### **Supporting Information for**

### Formal Intermolecular [2+2] Cycloaddition Reaction of Alleneamides

### with Alkenes via Gold Catalysis

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### **General Conditions**

All reactions were run under an inert atmosphere  $(N_2)$  with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. THF and CH<sub>2</sub>Cl<sub>2</sub> were obtained by fresh distilled over sodium/benzophenone or Calcium hydride respectively. Commercial reagents were used as supplied or purified by standard techniques where necessary. Column chromatography was performed using 200-300 mesh silica with the proper solvent system according to TLC analysis using KMnO<sub>4</sub> stain and UV light to visualize the reaction components. Unless otherwise noted, nuclear magnetic resonance spectra were recorded on 400 MHz spectrometer. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t =triplet, m = multiplet and bs = broad singlet), coupling constant in Hz and integration. Chemical shifts for <sup>13</sup>C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.0 ppm) as the internal standard. IR spectra were recorded on an FTIR spectrometer (KBr) and reported in reciprocal centimeters (cm<sup>-1</sup>). Low-resolution MS and HRMS data were obtained using ESI ionization. Mp data were measured with micro melting point apparatus.

Allenamides **2-10** were prepared according to the published methods.<sup>1, 2, 3</sup> Alkenes were obtained commercially and used without further purification.

#### **General Procedure for [2+2] cycloaddition reaction.**



To a solution of JohnphosAuCl/AgSbF<sub>6</sub> (2 mol%) in dry  $CH_2Cl_2$  (1 mL) containing 100mg activated 4Å MS, was added ether **a** (0.3 mmol) and a solution of alleneamide **5** (0.1 mmol) in  $CH_2Cl_2$  (1 mL) consecutively. The reaction mixture was stirred at rt until the complete consumption of the starting material (TLC monitoring). Then the mixture was concentrated in vacuum, and the residue was purified by chromatography on silica gel using hexane/EtOAc (20:1) as the eluent to afford 5a in 86% yield.

### General Procedure for the Synthesis of D-5



To a solution of Ph<sub>3</sub>PAuCl/AgSbF<sub>6</sub> (2 mol%) in dry  $CH_2Cl_2$  (1 mL) containing 100mg activated 4Å MS, was added alleneamide **5** (0.1 mmol) in 1 mL  $CH_2Cl_2$ . The reaction mixture was stirred at rt until the complete consumption of the starting material (TLC monitoring). Then the mixture was concentrated in vacuum, and the residue was purified by chromatography on silica gel using hexane/EtOAc (5:1) as the eluent to afford *D-5* in 90% yield.

### NOE data for compound anti-5i, syn-5i and 5n, 5o.



Compound anti-5i



Compound syn-5i





Compound 5n







The reaction of allene 5 with deuterated substrate o.



In the above spectrum, the total integral data for  $H_a$  and  $H_b$  is more than 1.19. The ratio of  $H_a/H_b$  is equal to 0.76/0.24. We repeated this reaction three times, similar results were obtained.

As compared with the ratio of  $H_a/H_b = 82\%/18\%$  in compound **o**, 6% of product underwent a possible isomerization to give the isomerized product.

#### The reaction of allene 5 with deuterated substrate i.





However, in the reaction of vinyl ether **i** with allene **5** (Eq. 5), The E/Z ratio of the substrate is equal to the anti/syn ratio of the product.

### **Characterization Data**

3-(propa-1,2-dien-1-yl)oxazolidin-2-one 4,<sup>2</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.81 (t, *J* = 6.4Hz, 1H), 5.39 (d, *J* = 6.3Hz, 2H), 4.37 (t, *J* = 7.9Hz, 2H), 3.56 (t, *J* = 8.2Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.4, 155.2, 96.9, 87.8, 62.3, 43.1.

### N-(4-fluorobenzyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 5



White solid; Mp 104.5-106.5°C; IR(neat) 1597, 1510, 1346, 1220, 1163, 1093, 908, 885, 588, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (d, *J* =8.2Hz, 2H), 7.32 (d, *J* =8.1Hz, 2H), 7.27 (dd, *J* =8.2, 5.4Hz, 2H), 6.96 (t, *J* = 5.3Hz, 2H), 6.81 (t, *J* = 6.2Hz, 1H), 5.15 (d, *J* = 6.2Hz, 2H), 4.30 (s, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.1, 162.1 (d, *J* = 244.3Hz), 143.9, 135.2, 131.8, 129.7, 129.5 (d, *J* = 8.1Hz), 127.1, 115.1 (d, *J* = 21.3Hz), 99.9, 88.0, 49.3, 21.5; HRMS (ESI) calcd for C<sub>17</sub>H<sub>17</sub>FNO<sub>2</sub>S [M+H]<sup>+</sup> 318.0964; found, 318.0963.

#### N-butyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 6



yellow oil; IR(neat) 2958, 1699, 1597, 1456, 1355, 1166, 1089, 920, 813, 665, 592, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (d, J = 8.3Hz, 2H), 7.30 (d, J = 8.2Hz, 2H), 6.81 (t, J = 6.2Hz, 1H), 5.28 (d, J = 6.2Hz, 2H), 3.09 (t, J = 7.2Hz, 2H), 2.42 (s, 3H), 1.55-1.47 (m, 2H), 1.35-1.26 (m, 2H), 0.89 (t, J = 7.3Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.6, 143.6, 135.6, 129.7, 127.2, 100.2, 87.4, 46.4, 30.0, 21.6, 19.8, 13.7; HRMS (ESI) calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> 266.1215; found, 266.1208.

### N-benzyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 7,<sup>4</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, J = 8.3Hz, 2H), 7.32 (d, J = 7.9Hz, 2H), 7.30-7.24 (m, 5H), 6.83 (t, J = 6.2Hz, 1H), 5.15 (d, J = 6.2Hz, 2H), 4.30 (s, 2H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.2, 143.8, 136.2, 135.4, 129.7, 128.3, 127.8, 127.4, 127.2, 100.1, 87.9, 50.0, 21.5.

4-methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 8, <sup>5</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, J = 8.3Hz, 2H), 7.31-7.26 (m, 5H), 7.10 (t, J = 6.3Hz, 1H), 7.01-6.98 (m, 2H), 5.02 (d, J = 6.3Hz, 2H), 2.43 (S, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 143.8, 137.1, 135.2, 129.5, 129.4, 128.6, 128.5, 127.6, 102.3, 87.4, 21.5.

### N-mesityl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide 9



White solid; mp 135.5-137.5°C; IR(neat) 1597, 1355, 1249, 1165, 1031, 979. 812, 661, 594, 542; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.2Hz, 2H), 7.29 (d, *J* = 6.3Hz, 2H), 7.15 (t, *J* = 6.2Hz, 1H), 6.82 (s, 2H), 5.01 (d, *J* = 6.2Hz, 2H), 2.43 (s, 3H), 2.25 (s, 3H), 1.92(s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.5, 143.6, 138.6, 138.4, 137.7, 132.1, 129.7, 129.3, 127.3, 101.2, 86.9, 21.5, 21.0, 18.2; HRMS (ESI) calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> 328.1371; found, 328.1367.

### 2-(propa-1,2-dien-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide 10



Yellow solid; mp 100.5-102.5°C; IR(neat) 1460, 1361, 1296, 1172, 1136, 750, 599, 567, 439; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, J = 7.8Hz, 1H), 7.63 (td, J = 7.5, 0.9Hz, 1H), 7.54 (t, J = 7.7Hz, 1H), 7.42 (d, J = 7.7Hz, 1H), 6.76 (t, J = 6.2Hz, 1H), 5.51 (d, J = 6.2Hz, 2H), 4.46 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.0, 134.8, 133.1, 132.8, 129.2, 124.6, 121.4, 95.3, 88.6, 48.6; HRMS (ESI) calcd for C<sub>10</sub>H<sub>10</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> 208.0432; found, 208.0423.

## 4-methyl-N-(naphthalen-2-ylmethyl)-N-(propa-1,2-dien-1-yl)benzenesulfonamide 11



Yellow oil; IR(neat) 2956, 2924, 1726, 1286, 1165, 1122, 1074, 744, 665, 592; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83-7.77 (m, 3H), 7.75 (d, *J* = 8.2Hz, 2H), 7.71 (s, 1H), 7.49-7.44 (m, 3H), 7.32 (d, *J* = 8.1Hz, 2H), 6.88 (t, *J* = 6.2Hz, 1H), 5.14 (d, *J* = 6.2Hz, 2H), 4.48 (s, 2H), 2.43 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.3, 143.9, 135.3, 133.6, 133.2, 132.8, 129.8, 128.1, 127.7, 127.6, 127.2, 126.9, 126.1, 125.9, 125.7, 100.1, 88.1, 50.3, 21.6; HRMS (ESI) calcd for C<sub>21</sub>H<sub>20</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> 350.1215; found, 350.1209.

### (Z)-3-(2-oxabicyclo[4.2.0]octan-8-ylidenemethyl)oxazolidin-2-one (4a)



18.2 mg white solid was obtained from 0.1 mmol scale reaction (82% yield), Rf = 0.25 (PE/EA = 5:1); mp 95.2-97.2°C; IR (neat) 2920, 1732, 1693, 1417, 1122, 1056, 1029, 752, 634; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.42 (d, *J* = 1.8Hz, 1H), 4.71 (dt, *J* = 6.8, 1.9Hz, 1H), 4.34 (t, *J* = 8.7Hz, 2H), 4.20-4.14 (m, 1H), 3.73 (q, *J* = 9.2Hz, 1H),

3.68-3.63 (m, 1H), 3.56-3.51 (m, 1H), 2.47-2.36 (m, 2H), 2.26-2.21 (m, 1H), 1.99-1.90 (m, 1H), 1.63-1.56 (m, 1H), 1.54-1.44 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 121.5, 118.4, 72.5, 63.3, 62.4, 44.3, 30.4, 30.3, 25.2, 22.0; HRMS (ESI) calcd for C<sub>11</sub>H<sub>15</sub>NNaO<sub>3</sub> [M+Na]<sup>+</sup> 232.0950; found, 232.0961.

## (Z)-N-(2-oxabicyclo[4.2.0]octan-8-ylidenemethyl)-N-(4-fluorobenzyl)-4-methylbe nzenesulfonamide (5a):



35.1 mg white solid was obtained from 0.1 mmol scale reaction (87% yield), Rf = 0.25 (PE/EA = 30:1); mp 102.7-104.7°C; IR (neat) 2926, 2852, 1508, 1348, 1220, 1165, 813, 663, 572, 545 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.28-7.26 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.35 (s, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.55 (d, *J* = 15.7Hz, 1H), 4.15 (d, *J* = 6.3Hz, 1H), 3.22 (dt, *J* = 11.2, 3.8 Hz, 1H), 2.72 (td, *J* = 11.4, 3.2 Hz, 1H), 2.42 (s, 3H), 2.25-2.17 (m, 2H), 1.98-1.92 (m, 2H), 1.33-1.26 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.3 (d, *J* = 243.9 Hz), 143.5, 136.3, 133.2, 129.6, 128.6 (d, *J* = 7.9 Hz), 127.1, 126.5, 120.0, 115.1 (d, *J* = 21.3 Hz), 72.2, 62.2, 49.4, 30.5, 30.0, 25.8, 22.3, 21.5; HRMS (ESI) calcd for C<sub>22</sub>H<sub>24</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup>424.1359; found, 424.1358.

### (Z)-tert-butyl 8-((N-(4-fluorobenzyl)-4-methylphenylsulfonamido)methylene)-2azabicyclo[4.2.0]octane-2-carboxylate (5b)



39 mg colorless oil was obtained from 0.1 mmol scale reaction (78% yield), Rf = 0.25 (PE/EA = 15:1); IR (neat) 2920, 2870, 1680, 1508, 1263, 1093, 1020, 800, 550, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (major) 7.65 (d, *J* = 7.7Hz, 2H), 7.32-7.26 (m, 4H), 6.99-6.92 (m, 2H), 6.01 (s, 1H), 5.20 (d, *J* = 7.9Hz, 1H), 4.70 (d, *J* = 15.3Hz, 1H),

4.32 (d, J = 15.8Hz, 1H), 3.35-3.29 (m, 1H), 2.48-2.37 (m, 5H), 2.10-2.04 (m, 1H), 1.95 (s, 1H), 1.85-1.77 (m, 1H), 1.47-1.43 (m, 11H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1(d, J = 242.6Hz), 154.7, 143.2, 137.2, 134.9, 132.8, 129.6(d, J = 25.6Hz), 127.0, 118.9, 115.0(d, J = 21.6Hz), 79.6, 51.9, 50.8, 41.2, 31.0, 30.6, 28.3, 26.7, 21.4, 20.8; HRMS (ESI) calcd for C<sub>27</sub>H<sub>33</sub>FN<sub>2</sub>O<sub>4</sub>NaS [M+Na]<sup>+</sup> 523.2043; found, 523.2043.

## (Z)-N-(2-oxabicyclo[3.2.0]heptan-7-ylidenemethyl)-N-(4-fluorobenzyl)-4-methylb enzenesulfonamide (5c)



34.5 mg white solid was obtained from 0.1 mmol scale reaction (89% yield), Rf = 0.25 (PE/EA = 20:1); mp 109.0-111.0°C; IR (neat) 2924, 2856, 1672, 1510, 1346, 1220, 1165, 813, 665, 563, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (d, *J* = 8.2Hz, 2H), 7.31 (d, *J* = 8.2Hz, 2H), 7.26-7.23 (m, 2H), 6.99 (t, *J* = 8.7Hz, 2H), 6.43 (s, 1H), 4.87 (d, *J* = 16.6Hz, 1H), 4.61 (d, *J* = 16.6Hz, 1H), 4.41 (d, *J* = 5.8Hz, 1H), 3.87 (t, *J* = 7.9Hz, 1H), 3.56-3.50 (m, 1H), 2.77-2.70 (m, 1H), 2.63-2.56 (m, 1H), 2.43 (s, 3H), 2.06-2.01 (m, 1H), 1.77-1.69 (m, 1H), 1.67-1.61 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1(d, *J* = 240.6Hz), 143.7, 136.2, 133.1, 129.7, 127.8 (d, *J* = 8.1), 126.8, 122.3, 122.1, 115.3 (d, *J* = 21.4Hz), 79.9, 66.2, 48.9, 35.7, 32.3, 30.3, 21.5; HRMS (ESI) calcd for C<sub>21</sub>H<sub>22</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup>410.1202; found, 410.1201.

## (Z)-tert-butyl 7-((N-(4-fluorobenzyl)-4-methylphenylsulfonamido)methylene)-2azabicyclo[3.2.0]heptane-2-carboxylate (5d)



42.3 mg yellow solid was obtained from 0.1 mmol scale reaction (87% yield), Rf = 0.25 (PE/EA = 20:1); mp 139.1-141.1°C; IR (neat) 2974, 2929, 1685, 1510, 1402, 1161, 815, 746, 570, 551, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (major) 7.62 (d, J = 8.1Hz, 2H), 7.38-7.26 (m, 4H), 6.98 (t, J = 8.7Hz, 2H), 6.16 (s, 1H), 5.21-5.07 (m,

1H), 4.93-4.84 (m, 1H), 4.73 (d, J = 15.4Hz, 1H), 3.88-3.80 (m, 1H), 2.95-2.79 (m, 2H), 2.60-2.56 (m, 1H), 2.42 (s, 3H), 2.11-2.03 (m, 1H), 1.72-1.59 (m, 1H), 1.53-1.40 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, J = 242.1Hz), 153.2, 143.3, 136.8, 132.9, 129.6, 129.0 (d, J = 15.3Hz), 126.9, 126.7, 115.2 (d, J = 20.6Hz), 79.6, 60.4, 48.3, 44.8, 35.9, 31.4, 30.5, 28.3, 21.5; HRMS (ESI) calcd for C<sub>26</sub>H<sub>31</sub>FN<sub>2</sub>O<sub>4</sub>NaS [M+Na]<sup>+</sup> 509.1886; found, 509.1886.

(Z)-N-(4-fluorobenzyl)-N-((3-methoxy-2-oxabicyclo[4.2.0]octan-8-ylidene)methyl) -4-methylbenzenesulfonamide (5e)



34 mg white solid was obtained from 0.1 mmol scale reaction (79% yield), Rf = 0.25 (PE/EA = 15:1); mp 127.6-129.6°C; IR (neat) 2926, 2856, 1510, 1346, 1222, 1163, 813, 565, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (major) 7.69 (d, J = 8.2Hz, 2H), 7.29 (d, J = 8.1Hz, 2H), 7.26-7.22 (m, 2H), 6.97 (t, J = 8.6Hz, 2H), 6.38 (s, 1H), 4.82 (d, J = 16.4Hz, 1H), 4.59 (d, J = 16.3Hz, 1H), 4.31 (t, J = 5.2Hz, 1H), 4.20 (d, J = 6.5Hz, 1H), 3.18 (s, 3H), 2.50-2.46 (m, 1H), 2.43 (s, 3H), 2.41-2.36 (m, 1H), 2.31-2.18 (m, 1H), 1.89-1.82 (m, 1H), 1.78-1.72 (m, 1H), 1.70-1.59 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.0 (d, J = 243.5Hz), 143.6, 136.2, 133.0, 129.6, 128.3 (d, J = 7.9Hz), 127.1, 123.9, 121.1, 115.3 (d, J = 21.3Hz), 98.5, 69.9, 55.2, 49.2, 31.5, 30.1, 27.1, 21.9, 21.5; HRMS (ESI) calcd for C<sub>23</sub>H<sub>26</sub>FNO<sub>4</sub>NaS [M+Na]<sup>+</sup> 454.1464; found, 454.1464.

(Z)-N-((2-ethoxycyclobutylidene)methyl)-N-(4-fluorobenzyl)-4-methylbenzenesul fonamide (5f)



28.4 mg colorless oil was obtained from 0.1 mmol scale reaction (73% yield), Rf =

0.25 (PE/EA = 30:1); IR (neat) 2926, 2850, 1598, 1515, 1336, 1222, 1163, 813, 572, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, J = 8.2Hz, 2H), 7.29 (d, J = 8.1Hz, 2H), 7.24 (dd, J = 8.3, 5.6Hz, 2H), 6.98 (t, J = 8.7Hz, 2H), 6.28 (s, 1H), 4.80 (d, J = 16.2Hz, 1H), 4.62 (d, J = 16.2Hz, 1H), 4.04-3.99 (m, 1H), 3.25-3.18 (m, 1H), 3.16-3.11 (m, 1H), 2.51-2.44 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.9 (d, J = 245.0Hz), 143.5, 136.5, 133.3, 129.6, 128.2 (d, J = 7.9Hz), 127.0, 126.0, 120.3, 115.1 (d, J = 21.3Hz), 75.8, 61.9, 49.5, 25.5, 22.7, 21.5, 15.3; HRMS (ESI) calcd for C<sub>21</sub>H<sub>24</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup>412.1359; found, 412.1357.

# (Z)-N-((2-butoxycyclobutylidene)methyl)-N-(4-fluorobenzyl)-4-methylbenzenesul fonamide (5g)



33.4 mg colorless oil was obtained from 0.1 mmol scale reaction (80% yield), Rf = 0.25 (PE/EA = 40:1); IR (neat) 2956, 2931, 2872, 1728, 1602, 1510, 1336, 1222, 1161, 815, 663, 576, 549; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.2Hz, 2H), 7.28 (d, *J* = 8.1Hz, 2H), 7.24 (dd, *J* = 8.5, 5.5Hz, 2H), 6.98 (t, *J* = 8.7Hz, 2H), 6.29 (s, 1H), 4.78 (d, *J* = 16.2Hz, 1H), 4.62 (d, *J* = 16.2Hz, 1H), 4.04-3.99 (m, 1H), 3.20-3.15 (m, 1H), 3.12-3.06 (m, 1H), 2.50-2.45 (m, 1H), 2.42 (s, 3H), 2.29-2.21 (m, 1H), 2.08-1.99 (m, 1H), 1.90-1.81 (m, 1H), 1.40-1.33 (m, 2H), 1.27-1.17 (m, 2H), 0.86 (t, *J* = 7.3Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.9 (d, *J* = 243.6Hz), 143.4, 136.5, 133.3, 129.6, 128.2 (d, *J* = 7.9Hz), 127.0, 125.9, 120.2, 115.1 (d, *J* = 21.4Hz), 75.8, 66.4, 49.3, 31.9, 25.6, 22.6, 21.5, 19.5, 13.9; HRMS (ESI) calcd for C<sub>23</sub>H<sub>29</sub>FNO<sub>3</sub>S [M+Na]<sup>+</sup>440.1672; found, 440.1644.

(Z)-N-(4-fluorobenzyl)-N-((2-methoxy-2-methylcyclobutylidene)methyl)-4-methyl benzenesulfonamide(5h)



26.8 mg white solid was obtained from 0.1 mmol scale reaction (69% yield), Rf = 0.25 (PE/EA = 20:1); mp 108.6-110.6°C; IR (neat) 2949, 2929, 1602, 1510, 1346, 1220, 1163, 813, 663, 570, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (d, *J* = 8.2Hz, 2H), 7.25 (d, *J* = 8.8Hz, 2H), 7.19 (dd, *J* = 8.5, 5.5Hz, 2H), 6.94 (t, *J* = 8.7Hz, 2H), 6.32 (s, 1H), 4.80 (s, 2H), 2.91 (s, 3H), 2.41 (s, 3H), 2.32-2.23 (m, 3H), 1.62-1.57 (m, 1H), 1.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.9 (d, *J* = 243.4Hz), 143.6, 136.5, 132.8, 129.5, 128.5 (d, *J* = 7.9Hz), 127.1, 119.6, 115.1 (d, *J* = 21.3Hz), 81.7, 50.6, 50.3, 28.0, 24.2, 21.8, 21.5; HRMS (ESI) calcd for C<sub>21</sub>H<sub>24</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup> 412.1359; found, 412.1386.

## *N*-((*Z*)-((*2S*\*,*3R*\*)-2-ethoxy-3-methylcyclobutylidene)methyl)-N-(4-fluorobenzyl)-4-methylbenzenesulfonamide(*anti*-5i)



33.8 mg yellow oil was obtained from 0.1 mmol scale reaction (84% yield), Rf = 0.25 (PE/EA = 30:1); IR (neat) 2927, 2873, 1724, 1602, 1510, 1332, 1222, 1161, 1091, 813, 663, 576, 549; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.3Hz, 2H), 7.28 (d, *J* = 8.2Hz, 2H), 7.24 (dd, *J* = 8.4, 5.5Hz, 2H), 6.98 (t, *J* = 8.7Hz, 2H), 6.22 (s, 1H), 4.78 (d, *J* = 16.1Hz, 1H), 4.58 (d, *J* = 16.1Hz, 1H), 3.59-3.56 (m, 1H), 3.32-3.24 (m, 1H), 3.22-3.15 (m, 1H), 2.63-2.55 (m, 1H), 2.42 (s, 3H), 2.29-2.19 (m, 1H), 1.78 (qd, *J* = 7.6, 2.3Hz, 1H), 1.04-1.00 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, *J* = 243.4Hz), 143.4, 136.5, 133.3, 129.6, 128.4 (d, *J* = 7.9Hz), 127.1, 120.3, 115.2 (d, *J* = 21.3Hz), 82.9, 62.5, 49.7, 34.3, 30.2, 21.5, 19.9, 15.4; HRMS (ESI) calcd for C<sub>22</sub>H<sub>26</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup> 426.1515; found, 426.1516.

### $N-((Z)-((2S^*,3S^*)-2-ethoxy-3-methylcyclobutylidene)methyl)-N-(4-fluorobenzyl)-$

4-methylbenzenesulfonamide(syn-5i)



33.8 mg yellow oil was obtained from 0.1 mmol scale reaction (84% yield), Rf = 0.25 (PE/EA = 80:1); IR (neat) 2972, 2927, 1600, 1510, 1338, 1222, 1163, 663, 584, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 8.3Hz, 2H), 7.28 (d, J = 7.9Hz, 2H), 7.26-7.23 (m, 2H), 6.97 (t, J = 8.7Hz, 2H), 6.10 (d, J = 1.4Hz, 1H), 4.78 (d, J = 15.8Hz, 1H), 4.52 (d, J = 15.8Hz, 1H), 4.00-3.98 (m, 1H), 3.31-3.23 (m, 1H), 3.22-3.14 (m, 1H), 2.42 (s, 3H), 2.40-2.32 (m, 2H), 1.87-1.83 (m, 1H), 1.03 (t, J = 7.0Hz, 3H), 0.92 (d, J = 6.8Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, J = 249.6Hz), 143.2, 136.4, 133.2, 130.0, 129.5, 128.7 (d, J = 7.9Hz), 127.2, 120.8, 115.2 (d, J = 21.3Hz), 64.4, 50.4, 31.4, 30.7, 21.5, 15.2, 14.1 (one peak was hided in the cdcl3); HRMS (ESI) calcd for C<sub>22</sub>H<sub>26</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup>426.1515; found, 426.1516.

(Z)-N-((2-(4-ethoxyphenyl)cyclobutylidene)methyl)-N-(4-fluorobenzyl)-4-methylb enzenesulfonamide (5j)



38.6 mg white solid was obtained from 0.1 mmol scale reaction (83% yield), Rf = 0.25 (PE/EA = 30:1); mp 104.7-106.7°C; IR (neat) 2980, 2926, 1606, 1580, 1352, 1244, 1163, 815, 572, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d, *J* = 8.1Hz, 2H), 7.31 (d, *J* = 8.0Hz, 2H), 6.98 (dd, *J* = 8.3, 5.6Hz, 2H), 6.91 (t, *J* = 8.6Hz, 2H), 6.86 (d, *J* = 8.5Hz, 2H), 6.64 (d, *J* = 8.5Hz, 2H), 5.88 (d, *J* = 1.5Hz, 1H), 4.36 (d, *J* = 15.5Hz, 1H), 4.00 (q, *J* = 7.0Hz, 2H), 3.91-3.87 (m, 1H), 3.75 (d, *J* = 15.5Hz, 1H), 2.72-2.58 (m, 2H), 2.48 (s, 3H), 2.37-2.28 (m,1H), 1.85-1.76 (m, 1H), 1.43 (t, *J* = 7.0Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, *J* = 232.8Hz), 157.3, 143.4, 136.3, 135.5,

132.4, 129.6, 128.9 (d, J = 8.0Hz), 128.0, 127.2, 118.0, 115.1 (d, J = 21.3Hz), 114.4, 63.3, 50.9, 46.8, 27.7, 26.8, 21.6, 14.9; HRMS (ESI) calcd for C<sub>27</sub>H<sub>28</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup> 488.1672; found, 488.1671.

(Z)-N-(4-fluorobenzyl)-4-methyl-N-((2-(p-tolyl)cyclobutylidene)methyl)benzenes ulfonamide (5k)



27.4 mg white solid was obtained from 0.1 mmol scale reaction (63% yield), Rf = 0.25 (PE/EA = 30:1); mp 96.3-98.3°C; IR (neat) 2925, 2846, 1604, 1510, 1354, 1163, 813, 572, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d, *J* = 8.2Hz, 2H), 7.31 (d, *J* = 8.0Hz, 2H), 6.98 (dd, *J* = 8.5, 5.8Hz, 2H), 6.93-6.88 (m, 4H), 6.85 (d, *J* = 8.0Hz, 2H), 5.91 (d, *J* = 1.8Hz, 1H), 4.37 (d, *J* = 15.7Hz, 1H), 3.92-3.88 (m, 1H), 3.75 (d, *J* = 15.6Hz, 1H), 2.75-2.59 (m, 2H), 2.49 (s, 3H), 2.39-2.34 (m, 1H), 2.32 (s, 3H), 1.86-1.77 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.3 (d, *J* = 226.9Hz), 143.4, 140.5, 136.3, 135.7, 135.6, 132.4, 129.6, 129.2, 128.8 (d, *J* = 7.9Hz), 127.2, 126.9, 118.1, 115.1 (d, *J* = 21.3Hz), 50.8, 47.2, 27.7, 26.9, 21.6, 21.1; HRMS (ESI) calcd for C<sub>26</sub>H<sub>27</sub>FNO<sub>2</sub>S [M+H]<sup>+</sup> 436.1747; found, 436.1749.

(Z)-N-((2-(4-(tert-butyl)phenyl)cyclobutylidene)methyl)-N-(4-fluorobenzyl)-4-me thylbenzenesulfonamide (5m)



32.4 mg white solid was obtained from 0.1 mmol scale reaction (68% yield), Rf = 0.25 (PE/EA = 100:1); mp 100.8-102.8°C; IR (neat) 2960, 2866, 1604, 1508, 1357, 1163, 827, 574, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d, *J* = 8.2Hz, 2H), 7.32 (d, *J* 

= 8.2Hz, 2H), 7.10 (d, J = 8.3Hz, 2H), 6.98 (dd, J = 8.5, 5.6Hz, 2H), 6.90 (t, J = 8.7Hz, 2H), 6.85 (d, J = 8.2Hz, 2H), 5.95 (d, J = 1.9Hz, 1H), 4.36 (d, J = 15.6Hz, 1H), 3.93-3.87 (m, 1H), 3.75 (d, J = 15.6Hz, 1H), 2.74-2.58 (m, 2H), 2.49 (s, 3H), 2.38-2.29 (m, 1H), 1.86-1.78 (m, 1H), 1.31(s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, J = 242.7Hz), 148.9, 143.4, 140.4, 136.4, 135.1, 132.5, 129.7, 128.8 (d, J = 7.9Hz), 127.3, 126.6, 125.3, 118.1, 115.1 (d, J = 21.3Hz), 50.6, 47.0, 34.4, 31.4, 27.7, 26.9, 21.6; HRMS (ESI) calcd for C<sub>29</sub>H<sub>33</sub>FNO<sub>2</sub>S [M+H]<sup>+</sup>478.2216; found, 478.2216.

N-(4-fluorobenzyl)-N-((Z)-((2R,3R)-2-(4-methoxyphenyl)-3-methylcyclobutyliden e)methyl)-4-methylbenzenesulfonamide (5n)



39.5 mg white solid was obtained from 0.1 mmol scale reaction (85% yield), Rf = 0.25 (PE/EA = 20:1); mp 116.4-118.4°C; IR (neat) 2951, 2920, 1606, 1510, 1346, 1247, 1163, 1035, 813, 572, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d, *J* = 8.0Hz, 2H), 7.34 (d, *J* = 8.0Hz, 2H), 7.04-7.00 (m, 2H), 6.95 (t, *J* = 8.6Hz, 2H), 6.85 (d, *J* = 8.4Hz, 2H), 6.65 (d, *J* = 8.3Hz, 2H), 5.95 (s, 1H), 4.38 (d, *J* = 15.4Hz, 1H), 3.82 (s, 3H), 3.75 (d, *J* = 15.5Hz, 1H), 3.34-3.32 (m, 1H), 2.85-2.78 (m, 1H), 2.50 (s, 3H), 2.22-2.32 (m, 2H), 1.08 (d, *J* = 6.2Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.0 (d, *J* = 241.0Hz), 158.0, 143.4, 136.4, 134.6, 133.2, 132.4, 129.2, 129.1 (d, *J* = 8.0Hz), 128.1, 127.3, 118.1, 115.1 (d, *J* = 21.2Hz), 113.7, 55.2, 55.1, 50.9, 37.1, 34.4, 21.5, 20.6; HRMS (ESI) calcd for C<sub>27</sub>H<sub>28</sub>FNO<sub>3</sub>NaS [M+Na]<sup>+</sup>488.1672; found, 488.1674.

(R,Z)-N-(4-fluorobenzyl)-N-((2-(4-methoxyphenyl)cyclobutylidene)methyl)-4-met hylbenzenesulfonamide, 50



36.5 mg colorless oil was obtained from 0.1 mmol scale reaction (80 % yield), Rf = 0.25 (PE/EA = 20:1); IR(neat) 2954, 2918, 1606, 1510, 1352, 1246, 1228, 1222, 1163, 1037, 815, 661, 572; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63(d, *J* = 8.3Hz, 2H), 7.31(d, *J* = 8.0Hz, 2H), 6.99-6.95(m, 2H), 6.92-6.86(m, 4H), 6.64(d, *J* = 8.7Hz, 2H), 5.86(d, *J* = 2.0Hz, 1H), 4.36(d, *J* = 15.5Hz, 1H), 3.89(d, *J* = 9.4Hz, 1H), 3.79(s, 3H), 3.73(d, *J* = 15.5Hz, 1H), 2.70-2.58(m, 2H), 2.47(s, 3H), 2.34-2.27(m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1(d, *J* = 243.7Hz), 157.9, 143.4, 136.4, 136.2, 135.5, 132.3, 129.6, 129.0(d, *J* = 8.0Hz), 128.0, 127.2, 118.0, 115.1(d, *J* = 21.3Hz), 113.8; HRMS (ESI) calcd for C<sub>26</sub>H<sub>26</sub>DFNO<sub>3</sub>S [M+H]<sup>+</sup> 453.1758, found, 453.1750.

## (Z)-N-(2-oxabicyclo[4.2.0]octan-8-ylidenemethyl)-N-butyl-4-methylbenzenesulfon amide (6a)



21.3 mg colorless oil was obtained from 0.1 mmol scale reaction (61% yield), Rf = 0.25 (PE/EA = 30:1); IR (neat) 2931, 2872, 1726, 1327, 1161, 1093, 663, 570, 551; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, *J* = 8.2Hz, 2H), 7.28 (d, *J* = 8.1Hz, 2H), 6.27 (s, 1H), 4.49 (d, *J* = 7.1Hz, 2H), 3.57-3.49 (m, 1H), 3.42-3.35 (m, 1H), 3.25-3.20 (m, 1H), 2.85-2.79 (m, 1H), 2.40 (s, 3H), 2.38-2.29 (m, 2H), 2.08 (d, *J* = 13.3Hz, 1H), 1.99-1.93 (m, 1H), 1.54-1.47 (m, 2H), 1.37-1.28 (m, 5H), 0.89 (t, *J* = 7.4Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.2, 136.7, 129.5, 127.1, 125.6, 120.2, 72.6, 62.3, 46.7, 30.7, 30.6, 30.2, 25.8, 22.3, 21.5, 19.7, 13.8; HRMS (ESI) calcd for C<sub>19</sub>H<sub>27</sub>NO<sub>3</sub>NaS [M+Na]<sup>+</sup> 372.1609; found, 372.1607.

### (Z)-N-(2-oxabicyclo [4.2.0] octan-8-ylidenemethyl)-N-benzyl-4-methylbenzenesulfo

namide (7a)



17.6 mg white solid was obtained from 0.1 mmol scale reaction (46% yield), Rf = 0.25 (PE/EA = 30:1); mp 142.8-144.8 °C; IR (neat) 2927, 2852, 1676, 1346, 1165, 574, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (d, *J* = 8.2Hz, 2H), 7.31-7.22 (m, 7H), 6.37 (s, 1H), 4.89 (d, *J* = 15.9Hz, 1H), 4.58 (d, *J* = 15.9Hz, 1H), 4.16-4.14 (m, 1H), 4.15 (d, *J* = 6.5Hz, 1H), 3.22 (dt, *J* = 7.2, 3.9Hz, 1H), 2.76-2.70 (m, 1H), 2.42 (s, 3H), 2.24-2.16 (m, 2H), 1.99-1.89 (m, 2H), 1.30-1.29 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.4, 137.5, 136.4, 129.6, 128.3, 127.2, 127.1, 126.9, 126.4, 120.2, 72.3, 62.2, 50.1, 30.6, 30.0, 25.8, 22.4, 21.5. HRMS (ESI) calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>3</sub>NaS [M+Na]<sup>+</sup> 406.1453; found, 406.1454.

## (Z)-N-(2-oxabicyclo[4.2.0]octan-8-ylidenemethyl)-4-methyl-N-phenylbenzenesulf onamide(8a)



9.2 mg colorless oil was obtained from 0.1 mmol scale reaction (25% yield), Rf = 0.25 (PE/EA = 30:1); IR (neat) 2922, 2850, 1650, 1353, 1166, 572, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, *J* = 8.3Hz, 2H), 7.27-7.25 (m, 4H), 7.23 (d, *J* = 8.3Hz, 2H), 7.11-7.09 (m, 2H), 6.59 (s, 1H), 3.77 (dt, *J* = 6.9, 1.9Hz, 1H), 3.48-3.42 (m, 1H), 3.28-3.23 (m, 1H), 2.41 (s, 3H), 2.31-2.25 (m, 1H), 2.20-2.14 (m, 1H), 2.14-2.09 (m, 1H), 1.93-1.85 (m, 1H), 1.48-1.38 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.7, 138.9, 135.3, 129.4, 129.2, 128.4, 127.7, 127.6, 126.8, 121.9, 72.2, 62.9, 30.5, 30.2, 25.7, 22.2, 21.5; HRMS (ESI) calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub>NaS [M+Na]<sup>+</sup> 392.1296; found, 392.1296.

#### (Z)-N-(2-oxabicyclo[4.2.0]octan-8-ylidenemethyl)-N-mesityl-4-methylbenzenesulf

onamide (9a)



34.9 mg white solid was obtained from 0.1 mmol scale reaction (85% yield), Rf = 0.25 (PE/EA = 30:1); mp 149.9-151.9 °C; IR (neat) 2922, 2848, 1690, 1348, 1163, 1085, 590, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (d, J = 8.2Hz, 2H), 7.27 (d, J = 7.8Hz, 2H), 6.85 (s, 1H), 6.78 (s, 1H), 6.63 (s, 1H), 3.48-3.43 (m, 1H), 3.15 (d, J = 4.9Hz, 1H), 2.92-2.88 (m, 1H), 2.59-2.54 (m, 1H), 2.42 (s, 3H), 2.26 (s, 3H), 2.11-2.04 (m, 1H), 2.00 (s, 3H), 1.85 (s, 3H), 1.59-1.49 (m, 2H), 1.45-1.41 (m, 1H), 1.32-1.27 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.5, 139.9, 138.2, 137.9, 137.4, 132.0, 129.5, 129.4, 128.6, 127.4, 119.9, 118.5, 72.9, 63.1, 31.5, 30.9, 23.9, 21.5, 21.2, 20.9, 18.9, 18.3; HRMS (ESI) calcd for C<sub>24</sub>H<sub>29</sub>NO<sub>3</sub>NaS [M+Na]<sup>+</sup> 434.1766; found, 434.1767.

### (Z)-2-(2-oxabicyclo[4.2.0]octan-8-ylidenemethyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (10a)



20.7 mg colorless oil was obtained from 0.1 mmol scale reaction (71% yield), Rf = 0.25 (PE/EA = 15:1); IR (neat) 2929, 2858, 1722, 1454, 1300, 1168, 759, 567, 530; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 7.8Hz, 1H), 7.62 (t, *J* = 7.2Hz, 1H), 7.53 (t, *J* = 7.6Hz, 1H), 7.43 (d, *J* = 7.6Hz, 1H), 6.48 (s, 1H), 5.13 (d, *J* = 14.7Hz, 1H), 4.83-4.82 (m, 1H), 4.58 (d, *J* = 14.7Hz, 1H), 3.74-3.69 (m, 1H), 3.64-3.59 (m, 1H), 2.48-2.46 (m, 2H), 2.23-2.17 (m, 1H), 2.09-2.04 (m, 1H), 1.61-1.51 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  133.8, 133.7, 132.9, 129.0, 124.5, 123.9, 121.4, 115.3, 72.4, 63.3, 50.3, 30.6, 30.5, 25.7, 22.4; HRMS (ESI) calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>

(Z)-3-((3-methylene-2-(2-oxooxazolidin-3-yl)cyclobutylidene)methyl)oxazolidin-2 -one (D-4)



14 mg white solid was obtained from 0.1 mmol scale reaction (56% yield), Rf = 0.25 (PE/EA = 2:1); mp 141.5-143.5°C; IR (neat) 1744, 1712, 1481, 1429, 1415, 1249, 1228, 1033, 752; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.61 (s, 1H), 5.62 (s, 1H), 5.19 (s, 1H), 5.14 (s, 1H), 4.38-4.33 (m, 4H), 3.85-3.73 (m, 2H), 3.62 (q, *J* = 8.5Hz, 1H), 3.48 (q, *J* = 8.2Hz, 1H), 3.32-3.19 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.5, 156.2, 142.7, 121.2, 115.6, 111.0, 62.6, 62.3, 58.1, 43.8, 40.0, 35.3; HRMS (ESI) calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>NaO<sub>4</sub> [M+Na]<sup>+</sup> 273.0851; found, 273.0868.

(Z)-N-(4-fluorobenzyl)-N-((2-(N-(4-fluorobenzyl)-4-methylphenylsulfonamido)-3-methylenecyclobutylidene)methyl)-4-methylbenzenesulfonamide(D-5)



57 mg white solid was obtained from 0.1 mmol scale reaction (90% yield), Rf = 0.25 (PE/EA = 10:1); mp>300°C; IR (neat) 2926, 2846, 1602, 1508, 1340, 1222, 1161, 1089, 815, 669, 565, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (d, *J* = 8.1Hz, 2H), 7.51 (d, *J* = 8.0Hz, 2H), 7.22 (d, *J* = 8.4Hz, 2H), 7.19 (d, *J* = 8.3Hz, 2H), 7.15 (d, *J* = 5.6Hz, 1H), 7.13 (d, *J* = 5.5Hz, 1H), 7.04 (d, *J* = 5.6Hz, 1H), 7.02 (d, *J* = 5.3Hz, 1H), 6.89-6.82 (m, 4H), 6.25 (s, 1H), 5.37 (d, *J* = 1.7Hz, 1H), 4.78 (d, *J* = 1.6Hz, 1H), 4.70

(d, J = 16.4Hz, 1H), 4.54 (d, J = 16.4Hz, 1H), 4.27 (d, J = 1.6Hz, 1H), 4.07 (s, 2H), 2.92 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.4 (d, J = 16.6Hz), 160.9 (d, J = 16.6Hz), 144.0, 143.9, 143.6, 137.7, 136.5, 132.4, 132.0, 130.7 (d, J = 8.1Hz), 129.7, 129.1 (d, J = 7.85Hz), 128.8, 127.3, 127.1, 123.3, 119.4, 115.2, 115.0 (d, J = 96.7Hz), 114.9, 111.6, 62.4, 50.1, 48.3, 35.5, 26.9, 21.5 (d, J = 5.69Hz); HRMS (ESI) calcd for C<sub>34</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>F<sub>2</sub>NaS<sub>2</sub> [M+Na] <sup>+</sup> 657.1669; found, 657.1674.

The X-ray structure of this compound is below:



(Z) - N-butyl - N-((2-(N-butyl-4-methylphenylsulfonamido) - 3-methylenecyclobutylidene) methyl) - 4-methylbenzenesulfonamide (D-6)



40.3 mg colorless oil was obtained from 0.1 mmol scale reaction (76% yield), Rf = 0.25 (PE/EA = 30:1); IR (neat) 2958, 2872, 1697, 1338, 1161, 1089, 815, 675, 570, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (d, *J* = 8.2Hz, 2H), 7.68 (d, *J* = 8.2Hz, 2H), 7.28 (d, *J* = 7.8Hz, 4H), 6.45 (s, 1H), 5.44 (s, 1H), 4.78 (d, J = 1.9Hz, 1H), 4.00 (d, *J* = 1.9Hz, 1H), 3.63-3.49 (m, 2H), 3.13-3.01 (m, 2H), 2.98-2.90 (m, 2H), 2.83-2.75 (m, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 1.43-1.33 (m, 4H), 1.28-1.21 (m, 2H), 1.06-0.97 (m, 2H), 0.89 (t, *J* = 14.2Hz, 3H), 0.75 (t, *J* = 14.7Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.7, 143.5, 137.8, 136.9, 129.6, 129.5, 127.3, 126.8, 122.6, 116.5, 110.8, 62.6, 46.8, 45.3, 35.3, 31.9, 30.9, 21.4, 20.0, 19.4, 13.9, 13.3; HRMS (ESI) calcd for C<sub>28</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>NaS<sub>2</sub> [M+Na]<sup>+</sup> 553.2171; found, 553.2169.

### (Z)-N-benzyl-N-((2-(N-benzyl-4-methylphenylsulfonamido)-3-methylenecyclobut

ylidene)methyl)-4-methylbenzenesulfonamide(D-7)



40.3 mg colorless oil was obtained from 0.1 mmol scale reaction (67% yield), Rf = 0.25 (PE/EA = 30:1); IR (neat) 2960, 2875, 1567, 1454, 1338, 1161, 1091, 813, 663, 565, 547; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (d, *J* = 8.2Hz, 2H), 7.52 (d, *J* = 8.2Hz, 2H), 7.21-7.15 (m, 14H), 7.06-7.04 (m, 2H), 6.20 (d, *J* = 1.7Hz, 1H), 5.41 (s, 1H), 4.75 (d, *J* = 2.2Hz, 1H), 4.71 (d, *J* = 16.2Hz, 1H), 4.45 (d, *J* = 16.3Hz, 2H), 4.11 (d, *J* = 15.0Hz, 1H), 3.97 (d, *J* = 15.2Hz, 1H), 2.89 (t, *J* = 2.2Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.4, 143.6, 143.3, 136.6, 136.4, 136.2, 129.5, 129.1, 128.2, 127.9, 127.6, 127.3, 127.2, 127.1, 123.4, 120.7, 111.4, 62.4, 51.0, 49.0, 35.5, 21.5, 21.4; HRMS (ESI) calcd for C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>NaS<sub>2</sub> [M+Na]<sup>+</sup> 621.1857; found, 621.1858.

(Z)-4-methyl-N-((2-(4-methyl-N-phenylphenylsulfonamido)-3-methylenecyclobut ylidene)methyl)-N-phenylbenzenesulfonamide(*D-8*)



21.7 mg white solid was obtained from 0.1 mmol scale reaction (38% yield), Rf = 0.25 (PE/EA=10:1); mp 170.7-172.7 °C; IR (neat) 2924, 2850, 1595, 1487, 1352, 1165, 1091, 813, 696, 584, 543; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56-7.45 (m, 4H), 7.38-7.34 (m, 7H), 7.24-7.21 (m, 3H), 7.19 (d, *J* = 8.2Hz, 1H), 7.15 (d, *J* = 8.2Hz, 1H), 6.35 (d, *J* = 2.3Hz, 1H), 5.08 (dd, *J* = 6.0, 2.3Hz, 1H), 4.97 (d, *J* = 2.2Hz, 1H), 4.94 (d, *J* = 2.1Hz, 1H), 2.84 (d, *J* = 2.0Hz, 1H), 2.75-2.73 (m, 1H), 2.39 (s, 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.4, 143.9, 143.1, 138.6, 137.7, 136.9, 134.2, 134.0, 132.0, 131.3, 129.9, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5,

128.4, 127.9, 127.8, 127.6, 127.5, 124.7, 123.3, 112.1, 63.9, 35.5, 21.6, 21.5; HRMS (ESI) calcd for C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>NaS<sub>2</sub> [M+Na]<sup>+</sup> 593.1545; found, 593.1541.

(Z)-4-methyl-N-((2-(4-methyl-N-(naphthalen-2-ylmethyl)phenylsulfonamido)-3methylenecyclobutylidene)methyl)-N-(naphthalen-2-ylmethyl)benzenesulfonami de(D-9)



49.5 mg yellow oil was obtained from 0.1 mmol scale reaction (71% yield), Rf = 0.25 (PE/EA = 10:1); IR (neat) 2974, 2866, 1699, 1568, 1346, 1161, 1091, 815, 563, 545; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78-7.75 (m, 2H), 7.66-7.64 (m, 3H), 7.62-7.60 (m, 3H), 7.55-7.52 (m, 2H), 7.45-7.40 (m, 6H), 7.32 (d, *J* = 8.5Hz, 1H), 7.18 (d, *J* = 8.5Hz, 1H), 7.13 (d, *J* = 8.1Hz, 2H), 7,07 (d, *J* = 8.1Hz, 2H), 6.28 (d, *J* = 1.8Hz, 1H), 5.52-5.51 (m, 1H), 4.91 (d, *J* = 16.2Hz, 1H), 4.73 (d, *J* = 2.1Hz, 1H), 4.65 (d, *J* = 16.2Hz, 1H), 4.54 (d, *J* = 2.3Hz, 1H), 4.31 (d, *J* = 15.2Hz, 1H), 4.16 (d, *J* = 15.3Hz, 1H), 2.87-2.86 (m, 2H), 2.33 (s, 3H), 2.55 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.3, 143.7, 143.4, 137.9, 136.5, 134.1, 133.5, 133.1, 132.9, 132.8, 132.7, 129.5, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.2, 127.0, 126.6, 126.0, 125.9, 125.8, 125.7, 123.6, 121.3, 111.5, 62.6, 51.4, 49.4, 35.6, 21.4, 21.3; HRMS (ESI) calcd for C<sub>42</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>NaS<sub>2</sub> [M+Na]<sup>+</sup> 721.2171; found, 721.2170.

(Z)-2-((2-(1,1-dioxidobenzo[d]isothiazol-2(3H)-yl)-3-methylenecyclobutylidene)m ethyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide(*D-10*)



23.2 mg white solid was obtained from 0.1 mmol scale reaction (56% yield), Rf =

0.25 (PE/EA = 5:1); mp 117.4-118.4°C; IR (neat) 2924, 2852, 1707, 1456, 1299, 1176, 756, 567, 557; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (dd, *J* = 13.7, 7.8Hz, 2H), 7.56 (dd, *J* = 13.5, 7.3Hz, 2H), 7.48 (dd, *J* = 17.2, 7.6Hz, 2H), 8.90 (t, *J* = 8.9Hz, 2H), 6.74 (s, 1H), 5.72 (s, 1H), 5.44 (s, 1H), 5.27 (s, 1H), 5.19 (d, *J* = 14.5Hz, 1H), 4.68 (d, *J* = 14.5Hz, 1H), 4.53 (d, *J* = 14.0Hz, 1H), 4.47 (d, *J* = 14.0Hz, 1H), 3.35 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.0, 134.5, 133.5, 133.4, 132.8, 129.1, 129.0, 124.9, 124.8, 121.2, 121.1, 118.6, 116.0, 112.7, 57.1, 50.5, 44.9, 35.2; HRMS (ESI) calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>NaS<sub>2</sub> [M+Na]<sup>+</sup> 437.0605; found, 437.0613.

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## H<sup>1</sup> NMR and C<sup>13</sup> NMR spectra

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