

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
11 August 2005 (11.08.2005)

PCT

(10) International Publication Number  
**WO 2005/073185 A1**

(51) International Patent Classification<sup>7</sup>: **C07C 327/00**

PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.

(21) International Application Number:  
PCT/US2005/001012

(22) International Filing Date: 12 January 2005 (12.01.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/537,832 21 January 2004 (21.01.2004) US

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, 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, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

#### Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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.

(71) Applicant (for all designated States except US): **BRISTOL-MYERS SQUIBB COMPANY** [US/US]; P.O. Box 4000, Route 206 and ProvinceLine Road, Princeton, New Jersey 08543-4000 (US).

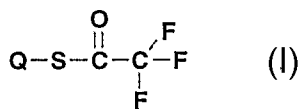
(72) Inventors; and

(75) Inventors/Applicants (for US only): **SHARMA, Padam N.** [US/US]; 9104 Cirrus Court, Manlius, New York 13104 (US). **GUBLO, Edward J.** [US/US]; 4176 Pisces Circle, Liverpool, NY 13090 (US). **BOETTGER, Susan D.** [US/US]; 7474 James Street, Fayetteville, NY 13066 (US). **RACHA, Saibaba** [US/US]; 7401 Highbridge Terrace, Fayetteville, New York 13066 (US). **USHER, John** [US/US]; 112 York Road, Dewitt, New York 13214 (US).

(74) Agents: **RODNEY, Burton** et al.; Bristol-Myers Squibb Company, P.O. Box 4000, Princeton, New Jersey 08543-4000 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GR, 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, NA, NI, NO, NZ, OM, PG,

(54) Title: NOVEL ALKYL- AND ARYL-THIOTRIFLUOROACETATES AND PROCESS



(57) Abstract: Novel C3-C19 alkyl- and aryl-thiotrifluoroacetates are provided which have the structure [Formula (I)], wherein Q is C9-C19 alkyl or aryl, and are useful protecting agents for the amino or hydroxy functional groups of amines, amino acids or primary or secondary alcohols or amino alcohols to enable formation of amide bonds in peptides or proteins which are useful

as screening agents, pharmaceuticals and cosmetics. A process for preparing C3-C19 alkyl- and aryl-thiotrifluoroacetates is also provided wherein a C3-C19 alkylthiol or arylthiol is treated with trifluoroacetic anhydride (TFAA) in the presence of organic base such as pyridine, a solvent such as dichloromethane (DCM) and dimethylaminopyridine (DMAP) as a catalyst to form the desired C3-C19 alkyl- or aryl-thiotrifluoroacetate. In addition, a process for protecting a primary or secondary amino group or a primary or secondary hydroxyl group or an amino alcohol with a trifluoroacetyl protecting group is provided wherein a primary or secondary amine, amino acid, a primary or secondary alcohol or an amino alcohol is treated with a C3 to C19 alkyl- or aryl-thiotrifluoroacetate in basic aqueous solution.

WO 2005/073185 A1