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Supporting Information

# C(sp<sup>3</sup>)–H fluorosulfonylvinylation/aza-Michael addition approach to FSO<sub>2</sub>-functionalized tetrahydropyridines

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#### **Supplementary Methods**

#### I. General Information

Unless otherwise stated, all glassware was oven dried. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise indicated. Reactions were monitored using Thin Layer Chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV light as the visualizing agent and High Performance Liquid Chromatography (HPLC) with UV detection at 254 nm. For HPLC yields, UV response factors relative to an internal standard (diphenyl sulfide). Flash column chromatography was performed using silica gel 60 (200-300 mesh). HRMS experiments were carried out on a ThermoFisher LTQ Orbitrap XL. All <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on Bruker DRX-600 and AMX-400 instruments. Chemical shifts were given in parts per million (ppm,  $\delta$ ), referenced to the solvent peak of CDCl<sub>3</sub>, defined at  $\delta = 7.26$  (<sup>1</sup>H NMR), defined at  $\delta = 77.16$  (<sup>13</sup>C NMR). Coupling constants were quoted in Hz (*J*). <sup>1</sup>H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). The diastereomeric ratios were determined by <sup>1</sup>H NMR analysis. FSO<sub>2</sub>Cl was prepared according to the literature procedure.<sup>[1]</sup>

#### **II. Preparation of Propargyl Alcohols**

Table S1. Propargyl alcohols used in this study.



Propargyl alcohols **1a**, **1u**, **1v**, **1w**, **1x**, **1y**, **1z**, **1aa**, **1ab**, **1ac**, **1ad**, **1ae**, **1af**, **1ag**, **1ah**, **1aj**, **1ak** are known compounds and were synthesized according to the literature. <sup>[2,3,4,6,7]</sup> The preparation of new propargyl alcohols and their characterization datas provided as follows.

Table S2. Unsuccessful propargyl alcohols



Table S3. Unsuccessful reactions



Procedure A: Synthesis of propargyl alcohol 1ai<sup>[2,3,5]</sup>



**Step 1**: Isopentylmagnesium bromide (10 mL, 2.0 equiv, 1 M in THF) was added dropwise to benzaldehyde (537.0 mg, 5 mmol, 1.0 equiv) in anhydrous THF (10 mL) at -20 °C. The reaction was warmed up to room temperature and stirred for 6 h. The reaction mixture was treated with saturated aqueous NH<sub>4</sub>Cl and extracted with EtOAc for three times. The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. The resultant crude alcohol was directly subjected to the oxidation by Dess-Martin periodinane (3.03 g, 7 mmol, 1.4 equiv) in DCM (25 mL) for 4 h. After the reaction completion, the crude reaction mixture was filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding ketone.

**Step 2**: To a solution of the ketone (463.5 mg, 2.5 mmol, 1.0 equiv) in THF (2.5 mL) was slowly added Lithium diisopropylamide (1.63 mL, 1.3 equiv, 2 M in THF) at -78 °C under N<sub>2</sub> atmosphere. After stirring for 1 h, MeI (236  $\mu$ L, 3.75 mmol, 1.5 equiv) was added dropwise and continued stirring for 20 min. Then the solution was allowed to warm to room temperature and stirred for 6 h. The reaction is quenched with saturated aqueous NH<sub>4</sub>Cl, extracted with EtOAc for three times. The combined extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography to afford the 2,4-dimethyl-1-phenylpentan-1-one.

**Step 3**: Ethynylmagnesium bromide (2.4 mL, 1.2 equiv, 0.5 M in THF) was added to the2,4-dimethyl-1-phenylpentan-1-one (190.3 mg, 1 mmol, 1.0 equiv) in anhydrous THF (2 mL) at 0 °C. Then the reaction was warmed up to room temperature and stirred overnight. The reaction mixture was treated with saturated aqueous NH<sub>4</sub>Cl and extracted with EtOAc for three times. The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel to afford the corresponding propargyl alcohol **1ai**.

4,6-Dimethyl-3-phenylhept-1-yn-3-ol (1ai)



Flash chromatography: 5% EtOAc in petroleum ether.

151.4 mg, 70% yield, *d.r.* = 1.65:1, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 – 7.59 (m, 5.3H, two isomers), 7.38 – 7.34 (m, 5.3H, two isomers), 7.32 – 7.28 (m, 2.65H, two isomers), 2.68 (s, 2.65H, two isomers), 2.40 (s, 2.65H, two isomers), 2.04 – 1.98 (m, 1.65H, one isomer), 1.64 – 1.60 (m, 1H, one isomer), 1.58 – 1.49 (m, 3.3H, one isomer), 1.25 – 1.19 (m, 2H, one isomer), 1.13 – 1.07 (m, 2.65H, two isomers), 1.05 (d, J = 6.6 Hz, 3H, one isomer), 0.93 (d, J = 6.5 Hz, 4.95H, one isomer), 0.87 – 0.80 (m, 12.9H, two isomers), 0.70 (d, J = 6.5 Hz, 3H, one isomer).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  143.7 & 143.5 (two isomers), 128.08 &128.05 (two isomers), 127.84 & 127.82 (two isomers), 126.32 & 126.28 (two isomers), 85.60 & 85.56 (two isomers), 77.14 & 77.11 (two isomers), 75.04 & 75.01 (two isomers), 43.03 & 43.00 (two isomers), 40.9 & 40.4 (two isomers), 25.7 & 25.5 (two isomers), 24.4 & 24.3 (two isomers), 21.4 & 21.1 (two isomers), 15.0 & 14.4 (two isomers).

**HRMS-ESI** (m/z)  $[M+H]^+$  calcd for  $C_{15}H_{21}O^+$  427.1098, found 427.1093.

#### III. Synthesis of FSO<sub>2</sub>-Functionalized Tetrahydropyridines

#### **General Procedure B**



The product **3** was prepared according to the method reported by Zhao et al.<sup>[4]</sup> After this reaction, the mixture was treated with cold saturated aqueous NaHCO<sub>3</sub>, the mixture was extracted with EtOAc for three times to a 10 mL tube and concentrated in *vacuo*. Then aniline (0.36 mmol, 1.8 equiv) and AcOH (60  $\mu$ L) were added, while this concentration had not been purified. The reaction mixture was stirred at 50 °C in oil bath for 12 h. After the reaction completion, the resulting mixture was diluted with 0.5 mL DCM and then directly purified by flash column chromatography on silica gel to afford the FSO<sub>2</sub>-THP **5**.

#### **Gram-Scale Reaction**

Typical procedure for gram-scale synthesis for 5a:



Step 1 was progressed according to the method mentioned above on 10mmol scale.<sup>[4]</sup> The reaction mixture was stirred under 35 W Blue LEDs at room temperature for 2 h. After treated with saturated aqueous NaHCO<sub>3</sub>, the mixture was extracted with EtOAc for three times to a 25 mL reaction flask and concentrated in *vacuo*. Then aniline (**4a**, 18 mmol, 1.65 mL, 1.8 equiv) and AcOH (3 mL) were added, while this concentration had not been purified. The reaction mixture was stirred at 50 °C in oil bath for 12 h. After the reaction completion, the resulting mixture was diluted with 25 mL DCM and then directly purified by flash column chromatography on silica gel to afford the FSO<sub>2</sub>-THP **5a** (3.27 g, 91%).

#### **Characterization Data**

(3,3-Dimethyl-6-phenyl-1-(aryl)-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5a)

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

61.8 mg, 86% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.37 (d, J = 7.3 Hz, 2H), 7.23 – 7.14 (m, 3H), 7.07 (t, J = 7.8 Hz, 2H), 6.94 (d, J = 7.9 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 5.48 (t, J = 3.7 Hz, 1H), 4.29 (d, J = 9.8 Hz, 1H), 3.79 (dd, J = 14.7, 10.0 Hz, 1H), 3.54 (dd, J = 14.6, 5.0 Hz, 1H), 2.13 (dd, J = 19.2, 4.2 Hz, 1H), 2.06 (dd, J = 19.2, 3.0 Hz, 1H), 1.09 (s, 3H), 0.90 (s, 3H). <sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 147.6, 138.9, 138.3, 128.7, 128.4, 127.7, 127.0, 121.6, 121.3, 110.7, 64.9, 50.5 (d, J = 13.0 Hz), 35.9 (d, J = 0.9 Hz), 35.1, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.4.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>23</sub>FNO<sub>2</sub>S<sup>+</sup> 360.1428, found 360.1413.

Methyl 4-(2-((Fluorosulfonyl)methyl)-3,3-dimethyl-6-phenyl-3,4-dihydropyridin-1(2H)-yl)benzoate (5b)



Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-methoxycarbonyl aniline.

Flash chromatography: 10 to 20% EtOAc in petroleum ether.

74.3 mg, 89% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 6.7 Hz, 2H), 7.23 – 7.16 (m, 3H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.58 (t, *J* = 3.7 Hz, 1H), 4.35 (d, *J* = 9.8 Hz, 1H), 3.81 (s, 3H), 3.78 (dd, *J* = 14.8, 10.1 Hz, 1H), 3.56 (dd, *J* = 14.6, 4.5 Hz, 1H), 2.15 (dd, *J* = 19.3, 4.2 Hz, 1H), 2.08 (dd, *J* = 19.4, 3.1 Hz, 1H), 1.11 (s, 3H), 0.87 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.0, 151.5, 138.2, 137.7, 130.7, 128.6, 128.0, 126.8, 122.6, 120.5, 112.5, 64.5, 51.9, 50.1 (d, *J* = 13.6 Hz), 36.2, 35.1, 27.8, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.2.

HRMS-ESI (m/z) [M+Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>24</sub>FNNaO<sub>4</sub>S<sup>+</sup> 440.1302, found 440.1280.

(1-(4-Cyanophenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5c)



Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-aminobenzonitrile. Flash chromatography: 10 to 20% EtOAc in petroleum ether.

48.4 mg, 63% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.31 (m, 4H), 7.26 – 7.20 (m, 3H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.63 (t, *J* = 3.7 Hz, 1H), 4.31 (d, *J* = 9.6 Hz, 1H), 3.77 (dd, *J* = 14.8, 10.1 Hz, 1H), 3.58 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.20 – 2.06 (m, 2H), 1.12 (s, 3H), 0.86 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 151.1, 137.7, 137.2, 133.0, 128.8, 128.2, 126.6, 121.0, 119.4, 113.5, 103.7, 64.5, 49.89 (d, *J* = 13.9 Hz), 36.3, 35.0, 27.7, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.2.

 $\label{eq:HRMS-ESI} \mbox{(m/z)} \mbox{[M+Na]}^+ \mbox{ calcd for } C_{21} \mbox{H}_{21} \mbox{FN}_2 \mbox{NaO}_2 \mbox{S}^+ \mbox{407.1200, found } \mbox{407.1186.}$ 

(1-(4-Acetylphenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5d)

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-aminoacetophenone.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

40.1 mg, 50% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 6.8 Hz, 2H), 7.21 (d, J = 7.5 Hz, 3H), 6.95 (d, J = 8.1 Hz, 2H), 5.59 (m, 1H), 4.36 (d, J = 9.8 Hz, 1H), 3.78 (dd, J = 14.6, 10.1 Hz, 1H), 3.57 (dd, J = 14.6, 3.6 Hz, 1H), 2.45 (s, 3H), 2.19 – 2.07 (m, 2H), 1.11 (s, 3H), 0.88 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 196.8, 151.7, 138.1, 137.7, 130.1, 129.6, 128.7, 128.0, 126.7, 120.4, 112.8, 64.5, 50.1 (d, *J* = 13.7 Hz), 36.2, 35.1, 27.8, 27.6, 26.3.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.2.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{22}H_{25}FNO_3S^+$  402.1534, found 402.1543.

(3,3-Dimethyl-1-(4-nitrophenyl)-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5e)



Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and p-nitroaniline.

Flash chromatography: 10 to 20% EtOAc in petroleum ether.

31.5 mg, 39% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, J = 9.3 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.25 – 7.20 (m, 3H), 6.96 (d, J = 8.8 Hz, 2H), 5.67 (t, J = 3.7 Hz, 1H), 4.37 (d, J = 9.7 Hz, 1H), 3.78 (dd, J = 14.9, 10.1 Hz, 1H), 3.59 (dd, J = 14.8, 3.5 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.14 (s, 3H), 0.88 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 152.9, 141.2, 137.7, 137.1, 128.9, 128.4, 126.7, 125.1, 120.2, 114.1, 64.6, 49.9 (d, *J* = 14.3 Hz), 36.4, 35.1, 27.68, 27.65.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.1.

HRMS-ESI (m/z) [M+Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>21</sub>FN<sub>2</sub>NaO<sub>4</sub>S<sup>+</sup> 427.1098, found 427.1093.

(1-(4-Iodophenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5f)

SO<sub>2</sub>F

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and p-iodoaniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

81.5 mg, 84% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>) *δ* 7.37 – 7.32 (m, 4H), 7.24 – 7.18 (m, 3H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.51 (t, *J* = 3.7 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.76 (dd, *J* = 14.8, 10.1 Hz, 1H), 3.54 (dd, *J* = 14.7, 4.1 Hz, 1H), 2.16 – 2.03 (m, 2H), 1.09 (s, 3H), 0.88 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 147.4, 138.3, 137.8, 137.6, 128.6, 127.9, 126.9, 123.5, 111.5, 84.3, 64.9, 50.30 (d, J = 13.1 Hz), 35.99 (d, J = 0.9 Hz), 35.0, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.4.

 $\label{eq:HRMS-ESI} \mbox{(m/z)} \mbox{[M+Na]}^+ \mbox{ calcd for } C_{20} \mbox{H}_{21} \mbox{FINNaO}_2 \mbox{S}^+ \mbox{508.0214, found 508.0197.}$ 

(1-(4-Bromophenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5g)

Br SO<sub>2</sub>F

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and p-bromoaniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

61.4 mg, 70% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.33 (m, 2H), 7.24 – 7.19 (m, 3H), 7.17 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.51 (t, *J* = 3.6 Hz, 1H), 4.21 (d, *J* = 9.7 Hz, 1H), 3.76 (dd, *J* = 14.7, 10.1 Hz, 1H), 3.54 (dd, *J* = 14.7, 4.0 Hz, 1H), 2.17 – 2.04 (m, 2H), 1.09 (s, 3H), 0.89 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 146.7, 138.4, 137.8, 131.7, 128.5, 127.9, 126.9, 123.1, 114.0, 111.3, 65.0, 50.3 (d, *J* = 13.2 Hz), 36.0 (d, *J* = 1.0 Hz), 35.0, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.4.

HRMS-ESI (m/z) [M+K]<sup>+</sup> calcd for C<sub>20</sub>H<sub>21</sub>BrFNKO<sub>2</sub>S<sup>+</sup> 476.0092, found 476.0095.

(1-(4-Chlorophenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5h)



Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and p-chloroaniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

72.5 mg, 92% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (d, *J* = 6.8 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.50 (t, *J* = 3.5 Hz, 1H), 4.20 (d, *J* = 9.8 Hz, 1H), 3.76 (dd, *J* = 14.7, 10.1 Hz, 1H), 3.54 (dd, *J* = 14.6, 4.3 Hz, 1H), 2.15 – 2.04 (m, 2H), 1.09 (s, 3H), 0.89 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 146.3, 138.5, 137.8, 128.8, 128.5, 127.9, 126.93, 126.5, 122.7, 111.2, 65.1, 50.4 (d, *J* = 13.3 Hz), 36.0 (d, *J* = 0.9 Hz), 35.1, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.4.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{20}H_{22}CIFNO_2S^+$  394.1038, found 394.1040.

(1-(4-Methoxyphenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5i)

MeO SO<sub>2</sub>F Ph

Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and *p*-methoxyaniline. Flash chromatography: 5 to 10% EtOAc in petroleum ether.

65.4 mg, 84% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J* = 7.1 Hz, 2H), 7.23 – 7.14 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 9.1 Hz, 2H), 5.45 – 5.40 (m, 1H), 4.19 (d, *J* = 9.5 Hz, 1H), 3.79 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.68 (s, 3H), 3.54 (dd, *J* = 14.6, 3.8 Hz, 1H), 2.16 – 2.03 (m, 2H), 1.09 (s, 3H), 0.94 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 154.4, 141.3, 139.2, 138.4, 128.3, 127.6, 127.1, 123.0, 114.0, 109.4, 65.4, 55.39, 50.8 (d, *J* = 12.6 Hz), 35.6 (d, *J* = 0.7 Hz), 35.0, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.7.

**HRMS-ESI** (m/z)  $[M+Na]^+$  calcd for  $C_{21}H_{24}FNNaO_3S^+$  412.1353, found 412.1351.

(1-(4-Hydroxyphenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5j)



Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-amino-phenol.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

30.0 mg, 40% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, J = 7.4 Hz, 2H), 7.21 – 7.13 (m, 3H), 6.84 (d, J = 8.3 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 5.42 – 5.39 (m, 1H), 4.40 (s, 1H), 4.15 (d, J = 9.8 Hz, 1H), 3.77 (dd, J = 14.6, 10.0 Hz, 1H), 3.53 (dd, J = 14.6, 4.3 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.07 (s, 3H), 0.92 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 150.1, 141.5, 139.2, 138.4, 128.3, 127.6, 127.1, 123.2, 115.6, 109.5, 65.4, 50.8 (d, *J* = 12.6 Hz), 35.7, 35.1, 28.2, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.7.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>23</sub>FNO<sub>3</sub>S<sup>+</sup> 376.1377, found 376.1375.

(1-(4-(Dimethylamino)phenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5k)

Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-amino-*N*,*N*-dimethylaniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

49.9 mg, 62% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J* = 6.5 Hz, 2H), 7.23 – 7.09 (m, 3H), 6.87 (d, *J* = 6.8 Hz, 2H), 6.63 – 6.42 (m, 2H), 5.42 – 5.33 (m, 1H), 4.16 (d, *J* = 9.3 Hz, 1H), 3.83 – 3.73 (m, 1H), 3.52 (d, *J* = 12.2 Hz, 1H), 2.81 (s, 6H), 2.16 – 2.00 (m, 2H), 1.07 (s, 3H), 0.94 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 145.4, 139.2, 138.6, 128.1, 127.3, 127.0, 122.8, 113.5, 113.4, 108.6, 65.2, 50.78 (d, *J* = 12.0 Hz), 41.1, 35.3, 35.0, 28.1, 27.4.

<sup>19</sup>**F** NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.7.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>28</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> 403.1850, found 403.1857.

(3,3-Dimethyl-6-phenyl-1-(p-tolyl)-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (51)



Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and p-toluidine.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

67.2 mg, 90% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) *δ* 7.38 (d, *J* = 7.3 Hz, 2H), 7.23 – 7.14 (m, 3H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 5.45 (t, *J* = 3.6 Hz, 1H), 4.25 (d, *J* = 9.8 Hz, 1H), 3.78 (dd, *J* = 14.7, 10.0 Hz, 1H), 3.54 (dd, *J* = 14.6, 4.5 Hz, 1H), 2.17 (s, 3H), 2.12 (dd, *J* = 19.1, 4.2 Hz, 1H), 2.06 (dd, *J* = 19.1, 2.7 Hz, 1H), 1.08 (s, 3H), 0.91 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 145.2, 139.0, 138.5, 130.6, 129.3, 128.3, 127.6, 127.0, 121.5, 110.1, 65.0, 50.6 (d, *J* = 12.7 Hz), 35.8 (d, *J* = 1.0 Hz), 35.1, 28.1, 27.6, 20.7.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.5.

HRMS-ESI (m/z) [M+K]<sup>+</sup> calcd for C<sub>21</sub>H<sub>24</sub>FKNO<sub>2</sub>S<sup>+</sup> 412.1143, found 412.1125.

(1-(4-Ethylphenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5m)



Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-aminoethylbenzene.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

56.6 mg, 73% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) *δ* 7.42 – 7.38 (m, 2H), 7.23 – 7.15 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.48 – 5.42 (m, 1H), 4.27 (d, *J* = 9.3 Hz, 1H), 3.79 (dd, *J* = 14.4, 10.2 Hz, 1H), 3.55 (dd, *J* = 14.6, 4.3 Hz, 1H), 2.49 (q, *J* = 7.6 Hz, 2H), 2.16 – 2.04 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.09 (s, 3H), 0.93 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 145.3, 139.0, 138.5, 137.0, 128.3, 128.0, 127.6, 127.0, 121.5, 110.1, 65.0, 50.6 (d, J = 12.4 Hz), 35.7, 35.1 (d, J = 2.2 Hz), 28.04, 27.96, 27.6, 15.4.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.5.

 $\label{eq:HRMS-ESI} \mbox{(m/z)} \mbox{[M+Na]}^+ \mbox{ calcd for } C_{22} H_{26} \mbox{FNNaO}_2 \mbox{S}^+ \mbox{410.1560, found } \mbox{410.1552.}$ 

(1-(4-(tert-Butyl)phenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5n)

SO<sub>2</sub>F

Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-(*tert*-butyl) aniline. Flash chromatography: 5 to 10% EtOAc in petroleum ether.

79.8 mg, 96% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J* = 7.3 Hz, 2H), 7.21 - 7.16 (m, 3H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.44 (t, *J* = 3.6 Hz, 1H), 4.26 (d, *J* = 9.8 Hz, 1H), 3.78 (dd, *J* = 14.7, 10.0 Hz, 1H), 3.53 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.12 (dd, *J* = 19.1, 4.1 Hz, 1H), 2.05 (dd, *J* = 19.1, 2.7 Hz, 1H), 1.20 (s, 9H), 1.08 (s, 3H), 0.91 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.0, 143.9, 139.0, 138.6, 128.3, 127.5, 127.0, 125.5, 121.1, 110.1, 64.9, 50.6 (d, *J* = 10.1, 2.7 Hz, 14.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 12.1, 13.1, 13.1, 13.1, 14.

12.7 Hz), 35.7, 35.1, 34.1, 31.5, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.4.

HRMS-ESI (m/z) [M+Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>30</sub>FNNaO<sub>2</sub>S<sup>+</sup> 438.1873, found 438.1856.

(1-(3,5-Dimethylphenyl)-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (50)

SO<sub>2</sub>F

Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 3,5-dimethylaminoaniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

61.2 mg, 79% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, J = 6.1 Hz, 2H), 7.20 (t, J = 6.9 Hz, 2H), 7.18 – 7.14 (m, 1H), 6.56 (s, 2H), 6.44 (s, 1H), 5.50 – 5.34 (m, 1H), 4.28 (d, J = 8.2 Hz, 1H), 3.84 – 3.74 (m, 1H), 3.54 (d, J = 10.9 Hz, 1H), 2.12 (s, 6H), 2.10 (s, 1H), 2.09 – 2.03 (m, 1H), 1.09 (s, 3H), 0.93 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 147.4, 139.1, 138.5, 137.9, 128.2, 127.4, 126.8, 123.1, 119.4, 110.2, 64.6, 50.5 (d, *J* = 16.7 Hz), 35.7 (d, *J* = 0.7 Hz), 35.0, 28.0, 27.5, 21.5.

<sup>19</sup>**F** NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.5.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>27</sub>FNO<sub>2</sub>S<sup>+</sup> 388.1741, found 388.1748.

(3,3-Dimethyl-6-phenyl-1-(o-tolyl)-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5p)

SO<sub>2</sub>F

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and o-toluidine.

Flash chromatography: 5 to 10% EtOAc in petroleum ether. **5p** was found to be too sensitive to obtain a clean NMR. 32.1 mg, 43% yield, *d.r.* = 2.2:1, pale yellow oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 (d, J = 7.2 Hz, 2.2H, one isomer), 7.16 – 7.09 (m, 15H, two isomers), 7.02 – 6.99 (m, 4.2H, two isomers), 6.96 – 6.91 (m, 4.2H, two isomers), 6.88 – 6.82 (m, 2.2H, one isomer), 6.74 (d, J = 7.3 Hz, 1H, one isomer), 5.38 – 5.34 (m, 1H, one isomer), 5.03 – 4.98 (m, 2.2H, one isomer), 4.01 (d, J = 15.4 Hz, 1H, one isomer), 3.97 – 3.86 (m, 6.4H, two isomers), 3.52 (d, J = 14.9 Hz, 2.2H, one isomer), 2.52 (s, 3H, one isomer), 2.33 (s, 6.6H, one isomer), 2.26 – 2.16 (m, 4.4H, one isomer), 2.12 – 2.03 (m, 2H, one isomer), 1.28 (s, 6.6H, one isomer), 1.15 (s, 6.6H, one isomer), 1.14 (s, 3H, one isomer), 1.02 (s, 3H, one isomer).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 146.0 & 143.8 (two isomers), 138.9 & 138.5 (two isomers), 132.9 & 132.1 (two isomers), 131.8 & 131.7 (two isomers), 128.2 & 128.0 (two isomers), 127.7 & 127.6 (two isomers), 127.3 & 127.0 (two isomers),

126.8 & 126.7 (two isomers), 125.8 & 124.81 (two isomers), 124.79 & 123.8 (two isomers), 63.5 & 62.9 (two isomers), 57.2 (d, *J* = 13.5 Hz) & 52.4 (d, *J* = 14.0 Hz) (two isomers), 35.49 & 34.48 (two isomers), 33.9 & 33.7 (two isomers), 28.2 & 28.1 (two isomers), 27.5 & 27.1 (two isomers), 20.4 & 18.9 (two isomers).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ 64.8 & 58.4 (two isomers).

HRMS-ESI (m/z) [M+Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>24</sub>FNNaO<sub>2</sub>S<sup>+</sup> 396.1404, found 396.1391.

#### (3,3-Dimethyl-1-(naphthalen-1-yl)-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5q)

Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 1-amino-naphthalene. Flash chromatography: 5 to 10% EtOAc in petroleum ether. **5q** was found to be too sensitive to obtain a clean NMR. 59.0 mg, 72% yield, d.r. = 2.8:1, pale yellow oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.44 (d, *J* = 8.5 Hz, 2.8H, one isomer), 8.36 (d, *J* = 8.4 Hz, 1H, one isomer), 7.83 (d, *J* = 8.1 Hz, 1H, one isomer), 7.75 (d, *J* = 8.1 Hz, 2.8H, one isomer), 7.65 (t, *J* = 7.2 Hz, 1H, one isomer), 7.54 – 7.50 (m, 3.8H, two isomers), 7.48 – 7.44 (m, 3.8H, two isomers), 7.42 – 7.35 (m, 4.8H, two isomers), 7.30 – 7.25 (m, 2H, one isomer), 7.24 – 7.20 (m, 5.6H, one isomer), 7.17 – 7.07 (m, 7.6H, two isomers), 7.03 – 6.98 (m, 8.4H, one isomer), 6.95 (d, *J* = 7.5 Hz, 1H, one isomer), 5.52 (t, *J* = 3.7 Hz, 1H, one isomer), 5.18 – 5.10 (m, 2.8H, one isomer), 4.25 – 4.16 (m, 4.8H, two isomers), 4.01 – 3.88 (m, 3.8H, two isomers), 3.65 – 3.55 (m, 2.8H, one isomer), 2.36 – 2.14 (m, 7.6H, two isomers), 1.44 (s, 8.4H, one isomer), 1.18 (s, 8.4H, one isomer), 1.11 (s, 3H, one isomer), 1.00 (s, 3H, one isomer).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  143.4 & 142.6 (two isomers), 141.9 & 141.8 (two isomers), 139.0 & 138.6 (two isomers), 135.04 & 135.01 (two isomers), 129.6 & 128.9 (two isomers), 128.8 & 128.3 (two isomers), 127.9 & 127.8 (two isomers), 127.3 & 126.6 (two isomers), 126.2 & 126.1 (two isomers), 126.0 & 125.79 (two isomers), 125.77 & 125.51 (two isomers), 125.46 & 125.1 (two isomers), 124.4 & 124.3 (two isomers), 123.8 & 123.8 (two isomers), 123.62 & 123.60 (two isomers), 109.8 & 104.4 (two isomers), 64.3 & 64.2 (two isomers), 57.5 (d, *J* = 13.7 Hz) & 52.6 (d, *J* = 14.2 Hz) (two isomers), 35.9 & 34.8 (two isomers), 34.7 & 34.0 (two isomers), 28.4 & 28.3 (two isomers), 27.6 & 27.5 (two isomers).

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ 63.5 & 58.1 (two isomers).

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>25</sub>FNO<sub>2</sub>S<sup>+</sup> 410.1585, found 410.1589.

#### (3,3-Dimethyl-1-(4-morpholinophenyl)-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5r)

SO<sub>2</sub>F

Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-morpholino-4-yl-phenylamine.

Flash chromatography: 20 to 40% EtOAc in petroleum ether.

72.0 mg, 81% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 7.6 Hz, 2H), 7.24 – 7.15 (m, 3H), 6.88 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 7.5 Hz, 2H), 5.41 (t, J = 3.5 Hz, 1H), 4.18 (d, J = 9.8 Hz, 1H), 3.85 – 3.77 (m, 5H), 3.53 (dd, J = 14.6, 4.4 Hz, 1H), 3.06 – 3.00 (m, 4H), 2.16 – 2.05 (m, 2H), 1.08 (s, 3H), 0.92 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  141.0, 139.1, 138.5, 128.3, 127.5, 127.1, 122.6, 116.36, 109.5, 67.0, 65.2, 50.7 (d, J = 12.4 Hz), 50.0, 35.6, 35.1, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.7.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{24}H_{30}FN_2O_3S^+$  445.1956, found 445.1962.

(3,3-Dimethyl-1-(4-(3-oxomorpholino)phenyl)-6-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5s)



Following **General Procedure B** on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and 4-(4-aminophenyl)-3-morpholinone.

Flash chromatography: 20 to 40% EtOAc in petroleum ether.

52.3 mg, 57% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d, J = 7.0 Hz, 2H), 7.22 – 7.15 (m, 3H), 7.05 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 5.49 (t, J = 3.6 Hz, 1H), 4.28 – 4.25 (m, 3H), 3.95 – 3.91 (m, 2H), 3.77 (dd, J = 14.7, 10.0 Hz, 1H), 3.67 – 3.57 (m, 2H), 3.54 (dd, J = 14.6, 4.0 Hz, 1H), 2.17 – 2.00 (m, 2H), 1.08 (s, 3H), 0.91 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 166.6, 146.1, 138.6, 138.1, 134.7, 128.5, 127.8, 126.9, 125.4, 121.8, 111.2, 68.6, 64.9, 64.2, 50.4 (d, J = 13.0 Hz), 49.6, 35.9, 35.1, 27.9, 27.7.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.4.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{24}H_{28}FN_2O_4S^+$  459.1748, found 459.1753.

(3,3-Dimethyl-6-phenyl-3,4-dihydro-2*H*-[1,3'-bipyridin]-2-yl)methanesulfonyl fluoride (5t)

SO Ph

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-phenylhept-1-yn-3-ol and pyridin-3-ylamine.

Flash chromatography: 10 to 20% EtOAc in petroleum ether.

20.2 mg, 28% yield, pale yellow solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 – 8.14 (m, 1H), 8.04 (d, *J* = 4.6 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.16 (m, 3H), 7.07 (dd, *J* = 8.4, 4.7 Hz, 1H), 5.55 (t, *J* = 3.6 Hz, 1H), 4.21 (d, *J* = 10.0 Hz, 1H), 3.79 (dd, *J* = 14.8, 10.1 Hz, 1H), 3.57 (dd, *J* = 14.7, 4.3 Hz, 1H), 2.19 – 2.05 (m, 2H), 1.10 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 143.9, 143.2, 141.9, 137.9, 137.1, 128.7, 128.24, 128.23, 127.0, 123.6, 111.8, 65.0, 50.2
(d, J = 13.7 Hz), 36.0 (d, J = 0.8 Hz), 35.0, 27.8, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.4.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>21</sub>FN<sub>2</sub>NaO<sub>2</sub>S<sup>+</sup> 383.1200, found 383.1195.

(6-(3-Bromophenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5u)



Following General Procedure B on 0.2 mmol scale with 3-(3-bromophenyl)-6-methylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

66.6 mg, 76% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 – 7.60 (m, 1H), 7.31 – 7.27 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.10 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.50 (t, *J* = 3.7 Hz, 1H), 4.27 (d, *J* = 9.4 Hz, 1H), 3.74 (dd, *J* = 14.7, 10.2 Hz, 1H), 3.58 – 3.52 (m, 1H), 2.17 – 2.01 (m, 2H), 1.08 (s, 3H), 0.89 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.2, 140.6, 137.8, 130.6, 129.9, 129.8, 128.9, 125.7, 122.5, 121.7, 121.6, 111.7, 64.9, 50.4 (d, *J* = 12.9 Hz), 35.9, 35.1, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.7.

HRMS-ESI (m/z)  $[M+K]^+$  calcd for  $C_{20}H_{21}BrFNKO_2S^+$  476.0092, found 476.0082.

(6-(4-Chlorophenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5v)



CI

Following General Procedure B on 0.2 mmol scale with 3-(4-chlorophenyl)-6-methylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

64.6 mg, 82% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 7.09 (t, J = 7.9 Hz, 2H), 6.92 (d, J = 7.8 Hz, 2H), 6.82 (t, J = 7.3 Hz, 1H), 5.47 (t, J = 3.2 Hz, 1H), 4.28 (d, J = 9.8 Hz, 1H), 3.76 (dd, J = 14.6, 10.2 Hz, 1H), 3.55 (dd, J = 14.6, 3.2 Hz, 1H), 2.16 - 2.03 (m, 2H), 1.09 (s, 3H), 0.90 (s, 3H)

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 147.3, 137.9, 136.8, 133.3, 128.9, 128.6, 128.2, 121.7, 121.6, 111.0, 64.9, 50.4 (d, *J* = 12.9 Hz), 35.9 (d, *J* = 0.9 Hz), 35.1, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) *δ* 60.8.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>22</sub>ClFNO<sub>2</sub>S<sup>+</sup> 394.1038, found 394.1043.

(6-(4-Fluorophenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5w)

SO<sub>2</sub>F

Following **General Procedure B** on 0.2 mmol scale with 3-(4-fluorophenyl)-6-methylhept-1-yn-3-ol and aniline. Flash chromatography: 5 to 10% EtOAc in petroleum ether.

52.1 mg, 69% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>) *δ* 7.35 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.89 (t, *J* = 8.7 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.43 (t, *J* = 3.6 Hz, 1H), 4.28 (d, *J* = 9.9 Hz, 1H), 3.79 (dd, *J* = 14.6, 10.2 Hz, 1H), 3.56 (dd, *J* = 14.6, 3.4 Hz, 1H), 2.23 – 1.98 (m, 2H), 1.09 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ 162.3 (d, J = 246.7 Hz), 147.4, 138.0, 134.3 (d, J = 3.1 Hz), 128.8, 128.6 (d, J = 8.0 Hz), 121.7, 121.5, 115.3 (d, J = 21.5 Hz), 110.3, 64.9, 50.4 (d, J = 12.8 Hz), 35.8 (d, J = 1.0 Hz), 35.1, 28.0, 27.6.

 $^{19}\mathrm{F}$  NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.7, -114.5.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{20}H_{22}F_2NO_2S^+$  378.1334, found 378.1324.

Methyl 4-(6-((fluorosulfonyl)methyl)-5,5-dimethyl-1-phenyl-1,4,5,6-tetrahydropyridin-2-yl)benzoate (5x)



Following General Procedure B on 0.2 mmol scale with methyl 4-(3-hydroxy-6-methylhept-1-yn-3-yl) benzoate and aniline.

Flash chromatography: 10 to 20% EtOAc in petroleum ether.

46.8 mg, 56% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.07 (t, J = 7.9 Hz, 2H), 6.91 (d, J = 7.8 Hz, 2H), 6.80 (t, J = 7.3 Hz, 1H), 5.59 (t, J = 3.7 Hz, 1H), 4.29 (d, J = 9.8 Hz, 1H), 3.85 (s, 3H), 3.75 (dd, J = 14.7, 10.2 Hz, 1H), 3.56 (dd, J = 14.6, 3.4 Hz, 1H), 2.20 – 2.06 (m, 2H), 1.09 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.0, 147.3, 142.9, 138.3, 129.7, 129.2, 128.9, 126.9, 121.7, 121.5, 112.5, 64.9, 52.1, 50.5 (d, *J* = 13.0 Hz), 35.8 (d, *J* = 0.6 Hz), 35.1, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.7.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>25</sub>FNO<sub>4</sub>S<sup>+</sup> 418.1483, found 418.1473.

(3,3-Dimethyl-1-phenyl-6-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5y)

SO<sub>2</sub>F

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-(4-(trifluoromethyl)phenyl)hept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

55.6 mg, 65% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.12 – 7.07 (m, 2H), 6.93 (d, J = 7.8 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 5.58 (t, J = 3.7 Hz, 1H), 4.30 (d, J = 9.4 Hz, 1H), 3.74 (dd, J = 14.6, 10.3 Hz, 1H), 3.60 – 3.55 (m, 1H), 2.19 – 2.07 (m, 2H), 1.10 (s, 3H), 0.91 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 147.2, 141.9, 137.9, 129.5 (q, *J* = 32.6 Hz), 129.0, 127.1, 125.4 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 273.2 Hz), 121.8, 121.6, 121.5, 112.6, 64.9, 50.4 (d, *J* = 13.0 Hz), 35.8 (d, *J* = 1.0 Hz), 35.1, 28.0, 27.6.

 $^{19}\mathrm{F}$  NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.9, -62.5.

 $\label{eq:HRMS-ESI} \mbox{(m/z)} \mbox{[M+H]}^+ \mbox{ calcd for } C_{21} \mbox{H}_{22} \mbox{F}_4 \mbox{NO}_2 \mbox{S}^+ \mbox{428.1302, found } \mbox{428.1310.}$ 

(6-(4-Cyanophenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5z)

SOAF

NC

Following **General Procedure B** on 0.2 mmol scale with 4-(3-hydroxy-6-methylhept-1-yn-3-yl)benzonitrile and aniline. Flash chromatography: 10 to 20% EtOAc in petroleum ether.

47.7 mg, 62% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) *δ* 7.50 – 7.45 (m, 4H), 7.09 (t, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 5.62 (t, *J* = 3.8 Hz, 1H), 4.29 (d, *J* = 9.3 Hz, 1H), 3.71 (dd, *J* = 14.6, 10.4 Hz, 1H), 3.57 (dd, *J* = 14.6, 1.9 Hz, 1H), 2.20 – 2.07 (m, 2H), 1.10 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 147.0, 143.0, 137.7, 132.2, 129.0, 127.5, 122.0, 121.5, 119.0, 113.4, 111.0, 64.9, 50.3 (d, *J* = 13.0 Hz), 35.8 (d, *J* = 0.8 Hz), 35.1, 28.0, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) *δ* 61.1.

 $\label{eq:HRMS-ESI} \textbf{(m/z)} \; [M+Na]^{+} \; calcd \; for \; C_{21}H_{21}FN_2NaO_2S^{+} \; 407.1200, \; found \; 407.1208.$ 

(6-(4-Methoxyphenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5aa)

SO<sub>2</sub>F

MeO

Following General Procedure B on 0.2 mmol scale with 3-(4-methoxyphenyl)-6-methylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

46.7 mg, 60% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d, J = 8.6 Hz, 2H), 7.09 (t, J = 7.8 Hz, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.80 (t, J = 7.3 Hz, 2H), 6.74 (d, J = 8.6 Hz, 1H), 5.44 – 5.33 (m, 1H), 4.28 (d, J = 9.8 Hz, 1H), 3.81 (dd, J = 14.5, 10.1 Hz, 1H), 3.73 (s, 3H), 3.55 (dd, J = 14.6, 4.4 Hz, 1H), 2.15 – 2.01 (m, 2H), 1.08 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 159.2, 147.8, 138.4, 130.8, 128.7, 128.1, 121.7, 121.2, 113.8, 109.1, 65.0, 55.3, 50.5 (d, *J* = 12.8 Hz), 35.9, 35.1, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.5.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>25</sub>FNO<sub>3</sub>S<sup>+</sup> 390.1534, found 390.1528.

#### (6-(4-(tert-Butyl)phenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5ab)



Following **General Procedure B** on 0.2 mmol scale with 3-(4-(*tert*-butyl)phenyl)-6-methylhept-1-yn-3-ol and aniline. Flash chromatography: 5 to 10% EtOAc in petroleum ether.

54.0 mg, 65% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.85 – 6.80 (m, 1H), 5.46 (s, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 3.79 (dd, *J* = 14.3, 10.1 Hz, 1H), 3.53 (dd, *J* = 14.5, 4.7 Hz, 1H), 2.19 – 2.06 (m, 2H), 1.26 (s, 9H), 1.09 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 150.7, 147.8, 135.3, 128.7, 126.5, 125.3, 121.6, 121.2, 110.3, 100.1, 65.0, 50.6 (d, J = 13.2 Hz), 35.9, 35.2, 34.6, 31.4, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.3.

**HRMS-ESI** (m/z)  $[M+H]^+$  calcd for  $C_{24}H_{31}FNO_2S^+$  416.2054, found 416.2046.

(3,3-Dimethyl-1-phenyl-6-(m-tolyl)-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5ac)

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-(m-tolyl) hept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

61.3 mg, 82% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 – 7.23 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.10 – 7.05 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 5.47 (t, *J* = 3.6 Hz, 1H), 4.29 (d, *J* = 9.3 Hz, 1H), 3.79 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.54 (dd, *J* = 14.7, 4.3 Hz, 1H), 2.27 (s, 3H), 2.15 – 2.02 (m, 2H), 1.09 (s, 3H), 0.91 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 147.7, 138.9, 138.3, 137.9, 128.7, 128.5, 128.2, 127.6, 124.2, 121.5, 121.2, 110.5, 64.9, 50.6 (d, *J* = 12.9 Hz), 35.9, 35.1, 28.0, 27.6, 21.6.

<sup>19</sup>**F** NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.3.

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>25</sub>FNO<sub>2</sub>S<sup>+</sup> 374.1585, found 374.1597.

(6-(3,5-Dimethylphenyl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5ad)

SOAF

Following General Procedure B on 0.2 mmol scale with 3-(3,5-dimethylphenyl)-6-methylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

62.0 mg, 80% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.08 (t, J = 7.8 Hz, 2H), 6.99 (s, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.82 – 6.76 (m, 2H), 5.48 – 5.39 (m, 1H), 4.27 (d, J = 9.6 Hz, 1H), 3.78 (dd, J = 14.6, 9.9 Hz, 1H), 3.53 (dd, J = 14.6, 5.1 Hz, 1H), 2.20 (s, 6H), 2.12 – 2.01 (m, 2H), 1.08 (s, 3H), 0.89 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 147.8, 139.0, 138.4, 137.7, 129.4, 128.7, 124.8, 121.4, 121.2, 110.5, 64.9, 50.6 (d, *J* = 12.9 Hz), 35.9, 35.1, 28.0, 27.6, 21.5.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.2.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{22}H_{27}FNO_2S^+$  388.1741, found 388.1748.

(6-([1,1'-Biphenyl]-4-yl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl) methanesulfonyl fluoride (5ae)

SO<sub>2</sub>F

Following **General Procedure B** on 0.2 mmol scale with 3-([1,1'-biphenyl]-4-yl)-6-methylhept-1-yn-3-ol and aniline. Flash chromatography: 5 to 10% EtOAc in petroleum ether.

38.3 mg, 44% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.43 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.58 – 5.52 (m, 1H), 4.32 (d, *J* = 9.8 Hz, 1H), 3.82 (dd, *J* = 14.7, 10.1 Hz, 1H), 3.57 (dd, *J* = 14.7, 4.4 Hz, 1H), 2.22 – 2.03 (m, 2H), 1.10 (s, 3H), 0.93 (s, 3H). <sup>13</sup>**C** NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 140.7, 140.3, 138.5, 137.3, 128.83, 128.82, 127.4, 127.3, 127.03, 127.00, 121.6,

121.4, 110.7, 65.0, 50.5 (d, *J* = 12.7 Hz), 35.9, 35.2, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.5.

HRMS-ESI (m/z) [M+Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>26</sub>FNNaO<sub>2</sub>S<sup>+</sup> 458.1560, found 458.1551.

(3,3-Dimethyl-1-phenyl-6-(thiophen-3-yl)-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5af)

Following General Procedure B on 0.2 mmol scale with 6-methyl-3-(thiophen-3-yl) hept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

36.5 mg, 50% yield, pale yellow solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 – 7.07 (m, 4H), 7.04 (d, *J* = 4.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 5.57 – 5.46 (m, 1H), 4.25 (d, *J* = 10.2 Hz, 1H), 3.80 (dd, *J* = 14.5, 10.5 Hz, 1H), 3.54 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.18 – 1.96 (m, 2H), 1.07 (s, 3H), 0.89 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 147.7, 139.8, 134.3, 128.7, 126.6, 125.2, 122.3, 121.4, 121.3, 109.3, 64.8, 50.3 (d, J = 12.6 Hz), 35.8 (d, J = 1.2 Hz), 34.9, 28.1, 27.7.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.8.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{18}H_{21}FNO_2S_2^+$  366.0992, found 366.0997.

(6-(Benzo[b]thiophen-3-yl)-3,3-dimethyl-1-phenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5ag)



Following **General Procedure B** on 0.2 mmol scale with 3-(benzo[*b*]thiophen-3-yl)-6-methylhept-1-yn-3-ol and aniline. Flash chromatography: 5 to 10% EtOAc in petroleum ether.

49.9 mg, 60% yield, pale yellow solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.28 (s, 1H), 7.02 (t, J = 7.8 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 5.68 – 5.53 (m, 1H), 4.32 (d, J = 9.9 Hz, 1H), 3.89 (dd, J = 14.6, 10.1 Hz, 1H), 3.60 (dd, J = 14.6, 1.7 Hz, 1H), 2.25 (dd, J = 19.1, 4.0 Hz, 1H), 2.10 – 2.04 (m, 1H), 1.12 (s, 3H), 0.98 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 147.5, 141.0, 137.7, 133.4, 133.0, 128.8, 125.8, 124.41, 124.35, 123.2, 123.0, 121.5, 120.7, 110.8, 64.7, 50.7 (d, *J* = 12.6 Hz), 35.8, 34.7, 28.1, 27.6.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.8.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{22}H_{23}FNO_2S_2^+$  416.1149, found 416.1143.

#### (3-Methyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5ah)

SO<sub>2</sub>F

Following General Procedure B on 0.2 mmol scale with 3-phenylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

29.7 mg, 43% yield, *d.r.* = 6:1, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, J = 7.4 Hz, 12H, one isomer), 7.34 (d, J = 7.3 Hz, 2H, one isomer), 7.22 – 7.12 (m, 33H, two isomers), 7.07 (d, J = 7.9 Hz, 14H, two isomers), 6.96 – 6.87 (m, 8H, two isomers), 6.80 (t, J = 7.0 Hz, 1H, one isomer), 5.69 – 5.59 (m, 6H, one isomer), 5.46 – 5.40 (m, 1H, one isomer), 4.55 (d, J = 8.9 Hz, 1H, one isomer), 4.31 (d, J = 10.4 Hz, 6H, one isomer), 4.22 – 4.16 (m, 1H, one isomer), 4.02 – 3.96 (m, 1H, one isomer), 3.86 – 3.76 (m, 6H, one isomer), 3.49 – 3.37 (m, 7H, two isomers), 2.51 – 2.40 (m, 7H, two isomers), 2.25 – 2.16 (m, 6H, one isomer), 2.16 – 2.11 (m, 1H, one isomer), 1.87 – 1.77 (m, 6H, one isomer), 1.01 (d, J = 6.8 Hz, 18H, one isomer), 0.96 (d, J = 6.9 Hz, 3H, one isomer).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.9, 140.3, 138.3, 129.0, 128.4, 127.9, 127.0, 124.1, 123.1, 111.4, 62.4, 48.4 (d, J = 13.4 Hz), 29.0, 28.0, 18.2.

<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ 61.4 & 60.1 (two isomers).

HRMS-ESI (m/z) [M+NH4]<sup>+</sup> calcd for C<sub>20</sub>H<sub>26</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> 363.1537, found 363.1553.

(3,3,5-Trimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (5ai)



Following General Procedure B on 0.2 mmol scale with 4,6-dimethyl-3-phenylhept-1-yn-3-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

57.5 mg, 77% yield, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, J = 7.4 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.01 (t, J = 7.9 Hz, 2H), 6.94 (d, J = 7.9 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 4.32 – 4.19 (m, 1H), 3.77 (dd, J = 14.7, 9.4 Hz, 1H), 3.56 (dd, J = 14.7, 3.6 Hz, 1H), 2.08 (t, J = 18.0 Hz, 1H), 1.89 – 1.83 (m, 4H), 1.08 (s, 3H), 0.92 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 148.2, 137.5, 133.0, 130.3, 128.5, 127.9, 127.1, 121.8, 121.0, 115.5, 64.8, 51.2 (d, *J* = 12.9 Hz), 41.5, 36.6 (d, *J* = 0.9 Hz), 28.1, 28.0, 20.3.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 60.2.

HRMS-ESI (m/z) [M+Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>24</sub>FNNaO<sub>2</sub>S<sup>+</sup> 396.1404, found 396.1390.

(2,3-Diphenyl-1,2,4a,5,6,7,8,8a-octahydroisoquinolin-1-yl)methanesulfonyl fluoride (5aj)

SO<sub>2</sub>F

Following General Procedure B on 0.2 mmol scale with 1-cyclohexyl-2-phenylbut-3-yn-2-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

39.3 mg, 51% yield, *d.r.* = 2.1:1, white solid.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, J = 7.2 Hz, 4.2H, one isomer), 7.34 (d, J = 7.1 Hz, 2H, one isomer), 7.21 – 7.12 (m, 13.5H, two isomers), 7.11 – 7.05 (m, 6.2H, two isomers), 6.94 – 6.90 (m, 4.1H, two isomers), 6.80 (t, J = 7.3 Hz, 1H, one isomer), 5.53 – 5.46 (m, 2.1H, one isomer), 5.22 – 5.17 (m, 1H, one isomer), 4.53 – 4.49 (m, 1H, one isomer), 4.27 (d, J = 10.8 Hz, 2.1H, one isomer), 4.05 – 3.98 (m, 1H, one isomer), 3.89 – 3.81 (m, 2.1H, one isomer), 3.52 (d, J = 14.5 Hz, 1H, one isomer), 3.44 – 3.38 (m, 2.1H, one isomer), 2.74 (s, 1H, one isomer), 2.06 (d, J = 12.8 Hz, 2H, one isomer), 1.99 – 1.93 (m, 2H, one isomer), 1.90 – 1.86 (m, 2.1H, one isomer), 1.85 – 1.79 (m, 4.2H, one isomer), 1.73 – 1.69 (m, 1H, one isomer), 1.65 – 1.61 (m, 4.2H, one isomer), 1.59 – 1.53 (m, 2.1H, one isomer), 1.48 – 1.31 (m, 7.2H, two isomers), 1.25 – 1.21 (m, 2.1H, one isomer), 1.19 – 1.15 (m, 1H, one isomer), 1.05 – 0.98 (m, 2.1H, one isomer).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.1 & 147.8 (two isomers), 140.2 & 138.8 (two isomers), 138.5 & 135.7 (two isomers), 129.0 & 128.8 (two isomers), 128.34 & 128.31 (two isomers), 127.8 & 127.6 (two isomers), 127.2 & 127.0 (two isomers), 124.4 & 123.2 (two isomers), 122.1 & 121.7 (two isomers), 116.3 & 100.1 (two isomers), 62.2 & 61.3 (two isomers), 53.4 (d, *J* = 12.1 Hz) & 49.86 (d, *J* = 12.7 Hz) (two isomers), 39.2 & 39.1 (two isomers), 37.4 & 33.00 (two isomers), 32.97 & 30.5 (two isomers), 29.7 & 26.9 (two isomers), 26.7 & 26.2 (two isomers), 25.6 & 22.2 (two isomers).

 $^{19}\mathrm{F}$  NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  61.6 & 60.4 (two isomers).

HRMS-ESI (m/z) [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>25</sub>FNO<sub>2</sub>S<sup>+</sup> 386.1585, found 386.1578.

(2,2-Dimethyl-4,5-diphenyl-3,4-dihydro-2H-1,4-oxazin-3-yl)methanesulfonyl fluoride (5ak)

Following General Procedure B on 0.2 mmol scale with 1-isopropoxy-2-phenylbut-3-yn-2-ol and aniline.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

21.7 mg, 30% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) *δ* 7.31 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.57 (s, 1H), 4.49 – 4.44 (m, 1H), 3.77 – 3.69 (m, 1H), 3.66 – 3.57 (m, 1H), 1.41 (s, 3H), 1.15 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 146.6, 135.1, 131.3, 129.1, 128.7, 127.1, 125.7, 121.6, 120.3, 119.1, 77.3, 60.7, 50.0 (d, *J* = 14.3 Hz), 26.3, 24.4.

 $^{19}\mathbf{F}$  NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  60.9.

**HRMS-ESI** (m/z)  $[M+H]^+$  calcd for  $C_{19}H_{21}FNO_3S^+$  362.1221, found 362.1231.

#### **IV. Further Transformations**

((2S,6S)-3,3-Dimethyl-1,6-diphenylpiperidin-2-yl)methanesulfonyl fluoride (6)

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

To a stirred solution of (3,3-dimethyl-1,6-diphenyl-1,2,3, 4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) in  $CH_2Cl_2$  (4 mL) were added NaBH<sub>3</sub>CN (66.0 mg, 1 mmol) at -40 °C followed by TFA (0.16 mL, 2.0 mmol). The resulting suspension was stirred for 5 h at this temperature. The reaction was quenched with saturated aqueous NaHCO<sub>3</sub>, diluted with  $CH_2Cl_2$  (10 mL) and the organic layer was separated. The aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in *vacuo* and the residue was purified by column chromatography to afford **6** as a white solid.

71.6 mg, 99% yield, white solid.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.23 (d, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.13 – 7.05 (m, 3H), 6.90 – 6.84 (m, 3H), 4.04 – 3.98 (m, 2H), 3.78 (d, *J* = 15.6 Hz, 1H), 3.70 – 3.63 (m, 1H), 1.94 – 1.86 (m, 1H), 1.84 – 1.79 (m, 1H), 1.59 (s, 3H), 1.55 – 1.51 (m, 2H), 1.13 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 149.0, 143.9, 128.8, 128.5, 127.2, 126.7, 125.1, 123.1, 67.9, 58.2, 47.3 (d, *J* = 15.0 Hz), 34.4, 33.3, 32.8, 28.0, 26.4.

<sup>19</sup>**F NMR** (565 MHz, CDCl<sub>3</sub>) δ 57.6.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{20}H_{25}FNO_2S^+$  362.1585, found 362.1584.

#### 2-Methoxyphenyl(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)me-thanesulfonate (7)



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.3 mg, 0.2 mmol) and *o*methoxy-phenol (25.3 mg, 0.24 mmol) were dissolved in MeCN (2 mL), and K<sub>2</sub>CO<sub>3</sub> (33.2 mg, 0.24 mmol) was added. The reaction was stirred at room temperature for 8 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **7** as a white solid.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

89.9 mg, 97% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.41 (m, 2H), 7.38 (dd, J = 7.9, 1.5 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.16 – 7.10 (m, 3H), 7.06 – 7.01 (m, 4H), 7.00 – 6.95 (m, 2H), 6.77 – 6.72 (m, 1H), 5.46 – 5.41 (m, 1H), 4.40 (dd, J = 9.6, 1.2 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.75 (s, 3H), 3.64 – 3.60 (m, 1H), 2.10 (s, 2H), 1.07 (s, 3H), 0.91 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 151.6, 148.0, 139.2, 138.8, 138.3, 128.4, 128.2, 128.1, 127.3, 127.2, 124.5, 121.7, 121.2, 120.7, 113.0, 110.4, 64.6, 55.8, 51.2, 35.9, 35.3, 28.0, 27.7.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{27}H_{30}NO_4S^+$  450.1734, found 450.1734.

#### 4-Allyl-2-methoxyphenyl(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonate (8)



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) and eugenol (39.8 mg, 0.24 mmol) were dissolved in MeCN (2 mL), and K<sub>2</sub>CO<sub>3</sub> (33.2 mg, 0.24 mmol) was added. The reaction was stirred at room temperature for 8 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **8** as a colorless oil.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

98.7 mg, 98% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.10 (m, 3H), 7.06 – 6.99 (m, 4H), 6.82 – 6.77 (m, 2H), 6.76 – 6.73 (m, 1H), 6.01 – 5.90 (m, 1H), 5.46 – 5.40 (m, 1H), 5.14 – 5.08 (m, 2H), 4.39 (d, *J* = 9.4 Hz, 1H), 3.83 – 3.77 (m, 1H), 3.74 (s, 3H), 3.61 (d, *J* = 14.4 Hz, 1H), 3.38 (d, *J* = 6.7 Hz, 2H), 2.09 (s, 2H), 1.07 (s, 3H), 0.91 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 151.4, 148.0, 140.5, 139.2, 138.9, 136.8, 136.6, 128.45, 128.2, 127.3, 127.2, 124.3, 121.8, 121.2, 120.7, 116.6, 113.2, 110.3, 64.7, 55.9, 51.2, 40.2, 36.0, 35.3, 28.0, 27.7.

HRMS-ESI (m/z) [M+NH<sub>4</sub>]<sup>+</sup> calcd forC<sub>30</sub>H<sub>37</sub>N<sub>2</sub>O<sub>4</sub>S<sup>+</sup> 507.2312, found 507.2305.

#### $\label{eq:2-Methyl-4-oxo-4} 2-Methyl-4-oxo-4H-pyran-3-yl(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl) methanesulfonat-e \eqref{eq:9} (9)$



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) and 3hydroxy-2-methyl-4-pyrone (30.9 mg, 0.24 mmol) were dissolved in MeCN (2 mL), and K<sub>2</sub>CO<sub>3</sub> (33.2 mg, 0.24 mmol) was added. The reaction was stirred at 50 °C for 4 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **9** as a colorless oil.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

82.9 mg, 89% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (d, *J* = 5.6 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.19 – 7.11 (m, 3H), 7.06 – 6.97 (m, 4H), 6.74 (d, *J* = 6.8 Hz, 1H), 6.41 (d, *J* = 5.6 Hz, 1H), 5.49 – 5.43 (m, 1H), 4.39 – 4.31 (m, 2H), 4.01 – 3.94 (m, 1H), 2.52 (s, 3H), 2.20 – 2.04 (m, 2H), 1.14 (s, 3H), 0.89 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 172.8, 163.3, 154.4, 148.2, 138.94, 138.90, 128.5, 128.2, 127.3, 127.2, 121.7, 120.7, 117.6, 110.9, 65.0, 53.3, 36.1, 35.3, 28.0, 27.8, 16.1.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{26}H_{28}NO_5S^+$  466.1683, found 466.1690.

2-Methyl-5-oxocyclopent-1-en-1-yl(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesul-fonate (10)



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) and methylcyclopentenolone (27.6 mg, 0.24 mmol) were dissolved in MeCN (2 mL), and K<sub>2</sub>CO<sub>3</sub> (33.2 mg, 0.24 mmol) was added. The reaction was stirred at 50°C for 6 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **10** as a colorless oil.

Flash chromatography: 10 to 20% EtOAc in petroleum ether.

75.9 mg, 84% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, J = 7.4 Hz, 2H), 7.20 – 7.11 (m, 3H), 7.08 – 6.98 (m, 4H), 6.75 (t, J = 6.9 Hz, 1H), 5.50 – 5.44 (m, 1H), 4.35 (d, J = 9.8 Hz, 1H), 4.05 (d, J = 14.2 Hz, 1H), 3.94 – 3.87 (m, 1H), 2.65 – 2.57 (m, 2H), 2.49 – 2.39 (m, 2H), 2.24 – 2.18 (m, 3H), 2.18 – 2.05 (m, 2H), 1.13 (s, 3H), 0.90 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) δ 200.1, 166.0, 148.1, 145.5, 138.90, 138.85, 128.4, 128.1, 127.23, 127.16, 121.6, 120.7, 110.8, 64.9, 53.1, 36.0, 35.2, 32.4, 28.1, 27.9, 27.7, 15.8.

HRMS-ESI (m/z)  $[M+Na]^+$  calcd for  $C_{26}H_{29}NNaO_4S^+$  460.1553, found 460.1539.

*N*-(3,4-Dimethoxyphenethyl)-1-(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfon-amide (11)



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) and 2-(3,4-dimethoxyphenyl)-ethylamine (74.8 mg, 0.4 mmol) were added in MeCN (2 mL), and DBU (62 µL, 0.4 mmol) was slowly added. The reaction was stirred at room temperature for 8 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **11** as a colorless oil.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

102.1 mg, 98% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (d, J = 7.2 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.06 – 6.98 (m, 4H), 6.79 – 6.69 (m, 3H), 6.66 (s, 1H), 5.42 – 5.38 (m, 1H), 4.56 – 4.44 (m, 1H), 4.19 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.42 – 3.32 (m, 2H), 3.24 – 3.17 (m, 1H), 2.96 (d, J = 14.2 Hz, 1H), 2.79 (t, J = 6.3 Hz, 2H), 2.04 – 1.91 (m, 2H), 0.98 (s, 3H), 0.84 (s, 3H).

<sup>13</sup>**C NMR** (150 MHz, CDCl<sub>3</sub>) *δ* 149.2, 148.1, 148.0, 138.9, 138.8, 130.5, 128.5, 128.3, 127.3, 126.9, 121.6, 121.0, 120.6, 112.0, 111.5, 110.8, 64.8, 56.0, 55.9, 52.1, 44.9, 36.4, 35.8, 35.2, 27.9, 27.7.

 $\label{eq:HRMS-ESI} \mbox{(m/z)} \mbox{[M+Na]}^+ \mbox{calcd for } C_{30} \mbox{H}_{36} \mbox{N}_2 \mbox{NaO}_4 \mbox{S}^+ \mbox{529.2131, found 529.2134.}$ 

#### 3,3-Dimethyl-1,6-diphenyl-2-((pyrrolidin-1-ylsulfonyl)methyl)-1,2,3,4-tetrahydropyridine (12)



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) were added in MeCN (2 mL), and tetrahydro pyrrole (84 µL, 1 mmol) was slowly added followed by DBU (62 µL, 0.4 mmol). The reaction was stirred at room temperature for 8 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **12** as a colorless oil.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

75.5 mg, 92% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, *J* = 7.3 Hz, 2H), 7.23 – 7.12 (m, 3H), 7.08 – 7.01 (m, 4H), 6.73 (s, 1H), 5.42 – 5.36 (m, 1H), 4.27 (d, *J* = 8.1 Hz, 1H), 3.44 – 3.37 (m, 4H), 3.33 – 3.26 (m, 1H), 3.06 (d, *J* = 13.9 Hz, 1H), 2.11 – 2.02 (m, 2H), 1.98 – 1.92 (m, 4H), 1.07 (s, 3H), 0.88 (s, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 148.2, 139.2, 128.4, 128.3, 127.3, 127.0, 122.3, 121.7, 120.5, 110.7, 64.4, 48.5, 47.9, 36.0, 35.3, 28.0, 27.8, 26.0.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{24}H_{31}N_2O_2S^+$  397.1944, found 397.1944.

#### 1-(3,3-Dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)-*N*-phenylmethanesulfonamide (13)



(3,3-dimethyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-2-yl)methanesulfonyl fluoride (73.2 mg, 0.2 mmol) and aniline (40  $\mu$ L, 0.4 mmol) were added in MeCN (2 mL), and DBU (62  $\mu$ L, 0.4 mmol) was slowly added. The reaction was stirred at room temperature for 8 h, the resulting mixture was concentrated in *vacuo* and the residue was purified by column chromatography to afford **13** as a colorless oil.

Flash chromatography: 5 to 10% EtOAc in petroleum ether.

51.9 mg, 60% yield, colorless oil.

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.10 – 7.00 (m, 7H), 6.75 (t, *J* = 7.0 Hz, 1H), 5.29 (t, *J* = 3.5 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 3.38 – 3.30 (m, 1H), 3.22 (d, *J* = 13.9 Hz, 1H), 1.90 (dd, *J* = 19.0, 4.1 Hz, 1H), 1.74 (dd, *J* = 19.0, 2.4 Hz, 1H), 0.88 (s, 3H), 0.82 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.1, 139.0, 138.8, 137.1, 129.9, 128.5, 128.2, 127.3, 127.0, 124.9, 121.6, 120.7, 119.7, 111.0, 64.7, 51.5, 35.9, 35.0, 27.8, 27.7.

HRMS-ESI (m/z)  $[M+H]^+$  calcd for  $C_{26}H_{29}N_2O_2S^+$  419.1788, found 419.1794.

### **Supplemental Reference**

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## Supplemental Data

## I. X-ray Crystal Data



Figure S1 X-ray structure of 5n (2183275).

Table S4 Crystal data and structure refinement for 5n.							
Identification code	5n						
Empirical formula	C24H30FNO2S						
Formula weight	415.55						
Temperature/K	150.1(4)						
Crystal system	triclinic						
Space group	P-1						
a/Å	8.0575(6)						
b/Å	10.2338(8)						
c/Å	13.7884(9)						
α/°	85.464(6)						
β/°	88.881(5)						
γ/°	84.269(6)						
Volume/Å <sup>3</sup>	1127.67(14)						
Z	2						

$\rho_{calc}g/cm^3$	1.224
µ/mm <sup>-1</sup>	0.171
F(000)	444.0
Crystal size/mm <sup>3</sup>	0.12  imes 0.11  imes 0.1
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
$2\Theta$ range for data collection/°	4.012 to 49.998
Index ranges	$-9 \le h \le 9, -11 \le k \le 12, -16 \le l \le 15$
Reflections collected	8377
Independent reflections	3978 [ $\mathbf{R}_{int} = 0.0252, \mathbf{R}_{sigma} = 0.0430$ ]
Data/restraints/parameters	3978/7/261
Goodness-of-fit on F <sup>2</sup>	1.053
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0544,  wR_2 = 0.1243$
Final R indexes [all data]	$R_1 = 0.0654, wR_2 = 0.1326$
Largest diff. peak/hole / e Å <sup>-3</sup>	1.11/-1.03

3379 3367 2667 2667 2687 1974 1197 1167 1167 1167 1167 1167 1167 1167	484	2294 278 809 809 792 555 551 553 553 553
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	$\checkmark$	



5a

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequence	cy 600

—1.087 —0.903

2.150 2.143 2.118 2.111 2.083 2.051 2.051 2.051







761 746 2220 2208 2222 208 2228 2208 2228 2228	586 580 574	353 337 337 308 308 777 757 757 757 757 757	173 166 166 134 134 059 059	105 370
000000000000000000000000000000000000000	2.5.5	446666666666		0.
	$\checkmark$			



5b

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequence	cy 600







--60.16

5b

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

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110	100	90	80	70	60	50	40	30	20	10	0 f1 (ppr	-10 n)	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	

7.349 7.334 7.319 7.317 7.319 7.317 7.319 7.317 7.246 7.221 7.221 6.959 6.944	5.634 5.628 5.622	4.318 3.791 3.791 3.766 3.756 3.756 3.563 3.563	2.190 2.158 2.158 2.151 2.151 2.151 2.175 2.077	— 1.118 — 0.864	
NC SO <sub>2</sub> F					
Ph				Parameter	Value
5c			1 S	olvent	CDCl3
			2 S	pectrometer Freque	ncy 600






	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

⊤ 0 f1 (ppm) 36 Т 110 100 90 80 50 40 30 -10 -20 -30 -90 -100 -110 70 60 20 10 -40 -50 -60 -70 -80







—60.19



5d

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

⊤ 0 f1 (ppm) 39 Т 110 100 90 80 70 60 50 40 30 -10 -20 -30 -50 -70 -80 -90 -100 -110 20 10 -40 -60







5e

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

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	110	100	90	80	70	60	50	40	30	20	10	0 f1 (ppn	-10 n)	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	









5f

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

Т 0 f1 (ppm) 45 110 100 90 80 70 60 50 40 30 -10 -20 -30 -70 -90 -100 -110 20 10 -40 -50 -60 -80







-60.43

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

					1 1		'	'	· ·	'	· · ·	· ·	·	·	'	·	'	· ·	· ·	· ·	· · ·		· · · ·
	110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
f1 (ppm)																							

7.348 7.336 7.260 7.197 7.197 7.197 7.197 7.197 6.866 6.866 6.866	5.504 5.492 5.492	4.213 4.197 3.783 3.758 3.741 3.552 3.520 3.520	2.148 2.141 2.116 2.075 2.075 2.045	— 1.087 — 0.885
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5h

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequenc	y 600







0 f1 (ppm) 51 110 100 90 80 70 60 50 40 30 20 10 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110







—60.68

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

⊤ 0 f1 (ppm) 54 Т 110 100 90 80 50 40 30 -10 -20 -30 -90 -100 -110 70 60 20 10 -40 -50 -60 -70 -80







## Т 0 f1 (ppm) 57 110 100 90 50 -10 -20 80 70 60 40 30 20 10 -30 -40 -50 -60 -70 -80 -90 -100 -110









—60.67

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

⊤ 0 f1 (ppm) 60 Т 110 100 90 80 70 60 50 40 30 -10 -20 -30 -70 -90 -100 -110 20 10 -40 -50 -60 -80

7.386 7.374 7.374 7.213 7.150 7.171 7.171 7.179 6.886 6.872 6.886 6.833	€5.453 5.447 5.441	4.254 4.254 3.803 3.779 3.779 3.552 3.552 3.552 3.552 3.552 3.552	2.174 2.174 2.135 2.135 2.103 2.103 2.075 2.073 2.039	— 1.084 — 0.914	
SO <sub>2</sub> F					
Pn ~			Γ	Parameter	Value
51			1	Solvent	CDCl3
			2	Spectrometer Frequer	ncy 600







51

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	7 565

⊤ 0 f1 (ppm) 63 Т 110 100 90 80 70 50 40 30 -10 -20 -30 -90 -100 -110 60 20 10 -40 -50 -60 -70 -80





5m

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	<del>,</del> 600

1.151
1.139
1.126
1.126
1.091
0.926



4.275 4.260 3.815 3.791 3.775 3.775 3.775 3.775 3.775 3.563 3.556 3.556 3.556 2.510 2.498 2.473 2.142 2.111 2.082 2.051





5m

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

Т 0 f1 (ppm) 66 110 100 90 80 70 60 50 40 30 -10 -20 -30 -70 -90 -100 -110 20 10 -40 -50 -60 -80







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

\_\_\_\_0 f1 (ppm) 69 Т 110 100 90 80 70 60 50 40 30 -10 -20 -30 -70 -90 -100 -110 20 10 -40 -50 -60 -80








Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

---0 f1 (ppm) 72 Т 110 100 90 80 50 40 30 -10 -20 -30 -90 -100 -110 70 60 20 10 -40 -50 -60 -70 -80











Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	150







5р

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

		·	'	'		1	·		1	·	'	· 1	'		· 1		·	- I	1	·	·	· · · ·
110	100	90	80	70	60	50	40	30	20	10	0 f1 (ppi	-10 m)	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110









—63.45 —58.07

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

Т 0 f1 (ppm) 78 110 100 90 -10 80 70 60 50 40 30 20 -20 -30 -50 -60 -70 -80 -90 -100 -110 10 -40

880 893 893 803 803 803 803 803 803 803 803 803 80	437 431 425	212	318 301 301 303 303 303 303 303 303 303 303	154 115 115 115 115 155 155 155 155 155	)98 943
4.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2	5 5 7 2 7 7	44		6666666666	0.1
	$\checkmark$	$\searrow$			



Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	7 600

5r







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

	1 1	1 1	1 1	1 1	1	'		'	'	'	1	'	·	'	. 1	'	'				'	- I - I
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
											f1 (ppm	)										
											81											





Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 600







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

Т 0 f1 (ppm) 84 110 100 90 80 50 40 30 -10 -20 -30 -90 -100 -110 70 60 20 10 -40 -50 -60 -70 -80

167 167 164 374 374 3350 333 350 3338 374 197 197 197 197 197 197 197 1082 0082 0068	558 551 546	218 201 812 787 787 770 577 553 553	182 175 150 143 104 099 072 067 040
××××××××××××××××××××××××××××××××××××××	ົນບົບ	4400000000	~~~~~~~~~~~~~~~~~
	$\checkmark$		



5t

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	600







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

⊤ 0 f1 (ppm) 87 Т 110 100 90 80 70 60 50 40 30 20 -10 -20 -30 -50 -70 -80 -90 -100 -110 10 -40 -60





Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequenc	y 600







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

⊤ 0 f1 (ppm) 90 Т 110 100 90 80 70 50 40 30 -10 -20 -30 -70 -90 -100 -110 60 20 10 -40 -50 -60 -80









Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

⊤ 0 f1 (ppm) 93 Т 110 100 90 80 70 60 50 40 30 20 -10 -20 -30 -50 -70 -90 -100 -110 10 -40 -60 -80







f1 (ppm) 95 -1 



Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

0 f1 (ppm) 96 110 100 90 80 70 50 40 30 -10 -20 -30 -50 -70 -90 -100 -110 60 20 10 -40 -60 -80





Parameter	Value				
1 Solvent	CDCl3				
2 Spectrometer Frequency 600					







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

' '		· ·	- I I	- I I	1 1	·	·	'	'	'	1	'	·	1	1	'		1		'	'	1	
11	0	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
												f1 (ppn	ר)										
												99											



 $CF_{3}$ 

5y



Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	600







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

	L

## 0 f1 (ppm) 102 110 100 90 80 70 60 50 40 30 -10 -20 -30 -50 -70 -80 -90 -100 -110 20 10 -40 -60









Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	150



/147.00 /142.97 /142.97 /132.23 /121.99 /111.04 /111.04



-61.12

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

-⊤ 0 f1 (ppm) 105 Т 110 100 90 80 70 50 40 30 -10 -20 -30 -90 -100 -110 60 20 10 -40 -50 -60 -70 -80






-1



Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

- 1		1	1			'	'				'		1		. 1	'	'				'	
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
										1	f1 (ppm	)										
											108											







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	y 565

'		1 1		'			'	'		'	1		· 1	'	. 1	'	1	'	'	· · ·	'	1	-
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	
											f1 (ppm	า)											
											111												







	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

1		1 1	1 1	1 1	1 1	1 1	1 1		- I I	1					·		1	'	· 1	'	·	
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
										1	f1 (ppm)	)										
											114											







Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	- I I	1			1		'	·	'		1 1		1	
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
										i	f1 (ppm)	)										
											117											





-1





	1 1			1 1	1	'	'	. 1		1	1	·	'	'	. 1		'	'		'		· · · ·
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
											f1 (ppm	)										
											120											



-5.519





Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	600







5af

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

·   ·		1 1	1 1	1 1	1 1	1 1	1 1	1 1			'	'	· 1	'	'	'	'		I	'	·	
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
											f1 (ppm)	)										
											123											



I
1 Solvent
Spectro

2.274 2.267 2.242 2.242 2.235 2.083



4.324 4.307 3.909 3.893 3.885 3.885 3.885 3.868 3.615 3.512 3.531 3.538





Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

-⊤ 0 f1 (ppm) 126 110 100 90 80 70 60 50 40 30 -10 -20 -30 -50 -70 -90 -100 -110 20 10 -40 -60 -80



Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	7 600







~61.40 ~60.08

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565









Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequenc	y 600







	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	565

1	, 1 ,	·   ·	, 1 ,		1 1			1		1	'	·	'	·	'	·	1	'	·	'	'	
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
											f1 (ppm	ı)										
											132											





5aj

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequence	cy 600







5aj

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565







5ak





Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	7 600







## Т 0 f1 (ppm) 138 110 100 90 50 -10 80 70 60 40 30 20 10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110





Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	600







-57.57

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	565

	1 1	1		1 1	1	'		'	. 1	1	'	1	'	'	. 1		'	'	1	'	'	
110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110
f1 (ppm)																						
											141											



0

Ő

7

Ph<sub>N</sub>

Ph

 $\hat{O}$ 



1		
	Parameter	Value
	1 Solvent	CDCl3
	2 Spectrometer Frequency	600






































Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	7 600



