

# Supporting Materials

## A regioselective synthesis of fused oxazepinone scaffolds through one-pot Smiles rearrangement tandem reaction

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### Experimental Section

General	P1
General Experimental Procedure for the Synthesis of (3a-l), (4b-m), (6a-d).	P1
Details of Crystal Data and Structure Refinement for Compound 4d.	P2
<sup>1</sup> H NMR and <sup>13</sup> C NMR Spectra of Compound 3a-l, 4b-m, 6a-d.	P3-P32

#### General

<sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) or 300 (300 MHz) spectrometer, using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on an XD-4 digital micro melting point apparatus. HRMS spectra were determined on a Q-TOF6510 spectrograph (Agilent). Single crystal X-ray diffraction were made on a Rigaku RAXIS-SPIDER IP diffractometer at 50 kV and 20 mA and data collection was performed at 298 K by using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å).

#### General Experimental Procedure for the Synthesis of (3a-l), (4b-m), (6a-d). Representative Procedure for the Synthesis of 10-ethyl-7-nitrodibenzo[b,f][1,4]oxazepin-11(10H)-one (3b).

To a solution of *N*-ethyl salicylamide (150 mg, 0.9 mmol) in dry DMF (10 mL) were added 1,2-difluoro-4-nitrobenzene (120 mg, 0.8 mmol) and K<sub>2</sub>CO<sub>3</sub> (310 mg, 2.3 mmol), then the mixture was stirred for 1 h at 80 °C (oil bath), and then H<sub>2</sub>O (30 mL) was added and the mixture was extracted with EtOAc (3×25 mL). The combined organic layers were washed with sat. brine (2×20 mL), dried over MgSO<sub>4</sub>, filtered, and evaporated in vacuo. The crude product was purified by

column chromatography on silica gel (PE/EtOAc = 5:1) to afford the desired product **3b** as a Pale yellow oil (207 mg, 96%).

**Table 1. Details of Crystal Data and Structure Refinement for Compound 4d**

<b>Empirical formula</b>	<b>C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub></b>	
<b>Formula weight</b>	<b>264.28</b>	
<b>Temperature</b>	<b>298 K</b>	
<b>Wavelength</b>	<b>0.71073 Å</b>	
<b>Crystal system</b>	<b>orthorhombic</b>	
<b>Space group</b>	<b>Pbca</b>	
<b>Unit cell dimensions</b>	<b>a = 11.4870(18) Å</b>	<b>alpha = 90</b>
<b>deg</b>	<b>b = 14.689(2) Å</b>	<b>beta = 90</b>
<b>deg</b>	<b>c = 15.200(2) Å</b>	<b>gamma =</b>
<b>90 deg</b>		
<b>Volume</b>	<b>2564.7(7) Å<sup>3</sup></b>	
<b>Z</b>	<b>7.0</b>	
<b>Calculated density</b>	<b>1.369 Mg/m<sup>3</sup></b>	
<b>Absorption coefficient</b>	<b>0.092 mm<sup>-1</sup></b>	
<b>F(000)</b>	<b>1104.0</b>	
<b>Crystal size</b>	<b>0.15 x 0.1 x 0.08 mm</b>	
<b>Theta range for data collection</b>	<b>2.62 to 23.33 deg</b>	
<b>Limiting indices</b>	<b>-11 ≤ h ≤ 12, -16 ≤ k ≤ 16, -12</b>	
<b>≤ l ≤ 16</b>		
<b>Reflections collected / unique</b>	<b>10308 / 1861 [R (int) = 0.0691]</b>	
<b>Completeness to theta = 23.33</b>	<b>99.9%</b>	
<b>Absorption correction</b>	<b>Semi-empirical from equivalents</b>	
<b>Max. and min. transmission</b>	<b>0.9927 and 0.9863</b>	
<b>Refinement method</b>	<b>Full-matrix least-squares on F<sup>2</sup></b>	
<b>Data / restraints / parameters</b>	<b>1861/0/182</b>	
<b>Goodness-of-fit on F<sup>2</sup></b>	<b>0.985</b>	
<b>Final R indices [I&gt;2sigma(I)]</b>	<b>R1 = 0.0420, wR2 = 0.0975</b>	
<b>R indices (all data)</b>	<b>R1 = 0.0762, wR2 = 0.1159</b>	
<b>Largest diff. peak and hole</b>	<b>0.157 and -0.147 e<sup>-3</sup></b>	

**<sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3a-l, 4b-m, 6a-d**







































































