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Metal Free Cycloaddition to Synthesize Naphtho[2,3-d][1,2,3]triazole-4,9-diones

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A metal free domino [3+2] cycloaddition is reported to construct naphtho[2,3-d][1,2,3]triazole-4,9-dione derivatives and an alternative approach to the azide-alkyne cycloadditions. The key features are easily available starting materials, mild conditions, atom economy, eco-friendly and with broad substrate scope in high yields.

Introduction-

Lewis acid-promoted cycloadditions are widely utilized approaches to construct useful heterocycles from simple starting materials.[1-2] Of particular importance, the [4+2], [4+1], and [3+2] cycloadditions *via* intramolecular or intermolecular type leads to build the biologically potent molecules.

In particular, [3+2] azide-alkyne cycloaddition reactions are well explored with metal salts such as Cu(CuAAC), Ru(RuAAC) and Ir(IrAAC).[3-6] Among them, the copper (I) catalyzed cyclo additions are well studied and the acetylide complexes are formed by using copper with terminal alkynes, it accelerates the cycloaddition reaction. Therefore, the CuAAC is limited to terminal alkynes, whereas the internal alkynes are challenging to react with azides to afford fully substituted triazoles due to their weak reactivity and difficulty in regioselectivity. This turn into a major problem of prevailing click reactions.

To overcome these drawbacks, recently some groups have developed alternative methods for [3+2] alkyne-azide cycloaddition reactions. In these reactions, the alkyne was replaced by the ketones, enals, β-ketoesters, and enones to give the respective 1,2,3-triazoles in high yields.[7-9] In this instance, recently Ramachary et. al., reported an efficient method to prepare substituted triazoles by using aldehydes and azides (Fig 1, Eq 1a).[3a] There is a demand in organic synthesis of simple methods by a sequential process to lead heterocyclic compounds. Inspired by this new concept, we want to explore this area and synthesized substituted fused triazoles from easily available staring materials as phenols or napthols was initiated.

Meanwhile, the fused triazoles have several biological applications like antibacterial, antimycotic, anticancer and several other applications.[7-8] Recently, they are also extensively utilized as ligands for catalysis,[10] directing groups for metal-catalyzed C–H activation,[11] and as building blocks in organic synthesis.[12] The most common methods available in the literature for synthesis of these scaffolds are less explored.[5c] By considering these facts, there is a need for the construction of fused triazoles by a simple method.[9,13] As part of our continuing research in the metal free reactions,[14] we herein envisioned a new metal free approach *via* oxidation followed by the alcohol azide cycloaddition to afford naphtho[2,3-*d*][1,2,3]triazole-4,9-dione derivatives (Fig 1, Eq 1b).

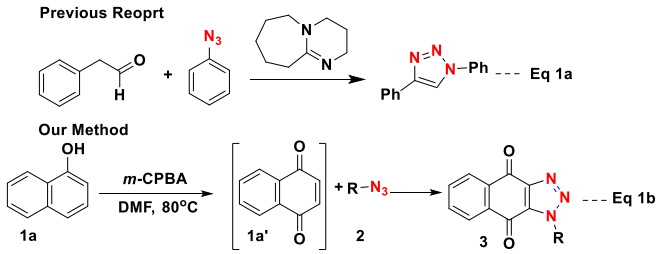

Figure 1 Substituted triazole synthesis.

Results and Discussions

The optimization studies were initiated with the alcohol **1a** in the presence of CuI/*m*-CPBA/K_2CO_3 in DMF at room temperature for 12h and then the azide **2a** was added. The desired compound **3a** was obtained in 60% yield (Table 1, entry 1). The reaction was screened with various copper salts as CuBr, CuCl, $CuSO_4$, $Cu(OAc)_2$, $Cu(OTf)_2$ and the yields are not satisfactory (entries 2-6). Without an additive K_2CO_3 the reaction yield was not varied (entry 7) and also without the catalyst CuI (entries 8), the reaction yields were not varied much from the entry 1. These results revealed that the catalyst and additive were not essential for this transformation. We next envisaged the feasibility of the reaction in the absence of metal salt and additive. Different solvents as DMSO, THF, H_2O,

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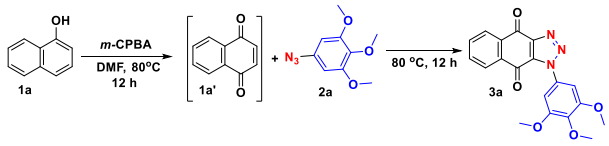
MeOH, EtOH, PhMe, C_6H_6, MeCN were scrutinized (entries 9-16) and among them DMF (entry 8) as shown the best result. The temperature was elevated to 80 °C and also increased to 100 °C, the reaction was good at 80 °C (entry 17-18). The yield was not increased even though the reaction was carried out for a longer time (entry 19). Finally, the entry 17 was chosen as the optimum condition and by using this condition the substrate scope is studied in Table 2 & 3.

Table 1 Optimization of reaction conditions to synthesize compound **3a** [a]

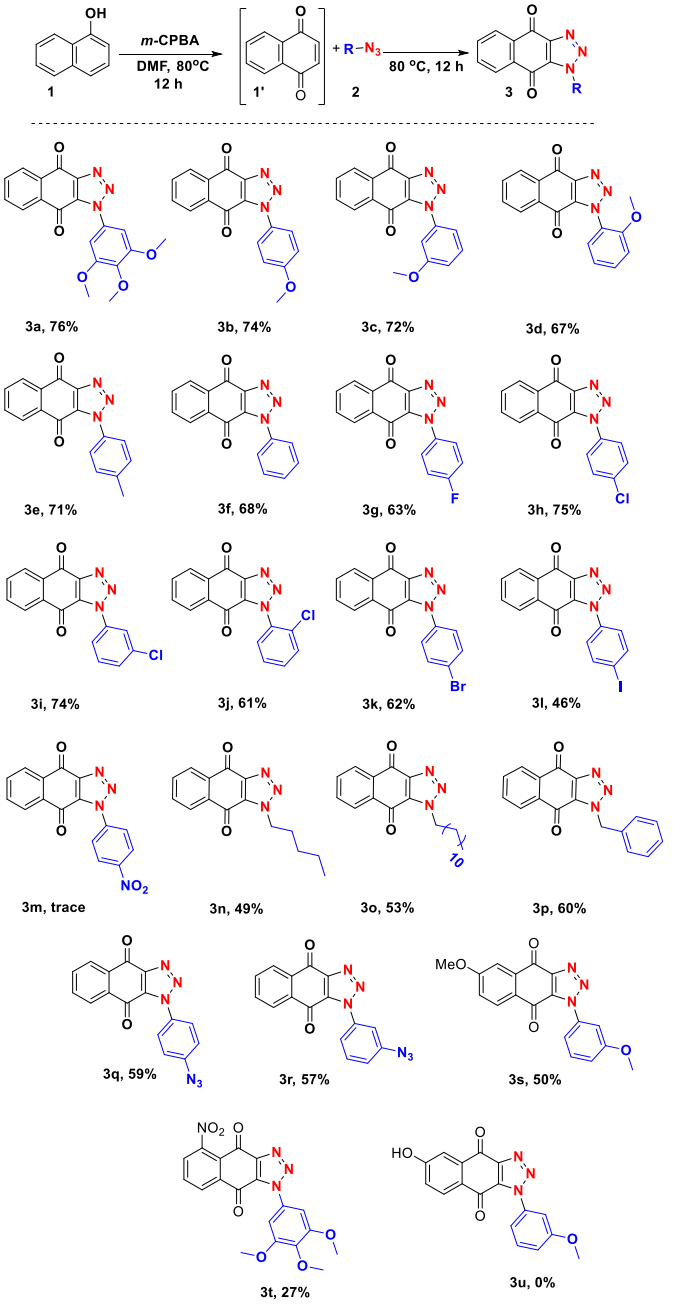


Entry	Oxidant	Solvent	Temp	Additive	3a[b]
1	CuI/ *m*-CPBA	DMF	rt	K_2CO_3	60
2	CuBr/ *m*-CPBA	DMF	rt	K_2CO_3	21
3	CuCl/ *m*-CPBA	DMF	rt	K_2CO_3	13
4	$CuSO_4$/ *m*-CPBA	DMF	rt	K_2CO_3	8
5	$Cu(OAc)_2$/ *m*-CPBA	DMF	rt	K_2CO_3	20
6	$Cu(OTf)_2$/ *m*-CPBA	DMF	rt	K_2CO_3	16
7	CuI/ *m*-CPBA	DMF	rt	none	55
8	*m*-CPBA	DMF	rt	none	57
9	*m*-CPBA	DMSO	rt	none	35
10	*m*-CPBA	THF	rt	none	42
11	*m*-CPBA	H_2O	rt	none	15
12	*m*-CPBA	MeOH	rt	none	8
13	*m*-CPBA	EtOH	rt	none	11
14	*m*-CPBA	PhMe	rt	none	20
15	*m*-CPBA	C_6H_6	rt	none	17
16	*m*-CPBA	MeCN	rt	none	19
17	*m*-CPBA	DMF	80	none	76
18	*m*-CPBA	DMF	100	none	73
19[c]	*m*-CPBA	DMF	80	none	70

[a] With **1** (1.0 mmol), *m*-CPBA (1.0 mmol) and DMF (2 mL) at 80 °C for 12 h then **2** (1.1 mmol) was added and stirred for 12 h. [b] Isolated yield. [c] 48 h.

With the optimized condition in hand, various functionalized azides were studied to give the desired naphtha [2,3-d][1,2,3]triazole-4,9-dione derivatives (Table 2). The aryl azides with electron donating groups as -OMe and -Me has given good yields **3a**-**3e**. The simple phenyl azide also tolerated well with the optimized conditions to give compound **3f**. With an electron withdrawing groups as F, Cl, Br and I groups the reaction proceeded smoothly to give the compounds **3g**-**3l**. Whereas, with nitro aryl azide the reaction was not successful to give the desired compound **3m**. It may be due to the strong electron withdrawing ability of $-NO_2$, which could decrease the nucleophilicity of azide. Next, we investigated the feasibility of reaction with alkyl azides, the desired products were observed in moderate yields (entries **3n** and **3o**). The study was continued with benzyl azide and it was succeeded with yield 60% by giving the compound **3p**. Surprisingly, the reactions with di-azide aryl compounds the reaction was succeeded to give the compounds **3q** and **3r** with moderate yields. To improve the substrate scope, the substituted napthols were tested. The electron donating group as –OMe produced the desired compound with moderate yield (3s). With electron withdrawing group as $-NO_2$ the product (3t) was observed in low yield with inseparable isomers. The reaction with hydroxyl substituted naphthol (3u) was failed.

Table 2 Scope of the reaction to synthesize naphtha [2,3-d][1,2,3]triazole-4,9-dione derivatives. [a, b]



[a] With **1** (1.0 mmol), *m*-CPBA (1.0 mmol) and DMF (2 mL) at 80 °C for 12 h then **2** (1.1 mmol) was added and stirred for 12 h. [b] Isolated yield.

Instead of napthols, the reaction scope was extended by using phenol. Interestingly, the bis-triazole moieties were observed with satisfactory yields (Table 3) by giving the

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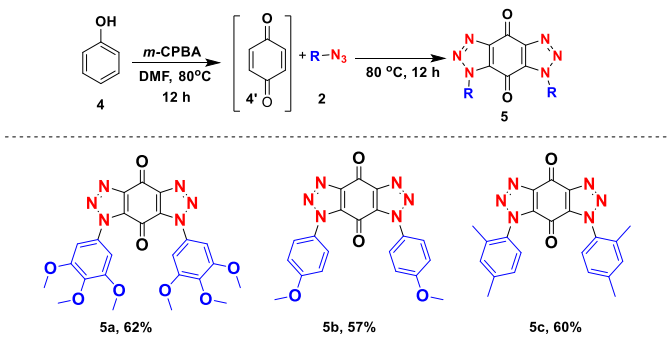
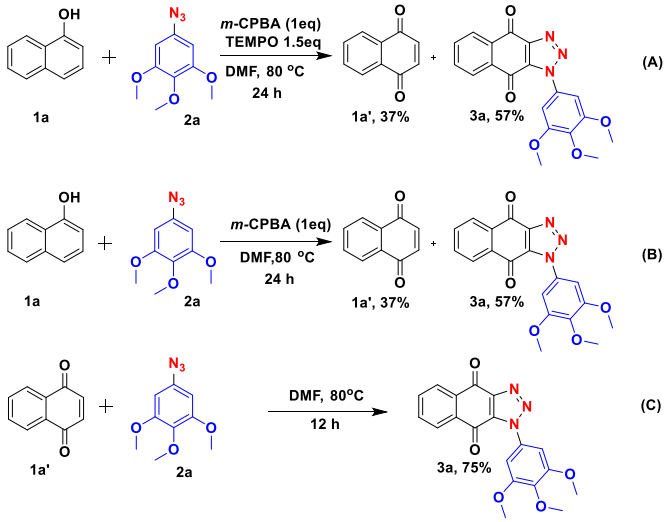
compounds **5a**-**5c**. The structures of compound **3f** and **5b** were confirmed by X-ray analysis (Figure 2).[15]

Table 3 Scope of the reaction to synthesize bistriazoles. [a,b]



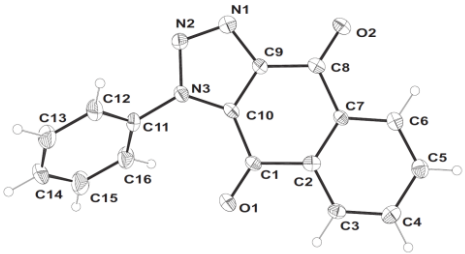
[a] With **1** (1.0 mmol), *m*-CPBA (1.0 mmol), and DMF (2 mL) at 80 °C for 12 h then **2** (2.0 mmol) added and stirred for 12 h. [b] Isolated yield.



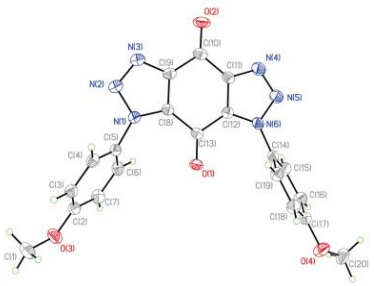
Scheme 1 Control experiments to confirm the mechanistic intermediates.

To understand the reaction mechanism, the control experiments are studied in Scheme 1. To confirm the reaction as it is following a radical pathway or cycloaddition, one pot synthesis was carried in the presence of TEMPO a radical scavenger. Surprisingly, the reaction was yielded with 57% of desired compound **3a** and the oxidized alcohol product **1a'** with yield 37% (Scheme 1A). This result shows that the one pot reaction feasibility as well as the reaction intermediate is quinone **1a'**. Next, the reaction was conducted without the TEMPO (Scheme 1B) and the reaction yield was not increased. By these results it was clear that the reaction was not inhibited by the TEMPO and the reaction is not proceeding *via* a radical mechanism. The experiment with quinone **1a'** was carried without an oxidant as *m*-CPBA and found that the reaction was smoothly undergoing to deserve the required compound **3a** (Scheme 1C).

The above results encouraged us to perform one pot method to synthesis naphtho[2,3-*d*][1,2,3]triazole-4,9-dione derivatives and the results were shown in Table 4. The reactions proceeded with moderate yields. Further optimization is required to increase the yields and they are under investigation.



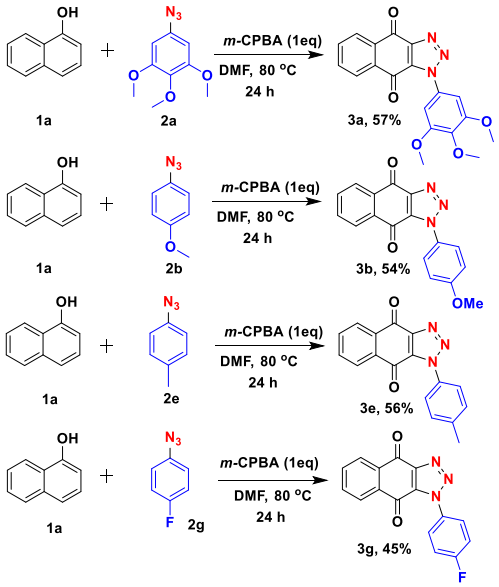
3f



5b

Figure 2. ORTEP diagram of **3f** and **5b.**

Table 4 One pot synthesis.



[a] Reactions were performed with 1 (1.0 mmol), 2 (1.0 mmol) and *m*-CPBA (1.0 mmol), DMF (2 mL)at 80 °C for 24-40 h. [b] Isolated yield.

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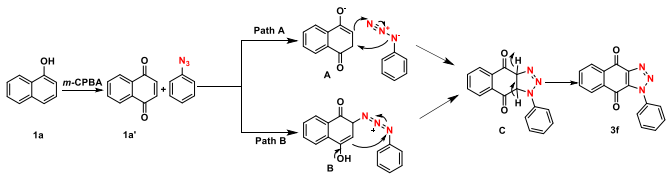
Based on these results, a plausible reaction mechanism was proposed in Scheme 2. The starting material **1a** was oxidized in the presence of *m*-CPBA to give benzoquinone **1a'**. The benzoquinone **1a'** undergoes a Michael type reaction to give an intermediate **A**. It undergoes a concerted [3+2] cycloaddition (Path A, intermediate **A**) or stepwise amination-cyclization reaction (Path B, intermediate **B**) to give the intermediate **C**. Intermediate **C** undergoes dehydrogenation to give the final compound **3f**.

Scheme 2 A plausible mechanism for the synthesis of Naphtho[2,3-d][1,2,3]triazole-4,9-dione derivatives.



Conclusions

In conclusion, we have developed a metal free synthesis *via* an oxidation followed by [3+2] cycloaddition to produce naptho[2,3-d][1,2,3]triazole-4,9-dione derivatives. For the first time, we have developed a metal-free alcohol-azide cycloaddition to synthesize the substituted fused triazoles. The notable features of the work include simple precursors, environmentally benign conditions, and with broad substrate scope.

Experimental

General procedure for the synthesis of Compound 2:

Corresponding compound **1** (100 mg, 1.0 mmol) was taken in DMF (2 mL) and the oxidant *m*-CPBA was (1.0 mmol) was added and the reaction was monitored by TLC after stirring at 12h at 80 °C. Then the compound **2** (1.0 mmol) was added to the reaction mixture. The reaction was monitored by TLC after stirring the reaction at 80 °C for 12h. The reaction mixture was cooled to room temperature and then water was added. Extracted with ethyl acetate (3 X 50 ml) followed by washing with water and brine. The combined extracts were dried over Na_2SO_4 and concentrated to give a crude residue. This was purified by flash column chromatography by using a gradient system of hexane/ethyl acetate and obtained the desired pure product **2**.

1-(3,4,5-trimethoxyphenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3a): Yellow solid (76%). mp = 232-234 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, J = 7.2, 1.2 Hz, 1H), 8.25 (dd, J = 7.2, 1.2 Hz, 1H), 7.88-7.83 (m, 2H), 7.02 (s, 2H), 3.96 (s, 3H) 3.95 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.9, 174.2, 153.3, 145.8, 139.8, 135.1, 134.5, 133.1, 132.9, 130.6, 127.7, 102.7, 61.1, 56.4. HRMS (ESI-ion trap, m/s) calcd for $C_{19}H_{15}N_3O_5Na$, calcd 388.0909, found 388.0903.

1-(4-methoxyphenyl)-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (3b):Yellow solid (74%). mp = 195-197 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (dd, J = 7.2, 1.6 Hz, 1H), 8.21 (dd, J = 7.2, 1.2 Hz, 1H), 7.88-7.79 (m, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.9, 174.3, 161.2, 145.7, 135.0, 134.4, 133.1, 133.0, 127.6, 127.5, 126.3, 114.3, 55.6. HRMS (ESI-ion trap, m/s) calcd for $C_{17}H_{11}N_3O_3Na$, calcd 328.0698, found 328.0690.

1-(3-methoxyphenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3c) : Yellow solid (72%). mp = 210-212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, J = 7.2, 1.6 Hz, 1H), 8.23 (dd, J=7.6, 1.2 Hz, 1H), 7.89-7.80 (m, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.0, 2.0Hz, 1H) ,7.286 (t, J = 2.4 Hz 1H) , 7.17 (dd, J = 8.4, 2.4Hz, 1H), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.9, 174.1, 160.0, 145.8, 136.1, 135.1, 134.5, 133.1, 130.0, 127.7, 127.6, 117.1, 116.7, 110.7, 55.7. HRMS (ESI-ion trap, m/s) calcd for $C_{17}H_{11}N_3O_3Na$, calcd 328.0698, found 328.0691

1-(2-methoxyphenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3d): Yellow solid (67%). mp = 222-226 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, J = 7.6, 1.6 Hz, 1H), 8.17 (dd, J = 8.0, 1.6 Hz, 1H), 7.87-7.77 (m, 2H), 7.63 (td, J = 7.6, 1.6Hz 1H), 7.53 (dd, J = 7.6, 1.6Hz, 1H) ,7.19 (m, 2H) , 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.0, 174.0, 153.8, 145.0, 134.9, 134.2, 133.3, 133.0, 132.4, 127.7, 127.3, 124.5, 120.7, 112.1, 55.8. HRMS (ESI-ion trap, m/s) calcd for $C_{17}H_{11}N_3O_3Na$, calcd 328.0698, found 328.0692.

1-(p-tolyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3e): Yellow solid (71%). mp = 126-128 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.35 (dd, J = 7.6, 1.6 Hz, 1H), 8.20 (dd, J = 7.6, 1.6 Hz, 1H), 7.88-7.79 (m, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.9, 174.1, 145.7, 141.2, 135.0, 134.4, 133.1, 133.0, 132.9, 132.7, 129.7, 127.6, 127.5, 124.7, 21.3. HRMS (ESI-ion trap, m/s) calcd for $C_{17}H_{11}N_3O_2Na$, calcd 312.0749, found 312.0741.

phenyl-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3f): Beige solid (68%). mp = 232-236 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (dd, J = 7.2, 1.2 Hz, 1H), 8.22 (dd, J = 7.6, 1.2 Hz, 1H), 7.89-7.80 (m, 2H), 7.75-7.73 (m, 2H), 7.65-7.61 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.9, 174.2, 145.8, 135.2, 135.1, 134.5, 133.1, 133.0, 132.9, 130.8, 129.2, 127.7, 127.6, 125.0. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_9N_3O_2Na$, calcd 298.0592, found 298.0585.

1-(4-fluorophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3g): Beige solid (63%). mp = 252-254 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, J = 7.2, 1.6 Hz, 1H), 8.22 (dd, J = 7.6, 1.2 Hz, 1H), 7.90-7.81 (m, 2H), 7.78-7.73 (m, 2H), 7.34-7.28 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.8, 174.3, 164.9, 162.4, 145.8, 135.2, 134.5, 133.0, 127.7, 127.6, 127.1, 116.5, 116.3. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2FNa$, calcd 316.0498, found 316.0495.

1-(4-chlorophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3h): Yellow solid (75%). mp = 220-222 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (dd, J = 7.6, 1.6 Hz, 1H), 8.22 (dd, J = 7.6, 1.6 Hz, 1H), 7.90-7.81 (m, 2H), 7.73 (d, J = 9.2 Hz, 2H), 7.61 (d, J = 9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 174.2,

145.9, 136.9, 135.2, 134.5, 133.6, 132.9, 129.5, 127.7, 127.6, 126.2. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 332.0203, found 332.0199.

1-(3-chlorophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3i) : Yellow solid (74%). mp = 212-214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (dd, J = 7.2, 1.6 Hz, 1H), 8.23 (dd, J = 7.2, 1.6 Hz, 1H), 7.90-7.81 (m, 2H), 7.80 (t, J = 2.0 Hz, 1H), 7.73 (dt, J = 7.6, 1.2 Hz, 1H), 7.63-7.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 174.1, 145.9, 136.0, 135.3, 135.0, 134.5, 133.0, 130.9, 130.2, 127.7, 125.3, 123.2. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 332.0203, found 332.0197.

1-(2-chlorophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3j): Beige solid (61%). mp = 238-242 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (dd, J= 7.6, 1.2 Hz, 1H), 8.18 (dd, J = 7.6, 1.2 Hz, 1H), 7.90-7.79 (m, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 174.1, 145.0, 135.2, 134.9, 134.4, 133.2, 132.7, 132.3, 131.1, 130.5, 128.3, 127.8, 127.4. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 332.0203, found 332.0196.

1-(4-bromophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3k): Yellow solid (62%). mp = 250-252 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, J = 7.6, 1.6 Hz, 1H), 8.23 (dd, J = 7.6, 1.6 Hz, 1H), 7.91-7.82 (m, 2H), 7.69-7.52 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 174.2, 145.9, 135.3, 134.5, 134.2, 132.9, 132.5, 127.8, 127.6, 126.4, 125.0. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 375.9698, found 375.9696.

1-(4-iodophenyl)-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (3l): Beige solid (46%). mp = 251-254 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (dd, J = 7.6, 1.6 Hz, 1H), 8.23 (dd, J = 7.6, 1.6 Hz, 1H), 7.98 (d, J = 8.4Hz, 2H), 7.90-7.81 (m, 2H), 7.52(d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.0, 174.4, 146.2, 138.7, 135.5, 134.8, 133.4, 133.2, 128.0, 127.9, 126.7, 97.0. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 375.9698, found 375.9696.

1-pentyl-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3n): Yellow solid (49%). mp = 88-90 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (dd, J = 6.8, 1.6 Hz, 1H), 8.24 (dd, J = 7.2, 1.6 Hz, 1H), 7.86-7.82 (m, 2H), 4.87 (t, J = 7.2 Hz, 2H), 2.06-1.99 (q, J = 7.2 Hz 2H), 1.43-1.36 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 175.3, 145.4, 135.0, 134.2, 133.2, 132.7, 127.7, 127.2, 50.5, 29.6, 28.3, 21.9, 13.7. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 292.1062, found 292.1054.

1-decyl-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (3o): Beige solid (53%). mp = 88-90 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (dd, J = 6.8, 1.6 Hz, 1H), 8.22 (dd, J = 7.2, 1.6 Hz, 1H), 7.88-7.80 (m, 2H), 4.87 (t, J = 7.2 Hz, 3H), 2.06-1.99 (m, 2H), 1.43-1.25 (m, 14H), 0.88 (t, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.6, 175.2, 145.3, 135.0, 134.1, 133.1, 127.5, 127.1, 50.5, 31.6, 29.8, 29.2, 29.0, 28.7, 26.1, 22.4, 13.9. HRMS (ESI-ion trap, m/s) calcd for $C_{20}H_{25}N_3O_2Na$, calcd 362.1844, found 362.1839.

benzyl-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3p): Beige solid (60%). mp = 119-123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (dd, J = 7.2, 2.0 Hz, 1H), 8.23(dd, J = 7.2, 1.2 Hz, 1H), 7.89-7.75 (m, 2H), 7.52 (dd, J = 8.0, 2.0 Hz, 2H), 7.38-7.308 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 175.3, 145.6, 135.1, 134.2, 128.6, 128.9, 127.8, 127.3, 123.5, 53.7. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_3O_2ClNa$, calcd 312.0749, found 312.0743.

1-(4-azidophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3q): Yellow solid (59%). mp = 172-176 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (dd, J = 7.6, 1.6 Hz, 1H), 8.22 (dd, J = 7.6, 1.6 Hz, 1H), 7.89-7.80 (m, 2H), 7.77 (d, J = 9.2 Hz, 2H), 7.26 (d, J = 9.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.8, 174.2, 145.8, 142.7, 135.2, 134.5, 133.0, 132.9, 127.7, 127.6, 126.5, 119.6. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_6O_2$, calcd 316.0709, found 316.0711.

1-(3-azidophenyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (3r): Beige solid (57%). mp = 135-138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (dd, J = 7.2, 1.2 Hz, 1H), 8.23 (dd, J = 7.6, 1.6 Hz, 1H), 7.90-7.81 (m, 2H), 7.63 (t, J = 8.0 Hz, 1H), 7.55-7.522 (m, 1H), 7.44 (t, J = 2.4 Hz, 1H), 7.31-7.28 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7, 174.1, 145.9, 141.5, 136.4, 135.2, 134.5, 133.0, 132.9, 130.5, 127.7, 121.3, 121.1, 115.9. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_6O_2$, calcd 316.0709, found 316.0711.

6-methoxy-1-(3-methoxyphenyl)-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (3s): Yellow solid. mp = 148-151 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 2.8 Hz, 1H), 7.42 (t, J = 8.4 Hz, 1H), 7.23-7.18 (m, 3H), 7.06 (dd, J = 8.8, 2.8 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.2, 174.1, 164.5, 160.0, 146.1, 136.1, 135.3, 133.3, 130.1, 129.9, 126.2, 120.7, 117.1, 116.7, 111.7, 110.7, 56.0, 55.7.

5-nitro-1-(3,4,5-trimethoxyphenyl)-1H-naphtho[2,3-d][1,2,3]triazole-4,9-dione (3t): Yellow sticky mass. The isomers are inseparable. ^{1}HNMR was attached in supporting information for reference. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (d, J = 8.0 Hz, 1H), 8.16 (t, J = 14.4 Hz, 1H), 7.96-7.85 (m, 2H), 7.75-7.71 (m, 1H), 6.94 (s, 1H), 6.41 (s, 1H), 3.89-3.77 (m, 11H).

1,7-bis(3,4,5-trimethoxyphenyl)benzo[1,2-*d*:4,5-*d*']bis([1,2,3]triazole)-4,8(1H,7H)-dione (5a): Beige solid (62%). mp = 256-258 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.90 (s, 2H), 3.93 (s, 3H), 3.89 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 163.5, 153.4, 146.1, 140.1, 134.0, 130.0, 102.9, 61.0, 56.51. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_6O_2$, calcd 545.1397, found 545.1393.

1,7-bis(4-methoxyphenyl)benzo[1,2-*d*:4,5-*d*']bis([1,2,3]triazole)-4,8(1H,7H)-dione (5b): Yellow solid (57%). mp = 230-232 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, J = 9.2 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 3.88 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 163.8, 161.4, 146.1, 133.8, 127.5, 126.4, 114.4, 55.6. HRMS (ESI-ion trap, m/s) calcd for $C_{16}H_8N_6O_2$, calcd 425.0974, found 425.0969.

1,7-bis(2,4-dimethylphenyl)benzo[1,2-d:4,5-d']bis([1,2,3]triazole)-4,8(1H,7H)-dione (5c): Beige solid (60%). mp = 157-159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18(m, 3H), 2.39 (s, 3H), 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 163.6, 145.9, 141.7, 134.8, 133.9, 131.9, 131.5, 127.6, 126.2, 21.2, 17.2.

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