Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 105–109
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

The synthesis of 4,4′-arylmethylene-bis(3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5-ol) in aqueous media without catalyst

Chang-Sheng Yao [a,b,*], Chen-Xia Yu [a,b], Shu-Jiang Tu [a,b], Da-Qing Shi [a,b], Xiang-Shan Wang [a,b], You-Quan Zhu [c], Hua-Zheng Yang [c]

[a] *Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China*
[b] *Key Laboratory of Biotechnology for Medical Plants of Jiangsu Province, Xuzhou 221116, People's Republic of China*
[c] *State Key Laboratory of Element-Organic Chemistry, Institute of Element-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China*

Received 11 September 2006; received in revised form 18 September 2006; accepted 1 October 2006
Available online 11 October 2006

Abstract

The synthesis of 4,4′-arylmethylene-bis(3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5-ol) was performed effectively in aqueous media without catalyst by the reaction of aryl aldehydes and 1-phenyl-3-trifluoromethylpyrazol-5-one. All of the compounds obtained were characterized by elemental analysis, FTIR and ^{1}H NMR. The structure of compound **3g** was further confirmed by the X-ray single crystal diffraction. The method has the advantages of mild condition, without any catalyst, high yields and environmentally benign procedure.

Keywords: Environment friendly; Aqueous media; Catalyst; 1-Phenyl-3-trifluoromethylpyrazol-5-one; 4,4′-Arylmethylene-bis(3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5-ol)

1. Introduction

Fluoro-containing organic compounds play an important role for the pharmaceutical as well as agrochemical industries, because of their often unique biological properties, such as the increased membrane permeability, enhanced hydrophobic binding and stability against metabolic oxidation [1–6]. Among them the trifluoromethylated molecules are of great significance, and attract continuous attention from various fields [7–10]. Since fluorine is virtually absent in the living organisms [11], fluorinated pharmaceuticals might have comparatively less environmental and mammalian toxicity. Today, many trifluoromethyl group-containing molecules have been developed as well-known drugs such as prozac (antidepressant), diflucan (anti-fungal agent), casodex (anticancer agent) and desflurane (inhalation anesthetic) [10]. Therefore, the development of synthetic methods for trifluoromethylated compounds is very significant to both organofluorine chemistry and organic synthetic chemistry.

Nowadays, the pyrazolone derivatives were paid much attention for their various biological activities, such as antitumor [12,13], selective COX-2 inhibitory [14]. Besides, they can be used as cytokine inhibitors [15], potent catalytic activity inhibitor of human telomerase [16], therapeutics for kinase mediated inflammatory disorders [17] and dyes [18,19]. The compounds that contain two pyrazolone ring can be used as extractant for some metal ions [20] and ligands [21,22]. In 1971, Buzykin and Lonshchakova performed the synthesis of aryl-bis(1-phenyl-3-methyl-5-pyrazolon-4-yl)methane using benzene as solvents [23]. Later, Li and co-worker reported the solid-state synthesis of these compounds [24] and Bai et al. employed the microwave irradiation to promote the solvent-free synthesis of these compounds [25]. Although the uses of organic solvents such as chloroform and methanol were avoided in the synthesis step, they must be present during workup.

Recently, the organic synthesis performed in aqueous media gained much interest for water is an easily available, economical, safe and environmentally benign solvent; it has thus been identified as a ''green'' solvent [26]. Consequently, conditions under which a wide range of reactions can be conducted in water have been developed, including those

* Corresponding author at: Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China. Fax: +86 516 83403164.
E-mail address: chshengyao@126.com (C.-S. Yao).

0022-1139/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2006.10.006

ordinarily thought to be intolerant of protic solvents, such as Lewis acid catalyzed and organometallic reactions [27]. Shi et al. [28] and Wang et al. [29] showed these compounds can be synthesized in aqueous media, but the reaction process need some catalyst, such as triethylbenzylammonium chloride (TEBA) [28] and sodium dodecyl sulfate (SDS) [29]. In addition, their workups need the organic solvent, ethanol, to isolate the product.

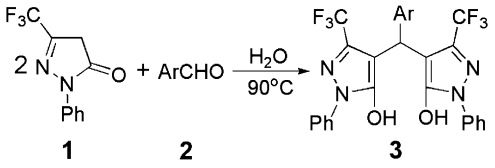
Because of the harmful effect of the toxic solvents to the environment, there is an urgent need to develop the green procedure for the synthesis of organic chemicals. To the best of our knowledge, there have been no report on the synthesis of 4,4′-arylmethylene-bis(3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5-ol). Here we shall report that the synthesis of these compounds in aqueous media. To further meet the demand of green chemistry, the reaction was performed without catalyst (Scheme 1 and Table 1).

2. Results and discussion

Due to the strong electron-withdrawing ability of the trifluoromethyl group, 3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5(4*H*)-one is very reactive. The results are summarized in Table 1, which shows that the reaction without any catalyst such as TEBA or SDS, in aqueous media gives the corresponding products in moderate to good yields (74–89%), although it involves the elimination of a molecule of water.

The workup is very simple, for just filtration can give the product. So this protocol is more economical, safe and environmentally benign than the known results [23–25,28,29].

To examine the generality of this process, several examples illustrating this method for the synthesis of those



Scheme 1.

Table 1
The synthesis of compound **3**

Entry	Product	ArCHO	Time (h)	Yield (%)[a]
1	**3a**	4-$NO_2C_6H_4CHO$	8	83
2	**3b**	4-BrC_6H_4CHO	7	74
3	**3c**	3,4-$OCH_2OC_6H_4CHO$	7	89
4	**3d**	4-ClC_6H_4CHO	8	86
5	**3e**	3-$NO_2C_6H_4CHO$	8	87
6	**3f**	4-$(CH_3)_2NC_6H_4CHO$	7	78
7	**3g**	2,4-$Cl_2C_6H_3CHO$	8	75
8	**3h**	4-$OHCC_6H_4CHO$	7	77
9	**3i**	4-FC_6H_4CHO	6	80
10	**3j**	C_6H_5CHO	7	86

[a] Isolated yield.

compounds were studied. As shown in Table 1, the effect of electron and the nature of substituents on the aromatic ring did not show strongly obvious effects in terms of yields under this reaction condition. Benzaldehyde and other aromatic aldehydes containing electron-withdrawing groups (such as a nitro group, halide) or electron-donating groups (such as a dimethylamino group) were employed and reacted well with 3-trifluoromethyl-l-phenyl-5-pyrazolone to give

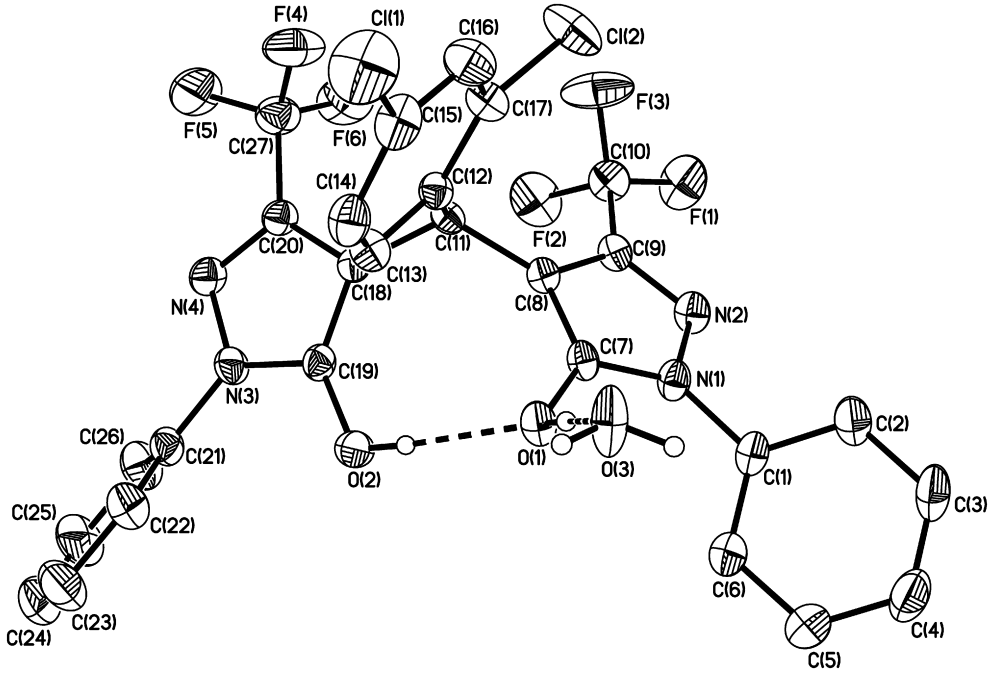


Fig. 1. The crystal structure of compound **3g**, the minor parts and the hydrogen atoms not involved hydrogen bond were omitted for clarity.

4,4′-arylmethylene-bis(3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5-ol) in moderate to good yields.

All the compounds were characterized by elemental analysis, FTIR and ^{1}H NMR. To further elucidate the structure of the product, a single crystal of **3g** was prepared and its structure was determined by X-ray diffraction. The crystal structure shows that the products exist as enol forms and there is an intramolecular hydrogen bond in it (Fig. 1).

3. Conclusion

In summary, we have developed an efficient, economical, safe and environmentally benign method to synthesize the 4,4′-arylmethylene-bis(3-(trifluoromethyl)-1-phenyl-1*H*-pyrazol-5-ol). The results showed that our strategies for the syntheses of some trifluoromethylated molecules are of great importance in both organofluorine and organic synthetic field, and should be applied to other clean syntheses of various potent bioactive trifluoromethylated compounds.

4. Experimental

4.1. General methods

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. The starting material, 1-phenyl-3-trifluoromethyl-pyrazol-5-one, **1**, was prepared according to Ref. [30]. NMR spectra were measured on a Bruker DPX 400, Data for ^{1}H are reported as follows: chemical shift (ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (Hz) and number. Infrared (IR) spectra were recorded on a Perkin-Elmer 500 FT-IR spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). Elemental analyses were performed on Yanaco-CHN CORDER elementary analyzer. Melting points were measured on a Thomas–Hoover apparatus and were not corrected. The single crystal diffraction data were gathered on a SMART CCD 1000 area diffractometer.

4.2. Synthesis of 3-(trifluoromethyl)-4-((3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl) arylmethyl)-1-phenyl-1H-pyrazol-5-ol (Table 1 and Scheme 1)

3-(Trifluoromethyl)-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2.0 mmol), aryl aldehyde (1.0 mmol) and 3 mL water were added to a 25 mL round bottom flask and were stirred at 90 °C for several hours (monitored by TLC). Then the mixture was cooled and filtered to give the pure product.

4.2.1. 3-(Trifluoromethyl)-4-((3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-nitrophenyl) methyl)-1-phenyl-1H-pyrazol-5-ol (**3a**)

mp: 152–153 °C; FTIR (KBr pallet, cm^{-1}): 3383, 3066, 2914, 1604, 1524, 1494, 1454, 1434, 1349, 1270, 1150, 1029, 1005, 888, 843, 758, 737, 691; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.29 (s, 1H, 4-methyl-H), 7.24 (t, J = 7.4 Hz, 2H, ArH), 7.41 (t, J = 8.0 Hz, 4H, ArH), 7.48 (d, J = 8.0 Hz, 2H, ArH), 7.85 (d, J = 8.0 Hz, 4H, ArH), 8.16 (d, J = 9.0 Hz, 2H, ArH); anal. calcd. for $C_{27}H_{17}F_6N_5O_4$: C, 55.02; H, 2.91; N, 11.88. Found: C, 55.12; H, 2.93; N, 11.78.

4.2.2. 4-((4-Bromophenyl)(3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methyl)-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-ol (**3b**)

mp: 153–154 °C; FTIR (KBr pallet, cm^{-1}): 3383, 3059, 2911, 1605, 1486, 1431, 1349, 1306, 1226, 1142, 1007, 851, 780, 730, 690; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.16 (s, 1H, 4-methyl-H), 7.17 (d, J = 8.0 Hz, 2H, ArH), 7.22 (t, J = 8.0 Hz, 2H, ArH), 7.40 (q, J = 8.0 Hz, 6H, ArH), 7.85 (d, J = 7.6 Hz, 4H, ArH); anal. calcd. for $C_{27}H_{17}BrF_6N_4O_2$: C, 52.02; H, 2.75; N, 8.99. Found: C, 52.15; H, 2.83; N, 8.78.

4.2.3. 4-((Benzo[d][1,3]dioxol-6-yl)(3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methyl)-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-ol (**3c**)

mp: 128–130 °C; FTIR (KBr pallet, cm^{-1}): 3385, 3069, 2893, 1600, 1489, 1431, 1303, 1241, 1152, 1039, 1004, 928, 881, 804, 754, 728, 698; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.09 (s, 1H, 4-methyl-H), 5.91 (s, 2H, OCH_2O), 6.65 (d, J = 8.0 Hz, 1H, ArH), 6.75 (d, J = 5.2 Hz, 2H, ArH), 7.20 (t, J = 7.4 Hz, 2H, ArH), 7.38 (t, J = 8.0 Hz, 4H, ArH), 7.83 (d, J = 8.0 Hz, 4H, ArH); anal. calcd. for $C_{28}H_{18}F_6N_4O_4$: C, 57.15; H, 3.08; N, 9.52. Found: C, 57.25; H, 2.85; N, 9.75.

4.2.4. 4-((4-Chlorophenyl)(3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methyl)-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-ol (**3d**)

mp: 148–149 °C; FTIR (KBr pallet, cm^{-1}): 3377, 3059, 1606, 1584, 1491, 1431, 1305, 1268, 1151, 1005, 880, 850, 755, 732, 690; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.16 (s, 1H, 4-methyl-H), 7.20 (t, J = 8.0 Hz, 4H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 7.38 (t, J = 8.0 Hz, 6H, ArH), 7.82 (d, J = 8.4 Hz, 2H, ArH); anal. calcd. for $C_{27}H_{17}ClF_6N_4O_2$: C, 56.02; H, 2.96; N, 9.68. Found: C, 56.15; H, 2.85; N, 9.78.

4.2.5. 3-(Trifluoromethyl)-4-((3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(3-nitrophenyl) methyl)-1-phenyl-1H-pyrazol-5-ol (**3e**)

mp: 226–228 °C; FTIR (KBr pallet, cm^{-1}): 3420, 3088, 1603, 1579, 1490, 1452, 1352, 1260, 1206, 1151, 1005, 800, 754, 732, 695; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.29 (s, 1H, 4-methyl-H), 7.22 (t, J = 7.2 Hz, 2H, ArH), 7.39 (t, J = 8.0 Hz, 4H, ArH), 7.56 (d, J = 8.0 Hz, 1H, ArH), 7.66 (d, J = 7.6 Hz, 1H, ArH), 7.82 (d, J = 8.0 Hz, 4H, ArH), 8.03 (d, J = 8.0 Hz, 1H, ArH), 8.08 (s, 1H, ArH); anal. calcd. for $C_{27}H_{17}F_6N_5O_4$: C, 55.02; H, 2.91; N, 11.88. Found: C, 55.15; H, 2.83; N, 11.85.

4.2.6. 4-((4-(Dimethylamino)phenyl)(3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methyl)-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-ol (**3f**)

mp: 174–176 °C; FTIR (KBr pallet, cm^{-1}): 3420, 3048, 1599, 1573, 1484, 1375, 1302, 1286, 1128, 1070, 1003, 872,

756, 700; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.12 (s, 6H, 2 × CH_3), 5.20 (s, 1H, 4-methyl-H), 7.21 (t, J = 7.4 Hz, 2H, ArH), 7.38–7.43 (m, 6H, ArH), 7.49 (d, J = 8.0 Hz, 2H, ArH), 7.83 (d, J = 7.6 Hz, 4H, ArH); anal. calcd. for $C_{29}H_{23}F_6N_5O_2$: C, 59.29; H, 3.95; N, 11.92. Found: C, 59.25; H, 3.85; N, 11.78.

*4.2.7. 4-((2,4-Dichlorophenyl)(3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methyl)-3-(trifluoromethyl)-1-phenyl-1H-pyrazol-5-ol (**3g**)*

mp: 174–176 °C; FTIR (KBr pallet, cm^{-1}): 3069, 1599, 1486, 1385, 1301, 1256, 1130, 1074, 1049, 1028, 1005, 913, 875, 851, 778, 755, 723, 693; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.60 (s, 1H, 4-methyl-H), 7.23 (t, J = 7.4 Hz, 2H, ArH), 7.35–7.43 (m, 5H, ArH), 7.47 (s, 1H, ArH), 7.67 (d, J = 3.2 Hz, 1H, ArH), 7.79 (d, J = 8.4 Hz, 4H, ArH); anal. calcd. for $C_{27}H_{16}Cl_2F_6N_4O_2$: C, 52.87; H, 2.63; N, 9.13. Found: C, 52.75; H, 2.76; N, 9.18.

*4.2.8. 4-((4-(Bis(5-hydroxyl-3-trifluoromethyl-1-phenyl-1H-pyrazol-4-yl)methyl)phenyl)(5-hydroxyl-3-trifluoromethyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-trifluoromethyl-1-phenyl-1H-pyrazol-5-ol (**3h**)*

mp: 198–200 °C; FTIR (KBr pallet, cm^{-1}): 3421, 3068, 2901, 1699, 1602, 1495, 1452, 1426, 1303, 1225, 1152, 1074, 1004, 756, 726, 691; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.10 (s, 2H, 4-methyl-H), 7.13 (s, 4H, ArH), 7.18 (t, J = 7.4 Hz, 4H, ArH), 7.35 (t, J = 7.8 Hz, 8H, ArH), 7.80 (d, J = 8.4 Hz, 8H, ArH); anal. calcd. for $C_{48}H_{30}F_{12}N_8O_4$: C, 57.04; H, 2.99; N, 11.09. Found: C, 57.15; H, 2.86; N, 11.18.

*4.2.9. 3-(Trifluoromethyl)-4-((3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-fluorophenyl)methyl)-1-phenyl-1H-pyrazol-5-ol (**3i**)*

mp: 202–204 °C; FTIR (KBr pallet, cm^{-1}): 3420, 3116, 2906, 1604, 1507, 1452, 1401, 1341, 1302, 1256, 1229, 1199, 1153, 1004, 912, 878, 852, 750, 726, 690; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.17 (s, 1H, 4-methyl-H), 7.03 (t, J = 8.4 Hz, 2H, ArH), 7.20–7.26 (m, 4H, ArH), 7.38 (t, J = 8.0 Hz, 4H, ArH), 7.83 (d, J = 8.4 Hz, 4H, ArH); anal. calcd. for $C_{27}H_{17}F_7N_4O_2$: C, 57.66; H, 3.05; N, 9.96. Found: C, 57.75; H, 2.96; N, 9.98.

*4.2.10. 3-(Trifluoromethyl)-4-((3-(trifluoromethyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(phenyl)methyl)-1-phenyl-1H-pyrazol-5-ol (**3j**)*

mp: 203–205 °C; FTIR (KBr pallet, cm^{-1}): 3064, 1601, 1493, 1430, 1303, 1257, 1206, 1150, 1004, 913, 854, 789, 754, 731, 688; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.22 (s, 1H, 4-methyl-H), 7.12 (t, J = 6.6 Hz, 1H, ArH), 7.23–7.29 (m, 6H, ArH), 7.40 (t, J = 8.0 Hz, 4H, ArH), 7.87 (d, J = 7.6 Hz, 4H, ArH); anal. calcd. for $C_{27}H_{18}F_6N_4O_2$: C, 59.56; H, 3.33; N, 10.29. Found: C, 59.65; H, 3.15; N, 10.18.

4.3. Crystal structure determination

The selected crystal of **3g** was mounted on a Bruker SMART CCD 1000 area diffractometer. Reflection data were measured at 294 (2) K, using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation and an φ–ω scan mode. A total of 5733 independent reflections were collected in the range of $2.02 < \theta < 26.42$, of which 2698 reflections with $I > 2\sigma$ (I) were considered to be observed and used in the succeeding refinement. The correction for Lp factors and empirical absorption were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL software package [31]. H atoms bonded to O atoms were located in a Fourier difference map and were refined freely, except for that on O1, where the instruction AFIX 3 was used to fix the atomic parameters. Other H atoms were placed in calculated positions, with C–H = 0.93 or 0.98, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(parent atom). In the molecular structure, the F atoms of one CF_3 group (F1, F2 and F3) were disordered over two positions, with refined site-occupancy factors of 0.889 (7) and 0.111 (7), for which the C–F bond lengths were restrained to 1.32 (1) Å. The C atoms of the C21–C26 aromatic ring and their attached H atoms were disordered over two positions also, with refined site-occupancy factors of 0.890 (3) and 0.110 (3). All non-H atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent C atoms. The final least-square cycle gave R_1 = 0.0571, R_w = 0.1016; the weighting scheme, $w = 1/[\sigma^2(Fo^2) + (0.0346P)^2 + 5.8586P]$ where $P = (Fo^2 + 2Fc^2)/3$. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-298349. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors appreciate the financial support of the Nature Science Foundation of Xuzhou Normal University (No. 05XLA07), National Natural Science Foundation of China (No. 20372057) and Natural Science Foundation of the Jiangsu Province (No. BK2006033).

References

[1] For recent advances, see:
(a) K.L. KirK, J. Fluorine Chem. 127 (2006) 1013–1029;
(b) J.-P. Bégué, D. Bonnet-Delpon, J. Fluorine Chem. 127 (2006) 992–1012.
[2] R.D. Chambers, D. Holling, G. Sandforda, A.S. Batsanov, J.A.K. Howard, J. Fluorine Chem. 125 (2004) 661–671.
[3] P.V. Ramachandran, in: Proceedings of the ACS Symposium Series, ACS, Washington, DC, 2000.
[4] T. Himaya, Organofluorine Compounds, Springer-Verlag, Berlin, Heidelberg, 2001.
[5] P. Kirsch, Modern Fluoroorganic Chemistry: Synthesis, Reactivity and Applications, Wiley–VCH, New York/Heidelberg, 2004.
[6] I. Ojima, J.R. McCarthy, J.T. Welch, Biomedical Frontiers of Fluorine Chemistry, American Chemical Society, Washington, DC, 1996.
[7] M.L. Quan, P.Y.S. Lam, Q. Han, D.J.P. Pinto, M.Y. He, R.H. Li, C.D. Ellis, C.A. Clark, J.H. Sun, R.S. Alexander, S. Bai, J.M. Luettgen, R.M. Knabb, P.C. Wong, R.R. Wexler, J. Med. Chem. 48 (2005) 1729–1744.

[8] O.G. Khudina, E.V. Shchegol'kov, Ya.V. Burgart, M.I. Kodess, O.N. Kazheva, A.N. Chekhlov, G.V. Shilov, O.A. Dyachenko, V.I. Saloutin, O.N. Chupakhin, J. Fluorine Chem. 126 (2005) 1230–1238.
[9] M. Schlosser, J.N. Volle, F. Leroux, K. Schenk, Eur. J. Org. Chem. (2002) 2913–2920.
[10] M. Abid, B. Török, Adv. Synth. Catal. 347 (2005) 1797–1803.
[11] S.C. O'Hagan, S.L. Cobb, J.T.G. Hamilton, D. Cormac, C.D. Murphy, Nature 416 (2002) 279.
[12] H.-J. Park, K. Lee, S.-J. Park, B. Ahn, J.-C. Lee, H.Y. Cho, K.-I. Lee, Bioorg. Med. Chem. Lett. 15 (2005) 3307–3312.
[13] M.P. Clark, S.K. Laughlin, M.J. Laufersweiler, R.G. Bookland, T.A. Brugel, A. Golebiowski, M.P. Sabat, J.A. Townes, J.C. VanRens, J.F. Djung, M.G. Natchus, B. De, L.C. Hsieh, S.C. Xu, R.L. Walter, M.J. Mekel, S.A. Heitmeyer, K.K. Brown, K. Juergens, Y.O. Taiwo, M.J. Janusz, J. Med. Chem. 11 (2004) 2724–2727.
[14] I.H. Cho, J.Y. Noh, S.W. Park, H.C. Ryu, J.W. Lim, J.H. Kim, M.Y. Chae, D.H. Kim, S.H. Jung, H.J. Park, Y.H. Kim, I.K. Min, US Patent 2 004 002 532 (2004).
[15] M.P. Clark, S.K. Laughlin, A. Golebiowski, T.A. Brugel, M. Sabat, WO Patent 2 005 047 287 (2005).
[16] K. Yasutaka, S. Narie, S.-M. Mieko, M. Hiromu, M.-M. Kimiko, Biochem. Biophys. Res. Commun. 4 (2004) 1351–1358.
[17] M.P. Clark, R.G. Bookland, Expert Opin. Ther. Pat. 11 (2005) 1617–1623.
[18] M. Ishida, WO Patent 2 006 006 212 (2006).
[19] M. Speckbacher, H.-J. Braun, WO Patent 2 006 012 934 (2006).
[20] H. Takeishi, Y. Kitatsuji, T. Kimura, Y. Meguro, Z. Yoshida, S. Kihara, Anal. Chim. Acta 1 (2001) 69–80.
[21] S.A. Abdel-Latif, Synth. React. Inorg. Metal-organic Chem. 8 (2001) 1355–1374.
[22] C. Pettinari, F. Marchetti, R. Pettinari, D. Martini, A. Drozdov, S. Troyanov, J. Chem. Soc., Dalton Trans. 11 (2001) 1790–1797.
[23] B.I. Buzykin, T.I. Lonshchakova, Russ. Chem. Bull. 10 (1971) 2224–2226.
[24] X.-L. Li, H. Ma, Y.-M. Wang, J.-B. Meng, Chem. J. Chin. Univ. 12 (1995) 1903–1906 (in Chinese).
[25] Y.-J. Bai, J. Lu, Z.-J. Wang, H.-Y. Gan, H.-R. Ma, Chin. J. Org. Chem. 6 (2004) 616–620 (in Chinese).
[26] J.M. DeSimone, Science 5582 (2002) 799–803.
[27] For recent advances, see:
(a) C.K.Z. Andrade, L.M. Alves, Curr. Org. Chem. 2 (2005) 195–218;
(b) M.C. Pirrung, Chem. Eur. J. 5 (2006) 1312–1317;
(c) C.-J. Li, Chem. Rev. 8 (2005) 3095–3165.
[28] D.-Q. Shi, J. Chen, N. Wu, Q.-Y. Zhuang, X.-S. Wang, Chin. J. Org. Chem. 4 (2005) 405–408.
[29] W. Wang, S.-X. Wang, X.-Y. Qin, J.-T. Li, Synth. Commun. 9 (2005) 1263–1269.
[30] C.-H. Mao, Y.-F. Lu, M.-Z. Huang, L. Huang, C. Chen, X.-M. Ou, Chin. J. Syn. Chem. 2 (2002) 167–169.
[31] SHELXTL (Version 5.1). Bruker AXS Inc., Madison, Wisconsin, USA.