

## Supplemental Data

Kapilashrami K. et al, 2012

Figure S1: Synthesis of 5R-TLM from D-alanine

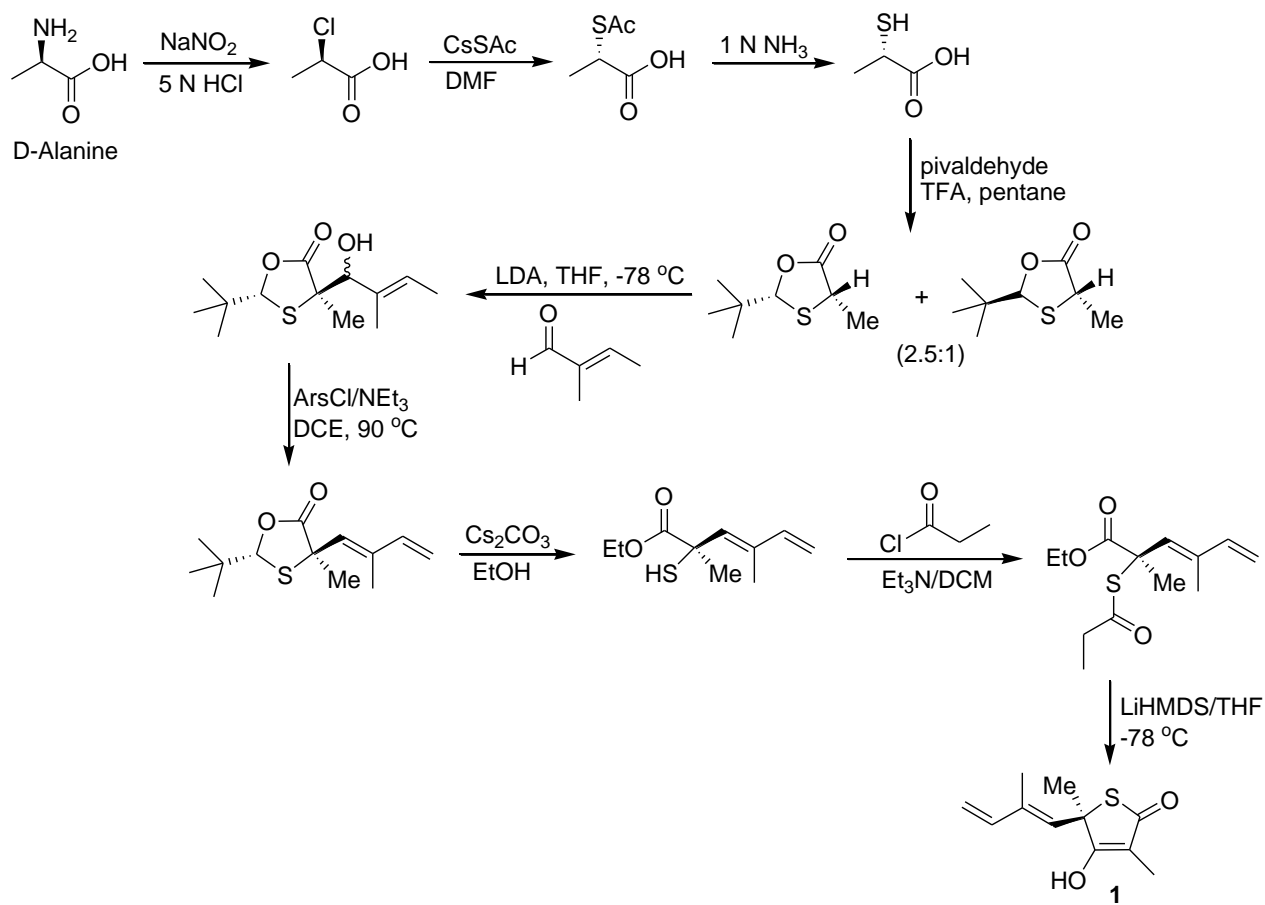
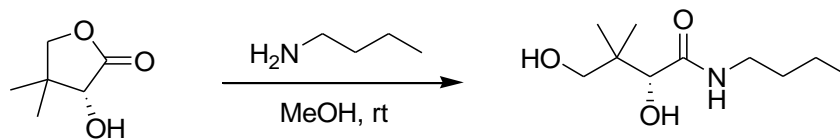
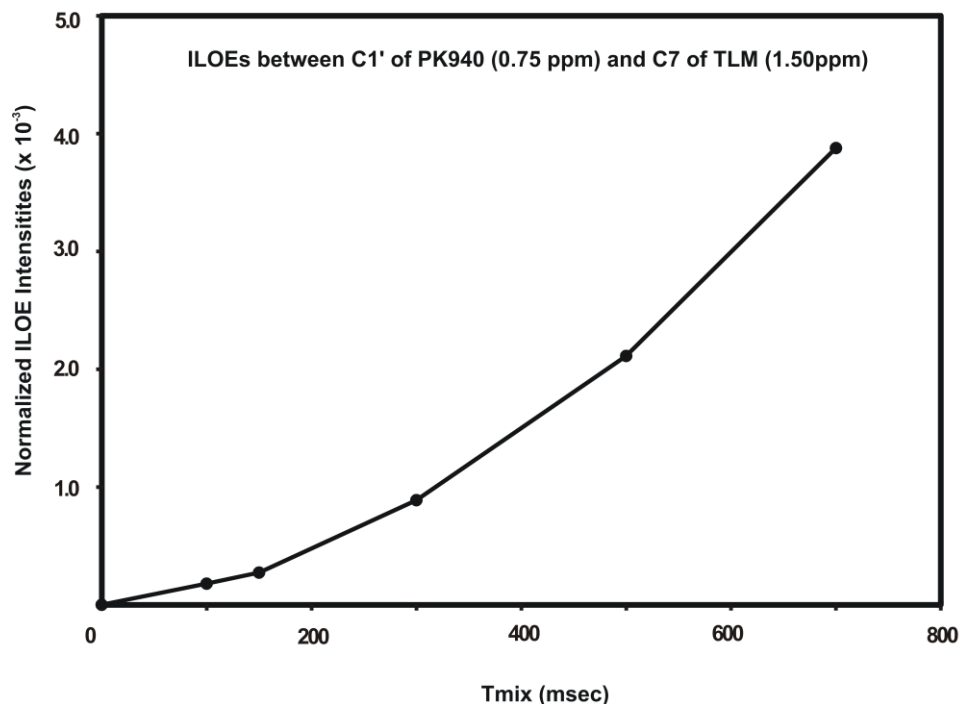


Figure S2: Synthesis of pantoylamide PK940



**Figure S3: Normalized ILOE between C1' of PK940 and C7 of TLM.**



#### **Analytical Data for 5R- Thiolactomycin**

##### **(5R)-4-Hydroxy-3,5-dimethyl-5-(2-methyl-buta-1,3-dienyl)-5-H-thiophen-2-one (Thiolactomycin)**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> and 5% MeOH-d<sub>4</sub>): δ 1.64, 1.65 (2s, 6 H), 1.73 (s, 3 H), 1.91 (s, 3 H), 4.96. (d, *J* = 11.0 Hz, 1 H), 5.15 (d, *J* = 17.0 Hz, 1 H), 5.53 (s, 1 H), 6.20-6.26 (dd, *J* = 11.0, 17.0 Hz, 1 H)

<sup>13</sup>C NMR spectra of Thiolactomycin in CDCl<sub>3</sub> and 5% MeOH-d<sub>4</sub> CDCl<sub>3</sub> and 5% Methanol-d<sub>4</sub> (125 MHz) δ 7.2, 11.6, 29.3, 55.1, 109.3, 113.2, 130.0, 139.1, 140.7, 180.6, 196.5.

MS spectra (ES<sup>-</sup>): 209.1 (M-1)

[α]<sub>D</sub><sup>23</sup> = +172.5 (*c* 1.2, MeOH), mp 119-121 °C, [(lit.(1) [α]<sub>D</sub><sup>23</sup> = +174 (*c* 0.6, MeOH), mp 119-121 °C)]; [(lit.(2) [α]<sub>D</sub><sup>20</sup> = +176 (*c* 1.0, MeOH), mp 120 °C)]

#### **Analytical Data for PK940**

##### **(R)-N-butyl-2,4-dihydroxy-3,3-dimethylbutanamide (PK940):**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (s, 3H), 0.94 (t,  $J = 8.6$  Hz, 3H), 0.98 (s, 3H), 1.36 (sextet,  $J = 8.6$  Hz, 2H), 1.49 (m, 2H), 3.15-3.36 (m, 2H), 3.47 (s, 2H), 3.71-4.31 (s, br, 2H), 4.01 (s, 1H), 6.89 (t, br,  $J = 5.8$  Hz, 1H);

$^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 20.2, 20.3, 21.4, 31.7, 39.0, 39.4, 71.4, 77.5, 173.7

HRMS (ESMS) calculated for  $\text{C}_{10}\text{H}_{22}\text{NO}_3$  [ $\text{M} + \text{H}^+$ ] 204.1600, found 204.1615.

#### References:

- (1) McFadden, J. M.; Frehywot, G. L.; Townsend, C. A. *Org Lett* **2002**, *4*, 3859-3862.
- (2) Szabo A.; Künzle N.; Mallat T.; Baiker A. *Tetrahedron: Asymmetry* **1999**, *10*, 61-76