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Quinidine derived organocatalysts for the nucleophile promoted asymmetric [4+2] cycloaddition reaction of salicyl *N*-tosylimine with allenic esters

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ABSTRACT

Cinchona alkaloid derived catalyst **cat. 5** prepared from β-isocupreidine (β-ICD) was found to be a fairly effective organocatalyst for the nucleophilic promoted asymmetric [4+2] cycloaddition reaction of salicyl *N*-tosylimines and allenic esters to give the corresponding adducts in up to 80% yield, 87% ee.

1. Introduction

2*H*-1-Chromenes or chromans are an important class of oxygenated heterocycles, which have attracted much synthetic interest because of the biological activity of naturally occurring representatives.[1,2] The synthesis of 2*H*-1-chromenes or chromans via the cyclization of suitably elaborated phenyl ethers commonly suffers from a lack of regioselective control at the key cyclization step. Recently, the reactions of salicyl aldehydes or salicylaldimines with various conjugated olefins,[3] allenic ketones, or esters[4–6] to give differently substituted chromenes or chromans have been reported. As a consequence, the exploitation of an efficient and novel catalytic asymmetric method for the synthesis of these compounds is highly desirable. In recent years, asymmetric methods that allow rapid access to this molecular architecture have attracted much attention because this asymmetric synthetic protocol is valuable in organic synthesis and chemical biology/medicinal chemistry. Herein, we report the synthesis of a series of quinidine derived organocatalysts and their applications in the reactions of salicyl *N*-tosylimine with various allenic esters, to give substituted chromans in good yields (up to 85% yield) and good ee values (up to 87% ee) under mild reaction conditions.

2. Results and discussion

Cinchona alkaloids derived catalysts β-isocupreidine (β-ICD) and **cat. 1**–**cat. 3** are known compounds and were synthesized according to the previous literature (Fig. 1).[7] Chiral catalysts **cat. 4**–**cat. 13** were synthesized from β-ICD according to our previous work (Fig. 1).[8] **Cat. 5** could also be transformed to **cat. 14** in 51% yield through thiocarbonylation using Lawesson's reagent[9] (Scheme 1). Both **cat. 15** and **cat. 16** could be synthesized from compound **7** via a Buchwald–Hartwig cross-coupling reaction in 50% yield and 25% yield, respectively (Scheme 2).

Initially, we used salicyl *N*-tosylimine **1a** (1.0 equiv) and allenic esters **2a** (1.2 equiv) as the substrates and multifunctional cinchona alkaloid β-isocupreidine (β-ICD) (Fig. 1) (10 mol %) as the catalyst in tetrahydrofuran (THF) to examine the reaction outcome; the results are shown in Table 1, entry 1. It was found that the corresponding substituted product **3aa** was obtained in 80% yield along with 10% ee at room temperature (25 °C) (Table 1, entry 1). We next turned our attention to screen other multifunctional cinchona alkaloid derived organocatalysts **cat. 1**–**cat. 3** (Fig. 1) in this reaction and found that the desired product **3aa** was formed in 50–60% yields along with 5–20% ee values (Table 1, entries 2–4).

Since these cinchona alkaloids derived catalysts are not particularly effective in this particular asymmetric substituted reaction, we attempted to use other multifunctional cinchona alkaloid derived organocatalysts (Fig. 1) in this reaction (Schemes 1 and 2). Therefore, using these new cinchona alkaloids derived organocatalysts, we investigated the reaction of **1a** with **2a** in the presence of **cat. 4**–**cat. 16** in THF at 25 °C and found that the substituent of the R′ group had a significant affect on the outcome of the reaction. We found that our organocatalysts **cat. 4**–**cat. 7** (10 mol %), in which R′ is an aliphatic group, could produce the corresponding product **3aa** in moderate to good yields along with 50–64% ee values (Table 1, entries 5–8). For example, **3aa** was formed in 85% yield and 64% ee in the presence of organocatalyst **cat. 5** (R′ = CH_3 and R″ = H) (Table 1, entry 6). The substituent on the aromatic R′ group can also have a significant affect on the reaction outcome. Introducing either no groups or strongly electron-donating methoxy groups at the 2-position or 3- and 5-position of the benzene ring (organocatalysts **cat. 8**–**cat. 10)** afforded the corresponding product **3aa** in low ee values (Table 1, entries 9–11). Using organocatalyst **cat.**

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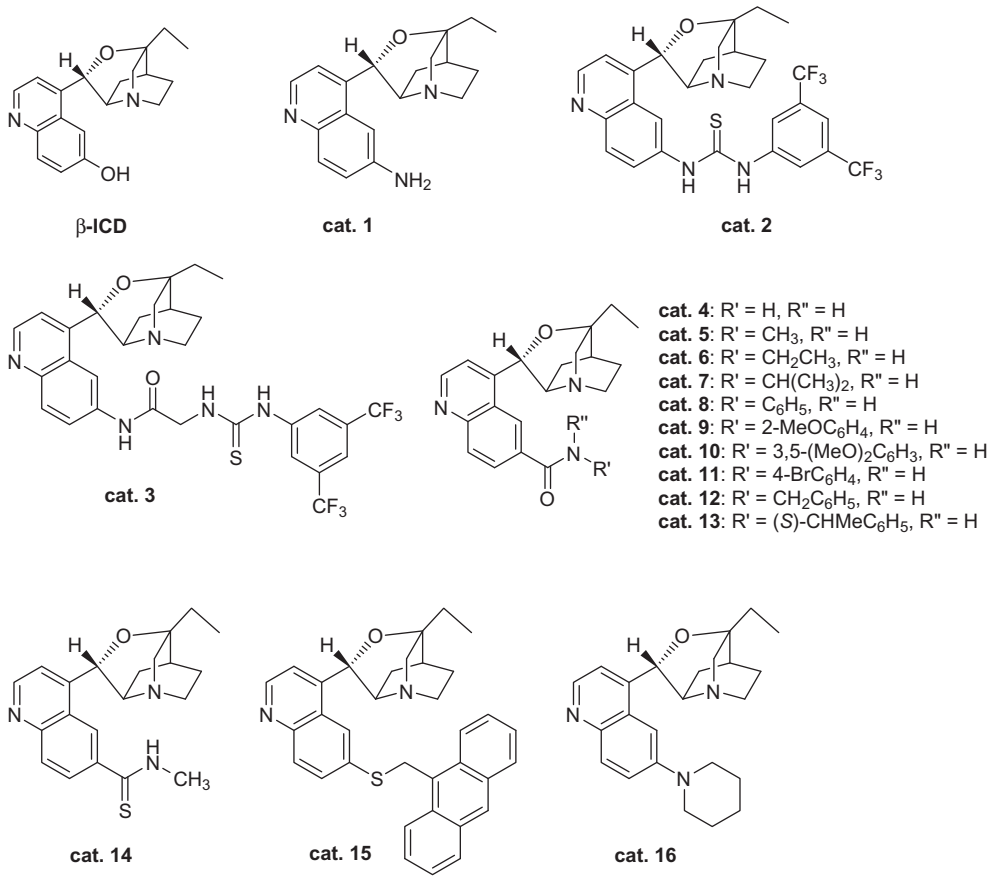
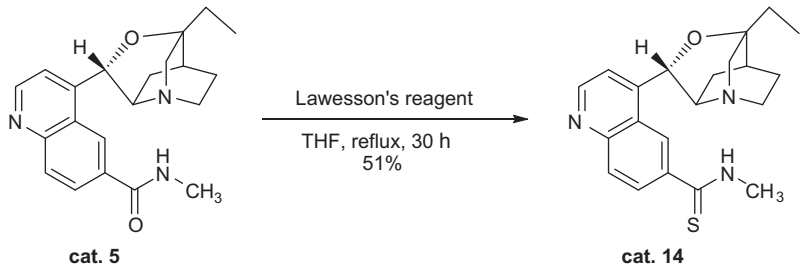


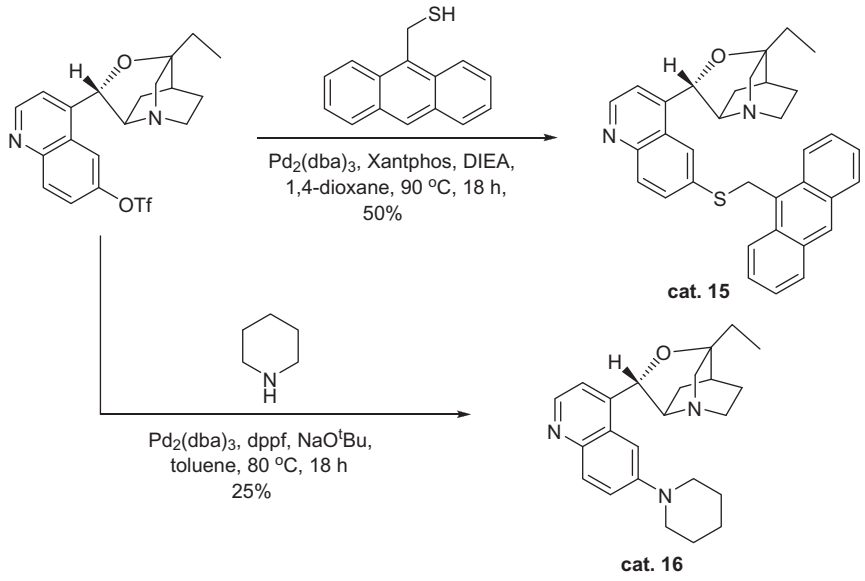
Figure 1. Multifunctional cinchona alkaloid derivatives.



Scheme 1. The synthetic route for the preparation of **cat. 14**.

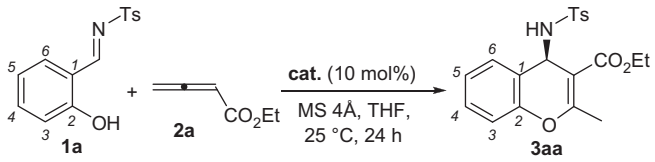
11, in which the aromatic R′ group has a bromine atom at the 4-position in this reaction furnished **3aa** in 72% yield and 54% ee (Table 1, entry 12). Organocatalysts **cat. 12** and **cat. 13**, in which R′ is a benzyl group or a substituted benzyl group and R" is a hydrogen atom, were also effective catalysts in this reaction, affording **3aa** in 88% yield with 60% ee and 73% yield with 51% ee, respectively (Table 1, entries 13 and 14). Furthermore, using organocatalyst **cat. 14** with a thiocarbonyl group as the catalyst produced the corresponding product **3aa** in 85% yield along with 54% ee (Table 1, entry 15). Organocatalysts **cat. 15** and **cat. 16**, in which the quinoline ring has a piperidyl substituent or an anthracenyl substituent, both catalyzed this reaction smoothly, affording **3aa** in 54% yield with 35% ee and 60% yield with 34% ee, respectively (Table 1, entries 16 and 17). Therefore, the optimal organocatalyst was identified as **cat. 5** (10 mol %) in this asymmetric [4+2] cycloaddition reaction to give the corresponding product in good yield along with a good ee value (64% ee).

Having identified the best organocatalyst for this reaction, we next carried out the reaction of **1a** with **2a** catalyzed by **cat. 5** in various solvents to examine the solvent effects in this reaction and the results are summarized in Table 1. It was found that Et_2O was the solvent of choice in comparison with those reactions carried out in other organic solvents, such as dichloromethane (DCM), CH_3CN, 1,4-dioxane, tetrahydrofuran (THF), toluene, and EtOAc (Table 2, entries 1–7). The reactant **1a** decomposed during the reaction without the formation of **3aa** in CH_3OH (Table 2, entry 8). In other ether solvents, such as methyl *tert*-butyl ether and isopropyl ether, compound **3aa** was formed in 75% yield along with 45% ee and 27% yield along with 57% ee, respectively (Table 2, entries 9 and 10). When lowering the reaction temperature to 0 °C ~ −20 °C, the reactions became sluggish and no improvement could be observed in Et_2O (Table 2, entries 11 and 12). Moreover, we also attempted to add some additives such as diisopropylethylamine (DIEA), *p*-toluenesulfonic acid (TsOH) and benzoic acid in



Scheme 2. The synthetic route for the preparation of **cat. 15** and **cat. 16**.

Table 1
Reaction of ethyl 2,3-butadienoate **2a** with salicyl *N*-tosylimine **1a** in the presence of cinchona alkaloids derived catalysts[a]



Entry	Cat	Yield[b] (%)	ee[c] (%)
1	β-ICD	80	10
2	**cat. 1**	62	20
3	**cat. 2**	51	5
4	**cat. 3**	50	10
5	**cat. 4**	90	51
6	**cat. 5**	85	64
7	**cat. 6**	70	57
8	**cat. 7**	75	50
9	**cat. 8**	85	9
10	**cat. 9**	68	10
11	**cat. 10**	85	6
12	**cat. 11**	72	54
13	**cat. 12**	88	60
14	**cat. 13**	73	51
15	**cat. 14**	85	54
16	**cat. 15**	54	35
17	**cat. 16**	60	34

[a] All reactions were carried out using **1a** (0.10 mmol) and **2a** (0.12 mmol) in THF (2.00 mL) for 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.

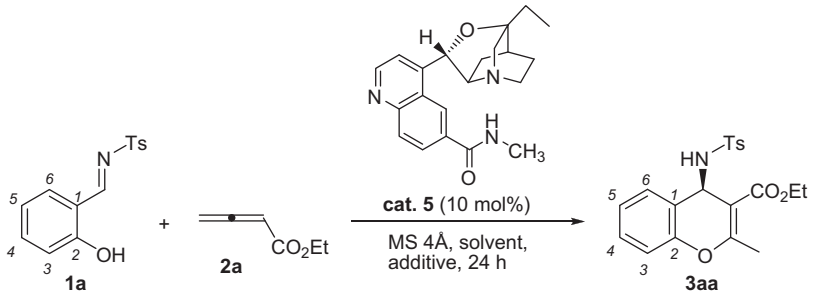
order to improve the enantiomeric excess of **3aa** in Et_2O at 25 °C. However, no improvements were observed under the standard conditions (Table 2, entries 13–15). Overall, this asymmetric [4+2] cycloaddition reaction should be carried out at 25 °C in Et_2O using organocatalyst **cat. 5** (10 mol %) as the catalyst.

The generality of this asymmetric [4+2] cycloaddition reaction was examined using a variety of salicyl *N*-tosylimines **1** and allenic esters **2** at 25 °C under the optimal conditions, and the results of these experiments are summarized in Table 3. As can be seen from Table 3, when salicyl *N*-tosylimines **1** bearing electron-withdrawing groups at the benzene ring were employed as the substrates, the reactions proceeded smoothly to give the desired products **3** in 56–85% yields along with 10–39% ee values (Table 3, entries 1–4). As for salicyl *N*-tosylimine **1f** and **1g**, which had electron-donating groups on the benzene ring, the corresponding products were formed in 82% yield along with 74% ee and 80% yield along with 69% ee, respectively, perhaps due to electronic properties (Table 3, entries 5 and 6). Other sulfonyl groups such as 4-nitrobenzenesulfonyl (Ns), 4-bromobenzenesulfonyl (Bs) and 2,4,6-triisopropylbenzenesulfonyl were also suitable substituents in this reaction to give the corresponding products **3ha**, **3ia**, and **3ja** in 50–69% yields along with 43–61% ee values (Table 3, entries 7–9). Changing the ester moiety of the allenic esters from OEt to OMe, O^{t}Bu, or O^{i}Pr could improve the reaction outcomes, affording the desired products **3ab**, **3ac,** and **3ad** in 75–85% yield along with 64–70% ee values (Table 3, entries 10–12). Applying isopropyl 2,3-butadienoate **2d** to this asymmetric [4+2] cycloaddition reaction, as for the salicyl *N*-tosylimines with electron-withdrawing groups on the benzene ring, gave the corresponding products in 21–80% yields along with 21–76% ee values (Table 3, entries 13–16). As for other salicyl *N*-tosylimines **1f**, **1g**, **1k,** and **1l**, which had electron-donating groups on the benzene ring, the reactions proceeded smoothly to give the desired products **3fd**, **3gd**, **3kd,** and **3ld** in 65–80% yields along with 64–87% ee values (Table 3, entries 17–20). Using other sulfonyl groups such as 4-nitrobenzenesulfonyl (Ns), 4-bromobenzenesulfonyl (Bs) and 2,4,6-triisopropylbenzenesulfonyl as the substrates afforded the desired products in 69–72% yield along with 55–65% ee values (Table 3, entries 21–23).

The absolute configurations of products **3** were unequivocally assigned as (*R*) by X-ray diffraction of **3cd** which bears a bromine atom on the benzene ring. Its ORTEP drawing is shown in Figure 2.[10]

Based on previous mechanistic studies by our group,[6a] a transition-state model was proposed and is shown in Figure 3. In the transition state, the substrate is bound *anti* to the quinoline ring of the organocatalyst **cat. 5** to minimize the steric interactions and so the allenic ester may attack the *Si*-face of the imine, consequently providing the corresponding asymmetric [4+2] cycloaddition products predominantly in the (*R*)-configuration.

Table 2
Optimization of the reaction conditions[a]



Entry	Temp (°C)	Solvent	Additive	Yield[b] (%)	ee[c] (%)
1	25	THF	—	85	64
2	25	DCM	—	75	55
3	25	CH_3CN	—	80	42
4	25	1.4-Dioxane	—	75	50
5	25	Et_2O	—	90	64
6	25	Toluene	—	75	50
7	25	EtOAc	—	85	60
8	25	CH_3OH	—	Trace	—
9	25	^{t}BuOMe	—	75	45
10[d]	25	^{i}PrO^{i}Pr	—	27	57
11[d]	0	Et_2O	—	90	64
12[d]	−20	Et_2O	—	86	64
13	25	Et_2O	DIEA	90	64
14	25	Et_2O	TsOH	Complex	—
15	25	Et_2O	PhCOOH	65	64

[a] All reactions were carried out using **1a** (0.10 mmol) and **2a** (0.12 mmol) in solvent (2.00 mL) for 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.
[d] Reaction was carried out for 36 h.

3. Conclusion

In conclusion, we have reported the first example of asymmetric [4+2] cycloaddition reaction of salicyl *N*-tosylimines and allenic esters in the presence of cinchona alkaloid derived catalyst **cat. 5** in Et_2O under mild conditions, affording the corresponding adducts in good yields along with moderate to good enantioselectivities. The multiplied functionalized 2*H*-1-chromenes or chromans obtained are useful building blocks in a variety of organic synthetic sequences. Efforts are currently in progress to use these novel multifunctional quinidine derived organocatalysts for other asymmetric catalysis.

4. Experimental

4.1. General remarks

Melting points were determined on a digital melting point apparatus and are uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. ^1H NMR spectra were recorded on a Bruker AM-300 and AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AM-300 and AM-400 spectrophotometers with complete proton decoupling spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H and IC-H columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd)). Mass spectra were recorded by EI, ESI, MALDI and HRMS was measured on a HP-5989 instrument. Organic solvents used were dried by standard methods when necessary.

4.2. General procedure for the synthesis of cat. 4–cat. 13

Cinchona alkaloid derived catalysts **cat. 4–cat. 13** are known compounds and were synthesized according to the literature.[8]

4.2.1. 6′-Formamide-β-ICD cat. 4

^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.04 (t, J = 7.6 Hz, 3H), 1.28 (dd, J = 12.4, 6.4 Hz, 1H), 1.53–1.58 (m, 1H), 1.64–1.78 (m, 4H), 2.18 (br s, 1H), 2.68 (d, J = 13.2 Hz, 1H), 2.97–2.99 (m, 2H), 3.47 (d, J = 6.4 Hz, 1H), 3.58 (d, J = 13.2 Hz, 1H), 6.04 (s, 1H), 6.15 (br s, 1H), 7.78 (d, J = 4.4 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 8.23 (br s, 1H), 8.37 (d, J = 8.8 Hz, 1H), 8.52 (s, 1H), 8.97 (d, J = 4.4 Hz, 1H).

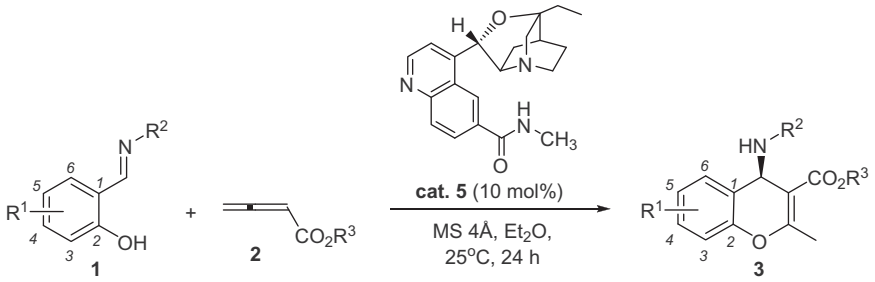
4.2.2. 6′-*N*-Methylformamide-β-ICD cat. 5

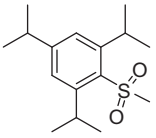
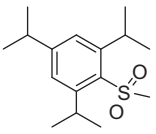
^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.02 (t, J = 7.5 Hz, 3H), 1.26 (m, 1H), 1.54–1.73 (m, 5H), 2.16 (br s, 1H), 2.67 (d, J = 13.5 Hz, 1H), 2.95–2.97 (m, 2H), 3.02 (d, J = 4.8 Hz, 3H), 3.45–3.54 (m, 2H), 6.01 (s, 1H), 7.65 (br s, 1H), 7.78 (d, J = 4.5 Hz, 1H), 8.13 (d, J = 9.3 Hz, 1H), 8.22–8.25 (m, 1H), 8.34 (s, 1H), 8.96 (d, J = 4.5 Hz, 1H).

4.2.3. 6′-*N*-Ethylformamide-β-ICD cat. 6

^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11 (t, J = 7.6 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.63 (dd, J = 13.6, 6.8 Hz, 1H), 1.83–1.88 (m, 2H), 2.01–2.07 (m, 2H), 2.09 (dd, J = 10.2, 6.8 Hz, 1H), 2.56 (br s, 1H), 3.25 (d, J = 13.2 Hz, 1H), 3.50–3.62 (m, 4H), 4.30–4.33 (m, 2H), 6.39 (s, 1H), 7.80 (d, J = 4.4 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 8.49 (d, J = 8.8 Hz, 1H), 8.65 (t, J = 5.2 Hz, 1H), 8.69 (s, 1H), 9.00 (d, J = 4.4 Hz, 1H).

Table 3
Substrate scope of the reactions of organocatalyst **cat. 5** catalyzed asymmetric [4+2] cycloaddition reaction of **1** with **2**[a]



Entry	No.	R^1	R^2	R^3	Yield[b] (%)	ee[c] (%)
1	**1b**	5-Cl	Ts	Et (**2a**)	**3ba**, 82	37
2	**1c**	5-Br	Ts	Et (**2a**)	**3ca**, 65	39
3	**1d**	3,5-Cl_2	Ts	Et (**2a**)	**3da**, 85	20
4	**1e**	3,5-Br_2	Ts	Et (**2a**)	**3ea**, 56	10
5	**1f**	3-OMe	Ts	Et (**2a**)	**3fa**, 82	74
6	**1g**	5-OMe	Ts	Et (**2a**)	**3ga**, 80	69
7	**1h**	H	Ns	Et (**2a**)	**3ha**, 65	43
8	**1i**	H	Bs	Et (**2a**)	**3ia**, 69	61
9	**1j**	H		Et (**2a**)	**3ja**, 50	50
10	**1a**	H	Ts	Me (**2b**)	**3ab**, 85	64
11	**1a**	H	Ts	^{t}Bu (**2c**)	**3ac**, 75	65
12	**1a**	H	Ts	^{i}Pr (**2d**)	**3ad**, 80	70
13	**1b**	5-Cl	Ts	^{i}Pr (**2d**)	**3bd**, 80	67
14	**1c**	5-Br	Ts	^{i}Pr (**2d**)	**3cd**, 72	76
15	**1d**	3.5-Cl_2	Ts	^{i}Pr (**2d**)	**3dd**, 27	38
16	**1e**	3.5-Br_2	Ts	^{i}Pr (**2d**)	**3ed**, 21	21
17	**1f**	3-OMe	Ts	^{i}Pr (**2d**)	**3fd**, 79	76
18	**1g**	5-OMe	Ts	^{i}Pr (**2d**)	**3gd**, 75	64
19	**1k**	3-Me	Ts	^{i}Pr (**2d**)	**3kd**, 80	87
20	**1l**	3,5-^{t}Bu$_2$	Ts	^{i}Pr (**2d**)	**3ld**, 65	72
21	**1h**	H	Ns	^{i}Pr (**2d**)	**3hd**, 69	65
22	**1i**	H	Bs	^{i}Pr (**2d**)	**3id**, 72	64
23	**1j**	H		^{i}Pr (**2d**)	**3jd**, 70	55

[a] All reactions were carried out using **1** (0.10 mmol) and **2** (0.12 mmol) in Et_2O (2.00 mL) for 24 h.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.

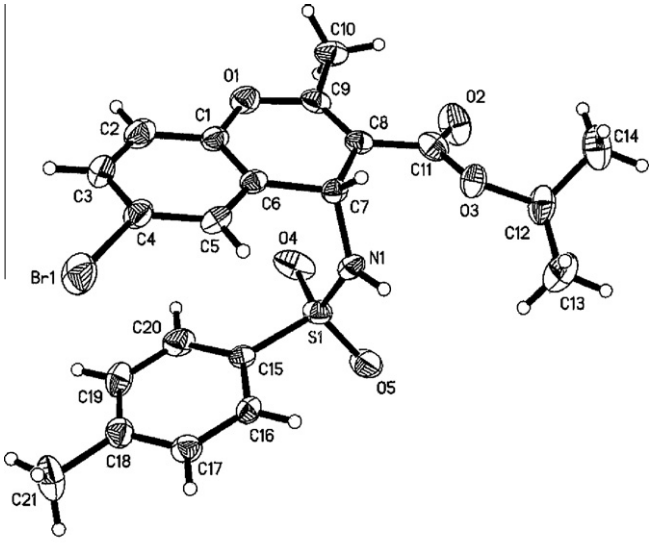


Figure 2. ORTEP drawing of **3cd**.

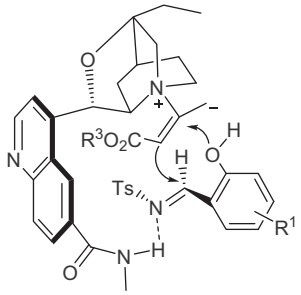


Figure 3. A plausible transition-state model.

4.2.4. 6′-*N*-Isopropylformamide-β-ICD cat. 7

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.03 (t, J = 7.6 Hz, 3H), 1.30–1.32 (m, 7H), 1.58–1.83 (m, 5H), 2.20 (br s, 1H), 2.70 (d, J = 13.6 Hz, 1H), 3.03–3.04 (m, 2H), 3.54–3.55 (m, 1H), 3.62–3.65 (m, 1H), 4.39–4.43 (m, 1H), 6.10 (s, 1H), 7.77 (d, J = 4.4 Hz, 2H), 8.15 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 8.8 Hz, 1H), 8.54 (s, 1H), 8.96 (d, J = 4.4 Hz, 1H).

4.2.5. 6′-*N*-Phenylformamide-β-ICD cat. 8

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.05 (t, J = 7.2 Hz, 3H), 1.40–1.48 (m, 1H), 1.68–1.78 (m, 4H), 1.91–1.97 (m, 1H), 2.35 (br s, 1H), 2.99 (d, J = 12.9 Hz, 1H), 3.31–3.34 (m, 2H), 4.05–4.07 (m, 2H), 6.33 (s, 1H), 7.05 (t, J = 6.6 Hz, 1H), 7.23–7.27 (m, 2H), 7.77–7.83 (m, 3H), 8.21 (d, J = 9.0 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.97–9.01 (m, 2H), 10.15 (s, 1H).

4.2.6. 6′-*N*-(2-Methoxyphenyl)formamide-β-ICD cat. 9

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.03 (t, J = 7.6 Hz, 3H), 1.21–1.25 (m, 1H), 1.45–1.60 (m, 1H), 1.63–1.75 (m, 4H), 2.09 (br s, 1H), 2.62 (d, J = 13.6 Hz, 1H), 2.95–2.98 (m, 2H), 3.49–3.56 (m, 2H), 3.88 (s, 3H), 6.04 (s, 1H), 6.85–6.94 (m, 1H), 6.98–7.02 (m, 1H), 7.06–7.10 (m, 1H), 7.82 (d, J = 4.0 Hz, 1H), 8.15–8.23 (m, 2H), 8.45 (d, J = 7.6 Hz, 1H), 8.56 (s, 1H), 8.82 (s, 1H), 9.00 (d, J = 4.8 Hz, 1H).

4.2.7. 6′-*N*-(3,5-Dimethoxyphenyl)formamide-β-ICD cat. 10

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.00 (t, J = 7.6 Hz, 3H), 1.20–1.31 (m, 1H), 1.50–1.51 (m, 1H), 1.61–1.75 (m, 4H), 2.13 (br s, 1H), 2.56 (d, J = 13.6 Hz, 1H), 2.87–2.89 (m, 2H), 3.41–3.46 (m, 2H), 3.63 (s, 6H), 5.95 (s, 1H), 6.09 (t, J = 2.0 Hz, 1H), 7.08 (d, J = 2.0 Hz, 2H), 7.76 (d, J = 4.4 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.41 (dd, J = 2.0 Hz, 8.8 Hz, 1H), 8.61 (s, 1H), 8.95 (d, J = 4.4 Hz, 1H), 9.78 (s, 1H).

4.2.8. 6′-*N*-(4-Bromophenyl)formamide-β-ICD cat. 11

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.06 (t, J = 7.2 Hz, 3H), 1.25–1.29 (m, 1H), 1.54–1.58 (m, 1H), 1.67–1.73 (m, 4H), 2.17 (br s, 1H), 2.67 (d, J = 13.6 Hz, 1H), 2.96–2.99 (m, 2H), 3.39 (d, J = 6.0 Hz, 1H), 3.58 (d, J = 13.6 Hz, 1H), 5.95 (s, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 4.4 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.44 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 8.58 (s 1H), 8.91 (d, J = 4.4 Hz, 1H), 10.09 (s, 1H).

4.2.9. 6′-*N*-Benzylformamide-β-ICD cat. 12

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.00 (t, J = 7.2 Hz, 3H), 1.19–1.26 (m, 1H), 1.49–1.52 (m, 1H), 1.59–1.74 (m, 4H), 2.14 (br s, 1H), 2.59 (d, J = 13.6 Hz, 1H), 2.89–2.92 (m, 2H), 3.39 (d, J = 6.4 Hz, 2H), 3.53 (d, J = 13.6 Hz, 2H), 4.60 (dd, J = 5.6, 14.8 Hz, 1H), 4.70 (dd, J = 5.6, 14.8 Hz, 1H), 5.98 (s, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.25 (t, J = 7.2 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 4.4 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 8.44 (d, J = 8.8 Hz, 1H), 8.52 (s, 1H), 8.92 (d, J = 4.4 Hz, 1H), 9.05 (t, J = 5.6 Hz, 1H).

4.2.10. 6′-(*S*)-*N*-(1-Phenylethyl)formamide-β-ICD cat. 13

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.00 (t, J = 7.2 Hz, 3H), 1.23–1.28 (m, 1H), 1.53–1.57 (m, 1H), 1.62–1.68 (m, 6H), 1.73–1.76 (m, 1H), 2.16 (br s, 1H), 2.62 (d, J = 13.6 Hz, 1H), 2.96–3.00 (m, 2H), 3.48 (d, J = 6.0 Hz, 1H), 3.57 (d, J = 13.6 Hz, 1H), 5.45–5.52 (m, 1H), 6.04 (s, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.28–7.34 (m, 4H), 7.49 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 4.4 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.61 (s, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.93 (d, J = 4.4 Hz, 1H).

4.3. General procedure for the synthesis of cat. 14

A mixture of **cat. 5** (70.2 mg, 0.2 mmol), Lawesson's reagent (90.0 mg, 1.2 equiv), and THF (3.0 mL) was refluxed at 70 °C for 30 h under an argon atmosphere. The mixture was washed with H_2O and then extracted with Et_2O. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (elution with DCM/MeOH = 20:1) to give **cat. 14** as a yellow solid (38.2 mg, 51% yield).

4.3.1. 6′-*N*-Methylethanethioamide-β-ICD cat. 14

A yellow solid (38.2 mg, 51% yield); $[\alpha]_D^{20} = -75.1$ (c 0.55, $CHCl_3$); mp 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.04 (t, J = 7.2 Hz, 3H), 1.21–1.25 (m, 1H), 1.52–1.56 (m, 1H), 1.65–1.70 (m, 4H), 2.15 (br s, 1H), 2.64 (d, J = 13.6 Hz, 1H), 2.95–2.97 (m, 2H), 3.37 (d, J = 4.4 Hz, 3H), 3.48–3.56 (m, 2H), 5.89 (s, 1H), 7.69 (d, J = 4.0 Hz, 1H), 8.07 (d, J = 8.8 Hz, 1H), 8.15 (br s, 1H), 8.69 (d, J = 8.8 Hz, 1H), 8.87 (d, J = 4.0 Hz, 1H), 9.80 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.3, 23.2, 23.5, 27.3, 32.8, 34.2, 46.1, 54.1, 56.9, 72.4, 77.3, 116.8, 119.6, 124.0, 130.2, 131.3, 136.9, 145.2, 148.8, 151.4, 157.1, 196.1; IR (neat) ν 3218, 2959, 1590, 1555, 1502, 1459, 1356, 1130, 1099, 1064, 1007, 854, 796 cm^{-1}; MS (ESI) m/e 368 (M+H); HRMS (ESI) for $C_{21}H_{26}N_3OS$ (M+H): 368.1791; found: 368.1789.

4.4. General procedure for the synthesis of cat. 15

A flame-dried flask provided with a water-cooled reflux condenser was charged with Pd_2dba_3 (18.8 mg, 0.02 mmol, 0.04 equiv), xantphos (5.0 mg, 0.03 mmol, 0.06 equiv), and 1,4-dioxane (1.0 mL). The condenser was capped with a rubber septum, evacuated, and backfilled with argon. This evacuation/backfilled sequence was repeated once more. Diisopropylethylamine (DIEA) (79.5 mg, 1.4 equiv), anthracen-9-ylmethanethiol (148 mg, 0.66 mmol, 1.5 equiv) and triflate **7** (200 mg, 0.44 mmol, 1.0 equiv) in solution in 1,4-dioxane (1.5 mL) were then added. The evacuation/backfilled sequence was performed twice. The mixture was then stirred at 100 °C for 16 h until the starting triflate had been completely consumed, as judged by TLC. The reaction was then cooled to room temperature, diluted with ethyl acetate, filtered on Celite, and concentrated in vacuo. The crude material was purified by flash chromatography (eluent: DCM/MeOH = 30:1) to give **cat. 15** as a yellow solid (116.0 mg, 50%).

4.4.1. 6′-Anthracen-9-ylmethanethiol-β-ICD cat. 15

A yellow solid (116.0 mg, 50%); $[\alpha]_D^{20} = +57.0$ (c 0.30, $CHCl_3$); mp 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 0.99 (t, J = 7.6 Hz, 3H), 1.16–1.20 (m, 1H), 1.41–1.46 (m, 1H), 1.53–1.70 (m, 4H), 2.06 (br s, 1H), 2.52 (d, J = 13.2 Hz, 1H), 2.84–2.89 (m, 2H), 3.26 (d, J = 5.6 Hz, 1H), 3.39 (d, J = 13.2 Hz, 1H), 5.21 (s, 2H), 5.81 (s, 1H), 7.38–7.46 (m, 4H), 7.70–7.74 (m, 2H), 7.92–7.96 (m, 3H), 8.04 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.8 Hz, 2H), 8.35 (s, 1H), 8.86 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.3, 23.5, 24.1, 27.3, 31.9, 32.8, 46.4, 54.5, 56.3, 72.8, 77.1, 119.6, 122.4, 123.9, 125.0, 125.9, 126.1, 127.2, 127.7, 129.0, 130.0, 130.6, 130.9, 131.3, 136.5, 143.9, 146.6, 149.8; IR (neat) ν 2963, 2922, 1747, 1730, 1586, 1492, 1448, 1350, 1103, 1064, 1017, 800, 726 cm^{-1}; MS (ESI) m/e 517 (M+H); HRMS (ESI) for $C_{34}H_{33}N_2OS$ (M+H): 517.2308; found: 517.2309.

4.5. General procedure for the synthesis of cat. 16

A flame-dried flask provided with a water-cooled reflux condenser was charged with Pd_2dba_3 (18.8 mg, 0.02 mmol, 0.04 equiv), 1,1′-bis(diphenylphosphino)ferrocene (dppf) (16.6 mg, 0.03 mmol, 0.06 equiv), and toluene (1.0 mL). The condenser was capped with a rubber septum, evacuated, and backfilled with argon. This evacuation/backfilled sequence was repeated once more. Next, NaO^{t}Bu (63.4 mg, 0.66 mmol, 1.5 equiv), piperidine (57.6 mg, 0.66 mmol, 1.5 equiv), and triflate **7** (200 mg, 0.44 mmol, 1.0 equiv) in a solution in toluene (1.5 mL) were added. The evacuation/backfilled sequence was performed twice. The mixture was then stirred at 80 °C for 16 h until the starting triflate had been completely consumed, as judged by TLC. The reaction was then cooled to room temperature, diluted with ethyl acetate, filtered on Celite, and concentrated in vacuo. The crude material was purified by a flash

chromatography (eluent: DCM:MeOH = 25:1) to give **cat. 16** as a yellow solid (41.5 mg, 25%).

4.5.1. 6′-Piperidine-β-ICD cat. 16

A yellow solid (41.5 mg, 25%); $[\alpha]_D^{20} = +27.0$ (*c* 0.50, $CHCl_3$); mp 138–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.42–1.47 (m, 1H), 1.61–1.67 (m, 2H), 1.74–1.81 (m, 8H), 1.99–2.04 (m, 1H), 2.38 (br s, 1H), 2.96 (d, *J* = 13.2 Hz, 1H), 3.27–3.30 (m, 1H), 3.39–3.47 (m, 5H), 4.00–4.04 (m, 2H), 6.09 (s, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 7.50 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H), 7.97 (d, *J* = 9.6 Hz, 1H), 8.69 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.3, 23.1, 23.7, 24.2, 25.8, 27.4, 29.7, 32.9, 46.4, 50.5, 54.4, 56.3, 72.6, 77.2, 103.5, 119.3, 122.5, 126.6, 130.8, 141.5, 143.2, 146.7, 150.4; IR (neat) *v* 2963, 2928, 1617, 1509, 1454, 1346, 1256, 1097, 1017, 800, 691 cm^{-1}; MS (ESI) *m*/*e* 378 (M+H); HRMS (ESI) for $C_{24}H_{32}N_3O$ (M+H): 378.2540; found: 378.2543.

4.6. Characterization data for the new salicyl *N*-tosylimines

4.6.1. *N*-(2-Hydroxybenzylidene)-4-nitrobenzenesulfonamide 1h

A yellow solid; mp 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.01–7.07 (m, 2H), 7.54–7.58 (m, 2H), 8.19 (d, *J* = 9.6 Hz, 2H), 8.41 (d, *J* = 9.6 Hz, 2H), 9.12 (s, 1H), 10.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.4, 118.2, 120.7, 124.6, 129.2, 135.9, 138.4, 143.9, 162.5, 173.4; IR (neat) *v* 1737, 1607, 1583, 1511, 1493, 1387, 1347, 1297, 1276, 1252, 1180, 1098, 886, 830, 756 cm^{-1}; MS (ESI) *m*/*e* 307 (M+H); HRMS (ESI) for $C_{13}H_{10}N_2NaO_5S$ (M+Na): 329.0203; found: 329.0193.

4.6.2. 4-Bromo-*N*-(2-hydroxybenzylidene)benzenesulfonamide 1i

A white solid; mp 147–149 °C ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.99–7.04 (m, 2H), 7.50–7.56 (m, 2H), 7.69–7.71 (m, 2H), 7.83–7.85 (m, 2H), 9.11 (s, 1H), 10.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.4, 118.0, 120.4, 129.2, 129.3, 132.7, 135.6, 137.1, 137.8, 162.2, 172.2; IR (neat) *v* 1741, 1624, 1593, 1509, 1389, 1327, 1258, 1159, 1088, 817, 763, 645 cm^{-1}; MS (ESI) *m*/*e* 340 (M+H); HRMS (ESI) for $C_{13}H_{11}BrNO_3S$ (M+H): 339.9638; found: 339.9648.

4.6.3. *N*-(2-Hydroxybenzylidene)-2,4,6-triisopropylbenzenesulfonamide 1j

A yellow solid; mp 143–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 12H), 2.92 (sept, *J* = 6.8 Hz, 1H), 4.28 (sept, *J* = 6.8 Hz, 2H), 7.01 (d, *J* = 6.8 Hz, 2H), 7.22 (s, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 9.11 (s, 1H), 10.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 24.6, 29.8, 34.2, 116.7, 117.7, 120.2, 124.0, 130.7, 135.2, 137.0, 151.1, 154.2, 161.8, 170.2; IR (neat) *v* 1743, 1619, 1591, 1559, 1488, 1457, 1427, 1389, 1357, 1317, 1275, 1039, 807, 672 cm^{-1}; MS (ESI) *m*/*e* 388 (M+H); HRMS (ESI) for $C_{22}H_{30}NO_3S$ (M+H): 388.1941; found: 388.1931.

4.7. General procedure for the reaction of salicyl *N*-tosylimine 1a with ethyl 2,3-butadienoate 2a in the presence of cat. 5

A solution of salicyl *N*-tosylimine **1a** (27.6 mg, 0.1 mmol), ethyl 2,3-butadienoate **2a** (13.6 μL, 0.12 mmol), MS 4 Å (50.0 mg) in Et_2O (2.0 mL) was stirred at 25 °C for 24 h in the presence of organocatalyst **cat. 5** (3.5 mg, 10 mol %) under an argon atmosphere. The reaction was monitored by TLC. When **1a** disappeared, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (eluent: EtOAc/petroleum ether = 1:4) to yield **3aa** (34.8 mg, 90%) as a colorless solid.

4.7.1. Ethyl 2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3aa

A white solid (34.8 mg, 90%); mp 138–140 °C; This is a known compound.[6a] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 2.39 (s, 3H), 3.86–3.90 (m, 1H), 4.06–4.11 (m, 1H), 5.30 (d, *J* = 6.4 Hz, 1H), 5.59 (d, *J* = 6.4 Hz, 1H), 7.00–7.04 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.22–7.26 (m, 1H), 7.33–7.35 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 2H); $[\alpha]_D^{20} = +6.9$ (*c* 1.20, $CHCl_3$) (64% ee); Chiralcel AD-H, hexane/^{i}PrOH = 75:25, 0.7 mL/min, 254 nm, t_{major} = 44.34 min, t_{minor} = 48.57 min.

4.7.2. Ethyl 6-chloro-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ba

A white solid (34.5 mg, 82%); mp 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 6H), 3.97–4.04 (m, 1H), 4.10–4.16 (m, 1H), 5.23 (d, *J* = 6.0 Hz, 1H), 5.47 (d, *J* = 6.0 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 7.15 (dd, *J* = 2.8 Hz, 8.8 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 19.7, 21.5, 47.7, 60.8, 102.9, 117.7, 120.9, 126.6, 129.2, 129.3, 129.4, 139.0, 143.1, 149.2, 163.1, 166.2; IR (neat) *v* 3308, 2962, 1733, 1682, 1521, 1348, 1324, 1277, 1259, 1225, 1154, 986, 764, 656 cm^{-1}; MS (ESI) *m*/*e* 444 (M+Na); HRMS (ESI) for $C_{20}H_{20}NNaClO_5S$ (M+Na): 444.0643; found: 444.0646. $[\alpha]_D^{20} = +17.8$ (*c* 0.40, $CHCl_3$) (37% ee); Chiralcel IC, hexane/^{i}PrOH = 70:30, 0.6 mL/min, 254 nm, t_{major} = 20.86 min, t_{minor} = 25.70 min.

4.7.3. Ethyl 6-bromo-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ca

A white solid (30.2 mg, 65%); mp 145–146 °C; This is a known compound.[6a] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.27 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 6H), 4.00–4.05 (m, 1H), 4.13–4.18 (m, 1H), 5.22 (d, *J* = 6.0 Hz, 1H), 5.46 (d, *J* = 6.0 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 7.18–7.20 (m, 3H), 7.29 (m, 1H), 7.49 (d, *J* = 8.5 Hz, 2H). $[\alpha]_D^{20} = +17.1$ (*c* 0.40, $CHCl_3$) (39% ee); Chiralcel OJ-H, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 13.73 min, t_{minor} = 18.23 min.

4.7.4. Ethyl 6,8-dichloro-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3da

A white solid (38.7 mg, 85%); mp 132–134 °C; This is a known compound.[6a] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 2.46 (s, 3H), 3.99–4.05 (m, 1H), 4.10–4.17 (m, 1H), 5.17 (s, 1H), 5.49 (s, 1H), 7.05–7.06 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.26–7.27 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 2H); $[\alpha]_D^{20} = +11.9$ (*c* 1.05, $CHCl_3$) (20% ee); Chiralcel IC, hexane/^{i}PrOH = 70:30, 0.5 mL/min, 254 nm, t_{major} = 19.59 min, t_{minor} = 24.86 min.

4.7.5. Ethyl 6,8-dibromo-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ea

A white solid (29.2 mg, 56%); mp 148–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (t, *J* = 6.8 Hz 6H), 2.41 (s, 3H), 2.45 (s, 3H), 3.99–4.06 (m, 1H), 4.10–4.17 (m, 1H), 5.31 (s, 1H), 5.48 (s, 1H), 7.19–7.22 (m, 3H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.6, 21.5, 47.7, 61.0, 103.7, 111.1, 116.7, 122.5, 126.7, 129.4, 131.4, 134.9, 138.7, 143.2, 146.9, 163.1, 165.7; IR (neat) *v* 3312, 2987, 1797, 1680, 1581, 1462, 1396, 1380, 1343, 1299, 1156, 1074, 758, 655 cm^{-1}; MS (ESI) *m*/*e* 565 (M+H); HRMS (ESI) for $C_{20}H_{19}NNaBr_2O_5S$ (M+H): 565.9243; found: 545.9228. $[\alpha]_D^{20} = +6.7$ (*c* 0.90, $CHCl_3$) (10% ee); Chiralcel IC, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 254 nm, t_{major} = 26.23 min, t_{minor} = 35.03 min.

4.7.6. Ethyl 8-methoxy-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3fa

A white solid (34.5 mg, 82%); mp 144–146 °C; This is a known compound.[6a] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.22 (t, J = 7.2 Hz, 3H), 2.35 (s, 3H), 2.40 (s, 3H), 3.85–3.93 (m, 4H), 4.05–4.13 (m, 1H), 5.04 (d, J = 6.8 Hz, 1H), 5.64 (d, J = 6.8 Hz, 1H), 6.81–6.83 (m, 1H), 6.97–7.00 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H); $[\alpha]_D^{20} = +17.2$ (c 0.40, $CHCl_3$) (74% ee); Chiralcel IC, hexane/^{i}PrOH = 70:30, 0.7 mL/min, 214 nm, t_{major} = 40.29 min, t_{minor} = 61.29 min.

4.7.7. Ethyl 6-methoxy-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ga

A white solid (34.5 mg, 82%); mp 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.22 (t, J = 7.2 Hz, 3H), 2.39 (s, 6H), 3.65 (s, 3H), 3.89–3.96 (m, 1H), 4.08–4.14 (m, 1H), 5.11 (d, J = 6.0 Hz, 1H), 5.56 (d, J = 6.0 Hz, 1H), 6.74–6.81 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H); $[\alpha]_D^{20} = +14.5$ (c 0.40, $CHCl_3$) (69% ee); Chiralcel AD-H, hexane/^{i}PrOH = 60:40, 0.7 mL/min, 214 nm, t_{major} = 26.13 min, t_{minor} = 30.63 min.

4.7.8. Ethyl 2-methyl-4-(4-nitrophenylsulfonamido)-4*H*-chromene-3-carboxylate 3ha

A white solid (27.2 mg, 65%); mp 148–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.26 (t, J = 7.2 Hz, 3H), 2.43 (s, 3H), 4.00–4.15 (m, 2H), 5.42 (d, J = 6.0 Hz, 1H), 5.62 (d, J = 6.0 Hz, 1H), 6.96 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.24–7.28 (m, 2H), 7.76 (d, J = 9.0 Hz, 2H), 8.19 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.0, 48.6, 60.9, 102.8, 116.5, 119.0, 123.7, 124.8, 129.5, 147.7, 149.5, 150.7, 163.8, 166.4; IR (neat) ν 3260, 2985, 2928, 1710, 1637, 1608, 1529, 1488, 1461, 1348, 1221, 1161, 1092, 989, 762, 746 cm^{-1}; MS (ESI) m/e 441 (M+Na); HRMS (ESI) for $C_{19}H_{18}N_2NaO_7S$ (M+Na): 441.0727; found: 441.0742. $[\alpha]_D^{20} = -9$ (c 0.20, $CHCl_3$) (43% ee); Chiralcel IC, hexane/^{i}PrOH = 70:30, 0.7 mL/min, 214 nm, t_{major} = 21.13 min, t_{minor} = 23.08 min.

4.7.9. Ethyl 4-(4-bromophenylsulfonamido)-2-methyl-4*H*-chromene-3-carboxylate 3ia

A white solid (31.1 mg, 69%); mp 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25 (t, J = 7.2 Hz, 3H), 2.40 (s, 3H), 2.39 (s, 3H), 3.93–4.01 (m, 1H), 4.08–4.16 (m, 1H), 5.28 (s, 1H), 5.58 (s, 1H), 6.99–7.05 (m, 2H), 7.23–7.30 (m, 3H), 7.47–7,53(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 19.9, 48.2, 60.7, 102.9, 116.3, 119.4, 124.8, 126.8, 128.3, 129.3, 129.6, 131.7, 141.2, 150.6, 163.4, 166.4; IR (neat) ν 2988, 2891, 1709, 1637, 1587, 1576, 1488, 1275, 1260, 1109, 750 cm^{-1}; MS (ESI) m/e 473 (M+Na); HRMS (ESI) for $C_{21}H_{26}N_3OS$ (M+Na): 473.9981; found: 473.9988. $[\alpha]_D^{20} = +2.8$ (c 0.40, $CHCl_3$) (61% ee); Chiralcel OJ-H, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 22.28 min, t_{minor} = 32.73 min.

4.7.10. Ethyl 2-methyl-4-(2,4,6-triisopropylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ja

A white solid (24.9 mg, 50%); mp 155–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.13 (d, J = 6.4 Hz, 6H), 1.18 (t, J = 7.2 Hz, 3H), 1.24 (d, J = 7.6 Hz, 12H), 2.45 (s, 3H), 2.88 (dsept, J = 7.2, 14.4 Hz, 1H), 3.74–3.82 (m, 1H), 4.01–4.11 (m, 3H), 4.70 (d, J = 7.6 Hz, 1H), 5.70 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 7.07 (s, 2H), 7.15–7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 19.6, 23.6, 23.7, 24.4, 24.7, 29.6, 34.1, 47.7, 60.4, 104.1, 116.2, 120.6, 123.3, 128.8, 129.3, 135.5, 149.2, 150.4, 152.1, 162.7, 166.3; IR (neat) ν 3285, 2958, 2867, 1706, 1630, 1487, 1462, 1363, 1217, 1145, 1064, 986, 777, 659 cm^{-1}; MS (ESI) m/e 522 (M+H); HRMS (ESI) for $C_{28}H_{37}NNaO_5S$ (M+Na): 522.2285; found: 522.2285. $[\alpha]_D^{20} = -13.2$ (c 1.10, $CHCl_3$) (50% ee); Chiralcel OD-H, hexane/^{i}PrOH = 99:1, 0.7 mL/min, 230 nm, t_{major} = 14.78 min, t_{minor} = 11.73 min.

4.7.11. Methyl 2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ab

A white solid (33.7 mg, 85%); mp 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.38 (s, 3H), 2.39 (s, 3H), 3.42 (s, 3H), 5.27 (s, 1H), 5.56 (s, 1H), 7.01–7.06 (m, 2H), 7.19–7.27 (m, 3H), 7.41 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 21.4, 47.6, 51.3, 102.7, 116.2, 120.3, 124.8, 126.7, 129.0, 129.2, 129.6, 139.2, 142.6, 150.4, 163.5, 166.6; IR (neat) ν 3275, 2988, 1696, 1633, 1489, 1434, 1329, 1275, 1261, 1151, 1066, 926, 788, 750, 615 cm^{-1}; MS (ESI) m/e 396 (M+H); HRMS (ESI) for $C_{19}H_{19}NNaO_5S$ (M+H): 396.0876; found: 396.0880. $[\alpha]_D^{20} = -7.8$ (c 0.35, $CHCl_3$) (64% ee); Chiralcel AD-H, hexane/^{i}PrOH = 75:25, 0.7 mL/min, 254 nm, t_{major} = 45.39 min, t_{minor} = 18.49 min.

4.7.12. *tert*-Butyl 2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ac

A white solid (31.1 mg, 75%); mp 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.46 (s, 9H), 2.33 (s, 3H), 2.38 (s, 3H), 5.04 (d, J = 6.0 Hz, 1H), 5.57 (d, J = 6.0 Hz, 1H), 6.95–7.02 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.20–7.28 (m, 2H), 7.53 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 21.4, 28.2, 48.2, 81.4, 104.3, 116.1, 119.9, 124.4, 126.8, 128.9, 129.1, 129.6, 139.2, 142.6, 150.7, 162.2, 165.7; IR (neat) ν 3357, 2924, 2853, 1664, 1588, 1488, 1363, 1150, 1031, 988, 777, 660 cm^{-1}; MS (ESI) m/e 438 (M+Na); HRMS (ESI) for $C_{22}H_{25}NNaO_5S$ (M+Na): 438.1346; found: 438.1350. $[\alpha]_D^{20} = +12.0$ (c 0.45, $CHCl_3$) (65% ee); Chiralcel IC, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 20.13 min, t_{minor} = 23.73 min.

4.7.13. Isopropyl 2-methyl-4-((4-methylphenylsulfonamido)-methyl)-4*H*-chromene-3-carboxylate 3ad

A white solid (33.9 mg, 80%); mp 157–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24 (d, J = 6.4 Hz, 3H), 1.28 (d, J = 6.4 Hz, 3H), 2.36 (s, 3H), 2.38 (s, 3H), 4.97–5.03 (m, 2H), 5.58 (d, J = 6.4 Hz, 1H), 6.96–7.04 (m, 2H), 7.16 (d, J = 7.6 Hz, 2H), 7.21–7.28 (m, 3H), 7.51 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 21.4, 21.8, 21.9, 48.1, 68.4, 103.2, 116.2, 119.7, 124.6, 126.8, 129.0, 129.1, 129.6, 139.2, 142.7, 150.7, 163.0, 166.0; IR (neat) ν 3272, 2926, 1708, 1637, 1587, 1489, 1461, 1381, 1343, 1291, 1262, 1159, 1106, 1063, 814, 760, 664 cm^{-1}; MS (ESI) m/e 424 (M+Na); HRMS (ESI) for $C_{21}H_{23}NO_5SNa$ (M+Na): 424.1189; found: 424.1189. $[\alpha]_D^{20} = +24.6$ (c 0.70, $CHCl_3$) (70% ee); Chiralcel IC, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 30.43 min, t_{minor} = 42.33 min.

4.7.14. Isopropyl 6-Cl-2-methyl-4-((4-methylphenylsulfonamido)methyl)-4*H*-chromene-3-carboxylate 3bd

A white solid (36.5 mg, 80%); mp 135–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (d, J = 6.0 Hz, 3H), 1.29 (d, J = 6.0 Hz, 3H), 2.39 (s, 3H), 2.39 (s, 3H), 5.02 (sept, J = 6.0 Hz, 1H), 5.24 (d, J = 5.6 Hz, 1H), 5.45 (d, J = 5.6 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 7.00 (br s, 1H), 7.12–7.18 (m, 3H), 7.47 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.4, 21.8, 21.9, 47.8, 68.6, 103.2, 117.6, 120.7, 126.6, 129.1, 129.18, 129.23, 139.0, 143.0, 149.3, 162.9, 165.8; IR (neat) ν 3207, 2924, 2877, 1654, 1633, 1479, 1373, 1328, 1278, 1236, 1151, 1088, 885, 763 cm^{-1}; MS (ESI) m/e 458 (M+Na); HRMS (ESI) for $C_{21}H_{22}NO_5SClNa$ (M+Na): 458.0799; found: 458.0809. $[\alpha]_D^{20} = +39$ (c 0.30, $CHCl_3$) (67% ee); Chiralcel OD-H, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 7.82 min, t_{minor} = 9.19 min.

4.7.15. Isopropyl 6-bromo-2-methyl-4-((4-methylphenylsulfonamido)methyl)-4*H*-chromene-3-carboxylate 3cd

A white solid (36.1 mg, 72%); mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (d, J = 6.4 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H), 2.39 (s, 3H), 2.40 (s, 3H), 5.02 (sept, J = 6.4 Hz, 1H), 5.34 (br s, 1H), 5.44 (d, J = 6.0 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 7.11 (d, J = 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.5, 21.8, 21.9, 47.7, 68.6, 103.3, 116.6, 118.0, 121.1, 126.6, 129.3, 131.9, 132.1, 138.9, 143.0, 149.8, 162.9, 165.8; IR (neat) ν 3672, 2972, 2901, 1709, 1652, 1633, 1602, 1376, 1328, 1234, 1066, 907, 777 cm^{-1}; MS (ESI) m/e 502 (M+Na); HRMS (ESI) for $C_{21}H_{22}BrNNaO_5S$ (M+Na): 502.0294; found: 502.0309. $[\alpha]_D^{20} = +20.8$ (c 0.35, $CHCl_3$) (76% ee); Chiralcel OD-H, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 8.58 min, t_{minor} = 10.33 min.

4.7.16. Isopropyl 6,8-dichloro-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3dd

A yellow solid (13.3 mg, 27%); mp 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (d, J = 6.4 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H), 2.40 (s, 3H), 2.44 (s, 3H), 5.03 (sept, J = 6.4 Hz, 1H), 5.13 (d, J = 6.0 Hz, 1H), 5.47 (d, J = 6.0 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 21.4, 21.8, 21.9, 47.8, 68.9, 103.8, 122.1, 122.3, 126.8, 127.7, 129.0, 129.3, 129.4, 138.8, 143.2, 145.6, 162.7, 165.4; IR (neat) ν 3005, 2926, 1683, 1580, 1364, 1275, 1257, 1158, 980, 750, 658 cm^{-1}; MS (ESI) m/e 492 (M+Na); HRMS (ESI) for $C_{21}H_{21}NO_5SCl_2Na$ (M+Na): 492.0410; found: 492.0427. $[\alpha]_D^{20} = +9.6$ (c 0.50, $CHCl_3$) (38% ee); Chiralcel IC, hexane/^{i}PrOH = 70:30, 0.5 mL/min, 214 nm, t_{major} = 19.21 min, t_{minor} = 25.54 min.

4.7.17. Isopropyl 6,8-dibromo-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ed

A white solid (12.2 mg, 21%); mp 155–157 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.27 (d, J = 6.0 Hz, 3H), 1.29 (d, J = 6.0 Hz, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 5.02–5.10 (m, 2H), 5.47 (d, J = 6.0 Hz, 1H), 7.14 (d, J = 2.1 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 21.5, 21.78, 21.85, 47.8, 68.9, 104.0, 111.1, 116.5, 122.4, 126.7, 129.3, 131.3, 134.9, 138.7, 143.2, 147.0, 162.8, 165.3; IR (neat) ν 3290, 3005, 1682, 1571, 1459, 1365, 1275, 1258, 1203, 1157, 1073, 1026, 979, 749, 657 cm^{-1}; MS (ESI) m/e 579 (M+Na); HRMS (ESI) for $C_{21}H_{21}NNaBr_2O_5S$ (M+Na): 579.9399; found: 579.9425. $[\alpha]_D^{20} = +6.4$ (c 0.35, $CHCl_3$) (21% ee); Chiralcel IC, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 19.83 min, t_{minor} = 28.38 min.

4.7.18. Isopropyl 8-methoxy-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3fd

A white solid (35.9 mg, 79%); mp 157–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24 (d, J = 6.0 Hz, 3H), 1.28 (d, J = 6.0 Hz, 3H), 2.21 (s, 3H), 2.38 (s, 3H), 3.81 (s, 3H), 4.98 (sept, J = 6.0 Hz, 1H), 5.27 (d, J = 7.2 Hz, 1H), 5.65 (d, J = 7.2 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.89–6.96 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 21.4, 21.7, 21.8, 47.7, 55.9, 68.4, 103.4, 110.8, 120.8, 121.3, 124.3, 126.8, 129.1, 139.2, 140.3, 142.6, 147.2, 162.5, 165.9; IR (neat) ν 3298, 2921, 1704, 1589, 1332, 1276, 1210, 1156, 1092, 1015, 764, 748, 660 cm^{-1}; MS (ESI) m/e 454 (M+Na); HRMS (ESI) for $C_{22}H_{25}NNaO_6S$ (M+Na): 454.1295; found: 454.1314. $[\alpha]_D^{20} = +22.0$ (c 0.20, $CHCl_3$) (76% ee); Chiralcel OJ-H, hexane/^{i}PrOH = 80:20, 0.7 mL/min, 214 nm, t_{major} = 20.09 min, t_{minor} = 29.13 min.

4.7.19. Isopropyl 6-methoxy-2-methyl-4-((4-methylphenylsulfonamido)methyl)-4*H*-chromene-3-carboxylate 3gd

A white solid (34.1 mg, 75%); mp 157–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.25 (d, J = 6.0 Hz, 3H), 1.27 (d, J = 6.0 Hz, 3H), 2.37 (s, 3H), 2.37 (s, 3H), 3.61 (s, 3H), 5.01 (sept, J = 6.0 Hz, 1H), 5.09 (d, J = 6.0 Hz, 1H), 5.54 (d, J = 6.0 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 6.77 (dd, J = 3.0 Hz, 9.0 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 7.16 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 21.3, 21.8, 21.9, 48.6, 55.3, 68.3, 102.4, 112.0, 116.4, 117.2, 119.9, 126.7, 129.0, 139.4, 142.6, 144.9, 156.1, 163.1, 166.2; IR (neat) ν 3288, 2924, 2877, 1658, 1494, 1374, 1340, 1289, 1224, 1204, 1155, 1073, 811, 762 cm^{-1}; MS (ESI) m/e 454 (M+Na); HRMS (ESI) for $C_{22}H_{25}NO_6SNa$ (M+Na): 454.1295; found: 454.1311. $[\alpha]_D^{20} = +17.4$ (c 0.50, $CHCl_3$) (64% ee); Chiralcel OD-H, hexane/^{i}PrOH = 95:5, 0.7 mL/min, 214 nm, t_{major} = 30.49 min, t_{minor} = 38.12 min.

4.7.20. Isopropyl 2,8-dimethyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3kd

A white solid (35.0 mg, 80%); mp 124–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.24 (d, J = 6.6 Hz, 3H), 1.26 (d, J = 6.6 Hz, 3H), 2.30 (s, 3H), 2.38 (s, 3H), 2.39 (s, 3H), 4.95–5.02 (m, 2H), 5.58 (d, J = 4.5 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 7.05–7.10 (m, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.6, 19.9, 21.5, 21.9, 22.0, 48.4, 68.4, 103.5, 119.6, 124.1, 125.5, 126.9, 127.1, 129.2, 130.3, 139.3, 142.7, 149.2, 163.0, 166.1; IR (neat) ν 3312, 2954, 2919, 1689, 1648, 1593, 1531, 1465, 1382, 1283, 1242, 1089, 763, 660 cm^{-1}; MS (ESI) m/e 438 (M+Na); HRMS (ESI) for $C_{22}H_{25}NNaO_5S$ (M+Na): 438.1346; found: 438.1349. $[\alpha]_D^{20} = +11.0$ (c 0.30, $CHCl_3$) (87% ee); Chiralcel IC, hexane/^{i}PrOH = 80:20, 1.0 mL/min, 220 nm, t_{major} = 22.28 min, t_{minor} = 33.38 min.

4.7.21. Isopropyl 6,8-di-*tert*-butyl-2-methyl-4-(4-methylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3ld

A white solid (34.8 mg, 65%); mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18 (s, 9H), 1.28 (d, J = 6.0 Hz, 3H), 1.30 (d, J = 6.0 Hz, 3H), 1.42 (s, 9H), 2.35 (s, 3H), 2.45 (s, 3H), 4.85 (d, J = 6.4 Hz, 1H), 5.06 (sept, J = 6.0 Hz, 1H), 5.58 (d, J = 6.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 2.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 19.7, 21.4, 21.8, 22.0, 30.0, 31.2, 34.4, 34.9, 48.9, 68.3, 103.7, 119.5, 123.6, 124.0, 126.7, 129.1, 136.5, 139.4, 142.5, 146.7, 162.9, 166.0; IR (neat) ν 3277, 2931, 2962, 2926, 1708, 1664, 1640, 1589, 1460, 1364, 1240, 1201, 1159, 1070, 760, 739, 663 cm^{-1}; MS (ESI) m/e 536 (M+Na); HRMS (ESI) for $C_{29}H_{39}NNaO_5S$ (M+Na): 536.2441; found: 536.2461. $[\alpha]_D^{20} = +50.6$ (c 0.35, $CHCl_3$) (72% ee); Chiralcel AD-H, hexane/^{i}PrOH = 90:10, 0.8 mL/min, 230 nm, t_{major} = 6.18 min, t_{minor} = 14.73 min.

4.7.22. Isopropyl 2-methyl-4-(4-nitrophenylsulfonamido)-4*H*-chromene-3-carboxylate 3hd

A white solid (29.8 mg, 69%); mp 152–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.23 (d, J = 6.0 Hz, 3H), 1.28 (d, J = 6.0 Hz, 3H), 2.42 (s, 3H), 5.00 (sept, J = 6.0 Hz, 1H), 5.32 (d, J = 4.2 Hz, 1H), 5.61 (d, J = 4.2 Hz, 1H), 6.93 (t, J = 8.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.21–7.26 (m, 2H), 7.75 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 21.9, 48.7, 68.7, 103.2, 116.5, 118.9, 123.7, 124.7, 128.1, 129.50, 129.52, 147.7, 149.5, 150.8, 163.4, 166.0; IR (neat) ν 3279, 2988, 1657, 1527, 1373, 1341, 1277, 1240, 1199, 1154, 1087, 1015, 764, 748 cm^{-1}; MS (ESI) m/e 455 (M+Na); HRMS (ESI) for $C_{20}H_{20}N_2NaO_7S$ (M+Na): 455.0883; found: 455.0890. $[\alpha]_D^{20} = -3.0$ (c 0.30, $CHCl_3$) (65% ee); Chiralcel AD-H, hexane/^{i}PrOH = 70:30, 0.6 mL/min, 214 nm, t_{major} = 31.21 min, t_{minor} = 52.54 min.

4.7.23. Isopropyl 4-(4-bromophenylsulfonamido)-2-methyl-4*H*-chromene-3-carboxylate 3id

A white solid (34.2 mg, 72%); mp 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25 (d, J = 6.4 Hz, 3H), 1.27 (d, J = 6.4 Hz, 3H), 2.39 (s, 3H), 5.00 (sept, J = 6.4 Hz, 1H), 5.24 (d, J = 4.2 Hz, 1H), 5.57 (d, J = 4.2 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 7.2 Hz, 2H), 7.44–7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.87, 21.91, 48.3, 68.6, 103.2, 116.3, 119.2, 124.6, 126.8, 128.4, 129.2, 129.6, 131.7, 141.2, 150.7, 163.1, 166.1; IR (neat) ν 3240, 2984, 1774, 1660. 1588, 1373, 1335, 1241, 1147, 1068, 1016, 988, 757 cm^{-1}; MS (ESI) m/e 488 (M+Na); HRMS (ESI) for $C_{20}H_{20}NNaBrO_5S$ (M+Na): 488.0138; found: 488.0156. $[\alpha]_D^{20} = +7.0$ (c 0.30, $CHCl_3$) (64% ee); Chiralcel IC, hexane/^{i}PrOH = 70:30, 0.6 mL/min, 214 nm, t_{major} = 15.04 min, t_{minor} = 16.63 min.

4.7.24. Isopropyl 2-methyl-4-(2,4,6-triisopropylphenylsulfonamido)-4*H*-chromene-3-carboxylate 3jd

A white solid (35.9 mg, 70%); mp 159–162 °C ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.07 (d, J = 6.8 Hz, 6H), 1.22–1.28 (m, 18H), 2.45 (s, 3H), 2.86 (dsept, J = 2.8 Hz, 6.8 Hz, 1H), 3.96–4.02 (m, 2H), 4.68 (d, J = 7.2 Hz, 1H), 5.02 (dsept, J = 6.4, 12.4 Hz, 1H), 5.69 (d, J = 7.2 Hz, 1H), 6.77 (t, J = 7.6 Hz, 1H), 6.91–6.93 (m, 1H), 6.98 (d, J = 7.6 Hz, 1H), 7.03 (s, 2H), 7.12–7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 21.7, 21.9, 23.7, 23.8, 24.2, 24.9, 34.1, 47.9, 68.5, 104.6, 116.2, 120.4, 123.3, 124.3, 128.7, 129.0, 135.7, 149.1, 150.6, 152.1, 162.4, 165.9; IR (neat) ν 3310, 2971, 2925, 1699, 1632, 1585, 1487, 1461, 1381, 1258, 1065, 880, 777, 658 cm^{-1}; MS (ESI) m/e 536 (M+Na); HRMS (ESI) for $C_{29}H_{39}NNaO_5S$ (M+Na): 536.2441; found: 536.2454. $[\alpha]_D^{20} = -9$ (c 0.20, $CHCl_3$) (55% ee); Chiralcel AD-H, hexane/^{i}PrOH = 70:30, 0.6 mL/min, 254 nm, 6.46 min, t_{minor} = 12.13 min.

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10. The crystal data of compound **3cd** have been deposited in the CCDC with number 814064. Empirical Formula: $C_{21}H_{22}BrNO_5S$; Formula Weight: 480.37; Crystal Color, Habit: colorless; Crystal Dimensions: 0.50 × 0.08 × 0.05 mm; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: a = 5.645(2) Å, b = 15.486(6) Å, c = 24.252(8) Å, α = 90°, β = 90°, γ = 90°, V = 2120.2(13) Å^3; Space group: $P2(1)2(1)2(1)$; Z = 4; D_{calcd} = 1.505 g/cm^3; $F(0\,0\,0)$ = 984; Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0459; wR_2 = 0.1142.