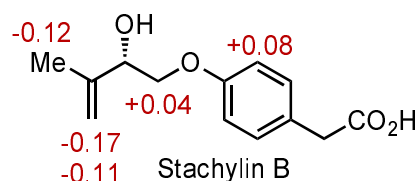


1. Establish the absolute configuration of Stachylin B using Mosher's method and the data given below.



7.20 (d, 8.4 Hz, 2H), 6.87 (d, 8.4 Hz, 2H, $\Delta\delta^{SR} = 0.08$), 5.08 (br s, 1H, $\Delta\delta^{SR} = -0.17$), 4.88 (br s, 1H $\Delta\delta^{SR} = -0.11$), 4.40 (dd, 4.0, 7.2 Hz, 1H), 4.01 (dd, 4.0, 9.8 Hz, 1H, $\Delta\delta^{SR} = 0.04$), 3.90 (dd, 7.2, 9.8 Hz, 1H), 3.51 (br s, 2H), 1.79 (s, 3H, $\Delta\delta^{SR} = -0.12$)

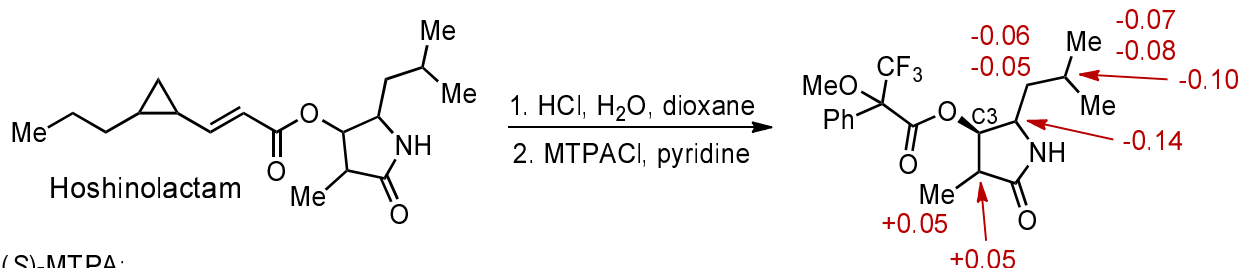
Almeida, C.; Part, N.; Bouhired, S.; Kehraus, S.; König, G. M. *J. Nat. Prod.* **2011**, 74, 21.

$$\Delta\delta^{SR} = \delta(\text{S-MTPA ester}) - \delta(\text{R-MTPA ester})$$

Those protons that have positive $\Delta\delta^{SR}$ values reside within R^1 , whereas those with negative values 'belong to' R^2 .

Hoye, T. R.; Jeffrey, C. S.; Shao, F. *Nat. Protocols* **2007**, 2, 2451.

2. Determine the absolute configuration of Hoshinolactam (at C3) given the data below.



(S)-MTPA:

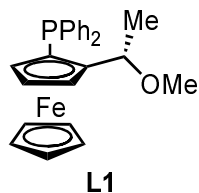
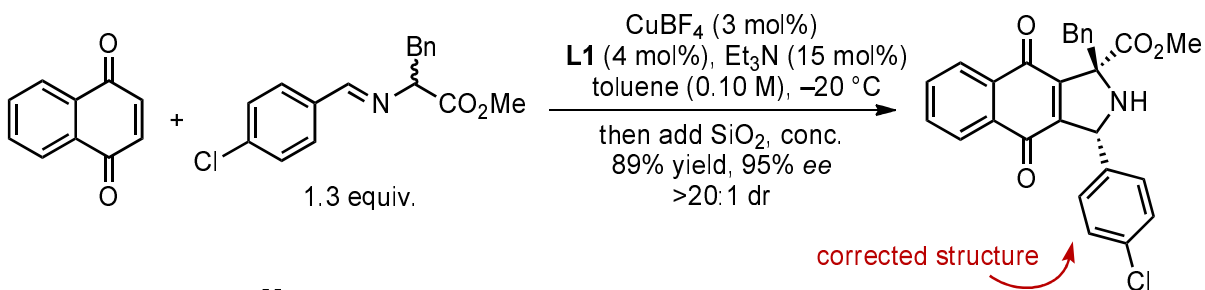
$^1\text{H-NMR}$ (400 MHz, C_6D_6) δ 7.62-7.57 (m, 2H), 7.09-7.01 (m, 3H), 4.98 (brs, NH), 4.80 (dd, $J = 5.6, 6.7$ Hz, 1H), 3.32 (s, 3H), 2.96 (ddd, $J = 5.3, 5.3, 9.2$ Hz, 1H), 2.30 (dq, $J = 7.6, 7.6$ Hz, 1H), 1.25 (d, $J = 7.5$ Hz, 3H), 1.03 (ddd, $J = 4.9, 8.0, 13.2$ Hz, 1H), 0.98-0.88 (m, 1H), 0.81 (ddd, $J = 5.4, 8.5, 13.2$ Hz, 1H), 0.54 (d, $J = 6.5$ Hz, 3H), 0.50 (d, $J = 6.5$ Hz, 3H)

(R)-MTPA:

$^1\text{H-NMR}$ (400 MHz, C_6D_6) δ 7.63-7.58 (m, 2H), 7.08-6.99 (m, 3H), 5.58 (brs, NH), 4.79 (dd, $J = 5.7, 6.4$ Hz, 1H), 3.32 (s, 3H), 3.10 (ddd, $J = 4.6, 4.6, 9.5$ Hz, 1H), 2.25 (dq, $J = 7.2, 7.2$ Hz, 1H), 1.20 (d, $J = 7.7$ Hz, 3H), 1.08 (m, 1H), 1.05-0.85 (m, 2H), 0.62 (d, $J = 6.4$ Hz, 3H), 0.57 (d, $J = 6.3$ Hz, 3H)

Ogawa, H.; Iwasaki, A.; Sumimoto, S.; Iwatsuki, M.; Ishiyama, A.; Hokari, R.; Otoguro, K.; Omura, S.; Suenaga, K. *Org. Lett.* **2017**, 19, 890.

3. The products of the following two reactions were characterized by NMR, HRMS, and X-ray. In both cases the structures were misassigned. Given the reaction conditions and the analytical data, suggest the correct structures.



Mp 112-115 $^\circ\text{C}$.

$[\alpha]_{\text{D}}^{25} = +97.4$ (c 1.60, CDCl_3).

$^1\text{H-NMR}$ (CDCl_3 , TMS, 300 MHz) δ 8.16 (d, $J = 7.5$ Hz, 1H), 7.88 (d, $J = 7.5$ Hz), 7.79-7.68 (m, 2H), 7.31-7.19 (m, 7H), 7.12 (m, 2H), 4.84 (s, 1H), 3.85 (s, 3H), 3.63 (d, $J = 13.8$ Hz, 1H), 3.46 (d, $J = 13.8$ Hz, 1H), 2.60-2.80 (br, 1H).

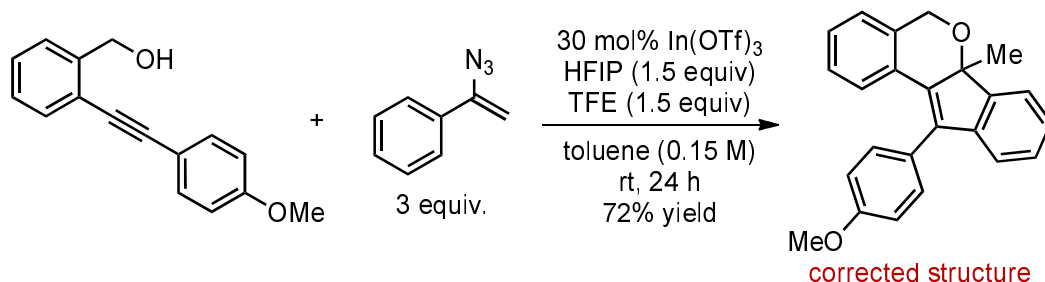
$^{13}\text{C-NMR}$ (CDCl_3 , TMS, 75 MHz) δ 182.3, 181.5, 172.5, 150.0, 146.4, 139.8, 135.4, 133.9, 133.6, 132.6, 130.7, 130.2, 129.2, 128.5, 128.3, 127.6, 127.1, 126.5, 126.3, 75.3, 66.3, 52.9, 41.6.

IR (KBr) ν 3380, 1741, 1667, 1637, 1594, 1491, 1339, 1219, 1089, 704 cm^{-1} .

HRMS: calcd. for $\text{C}_{27}\text{H}_{21}\text{ClNO}_4^+$: 458.1154, found 458.1148.

analytical data reported,
 matches the corrected structure

He, Z.; Liu, T.; Tao, H.; Wang, C.-J. *Org. Lett.* **2012**, *14*, 6230.



HFIP: hexafluoroisopropanol, TFE: 2,2,2-trifluoroethanol

Mp 124.5-127.4 $^\circ\text{C}$.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 7.52-7.54 (m, 1H), 7.36 (d, $J = 8.6$ Hz, 2H), 7.18-7.25 (m, 4H), 7.03-7.12 (m, 3H), 7.00 (d, $J = 8.7$ Hz, 2H), 5.22 (d, $J = 15.9$ Hz, 1H), 5.02 (d, $J = 15.9$ Hz, 1H), 3.89 (s, 3H), 1.55 (s, 3H).

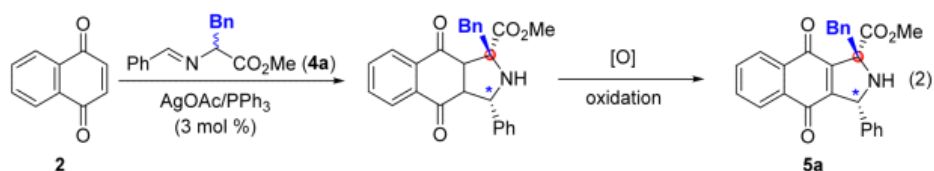
$^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 159.2, 147.2, 144.6, 140.3, 134.9, 134.1, 130.3, 128.9, 128.7, 127.5, 126.8, 126.5, 126.3, 126.2, 124.1, 121.9, 120.8, 114.2, 82.3, 64.5, 55.2, 20.3.

HRMS (EI, TOF) calcd for $\text{C}_{24}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 340.1463, found 340.1465.

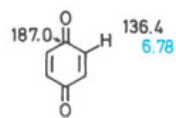
analytical data reported,
 matches the corrected structure

Siyang, H. X.; Ji, X. Y.; Wu, X. R.; Wu, X. Y.; Liu, P. N. *Org. Lett.* **2015**, *17*, 5220.

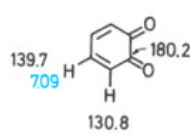
3. "Several compounds have a proton in the spectra between 2.60 and 2.70 ppm that was not reported in the experimental details section"



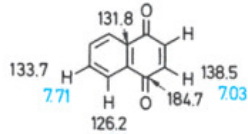
¹³C shifts for related compounds



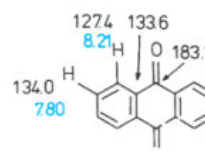
p-Benzochinon



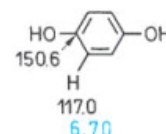
o-Benzochinon



1,4-Naphthochinon



9,10-Anthrachinon



Hydrochinon

4. New (top) and originally (below) proposed mechanism

