

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/083694 A1

(51) International Patent Classification⁷: **C07F 7/08**

(21) International Application Number: PCT/US02/11139

(22) International Filing Date: 9 April 2002 (09.04.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/833,757 12 April 2001 (12.04.2001) US

(71) Applicant: **UNIVERSITY OF PITTSBURGH** [US/US];
Cathedral of Learning, Pittsburgh, PA 15260 (US).

(72) Inventors: **CURRAN, Dennis, P.**; 506 Linden Avenue,
Pittsburgh, PA 15208 (US). **DU, Wu**; 11 Oakland Square,
Pittsburgh, PA 15213 (US).

(74) Agent: **BARTONY, Henry, E., Jr.**; Bartony & Hare, Suite
1800, Law & Finance Building, 429 Fourth Avenue, Pitts-
burgh, PA (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SYNTHESIS OF SILYL CAMPTOTHECINS AND SILYL HOMOCAMPTOTHECINS

(57) Abstract: A method of synthesizing 7-silyl camptothecins and 7-silyl homocamptothecins includes the step of mixing a camptothecin or a homocamptothecin having hydrogen at the C7 position with a silyl radical generator and a silyl radical precursor under conditions to generate a silyl radical $\text{SiR}^1\text{R}^2\text{R}^3$ wherein R^1 , R^2 and R^3 are independently a C_{1-10} alkyl group, a C_{2-10} alkenyl group, a C_{2-10} alkynyl group, an aryl group, $-(\text{CH}_2)_m\text{R}^{11}$ or $\text{SiR}^{12}\text{R}^{13}\text{R}^{14}$, wherein m is an integer within the range of 1 through 10 and R^{11} is a hydroxy group, an alkoxy group, an amino group, an alkylamino group, a dialkylamino group, F, Cl, a cyano group, $-\text{SR}^6$ or a nitro group, and wherein R^{12} , R^{13} and R^{14} are independently the same or different an alkyl group or an aryl group.



WO 02/083694 A1