

## Visible-light-induced alkylsulfonation/bicyclization cascade of 1,7-enynes with thianthrenium salts

Zhiyong Jiang,<sup>a</sup> Zhichao Chen,<sup>\*b,c</sup> Weigang Zhao,<sup>\*a</sup> and Xiaolan Xie,<sup>\*b,c</sup>

[a] College of Material Engineering, Fujian Agriculture and Forestry University, 63 Xiyuangong Road, Fuzhou 350002, PR China. E-mail: weigang-zhao@fafu.edu.cn

[b] College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, China. E-mail: xxl\_qztc@163.com; zchen@qztc.edu.cn.

[c] Key Laboratory of Chemical Materials and Green Nanotechnology, College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, China.

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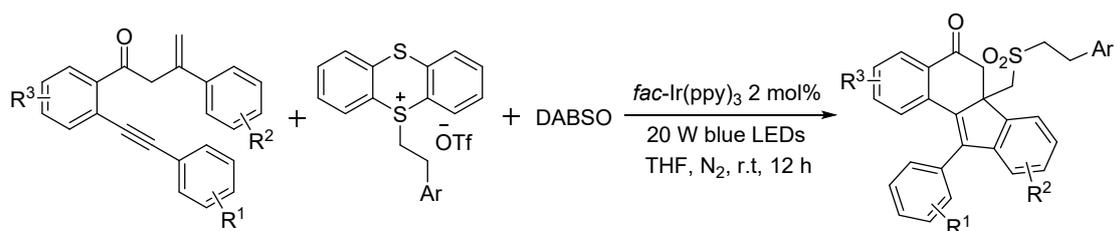
## 1. General information

Unless otherwise stated, all commercial materials and solvents were used directly without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a 400 MHz Bruker spectrometer ( $^1\text{H}$  400MHz,  $^{13}\text{C}$  100MHz,  $^{19}\text{F}$  NMR 376 MHz), using  $\text{CDCl}_3$  (spectra were referenced to the solvent peaks  $^1\text{H}$ : residual  $\text{CDCl}_3 = 7.26$  ppm,  $^{13}\text{C}$ :  $\text{CDCl}_3 = 77.0$  ppm) as the solvent. High-resolution mass spectra (HRMS) were measured on ESI-TOF. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluent. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Photochemical reactions were performed with a LED reactor WP-TEC-1020SL (WATTCAS, China).

## 2. General catalytic procedure for the synthesis of 3



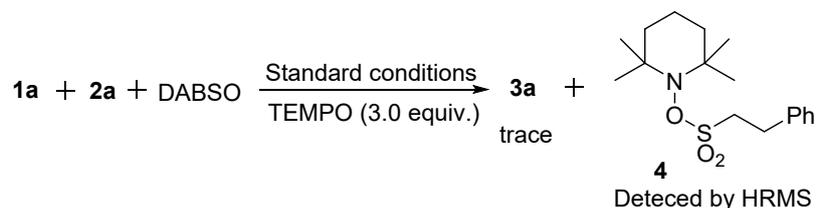
Figure S1 The WP-TEC-1020SL photochemical reaction system with the blue light LED



1,7-enynes **1** (0.2 mmol), thianthrenium salts **2** (0.3 mmol, 1.5 equiv), DABSO (0.3 mmol, 1.5 equiv),  $\text{fac-Ir(ppy)}_3$  (0.004 mmol, 0.02 equiv) and 2 mL THF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 20 W blue LED as light source under  $\text{N}_2$  atmosphere. After completion of the 1,7-enynes, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired products **3**.

### 3. Mechanism Exploration

#### (1) Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO)



1,7-enyne **1a** (0.2 mmol), thianthrenium salt **2a** (0.3 mmol, 1.5 equiv), DABSO (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, 0.02 equiv), TEMPO (0.6 mmol, 3.0 equiv) and 2 mL THF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 20 W blue LED as light source under N<sub>2</sub> atmosphere. The resulting mixture was monitored by TLC, and TEMPO adduct to sulfonyl radical was detected by HRMS (Figure S2). HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>28</sub>NO<sub>3</sub>S [M+H]<sup>+</sup> 326.1790, found 326.1798.

#### Elemental Composition Report

Page 1

##### Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

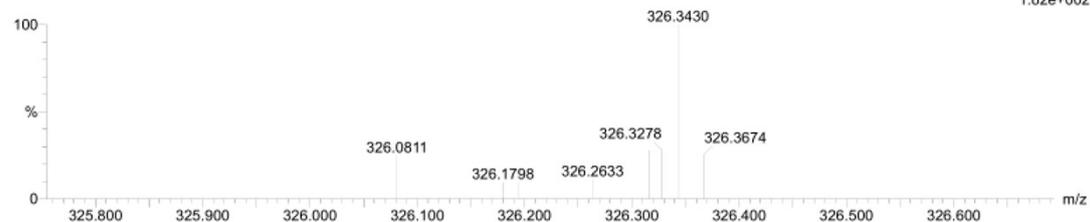
20 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-17 H: 0-28 N: 0-2 O: 0-3 S: 0-1

20250525-6-7-Pos 362 (1.436)

1: TOF MS ES+

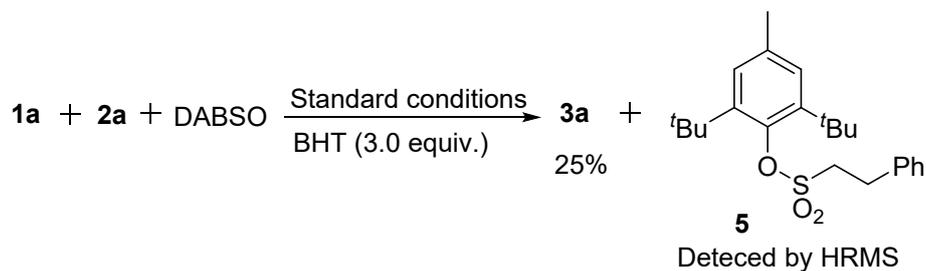


Minimum: -1.5  
Maximum: 5.0 10.0 50.0

| Mass     | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf (%) | Formula        |
|----------|------------|-----|-----|-----|-------|------|----------|----------------|
| 326.1798 | 326.1790   | 0.8 | 2.5 | 4.5 | 57.5  | n/a  | n/a      | C17 H28 N O3 S |

Figure S2

## (2) Trapping experiment with butylated hydroxytoluene (BHT)



1,7-enyne **1a** (0.2 mmol), thianthrenium salt **2a** (0.3 mmol, 1.5 equiv), DABSO (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, 0.02 equiv), BHT (0.6 mmol, 3.0 equiv) and 2 mL THF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 20 W blue LED as light source under N<sub>2</sub> atmosphere. The resulting mixture was monitored by TLC, and TEMPO adduct to sulfonyl radical was detected by HRMS (Figure S2). HRMS (ESI) *m/z* calcd for C<sub>23</sub>H<sub>33</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 389.2150, found 389.2161.

### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

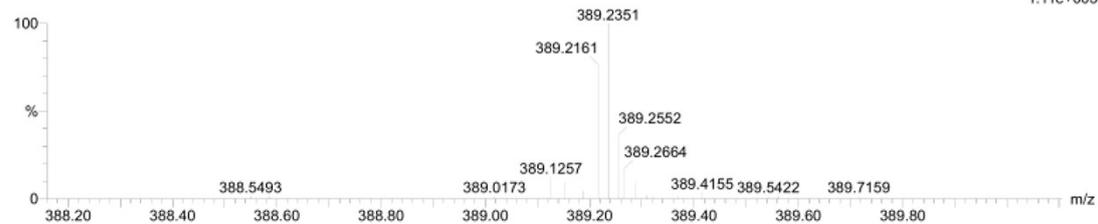
7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-23 H: 0-33 O: 0-3 S: 0-1

20250525-6-8-Pos 98 (0.403)

1: TOF MS ES+



|          |            |     |      |     |       |      |         |              |  |  |
|----------|------------|-----|------|-----|-------|------|---------|--------------|--|--|
| Minimum: |            |     |      |     | -1.5  |      |         |              |  |  |
| Maximum: |            | 5.0 | 10.0 |     | 50.0  |      |         |              |  |  |
| Mass     | Calc. Mass | mDa | PPM  | DBE | i-FIT | Norm | Conf(%) | Formula      |  |  |
| 389.2161 | 389.2150   | 1.1 | 2.8  | 7.5 | 112.1 | n/a  | n/a     | C23 H33 O3 S |  |  |

Figure S3

### (3) Light/dark experiments

In order to illustrate the reaction mechanism, the light/dark experiments were conducted. 1,7-enyne **1a** (0.2 mmol), thianthrenium salt **2a** (0.3 mmol, 1.5 equiv), DABSO (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, 0.02 equiv), BHT (0.6 mmol, 3.0 equiv) and 2 mL THF were added in a schlenk tube. The reaction mixture was exposed to 20 W blue LEDs irradiation under N<sub>2</sub> atmosphere at room temperature with stirring for 1 h, then stirring for 1 h without irradiation. The following product yields based on the irradiation with 20 W blue LEDs under N<sub>2</sub> atmosphere at room temperature for a certain time, and without irradiation for a certain time were also presented in the Figure S4.

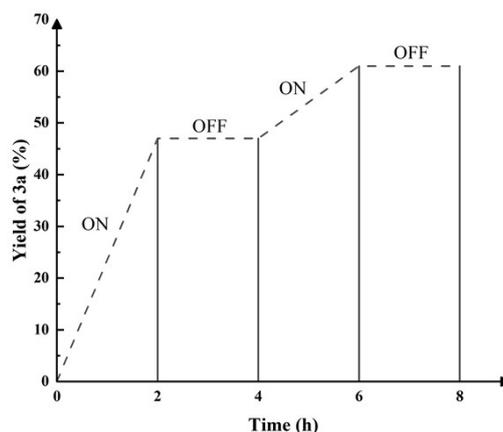
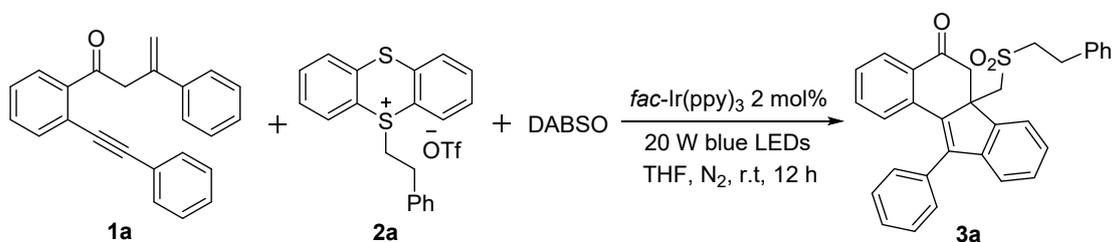


Figure S4 Light/dark experiments

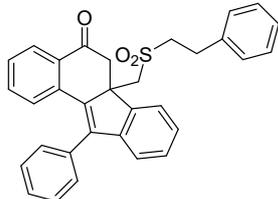
### 4. Large-scale synthesis of 3a



1,7-enyne **1a** (1 mmol), thianthrenium salt **2a** (1.5 mmol, 1.5 equiv), DABSO (1.5 mmol, 1.5 equiv), *fac*-Ir(ppy)<sub>3</sub> (0.004 mmol, 0.02 equiv) and 5 mL THF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 20 W blue LED as light source under N<sub>2</sub> atmosphere. After completion of the olefinic 1,7-enyne, the solvent was removed under reduced pressure by rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired products **3a**.

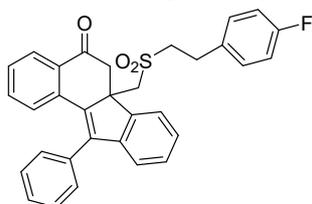
## 5. Characterization of compounds 3

### 6a-((Phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3a)



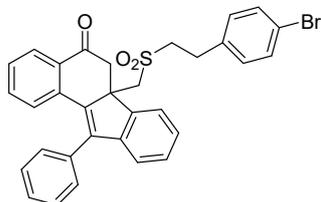
White solid. 79.7 mg. Yield: 81%.  $R_f = 0.50$  (PE/EA = 3:1). mp 145-146°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 – 8.07 (m, 1H), 7.63 (dd,  $J = 6.1, 1.9$  Hz, 1H), 7.53 – 7.44 (m, 3H), 7.42 – 7.32 (m, 6H), 7.29 – 7.15 (m, 5H), 6.96 – 6.89 (m, 2H), 3.67 (d,  $J = 14.7$  Hz, 1H), 3.46 (d,  $J = 16.5$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.89 – 2.79 (m, 2H), 2.75 – 2.59 (m, 2H), 2.55 (d,  $J = 16.5$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 146.7, 145.6, 140.7, 138.5, 137.4, 135.5, 134.2, 133.8, 129.7, 129.1, 128.9, 128.9, 128.8, 128.4, 128.3, 128.3, 128.2, 127.6, 126.9, 126.7, 122.6, 122.3, 58.0, 55.8, 53.3, 48.7, 27.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{27}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  491.1681, found 491.1682.

### 6a-(((4-Fluorophenethyl)sulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3b)



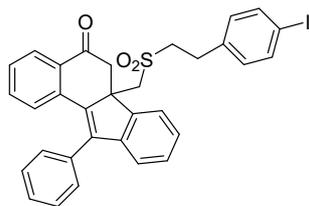
White solid. 68.9 mg. Yield: 68%.  $R_f = 0.50$  (PE/EA = 3:1). mp 165-167°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.08 (m, 1H), 7.64 (dd,  $J = 6.3, 1.7$  Hz, 1H), 7.52 – 7.42 (m, 3H), 7.42 – 7.31 (m, 6H), 7.29 – 7.25 (m, 1H), 7.19 – 7.13 (m, 1H), 6.95 – 6.86 (m, 4H), 3.68 (d,  $J = 14.7$  Hz, 1H), 3.48 (d,  $J = 16.5$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.82 (dd,  $J = 12.3, 4.4$  Hz, 2H), 2.71 – 2.51 (m, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 161.8 (d,  $J = 245.6$  Hz), 146.7, 145.6, 140.7, 138.5, 135.5, 134.2, 133.7, 133.1 (d,  $J = 3.1$  Hz), 129.8, 129.7, 129.7, 129.1, 128.9, 128.4 (d,  $J = 6.7$  Hz), 128.1, 127.6, 126.7, 122.7, 122.3, 115.6 (d,  $J = 21.6$  Hz), 58.2, 55.8, 53.3, 48.6, 26.7.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.58 (s). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{FO}_3\text{S}$   $[\text{M}+\text{H}]^+$  509.1587, found 509.1584.

### 6a-(((4-Bromophenethyl)sulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3c)



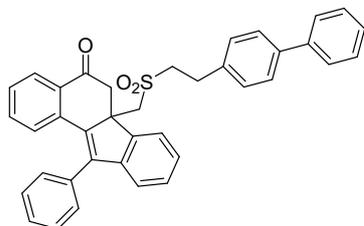
White solid. 77.7 mg. Yield: 68%.  $R_f = 0.50$  (PE/EA = 3:1). mp 152-153°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.07 (m, 1H), 7.68 – 7.61 (m, 1H), 7.52 – 7.42 (m, 3H), 7.41 – 7.30 (m, 8H), 7.29 – 7.23 (m, 1H), 7.20 – 7.13 (m, 1H), 6.80 (d,  $J = 8.4$  Hz, 2H), 3.70 (d,  $J = 14.7$  Hz, 1H), 3.48 (d,  $J = 16.5$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.78 (dd,  $J = 12.2, 4.7$  Hz, 2H), 2.71 – 2.49 (m, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 146.7, 145.6, 140.7, 138.5, 136.5, 135.5, 134.2, 133.7, 131.9, 130.0, 129.7, 129.1, 128.9, 128.9, 128.5, 128.4, 128.2, 127.6, 126.7, 122.7, 122.3, 120.8, 58.2, 55.4, 53.3, 48.6, 26.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{BrO}_3\text{S}$   $[\text{M}+\text{H}]^+$  569.0786, found 569.0784.

**6a-(((4-Iodophenethyl)sulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3d)**



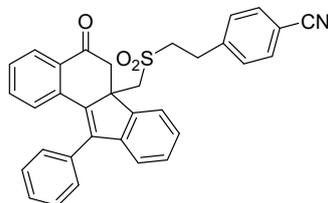
White solid. 82.3 mg. Yield: 67%.  $R_f = 0.50$  (PE/EA = 3:1). mp 158-159°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 – 8.05 (m, 1H), 7.66 – 7.61 (m, 1H), 7.54 (d,  $J = 8.3$  Hz, 2H), 7.52 – 7.43 (m, 3H), 7.41 – 7.32 (m, 6H), 7.28 – 7.24 (m, 1H), 7.20 – 7.14 (m, 1H), 6.67 (d,  $J = 8.3$  Hz, 2H), 3.69 (d,  $J = 14.7$  Hz, 1H), 3.47 (d,  $J = 16.5$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.81 – 2.73 (m, 2H), 2.70 – 2.50 (m, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 146.7, 145.6, 140.7, 138.5, 137.8, 137.1, 135.5, 134.2, 133.7, 130.3, 129.7, 129.1, 128.9, 128.9, 128.5, 128.4, 128.2, 127.6, 126.7, 122.7, 122.3, 92.2, 58.2, 55.4, 53.3, 48.6, 27.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{IO}_3\text{S}$   $[\text{M}+\text{H}]^+$  617.0647, found 617.0641.

**6a-(((2-([1,1'-Biphenyl]-4-yl)ethyl)sulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3e)**



White solid. 84.3 mg. Yield: 74%.  $R_f = 0.50$  (PE/EA = 3:1). mp 172-173°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.08 (m, 1H), 7.68 – 7.63 (m, 1H), 7.57 – 7.52 (m, 2H), 7.49 – 7.40 (m, 7H), 7.40 – 7.30 (m, 7H), 7.30 – 7.25 (m, 1H), 7.19 – 7.14 (m, 1H), 6.99 (d,  $J = 8.2$  Hz, 2H), 3.69 (d,  $J = 14.7$  Hz, 1H), 3.48 (d,  $J = 16.6$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.94 – 2.83 (m, 2H), 2.78 – 2.61 (m, 2H), 2.55 (d,  $J = 16.5$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 146.8, 145.6, 140.7, 140.5, 139.9, 138.5, 136.7, 135.5, 134.2, 133.8, 129.8, 129.1, 128.9, 128.9, 128.7, 128.4, 128.4, 128.2, 127.6, 127.4, 127.4, 127.0, 126.7, 122.7, 122.3, 58.1, 55.8, 53.4, 48.6, 27.2. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{38}\text{H}_{31}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  567.1994, found 567.1997.

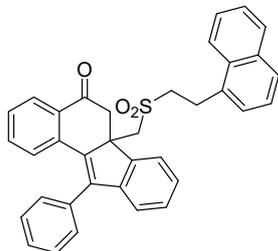
**4-(2-(((5-Oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)sulfonyl)ethyl)benzonitrile (3f)**



White solid. 78.3 mg. Yield: 76%.  $R_f = 0.50$  (PE/EA = 3:1). mp 198-199°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.07 (m, 1H), 7.65 (dd,  $J = 6.5, 1.3$  Hz, 1H), 7.56 – 7.43 (m, 5H), 7.43 – 7.32 (m, 6H), 7.30 – 7.25 (m, 1H), 7.20 – 7.14 (m, 1H), 7.06 (d,  $J = 8.3$  Hz, 2H), 3.74 (d,  $J = 14.8$  Hz, 1H), 3.48 (d,  $J = 16.5$  Hz, 1H), 3.35 (d,  $J = 14.7$  Hz, 1H), 2.90 (t,  $J = 8.1$  Hz, 2H), 2.75 – 2.63 (m, 1H), 2.61 – 2.49 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 146.7, 145.6, 143.1, 140.7, 138.4, 135.4, 134.3, 133.6,

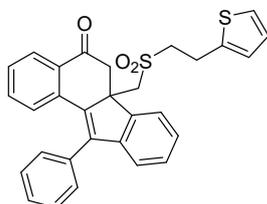
132.5, 129.7, 129.2, 129.1, 129.0, 128.8, 128.5, 128.4, 128.1, 127.6, 126.7, 122.7, 122.3, 118.6, 111.0, 58.3, 54.9, 53.3, 48.5, 27.4. HRMS (ESI)  $m/z$  calcd for  $C_{33}H_{26}NO_3S$   $[M+H]^+$  516.1633, found 516.1638.

**6a-(((2-(Naphthalen-1-yl)ethyl)sulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3g)**



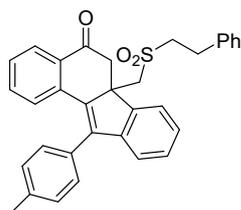
White solid. 84.9 mg. Yield: 78%.  $R_f$  = 0.50 (PE/EA = 3:1). mp 177-178°C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.09 (dd,  $J$  = 7.8, 1.3 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.73 (d,  $J$  = 7.8 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.41 (m, 5H), 7.37 – 7.23 (m, 7H), 7.21 – 7.17 (m, 1H), 7.13 – 7.06 (m, 2H), 3.71 (d,  $J$  = 14.7 Hz, 1H), 3.49 – 3.25 (m, 4H), 2.86 – 2.74 (m, 1H), 2.74 – 2.62 (m, 1H), 2.53 (d,  $J$  = 16.5 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  195.7, 146.6, 145.4, 140.8, 138.4, 135.5, 134.2, 133.9, 133.7, 133.5, 131.2, 129.8, 129.1, 129.0, 128.9, 128.8, 128.4, 128.3, 128.1, 127.9, 127.6, 126.7, 126.6, 126.4, 125.9, 125.5, 123.0, 122.7, 122.3, 58.4, 55.0, 53.4, 48.7, 24.5. HRMS (ESI)  $m/z$  calcd for  $C_{36}H_{29}O_3S$   $[M+H]^+$  541.1837, found 541.1833.

**11-Phenyl-6a-(((2-(thiophen-2-yl)ethyl)sulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3h)**



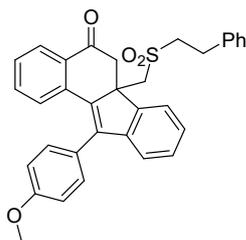
White solid. 62.3 mg. Yield: 63%.  $R_f$  = 0.50 (PE/EA = 2:1). mp 157-159°C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.14 – 8.08 (m, 1H), 7.65 – 7.59 (m, 1H), 7.52 – 7.43 (m, 3H), 7.42 – 7.33 (m, 6H), 7.30 – 7.24 (m, 1H), 7.21 – 7.16 (m, 1H), 7.11 (dd,  $J$  = 5.2, 1.1 Hz, 1H), 6.85 (dd,  $J$  = 5.1, 3.5 Hz, 1H), 6.60 (dd,  $J$  = 3.4, 0.9 Hz, 1H), 3.68 (d,  $J$  = 14.7 Hz, 1H), 3.45 (d,  $J$  = 16.5 Hz, 1H), 3.31 (d,  $J$  = 14.7 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.79 – 2.61 (m, 2H), 2.55 (d,  $J$  = 16.5 Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  195.6, 146.6, 145.5, 140.8, 139.5, 138.4, 135.5, 134.2, 133.7, 129.7, 129.1, 129.0, 128.9, 128.4, 128.4, 128.2, 127.6, 127.1, 126.8, 125.6, 124.4, 122.5, 122.3, 58.1, 55.9, 53.3, 48.7, 22.2. HRMS (ESI)  $m/z$  calcd for  $C_{30}H_{25}O_3S_2$   $[M+H]^+$  497.1245, found 497.1246.

**6a-((Phenethylsulfonyl)methyl)-11-(p-tolyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3i)**



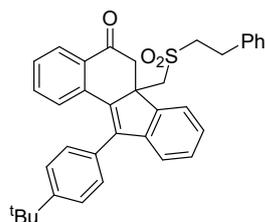
White solid. 84.8 mg. Yield: 84%.  $R_f = 0.50$  (PE/EA = 3:1). mp 166-168°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (dd,  $J = 6.0, 3.3$  Hz, 1H), 7.62 (dd,  $J = 6.2, 1.9$  Hz, 1H), 7.40 – 7.32 (m, 4H), 7.30 – 7.18 (m, 9H), 6.96 – 6.90 (m, 2H), 3.66 (d,  $J = 14.7$  Hz, 1H), 3.46 (d,  $J = 16.5$  Hz, 1H), 3.30 (d,  $J = 14.7$  Hz, 1H), 2.86 – 2.79 (m, 2H), 2.73 – 2.60 (m, 2H), 2.53 (d,  $J = 16.5$  Hz, 1H), 2.45 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 146.7, 145.7, 140.8, 138.2, 137.4, 135.7, 134.2, 130.6, 129.8, 129.7, 128.8, 128.8, 128.3, 128.2, 128.2, 127.6, 126.9, 126.6, 122.6, 122.3, 58.0, 55.8, 53.3, 48.6, 27.5, 21.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  505.1837, found 505.1838.

**11-(4-Methoxyphenyl)-6a-((phenethylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3j)**



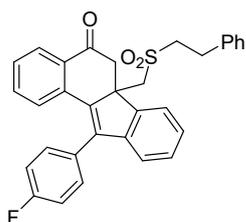
White solid. 59.8 mg. Yield: 57%.  $R_f = 0.50$  (PE/EA = 3:1). mp 173-175°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.08 (m, 1H), 7.66 – 7.59 (m, 1H), 7.41 – 7.28 (m, 7H), 7.27 – 7.18 (m, 4H), 7.00 (d,  $J = 8.8$  Hz, 2H), 6.93 (dd,  $J = 7.7, 1.5$  Hz, 2H), 3.89 (s, 3H), 3.66 (d,  $J = 14.7$  Hz, 1H), 3.45 (d,  $J = 16.6$  Hz, 1H), 3.30 (d,  $J = 14.7$  Hz, 1H), 2.86 – 2.80 (m, 2H), 2.74 – 2.59 (m, 2H), 2.53 (d,  $J = 16.5$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 159.6, 146.7, 145.7, 140.4, 138.1, 137.4, 135.7, 134.2, 130.2, 129.7, 128.8, 128.8, 128.3, 128.2, 128.2, 127.6, 126.9, 126.6, 125.7, 122.7, 122.2, 114.5, 58.0, 55.8, 55.4, 53.2, 48.6, 27.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_4\text{S}$   $[\text{M}+\text{H}]^+$  521.1787, found 521.1789.

**11-(4-(Tert-butyl)phenyl)-6a-((phenethylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3k)**



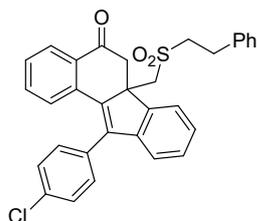
White solid. 83.7 mg. Yield: 77%.  $R_f = 0.50$  (PE/EA = 3:1). mp 155-157°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (dd,  $J = 6.1, 3.2$  Hz, 1H), 7.63 (dd,  $J = 6.2, 1.6$  Hz, 1H), 7.48 (d,  $J = 8.5$  Hz, 2H), 7.39 – 7.29 (m, 7H), 7.27 – 7.18 (m, 4H), 6.93 (dd,  $J = 7.7, 1.6$  Hz, 2H), 3.66 (d,  $J = 14.7$  Hz, 1H), 3.46 (d,  $J = 16.6$  Hz, 1H), 3.30 (d,  $J = 14.7$  Hz, 1H), 2.88 – 2.79 (m, 1H), 2.73 – 2.60 (m, 2H), 2.54 (d,  $J = 16.6$  Hz, 1H), 1.39 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 151.4, 146.8, 145.6, 140.7, 138.1, 137.4, 135.7, 134.2, 130.5, 129.7, 128.8, 128.7, 128.5, 128.3, 128.2, 128.2, 127.6, 126.9, 126.6, 125.9, 122.6, 122.4, 58.1, 55.8, 53.3, 48.6, 34.8, 31.4, 27.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{36}\text{H}_{35}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  547.2307, found 547.2306.

**11-(4-Fluorophenyl)-6a-((phenethylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3l)**



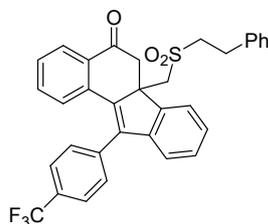
White solid. 73.1 mg. Yield: 72%.  $R_f = 0.50$  (PE/EA = 3:1). mp 152-153°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.07 (m, 1H), 7.61 (dd,  $J = 6.4, 1.6$  Hz, 1H), 7.43 – 7.32 (m, 6H), 7.27 – 7.12 (m, 7H), 6.97 – 6.88 (m, 2H), 3.66 (d,  $J = 14.6$  Hz, 1H), 3.44 (d,  $J = 16.6$  Hz, 1H), 3.30 (d,  $J = 14.6$  Hz, 1H), 2.90 – 2.78 (m, 2H), 2.73 – 2.57 (m, 2H), 2.53 (d,  $J = 16.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 162.7 (d,  $J = 247.8$  Hz), 146.6, 145.4, 139.6, 138.9, 137.4, 135.3, 134.3, 130.8 (d,  $J = 8.1$  Hz), 129.8, 129.7 (d,  $J = 3.5$  Hz), 128.9, 128.8, 128.5, 128.3, 128.1, 127.7, 127.0, 126.8, 122.6, 122.0, 116.3 (d,  $J = 21.6$  Hz), 57.9, 55.9, 53.3, 48.7, 27.5.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.87 (s). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{FO}_3\text{S}$   $[\text{M}+\text{H}]^+$  509.1587, found 509.1588.

**11-(4-Chlorophenyl)-6a-((phenethylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3m)**



White solid. 76.4 mg. Yield: 73%.  $R_f = 0.50$  (PE/EA = 3:1). mp 178-179°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.08 (m, 1H), 7.64 – 7.58 (m, 1H), 7.46 (d,  $J = 8.6$  Hz, 2H), 7.42 – 7.30 (m, 6H), 7.27 – 7.14 (m, 5H), 6.93 (dd,  $J = 7.7, 1.6$  Hz, 2H), 3.66 (d,  $J = 14.6$  Hz, 1H), 3.43 (d,  $J = 16.6$  Hz, 1H), 3.29 (d,  $J = 14.6$  Hz, 1H), 2.83 (t,  $J = 8.1$  Hz, 2H), 2.72 – 2.56 (m, 2H), 2.52 (d,  $J = 16.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 146.7, 145.2, 139.3, 139.1, 137.4, 135.2, 134.4, 134.4, 132.3, 130.4, 129.8, 129.4, 129.0, 128.8, 128.6, 128.3, 128.1, 127.7, 127.0, 126.8, 122.7, 122.0, 57.9, 55.9, 53.4, 48.6, 27.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{ClO}_3\text{S}$   $[\text{M}+\text{H}]^+$  525.1291, found 525.1295.

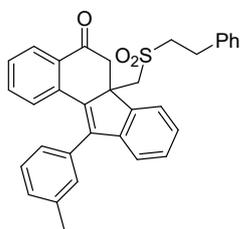
**6a-((Phenethylsulfonyl)methyl)-11-(4-(trifluoromethyl)phenyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3n)**



White solid. 83.1 mg. Yield: 74%.  $R_f = 0.50$  (PE/EA = 3:1). mp 166-167°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (dd,  $J = 6.0, 3.2$  Hz, 1H), 7.75 (d,  $J = 8.1$  Hz, 2H), 7.62 (dd,  $J = 5.9, 2.5$  Hz, 1H), 7.53 (d,  $J = 7.7$  Hz, 2H), 7.43 – 7.34 (m, 4H), 7.28 – 7.17 (m, 4H), 7.14 – 7.06 (m, 1H), 6.97 – 6.90 (m, 2H), 3.68 (d,  $J = 14.6$  Hz, 1H), 3.45 (d,  $J = 16.6$  Hz, 1H), 3.30 (d,  $J = 14.6$  Hz, 1H), 2.84 (t,  $J = 8.1$  Hz, 2H), 2.75 – 2.57 (m, 2H), 2.55 (d,  $J = 16.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.3, 146.6, 145.0,

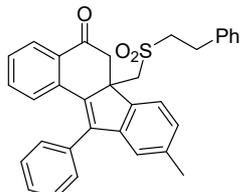
139.6, 139.0, 137.8, 137.4, 135.0, 134.4, 130.5 (q,  $J = 32.6$  Hz), 129.8, 129.5, 129.0, 128.8, 128.7, 128.3, 128.0, 127.8, 127.0, 126.9, 126.1 (q,  $J = 3.6$  Hz), 124.1 (q,  $J = 272.1$  Hz), 122.7, 121.9, 57.9, 56.0, 53.5, 48.6, 27.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.48 (s). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{26}\text{F}_3\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  559.1555, found 559.1552.

**6a-((Phenethylsulfonyl)methyl)-11-(m-tolyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3o)**



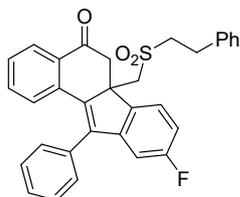
White solid. 60.1 mg. Yield: 60%.  $R_f = 0.50$  (PE/EA = 3:1). mp 147-148°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.07 (m, 1H), 7.62 (dd,  $J = 6.2, 1.8$  Hz, 1H), 7.40 – 7.32 (m, 5H), 7.29 – 7.14 (m, 8H), 6.96 – 6.90 (m, 2H), 3.68 (d,  $J = 14.7$  Hz, 1H), 3.45 (d,  $J = 16.5$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.88 – 2.78 (m, 2H), 2.74 – 2.58 (m, 2H), 2.53 (d,  $J = 16.5$  Hz, 1H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 146.7, 145.7, 140.9, 138.8, 138.2, 137.4, 135.6, 134.2, 133.7, 129.7, 129.3, 129.2, 129.0, 128.9, 128.8, 128.3, 128.2, 127.6, 126.9, 126.7, 126.0, 122.6, 122.3, 58.0, 55.8, 53.3, 48.7, 27.5, 21.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  505.1837, found 505.1836.

**9-Methyl-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3q)**



White solid. 69.5 mg. Yield: 69%.  $R_f = 0.50$  (PE/EA = 3:1). mp 163-165°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 – 8.06 (m, 1H), 7.53 – 7.43 (m, 4H), 7.41 – 7.30 (m, 4H), 7.27 – 7.19 (m, 3H), 7.19 – 7.13 (m, 2H), 7.05 (s, 1H), 6.96 – 6.89 (m, 2H), 3.66 (d,  $J = 14.7$  Hz, 1H), 3.43 (d,  $J = 16.5$  Hz, 1H), 3.31 (d,  $J = 14.7$  Hz, 1H), 2.83 (t,  $J = 8.2$  Hz, 2H), 2.71 – 2.50 (m, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 145.8, 144.0, 140.7, 139.0, 138.7, 137.5, 135.6, 134.2, 133.9, 129.7, 129.1, 128.9, 128.7, 128.3, 128.2, 128.2, 127.6, 127.5, 126.9, 122.8, 122.4, 58.2, 55.7, 53.0, 48.8, 27.5, 21.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  505.1837, found 505.1839.

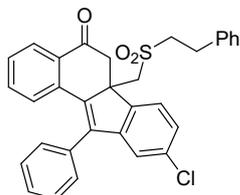
**9-Fluoro-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3r)**



White solid. 72.1 mg. Yield: 71%.  $R_f = 0.50$  (PE/EA = 3:1). mp 155-156°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 – 8.08 (m, 1H), 7.59 (dd,  $J = 8.2, 4.8$  Hz, 1H), 7.53 – 7.43 (m, 3H), 7.41 – 7.32 (m, 4H), 7.27 – 7.13 (m, 4H), 7.03 (td,  $J = 8.7, 2.4$  Hz, 1H), 6.99 – 6.90 (m, 3H), 3.60 (d,  $J = 14.6$  Hz, 1H), 3.48 (d,  $J = 16.6$  Hz, 1H), 3.24 (d,  $J = 14.5$  Hz, 1H), 2.91 – 2.69 (m, 4H), 2.52 (d,  $J = 16.5$  Hz, 1H).  $^{13}\text{C}$

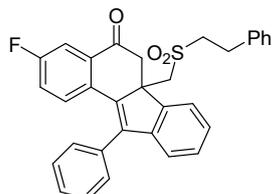
NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.4, 163.6 (d,  $J$  = 246.4 Hz), 147.6 (d,  $J$  = 8.8 Hz), 142.3, 142.2, 140.4, 139.9 (d,  $J$  = 3.0 Hz), 137.3, 135.1, 134.2, 133.2, 129.7, 129.2, 128.9, 128.8, 128.7, 128.7, 128.3, 128.2, 127.7, 127.0, 124.0 (d,  $J$  = 9.1 Hz), 113.4 (d,  $J$  = 23.4 Hz), 109.4 (d,  $J$  = 23.9 Hz), 57.8, 56.2, 52.9, 48.5, 27.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.52 (s). HRMS (ESI)  $m/z$  calcd for C<sub>32</sub>H<sub>26</sub>FO<sub>3</sub>S [M+H]<sup>+</sup> 509.1587, found 509.1590.

**9-Chloro-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3s)**



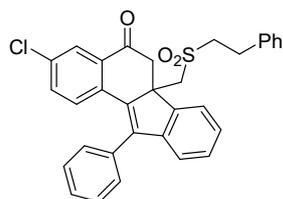
White solid. 73.5 mg. Yield: 70%.  $R_f$  = 0.50 (PE/EA = 3:1). mp 187-189°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 – 8.07 (m, 1H), 7.56 (d,  $J$  = 8.0 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.42 – 7.29 (m, 5H), 7.27 – 7.18 (m, 4H), 7.17 – 7.11 (m, 1H), 7.00 – 6.92 (m, 2H), 3.59 (d,  $J$  = 14.6 Hz, 1H), 3.47 (d,  $J$  = 16.6 Hz, 1H), 3.24 (d,  $J$  = 14.5 Hz, 1H), 2.91 – 2.69 (m, 4H), 2.51 (d,  $J$  = 16.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.2, 147.2, 145.0, 140.0, 139.8, 137.3, 135.0, 135.0, 134.3, 133.1, 129.7, 129.3, 128.9, 128.8, 128.7, 128.7, 128.3, 128.2, 127.7, 127.0, 126.6, 123.9, 122.4, 57.7, 56.2, 53.1, 48.3, 27.6. HRMS (ESI)  $m/z$  calcd for C<sub>32</sub>H<sub>26</sub>ClO<sub>3</sub>S [M+H]<sup>+</sup> 525.1291, found 525.1292.

**3-Fluoro-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3t)**



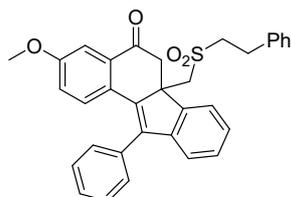
White solid. 68.5 mg. Yield: 67%.  $R_f$  = 0.50 (PE/EA = 3:1). mp 186-188°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (dd,  $J$  = 8.9, 2.8 Hz, 1H), 7.61 (dd,  $J$  = 6.2, 1.7 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.41 – 7.32 (m, 4H), 7.28 – 7.14 (m, 5H), 7.05 (td,  $J$  = 8.4, 2.8 Hz, 1H), 6.97 – 6.90 (m, 2H), 3.65 (d,  $J$  = 14.6 Hz, 1H), 3.47 (d,  $J$  = 16.6 Hz, 1H), 3.25 (d,  $J$  = 14.6 Hz, 1H), 2.85 (t,  $J$  = 8.1 Hz, 2H), 2.73 – 2.57 (m, 2H), 2.52 (d,  $J$  = 16.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  194.8 (d,  $J$  = 1.5 Hz), 162.3 (d,  $J$  = 250.7 Hz), 146.4, 145.5, 140.5, 137.6, 137.4, 133.6, 131.9 (d,  $J$  = 3.0 Hz), 131.7 (d,  $J$  = 6.5 Hz), 130.5 (d,  $J$  = 7.3 Hz), 129.2, 129.0, 128.9, 128.8, 128.5, 128.3, 127.0, 126.7, 122.6, 122.3, 121.9 (d,  $J$  = 22.6 Hz), 113.6 (d,  $J$  = 22.5 Hz), 58.0, 55.9, 53.3, 48.4, 27.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -110.62 (s). HRMS (ESI)  $m/z$  calcd for C<sub>32</sub>H<sub>26</sub>FO<sub>3</sub>S [M+H]<sup>+</sup> 509.1587, found 509.1585.

**3-Chloro-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3u)**



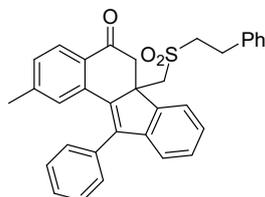
White solid. 48.2 mg. Yield: 46%.  $R_f = 0.50$  (PE/EA = 3:1). mp 151-153°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 2.2$  Hz, 1H), 7.65 – 7.59 (m, 1H), 7.53 – 7.43 (m, 3H), 7.42 – 7.33 (m, 4H), 7.32 – 7.17 (m, 5H), 7.11 (d,  $J = 8.5$  Hz, 1H), 6.98 – 6.90 (m, 2H), 3.64 (d,  $J = 14.6$  Hz, 1H), 3.46 (d,  $J = 16.6$  Hz, 1H), 3.24 (d,  $J = 14.6$  Hz, 1H), 2.85 (t,  $J = 8.1$  Hz, 2H), 2.75 – 2.56 (m, 2H), 2.52 (d,  $J = 16.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.6, 146.6, 145.4, 141.2, 137.5, 137.3, 134.5, 134.2, 133.9, 133.5, 130.9, 129.7, 129.2, 129.0, 128.8, 128.6, 128.3, 127.4, 127.0, 126.9, 122.6, 122.4, 57.9, 55.9, 53.1, 48.4, 27.6. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{ClO}_3\text{S}$   $[\text{M}+\text{H}]^+$  525.1291, found 525.1294.

### 3-Methoxy-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3v)



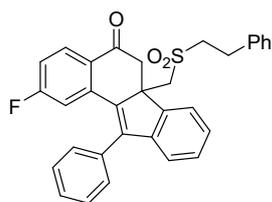
White solid. 79.6 mg. Yield: 76%.  $R_f = 0.50$  (PE/EA = 3:1). mp 175-176°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.60 (m, 1H), 7.57 (d,  $J = 2.8$  Hz, 1H), 7.50 – 7.42 (m, 3H), 7.41 – 7.30 (m, 4H), 7.27 – 7.16 (m, 4H), 7.09 (d,  $J = 8.7$  Hz, 1H), 6.97 – 6.89 (m, 3H), 3.85 (s, 3H), 3.66 (d,  $J = 14.7$  Hz, 1H), 3.48 (d,  $J = 16.5$  Hz, 1H), 3.28 (d,  $J = 14.7$  Hz, 1H), 2.90 – 2.79 (m, 2H), 2.75 – 2.58 (m, 2H), 2.53 (d,  $J = 16.5$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 159.6, 146.4, 145.8, 138.9, 138.4, 137.5, 134.0, 131.1, 129.6, 129.1, 129.0, 128.8, 128.8, 128.6, 128.3, 128.3, 126.9, 126.3, 122.7, 122.6, 121.9, 109.6, 58.3, 55.8, 55.6, 53.4, 48.4, 27.5. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_4\text{S}$   $[\text{M}+\text{H}]^+$  521.1787, found 521.1788.

### 2-Methyl-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3w)



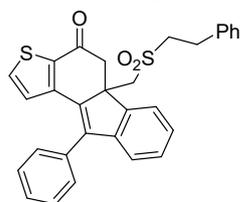
White solid. 72.5 mg. Yield: 72%.  $R_f = 0.50$  (PE/EA = 3:1). mp 162-164°C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.0$  Hz, 1H), 7.61 (dd,  $J = 6.3, 1.8$  Hz, 1H), 7.51 – 7.42 (m, 3H), 7.41 – 7.32 (m, 4H), 7.30 – 7.13 (m, 5H), 6.97 – 6.89 (m, 3H), 3.68 (d,  $J = 14.8$  Hz, 1H), 3.38 (dd,  $J = 20.5, 15.6$  Hz, 2H), 2.90 – 2.56 (m, 4H), 2.52 (d,  $J = 16.5$  Hz, 1H), 2.11 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.4, 146.8, 145.5, 145.2, 140.6, 138.5, 137.5, 135.4, 133.8, 129.5, 129.0, 128.9, 128.8, 128.8, 128.4, 128.4, 128.2, 127.7, 127.6, 126.9, 126.6, 122.6, 122.2, 58.1, 55.8, 53.4, 48.7, 27.5, 21.9. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{29}\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$  505.1837, found 505.1833.

### 2-Fluoro-6a-((phenethylsulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (3x)



White solid. 70.7 mg. Yield: 70%.  $R_f = 0.50$  (PE/EA = 3:1). mp 158-160°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (dd,  $J = 8.8, 5.9$  Hz, 1H), 7.64 – 7.59 (m, 1H), 7.55 – 7.45 (m, 3H), 7.42 – 7.33 (m, 4H), 7.30 – 7.17 (m, 4H), 7.03 (td,  $J = 8.4, 2.5$  Hz, 1H), 6.97 – 6.91 (m, 2H), 6.82 (dd,  $J = 9.7, 2.5$  Hz, 1H), 3.66 (d,  $J = 14.6$  Hz, 1H), 3.43 (d,  $J = 16.5$  Hz, 1H), 3.28 (d,  $J = 14.6$  Hz, 1H), 2.86 (t,  $J = 8.2$  Hz, 2H), 2.73 – 2.57 (m, 2H), 2.52 (d,  $J = 16.5$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.3, 166.0 (d,  $J = 256.4$  Hz), 146.7, 145.3, 142.0, 138.3 (d,  $J = 10.3$  Hz), 137.5, 137.5, 137.3, 133.2, 130.8 (d,  $J = 10.2$  Hz), 129.2, 129.0, 128.8, 128.7, 128.2, 127.1, 127.0, 126.4, 126.4, 122.6 (d,  $J = 3.5$  Hz), 116.1 (d,  $J = 22.8$  Hz), 114.4 (d,  $J = 23.3$  Hz), 58.0, 55.9, 53.3, 48.4, 27.6.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -101.61 (s). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{26}\text{FO}_3\text{S}$   $[\text{M}+\text{H}]^+$  509.1587, found 509.1582.

#### 5a-((Phenethylsulfonyl)methyl)-10-phenyl-5,5a-dihydro-4H-fluoreno[2,1-b]thiophen-4-one (3y)



White solid. 69.3 mg. Yield: 70%.  $R_f = 0.50$  (PE/EA = 2:1). mp 195-197°C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (dd,  $J = 6.1, 1.9$  Hz, 1H), 7.58 – 7.42 (m, 6H), 7.41 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.26 – 7.16 (m, 3H), 6.94 (d,  $J = 6.5$  Hz, 2H), 6.86 (d,  $J = 5.1$  Hz, 1H), 3.70 (d,  $J = 14.6$  Hz, 1H), 3.39 (dd,  $J = 15.4, 10.6$  Hz, 2H), 2.85 (t,  $J = 8.2$  Hz, 2H), 2.72 – 2.50 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.0, 146.7, 145.5, 143.5, 140.5, 137.4, 136.4, 135.6, 135.5, 133.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 127.0, 126.9, 126.6, 122.9, 122.5, 59.0, 55.9, 54.9, 48.0, 27.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{25}\text{O}_3\text{S}_2$   $[\text{M}+\text{H}]^+$  497.1245, found 497.1248.

## 6. Copies of the $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra

$^1\text{H}$  NMR spectrum of **3a**

$^{13}\text{C}$  NMR spectrum of **3a**

$^1\text{H}$  NMR spectrum of **3b**

$^{13}\text{C}$  NMR spectrum of **3b**

$^{19}\text{F}$  NMR spectrum of **3b**

$^1\text{H}$  NMR spectrum of **3c**

$^{13}\text{C}$  NMR spectrum of **3c**

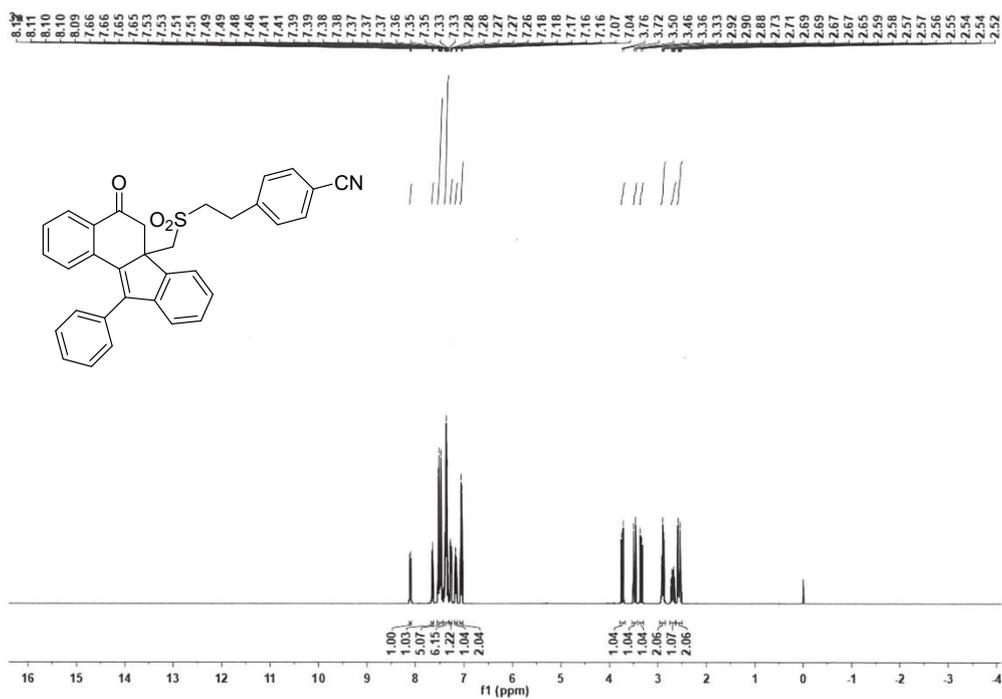
$^1\text{H}$  NMR spectrum of **3d**

$^{13}\text{C}$  NMR spectrum of **3d**

$^1\text{H}$  NMR spectrum of **3e**

$^{13}\text{C}$  NMR spectrum of **3e**

$^1\text{H}$  NMR spectrum of **3f**



<sup>13</sup>C NMR spectrum of **3f**

<sup>1</sup>H NMR spectrum of **3g**

<sup>13</sup>C NMR spectrum of **3g**

<sup>1</sup>H NMR spectrum of **3h**

<sup>13</sup>C NMR spectrum of **3h**

<sup>1</sup>H NMR spectrum of **3i**

$^{13}\text{C}$  NMR spectrum of **3i**

$^1\text{H}$  NMR spectrum of **3j**

$^{13}\text{C}$  NMR spectrum of **3j**

$^1\text{H}$  NMR spectrum of **3k**

$^{13}\text{C}$  NMR spectrum of **3k**

$^1\text{H}$  NMR spectrum of **3l**

$^{13}\text{C}$  NMR spectrum of **3l**

$^{19}\text{F}$  NMR spectrum of **3l**

$^1\text{H}$  NMR spectrum of **3m**

$^{13}\text{C}$  NMR spectrum of **3m**

$^1\text{H}$  NMR spectrum of **3n**

$^{13}\text{C}$  NMR spectrum of **3n**

$^{19}\text{F}$  NMR spectrum of **3n**

$^1\text{H}$  NMR spectrum of **3o**

$^{13}\text{C}$  NMR spectrum of **3o**

$^1\text{H}$  NMR spectrum of **3q**

$^{13}\text{C}$  NMR spectrum of **3q**

$^1\text{H}$  NMR spectrum of **3r**

$^{13}\text{C}$  NMR spectrum of **3r**

$^{19}\text{F}$  NMR spectrum of **3r**

$^1\text{H}$  NMR spectrum of **3s**

$^{13}\text{C}$  NMR spectrum of **3s**

$^1\text{H}$  NMR spectrum of **3t**

$^{13}\text{C}$  NMR spectrum of **3t**

$^{19}\text{F}$  NMR spectrum of **3t**

$^1\text{H}$  NMR spectrum of **3u**

$^{13}\text{C}$  NMR spectrum of **3u**

$^1\text{H}$  NMR spectrum of **3v**

$^{13}\text{C}$  NMR spectrum of **3v**

$^1\text{H}$  NMR spectrum of **3w**

$^{13}\text{C}$  NMR spectrum of **3w**

$^1\text{H}$  NMR spectrum of **3x**

$^{13}\text{C}$  NMR spectrum of **3x**

$^{19}\text{F}$  NMR spectrum of **3x**

$^1\text{H}$  NMR spectrum of **3y**

$^{13}\text{C}$  NMR spectrum of **3y**