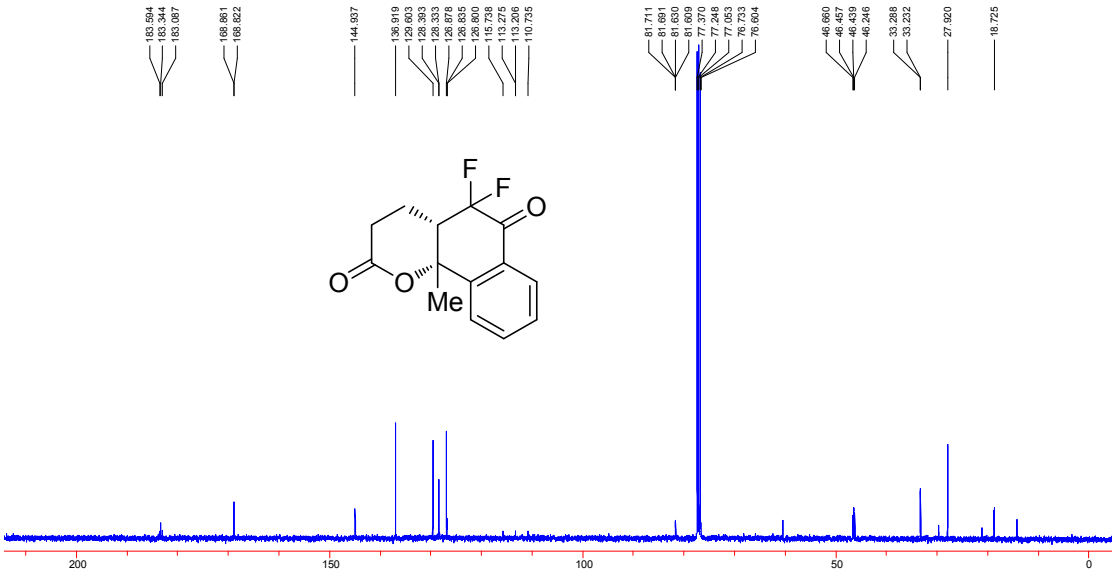

**4,4-difluoro-9b-hexyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ea)**

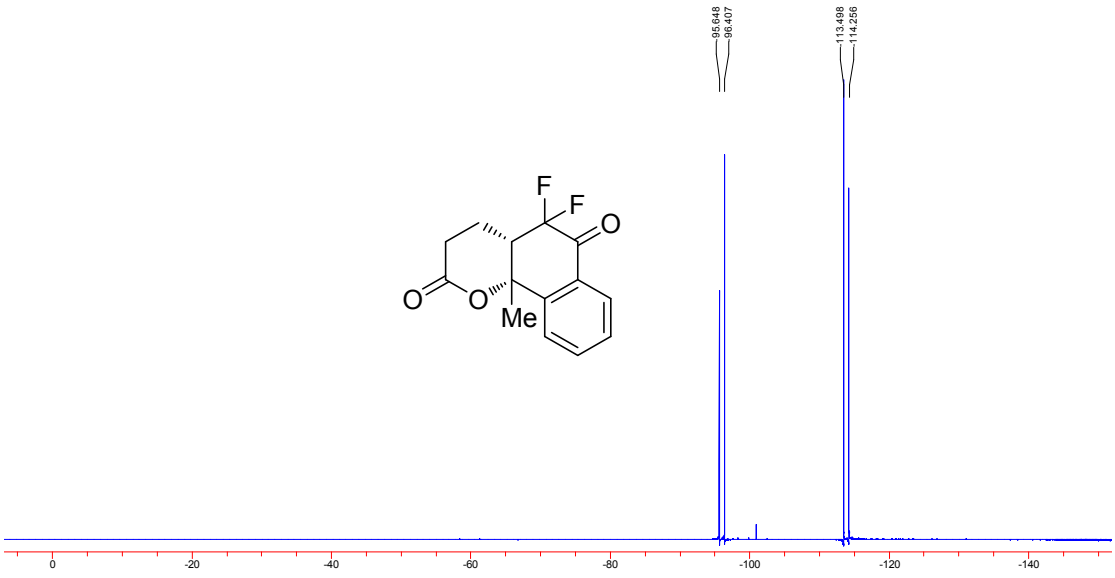




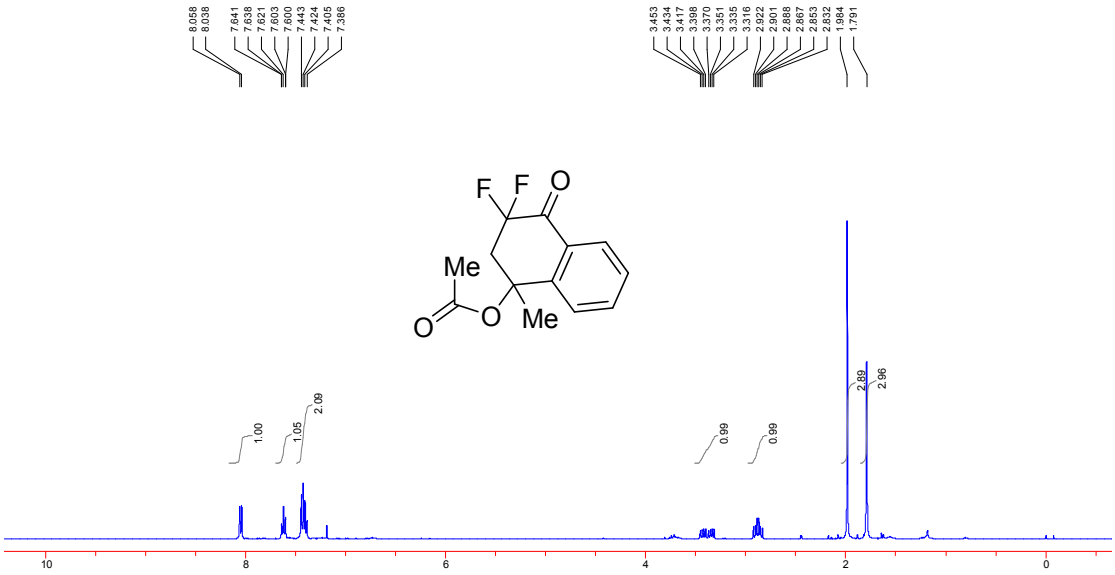

**5,5-difluoro-10b-methyl-3,4,4a,5-tetrahydro-2H-benzo[h]chromene-2,6(10bH)-dione (3fa)**

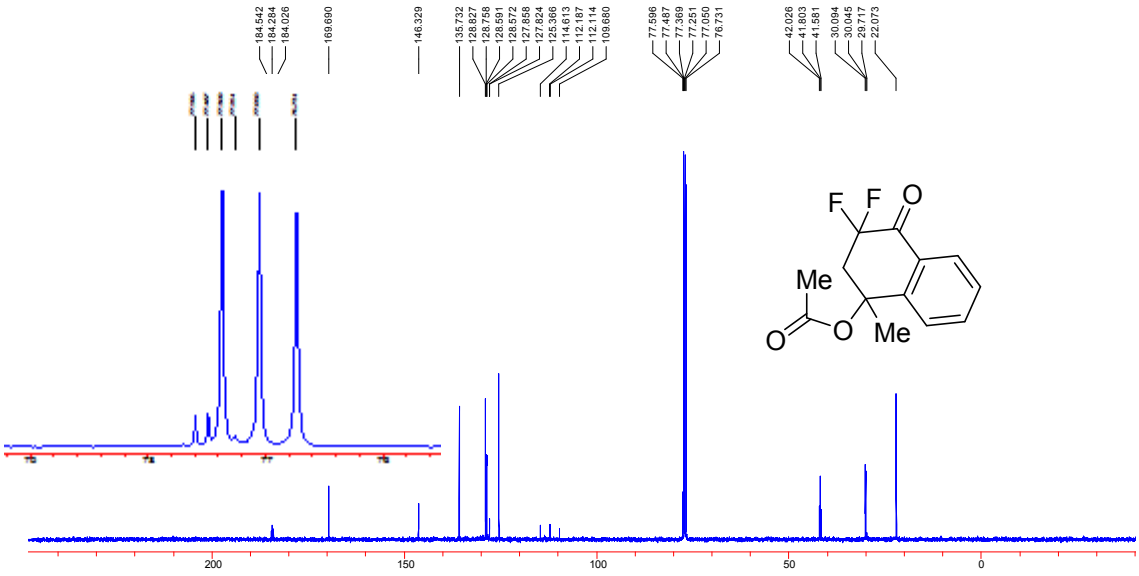

8.079
8.059
7.742
7.731
7.729
7.723
7.718
7.715
7.697
7.695
7.504
7.496
7.490
7.484
7.477
7.470
7.463
7.195
3.023
3.010
2.996
2.981
2.966
2.952
2.938
2.497
2.480
2.474
2.454
2.435
2.430
2.412
2.325
2.321
2.312
2.308
2.304
2.296
2.292
2.280
2.277
2.268
2.264
2.260
2.251
2.248
2.167
2.152
2.137
2.135
2.117
2.101
2.087
1.831
1.824
1.805
1.697
1.670
1.658
1.617
1.617
1.590
F
F
O
O
O
Me
0.94
1.84
1.14
0.94
1.04
1.10
1.12
2.86
1.27
12
10
8
6
4
2
0
-2

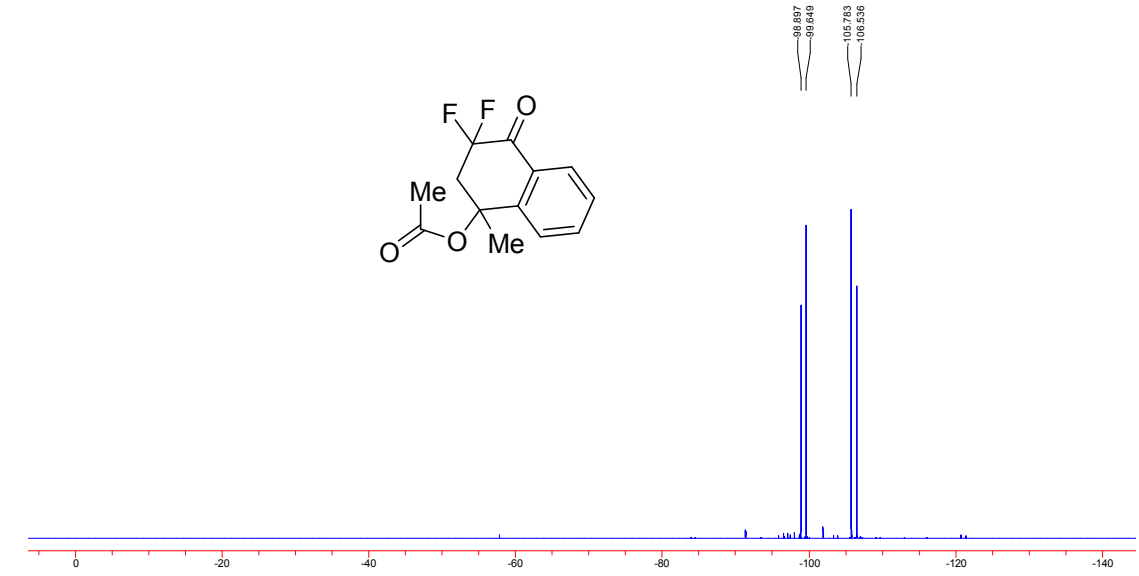

183.594
183.344
183.087
168.861
168.822
144.937
136.919
129.603
128.393
128.378
126.835
126.800
115.738
113.275
113.206
110.735
81.711
81.691
81.630
81.609
77.370
77.248
77.053
76.733
76.604
46.660
46.457
46.439
46.246
33.288
33.232
27.920
18.725
F
F
O
O
O
Me
200
150
100
50
0



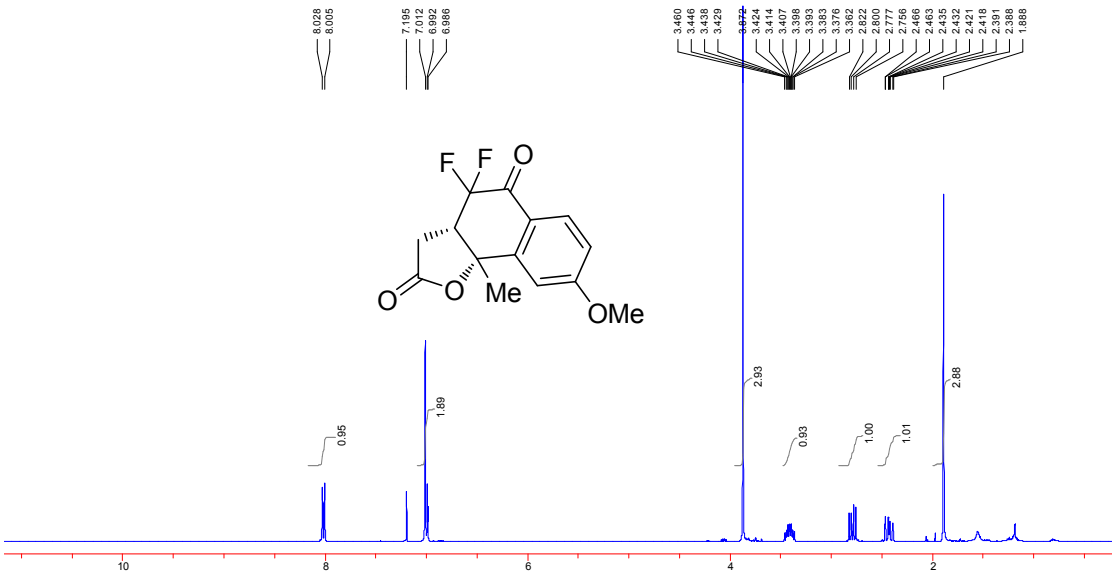

**3,3-difluoro-1-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate (3ga)**

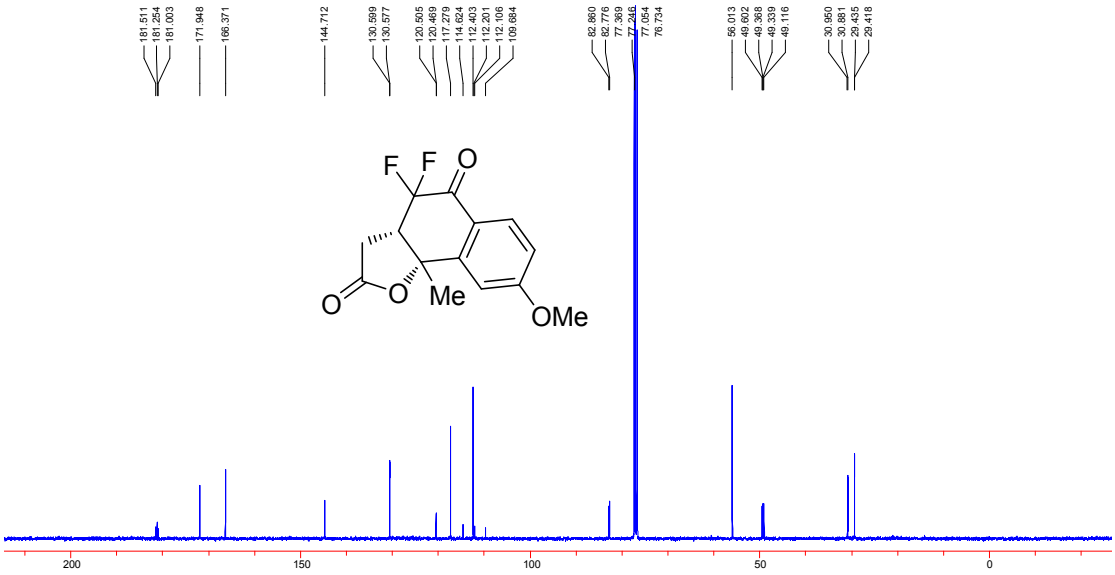


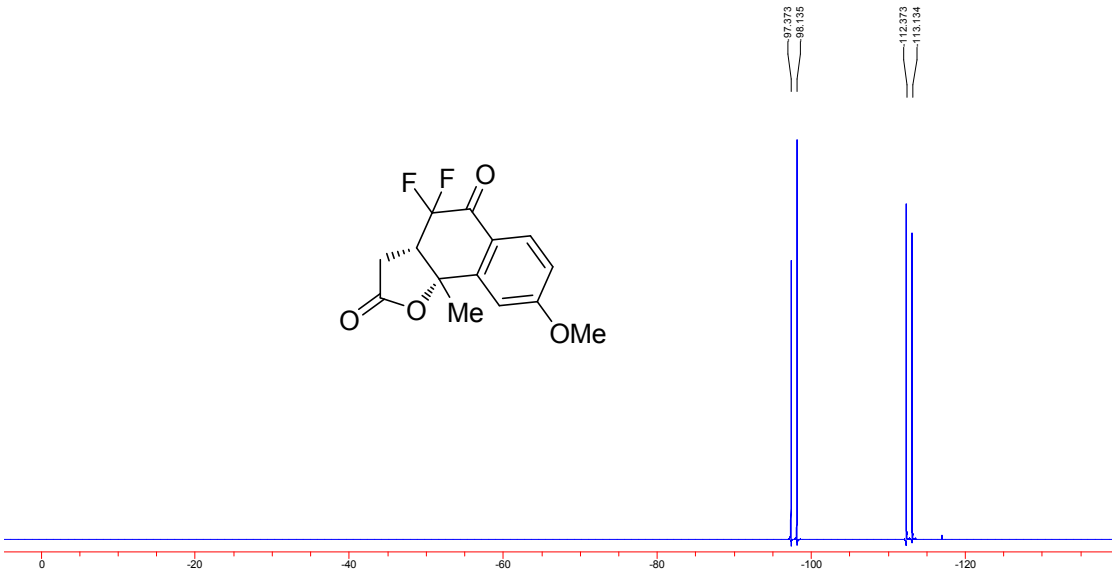


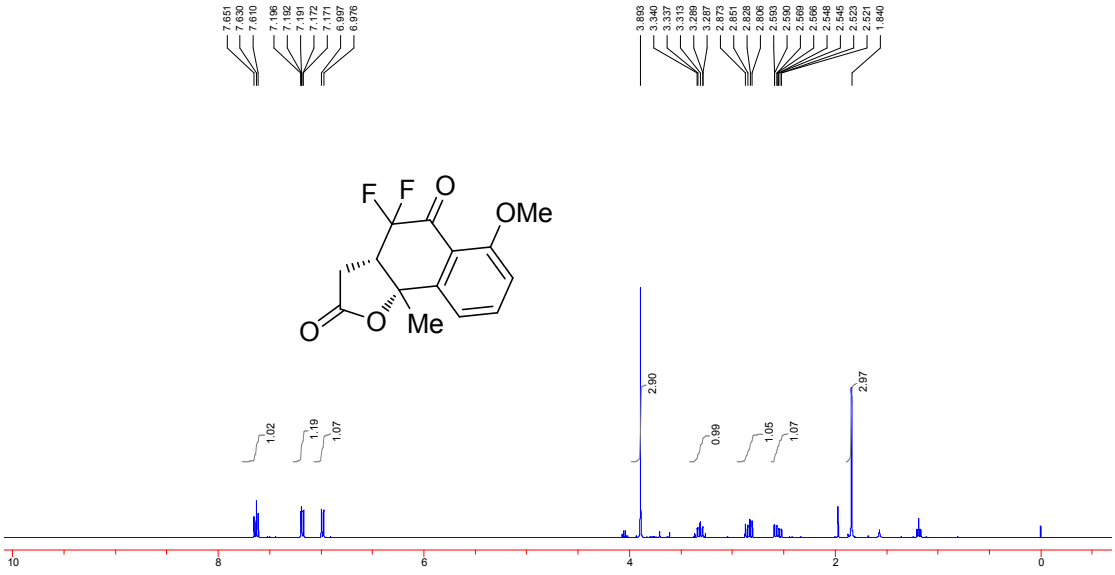

**4,4-difluoro-8-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ab)**

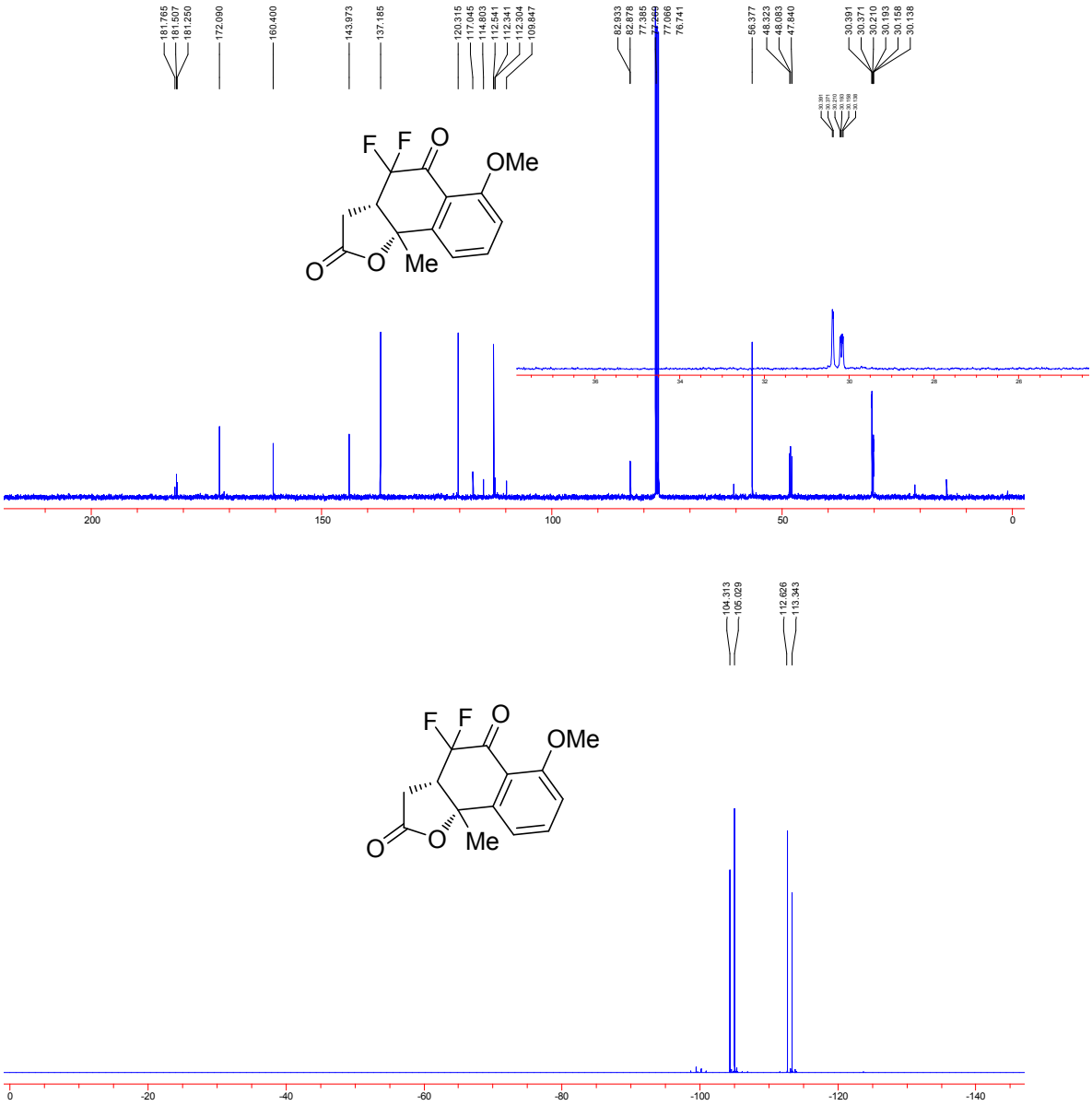

8.028
8.005
7.195
7.012
6.992
6.986
3.460
3.446
3.438
3.429
3.424
3.414
3.407
3.398
3.393
3.383
3.376
3.362
2.822
2.800
2.777
2.756
2.466
2.463
2.435
2.432
2.421
2.418
2.401
2.388
1.888
F
F
O
O
O
Me
OMe
0.95
1.89
2.93
0.93
1.00
1.01
2.88
10
8
6
4
2


181.511
181.254
181.003
171.948
166.371
144.712
130.599
130.577
120.505
120.469
117.279
114.624
112.403
112.201
112.106
109.684
82.860
82.776
77.369
77.246
77.054
76.734
56.013
49.602
49.368
49.339
49.116
30.950
30.861
29.435
29.418
F
F
O
O
O
Me
OMe
200
150
100
50
0



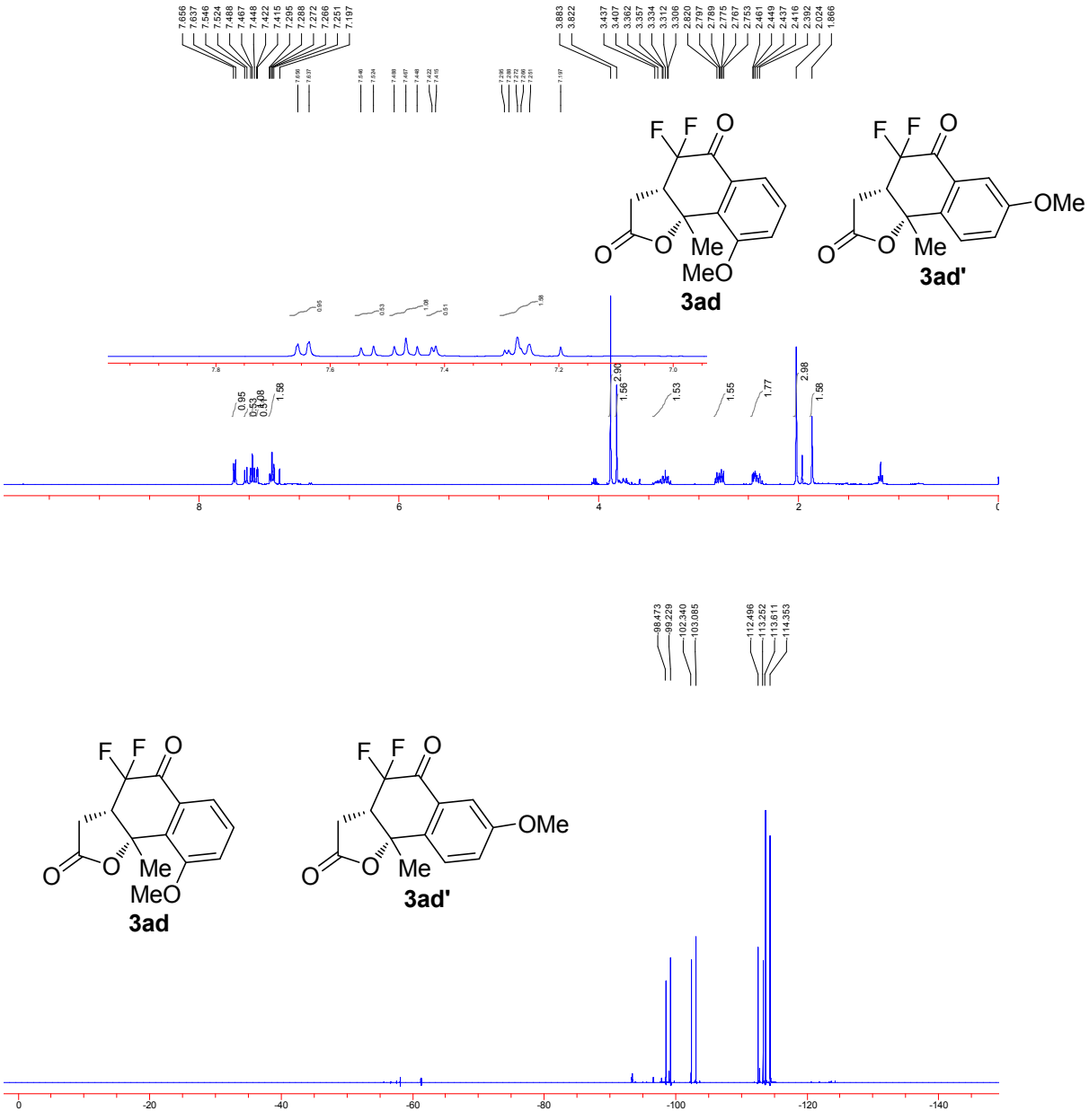

**4,4-difluoro-6-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ac)**



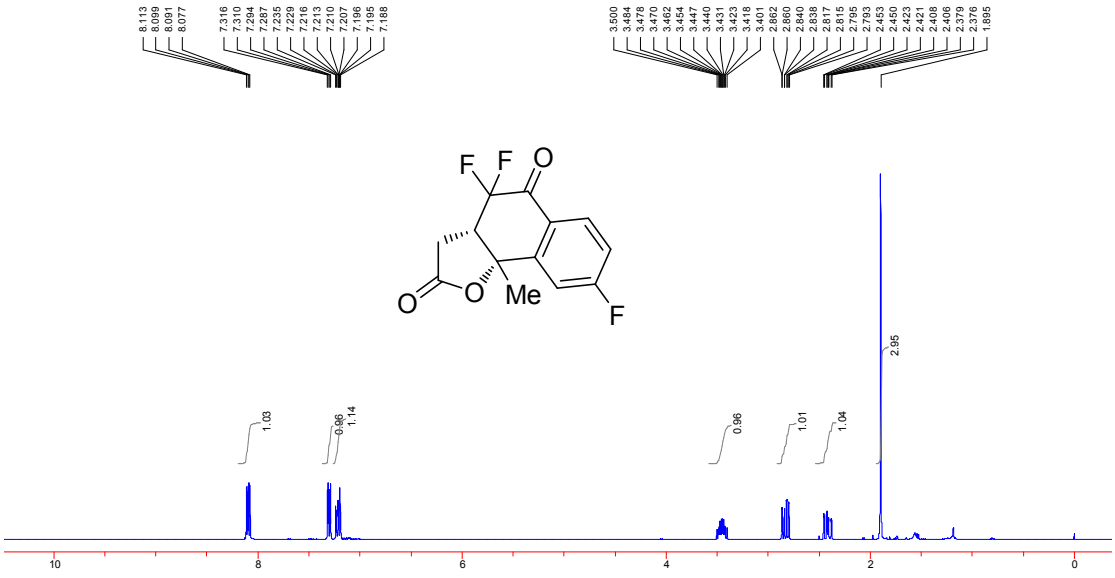


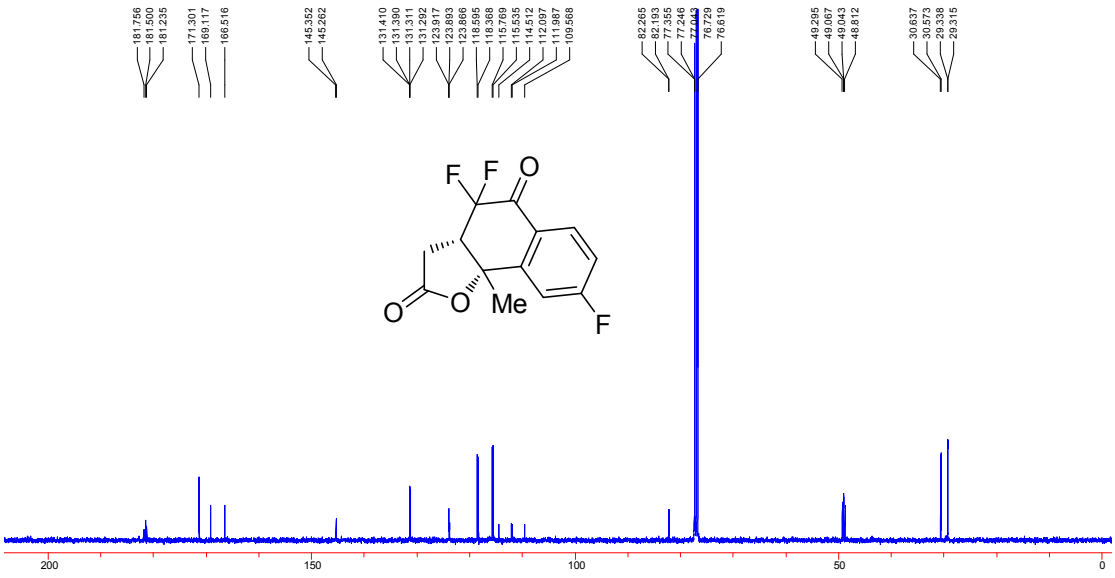

**4,4-difluoro-9-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad)**

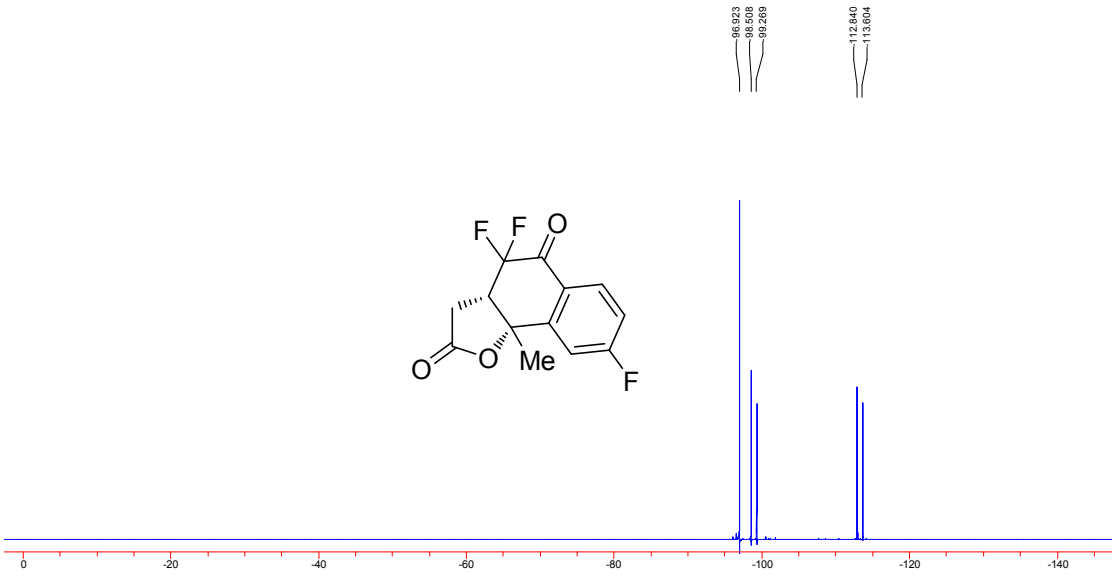
**4,4-difluoro-7-methoxy-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ad')**



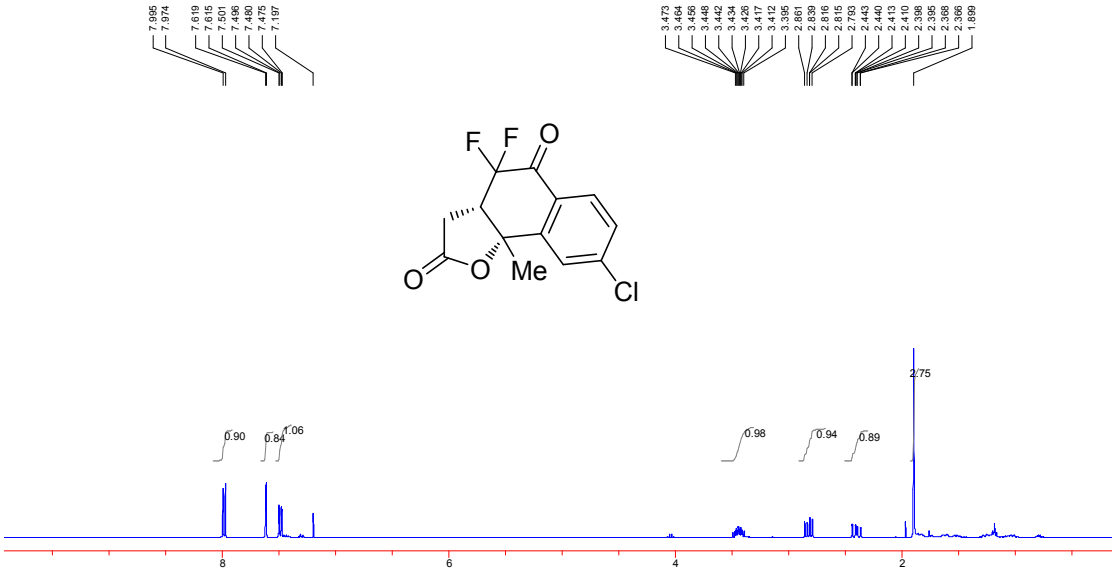

**4,4,8-trifluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione（3ae）**

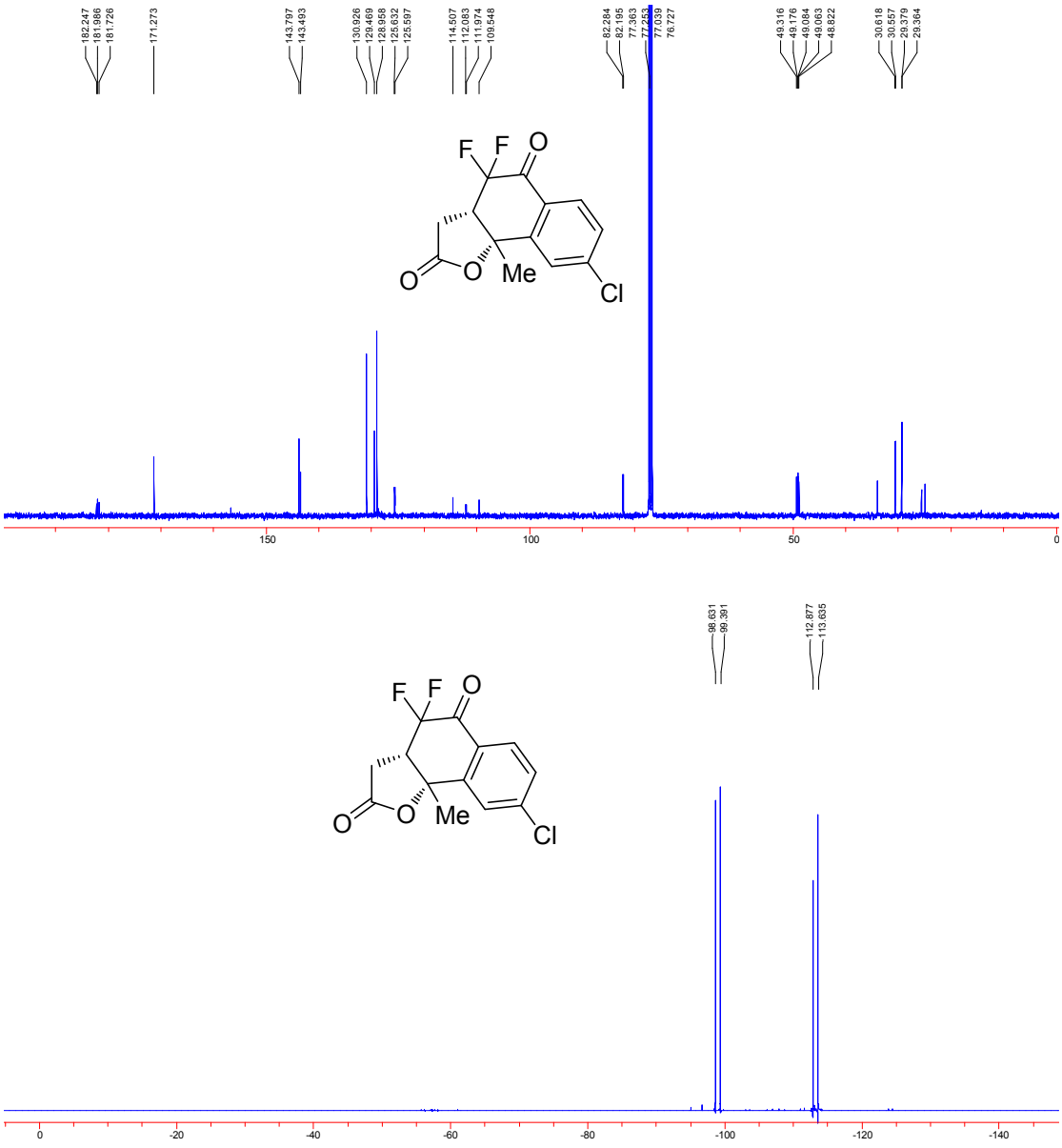

8.113
8.099
8.091
8.077
7.316
7.310
7.294
7.287
7.235
7.229
7.216
7.213
7.210
7.207
7.196
7.195
7.188
3.500
3.484
3.478
3.470
3.462
3.454
3.447
3.440
3.431
3.423
3.418
3.401
2.862
2.860
2.840
2.838
2.817
2.815
2.795
2.793
2.453
2.450
2.423
2.421
2.408
2.406
2.379
2.376
1.895
F
F
O
O
O
Me
F
1.03
0.98
1.14
0.96
1.01
1.04
2.95
10
8
6
4
2
0


181.756
181.500
181.235
171.301
169.117
166.516
145.352
145.262
131.410
131.390
131.311
131.292
129.017
123.893
123.866
118.595
118.368
115.769
115.535
114.512
112.097
111.987
109.568
82.265
82.193
77.355
77.246
77.043
76.729
76.619
49.295
49.067
49.043
48.812
30.637
30.573
29.338
29.315
F
F
O
O
O
Me
F
200
150
100
50
0

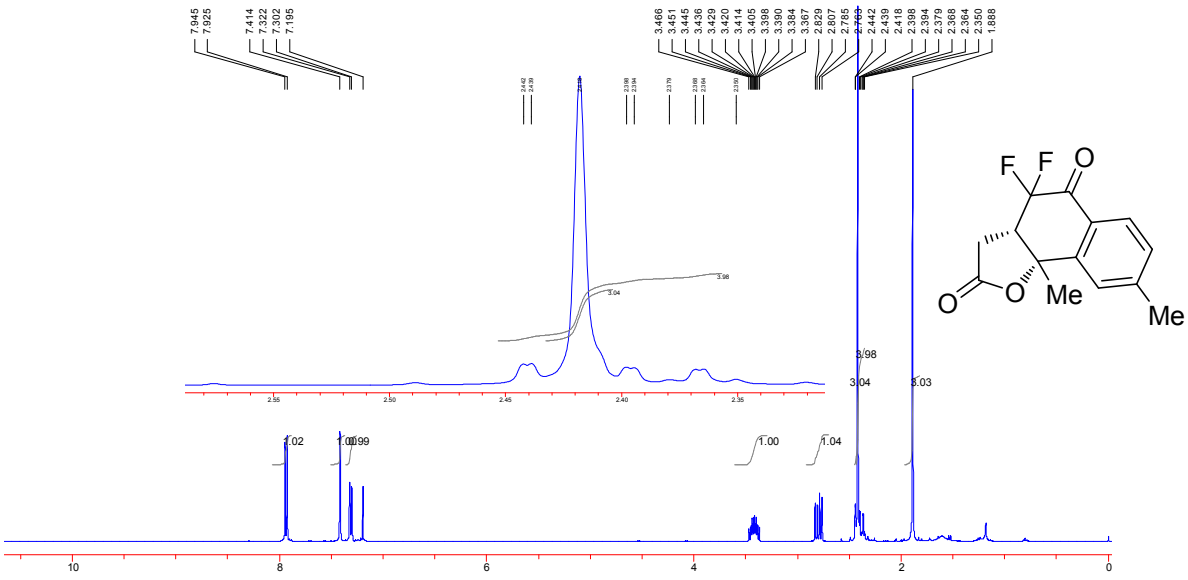


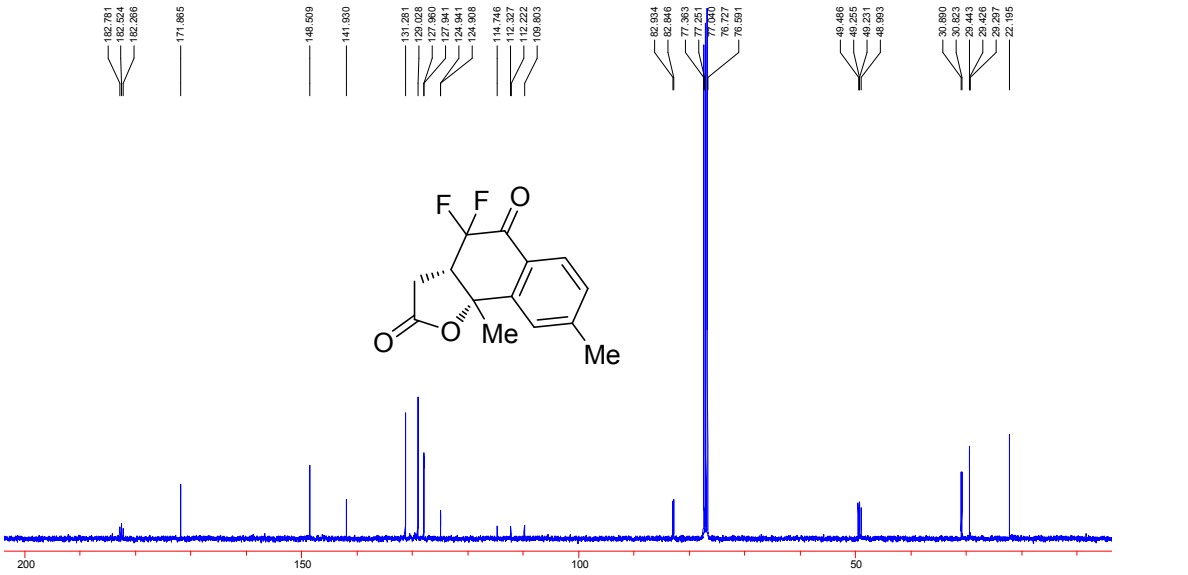

**8-chloro-4,4-difluoro-9b-methyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3af)**

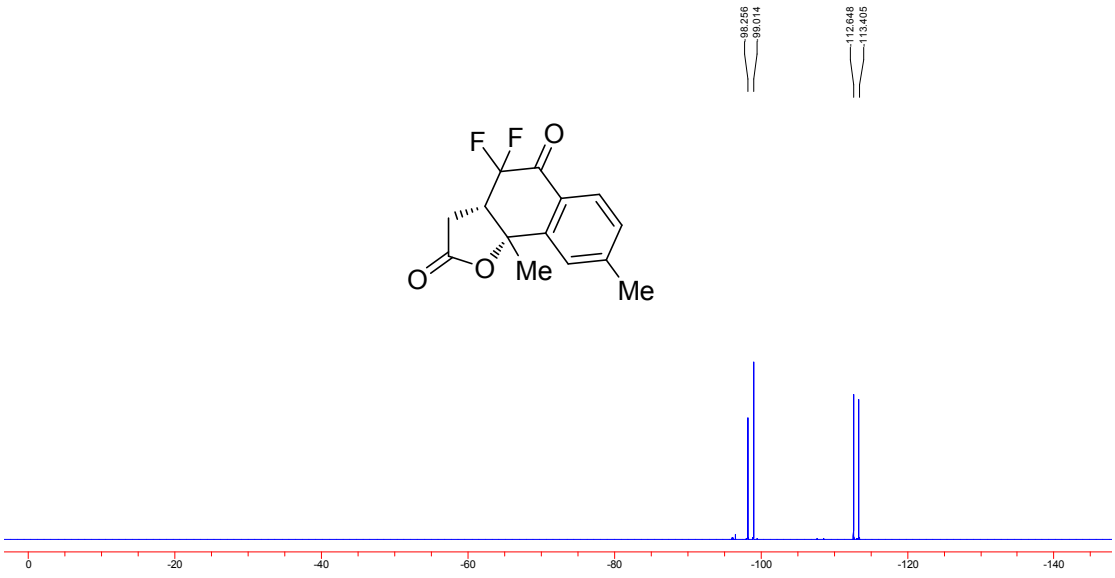





**4,4-difluoro-8,9b-dimethyl-3a,4-dihydronaphtho[1,2-b]furan-2,5(3H,9bH)-dione (3ag)**

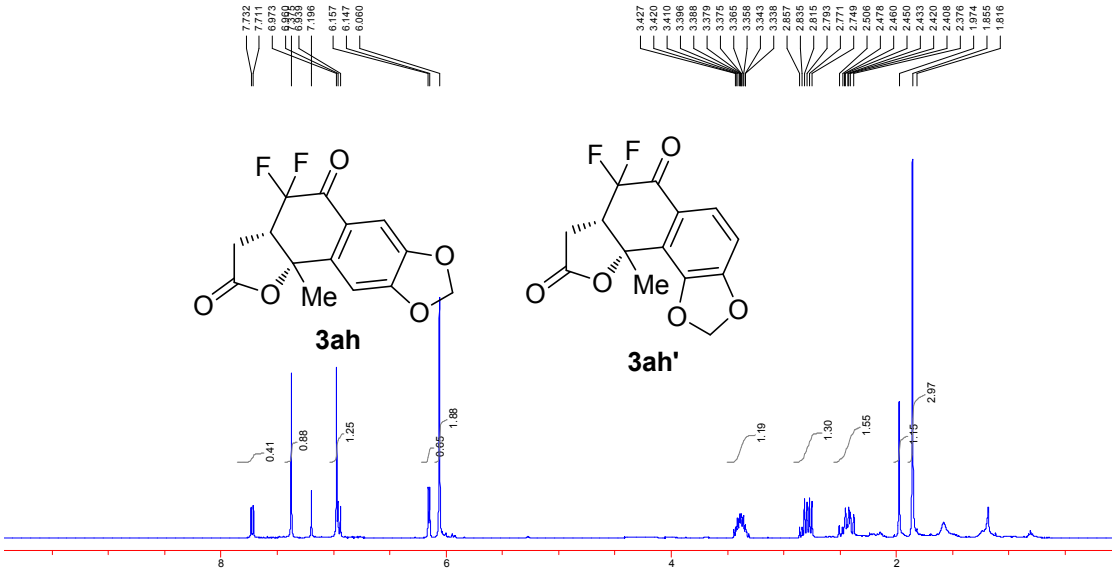

F
F
O
O
O
Me
Me
3.98
3.04
3.03
2.02
1.00
1.04

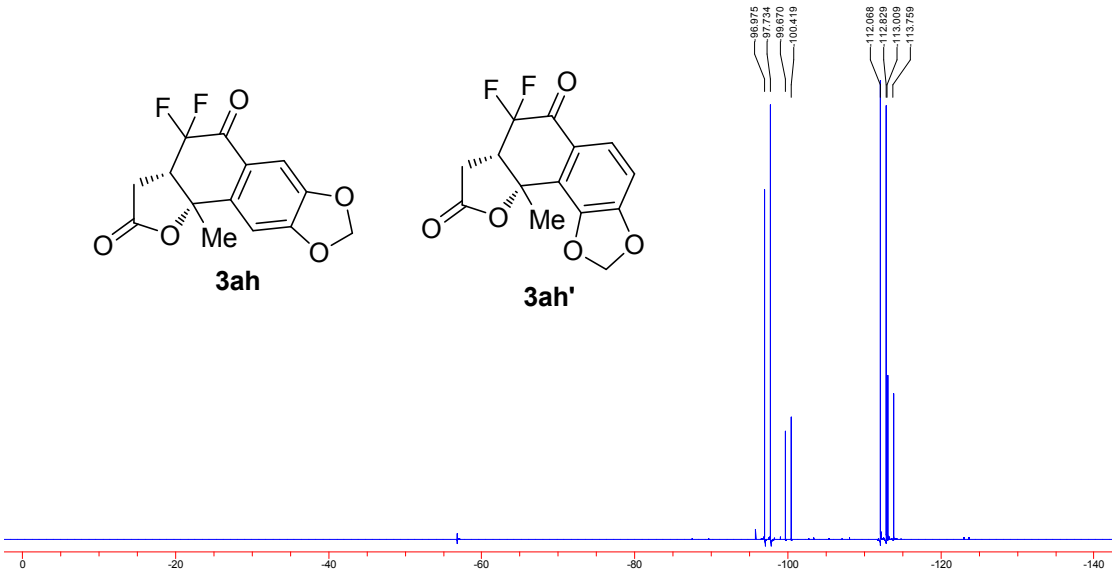

F
F
O
O
O
Me
Me



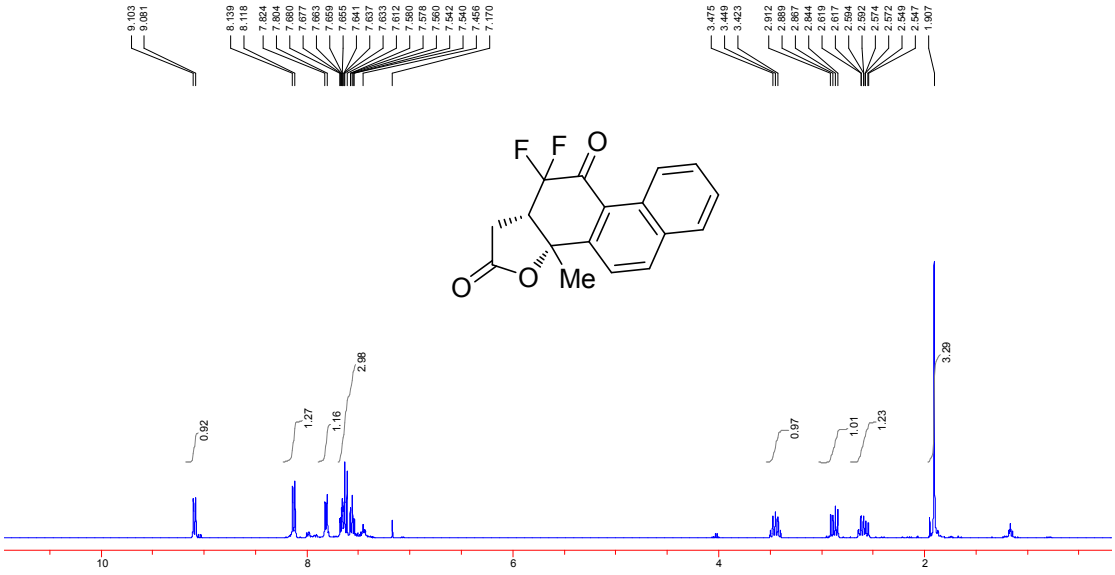

**4,4-difluoro-10b-methyl-3a,4-dihydrofuro[2',3':5,6]naphtho[2,3-d][1,3]dioxole-2,5(3H,10bH)-dione (3ah)**

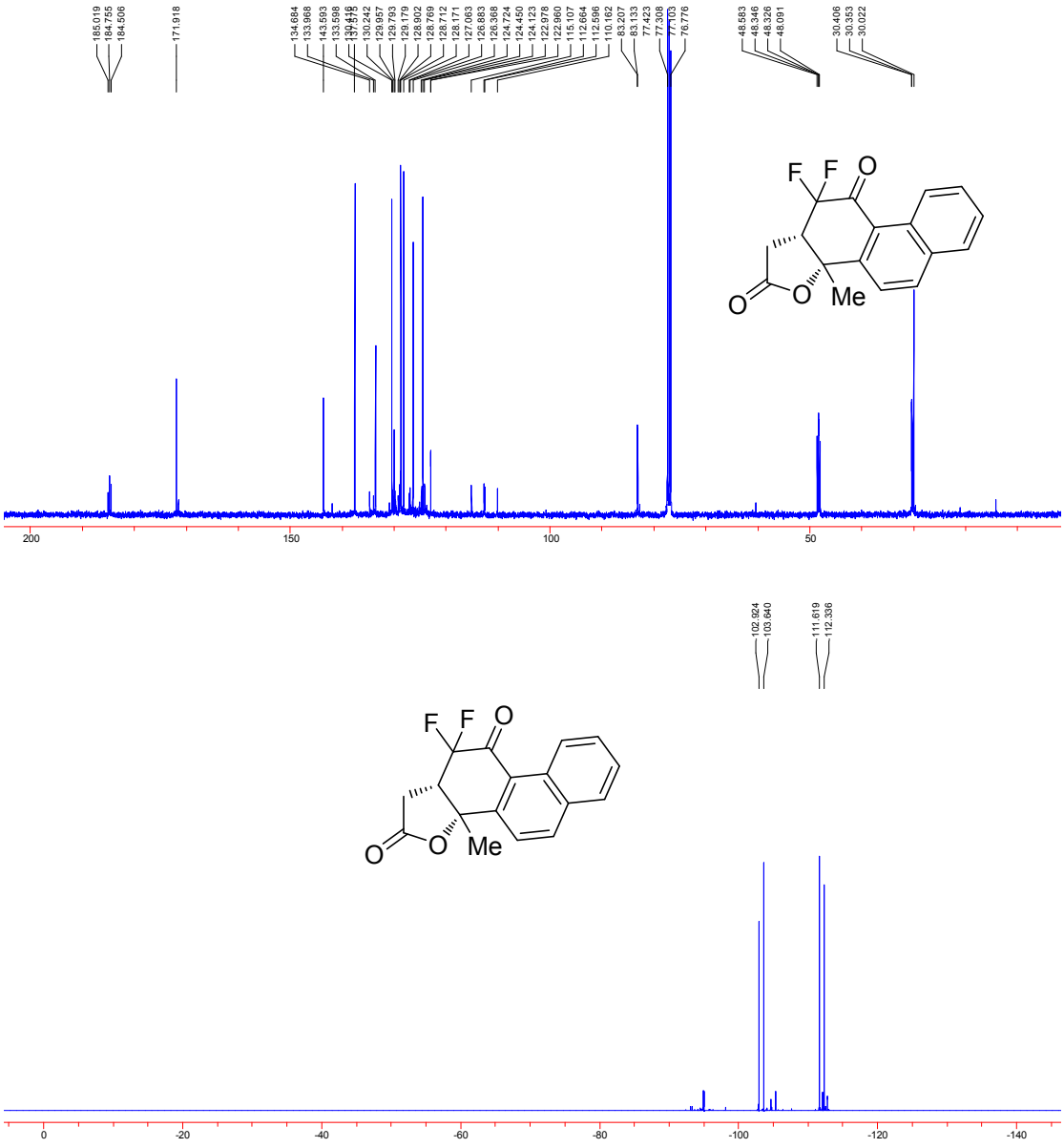
**7,7-difluoro-10a-methyl-7a,8-dihydrofuro[3',2':7,8]naphtho[1,2-d][1,3]dioxole-6,9(7H,10aH)-dione （3ah'）**



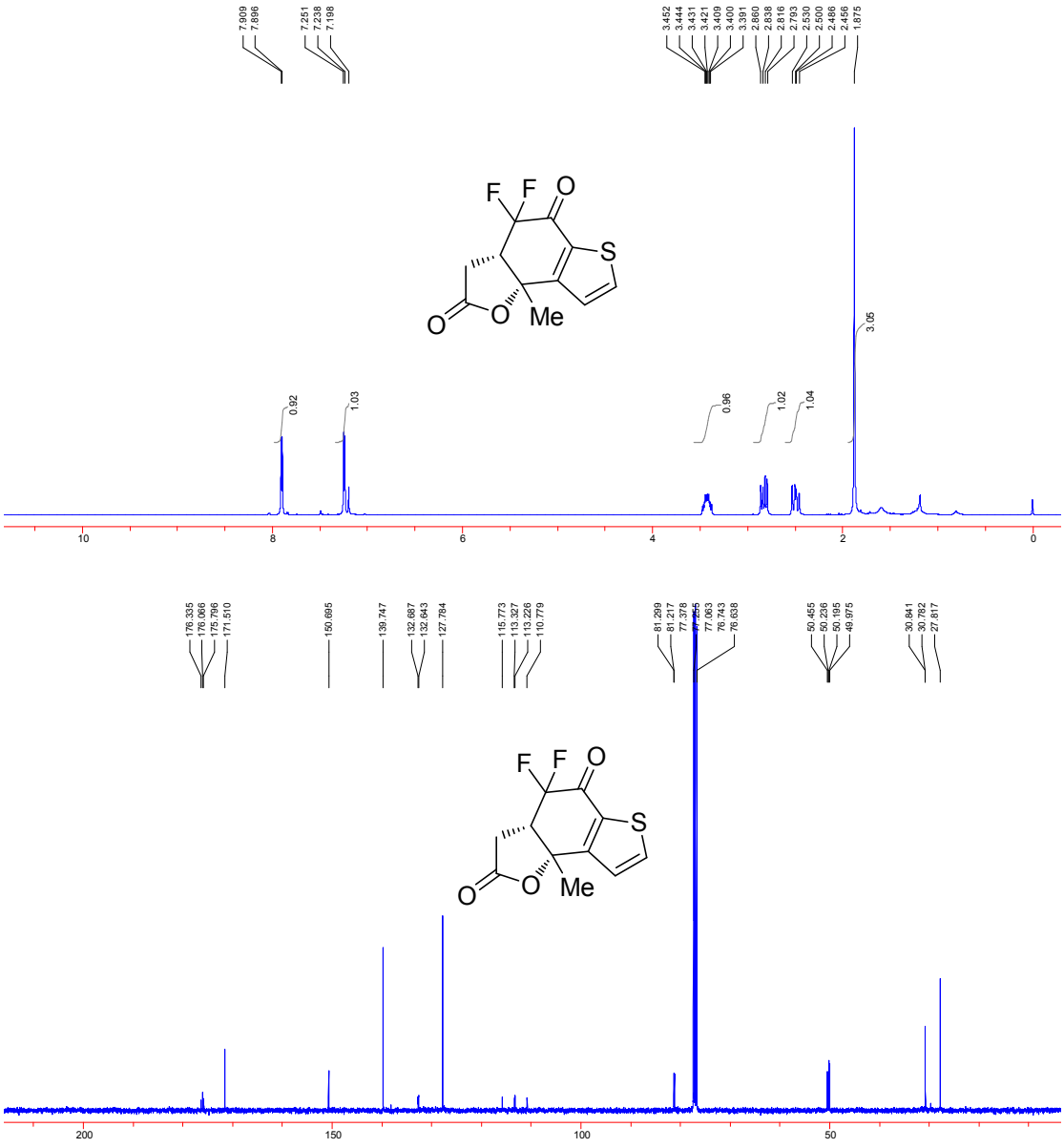


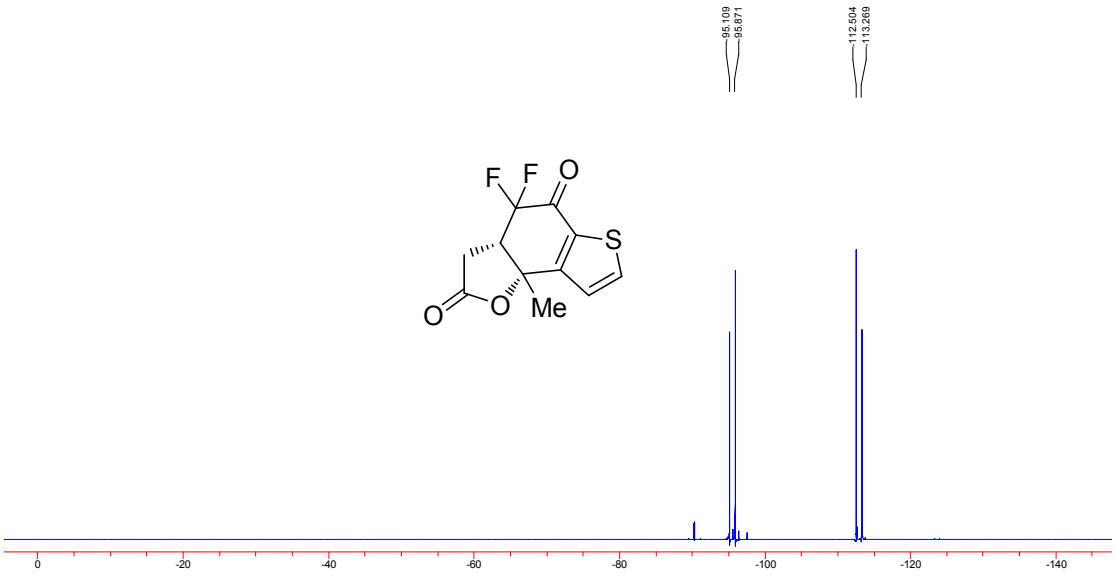

**11,11-difluoro-3a-methyl-11,11a-dihydrophenanthro[1,2-b]furan-2,10(1H,3aH)-dione （3ai）**





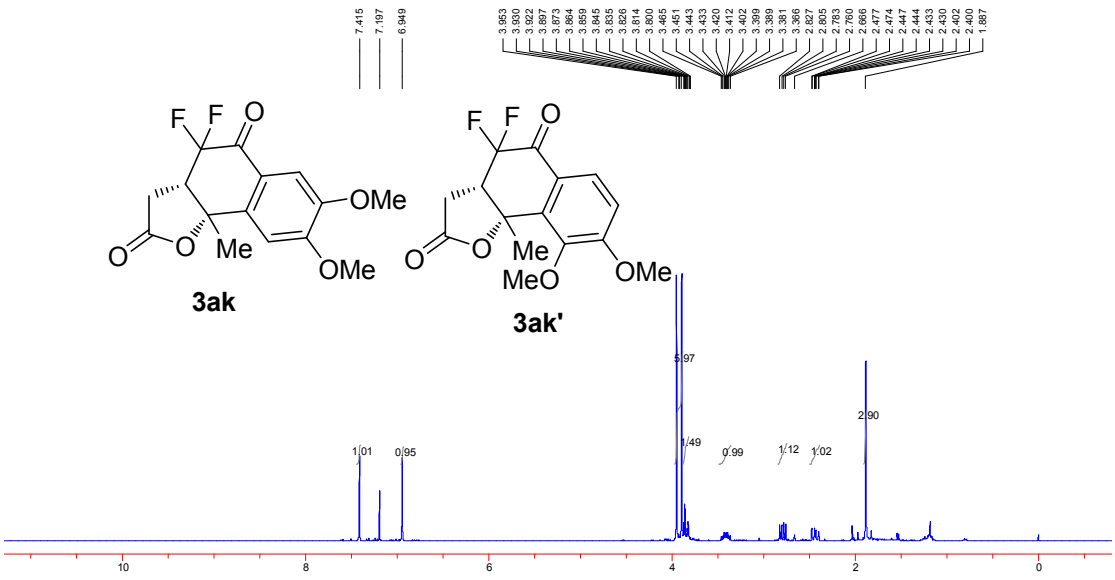

**4,4-difluoro-8b-methyl-3a,4-dihydrothieno[2,3-g]benzofuran-2,5(3H,8bH)-dione (3aj)**

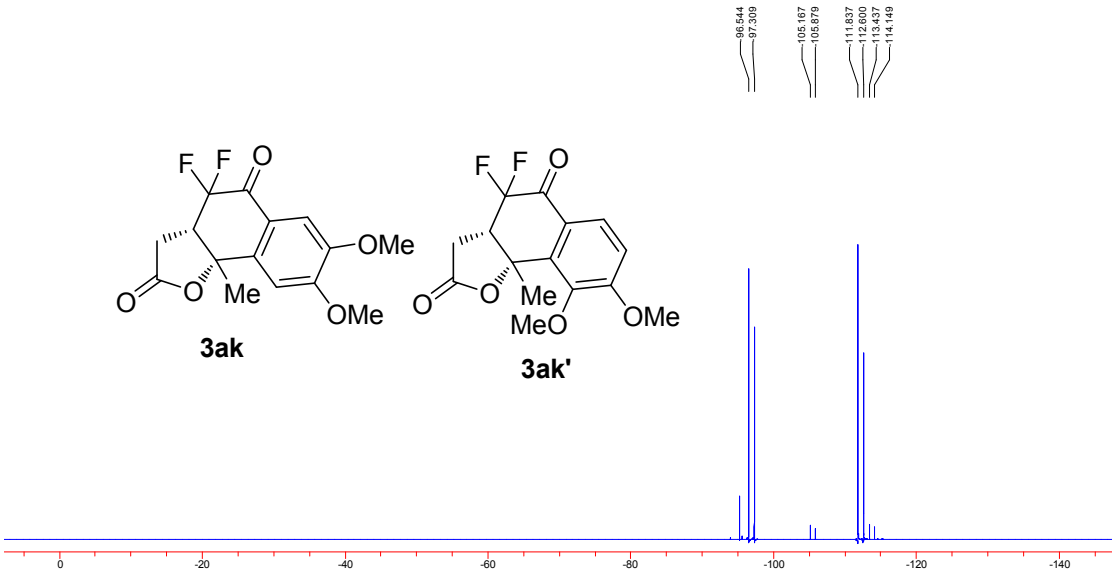

7.909
7.896
7.251
7.238
7.198
3.452
3.444
3.431
3.421
3.409
3.400
3.391
2.860
2.838
2.816
2.793
2.530
2.500
2.486
2.466
1.875
F
F
O
S
O
O
Me
0.92
1.03
0.96
1.02
1.04
3.05
10
8
6
4
2
0
176.335
176.066
175.796
171.510
150.695
139.747
132.687
132.643
127.784
115.773
113.327
113.226
110.779
61.299
61.217
77.316
77.063
76.743
76.638
50.455
50.236
50.195
49.975
30.841
30.782
27.817
F
F
O
S
O
O
Me
200
150
100
50




**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')**




96.544
97.309
105.167
105.879
111.837
112.600
113.437
114.149
F
F
O
OMe
O
O
Me
OMe
3ak
F
F
O
O
O
Me
MeO
OMe
3ak'
0
-20
-40
-60
-80
-100
-120
-140