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Alkyltriflate-Triggered Annulation of Arylisothiocyanates and Alkynes Leading to Multiply Substituted Quinolines through Domino Electrophilic Activation

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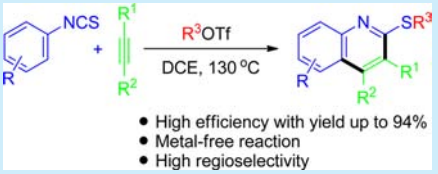
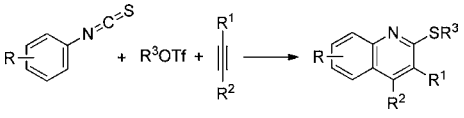
Supporting Information

ABSTRACT: The reaction of arylisothiocyanate, alkyltriflate, and alkynes leads to variously substituted quinolines in high yields. The reaction undergoes alkyltriflate-triggered domino electrophilic activation and avoids the use of a transition-metal catalyst. A variety of functional groups are tolerated in the quinoline ring.



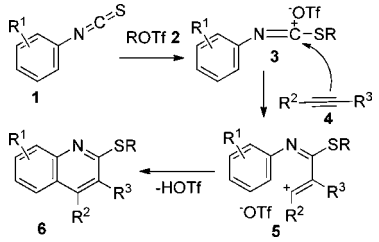
Quinoline scaffolds are found in a wide variety of pharmacologically and biologically active molecules.[1] They have also been employed as ligands for the preparation of OLED luminescent complexes[2] and organocatalysts for asymmetry synthesis.[3] Owing to the important application of quinolines, their synthesis had been extensively studied since the first discovery.[4,5] By far the most prevalent strategies for constructing quinoline rings are the classic annulation reactions such as Friedländer,[6] Combes,[7] and Conrad–Limpach–Knorr syntheses.[8] These named reactions generally proceed *via* condensation, Michael addition, or nucleophilic substitution, which usually lack tolerated functional groups. Recently, there are also many new metal-catalyzed protocols for preparing quinolines.[9] From the viewpoint of sustainable chemistry, the development of a new metal-free pathway toward quinoline is more attractive especially for the drug screen. Consequently, we sought to develop a convenient and diversifiable route under metal-free conditions. Herein, we report alkyltriflate-mediated domino electrophilic activation of arylisothiocyanates and alkynes to afford multiply substituted quinolines (Scheme 1).

Scheme 1. Alkyltriflate-Mediated Reaction of Arylisothiocyanates and Alkynes To Afford Quinolines



Alkyltriflate is often used as the alkylation reagent at a heteroatom such as nitrogen, oxygen, and sulfur, to induce an electrophilic center for carbon–carbon or carbon–heteroatom bond formation.[10] Inspired by this chemistry and part of our ongoing project on the formation of heterocycles,[11] we envisioned that the reaction of alkyltriflates, arylisothiocyanates, and alkynes would provide a general approach to substituted quinolines. The transformation consisted of a cascade reaction of the arylisothiocyanate **1** with alkyltriflate **2** to form alkylthio-substituted carbenium ion **3**, which followed the reaction with alkyne **4** to form intermediate **5**, and subsequent electrophilic annulation to give quinoline **6**, as the schematic representation indicates in Scheme 2.

Scheme 2. Proposed Mechanism



In the preliminary experiment, we used phenyl isothiocyanate **1a** (0.6 mmol), methyl triflate **2a** (0.6 mmol), and diphenylacetylene **4a** (0.5 mmol) as starting material in 1,2-dichloroethane (DCE) for 12 h at 60 °C, affording 2-(methylthio)-3,4-diphenylquinoline **6aaa** in 20% yield (Table 1, entry 1). When the reaction temperature was increased to 100 and 130 °C, the yield of the product increased to 60% and 67%, respectively (entries 2–3). Then, different solvents were screened such as THF, CH_3CN, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dichlomethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrachloromethane (CCl_4), and *n*-hexane (entries 4–11). DCE was found to be the superior solvent for this reaction (entry 3). When the ratio of the three components was converted to 1.2:1.5:1, the yield of **6aaa** increased to 80% (entry 12). The optimal ratio of three

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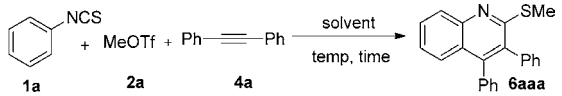
Table 1. Optimization of the Reaction Conditions for Formation of 6aaa[a]



entry	temp [°C]	time [h]	solvent	ratio [1a:2a:4a]	yield [%][b]
1	60	12	DCE	1.2:1.2:1	20
2	100	12	DCE	1.2:1.2:1	60
3	130	12	DCE	1.2:1.2:1	67
4	100	12	THF	1.2:1.2:1	NR
5	130	12	CH_3CN	1.2:1.2:1	NR
6	130	12	DMF	1.2:1.2:1	NR
7	130	12	DMSO	1.2:1.2:1	NR
8	100	12	CH_2Cl_2	1.2:1.2:1	52
9	100	12	$CHCl_3$	1.2:1.2:1	28
10	130	12	CCl_4	1.2:1.2:1	10
11	130	12	*n*-hexane	1.2:1.2:1	28
12	130	12	DCE	1.2:1.5:1	80
13	130	12	DCE	1.2:2:1	87
14	130	12	DCE	1.2:2.5:1	88
15	130	12	DCE	1.2:3:1	87
16	130	12	DCE	1.5:2.5:1	88
17	130	12	DCE	1.5:3:1	94 (80)
18	110	12	DCE	1.5:3:1	81
19	120	12	DCE	1.5:3:1	86
20	130	1	DCE	1.5:3:1	31
21	130	3	DCE	1.5:3:1	65
22	130	6	DCE	1.5:3:1	75

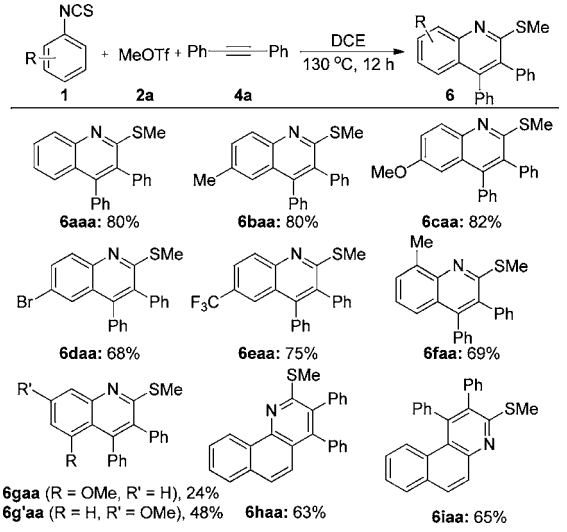
[a]The reaction was performed with 0.5 mmol of diphenylacetylene in sealed tube. [b]The yield was evaluated by ^1H NMR with CH_2Br_2 as the internal standard. Isolated yield was given in parentheses.

compounds was 1.5:3:1, in which the product **6aaa** was afforded in 94% yield (entry 17). When the reaction temperature was decreased to 120 and 110 °C, the desired product was formed in 86% and 81% yield, respectively (entries 18−19). Furthermore, the effect of reaction time was also examined; the yield of product was increased with the extended reaction time (entries 20−22). On the basis of the above results, the optimal conditions are shown in entry 17.

Under the optimized conditions, a study on the substrate scope was carried out. First, a variety of arylisothiocyanates **1** were used in the reaction with methyl triflate **2a** and diphenylacetylene **4a** to synthesize quinolines with a range of substituents of arylisothiocyanate, including 4-methyl, 4-methoxyl, 4-bromo, 4-trifluoromethyl, and 2-methyl groups. Some results are summarized in Scheme 3. In all cases, the reaction proceeded smoothly and the desired products were formed in satisfactory yields (Scheme 3, **6aaa**−**6faa**). The structure of **6caa** was further confirmed by single-crystal X-ray diffraction (see the Supporting Information). When 3-methoxyphenyl isothiocyanate **1g** was used in this reaction, the products were obtained as two isomers (**6gaa** = 24%; **6g′aa** = 48%). It is noteworthy that naphthalene nucleus substrates such as 1-naphthyl isothiocyanate **1h** and 2-naphthyl isothiocyanate **1i** were employed to afford the corresponding product in 63% and 65% yields, respectively (**6haa** and **6iaa**).

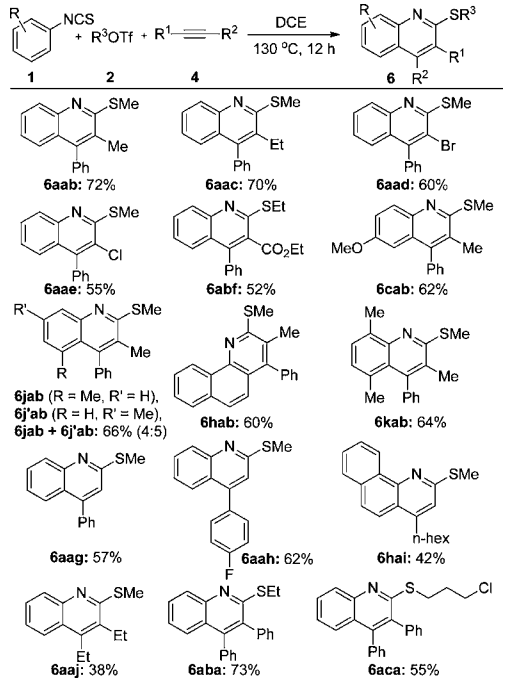
Second, a range of alkynes were handled with arylisothiocyanates and alkyltriflates to synthesize quinolines with a variety of substituents at the 3- and 4-positions. As shown in Scheme 4, the reaction of terminal or internal alkynes bearing aryl, alkyl, halogen, and ester groups proceeded smoothly under optimized

Scheme 3. Synthesis of Diphenyl-Substituted Quinolines from Variously Substituted Phenylisothiocyanates[a]



[a]The yields are of isolated products.

Scheme 4. Synthesis of Quinolines from Various Substrates[a]



[a]The yields are of isolated products.

conditions. This synthetic method gives quinolines with high regioselectivity when unsymmetric alkynes were used. The reaction of 1-phenyl-1-propyne **4b** or 1-phenyl-1-butyne **4c** afforded quinolones **6aab** or **6aac** in high yields with a phenyl group at the 4-position and an alkyl group at the 3-position. The structure of **6aac** was demonstrably confirmed by HMBC spectra analysis (see the Supporting Information). When 1-bromo-2-phenylacetylene **4d** and 1-chloro-2-phenylacetylene **4e** were used as substituents, the exclusive product was formed in good yields (**6aad** and **6aae**). To our delight, crystals of **6aad** suitable for X-ray analysis were obtained (see the Supporting Information). It clearly shows that the product **6aad** had a phenyl group in the 4-position and a bromo group at the 3-

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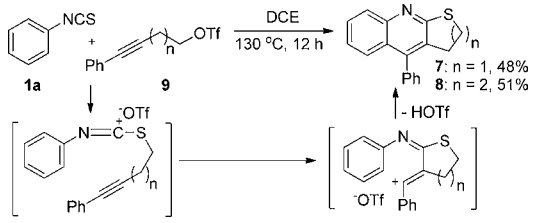
position. Furthermore, utilization of ethyl phenylpropiolate **4f** also afforded desired quinoline **6abf** in 52% yield with a phenyl group at the 4-position and an ester group at the 3-position. Terminal alkynes with an aryl group also gave the corresponding product in high yields with an aryl group at the 4-position (**6aag** and **6aah**). Their structures were confirmed by HMBC NMR spectra analysis. The high regioselectivity for unsymmetric alkynes may be attributed to the cation stabilizing nature of the aryl group for intermediate **5**. It is noteworthy that alkyl acetylenes were transformed into the corresponding quinolines in low yield (**6aaj** and **6hai**). Besides methyl triflate, other triflates such as ethyl triflate **2b** and 3-chloropropanyl triflate **2c** could also be used in this reaction and gave the desired product **6aba** and **6aca** in 73% and 55% yield, respectively. Notably, treatment of the reaction with HOTf led to the formation of a complex inseparable mixture. It is unlike the HOTf-induced transformation of 2-alkynylphenyl isothiocyanates.[12]

This new method provides opportunities for the construction of polycyclic quinolines which were exemplified in Scheme 5.

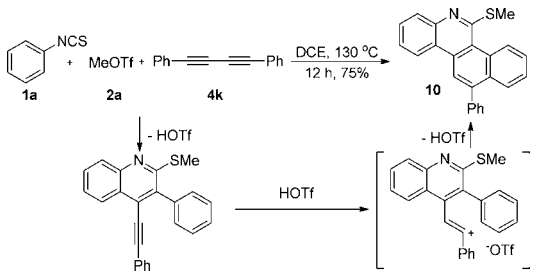
Scheme 5. Synthesis of Polycyclic Quinolines



Two polycyclic quinolines (**7** and **8**) were smoothly prepared from **1a** and *ω*-alkyn-1-yl-triflate **9** *via* a sequential intermolecular and intramolecular electrophilic activation transformation.

As shown in Scheme 6, a further application of our method is in the synthesis of benzo[*i*]phenanthridines that are useful

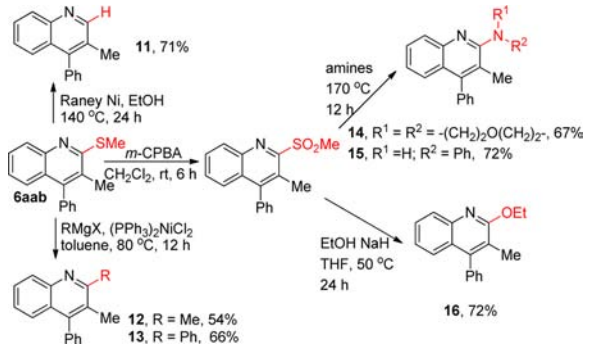
Scheme 6. Synthesis of Benzo[*i*]phenanthridine



compounds in organic photochromics.[13] Compound **10** was prepared from readily available **1a**, **2a**, and 1,4-diphenylbuta-1,3-diyne **4k** in one pot. The structure of product **10** was also confirmed by single-crystal X-ray diffraction (see Supporting Information).

In this reaction, there is a thioalkoxyl group at the 2-position of the quinoline ring, and there are many methods that can be used to convert the C−S bond into C−H, C−C, C−N, and C−O bonds. Scheme 7 shows examples for the transformation of the thiomethyl group to other substituents on the quinoline ring to extend the diversity. 3-Methyl-2-(methylthio)-4-phenylquinoline **6aab** can be transformed to the sulfur-free quinoline **11** by treatment with Raney-Ni in refluxing ethanol.[14] Also the

Scheme 7. Transformation of Thiomethyl Group to Other Substituents



2-(methylthio) group could be smoothly replaced by alkyl/aryl groups by treatment with either a methyl or phenyl Grignard reagent in the presence of bis(triphenylphosphino)nickel dichloride to obtain 2-methyl- and 2-phenylquinolines **12** and **13** in 54% and 66% yield,[14] respectively. Moreover, **6aab** could be oxidized by *m*-CPBA generating the 3-methyl-2-(methylsulfonyl)-4-phenylquinoline.[15] The 2-methylsulfonyl group on the quinoline ring could not only be easily substituted by morpholine and aniline producing 2-aminoquinoline **14** and **15** in 67% and 72% yield,[15] respectively, but also be easily replaced by ethanol generating the 2-ethyoxylquinoline **16** in 72% yield.

As illustrated in Scheme 2, the reaction of arylisothiocyanate with alkyltriflate is envisioned to give the adduct **3**. To verify the adduct **3** as an intermediate, we carried out the reaction of phenyl isothiocyanate **1a** and methyl triflate **2a**. Monitoring of this adduct by HRMS spectroscopy revealed the formation of the intermediate **3** (see Supporting Information). Introduction of diphenylacetylene **4a** to this mixture led to formation of product **6aaa** (50% NMR yield). This observation provides compelling evidence that **3** is a viable intermediate under the reaction conditions.

In summary, a concise, metal-free, and one-pot method has been developed for the facile synthesis of functionalized quinolines from readily available arylisothiocyanates, alkyltriflates, and alkynes. This method has been found to be generally useful for the preparation of a variety of substituted quinolines. The reaction demonstrates excellent reactivity, good functional group tolerance, complete regioselectivity, and high yields. The synthetic utilities were further displayed in convenient syntheses of polycyclic quinolines and benzo[*i*]-phenanthridines.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, full characterization including ^{1}H and ^{13}C NMR data for all new compounds, copies of spectra for all compounds, and the X-ray structure of product and X-ray data (CIF) for **6caa**, **6aad**, and **10**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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