RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2020, **10**, 44437

Enantioselective one-pot synthesis of 4*H*-chromene derivatives catalyzed by a chiral Ni(II) complex†

Xuan Yu, Wenjie Lan, Jiaqi Li, Hui Bai, Zhaohai Qin and Bin Fu*

Received 19th October 2020
Accepted 16th November 2020

DOI: 10.1039/d0ra08906k

rsc.li/rsc-advances

A Ni(II)–bis(oxazoline) complex and *p*-TSOH are used to form enantioenriched 4*H*-chromenes from *ortho*-quinone methides (*o*-QMs) and dicarbonyls, providing the desired products in up to 95% ee. The method is compatible with various β-ketoester substrates, and the products obtained could be converted into biologically active 4*H*-chromene derivatives.

The chromene skeleton is widespread in natural products and medicinal agents,[1] and the diverse biological activities[2] of chromene derivatives have intrigued pharmacologists and chemists. In particular, 4*H*-chromene is a privileged core structure that has received increasing attention in recent years. Natural and synthetic functionalized 4*H*-chromenes (Fig. 1) display a broad spectrum of biological activities,[3] including as cell-proliferation inhibitors (**A**), apoptosis inducers (**B**), and neuropeptide Y Y5 receptor antagonists (**C**), as well as improving cognitive deficit (**D**).

Over the past decade, extensive efforts have been devoted to the synthesis of 4*H*-chromene compounds. Most of the synthetic methods furnished racemic products,[4,5] though enantioselective routes have recently been developed. In 2009 and 2011, Xie *et al.* and Wang *et al.*[6] respectively, reported the organocatalytic synthesis of chiral 2-amino-4*H*-chromene derivatives from malononitrile. In 2011, Feng *et al.*[7] explored the first Lewis acid-catalyzed one-pot synthesis of enantioenriched 2-amino-4*H*-chromenes bearing indolyl moieties from malononitrile, salicylaldehyde and indole. In 2014, Schneider *et al.*[8] found the reaction of *ortho*-hydroxyl benzhydryl alcohols with β-diketones was catalyzed by a chiral phosphoric acid (CPA), giving rise to 4*H*-chromenes in high yield with excellent enantioselectivities (up to 98% ee); however, when the substrate was changed to ethyl acetoacetate, the ee value dropped to 84%. Subsequently, Rueping *et al.*[9] employed a chiral binol based *N*-trifly phosphoramide to promote the *in situ* generation of *ortho*-quinone methides (*o*-QMs) and their subsequent reaction with 1,3-cyclohexanedione, providing the desired 4*H*-chromene products with excellent enantioselectivities (up to 95% ee). In 2017, the Schneider group reported the oxidation of 2-alkyl-substituted phenols *in situ* by $Mn(dbm)_3$ (dbm = dibenzoylmethane) to give *o*-QMs that, upon the CPA-catalyzed conjugate addition of β-dicarbonyls, afforded 4*H*-chromenes in up to 79% yield and up to 74% ee,[10] indicating that the substrate structures have a remarkable influence on the reaction. Despite these notable advances, efficient and concise methods for the enantioselective synthesis of 4*H*-chromenes are still limited and highly desirable.

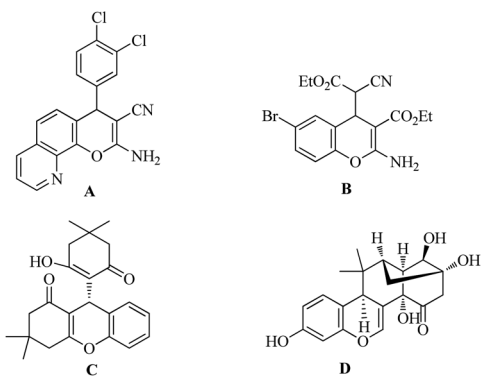


Fig. 1 Natural and synthetic bioactive 4*H*-chromene compounds.

o-QMs have been extensively applied in Michael additions and cycloadditions.[11,12] The reaction of some dicarbonyls with *o*-QMs generates chromene derivatives, and particularly the use of β-diketones has been well studied.

However, few reports mention the use of asymmetric catalysis to construct 4*H*-chromenes from β-ketoesters.[8,13] As part of a continuing effort to develop efficient catalytic asymmetric methods using readily available catalyst systems,[14] we explored the reaction of β-ketoesters with *o*-QMs catalyzed by a Ni(II)–bis(oxazoline) complex and subsequent *p*-TSOH, which gave 4*H*-chromenes in good yields and up to 95% ee. This one-pot, three-step sequence of enantioselective Michael addition, intramolecular ketalization and dehydration, was accomplished

Department of Applied Chemistry, China Agricultural University, West Yuanmingyuan Rd. 2, Beijing 100193, People's Repubic of China. E-mail: fubinchem@cau.edu.cn; Fax: +86-10-62730243; Tel: +86-10-62730243

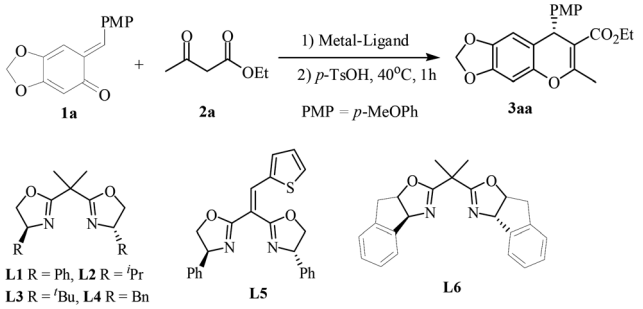
† Electronic supplementary information (ESI) available. CCDC 1941671. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra08906k

under mild conditions. The products could be transformed into potentially bioactive 4*H*-chromene compounds.

At the outset, *ortho*-quinone methide (*o*-QMs) **1a** (PMP = *p*-MeOPh) and ethyl acetoacetate **2a** were chosen as model substrates. The reaction was carried out in $CHCl_3$ at 0 °C in the presence of different metal complexes of ligand **L1**. For various Lewis acids including $Cu(OTf)_2$, $Mg(OTf)_2$, $Zn(OTf)_2$, $Ni(OTf)_2$ and $Ni(ClO_4)_2$, the reaction proceeded to completion within 5 minutes and giving product **3aa** in moderate to high yields (Table 1, entries 1–5). To our delight, $Ni(OTf)_2$ afforded the highest enantioselectivity (90% ee, entry 4). Encouraged by this result, the effect of solvent was tested. Other solvents did not show any positive effect on the reaction reactivity. Even the reaction was almost suppressed in tetrahydrofuran (THF) (Table 1, entry 8). Subsequently, different ligands were examined. No better results were achieved by $Ni(OTf)_2$ complexes of other bis(oxazoline) ligands. As expected, when lowering the reaction temperature to −40 °C the enantioselectivity could be improved to 95% ee regardless of a longer reaction time (entry 16). When the catalyst loading was reduced to 5 mol%, the reactivity was somewhat decreased although the enantioselectivity still remained (entry 17). The detailed screening data are illustrated in ESI.†

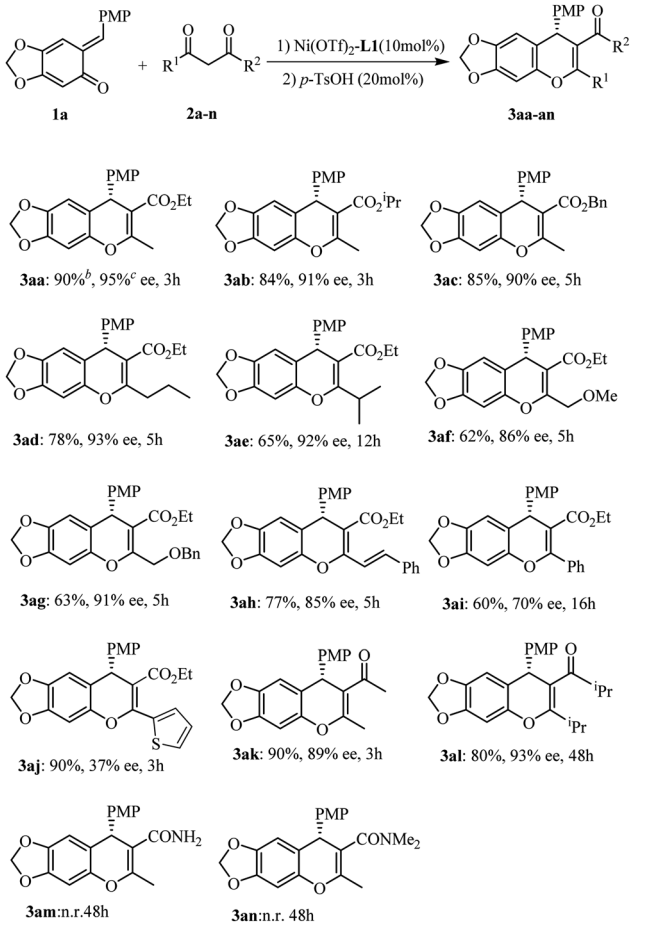
Initial optimization employing *ortho*-QM **1a** and ethyl acetoacetate **2a** provided **3aa** in 90% yield with 95% ee when the reaction was carried out at −40 °C in $CHCl_3$ using 10 mol% $Ni(OTf)_2$ and 11 mol% of the bis(oxazoline) **L1** (Scheme 1); thus we used these conditions to explore the reaction scope for β-dicarbonyl substrates (Scheme 1). The iso-propyl or benzyl acetoacetate reacted with *o*-quinone methide to furnish 4*H*-chromenes **3ab** and **3ac** in high yields and ee values similar to those obtained with the ethyl ester. β-Alkyl-substituents on the β-ketoesters were well tolerated, and a high level of enantioselectivity (86–93% ee for **3ad–3ag**) was observed. Even a β-styrenyl substituted β-ketoester was also a suitable substrate, affording chromene **3ah** in 84% ee. Regrettably, when β-aryl-substituted β-ketoesters **2i** and **2j** were used, the product was obtained with markedly lower ee (70% ee for **3ai** and 37% ee for **3aj**). Moreover, the same high enantioselectivities were obtained from chain β-diketones, giving rise to **3ak** and **3al** in 89% and 93% ee. However, in the case of 1,3-cyclohexanedione only the racemic 4*H*-chromene was obtained. In addition, considering

Table 1 Optimization of the reaction condition[a]

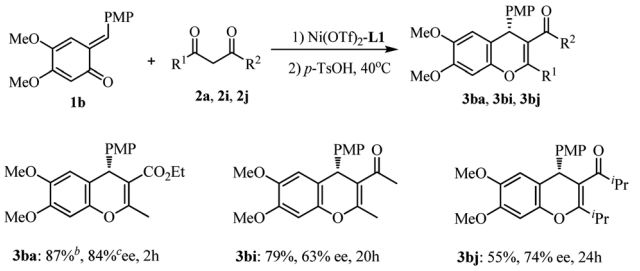


Entry	Ligand	Ni(II)	Solvent	Time	Yield[b] (%)	Ee[c] (%)
1	**L1**	$Cu(OTf)_2$	$CHCl_3$	5 min	77	30
2	**L1**	$Mg(OTf)_2$	$CHCl_3$	5 min	65	6
3	**L1**	$Zn(OTf)_2$	$CHCl_3$	5 min	84	36
4	**L1**	$Ni(OTf)_2$	$CHCl_3$	5 min	85	90
5	**L1**	$Ni(ClO_4)_2$	$CHCl_3$	5 min	54	67
6	**L1**	$Ni(OTf)_2$	Toluene	5 min	56	90
7	**L1**	$Ni(OTf)_{22}$	CH_2Cl_2	5 min	73	69
8	**L1**	$Ni(OTf)_2$	THF	5 min	Trace	—
9	**L1**	$Ni(OTf)_{22}$	EtOAc	5 min	46	88
10	**L2**	$Ni(OTf)_2$	$CHCl_3$	5 min	67	60
11	**L3**	$Ni(OTf)_2$	$CHCl_3$	5 min	79	20
12	**L4**	$Ni(OTf)_2$	$CHCl_3$	5 min	66	55
13	**L5**	$Ni(OTf)_2$	$CHCl_3$	5 min	88	52
14	**L6**	$Ni(OTf)_{22}$	$CHCl_3$	5 min	75	26
15[d]	**L1**	$Ni(OTf)_2$	$CHCl_3$	1 h	87	92
16[e]	**L1**	**$Ni(OTf)_2$**	**$CHCl_3$**	**3 h**	**90**	**95**
17[f]	**L1**	$Ni(OTf)_2$	$CHCl_3$	5 h	78	95

[a] All reactions were carried out in solvent (1.5 mL) using 10 mol% metal salt and 11 mol% ligand under nitrogen for indicated time before *p*-TSOH (20 mol%) was added at 40 °C. [b] Isolated yields. [c] Determined by HPLC. [d] −20 °C. [e] −40 °C. [f] 5 mol% catalyst at −40 °C.



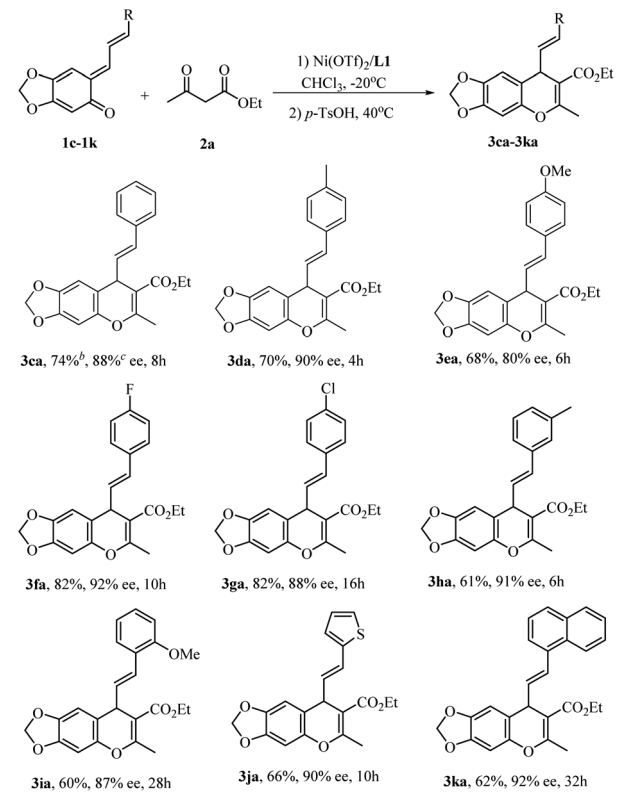
Scheme 1 The scope of β-dicarbonyls. [a]All reactions were conducted in $CHCl_3$ (1.5 mL) using $Ni(OTf)_2$ (10 mol%) and **L1** (11 mol%) at −40 °C under nitrogen for the indicated time before *p*-TSOH (20 mol%) was added at 40 °C; [b]isolated yields. [c]Determined by HPLC.



Scheme 2 The scope of *o*-QMs. [a]All reactions were conducted using $Ni(OTf)_2$ (10 mol%) and **L1** (11 mol%) in $CHCl_3$ (1.5 mL) at −40 °C under nitrogen for the indicated time before *p*-TSOH (20 mol%) was added at 40 °C; [b]isolated yields; [c]determined by HPLC.

the structural similarity with β-ketoesters, β-keto amides as substrates were also subjected to the above reaction condition, regrettably, the reaction didn't occur.

We next turned our attention to varying the *o*-QMs. Dimethoxy-substituted *o*-QM **1b** was evaluated under optimal conditions (Scheme 2), In the case of ethyl acetacetate, the reaction was complete at −40 °C within 2 h, and subsequent treatment with TsOH led to the annulation product **3ba** in 87% yield and 84% ee. However the reaction of **1b** with β-diketones required much longer time (20–24 h) and was less stereoselective (63% and 74% ee for **3bi** and **3bj**). Thus it is deducted that the substituents on both the quinone ring of the *o*-QMs and



Scheme 3 The extension to vinyl *o*-QMs. [a]All reactions were conducted using $Ni(OTf)_2$ (10 mol%) and **L1** (11 mol%) in $CHCl_3$ (1.5 mL) at −20 °C under nitrogen for the indicated time before *p*-TSOH (20 mol%) was added at 40 °C. [b]Isolated yields. [c]Determined by HPLC.

β-ketoester substrates have a remarkable impact on the reactivity and enantioselectivity.

The substrate scope could be expanded to other stable vinyl *o*-QMs.[15] At −40 °C the reaction of α-substituted vinyl *o*-QMs with ethyl acetoacetate occurred very sluggishly, but upon raising the temperature to −20 °C, a series of α-substituted vinyl *o*-QMs could be used, as shown in Scheme 3. Substituted vinyl *o*-QMs containing electron-withdrawing groups (**1f–1h**) were incorporated into chromenes in much higher yield than those bearing electron-donating groups (**1d**, **1e**, and **1i**). For all cases, good to high enantioselectivities were achieved (80–92% ee, **3ca–3ia**). Vinyl *o*-QMs with thienyl or naphthyl rings on the olefin were also suitable reactants and provided the desired products **3ja** and **3ka** in moderate yields with high enantioselectivities (90% and 92% ee).

On the basis of X-ray diffraction analysis, the single crystal of compound **3ab** was determined to be *S* (Fig. 2),[16] and the configuration of other products was also assigned by analogy. Considering the observed stereochemistry, a plausible asymmetric induction model was proposed (Fig. 2). The coordination of bisoxazoline ligand **L1** to a $Ni(OTf)_2$ resulted in a Ni(II)–**L1** complex, which interacted with acetoacetate to form an enolate. Simultaneously, the *o*-QMs **1a** also coordinated to the Ni(II) center from the axial direction. Steric congestion between the *p*-methoxyphenyl group of **1a** and the phenyl substituent of ligand **L1** disfavors an approach of the enolized acetoacetate to *o*-QMs from the *Si*-face, so the major product is formed from *Re*-face addition and subsequent treatment with *p*-TSOH form the *S*-isomer. Given the lower enantioselectivity afforded by β-aryl-substituted ketoesters in contrast to the corresponding alkyl group substrates, it is deducted that π–π stacking may be unfavorable for the asymmetric induction in the Michael addition step. The detailed mechanism remains to be further investigated.

The catalyst system was used to synthesize product **3aa** on a gram scale, in 85% yield and without compromising enantioselectivity (Scheme 4a). Treatment of product **3aa** with DIBALH (2.5 equiv.) in CH_2Cl_2 at −78 °C generated the corresponding alcohol **4**, which is an important intermediate; for example, subsequent reaction with DPPA/DBU resulted in azide

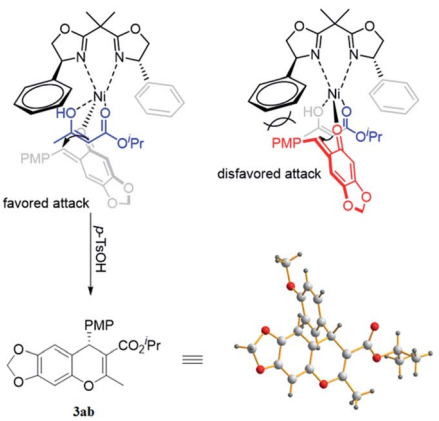
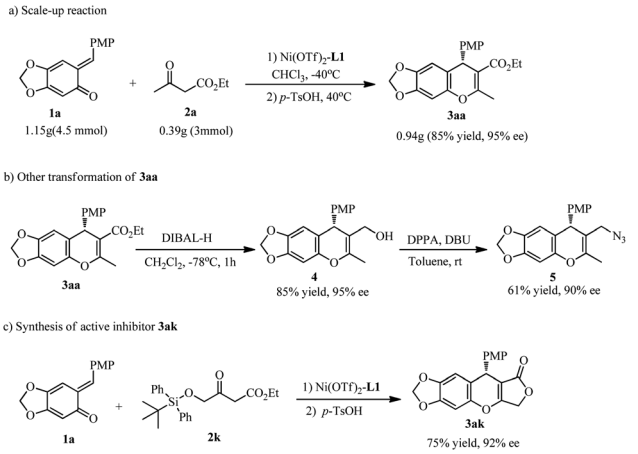


Fig. 2 Stereochemical induction model.



Scheme 4 The scale-up reaction and transformation of the products.

compound **5** with a slight loss of enantiopurity (Scheme 4b, 90% ee).

Finally, attempts to employ the β-silyloxymethylene-substituted β-ketoester **2k** led to the discovery of an unexpected cascade reaction that yielded a pharmaceutically interesting molecule. Following the conjugate addition under standard conditions and treatment with *p*-TsOH, the chromene lactone **3ak** was produced in 75% yield with 92% ee (Scheme 4c). Replacing the *p*-TsOH with other Brønsted acid or Lewis acids always yielded an intramolecular ketalization/dehydration accompanied by the deprotection of siloxyl group and subsequent intramolecular nucleophilic addition–elimination to give **3ak**. To the best our knowledge, this is a rare example of one-pot five-step reaction under mild conditions. The racemate of **3ak** is a potential inhibitor of tumor growth.[2f]

In conclusion, the Ni(OTf)$_2$/bis(oxazoline)-catalyzed asymmetric conjugate addition of β-dicarbonyls to *o*-QMs followed by treatment of *p*-TsOH generated 4*H*-chromenes in up to 95% ee. In particular, this method is amenable to the reaction of β-ketoesters, which well complements previous reports involving only 1,3-diketone substrates in this type of reaction.[8–10] Moreover, the catalytic products could be converted into biologically active and even pharmaceutically valuable 4*H*-chromene derivatives. Further application of this methodology is underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21572265, 21172255) and the Ministry of Science and Technology of China (No. 2015BAK45B01) for the financial support.

Notes and references

1 (*a*) W. S. Faraci and C. T. Walsh, *Biochemistry*, 1989, **28**, 431; (*b*) G. P. Ellis and I. M. Lockhart, in *The Chemistry of Heterocyclic Compounds, Chromenes, Chromanones, and Chromones*, ed. G. P. Ellis, Wiley-VCH, Weinheim, 2007, vol. 31, pp. 1–1196; (*c*) Y. Kashiwada, K. Yamazaki, Y. Ikeshiro, T. Yamagishi, T. Fujioka, K. Mihashi, K. Mizuki, L. M. Cosentino, K. Fowke, S. L. Morris-Natschke and K. H. Lee, *Tetrahedron*, 2001, **57**, 1559; (*d*) Y. Dong, K. Nakagawa-Goto, C.-Y. Lai, S. L. Morris-Natschke, K. F. Bastow, Y. Kim, E. Y.-H. P. Lee and K.-H. Lee, *J. Nat. Prod.*, 2012, **75**, 370; (*e*) M. Azizmohammadi, M. Khoobi, A. Ramazani, S. Emami, A. Zarrin, O. Firuzi, R. Miri and A. Shafiee, *Eur. J. Med. Chem.*, 2013, **59**, 15; (*f*) Y. L. N. Murthy, K. P. Suhasini, A. S. Pathania, S. Bhushan and Y. Nagendra Sastry, *Eur. J. Med. Chem.*, 2013, **62**, 545; (*g*) J. Mun, A. A. Jabbar, N. S. Devi, S. Yin, Y. Wang, C. Tan, D. Culver, J. P. Snyder, E. G. V. Meir and M. M. Goodman, *J. Med. Chem.*, 2012, **55**, 6738.

2 (*a*) K. C. Nicolaou, J. A. Pfefferkorn, A. J. Roecker, G. Q. Cao, S. Barluenga and H. J. Mitchell, *J. Am. Chem. Soc.*, 2000, **122**, 9939; (*b*) I. R. Hardcastle, X. l. Cockcroft, N. J. Curtin, M. D. El-Murr, J. J. Leahy, M. Stockley, B. T. Golding, L. Rigoreau, C. Richardson, G. C. M. Smith and R. J. Griffin, *J. Med. Chem.*, 2005, **48**, 7829; (*c*) D. J. Maloney, S. X. Chen and S. M. Hecht, *Org. Lett.*, 2006, **8**, 1925; (*d*) M. Kidwai, S. Saxena, M. K. R. Khan and S. S. Thukral, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 4295; (*e*) D. Tian, S. G. Das, J. M. Doshi, J. Peng, J. Lin and C. Xing, *Cancer Lett.*, 2008, **259**, 198; (*f*) L. Jurd, *J. Heterocycl. Chem.*, 1996, **33**, 1227; (*g*) N. Majumdar, N. D. Paul, S. Mandal, B. de Bruin and W. D. Wulff, *ACS Catal.*, 2015, **5**, 2329.

3 (*a*) D. C. Peter and W. A. Caerwyn, EP0599514A2, appl. no. 93308999.7, 1993; (*b*) J.-L. Wang, D. X. Liu, Z.-J. Zhang, S. M. Shan, X. B. Han, S. M. Srinivasula, C. M. Croce, E. S. Alnemri and Z. W. Huang, *Proc. Natl. Acad. Sci. U. S. A.*, 2000, **97**, 7124; (*c*) N. Sato, M. Jitsuoka, T. Shibata, T. Hirohashi, K. Nonoshita, M. Moriya, Y. Haga, A. Sakuraba, M. Ando, T. Ohe, H. Iwaasa, A. Gomori, A. Ishihara, A. Kanatani and T. Fukami, *J. Med. Chem.*, 2008, **51**, 4765; (*d*) O. Monthakantirat, W. Sukano, K. Umehara, H. Noguchi, Y. Chulikhit and K. Matsumoto, *Phytomedicine*, 2014, **21**, 1249.

4 For selected examples of racemic 4*H*-chromene, see: (*a*) Y. L. Shi and M. Shi, *Org. Lett.*, 2005, **7**, 3057; (*b*) Y. W. Fang and C. Z. Li, *J. Org. Chem.*, 2006, **71**, 6427; (*c*) L. W. Ye, X. L. Sun, C. Y. Zhu and Y. Tang, *Org. Lett.*, 2006, **8**, 3853; (*d*) Y. L. Shi and M. Shi, *Chem.–Eur. J.*, 2006, **12**, 3374; (*e*) L. Shi and M. Shi, *Org. Biomol. Chem.*, 2007, **5**, 1499; (*f*) K. Funabiki, T. Komeda, Y. Kubota and M. Matsui, *Tetrahedron*, 2009, **65**, 7457; (*g*) C. J. Reddy, J. Vijaykumar and R. Grée, *Synthesis*, 2010, **21**, 3715; (*h*) D. B. Ramachary, Y. V. Reddy and M. Kishor, *Org. Biomol. Chem.*, 2008, **6**, 4188; (*i*) D. Liang, M. Wang, B. Bekturhun, B. Xiong and Q. Liu, *Adv. Synth. Catal.*, 2010, **352**, 1593; (*j*) Y. Liu, J. Qian, S. Lou, J. Zhu and Z. Xu, *J. Org. Chem.*, 2010, **75**, 1309; (*k*) C. C. Malakar, D. Schmidt, J. Conrad and U. Beifuss, *Org. Lett.*, 2011, **13**, 1972; (*l*) F. Wang, M. Qu, F. Chen, L. Li and M. Shi, *Chem. Commun.*, 2012, **48**, 437.

5 J. Fan and Z. Wang, *Chem. Commun.*, 2008, **44**, 5381.
6 (*a*) J. W. Xie, X. Huang, L. P. Fan, D. C. Xu, X. S. Li, H. Su and Y. H. Wen, *Adv. Synth. Catal.*, 2009, **351**, 3077; (*b*) Q. Ren, W. Y. Siau, Z. Y. Du, K. Zhang and J. Wang, *Chem.–Eur. J.*, 2011, **17**, 7781.
7 W. l. Chen, Y. f. Cai, X. Fu, X. H. Liu, L. L. Lin and X. M. Feng, *Org. Lett.*, 2011, **13**, 4910.
8 O. El-Sepelgy, S. Haseloff, S. K. Alamsetti and C. Schneider, *Angew. Chem., Int. Ed.*, 2014, **53**, 7923.
9 C.-C. Hsiao, H.-H. Liao and M. Rueping, *Angew. Chem., Int. Ed.*, 2014, **53**, 13258.
10 K. Gebauer, F. Reuß, M. Spanka and C. Schneider, *Org. Lett.*, 2017, **19**, 4588.
11 For selected examples of conjugate addition, see: (*a*) Y. Luan and S. E. Schaus, *J. Am. Chem. Soc.*, 2012, **134**, 19965; (*b*) W. Zhao, Z. Wang, B. Chu and J. Sun, *Angew. Chem., Int. Ed.*, 2015, **54**, 1910; (*c*) Z. Wang, F. Ai, Z. Wang, W. Zhao, G. Zhu, Z. Lin and J. Sun, *J. Am. Chem. Soc.*, 2015, **137**, 383; (*d*) A. A. Jaworski and K. A. Scheidt, *J. Org. Chem.*, 2016, **81**, 10145; (*e*) H. Huang and J. Y. Kang, *Org. Lett.*, 2017, **19**, 5988; (*f*) J.-L. Wu, J.-Y. Wang, P. Wu, G.-J. Mei and F. Shi, *Org. Chem. Front.*, 2017, **4**, 2465; (*g*) B. Wu, Z. Yu, X. Gao, Y. Lan and Y.-G. Zhou, *Angew. Chem., Int. Ed.*, 2017, **56**, 4006; (*h*) X. Gu, H. Yuan, J. Jiang, Y. Wu and W.-J. Bai, *Org. Lett.*, 2018, **20**, 7229.
12 For selected examples of recent cycloaddition, see: (*a*) H. Lv, L. You and S. Ye, *Adv. Synth. Catal.*, 2009, **351**, 2822; (*b*) J. Izquierdo, A. Orue and K. A. Scheidt, *J. Am. Chem. Soc.*, 2013, **135**, 10634; (*c*) C.-C. Hsiao, S. Raja, H.-H. Liao, I. Atodiresei and M. Rueping, *Angew. Chem., Int. Ed.*, 2015, **54**, 5762; (*d*) S. K. Alamsetti, M. Spanka and C. Schneider, *Angew. Chem., Int. Ed.*, 2016, **55**, 2392; (*e*) H. P. Hu, Y. B. Liu, J. Guo, L. L. Lin, Y. L. Xu, X. H. Liu and X.-M. Feng, *Chem. Commun.*, 2015, **51**, 3835; (*f*) J. Zhou, M.-L. Wang, X. Gao, G.-F. Jiang and Y.-G. Zhou, *Chem. Commun.*, 2017, **53**, 3531; (*g*) B. Yang and S. Gao, *Chem. Soc. Rev.*, 2018, **47**, 7926; (*h*) T. Zhou, T. Xia, Z. Liu, L. Liu and J. Zhang, *Adv. Synth. Catal.*, 2018, **360**, 4475; (*i*) B. Wu, M.-W. Chen, Z.-S. Ye, C.-B. Yu and Y.-G. Zhou, *Adv. Synth. Catal.*, 2014, **356**, 383; (*j*) M.-W. Chen, L.-L. Cao, Z.-S. Ye, G.-F. Jiang and Y.-G. Zhou, *Chem. Commun.*, 2013, **49**, 1660; (*k*) F. Jiang, G.-Z. Luo, Z.-Q. Zhu, C.-S. Wang, G.-J. Mei and F. Shi, *J. Org. Chem.*, 2018, **83**, 10060; (*l*) Y. Xie and B. List, *Angew. Chem., Int. Ed.*, 2017, **56**, 4936; (*m*) X. Wu, L. Xue, D. Li, S. Jia, J. Ao, J. Deng and H. Yan, *Angew. Chem., Int. Ed.*, 2017, **56**, 13722; (*n*) J. Zhang, L. Lin, C. He, Q. Xiong, X. Liu and X. Feng, *Chem. Commun.*, 2018, **54**, 74; (*o*) Z. Wang and J. Sun, *Org. Lett.*, 2017, **19**, 2334; (*p*) J.-J. Zhao, S.-B. Sun, S.-H. He, Q. Wu and F. Shi, *Angew. Chem., Int. Ed.*, 2015, **54**, 5460; (*q*) G.-J. Mei, Z.-Q. Zhu, J.-J. Zhao, C.-Y. Bian, J. Chen, R.-W. Chen and F. Shi, *Chem. Commun.*, 2017, **53**, 2768; (*r*) H. Lv, W.-Q. Jia, L.-H. Sun and S. Ye, *Angew. Chem., Int. Ed.*, 2013, **52**, 8607; (*s*) Y.-H. Deng, W.-D. Chu, X.-Z. Zhang, X. Yan, K.-Y. Yu, L.-L. Yang, H. Huang and C.-A. Fan, *J. Org. Chem.*, 2017, **82**, 5433; (*t*) Y.-B. Shen, S.-S. Li, X. C. Liu, L. Yu, Y.-M. Sun, Q. Liu and J. Xiao, *J. Org. Chem.*, 2019, **84**, 3990; (*u*) S. Zhang, X. J. Yu, J. K. Pan, C. H. Jiang, H. S. Zhang and T. L. Wang, *Org. Chem. Front.*, 2019, **6**, 3799–3803.
13 L. Caruana, M. Mondatori, V. Corti, S. Morales, A. Mazzanti, M. Fochi and L. Bernardi, *Chem.–Eur. J.*, 2015, **21**, 6037.
14 (*a*) L. Liu, H.-L. Ma, Y.-M. Xiao, F.-P. Du, Z. H. Qin, N. Li and B. Fu, *Chem. Commun.*, 2012, **48**, 9281; (*b*) H.-L. Ma, J.-Q. Li, L. Sun, X.-H. Hou, Z. H. Zhang and B. Fu, *Tetrahedron*, 2015, **71**, 3625; (*c*) X. Hou, H. Ma, Z. Zhang, L. Xie, Z. Qin and B. Fu, *Chem. Commun.*, 2016, **52**, 1470; (*d*) H. Ma, L. Xie, Z. Zhang, J.-Q. Li, Z. Qin and B. Fu, *Adv. Synth. Catal.*, 2016, **358**, 1011; (*e*) L. Xie, X. Yu, J.-Q. Li, Z. H. Zhang, Z. Qin and B. Fu, *Eur. J. Org. Chem.*, 2017, 657; (*f*) H.-L. Ma, L. Xie, Z.-H. Zhang, L.-G. Wu, B. Fu and Z. H. Qin, *J. Org. Chem.*, 2017, **82**, 7353; (*g*) L. Xie, H.-L. Ma, J.-Q. Li, X. Yu, Z. H. Qin and B. Fu, *Org. Chem. Front.*, 2017, **4**, 1858.
15 (*a*) J.-l. Zhang, X. H. Liu, S. S. Guo, C. Q. He, W. l. Xiao, L. Lin and X. M. Feng, *J. Org. Chem.*, 2018, **83**, 10175; (*b*) C.-S. Wang, Y.-C. Cheng, J. Zhou, G.-J. Mei, S.-L. Wang and F. Shi, *J. Org. Chem.*, 2018, **83**, 13861; (*c*) Z. Wang, T.-l. Wang, W. J. Yao and Y. X. Lu, *Org. Lett.*, 2017, **19**, 4126; (*d*) X.-L. Jiang, S.-J. Liu, Y.-Q. Gu, G.-J. Mei and F. Shi, *Adv. Synth. Catal.*, 2017, **359**, 3341; (*e*) T. Zhou, T. Xia, Z. L. Liu, L. Liu and J. L. Zhang, *Adv. Synth. Catal.*, 2018, **360**, 4475.
16 Crystallographic Data Centre as supplementary publication number CCDC 1941671.†