DOI: 10.1002/chem.201403285

Synthetic Methods

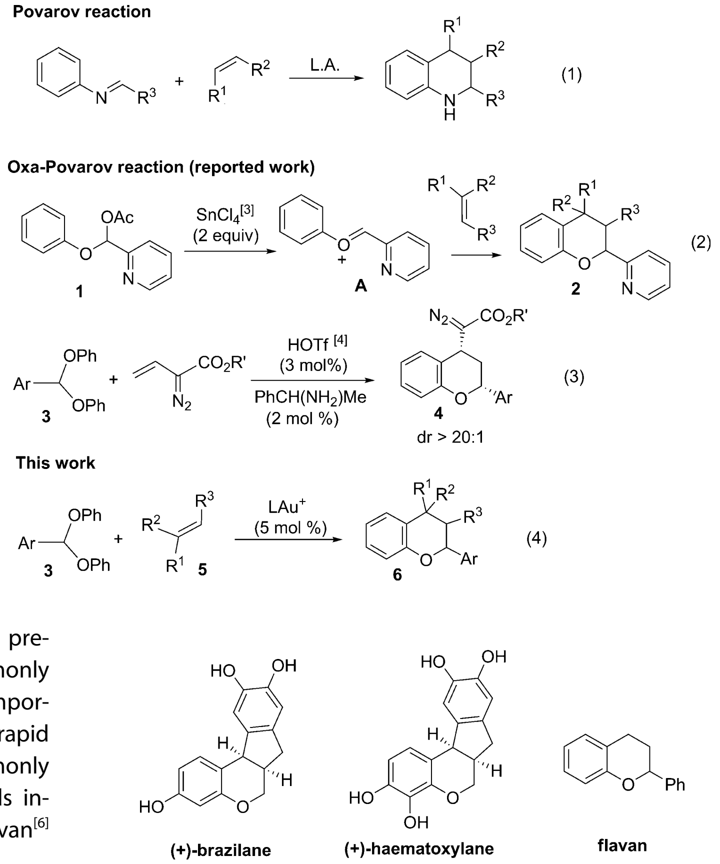
Gold-Catalyzed Oxa-Povarov Reactions for the Synthesis of Highly Substituted Dihydrobenzopyrans from Diaryloxymethylarenes and Olefins

Vinayak Vishnu Pagar, Chang-Chin Tseng, and Rai-Shung Liu*[a]

Abstract: Oxa-Povarov reactions involving readily available diaryloxymethylarenes and aryl-substituted alkenes are reported. Their [4+2] cycloadditions were efficiently catalyzed by $IPrAuSbF_6$ (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) with high diastereoselectivity. Product analysis revealed that the reactions likely proceed by a stepwise ionic mechanism, because both *E*- and *Z*-configured β-methylstyrene gave the same cycloadducts in the same proportions.

Introduction

Povarov reactions are formal [4+2] cycloadditions of *N*-aryl imines with electron-rich olefins, catalyzed by a Lewis acid (L.A.). Such reactions are powerful tools to construct tetrahydroquinoline cores [Eq. (1)], which are important skeletons for many bioactive molecules.[1,2] In contrast to this nitrogen system, metal-catalyzed oxa-Povarov reactions have remained largely unexplored, although the resulting dihydrobenzopyrans are also useful structural motifs. Batey and co-workers reported the first oxa-Povarov reactions involving [4+2] cycloadditions of alkenes with the oxonium intermediates **A**.[3] The reactions required the use of $SnCl_4$ (2.0 equiv) in stoichiometric proportions with special substrates such as aryl picolinates **1** [Eq. (2)]. We reported Povarov reactions of alkenyldiazocarbonyl compounds with diphenoxymethylbenzene, notably in a catalytic process using small amounts (2–3 mol%) of HOTf and α-phenylethylamine [Eq. (3)].[4] The examples in Equations (2) and (3) are not typical of oxa-Povarov reactions, because only special types of substrates and alkenes can be used. We report herein a logical extension of our preceding work to include diverse aryl acetals and commonly used alkenes with a suitable gold catalyst [Eq. (4)]. The importance of this new synthetic method is to provide a rapid access to the dihydrobenzopyran core, which is commonly found in numerous biologically active natural compounds including (+)-brazilane,[5] (+)-haematoxylane,[5] and flavan[6] (Scheme 1). Their specific biological activities are well documented.[7,8]



Scheme 1. Representative bioactive compounds.

Results and Discussion

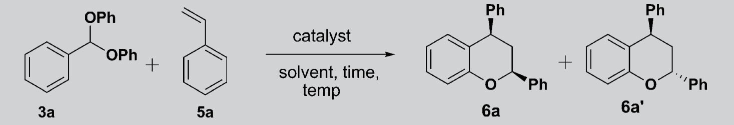
We tested the reactions of diphenoxymethylbenzene (**3a**) with styrene (**5a**) in the presence of various Lewis acid catalysts

---

[a] V. V. Pagar, C.-C. Tseng, Prof. Dr. R.-S. Liu
Department of Chemistry
National Tsing Hua University
Hsinchu, 30013 (Taiwan)
Fax: (+886) 3-5711082
E-mail: rsliu@mx.nthu.edu.tw

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403285.

Table 1. Catalyst screening and product stereoselectivity in the reaction of **3a** (1.0 equiv, 0.40 M) with **5a** (2 equiv).



Entry	Catalyst[a] (mol %)	Solvent	T [°C]	t [h]	d.r.	Yield [%][b]	
						6a	**6a**′
1	TfOH (3)/PhCH(NH$_2$)Me (2)	DCE	−20	2.4	1.8:1	43	23
2	TfOH (3)	DCE	−20	2.4	1.8:1	37	21
3	LAuCl/AgNTf$_2$ (5)	DCE	28	1.1	–[c]	–	–
4	SnCl$_4$ (5)	DCE	−20	3.0	1.5:1	40	27
5	BF$_3$(Et$_2$O) (5)	DCE	−20	3.5	3:1	42	14
6	IPrAuCl/AgSbF$_6$ (5)	DCE	28	0.2	1.2:1	48	40
7	IPrAuCl/AgSbF$_6$ (5)	DCE	−20	2.0	3:1	66	22
8	IPrAuCl/AgSbF$_6$ (5)	CH$_2$Cl$_2$	−20	2.0	8.1:1	81	10
9	IPrAuCl/AgSbF$_6$ (5)	toluene	−20	2.0	5.2:1	63	12
10	IPrAuCl/AgSbF$_6$ (5)	CHCl$_3$	−20	2.0	5:1	67	13
11	IPrAuCl/AgOTf (5)	CH$_2$Cl$_2$	−20	2.2	1:1.2	17	21

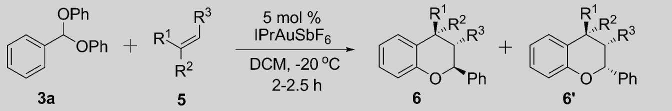
[a] IPr = 1,3-bis(diisopropy phenyl)imidazol-2-ylidene, L = P(tBu)$_2$(o-biphenyl). [b] Product yields are given after purification on a silica column. [c] Benzaldehyde and phenol were formed.

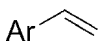
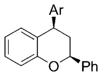
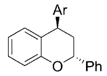
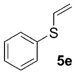
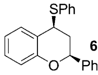
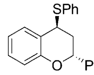
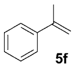
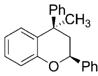
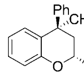
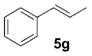
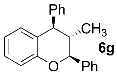
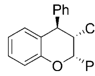
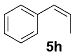
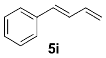
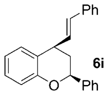
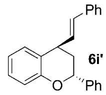
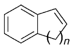
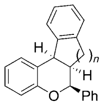
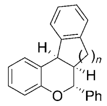
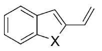
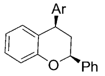
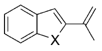
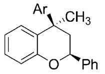
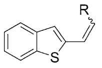
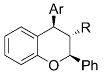
under optimized conditions (Table 1). In a typical reaction, **3a** (1 equiv) and **5a** (2 equiv) were mixed in a suitable solvent and then added slowly to a solution of the catalyst by using a syringe pump (ca. 0.2–1.0 h). The initial reaction was performed with **3a** and **5a** (2 equiv) in cold and dry dichloroethane (DCE, −20 °C) by using our previously reported combination of TfOH (3 mol %) and α-phenylethylamine (2 mol %). This gave desired cycloadducts **6a** and **6a**′ in 43 and 23 % yield, respectively (d.r. = 1.8:1; Table 1, entry 1). Hereby, hydrolysis of diphenoxymethylbenzene **3a** occurred to produce benzaldehyde and phenol in small amounts. For HOTf alone (3 mol %), the same reaction in cold DCE gave **6a** and **6a**′ in lower yields with d.r. = 1.8:1. The use of P(tBu)$_2$(o-biphenyl)AuCl/AgNTf$_2$ gave only benzaldehyde and phenol in DCE (28 °C, 1.1 h; Table 1, entry 3). Highly acidic catalysts such as SnCl$_4$ and BF$_3$·Et$_2$O gave **6a** and **6a**′ in 40–42 and 14–27 % yield, respectively (Table 1, entries 4 and 5). When less acidic IPrAuCl/AgSbF$_6$ (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) was employed in DCE at 28 °C, the respective yields of **6a** and **6a**′ were 48 and 40 %, albeit with a low d.r. of 1.2:1. At −20 °C, the diastereoselectivity improved to **6a**:**6a**′ = 3:1 with a satisfactory product yield of 66 % (Table 1, entry 7). The d.r. value and product yield improved significantly to **6a**:**6a**′ = 8.1:1 and 81 % in dichloromethane at −20 °C (Table 1, entry 8). The use of toluene and chloroform gave d.r. values of about **6a**:**6a**′ = 5.2:1 and 5:1, respectively (Table 1, entries 9 and 10). We then tested the reaction with IPrAuOTf, which is less acidic than IPrAuSbF$_6$, but the yields of **6a** (17 %) and **6a**′ (21 %) were poor in this case (Table 1, entry 11). The molecular structure of the major diastereomer **6a** was confirmed by X-ray diffraction.[9] The stereochemistry of compound **6a** is also readily identifiable from the ^{1}H NMR spectrum, in which one of the methylene protons has a coupling constant of 10–11 Hz, indicative of vicinal axial–axial coupling.

Table 2 assesses the generality of the oxa-Povarov reactions of diphenoxymethylbenzene (**3a**) with various alkenes (2 equiv) catalyzed by IPrAuSbF$_6$ (5 mol %); complete consumption of starting acetal **3a** was attained in all cases. Low temperatures (−20 °C) were maintained in CH$_2$Cl$_2$ to optimize the d.r. values. In entries 2–4, 6, 7, 9, and 10 of Table 2, the two diastereomeric products **6** and **6**′ were separable on silica columns. These cycloadditions worked well with various styrene derivatives **5b**–**5d** bearing 4-methoxy, 4-chloro, and 4-bromo substituents to give the corresponding cycloadducts **6b**–**6d** in good yields (68–78 %) and high diastereoselectivities (d.r. > 6.1:1; Table 2, entries 1–3). The reaction was extendible to phenyl vinyl sulfide (**5e**) to afford cycloadducts **6e** and **6e**′ in 76 and 8 % yield, respectively. The cycloaddition of α-methylstyrene (**5f**) proceeded highly stereoselectively to give dihydrobenzopyran **6f** exclusively (Table 2, entry 5). We prepared (E)- and (Z)-β-methylstyrene (**5g** and **5h**) to test the diastereoselectivity of the reaction, but both olefins gave products **6g** and **6g**′ with the same composition (**6g**:**6g**′ = 4:1; Table 2, entries 6 and 7). The molecular structure of the major diastereomer **6g** was determined by X-ray crystallography.[9] We observed excellent diastereoselectivity for (E)-1-phenylbuta-1,3-diene (**5i**) to afford compound **6i** exclusively in 87 % yield (Table 2, entry 8). By using indene **5j** and dihydronaphthalene **5k**, this new method provides access to polycyclic products **6j**,**6k** and **6j**′,**6k**′ in 60–61 and 8–10 % yield respectively (Table 2, entries 9 and 10). The reactions of 2-vinylbenzothiophene (**5l**) and 2-vinylbenzofuran (**5m**) with acetal **3a** also proceeded smoothly to give highly substituted cycloadducts **6l** and **6m** (d.r. > 20:1) in 75 and 58 % yield, respectively (Table 2, entries 11 and 12). The reactions of their α-methylvinyl derivatives **5n** and **5o** provided only single diastereomers **6n** and **6o** in 67 and 55 % yield, respectively (Table 2, entries 13 and 14). We also prepared substrates **5p** and **5q** with E:Z ratios of about 2:1; their reactions with acetal **3a** provided only dihydrobenzopyran derivatives **6p** and **6q** (Table 2, entries 15 and 16) in 78 and 55 % yield, respectively, whereby the Z forms of the substrates remained predominantly in the reaction mixture, as revealed by ^{1}H NMR spectroscopy. For compounds **6p** and **6q**, the ^{1}H NMR spectra of their crude products showed the presence of a single resonance in the region 4.5–5.5 ppm, assignable to the OCHPh protons. The reactions of acetal **3a** with cyclic or acyclic enol ethers such as 2,3-dihydrofuran and ethoxyethene were unsuccessful: only phenol and benzaldehydes were obtained.

We expanded the scope of this gold-catalyzed oxa-Povarov reaction with various acetals **3b**–**3g** (Table 3). We selected styrene (**5a**) and 2-vinylbenzothiophene (**5p**, 2.0 equiv, E:Z = 2:1) as the test alkenes to achieve both carbo- and heterocyclic frameworks. For acetals **3b** and **3c** containing 4-methoxy and 4-chloro substituents at their phenoxyl rings, the corresponding dihydrobenzopyran products **7b**,**7c** and **7b**′,**7c**′ were obtained in good yields (> 66 %) with d.r. > 6.1:1. The reactions were extendable to acetals **3d** and **3e** bearing 4-chloro and 4-

Table 2. Oxa-Povarov reactions of **3a** (0.40 M) with various alkenes (2 equiv).



Entry	Alkene	**6** (Yield [%])[a]	**6′** (Yield [%])[a]	d.r.
				
1	**5b** (Ar = 4-MeOC$_6$H$_4$)	**6b** (78)	**6b′** (trace)	> 20:1
2	**5c** (Ar = 4-ClC$_6$H$_4$)	**6c** (71)	**6c′** (10)	7.1:1
3	**5d** (Ar = 4-BrC$_6$H$_4$)	**6d** (68)	**6d′** (11)	6.1:1
4	 **5e**	 **6e** (76)	 **6e'** (8)	9.3:1
5	 **5f**	 **6f** (88)	 **6f'** (trace)	> 20:1
6	 **5g**	 **6g** (57)	 **6g'** (14)	4:1
7	 **5h**	**6g** (57)	**6g′** (14)	4:1
8	 **5i**	 **6i** (87)	 **6i'** trace)	> 20:1
				
9	**5j** ($n = 1$)	**6j** ($n = 1$, 61)	**6j′** ($n = 1$, 10)	6.1:1
10	**5k** ($n = 2$)	**6k** ($n = 2$, 60)	**6k′** ($n = 2$, 8)	7.3:1
				
11	**5l** (X = S)	**6l** (Ar = 2-benzothienyl, 75)		> 20:1
12	**5m** (X = O)	**6m** (Ar = 2-benzofuryl, 58)		> 20:1
				
13	**5n** (X = S)	**6n** (Ar = 2-benzothienyl, 67)		> 20:1
14	**5o** (X = O)	**6o** (Ar = 2-benzofuryl, 55)		> 20:1
				
	(E/z) = 2 : 1	(Ar = 2-benzothienyl)		
15	**5p** (R = Me)	**6p** (78)		> 20:1
16	**5q** (R = Et)	**6q** (55)		> 20:1

[a] Product yields are given after purification from a silica column.

bromo substituents at the phenylmethylacetal moiety to give desired **7d**,**7e** and **7d′**,**7e′** in 51–53 and 10% yield, respectively (Table 3, entries 3 and 4). Gold-catalyzed reactions of acetals **3f** and **3g** bearing a 2- or 4-methoxyphenylmethylacetal substituent with alkene **5p** yielded cycloadducts **7f** and **7g** in 73 and 41% yield, respectively. The gold-catalyzed reactions between alkene **5p** and acetals **3b**–**3d** delivered desired cycloadducts **7h**–**7j** with excellent yields (81–85%) and excellent d.r. > 20:1 (Table 3, entries 7–9).

In Scheme 2, we propose a plausible mechanism involving a stepwise ionic pathway with styrene-based alkenes as nucleophiles. We envisage that styrene approaches an oxonium intermediate in an *endo* conformation to generate a chairlike transition state **B** with two bulky phenyl groups located in the equatorial positions, which thus gives the observed major product **6a**. In Table 2, entries 6 and 7, both *cis*- and *trans*-β- methylstyrenes **5g** and **5h** gave cycloadducts with the same composition (**6g**:**6g′** = 4:1). We postulate that the *E*-configured olefin **5g** reacts with this oxonium intermediate via an antiperiplanar[10] conformation **A′**, which leads to an *anti* orientation between the bulky phenyl and PhCH=C moieties and thus generates a six-membered transition state **B′** bearing the three protons in the axial positions; this stereochemical course yields the observed major diastereomer **6g**. For the *cis*-configured β-methylstyrene, its antiperiplanar[10] conformation **A′′** generates a six-membered transition state **B′′** that has a bulky phenyl group at the axial position and thus suffer a 1,3-axial steric interaction. Intermediate **B″** thus undergoes a rearrangement to attain a more stable conformation **B′** that gives the observed major diastereomer **6g**.

Conclusion

We have reported gold-catalyzed[11–12] oxa-Povarov reactions involving readily available diaryloxymethyl arenes and aryl-substituted alkenes to give dihydrobenzopyrans;[13] their [4+2] cycloadditions are efficiently catalyzed by IPrAuSbF$_6$ with high diastereoselectivity. The cycloadditions were applicable to a reasonable range of substrates under ambient conditions. Our product analysis revealed that the reaction likely proceeds via a stepwise ionic mechanism, because both *E*- and *Z*-configured β-methylstyrene gave the same cycloadducts in the same proportions.

Experimental Section

General

Unless otherwise noted, the preparations of the substrates were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. Catalytic reactions were performed under argon atmosphere. DCE and CH$_2$Cl$_2$ were distilled from CaH$_2$ under nitrogen. THF and toluene were distilled from Na metal under nitrogen. Commercial reagents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz or Bruker 400, 500, 600 MHz spectrometers with CDCl$_3$ as internal standard.

Standard catalytic procedure for synthesis of dihydrobenzopyrans (6a):

A solution of IPrAuCl (12.3 mg, 0.02 mmol) and AgSbF$_6$ (6.8 mg, 0.02 mmol) in dichloromethane (1 mL) was stirred under argon atmosphere at −20 °C for 10 min. To this solution a solution of diphenoxymethylbenzene (**3a**, 110 mg, 0.40 mmol) and styrene (**5a**, 83 mg, 0.80 mmol) in dichloromethane (2 mL) was added dropwise by syringe pump (1.5 h). The resulting solution was stirred for a further 30 min and filtered over a short silica bed. The filtrate was concentrated and purified on a flash silica column (hexane:ethyl acetate 9:1) to give **6a** as a white solid (91 mg, 0.31 mmol, 81 %) and **6a′** as a semisolid (11 mg, 0.04 mmol, 10 %).

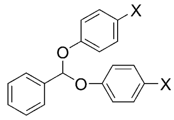
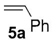
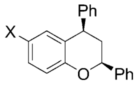
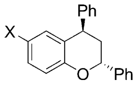
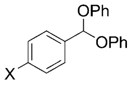
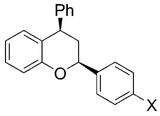
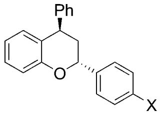
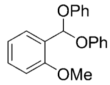
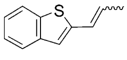
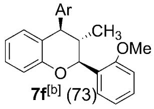
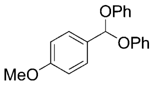
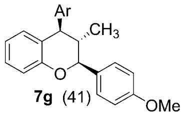
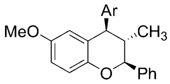
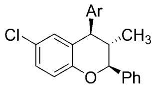
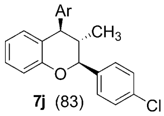
2,4-Diphenylchroman (6a): White solid (92 mg, 81 %), m.p. 122–124 °C; IR (neat): $\tilde{\nu}=3024$ (m), 1580 (s), 1486 (s), 1234 (m), 1061 (s), 757 cm^{-1} (s); ^{1}H NMR (600 MHz, CDCl$_3$): $\delta=7.46$ (dd, $J=8.4$, 1.3 Hz, 2H), 7.37 (t, $J=7.8$ Hz, 2H), 7.31–28 (m, 3H), 7.23–7.19 (m, 3H), 7.11 (t, $J=6.9$ Hz, 1H), 6.93 (d, $J=8.1$ Hz, 1H), 6.78–6.74 (m, 2H), 5.19 (dd, $J=11.4$, 1.6 Hz, 1H), 4.33 (dd, $J=12.1$, 5.8 Hz, 1H), 2.41–2.37 (m, 1H), 2.28–2.24 ppm (m, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): $\delta=155.5$, 144.5, 141.2, 129.8, 128.6, 128.5(CHx2), 128.0, 127.7, 126.7, 126.1, 125.7, 120.5, 117.0, 78.1, 43.5, 40.6 ppm; HRMS calcd for $C_{21}H_{18}O$: 286.1358; found: 286.1360.

2,4-Diphenylchroman (6a′): White semisolid (11 mg, 10 %); IR (neat): $\tilde{\nu}=3014$ (m), 1565 (s), 1468 (s), 1245 (m), 1059 (s), 752 cm^{-1} (s); ^{1}H NMR (600 MHz, CDCl$_3$): $\delta=7.34$–7.26 (m, 7H), 7.23–7.19 (m, 2H), 7.12 (d, $J=7.3$ Hz, 2H), 7.01 (dd, $J=8.2$, 0.9 Hz, 1H), 6.98 (dd, $J=7.6$,1.5 Hz, 1H), 6.88 (t, $J=7.5$ Hz, 1H), 5.04 (dd, $J=10.5$, 2.4 Hz, 1H), 4.22 (dd, $J=5.4$, 3.5 Hz, 1H), 2.46–2.43 (m, 1H), 2.26–2.23 ppm (m, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): $\delta=155.4$, 146.0, 141.4, 130.7, 128.5, 128.4(CHx2), 128.1, 127.7, 126.4, 126.0, 123.1, 120.5, 117.0, 73.2, 40.2, 38.2 ppm; HRMS calcd for $C_{21}H_{18}O$: 286.1358; found: 286.1355.

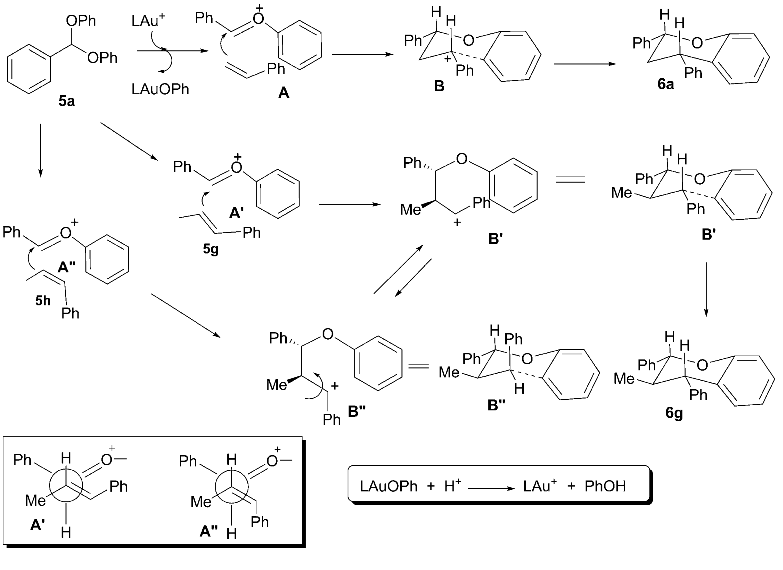
4-(4-Methoxyphenyl)-2-phenylchroman (6b): White solid (98 mg, 78 %), m.p. 130–132 °C; IR (neat): $\tilde{\nu}=2998$ (m), 1587 (s), 1490 (s), 1208 (m), 1059 (s), 751 cm^{-1} (s); ^{1}H NMR (600 MHz, CDCl$_3$): $\delta=7.48$–7.47 (m, 2H), 7.38 (t, $J=7.5$ Hz, 2H), 7.32 (t, $J=7.2$ Hz, 1H), 7.14–7.11 (m, 3H), 6.94 (dd, $J=7.9$, 0.3 Hz, 1H), 6.87–6.83 (m, 2H), 6.79–6.77 (m, 2H), 5.20 (dd, $J=11.4$,1.5 Hz, 1H), 4.31 (dd, $J=12.2$, 5.7 Hz, 1H), 3.79 (s, 3H), 2.39–2.36 (m, 1H), 2.27–2.23 ppm (m, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): $\delta=158.4$, 155.4, 141.2, 136.5, 129.7, 129.5, 128.5, 128.0, 127.7 (CH×2), 126.0, 120.5, 116.9, 114.0, 78.1, 55.2, 42.6, 40.7 ppm; HRMS calcd for $C_{22}H_{20}O_2$: 316.1463; found: 316.1468.

4-(4-Chlorophenyl)-2-phenylchroman (6c): White solid (90 mg, 71 %), m.p. 127–129 °C; IR (neat): $\tilde{\nu}=3034$ (m), 1580 (s), 1485 (s), 1265 (m), 737 cm^{-1} (s); ^{1}H NMR (600 MHz, CDCl$_3$): $\delta=7.47$ (d, $J=7.4$ Hz, 2H), 7.40 (t, $J=7.6$ Hz, 2H), 7.32 (t, $J=6.6$ Hz, 1H), 7.29 (d, $J=8.3$ Hz, 2H), 7.15 (d, $J=8.2$ Hz, 3H), 6.97 (d, $J=8.1$ Hz, 1H), 6.81 (t, $J=7.6$ Hz, 1H), 6.74 (d, $J=7.6$ Hz, 1H), 5.20 (d, $J=11.1$ Hz, 1H), 4.34 (dd, $J=12.1$, 5.7 Hz, 1H), 2.40–2.37 (m, 1H), 2.25–2.19 ppm (m, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): $\delta=155.4$, 143.0, 140.9, 132.4, 129.9, 129.6, 128.8, 128.6, 128.1, 127.9, 126.0, 125.0, 120.6, 117.1, 77.9,

Table 3. Oxa-Povarov reactions of various acetals **3** (0.40 M) with alkenes **5** (2 equiv).

Entry	Acetals	Alkene	**7** (yield [%])[a]	**7′** (yield [%])[a]	d.r.
		 **5a**			
1	**3b** (X=OMe)	**5a**	**7b** (75)	**7b′** (12)	6.1:1
2	**3c** (X=Cl)	**5a**	**7c** (66)	**7c′** (10)	6.7:1
					
3	**3d** (X=Cl)	**5a**	**7d** (53)	**7d′** (10)	5.3:1
4	**3e** (X=Br)	**5a**	**7e** (51)	**7e′** (10)	5.1:1
5	 **3f**	 **5p** (E/Z = 2:1)	 **7f**[b] (73)		>20:1
6	 **3g**	**5p**	 **7g** (41)		>20:1
7	**3b**	**5p**	 **7h** (81)		>20:1
8	**3c**	**5p**	 **7i** (85)		>20:1
9	**3d**	**5p**	 **7j** (83)		>20:1

[a] Product yields are given after purification from a silica column. [b] Ar=2-benzothienyl.



Scheme 2. Stereochemical course of cycloadditions.

42.8, 40.5 ppm; HRMS calcd for $C_{21}H_{17}ClO$: 320.0968; found: 320.0961.

4-(4-Chlorophenyl)-2-phenylchroman (6c′): White semisolid (13 mg, 10%); IR (neat): $\tilde{\nu}=3024$ (m), 1570 (s), 1491 (s), 1234 (m), 732 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.33$–726 (m, 7H), 7.19 (t, $J=8.3$ Hz, 1H), 7.05 (d, $J=6.6$ Hz, 2H), 7.00 (d, $J=8.2$ Hz, 1H), 6.93 (d, $J=7.7$ Hz, 1H), 6.87 (t, $J=7.3$ Hz, 1H), 4.97 (dd, $J=10.5$, 2.3 Hz, 1H), 4.18 (dd, $J=5.4$, 3.5 Hz, 1H), 2.46–2.41 (m, 1H), 2.20–2.17 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.3$, 144.5, 141.1, 132.3, 130.6, 129.9, 128.6, 128.5, 128.3, 127.8, 125.9, 122.5, 120.6, 117.2, 73.1, 39.6, 38.2 ppm; HRMS calcd for $C_{21}H_{17}ClO$: 320.0968; found: 320.0961.

4-(4-Bromophenyl)-2-phenylchroman (6d): Light yellow solid (99 mg, 68%), m.p. 149–153 °C; IR (neat): $\tilde{\nu}=3049$ (m), 1712 (s), 1473 (s), 1263 (m), 1059 (s), 739 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.46$ (d, $J=7.5$ Hz, 2H), 7.43 (d, $J=8.2$ Hz, 2H), 7.39 (t, $J=7.5$ Hz, 2H), 7.32 (t, $J=7.2$ Hz, 1H), 7.14 (t, $J=7.3$ Hz, 1H), 7.09 (d, $J=8.2$ Hz, 2H), 6.94 (d, $J=8.1$ Hz, 1H), 6.79 (t, $J=7.5$ Hz, 1H), 6.72 (d, $J=7.7$ Hz, 1H), 5.18 (d, $J=10.8$ Hz, 1H), 4.32 (dd, $J=12.1$, 5.8 Hz, 1H), 2.40–2.36 (m, 1H), 2.23–2.17 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.5$, 143.6, 141.0, 131.8, 130.3, 129.6, 128.6, 128.1, 128.0, 126.0, 125.0, 120.7, 120.5, 117.1, 77.9, 42.9, 40.5 ppm; HRMS calcd for $C_{21}H_{17}BrO$: 364.0463; found: 364.0455.

4-(4-Bromophenyl)-2-phenylchroman (6d′): Light yellow semisolid (16 mg, 11%); IR (neat): $\tilde{\nu}=3031$ (m), 1590 (s), 1441 (s), 1253 (m), 1065 (s), 772 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.41$ (dd, $J=6.8$,1.6 Hz, 1H), 7.34–7.26 (m, 6H), 7.20 (t, $J=8.5$ Hz, 1H), 7.00 (dd, $J=7.2$,4.5 Hz, 3H), 6.93 (d, $J=6.1$ Hz, 1H), 6.87 (t, $J=7.0$ Hz, 1H), 4.97 (dd, $J=10.5$,2.2 Hz, 1H), 4.17 (dd, $J=5.3$,3.4 Hz, 1H), 2.45–2.41 (m, 1H), 2.19–2.16 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.3$, 145.0, 141.1, 131.5, 130.6, 130.4, 128.5, 128.3, 127.8, 125.9, 122.4, 120.6, 120.4, 117.2, 77.2, 39.7, 38.1 ppm; HRMS calcd for $C_{21}H_{17}BrO$: 364.0463; found: 364.0462.

2-Phenyl-4-(phenylthio)chroman (6e): White solid (96 mg, 76%), m.p. 125–128 °C; IR (neat): $\tilde{\nu}=3300$ (br), 1578 (s), 1482 (s), 1265 (m), 737 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.77$ (d, $J=7.8$ Hz, 1H), 7.41–7.39 (m, 2H), 7.36 (dd, $J=6.5$, 1.7 Hz, 4H), 7.31–7.23 (m, 4H), 7.16 (t, $J=7.2$ Hz, 1H), 6.96 (t, $J=7.6$ Hz, 1H), 6.88 (dd, $J=8.2$,1.2 Hz, 1H), 4.99 (dd, $J=11.6$, 1.7 Hz, 1H), 4.66 (dd, $J=11.5$, 6.3 Hz, 1H), 2.45–2.42 (m, 1H), 2.29–2.23 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.4$, 140.6, 134.0, 132.6, 129.3, 129.0, 128.7, 128.6, 128.2, 127.6, 126.1, 122.1, 120.9, 117.3, 78.0, 43.9, 38.9 ppm; HRMS calcd for $C_{21}H_{18}OS$: 350.0799; found: 350.0794.

2-Phenyl-4-(phenylthio)chroman (6e′): White semisolid (10 mg, 8%); IR (neat): $\tilde{\nu}=3310$ (br), 1572 (s), 1489 (s), 1267 (m), 756 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.50$ (dd, $J=8.4$, 1.3 Hz, 2H), 7.41 (dd, $J=7.5$, 0.6 Hz, 2H), 7.38–7.27 (m, 7H), 7.19–7.17 (m, 1H), 6.93 (t, $J=8.6$ Hz, 2H), 5.51 (dd, $J=10.7$, 2.7 Hz, 1H), 4.57 (dd, $J=4.0$, 2.0 Hz, 1H), 2.25–2.20 (m, 2H), ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.3$, 141.0, 134.7, 132.5, 130.9, 129.2, 129.1, 128.6, 128.0, 127.7, 126.2, 120.5, 120.3, 117.4, 73.4, 43.9, 35.3 ppm; HRMS calcd for $C_{21}H_{18}OS$: 350.0799; found: 350.0796.

4-Methyl-2,4-diphenylchroman (6f): White solid (105 mg, 88%), m.p. 107–109 °C; IR (neat): $\tilde{\nu}=3019$ (m), 1585 (s), 1488 (s), 1237 (m), 1072 (s), 759 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.47$ (d, $J=7.4$ Hz, 2H), 7.38 (t, $J=7.5$ Hz, 2H), 7.32–7.27 (m, 5H), 7.18–7.13 (m, 2H), 6.99 (t, $J=8.6$ Hz, 1H), 6.81 (dd, $J=5.7$, 1.1 Hz, 2H), 5.25 (dd, $J=12.0$, 1.6 Hz, 1H), 2.41 (dd, $J=12.6$, 1.3 Hz, 1H), 2.12 ppm (dd, $J=14.1$, 1.9 Hz, 1H), 1.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.0$, 149.6, 141.2, 131.2, 129.9, 128.5, 128.1, 127.9, 127.4, 127.1, 126.1, 126.0, 120.8, 117.3, 75.0, 48.8, 41.0, 29.3 ppm; HRMS calcd for $C_{22}H_{20}O$: 300.1514; found: 300.1518.

3-Methyl-2,4-diphenylchroman (6g): White solid (68 mg, 57%), m.p. 117–120 °C; IR (neat): $\tilde{\nu}=3016$ (m), 1571 (s), 1492 (s), 1256 (m), 1082 (s), 767 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.44$ (d, $J=7.6$ Hz, 2H), 7.39 (t, $J=7.2$ Hz, 2H), 7.35–7.30 (m, 3H), 7.25 (t, $J=6.6$ Hz, 1H), 7.19 (dd, $J=8.4$, 1.3 Hz, 2H), 7.06 (t, $J=7.2$ Hz, 1H), 6.89 (d, $J=8.2$ Hz, 1H), 6.76 (t, $J=8.4$ Hz, 1H), 6.65 (d, $J=7.7$ Hz, 1H), 4.75 (d, $J=10.1$ Hz, 1H), 3.80 (d, $J=10.8$ Hz, 1H), 2.32–2.27 (m, 1H), 0.59 ppm (d, $J=6.6$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.3$, 143.8, 139.9, 130.1, 129.4, 128.5, 128.5, 128.4, 127.5, 127.4, 126.7, 126.4, 120.6, 116.6, 84.3, 51.1, 40.9, 15.7 ppm; HRMS calcd for $C_{22}H_{20}O$: 300.1514; found: 300.1521.

3-Methyl-2,4-diphenylchroman (6g′): White semisolid (17 mg, 14%); IR (neat): $\tilde{\nu}=3022$ (m), 1573 (s), 1461 (s), 1229 (m), 1048 (s), 782 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.30$ (t, $J=7.3$ Hz, 4H), 7.24–7.20 (m, 5H), 7.11–7.09 (m, 2H), 7.03 (dd, $J=8.2$, 0.8 Hz, 1H), 6.98 (dd, $J=7.6$, 1.3 Hz, 1H), 6.89 (t, $J=7.3$ Hz, 1H), 5.10 (d, $J=2.1$ Hz, 1H), 3.98 (d, $J=2.3$ Hz, 1H), 2.31–2.28 (m, 1H), 0.86 ppm (d, $J=7.0$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.9$, 146.4, 140.1, 131.6, 128.8, 128.4, 128.0, 127.9, 127.0, 126.4, 125.8, 121.8, 120.7, 116.7, 74.6, 48.3, 40.6, 13.3 ppm; HRMS calcd for $C_{22}H_{20}O$: 300.1514; found: 300.1517.

2-Phenyl-4-[(*E*)-styryl]chroman (6i): White solid (108 mg, 87%), m.p. 118–120 °C; IR (neat): $\tilde{\nu}=3027$ (m), 1578 (s), 1452 (s), 1239 (m), 1047 (s), 737 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.47$ (d, $J=7.2$ Hz, 2H), 7.40 (t, $J=8.4$ Hz, 4H), 7.34–7.31 (m, 3H), 7.23 (dd, $J=8.3$, 0.4 Hz, 2H), 7.17 (t, $J=0.8$ Hz, 1H), 6.94 (dd, $J=7.1$, 1.0 Hz, 1H), 6.90 (t, $J=8.5$ Hz, 1H), 6.64 (d, $J=15.8$ Hz, 1H), 6.13 (dd, $J=15.7$, 9.0 Hz, 1H), 5.15 (d, $J=11.5$ Hz, 1H), 3.95–3.90 (m, 1H), 2.32–2.28 (m, 1H), 2.12–2.06 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.9$, 141.2, 137.0, 132.2, 132.0, 129.2, 128.6, 128.5, 128.0 (CH × 2), 127.4, 126.2, 126.0, 124.0, 120.6, 117.0, 77.6, 40.8, 37.9 ppm; HRMS calcd for $C_{23}H_{20}O$: 312.1514; found: 312.1522.

6-Phenyl-6,6a,7,11b-tetrahydroindeno[2,1-*c*]chromene (6j): White solid (72 mg, 61%), m.p. 148–151 °C; IR (neat): $\tilde{\nu}=2998$ (m), 1603 (s), 1479 (s), 1231 (m), 751 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.53$–7.51 (m, 3H), 7.41 (t, $J=7.6$ Hz, 3H), 7.33 (t, $J=7.3$ Hz, 1H), 7.15 (t, $J=7.3$ Hz, 1H), 7.11–7.04 (m, 3H), 6.94–6.88 (m, 2H), 5.33 (d, $J=2.1$ Hz, 1H), 4.59 (d, $J=8.2$ Hz, 1H), 3.29–3.24 (m, 1H), 3.13 (dd, $J=15.6$, 4.6 Hz, 1H), 2.50 ppm (dd, $J=15.6$, 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.7$, 145.6, 142.4, 140.4, 129.2, 128.4, 127.4, 127.3, 127.2, 126.6, 125.6, 124.9, 124.8, 124.5, 121.6,117.7, 77.2, 46.5, 44.9, 30.4 ppm; HRMS calcd for $C_{22}H_{18}O$: 298.1358; found: 298.1353.

6-Phenyl-6,6a,7,11b-tetrahydroindeno[2,1-*c*]chromene (6j′): White semisolid (12 mg, 10%); IR (neat): $\tilde{\nu}=2997$ (m), 1598 (s), 1473 (s), 1237 (m), 758 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.52$ (d, $J=7.3$ Hz, 1H), 7.41–7.36 (m, 6H), 7.23 (dd, $J=6.6$,1.5 Hz, 1H), 7.20–7.16 (m, 3H), 7.04 (t, $J=7.6$ Hz, 1H), 6.92 (d, $J=8.1$ Hz, 1H), 4.40 (d, $J=6.1$ Hz, 1H), 4.39 (d, $J=10.6$ Hz, 1H), 3.09 (dd, $J=16.2$, 6.9 Hz, 1H), 2.98–2.95 (m, 1H), 2.58 ppm (d, $J=16.3$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.9$, 145.2, 140.6, 139.9, 130.4, 128.6, 128.4, 127.9, 127.7, 126.9, 126.6, 125.2, 124.2, 122.6, 120.7, 117.3, 78.1, 44.8, 42.7, 34.2 ppm; HRMS calcd for $C_{22}H_{18}O$: 298.1358; found: 298.1355.

6-Phenyl-6a,7,8,12b-tetrahydro-6*H*-naphtho[2,1-*c*]chromene (6k): White solid (74 mg, 60%), m.p. 153–155 °C; IR (neat): $\tilde{\nu}=2939$ (m), 1605 (s), 1483 (s), 1235 (m), 753 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.51$–7.50 (m, 2H), 7.44–7.39 (m, 3H), 7.34 (t, $J=7.4$ Hz, 1H), 7.27 (t, $J=7.2$ Hz, 1H), 7.21 (t, $J=7.5$ Hz, 1H), 7.12–7.08 (m, 3H), 6.96 (dd, $J=8.1$, 1.1 Hz,1H), 6.80 (t, $J=7.6$ Hz, 1H), 5.50 (d, $J=1.1$ Hz, 1H), 4.44 (d, $J=4.6$ Hz, 1H), 2.68–2.63 (m, 2H), 2.47–2.44 (m, 1H), 1.73–1.67 (m, 1H), 1.56–1.54 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.7$, 140.0, 137.0, 136.8, 131.5, 129.4, 129.0, 128.2, 127.6, 127.3, 126.9, 125.7, 125.2, 123.8, 120.7, 116.7, 79.5, 41.5, 37.7, 28.3, 17.1 ppm; HRMS calcd for $C_{23}H_{20}O$: 312.1514; found: 312.1517.

6-Phenyl-6a,7,8,12b-tetrahydro-6*H*-naphtho[2,1-*c*]chromene (6k′): White semisolid (10 mg, 8%); IR (neat): $\tilde{\nu}=3030$ (m), 1582 (s), 1484 (s), 1235 (m), 738 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=$ 7.34–7.32 (m, 4H), 7.31–7.29 (m, 1H), 7.19–7.13 (m, 6H), 6.95 (dd, $J=8.1$, 1.1 Hz, 1H), 6.89 (t, $J=7.2$ Hz, 1H), 4.90 (d, $J=7.0$ Hz, 1H), 3.90 (d, $J=5.1$ Hz, 1H), 2.82–2.79 (m, 2H), 2.68–2.65 (m, 1H), 1.96 (dd, $J=13.7$, 5.8 Hz, 1H), 1.53–1.50 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.8$, 140.7, 137.8, 137.0, 130.7, 129.6, 128.5, 128.5, 128.0, 127.9, 126.7, 126.5, 125.7, 123.0, 120.0, 116.8, 79.5, 37.1, 36.6, 27.5, 24.3 ppm; HRMS calcd for $C_{23}H_{20}O$: 312.1514; found: 312.1511.

4-(Benzo[*b*]thiophen-2-yl)-2-phenylchroman (6l): White solid (102 mg, 75%), m.p. 216–218 °C; IR (neat): $\tilde{\nu}=2921$ (m), 1511 (s), 1453 (s), 1234 (m), 736 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.73$ (dd, $J=19.6$, 7.6 Hz, 2H), 7.51–7.49 (m, 2H), 7.43–7.39 (m, 2H), 7.36–7.32 (m, 2H), 7.28 (td, $J=8.0$, 1.2 Hz, 1H), 7.25 (s, 1H), 7.20–7.16 (m, 1H), 7.06 (d, $J=7.6$ Hz, 1H), 6.97 (dd, $J=8.4$, 1.2 Hz, 1H), 6.84 (td, $J=7.6$, 1.2 Hz, 1H), 5.22 (dd, $J=11.6$, 2.0 Hz, 1H), 4.78 (dd, $J=12.0$, 6.0 Hz, 1H), 2.60–2.55 (m, 1H), 2.48–2.39 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.8, 148.3, 140.8, 139.5, 139.5, 129.4, 128.6, 128.4, 128.2, 126.1, 124.2, 124.2, 124.0, 123.1, 122.5, 122.4, 120.7, 117.1, 78.0, 40.6, 39.3 ppm; HRMS calcd for $C_{23}H_{18}OS$: 342.1078, found: 342.1076.

4-(Benzofuran-2-yl)-2-phenylchroman (6m): White solid (75 mg, 58%), m.p. 177–179 °C; IR (neat): $\tilde{\nu}=2945$ (m), 2851 (s), 1491 (s), 1269 (m), 1048 (s), 732 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.52–7.48 (m, 3H), 7.41–7.37 (m, 3H), 7.34–7.30 (m, 1H), 7.22–7.14 (m, 3H), 7.05 (d, $J=7.6$ Hz, 1H), 6.96 (d, $J=8.4$ Hz, 1H), 6.83 (t, $J=7.6$ Hz, 1H), 6.59 (s, 1H), 5.20 (dd, $J=10.8$, 2.8 Hz, 1H), 4.63 (dd, $J=11.6$, 6.4 Hz, 1H), 2.60–2.54 (m, 1H), 2.52–2.46 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.0$, 155.1, 154.9, 140.9, 128.8, 128.6, 128.4, 128.4, 128.2, 126.1, 123.7, 122.7, 121.9, 120.8, 120.6, 117.4, 111.1, 103.9, 77.8, 36.9, 36.4 ppm; HRMS calcd for $C_{23}H_{18}O_2$:326.1307, found: 326.1303.

4-(Benzo[*b*]thiophen-2-yl)-4-methyl-2-phenylchroman (6n): White solid (95 mg, 67%), m.p. 207–209 °C; IR (neat): $\tilde{\nu}=3003$ (m), 1510 (s), 1463 (s), 1265 (m), 739 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.68$ (dd, $J=12.0$, 7.6 Hz, 2H), 7.49–7.47 (m, 2H), 7.39 (t, $J=7.2$ Hz, 2H), 7.34–7.29 (m, 2H), 7.27 (dd, $J=8.4$, 1.2 Hz, 1H), 7.19 (s, 1H), 7.16–7.14 (m, 1H), 7.11–7.09 (m, 1H), 6.96 (dd, $J=8.4$, 1.2 Hz, 1H), 6.87–6.83 (m, 1H), 5.24 (dd, $J=12.0$, 1.6 Hz, 1H), 2.61 (t, $J=13.2$ Hz, 1H), 2.28 (dd, $J=14.0$, 2.0 Hz, 1H), 2.01 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=155.8$, 154.2, 140.7, 139.5, 139.4, 129.5, 129.4, 128.6, 128.5, 128.2, 128.1, 126.2, 124.1, 123.9, 123.1, 122.1, 120.8, 117.4, 74.9, 48.2, 40.1, 30.8 ppm; HRMS calcd for $C_{24}H_{20}OS$: 356.1235, found: 356.1230.

4-(Benzofuran-2-yl)-4-methyl-2-phenylchroman (6o): White solid (74 mg, 55%), m.p. 172–174 °C; IR (neat): $\tilde{\nu}=2976$ (m), 1507 (s), 1472 (s), 1266 (m), 735 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.51–7.48 (m, 3H), 7.39 (t, $J=7.6$ Hz, 2H), 7.35–7.31 (m, 2H), 7.20–7.12 (m, 3H), 7.03 (dd, $J=7.6$, 1.6 Hz, 1H), 6.97 (d, $J=7.6$ Hz, 1H), 6.84–6.80 (m, 1H), 6.63 (s, 1H), 5.26 (dd, $J=12.0$, 1.6 Hz, 1H), 2.79 (t, $J=13.2$ Hz, 1H), 2.12 (dd, $J=14.0$, 2.0 Hz, 1H), 1.90 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=163.5$, 154.8, 154.4, 140.9, 128.6, 128.5, 128.3, 128.1, 128.1, 127.0, 126.2, 123.7, 122.5, 120.9, 120.5, 117.6, 111.1, 102.9, 74.4, 42.9, 38.4, 28.7 ppm; HRMS calcd for $C_{24}H_{20}O_2$: 340.1463, found: 340.1468.

4-(Benzo[*b*]thiophen-2-yl)-3-methyl-2-phenylchroman (6p): White solid (110 mg, 78%), m.p. 212–214 °C; IR (neat): $\tilde{\nu}=2927$ (m), 1563 (s), 1485 (s), 1241 (m), 733 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.73$ (dd, $J=11.2$, 8.0 Hz, 2H), 7.46–7.44 (m, 2H), 7.42–7.39 (m, 2H), 7.37–7.31 (m, 2H), 7.29–7.25 (m, 2H), 7.13 (t, $J=7.6$ Hz, 1H), 6.94–6.89 (m, 2H), 6.81–6.78 (m, 1H), 4.77 (d, $J=10.4$ Hz, 1H), 4.24 (d, $J=11.2$ Hz, 1H), 2.44–2.37 (m, 1H), 0.73 ppm (d, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=154.6$, 147.7, 139.8, 139.5, 139.4, 129.7, 128.6, 128.5, 128.2, 127.5, 124.6, 124.2, 124.0, 123.9, 123.0, 122.5, 120.8, 116.7, 84.2, 47.0, 41.2, 16.0 ppm; HRMS calcd for $C_{24}H_{20}OS$: 356.1235, found: 356.1227.

4-(Benzo[*b*]thiophen-2-yl)-3-ethyl-2-phenylchroman (6q): White solid (80 mg, 55%), m.p. 219–221 °C; IR (neat): $\tilde{\nu}=3014$ (m), 1561 (s), 1482 (s), 1259 (m), 736 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 7.73 (dd, $J=12.4$, 8.0 Hz, 2H), 7.48–7.46 (m, 2H), 7.42–7.27 (m, 6H), 7.11 (t, $J=7.2$ Hz, 1H), 6.95 (d, $J=8.0$ Hz, 1H), 6.88 (d, $J=8.0$ Hz, 1H), 6.78 (t, $J=7.6$ Hz, 1H), 4.93 (d, $J=10.0$ Hz, 1H), 4.52 (d, $J=11.2$ Hz, 1H), 2.46–2.38 (m, 1H), 1.37–1.26 (m, 2H), 0.62 ppm (t, $J=7.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=154.4$, 148.0, 139.8, 139.4, 139.4, 129.9, 128.6, 128.6, 128.1, 127.6, 124.9, 124.2, 124.0, 123.7, 123.0, 122.5, 120.7, 116.7, 82.2, 45.7, 42.9, 21.4, 8.8 ppm; HRMS calcd for $C_{25}H_{22}OS$: 370.1391, found: 370.1392.

6-Methoxy-2,4-diphenylchroman (7b): Light yellow solid (77 mg, 75%), m.p. 126–128 °C; IR (neat): $\tilde{\nu}=2950$ (m), 1600 (s), 1490 (s), 1209 (m), 700 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.46$ (d, $J=7.5$ Hz, 2H), 7.37 (t, $J=7.4$ Hz, 2H), 7.30 (t, $J=7.4$ Hz, 3H), 7.21 (t, $J=7.2$ Hz, 3H), 6.88 (d, $J=8.8$ Hz, 1H), 6.71 (dd, $J=8.8$, 2.6 Hz, 1H), 6.30 (d, $J=2.3$ Hz, 1H), 5.13 (d, $J=11.2$ Hz, 1H), 4.32 (dd, $J=12.1$, 5.9 Hz, 1H), 3.60 (s, 3H), 2.39–2.36 (m, 1H), 2.23 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.4$, 149.7, 144.3, 141.3, 128.6, 128.5, 128.4, 128.0, 126.8, 126.2, 126.1, 117.5, 114.6, 113.6, 78.0, 55.6, 43.7, 40.7 ppm; HRMS calcd for $C_{22}H_{20}O_2$: 316.1463; found: 316.1459.

6-Methoxy-2,4-diphenylchroman (7b′): Light yellow semisolid (16 mg, 12%); IR (neat): $\tilde{\nu}=2953$ (m), 1600 (s), 1493 (s), 1215 (m), 1043 (s), 700 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=$7.32–7.29 (m, 7H), 7.22 (t, $J=7.6$ Hz, 1H), 7.14 (d, $J=8.3$ Hz, 2H), 6.94 (d, $J=8.9$ Hz, 1H), 6.79 (dd, $J=8.6$,3.1 Hz, 1H), 6.50 (d, $J=2.9$ Hz, 1H), 4.99 (dd, $J=10.5$, 2.3 Hz, 1H), 4.19 (dd, $J=5.6$, 3.3 Hz, 1H), 3.68 (s, 3H), 2.44–2.41 (m, 1H), 2.23–2.20 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=153.4$, 149.5, 145.9, 141.4, 128.6, 128.4, 128.3, 127.7, 126.4, 126.0, 123.4, 117.7, 114.7, 114.6, 73.0, 55.7, 40.5, 38.3 ppm; HRMS calcd for $C_{22}H_{20}O_2$: 316.1463; found: 316.1462.

6-Chloro-2,4-diphenylchroman (7c): White solid (67 mg, 66%), m.p. 121–123 °C; IR (neat): $\tilde{\nu}=3002$ (m), 1581 (s), 1485 (s), 1242 (m), 735 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.46$ (d, $J=7.3$ Hz, 2H), 7.38 (t, $J=7.3$ Hz, 2H), 7.34–7.32 (m, 3H), 7.27 (t, $J=7.3$ Hz, 1H), 7.20 (dd, $J=8.4.1.4$ Hz, 2H), 7.09–7.07 (m, 1H), 6.88 (d, $J=8.7$ Hz, 1H), 6.74 (d, $J=2.5$ Hz, 1H), 5.18 (dd, $J=11.5$,1.7 Hz, 1H), 4.30 (dd, $J=12.1$, 5.8 Hz, 1H), 2.41–2.38 (m, 1H), 2.27–2.21 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.1$, 143.5, 140.7, 129.3, 128.8, 128.6, 128.4, 128.2, 127.8, 127.3, 127.0, 126.0, 125.3, 118.4, 78.3, 43.4, 40.1 ppm; HRMS calcd for $C_{21}H_{17}ClO$: 320.0968; found: 320.0963.

6-Chloro-2,4-diphenylchroman (7c′): White semisolid (10 mg, 10%); IR (neat): $\tilde{\nu}=3011$ (m), 1582 (s), 1485 (s), 1239 (m), 752 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.32$–7.28 (m, 7H), 7.25 (t, $J=8.1$ Hz, 1H), 7.14 (dd, $J=6.8$, 3.0 Hz, 1H), 7.11 (d, $J=7.6$ Hz, 2H), 6.94 (d, $J=5.7$ Hz, 2H), 5.03 (dd, $J=10.3$, 2.3 Hz, 1H), 4.16 (t, $J=4.7$ Hz, 1H), 2.43–2.39 (m, 1H), 2.25–2.22 ppm (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=154.0$, 145.2, 140.9, 130.1, 128.6, 128.6, 128.5, 128.2, 127.9, 126.7, 125.9, 125.2, 124.7, 118.4, 73.4, 40.1, 37.8 ppm; HRMS calcd for $C_{21}H_{17}ClO$: 320.0968; found: 320.0981.

2-(4-Chlorophenyl)-4-phenylchroman (7 d): White solid (60 mg, 53 %), m.p. 165–168 °C; IR (neat): $\tilde{\nu}=3057$ (m), 1712 (s), 1484 (s), 1265 (m), 736 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.44$–7.42 (m, 2 H), 7.37 (d, $J=8.5$ Hz, 2 H), 7.33 (t, $J=7.3$ Hz, 2 H), 7.27 (t, $J=7.8$ Hz, 1 H), 7.22 (d, $J=8.4$ Hz, 2 H), 7.15 (t, $J=8.1$ Hz, 1 H), 6.95 (dd, $J=8.1$, 0.9 Hz, 1 H), 6.82–6.77 (m, 2 H), 5.20 (dd, $J=11.5$, 1.7 Hz, 1 H), 4.35 (dd, $J=12.2$, 5.8 Hz, 1 H), 2.41–2.38 (m, 1 H), 2.26–2.20 ppm (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.2$, 144.3, 139.7, 133.7, 129.8, 128.7(CHx2), 128.5, 127.8, 127.4, 126.8, 125.5, 120.7, 116.9, 77.3, 43.3, 40.6 ppm; HRMS calcd for $C_{21}H_{17}ClO$: 320.0968; found: 320.0969.

2-(4-Chlorophenyl)-4-phenylchroman (7 d′): White semisolid (11 mg, 10 %); IR (neat): $\tilde{\nu}=3051$ (m), 1711 (s), 1489 (s), 1270 (m), 735 (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.30$–7.27 (m, 4 H), 7.24–7.21 (m, 3 H), 7.20 (t, $J=6.9$ Hz, 1 H), 7.09 (dd, $J=7.4$ Hz, 2 H), 6.98 (dd, $J=8.2$, 0.9 Hz, 1 H), 6.95 (dd, $J=7.6$, 1.5 Hz, 1 H), 6.86 (t, $J=7.5$ Hz, 1 H), 4.99 (dd, $J=10.5$, 2.4 Hz, 1 H), 4.19 (dd, $J=5.4$, 3.5 Hz, 1 H), 2.40–2.35 (m, 1 H), 2.22–2.18 ppm (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.1$, 145.8, 140.0, 133.5, 130.8, 128.6, 128.6, 128.5, 128.2, 127.4, 126.5, 122.9, 120.7, 117.0, 72.5, 40.1, 38.3 ppm; HRMS calcd for $C_{21}H_{17}ClO$: 320.0968; found: 320.0967.

2-(4-Bromophenyl)-4-phenylchroman (7 e): Light brown solid (58 mg, 51 %), m.p. 174–176 °C; IR (neat): $\tilde{\nu}=3053$ (m), 1712 (s), 1265 (m), 736 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.53$–7.51 (m, 2 H), 7.38–7.36 (m, 2 H), 7.33 (t, $J=7.3$ Hz, 2 H), 7.26 (t, $J=6.4$ Hz, 1 H), 7.22 (dd, $J=7.0$,1.3 Hz, 2 H), 7.15 (t, $J=8.1$ Hz, 1 H), 6.95 (dd, $J=8.1$, 0.9 Hz, 1 H), 6.82–6.77 (m, 2 H), 5.18 (dd, $J=11.5$, 1.6 Hz, 1 H), 4.35 (dd, $J=12.1$, 5.8 Hz, 1 H), 2.41–2.38 (m, 1 H), 2.25–2.19 ppm (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.2$, 143.3, 140.2, 131.7, 129.8, 128.7, 128.5, 127.8, 127.7, 126.8, 125.5, 121.8, 120.7, 116.9, 77.3, 43.3, 40.5 ppm; HRMS calcd for $C_{21}H_{17}BrO$: 364.0463; found: 364.0466.

2-(4-Bromophenyl)-4-phenylchroman (7 e′): Light brown semisolid (11 mg, 10 %); IR (neat): $\tilde{\nu}=3049$ (m), 1705 (s), 1266 (m), 1059 (s), 736 cm^{-1} (s); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.44$–7.42 (m, 2 H), 7.29 (t, $J=7.5$ Hz, 2 H), 7.23–7.21 (m, 1 H), 7.20–7.17 (m, 3 H), 7.09 (d, $J=7.4$ Hz, 2 H), 6.99–6.94 (m, 2 H), 6.86 (t, $J=7.3$ Hz, 1 H), 4.97 (dd, $J=10.5$, 2.4 Hz, 1 H), 4.19 (dd, $J=5.3$, 3.4 Hz, 1 H), 2.38–2.35 (m, 1 H), 2.21–2.19 ppm (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=155.0$, 145.8, 140.5, 131.6, 130.8, 128.6, 128.5, 128.2, 127.7, 126.5, 122.9, 121.6, 120.7, 117.0, 72.6, 40.0, 38.3 ppm; HRMS calcd for $C_{21}H_{17}BrO$: 364.0463; found: 364.0459.

4-(Benzo[*b*]thiophen-2-yl)-2-(2-methoxyphenyl)-3-methylchroman (7 f): White solid (101 mg, 73 %), m.p. 223–225 °C; IR (neat): $\tilde{\nu}=2921$ (m), 1565 (s), 1483 (s), 1265 (m), 736 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.73$ (dd, $J=11.6$, 7.6 Hz, 2 H), 7.54 (dd, $J=7.6$, 1.6 Hz, 1 H), 7.35–7.25 (m, 4 H), 7.12 (t, $J=7.6$ Hz, 1 H), 7.05 (t, $J=7.6$ Hz, 1 H), 6.95–6.88 (m, 3 H), 6.79 (t, $J=7.6$ Hz, 1 H), 5.43 (d, $J=10.0$ Hz, 1 H), 4.29 (d, $J=10.8$ Hz, 1 H), 3.83 (s, 3 H), 2.47–2.37 (m, 1 H), 0.76 ppm (d, $J=6.4$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=157.1$, 155.1, 148.1, 139.8, 139.5, 129.7, 129.2, 128.1, 128.0, 127.7, 124.8, 124.2, 123.9, 123.8, 123.0, 122.5, 121.1, 120.5, 116.8, 115.7, 110.7, 55.5, 47.2, 41.5, 15.0 ppm; HRMS calcd for $C_{25}H_{22}O_2S$: 386.1341, found: 386.1345.

4-(Benzo[*b*]thiophen-2-yl)-2-(4-methoxyphenyl)-3-methylchroman (7 g): White solid (56 mg, 41 %), m.p. 231–233 °C; IR (neat): $\tilde{\nu}=2920$ (m), 1578 (s), 1473 (s), 1261 (m), 737 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.73$ (dd, $J=11.6$, 7.6 Hz, 2 H), 7.38–7.35 (m, 2 H), 7.33–7.31 (m, 1 H), 7.29–7.27 (m, 2 H), 7.11 (t, $J=7.6$ Hz, 1 H), 6.94–6.91 (m, 3 H), 6.89–6.87 (m, 1 H), 6.80–6.76 (m,1 H), 4.72 (d, $J=10.0$ Hz, 1 H), 4.22 (d, $J=10.8$ Hz, 1 H), 3.81 (s, 3 H), 2.41–2.34 (m, 1 H), 0.72 (d, $J=6.4$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.7$, 154.7, 147.9, 139.8, 139.4, 131.7, 129.7, 128.7, 128.1, 124.6, 124.2, 124.0, 123.9, 123.0, 122.5, 120.7, 116.7, 114.0, 83.8, 55.3, 47.1, 41.1, 16.0 ppm; HRMS calcd for $C_{25}H_{22}O_2S$: 386.1341, found: 386.1339.

4-(Benzo[*b*]thiophen-2-yl)-6-methoxy-3-methyl-2-phenylchroman (7 h): White solid (111 mg, 81 %), m.p. 226–228 °C; IR (neat): $\tilde{\nu}=2943$ (m), 1599 (s), 1493(s), 1219 (m), 700 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.73$ (dd, $J=13.6$, 8.0 Hz, 2 H), 7.45–7.25 (m, 8 H), 6.84 (d, $J=8.8$ Hz, 1 H), 6.73–6.70 (m, 1 H), 6.49 (d, $J=0.8$ Hz, 1 H), 4.70 (d, $J=10.0$ Hz, 1 H), 4.20 (d, $J=10.8$ Hz, 1 H), 3.60 (s, 3 H), 2.44–2.33 (m, 1 H), 0.71 ppm (d, $J=6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=153.6$, 148.8, 147.6, 139.9, 139.6, 139.4, 128.6, 128.5, 127.5, 125.2,124.2, 124.0, 123.9, 123.0, 122.5, 117.3, 114.6, 114.0, 84.2, 55.7, 47.3, 41.3, 16.0 ppm; HRMS calcd for $C_{25}H_{22}O_2S$: 386.1341, found: 386.1345.

4-(Benzo[*b*]thiophen-2-yl)-6-chloro-3-methyl-2-phenylchroman (7 i): White solid (106 mg, 85 %), m.p. 241–243 °C; IR (neat): $\tilde{\nu}=2928$ (m), 1712 (s), 1582 (s), 1261 (m), 737 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.75$ (dd, $J=12.4$, 6.0 Hz, 2 H), 7.43–7.28 (m, 8 H), 7.08–7.06 (m, 1 H), 6.89 (d, $J=1.2$ Hz, 1 H), 6.82 (d, $J=7.2$ Hz, 1 H), 4.74 (d, $J=8.0$ Hz, 1 H), 4.19 (d, $J=8.8$ Hz, 1 H), 2.41–2.33 (m, 1 H), 0.71 ppm (d, $J=5.6$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=153.2$, 146.6, 139.9, 139.4, 139.1, 129.2, 128.7, 128.7, 128.2, 127.5, 126.1, 125.6, 124.3, 124.2, 124.2, 123.1, 122.5, 118.2, 84.4, 46.8, 40.8, 15.9 ppm; HRMS calcd for $C_{24}H_{19}OSCl$: 390.0845, found: 390.0838.

4-(Benzo[*b*]thiophen-2-yl)-2-(4-chlorophenyl)-3-methylchroman (7 j): White solid (103 mg, 83 %), m.p. 251–253 °C; IR (neat): $\tilde{\nu}=2920$ (m), 1702 (s), 1484 (s), 1265 (m), 736 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.73$ (dd, $J=11.6$, 7.6 Hz, 2 H), 7.38–7.31 (m, 5 H), 7.29–7.25 (m, 2 H), 7.13 (t, $J=7.6$ Hz, 1 H), 6.93–6.87 (m, 2 H), 6.80 (t, $J=7.6$ Hz, 1 H), 4.74 (d, $J=10.0$ Hz, 1 H), 4.22 (d, $J=10.8$ Hz, 1 H), 2.37–2.30 (m, 1 H), 0.72 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=154.5$, 147.5, 139.8, 139.4, 138.0, 129.8, 129.6, 128.9, 128.8, 128.3, 124.3, 124.1, 124.0, 123.0, 122.5, 120.9, 117.5, 116.7, 83.4, 46.9, 41.2, 15.9 ppm; HRMS calcd for $C_{24}H_{19}ClOS$: 390.0845, found: 390.0844.

Acknowledgements

The authors wish to thank the National Science Council, Taiwan and the Ministry of Education for supporting this work.

Keywords: cycloaddition · diastereoselectivity · gold · oxygen heterocycles · synthetic methods

[1] Povarov reactions are formal [4+2] cycloadditions of *N*-aryl imines with enol ethers or enamines. For reviews, see: a) L. S. Povarov, *Russ. Chem. Rev.* **1967**, *36*, 656; b) V. V. Kouznetsov, *Tetrahedron* **2009**, *65*, 2721; c) D. Bello, R. Ramón, R. Lavilla, *Curr. Org. Chem.* **2010**, *14*, 332; d) M. A. McCarrick, Y. D. Wu, K. N. Houk, *J. Org. Chem.* **1993**, *58*, 3330; e) A. Whiting, C. M. Windsor, *Tetrahedron* **1998**, *54*, 6035.

[2] Selected examples of Povarov reactions catalyzed by Brønsted acids: a) H. Xu, S. J. Zuend, M. G. Woll, Y. Tao, E. N. Jacobson, *Science* **2010**, *327*, 986; b) T. Akiyama, H. Morita, K. Fuchibe, *J. Am. Chem. Soc.* **2006**, *128*, 13070; c) H. Liu, G. Dagousset, G. Masson, P. Retailleau, J. Zhu, *J. Am. Chem. Soc.* **2009**, *131*, 4598; d) G. Dagousset, J. Zhu, G. Masson, *J. Am. Chem. Soc.* **2011**, *133*, 14804; e) H. Ishitani, S. Kobayashi, *Tetrahedron Lett.* **1996**, *37*, 7357; f) G. Bergonzini, L. Gramigna, A. Mazzanti, M. Fochi, L. Bernardi, A. Ricci, *Chem. Commun.* **2010**, *46*, 327; g) L. He, M. Bekkaye, P. Retailleau, G. Masson, *Org. Lett.* **2012**, *14*, 3158.

[3] R. R. Taylor, R. A. Batey, *J. Org. Chem.* **2013**, *78*, 1404.

[4] A. M. Jadhav, V. V. Pagar, R.-S. Liu, *Angew. Chem.* **2012**, *124*, 11979; *Angew. Chem. Int. Ed.* **2012**, *51*, 11809.

[5] Y. Huang, J. Zhang, T. R. R. Pettus, *Org. Lett.* **2005**, *7*, 5841.

[6] A. R. Tapas, D. M. Sakarkar, R. B. Kakde, *Top. J. Pharm. Res.* **2008**, *7*, 1089.

[7] a) R. L. Tolman, A. C. Chin, Telomerase inhibitors and methods of their use. W. O. Patent 0, 193,864, Dec 13, **2001**; b) W. Mar, H. T. Lee, K. H. Je, H. Y. Choi, E. K. Seo, *Arch. Pharmacal Res.* **2003**, *26*, 147.

[8] a) E. J. Jacobsen, F. J. VanDoornik, D. E. Ayer, K. L. Belonga, J. M. Braughler, E. D. Hall, D. J. Houser, *J. Med. Chem.* **1992**, *35*, 4464; b) F. Cassidy, J. M. Evans, M. S. Hadley, A. H. Haladij, P. E. Leach, G. Stemp, *J. Med. Chem.* **1992**, *35*, 1623; c) C. Pouget, C. Fagnere, J.-P. Basly, H. Leveque, A.-J. Chulia, *Tetrahedron* **2000**, *56*, 6047.

[9] Crystallographic data of compounds **6a** and **6g** are provided in the Supporting Information. CCDC-996266 (**6a**) and CCDC-996267 (**6g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] a) L. F. Tietze, T. Kinzel, S. Schmatz, *J. Am. Chem. Soc.* **2006**, *128*, 11483; b) P. R. Carlier, K. M. Lo, M. M.-C. Lo, I. D. Williams, *J. Org. Chem.* **1995**, *60*, 7511; c) S. Tomoda, *Chem. Rev.* **1999**, *99*, 1243; d) A. J. Green, Y.-L. Kuan, J. M. White, *J. Org. Chem.* **1995**, *60*, 2734.

[11] For reviews on gold-catalyzed cycloaddition reactions, see: a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180; b) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208; c) N. T. Patil, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3395; d) S. M. Abu Sohel, R.-S. Liu, *Chem. Soc. Rev.* **2009**, *38*, 2269; e) F. López, J. L. Mascarenas, *Beilstein J. Org. Chem.* **2011**, *7*, 1075; f) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria, A. Simonneau, *Chem. Rev.* **2011**, *111*, 1954; g) D. Qian, J. Zhang, *Chem. Rec.* **2014**, *14*, 280.

[12] Selected papers: a) S. N. Karad, S. Bhunia, R.-S. Liu, *Angew. Chem.* **2012**, *124*, 8852; *Angew. Chem. Int. Ed.* **2012**, *51*, 8722; b) A. M. Jadhav, S. Bhunia, H.-Y. Liao, R.-S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 1769; c) C. H. Chen, Y. C. Tsai, R.-S. Liu, *Angew. Chem.* **2013**, *125*, 4697; *Angew. Chem. Int. Ed.* **2013**, *52*, 4599; d) M. W. Johnson, S. W. Bagley, N. P. Mankad, R. G. Bergman, V. Mascitti, F. D. Toste, *Angew. Chem.* **2014**, *126*, 4493; *Angew. Chem. Int. Ed.* **2014**, *53*, 4404; e) W. Zi, F. D. Toste, *J. Am. Chem. Soc.* **2013**, *135*, 12600; f) J. Bucher, T. Wurm, K. S. Nalivela, R. F. Rominger, A. S. K. Hashmi, *Angew. Chem.* **2014**, *126*, 3934; *Angew. Chem. Int. Ed.* **2014**, *53*, 3854; g) E. Rettenmeier, A. M. Schuster, M. Rudolph, F. Rominger, C. A. Gade, A. S. K. Hashmi, *Angew. Chem.* **2013**, *125*, 5993; *Angew. Chem. Int. Ed.* **2013**, *52*, 5880; h) Y. Wang, A. Yepremyan, S. Ghorai, R. Todd, D. H. Aue, L. Zhang, *Angew. Chem.* **2013**, *125*, 7949; *Angew. Chem. Int. Ed.* **2013**, *52*, 7795; i) B. Lu, Y. Li, Y. Wang, D. H. Aue, Y. Luo, L. Zhang, *J. Am. Chem. Soc.* **2013**, *135*, 8512; j) C. Obradors, A. M. Echavarren, *Chem. Eur. J.* **2013**, *19*, 3547.

[13] a) N. J. Willis, C. D. Bray, *Chem. Eur. J.* **2012**, *18*, 9160; b) S. J. Gharpure, A. M. Sathiyanarayanan, P. K. Vuram, *RSC Adv.* **2013**, *3*, 18279; c) S. B. Ferreira, F. de C. da Silva, A. C. Pinto, D. T. G. Gonzaga, V. F. Ferreira, *J. Heterocycl. Chem.* **2009**, *46*, 1080; d) R. W. Van de Water, T. R. R. Pettus, *Tetrahedron* **2002**, *58*, 5367; e) K. A. Korthals, W. D. Wulff, *J. Am. Chem. Soc.* **2008**, *130*, 2898; f) T. Inoue, S. Inoue, K. Sato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1647.

Received: April 28, 2014