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# Aryne click chemistry: synthesis of oxadisilole fused benzotriazoles or naphthotriazoles from arynes and azides

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ABSTRACT

The oxadisilole fused benzotriazoles or naphthotriazole derivatives have been synthesized by 1,3-dipolar cycloaddition of various azides with arynes generated in situ from benzobisoxadisilole or 2,3-naphthoxadisilole in good yields under mild conditions.

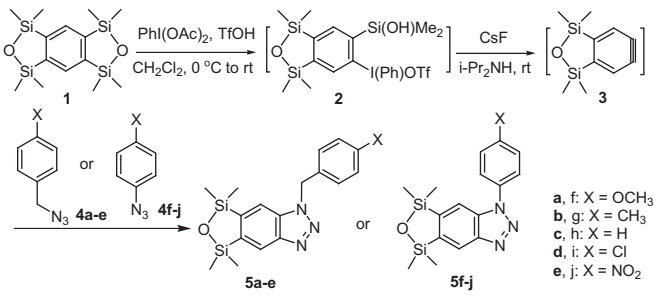


## 1. Introduction

The Cu-catalyzed [3+2] cycloaddition between terminal alkynes and azides,[1] termed 'click' chemistry,[2] has been extensively studied and applied to several areas of chemistry. Such chemistry included materials science,[3] chemical biology,[4] and medicinal chemistry.[5] Recently, Larock et al.[6a] reported the benzyne click chemistry, which involved the reaction of organic azide with benzyne, generated from *o*-(trimethylsilyl)aryl triflates to give the corresponding 1*H*-benzo[*d*][1,2,3]triazoles (hereafter referred as benzotriazoles).[6] Benzotrizole derivatives are important heterocyclic compounds. They play important roles as structural and functional units in many biological active compounds, natural products, and useful synthons.[7] Aryne is an important intermediate and synthon in organic synthesis.[8] Recently, we are interested in the chemistry of arynes generated from benzobisoxadisilole, benzotrisoxadisilole, and 2,3-naphthoxadisilole under very mild conditions. We found that benzobisoxadisilole can serve as the synthetic equivalent of benzdiyne. Their applications to the synthesis of functional acenes and benzoquinones have also been reported.[9] The chemistry was further extended to the synthesis of oxadisilole fused benzo[*d*]isoxazoline and naphtho[2,3-*d*]isoxazoline derivatives by 1,3-dipolar cycloaddition reaction of nitrones with arynes.[10] With this motif in mind, we envisioned [3+2] annulation of arynes by azides could be a very promising extension of the current click chemistry. Herein, we describe the 1,3-dipolar cycloaddition reactions of azides with arynes generated in situ from benzobisoxadisilole or 2,3-naphthoxadisilole, as a new aryne click chemistry.

## 2. Results and discussion

The synthesis of the oxadisilole fused benzotriazole derivatives **5a**–**j** or the naphthotriazole derivatives **9a**–**e** are outlined in Schemes 1 and 2. Arynes **3** and **8** were generated from benzobisoxadisilole **1** and 2,3-naphthoxadisilole **6**, respectively, through our previously reported phenyliodination fluoride induced desilylation protocol.[9a,b] Trapping benzyne **3** and naphthyne **8** at room temperature with azides **4a**–**j** via 1,3-dipolar cycloaddition reactions afforded the oxadisilole fused benzotriazole derivatives




**Scheme 1.**

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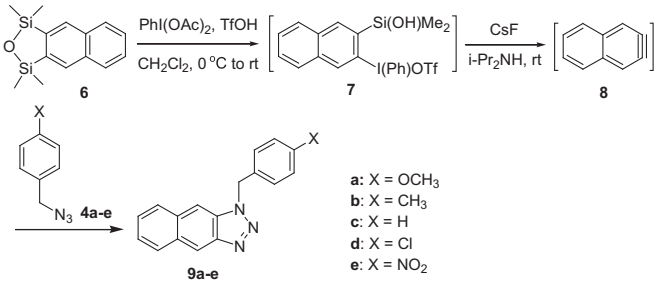


**Scheme 2.**

**5a**–**j** and naphthotriazole derivatives **9a**–**e** in good yields. Benzyl azides **4a**–**e** or aryl azides **4f**–**j** were prepared according to the literature procedures.[11]

Our investigation started with the reaction of phenyl azide **4h** and oxadisilole fused benzyne **3** generated in situ from benzobisoxadisilole. Phenyliodination of **1** with a 1.5:3 mixture of phenyliodium diacetate ($PhI(OAc)_2$) and trifluoromethanesulfonic acid (TfOH) took place readily at room temperature in dichloromethane (Scheme 1). Without isolation of the ring-opened iodination intermediate **2**, benzyne **3** could be generated in situ upon treatment with cesium fluoride (CsF). Trapping experiments were carried out with 10 equiv of phenyl azide **4h** (X=H) at room temperature to afford 52% isolated yields of the oxadisilole fused benzotriazole derivative **5h** in this three-step reaction (Scheme 1 and Table 1, entry 3). When acetonitrile was used as the solvent with CsF as the fluoride source, the yield of adduct **5h** dropped to 36%. At 80 °C, the yield was slightly increased to 39% (Table 1, entries 1 and 2). We tried tetrabutylammonium fluoride (TBAF) or CsF/18-crown-6 as the fluoride source in $CH_2Cl_2$, the isolated yields of **5h** were 45% and 50%, respectively (Table 1, entries 4 and 5).

**Table 1**
Cycloaddition of phenyl azide **4h** (10 equiv) with benzyne **3** generated from benzobisoxadisilole **1** in different fluoride sources and solvents

| Entry | Fluoride source | Solvent | *T*/°C | Yield[a] of **5h** (%) |
|---|---|---|---|---|
| 1 | CsF | $CH_3CN$ | rt | 36 |
| 2 | CsF | $CH_3CN$ | 80 | 39 |
| 3 | CsF | $CH_2Cl_2$ | rt | 52 |
| 4 | TBAF | $CH_2Cl_2$ | rt | 45 |
| 5 | CsF/18-crown-6 | $CH_2Cl_2$ | rt | 50 |

[a] Isolated yields.

With these preliminary results, we varied the amount of phenyl azide (**4h**) used. When molar ratio of benzobisoxadisilole **1** to phenyl azide **4h** was 4:1, we find that the yield of the oxadisilole fused benzotriazole derivative (**5h**) could be improved to 78% (Table 2, entry 6). We also tried other molar ratios, as shown in Table 2, the yields of **5h** have not been improved.

**Table 2**
Cycloaddition of phenyl azide **4h** with benzyne **3** generated from benzobisoxadisilole **1** at room temperature in $CH_2Cl_2$

| Entry | Molar ratio of **1**/**4h** | Yield[a] of **5h** (%) |
|---|---|---|
| 1 | 1:1.2 | 53 |
| 2 | 1:3 | 51 |
| 3 | 1:5 | 55 |
| 4 | 1:10 | 52 |
| 5 | 2:1 | 56 |
| 6 | 4:1 | 78 |

[a] Isolated yields.

We further studied the 1,3-dipolar cycloaddition reaction of benzyne **3** generated in situ from the benzobisoxadisilole **1** with benzyl azides **4a**–**e** or aryl azides **4f**–**j** at room temperature. The oxadisilole fused benzotriazole derivatives **5a**–**j** were formed in 56–92% yields (Scheme 1 and Table 3, entries 1–10). As shown from the chemical yields, this 1,3-dipolar cycloaddition of azides **4** to benzyne **3** is rather sensitive in the electronic nature (X=$OCH_3$, $CH_3$, H, Cl, $NO_2$) of the substituents on the benzyl or aryl azides. The results revealed that electron rich azides gave lower yields than electron deficient ones. Strengthening the electron donating of substituent X, the yield was decreased and the reactivity was weakened. On the contrary, strengthening the electron withdrawing of substituent X, the yield was increased and the reactivity was improved (Table 3). It should be pointed out that the lower yield of product **5j** than **5i** was observed in repeated experiments many times, may be due to a little denitrogenation competing reaction pathways of aryl azide to occur in 1,3-dipolar cycloaddition when the substituent is a so strong electron withdrawing group (X=$NO_2$).

**Table 3**
Cycloaddition of azides **4a**–**j** with benzyne **3** generated from benzobisoxadisilole **1** at room temperature

| Entry | Azide | X | Product | Yield[a] (%) |
|---|---|---|---|---|
| 1 | **4a** | $OCH_3$ | **5a** | 56 |
| 2 | **4b** | $CH_3$ | **5b** | 63 |
| 3 | **4c** | H | **5c** | 67 |
| 4 | **4d** | Cl | **5d** | 80 |
| 5 | **4e** | $NO_2$ | **5e** | 87 |
| 6 | **4f** | $OCH_3$ | **5f** | 61 |
| 7 | **4g** | $CH_3$ | **5g** | 75 |
| 8 | **4h** | H | **5h** | 78 |
| 9 | **4i** | Cl | **5i** | 92 |
| 10 | **4j** | $NO_2$ | **5j** | 74 |

[a] Isolated yields.

Our attention was then turned to the 1,3-dipolar cycloaddition reactions of naphthyne **8** generated in situ from the 2,3-naphthoxadisilole **6** with benzyl azides **4a**–**e**. To our delight, benzyl azides **4a**–**e** successfully participated in the cycloaddition reaction with naphthyne **8** at room temperature to afford the corresponding naphthotriazole derivatives **9a**–**e** in moderate yields (Scheme 2 and Table 4, entries 1–5). The structures of all the cycloadducts, **5a**–**j** and **9a**–**e**, were established by $^1H$ and $^{13}C$ NMR, MS, IR, elemental analysis, and HRMS.

**Table 4**
Cycloaddition of azides **4a**–**e** with 2,3-naphthyne **8** generated from 2,3-naphthoxadisilole **6** at room temperature

| Entry | Azide | X | Product | Yield[a] (%) |
|---|---|---|---|---|
| 1 | **4a** | $OCH_3$ | **9a** | 31 |
| 2 | **4b** | $CH_3$ | **9b** | 38 |
| 3 | **4c** | H | **9c** | 40 |
| 4 | **4d** | Cl | **9d** | 42 |
| 5 | **4e** | $NO_2$ | **9e** | 48 |

[a] Isolated yields.

In summary, a simple and efficient synthetic method of 1,3-dipolar cycloaddition of azides **4a**–**j** with arynes **3** or **8** generated in situ from benzobisoxadisilole **1** or 2,3-naphthoxadisilole **6** has been developed. The experimental results showed that the reaction was affected by electronic effects, wherein the presence of electron withdrawing groups show high reactivity compared to that of electron donating groups. The advantage of the method is not only good yields but also very mild conditions. These reactions could offer great opportunities for the synthesis of important heterocyclic compounds.

## 3. Experimental

### 3.1. General

IR spectra were recorded on a Bruker spectrometer and expressed in $cm^{-1}$ (KBr disc). NMR spectra were measured at

500 MHz for $^1H$ and 125 MHz for $^{13}C$ by Bruker DRX-500 NMR spectrometer. Chemical shifts of $^1H$ NMR were expressed in parts per million downfield from tetramethylsilane with reference to internal residual $CHCl_3$ ($\delta$=7.26) in $CDCl_3$. Chemical shifts of $^{13}C$ NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard ($\delta$=77.17) in $CDCl_3$. Coupling constants ($J$) are quoted in hertz. Low-resolution mass spectra were obtained on an Agilent LC/MSD SL spectrometer in EI mode and reported as $m/z$. High-resolution mass spectra (HRMS) were recorded on a Waters Micromass GCT instrument. Elemental analyses were measured on the Elemental Vario EL III. Melting points were determined on a WRS-1 digital melting point apparatus and are uncorrected. All reagents and solvents were obtained from commercial sources and used without purification, unless indicated otherwise. All non-aqueous reactions were carried out in oven-dried glassware under a slight positive pressure of nitrogen unless otherwise noted. Solvents were reagent grade and purified by standard techniques: THF was distilled from Na/benzophenone; $CH_2Cl_2$ was distilled from $CaH_2$. Crude products were purified by column chromatography on silica gel (G or $GF_{254}$). PE indicates petroleum ether (bp 60–80 °C).

### 3.2. General procedure for the preparation of oxadisilole fused benzotriazole derivatives 5a–j and naphthotriazole derivatives 9a–e

Trifluoromethanesulfonic acid (0.27 mL, 3.0 mmol) was added with a syringe to a stirred solution of phenyliodium diacetate (493 mg, 1.5 mmol in 10 mL of $CH_2Cl_2$) at 0 °C. The mixture was stirred under $N_2$ for 1 h at 0 °C and for 2 h at room temperature. The clear yellow solution was cooled again to 0 °C followed by dropwise addition of a cold (0 °C) solution of the benzobisoxadisilole **1** (or 2,3-naphthoxadisilole **6**) (1.0 mmol in 5 mL of $CH_2Cl_2$). The mixture was stirred for 0.5 h at 0 °C and warmed up to room temperature. After benzobisoxadisilole **1** (or 2,3-naphthoxadisilole **6**) disappeared (monitored by TLC), diisopropylamine (0.35 mL, 2.5 mmol) and azides **4** (0.25 mmol) were added followed by CsF (380 mg, 2.5 mmol). The mixture was stirred under $N_2$ for 5 h at room temperature. The organic solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using a gradient of 2–5% EtOAc in petroleum ether (60–80 °C) as eluent to afford cycloadducts **5a**–**j** and **9a**–**e**.

*3.2.1. 1-(4-Methoxylbenzyl)-5,6-oxadisilole fused benzotriazole (**5a**).* As a white solid; mp 111–112 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.37 (s, 6H), 0.40 (s, 6H), 3.78 (s, 3H), 5.80 (s, 2H), 6.86 (d, $J$=8.5 Hz, 2H), 7.25 (d, $J$=8.5 Hz, 2H), 7.55 (d, $J$=1.0 Hz, 1H), 8.22 (d, $J$=1.0 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.0, 1.1, 51.3, 55.0, 112.4, 114.1, 122.7, 126.8, 128.9, 133.8, 142.0, 146.5, 147.4, 159.4; IR (KBr) 3040, 2959, 2899, 1611, 1513, 1457, 1245, 1127, 1077, 932, 847 $cm^{-1}$; MS $m/z$ (%) (EI): 369 ($M^+$, 33), 340 (55), 326 (89), 310 (57), 121 (100); HRMS: $m/z$ $[M]^+$ calcd for $C_{18}H_{23}N_3O_2Si_2$: 369.1329; found 369.1330.

*3.2.2. 1-(4-Methylbenzyl)-5,6-oxadisilole fused benzotriazole (**5b**).* As a white solid; mp 140–141 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.37 (s, 6H), 0.40 (s, 6H), 2.32 (s, 3H), 5.82 (s, 2H), 7.14 (d, $J$=8.0 Hz, 2H), 7.19 (d, $J$=8.0 Hz, 2H), 7.55 (d, $J$=1.5 Hz, 1H), 8.22 (d, $J$=1.5 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.17, 1.21, 21.0, 51.7, 112.4, 122.9, 127.5, 129.5, 131.9, 134.0, 138.1, 142.1, 146.7, 147.5; IR (KBr) 3034, 2958, 2937, 1600, 1516, 1454, 1249, 1130, 1077, 943, 843 $cm^{-1}$; MS $m/z$ (%) (EI): 353 ($M^+$, 18), 324 (43), 310 (96), 105 (100); HRMS: $m/z$ $[M]^+$ calcd for $C_{18}H_{23}N_3OSi_2$: 353.1380; found 353.1382.

*3.2.3. 1-Benzyl-5,6-oxadisilole fused benzotriazole (**5c**).* As a white solid; mp 147–148 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.36 (s, 6H), 0.41 (s, 6H), 5.87 (s, 2H), 7.29–7.35 (m, 5H), 7.54 (d, $J$=1.0 Hz, 1H), 8.23 (d, $J$=1.0 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.2, 1.3, 52.1, 112.3, 123.1, 127.6, 128.5, 129.0, 134.1, 134.9, 142.3, 146.9, 147.6; IR (KBr) 3064, 2959, 2898, 1601, 1497, 1454, 1251, 1100, 1073, 923, 847 $cm^{-1}$; MS $m/z$ (%) (EI): 339 ($M^+$, 14), 310 (52), 296 (39), 91 (100); HRMS: $m/z$ $[M]^+$ calcd for $C_{17}H_{21}N_3OSi_2$: 339.1223; found 339.1229.

*3.2.4. 1-(4-Chlorobenzyl)-5,6-oxadisilole fused benzotriazole (**5d**).* As a white solid; mp 132–133 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.37 (s, 6H), 0.41 (s, 6H), 5.83 (s, 2H), 7.21 (d, $J$=8.5 Hz, 2H), 7.31 (d, $J$=8.5 Hz, 2H), 7.54 (d, $J$=1.0 Hz, 1H), 8.24 (d, $J$=1.0 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.22, 1.24, 51.2, 112.0, 123.1, 128.9, 129.1, 133.4, 133.9, 134.3, 142.5, 147.2, 147.5; IR (KBr) 3049, 2958, 2896, 1599, 1492, 1456, 1249, 1131, 1074, 942, 845 $cm^{-1}$; MS $m/z$ (%) (EI): 373 ($M^+$, 15), 344 (23), 330 (35), 310 (34), 125 (100); HRMS: $m/z$ $[M]^+$ calcd for $C_{17}H_{20}N_3OClSi_2$: 373.0833; found 373.0837.

*3.2.5. 1-(4-Nitrobenzyl)-5,6-oxadisilole fused benzotriazole (**5e**).* As a white solid; mp 172–173 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.37 (s, 6H), 0.42 (s, 6H), 5.97 (s, 2H), 7.40 (d, $J$=9.0 Hz, 2H), 7.54 (d, $J$=1.5 Hz, 1H), 8.20 (d, $J$=9.0 Hz, 2H), 8.27 (d, $J$=1.5 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.2, 1.3, 50.9, 111.6, 123.3, 124.3, 128.2, 134.0, 142.1, 143.0, 147.6, 147.8, 147.9; IR (KBr) 3080, 2959, 2901, 1608, 1520, 1456, 1252, 1130, 1072, 934, 849 $cm^{-1}$; MS $m/z$ (%) (EI): 384 ($M^+$, 52), 356 (76), 341 (100), 310 (23), 136 (75); HRMS: $m/z$ $[M]^+$ calcd for $C_{17}H_{20}N_4O_3Si_2$: 384.1074; found 384.1070.

*3.2.6. 1-(4-Methoxylphenyl)-5,6-oxadisilole fused benzotriazole (**5f**).* As a white solid; mp 118–119 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.40 (s, 6H), 0.44 (s, 6H), 3.92 (s, 3H), 7.14 (d, $J$=8.5 Hz, 2H), 7.66 (d, $J$=8.5 Hz, 2H), 7.81 (d, $J$=1.5 Hz, 1H), 8.30 (d, $J$=1.5 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.16, 1.20, 55.5, 112.8, 114.9, 123.0, 124.7, 129.8, 133.8, 142.6, 147.5, 159.8; IR (KBr) 3083, 2958, 1608, 1515, 1462, 1257, 1110, 1081, 938, 850 $cm^{-1}$; MS $m/z$ (%) (EI):355 ($M^+$, 4), 312 (100), 296 (7), 281 (2), 121 (2); HRMS: $m/z$ $[M]^+$ calcd for $C_{17}H_{21}N_3O_2Si_2$: 355.1172; found 355.1169.

*3.2.7. 1-(4-Methylphenyl)-5,6-oxadisilole fused benzotriazole (**5g**).* As a white solid; mp 135–136 °C; $^1H$ NMR (500 MHz, $CDCl_3$)) $\delta$ 0.40 (s, 6H), 0.44 (s, 6H), 2.49 (s, 3H), 7.44 (d, $J$=8.0 Hz, 2H), 7.65 (d, $J$=8.0 Hz, 2H), 7.85 (d, $J$=1.0 Hz, 1H), 8.30 (d, $J$=1.0 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.2, 1.3, 21.2, 113.0, 123.1, 123.2, 130.4, 133.6, 134.5, 138.8, 142.7, 147.68, 147.74; IR (KBr) 2957, 1600, 1516, 1443, 1250, 1112, 1083, 930, 845 $cm^{-1}$; MS $m/z$ (%) (EI): 339 ($M^+$, 4), 296 (100), 105 (4); HRMS: $m/z$ $[M]^+$ calcd for $C_{17}H_{21}N_3OSi_2$: 339.1223; found 339.1227.

*3.2.8. 1-Phenyl-5,6-oxadisilole fused benzotriazole (**5h**).* As an orange solid; mp 139–140 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.42 (s, 6H), 0.45 (s, 6H), 7.52–7.56 (m, 1H), 7.63–7.66 (m, 2H), 7.79–7.81 (m, 2H), 7.89–7.90 (m, 1H), 8.32 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.26, 1.29, 112.9, 123.1, 123.3, 128.8, 129.9, 133.5, 137.0, 143.0, 147.9, 148.0; IR (KBr) 3054, 2958, 1597, 1501, 1436, 1252, 1171, 1084, 934, 847 $cm^{-1}$; MS $m/z$ (%) (EI): 325 ($M^+$, 3), 282 (100), 77 (4); HRMS: $m/z$ $[M]^+$ calcd for $C_{16}H_{19}N_3OSi_2$: 325.1067; found 325.1065.

*3.2.9. 1-(4-Chlorophenyl)-5,6-oxadisilole fused benzotriazole (**5i**).* As a white solid; mp 159–160 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.42 (s, 6H), 0.45 (s, 6H), 7.62 (d, $J$=8.5 Hz, 2H), 7.75 (d, $J$=8.5 Hz, 2H), 7.84 (d, $J$=1.5 Hz, 1H), 8.32 (d, $J$=1.5 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 1.28, 1.30, 112.6, 123.4, 124.2, 130.2, 133.4, 134.5, 135.6, 143.3, 147.9, 148.4; IR (KBr) 3058, 2956, 1594, 1497, 1441, 1251, 1176, 1085, 928, 845 $cm^{-1}$; MS $m/z$ (%) (EI): 359 ($M^+$, 4), 316 (100), 296 (8), 281 (9), 111 (3); HRMS: $m/z$ $[M]^+$ calcd for $C_{16}H_{18}N_3OClSi_2$: 359.0677; found 359.0674.

*3.2.10. 1-(4-Nitrophenyl)-5,6-oxadisilole fused benzotriazole (**5j**).* As a white solid; mp 237–239 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 0.45 (s,

6H), 0.46 (s, 6H), 7.95 (d, *J*=1.0 Hz, 1H), 8.08 (d, *J*=9.0 Hz, 2H), 8.36 (d, *J*=1.0 Hz, 1H), 8.54 (d, *J*=9.0 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 1.3, 112.6, 122.6, 123.8, 125.7, 132.9, 142.1, 144.2, 146.9, 148.3, 149.6; IR (KBr) 3085, 2962, 1592, 1520, 1502, 1246, 1112, 1083, 939, 850 cm$^{-1}$; MS *m*/*z* (%) (EI): 370 ($M^+$, 8), 327 (100), 296 (72), 281 (95), 122 (2); HRMS: *m*/*z* $[M]^+$ calcd for $C_{16}H_{18}N_4O_3Si_2$: 370.0917; found 370.0922.

*3.2.11. 1-(4-Methoxybenzyl)naphthotriazole (**9a**).* As a brown solid; mp 145–146 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.71 (s, 3H), 5.82 (s, 2H), 6.81 (d, *J*=8.0 Hz, 2H), 7.24 (d, *J*=8.0 Hz, 2H), 7.35–7.42 (m, 2H), 7.74 (s, 1H), 7.82 (d, *J*=8.5 Hz, 1H), 7.96 (d, *J*=8.5 Hz, 1H), 8.57 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 51.9, 55.3, 105.6, 114.3, 117.9, 124.66, 126.5, 126.9, 128.0, 129.0, 129.3, 130.5, 131.4, 132.8, 145.5, 159.6; IR (KBr) 3043, 2963, 2934, 1610, 1512, 1461, 1246, 1140, 1087, 946, 853 cm$^{-1}$; MS *m*/*z* (%) (EI): 289 ($M^+$, 100), 260 (53), 240 (91), 230 (44), 121 (97). Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.45; H, 5.38; N, 13.93.

*3.2.12. 1-(4-Methylbenzyl)naphthatriazole (**9b**).* As a yellow solid; mp 156–157 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.29 (s, 3H), 5.87 (s, 2H), 7.11 (d, *J*=8.0 Hz, 2H), 7.20 (d, *J*=8.0 Hz, 2H), 7.37–7.44 (m, 2H), 7.75 (s, 1H), 7.83 (d, *J*=8.5 Hz, 1H), 7.98 (d, *J*=8.5 Hz, 1H), 8.59 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 21.1, 52.1, 105.5, 117.9, 124.6, 126.5, 127.5, 127.9, 129.3, 129.6, 130.5, 131.5, 131.9, 132.8, 138.2, 145.5; IR (KBr) 3046, 2972, 2851, 1614, 1512, 1441, 1257, 1141, 1093, 950, 855 cm$^{-1}$; MS *m*/*z* (%) (EI): 273 ($M^+$, 100), 244 (89), 230 (90), 105 (96); HRMS: *m*/*z* $[M]^+$ calcd for $C_{18}H_{15}N_3$: 273.1266; found 273.1265.

*3.2.13. 1-Benzylnaphthatriazole (**9c**).* As a white solid; mp 182–183 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.94 (s, 2H), 7.32 (s, 5H), 7.40–7.47 (m, 2H), 7.77 (s, 1H), 7.86 (d, *J*=8.0 Hz, 1H), 8.01 (d, *J*=8.0 Hz, 1H), 8.62 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 52.3, 105.5, 118.1, 124.8, 126.6, 127.6, 128.0, 128.5, 129.1, 129.4, 130.6, 131.6, 132.9, 135.0, 145.5; IR (KBr) 3059, 2961, 2928, 1629, 1497, 1453, 1258, 1103, 1072 cm$^{-1}$; MS *m*/*z* (%) (EI): 259 ($M^+$, 54), 230 (82), 91 (100). Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.20. Found: C, 78.35; H, 5.13; N, 16.01.

*3.2.14. 1-(4-Chlorobenzyl) naphthatriazole (**9d**).* As a white solid; mp 158–159 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.89 (s, 2H), 7.27–7.29 (m, 4H), 7.40–7.47 (m, 2H), 7.74 (s, 1H), 7.86 (d, *J*=8.5 Hz, 1H), 8.01 (d, *J*=8.5 Hz, 1H), 8.62 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 51.5, 105.3, 118.2, 124.9, 126.8, 127.9 128.9, 129.3, 129.4, 130.6, 131.4, 133.0, 133.4, 134.4, 145.4; IR (KBr) 3039, 2965, 2937, 1613, 1489, 1470, 1257, 1147, 1085, 932, 854 cm$^{-1}$; MS *m*/*z* (%) (EI): 293 ($M^+$, 54), 264 (43), 230 (52), 125 (100). Anal. Calcd for $C_{17}H_{12}ClN_3$: C, 69.51; H, 4.12; N, 14.30. Found: C, 69.30; H, 4.17; N, 14.15.

*3.2.15. 1-(4-Nitrobenzyl) naphthatriazole (**9e**).* As a yellow solid; mp 188–190 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.04 (s, 2H), 7.41–7.48 (m, 4H), 7.76 (s, 1H), 7.87 (d, *J*=8.5 Hz, 1H), 8.03 (d, *J*=8.5 Hz, 1H), 8.16 (d, *J*=8.5 Hz, 2H), 8.65 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 51.3, 104.9, 118.6, 124.3, 125.1, 127.1, 127.9, 128.3, 129.5, 130.8, 131.4, 133.2, 142.1, 145.4, 148.0; IR (KBr) 3102, 2967, 2940, 1605, 1526, 1443, 1257, 1108, 1090, 941, 856 cm$^{-1}$; MS *m*/*z* (%) (EI): 304 ($M^+$, 100), 275 (21), 229 (44), 136 (94); HRMS: *m*/*z* $[M]^+$ calcd for $C_{17}H_{12}N_4O_2$: 304.0960; found 304.0958.

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