Supporting Information

Catalyst-Controlled Divergent Transformations of N-Sulfonyl-1,2,3-triazoles into Isoquinolin-3-ones and 2-Aminoindanones

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List of Contents

1. General Information..............................................................................................................................................S2
2. General Procedure of Substrate 1 and 1a-d ...........................................................................................................S2
3. Table S1. Optimization for the Synthesis of 5a and 2a via Rh(II)- and Pd(0)-Catalysis.................................S3
4. Table S2. Optimization for the Synthesis of 2a Using Lewis Acid Catalyst.......................................................S4
5. Table S3. Optimization for the Synthesis of 3a via Tandem One-Pot Rh(II)/Pd(0) Catalysis.........................S5
6. All in One-Pot Rh(II)/Pd(0) Catalysis of 1a for the Synthesis of 3a.................................................................S5
7. General Procedure for the Synthesis of 2 ...........................................................................................................S6
8. General Procedure for Synthesis of 3 ................................................................................................................S6
9. General Procedure for Tandem Synthesis of 3a..............................................................................................S6
10. Deuterium Labeling Experiment.......................................................................................................................S7
11. Characterization Data........................................................................................................................................S9
12. X-ray Crystal Structure and Data of 2a...............................................................................................................S16
13. X-ray Crystal Structure and Data of 3a.............................................................................................................S17
14. Copies of 1H and 13C NMR Spectra................................................................................................................S18
1. General Information.

All reactions were performed under an argon atmosphere using standard Schelenk techniques. Reaction flasks were flame-dried under vacuum. All purchased reagents were used without further purification. Dry toluene was distilled prior to be used. Anhydrous solvent was transferred by an oven dried syringe of a cannula. All reactions were monitored by TLC with silica gel coated plates. Visualization on TLC was achieved by use of UV light (254 nm) or by staining with Cerium Ammonium Molybdate (CAM). NMR spectra were recorded on a Bruker 300 MHz for $^1$H, 75.5 MHz for $^{13}$C, and 282 MHz for $^{19}$F. The melting points were measured on a Fisher-Johns apparatus and uncorrected. HRMS, high resolution mass spectra were obtained by electron ionization (EI), fast atom bombardment (FAB) with a magnetic sector-electronic sector double focusing mass analyzer at the Daegu Center of the Korea Basic Science Institute.

2. General Procedure of Substrate 1 and 1a-d.

Under a nitrogen atmosphere, to a solution of dry THF (0.2 M) in a flame-dried round bottom flask was added acetylene S1a (1 equiv.) and stirred at -78 °C then added nBuLi (1.6 M in hexane, 1.1 equiv.) dropwise. The reaction mixture was stirred for an hour, then diluted with Et$_2$O and quenched with D$_2$O (10 equiv.). The resulting suspension was dried over MgSO$_4$ and filtered. The residue was concentrated under reduced pressure to afford compound S2. 1a-d was prepared from S2a according to the ref. (2) with additional D$_2$O (20 equiv.).

Reference


(2) J. Raushel and V. V. Fokin, Efficient Synthesis of 1-Sulfonyl-1,2,3-Triazoles. Org. Lett. 2010, 12, 4952-4955.
3. Table S1. Optimization for the Synthesis of 5a and 2a via Rh(II)- and Pd(0)-Catalysis.

In a glovebox, a flame-dried vial equipped with a stirrer bar was charged with triazole 1a (0.2 mmol), catalyst, 4 Å molecular sieves and sealed under an argon atmosphere. A solvent was added to the mixture and the solution was heated until all triazole was consumed (determined by TLC analysis). After being cooled to room temperature, the solvent was evaporated, dried under vacuum, and determined the product ratio from crude. 

<table>
<thead>
<tr>
<th>Entry</th>
<th>Rh Catalyst (mol%)</th>
<th>Pd Catalyst (mol%)</th>
<th>Ligand (mol%)</th>
<th>Solvent (M)</th>
<th>T (°C)</th>
<th>Yield (%)</th>
<th>2a : 5a ratioa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh₂(TMA)₄ (2)</td>
<td>Pd(PPh₃)₃ (2)</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>90 / 21</td>
<td>31</td>
<td>99&gt;1</td>
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<td>2</td>
<td>Rh₂(TMA)₄ (3)</td>
<td>Pd₂(dba)₃ (1)</td>
<td>Dppp (2)</td>
<td>Toluene (0.2)</td>
<td>120 / 1</td>
<td>53</td>
<td>1.63:1</td>
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<td>Rh₂(TMA)₄ (2)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
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<td>75</td>
<td>1:9</td>
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<td>Rh₂(TMA)₄ (2)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>&lt;80</td>
<td>N.R.</td>
<td>-</td>
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<td>5</td>
<td>Rh₂(TMA)₄ (2)</td>
<td>-</td>
<td>-</td>
<td>1,2-DCE (0.2)</td>
<td>90 / 2</td>
<td>64</td>
<td>1:10</td>
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<td>6</td>
<td>Rh₂(TMA)₄ (2)</td>
<td>-</td>
<td>-</td>
<td>PhCl (0.2)</td>
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<td>69</td>
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<td>-</td>
<td>MeCN (0.2)</td>
<td>90 / 7</td>
<td>13</td>
<td>3:7:1</td>
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<td>Rh₂(TMA)₄ (2)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
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<td>89</td>
<td>1&lt;99</td>
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<td>9</td>
<td>Rh₂(TMA)₄ (4)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>70 / 2.5</td>
<td>72</td>
<td>1&lt;99</td>
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<td>10</td>
<td>Rh₂(oc)₃ (4)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>70 / 21</td>
<td>30</td>
<td>1:2.3</td>
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<td>11</td>
<td>Rh₂(OAc)₄ (4)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>70 / 21</td>
<td>43</td>
<td>1.87:1</td>
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<td>Rh₂(exp)₂ (4)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>70 / 4</td>
<td>68</td>
<td>1&lt;99</td>
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<td>-</td>
<td>Toluene (0.2)</td>
<td>70 / 5</td>
<td>80</td>
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<td>14</td>
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<td>-</td>
<td>Toluene (0.2)</td>
<td>80 / 1</td>
<td>76</td>
<td>1&lt;99</td>
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<td>Rh₂(TMA)₄ (4)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>90 / 1</td>
<td>80</td>
<td>1&lt;99</td>
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<td>16</td>
<td>Rh₂(TMA)₄ (4)</td>
<td>-</td>
<td>-</td>
<td>Toluene (0.2)</td>
<td>100 / 1</td>
<td>83</td>
<td>1:32</td>
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<td>17</td>
<td>-</td>
<td>Pd(PPh₃)₃ (4)</td>
<td>-</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 6</td>
<td>61</td>
<td>99&gt;1</td>
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<tr>
<td>18</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>P(4-MeOPh)₃ (8)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 5</td>
<td>76</td>
<td>99&gt;1</td>
</tr>
<tr>
<td>19</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>P(4-MeOPh)₃ (8)</td>
<td>MeCN (0.13)</td>
<td>80 / 3</td>
<td>70</td>
<td>99&lt;1</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>P(4-MeOPh)₃ (8)</td>
<td>Toluene (0.13)</td>
<td>80 / 7</td>
<td>35</td>
<td>99&gt;1</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>P(4-MeOPh)₃ (8)</td>
<td>1,4-dioxane (0.13)</td>
<td>80 / 7</td>
<td>31</td>
<td>99&gt;1</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>Dppf (4)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 6</td>
<td>30</td>
<td>99&lt;1</td>
</tr>
<tr>
<td>23</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>PPh₃ (8)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 6</td>
<td>41</td>
<td>99&lt;1</td>
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<td>24</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>Xantphos (4)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 5</td>
<td>15</td>
<td>99&gt;1</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>rac-BINAP (4)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 5</td>
<td>N.D.</td>
<td>99&lt;1</td>
</tr>
<tr>
<td>26</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>Segphos (4)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 5</td>
<td>N.D.</td>
<td>99&lt;1</td>
</tr>
<tr>
<td>27</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>P(o-tolyl)PPh (8)</td>
<td>1,2-DCE (0.13)</td>
<td>80 / 5</td>
<td>72</td>
<td>99&lt;1</td>
</tr>
<tr>
<td>28</td>
<td>-</td>
<td>Pd₂(dba)₃ (2)</td>
<td>P(4-MeOPh)₃ (8)</td>
<td>1,2-DCE (0.13)</td>
<td>90 / 3</td>
<td>80</td>
<td>99&gt;1</td>
</tr>
</tbody>
</table>

aReactivation conditions: 1a (0.2 mmol), catalyst, and MS 4 Å in solvent at designated temperature. bTime for complete conversion of 1a determined by TLC. cIsolated yield. N.R.: No reaction occurred at all. d2a:5a ratio were determined by 1H NMR analysis. eStarting material was recovered in 46% yield. fOnly cyclic imidate intermediate 4a was detected.
4. **Table S2. Optimization for the Synthesis of 2a Using Lewis Acid Catalyst.**

![Reaction scheme]

In a glovebox, a flame-dried vial equipped with a stirrer bar was charged with triazole 1a (0.2 mmol), catalyst, 4 Å molecular sieves and sealed under an argon atmosphere. A solvent was added to the mixture and the solution was heated until all triazole was consumed (determined by TLC analysis). After being cooled to room temperature, the solvent was evaporated, dried under vacuum, and determined the product from crude ¹H NMR spectrum.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Lewis acid Catalyst (mol%)</th>
<th>time (h)ᵇ</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdCl₂(PhCN)₂ (4)</td>
<td>12</td>
<td>N.Dᵃ</td>
</tr>
<tr>
<td>2</td>
<td>PdCl₂(MeCN)₂ (4)</td>
<td>12</td>
<td>N.Dᵃ</td>
</tr>
<tr>
<td>3</td>
<td>PPh₃ (2)</td>
<td>12</td>
<td>No reaction</td>
</tr>
<tr>
<td>4</td>
<td>Sc(OTf)₃ (2)</td>
<td>12</td>
<td>Decomposed</td>
</tr>
<tr>
<td>5</td>
<td>Cu(OTf)₂ (2)</td>
<td>12</td>
<td>Decomposed</td>
</tr>
<tr>
<td>6</td>
<td>Zn(OTf)₂ (2)</td>
<td>6</td>
<td>N.Dᵃ</td>
</tr>
</tbody>
</table>

ᵃReaction conditions: 1a (0.2 mmol) Lewis acid cat. and MS 4 Å in 1,2-DCE (1.5 ml) at 80 °C.ᵇTime for complete conversion of 1a determined by TLC.  Only cyclic imidate intermediate was detected.
5. Table S3. Optimization for the Synthesis of 3a via Tandem One-Pot Rh(II)/Pd(0) Catalysis.a

To a flame-dried vial equipped with a stirrer bar was added Rh$_2$(TMA)$_4$, MS 4 Å, triazole 1a (0.2 mmol), and toluene (1 mL, 0.2 M) then the vial was sealed by the cap in a glove box. The solution was stirred and heated for 0.5 h to 1 h. After completion of the reaction, the mixture was cooled to room temperature, and charged with Pd cat. and ligand in a glovebox. The solution was stirred and heated until the reaction was completed (determined by TLC). The crude mixture was purified by column chromatography to afford the corresponding 2-aminooindanone 3a.

Note. Initial configuration of the product 3a was exclusively trans which was determined by $^1$H NMR analysis of the crude reaction mixture. However, the configuration of 3a was changed to trans/cis mixture after column chromatography due to highly enolizable α-proton to the carbonyl.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Rh catalyst (mol%)</th>
<th>T (°C) / time (h)$^b$</th>
<th>Pd Catalyst</th>
<th>Ligand</th>
<th>T (°C) / time (h)</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>-</td>
<td>60 / 12</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>-</td>
<td>60 / 12</td>
<td>decomposed</td>
</tr>
<tr>
<td>3</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>rac-BINAP</td>
<td>60 / 2</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>(R)-Segphos</td>
<td>60 / 12</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>dppph</td>
<td>60 / 12</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>dppp</td>
<td>60 / 12</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>dppf</td>
<td>60 / 12</td>
<td>20</td>
</tr>
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<td>8</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>xantphos</td>
<td>60 / 2</td>
<td>72</td>
</tr>
<tr>
<td>9</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$</td>
<td>xantphos</td>
<td>60 / 2 / 2</td>
<td>15</td>
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<tr>
<td>10</td>
<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd(OAc)$_2$</td>
<td>xantphos</td>
<td>60 / 1</td>
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<td>Rh$_2$(TMA)$_4$ (2)</td>
<td>120 / 0.5</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>xantphos</td>
<td>80 / 1</td>
<td>61</td>
</tr>
<tr>
<td>12</td>
<td>Rh$_2$(TMA)$_4$ (4)</td>
<td>90 / 1</td>
<td>Pd$_2$(dba)$_2$·CHCl$_3$</td>
<td>xantphos</td>
<td>60 / 2</td>
<td>72</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1a (0.2 mmol) Rh$_2$(TMA)$_4$ (4.0 x 10$^{-3}$ mmol) and MS 4 Å in toluene (1.0 ml) at designated temperature. $^b$Isolated yield of the cis and trans mixture. $^c$The reaction conditions with 4 mol% Rh$_2$(TMA)$_4$ at 90 °C were more suitable for other substrates than with 2 mol% Rh$_2$(TMA)$_4$ at 120 °C.

6. All in One-Pot Rh(II)/Pd(0) Catalysis of 1a for the Synthesis of 3a.

To a flame-dried vial equipped with a stirrer bar was added Rh$_2$(TMA)$_4$ (4.9 mg, 8.0 x 10$^{-3}$ mmol), Pd$_2$(dba)$_2$·CHCl$_3$ (5.5 mg, 5.0 x 10$^{-3}$ mmol), Xantphos (6.4 mg, 1.1 x 10$^{-2}$ mmol), MS 4 Å, triazole 1a (0.2 mmol), and toluene (1 mL, 0.2 M) then the vial was sealed by the cap in a glove box. The solution was stirred and heated to 120 °C for 1 h. The diastereomeric ratio of 3a was determined by $^1$H NMR of crude mixture (trans/cis=10:1). The reaction mixture was purified by column chromatography to afford the products 2a (8%) and 3a (53%).

In a glovebox, a flame-dried vial equipped with a stir bar was charged with Pd$_2$(dba)$_3$ (3.7 mg, 4.0 x 10$^{-3}$ mmol), P(4-MeOPh)$_3$ (5.6 mg, 1.6 x 10$^{-2}$ mmol), MS 4 Å and triazole 1 (0.2 mmol), then sealed by the pressure tube cap. To that mixture, 1,2-DCE (1.5 ml, 0.13 M) was added. The solution was heated at 90 °C until all triazole 1 was consumed (determined by TLC analysis). After being cooled to room temperature, the crude mixture was concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding 1,4-dihydro-isoquinolin-3(2H)-one 2.


In a glovebox, a flame-dried vial equipped with a stirrer bar was charged with Rh$_2$(TMA)$_4$ (4.9 mg, 8.0 x 10$^{-3}$ mmol), MS 4 Å, triazole (0.2 mmol) and toluene (1.0 mL, 0.2 M), then the vial was sealed by the cap. The solution was stirred and heated until all triazole 1 was consumed (determined by TLC). After cooled to room temperature, the reaction mixture was moved to a glovebox and charged with Pd$_2$(dba)$_3$·CHCl$_3$ (5.5 mg, 5.0 x 10$^{-3}$ mmol), and Xantphos (6.4 mg, 1.1 x 10$^{-2}$ mmol). The solution was stirred at 60 °C until the reaction was completed. The crude mixture was purified by column chromatography to afford the corresponding 2-aminoindanone 3.


A solution of S1a (47 mg, 0.3 mmol, 1.0 equiv), tosyl azide (71 mg, 0.36 mmol, 1.2 equiv), CuTC (2.9 mg, TC= thiophene-2-carboxylate), Rh$_2$(TMA)$_4$ (7.3 mg, 1.2 x 10$^{-2}$ mmol), and MS 4 Å in toluene (1.5 mL, 0.2 M) was stirred for 1.5 h at room temperature. Then, the mixture was heated to 90 °C for 0.5 h. After cooled to room temperature, the reaction mixture was moved to a glovebox and charged with Pd$_2$(dba)$_3$·CHCl$_3$ (7.8 mg, 7.5 x 10$^{-3}$ mmol), and Xantphos (9.5 mg, 1.65 x 10$^{-2}$ mmol). The solution was stirred at 60 °C for 4 h, then the crude mixture was purified by column chromatography to afford the corresponding 3a in 45 % overall yield.
10. Deuterium Labeling Experiment.

Deuterium labelled 2a-$d_{60\%}$ was produced from 1a-$d_{85\%}$ according to the general procedure.

Deuterium labelled 3a-$d_{77\%}$ was produced from 1a-$d_{85\%}$ according to the general procedure. The deuterium incorporation was observed by only in $^1$H NMR of the crude mixture since proton exchange occurred while conducting column chromatography.

Copies of $^1$H spectra of compound 1a-$d_{85\%}$

---

Current data Parameters
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BRN: 1
FRQMOD: 1

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SP02 18.10 MHz
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F2 - Processing parameters
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SF 300.180007 MHz
SSP 24
SSB 0
LB 10.0 Hz
WM 2
PC 1.00
Copies of $^1$H spectra of compound 2a-$d_{60\%}$

Copies of $^1$H spectra of crude mixture of compound 3a-$d_{77\%}$
11. Characterization Data

1-[2-[1-(4-Methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl]prop-2-en-1-ol (1a).
Yield: 75%; Eluent: n-hexane/ethyl acetate = 4/1; White solid; mp: 100–102 °C. 1H NMR (300 MHz, CDCl₃) δ 2.47 (s, 1H), 3.94 (brs, O–H), 5.09–5.20 (m, 1H), 5.26–5.39 (m, 2H), 5.96–6.12 (m, 1H), 7.32–7.47 (m, 4H), 7.47–7.60 (m, 2H), 8.00–8.09 (m, 2H), 8.34 (s, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 22.0, 71.8, 115.2, 121.6, 127.9, 128.3, 128.7, 129.0, 129.8, 130.0, 130.7, 132.9, 138.7, 141.1, 147.0, 147.8 ppm; HRMS (EI) Calcd m/z for C₁₈H₁₈N₂O₃S [M⁺]: 355.0991. Found: 355.0989.

1-[4-Methyl-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl]prop-2-en-1-ol (1b).
Yield: 70%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 98–100 °C. 1H NMR (300 MHz, CDCl₃) δ 2.36 (s, 3H), 2.47 (s, 3H), 3.89 (brs, O–H), 5.08–5.16 (m, 1H), 5.22–5.35 (m, 2H), 5.94–6.10 (m, 1H), 7.21 (dd, J = 7.9 Hz, J = 1.2 Hz, 1H), 7.30–7.37 (m, 1H), 7.38–7.46 (m, 3H), 8.00–8.10 (m, 2H), 8.35 (s, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 21.1, 22.0, 71.6, 115.0, 121.5, 127.7, 128.7, 128.9, 130.4, 130.6, 130.7, 133.0, 133.1, 138.2, 139.8, 147.0, 147.7 ppm; HRMS (EI) Calcd m/z for C₁₉H₁₉N₂O₃S [M⁺]: 369.1147. Found: 369.1144.

1-[5-Methoxy-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl]prop-2-en-1-ol (1c).
Yield: 50%; Eluent: n-hexane/ethyl acetate = 2/1; Yellow sticky solid; 1H NMR (300 MHz, CDCl₃) δ 2.46 (s, 3H), 3.83 (s, 3H), 4.00–4.13 (m, 1H), 5.07–5.21 (m, 1H), 5.21–5.39 (m, 2H), 5.91–6.11 (m, 1H), 6.89 (dd, J = 8.6 Hz, J = 2.7 Hz, 1H), 7.07 (d, J = 2.7 Hz, 1H), 7.38–7.47 (m, 3H), 8.00–8.09 (m, 2H), 8.26 (s, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 22.0, 55.5, 71.8, 113.7, 114.0, 115.3, 120.2, 120.9, 128.9, 130.7, 131.3, 133.0, 138.5, 142.8, 146.9, 147.7, 160.6 ppm; HRMS (EI) Calcd m/z for C₁₉H₁₉N₂O₃S [M⁺]: 385.1096. Found: 385.1093.

1-[6-[1-(4-Methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]-2H-1,3-benzodioxol-5-yl]prop-2-en-1-ol (1d).
Yield: 35%; Eluent: n-hexane/ethyl acetate = 2/1; Yellow solid; mp: 101–103 °C. 1H NMR (300 MHz, CDCl₃) δ 2.47 (s, 3H), 3.53–3.70 (m, O–H), 5.09–5.26 (m, 2H), 5.26–5.45 (m, 1H), 5.92–6.07 (m, 3H), 6.98 (d, J = 19.7, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.96–8.15 (m, 2H), 8.27 (s, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 22.0, 71.0, 101.8, 108.7, 109.6, 115.2, 121.2, 129.0, 130.7, 133.0, 135.8, 138.7, 146.6, 147.5, 147.8, 148.8 ppm; HRMS (FAB) Calcd m/z for C₁₉H₁₈N₃O₅S [M+H⁺]: 400.0967. Found: 400.0965.

1-[5-Fluoro-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl]prop-2-en-1-ol (1e).
Yield: 69%; Eluent: n-hexane/ethyl acetate = 4/1; Colorless oil; 1H NMR (300 MHz, CDCl₃) δ 2.47 (s, 3H), 3.98 (brs, O–H), 5.12–5.22 (m, 1H), 5.25–5.35 (m, 2H), 5.88–6.09 (m, 1H), 6.98–7.07 (m, 1H), 7.22–7.29 (m, 1H), 7.41–7.45 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 8.5 Hz, J = 5.6 Hz, 1H), 7.99–8.08 (m, 2H), 8.33 (s, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 22.0, 71.1 (d, J = 1.0 Hz), 115.2 (d, J = 22.0 Hz), 115.5 (d, J = 22.6 Hz), 115.8, 121.5, 123.8 (d, J = 3.3 Hz), 128.9, 130.7, 131.8 (d, J =
8.4 Hz), 132.8, 138.0, 143.8 (d, J = 6.9 Hz), 146.0, 147.9, 163.3 (d, J = 249.8 Hz) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -111.10 - -111.02 (m) ppm; HRMS (EI) Calcd m/z for C$_{18}$H$_{16}$FN$_3$O$_3$S [M]+: 373.0896. Found: 373.0894.

1-(2-Fluoro-6-(1-tosyl-1H-1,2,3-triazol-4-yl)phenyl)prop-2-en-1-ol (1f).

Yield: 50%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 2.48 (s, 3H), 4.76–4.89 (m, 1H), 4.96–5.11 (m, 1H), 5.59–5.72 (m, 1H), 5.81–5.99 (m, 1H), 7.09–7.21 (m, 1H), 7.22–7.28 (m, 1H), 7.29–7.38 (m, 1H), 7.43 (d, J = 8.2 Hz, 2H), 8.00–8.10 (m, 2H), 8.28 (s, 1H) ppm; $^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 22.0, 67.7 (d, J = 6.4 Hz), 114.8, 117.1 (d, J = 24.3 Hz), 122.1, 126.3 (d, J = 3.3 Hz), 128.9(6) (d, J = 13.8 Hz), 128.9(7), 129.5 (d, J = 9.8 Hz), 129.8 (d, J = 4.2 Hz), 130.7, 132.8, 138.6 (d, J = 1.7 Hz), 146.4 (d, J = 3.3 Hz), 147.9, 161.4 (d, J = 247.0 Hz) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$) δ -114.60 - -114.54 (m) ppm; HRMS (FAB) Calcd m/z for C$_{18}$H$_{17}$FN$_3$O$_3$S [M+H]+: 374.0975. Found: 374.0978.

1-4-Chloro-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl)prop-2-en-1-ol (1g).

Yield: 72%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 110–115 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 2.48 (s, 3H), 3.78 (bs, O–H), 5.12–5.22 (m, 1H), 5.24–5.39 (m, 2H), 5.93–6.08 (m, 1H), 7.34–7.40 (m, 1H), 7.42 (s, 1H), 7.45 (s, 1H), 7.47–7.54 (m, 2H), 8.00–8.11 (m, 2H), 8.37 (s, 1H) ppm; $^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 22.0, 71.1, 115.6, 122.0, 129.0, 129.5, 129.6, 130.2, 130.8, 132.9, 138.3, 139.5, 145.6, 148.0 ppm; HRMS (ESI) Calcd m/z for C$_{18}$H$_{16}$ClN$_3$O$_3$S [M]+: 389.0601. Found: 389.0604.

1-5-Bromo-2-[1-(4-methylbenzene-1-sulfonyl)-1H-1,2,3-triazol-4-yl]phenyl)prop-2-en-1-ol (1h).

Yield: 76%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 108–112 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 2.48 (s, 3H), 3.83 (d, J = 5.4 Hz, O-H), 5.15–5.26 (m, 1H), 5.25–5.31 (m, 1H), 5.31–5.41 (m, 1H), 5.91–6.11 (m, 1H), 7.36–7.40 (m, 1H), 7.42 (s, 1H), 7.44 (s, 1H), 7.50 (dd, J = 8.3 Hz, J = 2.1 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 8.00–8.11 (m, 2H) 8.35 (s, 1H) ppm; $^{13}$C NMR (75.5 MHz, CDCl$_3$) δ 22.1, 71.2, 116.0, 121.6, 124.1, 126.8, 129.0, 130.8, 131.3, 131.4, 131.8, 132.8, 137.9, 143.1, 146.0, 148.0 ppm; HRMS (ESI) Calcd m/z for C$_{18}$H$_{16}$BrN$_3$O$_3$S [M]+: 433.0096. Found: 433.0097.

1-(2-(1-Tosyl-1H-1,2,3-triazol-4-yl)-5-(trifluoromethyl)phenyl)prop-2-en-1-ol (1i).

Yield: 72%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 119–121 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 2.48 (s, 3H), 3.77 (d, J = 5.3 Hz, 1H), 5.18–5.30 (m, 1H), 5.32–5.46 (m, 2H), 5.92–6.14 (m, 1H), 7.44 (d, J = 9.0 Hz, 2H), 7.51–7.69 (m, 2H), 7.83 (s, 1H), 8.09–8.18 (m, 2H), 8.42 (s, 1H) ppm; $^{19}$F NMR (75.5 MHz, CDCl$_3$) δ 62.77 ppm; HRMS (EI) Calcd m/z for C$_{19}$H$_{16}$F$_3$N$_3$O$_3$S [M]+: 424.0943. Found: 424.0946.

S10
1-(3-(1-tosyl-1H-1,2,3-triazol-4-yl)benzo[b]thiophen-2-yl)prop-2-en-1-ol (1j).

Yield: 70%; Eluent: n-hexane/ethyl acetate = 4/1; Brown solid; mp: 148–156 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.60 (s, 1H), 5.17–5.29 (m, 1H), 5.32–5.42 (m, 2H), 7.36–7.50 (m, 2H), 7.53–7.62 (m, 2H), 8.36 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 42.7, 71.6, 115.2, 121.5, 127.5, 128.3, 128.6, 129.8, 129.9, 138.6, 140.8, 146.8 ppm; HRMS (FAB) Calcd m/z for C$_{20}$H$_{18}$N$_3$O$_3$S [$M+H]^+$: 412.0790. Found: 412.0787.

$^{-}$Ethenyl

1-[(Methylsulfonyl)-1H-1,2,3-triazol-4-yl]phenyl)prop-2-en-1-ol (1k).

Yield: 45%; Eluent: n-hexane/ethyl acetate = 4/1; Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.60 (s, 3H), 5.20–5.26 (m, 1H), 5.33–5.42 (m, 2H), 6.03–6.16 (m, 1H), 7.36–7.50 (m, 2H), 7.53–7.62 (m, 2H), 8.36 (s, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 42.7, 71.6, 115.2, 121.5, 127.5, 128.3, 128.6, 129.8, 129.9, 138.6, 140.9, 146.8 ppm; HRMS (FAB) Calcd m/z for C$_{12}$H$_{14}$N$_3$O$_3$S [$M+H]^+$: 280.0756. Found: 280.0758.

2-(Toluene-4-sulfonyl)-1-vinyl-1,4-dihydro-2H-isooquinolin-3-one (2a).

Yield: 80%; Eluent: n-hexane/ethyl acetate = 6/1; Light yellow solid; mp: 145–146 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.40 (s, 3H), 3.48 (d, $J$ = 18.5 Hz, 1H), 3.71 (dd, $J$ = 18.4 Hz, $J$ = 1.1 Hz, 1H), 5.12 (dd, $J$ = 17.0 Hz, $J$ = 1.4 Hz, 1H), 5.17–5.28 (m, 1H), 5.97 (dd, $J$ = 16.9 Hz, $J$ = 10.3 Hz, $J$ = 4.7 Hz, 1H), 6.13–6.20 (m, 1H), 7.04–7.19 (m, 1H), 7.22–7.40 (m, 5H), 7.84–8.00 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 21.8, 39.5, 62.5, 116.7, 126.3, 127.6, 127.7, 128.6, 129.2, 129.4, 130.9, 133.6, 135.1, 136.0, 145.1, 169.0 ppm; HRMS (FAB) Calcd m/z for [M+H]$^+$: C$_{15}$H$_{14}$NO$_3$S = 328.1007. Found: 328.1009.

1-Ethenyl-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2b).

Yield: 88%; Eluent: n-hexane/ethyl acetate = 4/1 to 2/1; White solid; mp: 140–142 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.32 (s, 1H), 2.39 (s, 1H), 3.42 (d, $J$ = 18.4 Hz, 1H), 3.68 (d, $J$ = 18.4 Hz, 1H), 5.11 (dd, $J$ = 16.9 Hz, $J$ = 1.6 Hz, 1H), 5.19 (dd, $J$ = 10.2 Hz, $J$ = 1.6 Hz, 1H), 5.88–6.03 (m, 1H), 6.09–6.17 (m, 1H), 6.93 (s, 1H), 7.07–7.15 (m, 1H), 7.18–7.24 (m, 1H), 7.25 (m, 1H), 7.28 (m, 1H), 7.85–7.95 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 21.2, 21.7, 39.5, 62.4, 116.4, 126.2, 128.2(6), 128.2(9), 129.1, 129.3, 130.6, 130.8, 135.4, 136.0, 138.6, 145.0, 169.2 ppm; HRMS (El) Calcd for C$_{19}$H$_{19}$NO$_3$S [M]$^+$: 341.1086. Found: 341.1083.

1-Ethenyl-7-methoxy-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2c).

Reaction temperature: 100 °C; Yield: 50%; Eluent: n-hexane/ethyl acetate = 4/1; Light yellow solid; mp: 140–142 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.40 (s, 1H), 3.43 (d, $J$ = 18.4 Hz, 1H), 3.63 (d, $J$ = 18.4 Hz, 1H), 3.83 (s, 1H), 5.14 (dd, $J$ = 16.9 Hz, $J$ = 1.6 Hz, 1H), 5.22 (dd, $J$ = 10.2 Hz, $J$ = 1.6 Hz, 1H), 5.95 (dd, $J$ = 16.9 Hz, $J$ = 10.3 Hz, $J$ = 4.7 Hz, 1H), 6.08–6.15 (m, 1H), 6.78–6.90 (m, 2H), 6.99–7.07 (m, 1H), 7.23–7.33 (m, 2H), 7.85–7.95 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 21.8, 38.8, 55.6, 62.6, 111.9, 114.2, 116.8, 122.7, 128.8, 129.2, 129.4, 134.7, 135.0, 136.1, 145.1, 159.1, 169.3 ppm; HRMS (El) Calcd for C$_{19}$H$_{19}$NO$_3$S [M]$^+$: 357.1035. Found: 357.1032.
5-Ethenyl-6-[(4-methylphenyl)sulfonyl]-5,8-dihydro[1,3]dioxolo[4,5-g]isoquinolin-7(6H)-one (2d).

Yield: 50%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow green solid; mp: 176–178 °C; 1H NMR (300 MHz, CDCl₃) δ 2.40 (s, 1H), 3.36 (d, J = 18.5 Hz, 1H), 3.61 (d, J = 18.4 Hz, 1H), 5.06–5.17 (m, 1H), 5.17–5.25 (m, 1H), 5.85–5.96 (m, 1H), 5.96–6.00 (m, 2H), 6.00–6.07 (m, 1H), 6.57 (s, 1H), 6.79 (s, 1H), 7.20–7.38 (m, 2H), 7.80–8.01 (m, 2H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 21.8, 39.4, 62.3, 101.6, 106.9, 108.0, 116.5, 124.3, 126.9, 129.1, 129.4, 135.0, 136.0, 145.1, 147.2, 148.0, 168.9 ppm; HRMS (EI) m/z Calcd for C₁₉H₁₇NO₃S [M]+: 371.0827. Found: 371.0825.

1-Ethenyl-7-fluoro-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2e).

Yield: 64%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 138–140 °C; 1H NMR (300 MHz, CDCl₃) δ 2.41 (s, 1H), 3.47 (d, J = 18.4 Hz, 1H), 3.65 (d, J = 18.5 Hz, 1H), 5.13 (dd, J = 16.9 Hz, J = 1.7 Hz, 1H), 5.25 (dd, J = 10.3 Hz, J = 1.7 Hz, 1H), 5.87–6.01 (m, 1H), 6.06–6.20 (m, 1H), 6.91–7.13 (m, 3H), 7.25–7.33 (m, 2H), 7.83–8.01 (m, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 21.8, 38.9, 62.1, 113.5 (d, J = 22.8 Hz), 115.7 (d, J = 21.6 Hz), 117.2, 126.7 (d, J = 3.2 Hz), 129.2, 129.3, 129.4 134.5, 135.5 (d, J = 7.6 Hz), 135.8, 145.3, 162.0 (d, J = 247.4 Hz), 168.7 ppm; 19F NMR (282 MHz, CDCl₃) δ -114.21 – -114.13 (m) ppm; HRMS (EI) m/z Calcd for C₁₉H₁₆FNO₃S [M]+: 345.0835. Found: 345.0837.

1-Ethenyl-8-fluoro-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2f).

Yield: 30%; Eluent: n-hexane/ethyl acetate = 6/1; Orange solid; mp: 138–140 °C. 1H NMR (300 MHz, CDCl₃) δ 2.41 (s, 1H), 3.52 (d, J = 18.5 Hz, 1H), 3.70 (d, J = 18.5 Hz, 1H), 5.18 (dd, J = 17.0 Hz, J = 1.6 Hz, 1H), 5.26 (dd, J = 10.3 Hz, J = 1.7 Hz, 1H), 5.95 (ddd, J = 16.9 Hz, J = 10.3 Hz, J = 4.8 Hz, 1H), 6.46 – 6.59 (m, 1H), 6.87 – 6.97 (m, 1H), 6.99 – 7.11 (m, 1H), 7.23 – 7.33 (m, 3H), 7.89 – 7.99 (m, 1H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 21.8, 39.2, 56.0 (d, J = 3.3 Hz), 114.4 (d, J = 21.0 Hz), 117.0, 121.2 (d, J = 16.4 Hz), 123.2 (d, J = 3.5 Hz), 129.3 (d, J = 8.1 Hz), 130.2 (d, J = 8.3 Hz), 133.5(8), 133.6(1), 135.8, 145.3, 158.4 (d, J = 249.1 Hz), 168.5 ppm; 19F NMR (282 MHz, CDCl₃) δ -119.74 – -119.69 (m) ppm; HRMS (FAB) Calcd m/z for C₁₈H₁₇FNO₃S [M]+: 346.0913. Found: 346.0910.

6-Chloro-1-ethenyl-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2g).

Reaction temperature: 100 °C; Yield: 41%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 132–134 °C; 1H NMR (300 MHz, CDCl₃) δ 2.41 (s, 1H), 3.45 (d, J = 18.5 Hz, 1H), 3.69 (d, J = 18.5 Hz, 1H), 5.11 (dd, J = 17.0 Hz, J = 1.7 Hz, 1H), 5.24 (dd, J = 10.3 Hz, J = 1.7 Hz, 1H), 5.87–6.02 (m, 1H), 6.08–6.20 (m, 1H), 7.13 (brs, 1H), 7.25–7.33 (m, 4H), 7.82–7.99 (m, 2H) ppm; 13C NMR (75.5 MHz, CDCl₃) δ 21.8, 39.2, 61.9, 117.0, 127.7, 127.7(8), 127.8(3), 129.2, 129.4, 132.1, 132.9, 134.5, 134.7, 135.8, 145.3, 168.2 ppm; HRMS (FAB) m/z Calcd for C₁₉H₁₇ClNO₃S [M]+: 362.0618. Found: 362.0621; C₁₉H₁₇ClNO₃S [M+2]+: 364.0593. Found: 364.0612.
7-bromo-1-ethenyl-2-[(4-methylphenyl)sulfonyl]-1,4-dihydroisoquinolin-3(2H)-one (2h).

Reaction temperature: 100 °C; Yield: 76%; Eluent: n-hexane/ethyl acetate = 4/1; White solid; mp: 177–179 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.41 (s, 1H), 3.45 (d, \(J = 18.5\) Hz, 1H), 3.63 (d, \(J = 18.3\) Hz, 1H), 5.14 (dd, \(J = 16.9\) Hz, \(J = 1.7\) Hz, 1H), 5.25 (dd, \(J = 10.3\) Hz, \(J = 1.7\) Hz, 1H), 5.94 (ddd, \(J = 16.9\) Hz, \(J = 10.3\) Hz, \(J = 4.7\) Hz, 1H), 6.07–6.16 (m, 1H), 6.97–7.04 (m, 1H), 7.26–7.34 (m, 2H), 7.40–7.46 (m, 1H), 7.46–7.53 (m, 1H), 7.84–7.99 (m, 2H) ppm; \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) \(\delta\) 21.8, 39.1, 61.9, 117.3, 121.3, 129.2, 129.3, 129.3(7), 129.4(4), 130.0, 131.7, 134.5, 135.6, 135.8, 145.3, 168.3 ppm; HRMS (FAB) \(m/z\) Calcd for C\(_{18}\)H\(_7\)BrNO\(_3\)S [M\(^\dagger\)]: 406.0113. Found: 406.0114; C\(_{18}\)H\(_{17}\)BrNO\(_3\)S [M\(^\dagger\)]: 408.0093. Found: 408.0134.

2-Tosyl-1-vinyl-1,4-dihydrobenzo[4,5]thieno[2,3-c]pyridin-3(2H)-one (2j).

Yield: 24%; Eluent: n-hexane/ethyl acetate = 4/1; Yellow solid; mp: 198–200 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.42 (s, 1H), 3.63 (dd, \(J = 20.4\) Hz, \(J = 1.4\) Hz, 1H), 3.84 (d, \(J = 20.4\) Hz, 1H), 5.28–5.36 (m, 1H), 5.36–5.48 (m 1H), 5.91–6.11 (m, 1H), 6.23–6.37 (m, 1H), 7.29–7.34 (m, 2H), 7.34–7.43 (m, 2H), 7.50–7.59 (m, 1H), 7.79–7.90 (m, 1H), 7.91–8.01 (m, 2H) ppm; \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) \(\delta\) 21.8, 33.7, 59.4, 117.9, 121.1,123.0, 124.9, 125.4, 125.7, 129.3, 129.4, 132.6, 135.8, 135.9, 137.0, 140.2, 145.2, 167.8 ppm; HRMS (FAB) Calcd \(m/z\) for C\(_{20}\)H\(_{18}\)NO\(_3\)S\(_2\) [M+H\(^\dagger\)]: 384.0728. Found: 384.0729.

1-Ethenyl-2-(methylsulfonyl)-1,4-dihydroisoquinolin-3(2H)-one (2k).

Yield: 64%; Eluent: n-hexane/ethyl acetate = 4/1 ; Light yellow liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.39 (s, 3H), 3.67 (d, \(J = 18.6\) Hz, 1H), 3.83 (d, \(J = 18.6\) Hz, 1H), 5.07–5.31 (m, 2H), 5.82–6.03 (m, 2H), 7.14–7.25 (m, 1H), 7.25–7.40 (m, 3H) ppm; \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) \(\delta\) 39.4, 42.6, 61.9, 116.8, 126.5, 127.7, 127.8, 128.8, 130.8, 133.2, 134.8, 170.5 ppm; HRMS (EI) \(m/z\) Calcd for C\(_{12}\)H\(_{13}\)NO\(_3\)S [M\(^\dagger\)]: 251.0616. Found: 251.0614.

\(N\)-[1-Ethenyl-3-oxo-2,3-dihydro-1H-inden-2-yl]-4-methylbenzene-1-sulfonamide (3a).

Yield: 72%; d.r > 99:1; Eluent: n-hexane/ethyl acetate = 4/1; White solid; mp: 135–138 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.43 (s, 3H), 3.78–3.90 (m, 2H), 5.22–5.39 (m, 3H), 5.84–6.01 (m, 1H), 7.31 (d, \(J = 8.1\) Hz, 2H), 7.38–7.48 (m, 2H), 7.62–7.76 (m, 2H), 7.83 (d, \(J = 8.3\) Hz, 2H) ppm; \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) \(\delta\) 21.7, 51.4, 65.2, 119.2, 124.3, 126.6, 127.8, 128.7, 129.8, 133.2, 136.2(0), 136.2(4), 136.6, 144.0, 152.9, 200.5 ppm. HRMS (EI) Calcd \(m/z\) for C\(_{19}\)H\(_{17}\)NO\(_3\)S\(_2\) [M\(^\dagger\)]: 327.0929. Found: 327.0930.

\(1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.42 (s, 3H), 4.22–4.26 (m, 1H), 4.32–4.37 (m, 1H), 4.80 (dt, \(J = 17.1\) Hz, \(J = 1.2\) Hz, 1H), 5.08–5.21 (m, 2H), 5.70–5.83 (m, 1H), 7.28–7.36 (m, 2H), 7.39–7.49 (m, 2H), 7.62–7.76 (m, 2H), 7.80–7.88 (m, 2H) ppm; \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)) \(\delta\) 21.7, 48.0, 62.9, 118.6, 124.4, 127.5(5), 127.5(7), 128.8, 129.9, 133.2, 136.1, 136.5, 136.6, 144.0, 152.8, 200.4 ppm. HRMS (EI) Calcd \(m/z\) for C\(_{19}\)H\(_{17}\)NO\(_3\)S\(_2\) [M\(^\dagger\)]: 327.0929. Found: 327.0930.

S13
N-[1-Ethenyl-5-methyl-3-oxo-2,3-dihydro-1H-inden-2-yl]-4-methylbenzene-1-sulfonamide (3b).

Yield: 71%; d.r > 99:1; Eluent: n-hexane/ethyl acetate = 4:1; Yellow solid; mp: 127–129 °C. ¹H NMR (300 MHz, CDCl₃) δ 2.38 (s, 3H), 2.42 (s, 3H), 3.72–3.86 (m, 2H), 5.29–5.33 (m, 2H), 5.39 (d, J = 4.5 Hz, 1H), 5.80–5.97 (m, 1H), 7.25–7.36 (m, 3H), 7.43–7.53 (m, 2H), 7.77–7.88 (m, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 21.2, 21.7, 51.0, 65.4, 118.8, 124.1, 126.2, 127.7, 129.7, 133.3, 136.4, 136.7, 137.4, 138.8, 143.8, 150.3, 200.5 ppm. HRMS (EI) Calcd m/z for C₁₉H₁₇NO₃S [M⁺]: 341.1086. Found: 341.1083.

N-(3-Ethenyl-5-methoxy-1-oxo-2,3-dihydro-1H-inden-2-yl)-4-methylbenzene-1-sulfonamide (3c).

Yield: 60 mol% of Rh₃(TMA)₄ was used at 60 °C; Yield: 65%; d.r > 99:1; Eluent: n-hexane/ethyl acetate = 4:1; Yellow solid; mp: 90–92 °C. ¹H NMR (300 MHz, CDCl₃) δ 2.42 (s, 3H), 3.71–3.84 (m, 2H), 3.88 (s, 3H), 5.24–5.39 (m, 2H), 5.81–5.99 (m, 1H), 6.77–6.87 (m, 1H), 6.89–6.97 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.5 Hz, 1H), 7.78–7.87 (m, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 21.6, 51.5, 55.8, 64.9, 109.6, 116.9, 119.2, 126.1(8), 126.1(9), 127.8, 129.8, 136.3, 136.4, 143.9, 156.4, 166.6, 198.3 ppm; HRMS (EI) Calcd m/z for C₁₉H₁₉NO₃S [M⁺]: 357.1035. Found: 357.1033.

N-(5-Ethenyl-7-oxo-6,7-dihydro-2H,5H-indeno[5,6-d][1,3]dioxol-6-yl)-4-methylbenzene-1-sulfonamide (3d).

Yield: 60 mol% of Rh₃(TMA)₄ was used at 60 °C; Yield: 51%, d.r = 91:9; Eluent: n-hexane/ethyl acetate = 4:1; Yellow solid; mp: 170–172 °C. ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3H), 3.65–3.82 (m, 2H), 5.18–5.40 (m, 3H), 5.79–5.94 (m, 1H), 6.08 (s, 2H), 6.77 (s, 1H), 7.03 (s, 1H), 7.28–7.36 (m, 2H), 7.78–7.86 (m, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 21.7, 51.3, 65.1, 102.6, 102.7, 105.9, 119.1, 127.7, 127.8, 129.8, 136.3(6), 136.4(2), 144.0, 149.2, 151.3, 155.6, 198.1 ppm; HRMS (EI) Calcd m/z for C₁₉H₁₇NO₃S [M⁺]: 371.0827. Found: 371.0827.

N-(3-Ethenyl-5-fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)-4-methylbenzene-1-sulfonamide (3e).

Yield: 78%; d.r > 99:1; Eluent: n-hexane/ethyl acetate = 4:1; colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3H), 3.77–3.90 (m, 2H), 5.22–5.42 (m, 3H), 5.82–5.99 (m, 1H), 7.05–7.17 (m, 2H), 7.32(d, J = 8.0 Hz, 2H), 7.68–7.79 (m, 1H), 7.79–8.72 (m, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 21.7, 51.3 (d, J = 7.5 Hz), 65.2, 113.5 (d, J = 22.6 Hz), 117.2 (d, J = 24.0 Hz), 119.8, 126.8, 126.9 (d, J = 10.4 Hz), 127.8, 129.6 (d, J = 2.0 Hz), 129.8, 135.6, 136.5, 144.1, 156.2 (d, J = 9.9 Hz), 168.1 (d, J = 259 Hz), 198.6 ppm; ¹⁹F NMR (282 MHz, CDCl₃) δ -99.19 – -99.11 (m) ppm; HRMS (EI) Calcd m/z for C₁₈H₁₆FNO₃S [M⁺]: 345.0835. Found: 345.0833.

N-(5-Chloro-1-ethenyl-3-oxo-2,3-dihydro-1H-inden-2-yl)-4-methylbenzene-1-sulfonamide (3g).

Yield: 61%; d.r = 91:9; Eluent: n-hexane/ethyl acetate = 4:1; Yellow solid; mp: 145–148 °C. ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3H), 3.74–3.92 (m, 2H), 5.22–5.39 (m, 3H), 5.88 (ddd, J = 17.0 Hz, J = 8.4 Hz, J = 10.2 Hz, 1H), 7.28–7.41 (m, 3H), 7.56–7.69 (m, 2H), 7.78–7.86 (m, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 21.7, 50.9, 65.5, 119.6, 123.9, 127.7, 127.9, 129.8, 134.6, 135.2, 135.7,
136.2, 136.6, 144.1, 150.9, 199.3 ppm; HRMS (EI) Calcd m/z for C_{18}H_{16}^{35}ClNO_{5}S [M]^{+}: 361.0539. Found: 361.0541; C_{18}H_{16}^{37}ClNO_{5}S [M+2]^{+}: 363.0515. Found: 363.0523.

N-(5-Bromo-1-oxo-3-vinyl-2,3-dihydro-1H-inden-2-yl)-4-methylbenzenesulfonamide (3h).

20 mol% of TFA was added in Pd catalysis step; Yield: 62%; d.r = 91:9; Eluent: n-hexane/ethyl acetate = 4/1; White solid; mp: 138–140 °C. "H NMR (300 MHz, CDCl$_3$) δ 2.43 (s, 3H), 3.72–3.93 (m, 2H), 5.22–5.45 (m, 3H), 5.78–5.99 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.53–7.63 (m, 3H), 7.77–7.87 (m, 2H) ppm; "C NMR (75.5 MHz, CDCl$_3$) δ 21.7, 51.2, 65.2, 119.9, 125.5, 127.8, 129.9, 130.0, 131.9, 132.0, 132.5, 135.5, 136.5, 144.1, 154.5, 199.3 ppm; HRMS (EI) Calcd m/z for C$_{19}$H$_{15}$BrNO$_{5}$S [M]$: 405.0034. Found: 405.0037; C$_{19}$H$_{16}^{38}$BrNO$_{5}$S [M]$^{+}$: 407.0015. Found: 407.0006.

4-Methyl-N-(1-oxo-5-(trifluoromethyl)-3-vinyl-2,3-dihydro-1H-inden-2-yl)benzenesulfonamide (3i).

Yield: 68%; d.r = 95:5; Eluent: n-hexane/ethyl acetate = 4/1; White solid; mp: 150–152 °C. "H NMR (300 MHz, CDCl$_3$) δ 2.45 (s, 3H), 3.83–4.02 (m, 2H), 5.27–5.49 (m, 3H), 5.81–6.01 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.64–7.77 (m, 2H), 7.84 (d, J = 8.3 Hz, 3H) ppm; "C NMR (75.5 MHz, CDCl$_3$) δ 21.7, 51.3, 65.6, 118.0–128.9 (m), 120.3, 123.7–123.8 (m), 124.9, 125.8–125.9 (m), 127.7, 129.8, 135.2, 135.8, 136.7, 136.7–138.1 (m), 144.1, 153.0, 199.7 ppm; "F NMR (282 MHz, CDCl$_3$) δ -63.04 ppm; HRMS (EI) Calcd m/z for C$_{19}$H$_{16}^{18}$F$_{3}$NO$_{5}$S [M]: 395.0803. Found: 395.0802.

N-(1-Ethenyl-3-oxo-2,3-dihydro-1H-inden-2-yl) methanesulfonamide (3j).

Yield: 50%; d.r = 91:9; Eluent: n-hexane/ethyl acetate = 4/1; Colorless oil; Major product "H NMR (300 MHz, CDCl$_3$) δ 3.21 (s, 3H), 3.73–3.84 (m, 1H), 4.20 (dd, J = 7.2 Hz, J = 6.1 Hz, 1H), 5.20–5.33 (m, 1H), 5.38–5.58 (m, 2H), 5.90–6.10 (m, 1H), 7.41–7.52 (m, 2H), 7.64–7.83 (m, 2H) ppm; "C NMR (75.5 MHz, CDCl$_3$) δ 43.2, 51.6, 65.8, 120.1, 124.3, 126.3, 128.9, 133.2, 135.9, 136.3, 152.1, 201.0 ppm; HRMS (EI) Calcd m/z for C$_{19}$H$_{15}$N$_{3}$O$_{5}$S [M]$: 251.0616. Found: 251.0615.

(Z)-4-Methyl-N-(1-vinylisochroman-3-ylidene) benzenesulfonamide (4a).

Yield: 66%; Eluent: n-hexane/ethyl acetate = 3/1; White solid; "H NMR (300 MHz, CDCl$_3$) δ 2.04 (s, 3H), 3.58–3.84 (m, 1.67H), 4.16–4.73 (brs, 0.26H), 5.26 (d, J = 16.7 Hz, 1H) 5.42 (d, J = 10.0 Hz, 1H), 5.76–6.09 (m, 2H), 7.12–7.44 (m, 6H), 7.81–7.94 (m, 2H) ppm; "C NMR (75.5 MHz, CDCl$_3$) δ 21.6, 35.4, 83.5, 120.5, 125.1, 127.5, 127.8, 129.0, 129.3, 129.4, 129.7, 132.2, 132.5, 138.5, 143.4, 168.1 ppm; HRMS (FAB) Calcd m/z for C$_{18}$H$_{18}^{18}$N_{3}O$_{5}$S [M+H]$: 251.1007. Found: 251.0810.

(Z)-4-Methyl-N-((3-vinylisobenzofuran-1(3H)-ylidene)methyl) benzenesulfonamide (5a).

Yield: 80%; Eluent: n-hexane/ethyl acetate = 6/1; Yellow oil; "H NMR (300 MHz, CDCl$_3$) δ 2.37 (s, 3H), 5.12–5.27 (m, 1H), 5.27–5.42 (m, 1H), 5.60–5.81 (m, 2H), 6.03 (d, J = 10.3 Hz, 1H) 6.37 (d, J = 10.3 Hz, 1H), 7.03–7.18 (m, 1H), 7.21–7.34 (m, 3H), 7.78 (d, J = 8.31, 2H) ppm; "C NMR (75.5 MHz, CDCl$_3$) δ 21.5, 86.6, 95.0, 117.9, 118.8, 122.0, 127.0, 128.5, 128.6, 129.7, 131.8, 135.4, 137.0, 140.7, 143.5, 145.1 ppm; HRMS (EI) Calcd m/z for C$_{18}$H$_{17}$NO$_{5}$S [M]: 327.0929. Found: 327.0928.
12. X-ray Crystal Structure and Data of 2a

Empirical formula: \( \text{C}_{18} \text{H}_{17} \text{N}_{3} \text{O}_{3} \text{S} \)

Formula weight: 327.39

Temperature: 223(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group: P-1

Unit cell dimensions:
- \( a = 8.3301(5) \text{ Å} \) \( \alpha = 106.868(2)^{\circ} \)
- \( b = 10.1313(5) \text{ Å} \) \( \beta = 106.256(2)^{\circ} \)
- \( c = 10.5314(6) \text{ Å} \) \( \gamma = 99.042(2)^{\circ} \)

Volume: 788.58(8) Å\(^3\)

Z: 2

Density (calculated): 1.379 Mg/m\(^3\)

Absorption coefficient: 0.220 mm\(^{-1}\)

\( F(000) \): 344

Crystal size: 0.19 x 0.15 x 0.10 mm\(^3\)

Theta range for data collection: 2.15 to 28.34°

Index ranges:
- \(-11 \leq h \leq 11\), \(-13 \leq k \leq 13\), \(-14 \leq l \leq 14\)

Reflections collected: 33101

Independent reflections: 3937 \( [R(int) = 0.0268] \)

Completeness to theta = 28.34°: 100.0%

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.9784 and 0.9594

Refinement method: Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters: 3937 / 0 / 209

Goodness-of-fit on \( F^2 \): 1.048

Final R indices [I>2sigma(I)]: \( R_1 = 0.0389, wR_2 = 0.1055 \)

R indices (all data): \( R_1 = 0.0458, wR_2 = 0.1112 \)

Largest diff. peak and hole: 0.394 and -0.227 e.Å\(^{-3}\)
### 13. X-ray Crystal Structure and Data of 3a

![Chemical structure of 3a](image)

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<th>Property</th>
<th>Value</th>
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<td>Theta range for data collection</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Refinement program</td>
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<tr>
<td>Function minimized</td>
<td>Σ w(Fo² - Fc²)²</td>
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<tr>
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<td>Goodness-of-fit on F2</td>
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<td>Final R indices</td>
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<td>all data R1 = 0.0685, wR2 = 0.1243</td>
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<td>Weighting scheme</td>
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<td>where P=(Fo²+2Fc²)/3</td>
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<td>Largest diff. peak and hole</td>
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<td>R.M.S. deviation from mean</td>
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14. Copies of $^1$H and $^{13}$C NMR Spectra

$^1$H spectra of compound 1a

$^{13}$C spectra of compound 1a

S18
$^1$H spectra of compound 1b

$^{13}$C spectra of compound 1b

S19
$^{1}H$ spectra of compound 1c

$^{13}C$ spectra of compound 1c
$^1$H spectra of compound 1d

$^1$C spectra of compound 1d
$^1$H spectra of compound 1e

$^1$C spectra of compound 1e
$^{19}$F spectra of compound 1e
$^1$H spectra of compound 1f

$^{13}$C spectra of compound 1f
$^{19}$F spectra of compound 1f
$^1$H spectra of compound 1g

$^{13}$C spectra of compound 1g
$^1$H spectra of compound 1g

$^1$C spectra of compound 1g
$^{1}H$ spectra of compound $\textit{II}$

$^{13}C$ spectra of compound $\textit{II}$
$^{19}$F spectra of compound II
$^1$H spectra of compound 1j

$^1$C spectra of compound 1j
$^1$H spectra of compound 1k

$^1$C spectra of compound 1k
$^1$H spectra of compound 2a

$^{13}$C spectra of compound 2a
$^1$H spectra of compound 2b

$^{13}$C spectra of compound 2b
$^1$H spectra of compound 2c

$^{13}$C spectra of compound 2c
$^1$H spectra of compound 2d

$^{13}$C spectra of compound 2d
$^1$H spectra of compound 2e

$^1^3$C spectra of compound 2e
$^{19}$F spectra of compound 2e
$^1$H spectra of compound 2f

$^{13}$C spectra of compound 2f
$^{19}$F spectra of compound 2f
$^1$H spectra of compound 2g

$^{13}$C spectra of compound 2g
$^1$H spectra of compound 2h

$^{13}$C spectra of compound 2h
$^1$H spectra of compound 2j

$^{13}$C spectra of compound 2j
$^1$H spectra of compound 2k

$^{13}$C spectra of compound 2k
\[ \text{1H spectra of compound 3a (crude)} \]

\[ \text{1H spectra of compound 3a (cis/trans mixture after column chromatography)} \]
\(^1\)H spectra of compound 3a \((trans)\)

\(^{13}\)C spectra of compound 3a \((trans)\)
$^1$H spectra of compound 3a' (cis)

$^{13}$C spectra of compound 3a' (cis)
\(^1\)H spectra of compound 3b (crude)

\(^1\)H spectra of compound 3b (cis/trans mixture after column chromatography)
$^1\text{H}$ spectra of compound 3b (trans)

$^{13}\text{C}$ spectra of compound 3b (trans)
$^1$H spectra of compound 3c (crude)

$^1$H spectra of compound 3c (cis/trans mixture after column chromatography)
$^1$H spectra of compound 3c (trans)

$^13$C spectra of compound 3c (trans)
$^1$H spectra of compound 3d (crude)

$^1$H spectra of compound 3d (cis/trans mixture after column chromatography)
$\text{S}\quad \text{52}$

13C spectra of compound 3d (trans)

155.56, 151.32, 149.24, 143.96, 136.42, 136.36, 129.80, 127.83, 127.70, 119.09

105.95, 102.69, 102.56

77.58, 77.16, 76.73

65.05

51.33

21.71

H spectra of compound 3d (trans)
\( ^1H \) spectra of compound 3e (crude)

\( ^1H \) spectra of compound 3e (cis/trans mixture after column chromatography)
$^1$H spectra of compound 3e (trans)

$^{13}$C spectra of compound 3e (trans)
$^{19}$F spectra of compound 3e
$^1$H spectra of compound 3g (crude)

$^1$H spectra of compound 3g (cis/trans mixture after column chromatography)
$^1$H spectra of compound 3g (trans)

$^{13}$C spectra of compound 3g (trans)
$^1$H spectra of compound 3h (cis/trans mixture after short silica filter)

Note.

The $^1$H NMR spectra of crude mixture of 3h was too complicated to be identified, in addition, cis/trans mixture of 3h was inseparable. Thus, $^1$H NMR spectra of cis/trans mixture after short silica filter has been attached above.

$^{13}$C spectra of compound 3h (trans)
$^1$H spectra of compound 3i (crude)

$^1$H spectra of compound 3i (cis/trans mixture after column chromatography)
$^1$H spectra of compound 3i (trans)

$^{13}$C spectra of compound 3i (trans)
$^{19}$F spectra of compound 3i
$^1$H spectra of compound 3k (crude)

Note.

The cis/trans mixture of 3k was inseparable. Thus, $^1$H NMR spectra of cis/trans mixture after silica column chromatography has been attached below.
$^1$H spectra of compound 3k (cis/trans mixture after column chromatography)

$^{13}$C spectra of compound 3k (trans)
$^1$H spectra of compound 4a

$^{13}$C spectra of compound 4a
DEPT-135 spectra of compound 4a
HSQC spectra of compound 4a

[Diagram of HSQC spectra with peaks labeled a, g, n, p, and chemical structure of compound 4a]
$^{1}$H spectra of compound 5a

$^{13}$C spectra of compound 5a