Electronic Supplementary Information for:

Asymmetric Michael Addition Reaction of 3-Aryl-N-Boc-Oxindole to Activated Terminal Alkene Catalyzed by Bifunctional Tertiary-Amine Thiourea Catalyst

Xin Li,* Zhi-Guo Xi,* Sanzhong Luo,* Jin-Pei Cheng**,*b

Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China and Department of Chemistry and State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin, 300071, China

luosz@iccas.ac.cn
Table S1. Optimization studies of Michael addition of oxindole to sulfone.

![Diagram of molecular structures]  

<table>
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<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield$^b$ (%)</th>
<th>ee$^c$ (%)</th>
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<td>THF</td>
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<td><strong>144</strong></td>
<td><strong>80</strong></td>
<td><strong>87</strong></td>
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$^a$ The reaction was carried out on a 0.1 mmol scale in 200 μL solvent at room temperature, and the molar ratio of oxindole 1d/5b is 1/3.  
$^b$ Isolated yield.  
$^c$ Determined by HPLC.  
$^d$ The reaction was carried out on a 0.1 mmol scale in 200 μL toluene with 4Å molecular formula at -20°C, and the molar ratio of oxindole 1d/5b is 1/3.  
$^e$ The reaction condition was same to the entry 10 except for 20 mol% 4d was used.
NMR spectrum for Michael products:

For the first spectrum:
- Chemical shifts (δ):
  - 7.00 ppm
  - 5.95 ppm
- Coupling constants (J):
  - J1 = 7.00 ppm
  - J2 = 3.80 ppm
  - J3 = 3.80 ppm
- HMBC shift parameters:
  - 22.00 ppm
  - 12.00 ppm
- 1H NMR shift parameters:
  - 1.00 ppm

For the second spectrum:
- Chemical shifts (δ):
  - 7.00 ppm
  - 5.95 ppm
- Coupling constants (J): 1H NMR shift parameters:
  - 1.00 ppm
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![Chemical Structure](Image)

**Data**
- **Current Data Parameters**
  - **NMR**
    - Probe: z5mm2H1, 500 MHz
    - Temperature: 298 K
    - Solvent: CDCl3
    - Impurity: 0.1%
  - **Mass Spectrometry**
    - Method: ESI-MS
    - Tune: 50 eV
    - Source Temp: 300 °C
    - Capillary: 3 kV
    - Spray: 3 MS gun
    - Ion Source: 2000 eV
    - Extract: 2000 eV
  - **UV-Visible Spectroscopy**
    - Wavelength: 190-800 nm
  - **Infrared Spectroscopy**
    - Wavenumber: 4000-400 cm⁻¹
  - **Differential Scanning Calorimetry**
    - Temperature: 50 °C
    - Heating Rate: 10 °C/min

**Results**
- **NMR Spectrum**
  - Peak at 6.5 ppm
  - Peak at 7.2 ppm
  - Peak at 8.1 ppm

**Discussion**
- The chemical structure 6a shows a Boc group attached to the nitrogen atom, with a sulfonamide functional group.
- The NMR spectrum provides information about the chemical shifts and coupling constants, which are crucial for the structural assignment.
- The mass spectrum confirms the molecular weight and allows for the identification of impurities.

**Conclusions**
- The data obtained from NMR and mass spectrometry support the proposed chemical structure for compound 6a.
- Further experiments are necessary to validate the structural integrity and purity of the compound.

**Acknowledgments**
- The authors thank the funding agencies for supporting this research.

**References**
HPLC spectrum for Michael products:

![HPLC spectrum](image)

**Peak results:**

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Chemical structures and HPLC chromatograms with peak results.

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\[
\begin{align*}
\text{CH}_3 &- \quad \begin{array}{c}
N \quad \text{Boc} \\
3g
\end{array} \\
\text{H}_3C &- \quad \begin{array}{c}
\text{O} \\
3g
\end{array} \\
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**Graph 1:**

- **Graph Title:** Prostar 325 Absorbance Channel 1 EL07010013
- **Peaks:**
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  - **Time (Min):** 5.57
  - **Quantity (% Area):** 92.04
  - **Height (mAU):** 922.0
  - **Area (mAU Min):** 119.1
  - **Area % (%):** 95.64

- **Index:** 2
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  - **Height (mAU):** 131.9
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- **Total:**
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  - **Height (mAU):** 147.7
  - **Area (mAU Min):** 100.0

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**Graph 2:**

- **Graph Title:** Prostar 325 Absorbance Channel 1 EL07019013
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  - **Area % (%):** 95.64

- **Index:** 2
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  - **Quantity (% Area):** 92.89
  - **Height (mAU):** 131.9
  - **Area (mAU Min):** 28.0
  - **Area % (%):** 15.76

- **Total:**
  - **Quantity (% Area):** 97.2
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| 2     | UNKNOWN  | 7.85       | 50.28        | 174.6        | 37.3           | 50.27%
| Total |          |            |              |              | 76.2          | 100.00%   |

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<td>58.3 100.000</td>
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Peak results:

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<th>Quantity (% Area)</th>
<th>Height</th>
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### Peak results:

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### Peak results:

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<th>Area (mAU Min)</th>
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Peak results:

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<th>Name</th>
<th>Time (Min)</th>
<th>Quantity (%)</th>
<th>Height (mAU)</th>
<th>Area (mAU Min)</th>
<th>Area %</th>
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Peak results:

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<th>Quantity (%)</th>
<th>Height (mAU)</th>
<th>Area (mAU Min)</th>
<th>Area %</th>
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8a

Peak results:

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<th>Time [Min]</th>
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Peak results:

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![Chemical Structure](image1)

**Peak results:**

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<tr>
<th>Index</th>
<th>Name</th>
<th>Time (Min)</th>
<th>Quantity (%)</th>
<th>Height (nA)</th>
<th>Area (nAU Min)</th>
<th>Area %</th>
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![Chromatogram](image2)

**Peak results:**

<table>
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<tr>
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<th>Name</th>
<th>Time (Min)</th>
<th>Quantity (%)</th>
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![Chromatogram](image3)
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![Chemical Structure](image)

### Peak results:

<table>
<thead>
<tr>
<th>Index</th>
<th>Name</th>
<th>Time (Min)</th>
<th>Quantity (% Area)</th>
<th>Height (mAU)</th>
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![Graph](image)

### Peak results:

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