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Transition-metal free C(sp^2)–C(sp^2) bond formation: arylation of 4-aminocoumarins using arynes as an aryl source†

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A mild, efficient and transition-metal free synthetic strategy has been developed for the α-arylation of 4-aminocoumarins. This synthetic strategy proceeds *via* C(sp^2)–C(sp^2) bond formation between 4-aminocoumarins and aryne precursors in a single step by simple treatment with a fluoride source in the absence of a metal-catalyst. Moreover, this methodology affords good yields of 4-amino-3-arylcoumarin derivatives bearing halide functionality.

Introduction

C–C bond formation reactions between two sp^2 hybridized carbon centers are one of the most fundamental reactions in organic synthesis which provide the foundation for the construction of molecular frameworks and have been in the forefront of research in organic synthesis.[1] There are several established synthetic strategies where different functionalized carbon centers have been used for the construction of such C–C bonds.[2] In this regard, transition-metal catalysts play a predominant role in the construction of C–C bonds.[3] A variety of metal catalysts such as Mn, Cu, Ni, Pd, Ag, Ru, Rh, Ir *etc.* have been extensively used for this task. Among the numerous synthetic methods for the construction of C–C bonds, transition-metal free reactions have gained predominance over others and are widely accepted in industrial practice due to their environmental friendliness. Additionally most of the transition metals are toxic in nature, and the removal of trace amounts of such transition-metal residues from the desired products is quite necessary and challenging in the pharmaceutical industries.[4] To overcome such issues, metal-free strategies have been developed for C–C bond formation *via* direct C–H/C–H cross coupling. In this regard, Itami and co-workers have reported a base-promoted metal-free coupling reaction of aryl halides with arenes.[5] Later, Shirakawa and Hayashi have reported a transition-metal free coupling reaction between aryl halides and aryl Grignard reagents for the construction of a C(sp^2)–C(sp^2) bond.[6] Furthermore, Wang and co-workers have reported a metal-free direct C–H arylation of quinones and naphthoquinones using diaryliodonium salts as an aryl source.[7] Later, Li *et al.* have developed a photocatalyst-free oxidative C(sp^2)–H thiocyanation of heteroarenes and arenes.[8] Similarly, Xie and his group have reported *C*-3 alkoxycarbonylation and *C*-3 alkylation of quinoxalin-2(1*H*)-ones.[9a,b] Recently, Xie and co-workers have reported visible light-induced organic dye-catalyzed *C*-2 sulfonylation of quinoline *N*-oxides.[9c] In addition to these, cross-dehydrogenative coupling (CDC) is another method which leads to the formation of C–C bonds directly between two unmodified C–H bonds.[10] This CDC strategy is particularly applicable to an sp^3 hybridized carbon center which is adjacent to the carbonyl group or heteroatom or at the allylic and benzylic positions. Therefore, the development of new synthetic strategies for direct C–C bond formation between two sp^2 hybridized carbon centers is highly desirable and necessary in organic synthesis.

On the other hand, arynes are versatile transient intermediates and have emerged as potent electrophiles for the atom economical synthesis of various building blocks and natural products.[11] In this context, Kobayashi's protocol using *o*-silyl aryl triflate[12] as a versatile aryne precursor is widely accepted in the synthetic community for the development of new-aryne based reactions which include muticomponent,[13] cycloaddition,[14] and insertion reactions.[15] Interestingly, various nucleophiles including N-heterocycles, urea and imines could be coupled with arynes to form their corresponding insertion products.[16] They also serve as key building blocks for the construction of transition-metal-free C–C bonds *via* coupling with a suitable nucleophile. However, metal-free *C*-arylation reactions using arynes as an aryl source are rare. In this regard,

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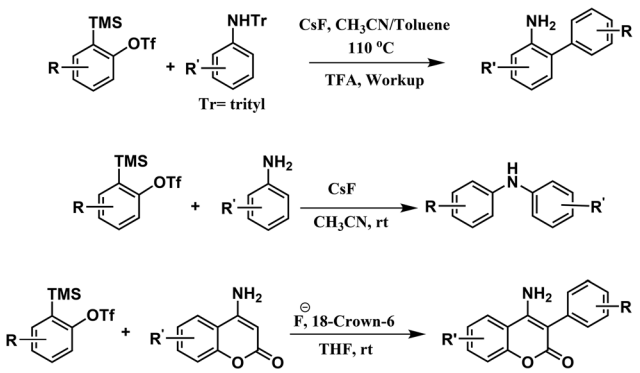
†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR and HRMS spectra of all products. See DOI: 10.1039/c9ob01919g

Chartrand and Ramtohul have reported a method for direct *C*-arylation of β-enamino esters and ketones employing arynes.[17] Also, Hu and co-workers have developed a nucleophilic fluoroalkylation of arynes using a nucleophilic fluoroalkylating agent.[18] Recently, Mhaske and co-workers have reported a metal-free *C*-arylation of malonamide esters employing aryne precursors.[19] Furthermore, Rodriguez *et al.* have developed a general method for *C*-arylation of β-ketoamides.[20] Moreover, arynes have also been used for direct *C*-arylation reactions involving $C(sp^2)$–$C(sp^2)$ bond formation. In this regard Greaney *et al.* have reported a transition-metal-free direct arylation of anilines *via* C–H arylation instead of N–H arylation due to steric hindrance around the nitrogen atom (Scheme 1a).[21] Later, they also developed a metal-free Truce–Smiles rearrangement for the synthesis of bis(hetero)aryls *via* coupling of two sp^2-carbon centers.[22] Another interesting chemistry was reported by Larock's group, where regioselective *N*-arylated products were obtained when amines and sulphonamides react with arynes (Scheme 1b).[23] These interesting reactions of *N*-arylation as well as *C*-arylation of aniline encouraged us to develop a new arylation strategy for 4-aminocoumarins. In our investigation, it is interesting to note that when 4-aminocoumarins were treated with an aryne precursor in the presence of a fluoride source, a *C*-arylated product was formed instead of an *N*-arylated product without the protection of amine functionality.

In continuation of our research on the development of new synthetic strategies involving aryne chemistry,[24] we present here the α-arylation of 4-aminocoumarins under transition-metal-free conditions (Scheme 1c). 4-Amino-3-arylcoumarin was previously synthesized *via* acylation of 2-hydroxybenzonitrile with α-ketoacid chlorides followed by treatment with $TiCl_3$ and Zn dust at refluxed temperature.[25] Besides the use of transition metals, this synthetic approach involves a multistep sequence. Therefore, a general and versatile synthetic method for efficient synthesis of 4-amino-3-arylcoumarin derivatives under mild conditions is highly desirable. To the best of our knowledge, there is no such synthetic methodology involving direct arylation of 4-aminocoumarins with arynes.

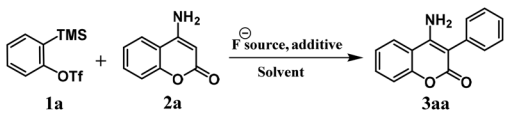


Scheme 1 Scope of *N- vs. C*-arylation.

Results and discussion

We initiated our optimization studies by treating benzyne derived *in situ* from 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.25 mmol) and CsF (0.5 mmol) with 4-aminocoumarin **2a** (0.25 mmol) in CH_3CN at room temperature for 6 h. Under these reaction conditions, the desired product **3aa** was obtained in 45% yield (Table 1, entry 1). To improve the

Table 1 Optimization studies[a]



1a **2a** **3aa**

Entry	F^- source (equiv.)	Additive (equiv.)	Solvent	Time (h)	Temp. (°C)	Yield[b] (%)
1	CsF (2.0)	—	CH_3CN	6	rt	45
2	KF (2.0)	—	CH_3CN	6	rt	50
3	TBAF (2.0)	—	CH_3CN	6	rt	Trace
4	KF (2.0)	18-Crown-6 (1.0)	CH_3CN	6	rt	65
5	KF (2.0)	18-Crown-6 (1.0)	THF	6	rt	70
6	KF (2.0)	18-Crown-6 (1.0)	DCM	6	rt	ND
7	KF (2.0)	18-Crown-6 (1.0)	Dioxane	6	rt	ND
8	KF (2.0)	18-Crown-6 (1.0)	DMF	6	rt	ND
9	KF (2.0)	18-Crown-6 (1.0)	DMSO	6	rt	ND
10	KF (2.0)	18-Crown-6 (1.0)	CH_3CN/THF (1 : 1)	6	rt	52
11	KF (3.0)	18-Crown-6 (1.0)	THF	6	rt	72
12	KF (4.0)	18-Crown-6 (1.0)	THF	6	rt	70
13	KF (3.0)	18-Crown-6 (1.5)	THF	6	rt	76
14	KF (3.0)	18-Crown-6 (1.5)	THF	3	60	67
15	—	—	THF	6	rt	ND

[a] Conditions: *o*-Silyl aryl triflate **1a** (0.25 mmol), 4-aminocoumarin **2a** (0.25 mmol), fluoride source (2 to 4 equiv.), additive (1 to 2 equiv.), solvent (3 mL) stirred at rt for 6 h. [b] Isolated yield. ND: not detected.

yield of the reaction product we used KF instead of CsF as the fluoride source. Under these reaction conditions, the desired product **3aa** was isolated in 50% yield (Table 1, entry 2).

When TBAF was used only traces of **3aa** were observed (Table 1, entry 3). The use of KF in the presence of 18-crown-6 in CH_3CN produced **3aa** in 65% yield (Table 1, entry 4). During our optimization studies, we also investigated the solvent effect by screening some common solvents, such as THF, DCM, dioxane, DMF, and DMSO and a solvent mixture of CH_3CN and THF. To our delight, a significantly improved yield of 70% was observed when the reaction was performed in THF (Table 1, entry 5). The use of a mixture of CH_3CN and THF gave **3aa** in 52% yield (Table 1, entry 10). The desired product **3aa** was not observed when DCM, dioxane, DMF and DMSO were used as solvents (Table 1, entries 6–9). After optimizing our fluoride source and reaction media, a few more experiments were performed by changing the amount of KF and 18-crown-6 (Table 1, entries 11 to 13). Interestingly, an improved yield of 76% was observed when the reaction was performed using 3 equiv. of KF as a fluoride source and 1.5 equiv. of 18-crown-6 as an additive in THF for 6 h (Table 1, entry 13), which were considered to be the optimized reaction conditions. Moreover, increasing the reaction temperature and decreasing the reaction time lowered the yield of product **3aa** (Table 1, entry 14). As a control experiment, when the reaction was performed in the absence of fluoride, product **3aa** was not observed (Table 1, entry 15). The coupled product **3aa** was characterized by ^{1}H NMR, ^{13}C NMR and HRMS analyses and compared with the reported data (see the ESI†).

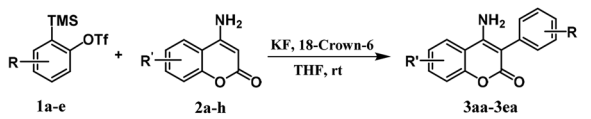
With the optimized reaction conditions in hand, we next generalized our transition-metal free C–C bond formation strategy for the synthesis of our targeted 4-amino-3-arylcoumarin derivatives (Table 2).

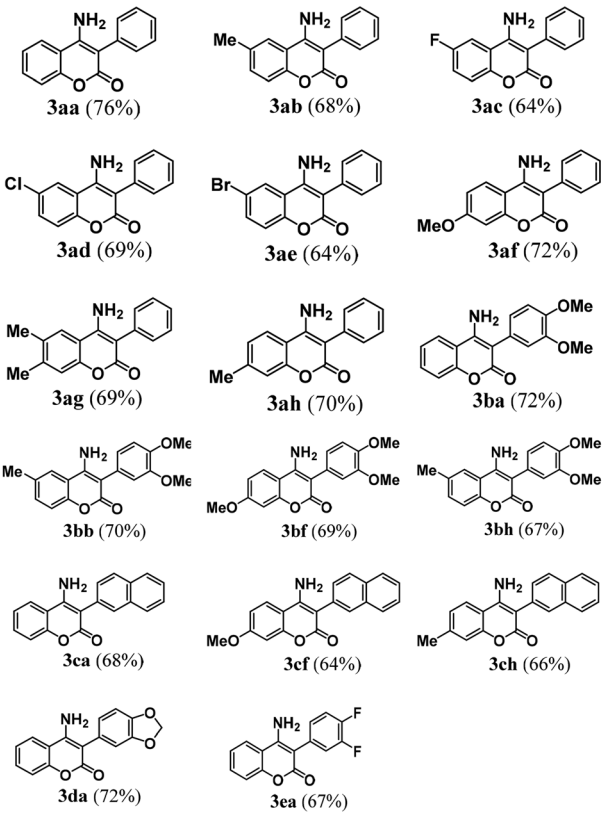
The cascade transition-metal free reactions of arynes with a wide range of 4-aminocoumarins for the one-pot synthesis of 4-amino-3-arylcoumarin derivatives are presented in Table 2. As shown in Table 2, *o*-silyl aryl triflate **1a** was treated with a variety of 4-aminocoumarins bearing methyl, fluoro, chloro, bromo and methoxy substituents leading to our desired 3-aryl-4-aminocoumarins being obtained in good yields (Table 2, **3aa–3ah**). It is noteworthy that both electron-rich and electron-deficient 4-aminocoumarins efficiently participated in the one-pot metal-free coupling process to provide the corresponding products (**3ab–3ah**) in good yields. This result confirms that the electronic effects of the substituents did not play any significant role in our reaction. Importantly, the chloro- and bromo-substituents tolerated the reaction conditions and can be used for further functionalization (Table 2, **3ad** and **3ae**). Moreover, 6,7 disubstituted 4-aminocoumarin **2ag** also provided the desired product **3ag** in good yield. Other symmetrical silyltriflates such as 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b**, 3-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **1c** and 5-(trimethylsilyl)benzo[*d*][1,3] dioxol-6-yl trifluoromethanesulphonate **1d** were also explored as aryne precursors for our one-pot synthetic strategy. In this regard, symmetrical silyl triflates **1b** and **1c** were treated with a variety of 4-aminocoumarins to obtain 4-amino-3-arylcoumarins in 72–66% yields (Table 2, **3ba–3ch**). Moreover, symmetrical aryne derived from **1d** was also treated with 4-aminocoumarin to furnish the desired product **3da** in good yield. In addition, an aryne precursor bearing an electron-withdrawing group such as 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1e** was also used as a suitable aryne precursor, leading to our desired product **3ea** in 67% yield.

Moreover, secondary amine **2i** was also used as a substrate for our coupling process. In this investigation, *o*-silyl aryl triflate **1a** is allowed to react with **2i** under our optimized reaction conditions to obtain the desired product 3-phenyl-4-(phenylamino)-2*H*-chromen-2-one in 62% yield (Scheme 2).

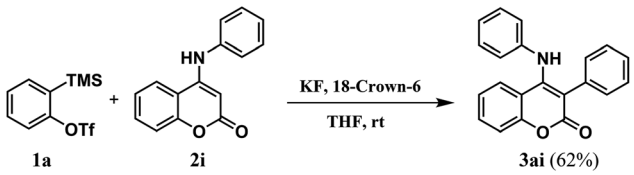
Similarly, secondary amine **2j** was also examined for our arylation process where *N*-protected iso-butyl aminocoumarin **2j** gives our desired product 4-(isobutylamino)-3-phenyl-2*H*-chromen-2-one in only 19% yield, which could be due to the steric hindrance of the iso-butyl group (Scheme 3).

Table 2 One-pot synthesis of 4-amino-3-arylcoumarins[a]



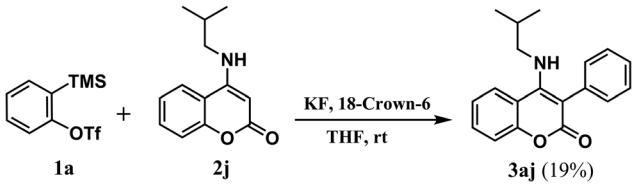


[a] Conditions: *o*-Silyl aryl triflate **1** (0.25 mmol), 4-aminocoumarin **2** (0.25 mmol), KF (0.75 mmol), 18-crown-6 (0.37 mmol), THF (3 mL) stirred at rt for 6 h.



1a 2i 3ai (62%)

Scheme 2 Synthesis of 3-phenyl-4-(phenylamino)-2*H*-chromen-2-one from aryne.



1a 2j 3aj (19%)

Scheme 3 Synthesis of 4-(isobutylamino)-3-phenyl-2*H*-chromen-2-one from aryne.

However, the yield of the product obtained from secondary aminocoumarins **2i** and **2j** is lower than that from primary aminocoumarins. This suggests that 4-aminocoumarin **2a** is a better substrate than secondary aminocoumarins **2i** and **2j**.

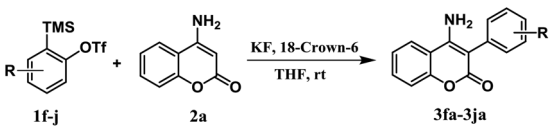
In order to explore the substrate scope, unsymmetrical benzyne precursors *i.e.* 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1f** and 4-methoxy-2-(trimethylsilyl) phenyl trifluoromethanesulfonate **1g** were treated with 4-aminocoumarin **2a** under our optimized reaction conditions (Table 3).

Benzyne precursors **1f** and **1g** gave 4-amino-3-arylcoumarin derivatives **3fa**/**3f′a** and **3ga**/**3g′a** as a mixture of regioisomers in good yields (Table 3, entries 1 and 2). The regioisomers were not separated into individual isomers and they are represented as mixtures. Interestingly, when unsymmetrical arynes derived from 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **1h**, 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** and 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate **1j** were treated with **2a**, single regioisomers **3ha**, **3ia** and **3ja** were obtained in 67%, 69% and 67% yields, respectively, with excellent regioselectivities.

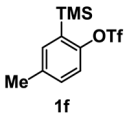
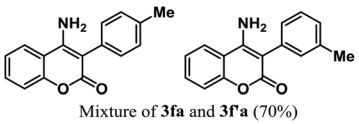
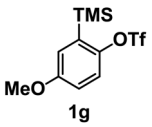
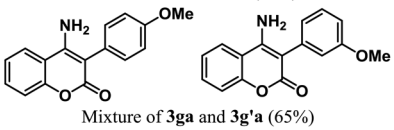
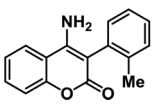
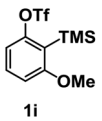
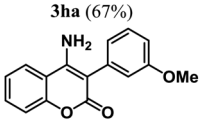
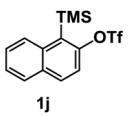
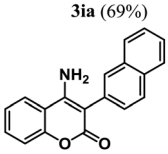
To gain insight into the reaction mechanism, a few deuterium-labelling experiments were performed. As shown in Scheme 4, when 4-aminocoumarin **2a** was treated with *o*-silyl aryl triflate **1a** under the optimized conditions, no deuterium incorporated product **3aa** was observed. Another independent experiment was performed using these two substrates in THF (dry) in the presence of D_2O as the fourth component under the same reaction conditions. Interestingly, this experiment gave the deuterium incorporated product **3aa-D** in 72% yield with quantitative incorporation of deuterium at the *ortho*-position, which was characterized by ^1H and ^{13}C NMR and HRMS analyses (Scheme 4).

Based on our experiments, a plausible reaction mechanism for the synthesis of 4-amino-3-arylcoumarin is proposed in Scheme 5. As shown in Scheme 5, the carbon atom of the enamine moiety of **2a** undergoes direct nucleophilic addition to arynes generated *in situ* from aryne precursor **1a** to form a zwitterionic intermediate **A**. Subsequently, intermediate **A** undergoes deprotonation at the activated methylene position followed by protonation at the aryl ring to form our desired product **3aa**.

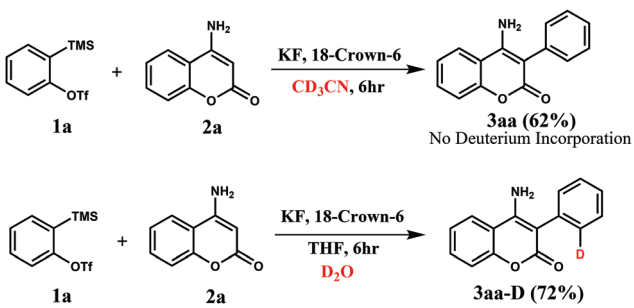
Table 3 Synthesis of 4-amino-3-arylcoumarins from unsymmetrical benzyne precursors[a]



1f-j 2a 3fa-3ja

Entry	Benzyne precursors (**1f–j**)	4-Amino-3-arylcoumarins (**3fa–3ja**)
1		 Mixture of **3fa** and **3f'a** (70%)
2		 Mixture of **3ga** and **3g'a** (65%)
3		 **3ha** (67%)
4		 **3ia** (69%)
5		 **3ja** (67%)

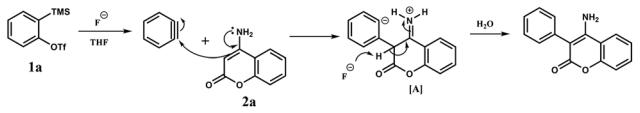
[a] Conditions: *o*-Silyl aryl triflate **1** (0.25 mmol), 4-aminocoumarin **2** (0.25 mmol), KF (0.75 mmol), 18-crown-6 (0.37 mmol), THF (3 mL) stirred at rt for 6 h.



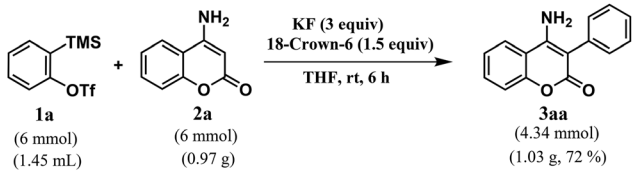
1a 2a 3aa (62%) No Deuterium Incorporation

1a 2a 3aa-D (72%)

Scheme 4 Deuterium labelling experiments.



Scheme 5 Probable reaction mechanism for the synthesis of 4-amino-3-arylcoumarin.



Scheme 6 Gram scale experiment for **3aa**.

Furthermore, to explore the practical utility of our synthetic strategy, the synthetic strategy was performed on a gram scale (Scheme 6). In our experiment, **1a** (6 mmol) was treated with **2a** (6 mmol) under our optimized conditions to give our desired product **3aa** in 72% yield.

Conclusion

In summary, we have developed a mild, efficient and transition-metal-free C(sp^2)–C(sp^2) bond forming strategy for the direct synthesis of 4-amino-3-arylcoumarins using aryne as an aryl source. A series of 4-amino-3-arylcoumarins have been synthesized using this one-pot synthetic strategy in good yields with excellent functional group compatibility including halides. Remarkably, this synthetic strategy gave a *C*-arylated product instead of an *N*-arylated product without protecting amine functionality.

Experimental section

General

All reactions involving oxygen- or moisture-sensitive compounds were carried out under an argon atmosphere using oven-dried or flame-dried glassware. All other solvents and reagents were purified according to the standard procedures or were used as received from TCI, Aldrich, Merck and Spectrochem. The reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed silica gel plates (0.2 mm thickness); the chromatograms were visualized with ultraviolet light (254 nm). Flash column chromatography was performed with silica gel 60 (100–200 or 200–400 mesh). HRMS data were recorded by electrospray ionization with a Q-TOF mass analyzer.

Starting materials

General procedure for the synthesis of 4-aminocoumarin. A mixture of 4-hydroxycoumarin (1 equiv.) and ammonium acetate (20 equiv.) was stirred at 130 °C overnight. After completion of the reaction, water (50 ml) was added. The mixture was stirred for 20 min, filtered and concentrated *in vacuo*. The residue was successively washed with water and ethanol to give 4-aminocoumarin **2a**. Compounds **2b–h** were prepared using the same method.

4-Amino-2*H*-chromen-2-one (2a).[26] Applying the general experimental procedure using 4-hydroxycoumarin (3 mmol, 1 equiv.) and ammonium acetate (60 mmol, 20 equiv.), 4-amino-2*H*-chromen-2-one **2a** was obtained as a light brown solid (0.430 g, 89% yield); mp 233–235 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.98 (dd, J_1 = 1.0 Hz, J_2 = 8.3 Hz, 1H), 7.56–7.59 (m, 1H), 7.40 (br s, 2H), 7.28–7.31 (m, 2H), 5.22 (s, 1H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.6, 155.5, 153.5, 132.0, 123.1, 122.8, 116.7, 114.3, 83.7; **IR ($CHCl_3$):** 3376, 3212, 2917, 2850, 1638, 1549, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_9H_8NO_2$ $[M + H]^+$**: 162.0555; found: 162.0564.

4-Amino-6-methyl-2*H*-chromen-2-one (2b).[26] Applying the general experimental procedure using 4-hydroxy-6-methylcoumarin (2 mmol, 1 equiv.) and ammonium acetate (40 mmol, 20 equiv.), 4-amino-6-methyl-2*H*-chromen-2-one **2b** was obtained as a light brown solid (0.287 g, 82% yield); mp 266–268 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.80 (d, J = 0.9 Hz, 1H), 7.39 (dd, J_1 = 1.8 Hz, J_2 = 8.4 Hz, 1H), 7.32 (br s, 2H), 7.17 (d, J = 8.4 Hz, 1H), 5.19 (s, 1H), 2.35 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.8, 155.5, 151.7, 132.8, 132.4, 122.7, 116.5, 114.0, 83.8, 20.4; **IR ($CHCl_3$):** 3376, 3207, 2922, 2845, 1621, 1570, 1218, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{10}H_{10}NO_2$ $[M + H]^+$**: 176.0712; found: 176.0710.

4-Amino-6-fluoro-2*H*-chromen-2-one (2c).[26] Applying the general experimental procedure using 6-fluoro-4-hydroxycoumarin (1 mmol, 1 equiv.) and ammonium acetate (20 mmol, 20 equiv.), 4-amino-6-fluoro-2*H*-chromen-2-one **2c** was obtained as a light brown solid (0.145 g, 80% yield); mp 298–300 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.89 (dd, J_1 = 2.9 Hz, J_2 = 9.7 Hz, 1H), 7.44–7.49 (m, 1H), 7.41 (br s, 2H), 7.34–7.37 (m, 1H), 5.24 (s, 1H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.4, 157.6 (d, J = 239.3 Hz), 154.8, 149.9, 119.4 (d, J = 24.2 Hz), 118.7 (d, J = 8.6 Hz), 115.3 (d, J = 8.7 Hz), 108.8 (d, J = 25.3 Hz), 84.2; **IR ($CHCl_3$):** 3368, 3203, 2922, 2835, 1635, 1551, 1220, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_9H_7FNO_2$ $[M + H]^+$**: 180.0461; found: 180.0461.

4-Amino-6-chloro-2*H*-chromen-2-one (2d).[26] Applying the general experimental procedure using 6-chloro-4-hydroxycoumarin (1 mmol, 1 equiv.) and ammonium acetate (20 mmol, 20 equiv.), 4-amino-6-chloro-2*H*-chromen-2-one **2d** was obtained as a light brown solid (0.158 g, 81% yield); mp 330–332 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.13 (d, J = 2.4 Hz, 1H), 7.61–7.63 (m, 1H), 7.46 (br s, 2H), 7.33 (d, J = 8.8 Hz, 1H), 5.23 (s, 1H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.1, 154.6, 152.3, 131.8, 127.4, 122.5, 118.8, 115.8, 84.2; **IR ($CHCl_3$):** 3367, 3198, 2917, 2845, 1626, 1570, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_9H_7ClNO_2$ $[M + H]^+$**: 196.0165; found: 196.0166.

4-Amino-6-bromo-2*H*-chromen-2-one (2e).[26] Applying the general experimental procedure using 6-bromo-4-hydroxycou-

marin (1 mmol, 1 equiv.) and ammonium acetate (20 mmol, 20 equiv.), 4-amino-6-bromo-2*H*-chromen-2-one **2e** was obtained as a light brown solid (0.197 g, 82% yield); mp 305–307 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.25 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.45 (br s, 2H), 7.26 (d, J = 8.8 Hz, 1H), 5.23 (s, 1H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.1, 154.5, 152.7, 134.6, 125.5, 119.1, 116.2, 115.2, 84.2; **IR ($CHCl_3$):** 3352, 3207, 2922, 2845, 1618, 1525, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_9H_7BrNO_2$ [M + H]$^+$:** 239.9660; found: 239.9669.

4-Amino-7-methoxy-2*H*-chromen-2-one (2f).[26] Applying the general experimental procedure using 7-methoxy-4-hydroxycoumarin (2 mmol, 1 equiv.) and ammonium acetate (40 mmol, 20 equiv.), 4-amino-7-methoxy-2*H*-chromen-2-one **2f** was obtained as a light brown solid (0.322 g, 84% yield); mp 299–301 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.89 (d, J = 8.9 Hz, 1H), 7.29 (br s, 2H), 6.89 (dd, J_1 = 2.5 Hz, J_2 = 8.9 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 5.07 (s, 1H), 3.82 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 162.3, 161.9, 155.9, 155.5, 124.1, 111.1, 107.5, 100.7, 81.7, 55.7; **IR ($CHCl_3$):** 3376, 3222, 2922, 2850, 1615, 1554, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{10}H_{10}NO_3$ [M + H]$^+$:** 192.0661; found: 192.0675.

4-Amino-6,7-dimethyl-2*H*-chromen-2-one (2g).[26] Applying the general experimental procedure using 4-hydroxy-6,7-dimethylcoumarin (1 mmol, 1 equiv.) and ammonium acetate (20 mmol, 20 equiv.), 4-amino-6,7-dimethyl-2*H*-chromen-2-one **2g** was obtained as a light brown solid (0.162 g, 86% yield); mp 299–301 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.73 (s, 1H), 7.27 (br s, 2H), 7.07 (s, 1H), 5.12 (s, 1H), 2.27 (s, 3H), 2.24 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 162.0, 155.7, 152.0, 141.6, 131.5, 122.9, 117.1, 111.8, 83.2, 19.5, 18.9; **IR ($CHCl_3$):** 3350, 3224, 2923, 2850, 1623, 1558, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{11}H_{12}NO_2$ [M + H]$^+$:** 190.0868; found: 190.0878.

4-Amino-7-methyl-2*H*-chromen-2-one (2h).[26] Applying the general experimental procedure using 4-hydroxy-7-methylcoumarin (2 mmol, 1 equiv.) and ammonium acetate (40 mmol, 20 equiv.), 4-amino-7-methyl-2*H*-chromen-2-one **2h** was obtained as a light brown solid (0.290 g, 83% yield); mp 262–264 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.85 (d, J = 7.9 Hz, 1H), 7.33 (br s, 2H), 7.09–7.11 (m, 2H), 5.16 (s, 1H), 2.36 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.8, 155.7, 153.7, 142.7, 124.2, 122.7, 116.7, 111.9, 83.1, 20.9; **IR ($CHCl_3$):** 3367, 3217, 2927, 2850, 1618, 1539, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{10}H_{10}NO_2$ [M + H]$^+$:** 176.0712; found: 176.0710.

General procedure for the synthesis of 4-(phenylamino)-2*H*-chromen-2-one (2i). A mixture of 4-hydroxycoumarin (1 equiv.) and aniline (3 equiv.) was stirred at 160 °C for 20 min. After completion of the reaction, the reaction mixture was dissolved in methanol (20 ml) and then aqueous NaOH solution was added dropwise. The mixture was stirred for 20 min. The precipitate so formed was washed with water and then with ethanol to obtain pure **2i**.[25]

4-(Phenylamino)-2*H*-chromen-2-one (2i).[27] Applying the general experimental procedure using 4-hydroxycoumarin (1 mmol, 1 equiv.) and aniline (3 mmol, 3 equiv.), 4-(phenylamino)-2*H*-chromen-2-one **2i** was obtained as a white solid (0.197 g, 83% yield); mp 258–260 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 9.33 (s, 1H), 8.24 (dd, J_1 = 1.2 Hz, J_2 = 8.1 Hz, 1H), 7.63–7.64 (m, 1H), 7.27–7.50 (m, 7H), 5.31 (s, 1H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.5, 153.3, 152.4, 138.1, 132.3, 129.5, 125.9, 125.0, 123.6, 122.7, 117.0, 114.4, 84.3; **IR ($CHCl_3$):** 3391, 3280, 2922, 2845, 1656, 1611, 1591, 1536, 1260, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{15}H_{12}NO_2$ [M + H]$^+$:** 238.0868; found: 238.0880.

General procedure for the synthesis of 4-(isobutylamino)-2*H*-chromen-2-one (2j).[26] A mixture of 4-hydroxycoumarin (1 equiv.) and *tert*-butylamine (10 equiv.) was refluxed in acetic acid overnight. After completion of the reaction, water was added until it precipitates. The mixture was stored in a fridge overnight and then filtered and concentrated *in vacuo*. The residue was successively washed with water and ethyl acetate to give 4-(isobutylamino)-2*H*-chromen-2-one (**2j**)[26]

4-(Isobutylamino)-2*H*-chromen-2-one (2j).[26] Applying the general experimental procedure using 4-hydroxycoumarin (1 mmol, 1 equiv.) and *tert*-butylamine (10 mmol, 10 equiv.), 4-(isobutylamino)-2*H*-chromen-2-one **2j** was obtained as a light brown solid (0.175 g, 80% yield); mp 144–146 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.08 (dd, J_1 = 1.1 Hz, J_2 = 8.0 Hz, 1H), 7.71 (t, J = 5.6 Hz, 1H), 7.57 (m, 1H), 7.28–7.32 (m, 2H), 5.13 (s, 1H), 3.04 (m, 2H), 1.94–2.02 (m, 1H), 0.92 (d, J = 6.6 Hz, 6H);**^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.6, 153.2, 153.0, 131.9, 123.3, 122.4, 116.9, 114.4, 81.2, 49.7, 26.5, 20.2; **IR ($CHCl_3$):** 3328, 3095, 2959, 2871, 1617, 1558, 1249, 767 cm^{-1}; **HRMS (+ESI) calcd for $C_{13}H_{16}NO_2$ [M + H]$^+$:** 218.1181; found: 218.1190.

General procedure for the synthesis of 4-amino-3-arylcoumarin derivatives from aryne precursors. An oven-dried round bottomed flask (50 mL) equipped with a magnetic stir bar was evacuated and purged with argon. *o*-Silyl aryl triflate (0.25 mmol, 1 equiv.), 4-aminocoumarin (0.25 mmol, 1.0 equiv.), KF (0.75 mmol, 3 equiv.), 18-crown-6 (0.37 mmol, 1.5 equiv.) and THF (3 mL) were successively added at room temperature. The reaction mixture was stirred at rt for 6 h. Water (10 mL) was added to the reaction mixture and the organic layer was extracted with EtOAc (20 × 2 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed, and the residue was purified by column chromatography on silica gel using hexanes/ethyl acetate as an eluent.

4-Amino-3-phenyl2*H*-chromen-2-one (3aa).[25] Applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.04 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-phenyl-2*H*-chromen-2-one **3aa** was obtained as a white solid (0.045 g, 76% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 180–182 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.28–7.58 (m, 9H), 5.00 (br s, 2H); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.9, 153.1, 149.7, 132.7, 131.9, 130.6, 129.2, 128.1, 123.6, 121.4, 117.5, 114.2, 101.0; **^{1}H NMR (500 MHz, DMSO-**

d_6): δ 8.15 (d, J = 7.8 Hz, 1H), 7.31–7.61 (m, 8H), 6.77 (br s, 2H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.8, 152.5, 150.8, 133.7, 131.9, 131.0, 128.6, 127.1, 123.5, 123.4, 116.5, 114.6, 97.4; **IR ($CHCl_3$):** 3450, 3340, 2920, 2850, 1673, 1628, 1606, 1548, 1501, 1428, 1286, 1207, 752 cm^{-1}; **HRMS (+ESI) calcd for $C_{15}H_{12}NO_2$ [M + H]$^+$:** 238.0868; found: 238.0870.

4-Amino-6-methyl-3-phenyl-2*H*-chromen-2-one (3ab). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-6-methylcoumarin (0.044 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-6-methyl-3-phenyl-2*H*-chromen-2-one **3ab** was obtained as a white solid (0.043 g, 68% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 277–279 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.99 (s, 1H), 7.41–7.46 (m, 3H), 7.30–7.35 (m, 3H), 7.22 (d, J = 8.4 Hz, 1H), 6.78 (br s, 2H), 2.38 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.9, 150.7, 150.6, 133.8, 132.6, 132.5, 130.9, 128.6, 127.0, 123.3, 116.2, 114.1, 97.4, 20.4; **IR ($CHCl_3$):** 3468, 3348, 2917, 2855, 1663, 1633, 1610, 1556, 1508, 1429, 1280, 1218, 771 cm^{-1}; **HRMS (+ESI) calcd for $C_{16}H_{14}NO_2$ [M + H]$^+$:** 252.1025; found: 252.1024.

4-Amino-6-fluoro-3-phenyl-2*H*-chromen-2-one (3ac). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-6-fluorocoumarin (0.045 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-6-fluoro-3-phenyl-2*H*-chromen-2-one **3ac** was obtained as a white solid (0.041 g, 64% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 282–284 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.08 (dd, J_1 = 2.9 Hz, J_2 = 10.0 Hz, 1H), 7.31–7.51 (m, 7H), 6.85 (brs, 2H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.6, 157.7 (d, J = 239.0 Hz), 150.1 (d, J = 1.9 Hz), 148.9, 133.4, 130.8, 128.6, 127.2, 119.1 (d, J = 23.3 Hz), 118.5 (d, J = 8.7 Hz), 115.6 (d, J = 8.9 Hz), 109.4 (d, J = 25.7 Hz), 97.9; **IR ($CHCl_3$):** 3468, 3337, 2915, 2847, 1669, 1633, 1610, 1556, 1504, 1435, 1410, 1212, 771 cm^{-1}; **HRMS (+ESI) calcd for $C_{15}H_{11}NO_2F$ [M + H]$^+$:** 256.0774; found: 256.0770.

4-Amino-6-chloro-3-phenyl-2*H*-chromen-2-one (3ad). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-6-chlorocoumarin (0.049 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-6-chloro-3-phenyl-2*H*-chromen-2-one **3ad** was obtained as a white solid (0.047 g, 69% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 292–294 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.33 (d, J = 2.4 Hz, 1H), 7.65 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.30–7.47 (m, 6H), 6.96 (br s, 2H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.5, 151.2, 149.9, 133.4, 131.6, 130.9, 128.6, 127.7, 127.3, 123.2, 118.6, 116.1, 97.9; **IR ($CHCl_3$):** 3444, 3323, 2927, 2845, 1674, 1626, 1605, 1552, 1498, 1428, 1399, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{15}H_{11}NO_2Cl$ [M + H]$^+$:** 272.0478; found: 272.0474.

4-Amino-6-bromo-3-phenyl-2*H*-chromen-2-one (3ae). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-6-bromocoumarin (0.060 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-6-bromo-3-phenyl-2*H*-chromen-2-one **3ae** was obtained as a white solid (0.051 g, 64% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 270–272 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.45 (d, J = 2.3 Hz, 1H), 7.76 (dd, J_1 = 2.2 Hz, J_2 = 8.8 Hz, 1H), 7.44–7.47 (m, 2H), 7.30–7.47 (m, 4H), 6.82 (br s, 2H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.5, 151.6, 149.8, 134.4, 133.4, 130.9, 128.7, 127.3, 126.1, 118.8, 116.5, 115.4, 98.0; **IR ($CHCl_3$):** 3454, 3332, 2922, 2850, 1672, 1628, 1601, 1545, 1496, 1428, 1398, 1219, 773 cm^{-1}; **HRMS (+ESI) calcd for $C_{15}H_{11}NO_2Br$ [M + H]$^+$:** 315.9973; found: 315.9974.

4-Amino-7-methoxy-3-phenyl-2*H*-chromen-2-one (3af). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-7-methoxycoumarin (0.048 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-7-methoxy-3-phenyl-2*H*-chromen-2-one **3af** was obtained as a white solid (0.048 g, 72% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 210–212 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.07 (d, J = 8.8 Hz, 1H), 7.30–7.45 (m, 5H), 6.89–6.93 (m, 2H), 6.87 (brs, 2H), 3.85 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.1, 161.0, 154.2, 151.0, 133.9, 131.0, 128.5, 126.9, 124.8, 111.2, 107.7, 100.4, 95.4, 55.7; **IR ($CHCl_3$):** 3454, 3342, 2922, 2850, 1638, 1602, 1546, 1513, 1431, 1272, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{16}H_{14}NO_3$ [M + H]$^+$:** 268.0974; found: 268.0974.

4-Amino-6,7-dimethyl-3-phenyl-2*H*-chromen-2-one (3ag). Applying the general experimental procedure using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-6,7-dimethylcoumarin (0.047 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-6,7-dimethyl-3-phenyl-2*H*-chromen-2-one **3ag** was obtained as a white solid (0.046 g, 69% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 220–222 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.94 (s, 1H), 7.29–7.44 (m, 5H), 7.13 (s, 1H), 6.54 (br s, 2H), 2.31 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.0, 150.8 (d, J = 1.7 Hz), 141.2, 133.9, 131.7, 130.9, 128.5, 126.9, 123.5, 116.7, 111.9, 96.8, 19.4, 18.4; **IR ($CHCl_3$):** 3458, 3342, 2922, 2845, 1664, 1613, 1546, 1431, 1216, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{17}H_{16}NO_2$[M + H]$^+$:** 266.1181; found: 266.1178.

4-Amino-7-methyl-3-phenyl-2*H*-chromen-2-one (3ah). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-amino-7-methylcoumarin (0.044 g; 0.25 mmol,

1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-7-methyl-3-phenyl-2*H*-chromen-2-one **3ah** was obtained as a white solid (0.044 g, 70% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 223–225 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.04 (d, J = 8.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.33–7.35 (m, 3H), 7.13–7.15 (m, 2H), 6.88 (brs, 2H), 2.40 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.0, 152.6, 150.9, 142.4, 133.9, 131.0, 128.6, 127.0, 124.5, 123.4, 116.5, 112.1, 96.8, 20.9; **IR ($CHCl_3$):** 3414, 3344, 2922, 2850, 1636, 1615, 1598, 1544, 1514, 1435, 1218, 770 cm^{-1}; **HRMS (+ESI) calcd for $C_{16}H_{14}NO_2$ [M + H]$^+$:** 252.1025; found: 252.1024.

4-Amino-3-(3,4-dimethoxyphenyl)-2*H*-chromen-2-one (3ba). Applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(3,4-dimethoxyphenyl)-2*H*-chromen-2-one **3ba** was obtained as a white solid (0.054 g, 72% yield) after purification by flash chromatography on silica gel (60% EtOAc/hexane); mp 256–258 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.14 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.30–7.32 (m, 2H), 7.02 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 1.6 Hz, 1H), 6.84 (dd, J_1 = 1.8 Hz, J_2 = 8.2 Hz, 1H), 6.74 (br s, 2H), 3.80 (s, 3H), 3.75 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.8, 152.4, 150.8, 148.7, 147.8, 131.6, 125.9, 123.4, 123.3, 123.2, 116.4, 114.6, 114.4, 111.9, 97.4, 55.4, 55.3; **IR ($CHCl_3$):** 3423, 3342, 2921, 2849, 1674, 1623, 1605, 1546, 1511, 1241, 1023, 751 cm^{-1}; **HRMS (+ESI) calcd for $C_{17}H_{16}NO_4$ [M + H]$^+$:** 298.1079; found: 298.1080.

4-Amino-3-(3,4-dimethoxyphenyl)-6-methyl-2*H*-chromen-2-one (3bb). Applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-amino-6-methylcoumarin (0.044 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(3,4-dimethoxyphenyl)-6-methyl-2*H*-chromen-2-one **3bb** was obtained as a white solid (0.055 g, 70% yield) after purification by flash chromatography on silica gel (60% EtOAc/hexane); mp 248–250 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.97 (s, 1H), 7.40 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.81–6.85 (m, 2H), 6.76 (br s, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 2.37 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.2, 150.9, 150.7, 148.8, 147.9, 132.6, 132.5, 126.1, 123.4, 123.3, 116.3, 114.5, 114.4, 112.0, 97.5, 55.5, 55.4, 20.6; **IR ($CHCl_3$):** 3421, 3340, 2922, 2855, 1667, 1638, 1603, 1549, 1510, 1219, 1025, 992, 771 cm^{-1}; **HRMS (+ESI) calcd for $C_{18}H_{18}NO_4$ [M + H]$^+$:** 312.1236; found: 312.1239.

4-Amino-3-(3,4-dimethoxyphenyl)-7-methoxy-2*H*-chromen-2-one (3bf). Applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-amino-7-methoxycoumarin (0.048 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(3,4-dimethoxyphenyl)-7-methoxy-2*H*-chromen-2-one **3bf** was obtained as a white solid (0.057 g, 69% yield) after purification by flash chromatography on silica gel (60% EtOAc/hexane); mp 250–252 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.04 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.89–6.92 (m, 2H), 6.80–6.85 (m, 2H), 6.78 (br s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 162.0, 161.2, 154.3, 151.3, 148.6, 147.7, 126.1, 124.7, 123.3, 114.5, 111.9, 111.2, 107.8, 100.4, 95.4, 55.7, 55.4, 55.3; **IR ($CHCl_3$):** 3409, 3338, 2923, 2850, 1633, 1597, 1539, 1510, 1219, 1025, 994, 770 cm^{-1}; **HRMS (+ESI) calcd for $C_{18}H_{18}NO_5$[M + H]$^+$:** 328.1185; found: 328.1182.

4-Amino-3-(3,4-dimethoxyphenyl)-7-methyl-2*H*-chromen-2-one (3bh). Applying the general experimental procedure using 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-amino-7-methylcoumarin (0.044 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(3,4-dimethoxyphenyl)-7-methyl-2*H*-chromen-2-one **3bh** was obtained as a white solid (0.052 g, 67% yield) after purification by flash chromatography on silica gel (60% EtOAc/hexane); mp 247–249 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.01 (d, J = 8.1 Hz, 1H), 7.00–7.15 (m, 3H), 6.81–6.85 (m, 2H), 6.74 (br s, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 2.40 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 161.0, 152.5, 151.0, 148.6, 147.8, 142.2, 126.0, 124.4, 123.3, 123.2, 116.4, 114.4, 112.1, 111.9, 96.7, 55.4, 55.3, 20.9; **IR ($CHCl_3$):** 3450, 3338, 2923, 2850, 1636, 1616, 1541, 1512, 1220, 1025, 992, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{18}H_{18}NO_4$[M + H]$^+$:** 312.1236; found: 312.1240.

4-Amino-3-(naphthalen-2-yl)-2*H*-chromen-2-one (3ca). Applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(naphthalen-2-yl)-2*H*-chromen-2-one **3ca** was obtained as a white solid (0.049 g, 68% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 252–254 °C; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 8.19 (d, J = 7.7 Hz, 1H), 7.94–7.96 (m, 3H), 7.87 (s, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.52–7.54 (m, 2H), 7.44 (dd, J_1 = 1.3 Hz, J_2 = 8.4 Hz, 1H), 7.35–7.38 (m, 2H), 6.92 (br s, 2H); **^{13}C NMR (126 MHz, DMSO-d_6):** δ 160.9, 152.6, 151.1, 133.3, 133.2, 131.8, 131.4, 129.8, 129.2, 127.9, 127.8, 127.4, 125.9, 125.7, 123.6, 123.4, 116.6, 114.6, 97.3; **IR ($CHCl_3$):** 3391, 3227, 2917, 2845, 1633, 1597, 1538, 1493, 1425, 1218, 1110, 768 cm^{-1}; **HRMS (+ESI) calcd for $C_{19}H_{14}NO_2$[M + H]$^+$:** 288.1025; found: 288.1023.

4-Amino-7-methoxy-3-(naphthalen-2-yl)-2*H*-chromen-2-one (3cf). Applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-amino-7-methoxycoumarin (0.048 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-7-methoxy-3-(naphthalen-2-yl)-2*H*-chromen-2-one **3cf** was obtained as a white solid (0.051 g, 64% yield) after purifi-

cation by flash chromatography on silica gel (40% EtOAc/hexane); mp 281–283 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.11 (d, J = 9.6 Hz, 1H), 7.92–7.96 (m, 3H), 7.86 (s, 1H), 7.50–7.54 (m, 2H), 7.44 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 6.94–6.96 (m, 2H), 6.92 (br s, 2H), 3.87 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 162.2, 161.2, 154.4, 151.5, 133.3, 132.1, 131.6, 129.9, 129.5, 127.9, 127.8, 127.4, 125.9, 125.8, 124.8, 111.3, 107.8, 100.5, 95.2, 55.8; **IR (CHCl$_3$):** 3318, 3178, 2922, 2855, 1672, 1635, 1593, 1535, 1509, 1423, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{20}H_{16}NO_3[M + H]^+$**: 318.1130; found: 318.1131.

4-Amino-7-methyl-3-(naphthalen-2-yl)-2*H*-chromen-2-one (3ch). Applying the general experimental procedure using 3-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-amino-7-methylcoumarin (0.044 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-7-methyl-3-(naphthalen-2-yl)-2*H*-chromen-2-one **3ch** was obtained as a white solid (0.050 g, 66% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 229–231 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.08 (d, J = 8.2 Hz, 1H), 7.93–7.97 (m, 3H), 7.87 (s, 1H), 7.50–7.54 (m, 2H), 7.45 (dd, J_1 = 1.7 Hz, J_2 = 8.4 Hz, 1H), 7.16–7.19 (m, 2H), 6.92 (br s, 2H), 2.43 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.1, 152.7, 151.3, 142.4, 133.3, 132.2, 131.6, 129.9, 129.4, 127.9, 127.8, 127.4, 125.9, 125.7, 124.5, 123.4, 116.5, 112.2, 96.6, 20.9; **IR (CHCl$_3$):** 3454, 3346, 2922, 2845, 1633, 1612, 1541, 1515, 1488, 1436, 1218, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{20}H_{16}NO_2[M + H]^+$**: 302.1181; found: 302.1178.

4-Amino-3-(benzo[*d*][1,3]dioxol-5-yl)-2*H*-chromen-2-one (3da). Applying the general experimental procedure using 5-(trimethylsilyl)benzo[*d*][1,3]dioxol-6-yl trifluoromethanesulphonate (0.05 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(benzo[*d*][1,3]dioxol-5-yl)-2*H*-chromen-2-one **3da** was obtained as a white solid (0.051 g, 72% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 252–254 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.10 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 1H), 7.57–760 (m, 1H), 7.29–7.32 (m, 2H), 6.97 (d, J = 7.9 Hz, 1H), 6.82 (d, J = 1.5 Hz, 1H), 6.46 (dd, J_1 = 1.6 Hz, J_2 = 7.9 Hz, 1H), 6.73 (br s, 2H), 6.02 (s, 2H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.1, 152.6, 151.3, 147.5, 146.4, 131.9, 127.2, 124.4, 123.6, 123.5, 116.6, 114.7, 111.4, 108.7, 100.9, 97.4; **IR (CHCl$_3$):** 3422, 3340, 2923, 2850, 1634, 1601, 1550, 1502, 1442, 1220, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{16}H_{12}NO_4[M + H]^+$**: 282.0766; found: 282.0765.

4-Amino-3-(3,4-difluorophenyl)-2*H*-chromen-2-one (3ea). Applying the general experimental procedure using 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(3,4-difluorophenyl)-2*H*-chromen-2-one **3ea** was obtained as a white solid (0.046 g, 67% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 287–289 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.16 (dd, J_1 = 1.4 Hz, J_2 = 8.4 Hz, 1H), 7.60–7.64 (m, 2H), 7.48 (dt, J_1 = 8.6 Hz, J_2 = 11.0 Hz, 1H), 7.32–7.39 (m, 2H), 7.14–7.15 (m, 1H), 6.98 (br s, 2H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 160.6, 151.9 (d, J = 142.4 Hz), 150.5 (d, J = 12.7 Hz), 149.6 (d, J = 12.5 Hz), 148.5 (d, J = 12.7 Hz), 147.7 (d, J = 12.7 Hz), 132.1, 131.4 (dd, J_1 = 3.7 Hz, J_2 = 6.5 Hz), 128.3 (dd, J_1 = 2.9 Hz, J_2 = 6.3 Hz), 123.5 (d, J = 11.8 Hz), 120.3 (d, J = 16.4 Hz), 117.5 (d, J = 17.0 Hz), 116.6, 114.5, 95.6; **IR (CHCl$_3$):** 3405, 3357, 2922, 2850, 1633, 1607, 1549, 1515, 751 cm^{-1}; **HRMS (+ESI) calcd for $C_{15}H_{10}NO_2F_2[M + H]^+$**: 274.0680; found: 274.0680.

3-Phenyl-4-(phenylamino)-2*H*-chromen-2-one (3ai). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-(phenylamino)-2*H*-chromen-2-one (0.059 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 3-phenyl-4-(phenylamino)-2*H*-chromen-2-one **3ai** was obtained as a white solid (0.049 g, 62% yield) after purification by flash chromatography on silica gel (30% EtOAc/hexane); mp 206–208 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.71 (s, 1H), 8.03 (dd, J_1 = 1.1 Hz, J_2 = 8.1 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 6.93–7.16 (m, 7H), 6.72–6.77 (m, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.4, 152.3, 146.8, 140.7, 134.1, 131.7, 130.5, 127.9, 127.2, 126.6, 124.3, 123.6, 122.1, 120.9, 116.9, 116.6, 106.8; **IR (CHCl$_3$):** 3322, 2922, 2850, 1673, 1594, 1560, 1524, 1495, 1439, 1380, 1170, 761 cm^{-1}; **HRMS (+ESI) calcd for $C_{21}H_{16}NO_2[M + H]^+$**: 314.1181; found: 314.1180.

4-(Isobutylamino)-3-phenyl-2*H*-chromen-2-one (3aj). Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-(isobutylamino)-2*H*-chromen-2-one (0.054 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-(isobutylamino)-3-phenyl-2*H*-chromen-2-one **3aj** was obtained as a yellow solid (0.014 g, 19% yield) after purification by flash chromatography on silica gel (20% EtOAc/hexane); mp 196–198 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.25 (d, J = 7.3 Hz, 1H), 8.14(d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.36–7.66 (m, 7H), 4.63 (d, J = 7.6 Hz, 2H), 2.19–2.27 (m, 1H), 0.94 (d, J = 6.6 Hz, 6H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 157.7, 152.8, 140.0, 139.8, 130.7, 124.9, 124.6, 123.4, 123.3, 122.8, 120.3, 117.9, 113.4, 111.8, 101.1, 51.4, 29.4, 19.5; **IR (CHCl$_3$):** 3399, 2958, 2924, 1648, 1590, 1524, 1460, 1219, 1025, 772 cm^{-1}; **HRMS (+ESI) calcd for $C_{19}H_{20}NO_2[M + H]^+$**: 294.1494; found: 294.1503.

4-Amino-3-(*p*-tolyl)-2*H*-chromen-2-one & 4-amino-3-(*m*-tolyl)-2*H*-chromen-2-one (3fa) & (3f'a). Applying the general experimental procedure using 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(*p*-tolyl)-2*H*-chromen-2-one & 4-amino-3-(*m*-tolyl)-2*H*-chromen-2-one **3fa** & **3f'a** were obtained as a white solid (0.044 g, 70% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp

202–204 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.15 (dd, J_1 = 3.2 Hz, J_2 = 7.8 Hz, 1H), 7.58–7.62 (m, 1H), 7.10–7.35 (m, 6H), 6.91 (br s, 2H), 2.34 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 160.9, 160.8, 152.6, 152.5, 150.8, 150.7, 137.6, 136.2, 133.6, 131.8, 131.7, 131.5, 130.8, 130.7, 129.2, 128.5, 127.9, 127.8, 123.5, 123.4, 116.6, 116.5, 114.7, 114.6, 97.6, 97.4, 21.0, 20.9; **IR (CHCl$_3$):** 3458, 3342, 2922, 2850, 1672, 1627, 1605, 1548, 1500, 1423, 1286, 1215, 970, 753 cm^{-1}; **HRMS (+ESI) calcd for C$_{16}$H$_{14}$NO$_2$[M + H]$^+$:** 252.1025; found: 252.1022.

4-Amino-3-(4-methoxyphenyl)-2*H*-chromen-2-one & 4-amino-3-(3-methoxyphenyl)-2*H*-chromen-2-one (3ga) & (3g′a). Applying the general experimental procedure using 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(4-methoxyphenyl)-2*H*-chromen-2-one & 4-amino-3-(3-methoxyphenyl)-2*H*-chromen-2-one **3ga** & **3g′a** were obtained as a white solid (0.044 g, 65% yield) after purification by flash chromatography on silica gel (60% EtOAc/hexane); mp 208–210 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.15 (t, J = 8.1 Hz, 1H), 7.56–7.62 (m, 1H), 7.23–7.38 (m, 3H), 6.87–7.01 (m, 3H), 6.85 (br s, 2H), 3.79 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.0, 160.7, 159.4, 158.3, 152.5, 152.4, 150.9, 150.8, 135.0, 132.0, 131.9, 131.7, 129.6, 125.6, 123.6, 123.5, 123.4, 123.3, 123.1, 116.5, 116.4, 116.3, 114.7, 114.6, 114.0, 112.8, 97.4, 97.2, 55.0, 54.3; **IR (CHCl$_3$):** 3454, 3342, 2922, 2855, 1674, 1626, 1603, 1547, 1281, 1219, 956, 773 cm^{-1}; **HRMS (+ESI) calcd for C$_{16}$H$_{14}$NO$_3$[M + H]$^+$:** 268.0974; found: 268.0972.

4-Amino-3-(*o*-tolyl)-2*H*-chromen-2-one (3ha). Applying the general experimental procedure using 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(*o*-tolyl)-2*H*-chromen-2-one **3ha** was obtained as a white solid (0.042 g, 67% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 204–206 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.15 (d, J = 8.4 Hz, 1H), 7.58–7.62 (m, 1H), 7.31–7.35 (m, 3H), 7.10–7.16 (m, 3H), 6.87 (br s, 2H), 2.34 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 160.8, 152.5, 150.8, 137.6, 133.6, 131.8, 131.5, 128.5, 127.9, 127.8, 123.5, 123.4, 116.5, 114.6, 97.6, 21.0; **IR (CHCl$_3$):** 3391, 3338, 2922, 2850, 1631, 1601, 1540, 1498, 1430, 1216, 1117, 773 cm^{-1}; **HRMS (+ESI) calcd for C$_{16}$H$_{14}$NO$_2$[M + H]$^+$:** 252.1025; found: 252.1027.

4-Amino-3-(3-methoxyphenyl)-2*H*-chromen-2-one (3ia). Applying the general experimental procedure using 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulphonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1 equiv.), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(3-methoxyphenyl)-2*H*-chromen-2-one **3ia** was obtained as a white solid (0.046 g, 69% yield) after purification by flash chromatography on silica gel (60% EtOAc/hexane); mp 214–216 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.13 (dd, J_1 = 1.4 Hz, J_2 = 8.4 Hz, 1H), 7.59–7.62 (m, 1H), 7.31–7.37 (m, 3H), 6.85–6.92 (m, 3H), 6.82 (br s, 2H), 3.76 (s, 3H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 160.9, 159.5, 152.6, 151.0, 135.0, 132.0, 129.8, 123.6, 123.5, 123.2, 116.7, 116.4, 114.6, 113.0, 97.5, 55.0; **IR (CHCl$_3$):** 3398, 3340, 2927, 2850, 1664, 1625, 1597, 1259, 1219, 1025, 989, 772 cm^{-1}; **HRMS (+ESI) calcd for C$_{16}$H$_{14}$NO$_3$[M + H]$^+$:** 268.0974; found: 268.0974.

4-Amino-3-(naphthalen-2-yl)-2*H*-chromen-2-one (3ja). Applying the general experimental procedure using 1-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate (0.07 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1equiv), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL), 4-amino-3-(naphthalen-2-yl)-2*H*-chromen-2-one **3ja** was obtained as a white solid (0.048 g, 67% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 274–276 °C; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 8.18 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.93–7.97 (m, 3H), 7.88 (s, 1H), 7.61–7.65 (m, 1H), 7.44 (dd, J_1 = 1.7 Hz, J_2 = 8.4 Hz, 2H), 7.33–7.38 (m, 3H), 6.97 (br s, 2H); **^{13}C NMR (126 MHz, DMSO-d$_6$):** δ 161.2, 152.7, 151.3, 133.4, 132.7, 132.1, 131.5, 129.9, 129.3, 128.1, 128.0, 127.6, 126.1, 125.9, 123.7, 123.6, 116.7, 114.7, 97.5; **IR (CHCl$_3$):** 3463, 3352, 2922, 2850, 1632, 1602, 1549, 1501, 1219, 772 cm^{-1}; **HRMS (+ESI) calcd for C$_{19}$H$_{14}$NO$_2$[M + H]$^+$:** 288.1025; found: 288.1025.

4-Amino-3-(phenyl-2-d)-2*H*-chromen-2-one {3aa-(D)}. Applying the general experimental procedure using 2-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.06 mL; 0.25 mmol, 1 equiv.), 4-aminocoumarin (0.040 g; 0.25 mmol, 1equiv), KF (0.043 g; 0.75 mmol, 3 equiv.), and 18-crown-6 (0.100 g; 0.37 mmol, 1.5 equiv.) in THF (3 mL) and D$_2$O (5.0 μL, 0.25 mmol), 4-amino-3-(phenyl-2-d)-2*H*-chromen-2-one **3aa-D** was obtained as a white solid (0.043 g, 72% yield) after purification by flash chromatography on silica gel (40% EtOAc/hexane); mp 208–210 °C; **^{1}H NMR (500 MHz, CDCl$_3$):** δ 8.17 (d, J = 8.0 Hz, 1H), 7.59–7.62 (m, 1H), 7.44–7.47 (m, 2H), 7.31–7.36 (m, 4H), 6.78 (br s, 2H); **^{13}C NMR (126 MHz, CDCl$_3$):** δ 160.9, 152.5, 150.8, 133.7 (d, J = 11.7 Hz), 131.9, 130.9, 128.6, 128.5, 127.1, 123.5 (d, J = 21.8 Hz), 116.5, 114.6, 97.4 (d, J = 4.1 Hz); **IR (CHCl$_3$):** 3468, 3342, 2917, 2855, 1672, 1628, 1607, 1548, 1500, 1427, 967, 771 cm^{-1}; **HRMS (+ESI) calcd for C$_{15}$H$_{11}$DNO$_2$ [M + H]$^+$:** 239.0931; found: 239.0925.

Conflicts of interest

There are no conflicts to declare.

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