## **Supporting Information**

### **Copper-Catalyzed N-H Olefination of Sulfonamides for** *N***-sulfonyl**

### **Enaminone Synthesis**

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#### **General Information**

Unless otherwise noted, all solvents and reagents were commercially available and used without further purification. All reagents were weighed and handled in air at room temperature. NMR Spectra were performed at 298K, and all NMR spectra were recorded on Bruker AVANCE 400 for <sup>1</sup>H NMR and <sup>13</sup>C NMR in CDCl<sub>3</sub>. The NMR chemical shift was reported in ppm relative to 7.26 and 77.20 ppm of CDCl<sub>3</sub> solvent as the standards of <sup>1</sup>H NMR and <sup>13</sup>C NMR. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. High-resolution mass spectra (HRMS) were tested on SHIMADZU LCMS-IT-TOF, which was equipped with an electrospray ion source (ESI) operating in positive ion mode. Single-crystal X-ray analysis was conducted on Gemini A Ultra X-ray single crystal diffractometer.

#### Optimization of solvent, time, temperature and additive



Entry	Catalyst	Oxidant (equiv)	Additives (equiv)	Yield <sup>b</sup>
1	CuI	-	byp (0.5)	trace <sup>c</sup>
2	CuI	-	byp (0.5)	trace
3	CuI	TBHP(2)	byp (0.5)	trace
4	CuI	DTBP (2)	byp (0.5)	trace
5	CuI	NFSI (2)	byp (0.5)	trace
6	CuI	Selectfluor (2)	byp (0.5)	trace
7	CuI	Oxone (2)	byp (0.5)	trace
8	CuI	TEMPO (2)	byp (0.5)	42
9	CuI	TEMPO (2)	DMAP (0.5)	55
10	CuI	TEMPO (2)	DMAP(1)	61
11	CuI	TEMPO (2)	DMAP(2)	56
12	CuI	4-CH <sub>3</sub> O-TEMPO (2)	DMAP(1)	69
13	CuI	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	78
14	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	88
15	CuTC	4-HO-TEMPO (3)	DMAP(1)	56
16	CuTC	4-Acetyl-TEMPO (3)	DMAP(1)	81
17	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	Et <sub>3</sub> N (1)	60
18	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	$Cs_2CO_3(1)$	trace
19	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	K <sub>3</sub> PO <sub>4</sub> (1)	55
20	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	Pyridine (1)	79
21	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	Phenanthroline (1)	65
22	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	$PPh_3(1)$	trace
23	CuTC	4-CH <sub>3</sub> O-TEMPO (3)	Proline (1)	trace
24	CuOAc	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	79
25	Cu(OAc) <sub>2</sub>	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	65
26	Cu(OTf) <sub>2</sub>	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	57
27	FeCl <sub>2</sub>	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	trace
28	AgOAc	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	15
29	NiCl <sub>2</sub>	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	trace
30	Pd(OAc) <sub>2</sub>	4-CH <sub>3</sub> O-TEMPO (3)	DMAP(1)	trace

<sup>*a*</sup> Reaction conditions: **1a** (0.9 mmol), **2a** (0.3mmol), metal catalyst (20 mol%), additives and oxidant were stirred in DMSO (2 mL) at 110 °C under O<sub>2</sub> condition (operating in Schlenk tube) for 24h. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Under air condition.

#### General experimental procedure

General Procedure for the Synthesis of N-sulfonyl Enaminone (3a)



Under oxygen atmosphere, propiophenone (0.9 mmol, **1a**), *N*-methyl-*p*-toluene sulfonamide (0.3 mmol, **2a**), Copper(I) thiophene-2-carboxylate (20 mol%), *p*-dimethylaminopyridine (100 mol%), 4-CH<sub>3</sub>O-TEMPO (3 equiv) in DMSO (2 mL) were stirred at 110 °C for 24 h in a 25 mL Schlenk tube. After cooling to room temperature, the mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over sodium sulfate, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 10/1) to get the desired product (**3a**). Such product could be further purified by means of recrystallization.

General Procedure for the Synthesis of Various N-methyl-p-toluene sulfonamide



Under air atmosphere, benzenesulfonyl chloride (2 mmol) was stirred in THF (4 mL) in a flask. Methylamine (40%, w/w, aq, 0.4mL) was slowly added to the mixture. After half an hour, the reaction ended. The mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over sodium sulfate, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 2/1) to get the desired *N*-methyl-*p*-toluene sulfonamide derivatives.

General Procedure for the Synthesis of  $\alpha,\beta$ -unsaturated ketone



Under air atmosphere, 3-Chloropropiophenone (2 mmol) wasstirred in CHCl<sub>3</sub> (4 mL) in a flask. Triethylamine (2 mmol) was slowly added to the mixture. After an hour, the reaction ended. The mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over sodium sulfate, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 10/1) to get the desired $\alpha$ ,  $\beta$ -unsaturated ketone.

### **TLC detection**



Collecting different samples from the same system at different reaction time (1-0.5h, 2-1h, 3-2h, 4-3h, 5-5h, 6-7h, 7-12h, 8-18h)

#### Characterization data for the products



## $(E) \text{-} N, 4 \text{-} dimethyl \text{-} N \text{-} (3 \text{-} oxo \text{-} 3 \text{-} phenyl prop-1 \text{-} en \text{-} 1 \text{-} yl) benzene sulfonamide} (3a, 88\%)^1$

White solid, m.p. 154-156 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, *J* = 13.4 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.15 (d, *J* = 13.4 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.39 (s), 145.02 (s), 143.76 (s), 138.49 (s), 134.42 (s), 132.46 (s), 130.25 (s), 128.53 (s), 128.08 (s), 127.23 (s), 103.14 (s), 32.50 (s), 21.65 (s).

HRMS (ESI, m/z) calcd. for C<sub>17</sub>H<sub>18</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 316.1002, found 316.1003.



(*E*)-*N*,4-dimethyl-*N*-(3-oxo-3-(p-tolyl)prop-1-en-1-yl)benzenesulfonamide (3b, 76%) White solid, m.p. 166-167  $^{\rm o}{\rm C}$ 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (d, *J* = 13.4 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 13.4 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 188.97 (s), 144.94 (s), 143.44 (s), 143.21 (s), 135.85 (s), 134.48 (s), 130.22 (s), 129.22 (s), 128.22 (s), 127.23 (s), 103.21 (s), 32.49 (s), 21.64 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 330.1158, found 330.1163.



(*E*)-*N*,4-dimethyl-*N*-(3-oxo-3-(m-tolyl)prop-1-en-1-yl)benzenesulfonamide (3c, 65%) White solid, m.p. 116-117  $^{\circ}$ C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d, *J* = 13.5 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.67 (dm, *J* = 6.1, 1.8 Hz, 1H), 7.37 – 7.32 (m, 4H), 6.12 (d, *J* = 13.5 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.61 (s), 144.95 (s), 143.63 (s), 138.55 (s), 138.33 (s), 134.50 (s), 133.20 (s), 130.23 (s), 128.65 (s), 128.37 (s), 127.23 (s), 125.26 (s), 103.41 (s), 32.50 (s), 21.64 (s), 21.40 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 330.1158, found 330.1154.



(*E*)-*N*-(3-(4-ethylphenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3d, 79%) White solid, m.p. 147-148 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (d, *J* = 13.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.14 (d, *J* = 13.4 Hz, 1H), 3.10 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.01 (s), 149.40 (s), 144.94 (s), 143.42 (s), 136.08 (s), 134.48 (s), 130.22 (s), 128.32 (s), 128.04 (s), 127.23 (s), 103.26 (s), 32.49 (s), 28.92 (s), 21.65 (s), 15.28 (s). HRMS (ESI, m/z) calcd. for C<sub>19</sub>H<sub>21</sub>NNaO<sub>3</sub>S (M+Na)<sup>+</sup> 366.1134, found 366.1130.



(*E*)-*N*-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3e, 91%) White solid, m.p. 164-165 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 13.4 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.10 (d, *J* = 13.4 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 187.95 (s), 145.12 (s), 144.14 (s), 138.75 (s), 136.80 (s), 134.33 (s), 130.28 (s), 129.49 (s), 128.80 (s), 127.24 (s), 102.42 (s), 32.51 (s), 21.66 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>17</sub>H<sub>16</sub>ClNNaO<sub>3</sub>S (M+Na)<sup>+</sup> 372.0432, found 372.0424.



(*E*)-*N*-(3-(3-chlorophenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3f, 67%) White solid, m.p. 124-125 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 13.4 Hz, 1H), 7.84 (s, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 6.06 (d, J = 13.4 Hz, 1H), 3.11 (s, 3H), 2.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 187.98 (s), 145.14 (s), 144.46 (s), 140.16 (s), 134.73 (s), 134.34 (s), 132.32 (s), 130.30 (s), 129.89 (s), 128.19 (s), 127.27 (s), 126.16 (s), 102.49 (s), 32.53 (s), 21.67 (s). HRMS (ESI, m/z) calcd. for C<sub>17</sub>H<sub>16</sub>ClNNaO<sub>3</sub>S (M+Na)<sup>+</sup> 372.0432, found 372.0422.



(*E*)-*N*-(**3**-(**4**-bromophenyl)-**3**-oxoprop-1-en-1-yl)-*N*,**4**-dimethylbenzenesulfonamide (**3**g, **8**4%) Light yellow solid, m.p. 163-164 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 13.4 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.08 (d, *J* = 13.4 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 188.14 (s), 145.12 (s), 144.20 (s), 137.23 (s), 134.34 (s), 131.79 (s), 130.28 (s), 129.63 (s), 127.41 (s), 127.25 (s), 102.38 (s), 32.52 (s), 21.66 (s). HRMS (ESI, m/z) calcd. for C<sub>17</sub>H<sub>17</sub>BrNO<sub>3</sub>S (M+H)<sup>+</sup> 394.0107, found 394.1114.

(*E*)-*N*-(3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3h, 80%) White solid, m.p. 172-173 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, J = 13.4 Hz, 1H), 7.92 (dd, J = 8.9, 5.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 6.11 (d, J = 13.4 Hz, 1H), 3.10 (s, 3H), 2.43 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  187.68 (s), 165.35 (d, J = 253.7 Hz), 145.08 (s), 143.91 (s), 134.78 (d, J = 3.0 Hz), 134.37 (s), 130.60 (d, J = 9.2 Hz), 130.27 (s), 127.23 (s), 115.58 (d, J = 21.8 Hz), 102.52 (s), 32.50 (s), 21.65 (s).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -106.31 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>17</sub>H<sub>17</sub>FNO<sub>3</sub>S (M+H)<sup>+</sup> 334.0908, found 334.0915.



(*E*)-*N*-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3i, 63%)

White solid, m.p. 119-121 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (d, *J* = 13.4 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.14 (d, *J* = 13.4 Hz, 1H), 3.87 (s, 3H), 3.10 (s, 3H), 2.43 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 187.76 (s), 163.11 (s), 144.88 (s), 143.12 (s), 134.53 (s), 131.25 (s), 130.32 (s), 130.21 (s), 127.23 (s), 113.70 (s), 102.98 (s), 55.48 (s), 32.50 (s), 21.64 (s). HRMS (ESI, m/z) calcd. for C<sub>18</sub>H<sub>20</sub>NO<sub>4</sub>S (M+H)<sup>+</sup> 346.1108, found 346.1114.



(*E*)-*N*-(3-(3,4-difluorophenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3j, 44%)

White solid, m.p. 144-145 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 13.3 Hz, 1H), 7.77 – 7.70 (m, 3H), 7.67 (ddd, *J* = 8.6, 4.2, 1.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.19 (m, 1H), 6.05 (d, *J* = 13.3 Hz, 1H), 3.11 (s, 3H), 2.44

(s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 186.51 (s), 154.40 (d, J = 13.0 Hz), 152.10 – 151.16 (m), 149.03 (s), 145.18 (s), 144.52 (s), 135.56 (s), 134.31 (s), 130.30 (s), 127.27 (s), 124.80 (dd, J = 7.3, 3.5 Hz), 117.40 (dd, J = 17.1, 6.2 Hz), 101.78 (s), 32.51 (s), 21.65 (s).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -130.94 (d, J = 20.9 Hz), -136.27 (d, J = 20.9 Hz). HRMS (ESI, m/z) calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub>NNaO<sub>3</sub>S (M+Na)<sup>+</sup> 374.0633, found 374.0619.



(*E*)-*N*-(3-(3,5-difluorophenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3k, 32%)

White solid, m.p. 133-135 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 (d, J = 13.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.44 – 7.31 (m, 4H), 6.98 (m, J = 8.5, 2.3 Hz, 1H), 6.00 (d, J = 13.3 Hz, 1H), 3.11 (s, 3H), 2.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  186.55 (s), 162.97 (dd, J = 250.6, 11.8 Hz), 145.25 (s), 145.00 (s),

141.65 (s), 134.26 (s), 130.32 (s), 127.29 (s), 111.79 – 110.32 (m), 107.59 (t, *J* = 25.4 Hz), 101.77 (s), 32.52 (s), 21.66 (s).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -108.34 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub>NNaO<sub>3</sub>S (M+Na)<sup>+</sup> 374.0633, found 374.0619.



## (*E*)-*N*-(3-(3,4-dichlorophenyl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3l, 55%)

Light yellow solid, m.p. 153-155 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, *J* = 13.3 Hz, 1H), 7.95 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 3H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.03 (d, *J* = 13.3 Hz, 1H), 3.11 (s, 3H), 2.44 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  186.78 (s), 145.22 (s), 144.74 (s), 138.14 (s), 136.83 (s), 134.27 (s), 133.07 (s), 130.65 (s), 130.32 (s), 130.05 (s), 127.28 (s), 127.15 (s), 101.83 (s), 32.55 (s), 21.67 (s). HRMS (ESI, *m*/*z*) calcd. for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 384.0222, found 384.0217.



(*E*)-*N*-(3-(furan-2-yl)-3-oxoprop-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (3m, 63%) White solid, m.p. 129-130  $^{\circ}$ C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 (d, J = 13.6 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.61 – 7.51 (m, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 3.5 Hz, 1H), 6.54 (dd, J = 3.5, 1.6 Hz, 1H), 6.10 (d, J = 13.6 Hz, 1H), 3.10 (s, 3H), 2.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.51 (s), 153.61 (s), 145.75 (s), 145.00 (s), 142.96 (s), 134.39 (s), 130.23 (s), 127.22 (s), 116.26 (s), 112.45 (s), 102.58 (s), 32.48 (s), 21.63 (s). HRMS (ESI, m/z) calcd. for C<sub>15</sub>H<sub>16</sub>NO<sub>4</sub>S (M+H)<sup>+</sup> 306.0795, found 306.0789.

(*E*)-*N*,4-dimethyl-*N*-(3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)benzenesulfonamide (3n, 67%) White solid, m.p. 146-148 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, *J* = 13.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.62 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.05 (d, *J* = 13.4 Hz, 1H), 3.11 (s, 3H), 2.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 181.21 (s), 145.58 (s), 145.03 (s), 143.08 (s), 134.38 (s), 133.04 (s), 130.83 (s), 130.25 (s), 128.08 (s), 127.23 (s), 102.84 (s), 32.52 (s), 21.65 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>15</sub>H<sub>16</sub>NO<sub>3</sub>S<sub>2</sub> (M+H)<sup>+</sup> 322.0566, found 322.0564.



(E)-N-methyl-N-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4a, 69%)

White solid, m.p. 125-126 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, J = 13.5 Hz, 1H), 7.89 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 7.3 Hz, 2H), 7.68 – 7.61 (m, 1H), 7.60 – 7.52 (m, 3H), 7.46 (t, J = 7.5 Hz, 2H), 6.16 (d, J = 13.5 Hz, 1H), 3.12 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.36 (s), 143.62 (s), 138.44 (s), 137.46 (s), 133.85 (s), 132.50 (s), 129.65 (s), 128.55 (s), 128.10 (s), 127.20 (s), 103.41 (s), 32.57 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>16</sub>H<sub>16</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 302.0845, found 302.0842.



#### (*E*)-4-chloro-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4b, 89%) White solid, m.p. 152-153 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 13.5 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.19 (d, *J* = 13.5 Hz, 1H), 3.12 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.15 (s), 143.15 (s), 140.61 (s), 138.30 (s), 135.84 (s), 132.63 (s),

130.01 (s), 128.63 (s), 128.58 (s), 128.10 (s), 103.77 (s), 32.61 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>16</sub>H<sub>15</sub>ClNO<sub>3</sub>S (M+H)<sup>+</sup> 336.0456, found 336.0461.



#### (*E*)-4-bromo-*N*-methyl-*N*-(3-oxo-3-phenyl prop-1-en-1-yl)benzenesulfonamide (4c, 81%) White solid, m.p. 155-156 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 13.5 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.70 (s, 4H), 7.55 (m, *J* = 6.6, 3.8, 1.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 3.12 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.15 (s), 143.14 (s), 138.30 (s), 136.38 (s), 133.00 (s), 132.63 (s), 129.18 (s), 128.66 (s), 128.59 (s), 128.10 (s), 103.81 (s), 32.61 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>16</sub>H<sub>14</sub>BrNNaO<sub>3</sub>S (M+Na)<sup>+</sup> 401.9770, found 401.9773.



(*E*)-4-iodo-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4d, 45%) White solid, m.p. 156-157 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 13.5 Hz, 1H), 7.90 (t, *J* = 8.5 Hz, 4H), 7.54 (d, *J* = 8.7 Hz, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.19 (d, *J* = 13.5 Hz, 1H), 3.12 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.16 (s), 143.16 (s), 138.95 (s), 138.31 (s), 137.04 (s), 132.62 (s), 128.58 (s), 128.44 (s), 128.10 (s), 103.81 (s), 101.75 (s), 32.61 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>16</sub>H<sub>15</sub>INO<sub>3</sub>S (M+H)<sup>+</sup> 427.9812, found 427.9812.



#### (*E*)-4-fluoro-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4e, 51%) White solid, m.p. 127-128 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (d, *J* = 13.5 Hz, 1H), 7.99 – 7.80 (m, 4H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 13.7, 5.1 Hz, 2H), 6.18 (d, *J* = 13.5 Hz, 1H), 3.12 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  189.18 (s), 165.73 (d, *J* = 257.2 Hz), 143.28 (s), 138.35 (s), 133.51 (d, *J* = 3.3 Hz), 132.58 (s), 130.07 (d, *J* = 9.6 Hz), 128.57 (s), 128.09 (s), 117.03 (d, *J* = 22.8 Hz), 103.64 (s), 32.56 (s).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -102.64 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>16</sub>H<sub>15</sub>FNO<sub>3</sub>S (M+H)<sup>+</sup> 320.0751, found 320.0755.



# (*E*)-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-2-(trifluoromethoxy)benzenesulfonamide (4f, 29%)

Light yellow solid, m.p. 138-140 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 13.5 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.75 – 7.64 (m, 1H), 7.59 – 7.51 (m, 1H), 7.50 – 7.38 (m, 4H), 6.21 (d, *J* = 13.5 Hz, 1H), 3.20 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.33 (s), 146.24 (s), 143.68 (s), 138.43 (s), 135.82 (s), 132.42 (s), 131.82 (s), 129.61 (s), 128.53 (s), 128.08 (s), 126.78 (s), 121.58 – 118.57 (m), 103.36 (s), 32.84 (s). HRMS (ESI, m/z) calcd. for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 386.0668, found 386.0669.



(*E*)-4-methoxy-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4g, 49%) White solid, m.p. 120-121 °C

1H NMR (400 MHz, CDCl3)  $\delta$  8.36 (d, J = 13.4 Hz, 1H), 7.89 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 9.0 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 6.15 (d, J = 13.4 Hz, 1H), 3.86 (s, 3H), 3.09 (s, 3H).

13C NMR (101 MHz, CDCl3)  $\delta$  189.38 (s), 163.82 (s), 143.81 (s), 138.51 (s), 132.44 (s), 129.46 (s), 128.75 (s), 128.53 (s), 128.07 (s), 114.82 (s), 102.90 (s), 55.80 (s), 32.44 (s). HRMS (ESI, *m*/*z*) calcd. for C<sub>17</sub>H<sub>18</sub>NO<sub>4</sub>S (M+H)<sup>+</sup> 332.0951, found 332.0955.



(*E*)-*N*-methyl-4-nitro-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4h, 40%) Yellow solid, m.p. 139-141°C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.41 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 13.5 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.25 (d, *J* = 13.5 Hz, 1H), 3.18 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 188.86 (s), 150.69 (s), 142.98 (s), 142.45 (s), 138.08 (s), 132.82 (s), 128.64 (s), 128.54 (s), 128.12 (s), 124.91 (s), 104.73 (s), 32.80 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>NaO<sub>5</sub>S (M+Na)<sup>+</sup> 369.1516, found 369.0492.



 $(E) \mbox{-}4\mbox{-}cyano-N\mbox{-}methyl-N\mbox{-}(3\mbox{-}oxo\mbox{-}3\mbox{-}phenylprop\mbox{-}1\mbox{-}n\mbox{-}1\mbox{-}yl) benzenesulfonamide}\ ) \ (4i,\ 82\%)$ 

White solid, m.p. 164-165 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (d, J = 13.5 Hz, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.92 – 7.84 (m, 4H), 7.59 – 7.53 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.24 (d, J = 13.5 Hz, 1H), 3.16 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 188.89 (s), 142.54 (s), 141.49 (s), 138.10 (s), 133.44 (s), 132.81 (s),

128.64 (s), 128.11 (s), 127.83 (s), 117.61 (s), 116.89 (s), 104.55 (s), 32.77 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>NaO<sub>3</sub>S (M+Na)<sup>+</sup> 349.0617, found 349.0619.



(*E*)-4-(tert-butyl)-*N*-methyl-*N*-(3-oxo-3-phenyl prop-1-en-1-yl)benzenesulfonamide (4j, 50%) White solid, m.p. 185-187  $^{\circ}$ C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, J = 13.5 Hz, 1H), 7.89 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.58 – 7.51 (m, 3H), 7.45 (t, J = 7.5 Hz, 2H), 6.15 (d, J = 13.5 Hz, 1H), 3.13 (s, 3H), 1.33 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.47 (s), 157.86 (s), 143.86 (s), 138.52 (s), 134.42 (s), 132.44 (s), 128.53 (s), 128.08 (s), 127.09 (s), 126.65 (s), 103.12 (s), 35.32 (s), 32.54 (s), 30.99 (s). HRMS (ESI, m/z) calcd. for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 358.1471, found 358.1476.



(*E*)-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)naphthalene-1-sulfonamide (4k, 73%) White solid, m.p. 135-137 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.57 (d, *J* = 13.4 Hz, 1H), 8.53 (d, *J* = 8.6 Hz, 1H), 8.30 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.70 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.15 (d, *J* = 13.4 Hz, 1H), 3.09 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.42 (s), 143.55 (s), 138.50 (s), 135.77 (s), 134.41 (s), 132.43 (s), 132.13 (s), 130.97 (s), 129.33 (s), 129.15 (s), 128.53 (s), 128.08 (s), 128.05 (s), 127.41 (s), 124.25 (s), 123.90 (s), 102.45 (s), 32.65 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>18</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 352.1002, found 352.0998.



(*E*)-*N*-methyl-*N*-(3-oxo-3-phenyl prop-1-en-1-yl)naphthalene-2-sulfonamide (4l, 84%) White solid, m.p. 122-124  $^{\circ}$ C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.45 (d, *J* = 13.4 Hz, 2H), 8.07 – 7.96 (m, 2H), 7.94 – 7.83 (m, 3H), 7.75 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.57 – 7.50 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.16 (d, *J* = 13.5 Hz, 1H), 3.15 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.43 (s), 143.72 (s), 138.46 (s), 135.22 (s), 134.15 (s), 132.49 (s), 132.10 (s), 130.17 (s), 129.58 (s), 129.46 (s), 129.14 (s), 128.54 (s), 128.10 (s), 128.04 (s), 121.71 (s), 103.29 (s), 32.62 (s).

HRMS (ESI, *m/z*) calcd. for C<sub>20</sub>H<sub>18</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 352.1002, found 352.1005.



#### (*E*)-*N*,2,4,6-tetramethyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4m, 45%) White solid, m.p. 142-143 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 13.4 Hz, 1H), 7.90 (d, *J* = 7.1 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.45 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.00 (s, 2H), 6.14 (d, *J* = 13.4 Hz, 1H), 3.02 (s, 3H), 2.59 (s, 6H), 2.32 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.59 (s), 144.14 (s), 143.93 (s), 140.43 (s), 138.69 (s), 132.54 (s), 132.28 (s), 130.73 (s), 128.49 (s), 128.05 (s), 100.63 (s), 31.81 (s), 22.94 (s), 21.06 (s). HRMS (ESI, m/z) calcd. for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 344.1315, found 344.1317.



## (*E*)-*N*-ethyl-4-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4n, 55%) White solid, m.p. 106-107 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, *J* = 13.7 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.54 (m, *J* = 6.5, 3.8, 1.2 Hz, 1H), 7.45 (m, *J* = 10.3, 4.6 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.19 (d, *J* = 13.7 Hz, 1H), 3.62 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  189.61 (s), 144.92 (s), 142.58 (s), 138.68 (s), 135.50 (s), 132.34 (s), 130.21 (s), 128.52 (s), 128.04 (s), 127.28 (s), 102.33 (s), 41.44 (s), 21.64 (s), 12.41 (s). HRMS (ESI, *m*/*z*) calcd. for C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 330.1158, found 330.1155.



#### (*E*)-*N*-butyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (40, 67%) White solid, m.p. 106-108 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.29 (d, J = 13.7 Hz, 1H), 7.93 – 7.80 (m, 4H), 7.64 (dd, J = 8.5, 6.3 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.46 (t, J = 7.4 Hz, 2H), 6.19 (d, J = 13.7 Hz, 1H), 3.60 – 3.34 (m, 2H), 1.82 – 1.54 (m, 2H), 1.52 – 1.28 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.58 (s), 142.94 (s), 138.61 (s), 138.42 (s), 133.76 (s), 132.40 (s), 129.60 (s), 128.55 (s), 128.04 (s), 127.20 (s), 102.98 (s), 46.47 (s), 28.98 (s), 20.06 (s), 13.66 (s). HRMS (ESI, m/z) calcd. for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 344.1315, found 344.1313.



#### (*E*)-*N*-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)methanesulfonamide (4p, 76%) White solid, m.p. 112-114 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 13.5 Hz, 1H), 7.92 (d, *J* = 7.1 Hz, 2H), 7.63 – 7.52 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 6.25 (d, *J* = 13.5 Hz, 1H), 3.28 (s, 3H), 3.04 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.33 (s), 143.35 (s), 138.39 (s), 132.58 (s), 128.60 (s), 128.11 (s), 103.20 (s), 39.74 (s), 32.70 (s).

HRMS (ESI, m/z) calcd. for C<sub>11</sub>H<sub>14</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 240.0689, found 240.0687.

#### (E)-3-(1,1-dioxido-1,2-thiazinan-2-yl)-1-phenylprop-2-en-1-one (4q, 32%)

Yellow solid, m.p. 120-121 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, J = 13.7 Hz, 1H), 7.89 (d, J = 7.1 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.46 (t, J = 7.5 Hz, 2H), 6.30 (d, J = 13.7 Hz, 1H), 4.05 – 3.91 (t, 2H), 3.26 – 3.10 (t, 2H), 2.35 – 2.23 (m, 2H), 1.83 – 1.72 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.82 (s), 142.58 (s), 138.61 (s), 132.39 (s), 128.54 (s), 128.05 (s), 102.08 (s), 51.10 (s), 47.09 (s), 23.87 (s), 21.96 (s).

HRMS (ESI, m/z) calcd. for C<sub>13</sub>H<sub>16</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 266.0845, found 266.0835.



#### $\label{eq:constraint} 2-((4-methoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1-phenylpropan-1-one$

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.05 (q, *J* = 7.1 Hz, 1H), 3.50 – 3.35 (m, 1H), 3.31 (s, 3H), 1.91 (d, *J* = 12.5 Hz, 1H), 1.79 (d, *J* = 12.5 Hz, 1H), 1.51 (d, *J* = 7.1 Hz, 3H), 1.46 – 1.27 (m, 5H), 1.24 (s, 3H), 1.11 (s, 3H), 0.92 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  201.56 (s), 135.10 (s), 133.13 (s), 129.13 (s), 128.54 (s), 86.04 (s), 71.54 (s), 59.97 (s), 59.95 (s), 55.74 (s), 45.02 (s), 44.97 (s), 34.19 (s), 33.76 (s), 21.34 (s), 21.23 (s), 19.27 (s).



#### 3-morpholino-1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propan-1-one

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 5.07 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.46 – 3.30 (m, 4H), 3.02 – 2.79 (m, 2H), 2.50 – 2.34 (m, 2H), 2.32 – 2.18 (m, 2H), 1.50 (s, 3H), 1.46 – 1.23 (m, 6H), 1.17 (s, 3H), 1.06 (s, 3H), 0.87 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  201.77 (s), 137.43 (s), 132.41 (s), 128.70 (s), 128.30 (s), 86.34 (s), 66.79 (s), 60.43 (s), 60.32 (s), 59.62 (s), 53.72 (s), 40.37 (s), 33.88 (s), 33.70 (s), 20.25 (s), 17.08 (s).

#### NMR Spectra for the products and key intermediates (*E*)-*N*,4-dimethyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (3a)





(E)-N,4-dimethyl-N-(3-oxo-3-(p-tolyl)prop-1-en-1-yl)benzenesulfonamide (3b)



(E)-N,4-dimethyl-N-(3-oxo-3-(m-tolyl)prop-1-en-1-yl)benzenesulfonamide (3c)



(E) - N - (3 - (4 - ethylphenyl) - 3 - oxoprop - 1 - en - 1 - yl) - N, 4 - dimethylbenzen esulfonamide (3d)





















-----106.3138











-127 -128 -129 -130 -131 -132 -133 -134 -135 -136 -137 -138 -139 -140 -141 -142 -143 -144 f1 (ppm)









(E) - N - (3 - (3, 4 - dichlorophenyl) - 3 - oxoprop - 1 - en - 1 - yl) - N, 4 - dimethyl benzenesulfonamide (3l)

































-----102.6439

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm) (E) - N - methyl- N - (3 - oxo- 3 - phenylprop- 1 - en- 1 - yl) - 2 - (trifluoromethoxy) benzenesulfonamide (4f)





(E) - 4 - methoxy - N - methyl - N - (3 - oxo - 3 - phenyl prop - 1 - en - 1 - yl) benzenesul fonamide (4g)











S43











(E)-N, 2, 4, 6-tetramethyl-N-(3-oxo-3-phenylprop-1-en-1-yl) benzenesul fonamide (4m)







#### (E)-N-butyl-N-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (4n)









#### (E)-3-(1,1-dioxido-1,2-thiazinan-2-yl)-1-phenylprop-2-en-1-one (4q)



#### 2-((4-methoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-1-phenylpropan-1-one





N-(2-((4-methoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-oxo-3-phenylpropyl)-N,4-dimethylbenzenesulfonamide



## Single-crystal X-ray analysis





#### Reference

1. X. Jie, Y. Shang, X. Zhang and W. Su, J. Am. Chem. Soc., 2016, 138, 5623-5633