Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 40–44
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Synthesis and structure of trifluoromethylated arylhydrazones formed from coupling of 4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one with diazonium salts

Huiling Jiang, Shizheng Zhu *

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

Received 8 June 2007; received in revised form 21 August 2007; accepted 22 August 2007
Available online 31 August 2007

Abstract

A series of trifluoromethyl-containing arylhydrazones were prepared via a direct azo-coupling of (*E*)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one (**1**) with different aromatic diazonium salts. Furthermore, we also discussed the non-covalent interactions existing in the crystal structure of compound (*E*)-4,4,4-trifluoro-2-(2-(4-iodophenyl)hydrazono)-3-oxobutanal (**3c**) by the X-ray diffraction analysis.

Keywords: Trifluoromethylated arylhydrazones; Diazonium salts; X-ray analysis; Non-covalent interaction

1. Introduction

Diazonium salts could react readily with nucleophiles containing an amino group, which have been extensively researched and widely used for the preparation of molecules with significance for both academia and industry [1]. The most important and most studied are arene diazoamino compounds prepared by coupling of diazonium ions with primary and secondary aromatic amines for their special stability [2]. A common character of aromatic diazonium ions is the high electrophilicity of the β-nitrogen which effects easy azo-coupling with appropriate nucleophiles. Since molecular nitrogen is an extremely good leaving group, some arene diazonium salts lose it very easily. In general, the stability of arene diazonium salts is strongly influenced by the pH of the solution, the anions, trace amount of contaminants such as transition metal ions and the presence or absence of water [3]. Furthermore, the stability also depends on the electronic character of R to which nitrogen is attached. Enaminones, regarded as potential agrochemicals or intermediates in dye and pharmaceutical industries, are attracting more and more attentions and have been successfully utilized to be good building blocks in the synthesis of a wide range of heterocycles [4,5]. Due to the potential versatility of these reactions for the construction of heterocycles, the demand for exploiting them has increased over the last 20 years. Thus, several publications on nucleophilic coupling of enaminones with diazonium salts have appeared [6]. Moreover, it is well known that various diazonium salts could also couple with fluorine-containing 1,3-dicarbonyl compounds, including fluorinated 1,3-keto esters, 1,3-diketones and so on, yielding corresponding hydrazones that could be used to synthesize multifarious significant compounds such as fluorinated heterocycles with antifungal and anti-inflammatory activity [2,7]. However, to the best of our knowledge, the direct coupling of trifluoromethyl-containing α,β-unsaturated ketones with diazonium salts has never been reported. Our longstanding interest in the chemical transformation of fluorine-containing alkenes has stimulated us to address this issue [8]. Initially, we studied the direct coupling of (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one with phenyldiazonium salt aimed at the preparation of novel trifluoromethylated hydrazone. However, the reaction failed to give the expected product. Then we replaced ethoxy group by dimethylamino group to prepare compound (*E*)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one (**1**) in order to enhance the nucleophilicity toward diazonium compounds. Subsequent research

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

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.08.011

indicated that compound (**1**) could couple readily with diazotized aromatic amines, affording corresponding fluorinated hydrazones with good yields. Herein, we wish to report these results and discuss the non-covalent interactions existing in the crystal structure of trifluoromethyl-containing arylhydrazones.

2. Results and discussion

2.1. Synthesis of 4,4,4-trifluoro-3-oxo-2-(2-arylhydrazono)butanal

A cold solution of phenyldiazonium salt (10 mmol) was prepared by adding a solution of $NaNO_2$ (10 mmol into 5 mL H_2O) to a cold solution of anilin hydrochloride (10 mmol of aniline **2a** in 5 mL conc. HCl). The resulting solution of anilin diazonium salt was added dropwise to a mixture of compound (**1**) (10 mmol) in ethanol (50 mL) containing NaOH (40 mmol) at 0 °C. The reaction mixture was stirred for 1 h at the same temperature and the precipitate was filtered off and purified by column chromatography on silica gel to give compound (*E*)-4,4,4-trifluoro-3-oxo-2-(2-phenylhydrazono)butanal (**3a**) in 87% yield (Table 1, entry 1).

Under the same reaction conditions, a series of trifluoromethyl-containing arylhydrazones were prepared with moderate to good yields (Table 1). When aryldiazonium salts bearing an electron-withdrawing group such as nitro or halogen atom were employed, corresponding arylhydrazones were obtained with satisfied yields from 72 to 79% (Table 1, entries 2–5). However, when substrates bore an electron-donating group such as methyl or dimethylamino, the corresponding diazonium salts were very unstable in the reaction mixture and evolution of nitrogen gas was observed during the reaction process, thus only a small quantity of products were isolated in 30–42% yields (Table 1, entries 6 and 7). Moreover, when 1-naphthylamine **2j** was used to react with compound **1** under the same reaction conditions, the corresponding product **3j** was gotten in 57% yield (Table 1, entry 8).

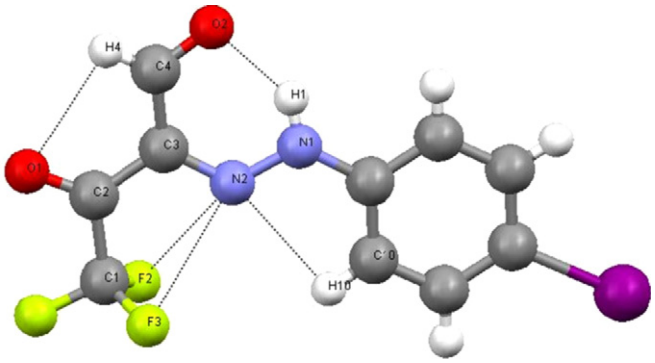


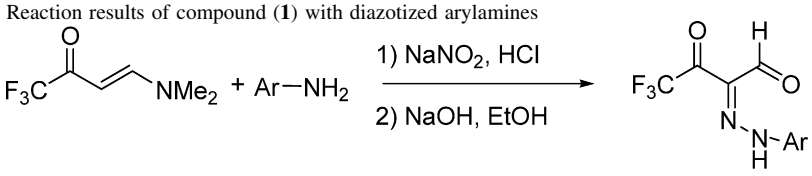
Fig. 1. Molecular structure of **3c**.

It was worthy to note that the product **3i** derived from 3-aminopyridine **2i** was unstable and observed to decompose at room temperature (Table 1, entry 9).

2.2. Single crystal structural analysis of compound (3c)

It is well known that non-covalent interactions play a significant role in determining the structures and properties of molecular assemblies in biology, chemistry and materials science [9]. During the past 10 years, a considerable amount of studies have concentrated on the intra- and intermolecular interactions existing in fluorinated molecules, such as hydrogen bonding (B···HY, B = Lewis base) and halogen bonding (B···XY, X = I, Br, Cl, F) [10]. In order to confirm the spatial configuration of trifluoromethylated arylhydrazones synthesized above, we subsequently analyzed the single crystal structure of compound (*E*)-4,4,4-trifluoro-2-(2-(4-iodophenyl)-hydrazono)-3-oxobutanal (**3c**) (Fig. 1, Table 2) and discussed the existent intra- and intermolecular non-covalent interactions (Figs. 1 and 2, Table 3). Just as our anticipation, a kind of strong intramolecular hydrogen bonding between oxygen atom of formyl and arylamino was observed ($d_{N1–H1\cdots O2} \cong 2.095$ Å and $\angle N1–H1–O2 \cong 125.2^{\circ}$). Furthermore, intramolecular hydrogen bonding between oxygen atom of trifluoroacetyl

Table 1
Reaction results of compound (**1**) with diazotized arylamines



Entry	1	2	Amine **2** (R=)	3	**3**[a] (yield, %)	mp (°)
1			**2a** (C_6H_5)		**3a** (87)	130–132
2			**2b** (C_6H_4Cl-*p*)		**3b** (79)	145–147
3			**2c** (C_6H_4I-*p*)		**3c** (78)	158–160
4			**2d** ($C_6H_4NO_2$-*p*)		**3d** (79)	98–100
5			**2e** (C_6H_4COOEt-*p*)		**3e** (72)	151–153
6			**2f** ($C_6H_4NMe_2$-*p*)		**3f** (42)	140–142
7			**2g** (C_6H_4Me-*p*)		**3g** (30)	156–158
8			**2h** ($C_{10}H_7$)		**3h** (57)	132–134
9			**2i** (C_5H_4N)		**3i** (44)	Oil

[a] Isolated yield.

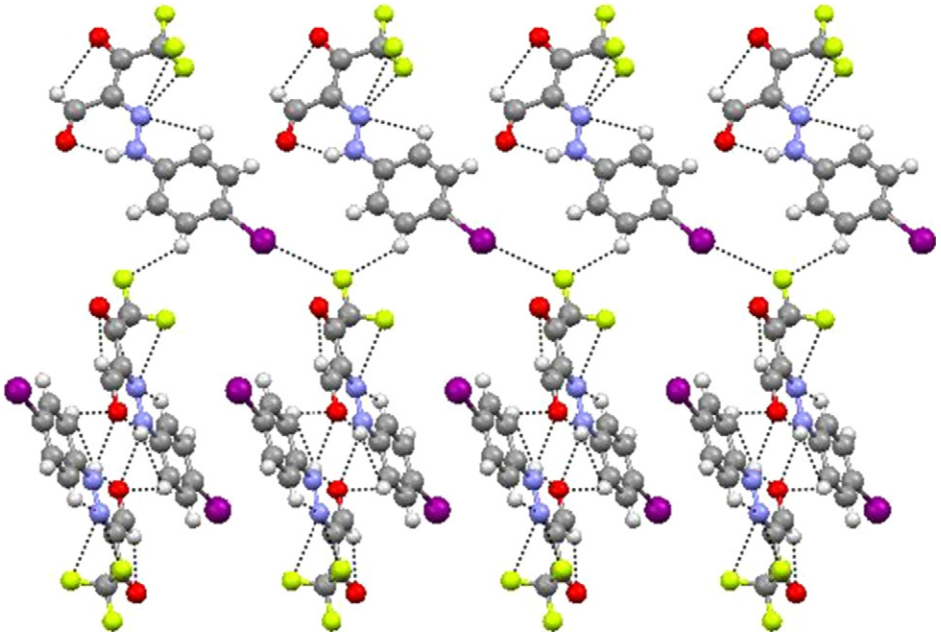


Fig. 2. Paking map of **3c**.

and hydrogen atom of formyl was also discovered. This intramolecular O···H distance is 2.591 Å, which is shorter than the sum of van der Waals radii of the contacting atoms by only ca. 0.129 Å and means a very weak intramolecular interaction. However, considering the torsional difficulty of the molecular framework, it is enough to show that intramolecular O···H interaction does exist. Both two hydrogen bonds greatly stabilized the spatial conformation of compound (**3c**). In addition, other weak intramolecular interactions, including a hydrogen bond C10–H10···N2 (≅2.493 Å, ≅97.9°) and two weak halogen bonds C1–F2···N2 (≅2.847 Å, ≅84.8°) and C1–F3···N2 (≅2.829 Å, ≅84.8°) also participate in stabilizing this conformation. Cooperation of all these weak interactions mentioned above, makes formyl and arylamino locate at the same side of the C=N bond; meanwhile, two C=O bonds and the C=N bond are observed to be coplanar, which could be confirmed by the sum of three angles ∠C4–C3–C2 (119.7°), ∠C4–C3–N2 (124.8°) and ∠C2–C3–N2 (115.5°).

Table 2
Selected bond length (Å) and angle (°) of **3c**

Bond length (Å)		Bond angle (°)	
C4–O2	1.217	∠O2–C4–C3	123.5
C4–C3	1.476	∠C4–C3–C2	119.7
C3–C2	1.459	∠C3–C2–O1	124.2
C2–O1	1.209	∠C4–C3–N2	124.8
C3–N2	1.337	∠C3–N2–N1	120.5
N2–N1	1.309	∠C2–C3–N2	115.5

Table 3
Selected non-covalent interaction data of **3c**

Distance (Å)		Angle (°)	
N1–H1···O2	2.095	∠N1–H1–O2	125.2
C4–H4···O1	2.591	∠C4–H4–O1	98.3
C10–H10···N2	2.493	∠C10–H10–N2	97.9
C1–F2···N2	2.847	∠C3–N2–F2	84.8
C1–F3···N2	2.829	∠C3–N2–F3	84.8
N3–H3···O4	2.545	∠N3–H3–O4	125.2
C16–H16···O4	2.580	∠C14–H14–O3	98.3
C1–F4···I	3.294	∠C1–F4–I	124.5
C1–F4···H7	2.588	∠C1–F4–H7	110.8

Besides intramolecular interactions, there also exist many intermolecular interactions in the crystal structure (Table 3), including a hydrogen bond N1–H1···O2 (≅2.545 Å, ≅125.2°) that makes molecules connect with each other to form dimers along the crystallographic *c* axis form. Furthermore, the dimeric structures are lined by two intermolecular interactions. One is a weak hydrogen bond existing between fluorine atom and hydrogen atom C6–H6···F1 (≅2.588 Å, ≅110.8°). It is worthy to note that the other non-covalent interaction is between fluorine atom and iodine atom along the crystallographic *a* axis form. The F···I distance is 3.294 Å, which is 0.156 Å shorter than the sum of their respective van der Waals radii and the C1–F1···I angle is 124.5°. All these intermolecular hydrogen and halogen bonds cooperate to stabilize the molecular assemblies.

3. Conclusion

In summary, we have described a novel method to prepare trifluoromethyl-containing arylhydrazones with moderate to good yields through a simple azo-coupling of (*E*)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one with various aromatic diazonium salts. The mild reaction conditions, straightforward procedure, synthetically useful products, high yielding and easy manipulation make this method potentially useful in organic synthesis. Furthermore, we also discussed the intra- and

intermolecular non-covalent interactions existing in the crystal structure of trifluoromethylated arylhydrazone. Further heterocyclization studies to develop new heterocycles bearing trifluoromethyl are underway in our laboratory.

4. Experimental

Melting points were measured on a Temp-Melt. apparatus and uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AM-300 or AM-400 instruments with Me_4Si and $CFCl_3$ as the internal standards, respectively. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low-resolution mass spectra (LRMS) or high-resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 or a Finnigan MAT-8430 instrument using the electron impact ionization technique (70 eV), respectively. Single crystal X-ray structure analysis was performed on a Bruker P4 instrument.

4.1. Experimental procedure

A solution of the aniline **2a** (1.28 g, 10 mmol) in a solution of conc. HCl (5 mL) was diazotized at 0 °C by slow addition of a solution of $NaNO_2$ (0.7 g, 10 mmol) in 5 mL H_2O. The solution of anilin diazonium salt was added dropwise to a mixture of compound (**1**) (1.67 g, 10 mmol) with NaOH (1.6 g, 40 mmol) and ethanol (50 mL) in ice-salt bath. The reaction mixture was stirred for 1 h at the same temperature, then TLC analysis showed that the reaction had finished. The resulting precipitate was filtered off. Purification by column chromatography on silica gel (hexane:AcOEt = 70:1) gave compound (*E*)-4,4,4-trifluoro-3-oxo-2-(2-phenylhydrazono)butanal (**3a**) in 87% yield.

4.1.1. (E)-4,4,4-Trifluoro-3-oxo-2-(2-phenylhydrazono)butanal (3a)

Yellow solid, mp: 130–132 °C. Yield: 87%. ^{1}H NMR ($CDCl_3$): δ 14.9 (1H, s, NH), 10.03 (1H, s, CHO), 7.53–7.45 (4H, m, Ph), 7.38–7.26 (1H, m, Ph). ^{19}F NMR ($CDCl_3$): −71.47 (s, CF_3). ^{13}C NMR ($CDCl_3$): δ 179.4 (q, $^{2}J_{C-F}$ = 34 Hz, C=O), 149.7 (CHO), 138.8 (C=N), 129.9 (C_6H_5), 125.7 (C_6H_5), 117.3 (C_6H_5), 116.9 (q, $^{1}J_{C-F}$ = 287 Hz, CF_3), 89.9 (C_6H_5). MS (*m/z*, %): 244 (M^+, 0.29), 242 (M^+–2H, 2.11), 215 (M^+–H–CO, 1.47), 121 (M^+–H–$PhNH_2$–CO, 0.28), 93 ($PhNH_2$, 9.11), 77 (Ph^+, 100), 69 (CF_3, 5.34). IR (cm^{-1}): 2923, 1682, 1605, 1195, 896. Anal. Calcd. for $C_{10}H_7F_3N_2O_2$ (%): C = 49.19, H = 2.89, N = 11.47; found C = 48.90, H = 3.03, N = 11.03.

4.1.2. (E)-2-(2-(4-Chlorophenyl)hydrazono)-4,4,4-trifluoro-3-oxobutanal (3b)

Red solid, mp: 145–147 °C. Yield: 79%. ^{1}H NMR ($CDCl_3$): δ 14.87 (1H, s, NH), 10.03 (1H, s, CHO), 7.45 (4H, s, Ph). ^{19}F NMR ($CDCl_3$): −71.50 (3F, s, CF_3). MS (*m/z*, %): 280 or 278 (M^+, 11.14 or 36.62), 243 (M^+–Cl, 6.60), 209 (M^+–CF_3, 2.93), 128 or 126 (*p*-$ClC_6H_4NH_2$, 29.56 or 81.63), 113 or 111 (*p*-$ClC_6H_4^+$, 32.15 or 100), 69 (CF_3, 26.91). IR (cm^{-1}): 2924, 1699, 1526, 1308, 1187, 1157, 897. Anal. Calcd. for $C_{10}H_6ClF_3N_2O_2$ (%): C = 43.11, H = 2.17, N = 10.05; found C = 43.16, H = 2.39, N = 10.05.

4.1.3. (E)-4,4,4-Trifluoro-2-(2-(4-iodophenyl)hydrazono)-3-oxobutanal (3c)

Red solid, mp: 158–160 °C. Yield: 78%. ^{1}H NMR ($CDCl_3$): δ 14.81 (1H, s, NH), 10.03 (1H, s, CHO), 7.80 (2H, d, $^{3}J_{HH}$ = 8 Hz, Ph), 7.30 (2H, d, $^{3}J_{HH}$ = 8 Hz, Ph). ^{19}F NMR ($CDCl_3$): −71.52 (3F, s, CF_3). MS (*m/z*, %): 370 (M^+, 100), 301 (M^+–CF_3, 2.66), 243 (M^+–I, 6.91), 218 (*p*-$IC_6H_4NH^+$, 63.55), 203 (*p*-$IC_6H_4^+$, 44.37), 69 (CF_3, 13.40). IR (cm^{-1}): 2924, 1697, 1645, 1527, 1154, 819. Anal. Calcd. for $C_{10}H_7F_3IN_2O_2$ (%): C = 32.46, H = 1.63, N = 7.57; found C = 32.69, H = 1.63, N = 7.58.

4.1.3.1. X-ray data. Formula $C_{10}H_6F_3IN_2O_2$; Mw = 370.07; triclinic, P-1; temperature 293(2) (K); a = 7.890(2) Å, b = 8.115(2) Å, c = 20.034(5) Å, α = 79.818(4)°, β = 83.897(5)°, γ = 86.060(5)°; V = 1253.8(6) $Å^3$; Z = 4, Dc = 1.961 Mg/m^3; absorption coefficient 2.587 mm^{-1}; $F(0\,0\,0)$ = 704; 1.04° < θ < 26.00°; reflections collected/unique 6796/4817 [R(int) = 0.1427]; absorption correction empirical; transmission 1.0000_{max}–0.73615_{min}; final R indices $R1$ = 0.0677, $wR2$ = 0.1680. The CCDC number is 649736.

4.1.4. (E)-4,4,4-Trifluoro-2-(2-(4-nitrophenyl)hydrazono)-3-oxobutanal (3d)

Red solid, mp: 98–100 °C. Yield: 79%. ^{1}H NMR ($CDCl_3$): δ 14.72 (1H, s, NH), 10.07 (1H, s, CHO), 8.20 (2H, d, $^{3}J_{HH}$ = 8 Hz, Ph), 7.62 (2H, d, $^{3}J_{HH}$ = 8 Hz, Ph). ^{19}F NMR ($CDCl_3$): −71.60 (3F, s, CF_3). MS (*m/z*, %): 289 (M^+, 27.06), 220 (M^+–CF_3, 4.45), 137 (*p*-$NO_2C_6H_4NH^+$, 44.56), 122 (*p*-$NO_2C_6H_4^+$, 100), 69 (CF_3, 44.69). IR (cm^{-1}): 3117, 1697, 1531, 1515, 1343, 1152, 861. Anal. Calcd. for $C_{10}H_6F_3N_3O_4$ (%): C = 41.54, H = 2.09, N = 14.53; found C = 41.77, H = 2.09, N = 14.87.

4.1.5. (E)-Ethyl 4-(2-(4,4,4-trifluoro-1,3-dioxobutan-2-ylidene)hydrazinyl)benzoate (3e)

Yellow solid, mp: 151–153 °C. Yield: 72%. ^{1}H NMR ($CDCl_3$): δ 14.79 (1H, s, NH), 10.06 (1H, s, CHO), 8.17 (2H, d, $^{3}J_{HH}$ = 9 Hz, Ph), 7.54 (2H, d, $^{3}J_{HH}$ = 9 Hz, Ph), 4.40 (2H, q, $^{3}J_{HH}$ = 7 Hz, CH_2), 1.41 (1H, t, $^{3}J_{HH}$ = 7 Hz, CH_3). ^{19}F NMR ($CDCl_3$): −71.56 (3F, s, CF_3). MS (*m/z*, %): 316 (M^+, 37.09), 220 (M^+–C_2H_5, 25.03), 271 (M^+–OC_2H_5, 20.52), 243 (M^+–CO–OC_2H_5, 8.01), 164 (*p*-$EtOOCC_6H_4NH^+$, 43.83), 149 (*p*-$EtOOCC_6H_4^+$, 100), 69 (CF_3, 23.72). IR (cm^{-1}): 2996, 1701, 1647, 1158, 856. Anal. Calcd. for $C_{13}H_{11}F_3N_3O_4$ (%): C = 49.38, H = 3.51, N = 8.86; found C = 49.27, H = 3.53, N = 8.75.

4.1.6. (E)-2-(2-(4-(Dimethylamino)phenyl)hydrazono)-4,4,4-trifluoro-3-oxobutanal (3f)

Red solid, mp: 140–142 °C. Yield: 42%. ^{1}H NMR ($CDCl_3$): δ 14.81 (1H, s, NH), 10.03 (1H, s, CHO), 7.80 (2H, d, $^{3}J_{HH}$ = 8 Hz, Ph), 7.30 (2H, d, $^{3}J_{HH}$ = 8 Hz, Ph). ^{19}F NMR ($CDCl_3$): −71.04 (3F, s, CF_3). MS (*m/z*, %): 287 (M^+, 30.13),

135 ($Me_2NC_6H_4^+$, 5.41), 69 (CF_3, 13.40). IR (cm^{-1}): 2916, 1681, 1604, 1193, 1149, 895. Anal. Calcd. for $C_{12}H_{12}F_3N_3O_2$ (%): C = 50.18, H = 4.21, N = 14.63; found C = 50.31, H = 4.17, N = 14.61.

4.1.7. (E)-4,4,4-Trifluoro-3-oxo-2-(2-p-tolylhydrazono)butanal (**3g**)

Yellow solid, mp: 156–158 °C. Yield: 30%. ^1H NMR ($CDCl_3$): δ 15.08 (1H, s, NH), 9.99 (1H, s, CHO), 7.75 (1H, d, $^3J_{HH}$ = 8 Hz, Ph), 7.30–7.19 (2H, m, Ph), 7.18–7.09 (1H, m, Ph), 2.39 (3H, s, Me). ^{19}F NMR ($CDCl_3$): −71.44 (3F, s, CF_3). MS (*m*/*z*, %): 258 (M^+, 23.49), 243 (M^+–Me, 4.49), 229 (M^+–H–CO, 5.16), 189 (M^+–CF_3, 1.35), 106 ($MeC_6H_4NH^+$, 30.99), 91 ($MeC_6H_4^+$, 100), 69 (CF_3, 5.40). IR (cm^{-1}): 2882, 1686, 1526, 1341, 1153, 896. Anal. Calcd. for $C_{11}H_9F_3N_2O_2$ (%): C = 51.17, H = 3.51, N = 10.85; found C = 51.28, H = 3.72, N = 10.76.

4.1.8. (E)-4,4,4-Trifluoro-2-(2-(naphthalen-1-yl)hydrazono)-3-oxobutanal (**3h**)

Yellow solid, mp: 132–134 °C. Yield: 57%. ^1H NMR ($CDCl_3$): δ 15.78 (1H, s, NH), 10.05 (1H, s, CHO), 7.96–7.80 (4H, m, Ph), 7.64–7.51 (3H, m, Ph). ^{19}F NMR ($CDCl_3$): −71.38 (3F, s, CF_3). MS (*m*/*z*, %): 294 (M^+, 18.89), 265 (M^+–H–CO, 4.46), 197 (M^+–CF_3–CO, 3.61), 142 ($C_{10}H_7NH^+$, 56.23), 127 ($C_{10}H_7^+$, 84.17), 115 ($C_9H_7^+$, 100), 69 (CF_3, 13.33). IR (cm^{-1}): 2924, 1690, 1533, 1507, 1188, 1156, 899. Anal. Calcd. for $C_{14}H_9F_3N_2O_2$ (%): C = 57.15, H = 3.08, N = 9.52; found C = 57.13, H = 3.16, N = 9.42.

4.1.9. (E)-4,4,4-Trifluoro-3-oxo-2-(2-(pyridin-3-yl)hydrazono)butanal (**3i**)

Yellow oil. Yield: 44%. ^1H NMR ($CDCl_3$): δ 10.03 (1H, s, CHO), 8.57 (1H, s, Ph), 8.33 (1H, d, $^3J_{HH}$ = 6 Hz, Ph), 7.45 (1H, dd, $^3J_{HH}$ = 6, 6 Hz, Ph), 7.22 (1H, dd, $^3J_{HH}$ = 6, 6 Hz, Ph). ^{19}F NMR ($CDCl_3$): −71.60 (3F, s, CF_3). ^{13}C NMR ($CDCl_3$): δ 187.4 (HC=O), 176.8 (–C=O, q, $^2J_{CF}$ = 31 Hz), 156.8 (C=N), 148.8 (Py.), 139.5 (Py.), 137.1 (Py.), 124.4 (Py.), 124.2 (Py.), 117.8 (CF_3, q, $^1J_{CF}$ = 288 Hz). MS (*m*/*z*, %): 245 (M^+, 8.23), 216 (M^+–H–CO, 1.43), 176 (M^+–CF_3, 1.10), 78 ($C_6H_4N^+$, 100), 69 (CF_3, 9.26). IR (cm^{-1}): 2932, 1668, 1586, 1186, 903. MS (*m*/*z*, %): 395 (M^+, 7.73), 366 (M^+–CO–H, 34.35), 337 (M^+–CO–NO, 12.25), 283 (M^+ + H–CO–NO–C_4H_7, 66.28), 180 ($C_6F_5CH_2$, 16.17), 77 ($C_6H_5^+$, 64.89), 55 ($C_4H_7^+$, 100). IR (cm^{-1}): 2946, 1725, 1522, 1503, 991. HRMS calcd. for $C_9H_6F_3N_3O_2$: 245.0412; found 245.0407.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NNSFC, No. 200532040) and the National Basic Research Program (No. 2007CB808000).

References

[1] (a) F.M. Abdelrazek, A.M.S. El-Din, A.E. Mekky, Tetrahedron 57 (2001) 1813–1817;
(b) R. Pellicciari, B. Natalini, B.M. Sadeghpour, M. Marinozzi, J.P. Snyder, B.L. Williamson, J.T. Kuethe, A. Padwa, J. Am. Chem. Soc. 118 (1996) 1–12.

[2] Y.V. Burgart, A.S. Fokin, O.G. Kuzueva, O.N. Chupakhin, V.I. Saloutin, J. Fluorine Chem. 92 (1998) 101–108.

[3] S. Patai (Ed.), The Chemistry of Diazonium and Diazo Groups, John Wiley & Sons, 1978.

[4] (a) M.H. Holschbach, D. Bier, W. Wutz, W. Sihver, M. Schüller, R.A. Olsson, Eur. J. Med. Chem. 40 (2005) 421–437;
(b) K. Tomita, Y. Tsuzuki, K. Shibamori, M. Tashima, F. Kajikawa, Y. Sato, S. Kashimoto, K. Chiba, K. Hino, J. Med. Chem. 45 (2002) 5564–5575.

[5] (a) N.A. Al-Awadi, M.H. Elnagdi, Y.A. Ibrahim, K. Kaul, A. Kumar, Tetrahedron 57 (2001) 1609–1614;
(b) S. Al-Mousawi, M.M. Abdelkhalik, E. John, M.H. Elnagdi, J. Heterocyclic Chem. 40 (2003) 689–695;
(c) F. Al-Omran, M.M.A. Khalik, A. Abou-Elkhair, M.H. Elnagdi, Synthesis 1997 (1997) 91–94.

[6] (a) S.A.S. Ghozlan, I.A. Abdelhamid, H.M. Gaber, M.H. Elnagdi, J. Heterocyclic Chem. 42 (2005) 1185–1189;
(b) M.A. Al-Shiekh, A.M.S. El-Din, E.A. Hafez, M.H. Elnagdi, J. Heterocyclic Chem. 41 (2004) 647–654;
(c) S. Al-Mousawi, M.M. Abdel-Khalik, S. El-Sherbiny, E. John, M.H. Elnagdi, J. Heterocyclic Chem. 38 (2001) 949–953.

[7] (a) O.G. Khudina, E.V. Shchegol'kov, Y.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;
(b) G. Urmila, S. Vineeta, K. Vineeta, C. Sanjana, Indian J. Heterocyclic Chem. 14 (2005) 265–266;
(c) G. Urmila, S. Vineeta, K. Vineeta, C. Sanjana, Indian J. Heterocyclic Chem. 12 (2002) 139–142;
(d) A.F. Shivanyuk, L.S. Kudryavtseva, M.O. Lozinskii, V.M. Neplyuev, Y.A. Fialkov, A.G. Bratolyubova, Ukrainskii Khimicheskii Zhurnal 47 (1981) 1078–1085 (Russian edition).

[8] (a) H.L. Jiang, S.Z. Zhu, Synlett 9 (2006) 1343–1346;
(b) Q.L. Chu, L.P. Song, G.F. Jin, S.Z. Zhu, J. Fluorine Chem. 108 (2001) 51–56;
(c) L.P. Song, Q.L. Chu, S.Z. Zhu, J. Fluorine Chem. 107 (2000) 107–112;
(d) Q.L. Chu, Y.L. Wang, S.Z. Zhu, Syn. Commun. 30 (2000) 677–687.

[9] G.R. Desiraju, T. Steiner (Eds.), The Weak Hydrogen Bond in Structural Chemistry and Biology. IUCr Monographs on Crystallography, vol. IX, Oxford University Press, New York, 2001.

[10] (a) M. Weck, R. Dunn, K. Matsumoto, G.W. Coates, E.B. Lobkovsky, R.H. Grubbs, Angew. Chem. Int. Ed. 38 (1999) 2741–2745;
(b) M.L. Renak, G.P. Bartholomew, S. Wang, P.J. Ricatto, R.J. Lachicotte, G.C. Bazan, J. Am. Chem. Soc. 121 (1999) 7787–7799;
(c) F. Ponzini, R. Zagha, K. Hardcastle, J.S. Siegel, Angew. Chem. Int. Ed. 39 (2000) 2323–2325;
(d) J.A.C. Clyburne, T. Hamilton, H.A. Jenkins, Cryst. Eng. 4 (2001) 1–9;
(e) M.R. Haneline, M. Tsunoda, F.P. Gabbai, J. Am. Chem. Soc. 124 (2002) 3737–3742;
(f) V.R. Vangala, A. Nangia, V.M. Lynch, Chem. Commun. (2002) 1304–1305;
(g) K. Müller-Dethlefs, P. Hobza, Chem. Rev. 100 (2000) 143–167.