# Selective Acylation Reactions of an Isotaxane Tetraol. A Direct Pathway to Introduction of the Oxetane Ring

Qingbei Zeng, Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210 USA

Fax 614-292-1685; E-mail: paquette.1@osu.edu

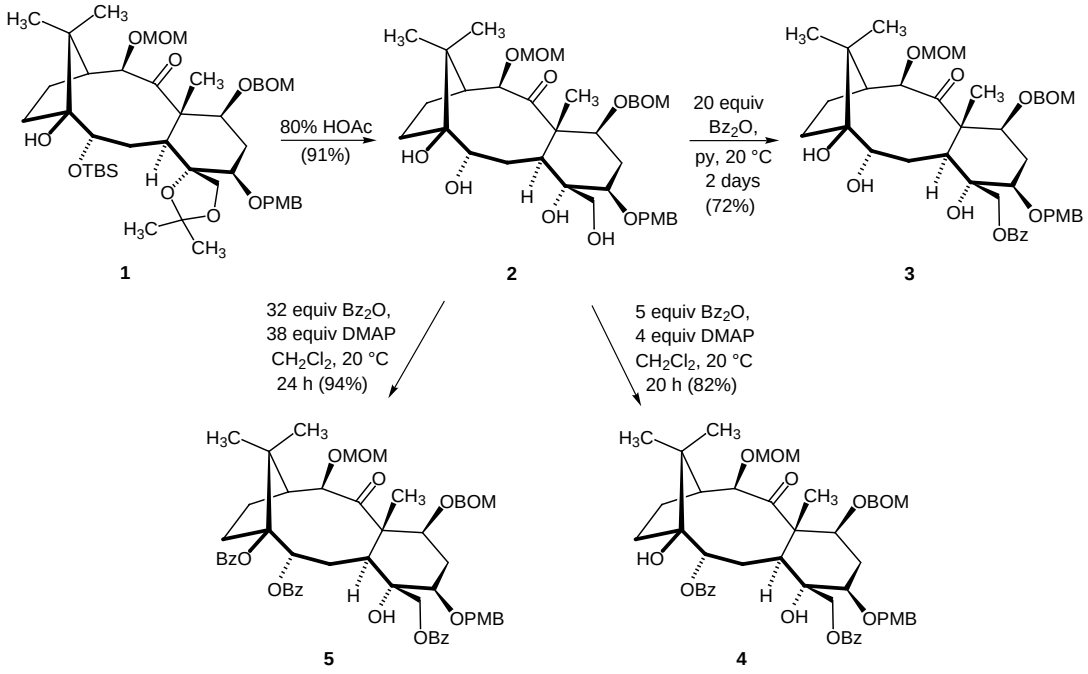
*Received 20 July 1999*

**Abstract:** An isotaxane fully functionalized as taxol in rings C and D was synthesized in six steps from tetraol **2** with complete chemical control over the four available hydroxyl substituents.

**Key words:** acylation, taxanes, oxetane, cyclization, benzoylation

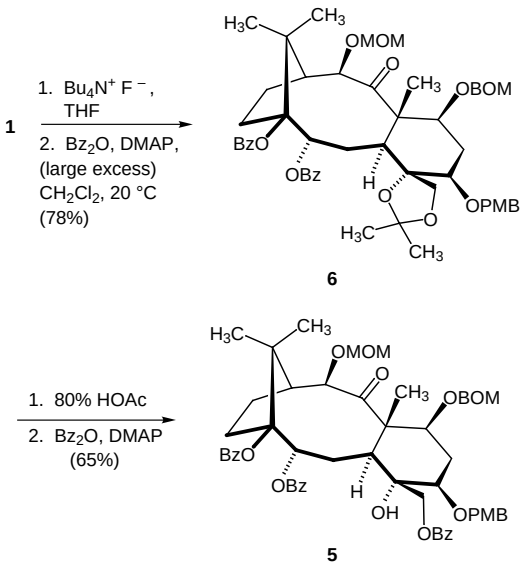
Intricate molecules such as members of the taxane family are generally synthesized through a linear sequence of reactions designed to increase structural complexity in systematic fashion. Considerable attention is paid to the proper selection of protecting groups that can subsequently be removed under relatively mild conditions at the appropriate time. In this laboratory, the tricyclic taxane framework has been assembled through the combined application of two "power" reactions, viz. an anionic Cope rearrangement and a 1,2-Wagner-Meerwein (for arrival at taxusin)[1] or α-ketol rearrangement (for taxol construction).[2] In an effort to streamline our approach and leapfrog past the often-utilized multiple hydroxyl masking steps,[3-8] we have evaluated the feasibility of advancing directly from the readily available enantiomerically pure tetraol intermediate **2**. Reported here are the regiocontrol elements associated with the selective benzoylation of **2** and the direct route to elaboration of a fused oxetane derivative that is thereby made possible.

The previously described **1**[9] experiences efficient hydrolysis to **2** in 80% acetic acid (Scheme 1). Remarkably, treatment of **2** with 20 equiv of benzoic anhydride in pyridine at 20 °C for 2 days resulted uniquely in esterification of the primary carbinol center and furnished **3**.[10] Some rate enhancement was noted on exposure of **2** and 5 equiv of benzoic anhydride to a solution of 4-(dimethylamino)pyridine (DMAP) in dichloromethane at 20 °C. After an elapsed time of 20 h, dibenzoate **4** was formed cleanly. We have examined a number of reaction conditions for more advanced esterification and have found that the combination of large excesses (ca 40 equivs) of both benzoic anhydride and DMAP in dichloromethane at room temperature for 24 h successfully effects conversion to a tribenzoate. Without DMAP, benzoylation occurs neither at the secondary nor tertiary hydroxyl groups.




**Scheme 1**

Since spectral analysis did not unambiguously reveal which of the two tertiary carbinols had undergone acylation, **5** was synthesized by the alternative route illustrated in Scheme 2.




**Scheme 2**

The desired structural comparison was readily accomplished by exhaustively benzoylating **1** to produce **6** in advance of chemoselective hydrolysis of the acetonide and esterification of the primary hydroxyl group. The sample of tribenzoate generated in this manner proved identical in all respects to **5**.

The striking difference in reactivity between the pair of tertiary carbinols lends itself conveniently to crafting of the taxol D ring. Subsequent to the conversion of **5** into the SEM derivative **7**, treatment with DDQ resulted in smooth conversion to alcohol **8**. When allowed to stir in methanolic 1% sodium hydroxide solution, **8** was transformed almost quantitatively into diol **9**. The involvement of a nearby polar functional group may be partially responsible for this heightened selectivity. At this point, it proved an easy matter to prepare the monomesylate of **9** and to bring about *in situ* cyclization to the oxetane **10**.

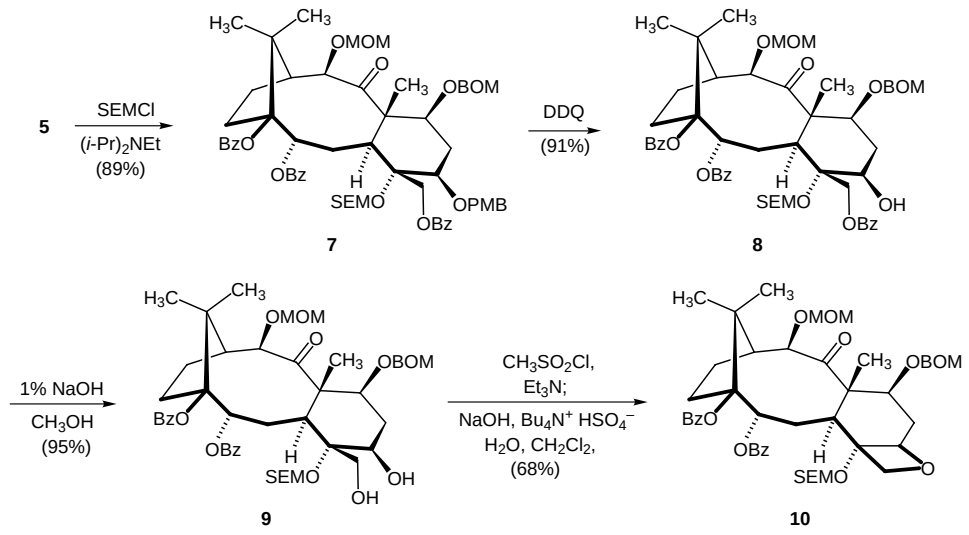
The six-step conversion of **2** into **10** is illustrative of the reaction economy that we consider desirable and necessary for an abbreviated route to taxol and analogues thereof.

## Acknowledgment

The authors are grateful to Eli Lilly and Company for their financial support.

## References and Notes

(1) (a) Paquette, L. A.; Zhao, M. *J. Am. Chem. Soc.* **1998**, *120*, 5203. (b) Paquette, L. A.; Wang, H.-L.; Su, Z.; Zhao, M. *J. Am. Chem. Soc.* **1998**, *120*, 5213.
(2) (a) Paquette, L. A.; Elmore, S. W.; Combrink, K. D.; Hickey, E. R.; Rogers, R. D. *Helv. Chim. Acta* **1992**, *75*, 1755. (b) Paquette, L. A.; Combrink, K. D.; Elmore, S. W.; Zhao, M. *Helv. Chim. Acta* **1992**, *75*, 1722. (c) Elmore, S. W.; Paquette, L. A. *J. Org. Chem.* **1993**, *58*, 4963. (d) Paquette, L. A.; Huber, S. K.; Thompson, R. C. *J. Org. Chem.* **1993**, *58*, 6874.
(3) (a) Holton, R. A.; Somoza, C.; Kim, H.-B.; Liang, F.; Biediger, R. J.; Boatman, P. D.; Shindo, M.; Smith, C. C.; Kim, S.; Nadizadeh, H.; Suzuki, Y.; Tao, C.; Vu, P.; Tang, S.; Zhang, P.; Murthi, K. K.; Gentile, L. N.; Liu, J. H. *J. Am.*




**Scheme 3**

*Chem. Soc.* **1994**, *116*, 1597. (b) Holton, R. A.; Kim, H. B.; Somoza, C.; Liang, F.; Biediger, R. J.; Boatman, P. D.; Shindo, M.; Smith, C. C.; Kim, S.; Nadizadeh, H.; Suzuki, Y.; Tao, C.; Vu, P.; Tang, S.; Zhang, P.; Murthi, K. K.; Gentile, L. N.; Liu, J. H. *J. Am. Chem. Soc.* **1994**, *116*, 1599.

(4) (a) Nicolaou, K. C.; Nantermet, P. G.; Ueno, H.; Guy, R. K.; Couladouros, E. A.; Sorensen, E. J. *J. Am. Chem. Soc.* **1995**, *117*, 624. (b) Nicolaou, K. C.; Liu, J.-J.; Yang, Z.; Ueno, H.; Sorensen, E. J.; Claiborne, C. F.; Guy, R. K.; Hwang, C.-K.; Nakada, M.; Nantermet, P. G. *J. Am. Chem. Soc.* **1995**, *117*, 634. (c) Nicolaou, K. C.; Yang, Z.; Liu, J.-J.; Nantermet, P. G.; Claiborne, C. F.; Renaud, J.; Guy, R. K.; Shibayama, K. *J. Am. Chem. Soc.* **1995**, *117*, 645. (d) Nicolaou, K. C.; Ueno, H.; Liu, J.-J.; Nantermet, P. G.; Yang, Z.; Renaud, J.; Paulvannan, K.; Chadha, R. *J. Am. Chem. Soc.* **1995**, *117*, 653.

(5) Danishefsky, S. J.; Masters, J. J.; Young, W. B.; Link, J. T.; Snyder, L. B.; Magee, T. V.; Jung, D. K.; Isaacs, R. C. A.; Bornmann, W. G.; Alaimo, C. A.; Coburn, C. A.; Di Grandi, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 2843.

(6) (a) Wender, P. A.; Badham, N. F.; Conway, S. P.; Floreancig, P. E.; Glass, T. E.; Gränicher, C.; Houze, J. B.; Jänichen, J.; Lee, D.; Marquess, D. G.; McGrane, P. L.; Meng, W.; Mucciaro, T. P.; Mühlebach, M.; Natchus, M. G.; Paulsen, H.; Rawlins, D. B.; Satkofsky, J.; Shuker, A. J.; Sutton, J. C.; Taylor, R. E.; Tomooka, K. *J. Am. Chem. Soc.* **1997**, *119*, 2755. (b) Wender, P. A.; Badham, N. F.; Conway, S. P.; Floreancig, P. E.; Glass, T. E.; Houze, J. B.; Krauss, N. E.; Lee, D.; Marquess, D. G.; McGrane, P. L.; Meng, W.; Natchus, M. G.; Shuker, A. J.; Sutton, J. C.; Taylor, R. E. *J. Am. Chem. Soc.* **1997**, *119*, 2757.

(7) Mukaiyama, T.; Shiina, I.; Iwadare, H.; Sakoh, H.; Tani, Y.; Hasegawa, M.; Saitoh, K. *Proc. Japan Acad., Ser. B* **1997**, *73*, 95.

(8) Morihira, K.; Hara, R.; Kawahara, S.; Nishimori, T.; Nakamura, N.; Kusama, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1998**, *120*, 12980.

(9) Paquette, L. A.; Montgomery, F. J.; Wang, T.-Z. *J. Org. Chem.* **1995**, *60*, 7857.

(10) **2**: colorless oil; $[\alpha]_D^{22}$-32.6 (*c* 0.05, $CHCl_3$); IR (film, $cm^{-1}$) 3393 (br), 1702, 1611, 1514, 1466; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.33 (br s, 5 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 4.83 (d, *J* = 7.6 Hz, 1 H), 4.74 (d, *J* = 7.5 Hz, 1 H), 4.69 (d, *J* = 11.7 Hz, 1 H), 4.53-4.45 (m, 4 H), 4.37 (d, *J* = 10.5 Hz, 1 H), 4.26 (d, *J* = 7.1 Hz, 1 H), 4.15-4.10 (m, 2 H), 4.04 (d, *J* = 11.6 Hz, 1 H), 3.79 (s, 3 H), 3.54-3.33 (m, 4 H), 3.30 (s, 3 H), 2.82-2.57 (m, 4 H), 2.32-2.30 (m, 1 H), 1.92-1.70 (m, 5 H), 1.27-1.17 (m, 2 H), 1.15 (s, 3 H), 1.00 (s, 3 H), 0.96 (s, 3 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 210.7, 159.6, 137.5, 129.4 (2 C), 129.2, 128.5 (2 C), 127.9, 127.8 (2 C), 114.1 (2 C), 95.3, 94.4, 86.8, 85.4, 81.1, 80.1, 74.8, 74.1, 72.4, 69.8, 61.0, 58.6, 57.1, 55.6, 55.3, 47.1, 36.3, 33.3, 32.6, 31.9, 28.7, 25.9, 17.1, 12.4. MS (FAB) ($M^+$) calcd 672.35, obsd 672.60.

**3**: colorless oil; $[\alpha]_D^{22}$-31.9 (*c* 0.16, $CHCl_3$); IR (film, $cm^{-1}$) 3396 (br), 1713, 1514, 1271; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.7 Hz, 2 H), 7.53-7.29 (m, 8 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 6.76 (d, *J* = 8.5 Hz, 2 H), 4.84 (d, *J* = 7.7 Hz, 1 H), 4.78-4.66 (m, 3 H), 4.58-4.42 (m, 7 H), 4.28 (d, *J* = 7.2 Hz, 1 H), 4.21 (dd, *J* = 11.3, 4.0 Hz, 1 H), 3.77 (s, 3 H), 3.65 (s, 1 H), 3.52 (dd, *J* = 12.3, 4.1 Hz, 1 H), 3.31 (s, 3 H), 2.82-2.67 (m, 4 H), 2.50-2.20 (m, 2 H), 2.04 (s, 1 H), 1.87-1.67 (m, 5 H), 1.15 (s, 3 H), 1.13 (s, 3 H), 1.02 (s, 3 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 210.9, 166.3, 159.2, 137.4, 133.0, 130.1, 129.9, 129.6 (2 C), 129.3, 129.2 (2 C), 128.5 (2 C), 128.3 (2 C), 127.8 (2 C), 113.7 (2 C), 95.1, 94.5, 87.1, 83.3, 81.1, 80.3, 74.9, 74.7, 72.1, 69.7, 63.2, 59.0, 57.2, 55.6, 55.2, 47.3, 37.6, 33.2, 32.4, 31.8, 28.3, 25.9, 17.0, 12.2.

**4**: colorless oil; $[\alpha]_D^{22}$-32.6 (*c* 0.05, $CHCl_3$); IR (film, $cm^{-1}$) 3504 (br), 1713, 1514, 1451, 1271, 1098; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.1 Hz, 2 H), 7.62 (d, *J* = 7.1 Hz, 2 H), 7.56 (t, *J* = 7.4 Hz, 1 H), 7.43-7.28 (m, 8 H), 7.23-7.10 (m, 4 H), 6.78 (d, *J* = 8.6 Hz, 2 H), 5.27-5.25 (m, 1 H), 4.86 (d, *J* = 7.6 Hz, 1 H), 4.80-4.57 (m, 4 H), 4.56 (d, *J* = 7.7 Hz, 2 H), 4.49 (t, *J* = 3.2 Hz, 2 H), 4.45 (s, 1 H), 4.33 (d, *J* = 7.2 Hz, 1 H), 4.14 (dd, *J* = 11.0, 3.3 Hz, 1 H), 3.78 (s, 3 H), 3.68 (s, 1 H), 3.58 (dd, *J* = 12.6, 4.0 Hz, 1 H), 3.33 (s, 3 H), 2.96-2.27 (series of m, 5 H), 2.05-1.54 (series of m, 6 H), 1.30 (s, 3 H), 1.11 (s, 3 H), 1.06 (s, 3 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 210.5, 166.7, 164.7, 159.1, 137.5, 133.1, 132.8, 130.3, 129.9, 129.6 (2 C), 129.5, 129.4 (2 C), 129.1 (2 C), 128.5 (2 C), 128.1 (2 C), 127.9 (2 C), 127.8, 113.7 (2 C), 95.3, 94.2, 84.7, 83.4, 81.1, 80.6, 75.9, 74.2, 72.5, 69.8, 64.1, 58.3, 56.6, 55.7, 55.2, 49.6, 39.4, 32.4, 31.7, 31.1, 28.3, 26.6, 17.2, 11.7. MS (FAB) ($M^+$) calcd 880.40, obsd 880.41.

**5**: colorless oil; $[\alpha]_D^{22}$+15.0 (*c* 0.03, $CHCl_3$); IR (film, $cm^{-1}$) 3403, 1720, 1287, 1110, 1037; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.5 Hz, 2 H), 7.81 (d, *J* = 7.6 Hz, 2 H), 7.59 (d, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.42-7.18 (m, 11 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 6.98 (t, *J* = 7.7 Hz, 2 H), 6.72 (d, *J* = 8.4 Hz, 2 H), 5.31 (d, *J* = 11.3 Hz, 1 H), 4.95 (d, *J* = 11.9 Hz, 1 H), 4.88 (d, *J* = 7.6 Hz, 1 H), 4.76-4.71 (m, 3 H), 4.58 (d, *J* = 10.7 Hz, 1 H), 4.50-4.28 (m, 5 H), 4.07 (dd, *J* = 11.3, 3.1 Hz, 1 H), 3.76 (s, 3 H), 3.60-3.56 (m, 2 H), 3.37 (s, 3 H), 3.32 (t, *J* = 13.0 Hz, 1 H), 2.82 (d, *J* = 13.1 Hz, 1 H), 2.68 (s, 2 H), 2.63 (d, *J* = 12.8 Hz, 1 H), 2.22-1.79 (m, 4 H), 1.45 (s, 3 H), 1.28 (s, 3 H), 1.25 (s, 3 H), 1.21-0.86 (m, 1 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 209.5, 166.1, 164.3, 159.0, 137.5, 132.8, 132.6, 132.5, 130.9, 130.0, 129.8, 129.6 (2 C), 129.4 (2 C), 129.1 (2 C), 128.4 (2 C), 128.3 (2 C), 128.1 (2 C), 127.9 (2 C), 127.74, 127.70, 113.6 (2 C), 95.3, 93.9, 89.9, 84.3, 81.7, 80.1, 75.5, 72.1, 69.7, 69.3, 63.1, 57.5, 55.7, 55.1, 55.0, 51.7, 40.1, 31.3, 30.8, 29.8, 29.6, 28.0, 17.8, 11.5. MS (FAB) ($M^+$) calcd 984.43, obsd 984.51.

**6**: colorless oil; $[\alpha]_D^{22}$+17.9 (*c* 0.07, $CHCl_3$); IR (film, $cm^{-1}$) 1721, 1286, 1249, 1098, 1037; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.1 Hz, 2 H), 7.61 (d, *J* = 7.1 Hz, 2 H), 7.52-7.45 (m, 2 H), 7.41-7.34 (m, 2 H), 7.33-7.26 (m, 5 H), 7.24 (d, *J* = 8.6 Hz, 2 H), 6.99 (t, *J* = 7.9 Hz, 2 H), 6.85 (d, *J* = 8.6 Hz, 2 H), 5.28 (dd, *J* = 12.3, 1.7 Hz, 1 H), 4.78 (d, *J* = 7.6 Hz, 1 H), 4.71-4.57 (m, 3 H), 4.53 (d, *J* = 1.4 Hz, 2 H), 4.45-4.36 (m, 3 H), 4.20 (d, *J* = 8.7 Hz, 1 H), 3.97-3.91 (m, 2 H), 3.79 (s, 3 H), 3.57 (dd, *J* = 12.3, 3.9 Hz, 1 H), 3.35 (s, 3 H), 3.24 (d, *J* = 13.7 Hz, 1 H), 2.72-2.65 (m, 3 H), 2.47 (d, *J* = 11.4 Hz, 1 H), 2.19-2.14 (m, 1 H), 2.00-1.97 (m, 1 H), 1.79 (s, 3 H), 1.77-1.70 (m, 1 H), 1.46 (s, 3 H), 1.45-1.41 (m, 2 H), 1.32 (s, 3 H), 1.27 (s, 3 H), 1.23 (s, 3 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 209.4, 165.5, 164.5, 159.1, 137.6, 133.6, 132.6, 132.4, 131.2, 130.2, 129.7 (2 C), 129.6 (2 C), 129.3 (2 C), 128.45, 128.42 (2 C), 128.3, 127.9 (2 C), 127.7 (2 C), 113.7 (2 C), 109.4, 95.2, 93.9, 89.9, 86.9, 81.3, 80.3, 80.1, 71.8, 69.6, 69.4, 64.2, 57.9, 55.7, 55.2, 54.8, 51.7, 39.2, 31.9, 31.3, 29.8, 29.2, 28.2, 26.8, 26.7, 17.7, 10.5. MS (FAB) ($M^+$) calcd 920.43, obsd 920.46.

**7**: colorless oil; $[\alpha]_D^{22}$-24.8 (*c* 0.6, $CHCl_3$); IR (film, $cm^{-1}$) 1719, 1286, 1111; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.2 Hz, 2 H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.55-7.49 (m, 4 H), 7.49-7.21 (m, 8 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 7.02-6.90 (m, 4 H), 6.82 (d, *J* = 8.1 Hz, 2 H), 5.31-5.15 (m, 3 H), 4.89 (d, *J* = 7.7 Hz, 1 H), 4.76-4.69 (m, 3 H), 4.56-4.36 (m, 6 H), 4.06-4.01 (m, 1 H), 3.87-3.67 (m, 3 H), 3.79 (s, 3 H), 3.57-3.48 (m, 1 H), 3.37 (s, 3 H), 2.87-2.82 (m, 1 H), 2.69-2.58 (m, 3 H), 2.27-2.00 (m, 3H), 1.78-1.61 (m, 1 H), 1.48 (s, 3 H), 1.43 (s, 1 H), 1.27 (s, 3 H), 1.25 s, 3H), 0.99-0.83 (m, 3 H), -0.04 (s, 9 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 209.7, 166.3, 165.7, 164.1, 159.1, 137.5, 132.6, 132.4, 132.3, 131.2, 129.95, 129.92,

129.7, 129.6, 129.4, 128.5, 128.3, 128.1, 127.9, 127.7, 127.6, 113.7, 95.3, 93.9, 91.4, 89.9, 83.1, 81.5, 80.1, 79.7, 70.9, 69.6, 67.4, 66.1, 62.8, 60.2, 57.9, 55.7, 55.2, 54.9, 51.7, 41.8, 31.5, 30.9, 30.8, 29.8, 28.1, 22.1, 18.3, 17.8, 11.0, -1.4. MS (FAB) ($M^+$) calcd 1114.50, obsd 1114.67.

**8**: colorless oil; $[\alpha]_D^{22}$-15.7 (*c* 0.15, $CHCl_3$); IR (film, $cm^{-1}$) 3409, 1720, 1601, 1287, 1110; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.1 Hz, 2 H), 7.96 (d, *J* = 7.1 Hz, 2 H), 7.54-7.46 (m, 3 H), 7.42-7.27 (m, 8 H), 7.26-7.21 (m, 1 H), 7.12-7.06 (m, 2 H), 6.93-6.88 (m, 2 H), 5.31-5.23 (m, 2 H), 5.10 (d, *J* = 8.4 Hz, 1 H), 5.00-4.95 (m, 2 H), 4.85 (d, *J* = 7.5 Hz, 1 H), 4.73-4.67 (m, 3 H), 4.64 (d, *J* = 14.2 Hz, 1 H), 4.48-4.43 (m, 2 H), 4.38 (d, *J* = 7.2 Hz, 1 H), 4.12 (dd, *J* = 11.9, 4.7 Hz, 1 H), 3.95-3.81 (m, 2 H), 3.79-3.37 (m, 3 H), 3.36 (s, 3 H), 2.66-2.50 (m, 4 H), 2.20-1.75 (m, 3 H), 1.62 (br s, 1 H), 1.48 (s, 3 H), 1.27 (s, 6 H), 1.05-0.95 (m, 2 H), 0.04 (s, 9 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 209.7, 166.2, 164.1, 137.6, 132.8, 132.7, 132.3, 131.2, 129.7 (2 C), 129.6 (2 C), 129.5 (2 C), 128.40 (2 C), 128.38 (2 C), 128.2 (2 C), 127.9 (2 C), 127.7, 127.6, 95.1, 93.9, 90.1, 89.2, 82.5, 81.3, 80.2, 73.9, 69.9, 69.2, 66.1, 60.9, 57.9, 55.7, 55.1, 51.7, 40.5, 33.5, 31.5, 30.8, 29.8, 28.2, 18.1, 17.8, 11.1, -1.5. MS (FAB) ($M^+$) calcd 994.45, obsd 994.52.

**9**: colorless gum; $[\alpha]_D^{22}$+7.3 (*c* 0.03, $CHCl_3$); IR (film, $cm^{-1}$) 3416, 1721, 1286, 1098, 1041; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.6 Hz, 2 H), 7.57 (d, *J* = 7.7 Hz, 2 H), 7.55-7.50 (m, 1 H), 7.41-7.28 (m, 8 H), 6.99-6.94 (t, *J* = 7.7 Hz, 2 H), 5.33 (s, 2 H), 5.28 (d, *J* = 5.1 Hz, 1 H), 5.23 (d, *J* = 10.8 Hz, 1 H), 4.83 (d, *J* = 7.5 Hz, 1 H), 4.72 (d, *J* = 7.5 Hz, 1 H), 4.67 (s, 2 H), 4.48-4.34 (m, 4 H), 4.29-4.26 (m, 1 H), 4.01-3.84 (m, 4 H), 3.50-3.47 (m, 1 H), 3.34 (s, 3 H), 3.32-3.01 (m, 1 H), 2.69-2.61 (m, 2 H), 2.36 (d, *J* = 12.8 Hz, 1 H), 2.13-1.90 (m, 2 H), 1.70-1.61 (m, 2 H), 1.43 (s, 3 H), 1.26 (s, 3 H), 1.23 (s, 3 H), 1.03 (t, *J* = 3.9 Hz, 2 H), 0.99-0.82 (m, 2 H), 0.77 (s, 9 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 209.6, 166.2, 164.2, 137.6, 132.8, 132.5, 130.9, 129.6 (2 C), 129.5 (2 C), 129.4, 128.3 (2 C), 127.9 (2 C), 127.7 (2 C), 127.6, 95.0, 93.8, 90.9, 90.1, 81.9, 81.2, 80.1, 76.4, 69.8, 69.0, 66.2, 63.9, 57.8, 55.7, 55.1, 51.7, 45.1, 39.9, 34.4, 31.8, 31.0, 29.90, 29.88, 29.6, 28.5, 18.3, 17.6, 11.3, -1.5. MS (FAB) ($M^+$) calcd 890.43, obsd 890.58.

**10**: colorless oil; $[\alpha]_D^{22}$+21.2 (*c* 0.31, $CHCl_3$); IR (film, $cm^{-1}$) 1721, 1286, 1269, 1108, 1045; $^1H$ NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.1 Hz, 1 H), 7.61 (d, *J* = 7.1 Hz, 2 H), 7.54 (d, *J* = 9.2 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.34-7.27 (m, 6 H), 6.99 (t, *J* = 8.0 Hz, 2 H), 5.29 (d, *J* = 12.2 Hz, 1 H), 5.24 (d, *J* = 7.8 Hz, 1 H), 5.16 (dd, *J* = 9.9, 5.9 Hz, 1 H), 5.09 (d, *J* = 7.8 Hz, 1 H), 4.74 (s, 2 H), 4.71-4.69 (m, 1 H), 4.61 (d, *J* = 8.7 Hz, 1 H), 4.49-4.40 (m, 3 H), 3.99-3.94 (m, 2 H), 3.76-3.70 (m, 1 H), 3.50-3.32 (m, 1 H), 3.34 (s, 3 H), 2.95-2.85 (m, 1 H), 2.75-2.50 (m, 3 H), 2.15-1.95 (m, 3 H), 1.90-1.80 (m, 1 H), 1.29 (s, 3 H), 1.25 (s, 6 H), 1.07-1.01 (m, 2 H), 0.90-0.83 (m, 3 H), 0.06 (s, 9 H). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 209.7, 166.0, 164.3, 137.5, 132.8, 132.6, 130.9, 129.7 (2 C), 129.6 (2 C), 129.5, 128.4 (2 C), 128.3 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7, 95.5, 93.7, 90.1, 89.7, 82.8, 81.0, 80.4, 75.2, 70.1, 68.8, 65.9, 55.6, 55.3, 55.2, 52.0, 39.5, 34.4, 31.3, 30.2, 30.0, 28.0, 18.1, 17.7, 14.1, 10.5, -1.3 (3 C). HRMS (EI) ($M^+$-CHO) calcd 842.4061, obsd 842.4072.

Article Identifier:
1437-2096,E;1999,0,10,1547,1550,ftx,en;S02599ST.pdf