### Supplementary information

### Aminofluorination: Transition-Metal-Free N-F Bond Insertion of Diazocarbonyl Compounds

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### **General information**

All reactions were carried out with standard Schlenk techniques under argon. All reagents were used as received from commercial suppliers unless otherwise stated. All solvents were purified by distillation following standard procedures. Reaction progress was monitored by thin layer chromatography (TLC) and components were visualized by observation under UV light at254nm.Flash column chromatography was performed using silica gel 60 (200-300 mesh). All <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded on Bruker AV-III 400 in CDCl<sub>3</sub>. Chemical shifts were reported in parts per million (ppm,  $\delta$ ). Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra is referenced to the peak of tetramethylsilane ( $\delta = 0.00$ ) and reported as follows: chemical shift (ppm), multiplicity (s = singlet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra is referenced to the solvent center peak of CDCl<sub>3</sub> ( $\delta = 77.0$ ).

**CAUTION!** Even though we have noted no explosive tendencies of the diazo compounds, it is strongly recommended that they should be handled with great care and proper protection.

### General procedure for preparation of diazoesters

Method A:

$$R^1 CO_2 R^2$$
 + TsN<sub>3</sub> DBU  $R^1 CO_2 R^2$  + TsN<sub>3</sub> CO<sub>2</sub> R<sup>2</sup>

According to a known procedure<sup>1-3</sup>, to the solution of ethyl phenylacetate (5mmol) and 4-methylbenzenesulfonyl azide ( $TsN_3$ ) (1.24 g, 6mmol) in anhydrous CH<sub>3</sub>CN or THF (40 mL) was added 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) (1.14 g, 7.5 mmol) slowly at room temperature. Then the reaction mixture was stirred at room temperature for 15 hours. After water (40 mL) was added, the resulting

mixture was extracted with diethyl ether (3  $\times$  40 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under reduced pressure, the residual was purified by column chromatography on silicagel to give **1a-1k**, **1m**, **1o-1q**, **1s-1v**.

Method B:

Ar-I + 
$$O$$
  $CO_2Et$   $Pd(PPh_3)_4$   $N_2$   
NaOH, EtOH  $Ar$   $CO_2Et$ 

According to a known procedure<sup>4</sup>, Pd(PPh<sub>3</sub>)<sub>4</sub> (144 mg, 5 mol%), NaOH (300.0 mg, 7.5 mmol) were suspended in ethanol (10.0 mL) and stirred for 30 minunder argon. Then aryl iodide (2.5 mmol) and ethyl 2-diazo-3-oxobutanoate (468 mg, 3.0 mmol) was added. The resulting solution was stirred at room temperature for 5 h. The mixture was filtered through a short path of silica gel with ethyl acetate as eluent. After removing the solvent under reduced pressure, the residual was purified by column chromatography on silica gel to give the products **11**, **1n** and **1w**.

# General procedure for the germinalaminofluorination of diazoesters

Method A:



The mixture of diazoesters (0.45mmol) and NFSI (0.3 mmol, 94.6 mg) in 3 mL DCE was stirred for 48 h under argon at 60 °C or 80 °C. After removing the solvent under reduced pressure, the residual was purified by column chromatography on silica gel to give 2. (It should be noted that according to the <sup>19</sup>F-NMR, the product 2 contains a small amount of impurities, ranging from 1 to 3%, which could not be removed by column chromatography.)





The mixture of diazoester **1a** (0.45mmol, 85.6 mg) and NFSI (0.3 mmol, 94.6 mg) in 3 mL DCE was irradiated under UV light ( $\lambda = 254$  nm) for 48 h. The yield of **2a** is obtained by <sup>19</sup>F NMR Spectroscopy.

### Method C: in the presence of radical scavenger (Scheme 3b)



The mixture of diazoester **1a** (0.45mmol, 85.6 mg), NFSI (0.3 mmol, 94.6 mg) and 2,6-di-tert-butyl-4-methylphenol (BHT) (0.3 mmol, 66.1 mg) in 3 mL DCE was stirred for 48 h under argon at 60 °C. After removing the solvent under reduced pressure, the residual was purified by a silica gel column chromatography to give **2a** as white solid.

### Method D: using selectfluor as fluorine source (Scheme 3c)



The mixture of diazoester **1a** (0.45mmol, 85.6 mg), selectfluor (0.3 mmol, 106 mg) and tetrapropylammoniumbenzenesulfonimide (0.3 mmol, 131 mg) in 3 mL DCE was stirred for 48 h under argon at 60 °C. The yield of **2a** is obtained by <sup>19</sup>F NMR Spectroscopy.

### Method E: in the presence of Brønsted acid



The mixture of diazoester **1a** (0.45mmol, 85.6 mg), NFSI (0.3 mmol, 94.6 mg) and Brønsted acid (2equivalent) in 3 mL DCE was stirred for 48 h under argon at 60 °C. The yield of **2a** is obtained by <sup>19</sup>F NMR Spectroscopy.





<sup>a</sup>All reaction was carried out in 0.30 mmol scale under argon at 60  $^{\circ}$ C, [**1a**] = 0.15 M, [NFSI] = 0.10 M, isolated yield.

### Nitrogen evolution

The solution of diazoester **1a** (0.45mmol) in 3 mL DCE was placed in a roundbottom flask with NFSI (0.3 mmol, 94.6 mg) or without NFSI. The flask was sealed with rubber septa and deaerated with DCE saturated argon for 15 min. Then, the solution was rigorously stirred at 60 °C. The nitrogen in the headspace was withdrawn by a deaerated Hamilton gas-tight syringe and immediately injected into a HP5890 GC/TCD fitted a Chrompack 5Å molecular sieve column (25 m × 0.32 mm) for analysis and quantified according to a calibration curve prepared by injecting known quantity of pure nitrogen gas into the reaction flask.



**Figure S1**. Plots of nitrogen evolution vs. time for the decomposition of **1a** in the presence of NFSI or without NFSI in DCE at 60 °C.

### **Kinetic Studies**

$$aA + bB \longrightarrow cC + dD$$

$$Rate = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = k[A]^{a}[B]^{b}$$

$$In(Rate) = In(k[A]^{a}[B]^{b})$$

$$= aIn[A] + bIn[B] + In(k)$$

A mixture of diazoester, NFSI and 1-bromo-4-fluorobenzenein 3 mL DCE was stirred under argon. 100  $\mu$ L of the mixture was sampled by a syringe and quenched by TFA (2 equivalent) at desired time. The concentration of **2a** is obtained by <sup>19</sup>F NMR Spectroscopy based on the internal standard (1-bromo-4-fluorobenzene). All reaction was monitored to 0~20 % yield of **2**. Initial rates were obtained by linear fit of the concentration-time plot (Figure S2 and Figure S3). A plot of ln(initial rate) vs. ln([**1a**]) or In([NFSI]) showed that the rate for the germinal aminofluorination of diazoesters is first-order in both **1a** and NFSI (Figure S4 and Figure S5, equation 1).

$$Rate = k[1a][NFSI]$$
(1)



Figure S2. Plots of concentration of 2a vs time for the reaction between diazoester 1a and NFSI in DCE at 50 °C. [Diazo] = 0.15 M.



Figure S3. Plots of concentration of 2a vs time for the reaction between diazoester 1a and NFSI in DCE at 50 °C. [NFSI] = 0.10 M.



**Figure S4**. Plot of ln(initial rate) vs ln([NFSI]). y = 1.1895x - 2.442,  $R^2 = 0.9605$ . The slope of the line is approximately 1, indicating that the rate for the germinal aminofluorination of diazoester is first-order in NFSI.



**Figure S5**. Plot of ln(initial rate) vs ln([1a]). y = 1.1862x - 2.531,  $R^2 = 0.9984$ . The slope of the line is approximately 1, indicating that the rate for the germinal aminofluorination of diazoester is first-order in 1a.

Effect of temperature. The effect of temperature on initial rate for the reaction between diazoesters (0.15 M) and NFSI (0.10 M) in DCE were studied from 313 to 353 K (Figure S6). The activation parameters were obtained from the plot of ln(initial rate/T) vs 1/T according to Eyring equation.  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  were found to be 17.1 kcal mol<sup>-1</sup> and -13.0 cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. The negative  $\Delta S^{\ddagger}$  value suggests that a bimolecular transition state involving NFSI and **1a** might be generated.

Eyring equation: 
$$\ln \frac{k}{T} = \frac{-\Delta H^{\dagger}}{R} \frac{1}{T} + \ln \frac{k_{B}}{h} + \frac{\Delta S^{\dagger}}{R}$$



Figure S6.Plot of ln(initial rate/T) vs 1/T for the reaction between 1a and NFSI in DCE, [1a] = 0.15 M, [NFSI] = 0.10 M, slope =  $-8.61 \times 10^3$ , y-intercept =  $1.27 \times 10$ , r<sup>2</sup> = 0.996.

**Hammett Correlation.** The electronic effects of substituent X in the *para*position of diazophenylacetates on the rate constants of this reactionhave been correlated by Hammett equation,  $log(k_X/k_H) = \rho\sigma^+$ . The plot of  $log(k_X/k_H)$  against  $\sigma^+$ shows a linear relationship (Figure S7), with the slope  $\rho = -0.81$ . The small negative  $\rho$ value suggests that the transition state is weakly polarized with a positive charge at the reaction center.



Figure S7. Hammett plot of  $log(k_X/k_H)$  vs  $\sigma^+$  for the reaction of NFSI with *para*substituted diazophenylacetate **1** in DCE at 50 °C, [**1**] = 0.15 M, [NFSI] = 0.10 M, slope = -0.81, y-intercept =  $0.4 \times 10^{-2}$ ,  $r^2 = 0.995$ .

### **Computational method**

All the calculations were carried out by using ORCA program package.<sup>5</sup> Full geometry optimization and frequency calculation were performed by using B3LYP functional<sup>6,7</sup> coupled with def2-SVP<sup>8</sup> basis set for all atoms. A larger basis set of def2-TZVPP4 was employed for single point energy corrections. To improve computational speed, the RIJCOSX approximation<sup>9-11</sup> in combination with def2-SVP/J and def2-TZVPP/J<sup>12</sup> auxiliary basis sets was applied. Dispersion effects were

computed by using the well-established dispersion corrections D3 with Becke-Johnson damping scheme.<sup>13,14</sup> Solvation effects were taken into account by the universal solvation model based on solute electron density (SMD)<sup>15</sup> with the conductor-like screening model (COSMO).<sup>16</sup>

### Calculated potential energy surface

As shown in Scheme S1, four possible transformation pathways from reactant **1a** to product **2a** were calculated to explore the reaction mechanism. The calculated barriers of the first step in each pathway are collected in Table S1.



Scheme S1. The first step of the four possible transformation pathways from reactant1a to product 2a. The major geometric differences were marked in red.

As can be seen from Table S1, pathway D is the lowest energy pathway where a fluorine transfer transition state  $(TS_D)$  is located with an enthalpy barrier of 16.2 kcal mol<sup>-1</sup>, which is in good agreement with experimental value of 17.1 kcal mol<sup>-1</sup>. The C–F and N–F bond lengths in TS<sub>D</sub> are 1.772 Å and 1.920 Å, respectively (Figure S8). The following intermediate **Int**<sub>1</sub> after C–F bond formation and C–N bond breaking is

exothermic by 25.6 kcal mol<sup>-1</sup>(Figure S9). Though the C-N bond has not been formed yet, these two atoms are quite close with a distance of 2.858 Å (Figure S8e), indicating the intermediate  $Int_1$  is an ionic pair. All attempts to find other possible mechanisms excluding those shown in Scheme S1 failed as the obtained energy barriers were higher than 32 kcal mol<sup>-1</sup> which were not possible in real experiment. The second step in pathway D was found to proceed in no barrier fashion with N<sub>2</sub> leaving. Thus, the corresponding intermediate  $Int_2$  is exothermic by 12.8 kcal mol<sup>-1</sup>. Like  $Int_1$ , this intermediate is also an ionic pair because the distance of C and N is 3.239 Å (Figure S8f). Finally, using the N–C distance as the scanning coordinate resulted in a downhill energy profile that fell down to the product. As a result, the total enthalpy change of the reaction is -84.8 kcal mol<sup>-1</sup>.

Table S2. B3LYP calculated transition state energies in the first step of four possible pathways. The SCF energy, enthalpy and free energy changes are in kcal mol<sup>-1</sup> while entropy changes are in cal mol<sup>-1</sup> K<sup>-1</sup>.

	$\Delta^{\ddagger}E$	$\Delta^{\ddagger}H$	$\Delta^{\ddagger}G$	$\Delta^{\ddagger}S$
А	33.6	32.0	29.0	10.1
В	52.7	51.6	50.9	2.5
С	58.2	54.5	57.9	-11.4
D	18.3	16.2	18.9	-9.0



Figure S8. Geometries of four transition states in Scheme S1.



**Figure S9.** DFT computed enthalpy change (red text, in kcalmol<sup>-1</sup>) for the reaction between **1a** and NFSI.

### <sup>1</sup>H and <sup>13</sup>C NMR Spectra datafor the prepared substrates

Ethyl 2-diazo-2-phenylacetate (1a)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.2,

128.9, 125.7, 125.6, 123.9, 60.9, 14.4.

### Methyl 2-diazo-2-phenylacetate (1b)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 3.86 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.6, 128.9, 125.8, 125.4, 123.9, 51.9.

Isobutyl 2-diazo-2-phenylacetate (1c)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, J = 7.5 Hz, 2H), 7.38 (t, J= 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 4.06 (d, J = 6.6 Hz, 2H), 2.07–1.94 (m, 1H), 0.97 (d, J = 6.6 Hz, 6H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>) δ 165.2, 128.9, 125.7, 125.6, 123.9, 70.9, 27.87, 19.0.

Benzyl 2-diazo-2-phenylacetate (1d)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, J = 7.4 Hz, 2H), 7.32 – 7.41 (m, 7H), 7.18 (t, J = 7.4 Hz, 1H), 5.32 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.0, 135.9, 128.9, 128.6, 128.3, 128.2, 66.5

125.9, 125.4, 124.0, 66.5.

### (+)-Menthyl 2-diazo-2-phenylacetate (1e)<sup>2</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.91–4.85 (m,1H), 2.14–2.10 (m, 1H), 1.96–1.88 (m, 1H), 1.73–1.67 (m, 2H), 1.54–1.48 (m, 1H), 1.44–1.41 (m, 1H), 1.15–1.02

(m, 2H), 0.93–0.90 (m, 6H), 0.88– 0.84 (m, 1H), 0.81 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.6, 128.8, 125.7, 125.5, 123.8, 74.9, 47.1, 41.3, 34.2, 31.4, 26.5, 23.6, 21.9, 20.6, 16.5.

#### 4-Diazo-isochroman-3-one (1f)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40–7.36 (m, 1H), 7.18–7.17 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 1H),5.35 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 134.5, 125.4, 124.0, 118.2, 116.7, 108.6, 26.7.

### **3-Diazo-1-methyl-2-indolinone** (1g)<sup>3</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20(t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 3.32 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 134.5, 125.4, 122.0, 118.2, 116.7, 108.6, 26.8.

#### Ethyl 2-diazo-2-(4-fluorophenyl)acetate (1h)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45–7.41 (m, 2H), 7.09–7.05 (m, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ165.1, 160.8 (d, J<sub>C-F</sub> = 245 Hz),

125.7 (d, $J_{C-F}$  = 7.9 Hz), 121.3 (d,  $J_{C-F}$ = 3.2 Hz), 115.8 (d,  $J_{C-F}$  = 21.8 Hz), 60.9, 14.3.

### Ethyl 2-(4-chlorophenyl)-2-diazoacetate (1i)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (d, J = 8.7 Hz, 2H),7.32 (d, J = 8.7 Hz, 2H), 4.32(q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.8, 131.3, 129.0,

125.0, 124.2, 61.1, 14.4.

### Ethyl 2-diazo-2-(3,4-dichlorophenyl)acetate (1j)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d, J = 2.2 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.28 (dd, J = 8.5 Hz, J = 2.2 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>) δ 164.3, 133.1, 130.6, 129.2, 126.1, 125.1, 122.5, 61.3, 14.4.

### Ethyl 2-(3-chlorophenyl)-2-diazoacetate (1k)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (s, 1H), 7.34–7.27 (m,2H), 7.14 (d, J = 7.4 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.6, 135.0,

130.0, 127.8, 125.6, 123.6, 121.5, 61.2, 14.4.

### Ethyl 2-diazo-2-(3,5-dichlorophenyl)acetate (11)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d, *J* = 1.8 Hz, 2H), 7.13(t, *J* = 1.8 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.0, 135.5, 129.5, 125.4, 121.5, 61.4, 14.4.

#### Ethyl 2-(4-bromophenyl)-2-diazoacetate (1m)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.8, 131.9, 125.3,

124.8, 119.2, 61.1, 14.4.

### Ethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (1n)<sup>4</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (s, 4H), 4.35 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.4, 130.2, 127.3 (q,  $J_{C-F}$  =32.6 Hz), 125.7 (q,  $J_{C-F}$ 

 $_{\rm F}$  = 3.8 Hz), 124.0 (q,  $J_{\rm C-F}$  = 270 Hz), 123.3, 61.3, 14.4.

### Ethyl 2-diazo-2-(3,4-dimethylphenyl)acetate (10)<sup>1</sup>



#### Ethyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate (1q)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H),  $\delta$  7.31 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 4.32(q, J = 6.8 Hz, 2H), 2.45 (s, 3H), 1.33 $(t, J = 6.8 \text{ Hz}, 3\text{H}); {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 164.8, 147.2, 145.4, 132.2, 129.8,$ 

128.5, 124.9, 124.7, 122.9, 61.1, 21.7, 14.4.

#### Ethyl 2-(4-(benzyloxy)phenyl)-2-diazoacetate (1r)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (d, J = 7.0 Hz, 2H), 7.40-7.36 (m, 4H), 7.34-7.30 (m, 1H), 5.06 (s, 2H), 4.31(q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>) δ 165.7, 157.1, 136.8, 128.6, 128.0, 127.4, 125.9, 117.4, 115.6, 70.1, 60.9, 14.5.

### Ethyl 2-diazo-2-(4-methoxyphenyl)acetate (1s)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.30(q, J = 7.1 Hz, 2H), 3.78 (s, 3H),1.32 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 165.6, 157.9, 125.7, 116.9, 114.4, 60.8, 55.2, 14.4.

### Ethyl 2-diazo-2-(4-methoxyphenyl)acetate (1t)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 (d, J = 1.5 Hz, 1H), 6.91–6.85 (m, 2H), 4.32(q, J = 7.1 Hz, 2H), 3.90 (s, 3H),3.88 (s, 3H),1.34 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100

 $MHz, CDCl_3) \ \delta \ 165.7, \ 149.4, \ 147.2, \ 117.5, \ 116.3, \ 111.6, \ 108.2, \ 60.9, \ 55.9, \ 55.8, \ 14.5.$ 

### Ethyl 2-diazo-2-(naphthalen-2-yl)acetate (1u)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (s,1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.50–7.42 (m, 2H), 4.38 (q, *J* = 6.8 Hz, 2H), 1.38 (t, *J* = 6.8

Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.3, 133.6, 131.4, 128.6, 127.6, 127.5, 126.6, 125.7, 122.8, 122.5, 121.9, 61.0, 14.5.

Vinyl 2-diazo-2-phenylacetate (1v)<sup>1</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) $\delta$ 7.48 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.02–5.93 (m, 1H), 5.40 (dd, *J* = 17.2Hz, *J* = 1.2Hz, 1H), 5.27 (d, *J* = 10.4Hz,

1H), 4.76 (t, J = 5.5 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.7, 132.0, 128.8, 125.7, 125.3, 123.9, 118.2, 65.3.

Vinyl 2-diazo-2-phenylacetate(1w)<sup>4</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54–7.52 (m, 4H), 7.47 -7.45 (m, 2H), 7.33-7.32 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.8, 132.1, 131.5, 128.3, 128.2, 125.7,

123.4, 123.2, 120.3, 89.6, 89.1, 61.1, 14.4.

### <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR Spectra data for the prepared products

### Ethyl 2-fluoro-2-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2a)



Compound 2a was obtained as a white solid in 97% yield; R<sub>f</sub> = 0.61 (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, J = 7.5 Hz, 4H), 7.61 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.5, 4H), 7.28–7.25 (m, 3H), 7.06 (t, J = 7.8, 2H), 4.38 – 4.22 (m, 2H), 1.30 (t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (d,  $J_{C-F} = 29.8$  Hz),

140.6, 133.9, 130.0, 129.9 (d,  $J_{C-F} = 24.9$  Hz), 128.7, 128.4 (d,  $J_{C-F} = 9.8$  Hz), 128.3, 127.4 (d,  $J_{C-F} = 1.7$  Hz), 100.3 (d,  $J_{C-F} = 232.5$  Hz), 63.4, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.7; IR (KBr) 1773, 1762, 1450, 1378, 1358, 1261, 1190, 1172, 1067, 1045, 1005, 836, 790, 760, 747, 723, 716, 694, 685, 605, 593, 553 cm<sup>-1</sup>; HRMS- $(DART) (m/z): (M + NH_4)^+ calcd for C_{22}H_{24}FN_2O_6S_2, 495.1060; found 495.1043.$ 

### Methyl 2-fluoro-2-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2b)



Compound 2a was obtained as a white solid in 95% yield;  $R_f = 0.55$  (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 7.8 Hz, 4H), 7.62 (t, J =

7.4 Hz, 2H), 7.47 (t, J = 7.8, 4H), 7.29–7.25 (m, 3H), 7.06 (t, J = 7.9, 2H), 3.84(s,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.6 (d,  $J_{C-F}$  = 30.0 Hz), 140.5, 133.9, 130.0, 129.8 (d,  $J_{C-F}$  = 25.0 Hz), 128.8, 128.4 (d,  $J_{C-F}$  = 10.1 Hz), 128.2, 127.5 (d,  $J_{C-F}$ = 1.7 Hz), 100.4 (d,  $J_{C-F}$  = 233.1 Hz), 53.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) $\delta$  -118.9; IR (KBr) 1772, 1753, 1450, 1387, 1360, 1279, 1208, 1194, 1194, 1087, 1065, 1045, 1034, 1007, 829, 822, 780, 752, 722, 682, 636, 606, 584, 561, 533 cm<sup>-1</sup>; HRMS- $(DART) (m/z): (M + NH_4)^+ calcd for C_{21}H_{22}FN_2O_6S_2, 481.0903; found 481.0893.$ 

### Isobutyl2-fluoro-2-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2c)



Compound 2c was obtained as a white solid in 95% yield;  $R_{f}$ = 0.39 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, J = 8.0 Hz, 4H), 7.61 (t, J =

7.4 Hz, 2H), 7.46 (t, J = 7.9, 4H), 7.27–7.24 (m, 3H), 7.05 (t, J = 7.8, 2H), 4.00 (d, J= 6.6 Hz, 2H), 2.04–1.93 (m, 1H), 0.882 (d, *J* = 6.6 Hz, 3H), 0.876 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.9 (d,  $J_{C-F}$  = 30.0 Hz), 140.6, 133.9, 130.1 (d,  $J_{C-F}$ = 25.1 Hz), 129.9, 128.7, 128.33, 128.36 (d,  $J_{C-F}$  = 9.6 Hz), 127.4 (d,  $J_{C-F}$  = 1.6 Hz), 100.4 (d,  $J_{C-F}$  = 232.5 Hz), 73.2, 27.4, 18.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.8; IR (KBr) 1768, 1452, 1381, 1357, 1262, 1246, 1208, 1190, 1174, 1162, 1083, 1066, 1042, 1007, 818, 777, 758, 748, 717, 684, 606, 591, 546; HRMS-(DART) (m/z): (M +  $NH_4$ )<sup>+</sup> calcd for C<sub>24</sub>H<sub>28</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 523.1373; found 523.1360.

### Benzyl2-fluoro-2-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2d)

 $(PhO_2S)_2N$ F CO<sub>2</sub>Bn 2d

= 0.63 (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) $\delta$  7.81 (d, J = 7.9 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.8, 4H), 7.33 – 7.31 (m, 5H), 7.25–7.19 (m, 3H), 7.01 (t, J = 7.7,

Compound 2d was obtained as a white solid in 94% yield;  $R_{f}$ 

2H), 5.28 (d, J = 12.1 Hz, 1H), 5.23 (d, J = 12.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.5 (d,  $J_{C-F}$  = 30.7 Hz), 140.4, 134.3, 133.9, 130.0, 129.7 (d,  $J_{C-F}$  = 24.9 Hz), 128.7, 128.48, 128.47 (d,  $J_{C-F} = 8.0$  Hz), 128.46, 128.3, 127.4 (d,  $J_{C-F} = 1.5$  Hz), 100.3 (d,  $J_{C-F} = 231.8$  Hz), 68.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.4; IR (KBr) 1771, 1751, 1450, 1381, 1363, 1267, 1190, 1174, 1080, 1068, 1044, 1004, 816, 772, 753, 723, 695, 680, 595, 555 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>27</sub>H<sub>26</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 557.1216; found 557.1204.

### (+)-Menthyl 2-fluoro-2-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2e)



Compound **2e** was obtained as a white solid in 92% yield;  $R_f = 0.57$  (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) $\delta$  7.88 - 7.84 (m, 8H), 7.61-7.58 (m, 4H), 7.47 - 7.43 (m, 8H), 7.27 - 7.23

(m, 6H), 7.08 – 7.02 (m, 4H), 4.79– 4.66 (m, 2H), 2.18(d, J = 12.2 Hz,1H), 2.03 – 1.99 (m, 1H), 1.80 (d, J = 11.9 Hz, 1H), 1.64 – 1.54 (m, 4H), 1.46 – 1.36 (m, 3H), 1.34 – 1.26 (m, 2H), 1.15 – 1.04 (m, 3H), 1.01 – 0.91 (m, 1), 0.89 – 0.83 (m, 8H), 0.79 (d, J = 6.6 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H), 0.53 (d, J = 7.0 Hz, 3H), 0.29 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (d,  $J_{C-F} = 27.9$  Hz), 165.6 (d,  $J_{C-F} = 28.8$  Hz), 140.6, 140.5, 133.83, 133.77, 130.1 (d,  $J_{C-F} = 11.9$  Hz), 129.9, 129.85 (d,  $J_{C-F} = 11.7$  Hz), 129.83, 128.65, 128.62, 128.5, 128.4, 128.36, 127.2 (d,  $J_{C-F} = 1.1$  Hz), 127.1 (d,  $J_{C-F} = 1.4$  Hz), 100.7 (d,  $J_{C-F} = 233.5$  Hz), 100.5 (d,  $J_{C-F} = 235.4$  Hz), 78.1, 77.7, 46.8, 46.7, 39.6, 39.2, 34.0, 33.9, 31.4, 31.2, 25.51, 25.55, 23.1, 23.0, 21.85, 21.81, 20.7, 20.1, 15.74, 15.70; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.4, -119.4; IR (KBr) 1742, 1450, 1380, 1289, 1269, 1174, 1080, 1045, 1006, 830, 786, 756, 719, 684, 596, 551 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>30</sub>H<sub>38</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 605.2155; found 605.2143.

### N-(4-fluoro-3-oxoisochroman-4-yl)-N-(phenylsulfonyl)benzenesulfonamide (2f)



Compound **2f**was obtained as a white solid in 97% yield;  $R_f = 0.29$  (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 6.2 Hz,

4H), 7.61 (t, J = 7.4, 2H), 7.52 (t, J = 7.7 Hz, 1H), 7.44 (t, J = 7.7 Hz, 4H), 7.38 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.5 Hz, 1H), 5.10 (d, J = 13.9 Hz, 1H), 4.89 (d, J = 13.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.1 (d,  $J_{C-F} = 26.4$  Hz), 139.5, 134.2, 133.9 (d,  $J_{C-F} = 5.5$  Hz), 130.7, 129.9 (d,  $J_{C-F} = 4.8$  Hz), 129.2 (d,  $J_{C-F} = 25.5$  Hz), 128.8, 128.6, 128.2, 124.6, 95.9 (d,  $J_{C-F} = 232.9$  Hz), 68.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -120.5;

IR (KBr) 1771, 1455, 1449, 1387, 1363, 1240, 1191, 1175, 1130, 1086, 1072, 1004, 989, 792, 758, 722, 702, 681, 670, 612, 592, 581, 547 cm<sup>-1</sup>; HRMS-(DART) (m/z):  $(M + NH_4)^+$  calcd for  $C_{21}H_{20}FN_2O_6S_2$ , 479.0747; found 479.0731.

## N-(3-fluoro-1-methyl-2-oxoindolin-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (2g)



Compound **2g** was obtained as a white solid in 83% yield;  $R_f = 0.36$  (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 – 7.80 (m, 5H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.50 –

7.46 (m, 5H), 7.16 (t, J = 7.6, 1H), 6.89 (t, J = 7.8 Hz, 1H), 3.20 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.9 (d,  $J_{C-F} = 21.9$  Hz), 144.6 (d,  $J_{C-F} = 5.8$  Hz), 139.9, 134.1, 133.2 (d,  $J_{C-F} = 3.5$  Hz), 128.7, 126.4, 123.6 (d,  $J_{C-F} = 3.1$  Hz), 123.0,122.8, 109.3 (d,  $J_{C-F} = 1.2$  Hz), 98.2 (d,  $J_{C-F} = 208.6$  Hz), 26.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -129.4; IR (KBr) 1751, 1617, 1473, 1450, 1382, 1362, 1180, 1169, 1114, 1084, 1064, 1028, 885, 762, 753, 719, 687, 610, 581 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>21</sub>H<sub>21</sub>FN<sub>3</sub>O<sub>5</sub>S<sub>2</sub>, 478.0907; found 478.0897.

#### Ethyl

#### 2-fluoro-2-(4-fluorophenyl)-2-(N-

### (phenylsulfonyl)phenylsulfonamido)acetate (2h)



Compound **2h** was obtained as a white solid in 96% yield;  $R_f$ = 0.44 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (d, *J* = 7.6 Hz, 4H), 7.63 (t, *J* = 7.4

Hz, 2H), 7.49 (t, J = 7.6 Hz, 4H), 7.27–7.23 (m, 2H), 6.74 (t, J = 8.6 Hz, 2H), 4.39– 4.23 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (d,  $J_{C-F} =$ 29.4 Hz), 163.6 (d,  $J_{C-F} = 250$  Hz), 140.4, 134.0, 130.8 (t,  $J_{C-F} = 9.4$  Hz), 128.8, 128.3, 125.7 (dd,  $J_{C-F} = 25.4$  Hz,  $J_{C-F} = 3.2$  Hz), 114.5 (dd,  $J_{C-F} = 21.7$  Hz,  $J_{C-F} = 1.2$  Hz), 100.0 (d,  $J_{C-F} = 233.0$  Hz), 63.6, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -110.0, 117.9; IR (KBr) 1746, 1603, 1509, 1449, 1381, 1357, 1303, 1270, 1239, 1184, 1176, 1168, 1074, 1045, 998, 903, 852, 812, 753, 722, 683, 619, 600, 575, 550 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>22</sub>H<sub>23</sub>F<sub>2</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 513.0966; found 513.0954.

### Ethyl

### (phenylsulfonyl)phenylsulfonamido)acetate (2i)

Compound 2i was obtained as a white solid in 98% yield; R<sub>f</sub> (PhO<sub>2</sub>S)<sub>2</sub>N F CO<sub>2</sub>Et = 0.43 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 CI MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, J = 7.4 Hz, 4H), 7.64 (t, J = 7.4 Hz, 2i 2H), 7.49 (t, J = 7.5 Hz, 4H), 7.20 (d, J = 8.8, 2H), 7.02 (d, J = 8.6 Hz, 2H), 4.39– 4.22 (m, 2H), 1.30 (t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.6 (d,  $J_{C-F} =$ 29.6 Hz), 140.4, 136.5, 134.1, 129.9 (d,  $J_{C-F} = 9.8$  Hz), 128.8, 128.5 (d,  $J_{C-F} = 25.7$ Hz), 128.3, 127.6 (d,  $J_{C-F} = 1.2$  Hz), 99.9 (d,  $J_{C-F} = 233.8$  Hz), 63.6, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.9; IR (KBr) 1748, 1491, 1451, 1381, 1385, 1300, 1266, 1182, 1175, 1162, 1096, 1075, 1048, 997, 907, 849, 813, 798, 754, 721, 685, 616, 608, 597, 560, 548 cm<sup>-1</sup>; HRMS-(DART) (m/z):  $(M + NH_4)^+$  calcd for  $C_{22}H_{23}ClFN_2O_6S_2$ , 529.0670; found 529.0658.

#### Ethyl2-(3,4-dichlorophenyl)-2-fluoro-2-(N-

### (phenylsulfonyl)phenylsulfonamido)acetate(2j)



Compound **2j** was obtained as a white solid in 94% yield;  $R_f = 0.43$  (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, *J* = 7.7 Hz, 4H), 7.66 (t, *J* = 7.4 Hz,

2H), 7.52 (t, J = 7.6 Hz, 4H), 7.30–7.23 (m, 2H), 7.16 (d, J = 1.8 Hz, 1H), 4.41– 4.22 (m, 2H), 1.31(t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.2 (d,  $J_{C-F} =$ 29.6 Hz), 140.1, 134.9, 134.3, 131.8 (d,  $J_{C-F} = 1.9$  Hz), 130.21 (d,  $J_{C-F} = 10.0$  Hz), 130.20 (d,  $J_{C-F} = 26.0$  Hz), 129.4, 128.9, 128.2, 128.1 ( $J_{C-F} = 10.2$  Hz), 99.2 (d,  $J_{C-F} =$ 234.8 Hz), 63.8, 13.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.5; IR (KBr) 1740, 1466, 1449, 1388, 1369, 1360, 1296, 1263, 1212, 1190, 1176, 1083, 1056, 1033, 1015, 909, 851, 827, 789, 760, 751, 724, 682, 616, 609, 579 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>22</sub>H<sub>22</sub>Cl2FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 563.0280; found 563.0269.

#### 2-(4-chlorophenyl)-2-fluoro-2-(N-

Ethyl

### (phenylsulfonyl)phenylsulfonamido)acetate (2k)



Compound 2k was obtained as a white solid in 85% yield;  $R_f$ CO<sub>2</sub>Et = 0.38 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 7.5 Hz, 4H), 7.64 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 4H), 7.33 (d, J = 7.9, 1H), 7.26 (d, J = 5.9 Hz, 1H), 7.10 (t, J = 8.0 Hz, 1H), 7.05 (s, 1H), 4.40–4.22 (m, 2H),1.30 (t, J = 7.1 Hz,3H); <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{CDCl}_3) \delta 165.4 \text{ (d}, J_{\text{C-F}} = 29.9 \text{ Hz}), 140.2, 134.2, 133.4 \text{ (d}, J_{\text{C-F}} = 2.2 \text{ Hz}),$ 132.0 (d,  $J_{C-F} = 25.6$  Hz), 130.3, 128.8, 128.7 (d,  $J_{C-F} = 6.1$  Hz), 128.4 (d,  $J_{C-F} = 10.1$ Hz), 128.2, 126.9 (d,  $J_{C-F} = 10.2$  Hz), 99.5 (d,  $J_{C-F} = 233.9$  Hz), 63.6, 13.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.4; IR (KBr) 1773, 1749, 1577, 1477, 1452, 1417, 1389, 1362, 1281, 1267, 1206, 1193, 1168, 1108, 1087, 1066, 1048, 1023, 998, 904, 835, 776, 753, 721, 683, 639, 606 cm<sup>-1</sup>; HRMS-(DART) (m/z):  $(M + NH_4)^+$  calcd for C<sub>22</sub>H<sub>23</sub>ClFN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 529.0670; found 529.0664.

### Ethyl2-(3,5-dichlorophenyl)-2-fluoro-2-(N-

### (phenylsulfonyl)phenylsulfonamido)acetate (21)



Compound **2I** was obtained as a white solid in 52% yield;  $R_f =$ 0.52 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, J = 7.8 Hz, 4H), 7.66 (t, J = 7.4 Hz, 2H), 7.53 (t, J = 7.8 Hz, 4H), 7.30 (s, 1H), 7.13 (s, 2H), 4.41

-4.22 (m, 2H),1.30(t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.1 (d,  $J_{C-F} =$ 30.0 Hz), 140.2, 134.4, 134.3 (d,  $J_{C-F} = 2.0$  Hz), 133.6 (d,  $J_{C-F} = 26.2$  Hz), 130.4, 128.9, 128.3, 127.0 ( $J_{C-F} = 10.4 \text{ Hz}$ ), 99.0 (d,  $J_{C-F} = 235.1 \text{ Hz}$ ), 63.9, 13.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.0.IR (KBr) 1770, 1471, 1450, 1382, 1358, 1298, 1261, 1245, 1208, 1190, 1175, 1163, 1083, 1065, 1041, 1006, 929, 898, 817, 777, 762, 758, 746, 716, 683, 633, 614, 606, 590, 560, 541 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>22</sub>H<sub>22</sub>Cl<sub>2</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 563.0280; found 563.0267.

### Ethyl

2-(4-bromophenyl)-2-fluoro-2-(N-

(phenylsulfonyl)phenylsulfonamido)acetate (2m)



Compound 2m was obtained as a white solid in 97% yield;  $R_f$ = 0.44 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, J = 7.6 Hz, 4H), 7.64 (t, J = 7.4 Hz,

2H), 7.49 (t, J = 7.7 Hz, 4H), 7.18 (d, J = 8.7, 2H), 7.13 (d, J = 8.8 Hz, 2H), 4.39– 4.22 (m, 2H), 1.30 (t, J = 7.1 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.5 (d,  $J_{C-F} =$ 29.3 Hz), 140.4, 134.1, 130.6 (d,  $J_{C-F} = 1.3$  Hz), 130.0 (d,  $J_{C-F} = 9.8$  Hz), 129.1 (d,  $J_{C-F}$ = 25.6 Hz), 128.8, 128.3, 124.9, 99.9 (d,  $J_{C-F}$  = 234.0 Hz), 63.7, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -119.1; IR (KBr) 1748, 1589, 1488, 1450, 1403, 1378, 1355, 1296, 1266, 1184, 1173, 1162, 1078, 1048, 996, 905, 847, 810, 754, 742, 720, 701, 683, 614, 605, 597, 559, 543 cm<sup>-1</sup>; HRMS-(DART) (m/z):  $(M + NH_4)^+$  calcd for C<sub>22</sub>H<sub>23</sub>BrFN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 573.0165; found 573.0160.

### Ethyl 2-fluoro-2-(N-(phenylsulfonyl)phenylsulfonamido)-2-(4-

### (trifluoromethyl)phenyl)acetate (2n)



Compound **2n** was obtained as a white solid in 55% yield;  $R_{f}$ = 0.45 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 7.6 Hz, 4H), 7.64 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.8 Hz, 4H), 7.42 (d, J = 8.2, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.40 – 4.22 (m, 2H), 1.30 (t, J = 7.1 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.3 (d,  $J_{C-F} =$ 29.7 Hz), 140.4, 134.2, 134.1 (d,  $J_{C-F} = 25.5$  Hz), 131.9 (q,  $J_{C-F} = 32.6$  Hz), 128.87 (d,  $J_{C-F} = 9.5$  Hz), 128.86, 128.3, 123.5 (q,  $J_{C-F} = 270.8$  Hz), 124.2 (m), 99.7 (d,  $J_{C-F} = 270.8$  Hz), 124.2 (m), 99.7 (d,  $J_{C-F} = 270.8$  Hz) 234.6 Hz), 63.8, 13.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.1, -119.3;IR (KBr) 1747, 1453, 1388, 1365, 1328, 1300, 1282, 1176, 1133, 1084, 1073, 1056, 1005, 998, 916, 856, 812, 763, 717, 687, 616, 605, 593, 559, 547 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M +  $NH_4$ )<sup>+</sup> calcd for  $C_{23}H_{23}F_4N_2O_6S_2$ , 563.0934; found 563.0924.

### Ethyl 2-fluoro-2-(N-(phenylsulfonyl)phenylsulfonamido)-2-(p-tolyl)acetate (20)



Compound **20** was obtained as a white solid in 95% yield;  $R_f =$ 

0.36 (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, *J* = 7.6 Hz, 4H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.13 (d, *J* = 8.2, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 4.38–4.21 (m, 2H),2.29 (s, 3H), 1.30 (t, *J* = 7.1 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 165.9 (d, *J*<sub>C-F</sub> = 29.5 Hz), 140.5, 140.2, 133.8, 128.6, 128.4 (d, *J*<sub>C-F</sub> = 9.8 Hz), 128.3,128.1 (d, *J*<sub>C-F</sub> = 1.6 Hz), 126.7 (d, *J*<sub>C-F</sub> = 25.0 Hz), 100.4 (d, *J*<sub>C-F</sub> = 232.3 Hz), 63.3, 21.1, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) $\delta$  -118.6; IR (KBr) 1747, 1450, 1377, 1356, 1315, 1298, 1271, 1183, 1174, 1162, 1107, 1050, 1028, 1014, 996, 906, 855, 845, 810, 792, 754, 722, 704, 685, 620, 612, 600, 576, 553, 532 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>23</sub>H<sub>26</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 509.1216; found 509.1210.

### Ethyl 2-fluoro-2-(N-(phenylsulfonyl)phenylsulfonamido)-2-(4-

#### (tosyloxy)phenyl)acetate (2q)

Compound 2q was obtained as a white solid in 92% yield;  $R_f$ (PhO<sub>2</sub>S)<sub>2</sub>N F CO<sub>2</sub>Et = 0.40 (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR TsO (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (d, J = 7.8 Hz, 4H), 7.74 (d, J = 2q 8.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.7 Hz, 4H), 7.35 (d, J = 8.1, 2H), 7.19 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 4.37–4.23 (m, 2H), 2.45 (s, 3H), 1.29(t, J = 7.2Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.5 (d,  $J_{C-F} = 29.9$  Hz), 150.7, 145.8, 140.3, 134.2, 132.2, 130.1 (d,  $J_{C-F} = 9.9$  Hz), 129.9, 128.9, 128.5 (d,  $J_{C-F} = 21.2$ Hz), 128.39, 128.35, 121.3(d,  $J_{C-F} = 1.1$  Hz), 99.8 (d,  $J_{C-F} = 232.9$  Hz), 63.6, 21.7, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.0; IR (KBr) 1771, 1750, 1597, 1502, 1451, 1380, 1363, 1295, 1268, 1203, 1179, 1157, 1078, 1048, 1004, 997, 867, 818, 770, 754, 722, 684, 661, 621, 600, 572, 557, 542 cm<sup>-1</sup>; HRMS-(DART) (m/z):  $(M + NH_4)^+$  calcd for C<sub>29</sub>H<sub>30</sub>FN<sub>2</sub>O<sub>9</sub>S<sub>3</sub>, 665.1097; found 665.1076.

### Ethyl 2-(4-(benzyloxy)phenyl)-2-fluoro-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2r)



Compound **2r** was obtained as a white solid in 44% yield;  $R_f = 0.63$  (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 7.7 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.34 (m, 9H), 7.13 (d, J = 8.7, 2H), 6.61 (d, J = 8.6 Hz, 2H), 5.05 (d, J = 12.0 Hz, 1H), 5.00 (d, J = 12.0 Hz, 1H), 4.37– 4.21 (m, 2H), 1.29 (t, J = 7.1 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8(d,  $J_{C-F} = 29.4$  Hz), 159.8, 140.5, 136.4, 133.8, 130.1 (d,  $J_{C-F} = 9.7$  Hz), 128.63, 128.62, 128.5, 128.2, 127.4, 121.4 (d,  $J_{C-F} = 25.1$  Hz), 113.7 (d,  $J_{C-F} = 1.0$  Hz), 100.3 (d,  $J_{C-F} = 231.6$  Hz), 69.8, 63.3, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -117.5; IR (KBr) 1769, 1748, 1607, 1583, 1510, 1450, 1378, 1362, 1257, 1180, 1075, 1045, 993, 846, 820, 800, 754, 731, 722, 683, 606, 550 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>29</sub>H<sub>30</sub>FN<sub>2</sub>O<sub>7</sub>S<sub>2</sub>, 601.1478; found 601.1467.

### Ethyl 2-fluoro-2-(4-methoxyphenyl)-2-(N-

### (phenylsulfonyl)phenylsulfonamido)acetate (2s)



Compound **2s** was obtained as a white solid in 43% yield;  $R_f = 0.20$  (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, J = 7.6 Hz, 4H), 7.61 (t, J =

### Ethyl 2-(3,4-dimethoxyphenyl)-2-fluoro-2-(N-

### (phenylsulfonyl)phenylsulfonamido)acetate (2t)



Compound **2t** was obtained as a white solid in 40% yield;  $R_f$ = 0.21 (petroleum ether : ethyl acetate = 3 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, *J* = 7.8 Hz, 4H), 7.61 (t, *J* =

7.4 Hz, 2H), 7.48 (t, J = 7.7 Hz, 4H), 6.86 (d, J = 7.5, 1H), 6.72 (s, 1H), 6.54 (d, J =

8.7, 1H), 4.40– 4.24 (m, 2H), 3.85 (s, 3H), 3.58 (s, 3H), 1.32 (t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (d,  $J_{C-F} = 29.4$  Hz), 150.3, 147.5, 140.6, 133.8, 128.7, 128.2, 122.1 (d,  $J_{C-F} = 10.2$  Hz), 121.3 (d,  $J_{C-F} = 25.2$  Hz), 111.4 (d,  $J_{C-F} = 10.2$  Hz), 109.6, 100.3 (d,  $J_{C-F} = 232.0$  Hz), 63.4, 55.9, 55.4, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -117.1;IR (KBr) 1770, 1750, 1518, 1465, 1448, 1376, 1361, 1266, 1248, 1189, 1171, 1150, 1082, 1056, 1039, 1024, 882, 856, 827, 800, 758, 722, 684, 625, 592, 550 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>24</sub>H<sub>28</sub>FN<sub>2</sub>O<sub>8</sub>S<sub>2</sub>, 555.1271; found 555.1258.

### Ethyl 2-fluoro-2-(naphthalen-2-yl)-2-(N-

### (phenylsulfonyl)phenylsulfonamido)acetate (2u)



Compound **2u** was obtained as a white solid in 90% yield;  $R_f = 0.39$  (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, J = 7.8 Hz, 4H), 7.77 (d, J =

10.8 Hz, 1H), 7.62–7.49 (m, 6H), 7.45–7.42 (m, 2H), 7.37 (d, J = 8.1 Hz, 4H), 4.41– 4.21 (m, 2H), 1.28 (t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (d,  $J_{C-F} =$ 29.7 Hz), 140.5, 133.9, 133.5, 131.6 (d,  $J_{C-F} = 1.4$  Hz), 128.870 (d,  $J_{C-F} = 9.9$  Hz), 128.872, 128.6, 128.3, 127.7, 127.3, 127.0, 126.9 (d,  $J_{C-F} = 1.6$  Hz), 126.3, 124.9 (d,  $J_{C-F} = 9.6$  Hz), 100.5 (d,  $J_{C-F} = 233.0$  Hz), 63.4, 13.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.2; IR (KBr) 1770, 1750, 1506, 1475, 1449, 1380, 1361, 1293, 1270, 1174, 1129, 1082, 1051, 1026, 943, 914, 860, 829, 810, 751, 722, 684, 630, 616, 611, 599, 580, 558, 543 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>26</sub>H<sub>26</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 545.1216; found 545.1203.

#### Allyl 2-fluoro-2-phenyl-2-(N-(phenylsulfonyl)phenylsulfonamido)acetate (2v)



Compound **2v** was obtained as a white solid in 96% yield;  $R_f = 0.38$  (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d, *J* = 7.6 Hz, 4H),

7.50 (d, J = 7.5 Hz, 2H),7.35 (t, J = 7.8 Hz, 4H), 7.19– 7.15 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H), 5.84–5.76 (m, 1H), 5.20– 5.10 (m, 2H), 4.68– 4.58 (m, 2H); <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>)  $\delta$  165.5 (d,  $J_{C-F}$  = 30.1 Hz), 140.4, 133.9, 130.7, 130.0, 129.7 (d,  $J_{C-F}$  = 24.9 Hz), 128.7, 128.4 (d,  $J_{C-F} = 9.8$  Hz), 128.2, 127.4 (d,  $J_{C-F} = 1.7$  Hz), 119.3, 100.3 (d,  $J_{C-F} = 232.7$  Hz), 67.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -118.8; IR (KBr) 1770, 1751, 1450, 1381, 1362, 1295, 1273, 1253, 1208, 1172, 1082, 1068, 1046, 1007, 931, 827, 777, 754, 721, 694, 683, 601, 553, 542 cm<sup>-1</sup>; HRMS-(DART) (m/z): (M + NH<sub>4</sub>)<sup>+</sup> calcd for C<sub>23</sub>H<sub>24</sub>FN<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 507.1060; found 507.1049.

### Ethyl 2-fluoro-2-(4-(phenylethynyl)phenyl)-2-(N-

(phenylsulfonyl)phenylsulfonamido)acetate (2w)

(PhO<sub>2</sub>S)<sub>2</sub>N F 2w Ph

Compound 2w was obtained as a white solid in 96% CO<sub>2</sub>Et yield;  $R_f = 0.45$  (petroleum ether : ethyl acetate = 5 : 1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, J = 7.5 Hz, 4H), 7.53 (t, J = 7.4 Hz, 2H), 7.45–7.43 (m, 2H), 7.39 (t, J = 7.6 Hz, 4H), 7.27–7.26 (m, 3H), 7.17–7.10 (m, 4H), 4.29–4.14 (m, 2H), 1.20(t, J = 7.2 Hz,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.5 (d,  $J_{C-F}$  = 29.7 Hz), 140.4, 134.0, 131.6, 130.3, 129.6 (d,  $J_{C-F}$  = 25.3 Hz), 128.76, 128.68, 128.41, 128.38, 128.3, 125.2, 122.6, 100.1 (d,  $J_{C-F} = 233.3$ Hz), 91.3, 88.2, 63.5, 13.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.9; IR (KBr) 1771, 1750, 1606, 1508, 1477, 1449, 1382, 1363, 1288, 1265, 1211, 1190, 1176, 1078, 1048, 1026, 997, 854, 812, 755, 722, 684, 617, 609, 600, 576, 551 cm<sup>-1</sup>; HRMS-(DART) (m/z):  $(M + NH_4)^+$  calcd for  $C_{30}H_{28}FN_2O_6S_2$ , 595.1373; found595.1362.

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