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Diastereo- and Enantioselective Organocatalytic Synthesis of Spirocyclopropyl Pyrazolones

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Dedicated to Professor Miquel Angel Pericàs Brondó on the occasion of his retirement from the Institute of Chemical Research of Catalonia, ICIQ,

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Abstract: A diastereo- and enantioselective synthesis of spirocyclopropylpyrazolones has been described through a Michael/alkylation cascade reaction of 4-arylidenepyrazol-5-ones with diethyl 2-bromomalonate catalyzed by $(DHQ)_2AQN$. The reaction afforded selectively the corresponding spirocyclic compounds with 30–83% yield, diastereoselectivities ranging from 60:40 to >95:5 and 26–93% enantiomeric excess under mild reaction conditions. Moreover, we performed two selective transformations with the corresponding chiral compounds.

Keywords: spirocyclic compounds; pyrazolones; cyclopropanes; organocatalysis; asymmetric synthesis

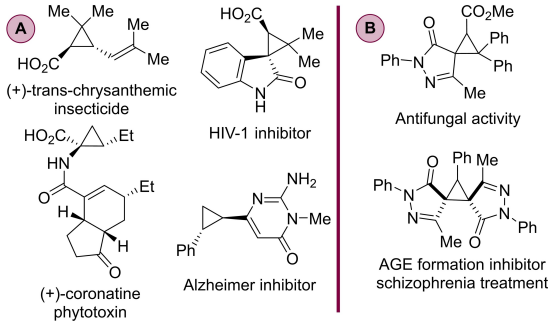


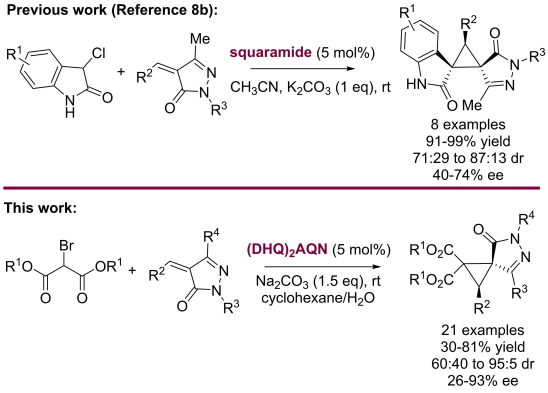
Figure 1. Natural products and biological active compounds containing cyclopropanes (1 A) and spirocyclopropyl pyrazolones (1B).

The chiral cyclopropane unit is a structural motif that is present in a large number of natural products and biological active compounds (Figure 1A).[1] Moreover, they are valuable building blocks for organic synthesis because of their unique properties such as the rigidness of the cyclopropyl ring and its inherent electrophilic reactivity, which are very useful for a wide range of transformations such as rearrangements, ring-opening or cycloaddition reactions.[2] Consequently, over the past years the synthesis of chiral cyclopropanes has become a hot topic in organic chemistry.[3] In this context, the catalytic enantioselective Michael-initiated ring closure (MIRC) reactions (or Michael/alkylation cascade reactions) of electron-poor olefins with enolates derived from α-carbonyl compounds or with ylides represent very efficient and convenient methodologies for the synthesis of chiral cyclopropanes, and among them, the organocatalytic approaches are the most attractive ones from a sustainable chemistry point of view.[4] In this context, spirocyclopropane compounds are an important class of cyclopropanes that have received the attention of synthetic and medicinal chemists, because these particular cyclopropyl rings are present in several pharmaceuticals.[5] In particular, spirocyclopropyl-pyrazolones (Figure 1B) have shown antifungal activity[6] or have been used for the treatment of schizophrenia.[7] Considering the possibilities and properties of the spirocyclopropylpyrazolone derivatives, several selective synthetic approaches have been described in the literature to obtain these class of compounds. However, most of the reported protocols

are limited to diastereoselective synthesis. Enantioselective examples remain limited[8] Du and coworkers described the enantioselective synthesis of spirocyclopropanes containing pyrazolones through a Michael/alkylation cascade reaction catalyzed by a squaramide organocatalyst (Scheme 1A).[8b] In their protocol, they shown eight examples with good yields and high diastereoselectivities but moderate enantiomeric excesses (40–74% ee). On the other hand, Wang and coworkers, described the asymmetric synthesis of spirocyclopropane-pyrazolones using 2,3-dioxopyrrolidines and halogenated pyrazolones as reagents and a phosphonium salt as organocatalyst.[8g] Therefore, the development of efficient strategies for the construction of spirocyclopropylpyrazolones derivatives in a selective way is highly valuable for medicinal chemistry and it is worth it for chemical synthesis.

Herein, we would like to present an efficient and selective organocatalytic cyclopropanation through a Michael/alkylation cascade reaction of dialkyl bromomalonates and arylidenepyrazolones catalyzed by a commercially available $(DHQ)_2AQN$ organocatalyst under phase-transfer conditions. The corresponding chiral and highly substituted spirocyclopropanes bearing a pyrazolone moiety are obtained with good yields (up to 67%), excellent diastereoselectivities (up to >95:5 dr) and high enantiomeric excesses (up to 93% ee).

Firstly, we chose the reaction between diethyl 2-bromomalonate (**1a**) and (*E*)-4-benzylidene-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) to optimize the reaction conditions (Table 1) using different organocatalysts derived from *Cinchona* alkaloids. When the quinine-derived squaramide **I** was used in combination with K_2CO_3 in DCM at room temperature, product **3aa** was obtained in 61% yield, after 5 days, with 80:20 dr, but as racemic mixture (Table 1, entry 1). Chiral quaternary ammonium salt **II** afforded the spirocyclopropane with 7% ee (Table 1, entry 2). At this point of the optimization, we decided to introduce

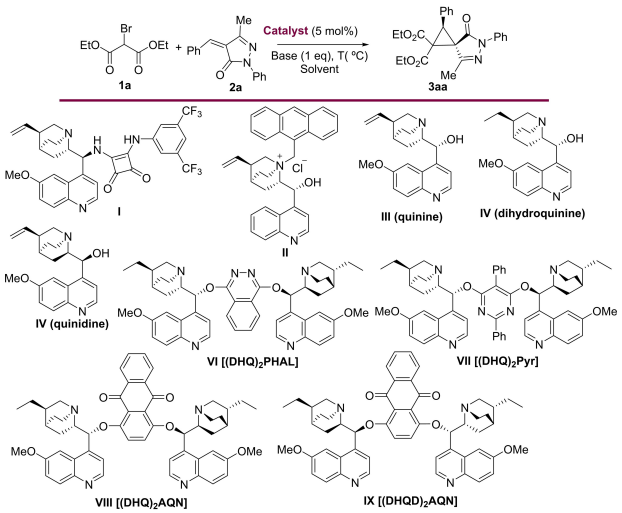


Scheme 1. Diastereo- and enantioselective organocatalytic synthesis of spirocyclopropylpyrazolones.

some water in order to have the conditions for phase transfer catalysis. Using catalyst **II** (5 mol%), K_2CO_3 as a base and a mixture 2:1 of DCM:H_2O as solvent, we observed similar yield and diastereoselectivity (72% yield and 64:36 dr), but the enantiomeric excess of **3aa** improved to 23% (Table 1, entry 3). The use of K_3PO_3 in combination with catalyst **II**, slightly enhance the ee of the cyclopropane **3aa** (Table 1, entry 4). When quinine **III** was used as catalyst, compound **3aa** was isolated with 34% ee (Table 1, entry 5). Seeking to improve the catalytic activity of quinine **III**, we decided to try other organic solvents like toluene (entry 6) or cyclohexane (entry 7), observing better stereoselectivities for compound **3aa**. Cyclohexane was the best organic solvent, providing the chiral cyclopropane in 68% yield, 88:12 dr and 63% ee after 2 days (Table 1, entry 7). The employment of Na_2CO_3 as base, gave better performance, and product **3aa** was obtained with the best results (81% yield, 87:13 dr and 67% ee) (Table 1, entry 8). Under these conditions, we decided to evaluate other organocatalysts derived from *Cinchona* alkaloids. Dihydroquinine **IV** gave similar stereoselectivities (entry 9) showing that the alkene moiety of the catalyst had no influence on the reaction outcome, while quinidine (**V**) (Table 1, entry 10) gave slightly lower enantioselectivity for the opposite enantiomer. Commercial available *bis-Cinchona* alkaloid catalysts $(DHQ)_2PHAL$ (**VI**), $(DHQ)_2Pyr$ (**VII**) and $(DHQ)_2AQN$ (**VIII**) were also tested (entries 11, 12 and 13, respectively). To our delight, $(DHQ)_2AQN$ (**VIII**) catalyzed efficiently the reaction and the chiral product **3aa** was obtained with 63% yield, 94:6 diastereoisomeric ratio and 90% enantiomeric excess (Table 1, entry 13). The use of a more diluted solution, slightly improved the enantioselectivity of the reaction and product **3aa** was isolated with 92% ee (Table 1, entry 14). Finally, the pseudoenantiomer $(DHQD)_2AQN$ (**IX**) was tested as organocatalyst (Table 1, entry 15), giving very similar results than **VIII**, although the diastereoselectivity was slightly lower (89:11) for the opposite enantiomer.[9]

With the optimized reaction conditions in hand (Table 1, entry 14), we proceeded to study the scope of the organocatalytic cyclopropanation reaction (Scheme 2). First we evaluated different dialkyl 2-bromomalonates to study the effect of the alkoxy groups on the stereoselectivity of the reaction. The dimethyl derivative **1b** gave the spirocyclopropylpyrazolone **3ba** in 41% yield, 87:13 dr and 87% enantiomeric excess, while diisopropyl 2-bromomalonate (**1c**) afforded product **3ca** in 59% yield with similar diastereoselectivity but lower enantioselectivity (70% ee). We also tested the dialkyl 2-chloromalonate derivatives, but in these reactions the products were obtained with lower stereoselectivities. Therefore, we decided to continue the evaluation of the scope of the reaction using diethyl 2-bromomalonate **1a** as reactant.

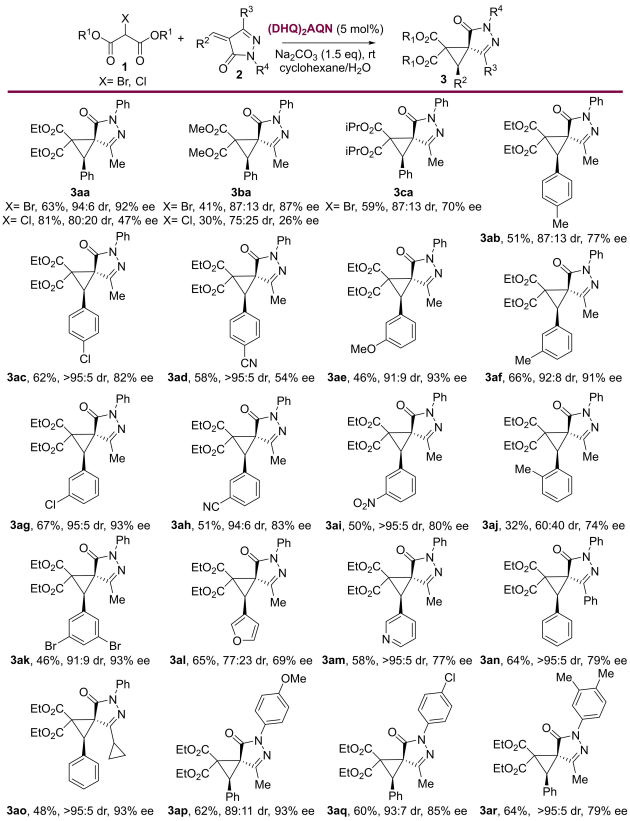
Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Base	Solvent	Yield (%)[b]	dr[c]	ee (%)[d]
1[e]	**I**	K_2CO_3	DCM	61	80:20	0
2[e]	**II**	K_2CO_3	DCM	62	70:30	7
3[f]	**II**	K_2CO_3	DCM/H_2O	72	64:36	23
4[g]	**II**	K_3PO_4	DCM/H_2O	67	60:40	26
5[h]	**III**	K_3PO_4	DCM/H_2O	48	70:30	34
6[i]	**III**	K_3PO_4	Tol/H_2O	80	74:26	52
7[i]	**III**	K_3PO_4	Cy/H_2O	68	88:12	63
8[g]	**III**	Na_2CO_3	Cy/H_2O	81	87:13	67
9[h]	**IV**	Na_2CO_3	Cy/H_2O	72	87:13	67
10[h]	**V**	Na_2CO_3	Cy/H_2O	83	85:15	63
11[i]	**VI**	Na_2CO_3	Cy/H_2O	27	73:27	44
12[i]	**VII**	Na_2CO_3	Cy/H_2O	51	83:17	79
13[i]	**VIII**	Na_2CO_3	Cy/H_2O	63	94:6	90
14[i,j]	**VIII**	Na_2CO_3	Cy/H_2O	63	94:6	92
15[i,j]	**IX**	Na_2CO_3	Cy/H_2O	71	89:11	90[k]

[a] Reaction conditions: 0.15 mmol **1a**, 0.1 mmol **2a**, 0.15 mmol of base and 5 mol% of catalyst were used with a biphasic system (1.5 mL; 2:1 solvent:H_2O) at room temperature.
[b] Isolated yield after column chromatography.
[c] Determined by ^1H NMR.
[d] Determined by chiral HPLC.
[e] The reaction time was 5 days.
[f] The reaction time was 6 days.
[g] The reaction time was 3 days.
[h] The reaction time was 1 day.
[i] The reaction time was 2 days.
[j] 2 mL of cyclohexane were used.
[k] The opposite enantiomer was obtained. DCM = CH_2Cl_2; Tol = toluene; Cy = cyclohexane.

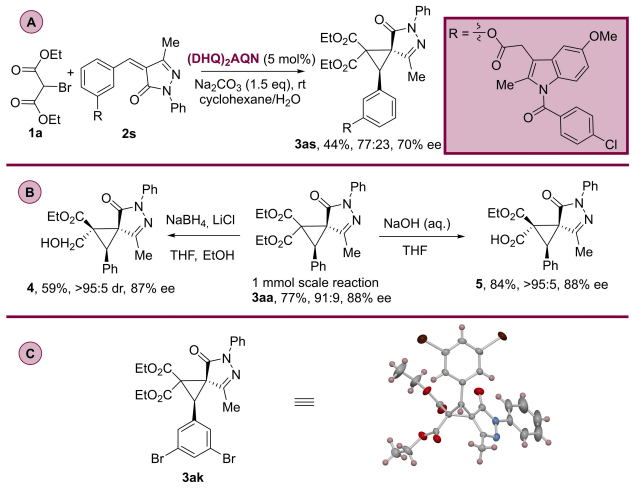
Later, we studied the effect of the substituents on the aromatic ring of the arylidenepyrazolone **2**. Starting materials with electron-donating (Me) or electron-withdrawing groups (Cl or CN) at *para* position afforded the corresponding products with excellent diastereoselectivities, but lower enantiomeric excesses. However, the reaction tolerates very well the presence of substituents at *meta* position, obtaining excellent stereoselectivities (>90:10 dr and 80–93% ee) with either electron-donating (MeO or Me) or electron-withdrawing groups (Cl, CN or NO_2). Nevertheless, the reactivity and stereoselectivity diminished if the substituent (Me) is at *ortho* position, probably due to an increase in v hindrance. 3,5-Dibromo benzylidene-pyrazolone was also compatible obtaining the spirocyclopropyl adduct **3ak**, with moderated yield (46%), but high diastereoselectivity (91:9) and excellent enantiomeric excess (93%). Moreover, heterocyclic



Scheme 2. Substrate scope of organocatalytic cyclopropanation reaction. Reaction conditions: **1** (0.15 mmol, **2** (0.1 mmol), Na_2CO_3 (0.15 mmol) and $(DHQ)_2AQN$ (5 mol%) in a mixture of cyclohexane (2 mL) and H_2O (0.5 mL) at rt. Isolated yields of **3** after column chromatography. Diastereoisomeric ratios determined by ^1H NMR. Enantiomeric excesses determined by chiral HPLC. Reactions carried out with bromomalonates under otherwise stated.

derivatives (furyl and pyridyl substituents) were tolerated, and the corresponding products **3 al** and **3 am** were obtained in good yields, but with moderate enantioselectivities (69% and 77% ee, respectively). In addition, we studied the influence of the substituent at 5-position of the pyrazolone. The reaction tolerates a cyclopropyl group at this position obtaining good results (93% ee), but the presence of a phenyl group decreased the enantioselectivity of the reaction (79% ee). Finally, we studied different substituted aromatic rings attached to the nitrogen of the pyrazolone. In general, the substituents are well tolerated, obtaining the corresponding chiral cyclopropane products (**3 am-3 ar**) with good yields, diastereoselectivities and enantiomeric excesses.

To showcase the robustness and utility of our methodology, the reaction was tested using a structurally complex drug-derived arylidenepyrazolone (Scheme 3A). For example, indomethacin (**2 s**), a nonsteroidal anti-inflammatory drug bearing a structurally



Scheme 3. A) Late-stage functionalization of structurally complex molecules; B) Synthetic transformations with the chiral cyclopropanes; C) X-ray structure of compound **3 ak**.

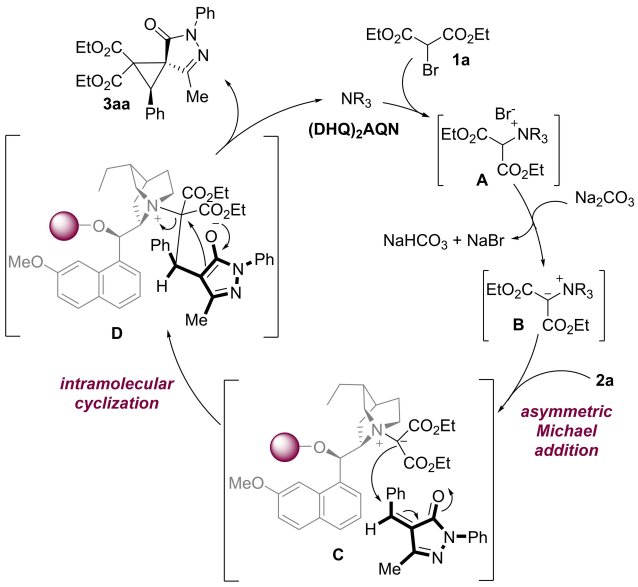
complex architecture and multiple functional groups,[10] was tolerated, although the chiral cyclopropane **3 as** was obtained with moderate stereoselectivity (77:23 dr and 70% ee). The reaction of **1 a** and **2 a** could be carried out at the 1 mmol scale (Scheme 3B) obtaining product **3 aa** with better yield (77%), but with a slightly decrease on the enantioselectivity (88% ee) with respect to the 0.1 mmol reaction.

To demonstrate the versatility and usefulness of our organocatalytic cyclopropanation protocol, we performed two chemical modifications of the chiral spirocyclopropane compound **3 aa** (Scheme 3B). The selective reduction of one of the ester groups was possible using a combination of $NaBH_4$ and LiCl, that provided product **4** bearing three stereogenic centers (two of them all-carbon quaternary stereocenters) in 59% yield, >95:5 dr without the erosion of the enantiomeric excess. Moreover, NaOH (aq.) promoted the selective hydrolisis of one of the ester groups giving the chiral cyclopronane **5** with three stereogenic centers (again with two of them fully substituted) in 84% yield, >95:5 dr and 88% ee. Finally, the absolute configuration of the stereogenic centers in product **3 ak**, was unambiguously determined by X-ray crystallography (Scheme 3C).[11] The configuration of the remaining products **3** was assigned on the assumption of a uniform mechanistic pathway. In addition, the relative configuration of compounds **4** and **5** were stablished by NOE experiments.[12] We explain the selective reduction and hydrolysis of one of the esters groups due to the steric hindrance. The less reactive ester is the one that is in *cis* position to the aromatic ring of the cyclopropane.

Based on previous literature procedures for asymmetric cyclopropanation reactions using *Cinchona* alkaloid organocatalysts,[13] a plausible reaction mecha-

nism is outlined in Scheme 4. Initially, $(DHQ)_2AQN$ reacts with bromomalonate **1a** affording the ammonium salt **A**, which is subsequently deprotonated by Na_2CO_3 forming the nucleophilic ammonium ylide **B**. We think that the biphasic system is beneficial to form these catalytic species by carrying the inorganic salts from the organic to the water phase. Subsequently, a Michael addition of **B** to the benzylidenepyrazolone **2a** generates the intermediate **D**, which could undergo an intramolecular susbtitution giving the corresponding chiral cyclopropane adduct **3aa** and regenerating the chiral organocatalyst $(DHQ)_2AQN$. Nevertheless, a phase transfer catalysis involving the quaternary ammonium salt **A** cannot be ruled out. The ammonium salt **A** may form a nucleophilic ionic pair with the ethyl bromomalonate enolate generated by deprotonation with Na_2CO_3 at the cyclohexane/water interphase. Then, this nucleophilic ionic pair may react in a stereoselectively with **2a** affording the chiral cyclopropane **3aa**.

In summary, we have developed an organocatalytic cyclopropanation reaction of arylidenepyrazolones with dialkyl 2-bromomalonates catalyzed by a commercial organocatalyst $(DHQ)_2AQN$. The reaction consists of a diastereo- and enantioselective Michael/alkylation cascade that affords the chiral cyclopropylpyrazolones (21 examples) with 30–81% yield, diastereoselectivities ranging from 60:40 to >95:5 and 26–93% enantiomeric excess. Furthermore, two synthetic transformations of the chiral spirocyclopropane compound **3aa** have been performed, showing the potential applicability of our methodology. The present organocatalytic protocol represents a powerful synthetic tool for the stereoselective synthesis of potentially bioactive spirocyclopropane adducts bearing a pyrazolone moiety.



Scheme 4. Plausible mechanistic pathway.

Experimental Section

General Procedure for the Diastereo- and Enantioselective Cyclopropanation of Arylidenepyrazolones 2

In a 5 mL vial, the corresponding alkylidene pyrazolone (**2**, 0.1 mmol, 1 eq.), diethyl bromomalonate (**1a**, 0.15 mmol, 1.5 eq., 26 µL), sodium carbonate (1.5 eq., 15.9 mg) and catalyst $(DHQ)_2AQN$ (**VIII**, 5 mol%, 4.2 mg) were dissolved in 2 mL of cyclohexane and 0.5 mL of H_2O. The reaction mixture was stirred at room temperature for 2 days. After this time, the reaction mixture was diluted with H_2O (10 mL), extracted with DCM (3x20 mL) and washed with H_2O (20 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude was purified via column chromatography with hexane:DCM mixtures as eluent to afford the corresponding enantiomerically enriched cyclopropanes **3**.

Selective reduction of 3aa with $NaBH_4$

To a solution of compound **3aa** (0.065 mmol, 1 eq.) in 1 mL of THF and 1 mL of EtOH, LiCl (1 eq.) and $NaBH_4$ (1 eq.) were added under stirring. The reaction mixture was left at room temperature for 15 h and then diluted with a solution of Rochelle Salt 10% (10 mL). Then, it was extracted with EtOAc (3x20 mL). The solvent was evaporated under vacuo and the crude was purified via column chromatography with mixtures hexane:EtOAc as eluent to obtain product **4**.

Selective hydrolysis of 3aa with NaOH

Compound **3aa** (0.05 mmol, 1 eq.) was dissolved in 1 mL THF. 1 M NaOH (0.05 mL, 1 eq.) was added to the solution and it was left stirring at room temperature for 8 h. The reaction mixture was then diluted with EtOAc (10 mL) and extracted with 10% aqueous NaOH (3x15 mL). The aqueous phase was acidified with 2 M aqueous HCl and extracted with DCM (3x20 mL). The organic phase was evaporated under reduced pressure to furnish product **5**.

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[9] For further optimization studies, see the supporting information.

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[11] CCDC 2263129 (**3 ak**) contains 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.

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