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[Pd(PPh$_3$)$_2$(saccharinate)$_2$]—general catalyst for Suzuki–Miyaura, Negishi cross-coupling and C–H bond functionalization of coumaryl and pyrone substrates

Parin Shah [a], M. Dolores Santana [b], Joaquín García [b], J. Luis Serrano [c], Minal Naik [d], Suhas Pednekar [d], Anant R. Kapdi [a,*]

[a] Institute of Chemical Technology, Matunga, Mumbai 400019, India
[b] Departamento de Química Inorgánica, Universidad de Murcia, 30071 Murcia, Spain
[c] Departamento de Ingeniería Minera, Geológica y Cartográfica, Universidad Politécnica de Cartagena, Área de Química Inorgánica, 30203 Cartagena, Spain
[d] Organic Chemistry Research Laboratory, Ramnarain Ruia College, Matunga, Mumbai 400019, India

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ABSTRACT

The potential of complex [Pd(PPh$_3$)$_2$(saccharinate)$_2$] **1** in catalyzing Suzuki–Miyaura cross-coupling of 4-halo and 4-bromomethyl coumaryl and pyrone substrates with different aryl boronic acids has been explored. Excellent yields of the desired products are obtained in competitive reaction time and under relatively mild conditions. Negishi cross-coupling of 4-coumaryl tosylate with aryl and alkylzinc reagents has also been performed with good yields of the cross-coupled products obtained in most cases. Intramolecular C–H bond functionalization of coumaryl ethers also furnished very high yields of synthetically attractive tetracyclic ring systems exhibiting the potential of **1** as a powerful catalyst in synthetically important reactions.

1. Introduction

Coumarins and 2-pyrones are important scaffolds that occupy a prominent place in the organic synthesis, as they are present in biologically active synthetic molecules and also in a wide variety of naturally occurring compounds.[1] Both synthetic and natural molecules containing the 4-substituted coumarin moiety have exhibited interesting biological and pharmacological properties.[2] This particularly applies for neoflavones (4-aryl coumarines), whose synthesis and isolation[3] have received continuous attention due to their activity anti-HIV, antimalarial, antibiotic, antibacterial, antifungal, or anticoagulant, among others.[4] Several research groups have reported recently on the cross-coupling of these structural moieties with aryl boronic acids.[4,5] Although good yields of the products were obtained, in most cases prolonged reaction time was required. Interestingly, despite its importance in various fields and as structural motifs with potential for further modification, palladium-mediated synthesis of benzyl coumarins has seldom been carried out.[6]

On the other hand, the mild nature of the organozinc reagents (easily accessible and high functional group tolerance) has rendered Negishi cross-coupling[7] as one of the most powerful synthetic tools. Few reports have emerged in the literature for the application of Negishi coupling of 4-tosylcoumarins,[8] and typically suffer from less than satisfactory yields in case of the cross-coupling with either the aryl or alkylzinc reagents.

Common commercial catalysts like Pd(AcO)$_2$, Pd(PPh$_3$)$_4$ and Pd(dppf)Cl$_2$ have usually been employed in both Suzuki and Negishi couplings above mentioned. In this sense, we have systematically investigated in collaboration with Fairlamb and coworkers[9] the potential in cross-coupling reactions of complexes containing imidate ligands, a variety of pseudohalides showing mixed σ-donating and π-accepting properties.[10] Our most recent contribution to this field has focused on the synthesis and characterization of novel monomeric and dimeric palladium(II) complexes with saccharinate as the imidate ligand.[11] A preliminary catalytic study was reported there giving a few examples of Suzuki–Miyaura cross-coupling of aryl and benzyl bromides. This study revealed complex [Pd(PPh$_3$)$_2$(saccharinate)$_2$] **1** as the one of outstanding performance,[11a] and encouraged us to explore in detail its catalytic potential against other substrates. We report here our results in Suzuki–Miyaura cross-coupling of benzyl and coumaryl halides with a variety of aryl boronic acids. Some important results, like the highly regioselective arylation of 4-bromomethyl coumarin or the C–H bond functionalization of coumaryl ethers to furnish synthetically challenging tetracyclic ring systems,[12] that prove the potential of complex **1** are also described. An efficient Neigishi

* Corresponding author. Tel.: +91 22 33612682; fax: +91 22 33611020; e-mail addresses: ar.kapdi@ictmumbai.edu.in, anant.kapdi@gmail.com (A.R. Kapdi).

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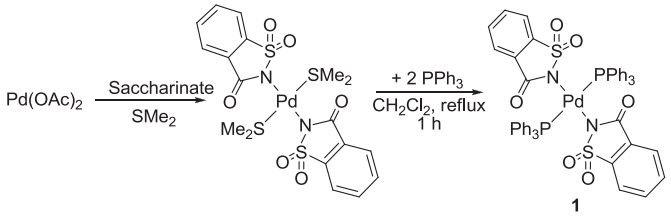
cross-coupling protocol for the synthesis of 4-alkyl or aryl substituted coumarins has also been presented.

2. Results and discussion

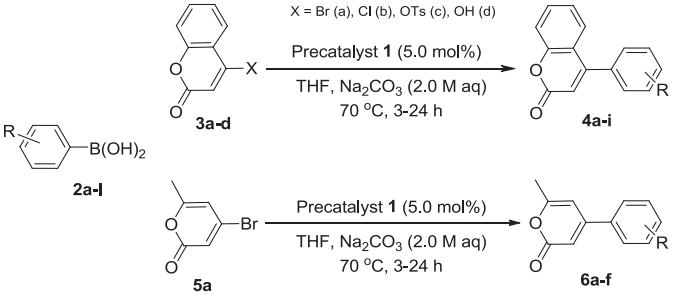
$[Pd(PPh_3)_2(saccharinate)_2]$ **1** was conveniently prepared in dichloromethane as displayed in Scheme 1 and fully characterized by X-ray diffraction analysis (CCDC nos. 817739 and 817740 for the polymorph containing CH_2Cl_2 as a co-crystallising solvent)[11a] and spectroscopic techniques.



Scheme 1. Synthesis of $[Pd(saccharinate)_2(PPh_3)_2]$ **1**.

Motivated by the results obtained with the cross-coupling of (hetero)aryl and benzyl halides with aryl boronic acids we envisaged the complex **1** to catalyze the cross-coupling of synthetically more relevant substrates (see Supplementary data). Accordingly, we became interested in testing this complex for the cross-coupling of substituted 4-halo coumarins and different aryl boronic acids with the view of developing a more efficient and practical procedure towards the synthesis of such structurally diverse molecules (Table 1). Initially, 4-bromocoumarin **3a** was cross-coupled with

Table 1
Suzuki–Miyaura cross-coupling of 4-halo coumarins and pyrones[a]



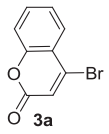
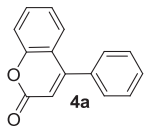
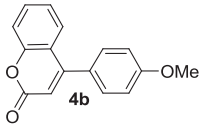
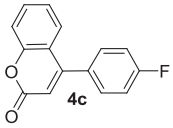
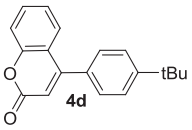
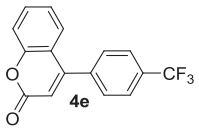
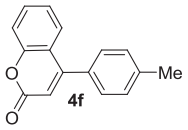
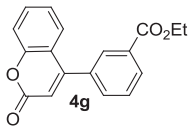
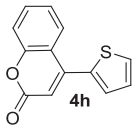
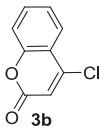
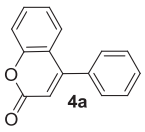
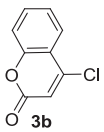
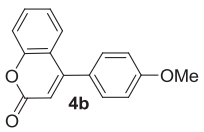
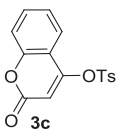
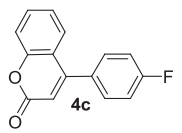
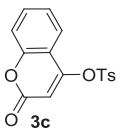
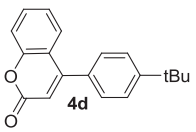
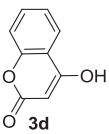
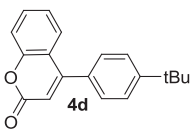
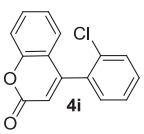
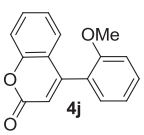
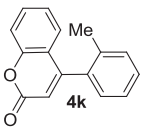
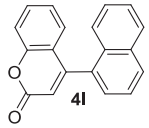
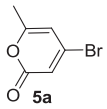
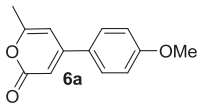
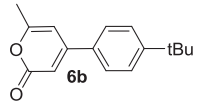
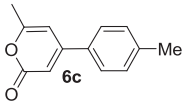
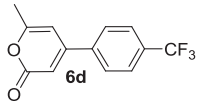
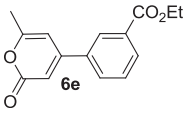
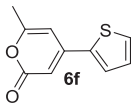
Entry	Reactant	Product	Yield[b] (%)
1			85
2	**3a**		97
3	**3a**		98
4	**3a**		93

Table 1 (*continued*)

Entry	Reactant	Product	Yield[b] (%)
5	**3a**		71
6	**3a**		89
7	**3a**		85
8	**3a**		87
9			93[c]
10			70[c]
11			97[d]
12			92[d]
13			91[e]
14	**3a**		80
15	**3a**		0
16	**3a**		0

(*continued on next page*)

Table 1 (*continued*)

Entry	Reactant	Product	Yield[b] (%)
17	**3a**	 **4l**	75
18	 **5a**	 **6a**	98
19	**5a**	 **6b**	94
20	**5a**	 **6c**	91
21	**5a**	 **6d**	64
22	**5a**	 **6e**	80
23	**5a**	 **6f**	91

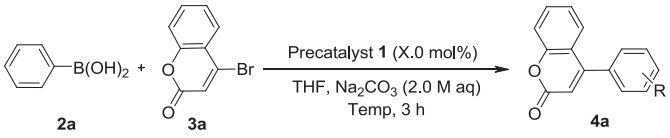
[a] Conditions: 1.0 mmol 4-bromocoumarin **3a** or 4-bromo-6-methyl-2-pyrone **5a**, 1.0 mmol aryl boronic acid, 5.0 mol % **1**, Na_2CO_3 (2.0 M 1.0 mL), THF (2.0 mL) for 3.0 h at 70 °C.
[b] Isolated yields.
[c] 4-Chlorocoumarin **3b** (1.0 mmol) used instead of **3a** (reaction time 24.0 h).
[d] 4-Tosylcoumarin **3c** (1.0 mmol) used instead of **3a** (reaction time 24.0 h).
[e] 4-Hydroxy coumarin **3d** (1.0 mmol), 1.0 mmol TsCl, 24.0 h at 70 °C.

phenyl boronic acid **2b** (Table 1, entry 1) in the presence of the complex **1** (5.0 mol %) at 70 °C to give the coupled product with very good yields in competitive reaction time. Several substituted aryl boronic acids **2a**–**i** (Table 1, entries 1–8) on coupling with 4-bromocoumarin **3a** under the given set of conditions gave 4-arylated coumarins in good to excellent yields. Employment of activated, electron-donating aryl boronic acids such as MeO-, *t*-Bu- and Me-, as well as deactivated, electron-withdrawing aryl boronic acids such as –F, $-CF_3$, CO_2Et showed excellent yields of the cross-coupled products. Heteroaryl boronic acid (2-thiophene boronic acid) when employed gave very good yields of the cross-coupled product (Table 1, entry 8). To improve the scope of the complex **1** synthetically more challenging 4-chloro (**3b**) and 4-tosyl coumarin (**3c**)[13–15] (Table 1, entries 9–12) were cross-coupled with aryl boronic acids. Although, longer reaction time was required to effect the transformation, excellent yields of the desired product were obtained. In situ activation of 4-hydroxy coumarin (**3d**)[16] with tosyl chloride and further cross-coupling with aryl boronic acid resulted in formation of the 4-arylated coumarin in very good yield (Table 1, entry 13). Increase in the bulk at the *ortho*-position by using *ortho*-substituted aryl boronic acids resulted in reduced yields for 2-Cl aryl boronic acid, however 2-Me and 2-MeO (Table 1, entries 14–16) gave no yields of the cross-coupled products **4i**–**k**, respectively. Interestingly, bulky 1-naphthyl boronic acid gave good yields of the cross-coupled product **4l** (Table 1, entry 17).

Synthetically useful 2-pyrone **5a** was also explored as potential electrophilic coupling partner for the Suzuki–Miyaura cross-coupling catalyzed by complex **1** (Table 1, entries 18–23). In most cases excellent yields of the cross-coupled products were obtained irrespective of the type of substituents present on the aryl boronic acid. The effect of catalyst concentration on the catalytic efficiency of palladacyclic complex **1** was next studied. Catalyst loading experiments are performed to determine the overall reactivity of the complex by varying its concentration in the reaction and is generally expressed in terms of its Turn Over Number (TON=mol product/mol catalyst).

Initial studies were carried out at 2.5 mol % catalyst concentration furnishing the cross-coupled product in 80% yield (Table 2, entry 2, TON=32 s^{-1}). At higher concentration of Pd (5.0 mol % Pd, Table 2, entry 1) led to higher yields of the product (85%, TON=17.0 s^{-1}). Lowering of catalyst concentration to 1.0 mol % (Table 2, entry 3, 75%, TON=75 s^{-1}) resulted in slight reduction in the product yield however high TON was observed in this case. Catalyst loading if reduced further led to either poor or no yield of the cross-coupled product suggesting the optimum concentration for high product yield and TON to be 1.0 mol %. Increase in the temperature of the reaction failed to bring about any improvement in the yield of the reaction.

Table 2
Catalyst loading and temperature studies[a]



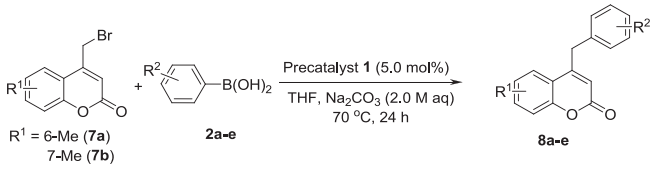
Entry	Complex **2** (mol %)	Temp (°C)	Yield[b] (%)	TON[c] (mol product/mol catalyst) (s^{-1})
1	5.0	70	85	17
2	2.5	70	80	32
3	1.0	70	75	75
4	0.1	70	0	0
5	0.1	90	0	0
6	5.0	40	0	0

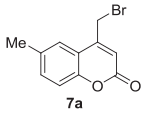
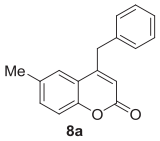
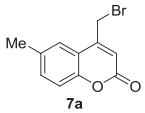
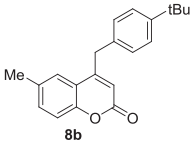
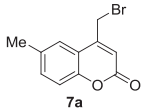
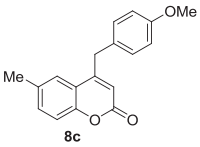
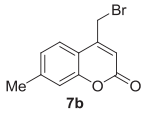
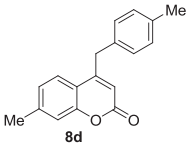
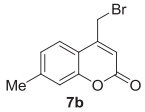
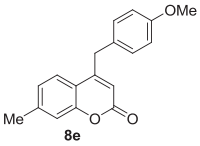
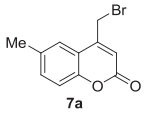
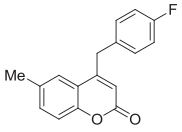
[a] Conditions: 1.0 mmol 4-bromocoumarin **3a**, 1.0 mmol aryl boronic acid, *X*.0 mol % **1**, Na_2CO_3 (2.0 M 1.0 mL), THF (2.0 mL) for 3.0 h.
[b] Isolated yields.
[c] TON=(mol product/mol catalyst) (s^{-1}).

We next turned our attention to the cross-coupling of 4-bromomethyl coumarins with aryl boronic acids. These substrates are expected to show similar reactivity compared to 4-halo coumarins. Accordingly, under the given set of conditions 4-halomethyl coumarins were cross-coupled with aryl boronic acids to obtain differently substituted 4-benzyl coumarins (4-methylcoumarin synthesis is one of the only similar examples for palladium-catalyzed)[17] (Table 3). Initially, the cross-coupling of unactivated phenyl boronic acid with 4-bromomethyl coumarin **7a** resulted in the formation of slightly reduced yield of the coupled products (Table 3, entries 1–3). Similar results were obtained for different electron-donating aryl boronic acids. 4-Bromomethyl coumarin **7b** also showed similar results with different aryl boronic acids (Table 3, entries 4 and 5). However, the use of electron-withdrawing aryl boronic acid failed to furnish the desired cross-coupled product. Studies are on-going to explain such an unusual behaviour (Table 3, entry 6).

In order to explore the reactivity of complex **1** further we turned our attention towards the Negishi cross-coupling of 4-

Table 3
Suzuki–Miyaura cross-coupling of 4-bromomethyl coumarins[a]



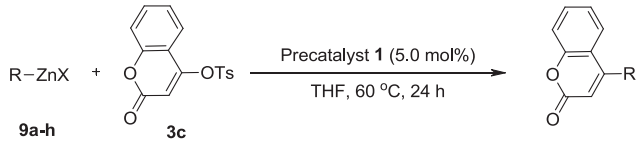
Entry	Reactants	Products	Yield[b] (%)
1			61
2			65
3			62
4			65
5			55
6			0

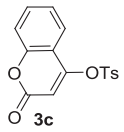
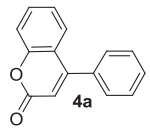
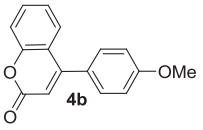
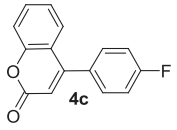
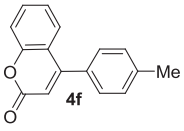
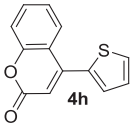
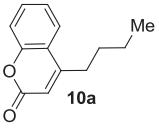
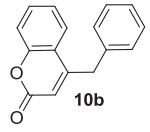
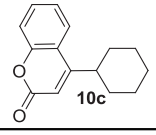
[a] Conditions: 1.0 mmol bromomethyl coumarin, 1.0 mmol aryl boronic acid, 5.0 mol % **1**, Na_2CO_3 (2.0 M 1.0 mL), THF (2.0 mL) for 24.0 h at 70 °C.
[b] Isolated yields.

tosylcoumarin with different alkyl and arylzinc reagents (entries 1–5, Table 4). Under relatively mild conditions good to excellent yields of the cross-coupled products were obtained, suggesting the efficiency of complex **1** to catalyze such transformations. Also to our surprise alkylzinc reagents under the given set of conditions furnished good yields of the coupled products in contrast to the examples reported in the literature[8] (entries 6–8, Table 4).

Furthermore, a complex system (**11a**–**c**) containing coumarin moiety was selected as possible substrate for achieving Suzuki–Miyaura cross-coupling to give arylated products or C–H bond functionalization to furnish synthetically challenging tetracyclic ring systems.[12] The Suzuki–Miyaura cross-coupling of **11a**–**c** was initiated under the same set of conditions used earlier for aryl or benzylic halides with phenyl boronic acid. Surprisingly, complete recovery of starting material was observed suggesting the inability of complex **1** to catalyze the cross-coupling reaction. Slight modification of the protocol, which involves carrying out the reaction under anhydrous conditions with the employment of a milder base

Table 4
Negishi cross-coupling of 4-tosylcoumarin[a]



Entry	Reactant	Product	Yield[b] (%)
1			96
2	**3c**		94
3	**3c**		91
4	**3c**		90
5	**3c**		95
6	**3c**		72
7	**3c**		82
8	**3c**		78

[a] Conditions: 1.0 mmol 4-tosylcoumarin **3c**, 1.5 mmol organozinc reagent, 5.0 mol % **2** THF (2.0 mL) for 24.0 h at 60 °C.
[b] Isolated yields.

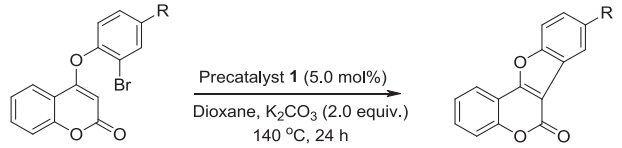
K_2CO_3 resulted in the quantitative formation of a tetracyclic ring product via C–H bond functionalization (Table 5).

Several substituted ethers **11a**–**c** were synthesized and submitted to C–H bond functionalization protocol. The complex **1** showed excellent reactivity against the range of substituted ethers. Electron-releasing substituent –Me (**11b**) showed comparable high reactivity with respect to –Cl (**11c**) (Table 5, entries 2 and 3).

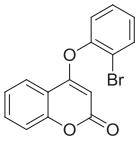
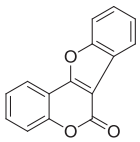
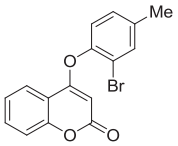
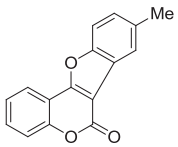
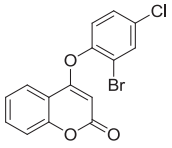
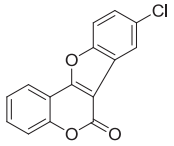
3. Conclusions

In summary, **1** has been shown to be a universal precatalyst for Suzuki–Miyaura cross-coupling of synthetically relevant coumaryl and pyrone halides with aryl and heteroaryl boronic acids. Catalyst

Table 5
Synthesis of coumarin based tetracyclic rings using complex **1**[a]



R = H (**11a**), Me (**11b**), Cl (**11c**) **12a-c**

Entry	Reactant	Product	Yield[b] (%)
1	 **11a**	 **12a**	80
2	 **11b**	 **12b**	83
3	 **11c**	 **12c**	89

[a] Conditions: 1.0 mmol coumaryl ethers **11a–c**, 5.0 mol % **1**, K_2CO_3 (2.0 mmol), 1,4-dioxane (2.0 mL) for 24.0 h at 140 °C.
[b] Isolated yields.

loading experiments were also performed, which allowed the catalyst concentration to be reduced to 1.0 mol % without any appreciable reduction in product yield. Interestingly, cross-coupling of 4-bromomethyl coumarins have exhibited excellent regioselectivity and could have further synthetic potential. Negishi cross-coupling of 4-tosylcourmain with alkyl and arylzinc reagents was also shown to proceed with excellent yields of the cross-coupled products. The complex **1** was also able to catalyze intra-molecular C–H bond functionalization of substrates **11a–c** affording the cyclized products in excellent yields.

4. Experimental section

4.1. General remarks

Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. Aryl bromides and other chemicals were obtained from commercial sources, and were used without further purification. Organozinc reagents were prepared by the reaction of zinc chloride with different Grignard reagents, which were obtained from commercial source. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^1H NMR. Flash chromatography: silica gel 60 (70–230 mesh). NMR data (^1H, ^{31}P) were recorded on Bruker 300 spectrometers. IR spectra were recorded on a Perkin–Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. ESI-MS analyses were performed on an Agilent VL mass-spectrometer. HRMS was carried out on ESI quadrapole mass analyzer. Elemental analysis was performed using a Carlo Erba instrument. General procedure for the synthesis of complexes and Suzuki cross-coupling of aryl and benzyl halides has been provided separately in the Supplementary data section.

4.2. General procedure for Suzuki–Miyaura cross-coupling of 4-halo coumarins

In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-halocoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution aryl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product.

4.3. General procedure for Suzuki–Miyaura cross-coupling of 4-bromomethyl coumarins

In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-bromomethyl coumarins (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution aryl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 24.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product.

4.4. Representative procedure for Negishi cross-coupling of 4-tosylcoumarin with alkyl and arylzinc reagents

To a solution of $ZnCl_2$ (1.60 mL, 1.60 mmol, 1.00 M in THF) was added dropwise *n*-butylmagnesium chloride (0.75 mL, 1.50 mmol, 2.00 M in THF) over 3 min at 0 °C. The solution was stirred at 0 °C for 1 h. In a second dry N_2-flushed Schlenk flask, a solution of **1** (25 mg, 5.0 mol %, 0.05 mmol) and 4-tosylcoumarin **3c** (316 mg, 1.00 mmol) in THF (2.00 mL) was stirred for 5 min at ambient temperature and the organozinc reagent was added. The reaction mixture was then stirred at 60 °C for 24 h. At ambient temperature, H_2O (5.0 mL) was added. The aqueous phase was extracted with EtOAc (2×10 mL). The combined organic phases were concentrated in vacuo. Purification by column chromatography (*n*-hexane/EtOAc: 100:1) yielded **4i** as a colourless liquid.

4.5. General procedure for C–H bond functionalization of substituted 4-(2-bromophenoxy)-coumarin

In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5 mol %) and substituted 4-(2-bromophenoxy)-coumarin (0.5 mmol) were taken in 1,4-dioxane (2 mL). The solutions were degassed (three freeze–pump-thaw cycles) and stirred for 10 min. After this time period, to the solution K_2CO_3 (1.5 mmol) was added and the mixture degassed. The reaction mixture was then refluxed for 24.0 h at 140 °C. The reaction was monitored by TLC. The reaction mixture was evaporated in vacuo. The resultant residue was purified by flash chromatography (silica gel) to afford the desired product.

All the cross-coupled products have been characterized by comparing with those found in the literature. 4-Bromo-2*H*-benzopyran-2-one (**3a**),[18] 4-chloro-2*H*-benzopyran-2-one (**3b**),[19] 4-tosyl-2*H*-benzopyran-2-one (**3c**),[20] 4-phenyl-2*H*-benzopyran-2-one (**4a**),[21] 4-(4-methoxyphenyl)-2*H*-benzopyran-2-one (**4b**),[16] 4-(4-fluorophenyl)coumarin (**4c**),[18] 4-(4-*tert*-butylphenyl)-2*H*-benzopyran-2-one (**4d**),[21] 4-(4-trifluoromethylphenyl)-2*H*-benzopyran-2-one (**4e**),[16] 4-(*p*-tolyl)-2*H*-benzopyran-2-one (**4f**),[21] 4-bromo-6-methyl-2-pyranone (**5a**),[5k] 4-(4-methoxyphenyl)-6-

methyl-2-pyranone (**6a**),[4k] 4-(4-*tert*-butylphenyl)-6-methyl-2-pyranone (**6b**),[22] 4-(4-methylphenyl)-6-methyl-2-pyranone (**6c**),[4k] 4-(4-trifluoromethylphenyl)-6-methyl-2-pyranone (**6d**),[4k] 4-(2-thiophene)-6-methyl-2-pyranone (**6f**),[23] 4-bromomethyl-6-methyl coumarin (**7a**),[24] 4-bromomethyl-7-methyl coumarin (**7b**),[24] 4-butylcoumarin (**10a**),[25] 4-(phenylmethyl)coumarin (**10b**),[8b] 4-cyclohexylcoumarin (**10c**),[8b] 4-(2-bromophenoxy)-coumarin (**11a**),[12a] benzofuro[3,2-*c*]coumarin (Comestan) (**12a**),[12] 4-methyl-benzofuro[3,2-*c*]coumarin (**12b**),[12b] 4-chloro-benzofuro[3,2-*c*] coumarin (**12c**),[12b] 4-(2-chlorophenyl)coumarin (**4i**),[16] 4-(1-naphthyl)coumarin (**4l**).[26]

Characterization of novel compounds synthesized during the course of this study is provided below.

4.5.1. 4-(3-Ethoxycarbonylphenyl)-2H-benzopyran-2-one ***4g***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %), 4-bromocoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 3-ethoxycarbonylphenyl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as a colourless solid. R_f 0.34 (E.A 10%/PE 90%); 249 mg, 85%. Mp 123–124 °C; IR (KBr, cm^{-1}): 3054, 1726, 1702, 1608, 1302, 1166, 1030, 747; ^{1}H NMR (300 MHz, DMSO-d_6) δ=8.12–8.16 (m, 1H, Ar–H), 8.05 (s, 1H, Ar–H), 7.43–7.54 (m, 2H, Ar–H), 7.31–7.38 (m, 2H, Ar–H), 7.15–7.26 (m, 2H, Ar–H), 6.34 (s, 1H, CH), 4.32 (q, J=7.4 Hz, 2H, OCH_2), 1.34 (t, J=7.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=165.9 (C_q), 160.6 (C_q), 154.8 (C_q), 154.2 (C_q), 135.4 (C_q), 132.6 (CH), 132.2 (CH), 131.3 (C_q), 130.7 (CH), 129.5 (CH), 129.4 (CH), 126.7 (CH), 124.4 (CH), 118.8 (C_q), 117.5 (CH), 115.6 (CH), 61.5 (OCH_2), 14.3 (CH_3). MS (ESI) m/z (relative intensity) 295 (100, M+H$^+$); HRMS (ESI, quadrapole): m/z calcd for $C_{18}H_{14}O_4$+H$^+$ 295.0970; found 295.0968. Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.45; H, 4.80%.

4.5.2. 2-(4-Coumarin)thiophene ***4h***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %), 4-bromocoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 2-thiophene boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as a pale yellow solid. R_f 0.43 (E.A 10%/PE 90%); 198 mg, 87%. Mp 84–85 °C. IR (KBr, cm^{-1}): 3084, 2954, 1730, 1603, 1302, 1427, 1369, 1182, 1050, 937, 749; ^{1}H NMR (300 MHz, DMSO-d_6): 7.98–8.03 (m, 2H, Ar–H), 7.31–7.79 (m, 5H, Ar–H), 6.63 (s, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6): 159.7 (C_q), 153.6 (C_q), 147.1 (C_q), 134.9 (C_q), 132.5 (CH), 130.3 (CH), 129.8 (CH), 128.5 (CH), 126.4 (CH), 124.6 (CH), 117.5 (C_q), 117.1 (CH), 114.3 (CH); MS (ESI) m/z (relative intensity) 229 (100, M+H$^+$); HRMS (ESI, quadrapole): m/z calcd for $C_{13}H_8O_2S$ 228.0245; found 228.0244. Anal. Calcd for $C_{13}H_8O_2S$: C, 68.40; H, 3.53; S, 14.05. Found: C, 68.41; H, 3.54; S, 14.05%.

4.5.3. 4-(3-Ethoxycarbonylphenyl)-6-methyl-2-pyranone ***6e***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %), 4-bromo-6-methyl-2-pyranone (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 3-ethoxycarbonylphenyl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as a colourless solid. R_f 0.36 (E.A 10%/PE 90%). Mp 148–150 °C; IR (KBr, cm^{-1}): 3048, 1731, 1706, 1621, 1304, 1173, 1050, 747; ^{1}H NMR (300 MHz, DMSO-d_6) δ=8.25 (s, 1H, Ar–H), 8.05–8.14 (m, 1H, Ar–H), 7.67–7.73 (m, 1H, Ar–H), 7.43–7.48 (m, 1H, Ar–H), 6.75 (s, 1H, CH), 6.64 (s, 1H, CH), 4.32 (q, J=7.5 Hz, 2H, OCH_2), 2.34 (s, 3H, CH_3), 1.34 (t, J=7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=165.1 (C_q), 162.7 (C_q), 162.1 (C_q), 153.6 (C_q), 135.5 (C_q), 131.5 (CH), 131.0 (CH), 130.8 (CH), 129.7 (CH), 127.1 (CH), 107.7 (CH), 102.7 (CH), 61.0 (OCH_2), 19.5 (CH_3), 14.1 (CH_3); MS (ESI) m/z (relative intensity) 259 (100, M+H$^+$); HRMS (ESI, quadrapole): m/z calcd for $C_{15}H_{15}O_4$ 259.0970; found 259.0969. Anal. Calcd for $C_{15}H_{15}O_4$: C, 69.76; H, 5.46. Found: C, 69.77; H, 5.46%.

4.5.4. 4-Benzyl-6-methyl coumarin ***8a***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-bromobenzyl-6-methylcoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution phenyl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as yellow solid. R_f 0.67 (E.A 20%/PE 80%). Mp 142–143 °C. IR (KBr, cm^{-1}): 3058, 2923, 1764, 1714, 1574, 1193, 1074, 1030, 828; ^{1}H NMR (300 MHz, DMSO-d_6) δ=7.66 (s, 1H, Ar-H), 7.21–7.38 (m, 7H, Ar–H), 6.15 (s, 1H, CH), 4.25 (s, 2H, CH_2), 2.34 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=159.9 (C_q), 155.3 (C_q), 151.3 (C_q), 137.0 (C_q), 133.5 (C_q), 132.8 (CH), 129.0 (CH), 128.7 (CH), 126.8 (CH), 125.1 (CH), 118.5 (C_q), 116.4 (CH), 114.6 (CH), 36.7 (CH_2), 20.4 (CH_3). MS (EI) m/z (relative intensity) 250 (100, M$^+$); HRMS (ESI, quadrapole): m/z calcd for $C_{17}H_{14}O_2$+H$^+$ 251.1072; found 251.1071. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.60; H, 5.65%.

4.5.5. 4-(4-tert-Butyl)benzyl-6-methyl coumarin ***8b***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-bromobenzyl-6-methylcoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 4-*tert*-butylphenyl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as colourless solid. R_f 0.73 (E.A 20%/PE 80%). Mp 120–121 °C; IR (KBr, cm^{-1}): 3057, 2961, 1725, 1573, 1268, 1197, 1058, 828; ^{1}H NMR (300 MHz, DMSO-d_6) δ=7.70 (s, 1H, Ar–H), 7.19–7.51 (m, 6H, Ar–H), 6.15 (s, 1H, CH), 4.18 (s, 2H, CH_2), 2.27 (s, 3H, CH_3), 1.22 (s, 9H, 3×CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=160.5 (C_q), 156.1 (C_q), 151.8 (C_q), 148.9 (C_q), 134.3 (C_q), 134.1 (C_q), 133.3 (CH), 129.2 (CH), 125.9 (CH), 125.6 (CH), 119.0 (C_q), 116.9 (CH), 114.9 (CH), 36.6 (CH_2), 34.6 (C_q), 31.6 (CH_3), 20.9 (CH_3). MS (EI) m/z (relative intensity) 306 (100, M$^+$); HRMS (ESI, quadrapole): m/z calcd for $C_{21}H_{22}O_2$+H$^+$ 307.1698; found 307.1696. Anal. Calcd For $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.32; H, 7.25 %.

4.5.6. 4-(4-Methoxy)benzyl-6-methyl coumarin ***8c***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-bromobenzyl-6-methylcoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 4-methoxyphenyl

boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as colourless solid. R_f 0.58 (E.A 20%/PE 80%). Mp 142–143 °C; IR (KBr, cm^{-1}): 3071, 2956, 1765, 1724, 1573, 1245, 1193, 1107, 1028, 838; ^1H NMR (300 MHz, DMSO-d_6) δ=7.67 (s, 1H, Ar–H), 7.24–7.46 (m, 4H, Ar–H), 6.91 (d, J=7.8 Hz, 2H, Ar–H), 6.16 (s, 1H, CH), 4.14 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=159.9 (C_q), 158.0 (C_q), 155.8 (C_q), 151.3 (C_q), 133.5 (C_q), 132.7 (CH), 130.1 (CH), 128.6 (CH), 125.1 (CH), 118.4 (C_q), 116.4 (CH), 114.5 (C_q), 114.3 (CH), 55.0 (OCH_3), 35.8 (CH_2), 20.4 (CH_3). MS (EI) m/z (relative intensity) 280 (100, M^+); HRMS (ESI, quadrapole): m/z calcd for $C_{18}H_{16}O_3$ 280.1099; found 280.1098. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.12; H, 5.76%.

4.5.7. 4-(4-Methyl)benzyl-7-methyl coumarin ***8d***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-bromobenzyl-7-methylcoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 4-methylphenyl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as yellow solid. R_f 0.73 (E.A 20%/PE 80%). Mp 104–105 °C; IR (KBr, cm^{-1}): 2922, 1731, 1619, 1259, 1143, 1014, 812; ^1H NMR (300 MHz, DMSO-d_6) δ=7.73 (d, J=7.9 Hz, 2H, Ar–H), 7.13–7.39 (m, 5H, Ar–H), 6.19 (s, 1H, CH), 4.17 (s, 2H, CH_2), 2.47 (s, 3H, CH_3), 2.27 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=160.0 (C_q), 155.5 (C_q), 153.3 (C_q), 142.7 (C_q), 135.8 (C_q), 133.9 (C_q), 129.2 (CH), 128.8 (CH), 125.3 (C_q), 125.2 (CH), 116.6 (CH), 113.6 (CH), 36.4 (CH_2), 20.9 (CH_3), 20.6 (CH_3). MS (EI) m/z (relative intensity) 264 (100, M^+); HRMS (ESI, quadrapole): m/z calcd for $C_{18}H_{16}O_2$+H^+ 265.1229; found 265.1226. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.78; H, 6.12%.

4.5.8. 4-(4-Methoxy)benzyl-7-methyl coumarin ***8e***. In a 30 mL Schlenk tube equipped with a magnetic stirring bar, complex **1** (5.0 mol %) and 4-bromobenzyl-7-methylcoumarin (1 mmol) were taken in THF (2 mL) and Na_2CO_3 solution (2.0 M, 1 mL). The solutions were degassed (three freeze–thaw cycles) and stirred for 10 min. After this time period, to the solution 4-methoxyphenyl boronic acid (1 mmol) was added and the mixtures degassed. The reaction mixtures were refluxed for 3.0 h. The reactions were monitored by TLC. The reaction mixtures were then evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as colourless solid. R_f 0.64 (E.A 20%/PE 80%). Mp 116–117 °C; IR (KBr, cm^{-1}): 2992, 1736, 1602, 1512, 1248, 1144, 1023, 858; ^1H NMR (300 MHz, DMSO-d_6) δ=7.67–7.76 (m, 1H, Ar–H), 7.11–7.37 (m, 4H, Ar–H), 6.92 (d, J=7.9 Hz, 2H, Ar–H), 6.31 (s, 1H, CH), 4.13 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=160.5 (C_q), 158.5 (C_q), 156.3 (C_q), 153.8 (C_q), 143.2 (C_q), 130.5 (CH), 129.3 (C_q), 125.7 (CH), 116.8 (CH), 116.6 (C_q), 114.5 (CH), 113.9 (CH), 55.5 (OCH_3), 36.5 (CH_2), 21.4 (CH_3). MS (ESI) m/z (relative intensity) 281 (100, M+H^+); HRMS (ESI, quadrapole): m/z calcd for $C_{18}H_{16}O_3$ 280.1099; found 280.1075. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.11; H, 5.77%.

4.5.9. 4-(2-Bromo-4-methyl-phenoxy)-coumarin ***9b***. In a 250 mL flask 4-chlorocoumarin (5.0 mmol) in acetonitrile (50 mL) was placed and to this were added K_2CO_3 (5.5 mmol) and 2-bromo-4-methylphenol (5.0 mmol). The reaction mixture was refluxed for 24 h and then quenched into water (150 mL). The organic layer was then extracted with EtOAc (50×3 mL) and the combined organic layer was evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as pale yellow solid. R_f- 0.70 (E.A 20%/PE 80%); 284 mg, 86%. Mp: 150–152 °C; IR (KBr, cm^{-1}): 3041, 2979, 1727, 1573, 1268, 1179, 1104, 1038, 858; ^1H NMR (300 MHz, DMSO-d_6) δ=8.05 (d, J=7.5 Hz, 1H, Ar–H), 7.71–7.76 (m, 1H, Ar–H), 7.68–7.69 (m, 1H, Ar–H), 7.35–7.50 (m, 4H, Ar–H), 5.10 (s, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ=165.1 (C_q), 161.3 (C_q), 153.5 (C_q), 147.0 (C_q), 139.3 (C_q), 134.6 (CH), 134.0 (CH), 130.9 (CH), 125.1 (CH), 123.8 (C_q), 123.6 (CH), 117.1 (CH), 114.9 (C_q), 93.2 (CH), 20.5 (CH_3); MS (ESI) m/z: 332 (100, M+H^+); HRMS (ESI, quadrapole) calcd for $C_{16}H_{11}BrO_3$: 329.9892, found: 329.9890. Anal. Calcd for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35; Br, 24.13. Found: C, 58.04; H, 3.35; Br, 24.12%.

4.5.10. 4-(2-Bromo-4-chlorophenoxy)-coumarin ***9c***. In a 250 mL flask 4-chlorocoumarin (5.0 mmol) in acetonitrile (50 mL) was placed and to this were added K_2CO_3 (5.5 mmol) and 2-bromo-4-chlorophenol (5.0 mmol). The reaction mixture was refluxed for 24 h and then quenched into water (150 mL). The organic layer was then extracted with EtOAc (50×3 mL) and the combined organic layer was evaporated in vacuo. The resultant residues were purified by flash chromatography (silica gel) to afford the desired product as white solid. R_f 0.65 (E.A 20%/PE 80%); 277 mg, 79%. Mp: 172–173 °C; IR (KBr, cm^{-1}): 3049, 2982, 1731, 1576, 1268, 1178, 1102, 1035, 828; ^1H NMR (300 MHz, $CDCl_3$) δ=7.96 (d, J=7.5 Hz, 1H, Ar–H), 7.65–7.67 (m, 1H, Ar–H), 7.55–7.58 (m, 1H, Ar–H), 7.27–7.38 (m, 2H, Ar–H), 7.13 (d, J=8.0 Hz, 2H, Ar–H), 5.23 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ=164.7 (C_q), 162.0 (C_q), 153.7 (C_q), 148.2 (C_q), 133.9 (CH), 133.2 (C_q), 133.1 (CH), 129.5 (CH), 124.3 (CH), 124.0 (CH), 123.1 (CH), 116.9 (CH), 116.7 (C_q), 114.7 (C_q), 93.8 (CH); MS (ESI) m/z: 352 (100, M+H^+); HRMS (ESI, quadrapole) calcd for $C_{15}H_8BrClO_3$+H^+: 350.9424, found: 350.9425. Anal. Calcd for $C_{15}H_8BrClO_3$: C, 51.24; H, 2.29; Br, 22.73; Cl, 10.08. Found: C, 51.24; H, 2.28; Br, 22.73, Cl, 10.07%.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.030.

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