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PAPER

Pd–carbene catalyzed carbonylation reactions of aryl iodides†

Liqin Xue,[a] Lijun Shi,[a] Yuan Han,[b] Chungu Xia,[a] Han Vinh Huynh*[b] and Fuwei Li*[a]

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A series of carbene complexes [$PdBr_2$(^{i}Pr_2-bimy)L] (**C2–C13**) with different types of co-ligands (L) have been tested for their catalytic activities in the carbonylative annulation of 2-iodophenol with phenylacetylene in DMF to afford the respective flavone **2a**. Complex **C12** with an *N*-phenylimidazole co-ligand showed the best activity and also afforded high yields when the substrate scope was extended to other aryl or pyridyl acetylenes. In addition, catalyst **C12** was also efficient in the carbonylative annulation of 2-iodoaniline with acid chlorides giving the desirable 2-substituted 4*H*-3,1-benzoxazin-4-ones (**4**) in good yields. Additionally, this Pd–NHC complex also proved to be a very efficient catalyst for the hydroxycarbonylation of iodobenzene derivatives at low catalyst loading and under low CO pressure. These results demonstrate the versatility and efficiency of this phosphine-free Pd(II)–NHC complex in different types of carbonylations of aryl iodides under mild conditions.

1. Introduction

The development of Pd-catalyzed, one-pot carbonylative annulation of multiple building blocks has attracted considerable attention, owing to the general and necessary focus on environmental sustainability, with the aim to reduce energy consumption and avoid waste production.[1] This approach allows an easy construction of important heterocycles such as flavones[2] (**2**) and 2-substituted-3,1-benzoxazin-4-ones[3] (**4**) through the cyclocarbonylation of *ortho*-functionalized aryl iodides with alkynes and acid chlorides, respectively, *via* the simultaneous formation of three new bonds.[1c,g,m] Although the fundamental metal-catalyzed carbonylation step itself is well established,[4,5] it is important to note that the most common catalyst systems require expensive phosphine ligands, relatively high catalyst loading and harsh reaction conditions.

As alternatives to phosphines, N-heterocyclic carbene ligands (NHCs) are currently widely used in homogeneous catalysis, especially in cross-coupling and olefin metathesis reactions.[6] Transition metal–NHC complexes have also shown excellent activities in the carbonylations of aryl halides to give carboxylic acid derivatives,[7] ketones[8] and amides.[9] However, and to the best of our knowledge, there is no account on the synthesis of heterocycles *via* Pd–NHC catalyzed cyclocarbonylation of aryl halides.[10] Since such transformations generally proceed *via* oxidative additions of aryl halides under harsh conditions, we believe that electron rich Pd–NHC complexes may be a good choice due to their stronger Pd–C bonds.

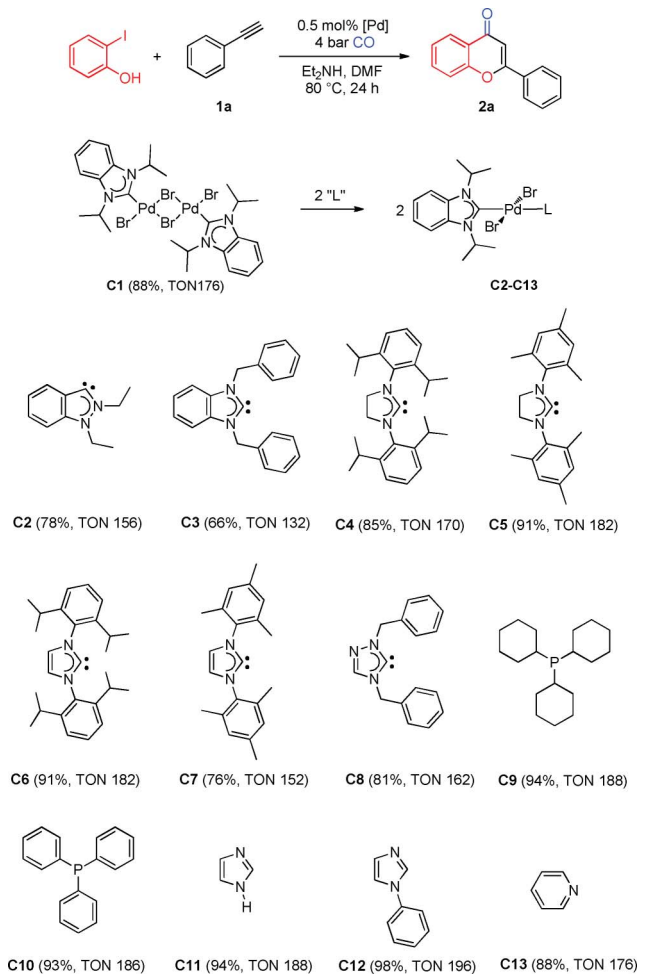
As part of our continuing studies on the preparation and catalytic applications of Pd–NHC complexes,[11] we herein describe the catalytic activities of palladium(II) benzimidazolin-2-ylidene complexes (Scheme 1) in the carbonylative annulation of *ortho*-functionalized aryl iodides to yield flavones and 3,1-benzoxazin-4-ones as well as in the hydroxycarbonylation of iodobenzenes to afford benzonic acids under low catalyst loading and mild conditions.

2. Results and discussion

2.1 Screening of catalyst

A range of mixed benzimidazolin-2-ylidene/co-ligand Pd(II) complexes of the general formula [$PdBr_2$(^{i}Pr_2-bimy)L] (**C2–C13**) (^{i}Pr_2-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) have been formally synthesized by bridge-cleavage reactions of the parent dimer [$PdBr_2$(^{i}Pr_2-bimy)]$_2$ (**C1**)[11g] with 2 equivalents of co-ligand L. Recently, we have used these complexes as probes to study the donor abilities of their respective ligands L by ^{13}C NMR spectroscopy.[11c] In this study, the donor strengths of the chosen co-ligands gradually decrease from catalyst **C2** to **C13**. For the purpose of comparison we have also included the parent dimer **C1**. In order to discern any co-ligand effects on the catalytic activities, these complexes have been tested in the cyclocarbonylation of 2-iodophenol with phenylacetylene **1a** as a benchmark reaction. These reactions were performed at 80 °C and under a relatively low CO pressure of 4.0 bar with 0.5 mol% catalyst loading. As summarized in Scheme 1, the *trans*-hetero-bis(carbene) complexes **C2–C8** could catalyze the cyclocarbonylations smoothly giving moderate to good isolated yields of flavone **2a**, ranging from 66–91%. Unfortunately, no obvious electronic and steric effects of

[a]*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 73000, China. E-mail: fuweili@licp.cas.cn; Fax: (+86)-931-4968129*
[b]*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543, Singapore. E-mail: chmhhv@nus.edu.sg*
† Electronic supplementary information (ESI) available: NMR spectra of the representative products. See DOI: 10.1039/c1dt10433k



Scheme 1 Screening of different *trans*-[$PdBr_2$(^{i}Pr_2-bimy)L] catalysts in the carbonylative annulation of 2-iodophenol with phenylacetylene.

the NHC co-ligand could be observed. For example, the strongest (**C2**, indazolin-3-ylidene) and the weakest donating (**C8**, triazolin-5-ylidene) NHC co-ligands gave similar yields of 78 and 81%, respectively. The mixed phosphine/NHC complexes **C9** and **C10** performed better with almost identical high yields of 94 and 93%, respectively. This observation corroborates again that the donating power of the co-ligand has essentially no notable effect on the cyclocarbonylation.

When the co-ligand was changed to commercially available N-donors such as imidazoles (**C11**, **C12**) or pyridine (**C13**), excellent yields (88–98%) of **2a** were still achieved. Finally, the parent dimer **C1** could also catalyze the formation of **2a** with a good yield of 88%.[11c] For comparison, the classical phosphine-based carbonylation catalyst [$PdCl_2(PPh_3)_2$] gave a lower yield of 75% under the same reaction conditions. Overall, the high activity at a low catalyst loading of 0.5 mol% is remarkable, since reported procedures generally operate at higher temperatures using 5 mol% loading.[1q] In an attempt to extend the substrate scope to aryl bromides, we also tested the carbonylation reaction of bromobenzene in the presence of phenylacetylene. However, no significant conversion was observed. This is not surprising, since to the best of our knowledge there are no reports on the carbonylative annulation of bromophenols, highlighting the current challenge in this reaction.

Overall, these results indicate that this series of [$PdBr_2$(^{i}Pr_2-bimy)L] complexes are useful and efficient alternatives to the classical pure metal–phosphine catalysts in carbonylative annulation reactions. Furthermore, it was found that the nature of the co-ligand in the catalysts **C1–C13** have only a small influence on the activity. In analogy to the chloropyridine ligand in the commercially available PEPPSI™ catalyst, their role may be defined as a "throw-away" ligand, which provides added stability and at the same time allows easy catalyst initiation.

Pd–NHC catalyzed carbonylative annulation of 2-iodophenol with acetylenes

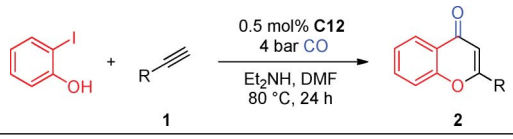
Compound **C12** bearing a simple *N*-phenylimidazole co-ligand proved to be the best catalyst in terms of activity and availability. Thus, **C12** was subsequently applied to the carbonylative annulation of 2-iodophenol with a range of other acetylenes (**1b–1j**) in order to extend the substrate scope.

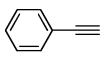
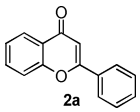
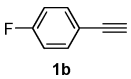
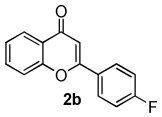
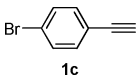
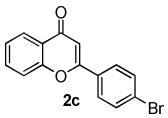
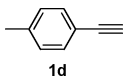
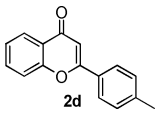
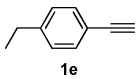
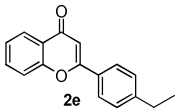
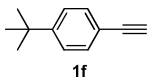
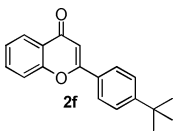
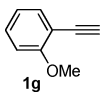
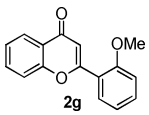
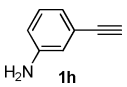
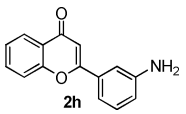
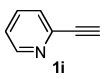
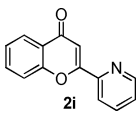
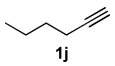
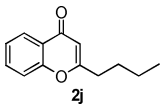
As shown in Table 1, the annulation with deactivated or electron-poor phenylacetylenes **1b** and **1c** (entries 2 and 3) proceeded smoothly giving high isolated yields of the desired flavones **2b** and **2c**, which were however slightly lower than that obtained for **2a** using the parent phenylacetylene (entry 1). Comparatively better and near quantitative yields of the desired flavones (**2d–2f**, entries 4–6) were obtained with electron rich 4-alkyl phenylacetylenes (**1d–1f**). The sterically hindered *ortho*-methoxy phenylacetylene **1g** could also be efficiently coupled at a low catalyst loading yielding 84% of **2g** (entry 7). A free amino function on the aryl acetylene (**1h**) is efficiently tolerated in the cyclocarbonylation as evidenced by a high 93% yield of aminoflavone **2h** (entry 8). Notably, no amide byproducts were observed that could have resulted from a competitive carbonylation between 2-iodophenol and the amino-substituent of the aryl acetylene. The observed high selectivity indicates that this reaction involves a Sonogashira carbonylation across the C–I bond of 2-iodophenol with acetylene to give an alkynone intermediate, which subsequently undergoes internal hydroalkoxylation by addition of the –OH moiety to the triple bond to afford the final product. Compared to advances in the carbonylation of common aryl substrates, the use of heterocycles has been plagued with problems, especially when palladium catalysts are used, probably due to competing and irreversible coordination to the active species. Importantly, this was not observed with **C12**, and the carbonylative annulation of pyridyl acetylene resulted in the desired pyridyl flavone (**2i**) in near quantitative yields with a considerably lower catalyst loading (entry 9). Unfortunately, the reaction of alkyl acetylene gave only a low 25% yield of flavone **2j** under the same reaction conditions (entry 10).

In recent years, ionic liquids (ILs) have received much attention in catalysis due to their potential as a "green" recyclable alternative to traditional organic solvents.[12] In many cases, the use of ILs has led to an improvement of the catalytic reactions. Encouraged by the observed catalytic efficiency of the Pd–NHC complex **C12** for the homogeneous cyclocarbonylative annulation, we also tested it's performance in imidazolium based ILs as a reaction media (Table 2)

Disappointingly, only trace amounts **2a** were obtained in the cyclocarbonylation of 2-iodophenol and phenylacetylene when [bmim]Cl (bmim = 1-butyl-3-methylimidazolium cation) was used

Table 1 **C12** catalyzed carbonylative annulation of 2-iodophenol with acetylenes[a]



Entry	Acetylene	Flavone	Yield[b] (TON)
1	 1a	 2a	98% (196)
2	 1b	 2b	83% (166)
3	 1c	 2c	85% (170)
4	 1d	 2d	94% (188)
5	 1e	 2e	95% (190)
6	 1f	 2f	95% (190)
7	 1g	 2g	84% (168)
8	 1h	 2h	93% (186)
9	 1i	 2i	96% (192)
10	 1j	 2j	25% (50)

[a] Reaction conditions: 2-iodophenol (0.5 mmol), acetylene (0.6 mmol), **C12** (0.5 mol%), Et_2NH (1.0 mmol), CO (4.0 bar), DMF (1.0 mL), 80 °C, 24 h. [b] Isolated yields based on 2-iodophenol after silica gel chromatography and all results are average from two runs.

Table 2 Effect of selected imidazolium-based ionic liquids (ILs) on the catalytic activity in the cyclocarbonylation of 2-iodophenol with phenylacetylene[a]

Entry	ILs	Yield[b] (TON)
1	[bmim]Cl	Trace
2	[bmim]Br	43% (86)
3	[bmim]BF_4	48% (96)

[a] Reaction condition: ILs : substrate = 5 : 1 and other conditions are the same as shown in Table 1. [b] Isolated yield.

as a solvent (entry 1). Changing the counter anion to Br^- led to an improvement in the yield to 43% (entry 2). Attempts to further improve the yield by using ILs with the non-coordinating anion BF_4^- were not met with success as only 48% was obtained (entry 3). These results clearly demonstrate that all the reactions in imidazolium ILs are much slower than the reactions in DMF, which suggests that the imidazolium salts probably inhibit the carbonylation. A similar observation has been described for the methoxycarbonylation of iodobenzene in [bmim]X in the presence of palladium complexes.[13] We attribute this to the non-innocent behavior of the imidazolium salts, which upon base mediated C–H activation may react further with the palladium catalyst to form unreactive species (*e.g.* $[PdX_2L_2]$) shutting down the catalytic cycle.

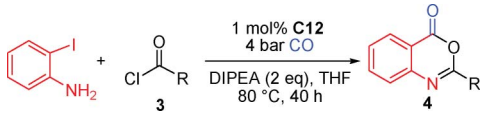
Pd–NHC catalyzed carbonylative annulation of 2-iodoaniline with acid chlorides

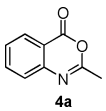
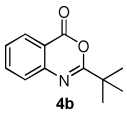
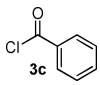
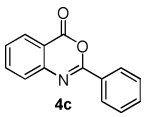
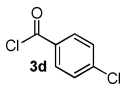
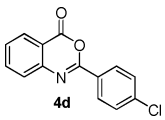
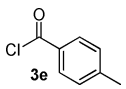
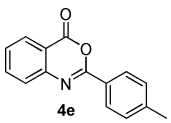
Another interesting target to study the catalytic application of Pd–NHC complex **C12** could also be the three-component carbonylative annulation of 2-iodoaniline with acid chlorides. This reaction was developed by Alper and co-workers using 2.0 mol% $Pd(OAc)_2$ and 20 bar CO at 130 °C.[14] We were pleased to observe that 2-iodoaniline and representative acid chlorides could be efficiently annulated to give the desired 2-substituted 4*H*-3,1-benzoxazin-4-ones at a lower catalyst loading (1.0 mol%) of **C12** using diisopropyl ethyl amine (DIPEA) as a base and under milder reaction conditions (4.0 bar and 80 °C), and the results are shown in Table 3.

The cyclocarbonylation of 2-iodoaniline with acetyl chloride (**3a**) gave 2-methyl-4*H*-3,1-benzoxazin-4-one (**4a**) in a moderate yield of 60% (entry 1). The more bulky and electron rich pivaloyl chloride (**3b**) afforded excellent isolated yields (90%) of the respective heterocyclic product **4b** (entry 2). Likewise, annulation of the aromatic benzoyl chloride **3c** proceeded smoothly giving an 86% yield of **4c** (entry 3). The introduction of *para*-substituents in this system did not affect the yield to a great extent. However, it was observed that the electron-withdrawing chloro substituent led to a slight decrease, whereas an electron donating methyl group led to an increase in the yields of the corresponding heterocycles **4d** and **4e** (entries 4 and 5), respectively.

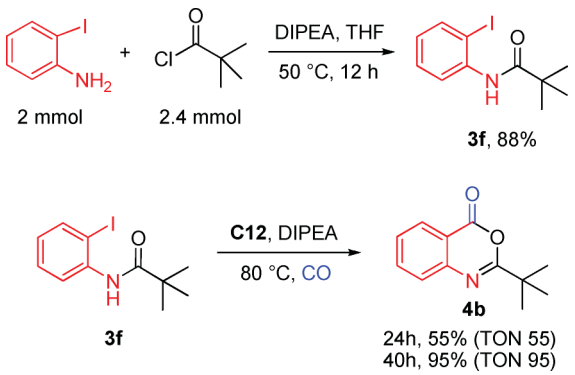
To gain a more detailed understanding of this carbonylative annulation, we further investigated the two-step synthesis of **4b** as a model reaction represented in Scheme 2. Heating the mixture of 2-iodoaniline and pivaloyl chloride (**3b**) in the presence of DIPEA gave an 88% yield of the aromatic amide **3f**, which was subsequently cyclocarbonylated under the same conditions. After 40 h **4b** was isolated in a near quantitative yield, which is comparable

Table 3 **C12** catalyzed carbonylative annulation of 2-iodoaniline with acid chlorides (**3**) under mild conditions[a]



Entry	ClCOR	Product	Yield[b] (TON)
1			60% (60)
2			90% (90)
3			86% (86)
4			76% (76)
5			90% (90)

[a] Reaction conditions: 2-iodoaniline (0.5 mmol), acid chloride (0.6 mmol), **C12** (1.0 mol%), DIPEA (1.0 mmol), CO (4.0 bar), THF (2.0 mL), 80 °C, 40 h. [b] Isolated yields are based on 2-iodoaniline after silica gel chromatography and all results are average from two runs.

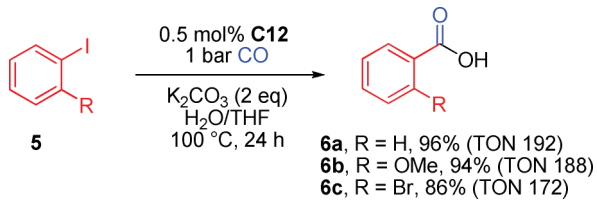


Scheme 2 Two-step synthesis of **4b**. Reaction conditions of the carbonylation are the same as shown in Table 3.

to the one-step three-component carbonylation reaction shown in Table 3. This result agrees well with the previously proposed two-step mechanism by Alper and coworkers.[14a]

Pd–NHC catalyzed hydroxycarbonylation of iodobenzene derivatives

Besides the two types of carbonylative annulation reactions of *ortho*-NH_2 and –OH substituted aryl iodides with alkynes and acid chlorides discussed above, the application of **C12** in the hydroxycarbonylation of iodobenzene derivatives was also investigated (Scheme 3). Using only a 0.5 mol% catalyst loading and 1 bar of CO in wet THF, iodobenzene was very efficiently converted into the benzoic acid with a yield of 96%. The use of aryl iodides with either an electron donating methoxy (**5b**) or a withdrawing bromido (**5c**) *ortho*-substituent did not hamper the catalysis significantly giving the desired carboxylic acids (**6b** and **6c**) in excellent to very good isolated yields of 94% and 86%, respectively.



Scheme 3 **C12** catalyzed hydroxycarbonylation of iodobenzene derivatives.

Conclusion

In summary, a series of mixed carbene/co-ligand Pd(II) complexes of the type [$PdBr_2$(^{i}Pr_2-bimy)L] (**C2–C13**) and its parent dimer **C1** was tested for their catalytic activities in the carbonylative annulation of 2-iodophenol with phenyl acetylene to give the respective flavone. All complexes can be easily prepared and are air stable, which allows easy handling under aerobic conditions. Complex **C12** bearing a phenylimidazole co-ligand was identified as the most efficient phosphine-free catalyst, which could also be employed to a broader substrate scope affording a range of flavone derivatives as important heterocyclic building blocks. Attempts to apply this catalytic system in ILs were met with limited success possibly due to non-innocent behavior of the solvent. Furthermore, the catalytic utility of **C12** has been successfully extended to the cyclocarbonylation of 2-iodoaniline with acid chlorides and the hydroxycarbonylation of iodobenzenes giving the desired products in high yields. The observed higher catalytic activities of this Pd(II)–benzimidazolin-2-ylidene complex compared to phosphine analogues demonstrates the potential of NHCs as suitable and highly effective ligands in promoting carbonylative catalysis. Current work in our laboratories is ongoing to extend the scope of transition metal–NHC complexes in efficient carbonylative reactions for the synthesis of important heterocyclic intermediates.

Experimental

General remarks

All the chemicals and solvents were used as received without further purification with the exception of THF, which was dried over sodium–benzophenone and freshly distilled prior to use. All [$PdBr_2$(^{i}Pr_2-bimy)L] complexes (**C2–C13**) and the parent dimer (**C1**) were synthesized according to our previous reported procedures.[11c] Ionic liquids were synthesized by standard methodologies.[12] NMR spectra of the products were recorded using a Bruker Avance TM III spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. Elemental analyses were carried out on a Vario EL analyzer. Ions

for low resolution mass spectra (MS) EI data were run on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 N mass spectrometer. High resolution mass spectrum were obtained on a Bruker Daltonics micrO TOF-Q^{II} spectrometer.

Carbonylation procedures

General procedure for the carbonylative annulation of 2-iodophenol with acetylenes. 2-Iodophenol (0.5 mmol), acetylene (0.6 mmol), [$PdBr_2$(^{i}Pr_2-bimy)L] (0.0025 mmol), Et_2NH (1.0 mmol) and DMF (1.0 mL) were introduced into a 100 mL stainless steel autoclave with magnetic stirring. The autoclave was closed and purged three times with CO before it was finally pressurized with 4.0 bar CO gas. Then the reactor was immersed in an oil bath preheated at 80 °C for 24 h. After cooling to room temperature, excess CO was discharged and the resultant reaction mixture was purified by flash chromatography using silica gel (petroleum ether–ethyl acetate = 10 : 1) to afford the corresponding flavones (**2**).

General procedure for the carbonylative annulation of 2-iodoaniline with acyl chlorides. A 100 mL stainless steel autoclave equipped with a magnetic stir bar was charged with 2-iodoaniline (0.5 mmol), acyl chloride (0.6 mmol), **C12** (0.005 mmol), DIPEA (1.0 mmol) and THF (2.0 mL). The autoclave was sealed and then pressurized with 4.0 bar CO after being purged three times with pure CO at room temperature. Then the reactor was stirred at 80 °C for 40 h. Excess CO was discharged at room temperature. The reaction mixture was purified by flash chromatography using silica gel (petroleum ether–ethyl acetate = 3 : 2) yielding the desired products (**4**).

General procedure for the hydroxycarbonylation of iodobenzenes with CO in H_2O–THF. Iodobenzene derivatives (0.5 mmol), **C12** (0.0025 mmol), K_2CO_3 (1.0 mmol) and a mixture of H_2O–THF (6.0 mL, volume ratio around 5 : 1) were added to a 100 mL autoclave. The autoclave was pressurized with 1.0 bar CO at room temperature after three cycles of filling and degassing of pure CO. The reactor was immersed in an oil bath preheated at 100 °C and stirred for 24 h. After the completion of the reaction, the resultant reaction mixture was acidified carefully with aqueous HCl (pH value ~2.0) and extracted with CH_2Cl_2 (2 × 5 mL). The organic extracts were combined, dried over Na_2SO_4, filtered and the filtrate dried to give the desired products.

Representative spectroscopic data

2-Phenyl-4*H*-chromen-4-one (2a), White solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (dd, J = 8.0 and 1.2 Hz, 1H), 7.93–7.95 (m, 2H), 7.70–7.74 (m, 1H), 7.53–7.60 (m, 4H), 7.43 (t, J = 8.0 Hz, 1H), 6.89 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.6 (C═O), 163.9, 156.4, 134.1, 131.9, 131.7, 129.2, 126.5, 125.8, 125.5, 123.8, 118.2, 107.5 (Ar–C). HRMS (ESI) for [$C_{15}H_{10}NaO_2$] calculated 245.0573, found 245.0565.

2-(4-Fluorophenyl)-4*H*-chromen-4-one (2b), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (dd, J = 8.0 and 1.6 Hz, 1H), 7.92–7.95 (m, 2H), 7.69–7.73 (m, 1H), 7.55–7.57 (m, 1H), 7.41–7.45 (m, 1H), 7.20–7.24 (m, 2H), 6.77 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.4 (C═O), 166.2, 163.6, 162.5, 156.3, 134.0, 128.7, 128.6, 125.9, 125.5, 124.0, 118.1, 116.6, 116.3, 107.5 (Ar–C). HRMS (ESI) for [$C_{30}H_{18}F_2NaO_4$] calculated 503.1065, found 503.1059. Anal. Calcd for $C_{15}H_9O_2F$: C, 74.99; H, 3.776; Found: C, 74.38; H, 3.791.

2-(4-Bromophenyl)-4*H*-chromen-4-one (2c), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (dd, J = 8.0 and 1.6 Hz, 1H), 7.78–7.80 (m, 2H), 7.69–7.73 (m, 1H), 7.64–7.67 (m, 2H), 7.55–7.57 (m, 1H), 7.41–7.45 (m, 1H), 6.80 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.4 (C═O), 162.4, 156.2, 134.0, 132.5, 130.8, 127.8, 126.4, 125.8, 125.5, 124.0, 118.2, 107.8 (Ar–C). HRMS (ESI) for [$C_{30}H_{18}Br_2NaO_4$] calculated 624.9446, found 624.9444. Anal. Calcd for $C_{15}H_9O_2Br$: C, 59.83; H, 3.012; Found: C, 57.67; H, 3.050.

2-*p*-Toyl-4*H*-chromen-4-one (2d), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (dd, J = 8.0 and 1.6 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.68–7.72 (m, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 6.81 (s, 1H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.6 (C═O), 163.8, 156.4, 142.4, 133.8, 129.9, 129.1, 126.4, 125.8, 125.3, 124.1, 118.2, 107.1 (Ar–C), 21.7. HRMS (ESI) for [$C_{16}H_{13}O_2$] calculated 237.0910, found 237.0907.

2-(4-Ethylphenyl)-4*H*-chromen-4-one (2e), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (dd, J = 8.0 and 1.6 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.66–7.70 (m, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.38–7.42 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.80 (s, 1H), 2.72 (q, J = 8.0 Hz, 2H), 1.28 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.6 (C═O), 163.7, 156.3, 148.6, 133.7, 129.2, 128.7, 126.4, 125.7, 125.2, 124.0, 118.1, 107.1 (Ar–C), 28.9, 15.4. HRMS (ESI) for [$C_{34}H_{28}NaO_4$] calculated 523.1880, found 523.1882.

2-(4-*tert*-Butylphenyl)-4*H*-chromen-4-one (2f), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (dd, J = 8.0 and 1.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.68–7.73 (m, 1H), 7.54–7.59 (m, 3H), 7.41–7.45 (m, 1H), 6.84 (s, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.7 (C═O), 163.8, 156.5, 155.5, 133.9, 129.1, 126.3, 126.2, 125.9, 125.3, 124.1, 118.2, 107.2 (Ar–C), 35.2, 31.3. HRMS (ESI) for [$C_{38}H_{36}NaO_4$] calculated 579.2506, found 579.2502.

2-(2-Methoxylphenyl)-4*H*-chromen-4-one (2g), pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (dd, J = 8.0 and 1.6 Hz, 1H), 7.88 (dd, J = 8.0 and 1.6 Hz, 1H), 7.63–7.67 (m, 1H), 7.43–7.51 (m, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.07–7.10 (m, 1H), 7.01 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.9 (C═O), 160.8, 158.0, 156.5, 133.6, 132.5, 129.3, 125.6, 124.9, 123.8, 120.7, 118.1, 112.6, 111.8 (Ar–C), 55.7. HRMS (ESI) for [$C_{16}H_{13}O_3$] calculated 253.0859, found 253.0856.

2-(3-Aminophenyl)-4*H*-chromen-4-one (2h), yellow green solid. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.04 (dd, J = 8.0 and 1.6 Hz, 1H), 7.79–7.84 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.46–7.50 (m, 1H), 7.21–7.25 (m, 1H), 7.20–7.21 (m, 2H), 6.78–6.81 (m, 2H), 5.44 (s, 2H). ^{13}C NMR (d_6-DMSO, 100 MHz): δ 177.0 (C═O), 163.7, 155.7, 149.3, 134.3, 131.7, 129.7, 125.5, 124.8, 123.4, 118.4, 117.3, 113.9, 111.0, 106.5 (Ar–C). HRMS (ESI) for [$C_{15}H_{12}NO_2$] calculated 238.0863, found 238.0859. Anal. Calcd for $C_{15}H_{11}O_2N$: C, 75.94; H, 4.674; N, 5.91. Found: C, 75.42; H, 4.739; N, 5.81.

2-Pyridyl-4*H*-chromen-4-one (2i), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.73–8.75 (m, 1H), 8.25 (dd, J = 8.0 and 1.6 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.87–7.91 (m, 1H), 7.69–7.74 (m, 1H), 7.58–7.61 (m, 1H), 7.41–7.45 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.7 (C═O), 161.7, 156.2, 150.2, 149.6, 137.2, 134.0, 126.0, 125.7, 125.4, 124.5, 121.1, 118.2, 108.9 (Ar–C). HRMS (ESI) for [$C_{28}H_{18}N_2NaO_4$] calculated 469.1159, found 469.1149.

2-Butyl-4*H*-chromen-4-one (2j), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (dd, J = 8.0 and 1.6 Hz, 1H), 7.62–7.67 (m, 1H), 7.42–7.44 (m, 1H), 7.36–7.40 (m, 1H), 6.18 (s, 1H), 2.63 (t, J = 8.0 Hz, 2H), 1.69–1.77 (m, 2H), 1.39–1.48 (m, 2H), 0.97 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5 (C═O), 170.0, 156.6, 133.5, 125.8, 125.0, 123.8, 118.0, 109.9 (Ar–C), 34.1, 29.0, 22.2, 13.8. MS (EI) m/z 202 (M^+).

***N*-(2-iodophenyl)pivalamide (3f)**, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.65 (t, J = 8.0 Hz, 1H), 1.22 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.2 (C═O), 138.4, 138.1, 128.9, 125.5, 121.7, 90.2 (Ar–C), 39.8, 27.5. HRMS (ESI) for [$C_{11}H_{14}INNaO$] calculated 326.0012, found 326.0009.

2-Methyl-4*H*-benzo[d][1,3]oxazin-4-one (4a), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (dd, J = 8.0 and 1.2 Hz, 1H), 7.78–7.82 (m, 1H), 7.30–7.55 (m, 2H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3 (C═O), 159.7 (C═N), 146.4, 136.6, 128.5, 128.2, 126.4, 116.7 (Ar–C), 21.4. MS (EI) m/z 161 (M^+).

2-*tert*-Butyl-4*H*-benzo[d][1,3]oxazin-4-one (4b), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (dd, J = 8.0 and 1.2 Hz, 1H), 7.76–7.80 (m, 1H), 7.58–7.60 (m, 1H), 7.46–7.51 (m, 1H), 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.3 (C═O), 160.1 (C═N), 146.6, 136.3, 128.3, 128.1, 127.0, 116.9 (Ar–C), 38.0, 27.8. MS (EI) m/z 203 (M^+).

2-Phenyl-4*H*-benzo[d][1,3]oxazin-4-one (4c), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31–8.33 (m, 2H), 8.25 (dd, J = 8.0 and 1.2 Hz, 1H), 7.81–7.86 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.57–7.60 (m, 1H), 7.50–7.54 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.7 (C═O), 157.3 (C═N), 147.1, 136.7, 132.8, 130.4, 128.9, 128.8, 128.5, 128.4, 127.4, 117.2 (Ar–C). MS (EI) m/z 223 (M^+).

2-*p*-Chlorophenyl-4*H*-benzo[d][1,3]oxazin-4-one (4d), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23–8.26 (m, 3H), 7.82–7.86 (m, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.51–7.55 (m, 1H), 7.47–7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4 (C═O), 156.4 (C═N), 146.9, 139.2, 136.8, 129.7, 129.3, 128.9, 128.8, 128.6, 127.4, 117.1 (Ar–C). MS (EI) m/z 257 (M^+).

2-*p*-Toyl-4*H*-benzo[d][1,3]oxazin-4-one (4e), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (dd, J = 8.0 and 1.2 Hz, 1H), 8.20 (d, J = 8.0 Hz, 2H), 7.80–7.84 (m, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.48–7.52 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.9 (C═O), 157.5 (C═N), 147.3, 143.5, 136.7, 129.7, 128.7, 128.5, 128.1, 127.6, 127.2, 117.1 (Ar–C), 21.8. MS (EI) m/z 223 (M^+).

Benzoic acid (6a), white solid. ^{1}H NMR($CDCl_3$, 400 MHz): δ 8.12–8.14 (m, 2H), 7.60–7.65 (m, 1H), 7.49 (t, J = 8.0 Hz, 2H). ^{13}C NMR($CDCl_3$, 100 MHz): δ 172.4 (C═O), 134.0, 130.4, 129.5, 128.6 (Ar–C).

2-Methoxybenzoic acid (6b), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.95 (s, 1H), 8.15 (dd, J = 8.0 and 1.6 Hz, 1H), 7.56–7.60 (m, 1H), 7.06–7.14 (m, 2H), 4.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0 (C═O), 158.2, 135.2, 133.6, 122.1, 117.6, 111.8 (Ar–C), 56.7. HRMS (ESI) for [$C_8H_8NaO_3$] calculated 175.0366, found 175.0357.

2-Bromobenzoic acid (6c), white solid. ^{1}H NMR($CDCl_3$, 400 MHz): δ 8.00–8.02 (m, 1H), 7.71–7.74 (m, 1H), 7.38–7.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.3 (C═O), 135.0, 133.7, 132.6, 130.4, 127.5, 122.7 (Ar–C).

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