JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo401324k • Publication Date (Web): 22 Aug 2013

Gold-Catalyzed Cyclization of 3-(2'-Azidoaryl)-1-Arylpropargyl Carbonates or 3-Aryl-1-(2'-Azidoaryl)propargyl Carbonates to Produce Quinolines

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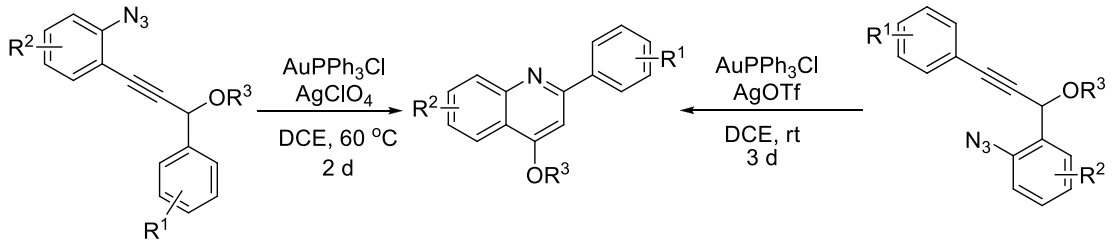


Abstract:

A gold-catalyzed cyclization of 3-(2'-azidoaryl)-1-arylpropargyl carbonates to generate substituted quinolines via a sequence of 3,3-rearrangement, 6-*endo*-trig cyclization and denitrogenation has been developed. Similar products could be obtained from 3-aryl-1-(2'-azidoaryl)propargyl carbonates under different gold catalytic conditions via a sequential 6-*endo*-dig cyclization, denitrogenation and 1,2-H shift process.

INTRODUCTION:

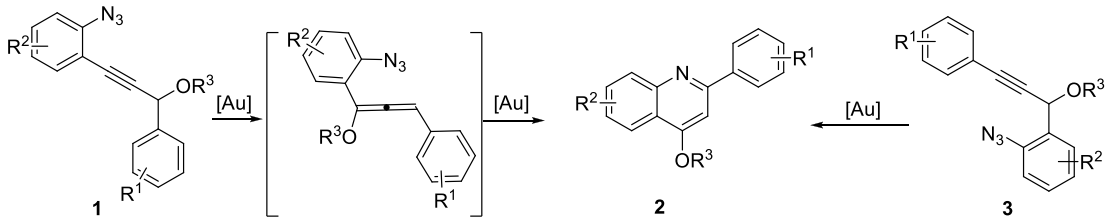
Quinolines represent an important group of heterocycles. Several quinoline

derivatives have been found to exert important biological activities as antimalarial, anti-inflammatory, antiasthamatic, antibacterial, antihypertensive, and tyrosine kinase inhibiting agents.[3-5] In addition, quinolines have been used for the preparation of nano and mesostructures with enhanced electronic and photonic properties.[6] Consequently, the study on quinolines continues to be an active research area, and continuous efforts have been directed to the development of new and efficient synthetic methods towards quinolines.[7]

In recent years, gold-catalyzed rearrangement reactions have attracted much attention owing to their synthetic utility for the construction of natural products and complex molecules.[8] The most important and interesting rearrangement reactions are conducted with propargyl esters; the latter can undergo 1,2-acyloxy migration[9] or 3,3-rearrangement.[10] Many research groups have intensively investigated this type of reactions. The gold catalyzed 3,3-rearrangement of propargyl esters leads to the formation of in situ carboxyallenes, which can be further converted into various acyloxocarbenium ion intermediates by the same gold catalyst. By employing this strategy, a variety of polycyclic compounds were prepared highly efficiently from readily available starting materials.[11]

We envisioned that the in situ generated allene intermediate from 3-(2'-azidoaryl)-1-arylpropargyl carbonates might react with an intramolecular azide group, leading to useful azacyclic compounds after a series of subsequent transformations (Scheme 1). Herein, we report our results on tandem cationic Au(I)-catalyzed activations of both propargylic carbonates and the in situ generated allenylic carbonates, resulting in the expeditious formation of substituted quinolines via sequential 3,3-rearrangement and cyclization. Furthermore, we also present our study on the Au(I)-catalyzed cyclization of 3-aryl-1-(2'-azidoaryl)propargyl carbonates, which was found to proceed via a distinct pathway to give similar products (Scheme 1).

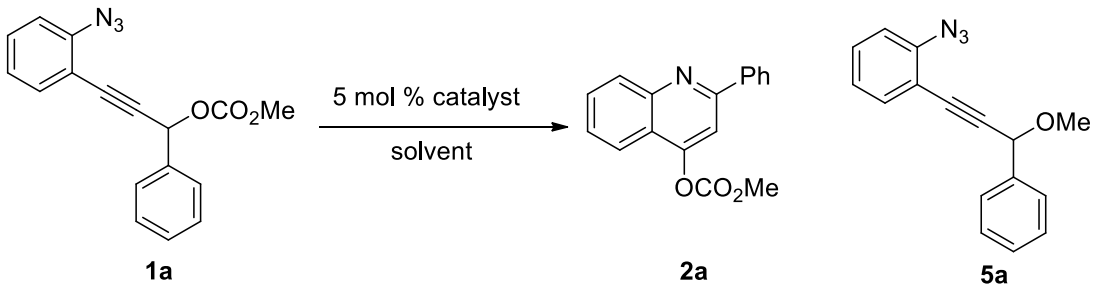
Scheme 1



RESULTS AND DISCUSSION:

We selected **1a** as the standard substrate to search for potential catalysts under suitable reaction conditions. Treatment of propargyl carbonate **1a** with 5 mol % of $Ph_3PAuCl/AgSbF_6$ in DCE at 60°C furnished the desired **2a** in 42% yield (entry 1). When the reaction was performed at 80 °C, the yield was not improved. Other solvents such as toluene, DMF, CH_2Cl_2 and CH_3CN were examined with no improvement (Table 1, entries 5-9). When THF was employed as the solvent, the decarboxylation compound 1-azido-2-(3-methoxy-3-phenylprop-1-yn-1-yl)benzene (**5a**) was isolated in 75% yield. Silver salts were screened: $AgClO_4$ was slightly better while AgOTf was ineffective. The reaction failed to afford the product **2a** when Ph_3PAuCl or $AgClO_4$ was used as catalyst alone (Table 1, entries 10 and 11). However, screening of gold catalysts revealed that AuCl, $AuCl_3$, Au(IPr)Cl and PPh_3AuNTf_2 were less effective (Table 1, entries 12 -17).

Table 1. Optimization of reaction conditions for the cyclization of **1a** forming quinoline **2a**[a]



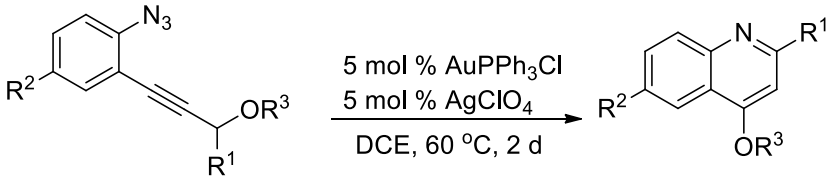
1a **2a** **5a**

entry	catalyst (5 mol %)	solvent	temp (°C)	time	yield of **2a** (%)[b]
1	$PPh_3AuCl/AgSbF_6$	DCE	60	3 d	42
2	$PPh_3AuCl/AgSbF_6$	DCE	80	2 d	40
3	$PPh_3AuCl/AgSbF_6$	tolouene	80	3 d	20
4	$PPh_3AuCl/AgSbF_6$	DMF	60	1 d	0
5	$PPh_3AuCl/AgSbF_6$	CH_2Cl_2	rt	3 d	trace
6	$PPh_3AuCl/AgSbF_6$	CH_3CN	60	2 d	28
7	$PPh_3AuCl/AgSbF_6$	THF	60	2 h	0[c]
8	$PPh_3AuCl/AgClO_4$	DCE	60	2 d	45
9	$PPh_3AuCl/AgOTf$	DCE	60	2 d	trace
10	PPh_3AuCl	DCE	60	2 d	0[d]
11	$AgClO_4$	DCE	60	2 d	0
12	AuCl	DCE	60	2 d	17
13	$AuCl/AgClO_4$	DCE	60	2 d	21
14	$AuCl_3$	DCE	60	2 d	26
15	$AuCl_3/AgClO_4$	DCE	60	2 d	20
16	$Au(IPr)Cl/AgClO_4$	DCE	60	2 d	31
17	$AuPPh_3NTf_2$	DCE	60	2 d	37

[a] Reactions were carried out on a 0.3 mmol scale in 3.0 mL of solvent under N_2 atmosphere for the specified period of time with 5 mol% of the catalyst. [b] Isolated yields. [c] 75% decarboxylation compound **5a** was isolated. [d] 88% starting material was recovered.

Under the optimal conditions, the scope of this reaction was explored. Some typical results are summarized in Table 2. As for substrate **1** wherein R^1 is an aromatic group such as phenyl, *p*-bromoylphenyl, *p*-fluorophenyl and *o*-methoxyphenyl group, the reactions proceeded smoothly under the established conditions, delivering the quinolines **2** in moderate yields (Table 2, entries 1–4). However, when R^1 is methyl, no expected product was observed and 86% of **1i** was recovered (Table 2, entry 9). The substituent on the azido-substituted phenyl unit (R^2) can be methyl, and chloride; R^3 can be Ac and CO_2Me. All of the products were characterized by spectroscopic methods, and **2c** was further confirmed by X-ray crystallography (See **Fig. S1** in Supporting Information).

Table 2. Gold-catalyzed formation of quinolines **2**[a]



1 **2**

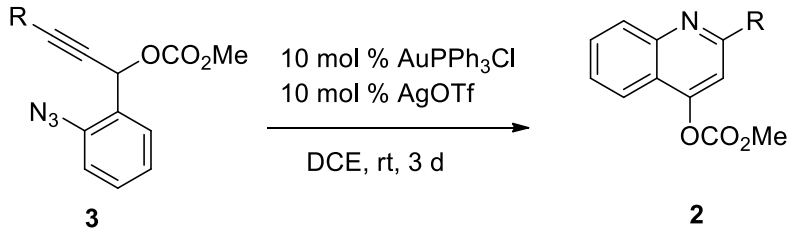
entry	**1**				yield of **2** (%)[b]
	R^1	R^2	R^3		
1	C_6H_5	H	CO_2Me	**1a**	45 (**2a**)
2	*p*-BrC_6H_4	H	CO_2Me	**1b**	51 (**2b**)
3	*p*-FC_6H_4	H	CO_2Me	**1c**	48 (**2c**)
4	*o*-BrC_6H_4	H	CO_2Me	**1d**	47 (**2d**)
5	C_6H_5	Me	CO_2Me	**1e**	38 (**2e**)
6	C_6H_5	Cl	CO_2Me	**1f**	41 (**2f**)
7	C_6H_5	H	Ac	**1g**	52 (**2g**)
8	C_6H_5	Cl	Ac	**1h**	55 (**2h**)
9	Me	H	CO_2Me	**1i**	0[c]

[a] Reactions were carried out using **1** (0.3 mmol), [$(PPh_3)AuCl$]/$AgClO_4$ (5 mol%) in DCE (3 mL) at 60 °C under N_2 atmosphere. [b] Isolated yields. [c] 86% of **1i** was recovered.

Furthermore we also synthesized 3-aryl-1-(2'-azidoaryl)propargyl carbonatess **3** to examine the gold catalyzed reaction in order to get the differently substituted quinolines. To our surprise, in the presence of 10 mol % of PPh_3AuCl/AgOTf, the reaction of **3** also afforded the quinolines **2** with substituents at different locations in moderate yields at room temperature. Several examples are presented in Table 3. For R, aromatic groups including *p*-F, *p*-CF_3, *p*-Me, and *p*-Cl substituted phenyl groups are applicable (Table 3, entries 2-5). After hydrolysis of **2c**, we obtained 2-(4-fluorophenyl)quinolin-4(1H)-one (**4c)**, and its structure was confirmed by X-ray

crystallography (See **Fig. S2** in Supporting Information).

Table 3 Gold-catalyzed formation of quinolines **2**[a]



3 **2**

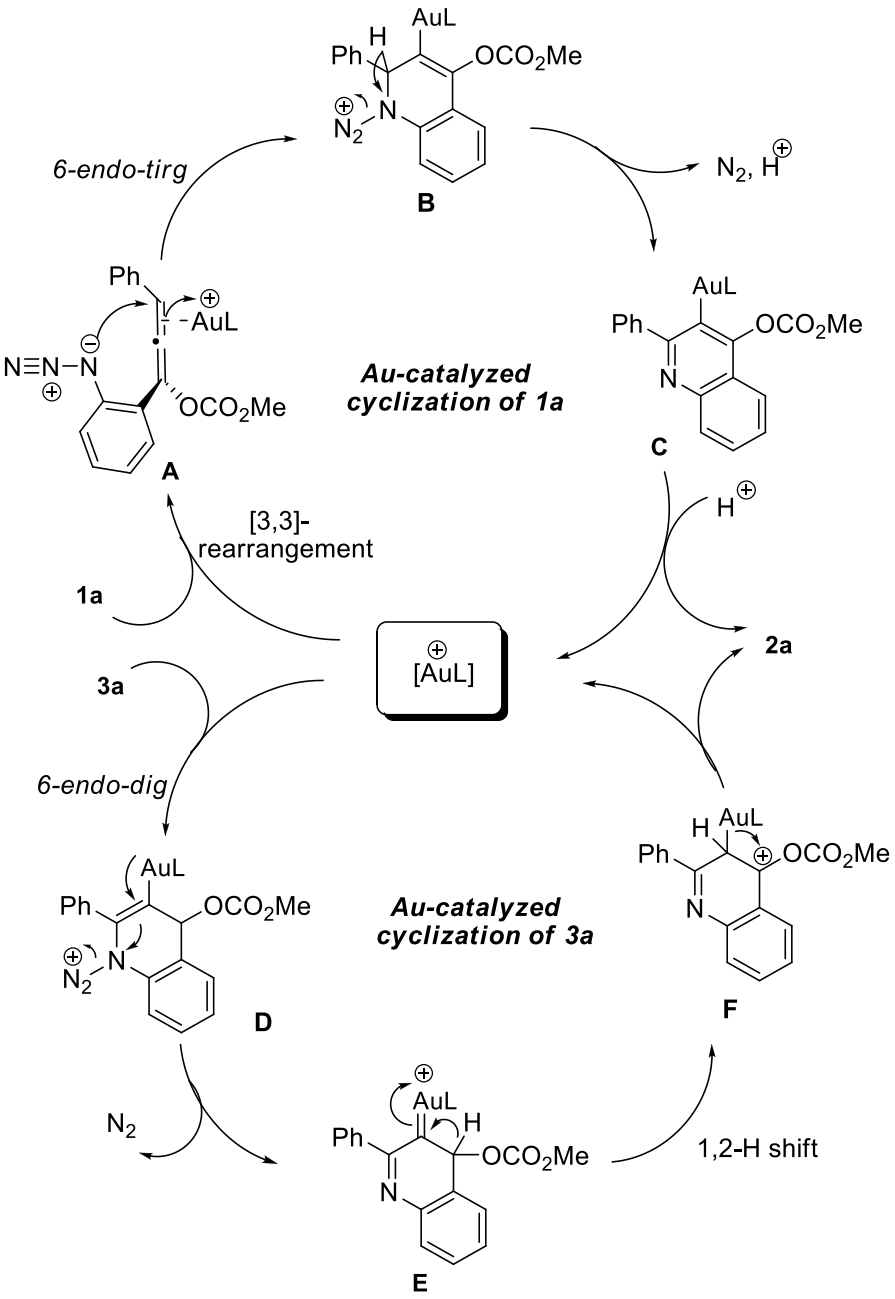
entry	**3** R		yield of **2** (%)[b]
1	C_6H_5	**3a**	55 (**2a**)
2	*p*-FC_6H_4	**3c**	53 (**2c**)[c]
3	*p*-$CF_3C_6H_4$	**3i**	51 (**2i**)[c]
4	*p*-MeC_6H_4	**3j**	53 (**2j**)[c]
5	*p*-ClC_6H_4	**3k**	48 (**2k**)[c]

[a] Reactions were carried out using **3** (0.3 mmol), [(PPh_3)AuCl]/AgOTf (10 mol%) in DCE (3 mL) at rt under N_2 atmosphere. [b] Isolated yields. [c] A small amount of byproduct was observed.

Based on the above results and literature precedents, two catalytic cycles were proposed to rationalize the above reactions which produce the same product **2a** from different substrate **1a** or **3a** (Scheme 2).[12] The cyclization of **1a** is initialed by an Au-catalyzed [3,3]-sigmatropic rearrangement of the substrate to give an allenylic carbonate **A**. Subsequently, **A** undergoes an Au-induced 6-*endo*-trig cyclization to form intermediate **B**, which loses a molecule of N_2 and proton to afford the quinolinyl

gold intermediate **C**. Protodemetallation of **C** gave the product **2a** (Scheme 2, top cycle). The Au-catalyzed cyclization of **3a** first involves an intramolecular nucleophilic attack of the azide group to the Au-activated triple bonds in a 6-*endo*-dig manner to give the intermediate **D**. Loss of a molecule of N_2 leads to the formation of a gold carbenoid **E**. The subsequent 1,2-H shift of **E** leads to the formation of a gold intermediate **G** which finally transforms to the product **2a**, and the cationic gold(I) catalyst is regenerated (Scheme 2, bottom cycle).

Scheme 2 Proposed mechanisms for the Au-catalyzed sequential reactions for the synthesis of quinolines



CONCLUSIONS:

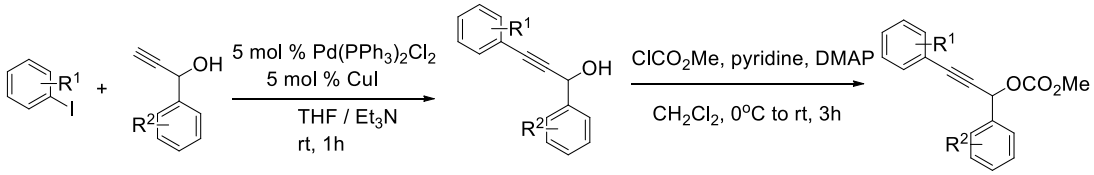
In summary, we have developed two sets of gold(I) catalyzed cyclization reactions, providing a facile synthesis of substituted quinolines from the easily accessible 3-(2'-azidoaryl)-1-arylpropargyl carbonates or 3-aryl-1-(2'-azidoaryl)propargyl carbonates. Although producing the same type of

products, mechanistically the reactions take place via different pathways. The reaction of 3-(2'-azidoaryl)-1-arylpropargyl carbonates involves a reaction sequence of [3,3]-sigmatropic rearrangement, 6-endo-trig cyclization and denitrogenation, while the cyclization of 3-aryl-1-(2'-azidoaryl)propargyl carbonates proceeds via a sequential 6-endo-dig cyclization, denitrogenation and 1,2-H shift process. Our study that two regioisomeric substrates lead to the same type of products in the presence of a similar gold(I) catalyst provide an interesting example of convergence in homogenous gold catalysis.

EXPERIMENTAL SECTION:

General: All reactions were performed under an N_2 atmosphere. Anhydrous solvents were distilled prior to use: THF was distilled from sodium wire using benzophenone as the indicator; DMF was distilled from CaH_2. Petroleum ether refers to the fraction with the boiling point in the range 60–90 °C. All ^1H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. Starting materials: Propargylic alcohols were prepared according to the literature.

General procedure for the preparation of propargylic compounds 1a-i and 3a-k.



6 **7** **8** **1/3**

An oven-dried Schlenk tube containing a Teflon-coated stirring bar was charged with $Pd(PPh_3)_2Cl_2$ (70 mg, 5 mol %), CuI (19 mg, 5 mol %), and substituted iodobenzene (2 mmol). The Schlenk tube was sealed, evacuated and backfilled with N_2 (3 cycles). A solution of propargylic alcohol (2.4 mmol) in 10 mL of THF and 3 mL of Et_3N was subsequently injected to the Schlenk tube. The reaction mixture was stirred for 1 h at

room temperature. After 1h the reaction was complete as monitored by TLC, the reaction was quenched with an aqueous saturated solution of NH_4Cl and extracted with diethyl ether (3 × 20 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Filtration, evaporation and column chromatography on silica gel (Petroleum ether – ethyl acetate 4:1) afforded propargylic alcohols.

To a solution of propargylic alcohol prepared above (1.0 mmol), pyridine (0.32 g, 4.0 mmol), and DMAP (22.4 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added at 0 °C ethyl chloroformate (0.44 g, 4.0 mmol). After being stirred for 2 h at room temperature, the reaction mixture was diluted with CH_2Cl_2. The CH_2Cl_2 solution was washed with a saturated aqueous copper sulfate solution, water, dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica gel (Petroleum ether – ethyl acetate 10:1) to afford the corresponding propargylic compounds.

3-(2-azidophenyl)-1-phenylprop-2-yn-1-yl methyl carbonate (1a): Yield: 83% (254 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 2H), 7.46-7.32 (m, 5H), 7.11-7.05 (m, 2H), 6.57 (s, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 141.6, 136.2, 133.9, 130.2, 129.2, 128.7, 127.9, 124.5, 118.6, 114.0, 90.5, 83.7, 70.1, 55.1 ppm; MS (EI, 70ev) m/z (%) 307 (M^+, 8.56), 220 (100); IR (neat): 2956, 2128, 1747, 1489, 1297, 1096 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{13}N_3O_3$ (M^+): 307.0957; found: 307.0954.

3-(2-azidophenyl)-1-(4-bromophenyl)prop-2-yn-1-yl methyl carbonate (1b): Yield: 77% (296 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.52 (m, 4H), 7.45 (d, J = 9.2 Hz, 1H), 7.39-7.35 (m, 1H), 7.13-7.07 (m, 2H), 6.51 (s, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 141.7, 135.3, 133.9, 131.9, 130.3, 129.6, 124.6, 123.5, 118.6, 113.8, 89.9, 84.0, 69.4, 55.2 ppm; MS (EI, 70ev) m/z (%) 385 (M^+, 11.28), 219 (100); IR (neat): 2961, 2128, 1747, 1486, 1252, 1010 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}{}^{79}Br\,N_3O_3$ (M^+): 385.0062; found: 385.0067.

3-(2-azidophenyl)-1-(4-fluorophenyl)prop-2-yn-1-yl methyl carbonate (1c): Yield: 81% (263 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.62 (m, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.38-7.33 (m, 1H), 7.12-7.06 (m, 4H), 6.54 (s, 1H), 3.82 (s, 3H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (J = 247.1 Hz), 154.8, 141.6, 133.9, 132.2 (J = 2.9 Hz), 130.3, 130.0 (J = 8.6 Hz), 124.5, 118.6, 115.6 (J = 1.9 Hz), 113.8, 90.2, 83.9, 69.4, 55.1 ppm; MS (EI, 70ev) m/z (%) 325 (M^+, 7.35), 238 (100); IR (neat): 2958, 2129, 1747, 1572, 1488, 1159 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}FN_3O_3$ (M^+): 325.0863; found: 325.0869.

3-(2-azidophenyl)-1-(2-bromophenyl)prop-2-yn-1-yl methyl carbonate (1d): Yield: 80% (308 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-7.92 (m, 1H), 7.61-7.59 (m, 1H), 7.47-7.33 (m, 3H), 7.26-7.25 (m, 1H), 7.12-7.08 (m, 2H), 6.87 (s, 1H), 3.85 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 141.7, 135.4, 134.0, 133.0, 130.7, 130.3, 130.0, 127.8, 124.5, 123.4, 118.6, 113.9, 89.7, 84.0, 69.4, 55.2 ppm; MS (EI, 70ev) m/z (%) 385 (M^+, 14.38), 219 (100); IR (neat): 2956, 2127, 1750, 1488, 1252, 1120 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}{}^{79}BrN_3O_3$ (M^+): 385.0062; found: 385.0063.

3-(2-azido-5-methylphenyl)-1-phenylprop-2-yn-1-yl methyl carbonate (1e): Yield: 74% (238 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.2 Hz, 2H), 7.42-7.37 (m, 3H), 7.25 (d, J = 6.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.56 (s, 1H), 3.81 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 138.8, 136.2, 134.3, 134.2, 131.0, 129.2, 128.7, 127.9, 118.5, 113.7, 90.1, 83.8, 70.2, 55.0, 20.5 ppm; MS (EI, 70ev) m/z (%) 321 (M^+, 11.46), 234 (100); IR (neat): 2959, 2120, 1747, 1493, 1248, 1104 cm^{-1}; TOF HRMS (EI) calcd. for $C_{18}H_{15}N_3O_3$ (M^+): 321.1113; found: 321.1118.

3-(2-azido-5-chlorophenyl)-1-phenylprop-2-yn-1-yl methyl carbonate (1f): Yield: 78% (266 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.61 (m, 2H), 7.42-7.40 (m, 4H), 7.30-7.28 (m, 1H), 7.01 (d, J = 8.8 Hz, 1H), 6.55 (s, 1H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 140.2, 135.9, 133.4, 130.2, 129.7, 129.3, 128.7, 127.8, 119.8, 115.4, 91.7, 82.3, 69.9, 55.1 ppm; MS (EI, 70ev) m/z (%) 341 (M^+, 13.48), 184 (100); IR (neat): 2956, 2117, 1747, 1484, 1251, 1154, 933, 762 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}{}^{35}ClN_3O_3$ (M^+): 341.0567; found: 341.0561.

3-(2-azidophenyl)-1-phenylprop-2-yn-1-yl acetate (1g): Yield: 76% (221 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.6 Hz, 2H), 7.45-7.33 (m, 5H),

7.10-7.06 (m, 2H), 6.74 (s, 1H), 2.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 141.5, 136.8, 133.9, 130.0, 128.9, 128.6, 127.9, 124.5, 118.6, 114.2, 91.3, 82.6, 66.0, 21.0 ppm; MS (EI, 70ev) m/z (%) 291 (M^+, 17.28), 255 (100); IR (neat): 3066, 2116, 1739, 1590, 1218, 1017, 952, 697 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{13}N_3O_2(M^+)$: 291.1008; found: 291.1005.

3-(2-azido-5-chlorophenyl)-1-phenylprop-2-yn-1-yl acetate (1h): Yield: 83% (270 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62-7.60 (m, 2H), 7.43-7.35 (m, 4H), 7.29-7.24 (m, 1H), 7.00 (d, J = 9.2 Hz, 1H), 6.71 (s, 1H), 2.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 140.1, 136.5, 133.4, 130.1, 129.7, 129.0, 128.7, 127.8, 119.8, 115.6, 92.5, 81.3, 65.8, 21.0 ppm; MS (EI, 70ev) m/z (%) 325 (M^+, 5.83), 221 (100); IR (neat): 3064, 2127, 1738, 1571, 1297, 1097, 950, 753 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}{}^{35}Cl\,N_3O_2(M^+)$: 325.0618; found: 325.0612.

4-(2-azidophenyl)but-3-yn-2-yl methyl carbonate (1i): Yield: 88% (215 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.41 (m, 1H), 7.36-7.32 (m, 1H), 7.10-7.06 (m, 2H), 5.59 (q, J = 6.8 Hz, 1H), 3.82 (s, 3H), 1.65 (d, J = 8.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 141.2, 134.0, 130.0, 124.5, 118.8, 114.3, 92.5, 81.0, 64.8, 54.9, 21.3 ppm; MS (EI, 70ev) m/z (%) 245 (M^+, 13.58), 130 (100); IR (neat): 2958, 2129, 1745, 1574, 1257, 1021, 939, 758 cm^{-1}; TOF HRMS (EI) calcd. for $C_{12}H_{11}N_3O_3(M^+)$: 245.0800; found: 245.0807.

1-(2-azidophenyl)-3-phenylprop-2-yn-1-yl methyl carbonate (3a): Yield: 79% (243 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.6 Hz, 1H), 7.48-7.41 (m, 3H), 7.34-7.29 (m, 3H), 7.23-7.19 (m, 2H), 6.76 (s, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 138.0, 131.9, 130.6, 129.5, 128.9, 128.3, 127.4, 125.0, 121.9, 118.3, 87.9, 84.3, 65.2, 55.1 ppm; MS (EI, 70ev) m/z (%) 307 (M^+, 11.76), 204 (100); IR (neat): 2927, 1748, 1494, 1256, 1105, 948, 857, 756 cm^{-1}; MS: *m*/*z* (%) = 307 (M^+, 4.66), 224 (100); IR (neat): 2957, 2230, 1750, 1490, 1244, 1093 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{13}N_3O_3$ (M^+): 307.0957; found: 307.0951.

1-(2-azidophenyl)-3-(4-fluorophenyl)prop-2-yn-1-yl methyl carbonate (3c): Yield: 72% (233 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.0 Hz, 1H), 7.47-7.40 (m, 3H), 7.22-7.18 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.74 (s, 1H), 3.84 (s,

3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (J = 248.5 Hz), 154.7, 138.0, 133.9 (J = 7.7 Hz), 130.6, 129.4, 127.3, 125.0, 118.3, 117.9 (J = 4.3 Hz), 115.6 (J = 21.9 Hz), 86.8, 84.1, 65.1, 55.1 ppm; MS (EI, 70ev) m/z (%) 325 (M^+, 12.48), 222 (100); IR (neat): 2957, 1750, 1443, 1244, 1157, 1092 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}FN_3O_3$ (M^+): 325.0863; found: 325.0866.

1-(2-azidophenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl methyl carbonate (3i): Yield: 69% (259 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.6 Hz, 1H), 7.57 (s, 4H), 7.43 (t, J = 7.6 Hz, 1H), 7.25-7.19 (m, 2H), 6.77 (s, 1H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 138.0, 132.2, 130.8, 130.4, 129.3, 127.0, 125.7, 125.1 (q, J = 4.5 Hz), 122.4, 118.3, 86.8, 86.3, 64.9, 55.2 ppm; MS (EI, 70ev) m/z (%) 375 (M^+, 18.84), 302 (100); IR (neat): 2961, 2128, 1752, 1489, 1248, 1125 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}F_3N_3O_3$ (M^+): 375.0831; found: 375.0836.

1-(2-azidophenyl)-3-(p-tolyl)prop-2-yn-1-yl methyl carbonate (3j): Yield: 76% (244 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.6 Hz, 1H), 7.42-7.35 (m, 3H), 7.23-7.15 (m, 2H), 7.10 (d, J = 7.6 Hz, 2H), 6.75 (s, 1H), 3.82 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 139.1, 137.9, 131.8, 130.5, 129.5, 128.9, 127.5, 125.0, 118.7, 118.2, 88.1, 83.6, 65.2, 55.0, 21.4 ppm; MS (EI, 70ev) m/z (%) 321 (M^+, 17.68), 218 (100); IR (neat): 2954, 2229, 2131, 1750, 1585, 1261 cm^{-1}; TOF HRMS (EI) calcd. for $C_{18}H_{15}N_3O_3$ (M^+): 321.1113; found: 321.1118.

1-(2-azidophenyl)-3-(4-chlorophenyl)prop-2-yn-1-yl methyl carbonate (3k): Yield: 84% (286 mg). Oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.6 Hz, 1H), 7.31-7.26 (m, 3H), 7.16-7.04 (m, 4H), 6.64 (s, 1H), 3.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 137.9, 134.9, 133.0, 130.6, 129.3, 128.5, 127.1, 124.9, 120.2, 118.2, 86.8, 85.3, 64.9, 55.0 ppm; MS (EI, 70ev) m/z (%) 341 (M^+, 12.44), 219 (100); IR (neat): 2959, 2126, 1750, 1488, 1244, 1013 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}{}^{35}ClN_3O_3$ (M^+): 341.0567; found: 341.0561.

Procedure for Synthesis of 2a−k: Typical Procedure for preparation of (2-Phenylquinolin-4-yl) methyl carbonate (2a)

Typical Procedure I: To a dried Schlenk tube were added $AgClO_4$ (3.1 mg, 0.015

mmol), $Au(PPh_3)Cl$ (7.6 mg, 0.015 mmol), and DCE (1 mL) sequentially under a nitrogen atmosphere at room temperature. The resulting mixture was stirred at room temperature for about 10 min, which was followed by the addition of **1a** (92.1 mg, 0.30 mmol) and 2 mL of DCE. The resulting mixture was then submerged in an oil bath preheated to 60 ^oC. After complete consumption of the starting material as monitored by TLC, the mixture was transferred with 30 mL of Et_2O and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford **2a** (37.7 mg, 45%): solid; m.p. 142-146 ^oC (petroleum ether /$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.18 (d, J = 8.8 Hz, 1H), 8.16-8.14 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 8.8 Hz, 1H), 7.89 (s, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.58-7.47 (m, 4H), 4.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 154.8, 153.0, 149.9, 139.1, 130.4, 129.8, 129.7, 128.8, 127.6, 126.7, 120.9, 120.8, 109.8, 55.9 ppm; MS (EI, 70ev) m/z (%) 279 (M^+, 100); IR (neat): 2936, 1771, 1491, 1244, 1154 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{13}NO_3$ (M^+): 279.0895; found: 279.0899.

2-(4-Bromophenyl)quinolin-4-yl methyl carbonate (2b)

The reaction of **1b** (115.5 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol) and $Au(PPh_3)Cl$ (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2b** (54.6 mg, 51%) (eluent: petroleum ether/ethyl acetate = 20/1): solid; m.p. 132-136 ^oC (petroleum ether /$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 8.8 Hz, 3H), 7.85 (s, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 4.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 154.9, 153.0, 149.8, 137.9, 132.0, 130.5, 129.7, 129.0, 126.9, 124.3, 120.9, 120.8, 109.3, 55.9 ppm; MS (EI, 70ev) m/z (%) 359 (M^+(^{81}Br), 99), 357 (M^+(^{79}Br), 100); IR (neat): 2923, 2203, 2117, 1720, 1629, 1598, 1567, 1397, 912 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_3{}^{79}Br$ (M^+): 357.0001; found: 356.9996.

2-(4-Fluorophenyl)quinolin-4-yl methyl carbonate (2c)

The reaction of **1c** (97.5 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol) and $Au(PPh_3)Cl$ (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2c** (42.8 mg, 48%) (eluent: petroleum ether/ethyl acetate = 10/1): solid; m.p. 151-154 ^oC (petroleum ether

/$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18-8.12 (m, 3H), 8.02 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.20 (t, J = 8.4 Hz, 2H), 4.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (J = 247.7 Hz), 157.1, 154.9, 153.0, 149.8, 135.2 (J = 2.9 Hz), 130.5, 129.6, 129.5 (J = 9.2 Hz), 126.7, 120.9, 120.6, 115.8 (J = 21.1 Hz), 109.4, 55.9 ppm; MS (EI, 70ev) m/z (%) 297 (M^+, 100); IR (neat): 2983, 1548, 1406, 1250, 1052 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_3F$ (M^+): 297.0801; found: 297.0807.

2-(2-Bromophenyl)quinolin-4-yl methyl carbonate (2d)

The reaction of **1d** (116.2 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol) and Au(PPh3)Cl (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2d** (50.3 mg, 47%) (eluent: petroleum ether/ethyl acetate = 20/1): solid; m.p. 146-149 ^{o}C (petroleum ether /$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.80-7.60 (m, 5H), 7.47-7.43 (m, 1H), 7.32 (t, J = 7.6 Hz, 1H), 4.00 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 153.6, 152.9, 149.5, 141.0, 133.3, 131.6, 130.4, 130.2, 129.7, 127.7, 127.2, 121.7, 121.0, 120.8, 113.6, 55.9 ppm; MS (EI, 70ev) m/z (%) 359 (M^+(^{81}Br), 12.30), 357 (M^+(^{79}Br), 12.20) , 105 (100); IR (neat): 2973, 1766, 1474, 1253, 1153 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_3{}^{79}Br$ (M^+): 357.0001; found: 357.0010.

(6-Methyl-2-phenylquinolin-4-yl) methyl carbonate (2e)

The reaction of **1e** (96.3 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol) and Au(PPh3)Cl (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2e** (33.4 mg, 38%) (eluent: petroleum ether/ethyl acetate = 10/1): solid; m.p. 148-152 ^{o}C (petroleum ether /$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14-8.07 (m, 3H), 7.83 (s, 1H), 7.77 (s, 1H), 7.58 (d, J = 9.2 Hz, 1H), 7.51-7.43 (m, 3H), 4.01 (s, 3H), 2.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 154.2, 153.1, 148.6, 139.2, 136.9, 132.7, 129.4, 128.8, 127.4, 120.7, 119.6, 109.9, 55.9, 21.8 ppm; MS (EI, 70ev) m/z (%) 293 (M^+, 100) ; IR (neat): 2980, 1770, 1494, 1251, 1152 cm^{-1}; TOF HRMS (EI) calcd. for $C_{18}H_{15}NO_3$ (M^+): 293.1052; found: 293.1057.

6-Chloro-2-phenylquinolin-4-yl methyl carbonate (2f)

The reaction of **1f** (102.3 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol)

and $Au(PPh_3)Cl$ (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2f** (38.5 mg, 41%) (eluent: petroleum ether/ethyl acetate = 20/1): solid; m.p. 128-132 ^oC (petroleum ether /$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.14-8.11 (m, 3H), 8.02-8.01 (m, 1H), 7.93 (s, 1H), 7.69 (dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, 1H), 7.53-7.48 (m, 3H), 4.03 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 153.9, 152.8, 148.2, 138.7, 132.7, 131.35, 131.33, 129.9, 128.9, 127.5, 121.4, 120.1, 110.4, 56.1 ppm; MS (EI, 70ev) m/z (%) 315 ($M^+(^{37}Cl)$, 35.40), 313 ($M^+(^{35}Cl)$, 100); IR (neat): 2957, 1769, 1486, 1247, 1116 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_3{}^{35}Cl$ (M^+): 313.0506; found: 313.0511.

2-Phenylquinolin-4-yl acetate (2g)

The reaction of **1g** (87.3 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol) and $Au(PPh_3)Cl$ (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2g** (41.0 mg, 52%) (eluent: petroleum ether/ethyl acetate = 10/1): oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20-8.13 (m, 3H), 7.92 (d, J = 8.8 Hz, 1H), 7.77-7.75 (m, 2H), 7.54-7.48 (m, 4H), 2.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 158.3, 154.7, 150.0, 139.2, 130.2, 129.9, 129.6, 128.8, 127.6, 126.6, 121.2, 121.0, 110.9, 21.2 ppm; MS (EI, 70ev) m/z (%) 263 (M^+, 25.00), 221 (100); IR (neat): 2925, 1773, 1499, 1254, 1142 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{13}NO_2$ (M^+): 263.0946; found: 263.0949.

6-Chloro-2-phenylquinolin-4-yl acetate (2h)

The reaction of **1h** (97.5 mg, 0.30 mmol) catalyzed by $AgClO_4$ (3.1 mg, 0.015 mmol) and $Au(PPh_3)Cl$ (7.6 mg, 0.015 mmol) in 3 mL of DCE afforded **2h** (49.1 mg, 55%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.17-8.12 (m, 3H), 7.92 (d, J = 2.4 Hz, 1H), 7.83(s, 1H), 7.70 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.57-7.47 (m, 3H), 2.54 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 158.5, 153.7, 148.3, 138.8, 132.5, 131.5, 131.2, 129.8, 128.9, 127.5, 121.8, 120.1, 111.5, 21.2 ppm; MS (EI, 70ev) m/z (%) 299 ($M^+(^{37}Cl)$, 8.52), 297 ($M^+(^{35}Cl)$, 25.00), 255 (100); IR (neat): 2959, 1763, 1496, 1257, 1196 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_2{}^{35}Cl$ (M^+): 297.0557; found: 297.0554.

(2-Phenylquinolin-4-yl) methyl carbonate (2a)

Typical Procedure □: To a dried Schlenk tube were added AgOTf (9.3 mg, 0.030 mmol), $Au(PPh_3)Cl$ (15.2 mg, 0.030 mmol), and DCE (1 mL) sequentially under a

nitrogen atmosphere at room temperature. The resulting mixture was stirred at room temperature for about 10 min, which was followed by the addition of **3a** (92.4 mg, 0.30 mmol) and 2 mL of DCE. After complete consumption of the starting material as monitored by TLC, the mixture was transferred with 30 mL of Et_2O and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford **2a** (46.1 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.18 (d, J = 8.8 Hz, 1H), δ = 8.16-8.14 (d, J = 7.6 Hz, 2H), 8.03 (d, J = 8.8 Hz, 1H), 7.89 (s, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.58-7.47 (m, 4H), 4.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 154.8, 153.0, 149.9, 139.1, 130.4, 129.8, 129.7, 128.8, 127.6, 126.7, 120.9, 120.8, 109.8, 55.9 ppm.

2-(4-Fluorophenyl)quinolin-4-yl methyl carbonate (2c)

The reaction of **3c** (97.5 mg, 0.30 mmol) catalyzed by AgOTf (9.3 mg, 0.030 mmol) and $Au(PPh_3)Cl$ (15.2 mg, 0.030 mmol) in 3 mL of DCE afforded **2c** (47.3 mg, 53%) (eluent: petroleum ether/ethyl acetate = 20/1): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18-8.12 (m, 3H), 8.02 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.76 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.22-7.18 (m, 2H), 4.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (J = 247.7 Hz), 157.1, 154.9, 153.0, 149.8, 135.2 (J = 2.9 Hz), 130.5, 129.6, 129.5 (J = 9.2 Hz), 126.7, 120.9, 120.6, 115.8 (J = 21.1 Hz), 109.4, 55.9 ppm.

(2-(4-(Trifluoromethyl)phenyl)quinolin-4-yl) methyl carbonate (2i)

The reaction of **3i** (112.5 mg, 0.30 mmol) catalyzed by AgOTf (9.3 mg, 0.030 mmol) and $Au(PPh_3)Cl$ (15.2 mg, 0.030 mmol) in 3 mL of DCE afforded **2i** (52.1 mg, 51%) (eluent: petroleum ether/ethyl acetate = 20/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.91 (s, 1H), 7.80-7.76 (m, 3H), 7.59 (t, J = 7.6 Hz, 1H), 4.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 155.0, 153.0, 149.9, 142.3, 130.7, 129.9, 127.8, 127.2, 125.7 (q, J = 2.5 Hz), 121.0, 109.6, 56.0 ppm; MS (EI, 70ev) m/z (%) 347 (M^+, 100); IR (neat): 2966, 1769, 1442, 1322, 1238, 1162 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_3CF_3$ (M^+): 347.0769; found: 347.0772.

(2-(P-tolyl)quinolin-4-yl) methyl carbonate (2j)

The reaction of **3j** (96.3 mg, 0.30 mmol) catalyzed by AgOTf (9.3 mg, 0.030 mmol) and Au(PPh3)Cl (15.2 mg, 0.030 mmol) in 3 mL of DCE afforded **2j** (46.6 mg, 53%) (eluent: petroleum ether/ethyl acetate = 30/1): solid; m.p. 115-119 ^{o}C (petroleum ether /$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.8 Hz, 1H), 8.06-8.00 (m, 3H), 7.86 (s, 1H), 7.74 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 4.00 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 154.7, 153.1, 149.9, 139.8, 136.3, 130.3, 129.7, 129.6, 127.4, 126.5, 120.8, 120.7, 109.6, 55.9, 21.3 ppm; MS (EI, 70ev) m/z (%) 293 (M^+, 100); IR (neat): 1766, 1606, 1503, 1430, 1254, 1009 cm^{-1}; TOF HRMS (EI) calcd. for $C_{18}H_{15}NO_3$ (M^+): 293.1052; found: 293.1051.

2-(4-Chlorophenyl)quinolin-4-yl methyl carbonate (2k)

The reaction of **3k** (102.3 mg, 0.30 mmol) catalyzed by AgOTf (9.3 mg, 0.030 mmol) and Au(PPh3)Cl (15.2 mg, 0.030 mmol) in 3 mL of DCE afforded **2k** (45.1 mg, 48%) (eluent: petroleum ether/ethyl acetate = 20/1): solid; m.p. 126-130 ^{o}C (petroleum ether /$CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.2 Hz, 1H), 7.86 (s, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H), 4.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 154.9, 153.0, 149.9, 137.5, 135.9, 130.5, 129.7, 129.0, 128.8, 126.9, 120.9, 120.8, 109.4, 56.0 ppm; MS (EI, 70ev) m/z (%) 315 (M^+(^{37}Cl), 34.50), 313 (M^+(^{35}Cl), 100); IR (neat): 3053, 1769, 1438, 1270, 1089, 1013 cm^{-1}; TOF HRMS (EI) calcd. for $C_{17}H_{12}NO_3{}^{35}Cl$ (M^+): 313.0506; found: 313.0504.

Procedure for preparation of

1-Azido-2-(3-methoxy-3-phenylprop-1-yn-1-yl)benzene (5a)

To a dried Schlenk tube were added $AgSbF_6$ (5.2 mg, 0.015 mmol), Au(PPh3)Cl (7.6 mg, 0.015 mmol), and DCE (1 mL) sequentially under a nitrogen atmosphere at room temperature. The resulting mixture was stirred at room temperature for about 10 min, which was followed by the addition of **1a** (93.1 mg, 0.30 mmol) and 2 mL of THF. The resulting mixture was then submerged in an oil bath preheated to 60 ^{o}C. After complete consumption of the starting material as monitored by TLC, the mixture was transferred with 30 mL of Et2O and concentrated under reduced pressure. The residue

was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford **5a** (59.2 mg, 75%): oil ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 7.2 Hz, 2H), 7.46-7.30 (m, 5H), 7.12-7.04 (m, 2H), 5.36 (s, 1H), 3.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 138.2, 133.7, 129.7, 128.5, 128.4, 127.5, 124.5, 118.5, 114.6, 92.5, 83.3, 73.5, 55.9 ppm; MS (EI, 70ev) m/z (%) 263 (M^+, 15) , 79 (100); IR (neat): 2932, 2126, 2101, 1720, 1597, 1487, 1447, 1279, 1189, 1075 cm^{-1}; TOF HRMS (EI) calcd. for $C_{16}H_{13}N_3O$ (M^+): 263.1059; found: 263.1052.

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[§] Prof. Xian Huang passed away on March 6, 2010. He had been fully in charge of this project. At this moment, Prof. Luling Wu is helping him to finish all the projects with the help from Prof. Shengming Ma.

ACKNOWLEDGMENT

We are grateful to the National Natural Science Foundation of China (Project Nos. 20872127 and J0830431) and National Basic Research Program of China (973 Program, 2009CB825300) and CAS Academician Foundation of Zhejiang Province and the Fundamental Research Funds for the Central Universities for financial support.

Supporting Information. Figures 1 and 2, copies of ^{1}H and ^{13}C NMR spectra for compounds **1, 2,** and **3** and CIF files for **2c**, and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES

(1) C X–ray crystal data for **2c**: $C_{17}H_{12}NO_3F$; M= 297.28; crystal system: monoclinic; space group: C 2/c; final R indices ($I > 2\sigma(I)$) $R1$= 0.0404, $wR2$= 0.0737, R indices (all data) $R1$= 0.0634, $wR2$= 0.0843; a=3.8270(4) Å, b=19.9545(12) Å, c=8.9557(6) Å; α=90.00, β= 90.076, γ=90.00, V= 683.86(9) $Å^3$, T=293(2) K, Z= 2; reflections collected/unique: 4885/2466 (R(int)= 0.0314); number of observations (> 2$\sigma(I)$):

1884; parameters: 200. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 886294.

(2) C X–ray crystal data for **4c**: $C_{15}H_{10}NOF$; *M*= 239.24; crystal system: monoclinic; space group: *C* 2/c; final *R* indices ($I > 2\sigma(I)$) *R*1= 0.0348, *wR*2= 0.0918, R indices (all data) *R*1= 0.0420, *wR*2= 0.0968; *a*=11.7400(5) Å, *b*=7.1758(3) Å, *c*=13.2748(7) Å; α=90.00, β= 92.215(4), γ=90.00, *V*= 1117.49(9) $Å^3$, *T*=293(2) K, *Z*= 4; reflections collected/unique: 4857/1738 (*R*(int)= 0.0162); number of observations (> 2σ(*I*)): 1738; parameters: 164. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 886297.

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