

## Supporting information

# Red Light-Mediated Photoredox Catalysis Promotes Regioselective Switch in the Difunctionalization of Alkenes

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## Contents

|                                                                                               |    |
|-----------------------------------------------------------------------------------------------|----|
| Supporting information.....                                                                   | 1  |
| 1.1 Chemicals and solvents .....                                                              | 3  |
| 1.2 Analysis .....                                                                            | 3  |
| 1.2.1 Nuclear magnetic resonance.....                                                         | 3  |
| 1.2.2 Chromatography .....                                                                    | 3  |
| 1.3 General procedure and optimizations .....                                                 | 4  |
| 1.4 Mechanistic investigation .....                                                           | 9  |
| 1.4.1 Electrochemical measurements .....                                                      | 9  |
| 1.4.2 Quenching experiment and radical probe experiment.....                                  | 11 |
| 1.4.3 Analysis of Cu-CF <sub>3</sub> complex.....                                             | 13 |
| 1.5 Experiments.....                                                                          | 19 |
| 1.5.1 Photocatalytic reaction setup .....                                                     | 19 |
| 1.5.2 Procedure for synthesis of TT-CF <sub>3</sub> <sup>+</sup> OTF <sup>-</sup> .....       | 19 |
| 1.5.3 Procedure for synthesis of Os(bptpy) <sub>2</sub> (PF <sub>6</sub> ) <sub>2</sub> ..... | 20 |
| 1.5.4 Procedure for the synthesis of olefins from phenols .....                               | 20 |
| 1.5.5 Procedure for synthesis of olefins from acids .....                                     | 21 |
| 1.5.6 Procedure for sulfonyltrifluoromethylation of olefins.....                              | 22 |
| 1.6 Characterization.....                                                                     | 23 |
| 1.7 Reference .....                                                                           | 40 |
| 1.8 Spectra .....                                                                             | 41 |

## **1.1 Chemicals and solvents**

All reagents and solvents were purchased from certified chemical vendors and used without prior purification. Demineralized water was obtained through deionization of tap water using a EUROTEC L4 reverse osmosis installation. This instrument filters out salts by means of a semi-permeable membrane. Water that was used never exceeded a conductivity of 0.5  $\mu\text{S}/\text{cm}$ . Gases were purchased in high-pressured cylinders (200 bar) and converted to the desired pressure by means of a pressure regulator.

## **1.2 Analysis**

### **1.2.1 Nuclear magnetic resonance**

$^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (101 MHz) spectra were recorded by using a Bruker Avance III Fourier Transform NMR spectrometer at 300 K unless explicitly stated otherwise, using deuterated solvents as internal standard ( $^1\text{H}$ :  $\delta$  7.26 ppm and  $^{13}\text{C}$  { $^1\text{H}$ }:  $\delta$  77.2 ppm in  $\text{CDCl}_3$ ;  $^1\text{H}$ :  $\delta$  2.50 ppm and  $^{13}\text{C}$  { $^1\text{H}$ }:  $\delta$  39.52 in  $\text{DMSO}-d_6$ ). Chemical shifts ( $\delta$ ) were expressed in ppm and coupling constants ( $J$ ) in Hertz (Hz). Splitting patterns are reported as: s (singlet), d (doublet), t (triplet), q (quadruplet), p (pentuplet), m (multiplet) or combinations thereof. Integration of the signals is presented as the number of hydrogen atoms.

### **1.2.2 Chromatography**

Thin-layer chromatography was performed by using a heptane/ethyl acetate (EtOAc) solvent system as mobile phase and a 0.20 mm silica gel on an aluminium plate (Machery-Nagel Precoated TLC sheets Alugram® SIL G/UV254) as stationary phase. Visualization of the 'spots' was enhanced by illumination with UV-light (254 nm).

Flash chromatography was performed by using an automatic chromatographic system (Biotage® or Combiflash®) with on-line UV-detection (254 nm and 280 nm unless explicitly stated otherwise). A heptane/EtOAc solvent system was used as mobile phase and commercial silica cartridges (12-80 g, Grace®) as stationary phase.

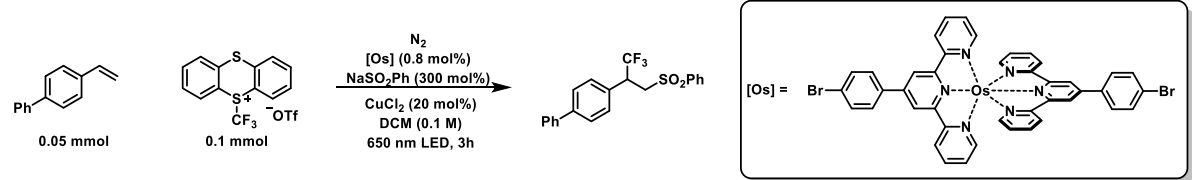
## 1.3 General procedure and optimizations

### General procedure for optimizations:

A dried 8 mL reaction vial with magnetic stirring bar was charged with photocatalyst, CF<sub>3</sub>-source, co-catalyst, sodium sulfinate salts (RSO<sub>2</sub>Na) and 4-vinylbiphenyl (0.05 mmol, 1 equiv.) after which the vessel was evacuated using Schlenk techniques and flushed with N<sub>2</sub> three times. Dry DCM was added by using a syringe flushed with inert gas. The resulting mixture was stirred for 3-4 h under irradiation of blue LED (40 W, 456 nm) or red light (EvoluChem™ LED 650PF, 650 nm, 20 mW/cm<sup>2</sup>) with the EvoluChem PhotoRedOx Box at room temperature. After 3-4 h, trifluorotoluene (prepared in stock solution) was added as an internal standard. After shaking the vial, the mixture was filtered by celite and was submitted to the NMR to determine the yield through <sup>19</sup>F NMR.

### 1.3.1 Optimizations based on red light system:

**Table S1.** Investigation of the amount of sulfinate salts and CF<sub>3</sub> reagent and addition of ligands.

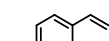
|  |                                     |                        |
|--------------------------------------------------------------------------------------|-------------------------------------|------------------------|
| Entry                                                                                | Variations                          | Yield (%) <sup>a</sup> |
| 1                                                                                    | none                                | 76(73 <sup>b</sup> )   |
| 2                                                                                    | 2 equiv. NaSO <sub>2</sub> Ph       | 50                     |
| 3                                                                                    | 1.5 equiv. CF <sub>3</sub> -reagent | 66                     |
| 4                                                                                    | DCM (0.05 M)                        | 43                     |
| 5                                                                                    | 30 mol% bpy ligand                  | 0                      |
| 6                                                                                    | 30 mol% 1,10-phen ligand            | 0                      |

<sup>a</sup>Yield was determined by <sup>19</sup>F NMR with trifluorotoluene as internal standard. <sup>b</sup>Isolated yields.

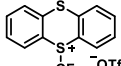
The amount of each of the component was evaluated: Lower concentration or equivalent of -CF<sub>3</sub> reagent and sulfinate salts provided comparably lower yield of product, which can be attributed to the kinetic effect. Since the presence of Cu-salts, commonly used ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (1,10-

phen) were added in the reactions, however, both of the ligands did not provide any product.

**Table S2.** Investigations of -CF<sub>3</sub> reagents by the irradiation of red light.



0.05 mmol



0.1 mmol

N<sub>2</sub>

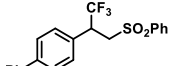
[Os] (0.8 mol%)

NaSO<sub>2</sub>Ph (300 mol%)

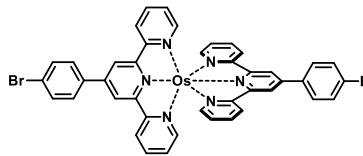
CuCl<sub>2</sub> (20 mol%)

DCM (0.1 M)

650 nm LED, 3h



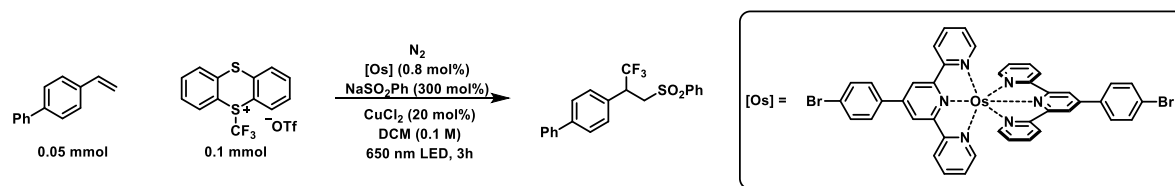
[Os] =



| Entry | Variations                                      | Yield (%) <sup>a</sup> |
|-------|-------------------------------------------------|------------------------|
| 1     | 2.0 equiv. Togni I                              | trace                  |
| 2     | 2.0 equiv. Togni II                             | 8                      |
| 3     | 2.0 equiv. Umemoto reagent                      | 20                     |
| 4     | 2.0 equiv. Mes-Umemoto reagent                  | trace                  |
| 5     | 2.0 equiv. bpyCu(CF <sub>3</sub> ) <sub>3</sub> | 0                      |

<sup>a</sup>Yield was determined by <sup>19</sup>F NMR with trifluorotoluene as internal standard.

When alternative electrophilic -CF<sub>3</sub> sources such as Togni reagents, Umemoto reagents, and Cu(CF<sub>3</sub>)<sub>3</sub>bpy were exploited, we observed substantially lower or negligible yields of the desired product. For Togni's reagents, Cu-salts directly reacted with them to form the Cu-CF<sub>3</sub> complexes, which caused lower selectivity and reactivity in the reaction. When Umemoto reagent was used as the -CF<sub>3</sub> source, the Os-catalyst at the excited state directly reduced it to the corresponding -CF<sub>3</sub> radical, which generated the free -CF<sub>3</sub> radical and caused the formation of side products, β-trifluoromethylated product. Compared to Umemoto reagent, Mes-Umemoto reagent was more difficult to be reduced by the Os-catalyst. Therefore, only trace quantity of product was detected. At last, Cu(CF<sub>3</sub>)<sub>3</sub>bpy was also examined and no product was obtained. From the <sup>19</sup>F NMR spectra, Cu(CF<sub>3</sub>)<sub>3</sub>bpy was intact under this reaction conditions.

**Table S3.** Investigation of Cu-salts and solvents in the difunctionalization reaction.

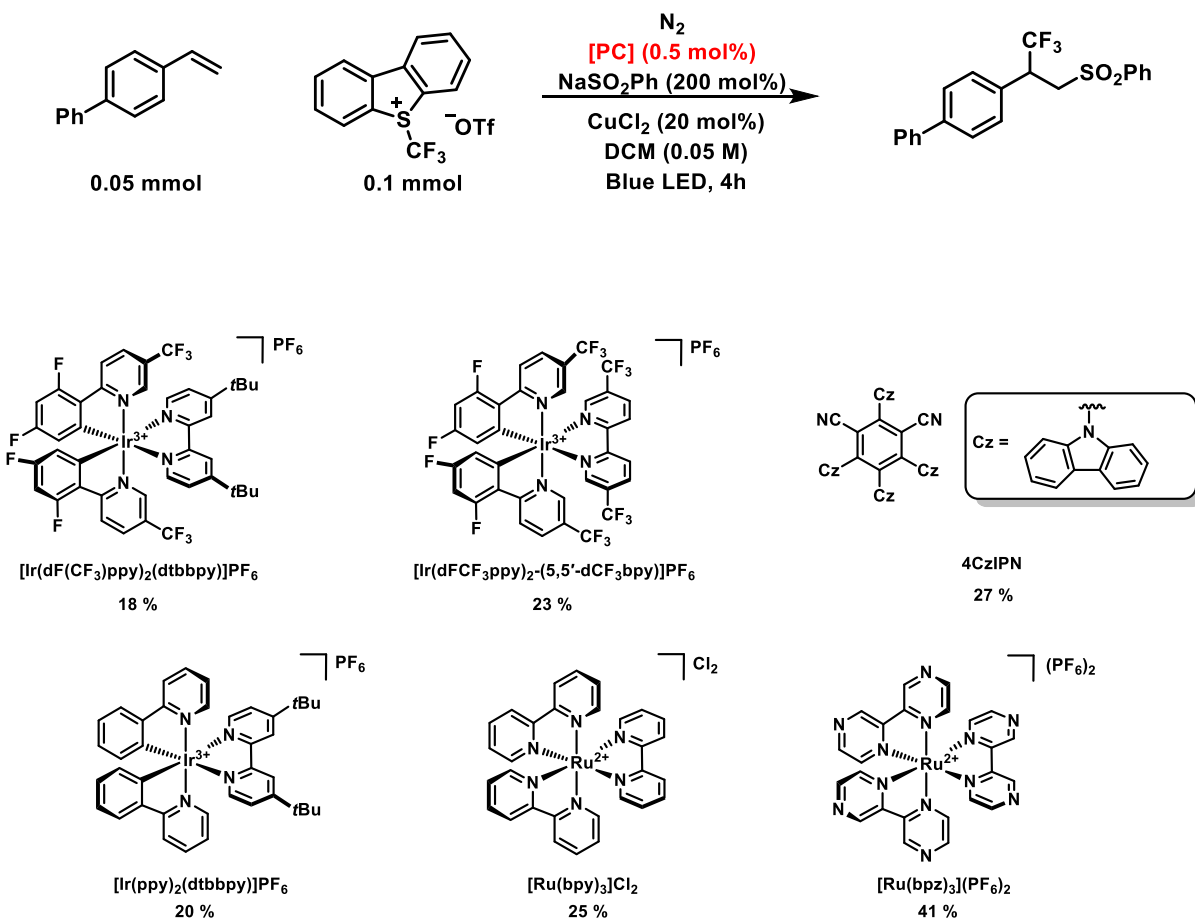
| Entry | Variations                    | Yield (%) <sup>a</sup> |
|-------|-------------------------------|------------------------|
| 1     | 20 mol% CuCl                  | 51                     |
| 2     | 20 mol% Cu powder             | 0                      |
| 3     | MeCN (0.1 M)                  | 26                     |
| 4     | EtOAc (0.1 M)                 | 30                     |
| 5     | 6 h                           | 61                     |
| 6     | No CuCl <sub>2</sub>          | 0                      |
| 7     | No [Os]                       | 0                      |
| 8     | No light                      | 0                      |
| 9     | 40 W NIR Kessil lamp (740 nm) | 24                     |
| 10    | w/o EvoluChem PhotoRedOx Box  | 52                     |

<sup>a</sup>Yield was determined by <sup>19</sup>F NMR with trifluorotoluene as internal standard. <sup>b</sup>Isolated yields.

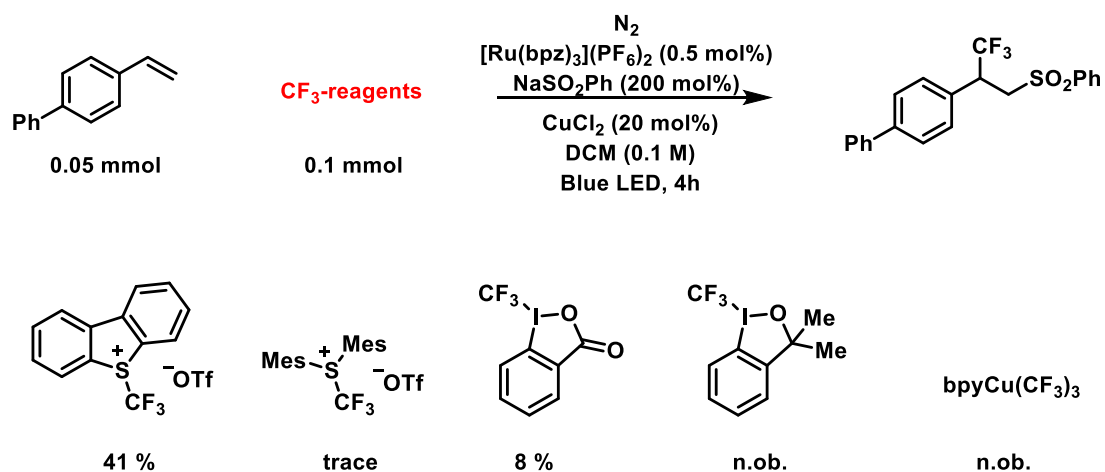
Investigations were conducted to find out whether variations in the valence state of Cu, specifically by involving Cu<sup>I</sup> salt (such as CuCl) and Cu<sup>0</sup> in the form of fresh copper powder, had an influence in the reaction. The results indicated that the presence of CuCl promoted the reaction to obtain the product, albeit resulting in a slightly reduced yield of approximately 20%. We assumed that the concentration of chloride was also crucial for achieving high photocatalytic activity (more details is found in **Scheme S8**). However, Cu-powder was not efficient under these conditions, giving no product. Additionally, two frequently used solvents in photocatalytic functionalization of -CF<sub>3</sub> group, namely MeCN and EtOAc, were also evaluated, however, no improvement was found. At last, to further increase the yield of product, we prolonged the reaction time to 6 hours, however, it revealed that extending the reaction time resulted in a marginal reduction in yield. To assess the necessity of the photocatalyst, Cu-salts, and light, a series of control experiments were meticulously conducted, elucidating their necessity in propelling the reaction.

### 1.3.2 Optimizations based on blue light system:

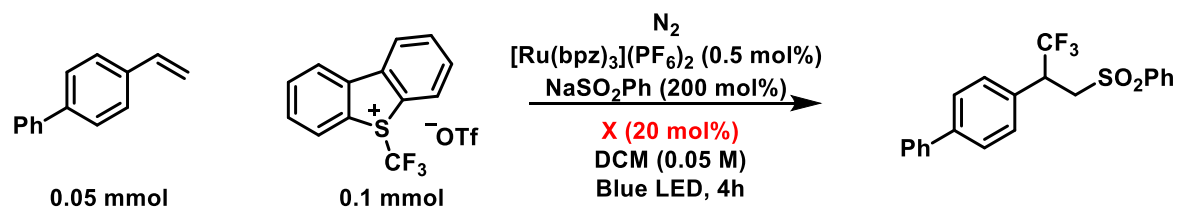
#### Investigation of the photocatalysts



#### Investigation of CF<sub>3</sub>-sources

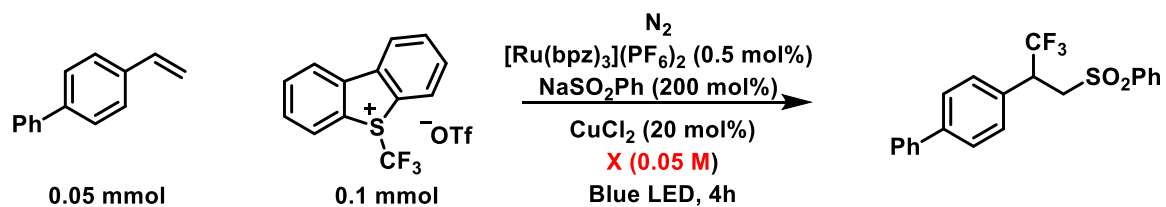


## Investigations of co-catalysts



| X                                            | Yield (%) |
|----------------------------------------------|-----------|
| $\text{CuCl}_2$                              | 41        |
| $\text{CuCl}$                                | 30        |
| $\text{Cu}(\text{CH}_3\text{CN})\text{PF}_6$ | 0         |
| $\text{Cu}(\text{OTf})_2$                    | 0         |
| $\text{CuCN}$                                | 31        |
| $\text{FeCl}_2$                              | 0         |
| $\text{MnCl}_2$                              | 0         |

## Investigation of solvents

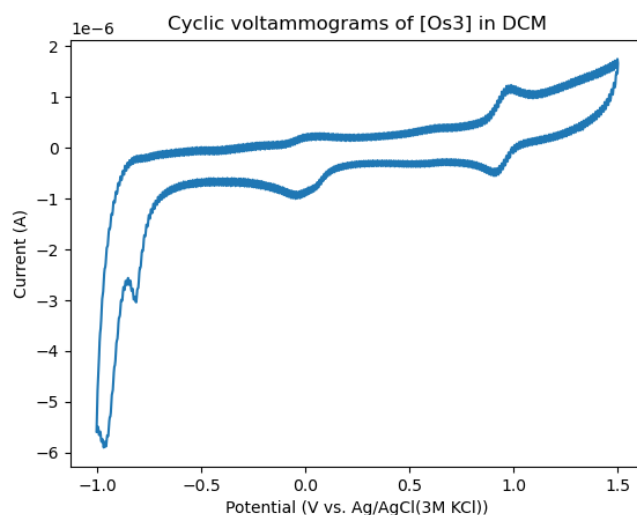


| X           | Yield (%) |
|-------------|-----------|
| MeCN        | 34        |
| DMSO        | trace     |
| DCM         | 41        |
| 1,2-DCE     | 28        |
| DMF         | 0         |
| Acetone     | trace     |
| EtOAc       | 27        |
| DCM (0.1 M) | 42        |

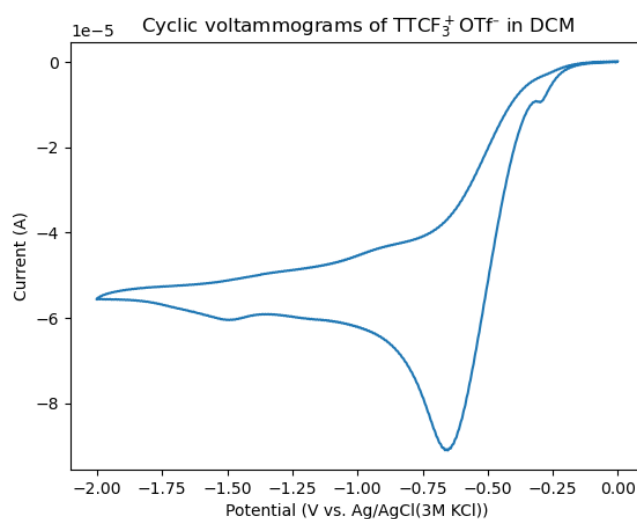
## 1.4 Mechanistic investigation

### 1.4.1 Electrochemical measurements

The electrochemical redox potentials were obtained by using a Metrohm Autolab potentiostat-galvanostat PGSTAT204 fitted with a glassy carbon (GC) working electrode (diameter = 3 mm), an Ag/AgCl (3 M KCl) reference electrode and a Pt-foil counter electrode, attached to a PC by using Nova v2.1.5 software. 0.1 mmol samples were dissolved in 15 mL 0.1 M tetra-*n*-butylammonium hexafluorophosphate ( $n\text{Bu}_4\text{NPF}_6$ ) in dry, degassed DCM. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction. The obtained value was referenced to Ag/AgCl (3 M KCl).



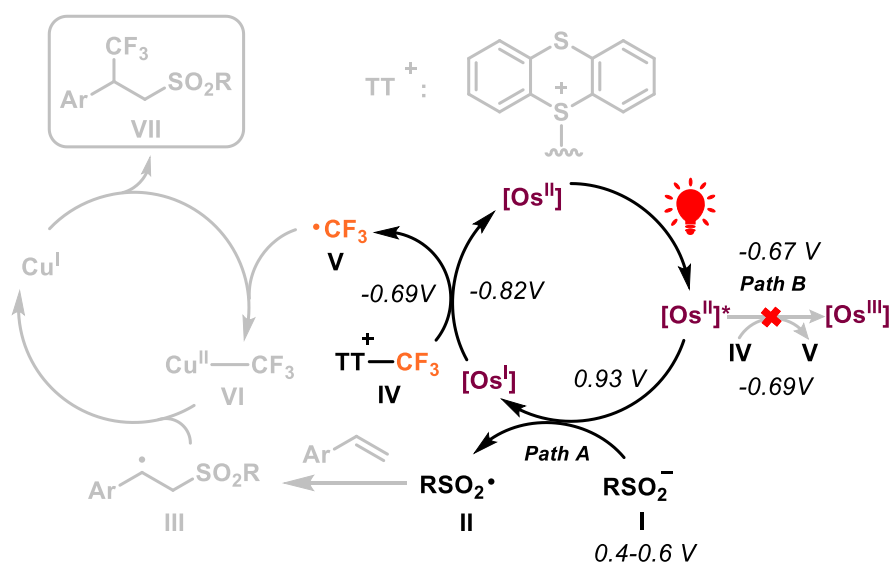
**Scheme S1.** Redox potential analysis of  $[\text{Os}]$ -catalyst *via* cyclic voltammetry.



**Scheme S2.** Redox potential analysis of  $\text{TT-CF}_3^+\text{OTf}^-$  catalyst *via* cyclic voltammetry.

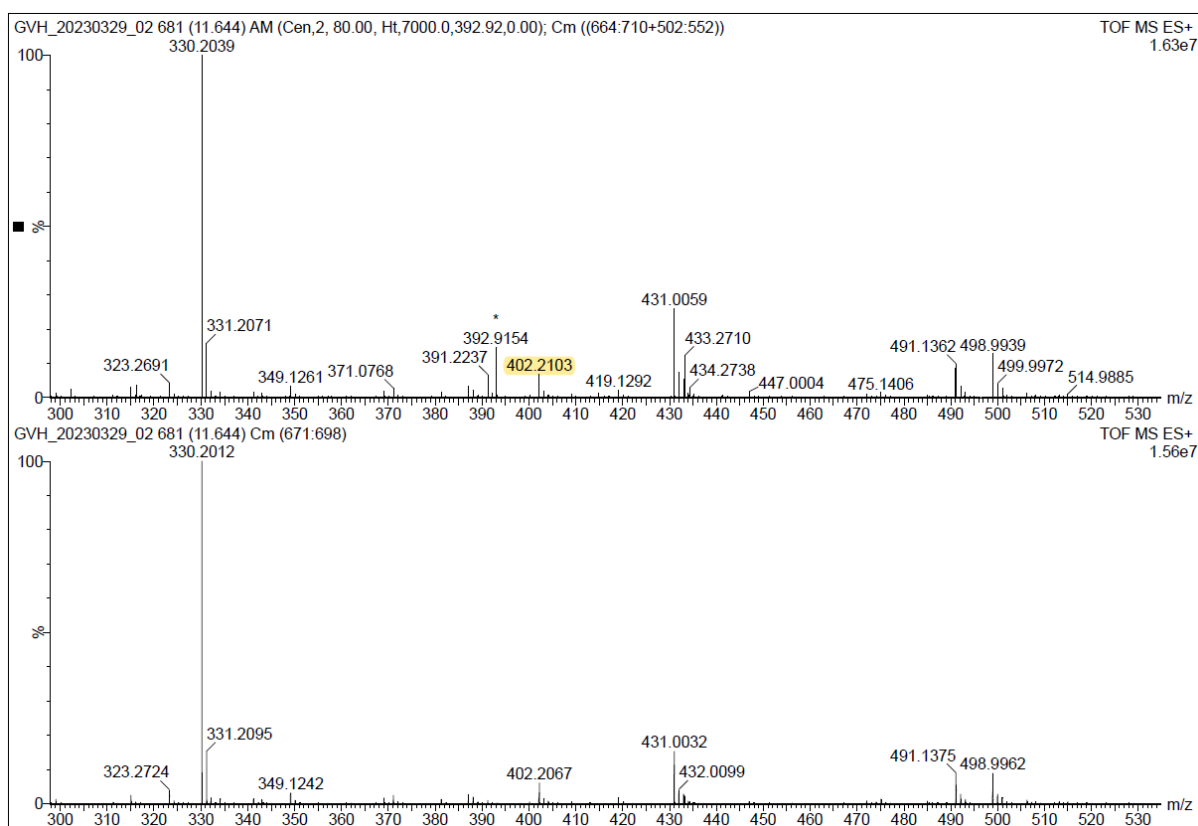
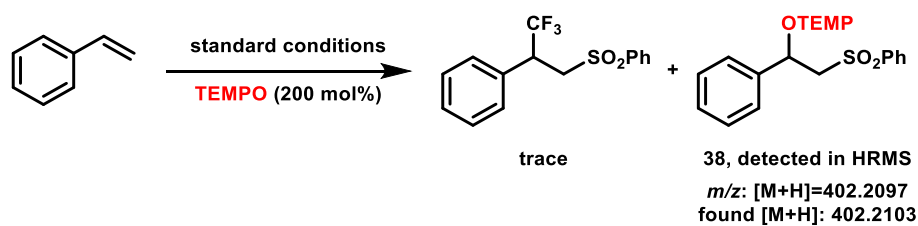
The redox potentials of Os-photocatalyst and  $\text{TTCF}_3^+\text{OTF}^-$  were measured in DCM (0.1 M). The  $E_{\text{ox}}$  and  $E_{\text{red}}$  of [Os] were 1.05 V and -0.82 V vs. Ag/AgCl (3 M KCl), respectively. Although the solvent was different from the reference, those values were consistent with the reference.<sup>1</sup> Therefore, the redox potential of the excited state was estimated same as the reference. The reduction potential of  $\text{TTCF}_3^+\text{OTF}^-$  was ca. -0.69 V vs. Ag/AgCl (3 M KCl).

According to these redox potentials, we demonstrated that the excited state of photocatalyst  $[\text{Os}^{\text{II}}]^*$  would exclusively undergo reduction by **I** to form the sulfonyl radical **II** (*Path A*) rather than oxidation by **IV** to generate the free  $-\text{CF}_3$  radical **V** (*Path B*). We highlighted the aspect of mechanism we verified in this part.



The obtained value was referenced to Ag/AgCl (3 M KCl).

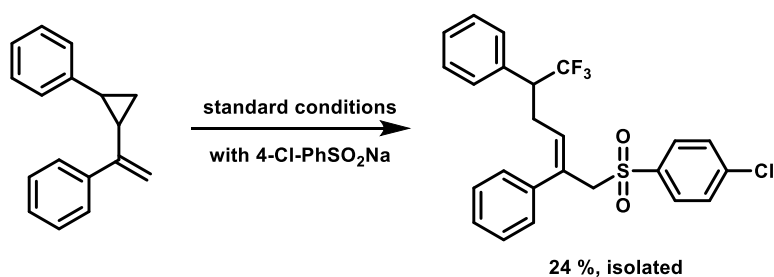
### 1.4.2 Quenching experiment and radical probe experiment



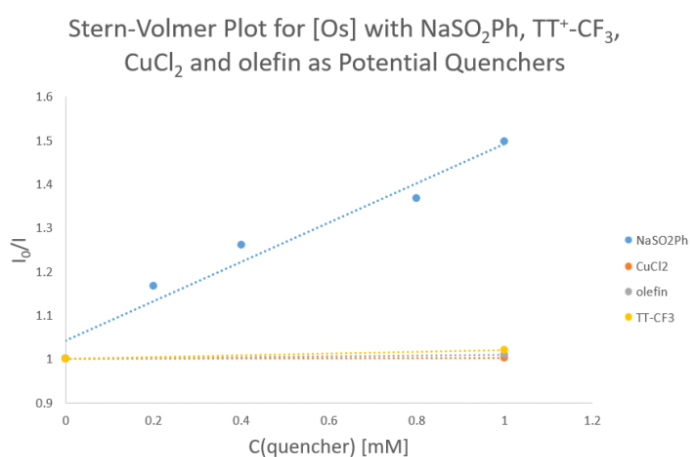
**Scheme S3.** HRMS analysis of carbon-centered radical (**III**) trapped by TEMPO.

The quenching experiment was carried out with 2 equiv. TEMPO and the carbon-centered radical **III** was captured by TEMPO which was detected by HRMS.

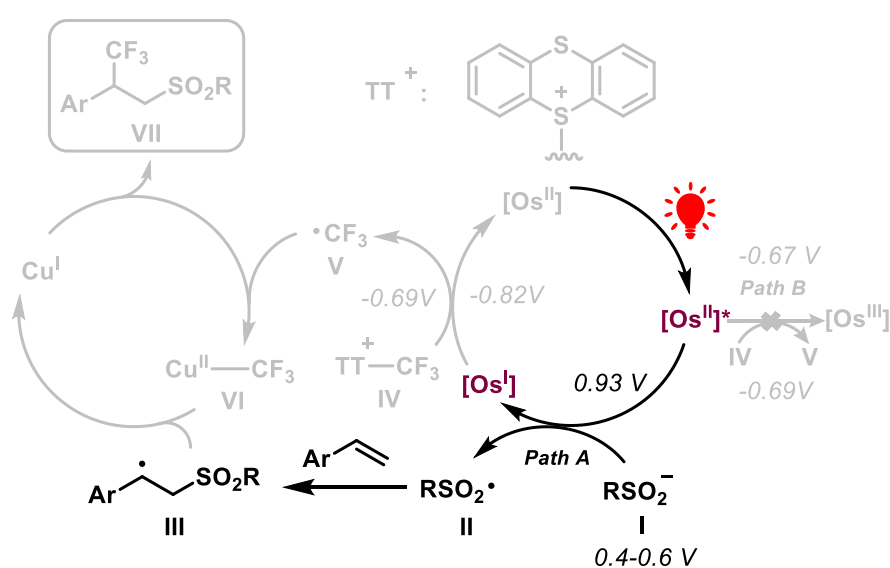
### Radical probe experiment via ring-opening reaction



### Fluorescence quenching experiments

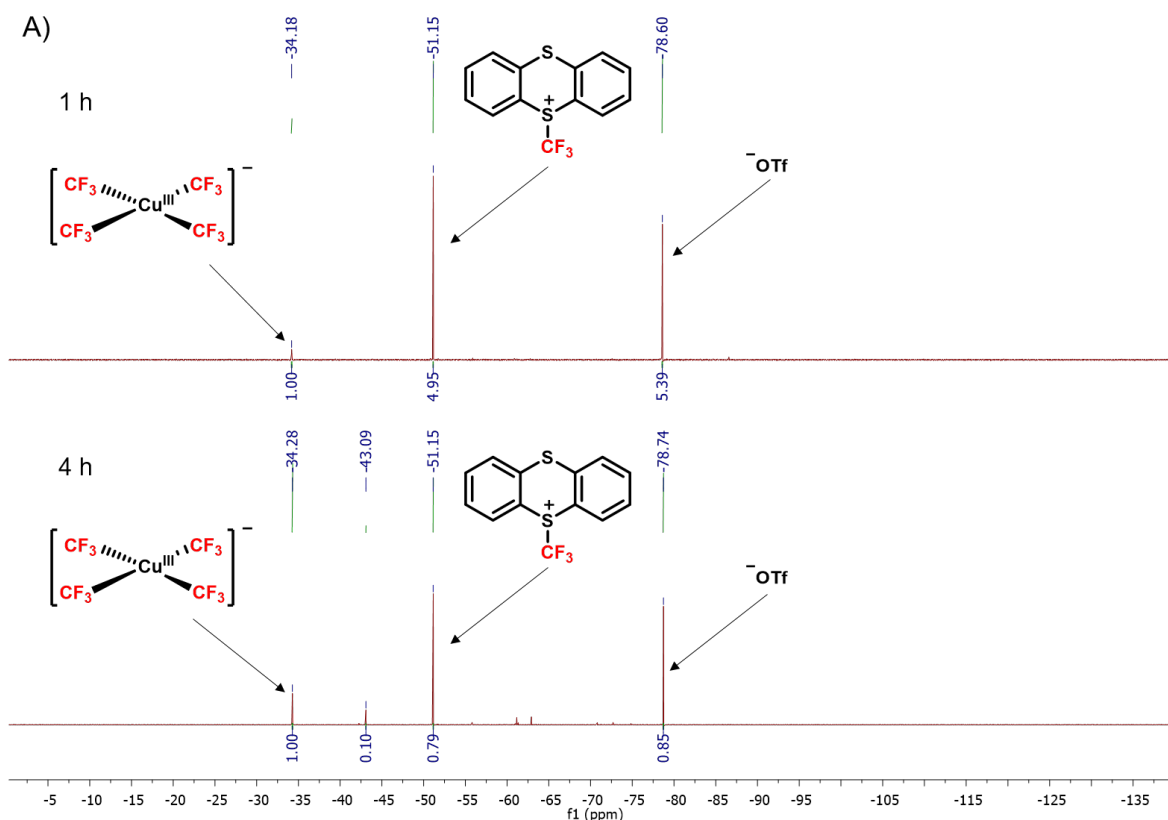


The radical probe experiment and Stern-Volmer analysis were also carried out. These results verified that the excited state of the photocatalyst [Os<sup>II</sup>]<sup>\*</sup> was quenched by the sulfinate anion and the following steps involved radical process. *We highlighted the aspect of mechanism that we had verified in this part.*



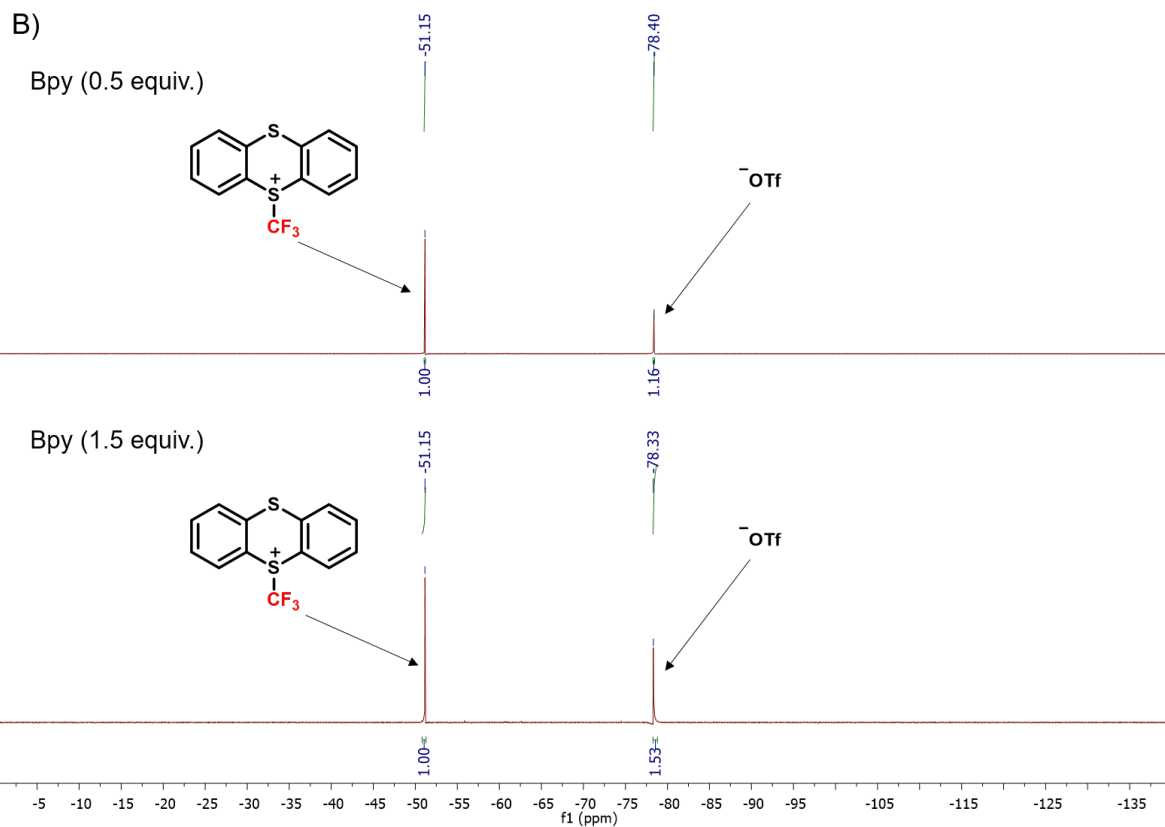
The obtained value was referenced to Ag/AgCl (3 M KCl).

### 1.4.3 Analysis of Cu-CF<sub>3</sub> complex



**Scheme S4.** <sup>19</sup>F NMR analysis of the reaction in the absence of styrene in 1 and 4 hours.

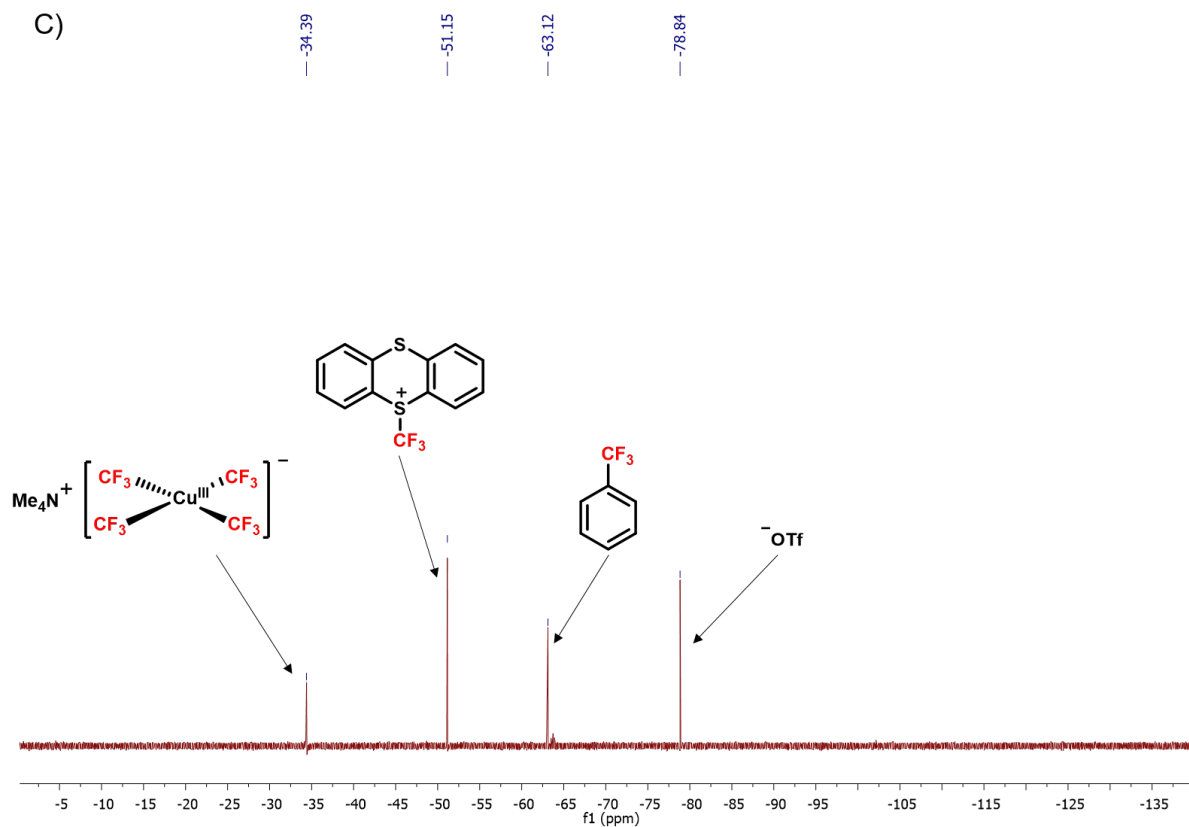
To analyze the possible Cu-CF<sub>3</sub> active species, various control experiments were carried out. Initially, we attempted to detect the active species in the absence of any styrene. While no new peak corresponding to Cu<sup>II</sup>-CF<sub>3</sub> was observed, we observed the presence of the Cu<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub> anion peak (**Scheme S4**).



**Scheme S5.** <sup>19</sup>F NMR analysis of the reaction in the absence of styrene and adding 2,2'-bipyridine (bpy) ligand.

To capture the active species, the 2,2'-bipyridine (bpy) ligand was added into the system. Unfortunately, only peak of TTCF<sub>3</sub><sup>+</sup>OTf<sup>-</sup> was observed in <sup>19</sup>F NMR (**Scheme S5**). Therefore, it was necessary to examine whether the Cu<sup>III</sup>(CF<sub>3</sub>)<sub>4</sub> anion complex was the active species.

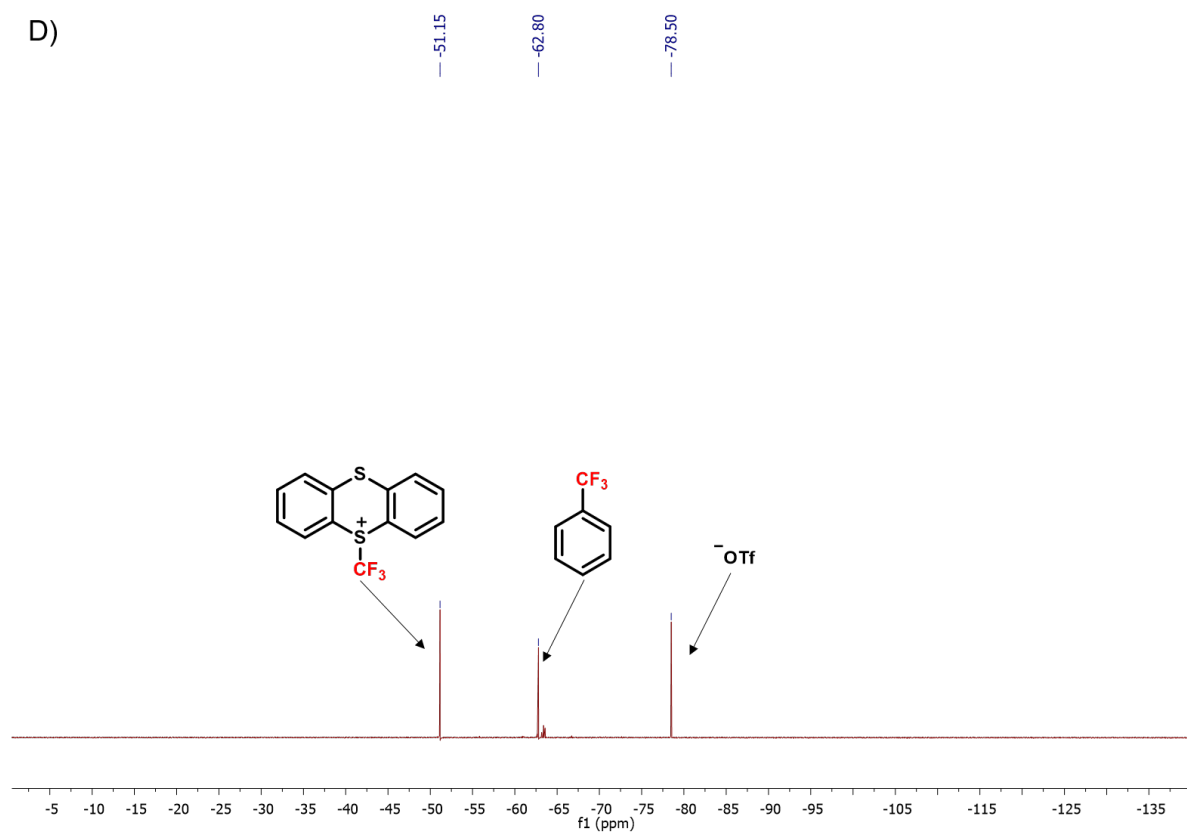
C)



**Scheme S6.**  $^{19}\text{F}$  NMR analysis of the reaction with  $\text{Me}_4\text{NCu}^{\text{III}}(\text{CF}_3)_4$  complex instead of  $\text{CuCl}_2$ .

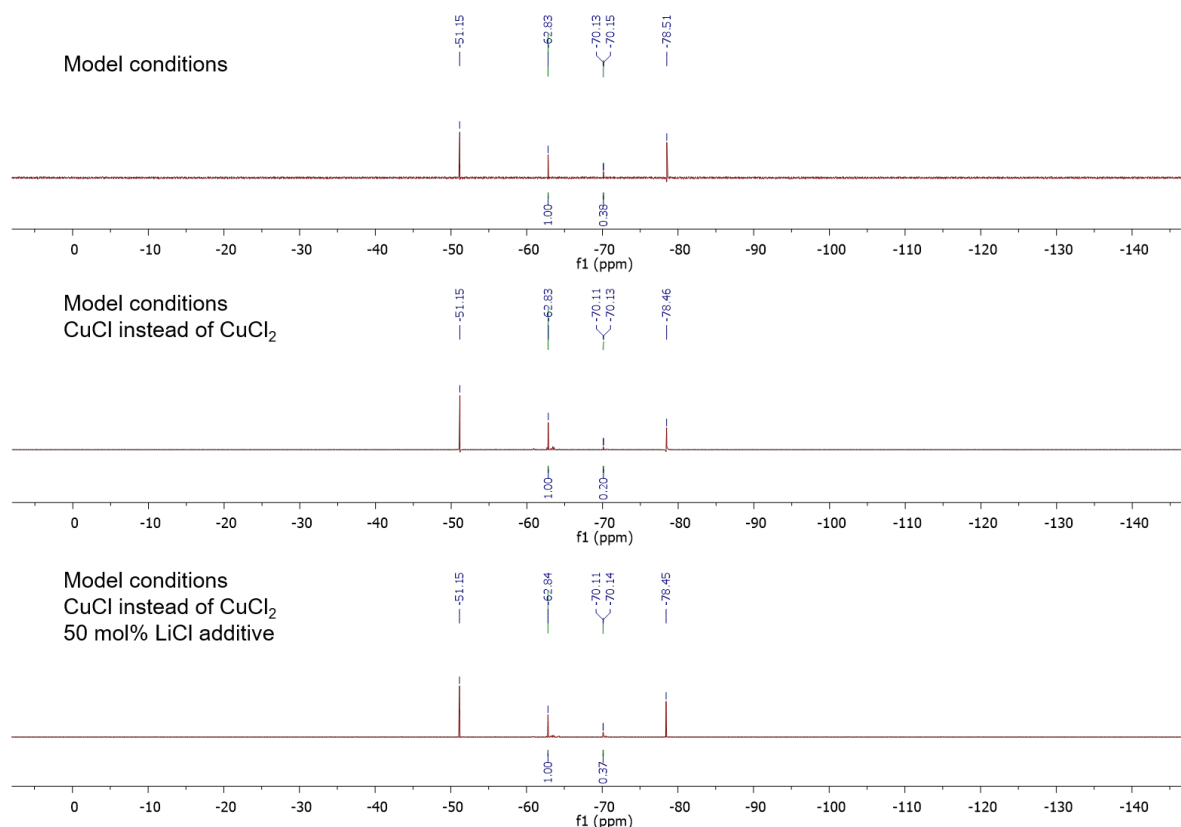
The styrene was added to system, however, no desired sulfonyltrifluoromethylated product was obtained. To further examine the  $\text{Cu}^{\text{III}}(\text{CF}_3)_4$  anion complex, we synthesized stable  $\text{Me}_4\text{NCu}^{\text{III}}(\text{CF}_3)_4$  complex according to the reference.<sup>2</sup> As expected, no product was obtained by using  $\text{Me}_4\text{NCu}^{\text{III}}(\text{CF}_3)_4$  complex instead of  $\text{CuCl}_2$  (**Scheme S6**).

D)



**Scheme S7.**  $^{19}\text{F}$  NMR analysis of the reaction with fresh  $\text{Cu}^0$  powder instead of  $\text{CuCl}_2$ .

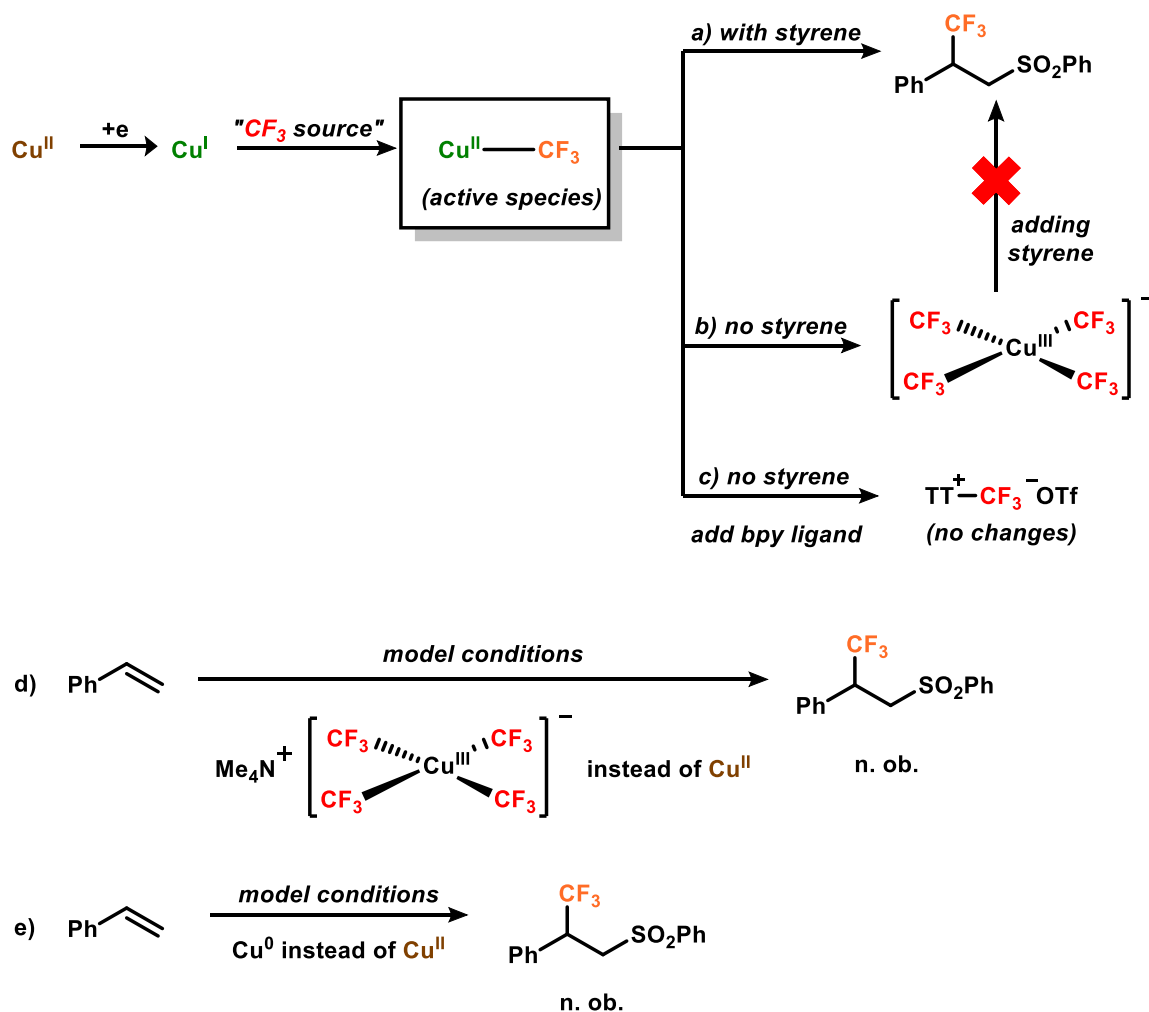
Fresh  $\text{Cu}^0$  powder was also used as catalyst instead of  $\text{CuCl}_2$ , and no product was found in the system.



**Scheme S8.** Top:  $^{19}\text{F}$  NMR analysis of the model reaction. Middle:  $^{19}\text{F}$  NMR analysis of the reaction with CuCl instead of  $\text{CuCl}_2$ . Bottom:  $^{19}\text{F}$  NMR analysis of the reaction with CuCl with 50 mol% LiCl instead of  $\text{CuCl}_2$ .

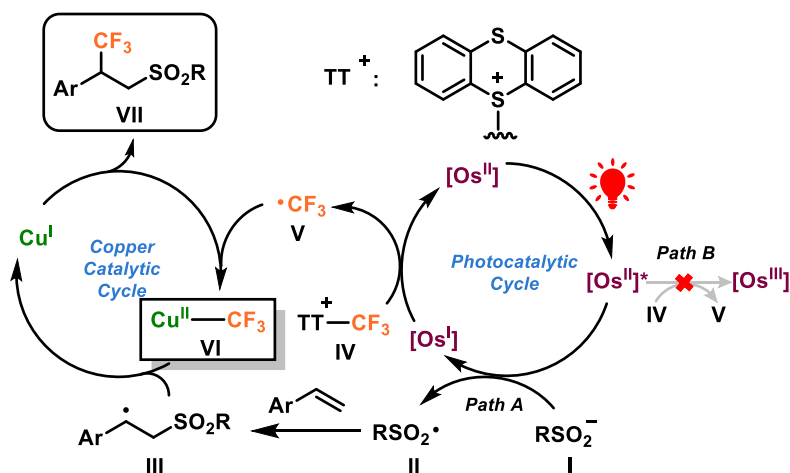
As elucidated in the optimization table, the introduction of CuCl instead of  $\text{CuCl}_2$  resulted in a decrease in yield by approximately 20%. As expected, if  $\text{Cu}^{\text{I}}$  effectively captured the  $-\text{CF}_3$  radical to form the active species, the yield should have been comparable to that obtained with  $\text{Cu}^{\text{II}}$  salts, which generated  $\text{Cu}^{\text{I}}$  *in situ*. We hypothesized that the concentration of chloride anion ( $\text{Cl}^-$ ) might also play a crucial role in the reaction, as reported in the literature.<sup>3</sup>

Consequently, the addition of 50 mol% of LiCl was incorporated as an additive to the system, resulting in an increased yield comparable to that of the model reaction.



**Scheme S9.** The comprehensive analysis of Cu-CF<sub>3</sub> complexes.

Based on this analysis, we assumed that Cu<sup>II</sup>-CF<sub>3</sub> (**VI**) was the possible active species for conducting the desired product *via* cross-coupling with **III**. The total mechanism of this reaction is proposed as follow:



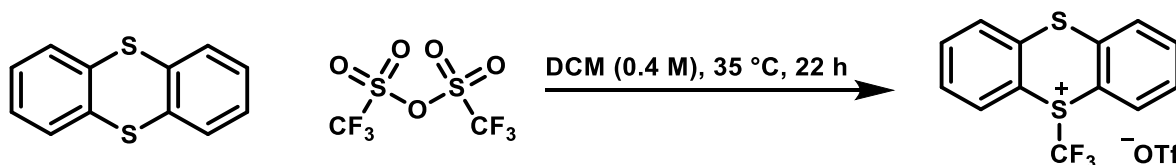
## 1.5 Experiments

### 1.5.1 Photocatalytic reaction setup

The reaction was carried out with the red LED light (EvoluChem™ LED 650PF HCK1012-XX-014 650 nm 20 mW/cm<sup>2</sup>) in the EvoluChem PhotoRedOx Box. In the box, it contained an electric fan to cool down the reaction. The reaction holder supported 8 reaction vials simultaneously. The reaction mixture was stirred by using a magnetic stirring plate and stirring bar at 800 rpm on average.

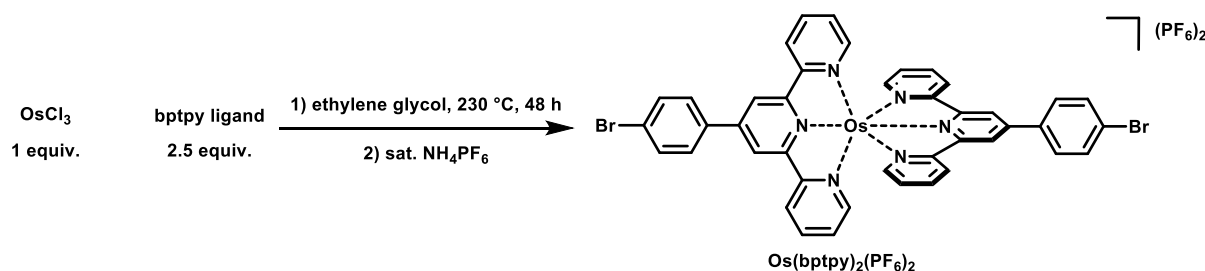


### 1.5.2 Procedure for synthesis of TT-CF<sub>3</sub><sup>+</sup>OTF<sup>-</sup>



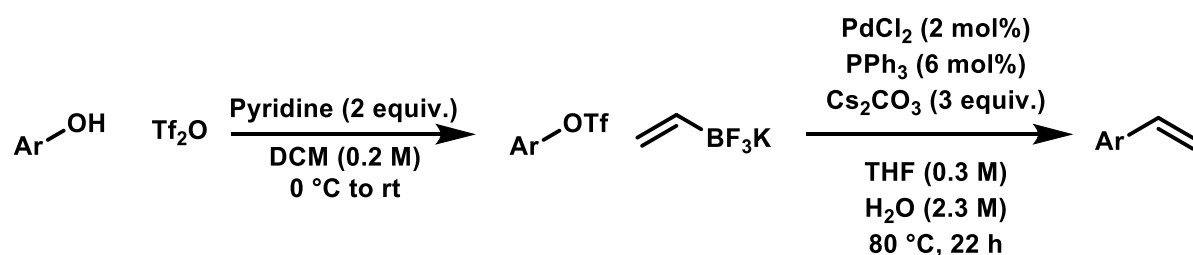
The S-(trifluoromethyl)thianthrenium triflate was prepared according to the literature.<sup>4</sup> A dried 250 mL round-bottom flask with magnetic stirring bar was charged with thianthrene (40 mmol, 1 equiv.) and DCM (100 mL, 0.4 M) under an ambient atmosphere. Subsequently, triflic anhydride (44 mmol, 1.1 equiv.) was added in one portion. The reaction mixture was stirred at 35 °C for 22 h. Followed by this, a saturated aqueous NaHCO<sub>3</sub> solution (50 mL) was added carefully. The organic layer was separated and concentrated in vacuo. Et<sub>2</sub>O (50 mL) was added to the residue and the suspension was stirred vigorously at room temperature for 30 min. The mixture was allowed to stand for 5 minutes, and the solvent was decanted carefully. The resulting yellow slurry was concentrated to dryness in vacuo and TT-CF<sub>3</sub><sup>+</sup>OTF<sup>-</sup> salts can be used without further purification.

### 1.5.3 Procedure for synthesis of $\text{Os}(\text{bptpy})_2(\text{PF}_6)_2$



A dried 50 mL pressure tube with magnetic stirring bar was charged with OsCl<sub>3</sub> (1 equiv.) and bptpy ligand (2.5 equiv.), followed by the addition of anhydrous ethylene glycol (0.075 M) in glovebox. The tube was sealed and heated at 230 °C in a sand bath (*Caution*: a blast shield is required for all sealed tube reactions since pressure develops in the tube.). After 48 h, the reaction was allowed to cool to 60 °C. Then, NH<sub>4</sub>PF<sub>6</sub> (10 equiv.) was added to the flask under an ambient atmosphere, followed by adding equal volume of distilled water. After 45 minutes, a dark precipitate was collected on filter paper and was washed with water, methanol, DCM and Et<sub>2</sub>O to obtain the pure catalyst. The catalyst was dried under vacuum and was used without further purification.<sup>1</sup>

### 1.5.4 Procedure for the synthesis of olefins from phenols

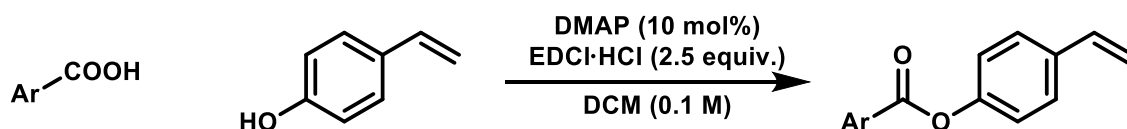


The olefin substrates were synthesized according to a reported procedure.<sup>5</sup> A dried Schlenk flask with magnetic stirring bar was charged with phenol (1.0 mmol, 1.0 equiv), after which the vessel was evacuated by using Schlenk techniques and was flushed with N<sub>2</sub> for three times. Under nitrogen atmosphere, DCM (5.0 mL, 0.20 M) and pyridine (2.0 mmol, 2.0 equiv) were added. The resulting mixture was cooled to 0 °C. Subsequently, Tf<sub>2</sub>O (1.5 mmol, 1.5 equiv) was added dropwise over 5 minutes. The reaction mixture was then warmed to room temperature and stirred for 5 hours. After 5 h, the reaction mixture was quenched by adding distilled water (15 mL). The

organic phase was extracted by DCM (3 × 20 mL) and was concentrated in vacuo. Purification proceeded to obtain *triflate substrate* via flash column chromatography.

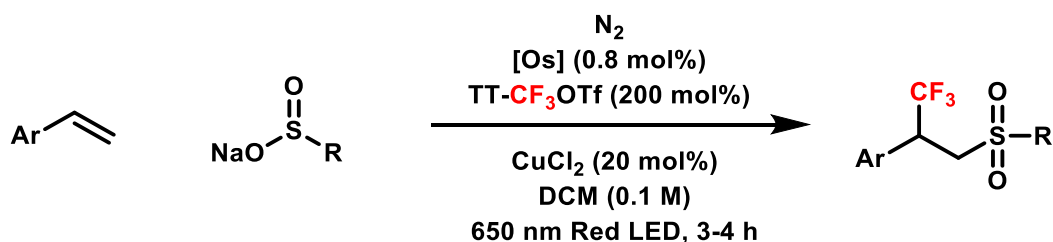
A dried two-necked flask with stirring bar was charged with *triflate substrate* (0.5 mmol, 1.00 equiv) from previous step, potassium vinyltrifluoroborate (0.6 mmol, 1.2 equiv), PdCl<sub>2</sub> (0.01 mmol, 2.00 mol%), PPh<sub>3</sub> (0.03 mmol, 6.00 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.5 mmol, 3.00 equiv), after which the vessel was evacuated by using Schlenk techniques and flushed with N<sub>2</sub> for three times. Distilled THF (2.00 mL) and degassed distilled water (0.25 mL) were added. After stirring at 80 °C for 22 h, the reaction mixture was quenched by adding DCM (15.0 mL) and water (20.0 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 × 15 mL). The organic phase was extracted and concentrated in vacuo. The residue was purified by flash column chromatography.

### 1.5.5 Procedure for synthesis of olefins from acids



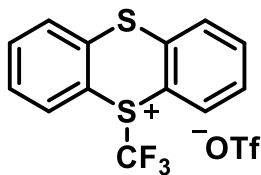
These olefins were prepared by following reported literature procedure.<sup>6</sup> A dried two-necked flask with stirring bar was charged with acid (2 mmol, 1 equiv.), DMAP (0.2 mmol, 10 mol%) and EDCI·HCl (5 mmol, 2.5 equiv.), after which the vessel was evacuated by using Schlenk techniques and flushed with N<sub>2</sub> for three times. Under nitrogen gas flow, 4-vinylphenol (2 mmol, 1 equiv.) and DCM (0.1 M) were added by using a syringe flushed with inert gas. The mixture was stirred at room temperature under N<sub>2</sub> until the reaction was completed which was checked by TLC monitoring. After the completion of the reaction, the mixture was diluted with water and the organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification proceeded *via* flash column chromatography.

### 1.5.6 Procedure for sulfonyltrifluoromethylation of olefins



A dried reaction vial with magnetic stirring bar was charged with Os(btpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (0.0008 mmol, 0.8 mol%), CuCl<sub>2</sub> (0.02 mmol, 20 mol%), TT-CF<sub>3</sub><sup>+</sup>OTF<sup>-</sup> (0.2 mmol, 2 equiv.) and sodium sulfinates (0.3 mmol, 3 equiv.), after which the vessel was evacuated by using Schlenk techniques and flushed with N<sub>2</sub> for three times. Under nitrogen gas flow, olefin (0.1 mmol, 1 equiv.) (if liquid, otherwise added before flushing cycle) and dry DCM (0.1 M) were added by using a syringe flushed with inert gas. The resulting mixture was stirred for 3-4 h under the irradiation of red LED light (EvoluChem™ LED 650PF HCK1012-XX-014 650 nm 20 mW/cm<sup>2</sup>) in the EvoluChem PhotoRedOx Box. After completion of the reaction, the reaction mixture was quenched by adding distilled water (2 mL). The organic phase was extracted and concentrated in vacuo. 1,1,1-Trifluorotoluene was added as an internal standard to determine the NMR yield of the functionalised product through <sup>19</sup>F NMR. Purification proceeded *via* flash column chromatography.

## 1.6 Characterization

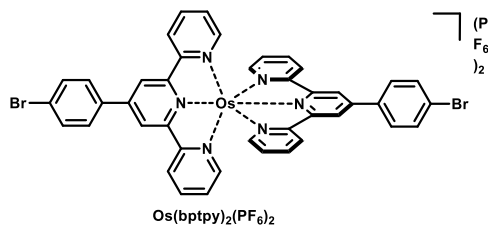


TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.58 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.82 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.79 – 7.74 (m, 1H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -51.11 (s), -78.39 (s).

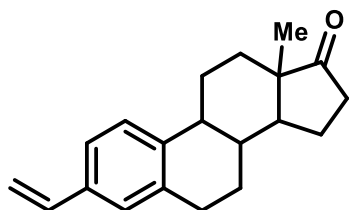
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.90, 136.81, 136.65, 130.33, 129.41, 124.43 (q, *J* = 337.2 Hz), 120.68 (q, *J* = 320.3 Hz), 108.95.



**<sup>1</sup>H NMR** (400 MHz, DMSO) δ 9.40 (s, 4H), 8.97 (d, *J* = 8.2 Hz, 4H), 8.27 (d, *J* = 8.5 Hz, 4H), 7.88 (d, *J* = 8.5 Hz, 4H), 7.81 (t, *J* = 7.8 Hz, 4H), 7.31 (d, *J* = 5.6 Hz, 4H), 7.09 (t, *J* = 6.5 Hz, 4H).

**<sup>19</sup>F NMR** (376 MHz, DMSO) δ -70.18 (d, *J* = 711.2 Hz).

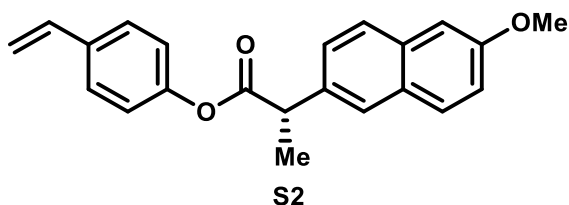
**<sup>13</sup>C NMR** (101 MHz, DMSO) δ 160.12, 155.18, 152.96, 152.75, 138.30, 135.09, 132.58, 130.43, 128.47, 125.49, 124.64, 120.10.



S1

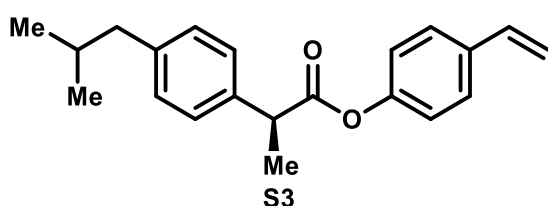
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.21 (dd, *J* = 17.6, 8.2 Hz, 2H), 7.12 (s, 1H), 6.68 – 6.55 (m, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 2.90 (dd, *J* = 8.6, 3.9 Hz, 2H), 2.44 (ddd, *J* = 17.4, 16.0, 6.8 Hz, 2H), 2.25 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.19 – 1.89 (m, 4H), 1.67 – 1.33 (m, 6H), 0.89 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 220.9, 139.57, 136.64, 136.57, 135.24, 126.90, 125.55, 123.64, 113.16, 50.55, 47.98, 44.47, 38.20, 35.86, 31.65, 29.41, 26.53, 25.76, 21.62, 13.88.



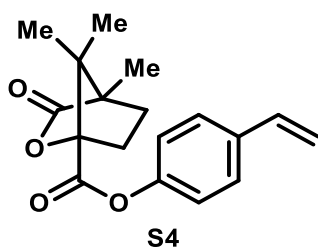
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.80 – 7.69 (m, 3H), 7.50 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.16 (dt, *J* = 7.2, 2.4 Hz, 2H), 7.00 – 6.88 (m, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.67 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.21 (dd, *J* = 10.9, 0.7 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 1.69 (d, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 173.10, 157.80, 150.42, 135.91, 135.31, 135.14, 133.85, 129.33, 129.03, 127.38, 127.07, 126.15, 126.13, 121.45, 119.11, 113.93, 105.67, 55.34, 45.61, 18.52.



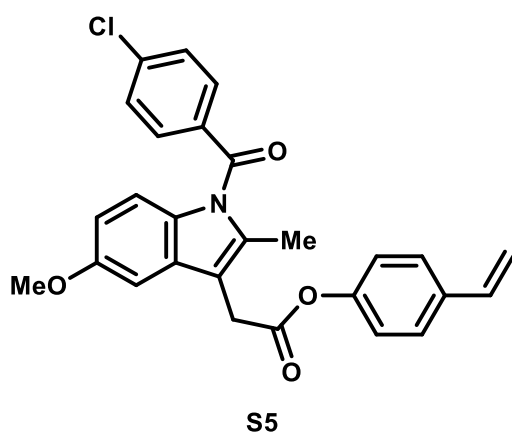
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.34 (m, 2H), 7.32 – 7.23 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.93 (m, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.68 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.22 (dd, *J* = 10.9, 0.6 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.97 – 1.79 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 173.16, 150.47, 140.83, 137.24, 135.94, 135.27, 129.51, 127.22, 127.07, 121.46, 113.90, 45.29, 45.07, 30.18, 22.39, 18.53.



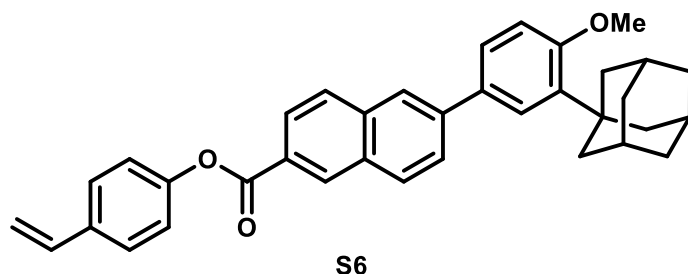
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.37 (m, 2H), 7.15 – 7.06 (m, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.6, 0.5 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 2.57 (ddd, *J* = 13.5, 10.8, 4.3 Hz, 1H), 2.20 (ddd, *J* = 13.6, 9.3, 4.6 Hz, 1H), 1.99 (ddd, *J* = 13.2, 10.8, 4.6 Hz, 1H), 1.77 (ddd, *J* = 13.4, 9.4, 4.3 Hz, 1H), 1.16 (d, *J* = 7.6 Hz, 6H), 1.11 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 177.79, 166.08, 149.49, 135.71, 127.31, 121.36, 114.49, 90.83, 54.91, 54.68, 30.78, 28.99, 16.89, 9.73.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 – 7.62 (m, 2H), 7.55 – 7.45 (m, 2H), 7.41 – 7.35 (m, 2H), 7.04 (ddd, *J* = 11.2, 6.9, 2.5 Hz, 3H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.75 – 6.62 (m, 2H), 5.69 (dd, *J* = 17.6, 0.6 Hz, 1H), 5.24 (dd, *J* = 10.9, 0.5 Hz, 1H), 3.90 (s, 2H), 3.84 (s, 3H), 2.46 (s, 3H).

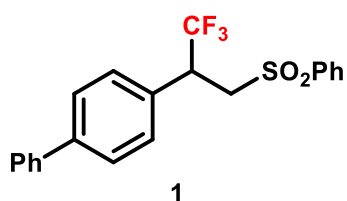
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 169.24, 168.31, 156.18, 150.26, 139.37, 136.22, 135.83, 135.52, 133.88, 131.21, 130.90, 130.52, 129.16, 127.16, 121.44, 115.03, 114.15, 112.00, 111.85, 101.28, 55.75, 30.59, 13.42.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.78 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 8.01 (dd, *J* = 23.4, 9.1 Hz, 3H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.62 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 17.7,

10.8 Hz, 1H), 5.75 (d,  $J$  = 17.5 Hz, 1H), 5.28 (d,  $J$  = 10.8 Hz, 1H), 3.92 (d,  $J$  = 1.1 Hz, 3H), 2.20 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.37, 159.05, 150.69, 141.83, 139.10, 136.31, 136.01, 135.45, 132.48, 131.72, 131.27, 129.84, 128.46, 127.29, 126.68, 126.23, 126.02, 125.82, 125.77, 124.78, 121.85, 114.03, 112.18, 55.19, 40.66, 37.26, 37.16, 29.15.

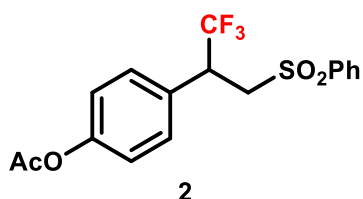


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.57 (m, 2H), 7.52 – 7.42 (m, 5H), 7.40 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.17 (d,  $J$  = 8.2 Hz, 2H), 4.08 – 3.98 (m, 1H), 3.80 (qd,  $J$  = 14.7, 6.8 Hz, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.95 (d,  $J$  = 9.1 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.84, 140.18, 139.12, 133.47, 129.84, 129.56, 129.04, 128.88, 127.88, 127.72, 127.42, 127.02, 126.80, 55.48, 45.67 (q,  $J$  = 28.6 Hz).

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{21}\text{H}_{17}\text{SO}_2\text{F}_3$  391.0974, found 391.0976.

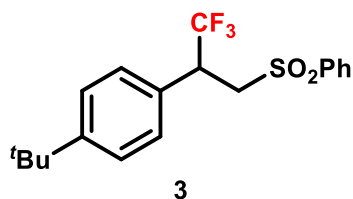


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.48 (m, 3H), 7.43 – 7.30 (m, 2H), 7.11 (d,  $J$  = 8.5 Hz, 2H), 6.96 – 6.86 (m, 2H), 4.08 – 3.92 (m, 1H), 3.74 (m, 2H), 2.29 (s, 3H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.06 (d,  $J$  = 9.0 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.81, 151.11, 138.91, 133.84, 130.16, 129.24, 128.49, 127.77, 126.66, 121.95, 55.50, 45.39 (q,  $J$  = 29.0 Hz), 21.10.

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{17}\text{H}_{15}\text{SO}_4\text{F}_3$  373.0716, found 373.0718.

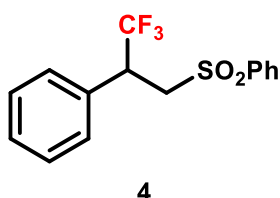


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.52 (m, 2H), 7.48 – 7.39 (m, 1H), 7.33 – 7.22 (m, 2H), 7.20 – 7.08 (m, 2H), 6.99 (d,  $J$  = 8.3 Hz, 2H), 3.96 (pd,  $J$  = 9.2, 3.3 Hz, 1H), 3.85 – 3.68 (m, 2H), 1.27 (s, 9H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.14 (d,  $J$  = 9.1 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.77, 139.13, 133.45, 128.92, 128.74, 127.87, 127.75, 126.86, 125.64, 55.38, 45.54 (q,  $J$  = 28.5 Hz), 34.49, 31.20.

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{19}\text{H}_{21}\text{SO}_2\text{F}_3$  371.1287, found 371.1292. [ $\text{M}+\text{Na}^+$ ] 393.1107, found 393.1114.

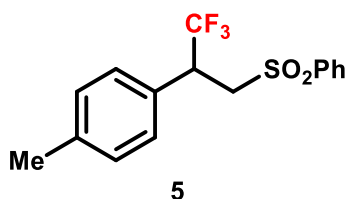


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.58 (m, 2H), 7.50 (ddd,  $J$  = 8.7, 2.4, 1.2 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.25 – 7.17 (m, 3H), 7.13 (d,  $J$  = 7.4 Hz, 2H), 3.98 (pd,  $J$  = 9.1, 3.9 Hz, 1H), 3.83 – 3.69 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.02 (d,  $J$  = 9.1 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.07, 133.65, 131.10, 129.12, 129.08, 128.91, 128.77, 127.85, 126.80, 55.42, 45.86 (q,  $J$  = 28.7 Hz).

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{15}\text{H}_{13}\text{SO}_2\text{F}_3$  315.0661, found 315.0668.

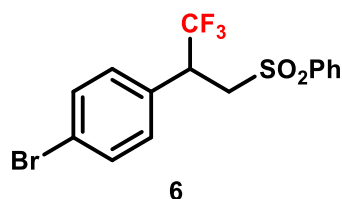


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.58 (m, 1H), 7.57 – 7.46 (m, 1H), 7.41 – 7.29 (m, 1H), 7.03 – 6.98 (m, 2H), 3.93 (pt,  $J$  = 8.4, 4.1 Hz, 1H), 3.81 – 3.65 (m, 1H), 2.31 – 2.25 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.16 (d,  $J$  = 9.1 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.16, 138.79, 133.45, 129.44, 129.01, 128.98, 128.06, 127.88, 124.07, 55.54, 45.44 (q, *J* = 28.6 Hz), 21.04.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>16</sub>H<sub>15</sub>SO<sub>2</sub>F<sub>3</sub> 329.0818, found 329.0827.

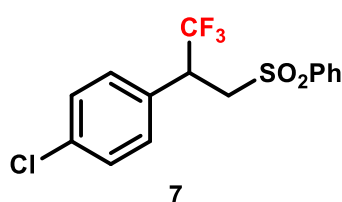


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.52 (m, 3H), 7.45 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.04 – 3.87 (m, 1H), 3.78 – 3.64 (m, 2H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.04 (d, *J* = 9.0 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 138.99, 133.74, 131.97, 130.76, 130.03, 129.22, 127.81, 126.47, 123.34, 55.25, 45.40.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>15</sub>H<sub>12</sub>SO<sub>2</sub>F<sub>3</sub>Br 392.9766, found 392.9778.  
[M+Na<sup>+</sup>] 414.9586, found 414.9603.

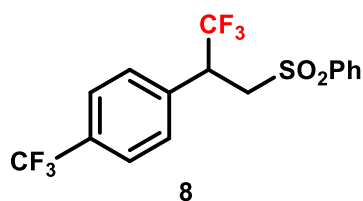


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.50 (m, 1H), 7.45 – 7.33 (m, 1H), 7.22 – 7.13 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 4.03 – 3.89 (m, 1H), 3.72 (d, *J* = 7.0 Hz, 1H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.07 (d, *J* = 8.9 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.01, 135.17, 133.76, 130.47, 129.55, 129.20, 129.01, 127.82, 126.55, 55.31, 45.30.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>15</sub>H<sub>12</sub>SO<sub>2</sub>F<sub>3</sub>Cl 349.0271, found 349.0275.  
[M+Na<sup>+</sup>] 371.0091, found 371.0099.

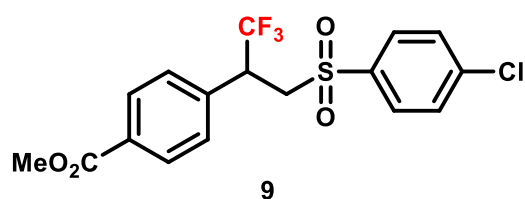


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.55 (m, 2H), 7.55 – 7.49 (m, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 10.8, 4.9 Hz, 2H), 7.27 (m, 2H), 4.07 (pd, *J* = 8.9, 4.9 Hz, 1H), 3.83 – 3.71 (m, 2H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.05, -69.78 (d, *J* = 8.8 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 138.88, 134.96, 134.06, 133.91, 129.68, 129.22, 127.76, 125.73, 125.69, 123.65, 55.08, 45.75 (d, *J* = 28.8 Hz).

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+Na<sup>+</sup>] calcd. for C<sub>16</sub>H<sub>12</sub>SO<sub>2</sub>F<sub>6</sub> 405.0354, found 405.0351.

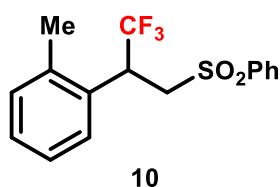


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.86 (m, 2H), 7.56 – 7.48 (m, 2H), 7.35 – 7.29 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.04 (pd, *J* = 8.8, 5.0 Hz, 1H), 3.93 (s, 3H), 3.80 – 3.69 (m, 2H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -69.68 (d, *J* = 8.8 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.12, 140.90, 137.26, 135.70, 130.97, 130.01, 129.50, 129.32, 126.41, 126.13, 55.29, 52.32, 45.77 (d, *J* = 29.0 Hz).

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>17</sub>H<sub>14</sub>SO<sub>4</sub>F<sub>3</sub>Cl 407.0326, found 407.0330.

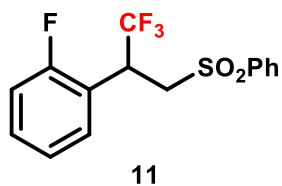


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.52 (m, 2H), 7.51 – 7.44 (m, 1H), 7.36 – 7.28 (m, 2H), 7.11 (ddd, *J* = 11.3, 9.2, 4.5 Hz, 2H), 6.90 (dt, *J* = 7.9, 4.4 Hz, 2H), 4.40 (pd, *J* = 9.1, 3.5 Hz, 1H), 3.79 (qd, *J* = 14.7, 6.8 Hz, 2H), 2.45 (s, 3H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -69.97 (d, *J* = 9.0 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.20, 138.15, 133.55, 130.82, 129.46, 129.00, 128.65, 127.54, 127.17, 127.05, 126.27, 55.69, 40.38 (d, *J* = 29.8 Hz), 19.84.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>16</sub>H<sub>15</sub>SO<sub>2</sub>F<sub>3</sub> 329.0818, found 329.0821.

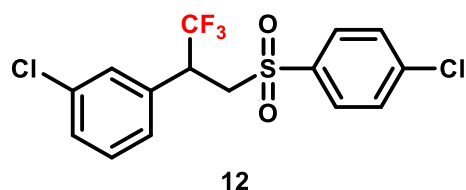


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (dt,  $J$  = 8.6, 1.6 Hz, 2H), 7.57 – 7.48 (m, 1H), 7.41 – 7.36 (m, 2H), 7.28 – 7.21 (m, 1H), 7.14 (t,  $J$  = 7.4 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.97 – 6.88 (m, 1H), 4.36 – 4.25 (m, 1H), 3.87 (dd,  $J$  = 14.7, 10.9 Hz, 1H), 3.71 (dd,  $J$  = 14.7, 2.6 Hz, 1H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.04 (dd,  $J$  = 8.9, 6.0 Hz), -115.26.

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.31, 159.83, 138.56, 133.89, 130.91/130.83, 129.95, 129.18, 127.94, 124.49/ 124.45, 118.48/118.36, 116.13/115.91, 54.11, 39.19 (q,  $J$  = 30.0 Hz).

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{15}\text{H}_{12}\text{SO}_2\text{F}_4$  333.0567, found 333.0572.

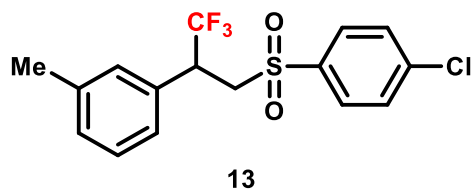


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.46 (m, 2H), 7.38 – 7.31 (m, 2H), 7.26 (ddd,  $J$  = 8.0, 1.9, 1.1 Hz, 1H), 7.17 (t,  $J$  = 7.8 Hz, 2H), 7.09 – 6.97 (m, 2H), 4.00 – 3.87 (m, 1H), 3.80 – 3.66 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.93 (d,  $J$  = 8.8 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.89, 137.21, 134.87, 132.62, 130.14, 129.43, 129.22, 127.59, 126.38, 123.59, 55.13, 45.67 (q,  $J$  = 29.0 Hz).

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{Na}^+$ ] calcd. for  $\text{C}_{15}\text{H}_{11}\text{SO}_2\text{F}_3\text{Cl}_2$  404.9701, found 404.9704.

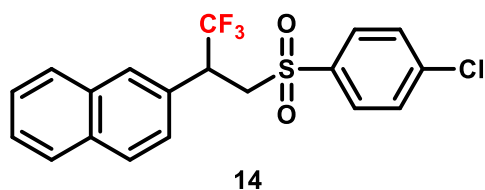


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.38 (m, 2H), 7.25 (dt,  $J$  = 4.4, 1.9 Hz, 2H), 7.12 – 7.03 (m, 2H), 6.92 (d,  $J$  = 7.2 Hz, 1H), 6.76 (s, 1H), 3.98 – 3.84 (m, 1H), 3.82 – 3.70 (m, 2H), 2.21 (s, 3H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.07 (d,  $J$  = 8.9 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.36, 138.57, 137.44, 130.47, 130.25, 129.66, 129.60, 129.26, 129.11, 128.76, 126.51, 55.38, 45.98 (dd, *J* = 57.6, 28.9 Hz), 21.10.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+Na<sup>+</sup>] calcd. for C<sub>16</sub>H<sub>14</sub>SO<sub>2</sub>F<sub>3</sub>Cl 385.0247, found 385.0253.

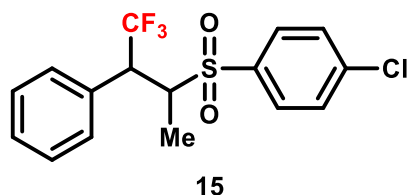


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.76 (m, 1H), 7.67 (ddd, *J* = 19.1, 9.4, 6.0 Hz, 2H), 7.57 – 7.47 (m, 3H), 7.39 – 7.32 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.00 – 6.89 (m, 2H), 4.20 – 4.05 (m, 1H), 3.86 (ddd, *J* = 17.9, 14.8, 6.9 Hz, 2H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -69.75 (d, *J* = 8.9 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.35, 137.35, 133.18, 132.81, 129.69, 129.48, 129.19, 129.10, 128.95, 128.80, 127.71, 127.55, 127.09, 126.89, 125.51, 55.46, 46.24.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>19</sub>H<sub>14</sub>SO<sub>2</sub>F<sub>3</sub>Cl 399.0428, found 399.0427.  
[M+Na<sup>+</sup>] 421.0247, found 421.0248.

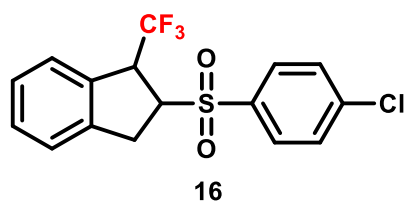


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.30 (m, 2H), 7.18 (m, 6H), 4.19 (d, *J* = 9.8 Hz, 1H), 3.51 – 3.34 (m, 1H), 1.79 (d, *J* = 7.0 Hz, 3H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -68.40 (d, *J* = 8.0 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.16, 136.74, 132.67, 130.08, 129.73, 129.02, 128.71, 128.61, 71.43, 40.82 (dd, *J* = 52.3, 26.1 Hz), 30.89, 12.84.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+Na<sup>+</sup>] calcd. for C<sub>16</sub>H<sub>14</sub>SO<sub>2</sub>F<sub>3</sub>Cl 385.0247, found 385.0252.

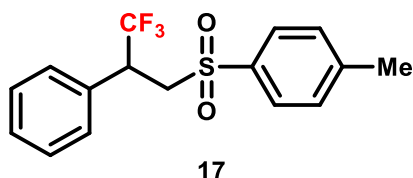


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.84 – 7.80 (m, 2H), 7.54 – 7.48 (m, 2H), 7.35 – 7.17 (m, 4H), 4.32 (qd, *J* = 9.0, 2.4 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.57 – 3.43 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.74 (d,  $J$  = 9.1 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.19, 141.06, 135.24, 133.52, 130.29, 129.71, 129.56, 127.70, 125.84, 124.68, 63.55, 50.96 (q,  $J$  = 29.5 Hz), 33.20, 29.69.

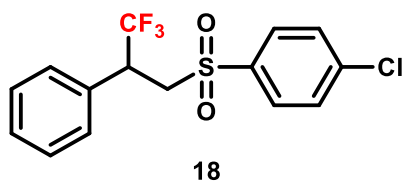
**HRMS** ( $\text{ESI}^+$ ,  $m/z$ )  $[\text{M}+\text{H}^+]$  calcd. for  $\text{C}_{16}\text{H}_{12}\text{SO}_2\text{F}_3\text{Cl}$  361.0271, found 361.0278.



**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.43 (m, 2H), 7.29 – 7.18 (m, 3H), 7.13 (dd,  $J$  = 7.6, 4.2 Hz, 4H), 3.94 (pd,  $J$  = 9.1, 4.2 Hz, 1H), 3.80 – 3.65 (m, 2H), 2.37 (s, 3H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.03 (d,  $J$  = 9.0 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.45, 144.76, 136.04, 131.31, 130.00, 129.70, 129.14, 128.71, 127.91, 55.48, 45.85, 21.53.

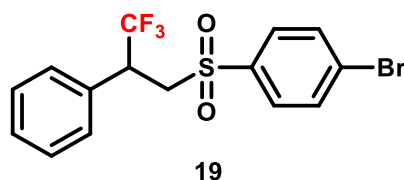


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.42 (m, 2H), 7.32 – 7.24 (m, 3H), 7.20 (dd,  $J$  = 10.3, 4.8 Hz, 2H), 7.10 (d,  $J$  = 7.6 Hz, 2H), 3.96 (pd,  $J$  = 9.1, 4.5 Hz, 1H), 3.84 – 3.68 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.05 (d,  $J$  = 9.1 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.50, 137.44, 130.81, 129.31, 129.16, 128.97, 128.85, 126.69, 123.90, 55.50, 45.98 (q,  $J$  = 28.6 Hz).

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ )  $[\text{M}+\text{Na}^+]$  calcd. for  $\text{C}_{15}\text{H}_{12}\text{SO}_2\text{F}_3\text{Cl}$  371.0091, found 371.0097.

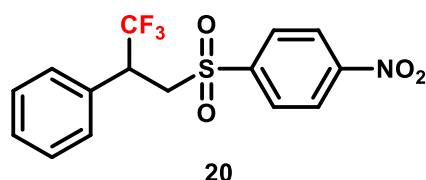


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.36 (m, 4H), 7.31 – 7.26 (m, 1H), 7.23 – 7.17 (m, 2H), 7.09 (d,  $J$  = 7.6 Hz, 2H), 3.95 (pt,  $J$  = 8.0, 3.9 Hz, 1H), 3.82 – 3.68 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.05 (d,  $J$  = 9.0 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.95, 132.32, 130.78, 129.34, 129.16, 129.10, 128.95, 128.87, 126.68, 55.49, 45.97 (q,  $J$  = 28.7 Hz).

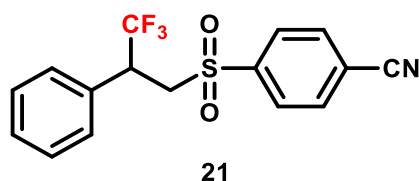
**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{15}\text{H}_{12}\text{SO}_2\text{F}_3\text{Br}$  392.9766, found 392.9759.  
[ $\text{M}+\text{Na}^+$ ] 414.9586, found 414.9589.



**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 – 8.07 (m, 2H), 7.71 – 7.66 (m, 2H), 7.24 (dt,  $J$  = 2.6, 1.7 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.08 (d,  $J$  = 7.6 Hz, 2H), 4.07 – 3.94 (m, 1H), 3.90 – 3.77 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.02 (d,  $J$  = 8.8 Hz).

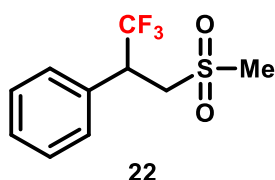
**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.47, 144.52, 130.43, 130.41, 129.31, 129.26, 128.92, 126.52, 123.98, 55.56, 46.05 (q,  $J$  = 29.0 Hz).



**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.52 (m, 4H), 7.30 – 7.23 (m, 1H), 7.21 – 7.14 (m, 2H), 7.07 (d,  $J$  = 7.6 Hz, 2H), 3.99 (pd,  $J$  = 8.9, 4.8 Hz, 1H), 3.89 – 3.75 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.03 (d,  $J$  = 8.8 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.10, 132.59, 130.44, 129.24, 129.21, 128.93, 128.53, 126.54, 123.75, 117.30, 116.84, 55.45, 46.02 (q,  $J$  = 28.9 Hz).

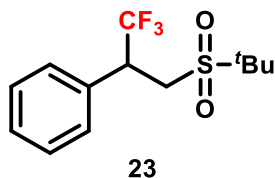


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.38 (m, 5H), 4.13 – 3.93 (m, 1H), 3.69 – 3.53 (m, 2H), 2.36 (s, 3H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.61 (d,  $J$  = 9.0 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  129.62, 129.49, 129.30, 129.20, 127.14, 54.94, 46.13 (d,  $J$  = 28.9 Hz), 42.27.

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{Na}^+$ ] calcd. for  $\text{C}_{10}\text{H}_{11}\text{SO}_2\text{F}_3$  275.0324, found 275.0326.

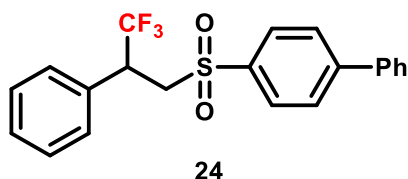


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.34 (m, 5H), 4.12 (pd,  $J$  = 9.4, 3.1 Hz, 1H), 3.51 (qd,  $J$  = 13.6, 6.4 Hz, 2H), 1.38 (s, 9H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.53 (d,  $J$  = 9.3 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.64, 129.08, 129.00, 128.91, 124.49, 60.03, 45.61, 44.14, 23.24.

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{Na}^+$ ] calcd. for  $\text{C}_{13}\text{H}_{17}\text{SO}_2\text{F}_3$  317.0794, found 317.0793.

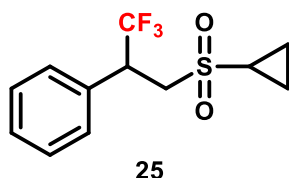


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.62 (m, 2H), 7.58 – 7.45 (m, 7H), 7.27 – 7.13 (m, 5H), 4.02 (pd,  $J$  = 9.1, 3.4 Hz, 1H), 3.82 (qd,  $J$  = 14.7, 6.7 Hz, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.03 (d,  $J$  = 9.0 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.63, 139.09, 137.40, 131.09, 129.20, 129.11, 128.77, 128.75, 128.73, 128.38, 127.67, 127.31, 126.80, 55.48, 45.98 (q,  $J$  = 28.7 Hz).

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{21}\text{H}_{17}\text{SO}_2\text{F}_3$  391.0974, found 391.0980.

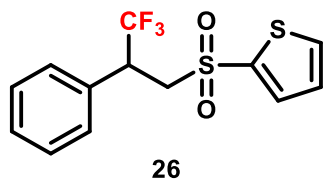


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.36 (m, 5H), 4.12 – 3.95 (m, 1H), 3.65 (ddd,  $J$  = 17.6, 14.7, 6.8 Hz, 2H), 1.71 – 1.58 (m, 1H), 1.20 – 1.11 (m, 1H), 1.08 – 0.97 (m, 1H), 0.82 – 0.63 (m, 2H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -69.77 (d,  $J$  = 9.0 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 132.16, 129.37, 129.32, 129.15, 126.95, 53.79, 45.79, 30.95, 5.51, 5.33.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>12</sub>H<sub>13</sub>SO<sub>2</sub>F<sub>3</sub> 301.0481, found 301.0485.

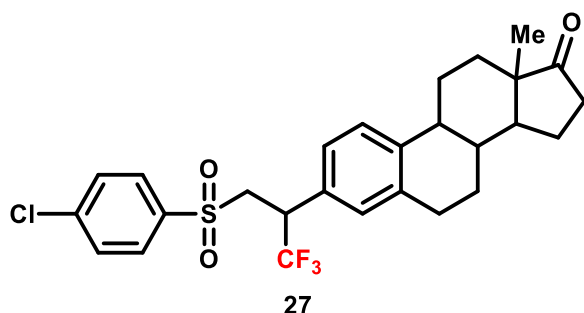


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.33 – 7.16 (m, 6H), 6.91 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.08 – 3.93 (m, 1H), 3.93 – 3.79 (m, 2H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.00 (d, *J* = 8.9 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.88, 134.71, 134.49, 131.22, 129.07, 128.97, 128.84, 127.78, 126.75, 56.8, 46.11 (q, *J* = 28.6 Hz).

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>13</sub>H<sub>11</sub>S<sub>2</sub>O<sub>2</sub>F<sub>3</sub> 321.0225, found 321.0231. [M+Na<sup>+</sup>] 343.0045, found 343.0053.

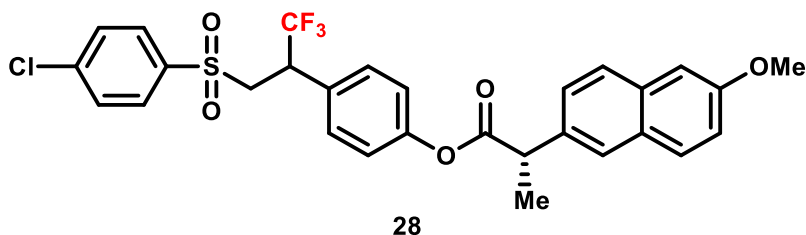


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.37 (m, 2H), 7.23 – 7.18 (m, 2H), 7.09 (2d, *J* = 8.1 Hz, 1H), 6.88 (2d, *J* = 8.1 Hz, 1H), 6.62 (2s, 1H), 3.95 – 3.83 (m, 1H), 3.80 – 3.66 (m, 2H), 2.82 – 2.46 (m, 3H), 2.43 – 2.30 (m, 1H), 2.25 – 1.93 (m, 5H), 1.70 – 1.33 (m, 6H), 0.95 (2s, 3H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.12 (d, *J* = 8.8 Hz), -70.17 (d, *J* = 8.8 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 220.38, 140.92/140.87, 139.96/139.90, 137.66/137.63, 136.91/136.89, 129.72, 129.31/129.29, 129.06, 128.86, 127.67/127.56, 127.21, 126.55, 125.83/125.81, 55.29/55.15, 53.40, 50.53/50.52, 47.94/47.89, 45.74 (q, *J* = 28.8 Hz), 44.30/44.24, 37.99/37.97, 35.80, 31.58/31.56, 29.20/29.18, 26.24, 25.74/25.58, 21.56, 14.01/13.90.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>27</sub>H<sub>28</sub>SO<sub>4</sub>F<sub>3</sub>Cl 525.1473, found 525.1482.

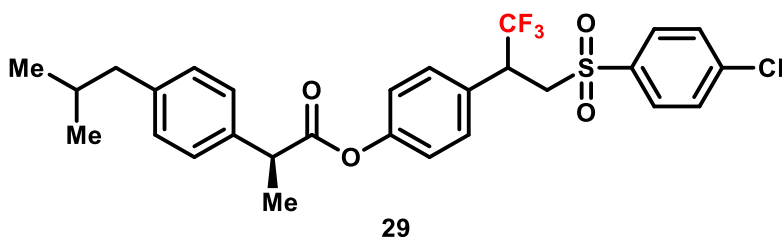


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.69 (m, 3H), 7.49 (dt,  $J$  = 8.6, 1.6 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.33 – 7.26 (m, 2H), 7.20 – 7.12 (m, 2H), 7.03 (d,  $J$  = 8.6 Hz, 2H), 6.87 – 6.79 (m, 2H), 4.16 – 4.04 (m, 1H), 4.00 – 3.86 (m, 4H), 3.76 – 3.61 (m, 2H), 1.71 (d,  $J$  = 7.1 Hz, 3H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.13 (d,  $J$  = 8.8 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.59, 157.86, 151.40, 140.63, 137.34, 134.86, 134.81, 133.91, 130.09, 129.52, 129.32, 129.15, 129.02, 128.05, 127.43, 126.17, 126.06, 126.04, 121.87, 119.18, 105.68, 55.56, 55.35, 45.56, 18.36.

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{29}\text{H}_{24}\text{SO}_5\text{F}_3\text{Cl}$  577.1058, found 577.1053.

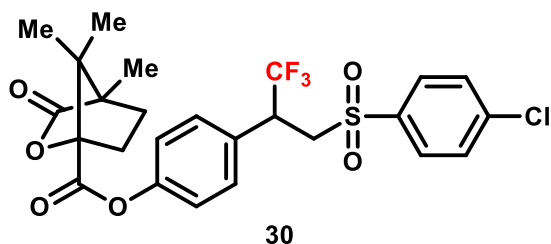


**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.38 (m, 2H), 7.30 (ddd,  $J$  = 6.9, 4.6, 1.7 Hz, 4H), 7.15 (d,  $J$  = 7.9 Hz, 2H), 7.04 (d,  $J$  = 8.5 Hz, 2H), 6.85 (d,  $J$  = 8.5 Hz, 2H), 4.02 – 3.87 (m, 2H), 3.76 – 3.65 (m, 2H), 2.48 (d,  $J$  = 7.2 Hz, 2H), 1.87 (dp,  $J$  = 13.5, 6.7 Hz, 1H), 1.62 (d,  $J$  = 7.2 Hz, 3H), 0.92 (d,  $J$  = 6.6 Hz, 6H).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -70.13 (dd,  $J$  = 8.9, 4.9 Hz).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.63, 151.44, 140.96, 140.64, 138.40, 137.37, 137.35, 136.97, 136.93, 130.08, 129.54, 129.15, 127.97, 127.20, 121.87, 55.59, 45.26, 45.06, 30.18, 22.38, 18.39.

**HRMS** ( $\text{ESI}^+$ ,  $m/z$ ) [ $\text{M}+\text{H}^+$ ] calcd. for  $\text{C}_{28}\text{H}_{28}\text{SO}_4\text{F}_3\text{Cl}$  553.1422, found 553.1413.

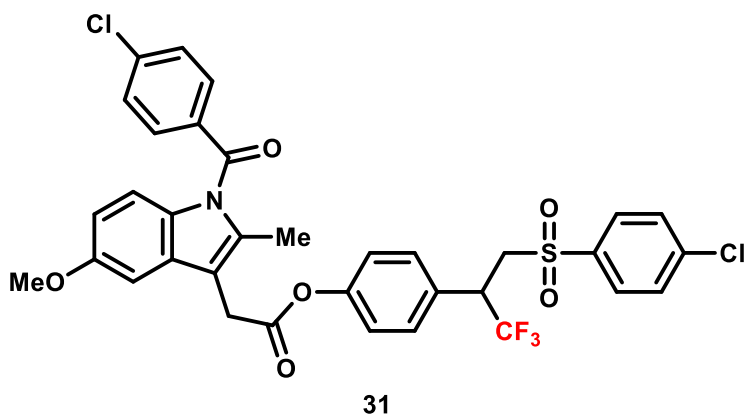


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.34 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.07 – 3.92 (m, 1H), 3.75 (m, 2H), 2.63 – 2.50 (m, 1H), 2.20 (dddd, *J* = 13.6, 9.3, 4.5, 2.2 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.78 (ddd, *J* = 13.4, 9.3, 4.2 Hz, 1H), 1.17 (d, *J* = 5.7 Hz, 6H), 1.11 (s, 3H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.06 (d, *J* = 8.8 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 177.68, 165.67/165.64, 150.46, 140.65, 137.43, 137.40, 130.41, 129.58, 129.21, 128.93, 121.79, 90.70, 55.50, 54.92, 54.72, 45.89, 45.60, 45.31, 45.02, 30.82/30.78, 28.96, 16.89/16.86, 9.72.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>25</sub>H<sub>24</sub>SO<sub>6</sub>F<sub>3</sub>Cl 545.1007, found 545.1004.

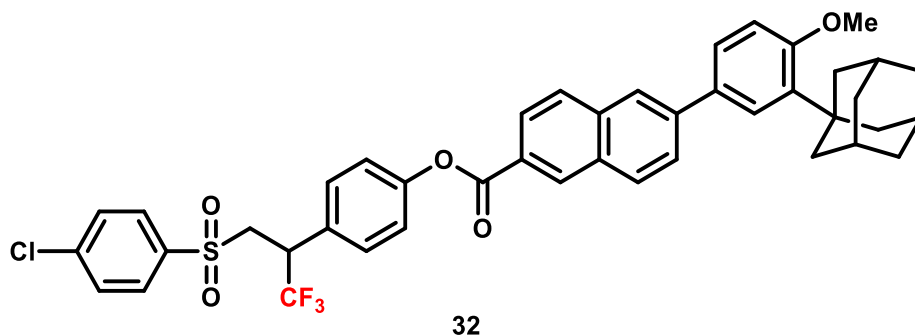


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.73 – 7.65 (m, 2H), 7.51 – 7.41 (m, 4H), 7.33 – 7.28 (m, 2H), 7.07 (dd, *J* = 12.2, 5.5 Hz, 3H), 6.96 – 6.84 (m, 3H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.96 (ddd, *J* = 15.8, 7.8, 4.5 Hz, 1H), 3.91 (s, 2H), 3.85 (s, 3H), 3.71 (m, 2H), 2.47 (s, 3H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.08 (d, *J* = 8.9 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 168.67, 168.30, 156.19, 151.22, 140.64, 139.44, 137.38, 136.35, 133.81, 131.21, 130.91, 130.46, 130.20, 129.55, 129.19, 128.37, 121.89, 115.04, 111.72, 101.39, 55.78, 55.55, 45.40 (d, *J* = 29.0 Hz), 30.52, 13.38.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+H<sup>+</sup>] calcd. for C<sub>34</sub>H<sub>26</sub>NSO<sub>6</sub>F<sub>3</sub>Cl<sub>2</sub> 704.0883, found 704.0882.

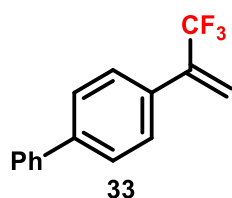


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.79 (d, *J* = 10.8 Hz, 1H), 8.19 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.02 (dd, *J* = 20.9, 9.2 Hz, 3H), 7.85 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.63 (d, *J* = 2.3 Hz, 1H), 7.57 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.43 – 7.38 (m, 2H), 7.21 – 7.13 (m, 4H), 7.02 (d, *J* = 8.5 Hz, 1H), 4.10 – 3.98 (m, 1H), 3.92 (s, 3H), 3.79 (d, *J* = 6.9 Hz, 2H), 2.20 (d, *J* = 2.4 Hz, 6H), 2.12 (s, 3H), 1.82 (s, 6H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -70.01 (d, *J* = 8.9 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 164.80, 159.09, 152.14, 151.71, 141.99, 140.74, 139.13, 137.45, 136.39, 132.40, 131.83, 131.24, 130.31, 129.86, 129.63, 129.27, 128.57, 126.78, 126.01, 125.86, 125.78, 125.71, 124.78, 122.31, 112.19, 55.19, 40.66, 37.26, 37.15, 29.70, 29.14.

**HRMS** (ESI<sup>+</sup>, *m/z*) [M+Na<sup>+</sup>] calcd. for C<sub>43</sub>H<sub>38</sub>SO<sub>5</sub>F<sub>3</sub>Cl 781.1973, found 781.1963.

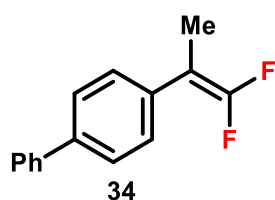


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.55 (m, 4H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 5.95 (d, *J* = 1.1 Hz, 1H), 5.79 (d, *J* = 1.6 Hz, 1H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -64.78.

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 141.90, 140.30, 138.67 (q, *J* = 30.0 Hz), 132.51, 128.91, 127.78, 127.73, 127.30, 127.11, 123.46 (q, *J* = 274.1 Hz), 120.20 (q, *J* = 5.8 Hz).

**GCMS** (EI, *m/z*) [M<sup>+</sup>] calcd. for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub> 248.0807, found 248.0804.

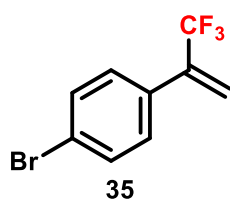


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.57 (m, 4H), 7.48 – 7.40 (m, 4H), 7.40 – 7.30 (m, 1H), 2.02 (t, *J* = 3.4 Hz, 3H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -89.82 (dq, *J* = 42.9, 3.3 Hz), 90.20 (dq, *J* = 42.8, 3.3 Hz).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 153.59 (dd, *J* = 290.7, 286.3 Hz), 140.60, 139.88, 133.84 (t, *J* = 4.2 Hz), 128.81, 127.83 (dd, *J* = 4.7, 3.4 Hz), 127.38, 127.04, 127.01, 87.23 (dd, *J* = 22.6, 14.1 Hz), 13.15 (t, *J* = 1.8 Hz).

**GCMS** (EI, *m/z*) [*M*<sup>+</sup>] calcd. for C<sub>15</sub>H<sub>12</sub>F<sub>2</sub> 230.0902, found 230.0899.

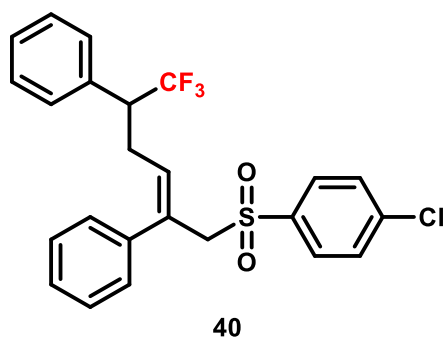


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.50 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.98 (q, *J* = 1.3 Hz, 1H), 5.78 (q, *J* = 1.6 Hz, 1H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -64.95 (s).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 138.28 (q, *J* = 30.5 Hz), 132.67, 131.95, 129.16, 123.54, 122.04 (q, *J* = 273.9 Hz), 121.03 (q, *J* = 5.7 Hz).

**GCMS** (EI, *m/z*) [*M*<sup>+</sup>] calcd. for C<sub>9</sub>H<sub>6</sub>F<sub>3</sub>Br 251.9579, found 251.9577.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.37 (m, 4H), 7.31 – 7.27 (m, 4H), 7.15 – 7.11 (m, 2H), 6.95 – 6.88 (m, 2H), 5.78 (t, *J* = 7.4 Hz, 1H), 4.26 (s, 2H), 3.49 – 3.37 (m, 1H), 2.98 – 2.88 (m, 1H), 2.84 – 2.73 (m, 1H).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -69.30 (d, *J* = 9.2 Hz).

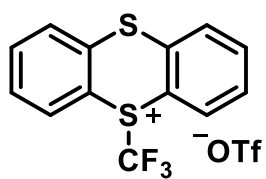
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.48, 140.17, 137.35, 133.53, 130.29, 129.85, 129.18, 128.98, 128.92, 128.86, 128.48, 128.36, 128.20, 127.55, 126.37, 57.90, 49.77, 29.23.

**HRMS** (ESI<sup>+</sup>, *m/z*) [*M*+*H*<sup>+</sup>] calcd. for C<sub>24</sub>H<sub>20</sub>SO<sub>2</sub>F<sub>3</sub>Cl 465.0897, found 465.0911.

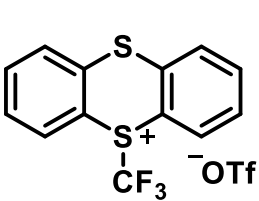
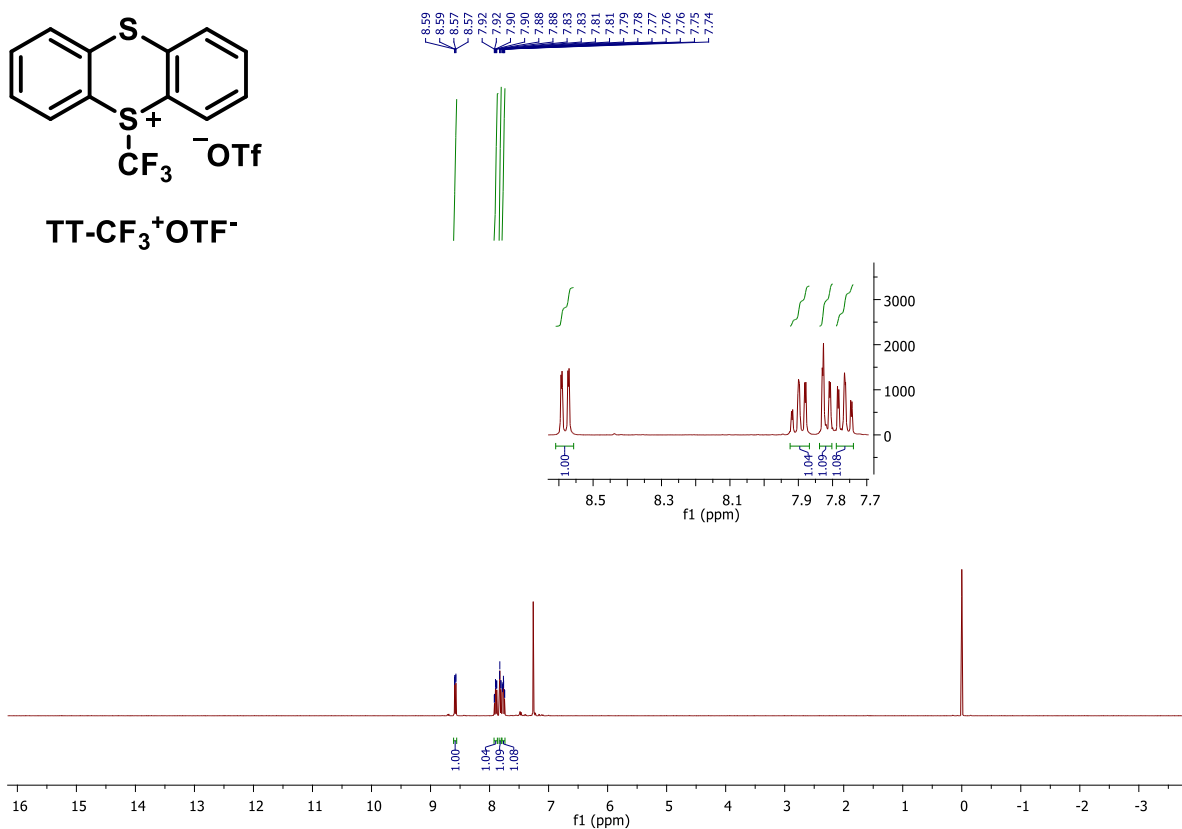
## 1.7 Reference

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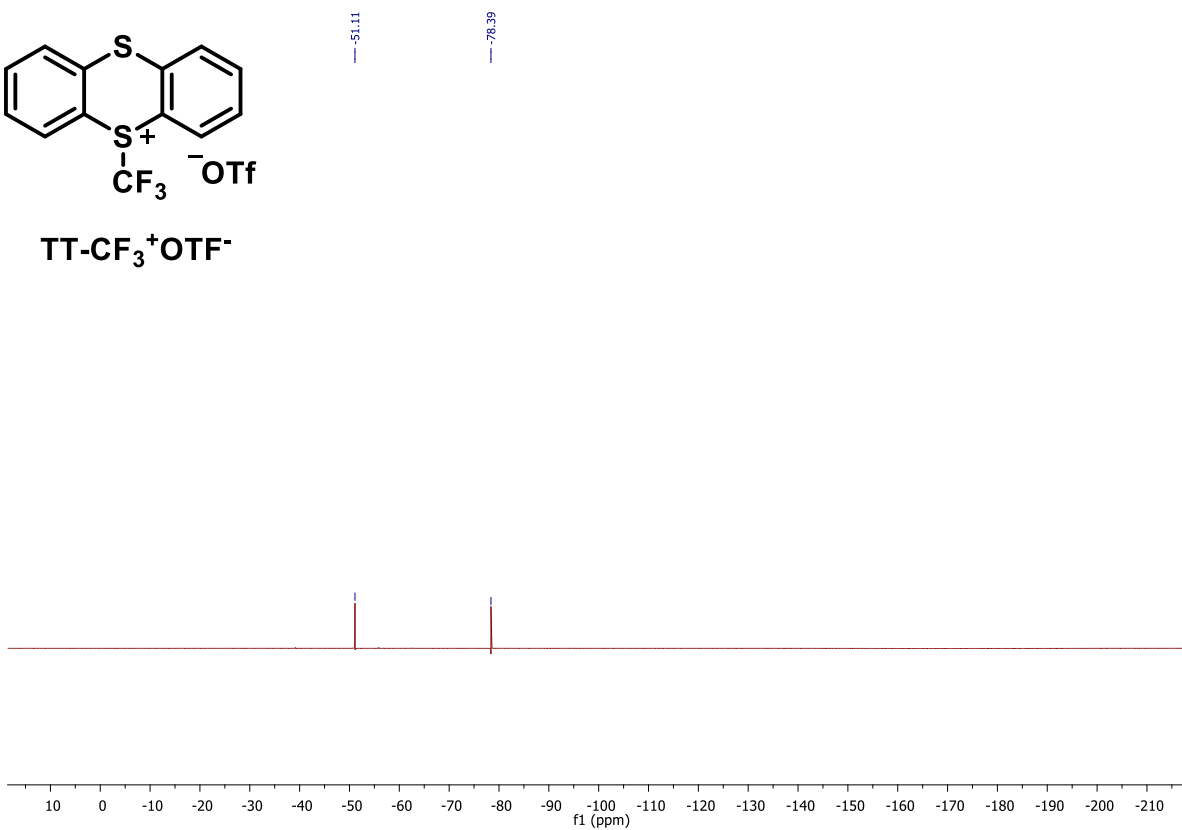
## 1.8 Spectra

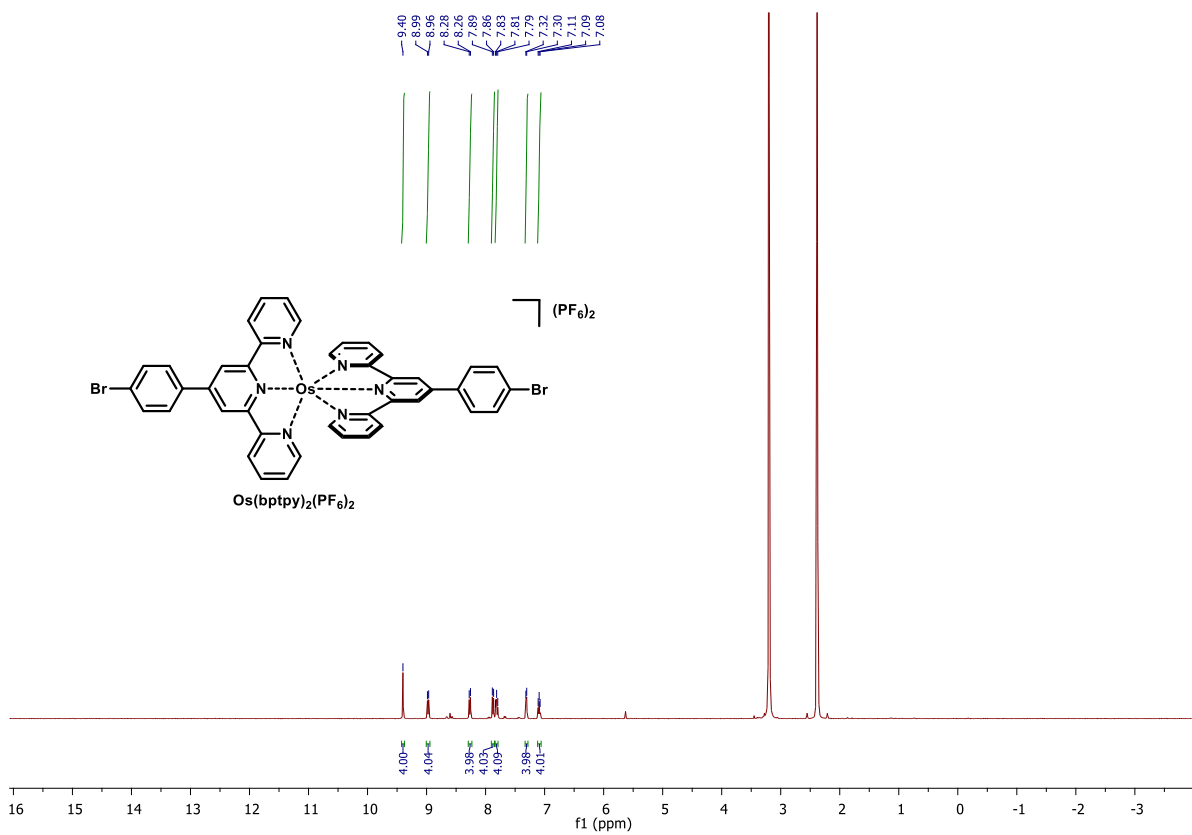
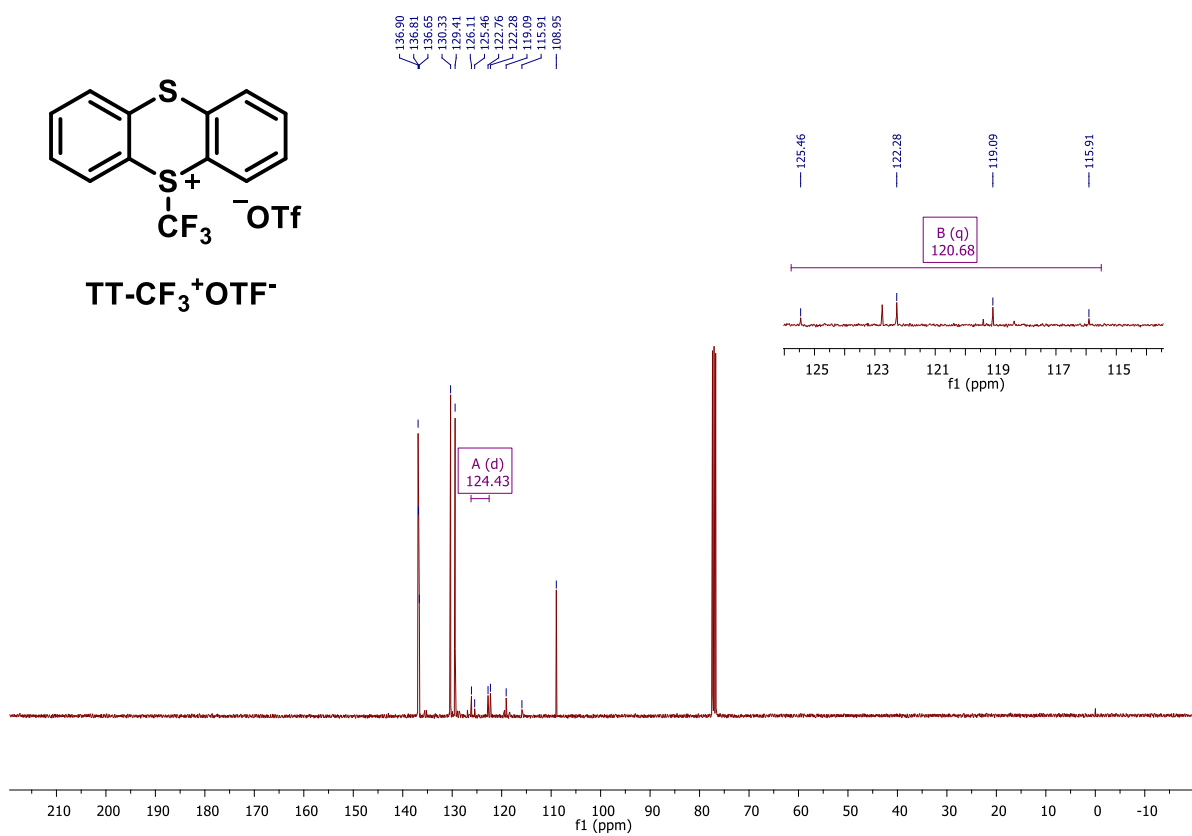


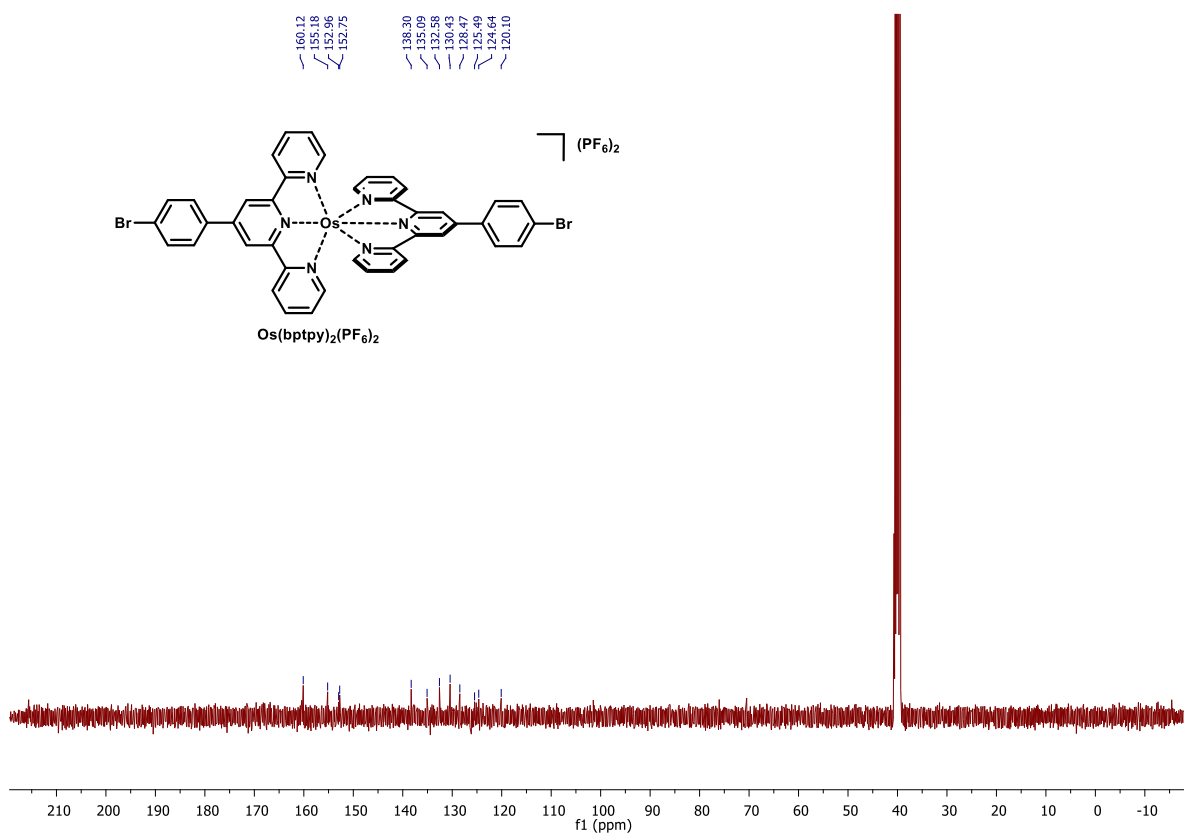
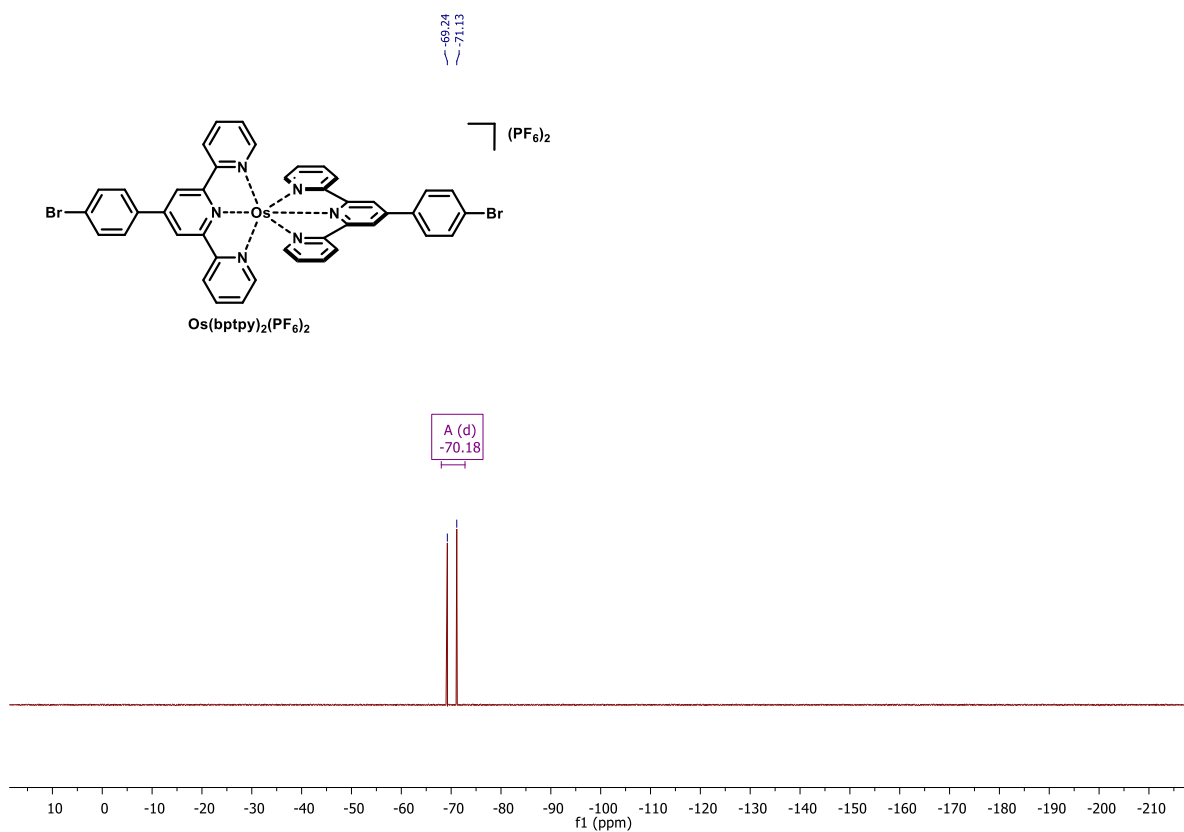
TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup>

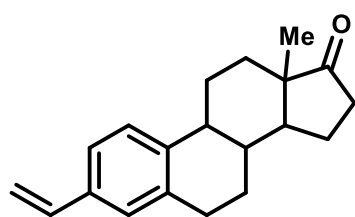


TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup>









S1

