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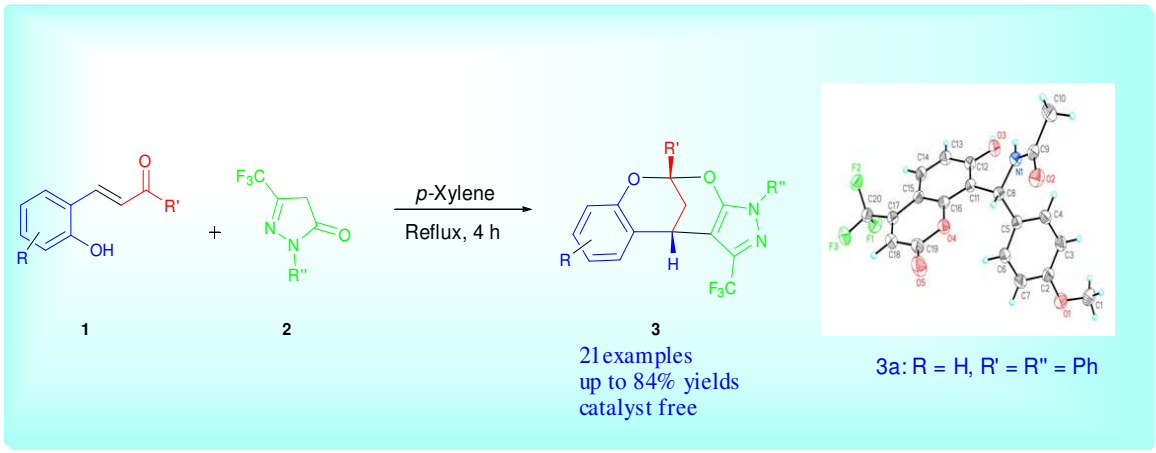

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ARTICLE TYPE

A simple and catalyst free one pot access to the pyrazolone fused 2,8-dioxabicyclo[3.3.1]nonanes

Chiranjeevi Bingi,[a] Narender Reddy Emmadi,[a] Madhu Chennapuram,[a] Jagadeesh Babu Nanubolu[b] and Krishnaiah Atmakur*[a,c]

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Synthesis of a series of novel aryl and heteroaryl fused 2,8-dioxabicyclo[3.3.1]nonanes (**3**) were accomplished by one pot, catalyst free reaction of 2-hydroxy chalcone (**1**) with 3-trifluoromethyl substituted pyrazolone (**2**) in xylene at reflux temperature. The role of trifluoromethyl functional in formation of **3** was confirmed by comparative studies with 3-methyl substituted pyrazolones (**2c-d**) and the outcome is presented.

1. Introduction

The 2,8-dioxabicyclo[3.3.1]nonane is a unique bicyclo frame work which is widely found in natural products and biological active compounds.[1] Trogers base,[2] a prominent methylene bridged bicyclic compound and its derivatives have been widely employed as molecular tweezers,[3] ion receptors[4] and high affinity DNA targeting fluorescent supramolecular scaffolds[5] owing to their rigidity. Similarly, 2,8-dioxabicyclo[3.3.1]nonanes e.g. dracoflavan C, dracoflavan D and procyanidin A1 (Fig. 1) an important methylene bridged bicyclic compounds have been found in medicinal plant sources.

Several reports have appeared on the construction of 2,8-dioxabicyclo[3.3.1]nonane frame work with varied structural analogues. For example, Manolov[6] reported 1-phenyl or methyl 2,8-dioxabicyclo[3. 3.1]nonanes by a base catalyzed reaction of 3-benzoyl or acetyl coumarin with 4-hydroxy coumarin. Yang[7] reported the reaction of 2-phenyl chroman-4-ol with 4-hydroxy comarin catalyzed by aluminium chloride. Weinges[8] described a three step sequence to bicyclic core by reacting (2-benzyloxy chalcone and 2-benzyloxy phenyl magnesium bromide, Meetsma[9] reported 1-methyl substituted 2,8-dioxa bicyclo[3.3.1]nonanes from β-napthol, salicilaldehyde and excess ethyl acetoacetate catalyzed by Lewis acid and more general methods[10] were appeared to access this frame work by condensing flavylium salts and polyphenols.

More recently, Anxinwu[11] described the stereo selective synthesis of 2,8-dioxabicyclo[3.3.1]nonanes by the reaction of 3-(2-hydroxy phenyl)-1-phenyl prop-2-en-1-one with 4-hydroxy coumarin, 1,3-dione and also with 1,4-napthaquinone. Min shi[12] reported the construction of [3.3.1] bicyclic ketals by enantioselective Pd (II) catalyzed reaction of 2-hydroxy phenyl boronic acid and 2-hydroxy chalcone.

[a] *Division of Crop Protection Chemicals, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500 007, India.*

[b] *Laboratory of X-ray crystallography, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500 007, India*

[c] *AcSIR- Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500 007, India.*

E-mail: srikrishnua@yahoo.com; Tel: +91- 40-27191436

Guodong Yin[13] reported the Ag(OTf) catalyzed synthesis of di-aryl fused [3.3.1] bicyclic nonanes by reacting 2-hydroxy chalcones with napthols and also with substituted phenols. The latest report[14] was by the reaction of 2-hydoxy chalcones with napthols catalyzed by (D, L)-10-camphorsulfonic acid to furnish diaryl fused 2,8-dioxabicyclo[3. 3.1]nonanes. Thus a great deal of effort has been done to prepare these derivatives. However all these reports are on diaryl fused bicyclo nonanes which are sometime requiring using expensive catalysts.

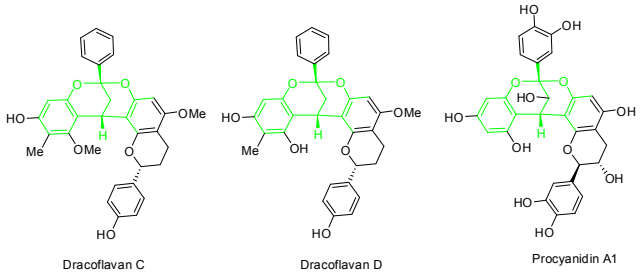


Figure 1 2,8-dioxabicyclo[3.3.1]nonane containing bioactive natural products.

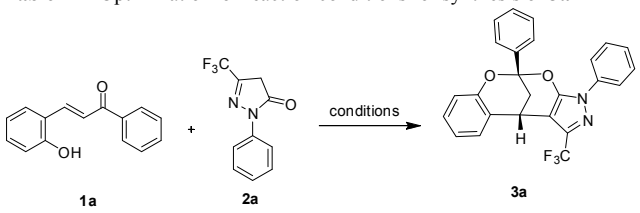
On the other hand, pyrazolone is a key structure in numerous compounds of therapeutic importance and have been the focus of medicinal chemists because of the outstanding pharmacological properties shown by several of its derivatives e.g. ampyrone, metanizole etc. Further, pyrazolone is a constituent structural feature of many NSAIDS clinically useful in the treatment of arthritis and other musculo skeletal and joint disorders.[15] Therefore, the investigation on the chemistry of pyrazolones have been, and continuous to be one of the most active area of heterocyclic chemistry. Realising the importance of pyrazolones and the significance of 2,8-dioxabicyclo[3.3.1] nonanes in one way, nowadays keen research interest on synthesis and derivatization of complex structural motifs with an attached bicyclo[3.3.1]nonane frame work[16] on the other way, we planned to synthesize a new series of 2,8-dioxabicyclo[3.3.1]nonane compounds by fusing 2-hydroxy chalcones (**1**) with trifluoromethyl substituted

pyrazolones (**2**). Additionally, presence of fluorine, especially trifluoromethyl group at a specified position in a molecule alters the reactivity because of its strong electron withdrawing character, lipophilicity and metabolic stability. In this context, the literature survey at this stage revealed that, no reports are available on the aryl and hetero aryl fused 2,8-dioxabicyclo [3.3.1]nonanes. With this background and also as a part of our continuous endeavour to synthesize new bio-active molecules,[17] we herein report for the first time an aryl and pyrazolone fused 2,8-dioxabicyclo[3.3.1]nonane (**3**) derivatives in a one pot reaction without any catalyst.

2. Results and Discussions

Before testing the feasibility of our hypothesis to construct the 2,8-dioxabicyclo[3.3.1]nonane framework with aryl and hetero aryl moieties, 2-hydroxy chalcone (**1a**) was prepared by known procedure[18] and a model reaction was attempted with compound (**1a**) and pyrazolone (**2a**) in methanol and ethanol separately without any catalyst (Table 1). However, formation of the desired product **3** was observed in very poor yields upon long refluxing. Further, the same reaction was studied independently in n-propyl alcohol, 1,4-dioxane and water. All these studies resulted in formation of bicyclic compound **3** in poor yields.

Table 1 Optimization[a] of reaction conditions for synthesis of **3a**



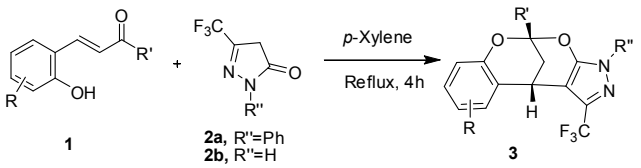
Entry	Solvent	Catalyst	Time (h)	Yield[b] (%)
1	Methanol	**-**	24	20
2	Ethanol	-	24	34
3	*n*-Pr OH	-	10	58
4	1,4-dioxane	-	24	36
5	Water	-	8	55
6	*n*-Pr OH	$CuCl_2.2H_2O$	10	59
7	1,4-dioxane	$CuCl_2.2H_2O$	10	50
8	Toluene	-	8	61
9	Toluene	$Cu(OTf)_2$	8	62
10	Toluene	$CuCl_2.2H_2O$	8	71
11	***p*-Xylene**	**-**	**4**	**81**
12	*p*-xylene	$CuCl_2.2H_2O$	4	76
13	*p*-xylene	$Cu(OTf)_2$	4	72
14	*p*-xylene	$Zn(OTf)_2$	4	67
15	*p*-xylene	CSA	8	74
16	*p*-xylene	CuBr	8	71

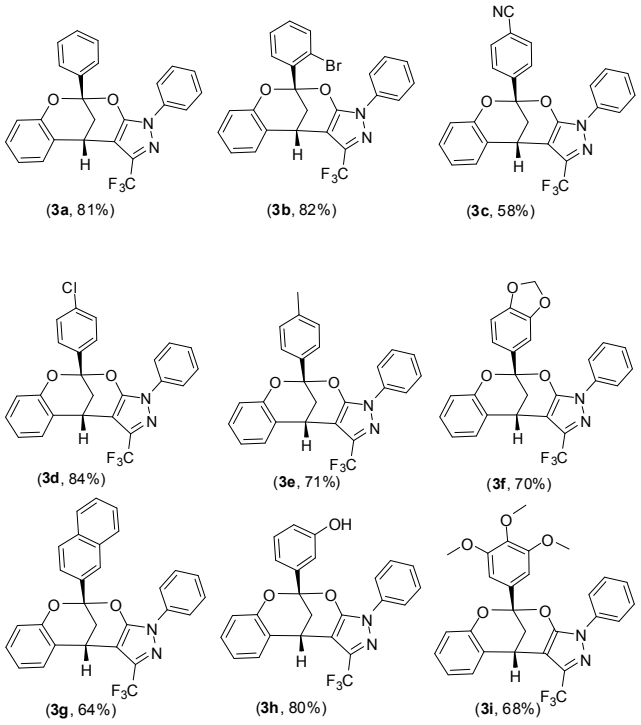
---- No catalyst

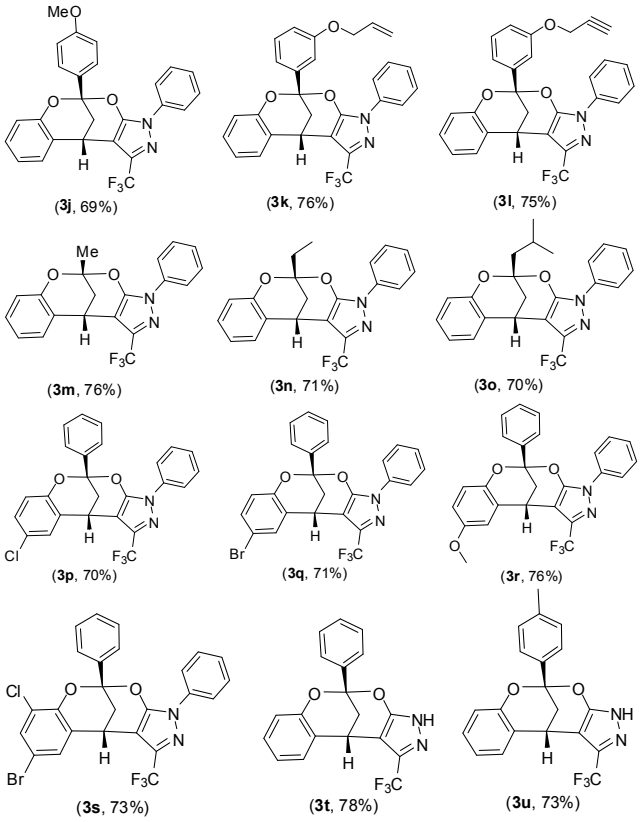
[a] All the reactions were performed with 2-hydroxy chalcone (**1a**, 0.1mmol), 3-trifluoromethyl pyrazolone (**2a**, 0.1mmol) and catalyst (30 mol%) in appropriate solvent were refluxed under above mentioned. [b] Yield refers to pure products after column chromatography.

Continued studies to improve the yields of **3**, by employing Lewis acid catalysts (entry 6, 7, Table 1) resulted in formation of **3** in moderate yields. Subsequently, next reaction was conducted in high boiling solvent like toluene at reflux temperature and interestingly yields of **3** were improved to 61%. When the same reaction was conducted by employing Lewis acid catalysts (entry-9, 10, Table 1) a perceptible increase in yields 71% were observed. Next, the reaction was conducted in xylene medium at reflux temperature. Surprisingly, yields of **3** were dramatically improved to 81%. Subsequent studies by employing the Lewis acid catalysts in xylene medium as indicated in table 1 could not enhance the yields. Encouraged by the remarkable results obtained in xylene without any catalyst, the generality and scope of this protocol was explored by synthesizing a series of new compounds by varying the substitution (Table 2). A wide range of functional groups such as electron withdrawing and electron releasing groups on **1** were well tolerated. However, the yields were varied. Compounds bearing electron withdrawing groups gave the better yields and the compounds with electron releasing groups could not make much impact when compared with simple aryl groups. Further, aliphatic groups such as methyl, ethyl and isobutyl adjacent to α, β-unsaturated ketone on **1** also gave the products **3m-o** in 70% yields under these set of reaction conditions.

Table 2 Scope of reaction between chalcones and 3-trifluoromethyl pyrazolones







[a]All the products were characterized by NMR, IR and mass spectrometry. [b]Yield refers to pure products after column chromatography.

Structure of compound **3** was well characterized by NMR, IR, Mass spectrometry and a representative sample **3a** was unambiguously confirmed by X-Ray crystallography[19] (Fig. 2).

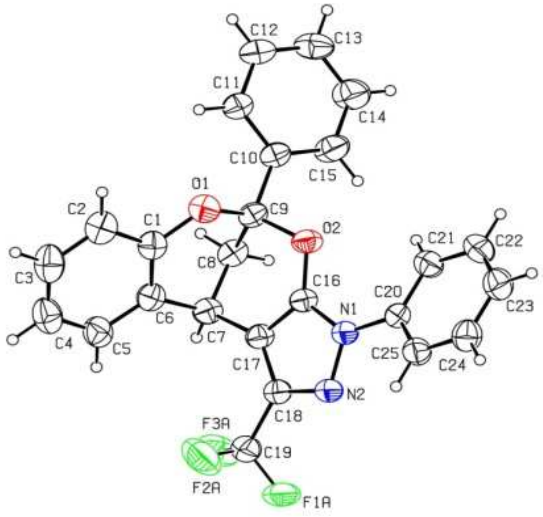
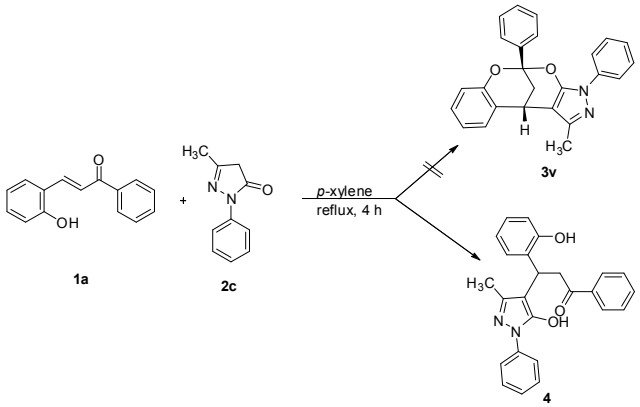


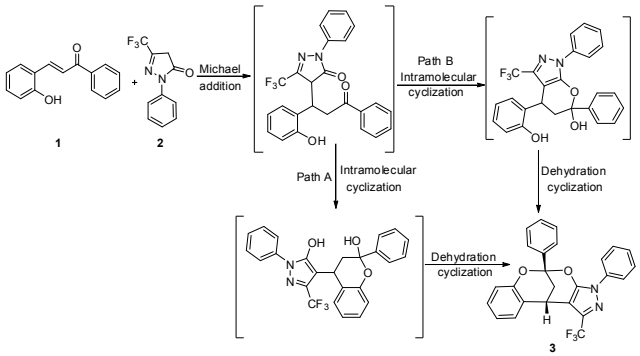
Figure 2 ORTEP Diagram of compound **3a**

In order to find out the role of $-CF_3$ if any on the formation of **3**, this protocol was verified by reacting 2-hydroxy chalcone (**1a**) with 3-methyl-1-phenyl substituted pyrazolone (**2c**) (scheme 1). Surprisingly, there was no formation of desired product **3.** Instead, only a Michael adduct **4** was observed in poor yields along with other unidentifiable compounds. Further heating of compound **4** also didn't lead to the desired product; instead it decomposed into unidentifiable compounds. This indicates the $-CF_3$ influence in formation of **3**. To confirm this, compound **1a** was further reacted with 3-methyl pyrazolone (**2d**) under similar set of reaction condition. However, it failed to produce either **3** or **4**. This clearly indicates the $-CF_3$ influence in formation product **3**. Additionally, formation of **3t-u** in high yields by the reaction of 2-hydroxychalcone with 3-trifluoromethyl pyrazolone (**2b**) without *N*-phenyl (aromatic) substitution substantiate the remarkable influence of $-CF_3$.

Influence of $-CF_3$ in formation of **3** can be explained by the fact that, as a most electronegative atom, fluorine has a very strong effect on the acidity or basicity of nearby functional groups.[20-22] Thus, in case of **2a**, due to the strong electron withdrawing nature of $-CF_3$, the methylene protons on C-4 may becoming highly acidic resulting to enolize quickly and involve in Michael addition, intramolecular cyclization followed by water elimination to give the desired product **3** through either path **A** or path **B** (scheme 2). Experimental observation also espouse this explanation as the formation of **3** was observed directly not followed by the Michael adduct.



Scheme 1



Scheme 2 Plausible Mechanism for **3.**

3. Conclusions

In closing, we have developed a simple, efficient and catalyst free protocol to synthesize a series of novel 3-trifluomethyl substituted aryl and heteroaryl fused 2,8-dioxabicyclo[3.3.1]nonanes (**3**) for the first time. Confirmed the $-CF_3$ influence on the formation of **3** by comparative studies and provided adequate reason. Higher yields, simple reaction

condition, and environmentally benign synthesis are the advantages of this protocol.

4. Experimental

4.1 General

Melting points were measured by CINTEX programmable melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra of samples in $CDCl_3$ and DMSO-d_6 were recorded on AVANCE- 300 MHz and 500 MHz spectrometers. Chemical shifts (δ) are reported relative to TMS (δ = 0.0) as the internal standard. Mass spectra were recorded in ESI spectrometers. All high resolution mass spectra were recorded on QSTAR XL hybrid ms/ms system (Applied Bio systems/MDS sciex, foster city, USA), equipped with an ESI source (IICT, Hyderabad). IR was recorded on Thermo Nicolet nexus-670 spectrometer with reference to KBr.TLC was performed on Merck 60 F-254 silica gel plates. The chemicals used in this work were obtained from commercial channels and were used without purification.

4.2. General Procedure for the synthesis of 1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one 2a.

A mixture of ethyl 4,4,4-trifluoro-3-oxobutanoate (5 g, 0.1 mmol) and phenyl hydrazine (2.9 g, 0.1 mmol) in acetic acid, in a round bottom flask was heated to reflux till the completion of the reaction (monitored by TLC). Then the neat reaction mass was allowed to come to room temperature, acetic acid was removed by rotary evaporator and the leftover residual solid mass was washed with water and hexane to obtain the pure solid **2a**.

4.2.1 1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (2a). Yield 90%; Mp 185-186 °C; IR (KBr): 3014, 1603, 1508, 1139, 995 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6): δ 7.75 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.3 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 5.82 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO-d_6): δ 152.0, 139.4 (q, $^2J_{C\text{-}F}$ = 38.1 Hz), 136.5, 127.2, 125.2, 120.6, 119.7 (q, $^1J_{C\text{-}F}$ = 268.8 Hz), 84.0 ppm; ESI-MS: m/z 229 [M+H]$^+$.

4.2.2 3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (2b). Yield 88%; Mp 210-215 °C; IR (KBr): 3121, 2804, 1731, 1598, 1492, 1259, 985 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6): δ 5.65 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+ DMSO-d_6): 153.9, 138.8 (q, $^2J_{C\text{-}F}$ = 37.4 Hz), 120.1(q, $^1J_{C\text{-}F}$ = 267.9 Hz), 82.9 ppm; ESI-MS: m/z 153 [M+H]$^+$.

4.3 General Procedure for the Synthesis of 5-(aryl/alkyl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11–methanobenzo [7,8][1,3]dioxocino[4,5-c]pyrazole derivatives (3).

A mixture of 3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one derivatives (**1**, 0.1 mmol) and 1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5(4H)-one (**2**, 0.1 mmol) was heated to reflux in *p*-xylene (10 mL) while stirring in a round bottom flask. The solution became homogeneous and dark brown on heating. After completion of the reaction in 4 h, as indicated by TLC, it was cooled to room temperature and solvent was removed by rotary evaporator under reduced pressure. Then, the residue was passed through column chromatography by eluting with 5-10% (ethyl acetate: hexane) to furnish the pure compound.

4.3.1 3,5-Diphenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3a). Yield 81%; Mp 155-157 °C; IR (KBr): 3065, 2953, 1952, 1596, 1481, 1227, 1131, 1015, 861, 757 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83-7.75 (m, 2H), 7.73-7.65 (m, 2H), 7.51-7.35 (m, 5H), 7.34-7.16 (m, 3H), 7.10-6.98 (m, 2H), 4.28 (s, 1H), 2.56 (dd, J = 13.6, 3.0 Hz, 1H), 2.35 (dd, J = 13.6, 3.0 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 149.0, 139.5, 137.6, 137.1 (q, $^2J_{C\text{-}F}$ = 37.9 Hz), 129.3, 129.0, 128.5, 128.2, 127.1, 126.9, 126.2, 125.6, 122.2, 121.4 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 121.0, 116.4, 103.1, 101.8, 34.4, 27.1 ppm; ESI-MS: m/z 435 [M+H]$^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{18}F_3N_2O_2$ m/z 435.1314 [M+H]$^+$, found 435.1306.

4.3.2 5-(2-Bromophenyl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3b). Yield 82%; Mp 139-141 °C; IR (KBr): 3068, 2942, 1597, 1482, 1456, 1311, 1233, 1129, 1016, 872, 755 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01-7.93 (m, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 7.0 Hz, 1H), 7.44-7.33 (m, 3H), 7.32-7.13 (m, 4H), 7.10-6.93 (m, 2H), 4.30 (s, 1H), 2.98 (dd, J = 13.5, 3.0 Hz, 1H), 2.5 (dd, J = 13.5, 3.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.5, 148.3, 137.5, 137.2, 137.0 (q, $^2J_{C\text{-}F}$ = 38.1 Hz), 135.4, 130.9, 129.0, 128.6, 128.2, 127.6, 127.2, 126.9, 126.2, 122.3, 121.4 (q, $^1J_{C\text{-}F}$ = 269.7 Hz), 121.3, 121.0, 116.7, 102.9, 102.0, 30.5, 26.7 ppm; ESI-MS: m/z 513 [M+H]$^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{17}BrF_3N_2O_2$ m/z 513.0420 [M+H]$^+$, found 513.0421.

4.3.3 4-(3-Phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazol-5-yl)benzonitrile (3c). Yield 58%; Mp 181-184 °C; IR (KBr): 2924, 2853, 2230, 1594, 1481, 1310, 1233, 1130, 1014, 886, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87-7.68 (m, 6H), 7.48-7.38 (m, 2H), 7.36-7.18 (m, 3H), 7.11-6.98 (m, 2H), 4.32 (s, 1H), 2.57 (dd, J = 13.5, 3.0 Hz, 1H), 2.34 (dd, J = 13.5, 2.8 Hz, 1H) ppm; ^{13}C NMR(125 MHz, $CDCl_3$): δ 151.4, 148.3, 144.2, 137.3, 137.1 (q, $^2J_{C\text{-}F}$ = 38.1 Hz), 132.5, 129.2, 128.5, 127.4, 127.0, 126.6, 125.8, 122.6, 121.2 (q, $^1J_{C\text{-}F}$ = 268.8 Hz), 121.1, 118.1, 116.4, 113.5, 102.3, 101.6, 34.1, 26.9 ppm; ESI-MS: m/z 460 [M+H]$^+$; HRMS (ESI) Anal. calcd. for $C_{26}H_{17}F_3N_3O_2$ m/z 460.1267 [M+H]$^+$, found 460.1276.

4.3.4 5-(4-Chlorophenyl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3d). Yield 84%; Mp 176-177 °C; IR (KBr): 3172, 2930, 1908, 1592, 1496, 1235, 1134, 1092, 1011, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.74 (m, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.47-7.39 (m, 4H), 7.33-7.27 (m, 2H), 7.24-7.18 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 4.29 (s, 1H), 2.56 (dd, J = 13.7, 3.2 Hz, 1H), 2.34 (dd, J = 13.7, 2.8 Hz, 1H) ppm ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6, 148.7, 138.1, 137.5, 137.1 (q, $^2J_{C\text{-}F}$ = 38.1 Hz), 135.5, 129.1, 128.8, 128.3, 127.3, 127.2, 127.0, 126.0, 122.4, 121.3 (q, $^1J_{C\text{-}F}$ = 267.9 Hz), 121.1, 116.4, 102.6, 101.7, 34.3, 27.0 ppm; ESI-MS: m/z 469 [M+H]$^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{17}ClF_3N_2O_2$ m/z 469.0925 [M+H]$^+$, found 469.0929.

4.3.5 3-Phenyl-5-(p-tolyl)-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3e). Yield 71%; Mp 154-156 °C; IR (KBr): 3066, 3037, 2950, 1597, 1481, 1229, 1139, 1107, 1015, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33-7.16 (m, 5H), 7.09-6.96 (m, 2H), 4.28 (s, 1H), 2.57 (dd, *J* = 13.5, 3.0 Hz, 1H), 2.42 (s, 3H), 2.36 (dd, *J* = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 149.1, 139.3, 137.6, 137.1 (q, $^2J_{C-F}$ = 38.1 Hz), 136.7, 129.2, 129.1, 128.2, 127.1, 126.9, 126.2, 125.5, 122.1, 121.4 (q, $^1J_{C-F}$ = 269.7 Hz), 121.1, 116.5, 103.1, 101.7, 34.5, 27.2, 21.1 ppm; ESI-MS: m/z 449 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{26}H_{20}F_3N_2O_2$ m/z 449.1471 $[M+H]^+$, found 449.1469.

4.3.6 5-(Benzo[d][1,3]dioxol-5-yl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo [7,8][1,3]dioxocino[4,5-c]pyrazole (3f). Yield 70%; Mp 165-167 °C; IR (KBr): 2899, 1736, 1598, 1487, 1256, 1134, 1037, 1012, 762 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.31-7.27 (m, 2H), 7.22-7.17 (m, 2H), 7.15 (d, *J* = 1.6 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H), 4.27 (s, 1H), 2.55 (dd, *J* = 13.7, 3.0 Hz, 1H), 2.34 (dd, *J* = 13.8, 2.8 Hz, 1H) ppm; ^{13}C NMR(125 MHz, $CDCl_3$): δ 151.8, 148.9, 148.4, 147.8, 137.5, 137.1 (q, $^2J_{C-F}$ = 38.1 Hz), 133.5, 129.1, 128.2, 127.1, 126.9, 126.1, 122.2, 121.3 (q, $^1J_{C-F}$ = 269.7 Hz), 121.1, 119.5, 116.4, 108.1, 106.5, 103.0, 101.7, 101.4, 34.6, 27.2 ppm; ESI-MS: m/z 479 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{26}H_{18}F_3N_2O_4$ m/z 479.1213 $[M+H]^+$, found 479.1216.

4.3.7 5-(Naphthalen-2-yl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3g). Yield 64%; Mp 139-141 °C; IR (KBr): 3049, 2923, 1596, 1481, 1234, 1134, 1018, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.00-7.78 (m, 6H), 7.75-7.71 (m, 1H), 7.57-7.50 (m, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.33-7.21 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.32 (s, 1H), 2.66 (dd, *J* = 13.7, 3.0 Hz, 1H), 2.43 (dd, *J* = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 149.0, 137.6, 137.1 (q, $^2J_{C-F}$ = 38.1 Hz), 136.6, 133.5, 132.7, 129.1, 128.5, 128.3, 127.7, 127.6, 127.1, 127.0, 126.9, 126.6, 126.2, 125.1, 123.0, 122.3, 121.4 (q, $^1J_{C-F}$ = 269.7 Hz), 121.0, 116.5, 103.2, 101.8, 34.3, 27.2 ppm; ESI-MS: m/z 485 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{29}H_{20}F_3N_2O_2$ m/z 485.1471 $[M+H]^+$, found 485.1474.

4.3.8 3-(3-Phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazol-5-yl)phenol (3h). Yield 80%; Mp 172-173 °C; IR (KBr): 3306, 3068, 2951, 1483, 1453, 1228, 1141, 1111, 1014, 761, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.42-7.27 (m, 5H), 7.23-7.16 (m, 2H), 7.08-6.9 (m, 4H), 4.24 (s, 1H), 2.23 (d, *J* = 2.6 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6): δ 157.7, 151.5, 148.6, 140.3, 137.1, 136.6 (q, $^2J_{C-F}$ = 37.9 Hz), 129.2, 128.7, 127.8, 126.8, 126.5, 125.9, 121.7,121.0 (q, $^1J_{C-F}$ = 269.0 Hz), 120.7, 116.2, 116.1, 116.0, 112.6, 102.7, 101.4, 33.9, 26.6 ppm; ESI-MS: m/z 451 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{18}F_3N_2O_3$ m/z 451.1264 $[M+H]^+$, found 451.1268.

4.3.9 3-Phenyl-1-(trifluoromethyl)-5-(3,4,5-trimethoxy phenyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3] dioxocino[4,5-c]pyrazole (3i). Yield 68%; Mp 154-156 °C; IR (KBr): 3037, 3004, 2936, 2836, 1512, 1240, 1126, 1011, 844, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33-7.28 (m, 2H), 7.24-7.19 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.92 (s, 2H), 4.31 (s, 1H), 3.90 (s, 3H), 3.88 (s, 6H), 2.59 (dd, *J* = 13.7, 3.2 Hz, 1H), 2.43 (dd, *J* = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 151.7, 148.9, 138.8, 137.5, 137.0 (q, $^2J_{C-F}$ = 38.1 Hz), 134.9, 129.0, 128.3, 127.1, 127.0, 126.0, 122.3, 121.3 (q, $^1J_{C-F}$ = 268.8 Hz), 120.9, 116.4, 103.09, 103.02, 101.8, 60.8, 56.1, 34.3, 27.1 ppm; ESI-MS: m/z 525 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{28}H_{24}F_3N_2O_5$ m/z 525.1631 $[M+H]^+$, found 525.1621.

4.3.10 5-(4-Methoxyphenyl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3j). Yield 69%; Mp 159-161 °C; IR (KBr): 3062, 2938, 2843, 1599, 1480, 1311, 1256, 1139, 1109, 1018, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.32-7.27 (m, 2H), 7.22-7.17 (m, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 7.02-6.96 (m, 3H), 4.28 (s, 1H), 3.85 (s, 3H), 2.56 (dd, *J* = 13.7, 3.0 Hz, 1H), 2.36 (dd, *J* = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 151.9, 149.1, 137.6, 137.1 (q, $^2J_{C-F}$ = 38.1 Hz), 131.7, 130.5, 129.1, 128.2, 127.0, 126.2, 122.1, 121.4 (q, $^1J_{C-F}$ = 268.8 Hz), 121.1, 116.5, 113.8, 113.6, 103.1, 101.7, 55.3, 34.5, 27.2 ppm; ESI-MS: m/z 465 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{26}H_{20}F_3N_2O_3$ m/z 465.1420 $[M+H]^+$, found 465.1420.

4.3.11 5-(4-(Allyloxy)phenyl)-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3k). Yield 74%; Mp 145-147 °C; IR (KBr): 3071, 2922, 2856, 1598, 1484, 1439, 1311, 1227, 1137, 1012, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.45-7.34 (m, 3H), 7.32-7.16 (m, 5H), 7.10-6.96 (m, 3H), 6.12-5.98 (m, 1H), 5.41 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.56 (d, *J* = 5.0 Hz, 2H), 4.28 (s, 1H), 2.56 (dd, *J* = 13.7, 3.2 Hz, 1H), 2.35 (dd, *J* = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 151.8, 148.9, 141.0, 137.5, 137.0 (q, $^2J_{C-F}$ = 38.1 Hz), 132.9, 129.6, 129.0, 128.2, 127.1, 126.9, 126.1, 122.2, 121.4 (q, $^1J_{C-F}$ = 269.7 Hz), 121.0, 118.1, 117.8, 116.4, 115.4, 112.5, 102.9, 101.7, 68.8, 34.4, 27.1 ppm; ESI-MS: m/z 491 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{28}H_{22}F_3N_2O_3$ m/z 491.1577 $[M+H]^+$, found 491.1588.

4.3.12 3-Phenyl-5-(4-(prop-2-yn-1-yloxy)phenyl)-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo [7,8][1,3]dioxocino[4,5-c]pyrazole (3l). Yield 75%; Mp 137-140 °C; IR (KBr): 3309, 3039, 2925, 2122, 1599, 1483, 1444, 1311, 1286, 1138, 1112, 1019, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 3H), 7.37-7.17 (m, 5H), 7.11-6.96 (m, 3H), 4.73 (d, *J* = 2.4 Hz, 2H), 4.29 (s, 1H), 2.58 (dd, *J* = 13.5, 3.0 Hz, 1H), 2.49 (t, *J* = 2.2 Hz, 1H), 2.36 (dd, *J* = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 151.8, 148.8, 141.1, 137.6 (q, $^2J_{C-F}$ = 37.3 Hz), 137.5, 129.6, 129.0, 128.2, 127.1, 126.9, 126.1, 121.3 (q, $^1J_{C-F}$ = 267.8

Hz), 122.2, 121.1, 118.8, 116.4, 115.5, 112.8, 102.8, 101.7, 78.1, 75.8, 55.8, 34.3, 27.0 ppm; ESI-MS: m/z 489 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{28}H_{20}F_3N_2O_3$ m/z 489.1420 $[M+H]^+$, found 489.1431

4.3.13 5-Methyl-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3m). Yield 76%; Mp 148-150 °C; IR (KBr): 2950, 1599, 1482, 1228, 1129, 1072, 1014, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 2H), 7.34-7.19 (m, 2H), 7.17-7.09 (m, 1H), 6.98-6.84 (m, 2H), 4.2 (s, 1H), 2.37 (dd, J = 13.4, 3.2 Hz, 1H), 2.26 (dd, J = 13.5, 3.0 Hz, 1H), 1.96 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6, 149.1, 137.6, 136.9 (q, $^2J_{C-F}$ = 37.2 Hz), 129.0, 128.0, 127.1, 126.9, 125.9, 121.8, 121.4 (q, $^1J_{C-F}$ = 269.7 Hz), 121.2, 116.3, 102.4, 101.8, 32.2, 26.75, 26.72 ppm; ESI-MS: m/z 373 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{20}H_{16}F_3N_2O_2$ m/z 373.1158 $[M+H]^+$, found 373.1161.

4.3.14 5-ethyl-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3n). Yield 71%; Mp 105-106 °C; IR (KBr): 3066, 2984, 2941, 1597, 1531, 1484, 1399, 1133, 1012, 854, 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, J = 7.7 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.34-7.19 (m, 2H), 7.16-7.08 (m, 1H), 6.96-6.85 (m, 2H), 4.20 (s, 1H), 2.35-2.16 (m, 4H), 1.18 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8, 149.1, 137.6, 136.9 (q, $^2J_{C-F}$ = 38.1 Hz), 129.0, 128.0, 127.0, 126.9, 126.2, 121.7, 121.4 (q, $^1J_{C-F}$ = 268.8 Hz), 121.0, 116.2, 104.4, 101.9, 32.6, 30.0, 26.5, 7.7 ppm; ESI-MS: m/z 387 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{21}H_{18}F_3N_2O_2$ m/z 387.1314 $[M+H]^+$, found 387.1320.

4.3.15 5-Isobutyl-3-phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3o). Yield 70%; Mp 138-139 °C; IR (KBr): 3073, 3027, 2956, 2930, 1511, 1482, 1237, 1117, 1014, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, J = 7.7 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.32-7.19 (m, 2H), 7.16-7.08 (m, 1H), 6.96-6.82 (m, 2H), 4.18 (s, 1H), 2.31 (dd, J = 13.4, 3.2 Hz, 1H), 2.21 (dd, J = 13.4, 3.0 Hz, 1H), 2.15-2.02 (m, 3H), 1.07 (q, J = 6.2, 3.2 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6, 149.0, 137.6, 137.0 (q, $^2J_{C-F}$ = 37.9 Hz), 128.9, 128.0, 127.0, 126.8, 126.3, 121.7, 121.4 (q, $^1J_{C-F}$ = 269.5 Hz), 121.1, 116.3, 104.4, 101.8, 47.7, 30.8, 26.5, 24.1, 23.8 ppm; ESI-MS: m/z 415 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{23}H_{22}F_3N_2O_2$ m/z 415.1627 $[M+H]^+$, found 415.1627.

4.3.16 9-Chloro-3,5-diphenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3p). Yield 70%; Mp 190-192 °C; IR (KBr): 2927, 1480, 1450, 1401, 1316, 1279, 1232, 1138, 1011, 855 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 7.5 Hz, 2H), 7.70-7.63 (m, 2H), 7.53-7.38 (m, 5H), 7.33-7.27 (m, 2H), 7.19-7.13 (m, 1H), 7.03-6.97 (m, 1H), 4.25 (s, 1H), 2.58 (dd, J = 13.5, 3.0 Hz, 1H), 2.34 (dd, J = 13.5, 3.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6): δ 150.0, 148.3, 138.3, 136.8, 136.4 (q, $^2J_{C-F}$ = 38.5 Hz), 129.0, 128.6, 128.0, 127.5, 127.3, 126.8, 126.1, 125.9, 124.9, 120.7 (q, $^1J_{C-F}$ = 269.5 Hz), 120.5, 117.3, 102.6, 100.5, 33.3, 26.3 ppm; ESI-MS: m/z 469 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{17}ClF_3N_2O_2$ m/z 469.0925 $[M+H]^+$, found 469.0932.

4.3.17 9-Bromo-3,5-diphenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3q). Yield 71%; Mp 192-194 °C; IR (KBr): 2925, 2853, 1478, 1451, 1315, 1232, 1140, 1072, 1013, 876 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.70-7.62 (m, 2H), 7.53-7.37 (m, 6H), 7.35-7.27 (m, 2H), 6.95 (d, J = 8.3 Hz, 1H), 4.25 (s, 1H), 2.58 (dd, J = 13.5, 3.0 Hz, 1H), 2.34 (dd, J = 13.5, 3.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 148.9, 139.0, 137.4, 137.1 (q, $^2J_{C-F}$ = 38.1 Hz), 131.1, 129.5, 129.1, 128.6, 128.2, 128.0, 127.3, 125.5, 121.3 (q, $^1J_{C-F}$ = 269.7 Hz), 121.1, 118.3, 114.2, 103.0, 101.0, 34.1, 27.0 ppm; ESI-MS: m/z 513 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{17}BrF_3N_2O_2$ m/z 513.0420 $[M+H]^+$, found 513.0436.

4.3.18 9-Methoxy-3,5-diphenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3r). Yield 76%; Mp 162-165 °C; IR (KBr): 2927, 2854, 1493, 1451, 1314, 1284, 1213, 1141, 1010, 851 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 8.5 Hz, 2H), 7.71-7.66 (m, 2H), 7.50-7.44 (m, 3H), 7.41 (t, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 6.85-6.82 (m, 1H), 6.77-6.73 (m, 1H), 4.23 (s, 1H), 3.79 (s, 3H), 2.56 (dd, J = 13.7, 3.2 Hz, 1H), 2.35 (dd, J = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.5, 149.2, 145.7, 139.6, 137.6, 137.0 (q. $^2J_{C-F}$ = 38.1 Hz), 129.3, 129.1, 128.5, 127.1, 126.8, 125.6, 121.4 (q, $^1J_{C-F}$ = 269.7 Hz), 121.1, 117.1, 113.8, 111.7, 103.2, 101.5, 55.7, 34.4, 27.4 ppm; ESI-MS: m/z 465 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{26}H_{20}F_3N_2O_3$ m/z 465.1420 $[M+H]^+$, found 465.1424.

4.3.19 9-Bromo-7-chloro-3,5-diphenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3s). Yield 70%; Mp 200-204 °C; IR (KBr): 2944, 1595, 1480, 1456, 1316, 1247, 1132, 1031, 1015, 871 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (t, J = 7.7 Hz, 4H), 7.53-7.48 (m, 3H), 7.46 (d, J = 2.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.24 (s, 1H), 4.27 (s, 1H), 2.65 (dd, J = 13.8, 3.2 Hz, 1H), 2.27 (dd, J = 14.0, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.7, 147.7, 138.4, 137.3, 137.1 (q, $^2J_{C-F}$ = 38.1 Hz), 131.4, 129.6, 129.1, 128.8, 128.6, 127.3, 127.2, 125.8, 121.2 (q, $^1J_{C-F}$ = 269.7 Hz), 121.1, 111.0, 103.7, 100.2, 34.1, 27.3 ppm; ESI-MS: m/z 547 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{16}BrClF_3N_2O_2$ m/z 547.0030$[M+H]^+$, found 547.0053.

4.3.20 5-Phenyl-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3t). Yield 78%; Mp 89-91 °C; IR (KBr): 3115, 2928, 1598, 1498, 1289, 1236, 1180, 1132, 1017, 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75-7.65 (m, 2H), 7.50-7.39 (m, 3H), 7.24-7.14 (m, 2H), 7.10-6.93 (m, 2H), 4.23 (s, 1H), 2.49 (dd, J = 13.7, 3.2 Hz, 1H), 2.33 (dd, J = 13.5, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 152.1, 139.7,133.2 (q, $^2J_{C-F}$ = 37.2 Hz), 129.1, 128.3, 128.2, 126.8, 126.0, 125.7, 121.9, 120.6 (q, $^1J_{C-F}$ = 269.5 Hz), 116.5, 102.3, 101.9, 34.6, 26.8 ppm; ESI-MS: m/z 359 $[M+H]^+$;

HRMS (ESI) Anal. calcd. for $C_{19}H_{14}F_3N_2O_2$ m/z 359.1001 $[M+H]^+$, found 359.1015.

4.3.21 5-(p-Tolyl)-1-(trifluoromethyl)-3,11-dihydro-5,11-methanobenzo[7,8][1,3]dioxocino[4,5-c]pyrazole (3u). Yield 73%; Mp 88-89 °C; IR (KBr): 3119, 2925, 1599, 1498, 1235, 1180, 1134, 1109, 1017, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 11.75 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.25-7.13 (m, 4H), 7.01 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.3 Hz, 1H), 4.19 (s, 1H), 2.43 (dd, J = 13.7, 3.0 Hz, 1H), 2.38 (s, 3H), 2.30 (dd, J = 13.7, 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 152.1, 138.9, 136.9, 133.3 (q, $^2J_{C-F}$ = 37.9 Hz), 128.9, 128.1, 126.8, 126.0, 125.6, 121.8, 120.6 (q, $^1J_{C-F}$ = 269.0 Hz), 116.5, 102.1, 102.0, 34.5, 26.8, 21.0 ppm; ESI-MS: m/z 373 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{20}H_{16}F_3N_2O_2$ m/z 373.1158 $[M+H]^+$, found 373.1175.

4.3.22 3-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-3-(2-hydroxyphenyl)-1-phenylpropan-1-one (4). Yield 59%; Mp 166-168 °C; IR (KBr): 3400, 3063, 2924, 1682, 1598, 1406, 1368, 1311, 1101, 752, 689 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 10.96 (br s, 1H), 9.64 (br s, 1H), 7.95 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.45-7.25 (m, 4H), 7.19-7.10 (m, 4H), 7.02-6.94 (m, 2H), 6.84-6.78 (m, 1H), 4.57-4.94 (m, 2H), 3.58 (dd, J = 16.9, 2.5 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 155.6, 146.8, 137.5, 136.9, 135.2, 133.2, 130.5, 130.3, 128.8, 128.5, 128.0, 126.1, 124.4, 120.3, 120.18, 120.11, 119.8, 39.5, 34.3, 11.0 ppm; ESI-MS: m/z 399 $[M+H]^+$; HRMS (ESI) Anal. calcd. for $C_{25}H_{23}N_2O_3$ m/z 399.17032 $[M+H]^+$, found 399.16996.

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Notes and References

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