RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2022, **12**, 16684

Diastereoselective synthesis of chroman bearing spirobenzofuranone scaffolds *via* oxa-Michael/1,6-conjugated addition of *para*-quinone methides with benzofuranone-type olefins†

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Received 13th May 2022
Accepted 29th May 2022

DOI: 10.1039/d2ra03031d

rsc.li/rsc-advances

A simple and convenient cyclization of *ortho*-hydroxyphenyl-substituted *para*-quinone methides with benzofuran-2-one type active olefins *via* oxa-Michael/1,6-conjugated addition has been developed, which afforded an easy access to enriched functionalized chroman-spirobenzofuran-2-one scaffolds with good to excellent yields (up to 90%) and diastereoselectivities (up to >19 : 1 dr). This reaction provided an efficient method for constructing desired spirocyclic compounds combining both well-known heterocyclic pharmacophores chroman and benzofuran-2-one.

The chroman framework represents a privileged heterocyclic core commonly found within a wide variety of biologically active natural products[1] and synthetic compounds of medicinal interest (Fig. 1).[2] Owing to the wide application of these heterocyclic molecules, over the past few decades, numerous efforts have been devoted to the efficient synthesis of chroman nucleus motifs.[3,4] In particular, incorporating chroman into spiro-bridged and spiro-fused heterocyclic systems is appealing due to its fascinating molecular architecture and proven biological activity.[5] Among the existing methods, the [4 + m] cycloaddition of *para*-quinone methides (*p*-QMs) is found to be an efficient pathway to access these valuable spirocyclic skeletons.[6] For instance, the Enders group synthesized functionalized chromans with an oxindole motif by the asymmetric organocatalytic domino oxa-Michael/1,6-addition reaction.[7] After that, the Hao,[8a] Peng,[8b] Shi,[8c,d] Zhou,[8e] Liang[8f] and Wang[8g] groups developed convenient methods to construct chromans bearing spirocyclic skeletons from *p*-QMs, respectively. Despite all these shining achievements, however, it is still very challenging to simply and conveniently construct chromans bearing quaternary carbon spirals for organic chemical or drug discovery among these [4 + m] cycloaddition reactions.

Benzofuran-2-(3*H*)-ones as one of the important oxygen-containing heterocycles that exist in a broad array of natural products[9] and potential medicines.[10] The streamlined synthesis of benzofuran-2-ones pose considerable challenge due to their quaternary carbon centers at the C-3 position,[11] especially those featuring relatively congested spirocyclic motifs represent challenging synthetic targets.[12,13] In our continuous interests in developing efficient method for the synthesis of spirocyclic compounds based on cyclization reaction,[14] we wish to report a cycloaddition of *para*-quinone methides with benzofuranone derived olefins, affording the spiro-cycloadducts in good to excellent yields and diastereoselectivities. This cyclization features the simultaneous formation of chroman and spirobenzofuran-2-one skeletons in a single step (Scheme 1), which may be potentially applied as pharmaceutical agents.

We initiated our investigations with the readily available *ortho*-hydroxyphenyl-substituted *para*-quinone methides **1a** and 3-benzylidenebenzofuran-2-one **2a** in toluene at room temperature in the presence of base. Unfortunately, no desired

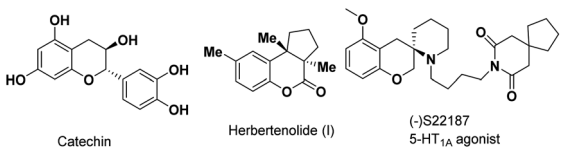
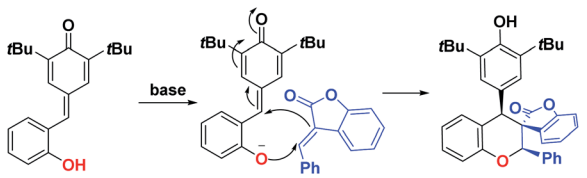


Fig. 1 Representative chroman compounds.



Scheme 1 Strategy for the synthesis of chroman-spirobenzofuran-2-one.

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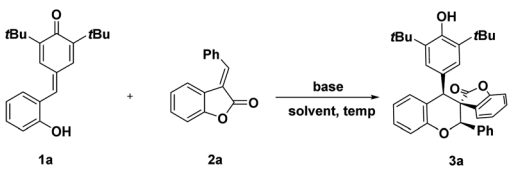
† Electronic supplementary information (ESI) available. CCDC 2128983. For ESI and crystallographic data in CIF or other electronic format see https://doi.org/10.1039/d2ra03031d

chroman derivatives bearing spirobenzofuranone scaffolds **3a** was isolated in the presence of 2 eq. Na_2CO_3 after stirring at room temperature for 48 h (entry 1, Table 1). A base survey showed that K_2CO_3 and CsF led to desired cycloaddcuts **3a** even if with a disappointing yield (entries 2–4, Table 1). Gratifyingly, Cs_2CO_3 furnished the desired product in 70% yield and with a generally acceptable 6 : 1 dr value (entry 5, Table 1). A solvent screening indicated that the yield and diastereoselectivity are both dependent on the solvent (Table 1). Thus, the oxygenated solvents such as THF, diethyl ether and 1,4-dioxane gave comparably high yields and diastereoselectivities than polar solvents as exemplified by CH_3CN or DMF (entries 5–10). To our delight, performing the reaction in THF led to desired chroman-spirobenzofuranone **3a** with an excellent diastereoselectivity, albeit with a very subtle erosion of the yield (entry 6). Further optimization of the reaction conditions by varying the temperature was also investigated. When higher temperature was used, no improvement in the final yield was observed (entry 11). Performing the reaction at lower 10 °C resulted in a increase of the yield accompanied with no erosion in diastereoselectivity (entry 12). However, the yield decreased to 64% when the reaction performed at lower 0 °C (entry 13).

With the optimized reaction conditions in hand, we explored the substrate scope of this cyclization reaction with a selection of benzofuranones. The results are shown in Table 2. To our pleasure, a wide range of benzofuran-2-ones derived olefins were compatible affording the corresponding chromans-spirobenzofuranone scaffolds **3** in good results. In detail, the steric hindrance of substituents had a significant impact on the cyclization reaction. The substrates with substituents on *para*- or *meta*-position on phenyl ring were tolerable affording the desired cycloadducts in good yields regardless of the electronic nature of substituents (entries 5–14). However, good diastereoselectivities were also observed in *ortho*-substituted substrates (entries 2–4). Furthermore, 2-naphthyl derived substrate gave also good yield and sole diastereoselectivity (entry 15). Multi-substituted substrate was also able to participate in this cyclization, for example, 3,4,5-trimethoxylphenyl substituted benzofuranone delivered cycloadduct **3p** in 88% yield and with 12 : 1 dr value (entry 16). Interestingly, the extension of the reaction conditions to heteroaromatic substrates including 3-pyridyl and 3-thiophenyl benzofuranones were proceeded smoothly, giving rise to cyclization products **3q** and **3r** in 79% and 80% yield, respectively (entries 17–18).

Subsequently, the generality of this cyclization reaction was further evaluated through varying *p*-QMs **1**. As shown in Table 3. It turned out that various *p*-QMs **1** can be employed to the reaction, which delivered functionalized chroman-spirobenzofuran-2-ones scaffolds **4** in high yields (up to 90%) and with good diastereoselectivities. It seems that the position of the substituents had some delicate influence on the reaction. The C5-methoxyl- or methyl-substituted substrates *p*-QMs **1** generated the products with a higher yield than those of the C4-substituted counterparts (entries 3–6). Moreover, the C5-chloro- and bromo-substituted *p*-QMs **1** afforded the products **4a** and **4b** in moderate yield (entries 1–2).

Table 1 Optimization of conditions[a]

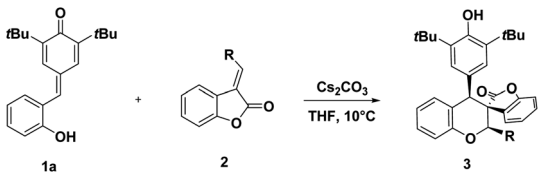


1a 2a 3a

Entry	Base	Solvent	Yield[b] (%)	Dr[c]
1	Na_2CO_3	Toluene	—	—
2	DMAP	Toluene	—	—
3	K_2CO_3	Toluene	25	3 : 1
4	CsF	Toluene	52	5 : 1
5	Cs_2CO_3	Toluene	70	6 : 1
6	Cs_2CO_3	THF	68	>19 : 1
7	Cs_2CO_3	Et_2O	60	8 : 1
8	Cs_2CO_3	Dioxane	53	7 : 1
9	Cs_2CO_3	CH_3CN	50	>19 : 1
10	Cs_2CO_3	DMF	31	15 : 1
11[d]	Cs_2CO_3	THF	65	>19 : 1
12[e]	Cs_2CO_3	THF	75	>19 : 1
13[f]	Cs_2CO_3	THF	64	>19 : 1

[a] Reaction conditions: *p*-QMs **1a** (0.1 mmol), benzofuranones **2a** (0.12 mmol) and base (0.2 mmol) in 2 mL of solvent for 6–48 h. [b] Isolated yields. [c] Determined by crude ^{1}H NMR analysis. [d] Performed at 30 °C. [e] Performed at 10 °C. [f] Performed at 0 °C.

Table 2 Substrate scope of diastereoselective synthesis of chroman-spirobenzofuran-2-one[a]

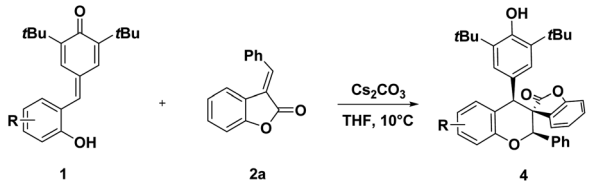


1a 2 3

Entry	R	3	Yield[b] (%)	Dr[c]
1	C_6H_5	**3a**	75	>19 : 1
2	2-ClC_6H_4	**3b**	69	>19 : 1
3	2-BrC_6H_4	**3c**	67	15 : 1
4	2-$CH_3C_6H_4$	**3d**	64	>19 : 1
5	3-$CH_3C_6H_4$	**3e**	75	>19 : 1
6	3-$MeOC_6H_4$	**3f**	72	>19 : 1
7	3-$NO_2C_6H_4$	**3g**	71	>19 : 1
8	3-BrC_6H_4	**3h**	75	>19 : 1
9	4-$CH_3C_6H_4$	**3i**	73	10 : 1
10	4-$MeOC_6H_4$	**3j**	86	>19 : 1
11	4-$CF_3C_6H_4$	**3k**	82	12 : 1
12	4-$NO_2C_6H_4$	**3l**	85	12 : 1
13	4-ClC_6H_4	**3m**	83	>19 : 1
14	4-BrC_6H_4	**3n**	81	12 : 1
15	2-Naphthyl	**3o**	74	>19 : 1
16	3,4,5-$(OMe)_3C_6H_2$	**3p**	88	12 : 1
17	3-Pyridinyl	**3q**	79	>19 : 1
18	3-Thiophenyl	**3r**	80	>19 : 1

[a] Reaction conditions: *p*-QMs **1a** (0.1 mmol), benzofuranones **2** (0.12 mmol) and Cs_2CO_3 (0.2 mmol) in 2 mL of THF. [b] Isolated yields for 4–48 h. [c] Determined by crude ^{1}H NMR analysis.

Table 3 Substrate scope of *p*-QMs[a]



Entry	R	4	Yield[b] (%)	Dr[c]
1	5-Cl	**4a**	73	>19 : 1
2	5-Br	**4b**	65	>19 : 1
3	5-CH_3	**4c**	90	>19 : 1
4	5-OCH_3	**4d**	80	10 : 1
5	4-CH_3	**4e**	72	>19 : 1
6	4-OCH_3	**4f**	66	10 : 1

[a] Reaction conditions: *p*-QMs **1** (0.1 mmol), benzofuranones **2a** (0.12 mmol) and Cs_2CO_3 (0.2 mmol) in 2 mL of THF for 6–48 h. [b] Isolated yields. [c] Determined by crude ^1H NMR analysis.

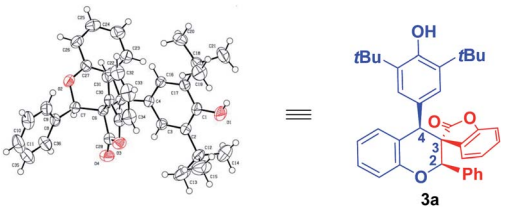


Fig. 2 X-ray crystal structure of **3a**.

The structure and relative configuration of **3a** were determined by HRMS, NMR spectroscopy and single-crystal X-ray analysis.[15] The relative configuration of other cycloadducts were tentatively assigned by analogy (Fig. 2 and see ESI†).

Conclusions

In conclusion, we described a cyclization reaction of *ortho*-hydroxyphenyl-substituted *para*-quinone methides with benzofuran-2-one derived olefins *via* oxa-Michael/1,6-conjugated addition, which efficiently constructed enriched functionalized spirocyclic compounds combining both well-known heterocyclic pharmacophores chroman and benzofuran-2-one in good to excellent yields (up to 90%) and diastereoselectivities (up to 19 : 1 dr).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (21772158), Scientific Research Funds of Guiyang University [GYU-KY-2022] and Guizhou Education Department Youth Science and Technology Talents Growth Project KY[2019]094.

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