有机化学 DOI: 10.6023/cjoc202111030 研究论文
Chinese Journal of Organic Chemistry ARTICLE

手性方酰胺催化环状 1,3-二羰基化合物对 β,γ-不饱和-α-酮酯的不对称 Michael 加成反应

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摘要 发展了新型手性双功能叔胺-方酰胺催化的环状 1,3-二羰基化合物和 β,γ-不饱和-α-酮酯之间的不对称 Michael 加成反应, 反应条件温和, 底物适用范围广泛, 相应产物的产率和对映选择性分别高达 97%和 97% *ee*, 为合成和医药上极为重要的手性色烯衍生物的立体选择性合成提供了一种实用的方法.

关键词 Michael 加成; 有机催化; 叔胺-方酰胺; 环状 1,3-二羰基化合物; β,γ-不饱和-α-酮酯

Chiral Squaramide Catalyzed Enantioselective Michael Addition of Cyclic 1,3-Diketones to β,γ-Unsaturated α-Keto Esters

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Abstract A stereoselective methodology was developed to construct synthetically and pharmaceutically useful chiral chromene derivatives. In the presence of a newly designed bifunctional tertiary amine-squaramide organocatalyst, the Michael addition between cyclic 1,3-diketones and β,γ-unsaturated α-ketoesters occurred smoothly to provide the desired products with high to excellent yields (84%～97%) and enantioselectivies (79%～97% *ee*). This catalytic protocol was compatible with a range of structurally distinct β,γ-unsaturated α-ketoesters.

Keywords Michael addition; organocatalysis; tertiary amine-squaramide; cyclic diketone; β,γ-unsaturated α-ketoesters

1 Introduction

Asymmetric Michael reaction is generally considered to be one of the most effective and widely used tools for the formation of C—C bond in synthetic chemistry.[1] In a wide range of such transformations, catalytic Michael additions of 1,3-dicarbonyl compounds to α,β-unsaturated carbonyl compounds have attracted extensive attention because a variety of useful skeletons widely existing in bioactive compounds can be obtained by this simple and effective method.[2] As a sort of commonly-used carbonyl derivatives, the β,γ-unsaturated α-ketoesters have special advantages owing to high reactivity and potential conversion to a range of different functionalities.[3] As early as in 2003, Jørgensen and co-workers reported the first Michael reaction of cyclic 1,3-dicarbonyl compounds to β,γ-unsaturated α-ketoesters catalyzed by chiral bisoxazoline-copper(II) complexes, quantitative yields and up to 92% *ee* were obtained.[4] From then on, this asymmetric process has drawn intensive attention and a variety of catalysts have also been utilized in recent years.[5] However, only a few of organocatalysts have provided excellent enantioselectivity for the transformations of this type,[5b-5g] the development of a novel and efficient chiral organocatalyst is in high demand, yet remaining an elusive challenge.

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Received November 22, 2021; revised January 2, 2022; published online January 20, 2022.
Project supported by the Natural Science Foundation of Henan Province (No. 202300410188) and the Training Plan for Young Key Teachers in Colleges and Universities in Henan Province (No. 2021GGJS173).
河南省自然科学基金(No. 202300410188)和河南省高等学校青年骨干教师培养计划(No. 2021GGJS173)资助项目.
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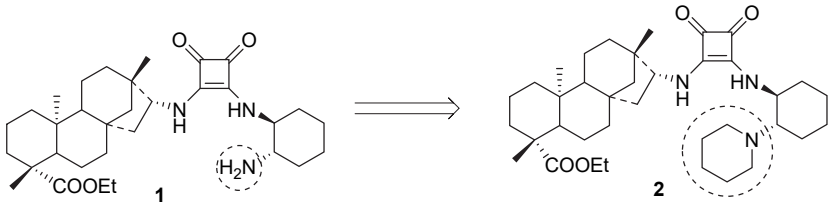
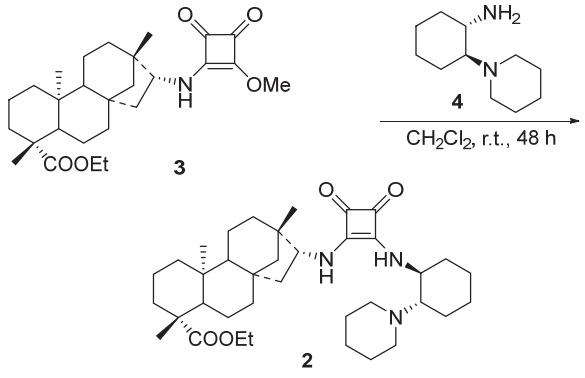


Figure 1 Chiral amine-squaramide

Amine-squaramide is a kind of effective hydrogen bonding-donor bifunctional catalyst to promote many asymmetric transformations.[6] Since Rawal's pioneering work,[7] these catalysts have been successfully applied to various asymmetric reactions.[8] Chiral primary amine-squaramide **1**, developed by our group, was found to be efficient for asymmetric Michael addition of isobutyraldehyde to maleimides.[9] Inspired by this, we envisaged that cyclic 1,3-diketones and *β*,*γ*-unsaturated *α*-ketoesters might be suitably activated and orientated by the newly designed tertiary amine-squaramide **2**, which were obtained by means of the replacement of primary amino group with tertiary amino group, and it is possible that the tetracyclic diterpene skeleton provides the appropriate sterically hindered microenvironment to promote the stereoselectivity of the target Michael addition. Herein we report a highly enantioselective Michael addition of cyclic 1,3-diketones to *β*,*γ*-unsaturated *α*-ketoesters using a newly synthesized tertiary amine-squaramide organocatalyst.

2 Results and discussion

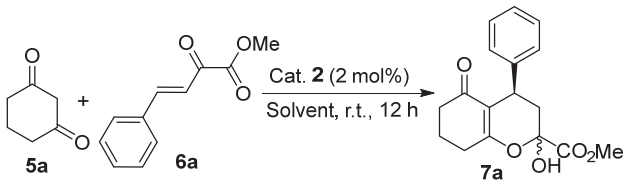
The chemical structure and synthetic pathway of squaramide **2** are shown in Scheme 1. The mono-squaramide **3**, which could be readily prepared from commercially available natural product stevioside,[9] reacted with 2-(piperidin-1-yl)cyclohexanamine **4**[10] in dichloromethane afforded the chiral amine-squaramide **2** in 79% yield.



Scheme 1 Synthetic routes of tertiary amine-squaramide **2**

With the novel tertiary amine-squaramide **2** in hand, a model reaction of 1,3-cyclohexanedione **5a** with *β*,*γ*-unsaturated-*α*-keto ester **6a** was chosen to screen the effects of the catalyst (Table 1, Entry 1). Gratifyingly, as expected, the catalyst **2** was efficient and provided *R*-enriched adduct with good enantioselectivity (83% *ee*) and yield (94%). The product **7a** was obtained as a mixture of epimeric hemiacetal and open chain, which was consistent with Jørgensen's early discovery.[4] Inspired by this, other reaction parameters were investigated to improve the enantioselectivity of the adduct. Solvent screening showed that Et_2O performed the best and gave **7a** in 93% yield and 85% *ee* (Table 1, Entry 2). Decreasing the catalyst loading from 2 mol% to 1 mol%, the enantioselectivity gradually increased from 85% *ee* to 91% *ee* (Entries 6 vs. 2). When 0.5 mol% catalyst was used, no better results were obtained with a slight sacrifice of the yield (Entry 7). When the reaction was conducted at 0 ℃, the yield further decreased (Entry 8). To conclude, the reaction of 0.12 mmol of **5a** (1.2 equiv.) and 0.10 mmol of **6a** (1.0 equiv.) was best performed in 1.0 mL of Et_2O with 1 mol% catalyst **2** at room temperature.

Table 1 Optimization of the reaction conditions[a]



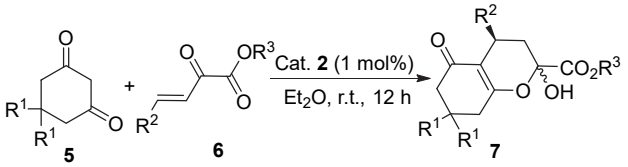
Entry	Solvent	Yield[b]/%	*ee*[c]/%
1	CH_2Cl_2	94	83
2	Et_2O	93	85
3	THF	89	77
4	Toluene	91	71
5	CH_3OH	46	20
6[d]	Et_2O	95	91
7[e]	Et_2O	76	91
8[f]	Et_2O	70	90

[a] Unless otherwise specified, all reactions were carried out with 1,3-cyclohexanedione (**5a**, 0.12 mmol), *β*,*γ*-unsaturated-*α*-keto ester (**6a**, 0.10 mmol) and 2 mol% catalyst **2** in Et_2O (1.0 mL) at room temperature for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase. [d] 1 mol% catalyst **2**. [e] 0.5 mol% catalyst **2**. [f] The reaction was conducted at 0 ℃.

After the optimized reaction conditions were established, the generality of this reaction were further explored and the results are summarized in Table 2. 1,3-Cyclohexanedione **5a** reacted smoothly to *β*,*γ*-unsaturated *α*-keto esters **6** bearing a *γ*-aryl substituent within 12 h with high yields (90%～95%) and enantioselectivities (86%～91% *ee*), irrespective of the electronic nature or position of the substituents on the phenyl ring (Table 2, Entries 1～6). Besides, using *β*,*γ*-unsaturated *α*-keto esters with a heteroar-

omatic or naphth-2-yl substituent as the starting material, the corresponding products were also obtained with good yields and enantioselectivities (Entries 7, 8). Moreover, the β,γ-unsaturated α-ketoester bearing a relative big substituent on ester moiety (R^2) was also suitable for this reaction, which gave the product in 97% yield and 89% *ee* (Entry 9).

Table 2 Substrate studies of the Michael addition[a]

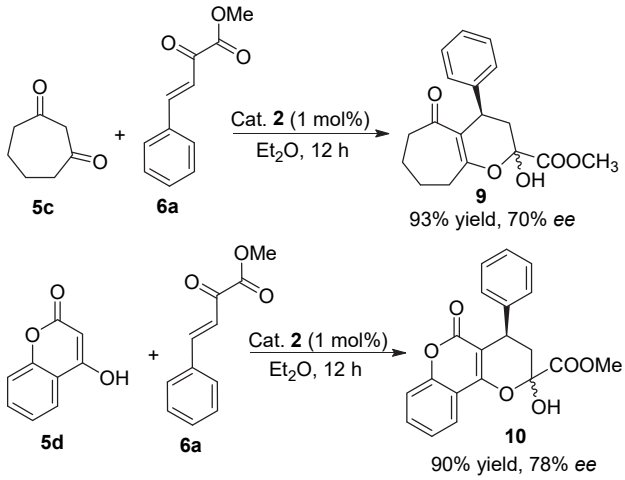


Entry	R^1 (**5**)	R^2, R^3 (**6**)	**7**	Yield[b]/%	*ee*[c]/%
1	H (**5a**)	Ph, CH_3 (**6a**)	**7a**	95	91
2	H (**5a**)	4-$CH_3C_6H_4$, CH_3 (**6b**)	**7b**	93	86
3	H (**5a**)	4-$CH_3OC_6H_4$, CH_3 (**6c**)	**7c**	93	90
4	H (**5a**)	4-FC_6H_4, CH_3 (**6d**)	**7d**	90	87
5	H (**5a**)	4-ClC_6H_4, CH_3 (**6e**)	**7e**	91	88
6	H (**5a**)	4-BrC_6H_4, CH_3 (**6f**)	**7f**	92	86
7	H (**5a**)	2-Thienyl, CH_3 (**6g**)	**7g**	85	82
8	H (**5a**)	2-Naphthyl, CH_3 (**6h**)	**7h**	86	88
9	H (**5a**)	Ph, Bn (**6i**)	**7i**	97	89
10	CH_3 (**5b**)	Ph, CH_3 (**6a**)	**8a**	95	97
11	CH_3 (**5b**)	4-$CH_3C_6H_4$, CH_3 (**6b**)	**8b**	92	90
12	CH_3 (**5b**)	4-$CH_3OC_6H_4$, CH_3 (**6c**)	**8c**	93	90
13	CH_3 (**5b**)	4-FC_6H_4, CH_3 (**6d**)	**8d**	94	84
14	CH_3 (**5b**)	4-ClC_6H_4, CH_3 (**6e**)	**8e**	91	89
15	CH_3 (**5b**)	4-BrC_6H_4, CH_3 (**6f**)	**8f**	91	79
16	CH_3 (**5b**)	2-Thienyl, CH_3 (**6g**)	**8g**	87	84
17	CH_3 (**5b**)	2-Naphthyl, CH_3 (**6h**)	**8h**	84	88
18	CH_3 (**5b**)	Ph, Bn (**6i**)	**8i**	94	88
19	CH_3 (**5b**)	Ph, Et (**6j**)	**8j**	95	84
20	CH_3 (**5b**)	Et, Et (**6k**)	**8k**	93	80

[a] Unless otherwise specified, all reactions were carried out with cyclic diketone (**5**, 0.12 mmol), β,γ-unsaturated-α-keto ester (**6**, 0.10 mmol) and 1 mol% catalyst **2** in Et_2O (1.0 mL) at room temperature for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase.

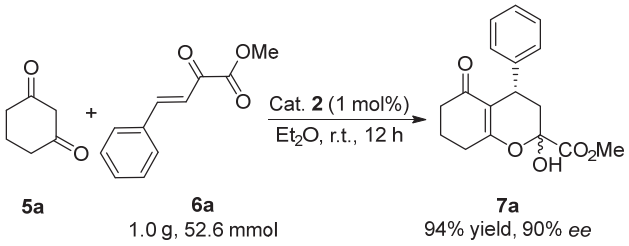
To further explore the potential of this catalytic system, cyclohexane-1,3-dione with the same R^1-substituent such as dimedone **5b** was also applied as Michael donor to react with β,γ-unsaturated α-keto esters. As shown in Table 2 (Entries 10～20), in all cases, the reactions proceeded smoothly, the efficiency and enantioselectivity remained almost the same compared with the results obtained by using cyclohexane-1,3-dione **5a**. It is noteworthy that substrate with an alkyl group also provided the desired product in good yield with good enantioselectivity (Entry 20).

Acyclic 1,3-diketone and other cyclic 1,3-diketones were also tried as Michael donors, such as acetylacetone, 1,3-cyclopentanedione and 1,3-cycloheptandione. However, a significant conversion did not observe by prolonging the reaction time for acetylacetone and 1,3-cyclopentanedione. Notably, 1,3-cycloheptandione **5c** reacted with β,γ-unsaturated α-keto ester **6a** smoothly to give the adduct **9** in high yield and good enantioselectivity (Scheme 2). Besides, this catalytic system was also suitable for 4-hydroxycoumarin **5d**, which gave the product **10** in 90% yield and 78% *ee* (Scheme 2).



Scheme 2 Asymmetric Michael reaction by using cycloheptane-1,3-dione and 4-hydroxycoumarin as Michael donors

Large-scale asymmetric Michael reaction with 1.0 g of β,γ-unsaturated α-keto ester **6a** was further performed. The same catalyst loading of 1 mol% as in the experimental scale was used. The large-scale experiments can be easily carried out using the same procedure as for the experimental scale reactions. As can be seen from the results summarized in Scheme 3, both the yield and enantioselectivity were maintained at the same level for the large-scale reactions, which offers a great possibility for application in industry.



Scheme 3 Large-scale asymmetric Michael addition

On the basis of the experimental results described above and the previous asymmetric Michael reactions,[5] a possible transition state model was hypothesized based on the dual activation mechanism of tertiary amine-squaramide catalyst. As illustrated in Figure 2, the β,γ-unsaturated α-keto ester was fixed and activated by the squaramide moiety via double H-bonding between the NH groups and the α-keto ester group. Meanwhile, after deprotonation, cyclic diketone was activated by protonated tertiary amine group via H-bonding. With the spatial alignment, the cyclic diketone would attack from the *Re*-face of the β,γ-unsaturated α-keto ester to give the observed stereochemistry of the product.

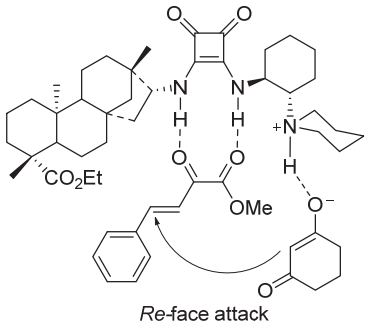


Figure 2 Proposed transition-state model for the Michael addition

3 Conclusions

In summary, a novel tertiary amine-squaramide organocatalyst was synthesized and demonstrated to be effective for the asymmetric Michael addition of cyclic 1,3-diketones to β,γ-unsaturated α-keto esters. A broad range of substrates are well-tolerated to give the desired Michael products in high yields (84%～97%) with good to high enantioselectivities (up to 97% *ee*). Further study on the application of this catalyst to other reactions is ongoing in our laboratory.

4 Experimental section

4.1 Reagents and instruments

All chemicals were used as received unless otherwise noted. Reagent grade solvents were redistilled prior to use. ^{1}H NMR and ^{13}C NMR spectra were collected with a Bruker DPX 400 NMR spectrometer with TMS as internal reference. IR spectra were determined with a Thermo Nicolet IR200 unit. ESI mass spectra were carried out on an HPLC Q-Exactive HRMS spectrometer (Thermo, USA) by using methanol as mobile phase. Chromatography was performed on silica gel (200～300 mesh). Melting points were determined with an aXT5 A apparatus and were uncorrected. Optical rotations were determined with a Perkin-Elmer 341 polarimeter. Enantiomeric excesses were determined by chiral HPLC at room temperature with use of a Labtech 2006 pump, a Labtech UV600 ultra detector, and Chiralcel AD-H (4.6 mm×250 mm) columns.

4.2 Synthetic procedure of tertiary amine-squaramide **2**

To a stirred solution of (1*S*,2*S*)-2-(piperidin-1-yl)cyclohexanamine **4** (0.18 g, 1.0 mmol) in dry CH_2Cl_2 (25 mL), the mono-squaramide **3**[11] (0.46 g, 1.0 mmol) was added. Then the reaction mixture was stirred at room temperature for 48 h. After removing of the solvent, the crude product was purified by column chromatography on silica gel (CH_3OH/CH_2Cl_2, V/V=1/10) to give the tertiary amine-squaramide (**2**) as light yellow solid, yield 80%. m.p. 203.9～204.7 ℃; $[\alpha]_D^{20}$ +38.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 0.71 (s, 3H), 0.83～0.89 (m, 2H), 0.95 (s, 3H), 0.98～1.16 (m, H), 1.16 (s, 3H), 1.24 (t, J=6.8 Hz, 3H), 1.24～1.44 (m, 10H), 1.54～1.95 (m, 15H), 2.14 (d, J=12.8 Hz, 1H), 2.36 (s, 3H), 2.65 (s, 2H), 3.78 (s, 1H), 4.00～4.26 (m, 3H), 6.85 (s, 2H); ^{13}C NMR (101 MHz, $CHCl_3$) δ: 13.4, 14.1, 18.9, 20.5, 21.6, 24.7, 25.4, 26.8, 28.9, 33.4, 34.8, 38.0, 39.9, 41.3, 43.7, 49.5, 54.2, 55.7, 56.9, 59.9, 62.8, 68.7, 168.4, 177.4, 182.4; IR (KBr) v: 974, 1032, 1097, 1150, 1180, 1222, 1375, 1466, 1528, 1581, 1669, 1723, 1794, 2850, 2933, 3263 cm^{-1}; HRMS calcd for $C_{37}H_{58}N_3O_4$ $[M+H]^+$ 608.4427, found 608.4426.

4.3 Typical procedure for asymmetric Michael addition

A mixture of cyclic diketone (0.12 mmol), β,γ-unsaturated α-keto ester (0.1 mmol) and the catalyst (0.001 mmol) in Et_2O (1.0 mL) was stirred at room temperature for 12 h [monitored by thin-layer chromatography (TLC)]. The crude product was purified by column chromatography on silica gel, eluted by CH_3OH/CH_2Cl_2 to afford the desired Michael adduct. Absolute configurations of the products were assigned by correlation to literature data and considering the similarity in the stereochemical reaction pathway.[5e,5h,12-13]

(*R*)-Methyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-phenylbutanoate (**7a**):[5h] White solid, 28.7 mg, 95% yield. m.p. 148.0～149.3 ℃; $[\alpha]_D^{20}$ +15.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, V/V=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=20.4 min (major), 28.8 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28～7.24 (m, 3.06H), 7.17～7.14 (m, 3H), 4.58 (s, 0.66H), 4.22 (s, 0.36H), 4.11 (d, J=7.2 Hz, 0.36H), 3.92～3.87 (m, 0.71H), 3.85 (s, 0.94H), 3.77 (s, 1.90H), 2.61～2.23 (m, 6.37H), 2.12～1.97 (m, 2.20H); HRMS calcd for $C_{17}H_{19}O_5$ $[M+H]^+$ 303.1232, found 303.1225.

(*R*)-Methyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-(*p*-tolyl)butanoate (**7b**):[5h] White solid, 29.4 mg, 93% yield. m.p. 149.6~150.8 ℃; $[\alpha]_D^{20}$ +3.0 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, V/V=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=28.6 min (major), 35.5 min (minor); ^{1}H NMR (400 MHz, CDCl3) δ: 7.06 (m, 4H), 4.57 (s, 0.58H), 4.23 (s, 0.34H), 4.07 (d, J=6.4 Hz, 0.37H), 3.88～3.85 (m, 1.71H), 3.77 (s, 2H), 2.60～2.21 (m, 9H), 2.10～1.97 (m, 2H); HRMS calcd for $C_{18}H_{21}O_5$ $[M+H]^+$ 317.1389, found 317.1381.

(*R*)-Methyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-4-(4-methoxyphenyl)-2-oxobutanoate (**7c**)[5h]: White solid, 30.9 mg, 93% yield. m.p. 159.3～161.2 ℃; $[\alpha]_D^{20}$ −2.0 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, V/V=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=17.9 min (major), 29.2 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08～7.04 (m, 2.02H), 6.80～6.78 (m, 2H), 5.26 (s, 0.64H), 4.68 (s, 0.32H), 4.00～4.02 (m, 0.34H), 3.88～3.83 (m, 0.83H), 3.82 (s, 0.94H), 3.75 (d, J=1.6 Hz, , 3H), 3.67～3.64 (m, 2H), 2.58～2.18 (m, 6.29H), 2.08～1.97 (m, 2.65H); HRMS calcd for $C_{18}H_{21}O_6$ $[M+H]^+$ 333.1338, found 333.1331.

(*R*)-Methyl 4-(4-fluorophenyl)-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-oxobutanoate (**7d**):[5h] White solid,

28.8 mg, 90% yield. m.p. 154.9～156.2 ℃; $[\alpha]_D^{20}$ +13.6 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=13.3 min (major), 20.9 min (minor); ^{1}H NMR (400 MHz, CDCl3) δ: 7.19～7.09 (m, 2.01H), 6.97～6.90 (m, 2H), 4.92 (s, 0.63H), 4.55 (s, 0.32H), 4.05～4.02 (m, 0.33H), 3.91～3.86 (m, 0.70H), 3.84 (s, 0.97H), 3.75 (s, 1.97H), 2.58～2.15 (m, 6.25H), 2.11～1.95 (m, 2.20H); HRMS calcd for $C_{17}H_{18}FO_5$ $[M+H]^+$ 321.1138, found 321.1129.

(*R*)-Methyl 4-(4-chlorophenyl)-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-oxobutanoate (**7e**):[5h] White solid, 30.6 mg, 91% yield. m.p. 159.0～160.3 ℃; $[\alpha]_D^{20}$ −12.3 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=15.0 min (major), 22.2 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23～7.19 (m, 2H), 7.09～7.07 (m, 2H), 5.13 (s, 0.67H), 4.74 (s, 0.33H), 4.02～4.00 (m, 0.34H), 3.89～3.87 (m, 0.63H), 3.84 (s, 1.02H), 3.74 (s, 1.97H), 2.58～2.13 (m, 6.23H), 2.09 ～ 1.97 (m, 2.16H); HRMS calcd for $C_{17}H_{18}ClO_5$ $[M+H]^+$ 337.0843, found 3337.0836.

(*R*)-Methyl 4-(4-bromophenyl)-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-oxobutanoate (**7f**):[5h] White solid, 35.0 mg, 92% yield. m.p. 143.2～144.3 ℃; $[\alpha]_D^{20}$ −11.4 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=15.8 min (major), 24.0 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.34 (m, 2H), 7.06～7.03 (m, 2H), 4.64 (s, 0.57H), 4.37 (s, 0.27H), 4.02 (d, *J*=6.8 Hz, 0.35H), 3.88～3.80 (m, 3.73H), 2.57～2.16 (m, 6H), 2.08～1.97 (m, 2H); HRMS calcd for $C_{17}H_{18}BrO_5$ $[M+H]^+$ 381.0338, found 381.0332.

(*S*)-Methyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-(thiophen-2-yl)butanoate (**7g**):[5h] White solid, 26.2 mg, 85% yield. m.p. 159.0～160.6 ℃; $[\alpha]_D^{20}$ +36.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=44.1 min (major), 52.5 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (ddd, *J*=16.4, 4.8, 1.2 Hz, 1H), 6.89～6.85 (m, 1H), 6.80～6.78 (m, 1H), 4.93 (s, 0.55H), 4.44 (s, 0.39H), 4.39～4.38 (m, 0.48H), 4.27～4.23 (m, 0.62H), 3.86 (s, 1.39H), 3.71 (s, 1.81H), 2.60～2.37 (m, 5.39H), 2.33～2.24 (m, 1.40H), 2.10～1.97 (m, 2.36H); HRMS calcd for $C_{15}H_{17}O_5S$ $[M+H]^+$ 309.0797, found 309.0789.

(*R*)-Methyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-4-(naphthalen-2-yl)-2-oxobutanoate (**7h**):[5h] White solid, 30.3 mg, 86% yield. m.p. 182.9～184.1 ℃; $[\alpha]_D^{20}$ −40.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=20.4 min (major), 30.8 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77～7.72 (m, 3H), 7.58 (d, *J*=17.6 Hz, 1H), 7.43～7.28 (m, 3H), 4.66 (s, 0.59H), 4.30 (m, 0.74H), 4.06 (t, *J*=9.2 Hz, 0.72H), 3.84 (s, 1H), 3.72 (s, 2H), 2.63～2.29 (m, 6H), 2.17～2.00 (m, 2H); HRMS calcd for $C_{21}H_{21}O_5$ $[M+H]^+$ 353.1389, found 353.1382.

(*R*)-Benzyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-phenylbutanoate (**7i**): White solid, 36.7 mg, 97% yield. m.p. 154.8～155.6 ℃; $[\alpha]_D^{20}$ +16.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=17.3 min (major), 27.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.21 (m, 7.35H), 7.16～7.13 (m, 3H), 5.24～5.02 (m, 2.06H), 4.92 (s, 0.58H), 4.51 (s, 0.33H), 4.03～4.05 (m, 0.35H), 3.91～3.87 (m, 0.65H), 2.59～2.19 (m, 6.18H), 2.05～1.95 (m, 2.15H); HRMS calcd for $C_{23}H_{23}O_5$ $[M+H]^+$ 379.1545, found 379.1538.

(*R*)-Methyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-phenylbutanoate (**8a**):[12] White solid, 31.4 mg, 95% yield. m.p. 141.5～143.0 ℃; $[\alpha]_D^{20}$ −14.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=14.1 min (major), 25.6 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20～7.16 (m, 2.44H), 7.10～7.05 (m, 3H), 4.74 (s, 0.60H), 4.34 (s, 0.32H), 3.98～4.00 (m, 0.35H), 3.84～3.79 (m, 0.71H), 3.76 (s, 1.02H), 3.62 (d, *J*=0.8 Hz, 1.95H), 2.51～2.12 (m, 6.35H), 1.11 (d, *J*=8.0 Hz, 3.16H), 1.02 (d, *J*=8.4 Hz, 3.23H); HRMS calcd for $C_{19}H_{23}O_5$ $[M+H]^+$ 331.1545, found 331.1538.

(*R*)-Methyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-(p-tolyl)butanoate (**8b**):[12] White solid, 31.7 mg, 92% yield. m.p. 136.1～137.2 ℃; $[\alpha]_D^{20}$ −20.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=16.1 min (major), 25.0 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.00～6.94 (m, 4H), 4.75 (s, 0.60H), 4.36 (s, 0.36H), 3.96 (m, 0.39H), 3.80～3.77 (m, 0.72H), 3.76 (s, 1.07H), 3.63 (d, *J*=3.6 Hz, 1.92H), 2.48～2.23 (m, 3.72H), 2.20 (d, *J*=2.0 Hz, 3.10H), 2.18～2.11 (m, 2.70H), 1.10 (d, *J*=8.8 Hz, 3.18H), 1.01 (d, *J*=9.2 Hz, 3.19H); HRMS calcd for $C_{20}H_{25}O_5$ $[M+H]^+$ 345.1702, found 345.1696.

(*R*)-Methyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-4-(4-methoxyphenyl)-2-oxobutanoate (**8c**):[12] White solid, 33.5 mg, 93% yield. m.p. 135.0～135.9 ℃; $[\alpha]_D^{20}$ −19.4 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=15.2 min (major), 30.3 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03～6.98 (m, 2H), 6.75～6.72 (m, 2H), 4.49 (s, 0.60H), 4.18 (s, 0.40H), 3.98 (d, *J*=6.4 Hz, 0.40H), 3.80～3.76 (m, 1.82H), 3.69～3.68 (m, 4.86H), 2.48～2.09 (m, 6.19H), 1.10 (d, *J*=10.8 Hz, 3.10H), 1.02 (d, *J*=13.6 Hz, 3.05H); HRMS calcd for $C_{20}H_{25}O_6$ $[M+H]^+$ 361.1651, found 361.1644.

(*R*)-Methyl 4-(4-fluorophenyl)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-oxobutanoate (**8d**):[12] White solid, 32.7 mg, 94% yield. m.p. 175.8～177.2 ℃; $[\alpha]_D^{20}$ +2.0 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=11.2 min (major), 23.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07～7.02 (m, 2H), 6.90～6.83 (m, 2H), 3.99～3.98 (m, 0.54H), 3.83～3.79 (m, 1.78H), 1.89 (s, 1.89H), 2.51～2.13 (m, 6.36H), 1.10 (d, *J*=11.2 Hz, 3.05H), 1.02 (d, *J*=8.4 Hz, 3.30H); HRMS calcd for $C_{19}H_{22}FO_5$ $[M+H]^+$ 349.1451, found 349.1443.

(*R*)-Methyl 4-(4-chlorophenyl)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-oxobutanoate (**8e**):[12] White solid, 33.1 mg, 91% yield. m.p. 161.0～162.9 ℃;

$[\alpha]_D^{20}$ −21.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=12.1 min (major), 25.0 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25～7.19 (m, 2H), 7.10～7.09 (m, 2H), 4.51 (s, 0.61H), 4.29 (s, 0.36H), 4.05～4.03 (m, 0.39H), 3.88～3.84 (m, 1.75H), 3.80 (s, 1.91H), 2.58～2.16 (m, 6.35H), 1.17 (d, *J*=12.0 Hz, 3.15H), 1.09 (d, *J*=8.4 Hz, 3.15H); HRMS calcd for $C_{19}H_{22}ClO_5$ $[M+H]^+$ 365.1156, found 365.1150.

(*R*)-Methyl 4-(4-bromophenyl)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-oxobutanoate (**8f**):[12] White solid, 37.1 mg, 91% yield. m.p. 152.3～153.9 ℃; $[\alpha]_D^{20}$ −30.4 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=12.7 min (major), 26.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.35 (m, 2H), 7.04 (d, *J*=8.0 Hz, 2H), 4.49 (s, 0.61H), 4.31 (t, *J*=6.8 Hz, 0.30H), 4.02 (d, *J*=8.8 Hz, 0.39H), 3.86～3.81 (m, 3.72H), 2.58～2.20 (m, 6H), 1.16 (d, *J*=12.0 Hz, 3H), 1.09 (d, *J*=8.0 Hz, 3H); HRMS calcd for $C_{19}H_{22}BrO_5$ $[M+H]^+$ 409.0651, found 409.0643.

(*S*)-Methyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-*oxo*-4-(thiophen-2-yl)butanoate (**8g**): White solid, 29.2 mg, 87% yield. m.p. 144.0～145.3 ℃; $[\alpha]_D^{20}$ +20.8 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=24.1 min (major), 28.6 min (minor); 1H NMR (400 MHz, $CDCl_3$) δ: 7.02 (dd, *J*=13.6, 4.2 Hz, 1H), 6.82～6.79 (m, 1H), 6.74～6.73 (m, 1H), 4.60 (s, 0.49H), 4.30～4.28 (m, 0.90H), 4.18 (t, *J*=8.0 Hz, 0.55H), 3.79 (s, 1.37H), 3.65 (s, 1.63H), 2.47～2.16 (m, 6H), 1.11 (d, *J*=6.0 Hz, 3H), 1.02 (d, *J*=7.6 Hz, 3H); HRMS calcd for $C_{17}H_{21}O_5S$ $[M+H]^+$ 337.1110, found 337.1103.

(*R*)-Methyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-4-(naphthalen-2-yl)-2-oxobutanoate (**8h**): White solid, 31.9 mg, 84% yield. m.p. 133.2～134.4 ℃; $[\alpha]_D^{20}$ −40.6 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=18.0 min (major), 24.3 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69～7.65 (m, 3.03H), 7.50 (s, 1H), 7.35～7.17 (m, 3.46H), 4.14 (s, 0.44H), 3.97 (t, *J*=8.4 Hz, 0.72H), 3.74 (s, 0.99H), 3.54 (s, 1.95H), 2.56～2.09 (m, 6.13H), 1.14 (d, *J*=11.2 Hz, 3.23H), 1.02 (d, *J*=13.2 Hz, 3.21H); HRMS calcd for $C_{23}H_{25}O_5$ $[M+H]^+$ 381.1702, found 381.1695.

(*R*)-Benzyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-oxo-4-phenylbutanoate (**8i**):[13] White solid, 38.2 mg, 94% yield. m.p. 140.3～141.6 ℃; $[\alpha]_D^{20}$ −12.0 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=17.9 min (major), 32.2 min (minor); 1H NMR (400 MHz, CDCl3) δ: 7.28～7.15 (m, 7.53H), 7.09～7.05 (m, 3H), 5.17～4.93 (m, 2.08H), 3.96 (s, 0.41H), 3.82 (t, *J*=8.4 Hz, 0.64H), 2.52～2.07 (m, 5.99H), 1.08 (d, *J*=4.0 Hz, 3.01H), 0.99 (d, *J*=3.2 Hz, 3.19H); HRMS calcd for $C_{25}H_{27}O_5$ $[M+H]^+$ 407.1858, found 407.1851.

(*R*)-Ethyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-oxo-4-phenylbutanoate (**8j**):[5e] White solid, 32.7 mg, 95% yield. m.p. 117.8～118.9 ℃; $[\alpha]_D^{20}$ −3.0 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=15.8 min (major), 29.5 min (minor); ^{1}H NMR (400 MHz, CDCl3) δ: 7.29～7.23 (m, 2H), 7.18～7.16 (m, 3H), 4.57 (s, 0.60H), 4.32～4.15 (m, 2.43H), 4.09 (d, *J*=5.6 Hz, 0.30H), 3.89 (t, *J*=9.2 Hz, 0.70H), 1.34～1.26 (m, 3H), 1.20 (s, 1.06H), 1.17 (s, 1.94H), 1.11 (s, 1.06H), 1.09 (s, 1.94H); HRMS calcd for $C_{20}H_{25}O_5$ $[M+H]^+$ 345.1702, found 345.1696.

(*S*)-Ethyl 4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-oxohexanoate (**8k**):[5e] Colourless oil; 27.5 mg, 93% yield. $[\alpha]_D^{20}$ +20.4 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V* = 85/15, flow rate = 0.6 mL/min, λ = 254 nm): t_R = 11.3 min (major), 20.0 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.52 (s, 0.59H), 4.32～4.27 (m, 2.35H), 2.72～2.60 (m, 0.97H), 2.28～2.23 (m, 4H), 2.11 (m, 1.22H), 2.01～1.97 (m, 0.85H), 1.33～1.25 (m, 4.73H), 1.07～1.05 (m, 6H), 0.94～0.83 (m, 3.46H); HRMS (*m*/*z*): calcd for $C_{16}H_{25}O_5$ $[M+H]^+$ 297.1702, found 297.1694.

(*R*)-Methyl 4-(2-hydroxy-7-oxocyclohept-1-en-1-yl)-2-*oxo*-4-phenylbutanoate (**9**):[12] White solid, 29.4 mg, 93% yield. m.p. 108.9～110.2 ℃; $[\alpha]_D^{20}$ −1.8 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V* = 80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=14.3 min (major), 20.9 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26～7.21 (m, 2H), 7.18～7.12 (m, 3H), 4.82 (s, 0.65H), 4.36 (s, 0.35H), 4.24～4.23 (m, 0.35H), 4.03 (t, *J*=8.8 Hz, 0.65H), 3.82 (s, 1H), 3.66 (s, 2H), 2.73～2.46 (m, 5H), 2.30～2.14 (m, 2H), 1.88～1.77 (m, 3H); HRMS (*m*/*z*): calcd for $C_{18}H_{21}O_5$ $[M+H]^+$ 317.1389, found 317.1380.

(*R*)-Methyl 4-(4-hydroxy-2-*oxo*-2*H*-chromen-3-yl)-2-*oxo*-4-phenylbutanoate (**10**): White solid, 31.7 mg, 90% yield. m.p. 182.0～183.5 ℃; $[\alpha]_D^{20}$ −9.2 (*c* 1.0, CH_2Cl_2); HPLC: Chiralpak AD-H (hexanes/*i*-PrOH, *V*/*V*=80/20, flow rate=0.6 mL/min, λ=254 nm): t_R=19.1 min (major), 36.9 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J*=8.0 Hz, 0.32H), 7.78 (d, *J*=8.0 Hz, 0.63H), 7.59～7.51 (m, 1H), 7.37～7.19 (m, 7H), 4.76 (s, 0.63H), 4.51 (s, 0.32H), 4.34 (dd, *J*=3.2, 7.2 Hz, 0.34H), 4.20 (t, *J*=8.8 Hz, 0.75H), 3.91～3.88 (m, 3H), 2.79 (dd, *J*=7.2, 14.4 Hz, 0.36H), 2.54 (dd, *J*=3.2, 14.4 Hz, 0.38H), 2.46 (d, *J*=9.2 Hz, 1.35H); HRMS calcd for $C_{20}H_{17}O_6$ $[M+H]^+$ 353.1025, found 353.1017.

Supporting Information NMR spectra of tertiary amine-squaramide **2**, NMR and HPLC spectra of Michael adducts **7a**～**7i**, **8a**～**8k**, **9** and **10**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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