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The $Rh_2(OAc)_4$-catalyzed reactions of 3-trifluoromethyl-4-diazopyrazolinones with aromatic compounds

Huafang Fan [a,b], Zhenhua Zhang [b], Xinjin Li [b], Jingwei Zhao [b], Jinming Gao [a,*], Shizheng Zhu [b,*]

[a] Shaanxi Engineering Center of Bioresource Chemistry and Sustainable Utilization, College of Science, Northwest A & F University, Yangling 712100, Shaanxi, China
[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

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ABSTRACT

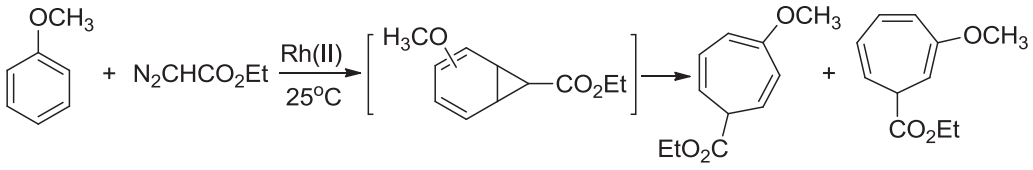
The C–H insertion reactions of 3-trifluoromethyl-4-diazopyrazolinones **1** with benzene and its derivatives catalyzed by $Rh_2(OAc)_4$ were studied. It was found that the Csp^2-H insertion products were obtained in good yields when anisole or xylene etc. was used, while the aromatic compounds with electronic-withdrawing groups, such as fluorobenzene, chlorobenzene, and benzonitrile, did not react with the diazo compounds **1**.

1. Introduction

Diazo compounds are notably versatile building blocks in organic synthesis.[1] Thermally or photochemically induced expulsion of molecular nitrogen provides access to carbene chemistry[2] and transition-metal-catalyzed dediazoniation typically generates short-lived metal-carbene complexes.[3] Several metals have been reported to mediate this transformation effectively, and the appropriate selection of ligands has permitted excellent selectivities.[4] In general, rhodium(II)-catalyzed decomposition of alkyl diazoacetates in a large access of aromatic substrate at room temperature produces kinetically controlled cycloheptatrienyl esters in excellent yield (Scheme 1).[5]

To our best knowledge, the functionalization of aromatic Csp^2-H bonds with this strategy has been somewhat developed for intramolecular processes, while the intermolecular version is still quite rare.[6] It is well known that the introduction of fluorine atoms into a molecule can often bring some unpredictable influence on its bioactivity.[7] However, there are few reports on the synthesis of fluorine substituted pyrazole compounds.[8]

In our group, we have recently successfully prepared 3-trifluoromethyl-4-diazopyrazolinones **1** using perfluoroalkane sulfonyl azide as diazo-transfer reagents and reported a facile synthesis of novel CF_3-substituted ring-fused furo [2,3-*c*] pyrazoles through $Rh_2(OAc)_4$ catalyzed [3+2] cycloaddition of 4-diazo-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5(4*H*)-one with aromatic



Scheme 1. Rhodium(II)-catalyzed the reaction of alkyl diazoacetates with aromatic substrate.

alkynes (Scheme 2).[9] Herein, we report the reactions of 3-trifluoromethyl-4-diazo pyrazolinones **1** with aromatic compounds catalyzed by $Rh_2(OAc)_4$.

* Corresponding authors. E-mail address: zhusz@mail.sioc.ac.cn (S. Zhu).

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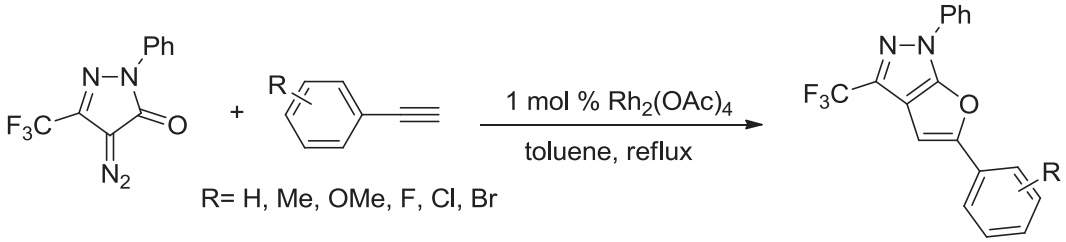
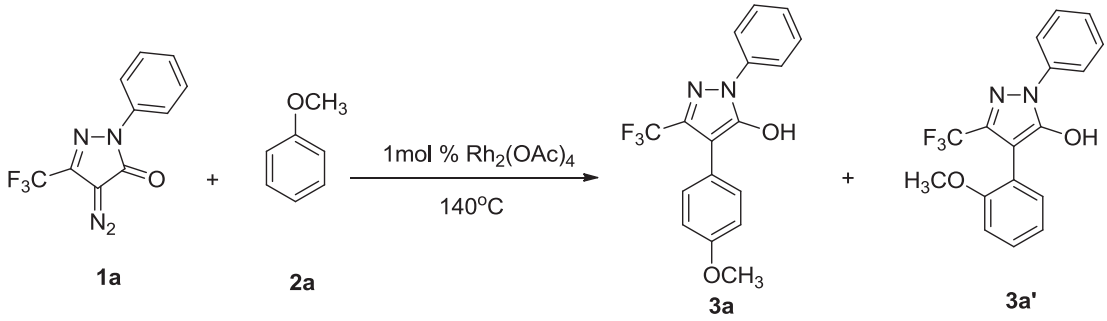


Scheme 2. Reactions of 4-diazo-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one with aromatic alkynes catalyzed by $Rh_2(OAc)_4$.

2. Results and discussions

The reaction of 3-trifluoromethyl-4-diazo pyrazolinone **1a** (254 mg, 1 mmol) and $Rh_2(OAc)_4$ (4 mg, 0.01 mmol) in excess of anisole **2a** (5.0 mL) at 140 °C was firstly investigated (Scheme 3). The reaction was complete within 3 h monitored by TLC, the products **3a** and **3a′** were isolated by column chromatography as colorless solids and got in yields of 63% and 13%, respectively. The products identified by NMR and mass spectra. The ^{19}F NMR spectra of the products **3a** and **3a′** showed a single peak at −60.87 ppm and −59.96 ppm respectively different from the spectrum of the starting diazo compound **1a** (−63.9 ppm). The ^{1}H NMR spectra of the products showed



Scheme 3. The reaction of 3-trifluoromethyl-4-diazo pyrazolinone with anisole catalyzed by $Rh_2(OAc)_4$.

that the typical peaks were observed at δ 7.25 and 6.91 ppm, which indicated to be a *para*-methoxyl-compound **3a**. Meanwhile, a higher-order spectrum indicated an *ortho*-isomer compound **3a′**. Mass spectra showed that the molecular weight of **3a** and **3a′** are both 334.

After that, we screened conditions for the reactions of 3-trifluoromethyl-4-diazo pyrazolinone **1a** with other aromatic compounds and the results were listed in Table 1. It was not a surprise that no reaction took place without $Rh_2(OAc)_4$ (Table 1, **entry 1**). After different catalysts were examined, 1 mol % $Rh_2(OAc)_4$ was effective to catalyze this reaction. It was also noticed that the product was obtained in a low yield when the substrate was benzene (Table 1, **entry 6**). What is more, the aromatic compounds with an electronic-withdrawing group, such as fluorobenzene, chlorobenzene or benzonitrile, did not react with the diazo compound **1a**.

Table 1
Reactions of **1a** with aromatic compounds under different conditions[a]

Entry	Substrate	Cat. (mol %)	Temp	Time (h)	Yield (%) [b]
1	Anisole	—	140 °C	8	N.R
2	Anisole	$Rh_2(OAc)_4$ (1)	100 °C	16	56 and11
3	Anisole	$Rh_2(OAc)_4$ (1)	140 °C	3	63 and 13
4	Anisole	CuI (10)	140 °C	15	N.R
5	Anisole	$Cu(OTf)_2$(1)	140 °C	8	N.R
6	Benzene	$Rh_2(OAc)_4$ (1)	Reflux	20	2
7	Fluorobenzene	$Rh_2(OAc)_4$ (1)	140 °C	3	N.R
8	Chlorobenzene	$Rh_2(OAc)_4$ (1)	140 °C	3	N.R
9	Benzonitrile	$Rh_2(OAc)_4$ (1)	140 °C	3	N.R

[a] Reactions were carried out with **1a** (1 mmol), **2** (5 mL) and $Rh_2(OAc)_4$ (4 mg).
[b] Isolated yields by column chromatography.

With the optimized reaction condition in hand, a series of CF_3-substituted pyrazolol derivatives (**3a**–**3k**) were obtained in moderate to good yields. The results were summarized in Table 2. The results showed that both *para*- and *ortho*-substituted products were formed when anisole was participated in the reaction. When xylene or 1,3,5-trimethylbenzene was employed, only one product was isolated in a moderate yield (Table 2, **entries 2**–**4**). However, the yield was lower when the aromatic compound was toluene.

All of the novel CF_3-substituted pyrazolols were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and mass spectrometry. For the compound **3e**, it was further confirmed by X-ray single crystal diffraction analysis (Fig. 1). It disclosed that the dihedral angle between pyrazole ring and benzene ring is 83.73 °C, and that is 86.22 °C between pyrazole ring and the methyl substituted benzene ring.

In our previous study, the reaction of 3-trifluoromethyl-4-diazopyrazolinones with aromatic terminal alkynes catalyzed by $Rh_2(OAc)_4$ in toluene indeed afford the corresponding products and no C–H products were found (Scheme 2).[9] It was indicated that the metal-carbene intermediate was much easier to occur [3+2] cycloaddition reaction. According to the above results, it was indicated that the reaction activity of metal-carbene intermediate was [3+2] cycloaddition > Csp^2-H insertion.

It was also found that the reaction of **1a** with pyridine or its derivatives did not give corresponding products or C–H insertion products (Scheme 4).

Under the same reaction conditions, 3-trifluoromethyl-4-diazopyrazolinethione **4**, which was obtained by the reaction of **1** with Lawesson's, did not react with toluene, anisole or xylene and **4** was recovered quantitatively in all these reactions (Scheme 5).

In our studies, we also noticed that in case of cyclohexene with compound **1a**, no corresponding cyclopropanation products were isolated, which indicated the resulting metal-carbene intermediate did not add to the carbon–carbon double bond (Scheme 6).

Considering all the results, neither cyclopropanation compounds nor cycloheptatriene derivatives were found in the reaction of 1 with benzene derivatives. We proposed a possible mechanism

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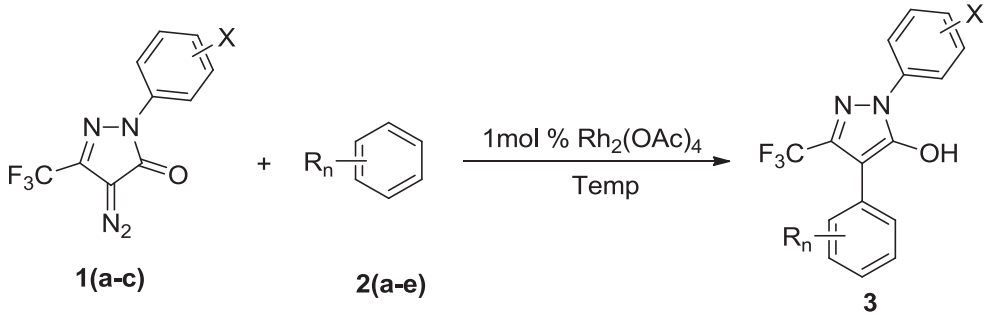
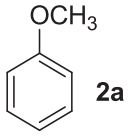
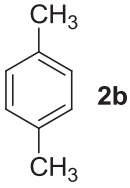
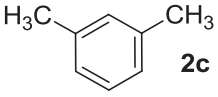
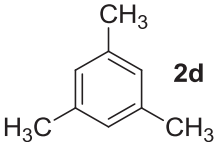
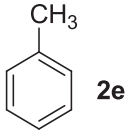
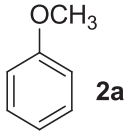
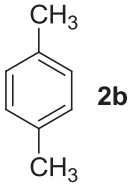
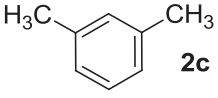
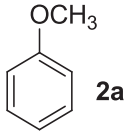
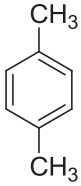
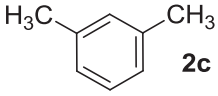
Table 2
Reactions of 3-trifluoromethyl-4-diazopyrazolinones with aromatic compounds catalyzed by $Rh_2(OAc)_4$



Entry	X **1**	**2**	Temp (°C)	Time (h)	**3**	Yield (%)[a]
1	H **1a**	 **2a**	140	3	**3a**(*p*-) and **3a′**(*o*-)	63 and 13
2	H **1a**	 **2b**	Reflux	4	**3b**	56
3	H **1a**	 **2c**	Reflux	4	**3c**(*p*-)	61
4	H **1a**	 **2d**	140	9	**3d**	45
5	H **1a**	 **2e**	Reflux	22	**3e**	15
6	*p*-CH_3 **1b**	 **2a**	140	3	**3f**(*p*-) and **3f′**(*o*-)	65 and 17
7	*p*-CH_3 **1b**	 **2b**	Reflux	4	**3g**	68
8	*p*-CH_3 **1b**	 **2c**	Reflux	4	**3h**(*p*-)	71
9	*p*-Cl **1c**	 **2a**	140	3	**3i**(*p*-) and **3i′** (*o*-)	71 and 7

(*continued on next page*)

Table 2 (*continued*)

Entry	X **1**	**2**	Temp (°C)	Time (h)	**3**	Yield (%)[a]
10	*p*-Cl **1c**	 **2b**	Reflux	4	**3j**	69
11	*p*-Cl **1c**	 **2c**	Reflux	4	**3k**(*p*-)	63

[a] Isolated yields by column chromatography.

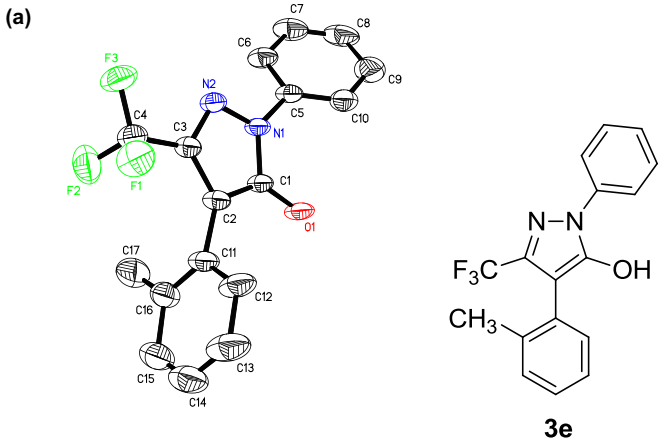


Fig. 1. (a) The structure of compound **3e**. (b) Packing map of molecular **3e**.

for the formation of CF_3-substituted pyrazolols on the basis of previous investigations.[10] A π- or σ-complex was postulated as the intermediate for these reactions. That is to say, the cyclopropane product was not formed in this reaction. However, a π- or σ-complex may be formed first, by the donor-acceptor interaction between the aromatic compounds and the electron-deficient diazo compounds. The π- or σ-complex is followed by 1,2-H shift to give the final product 3-trifluoromethyl-4-aryl-pyrazolol (Scheme 7).

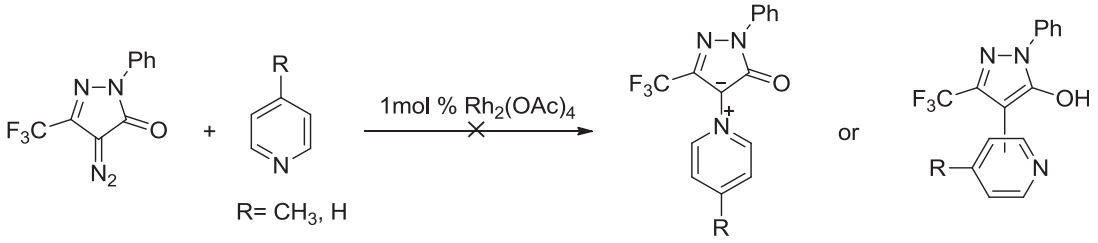
3. Conclusions

In summary, we developed a convenient method for preparation of CF_3-substituted pyrazolols through C—H insertion reactions of diazocarbonyl compounds with electronic-rich benzene derivatives catalyzed by $Rh_2(OAc)_4$. However, the aromatic compounds with an electronic-withdrawing group, such as fluorobenzene, chlorobenzene or benzonitrile, did not react with diazo compounds **1**.

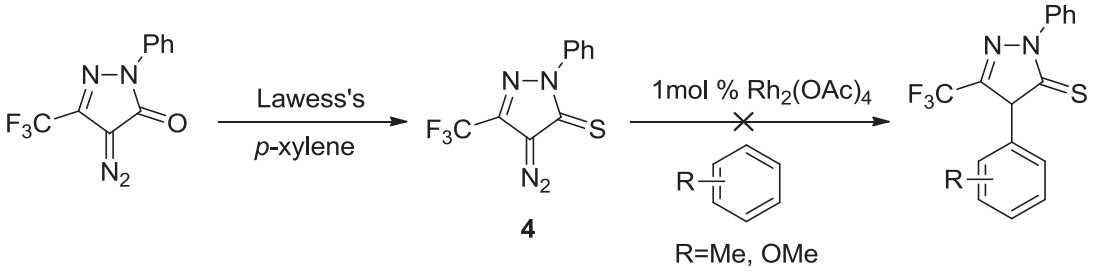
4. Experimental

4.1. General remarks and methods

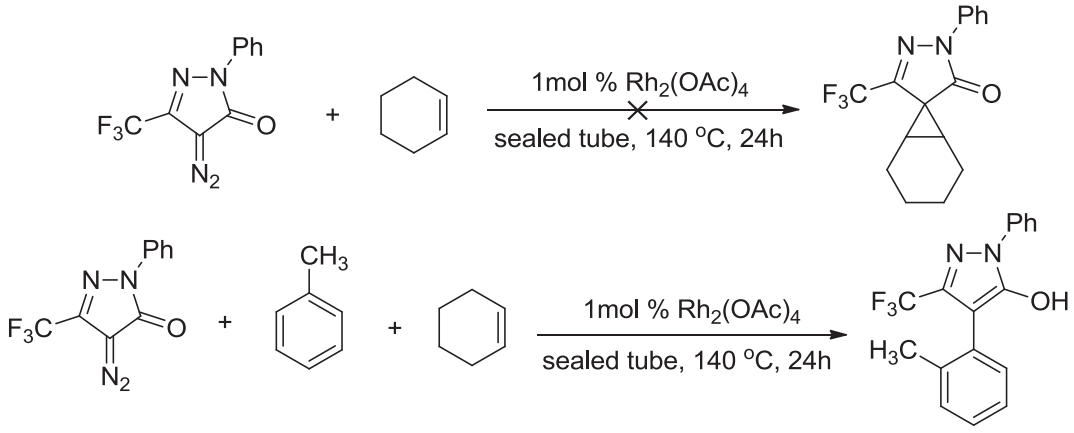
Commercial reagents were used without further purification. All solvents used were dried and purified by distillation. The starting pyrazolinones **1** were prepared according to described procedure.[9] Melting points were measured in Temp-Melt apparatus without calibration. ^1H and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker AM-300 instruments with Me_4Si and $CFCl_3$ (with upfield negative) as the internal and external standards, respectively. ^{13}C NMR spectra were recorded in $CDCl_3$ with Bruker AMX at 100 MHz and chemical shifts were given in parts per million relative to Me_4Si. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Lower resolution mass spectra or high-resolution mass spectra (HRMS) were obtained on a FinniganMAT-8430 instrument using the electron impact ionization technique (70 eV). X-ray diffraction crystal structure analysis was obtained on Bruker P4 instrument. All reaction as well as column chromatography were monitored routinely with the aid of TLC or ^{19}F NMR spectroscopy.



Scheme 4. No reactions of 3-trifluoromethyl-4-diazo pyrazolinone with pyridine or its derivatives under the same conditions.



Scheme 5. Synthesis of 3-trifluoromethyl-4-diazopyrazolinethione and the reactions of it with toluene, anisole or xylene.

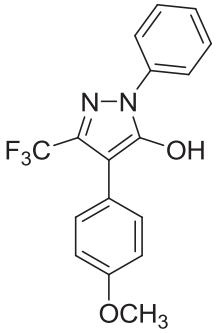


Scheme 6. Compared reaction of 3-trifluoromethyl-4-diazo pyrazolinone with cyclohexene under the same conditions.

4.2. General procedure for the synthesis of compounds 3

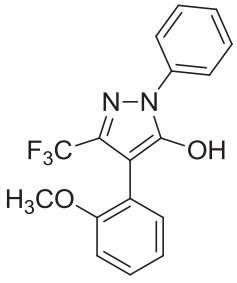
3-Trifluoromethyl-4-diazopyrazolinones **1** (254 mg, 1 mmol) and $Rh_2(OAc)_4$ (4 mg) were dissolved in anisole (5 mL). The reaction mixture was stirred at 140 °C for about 3 h, until the starting material of CF_3-substituted diazo compound disappeared while monitoring by TLC. The solvent was removed in vacuum and the residue was purified on silica gel using petroleum ether/ethyl acetate (20:1) as eluent to afford the corresponding products.

*4.2.1. 4-(4-Methoxyphenyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3a**).*



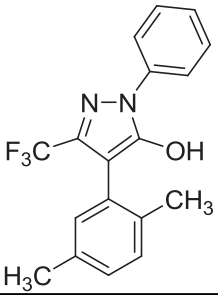
Yield 63%, 210.5 mg; white solid; mp 147–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.64 (d, J=7.8 Hz, 2H), 7.43 (t, J=7.8 Hz, 2H), 7.35 (d, J=7.2 Hz, 1H), 7.25 (d, J=8.1 Hz, 2H), 6.91 (d, J=8.1 Hz, 2H), 3.80 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−60.87 (s, 3F). IR (KBr) cm^{-1}: 2934, 2837, 1530, 1503, 1484, 1337, 1256, 1125, 985, 762. MS: m/z (%)=334 (M^+, 57), 210 (22), 135 (50), 91 (19), 78 (18), 77 (100), 51 (24), 41 (19). HRMS (EI): Calcd for $C_{17}H_{13}F_3N_2O_2$: 334.0929; found: 334.0927.

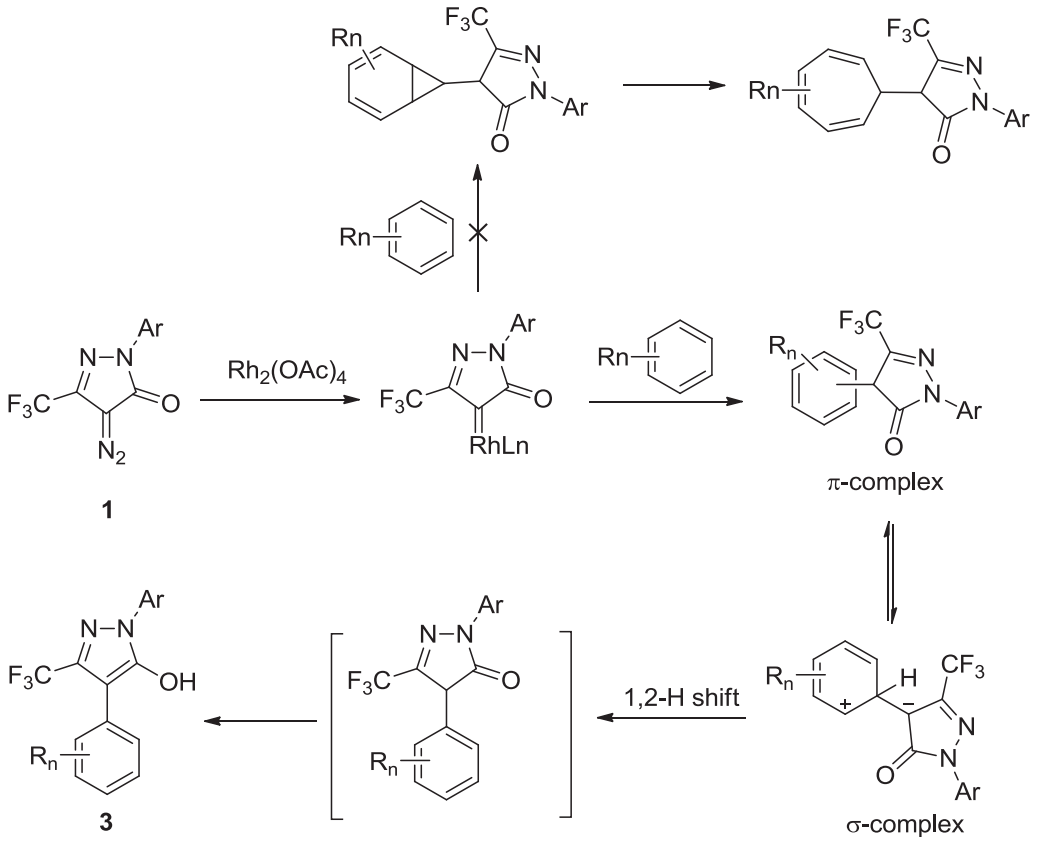
*4.2.2. 4-(2-Methoxyphenyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3a′**).*



Yield 13%, 43.4 mg; white solid; mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (d, J=8.4 Hz, 2H), 7.46-7.56 (m, 3H), 7.35–7.40 (m, 2H), 7.08–7.18 (m, 2H), 3.99 (s, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ=−59.96 (s, 3F). IR (KBr) cm^{-1}: 2948, 1485, 1456, 1333, 1275, 1250, 1170, 1133, 1114, 987, 759, 693. MS: m/z (%)=334 (M^+, 40), 299 (17), 146 (18), 77 (100), 58 (18), 51 (25), 44 (25), 41 (21). HRMS (EI): Calcd for $C_{17}H_{13}F_3N_2O_2$: 334.0929; found: 334.0931.

*4.2.3. 4-(2,5-Dimethylphenyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3b**).*

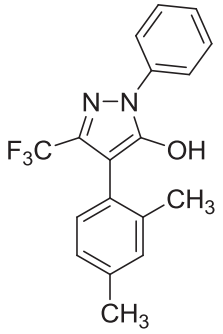




Scheme 7. Possible mechanism for this reaction.

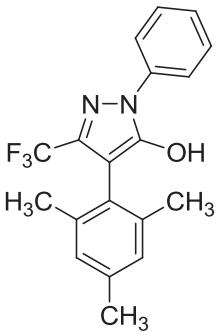
Yield 56%, 186.0 mg; white solid; mp 162–163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.73 (d, J=8.1 Hz, 2H), 7.47 (t, J=7.5 Hz, 2H), 7.36 (t, J=7.5 Hz, 1H), δ=7.17 (d, J=7.8 Hz, 1H), 7.11 (d, J=7.6 Hz, 1H), 7.03 (s, 1H), 2.33 (s, 3H), 2.14 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−61.60 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ=148.8, 139.4 (q, $^2J_{C-F}$=40.8 Hz), 137.4, 135.3, 135.2, 132.3, 130.0, 129.6, 129.0, 127.7, 127.4, 123.0, 121.1 (q, $^1J_{C-F}$=268.4 Hz), 102.3 (m, $^3J_{C-F}$), 20.8, 19.2. IR (KBr) cm^{-1}: 3418, 2924, 1598, 1485, 1409, 1329, 1127, 1006, 768, 693. MS: m/z (%)=332 (M^+, 81), 333 (20), 289 (35), 128 (21), 93 (26), 78 (23), 77 (100), 57 (18). HRMS (EI): Calcd for $C_{18}H_{15}F_3N_2O$: 332.1136; found: 332.1141.

*4.2.4. 4-(2,4-Dimethylphenyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3c**).*



Yield 61%, 202.6 mg; white solid; mp 159–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.74 (d, J=8.1 Hz, 2H), 7.47 (t, J=7.5 Hz, 2H), 7.36 (t, J=7.5 Hz, 1H), δ=7.03–7.11 (m, 3H), 2.36 (s, 3H), 2.16 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−61.60 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$): δ=149.3, 139.4 (q, $^2J_{C-F}$=36.4 Hz), 138.4, 138.2, 137.2, 131.6, 130.9, 128.9, 127.7, 126.4, 124.7, 123.1, 120.0 (q, $^1J_{C-F}$=269.0 Hz), 102.2 (m, $^3J_{C-F}$), 21.2, 19.6. IR (KBr) cm^{-1}: 2924, 1599, 1481, 1457, 1406, 1291, 1192, 1156, 1122, 988,767, 692. MS: m/z (%)=332 (M^+, 82), 333 (18), 289 (32), 135 (25), 105 (21), 93 (19), 77 (100), 51 (26). HRMS (EI): Calcd for $C_{18}H_{15}F_3N_2O$: 332.1136; found: 332.1131.

*4.2.5. 4-Mesityl-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3d**).*



Yield 45%, 155.8 mg; white solid; mp 165–166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.81 (d, J=8.1 Hz, 2H), 7.49 (t, J=7.8 Hz, 2H), 7.36 (t, J=7.5 Hz, 1H), 6.97 (s, 2H), 2.33 (s, 3H), 2.10 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−63.09 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=139.0, 138.4, 137.8, 137.2 (q, $^2J_{C-F}$=30.8 Hz), 129.7, 129.0, 128.9, 128.1, 127.9, 127.2, 127.1, 122.2, 121.8 (q, $^1J_{C-F}$=267.6 Hz),

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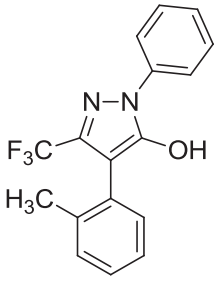
118.5 (m, $^3J_{C-F}$), 20.2, 19.7. IR (KBr) cm^{-1}: 3418, 2923, 1598, 1506, 1482, 1457, 1284, 1154, 1128, 987, 770. MS: *m*/*z* (%)=346 (M^+, 29), 213 (51), 212 (64), 119 (96), 106 (55), 91 (46), 78 (100), 77 (69), 63 (45). HRMS (EI): Calcd for $C_{19}H_{17}F_3N_2O$: 346.1293; found: 346.1296.

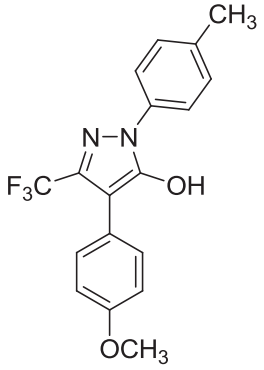
*4.2.6. 4-(o-Tolyl)-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3e**).*



Yield 15%, 47.7 mg; white solid; mp 102–103 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.72 (d, *J*=8.1 Hz, 2H), 7.48 (t, *J*=8.1 Hz, 2H), 7.37 (t, *J*=7.5 Hz, 1H), 7.26–7.28 (m, 4H), 2.40 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−61.35 (s, 3F). IR (KBr) cm^{-1}: 2924, 1597, 1531, 1502, 1481, 1334, 1127, 987, 765, 690. MS: *m*/*z* (%)=318 (M^+, 100), 319 (15), 275 (15), 194 (42), 115 (23), 78 (19), 77 (88), 51 (18). HRMS (EI): Calcd for $C_{17}H_{13}F_3N_2O$: 318.0980; found: 318.0981.

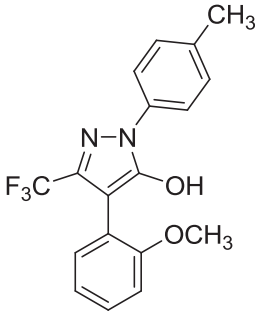
Crystal data of **3e**. CCDC reference number is 872812. $C_{17}H_{13}F_3N_2O$: MW=318.29, Monoclinic, space group P2(1)/c, *a*=18.3444(10), *b*=20.8512(11), *c*=18.2354(10) Å, α=90.00, β=116.9840(10), γ=90.00, *V*=6215.7(6) $Å^3$, *Z*=16, *Dc*=1.361 mg/m^3, *F* (000)=2624, radiation, Mo Ka (λ=0.71073 Å), $1.58 \le 2\theta \le 25.25$, intensity data were collected at 293 K with a Bruker AXS D8 diffractometer, and employing $\omega/2\theta$ scanning technique, in the range of $-22 \le h \le 22$, $-25 \le k \le 21$, $-20 \le l \le 20$.

*4.2.7. 4-(4-Methoxyphenyl)-1-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3f**).*



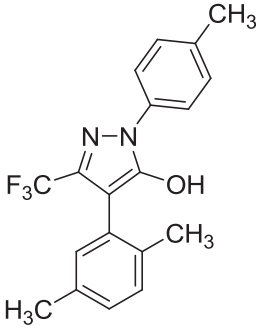
Yield 65%, 226.3 mg; white solid; mp 165–166 °C. ^1H NMR (300 MHz, acetone-d_6): δ=7.70 (d, *J*=8.1 Hz, 2H), 7.34 (t, *J*=8.4 Hz, 4H), 6.98 (d, *J*=8.7 Hz, 2H), 3.83 (s, 3H), 2.40 (s, 3H). ^{19}F NMR (282 MHz, acetone-d_6): δ=−60.85 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=159.4, 149.8, 138.4 (q, $^2J_{C-F}$=35.7 Hz), 137.3, 135.9, 131.4, 129.5, 122.8, 122.0 (q, $^1J_{C-F}$=267.8 Hz), 121.7, 113.8, 103.2 (m, $^3J_{C-F}$), 54.7, 20.1. IR (KBr) cm^{-1}: 2963, 2837, 1527, 1508, 1483, 1135, 1251, 1179, 1127, 938, 822. MS: *m*/*z* (%)=348 (M^+, 6), 228 (88), 161 (40), 118 (28), 105 (36), 91 (35), 78 (19), 77 (100), 51 (25). HRMS (EI): Calcd for $C_{18}H_{15}F_3N_2O_2$: 348.1086; found: 348.1081.

*4.2.8. 4-(2-Methoxyphenyl)-1-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3f'**).*



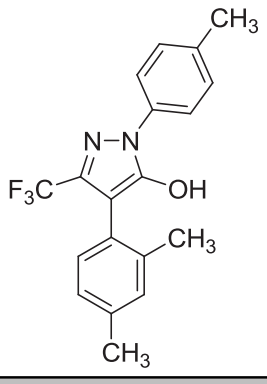
Yield 17%, 59.2 mg; white solid; mp 134–135 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.66 (d, *J*=8.1 Hz, 2H), 7.54 (d, *J*=7.8 Hz, 1H), 7.38 (t, *J*=8.4 Hz, 1H), 7.29 (d, *J*=8.7 Hz, 2H), 7.15 (t, *J*=7.8 Hz, 1H), 7.10 (d, *J*=7.5, 1H), 3.99 (s, 3H), 2.41(s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−60.34 (s, 3F). IR (KBr) cm^{-1}: 3006, 2947, 1535, 1487, 1290, 1276, 1251, 1130, 1113, 986, 821, 759. MS: *m*/*z* (%)=348 (M^+, 63), 131 (44), 91 (100), 77 (38), 69 (47), 68 (43), 43 (38). HRMS (EI) Calcd for $C_{18}H_{15}F_3N_2O_2$: 348.1086; found: 348.1088.

*4.2.9. 4-(2,5-Dimethylphenyl)-1-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3g**).*



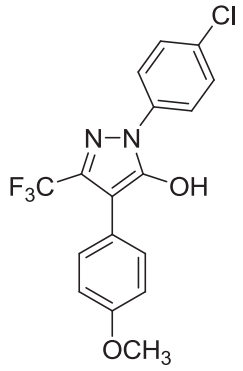
Yield 68%, 235.4 mg; white solid; mp 152–153 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=7.61 (d, *J*=8.1 Hz, 2H), 7.27 (d, *J*=6.9 Hz, 2H), 7.12-7.20 (m, 2H), 7.06 (s, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.16 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.14 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=149.8, 138.8 (q, $^2J_{C-F}$=35.7 Hz), 137.1, 136.1, 135.5, 134.7, 132.5, 129.7, 129.5, 129.2, 128.7, 122.5, 121.9 (q, $^1J_{C-F}$=267.6 Hz), 102.0 (m, $^3J_{C-F}$), 20.1, 20.0, 18.8. IR (KBr) cm^{-1}: 2925, 1521, 1490, 1330, 1309, 1208, 1158, 1119, 1005, 822. MS: *m*/*z* (%)=346 (M^+, 100), 347 (19), 303 (31), 249 (17), 107 (17), 106 (13), 91 (53), 65 (16). HRMS (EI): Calcd for $C_{19}H_{17}F_3N_2O$: 346.1293; found: 346.1291.

*4.2.10. 4-(2,4-Dimethylphenyl)-1-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3h**).*



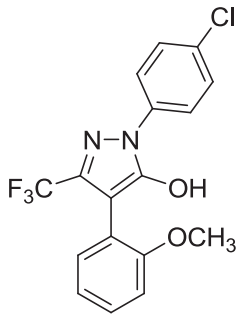
Yield 71%, 245.8 mg; white solid; mp 176–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.57 (d, J=8.4 Hz, 2H), 7.25 (d, J=8.1 Hz, 2H), 7.08 (d, J=8.4 Hz, 2H), 7.04 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.13 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.16 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=149.9, 138.9 (q, $^2J_{C-F}$=35.0 Hz), 138.4, 138.0, 137.1, 136.1, 132.0, 130.5, 129.5, 126.2, 125.9, 122.4, 121.9 (q, $^1J_{C-F}$=267.6 Hz), 101.7 (m, $^3J_{C-F}$), 20.2, 20.1, 19.2. IR (KBr) cm^{-1}: 2925, 1520, 1484, 1417, 1330, 1182, 1142, 1128, 991, 821. MS: m/z (%)=346 (M^+, 100), 347 (23), 303 (30), 249 (13), 222 (12), 107 (10), 91 (40), 65 (11). HRMS (EI): Calcd for $C_{19}H_{17}F_3N_2O$: 346.1293; found: 346.1297.

*4.2.11. 4-(4-Methoxyphenyl)-1-(4-chlorophenyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3i**).*



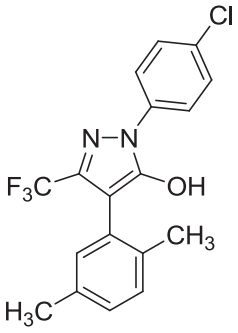
Yield 71%, 261.3 mg; white solid; mp 144–145 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ=7.90 (d, J=9.0 Hz, 2H), δ=7.59 (d, J=9.0 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 6.99 (d, J=8.7 Hz, 2H), 3.84 (s, 3H). ^{19}F NMR (282 MHz, acetone-d_6): δ=−62.63 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=159.5, 150.1, 139.2 (q, $^2J_{C-F}$=35.8 Hz), 137.1, 132.4, 131.5, 129.1, 124.0, 121.8 (q, $^1J_{C-F}$=267.6 Hz), 121.4, 113.9, 103.4 (m, $^3J_{C-F}$), 54.7. IR (KBr) cm^{-1}: 2967, 2839, 1526, 1498, 1480, 1340, 1252, 1182, 1129, 984, 838. MS: m/z (%)=368 (M^+, 100), 370 (32), 369 (20), 200 (28), 113 (23), 111 (67), 77 (30), 75 (32). HRMS (EI): Calcd for $C_{17}H_{12}ClF_3N_2O_2$: 368.0539; found: 368.0541.

*4.2.12. 4-(2-Methoxyphenyl)-1-(4-chlorophenyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3i′**).*



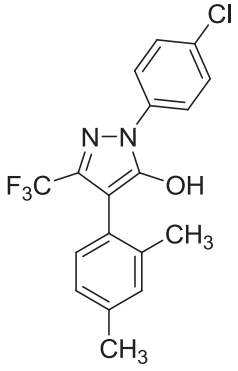
Yield 7%, 25.8 mg; white solid; mp 183–184 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ=7.92 (d, J=9.0 Hz, 2H), 758 (d, J=9.3 Hz, 2H), 7.28–7.41 (m, 2H), 7.06 (d, J=9.3 Hz, 1H), 7.00 (d, J=7.2 Hz, 1H), 3.82 (s, 3H). ^{19}F NMR (282 MHz, acetone-d_6): δ=−62.34 (s, 3F). IR (KBr) cm^{-1}: 3007, 2948, 1591, 1486, 1414, 1276, 1170, 1131, 1096, 986, 833, 756. MS: m/z (%)=368 (M^+, 58), 113 (31), 111 (100), 75 (37), 57 (25), 56 (30), 43 (41), 41 (36). HRMS (EI): Calcd for $C_{17}H_{12}ClF_3N_2O_2$: 368.0539; found: 368.0537.

*4.2.13. 4-(2,5-Dimethylphenyl)-1-(4-chlorophenyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3j**).*



Yield 69%, 252.6 mg; white solid; mp 146–147 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ=7.93 (d, J=8.7 Hz, 2H), δ=7.59 (d, J=9.0 Hz, 2H), 7.09-7.18 (m, 2H), 7.05 (s, 1H), 2.30 (s, 3H), 2.16 (s, 3H). ^{19}F NMR (acetone-d_6, 282 MHz): δ=−62.66 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=150.1, 139.5 (q, $^2J_{C-F}$=35.0 Hz), 137.3, 135.5, 134.8, 132.5, 132.2, 129.8, 129.3, 129.1, 128.4, 123.7, 121.7 (q, $^1J_{C-F}$=267.6 Hz), 102.2 (m, $^3J_{C-F}$), 20.0, 18.8. IR (KBr) cm^{-1}: 2927, 1597, 1533, 1486, 1416, 1330, 1207, 1132, 1004, 833, 808. MS: m/z (%)=366 (M^+, 85), 323 (48), 111 (100), 75 (56), 57 (68), 56 (44), 43 (87), 41 (67). HRMS (EI): Calcd for $C_{18}H_{14}ClF_3N_2O$: 366.0747; found: 366.0750.

*4.2.14. 4-(2,4-Dimethylphenyl)-1-(4-chlorophenyl)-3-(trifluoromethyl)-1H-pyrazol-5-ol (**3k**).*



Yield 63%, 230.6 mg; white solid; mp 181–182 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ=7.93 (d, J=9.0 Hz, 2H), δ=7.59 (d, J=8.7 Hz, 2H), 7.02–7.12 (m, 3H), 2.33 (s, 3H), 2.16 (s, 3H). ^{19}F NMR (acetone-d_6, 282 MHz): δ=−62.68 (s, 3F). ^{13}C NMR (100 MHz, acetone-d_6): δ=150.2, 139.6 (q, $^2J_{C-F}$=35.8 Hz), 138.5, 138.1, 137.3, 132.2, 131.9, 130.5, 129.1, 126.3, 125.7, 125.5, 123.7, 121.7 (q, $^1J_{C-F}$=267.6 Hz), 101.9 (m, $^3J_{C-F}$), 20.2, 19.1. IR (KBr) cm^{-1}: 2924, 1594, 1482, 1413, 1331, 1180, 1130, 991, 833, 808. MS: m/z (%)=366 (M^+, 100), 368 (32), 323 (41), 127 (28), 115 (28), 111 (85), 77 (32), 43 (35). HRMS (EI): Calcd for $C_{18}H_{14}ClF_3N_2O$: 366.0747; found: 366.0746.

4.3. General procedure for the synthesis of compounds 4

3-Trifluoromethyl-4-diazopyrazolinones **1a** (254 mg, 1 mmol) and Lawesson reagent (404 mg, 1 mmol) were dissolved in xylene (10 mL). The reaction mixture was stirred at reflux for about 5 h, until the starting material of **1** disappeared while monitoring by TLC. The solvent was removed in vacuum and the residue was purified on silica gel using petroleum ether/ethyl acetate (10:1) as eluent to afford the corresponding product **4**.

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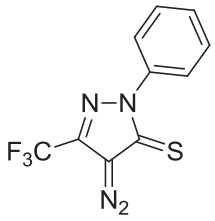
*4.3.1. 4-Diazo-1-phenyl-3-(trifluoromethyl)-1H-pyrazole-5(4H)-thione (**4**).*



Yield 86%, 232.2 mg; white solid; mp 93–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.76 (d, J=7.5 Hz, 2H), 7.59 (t, J=7.5 Hz, 2H), 7.45 (t, d, J=7.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ=−61.15 (s, CF_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ=156.1, 147.8, 138.0, 132.2 (q, $^2J_{C-F}$=41.5 Hz), 130.1, 128.3, 119.8 (q, $^1J_{C-F}$=268.4 Hz), 118.2. IR (KBr) cm^{-1}: 2354, 1594, 1532, 1504, 1478, 1427, 1296, 1197, 1029, 894, 758. MS: m/z (%)=270 (M+, 18), 242 (21), 105 (9), 87 (11), 77 (100), 51 (23), 50 (7). HRMS (EI): Calcd for $C_{10}H_5F_3N_4S$: 270.0187; found: 270.0191.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.077. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Regitz, M.; Maas, G. *Diazo Compounds – Properties and Synthesis*; Academic: Orlando, FL, 1986; (b) Maas, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 8186–8195.
2. Smith, M. R.; Blake, A. J.; Hayes, C. J.; Stevens, M. F. G.; Moody, C. J. *J. Org. Chem.* **2009**, *74*, 9372–9380.
3. (a) Rosenfeld, M. J.; Ravi Shankar, B. K.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2699–2703; (b) Yang, M.; Webb, T. R.; Livant, P. *J. Org. Chem.* **2001**, *66*, 4945–4948.
4. Fructos, M. R.; Belderrain, T. R.; Fremont, P.; Scott, N. M.; Nolan, S. P.; Diaz-Requejo, M. M.; Perez, P. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 5284–5288.
5. (a) Anciaux, A. J.; Demonceau, A.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyesil, P. *J. Chem. Soc., Chem. Commun.* **1980**, *16*, 765–766; (b) Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssil, P. *J. Org. Chem.* **1981**, *46*, 873–876.
6. Rivilla, I.; Gomez-Emeterio, B. P.; Fructos, M. R.; Díaz-Requejo, M. M.; Perez, P. *J. Organometallics* **2011**, *30*, 2855–2860.
7. (a) Jiang, B.; Zhang, X. B.; Luo, Z. H. *Org. Lett.* **2002**, *4*, 2453–2455; (b) Shi, G. Q.; Xu, Y. Y.; Xu, M. *J. Fluorine Chem.* **1991**, *52*, 149–157; (c) Shi, G. Q.; Cao, Z. Y.; Cai, W. L. *Tetrahedron* **1995**, *51*, 5011–5018; (d) Hoffmann, M. G.; Wenkert, E. *Tetrahedron* **1993**, *49*, 1057–1062.
8. (a) Abdou, I. M.; Saleh, A. M.; Zohdi, H. F. *Molecules* **2004**, *9*, 109–116; (b) Beverina, L.; Crippa, M.; Sassi, M.; Monguzzi, A.; Meinardi, F.; Tubino, R.; Pagani, G. A. *Chem. Commun.* **2009**, 5103–5105; (c) Soliman, A. A. *Spectrochim. Acta, Part A* **2007**, *67*, 852–857; (d) Zhang, Z. H.; Wang, X. W.; Song, T.; Zhu, S. Z. *Tetrahedron* **2012**, *68*, 5969–5978.
9. Zhang, Z. H.; Han, J. W.; Zhu, S. Z. *Tetrahedron* **2011**, *67*, 8496–8501.
10. Zhu, S. Z.; He, P. *Tetrahedron* **2005**, *61*, 5679–5685.