

Photocatalytic radical addition/bicyclization of 1,7-enynes with *N*-sulfonylaminopyridinium salts/sulfamoyl chlorides: access to sulfonamide-containing benzo[*a*]fluoren-5-ones

Zhichao Chen,^{*a,b} Zhiyong Jiang,^c Fengjiao Lv,^{a,b} Xiaolan Xie^{*a,b}

^aCollege of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, China. E-mail: zcchen@qztc.edu.cn; xxl_qztc@163.com.

^bKey Laboratory of Chemical Materials and Green Nanotechnology, College of Chemical Engineering and Materials Science, Quanzhou Normal University, Quanzhou 362000, China.

^cCollege of Material Engineering, Fujian Agriculture and Forestry University, 63 Xiyuangong Road, Fuzhou 350002, PR China.

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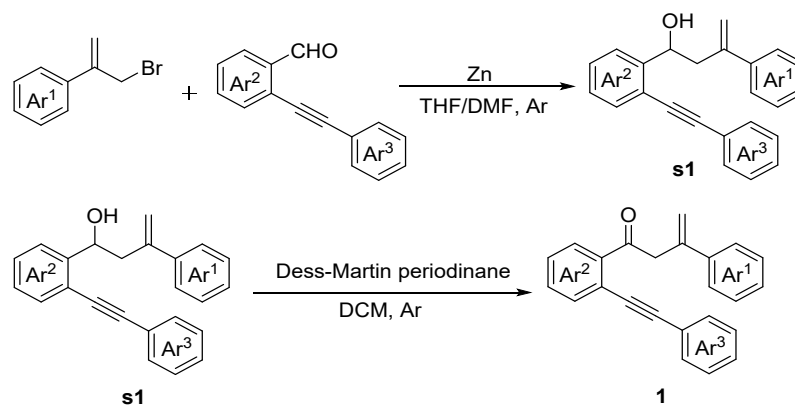
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1. General information

Unless otherwise stated, all commercial materials and solvents were used directly without further purification. ^1H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^1H 400MHz, ^{13}C 100MHz, ^{19}F NMR 376 MHz), using CDCl_3 (spectra were referenced to the solvent peaks ^1H : residual $\text{CDCl}_3 = 7.26$ ppm, ^{13}C : $\text{CDCl}_3 = 77.0$ ppm) as the solvent. The following abbreviations were used to describe peak splitting patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet). 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). Products were purified by flash chromatography on silica gels, eluting with petroleum ether/ethyl acetate. Crystal Growth Procedure: Approximately 30 mg of the sample (**3aa**) was dissolved in DCM (10 mL) and filtered, a small piece of cotton was used to ensure no solid particles would be present in the solubilized sample, this solution was transferred to a 25 mL vial, this vial was completed with hexanes (10 mL) and then closed, the crystal was formed within 5 days, the crystal was then analyzed. X-ray analysis was performed with a single-crystal X-ray diffractometer (Gemini E) from Agilent. 1,7-enynes **1** were prepared according to the reported literature.¹ *N*-sulfonylaminopyridinium salts **2** were prepared according to the reported literature.² All sulfamoyl chlorides were purchased from commercial sources (Adamas).

2. General experimental procedures

(1) General procedure for the synthesis of 1,7-enynes **1**¹

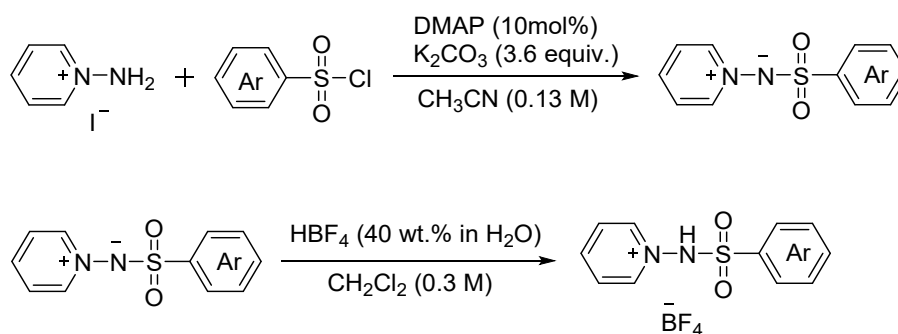


Under argon conditions, Zn powder (12.0 mmol, 3.0 equiv) and co-solvent of THF and DMF (10.0 mL) were added into a dried flask. Then 2-(phenylethynyl)benzaldehyde (4.0 mmol, 1.0 equiv) were added into this system. To this suspension, a solution of (3-bromoprop-1-en-2-yl)benzene (4.0 mmol, 1.0 equiv) in THF (2.8 mL) was dropwise and stirred for 16 h. After that, it was quenched by saturated aqueous NH_4Cl and extracted with ethyl acetate. Purification by column chromatography over silica gel (200-300 mesh) using mixtures of petroleum ether and acetic ester (petroleum ether /acetic ester, 20:1, v/v) afforded compound **s1**.

Under argon conditions, Dess-Martin periodinane (3.0 mmol, 1.5 equiv) and CH_2Cl_2 (3 mL) were

added into a dried flask. Then, the mixture was cooled down to 0 °C. Next, compound **s1** (2.0 mmol, 1.0 equiv) was dropwise. After stirring at this temperature for 2.0 h, and it was quenched by saturated aqueous NaHCO₃. Then the mixture was extracted with DCM and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (200-300 mesh) using mixtures of petroleum ether /acetic ester, 50:1, v/v) afforded 1,7-enynes **1**.

(2) General procedure for the synthesis of *N*-sulfonylaminopyridinium salts **2**²

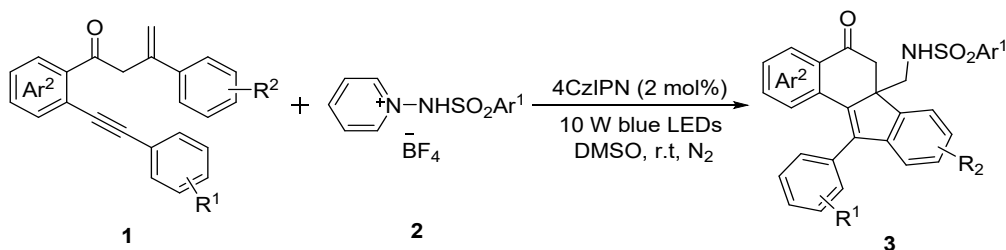


To a solution of 1-aminopyridinium iodide (10 mmol, 2.22 g) and distilled-CH₃CN (77 mL, 0.13 M) were added DMAP (10 mol%, 122 mg), K₂CO₃ (36 mmol, 4.96 g) and sulfonyl chloride (10 mmol, 1.9 g) at 0 °C (ice water bath) under N₂. Then, the cooling bath was removed and the reaction mixture was stirred at room temperature for 6 h. The suspension was filtered and concentrated in vacuo. The residue was suspended in DCM and filtered to remove inorganic impurities. After the solvent was removed under reduced pressure, The crude product was purified by column chromatography on silica gel with DCM/MeOH (20:1) as eluent to afford pure product. The obtained ylide (5 mmol, 1.24 g) was dissolved in DCM (17 mL, 0.3 M) and tetrafluoroboric acid solution (40 wt.% in H₂O) (7.5 mmol, 653 uL) was added to the solution at room temperature. The reaction mixture was stirred for 30 min, then the product was precipitated with Et₂O. The resulting precipitate was filtered off, washed with Et₂O and dried under vacuum.

(3) General procedure for preparation of benzo[a]fluoren-5-ones **3**.

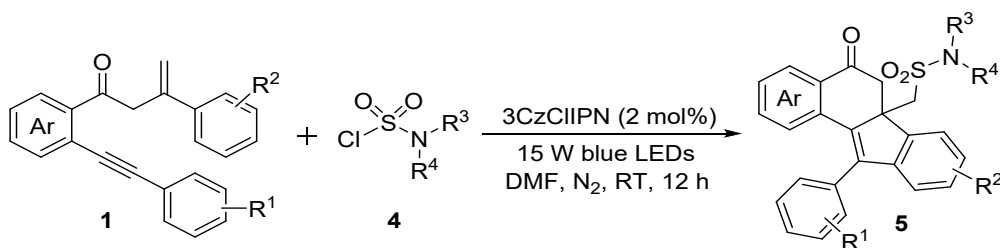


Figure S1 The WP-TEC-1020SL photochemical reaction system with the blue light LED



1,7-enynes **1** (0.2 mmol), *N*-sulfonylaminopyridinium salts **2** (0.24 mmol, 1.2 equiv), 4CzIPN (0.004 mmol, 0.02 equiv) and 2 mL DMSO were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor (Figure S1) with 10 W blue LED as light source under N₂ atmosphere. Upon completion of the reaction, the reaction was then diluted with H₂O (30 mL), the aqueous layer was then extracted with CH₂Cl₂ (3×20 mL) and all organics combined and dried (Na₂SO₄). The suspension was then filtered, concentrated and purified by flash chromatography (EtOAc/PE: 1/6) to give the desired products **3**.

(4) General procedure for preparation of benzo[a]fluoren-5-ones **5**.



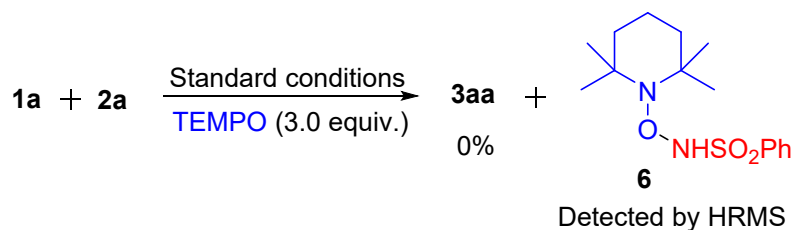
1,7-enynes **1** (0.2 mmol), sulfamoyl chlorides **4** (0.4 mmol, 2.0 equiv), 3CzClIPN (0.004 mmol, 0.02 equiv) and 2 mL DMF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor (Figure S1) with 15 W blue LED as light source under N₂ atmosphere. Upon completion of the reaction, the reaction was then diluted with H₂O (30 mL), the aqueous layer was then extracted with CH₂Cl₂ (3×20 mL) and all organics combined and dried (Na₂SO₄). The suspension was then filtered, concentrated and purified by flash chromatography (EtOAc/PE: 1/8) to give the desired products **5**.

3. References

- [1] Huang, M.-H.; Zhu, Y.-L.; Hao, W.-J.; Wang, A.-F.; Wang, D.-C.; Liu, F.; Wei, P.; Tu, S.-J.; Jiang, B. Visible-Light Photocatalytic Bicyclization of 1,7-Enynes toward Functionalized Sulfone-Containing Benzo[a]fluoren-5-ones. *Adv. Synth. Catal.* **2017**, *359*, 2229-2234.
- [2] (a) Pan, C.; Luo, S.; Wu, Y.; Yu, J.-T.; Zhu, C. Photo-Induced Cyclization of Olefinic Amides towards Sulfonamidylated Iminoisobenzofurans and Benzoxazines. *Org. Chem. Front.* **2023**, *10*, 3479-3484. (b) Pan, C.; Yang, Z.; Wu, X.; Yu, J.-T.; Zhu, C. Substituent-Controlled Regioselective Photoinduced Cyclization of *N*-Allylbenzamides with *N*-Sulfonylaminopyridinium Salts. *Org. Lett.* **2023**, *25*, 494-499.

4. Mechanism Exploration

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



1,7-enyne **1a** (0.2 mmol), *N*-sulfonylaminopyridinium salt **2a** (0.24 mmol, 1.2 equiv), 4CzIPN (0.004 mmol, 0.02 equiv), TEMPO (0.6 mmol, 3.0 equiv) and 2 mL DMSO were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 10 W blue LED as light source under N₂ 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 C₁₅H₂₅N₂O₃S [M+H]⁺ 313.1586, found 313.1580.

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

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

Elements Used:

C: 0-15 H: 0-25 N: 0-2 O: 0-3 S: 0-1

20250525-6-1-Pos 173 (0.698)

1: TOF MS ES+

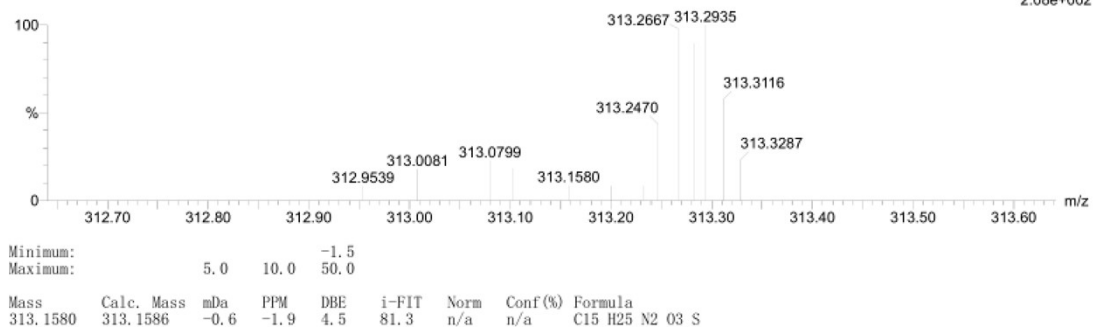
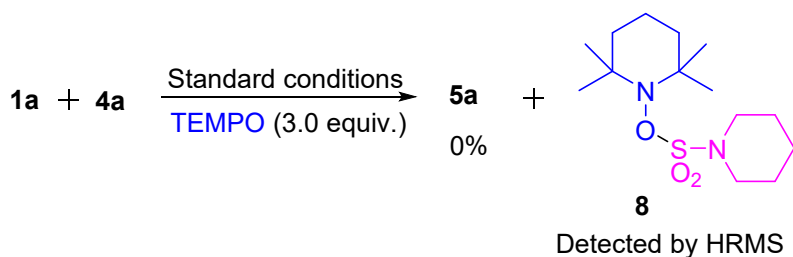


Figure S2



1,7-enyne **1a** (0.2 mmol), sulfamoyl chlorides **4a** (0.4 mmol, 2.0 equiv), 3CzCIIPN (0.004 mmol, 0.02 equiv), TEMPO (0.6 mmol, 3.0 equiv) and 2 mL DMF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 10 W blue LED as light source under N₂ atmosphere. The resulting mixture was monitored by TLC, and TEMPO adduct to sulfuryl radical was detected by HRMS (Figure S3). HRMS (ESI) m/z calcd for C₁₄H₂₉N₂O₃S [M+H]⁺ 305.1899, found 305.1899.

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

725 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

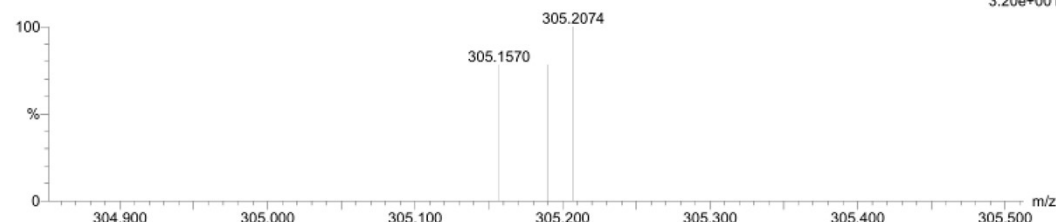
Elements Used:

C: 14-14 H: 29-29 N: 0-100 O: 0-100 Na: 0-1 S: 1-3

26

260123-15-CZL-15 44 (0.264)

1: TOF MS ES+
3.20e+001

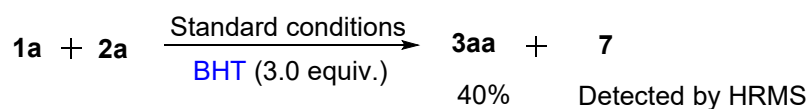


Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
305.1899	305.1899	0.0	0.0	1.5	19.2	n/a	n/a	C14 H29 N2 O3 S

Figure S3

(2) Trapping experiment with butylated hydroxytoluene (BHT)



1,7-enyne **1a** (0.2 mmol), *N*-sulfonylaminopyridinium salt **2a** (0.24 mmol, 1.2 equiv), 4CzIPN (0.004 mmol, 0.02 equiv), BHT (0.6 mmol, 3.0 equiv) and 2 mL DMSO were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 10 W blue LED as light source under N₂ atmosphere. The resulting mixture was monitored by TLC, and TEMPO adduct to sulfuryl radical was detected by HRMS (Figure S4). HRMS (ESI) m/z calcd for C₂₁H₃₀NO₃S [M+H]⁺ 376.1946, found 376.1945.

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: 0-21 H: 0-30 N: 0-2 O: 0-3 S: 0-1

20250525-6-2-Pos 235 (0.939)

1: TOF MS ES+

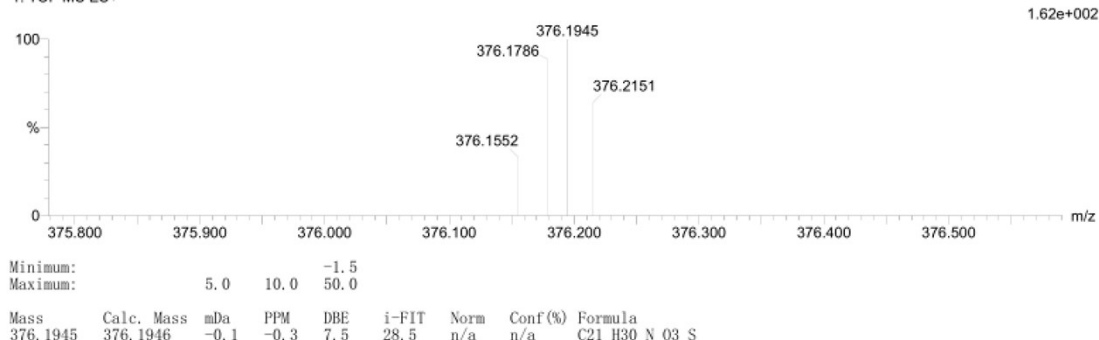
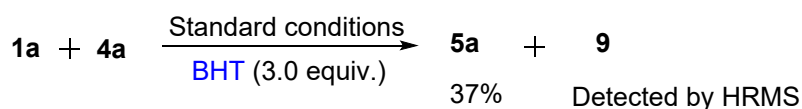


Figure S4



1,7-enyne **1a** (0.2 mmol), sulfamoyl chlorides **4a** (0.4 mmol, 2.0 equiv), 3CzCIIPN (0.004 mmol, 0.02 equiv), BHT (0.6 mmol, 3.0 equiv) and 2 mL DMF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 12 h in the photochemical reactor with 15 W blue LED as light source under N₂ atmosphere. The resulting mixture was monitored by TLC, and BHT adduct to sulfuryl radical was detected by HRMS (Figure S5). HRMS (ESI) m/z calcd for C₂₀H₃₄NO₃S [M+H]⁺ 368.2259, found 368.2254.

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

1202 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 20-20 H: 34-34 N: 0-100 O: 0-100 Na: 0-1 S: 1-3

26

260123-15-CZL-16 13 (0.093)

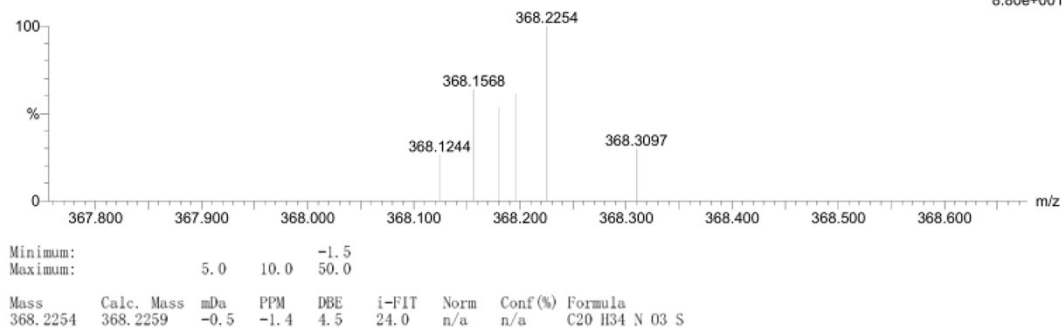
1: TOF MS ES+
8.80e+001

Figure S5

(3) Light/dark experiments

In order to illustrate the reaction mechanism, the light/dark experiments were conducted.

1,7-enyne **1a** (0.2 mmol), *N*-sulfonylaminopyridinium salt **2a** (0.24 mmol, 1.2 equiv), 4CzIPN (0.004 mmol, 0.02 equiv) and 2 mL DMSO were added in a schlenk tube. The reaction mixture was exposed to 10 W blue LEDs irradiation under N₂ atmosphere at room temperature with stirring for 2 h, then stirring for 2 h without irradiation. The following product yields based on the irradiation with 10 W blue LEDs under N₂ atmosphere at room temperature for a certain time, and without irradiation for a certain time were also presented in the Figure S6.

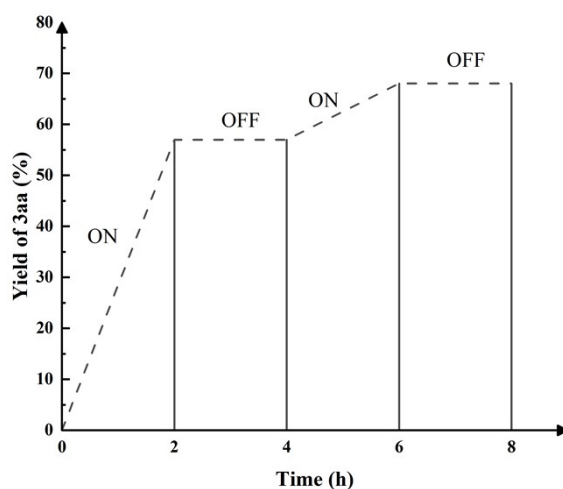


Figure S6 Light/dark experiments (1a + 2a)

1,7-enyne **1a** (0.2 mmol), sulfamoyl chlorides **4a** (0.4 mmol, 2.0 equiv), 3CzCIIPN (0.004 mmol, 0.02 equiv) and 2 mL DMf were added in a schlenk tube. The reaction mixture was exposed to 15 W blue LEDs irradiation under N₂ atmosphere at room temperature with stirring for 2 h, then stirring for 2 h without irradiation. The following product yields based on the irradiation with 10 W blue LEDs under N₂ atmosphere at room temperature for a certain time, and without irradiation for a certain time were also presented in the Figure S7.

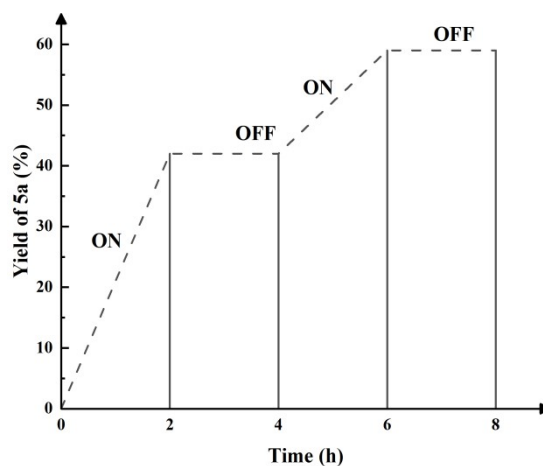
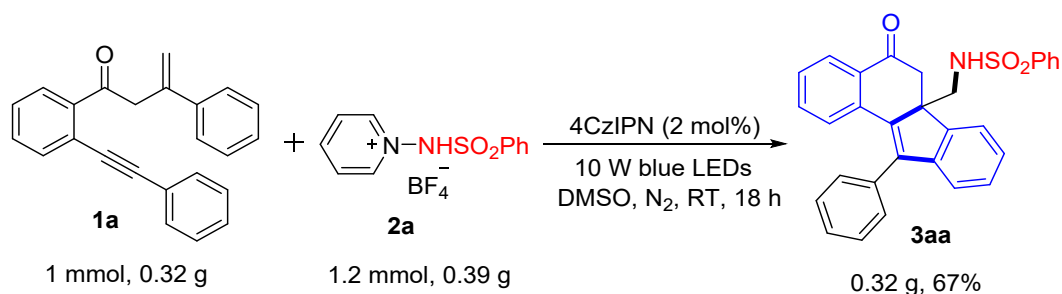
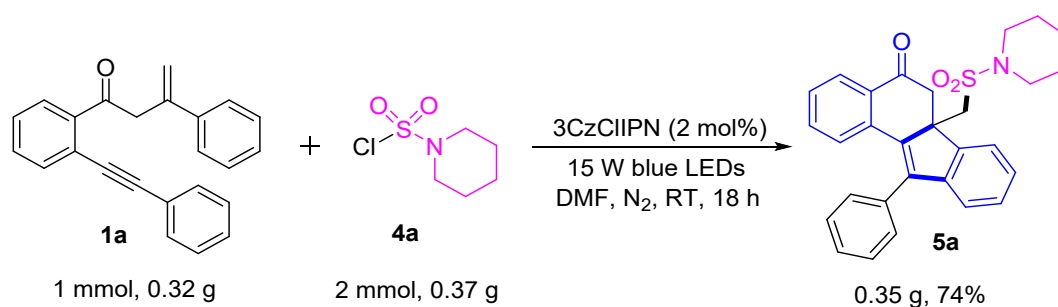


Figure S7 Light/dark experiments (1a + 4a)

5. Large-scale synthesis of 3aa and 5a



1,7-enyne **1a** (1 mmol, 0.32 g), thianthrenium salt **2a** (1.2 mmol, 0.39 g, 1.2 equiv), 4CzIPN (0.02 mmol, 0.02 equiv) and 5 mL DMSO were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 18 h in the photochemical reactor with 10 W blue LED as light source under N₂ atmosphere. Upon completion of the reaction, 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 **3aa** in 67% yield (0.32 g).



1,7-enyne **1a** (1 mmol, 0.32 g), sulfamoyl chlorides **4a** (2.0 mmol, 0.37 g, 2.0 equiv), 3CzCIIPN (0.02 mmol, 0.02 equiv) and 5 mL DMF were added in a schlenk tube. The mixture was stirred at room temperature (rt) for 18 h in the photochemical reactor with 15 W blue LED as light source under N₂ atmosphere. Upon completion of the reaction, 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 **5a** in 74% yield (0.35 g).

6. Crystal structures and data of 3aa

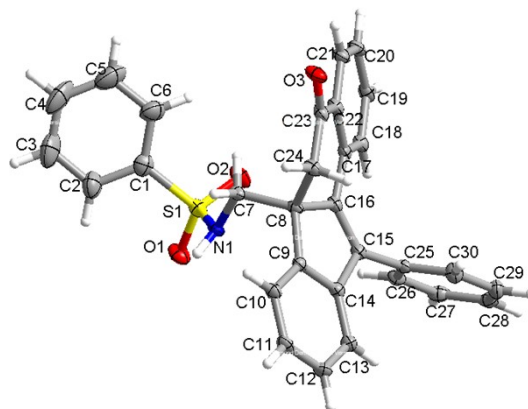


Figure S5 X-ray Crystallography Structure of Compounds **3aa** (CCDC 2516414)

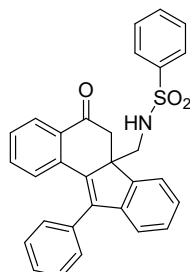
Displacement ellipsoids are shown at the 50% probability level

Table 1 Crystal data and structure refinement for 3aa.

Identification code	3aa
Empirical formula	C ₃₀ H ₂₃ NO ₃ S
Formula weight	477.55
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.58611(18)
b/Å	12.4288(3)
c/Å	20.4263(5)
α/°	86.498(2)
β/°	83.6531(18)
γ/°	88.7926(18)
Volume/Å ³	2413.98(10)
Z	4
ρ _{calc} /cm ³	1.314
μ/mm ⁻¹	0.167
F(000)	1000.0
Crystal size/mm ³	0.17 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.276 to 52.742
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -25 ≤ l ≤ 25
Reflections collected	30065
Independent reflections	9835 [R _{int} = 0.0371, R _{sigma} = 0.0432]
Data/restraints/parameters	9835/0/639
Goodness-of-fit on F ²	1.072
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0529, wR ₂ = 0.1243
Final R indexes [all data]	R ₁ = 0.0753, wR ₂ = 0.1317
Largest diff. peak/hole / e Å ⁻³	0.28/-0.38

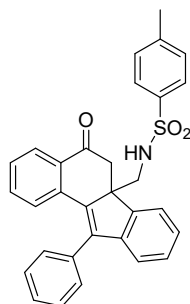
7. Characterization of compounds 3 and 5

N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3aa**)



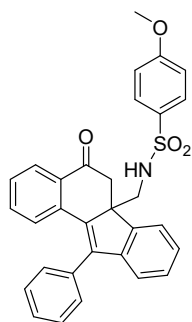
White solid. 71.3 mg. Yield: 75%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 195-197°C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.53 – 7.43 (m, 6H), 7.39 (d, *J* = 6.8 Hz, 2H), 7.35 – 7.21 (m, 8H), 7.05 – 6.99 (m, 1H), 4.08 (t, *J* = 6.2 Hz, 1H), 3.49 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.31 – 3.18 (m, 2H), 2.55 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.0, 146.7, 145.6, 141.3, 139.3, 138.1, 134.8, 133.9, 133.8, 132.5, 130.1, 129.1, 129.0, 128.6, 128.4, 128.2, 127.7, 127.6, 126.8, 126.8, 122.0, 121.8, 55.4, 47.7, 45.8. HRMS (ESI) *m/z* calcd for C₃₀H₂₄NO₃S [M+H]⁺ 478.1477, found 478.1476.

4-Methyl-*N*-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3ab**)



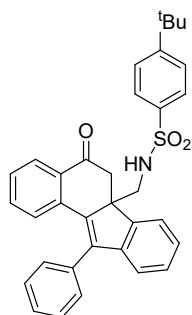
White solid. 58.4 mg. Yield: 59%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 197-199°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.37 (d, *J* = 8.2 Hz, 4H), 7.33 – 7.25 (m, 4H), 7.25 – 7.18 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.05 – 7.00 (m, 1H), 4.22 (t, *J* = 6.2 Hz, 1H), 3.46 (dd, *J* = 12.4, 5.9 Hz, 1H), 3.28 – 3.14 (m, 2H), 2.52 (d, *J* = 16.8 Hz, 1H), 2.36 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.1, 146.8, 145.5, 143.2, 141.3, 138.1, 136.3, 134.8, 133.9, 133.7, 130.1, 129.6, 129.1, 129.1, 128.5, 128.4, 128.1, 127.7, 127.5, 126.9, 126.7, 122.0, 121.9, 55.4, 47.7, 45.8, 21.5. HRMS (ESI) *m/z* calcd for C₃₁H₂₆NO₃S [M+H]⁺ 492.1633, found 492.1636.

4-Methoxy-*N*-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3ac**)



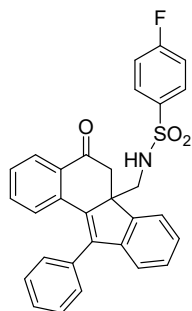
White solid. 67.5 mg. Yield: 67%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 196-198°C. ^1H NMR (400 MHz, CDCl_3) δ 8.05 – 7.99 (m, 1H), 7.50 – 7.35 (m, 7H), 7.33 – 7.19 (m, 6H), 7.02 (dd, $J = 7.6, 1.2$ Hz, 1H), 6.78 – 6.71 (m, 2H), 4.19 (t, $J = 6.2$ Hz, 1H), 3.81 (s, 3H), 3.46 (dd, $J = 12.4, 5.9$ Hz, 1H), 3.28 – 3.14 (m, 2H), 2.52 (d, $J = 16.7$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.1, 162.7, 146.8, 145.5, 141.3, 138.1, 134.8, 133.9, 133.7, 130.7, 130.1, 129.1, 129.0, 128.5, 128.4, 128.1, 127.7, 127.5, 126.7, 122.0, 121.9, 114.1, 55.6, 55.3, 47.6, 45.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 508.1583, found 508.1580.

4-(Tert-butyl)-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide (**3ad**)



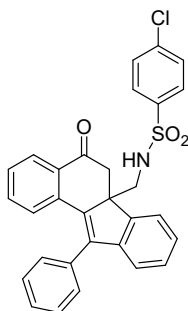
White solid. 69.2 mg. Yield: 65%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 251-252°C. ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.01 (m, 1H), 7.52 – 7.44 (m, 3H), 7.40 (t, $J = 7.0$ Hz, 4H), 7.34 – 7.21 (m, 8H), 7.06 – 7.00 (m, 1H), 4.07 (t, $J = 6.3$ Hz, 1H), 3.49 (dd, $J = 12.5, 5.8$ Hz, 1H), 3.30 – 3.18 (m, 2H), 2.55 (d, $J = 16.8$ Hz, 1H), 1.30 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.0, 156.2, 146.8, 145.5, 141.2, 138.2, 136.3, 134.8, 133.9, 133.7, 130.1, 129.1, 129.0, 128.5, 128.4, 128.2, 127.7, 127.6, 126.7, 126.0, 122.0, 121.8, 55.4, 47.7, 45.9, 35.1, 31.1. HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{32}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 534.2103, found 534.2105.

4-Fluoro-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide (**3ae**)



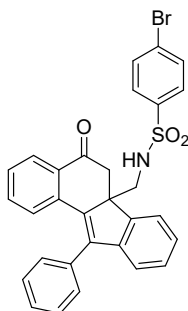
White solid. 64.6 mg. Yield: 65%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 213-215°C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.55 – 7.44 (m, 5H), 7.41 – 7.35 (m, 2H), 7.34 – 7.26 (m, 4H), 7.25 – 7.20 (m, 2H), 7.02 – 6.92 (m, 3H), 4.22 (t, *J* = 6.1 Hz, 1H), 3.51 (dd, *J* = 12.5, 5.8 Hz, 1H), 3.28 – 3.17 (m, 2H), 2.54 (d, *J* = 16.7 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.0, 164.9 (d, *J* = 254.6 Hz), 146.6, 145.5, 141.4, 137.9, 135.4 (d, *J* = 3.2 Hz), 134.7, 133.8, 133.8, 130.0, 129.6 (d, *J* = 9.4 Hz), 129.1, 129.0, 128.6, 128.5, 128.3, 127.6, 126.8, 122.1, 121.8, 116.2 (d, *J* = 22.6 Hz), 55.3, 47.7, 45.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -105.40 (s). HRMS (ESI) *m/z* calcd for C₃₀H₂₃FNO₃S [M+H]⁺ 496.1383, found 496.1387.

4-Chloro-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide(**3af**)



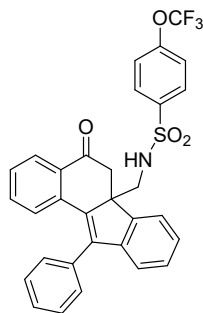
White solid. 61.2 mg. Yield: 60%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 177-178°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.42 – 7.26 (m, 8H), 7.25 – 7.19 (m, 4H), 6.97 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.24 (t, *J* = 6.0 Hz, 1H), 3.53 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.28 – 3.16 (m, 2H), 2.53 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.0, 146.6, 145.5, 141.4, 139.0, 137.8, 134.6, 133.8, 130.0, 129.3, 129.1, 129.0, 128.6, 128.5, 128.2, 127.6, 127.6, 126.8, 55.3, 47.6, 45.9. HRMS (ESI) *m/z* calcd for C₃₀H₂₃ClNO₃S [M+H]⁺ 512.1087, found 512.1086.

4-Bromo-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide(**3ag**)



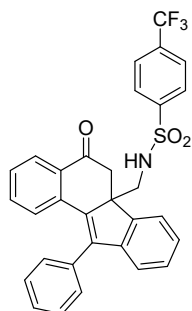
White solid. 72.8 mg. Yield: 65%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 210-211°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.42 – 7.25 (m, 10H), 7.25 – 7.19 (m, 2H), 6.96 (dd, *J* = 7.7, 0.9 Hz, 1H), 4.24 (t, *J* = 6.1 Hz, 1H), 3.53 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.28 – 3.17 (m, 2H), 2.53 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.93, 146.5, 145.5, 141.4, 138.4, 137.8, 134.6, 133.8, 133.8, 132.2, 130.0, 129.1, 129.0, 128.6, 128.5, 128.3, 128.2, 127.6, 127.6, 127.5, 126.9, 122.1, 121.8, 55.3, 47.6, 45.9. HRMS (ESI) *m/z* calcd for C₃₀H₂₃BrNO₃S [M+H]⁺ 556.0582, found 556.0574.

N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)-4-(trifluoromethoxy)benzenesulfonamide (**3ah**)



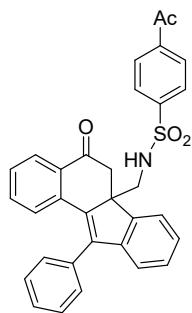
White solid. 79.5 mg. Yield: 71%. Purification by column chromatography (EtOAc/Pe, 1:5 v/v). mp 185-186°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 – 7.42 (m, 5H), 7.36 (dd, *J* = 5.5, 1.9 Hz, 2H), 7.33 – 7.16 (m, 6H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.99 (dd, *J* = 7.7, 0.8 Hz, 1H), 4.44 (d, *J* = 5.6 Hz, 1H), 3.55 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.29 – 3.18 (m, 2H), 2.52 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.0, 151.8, 146.7, 145.5, 141.5, 137.8, 137.8, 134.7, 133.8, 133.7, 130.1, 129.1, 129.0, 128.9, 128.6, 128.5, 128.3, 127.6, 126.7, 122.0, 121.8, 120.8, 120.2 (q, *J* = 259.1 Hz), 55.3, 47.7, 45.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.62 (s). HRMS (ESI) *m/z* calcd for C₃₁H₂₃F₃NO₄S [M+H]⁺ 562.1300, found 562.1305.

N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)-4-(trifluoromethyl)benzenesulfonamide (**3ai**)



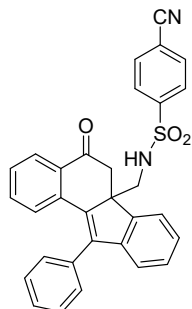
White solid. 63.1 mg. Yield: 58%. Purification by column chromatography (EtOAc/Pe, 1:5 v/v). mp 191-193°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (q, *J* = 8.5 Hz, 4H), 7.51 – 7.44 (m, 3H), 7.36 (dd, *J* = 5.7, 1.8 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.15 (m, 2H), 6.99 – 6.93 (m, 1H), 4.38 (t, *J* = 6.0 Hz, 1H), 3.58 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.32 – 3.18 (m, 2H), 2.53 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.9, 146.5, 145.5, 143.1, 141.5, 137.7, 134.6, 134.2, 133.9, 133.8, 133.7, 130.0, 129.1, 128.9, 128.7, 128.5, 128.3, 127.6, 127.5, 127.2, 126.8, 126.1 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 272.9 Hz), 122.1, 121.7, 55.3, 47.7, 45.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.12 (s). HRMS (ESI) *m/z* calcd for C₃₁H₂₃F₃NO₃S [M+H]⁺ 546.1351, found 546.1355.

4-Acetyl-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide(**3aj**)



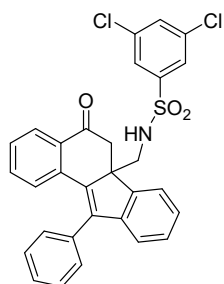
White solid. 69.7 mg. Yield: 67%. Purification by column chromatography (EtOAc/Pe, 1:5 v/v). mp 227-229°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.60 – 7.53 (m, 2H), 7.52 – 7.43 (m, 3H), 7.41 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 7.26 – 7.18 (m, 3H), 6.99 (dd, *J* = 7.8, 0.8 Hz, 1H), 4.28 (t, *J* = 6.1 Hz, 1H), 3.54 (dd, *J* = 12.6, 5.7 Hz, 1H), 3.32 – 3.17 (m, 2H), 2.61 (s, 3H), 2.55 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.7, 195.9, 146.6, 145.5, 143.3, 141.5, 139.8, 137.8, 134.7, 133.8, 133.8, 130.0, 129.2, 129.0, 128.8, 128.7, 128.5, 128.2, 127.6, 127.1, 126.8, 122.1, 121.8, 55.3, 47.8, 45.8, 26.9. HRMS (ESI) *m/z* calcd for C₃₂H₂₆NO₄S [M+H]⁺ 520.1583, found 520.1580.

4-Cyano-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide(**3ak**)



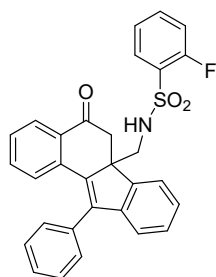
White solid. 58.7 mg. Yield: 58%. Purification by column chromatography (EtOAc/Pe, 1:5 v/v). mp 194-196°C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.57 (s, 4H), 7.53 – 7.46 (m, 3H), 7.39 – 7.26 (m, 6H), 7.25 – 7.20 (m, 2H), 6.97 (dd, *J* = 7.8, 0.7 Hz, 1H), 4.32 (t, *J* = 6.1 Hz, 1H), 3.58 (dd, *J* = 12.7, 5.7 Hz, 1H), 3.32 – 3.17 (m, 2H), 2.55 (d, *J* = 16.7 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.8, 146.4, 145.5, 143.8, 141.6, 137.6, 134.5, 133.8, 133.6, 132.8, 130.0, 129.2, 128.9, 128.8, 128.6, 128.4, 127.7, 127.5, 127.3, 126.9, 122.2, 121.7, 117.3, 116.2, 55.3, 47.8, 45.8. HRMS (ESI) *m/z* calcd for C₃₁H₂₃N₂O₃S [M+H]⁺ 503.1429, found 503.1431.

3,5-Dichloro-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide(**3al**)



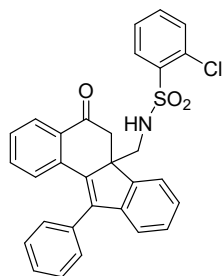
White solid. 70.2 mg. Yield: 64%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 232-233°C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.41 – 7.26 (m, 9H), 7.26 – 7.20 (m, 2H), 6.99 (dd, *J* = 7.7, 0.9 Hz, 1H), 4.27 (t, *J* = 6.0 Hz, 1H), 3.61 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.33 (dd, *J* = 12.8, 6.6 Hz, 1H), 3.23 (d, *J* = 16.8 Hz, 1H), 2.56 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.8, 146.4, 145.5, 142.6, 141.6, 137.7, 135.8, 134.5, 133.9, 133.7, 132.6, 130.0, 129.2, 128.9, 128.9, 128.5, 128.4, 127.7, 127.4, 126.8, 125.1, 122.0, 121.7, 55.3, 47.7, 45.8. HRMS (ESI) *m/z* calcd for C₃₀H₂₂Cl₂NO₃S [M+H]⁺ 546.0697, found 546.0698.

2-Fluoro-N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide(**3am**)



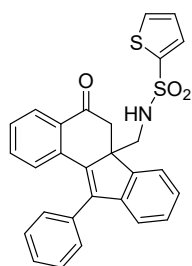
White solid. 56.1 mg. Yield: 57%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 216-218°C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.58 (td, *J* = 7.6, 1.7 Hz, 1H), 7.53 – 7.40 (m, 6H), 7.33 – 7.16 (m, 6H), 7.10 (td, *J* = 7.7, 0.8 Hz, 1H), 7.03 – 6.91 (m, 2H), 4.34 (t, *J* = 5.9 Hz, 1H), 3.61 (dd, *J* = 12.7, 5.8 Hz, 1H), 3.33 (dd, *J* = 12.7, 6.2 Hz, 1H), 3.23 (d, *J* = 16.8 Hz, 1H), 2.55 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.9, 158.4 (d, *J* = 254.3 Hz), 146.6, 145.5, 141.5, 137.8, 134.7, 134.7, 134.6, 133.9, 133.8, 130.1, 129.9, 129.1 (d, *J* = 12.6 Hz), 128.7, 128.3 (d, *J* = 22.4 Hz), 127.6, 127.56 (d, *J* = 12.9 Hz), 126.8, 124.3 (d, *J* = 3.7 Hz), 122.0, 121.7, 116.9 (d, *J* = 21.0 Hz), 55.4, 47.9, 45.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.23 (s). HRMS (ESI) *m/z* calcd for C₃₀H₂₃FNO₃S [M+H]⁺ 496.1383, found 496.1382.

2-Chloro-*N*-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3an**)



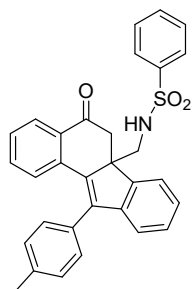
White solid. 69.3 mg. Yield: 68%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 204-206°C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 1H), 7.79 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.35 (m, 6H), 7.33 – 7.23 (m, 7H), 7.21 – 7.15 (m, 1H), 7.07 – 7.01 (m, 1H), 4.51 (t, *J* = 5.8 Hz, 1H), 3.56 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.28 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.20 (d, *J* = 16.8 Hz, 1H), 2.53 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.9, 146.6, 145.5, 141.4, 137.9, 136.6, 134.6, 133.8 (d, *J* = 1.4 Hz), 133.5, 131.5, 131.2, 130.9, 130.0, 129.1, 129.0, 128.6, 128.5, 128.3, 127.7, 127.6, 127.0, 126.8, 122.1, 121.6, 55.4, 48.0, 46.1. HRMS (ESI) *m/z* calcd for C₃₀H₂₃ClNO₃S [M+H]⁺ 512.1087, found 512.1089.

N-((5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)thiophene-2-sulfonamide(**3ao**)



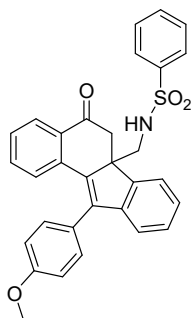
White solid. 63.7 mg. Yield: 66%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 231-232°C. ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 8.01 (m, 1H), 7.52 – 7.36 (m, 6H), 7.35 – 7.28 (m, 4H), 7.27 – 7.22 (m, 3H), 7.09 – 7.04 (m, 1H), 6.89 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.29 (t, *J* = 6.0 Hz, 1H), 3.56 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.36 – 3.21 (m, 2H), 2.56 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.1, 146.7, 145.5, 141.4, 140.2, 138.0, 134.8, 133.9, 133.8, 132.2, 132.0, 130.1, 129.1, 129.1, 128.6, 128.4, 128.3, 127.8, 127.6, 127.2, 126.8, 122.1, 121.8, 55.3, 48.0, 45.9. HRMS (ESI) *m/z* calcd for C₂₈H₂₂NO₃S₂ [M+H]⁺ 484.1041, found 484.1053.

N-((5-oxo-11-(*p*-tolyl)-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3ba**)



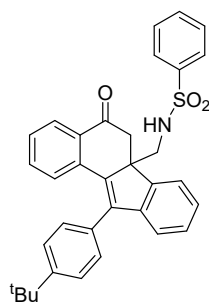
White solid. 59.5 mg. Yield: 61%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 188-189°C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 8.00 (m, 1H), 7.53 – 7.43 (m, 3H), 7.36 – 7.18 (m, 13H), 7.07 (dd, *J* = 4.3, 2.4 Hz, 1H), 4.11 – 4.06 (m, 1H), 3.48 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.28 – 3.19 (m, 2H), 2.53 (d, *J* = 16.8 Hz, 1H), 2.45 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.1, 146.7, 145.7, 141.3, 139.3, 138.2, 137.7, 134.9, 133.8, 132.5, 130.7, 130.1, 129.8, 129.0, 128.9, 128.5, 128.1, 127.7, 127.5, 126.8, 126.7, 122.1, 121.7, 55.3, 47.7, 45.8, 21.5. HRMS (ESI) *m/z* calcd for C₃₁H₂₆NO₃S [M+H]⁺ 492.1633, found 492.1639.

N-((11-(4-methoxyphenyl)-5-oxo-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bb**)



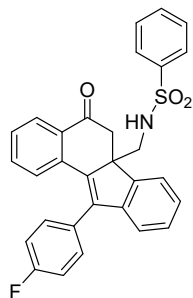
White solid. 48.2 mg. Yield: 47%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 174-175°C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 1H), 7.51 – 7.43 (m, 3H), 7.35 – 7.26 (m, 8H), 7.25 – 7.19 (m, 2H), 7.11 – 7.06 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.11 (t, *J* = 6.2 Hz, 1H), 3.89 (s, 3H), 3.48 (dd, *J* = 12.4, 5.8 Hz, 1H), 3.28 – 3.16 (m, 2H), 2.52 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.1, 159.6, 146.7, 145.7, 141.0, 139.3, 137.7, 135.0, 133.8, 132.5, 130.3, 130.1, 129.0, 128.5, 128.1, 127.6, 127.5, 126.8, 126.7, 125.9, 122.0, 121.8, 114.5, 55.4, 55.2, 47.7, 45.8. HRMS (ESI) *m/z* calcd for C₃₁H₂₆NO₄S [M+H]⁺ 508.1583, found 508.1587.

N-((11-(4-(*tert*-butyl)phenyl)-5-oxo-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bc**)



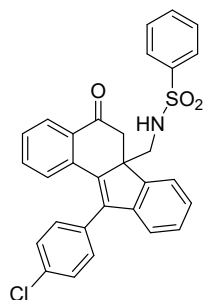
White solid. 63.3 mg. Yield: 59%. mp 195-197°C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 1H), 7.50 – 7.44 (m, 5H), 7.35 – 7.24 (m, 9H), 7.23 – 7.17 (m, 1H), 7.12 – 7.08 (m, 1H), 4.22 (t, *J* = 5.9 Hz, 1H), 3.47 (dd, *J* = 12.4, 5.8 Hz, 1H), 3.30 – 3.17 (m, 2H), 2.53 (d, *J* = 16.8 Hz, 1H), 1.39 (s, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.2, 151.4, 146.7, 145.7, 141.3, 139.3, 137.7, 135.0, 133.8, 132.5, 130.7, 130.1, 129.0, 128.7, 128.5, 128.1, 127.7, 127.5, 126.8, 126.7, 125.9, 122.2, 121.8, 55.3, 47.7, 45.8, 34.8, 31.4. HRMS (ESI) *m/z* calcd for C₃₄H₃₂NO₃S [M+H]⁺ 534.2103, found 534.2108.

N-((11-(4-fluorophenyl)-5-oxo-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide (**3bd**)



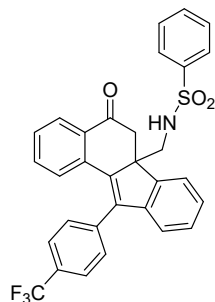
White solid. 62.2 mg. Yield: 63%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 226-228°C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 8.01 (m, 1H), 7.51 – 7.44 (m, 3H), 7.40 – 7.29 (m, 7H), 7.29 – 7.14 (m, 5H), 7.03 – 6.98 (m, 1H), 4.19 (t, *J* = 6.2 Hz, 1H), 3.48 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.30 – 3.17 (m, 2H), 2.52 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.9, 162.7 (d, *J* = 247.9 Hz), 146.6, 145.4, 140.2, 139.3, 138.5, 134.6, 133.9, 132.6, 130.9, 130.9, 130.1, 129.8 (d, *J* = 3.5 Hz), 129.0, 128.6, 128.4, 127.6 (d, *J* = 8.7 Hz), 126.9, 126.8, 121.9, 121.8, 116.3 (d, *J* = 21.4 Hz), 55.4, 47.7, 45.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.81 (s). HRMS (ESI) *m/z* calcd for C₃₀H₂₃FNO₃S [M+H]⁺ 496.1383, found 496.1393.

N-((11-(4-chlorophenyl)-5-oxo-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide (**3be**)



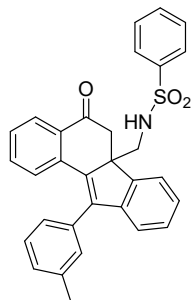
White solid. 63.7 mg. Yield: 62%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 223-225°C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 1H), 7.45 (dd, *J* = 14.2, 8.2 Hz, 5H), 7.35 – 7.26 (m, 8H), 7.20 (dd, *J* = 16.8, 7.4 Hz, 2H), 7.01 (dd, *J* = 6.6, 2.3 Hz, 1H), 4.38 (t, *J* = 6.2 Hz, 1H), 3.47 (dd, *J* = 12.5, 5.9 Hz, 1H), 3.28 – 3.16 (m, 2H), 2.50 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.9, 146.7, 145.1, 139.9, 139.3, 138.7, 134.5, 134.3, 133.9, 132.5, 132.4, 130.5, 130.1, 129.4, 129.0, 128.6, 128.4, 127.6, 127.6, 126.9, 126.8, 121.9, 121.7, 55.5, 47.7, 45.8. HRMS (ESI) *m/z* calcd for C₃₀H₂₃ClNO₃S [M+H]⁺ 512.1087, found 512.1082.

N-((5-oxo-11-(4-(trifluoromethyl)phenyl)-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bf**)



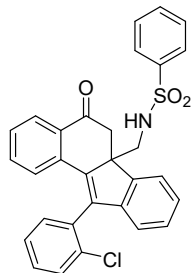
White solid. 88.7 mg. Yield: 81%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 203-205°C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.41 (m, 5H), 7.36 – 7.26 (m, 6H), 7.20 (dd, *J* = 10.8, 3.9 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.95 (dd, *J* = 7.6, 1.0 Hz, 1H), 4.60 (q, *J* = 6.0 Hz, 1H), 3.49 (dd, *J* = 12.6, 6.1 Hz, 1H), 3.31 – 3.13 (m, 2H), 2.51 (d, *J* = 16.8 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.8, 146.78, 144.9, 139.7, 139.4, 139.2, 137.9, 134.3, 134.0, 132.5, 130.4 (q, *J* = 32.7 Hz), 130.2, 129.6, 129.0, 128.6, 127.7, 127.6, 127.0, 126.8, 126.1, 126.1, 126.0, 126.0, 124.1 (q, *J* = 272.8 Hz), 122.0, 121.7, 55.7, 47.8, 45.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.45 (s). HRMS (ESI) *m/z* calcd for C₃₁H₂₃F₃NO₃S [M+H]⁺ 546.1351, found 546.1366.

N-((5-oxo-11-(*m*-tolyl)-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bg**)



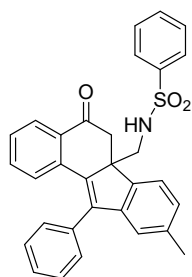
White solid. 58.5 mg. Yield: 60%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 196-198°C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 8.00 (m, 1H), 7.52 – 7.43 (m, 3H), 7.39 – 7.26 (m, 7H), 7.25 – 7.13 (m, 4H), 7.07 – 7.02 (m, 1H), 4.17 – 4.07 (m, 1H), 3.48 (dd, *J* = 12.4, 5.8 Hz, 1H), 3.29 – 3.18 (m, 2H), 2.54 (d, *J* = 16.7 Hz, 1H), 2.40 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.1, 146.7, 145.6, 141.5, 139.3, 138.8, 137.8, 134.9, 133.8, 132.5, 130.1, 129.5, 129.1, 129.0, 128.5, 128.2, 127.7, 127.5, 126.8, 126.7, 126.0, 122.1, 121.7, 55.3, 47.7, 45.8, 21.5. HRMS (ESI) *m/z* calcd for C₃₁H₂₆NO₃S [M+H]⁺ 492.1633, found 492.1637.

N-((11-(2-chlorophenyl)-5-oxo-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide (**3bh**)



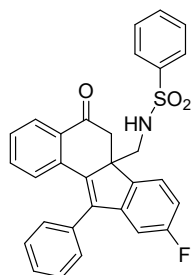
White solid. 64.3 mg. Yield: 63%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 180-181°C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.55 – 7.41 (m, 6H), 7.36 – 7.22 (m, 7H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.96 – 6.91 (m, 1H), 4.08 (t, *J* = 6.1 Hz, 1H), 3.50 (dd, *J* = 12.5, 5.3 Hz, 1H), 3.40 – 3.11 (m, 1H), 2.58 (d, *J* = 16.5 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.0, 146.5, 145.3, 140.3, 139.4, 138.2, 135.3, 134.2, 132.8, 132.7, 132.6, 131.6, 130.5, 129.9, 129.4, 129.0, 128.7, 128.5, 127.5, 127.2, 126.9, 126.8, 126.4, 121.8, 121.7, 55.8, 47.8, 46.2. HRMS (ESI) *m/z* calcd for C₃₀H₂₃ClNO₃S [M+H]⁺ 512.1087, found 512.1084.

N-((9-methyl-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide (**3bi**)



White solid. 63.7 mg. Yield: 65%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 248-250°C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.53 – 7.44 (m, 6H), 7.38 (d, *J* = 6.6 Hz, 2H), 7.35 – 7.23 (m, 4H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.08 – 6.97 (m, 3H), 4.00 (t, *J* = 6.2 Hz, 1H), 3.46 (dd, *J* = 12.4, 5.4 Hz, 1H), 3.30 – 3.16 (m, 2H), 2.54 (d, *J* = 16.7 Hz, 1H), 2.35 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.1, 145.8, 143.8, 141.3, 139.4, 138.6, 138.3, 134.8, 134.0, 133.8, 132.5, 130.1, 129.1, 129.0, 129.0, 128.4, 128.1, 127.6, 127.6, 127.6, 126.8, 122.7, 121.5, 55.0, 47.8, 46.0, 21.6. HRMS (ESI) *m/z* calcd for C₃₁H₂₆NO₃S [M+H]⁺ 492.1633, found 492.1635.

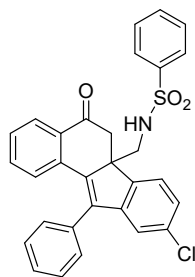
N-((9-fluoro-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide (**3bj**)



White solid. 92.3 mg. Yield: 93%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 223-225°C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 (dt, *J* = 7.3, 6.7 Hz, 6H),

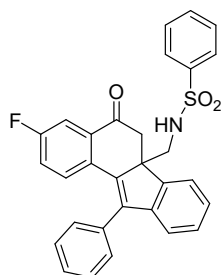
7.40 – 7.27 (m, 6H), 7.20 (dd, $J = 8.2, 4.8$ Hz, 1H), 7.04 (dd, $J = 7.6, 1.0$ Hz, 1H), 6.88 (dd, $J = 13.5, 5.7$ Hz, 2H), 4.11 (t, $J = 6.3$ Hz, 1H), 3.48 (dd, $J = 12.7, 6.2$ Hz, 1H), 3.29 – 3.16 (m, 2H), 2.54 (d, $J = 16.8$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 195.6, 163.4 (d, $J = 246.1$ Hz), 147.7, 147.6, 142.2, 142.1, 140.5, 140.5, 140.0, 139.4, 134.4, 133.9, 133.3, 132.6, 130.1, 129.3, 129.0, 128.9, 128.7 (d, $J = 4.4$ Hz), 127.6, 126.8, 122.8 (d, $J = 9.2$ Hz), 113.4 (d, $J = 23.4$ Hz), 109.3 (d, $J = 24.0$ Hz), 55.0, 47.7, 45.8. ^{19}F NMR (376 MHz, CDCl_3) δ -113.00 (s). HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{FNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 496.1383, found 496.1389.

N-((9-chloro-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bk**)



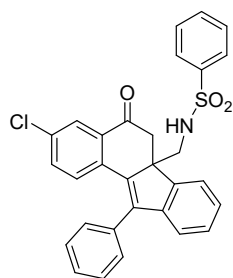
White solid. 72.6 mg. Yield: 71%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 246-247°C. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.50 (d, $J = 7.5$ Hz, 6H), 7.39 – 7.28 (m, 6H), 7.20 – 7.12 (m, 3H), 7.07 – 7.02 (m, 1H), 4.10 (t, $J = 6.4$ Hz, 1H), 3.49 (dd, $J = 12.8, 6.4$ Hz, 1H), 3.30 – 3.17 (m, 2H), 2.53 (d, $J = 16.8$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 195.5, 147.2, 145.0, 140.4, 139.6, 139.4, 134.7, 134.3, 133.9, 133.2, 132.6, 130.1, 129.3, 129.0, 128.9, 128.7, 127.7, 127.7, 126.7, 126.6, 122.7, 122.1, 55.2, 47.6, 45.5. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{ClNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 512.1087, found 512.1089.

N-((3-fluoro-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bl**)



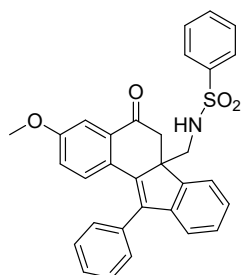
White solid. 67.9 mg. Yield: 69%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 178-180°C. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (dd, $J = 8.9, 2.6$ Hz, 1H), 7.54 – 7.43 (m, 6H), 7.41 – 7.29 (m, 5H), 7.28 – 7.20 (m, 3H), 7.05 – 6.93 (m, 2H), 4.11 (t, $J = 6.3$ Hz, 1H), 3.47 (dd, $J = 12.5, 5.5$ Hz, 1H), 3.30 – 3.17 (m, 2H), 2.54 (d, $J = 16.8$ Hz, 1H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 195.1, 162.2 (d, $J = 250.8$ Hz), 146.3, 145.5, 141.1, 139.4, 137.1, 133.7, 132.6, 132.1, 132.0, 131.2 (d, $J = 3.1$ Hz), 129.9 (d, $J = 7.3$ Hz), 129.2, 129.0 (d, $J = 6.8$ Hz), 128.7, 128.5, 126.8, 126.8, 122.1, 121.8, 121.5 (d, $J = 22.6$ Hz), 113.6 (d, $J = 22.5$ Hz), 55.4, 47.8, 45.6. ^{19}F NMR (376 MHz, CDCl_3) δ -110.71 (s). HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{FNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 496.1383, found 496.1380.

N-((3-chloro-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bm**)



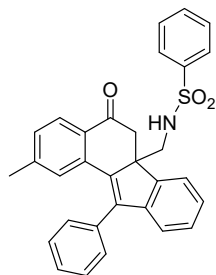
White solid. 72.1 mg. Yield: 70%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 200-202°C. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 2.3$ Hz, 1H), 7.53 – 7.44 (m, 6H), 7.39 – 7.27 (m, 6H), 7.26 – 7.17 (m, 3H), 6.95 (d, $J = 8.5$ Hz, 1H), 4.19 (t, $J = 6.2$ Hz, 1H), 3.48 (dd, $J = 12.6, 5.6$ Hz, 1H), 3.29 – 3.16 (m, 2H), 2.52 (d, $J = 16.8$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.9, 146.5, 145.4, 141.9, 139.3, 137.0, 134.4, 133.8, 133.6, 133.2, 132.6, 131.2, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 127.4, 127.0, 126.8, 122.2, 121.8, 55.2, 47.7, 45.6. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{ClNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 512.1087, found 512.1091.

N-((3-methoxy-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide (**3bn**)



White solid. 70.7 mg. Yield: 70%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 200-202°C. ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.42 (m, 7H), 7.40 – 7.23 (m, 6H), 7.22 – 7.15 (m, 2H), 6.95 (d, $J = 8.7$ Hz, 1H), 6.83 (dd, $J = 8.7, 2.8$ Hz, 1H), 4.24 (t, $J = 6.2$ Hz, 1H), 3.83 (s, 3H), 3.48 (dd, $J = 12.4, 5.9$ Hz, 1H), 3.28 – 3.16 (m, 2H), 2.52 (d, $J = 16.8$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.1, 159.5, 146.4, 145.7, 139.4, 138.0, 134.1, 132.5, 131.5, 129.2, 129.1, 129.1, 129.0, 128.5, 128.3, 127.9, 126.8, 126.4, 122.2, 121.8, 121.6, 109.5, 55.6, 55.3, 48.0, 45.7. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 508.1583, found 508.1587.

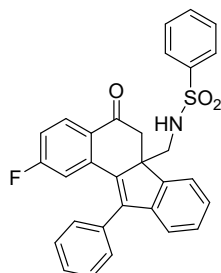
N-((2-methyl-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methyl)benzenesulfonamide (**3bo**)



White solid. 58.4 mg. Yield: 59%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 191-193°C. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 1H), 7.52 – 7.43 (m, 6H), 7.41 – 7.35 (m, 2H), 7.32 (dd, $J = 11.0, 4.5$ Hz, 3H), 7.27 – 7.18 (m, 3H), 7.11 (dd, $J = 8.0, 1.0$ Hz, 1H), 6.77 (s,

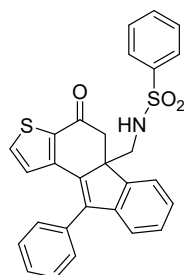
1H), 4.14 (t, $J = 6.2$ Hz, 1H), 3.48 (dd, $J = 12.4, 5.7$ Hz, 1H), 3.30 – 3.15 (m, 2H), 2.51 (d, $J = 16.7$ Hz, 1H), 2.12 (s, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.8, 146.7, 145.45, 144.5, 141.0, 139.3, 138.3, 134.7, 133.9, 132.4, 129.4, 129.0, 129.0, 128.9, 128.5, 128.4, 128.0, 127.9, 127.6, 126.9, 126.7, 122.0, 121.8, 55.4, 47.8, 45.8, 21.9. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 492.1633, found 492.1630.

N-((2-fluoro-5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[*a*]fluoren-6a-yl)methyl)benzenesulfonamide(**3bp**)



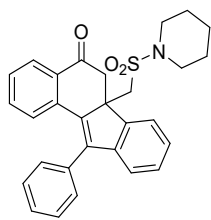
White solid. 65.5 mg. Yield: 66%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 193-195°C. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (dd, $J = 8.8, 6.0$ Hz, 1H), 7.48 (dt, $J = 14.2, 7.4$ Hz, 6H), 7.39 – 7.28 (m, 6H), 7.27 – 7.20 (m, 2H), 6.94 (td, $J = 8.4, 2.5$ Hz, 1H), 6.54 (dd, $J = 9.8, 2.5$ Hz, 1H), 4.33 (dd, $J = 7.0, 5.5$ Hz, 1H), 3.51 (dd, $J = 12.6, 5.3$ Hz, 1H), 3.29 – 3.16 (m, 2H), 2.50 (d, $J = 16.8$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.7, 165.6 (d, $J = 255.7$ Hz), 146.6, 145.3, 142.7, 139.4, 137.5 (d, $J = 10.2$ Hz), 137.0 (d, $J = 2.3$ Hz), 133.3, 132.6, 130.7 (d, $J = 10.1$ Hz), 129.3, 129.0, 128.8, 128.7, 128.7, 127.2, 126.8, 126.7, 126.7, 122.3, 121.9, 115.9 (d, $J = 22.6$ Hz), 113.8 (d, $J = 23.3$ Hz), 55.5, 47.7, 45.6. ^{19}F NMR (376 MHz, CDCl_3) δ -102.26 (s). HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{23}\text{FNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 496.1383, found 496.1385.

N-((4-oxo-10-phenyl-4,5-dihydro-5aH-fluoreno[2,1-*b*]thiophen-5a-yl)methyl)benzenesulfonamide(**3bq**)



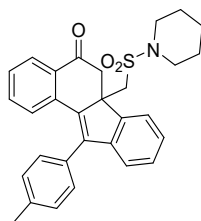
White solid. 82.5 mg. Yield: 85%. Purification by column chromatography (EtOAc/Pe, 1:6 v/v). mp 188-189°C. ^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.41 (m, 9H), 7.38 – 7.22 (m, 6H), 6.71 (d, $J = 5.1$ Hz, 1H), 4.24 (t, $J = 6.4$ Hz, 1H), 3.48 (dd, $J = 12.6, 5.7$ Hz, 1H), 3.35 (dd, $J = 12.6, 7.4$ Hz, 1H), 3.16 (d, $J = 16.5$ Hz, 1H), 2.58 (d, $J = 16.5$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.5, 146.7, 145.5, 142.7, 141.0, 139.6, 136.1, 136.1, 134.8, 133.5, 132.6, 129.1, 129.0, 128.9, 128.7, 127.0, 126.8, 126.3, 122.3, 122.1, 57.1, 49.2, 45.1. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{22}\text{NO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 484.1041, found 484.1050.

11-Phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[*a*]fluoren-5-one (**5a**)



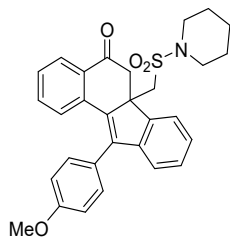
White solid. 78.9 mg. Yield: 84%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 177-179°C. ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.05 (m, 1H), 7.72 – 7.63 (m, 1H), 7.53 – 7.39 (m, 5H), 7.38 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 7.24 – 7.17 (m, 1H), 3.60 (d, *J* = 14.4 Hz, 1H), 3.51 (d, *J* = 16.5 Hz, 1H), 3.22 (d, *J* = 14.4 Hz, 1H), 2.84 (dd, *J* = 11.3, 6.4 Hz, 2H), 2.70 (dd, *J* = 12.4, 5.1 Hz, 2H), 2.48 (d, *J* = 16.5 Hz, 1H), 1.48 – 1.32 (m, 4H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.2, 147.5, 145.3, 140.0, 139.3, 135.8, 134.0, 133.9, 129.8, 129.0, 128.4, 128.3, 128.1, 127.4, 126.4, 122.8, 54.0, 53.5, 48.6, 45.9, 25.5, 23.7. HRMS (ESI) *m/z* calcd for C₂₉H₂₈NO₃S [M+H]⁺ 470.1790, found 470.1799.

6a-((Piperidin-1-ylsulfonyl)methyl)-11-(p-tolyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5b**)



White solid. 60.0 mg. Yield: 62%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 202-203°C. ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.04 (m, 1H), 7.66 (dd, *J* = 5.8, 2.7 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.30 – 7.24 (m, 6H), 3.57 (d, *J* = 14.4 Hz, 1H), 3.50 (d, *J* = 16.5 Hz, 1H), 3.21 (d, *J* = 14.4 Hz, 1H), 2.84 (dd, *J* = 11.1, 6.3 Hz, 2H), 2.70 (dd, *J* = 12.2, 5.1 Hz, 2H), 2.51 – 2.40 (m, 4H), 1.45 – 1.36 (m, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.3, 147.5, 145.4, 140.1, 139.0, 138.0, 136.0, 133.9, 130.9, 129.8, 129.7, 128.9, 128.3, 128.3, 128.0, 127.4, 126.4, 122.8, 122.0, 54.0, 53.4, 48.6, 45.9, 25.5, 23.7, 21.5. HRMS (ESI) *m/z* calcd for C₃₀H₃₀NO₃S [M+H]⁺ 484.1946, found 484.1946.

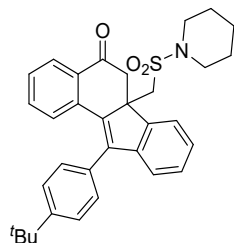
11-(4-Methoxyphenyl)-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5c**)



White solid. 64.0 mg. Yield: 64%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 190-192°C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.73 – 7.59 (m, 1H), 7.42 – 7.32 (m, 6H), 7.31 – 7.26 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.57 (d, *J* = 14.4 Hz, 1H), 3.50 (d, *J* = 16.5 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 2.84 (dd, *J* = 11.2, 6.4 Hz, 2H), 2.70 (dd, *J* = 12.3, 5.0 Hz, 2H), 2.47 (d, *J* = 16.5 Hz, 1H), 1.45 – 1.37 (m, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.3, 159.5, 147.5, 145.5, 139.7, 138.9, 136.0, 133.9, 130.3, 129.8, 128.3, 128.2, 128.0, 127.4, 126.4, 126.0,

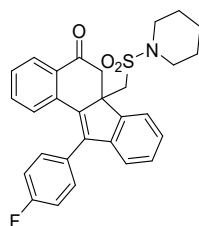
122.8, 121.9, 114.4, 55.3, 54.0, 53.3, 48.5, 45.9, 25.5, 23.7. HRMS (ESI) m/z calcd for $C_{30}H_{30}NO_4S$ $[M+H]^+$ 500.1896, found 500.1999.

11-(4-(Tert-butyl)phenyl)-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (5d)



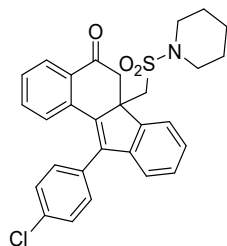
White solid. 65.2 mg. Yield: 62%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 180-181°C. 1H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 7.69 – 7.62 (m, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.41 – 7.27 (m, 8H), 3.58 (d, J = 14.5 Hz, 1H), 3.50 (d, J = 16.5 Hz, 1H), 3.21 (d, J = 14.4 Hz, 1H), 2.89 – 2.79 (m, 2H), 2.75 – 2.64 (m, 2H), 2.48 (d, J = 16.5 Hz, 1H), 1.42 – 1.39 (m, 15H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.3, 151.2, 147.6, 145.5, 140.0, 138.9, 136.0, 133.9, 130.8, 129.8, 128.6, 128.3, 128.3, 128.0, 127.3, 126.3, 125.8, 122.8, 122.1, 54.1, 53.5, 48.6, 45.9, 34.8, 31.4, 25.5, 23.7. HRMS (ESI) m/z calcd for $C_{33}H_{36}NO_3S$ $[M+H]^+$ 526.2416, found 526.2412.

11-(4-Fluorophenyl)-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (5e)



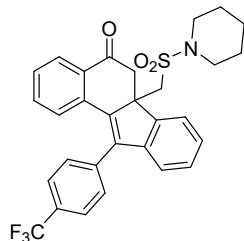
White solid. 57.5 mg. Yield: 59%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 179-180°C. 1H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.04 (m, 1H), 7.65 (dd, J = 5.8, 2.7 Hz, 1H), 7.48 – 7.32 (m, 6H), 7.26 – 7.14 (m, 4H), 3.57 (d, J = 14.4 Hz, 1H), 3.48 (d, J = 16.5 Hz, 1H), 3.21 (d, J = 14.4 Hz, 1H), 2.83 (dd, J = 11.2, 6.4 Hz, 2H), 2.70 (dd, J = 12.3, 5.0 Hz, 2H), 2.48 (d, J = 16.5 Hz, 1H), 1.41 (d, J = 6.1 Hz, 6H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.1, 162.7 (d, J = 247.5 Hz), 147.4, 145.2, 139.6, 139.0, 135.7, 134.0, 130.9 (d, J = 8.0 Hz), 129.9 (d, J = 3.5 Hz), 129.8, 128.4, 128.2, 128.1, 127.5, 126.5, 122.8, 121.8, 116.2 (d, J = 21.6 Hz), 53.9, 53.5, 48.6, 45.9, 25.5, 23.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.11 (s). HRMS (ESI) m/z calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$ 488.1696, found 488.1699.

11-(4-Chlorophenyl)-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5f**)



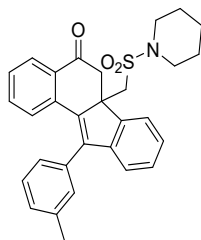
White solid. 75.6 mg. Yield: 75%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 180-181°C. ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.08 (m, 1H), 7.67 – 7.61 (m, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.33 (m, 6H), 7.25 – 7.17 (m, 2H), 3.57 (d, *J* = 14.4 Hz, 1H), 3.48 (d, *J* = 16.5 Hz, 1H), 3.21 (d, *J* = 14.3 Hz, 1H), 2.83 (dd, *J* = 11.1, 6.5 Hz, 2H), 2.70 (dd, *J* = 12.4, 5.0 Hz, 2H), 2.48 (d, *J* = 16.5 Hz, 1H), 1.41 (d, *J* = 5.8 Hz, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.0, 147.4, 145.0, 139.8, 138.7, 135.5, 134.2, 134.1, 132.5, 130.5, 129.8, 129.4, 128.5, 128.3, 128.1, 127.5, 126.6, 122.8, 121.7, 53.9, 53.5, 48.6, 45.9, 25.5, 23.7. HRMS (ESI) *m/z* calcd for C₂₉H₂₇ClNO₃S [M+H]⁺ 504.1400, found 504.1405.

6a-((Piperidin-1-ylsulfonyl)methyl)-11-(4-(trifluoromethyl)phenyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5g**)



White solid. 72.0 mg. Yield: 67%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 166-168°C. ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.09 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.33 (m, 4H), 7.24 – 7.19 (m, 1H), 7.17 – 7.11 (m, 1H), 3.59 (d, *J* = 14.3 Hz, 1H), 3.49 (d, *J* = 16.6 Hz, 1H), 3.23 (d, *J* = 14.3 Hz, 1H), 2.84 (dd, *J* = 11.0, 6.5 Hz, 2H), 2.71 (dd, *J* = 12.3, 4.9 Hz, 2H), 2.51 (d, *J* = 16.6 Hz, 1H), 1.41 (s, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.8, 147.4, 144.8, 140.3, 138.5, 138.1, 135.3, 134.2, 130.4 (q, *J* = 32.5 Hz), 129.8, 129.6, 128.5, 128.5, 128.1, 127.6, 126.7, 126.0 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 272.2 Hz), 122.8, 121.6, 53.8, 53.7, 48.6, 45.9, 25.5, 23.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.49 (s). HRMS (ESI) *m/z* calcd for C₃₀H₂₇F₃NO₃S [M+H]⁺ 538.1664, found 538.1667.

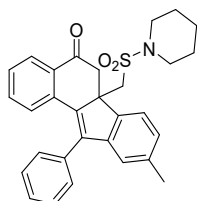
6a-((Piperidin-1-ylsulfonyl)methyl)-11-(*m*-tolyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5h**)



White solid. 73.5 mg. Yield: 76%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 182-184°C. ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.06 (m, 1H), 7.66 (dd, *J* = 5.9, 2.7 Hz, 1H), 7.41 –

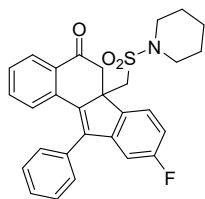
7.32 (m, 5H), 7.30 – 7.17 (m, 5H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.50 (d, $J = 16.5$ Hz, 1H), 3.21 (d, $J = 14.4$ Hz, 1H), 2.85 (dd, $J = 11.3, 6.3$ Hz, 2H), 2.71 (dd, $J = 12.3, 5.1$ Hz, 2H), 2.48 (d, $J = 16.5$ Hz, 1H), 2.39 (s, 3H), 1.44 – 1.37 (m, 6H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 196.3, 147.5, 145.5, 140.3, 139.0, 138.7, 135.9, 133.9, 133.9, 129.8, 129.5, 129.0, 128.9, 128.3, 128.3, 128.0, 127.3, 126.4, 126.1, 122.8, 122.0, 54.0, 53.4, 48.6, 45.9, 25.5, 23.7, 21.5. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{30}\text{NO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 484.1946, found 484.1948.

9-Methyl-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[*a*]fluoren-5-one (**5i**)



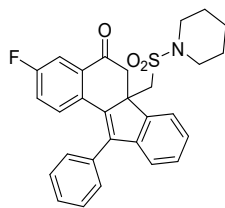
White solid. 64.8 mg. Yield: 67%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 203-205°C. ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.06 (m, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.52 – 7.44 (m, 3H), 7.43 – 7.31 (m, 4H), 7.21 – 7.15 (m, 2H), 7.05 (s, 1H), 3.54 (d, $J = 4.2$ Hz, 1H), 3.51 (d, $J = 6.4$ Hz, 1H), 3.17 (d, $J = 14.3$ Hz, 1H), 2.86 (dd, $J = 11.4, 6.2$ Hz, 2H), 2.74 (dd, $J = 12.4, 5.2$ Hz, 2H), 2.47 (d, $J = 16.5$ Hz, 1H), 2.36 (s, 3H), 1.47 – 1.37 (m, 6H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 196.3, 145.5, 144.8, 140.1, 139.4, 138.3, 135.9, 134.2, 133.8, 129.8, 129.0, 129.0, 128.2, 128.0, 127.4, 127.2, 122.7, 122.5, 53.9, 53.1, 48.6, 46.0, 25.5, 23.7, 21.6. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{30}\text{NO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 484.1946, found 484.1949.

9-Fluoro-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[*a*]fluoren-5-one (**5j**)



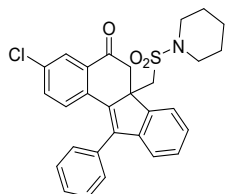
White solid. 65.3 mg. Yield: 67%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 179-180°C. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (dd, $J = 6.0, 3.2$ Hz, 1H), 7.63 (dd, $J = 8.3, 4.9$ Hz, 1H), 7.53 – 7.44 (m, 3H), 7.38 (dt, $J = 7.3, 4.0$ Hz, 4H), 7.23 – 7.16 (m, 1H), 7.04 (td, $J = 8.8, 2.4$ Hz, 1H), 6.94 (dd, $J = 8.9, 2.4$ Hz, 1H), 3.52 (t, $J = 15.5$ Hz, 2H), 3.14 (d, $J = 14.3$ Hz, 1H), 2.88 (dd, $J = 11.4, 6.4$ Hz, 2H), 2.78 (dd, $J = 12.3, 5.0$ Hz, 2H), 2.48 (d, $J = 16.5$ Hz, 1H), 1.45 (dd, $J = 9.0, 4.7$ Hz, 6H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 195.8, 163.4 (d, $J = 245.4$ Hz), 147.4 (d, $J = 8.8$ Hz), 142.9, 142.9, 141.1, 139.3 (d, $J = 3.0$ Hz), 135.3, 134.0, 133.4, 129.8, 129.2, 128.9, 128.5, 128.4, 128.2, 127.5, 124.1 (d, $J = 9.0$ Hz), 113.1 (d, $J = 23.3$ Hz), 109.1 (d, $J = 23.9$ Hz), 53.7, 53.0, 48.3, 46.1, 25.5, 23.7. ^{19}F NMR (376 MHz, CDCl_3) δ -113.41 (s). HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{27}\text{FNO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 488.1696, found 488.1700.

3-Fluoro-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[*a*]fluoren-5-one (**5k**)



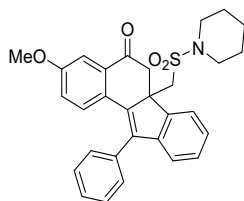
White solid. 76.1 mg. Yield: 78%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 168-170°C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.65 (dd, *J* = 5.6, 2.8 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.42 – 7.33 (m, 4H), 7.29 – 7.25 (m, 1H), 7.21 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.08 (td, *J* = 8.4, 2.8 Hz, 1H), 3.54 (dd, *J* = 20.5, 15.5 Hz, 2H), 3.18 (d, *J* = 14.4 Hz, 1H), 2.85 (dd, *J* = 11.4, 6.4 Hz, 2H), 2.72 (dd, *J* = 12.3, 5.0 Hz, 2H), 2.48 (d, *J* = 16.6 Hz, 1H), 1.49 – 1.37 (m, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.3, 162.2 (d, *J* = 250.4 Hz), 147.3, 145.3, 139.9, 138.3, 133.8, 132.2 (d, *J* = 3.3 Hz), 131.7, 131.7, 130.5 (d, *J* = 7.3 Hz), 129.1, 129.0, 128.4 (d, *J* = 8.2 Hz), 126.5, 122.7, 122.0, 121.6 (d, *J* = 22.5 Hz), 113.4 (d, *J* = 22.5 Hz), 53.9, 53.4, 48.4, 46.0, 25.5, 23.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.11 (s). HRMS (ESI) *m/z* calcd for C₂₉H₂₇FNO₃S [M+H]⁺ 488.1696, found 488.1697.

3-Chloro-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5l**)



White solid. 75.6 mg. Yield: 75%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 192-193°C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 2.3 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.52 – 7.44 (m, 3H), 7.42 – 7.26 (m, 6H), 7.15 (d, *J* = 8.5 Hz, 1H), 3.54 (dd, *J* = 22.2, 15.5 Hz, 2H), 3.17 (d, *J* = 14.3 Hz, 1H), 2.86 (dd, *J* = 11.3, 6.4 Hz, 2H), 2.72 (dd, *J* = 12.2, 5.0 Hz, 2H), 2.47 (d, *J* = 16.6 Hz, 1H), 1.47 – 1.37 (m, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 195.1, 147.4, 145.2, 140.7, 138.2, 134.3, 134.2, 134.0, 133.7, 130.9, 129.7, 129.1, 128.9, 128.5, 128.5, 127.2, 126.7, 122.7, 122.1, 53.9, 53.3, 48.4, 46.0, 25.5, 23.7. HRMS (ESI) *m/z* calcd for C₂₉H₂₇ClNO₃S [M+H]⁺ 504.1400, found 504.1397.

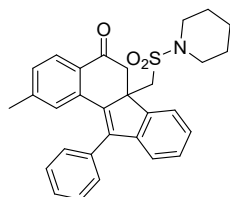
3-Methoxy-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5m**)



White solid. 63.0 mg. Yield: 63%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 202-203°C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.64 (m, 1H), 7.57 (d, *J* = 2.7 Hz, 1H), 7.49 – 7.40 (m, 5H), 7.36 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 6.95 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.86 (s, 3H), 3.55 (dd, *J* = 15.4, 10.7 Hz, 2H), 3.17 (d, *J* = 14.4 Hz, 1H), 2.86 (dd, *J* = 11.3, 6.2 Hz, 2H), 2.72 (dd, *J* = 12.1, 5.0 Hz, 2H), 2.47 (d, *J* = 16.5 Hz, 1H), 1.49 – 1.33 (m, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 196.2, 159.4, 147.2, 145.5, 139.3, 138.3, 134.2, 131.1, 129.7, 129.1, 129.0, 129.0,

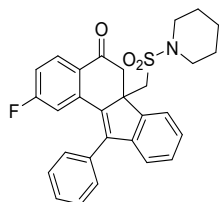
128.3, 128.2, 126.1, 122.9, 122.3, 121.6, 109.3, 55.6, 54.1, 53.5, 48.3, 46.0, 25.5, 23.7. HRMS (ESI) m/z calcd for $C_{30}H_{30}NO_4S$ $[M+H]^+$ 500.1869, found 500.1865.

2-Methyl-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5n**)



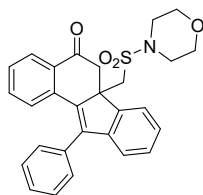
White solid. 69.6 mg. Yield: 72%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 156-158°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, $J = 8.0$ Hz, 1H), 7.65 (dd, $J = 5.9, 2.6$ Hz, 1H), 7.51 – 7.33 (m, 7H), 7.28 (d, $J = 5.0$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 1H), 6.99 (s, 1H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.46 (d, $J = 16.5$ Hz, 1H), 3.23 (d, $J = 14.4$ Hz, 1H), 2.85 (dd, $J = 11.2, 6.2$ Hz, 2H), 2.69 (dd, $J = 12.1, 5.0$ Hz, 2H), 2.46 (d, $J = 16.5$ Hz, 1H), 2.17 (s, 3H), 1.48 – 1.36 (m, 6H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.9, 147.5, 145.4, 144.8, 139.8, 139.5, 135.8, 134.1, 129.2, 129.0, 128.9, 128.6, 128.3, 128.2, 127.6, 127.4, 126.3, 122.8, 121.9, 54.1, 53.5, 48.6, 45.9, 25.5, 23.7, 21.9. HRMS (ESI) m/z calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$ 484.1946, found 484.1950.

2-Fluoro-11-phenyl-6a-((piperidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5o**)



White solid. 48.8 mg. Yield: 50%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 188-190°C. 1H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, $J = 8.7, 5.9$ Hz, 1H), 7.64 (dd, $J = 5.6, 2.6$ Hz, 1H), 7.55 – 7.44 (m, 3H), 7.44 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 7.02 (td, $J = 8.5, 2.5$ Hz, 1H), 6.85 (dd, $J = 9.8, 2.5$ Hz, 1H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.47 (d, $J = 16.5$ Hz, 1H), 3.22 (d, $J = 14.4$ Hz, 1H), 2.85 (dd, $J = 11.2, 6.4$ Hz, 2H), 2.71 (dd, $J = 12.2, 5.0$ Hz, 2H), 2.47 (d, $J = 16.5$ Hz, 1H), 1.48 – 1.37 (m, 6H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.8, 165.9 (d, $J = 255.9$ Hz), 147.5, 145.1, 141.4, 138.7, 138.5, 138.2, 138.1, 130.5 (d, $J = 10.2$ Hz), 129.2, 128.8, 128.5 (d, $J = 11.8$ Hz), 126.8, 126.5 (d, $J = 2.5$ Hz), 122.7, 122.3, 115.9 (d, $J = 22.6$ Hz), 114.4 (d, $J = 23.3$ Hz), 54.0, 53.5, 48.4, 45.9, 25.5, 23.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.20 (s). HRMS (ESI) m/z calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$ 488.1696, found 488.1700.

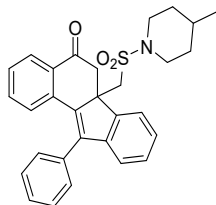
6a-((Morpholinosulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5p**)



White solid. 61.3 mg. Yield: 65%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 194-196°C. 1H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 1H), 7.66 (dd, $J = 5.7, 2.7$ Hz, 1H), 7.53 – 7.43 (m, 3H), 7.44 – 7.34 (m, 6H), 7.31 – 7.27 (m, 1H), 7.23 – 7.17 (m, 1H), 3.61 (d, $J = 14.4$ Hz, 1H),

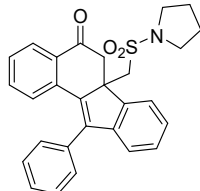
3.55 – 3.47 (m, 5H), 3.25 (d, $J = 14.4$ Hz, 1H), 2.90 (dt, $J = 12.2, 4.7$ Hz, 2H), 2.78 (dt, $J = 12.4, 4.7$ Hz, 2H), 2.51 (d, $J = 16.5$ Hz, 1H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.0, 147.3, 145.3, 140.2, 139.0, 135.7, 134.0, 133.9, 129.8, 129.1, 129.0, 128.6, 128.3, 128.2, 127.5, 126.6, 122.7, 122.1, 66.4, 54.0, 53.4, 48.5, 45.1. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 472.1583, found 472.1890.

6a-(((4-Methylpiperidin-1-yl)sulfonyl)methyl)-11-phenyl-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5q**)



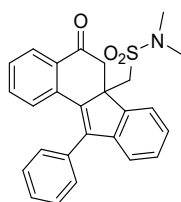
White solid. 82.2 mg. Yield: 85%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 197-198°C. ^1H NMR (400 MHz, CDCl_3) δ 8.13 – 8.07 (m, 1H), 7.68 – 7.63 (m, 1H), 7.51 – 7.39 (m, 5H), 7.38 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 1H), 3.61 (d, $J = 14.5$ Hz, 1H), 3.49 (d, $J = 16.5$ Hz, 1H), 3.43 – 3.33 (m, 2H), 3.24 (d, $J = 14.4$ Hz, 1H), 2.48 (d, $J = 16.5$ Hz, 1H), 2.32 (td, $J = 12.2, 2.5$ Hz, 1H), 2.06 (td, $J = 12.3, 2.5$ Hz, 1H), 1.53 – 1.42 (m, 2H), 1.34 – 1.19 (m, 1H), 1.09 – 0.94 (m, 2H), 0.84 (d, $J = 6.5$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.2, 147.5, 145.4, 140.0, 139.2, 135.8, 134.0, 133.9, 129.8, 129.0, 128.4, 128.3, 128.1, 127.4, 126.4, 122.7, 122.0, 54.2, 53.5, 48.7, 45.4, 45.3, 33.7, 33.6, 30.3, 21.6. HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{30}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 484.1946, found 484.1949.

11-Phenyl-6a-((pyrrolidin-1-ylsulfonyl)methyl)-6,6a-dihydro-5H-benzo[a]fluoren-5-one (**5r**)



White solid. 47.4 mg. Yield: 52%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 158-160°C. ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.07 (m, 1H), 7.67 – 7.63 (m, 1H), 7.51 – 7.39 (m, 5H), 7.38 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 1H), 3.72 (d, $J = 14.7$ Hz, 1H), 3.46 (d, $J = 16.5$ Hz, 1H), 3.35 (d, $J = 14.7$ Hz, 1H), 3.04 – 2.95 (m, 2H), 2.88 – 2.78 (m, 2H), 2.49 (d, $J = 16.5$ Hz, 1H), 1.67 – 1.59 (m, 4H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.1, 147.6, 145.3, 140.0, 139.2, 135.9, 134.0, 133.9, 129.8, 129.0, 129.0, 128.3, 128.3, 128.2, 128.1, 127.4, 126.4, 122.4, 121.9, 54.9, 53.6, 48.7, 46.9, 25.6. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 456.1633, found 456.1643.

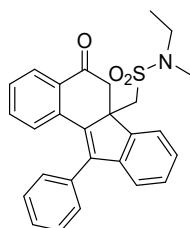
N,N-dimethyl-1-(5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methanesulfonamide (**5s**)



White solid. 54.1 mg. Yield: 63%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 158-159°C. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (dd, $J = 7.1, 2.1$ Hz, 1H), 7.67 – 7.62 (m, 1H), 7.51 –

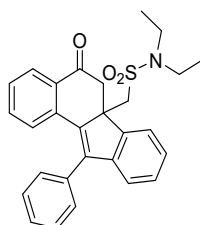
7.40 (m, 5H), 7.39 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 – 7.19 (m, 1H), 3.66 (d, $J = 14.6$ Hz, 1H), 3.47 (d, $J = 16.5$ Hz, 1H), 3.31 (d, $J = 14.6$ Hz, 1H), 2.50 (d, $J = 16.5$ Hz, 1H), 2.42 (s, 6H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.1, 147.4, 145.4, 140.0, 139.2, 135.8, 134.0, 133.9, 129.8, 129.0, 128.5, 128.3, 128.2, 128.1, 127.4, 126.4, 122.5, 122.1, 53.5, 53.5, 48.8, 36.5. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 430.1477, found 430.1474.

N-ethyl-N-methyl-1-(5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methanesulfonamide (**5t**)



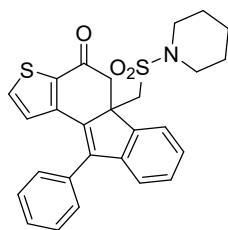
White solid. 60.3 mg. Yield: 68%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 160-162°C. ^1H NMR (400 MHz, CDCl_3) δ 8.15 – 8.06 (m, 1H), 7.64 (dd, $J = 5.8, 2.7$ Hz, 1H), 7.51 – 7.39 (m, 5H), 7.39 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 7.24 – 7.19 (m, 1H), 3.66 (d, $J = 14.6$ Hz, 1H), 3.47 (d, $J = 16.5$ Hz, 1H), 3.30 (d, $J = 14.5$ Hz, 1H), 2.84 (dq, $J = 14.2, 7.1$ Hz, 1H), 2.67 (dq, $J = 14.1, 7.1$ Hz, 1H), 2.49 (d, $J = 16.5$ Hz, 1H), 2.40 (s, 3H), 0.97 (t, $J = 7.1$ Hz, 3H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.2, 147.4, 145.3, 140.0, 139.3, 135.8, 134.0, 129.8, 129.0, 128.4, 128.3, 128.2, 128.1, 127.4, 126.4, 122.7, 122.0, 54.7, 53.6, 48.9, 44.1, 32.9, 13.4. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 466.1453, found 466.1453.

N,N-diethyl-1-(5-oxo-11-phenyl-5,6-dihydro-6aH-benzo[a]fluoren-6a-yl)methanesulfonamide (**5u**)

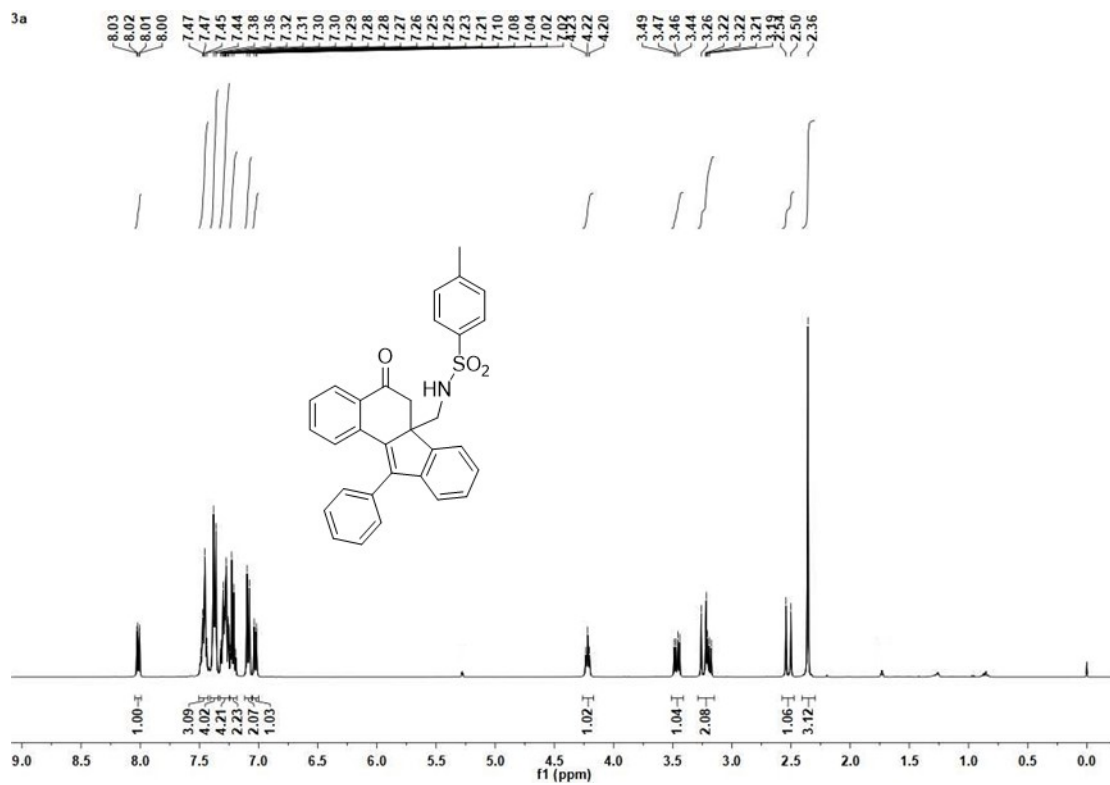


White solid. 60.4 mg. Yield: 66%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 168-170°C. ^1H NMR (400 MHz, CDCl_3) δ 8.13 – 8.08 (m, 1H), 7.68 (dd, $J = 5.6, 2.9$ Hz, 1H), 7.51 – 7.40 (m, 5H), 7.39 – 7.32 (m, 4H), 7.28 – 7.25 (m, 1H), 7.23 – 7.19 (m, 1H), 3.57 (t, $J = 15.9$ Hz, 2H), 3.22 (d, $J = 14.3$ Hz, 1H), 2.99 – 2.79 (m, 4H), 2.50 (d, $J = 16.5$ Hz, 1H), 0.98 (t, $J = 7.1$ Hz, 6H). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 196.3, 147.4, 145.3, 140.2, 139.2, 135.8, 134.1, 133.9, 129.8, 129.0, 128.4, 128.2, 128.2, 128.0, 127.4, 126.4, 123.0, 121.9, 56.5, 53.7, 48.5, 41.7, 14.6. HRMS (ESI) m/z calcd for $\text{C}_{28}\text{H}_{28}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 458.1790, found 458.1792.

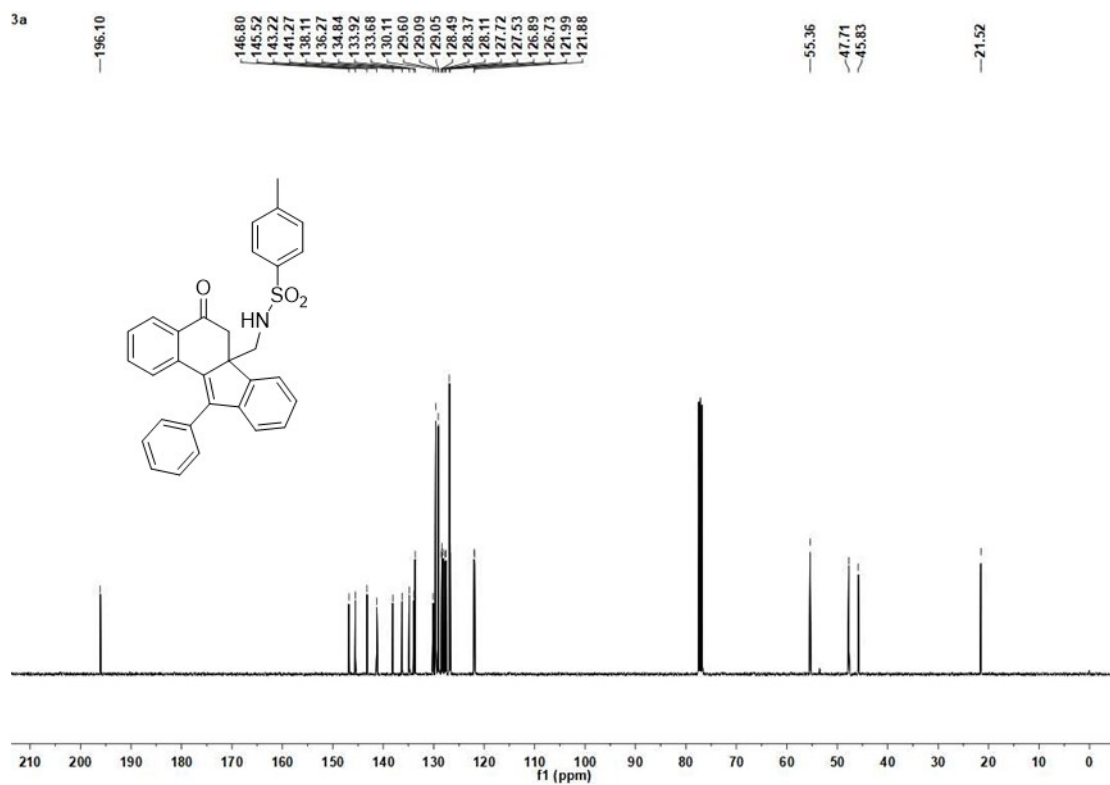
10-Phenyl-5a-((piperidin-1-ylsulfonyl)methyl)-5,5a-dihydro-4H-fluoreno[2,1-b]thiophen-4-one (**5v**)



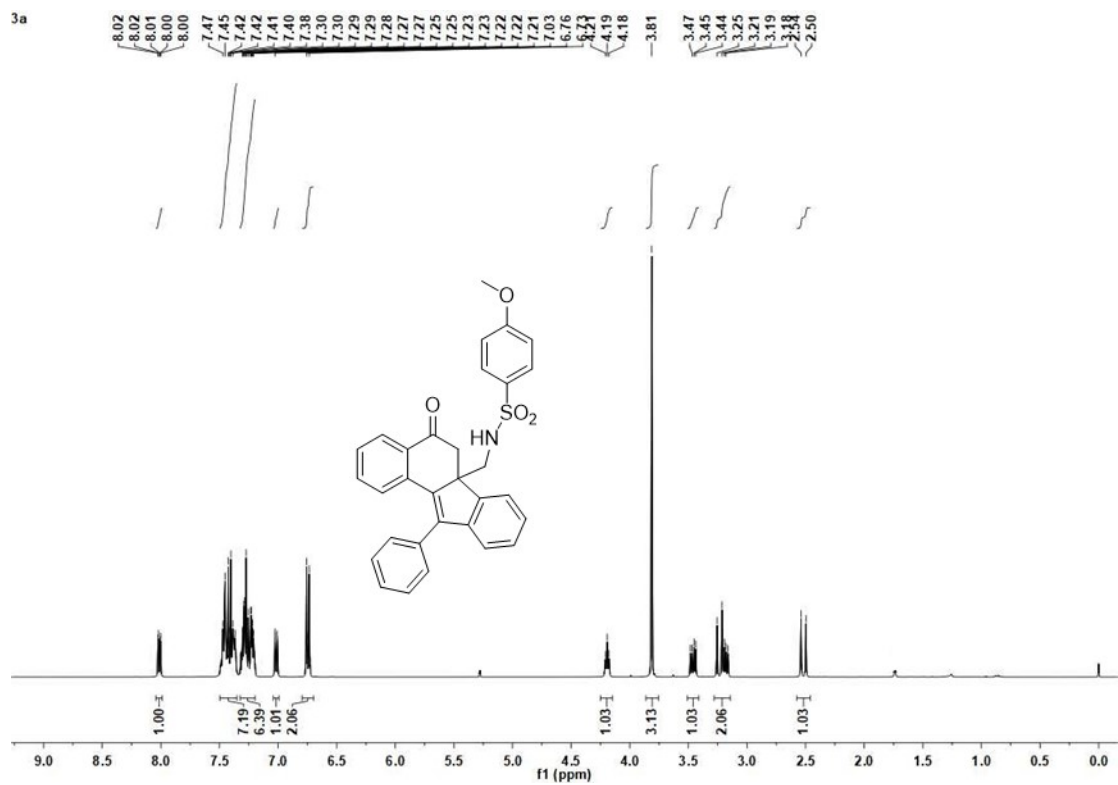
White solid. 65.6 mg. Yield: 69%. Purification by column chromatography (EtOAc/Pe, 1:8 v/v). mp 197-199°C. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 5.6, 2.8 Hz, 1H), 7.57 (d, *J* = 5.1 Hz, 1H), 7.54 – 7.44 (m, 5H), 7.40 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 6.89 (d, *J* = 5.1 Hz, 1H), 3.61 (d, *J* = 14.3 Hz, 1H), 3.43 (d, *J* = 16.2 Hz, 1H), 3.28 (d, *J* = 14.2 Hz, 1H), 2.96 – 2.85 (m, 2H), 2.78 (dd, *J* = 12.5, 5.1 Hz, 2H), 2.53 (d, *J* = 16.2 Hz, 1H), 1.49 – 1.37 (m, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 190.6, 147.5, 145.2, 143.7, 140.1, 137.1, 135.5, 135.0, 133.7, 129.1, 128.8, 128.6, 128.5, 126.7, 126.7, 123.0, 122.2, 55.0, 54.9, 47.8, 46.0, 25.5, 23.7. HRMS (ESI) *m/z* calcd for C₂₇H₂₆NO₃S₂ [M+H]⁺ 476.1354, found 476.1350.



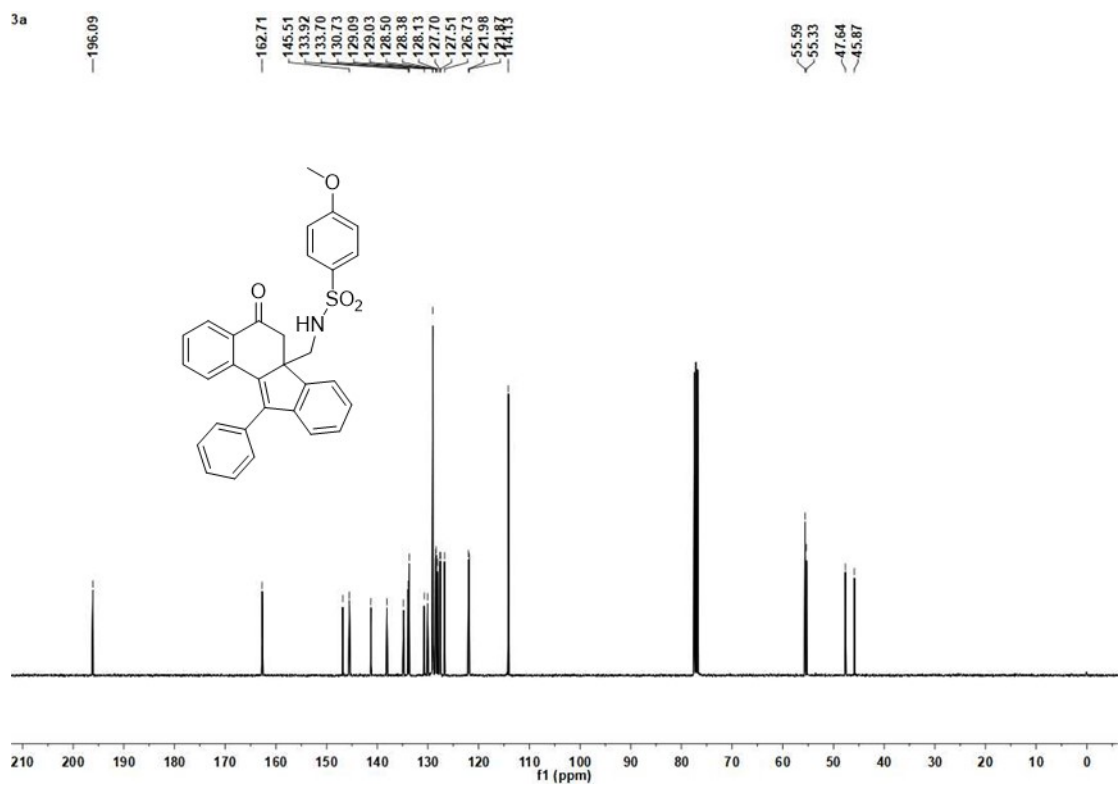
¹³C NMR spectrum of 3ab



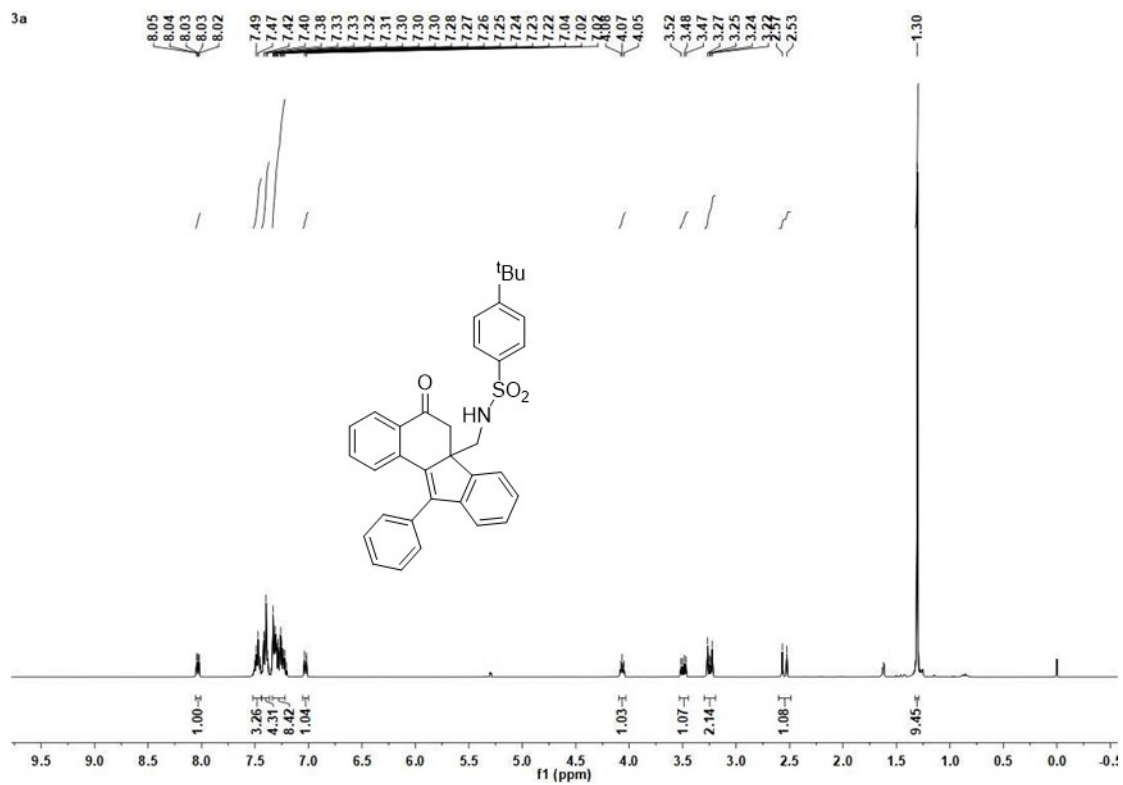
¹H NMR spectrum of 3ac



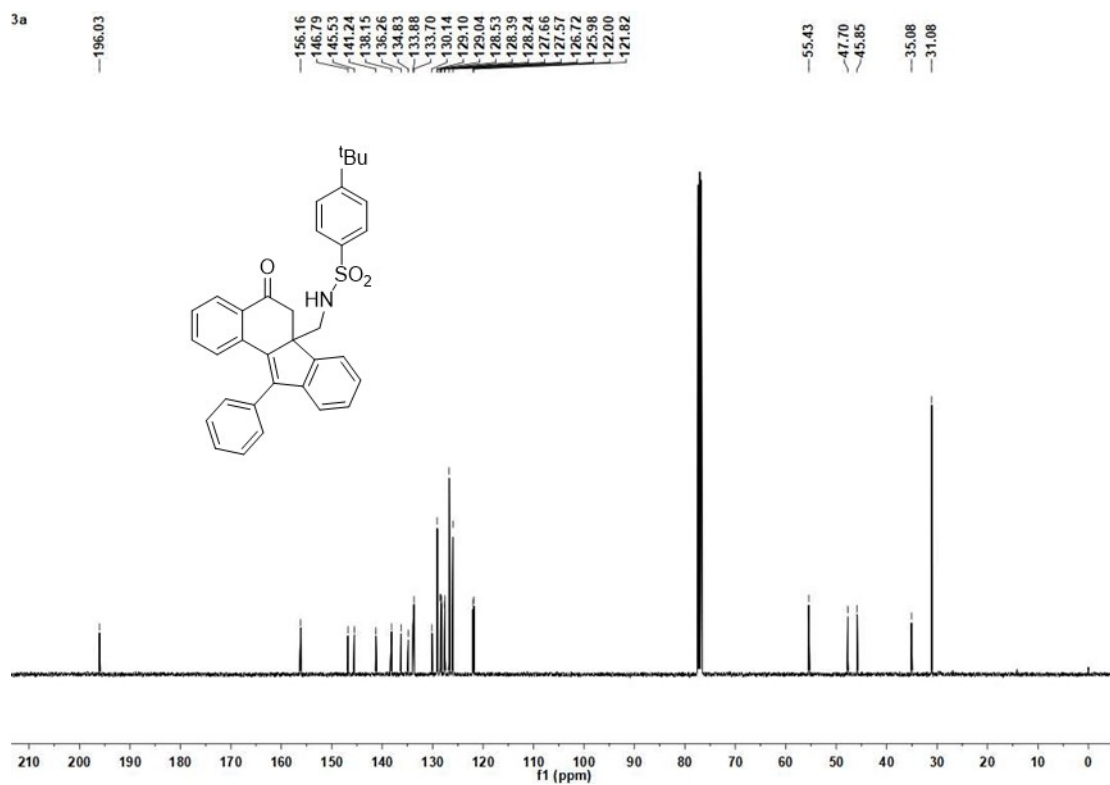
¹³C NMR spectrum of **3ac**



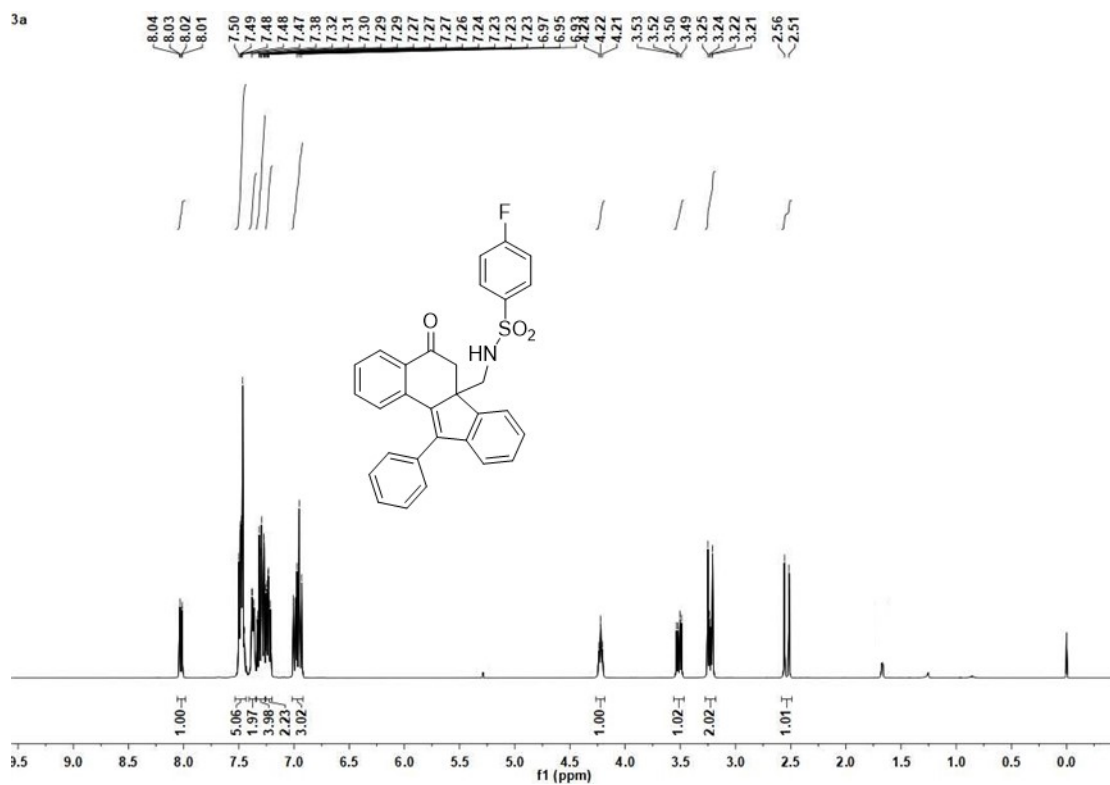
¹H NMR spectrum of **3ad**



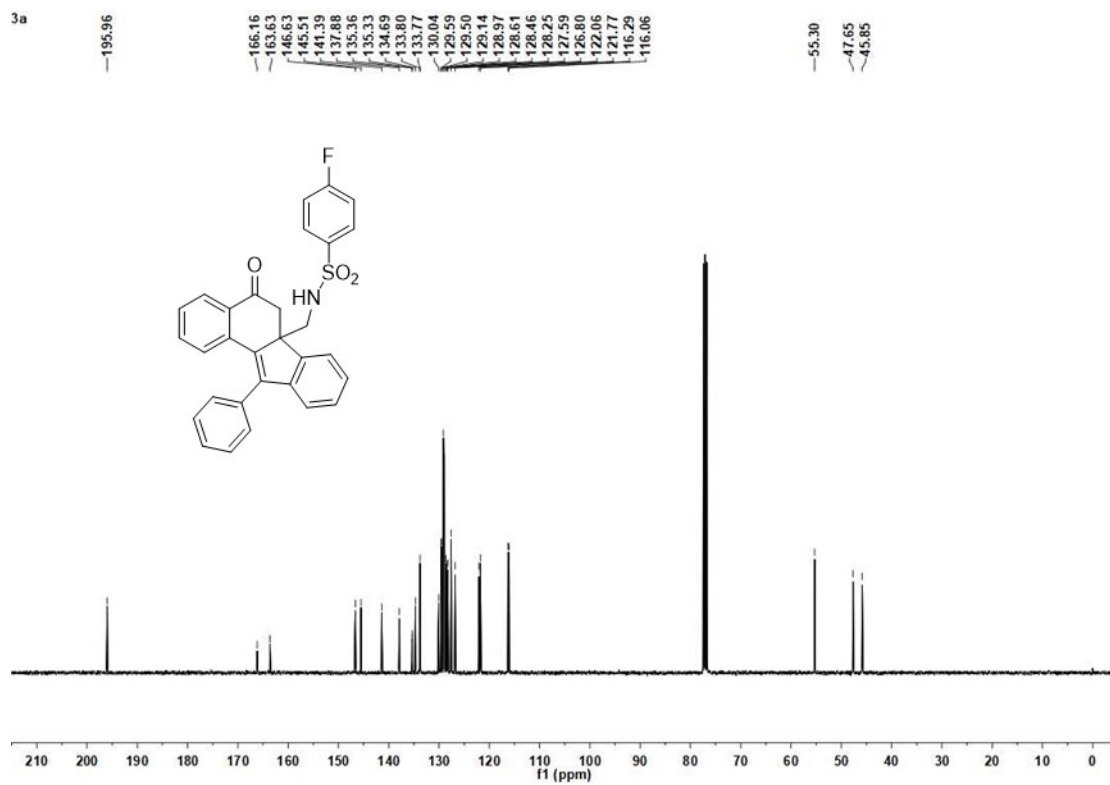
^{13}C NMR spectrum of 3ad



^1H NMR spectrum of 3ae

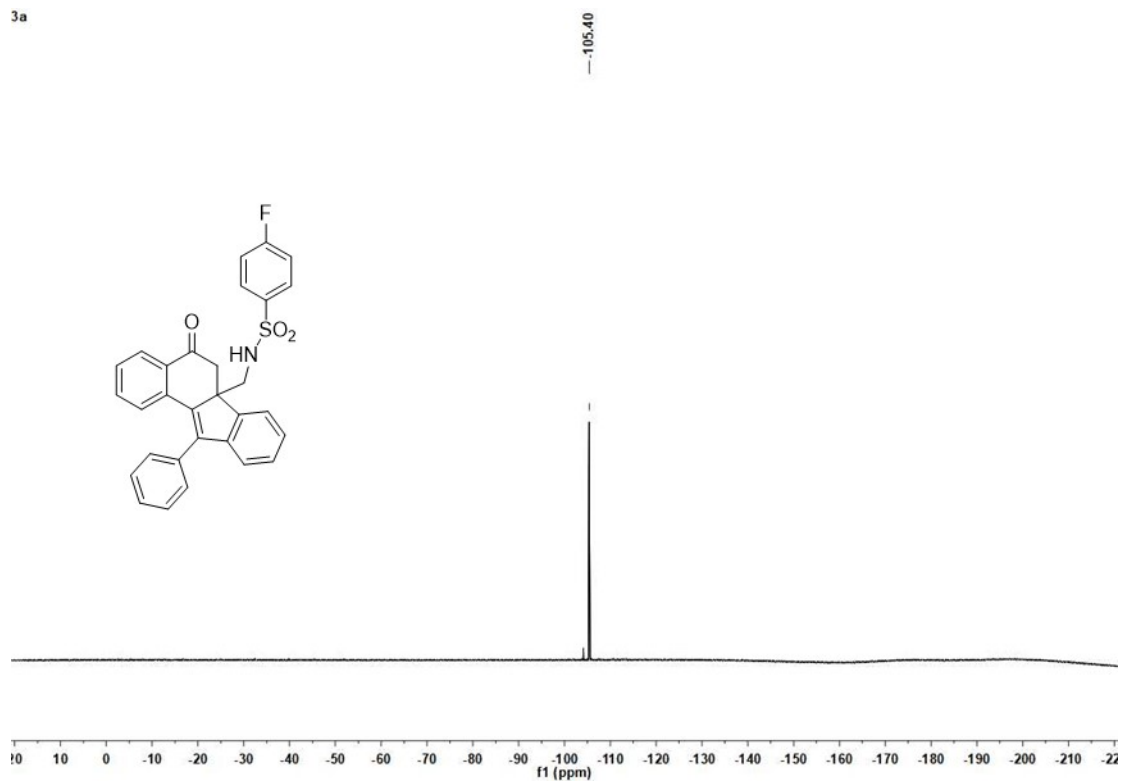


¹³C NMR spectrum of 3a

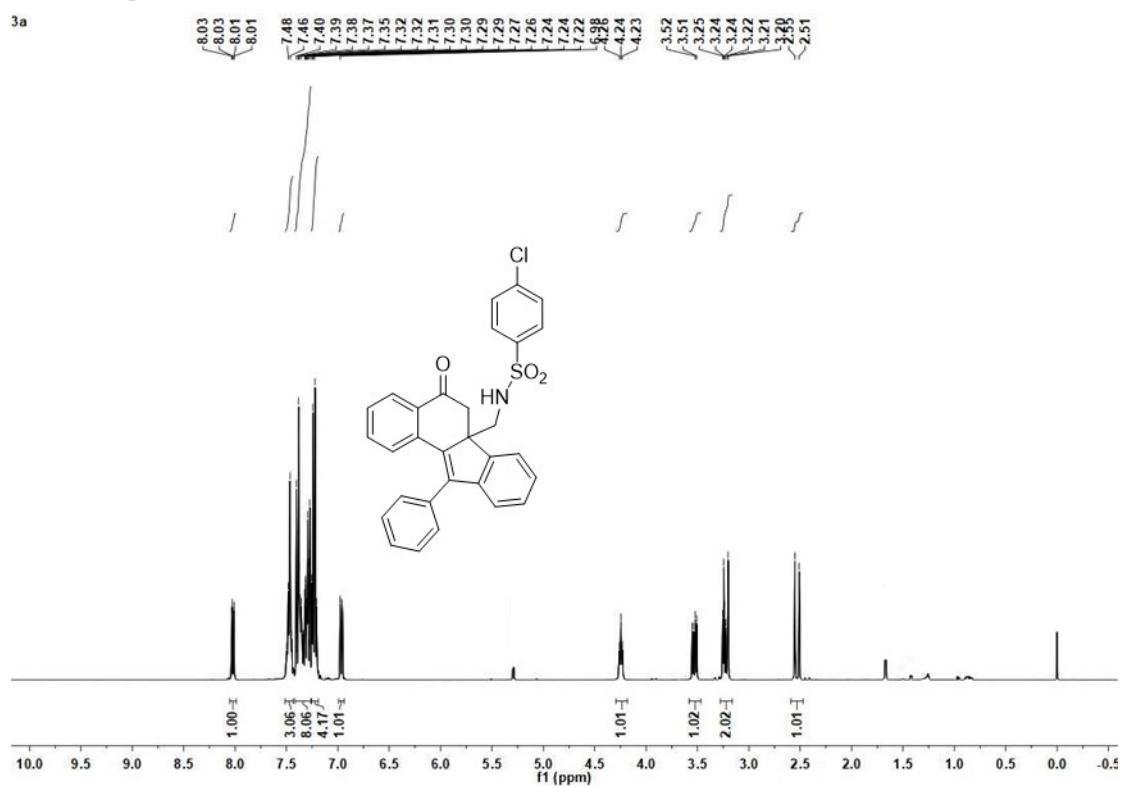


¹⁹F NMR spectrum of 3a

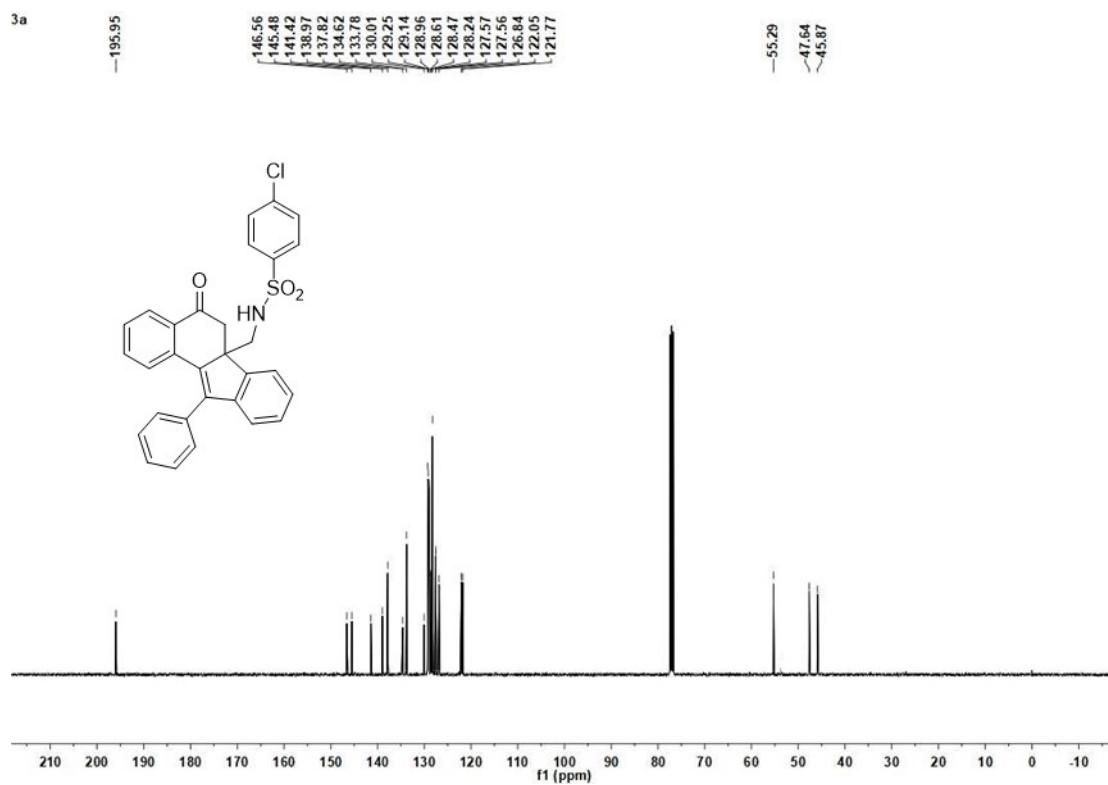
3a



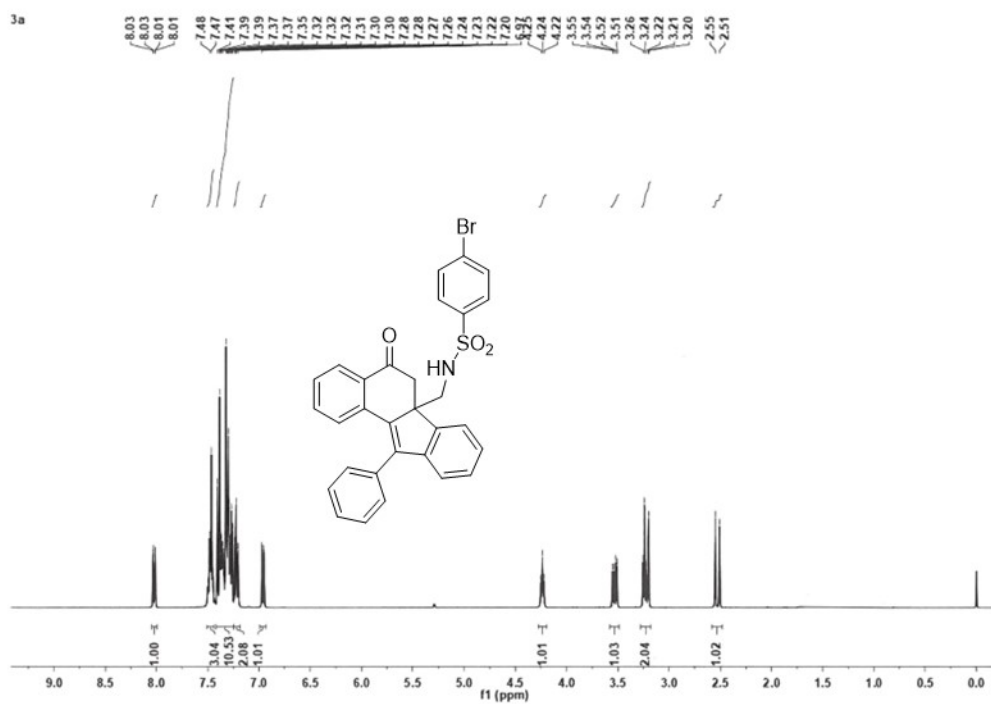
¹H NMR spectrum of 3af



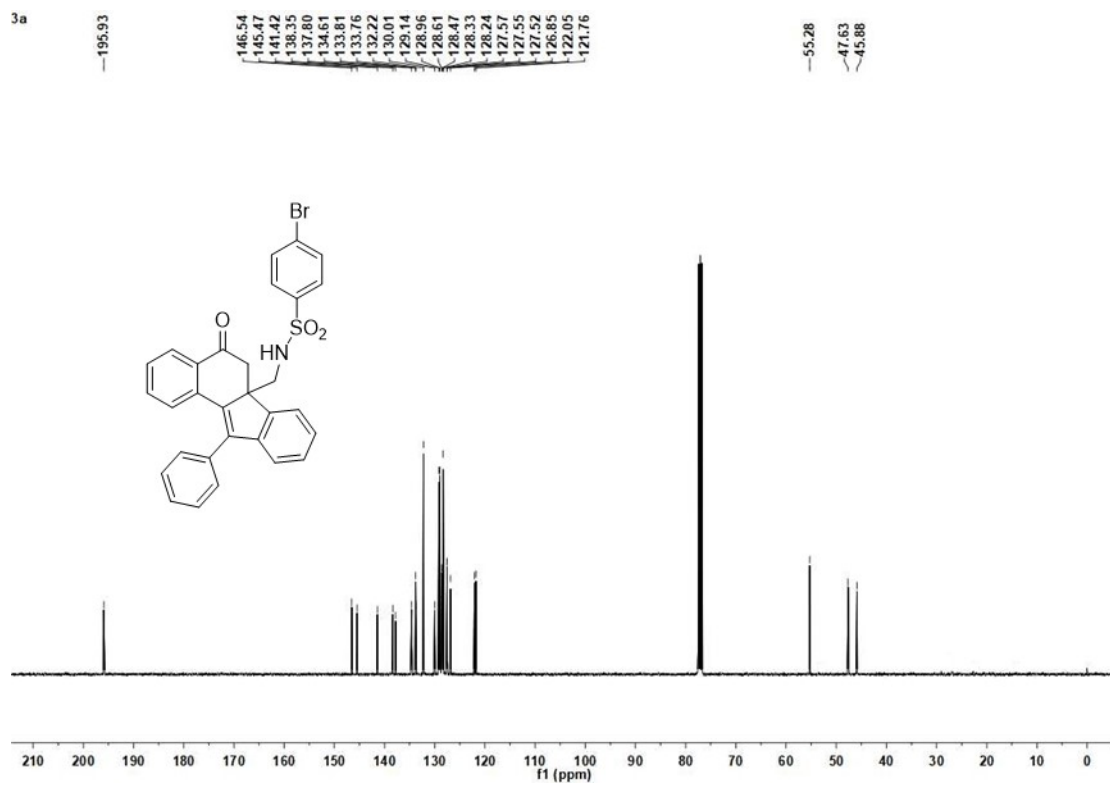
¹³C NMR spectrum of 3af



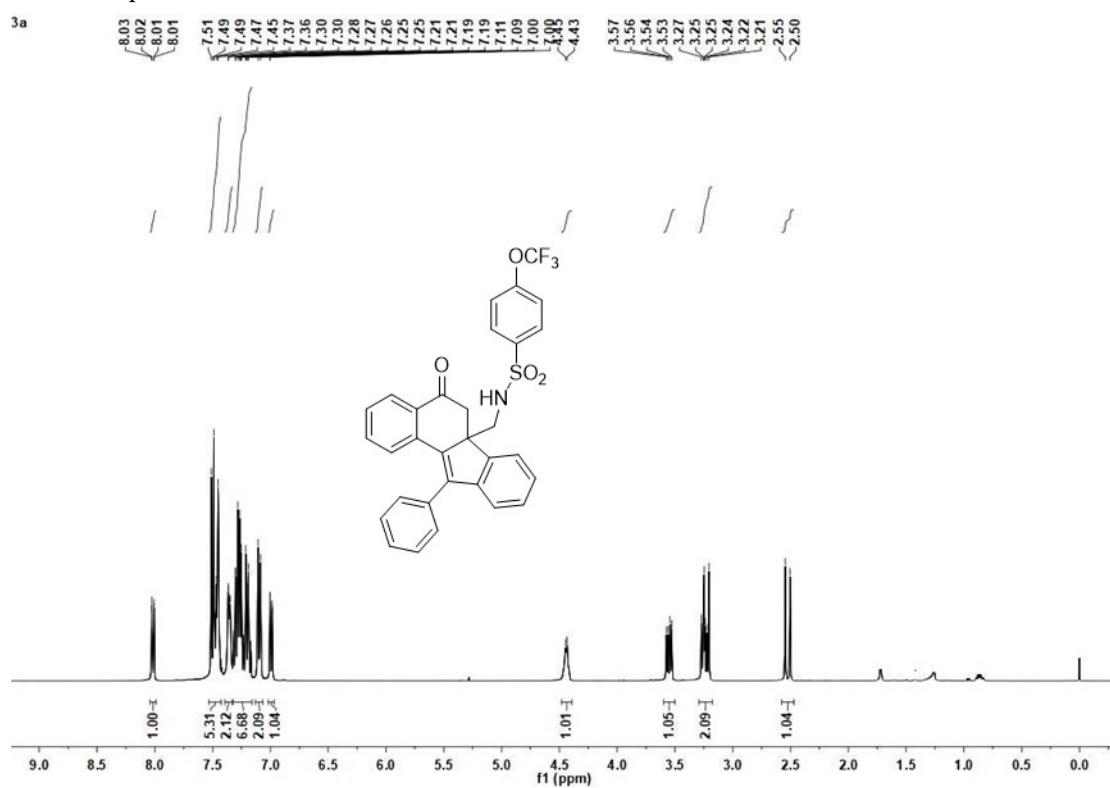
¹H NMR spectrum of 3ag



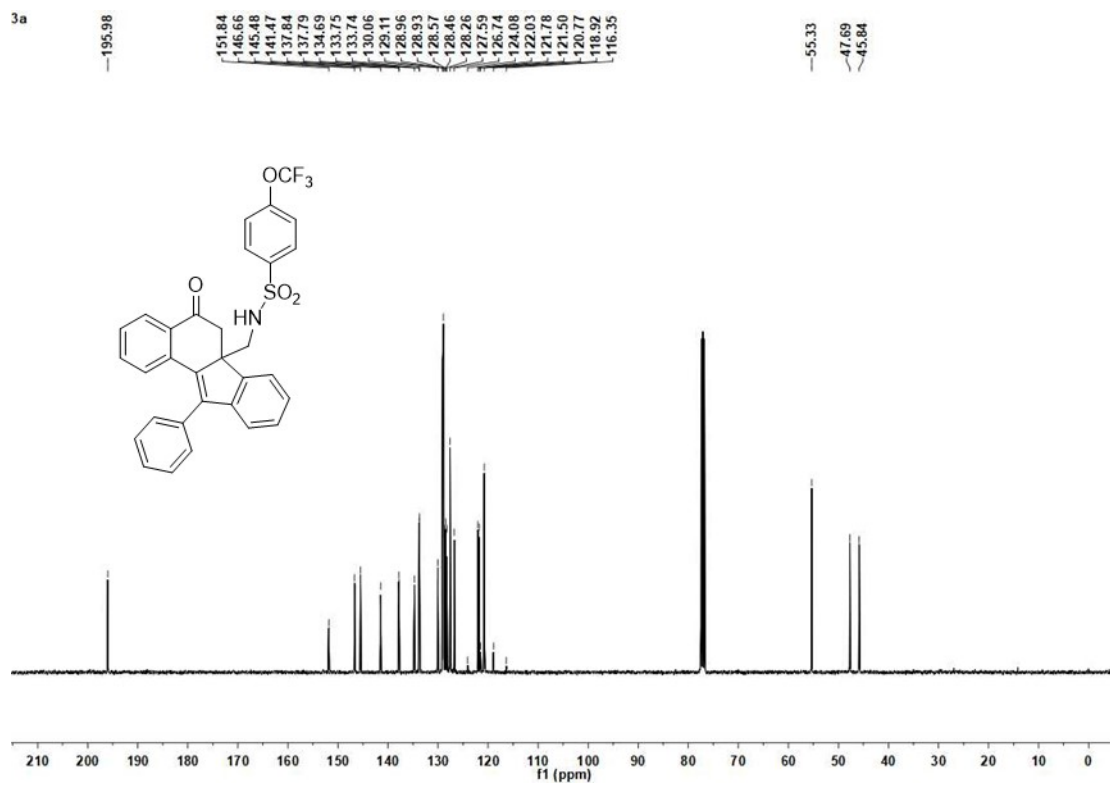
¹³C NMR spectrum of 3ag



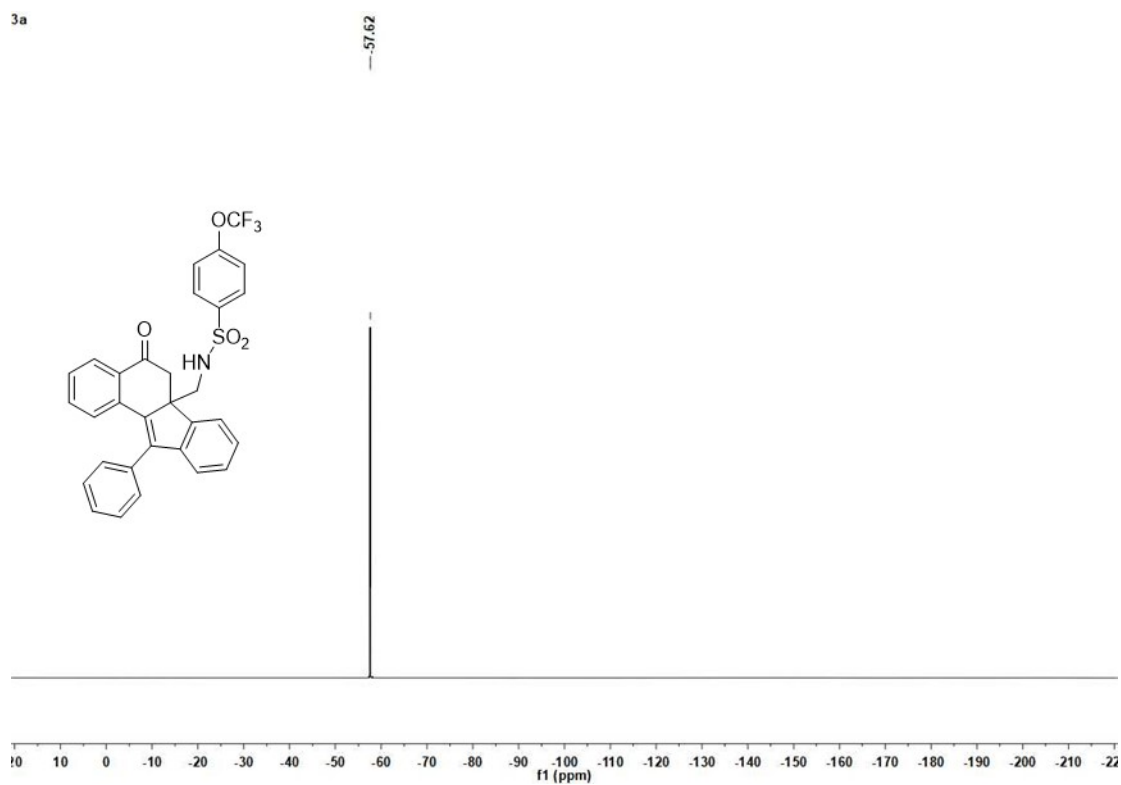
¹H NMR spectrum of 3ah



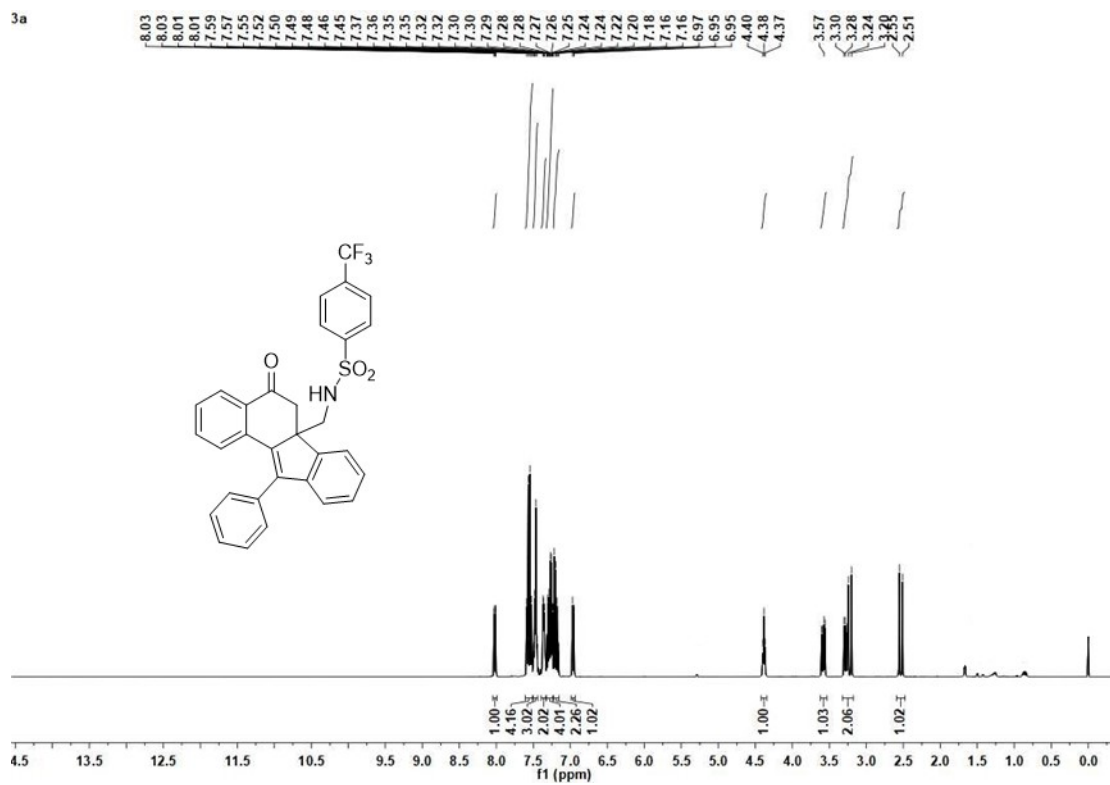
¹³C NMR spectrum of 3ah



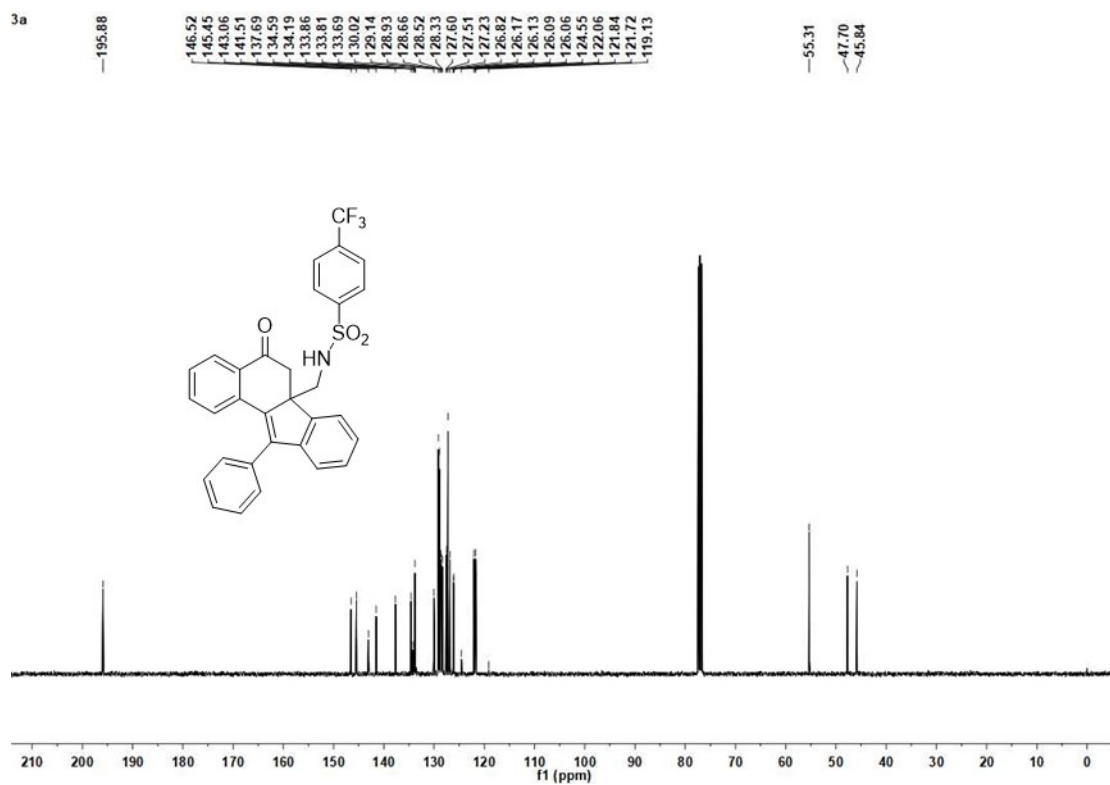
¹⁹F NMR spectrum of 3ah



¹H NMR spectrum of 3ai



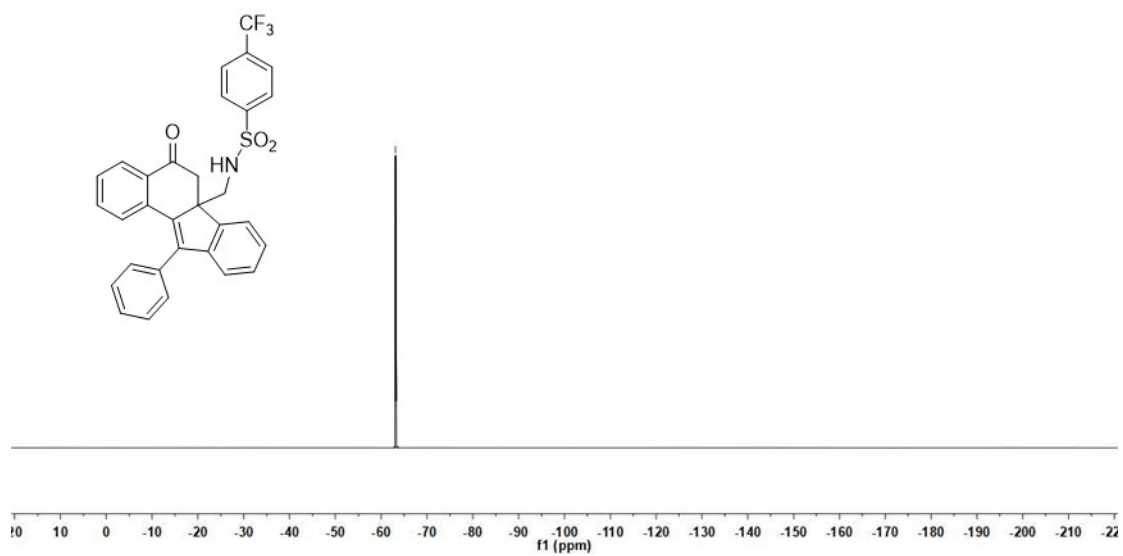
¹³C NMR spectrum of **3ai**



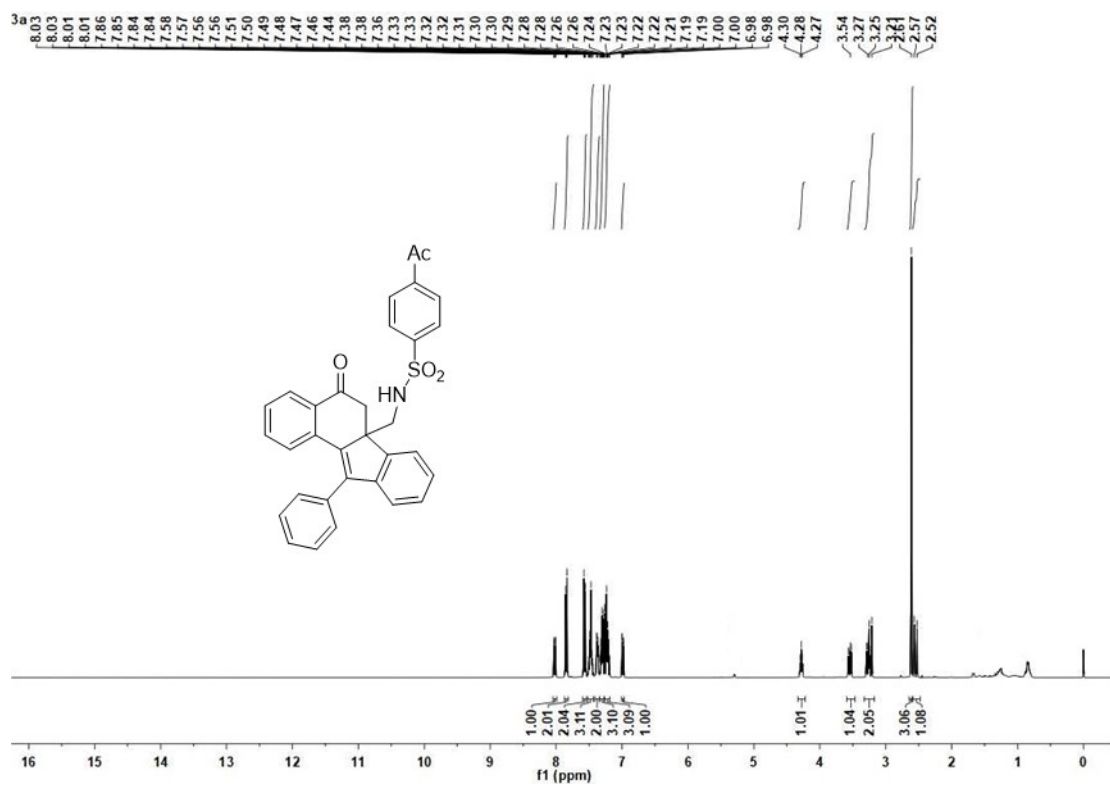
¹⁹F NMR spectrum of **3ai**

3a

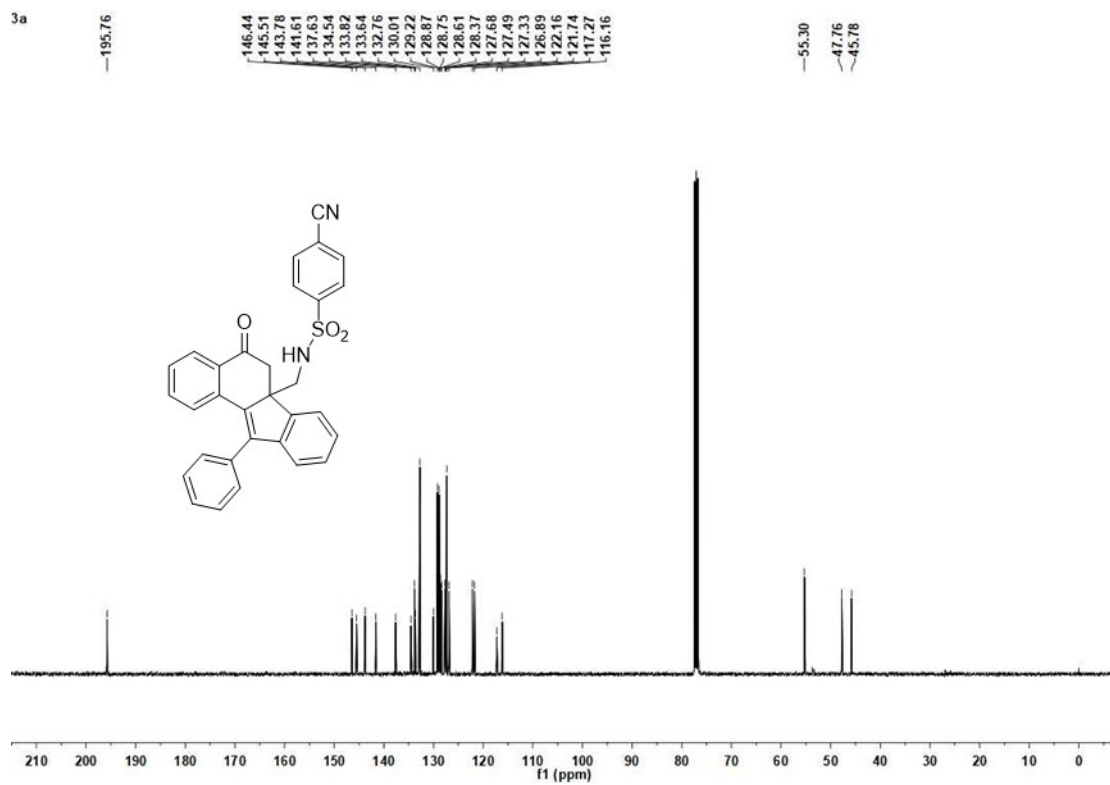
—63.12



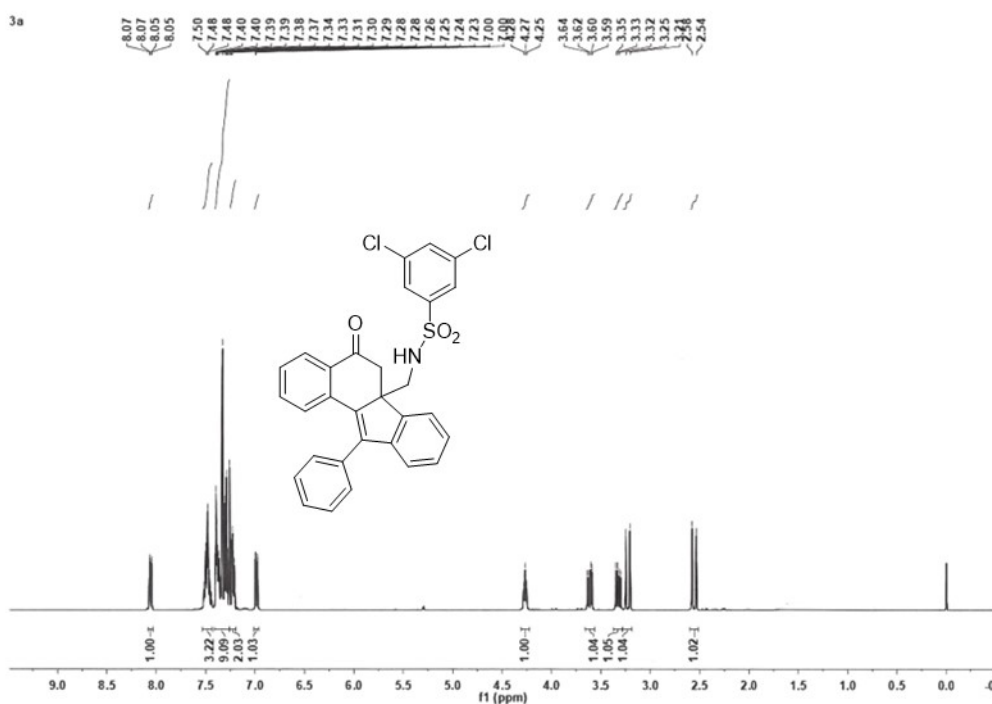
¹H NMR spectrum of 3aj



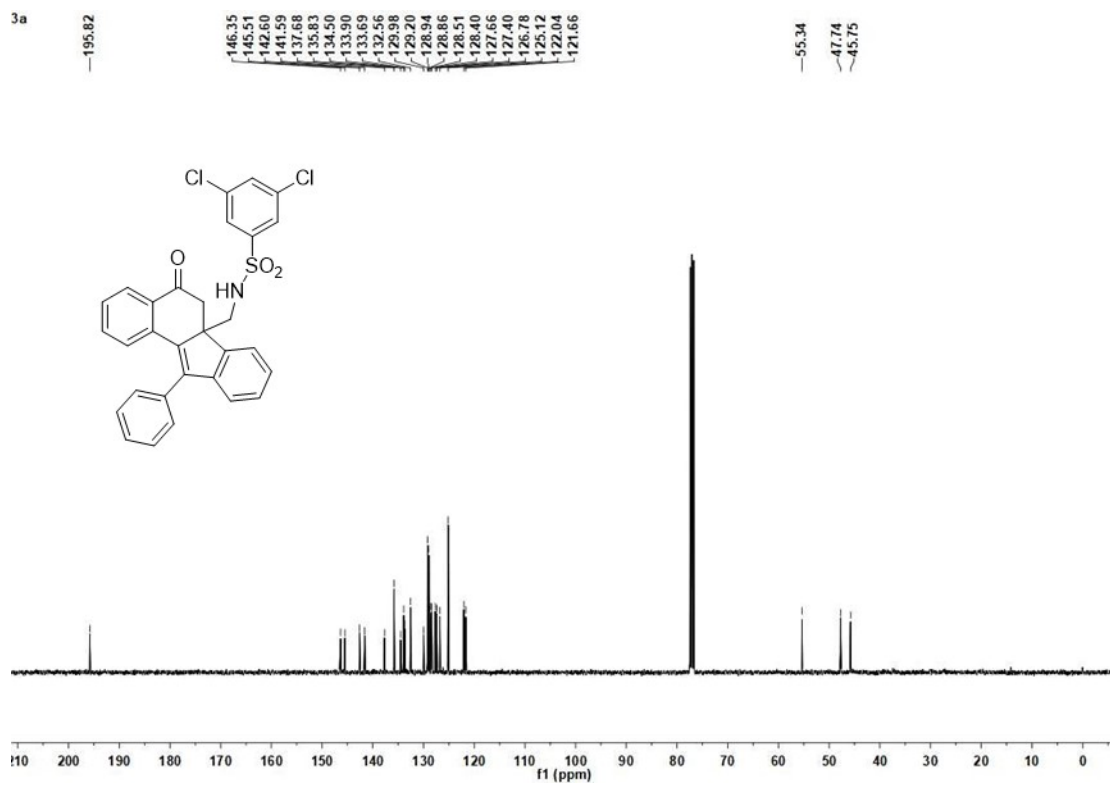
¹³C NMR spectrum of 3aj



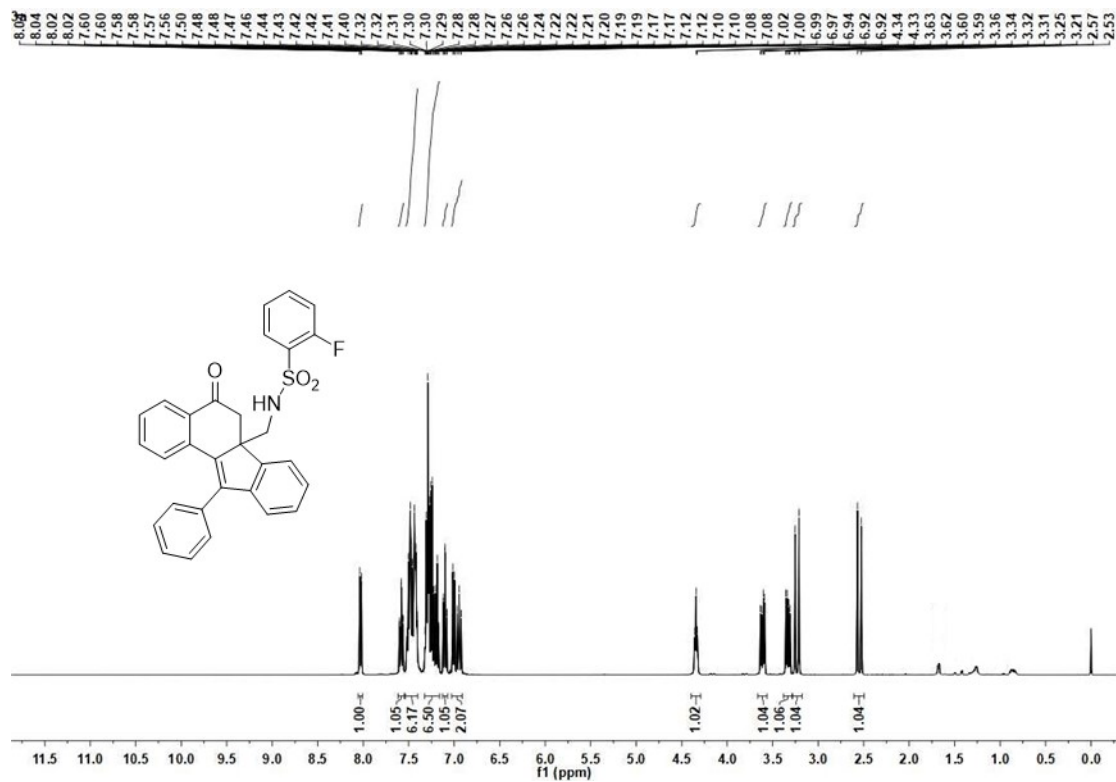
¹H NMR spectrum of 3a



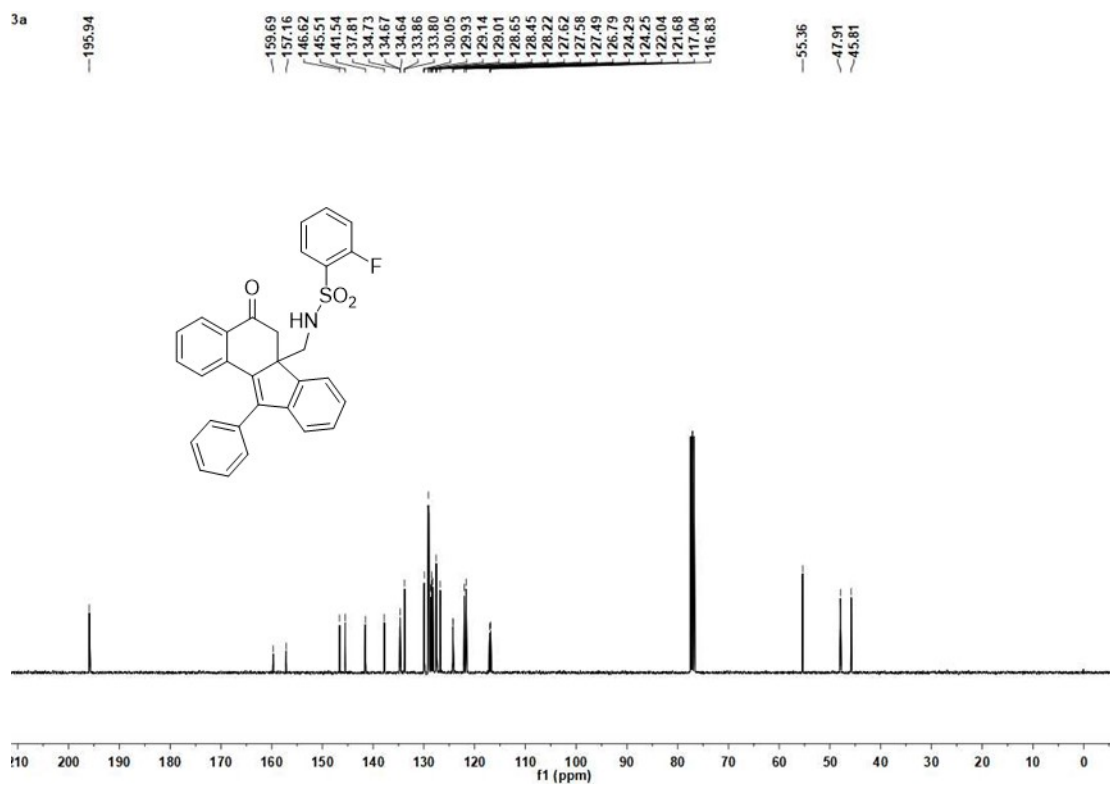
¹³C NMR spectrum of 3a



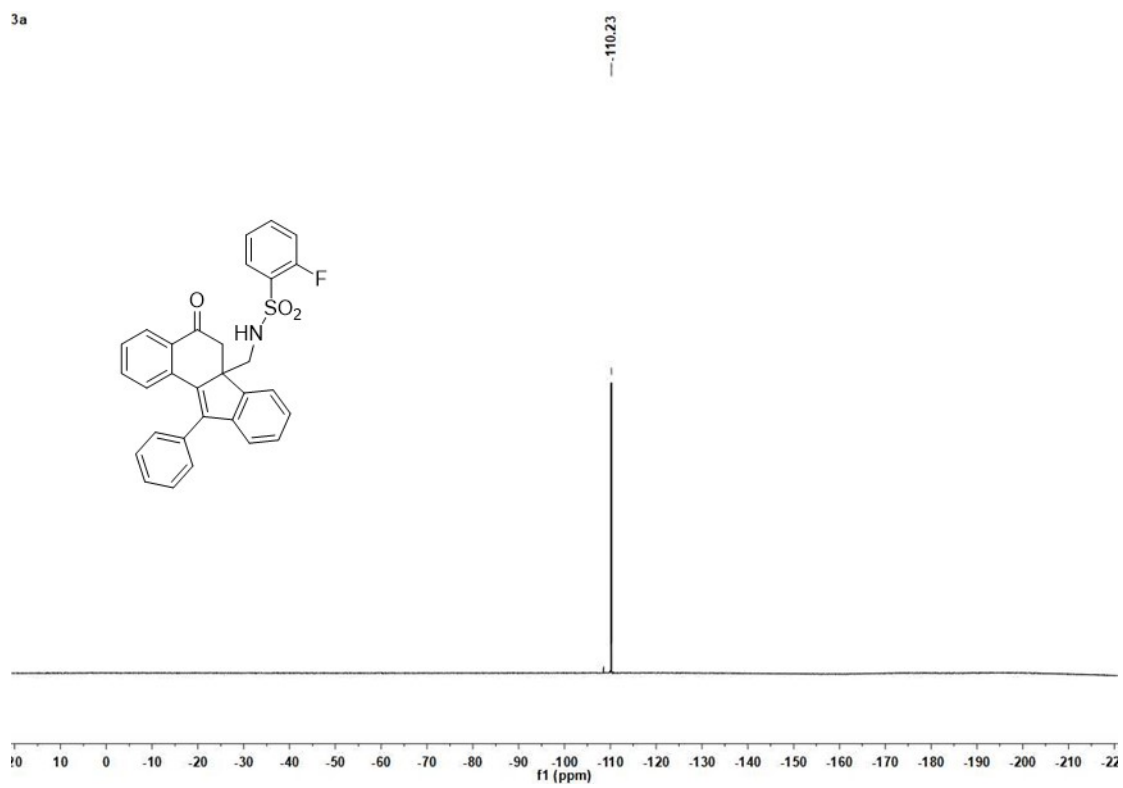
¹H NMR spectrum of 3am



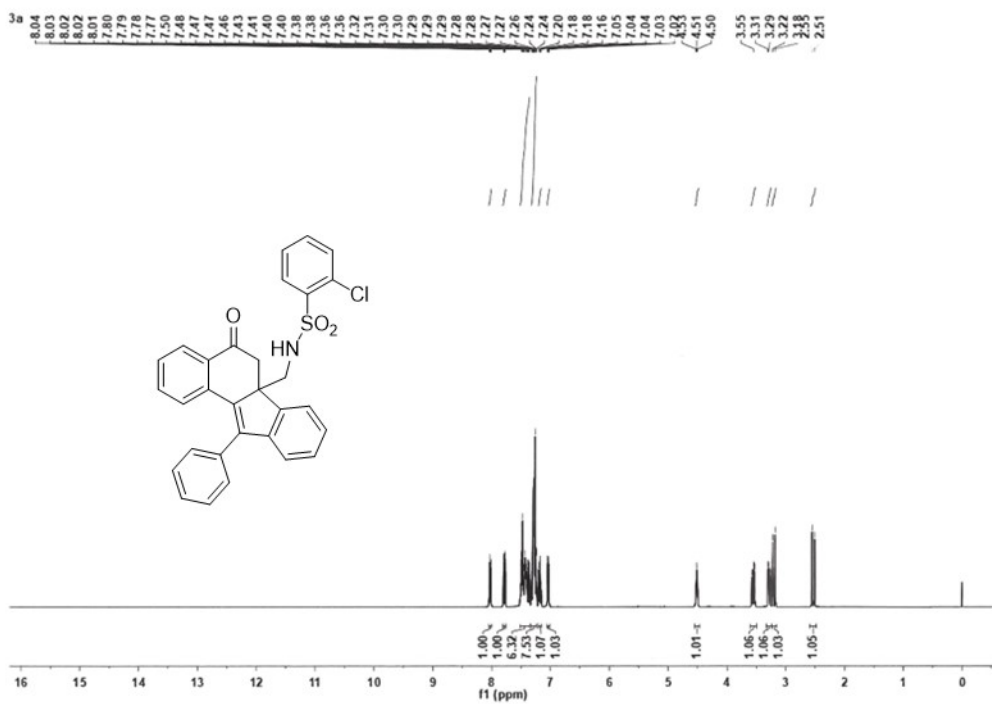
¹³C NMR spectrum of 3am



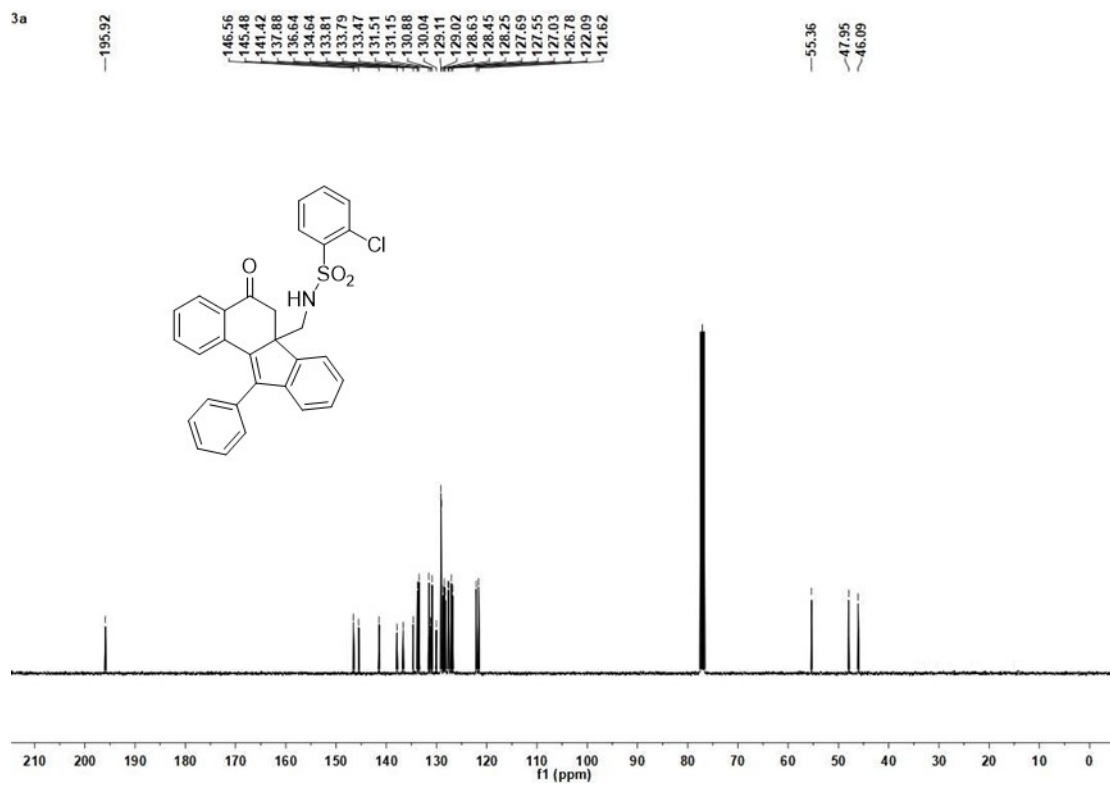
¹⁹F NMR spectrum of **3am**



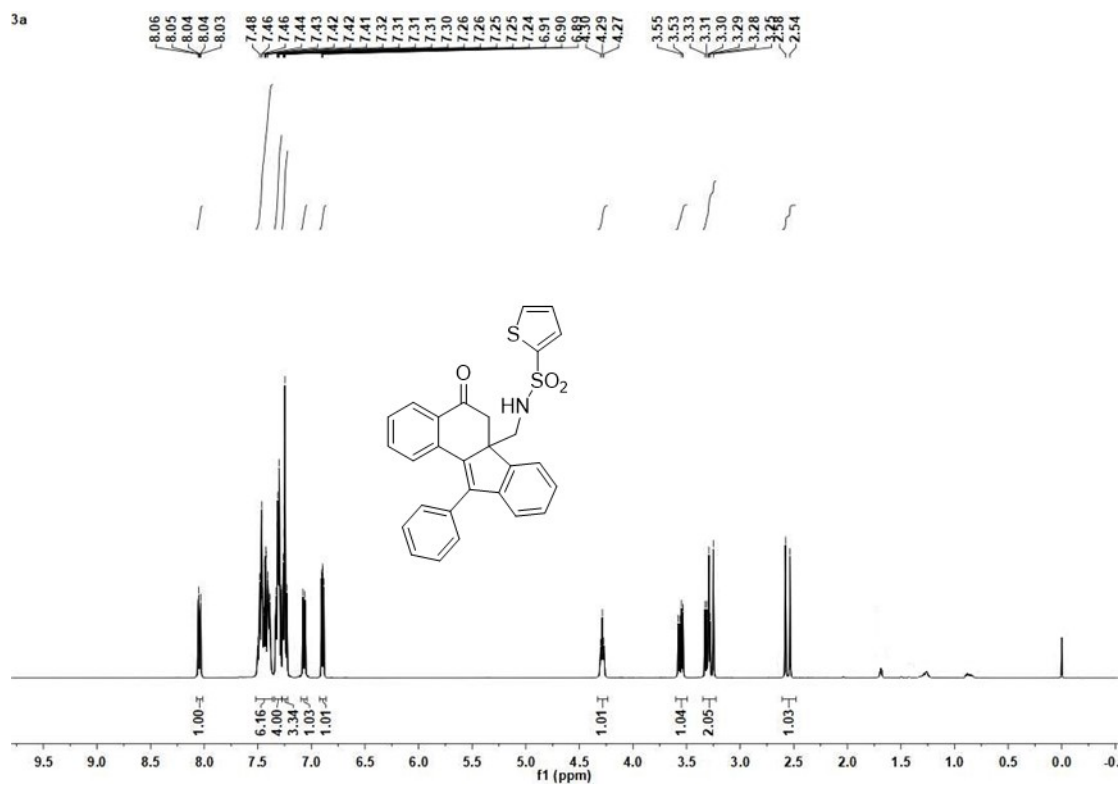
¹H NMR spectrum of **3an**



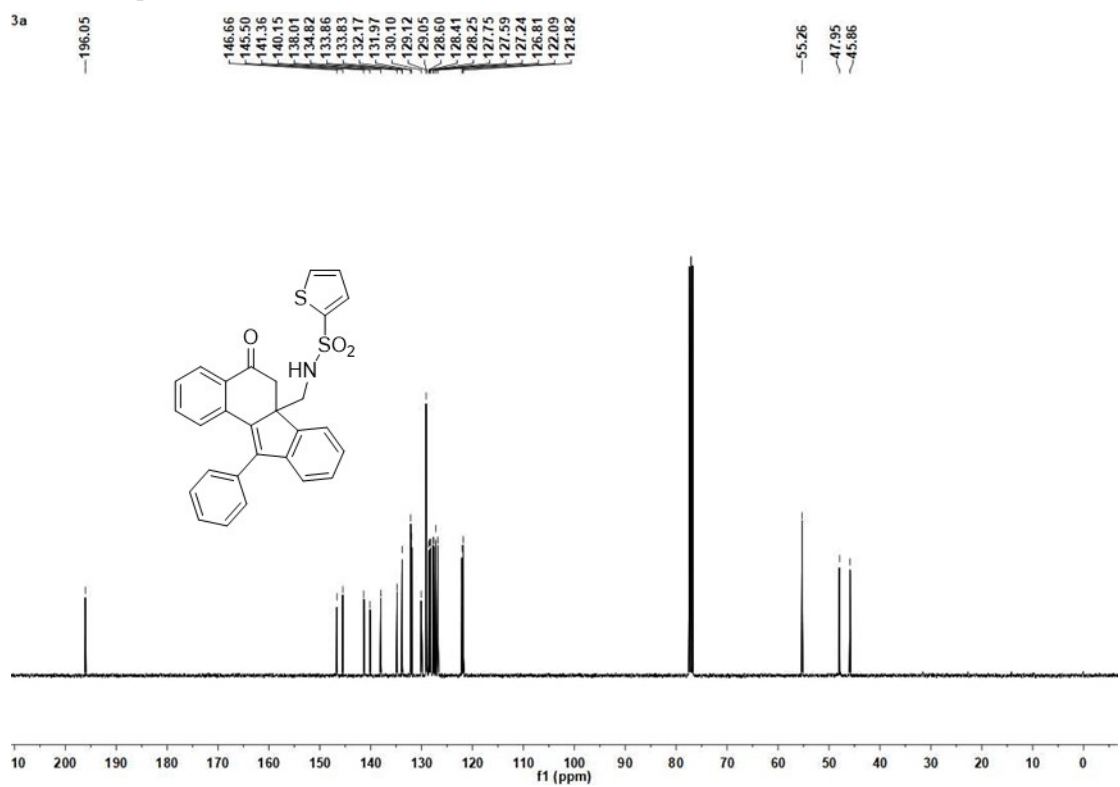
^{13}C NMR spectrum of **3an**



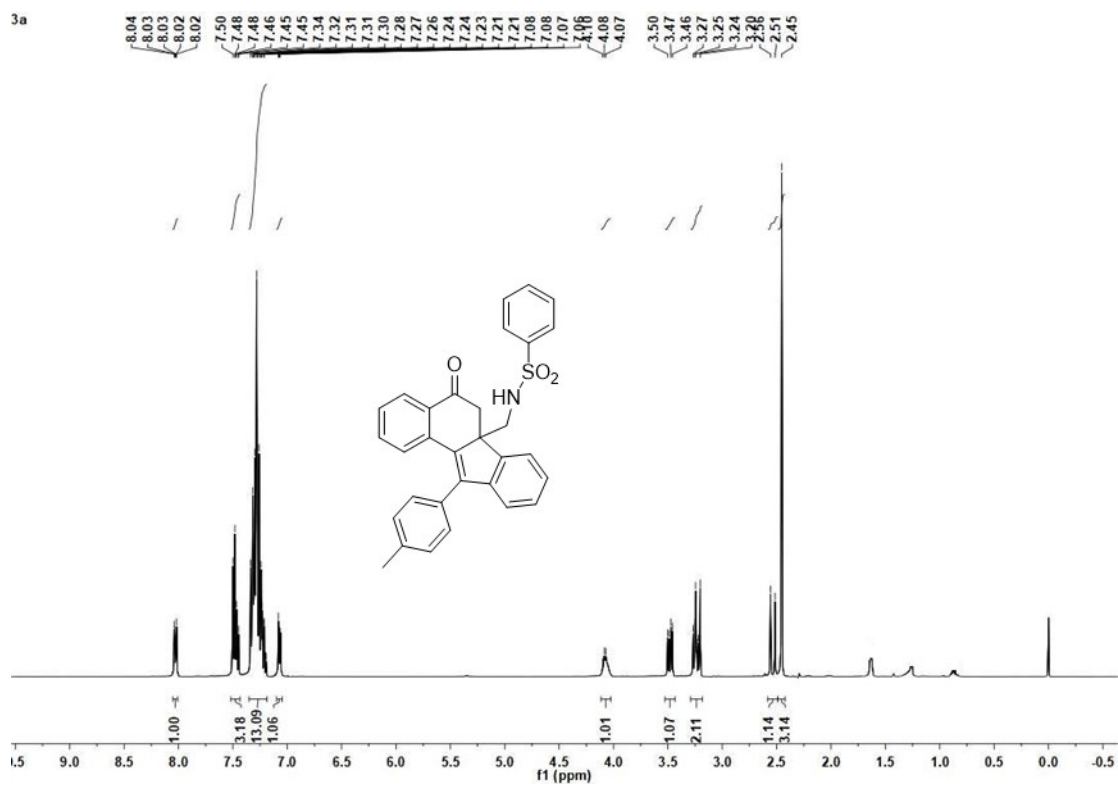
¹H NMR spectrum of 3a



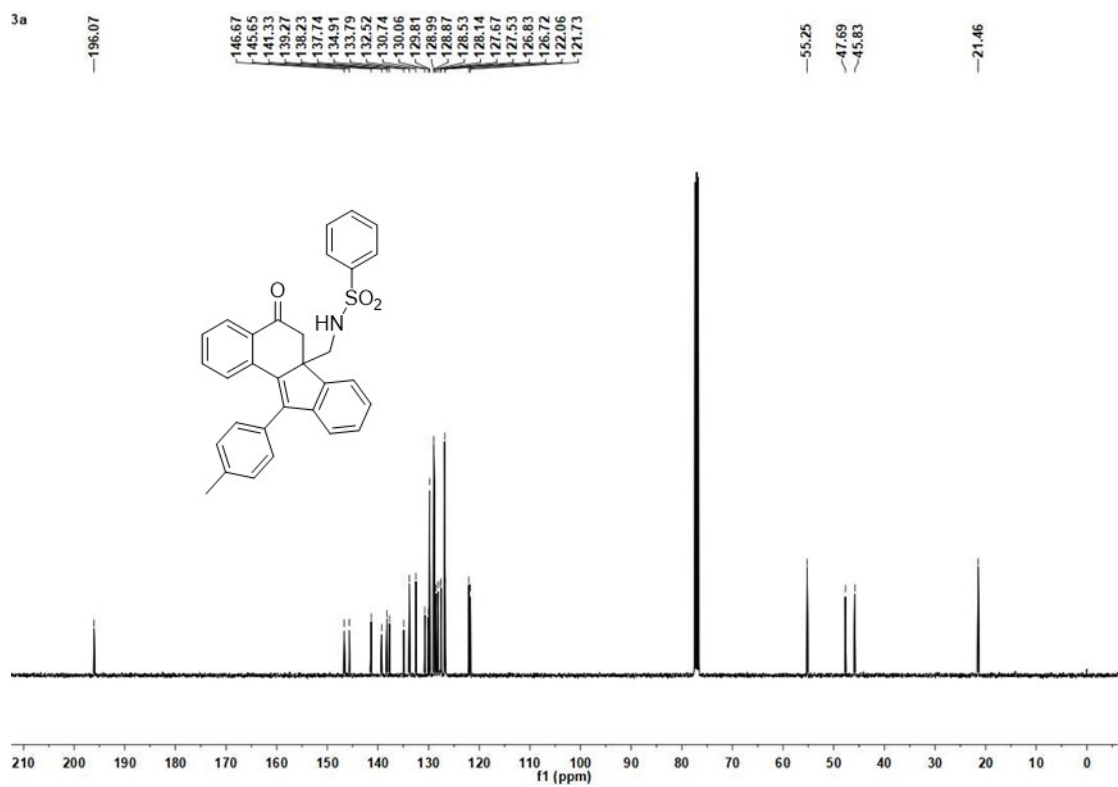
¹³C NMR spectrum of 3a



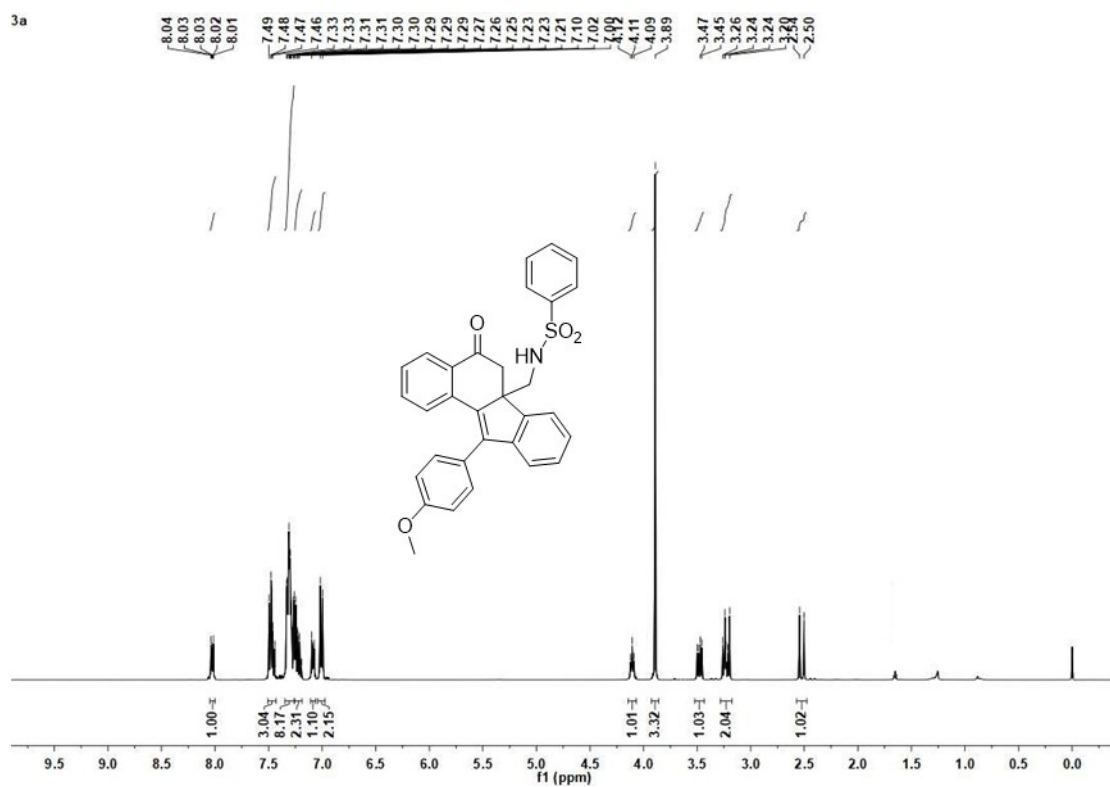
¹H NMR spectrum of **3ba**



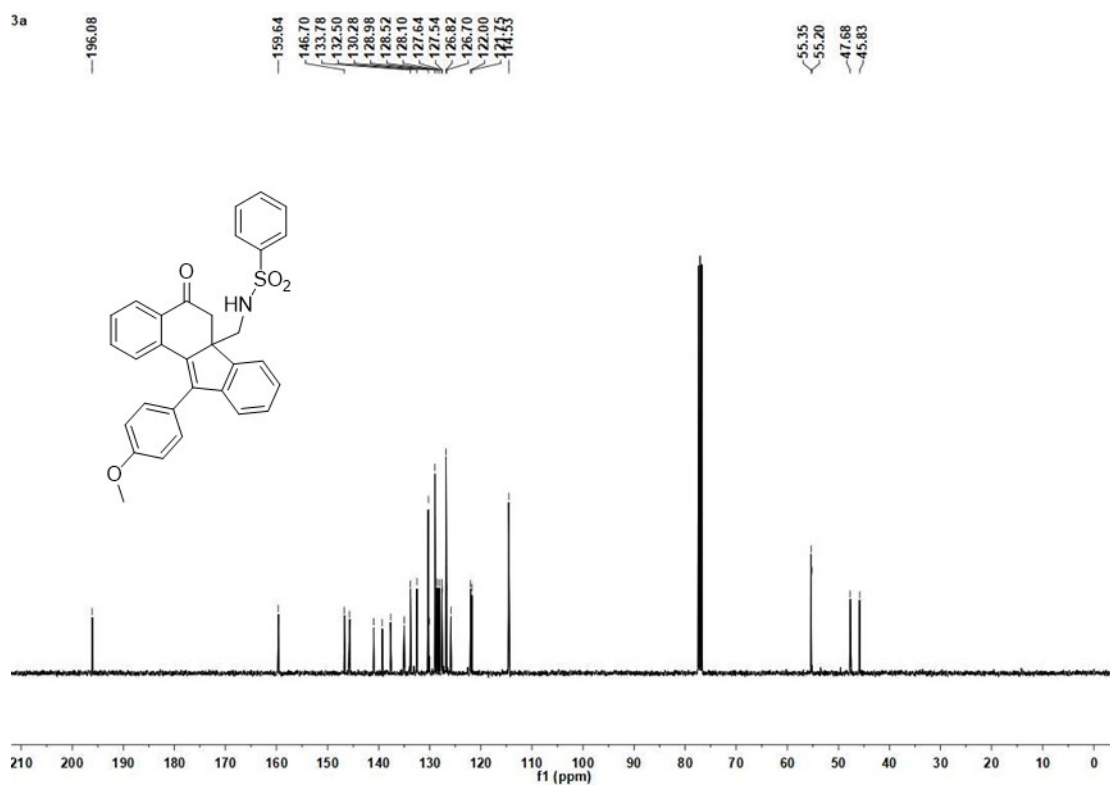
¹³C NMR spectrum of **3ba**



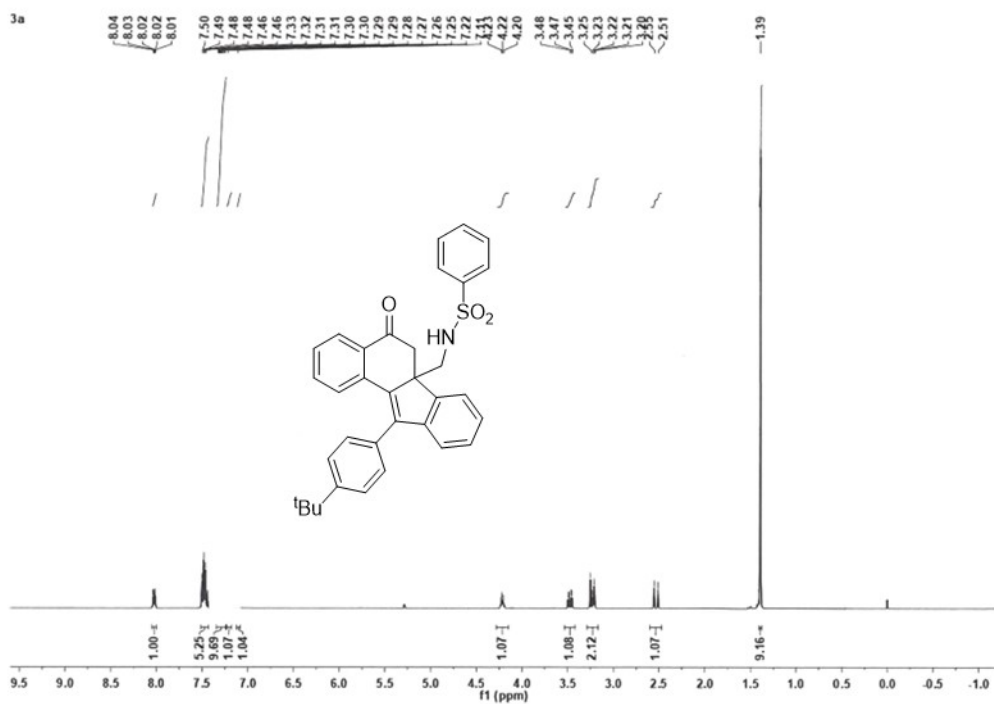
¹H NMR spectrum of **3bb**



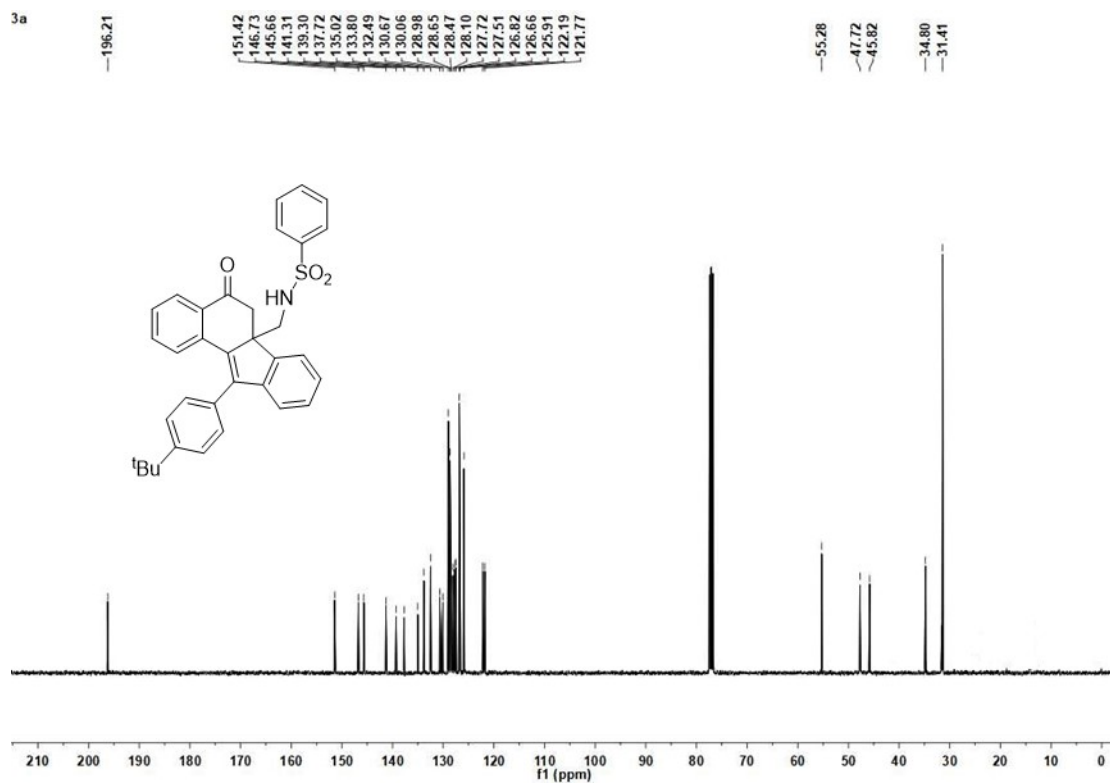
¹³C NMR spectrum of **3bb**



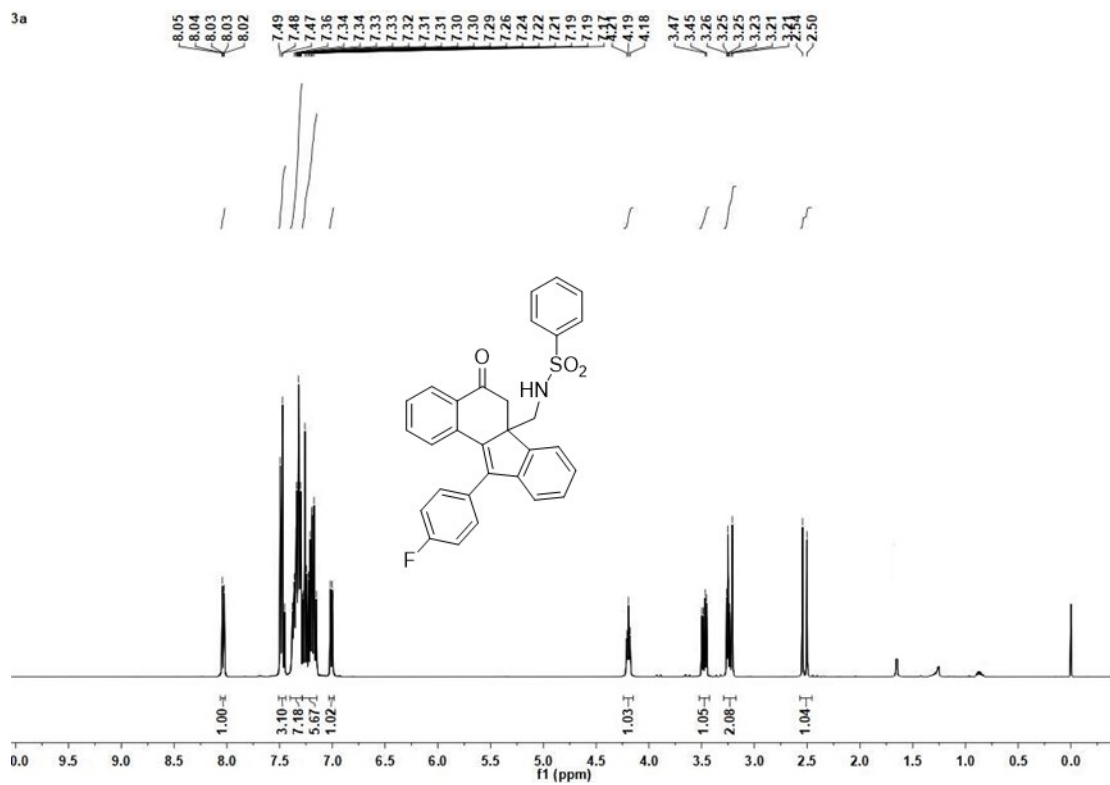
¹H NMR spectrum of **3bc**



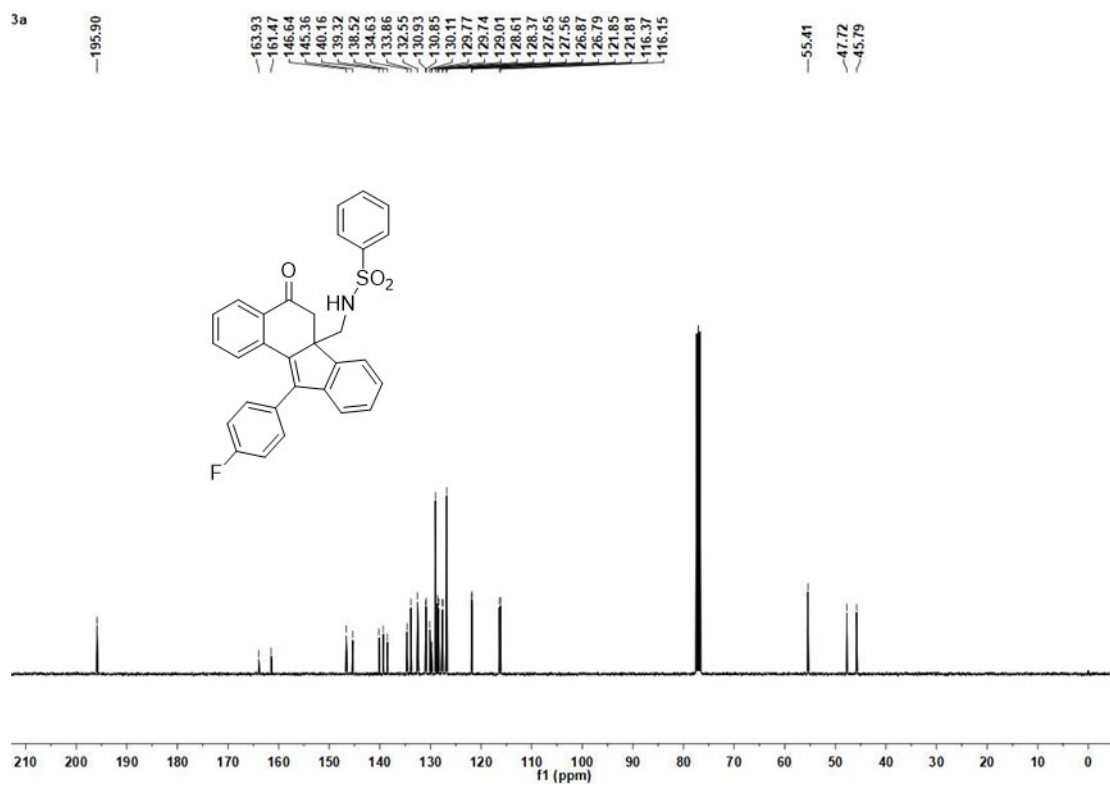
¹³C NMR spectrum of **3bc**



¹H NMR spectrum of **3bd**

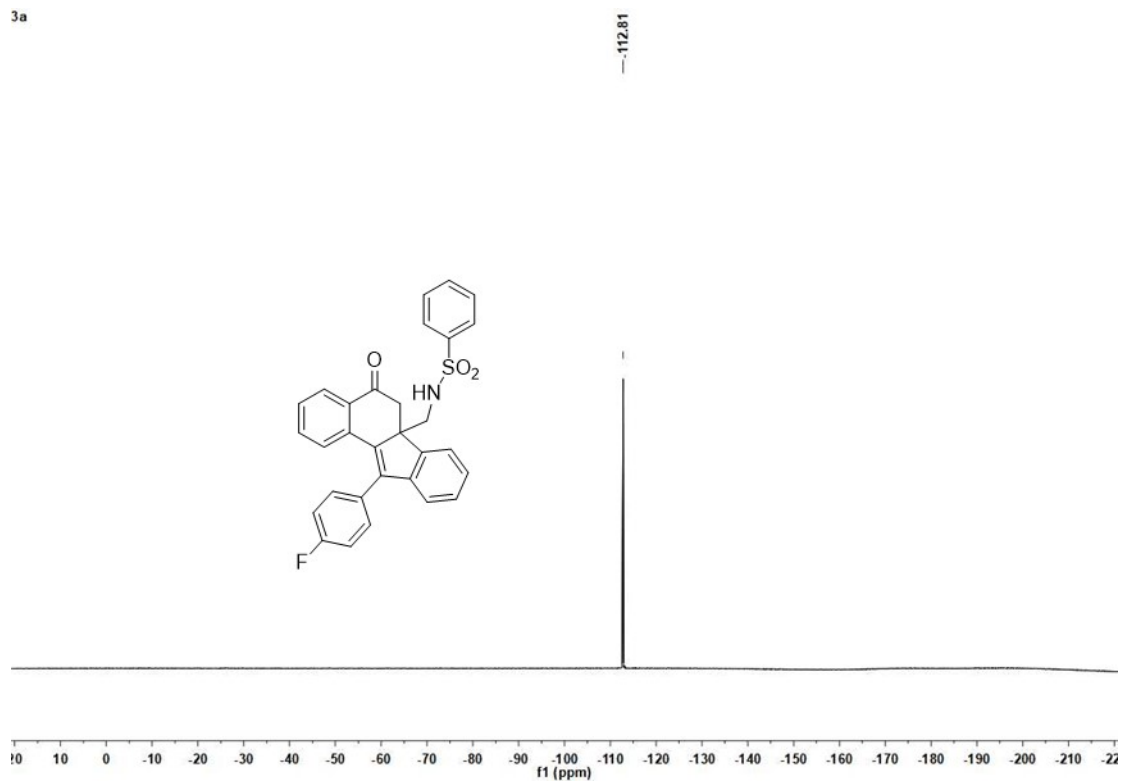


¹³C NMR spectrum of **3bd**

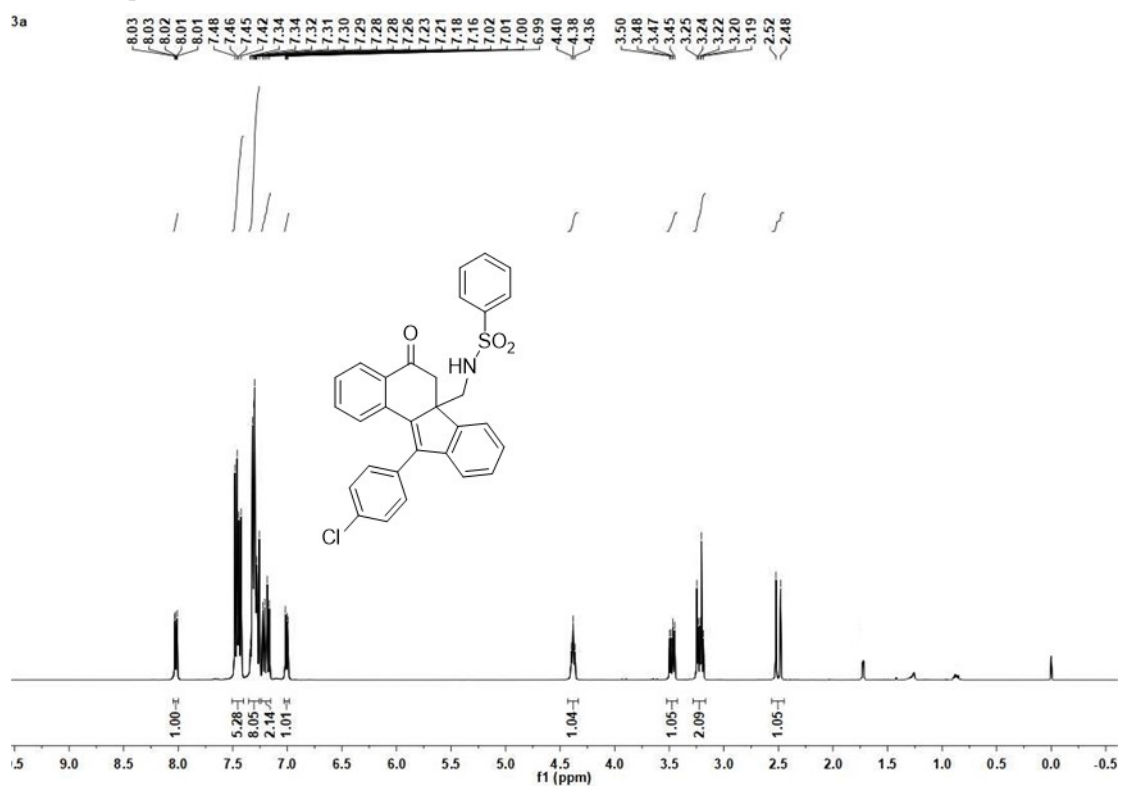


¹⁹F NMR spectrum of **3bd**

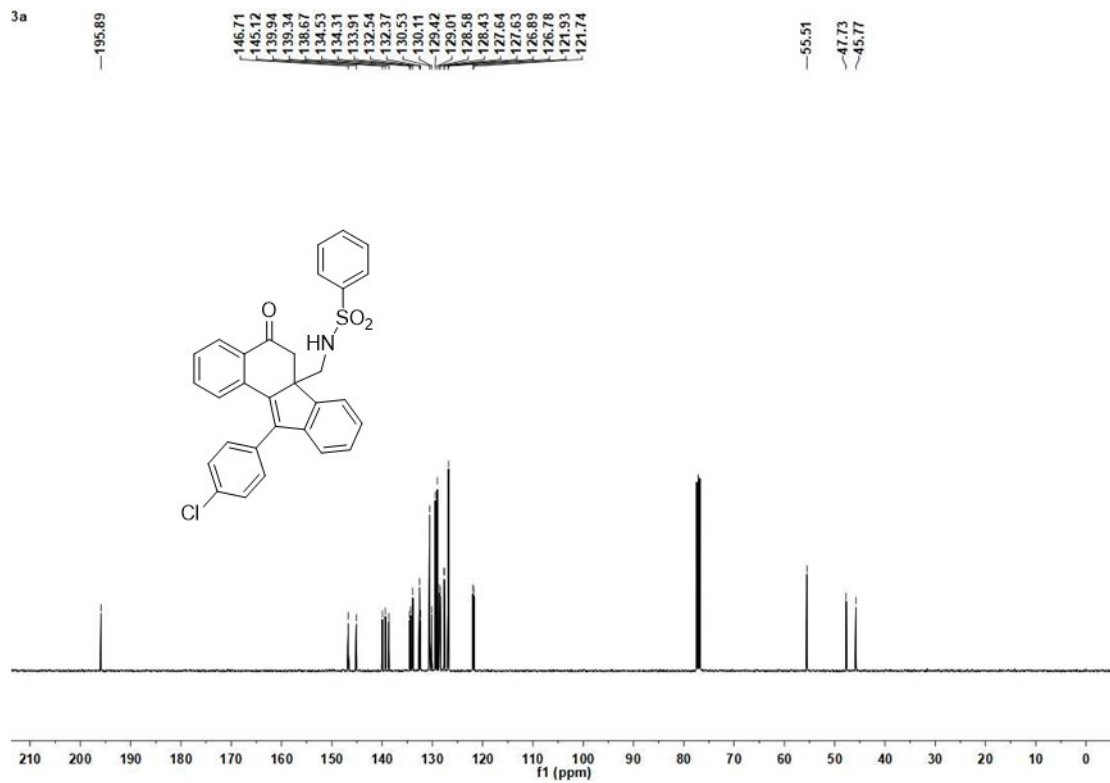
3a



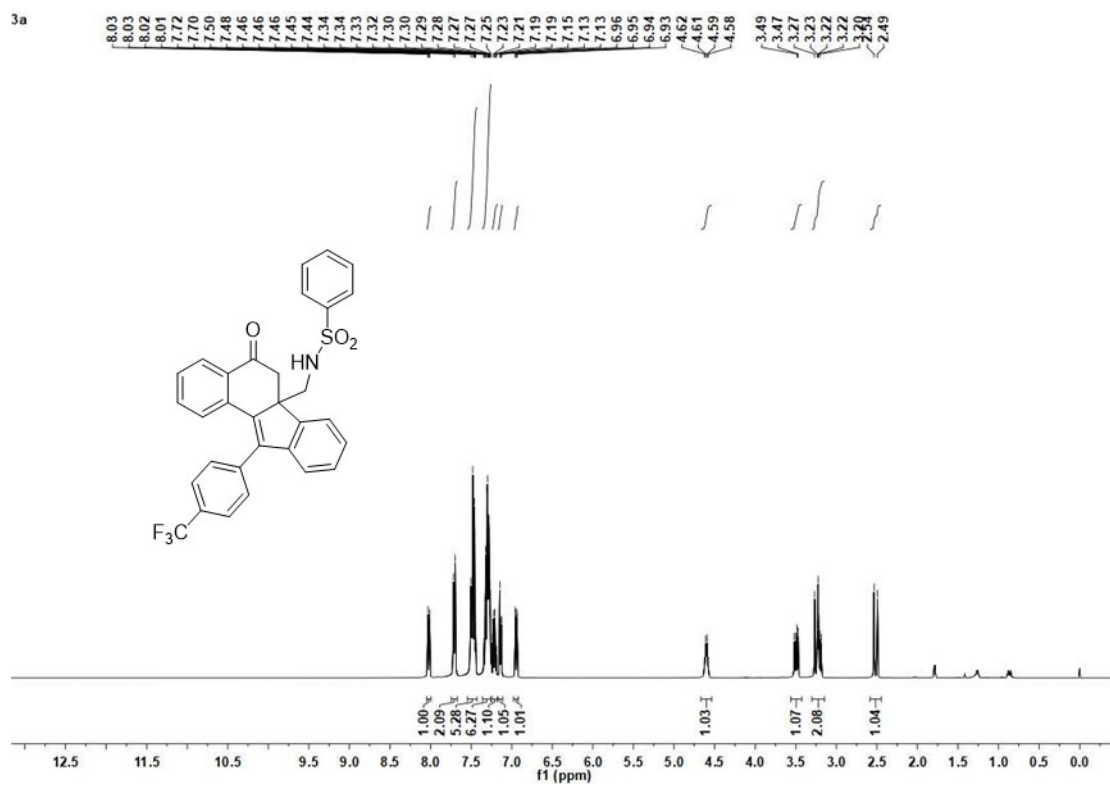
¹H NMR spectrum of 3be



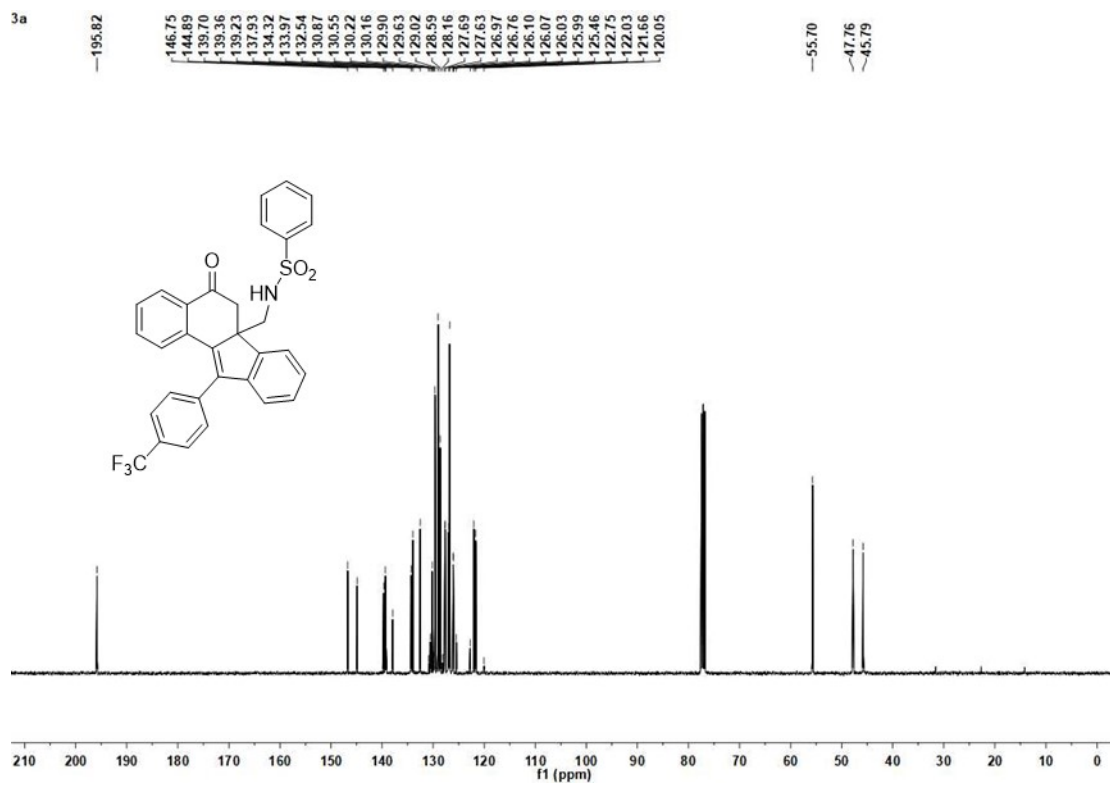
¹³C NMR spectrum of 3be



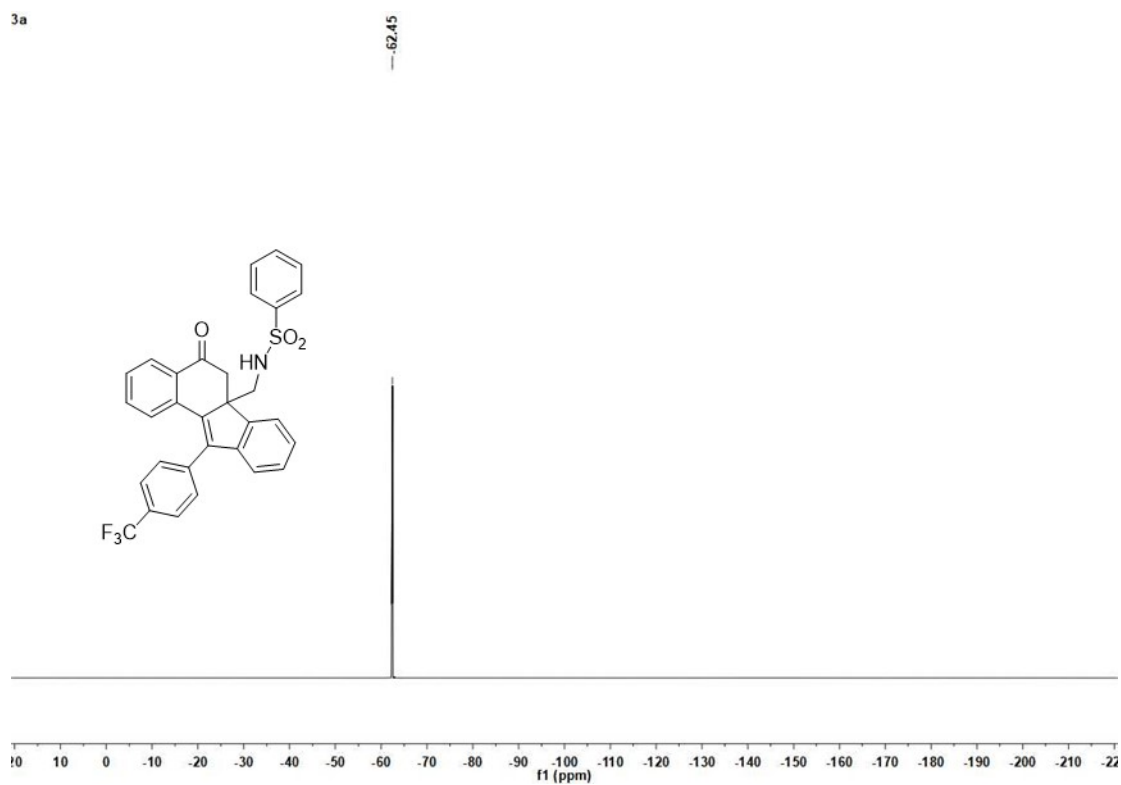
¹H NMR spectrum of **3bf**



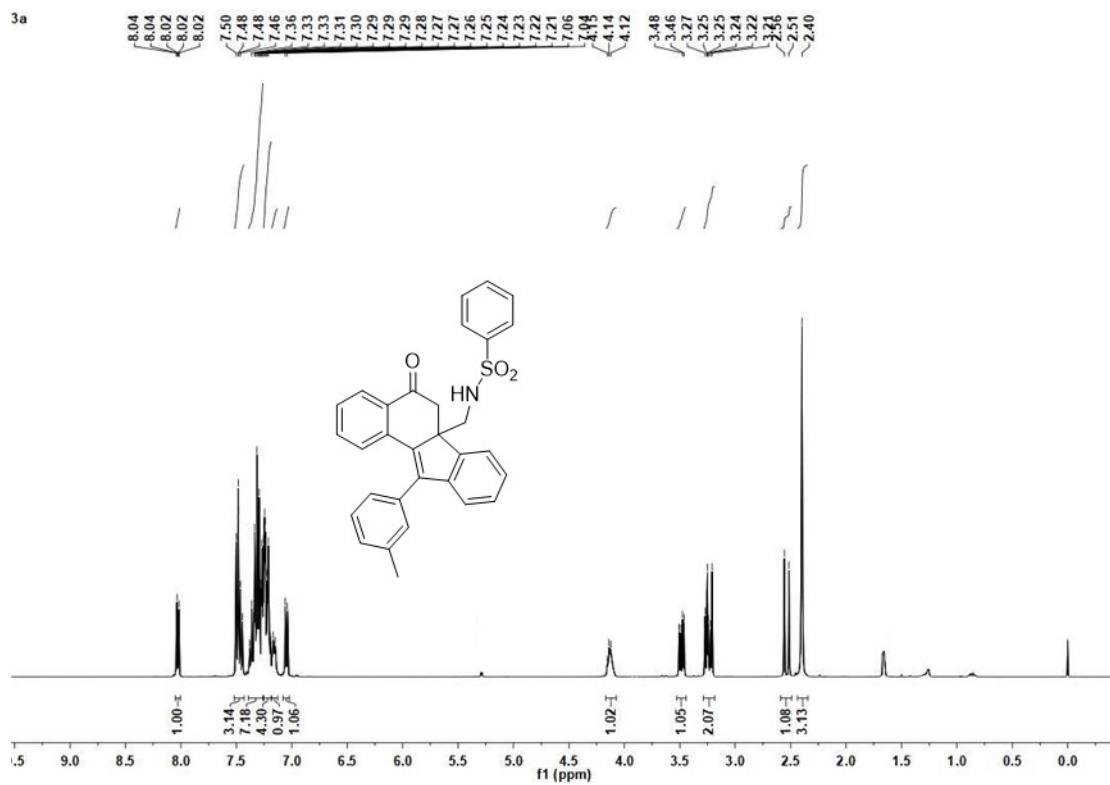
¹³C NMR spectrum of **3bf**



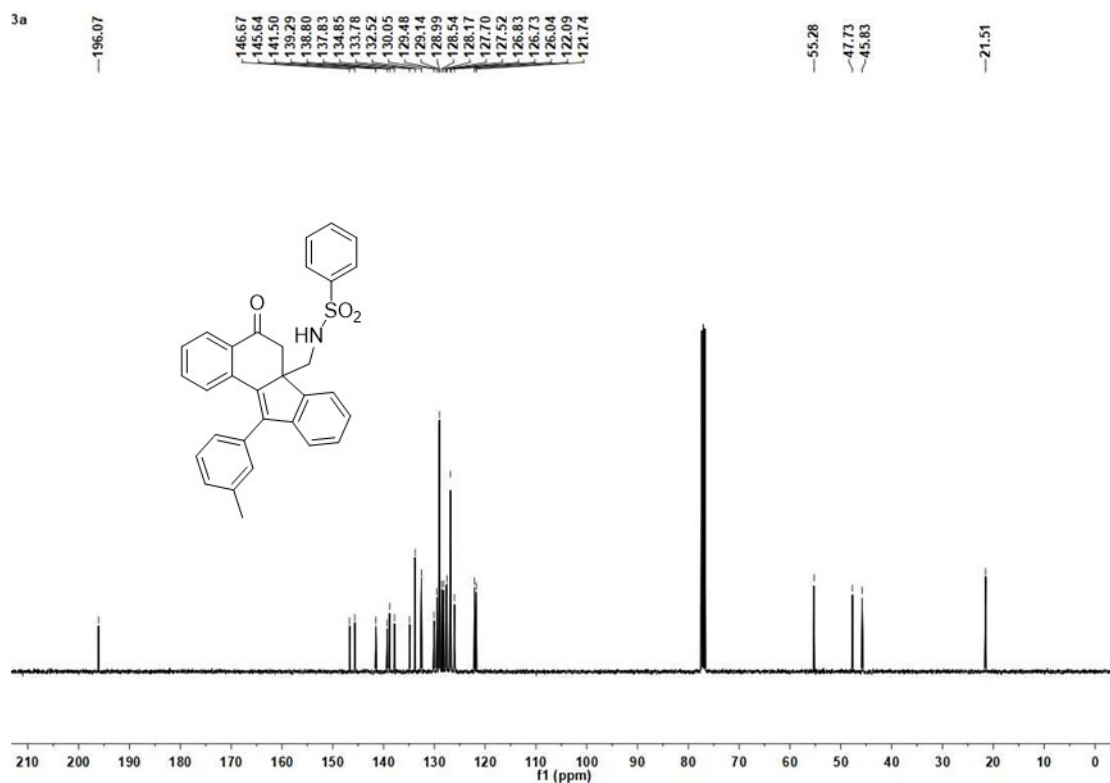
¹⁹F NMR spectrum of **3bf**



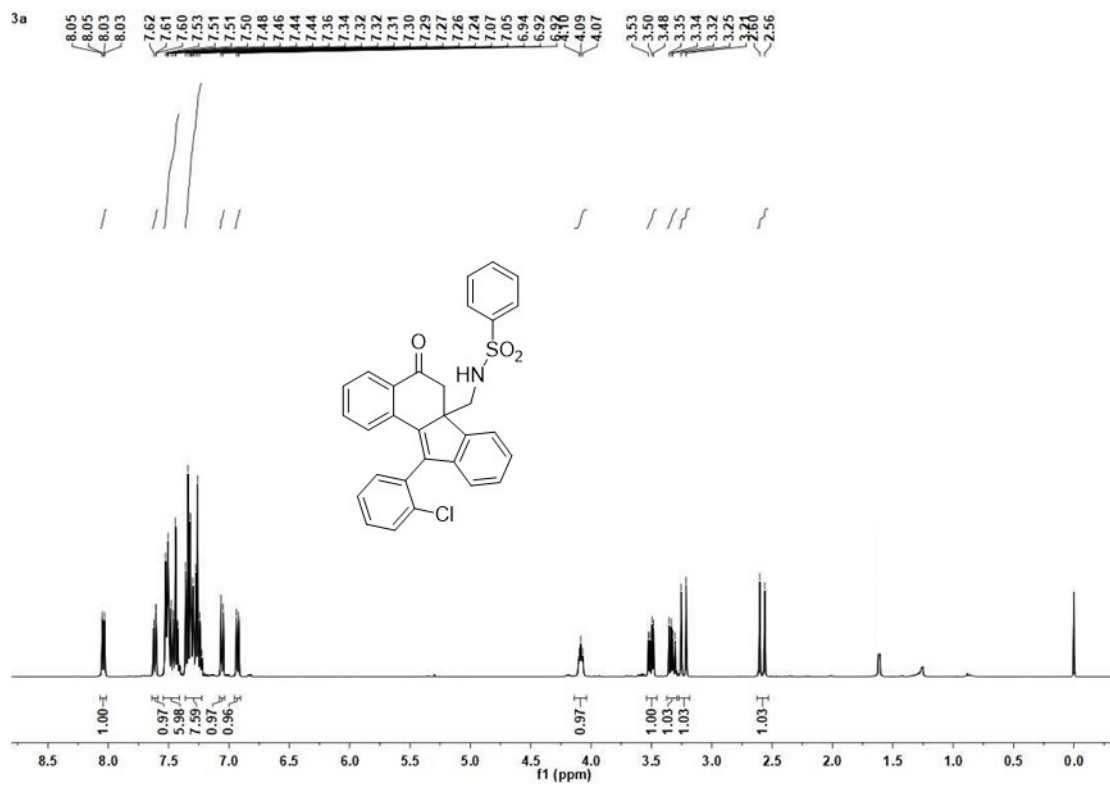
¹H NMR spectrum of **3bg**



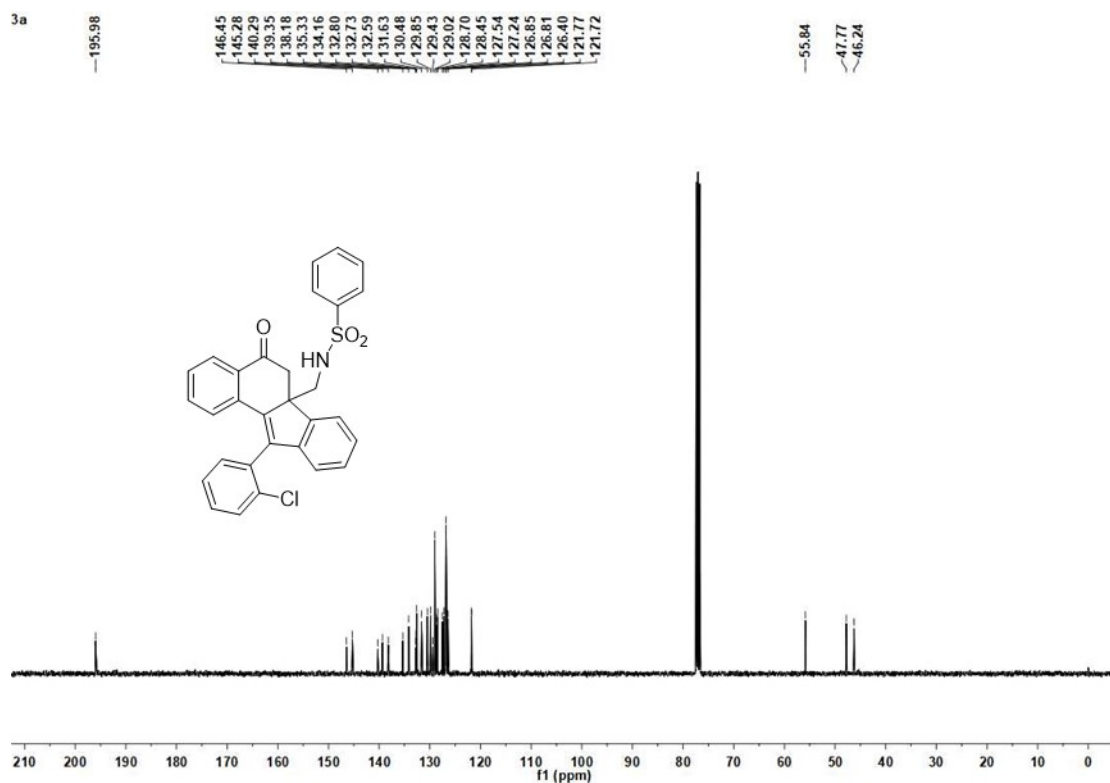
¹³C NMR spectrum of **3bg**



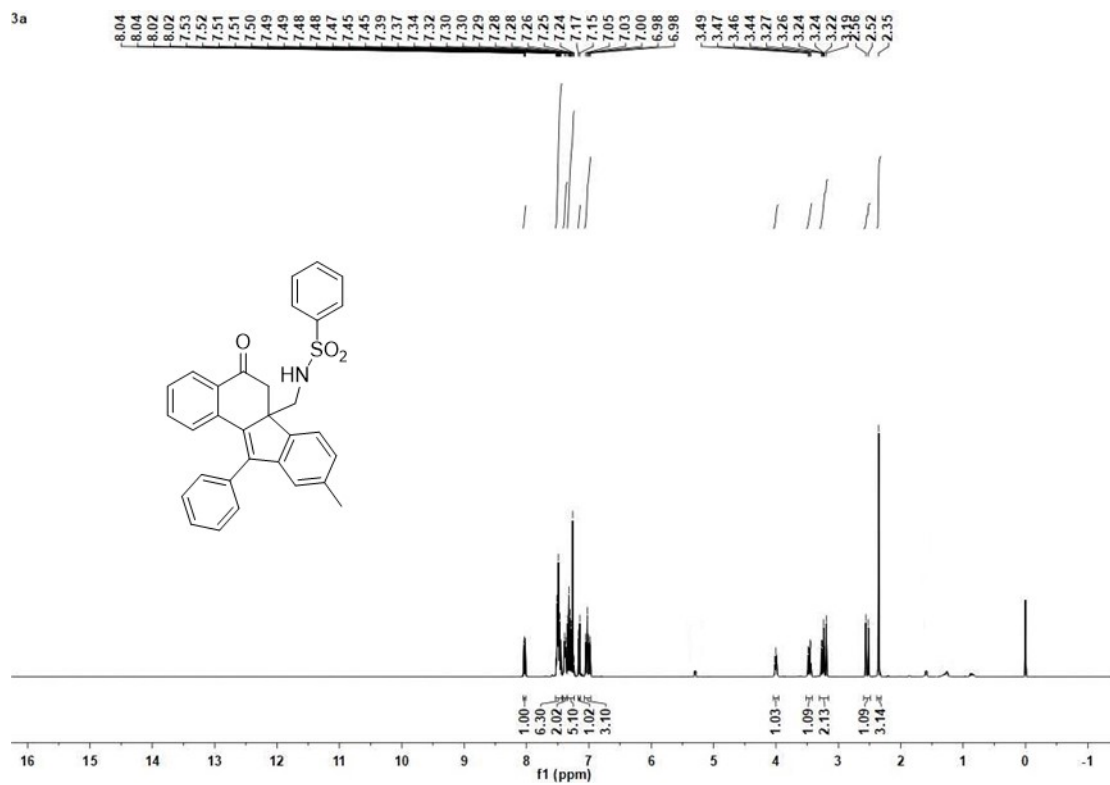
¹H NMR spectrum of **3bh**



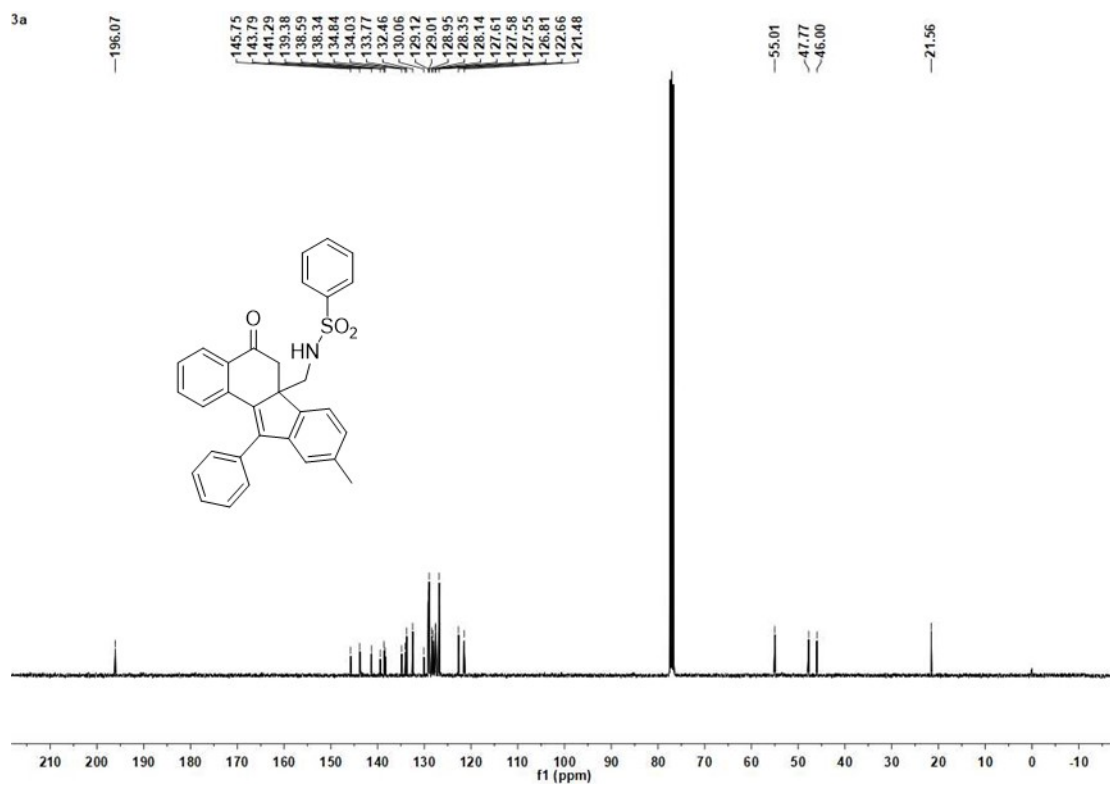
¹³C NMR spectrum of **3bh**



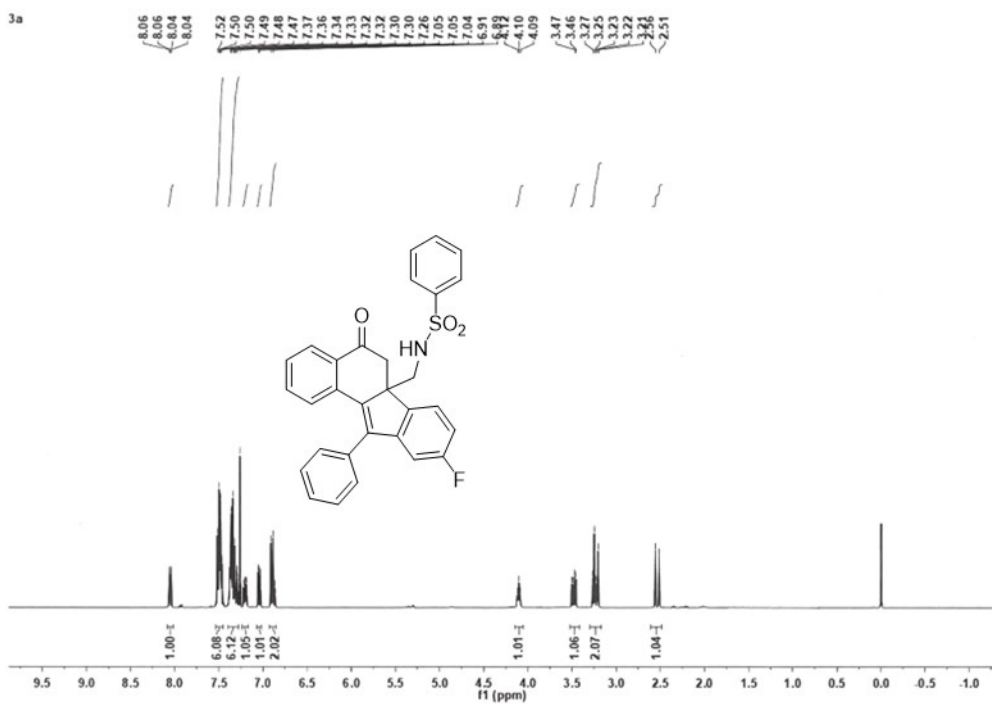
¹H NMR spectrum of **3bi**



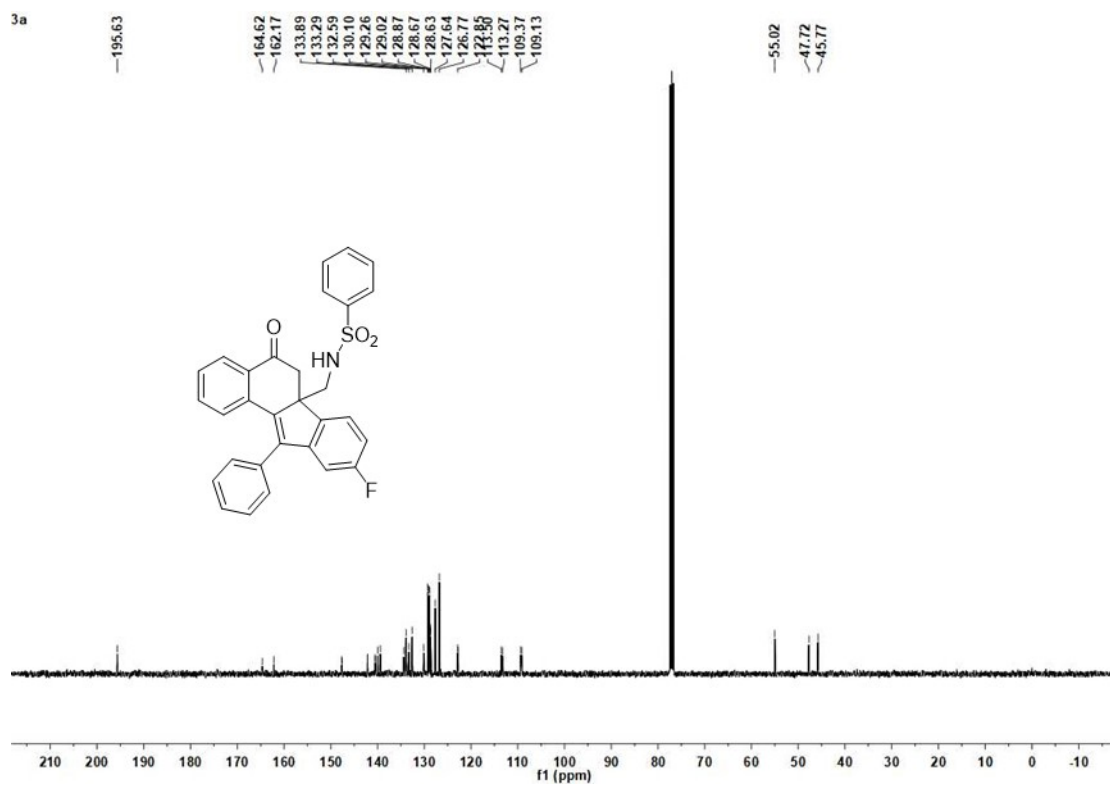
¹³C NMR spectrum of 3bi



¹H NMR spectrum of 3bj

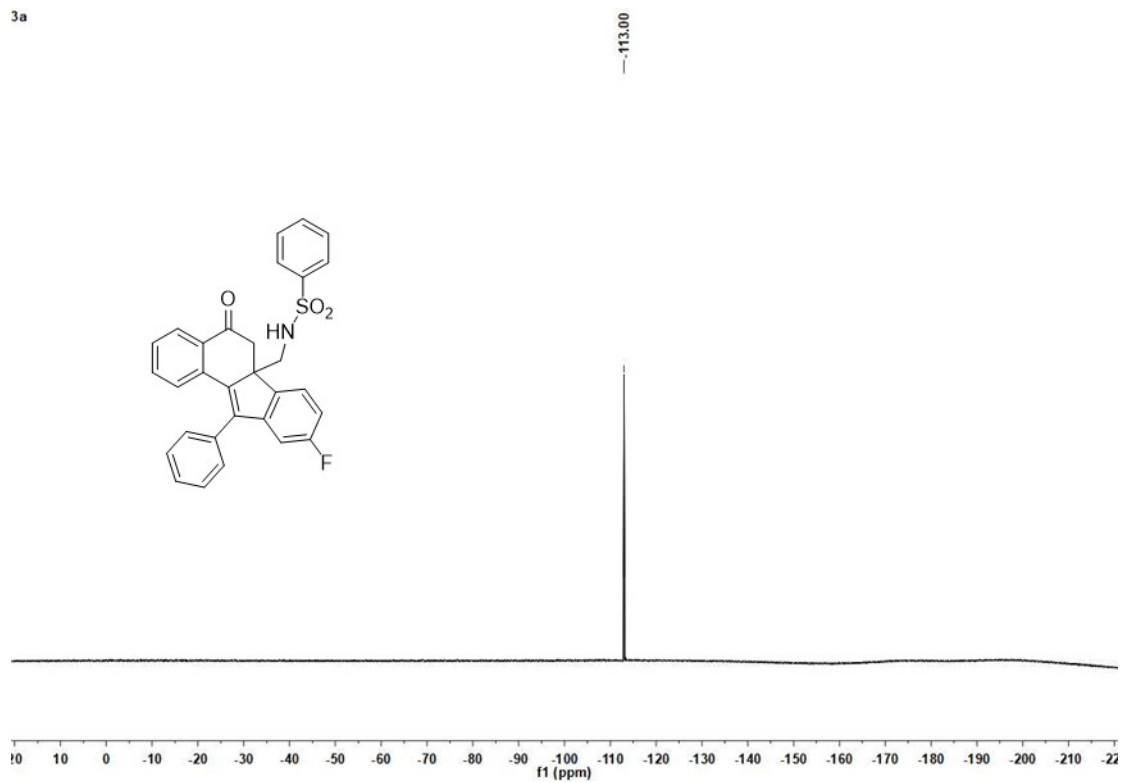


¹³C NMR spectrum of **3bj**

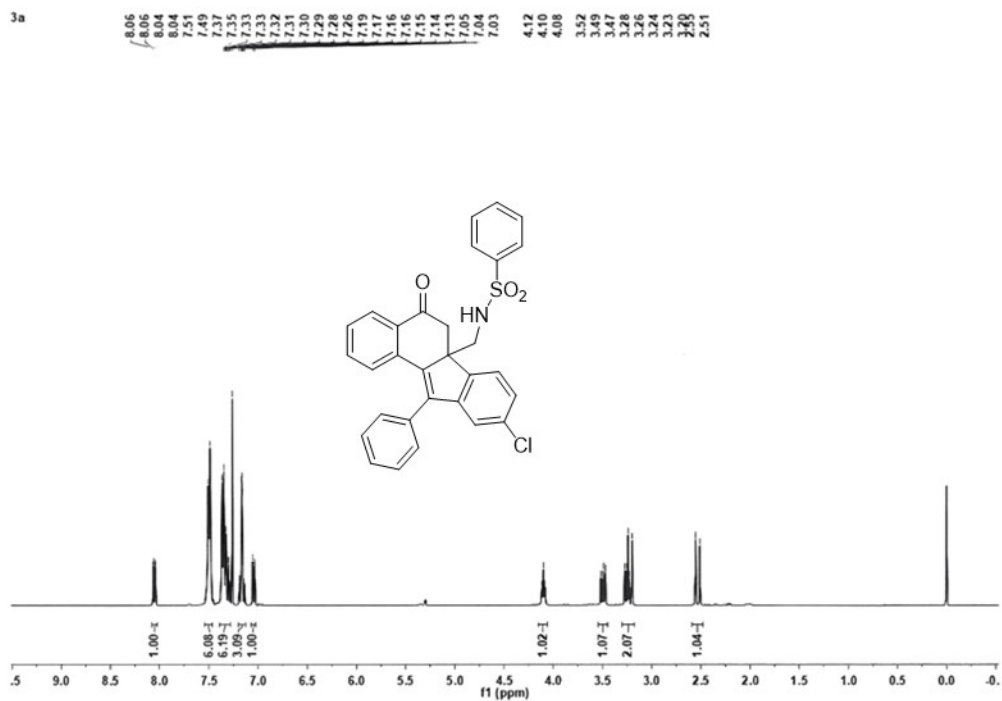


¹⁹F NMR spectrum of **3bj**

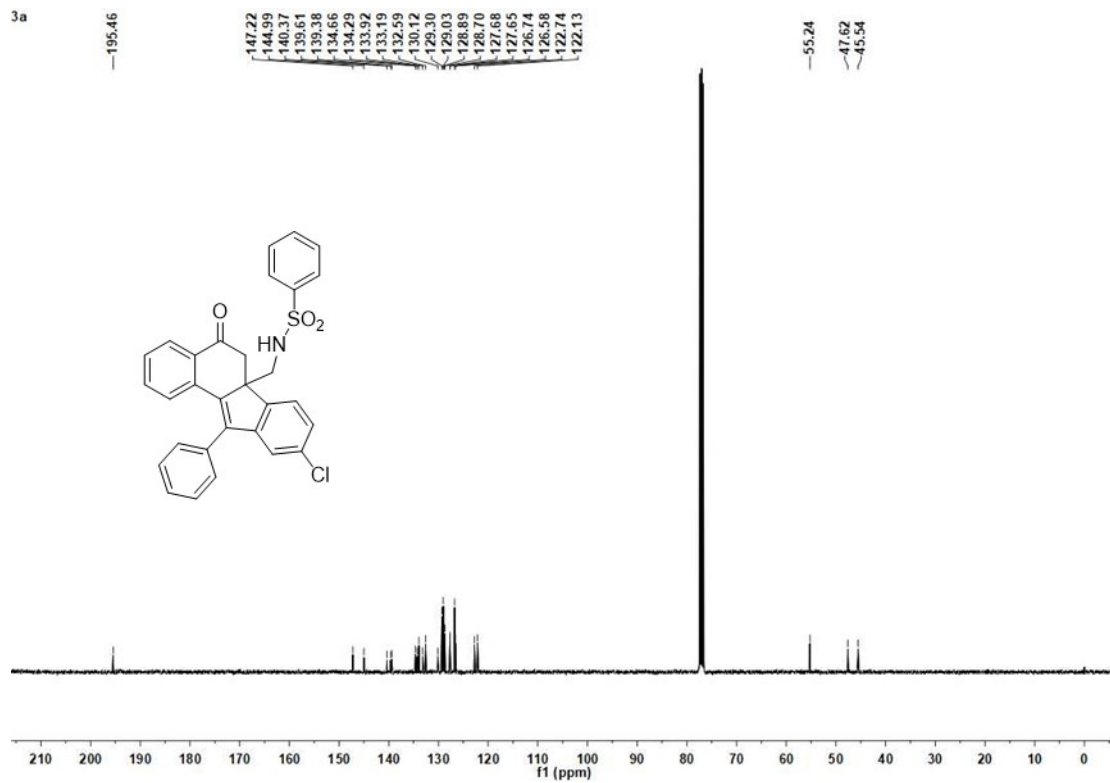
3a



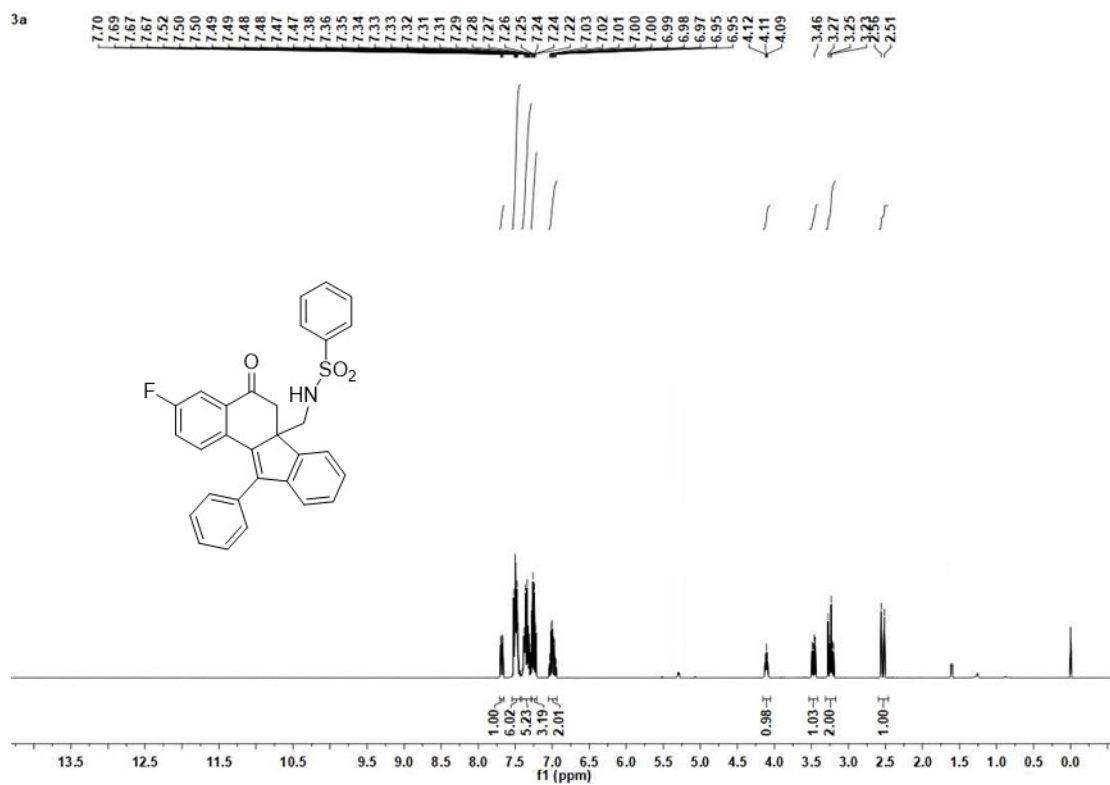
¹H NMR spectrum of **3bk**



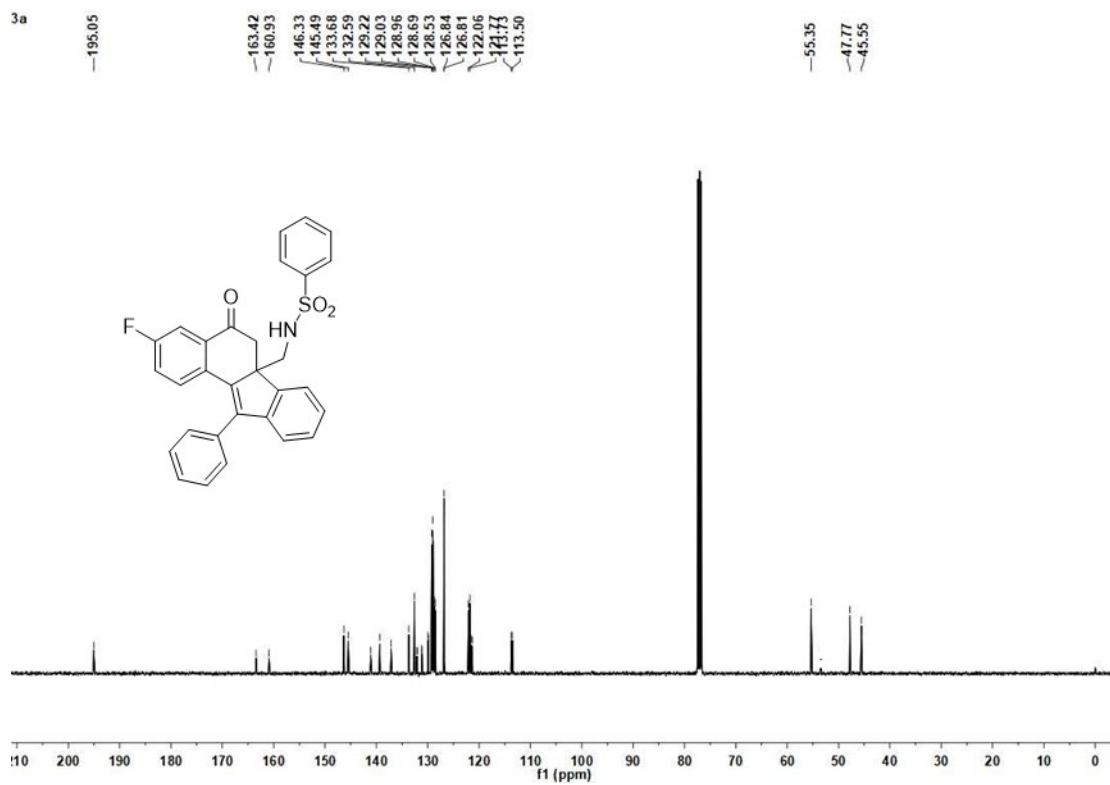
¹³C NMR spectrum of **3bk**



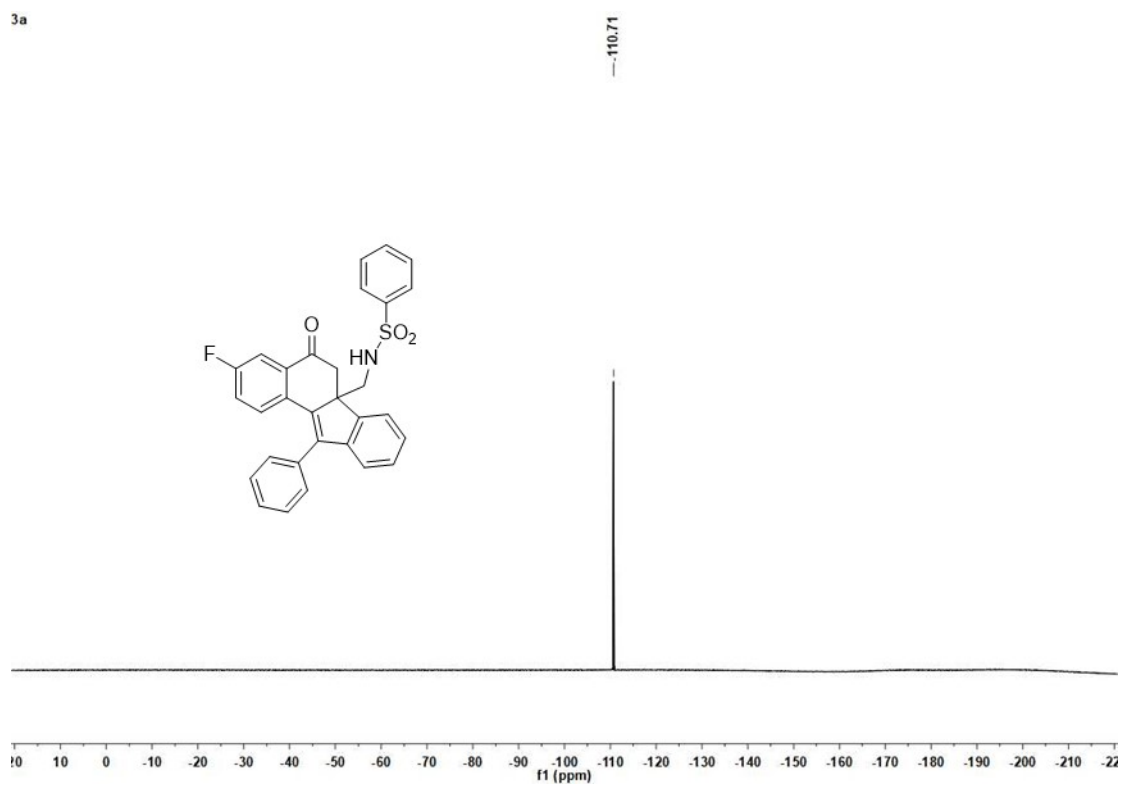
¹H NMR spectrum of 3bl



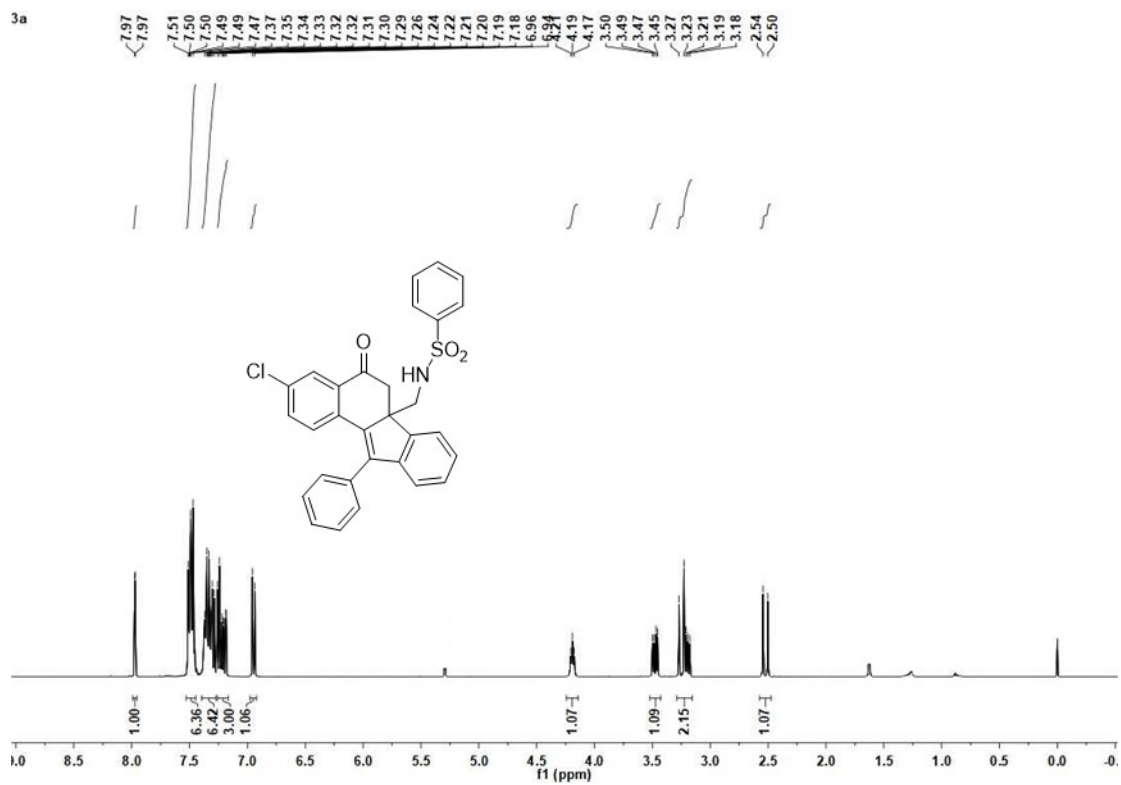
¹³C NMR spectrum of 3bl



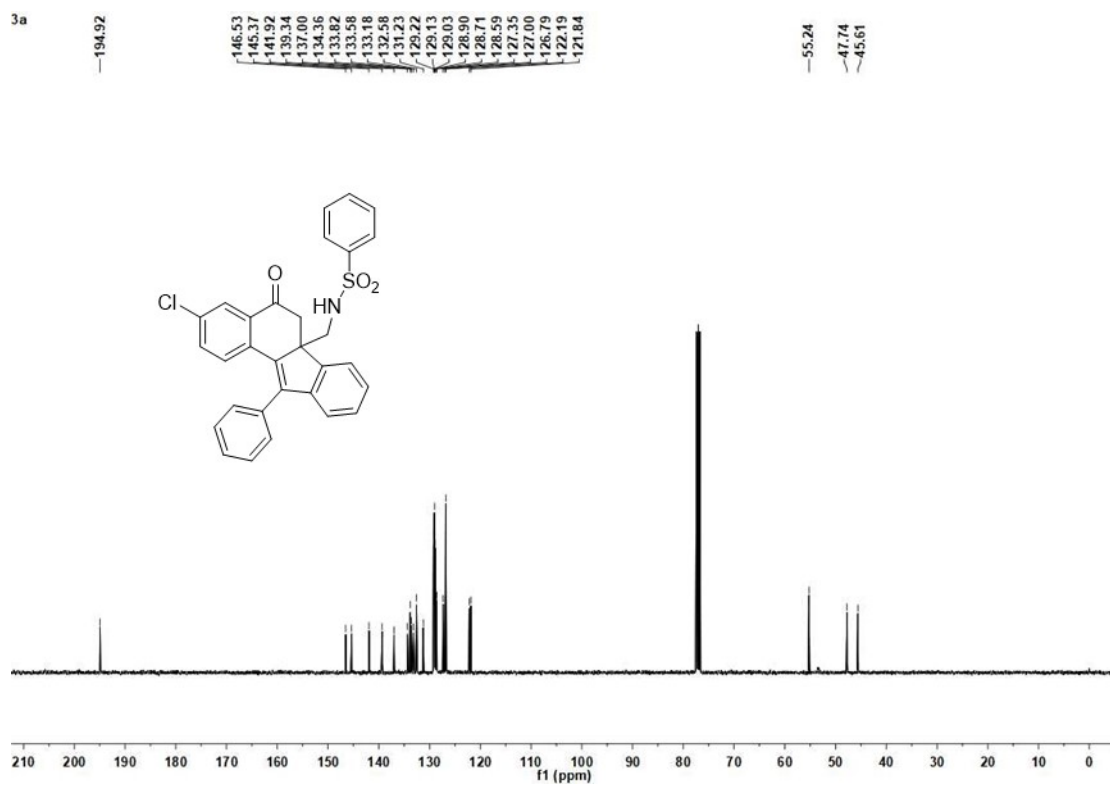
^{19}F NMR spectrum of **3bl**



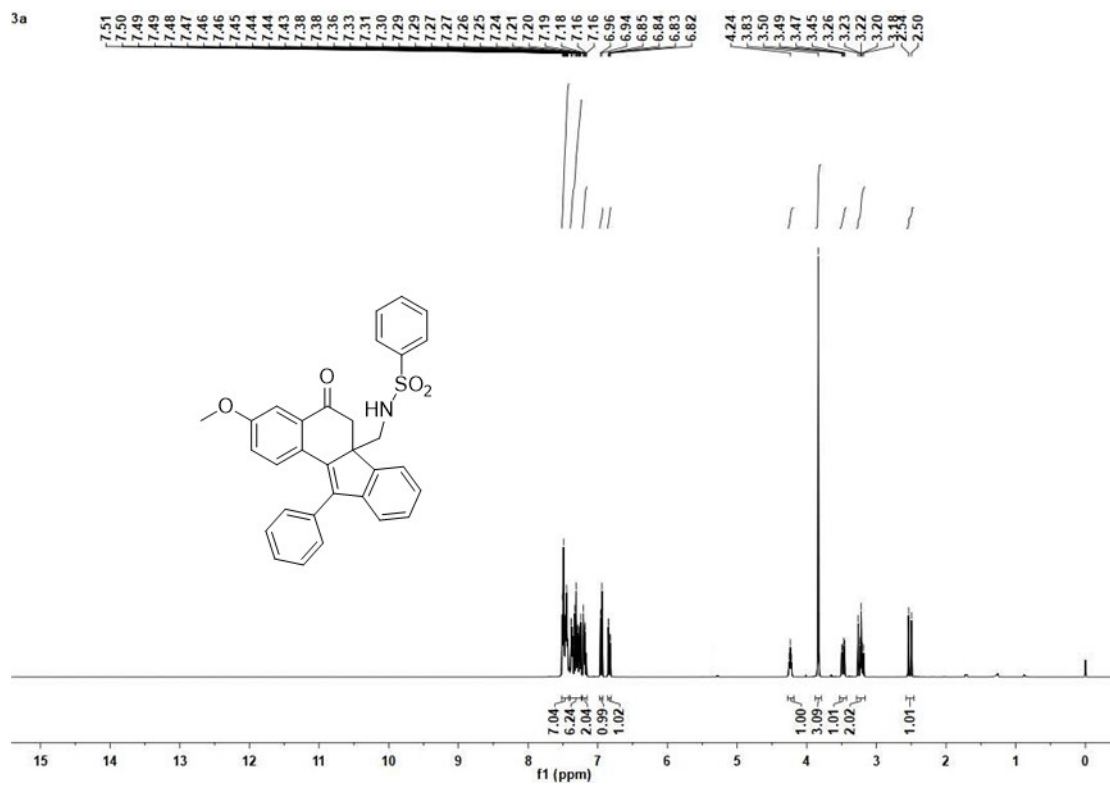
^1H NMR spectrum of **3bm**



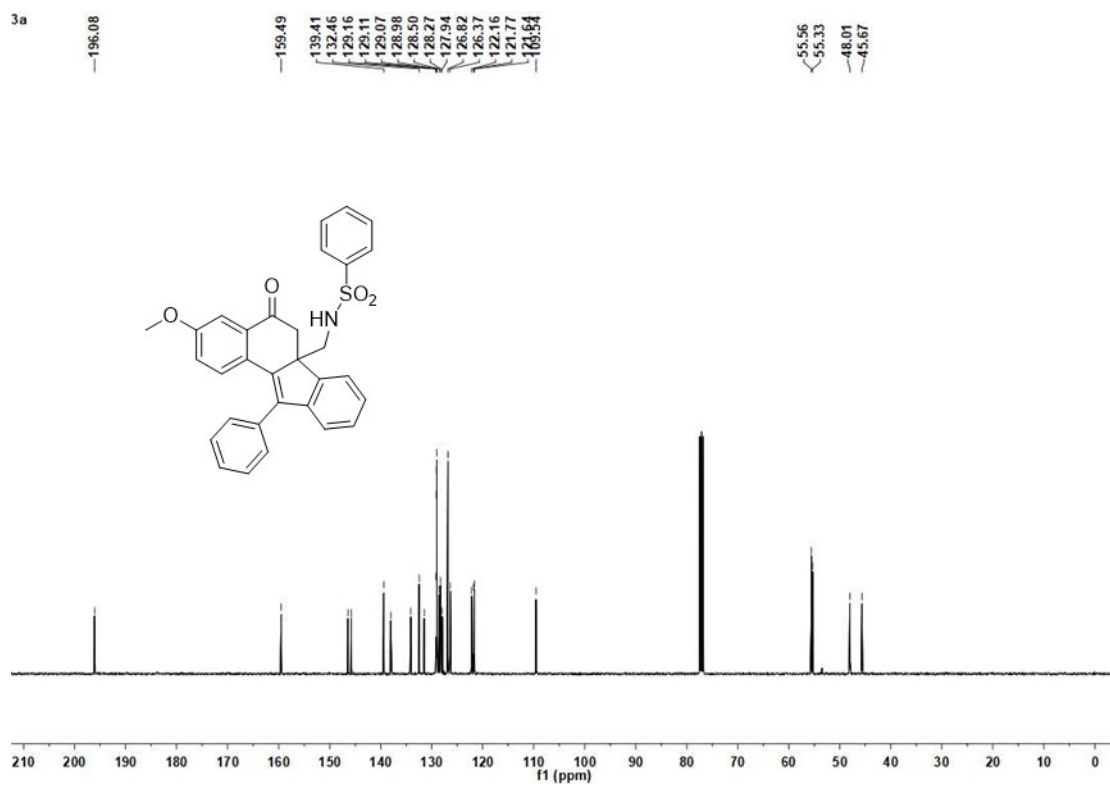
¹³C NMR spectrum of 3bm



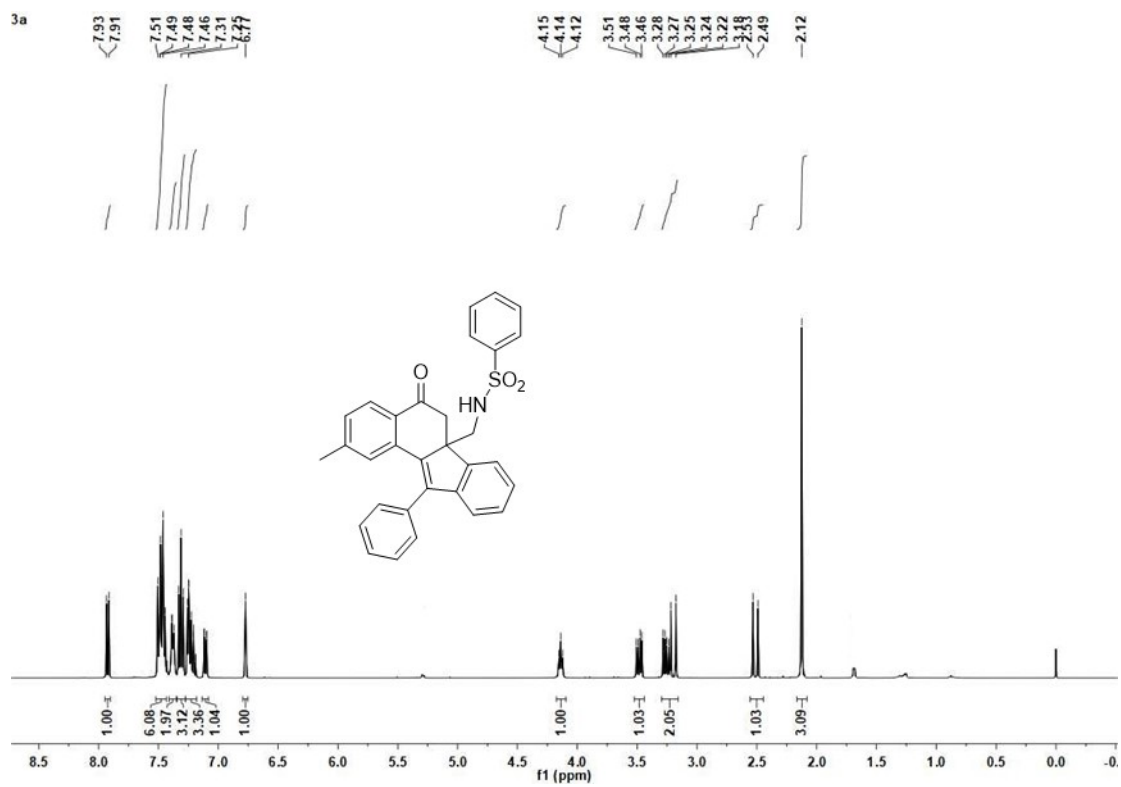
¹H NMR spectrum of 3bn



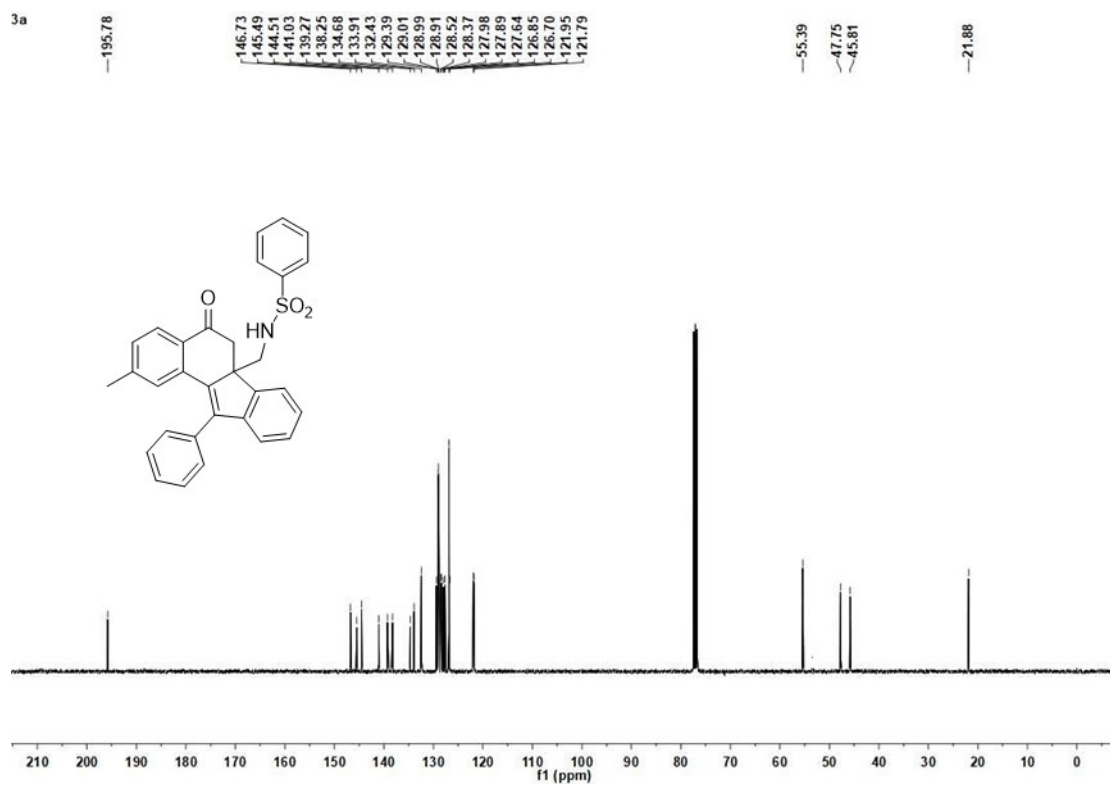
¹³C NMR spectrum of 3bn



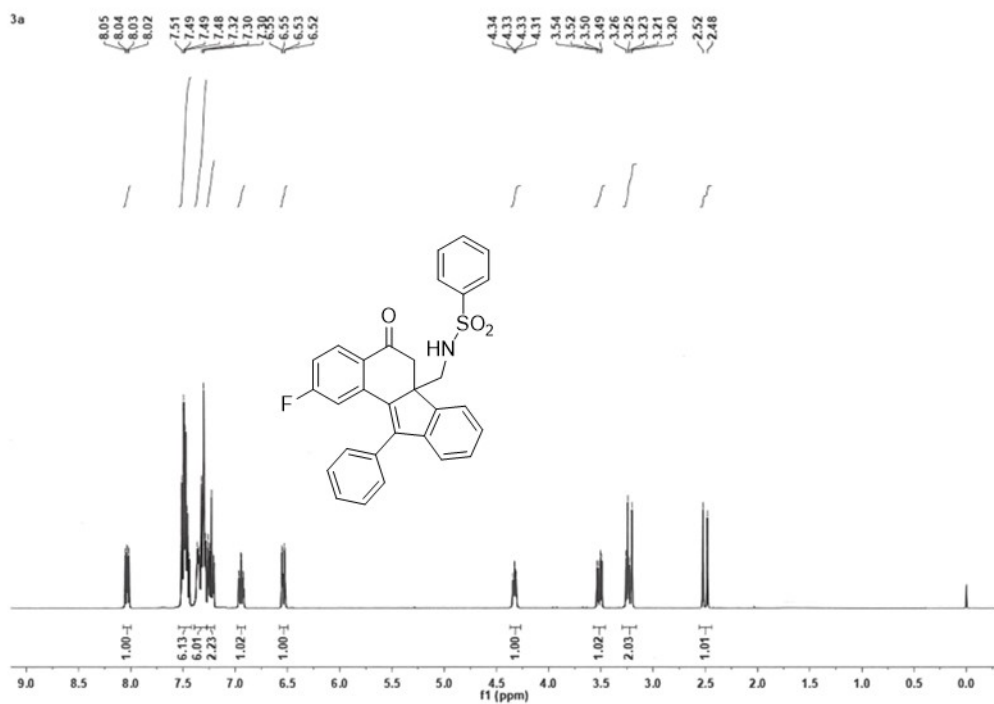
¹H NMR spectrum of 3bo



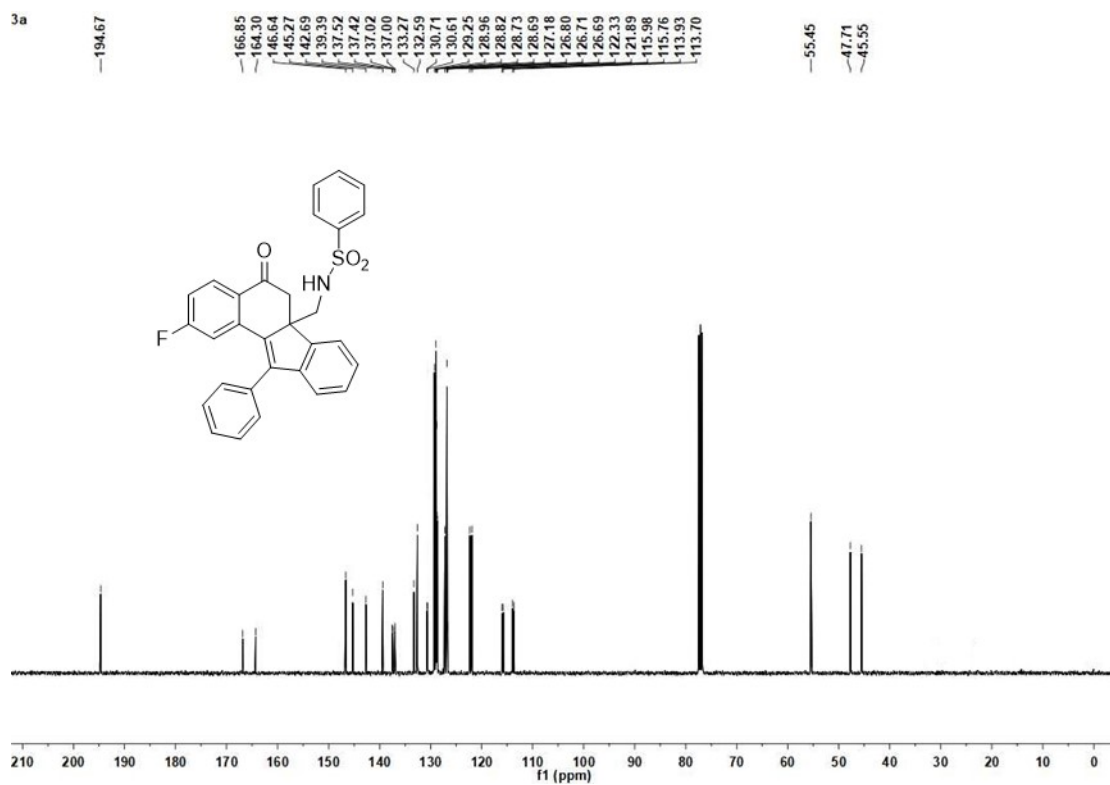
¹³C NMR spectrum of **3bo**



¹H NMR spectrum of **3bp**

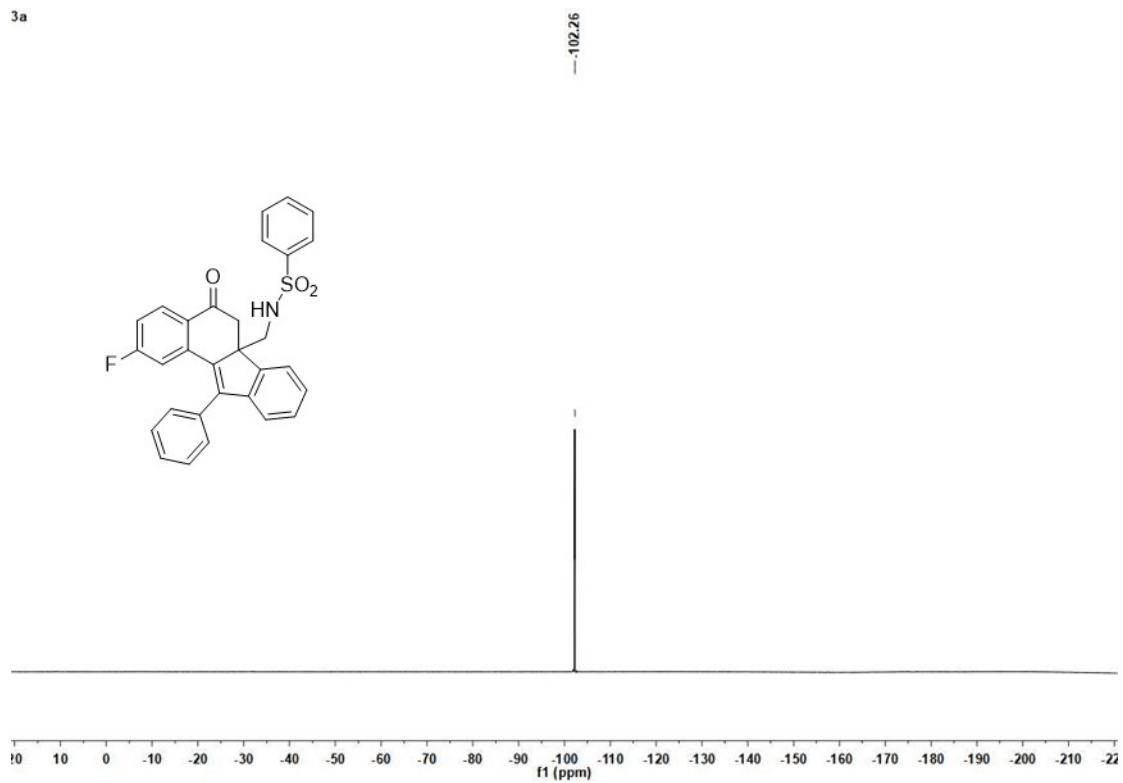


¹³C NMR spectrum of **3bp**

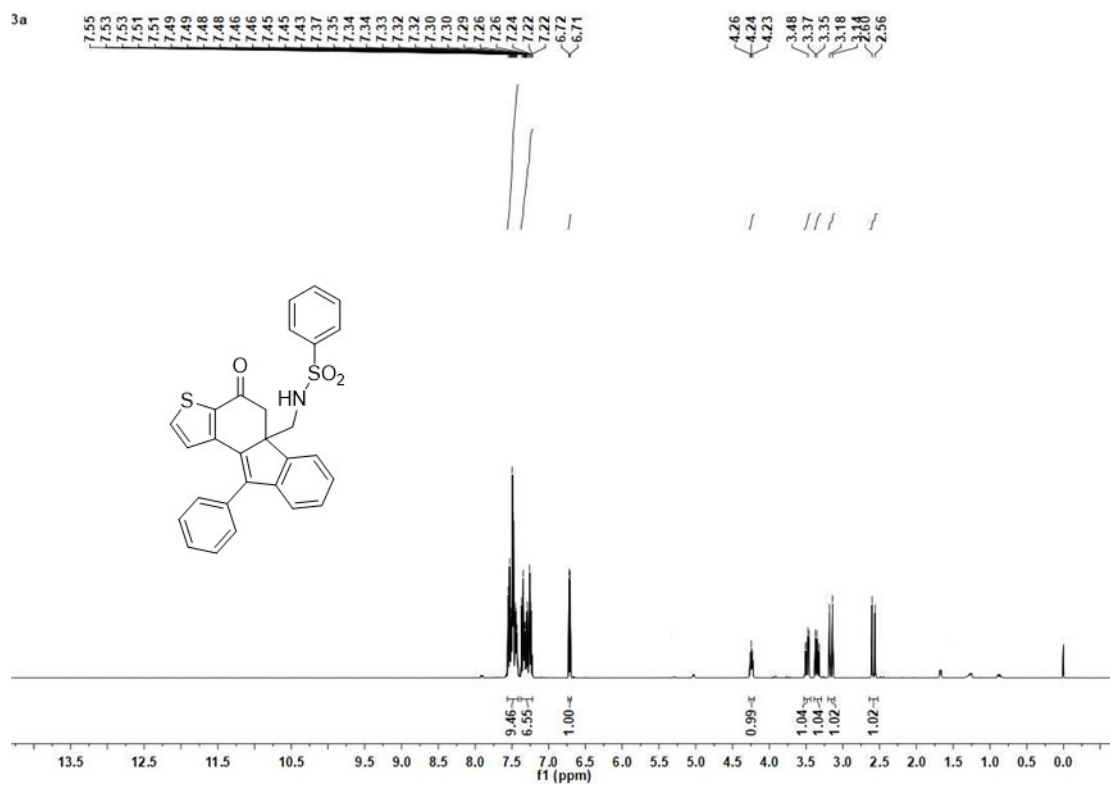


¹⁹F NMR spectrum of **3bp**

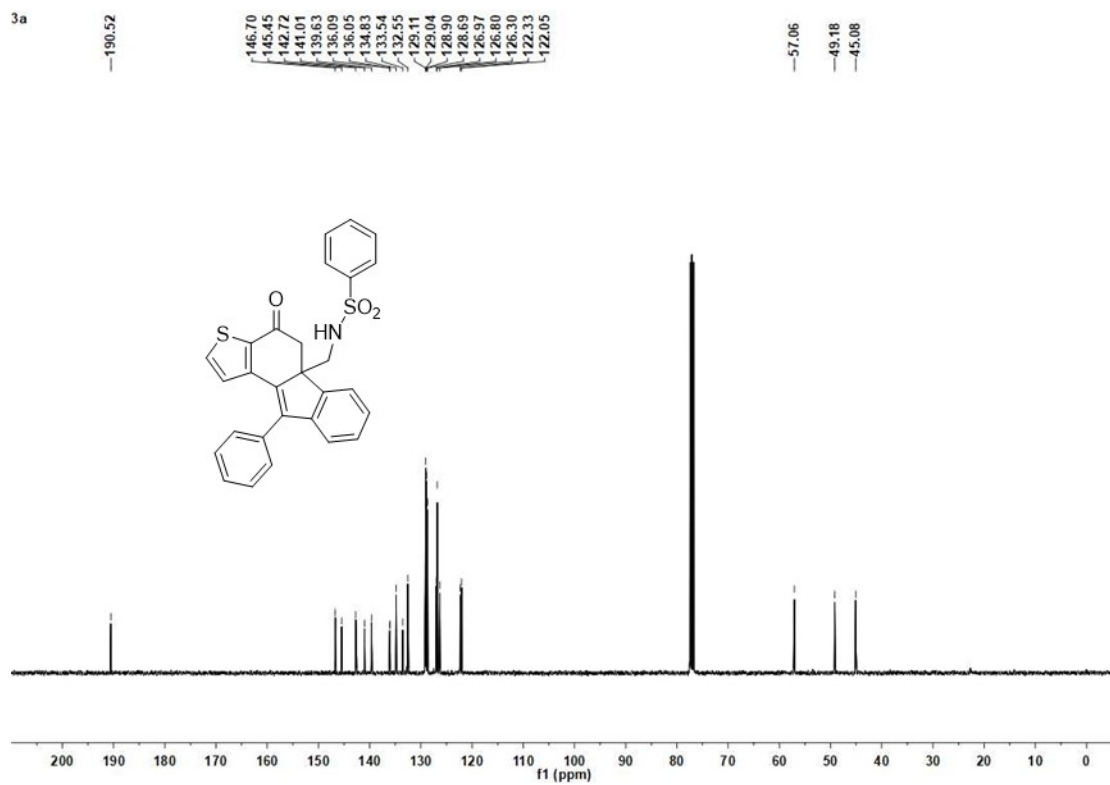
3a



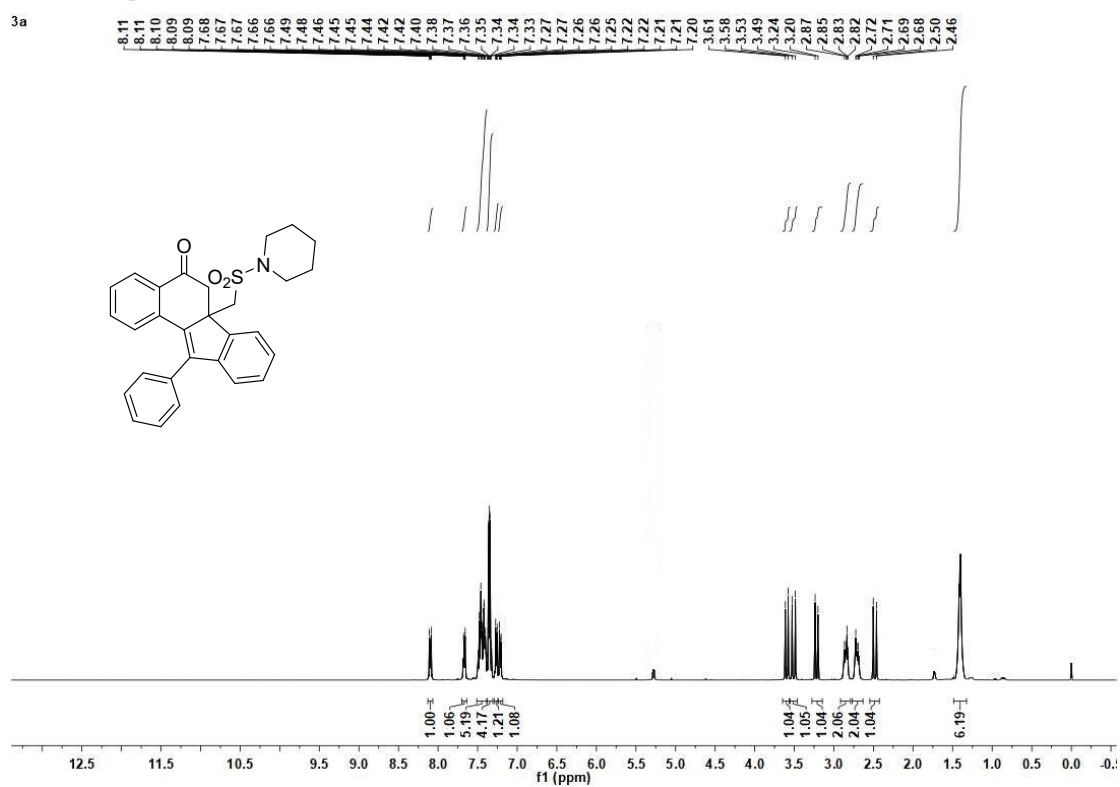
^1H NMR spectrum of 3bq



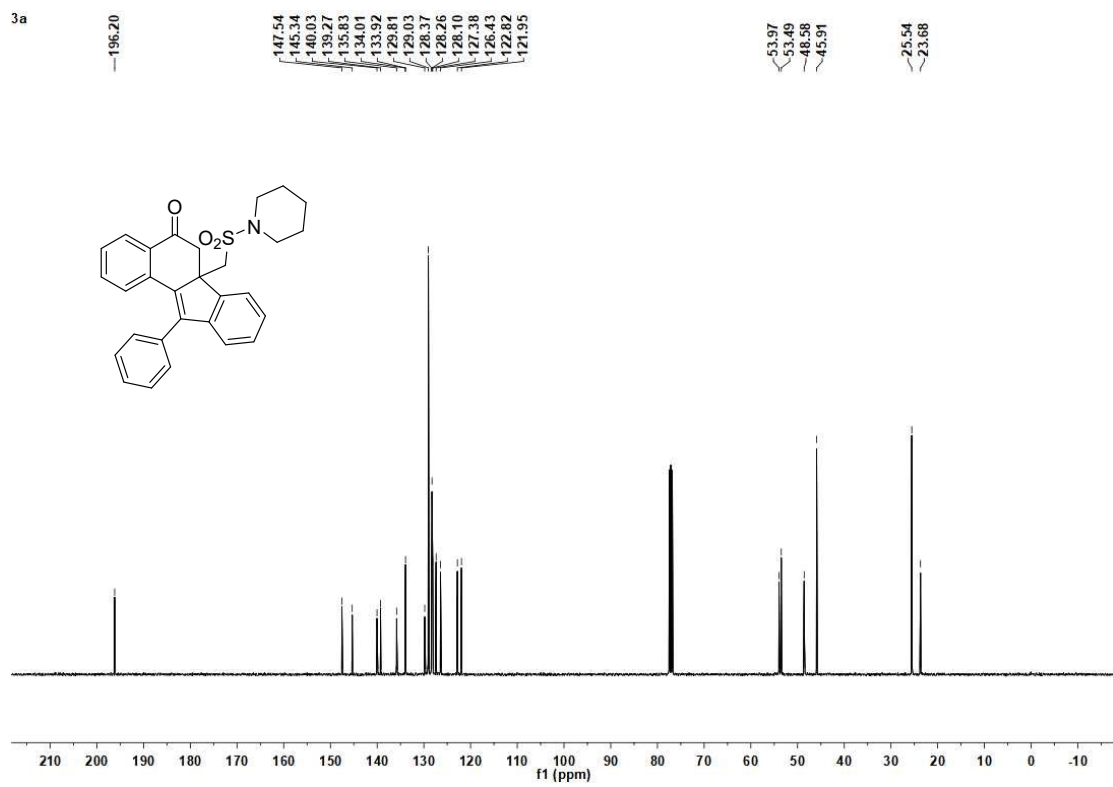
^{13}C NMR spectrum of 3bq



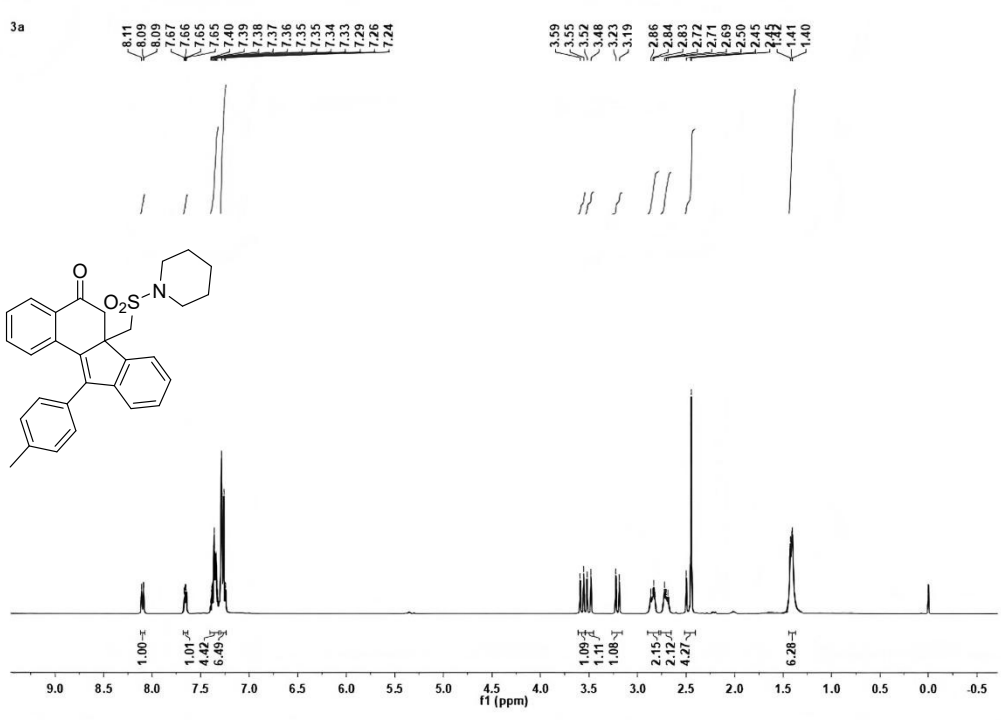
¹H NMR spectrum of 5a



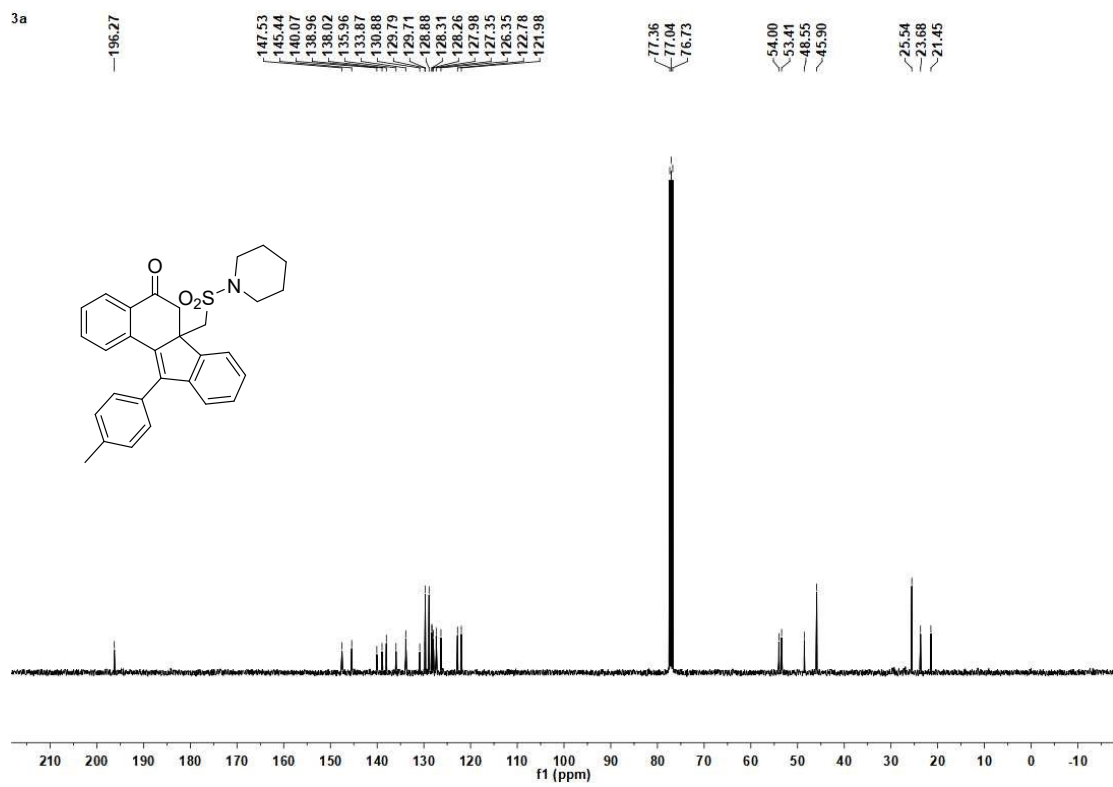
¹³C NMR spectrum of 5a



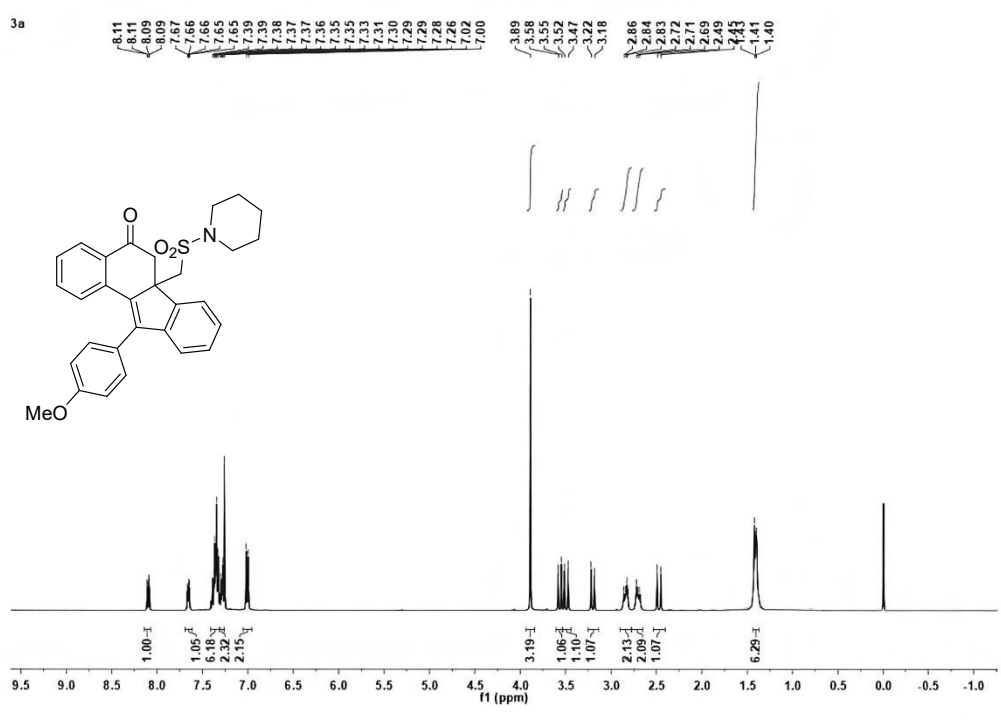
¹H NMR spectrum of 5b



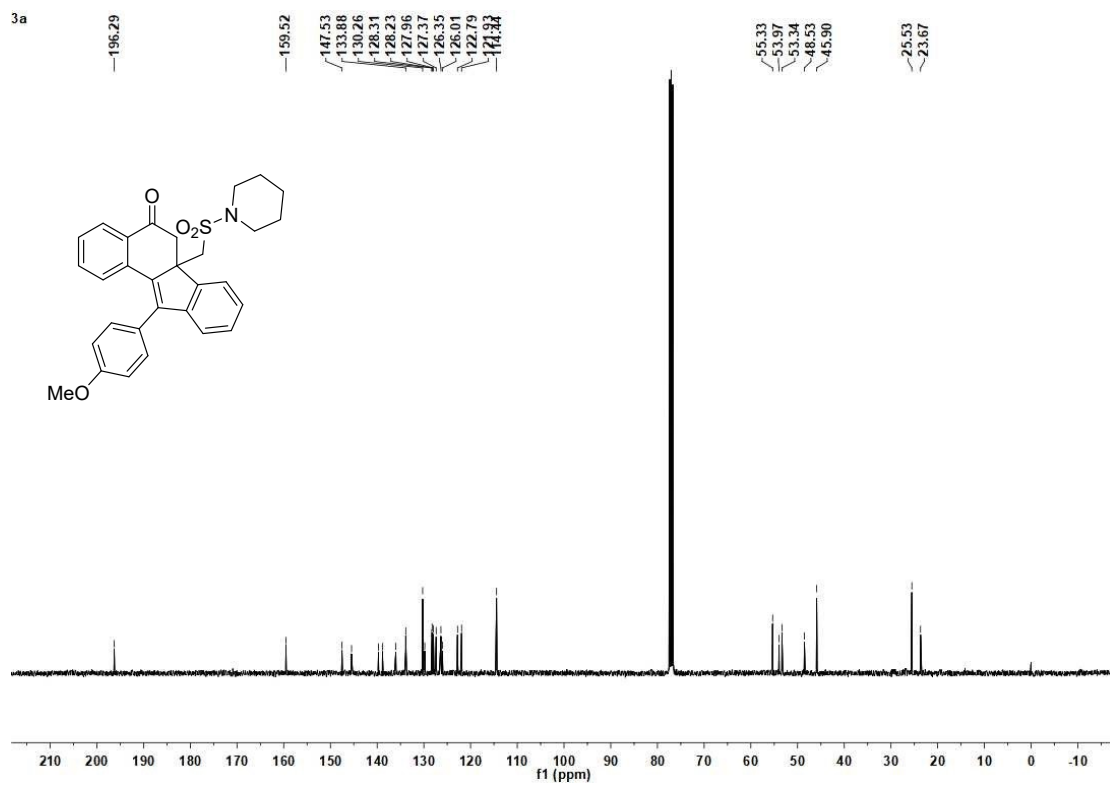
¹³C NMR spectrum of 5b



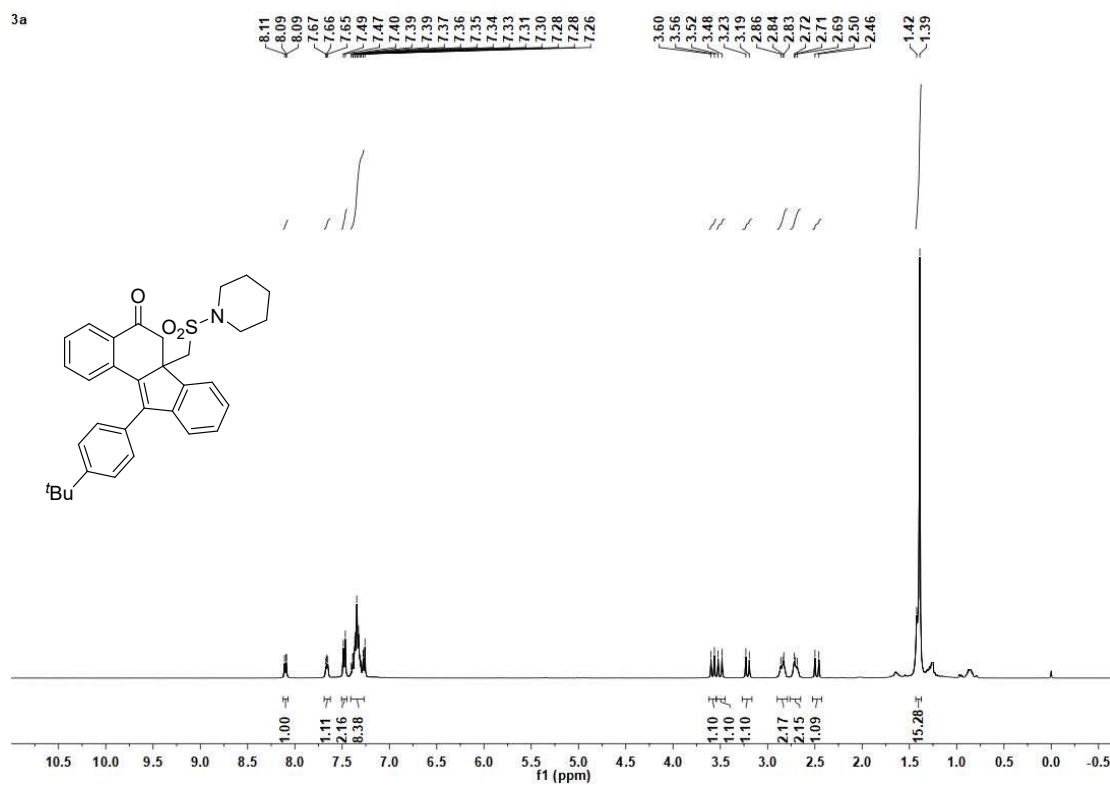
¹H NMR spectrum of 5c



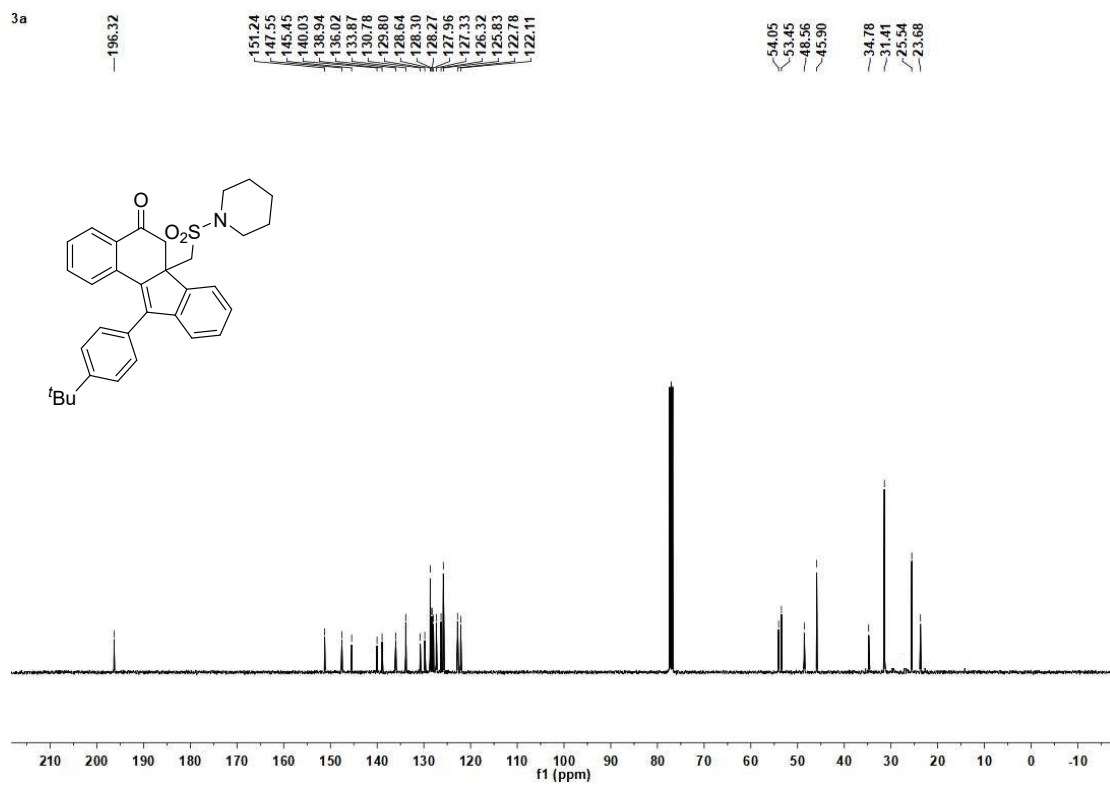
¹³C NMR spectrum of 5c



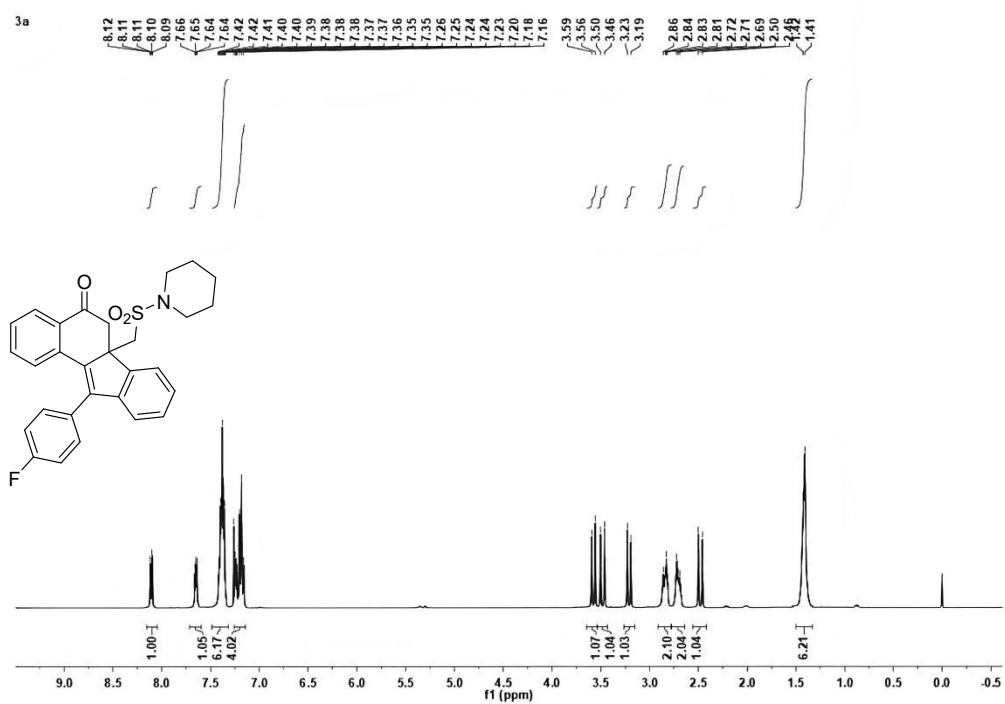
¹H NMR spectrum of 5d



¹³C NMR spectrum of 5d

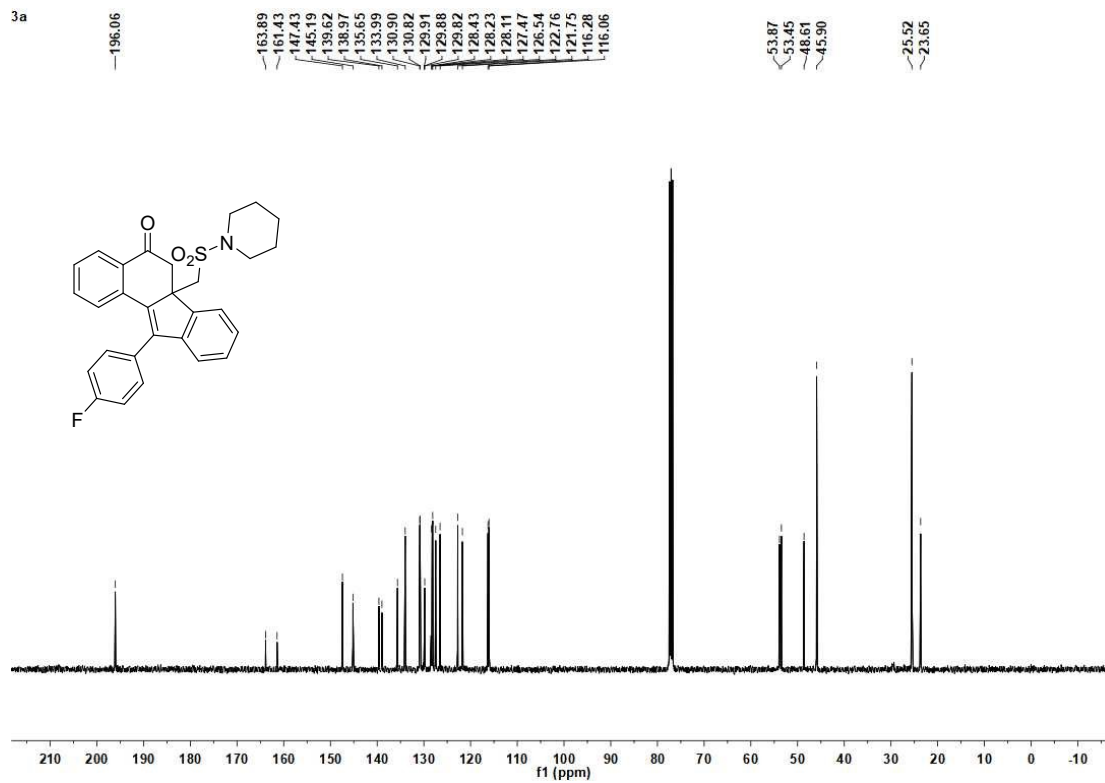


¹H NMR spectrum of 5e



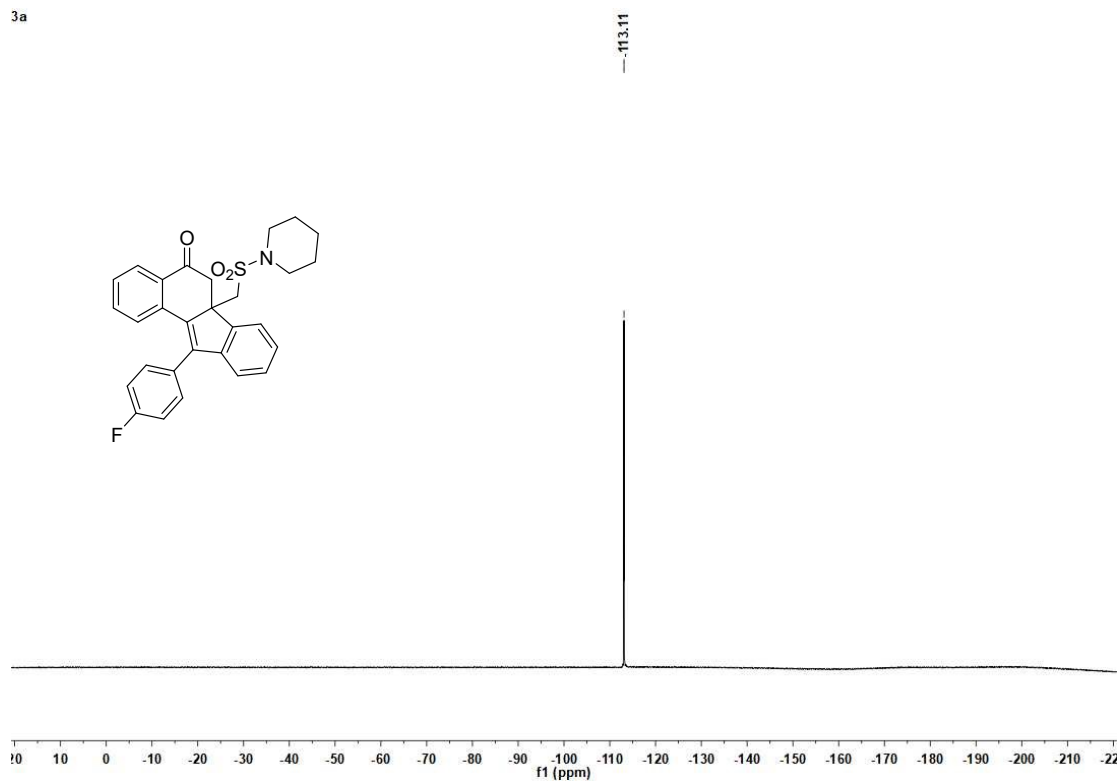
¹³C NMR spectrum of 5e

3a

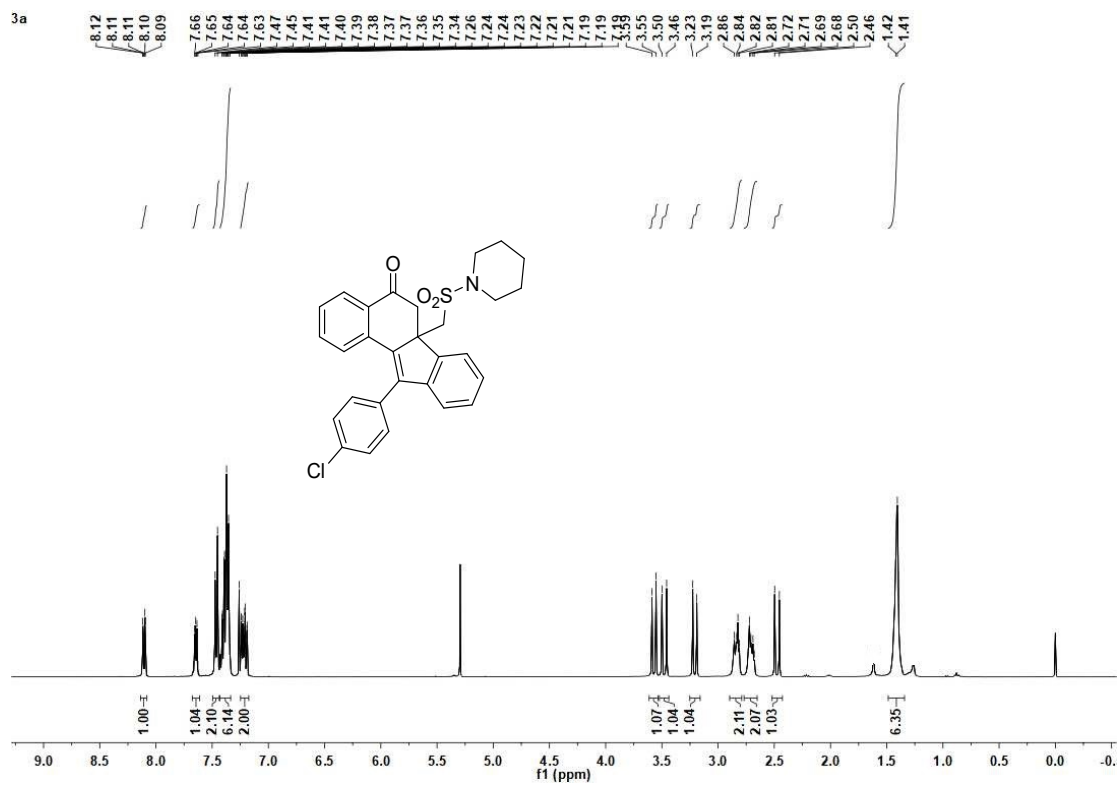


¹⁹F NMR spectrum of 5e

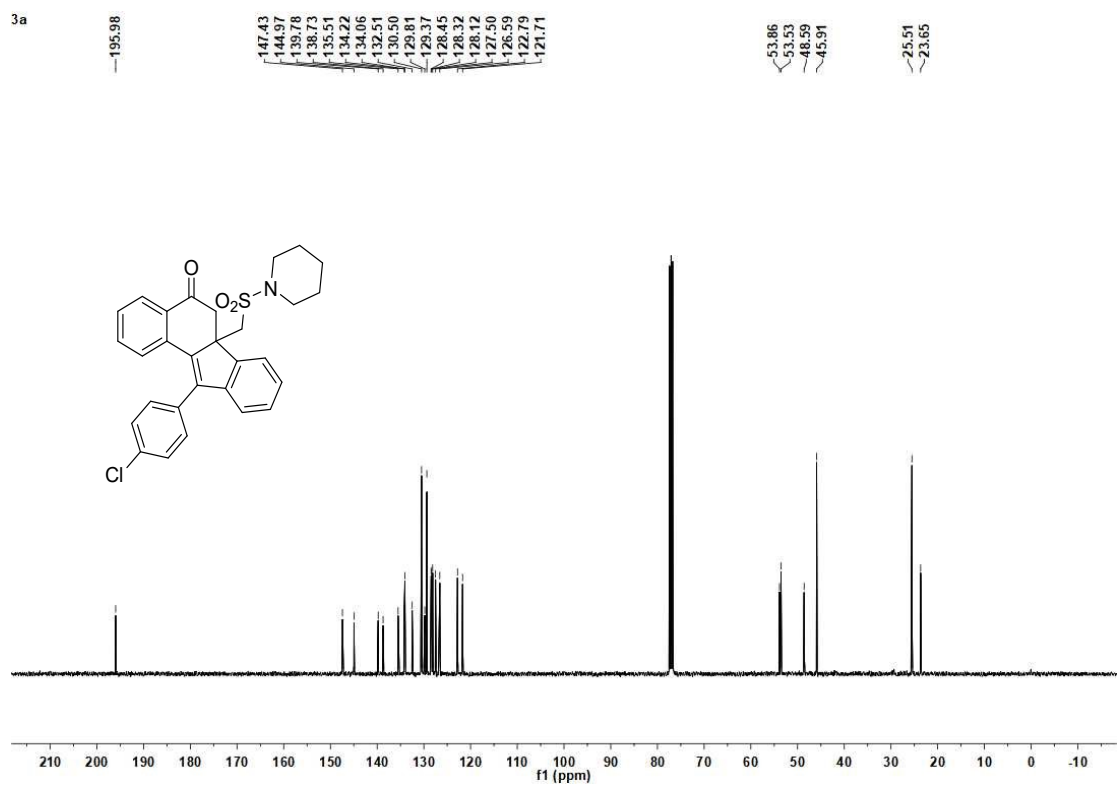
3a



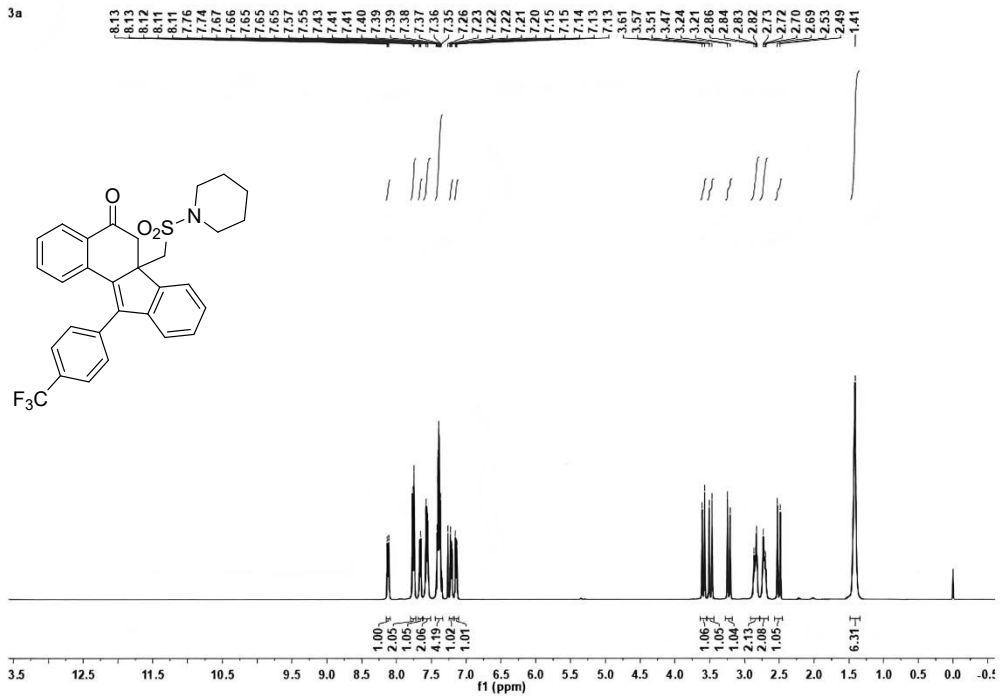
¹H NMR spectrum of 5f



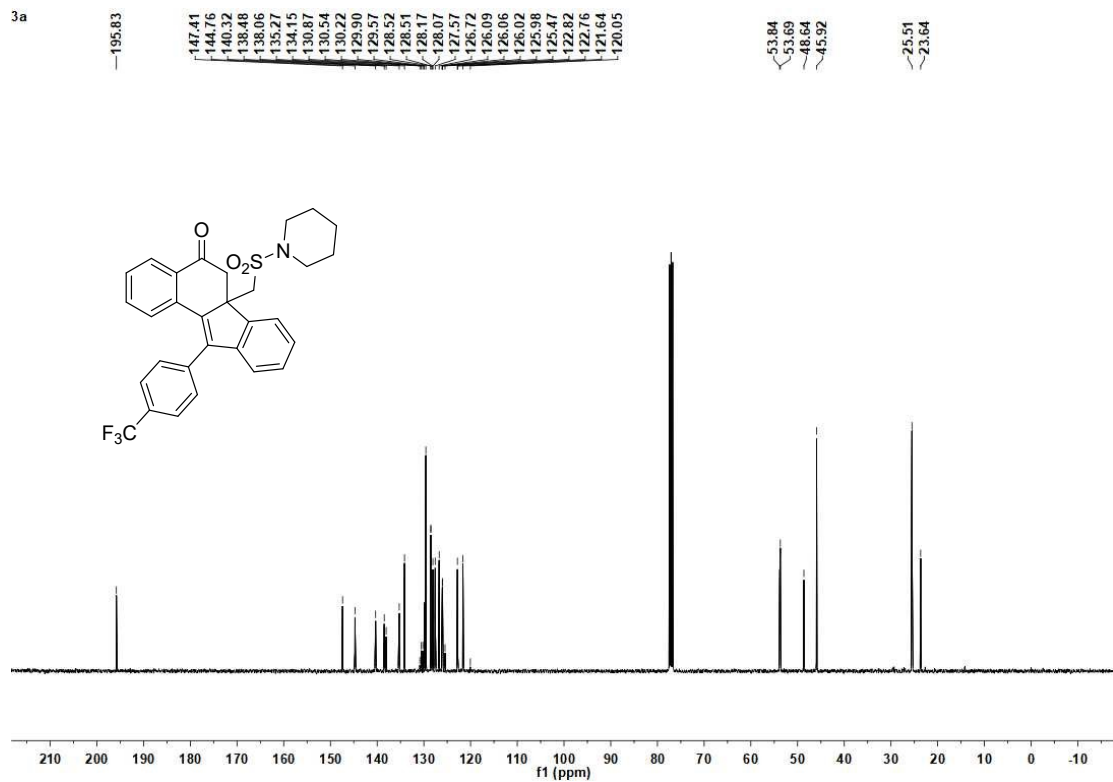
¹³C NMR spectrum of 5f



¹H NMR spectrum of 5g

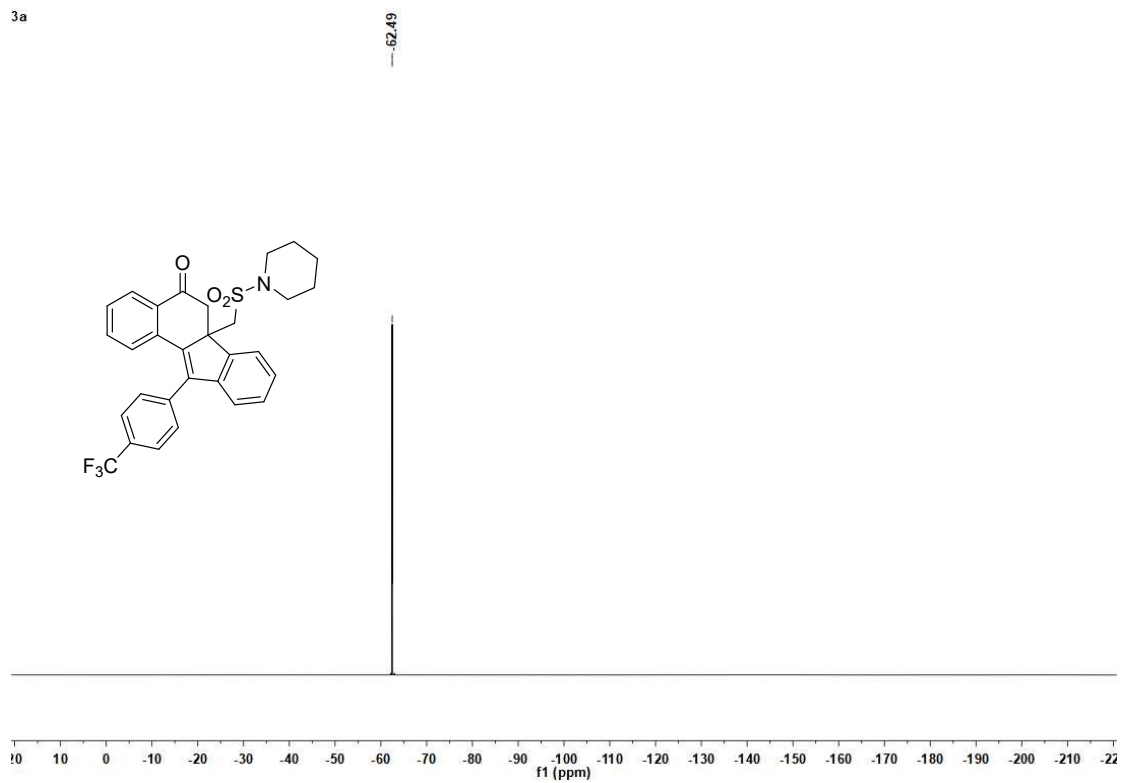


¹³C NMR spectrum of 5g

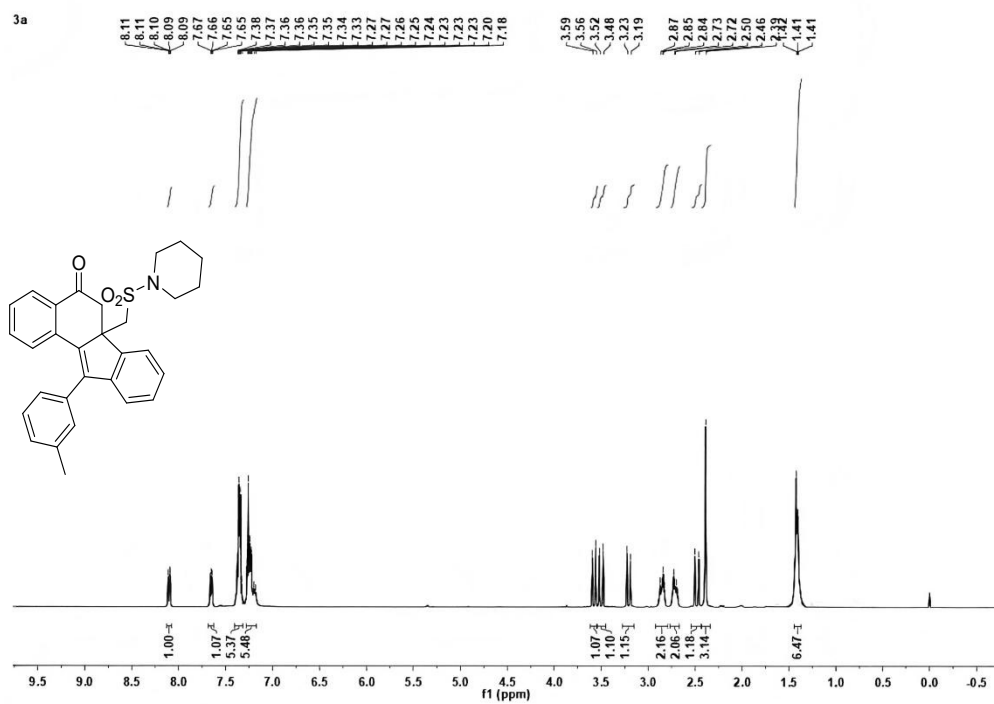


¹⁹F NMR spectrum of 5g

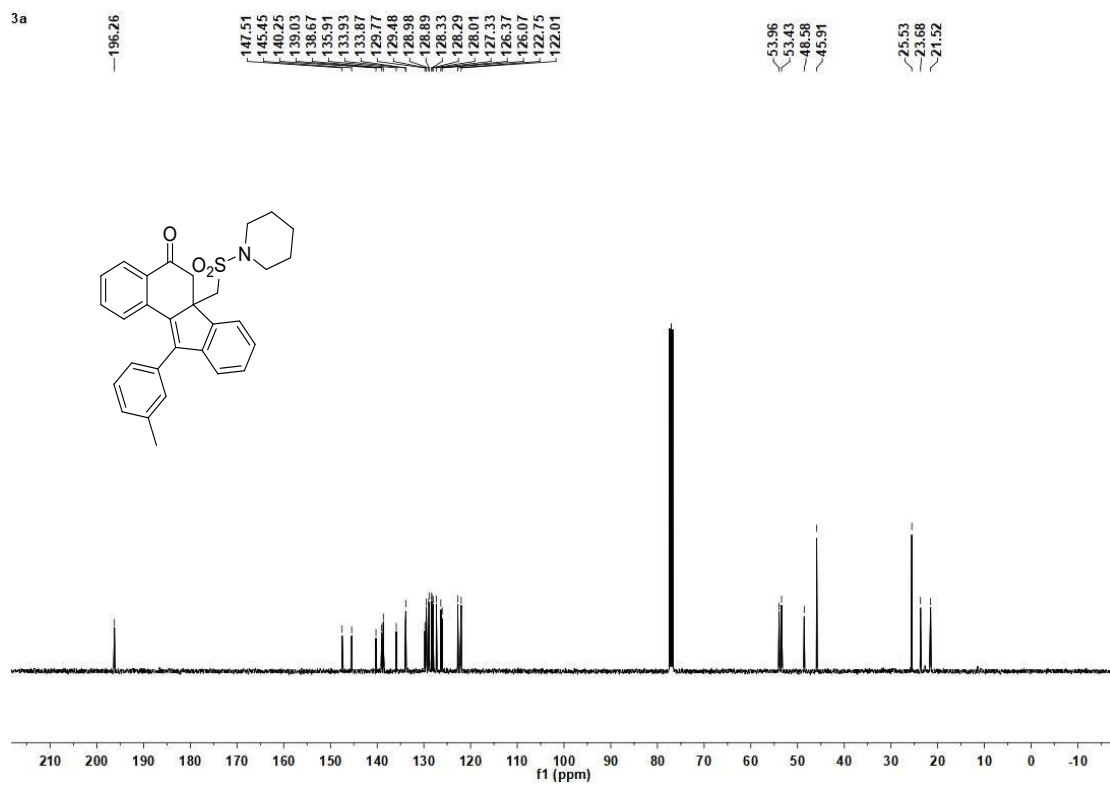
3a



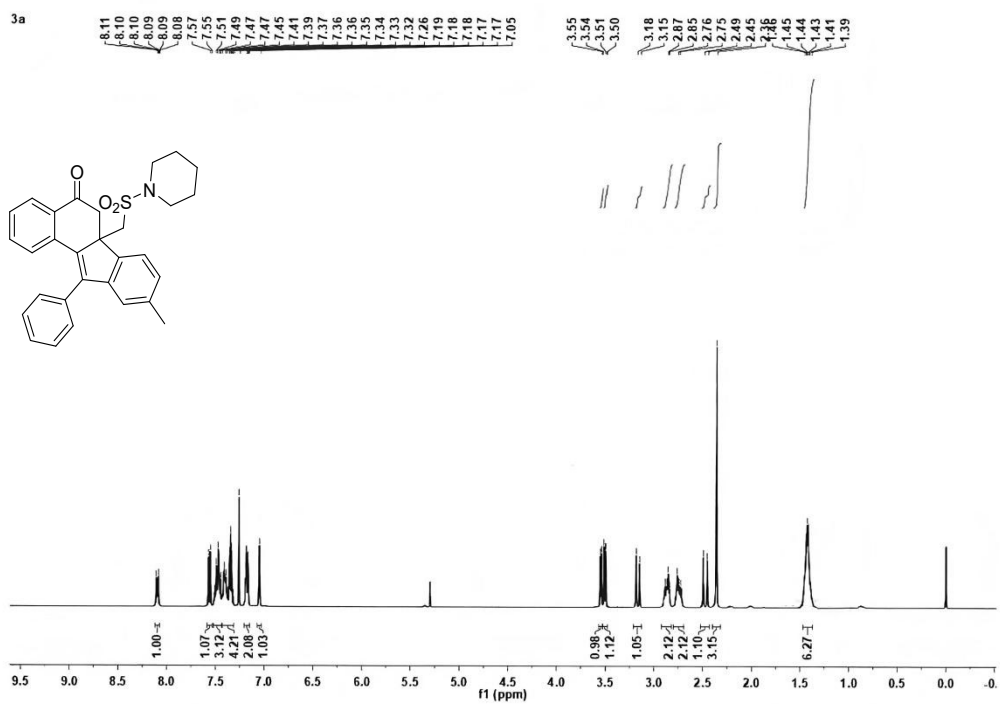
¹H NMR spectrum of 5h



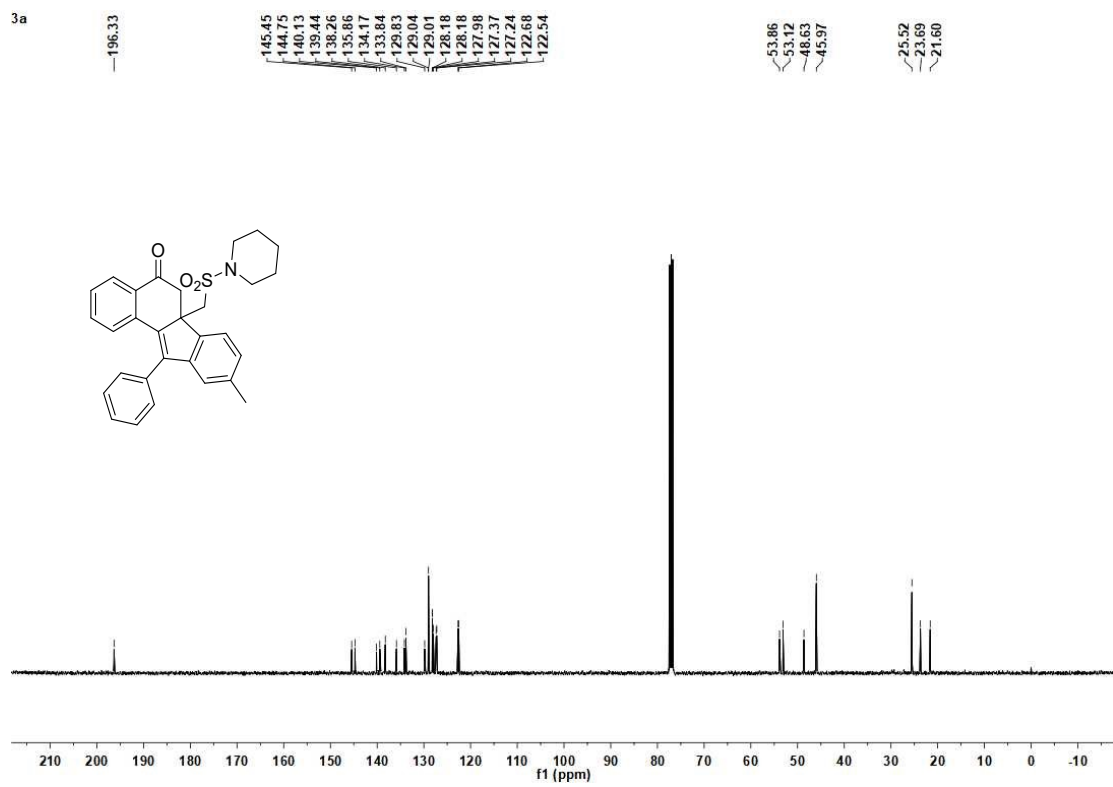
¹³C NMR spectrum of 5h



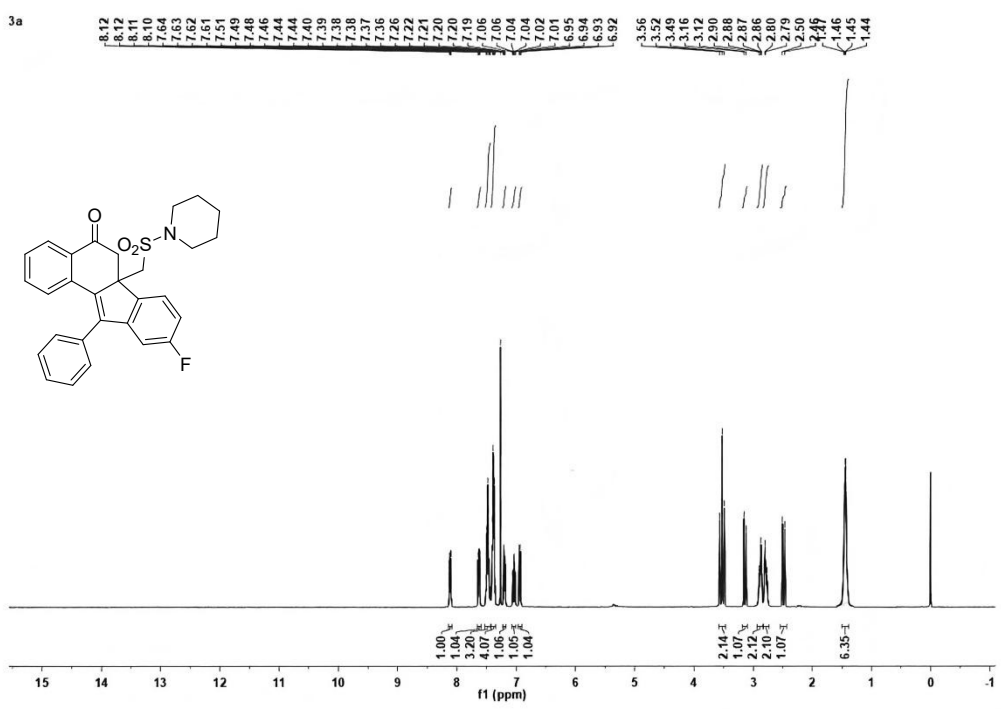
^1H NMR spectrum of **5i**



^{13}C NMR spectrum of **5i**

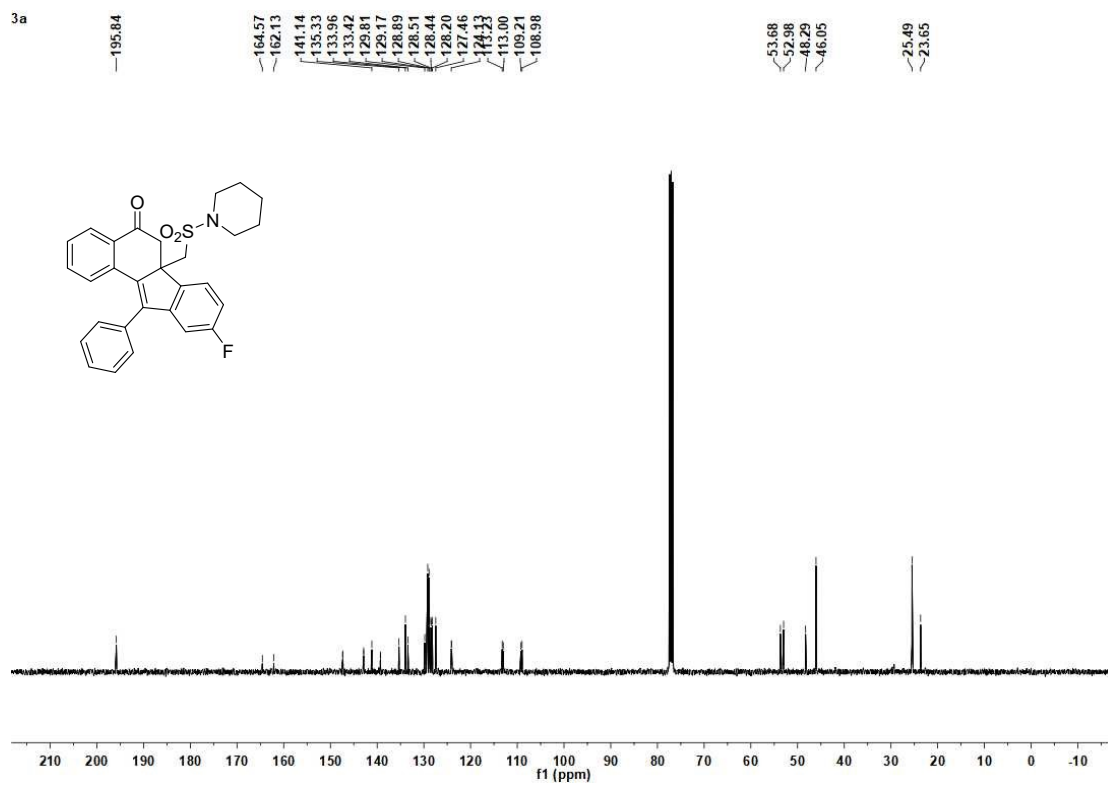


¹H NMR spectrum of 5j



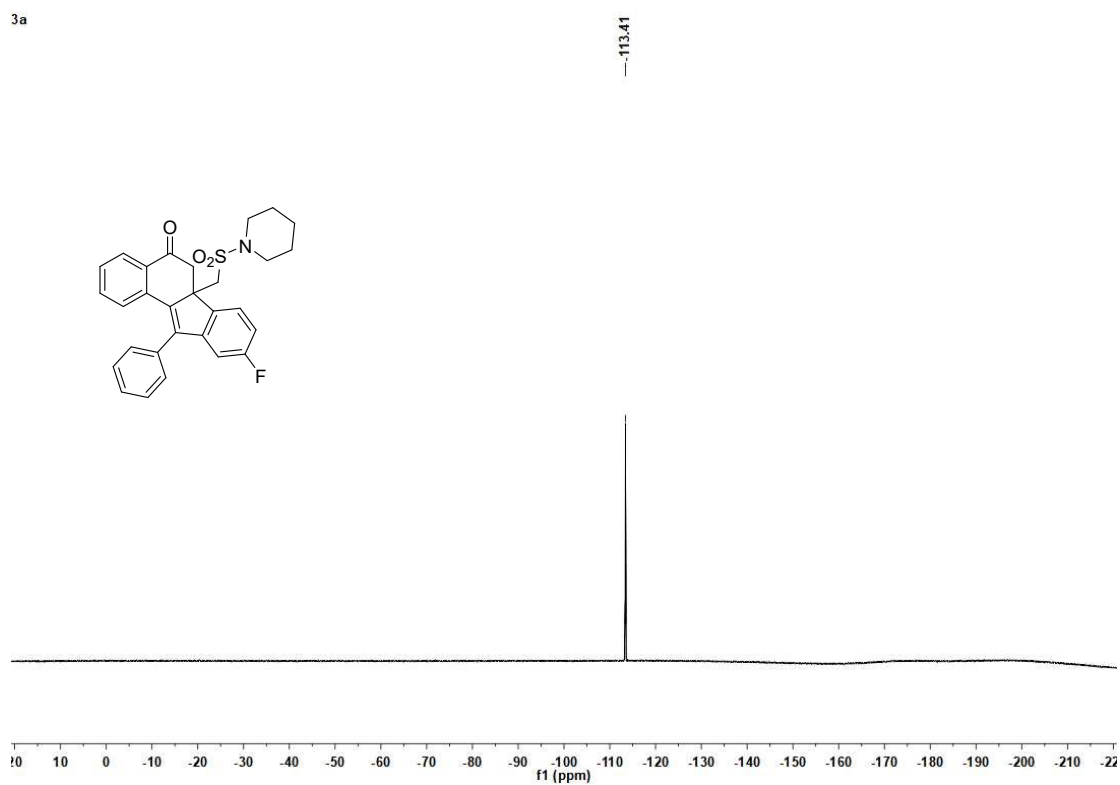
¹³C NMR spectrum of 5j

3a

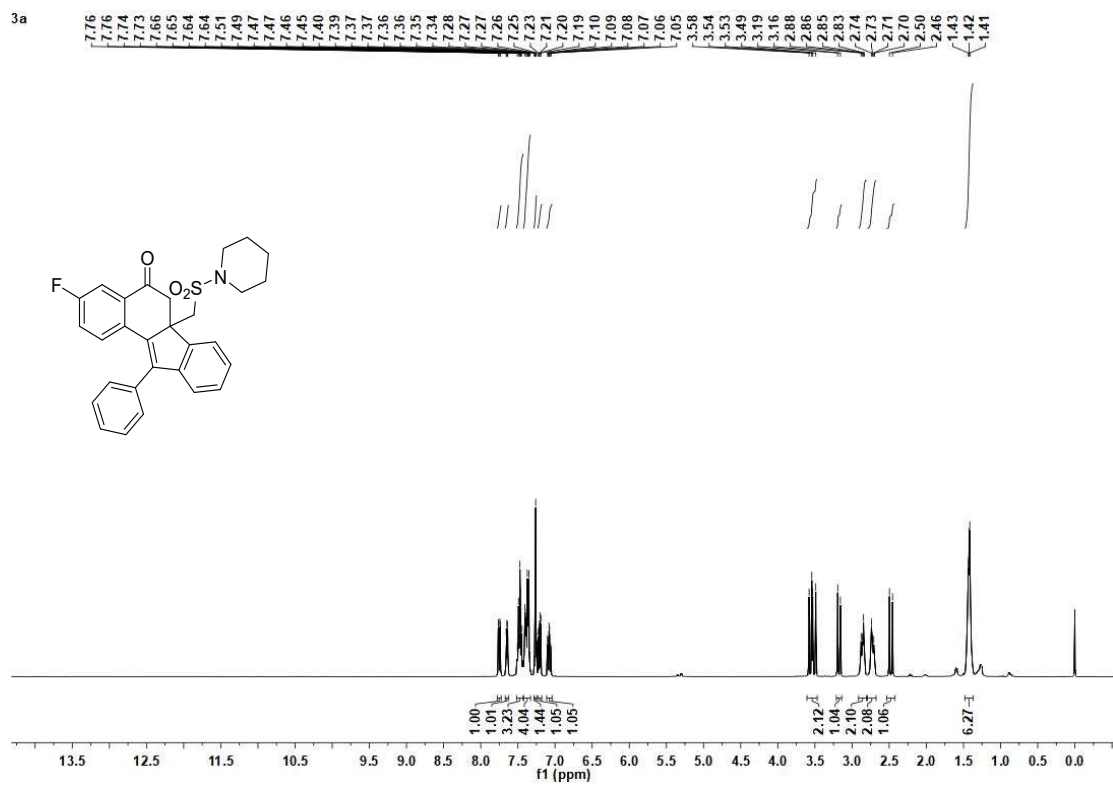


¹⁹F NMR spectrum of 5j

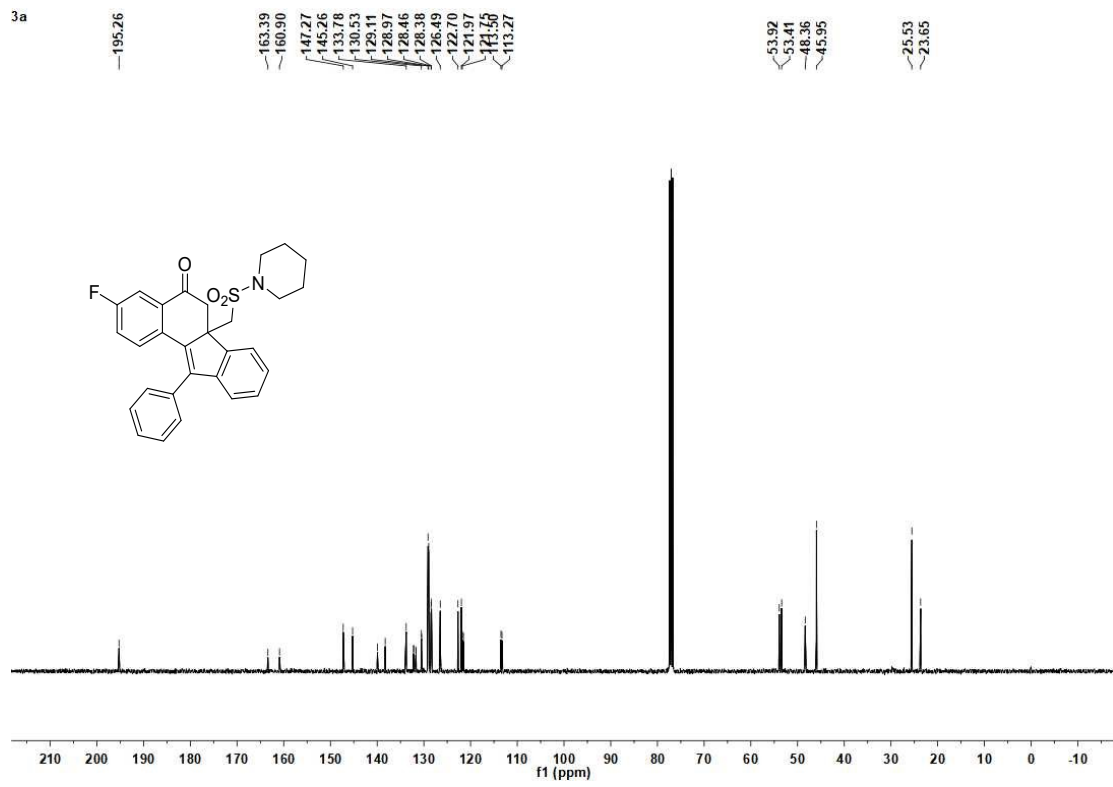
3a



¹H NMR spectrum of 5k

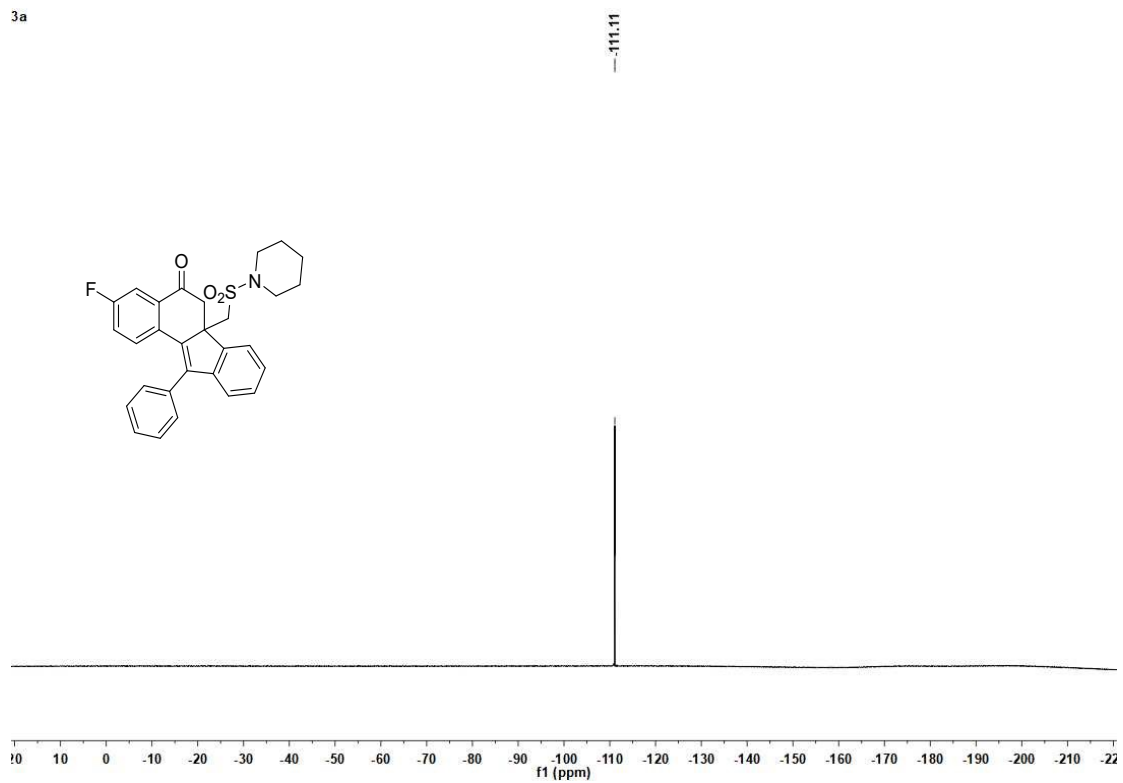
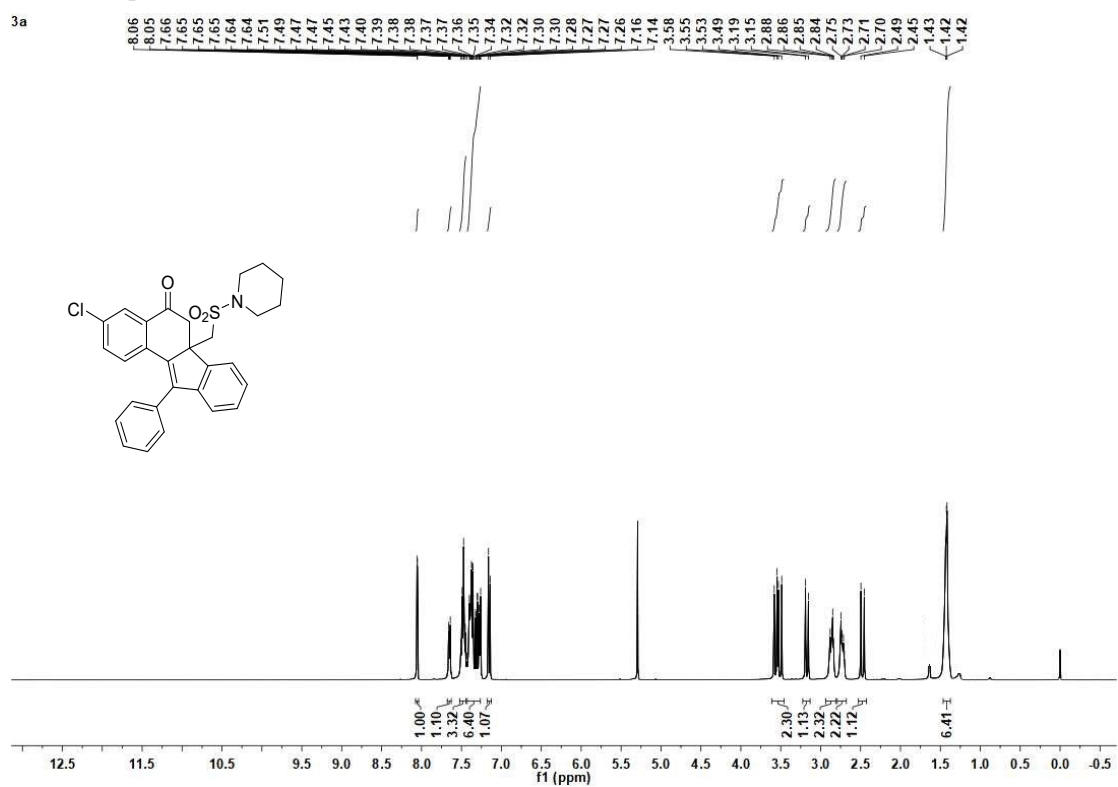


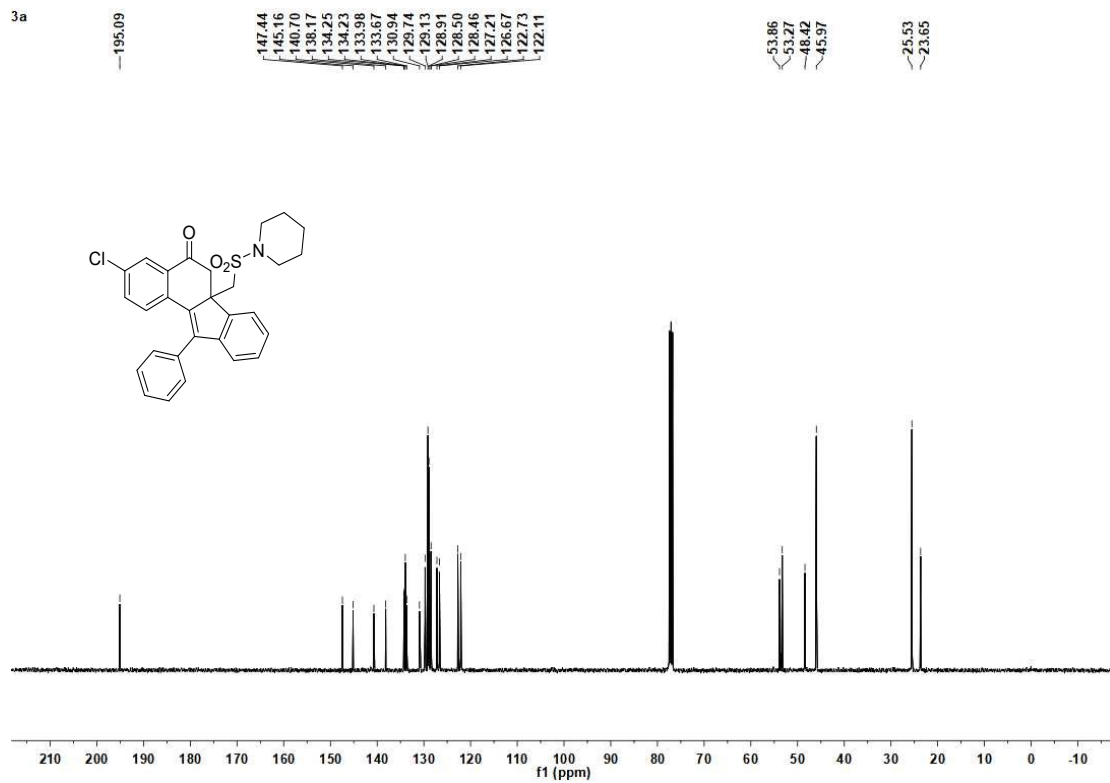
¹³C NMR spectrum of 5k



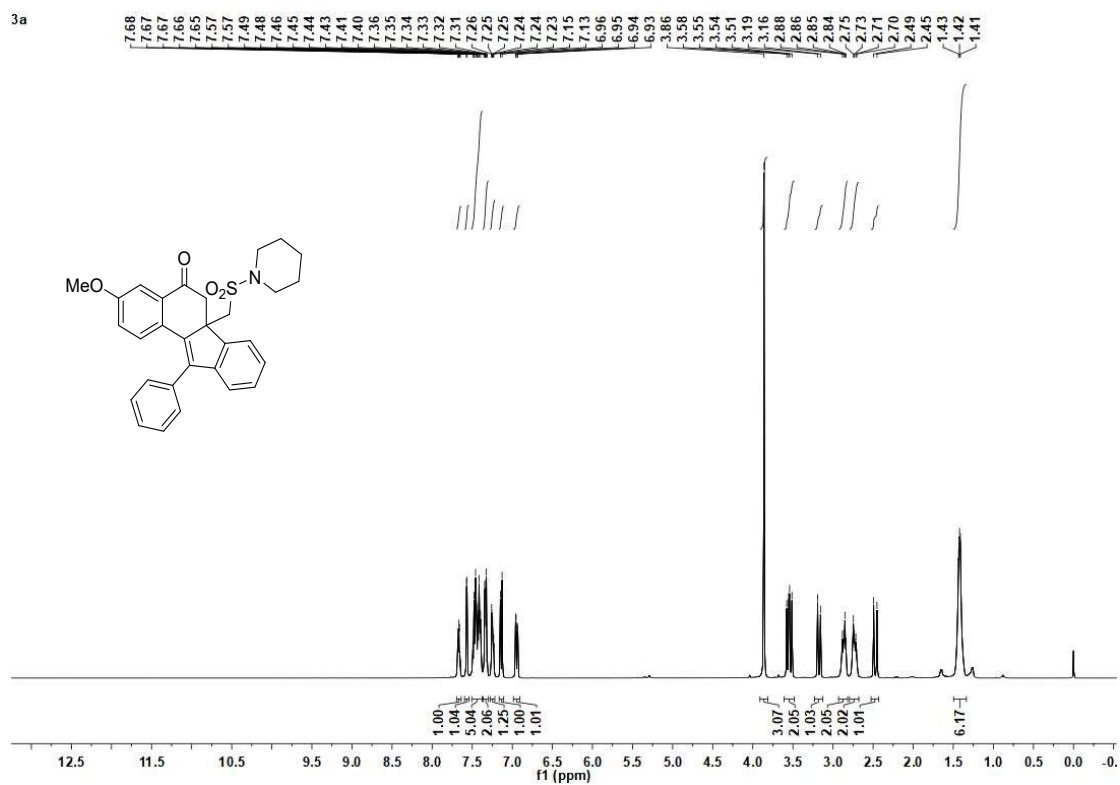
¹⁹F NMR spectrum of 5k

3a

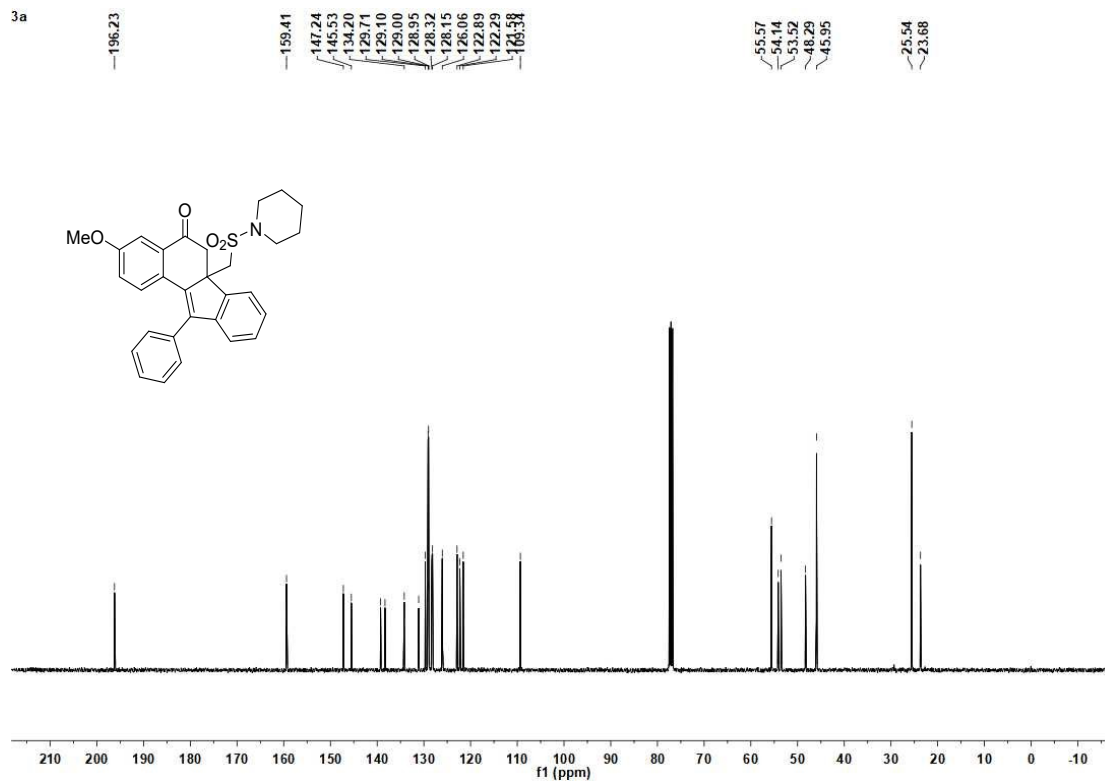
¹H NMR spectrum of 5I¹³C NMR spectrum of 5I



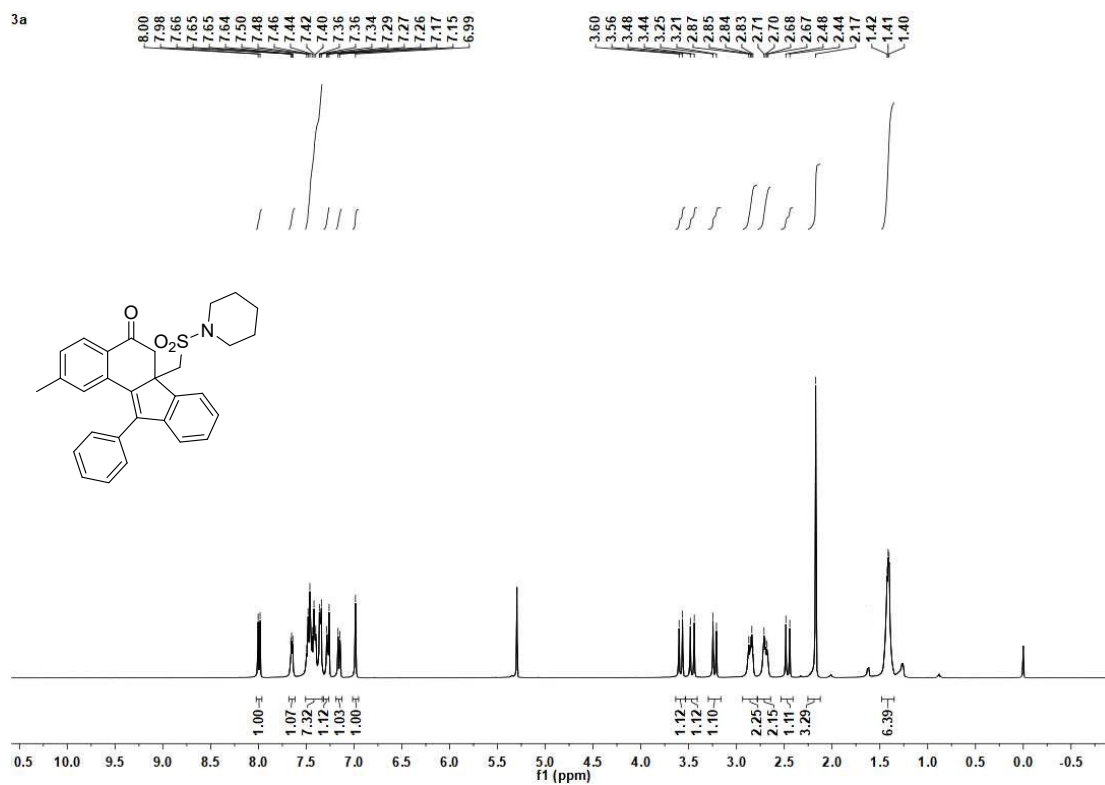
¹H NMR spectrum of 5m



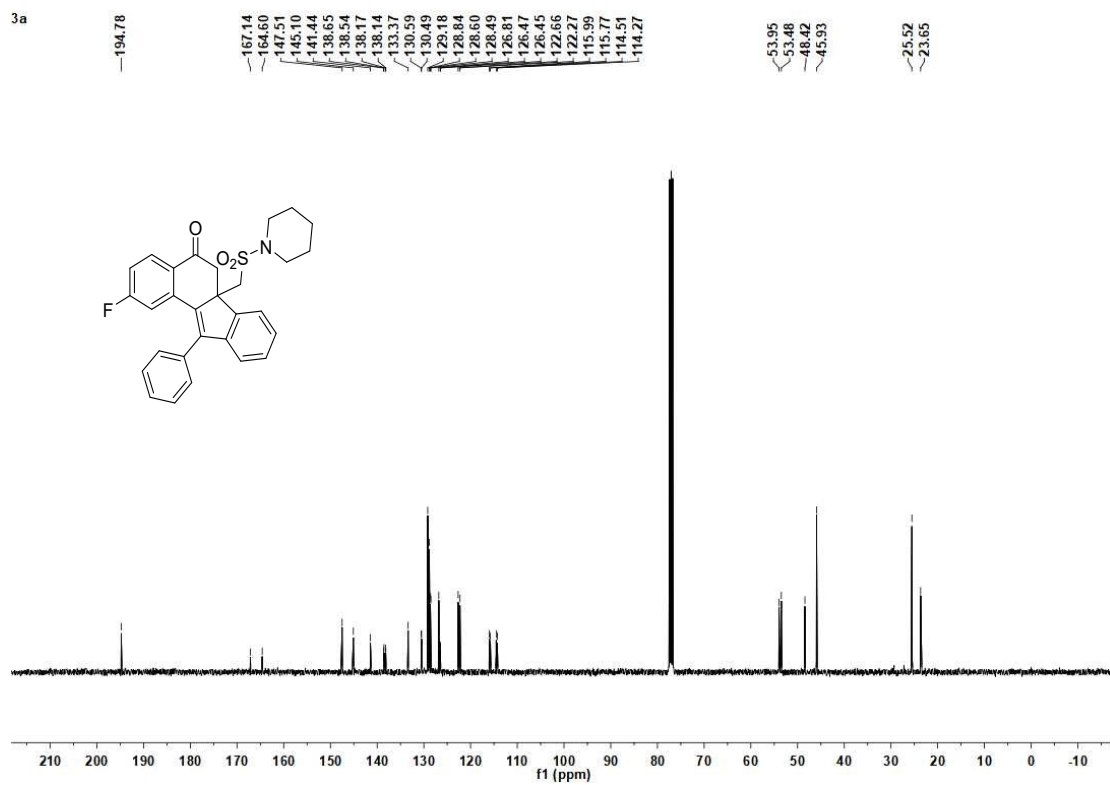
¹³C NMR spectrum of 5m



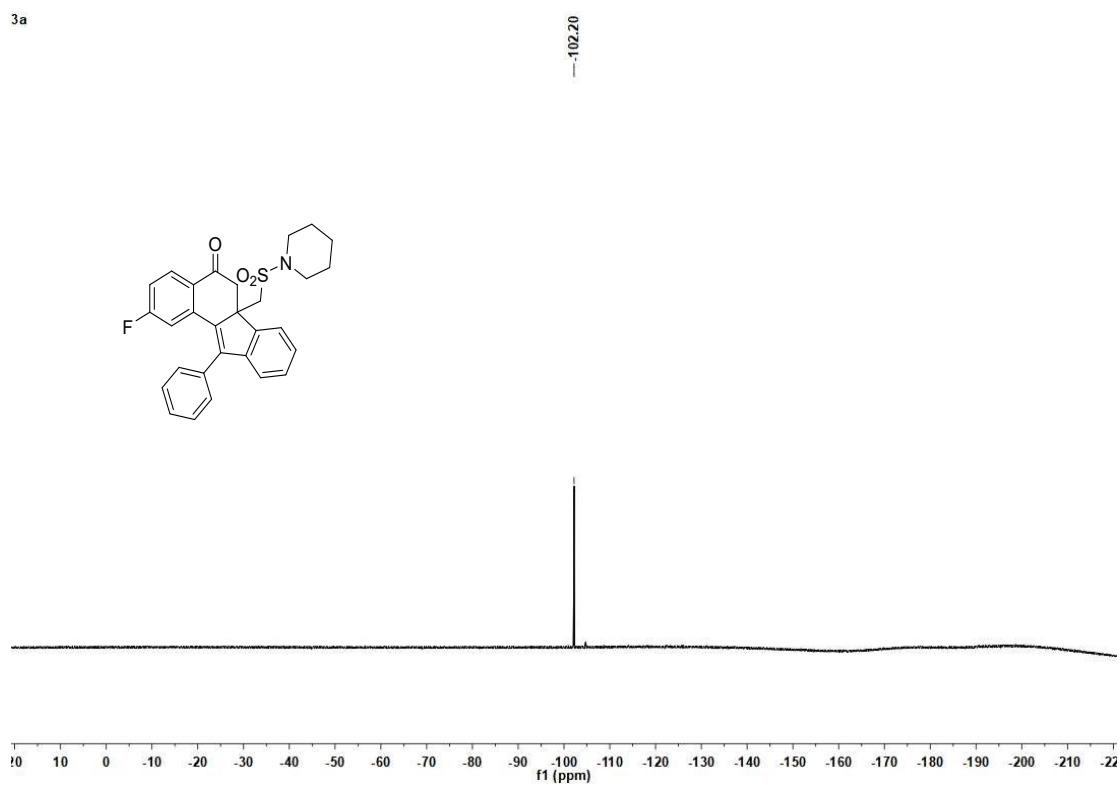
¹H NMR spectrum of 5n



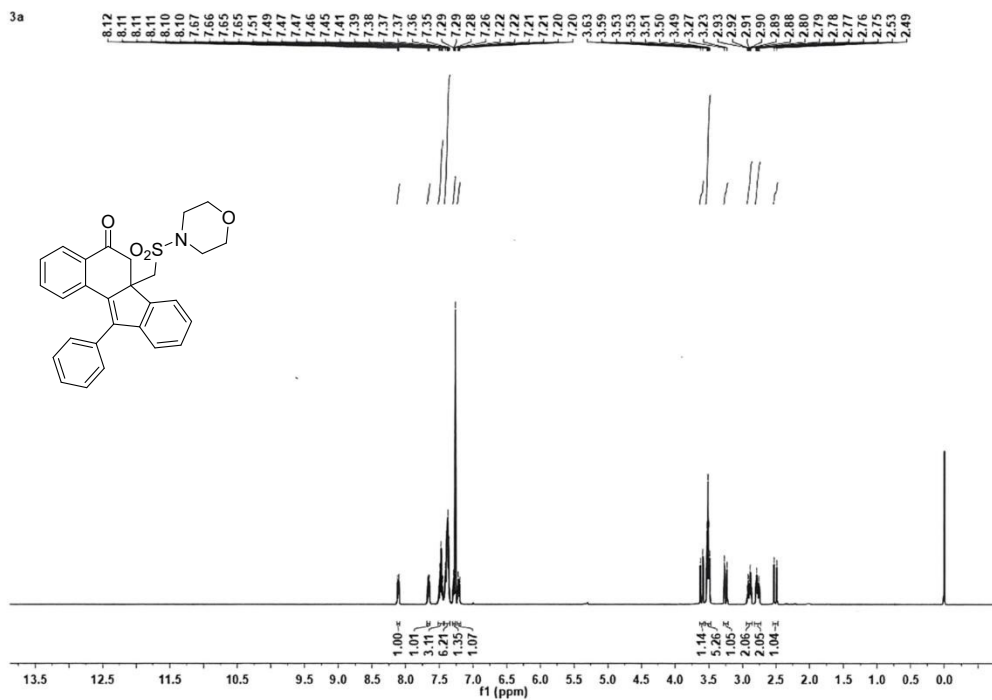
¹³C NMR spectrum of 5n



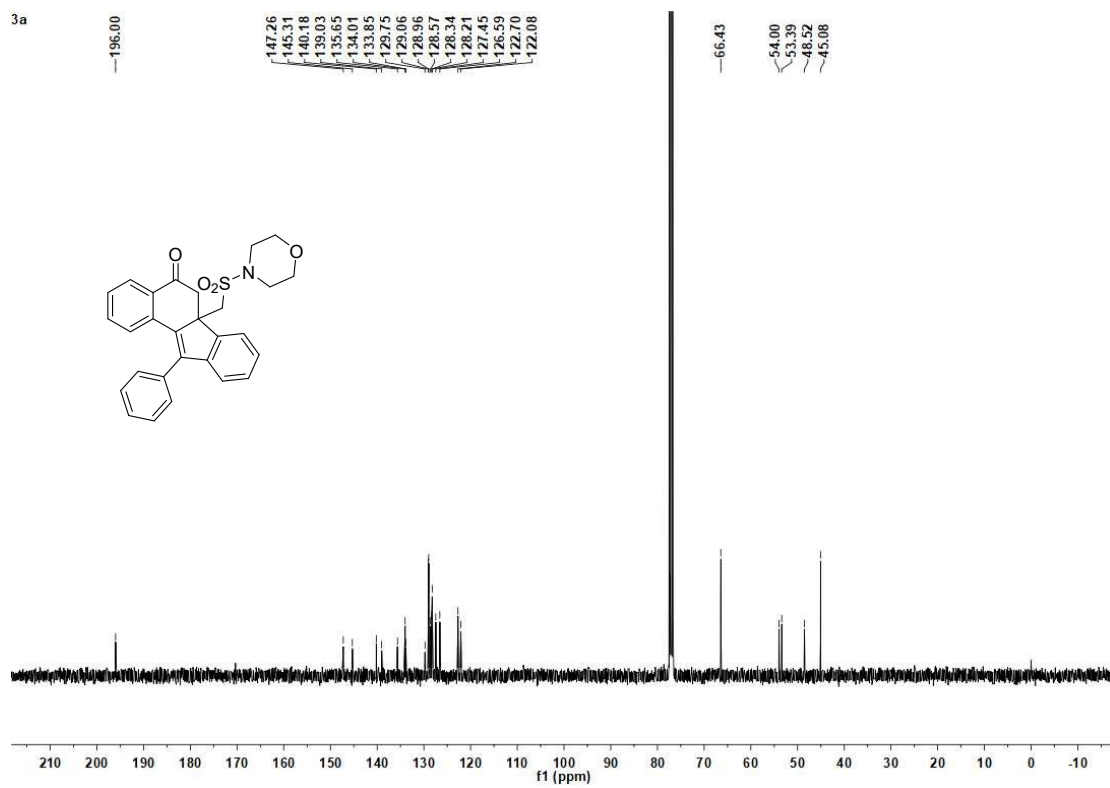
^{19}F NMR spectrum of **5o**



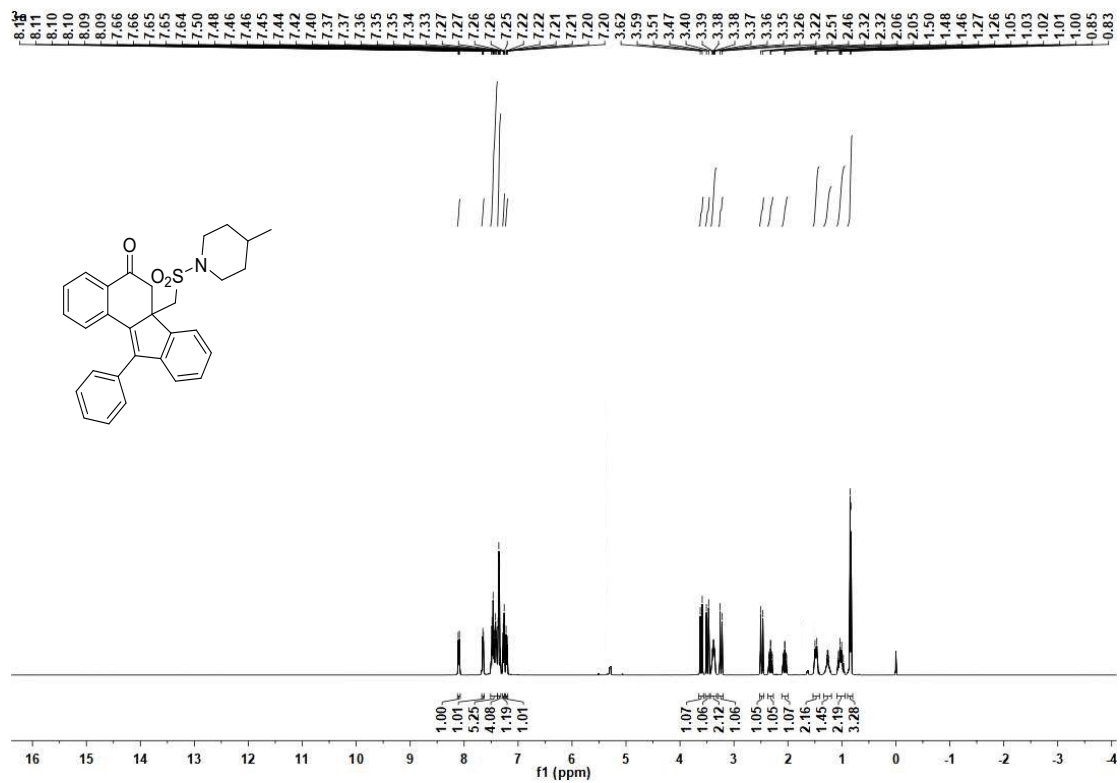
^1H NMR spectrum of **5p**



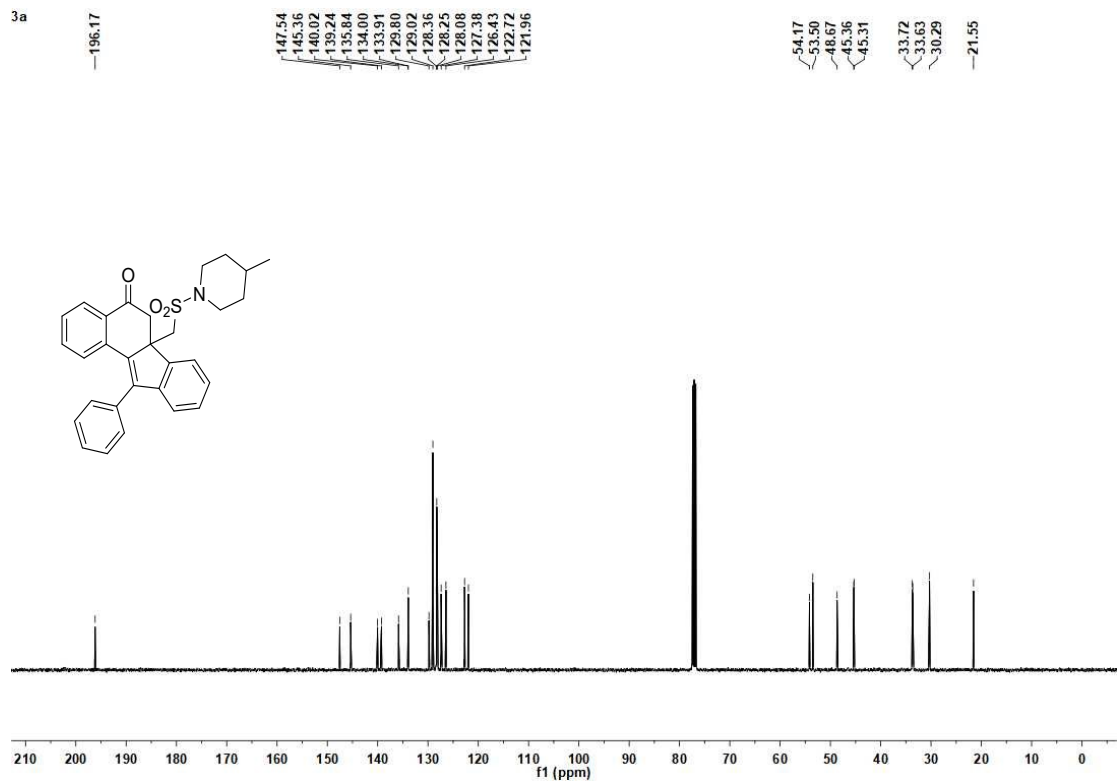
¹³C NMR spectrum of 5p



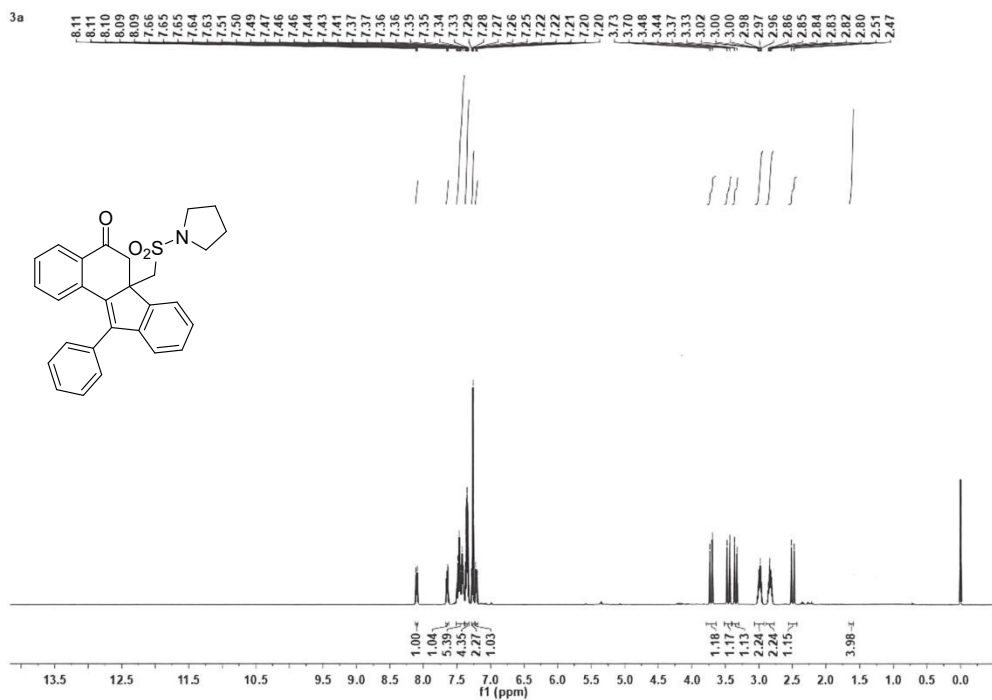
¹H NMR spectrum of 5q



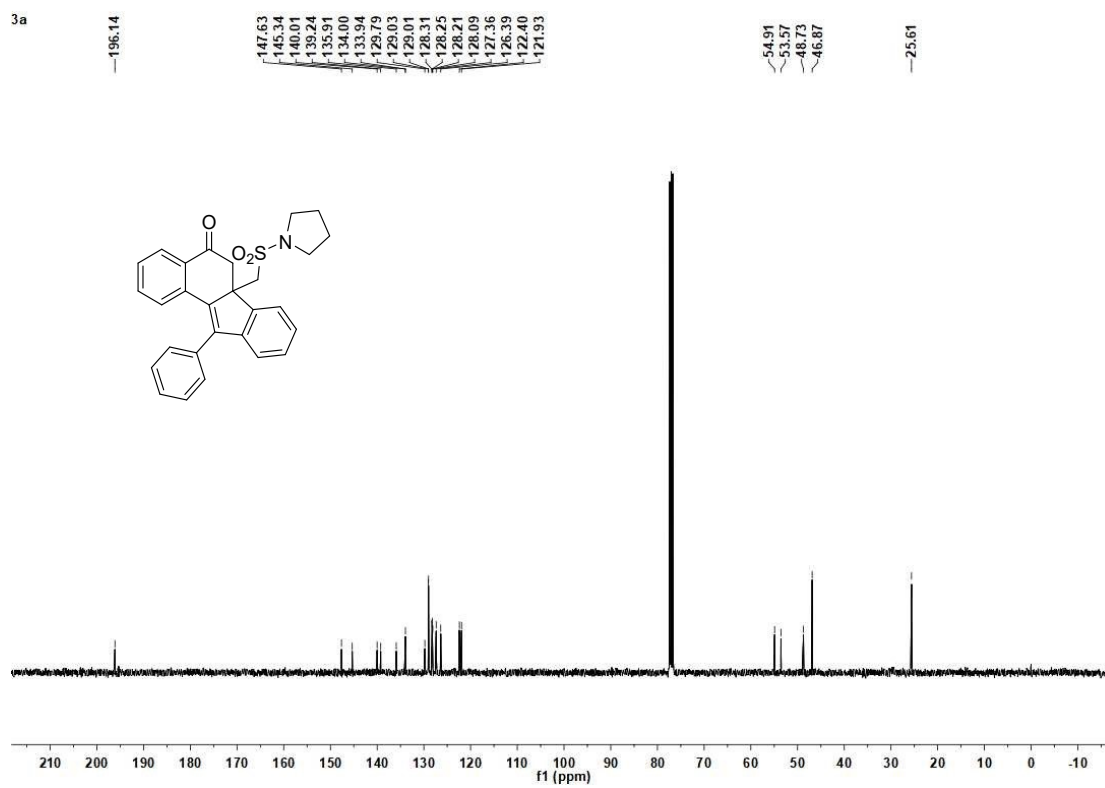
¹³C NMR spectrum of 5q



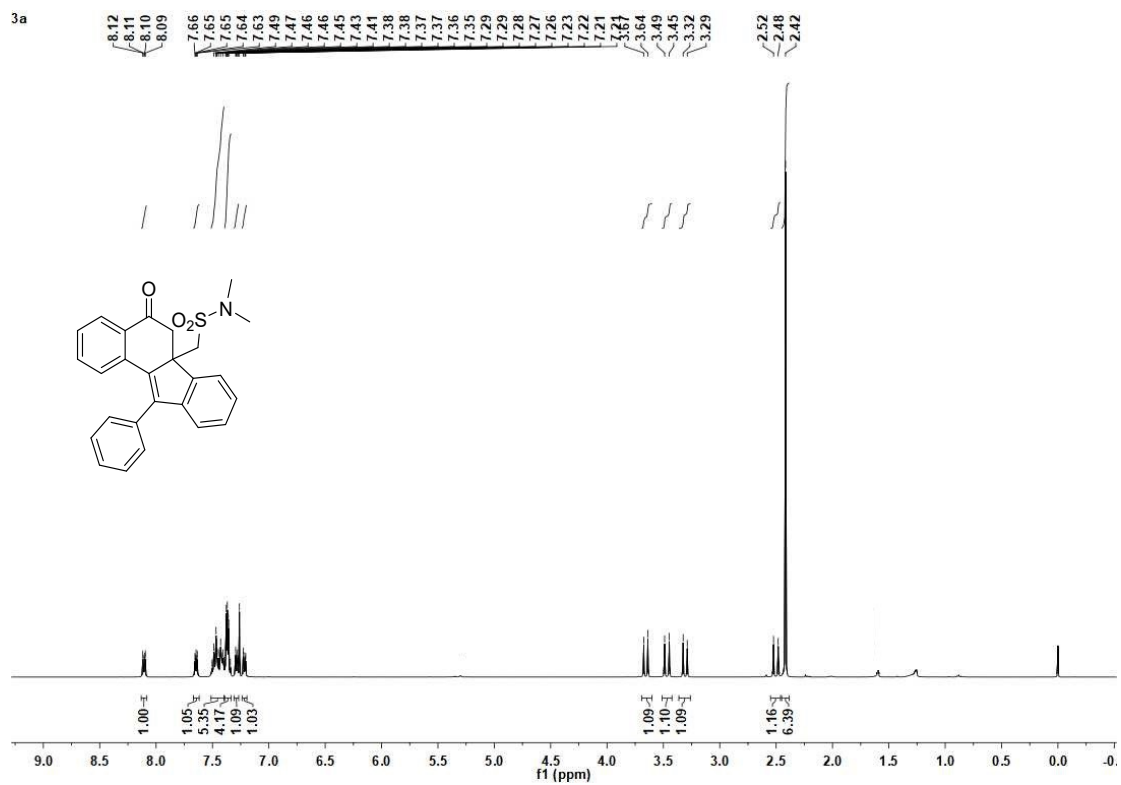
¹H NMR spectrum of 5r



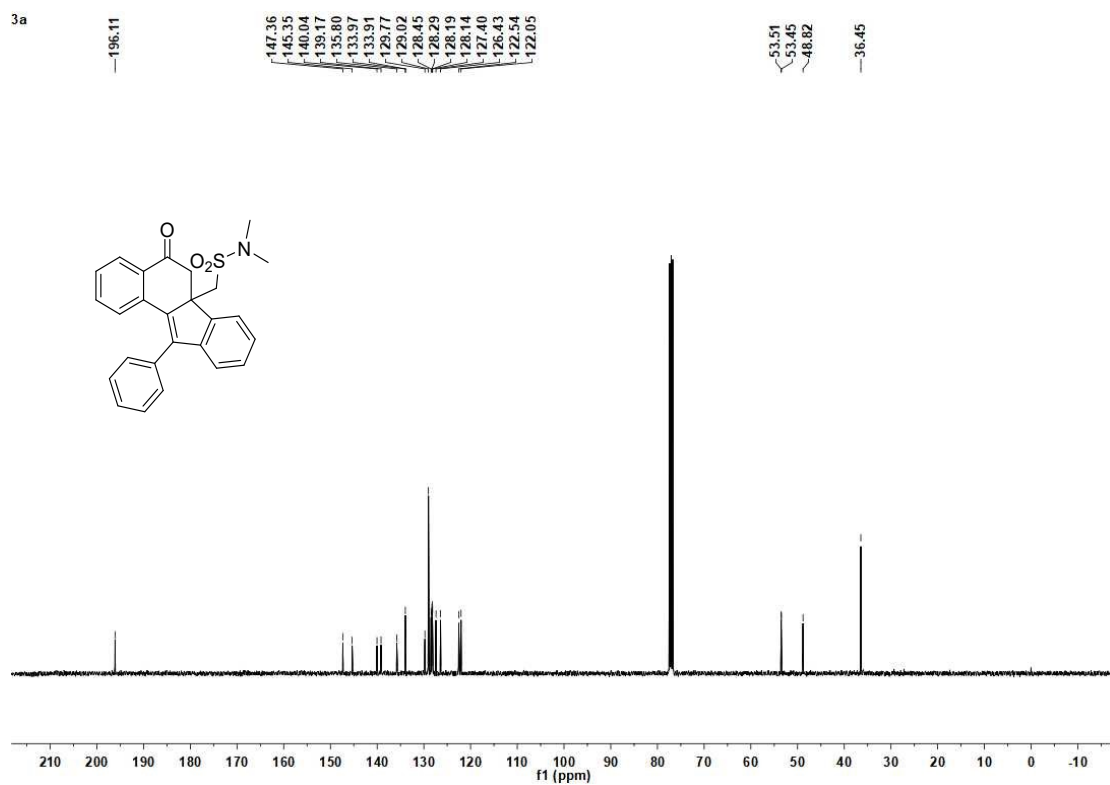
¹³C NMR spectrum of 5r



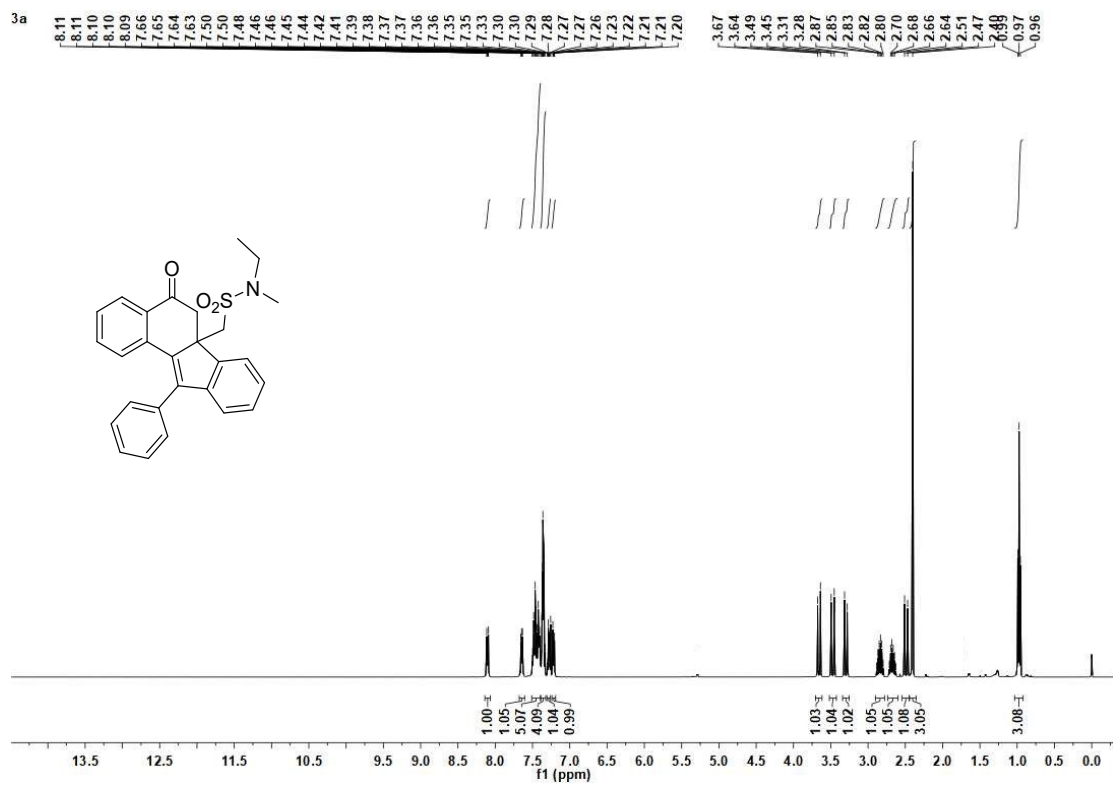
¹H NMR spectrum of 5s



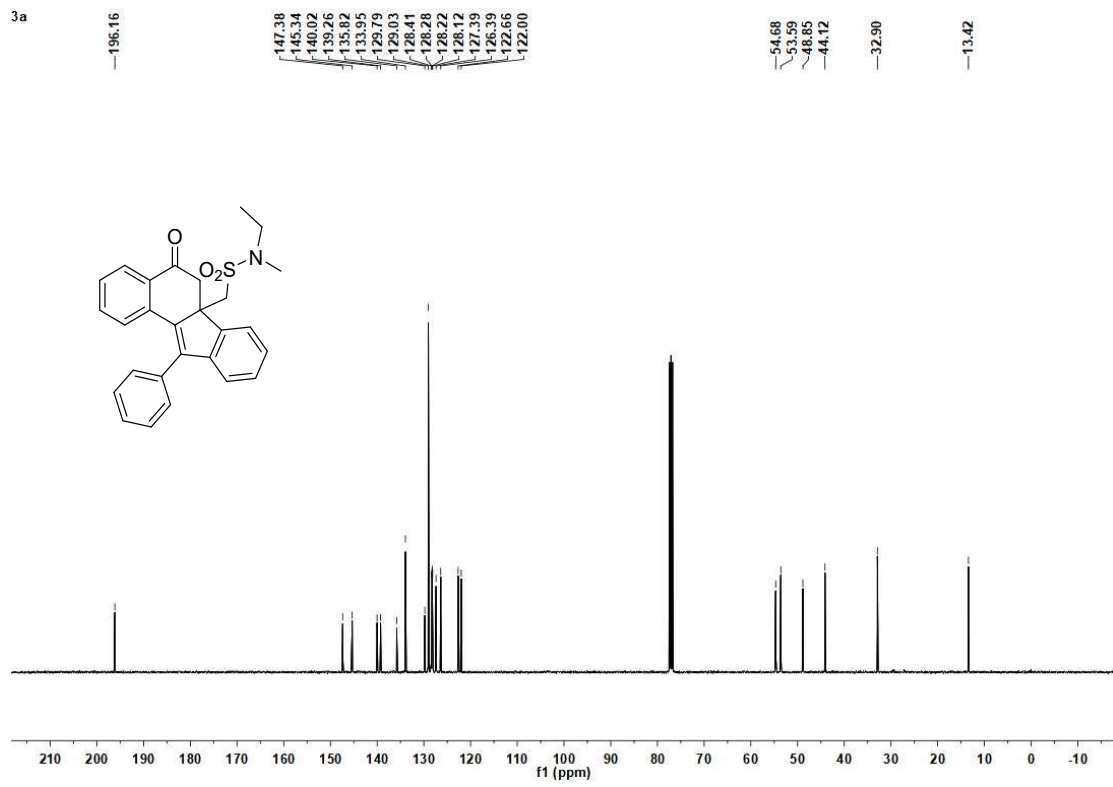
¹³C NMR spectrum of 5s



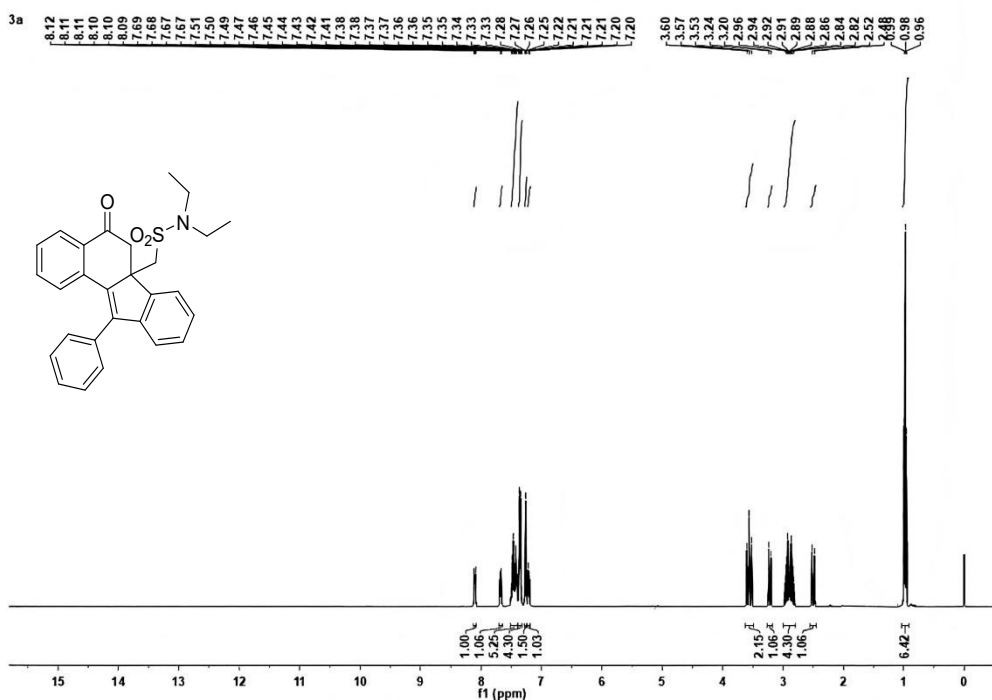
¹H NMR spectrum of 5t



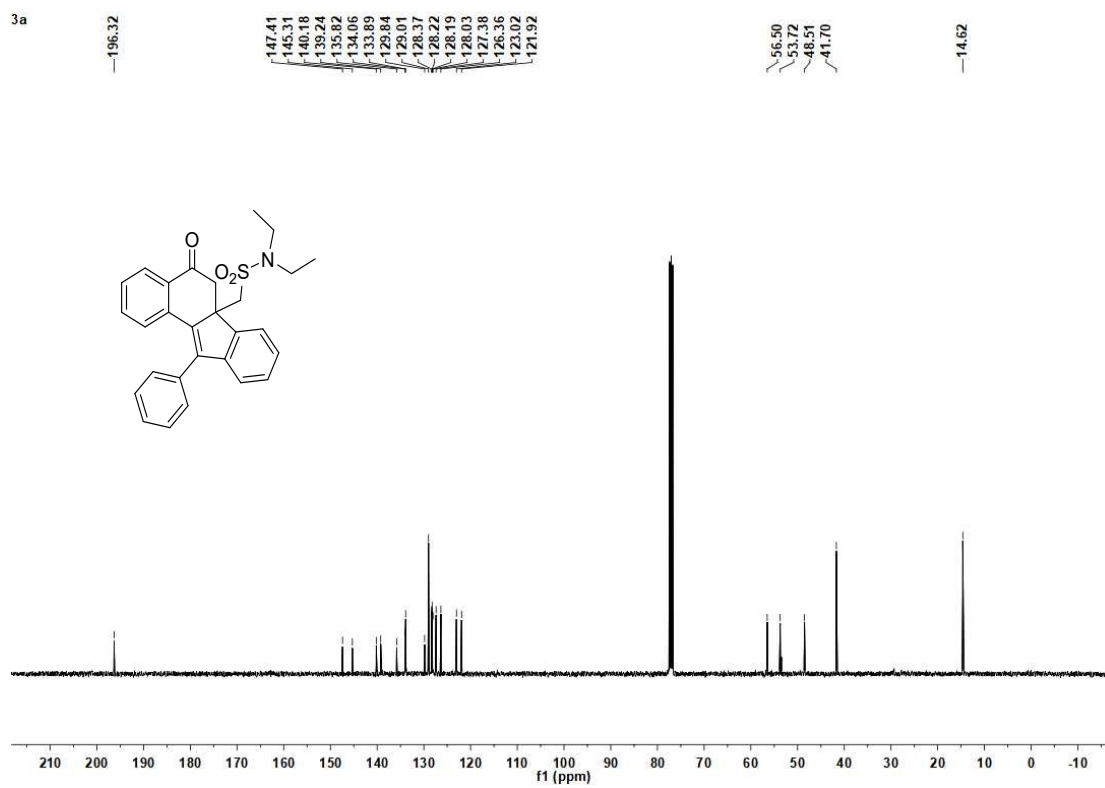
¹³C NMR spectrum of 5t



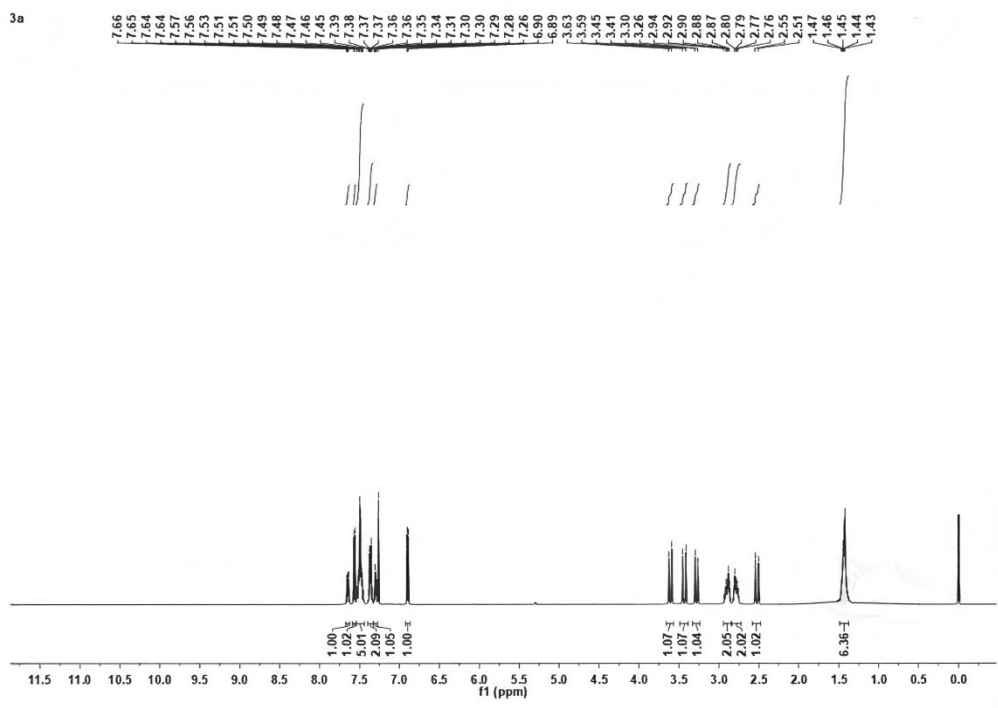
¹H NMR spectrum of 5u



¹³C NMR spectrum of 5u



¹H NMR spectrum of 5v



^{13}C NMR spectrum of 5v

