2-(Azidomethyl)arylboronic Acids in the Synthesis of Coumarin-Type Compounds

Mikael I. Naumov,[a] Alexander V. Nuchev,[a] Nikolay S. Sitnikov,[a] Yulia B. Malysheva,[a] Andrew S. Shavyrin,[b] Irina P. Beletskaya,[c] Andrei E. Gavryushin,[d] Sebastien Combes,[e] Alexey Yu. Fedorov*[a]

[a] Department of Organic Chemistry, Nizhnii Novgorod N. I. Lobachevsky State University, 23 Gagarin Avenue, 603950 Nizhnii Novgorod, Russian Federation
Fax +7(831)4658592; E-mail: afnn@rambler.ru

[b] G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina Street 49, 603600 Nizhnii Novgorod, Russian Federation
E-mail: andrew@imoc.sinn.ru

[c] Department of Chemistry, M.V. Lomonosov State University, Leninskie Gori, 119992 Moscow, Russian Federation
E-mail: beletska@org.chem.msu.ru

[d] Department Chemie and Biochemie, Ludwig Maximilians-Universität München, Butenandtstr. 5–13, Haus F, 81377 München, Germany
E-mail: gavch@cup.uni-muenchen.de

[e] UMR 6264, Faculte des Sciences Saint-Jerome, Universite d'Aix Marseille 1 et 2, 13397 Marseille Cedex 20, France
E-mail: Sebastien.Combes@univ-provence.fr

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Dedicated to the memory of Professor Jean-Pierre Finet

Abstract: Several 2-(azidomethyl)arylboronic acids were synthesized. Their involvement into organolead-mediated Pinhey arylation reaction with 4-hydroxycoumarins afforded 3-[2-(azidomethyl)aryl]-4-hydroxycoumarins or [4,3-*c*]isoquinolinocoumarins in reasonable yields via two- or four-step one-pot reaction sequence. Palladium-catalyzed cross-coupling of organoboron reagents with 4-trifluoromethylsulfonyloxycoumarins under Suzuki reaction conditions gave 4-[2-(azidomethyl)aryl]coumarins in good yields. 2-(Azidomethyl)arylboronic acid, as well as azide-containing iso- and neoflavonoid compounds underwent catalytic alkyne-azide cycloaddition in THF–water, providing 1,4-triazole compounds regioselectively in good to excellent yields.

Key words: coumarins, azides, arylation, cross-coupling, cycloaddition

3-Arylcoumarins, 4-arylcoumarins, and related compounds represent a class of naturally occurring flavonoids found in plants belonging to the families *Guttiferae*, *Rubiaceae*, *Leguminosae*, *Passifloraceae*, and *Millettia grifonianas*.[1] The presence of two noncoplanar *syn*-aryl fragments linked by a rigid C–C bond in 4-arylcoumarins determines their structural analogies with combretastatin A-4 – a promising natural molecule able to disrupt efficiently normal mitotic spindle functions (Figure 1).[2] Indeed, neoflavonoid **1a**, isolated recently from endophytic *Streptomyces aureofaciens,* inhibits cell proliferation and acts on oncoprotein expression.[3] Its synthetic analogues **1b**,**c** display potent antimitotic properties.[4] On the other hand, the effects of soy isoflavones[5] daidzein **2a** and genistein **2b** are associated with a decreased incidence of hormone dependent cancers[6] and have been also implicated in the prevention of cardiovascular diseases,[7] lessening the symptoms of menopause,[8] and protection against osteoporosis.[9] This type of compounds, due to the presence of two *anti*-aryl fragments **A** and **B** is close to resveratrol (Figure 1),[10] a *trans*-stilbene, which is present in grapes and manifests preventive activity against cardiovascular diseases[11] and cancer.[12]

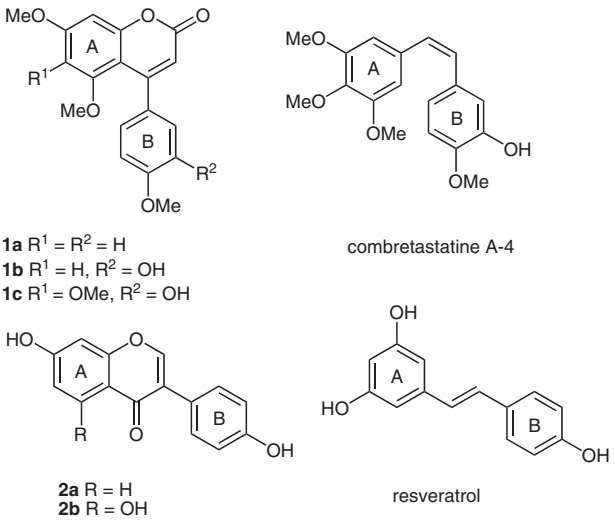

Figure 1 Naturally occurring stilbenes and their structural analogues

Herein, we report the synthesis of several families of flavonoid compounds (Scheme 1) – rigid analogues of resveratrol (compounds **A**, **B**, and **D**) and combretastatin A-4 (molecules **C** and **E**). Derivatives **A**–**D** are stable towards isomerization, in contrast to their stilbene prototypes. Importantly, such easy *cis-trans* isomerization of stilbenes can dramatically influence on the biological activity of combretastatin A-4 and resveratrol molecules.[13]

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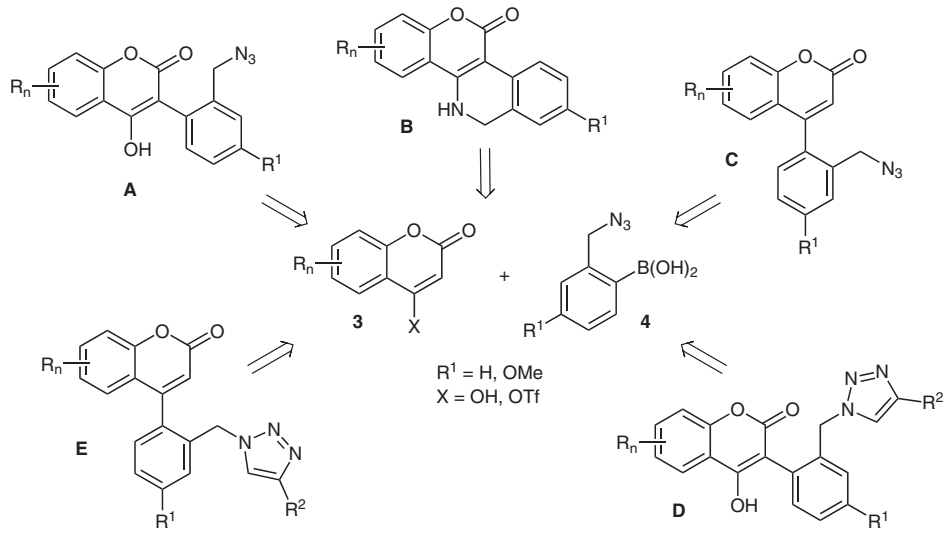


Scheme 1 Synthetic pathways to compounds **A**–**E**

The key step for the synthesis of **A**–**D** derivatives is arylation at positions 3 and 4 of the coumarin skeleton using azide-containing boronic acid **4**. Due to the good tolerance to functional groups, air and moisture stability and low toxicity[14] of boronic acids, the Suzuki–Miyaura reaction has become one of the most useful catalytic approaches to a new C–C bond formation.[15] It can be also used for the synthesis of **C** and **E** types of our neoflavonoid compounds, starting from 4-trifluoromethylsulfonyloxycoumarins (Scheme 1).

Besides cross-coupling reactions, arylboronic acids can be easily transformed into the corresponding aryllead triacetates[16] – efficient C-arylating agents, permitting to activate directly C–H bonds of phenols or enolizable substrates.[17,18] This synthetic methodology can be used as a good alternative to the Suzuki arylation[15] and to the palladium-catalyzed α-arylation of enolizable substrates.[19] It has been applied to the synthesis of a number of naturally occurring molecules.[1b,c,20] We were interested in the application of this procedure to the synthesis of **A**, **B**, and **D** families of the flavonoid compounds.

Arylboronic acids bearing an azido group are very scarcely documented in literature. In a recent precedent, three examples of 2-(azidomethyl-2,3-dihydrobenzo[*b*]furan-7-yl)boronic acid and 5-(2-azidoethyl)-2-methoxyphenylboronic acids were synthesized using halogen–lithium–boron exchange.[21] Preparation of these arylboronic acids was performed via the formation of aryllithium intermediates **5a**,**b**, stabilized by an intramolecular chelation (Figure 2). The lithiation of 2-(azidomethyl)aryl bromide or iodide, necessary for the synthesis of boronic acid **4**, gives nonstabilized aryllithium reagent **5c** (Figure 2). This last reagent is able to attack intramolecularly or intermolecularly another azido group, leading to a complex mixture of nitrogen-containing compounds.[22]

Application of the Knochel's metalation procedure[23] for modification of 2-(azidomethyl)aryl bromide as well as *i*-PrMgCl (or *n*-BuLi)/bis[2-(*N*,*N*-dimethylamino)ethyl]ether complex[24,25] did not afford the desired product **4**. On the other hand, the treatment of 2-(bromomethyl)arylboronic acids **6a**,**b**[26] with NaN_3 in THF–water afforded boronic acids **4a**,**b** in 61 and 63% yield, respectively (Scheme 2), which can exist along with boroxine forms of boronic acids.[27]

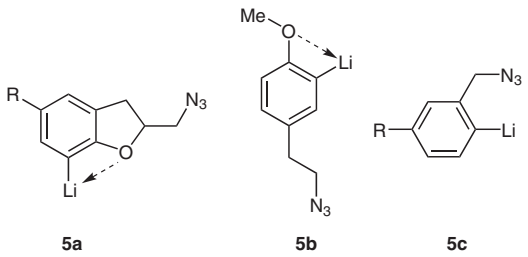
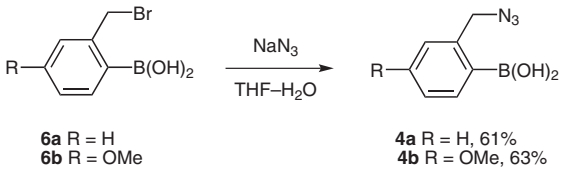


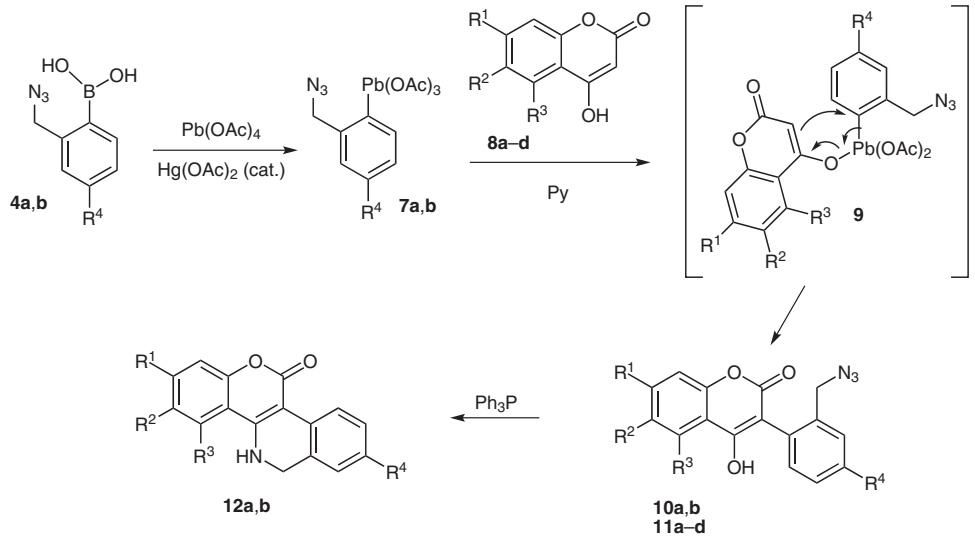
Figure 2 Azide-bearing organolithium intermediates



Scheme 2 Synthesis of 2-(azidomethyl)arylboronic acids **4a**,**b**

The synthesis of type **A** isoflavonoid compounds implies a two-step one-pot reaction sequence (Scheme 3). The transmetalation of arylboronic acids **4a**,**b** with lead triacetate in the presence of a catalytic amount of mercuric acetate according to the Pinhey's procedure[16] afforded the aryllead triacetates **7a**,**b**, which reacted in situ with 4-hydroxycoumarins **8a**–**d** in the presence of pyridine.

This step involves a reductive ligand coupling[28] C-arylation reaction, which has been realized by using aryl derivatives of lead,[17,18] bismuth,[17,29] iodine,[17,30] and some other heteroatoms.[17] Supposedly, this process involves the formation of the covalent intermediate **9**,[18,31] which under-



Scheme 3 Synthesis of isoflavonoids **10a**,**b** and **11a–d** and isoquinolinocoumarins **12a**,**b**

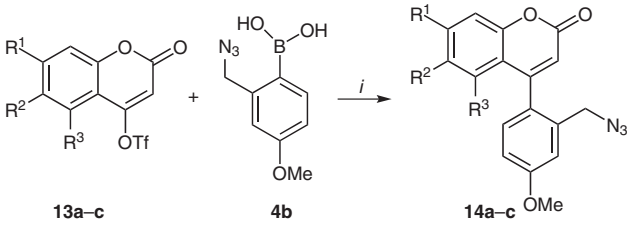
goes a reductive elimination leading to the α-arylation products **10a**,**b** and **11a–d** in 45–68% yields (Table 1). Although organolead-mediated arylation reactions sometimes give mixtures of mono- and polyarylated products,[17,18] only mono-α-arylated products **10a**,**b** and **11a–d** were isolated in all of the presently reported cases. The good yields of the desired isoflavonoid products demonstrate the high efficiency of organolead-mediated arylation reactions for the transfer of aryl fragments bearing a susceptible group in the side chain of the aryl moiety.

Table 1 Isoflavonoids **10a**,**b**, **11a–d**, and Isoquinolinocoumarins **12a**,**b**

Product	R^1	R^2	R^3	R^4	Yield (%)
10a	H	H	H	H	45
10b	OMe	OMe	H	H	51
11a	H	H	H	OMe	68
11b	OMe	OMe	H	OMe	44
11c	OMe	H	OMe	OMe	62
11d	OMe	OMe	OMe	OMe	62
12a	H	H	H	H	21
12b	OMe	OMe	H	H	15

In situ reduction of the azido group of isoflavonoid compounds **10a**,**b** with triphenylphosphine[32] afforded the corresponding isoquinolinocoumarins **12a** and **12b** in 21 and 15% overall yield, respectively (Table 1). The synthesis of these compounds implies four-step one-pot reaction sequence, namely: the preparation of the arylation agent, the ligand coupling stage, Staudinger reaction, aza-Wittig reaction, and finally, isomerization of the imine product into the enamine form.

The regioselectivity of the reactions presented in Scheme 3 and the nature of the resulting products show that the reactive center on the aryl moiety, bonded directly to the boron or to the lead atoms in compounds **4a**,**b** and **7a**,**b**, is more reactive in comparison with the *ortho*-benzylic electrophilic center. This observation prompted us to test the behavior of 2-(azidomethyl)arylboronic acids in the Suzuki–Miyaura reaction[15] in order to obtain azide-containing analogues of naturally occurring 4-arylcoumarin **1a**. The azido function is known to undergo numerous transformations in the presence of transition metal complexes.[32,33] To our delight, the cross-coupling of 4-trifluoromethylsulfonyloxycoumarins **13a–c** with boronic acid **4b** using $Pd(dppf)Cl_2$ (0.05 equiv)/K_3PO_4 (3.0 equiv)/Bu_4NBr (0.1 equiv) catalytic system[34] afforded the neoflavonoid derivatives **14a–c** in good yields (Scheme 4, Table 2). These coupling reactions have to be performed under mild conditions, since above 45 °C decomposition processes, probably involving the azide group, take place leading to a complex mixture of products.

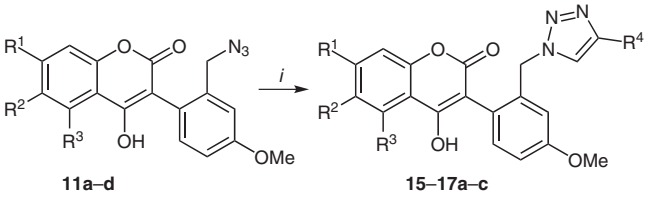


Scheme 4 *Reagents and conditions*: *i*) $Pd(dppf)Cl_2$ (0.05 equiv), K_3PO_4 (3.0 equiv), Bu_4NBr (0.1 equiv), MeCN, 40–45 °C.

Table 2 Neoflavonoids **14**

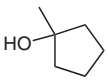
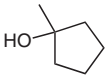
Product	R^1	R^2	R^3	Yield (%)
14a	H	H	H	58
14b	OMe	H	OMe	74
14c	OMe	OMe	OMe	82

Iso- and neoflavonoid compounds **11a–d** and **14a–c** bearing a benzylic azide group smoothly undergo a copper-mediated [3+2] dipolar cycloaddition reactions[35–37] with terminal alkynes in the presence of copper sulfate and sodium ascorbate (AscNa) in THF–water (Schemes 5 and 6). These reactions lead to corresponding triazole compounds **15–20**. In the case of the functionalization of 3-arylcoumarins **11a–d** (Scheme 5, Table 3), the proposed methodology permitted the synthesis of exclusively 1,4-regioisomers **15–17a–c** in good to excellent yields, carrying different substitution patterns in the azole site of the flavonoid molecule.



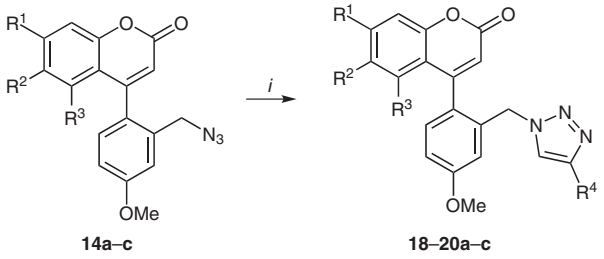
Scheme 5 *Reagents and conditions*: *i*) terminal acetylene (1.5 equiv), $CuSO_4$ (0.07 equiv), AscNa (0.2 equiv), THF–H_2O emulsion (1:1).

Table 3 Triazoles **15–17**

Product	R^1	R^2	R^3	R^4	Yield (%)
15a	H	H	H	Pr	62
15b	H	H	H	Ph	84
15c	H	H	H	OEt	61
16a	OMe	H	OMe	Pr	96
16b	OMe	H	OMe		95
16c	OMe	H	OMe	CH_2OAc	98
17a	OMe	OMe	OMe	Pr	95
17b	OMe	OMe	OMe		48
17c	OMe	OMe	OMe	OEt	97

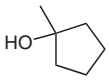
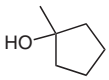
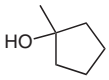
4-[2-(Azidomethyl)aryl]coumarins **14a–c** manifest almost the same reactivity in the Cu(I)-catalyzed alkyne-azide cycloaddition as their isoflavonoid analogues **11a–d**. The 1,4-substituted triazoles **18–20a–c** were obtained regioselectively in good to high yields (Scheme 6, Table 4) independent of the number of methoxy groups in the coumarin substrate and the nature of the substituent in the terminal acetylene.

The scope of the performed copper-mediated reactions led us to consider whether it is possible to accomplish the 'click' transformations using directly 2-(azidomethyl)phenylboronic acids **4a**,**b**. Such cycloaddition procedures can give a simple synthetic way to arylboronic acids bearing 1,4-substituted triazole fragment in the side chain

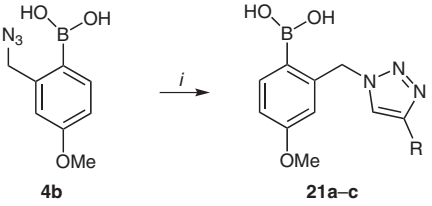


Scheme 6 *Reagents and conditions*: *i*) terminal acetylene (1.5 equiv), $CuSO_4$ (0.07 equiv), AscNa (0.2 equiv), THF–H_2O emulsion (1:1).

Table 4 Triazoles **18–20**

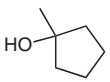
Product	R^1	R^2	R^3	R^4	Yield (%)
18a	H	H	H	CH_2OAc	71
18b	H	H	H		85
18c	H	H	H	Pr	86
19a	OMe	H	OMe	CH_2OAc	91
19b	OMe	H	OMe		47
20a	OMe	OMe	OMe	CH_2OAc	85
20b	OMe	OMe	OMe		73
20c	OMe	OMe	OMe	Pr	49

of the aryl moiety. Indeed, the use of 10 mol% of $CuSO_4$ as a catalyst led to triazole-containing arylboronic acids in good yields, partly in the forms of boroxines[38] (Scheme 7, Table 5).

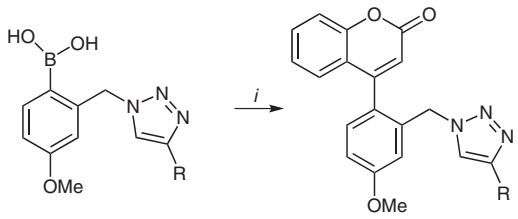


Scheme 7 *Reagents and conditions*: *i*) terminal acetylene (1.5 equiv), $CuSO_4$ (0.01 equiv), AscNa (0.3 equiv), THF–H_2O emulsion (1:1).

Table 5 Triazoles **21** Prepared

	R	Yield (%)
21a	CH_2OAc	73
21b		75
21c	Pr	71

Compounds **21a–c** smoothly react with the coumarin triflate **13a** under palladium catalysis to form the neoflavonoid compounds **18a–c** in 85, 61, and 67% yield, respectively (Scheme 8).



21a–c 18a–c

Scheme 8 *Reagents and conditions*: *i*) **13a** (1.0 equiv), $Pd(dppf)Cl_2$ (0.05 equiv), K_3PO_4 (3.0 equiv), Bu_4NBr (0.1 equiv), MeCN, 80 °C.

In conclusion, new 2-(azidomethyl)arylboronic acids showed to be useful reagents for the lead- or palladium-mediated arylation reactions, as well as for the copper-catalyzed [3+2] cycloadditions. This broad range of transformations, involving application of newly synthesized azido-containing boronic acids permitted to prepare different families of flavonoid compounds in reasonable yields. The presence of an azido group in the vicinity to the boron, lead or palladium heteroatomic center does not interfere with the arylating ability of this type of reagents, useful for the transfer of aryl fragments bearing easily functionalizable groups.

Melting points were recorded with a Büchi capillary apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were obtained with Bruker AC-200P spectrometer. Chemical shifts (δ) are reported in ppm for a solution in $CDCl_3$, with $SiMe_4$ as an internal reference. *J* values are given in Hertz. Separations by column chromatography (CC) were performed using Merck Kieselgel 60 (70–230 mesh). All solvents were purified by standard techniques. 4-Hydroxycoumarins **8a–d** and 4-trifluoromethylsulfonyloxycoumarins **13a–c** were prepared as previously reported.[1b,c,4a,39] All commercially available reagents were obtained from Aldrich and used as received without further purification. Light petroleum (PE) used refers to the fraction boiling in the range 40–70 °C.

2-(Azidomethyl)phenylboronic Acid (4a); Typical Procedure

2-(Bromomethyl)phenylboronic acid (**6a**;[26] 1 g, 4.6 mmol) was dissolved in THF (7 mL) and distilled H_2O (2 mL) was added. After the addition of NaN_3 (0.9 g, 13.8 mmol), the reaction mixture was vigorously stirred at r.t. for 12 h. The resulting mixture was extracted with Et_2O (40 mL) and the organic layer was washed by H_2O (3 × 10 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was recrystallized from CH_2Cl_2–PE (1:1) to give **4a** (0.5 g, 61%) as white crystals; mp 64 °C.

IR (KBr): 2105 cm^{-1} (N_3).

^1H NMR (200 MHz, $CDCl_3$): δ = 4.89 (s, 2 H), 7.31–7.66 (m, 3 H), 8.28 (dd, *J* = 7.1, 1.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.2, 128.2, 129.8, 132.9, 137.5, 142.3.

Anal. Calcd for $C_7H_8BN_3O_2$: C, 47.51; H, 4.56; N, 23.74. Found: C, 47.32; H, 4.84; N, 23.91.

2-(Azidomethyl)-4-methoxyphenylboronic Acid (4b)

Prepared as stated above starting from **6b**;[26] recrystallized from CH_2Cl_2–Et_2O–PE; pale yellow solid (63%); mp 64 °C.

IR (KBr): 2103 cm^{-1} (N_3).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 4.87 (s, 2 H), 6.99–7.05 (m, 2 H), 8.24 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.1, 55.2, 55.3, 56.2, 112.8, 113.0, 115.8, 116.4, 137.9, 139.8, 141.2, 144.6, 161.5, 163.3.

Anal. Calcd for $C_8H_{10}BN_3O_3$: C, 46.42; H, 4.87; N, 20.30. Found: C, 46.28; H, 4.88; N, 20.34.

Compounds 10a,b and 11a–d; 3-(2′-Azidomethylphenyl)-4-hydroxychromen-2-one (10a); Typical Procedure

A solution of boronic acid **4a** (0.107 g, 0.6 mmol) in $CHCl_3$ (2 mL) was added dropwise at 35 °C under an inert atmosphere to a stirred mixture of $Pb(OAc)_4$ (0.266 g, 0.6 mmol) and $Hg(OAc)_2$ (0.019 g, 0.06 mmol) in anhyd $CHCl_3$ (3 mL). The reaction mixture was stirred at 45 °C for 1.5 h and then kept at r.t. for 20 h. The substrate **8a** (0.089 g, 0.55 mmol) and pyridine (1.8 mmol, 3.0 equiv) in anhyd $CHCl_3$ (2 mL) were added. The mixture was stirred at 40 °C for 1 h and then at r.t. for 12 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: Et_2O–PE, 4:1) to afford **10a** (0.073 g, 45%) as colorless crystals; mp 173–174 °C.

IR (Nujol): 2090 (N_3), 3210 cm^{-1} (OH).

^1H NMR (200 MHz, $CDCl_3$): δ = 4.28 (d, *J* = 14.0 Hz, 1 H), 4.38 (d, *J* = 14.0 Hz, 1 H), 7.30–7.63 (m, 7 H), 7.93 (dd, *J* = 7.6, 1.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.9, 104.5, 114.8, 117.0, 123.8, 124.2, 128.5, 129.4, 130.1, 130.2, 131.7, 132.8, 137.0, 153.2, 160.8, 161.7.

Anal. Calcd for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.78; N, 14.33. Found: C, 65.24; H, 3.47; N, 14.16.

3-(2′-Azidomethylphenyl)-4-hydroxy-6,7-dimethoxychromen-2-one (10b)

CC (eluent: Et_2O–PE, 1:1); colorless crystals (51%); mp 176–177 °C.

IR (Nujol): 2095 (N_3), 3205 cm^{-1} (OH).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.93 (s, 3 H), 3.99 (s, 3 H), 4.26 (d, *J* = 14.3 Hz, 1 H), 4.38 (d, *J* = 14.3 Hz, 1 H), 6.83 (s, 1 H), 6.94 (s, 1 H), 7.31–7.50 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.5, 56.6, 67.9, 100.1, 103.4, 108.4, 115.6, 128.1, 128.7, 129.4, 129.8, 130.5, 135.5, 149.4, 154.1, 156.8, 161.4, 166.6.

Anal. Calcd for $C_{18}H_{15}O_5N_3$: C, 61.19; H, 4.28; N, 11.89. Found: C, 60.90; H, 3.97; N, 12.01.

3-(2′-Azidomethyl-4′-methoxyphenyl)-4-hydroxychromen-2-one (11a)

CC (eluent: EtOAc–PE, 1:1); polycrystalline colorless solid (68%); mp 65 °C.

IR (KBr): 2105 (N_3), 3207 cm^{-1} (OH).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.82 (s, 3 H) 4.41 (s, 2 H), 6.89 (dd, *J* = 8.4, 2.6 Hz, 1 H), 7.04 (d, *J* = 2.6 Hz, 1 H), 7.26–7.38 (m, 3 H), 7.48–7.57 (m, 1 H), 7.92 (dd, *J* = 7.8, 1.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.9, 55.4, 104.2, 114.6, 114.8, 115.7, 116.7, 119.9, 123.8, 124.2, 132.7, 132.9, 138.5, 153.2, 160.8, 160.9, 161.9.

Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.29; H, 4.11; N, 12.96.

3-(2′-Azidomethyl-4′-methoxyphenyl)-4-hydroxy-6,7-dimethoxychromen-2-one (11b)
CC (eluent: EtOAc–PE, 2:3); polycrystalline colorless solid (44%); mp 136 °C.

IR (KBr): 2096 (N_3), 3207 cm^{-1} (OH).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 3.96 (s, 3 H), 3.98 (s, 3 H), 4.32 (d, *J* = 4.2 Hz, 2 H), 6.88 (s, 1 H), 6.94 (dd, *J* = 8.2, 2.4 Hz, 1 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 7.25 (d, *J* = 8.2 Hz, 1 H), 7.34 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.9, 55.4, 56.4, 56.4, 99.6, 101.8, 103.9, 107.0, 114.4, 115.5, 120.7, 133.0, 138.5, 141.7, 146.4, 149.2, 153.6, 160.5, 161.3.

Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.26; H, 4.44; N, 10.88.

3-(2′-Azidomethyl-4′-methoxyphenyl)-4-hydroxy-5,7-dimethoxychromen-2-one (11c)
CC (eluent: EtOAc–PE, 1:1); polycrystalline colorless solid (62%); mp 141 °C.

IR (KBr): 2090 (N_3), 3210 cm^{-1} (OH).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 3.89 (s, 3 H), 4.03 (s, 3 H), 4.31 (s, 2 H), 6.40 (d, *J* = 2.2 Hz, 1 H), 6.55 (d, *J* = 2.2 Hz, 1 H), 6.93 (dd, *J* = 8.2, 2.4 Hz, 1 H), 7.03 (d, *J* = 2.8 Hz, 1 H), 7.24 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.9, 55.3, 56.0, 57.0, 94.4, 95.7, 98.6, 100.0, 101.4, 113.8, 114.2, 122.6, 132.8, 136.8, 156.0, 157.1, 159.6, 162.4, 163.4.

Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.38; H, 4.48; N, 10.95.

3-(2′-Azidomethyl-4′-methoxyphenyl)-4-hydroxy-5,6,7-trimethoxychromen-2-one (11d)
CC (eluent: EtOAc–PE, 2:3); polycrystalline colorless solid (62%); mp 136 °C.

IR (KBr): 2098 (N_3), 3209 cm^{-1} (OH).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.89 (s, 3 H), 3.95 (s, 3 H), 4.18 (s, 3 H), 4.31 (s, 2 H), 6.72 (s, 1 H), 6.94 (dd, *J* = 8.4, 2.6 Hz, 1 H), 7.03 (d, *J* = 2.6 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 10.10 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.9, 55.3, 56.5, 61.4, 62.8, 96.9, 100.9, 102.4, 113.8, 114.3, 122.4, 132.7, 136.8, 137.6, 149.1, 150.4, 157.2, 159.7, 162.1, 162.3.

Anal. Calcd for $C_{20}H_{19}N_3O_7$: C, 58.11; H, 4.63; N, 10.16. Found: C, 58.05; H, 4.63; N, 10.12.

5,6-Dihydro-11*H*-[1]benzopyrano[4,3-*c*]isoquinolin-11-one (12a); Typical Procedure
A solution of boronic acid **4a** (0.112 g, 0.63 mmol) in $CHCl_3$ (2 mL) was added dropwise at 45 °C under an inert atmosphere to a stirred mixture of $Pb(OAc)_4$ (0.28 g, 0.63 mmol) and $Hg(OAc)_2$ (0.020 g, 0.063 mmol) in anhyd $CHCl_3$ (3 mL). The reaction mixture was stirred at this temperature for 1.5 h and then at r.t. for 20 h. The substrate **8a** (0.071 g, 0.44 mmol) and pyridine (0.104 g, 1.32 mmol) in anhyd $CHCl_3$ (2 mL) were added and the mixture was stirred at 40 °C for 1 h and at 20 °C for 12 h. Then Ph_3P (0.115 g, 0.44 mmol) was added and the stirring was continued at 40 °C for 12 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent $CHCl_3$-Et_2O–PE, 2:2:1) followed by preparative TLC on silica gel with the same eluent to afford **12a** (0.023 g, 21%) as colorless crystals; mp 138 °C.

IR (Nujol): 3375 cm^{-1} (NH).

^1H NMR (200 MHz, $CDCl_3$): δ = 5.50 (s, 2 H), 7.10 (d, *J* = 7.4 Hz, 1 H), 7.26 (t, *J* = 6.8 Hz, 1 H), 7.35–7.52 (m, 3 H), 7.68 (dt, *J* = 7.4, 1.3 Hz, 1 H), 8.29 (d, *J* = 7.6 Hz, 1 H), 8.83 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 71.7, 98.0, 117.1, 123.6, 123.7, 125.2, 125.4, 125.8, 126.4, 127.0, 129.0, 127.9, 133.1, 152.3, 165.8, 176.0.

Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.23; H, 4.68; N, 5.67.

2,3-Dimethoxy-5,6-dihydro-11*H*-[1]benzopyrano[4,3-*c*]isoquinolin-11-one (12b)
CC (eluent: $CHCl_3$–EtOH, 44:1); colorless crystals (15%); mp 158 °C.

IR (Nujol): 3380 cm^{-1} (NH).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.97 (s, 3 H), 4.00 (s, 3 H), 5.47 (s, 2 H), 6.84 (s, 1 H), 7.09 (d, *J* = 6.1 Hz, 1 H), 7.26 (dt, *J* = 6.5, 1.7 Hz, 1 H), 7.40 (dt, *J* = 6.6, 1.8 Hz, 1 H), 7.64 (s, 1 H), 8.83 (d, *J* = 6.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.3, 56.4, 71.67, 97.4, 99.2, 105.4, 116.8, 123.6, 125.2, 125.9, 126.9, 128.2, 128.9, 147.6, 147.8, 153.8, 165.4, 175.5.

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.81; H, 4.75; N, 4.56.

4-(2′-Azidomethyl-4′-methoxyphenyl)chromen-2-one (14a); Typical Procedure
A mixture of 4-trifluoromethylsylfonyloxycoumarin (**13a**; 0.088 g, 0.30 mmol), arylboronic acid **4b** (0.068 g, 0.33 mmol), 1,1′-bis(diphenylphosphino)ferrocene-palladium(II) dichloride chloroform complex (0.009 g, 0.015 mmol), Bu_4NBr (0.0096 g, 0.03 mmol), and K_3PO_4 (0.127 g, 0.60 mmol) in anhyd MeCN (2–3 mL) was stirred at 45 ° under argon until the substrate was completely consumed (4 h, monitored by TLC). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent EtOAc–PE, 1:5) to afford **14a** (0.053 g, 58%) as viscous colorless oil.

IR (KBr): 2096 cm^{-1} (N_3).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 4.16 (d, *J* = 14.4 Hz, 1 H), 4.25 (d, *J* = 14.4 Hz, 1 H), 6.34 (s, 1 H), 7.01 (dd, *J* = 6.0, 2.6 Hz, 1 H), 7.07–7.11 (m, 2 H), 7.16–7.23 (m, 2 H), 7.40 (dd, *J* = 8.3, 1.7 Hz, 1 H), 7.55 (dt, *J* = 8.4, 1.7 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.3, 55.3, 114.0, 114.9, 116.5, 117.2, 119.8, 124.4, 126.4, 126.4, 126.7, 130.5, 132.2, 134.8, 154.1, 160.4, 160.5.

Anal. Calcd for $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.67. Found: C, 66.60; H, 4.26; N, 13.71.

4-(2′-Azidomethyl-4′-methoxyphenyl)-5,7-dimethoxychromen-2-one (14b)
CC (eluent: EtOAc–PE, 1:4); polycrystalline colorless solid (74%); mp 122 °C.

IR (KBr): 2097 cm^{-1} (N_3).

^1H NMR (200 MHz, $CDCl_3$): δ = 3.40 (s, 3 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 4.15 (s, 2 H), 5.95 (s, 1 H), 6.20 (d, *J* = 2.2 Hz, 1 H), 6.52 (d, *J* = 2.2 Hz, 1 H), 6.88 (dd, *J* = 8.6, 2.4 Hz, 1 H), 6.96 (d, *J* = 2.4 Hz, 1 H), 7.09 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.4, 55.4, 55.8, 55.8, 93.6, 95.6, 103.9, 111.7, 113.0, 113.5, 128.7, 131.6, 133.6, 153.7, 156.9, 158.1, 159.4, 160.6, 163.5.

Anal. Calcd for $C_{19}H_{17}N_3O_5$: C, 62.12; H, 4.66; N, 11.44. Found: C; 61.96, H; 4.64, N, 11.39.

4-(2′-Azidomethyl-4′-methoxyphenyl)-5,6,7-trimethoxychromen-2-one (14c)
CC (eluent: EtOAc–PE, 3:7); colorless oil (82%).

IR (KBr): 2099 cm^{-1} (N_3).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.22 (s, 3 H), 3.77 (s, 3 H), 3.89 (s, 3 H), 3.94 (s, 3 H), 4.14 (d, *J* = 14.4 Hz, 1 H), 4.25 (d, *J* = 14.4 Hz, 1 H), 6.04 (s, 1 H), 6.72 (s, 1 H), 6.89 (dd, *J* = 8.2, 2.4 Hz, 1 H), 6.99 (d, *J* = 2.4 Hz, 1 H), 7.14 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.5, 55.4, 56.3, 60.9, 61.0, 96.4, 107.6, 112.5, 113.6, 114.6, 128.7, 130.7, 134.6, 139.4, 150.8, 151.3, 153.4, 157.0, 159.6, 160.4.

Anal. Calcd for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.57. Found: C, 60.54; H, 4.83; N, 10.61.

Triazoles 15a–c, 16a–c, 17a–c, 18a–c, 19a,b, and 20a–c; 4-Hydroxy-3-{4′-methoxy-2′-[(4″-propyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]phenyl}chromen-2-one (15a) Typical Procedure
Compound **11a** (0.075 g, 0.208 mmol) and pent-1-yne (0.021 g, 0.312 mmol) were dissolved in H_2O–THF mixture (1:1, 1.5 mL). Sodium ascorbate (0.42 mL, 0.042 mmol of freshly prepared 0.1 M aqueous solution) was added to a vigorously stirred mixture, followed by addition of aq 0.1 M $CuSO_4$ (0.15 mL, 0.015 mmol). The resulting mixture was stirred at r.t. until the substrate was completely consumed (TLC monitoring). After removal of the solvent, the product **15a** was isolated using column chromatography on silica gel (eluent: EtOAc–EtOH, 9:1) as polycrystalline colorless solid (0.050 g, 62%); mp 91 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.0 Hz, 3 H), 1.41–1.52 (m, 2 H), 2.40 (t, *J* = 7.4 Hz, 2 H), 3.61 (s, 3 H), 5.16 (d, *J* = 15.6 Hz, 1 H), 5.39 (d, *J* = 15.6 Hz, 1 H), 6.34 (d, *J* = 1.8 Hz, 1 H), 6.78 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.19–7.31 (m, 4 H), 7.52 (t, *J* = 7.8 Hz, 1 H), 7.91 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 22.3, 27.3, 51.8, 55.3, 103.8, 110.1, 113.9, 114.5, 116.3, 116.5, 122.1, 124.0, 124.3, 132.4, 133.1, 137.5, 153.2, 158.0, 160.3, 162.8, 163.0.

Anal. Calcd for $C_{22}H_{21}N_3O_4$: C, 67.51; H, 5.41; N, 10.74. Found: C, 67.21; H, 5.42; N, 10.70.

4-Hydroxy-3-{4′-methoxy-2′-[(4″-phenyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]phenyl}chromen-2-one (15b)
CC (eluent: EtOAc–EtOH, 9:1); polycrystalline colorless solid (84%); mp 144 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.55 (s, 3 H), 5.36 (d, *J* = 15.4 Hz, 1 H), 5.52 (d, *J* = 15.4 Hz, 1 H), 6.37 (d, *J* = 2.2 Hz, 1 H), 6.55 (dd, *J* = 7.1, 2.2 Hz, 1 H), 7.17–7.41 (m, 6 H), 7.49–7.61 (m, 3 H), 7.72 (s, 1 H), 8.00 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 51.9, 55.2, 103.7, 113.6, 114.3, 116.0, 116.5, 121.5, 124.1, 124.2, 125.7, 128.3, 128.7, 129.7, 132.5, 133.1, 137.1, 147.2, 153.2, 160.3, 162.7, 162.9.

Anal. Calcd for $C_{25}H_{19}N_3O_4$: C, 70.58; H, 4.50; N, 9.88. Found: C, 70.69; H, 4.49; N, 9.94.

3-{2′-[(4″-Ethoxy-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}-4-hydroxychromen-2-one (15c)
CC (eluent: EtOAc–EtOH, 9:1); colorless oil (61%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1 Hz, 3 H), 3.72 (s, 3 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 5.20 (d, *J* = 15.0 Hz, 1 H), 5.37 (d, *J* = 15.0 Hz, 1 H), 6.63 (d, *J* = 1.8 Hz, 1 H), 6.91 (dd, *J* = 7.4, 1.8 Hz, 1 H), 7.05 (s, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 7.32–7.38 (m, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.94 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 52.6, 55.3, 66.3, 104.1, 114.5, 114.9, 116.6, 121.6, 124.1, 132.5, 135.2, 137.1, 144.6, 153.1, 160.5, 162.4, 162.8.

Anal. Calcd for $C_{21}H_{19}N_3O_5$ (433.16): C, 64.12; H, 4.87; N, 10.68. Found: C, 64.34; H, 4.90; N, 10.71.

4-Hydroxy-5,7-dimethoxy-3-{4′-methoxy-2′-[(4″-propyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]phenyl}chromen-2-one (16a)
CC (eluent: EtOAc–PE, 7:3); polycrystalline colorless solid (96%); mp 174 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 3 H), 1.56–1.67 (m, 2 H), 2.60 (t, *J* = 7.2 Hz, 2 H), 3.76 (s, 3 H), 3.88 (s, 3 H), 4.03 (s, 3 H), 5.34 (d, *J* = 15.1 Hz, 1 H), 5.52 (d, *J* = 15.1 Hz, 1 H), 6.39 (d, *J* = 1.8 Hz, 1 H), 6.54 (d, *J* = 1.8 Hz, 1 H), 6.72 (d, *J* = 2.4 Hz, 1 H), 6.95 (dd, *J* = 8.6, 2.4 Hz, 1 H), 7.25–7.29 (m, 2 H), 9.59 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 22.6, 27.7, 52.1, 55.3, 56.0, 57.1, 94.4, 98.5, 95.8, 100.9, 114.1, 114.4, 121.0, 122.8, 133.1, 136.1, 148.4, 156.0, 157.1, 159.8, 162.6, 162.7, 163.5.

Anal. Calcd for $C_{24}H_{25}N_3O_6$: C, 63.85; H, 5.58; N, 9.31. Found: C, 64.29; H, 5.59; N, 9.33.

4-Hydroxy-3-(2′-{[4″-(1‴-hydroxycyclopentyl)-1*H*-1″,2″,3″-triazol-1″-yl]methyl}-4′-methoxyphenyl)-5,7-dimethoxychromen-2-one (16b)
CC (eluent: EtOAc); polycrystalline colorless solid (95%); mp 126 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74–2.08 (m, 8 H), 3.80 (s, 3 H), 3.89 (s, 3 H), 4.02 (s, 3 H), 5.37 (d, *J* = 15.1 Hz, 1 H), 5.53 (d, *J* = 15.1 Hz, 1 H), 6.39 (d, *J* = 1.8 Hz, 1 H), 6.53 (d, *J* = 1.8 Hz, 1 H), 6.83 (d, *J* = 2.4 Hz, 1 H), 6.97 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.23 (d, *J* = 8.4 Hz, 1 H), 7.39 (s, 1 H), 9.60 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.5, 23.6, 40.8, 41.0, 52.7, 55.4, 56.0, 57.0, 78.8, 94.4, 95.8, 98.4, 100.7, 114.3, 114.9, 123.1, 133.3, 135.6, 155.9, 157.1, 159.8, 162.6, 162.7, 163.5.

Anal. Calcd for $C_{26}H_{27}N_3O_7$: C, 63.28; H, 5.51; N, 8.51. Found: C, 63.15; H, 5.51; N, 8.50.

3-{2′-[(4″-Acetyloxymethyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}-4-hydroxy-5,7-dimethoxychromen-2-one (16c)
CC (eluent: EtOAc); polycrystalline colorless solid (98%); mp 137 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (s, 3 H), 3.77 (s, 3 H), 3.89 (s, 3 H), 4.04 (s, 3 H), 5.12 (s, 2 H), 5.38 (d, *J* = 14.8 Hz, 1 H), 5.50 (d, *J* = 14.8 Hz, 1 H), 6.40 (d, *J* = 1.8 Hz, 1 H), 6.54 (d, *J* = 1.8 Hz, 1 H), 6.76 (d, *J* = 2.6 Hz, 1 H), 6.96 (dd, *J* = 8.4, 2.6 Hz, 1 H), 7.24 (d, *J* = 8.4 Hz, 1 H), 7.58 (s, 1 H), 9.62 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 52.2, 55.3, 56.0, 57.1, 57.7, 94.4, 95.8, 98.5, 100.8, 114.3, 114.5, 123.0, 123.9, 133.2, 135.7, 156.0, 157.2, 159.8, 162.5, 162.8, 163.6, 170.7.

Anal. Calcd for $C_{24}H_{23}N_3O_8$: C, 59.87; H, 4.82; N, 8.73. Found: C, 59.75; H, 4.80; N, 8.76.

4-Hydroxy-5,6,7-trimethoxy-3-{4′-methoxy-2′-[(4″-propyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]phenyl}chromen-2-one (17a)
CC (eluent: EtOAc–PE, 1:1); polycrystalline colorless solid (95%); mp 152 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.2 Hz, 3 H), 1.48–1.60 (m, 2 H), 2.52 (t, *J* = 7.3 Hz, 2 H), 3.70 (s, 3 H), 3.81 (s, 3 H), 3.88 (s, 3 H), 4.11 (s, 3 H), 5.27 (d, *J* = 14.8 Hz, 1 H), 5.45 (d, *J* = 14.8 Hz, 1 H), 6.63 (s, 1 H), 6.69 (d, *J* = 2.6 Hz, 1 H), 6.89 (dd, *J* = 8.4, 2.6 Hz, 1 H), 7.19 (s, 1 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 10.03 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.6, 27.6, 52.2, 55.3, 56.4, 61.4, 62.9, 96.8, 100.7, 101.7, 114.3, 121.0, 122.7, 133.0, 136.1, 137.5, 148.4, 149.0, 150.3, 157.3, 159.8, 162.3, 162.4.

Anal. Calcd for $C_{25}H_{27}N_3O_7$: C, 62.36; H, 5.65; N, 8.73. Found: C, 62.19; H, 5.67; N, 8.74.

4-Hydroxy-3-(2′-{[4″-(1‴-hydroxycyclopentyl)-1*H*-1″,2″,3″-triazol-1″-yl]methyl}-4′-methoxyphenyl)-5,6,7-trimethoxychromen-2-one (17b)

CC (eluent: EtOAc–EtOH, 9:1); polycrystalline colorless solid (48%); mp 184 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74–2.00 (m, 8 H), 3.80 (s, 3 H), 3.87 (s, 3 H), 3.94 (s, 3 H), 4.18 (s, 3 H), 5.40 (d, *J* = 15.0 Hz, 1 H), 5.50 (d, *J* = 15.0 Hz, 1 H), 6.68 (s, 1 H), 6.85 (d, *J* = 2.7 Hz, 1 H), 6.98 (dd, *J* = 8.4, 2.7 Hz, 1 H), 7.23 (d, *J* = 8.4 Hz, 1 H), 7.39 (s, 1 H), 10.11 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.5, 23.6, 41.0, 41.3, 52.6, 55.4, 56.5, 61.4, 62.9, 78.8, 96.8, 100.7, 101.6, 114.3, 114.9, 119.9, 122.9, 133.3, 135.8, 137.5, 149.0, 150.3, 154.2, 157.3, 159.8, 162.2, 162.4.

Anal. Calcd for $C_{27}H_{29}N_3O_8$: C, 61.94; H, 5.58; N, 8.03. Found: C, 61.89; H, 5.59; N, 8.00.

3-{2′-[(4″-Ethoxy-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}-4-hydroxy-5,6,7-trimethoxychromen-2-one (17c)

CC (eluent: EtOAc); polycrystalline colorless solid (97%); mp 180 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3 H), 3.77 (s, 3 H), 3.87 (s, 3 H), 3.94 (s, 3 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 4.18 (s, 3 H), 5.28 (d, *J* = 15.2 Hz, 1 H), 5.42 (d, *J* = 15.2 Hz, 1 H), 6.69 (d, *J* = 2.7 Hz, 1 H), 6.77 (s, 1 H), 6.93–6.95 (m, 2 H), 7.23 (d, *J* = 8.3 Hz, 1 H), 10.11 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.7, 53.1, 55.3, 56.4, 61.3, 62.9, 66.2, 96.7, 100.7, 101.6, 106.2, 114.3, 122.7, 133.0, 135.8, 137.5, 149.0, 150.3, 157.3, 159.8, 161.0, 162.3, 162.4.

Anal. Calcd for $C_{24}H_{25}N_3O_8$: C, 59.62; H, 5.21; N, 8.69. Found: C, 59.80; H, 5.21; N, 8.66.

4-{2′-[(4″-Acetyloxymethyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}chromen-2-one (18a)

CC (eluent: EtOAc–PE, 7:3); polycrystalline colorless solid (71%); mp 100 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 3.85 (s, 3 H), 5.08 (s, 2 H), 5.29 (d, *J* = 15.2 Hz, 1 H), 5.42 (d, *J* = 15.2 Hz, 1 H), 6.28 (s, 1 H), 6.86 (d, *J* = 2.2 Hz, 1 H), 7.00–7.04 (m, 2 H), 7.16–7.28 (m, 2 H), 7.35–7.42 (m, 2 H), 7.56 (dt, *J* = 7.9, 1.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 51.5, 57.8, 57.3, 114.4, 115.0, 116.5, 117.3, 119.4, 123.8, 124.5, 126.2, 126.4, 130.7, 132.1, 133.7, 143.1, 153.6, 153.7, 160.0, 160.7, 170.8.

Anal. Calcd for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.37. Found: C, 65.02; H, 4.70; N, 10.39.

4-(2′-{[4″-(1‴-Hydroxycyclopentyl)-1*H*-1″,2″,3″-triazol-1″-yl]methyl}-4′-methoxyphenyl)chromen-2-one (18b)

CC (eluent: EtOAc–PE, 7:3); polycrystalline colorless solid (85%); mp 74 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78–1.93 (m, 8 H), 3.85 (s, 3 H), 5.26 (d, *J* = 15.4 Hz, 1 H), 5.38 (d, *J* = 15.4 Hz, 1 H), 6.24 (s, 1 H), 6.89 (d, *J* = 2.0 Hz, 1 H), 7.00–7.04 (m, 2 H), 7.15–7.23 (m, 3 H), 7.40 (d, *J* = 7.8 Hz, 1 H), 7.59 (dt, *J* = 8.5, 1.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.6, 23.7, 41.2, 41.3, 51.6, 55.5, 78.7, 114.4, 115.3, 116.5, 117.4, 119.6, 119.8, 124.5, 126.3, 126.5, 130.7, 132.4, 134.0, 153.7, 153.8, 160.2, 160.7.

Anal. Calcd for $C_{24}H_{23}N_3O_4$: C, 69.05; H, 5.55; N, 10.07. Found: C, 69.21; H, 5.57; N, 10.06.

4-{4′-Methoxy-2′-[(4″-propyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]phenyl}chromen-2-one (18c)

CC (eluent: EtOAc–PE, 3:2); polycrystalline colorless solid (86%); mp 74–76 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3 H), 1.50–1.69 (m, 2 H), 2.58 (t, *J* = 7.4 Hz, 2 H), 3.83 (s, 3 H), 5.24 (d, *J* = 15.6 Hz, 1 H), 5.38 (d, *J* = 15.6 Hz, 1 H), 6.31 (s, 1 H), 6.81 (d, *J* = 2.6 Hz, 1 H), 6.98–7.07 (m, 3 H), 7.16–7.23 (m, 2 H), 7.41 (d, *J* = 7.4 Hz, 1 H), 7.50–7.57 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 22.5, 27.5, 51.3, 55.5, 114.4, 114.6, 116.5, 117.3, 119.6, 120.7, 124.5, 126.0, 126.5, 130.5, 132.4, 134.4, 148.6, 153.7, 153.9, 160.2, 160.7.

Anal. Calcd for $C_{22}H_{21}N_3O_3$: C, 70.38; H, 5.64; N, 11.19. Found: C, 70.55; H, 5.60; N, 11.21.

4-{2′-[(4″-Acetyloxymethyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}-5,7-dimethoxychromen-2-one (19a)

CC (eluent: EtOAc–PE, 7:3); polycrystalline colorless solid (91%); mp 83 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 3.39 (s, 3 H), 3.81 (s, 3 H), 3.87 (s, 3 H), 5.11 (s, 2 H), 5.25 (d, *J* = 15.47 Hz, 1 H), 5.36 (d, *J* = 15.47 Hz, 1 H), 5.90 (s, 1 H), 6.20 (d, *J* = 2.0 Hz, 1 H), 6.52 (d, *J* = 2.0 Hz, 1 H), 6.70 (d, *J* = 2.0 Hz, 1 H), 6.89 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.09 (d, *J* = 8.4 Hz, 1 H), 7.31 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 51.7, 55.4, 55.8, 55.8, 57.5, 93.8, 95.8, 103.7, 113.0, 113.3, 113.6, 128.9, 131.5, 132.7, 153.1, 156.9, 157.9, 159.6, 160.3, 163.8, 170.8.

Anal. Calcd for $C_{24}H_{23}N_3O_7$: C, 61.93; H, 4.98; N, 9.03. Found: C, 61.77; H, 5.00; N, 8.99.

4-(2′-{[4″-(1‴-Hydroxycyclopentyl)-1*H*-1″,2″,3″-triazol-1″-yl]methyl}-4′-methoxyphenyl)-5,7-dimethoxychromen-2-one (19b)

CC (eluent: EtOAc); polycrystalline colorless solid (47%); mp 88 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.76–2.08 (m, 8 H), 3.39 (s, 3 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 5.23 (d, *J* = 15.1 Hz, 1 H), 5.34 (d, *J* = 15.1 Hz, 1 H), 5.85 (s, 1 H), 6.19 (d, *J* = 2.4 Hz, 1 H), 6.52 (d, *J* = 2.4 Hz, 1 H), 6.76 (d, *J* = 2.4 Hz, 1 H), 6.89 (dd, *J* = 8.3, 2.4 Hz, 1 H), 7.07 (d, *J* = 8.4 Hz, 1 H), 7.15 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.5, 23.5, 41.0, 41.1, 51.9, 55.4, 55.8, 55.8, 78.7, 93.8, 95.8, 103.8, 112.9, 113.1, 114.0, 120.0, 128.9, 131.6, 132.9, 153.2, 154.3, 156.9, 157.9, 159.6, 160.5, 163.7.

Anal. Calcd for $C_{26}H_{27}N_3O_6$: C, 65.40; H, 5.70; N, 8.80. Found: C, 65.62; H, 5.72; N, 8.83.

4-{2′-[(4″-Acetyloxymethyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}-5,6,7-trimethoxychromen-2-one (20a)

CC (eluent: EtOAc–PE, 7:3); polycrystalline colorless solid (85%); mp 71–72 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 3.22 (s, 3 H), 3.80 (s, 6 H), 3.94 (s, 3 H), 5.14 (s, 2 H), 5.36 (s, 2 H), 5.95 (s, 1 H), 6.15 (m, 1 H), 6.59–6.79 (m, 2 H), 6.91 (dd, *J* = 8.4, 1.9 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 1 H), 7.43 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 29.7, 51.9, 55.4, 56.3, 57.5, 61.1, 96.7, 107.4, 112.9, 113.7, 114.8, 123.9, 129.0, 130.5, 134.0, 139.6, 150.5, 151.4, 152.8, 157.3, 159.5, 160.0, 170.8.

Anal. Calcd for $C_{25}H_{25}N_3O_8$: C, 60.60; H, 5.09; N, 8.48. Found: C, 60.70; H, 5.08; N, 8.50.

4-(2′-{[4″-(1‴-Hydroxycyclopentyl)-1*H*-1″,2″,3″-triazol-1″-yl]methyl}-4′-methoxyphenyl)-5,6,7-trimethoxychromen-2-one (20b)
CC (eluent: EtOAc); polycrystalline colorless solid (73%); mp 72 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78–2.05 (m, 8 H), 3.24 (s, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 3.95 (s, 3 H), 5.34 (s, 2 H), 5.87 (s, 1 H), 6.70–6.76 (m, 2 H), 6.92 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 7.27 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.5, 23.6, 41.0, 41.1, 52.1, 55.4, 56.3, 61.0, 61.1, 78.8, 96.6, 107.4, 112.8, 114.1, 114.5, 120.1, 128.9, 130.6, 134.2, 139.5, 150.4, 151.3, 152.8, 157.2, 159.8, 160.3.

Anal. Calcd for $C_{27}H_{29}N_3O_7$: C, 63.89; H, 5.76; N, 8.28. Found: C, 63.69; H, 5.77; N, 8.28.

5,6,7-Trimethoxy-4-{4′-methoxy-2′-[(4″-propyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]phenyl}chromen-2-one (20c)
CC (eluent: EtOAc–PE, 7:3); polycrystalline colorless solid (49%); mp 63 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.1 Hz, 3 H), 1.62–1.65 (m, 2 H), 2.62 (t, *J* = 6.9 Hz, 2 H), 3.23 (s, 3 H), 3.78 (s, 3 H), 3.80 (s, 3 H), 3.94 (s, 3 H), 5.26 (d, *J* = 15.5 Hz, 2 H), 5.38 (d, *J* = 15.5 Hz, 2 H), 5.98 (s, 1 H), 6.62 (d, *J* = 2.4 Hz, 1 H), 6.73 (s, 1 H), 6.89 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.10–7.19 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 22.5, 27.6, 51.6, 55.4, 56.3, 61.0, 61.1, 96.6, 107.5, 112.9, 113.2, 114.7, 128.8, 130.3, 134.6, 139.6, 140.8, 150.5, 151.3, 153.0, 157.2, 159.9, 160.2.

Anal. Calcd for $C_{25}H_{27}N_3O_6$: C, 64.50; H, 5.85; N, 9.03. Found: C, 64.62; H, 5.84; N, 9.00.

2-[(4′-Acetyloxymethyl-1*H*-1′,2′,3′-triazol-1′-yl)methyl]-4-methoxyphenylboronic Acid (21a); Typical Procedure
Compound **4b** (0.062 g, 0.3 mmol) and propargyl acetate (0.044 g, 0.45 mmol) were dissolved in H_2O–THF mixture (1:1, 1.5 mL). Sodium ascorbate (1.2 mL, 0.12 mmol of freshly prepared 0.1 M aqueous solution) was added to a virgiously stirred mixture, followed by the addition of aq 0.1 M $CuSO_4$ (0.3 mL, 0.03 mmol). The resulting mixture was stirred at r.t. until the substrate was completely consumed (TLC monitoring). After removal of the solvent, the product **21a** was isolated by recrystallization from PE–$CHCl_3$–Et_2O as polycrystalline colorless solid (0.067 g, 73%); mp 48 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00 (s, 3 H), 3.80 (s, 3 H), 5.05 (s, 2 H), 5.84 (br s, 2 H), 6.8 (br s, 1 H), 6.93 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.70 (br s, 1 H), 7.96 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.7, 53.8, 55.1, 57.1, 113.2, 114.5, 136.8, 138.0, 139.1, 141.3, 161.1, 170.6.

Anal. Calcd for $C_{13}H_{16}BN_3O_5$: C, 51.18; H, 5.29; N, 13.77. Found: C, 51.43; H, 4.91; N, 13.96.

2-{[4′-(1″-Hydroxycyclopentyl)-1*H*-1′,2′,3′-triazol-1′-yl]methyl}-4-methoxyphenylboronic Acid (21b)
Purified by recrystallization from PE–$CHCl_3$–Et_2O; colorless oil (75%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.80–1.86 (m, 8 H), 3.80 (br s, 3 H), 5.79 (br s, 2 H), 6.83 (d, *J* = 2.2 Hz, 1 H), 6.93 (dd, *J* = 8.3, 2.3 Hz, 1 H), 7.54 (s, 1 H), 7.95 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.4, 23.5, 40.7, 40.8, 53.7, 55.2, 78.8, 113.3, 114.7, 121.5, 136.6, 139.3, 153.5, 161.0.

Anal. Calcd for $C_{15}H_{20}BN_3O_4$: C, 56.81; H, 6.36; N, 13.25. Found: C, 56.94; H, 6.36; N, 13.29.

4-Methoxy-2-[(4′-propyl-1*H*-1′,2′,3′-triazol-1′-yl)methyl]phenylboronic Acid (21c)
Purified by recrystallization from PE–$CHCl_3$–Et_2O; colorless oil (71%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3 H), 1.56 (m, 2 H), 2.53 (m, 2 H), 3.80 (s, 3 H), 5.80 (br s, 2 H), 6.78 (d, *J* = 2.0 Hz, 1 H), 6.92 (dd, *J* = 8.2, 2.0 Hz, 1 H), 7.35 (br s, 1 H), 7.98 (d, *J* = 8.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 22.4, 27.6, 53.6, 55.2, 113.3, 114.1, 122.3, 130.1, 136.6, 139.6, 161.0.

Anal. Calcd for $C_{13}H_{18}BN_3O_3$: C, 56.75; H, 6.59; N, 15.27. Found: C, 56.92; H, 6.56; N, 15.32.

Compounds 18a–c Starting from Arylboronic Acids 21a–c; 4-{2′-[(4″-Acetyloxymethyl-1*H*-1″,2″,3″-triazol-1″-yl)methyl]-4′-methoxyphenyl}chromen-2-one (18a); Typical Procedure
A mixture of 4-trifluoromethylsylfonyloxycoumarin (**13a**; 0.035 g, 0.113 mmol), arylboronic acid **21a** (0.038 g, 0.125 mmol), 1,1′-bis(diphenylphosphino)ferrocene-palladium(II) dichloride chloroform complex (0.0034 g, 0.0057 mmol), Bu_4NBr (0.0035 g, 0.011 mmol), and K_3PO_4 (0.0718 g, 0.339 mmol) in anhyd MeCN (2–3 mL) was stirred at 80 °C under argon until the substrate was completely consumed (1.5 h, monitored by TLC). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent EtOAc–PE, 7:3) to afford **18a** (0.039 g, 85%) as polycrystalline colorless solid; mp 100 °C.

18b
CC (eluent EtOAc–PE, 7:3); polycrystalline colorless solid (61%); mp 74 °C.

18c
CC (eluent EtOAc–PE, 2:3); polycrystalline colorless solid (67%); mp 74–76 °C.

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