dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The obtained residue was purified by flash column chromatography (0% to 20% EtOAc in hexanes) to afford epidithiodiketopiperazine **251c** (5.0 mg, 0.009 mmol, 54% yield).

*Epidithiodiketopiperazine **251a***: $[\alpha]_D^{25} = -576°$ ($c = 0.390$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (td, $J = 7.7, 1.2$ Hz, 1H), 7.07 (dd, $J = 7.3, 0.7$ Hz, 1H), 6.76 (td, $J = 7.5, 0.7$ Hz, 1H), 6.45 (d, $J = 7.8$ Hz, 1H), 5.34 (s, 1H), 3.27 (d, $J = 14.7$ Hz, 1H), 3.07 (s, 3H), 2.59 (d, $J = 14.7$Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 149.2, 133.9, 128.9, 121.7, 118.4, 107.0, 90.7, 52.1, 44.3, 34.9, 25.1; FTIR (NaCl/thin film): 3052, 3020, 2959, 2925, 2867, 1693, 1608, 1493, 1445, 1384, 1357, 1324, 1302, 1274, 1185, 1124, 1104, 1093, 1060, 1020, 997, 941, 797, 742 cm^{-1}; HRMS (APCI) calc'd for $C_{26}H_{27}N_4O_2$ $[M+H–S_2]^+$ 491.1570, found 491.1576.

*Epidithiodiketopiperazine **251b***: $[\alpha]_D^{25} = -613°$ ($c = 0.355$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 7.08 (dd, $J = 7.5, 0.9$ Hz, 1H), 7.04 (d, $J = 2.0$ Hz, 1H), 6.76 (td, $J = 7.4, 0.9$ Hz, 1H), 6.46 (d, $J = 7.8$ Hz, 1H), 5.99 (dd, $J = 17.3, 10.5$ Hz, 1H), 5.35 (s, 1H), 5.32 (s, 1H), 5.02 (dd, $J = 11.0, 1.5$ Hz, 1H), 4.99 (dd, $J = 7.2, 1.4$ Hz, 1H), 3.28 (d, $J = 2.2$ Hz, 1H), 3.25 (d, $J = 2.2$ Hz, 1H), 3.09 (s, 3H), 3.04 (s, 3H), 2.59 (dd, $J = 14.5, 8.7$ Hz, 2H), 1.51 (s, 3H), 1.50 (s, 3H), 1.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 164.4, 149.2, 148.6, 147.4, 138.9, 133.9, 133.7, 128.9, 126.3, 121.7, 112.0, 118.4, 110.3, 107.0, 106.6, 91.2, 90.7, 76.0, 75.9, 52.3, 52.1, 44.4, 44.4, 40.7, 35.0, 34.9, 28.5, 28.5, 25.1, 24.7; FTIR (NaCl/thin film): 2961, 2925, 2868, 1693, 1608, 1494, 1358, 1317, 1302, 1186, 1120, 1053, 997, 911, 812, 753 cm^{-1}; HRMS (APCI) calc'd for $C_{31}H_{35}N_4O_2$ $[M+H–S_2]^+$ 559.2196, found 559.2183.

Epidithiodiketopiperazine ***251c***: $[\alpha]_D^{25} = -577°$ ($c = 0.210$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.1, 2.0 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.40 (d, J = 8.3 Hz, 1H), 5.99 (dd, J = 17.5, 10.6 Hz, 1H), 5.32 (s, 1H), 5.02 (dd, J = 11.1, 1.2 Hz, 1H), 4.99 (dd, J = 4.4, 1.2 Hz, 1H), 3.26 (d, J = 14.4 Hz, 1H), 3.05 (s, 3H), 2.59 (dd, J = 14.7 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 148.6, 147.4, 138.9, 133.8, 126.3, 119.7, 110.3, 106.5, 91.2, 52.3, 44.4, 40.7, 35.0, 28.55, 28.50, 24.7; FTIR (NaCl/thin film): 3079, 2962, 2926, 2869, 2824, 1695, 1619, 1498, 1446, 1431, 1411, 1358, 1315, 1287, 1185, 1136, 1117, 1099, 1053, 996, 910, 809, 754 cm^{-1}; HRMS (APCI) calc'd for $C_{36}H_{43}N_4O_2$ $[M+H-S_2]^+$ 627.2822, found 627.2819.

2.6 NOTES AND REFERENCES

(1) Anthoni, U.; Christophersen, C.; Nielsen, P. H. In *Alkaloids: Chemical and Biological Perspectives*; Pelletier, S. W., Ed.; Pergamon: 1999; Vol. Volume 13, p 163.

(2) Yanagihara, M.; Sasaki-Takahashi, N.; Sugahara, T.; Yamamoto, S.; Shinomi, M.; Yamashita, I.; Hayashida, M.; Yamanoha, B.; Numata, A.; Yamori, T.; Andoh, T. *Cancer Sci.* **2005**, *96*, 816.

(3) Tuntiwachwuttikul, P.; Taechowisan, T.; Wanbanjob, A.; Thadaniti, S.; Taylor, W. C. *Tetrahedron* **2008**, *64*, 7583.

(4) Crich, D.; Chan, C.-O.; Davies, J. W.; Natarajan, S.; Vinter, J. G. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2233.

(5) Raju, R.; Piggott, A. M.; Huang, X.-C.; Capon, R. J. *Org. Lett.* **2011**, *13*, 2770.

(6) Repka, L. M.; Reisman, S. E. *J. Org. Chem.* **2013**, *78*, 12314.

(7) Marsden, S. P.; Depew, K. M.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 11143.

(8) López, C. S.; Pérez-Balado, C.; Rodríguez-Graña, P.; de Lera, Á. R. *Org. Lett.* **2008**, *10*, 77.

(9) Wang, M.; Feng, X.; Cai, L.; Xu, Z.; Ye, T. *Chem. Commun.* **2012**, *48*, 4344.

(10) Espejo, V. R.; Li, X.-B.; Rainier, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 8282.

(11) Kim, J.; Movassaghi, M. *J. Am. Chem. Soc.* **2011**, *133*, 14940.

(12) Movassaghi, M.; Schmidt, M. A.; Ashenhurst, J. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 1485.

(13) He, B.; Song, H.; Du, Y.; Qin, Y. *J. Org. Chem.* **2008**, *74*, 298.
(14) Zhang, D.; Song, H.; Qin, Y. *Acc. Chem. Res.* **2011**, *44*, 447.
(15) Kieffer, M. E.; Chuang, K. V.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 5557.
(16) Ashimori, A.; Matsuura, T.; Overman, L. E.; Poon, D. J. *J. Org. Chem.* **1993**, *58*, 6949.
(17) Trost, B. M.; Zhang, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4590.
(18) Bui, T.; Syed, S.; Barbas, C. F. *J. Am. Chem. Soc.* **2009**, *131*, 8758.
(19) Ma, S.; Han, X.; Krishnan, S.; Virgil, S. C.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 8037.
(20) Li, X.; Luo, S.; Cheng, J.-P. *Chem. Eur. J.* **2010**, *16*, 14290.
(21) Hills, I. D.; Fu, G. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 3921.
(22) DeLorbe, J. E.; Jabri, S. Y.; Mennen, S. M.; Overman, L. E.; Zhang, F.-L. *J. Am. Chem. Soc.* **2011**, *133*, 6549.
(23) Zhu, S.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2012**, *134*, 10815.
(24) Repka, L. M.; Ni, J.; Reisman, S. E. *J. Am. Chem. Soc.* **2010**, *132*, 14418.
(25) Ni, J.; Wang, H.; Reisman, S. E. *Tetrahedron* **2013**, *69*, 5622.
(26) Yang, Y.; Buchwald, S. L. *J. Am. Chem. Soc.* **2013**, *135*, 10642.
(27) King, S. B.; Ganem, B. *J. Am. Chem. Soc.* **1994**, *116*, 562.
(28) Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606.
(29) Depew, K. M.; Marsden, S. P.; Zatorska, D.; Zatorski, A.; Bornmann, W. G.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 11953.
(30) Boyer, N.; Morrison, K. C.; Kim, J.; Hergenrother, P. J.; Movassaghi, M. *Chem. Sci.* **2013**, *4*, 1646.
(31) Gardiner, D. M.; Waring, P.; Howlett, B. J. *Microbiology* **2005**, *151*, 1021.
(32) Welch, T. R.; Williams, R. M. *Nat. Prod. Rep.* **2014**, *31*, 1376.
(33) Kim, J.; Ashenhurst, J. A.; Movassaghi, M. *Science* **2009**, *324*, 238.
(34) Takano, S.; Moriya, M.; Iwabuchi, Y.; Ogasawara, K. *Chem. Lett.* **1990**, 109.
(35) Nicolaou, K. C.; Giguère, D.; Totokotsopoulos, S.; Sun, Y.-P. *Angew. Chem. Int. Ed.* **2012**, *51*, 728.
(36) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(37) Navarre, L.; Martinez, R.; Genet, J.-P.; Darses, S. *J. Am. Chem. Soc.* **2008**, *130*, 6159.
(38) Firouzabadi, H.; Vessal, B.; Naderi, M. *Tetrahedron Lett.* **1982**, *23*, 1847.
(39) Ni, J. Thesis Development of Asymmetric Protonation Reactions for the Synthesis of Indoline Alkaloids. Ph.D. Dissertation, California Institute of Technology, 2015.