Synthesis A. Kafle et al. Paper

An Unusual Triazole Synthesis from Aurones

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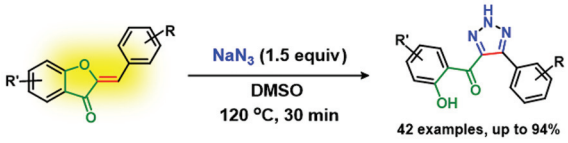

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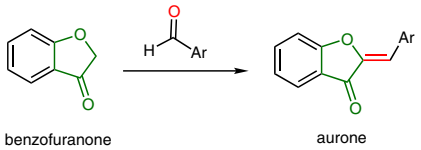
Abstract Attempts to prepare azido-substituted aurones via a copper-catalyzed azidation failed to afford the desired product, but instead resulted in an unusual triazole formation reaction. Further efforts noted that copper was not required for this reaction, but simply thermal treatment with sodium azide in a polar aprotic solvent. A wide range of substitution patterns were tolerated in this reaction to afford the interesting salicyl-substituted triazoles in modest to excellent yield. While the mechanism is not yet clear, a simple elimination/cyclization pathway seems unlikely given the failure of the reaction on the corresponding thioaurones, which feature an even better thiol leaving group. Regardless, the potential utility of these easily accessible, multifunctional compounds should engender further interest and applications.

Key words aurones, triazoles, cycloaddition, metal-free, polar aprotic

Aurones are an interesting minor sub-family of the flavonoid family of natural products.[1] Although known for some time, they have received comparatively little interest until fairly recently. Even this current interest has been fairly limited in terms of its diversity. In part, this situation is the result of most efforts being determined by the synthetic approach employed to access the aurone framework. In virtually all cases, this approach is the Knoevenagel-type condensation of a benzofuranone with an aromatic aldehyde[2] (Scheme 1).



Scheme 1 Condensation route to aurones

While it is true that there are many commercially available aldehydes as well as a number of commercially available benzofuranones, we were interested in potentially combining our recently reported azidation/click reaction of aryl halides to further diversify and functionalize halogen containing aurones.[3] In this way, even greater structural diversity could be accessed without the need to synthesize a new aldehyde for each new aurone.

In addition, this same azidation chemistry in the absence of an alkyne should afford the unknown 4-azidoaurone. This compound or similar azidoaurones are expected to be suitable substrates for photoaffinity labeling via nitrene generation and thus find application in studies to better understand the interaction of these compound with biological systems.[4]

With these twin goals in mind, iodoaurone **1** was selected as a substrate for an in situ azidation/click reaction. Initial attempts did result in consumption of the iodoaurone, but failed to afford any of the anticipated triazole **2** (Scheme 2). In an effort to understand the failure of this transformation, iodoaurone **1** was simply subjected to our standard azidation conditions but without the alkyne [sodium azide, catalytic copper(I) iodide and *N*,*N*′-dimethylethylenediamine in choline chloride/glycerol (CC/G)]. Again, this consumed the starting material, but failed to afford any azide **3**. Further variations in solvent, catalyst, and temperature likewise only resulted in conversion to a new unknown product that did not contain an azide, but featured most of the anticipated spectral features of an aurone with the exception of the very characteristic enone β-proton.

After several other failed attempts, new attempts were made to react cyanoaurone **5a** with sodium azide to form the corresponding tetrazole **4** (Scheme 3). Again, the reaction failed to afford the anticipated tetrazole but did result in consumption of the starting material and the formation of a new polar product that showed considerable similarity

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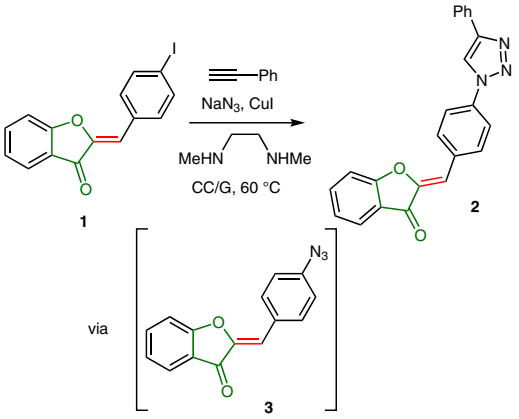
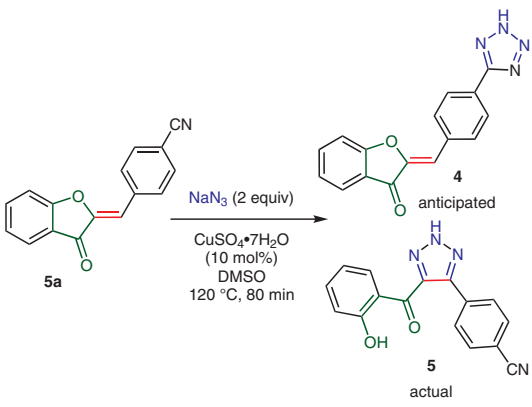


Scheme 2 Azidation/click attempt

to that obtained from the reactions with iodoaurone **1**. This product could be isolated as a solid that could be crystallized to afford crystals suitable for X-ray diffraction analysis[5] (Scheme 3). This analysis confirmed that the product was indeed not a tetrazole, but actually the triazole **5**.

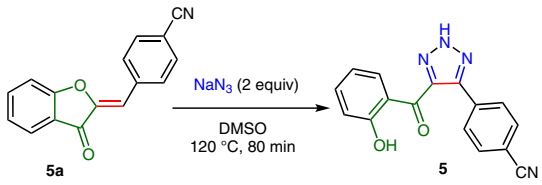


Scheme 3 New triazole formation

With this structural confirmation, reexamination of the products from the reaction with iodoaurone **1** proved to have similarly afforded these unusual triazole products. Further optimization of this transformation was conducted using cyanoaurone **5a** (Table 1).

Using sodium azide in DMSO without any catalyst also afforded the triazole product **5**. Further attempts at optimization of this transformation noted that polar aprotic solvents were good for this reaction, affording modest to good yields of the triazole after short reaction times at moderate temperature (120 °C). Decreasing the temperature resulted in slower conversion to the triazole, with the reaction at 100 °C requiring 3 hours and one at 80 °C requiring 6 hours. Further reduction in temperature resulted in a very sluggish and unclean reaction. Less polar solvents (THF and 1,4-dioxane) were not effective, while a protic solvent (EtOH) was slower, but did afford the product in a reduced yield.

Table 1 Reaction Conditions Study



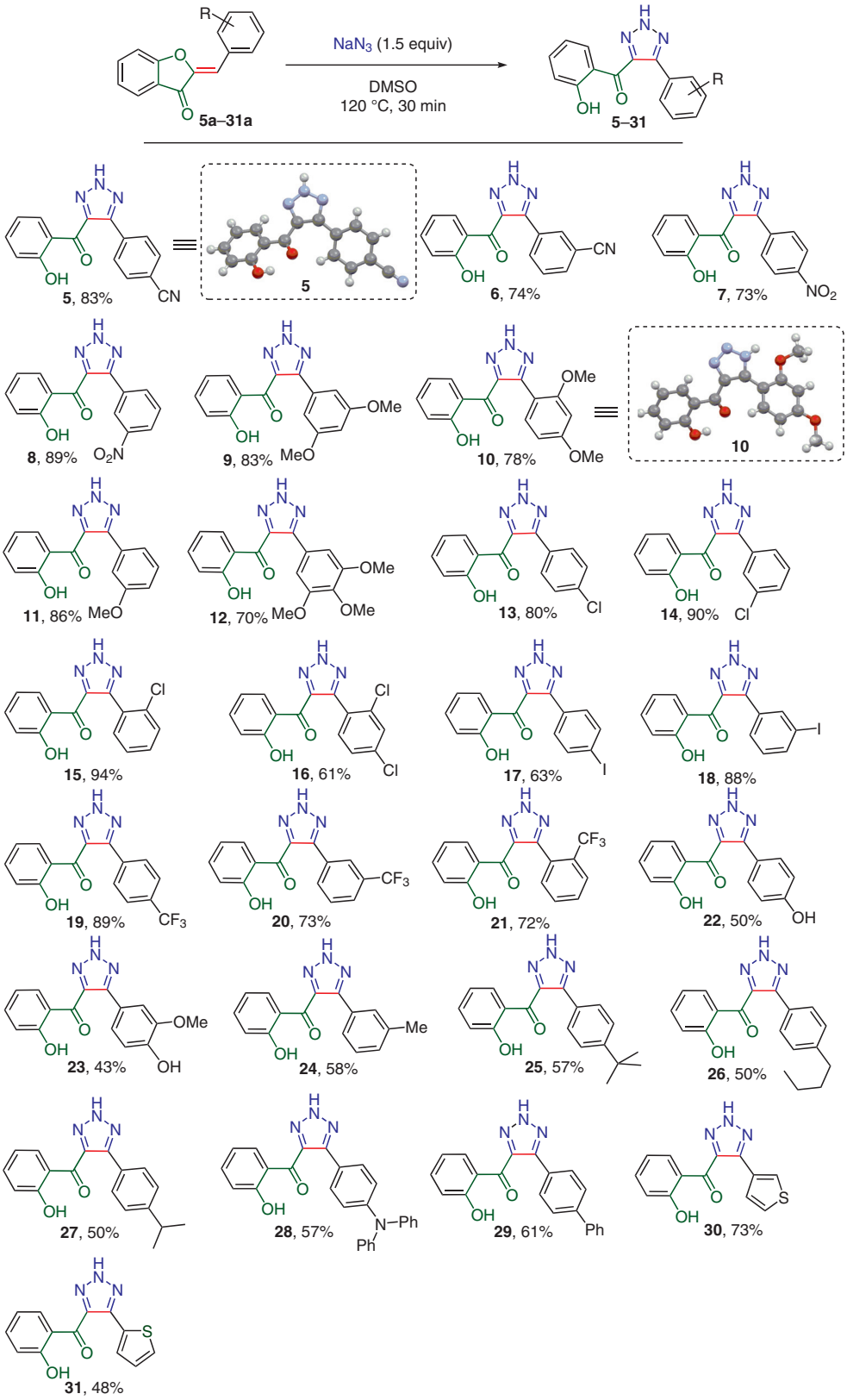
Entry	Condition modification	Time	Yield (%)[a]
1	$CuSO_4$, 140 °C	80 min	100 (75)
2	none	30 min	100 (83)
3	80 °C	6 h	100 (ND)
4	100 °C	3 h	100 (ND)
5	DMF, 105 °C	20 min	100 (88)
6	1,4-dioxane, 105 °C	15 h	NR
7	THF, 65 °C	24 h	NR
8	EtOH (95%), 105 °C	15 h	75 (ND)
9	glacial AcOH, 120 °C	12 h	NR

[a] Conversion yields by ^{1}H NMR analysis (values in parentheses are isolated yields). ND = Not determined; NR = no reaction.

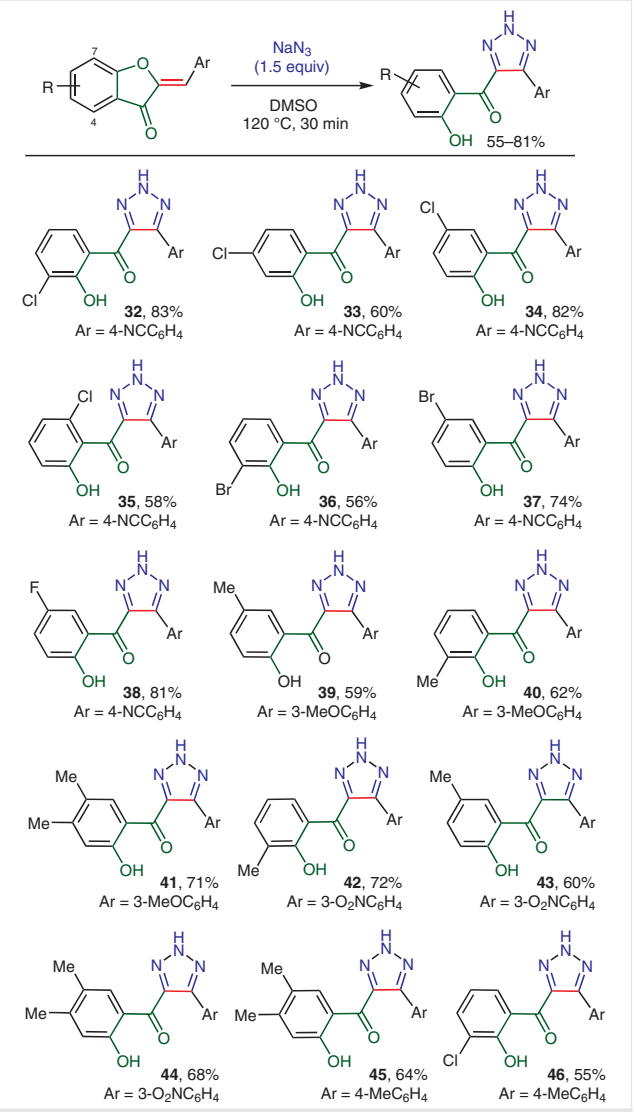
While the results in Table 1 might appear to indicate that DMF was the best solvent, further examples did not demonstrate this to be a consistent result. Further, one major challenge with this chemistry was product isolation. The triazole products are quite polar and frequently do not afford good recovery following chromatography. DMSO could be removed much more readily from the reactions than DMF and was used in all subsequent examples.

In examining the scope of the reaction, variations of the aryl group proved to be well tolerated (Scheme 4). While the isolated yields varied from near 50% to just under 90%, there was no clear trend. Electron-withdrawing groups afforded high yields, as did methyl ethers. Most halogens were similarly efficient. Curiously, free hydroxyl groups and alkyl groups tended to afford the lowest yields. In the case of free hydroxyl groups, this is likely due to their highly polar nature, making isolation and purification difficult. It is worth noting that NMR analysis of the crude reaction mixtures showed clean conversion to product, with only small amounts (<10%) of starting material or unidentified byproducts as well as residual solvent. Further, mass balance was near quantitative, demonstrating that the yield challenge is clearly in the purification step. Two heteroaromatics that were explored afforded similar yields.

In probing the utility of the reaction with respect to the benzofuranone portion, it proved to be equally general (Scheme 5). Halogens were tolerated at all positions as were methyl groups at all 3 positions that were tested. Yields ranged from 55–81%.



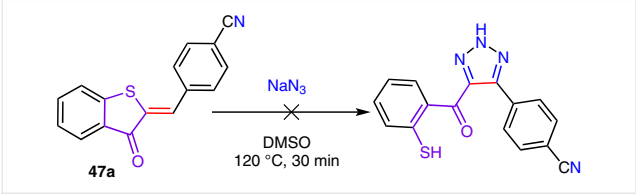
Scheme 4 Aurone variations



Scheme 5 Benzofuranone variations

Additional peaks observed, which were particularly evident in the ^{13}C NMR of some triazoles, suggested the presence of tautomeric mixtures that depend on the concentration and type of solvent used. Tautomerism has been reported as a common phenomenon in 1,2,3-triazoles,[6] which in our case, was further evidenced in the crystal structures of triazoles **5** and **10** which feature the N2 and N1 tautomers respectively (Figure S1).[5] This tautomerization is evident from the hybridization and bond lengths indicated in the crystal structures and the inferred location of hydrogen atoms.

With respect to the reaction mechanism, it is unclear at this point whether some form of Michael addition/elimination/cyclization sequence, a cycloaddition/elimination sequence, or an elimination to an intermediate ynone followed by cycloaddition is occurring. Considering that ynones are known to readily undergo reaction with sodium azide to afford triazoles, elimination/cycloaddition would appear to be the simplest mechanistic explanation.[7] Unfortunately, attempts to observe a ynone intermediate have not been successful and reactions under the same reaction conditions using thioaurone **47a** afforded only recovered starting material even though it would be expected that elimination of the better thiol leaving group would be more facile and thus afford better yields of the triazole product (Scheme 6). Additionally, attempts to induce elimination using DBU in DMSO at temperatures up to 120 °C for up to 12 hours have resulted only in recovery of the starting aurone, as has thermal treatment of the aurone in the absence of sodium azide.



Scheme 6 Thioaurone attempt

From the literature, the closest transformation was reported a number of years ago by Bognar and co-workers on the conversion of dibromochalcones with sodium azide in DMF into a number of different compounds including a triazole.[8] Even in this case, the mechanism is unclear, and a number of possible pathways are proposed. Ring openings of aurones using methyl isocyanoacetate have been reported recently by Shao and co-workers for which a more complicated cyclization/ring opening pathway has been proposed.[9] However, this reaction also requires a base catalyst and proceeds best in protic solvents, unlike our conversion to triazoles. Msadek and co-workers have reported the ring-opening synthesis of pyrazoles from aurones by reaction with aryldiazomethanes under mild thermal conditions. They propose that this reaction occurs via cycloaddition followed by elimination to afford the aromatic pyrazole, but no mechanistic evidence is provided.[10] As a result, the mechanism for this transformation to triazoles is far from clear at present.

In conclusion, we have observed an unusual ring-opening triazole formation by the reaction of aurones with sodium azide. The product triazoles feature two clear sites for alkylation chemistry as well as great opportunity for modification at many sites in the ring system. Given this potential and their ease of access, it is anticipated that they could prove to be new, unexplored scaffolds for further development.

All the reactions were done under an air atmosphere. ^{1}H and ^{13}C NMR of all the compounds were recorded on JEOL AS (500 and 300 MHz) NMR instrument and chemical shifts were recorded in ppm. All the chemical shifts were recorded taking $CDCl_3$ or DMSO, or acetone as a standard reference.[11] Standard abbreviations are used for multiplicities. Cary 630 FT-IR (Agilent Technologies) was used to collect IR spectra. All mass spectra were acquired on a Waters Synapt HDMS QToF with Ion Mobility. All extracts were concentrated under reduced pressure using a Büchi Rotary Evaporator. During purification and identification of compounds, TLC was performed on silica gel coated TLC plates and monitored by short wavelength (254 nm) UV light. Products were purified by silica gel column chromatography. ACS grade reagents were employed during the experiments.

The synthesis and characterization of starting aurones are described in the Supporting Information.

Triazoles; General Procedure

In a 3-dram glass vial, aurone (1 equiv) and NaN_3 (1.5 equiv) were combined and dissolved in regular DMSO (1.5 mL). The reaction mixture was then stirred for 30 min at 120 °C in a sand bath. The mixture immediately changed its color to dark brown. The reaction was monitored by TLC. After 30 min, the mixture was transferred to a 50 mL centrifuge tube, diluted with distilled H_2O, and extracted several times with EtOAc. To remove residual DMSO, the organic fraction was then washed with distilled H_2O followed by brine. The organic fraction was concentrated in vacuo and the crude material was further purified by flash column chromatography using mixtures of hexane and EtOAc (20–50% EtOAc/hexane) to obtain the desired triazole.

4-[5-(2-Hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (5)

From aurone **5a** (215 mg, 0.87 mmol), no chromatographic separation was needed; yield: 241 mg (83%); yellow solid; mp 162–164 °C.

IR (neat): 3160, 2997, 2924, 2238, 1737, 1628, 1469, 1432, 1264, 1233, 1153, 991, 920, 747 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.29–8.20 (m, 1 H), 8.02 (d, *J* = 8.5 Hz, 2 H), 7.88 (d, *J* = 8.5 Hz, 2 H), 7.62 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.04 (dd, *J* = 8.5, 0.9 Hz, 1 H), 6.98 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1 H).

^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 193.4, 164.3, 138.1, 135.5, 134.9, 133.1, 133.0, 130.2, 130.1, 120.5, 119.9, 119.0, 118.8, 113.4 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* calcd [M + H] for $C_{16}H_{11}N_4O_2$: 291.0882; found: 291.0885.

3-[5-(2-Hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (6)

From aurone **6a** (94 mg, 0.38 mmol); eluent: 40% EtOAc/hexane; yield: 82 mg (74%); yellow solid; mp 159–161 °C.

IR (neat): 3306, 3073, 2924, 2231, 1628, 1600, 1475, 1315, 1145, 1119, 924, 760, 732 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.31 (d, *J* = 7.5 Hz, 1 H), 8.24 (s, 1 H), 8.13 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.88–7.85 (m, 1 H), 7.70 (dd, *J* = 10.0, 6.0 Hz, 1 H), 7.61 (ddd, *J* = 10.0, 6.0, 1.5 Hz, 1 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.98 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1 H).

^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 193.1, 164.3, 138.0, 134.9, 133.9, 133.4, 132.2, 132.9, 132.5, 131.8, 130.6, 120.5, 119.9, 118.9, 118.7, 113.4 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{11}N_4O_2$: 291.0882; found: 291.0879.

(2-Hydroxyphenyl)[5-(4-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (7)

From aurone **7a** (80 mg, 0.30 mmol); eluent: 40% EtOAc/hexane; yield: 68 mg (73%); yellow solid; mp 200–202 °C.

IR (neat): 3471, 2903, 1596, 1467, 1438, 1207, 1162, 1149, 1041, 929, 834, 754 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.34 (d, *J* = 9.0 Hz, 2 H), 8.26 (dd, *J* = 8.0, 1.5 Hz, 1 H), 8.10 (d, *J* = 9.0 Hz, 2 H), 7.63 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.99 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1 H).

^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 193.4, 164.3, 149.0, 138.2, 136.8, 134.9, 130.6, 130.5, 124.4, 120.5, 119.9, 118.8 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}N_4O_4$: 311.0780; found: 311.0781.

(2-Hydroxyphenyl)[5-(3-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (8)

From aurone **8a** (101.5 mg, 0.38 mmol); eluent: 50% EtOAc/hexane; yield: 105 mg (89%); yellow solid; mp 157–158 °C.

IR (neat): 3110, 2903, 1628, 1534, 1482, 1350, 1253, 1153, 1100, 925, 817, 747 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.72 (br s, 1 H), 8.32 (t, *J* = 7.5 Hz, 2 H), 8.27 (d, *J* = 8.5 Hz, 1 H), 7.79 (t, *J* = 8.0 Hz, 1 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.99 (t, *J* = 7.5 Hz, 1 H).

^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 193.2, 164.3, 149.2, 138.1, 134.9, 132.2, 130.7, 124.6, 124.4, 124.2, 124.0, 120.5, 119.9, 118.8 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}N_4O_4$: 311.0780; found: 311.0783.

[5-(3,5-Dimethoxyphenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (9)

From aurone **9a** (107.3 mg, 0.38 mmol); eluent: 50% EtOAc/hexane; yield: 103 mg (83%); waxy solid; mp 79–82 °C.

IR (neat): 3478, 3070, 2905, 2838, 1600, 1596, 1469, 1439, 1289, 1248, 1151, 1069, 752, 678 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.99 (s, 1 H), 7.99 (d, *J* = 6.0 Hz, 1 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.02 (d, *J* = 8.5 Hz, 1 H), 6.85 (d, *J* = 7.5 Hz, 1 H), 6.82 (s, 2 H), 6.49 (d, *J* = 2.5 Hz, 1 H), 3.74 (s, 6 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 192.4, 163.6, 160.9, 137.4, 133.8, 119.6, 119.3, 118.3, 106.7, 102.1, 55.6.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{17}H_{16}N_3O_4$: 326.1141; found: 326.1138.

(2-Hydroxyphenyl)[5-(3-methoxyphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (10)

From aurone **10a** (96 mg, 0.38 mmol); eluent: 50% EtOAc/hexane; yield: 96 mg (78%); yellow solid; mp 94–96 °C.

IR (neat): 3078, 2959, 2907, 1628, 1598, 1585, 1484, 1441, 1225, 1150, 1033, 1009, 752 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.03 (s, 1 H), 8.05 (d, *J* = 5.0 Hz, 1 H), 7.51 (ddd, *J* = 8.5, 3.0, 1.5 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.27 (overlapped with residual $CHCl_3$ in the solvent, 1 H) 7.23 (d, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.96 (d, *J* = 8.1 Hz, 1 H), 6.87 (t, *J* = 8.0 Hz, 1 H), 3.79 (s, 3 H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 192.3, 163.5, 159.6, 140.7, 137.3, 133.8, 129.9, 128.6, 121.0, 119.5, 119.3, 118.3, 115.8, 114.1, 55.4.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{14}N_4O_3$: 296.1035; found: 296.1038.

[5-(2,4-Dimethoxyphenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (11)

From aurone **11a** (107.3 mg, 0.38 mmol); eluent: 50% EtOAc/hexane; yield: 96 mg (86%); yellow solid; mp 194–195 °C.

IR (neat): 3237, 1624, 1581, 1499, 1458, 1441, 1210, 1032, 925, 819, 756 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 11.55 (s, 1 H), 7.8 (br s, 1 H), 7.46 (dd, *J* = 18.6, 7.5 Hz, 2 H), 6.95 (d, *J* = 8.1 Hz, 1 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 6.62 (dd, *J* = 8.5, 2.1 Hz, 1 H), 6.53 (s, 1 H), 3.79 (s, 3 H), 3.43 (s, 3 H).

$^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ = 194.5, 164.1, 163.3, 158.3, 137.4, 134.6, 131.8, 120.6, 119.7, 118.5, 106.4, 99.2, 55.8, 55.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{17}H_{16}N_3O_4$: 326.1141; found: 326.1143.

(2-Hydroxyphenyl)[5-(3,4,5-trimethoxyphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (12)

From aurone **12a** (62.5 mg, 0.20 mmol); eluent: 50% EtOAc/hexane; yield: 50 mg (70%); yellow solid; mp 211–213 °C.

IR (neat): 2957, 2928, 1631, 1596, 1482, 1441, 1248, 1132, 983, 935, 760 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 7.77 (s, 1 H), 7.52–7.42 (m, 1 H), 7.10 (s, 2 H), 6.93 (m, 2 H), 3.77 (m, 6 H), 3.69 (m, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6): δ = 190.7, 159.3, 152.7, 138.3, 134.9, 131.9, 123.5, 118.9, 117.2, 106.1, 60.1, 55.9.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{18}H_{18}N_3O_5$: 356.1247; found: 356.1246.

[5-(4-Chlorophenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (13)

From aurone **13a** (97.5 mg, 0.38 mmol); eluent: 40% EtOAc/hexane; yield: 91 mg (80%); yellow solid; mp 147–149 °C.

IR (neat): 3150, 2913, 2825 (br), 1626, 1596, 1443, 1259, 1318, 1259, 1222, 1154, 1099, 924, 791 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 12.03 (br s, 1 H), 8.28 (d, *J* = 9.0 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.59 (ddd, *J* = 8.5, 4.5, 0.7 Hz, 1 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 6.96 (dd, *J* = 7.2 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ = 193.5, 164.3, 137.9, 135.6, 134.9, 131.1, 130.9, 129.4, 129.3, 120.5, 119.8, 118.7 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}ClN_3O_2$: 300.0540; found: 300.0545.

[5-(3-Chlorophenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (14)

From aurone **14a** (97.5 mg, 0.38 mmol); eluent: 30% EtOAc/hexane; yield: 103 mg (90%); waxy solid; mp 67–69 °C.

IR (neat): 3161 (br), 2920, 1626, 1598, 1445, 1255, 1153, 925, 754, 680 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 11.98 (s, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 1.5 Hz, 1 H), 7.57–7.49 (m, 2 H), 7.40–7.29 (m, 1 H), 7.05 (d, *J* = 8.5 Hz, 1 H), 6.87 (t, *J* = 7.6 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 191.9, 163.6, 141.1, 137.6, 134.8, 133.7, 129.9, 128.7, 126.9, 119.4, 118.5 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}ClN_3O_2$: 300.0540; found: 300.0541.

[5-(2-Chlorophenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (15)

From aurone **15a** (97.5 mg, 0.38 mmol); eluent: 40% EtOAc/hexane; yield: 107 mg (94%); yellow solid; mp 102–105 °C.

IR (neat): 3460, 3091, 2812, 1601, 1473, 1452, 1249, 1153, 1037, 992, 752 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.91 (s, 1 H), 8.36 (br s, 1 H), 7.56–7.54 (m, 1 H), 7.51 (d, *J* = 7.0 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.44–7.38 (m, 2 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.93 (t, *J* = 7.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.1, 163.6, 137.2, 133.5, 133.4, 131.5, 131.1, 130.1, 127.2, 119.3, 119.1, 118.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}ClN_3O_2$: 300.0540; found: 300.0538.

[5-(2,4-Dichlorophenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (16)

From aurone **16a** (128 mg, 0.44 mmol); eluent: 30% EtOAc/hexane; yield: 90 mg (61%); yellow waxy solid; mp 62–64 °C.

IR (neat): 3132, 2909, 1626, 1601, 1447, 1248, 1151, 922, 618 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.88 (s, 1 H), 8.35 (br s, 1 H), 7.56–7.52 (m, 1 H), 7.51–7.49 (m, 2 H), 7.39 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.94 (t, *J* = 7.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 190.8, 163.7, 137.3, 136.5, 134.2, 133.4, 132.3, 129.9, 127.6, 119.3, 119.0, 118.4.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{10}Cl_2N_3O_2$: 334.0150; found: 334.0151.

(2-Hydroxyphenyl)[5-(4-iodophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (17)

From aurone **17a** (250.7 mg, 0.72 mmol); eluent: 30% EtOAc/hexane; yield: 177 mg (63%); yellow solid; mp 161–163 °C.

IR (neat): 3132, 2909, 1626, 1601, 1447, 1248, 1151, 922, 618 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.98 (s, 1 H), 8.08 (br s, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.55 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.26 (s, 1 H), 7.06 (dd, *J* = 8.5, 1.0 Hz, 1 H), 6.91 (t, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.1, 163.58, 138.0, 137.6, 133.7, 130.3, 119.5, 119.4, 118.6, 96.5.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}IN_3O_2$: 391.9896; found: 391.9896.

(2-Hydroxyphenyl)[5-(3-iodophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (18)

From aurone **18a** (212.4 mg, 0.61 mmol); eluent: 30% EtOAc/hexane; yield: 209 mg (88%); waxy solid; mp 60–61 °C.

IR (neat): 2887, 3060 (br), 2920, 1628, 1443, 1257, 1218, 1153, 1009, 924, 752 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.27 (d, *J* = 8.0 Hz, 1 H), 8.21 (t, *J* = 1.5 Hz, 1 H), 7.83 (t, *J* = 7.5 Hz, 2 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.98 (t, *J* = 7.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 209.5, 192.1, 163.6, 145.5, 141.1, 138.5, 137.3, 133.8, 130.2, 128.0, 119.5, 119.3, 118.4, 94.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}IN_3O_2$: 391.9896; found: 391.9898.

(2-Hydroxyphenyl){5-[4-(trifluoromethyl)phenyl]-2*H*-1,2,3-triazol-4-yl}methanone (19)

From aurone **19a** (98.7 mg, 0.34 mmol), no chromatographic separation was needed; yield: 101 mg (89%); yellow solid; mp 127–129 °C.

IR (neat): 3226, 2828, 1626, 1607, 1479, 1450, 1432, 1322, 1158, 1110, 920, 845 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.96 (s, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.56 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.08 (d, *J* = 8.5 Hz, 1 H), 6.92 (t, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 192.1, 163.7, 146.2, 141.3, 137.8, 133.6, 131.8 (q, $^2J_{C,F}$ = 30 Hz), 129.1, 127.4 (q, $^1J_{C,F}$ = 240 Hz), 125.7 (q, $^3J_{C,F}$ = 4.5 Hz), 119.5, 119.4, 118.6 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{11}F_3N_3O_2$: 334.0803; found: 334.0800.

(2-Hydroxyphenyl){5-[3-(trifluoromethyl)phenyl]-2*H*-1,2,3-triazol-4-yl}methanone (20)

From aurone **20a** (119 mg, 0.41 mmol); eluent: 30% EtOAc/hexane; yield: 99 mg (73%); mp 113–115 °C.

IR (neat): 3226, 2828, 1626, 1607, 1479, 1432, 1322, 1110, 920, 758 cm^{-1}.

^1H NMR (301 MHz, $CDCl_3$): δ = 11.97 (s, 1 H), 8.07 (d, *J* = 9.0 Hz, 2 H), 7.91 (d, *J* = 7.5 Hz, 1 H), 7.69 (d, *J* = 7.4 Hz, 1 H), 7.54 (t, *J* = 7.8 Hz, 2 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 6.89 (t, *J* = 7.7 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.9, 163.6, 141.1, 137.7, 133.6, 132.1, 131.2 (q, $^2J_{C,F}$ = 32.5 Hz), 129.3, 129.1, 126.4 (q, $^3J_{C,F}$ = 2.5 Hz), 125.6 (q, $^3J_{C,F}$ = 3.75 Hz), 123.8 (q, $^1J_{C,F}$ = 270 Hz), 119.4, 119.3, 118.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{11}F_3N_3O_2$: 334.0803; found: 334.0801.

(2-Hydroxyphenyl){5-[2-(trifluoromethyl)phenyl]-2*H*-1,2,3-triazol-4-yl}methanone (21)

From aurone **21a** (41 mg, 0.14 mmol); eluent: 30% EtOAc/hexane; yield: 36 mg (72%); yellow solid; mp 147–150 °C.

IR (neat): 3084, 2855, 1629, 1574, 1439, 1328, 1253, 1076, 973, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.90 (s, 1 H), 8.48 (d, *J* = 7.5 Hz, 1 H), 7.77 (d, *J* = 7.5 Hz, 1 H), 7.61 (td, *J* = 15.0, 7.3 Hz, 2 H), 7.53–7.46 (m, 2 H), 6.99 (d, *J* = 8.0 Hz, 1 H), 6.93 (t, *J* = 7.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 190.3, 163.6, 143.3, 137.1, 133.61, 132.3, 131.8, 129.9, 129.3 (q, $^2J_{C,F}$ = 30 Hz), 127.5, 126.5 (q, $^3J_{C,F}$ = 5 Hz), 123.7 (q, $^1J_{C,F}$ = 272.5 Hz), 120.4, 119.3, 118.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{11}F_3N_3O_2$: 334.0803; found: 334.0804.

(2-Hydroxyphenyl)[5-(4-hydroxyphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (22)

From aurone **22a** (100 mg, 0.42 mmol); eluent: 50% EtOAc/hexane; yield: 59 mg (50%); yellow solid; mp 130–132 °C.

IR (neat): 3131, 2961, 1615, 1592, 1434, 1223, 922, 748 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.26 (d, *J* = 6.0 Hz, 1 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 7.56–7.50 (m, 1 H), 6.98 (d, *J* = 8.5 Hz, 1 H), 6.92–6.87 (m, 3 H) (peaks for another tautomer were also observed).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 193.8, 164.3, 159.5, 137.6, 135.0, 131.0, 130.8, 120.7, 119.7, 118.6, 116.3, 116.0 (peaks for another tautomer were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{11}N_3O_3$: 282.0878; found: 282.0875.

[5-(4-Hydroxy-3-methoxyphenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (23)

From aurone **23a** (110 mg, 0.41 mmol); eluent: 50% EtOAc/hexane; yield: 55 mg (43%); yellow solid; mp 186–187 °C.

IR (neat): 3181, 2939, 1628, 1594, 1486, 1445, 1214, 927, 789 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 12.08 (s, 1 H), 8.26 (s, 1 H), 7.60 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.46 (d, *J* = 1.5 Hz, 1 H), 7.30 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.02 (d, *J* = 8.5 Hz, 1 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 3.87 (s, 3 H) (peaks for another tautomer were also observed).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 194.0, 164.3, 148.9, 148.3, 137.7, 135.1, 122.9, 120.9, 119.8, 118.7, 116.0, 113.1, 56.3 (peaks for other tautomers were also observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{14}N_3O_4$: 312.0984; found: 312.0981.

(2-Hydroxyphenyl)[5-(*m*-tolyl)-2*H*-1,2,3-triazol-4-yl]methanone (24)

From aurone **24a** (45 mg, 0.19 mmol); eluent: 30% EtOAc/hexane; yield: 31 mg (58%); waxy solid.

IR (neat): 3134, 2918, 1626, 1445, 1309, 1257, 1151, 925, 754 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.05 (s, 1 H), 8.11 (d, *J* = 8.0 Hz, 1 H), 7.53–7.46 (m, 2 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.23 (d, *J* = 7.5 Hz, 1 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 2.34 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.3, 163.7, 141.1, 138.7, 137.3, 133.9, 130.8, 129.3, 128.8, 127.6, 125.9, 119.7, 119.3, 118.4, 77.4, 77.2, 76.9, 21.5.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{14}N_3O_2$: 280.1086; found: 280.1084.

{5-[4-(*tert*-Butyl)phenyl]-2*H*-1,2,3-triazol-4-yl}(2-hydroxyphenyl)methanone (25)

From aurone **25a** (142 mg, 0.51 mmol); eluent: 20% EtOAc/hexane; yield: 93 mg (57%); yellow solid; mp 138–139 °C.

IR (neat): 3272, 2969, 1628, 1452, 1328, 1205, 998, 922, 756 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.07 (s, 1 H), 8.14 (s, 1 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.50 (t, *J* = 7.8 Hz, 1 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.86 (t, *J* = 7.6 Hz, 1 H), 1.32 (s, 9 H) (COSY, HMQC, HMBC data are provided in the Supporting Information).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.3, 163.7, 153.4, 137.2, 133.9, 128.4, 125.9, 119.7, 119.3, 118.4, 34.9, 31.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{19}H_{20}N_3O_2$: 322.1555; found: 322.1556.

[5-(4-Butylphenyl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (26)

From aurone **26a** (147.5 mg, 0.53 mmol); eluent: 20% EtOAc/hexane; yield: 85 mg (50%); brown oil.

IR (neat): 3105, 2928, 1628, 1469, 1253, 1151, 922, 756 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.08 (s, 1 H), 8.16 (s, 1 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 0.7 Hz, 2 H), 7.05 (d, *J* = 8.5 Hz, 1 H), 6.90 (t, *J* = 7.5 Hz, 1 H), 2.65 (t, *J* = 7.5 Hz, 2 H), 1.62 (dt, *J* = 13.0, 7.5 Hz, 2 H), 1.37 (dq, *J* = 14.5, 7.5 Hz, 2 H), 0.93 (t, *J* = 7.5 Hz, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.4, 163.6, 145.2, 140.7, 137.2, 133.9, 128.9, 128.6, 119.7, 119.2, 118.3, 35.6, 33.4, 22.5, 14.0.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{19}H_{20}N_3O_2$: 322.1555; found: 322.1554.

(2-Hydroxyphenyl)[5-(4-isopropylphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (27)

From aurone **27a** (129.5 mg, 0.49 mmol); eluent: 20% EtOAc/hexane; yield: 75 mg (50%); yellow solid; mp 125–126 °C.

IR (neat): 3250, 2961, 1618, 1488, 1452, 1244, 1210, 1162, 998, 924, 761 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.06 (s, 1 H), 8.12 (d, *J* = 7.5 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 2.0 Hz, 1 H), 7.24 (d, *J* = 1.0 Hz, 1 H), 7.03 (d, *J* = 8.5 Hz, 1 H), 6.84 (t, *J* = 7.5 Hz, 1 H), 3.12–2.81 (m, 1 H), 1.24 (d, *J* = 7.0 Hz, 6 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.3, 163.7, 151.1, 140.8, 137.2, 133.9, 128.7, 127.1, 119.7, 119.2, 118.4, 34.1, 23.8.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{18}H_{18}N_3O_2$: 308.1399; found: 308.1401.

{5-[4-(Diphenylamino)phenyl]-2*H*-1,2,3-triazol-4-yl}(2-hydroxyphenyl)methanone (28)

From aurone **28a** (210 mg, 0.54 mmol); eluent: 30% EtOAc/hexane; yield: 133 mg (57%); orange solid; mp 88–90 °C.

IR (neat): 3159, 2922, 1600, 1590, 1486, 1447, 1253, 1151, 920, 821, 754, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.07 (s, 1 H), 8.13 (s, 1 H), 7.55 (dd, *J* = 8.5, 2.0 Hz, 2 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.26 (t, *J* = 7.0 Hz, 4 H), 7.10 (d, *J* = 8.0 Hz, 4 H), 7.06 (t, *J* = 7.5 Hz, 2 H), 7.04–6.99 (m, 3 H), 6.81 (t, *J* = 7.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.4, 163.7, 149.6, 147.0, 137.2, 133.9, 129.6, 125.5, 124.1, 121.7, 119.7, 119.2, 118.4.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{27}H_{21}N_4O_2$: 433.1664; found: 433.1665.

[5-([1,1′-Biphenyl]-4-yl)-2*H*-1,2,3-triazol-4-yl](2-hydroxyphenyl)methanone (29)

From aurone **29a** (137 mg, 0.46 mmol); eluent: 20% EtOAc/hexane; yield: 94 mg (61%); yellow solid; mp 165–166 °C.

IR (neat): 3071, 2920, 1628, 1596, 1475, 1445, 1259, 1223, 1156, 924, 735 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.06 (s, 1 H), 8.15 (d, *J* = 6.5 Hz, 1 H), 7.78 (d, *J* = 8.5 Hz, 2 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 7.61–7.59 (m, 2 H), 7.54–7.50 (m, 1 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.38 (ddd, *J* = 7.5, 4.0, 1.5 Hz, 1 H), 7.05 (dd, *J* = 8.0, 1.0 Hz, 1 H), 6.90–6.87 (m, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 206.8, 192.3, 163.7, 142.7, 140.9, 140.0, 137.4, 133.9, 129.1, 129.0, 127.9, 127.5, 127.2, 119.6, 119.3, 118.4.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{21}H_{16}N_3O_2$: 342.1242; found: 342.1238.

(2-Hydroxyphenyl)[5-(thiophen-3-yl)-2*H*-1,2,3-triazol-4-yl]methanone (30)

From aurone **30a** (89 mg, 0.39 mmol); eluent: 20% EtOAc/hexane; yield: 77 mg (73%); yellow solid; mp 125–126 °C.

IR (neat): 2883, 2922, 1628, 1600, 1445, 1309, 1255, 1108, 931, 732 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.11 (s, 1 H), 8.17 (d, *J* = 8.0 Hz, 1 H), 8.07 (d, *J* = 2.0 Hz, 1 H), 7.52 (dd, *J* = 12.0, 6.0 Hz, 2 H), 7.38 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 6.89 (t, *J* = 7.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.0, 163.7, 140.8, 137.3, 133.9, 127.6, 127.3, 126.6, 119.7, 119.3, 118.5.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{13}H_{10}N_3O_2S$: 272.0493; found: 272.0491.

(2-Hydroxyphenyl)[5-(thiophen-2-yl)-2*H*-1,2,3-triazol-4-yl]methanone (31)

From aurone **31a** (105 mg, 0.46 mmol); eluent: 30% EtOAc/hexane; yield: 60 mg (48%); yellow solid; mp 131–132 °C.

IR (neat): 3080, 2928, 1626, 1596, 1467, 1443, 1255, 1161, 985, 912, 752 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.5 Hz, 1 H), 7.80 (dd, *J* = 4.0, 1.0 Hz, 1 H), 7.54 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1 H), 7.45 (dd, *J* = 5.0, 1.0 Hz, 1 H), 7.12 (dd, *J* = 5.0, 3.5 Hz, 1 H), 7.08–7.05 (dd, *J* = 8.5, 1.0 Hz, 1 H), 6.92 (t, *J* = 7.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.7, 163.8, 140.5, 137.3, 133.8, 129.5, 128.4, 127.9, 119.7, 119.3, 118.5.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{13}H_{10}N_3O_2S$: 272.0493; found: 272.0490.

4-[5-(3-Chloro-2-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (32)

From aurone **32a** (113 mg, 0.40 mmol); eluent: 50% EtOAc/hexane; yield: 108 mg (83%); yellow solid; mp 182–183 °C.

IR (neat): 3170, 2922, 2231, 1624, 1430, 1261, 1143, 951, 737 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 8.33 (dd, *J* = 8.1, 1.5 Hz, 1 H), 8.05 (d, *J* = 8.7 Hz, 2 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.76 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.03 (t, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 192.9, 170.9, 159.7, 148.1, 142.1, 141.6, 137.7, 135.4, 134.6, 133.7, 133.1, 133.0, 130.3, 130.2, 122.8, 121.6, 120.2, 118.9, 113.5, 113.3 (tautomers).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{10}ClN_4O_2$: 325.0492; found: 325.0493.

4-[5-(4-Chloro-2-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (33)

From aurone **33a** (113 mg, 0.40 mmol); eluent: 50% EtOAc/hexane; yield: 78 mg (60%); yellow solid; mp 200–201 °C.

IR (neat): 3203, 2922, 2237, 1596, 1469, 1292, 1128, 935, 782 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 8.37 (d, *J* = 8.7 Hz, 1 H), 8.03 (d, *J* = 8.7 Hz, 2 H), 7.88 (d, *J* = 8.7 Hz, 2 H), 7.09 (d, *J* = 2.1 Hz, 1 H), 7.03 (dd, *J* = 8.7, 2.1 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ = 192.25, 164.91, 143.09, 138.15, 136.38, 134.69, 133.12, 133.05, 130.40, 130.29, 130.23, 120.45, 119.96, 119.36, 119.02, 118.57, 113.56 (tautomers).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{10}ClN_4O_2$: 325.0492; found: 325.0495.

4-[5-(5-Chloro-2-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (34)

From aurone **34a** (113 mg, 0.40 mmol); eluent: 50% EtOAc/hexane; yield: 106 mg (82%); yellow solid; mp 212–214 °C.

IR (neat): 3155, 2995, 2922, 2237, 1737, 1628, 1467, 1257, 1158, 937, 827, 737 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.42 (d, *J* = 2.0 Hz, 1 H), 8.05 (d, *J* = 8.5 Hz, 2 H), 7.90 (d, *J* = 8.5 Hz, 2 H), 7.62 (dd, *J* = 9.0, 2.5 Hz, 1 H), 7.08 (d, *J* = 8.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 190.9, 161.9, 141.4, 136.6, 133.9, 132.9, 132.3, 129.7, 129.6, 123.3, 120.6, 119.9, 118.2, 112.8.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{10}ClN_4O_2$: 325.0492; found: 325.0490.

4-[5-(2-Chloro-6-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (35)

From aurone **35a** (113 mg, 0.40 mmol); eluent: 50% EtOAc/hexane; yield: 75 mg (58%); yellow solid; mp 177–179 °C.

IR (neat): 3177, 2924, 2235, 1672, 1588, 1287, 1140, 905, 780 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 8.23 (d, *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 6.9 Hz, 1 H), 7.29 (t, *J* = 8.1 Hz, 1 H), 6.96 (dd, *J* = 13.2, 8.2 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 187.2, 155.7, 145.5, 134.1, 132.2, 131.3, 130.8, 129.7, 129.6, 127.9, 120.3, 118.3 114.6, 112.2 (tautomers).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{10}ClN_4O_2$: 325.0492; found: 325.0494.

4-[5-(3-Bromo-2-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (36)

From aurone **36a** (130 mg, 0.40 mmol); eluent: 50% EtOAc/hexane; yield: 83 mg (56%); yellow solid; mp 217–218 °C.

IR (neat): 3287, 2231, 1622, 1564, 1426, 1330, 1223, 1138, 996, 765 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.38 (dd, *J* = 8.0, 1.4 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 2 H), 7.93–7.86 (m, 3 H), 6.97 (t, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 206.3, 192.9, 160.5, 148.1, 142.0, 141.5, 140.9, 135.4, 134.5, 133.1, 130.4, 130.3, 121.5, 120.8, 118.9, 113.5, 113.3, 111.9 (tautomers).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{10}BrN_4O_2$: 368.9987; found: 368.9989.

4-[5-(5-Bromo-2-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (37)

From aurone **37a** (98 mg, 0.30 mmol), no chromatographic separation was needed; yield: 82 mg (74%); yellow solid; mp 240–243 °C.

IR (neat): 3162, 2922, 2238, 1626, 1467, 1231, 1158, 991, 726 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 8.55 (s, 1 H), 8.05 (d, *J* = 8.2 Hz, 2 H), 7.89 (d, *J* = 7.9 Hz, 2 H), 7.72 (d, *J* = 8.9 Hz, 1 H), 7.01 (d, *J* = 8.9 Hz, 1 H).

$^{13}C\{^1H\}$NMR (75 MHz, acetone-d_6): δ = 191.6, 163.1, 140.2, 136.7, 133.0, 130.5, 121.9, 121.10, 119.03, 113.52, 110.94.

HRMS (EI): *m*/*z* [M + H], calcd for $C_{16}H_{10}BrN_4O_2$: 368.9987; found: 368.9984.

4-[5-(5-Fluoro-2-hydroxybenzoyl)-2*H*-1,2,3-triazol-4-yl]benzonitrile (38)

From aurone **38a** (106 mg, 0.40 mmol); no chromatographic separation was needed; yield: 100 mg (81%); yellow solid; mp 220–223 °C.

IR (neat): 3153, 2995, 2922, 2240, 1611, 1469, 1430, 1244, 1141, 991, 789 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.16 (dd, *J* = 10.0, 3.5 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 2 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 7.47–7.43 (m, 1 H), 7.06 (dd, *J* = 9.0, 4.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 191.8, 160.6, 155.6 (d, $^1J_{C,F}$ = 235 Hz), 148.3, 141.7, 135.5, 134.7, 133.1, 125.3 (d, $^2J_{C,F}$ = 25 Hz), 120.3 (d, $^3J_{C,F}$ = 7.5 Hz), 120.1 (d, $^3J_{C,F}$ = 7.5 Hz), 119.4 (d, $^2J_{C,F}$ = 25 Hz), 119.0, 113.6, 113.3.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{10}FN_4O_2$: 309.0788; found: 309.0791.

(2-Hydroxy-5-methylphenyl)[5-(3-methoxyphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (39)

From aurone **39a** (77 mg, 0.29 mmol); eluent: 50% EtOAc/hexane; yield: 55 mg (59%); yellow solid; mp 119–121 °C.

IR (neat): 3466, 3347, 2667, 1605, 1585, 1477, 1261, 1033, 955, 830, 795 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.85 (s, 1 H), 7.77 (s, 1 H), 7.32 (t, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 6.97–6.91 (m, 2 H), 3.80 (s, 3 H), 2.21 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 161.7, 159.8, 138.6, 133.3, 130.0, 128.5, 121.0, 119.3, 118.2, 115.8, 114.0, 55.5, 20.6.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{17}H_{16}N_3O_3$: 310.1191; found: 310.1187.

(2-Hydroxy-3-methylphenyl)[5-(3-methoxyphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (40)

From aurone **40a** (133 mg, 0.50 mmol); eluent: 30% EtOAc/hexane; yield: 96 mg (62%); yellow solid; mp 77–80 °C.

IR (neat): 3470, 2890, 1605, 1425, 1259, 1041, 849, 756 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.30 (s, 1 H), 7.82 (d, *J* = 6.0 Hz, 1 H), 7.38 (d, *J* = 7.5 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.28 (s, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 6.96 (dd, *J* = 8.3, 2.5 Hz, 1 H), 6.77 (t, *J* = 8.0 Hz, 1 H), 3.80 (s, 3 H), 2.30 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 192.8, 162.1, 159.8, 138.2, 131.4, 129.9, 127.4, 120.9, 118.9, 118.6, 115.8, 113.9, 55.5, 15.7.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{17}H_{16}N_3O_3$: 310.1191; found: 310.1189.

(2-Hydroxy-4,5-dimethylphenyl)[5-(3-methoxyphenyl)-2*H*-1,2,3-triazol-4-yl]methanone (41)

From aurone **41a** (118 mg, 0.38 mmol); eluent: 50% EtOAc/hexane; yield: 87 mg (71%); waxy solid; mp 75–78 °C.

IR (neat): 3458, 2920, 1639, 1579, 1451, 1264, 1246, 1030, 901, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.91 (s, 1 H), 7.68 (s, 1 H), 7.32–7.25 (m, 2 H, 7.22 (d, *J* = 7.4 Hz, 1 H), 6.94 (dd, *J* = 5.8, 4.7 Hz, 1 H), 6.83 (s, 1 H), 3.78 (s, 3 H), 2.25 (s, 3 H), 2.09 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.9, 162.1, 159.8, 148.5, 141.1, 133.6, 129.9, 127.8, 120.9, 118.9, 117.6, 115.8, 113.9, 55.5, 20.8, 18.9.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{18}H_{18}N_3O_3$: 324.1348; found: 324.1350.

(2-Hydroxy-3-methylphenyl)[5-(3-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (42)

From aurone **42a** (120 mg, 0.43 mmol); eluent: 30% EtOAc/hexane, yield: 101 mg (72%); yellow solid; mp 170–171 °C.

IR (neat): 3200, 2922, 1605, 1540, 1426, 1356, 1268, 1074, 968, 737 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.72–8.70 (m, 1 H), 8.35–8.30 (m, 1 H), 8.26 (d, *J* = 7.5 Hz, 1 H), 8.12 (t, *J* = 7.0 Hz, 1 H), 7.80 (t, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 7.5 Hz, 1 H), 6.89 (t, *J* = 8.0 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 193.7, 162.9, 149.2, 138.9, 135.1, 132.7, 132.3, 130.8, 130.7, 127.7, 124.6, 124.4, 124.1, 123.9, 119.7, 119.4, 15.5.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{13}N_4O_4$: 325.0937; found: 325.0941.

(2-Hydroxy-5-methylphenyl)[5-(3-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (43)

From aurone **43a** (130 mg, 0.46 mmol); eluent: 30% EtOAc/hexane; yield: 90 mg (60%); yellow solid; mp 152–153 °C.

IR (neat): 3276, 2920, 1631, 1592, 1469, 1255, 1100, 955, 730 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.77 (s, 1 H), 8.69 (t, *J* = 2.0 Hz, 1 H), 8.30–8.27 (m, 1 H), 8.12–8.09 (m, 1 H), 7.85 (s, 1 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 7.38 (dd, *J* = 8.5, 2.0 Hz, 1 H), 6.99 (d, *J* = 8.5 Hz, 1 H), 2.27 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 193.1, 162.3, 149.1, 139.1, 135.6, 134.5, 134.4, 132.2, 130.7, 130.62, 128.95, 124.49, 124.06, 120.16, 118.57, 20.41 (tautomeric mixture).

HRMS (EI): *m*/*z* [M + H], calcd for $C_{16}H_{13}N_4O_4$: 325.0937; found: 325.0936.

(2-Hydroxy-4,5-dimethylphenyl)[5-(3-nitrophenyl)-2*H*-1,2,3-triazol-4-yl]methanone (44)

From aurone **44a** (121 mg, 0.41 mmol); eluent: 40% EtOAc/hexane; yield: 92 mg (68%); yellow solid; mp 155–157 °C.

IR (neat): 3330, 3185, 1639, 1534, 1352, 1268, 991, 735 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.84 (s, 1 H), 8.68 (s, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.75 (s, 1 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 2.28 (s, 3 H), 2.15 (s, 3 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.2, 162.3, 149.0, 148.4, 134.7, 133.3, 130.9, 129.7, 128.0, 124.1, 123.8, 119.1, 117.4, 20.8, 19.0.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{17}H_{15}N_4O_4$: 339.1093; found: 339.1089.

(2-Hydroxy-4,5-dimethylphenyl)[5-(*p*-tolyl)-2*H*-1,2,3-triazol-4-yl]methanone (45)

From aurone **45a** (80 mg, 0.30 mmol); eluent: 30% EtOAc/hexane; yield: 59 mg (64%); yellow solid; mp 129–132 °C.

IR (neat): 3209, 2918, 1631, 1603, 1467, 1432, 1266, 1186, 897, 799 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 11.96 (s, 1 H), 7.78 (s, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.80 (s, 1 H), 2.33 (s, 3 H), 2.23 (s, 3 H), 2.05 (s, 3 H) (tautomeric peaks observed).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.7, 162.0, 148.2, 140.0, 133.7, 129.5, 128.5, 127.7, 126.5, 118.8, 117.6, 21.5, 20.7, 18.8 (tautomeric peaks observed).

HRMS (EI): *m*/*z* [M + H] calcd for $C_{18}H_{18}N_3O_2$: 308.1399; found: 308.1401.

(3-Chloro-2-hydroxyphenyl)[5-(*p*-tolyl)-2*H*-1,2,3-triazol-4-yl]methanone (46)

From aurone **46a** (97 mg, 0.36 mmol); eluent: 20% EtOAc/hexane; yield: 63 mg (55%); yellow solid; mp 107–109 °C.

IR (neat): 2998, 1624, 1598, 1430, 1264, 1147, 1007, 955, 737 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 12.63 (s, 1 H), 8.22 (s, 1 H), 7.63 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.26 (dd, *J* = 8.5, 0.5 Hz, 1 H), 6.88 (t, *J* = 8.0 Hz, 1 H), 2.41 (s, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.7, 159.2, 140.7, 137.0, 132.49, 129.7, 128.6, 122.8, 120.5, 119.3, 21.6.

HRMS (EI): *m*/*z* [M + H] calcd for $C_{16}H_{13}ClN_3O_2$: 314.0696; found: 314.0700.

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Supporting Information

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