Journal of Fluorine Chemistry 132 (2011) 402–408

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Catalyst free 1,3-dipolar cycloaddition of 3-oxo-1,2-pyrazolidinium ylides to β-trifluoroacetyl vinyl ethyl ether: Synthesis of 6-trifluoroacetyl substituted bicyclic pyrazolidinones

Yong Xin, Jingwei Zhao, Jiwei Gu, Shizheng Zhu *

Key Laboratory of Organouorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

ARTICLE INFO

Article history:
Received 10 March 2011
Received in revised form 26 March 2011
Accepted 29 March 2011
Available online 5 April 2011

Keywords:
1,3-Dipolar
Cycloaddition
Ylides
Trifluoroacetyl
Pyrazolidinones

ABSTRACT

A catalyst free cycloaddition reaction of 3-oxo-1,2-pyrazolidinium ylides with β-trifluoroacetyl vinyl ethyl ether is reported, which proceeded smoothly at ambient temperature and afford the bicyclic pyrazolidinone products in good yield. This is the first report of synthesis of 6-trifluoroacetyl substituted bicyclic pyrazolidinones that are potentially anti-microbial and herbicidal.

1. Introduction

1,3-Dipolar cycloadditions are powerful methods for constructing a variety of five-membered heterocycles in a convergent manner of relatively simple precursors [1]. Among the well-developed dipoles, azomethine imines represents a series of powerful building blocks, which are stable, easily handled, inexpensive and atom economic [2]. The cyclic azomethine imine, 3-oxo-1,2-diazetidinium ylides, was firstly synthesized by Murckmann in 1911 [3]. However, the very first time it was recognized as a 1,3-dipole was 1968 [4], from when the detailed chemical properties [5], thermic behavior and photochromic properties [6] were investigated. During the past two decades, it was successfully employed in the reactions with dipolephiles, such as alkynes [7], alkenes (including unstaturated aldehydes [8], unsaturated ketones and esters [9] and others [10]), and so on [11]. Cycloadditions of these dipoles, even with highly electron-deficient alkynes (e.g., dimethyl acetylenedicarboxylate), are often conducted at elevated temperatures and, in the case of unsymmetrical alkynes, generally furnish mixtures of regioisomeric heterocycles. Only during recent years, along with the development of click chemistry, 3-oxo-1,2-diazetidinium ylides were efficiently used in the cycloaddition reactions in the presence of Cu (I) catalyst [7(a), (b), (c)–12]. Especially, Shibata et al. [10(e)] reported a noncatalytic 1,3-dipolar cyclization of azomethine imines with tert-butyl 2-(trifluoromethyl)prop-2-enoate at room temperature.

In the course of our study on the chemical transformation of β-trifluoroacetyl vinyl ethyl ether 1, we found it a dipolephilic partner of high activity [13]. Thus, we investigated the 1,3-dipolar cycloaddition reaction of 1 with cyclic azomethine imines, 3-oxo-1,2-pyrazolidinium ylides. Herein, we report a convenient synthesis of trifluoroacetyl bearing bicyclic pyrazolidinones, using the catalyst free cycloaddition reaction of 3-oxo-1,2e-pyrazolidinium ylides with β-trifluoroacetyl vinyl ethyl ether at room temperature.

2. Results and discussion

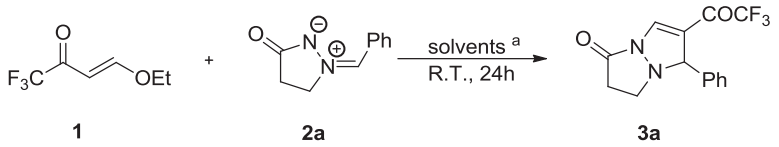
Initially, we examined the reaction of 1 with 3-oxo-1,2-pyrazolidinium ylide 2a at room temperature in dichloromethane which was generally used as solvent in this type of cycloaddition reaction. Unfortunately, according to ^{19}F NMR, only imperceptible product was formed. After stirring for 3 days, the reaction proceeded only near 50%, and after regular isolation the desired product 3a was isolated in a yield of 40% as yellow oil. The result encouraged us to screening the solvents in order to improve the efficiency of the reaction, and the results are listed in Table 1. The yields were determined by ^{19}F NMR, using 0.1 mmol trifluoromethylbenzene (−63 ppm) as internal standard, while the chemical shifts of 1 and correspongding product 3a are −78 ppm and −73 ppm, respectively.

We found DMSO as the best solvent. To the best of our knowledge, the more polar solvent is, the better the 1,3-dipolar

* Corresponding author. Tel.: +86 21 54925185; fax: +86 21 64166128.
E-mail addresses: zhusz@sioc.ac.cn, zhusz@mail.sioc.ac.cn (S. Zhu).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.03.023

Table 1
1,3-Dipolar cycloaddition of 3-oxo-1,2-pyrazolidinium ylide **2a** to β-trifluoroacetyl vinyl ethyl ether **1**: effect of solvents on the yield of the reaction.

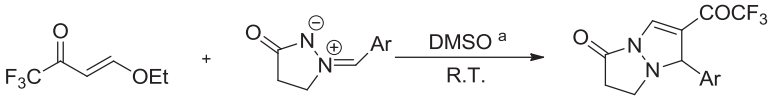


1 2a 3a

Entry	Solvents	Yield (%)[b]
1	CH_2Cl_2	35
2	$CHCl_3$	32
3	CCl_4	20
4	DCE	56
5	Et_2O	12
6	THF	12
7	DME	24
8	DMF	80
9	EtOAc	12
10	Benzene	42
11	Toluene	40
12	CH_3CN	77
13	DMSO	83
14	Acetone	41
15	Methanol	15
16	Ethanol	43

[a]The reactions were conducted in varies of solvents at room temperature between 0.1 mmol of β-trifluoroacetyl vinyl ethyl ether 1 and 0.1 mmol of 3-oxo-1,2-pyrazolidinium ylide **2a**. The solvents were used without pre-purification.
[b] Determined by ^{19}F NMR.

Table 2
Reaction scope: 3-oxo-1,2-pyrazolidinium ylides.



1 2a-j 3a-j

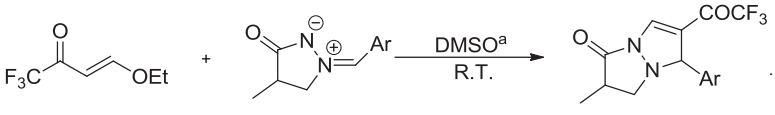
Entry	Ar	Time (h)	Product	Yield (%)[b]
1	Ph (**2a**)	3	**3a**	85
2	4-$MeOC_6H_4$ (**2b**)	6	**3b**	88
3	3-$NO_2C_6H_4$ (**2c**)	5	**3c**	89
4	2-FC_6H_4 (**2d**)	10	**3d**	80
5	3-FC_6H_4 (**2e**)	10	**3e**	73
6	4-FC_6H_4 (**2f**)	10	**3f**	78
7	2,3-$2FC_6H_3$ (**2g**)	14	**3g**	88
8	4-ClC_6H_4 (**2h**)	8	**3h**	79
9	4-BrC_6H_4 (**2i**)	8	**3i**	82
10	2-furanyl (**2j**)	7	**3j**	44

[a]The reactions were conducted between 1.0 mmol of 1 and 1.0 mmol of **2a–j** in 2 mL of DMSO at room temperature.
[b] Isolated yield.

cycloaddition reaction proceeds. However, in our case, comparing entry 15, 16 with entry 12 in Table 1, solubility of 2a in solvents has a great impact of the efficiency of the reaction. In addition, the 3-oxa 2a dissolved better in benzene and toluene (Table 1, entry 10 and 11), which are non-polar solvents; but the reaction was less efficient in ether (Table 1, entry 5 and 6) and ethyl acetate (Table 1, entry 9), which are more polar solvents.

In the subsequent research, with optimized condition in hand, we examined the scope of substrates 2. It was found that the aromatic ylides, regardless of electron-donating or electron-withdrawing

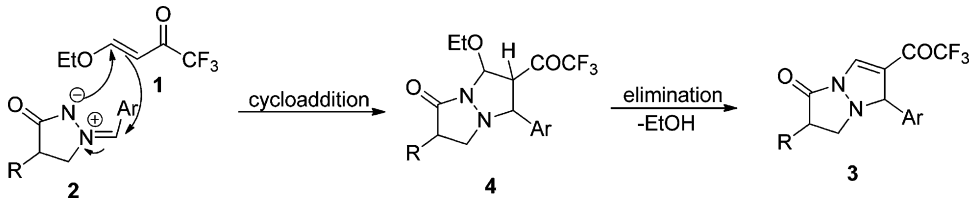
Table 3
Reaction scope: 4-methyl-3-oxo-1,2-pyrazolidinium ylides.



1 2k-m 3k-m

Entry	Ar	Time (h)	Product[b]	dr[c]	Yield (%)[d]
1	Ph (2k)	8	**3k**	3: 5	79
2	4-$MeOC_6H_4$ (2l)	9	**3l**	4: 5	88
3	3-$NO_2C_6H_4$ (2m)	9	**3m**	1: 3	82

[a]The reactions were conducted between 1.0 mmol of **1** and 1.0 mmol of **2k–m** in 2 mL of DMSO at room temperature.
[b] The diasteroisomers were hard to be isolated by flash chromatography and the products were the mixture of diasteroisomers.
[c] The dr was determined by ^1H NMR of the products, and the *cis*- and *trans*-isomers were not specified.
[d] Isolated yield.



Scheme 1. Reaction pathway.

substituents on the phenyl ring, participated in this process with high efficiency (Table 2). Further more, heterocyclic aldehyde also worked well, but the yield was much lower (Table 2, entry 10).

To further explore the scope of the reaction, we prepared 4-methyl-3-oxo-1,2-pyrazolidinium ylides 2k-m and they were subjected with 1. To our delight, the reaction also proceeded smoothly and gave the diastereoisomers in good yields (Table 3).

Formation of cycloadducts 3 is explainable by initial 1,3-dipolar cycloaddition of alkene 1 to azomethine imines 2 to give the fully saturated cycloadduct 4, which then undergoes elimination of ethanol to afford the 2,3-dihydropyrazolo[1,2-a]pyrazolone 3 (Scheme 1).

3. Conclusion

In summary, we here report a first synthesis of 6-trifluoroacetyl substituted bicyclic pyrazolidinones through a 1,3-dipolar cycloaddition of 3-oxo-1,2-pyrazolidinium ylides to β-trifluoroacetyl vinyl ethyl ether. The reaction proceeded efficiently in DMSO at room temperature and afforded the desired products in moderate to good yield, which are potentially anti-microbial and herbicidal [14]. A wide range of 3-oxo-1,2-pyrazolidinium ylides could participate in the process successfully.

4. Experimental

4.1. General Information

Melting points are measured on a Temp-Melt apparatus and are uncorrected. ^{1}H (300 MHz) and ^{19}F NMR (282 MHz) spectra were recorded on a Bruker AM-300 ultra shield, 300 MHz, high performance digital FT-NMR spectrometer with Me_4Si and $CFCl_3$ as the internal and external standards, respectively. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AV-400 ultra shield plus, 400 MHz, high performance digital FT-NMR spectrometer with Me_4Si as the internal standard. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV) or Electrospray Ionization. Elemental analyses were performed by this institute. All solvents and reagents were used without further purification unless otherwise stated.

4.2. General procedure and spectra data of 2a–m

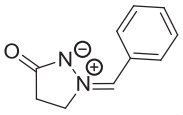
4.2.1. General procedure to prepare 3-oxo-1,2-pyrazolidinium ylide 2a–j

Cooled in an ice bath, methacrylate 30 mL was added to the solution of hydrazine hydrate 60 mL in ethanol 240 mL. After addition, the mixture was heated to reflux for 8 h. Then the solvent and the volatile components were removed under reduced pressure. The thick colorless oil, crude pyrazolidin-3-one, was obtained in 80% yield.

By subjecting pyrazolidin-3-one (1.1 equiv.) to various aromatic aldehydes (1.0 equiv.) in methanol (20 mmol in 15 mL methanol) at room temperature, the crude products of desired 3-oxo-1,2-pyrazolidinium ylides were formed. After removing the solvent methanol, the crude product was recrystallized in ethanol. Washed by ethyl acetate and dried under vacuum, the pure product 2 was obtained in moderate yield.

4.2.2. Characterisation data of 2a–2j

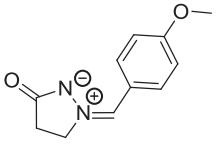
4.2.2.1. Benzylidene-5-oxopyrazolidin-2-ium-1-ide (2a) [7(b)].



2.2g, 65%

White solid, mp 194–195 °C (lit. mp 192–194 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.30–8.28 (m, 2H), 7.48–.45 (m, 3H), 7.14 (s, 1H), 4.52 (td, 2H, J = 8.1 Hz, 2.1 Hz), 2.79 (m, 2H).

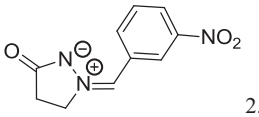
4.2.2.2. (4-Methoxybenzylidene)-5-oxopyrazolidin-2-ium-1-ide (2b) [15a].



2.8g, 69%

White solid, mp 173–175 °C (lit. mp 183–86 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.29 (d, 2H, J = 8.7 Hz), 7.84 (d, 2H, J = 8.7 Hz), 4.56 (t, 2H, J = 8.1 Hz), 3.89 (s, 3H), 2.92 (t, 2H, J = 8.1 Hz).

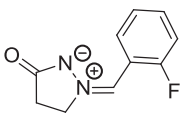
4.2.2.3. (3-Nitrobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (2c) [15b].



2.9g, 66%

Yellow solid, mp 240 °C (lit. mp 236–38 °C). ^{1}H NMR (DMSO, 300 MHz): δ 9.34 (s, 1H), 8.54 (d, 1H, J = 7.8 Hz), 8.34 (dd, 1H, J = 8.1 Hz, 1.8 Hz), 7.87-7.81 (m, 2H), 4.66 (t, 2H, J = 8.1 Hz), 2.64 (t, 2H, J = 8.1 Hz).

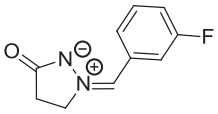
4.2.2.4. (2-Fluorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (2d) [7(b)].



2.2g, 58%

White solid, mp 233–34 °C (lit. mp 230–231 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.23 (t, 1H, J = 7.8 Hz), 7.50–7.43 (m, 2H), 7.31–7.09 (m, 3H), 4.59 (t, J = 8.1 Hz), 2.85 (t, J = 8.1 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −116.8 (s, 1F).

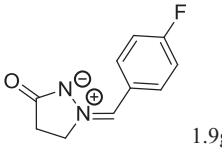
*4.2.2.5. (3-Fluorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**2e**).*



1.8g, 47%

White solid, mp 233–235 °C. ^{1}H NMR (DMSO, 300 MHz): δ 8.33 (d, 1H, J = 10.5 Hz), 7.94 (d, 1H, J = 7.8 Hz), 7.70 (s, 1H), 7.59 (q, 1H, J = 6.3 Hz), 7.37 (td, 1H, J = 8.7 Hz, 1.5 Hz), 4.60 (t, J = 7.8 Hz), 2.59 (t, 7.8 Hz). ^{19}F NMR (DMSO, 282 MHz): δ −112.1 (dd, J = 9.3 Hz, 8.2 Hz). EI-MS m/z (%): 192 (M^+, 36), 191 (72), 108 (100). Anal. Calcd. For C10H9FN2O C62.49, H4.72, N14.58; Found C62.51, H4.81, N14.55. FT-IR (KBr, cm^{-1}): 1680, 1654, 1609, 1575, 1540, 1451, 1347, 1331, 1292, 1276, 1248, 948, 787, 687.

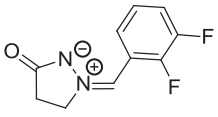
*4.2.2.6. (4-Fluorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**2f**) [9(a)].*



1.9g, 51%

White solid, mp 223 °C (lit. mp not available). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.35 (s, 1H), 7.25–7.13 (m, 4H), 4.53 (t, 2H, J = 8.1 Hz), 2.83 (t, 2H, J = 8.1 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −104.8 (s, 1F).

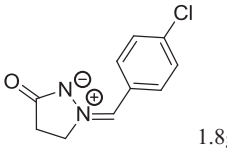
*4.2.2.7. (2,3-Difluorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**2g**).*



2.3g, 55%

Yellow solid, mp 243–245 °C. ^{1}H NMR (DMSO, 300 MHz): δ 8.81 (td, 1H, J = 6.6 Hz, 1.5 Hz), 7.74 (s, 1H), 7.61 (q, 1H, J = 10.2 Hz), 7.41 (m, 1H), 4.66 (t, 2H, J = 8.1 Hz), 2.60 (t, 2H, J = 8.1 Hz). ^{19}F NMR (DMSO, 282 MHz): δ −139.1 to 139.3 (m, 1F), −142.4 to 142.5 (m, 1F). EI-MS m/z (%): 210 (M^+, 32), 126 (100). Anal. Calcd. For C10H8F2N2O: C57.14, H3.84, N13.33; Found C57.10, H3.84, N13.33. FT-IR (KBr, cm^{-1}): 1679, 1652, 1597, 1476, 1463, 1436, 1343, 1296, 1108, 949, 817, 668.

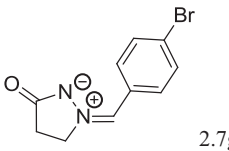
*4.2.2.8. (4-Chlorobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**2h**) [9(a)].*



1.8g, 44%

White solid, mp 219–220 °C (lit. mp 214–217 °C). ^{1}H NMR (DMSO, 300 MHz): δ 8.32 (d, 2H, J = 8.7 Hz), 7.69 (s, 1H), 7.62 (d, 2H, J = 8.7 Hz), 4.57 (t, 2H, J = 7.5 Hz), 2.57 (t, 2H, J = 7.5 Hz).

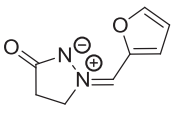
*4.2.2.9. (4-Bromobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**2i**) [9(a)].*



2.7g, 53%

Yellow solid, mp 239–240 °C (lit. mp not available). ^{1}H NMR (DMSO, 300 MHz): δ 8.24 (d, 2H, J = 8.7 Hz), 7.76 (d, 2H, J = 8.7 Hz), 7.67 (s, 1H), 4.56 (t, 2H, J = 7.8 Hz), 2.57 (t, 2H, J = 7.8 Hz).

*4.2.2.10. (Furan-2-ylmethylene)-5-oxopyrazolidin-2-ium-1-ide (**2j**) [15a].*



1.1g, 34%

Dark yellow solid, mp 215–217 °C (lit. mp not available). ^{1}H NMR (DMSO, 300 MHz): δ 7.98 (s, 1H), 7.78 (s, 1H), 7.58 (d, 1H, J = 3.3 Hz), 6.80–6.78 (m, 1H), 4.48 (t, 2H, J = 7.8 Hz), 2.58 (t, 2H, J = 7.8 Hz).

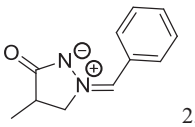
4.3. General procedure to prepare 4-methyl-3-oxo-1,2-pyrazolidinium ylide 2k–m

Cooled in an ice bath, methyl methacrylate 60 mL was added to the solution of hydrazine hydrate 26 mL in ethanol 240 mL. After addition, the mixture was heated to reflux for 12 h. Then the solvent and the volatile components were removed under reduced pressure. The thick colorless oil, crude 4-methyl pyrazolidin-3-one, was obtained in 77% yield.

By subjecting 4-methyl pyrazolidin-3-one (1.1 equiv.) to various aromatic aldehydes (1.0 equiv.) in methanol (20 mmol in 15 mL methanol) at room temperature, the crude products of desired 4-methyl-3-oxo-1,2-pyrazolidinium ylides were formed. After removing the solvent methanol, the crude product was recrystallized in ethanol. Washed by ethyl acetate and dried under vacuum, the pure product 2 was obtained in good yield.

*4.4. Characterisation data of **2k–2m***

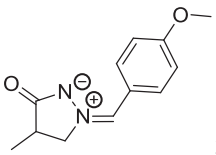
*4.4.1.1. Benzylidene-4-methyl-5-oxopyrazolidin-2-ium-1-ide (**2k**) [4(a)]*



2.8g, 75%

White solid, mp 123–124 °C (lit. mp 141–142 °C). ^{1}H NMR (DMSO, 300 MHz): δ 8.32–8.28 (m, 2H), 7.66 (s, 1H), 7.54-7.51 (m, 3H), 4.75 (dd, J = 9.3 Hz, 13.5 Hz), 4.21 (dd, J = 7.2 Hz, 13.5 Hz), 2.80–2.67 (m, 1H), 1.18 (d, 3H, J = 6.9 Hz).

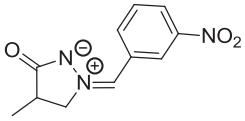
*4.4.1.2. (4-Methoxybenzylidene)-4-methyl-5-oxopyrazolidin-2-ium-1-ide (**2l**) [15b]*



3.4g, 78%

White solid, mp 145 °C (lit. mp not avilable). ^{1}H NMR (DMSO, 300 MHz): δ 8.29 (d, 2H, J = 8.7 Hz), 7.60 (s, 1H), 7.11 (d, 2H, J = 8.7 Hz), 4.70 (dd, 1H, J = 13.2 Hz, 9.6 Hz), 4.15 (dd, 1H, J = 13.2 Hz, 6.9 Hz), 3.85 (s, 3H), 2.75–2.67 (m, 1H), 1.17 (d, 3H, J = 7.2 Hz).

*4.4.1.3. Methyl-2-(3-nitrobenzylidene)-5-oxopyrazolidin-2-ium-1-ide (**2m**) [15b]*



3.8g, 81%

Yellow solid, mp 187–188 °C (lit. mp not avilable). ^{1}H NMR (DMSO, 300 MHz): δ 9.35 (s, 1H), 8.53 (d, 1H, J = 7.5 Hz), 8.33 (d, 1H, J = 8.7 Hz), 7.85-7.80 (m, 2H), 4.81 (dd, 1H, J = 13.2 Hz, 9.6 Hz), 4.29 (dd, 1H, J = 13.5 Hz, 6.6 Hz), 2.85-2.73 (m, 1H), 1.20 (d, 3H, J = 7.2 Hz).

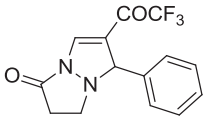
4.5. General procedure and spectra data of 3a–m

4.5.1. General procedure of the 1,3-dipolar cycloaddition of 2 to β-trifluoroacetyl vinyl ethyl ether (1)

To a solution of β-trifluoroacetyl vinyl ethyl ether **1** (1.0 mmol, 0.168 g) in 2 mL of DMSO, compound **2** (1.0 mmol) was added. After stirring for 8 h, monitored by TLC, the reaction completed and a yellow spot (TLC Rf = 0.3, using hexanes: ethyl acetate, 2: (1) was generated cleanly. The mixture was poured into brine 50 mL and stirred for 5 min. The water phase was extracted by ethyl ether (3 × 30 mL) till the water phase became colorless. The organic phase was dried over $MgSO_4$ for 0.5–1 h, filtered, and the filtrate was evaporated in vacuo. The crude product was purified on silica gel using hexanes: ethyl acetate (5:1–3:1) as eluent. The product 3 was obtained as yellow oil or solid.

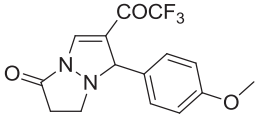
4.5.2. Characterisation data of 3a–m

*4.5.2.1. Phenyl-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3a**).*



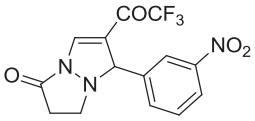
Yellow oil. 0.251 g, 85%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79 (s, 1H), 7.39–7.34 (m, 5H), 5.35 (s, 1H), 3.44–3.37 (m, 1H), 3.15–3.07 (m, 1H), 3.0–2.81 (m, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.9 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5(q, J = 34.5 Hz), 165.8, 136.8, 132.2 (q, J = 4.4 Hz), 128.9, 128.8, 128.1, 118.8, 116.2 (q, J = 289.0 Hz), 72.6, 50.9, 35.5. ESI-MS m/z: 319 $[M+Na]^+$. HRMS-EI: calc. mass 296.0773, mass 296.0771, formula C14 H11 N2 O2 F3. FT-IR (neat, cm^{-1}): 3066, 2095, 1738, 1712, 1675, 1606, 1563, 1509, 1426, 1193, 1144, 905, 841.

*4.5.2.2. (4-Methoxyphenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3b**).*



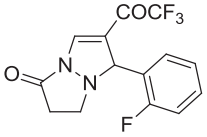
Yellow solid. Mp: 110–112 °C. 0.287 g, 88%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79 (s, 1H), 7.28 (d, 2H, J = 8.7 Hz), 6.91 (d, 2H, J = 8.7 Hz), 5.33 (s, 1H), 3.81 (s, 3H), 3.4-3.33 (m, 1H), 3.13-2.81 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ -72.9 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 36.4 Hz), 165.8. 160.1, 132.0 (q, J = 4.4 Hz), 129.3, 128.7, 118.9, 116.3 (q, J = 288.0 Hz), 114.2, 71.8, 55.3, 50.4, 35.6. ESI-MS: 327 $[M+H]^+$. HRMS-ESI: $[M+H]^+$: calc. mass 327.09510, mass 327.09572, formula C15 H14 F3 N2 O3. FT-IR (neat, cm^{-1}): 3089, 2926, 1749, 1659, 1565, 1515, 1368, 1250, 1197, 1138, 1026, 994, 904, 833, 714.

*4.5.2.3. (3-Nitrophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3c**).*



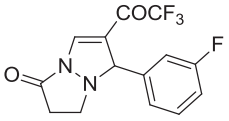
Yellow solid. Mp 102–104 °C. 0.303 g, 89%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.36 (t, 1H, J = 2.1 Hz), 8.52 (d, 1H, J = 8.1 Hz), 7.81 (s, 2H), 7.57 (t, 1H, J = 8.4 Hz), 5.43 (s, 1H), 3.64 (t, 1H, J = 6.3 Hz), 3.23–3.02 (m, 2H), 2.91-2.86 (m, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.58 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 36.4 Hz), 166.0, 148.4, 140.5, 134.5, 133.0 (q, J = 5.1 Hz), 129.5, 123.6, 123.2, 117.5, 116.1 (q, J = 288.7 Hz), 72.6, 52.2, 35.3. EI-MS m/z (%): 341 (M^+, 6), 219 (52), 55 (100). ESI-MS m/z: 342 $[M+H]^+$. HRMS-EI: calc. mass 341.0623, mass 341.0618, formula C14 H10 N3 O4 F3.FT-IR (neat, cm^{-1}): 3069, 2909, 2845, 1747, 1670, 1558, 1531, 1418, 1350, 1193, 1142, 999, 822, 738, 714, 580.

*4.5.2.4. (2-Fluorophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3d**).*



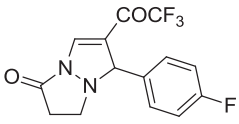
Yellow oil. 0.251 g, 80%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (s, 1H), 7.37-7.10 (m, 4H), 5.70 (s, 1H), 3.45–3.41 (m, 1H), 3.20 (dd, 1H, J = 8.4 Hz, 8.7 Hz), 2.94–2.85 (m, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.9 (s, 3F), −118.1(m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.4 (q, J = 36.4 Hz), 165.9, 161.1 (d, J = 246.4 Hz), 132.9 (q, J = 4.4 Hz), 130.6 (d, J = 8.0 Hz), 129.1 (d, J = 3.7 Hz), 124.6 (d, J = 3.7 Hz), 123.8 (d, J = 12.4 Hz), 117.2, 116.3 (q, J = 288.8 Hz), 115.9 (d, J = 21.9 Hz), 65.8 (d, J = 2.9 Hz), 50.9, 35.5. ESI-MS: 315 $[M+H]^+$. HRMS-ESI: $[M+H]^+$ calc. mass 315.0764, mass 315.0751, formula C14 H11 N2 O2 F4. FT-IR (neat, cm^{-1}): 3079, 2925, 2851, 1731, 1709, 1670, 1560, 1494, 1411, 1361, 1185, 1142, 818, 759, 727, 708.

*4.5.2.5. (3-Fluorophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3e**).*



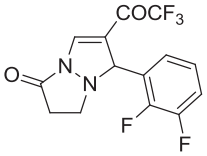
Yellow oil. 0.229 g, 73%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80 (s, 1H), 7.34 (dd, 1H, J = 7.8 Hz, 6.0 Hz), 7.20–7.00 (m, 3H), 5.32 (s, 1H), 3.47 (td, 1H, J = 8.4 Hz, 2.4 Hz), 3.15–3.80 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.0 (s, 3F), −112.1 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 36.4 Hz), 165.9, 163.0 (d, J = 245.0 Hz), 140.0 (d, J = 6.6 Hz), 132.5(q, J = 3.6 Hz), 132.2 (d, J = 8.0 Hz), 123.9 (d, J = 2.9 Hz), 118.2, 116.2 (q, J = 288.7 Hz), 115.8 (d, J = 21.1 Hz), 115.0 (d, J = 21.9 Hz), 72.3, 51.3, 35.4. EI-MS m/z (%): 314 (M^+, 9), 261 (78), 219 (42), 189 (53), 133 (43), 55 (100). HRMS-EI: calc. mass 314.0681, mass 314.0678, formula C14 H10 N2 O2 F4. FT-IR (neat, cm^{-1}): 3085, 2930, 2845, 1736, 1704, 1677, 1664, 1563, 1427, 1358, 1193, 1137, 911, 780, 714.

*4.5.2.6. (4-Fluorophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3f**).*



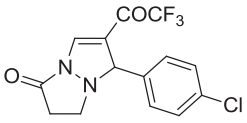
Yellow oil. 0.245 g, 78%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79 (s, 1H), 7.37 (dd, 1H, J = 8.4 Hz, 5.7 Hz), 7.06 (t, 1H, J = 8.4 Hz), 5.32 (s, 1H), 3.45 (td, J = 8.4 Hz, 2.7 Hz), 3.14–2.80 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.0 (s, 3F), −112.9 (m, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 36.5 Hz), 165.9, 162.9 (d, 245.8 Hz), 133.2 (d, 2.9 Hz), 132.3 (q, 4.3 Hz), 129.8 (d, 8 Hz), 118.5, 116.2 (q, 288.0 Hz), 115.6 (d, 21.2 Hz), 72.1, 51.2, 35.5. ESI-MS: 315 $[M+H]^+$. HRMS-EI: calc. mass 314.0678, mass 314.0676, formula C14 H10 N2 O2 F4. FT-IR (neat, cm^{-1}): 3078, 2926, 1739, 1712, 1563, 1509, 1426, 1362, 1193, 905, 883, 840, 778, 713.

*4.5.2.7. (2,3-Difluorophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3g**).*



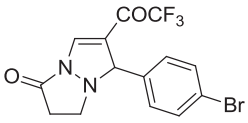
Yellow solid. Mp 102–104 °C. 0.292 g, 88%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.83 (s, 1H), 7.18-7.00 (m, 3H), 5.70 (s, 1H), 3.52 (td, 1H, J = 8.4 Hz, 3.3dHz), 3.22 (q, 1H, J = 8.7 Hz), 3.03–2.84 (m, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.2 (s, 3F), -137.7 (s, 1F), −143.5 (s, 1F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.3 (q, J = 36.5 Hz), 165.9, 149.9 (qd, J = 115.2 Hz, 13.1 Hz,), 133.2 (q, J = 4.4 Hz), 126.8 (d, J = 9.5 Hz), 124.5 (t, J = 5.1 Hz), 123.8, 117.7, 117.5, 116.2 (q, J = 288.7 Hz), 116.6, 65.8, 51.4, 35.4.EI-MS m/z (%): 332 (M^+, 9), 219 (51), 151 (46), 55 (100). HRMS-EI: calc. mass 332.0583, mass 332.0584, formula C14 H9 N2 O2 F5. FT-IR (neat, cm^{-1}): 3069, 2920, 2851, 1744, 1664, 1565, 1488, 1425, 1409, 1362, 1277, 1223, 1194, 1144, 1022, 977, 929, 819, 786, 768, 747, 717.

*4.5.2.8. (4-Chlorophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3h**).*



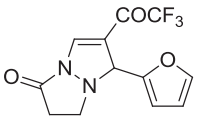
Yellow oil. 0.261 g, 79%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (s, 1H), 7.61–7.55 (m, 4H), 5.54 (s, 1H), 3.74–3.68 (m, 1H), 3.39–3.04 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.6 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.0 (q, J = 35.7 Hz), 165.9, 135.9, 134.7, 132.4 (q, J = 4.4 Hz), 129.4, 128.9, 118.4, 116.2 (q, J = 288.7 Hz), 72.2, 51.3, 35.5. EI-MS m/z (%): 330 (M^+, 17) 332 ($M+2^+$, 6), 219 (95), 55 (100). ESI-MS m/z: 331 $[M+H^+]$, 333 $[M+2+H^+]$. HRMS-EI: calc. mass. 330.0383, mass 330.0386, formula C14 H10 N2 O2 F3 Cl.FT-IR (neat, cm^{-1}): 3033, 2920, 2840, 1674, 1562, 1425, 1361, 1194, 1142, 905, 733, 715.

*4.5.2.9. (4-Bromophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3i**).*



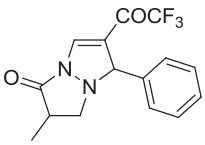
Yellow solid. Mp 92–94°C. 0.306 g, 82%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97 (s, 1H), 7.70 (d, 2H, J = 8.1 Hz), 7.47 (d, 2H, J = 8.1 Hz), 5.48 (s, 1H), 3.66 (td, 1H, J = 8.1 Hz, 3.0 Hz), 3.34–3.01 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.1 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 36.5 Hz), 165.8, 136.5, 132.5 (q, J = 4.4 Hz), 131.9, 129.8, 122.8, 118.2, 116.2 (q, J = 288.8 Hz), 72.3, 51.4, 35.5. EI-MS m/z (%): 374 (M^+, 4), 376 ($M+2^+$, 4), 219 (70), 55 (100). ESI-MS m/z: 375 $[M+H]^+$, 377 $[M+2+H]^+$. HRMS-EI: calc. mass 373.9878, mass 373.9882, formula C14 H10 N2 O2 F3 Br.FT-IR (neat, cm^{-1}): 3025, 2925, 2835, 1736, 1667, 1560, 1480, 1417, 1355, 1193, 1142, 1009, 996, 879, 818, 708.

*4.5.2.10. (Furan-2-yl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3j**).*



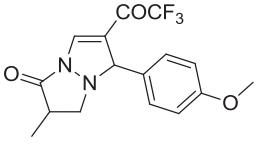
Dark yellow oil. 0.126 g, 44%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79 (s, 1H), 7.42 (s, 1H), 6.35 (d, 2H, J = 8.4 Hz), 5.5 (s, 1H), 3.25–3.17 (m, 1H), 3.08-2.78 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.6 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz):δ 175.4 (q, J = 36.3 Hz), 165.4, 148.7, 143.6, 132.4 (q, J = 4.8 Hz), 116.2 (q, J = 2883.3 Hz), 116.3, 110.7, 110.3, 63.3, 48.7, 35.7. EI-MS m/z (%): 286 (M^+, 65), 55 (100). ESI-MS m/z: 287 $[M+H]^+$. HRMS-EI: calc. mass 286.0565, mass 286.0563, formula C12 H9 N2 O3 F.FT-IR (neat, cm^{-1}): 3126, 2929, 1739, 1709, 1675, 1564, 15187, 1364, 1146, 1015, 913, 198, 745, 708, 618, 594.

*4.5.2.11. Methyl-5-phenyl-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3k**).*



Yellow oil. dr: 3:5. 0.245 g, 79%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.16 (s, 1H), 8.12 (s, 0.6H), 7.70–7.63 (m, 6H), 7.57–7.55 (m, 2H), 5.81 (s, 1H), 5.55 (s, 0.6H), 4.03 (t, 0.6H, J = 8.4 Hz), 3.48-3.35 (m, 2.7H), 3.08 (dd, 0.6H, J = 6.6 Hz, 3.0 Hz), 2.86 (t, 1H, J = 8.1 Hz), 1.60 (d, 2.4H, J = 7.2 Hz), 1.52 (d, 3H, J = 6.9 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.7 (s, 3F), −72.8 (s, 1.8F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 35.6 Hz), 175.3 (q, J = 35.5 Hz), 169.4, 168.6, 138.3, 134.5, 132.8, 132.0, 129.1, 128.9, 128.8, 128.6, 128.2, 128.0, 119.0, 118.3, 116.4 (q, J = 289.1 Hz), 116.3 (q, J = 288.3 Hz), 73.7, 69.8, 59.7, 55.1, 42.1, 41.5, 13.2, 12.2. EI-MS m/z (%): 310 (M^+, 13), 233 (56), 69 (100). HRMS-EI: calc. mass 310.0929, mass 310.0925, formula C15 H13 N2 O2 F3.FT-IR (neat, cm^{-1}): 3016, 2981, 1712, 1560, 1542, 1422, 1194, 1145, 903, 699.

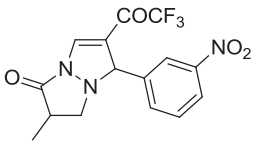
*4.5.2.12. (4-Methoxyphenyl)-2-methyl-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3l**).*



Yellow oil. dr: 4:5. 0.299 g, 88%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 8.02 (s, 0.8H), 7.97 (s, 1H), 7.51 (d, 2H, J = 8.7 Hz), 7.34 (d, 1.6H, J = 8.7 Hz), 7.09 (d, 4H, J = 8.7 Hz), 5.69 (s, 0.8H), 5.40 (s, 1H), 3.99 (s, 5.4H), 3.93–3.88 (m, 1H), 3.37–3.24 (m, 2.8H), 2.98–2.91 (m, 1H), 2.72–2.68 (m, 0.8H), 1.49 (dd, 3H, J = 7.2 Hz, 2.4 Hz), 1.40 (dd, 3H, J = 7.2 Hz, 2.4 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −72.9 (s, 2.4F), -73.0 (s, 3F). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5 (q, J = 36.3 Hz), 175.3 (q, J = 36.3 Hz), 169.3, 168.5, 160.3, 159.9, 132.6 (q, J = 3.9 Hz), 131.7 (q, J = 4.7 Hz), 131.2, 130.2, 129.5, 129.2, 119.2, 118.6, 116.3 (q, J = 289.1 Hz), 116.2 (q, J = 288.3 Hz), 114.4, 114.1, 73.2, 68.9, 60.4, 59.5, 55.2, 54.7, 42.1, 41.5, 13.0, 12.3. EI-MS m/z (%): 340 (M^+, 26), 69 (100). HRMS-EI: calc. mass 340.1035, mass 340.1036, formula C16

H15 N2 O3 F3.FT-IR (neat, cm^{-1}): 3017, 2938, 2841, 1708, 1612, 1563, 1423, 1362, 1148, 1063, 1031, 903, 835, 720.

*4.5.2.13. Methyl-5-(3-nitrophenyl)-6-(2,2,2-trifluoroacetyl)-2,3-dihydropyrazolo[1,2-a]pyrazol-1(5H)-one (**3m**).*



Yellow oil. dr: 1:3. 0.291 g, 82%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.62 (s, 0.3H), 8.53 (s, 1H), 8.45–8.43 (m, 1.3H), 8.11 (s, 1.6H), 8.02 (d, J = 6.6 Hz), 7.86–7.81 (m, 1.3H), 5.79 (s, 1H), 5.67 (s, 0.3H), 4.39–4.31 (m, 0.5H), 4.10–4.05 (m, 0.3H), 3.59–3.10 (m, 3.9H), 1.61 (d, 3H, J = 6.9 Hz), 1.50 (d, 1H, J = 7.2 Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −73.2 (s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.4 (q, J = 36.3 Hz), 175.3 (q, J = 36.3 Hz), 169.3, 169.0, 148.5, 148.3, 141.1, 139.2, 134.5, 134.4, 133.4, 132.9, 129.7, 129.4, 123.7, 123.4, 123.2, 123.1, 117.7, 117.2, 116.2 (q, J = 288.3 Hz), 116.1 (q, J = 288.3 Hz), 72.9, 71.0, 59.9, 57.1, 42.1, 41.3, 14.1, 11.9. EI-MS m/z (%): 355 (M^+, 5), 233 (48), 69 (100). HRMS-EI: calc. mass 355.0780, mass 355.0782, formula C15 H12 N3 O4 F3.FT-IR (neat, cm^{-1}): 3078, 2981, 2937, 2854, 1743, 1668, 1558, 1513, 1429, 1359, 1236, 1163, 927, 711.

Acknowledgement

We are grateful to the National Natural Science Foundation of China (NNSFC No. 21032006) for the financial support on this research.

References

[1] For reviews of 1,3-dipolar cycloadditions, see;
(a) Synthetic applications of 1,3-dipolar cycloaddition chemistry toward heterocycles and natural products. In: A. Padwa. W.H. Pearson. (Eds.), vol. 59. Wiley: New York, 2003.
(b) K.V. Gothelf, K.A. Jørgensen, Chem. Rev. 98 (1998) 863–909.
[2] (a) A. Padwa (Ed.), 1,3-Dipolar Cycloaddition Chemistry, vol. 1, John Wiley & Sons, New York, 1984;
(b) E. Vedejs, F.G. West, Chem. Rev. 86 (1986) 941–955;
(c) O. Tsuge, S. Kanemasa, in: A.R. Katritzky (Ed.), Advances in Heterocyclic Chemistry, vol. 45, Academic Press, San Diego, 1989, pp. 231–349.
[3] E. Muckermann, J. Prakt. Chem. 84 (1911) 278–292.
[4] (a) H. Dorn, A. Otto, Angew. Chem. Int. Ed. 7 (1968) 214–215;
(b) H. Dorn, A. Otto, Tetrahedron 24 (1968) 6809–6811.
[5] (a) H. Dorn, T. Kreher, Tetrahedron Lett. 29 (1988) 2939–2942;
(b) E.C. Taylor, N.F. Haley, R.J. Clemens, J. Am. Chem. Soc. 103 (1981) 7743–7752.
[6] (a) G. Tomaschewski, G. Geissler, G. Schauer, J. Prakt. Chem. 322 (1980) 623–628;
(b) G. Geissler, I. Menz, K. Angermüller, G. Tomaschewski, J. Prakt. Chem. 325 (1983) 197–204.
[7] (a) A. Suárez, C.W. Downey, G.C. Fu, J. Am. Chem. Soc. 127 (2005) 11244–11245;
(b) R. Shintani, G.C. Fu, J. Am. Chem. Soc. 125 (2003) 10778–10779;
(c) T. Oishi, K. Yoshimura, K. Yamaguchi, N. Mizuno, Chem. Lett. 39 (2010) 1086–1087;
(d) L. Pezdirc, U. Grošelj, A. Meden, B. Stanovnik, J. Svete, J. Heterocycl. Chem. 45 (2008) 181–188;
(e) A. Preseren, J. Svete, B. Stanovnik, J. Heterocycl. Chem. 36 (1999) 799–801;
(f) J. Svete, A. Preseren, B. Stanovnik, L. Golic, S. Golic-Grdadolnik, J. Heterocycl. Chem. 34 (1997) 1323–1328;
(g) L. Pezdirc, B. Stanovnik, J. Svete, Aust. J. Chem 62 (2009) 1661–1666;
(h) M. Keller, A.S.S. Sido, P. Pale, J. Sommer, Chem. Eur. J 15 (2009) 2810–2817;
(i) N. Mizuno, K. Kamata, Y. Nakagawa, T. Oishi, K. Yamaguchi, Catal. Today 157 (2010) 359–363;
(j) C. Turk, J. Svete, B. Stanovnik, L. Golič, S. Golič-Grdadolnik, A. Golobič, L. Selič, Helv. Chem. Acta 84 (2001) 146–156;
(k) C. Turk, L. Golič, L. Selič, S. Svete, B. Stanovnik, ARKIVOC V (2001) 87–97;
(l) For patents see: US728733, US4734504, US4902707 and EP0202047.
[8] (a) L. Pezdirc, V. Jovanovski, D. Bevk, R. Jakše, S. Pirc, A. Meden, B. Stanovnik, J. Svete, Tetrahedron 61 (2005) 3977–3990;
(b) W. Chen, X.H. Yuan, R. Li, W. Du, Y. Wu, L.S. Ding, Y.C. Chen, Adv. Synth. Catal. 348 (2006) 1818–1822.
[9] (a) W. Chen, W. Du, Y.Z. Duan, Y. Wu, S.Y. Yang, Y.C. Chen, Angew. Chem. Int. Ed. 46 (2007) 7667–7670;
(b) M.P. Sibi, D. Rane, L.M. Stanley, T. Soeta. Org. Lett. 10 (2008) 2971–2974;
(c) L. Pezdirc, B. Stanovnik, J. Svete, Z. Naturforsch 63b (2008) 375–383.
[10] (a) K. Tanaka, T. Kato, Y. Ukaji, K. Inomata, Heterocycles 80 (2010) 887–893;
(b) T. Kato, S. Fujinami, Y. Ukaji, K. Inomata, Chem. Lett. 37 (2008) 342–343;
(c) R. Huisgen, R. Weinberger, Tetrahedron Lett. 26 (1985) 5119–5122;
(d) H. Dorn, Tetrahedron Lett. 26 (1985) 5123–5126;
(e) S. Ogawa, T. Nishimine, E. Tokunaga, N. Shibata, Synthesis (2010) 3274–3281.
[11] (a) T.H. Chuang, K.B. Sharpless, Helv. Chem. Acta 83 (2000) 1734–1743;
(b) R. Shintani, T. Hayashi, J. Am. Chem. Soc. 128 (2006) 6330–6331;
(c) N.D. Shapiro, Y. Shi, F.D. Toste, J. Am. Chem. Soc. 131 (2009) 11654–11655;
(d) B. Qian, M.J. Fan, Y.X. Xie, L.Y. Wu, Y. Shi, Y.M. Liang, Synthesis (2009) 1689–1693;
(e) I. Panfil, Z. Urbańczyk-Lipkowska, K. Suwińska, J. Solecka, M. Chmielewski, Tetrahedron 58 (2002) 1199–1212;
(f) E.C. Taylor, D.M. Sobieray, Tetrahedron 47 (1991) 9599–9620;
(g) W. Duczek, H.J. Niclas, Tetrahedron Lett. 36 (1995) 2457–2458;
(h) T. Jin, F. Yang, Y. Yamamoto, Collect. Czech. Chem. Commun. 74 (2009) 957–972.
[12] For review see S. Chassaing, A. Alix, T. Boningari, K. Sani Souna Sido, M. Keller, P. Kuhn, B. Louis, J. Sommer, P. Pale, Synthesis, (2010) 1557–1567.
[13] (a) H.L. Jiang, W.M. Yue, H.H. Xiao, S.Z. Zhu, Tetrahedron 63 (2007) 2315–2319;
(b) Y. Xin, J.W. Zhao, J.W. Han, S.Z. Zhu, J. Fluorine Chem. 131 (2010) 642–645.
[14] (a) J.M. Indelicato, C.E. Pasini, J. Med. Chem. 31 (1988) 1227–1230;
(b) D.J. Steenkamp, D. Weldrick, H.S.C. Spies, Eur. J. Biochem. 242 (1996) 557–566.
[15] (a) H. Dorn, A. Otto, Chem. Ber. 101 (1968) 3287–3301;
(b) S. Manfred, W. Gerd, M. Uta, H. Dietmar, J. Prakt. Chem. 318 (1976) 946.