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Full Paper

C-Alkynylation of Chromones by Sonogashira Reaction

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Sonogashira reaction of bromochromones and -flavones with a bromine atom on their benzene or heterocyclic ring with various terminal alkynes gave the desired products with nearly the same efficiency as the previously used iodine derivatives. The coupling reactions were performed in the presence of [tetrakis(triphenylphosphine)palladium(0)], copper(I) co-catalyst, and triethylamine, resulting in the formation of numerous hitherto unknown alkynylated oxygen heterocycles, and provide further proof for the applicability of this reaction for these *O*-heterocycles. Chromones with ethynyl functionality were prepared by removal of the trimethylsilyl protecting group and used as terminal alkynes in a second cross-coupling reaction.

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Introduction

The palladium-catalyzed coupling of terminal alkynes with aryl and vinyl halides (Sonogashira coupling) is an important and widely used reaction for carbon–carbon bond formation.[1] These reactions are often used in the field of *N*-heterocycles, but relatively little has been published in the field of *O*-heterocycles. In 1998, Tsukayama and his coworkers reported the coupling of 5,7,4′-tribenzyloxy-8-iodoisoflavone with 2-methyl-3-butyn-2-ol in the presence of $PdCl_2$ and CuI to give the expected Sonogashira product.[2a] The same protocol was also successfully used for 6-iodoisoflavones to give various naturally occurring derivatives.[2b–2e] In 1999, Johnson, Chandraratna, and their coworkers reported on the coupling of 6-bromo-1-thiochromanone, 2,2-dimethyl-6-triflyloxy-1-thiochromanone, and 6-bromo-2,2-dimethylchromanone with various alkynes. Some of the prepared compounds showed high affinity for retinoid acid receptors.[3] In 2001, the Sonogashira–Hagihara cross-coupling of 3-bromocoumarin and phenylacetylene in excellent yield was reported.[4] In 2002, Cho and his coworkers coupled 3,5-dibromo-2-pyrone with various alkynes in the presence of triethylamine as base and dioxane or DMF as solvent, using $Pd(PPh_3)_2Cl_2$ as ligand, to give rise to the corresponding 3-alkynyl-5-bromo-2-pyrones with good-to-excellent yield and regioselectivity; the bromo substituent adjacent to the lactone group showed higher reactivity.[5] One year later, Pal, Yeleswarapu, and their coworkers reported the coupling of 3-iodoflavones with four different terminal alkynes in the presence of $Pd(PPh_3)_2Cl_2$ as catalyst, CuI as co-catalyst, and (*S*)-prolinol as base to give 3-(substituted)alkynylflavones in 52–81% yields.[6a,b] In addition, a double adduct, i.e. 3-enynyl derivatives were obtained as major products when 3-iodoflavones were treated with a terminal alkyne in the absence of CuI (Heck conditions) followed by the addition of a further equivalent of alkyne and Cu^I co-catalyst.[6b] Reaction of 3-iodochromones and 3-iodo-1-thiochromones with various alkynes under copper-free conditions led to the formation of benzannulated double adducts.[6c] 3-Iodo-4′-methoxyflavone was alkynylated with a paramagnetic alkyne compound under very similar conditions.[7] 6-, 7-, and 4′-Iodoflavones were alkynylated with 3-hydroxy-3-methylbut-1-yne and 3-methylbut-3-en-1-yne. The products were tested for antimicrobial and cytotoxic activities but no marked effect was found.[8] Larock and his coworkers reported the synthesis of 3-iodochromones and flavones and their thio analogues from the corresponding aryl alkynyl ketones in the presence of ICl, their transformation into 3-iodochromones and flavones, and the ring-closure of the 2-alkynyl ketone fragment into a furan ring accompanied by incorporation of an alkoxy group from the solvent in the presence of a gold(III) catalyst.[9] A similar ring-closure leading to furans in the presence of copper(I) salts was also reported by Yamamoto and his coworkers.[10] 3-Iodochromone was coupled with phenylacetylene and its 4-substituted derivatives in the presence of $Pd(PPh_3)_2Cl_2$, CuI, and PPh_3 ligand to give derivatives with interesting electrogenerated chemiluminesce (ECL) properties; X-ray structures and density functional theory calculations were also presented.[11] 4-Hydroxycoumarin was tosylated with 4-toluenesulfonyl chloride, and the intermediate, after replacement of the solvent and without isolation, was reacted with phenylacetylene and various aliphatic alkynes under copper-free conditions in the presence of Pd^{II}-acetate and PPh_3 to give the expected 4-alkynylcoumarins in moderate to good yield.[12]

Recently, we published our results on the palladium-catalyzed cross-coupling (Heck–Mizoroki reaction) of bromochromones and bromoflavones with various terminal alkenes and pointed out that this methodology offers a new route to the

C-alkenylation of these oxygen heterocycles including various naturally occurring systems.[13] The usefulness of Suzuki–Miyaura cross-couplings for the arylation of (triflyloxy) coumarins and -flavones has also been demonstrated.[14] Cross-coupling of similar substrates with terminal alkynes is also a promising approach; *C*-alkynylation in the presence of a neighbouring XH functionality followed by a subsequent ring-closure may lead to tricyclic systems such furochromones and pyranochromones frequently isolated from natural sources. In this contribution, we present our results of the Sonogashira reaction of simple bromochromones and -flavones with various terminal alkynes and some transformation of the resulting products.

Results and Discussion

As indicated in the Introduction, most Sonogashira couplings in the field of oxygen heterocycles were performed by starting from iodo derivatives up to now. However, the synthesis of iodochromones and -flavones other than the 3-iodo substrates is laborious, less efficient, and costly. Therefore, we wanted to investigate the reactivity and usefulness of bromochromones and -flavones in the preparation of various alkynylated compounds. The starting material bromochromones **1**, **9a**–**d** and bromoflavones **2**, **10** were prepared according to previously published methods.[13a,c,15]

First, we tried to find optimal conditions for the Sonogashira coupling using 3-bromochromone (**1**) as substrate and phenylacetylene as the terminal alkyne (Scheme 1). In our attempts, the classical combination of the tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] catalyst, copper(I) iodide co-catalyst,[1b] and triphenylphosphine ligand was studied; representative results are shown in Table 1.

Triethylamine (TEA) as base and tetrahydrofuran (THF) as solvent at elevated temperature gave a moderate yield (Table 1, entry 2); no reaction was observed at room temperature (Table 1, entry 1). Other bases such as pyrrolidine or diazabicyclo[2.2.2]octane (DABCO) in THF resulted in much worse yields, if any (Table 1, entries 3, 4). In *N*,*N*-dimethylformamide (DMF), only a marginal yield was achieved (Table 1, entry 5) but the use of TEA as base and solvent gave a better result in a shorter reaction period (Table 1, entry 6). As 3-bromochromone (**1**) is a base-sensitive substrate, the moderate yield seemed acceptable and we applied these conditions to further cross-coupling experiments.

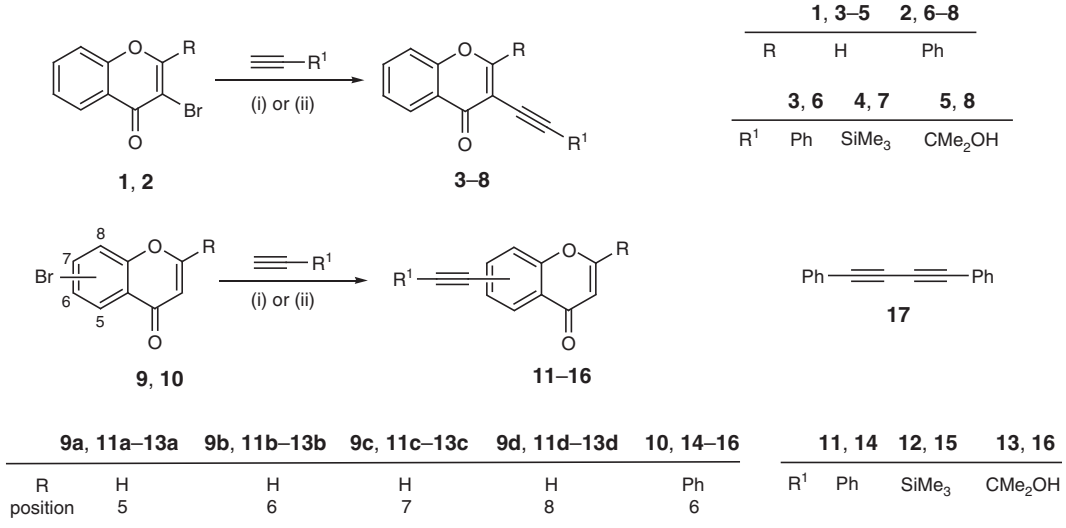
Then, we tested the cross-coupling reaction with 3-bromochromone (**1**) and other substrates such as bromochromones **9a**–**d**, which have the halo substituent in their ring A and bromoflavones **10**, **11**. In addition to the model reactant phenylacetylene used previously, trimethylsilylacetylene and 3-methyl-1-butyn-3-ol were used as terminal alkynes because in both cases the coupled products have a removable end-group, giving the corresponding ethynyl derivatives after cleavage. Moreover, 3-hydroxy-3-methylbutynylated chromones and flavones with an *ortho*-hydroxy function are reasonable intermediates for naturally occurring tricyclic oxygen heterocycles with a 2,2-dimethylpyran motif after diastereoselective reduction and subsequent ring-closure. The results of the C–C couplings are shown in Table 2. With only one exception, the desired alkynylated chromones **4**, **5**, **11a**–**d**, **12a**–**d**, and **13a**–**d**, and flavones **6**–**8** and **14**–**16** were obtained. Surprisingly, no cross-coupled product **11a** but only the Glaser–Hay[16] product **17** was obtained in the reaction of 5-bromochromone (**9a**) and phenylacetylene. This by-product was not indentified in the other reactions. The yields varied over a wide range (23–92 %) but typically, moderate to good yields were obtained (Table 2). It is noteworthy that the position of the halogen atom had no

Table 1. Optimization of the Sonogashira reaction of 3-bromochromone (1) and phenylacetylene

DABCO, diazabicyclo[2.2.2]octane; TEA, triethylamine

Entry	Solvent	Base	Temperature [°C]	Reaction time [h]	Yield [%][A]
1	THF	TEA	RT	72	0
2	THF	TEA	60	7	42
3	THF	Pyrrolidine	70	6	0
4	THF	DABCO	70	7	19
5	DMF	TEA	70	7	9
6	TEA		70	2	46

[A]Yields refer to isolated pure products.



Scheme 1. Synthesis of ethynylchromones **3–8** and **11–16**. Reagents and conditions: (i) alkyne/CuI/$Pd(PPh_3)_4$/PPh_3/triethylamine (TEA)/60–90°C; (ii) alkyne/Pd-C/PPh_3/TEA/80–90°C.

marked effect on the reaction conditions or the yields of the Sonogashira couplings, which is in sharp contrast with the Heck–Mizoroki reactions of bromochromones, where the 7-bromo derivative has considerably higher reactivity in comparison with the 6-bromo analogue.[13a] Similarly, we demonstrated the greater reactivity of position 7 in the Suzuki coupling of 5,7- and 7,8-*bis*(trifluoromethanesulfonyloxy)flavones. The difference in the reactivities allowed the regioselective monoarylation of these substrates.[14c,e]

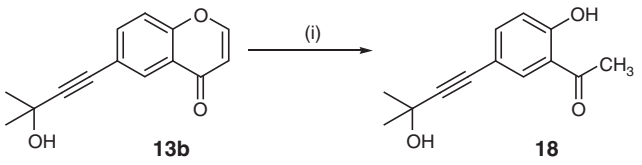
Since 1990, it has been known that Pd/C can be used as a palladium source in Sonogashira cross-coupling;[17a] in 2002, German researchers reported the successful application of Pd/C as catalyst in Heck–Mizoroki, Suzuki–Miyaura, and Sonogashira reactions.[17b] Therefore, we also tested this possibility. As shown in Table 2 (entries 3, 6, 12, 22), alkynylation using Pd/C instead of the more expensive tetrakis(triphenylphosphine)palladium(0) led to the expected products in all cases but the yields were lower, with the exception of trimethylsilylacetylene (see entry 2 versus entry 3). However, these conditions could be considered if scaling up of these coupling reactions was necessary.

The products were characterized on the basis of their IR, ^{1}H, and ^{13}C NMR spectra. The only special and noteable spectral feature observed in the IR spectra of the (trimethylsilyl)ethynyl derivatives **4**, **7**, **12a**–**d**, and **15** was the intensive C≡C stretch observed between 2140 and 2170 cm^{-1}. In the case of the other alkyne derivatives, this band was much weaker.

We can conclude that the results summarized in Tables 1 and 2 clearly show the generality and the synthetic value of the Sonogashira cross-coupling in the field of benzopyranoids.

Next, we investigated the removal of the end-group from 3-hydroxy-3-methylbutynylated derivatives in the form of acetone, which could lead to an ethynylchromone derivative. This type of cleavage is usually performed under basic conditions such as sodium hydroxide in refluxing toluene,[18] sodium hydride in refluxing toluene,[19] or potassium hydroxide in hot diisopropyl amine.[19] Some of these reactions have also been applied in tandem or domino couplings.[19,20] In our case, the attempted deprotection of 6-(3-hydroxy-3-methyl-1-butynyl) chromone (**13b**) failed to give any desired product with either sodium hydroxide or sodium hydride in hot toluene; no reaction was observed.

When compound **13b** was reacted with 5 M aqueous sodium hydroxide in the presence of 10 mol-% tetrabutylammonium iodide (TBAI) in toluene at 80°C,[21] no cleavage of the end-group but opening of the chromone ring followed by a *retro*-Claisen reaction took place and 2′-hydroxy-5′-(3-hydroxy-3-methyl-1-butynyl)acetophenone (**18**) was obtained in moderate yield (Scheme 2).

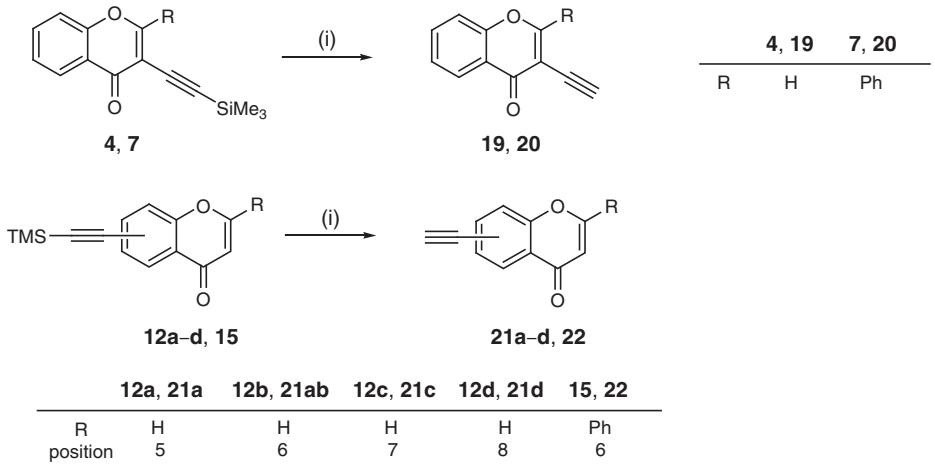


Scheme 2. Attempted deprotection of ethynylchromone **13b**. Reagents and conditions: (i) 3 equiv. 5M aqueous NaOH/tetrabutylammonium iodide (10 mol-%)/PhMe/80°C.

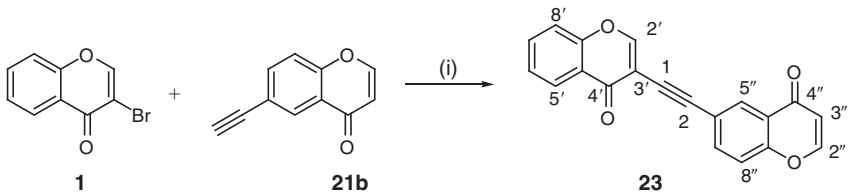
Table 2. Sonogashira reaction of bromochromones and -flavones 1, 2, 9a–d, 10 and various alkynes
Conditions A: alkyne/CuI/$Pd(PPh_3)_4$/PPh_3/triethylamine (TEA)/70°C; Conditions B: alkyne/Pd-C/PPh_3/TEA/70°C

Entry	Starting material	R	R^1	Conditions	Reaction time [h]	Product	Yield [%][A]
1	**1**	H	Ph	A	2	**3**	46
2	**1**	H	$SiMe_3$	A	3	**4**	63
3	**1**	H	$SiMe_3$	B	4	**4**	79
4	**1**	H	CMe_2OH	A	3	**5**	48
5	**2**	Ph	Ph	A	3	**6**	85
6	**2**	Ph	Ph	B	4	**6**	64
7	**2**	Ph	$SiMe_3$	A	5	**7**	23[B]
8	**2**	Ph	CMe_2OH	A	4	**8**	80[C]
9	**9a**	H	Ph	A	3	**11a**	0[D]
10	**9b**	H	Ph	A	4.5	**11b**	72
11	**9c**	H	Ph	A	3.75	**11c**	89
12	**9c**	H	Ph	B	4	**11c**	53
13	**9d**	H	Ph	A	2.5	**11d**	64
14	**9a**	H	$SiMe_3$	A	1	**12a**	36
15	**9b**	H	$SiMe_3$	A	0.5	**12b**	76
16	**9c**	H	$SiMe_3$	A	0.5	**12c**	48
17	**9d**	H	$SiMe_3$	A	2	**12d**	62
18	**9a**	H	CMe_2OH	A	2	**13a**	50
19	**9b**	H	CMe_2OH	A	1.5	**13b**	48
20	**9c**	H	CMe_2OH	A	0.5	**13c**	54
21	**9d**	H	CMe_2OH	A	4	**13d**	73
22	**9d**	H	CMe_2OH	B	4	**13d**	61
23	**10**	Ph	Ph	A	3	**14**	28
24	**10**	Ph	$SiMe_3$	A	1.5	**15**	90
25	**10**	Ph	CMe_2OH	A	3	**16**	92

[A]Yields refer to isolated pure products.
[B]Reaction performed at 90°C.
[C]Reaction performed at 80°C.
[D]Only homo-coupled product **17** was obtained (35 %).



Scheme 3. Deprotection of (trimethylsilyl)ethynylchromones **4**, **7**, **12a**–**d** and **15**. Reagents and conditions: (i) TBAF/THF, room temperature.



Scheme 4. Synthesis of ethynyl-bridged *bis*-chromone **23**.

Then, we studied the removal of the trimethylsilyl group from derivatives **4**, **7**, **12**, and **15**. Several methods have been published in the literature. 6-[(2-Trimethylsilyl)ethynyl] thiochromanones have been deprotected by potassium carbonate in methanol[3] but this approach seemed risky because of the sensitivity of the chromone ring towards bases (see above). Copper(I) and silver(I) ions could also cleave the trimethylsilyl functionality[20,22,23] but in the case of the copper(I) ion, dimerization into the corresponding butadiynes has been observed.[20,23] We decided to apply the 'classical' fluoride ion-promoted cleavage.[24] To our delight, the treatment of chromone and flavone derivatives **4**, **7**, **12**, and **15** with tetrabutylammonium fluoride (TBAF) in THF solution smoothly gave the desired deprotected compounds **19**–**22**, in good to excellent yields (61–92 %) (Scheme 3). The only exception was the base-sensitive 3-[2-(trimethylsilyl)ethynyl]chromone (**4**), which gave the deprotected product only in 27 % yield. Chromones **4** and **12** gave the corresponding products in a short (10–20 min) reaction period; flavones **7** and **15** required longer treatment.

The successful deprotection was proved by the appearance of the signal belonging to the terminal alkyne hydrogens in the range δ 3.0–3.5 ppm of their ^{1}H NMR spectra. These ethynylchromone derivatives are useful building blocks. For instance, they can act as substrates in 'Click' reactions to afford 1,4-disubstituted-1,2,3-triazoles of complex structure.[25] Another application is shown in Scheme 4, the reaction of 6-ethynylchromone (**21**) with 3-bromochromone (**1**) in a Sonogashira coupling resulting in the ethynyl-bridged *bis*-chromone **23** in moderate yield (Scheme 4).

In conclusion, we have demonstrated that Sonogashira cross-coupling reaction of bromochromones with various alkynes allows the synthesis of a wide range of hitherto unknown oxygen heterocycles including the useful building blocks ethynylchromones as secondary products. Extension of the coupling to *ortho*-substituted starting materials can open the way to various naturally occurring products such as tricyclic systems. Such exploitation of the coupling will be presented soon.

Experimental

Thin-layer chromatography was carried out on Kieselgel 60 F_{254} (0.25-mm layer thickness, Merck). Chromatographic separations were performed using silica gel (Merck, 70–230 mesh); eluting mixtures are shown. Melting points were determined on a Boetius hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM 360 (360 MHz for ^{1}H, 90 MHz for ^{13}C nuclei) spectrometer (internal standard TMS, δ 0 ppm, or residual $CHCl_3$ peaks (δ 7.26 ppm) for ^{1}H NMR and (δ 77.00 ppm) for ^{13}C NMR)). ^{13}C NMR assignments were supported by the J-echo technique. IR spectra were recorded with Perkin–Elmer 16 PC-FT-IR (Fourier-transform IR) or Jasco FT-IR 4100A instruments with KBr discs. The mass spectra were recorded on an AutoSpecEQ EI+ spectrometer. Elemental analyses were performed in-house with Carlo Erba 1106 EA and Elementar Vario MicroCube instruments. Triethylamine was distilled from lithium aluminium hydride.

Bromochromones (**1**, **9a**–**d**) were prepared as previously reported.[13a] 3-Bromoflavone (**2**) was prepared according to a literature procedure[15] by heating flavone with 1.67 equiv. of *N*-bromosuccinimide (NBS) and 0.25 equiv. of pyridine in dry carbon tetrachloride in 77 % yield. (**CAUTION**: because of the adverse health effects of the solvent, reaction and workup should be performed in a well-ventilated hood!). The product was

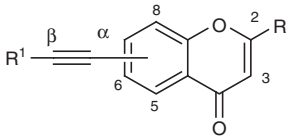


Chart 1.

identified by its literature mp[25,26] and its ^{1}H NMR spectrum. 6-Bromoflavone (**10**) was synthetized by our methodology (iodine-catalyzed dehydrogenation in hot DMSO solution)[27] in 53 % yield and was identified by its literature mp[28] and its ^{1}H NMR spectrum.

For numbering of the products, see Chart 1.

General Procedure for the Synthesis of (2-Substituted Ethynyl)chromones

Conditions A: A mixture of bromochromone **1**, **9a**–**d** or bromoflavone **2**, **10** (2.5 mmol), 1-alkyne (3.75 mmol), tetrakis (triphenylphosphine)palladium(0) (71.9 mg, 0.0622 mmol), triphenylphosphine (16.3 mg, 0.0622 mmol), and copper(I) iodide (6.0 mg, 0.0315 mmol) in triethylamine (15 mL) was heated at 70°C under a nitrogen atmosphere. When the starting material had disappeared (TLC monitoring; for details see Tables 1 and 2), the solvent was removed under reduced pressure, and the residue was subjected to column chromatography (eluent: hexane/acetone 4 : 1 v/v unless otherwise stated).

Conditions B: The reaction was performed and worked up as given in Conditions A but 72 mg 10 % palladium-on-charcoal catalyst was used as the palladium source.

3-(2-Phenylethynyl)chromone ***3***

Yield: 46 % (Conditions A, reaction period: 2 h), mp 174.5–178°C (lit.[9a] 179–181°C). ν_{max} (KBr)/cm^{-1} 3074 (CH), 1650 (C=O), 1616 (C=C), 1464, 1380, 1302, 1216, 754. δ_H ($CDCl_3$) 7.35 (m, 3H, 3′,5′-H, 4′-H), 7.42–7.50 (m, 2H, 6-H, 8-H), 7.60 (m, 2H, 2′,6′-H), 7.70 (m, 1H, 7-H), 8.24 (s, 1H, 2-H), 8.29 (dd, *J* 7.9, 1.6, 1H, 5-H). δ_C ($CDCl_3$) 79.5 (C_α), 95.0 (C_β), 111.4 (C-3), 118.2 (C-8), 122.6, 123.5 (C-4a, C-1′), 125.7, 126.2 (C-6, C-4′), 128.2, 128.6 (C-5, C-3′,5′), 131.8 (C-2′,6′), 133.9 (C-7), 155.9 (C-8a), 157.8 (C-2), 175.3 (C-4). (Found: C 83.04, H 3.99. $C_{17}H_{10}O_2$ requires: C 82.91, H 4.09 %).

3-(2-(Trimethylsilyl)ethynyl)chromone ***4***

Yield: 63 % (Conditions A, reaction period: 3 h); 79 % (Conditions B, reaction period: 4 h), mp 95–96°C. ν_{max} (KBr)/cm^{-1} 2956, 2164 (C≡C), 1648 (C=O), 1614 (C=C), 1464, 1218, 1188, 860, 842, 762. δ_H ($CDCl_3$) 0.27 (s, 9H, Me_3), 7.38–7.49 (m, 2H, 6-H, 8-H), 7.68 (m, 1H, 7-H), 8.18 (s, 1H, 2-H), 8.24 (dd, 1H, *J* 8.6, 1.4, 5-H). δ_C ($CDCl_3$) 0.2 (Me_3), 94.9 (C_α), 101.3 (C_β), 111.5 (C-3), 118.5 (C-8), 123.8 (C-4a), 126.1, 126.5 (C-5, C-6), 134.3 (C-7), 156.1 (C-8a), 159.1 (C-2), 175.6 (C-4). (Found: C 69.12, H 5.65. $C_{14}H_{14}O_2Si$ requires: C 69.38, H 5.82 %).

3-(3-Hydroxy-3-methyl-1-butynyl)chromone ***5***

Yield: 48 % (Conditions A, reaction period: 3 h), mp 109–111°C. ν_{max} (KBr)/cm^{-1} 3416 (C–OH), 3072 (C–H), 1652 (C=O), 1614 (C=C), 1466, 1284, 1232, 1166 (C–O), 768. δ_H ($CDCl_3$) 1.64 (s, 6H, Me_2), 3.60–3.80 (br s, 1H, OH), 7.36–7.50 (m, 2H, 6-H, 8-H), 7.69 (m, 1H, 7-H), 8.14 (s, 1H, 2-H), 8.22 (dd, *J* 7.1, 1.4, 1H, 5-H). δ_C ($CDCl_3$) 31.5 (Me_2), 65.4 (*C*Me_2OH), 72.2 (C_α), 101.1 (C_β), 111.0 (C-3), 118.5 (C-8), 123.5 (C-4a), 126.1, 126.4 (C-5, C-6), 134.4 (C-7), 156.2 (C-8a), 158.2 (C-2), 176.3 (C-4). (Found: C 73.55, H 5.41. $C_{14}H_{12}O_3$ requires: C 73.67, H 5.30 %).

3-(2-Phenylethynyl)flavone ***6***

Yield: 85 % (Conditions A, reaction period: 3 h); 64 % (Conditions B, reaction period: 4 h), mp 161–163°C. ν_{max} (KBr)/cm^{-1} 3058, 1645 (C=O), 1615 (C=C), 1554, 1464, 1396 (flavone skeleton), 1306, 1120, 753, 705. δ_H ([D6]DMSO) 7.44 (br s, 5H, Ar–H), 7.57 (m, 1H, 6-H), 7.67 (br s, 3H, Ar–H), 7.79 (d, *J* 8.4, 1H, 8-H), 7.89 (m, 1H, 7-H), 8.13 (d, *J* 7.9, 1H, 5-H), 8.23 (m, 2H, 2′,6′-H). δ_H ([D6]DMSO) 82.0 (C_α), 96.1 (C_β), 105.6 (C-3), 118.1 (C-8), 121.0, 121.8 (C-4a, C-1′), 122.0 (C-6), 124.7, 125.6 (C-4′, C-4″), 128.0, 128.3, 128.4, 130.5 (C-2′,6′, C-3′,5′, C-2″,6″, C-3″,5″), 130.1 (C-1′), 131.4 (C-5), 134.3 (C-7), 154.6 (C-8a), 174.8 (C-4). (Found: C 85.61, H 4.48. $C_{23}H_{14}O_2$ requires: C 85.70, H 4.38 %).

3-(2-(Trimethylsilyl)ethynyl)flavone ***7***

Yield: 23 % (Conditions A, reaction period: 5 h, reaction temperature: 90°C), mp 58–59°C. ν_{max} (KBr)/cm^{-1} 2959, 2153 (C≡C), 1651 (C=O), 1614 (C=C), 1465, 1381 (flavone skeleton), 1250, 1183, 1140, 895, 859. δ_H ($CDCl_3$) 0.27 (s, 9H, Me_3), 7.44 (m,1H, 6-H), 7.54–7.58 (m, 4H, 8-H, 3′,5′-H, 4′-H), 7.70 (m, 1H, 7-H), 8.22–8.29 (overlapping dd, 3H, 5-H, 2′,6′-H). δ_C ($CDCl_3$) 0.2 (Me_3), 94.6 (C_α), 104.9 (C_β), 118.1 (C-8), 119.0 (C-3), 123.9 (C-4a), 125.1, 126.1 (C-5, C-6), 127.1 (C-2′,6′), 128.2 (C-3′,5′), 130.1 (C-4′), 132.8 (C-1′), 134.2 (C-7), 157.0 (C-8a), 158.9 (C-2), 178.5 (C-4). (Found: C 75.40, H 5.58. $C_{20}H_{18}O_2Si$ requires: C 75.43, H 5.70 %).

3-(3-Hydroxy-3-methyl-1-butynyl)flavone ***8***

Yield: 80 % (Conditions A, reaction period: 4 h, reaction temperature: 80°C, column chromatography: toluene/ethyl acetate, 4 : 1 v/v), mp 138.5–141°C. ν_{max} (KBr)/cm^{-1} 3437 (C–OH), 2982, 1630 (C=O), 1615 (C=C), 1466, 1386 (flavone skeleton), 1239, 1135, 953, 760. δ_H ($CDCl_3$) 1.60 (s, 6H, Me_2), 7.43 (m, 1H, 6-H), 7.47–7.56 (m, 4H, 8-H, 3′,5′-H, 4′-H), 7.71 (m, 1H, 7-H), 8.18 (dd, *J* 8.0, 2.1,1H, 8-H), 8.25 (dd, 1H, *J* 8.2, 1.9, 5-H). δ_C ($CDCl_3$) 32.6 (Me_2), 64.9 (*C*Me_2OH), 85.6 (C_α), 111.1, 112.1 (C-3, C_β), 117.9 (C-8), 124.6 (C-6), 125.5, 125.7 (C-4a, C-5), 127.3 (C-2′,6′), 128. 6 (C-3′,5′), 130.4 (C-4′), 132.9 (C-1′), 135.5 (C-7), 156.8, 157.3 (C-2, C-8a), 179.6 (C-4). (Found: C 79.08, H 5.28. $C_{20}H_{16}O_3$ requires: C 78.93, H 5.30 %).

6-(2-Phenylethynyl)chromone ***11b***

Yield: 72 % (Conditions A, reaction period: 4.5 h), mp 116–117°C. ν_{max} (KBr)/cm^{-1} 3066, 1648 (C=C), 1610 (C=C), 1492, 1440, 1318, 836, 754. δ_H ($CDCl_3$) 6.34 (d, *J* 6.4, 1H, 3-H), 7.29–7.39 (m, 3H, 3′,5′-H, 4′-H), 7.43 (d, *J* 8.4, 1H, 8-H), 7.52 (m, 2H, 2′,6′-H), 7.77 (dd, *J* 8.4, 2.1, 1H, 7-H), 7.84 (d, *J* 6.4, 1H, 2-H), 8.36 (d, *J* 2.1, 1H, 5-H). δ_C ($CDCl_3$) 88.0, 90.8 (C_α, C_β), 113.4 (C-3), 118.9 (C-8), 121.1 (C-6), 123.0, 125.1 (C-4a, C-1′), 128.7 (C-3′,5′), 129.0, 129.4 (C-5, C-4′), 132.0 (C-2′,6′), 136.8 (C-7), 155.6 (C-2), 156.2 (C-8a), 177.1 (C-4). (Found: C 82.88, H 3.91. $C_{17}H_{10}O_2$ requires: C 82.91, H 4.09 %).

7-(2-Phenylethynyl)chromone ***11c***

Yield: 89 % (Conditions A, reaction period: 3.75 h), 53 % (Conditions B, reaction period: 4 h), mp 129–130°C. ν_{max} (KBr)/cm^{-1} 3064, 2204 (C≡C), 1648 (C=O), 1616 (C=C), 1422,

1348, 1308, 1028, 828. δ_H ($CDCl_3$) 6.34 (d, *J* 6.0, 1H, 3-H), 7.38, 7.49–7.60 (m, 7H, Ar-H), 7.84 (d, *J* 6.0, 1H, 2-H), 8.17 (d, *J* 8.4, 1H, 5-H). δ_C ($CDCl_3$) 87.7 (C_α), 93.3 (C_β), 113.2 (C-3), 120.8 (C-8), 122.2, 124.1 (C-4a, C-1′), 125.8 (C-6), 128.3 (C-4′), 128.4 (s, C-3′,5′), 129.0 (C-7), 129.0 (C-5), 131.8 (C-2′,6′), 155.3 (C-2), 156.1 (C-8a), 177.0 (C-4). (Found: C 83.04, H 3.99. $C_{17}H_{10}O_2$ requires: C 82.91, H 4.09 %).

8-(2-Phenylethynyl)chromone ***11d***

Yield: 64 % (Conditions A, reaction period: 2.5 h), mp 94–96°C. ν_{max} (KBr)/cm^{-1} 3066, 3070, 1658 (C=O), 1588, 1574, 1476, 1432, 1406, 1334, 1246, 800, 760. δ_H ($CDCl_3$) 6.39 (d, *J* 6.4, 1H, 3-H), 7.33–7.45 (m, 4H, 6-H, 3′,5′-H, 4′-H), 7.53–7.66 (m, 2H, 2′,6′-H), 7.85 (dd, *J* 6.4, 1.4, 1H, 7-H), 7.95 (d, *J* 6.4, 1H, 2-H), 8.17 (dd, *J* 7.6, 1.4, 1H, 5-H). δ_C ($CDCl_3$) 82.7 (C_α), 96.1 (C_β), 113.2 (C-3), 114.2 (C-8), 122.5 (C-1′), 124.8, 125.0 (C-4a, C-6), 125.8 (C-4′), 128.4 (C-3′,5′), 128. 9 (C-5), 131.7 (C-2′,6′), 137.2 (C-7), 155.4 (C-2), 156.1 (C-8a), 177.2 (C-4). (Found: C 82.97, H 3.91. $C_{17}H_{10}O_2$ requires: C 82.91, H 4.09 %).

5-(2-(Trimethylsilyl)ethynyl)chromone ***12a***

Yield: 36 % (Conditions A, reaction period: 1 h), mp 76–77°C. ν_{max} (KBr)/cm^{-1} 2959, 2142 (C≡C), 1661, 1645 (C=O), 1592, 1470, 1400, 1343, 1250, 985, 842, 760. δ_H ($CDCl_3$) 0.37 (s, 9H, Me_3), 6.30 (d, *J* 5.6, 1H, 3-H), 7.38 (m, 1H, 7-H), 7.55 (m, 2H, 6-H, 8-H), 7.75 (d, *J* 5.6, 1H, 2-H). δ_C ($CDCl_3$) 0.2 (Me_3), 102.5, 102.6 (C_α, C_β), 112.8 (C-3), 119.0 (C-8), 123.8 (C-4a), 126.8 (C-6), 126.9 (C-5), 133.2 (C-7), 155.1 (C-8a), 157.1 (C-2), 176.0 (C-4). (Found: C 69.49, H 5.72. $C_{14}H_{14}O_2Si$ requires: C 69.38, H 5.82 %).

6-(2-(Trimethylsilyl)ethynyl)chromone ***12b***

Yield: 76 % (Conditions A, reaction period: 0.5 h, column chromatography: hexane/acetone, 8 : 1 v/v), mp 98–100°C. ν_{max} (KBr)/cm^{-1} 2959, 2142, 2166 (C≡C), 1650 (C=O), 1614 (C=C), 1474, 1438, 1246, 914, 834. δ_H ($CDCl_3$) 0.28 (s, 9H, Me_3), 6.33 (d, *J* 6.0, 1H, 3-H), 7.46 (d, *J* 8.7, 1H, 8-H), 7.72 (dd, *J* 8.7, 2.1, 1H, 7-H), 7.84 (d, *J* 6.0, 1H, 2-H), 8.31 (d, *J* 2.1, 1H, 5-H). δ_C ($CDCl_3$) 0.5 (Me_3), 96.5 (C_β), 103.8 (C_α), 113.8 (C-3), 119.1 (C-8), 121.3 (C-6), 125.3 (C-4a), 130.4 (C-5), 137.4 (C-7), 156.0 (C-2), 156.4 (C-8a), 177.4 (C-4). (Found: C 69.29, H 5.69. $C_{14}H_{14}O_2Si$ requires: C 69.38, H 5.82 %).

7-(2-(Trimethylsilyl)ethynyl)chromone ***12c***

Yield: 48 % (Conditions A, reaction period: 0.5 h, column chromatography: hexane/acetone, 8 : 1 v/v), mp 156–159°C. ν_{max} (KBr)/cm^{-1} 3068, 2964, 2902 (C–H), 2160 (C≡C), 1648 (C=O), 1618 (C=C), 1424, 1250, 936, 874, 844, 822. δ_H ($CDCl_3$) 0.28 (s, 9H, Me_3), 6.33 (d, *J* 6.0, 1H, 3-H), 7.46 (d, *J* 8.7, 1H, 6-H), 7.57 (br s, 1H, 8-H), 7.85 (d, *J* 6.0, 1H, 2-H), 8.17 (d, *J* 8.7, 1H, 5-H). δ_C ($CDCl_3$) 0.4 (Me_3), 99.7 (C_β), 103.6 (C_α), 113.9 (C-3), 122.0 (C-8), 125.1 (C-4a), 126.4 (C-6), 129.3 (C-5), 129.4 (C-7), 156.1 (C-2), 156.7 (C-8a), 177.6 (C-4). (Found: C 69.33, H 5.71. $C_{14}H_{14}O_2Si$ requires: C 69.38, H 5.82 %).

8-(2-(Trimethylsilyl)ethynyl)chromone ***12d***

Yield: 62 % (Conditions A, reaction period: 2 h, column chromatography: hexane/acetone, 8 : 1 v/v), mp 96–98°C. ν_{max} (KBr)/cm^{-1} 2152 (C≡C), 1660 (C=O), 1572, 1476, 1432, 1402, 1326, 1242, 1030, 844, 808, 754. δ_H ($CDCl_3$) 0.31 (s, 9H, Me_3), 6.37 (d, *J* 6.5, 1H, 3-H), 7.35 (m, 1H, 6-H), 7.81 (dd, *J* 7.5, 1.4, 1H, 7-H), 7.94 (d, *J* 6.5, 1H, 2-H), 8.16 (dd, *J* 7.5, 1.4, 1H, 5-H). δ_C ($CDCl_3$) 0.2 (Me_3), 98.2 (C_β), 102.5 (C_α), 113.5 (C-3), 114.3 (C-8), 125.0 (C-6), 125.3 (C-4a), 126.4 (C-5), 138.2 (C-7), 155.7 (C-2), 156.7 (C-8a), 177.5 (C-4). (Found: C 69.47, H 5.84. $C_{14}H_{14}O_2Si$ requires: C 69.38, H 5.82 %).

5-(3-Hydroxy-3-methyl-1-butynyl)chromone ***13a***

Yield: 50 % (Conditions A, reaction period: 2 h, column chromatography: hexane/acetone 8 : 1 v/v), mp 101.5–103.5°C. ν_{max} (KBr)/cm^{-1} 3404 (OH), 2980, 1653 (C=O), 1594, 1474, 1400, 1388, 1344, 1171 (C–O), 954, 845, 768. δ_H ($CDCl_3$) 1.72 (s, 6H, Me_2), 2.94 (s, 1H, OH), 6.29 (d, *J* 5.8, 1H, 3-H), 7.39 (d, *J* 7.8, 1H, 8-H), 7.45 (d, *J* 7.4, 1H, 6-H), 7.56 (m, 1H, 7-H), 7.77 (d, *J* 5.8, 1H, 2-H). δ_H ([D6]DMSO) 1.55 (s, 6H, Me_2), 5.66 (s, 1H, OH), 6.44 (d, *J* 6.0, 1H, 3-H), 7.48 (m, 1H, 7-H), 7.87 (d, *J* 6.6, 1H, 8-H), 8.03 (d, *J* 7.4, 1H, 6-H), 8.41 (d, *J* 6.0, 1H, 2-H). δ_C ([D6]DMSO) 31.0 (Me_2), 63.3 (*C*Me_2OH), 73.7 (C_α), 102.4 (C_β), 112.1 (C-3), 112.9 (C-4a), 124.0 (C-5), 124.5, 124.7 (C-6, C-8), 136.9 (C-7), 155.9 (C-8a), 156.5 (C-2), 175.6 (C-4). (Found: C 73.79, H 5.22. $C_{14}H_{12}O_3$ requires: C 73.67, H 5.30 %).

6-(3-Hydroxy-3-methyl-1-butynyl)chromone ***13b***

Yield: 48 % (Conditions A, reaction period: 1.5 h, column chromatography: toluene/ethyl acetate, 4 : 1 v/v), mp 127.5–128.5°C. ν_{max} (KBr)/cm^{-1} 3378 (OH), 2980, 1632 (C=O), 1608, (C=C), 1600, 1478, 1442, 1228, 1166 (C–O), 928, 846, 826. δ_H ($CDCl_3$) 1.64 (s, 6H, Me_2), 2.96 (s, 1H, OH), 6.36 (d, *J* 6.0, 1H, 3-H), 7.38 (d, *J* 9.1, 1H, 8-H), 7.65 (dd, *J* 9.1, 2.0, 1H, 7-H), 7.86 (d, *J* 6.0, 1H, 2-H), 8.23 (d, *J* 2.0, 1H, 5-H). δ_C ($CDCl_3$) 32.0 (Me_2), 66.1 (*C*Me_2OH), 81.0 (C_α), 95.8 (C_β), 113.7 (C-3), 119.0 (C-8), 121.0 (C-6), 125.2 (C-4a), 129.8 (C-5), 137.2 (C-7), 156.1 (C-2), 156.4 (C-8a), 177.6 (C-4). (Found: C 73.72, H 5.21. $C_{14}H_{12}O_3$ requires: C 73.67, H 5.30 %).

7-(3-Hydroxy-3-methyl-1-butynyl)chromone ***13c***

Yield: 54 % (Conditions A, reaction period: 0.5 h, column chromatography: toluene/ethyl acetate, 4 : 1 v/v), mp 121–122°C. ν_{max} (KBr)/cm^{-1} 3436 (OH), 2976, 1654, 1632 (C=O), 1618 (C=C), 1590, 1428, 1352, 1274, 1162 (C–O), 1146, 856, 824. δ_H ($CDCl_3$) 1.65 (s, 6H, Me_2), 3.06 (s, 1H, OH), 6.35 (d, *J* 6.4, 1H, 3-H), 7.35 (d, *J* 8.9, 1H, 6-H), 7.42 (br s, 1H, 8-H), 7.84 (d, *J* 6.4, 1H, 2-H), 8.10 (d, *J* 8.9, 1H, 5-H). δ_C ($CDCl_3$) 31.9 (Me_2), 66.1 (*C*Me_2OH), 81.0 (C_α), 98.9 (C_β), 113.8 (C-3), 121.6 (C-8), 124.8 (C-4a), 126.4 (C-6), 129.1 (C-5), 129.4 (C-7), 156.2 (C-2), 156.7 (C-8a), 177.8 (C-4). (Found: C 73.71, H 5.19. $C_{14}H_{12}O_3$ requires: C 73.67, H 5.30 %).

8-(3-Hydroxy-3-methyl-1-butynyl)chromone ***13d***

Yield: 73 % (Conditions A, reaction period: 4 h, column chromatography: toluene/ethyl acetate, 4 : 1 v/v); 51 % (Conditions B, reaction period: 4 h), mp 131–132°C. ν_{max} (KBr)/cm^{-1} 3380 (OH), 2980, 1636 (C=O), 1586, 1410, 1332, 1242, 1174 (C-O), 808, 756. δ_H ($CDCl_3$) 1.68 (s, 6H, Me_2), 3.03 (s, 1H, OH), 6.38 (d, *J* 5.8, 1H, 3-H), 7.31 (m, *J* 7.3, 1H, 6-H), 7.69 (dd, *J* 7.3, 1.4, 1H, 7-H), 7.87 (d, *J* 5.8, 1H, 2-H), 8.14 (dd, *J* 7.3, 1.4, 1H, 5-H). δ_C ($CDCl_3$) 31.6 (Me_2), 65.8 (*C*Me_2OH), 75.6 (C_α), 101.4 (C_β), 113.4 (C-3), 114.0 (C-8), 125.0, 126.1 (C-5, C-6), 125.1 (C-4a), 137.7 (C-7), 155.7 (C-2), 156.4 (C-8a), 177.8 (C-4). (Found: C 73.55, H 5.45. $C_{14}H_{12}O_3$ requires: C 73.67, H 5.30 %).

6-(2-Phenylethynyl)flavone ***14***

Yield: 28 % (Conditions A, reaction period: 3 h), mp 178–181°C. ν_{max} (KBr)/cm^{-1} 3061, 1657 (C=O), 1614 (C=C), 1567, 1497, 1449, 1356 (flavone skeleton), 842, 769, 759. δ_H ($CDCl_3$) 6.84 (s, 1H, 3-H), 7.37 (m, 3H, 8-H, 4′-H, 4′-H), 7.56 (m, 6H, 3′,5′-H, 2′,6′-H, 3′,5′-H), 7.83 (dd, *J* 8.1, 1.9, 1H, 7-H), 7.94 (dd, *J* 8.0, 2.0, 2H, 2′,6′-H), 8.39 (d, *J* 1.9, 1H, 5-H). δ_C ($CDCl_3$) 87.8, 90.6 (C_α, C_β), 107.8 (C-3), 118.6 (C-8), 120.9, 122.9, 124.1 (C-4a, C-6, C-1″), 126.4 (C-3″,5″), 128.7 (C-3′,5′), 128.8, 129.1 (C-4′, C-4″), 129.2 (C-2′,6′), 131.7 (C-1′), 131.8 (C-2′,6′), 131.9 (C-5), 136.6 (C-7), 155.8 (C-8a), 163.6 (C-2), 177.8 (C-4). (Found: C 85.56, H 4.41. $C_{23}H_{14}O_2$ requires: C 85.70, H 4.38 %).

6-(2-(Trimethylsilyl)ethynyl)flavone ***15***

Yield: 90 % (Conditions A, reaction period: 1.5 h, reaction temperature: 80°C, column chromatography: toluene/ethyl acetate, 4 : 1 v/v)), mp 158–160°C. ν_{max} (KBr)/cm^{-1} 3066, 2957, 2166 (C≡C), 1640 (C=O), 1612 (C=C), 1566, 1477, 1452, 1433, 1360 (flavone skeleton), 832, 776. δ_H ($CDCl_3$) 0.33 (s, 9H, Me_3), 6.84 (s, 1H, 3-H), 7.54 (m, 4H, 8-H, 3′,5′-H, 4′-H), 7.75 (dd, *J* 8.3, 2.1, 1H, 7-H), 7.91 (dd, *J* 8.6, 1.9, 2H, 2′,6′-H), 8.34 (d, *J* 1.8, 1H, 5-H). δ_C ($CDCl_3$) −0.2 (Me_3), 95.6 (C_α), 103.2 (C_β), 107.5 (C-3), 118.2 (C-8), 120.5 (C-6), 123.6 (C-4a), 126.2 (C-3′,5′), 129.0 (C-2′,6′), 129.5 (C-4′), 131.5 (C-1′), 131.7 (C-5), 136.6 (C-7), 155.0 (C-8a), 163.3 (C-2), 177.4 (C-4). (Found: C 75.59, H 5.61. $C_{20}H_{18}O_2Si$ requires: C 75.43, H 5.70 %).

6-(3-Hydroxy-3-methyl-1-butynyl)flavone ***16***

Yield: 92 % (Conditions A, reaction period: 3 h, reaction temperature: 80°C), mp 129–132°C. ν_{max} (KBr)/cm^{-1} 3458 (OH), 2978, 1643 (C=O), 1613 (C=C), 1565, 1450, 1434, 1358 (flavone skeleton), 1214 (C–OH), 1170, 843. δ_H ([D6] DMSO) 1.53 (s, 6H, Me_2), 5.60 (s, 1H, OH), 7.06 (s, 1H, 3-H), 7.60 (m, 5H, Ph), 7.79 (m, 2H, 6-H, 7-H), 7.98 (s, 1H, 5-H), 8.10 (d, *J* 6.9, 2H, 2′,6′-H). δ_C ([D6]DMSO) 38.5 (Me_2), 63.1 (*C*Me_2OH), 78.5 (C_α), 96.5 (C_β), 106.5 (C-3), 118.8 (C-8), 119.3 (C-6), 122.8 (C-4a), 125.9 (C-3′,5′), 126.9 (C-4′), 128.6 (C-2′,6′), 130.4 (C-1′), 131.4 (C-5), 135.9 (C-7), 154.5 (C-8a), 162.2 (C-2), 175.8 (C-4). (Found: C 78.79, H 5.42. $C_{20}H_{16}O_3$ requires: C 78.93, H 5.30 %).

This compound has been reported previously[8] without melting point or any spectral data.

1,4-Diphenyl-1,3-butadiyne ***17***

Yield: 35 % (Conditions A, reaction period: 3 h), mp 81–83°C (lit.[29] 87–88°C). The ^{1}H NMR spectrum was identical to that reported.[30]

2′-Hydroxy-5′-(3-hydroxy-3-methyl-1-butynyl) acetophenone ***18***

A mixture of 6-(3-hydroxy-3-methyl-1-butynyl)chromone (**13b**) (250 mg, 1.095 mmol), TBAI (40 mg, 0.1083 mmol), 5 M sodium hydroxyde solution (0.66 mL, 3.300 mmol), and toluene (15 mL) was heated at 80°C for 30 min, then the solvent was removed under reduced pressure and the residue was separated by column chromatography (eluent: hexane/acetone 4 : 1 v/v) to give 94 mg (39 %) of acetophenone **18**, mp: 56.5–57.5°C. ν_{max} (KBr)/cm^{-1} 3629 (OH), 2986, 1648 (C=O), 1566, 1478, 1364, 1321, 1302, 1235, 1194, 1152, 968, 930, 817. δ_C ($CDCl_3$) 1.63 (s, 6H, Me_2), 2.04 (s, 1H, CMe_2O*H*), 2.64 (s, 3H, COMe), 6.93 (d, *J* 8.6, 1H, 3′-H), 7.50 (dd, *J* 8.6, 1.9, 1H, 4′-H), 7.81 (d, *J* 1.9, 1H, 6′-H), 12.34 (s, 1H, 2′-OH). δ_C ($CDCl_3$) 29.2 (C-2), 32.5 (Me_2), 64.6 (*C*Me_2OH), 78.2 (C_α), 93.0 (C_β), 115.9 (C-3′), 119.0 (C-5′), 126.7 (C-1′), 129.8 (C-6′), 137.6 (C-4′), 160.2 (C-2′), 188.2 (C-1). (Found: C 71.39, H 6.42. $C_{13}H_{14}O_3$ requires: C 71.54, H 6.47 %).

General Procedure for the Synthesis of Ethynylchromones and -Flavones by Removal of the Trimethylsilyl End-group

To a solution of trimethylsilyl derivatives **4**, **7**, **12a**–**d**, or **15** (0.4545 mmol) in THF (5 mL) was added 1 M tetrabutylammonium fluoride in THF (0.15 mL); the mixture was stirred under nitrogen at room temperature and the reaction was monitored by thin-layer chromatography. After completion, the solvent was removed under reduced pressure and the residue was separated by column chromatography (eluent: hexane/acetone 2 : 1 v/v).

3-Ethynylchromone ***19***

Yield: 27 %, reaction period: 20 min, mp 126–129°C. ν_{max} (KBr)/cm^{-1} 3245 (≡CH), 1639 (C=O), 1614 (C=C), 1464, 1378, 1346, 1166, 850, 757. δ_H ($CDCl_3$) 3.28 (s, 1H, ≡CH), 7.36–7.50 (m, 2H, 6-H, 8-H), 7.70 (m, 1H, 7-H), 8.19 (s, 1H, 2-H), 8.26 (1H, dd, *J* 7.8, 1.8, 5-H). δ_C ($CDCl_3$) 74.0 (C_β), 83.6 (C_α), 110.7 (C-3), 118.5 (C-8), 123.8 (C-4a), 126.2, 126.6 (C-5, C-6), 134.5 (C-7), 155.3 (C-8a), 159.2 (C-2), 175.5 (C-4). (Found: C 77.47, H 3.67. $C_{11}H_6O_2$ requires: C 77.64, H 3.55 %).

3-Ethynylflavone ***20***

Yield: 72 %, reaction period: 45 min, mp 165–167°C. ν_{max} (KBr)/cm^{-1} 3205 (≡CH), 2094 (C≡C), 1631 (C=O), 1614 (C=C), 1546, 1468, 1373 (flavone skeleton), 758. δ_H ($CDCl_3$) 3.44 (s, 1H, ≡CH), 7.44 (m, 1H, 6-H), 7.56 (m, 4H, 8-H, 3′,5′-H, 4′-H), 7.70 (m, 1H, 7-H), 8.18 (dd, *J* 8.4, 1.9, 8-H), 8.29 (dd, *J* 7.9, 1.7, 1H, 5-H). δ_C ($CDCl_3$) 75.9 (C_β), 86.5 (C_α), 106.3 (C-3), 118.1 (C-8), 122.1 (C-4a), 125.8, 126.2 (C-5, C-6), 128.4, 129.0 (C-2′,6′, C-3′,5′), 131.8 (C-5), 132.1 (C-1′), 134.3 (C-7), 155.5 (C-8a), 167.1 (C-2), 176.8 (C-4). (Found: C 83.07, H 3.98. $C_{17}H_{10}O_2$ requires: C 82.91, H 4.09 %).

5-Ethynylchromone ***21a***

Yield: 79 %, reaction period: 15 min, mp 122–124°C. ν_{max} (KBr)/cm^{-1} 3236 (≡CH), 2095 (C≡C), 1639 (C=O), 1593, 1472, 1401, 1347, 1291, 1210, 966, 833, 763, 715. δ_H ($CDCl_3$) 3.54 (s, 1H, ≡CH), 7.33 (d, *J* 6.0, 1H, 3-H), 7.42 (m 1H, 7-H), 7.58 (m, 2H, 6-H, 8-H), 7.77 (d, *J* 6.0, 1H, 2-H). δ_C ($CDCl_3$) 82.0, 83.3 (C_α, C_β), 113.8 (C-3), 118.9 (C-8), 121.0 (C-4a), 125.3 (C-5), 132.4, 132.6 (C-6, C-7), 154.1 (C-2), 156.9 (C-8a), 172.2 (C-4). (Found: C 77.71, H 3.52. $C_{11}H_6O_2$ requires: C 77.64, H 3.55 %).

6-Ethynylchromone ***21b***

Yield: 66 %, reaction period: 15 min, mp 182–185°C. ν_{max} (KBr)/cm^{-1} 3216 (≡CH), 2104 (C≡C), 1647 (C=O), 1615 (C=C), 1474, 1437, 1313, 1196, 832. δ_H ([D6]DMSO) 4.36 (s, 1H, ≡CH), 6.40 (d, *J* 6.5, 1H, 3-H), 7.69 (d, *J* 8.9, 1H, 8-H), 7.87 (d, *J* 8.9, 1H, 7-H), 8.05 (brs, 1H, 5-H), 8.33 (d, *J* 6.5, 1H, 2-H). δ_C ([D6]DMSO) 78.5, 80.5 (C_α, C_β), 111.5 (C-3), 117.6 (C-8), 118.0 (C-6), 123.2 (C-4a), 127.7 (C-5), 135.4 (C-7), 154.7 (C-8a), 154.8 (C-2), 174.4 (C-4). (Found: C 77.59, H 3.61. $C_{11}H_6O_2$ requires: C 77.64, H 3.55 %).

7-Ethynylchromone ***21c***

Yield: 68 %, reaction period: 10 min, mp 161.5–162.5°C. ν_{max} (KBr)/cm^{-1} 3244 (≡CH), 2106 (C≡C), 1665, 1643 (C=O), 1599, 1428, 1343, 1298, 1212, 876, 820. δ_H ($CDCl_3$) 3.30 (s, 1H, ≡CH), 6.34 (d, *J* 6.0, 1H, 3-H), 7.49 (d, *J* 8.6, 1H, 6-H), 7.58 (br s, 1H, 8-H), 7.85 (d, *J* 6.0, 1H, 2-H), 8.15 (d, *J* 8.6, 1H, 5-H). δ_C ($CDCl_3$) 81.0, 82.3 (C_α, C_β), 113.2 (C-3), 121.7 (C-8), 125.5 (C-4a), 125.9 (C-8), 127.7 (C-7), 128.6 (C-5), 155.4 (C-2), 156.0 (C-8a), 180.8 (C-4). (Found: C 77.52, H 3.49. $C_{11}H_6O_2$ requires: C 77.64, H 3.55 %).

8-Ethynylchromone ***21d***

Yield: 61 %, reaction period: 10 min, mp 233–235°C. ν_{max} (KBr)/cm^{-1} 3217 (≡CH), 2106 (C≡C), 1649 (C=O), 1589, 1574, 1478, 1434, 1410, 1336, 805, 754. δ_H ($CDCl_3$) 3.48 (s, 1H, ≡CH), 6.38 (d, *J* 6.1, 1H, 3-H), 7.38 (m, 1H, 6-H), 7.84 (dd, *J* 7.9, 1.8, 1H, 7-H), 7.94 (d, *J* 6.1, 1H, 2-H), 8.20 (dd, *J* 7.8, 1.8, 5-H). δ_C ($CDCl_3$) 80.1, 81.1 (C_α, C_β), 110.0 (C-8), 116.0 (C-3), 124.7 (C-4a), 125.5 (C-6), 128.2, 129.1 (C-5, C-7), 155.7 (C-2), 158.0 (C-8a), 179.5 (C-4). (Found: C 77.80, H 3.53. $C_{11}H_6O_2$ requires: C 77.64, H 3.55 %).

6-Ethynylflavone ***22***

Yield: 91 %, reaction period: 45 min (column chromatography: toluene/ethyl acetate, 4 : 1 v/v), mp 167.5–168.5°C. ν_{max} (KBr)/cm^{-1} 3286 (≡CH), 1652 (C=O), 1603, 1567, 1458, 1435, 1356 (flavone skeleton), 773. δ_H ($CDCl_3$) 3.15 (s, 1H, ≡CH), 6.83 (s, 1H, 3-H), 7.53 (m, 4H, 8-H, 3′,5′-H, 4′-H), 7.78 (dd, 1H, *J* 8.3, 2.0, 7-H), 7.92 (dd, *J* 8.0, 1.9, 2H, 2′,6′-H), 8.37 (d, *J* 2.0, 1H, 5-H). δ_C ($CDCl_3$) 78.5, 82.1 (C_α, C_β), 107.8 (C-3), 118.6 (C-8), 119.6 (C-6), 123.9 (C-4a), 126.4 (C-3′,5′), 129.2 (C-2′,6′), 129.9 (C-4′), 131.5 (C-1′), 131.9 (C-5), 137.0 (C-7), 156.0 (C-8a), 163.6 (C-2), 177.5 (C-4). (Found: C 82.81, H 4.20. $C_{17}H_{10}O_2$ requires: C 82.91, H 4.09 %).

*1-(4-Oxo-4*H*-1-benzopyran-3-yl)-2-(4-oxo-4*H*-1-benzopyran-6-yl)ethyne* ***23***

A mixture of 3-bromochromone (**1**) (220 mg, 0.978 mmol), 6-ethynylchromone (**21b**) (250 mg, 1.470 mmol), tetrakis(triphenylphosphine)palladium(0) (29 mg, 0.0251 mmol), triphenylphosphine (6 mg, 0.0229 mmol), and copper(I)iodide (3 mg, 0.0158 mmol) in triethylamine (15 mL) was heated at 110°C under a nitrogen atmosphere for 2.5 h; then the solvent was removed under reduced pressure and the residue was subjected to column chromatography (eluent: hexane/acetone 2 : 1 v/v) to give 140 mg (46 %) ethyne **23**, mp 264–267°C. ν_{max} (KBr)/cm^{-1} 1666 br (C=O), 1615 (C=C), 1481, 1225, 1140, 834, 761. δ_H ([D6]DMSO) 6.42 (d, *J* 6.5, 1H, 3′-H), 7.57 (m, 1H, 6′-H), 7.74 (m, 2H, 8′-H, 8′-H), 7.85–7.94 (m, 3H, 7′-H, 5′-H, 7′-H), 8.14 (dd, *J* 7.9, 1.7, 1H, 5′-H), 8.34 (d, *J* 6.5, 1H, 2′-H), 8.90 (s, 1H, 2′-H). δ_C ([D6]DMSO) 81.8 (C-1), 92.4 (C-2), 109.4 (C-3′), 112.5 (C-3′), 118.7, 119.7 (C-8′, C-8′), 119.3 (C-6′), 124.4, 122.1 (C-4a′, C-4a′), 125.3, 126.3 (C-5′, C-6′), 127.9 (C-5′), 134.8, 136.4 (C-7′, C-7′), 155.5, 155.7 (C-8a′, C-8a′), 174.5 (C-4′), 175.6 (C-4′). (Found: C 76.29, H 3.31. $C_{20}H_{10}O_4$ requires: C 76.43, H 3.21 %).

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