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Iron-Catalyzed Regioselective Hydroaryloxylation of C≡C Triple Bonds: An Efficient Synthesis of 2*H*-1-Benzopyran Derivatives

Xiaobing Xu,[a] Jun Liu,[a] Linfeng Liang,[a] Hongfeng Li,[a] and Yanzhong Li[a,*]

[a] Institute of Medicinal Chemistry, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, People's Republic of China
Fax: (+86)-021-6223-3969; e-mail: yzli@chem.ecnu.edu.cn

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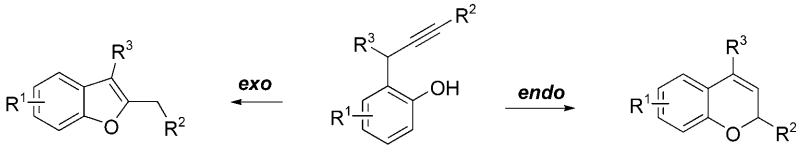
Abstract: An efficient, regioselective, iron-catalyzed intramolecular hydroaryloxylation of 2-propargylphenols or naphthols is reported. The reactions proceed through an *endo-dig* cyclization to afford benzopyran or naphthopyran derivatives in good to high yields using iron(III) chloride as the catalyst with the assistance of aniline in dimethylformamide (DMF).

Keywords: benzopyrans; hydroaryloxylation; iron catalysis; naphthopyrans; regioselective cyclization

The transition metal-catalyzed or -mediated intramolecular O–H addition across unsaturated C–C bonds represents one of the most effective and atom-economical routes to oxygen-containing heterocycles.[1] These catalysts include lanthanide,[1a–c] Pt,[1d,i] Ru,[1p] Au,[1d,g,m,r] Ag,[1k,n] Cu[1e] etc. Oxygen-containing heterocyclic moieties such as benzopyran rings represent key structural units of a variety of natural compounds with interesting biological activities.[2] Different synthetic approaches to these compounds were reported in the literature, such as metal-catalyzed intramolecular ring closure,[1,3] acid-mediated condensation[4] and others.[5] Due to the drawbacks of the reported methods, for example, low yields, requirement of a large excess amount of one of the reagents or high catalyst costs, the development of sustainable, environmentally friendly and less expensive catalysts to accomplish the carbon-heteroatom bond forming process is highly desired. As a result, iron-catalyzed C–C and C–X bond formation has attracted considerable attention, because iron compounds are usually less toxic, low priced and easy to synthesize. There have been a lot of reports concerning the Fe-catalyzed C–C forming reactions with the assistance of Grignard reagents.[6,7] In the past few years, Fe-catalyzed C–C and C–X bond forming reactions without the utilization of Grignard reagents have also appeared.[8,9] In the course of our ongoing study on the development of new, transition metal-catalyzed, selective heterocycle forming protocols,[10] we found that iron-catalyzed benzopyran ring formation was accomplished with high regioselectivity with the assistance of amines. Herein we would like to present our results of the iron-catalyzed regioselective synthesis of 2*H*-1-benzopyran derivatives by the intramolecular hydroaryloxylation of C≡C triple bonds.

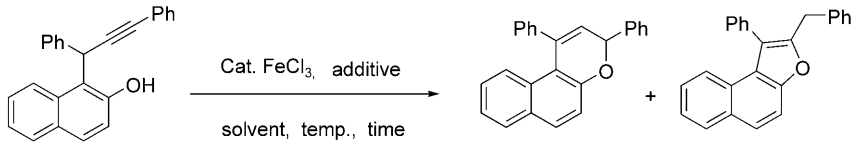
For intramolecular 2-propargylphenol hydroaryloxylations, there exist two possible pathways, namely *exo-dig* or *endo-dig* cyclization to five- or six-membered rings according to Baldwin's rules[11] (Scheme 1). Generally, metal-mediated hydroaryloxylation facilitates an *exo-attack* to give five-membered rings[1a–e,12] there is only one example of the six-membered ring formation catalyzed by Ru.[1p] It is therefore attractive to develop a metal-catalyzed, regioselective hydroaryloxylation for six-membered ring formation.



Scheme 1.

We began our investigation with 1-(1,3-diphenylprop-2-ynyl)naphthalen-2-ol (**1a)**, which was synthesized according to a modified literature method.[12b] Treatment of **1a** with Fe catalyst and additives was selected as the prototypical case to screen the experimental conditions. The results are summarized in Table 1. We first carried out the reaction using $FeCl_3$ (10 mol%) as the catalyst without any additives in DMF at 135 °C, the *endo-dig* cyclization product **2a** was obtained in 15% as the sole product (Table 1, entry 1). Addition of 2.0 equiv. of Na_2CO_3 resulted in the formation of the *exo-dig* cyclizaiton product **3a** in 70% yield, **2a** was not detected (Table 1, entry 2). It is interesting to note when 2.0 equiv. of triethylamine were used, both 5- and 6-membered ring compounds were produced in 63% yield with a ratio 1:1(Table 1, entry 3). Changing the amine to *N*-methylbenzenamine furnished the desired naphthopyran **2a** in 36% yield without the detection of **3a** (Table 1, entry 4). The use of aniline gave rise to **2a** as the only product

Table 1. Optimization of reaction conditions for regioselective formation of **2a**.



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

Entry	$FeCl_3$	Additive	Solvent	Temp.	Time	Product	Yield[a]
1	10%	None	DMF	135 °C	10 h	**2a**	15%
2	10%	Na_2CO_3 (2.0 equiv.)	DMF	135 °C	1 h	**3a**	70%
3	10%	Et_3N (2.0 equiv.)	DMF	135 °C	1 h	**2a** + **3 a**	63%[b]
4	10%	PhMeNH (2.0 equiv.)	DMF	135 °C	5 h	**2a**	36%
5	10%	$PhNH_2$ (2.0 equiv.)	DMF	135 °C	5 h	**2a**	43%
6	20%	$PhNH_2$ (2.0 equic.)	DMF	135 °C	5 h	**2a**	52%
7	5%	$PhNH_2$ (2.0 equiv.)	DMF	135 °C	5 h	**2a**	34%
8	None	$PhNH_2$ (2.0 equiv.)	DMF	135 °C	3 h	**2a** + **3a**	48%[c]
9	20%	$PhNH_2$ (1.0 equiv.)	DMF	135 °C	5 h	**2a**	50%
10	20%	$PhNH_2$ (0.2 equiv.)	DMF	135 °C	5 h	**2a**	49%
11	10%	$PhNH_2$ (2.0 equiv.)	DMF	120 °C	8 h	**2a**	47%
12	10%	$PhNH_2$ (2.0 equiv.)	DMF	100 °C	12 h	**2a**	trace
13	20%	$PhNH_2$ (2.0 equiv.)	DMA	150 °C	3 h	**2a**	38%
14	20%	$PhNH_2$ (2.0 equiv.)	DMA	135 °C	5 h	**2a**	42%
14[d]	20%	$PhNH_2$ (2.0 equiv.)	DMSO	135 °C	5 h	–	–
15	20%	$PhNH_2$ (2.0 equiv.)	Toluene	120 °C	12 h	–	0
16	20%	$PhNH_2$ (2.0 equiv.)	Dioxane	110 °C	12 h	–	0
17	10%	$BuNH_2$ (2.0 equiv.)	DMF	135 °C	1 h	**3a**	76%
18	none	$BuNH_2$ (2.0 equiv.)	DMF	135 °C	1 h	**3a**	71%
19	none	$BuNH_2$ (0.2 equiv.)	DMF	135 °C	1 h	**3a**	66%

[a] Isolated yields.
[b] **2a**:**3a** = 1:1.
[c] **2a**:**3a** = 4:5.
[d] The reaction mixture was complicated.

in 43% yield (Table 1, entry 5). Increasing $FeCl_3$ to 20 mol% resulted in the formation of **2a** in 52% yield (Table 1, entry 6). The structure of **2a** was unequivocally confirmed by X-ray crystal analysis (Figure 1),

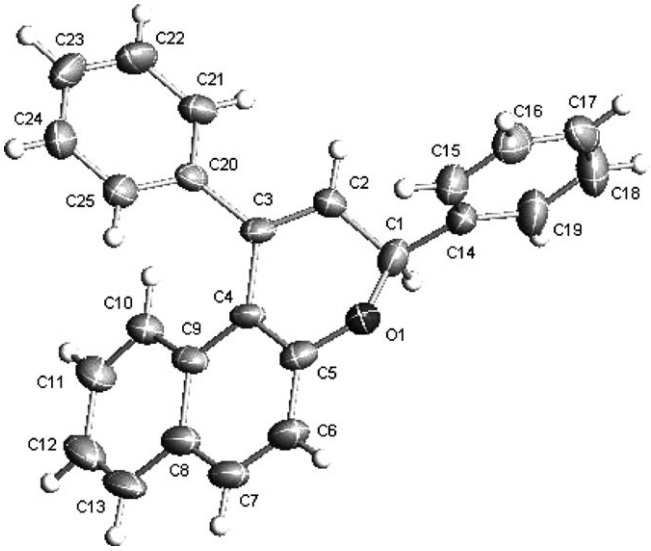


Figure 1. The X-ray crystal structure of **2a**.

which clearly shows the six-membered pyran ring. One equivalent or 20 mol% of aniline gave the similar results as 2.0 equiv. (Table 1, entries 9 and 10). Other solvents such as DMA, DMSO, 1,4-dioxane or toluene failed to accomplish the hydroaryloxylation reaction or gave lower yields of the naphthopyran, respectively (Table 1, entries 13–16). A control reaction in the absence of $FeCl_3$ led to the formation of both 5- and 6-membered rings (Table 1, entry 8). Switching to butan-1-amine afforded the 5-memberd ring compound as the sole product (Table 1, entries 17–19). It is interesting to note that the addition of aniline or butylamine resulted in completely different products, and the optimized reaction conditions for 6-membered ring formation were to use 20 mol% $FeCl_3$ as the catalyst with the addition of 20 mol% to 2.0 equiv. of aniline in DMF at 135 °C.

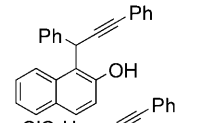
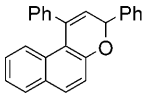
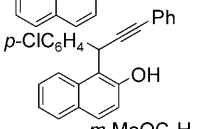
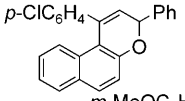
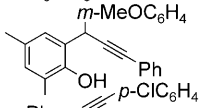
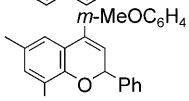
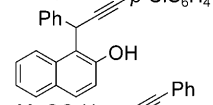
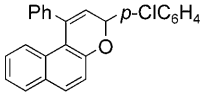
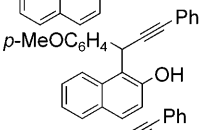
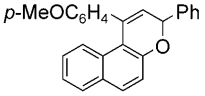
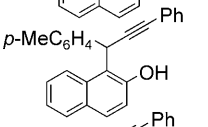
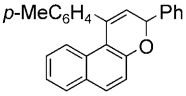
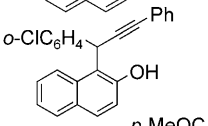
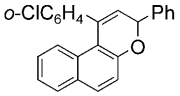
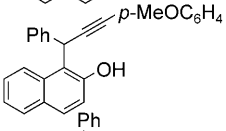
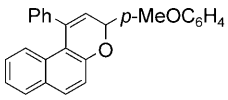
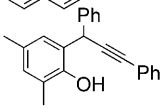
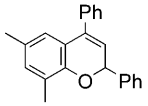
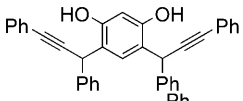
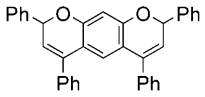
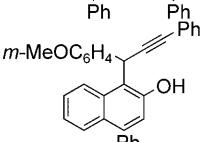
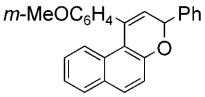
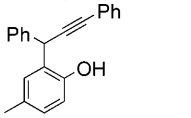
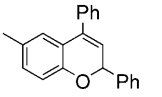
Having established an effective catalytic system for the hydroalkoxylation reactions, we next synthesized a variety of 2-propargylphenol derivatives to explore the scope of the regioselective cyclization reaction under the optimized conditions. Representative results are shown in Table 2. The reaction was applicable to various propargylnaphthols and phenols. Naphthol **1b** with an electron-withdrawing (*p*-Cl) aryl group at the propargylic position cyclized smoothly to give the naphthopyran **2b** in 80% yield (Table 2, entry 2), the electron-withdrawing (*o*-Cl) aryl group naphthol **1g** afforded **2g** in 72% yield (Table 2, entry 7). Whilst **1e** with an electron-donating (*p*-OMe) aryl group gave rise to the corresponding **2e** in 64% yield, the regioselectivity of naphthopyran to naphthofuran was 87:13 (Table 2, entry 5). When **1k** with a similar electron-donating (*m*-OMe) aryl group was employed, the corresponding naphthopyran was produced in 56% yield with a better regioselectivity of 95:5 (Table 2, entry 11). The naphthol bearing a (*p*-Me) aryl group **1f** furnished the desired naphthopyran **2f** in 72% isolated yield (Table 2, entry 6). It seems that naphthols with an electron-withdrawing group at the propargylic position gave better yields in the *endo-dig* cyclization products.

The regioselective effect of the substituents on the triple bond was also investigated. Naphthols with an electron-withdrawing (*p*-Cl) aryl group on the triple bond, e.g., **1d**, gave the *endo-dig* compound **2d** in 60% yield as the sole product (Table 2, entry 4), **1h** with an electron-donating (*p*-OMe) aryl group gave rise to the corresponding **2h** in lower yield and selectivity(Table 2, entry 8).

The substrate scope of the reaction could be extended to various phenols, the desired benzopyrans were obtained in good to high yields with high regioselectivity. When the propargylphenol with an electron-donating (*p*-OMe) aryl group at the propargylic position **1c** was used, the reaction was completed cleanly to afford **2c** in 72% yield (Table 2, entry 3). Dimethylarylphenol **1i** furnished **2i** in 67% yield (Table 2, entry 9). Interestingly, the diynyldiol **1j** gave the corresponding tricyclic compound **2j** as two diastereoisomers in good yield (Table 2, entry 10).

In order to further probe the scope of this process, we also examined the alkyl-substituted phenols and less substituted substrates under the optimized reaction conditions, the results are shown in Table 3. When a propargylnaphthol with a butyl group at the triple bond, **1m**, was used, only the desired six-membered ring was detected after 24 h, although the yield was low (*ca.*10%). This could be improved by using a higher catalyst loading (100 mol%), however, the selectivity was decreased to 3:1 (Table 3, entry 1). When a naphthol with a propyl group at the propargylic position, **1n**, was employed, neither 5- nor 6-membered ring compound could be obtained with most of the starting material being recovered, increasing $FeCl_3$ to 50 mol% resulted in the formation of only five-membered ring product **3n** in low yield (Table 3, entry 2). The phenol bearing a terminal alkyne, **1o**, gave rise to the production of both benzopyran (**2o**) and benzofuran (**3o**) in moderate yields with a ratio 3:1(Table 3, entry 3). A trimethylsilyl-substituted phenol, **1p**, reacted smoothly to produce the respective benzopyran and benzofuran in 23% and 39% yields, respectively (Table 3, entry 4). When a phenol without any substituents at the propargylic position, namely 2-(3-phenylprop-2-ynyl)phenol, was employed, no reaction occurred after 24 h. It seems that substrates without any

Table 2. $FeCl_3$-catalyzed regioselective formation of benzopyrans.

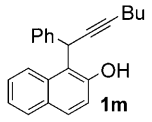
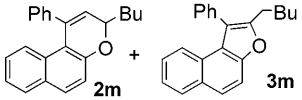
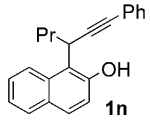
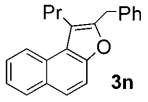
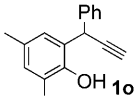
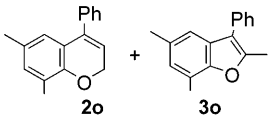
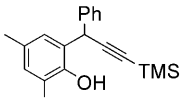
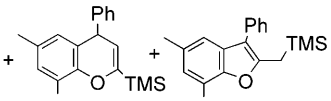
Entry	Phenol		Product		Yield [%][a]
1		**1a**		**2a**	52
2		**1b**		**2b**	80
3		**1c**		**2c**	72
4		**1d**		**2d**	60
5		**1e**		**2e**	64[c,e]
6		**1f**		**2f**	72[d]
7		**1g**		**2g**	74[d]
8		**1h**		**2h**	36[d]
9		**1i**		**2i**	67[d]
10		**1j**		**2j**	59[d,e]
11		**1k**		**2k**	56[d]
12		**1l**		**2l**	70[b,e]

[a] Isolated yields.
[b] The regioselectivity of the crude mixture was **2**:**3** = 91:9.
[c] **2**:**3** = 87:13.
[d] **2**:**3** = 95:5.
[e] Products were isolated as a mixture of **2** + **3**.

substituents or with an alkyl group at the propargylic position have low reactivity and prefer to give the 5-membered ring compound, while substrates with an aryl group at the propargylic position result in the formation of 6-membered rings with good to excellent regioselectivity.

In summary, we have reported an efficient, regioselective, intramolecular hydroaryloxylation of 2-propargylphenols to benzopyrans, good to excellent regioselectivities were achieved when diaryl-substituted phenols were employed. The reactions proceed to afford the benzopyran or naphthopyran derivatives in good to high yields using $FeCl_3$ as the catalyst with the assistance of aniline in DMF. Further applications of this novel iron-catalyzed hydroaryloxylation proce-

Table 3. $FeCl_3$-catalyzed cyclization reactions of alkyl-substituted phenols.

Entry	Phenol	Product	Yield[a]
1[b]	 **1m**	 **2m** + **3m**	**2m**: 32% **3m**: 12%
2[c]	 **1n**	 **3n**	24%
3	 **1o**	 **2o** + **3o**	**2o**: 32% **3o**: 17%
4	 **1p**	**2o** +  **2p** + **3p**	**2o** + **2p**: 23% **3p**: 39%

[a] Isolated yields; unless otherwise noted, reactions were carried out using 20 mol% $FeCl_3$, 2.0 equiv. $PhNH_2$ at 135 °C in DMF for 24 h.
[b] 100 mol% $FeCl_3$ and 4.0 equiv. $PhNH_2$ were used.
[c] 50 mol% $FeCl_3$ were used.

dure to extend the scope of synthetic utility of the reaction are under progress in our group.

Experimental Section

Typical Procedure for the Fe-Catalyzed Formation of 1,3-Diphenyl-3*H*-benzo[*f*]chromene (2a)

A 20-mL Schlenk tube was charged with naphthol **1a** (104 mg, 0.5 mmol) and $FeCl_3$ (16 mg, 0.1 mmol). The reaction mixture was heated to 135 °C for 5 h and then cooled down to room temperature. The mixture was quenched with 3 M HCl and extracted with dichloromethane (3×15 mL). The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel to give the white solid product 1,3-diphenyl-3*H*-benzo[*f*]chromene (**2a**); yield: 87 mg (52%); mp 172–173 °C. ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 5.71$ (d, $J = 4.0$ Hz, 1H), 5.96 (d, $J = 4.0$ Hz, 1H), 7.03–7.58 (m, 10H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 76.53$, 117.13, 118.04, 123.30, 124.56, 125.22, 126.55, 127.33, 127.55, 127.89, 128.38, 128.42, 128.57, 129.96, 130.33, 130.76, 138.16, 139.77, 141.02, 154.03; HR-MS: $m/z = 334.1362$, calcd for $C_{25}H_{18}O$: 334.1358.

Supporting Information

Experimental details and spectroscopic characterization of all new compounds are given in the Supporting Information file.

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[13] CCDC 739832 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223–336–033; or deposit@ccdc.cam.ac.uk.

