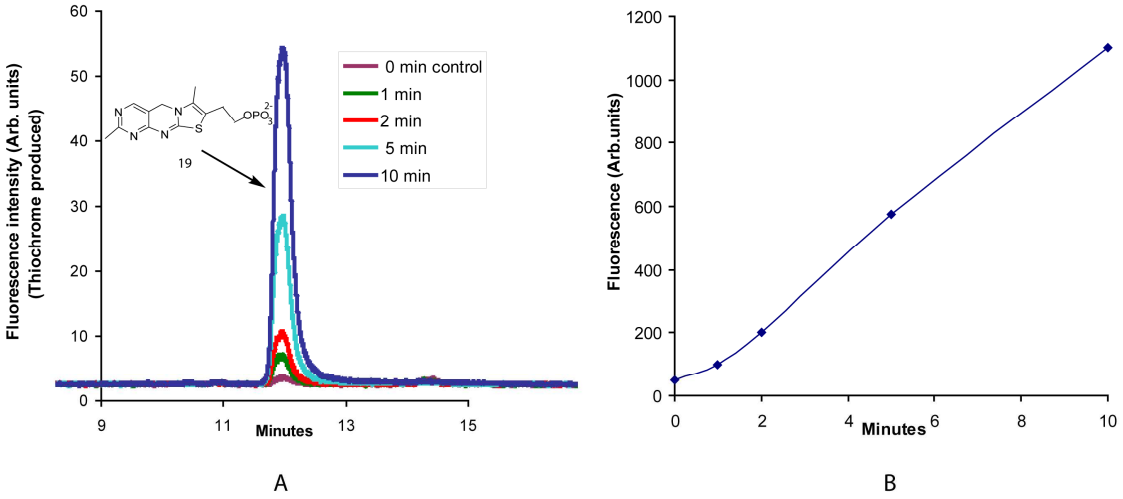
Supplementary figures:



A B

Figure 1: A) HPLC chromatogram showing the time-course for the thiazole reconstitution reaction using the thiochrome assay. (Reaction times = 0min, 1 min, 2 min, 10 min and 30min). B) Plot of product formation (as measured by peak area from the chromatogram) versus time.

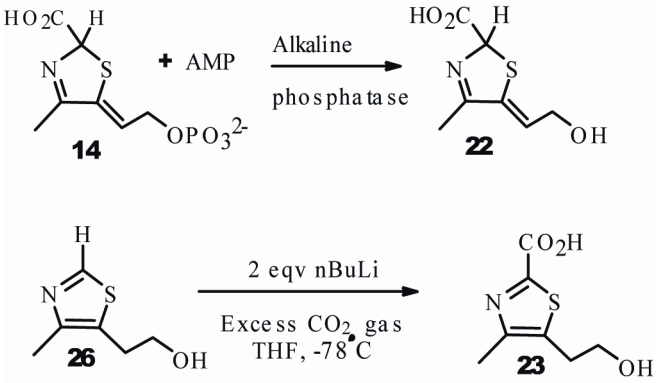


Figure 2: Procedures for the production of reference compounds **22** and **23**.

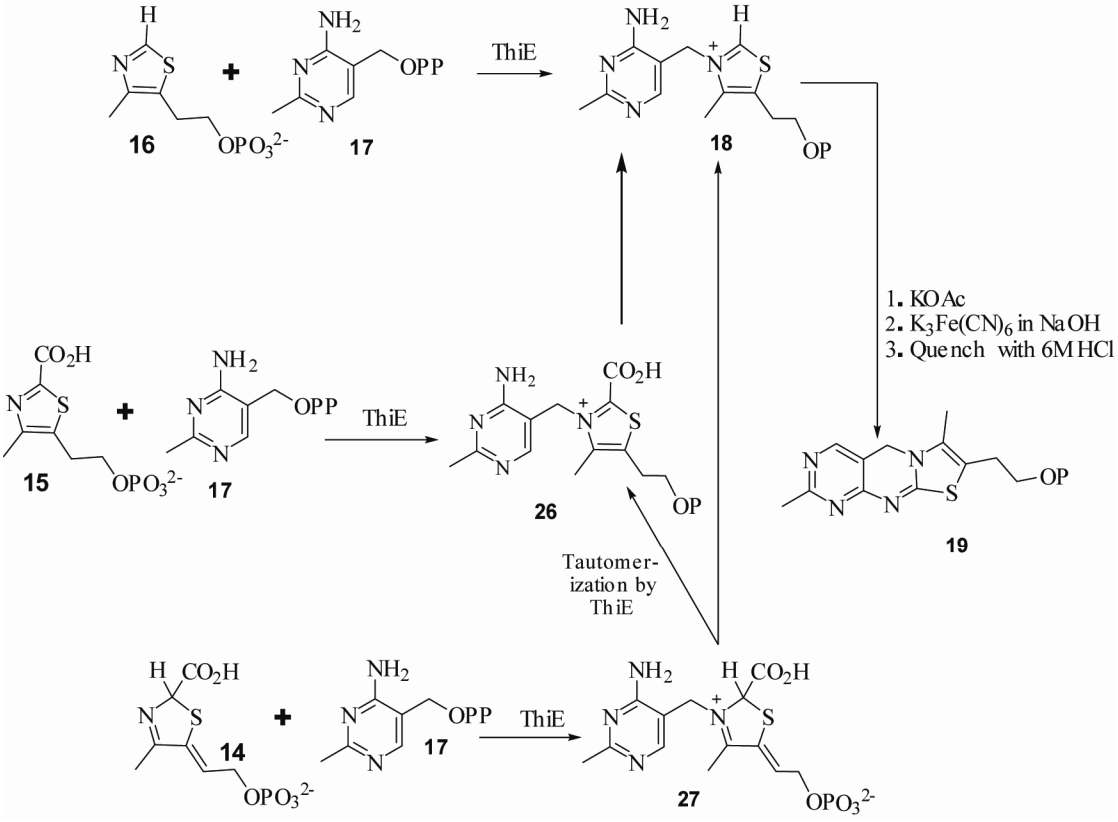


Figure 3: The experimentally observed conversion of thiazoles **14**, **15** and **16** to thiochrome phosphate **19** (unpublished results). Compound **26** is likely to undergo either enzymatic or spontaneous decarboxylation to give **18** via the well-characterized thiamin ylide. Compound **27** may aromatize either by deprotonation to give 26 or by decarboxylation to give **18**.

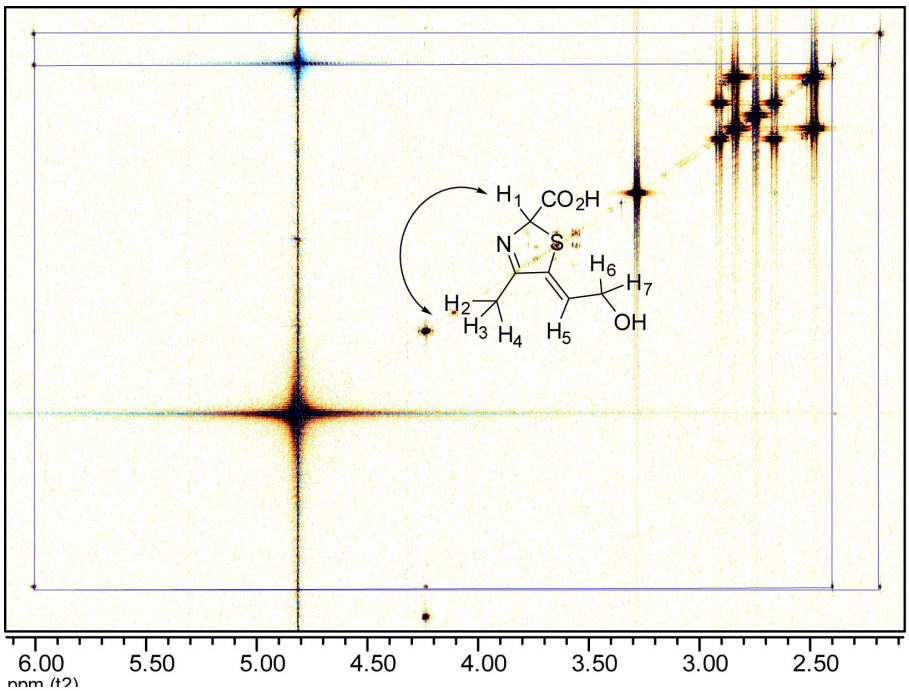


Figure 4: Cross-peak for H1 (6.02 ppm) and H2/H3/H4 (2.2 ppm and 2.4 ppm) observed in the 2-D dqf-COSY experiment

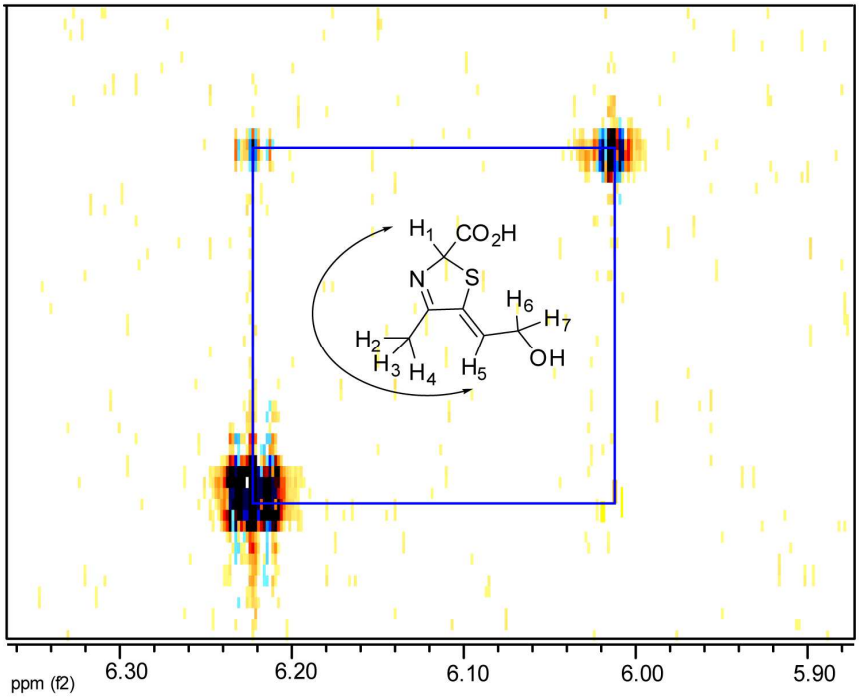


Figure 5: Cross-peak for H1 (6.02 ppm) and H5 (6.22 ppm) observed in the 2-D dqf-COSY experiment

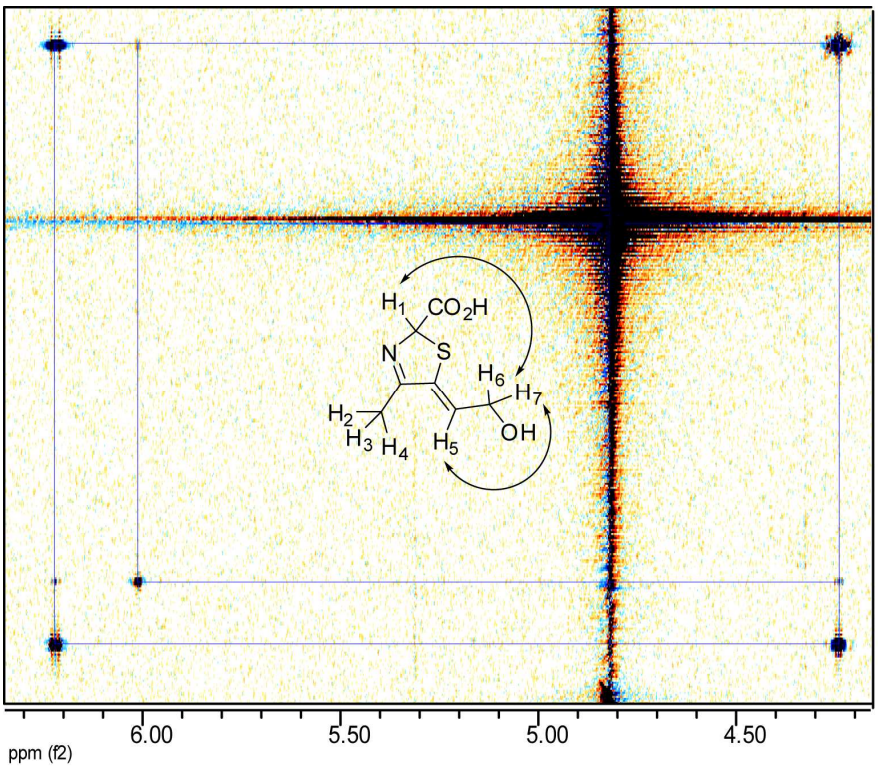


Figure 6: Cross-peak for H1 (6.02 ppm) and H5 (4.24 ppm) observed in the 2-D dqf-COSY experiment.