

## Supplementary Information

### First Asymmetric Reduction of Isatin by Marine-Derived Fungi

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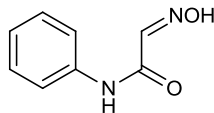
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Rio de Janeiro-RJ, Brazil

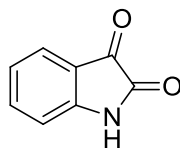
Spectral data

2-(Hydroxyimino)-*N*-phenylacetamide



<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>)  $\delta_{\text{H}}$  6.45 (t, 1H, *J* 8.0 Hz), 6.67 (t, 2H, *J* 8.0 Hz), 6.69 (s, 1H), 7.01 (d, 2H, *J* 8.0 Hz), 9.09 (s, 1H), 11.39 (s, 1H); <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>)  $\delta_{\text{C}}$  118.7, 122.6, 127.3, 136.8, 142.5, 159.2.

Isatin **1**



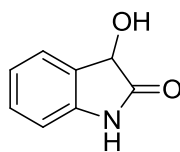
<sup>1</sup>H NMR (200 MHz, DMSO)  $\delta_{\text{H}}$  6.89 (d, 1H, *J* 8 Hz), 7.04 (td, 1H, *J* 2 and 8 Hz), 7.48 (d, 1H, *J* 8 Hz), 7.57 (td, 1H, *J* 2 and 8 Hz), 11.03 (s, 1H); <sup>13</sup>C NMR (50 MHz, DMSO)  $\delta_{\text{C}}$  112.8, 118.3, 123.3, 125.2, 138.9, 151.3, 159.9, 184.9; GC-MS (EI) *m/z* 147 (60), 119 (100), 92 (95), 64 (45), 50 (32).

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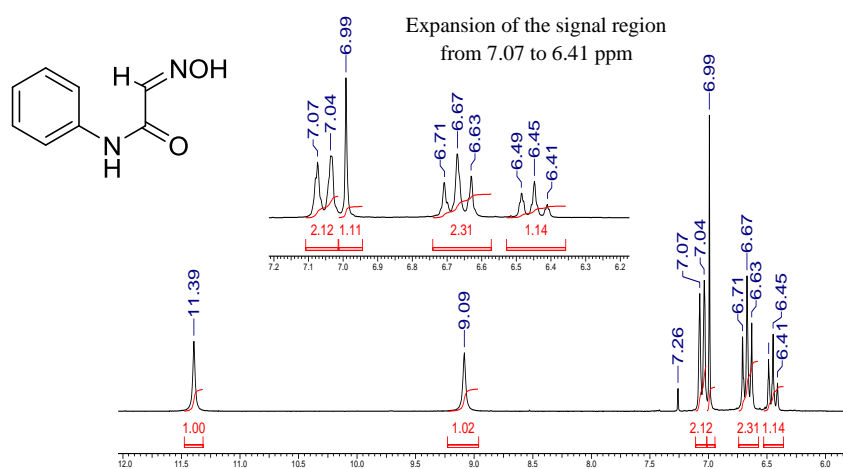
<sup>†</sup>This paper is dedicated to the memory of our wonderful Professor Angelo da Cunha Pinto.

## Dioxindole 2

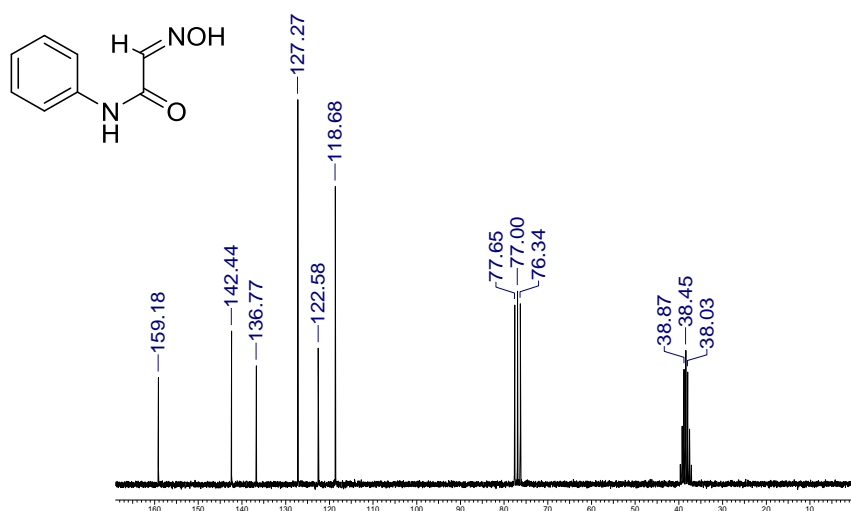


$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta_{\text{H}}$  4.83 (s, 1H), 6.16 (s, 1H), 6.57-6.87 (m, 2H), 6.93 (t, 1H,  $J$  10 Hz), 7.06-7.16 (m, 1H), 10.22 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta_{\text{C}}$  69.2, 109.48, 121.50, 124.78, 128.93, 129.32, 142.19, 177.9; GC-MS (EI)  $m/z$  149 (70), 121 (30), 105 (10), 93 (100), 51 (30).

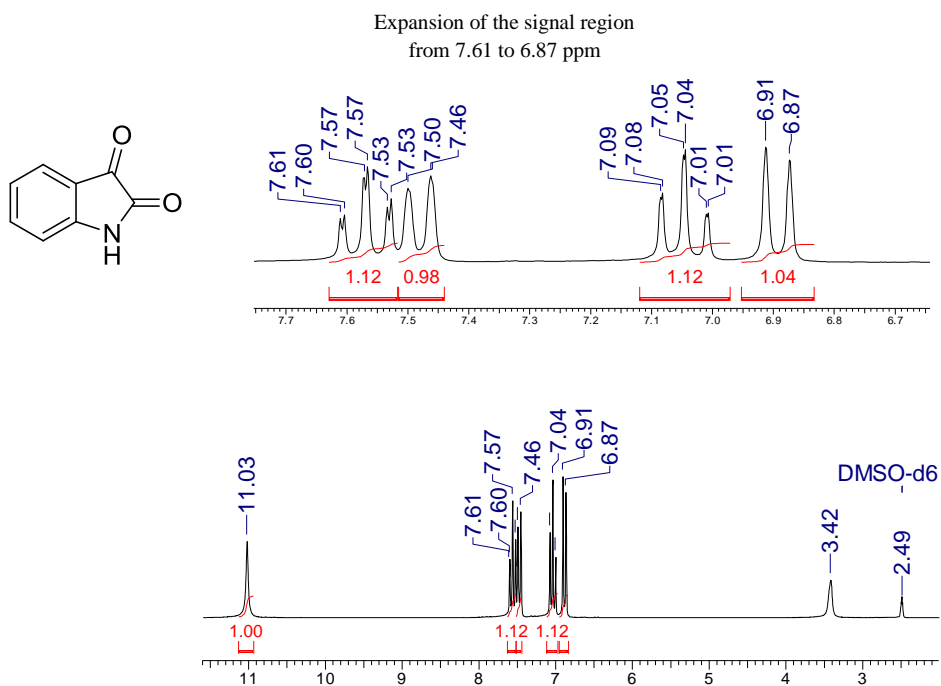
## NMR spectra



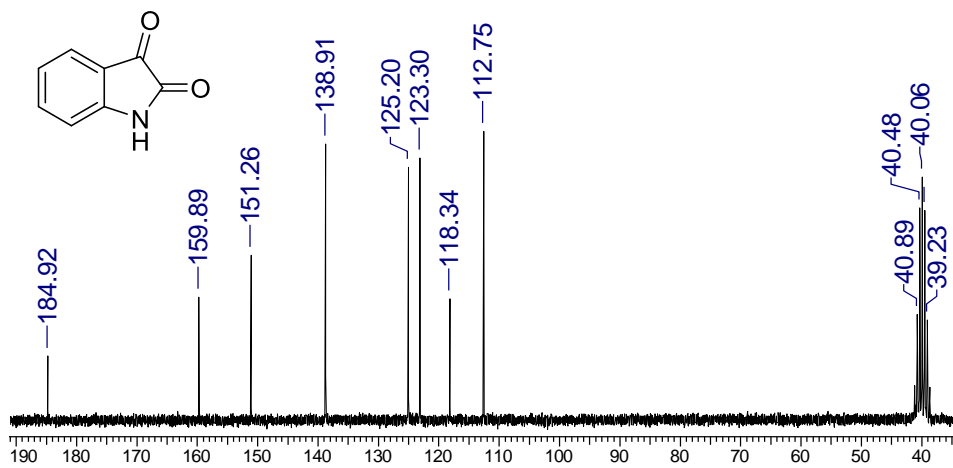
**Figure S1.** Spectrum of  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3 + \text{DMSO-}d_6$ ) of the isonitrosoacetanilide.



**Figure S2.** Spectrum of  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3 + \text{DMSO-}d_6$ ) of the isonitrosoacetanilide.



**Figure S3.** Spectrum of  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO}$ ) of the isatin.



**Figure S4.** Spectrum of  $^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO-d}_6$ ) of the isatin.

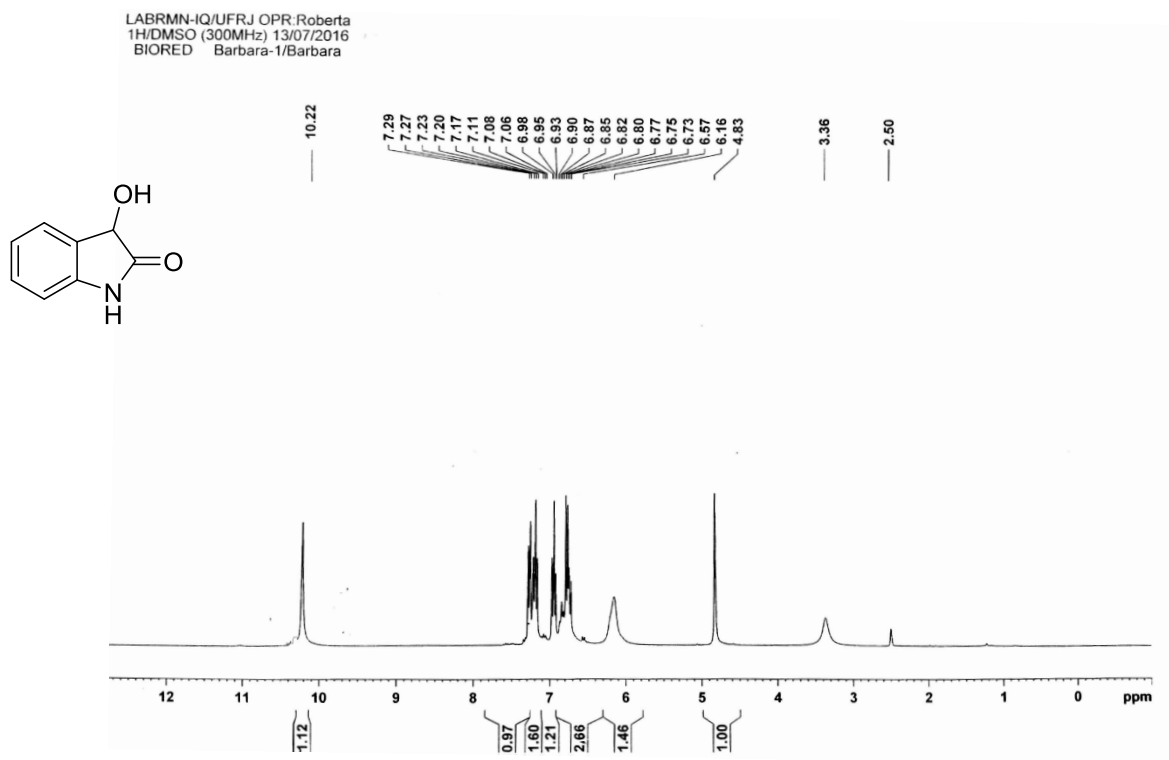


Figure S5. Spectrum of  $^1\text{H}$  NMR (500 MHz, DMSO) of the dioxindole.

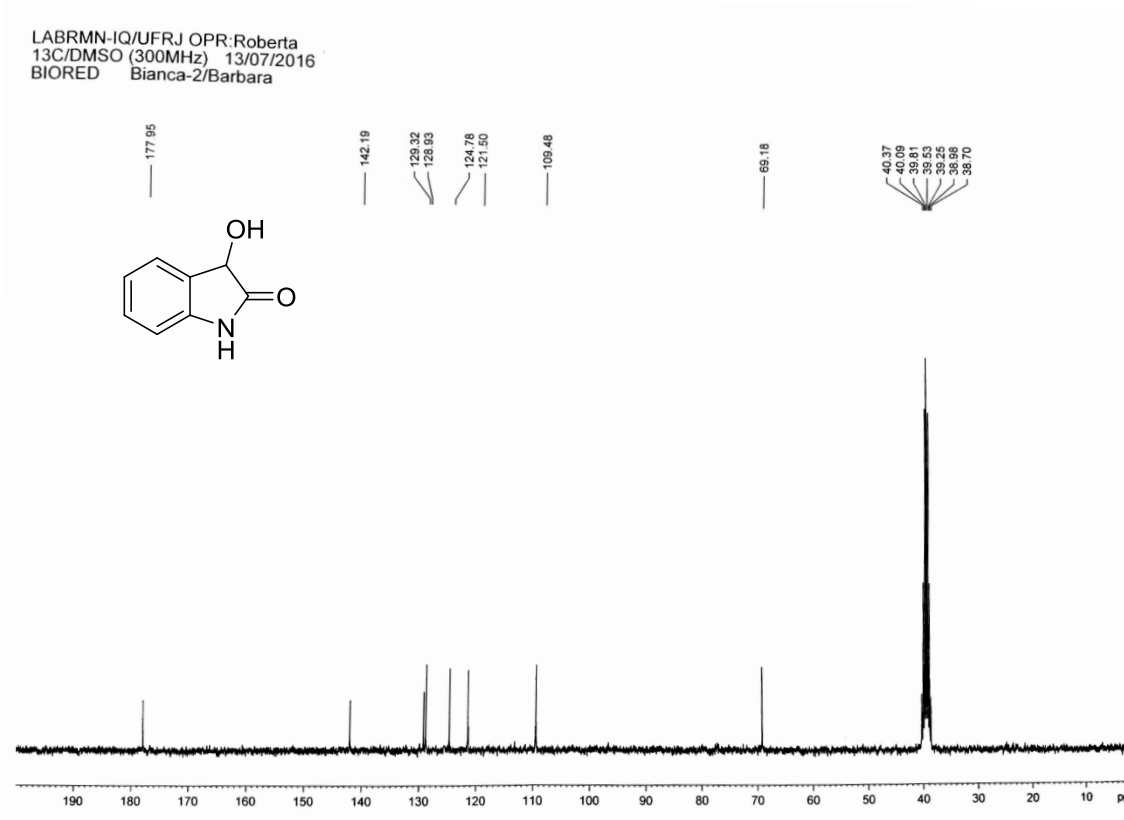
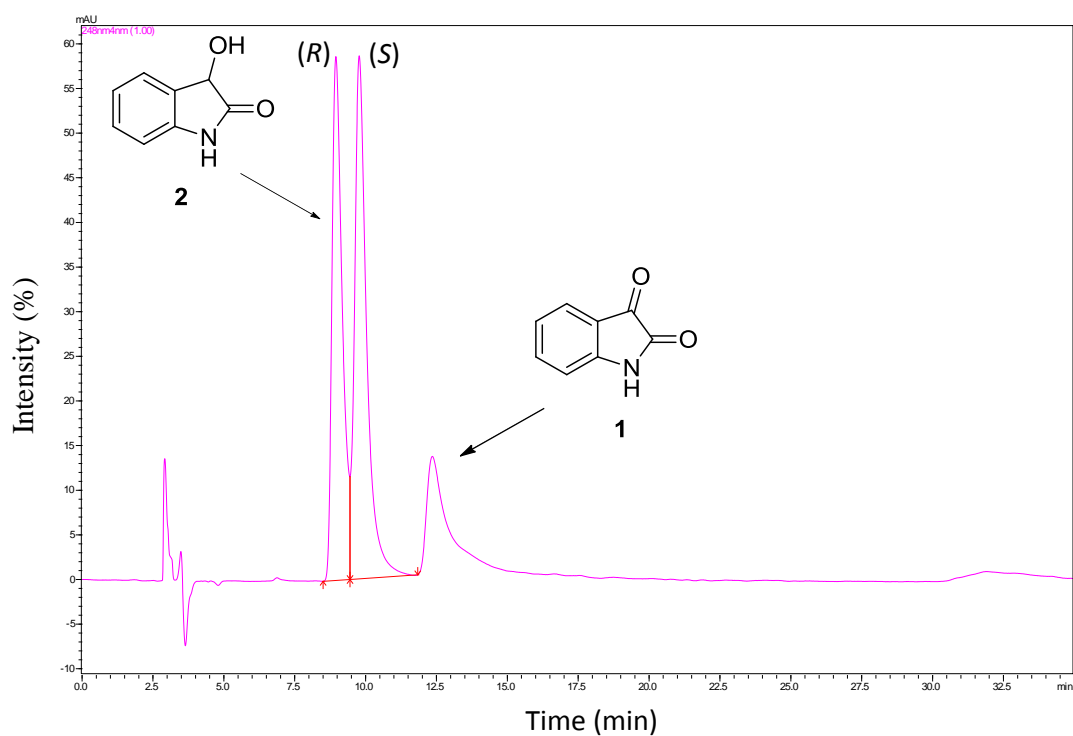
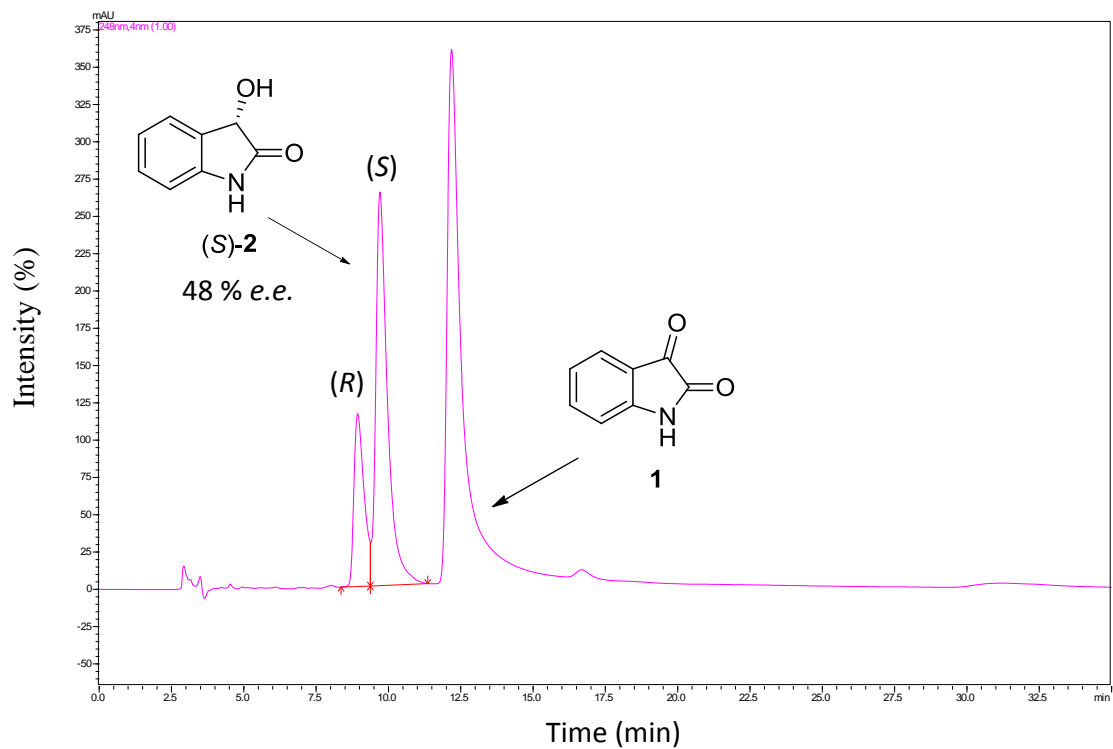


Figure S6. Spectrum of  $^{13}\text{C}$  NMR (125 MHz, DMSO) of the dioxindole.

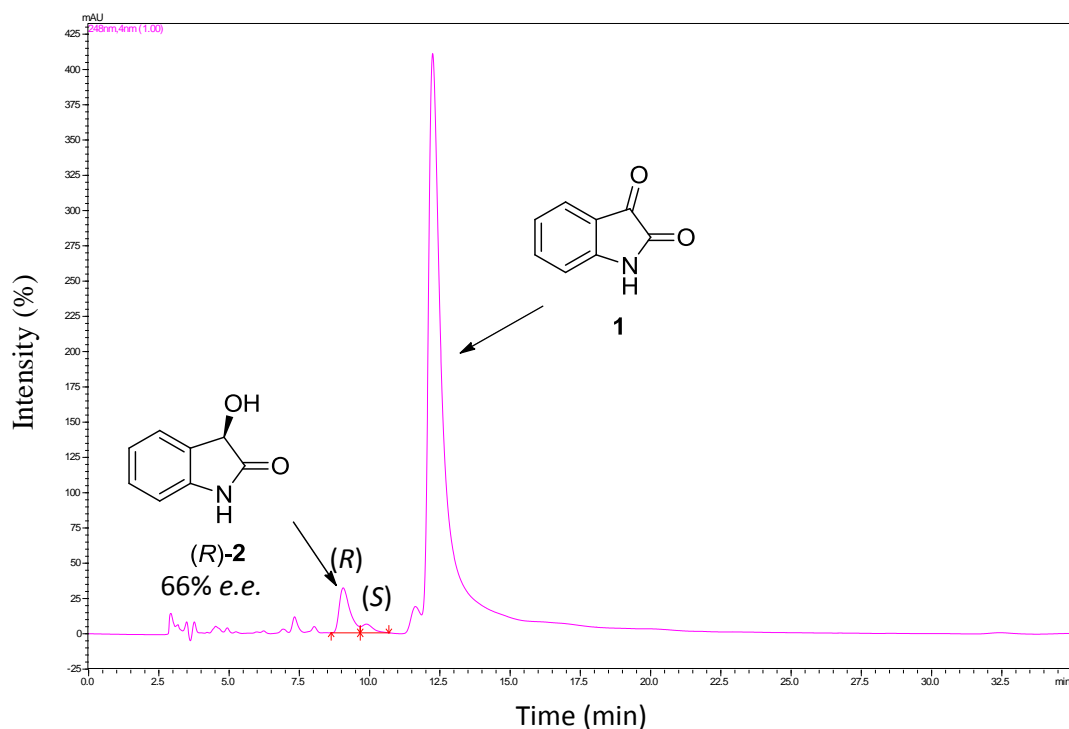
## Chromatographic analysis



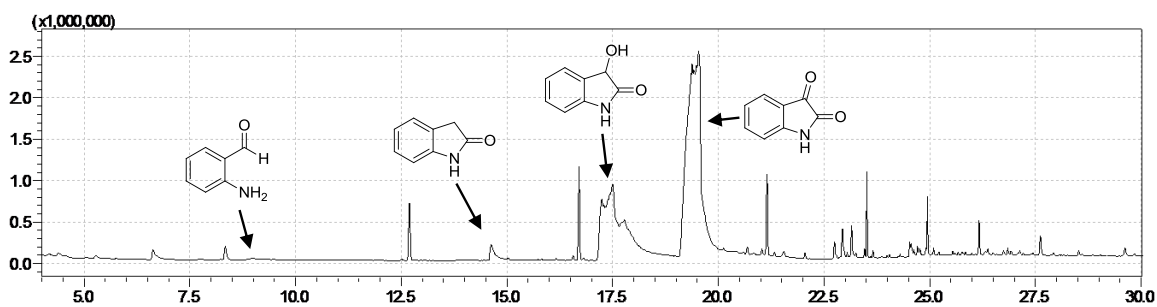
**Figure S7.** Chromatogram obtained by HPLC of dioxindole racemic **2** and isatin **1** standard. Retention time; (R)-**2** = 9.2 min; (S)-**2** = 9.8 min; isatin = 12.5 min.



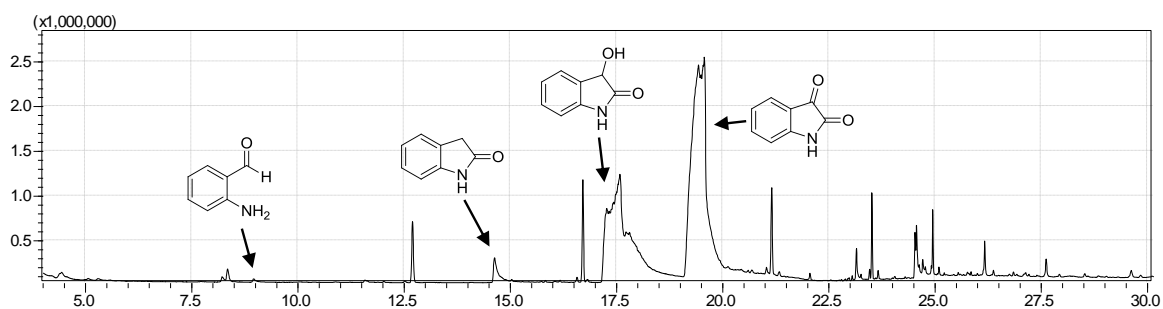
**Figure S8.** Chromatogram obtained by HPLC of (S)-**2** and isatin **1** of the reaction with marine-derived fungi *Acremonium* sp. CBMAI 1676. Retention time; (R)-**2** = 9.2 min; (S)-**2** = 9.8 min; isatin = 12.5 min.



**Figure S9.** Chromatogram by HPLC of (*S*)-**2** and isatin **1** of the reaction of *A. sydowii* CBMAI 935. Retention time; (*R*)-**2** = 9.2 min; (*S*)-**2** = 9.8 min; isatin = 12.5 min.



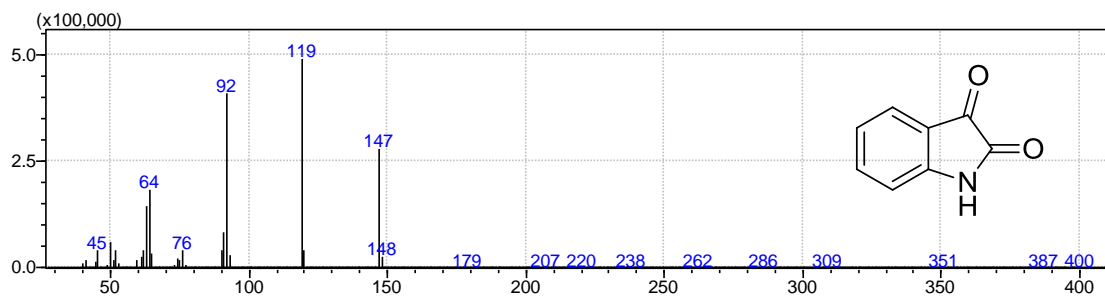
**Figure S10.** Chromatogram obtained by GC-MS (70 eV) of biotransformation reaction of compound **1** by *Acremonium* sp. CBMAI 1676 in 2% malt medium for 3 days.



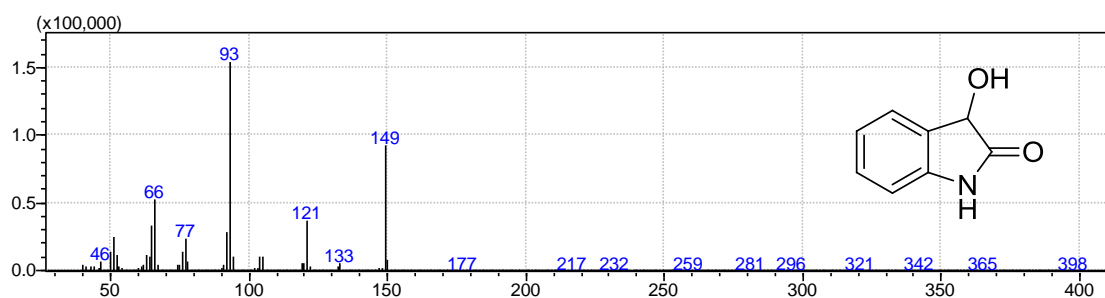
**Figure S11.** Chromatogram obtained by GC-MS (70 eV) of biotransformation reaction of compound **1** by *A. sydowii* CBMAI 935 in 2% malt medium for 3 days.

## Mass spectrum analysis

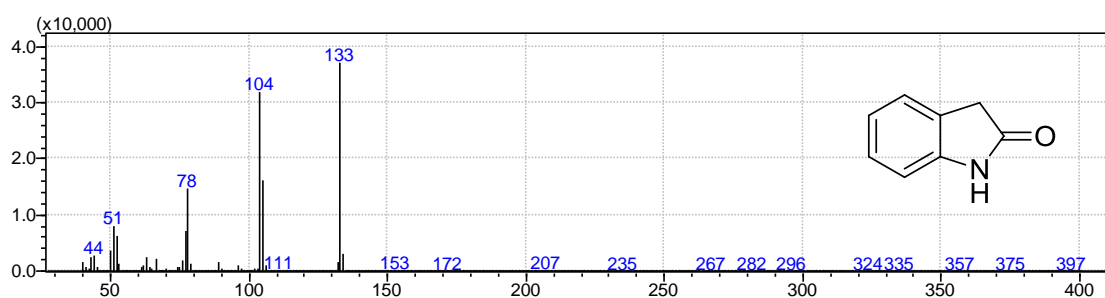
(A)



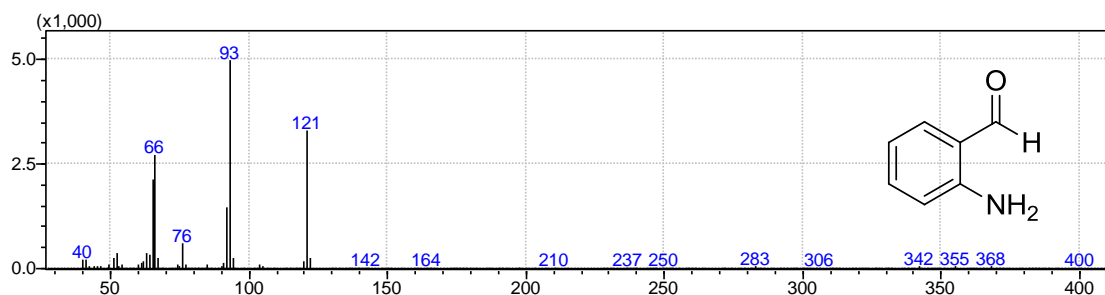
(B)



(C)



(D)



**Figure S12.** Mass spectrum (70 eV) of the (A) isatin **1** (96% similarity) biotransformation to (B) dioxindole **2** (87% similarity), (C) indolin-2-one **3** (90% similarity) and (D) 2-aminobenzaldehyde **4** (92% similarity) by *Acremonium* sp. CBMAI 1676.