JOC The Journal of Organic Chemistry

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Palladium-Catalyzed Oxidative Heck Coupling Reaction for Direct Synthesis of 4-Arylcoumarins Using Coumarins and Arylboronic Acids

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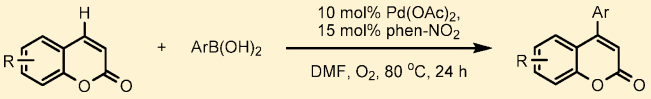
Supporting Information

ABSTRACT: An efficient protocol for the direct synthesis of 4-arylcoumarins via palladium-catalyzed oxidative Heck coupling reaction of coumarins and arylboronic acids was developed. 4-Arylcoumarins were obtained in moderate to excellent yields, and the reaction also showed tolerance toward functional groups such as hydro, methoxy, diethylamino, nitro, and chloro groups.



4-Arylcoumarins (neoflavones) as the family members of flavonoids are widely distributed in natural products such as *Clusiaceae, Fabaceae, Rubiaceae, Rutaceae, Passifloraceae, Asteraceae,* and *Thelypteridaceae.*[1] Besides, they exhibit several important biological activities[1,2] such as antitumor,[3] antimalarial,[4] cytotoxic,[5] antibacterial,[6] anti-inflammatory,[7] anti-HIV,[8] antiprotozoal,[9] antidiabetic,[10] and antivirus properties.[11] Without a doubt, many future pharmaceutical applications will require the development of 4-arylcoumarins to fulfill the increasing demand and practical requirements (Figure 1).

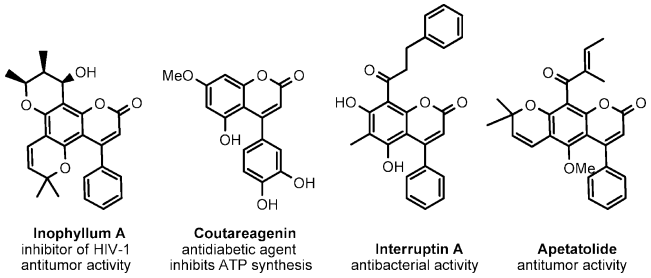
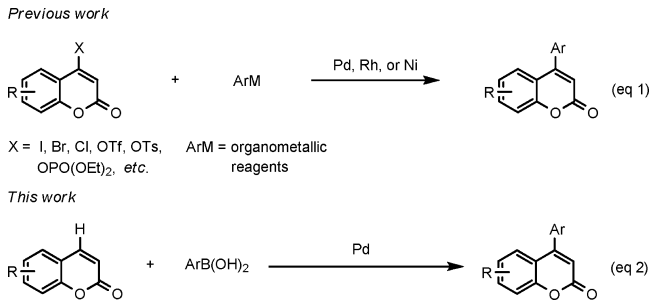


Figure 1. Examples of 4-arylcoumarins medical intermediates.

The general methods for the preparation of 4-arylcoumarins based on the palladium-catalyzed Suzuki-type coupling reaction or Stille coupling reaction using organoboron,[12] organobismuth,[13] organozinc,[14] organoindium,[15] or organotin[16] as organometallic reagents with aryl halogen, triflate, tosylate, phosphonate, or *N,N*-dimethylcarbamate as aryl electrophilic reagents, correspondingly, have been developed recently. Furthermore, rhodium[17] and nickel[18] as catalysts for the Suzuki–Miyaura coupling and Negishi-type coupling to synthesis of 4-arylcoumarins were reported (Scheme 1, eq 1). Other procedures for the synthesis of 4-arylcoumarins involving cyclization reactions such as Pechmann or Perkin reactions have been published as well.[19] However, these routes suffer from poor atom-economic, stoichiometric amounts of mineral or Lewis acids, toxic reagents, and poor yields.[11,12e,15,19d,20]

Scheme 1. Methods for the Preparation of 4-Arylcoumarins



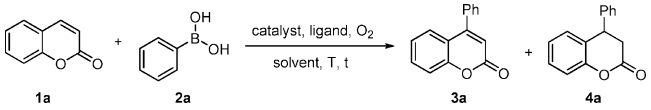
Transition-metal-catalyzed oxidative Heck reaction as a synthetic strategy for C–C bond formation received much attention in the past years.[21] Palladium-catalyzed direct oxidative coupling by the C–H bond activation of coumarins with arylboronic acids is an atom-economic protocol for the preparation of 4-arylcoumarins, and to the best of our knowledge, there is no such work published up to now. Herein, we disclose an efficient, atom-economic route for rapid synthesis of 4-arylcoumarins via palladium-catalyzed direct arylation of 4-unsubstituted coumarins with arylboronic acids (Scheme 1, eq 2).

To establish efficient cross-coupling conditions, coumarin **1a** and phenylboronic acid **2a** were selected as the model to screen the reaction parameters (Table 1). Our initial experiments showed that $Pd(OAc)_2$/phen/O_2/DMF as catalytic system was able to give the coupling product **3a** in 60% GC yield and conjugate addition byproduct **4a** in 5% yield, respectively (Table 1, entry 1). However, no coupling product was detected in the case of $PdCl_2$ as catalyst (Table 1, entry 2). Next, various ligands were investigated in order to find the most efficient one (Table 1, entries 3–12). With bpy as ligand, the yield of **3a** gave rise to 79%; meanwhile, 3% Michael addition byproduct

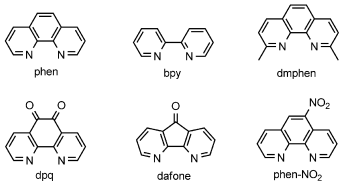
Received: December 17, 2011
Published: January 17, 2012

dx.doi.org/10.1021/jo202577m | J. Org. Chem. 2012, 77, 2053–2057

Table 1. Optimized Conditions for the Synthesis of 4-Phenylcoumarins[a]



entry	ligand	solvent	T (°C)	t (h)	GC yield (%)
1	phen	DMF	60	20	60(5)[c]
2[b]	phen	DMF	60	20	nd
3	bpy	DMF	60	20	79(3)[c]
4	dmphen	DMF	60	20	nd
5	dafone	DMF	60	20	5
6	DMEDA	DMF	60	20	7
7	TMEDA	DMF	60	20	38(19)[c]
8	dppe	DMF	60	20	nd
9	dppp	DMF	60	20	nd
10	dppf	DMF	60	20	nd
11	dpq[d]	DMF	60	20	54(28)[c]
12	phen-NO_2[e]	DMF	60	20	72(<0.2)[c]
13	phen-NO_2	CH_3CN	80	24	nd
14	phen-NO_2	DMSO	60	24	5
15	phen-NO_2	DCE	60	20	11
16	phen-NO_2	DMAc	60	22	46(2)[c]
17	phen-NO_2	NMP	60	22	6
18	phen-NO_2	DMF	80	24	76
19[f]	phen-NO_2	DMF	80	24	99
20[f]	phen-NO_2	DMF	60	24	88
21[f,g]	phen-NO_2	DMF	100	24	61



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (0.02 mmol), ligand (0.03 mmol), and dry solvent (1 mL) under O_2 for desired time. [b]10 mol % $PdCl_2$ as catalyst. [c]Yield of Michael addition product **4a**. [d]1,10-phenanthroline-5,6-quinone. [e]5-nitro-1,10-phenanthroline. [f]3 equiv of $PhB(OH)_2$. [g]5 mol % of $Pd(OAc)_2$.

4a was observed (Table 1, entry 3). However, in the case of dmphen, no coupling product was observed, indicating that ligand's steric hindrance might inhibit the coupling reaction (Table 1, entry 4). Phosphine ligands such as dppe, dppp, and dppf also failed to give the desired products **3a** (Table 1, entries 8–10). On the other hand, *N*,*N*-ligands, such as dafone, DMEDA, TMEDA, and dpq could catalyze reaction to produce **3a** in the yields of 5, 7, 38, and 54%, respectively (Table 1, entries 5–7 and 11). The above results indicated that the ligand had a great effect on the selectivity of coupling products. To our delight, we found that phen-NO_2 was the best choice, which gave slightly lower yield than bpy but with only negligible byproduct **4a** (Table 1, entry 12). The solvent also affected the coupling reaction of coumarin and phenylboronic acid. No product was found with CH_3CN as solvent (Table 1, entry 13), and only poor to moderate yields of products were obtained when other solvents such as DMSO, DCE, DMAc, or NMP were employed (Table 1, entries 14–17). Therefore, DMF is the best solvent. The yield of **3a** enhanced from 72 to 76% when the temperature was increased to 80 °C (Table 1, entry 18). Considering that the phenylboronic acid rapidly underwent protodeborylation, we increased the amount of **2a** to 3 equiv. We were pleased to find that 99% yield of **3a** was obtained at 80 °C for 24 h (Table 1, entry 19). However, the **3a** was observed in 88% yield at 60 °C for 24 h (Table 1, entry 20), and only 61% yield of **3a** was detected in the presence of 5 mol % $Pd(OAc)_2$ catalyst at 100 °C for 24 h (Table 1, entry 21).

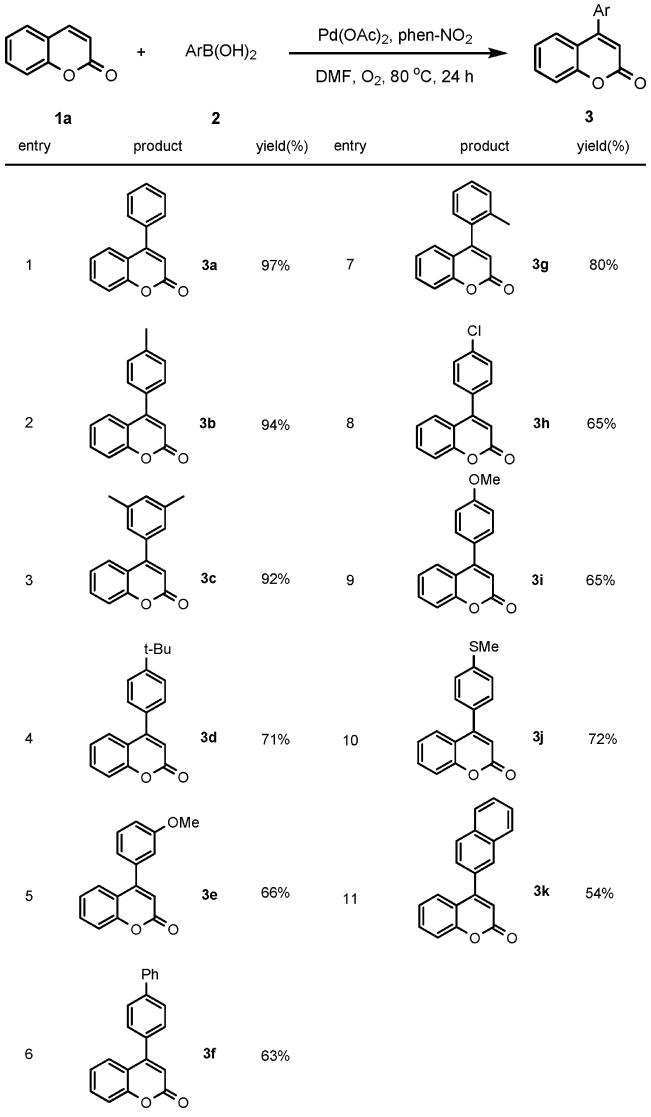
Under the optimized reaction conditions (Table 1, entry 19), we tested a wide range of arylboronic acids **2** to evaluate the group tolerance. As shown in Table 2, this protocol was proven to be efficient for coupling coumarin **1a** with various arylboronic acids bearing electron-donating groups such as methyl, *tert*-butyl, methoxy, and methylthio, and it afforded the corresponding coupling products in good yields. **3g** was generated in 80% yield with 2-methylphenylboronic acid as substrate, indicating that steric hindrance has little effect on the reaction. The weak electron-withdrawing chloro group was also well tolerated and generated **3h** in 65% yield. Furthermore, a large substituent at arylboronic acids **2** affected the selectivity of oxidative Heck and Michael addition products; for example, 4-biphenylboronic acid and 2-naphthylboronic acid gave 4-arylated products **3f** and **3k** in 63 and 54% yield, respectively. In addition, 4-bromophenylboronic acid as a substrate was investigated; the peak area ratio of the Michael addition product to the oxidative Heck product was about 30:70 (see the Supporting Information for more details).

In order to further explore the generality of this procedure, a series of coumarins **1** were investigated under the given conditions (Table 3). These coumarins **1** bearing electron-donating or electron-withdrawing groups were well tolerated and smoothly underwent oxidative Heck reactions to result in variously functionalized 4-arylcoumarins in moderate to excellent yields. For example, corresponding 4-arylated products **3l–m**, **3o–p**, and **3r–s** were formed in fairly good yields when coumarins bearing methyl, methoxy, hydro, and chloro substituents were used. A 42% yield of **3n** was obtained even with electron-poor 6-nitrocoumarin. More importantly, coumarins bearing diethylamino were also able to efficiently transform into their 4-arylated products, which provided a new protocol to synthesize the strong fluorescence compound **3n**.[22]

In conclusion, we have developed an efficient protocol for the synthesis of 4-arylcoumarins via palladium-catalyzed

dx.doi.org/10.1021/jo202577m | J. Org. Chem. 2012, 77, 2053–2057

Table 2. Palladium-Catalyzed Direct 4-Arylation of Coumarin 1a with Different Boronic Acids 2[a]



entry	product	yield(%)	entry	product	yield(%)
1	**3a**	97%	7	**3g**	80%
2	**3b**	94%	8	**3h**	65%
3	**3c**	92%	9	**3i**	65%
4	**3d**	71%	10	**3j**	72%
5	**3e**	66%	11	**3k**	54%
6	**3f**	63%			

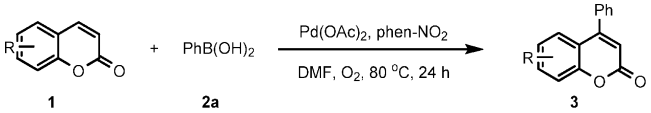
[a]Reaction conditions: coumarin (0.3 mmol), $ArB(OH)_2$ (3 equiv), $Pd(OAc)_2$ (10 mol %), phen-NO_2 (15 mol %), and dry DMF (1.5 mL) at 80 °C under O_2 for 24 h.

oxidative Heck coupling reaction of coumarins and arylboronic acids. The reaction represents a convenient, atom-economic approach with good functional group tolerance.

EXPERIMENTAL SECTION

General Information. All reagents were obtained from commercial sources (>99%) and used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was carried out with silica gel GF 254 precoated plates. Visualization was accomplished with a UV lamp. The reactions were carried out under O_2 atmosphere, and the products were isolated by column chromatography on silica gel (300−400 mesh) using petroleum ether (60−90 °C) and ethyl acetate. All compounds were characterized by ^1H NMR, ^{13}C NMR, and mass spectroscopy. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra in $CDCl_3$ or DMSO-d_6 as solvent were determined. Chemical shifts are reported in ppm with TMS as internal standard. Gas chromatography analyses were performed with an FID detector. GC−MS data were also performed. High resolution mass spectrometry (HRMS) data were performed on Q-TOF MS.

Table 3. Palladium-Catalyzed Direct 4-Arylation of Different Coumarins 1 with Phenylboronic Acid 2a[a]



entry	product	yield(%)	entry	product	yield(%)
1	**3l**	90%	5	**3p**	87%
2	**3m**	87%	6	**3q**	42%
3	**3n**	53%	7	**3r**	86%
4	**3o**	85%	8	**3s**	84%

[a]Reaction conditions: coumarins (0.3 mmol), $PhB(OH)_2$ (3 equiv), $Pd(OAc)_2$ (10 mol %), phen-NO_2 (15 mol %), and dry DMF (1.5 mL) at 80 °C under O_2 for 24 h.

General Procedure for Palladium-Catalyzed Preparation of 4-Arylcoumarins. A dried Schlenk test tube containing a magnetic stirring bar was charged under air with coumarins (0.3 mmol), arylboronic acids (0.9 mmol), $Pd(OAc)_2$ (10 mol %), phen-NO_2 (15 mol %), and dry DMF (1.5 mL). Then, the O_2 was introduced to the tube to form an O_2 balloon. The tube was sealed, and the mixture was treated at 80 °C for 24 h. The resulting mixture was allowed to room temperature and extracted with ethyl acetate three times. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with petroleum/EtOAc (20/1−2/1) to afford the desired product.

4-Phenyl-2*H*-chromen-2-one (3a, CAS No. 15185-05-4).[13] The title compound was prepared according to the general procedure for 4-arylated of coumarin with phenylboronic acid to give a colorless solid, 64.7 mg, 97% yield: mp 97−98 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.39 (m, 8H), 7.24 (dd, J = 13.9, 6.4 Hz, 1H), 6.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 155.8, 154.3, 135.3, 132.1, 129.8, 129.0, 128.6, 127.2, 124.3, 119.1, 117.5, 115.3; GC−MS (EI) m/z = 222 $[M]^+$.

4-(*p*-Tolyl)-2*H*-chromen-2-one (3b, CAS No. 76103-24-7).[19b] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 4-methyl-phenylboronic acid to give a colorless solid, 66.6 mg, 94% yield: mp 106−107 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.49 (m, 2H), 7.40−7.30 (m, 5H), 7.22 (ddd, J = 8.2, 7.5, 1.1 Hz, 1H), 6.34 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 155.7, 154.2, 134.0, 132.3, 131.9, 129.6, 128.4, 127.1, 124.2, 119.1, 117.3, 114.9, 21.4; GC−MS (EI) m/z = 236 $[M]^+$.

4-(3,5-Dimethylphenyl)-2*H*-chromen-2-one (3c, CAS No. 852171-78-9).[18d] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 3,5-dimethylphenylboronic acid to give a colorless solid, 69.1 mg, 92% yield: mp 138−140 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 12.8, 4.6 Hz, 2H), 7.38 (d, J = 8.1 Hz, 1H), 7.25−7.19 (m, 1H), 7.15

dx.doi.org/10.1021/jo202577m | J. Org. Chem. 2012, 77, 2053−2057

(s, 1H), 7.05 (s, 2H), 6.33 (s, 1H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 156.2, 154.2, 138.7, 135.2, 131.9, 131.4, 127.3, 126.3, 124.2, 119.2, 117.3, 115.0, 21.5; GC−MS (EI) m/z = 250 $[M]^+$.

4-(4-*tert*-Butylphenyl)-2*H*-chromen-2-one (3d, CAS No. 852171-80-3).[19a] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 4-*tert*-butylphenylboronic acid to give a colorless solid, 59.3 mg, 71% yield: mp 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.52 (m, 4H), 7.40 (dd, J = 8.3, 1.8 Hz, 3H), 7.26−7.21 (m, 1H), 6.38 (s, 1H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 155.8, 154.3, 153.2, 132.4, 132.0, 128.4, 127.3, 126.0, 124.2, 119.2, 117.4, 115.0, 35.0, 31.4; GC−MS (EI) m/z = 278 $[M]^+$.

4-(3-Methoxyphenyl)-2*H*-chromen-2-one (3e, CAS No. 131575-58-1).[19a] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 3-methoxyphenylboronic acid to give a colorless solid, 49.9 mg, 66% yield: mp 145−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.58 (m, 2H), 7.38−7.46 (m, 2H), 7.26−7.20 (m, 1H), 7.08−7.00 (m, 2H), 6.99−6.95 (m, 1H), 6.38 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 159.9, 155.7, 154.3, 136.6, 132.1, 130.1, 127.2, 124.3, 120.9, 119.1, 117.4, 115.2, 115.2, 114.2, 55.6; GC−MS (EI) m/z = 252 $[M]^+$.

4-(Biphenyl-4-yl)-2*H*-chromen-2-one (3f, CAS No. 864354-17-6).[19a] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 4-biphenylboronic acid to give a white solid, 56.4 mg, 63% yield: mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.72 (m, 2H), 7.66 (dd, J = 5.2, 3.2 Hz, 2H), 7.61−7.45 (m, 6H), 7.43−7.38 (m, 2H), 7.25 (td, J = 7.8, 1.2 Hz, 1H), 6.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 155.5, 154.3, 142.8, 140.1, 134.1, 132.1, 129.1, 129.0, 128.1, 127.7, 127.3, 127.2, 124.4, 119.1, 117.5, 115.2; GC−MS (EI) m/z = 298 $[M]^+$.

4-(*o*-Tolyl)-2*H*-chromen-2-one (3g, CAS No. 852171-79-0).[19b] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 2-methylphenylboronic acid to give a white solid, 56.7 mg, 80% yield: mp 98−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.37−7.44 (m, 2H), 7.37−7.29 (m, 2H), 7.21−7.14 (m, 2H), 7.07 (dd, J = 7.9, 1.6 Hz, 1H), 6.32 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 156.2, 153.9, 135.4, 134.8, 132.1, 130.6, 129.4, 128.5, 127.1, 126.2, 124.4, 119.5, 117.2, 115.8, 19.9; GC−MS (EI) m/z = 236 $[M]^+$.

4-(4-Chlorophenyl)-2*H*-chromen-2-one (3h, CAS No. 1092835-45-4).[19b] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 4-chlorophenylboronic acid to give a colorless solid, 50.1 mg, 65% yield: mp 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.55 (m, 1H), 7.54−7.50 (m, 2H), 7.47−7.38 (m, 4H), 7.28−7.22 (m, 1H), 6.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 154.6, 154.3, 136.1, 133.7, 132.3, 130.0, 129.4, 126.8, 124.5, 118.8, 117.6, 115.5; GC−MS (EI) m/z = 256 $[M]^+$.

4-(4-Methoxyphenyl)-2*H*-chromen-2-one (3i, CAS No. 170456-76-5).[19b] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 4-methoxyphenylboronic acid to give a white solid, 49.2 mg, 65% yield: mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.51 (m, 2H), 7.45−7.37 (m, 3H), 7.28−7.21 (m, 1H), 7.08−7.01 (m, 2H), 6.35 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 161.0, 155.5, 154.4, 132.0, 130.1, 127.6, 127.2, 124.2, 119.3, 117.5, 114.8, 114.5, 55.6; GC−MS (EI) m/z = 252 $[M]^+$.

4-(4-Methylthiophenyl)-2*H*-chromen-2-one (3j). The title compound was prepared according to the general procedure for 4-arylated of coumarin with 4-methylthiophenylboronic acid to give a colorless solid, 58.0 mg, 72% yield: mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.50 (m, 2H), 7.41−7.34 (m, 5H), 7.26−7.20 (m, 1H), 6.34 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 155.2, 154.3, 141.5, 132.0, 131.5, 129.0, 127.0, 126.2, 124.3, 118.9, 117.4, 114.9, 15.4; GC−MS (EI) m/z = 268 $[M]^+$; HRMS (ESI-TOF) calcd. for $C_{16}H_{12}O_2SNa$ $[M + Na]^+$ 291.0456, found 291.0458.

4-(Naphthalene-2-yl)-2*H*-chromen-2-one (3k, CAS No. 76103-22-5).[19b] The title compound was prepared according to the general procedure for 4-arylated of coumarin with 2-naphthaleneylboronic acid to give a colorless solid, 44.1 mg, 54% yield: mp 171−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.5 Hz, 1H), 7.98−7.91 (m, 3H), 7.64−7.53 (m, 5H), 7.47−7.43 (m, 1H), 7.24 (dd, J = 11.7, 4.8 Hz, 1H), 6.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 155.9, 154.4, 133.8, 133.2, 132.8, 132.2, 128.8, 128.6, 128.3, 128.1, 127.5, 127.3, 127.2, 125.9, 124.4, 119.3, 117.6, 115.7; GC−MS (EI) m/z = 272 $[M]^+$.

6,8-Dimethyl-4-phenyl-2*H*-chromen-2-one (3l, CAS No. 859821-52-6).[23] The title compound was prepared according to the general procedure for 4-arylated of 6,8-dimethylcoumarin with phenylboronic acid to give a colorless solid, 67.6 mg, 90% yield: mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 6.4, 3.7 Hz, 3H), 7.39−7.45 (m, 2H), 7.21 (s, 1H), 7.07 (s, 1H), 6.32 (s, 1H), 2.46 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 156.1, 150.7, 135.8, 134.5, 133.3, 129.6, 128.9, 128.5, 126.4, 124.6, 118.5, 114.9, 21.0, 15.8; GC−MS (EI) m/z = 250 $[M]^+$; HRMS (ESI-TOF) calcd. for $C_{17}H_{14}O_2Na$ $[M + Na]^+$ 273.0891, found 273.0886.

6-Methyl-4-phenyl-2*H*-chromen-2-one (3m, CAS No. 16299-22-2).[13] The title compound was prepared according to the general procedure for 4-arylated of 6-methylcoumarin with phenylboronic acid to give a colorless solid, 61.7 mg, 87% yield: mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.50 (m, 3H), 7.44 (dd, J = 6.6, 3.0 Hz, 2H), 7.35 (dd, J = 8.4, 1.6 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.25 (s, 1H), 6.33 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 155.7, 152.4, 135.4, 134.0, 133.0, 129.7, 128.9, 128.5, 126.8, 118.7, 117.1, 115.2, 21.0; GC−MS (EI) m/z = 236 $[M]^+$.

7-(Diethylamino)-4-phenyl-2*H*-chromen-2-one (3n, CAS No. 154869-90-6).[22] The title compound was prepared according to the general procedure for 4-arylated of 7-diethylaminocoumarin with phenylboronic acid to give a melicera orange oil, 46.6 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.40 (m, 5H), 7.29−7.22 (m, 1H), 6.57 (d, J = 2.5 Hz, 1H), 6.52 (dd, J = 9.0, 2.6 Hz, 1H), 6.01 (s, 1H), 3.41 (q, J = 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 156.9, 156.2, 150.7, 136.3, 129.3, 128.7, 128.5, 128.0, 108.6, 108.4, 108.0, 97.9, 44.9, 12.6; GC−MS (EI) m/z = 293 $[M]^+$.

7-Hydro-4-phenyl-2*H*-chromen-2-one (3o, CAS No. 2555-30-8).[19c] The title compound was prepared according to the general procedure for 4-arylated of 7-hydrocoumarin with phenylboronic acid to give a colorless solid, 60.8 mg, 85% yield: mp 210−211 °C; ^{1}H NMR (400 MHz, DMSO) δ 10.70 (br, s, 1H), 7.57 (dt, J = 7.0, 3.9 Hz, 5H), 7.31 (d, J = 8.6 Hz, 1H), 6.84 (d, J = 2.2 Hz, 1H), 6.81 (dd, J = 8.7, 2.1 Hz, 1H), 6.18 (s, 1H); ^{13}C NMR (100 MHz, DMSO) δ 161.4, 160.2, 155.6, 155.4, 135.2, 129.6, 128.8, 128.4, 128.1, 113.2, 110.7, 110.4, 102.7; GC−MS (EI) m/z = 238 $[M]^+$.

6-Chloro-4-phenyl-2*H*-chromen-2-one (3p, CAS No. 26152-84-1).[15] The title compound was prepared according to the general procedure for 4-arylated of 6-chlorocoumarin with phenylboronic acid to give a colorless solid, 67.0 mg, 87% yield: mp 151−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.53 (m, 3H), 7.50 (dd, J = 8.8, 2.4 Hz, 1H), 7.41−7.47 (m, 3H), 7.35 (d, J = 8.8 Hz, 1H), 6.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 154.7, 152.7, 134.6, 132.0, 130.1, 129.8, 129.2, 128.4, 126.5, 120.3, 118.9, 116.3; GC−MS (EI) m/z = 256 $[M]^+$.

6-Nitro-4-phenyl-2*H*-chromen-2-one (3q). The title compound was prepared according to the general procedure for 4-arylated of 6-nitrocoumarin with phenylboronic acid to give a white solid, 33.7 mg, 42% yield: mp 217−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47−8.39 (m, 2H), 7.65−7.57 (m, 3H), 7.55 (d, J = 9.5 Hz, 1H), 7.48 (dd, J = 6.5, 2.9 Hz, 2H), 6.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.9, 154.8, 144.2, 134.0, 130.7, 129.6, 128.4, 126.9, 123.2, 119.5, 118.7, 116.9; GC−MS (EI) m/z = 267 $[M]^+$; HRMS (ESI-TOF) calcd. for $C_{15}H_9NO_4Na$ $[M + Na]$ 290.0429, found 290.0425.

6-Methoxy-4-phenyl-2*H*-chromen-2-one (3r, CAS No. 40547-03-3).[24] The title compound was prepared according to the general procedure for 4-arylated of 6-methoxycoumarin with phenylboronic acid to give a colorless solid, 65.1 mg, 86% yield: mp 148−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.50 (m, 3H), 7.46 (dd, J = 6.6, 2.9 Hz, 2H), 7.34 (d, J = 9.0 Hz, 1H), 7.13 (dd, J = 9.0, 2.9 Hz, 1H), 6.93 (d, J = 2.9 Hz, 1H), 6.38 (s, 1H), 3.74 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 161.1, 156.0, 155.5, 148.7, 135.4, 129.7, 129.1, 128.5, 119.6, 119.1, 118.4, 115.8, 110.1, 55.9; GC–MS (EI) m/z = 252 $[M]^+$.

7-Methoxy-4-phenyl-2*H*-chromen-2-one (3s, CAS No. 2555-31-9).[18c] The title compound was prepared according to the general procedure for 4-arylated of 7-methoxycoumarin with phenylboronic acid to give a white solid, 63.6 mg, 84% yield: mp 106–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.47 (m, 3H), 7.47–7.40 (m, 2H), 7.38 (d, J = 8.9 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 6.79 (dd, J = 8.9, 2.5 Hz, 1H), 6.20 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 161.2, 156.0, 155.9, 135.6, 129.7, 128.9, 128.4, 128.0, 112.5, 112.3, 111.9, 101.2, 55.9; GC–MS (EI) m/z = 252 $[M]^+$.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR, ^{13}C NMR and MS(EI) spectra of all compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC) (Project No. 21176039, 20876021, and 20923006) and the Education Department of Liaoning Province (2009S021).

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