Copper-mediated cascade radical cyclization of olefins with naphthalenyl iododifluoromethyl ketones

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1. General procedures.
All reactions were carried out under argon atmosphere. All reagents were commercially available and used without further purification unless indicated otherwise. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on GF254 plates (0.25 mm layer thickness) using UV light as visualizing agent. Flash chromatography was performed with 400-500 mesh silica gels.

All NMR spectra were recorded on a Bruker Avance 500 (resonance frequencies 500 MHz for $^1$H and 125 MHz for $^{13}$C) equipped with a 5 mm inverse broadband probe head with z-gradients at 295.8 K with standard Bruker pulse programs. The samples were dissolved in 0.6 ml CDCl$_3$ (99.8% D.TMS). Chemical shifts were given in values of $\delta^H$ and $\delta^C$ referenced to residual solvent signals ($\delta^H$ 7.26 for $^1$H, $\delta^C$ 77.0 for $^{13}$C in CDCl$_3$). The $^{19}$F NMR spectra were obtained using a 500 spectrometer (470 MHz) using trifluorotoluene as external standard. High resolution mass spectra (HRMS) were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight).

2. The procedure for preparation of Compound 3.
To a solution of 2-iodo-2,2-difluorocacetophenones $^1$ (1 mmol, 1.0 equiv.) in DMF (2mL) was added alkene $^2$ (1mmol, 1.0 equiv.), copper (1 mmol, 1.0 equiv.). The mixture was stirred at 120°C under N$_2$ protection for 1h. The reaction was quenched with water (10mL), and extracted with ethyl acetate (3 x 10mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether/Ethyl acetate (50:1, 40:1) to afford the product $^3$ as yellow oil (32-70%).

$^{(3a)}$ 2,2-difluoro-4-hexyl-3,4-dihydrophenanthren-1$^{(2H)}$-one

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one ($^1$a) with 1-octene ($^2$a), and purified by flash column chromatography as white solid (221.0 mg, 70% yield).

$^\delta$H (500 MHz, CDCl$_3$, Me$_4$Si) 8.10(2H, t, $J=5.0$Hz), 7.90(1H, d, $J = 10.0$Hz), 7.82(1H, d, $J=10.0$ Hz), 7.66 (2H, m), 3.89 (1H, d, $J = 5.0$ Hz), 2.97(1H, t, $J = 15.0$ Hz), 2.56 (1H, m), 1.84(2H, dd, $J = 10.0, 5.0$ Hz), 1.73 (1H, m), 1.53(1H, m), 1.37 (6H, m), 0.90(3H, d, $J = 5.0$ Hz).

$^\delta$F (470 MHz, CDCl$_3$) -98.4(1F, d, $J = 285.0$ Hz), -102.8(1F, d, $J = 285.0$ Hz).

$^\delta$C (125 MHz, CDCl$_3$) 185.7(t, $J = 25.0$ Hz), 147.9, 136.8, 130.1, 129.4(d, $J = 5.0$Hz), 128.4, 127.5, 125.0, 123.2, 113.0(t, $J = 246.3$ Hz), 36.1(d, $J = 3.8$Hz), 33.9(t, $J = 21.3$ Hz), 33.4(d, $J = 10.0$ Hz), 31.7, 29.1, 28.0, 22.6, 14.1.

HRMS (EI-TOF) calculated [M]$^+$ for C$_{20}$H$_{22}$F$_2$O 316.1639, found 316.1638.
(3b) 2,2-difluoro-4-(phenoxymethyl)-3,4-dihydrophenanthren-1(2H)-one

![Chemical Structure](image)

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with (allyloxy)benzene (2b), and purified by flash column chromatography as yellow oil (226.5 mg, 67% yield).

δH (500 MHz, CDCl3, Me4Si) 8.23(1H, d, J = 10.0 Hz), 8.16(1H, d, J = 10.0 Hz), 7.92(2H, dd, J = 10.0,5.0 Hz), 7.67(2H, m), 7.26(2H, t, J = 10.0 Hz), 6.96(1H, t, J = 10.0 Hz), 6.88(2H, d, J = 5.0 Hz), 4.45(1H, s), 4.26(2H, m), 3.35(1H, t, J = 15.0 Hz), 2.68 (1H, m).

δF (470 MHz, CDCl3) -97.8(1F, d, J = 285.0 Hz), -104.6(1F, d, J = 285.0 Hz).

δC (125 MHz, CDCl3) 185.3(t, J = 25.0 Hz), 158.4, 141.5, 136.7, 130.5, 129.6, 129.4(d, J = 5.0 Hz), 127.9, 125.0, 123.3, 121.4, 114.7, 112.9(t, J = 242.5 Hz), 69.9, 34.1(d, J = 10.0 Hz), 33.3(t, J = 21.3 Hz).


(3c) 4-(butoxymethyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one

![Chemical Structure](image)

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with 1-(allyloxy)butane (2c), and purified by flash column chromatography as yellow oil (190.8 mg, 60% yield).

δH (500 MHz, CDCl3, Me4Si) 8.24(1H, d, J = 5.0 Hz), 8.13(1H, d, J = 5.0 Hz), 7.91(1H, d, J = 2.0 Hz), 7.86(2H, d, J = 2.0 Hz, 7.67(2H, m), 4.22(1H, s), 3.80(1H, d, J = 10.0 Hz), 3.64(1H, td, J = 10.0, 2.0 Hz), 2.48 (1H, m), 3.24(1H, t, J = 15.0 Hz), 2.56 (1H, m), 1.60(2H, td, J = 15.0, 5.0 Hz), 1.42(2H, td, J = 15.0, 5.0 Hz ), 0.943(3H, t, J = 5.0 Hz).

δF (470 MHz, CDCl3) -97.8(1F, d, J = 285.0 Hz), -104.6(1F, d, J = 285.0 Hz).

δC (125 MHz, CDCl3) 185.3(t, J = 36.8 Hz), 142.6, 136.6, 130.6, 129.2(t, J =26.3 Hz), 127.6, 125.2, 123.2, 112.9(t, J =248.8 Hz), 72.9(d, J =3.8 Hz), 71.2, 34.5(d, J=10.0 Hz), 33.2(t, J=21.5 Hz), 19.3, 13.9.


(3d) 4-benzyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one

![Chemical Structure](image)
The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with allylbenzene (2d), and purified by flash column chromatography as yellow oil (206.0 mg, 64% yield).

δH (500 MHz, CDCl₃, Me₂Si) 8.32(1H, d, J = 10.0 Hz), 8.17(1H, d, J = 5.0 Hz), 7.93(1H, t, J = 5.0 Hz), 7.87(1H, d, J = 10.0 Hz), 7.71(m, 2H), 7.42(4H, d, J = 5.0 Hz), 7.31(m, 1H), 4.18(1H, d, J = 10.0 Hz), 3.28(1H, d, J = 15.0 Hz), 2.97(1H, m), 2.77(1H, t, J = 15.0 Hz), 2.42(1H, m).

δF (470 MHz, CDCl₃) -96.7(1F, d, J = 289.8 Hz), -103.5(1F, d, J = 289.8 Hz).

δC (125 MHz, CDCl₃) 185.5(t, J = 25.0 Hz), 146.0, 139.1, 136.9, 130.0, 129.5(d, J = 17.5 Hz), 128.9(d, J = 6.3 Hz), 127.8, 127.0, 124.8, 123.3, 113.1(t, J = 245.0 Hz), 41.5(d, J = 3.8 Hz), 35.6(d, J = 10.0 Hz), 33.2(t, J = 20.0 Hz).

HRMS (EI-TOF) calculated [M]+ for C₂₁H₁₆F₂O 322.1169, found 322.1170.

(3e) 4-butyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with 1-Hexene (2e), and purified by flash column chromatography as yellow oil (149.8 mg, 52% yield).

δH (500 MHz, CDCl₃, Me₂Si) 8.10(2H, t, J = 5.0 Hz), 7.90(1H, d, J = 5.0 Hz), 7.82(1H, d, J = 5.0 Hz), 7.67(2H, m), 3.88(1H, s), 2.96(1H, t, J = 10.0 Hz), 2.56(1H, m), 1.84(2H, d, J = 10.0 Hz), 1.54(1H, m), 1.40(2H, m), 0.95(3H, t, J = 10.0 Hz).

δF (470 MHz, CDCl₃) δ= -98.4(d, J = 357.2 Hz, 1F), -102.8(d, J = 357.2 Hz, 1F).

δC (125 MHz, CDCl₃), δ=185.7(t, J = 26.3 Hz), 147.8, 136.8, 130.1, 129.3(d, J = 2.5 Hz), 128.4, 127.5, 125.0, 123.2, 113.0(t, J = 243.8 Hz), 35.8(d, J = 3.8 Hz), 34.0(t, J = 21.3 Hz), 33.4(d, J = 10.0 Hz), 30.2, 22.5, 14.0.

HRMS (EI-TOF) calculated [M]+ for C₁₈H₁₈F₂O for 288.1326, found 288.1325

(3f) Methyl-2,2-difluoro-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with ethyl acrylate (2f), and purified by flash column chromatography as white solid (191.5 mg, 63% yield).

δH (500 MHz, CDCl₃, Me₂Si) 8.13(1H, d, J = 10.0 Hz), 7.91(3H, t, J = 7.0 Hz), 7.65(2H, m), 4.82(1H, d, J = 5.5 Hz), 4.17(2H, dd, J = 14.0, 7.0 Hz), 3.33(1H, m), 2.84(2H, m), 1.16 (3H, t, J = 7.0 Hz).

δF (470 MHz, CDCl₃) -105.0(1F, d, J = 277.3 Hz), -109.6(1F, d, J = 277.3 Hz).

δC (125 MHz, CDCl₃) δ=184.7(t, J = 250.0 Hz), 171.1, 138.5, 136.5, 131.2, 129.7, 129.5, 129.2, 127.9, 124.7, 122.9, 112.8(t, J = 250.0 Hz), 62.1, 39.9(d, J = 8.8 Hz), 35.7(t, J = 23.8 Hz), 13.9.
HRMS (EI-TOF) calculated [M]$^+$ for $C_{17}H_{14}F_2O_3$ 304.0911, found 304.0913.

(3g) 2,2-difluoro-4-phenyl-3,4-dihydrophenanthren-1(2H)-one

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with styrene (2g), and purified by flash column chromatography as yellow oil (163.2 mg, 53% yield).

δH (500 MHz, CDCl$_3$, Me$_4$Si) 8.24(1H, d, $J$ = 10.0 Hz), 7.94(1H, d, $J$ = 10.0 Hz), 7.89(1H, d, $J$ = 10.0 Hz), 7.79(1H, d, $J$ = 10.0 Hz), 7.58(1H, t, $J$ = 10.0 Hz), 7.40(1H, m), 7.22(3H, m), 7.00(2H, d, $J$ = 10.0 Hz), 5.28(1H, m), 3.02(2H, m).

δF (470 MHz, CDCl$_3$) -102.3(1F, d, $J$ = 343.1 Hz), -107.6(1F, d, $J$ = 343.1 Hz).

δC (125 MHz, CDCl$_3$) 185.7(t, $J$=25.0 Hz), 143.4, 142.9, 136.8, 130.8, 129.3(d, $J$=8.8 Hz), 129.0, 128.8, 127.9(d, $J$=1.3 Hz), 127.5, 127.0, 126.5, 122.9, 112.5(t, $J$=247.5 Hz), 40.2(t, $J$=20.0 Hz), 39.9(d, $J$=8.8 Hz).

HRMS (EI-TOF) calculated [M]$^+$ for $C_{20}H_{14}F_2O$ 308.1014, found 308.1014.

(3h) 4-(4-chlorophenyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with 1-chloro-4-vinylbenzene (2h), and purified by flash column chromatography as yellow oil (193.4 mg, 58% yield).

δH (500 MHz, CDCl$_3$, Me$_4$Si) 8.15(1H, d, $J$ = 10.0 Hz), 7.87(1H, d, $J$ = 10.0 Hz), 7.82(1H, d, $J$ = 10.0 Hz), 7.65(1H, d, $J$ = 5.0 Hz), 7.35(1H, m), 7.12(2H, d, $J$ = 10.0 Hz), 6.22(2H, d, $J$ = 10.0 Hz), 6.21(2H, d, $J$ = 10.0 Hz), 6.94(2H, d, $J$ = 5.0 Hz), 5.18(1H, m), 2.91(2H, m).

δF (470 MHz, CDCl$_3$) -101.8(1F, d, $J$ = 347.8 Hz), -106.9(1F, d, $J$ = 347.8 Hz).

δC (125 MHz, CDCl$_3$) 185.4(t, $J$=25.0 Hz), 143.4, 142.9, 136.8, 132.9, 129.6, 129.4(d, $J$=8.8 Hz), 129.1(d, $J$=8.8 Hz), 127.7, 126.2, 123.0, 112.4(t, $J$=246.3 Hz), 53.4, 40.0(t, $J$=21.3 Hz), 39.2(d, $J$=7.5 Hz).

HRMS (EI-TOF) calculated [M]$^+$ for $C_{20}H_{14}F_2Cl$ 342.0623, found 342.0622.

(3i) Methyl-2,2-difluoro-3-methyl-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate
The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with methyl crotonate (2i), and purified by flash column chromatography as yellow oil (133.8 mg, 44% yield).

\[ \delta H (500 \text{ MHz, CDCl}_3, \text{Me}_4\text{Si}) \ 8.14(1H, \text{ d, } J = 10.0 \text{ Hz}), \ 7.92(3H, \text{ t, } J = 10.0 \text{ Hz}), \ 7.66(2H, \text{ m}), \ 4.59(1H, \text{ t, } J = 5.0 \text{ Hz}), \ 3.68(1H, \text{ s}), \ 3.50(1H, \text{ m}), \ 1.28(3H, \text{ d, } J = 10.0 \text{ Hz}). \]

\[ \delta F (470 \text{ MHz, CDCl}_3) \ -106.0(1F, \text{ d, } J = 338.4 \text{ Hz}), \ -119.2(1F, \text{ d, } J = 338.4 \text{ Hz}). \]

\[ \delta C (125 \text{ MHz, CDCl}_3) \ 184.6(1t, J=26.3 \text{ Hz}), \ 172.0, \ 136.7, \ 136.6, \ 131.8, \ 129.6, \ 129.3(d, J=8.8 \text{ Hz}), \ 127.9, \ 124.5, \ 122.7, \ 114.2(t, J=243.8 \text{ Hz}), \ 53.0(d, J=1.3 \text{ Hz}), \ 47.8(d, J=6.3 \text{ Hz}), \ 40.5(t, J=21.3 \text{ Hz}), \ 13.5(d, J=7.5 \text{ Hz}). \]

HRMS (EI-TOF) calculated [M]^+ \text{ C}_{17}\text{H}_{14}\text{F}_2\text{O}_3 \text{ for } 304.0911 \text{, found } 304.0909.

\[(3j) \ 5,5\text{-difluoro-1,3,4,4a,5,12c-hexahydrobenzo[c]phenanthren-6(2H)-one} \]

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-2-yl)ethan-1-one (1a) with methyl crotonate (2i), and purified by flash column chromatography as yellow oil (134.4 mg, 47% yield).

\[ \delta H (500 \text{ MHz, CDCl}_3, \text{Me}_4\text{Si}) \ 8.05(2H, \text{ d, } J = 10.0 \text{ Hz}, 5Hz), \ 7.82(1H, \text{ m}), \ 7.74(1H, \text{ d, } J = 10.0 \text{ Hz}), \ 7.57(2H, \text{ m}), \ 3.72(1H, \text{ m}), \ 2.65(1H, \text{ m}), \ 2.47(1H,m), \ 2.11(1H, \text{ d, } J = 10.0 \text{ Hz}), \ 1.91(1H, \text{ d, } J = 10.0 \text{ Hz}), \ 1.78(1H, \text{ m}), \ 1.70(3H, \text{ d, } J = 10.0 \text{ Hz}), \ 1.60(1H, \text{ m}). \]

\[ \delta F (470 \text{ MHz, CDCl}_3) \ -103.1(1F, \text{ d, } J = 352.5 \text{ Hz}), \ -112.7(1F, \text{ d, } J = 338.4 \text{ Hz}). \]

\[ \delta C (125 \text{ MHz, CDCl}_3) \ 185.8(t, J=25.0 \text{ Hz}), \ 147.8, \ 136.7, \ 130.0, \ 129.3(d, J=5.0 \text{ Hz}), \ 128.4, \ 127.4, \ 125.1, \ 123.3, \ 115.3(t, J=247.5 \text{ Hz}), \ 39.9(t, J=20.0 \text{ Hz}), \ 37.3(d, J=8.8 \text{ Hz}), \ 26.2, \ 24.2, \ 22.2(d, J=5.0 \text{ Hz}). \]

HRMS (EI-TOF) calculated [M]^+ \text{ C}_{18}\text{H}_{16}\text{F}_2\text{O} \text{ for } 286.1169 \text{, found } 286.1168.

\[(3k) \ 3,3\text{-difluoro-1-hexyl-2,3-dihydrophenanthren-4(1H)-one} \]

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-1-yl)ethan-1-one (1b) with 1-octene (2a), and purified by flash column chromatography as yellow oil (116.9 mg, 37% yield).

\[ \delta H (500 \text{ MHz, CDCl}_3, \text{Me}_4\text{Si}) \ 9.31(1H, \text{ t, } J = 10.0 \text{ Hz}), \ 8.04(1H, \text{ d, } J = 10.0 \text{ Hz}), \ 7.84(1H, \text{ d, } J = 10.0 \text{ Hz}). \]
Hz), 7.68(1H, t, \( J = 5.0 \) Hz), 7.55(1H, t, \( J = 5.0 \) Hz), 7.41(1H, d, \( J = 10.0 \) Hz), 3.32(1H, s), 2.63 (2H, m), 1.83(2H, d, \( J = 5.0 \) Hz), 1.32(8H, d, \( J = 25.0 \) Hz), 0.88(3H, s).

\( \delta F \) (470 MHz, CDCl\(_3\) ) -102.2(1F, d, \( J = 338.4 \) Hz), -103.0(1F, , \( J = 338.4 \) Hz).

\( \delta C \) (125 MHz, CDCl\(_3\)) 187.1(t, \( J = 25.0 \) Hz), 150.1, 136.1, 132.6, 131.5, 129.7, 128.5, 126.8, 126.2, 125.9, 124.4, 113.7(t, \( J = 245.0 \) Hz), 37.2(t, \( J = 3.8 \) Hz), 36.8, 35.1(t, \( J = 21.3 \) Hz), 31.7, 29.2, 27.0, 22.6, 14.1.

HRMS (EI-TOF) calculated [M]+ for C\(_{20}\)H\(_{22}\)F\(_2\)O 316.1639, found 316.1638.

\( 3l \)

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-1-yl)ethan-1-one (1b) with 1-Octene (2a), and purified by flash column chromatography as yellow oil (111.3 mg, 35% yield).

\( \delta H \) (500 MHz, CDCl\(_3\), Me\(_4\)Si) \( \delta = 8.32(d, J=10.0Hz, 1H), 8.05(d, J=10.0Hz, 1H), 7.85(d, J=10.0 Hz, 1H), 7.69(t, J=10.0 Hz, 1H), 7.57(t, J=10.0 Hz, 1H), 7.51(d, J=10.0 Hz, 1H), 4.22(s, 1H), 3.74(m, 2H), 3.59(t, J=5.0 Hz, 1H), 3.47(td, J=15.0, 5.0 Hz, 2H), 2.74(m, 2H), 1.56 (m, 2H), 1.36(td, J=15.0,10.0 Hz, 2H), 0.91(t, J=10.0 Hz, 3H).

\( \delta F \) (470 MHz, CDCl\(_3\) ) \( \delta = -102.6(d, J = 338.4 \) Hz, 1F), -104.3(d, \( J = 333.7 \) Hz, 1F).

\( \delta C \) (125 MHz, CDCl\(_3\)), \( \delta = 186.8(t, J=25.0 \) Hz), 146.3, 136.0, 132.8, 131.5, 129.7, 128.5, 126.9, 126.3, 126.0, 113.6(t, J=246.3 Hz), 74.1(d, J=1.3 Hz), 71.3, 53.4, 38.0(dd, \( J = 6.3, 2.5 \) Hz), 33.7(t, \( J = 22.5 \) Hz), 31.6, 19.3, 13.9.

HRMS (EI-TOF) calculated [M]+ for C\(_{19}\)H\(_{20}\)F\(_2\)O\(_2\) 318.1431 , found 318.1432.

\( 3m \)

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-1-yl)ethan-1-one (1b) with (allyloxy)benzene (2b), and purified by flash column chromatography as yellow oil (125.1 mg, 37% yield).

\( \delta H \) (500 MHz, CDCl\(_3\), Me\(_4\)Si) 9.33(1H, d, \( J = 10.0 \) Hz), 8.05(1H, d, \( J = 10.0 \) Hz), 7.85(1H, d, \( J = 10.0 \) Hz), 7.68(1H, t, \( J = 8.0 \) Hz), 7.56(1H, t, \( J = 7.5 \) Hz), 7.51 (1H, d, \( J = 6.5 \) Hz), 7.27(2H, t, \( J = 8.0 \) Hz), 6.96(1H, t, \( J = 7.0 \) Hz), 6.88(1H, d, \( J = 8.0 \) Hz). 4.29(2H, m), 3.80(1H, t, \( J = 5.0 \) Hz), 2.84(2H, m).

\( \delta F \) (470 MHz, CDCl\(_3\) ) -102.4(1F, d, \( J = 329.0Hz), -104.4(1F, d, J = 333.7 Hz).

\( \delta C \) (125 MHz, CDCl\(_3\)) 186.7(t, \( J = 25.0 \) Hz), 158.3, 145.2, 136.4, 133.0, 131.5, 129.9, 129.7, 128.6, 127.2, 126.3, 125.8, 121.5, 114.7, 114.0(t, \( J = 246.0 \) Hz), 70.9, 37.6(dd, \( J = 6.3, 5.0 \) Hz), 33.8(t, \( J = 22.5 \) Hz).
HRMS (EI-TOF) calculated [M]+ for C_{21}H_{16}F_{2}O_{2} 338.1118, found 338.1119.

(3n) 3,3-difluoro-1-phenyl-2,3-dihydrophenanthrene-4(1H)-one

\[
\text{O} \quad \text{F} \quad \text{F} \\
\text{3n}
\]

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-1-yl)ethan-1-one (1b) with styrene (2g), and purified by flash column chromatography as yellow oil (175.6 mg, 57% yield).

\[
\delta H (500 \text{ MHz, CDCl}_3, \text{Me}_4\text{Si}) \ 9.31(1\text{H}, \text{d}, J = 10.0 \text{ Hz}), 7.75(1\text{H}, \text{d}, J = 8.5 \text{ Hz}), 7.67(1\text{H}, \text{d}, J = 8.0 \text{ Hz}), 7.58(1\text{H}, \text{t}, J = 8.0 \text{ Hz}), 7.44(1\text{H}, \text{t}, J = 7.5 \text{ Hz}), 7.22(3\text{H}, \text{m}), 7.03(2\text{H}, \text{d}, J = 7.0 \text{ Hz}), 6.86(1\text{H}, \text{d}, J = 8.5 \text{ Hz}), 4.53(1\text{H}, \text{dd}, J = 10.5, 5.5 \text{ Hz}), 2.86(1\text{H}, \text{m}), 2.55(1\text{H}, \text{m}).
\]

\[
\delta F (470 \text{ MHz, CDCl}_3) \ -108.3(1\text{F}, \text{d}, J = 324.3 \text{Hz}), -110.0(1\text{F}, \text{d}, J = 329.0 \text{Hz}).
\]

\[
\delta C (125 \text{ MHz, CDCl}_3) \ 186.9(\text{t}, J = 25.0 \text{ Hz}), 148.4, 142.9, 136.0, 132.7, 131.3, 129.9, 129.3, 128.8, 128.6, 127.7, 127.1, 127.0, 126.3, 113.3(\text{t}, J = 250.0 \text{ Hz}), 43.59(\text{dd}, J = 7.5, 2.5 \text{ Hz}), 40.7(\text{t}, J = 22.5 \text{ Hz}).
\]

HRMS (EI-TOF) calculated [M]+ for C_{20}H_{14}F_{2}O 308.1013, found 308.1012.

(3o) methyl 3,3-difluoro-2-methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-1-carboxylate

\[
\text{O} \quad \text{F} \quad \text{F} \\
\text{3o}
\]

The title compound was prepared according to the general procedure described above by the reaction between 2,2-difluoro-2-iodo-1-(naphthalen-1-yl)ethan-1-one (1b) with methyl crotonate (2i), and purified by flash column chromatography as yellow oil (103.4 mg, 34% yield).

\[
\delta H (500 \text{ MHz, CDCl}_3, \text{Me}_4\text{Si}) \ 9.27(1\text{H}, \text{d}, J = 10.0 \text{ Hz}), 8.99(1\text{H}, \text{d}, J = 10.0 \text{ Hz}), 7.79(1\text{H}, \text{d}, J = 10.0 \text{ Hz}), 7.64(1\text{H}, \text{t}, J = 8.0 \text{ Hz}), 7.52(1\text{H}, \text{t}, J = 7.0 \text{ Hz}), 7.23(1\text{H}, \text{d}, J = 8.5 \text{ Hz}), 4.06(1\text{H}, \text{d}, J = 8.5 \text{ Hz}), 3.06(1\text{H}, \text{m}), 3.06(1\text{H}, \text{m}), 1.26(3\text{H}, \text{d}, J = 7.0 \text{ Hz}).
\]

\[
\delta F (470 \text{ MHz, CDCl}_3) \ -116.7(1\text{F}, \text{d}, J = 324.3 \text{Hz}), -120.4(1\text{F}, \text{d}, J = 319.6 \text{Hz}).
\]

\[
\delta C (125 \text{ MHz, CDCl}_3) \ 186.2(\text{t}, J = 25.0 \text{ Hz}), 171.8, 140.9, 136.5, 133.0, 131.4, 130.1, 129.6, 127.3, 126.3, 125.0, 114.0(\text{t}, J = 250.0 \text{ Hz}), 52.9, 51.8(\text{d}, J = 5.0 \text{ Hz}), 39.3(\text{t}, J = 22.5 \text{ Hz}), 11.2(\text{t}, J = 2.5 \text{ Hz}).
\]

HRMS (EI-TOF) calculated [M]+ for C_{17}H_{14}F_{3}O for 304.0911, found 304.0909.

(3p) 2,2-difluoro-4-hexyl-3,4-dihyronaphthalen-1(2H)-one

\[
\text{3p}
\]
The title compound was prepared according to the general procedure described above by the reaction between 2-iodo-2,2-difluoroacetophenone (1c) with 1-octene (2a), and purified by flash column chromatography as yellow oil (87.8 mg, 33% yield).

δH (500 MHz, CDCl₃, Me₄Si) 8.12(1H, d, J = 10.0 Hz), 7.63(1H, t, J = 5.0 Hz), 7.87(1H, t, J = 10.0 Hz), 7.41(2H, m), 2.64(1H, m), 2.43(1H, m), 1.59(1H, s), 1.48(1H, m), 1.35(6H, m), 0.90(3H, t, J = 6.5 Hz).

δF (470 MHz, CDCl₃) -105.1(1F, d, J = 277.3 Hz), -106.5(1F, d, J = 277.3 H).

δC (125 MHz, CDCl₃) 185.6(t, J = 25.0 Hz), 147.0, 135.1, 129.7, 128.8, 127.9, 127.4, 113.6(t, J = 250.0 Hz), 36.2(t, J = 20.0 Hz), 35.6(t, J = 5.0 Hz), 35.3, 29.2, 26.6, 22.7, 14.1.

HRMS (EI-TOF) calculated [M]+ for C₁₆H₂₀F₂O 266.1482, found 266.1481.

3. The reaction of other naphthalenyl halodifluoromethyl ketones with 1-octene

To a solution of 2-halo-2,2-difluoroacetophenones (1 mmol, 1.0 equiv.) in DMF (2mL) was added alkene 2a (1mmol, 1.0 equiv.), copper (1 mmol, 1.0 equiv.), AgNO₃ (1 mmol, 1.0 equiv.). The mixture was stirred at 120°C under N₂ protection for 1h. The reaction was quenched with water (10mL), and extracted with ethyl acetate (3 x 10mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether/Ethyl acetate (50:1, 40:1) to afford the product 3 as yellow oil (75% yield, halo = Br; 54% yield, halo = Cl).

4. Studies on Reaction Mechanism

4.1 Control experiment

We added the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to this cyclization reaction under standard conditions and found that the reaction was suppressed. Similarly, when butylated hydroxytoluene (BHT) and nitrobenzene were subjected to the standard reaction system respectively, the yield of the desired cyclic product 3a was declined sharply (Scheme 1a). These results indicated that the reaction might undergo a tandem radical addition and cyclization process. Then, the addition compound 6 was prepared and used to perform the intramolecular cyclization in the presence of copper under standard condition. However, the desired product 3a was not obtained (Scheme 1b),

![Scheme 1](image-url)
4.2 Computational Methods

We employed the DFT method with M06-2X hybrid meta-GGA functional as default to describe the all molecules. It is well-known that B3LYP functional has many shortcomings, such as (1) it systematically underestimates activation barrier heights of transition states (TSs), and (2) it is not enough to treat medium-range VDW interactions, for example, aromatic-aromatic stacking energies. Recently, Zhao et al. developed new density functionals, called M06-class, for a variety of databases. The M06-2X is a hybrid meta functional and has excellent performances for accurately predicting main-group thermochemistry, electronic excitation energies, and aromatic-aromatic stacking interactions. This functional could be considered to describe the noncovalent interactions as reliably as the Møller-Plesset second-order perturbation theory (MP2) with the affordable computational costs for very large systems.

During structural optimization, molecular structures were allowed to relax. The frequency calculations were performed at the same level of theory. The 6-31G(d,p) basis set was employed for O, C, F, and H atoms and LANL2DZ effective core potential basis set was used for Cu and I atoms. Single-point energy calculations were carried out at the M06-2X/6-311++G(2d,2p) levels using the abovementioned M06-2X/6-31G(d,p) optimized structures in order to obtain more reliable interaction energies. A polarized continuum model (PCM-SMD) was utilized to simulated the solvent effect of n,n-DiMethylFormamide (DMF). Unless otherwise mentioned, the Gibbs free energies are used at the M06-2X/6-311++G(2d,2p) level in DMF solution. All the calculations were performed using the Gaussian 09 code.

4.3 Description of Reaction Mechanism

As given in Figure 1, the A can be formed from 1a by Cu catalyst and need the energy of 258.58 kJ/mol. Furthermore, the B can be obtained by a dimerization step and are energetically favorable due to a large exothermic step (-163.87 kJ/mol). The B radical will experience a cyclization step and two intermediates, C and D, are produced. The C is further reduced by losing an electron to produce E (250.90 kJ/mol), followed by a deprotonation step (414.53 kJ/mol). The main product 3a is finally formed. All molecular structures are shown in Figure 2.
Figure 1. Plausible copper oxidation quenching mechanism for the formation of 3a
Figure 2. The optimized structures of 1a, A-E, 3a molecules at the level of M06-2X/6-31G(d,p).

5. X-Ray Data Collection and Structure Refinement Details

X-Ray data for compound 3a were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5° steps at 296(2) K. Cell determination, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24[1] software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

Figure 3. ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the
crystallographic structure of compound 3a determined at 296 K.

Crystallization: Crystal of compound 3a was grown from the solvents PE + EA by slow evaporation method.

Table 1. Crystal data and structure refinement for 3a.

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<th>Compound</th>
<th>3a</th>
</tr>
</thead>
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</tr>
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</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
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</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P 21/c</td>
</tr>
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</table>
| Unit cell dimensions | a = 10.0026(6) Å \( \equiv 90^\circ \),  
                      | b = 25.7449(14) Å \( \equiv 103.519(2)^\circ \),  
                      | c = 7.0051(4) Å \( \equiv 90^\circ \).  
                      | Volume | 1753.94(17) Å³ |
| Z                 | 4                         |
| Density (calculated) | 1.198 Mg/m³  |
| Absorption coefficient | 0.086 mm⁻¹  |
| F(000)            | 672                       |
| Crystal size      | 0.20 x 0.16 x 0.13 mm³    |
| Theta range for data collection | 2.625 to 24.997°.  
| Index ranges      | -11\leq h\leq 11, -30\leq k\leq 30, -8\leq l\leq 8  |
| Reflections collected | 8890  |
| Independent reflections | 3050 [R(int) = 0.0404]  |
| Completeness to theta = 25.242° | 96.1 %  |
| Absorption correction | Semi-empirical from equivalents  |
| Max. and min. transmission | 0.7456 and 0.6097  |
| Refinement method | Full-matrix least-squares on F²  |
| Data / restraints / parameters | 3050 / 72 / 265  |
| Goodness-of-fit on F² | 1.033  |
| Final R indices [I>2\sigma(I)] | R₁ = 0.0747, wR₂ = 0.2071  |
| R indices (all data) | R₁ = 0.1057, wR₂ = 0.2380  |
| Largest diff. peak and hole | 0.201 and -0.203 e.Å⁻³  |
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 3a. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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Table 3. Bond lengths [Å] and angles [°] for 3a.

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C(18')-H(18D) 0.9700
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C(2)-C(1)-C(10) 122.9(2)
C(6)-C(1)-C(10) 119.4(2)
C(9)-C(10)-C(1) 117.8(2)
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Table 4. Anisotropic displacement parameters (Å² x 10³) for 3a.

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Table 5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) for 3a.

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Table 6. Torsion angles [°] for 3a.

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<th>Bond</th>
<th>Torsion Angle</th>
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<td>C(2)-C(1)-C(10)-C(9)</td>
<td>179.5(3)</td>
</tr>
<tr>
<td>C(6)-C(1)-C(10)-C(9)</td>
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</tr>
<tr>
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<tr>
<td>C(6)-C(1)-C(10)-C(14)</td>
<td>-179.0(3)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(6)-C(7)</td>
<td>-179.8(3)</td>
</tr>
<tr>
<td>C(10)-C(1)-C(6)-C(7)</td>
<td>-1.2(4)</td>
</tr>
<tr>
<td>C(2)-C(1)-C(6)-C(5)</td>
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</tr>
<tr>
<td>C(10)-C(1)-C(6)-C(5)</td>
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</tr>
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<td>-0.3(4)</td>
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<tr>
<td>C(14)-C(10)-C(9)-C(8)</td>
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<td>C(1)-C(10)-C(9)-C(11)</td>
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<tr>
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<td>C(6)-C(1)-C(2)-C(3)</td>
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<tr>
<td>C(10)-C(1)-C(2)-C(3)</td>
<td>-177.9(3)</td>
</tr>
<tr>
<td>C(10)-C(9)-C(8)-C(7)</td>
<td>-0.1(4)</td>
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<td>C(11)-C(9)-C(8)-C(7)</td>
<td>179.4(3)</td>
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<td>C(7)-C(6)-C(5)-C(4)</td>
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<td>C(1)-C(6)-C(5)-C(4)</td>
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</tr>
<tr>
<td>C(9)-C(8)-C(7)-C(6)</td>
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<tr>
<td>C(5)-C(6)-C(7)-C(8)</td>
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</tr>
<tr>
<td>C(1)-C(6)-C(7)-C(8)</td>
<td>0.8(4)</td>
</tr>
<tr>
<td>C(9)-C(10)-C(14)-C(15)</td>
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<td>C(1)-C(10)-C(14)-C(15)</td>
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<td>C(9)-C(10)-C(14)-C(13)</td>
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<td>C(1)-C(10)-C(14)-C(13)</td>
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<td>C(12)-C(13)-C(14)-C(15)</td>
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C(12)-C(13)-C(14)-C(10) 49.4(4)
C(12)-C(13)-C(14)-C(15') -74.1(12)
C(10)-C(9)-C(11)-O(1) -175.5(3)
C(8)-C(9)-C(11)-O(1) 4.9(4)
C(10)-C(9)-C(11)-C(12) 3.9(4)
C(8)-C(9)-C(11)-C(12) -175.6(3)
C(14)-C(13)-C(12)-F(2) 75.2(3)
C(14)-C(13)-C(12)-F(1) -168.8(3)
C(14)-C(13)-C(12)-C(11) -46.8(4)
O(1)-C(11)-C(12)-F(2) 74.4(4)
C(9)-C(11)-C(12)-F(2) -105.1(3)
O(1)-C(11)-C(12)-F(1) -37.2(4)
C(9)-C(11)-C(12)-F(1) 143.3(3)
C(10)-C(14)-C(15)-C(16) 159.5(5)
C(13)-C(14)-C(15)-C(16) -73.0(8)
C(15')-C(14)-C(15)-C(16) -53(3)
C(14)-C(15)-C(16)-C(17) 176.1(8)
C(15)-C(16)-C(17)-C(18) -165.4(8)
C(16)-C(17)-C(18)-C(19) -87.6(14)
C(17)-C(18)-C(19)-C(20) -174.6(10)
C(15)-C(14)-C(15')-C(16') 37(16)
C(10)-C(14)-C(15')-C(16') -177(2)
C(13)-C(14)-C(15')-C(16') -53(3)
C(14)-C(15')-C(16')-C(17') -95(3)
C(15')-C(16')-C(17')-C(18') 170.3(16)
C(16')-C(17')-C(18')-C(19') 101(3)
C(17')-C(18')-C(19')-C(20') 92(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 3a [Å and °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-H...A</td>
<td>d(D-H)</td>
<td>d(H...A)</td>
<td>d(D...A)</td>
<td>&lt;(DHA)</td>
</tr>
</tbody>
</table>
C(13)-H(13B)...O(1)#1 0.97 2.61 3.520(5) 156.3
C(13)-H(13B)...O(1)#1 0.97 2.61 3.520(5) 156.3

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z-1/2

6. The transformation reactions of gem-difluorodihydrophenanthrenones.

6.1 The procedure for preparation of 9 4-(4-chlorophenyl)-2,2-difluoro-N-methyl-1,2,3,4-tetrahydrophenanthren-1-amine.

To a solution of 4-(4-chlorophenyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one 3h (1 mmol, 1.0 equiv.) in MeOH (5mL) was added CH$_3$NH$_2$ (25% in EtOH, 10 mmol, 10.0 equiv.), Na(CN)BH$_3$ (1.25 mmol, 1.25 equiv.), ZnCl$_2$ (1 mmol, 1.0 equiv.) . The mixture was stirred at rt under N$_2$ protection overnight. The solvent was evaporated in vacuo, and extracted with DCM (3 x 20mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether/Ethyl acetate (100:1, 80:1) to afford the product 9 as yellow oil(125.3 mg, 35% yield).

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

$\delta$H (500 MHz, CDCl$_3$, Me$_4$Si) 7.81(2H, t, $J = 10.0$ Hz), 7.56(2H, dd, $J = 20.0, 5.0$ Hz), 7.39 (1H, t, $J = 10.0$ Hz), 7.27(1H, d, $J = 5.0$ Hz), 7.18(2H, t, $J = 5.0$ Hz), 6.97(2H, d, $J = 5.0$ Hz), 4.91(1H, t, $J = 9.0$ Hz), 4.02(1H, t, $J = 9.0$ Hz), 2.71(5H, m).

$\delta$F (470 MHz, CDCl$_3$) -98.7(1F, m), -107.2(1F, m).

$\delta$C (125 MHz, CDCl$_3$), 144.7, 133.7, 132.0, 131.3, 128.9(d, $J = 12.5$ Hz), 128.6(d, $J = 12.5$ Hz), 127.5, 126.3, 125.8, 125.5, 63.3(dd, $J = 27.5, 22.5$ Hz), 41.1(t, $J = 5.0$ Hz), 37.6(t, $J = 21.3$ Hz), 36.2, 1.0.

HRMS (EI-TOF) calculated [M]$^+$ for C$_{21}$H$_{18}$F$_2$NCl 358.1168, found 358.1168.

6.2 The procedure for preparation of 10 1,1,2,2-tetrafluoro-4-phenyl-1,2,3,4-tetrahydrophenanthrene

To a solution of 4-(4-chlorophenyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one 3h (1 mmol, 1.0 equiv.) in DCM (5mL) was added DAST (15 mmol, 15.0 equiv.). The mixture was stirred at 30$^\circ$C under N$_2$ protection overnight. The solvent was added to the 50mL sat. NaHCO$_3$(aq), then extracted with DCM (3 x 20mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether/Ethyl acetate (100:1) to afford the product 10 as yellow oil(282.4 mg, 80% yield).
\(\delta H (500 \text{ MHz, } \text{CDCl}_3, \text{Me}_4\text{Si})\): 8.01 (1H, d, \(J = 10.0 \text{ Hz}\)), 7.91 (2H, d, \(J = 10.0 \text{ Hz}\)), 7.70 (1H, d, \(J = 10.0 \text{ Hz}\)), 7.52 (1H, t, \(J = 10.0 \text{ Hz}\)), 7.36 (1H, t, \(J = 10.0 \text{ Hz}\)), 7.27 (2H, t, \(J = 5.0 \text{ Hz}\)), 7.23 (1H, t, \(J = 10.0 \text{ Hz}\)), 7.03 (2H, d, \(J = 10.0 \text{ Hz}\)), 5.15 (1H, s), 3.08 (1H, m), 2.74 (1H, m).

\(\delta F \text{ NMR (470 MHz, } \text{CDCl}_3\)): -105.4 (1F, ddd, \(J = 23.5, 18.8, 9.4 \text{ Hz}\)), -110.1 (1F, d, \(J = 23.5, 18.8, 9.4 \text{ Hz}\)), -118.0 (1F, ddd, \(J = 23.5, 14.1, 4.7 \text{ Hz}\)), -118.7 (1F, ddd, \(J = 23.5, 14.1, 4.7 \text{ Hz}\)).

\(\delta C \text{ NMR (125 MHz, } \text{CDCl}_3\)): 144.8, 135.0, 134.0 (t, \(J = 6.3 \text{ Hz}\)), 130.6, 130.0, 128.9 (d, \(J = 13.8 \text{ Hz}\)), 127.7, 127.4, 126.9 (d, \(J = 16.3 \text{ Hz}\)), 126.1, 121.5 (t, \(J = 3.8 \text{ Hz}\)), 115.9 (t, \(J = 26.3 \text{ Hz}\)), 113.0 (t, \(J = 27.5 \text{ Hz}\)), 40.8 (d, \(J = 3.8 \text{ Hz}\)), 37.3 (t, \(J = 20.0 \text{ Hz}\)) ppm.

HRMS (EI-TOF) calculated \([M]^+ \text{ for C}_{20}H_{14}F_3\) 353.0923, found 353.0929.

References
7. Spectral data

$^1$H NMR spectrum of 2,2-difluoro-4-hexyl-3,4-dihydrophenanthren-1(2H)-one(3a)

$^{19}$F NMR spectrum of 2,2-difluoro-4-hexyl-3,4-dihydrophenanthren-1(2H)-one(3a)
$^{13}$C NMR spectrum of 2,2-difluoro-4-hexyl-3,4-dihydrophanthrene-1(2H)-one(3a)

$^1$H NMR spectrum of 2,2-difluoro-4-(phenoxymethyl)-3,4-dihydrophanthrene-1(2H)-one(3b)
$^{19}$F NMR spectrum of 2,2-difluoro-4-(phenoxymethyl)-3,4-dihydrophenanthren-1(2H)-one(3b)

$^{13}$C NMR spectrum of 2,2-difluoro-4-(phenoxymethyl)-3,4-dihydrophenanthren-1(2H)-one(3b)
$^1$H NMR spectrum of 4-(butoxymethyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one (3c)

$^{19}$F NMR spectrum of 4-(butoxymethyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one (3c)
$^{13}$C NMR spectrum of 4-(butoxymethyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one (3c)

$^1$H NMR spectrum of 4-benzyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one (3d)
$^{19}$F NMR spectrum of 4-benzyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one(3d)

$^{13}$C NMR spectrum of 4-benzyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one(3d)
$^1$H NMR spectrum of 4-butyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one (3e)

$^{19}$F NMR spectrum of 4-butyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one (3e)
$^{13}$C NMR spectrum of 4-butyl-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one(3e)

$^1$H NMR spectrum of Methyl-2,2-difluoro-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3f)
$^{19}$F NMR spectrum of Methyl-2,2-difluoro-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3f)

$^{13}$C NMR spectrum of Methyl-2,2-difluoro-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3f)
$^1$H NMR spectrum of 2,2-difluoro-4-phenyl-3,4-dihydrophenanthren-1(2H)-one (3g)

$^{19}$F NMR spectrum of 2,2-difluoro-4-phenyl-3,4-dihydrophenanthren-1(2H)-one (3g)
$^{13}$C NMR spectrum of 2,2-difluoro-4-phenyl-3,4-dihydrophenanthren-1(2H)-one(3g)

$^1$H NMR spectrum of 4-(4-chlorophenyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one(3h)
$^{19}$F NMR spectrum of 4-(4-chlorophenyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one(3h)

$^{13}$C NMR spectrum of 4-(4-chlorophenyl)-2,2-difluoro-3,4-dihydrophenanthren-1(2H)-one(3h)
$^1$H NMR spectrum of Methyl-2,2-difluoro-3-methyl-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3i)

$^{19}$F NMR spectrum of Methyl-2,2-difluoro-3-methyl-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3i)
$^{13}$C NMR spectrum of Methyl-2,2-difluoro-3-methyl-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3i)

The NOESY spectrum of Methyl-2,2-difluoro-3-methyl-1-oxo-1,2,3,4-tetrahydrophenanthrene-4-carboxylate(3i)
$^1$H NMR spectrum of 5,5-difluoro-1,3,4,4a,5,12c-hexahydrobenzo[c]phenanthren-6(2H)-one(3j)

$^{19}$F NMR spectrum of 5,5-difluoro-1,3,4,4a,5,12c-hexahydrobenzo[c]phenanthren-6(2H)-one(3j)
\(^{13}\)C NMR spectrum of 5,5-difluoro-1,3,4,4a,5,12c-hexahydrobenzo[c]phenanthren-6(2H)-one (3j)

The NOESY spectrum of 5,5-difluoro-1,3,4,4a,5,12c-hexahydrobenzo[c]phenanthren-6(2H)-one (3j)
$^1$H NMR spectrum of 3,3-difluoro-1-hexyl-2,3-dihydrophenanthren-4(1H)-one (3k)

$^{19}$F NMR spectrum of 3,3-difluoro-1-hexyl-2,3-dihydrophenanthren-4(1H)-one (3k)
$^{13}$C NMR spectrum of 3,3-difluoro-1-hexyl-2,3-dihydrophenanthren-4(1H)-one (3k)

$^1$H NMR spectrum of butoxy-3,3-difluoro-2,3-dihydrophenanthren-4(1H)-one (3l)
$^{19}$F NMR spectrum of butoxy-3,3-difluoro-2,3-dihydrophenanthrene-4(1H)-one (3I)

$^{13}$C NMR spectrum of butoxy-3,3-difluoro-2,3-dihydrophenanthrene-4(1H)-one (3I)
$^1$H NMR spectrum of 3,3-difluoro-1-(phenoxy)methyl-2,3-dihydrophenanthren-4(1H)-one (3m)

$^{19}$F NMR spectrum of 3,3-difluoro-1-(phenoxy)methyl-2,3-dihydrophenanthren-4(1H)-one (3m)
$^{13}$C NMR spectrum of 3,3-difluoro-1-(phenoxymethyl)-2,3-dihydrophenanthren-4(1H)-one(3m)

$^1$H NMR spectrum of 3,3-difluoro-1-phenyl-2,3-dihydrophenanthren-4(1H)-one(3n)
$^{19}$F NMR spectrum of 3,3-difluoro-1-phenyl-2,3-dihydrophenanthren-4(1H)-one(3n)

$^{13}$C NMR spectrum of 3,3-difluoro-1-phenyl-2,3-dihydrophenanthren-4(1H)-one(3n)
$^1$H NMR spectrum of methyl 3,3-difluoro-2-methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-1-
carboxylate(3o)

$^{19}$F NMR spectrum of methyl 3,3-difluoro-2-methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-1-
carboxylate(3o)
$^{13}$C NMR spectrum of methyl 3,3-difluoro-2-methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-1-carboxylate(3o)

The NOESY spectrum of methyl 3,3-difluoro-2-methyl-4-oxo-1,2,3,4-tetrahydrophenanthrene-1-carboxylate(3o)
$^1$H NMR spectrum of 2,2-difluoro-4-hexyl-3,4-dihydronaphthalen-1(2H)-one(3p)

$^{19}$F NMR spectrum of 2,2-difluoro-4-hexyl-3,4-dihydronaphthalen-1(2H)-one(3p)
$^{13}$C NMR spectrum of 2,2-difluoro-4-hexyl-3,4-dihydronaphthalen-1(2H)-one(3p)

$^1$H NMR spectrum of 4-(4-chlorophenyl)-2,2-difluoro-N-methyl-1,2,3,4-tetrahydrophenanthren-1-amine(9)
$^{19}F$ NMR spectrum of 4-(4-chlorophenyl)-2,2-difluoro-N-methyl-1,2,3,4-tetrahydrophenanthren-1-amine(9)

$^{13}C$ NMR spectrum of 4-(4-chlorophenyl)-2,2-difluoro-N-methyl-1,2,3,4-tetrahydrophenanthren-1-amine(9)
The NOESY spectrum of 4-(4-chlorophenyl)-2,2-difluoro-N-methyl-1,2,3,4-tetrahydrophenanthren-1-amine (9)

$^1$H NMR spectrum of 1,1,2,2-tetrafluoro-4-phenyl-1,2,3,4-tetrahydrophenanthrene (10)
$^{19}$F NMR spectrum of 1,1,2,2-tetrafluoro-4-phenyl-1,2,3,4-tetrahydrophenanthrene(10)

$^{13}$C NMR spectrum of 1,1,2,2-tetrafluoro-4-phenyl-1,2,3,4-tetrahydrophenanthrene(10)