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Catalytic Enantioselective Aziridoarylation of Aryl Cinnamyl Ethers toward Synthesis of *trans*-3-Amino-4-arylchromans

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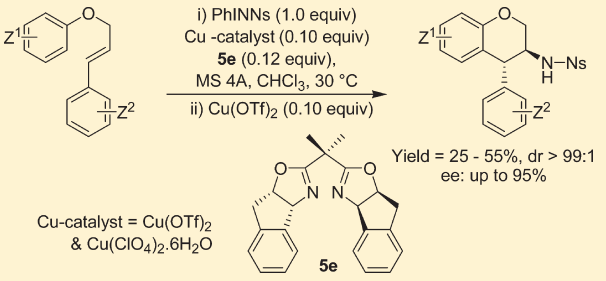
Supporting Information

ABSTRACT: Catalytic enantioselective one-pot aziridoarylation reaction of aryl cinnamyl ethers has been demonstrated in detail. Combination of suitable copper catalyst and chiral bis-oxazoline ligand was found to be very efficient for asymmetric aziridination followed by intramolecular arylation (Friedel−Crafts) reaction to provide a general and direct method for the synthesis of *trans*-3-amino-4-arylchromans with high regio-, diastereo- (dr > 99:1), and enantioselectivity (up to 95% ee) with moderate yield. *trans*-3-Amino-4-arylchroman is an advanced intermediate for the synthesis of chromenoisoquinoline compounds such as doxanthrine, a potent and selective full agonist for the dopamine-D_1 receptor.



INTRODUCTION

The aziridine ring provides a balanced combination of reactivity and flexibility and therefore can serve as an important synthetic intermediate. Stereoselective construction of aziridine followed by its selective opening offers an important chemical tool to the 1,2-bifunctionalization of alkenes. Asymmetric aziridination has been studied quite extensively on styrene, cinnamate, and chalcone double bonds.[1] Ring-opening chemistry with the corresponding aziridines has also been broadly addressed.[2−4] Carbon nucleophile-based aziridine opening is more frequent with metallo-carbon nucleophiles[2a,c] compared to π-nucleophilic heteroaromatics[3] and benzoaromatics.[4] However, cinnamyl alcohol derivatives are infrequent in this array of aziridine-mediated functionalization techniques. There are only a few reports on intramolecular aziridination of cinnamyl carbamates.[5] Specific examples of aziridination of a cinnamyl alcohol,[6] ester,[7] and ether[8] are also known in the literature. However, detailed study on aziridination of aryl cinnamyl ethers, in particular, the asymmetric reaction and subsequent aziridine opening reaction, has not been investigated. It was presumed that aryl cinnamyl ethers **1**, upon reaction with a suitable nitrene source, would produce reactive aziridines **2** that would undergo further intramolecular arylation to provide *trans*-3-amino-4-arylchromans **3** (Scheme 1).

Chromans are ubiquitous in medicinal and natural product chemistry. In particular, the chromenoisoquinoline framework is receiving increasing interest in synthetic and pharmacological chemistry. Recently, the Nichols group has emphasized the synthesis and pharmacological characterization of some synthetic trans-fused chromenoisoquinoline derivatives, such as doxanthrine[9] **4**, which is a potent and selective full agonist for the dopamine-D_1 receptor. *trans*-3-Amino-4-arylchroman **3** could be an advanced intermediate for the synthesis of trans-fused chromenoisoquinoline via Pictet−Spengler reaction. To date, there is no report on asymmetric synthesis of aminochromans.[10] This led us to study the aziridoarylation of aryl cinnamyl ethers. We herewith describe a detailed study on catalytic enantioselective aziridination of aryl cinnamyl ethers **1** followed by intramolecular 6-exotet arylation [Friedel−Crafts (F−C) cyclialkylation] of the tethered aziridines **2** that lead to the one-pot synthesis of *trans*-3-amino-4-aryl-chromans **3** (Scheme 1) with high diastereo- (dr > 99:1) and enantioselectivity (up to 95%) and moderate yields.

RESULTS AND DISCUSSION

One of the most convenient ways for direct and stereoselective alteration of alkene to aziridine is by the action of iodinane ylides (ArI═NSO_2Ar) under copper-catalyzed reaction conditions.[1,11−15] Recently $Cu(OTf)_2$ was found to act as an efficient dual catalyst for aziridination and subsequent intramolecular F−C reaction of the in situ-generated aziridine intermediate.[16] In allied studies, PhINSO_2(4-$NO_2C_6H_4$) [PhINNs] was recognized as a better nitrene precursor than PhINSO_2(4-MeC_6H_4) [PhINTs]. Thus, cinnamyl phenyl ether **1a** (5.0 equiv) was made to react with nitrenoid reagent PhINNs (1.0 equiv) in the presence of 0.10 equiv of $Cu(OTf)_2$ as a catalyst and molecular sieves (MS 4A) in acetonitrile at 30 °C (Scheme 2). Within 30 min, the corresponding *trans*-aziridine (±)-**2a** was produced in 58% yield. The same reaction, when carried out in dichloromethane, showed similar aziridination followed by in situ intramolecular 6-exotet arylcyclization. In the crude reaction mixture, the presence of both chroman (±)-**3a** and aziridine (±)-**2a** was detected (Scheme 2). The remainder of the intermediate aziridine was fully cyclized upon stirring (1 h) with supplementary $Cu(OTf)_2$ (0.10 equiv). Finally, chroman (±)-**3a** was obtained in 51% overall yield after column chromatographic purification. In the case of acetonitrile

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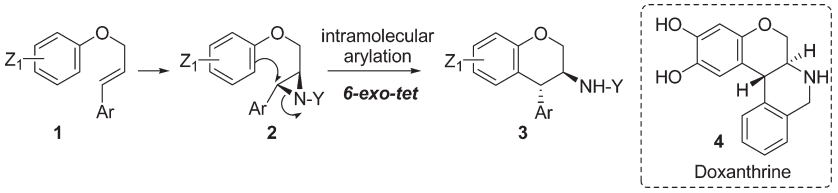
Scheme 1. Proposed Aziridoarylation of Aryl Cinnamyl Ethers 1



Scheme 2. Aziridoarylation Reaction of Allyl Phenyl Ethers

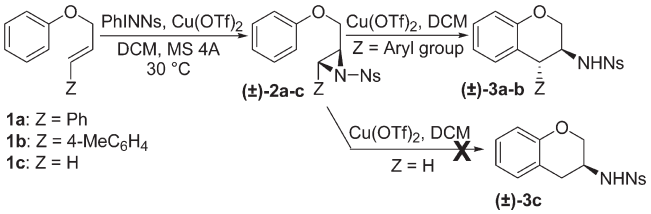
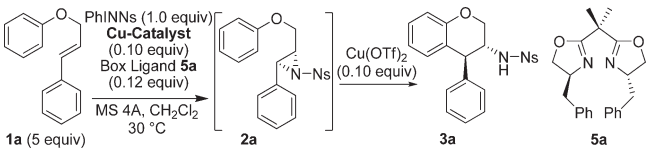


Table 1. Screening of Copper Complexes for Aziridoarylation Reaction

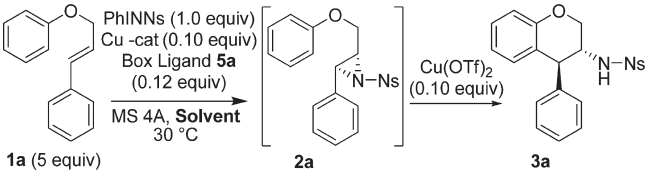


entry	catalyst	yield of **3a** (%)[a]	ee (%)[b]
1	$CuCl_2$[c]	14	8
2	$Cu(acac)_2$[c]	20	46
3	$CuSO_4$[d]	NR	–
4	$Cu(ClO_4)_2 \cdot 6H_2O$[e]	32	58
5	$Cu(OAc)_2 \cdot H_2O$[e]	11	13
6	Cu_2Cl_2[c]	NR	–
7	Cu_2I_2[c]	24	16
8	$Cu(OTf)_2$[c]	25	50

[a] Isolated yields after column chromatography, calculated against the amount of PhINNs. [b] Enantioselectivity of **3a** was determined by HPLC using a chiral column. [c] $CuCl_2$, Cu_2Cl_2, Cu_2I_2, $Cu(acac)_2$, and $Cu(OTf)_2$ were dried and activated by heating (100 °C) under vacuum (10 mm of Hg) for 2 h. [d] $CuSO_4$ was dehydrated with Dean–Stark apparatus using benzene. [e] For the reaction procedure with hydrated copper salts, see Experimental Section. NR: no reaction.

as the solvent, the intermediate aziridine could not be cyclized with additional $Cu(OTf)_2$ catalyst in one-pot fashion. Isolated aziridine (±)-**2a** was cyclized quantitatively to (±)-**3a** in dichloromethane upon treatment with 0.10 equiv of $Cu(OTf)_2$ as the Lewis acid catalyst. Trans stereochemistry of chromans **3** was confirmed by single crystal X-ray analysis of compound (±)-**3b**,[17] obtained by a similar reaction with **1b** (63% yield) and crystallized from toluene–hexane. When allyl phenyl ether **1c** was subjected to the same reaction in dichloromethane under similar conditions, it failed to undergo cyclization and thereby terminated at aziridine (±)-**2c** (Scheme 2). Hence, an aryl substituent on the double bond is essential under the present conditions for intramolecular cyclialkylation via benzylic substitution.

Table 2. Effect of Solvents on Asymmetric Aziridoarylation of 1a



		$Cu(OTf)_2$		$Cu(ClO_4)_2 \cdot 6H_2O$	
entry	solvent	yield (%)[a]	ee (%)[b]	yield (%)[a]	ee (%)[b]
1	CH_2Cl_2	25	50	32	58
2	$CHCl_3$	26	64	32	76
3	CH_3CN[c]	29	49	39	35
4	C_6H_6	19	35	12	53
5	$C_6H_5CH_3$	23	16	12	43
6	CCl_4	15	20	16	51
7	$MeOCH_2CH_2OMe$[c]	21	40	8	50
8	1,4-dioxane[c]	10	34	11	57
9	$ClCH_2CH_2Cl$	18	57	30	48
10	C_6H_5Cl	18	42	13	14

[a] Isolated yield after column chromatography. [b] Enantioselectivity was determined by HPLC using a chiral column. The absolute configuration of the major enantiomer was assigned by analogy with the literature report.[11b] [c] Intermediate aziridine **2** did not cyclize in one pot; it was isolated and cyclized separately in dichloromethane with additional $Cu(OTf)_2$.

The reaction was then examined with chiral bis-oxazoline (Box) chelated copper catalyst for enantioinduction. Cinnamyl phenyl ether **1a** and the benzyl-Box ligand **5a** were selected as a model substrate and ligand, respectively. Various copper reagents were screened and found that yield and selectivity both depend on the conjugate anion of copper complexes (Table 1). Copper(II) triflate and perchlorate salts were superior to the other copper catalysts for one-pot aziridoarylation reaction.

The aziridination was found to be very sensitive toward substrate concentration and temperature. Yield of the given reaction, under $Cu(OTf)_2$-mediated conditions, dropped to 16% when only a stoichiometric amount of substrate was used. With lowering temperature, the reaction rate retarded significantly, and below 18 °C, there was no aziridine formation at all. Therefore, with both of the selected Cu-salts, the variation of solvents and ligands (Tables 2 and 3, respectively) was studied at 30 °C using 5 molar multiples of substrate relative to the nitrene reagent. It is noteworthy that with both $Cu(OTf)_2$ and $Cu(ClO_4)_2 \cdot 6H_2O$, yields were maximum (entry 3, Table 2) in acetonitrile with moderate enantioselectivity (49% and 35%). Solvents such as 1,2-dimethoxyethane and 1,4-dioxane gave very

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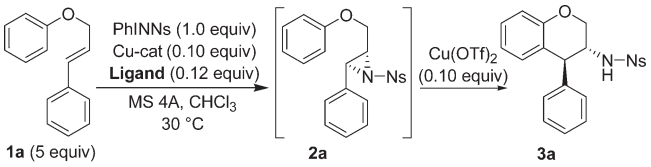
poor yields (entries 7 and 8). Among the solvents, chloroform showed high enantioselectivity with moderate yield (entry 2).

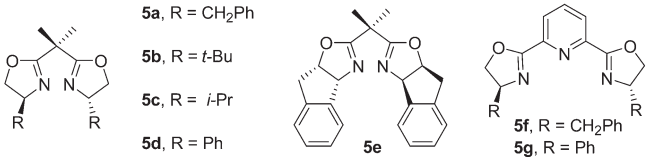
In the ligand study, indanolamine-derived Box ligand **5e** was found to work well in combination with chloroform for both $Cu(OTf)_2$ and $Cu(ClO_4)_2$ salts (85% and 83% ee, respectively; entry 5, Table 3). Enantioselectivity exhibited by benzyl Box **5a** and isopropyl Box **5c** were moderate (entries 1 and 3). Unlike the reported styrene substrates lacking an additional binding site, sterically demanding *tert*-butyl-Box **5b** and phenyl-Box **5d** showed poor enantioselectivity.[11,16b] Replacement of the Box ligands with Pybox analogues **5f**−**g** improved the yield but at the expense of selectivity (entries 6 and 7).

In order to generalize the scope, this technique was employed for a variety of aryl cinnamyl ethers, and enantioselectivity up to 95% was achieved (Table 4). All substrates underwent smooth one-pot aziridoarylation reaction, except for aryl cinnamyl ethers with chloro and fluoro substituents such as **3j** and **3k**. Those corresponding aziridines were isolated and cyclized separately in dichloromethane using 0.10 equiv of $Cu(OTf)_2$ (entries 9 and 10). This might be because of the low π-nucleophilicity of aryl units. In contrast to the formation of a mixture of aziridine and chroman in ligand-free racemic reactions, only aziridine was formed in the chiral Cu-complex-catalyzed enantioselective reactions, which required additional 0.10 equiv of $Cu(OTf)_2$ for cyclization. Yields obtained in enantioselective reactions were also lower than those in corresponding racemic reactions and did not exceed 50% except for **3j** having a 2-chlorophenyl unit. Substrates with electron-rich arenes and heteroarenes at either end were studied and found to produce a mixture of uncharacterized products. The purity of the nitrene reagent PhINNs is very important; contaminated reagent not only decreases the yield but also lowers the ee up to 15%.

In all cases, only *trans*-chroman product **3a**−**k** (dr > 99:1) was isolated with high regio- and stereoselectivity. Overall retention of substrate stereochemistry over to the product indicates that there is no radical pathway for aziridination in the present system. The concerted addition of the electrophilic nitrene results in geometrically stereospecific conversion of the pure *trans*-alkene to *trans*-aziridine. In the second step, the stereospecific anti-opening

Table 3. Screening of Ligands in Aziridoarylation of 1a

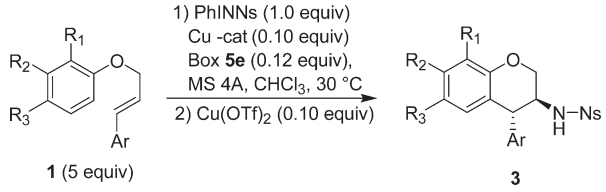




			$Cu(OTf)_2$		$Cu(ClO_4)_2 \cdot 6H_2O$	
entry	Box/Pybox Ligand	R	yield (%)[a]	ee (%)[b]	yield (%)[a]	ee (%)[b]
1	**5a**	CH_2Ph	26	64	32	76
2	**5b**	*t*-Bu	15	57	23	43
3	**5c**	*i*-Pr	22	77	30	58
4	**5d**	Ph	30	23	33	21
5	**5e**[c]	indenyl	28	−85	31	- 83
6	**5f**	CH_2Ph	35	0	–	–
7	**5g**	Ph	42	4	–	–

[a] Isolated yield after column chromatography. [b] Enantioselectivity was determined by HPLC using a chiral AD-H column. [c] The enantiomeric population of the product was reversed.

Table 4. Generalization of Aziridoarylation for the Synthesis of Aminoarylchromans 3



					$Cu(OTf)_2$		$Cu(ClO_4)_2 \cdot 6H_2O$	
entry	substrate	R_1, R_2, R_3	Ar	product	yield/%[a] (time/h)[b]	ee (%)[c]	yield/%[a] (time/h)[b]	ee (%)[c]
1	**1a**	H, H, H	Ph	**3a**	28 (0.5)	85	31 (0.5)	83
2	**1b**	H, H, H	4-MeC_6H_4	**3b**	40 (0.5)	90	32 (0.5)	71
3	**1d**	H, H, Me	Ph	**3d**	48 (0.5)	95	37 (0.5)	86
4	**1e**	H, H, Cl	Ph	**3e**	48 (1.0)	81	30 (1.5)	48
5	**1f**	H, H, H	4-ClC_6H_4	**3f**	25 (1.5)	85	33 (1.0)	61
6	**1g**	H, H, Me	4-ClC_6H_4	**3g**	28 (0.5)	83	27 (0.5)	56
7	**1h**	H, H, Cl	4-MeC_6H_4	**3h**	29 (1.0)	66	26 (0.5)	70
8	**1i**	H, H, Me	4-MeC_6H_4	**3i**	32 (0.5)	73	45 (0.5)	66
9[d]	**1j**	Cl, H, H	Ph	**3j**	55 (1.0)	90	42 (1.0)	67
10[d]	**1k**	H, H, F	Ph	**3k**	26 (1.0)	80	31 (1.5)	74

[a] Isolated yield after column chromatography. [b] Values in parentheses refer to the aziridination reaction time. [c] Enantioselectivity was determined by HPLC using a chiral column. [d] Aziridine did not cyclize in one pot; it was isolated and cyclized separately in CH_2Cl_2 using an additional 0.10 equiv of $Cu(OTf)_2$ catalyst.

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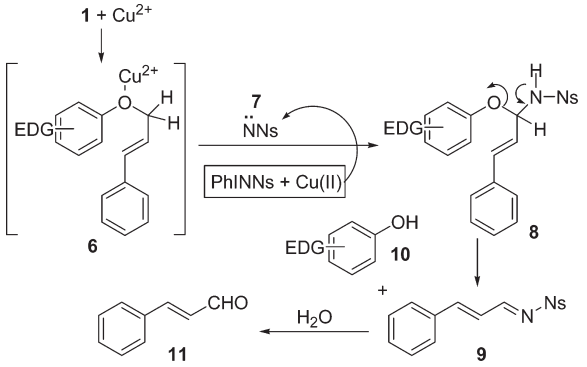
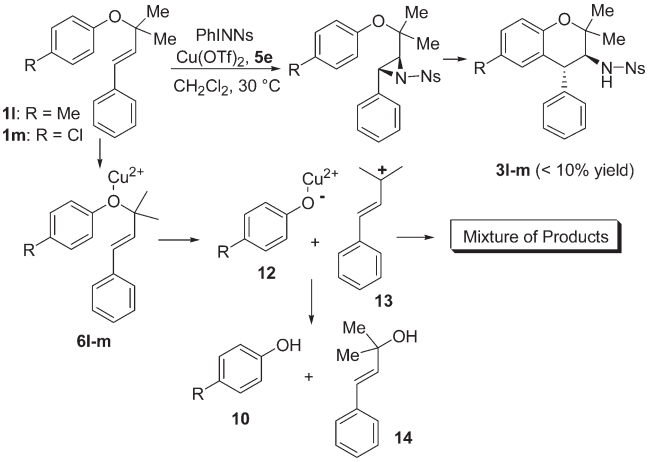
Scheme 3. C−H Insertion of Nitrene Followed by Oxidative Cleavage



Scheme 4. Aziridoarylation of Aryl Cinnamyl Ethers 1l and 1m



of the aziridine by the intramolecular aromatic nucleophile produces aminoarylchroman with trans-stereochemistry.[16]

Average yield of the desired aziridines was low to moderate, and formation of some side products such as cinnamyl imine and cinnamaldehyde was detected. Formation of the imine **9** is reasonable from a nitrene insertion mechanism into the C−H bond (Scheme 3).[18] The enhanced activation of the oxy-methylene group upon binding with copper makes it facile for nitrene insertion. Insertion followed by oxidative cleavage of the ethereal bond finally results in phenol **10** and imine **9**, which in turn give cinnamaldehyde **11**. In comparison to our earlier report on the aziridoarylation reaction of arylethyl styrenes,[16] the present method with the ether variant is relatively faster; however, because of the additional oxygen−metal binding, it requires higher catalyst loading and provides poor to moderate yields.

To eliminate this undesired nitrene insertion reaction, *gem*-dimethylcinnamyl phenyl ethers **1l** and **1m** were used (Scheme 4), but under both chiral and achiral reaction conditions, these substrates could not circumvent the ethereal cleavage, and only <10% of chromans **3l,m** was detected in the complex mixture of products by ^{1}H NMR. Among the many side products, phenol **10** and *gem*-dimethylcinnamyl alcohol **14** were detected in the reaction mixture, which supports the mechanism of Lewis acid-catalyzed ethereal cleavage.

CONCLUSIONS

In summary, this is the first study on catalytic and enantioselective aziridination of aryl cinnamyl ethers and one-pot intramolecular arylation of the in situ-generated tethered aziridine. This method provides an easy access of *N*-sulfonyl-protected *trans*-3-amino-4-arylchromans with high regio-, diastereo- (dr > 99:1), and enantioselectivity (ee up to 95%). These chiral aminochromans could be advanced intermediates for the synthesis of biologically active chromenoisoquinoline compounds such as doxanthrine, via Pictet−Spengler cyclization. Competitive C−H insertion of nitrene at the O−CH $_2$ unit followed by oxidative cleavage is the major side reaction, which lowers the overall yield.

EXPERIMENTAL SECTION

Melting points (mp) of solid compounds are reported without correction. ^{1}H NMR chemical shifts are expressed in parts per million (δ ppm) downfield to $CHCl_3$ (δ = 7.26), C_2D_6SO (δ = 2.48); ^{13}C NMR chemical shifts are expressed in ppm (δ) relative to the central $CDCl_3$ resonance (δ = 77.0) and DMSO-d_6 (δ = 39.7). Enantioselectivities were determined by HPLC using Chiralpak AD-H chiral column (0.46 × 15.0 cm^2 each) with *i*-PrOH/*n*-hexane (10:90) solvent, flow rate 1 mL/min, UV wavelength 220 nm, 20 nm (ref off). Specific rotation values are reported only for the Cu(OTf)$_2$-catalyzed reactions.

General Procedure for Synthesis of Aryl Cinnamyl Ethers. Allylaryl ethers **1** were prepared by conventional alkylation method via the reaction of phenol derivatives with corresponding allyl- or cinnamyl bromides in the presence of K_2CO_3 in acetone.

Cinnamyl Phenyl Ether, ***1a***. Yield = 81%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48−7.39 (m, 2H), 7.38−7.25 (m, 5H), 7.05−6.90 (m, 3H), 6.74 (d, *J* = 15.8 Hz, 1H), 6.42 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.71 (dd, *J* = 5.6, 1.4 Hz, 2H).

1-Methyl-4-(3-phenylallyloxy)benzene, ***1b***. Yield = 78%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48−7.15 (m, 5H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.42 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.68 (dd, *J* = 5.6, 1.2 Hz, 2H), 2.30 (s, 3H).

Allyl Phenyl Ether, ***1c***. Yield = 86%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.38−7.21 (m, 2H), 7.04−6.89 (m, 3H), 6.14−5.97 (m, 1H), 5.48−5.25 (m, 2H), 4.57−4.51 (m, 2H).

1-Methyl-4-(3-phenoxypropenyl)benzene, ***1d***. Yield = 71%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39−7.22 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04−6.89 (m, 3H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.38 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.70 (dd, *J* = 5.8, 1.0 Hz, 2H), 2.35 (s, 3H).

1-Chloro-4-(3-phenylallyloxy)benzene, ***1e***. Yield = 77%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.49−7.17 (m, 7H), 6.89 (d, *J* = 9.2 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.39 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.66 (dd, *J* = 5.8, 1.4 Hz, 2H).

1-Chloro-4-(3-phenoxypropenyl)benzene, ***1f***. Yield = 73%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.43−7.28 (m, 6H), 7.08−6.92 (m, 3H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.74 (dd, *J* = 5.6, 1.4 Hz, 2H).

4-Chlorocinnamyl-4-methylphenyl Ether, ***1g***. Yield = 80%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.38−7.23 (m, 4H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 16.0, 5.4 Hz, 1H), 4.63 (dd, *J* = 5.6, 1.2 Hz, 2H), 2.27 (s, 3H).

4-Methylcinnamyl-4-chlorophenyl Ether, ***1h***. Yield = 75%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.30−7.18 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.62 (d, *J* = 5.8 Hz, 2H), 2.31 (s, 3H).

4-Methylcinnamyl-4-methylphenyl Ether, ***1i***. Yield = 71%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.12−7.03 (m, 4H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.8, 5.8 Hz, 1H), 4.63 (d, *J* = 5.8 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 3H).

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1-Chloro-2-(3-phenylallyloxy)benzene, ***1j***. Yield = 87%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.43−7.14 (m, 7H), 6.99−6.83 (m, 2H), 6.75 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 13.4, 5.6 Hz, 1H), 4.76 (dd, J = 5.6, 1.4 Hz, 2H).

1-Fluoro-4-(3-phenylallyloxy)benzene, ***1k***. Yield = 70%, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45−7.22 (m, 5H), 7.05−6.80 (m, 4H), 6.70 (d, J = 16.0 Hz, 1H), 6.37 (dt, J = 16.0, 5.8 Hz, 1H), 4.63 (dd, J = 5.8, 1.4 Hz, 2H).

Synthesis of 1-Substututed-4-(1,1-dimethyl-3-phenylallyloxy)benzene, ***1l,m***. Mitsunobu coupling of dimethylcinnamyl alcohol with corresponding *p*-methyl- and *p*-chlorophenols afforded the modified substrates **1l,m**.

1-(1,1-Dimethyl-3-phenylpropoxy)-4-methylbenzene, ***1l***. Colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36−7.18 (m, 5H), 7.04 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 16.2 Hz, 1H), 6.35 (d, J = 16.2 Hz, 1H), 2.27 (s, 3H), 1.43 (s, 6H).

1-Chloro-4-(1,1-dimethyl-3-phenylpropoxy)benzene, ***1m***. Colorless liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.42−7.28 (m, 5H), 7.20 (d, J = 9.0 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 6.60 (d, J = 16.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 1.43 (s, 6H).

General Procedure for One-Pot Enantioselective Synthesis of N-Protected-3-amino-4-arylchromans 3 and Aziridines 2. In dichloromethane, the corresponding copper catalyst (0.10 equiv) was stirred with the ligand (**5**, 0.12 equiv) in the presence of molecular sieves (MS 4A) at rt. [In the case of hydrated copper salts (e.g., copper acetate and perchlorate), it was stirred with the corresponding ligand for 30 min in dichloromethane, and then the solvent was removed under vacuum (1.0 mm of Hg) at 50 °C for 20 min. It was cooled to 30 °C, and chloroform and activated molecular sieves (MS 4A) were added further and stirred at rt.] After 1 h, alkene **1** (5.0 equiv) and PhINNs (1.0 equiv) were added and stirred at 30 °C. It was a heterogeneous reaction mixture, and completion of the aziridination step was indicated by the complete dissolution of the reagent. Then a supplementary amount of $Cu(OTf)_2$ (0.10 equiv) was added. Conversion of the aziridine to chroman was monitored by TLC (approximately 2 h), and upon completion, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a short plug of silica gel. The silica gel was washed with an additional 10 mL of ethyl acetate. The filtrate was concentrated by rotary evaporation under reduced pressure. N-Protected 3-amino-4-arylchroman **3** was isolated by flash column chromatography, using a combination of ethyl acetate and hexane as an eluent. Enantioselectivity was determined by HPLC (Solvent: *n*-hexane/*i*-PrOH = 90/10; flow rate: 1.0 mL/min; wavelength: 220 nm, bandwidth: 20 nm, column: CHIRALPAK AD-H, 0.46 cm × 15.0 cm).

1-(4-Nitrobenzenesulfonyl)-2-phenoxymethyl-3-phenylaziridine, (±)- ***2a***. White solid, mp: 164 °C. FTIR (KBr, cm^{-1}): 1654, 1527, 1490, 1342, 1305, 1238, 1166, 1086, 1041, 917, 855; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.31 (d, J = 7.2 Hz, 2H), 8.14 (d, J = 7.2 Hz, 2H), 7.40−7.15 (m, 7H), 7.01 (quasi-t, J = 7.4 Hz, 1H), 6.91−6.86 (m, 2H), 4.69 (dd, J = 10.8, 6.4 Hz, 1H), 4.52 (dd, J = 10.8, 5.6 Hz, 1H), 3.51−3.42 (m, 1H), 4.12 (d, J = 4.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.9, 150.5, 145.3, 133.3, 129.7 (2C), 129.0, 128.9 (2C), 128.8 (2C), 126.9 (2C), 124.2 (2C), 121.8, 114.7 (2C), 64.8, 50.4, 47.4. Anal. (CHN %) Calcd for $C_{21}H_{18}N_2O_5S$: C, 61.45; H, 4.42; N, 6.83. Found: C, 61.66; H, 4.39; N, 6.59.

1-(4-Nitrobenzenesulfonyl)-2-phenoxymethylaziridine, (±)- ***2c***. White solid, mp: 132−133 °C. FTIR (KBr, cm^{-1}): 2100, 1655, 1560, 1527, 1348, 1220, 1167, 772; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.43 (d, J = 9.0 Hz, 2H), 8.13 (d, J = 9.0 Hz, 2H), 7.25−7.15 (m, 2H), 6.93 (quasi-t, J = 7.4 Hz, 1H), 6.69 (dd, J = 7.8, 1.2 Hz, 2H), 4.19 (dd, J = 10.1, 3.4 Hz, 1H), 3.85 (dd, J = 10.1, 6.8 Hz, 1H), 3.34−3.21 (m, 1H), 2.94 (d, J = 7.2 Hz, 1H), 2.46 (d, J = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 150.6, 143.4, 129.5 (2C), 129.3 (2C), 124.1 (2C), 121.4, 114.2 (2C), 66.5, 39.4, 31.0. Anal. (CHN %) Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.88; H, 4.22; N, 8.38. Found: C, 53.54; H, 4.01; N, 7.99.

4-Nitro-N-(4-phenylchroman-3-yl)benzenesulfonamide, ***3a***. White solid, mp: 157−158 °C. FTIR (KBr, cm^{-1}): 1523, 1489, 1458, 1448, 1438, 1348, 1309, 1229, 1164, 1099; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.25−7.15 (m, 4H), 6.94−6.90 (m, 3H), 6.85 (quasi-t, J = 7.6 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 5.03 (d, J = 7.6 Hz, 1H), 4.24 (dd, J = 11.2, 2.0 Hz, 1H), 4.03 (d, J = 5.2 Hz, 1H), 3.85 (dd, J = 11.2, 6.0 Hz, 1H), 3.77−3.71 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.8, 149.9, 145.9, 141.8, 131.2, 129.0, 128.8 (2C), 128.7 (2C), 127.9 (2C), 127.4, 124.3 (2C), 121.8, 120.8, 116.8, 65.5, 53.7, 47.8. Anal. (CHN %) Calcd for $C_{21}H_{18}N_2O_5S$: C, 61.45; H, 4.42; N, 6.83. Found: C, 61.39; H, 4.16; N, 6.79; LRMS (electrosprayionization-MS): Calcd 409.0936 m/z $(M - H)^-$, found 409.0855 m/z. HPLC (0.46 × 15.0 cm^2 Chialpak AD-H, 90:10 *n*-hexane/*i*-PrOH, 1 mL/min, 220, 20 nm wavelength, ref off. Similar HPLC condition was followed for all other samples): $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 14.34 min, t_r (major) 16.28 min, 85% ee; $[\alpha]^{28}_D$ = +29.1 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2 \cdot 6H_2O$-catalyzed reaction, 83% ee.

4-Nitro-N-(4-p-tolylchroman-3-yl)benzenesulfonamide, ***3b***. White solid, mp: 169−170 °C. FTIR (KBr, cm^{-1}): 2924, 2869, 1606, 1528, 1512, 1488, 1348, 1335, 1312, 1228, 1163, 1097, 1069, 1050; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.17 (quasi-t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.85−6.80 (m, 1H), 6.79 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 7.2 Hz, 1H), 5.01 (d, J = 7.6 Hz, 1H), 4.28 (dd, J = 11.2, 2.4 Hz, 1H), 3.95 (d, J = 5.6 Hz, 1H), 3.85 (dd, J = 11.2, 6.4 Hz, 1H), 3.73−3.65 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.9, 149.9, 145.8, 138.7, 137.4, 131.1, 129.5 (2C), 128.7 (3C), 128.1 (2C), 124.2 (2C), 121.7, 121.4, 116.8, 66.1, 53.9, 47.7, 20.9. Anal. (CHN %) Calcd for $C_{22}H_{20}N_2O_5S$: C, 62.25; H, 4.75; N, 6.60. Found: C, 62.50; H, 5.10; N, 6.72; LRMS (EI): Calcd 423.1093 m/z $(M - H)^-$, found 423.1013 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 15.04 min, t_r (major) 17.27 min, 90% ee; $[\alpha]^{28}_D$ = −59.2 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2 \cdot 6H_2O$-catalyzed reaction, 71% ee.

N-(6-Methyl-4-phenylchroman-3-yl)-4-nitrobenzenesulfonamide, ***3d***. White solid, mp: 203−204 °C. FTIR (KBr, cm^{-1}): 2929, 2373, 1530, 1499, 1426, 1347, 1307, 1222, 1164, 1092; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.22−7.20 (m, 3H), 6.99 (d, J = 8.4 Hz, 1H), 6.96−6.93 (m, 2H), 6.81 (d, J = 8.4 Hz, 1H), 6.52 (s, 1H), 5.05 (d, J = 8.0 Hz, 1H), 4.18 (dd, J = 11.2, 2.0 Hz, 1H), 4.00 (d, J = 4.8 Hz, 1H), 3.80 (dd, J = 11.2, 5.6 Hz, 1H), 3.75−3.70 (m, 1H), 2.15 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.9, 149.6, 146.5, 142.4, 131.2, 130.7, 129.1, 129.0 (2C), 128.6 (2C), 127.9 (2C), 127.1, 124.1 (2C), 121.5, 116.5, 66.4, 54.2, 47.6, 20.4. Anal. (CHN %) Calcd for $C_{22}H_{20}N_2O_5S$: C, 62.25; H, 4.75; N, 6.60. Found: C, 62.15; H, 4.42; N, 6.64; LRMS (EI): Calcd 423.1093 m/z $(M - H)^-$, found 423.1019 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 12.30 min, t_r (major) 13.46 min, 95% ee; $[\alpha]^{28}_D$ = −53.2 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2 \cdot 6H_2O$-catalyzed reaction, 86% ee.

N-(6-Chloro-4-phenyl-chroman-3-yl)-4-nitrobenzenesulfonamide, ***3e***. White solid, mp: 217 °C. FTIR (KBr, cm^{-1}): 1524, 1484, 1420, 1349, 1314, 1260, 1224, 1162, 1096, 1021, 1002; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.8 Hz, 2H), 7.23−7.18 (m, 3H), 7.14 (dd, J = 8.8, 2.4 Hz, 1H), 6.94−6.91 (m, 2H), 6.86 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 5.01 (d, J = 7.6 Hz, 1H), 4.25 (dd, J = 11.2, 2.4 Hz, 1H), 4.01 (d, J = 5.2 Hz, 1H), 3.85 (dd, J = 11.2, 6.0 Hz, 1H), 3.75−3.69 (m, 1H); ^{13}C NMR (50 MHz, DMSO-d_6): δ 152.8, 149.5, 146.5, 141.5, 130.3, 129.0 (2C), 128.6 (2C), 128.2, 127.7 (2C), 127.3, 125.9, 124.4, 124.0 (2C), 118.1, 67.2, 53.7, 47.3. Anal. (CHN %) Calcd for $C_{21}H_{17}ClN_2O_5S$: C, 56.69; H, 3.85; N, 6.30. Found: C, 56.41; H, 3.78; N, 5.92; LRMS (EI): Calcd 443.0547 m/z $(M - H)^-$, found 443.0468 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 13.08 min, t_r (major) 15.77 min, 81% ee; $[\alpha]^{28}_D$ = −25.8 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2 \cdot 6H_2O$-catalyzed reaction, 48% ee.

N-[4-(4-Chlorophenyl)chroman-3-yl]-4-nitrobenzenesulfonamide, ***3f***. White solid, mp: 215−216 °C. FTIR (KBr, cm^{-1}): 1530, 1489, 1346, 1310, 1223, 1165, 1090, 1014, 997; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.8 Hz, 2H), 7.89 (d. J = 8.8 Hz, 2H), 7.23−7.15 (m, 3H), 6.93−6.85 (m, 4H), 6.73 (d, J = 7.6 Hz, 1H), 5.07 (d, J = 8.4 Hz, 1H), 4.17 (dd, J = 11.2, 2.0 Hz, 1H), 4.04 (d, J = 4.8 Hz, 1H), 3.84 (dd, J = 11.2, 5.6 Hz, 1H), 3.75−3.65 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.8, 150.1, 146.0, 140.5, 133.6, 131.2, 130.1 (2C), 129.0 (3C), 128.0 (2C), 124.4 (2C), 122.0, 120.4, 117.1, 65.5, 53.9, 47.4. Anal. (CHN %) Calcd for $C_{21}H_{17}ClN_2O_5S$: C, 56.69; H, 3.85; N, 6.30. Found: C, 56.42; H, 3.90; N, 6.49; LRMS (EI): Calcd 443.0547 m/z $(M - H)^-$, found 443.0469 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 17.85 min, t_r (major) 19.21 min, 85% ee; $[\alpha]^{28}_D$ = −81.5 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2\cdot 6H_2O$-catalyzed reaction, 61% ee.

N-[4-(4-Chlorophenyl)-6-methylchroman-3-yl]-4-nitrobenzenesulfonamide, ***3g***. Pale yellow solid, mp: 202 °C. FTIR (KBr, cm^{-1}): 1605, 1530, 1498, 1430, 1350, 1310, 1226, 1165, 1091, 1014; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 6.4 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 1H), 6.51 (s, 1H), 5.09 (d, J = 8.4 Hz, 1H), 4.12 (dd, J = 11.2, 2.0 Hz, 1H), 4.01 (d, 4.8 Hz, 1H), 3.79 (dd, J = 11.2, 5.2 Hz, 1H), 3.72−3.67 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.9, 149.3, 146.5, 140.8, 132.9, 130.7, 130.5, 130.4 (2C), 129.0, 128.4 (2C), 127.7 (2C), 123.9 (2C), 122.1, 116.4, 67.5, 54.4, 46.9, 20.4. Anal. (CHN %) Calcd for $C_{22}H_{19}ClN_2O_5S$: C, 57.58; H, 4.17; N, 6.10. Found: C, 57.34; H, 4.03; N, 5.89; LRMS (EI): Calcd 457.0703 m/z $(M - H)^-$, found 457.0620 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 14.64 min, t_r (major) 17.09 min, 83% ee; $[\alpha]^{28}_D$ = −45.2 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2\cdot 6H_2O$-catalyzed reaction, 56% ee.

N-(6-Chloro-4-p-tolylchroman-3-yl)-4-nitrobenzenesulfonamide, ***3h***. Pale yellow solid, mp: 178−180 °C. FTIR (KBr, cm^{-1}): 1608, 1527, 1483, 1438, 1347, 1312, 1229, 1164, 1101, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.12 (dd, J = 8.8, 2.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.8 Hz, 1H), 6.78 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 2.4 Hz, 1H), 4.95 (d, J = 7.2 Hz, 1H), 4.29 (dd, J = 11.2, 2.8 Hz, 1H), 3.92 (d, J = 6.4 Hz, 1H), 3.85 (dd, J = 11.2, 6.4 Hz, 1H), 3.68−3.61 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.5, 149.9, 145.6, 137.8, 137.7, 130.4, 129.6 (2C), 128.7, 128.6 (2C), 128.0 (2C), 126.5, 124.2 (2C), 123.3, 118.3, 66.4, 53.6, 47.5, 20.9. Anal. (CHN %) Calcd for $C_{22}H_{19}ClN_2O_5S$: C, 57.58; H, 4.17; N, 6.10. Found: C, 57.20; H, 4.14; N, 5.78; LRMS (EI): Calcd 457.0703 m/z $(M - H)^-$, found 457.0626 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 12.66 min, t_r (major) 15.64 min, 66% ee; $[\alpha]^{28}_D$ = +51.7 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2\cdot 6H_2O$-catalyzed reaction, 70% ee.

N-(6-Methyl-4-p-tolylchroman-3-yl)-4-nitrobenzenesulfonamide, ***3i***. White solid, mp: 156 °C. FTIR (KBr, cm^{-1}): 3106, 2924, 2866, 1608, 1530, 1498, 1420, 1348, 1313, 1224, 1166, 1095, 1066, 1040; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.00−6.95 (m, 3H), 6.82−6.77 (m, 3H), 6.50 (s, 1H), 5.02 (d, J = 7.2 Hz, 1H), 4.22 (dd, J = 11.2, 2.0 Hz, 1H), 3.93 (d, J = 5.2 Hz, 1H), 3.80 (dd, J = 11.2, 6.0 Hz, 1H), 3.70−3.65 (m, 1H), 2.30 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.7, 149.9, 146.0, 139.0, 137.3, 131.2, 131.1, 129.5 (2C), 129.4, 128.7 (2C), 128.1 (2C), 124.2 (2C), 120.8, 116.5, 65.8, 54.1, 47.6, 20.9, 20.4. Anal. (CHN %) Calcd for $C_{23}H_{22}N_2O_5S$: C, 63.00; H, 5.06; N, 6.39. Found: C, 62.85; H, 4.94; N, 6.28; LRMS (EI): Calcd 437.1249 m/z $(M - H)^-$, found 437.1176 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 11.79 min, t_r (major) 13.49 min, 73% ee; $[\alpha]^{28}_D$ = −19.9 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2\cdot 6H_2O$-catalyzed reaction, 66% ee.

N-(8-Chloro-4-phenylchroman-3-yl)-4-nitrobenzenesulfonamide, ***3j***. White solid, mp: 198 °C. FTIR (KBr, cm^{-1}): 1606, 1527, 1475, 1448, 1350, 1240, 1163, 1094, 1078, 1062, 1027; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.29 (dd, J = 8.0, 1.2 Hz, 1H), 7.22−7.19 (m, 3H), 6.95−6.92 (m, 2H), 6.81 (quasi-t, J = 8.0 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 5.03 (d, J = 7.6 Hz, 1H), 4.34 (dd, J = 11.2, 2.4 Hz, 1H), 4.10 (d, J = 5.2 Hz, 1H), 3.97 (dd, J = 11.2, 5.6 Hz, 1H), 3.79−3.74 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.0, 149.6, 145.7, 141.3, 129.7, 129.3, 129.0 (2C), 128.7 (2C), 128.0 (2C), 127.7, 124.4 (2C), 122.9, 121.9 (2C), 66.3, 53.5, 48.0. Anal. (CHN %) Calcd for $C_{21}H_{17}ClN_2O_5S$: C, 56.69; H, 3.85; N, 6.30. Found: C, 57.03; H, 3.73; N, 6.11; LRMS (EI): Calcd 443.0547 m/z $(M - H)^-$, found 443.0466 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (major) 11.34 min, t_r (minor) 12.84 min, 90% ee; $[\alpha]^{28}_D$ = −26.1 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2\cdot 6H_2O$-catalyzed reaction, 67% ee.

N-(6-Fluoro-4-phenylchroman-3-yl)-4-nitrobenzenesulfonamide, ***3k***. White solid, mp: 214 °C. FTIR (KBr, cm^{-1}): 1606, 1521, 1492, 1421, 1348, 1306, 1258, 1196, 1162, 1098, 1022, 1005, 937; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.22−7.17 (m, 3H), 6.94−6.91 (m, 2H), 6.90−6.86 (m, 2H), 6.43 (dd, J = 8.8, 2.8 Hz, 1H), 5.01 (d, J = 7.6 Hz, 1H), 4.24 (dd, J = 11. 2, 2.4 Hz, 1H), 4.01 (d, J = 5.2 Hz, 1H), 3.83 (dd, J = 11.2, 6.4 Hz, 1H), 3.74−3.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 156.2, 149.8, 145.6, 141.1, 128.9 (2C), 128.6 (2C), 127.9 (2C), 127.7, 124.3 (2C), 122.2 (d, J = 7.4 Hz), 118.0 (d, J = 8.1 Hz), 116.7 (d, J = 23.2 Hz), 115.9 (d, J = 23.4 Hz), 65.8, 53.5, 48.1. Anal. (CHN %) Calcd for $C_{21}H_{17}FN_2O_5S$: C, 58.87; H, 4.00; N, 6.54. Found: C, 59.04; H, 3.65; N, 6.21; LRMS (EI): Calcd 427.0842 m/z $(M - H)^-$, found 427.0764 m/z. HPLC: $Cu(OTf)_2$-catalyzed reaction, t_r (minor) 13.08 min, t_r (major) 15.81 min, 80% ee; $[\alpha]^{28}_D$ = −12.6 (c 0.10, $CHCl_3$); $Cu(ClO_4)_2\cdot 6H_2O$-catalyzed reaction, 74% ee.

■ ASSOCIATED CONTENT

Supporting Information. CIF and ORTEP diagram of compound (±)-**3b**, ^{1}H and ^{13}C NMR spectra of compounds (±)-**2a**, (±)-**2c**, and **3a**−**k** and mass spectra and HPLC chromatogram of **3a**−**k**. This material is available free of charge via the Internet at http://pubs.acs.org.

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