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SILVER-CATALYZED OXIDATIVE COUPLING OF TERMINAL AROMATIC ALKYNES AND BENZYLIC ETHERS

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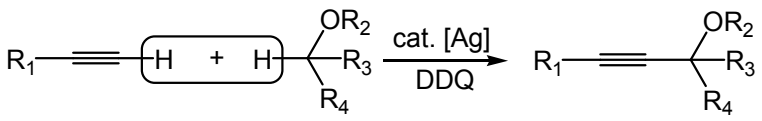
Abstract – The Cross-Dehydrogenative-Coupling (CDC) of terminal aromatic alkynes and benzylic ethers was achieved through the use of a catalytic amount of silver triflate and employing 2,3-dichloro-5,6-dicyanoquinone (DDQ) as the oxidant.

INTRODUCTION

Direct C-C bond formation through metal catalyzed C-H bond activation continues to attract interest as it provides organic chemists with an alternative to traditional functional group derivatization for organic synthesis.[1] This allows for better atom economy and reduces the number of steps in the synthetic process.[2] In an effort to completely eliminate highly functionalized starting material our group has focused on the development by direct activation of simple starting material. The method of activation and subsequent coupling of C-H bonds in both substrates was termed Cross-Dehydrogenative-Coupling (CDC).[3,4]

Among the strategies for activation of the *sp* C-H bond of terminal alkynes, there are few reports of using silver for *in situ* generation of acetylides.[5] Previously, our group has published reports showing Ag (I) to be an effective catalyst for the nucleophilic addition of terminal alkynes to C=O and C=N bonds.[6] To our knowledge the oxidative coupling of alkynes and benzylic ethers has not yet been reported. Herein, we report the first silver-catalyzed *sp*-*sp*^{3} CDC reaction of terminal aromatic alkynes and benzylic ethers (Scheme 1).

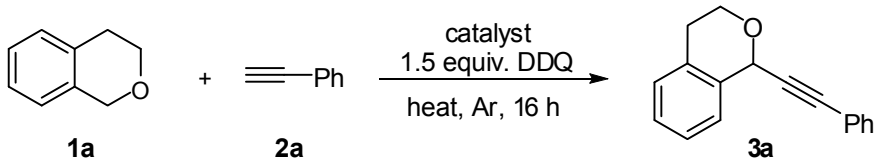


Scheme 1. Cross-Dehydrogenative-Coupling of a terminal alkyne and an ether.

Dedicated to Professor Dr. Albert Eschenmoser on the occasion of his 85th birthday.

RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions for the Oxidative Alkynylation of Isochroman



1a **2a** **3a**

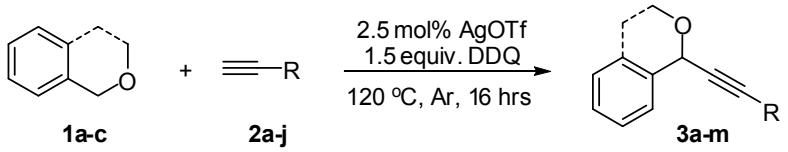
Entry[a]	Catalyst (mol%)	Additive (mol% / mL)	Solvent (mL)	Yield[b]
1	$AuClPPh_3$(5)	AgOTf (5)	neat	17
2	$AuClPPh_3$ (5)	AgOTf (5)	C_6H_5Cl (0.5)	34
3[c]	$AuClPPh_3$ (5)	AgOTf (5)	DCE (1.0)	22
4	$AuClPPh_3$ (5)	-	C_6H_5Cl (0.5)	22
5	AgOTf (5)	-	C_6H_5Cl (0.5)	59
6[c]	AgOTf (5)	-	DCE	60
7	AgOTf (5)	-	toluene (2.0)	73
8	AgOTf (2.5)	-	toluene (2.0)	73
9	AgOTf (2.5)	C_6H_5Cl (0.5)	toluene (2.0)	78
10	-	C_6H_5Cl (0.5)	toluene (2.0)	0
11	$Cu(OTf)_2$ (2.5)	C_6H_5Cl (0.5)	toluene (2.0)	70
12	$Cu(OTf)_2$ (1)	C_6H_5Cl (0.5)	toluene (2.0)	78
13[d]	AgOTf (2.5)	C_6H_5Cl (2.5)	toluene (1.0)	88

[a]Reaction conditions: 0.2 mmol phenylacetylene, 5 equiv. isochroman, 1.5 equiv. DDQ at 120 °C under argon for 16 h. [b]NMR yield calculated using an internal standard. [c]Reaction temperature 70 °C. [d] Reaction run on a 0.1 mmol scale.

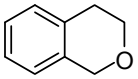
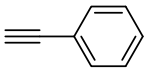
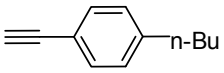
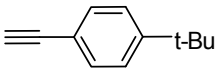
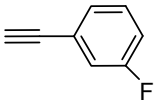
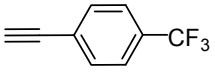
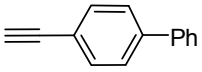
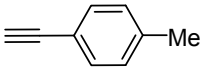
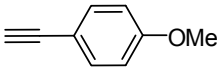
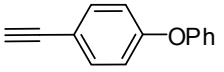
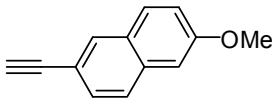
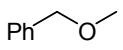
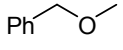
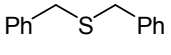
We chose isochroman (**1a**) and phenylacetylene (**2a**) as the standard substrates for the optimization of reaction conditions. 2,3-Dichloro-5,6-dicyanoquinone **(**DDQ)[7] was employed as the oxidant since we[8] and others[9] have had previous success using it for C-H activation reactions. To begin our study we initially tested 5 mol% each of $AuClPPh_3$ and AgOTf under neat conditions at 120 °C, which produced the desired compound (**3a**) in a 17% yield (Table 1, entry 1). The product yield could be increased to 34% when the reaction was run in 0.5 mL chlorobenzene (C_6H_5Cl) at 120 °C (entry 2). When AgOTf was removed, $AuClPPh_3$ could only furnish the product in a 22% yield. Surprisingly using AgOTf as the lone catalyst the yield jumped to 59% (entry 5). A comparable yield could be obtained at a milder temperature of 70 °C in 1.0 mL dichloroethane (DCE) (entry 6); however it could not be further optimized at this temperature. A better yield of 73% was obtained when the reaction was run in 2.0 mL toluene at 120 °C; we could get the same yield at lower catalyst loading of 2.5 mol% (entries 7 and 8). The addition of 0.5 mL of the more polar solvent chlorobenzene was found to be beneficial to the reaction (entry 9).[10] Changing the metal catalyst to 1 mol% copper (II) triflate, **3a** was produced in comparable yields to our best conditions (entries 9 and 12). However, when we turned to the scope of the reaction, silver triflate

was found to provide better NMR yields for functionalized alkynes such as 3-fluorophenylacetylene. The best condition was obtained when the reaction was performed on a 0.1 mmol scale (entry 13). The silver catalyst is instrumental to the reaction; **3a** was not obtained when the catalyst was removed from the reaction mixture (entry 10).

Table 2. Scope of the Silver-Catalyzed Alkynylation of Isochroman



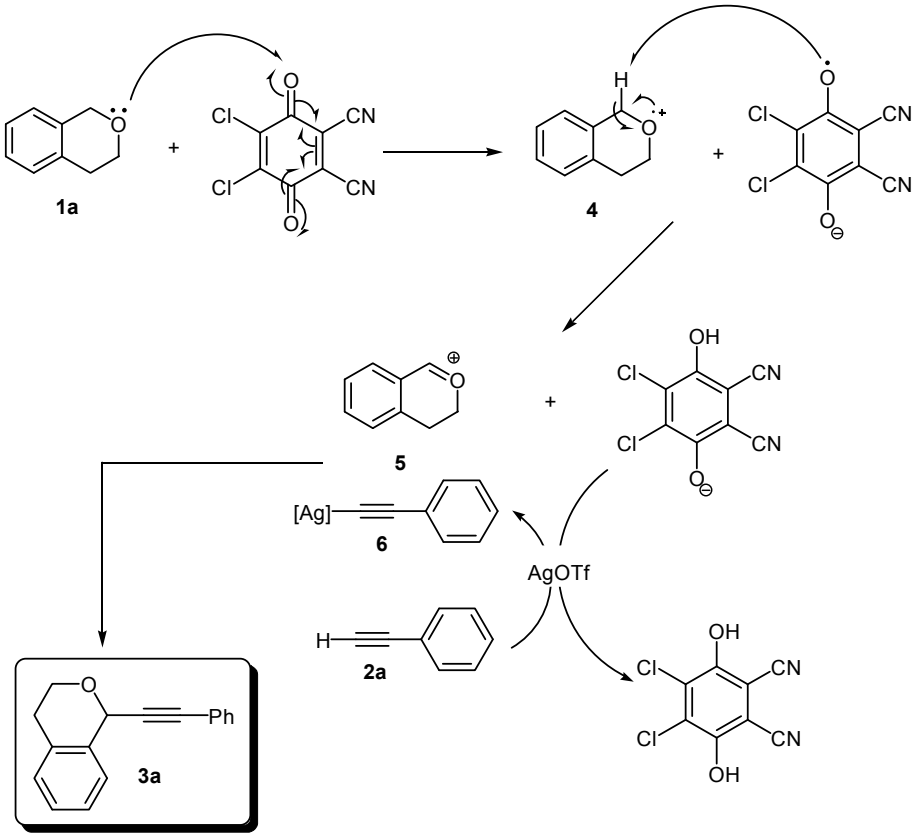
1a-c + **2a-j** → **3a-m**

Entry[a]	Benzylic Ether	Alkyne	Product	Yield (%)[b]
1	**1a** 	**2a** 	**3a**	83
2	**1a**	**2b** 	**3b**	73
3	**1a**	**2c** 	**3c**	62
4[c]	**1a**	**2d** 	**3d**	42
5[c]	**1a**	**2e** 	**3e**	15
6	**1a**	**2f** 	**3f**	74
7	**1a**	**2g** 	**3g**	52
8	**1a**	**2h** 	**3h**	44
9	**1a**	**2i** 	**3i**	53
10	**1a**	**2j** 	**3j**	55
11	**1b** 	**2a**	**3k**	28
12	**1b** 	**2f**	**3l**	14
13	**1c** 	**2a**	**3m**	0

[a]Conditions: 0.1 mmol alkyne, 5 equiv. benzylic ether, 1.5 equiv. DDQ, 2.5 mol% AgOTf in 1.25 mL of 4:1 toluene:chlorobenzene at 120 °C for 16 h under argon. [b]Isolated yield. [c]Solvent used was 0.5 mL chlorobenzene.

With our best conditions, as set out in Table 1 entry 13, we then examined the scope of the reaction (Table 2). Phenylacetylene was found to be the best substrate affording the corresponding product (**3a**) in high yield (entry 1). Weakly donating or withdrawing groups provided the product in moderate to good yields. Aromatic alkynes with strong donating groups (**2h**,**i**) were also feasible and the corresponding products were obtained in moderate yields. Gratifyingly, it was also possible to use strong withdrawing groups such as *m*-F and *p*-CF_3 (**2d**,**e**); however owing to their reduced reactivity yields were only moderate.[11] Isochroman appeared to be the best benzylic ether substrate for this reaction. Although the reaction could also be realized with the acyclic methyl benzyl ether, poor yields were obtained (entries 11 and 12). Dibenzyl sulfide was not reactive under these conditions.

The reaction is likely initiated by a single electron transfer from isochroman to DDQ to form the radical cation **4**. H-radical abstraction from **4** would yield the highly reactive benzoxy cation intermediate **5**.[12] In the presence of silver triflate, the reduced hydroquinone anion can react with phenyl acetylene producing the silver acetylide **6** which would then add to **5** to form the product **3a** (Scheme 2).



Scheme 2. Proposed Mechanism for the DDQ Mediated Alkynylation of Isochroman

In summary, we developed a novel silver-catalyzed *sp*-*sp*^{3} Cross-Dehydrogenative-Coupling of terminal aromatic alkynes and benzylic ethers utilizing DDQ as the oxidant. The in-situ generated acetylide is

formed under low catalyst loadings and the CDC reaction allows direct use of the alkyne and ether which are simple starting materials. The application and further expansion of the scope of this reaction is still under investigation.

EXPERIMENTAL

Typical Procedure: AgOTf (0.0025 mmol) and DDQ (0.15 mmol) was placed in a sealable tube. To this 1 mL toluene and 0.25 mL chlorobenzene, phenylacetylene (0,1 mmol) and isochroman (0.5 mmol) were then added. The tube was sealed and flushed with argon, then stirred for 16 h at 120 ^{o}C. The reaction mixture was cooled to room temperature and flushed through a short column of silica gel with EtOAc. The solvent was then removed under vacuum. The product was isolated from the dark purple crude mixture by flash column chromatography using CH_2Cl_2.[13]

1-(2-Phenylethynyl)-3,4-dihydro-1*H*-isochromene (3a). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.51-7.49 (m, 2H), 7.40-7.39 (m, 1H), 7.36-7.32 (m, 3H), 7.30-7.25 (m, 2H), 7.19-7.18 (m, 1H), 5.82 (s, 1H), 4.38-4.33 (m, 1H), 4.07 (dt, *J* = 5.4 Hz, 11.5 Hz, 1H), 3.02-2.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 135.0, 132.8, 131.9, 129.0, 128.5, 128.2, 127.3, 126.4, 126.1, 122.6, 88.1, 85.7, 67.3, 62.7, 28.1; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{17}H_{13}O$: 233.09609; found: 233.09616.

1-(2-(4-Butylphenyl)ethynyl)-3,4-dihydro-1*H*-isochromene (3b). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.37-7.34 (m, 3H), 7.23-7.21 (m, 2H), 7.15-7.13 (m, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.77 (s, 1H), 4.33-4.29 (m, 1H,), 4.02 (dt, *J* = 5.4 Hz, 14.5Hz, 1H), 2.97-2.86 (m, 2H) 2.59 (t, *J* = 7.8 Hz, 2H), 1.63-1.55 (m, 2H), 1.34 (q, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 143.6, 135.1, 132.8, 131.8, 128.9, 128.3, 127.2, 126.3, 126.1, 119.7, 87.4, 85.9, 67.4, 62.7, 35.5, 33.4, 28.1, 22.3, 13.9; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{21}H_{21}O$: 289.15869; found: 289.15873.

1-(2-(4-Tert-butylphenyl)ethynyl)-3,4-dihydro-1*H*-isochromene (3c). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.37-7.31 (m, 3H), 7.24-7.21 (m, 2H), 7.16-7.13 (m, 1H), 5.77 (s, 1H), 4.34-4.29 (m, 1H), 4.02 (dt, *J* = 5.4 Hz, 14.5 Hz, 1H), 2.97-2.87 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 151.7, 135.1, 132.8, 131.6, 128.9, 127.2, 126.3, 126.1, 125.2, 119.5, 87.4, 85.8, 67.4, 62.7, 34.8, 31.1, 28.1; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{21}H_{21}O$: 289.15869; found: 289.15866.

1-(2-(3-Fluorophenyl)ethynyl)-3,4-dihydro-1*H*-isochromene (3d). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.39-7.31 (m, 1H), 7.29-7.22 (m,4H), 7.16-7.14 (m, 2H), 7.04-7.02 (m, 1H), 5.77 (s, 1H), 4.32-4.27 (m, 1H), 4.04 (dt, *J* = 5.4 Hz, 11.5 Hz, 1H), 2.98-2.86 (m, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 162.3 (d, *J* = 245.1 Hz), 134.6, 132.8, 129.8 (d, *J* = 8.8 Hz), 129.0, 127.7 (d, *J* = 3.3 Hz), 127.3 126.4, 125.9, 124. 3 (d, *J* = 9.8 Hz), 118.6 (d, *J* = 23.1 Hz), 115.8 (d, *J* = 21.2 Hz), 89.1, 84.4 (d, *J* = 3.3 Hz), 67.2, 62.7, 28.0; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{17}H_{12}FO$: 251.08667; found: 251.08661.

1-(2-(4-(Trifluoromethyl)phenyl)ethynyl)-3,4-dihydro-1*H*-isochromene (3e). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.56 (s, 4H), 734-7.32 (m, 1H), 7.25-7.24 (m, 2H), 7.17-7.15 (m, 1H), 5.79 (s, 1H), 4.32-4.27 (m, 1H), 4.05 (dt, *J* = 5.4Hz, 11.5 Hz, 1H), 2.99-2.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 134.4, 132.8, 132.1, 130.2 (q, *J* = 32.4 Hz), 129.1, 127.4, 126.6, 126.5, 125.9, 125.2 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 270.6 Hz), 90.6, 84.2, 67.1, 62.8, 28.0; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{18}H_{12}F_3O$: 301.08348; found: 301.08346.

1-(2-*p*-Biphenylethynyl)-3,4-dihydro-1*H*-isochromene (3f). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.59 (d, *J* = 7.1 Hz, 2H), 7.54 (s, 4H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.39-7.36 (m, 2H), 7.26-7.24 (m, 2H), 7.17-7.16 (m, 1H), 5.82 (s, 1H), 4.36-4.32 (m, 1H), 4.05 (dt, *J* = 5.4 Hz, 11.5 Hz, 1H), 3.0-2.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 141.2, 140.3, 134.9, 132.8, 132.3, 129.0, 128.8, 127.7, 127.3, 127.0, 126.9, 126.4, 126.1, 121.5, 88.8, 85.6, 67.4, 62.7, 28.1; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{23}H_{17}O$: 309.12739; found: 309.12744.

1-(2-*p*-Tolylethynyl)-3,4-dihydro-1*H*-isochromene (3g). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.34 (d, 3H, *J* = 8.1 Hz), 7.24-7.20 (m, 2H), 7.18-7.13 (m, 1H), 7.10 (d, 8.5 Hz, 2H), 5.76 (s, 1H), 4.33-4.28 (m, 1H), 4.02 (dt, *J* = 5.4 Hz, 11.5 Hz, 1H), 2.96-2.86 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 138.6, 135.1, 132.8, 131.7, 128.9, 128.9, 127.2, 126.3, 126.1, 119.5, 87.3, 85.8, 67.4, 62.7, 28.1, 21.5; HRMS (ESI): *m/z*: $[M-H]^+$ calculated for $C_{18}H_{15}O$: 247.11174; found: 247.11149.

1-(2-(4-Methoxyphenyl)ethynyl)-3,4-dihydro-1*H*-isochromene (3h). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.41-7.7.38 (m, 2H), 7.36-7.34 (m, 1H), 723-7.22 (m, 2H), 7.15-7.13 (m, 1H), 6.84-6.81 (m, 2H), 5.76 (s, 1H), 4.33-4.28 (m, 1H), 4.02 (dt, *J* = 5.2 Hz, 11.7 Hz, 1H), 2.99-2.86 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 159.7, 135.2, 133.3, 132.8, 128.9, 127.1, 126.3, 126.1, 114.6, 113.8, 86.7, 85.6, 67.4, 62.7, 55.3, 28.1; HRMS (ESI): *m/z*: $[M+H]^+$ calculated for $C_{18}H_{17}O_2$: 265.12231; found: 265.12233.

1-(2-(4-Phenoxyphenyl ethynyl)-3,4-dihydro-1*H*-isochromene (3i). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.37-7.34 (m, 3H), 7.24-7.22 (m, 2H), 7.16-7.14 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.92-6.91 (m, 2H), 5.77 (s, 1H), 4.33-4.29 (m, 1H), 4.03 (dt, *J* = 5.2 Hz, 11.7 Hz, 1H), 2.98-2.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 157.8, 156.4, 133.5, 132.8, 129.9, 129.0, 127.2, 126.4, 123.9, 119.4, 118.2, 117.2, 117.1, 87.4, 85.2, 67.4, 62.7, 28.1; HRMS (ESI): *m/z*: $[M+H]^+$ calculated for $C_{23}H_{19}O_2$: 327.13796; found: 327.13800.

1-(2-(6-Methoxynaphthalen-2-yl)ethynyl)-3,4-dihydro-1*H*-isochromene (3j). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.91 (s, 1H), 7.66 (t, *J*= 9.6 Hz, 2H), 7.47 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.41-7.39 (m, 1H), 7.25-7.24 (m, 2H), 7.17-7.13 (m, 2H), 7.09(d, *J* = 2.4 Hz, 1H), 5.82 (s, 1H), 4.37-4.32 (m, 1H), 4.05 (dt, *J* = 5.4 Hz, 11.5 Hz, 1H), 3.92 (s, 3H), 2.99-2.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 158.4, 135.1, 134.2, 132.8, 131.7, 129.3, 129.1, 129.0, 128.3, 127.2, 126.7, 126.4, 126.1, 119.4, 117.4, 105.8,

87.7, 86.2, 67.4, 62.7, 55.3, 28.1; HRMS (ESI): *m/z*: $[M+H]^+$ calculated for $C_{22}H_{19}O_2$: 315.13796; found: 315.13801.

3-Methoxy-(1-diphenyl)(3-phenyl)prop-1-yne (3l). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.60-7.58 (m, 3H), 7.56 (s, 3H), 7.46-7.35 (m, 8H), 5.34 (s, 1H), 3.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 140.3, 138.5, 132.2, 128.9, 128.5, 128.5, 127.7, 127.5, 127.0, 127.0, 126.8, 121.4, 87.6, 87.3, 73.6, 56.0; HRMS (ESI): *m/z*: $[M+H]^+$ calculated for $C_{22}H_{19}O$: 299.14304; found: 299.14310.

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