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An efficient and highly stereoselective synthesis of novel trifluoromethylated *trans*-dihydrofuro[2,3-*c*]pyrazoles using arsonium ylides

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ABSTRACT

An efficient approach of highly stereoselective synthesis of novel trifluoromethylated *trans*-4,5-dihydrofuro[2,3-*c*]pyrazoles has been described. Arsonium bromides **1** reacted smoothly with the electron-deficient alkenes (*Z*)-4-aryl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrozol-5(4*H*)-ones **2** to give products *trans*-dihydrofuro[2,3-*c*]pyrazoles **3** with high stereoselectivity and in good to excellent yields, using CH_2Cl_2 as solvent and K_2CO_3 as base.

1. Introduction

Pyrazoles, including their fluorinated derivatives, have demonstrated a broad spectrum of biological activities and represented an important structural class in pharmaceuticals and agrochemicals.[1–4] Much work has been done on the design and the synthesis of complex pyrazoles, giving particular relevance to the functionalization of the scaffold in different regions[5] and in particular, to the synthesis of ring-condensed structures.[6] Indeed, the preparation of pyrazole-fused ring derivatives is very important and challenging from the synthetic point of view.

Dihydrofurans belong to an important class of compounds, which show a wide range of biological activities and form the core structure of many natural products.[7] Among them, 2,3-dihydrofurans have gained importance as structural features of natural products, such as aflatoxins,[8] natural germination inhibitor (+)-erigeronic acid A,[9] monomers for the synthesis of biodegradable polymers (e.g., naturally occurring polyethers),[10] and other useful synthetic intermediates.[7c]

In the course of investigations concerning the exploitation of novel bioactive molecules, the usual design was to combine the known pharmacophore into a single molecule as a central scaffold.[3,6] Therefore, the integration of a pyrazole ring with CF_3-group and a substituted dihydrofuran ring in one molecule could lead to the novel trifluoromethylated dihydrofuropyrazoles, which may show a modified biological activity. The literature survey showed that there are no reports of CF_3-substituted dihydrofuro[2,3-*c*]pyrazoles and their stereoselective synthesis. Furthermore, arsonium ylides are known to show their high reactivity and high diastereoselectivity in heterocycle and carbocycle synthesis in the reactions with the electron-deficient alkenes.[11] Thus, in our continuing efforts of synthesizing new fluorinated compounds with promising biological properties,[12] herein, we reported an efficient synthetic method for the synthesis of novel trifluoromethylated *trans*-4,5-dihydrofuro[2,3-*c*]pyrazoles **3** via the high stereoselective reaction of arsonium bromides **1** and the electron-deficient alkenes (*Z*)-4-aryl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrozol-5(4*H*)-ones **2** in CH_2Cl_2 under reflux, using K_2CO_3 as base (Scheme 1).

2. Results and discussion

Choosing an appropriate solvent is of crucial importance for the successful organic reactions. To search the optimal solvent, the

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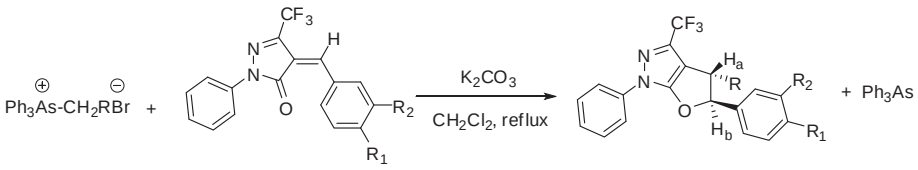


1

R = CO_2Me, **1A**
R = COMe, **1B**
R = COPh, **1C**
R = furoyl, **1D**

2

R_1 = Me, R_2 = H **2a**
R_1 = H, R_2 = H **2b**
R_1 = Cl, R_2 = H **2c**
R_1 = Br, R_2 = H **2d**
R_1 = F, R_2 = H **2e**
R_1 = H, R_2 = Cl **2f**

3

Scheme 1. Synthesis of trifluoromethylated *trans*-4,5-dihydrofuro[2,3-*c*]pyrazoles **3**.

reaction of arsonium bromide **1A** with (*Z*)-4-benzylidene-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5(4*H*)-one **2b** was examined using 1,2-dimethoxyethane (DME), acetonitrile, tetrahydrofuran (THF), chloroform, and dichloromethane (DCM) as solvents, respectively, at room temperature to synthesize **3Ab**. The results were summarized in Table 1 and the reaction in DCM resulted in the product with a higher yield (entry 5).

Table 1
Optimization for the synthesis of **3Ab**

Entry	Solvent	Base	Ratio (**2b**/**1A**/base)	Temp (°C)	Time (h)	Isolated yield (%)
1	CH_3CN	K_2CO_3	1:1.2:2	rt	48	30
2	$CHCl_3$	K_2CO_3	1:1.2:2	rt	48	32
3	THF	K_2CO_3	1:1.2:2	rt	48	16
4	DME	K_2CO_3	1:1.2:2	rt	48	24
5	CH_2Cl_2	K_2CO_3	1:1.2:2	rt	48	58
6	CH_2Cl_2	Cs_2CO_3	1:1.2:2	rt	48	43
7	CH_2Cl_2	$KF{\cdot}2H_2O$	1:1.2:2	rt	48	20
8	CH_2Cl_2	K_2CO_3	1:1.8:2	rt	12	64
9	CH_2Cl_2	K_2CO_3	1:1.2:3	rt	12	48
10	CH_2Cl_2	K_2CO_3	1:1.8:3	rt	12	50
11	**CH_2Cl_2**	**K_2CO_3**	**1:1.8:2**	**40**	**36**	**82**

Bold value represents optimized reaction conditions.

Other reaction conditions, including reaction temperature, base and the molar ratio of **2b** to **1A** and base, were then investigated. A series of experiments revealed that 1.0 equiv of **2b**, 1.8 equiv of **1A**, and 2.0 equiv of base were sufficient for the synthesis of **3Ab** and K_2CO_3 was found to be the best base among those tested (entries 5–11). And the optimal result was obtained when the reaction was performed in DCM under reflux, whereby the yield of **3Ab** reached 82% (entry 11).

Having established the optimized conditions for the CF_3-substituted ring-fused dihydrofuropyrazoles synthesis, we intended to determine its scope with respect to arsonium bromides **1** and the fluorinated electron-deficient alkenes **2**. A series of trifluoromethylated *trans*-4,5-dihydrofuro[2,3-*c*]pyrazoles **3** were synthesized under the identical conditions. All the reactions proceeded smoothly to afford the products in good to excellent yields (Table 2). Still, it was observed that the reaction was significantly affected by electronic effects of the substituents on pyrazole substrates. The alkenes **2** with electronically poor aryl group at the α position to olefinic bond of pyrazole substrates showed higher activity than those bearing electronically neutral substituents. For example, the reactions of compounds **2** with R_1 substituents as halogen completed faster than those reactions of compounds **2** with R_1 substituent as methyl group or hydrogen atom (Table 2, entries 1, 2 vs 3–6). Moreover, steric effects have been found to play an important role in this reaction. It was noted that arsonium bromides **1** with R group as methyl or methoxy rendered the reaction faster and gave better yields than those with the aryl or heteroaryl groups (entries 1, 7 vs 8, 9).

The structures of the products were identified by ^1H NMR, ^{13}C NMR, ^{19}F NMR, MS, and IR. It was found that their ^1H NMR spectra were all in the similar manner. The coupling constant between H_a and H_b on the fused dihydrofuran was 5.5–6.5 Hz, which confirmed the trans configuration of compounds **3**.[13] An X-ray diffraction

Table 2
Synthesis of trifluoromethylated *trans*-4,5-dihydrofuro[2,3-*c*]pyrazoles **3**[a]

Entry	R	Arsonium bromides **1**	R_1	R_2	The fluorinated electron-deficient alkenes **2**	Time (h)	Product **3**	Isolated yield (%)
1	CO_2Me	**1A**	CH_3	H	**2a**	24	**3Aa**	78
2	CO_2Me	**1A**	H	H	**2b**	36	**3Ab**	82
3	CO_2Me	**1A**	Cl	H	**2c**	10	**3Ac**	81
4	CO_2Me	**1A**	Br	H	**2d**	6	**3Ad**	85
5	CO_2Me	**1A**	F	H	**2e**	15	**3Ae**	84
6	CO_2Me	**1A**	H	Cl	**2f**	20	**3Af**	80
7	COMe	**1B**	CH_3	H	**2a**	20	**3Ba**	80
8	COPh	**1C**	CH_3	H	**2a**	28	**3Ca**	73
9	Furoyl	**1D**	CH_3	H	**2a**	36	**3Da**	70
10	COMe	**1B**	Cl	H	**2c**	11	**3Bc**	82
11	COPh	**1C**	Cl	H	**2c**	19	**3Cc**	76
12	Furoyl	**1D**	Cl	H	**2c**	27	**3Dc**	82
13	COMe	**1B**	Br	H	**2d**	10	**3Bd**	89
14	COMe	**1B**	F	H	**2e**	12	**3Be**	85
15	COMe	**1C**	H	H	**2b**	16	**3Bb**	83
16	COPh	**1C**	H	H	**2b**	21	**3Cb**	75
17	COPh	**1C**	Br	H	**2d**	20	**3Cd**	80
18	COPh	**1C**	H	Cl	**2f**	20	**3Cf**	73

[a] Conditions: fluorinated electron-deficient alkenes **2** 1.0 mmol, arsonium bromide **1** 1.8 equiv, K_2CO_3 2.0 equiv, CH_2Cl_2 5 mL, reflux.

method was used to further elucidate the structures of **3**. It was proved that the 3D perspective view of the crystal structure of **3Ac** was unequivocally the trans-isomer by X-ray crystallographic analysis (Fig. 1).[14]

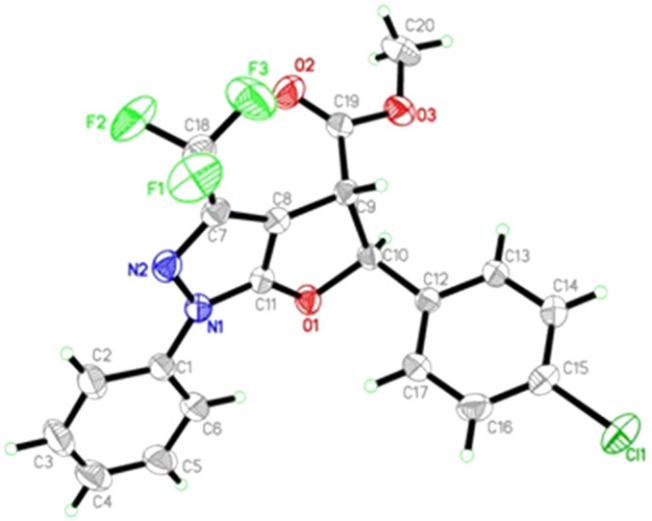


Fig. 1. X-ray structure of compound **3Ac**.

Based on the published results,[15,16] a plausible mechanism of this reaction was hypothesized as shown in Scheme 2. Firstly, the Michael addition of arsonium ylide **4**, derived from arsonium salt **1** with K_2CO_3 as base, to compound **2**, can potentially lead to two possible intermediates **5** or **6**. Due to the steric repulsion between two bulky groups (R and Ar) in the intermediate of **5**, the intermediate **6** should be more stable and favored. However, the size of R group could still influence the stability of the intermediate **6**. The bigger size of R group could lead to the more intense repulsion between R and CF_3-group in the conformation of **6**. As a result, arsonium bromide **1** with small R group as methyl or methoxy gave the higher yield in shorter time as shown in Table 2. The intramolecular ring closure of the intermediate **6** provided transient *trans*-cyclopropane **7** as a typical donor–acceptor cyclopropane.[15] The donor group Ar served to stabilize the partial positive charge on zwitterion **8** that was created as the C_1–C_2 bond cleavage of **7**. Subsequently, the oxygen anion in intermediate **9**, formed through enolation of **8**, attacked the carbon cation stereoselectively to give the final cyclized product *trans*-isomer **3**. cis-Isomer was not obtained due to the repulsion interaction between R and Ar groups, which are both situated on the same side of the dihydrofuran ring in the structure of **11**. Furthermore, the reason that compound **2** more readily underwent reaction when R_1 or R_2 was the electron-withdrawing group was attributed to that the carbon cation in zwitterion **8** was more electrophilic and thus showed higher activity owing to the electron-withdrawing effect.

3. Conclusion

In summary, an efficient method for the stereoselective synthesis of new CF_3-substituted *trans*-dihydrofuro[2,3-*c*]pyrazoles was first developed. This protocol provided a new avenue for developing pyrazole-fused derivatives. The best result was obtained with arsonium bromides, (*Z*)-4-aryl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrozol-5(4*H*)-ones, K_2CO_3 base, and DCM solvent under reflux. A possible reaction pathway is proposed, which proceeds through a tandem Michael addition, cyclopropanation, the opening of three-membered ring, and stereoselective cyclization.

4. Experimental

4.1. General information

All reagents and solvents were purchased from commercial sources and used without further purification, except that arsonium bromides **1**[13c] and (*Z*)-1-phenyl-3-(trifluoromethyl)-1*H*-pyrozol-5(4*H*)-one derivatives **2**[17] were prepared according to the known literature. Melting points were recorded on a WRS-1 instrument and uncorrected. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker DRX-500 MHz spectrometer. All chemical shifts are reported in parts per million downfield (positive) of the standard: C_6F_6 for ^{19}F, TMS for ^1H and ^{13}C NMR spectra. IR spectra were obtained on an AVATAR370 FT-IR spectrometer. Elemental analysis was performed on an Elementar Vario EL-III instrument. LRMS was run on an Agilent LC/MSD SL mass spectrometer. HRMS was run on an APEXIII 7.0 TESLA FTMS mass spectrometer. X-ray analysis was performed on a Bruker Smart Apex2 CCD spectrometer. Compounds previously described in the literature were characterized by comparing their ^1H NMR spectra to the published data. All yields reported in this publication refer to isolated ones of compounds and their purity was determined by ^1H NMR.

4.2. General procedure for preparation of compound 2

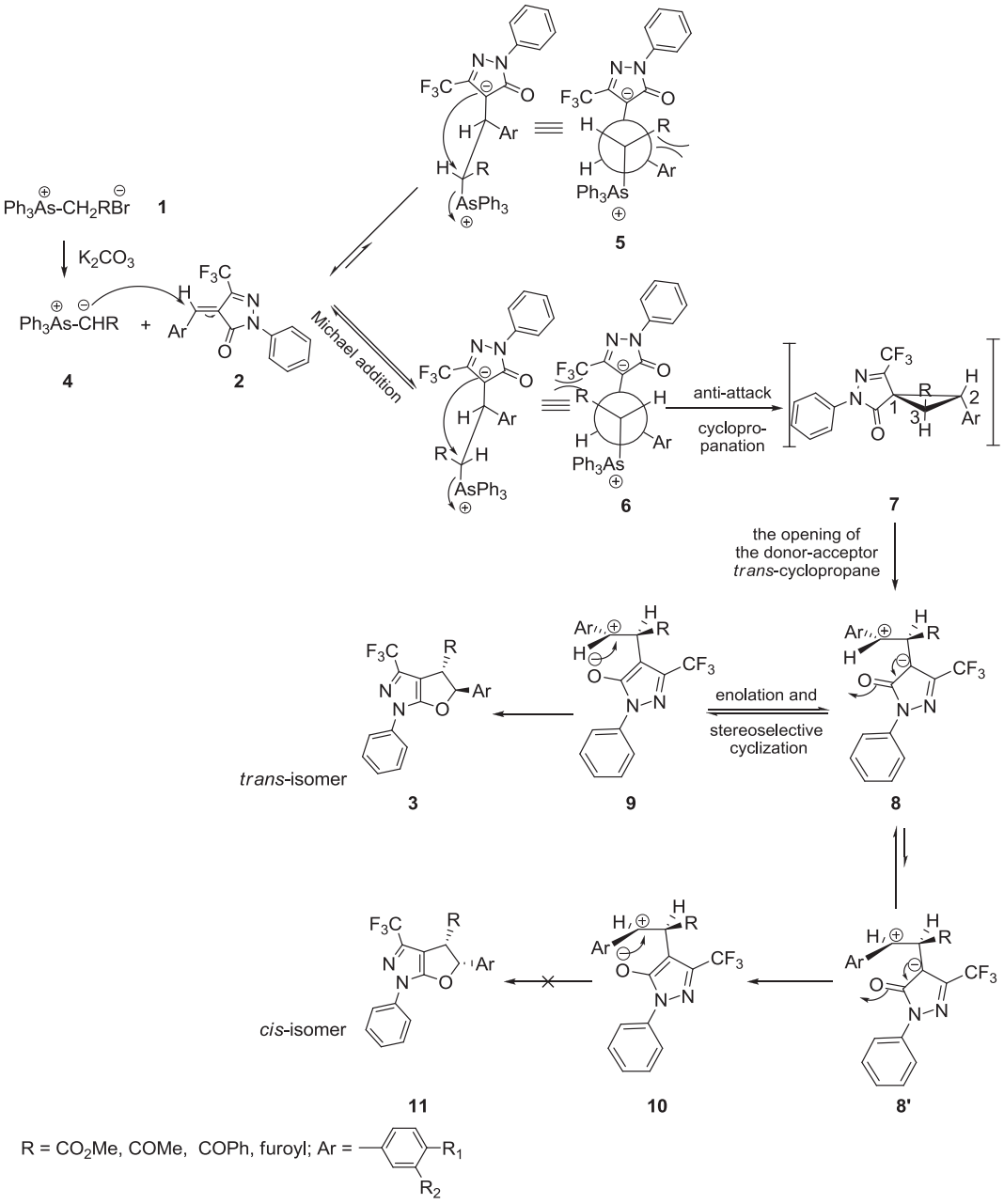
Ethyl 4,4,4-trifluoroacetoacetate 9.20 g (0.05 mol) and phenylhydrazine 5.40 g (0.05 mol) were mixed and refluxed in AcOH (30 mL) for 6 h. Then the mixture was cooled to room temperature. After filtration, the residue was recrystallized from ethanol to give the pure 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one 10.23 g, yield 90%.

Aromatic aldehyde (0.012 mol) and 1-phenyl-3-(trifluoromethyl)-2-pyrazolin-5-one 2.28 g (0.010 mol) were heated in an oil-bath at 160–170 °C for 4–6 h. The reaction mixture was cooled, triturated in ethyl ether (20 mL) and filtered off. The colored filter cake was recrystallized to afford the corresponding (*Z*)-4-aryl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrozol-5(4*H*)-ones **2** as colored crystals. The *Z* configuration of compound **2** was confirmed by single-crystal X-ray diffraction analysis.[14]

*4.2.1. (Z)-4-(4-Methylbenzylidene)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2a**).* Red solid; yield: 67%; mp: 156.3–157.8 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 2.47 (s, 3H), 7.27–7.29 (m, 1H), 7.35 (d, J=8.0 Hz, 2H), 7.44–7.47 (m, 2H), 7.73 (s, 1H), 7.91 (d, J=8.0 Hz, 2H), 8.46 (d, J=8.0 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −63.37 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.2, 150.2, 146.6, 140.8 (q, $^2J_{C-F}$=37.5 Hz), 137.6, 135.0, 130.2, 129.9, 129.0, 126.1, 120.4, 119.9 (q, $^1J_{C-F}$=270.0 Hz), 119.8, 22.1 ppm; IR (KBr): ν 3042, 1693, 1589, 1547, 1497, 1432, 1334, 1317, 1178, 1128, 1113, 959, 817, 754 cm^{-1}; MS (EI) m/z (%): 331 (M^+); Anal. Calcd for $C_{18}H_{13}F_3N_2O$: C 65.45; H 3.97; found: C 65.50; H 3.90.

*4.2.2. (Z)-4-Benzylidene-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2b**).* Red solid; yield: 59%; mp: 132.1–133.9 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.26–7.30 (m, 1H), 7.44–7.47 (m, 2H), 7.54–7.57 (m, 2H), 7.62–7.65 (m, 1H), 7.77 (s, 1H), 7.91 (d, J=7.5 Hz, 2H), 8.53 (d, J=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −63.45 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.1, 150.7, 140.8 (q, $^2J_{C-F}$=37.5 Hz), 137.5, 134.6, 132.5, 129.0, 127.9, 126.3, 123.1, 121.5, 120.0 (q, $^1J_{C-F}$=262.5 Hz), 119.9 ppm; IR (KBr): ν 1699, 1608, 1596, 1499, 1433, 1319, 1176, 1149, 1118, 959, 753, 688 cm^{-1}; MS (EI) m/z (%): 317 (M^+); Anal. Calcd for $C_{17}H_{11}F_3N_2O$: C, 54.56; H, 3.51; found: C 54.61; H 3.57.

*4.2.3. (Z)-4-(4-Chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2c**).* Red solid; yield: 78%; mp: 166.8–167.9 °C (lit.[17]: 166.0–167.0 °C); ^1H NMR (500 MHz, $CDCl_3$):



Scheme 2. Proposed mechanism for the formation of product **3**.

δ 7.27–7.30 (m, 1H), 7.44–7.51 (m, 4H), 7.69 (s, 1H), 7.89 (d, J=7.5 Hz, 2H), 8.49 (d, J=8.5 Hz, 2H) ppm.

*4.2.4. (Z)-4-(4-Bromobenzylidene)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2d**).* Red solid; yield: 80%; mp: 177.7–179.0 °C (lit.[17]: 157.0–159.0 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.30 (m, 1H), 7.44–7.47 (m, 2H), 7.66–7.68 (m, 3H), 7.88 (d, J=7.5 Hz, 2H), 8.40 (d, J=8.5 Hz, 2H) ppm.

*4.2.5. (Z)-4-(4-Fluorobenzylidene)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2e**).* Red solid; yield: 48%; mp: 112.4–113.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (m, 2H), 7.28 (m, 1H), 7.46 (m, 2H), 7.69 (s, 1H), 7.90 (d, J=8.0 Hz, 2H), 8.60–8.62 (m, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −63.46 (s, CF_3), −100.09 (m, Ar–F) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.3 (d, $^1J_{C-F}$=250.0 Hz), 161.1, 148.9, 140.4 (q, $^2J_{C-F}$=37.5 Hz), 137.6, 137.4, 129.0, 126.3, 121.4 (q, $^1J_{C-F}$=275.0 Hz), 119.8, 118.7, 116.4 (d, $^2J_{C-F}$=21.2 Hz) ppm; IR (KBr): ν 1698, 1596, 1556, 1498, 1434, 1322, 1245, 1174, 1162, 1137, 1119, 1096, 961, 850, 753 cm^{-1}; MS (EI) m/z (%): 334 (M^+); Anal. Calcd for $C_{17}H_{10}F_4N_2O$: C 61.08; H 3.02; found: C 61.10; H 3.05.

*4.2.6. (Z)-4-(3-Chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2f**).* Red solid; yield: 43%; mp: 163.3–164.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24–7.28 (m, 1H), 7.42–7.49 (m, 4H), 7.66 (s, 1H), 7.86–7.88 (m, 2H), 8.46–8.78 (m, 2H) ppm ^{19}F NMR (470 MHz, $CDCl_3$) δ: −63.58 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.0, 148.8, 140.5 (q, $^2J_{C-F}$=37.5 Hz), 137.3, 135.7, 132.3, 131.2, 130.1, 129.0, 126.4, 121.9, 120.0 (q, $^1J_{C-F}$=275.0 Hz), 119.9, 118.6 ppm; IR (KBr): ν 1700, 1610, 1590, 1570, 1489, 1431, 1305, 1252, 1200, 1149, 1004, 965, 876, 754 cm^{-1}; MS (EI) m/z (%): 350 (M^+); Anal. Calcd for $C_{17}H_{10}ClF_3N_2O$: C 58.22; H 2.87; found: C 58.24; H 2.88.

4.3. General procedure for preparation of compound 3

To 5 mL DCM, arsonium bromide **1** (1.8 mmol), (*Z*)-4-aryl-1-phenyl-3-(trifluoromethyl)-1*H*-pyrozol-5(4*H*)-one derivative **2** (1.0 mmol), and K_2CO_3 (2.0 mmol) were added. The mixture was stirred under reflux. After the completion of the reaction (monitored by TLC), the solid was filtered off and the filtrate was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel, using petroleum ether (60–90 °C)/ethyl acetate as eluent to give the desired product **3**.

*4.3.1. trans-Methyl 1-phenyl-5-p-tolyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazole-4-carboxylate (**3Aa**).* White solid; yield: 78%; mp: 76.3–77.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.82 (s, 3H), 4.31 (d, *J*=6.5 Hz, 1H), 6.76 (d, *J*=6.5 Hz, 1H), 7.23–7.45 (m, 7H), 7.80 (d, *J*=8.0 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.80 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 160.0, 140.0, 137.4, 136.2 (q, $^2J_{C-F}$=38.8 Hz), 135.2, 130.0, 126.1, 129.4, 127.0, 125.9, 122.7 (q, $^1J_{C-F}$=267.5 Hz), 119.6, 100.1, 52.9, 51.0, 21.3 ppm; IR (KBr): ν 2950, 2938, 1734, 1601, 1543, 1523, 1485, 1457, 1407, 1250, 1220, 1176, 1127, 943, 805, 754 cm^{-1}; MS (EI) *m*/*z* (%): 402 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{21}H_{17}F_3N_2O_3$ [$(M+Na)^+$]: 425.1099; found: 425.1084.

*4.3.2. trans-Methyl 1,5-diphenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazole-4-carboxylate (**3Ab**).* White solid; yield: 82%; mp: 70.1–70.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.84 (s, 3H), 4.33 (d, *J*=6.0 Hz, 1H), 6.82 (d, *J*=6.0 Hz, 1H), 7.28–7.31 (m, 1H), 7.47–7.46 (m, 7H), 7.81–7.83 (m, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.80 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 160.0, 138.3, 137.3, 136.2 (q, $^2J_{C-F}$=38.8 Hz), 129.5, 129.2, 127.0, 125.8, 121.3 (q, $^1J_{C-F}$=267.5 Hz), 119.6, 100.0, 52.9, 51.0 ppm; IR (KBr): ν 2958, 2941, 1730, 1601, 1545, 1486, 1459, 1408, 1253, 1180, 1126, 948, 832, 753 cm^{-1}; MS (EI) *m*/*z* (%): 388 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{15}F_3N_2O_3$ [$(M+Na)^+$]: 411.0944; found: 411.0927.

*4.3.3. trans-Methyl 5-(4-chlorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazole-4-carboxylate (**3Ac**).* White solid; yield: 81%; mp: 93.7–94.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 3H), 4.28 (d, *J*=6.5 Hz, 1H), 6.80 (d, *J*=6.5 Hz, 1H), 7.31–7.49 (m, 7H), 7.81 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.85 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 160.0, 137.2, 136.8, 136.2 (q, $^2J_{C-F}$=38.8 Hz), 129.5, 127.2, 120.6 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 98.9, 53.2, 51.0 ppm; IR (KBr): ν 2956, 1724, 1603, 1543, 1489, 1459, 1409, 1251, 1178, 1137, 1126, 1091, 951, 809, 756 cm^{-1}; MS (EI) *m*/*z* (%): 422 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{14}ClF_3N_2O_3$ [$(M+Na)^+$]: 445.0551; found: 445.0547.

*4.3.4. trans-Methyl 5-(4-bromophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazole-4-carboxylate (**3Ad**).* White solid; yield: 85%; mp: 96.5–97.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 4.25 (d, *J*=6.5 Hz, 1H), 6.75 (d, *J*=6.5 Hz, 1H), 7.26–7.32 (m, 3H), 7.43–7.46 (m, 2H), 7.56 (d, *J*=8.5 Hz, 2H), 7.78 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.84 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 159.5, 137.2, 136.2 (q, $^2J_{C-F}$=38.8 Hz), 132.3, 129.5, 127.4, 127.1, 123.7, 120.4 (q, $^1J_{C-F}$=267.5 Hz), 98.9, 53.0, 50.9 ppm; IR (KBr): ν 2956, 1725, 1602, 1543, 1488, 1459, 1250, 1178, 1138, 1126, 1111, 950, 834, 757 cm^{-1}; MS (EI) *m*/*z* (%): 466 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{14}BrF_3N_2O_2$ [$(M+Na)^+$]: 489.0015; found: 489.0032.

*4.3.5. trans-Methyl 5-(4-fluorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazole-4-carboxylate (**3Ae**).* White solid; yield: 84%; mp: 93.0–94.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 4.31 (d, *J*=6.5 Hz, 1H), 6.80 (d, *J*=6.5 Hz, 1H), 7.15 (m, 2H), 7.30–7.36 (m, 1H), 7.44–7.48 (m, 4H), 7.81–7.83 (m, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.84 (s, CF_3), −111.43 (m, Ar–F) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 163.2 (d, $^1J_{C-F}$=247.5 Hz), 159.5, 137.3, 136.2 (q, $^2J_{C-F}$=38.8 Hz), 134.2, 129.5, 127.4, 127.0, 120.6 (q, $^1J_{C-F}$=267.5 Hz), 118.7, 116.0, 99.2, 53.0, 51.0 ppm; IR (KBr): ν 2964, 1727, 1601, 1545, 1512, 1485, 1456, 1408, 1253, 1223, 1180, 1130, 1039, 950, 840, 756 cm^{-1}; MS (EI) *m*/*z* (%): 406 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{14}F_4N_2O_3$ [$(M+Na)^+$]: 429.0825; found: 429.0833.

*4.3.6. trans-Methyl 5-(3-chlorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazole-4-carboxylate (**3Af**).* White solid; yield: 80%; mp: 94.5–95.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3H), 4.27 (d, *J*=6.5 Hz, 1H), 6.77 (d, *J*=6.5 Hz, 1H), 7.29–7.47 (m, 7H), 7.80 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.84 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 159.5, 140.2, 137.2, 136.2 (q, $^2J_{C-F}$=38.8 Hz), 135.1, 130.5, 129.5, 127.1, 125.8, 123.8, 120.6 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 98.6, 53.0, 51.0 ppm; IR (KBr): ν 2955, 1742, 1600, 1542, 1486, 1457, 1408, 1261, 1209, 1178, 1132, 1042, 950, 788, 759 cm^{-1}; MS (EI) *m*/*z* (%): 422 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{14}ClF_3N_2O_3$ [$(M+Na)^+$]: 445.0551; found: 445.0547.

*4.3.7. (trans-1-Phenyl-5-p-tolyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)ethanone (**3Ba**).* White solid; yield: 80%; mp: 95.9–96.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 2.37 (s, 3H), 4.32 (d, *J*=5.5 Hz, 1H), 6.77 (d, *J*=5.5 Hz, 1H), 7.21–7.30 (m, 5H), 7.42–7.45 (m, 2H), 7.80 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.78 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.8, 160.0, 139.6. 137.3, 135.7 (q, $^2J_{C-F}$=40.0 Hz), 135.5, 129.8, 129.4, 127.0, 125.8, 120.8 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 99.3, 58.5, 28.8, 21.3 ppm; IR (KBr): ν 2937, 2922, 1709, 1601, 1540, 1484, 1457, 1407, 1273, 1179, 1113, 1040, 950, 810, 754 cm^{-1}; MS (EI) *m*/*z* (%): 386 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{21}H_{17}F_3N_2O_2$ [$(M+Na)^+$]: 409.1123; found: 409.1135.

*4.3.8. (trans-1,5-Diphenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)ethanone (**3Bb**).* White solid; yield: 83%; mp: 97.2–97.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 4.34 (d, *J*=5.5 Hz, 1H), 6.84 (d, *J*=5.5 Hz, 1H), 7.29–7.31 (m, 1H), 7.39–7.46 (m, 7H), 7.82 (d, *J*=8.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.71 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.7, 160.0, 138.5. 137.3, 135.7 (q, $^2J_{C-F}$=38.8 Hz), 129.5, 129.2, 127.1, 125.6, 120.8 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 99.0, 58.6, 28.8 ppm; IR (KBr): ν 2910, 1718, 1598, 1552, 1488, 1453, 1400, 1271, 1186, 1125, 1041, 947, 765, 699 cm^{-1}; MS (EI) *m*/*z* (%): 372 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{15}F_3N_2O_2$ [$(M+Na)^+$]: 395.0972; found: 395.0978.

*4.3.9. (trans-5-(4-Chlorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)ethanone (**3Bc**).* White solid; yield: 82%; mp: 111.0–113.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 4.27 (d, *J*=5.5 Hz, 1H), 6.82 (d, *J*=5.5 Hz, 1H), 7.29–7.32 (m, 3H), 7.38 (d, *J*=8.0 Hz, 2H), 7.43–7.46 (m, 2H), 7.80 (d, *J*=8.0 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.68 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.4, 160.0, 137.2. 137.0, 135.7 (q, $^2J_{C-F}$=38.8 Hz), 135.3, 129.5, 129.4 127.2, 127.1, 120.7 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 98.0, 58.6, 28.7 ppm; IR (KBr): ν 2931, 1714, 1600, 1543, 1492, 1458, 1405, 1273, 1185, 1116, 1089, 961, 819, 758 cm^{-1}; MS (EI) *m*/*z* (%): 406 (M^+); HRMS (ESI) *m*/*z* calcd for $C_{20}H_{14}ClF_3N_2O_2$ [$(M+Na)^+$]: 429.0591; found: 429.0588.

*4.3.10. (trans-5-(4-Bromophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)ethanone (**3Bd**).* White solid; yield: 89%; mp: 112.7–113.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 (s, 3H), 4.27 (d, *J*=5.5 Hz, 1H), 6.83 (d, *J*=5.5 Hz, 1H), 7.26–7.35 (m, 3H), 7.46–7.49 (m, 2H), 7.57 (d, *J*=8.0 Hz, 2H), 7.82 (d, *J*=8.0 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.68 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.4, 160.0, 137.5, 137.2, 135.7 (q, $^2J_{C-F}$=38.8 Hz), 132.4, 129.5, 127.3, 127.2, 123.5, 120.7 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 98.0, 58.5, 28.8 ppm; IR (KBr): ν 2921, 1707,

1600, 1540, 1487, 1458, 1406, 1269, 1242, 1193, 1125, 1040, 960, 805, 755 cm^{-1}; MS (EI) *m/z* (%): 450 (M^+); HRMS (ESI) *m/z* calcd for $C_{20}H_{14}BrF_3N_2O_2$ [$(M+Na)^+$]: 473.0078; found: 473.0083.

*4.3.11. (trans-5-(4-Fluorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)ethanone (**3Be**).* White solid; yield: 85%; mp: 117.1–119.3 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 4.28 (d, *J*=5.5 Hz, 1H), 6.81 (d, *J*=5.5 Hz, 1H), 7.08–7.12 (m, 2H), 7.29–7.46 (m, 5H), 7.79 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.68 (s, CF_3), −111.43 (m, Ar–F) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.5, 163.2 (d, $^1J_{C-F}$=247.5 Hz), 159.8, 137.2, 135.7 (q, $^2J_{C-F}$=38.8 Hz), 134.4, 129.5, 127.7, 127.2, 120.0 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 116.3, 98.3, 58.6, 28.8 ppm; IR (KBr): ν 2922, 1714, 1602, 1536, 1512, 1483, 1456, 1408, 1271, 1244, 1181, 1133, 1109, 1039, 960, 835, 757 cm^{-1}; MS (EI) *m/z* (%): 390 (M^+); HRMS (ESI) *m/z* calcd for $C_{20}H_{14}F_4N_2O_2$ [$(M+Na)^+$]: 413.0877; found: 413.0884.

*4.3.12. (trans-1-Phenyl-5-p-tolyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)(phenyl)methanone (**3Ca**).* Yellow oil; yield: 73%; ^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (s, 3H), 5.32 (d, *J*=6.0 Hz, 1H), 6.78 (d, *J*=6.0 Hz, 1H), 7.26–7.34 (m, 5H), 7.44–7.51 (m, 4H), 7.65 (m, 1H), 7.83 (d, *J*=7.5 Hz, 2H), 7.93 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.75 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8, 150.4, 138.2 (q, $^2J_{C-F}$=38.8 Hz), 137.5, 137.2, 135.4, 134.1, 133.1, 132.2, 129.4, 129.1, 129.0, 128.8, 128.3, 127.3, 121.5, 121.1 (q, $^1J_{C-F}$=267.5 Hz), 96.2, 53.2, 20.9 ppm; IR (KBr): ν 2923, 1702, 1682, 1597, 1513, 1480, 1456, 1449, 1218, 1135, 1019, 974, 808, 761 cm^{-1}; MS (EI) *m/z* (%): 448 (M^+); HRMS (ESI) *m/z* calcd for $C_{26}H_{19}F_3N_2O_2$ [$(M+Na)^+$]: 471.1298; found: 471.1278.

*4.3.13. (trans-1,5-Diphenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)(phenyl)methanone (**3Cb**).* Yellow oil; yield: 75%; ^1H NMR (500 MHz, $CDCl_3$): δ 5.34 (d, *J*=6.0 Hz, 1H), 6.86 (d, *J*=6.0 Hz, 1H), 7.30–7.34 (m, 1H), 7.44–7.52 (m, 9H), 7.66 (m, 1H), 7.85 (m, 2H), 7.95 (m, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.16 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.2, 160.3, 138.4, 137.4, 135.8 (q, $^2J_{C-F}$=38.8 Hz), 135.5, 134.2, 129.7, 129.4, 129.3, 129.0, 128.9, 127.0, 126.0, 120.5 (q, $^1J_{C-F}$=267.5 Hz), 118.9, 100.8, 53.2 ppm; MS (EI) *m/z* (%): 434 (M^+); IR (KBr): ν 1685, 1598, 1579, 1541, 1524, 1454, 1407, 1272, 1219, 1172, 1136, 1041, 1007, 760 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{17}F_3N_2O_2$ [$(M+Na)^+$]: 457.1134; found: 457.1134.

*4.3.14. (trans-5-(4-Chlorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)(phenyl)methanone (**3Cc**).* Yellow oil; yield: 76%; ^1H NMR (500 MHz, $CDCl_3$): δ 5.28 (d, *J*=6.0 Hz, 1H), 6.84 (d, *J*=6.0 Hz, 1H), 7.31–7.38 (m, 3H), 7.43–7.53 (m, 6H), 7.67 (m, 1H), 7.82 (d, *J*=7.8 Hz, 2H), 7.94 (d, *J*=7.8 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.17 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.9, 160.0, 143.3, 138.0, 137.2 (q, $^2J_{C-F}$=38.8 Hz), 136.4, 135.5, 135.4, 134.4, 133.4, 133.0, 129.6, 129.3, 128.7, 128.5, 127.4, 122.4, 120.4 (q, $^1J_{C-F}$=267.5 Hz), 118.8, 99.8, 53.1 ppm; IR (KBr): ν 1685, 1671, 1597, 1481, 1456, 1448, 1215, 1133, 1013, 965, 824, 757 cm^{-1}; MS (EI) *m/z* (%): 468 (M^+); HRMS (ESI) *m/z* calcd for $C_{25}H_{16}ClF_3N_2O_2$ [$(M+Na)^+$]: 491.0751; found: 491.0747.

*4.3.15. (trans-5-(4-Bromophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)(phenyl)methanone (**3Cd**).* Yellow oil; yield: 80%; ^1H NMR (500 MHz, $CDCl_3$): δ 5.28 (d, *J*=6.5 Hz, 1H), 6.84 (d, *J*=6.5 Hz, 1H), 7.29–7.34 (m, 3H), 7.46–7.53 (m, 5H), 7.58–7.60 (m, 1H), 7.65–7.68 (m, 1H), 7.83 (d, *J*=7.5 Hz, 2H), 7.94 (d, *J*=7.5 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.15 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.9, 160.0, 137.4, 137.3, 135.6, 135.2 (q, $^2J_{C-F}$=38.8 Hz), 134.4, 132.4, 129.5, 129.0, 127.6, 127.1, 123.7, 120.3 (q, $^1J_{C-F}$=267.5 Hz), 118.9, 99.8, 53.1 ppm; IR (KBr): ν 1681, 1658, 1605, 1542, 1485, 1457, 1446, 1265, 1219, 1120, 1009, 979, 819, 757 cm^{-1}; MS (EI) *m/z* (%): 512 (M^+); HRMS (ESI) *m/z* calcd for $C_{25}H_{16}BrF_3N_2O_2$ [$(M+Na)^+$]: 535.0245; found: 535.0238.

*4.3.16. (trans-5-(3-Chlorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)(phenyl)methanone (**3Cf**).* Yellow oil; yield: 73%; ^1H NMR (500 MHz, $CDCl_3$): δ 5.27 (d, *J*=6.5 Hz, 1H), 6.84 (d, *J*=6.5 Hz, 1H), 7.24–7.51 (m, 9H), 7.63–7.65 (m, 1H), 7.81 (d, *J*=7.8 Hz, 2H), 7.94 (d, *J*=7.4 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.17 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.0, 160.0, 143.3, 138.0, 137.2, 136.3 (q, $^2J_{C-F}$=38.8 Hz), 135.6, 135.4, 134.3, 133.4, 133.0, 129.6, 129.3, 128.7, 128.5, 127.4, 122.4, 120.4 (q, CF_3, $^1J_{C-F}$=267.5 Hz), 118.8, 99.8, 53.1 ppm; IR (KBr): ν 1697, 1598, 1541, 1484, 1456, 1384, 1230, 1180, 1121, 1040, 950, 904, 757 cm^{-1}; MS (EI) *m/z* (%): 468 (M^+); HRMS (ESI) *m/z* calcd for $C_{25}H_{16}ClF_3N_2O_2$ [$(M+Na)^+$]: 491.0751; found: 491.0747.

*4.3.17. trans-(Furan-2-yl)(5-(p-tolyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)methanone (**3Da**).* Colorless oil; yield: 70%; ^1H NMR (500 MHz, $CDCl_3$): δ 2.38 (s, 3H), 5.11 (d, *J*=6.0 Hz, 1H), 6.58–6.59 (m, 1H), 6.82 (d, *J*=6.0 Hz, 1H), 7.22–7.32 (m, 6H), 7.43 (m, 2H), 7.64 (m, 1H), 7.80 (d, *J*=8.0 Hz, 2H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): −62.83 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 184.4, 160.2, 151.5, 147.8, 139.7, 137.4, 135.7 (q, $^2J_{C-F}$=38.8 Hz), 135.4, 129.8, 129.3, 126.9, 126.1, 120.5 (q, $^1J_{C-F}$=267.5 Hz), 119.4, 118.9, 113.0, 100.2, 53.5, 21.3 ppm; IR (KBr): ν 2923, 1679, 1600, 1568, 1542, 1489, 1461, 1406, 1269, 1183, 1123, 1041, 1022, 814, 758 cm^{-1}; MS (EI) *m/z* (%): 438 (M^+); HRMS (ESI) *m/z* calcd for $C_{24}H_{17}F_3N_2O_3$ [$(M+Na)^+$]: 461.1089; found: 461.1077.

*4.3.18. trans-(Furan-2-yl)(5-(4-chlorophenyl)-1-phenyl-3-(trifluoromethyl)-4,5-dihydro-1H-furo[2,3-c]pyrazol-4-yl)methanone (**3Dc**).* Yellow oil; yield: 82%; ^1H NMR (500 MHz, $CDCl_3$): δ 5.07 (d, *J*=6.5 Hz, 1H), 6.80 (d, *J*=6.5 Hz, 1H), 7.14–7.16 (m, 1H), 7.28–7.46 (m, 7H), 7.66–7.67 (m, 1H), 7.76–7.81 (m, 3H) ppm; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.25 (s, CF_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5, 160.2, 142.5, 137.3, 136.8, 136.4, 135.8 (q, $^2J_{C-F}$=38.8 Hz), 135.6, 133.8, 129.5, 128.7, 127.5, 127.2, 123.7, 120.5 (q, $^1J_{C-F}$=267.5 Hz), 118.9, 100, 54.6 ppm; IR (KBr): ν 1661, 1600, 1542, 1486, 1457, 1411, 1268, 1218, 1192, 1123, 1041, 969, 861, 762 cm^{-1}; MS (EI) *m/z* (%): 458 (M^+); HRMS (ESI) *m/z* calcd for $C_{23}H_{14}ClF_3N_2O_3$ [$(M+Na)^+$]: 481.0527; found: 481.0537.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.01.030. These data include MOL files and InChiKeys of the most important compounds described in this article.

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14. CCDC-822551 (**3Ac**) and CCDC-797937 (**2a**) contain all crystallographic details of this publication and are available free of charge at or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk. Unit cell parameters (**3Ac**): *a*: 7.935(2) Å; *b*: 15.050(4) Å; *c*: 16.356(4) Å; α: 90.000; β: 103.254(3); γ: 90.000; space group: *P*2(1)/*c*. Unit cell parameters (**2a**): *a*: 21.66(3) Å; *b*: 9.463(15) Å; *c*: 17.19(3) Å; α: 90.000; β: 116.564(19); γ: 90.000; space group: *C*2/*c*.
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