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Silver-Catalyzed Nitration/Annulation of α-Alkynyl Arylols toward 3-Nitrated Benzofurans

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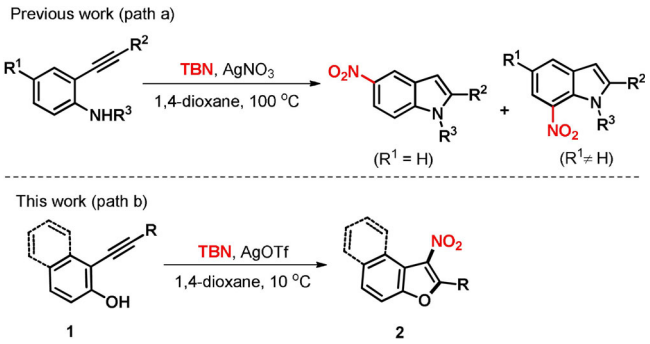
Abstract: A silver-catalyzed nitration/annulation of α-alkynyl arylols is reported by using *tert*-butyl nitrite (TBN) as a NO_2 radical precursor, from which a set of 3-nitrated benzofurans were synthesized with moderate to good yields. This transformation initiated by an in situ generated NO_2 radical proceeds efficiently under mild and neutral redox conditions, which provides a new pathway toward the 3-nitrobenzofuran framework via catalytic difunctionalization of internal alkynes.

Introduction

Catalytic addition of alkynes toward their functionalization remains one of the hot topics in modern organic synthesis,[1] providing economical and efficient methods for numerous functionalized molecular libraries. Specifically, difunctionalization of alkynes via addition of heteroatoms across carbon-carbon multiple bond has been recognized as a step- and atom-economic synthetic strategy for the assembly of heteroatom-containing molecules with high stereoselectivity.[2] Among them, radical-induced addition/intramolecular annulations of internal alkynes have been one of the most attractive targets in the organic community since such transformations not only realize alkyne difunctionalization but also construct bioactive heterocyclic system in a highly regioselective manner, and thus has drawn considerable attention from chemists.[3] On the other hand, *tert*-butyl nitrite (TBN) emerges as a powerful NO_2 radical precursor, which have been widely applied in the synthesis of nitrogen-containing compounds including nitroarenes.[4] Recently, our group reported a silver-catalyzed nitration-annulation of 2-alkynylanilines with TBN, leading to the selective generation of a variety of C5/7-nitroindoles (Scheme 1, path a).[5] However, NO_2 radical-triggered difunctionalization of internal alkynes remains almost unexplored,[6] probably because of their strong bond energy and difficulty in the regioselectivity.[7]

One the other hand, benzofurans are an important structural scaffold in the pharmaceutical application and have exhibited a remarkable biological and pharmacological activities.[8] For instance, 3-nitrobenzofurans have been found to show antibacterial, parasiticidal[9] and antimicrobial[10] activities. With these contributions in mind, considerable effort has been made to identify efficient methods for the synthesis of these 3-nitrobenzofurans, including traditional electrophilic substitution of benzofurans using HNO_3 as nitrating reagents[11] and cyclization of benzoquinones with nitro compounds.[12] However, these methods often suffer from over-nitration and poor regioselectivity, narrow substrate scope and limited functional group tolerance, thereby limiting their further applications to a certain extent. To search a new entry to construct 3-nitrobenzofuran skeleton and to continue our efforts on radical transformations,[13] we found that by using α-alkynyl arylols **1** as internal alkynes[14] and TBN as a nitrating reagent, a silver-catalyzed reaction proceeded readily in a highly regioselective manner, enabling nitro radical addition/intramolecular annulation to access a vast array of structurally diverse 3-nitrobenzofurans **2** in moderate to good yields (Scheme 1, path b). Herein, we elaborate this attractive transformation for the achievement of NO_2 radical difunctionalization of internal alkynes.



Scheme 1. Profiles of nitration-annulation of TBN.

Results and Discussion

We initiated our investigations with 1-(phenylethynyl)naphthalen-2-ol (**1a**) and commercially available TBN as the nitrating

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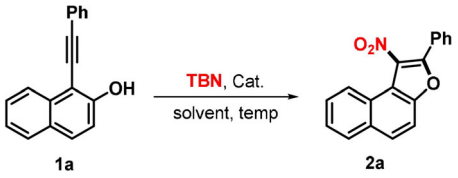
agent. The reaction of **1a** with in a 1:1 mol ratio worked in the presence of $AgNO_3$ (10 mol%) at 10 °C in tetrahydrofuran (THF) under air conditions. To our delight, 1-nitronaphtho[2,1-*b*]furan product **2a** was obtained in 45% yield (Table 1, entry 1). Without $AgNO_3$, the reaction did not proceed, indicating silver salts are crucial for this transformation (entry 2). Reducing reaction temperature to 0 °C resulted in a slightly dropped yield of **2a** (43%, entry 3). In contrast, the yield of **2a** remarkably decreased when the temperature was raised to 25 °C (entry 4). As the next optimization step, we examined the solvent effect by adjusting reaction media, including 1,4-dioxane, toluene, dimethylformamide (DMF), dichloroethane (DCE) and acetonitrile (entries 5–9). After carful screening of these solvents, we found that 1,4-dioxane was proven to be the best one, affording **2a** in 50% yield (entry 5). The yield of **2a** levelled off by increasing the amount of TBN (entry 10). Subsequently, an increase in the loading of $AgNO_3$ to 0.5 equivalent facilitated the transformation, providing **2a** in 53% yield (entry 11). Further increasing $AgNO_3$ loading to 1.0 equivalent did not show any improvement on the yield of **2a** (entry 12). The following screening of other silver catalysts such as $AgBF_4$, AgOTf and Ag_2CO_3 (entries 13–15) revealed that AgOTf was the best choice, delivering a higher yield than $AgNO_3$ (entry 14 vs. entry 11).

Table 1. Optimization Conditions for Forming **2a**.[a]

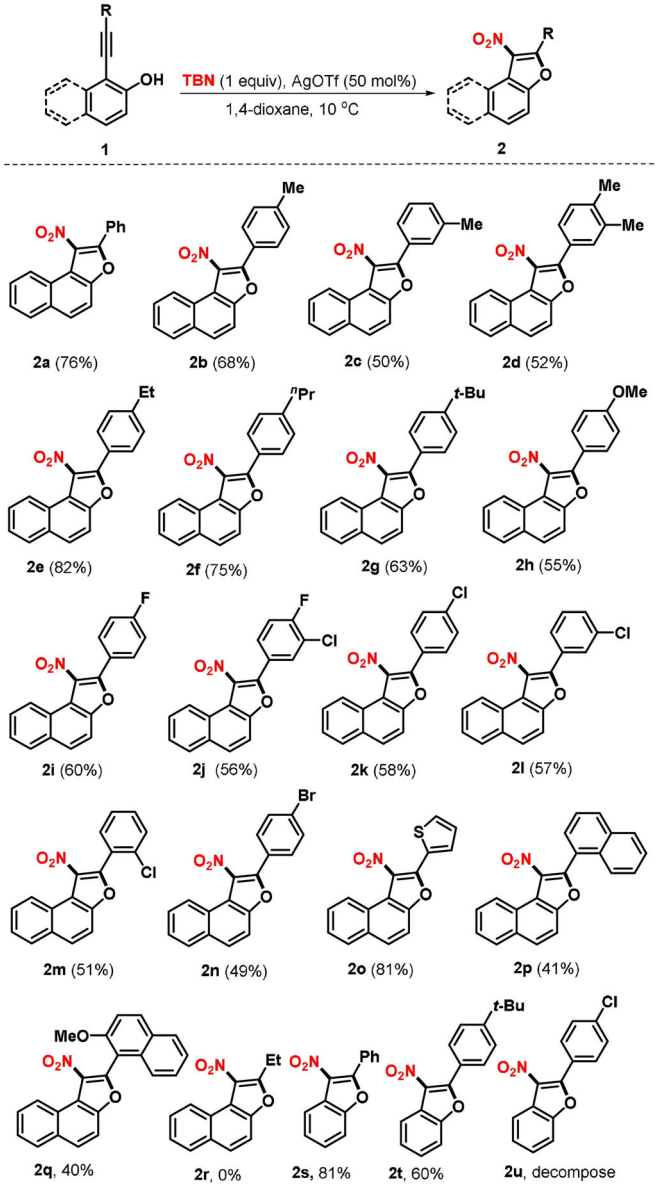


1a **2a**

Entry	Ag-cat. [mol%]	Ratio [**1a**/TBN]	Solvent	*t* [°C]	Yield [%][b]
1	$AgNO_3$ (0.1)	1:1	THF	10	45
2	–	1:1	THF	10	N.R.
3	$AgNO_3$ (0.1)	1:1	THF	0	43
4	$AgNO_3$ (0.1)	1:1	THF	25	17
5	$AgNO_3$ (0.1)	1:1	1,4-dioxane	10	50
6	$AgNO_3$ (0.1)	1:1	toluene	10	N.R.
7	$AgNO_3$ (0.1)	1:1	DMF	10	N.D.
8	$AgNO_3$ (0.1)	1:1	DCE	10	24
9	$AgNO_3$ (0.1)	1:1	CH_3CN	10	N.D.
10	$AgNO_3$ (0.1)	1:2	1,4-dioxane	10	51
11	$AgNO_3$ (0.5)	1:1	1,4-dioxane	10	53
12	$AgNO_3$ (1.0)	1:1	1,4-dioxane	10	53
13	$AgBF_4$ (0.5)	1:1	1,4-dioxane	10	42
14	AgOTf (0.5)	1:1	1,4-dioxane	10	76
15	Ag_2CO_3 (0.5)	1:1	1,4-dioxane	10	40

[a] Reaction conditions: **1a** (0.2 mmol), solvent (2.0 mL), 0.5 h in a sealed tube. [b] Isolated yield.

With the optimized reaction conditions in hands, we then investigated the scope of this nitration-annulation reaction by examining various α-alkynyl arylols under standard conditions (Scheme 2). The presence of substituents on the aryl ring (R) relative to the alkynyl moiety did not hamper the reaction process. Both electronically rich and poor groups at different positions could show highly reactive profiles, delivering the corresponding 1-nitronaphtho[2,1-*b*]furans **2b**–**2q** in 40–82% yields. Obviously, the radical system can readily endure various substituents, such as methyl (**1b**, **1c** and **1d**), ethyl (**1e**), *n*-propyl (**1f**), *tert*-butyl (**1g**), fluoro (**1i** and **1j**), chloro (**1k**, **1l** and **1h**), and bromo (**1n**). Among them, both Cl and Br groups provide the possibility for further functionalization. Alternatively, 2-thienyl analogue **1o** did not influence the reaction output, affording product **2o** in 81% yield. Moreover, sterically more demanding 1-naphthyl (1-Np) **1p** and 2-methoxynaphthalen-1-yl (1-(2-MeO)Np) **1q** were suitable surrogates for the alkyne difunctionalization, albeit with remarkably declining yields of products **2p** and **2q**. However, α-alkynyl arylol **1r** bearing an ethyl group did not work in this transformation.



Scheme 2. Synthesis of 3-nitrofurans.

To broaden the scope of this protocol, representative α-alkynylphenols **1s**–**1u** were employed to react with TBN. All these reactions worked well under standard conditions. In cases of **1s** and **1t**, products **2s** and **2t** were offered in 81% and 60%

yields, respectively. The desired product **2u** was observed but extremely decomposed during purification process and failed to be isolated. The structures of products **2** have been fully characterized by NMR and HRMS analyses. Furthermore, the structure of **2k** has been determined by X-ray diffraction analysis (Figure 1, see the Supporting Information).[15]

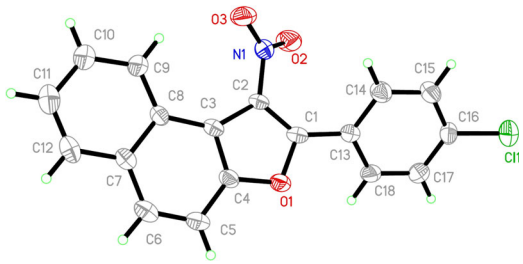
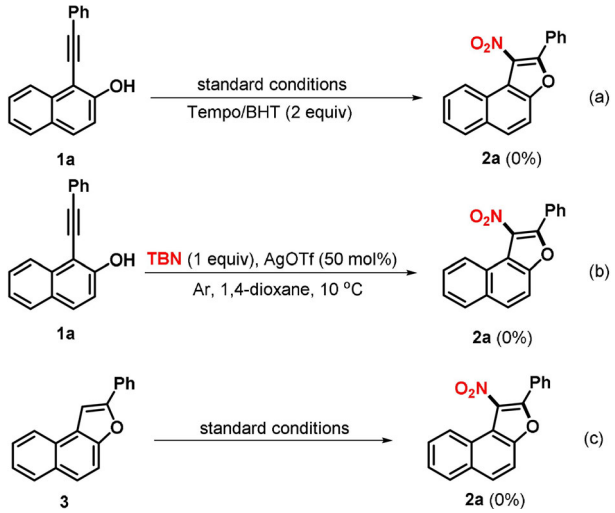


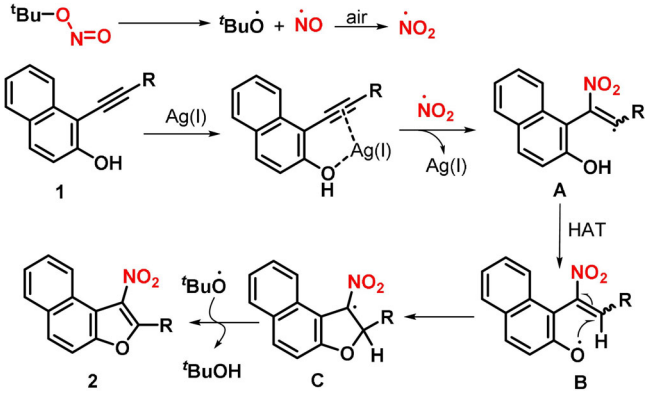
Figure 1. X-ray Structure of **2k**.

In order to gain insights on the mechanistic pathway, several control experiments were conducted. 2.0 Equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the radical scavenger was first subjected to the reaction mixture of **1a** and TBN under the standard conditions, the reaction was completely inhibited. The similar outcome was observed as the antioxidant butylated hydroxytoluene (BHT) was used (Scheme 3a). These results show that the mechanism may include a radical process. Next, the reaction of **1a** with TBN under argon (Ar) conditions failed to generate the desired product **2a** with the starting materials remaining unconsumed (Scheme 3b), showing that O_2 may participate in the reaction process. To further confirm the sequence of nitration and annulation, subjecting the preformed 2-phenylnaphtho[2,1-*b*]furan **3** to the standard conditions failed to generate any desired product **2a** with the starting materials remaining unconsumed (Scheme 3c), indicating that the nitration drove annulation reaction.



Scheme 3. Control experiments.

Combining the above experimental results and literature survey, a reasonable mechanism for forming 3-nitrofurans was proposed (Scheme 4). Initially, the decomposition of TBN yields *t*BuO$^{\bullet}$ together with NO radical (·NO), followed oxidized by O_2 from air to give NO_2 radical (·NO_2). Next, addition of NO_2 radical to carbon-carbon triple bond of **1** activated by silver catalyst



Scheme 4. Plausible mechanism.

gives alkenyl radical intermediate **A**, which undergoes 1,5-hydrogen atom transfer (HAT) to give alkenyl *O*-centered radical intermediate **B**. Subsequent intramolecular 5-*endo*-*trig* cyclization of intermediate **B** occurs, providing *C*-centered radical intermediate **C**. Finally, *t*BuO$^{\bullet}$ abstracts hydrogen atom to afford the desired products **2**.

Conclusions

In summary, we have successfully established an efficient radical-enabled difunctionalization of internal alkynes with TBN via a silver-catalyzed nitration–annulation cascade, providing a wide range of 3-nitrated benzofurans with moderate to good yields. The transformation offered a new entry to prepare the 3-nitrobenzofuran skeleton, avoiding the use of traditional HNO_3 as a NO_2 source. Further investigation and application of this nitration–annulation reaction is underway in our laboratory.

Experimental Section

General Information

All one-pot reactions were carried out in a 10-mL Schlenk tube equipped with a magnetic stir bar under air. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a 400 MHz instrument with TMS as internal standard. Chemical shifts (δ) were reported in ppm with respect to TMS. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = oublet, m = multiples), coupling constant (J, Hz) and integration. HRMS analyses were carried out using a TOF-MS instrument with an APCI source. X-Ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer.

General Procedure for the Synthesis of Products 2.

Example for the synthesis of 2a:

A suspension of $AgNO_3$ (0.1 mmol, 0.5 equiv), *t*BuONO (0.2 mmol, 1.0 equiv) in 1.0 mL of 1,4-dioxane was stirred at 10 °C under air conditions. Subsequently, 1-(phenylethynyl)naphthalen-2-ol **1a** (0.2 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) was added into the suspension over 30 min via a syringe pump. Next, the mixture was sealed and stirred for 30 min until TLC (petroleum ether: ethyl acetate = 1:15, v/v) revealed that conversion of the starting material **1a** was completed. The reaction system was evaporated under vacuum and purified by flash column chromatography (silica gel, mixtures of petroleum ether/ ethyl acetate = 1:50, v/v) to afford the desired product **2a**.

1-nitro-2-phenylnaphtho[2,1-b]furan (2a)

Light yellow solid, 44 mg, 76% yield; mp 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.91–7.85 (m, 3H), 7.70–7.62 (m, 2H), 7.61–7.56 (m, 1H), 7.56–7.51 ppm (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 150.4, 131.5, 130.9, 129.3, 128.9, 128.8, 128.2, 127.5, 127.4, 125.9, 125.9, 123.9, 115.3, 111.9 ppm. IR (KBr): $\tilde{\nu}$ = 1507, 1453, 1388, 1356, 1200, 1131, 1020, 802, 750 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{12}NO_3$ $[M+H]^+$ 290.0817, found 290.0835.

1-nitro-2-(p-tolyl)naphtho[2,1-b]furan (2b)

Light yellow solid, 41 mg, 68% yield; mp 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.89–7.83 (m, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.69–7.60 (m, 2H), 7.60–7.54 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 2.45 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 150.2, 141.5, 131.4, 129.6, 129.3, 128.6, 128.2, 127.4, 125.9, 125.8, 124.6, 124.0, 115.4, 111.9, 21.7 ppm. IR (KBr): $\tilde{\nu}$ = 1506, 1389, 1356, 1213, 1015, 801, 736 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{19}H_{14}NO_3$ $[M+H]^+$ 304.0974, found 304.0981.

1-nitro-2-(m-tolyl)naphtho[2,1-b]furan (2c)

Light yellow solid, 30 mg, 50% yield; mp 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.71–7.66 (m, 3H), 7.66–7.61 (m, 1H), 7.61–7.55 (m, 1H), 7.45–7.39 (m, 1H), 7.34 (d, J = 7.6 Hz, 1H), 2.46 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 150.3, 138.7, 131.8, 131.4, 129.3, 128.8, 128.7, 128.6, 127.5, 127.3, 125.9, 125.3, 123.9, 115.4, 111.9, 21.5 ppm. IR (KBr): $\tilde{\nu}$ = 1565, 1505, 1392, 1362, 1192, 1089, 1007, 812, 745 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{19}H_{14}NO_3$ $[M+H]^+$ 304.0974, found 304.0970.

2-(3,4-dimethylphenyl)-1-nitronaphtho[2,1-b]furan (2d)

Light yellow solid, 33 mg, 52% yield; mp 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.67–7.61 (m, 4H), 7.59–7.54 (m, 1H), 7.27 (d, J = 8.4 Hz, 1H), 2.35 (s, 3H), 2.34 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 150.1, 140.2, 137.3, 131.4, 130.1, 129.3, 129.0, 128.5, 127.4, 125.9, 125.8, 125.7, 124.9, 124.0, 115.4, 111.9, 20.0, 19.9 ppm. IR (KBr): $\tilde{\nu}$ = 1506, 1391, 1359, 1255, 1212, 1180, 1006, 817, 795, 748 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{20}H_{16}NO_3$ $[M+H]^+$ 318.1130, found 318.1125.

2-(4-ethylphenyl)-1-nitronaphtho[2,1-b]furan (2e)

Light yellow solid, 52 mg, 82% yield; mp 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88–7.78 (m, 3H), 7.68–7.61 (m, 2H), 7.60–7.54 (m, 1H), 7.36 (d, J = 8.0 Hz, 2H), 2.79–2.70 (m, 2H), 1.31 ppm (t, J = 7.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 150.2, 147.7, 131.4, 129.3, 128.6, 128.4, 128.3, 127.4, 125.9, 125.8, 124.7, 124.0, 115.4, 111.9, 29.0, 15.3 ppm. IR (KBr): $\tilde{\nu}$ = 1496, 1392, 1360, 1213, 1116, 1017, 840, 785 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{20}H_{16}NO_3$ $[M+H]^+$ 318.1130, found 318.1141.

1-nitro-2-(4-propylphenyl)naphtho[2,1-b]furan (2f)

Light yellow solid, 50 mg, 75% yield; mp 80–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 8.4 Hz, 1H), 8.01–7.94 (m, 1H), 7.90–7.84 (m, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.70–7.61 (m, 2H), 7.60–7.54 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.71–2.64 (m, 1H), 1.76–1.65 (m, 2H), 0.99 ppm (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 150.2, 146.2, 131.5, 129.3, 129.0, 128.6, 128.2, 127.4, 125.9, 125.8, 124.8, 124.0, 115.4, 111.9, 38.1, 24.3, 13.9 ppm. IR (KBr): $\tilde{\nu}$ = 1506, 1383, 1341, 1219, 1187, 1007, 835, 769 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{21}H_{18}NO_3$ $[M+H]^+$ 332.1287, found 332.1282.

2-(4-(tert-butyl)phenyl)-1-nitronaphtho[2,1-b]furan (2g)

Light yellow solid, 44 mg, 63% yield; mp 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.89–7.82 (m, 3H), 7.68–7.61 (m, 2H), 7.60–7.52 (m, 3H), 1.39 ppm (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 152.9, 150.2, 131.4, 129.3, 128.6, 128.0, 127.4, 125.9, 125.8, 124.5, 124.0, 115.4, 111.9, 35.1, 31.2 ppm. IR (KBr): $\tilde{\nu}$ = 1573, 1508, 1393, 1357, 1210, 1143, 1014, 827, 802, 754 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{22}H_{20}NO_3$ $[M+H]^+$ 346.1443, found 346.1429.

2-(4-ethylphenyl)-1-nitronaphtho[2,1-b]furan (2h)

Light yellow solid, 35 mg, 55% yield; mp 143–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.90–7.82 (m, 3H), 7.67–7.61 (m, 2H), 7.59–7.54 (m, 1H), 7.06–7.01 (m, 2H), 3.89 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 153.2, 150.0, 131.5, 130.2, 129.3, 128.4, 127.3, 125.9, 125.7, 124.1, 119.8, 115.5, 114.3, 111.8, 55.5 ppm. IR (KBr): $\tilde{\nu}$ = 1608, 1506, 1389, 1351, 1256, 1176, 1021, 825, 796 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{19}H_{14}NO_4$ $[M+H]^+$ 320.0923, found 320.0930.

2-(4-fluorophenyl)-1-nitronaphtho[2,1-b]furan (2i)

Light yellow solid, 37 mg, 60% yield; mp 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.93–7.86 (m, 3H), 7.68–7.63 (m, 2H), 7.61–7.56 (m, 1H), 7.26–7.19 ppm (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1 ($^1J_{CF}$ = 251.6 Hz), 151.75, 150.32, 131.49, 130.72, 130.64, 129.33, 128.94, 127.55, 125.95, 125.85, 124.01, 123.65, 123.61, 116.2 ($^2J_{CF}$ = 22.0 Hz), 115.24, 111.81 ppm. IR (KBr): $\tilde{\nu}$ = 1606, 1508, 1362, 1237, 1164, 1102, 831, 795, 752 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{11}FNO_3$ $[M+H]^+$ 308.0723, found 308.0719.

2-(3-chloro-4-fluorophenyl)-1-nitronaphtho[2,1-b]furan (2j)

Light yellow solid, 38 mg, 56% yield; mp 152–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, J = 8.4 Hz, 1H), 8.02–7.95 (m, 2H), 7.90 (d, J = 8.8 Hz, 1H), 7.83–7.77 (m, 1H), 7.70–7.64 (m, 2H), 7.62–7.57 (m, 1H), 7.33–7.27 ppm (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5 ($^1J_{CF}$ = 253.8 Hz), 150.5, 150.1, 131.5, 130.9, 129.4, 129.4,

128.5 ($^3J_{CF}$ = 7.9 Hz), 127.7, 126.1, 125.8, 124.6 ($^4J_{CF}$ = 4.1 Hz), 124.0, 122.2, 122.0, 117.3, 117.11 ($^2J_{CF}$ = 21.7 Hz), 115.1, 111.8 ppm. IR (KBr): $\tilde{\nu}$ = 1508, 1392, 1363, 1266, 1212, 1122, 1061, 900, 817 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{10}ClFNO_3$ $[M+H]^+$ 342.0333, found 342.0335.

2-(4-chlorophenyl)-1-nitronaphtho[2,1-b]furan (2k)

Light yellow solid, 38 mg, 58% yield; mp 153–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.86–7.81 (m, 2H), 7.69–7.63 (m, 2H), 7.62–7.56 (m, 1H), 7.53–7.47 ppm (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2, 150.5, 137.2, 131.5, 129.5, 130.0, 129.2, 129.1, 127.6, 126.0, 125.8, 123.9, 115.3, 111.8 ppm. IR (KBr): $\tilde{\nu}$ = 1510, 1483, 1392, 1354, 1199, 1093, 1012, 805, 747 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{11}ClNO_3$ $[M+H]^+$ 324.0427, found 324.0430.

2-(3-chlorophenyl)-1-nitronaphtho[2,1-b]furan (2l)

Light yellow solid, 37 mg, 57% yield; mp 135–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.91–7.85 (m, 2H), 7.78–7.74 (m, 1H), 7.69–7.62 (m, 2H), 7.61–7.56 (m, 1H), 7.51–7.43 ppm (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 150.5, 135.0, 131.5, 130.9, 130.2, 129.4, 129.3, 129.0, 128.1, 127.7, 126.2, 126.1, 125.8, 123.9, 115.2, 111.8 ppm. IR (KBr): $\tilde{\nu}$ = 1560, 1509, 1475, 1359, 1145, 1080, 997, 792 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{11}ClNO_3$ $[M+H]^+$ 324.0427, found 324.0435.

2-(2-chlorophenyl)-1-nitronaphtho[2,1-b]furan (2m)

Light yellow solid, 33 mg, 51% yield; mp 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.92–7.85 (m, 2H), 7.79–7.73 (m, 1H), 7.69–7.62 (m, 2H), 7.61–7.56 (m, 1H), 7.51–7.43 ppm (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 150.4, 135.0, 131.5, 130.9, 130.2, 129.4, 129.3, 129.0, 128.1, 127.7, 126.2, 126.1, 125.8, 123.9, 115.2, 111.8 ppm. IR (KBr): $\tilde{\nu}$ = 1560, 1509, 1475, 1359, 1211, 1145, 1080, 997, 804 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{11}ClNO_3$ $[M+H]^+$ 324.0427, found 324.0436.

2-(4-bromophenyl)-1-nitronaphtho[2,1-b]furan (2n)

Light yellow solid, 36 mg, 49% yield; mp 160–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.79–7.75 (m, 2H), 7.70–7.63 (m, 4H), 7.62–7.57 ppm (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 150.5, 132.2, 131.5, 129.6, 129.4, 129.2, 127.6, 126.3, 126.0, 125.8, 125.6, 123.9, 115.3, 111.8 ppm. IR (KBr): $\tilde{\nu}$ = 1596, 1506, 1356, 1213, 1134, 1075, 1012, 833, 802 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{11}BrNO_3$ $[M+H]^+$ 367.9922, found 367.9917.

1-nitro-2-(thiophen-2-yl)naphtho[2,1-b]furan (2o)

Light yellow solid, 48 mg, 81% yield; mp 163–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.4 Hz, 1H), 8.13–8.08 (m, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.70–7.62 (m, 3H), 7.61–7.55 (m, 1H), 7.26–7.23 ppm (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 150.1, 131.7, 131.7, 131.6, 129.3, 129.3, 128.9, 128.2, 127.4, 126.0, 125.9, 125.0, 115.2, 111.6 ppm. IR (KBr): $\tilde{\nu}$ = 1556, 1493, 1419, 1360, 1224, 1123, 1056, 806 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{16}H_{10}NO_3S$ $[M+H]^+$ 296.0381, found 296.0385.

2-(naphthalen-1-yl)-1-nitronaphtho[2,1-b]furan (2p)

Light yellow solid, 28 mg, 41% yield; mp 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.97 (m, 2H), 7.84 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (m, 2H), 7.63 (m, 2H), 7.60–7.50 ppm (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 151.2, 133.5, 131.7, 131.7, 131.5, 129.6, 129.3, 129.0, 128.8, 127.6, 126.7, 126.1, 126.0, 125.2, 125.0, 124.9, 124.7, 114.6, 112.1 ppm. IR (KBr): $\tilde{\nu}$ = 1506, 1447, 1320, 1301, 1219, 1134, 829 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{22}H_{13}NO_3$ $[M+H]^+$ 340.0974, found 340.1012.

2-(2-methoxynaphthalen-1-yl)-1-nitronaphtho[2,1-b]furan (2q)

Light yellow solid, 30 mg, 40% yield; mp 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.64–7.58 (m, 2H), 7.51–7.45 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 3.93 ppm (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 151.6, 133.3, 133.1, 131.6, 129.2, 128.8, 128.6, 128.5, 128.0, 127.4, 126.2, 125.8, 125.1, 124.3, 124.0, 112.7, 112.2, 56.5 ppm. IR (KBr): $\tilde{\nu}$ = 1506, 1411, 1357, 1329, 1183, 1131, 1042, 865, 746 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{23}H_{16}NO_4$ $[M+H]^+$ 370.1079, found 370.1054.

3-nitro-2-phenylbenzofuran (2s)

Light yellow solid, 39 mg, 81% yield; mp 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 2.0 Hz, 1H), 8.25–8.20 (m, 1H), 7.91–7.86 (m, 2H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.53–7.47 (m, 2H), 7.46–7.40 (m, 1H), 7.14 ppm (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 157.6, 144.3, 129.7, 129.7, 129.2, 129.1, 125.3, 120.1, 117.3, 111.5, 101.6 ppm. IR (KBr): $\tilde{\nu}$ = 1514, 1440, 1348, 1262, 1069, 1016, 862 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{14}H_{10}NO_3$ $[M+H]^+$ 240.0661, found 240.0670.

2-(4-(tert-butyl)phenyl)-3-nitrobenzofuran (2t)

Light yellow solid, 15 mg, 26% yield; mp 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.07 (m, 1H), 7.91–7.83 (m, 3H), 7.54–7.49 (m, 2H), 7.37–7.30 (m, 1H), 7.07 (s, 1H), 1.37 ppm (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 153.1, 146.9, 133.8, 133.4, 127.3, 126.3, 126.0, 125.3, 122.8, 120.2, 100.2 ppm. IR (KBr): $\tilde{\nu}$ = 1516, 1497, 1321, 1150, 1036, 997, 862 cm^{-1}. HRMS (APCI-TOF, *m/z*): calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$ 296.1287, found 296.1292.

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Conflict of interest

The authors declare no conflict of interest.

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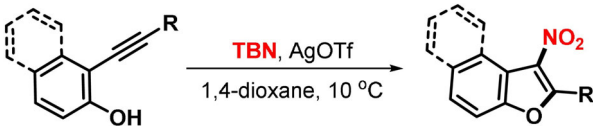

A silver-catalyzed NO_2 radical-triggered nitration/annulation of α-alkynyl arylols is reported by using *tert*-butyl nitrite (TBN), and a set of 3-nitrated benzofurans were synthesized in moderate to good yields. The control experiments suggested that this transformation involved NO_2 radical addition, 1,5-HAT, 5-*endo-trig* cyclization and H-abstraction, thus providing a direct pathway for the formation of 3-nitrobenzofurans via catalytic difunctionalization of internal alkynes.

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Silver-Catalyzed Nitration/Annulation of α-Alkynyl Arylols toward 3-Nitrated Benzofurans