Tetrahedron 69 (2013) 11164–11168

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Palladium-catalyzed domino protodecarboxylation/oxidative Heck reaction: regioselective arylation of coumarin-3-carboxylic acids

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ARTICLE INFO

Article history:
Received 12 August 2013
Received in revised form 17 October 2013
Accepted 28 October 2013
Available online 1 November 2013

Keywords:
Domino reaction
Neoflavone
Oxidative Heck reaction
Palladium
Protodecarboxylation

ABSTRACT

A protocol for straightforward and step-economical synthesis of neoflavones from coumarin-3-carboxylic acids is developed. This approach enables controlled protodecarboxylation/regioselective C–H arylation of coumain-3-carboxylic acids in one-pot using a monometallic catalytic system. A wide variety of electron-donating and -withdrawing substituents on both coumarins and arylboronic acid are tolerated under the reaction conditions and 4-aryl coumarins are constructed in high yields.

1. Introduction

The regioselective synthesis of arylcoumarins has become increasingly important, because of their presence in a variety of natural products and their diverse pharmacological and biological properties.[1] For instance, neoflavones (4-aryl coumarins) of type **I** show relevant cytotoxic and antitubulin activities (Fig. 1).[2] Also *Calophyllum* coumarins, such as calophyllolide **II** are reported to have anti-coagulant, anti-tuberculosis, anti-inflammatory, and anti-arthritis activities (Fig. 1).[3]

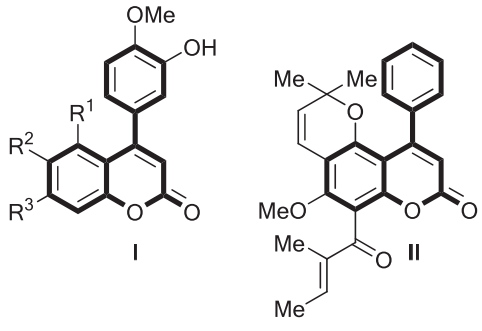

Fig. 1. 4-Aryl coumarins with biological activities.

Among various methods reported for construction of these privileged structural motifs, transition-metal-catalyzed cross-coupling reactions of coumarin frameworks activated at the C-4 position are among the most important.[4] Very recently, we and others have developed more efficient palladium-catalyzed C–H functionalization reactions for direct arylation of coumarins at C-4 via oxidative addition of arylboronic acids and arenes to coumarins.[5] On the other hand, the convenient ring-closure reactions for construction of coumarins[6] leaves behind a surplus carboxylate group at C-3, which should be removed before arylation of coumarins. One might therefore expect that decarboxylative arylation of these scaffolds would find significant utility in organic synthesis. The documented combination of C–H functionalization of aromatic carboxylic acids with a concomitant decarboxylation is limited exclusively to arenes.[7] The direct C–H arylation of *ortho*-substituted heteroarene carboxylic acids with a subsequent removal of the carboxylate group by in situ protodecarboxylation however remains largely unexplored.[8]

In this context, we have demonstrated an efficient palladium-catalyzed arylation of coumarin-3-carboxylic acids with iodoarenes (Scheme 1, Path **a**).[9] In this work, C-3 arylation proceeded regioselectively, and 4-arylated coumarins were not detected. In this paper, we set out to explore C-4 arylation of these heteroarene

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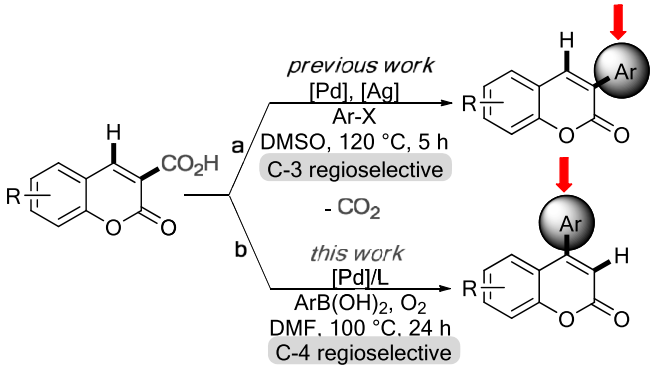
http://dx.doi.org/10.1016/j.tet.2013.10.089

carboxylic acids using arylboronic acids in place of iodoarenes (Scheme 1, Path **b**). This transformation could be achieved by a two-step sequence involving protodecarboxylation of coumarin-3-carboxylic acid[10] and subsequent oxidative cross-coupling with arylboronic acid coupling partners[11] using the same catalytic system. The reaction features attractive synthetic attributes, such as protodecarboxylation/direct arylation in one-pot, regioselective functionalization, tolerance of a wide variety of functional groups and mild reaction conditions without the requisite for addition of Ag salts or acids for protodecarboxylation.

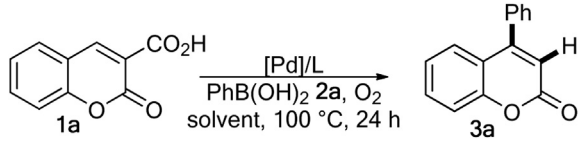


Scheme 1. Regioselectivity in arylation of coumarin-3-carboxylic acids.

2. Results and discussion

We initially focused on the cross-coupling of coumarin **1a** and phenylboronic acid **2a** as test substrates to explore the prospect of the proposed palladium-catalyzed direct arylation reaction. Negligible activity was observed applying our previous reaction conditions for decarboxylative arylation of coumarin-3-carboxylic acids (Table 1, entry 1). Next we examined protodecarboxylation/arylation reaction of coumarin using a catalytic system comprising $PdCl_2$/phen, and gratifyingly 4-phenylcoumarin **3a** was obtained albeit in a 15% yield (entry 2). Using other palladium sources in place of $PdCl_2$, established $Pd(OAc)_2$ as the most effective catalyst for promoting the cross-coupling reaction where, desired 4-phenylcoumarin **3a** was obtained in 80% yield (entries 3–5). Further optimizations, which included screening ligands and the addition of bases, did not give any satisfactory results (entries 6–9). No biaryl product was observed in the absence of the oxidant, and the oxidant's properties were critical to the cross-coupling efficiency, evidenced by the observation that replacing O_2 with $Na_2S_2O_8$ dramatically diminished the yield (entry 10). Finally, a solvent screen was performed; DMF was replaced with solvents, such as 1,4-dioxane, amyl alcohol, *n*-butanol and H_2O, but the desired product was obtained in lower yields (entries 11–13).

Table 1
Screening of the reaction conditions for domino C–H arylation and decarboxylation of **1a**[a]



Entry	Catalyst	Ligand	Base	Solvent	Yield (%)[b]
1	$PdCl_2$	—	Ag_2CO_3	DMF	0
2	$PdCl_2$	Phen	—	DMF	15
3	$Pd(acac)_2$	Phen	—	DMF	30
4	$Pd(PPh_3)_2$	Phen	—	DMF	14
5	**$Pd(OAc)_2$**	**Phen**	—	**DMF**	**80**[c]
6	$Pd(OAc)_2$	Dmphen	—	DMF	Trace
7	$Pd(OAc)_2$	Bpy	—	DMF	30
8	$Pd(OAc)_2$	Phen	Cs_2CO_3	DMF	0
9	$Pd(OAc)_2$	Phen	K_2CO_3	DMF	0
10	$Pd(OAc)_2$	Phen	—	DMF	20[d]
11	$Pd(OAc)_2$	Phen	—	1,4-Dioxane	15
12	$Pd(OAc)_2$	Phen	—	Amyl alcohol	20
13	$Pd(OAc)_2$	Phen	—	H_2O	12

[a] All reactions were run under the following conditions: phenylboronic acid (2 equiv), catalyst (10 mol %), ligand (20 mol %), base (2 equiv), O_2 (balloon pressure) in solvent (0.3 M) were heated in a sealed tube at 100 °C for 24 h.
[b] Isolated yields.
[c] Optimized reaction conditions.
[d] $Na_2S_2O_8$ was used as oxidant.

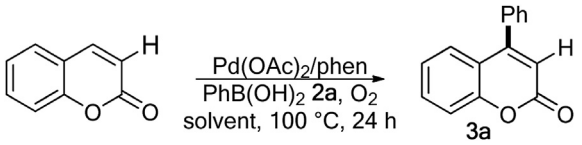
We were pleased to see that under the optimized reaction conditions a tandem protodecarboxylation/C–H arylation reaction occurred, leading to the exclusive formation of C-4 arylated product despite the presence of the carboxylic acid group at the C-3 position. 3-Arylcoumarin was not observed and regioselective efficient C-4 arylation of coumarin was accompanied with CO_2 extrusion/protonation at C-3 in 80% yield. It is also noteworthy that protodecarboxylation was accomplished in the absence of silver salts or catalytic amounts of acids in lower temperature compared with the previous protodecarboxylation reactions.[10]

With the optimized reaction conditions in hand, we next studied the scope and limitations of the protodecarboxylation cross-coupling procedure with various substituted coumarins and arylboronic acids (Table 2). The results showed that various electron-donating and electron-withdrawing substituents including alkyl, halo, methoxy and nitro groups were tolerated under the optimized reaction conditions. To our delight, the C-4 functionalization and protodecarboxylation of coumarins with *p*-fluoro and -bromophenylboronic acids were accomplished in 80% and 65% yields, respectively (**3b** and **3c**). With alkyl substituted boronic acids and coumarins, 4-aryl coumarins **3d–f** were also obtained in high yields. It is noteworthy that coumarins containing relatively labile C–Br bonds were tolerated under the reaction conditions, offering an opportunity for further arylation or alkenylation reactions at C-6 and facilitating synthesis of π-electron extended coumarins. The cross-coupling reaction of 6-bromocoumarin with unsubstituted and *p*-chloro substituted arylboronic acids proceeded successfully, affording the desired products **3h** and **3i** in yields exceeding 70%.

Next it was desirable to extend the scope of this regioselective arylation reaction to construct methoxy neoflavones as the presence of methoxyphenyl moieties in these compounds, increase their potent antileishmanial activity.[1c] In this context, 7-methoxy coumarin was reacted with phenylboronic acid and, gratifyingly, C-4 arylated coumarin **3g** was obtained in high yield. Regioselective C-4 arylation of 6-nitrocoumarins, which is not feasible in direct arylation reactions with simple arenes, were also proceeded smoothly to give desired products **3j–l** in good to high yields. Direct arylation of coumarin with 2,4-difluorophenyl boronic acid, however, was not successful. Further investigations showed that *p*-methoxy substituted boronic acid was also amenable to this arylation reaction and the related product **3n** was obtained in satisfactory yield. 3,5-Dimethylphenylboronic acid and a sterically hindered boronic acid with an *o*-methyl substituent also afforded the desired 4-aryl coumarins **3o** and **3p** in good to moderate yields. We also investigated the reaction scope with electron-deficient boronic acids with a nitro substituent. Unfortunately, the corresponding arylated coumarin **3r** was not observed.

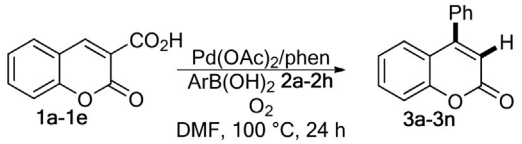
This process is likely to proceed via a tandem protodecarboxylation/arylation, as depicted in Scheme 2. A palladium-catalyzed controlled protodecarboxylation at C-3 is followed by a regioselective oxidative Heck reaction at C-4 (Scheme 2). When coumarin-3-carboxylic acid was submitted to the reaction conditions in the absence of arylboronic acid, protodecarboxylated coumarin was isolated in 46% yield. Also beside the desired 4-aryl

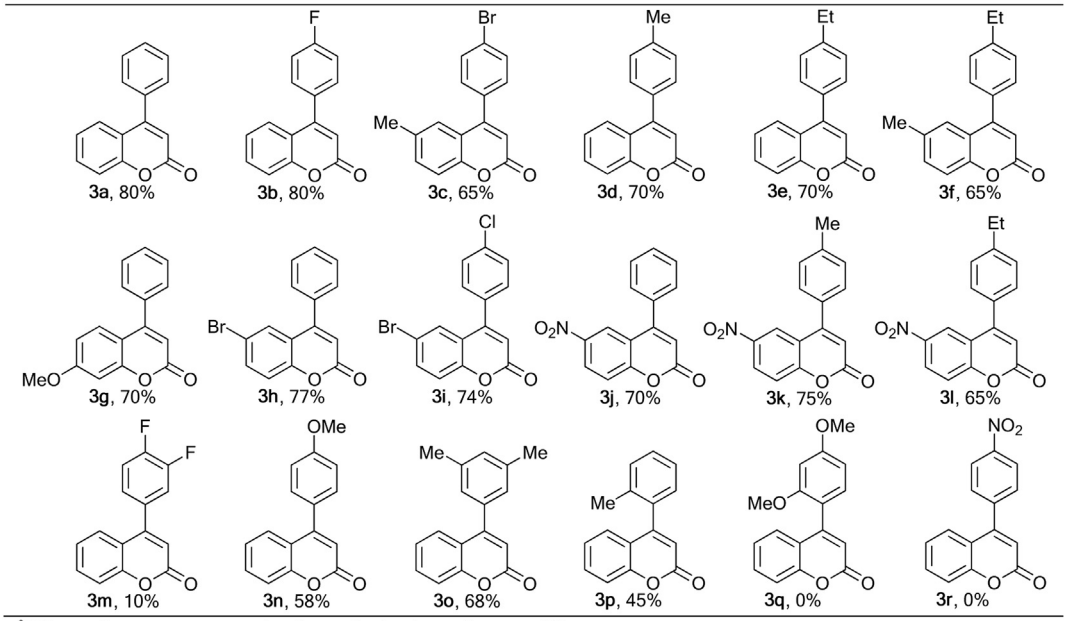
coumarin, coumarin was observed during the reaction. When the reaction of coumarin-3-carboxylic acid **1a** and phenylboronic acid **2a** was interrupted at different time intervals of 4, 8 and 12 h, the protodecarboxylated coumarin was obtained in 24%, 38% and 10% yields, respectively. The results show an initial formation of protodecarboxylated coumarin in the course of reaction, which is then consumed to afford the desired arylated coumarin.



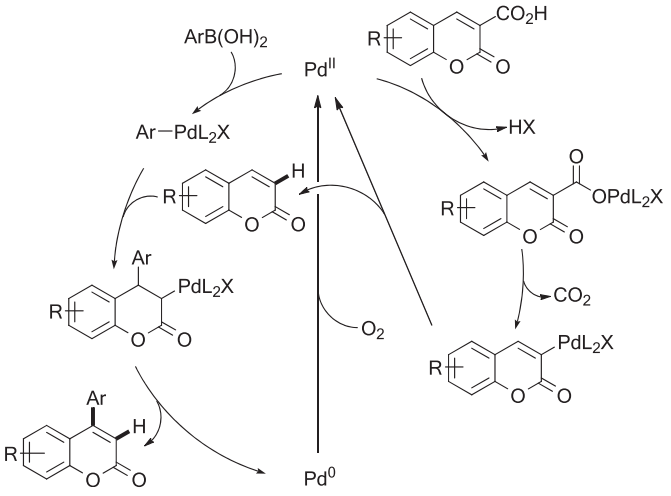
Scheme 3. Direct arylation of coumarin at C-4.

Table 2
Scope of domino protodecarboxylation/oxidative Heck reaction of coumarins[a]





[a]All reactions were run under the optimized reaction conditions



Scheme 2. Plausible reaction mechanism.

Furthermore, the reaction of coumarin and phenylboronic acid under the optimized reaction condition afforded the desired 4-aryl coumarin in 82% isolated yield (Scheme 3).

3. Summary and conclusions

In summary, we have developed a monometallic catalyst for efficient, regioselective and step-economical domino protodecarboxylation/arylation of coumarin-3-carboxylic acids. No base or co-catalyst was required for protodecarboxylation and O_2 was successfully utilized as the sole oxidant for the oxidative Heck coupling. Protodecarboxylation of a wide range of coumarin-3-carboxylic acids regardless of their substitution pattern was proceeded smoothly and followed by direct arylation with a wide range of arylboronic acids. This protocol provided a new route to neoflavone backbones, which are privileged motifs in many biologically active compounds. Expansion of the derived methodology to heterocycles and their subsequent functionalizations are under investigation.

4. Experimental section

4.1. General remarks

Anhydrous solvents were systematically used. DMF and amyl alcohol were distilled under nitrogen from CaH_2 and immediately used or stored under 4 Å molecular sieves. 1,4-Dioxane was refluxed over Na and benzophenone, distilled and stored over 4 Å molecular sieves in the dark. Other reagents, palladium catalysts

and ligands were commercially available and used as received. These reactions were carried out in an oil bath using microwave vials (2–5 mL). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on 500 MHz spectrometers using $CDCl_3$ as the NMR solvent. ^{1}H NMR spectra are referenced to tetramethylsilane and ^{13}C NMR spectra are referenced from the solvent central peak. Chemical shifts are given in parts per million. IR is reported as characteristic bands (cm^{-1}) in their maximal intensity.

4.2. Synthesis of 4-aryl coumarins

*4.2.1. 4-Phenyl-2H-chromen-2-one (**3a**).* A vial equipped with a stir bar was charged with coumarin-3-carboxylic acid (0.1 mmol), phenylboronic acid (0.2 mmol, 2 equiv), $Pd(OAc)_2$ (10 mol %), phenanthroline (20 mol %). DMF (0.3 M) was added and the vial was capped and degassed. The resulting mixture was heated under O_2 (balloon pressure) in an oil bath at 100 °C for 24 h, cooled then filtered through a short plug of silica. Purification of the crude product by flash column chromatography (10% EtOAc/hexane) afforded the corresponding product **3a** as white solid (0.018 g, 80%), mp 79–81 °C (Ref. 4g 74–76 °C); ν_{max} 1765 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.40 (1H, s, =C*H*), 7.26 (1H, t, *J* 7.5 Hz, Ph), 7.42–7.57 (8H, m, Ph); δ_C (125 MHz, $CDCl_3$) 115.1, 117.3, 124.2, 126.9, 128.4, 128.9, 129.7, 130.9, 131.9, 135.2, 154.2, 155.7, 160.8.

*4.2.2. 4-(4-Fluorophenyl)-2H-chromen-2-one (**3b**).* Operation as above with coumarin-3-carboxylic acid (0.1 mmol), (4-fluorophenyl)boronic acid (0.2 mmol, 2 equiv), compound **3b** was obtained as white solid (0.019 g, 80%), mp 154–156 °C (Ref. 12 156–157 °C); ν_{max} 1732 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.38 (1H, s, =C*H*), 7.24–7.27 (4H, m, Ph), 7.42–7.46 (3H, m, Ph), 7.58 (1H, t, *J* 7.3 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 115.6, 116.4, 117.7, 119.2, 124.6, 127.1, 130.6, 130.7, 132.4, 146.7, 154.5, 154.7, 160.9.

*4.2.3. 4-(4-Bromophenyl)-6-methyl-2H-chromen-2-one (**3c**).* Operation as above with 6-methyl-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), (4-bromophenyl)boronic acid (0.2 mmol, 2 equiv), compound **3c** was obtained as white solid (0.020 g, 65%), mp 105–106 °C (Ref. 5a 104–106 °C); ν_{max} 1725 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.35 (3H, s, C*H*$_3$), 6.34 (1H, s, =C*H*), 7.19 (1H, s, Ph), 7.31–7.39 (4H, m, Ph), 7.68 (2H, d, *J* 8.1 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 20.4, 114.8, 116.7, 117.8, 123.5, 125.8, 129.5, 130.6, 132.6, 133.5, 133.7, 151.8, 153.9, 160.2.

*4.2.4. 4-(p-Tolyl)-2H-chromen-2-one (**3d**).* Operation as above with coumarin-3-carboxylic acid (0.1 mmol), *p*-tolylboronic acid (0.2 mmol, 2 equiv), compound **3d** was obtained as white solid (0.017 g, 70%), mp 81–83 °C (Ref. 5a 79–81 °C); ν_{max} 1745 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.46 (3H, s, C*H*$_3$), 6.38 (1H, s, =C*H*), 7.24 (1H, t, *J* 7.8 Hz, Ph), 7.33–7.37 (4H, m, Ph), 7.42 (1H, d, *J* 7.8 Hz, Ph), 7.53–7.57 (2H, m, Ph); δ_C (125 MHz, $CDCl_3$) 21.3, 114.8, 117.3, 119.0, 124.1, 127.0, 128.4, 129.5, 131.8, 132.3, 139.9, 154.2, 155.7, 160.8.

*4.2.5. 4-(4-Ethylphenyl)-2H-chromen-2-one (**3e**).*[5a] Operation as above with coumarin-3-carboxylic acid (0.1 mmol), (4-ethylphenyl) boronic acid (0.2 mmol, 2 equiv), compound **3e** was obtained as an oil (0.018 g, 70%); ν_{max} 1724 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, *J* 7.6 Hz, C*H*$_3$), 2.77 (2H, q, *J* 7.6 Hz, C*H*$_2$), 6.38 (1H, s, =C*H*), 7.24 (1H, dt, *J* 8.4, 1.2 Hz, Ph), 7.35–7.41 (4H, m, Ph), 7.42 (1H, d, *J* 8.4 Hz, Ph), 7.54–7.57 (2H, m, Ph); δ_C (125 MHz, $CDCl_3$) 15.4, 28.7, 114.9, 117.3, 119.0, 124.0, 127.0, 128.3, 128.5, 131.8, 132.5, 146.2, 154.2, 155.7, 160.9.

*4.2.6. 4-(4-Ethylphenyl)-6-methyl-2H-chromen-2-one (**3f**).*[5a] Operation as above with 6-methyl-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), (4-ethylphenyl)boronic acid (0.2 mmol, 2 equiv), compound **3f** was obtained as white solid (0.017 g, 65%), mp 42–44 °C (Ref. 1 41–44 °C); ν_{max} 1737 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.35 (3H, t, *J* 7.5 Hz, CH$_2$–C*H*$_3$), 2.35 (3H, s, C*H*$_3$), 2.77 (2H, q, *J* 7.5 Hz, C*H*$_2$–CH$_3$), 6.35 (1H, s, =C*H*), 7.30–7.31 (2H, d, *J* 8.3 Hz, Ph), 7.35–7.40 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 15.3, 20.9, 28.4, 114.8, 117.0, 118.7, 126.7, 127.3, 128.5, 128.6, 132.7, 133.6, 146.0, 152.3, 155.7, 161.1.

*4.2.7. 7-Methoxy-4-phenyl-2H-chromen-2-one (**3g**).* Operation as above with 7-methoxy-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), phenylboronic acid (0.2 mmol, 2 equiv), compound **3g** was obtained as white solid (0.018 g, 70%), mp 116–118 °C (Ref. 5a 114–116 °C); ν_{max} 1734 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.89 (3H, s, OC*H*$_3$), 6.23 (1H, s, =C*H*), 6.81 (1H, dd, *J* 8.9, 2.4 Hz, Ph), 6.90 (1H, d, *J* 2.4 Hz, Ph), 7.39 (1H, d, *J* 8.9 Hz, Ph), 7.43–7.45 (2H, m, Ph), 7.51–7.53 (3H, m, Ph); δ_C (125 MHz, $CDCl_3$) 55.8, 101.1, 111.8, 112.3, 127.9, 128.3, 128.8, 129.6, 130.9, 132.3, 135.6, 155.8, 161.2, 162.8.

*4.2.8. 6-Bromo-4-phenyl-2H-chromen-2-one (**3h**).* Operation as above with 6-bromo-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), phenylboronic acid (0.2 mmol, 2 equiv), compound **3h** was obtained as white solid (0.023 g, 77%), mp 163–165 °C (Ref. 13 161–163 °C); ν_{max} 1727 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.42 (1H, s, =C*H*), 7.31 (1H, d, *J* 8.5 Hz, Ph), 7.45–7.57 (6H, m, Ph), 7.65 (1H, d, *J* 8.5 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 116.1, 117.1, 119.0, 120.6, 126.8, 128.4, 128.7, 129.1, 130.0, 134.4, 134.8, 153.1, 154.5, 160.1.

*4.2.9. 6-Bromo-4-(4-chlorophenyl)-2H-chromen-2-one (**3i**).* Operation as above with 6-bromo-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), (4-chlorophenyl)boronic acid (0.2 mmol, 2 equiv), compound **3i** was obtained as white solid (0.025 g, 74%), mp 207–209 °C; ν_{max} 1732 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.40 (1H, s, =C*H*), 7.32 (1H, d, *J* 8.7 Hz, Ph), 7.40 (2H, d, *J* 7.5 Hz, Ph), 7.54–7.57 (3H, m, Ph), 7.67 (1H, dd, *J* 8.8, 2.2 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 160.6, 154.6, 153.3, 136.1, 134.7, 130.2, 129.2, 128.5, 126.8, 123.5, 119.2, 117.2, 115.1. $C_{15}H_8BrClO_2$ (335.58): calcd C, 53.69; H, 2.40; found C, 53.97; H, 2.51.

*4.2.10. 6-Nitro-4-phenyl-2H-chromen-2-one (**3j**).* Operation as above with 6-nitro-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), phenylboronic acid (0.2 mmol, 2 equiv), compound **3j** was obtained as white solid (0.019 g, 70%), mp 208–210 °C (Ref. 5a 208–210 °C); ν_{max} 1327, 1511, 1729 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.53 (1H, s, =C*H*), 7.47–7.49 (3H, m, Ph), 7.54–7.56 (2H, m, Ph), 7.60 (1H, dd, *J* 7.2, 2.2 Hz, Ph), 8.42–8.44 (2H, m, Ph); δ_C (125 MHz, $CDCl_3$) 116.7, 118.5, 123.0, 126.7, 128.2, 129.4, 130.5, 133.7, 143.9, 154.6, 157.7, 158.0.

*4.2.11. 6-Nitro-4-(p-tolyl)-2H-chromen-2-one (**3k**).* Operation as above with 6-nitro-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), *p*-tolylboronic acid (0.2 mmol, 2 equiv), compound **3k** was obtained as white solid (0.021 g, 75%), mp 215–217 °C (Ref. 5a 214–216 °C); ν_{max} 1338, 1516, 1731 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.48 (3H, s, C*H*$_3$), 6.50 (1H, s, =C*H*), 7.35–7.40 (4H, m, Ph), 7.53 (1H, d, *J* 8.9 Hz, Ph), 8.42 (1H, dd, *J* 8.9, 2.7 Hz, Ph), 8.47 (1H, d, *J* 2.7 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 21.4, 116.3, 118.4, 119.4, 123.1, 126.6, 128.2, 130.1, 130.8, 140.9, 143.9, 154.7, 157.7, 159.0.

*4.2.12. 4-(4-Ethylphenyl)-6-nitro-2H-chromen-2-one (**3l**).*[5a] Operation as above with 6-nitro-2-oxo-2*H*-chromene-3-carboxylic acid (0.1 mmol), 4-ethylphenylboronic acid (0.2 mmol, 2 equiv), compound **3l** was obtained as an oil (0.019 g, 65%); ν_{max} 1337, 1505, 1730 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.33 (3H, t, *J* 7.6 Hz, C*H*$_3$), 2.80 (2H, q, *J* 7.6 Hz, C*H*$_2$), 6.51 (1H, s, =C*H*), 7.39–7.44 (4H, m, Ph), 7.54 (1H, d, *J* 9.0 Hz, Ph), 8.42 (1H, dd, *J* 9.0, 2.6 Hz, Ph), 8.49 (1H, d, *J* 2.6 Hz, Ph); δ_C (125 MHz, $CDCl_3$) 15.3, 28.7, 116.3, 118.4, 119.4, 123.1, 126.5, 128.3, 128.9, 131.0, 143.9, 147.1, 154.7, 157.7, 159.0.

*4.2.13. 4-(4-Methoxyphenyl)-2H-chromen-2-one (**3n**).* Operation as above with 2*H*-chromene-3-carboxylic acid (0.1 mmol), 4-

methoxyphenylboronic acid (0.2 mmol, 2 equiv), compound **3n** was obtained as white solid (0.015 g, 58%), mp 127–128 °C (Ref. 5b 128–129 °C); δ_H (500 MHz, $CDCl_3$) 3.91 (3H, s, CH_3), 6.36 (1H, s, =C*H*), 7.00–7.09 (2H, m, Ph), 7.22–7.29 (1H, m, Ph), 7.38–7.47 (3H, m, Ph), 7.52–7.61 (2H, m, Ph); δ_C (125 MHz, $CDCl_3$) 55.7, 114.4, 114.8, 117.6, 119.4, 124.3, 127.3, 127.6, 130.2, 132.0, 154.5, 155.5, 161.1, 161.2.

*4.2.14. 4-(3,5-Dimethylphenyl)-2H-chromen-2-one (**3o**).* Operation as above with 2*H*-chromene-3-carboxylic acid (0.1 mmol), (3,5-dimethylphenyl)boronic acid (0.2 mmol, 2 equiv), compound **3o** was obtained as white solid (0.017 g, 68%), mp 136–139 °C (Ref. 5b 138–140 °C); δ_H (500 MHz, $CDCl_3$) 2.39 (6H, s, 2CH_3), 6.33 (1H, s, =C*H*), 7.04–7.05 (2H, m, Ph), 7.14–7.15 (1H, m, Ph), 7.20–7.24 (1H, m, Ph), 7.37 (1H, d, *J* 8.2 Hz, Ph), 7.51–7.55 (2H, m, Ph); δ_C (125 MHz, $CDCl_3$) 21.4, 115.0, 117.3, 119.2, 124.2, 126.2, 127.4, 131.4, 132.0, 135.2, 138.8, 154.3, 156.1, 161.0.

*4.2.15. 4-(o-Tolyl)-2H-chromen-2-one (**3p**).* Operation as above with 2*H*-chromene-3-carboxylic acid (0.1 mmol), *o*-tolylboronic acid (0.2 mmol, 2 equiv), compound **3p** was obtained as white solid (0.011 g, 45%), mp 97–99 °C (Ref. 5b 98–99 °C); δ_H (500 MHz, $CDCl_3$) 2.16 (3H, s, CH_3), 6.31 (1H, s, =C*H*), 7.06–7.08 (1H, m, Ph), 7.16–7.19 (2H, m, Ph), 7.30–7.39 (2H, m, Ph), 7.40–7.42 (2H, m, Ph), 7.51–7.55 (1H, m, Ph); δ_C (125 MHz, $CDCl_3$) 20.0, 115.8, 117.2, 119.5, 124.4, 126.3, 127.2, 128.6, 129.4, 130.7, 132.1, 134.9, 135.4, 154.0, 156.3, 161.0.

Acknowledgements

We gratefully acknowledge the financial support of the Pharmaceutical Science Research Center, Iranian National Elites Foundation (INEF), Iran National Science Foundation (INSF) and the University of Tehran.

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.10.089.

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