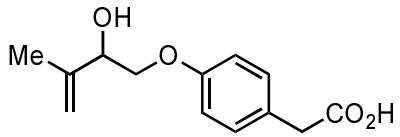
1. Establish the absolute configuration of Stachylin B using Mosher's method and the data given below.

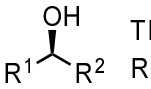


Stachylin B

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.

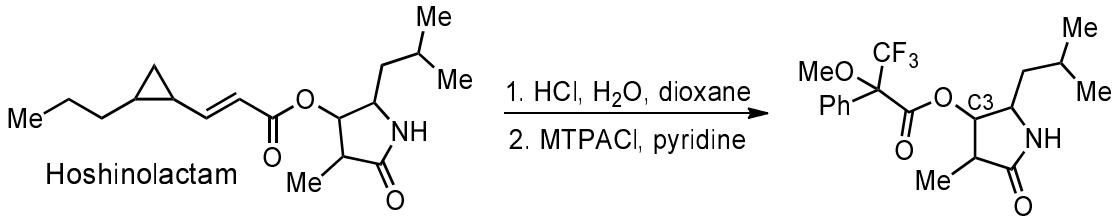
$\Delta\delta^{SR} = \delta$(*S*-MTPA ester) – δ(*R*-MTPA ester)



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.



Hoshinolactam

(*S*)-MTPA:

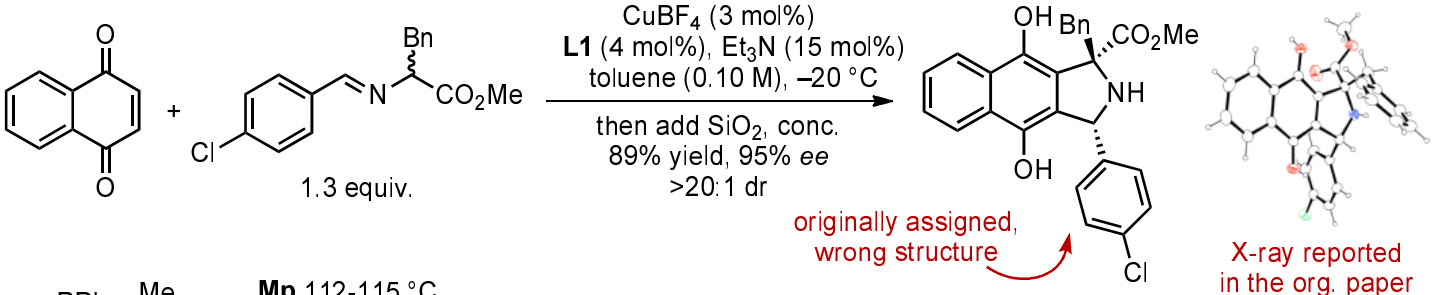
^{1}H-NMR (400 MHz, C_6D_6) δ 7.62-7.57 (m, 2H), 7.09-7.01 (m, 3H), 4.98 (brs, NH), 4.80 (dd, *J* = 5.6, 6.7 Hz, 1H), 3.32 (s, 3H), 2.96 (ddd, *J* = 5.3, 5.3, 9.2 Hz, 1H), 2.30 (dq, *J* = 7.6, 7.6 Hz, 1H), 1.25 (d, *J* = 7.5 Hz, 3H), 1.03 (ddd, *J* = 4.9, 8.0, 13.2 Hz, 1H), 0.98-0.88 (m, 1H), 0.81 (ddd,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

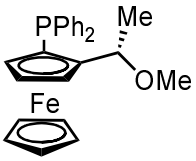
^{1}H-NMR (400 MHz, C_6D_6) δ 7.63-7.58 (m, 2H), 7.08-6.99 (m, 3H), 5.58 (brs, NH), 4.79 (dd, *J* = 5.7, 6.4 Hz, 1H), 3.32 (s, 3H), 3.10 (ddd, *J* = 4.6, 4.6, 9.5 Hz, 1H), 2.25 (dq, *J* = 7.2, 7.2 Hz, 1H), 1.20 (d, *J* = 7.7 Hz, 3H), 1.08 (m, 1H), 1.05-0.85 (m, 2H), 0.62 (d, *J* = 6.4 Hz, 3H), 0.57 (d,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



X-ray reported in the org. paper



L1

Mp 112-115 °C.

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

^{1}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}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.

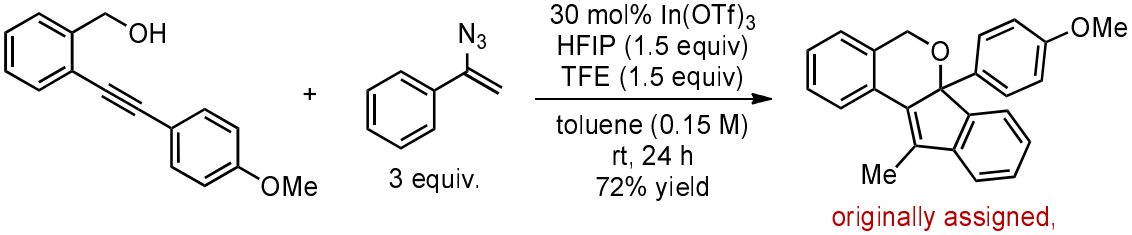
IR (KBr) ν 3380, 1741, 1667, 1637, 1594, 1491, 1339, 1219, 1089, 704 cm^{-1}.

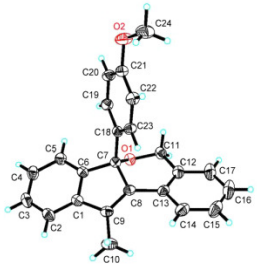
HRMS: calcd. for $C_{27}H_{21}ClNO_4^+$: 458.1154, found 458.1148.

analytical data reported, matches the corrected structure

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

*the signal at 2.60 ppm was not reported in the org. paper but is not of importance for the problem here





X-ray reported in the org. paper

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

Mp 124.5-127.4 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °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}C-NMR (100.6 MHz, $CDCl_3$, 25 °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 $C_{24}H_{20}O_2$ $[M]^+$ 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.