Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers. This journal is © the Partner Organisations 2023

Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers. This journal is © The Royal Society of Chemistry 2022

# **Electronic Supplementary Information for:**

# Visible-light promoted generation of p-(N,N-dimethyl)benzyl equivalents and their reactions with quinols: an easy access to diarylalkanes

Baihui Zheng, Xiaotong Li, Shuyang Meng, Yifei Li, Qun Liu & Ling Pan\*

Jilin Province Key Laboratory of Organic Functional Molecular, Design & Synthesis, Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun, 130024, China.

E-mail: panl948@nenu.edu.cn

## **Table of Contents**

| I. General information  | S2  |
|---|-----|
| II. Additional optimization of reaction conditions                                    | S3  |
| III. Mechanistic studies  | S3  |
| IV. Experimental procedures and analytical data                                       | S10 |
| V. Crystal data of compound <b>3d</b>   | S22 |
| VI. Copies of <sup>1</sup> H NMR, <sup>13</sup> C NMR and <sup>19</sup> F NMR spectra | S24 |

#### I. General information

All reagents and catalysts were purchased from commercial sources and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254) using UV light as visualizing agent. Tsingdao silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Brüker Advance 600 (<sup>1</sup>H: 600 MHz, <sup>13</sup>C: 150 MHz, <sup>19</sup>F NMR: 565 MHz) and Brüker Advance 500 (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0 ppm) for <sup>1</sup>H NMR and CDCl<sub>3</sub> (77.0 ppm) for <sup>13</sup>C NMR. All <sup>1</sup>H NMR spectra were reported in delta (d) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared spectroscopy (IR) was obtained by Fourier Transform Infrared Spectrometer (FT-IR). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focusspectrometer (ESI).

Blue LEDs (5 W,  $\lambda = 465$  nm) was purchased from Wattecs (parallel light reactor, WP-TEC-1020HC). Quartz tube (15 mL) was used as the irradiation vessel and the Blue LEDs irradiated at the bottom with a 1–1.5 cm distance. Blue LEDs (15 W,  $\lambda = 465-470$  nm) was purchased from Merck (SynLEDZ742680). Airtight glass tube (10 mL) was used as the irradiation vessel and the Blue LEDs irradiated at the bottom with a 1–1.5 cm distance. Blue LEDs (40 W,  $\lambda = 456$  nm) was purchased from Kessil (PR160) with flask (15 mL and 75mL) as the irradiation vessel with a 5–6 cm distance.

Varian cary50 was used for UV-*vis* absorption analysis; spectrofluorometer (Edinburgh FS5) was used for Stern-Volmer fluorescence quenching experiments; and CH Instruments (CHI 660E) was used for Cyclic Voltammetry experiments.

#### **II.** Additional optimization of reaction conditions

#### The effect of light source<sup>*a*</sup>

| CF <sub>3</sub> OTMS | Light Source<br>[Ir(dtbbpy)(ppy) <sub>2</sub> ][PF <sub>6</sub> ] (1 r<br>48 h, DCE, N <sub>2</sub> | nol%)<br>CF <sub>3</sub>            |
|----------------------|---|-------------------------------------|
| 1a                   | 2a  | 3a                                  |
| Entry                | Light source  | Yield of <b>3a</b> (%) <sup>b</sup> |
| 1                    | Blue light (15 W)   | 56                                  |
| 2                    | White light (5 W)   | 49                                  |
| 3                    | UV light (5 W)  | Trace                               |
| 4                    | Green light (5 W)   | 21                                  |
| 5                    | Yellow light (5 W)  | N. R. <sup><i>c</i></sup>           |
| 6                    | Blue light (5 W)  | 50                                  |
| 7                    | Blue light (40 W)   | 52                                  |

<sup>*a*</sup> **1a** (0.3 mmol), **2a** (5.0 eq), [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>] (1 mol%) in DCE (2 mL) at room temperature for 48 h under irradiation with 15 W blue LED light. <sup>*b*</sup> Isolated yields. <sup>*c*</sup> No reaction was observed.

## **III.** Mechanistic studies

## a. UV-vis Absorption Spectra

UV-*vis* spectra were carried out using the DCE solution of trifluoromethyl-containing quinol **1a**  $(2 \times 10^{-5} \text{ mol}, 2 \times 10^{-4} \text{ M} \text{ in DCE})$ , *N,N*-dimethyl aniline **2a**  $(2 \times 10^{-5} \text{ mol}, 2 \times 10^{-4} \text{ M} \text{ in DCE})$ , [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>]  $(1 \times 10^{-6} \text{ mol}, 6 \times 10^{-6} \text{ M} \text{ in DCE})$  respectively, and their mixture. It was shown that [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>] has strongest ultraviolet absorption at the reaction wavelength (465 nm) and is the best photosensitizer.



Figure S1. UV-*vis* spectra of trifluoromethyl-containing quinol 1a, N,N-dimethyl aniline 2a, [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>] respectively and their mixture.

## b. Emission Quenching Studies

Emission intensities were recorded by spectrofluorometer (Edinburgh FS5) at ambient temperature. The DCE solution of  $[Ir(dtbbpy)(ppy)_2][PF_6]$  were excited at 485 nm and the emission intensity at 562 nm was observed. Firstly, the emission spectrum of a  $5 \times 10^{-5}$  M solution of  $[Ir(dtbbpy)(ppy)_2][PF_6]$  in DCE was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. The Stern-Volmer emission quenching studies tell that the *N*,*N*-dimethyl arylamine is easier than trifluoromethylated quinol to quench the excited photosensitizer.



Figure S2.  $Ir(dtbbpy)(ppy)_2][PF_6]$  emission quenching by trifluoromethylated quinol 1a.



Figure S3. [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>] emission quenching by *N*,*N*-dimethyl aniline 2a.



Figure S4. [Ir(dtbbpy)(ppy)<sub>2</sub>][PF<sub>6</sub>] emission quenching by 4-trifluoromethyl-*p*-quinol 1w.



**Figure S5**. Emission-quenching experiments of  $[Ir(dtbbpy)(ppy)_2][PF_6]$  with trifluoromethylated quinol **1a**, *N*,*N*-dimethyl aniline **2a** and 4-trifluoromethyl-*p*-quinol **1w**.

#### c. Cyclic Voltammetry Experiments

For the electrochemical measurements, a three-electrode system connected to an electrochemical station was used: A reference electrode, Ag/AgCl in 0.1 M KCl; A glassy carbon electrode as the working electrode; and a Pt wire as the counter electrode. All electrochemical measurements were performed in degassed DMF under dry  $N_2$  atmosphere.



**Figure S6.** CV spectra of trifluoromethylated quinol **1a** (3 mM), *N*,*N*-dimethyl aniline **2a** (3 mM) and  $[Ir(dtbbpy)(ppy)_2][PF_6]$  (3 mM) in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed DMF (20 mL) with scan rate 100 mV/s.



## **Plausible Mechanism**

# d. Radical trapping experiments



#### e. Detection of by-product

#### Detection of N-methylaniline by GC-MS



#### f. Capture of intermediate B

## i) Synthesis of intermediate A<sup>1</sup>



In a round-bottomed flask, the salt of 4-(bromomethyl)-*N*,*N*-dimethylaniline (426 mg, 2 mmol) was dissolved in 5 mL of acetone, neutralized with K<sub>2</sub>CO<sub>3</sub> (304 mg, 2.2 mmol), and stirred for 5 min. This reaction mixture was added to a 25 mL round-bottomed flask equipped with a magnetic stirring bar, followed by the addition of of *N*-methylaniline (216  $\mu$ L, 2 mmol) and residual K<sub>2</sub>CO<sub>3</sub> (304 mg, 2.2 mmol) in 10 mL of dimethylformamide (DMF). The reaction was stirred for 48 h at room temperature. After the completion of the reaction as indicated by TLC, the solution was concentrated in vacuo. Then the residue was purified by silica gel column chromatography (PE/EA = 15/1) to afford product, intermediate A (173 mg, 36%)

<sup>1.</sup> L. Leng, Y. Fu, P. Liu and J. M. Ready, Regioselective, Photocatalytic α-Functionalization of Amines. J. Am. Chem. Soc., 2020, **142**, 11972–11977.

## ii) Analysis for intermediate A and 1a by GC-MS



To a glass tube (10 mL) equipped with a stir-bar was added trifluoromethylated quinol **1a** (0.09 g, 0.3 mmol),  $[Ir(dtbbpy)(ppy)_2][PF_6]$  (8.2 mg, 0.009 mmol) and degassed with N<sub>2</sub>. Then intermediate **A** (144 mg, 2 equiv.) and DCE (2 mL) were added under nitrogen atmosphere. The reaction mixture was stirred for 72 h under the irradiation of blue LED light (15 W). After the completion of the reaction as indicated by TLC. Intermediate *N*-methylaniline **F** and **G**, which was proposed to come from *p*-(*N*,*N*-dimethyl)benzyl equivalent **B** was dectected from GC-MS analysis, indicating the formation of *p*-(*N*,*N*-dimethyl)benzyl equivalents **B** in this visible-light mediated transformations.

#### Detection of aromatization derivative G by GC-MS



## IV. Experimental procedures and analytical data



**Typical synthetic procedure** (with **3a** as an example): To a glass tube (10 mL) equipped with a stir-bar was added trifluoromethylated quinol **1a** (0.09 g, 0.3 mmol),  $[Ir(dtbbpy)(ppy)_2][PF_6]$  (8.2 mg, 0.009 mmol) and degassed with N<sub>2</sub>. Then *N*,*N*-dimethyl aniline **2a** (190 µL, 1.5 mmol) and DCE (2 mL) were added under nitrogen atmosphere. The reaction mixture was stirred for 72 h under the irradiation of blue LED light (15 W). After the completion of the reaction as indicated by TLC, the solution was concentrated in vacuo. Then the residue was purified by silica gel column chromatography (PE/EA = 5/1) to afford product **3a** (79.6 mg, 77%).



#### 3a: 2-(4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow oil. 79.6 mg (77%). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.23 (d, J = 9.0 Hz, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.73 (s, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 5.76 (br, 1H), 4.10 (s, 2H), 2.94 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  153.0, 150.0, 129.5, 129.2, 128.3 (q, J = 5.9 Hz), 127.4, 125.8, 125.4, 124.9, 125.0 (q, J = 270.9 Hz), 124.0 (q, J = 2.1 Hz), 122.2, 118.3, 118.1 (q, J = 30.0 Hz), 113.3, 40.6, 36.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -55.59. **HRMS** (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>F<sub>3</sub>NO<sup>+</sup> 346.1413; Found 346.1415.



## 3b: 2-(4-(dimethylamino)-2-methylbenzyl)-4-(trifluoromethyl)naphthalen-1-ol

Brown oil. 73.2 mg (68%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.66 (s, 1H), 6.59 (d, J = 8.4 Hz, 1H), 5.87 (br, 1H), 4.08 (s, 2H), 2.96 (s, 6H), 2.28 (s, 3H). <sup>13</sup>C NMR

(150 MHz, CDCl<sub>3</sub>):  $\delta$  153.1, 150.1, 137.9, 129.5, 128.2 (q, *J* = 5.9 Hz), 127.3, 125.7, 125.4, 124.5 (q, *J* = 270.6 Hz), 124.1, 123.9 (q, *J* = 2.1 Hz), 123.1, 122.3, 118.1 (q, *J* = 29.9 Hz), 117.4, 115.4, 110.8, 40.6, 34.6, 20.4. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.20. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>NO<sup>+</sup> 360.1570; Found 360.1569.



## 3c: 2-(4-(dimethylamino)-2-ethylbenzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow oil. 77.2 mg (69%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.26 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.72 (s, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 6.72 (s, 1H), 6.60 (d, J = 8.5 Hz, 1H), 5.98 (br, 1H), 4.13 (s, 2H), 2.98 (s, 6H), 2.67 (q, J = 7.5 Hz, 2H), 1.21 (t, J = 7.5 Hz, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  153.0, 150.3, 143.7, 129.8, 129.3, 128.2 (q, J = 6.9 Hz), 127.3, 127.0 (q, J = 277.7 Hz), 125.7, 125.4, 123.9 (q, J = 2.3 Hz), 122.6, 122.3, 118.1 (q, J = 35.9 Hz), 117.8, 113.8, 111.1, 40.6, 33.8, 26.5, 14.8. <sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.53. **HRMS** (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>22</sub>H<sub>23</sub>F<sub>3</sub>NO<sup>+</sup> 374.1726; Found 374.1726.



#### 3d: 2-(4-(dimethylamino)-2-isopropylbenzyl)-4-(trifluoromethyl)naphthalen-1-ol

White solid. 81.3 mg (70%). mp: 116–117 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.71 (s, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.80 (s, 1H), 6.61 (d, J = 8.5 Hz, 1H), 6.02 (br, 1H), 4.17 (s, 2H), 3.22–3.17 (m, 1H), 3.00 (s, 6H), 1.22 (d, J = 7.0 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  153.0, 150.5, 148.5, 130.0, 129.2, 128.0 (q, J = 6.0 Hz), 127.3, 125.7, 125.4, 125.0 (q, J = 270.6 Hz), 123.9 (q, J = 2.0 Hz), 122.2, 121.7, 118.1 (q, J = 30.0 Hz), 118.0, 111.0, 110.6, 40.6, 34.0, 29.5, 23.6. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.51. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>23</sub>H<sub>25</sub>F<sub>3</sub>NO<sup>+</sup> 388.1883; Found 388.1895.



## 3e: 2-(2-(tert-butyl)-4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow solid. 44.5 mg (37%). mp: 112–113 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.22 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.67 (s, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.92 (s, 1H), 6.52 (d, J = 8.5 Hz, 1H), 5.76 (br, 1H), 4.39 (s, 2H), 2.96 (s, 6H), 1.53 (s, 9H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.7, 149.7, 149.0, 132.2, 129.3, 128.5 (q, J = 6.0 Hz), 127.3, 125.7, 125.5, 125.0 (q, J = 270.6 Hz), 123.9 (q, J = 2.1 Hz), 122.3, 118.8, 118.0 (q, J = 30.2 Hz), 111.5, 111.1, 40.6, 36.2, 35.6, 31.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.61. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>24</sub>H<sub>27</sub>F<sub>3</sub>NO<sup>+</sup> 402.2039. Found 402.2040.



#### 3f: 2-((5-(dimethylamino)-[1,1'-biphenyl]-2-yl)methyl)-4-(trifluoromethyl)naphtalen-1-ol

Brown oil. 102.3 mg (81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.21 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 7.0 Hz, 1H), 7.41 (s, 4H), 7.32 (s, 2H), 7.22 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 6.72 (s, 1H), 5.59 (br, 1H), 4.06 (s, 2H), 2.99 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.5, 149.6, 143.1, 141.7, 130.0, 129.1, 128.9, 128.3, 128.2 (q, J = 5.9 Hz), 127.3, 127.1, 125.6, 125.2, 124.9 (q, J = 270.6 Hz), 123.8 (q, J = 2.0 Hz), 122.8, 122.2, 118.6, 117.8 (q, J = 30.0 Hz), 114.7, 112.3, 40.4, 34.1. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.53. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>26</sub>H<sub>23</sub>F<sub>3</sub>NO<sup>+</sup> 422.1726; Found 422.1732.



3g: 2-(4-(dimethylamino)-2-fluorobenzyl)-4-(trifluoromethyl)naphthalen-1-ol

Red oil. 65.3 mg (60%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.26 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.72 (s, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.02 (t, J = 9.0 Hz, 1H), 6.44–6.42 (m, 2H), 5.91 (br, 1H), 4.04 (s, 2H), 2.92 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  161.6 (d, J = 239.0 Hz), 152.3, 151.4 (d, J = 11.0 Hz), 130.4 (d, J = 6.5 Hz), 129.4, 128.0 (q, J = 6.0 Hz), 127.4, 125.9, 125.3, 124.9 (q, J = 270.9 Hz), 124.0, 122.3, 118.4 (q, J = 30.0 Hz), 117.4, 111.6 (d, J = 16.5 Hz), 108.6 (d, J = 2.3 Hz), 99.5 (d, J = 26.9 Hz), 40.4, 28.8 (d, J = 2.6 Hz). <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.70 (s, 3F), -116.4 (s, 1F). HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>F<sub>4</sub>NO<sup>+</sup> 364.1319; Found 364.1313.



#### 3h: 2-(2-chloro-4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Brown solid. 77.3 mg (68%). mp: 119–120 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.60 (t, J = 8.4 Hz, 1H), 7.55 (t, J = 8.4 Hz, 1H), 6.97–6.95 (m, 2H), 6.58 (d, J = 8.4 Hz, 1H), 5.79 (br, 1H), 4.16 (s, 2H), 2.92 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.5, 150.6, 130.3, 129.4, 128.2 (q, J = 6.0 Hz), 127.4, 125.9, 125.3, 125.2, 124.9 (q, J = 270.8 Hz), 124.0 (q, J = 2.6 Hz), 123.9, 122.3, 118.3 (q, J = 30.2 Hz), 117.2, 116.3, 112.2, 40.3, 35.6. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.63. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>ClF<sub>3</sub>NO<sup>+</sup> 380.1024; Found 380.1026.



#### 3i: 2-(2-bromo-4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow solid. 77.9 mg (63%). mp: 107–108 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 6.96–6.95 (m, 2H), 6.58 (d, J = 8.4 Hz, 1H), 5.86 (br, 1H), 4.16 (s, 2H), 2.92 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.5, 150.6, 130.3, 129.4, 128.2 (q, J = 5.9 Hz), 127.4, 126.7 (q, J = 284.6 Hz), 125.9, 125.3, 125.2, 124.0 (q, J = 2.4 Hz), 123.9, 122.3, 118.3 (q, J = 30.0 Hz), 117.2, 116.3, 112.2, 40.3, 35.6. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.66. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>BrF<sub>3</sub>NO<sup>+</sup> 424.0518; Found 424.0521.



## 3j: 2-(4-(dimethylamino)-2-iodobenzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow oil. 110.2 mg (78%). <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.67 (s, 1H), 7.62 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.24 (s, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.62 (d, J = 8.5 Hz, 1H), 5.66 (br, 1H), 4.14 (s, 2H), 2.92 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.6, 150.4, 129.4, 129.4, 128.3 (q, J = 6.3 Hz), 127.4, 127.2, 125.9, 125.3, 125.1 (q, J = 270.5 Hz), 124.0, 123.1, 122.3, 118.4 (q, J = 30.0 Hz), 117.4, 113.0, 102.0, 40.6, 40.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.63. **HRMS** (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>IF<sub>3</sub>NO<sup>+</sup> 472.0380; Found 472.0376.



## 3k: 2-(4-(dimethylamino)-2-ethynylbenzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow oil. 33.2 mg (30%). <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.27 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.77 (s, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.88 (s, 1H), 6.68 (d, J = 8.5 Hz, 1H), 6.21 (br, 1H), 4.23 (s, 2H), 3.45 (s, 1H), 2.92 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.5, 149.2, 129.6, 129.4, 128.3 (q, J = 6.0 Hz), 128.0, 127.3, 125.8, 125.3, 125.0 (q, J = 258.8 Hz), 123.9 (q, J = 2.4 Hz), 122.5, 121.3, 118.1 (q, J = 30.0 Hz), 117.9, 116.3, 114.5, 83.2, 81.7, 40.4, 33.9. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.66. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>22</sub>H<sub>19</sub>F<sub>3</sub>NO<sup>+</sup> 370.1413; Found 370.1413.



## 3n: 2-(4-(dimethylamino)-2,6-dimethylbenzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow solid. 79.5 mg (71%). mp: 110–111 °C. <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.53 (s, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 6.54 (s,

2H), 6.23 (br, 1H), 4.14 (s, 2H), 2.97 (s, 6H), 2.27 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  153.0, 149.9, 138.3, 128.9, 127.3 (q, J = 5.7 Hz), 127.2, 125.7, 125.4, 125.0 (q, J = 270.3 Hz), 123.9, 122.2, 121.2, 118.0 (q, J = 30.3 Hz), 116.5, 113.3, 40.5, 30.9, 21.1. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.62. **HRMS** (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>22</sub>H<sub>23</sub>F<sub>3</sub>NO<sup>+</sup> 374.1726; Found 374.17328.



## 30: 2-(2-chloro-4-(dimethylamino)-6-methylbenzyl)-4-(trifluoromethyl)naphthalen-1-ol

White solid. 77.8 mg (66%). mp: 182–183 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.24 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.48 (s, 1H), 6.69 (s, 1H), 6.52 (s, 1H), 6.00 (br, 1H), 4.22 (s, 2H), 2.96 (s, 6H), 2.24 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.3, 150.1, 139.7, 135.6, 129.1, 127.2, 127.1 (q, J = 6.0 Hz), 125.8, 125.2, 125.0 (q, J = 270.9 Hz), 124.0, 122.0, 120.8 (q, J = 3.2 Hz), 118.2 (q, J = 30.5 Hz), 116.7, 113.8, 111.1, 40.3, 30.3, 21.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.63. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>ClF<sub>3</sub>NO<sup>+</sup> 394.1180; Found 394.1175.



#### 3p: 2-(4-(dimethylamino)benzyl)-4-(perfluoroethyl)naphthalen-1-ol

Yellow oil. 85.3 mg (72%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 5.84 (br, 1H), 4.11 (s, 2H), 2.94 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  153.4, 149.9, 130.8 (t, J = 8.4 Hz), 130.4, 129.5, 129.2, 127.3, 125.6, 125.5, 124.8, 124.4, 122.3, 118.7, 115.9 (qt, J = 253.2 Hz, J = 21.9 Hz), 115.4 (tq, J = 263.3 Hz, J = 38.9 Hz), 113.3, 40.6, 36.4. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -83.47 (s, 3F), -107.48 (s, 2F). HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>F<sub>5</sub>NO<sup>+</sup> 396.1381; Found 3496.1380.



## 3q: 2-(4-(dimethylamino)benzyl)-6-methoxy-4-(trifluoromethyl)naphthalen-1-ol

Brown solid. 60.7 mg (54%). mp: 102–103 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.13 (d, J = 9.0 Hz, 1H), 7.70 (s, 1H), 7.41 (s, 1H), 7.17 (d, J = 9.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 5.72 (br, 1H), 4.05 (s, 2H), 3.95 (s, 3H), 2.93 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  158.7, 153.2, 149.9, 131.1, 129.2, 128.9 (q, J = 5.9 Hz), 125.2 (q, J = 270.5 Hz), 125.1, 124.0, 120.6, 118.2, 116.8 (q, J = 30.0 Hz), 116.4, 113.3, 102.7, 55.3, 40.5, 36.2. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -59.32. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> 376.1519; Found 376.1527.



## 3r: 2-(4-(dimethylamino)benzyl)-7-methoxy-4-(trifluoromethyl)naphthalen-1-ol

Brown solid. 49.5 mg (44%). mp: 98–99 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.07 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.54 (s, 1H), 7.28 (d, J = 9.0 Hz, 1H), 7.16 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 5.65 (br, 1H), 4.10 (s, 2H), 3.93 (s, 3H), 2.96 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  157.5, 151.9, 149.9, 129.2, 126.8, 125.0 (q, J = 271.2 Hz), 125.7 (q, J = 5.7 Hz), 125.6, 124.9, 124.8, 120.0, 118.8, 118.2 (q, J = 30.0 Hz), 113.3, 100.6, 55.2, 40.5, 36.4. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.45. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> 376.1519; Found 376.1534.



## 3s: 6-bromo-2-(4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow oil. 67.1 mg (53%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (s, 1H), 8.09 (d, J = 9.0 Hz, 1H), 7.72 (s, 1H), 7.58 (d, J = 9.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 5.85 (br, 1H), 4.06 (s, 2H), 2.93 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  153.3, 150.0, 130.5, 129.4 (q, J = 5.7 Hz), 129.2, 129.2, 126.2 (q, J = 2.6 Hz), 124.7 (q, J = 270.6 Hz), 124.3, 124.0, 122.3, 118.8,

117.3 (q, J = 30.5 Hz), 113.3, 40.5, 36.4. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -58.71. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>BrF<sub>3</sub>NO<sup>+</sup> 424.0518; Found 424.0519. For details please see the following HMBC spectra analysis of 3s and 3t.



## 3t: 7-bromo-2-(4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Yellow oil. 62.3 mg (49%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.39 (s, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.71 (s, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 5.81 (br, 1H), 4.08 (s, 2H), 2.93 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.2, 150.0, 130.7, 129.2, 128.6 (q, J = 5.9 Hz), 127.9, 126.7, 125.6 (q, J = 2.1 Hz), 125.0, 124.7 (q, J = 270.6 Hz), 124.3, 120.2, 119.4, 118.3 (q, J = 30.3 Hz), 113.4, 40.5, 36.4. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.72. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>BrF<sub>3</sub>NO<sup>+</sup> 424.0518; Found 424.0511.

For details please see the following HMBC spectra analysis of 3s and 3t.



## 3u: 2-(4-(dimethylamino)benzyl)-6,7-dimethyl-4-(trifluoromethyl)naphthalen-1-ol

Yellow solid. 64.9 mg (58%). mp: 114–115 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.94 (s, 1H), 7.84 (s, 1H), 7.61 (s, 1H), 7.11 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 5.62 (br, 1H), 4.06 (s, 2H), 2.92 (s, 6H), 2.45 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.3, 149.8, 137.3, 135.6, 129.5, 129.2, 127.4 (q, J = 5.7 Hz), 125.4, 125.2 (q, J = 270.0 Hz), 124.2, 123.6, 121.6, 117.5, 117.3 (q, J = 29.7 Hz), 113.3, 40.6, 36.2, 20.5, 20.2. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.59. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>22</sub>H<sub>23</sub>F<sub>3</sub>NO<sup>+</sup> 374.1726; Found 374.1736.



#### 3v: 6,7-dibromo-2-(4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-ol

Green solid. 63.1 mg (42%). mp: 111–112 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.50 (s, 1H), 8.36 (s, 1H), 7.72 (s, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.95 (br, 1H), 4.05 (s, 2H), 2.93 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  152.3, 150.0, 129.6 (q, J = 5.7 Hz), 129.2, 128.9, 128.5 (q, J = 2.4 Hz), 127.4, 125.3, 124.5, 124.4 (q, J = 270.6 Hz), 123.9, 122.5, 119.6, 117.3 (q, J = 30.6 Hz), 113.3, 40.5, 36.4. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -58.72. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>Br<sub>2</sub>F<sub>3</sub>NO<sup>+</sup> 501.9624; Found 503.9590.

#### Synthesis of compound 5

To a solution of **3a** (104 mg, 0.3 mmol) in DMF (3 mL) was added K<sub>2</sub>CO<sub>3</sub> (50 mg, 1.2 eq) and MeI (22.4  $\mu$ L, 1.2 eq). The reaction mixture was stirred at room temperature until **3a** was completely consumed (TLC). The reaction was quenched by adding H<sub>2</sub>O (25 mL) and extracted with ethyl acetate (3×5 mL). The organic layer was washed with water (3×10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated in vacuo and purified via column chromatography using PE/EA (8:1 v/v) to obtain Yellow oil **5** (70.0 mg, 65%).



#### 5: 4-((1-methoxy-4-(trifluoromethyl)naphthalen-2-yl)methyl)-N,N-dimethylaniline

Yellow oil. 70.0 mg (65%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.23–8.22 (m, 1H), 8.18–8.16 (m, 1H), 7.72 (s, 1H), 7.62–7.60 (m, 2H), 7.12 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 4.15 (s, 2H), 3.95 (s, 3H), 2.93 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  156.6, 149.3, 129.4, 128.8, 128.7, 128.2 (q, J = 5.9 Hz), 127.9, 127.1, 126.5, 124.6 (q, J = 271.5 Hz), 124.5 (q, J = 2.3 Hz), 122.8, 122.0 (q, J = 30.0 Hz), 113.0, 62.3, 40.7, 34.3. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -59.10. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>NO<sup>+</sup> 360.1570; Found 360.1559.

#### Synthesis of compound 6

A solution of the **3a** (93.0 mg, 0.2 mmol) in DCM (2 mL) was cooled to 0 °C, pyridine (32.4  $\mu$ L, 0.4 mmol) was added to the above solution, and trifluoromethanesulfonic anhydride (40.4  $\mu$ L, 0.24 mmol) was added dropwise with stirring. The reaction was completed until **3a** was consumed (TLC). The reaction was quenched by adding H<sub>2</sub>O and extracted with DCM (3×5 mL). The organic layer was washed with water (3×10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated in vacuo and purified via column chromatography using PE/EA (10:1 v/v) to obtain pink oil **6** (60.1 mg, 63%).



**6:** 2-(4-(dimethylamino)benzyl)-4-(trifluoromethyl)naphthalen-1-yltrifluoromethanesulfonate Pink oil. 60.1 mg (63%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.27 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.77–7.74 (m, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 4.28 (s, 2H), 2.97 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 149.6, 144.4, 131.5, 129.8, 129.2, 128.3, 128.2, 127.8, 127.5 (q, J = 6.0 Hz), 126.6 (q, J = 30.4 Hz), 125.4, 124.5 (q, J = 2.9 Hz), 123.8 (q, J = 272.3 Hz), 122.1, 118.7 (q, J = 318.3 Hz), 113.0, 40.5, 35.0. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>): δ -59.68 (s, 3F), -72.69 (s, 3F). HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>21</sub>H<sub>18</sub>F<sub>6</sub>NO<sub>3</sub>S<sup>+</sup> 478.0906; Found 478.0917.

#### Synthesis of compound 7

To a solution of **3a** (104 mg, 0.3 mmol) and K<sub>3</sub>PO<sub>4</sub> (96 mg, 0.45 mmol) in dry DCE (3 mL) was added PhIO (99 mg, 0.45 mmol), and the mixture was stirred at room temperature. The completion of reaction was monitored by TLC. Then the insolubles were filtered off, and the solution was extracted with  $CH_2Cl_2$  (3×5 mL). Then, the solvent was removed by evaporation. The residue was purified via column chromatography using PE/EA (8:1 v/v) to obtain product 7 as a yellow solid (36.6 mg, 34%).



#### 7: (4-(dimethylamino)phenyl)(1-hydroxy-4-(trifluoromethyl)naphthalen-2-yl)methanone

Yellow solid. 36.6 mg (34%). mp: 123–124 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.59 (d, J = 8.5 Hz, 1H), 8.15 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.77–7.73 (m, 3H), 7.62 (t, J = 8.5 Hz, 1H), 6.75 (d, J = 9.0 Hz, 2H), 3.09 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  198.1, 165.8, 153.3, 132.2, 132.0, 131.0, 127.3 (q, J = 6.1 Hz), 126.4, 126.1, 124.9, 124.7 (q, J = 270.6 Hz), 124.1 (q, J = 2.4 Hz), 124.0, 115.6 (q, J = 30.3 Hz), 111.1, 110.9, 40.0. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>):  $\delta$  -59.33. HRMS (ESI) m/z: (M+H)<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> 360.1206; Found 360.1215.

## HMBC spectra analysis of 3s and 3t



Synthetic procedure: To a glass tube (10 mL) equipped with a stir-bar was added trifluoromethylated quinol 1s and 1t (total 0.23 g, 0.6 mmol, the ratio of 1s/1t is nearly 1:1),  $[Ir(dtbbpy)(ppy)_2][PF_6]$  (16.5 mg, 0.018 mmol) and degassed with N<sub>2</sub>. Then *N*,*N*-dimethyl aniline 2a (380 µL, 1.5 mmol) and DCE (4 mL) were added under nitrogen atmosphere. The reaction mixture was stirred for 72 h under the irradiation of blue LED light (15 W). After the completion of the reaction as indicated by TLC, the solution was concentrated in vacuo. Then the residue was purified by silica gel column chromatography (PE/EA = 5/1) to afford product 3s (67.1 mg, 53%) and 3t (62.3 mg, 49%) separately.

## <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of compound 1s and 1t

## The ratio of **1s/1t** is nearly 1:1.











#### V. Crystal data of compound 3d

Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-K $\alpha$  ( $\lambda$  =0.71073 Å) radiation with a  $\omega$  scan technique. The crystal structures were solved bydirect method of SHELXS-97<sup>2</sup> and refined by full-matrix least-squares techniques usingthe SHELXL-97 program. Drawing of the compound shows ellipsoid contour at the 30% probability level. Non-hydrogen atoms were refined anisotropic. CCDC deposition number: 2159660 (**3d**). Data can be obtained free of charge viawww.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

The single crystal of 3d was cultivated from the mixed solvent of dichloromethane, ethyl acetate and petroleum ether with a volume ratio of 4:1:10 via solvent volatilization.





| Table S1. Crystallographic data and structural refinement for 3d. |                         |  |  |  |
|---|-------------------------|--|--|--|
| Empirical formula   | $C_{23}H_{24}F_3NO$     |  |  |  |
| Formula weight  | 387.43                  |  |  |  |
| Crystal system  | Triclinic               |  |  |  |
| Space group   | P - 1                   |  |  |  |
| a (Å)   | 8.8092(7)               |  |  |  |
| b (Å)   | 9.8034(8)               |  |  |  |
| c (Å)   | 12.4843(10)             |  |  |  |
| α (deg)   | 71.412(8)               |  |  |  |
| $\beta$ (deg)   | 74.369(7)               |  |  |  |
| γ (deg)   | 85.988(7)               |  |  |  |
| Volume (Å3)   | 983.96(15)              |  |  |  |
| Z   | 4                       |  |  |  |
| Calculated density (mg/m <sup>3</sup> )                           | 1.291                   |  |  |  |
| Absorption coefficient (mm-1)                                     | 0.096                   |  |  |  |
| F(000)  | 400.0                   |  |  |  |
| Theta range for data collection (deg)                             | 3.557 to 29.430         |  |  |  |
| Reflections collected/unique                                      | 4548/3012               |  |  |  |
| Goodness-of-fit on F2   | 1.048                   |  |  |  |
| Final R indices $[I > 2\sigma(I)]$                                | R1=0.0667, WR2 = 0.1749 |  |  |  |
| R indices (all data)  | R1= 0.0984, WR2 =0.2078 |  |  |  |

<sup>2.</sup> G. M. Sheldrick, SHELXS-97, Programs for X-ray crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.

|                  | e        | 2 3 0 2 3         |            |
|------------------|----------|-------------------|------------|
| O(1)-C(4)        | 1.354(3) | C(5)-N(1)-C(24)   | 115.28(18) |
| N(1)-C(5)        | 1.441(3) | C(5)-N(1)-C(25)   | 111.50(18) |
| N(1)-C(24)       | 1.465(3) | C(24)-N(1)-C(25)  | 110.5(2)   |
| N(1)-C(25)       | 1.470(3) | C(14)-C(3)-C(4)   | 119.2(2)   |
| C(3)-C(4)        | 1.430(3) | C(16)-C(3)-C(4)   | 121.8(2)   |
| C(3)-C(14)       | 1.421(3) | C(16)-C(3)-C(14)  | 118.97(19) |
| C(3)-C(16)       | 1.414(3) | O(1)-C(4)-C(3)    | 121.44(19) |
| C(4)-C(12)       | 1.371(3) | O(1)-C(4)-C(12)   | 116.99(18) |
| C(5)-C(8)        | 1.390(3) | C(12)-C(4)-C(3)   | 121.5(2)   |
| C(5)-C(10)       | 1.377(3) | C(8)-C(5)-N(1)    | 123.73(19) |
| C(6)-C(7)        | 1.390(3) | C(10)-C(5)-N(1)   | 118.42(17) |
| C(6)-C(9)        | 1.523(3) | C(10)-C(5)-C(8)   | 117.85(19) |
| C(6)-C(13)       | 1.400(3) | C(7)-C(6)-C(9)    | 119.06(18) |
| C(7)-C(10)       | 1.376(3) | C(7)-C(6)-C(13)   | 117.55(18) |
| C(8)-C(13)       | 1.395(3) | C(13)-C(6)-C(9)   | 123.38(17) |
| C(9)-C(12)       | 1.510(3) | C(10)-C(7)-C(6)   | 122.65(19) |
| C(11)-C(12)      | 1.400(3) | C(5)-C(8)-C(13)   | 122.44(19) |
| C(11)-C(15)      | 1.371(3) | C(12)-C(9)-C(6)   | 112.47(16) |
| C(13)-C(23)      | 1.528(3) | C(7)-C(10)-C(5)   | 120.35(18) |
| C(14)-C(15)      | 1.429(3) | C(15)-C(11)-C(12) | 122.7(2)   |
| C(14)-C(17)      | 1.419(3) | C(4)-C(12)-C(9)   | 120.9(2)   |
| C(15)-C(26)      | 1.487(4) | C(4)-C(12)-C(11)  | 118.25(19) |
| C(16)-C(18)      | 1.361(3) | C(11)-C(12)-C(9)  | 120.8(2)   |
| C(17)-C(20)      | 1.359(4) | C(6)-C(13)-C(23)  | 121.34(19) |
| C(18)-C(20)      | 1.397(4) | C(8)-C(13)-C(6)   | 119.13(18) |
| F(3)-C(26)       | 1.329(4) | C(8)-C(13)-C(23)  | 119.52(19) |
| F(2)-C(26)       | 1.339(4) | C(3)-C(14)-C(15)  | 117.96(19) |
| F(1)-C(26)       | 1.330(4) | C(17)-C(14)-C(3)  | 117.9(2)   |
| C(23)-C(27)      | 1.527(5) | C(17)-C(14)-C(15) | 124.1(2)   |
| C(23)-C(28)      | 1.479(4) | C(11)-C(15)-C(14) | 120.1(2)   |
|                  |          | C(11)-C(15)-C(26) | 119.5(2)   |
|                  |          | C(14)-C(15)-C(26) | 120.4(2)   |
|                  |          | C(18)-C(16)-C(3)  | 121.3(2)   |
|                  |          | C(20)-C(17)-C(14) | 121.1(2)   |
|                  |          | C(16)-C(18)-C(20) | 119.7(2)   |
|                  |          | C(17)-C(20)-C(18) | 121.0(2)   |
|                  |          | C(27)-C(23)-C(13) | 113.2(2)   |
|                  |          | C(28)-C(23)-C(13) | 111.2(2)   |
|                  |          | C(28)-C(23)-C(27) | 109.3(3)   |
| F(2)-C(26)-C(15) | 112.8(2) | F(3)-C(26)-C(15)  | 113.2(3)   |
| F(1)-C(26)-C(15) | 113.4(2) | F(3)-C(26)-F(2)   | 105.2(3)   |
| F(1)-C(26)-F(2)  | 105.8(3) | F(3)-C(26)-F(1)   | 105.8(3)   |

 Table S2. Bond lengths [Å] and angles [°] for 3d.





<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3a



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)





<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3b



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3c



40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 f1 (ppm)



<sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of compound 3d



65 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 65 80 75 70 65 60 55 50 45 40 35 30 25 20 15 1 fl (ppm)

<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3d



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)









20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)



## <sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3f



60 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 1 f1 (ppm)









<sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3g



.70 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 fl (ppm)





## <sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3h



165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 55 50 75 70 65 60 55 50 45 40 35 30 f1 (ppm)

<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3h





<sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3i



165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 fl (ppm)









<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3j













0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 f1 (ppm)



160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 25 30 25 20 f1 (ppm)













<sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3q









10 0 -10 -20 -30 -40 -50 -60 -70 -50 -90 -100 -110 -120 -130 -140 -150 -160 -170 -150 -190 -200 -210 f1 (ppm)

## <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of compound 1s and 1t







<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 3s





<sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3t







4.0 f1 (ppm) 2.5 .5 3.0 8.0 7.0 5.5 4.5 3.5 7.5 6.5 6.0 5.0 2.0 1.5 0.5 0.0 -0. 1.0

## <sup>13</sup>C spectrum (150 MHz, CDCl<sub>3</sub>) of compound 3u



160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 f1 (ppm)





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl (ppm)



**S53** 



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)









165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 3 f1 (ppm)

![](_page_54_Figure_3.jpeg)

![](_page_54_Figure_4.jpeg)

## <sup>1</sup>H spectrum (500 MHz, CDCl<sub>3</sub>) of compound 6

![](_page_55_Figure_1.jpeg)

<sup>13</sup>C spectrum (125 MHz, CDCl<sub>3</sub>) of compound 6

![](_page_55_Figure_3.jpeg)

## <sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 6

![](_page_56_Figure_1.jpeg)

![](_page_57_Figure_0.jpeg)

![](_page_57_Figure_1.jpeg)

<sup>19</sup>F spectrum (565 MHz, CDCl<sub>3</sub>) of compound 7

![](_page_57_Figure_3.jpeg)

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (spm)