

Carbonylative annulation of unsaturated compounds using molybdenum hexacarbonyl: an efficient synthesis of 2(1*H*)-quinolones

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Abstract

A ligand- and CO gas-free condition is developed in palladium-catalyzed three-component reaction of iodoanilines, unsaturated compounds and Mo(CO)₆ as a solid carbon monoxide source. The approach allows for smooth construction of biologically interesting 3,4-disubstituted (dihydro)quinolin-2(1*H*)-ones in presence of catalytic amounts of palladium and avoids the problematic use of gaseous carbon monoxide.

Keywords: 2-Quinolone, palladium, carbonylation, Mo(CO)₆, iodoaniline, internal alkyne, norbornene

Introduction

Palladium-catalyzed carbonylation reactions as a highly efficient and selective way for converting fine chemicals into a diverse range of products have found widespread use in organic synthetic applications.¹⁻⁶ Introduction of a carbonyl functionality into organic molecules which is pioneered by Heck and co-workers⁷⁻⁸ and combination of the process with subsequent intramolecular cyclization reactions, have permitted an efficient access to various biologically interesting heterocycles.⁹⁻¹⁶

Although carbonylations of a wide spectrum of organometallic reagents have been performed using gaseous carbon monoxide but the use of highly toxic flammable gaseous carbon monoxide is often impractical as it associates with risky and troublesome handling and needs highly specialized equipments. According to limited synthetic applications of gaseous carbon monoxide, employing alternative CO sources including metal carbonyls generating carbon monoxide in situ during the reaction would be more appealing. Among them, Mo(CO)₆ represents an ideal easily handled solid reagent for in situ release of carbon monoxide. In this regard, several groups have reported on various CO-gas free methods including microwave-

assisted palladium-catalyzed $\text{Mo}(\text{CO})_6$ -mediated carbonylative coupling reactions.¹⁷⁻³² Recently we also reported a facile route to diaryl ketones through palladium-catalyzed three-component cross-coupling of aryl and heteroaryl halides, $\text{Mo}(\text{CO})_6$ and boronic acids and offered a mild base/solvent combination for efficient microwave-free extrusion of carbon monoxide in the course of the reaction.³³ Continuing our interest in carbonylation reactions, we further attempted to synthesize (dihydro)quinolones via carbonylative annulation reactions of readily available 2-iodoanilines and unsaturated compounds. Quinolones are interesting structural motifs found in numerous biologically active natural products. Several synthetic quinolinone derivatives have been also found to possess various pharmacological activities.³⁴⁻³⁵ For instance compounds of type **1** and **2** are known to be selective Androgen receptor modulators and to have positive inotropic effects, respectively (Figure 1).³⁶ Linomide **3**, a synthetic immunomodulator, has been also investigated in treatment of various types of cancers and autoimmune disorders (Figure 1).³⁷ Thus, general and versatile synthetic methods for construction of these interesting frameworks are of great interest in synthetic organic chemistry.

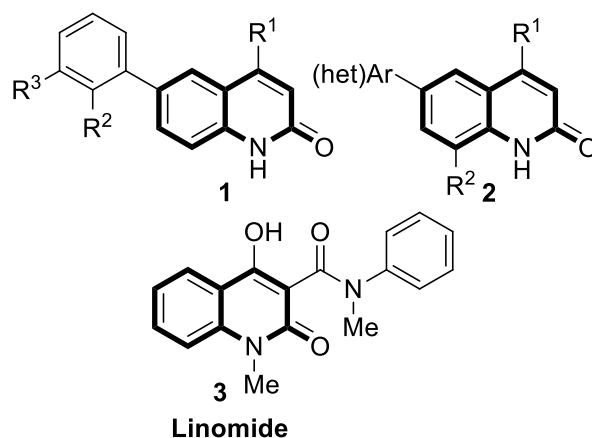


Figure 1. Biologically active quinolones.

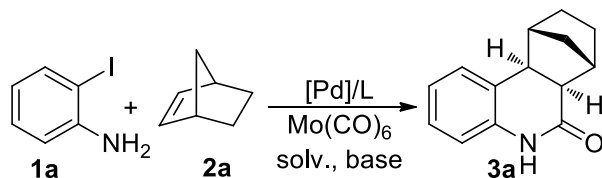
Although various classic methodologies exist for construction of 2-quinolinones,³⁸⁻⁴⁷ their utility in construction of 3,4-disubstituted quinolones are limited and they usually lead to monosubstituted scaffolds. On the other hand, only few examples of metal-catalyzed strategies which provide more powerful and practical route to heterocycles, are reported for construction of substituted quinolones.⁴⁸⁻⁶⁰ Some recent developments in metal-catalyzed construction of these privileged scaffolds include cycloaddition of *o*-cyanophenylbenzamides⁶¹⁻⁶² and *N*-arylcabamoyl chlorides⁶³ with internal alkynes, ring closing metathesis (RCM) reaction of *N*-phenylacrylamides,⁶⁴ domino Heck/Buchwald–Hartwig reaction of *o*-bromocinnamamide and iodoarenes⁶⁵ and cyclization of 3,3-diarylacrylamides through intramolecular C-H amination⁶⁶ which often require employing complicated starting materials. Larock et al. developed a palladium-catalyzed carbonylative annulation of alkynes with readily available anilines employing gaseous CO.⁶⁷⁻⁶⁸ Recently Xiao et al. further developed this strategy through a

microwave- assisted Pd(OAc)₂/dppe catalyzed carbonylative annulation of terminal alkynes with iodoanilines using solid carbon monoxide source.⁶⁹ The protocol however encountered some limitations where no reactivity was observed with internal alkynes or N-protected 2-iodoanilines and the approach typically led to only monosubstituted quinolones.

Prompted by the recent advances in CO gas-free carbonylative reactions and continuing our interest in the field, we attempted to construct 3,4-disubstituted quinolone scaffold through a palladium-catalyzed three-component reaction of iodoaniline, internal alkynes/alkenes and Mo(CO)₆ as a solid carbon monoxide source. The protocol is experimentally simple, uses readily available starting materials and is a ligand and microwave-free choice for construction of 3,4-disubstituted (dihydro)quinolin-2(1*H*)-ones. Furthermore, the annulation reactions proceed with insertion of unsaturated compounds into the arylpalladium bond in preference to insertion of carbon monoxide where no isomeric quinolones were observed.

Results and Discussion

Initially when iodoaniline **1a** and norbornene **2a** were reacted under the conditions applied for construction of diarylketones, only traces of the desired product **3a** was obtained. Next optimization reactions with respect to catalyst, base and solvents were conducted (Table 1). When PdCl₂ as the catalyst and DBU as an organic base in presence of an additive (TBAC) in THF were employed, a 30% of the desired annulated product **3a** was obtained (entry 1). Upon optimization of the palladium catalyst and base, Pd(OAc)₂ and py showed superior reactivity (entries 2-5). As screening reactions with respect to ligands including PPh₃, Pcy₃, Pcy₃.HBF₄, dppe and TFP, resulted in only comparable or lower yields of tricyclic product, ligand-free condition was established for later investigations (entries 6-10). Finally, between various solvents investigated, the carbonylation/cyclization reaction proceeded in higher yield in DMF (entries 11-15). The optimal conditions of *o*-iodoaniline, norbornene (5 equiv.), py (3 equiv.), Pd(OAc)₂ (10 mol%) and Mo(CO)₆ (1.5 equiv.) in DMF at 160 °C for 12 h, led to formation of hexahydrophenanthridinone **3a** in 45% isolated yield (Table 2, entry 1). It is noteworthy that norbornene adds to the arylpalladium intermediate in a *cis*-*exo* manner followed by CO insertion and intramolecular amination. The slow CO liberation in the course of reaction also provides an efficient pressure of the gas to promote the carbonylative reaction. This protocol merges three Heck, carbonylation and amination reactions to construct two C-C and one C-N bonds in one pot.

Table 1. Optimization of carbonylative annulation reaction^a

Entry	[Pd]	Base	L	Solv.	Yield (%)
1	PdCl ₂	DBU		THF	30
2	Pd(OAc) ₂	DBU		THF	33
3	Pd(OH) ₂ /C	DBU		THF	15
4	Pd(dppe) ₂	DBU		THF	25
5	Pd(OAc) ₂	py		THF	36
6	Pd(OAc) ₂	py	PPh ₃	THF	31
7	Pd(OAc) ₂	py	Pcy ₃	THF	25
8	Pd(OAc) ₂	py	Pcy ₃ .HBF ₄	THF	28
9	Pd(OAc) ₂	py	dppe	THF	22
10	Pd(OAc) ₂	py	TFP	THF	12
11	Pd(OAc) ₂	py		ACN	35
12	Pd(OAc) ₂	py		DMA	35
13	Pd(OAc) ₂	py		DME	33
14	Pd(OAc) ₂	py		Toluene:ACN	41
15	Pd(OAc) ₂	py		DMF	45 ^b

^aReactions conditions: o-Iodoaniline (0.2 mmol), norbornene (1.0 mmol), Base (0.6 mmol), n-Bu₄NCl (0.2 mmol), catalyst (10 mol%), ligand (20 mol%) and Mo(CO)₆ (0.3 mmol), solvent (2 mL) at 100 °C for 12 h. ^b160 °C.

Next protection of the amino group of the aniline was explored. Gratifyingly, with an ethoxycarbonyl protecting group, tricyclic adduct **3a** was obtained in almost quantitative yield (95%, entry 2). Ethyl ester deprotection proceeded in the course of the reaction and completed during the workup. Encouraged by the results, we explored some other protecting groups. The carbonylative annulation reaction of norbornene with *N*-tosyl-*o*-iodoaniline afforded the desired product in 80% yield (entry 3). Sulfonyl and acyl protecting groups also resulted in the annulated products in 85 and 87% yields, respectively (entries 4-5). Next internal alkynes were employed to investigate the scope and limitations of the approach in constructing 3,4-disubstituted quinolones. Although annulation reaction of dipropyl acetylene with unprotected iodoaniline afforded only 25% of the desired quinolone **3b**, but protected anilines resulted in the same product in high to excellent yields exceeding 85% (entries 6-9).

Table 2. Scope of annulation reactions of N-substituted o-iodoanilines

$$\begin{array}{c}
 \text{R}^1 \text{---} \text{C}_6\text{H}_3 \text{---} \text{I} \\
 | \\
 \text{NHR} \\
 \mathbf{1a-1f}
 \end{array}
 +
 \begin{array}{c}
 \text{R}^2 \\
 | \\
 \text{---} \text{C} = \text{C} \text{---} \\
 | \\
 \text{R}^2 \\
 \mathbf{2a-2c}
 \end{array}
 \xrightarrow[\text{DMF, 160 }^\circ\text{C, 12h}]{\text{Pd(OAc)}_2, \text{py, n-Bu}_4\text{NCl, Mo(CO)}_6}
 \begin{array}{c}
 \text{R}^2 \\
 | \\
 \text{C} \\
 | \\
 \text{C} \\
 | \\
 \text{R}^1 \text{---} \text{C}_6\text{H}_3 \text{---} \text{N} \text{---} \text{H} \\
 | \\
 \text{C} = \text{O} \\
 \mathbf{3a-3d}
 \end{array}$$

Entry	Amine	Alkene/Alkyne	Product	Yield(%)
1				45
2		2a	3a	95
3		2a	3a	80
4		2a	3a	85
5		2a	3a	87
6	1a	2b <i>n</i> -Pr \equiv <i>n</i> -Pr		25
7	1b	2b	3b	96
8	1d	2b	3b	88
9	1e	2b	3b	85
10	1c	2b	3b	60
11	1b	2c <i>n</i> -Bu \equiv <i>n</i> -Bu		75
12		2b		78

When aniline with tosyl protecting group was used in the reaction, a moderate yield of the desired product was obtained (entry 10). 5-Decyne also was employed in annulation reaction and afforded product **3c** in high yield (entry 11). Next the reactivity of substituted iodoaniline was examined in the carbonylative annulation reaction of alkynes. Accordingly, *o*-iodoaniline **1f** was reacted with 4-octyne and the desired quinolone **3d** was obtained in 78% isolated yield (entry 12). Unfortunately, diphenylacetylene did not participate in this annulation reaction and only traces of the desired product were obtained. Homo-coupling and polymerization of diarylacetylene, could not be overcome during the liberation of carbon monoxide in the course of reaction.

Conclusions

We have developed a versatile and efficient route to 3,4-disubstituted 2-quinolones via palladium catalyzed carbonylative annulation of internal alkynes as well as norbornene under mild reaction conditions. The presented methodology employs readily available starting materials including iodoanilines, unsaturated compounds and Mo(CO)₆ and establishes CO gas free conditions which seems to overcome the trouble of using gaseous carbon monoxide and looks suitable for high-throughput carbonylative reactions. Furthermore, the reaction is compatible with various N-protected anilines and results in deprotected amines in the course of the reaction.

Experimental Section

General. All reagents and metal catalysts were commercially available and used as received. All carbonylative annulation reactions were carried out in an oil bath using Microwave Vials (2-5 mL). IR spectra were recorded on a Shimadzu FT-IR 4300 spectrometer. IR is reported as characteristic bands (cm⁻¹) in their maximal intensity. ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker AC 300 MHz or 500 MHz spectrometers using CDCl₃ as the NMR solvent. Mass spectra of the products were obtained with a HP (Agilent Technologies) 5937 Mass Selective Detector. Elemental analyses were obtained using a Flash EA 1112 elemental analysis instrument.

General procedure for the Pd-catalyzed synthesis of 3,4-disubstituted 2-quinolones. A vial equipped with a stir bar was charged with 2-iodoaniline (0.2 mmol, 1.0 equiv), alkene or alkyne (1.0 mmol), pyridine (0.6 mmol), *n*-Bu₄NCl (0.2 mmol), Pd(OAc)₂ (10 mol %) and Mo(CO)₆ (0.3 mmol). DMF (2 mL) was then added and the vial was capped. The resulting mixture was heated in an oil bath at 160 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The residue was treated with 2 mL of 1M ethanolic NaOH at room temperature for 30 min. The resulting mixture was then extracted with DCM. Organic

fractions were combined, washed with brine, dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel.

6a,7,8,9,10,10a-Hexahydro-7,10-methanophenanthridin-6(5H)-one (3a). White solid, mp 161-163 °C; IR (ν_{max} , cm^{-1}): 1665 (C=O). ^1H NMR (500 MHz, CDCl_3): δ_{H} 1.18 (1H, d, J 10.3 Hz, CH), 1.45 (1H, d, J 10.3 Hz, CH), 1.54 (2H, m, 2CH), 1.69 (2H, m, 2CH), 2.45 (1H, d, J 2.7 Hz, CH), 2.74 (1H, d, J 9.8 Hz, CH), 2.88 (1H, d, J 3.1 Hz, CH), 3.13 (1H, d, J 9.8 Hz, CH), 6.72 (1H, d, J 7.8 Hz, Ar-H), 6.98 (1H, t, J 7.3 Hz, Ar-H), 7.09 (1H, t, J 7.4 Hz, Ar-H), 7.16 (1H, d, J 7.5 Hz, Ar-H), 9.12 (1H, s, NH). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 28.9, 29.6, 34.7, 44.2, 45.5, 48.1, 48.6, 115.4, 123.1, 124.0, 127.1, 129.2, 136.0, 171.7 (C=O). MS, m/z (%) = 213 (M^+ , 70), 196 (34), 146 (100), 76 (23). Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}$ (213.28): C, 78.84; H, 7.09; N, 6.57%. Found: C, 79.11; H, 7.20; N, 6.71%.

3,4-Dipropyl-2(1H)-quinolinone (3b): White solid, mp 188-190 °C (Ref.⁶⁷ 159-160 °C); IR (ν_{max} , cm^{-1}): 1651 (C=O). ^1H NMR (300 MHz, CDCl_3): δ_{H} 1.06-1.12 (6H, m, 2 CH_3), 1.63-1.67 (4H, m, 2 CH_2), 2.73-2.77 (2H, m, CH_2), 2.86-2.90 (2H, m, CH_2), 7.18-7.22 (1H, m, Ar-H), 7.40-7.44 (2H, m, Ar-H), 7.68 (1H, d, J 8.1 Hz, Ar-H), 12.17 (1H, s, NH). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 14.5, 14.6, 22.7, 23.3, 29.1, 30.9, 116.3, 120.1, 122.0, 124.3, 129.0, 131.2, 137.3, 147.3, 164.0 (C=O). MS, m/z (%) = 229 (M^+ , 49), 214 (62), 186 (36), 129 (46), 83 (58), 71 (61), 57 (100), 43 (95). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ (229.32): C, 78.56; H, 8.35; N, 6.11. Found: C, 78.80; H, 8.47; N, 6.27.

3,4-Dibutyl-2(1H)-quinolinone (3c): White solid, mp 133-134 °C (Ref.⁶³ 134-135 °C); IR (ν_{max} , cm^{-1}) 1656 (C=O). ^1H NMR (300 MHz, CDCl_3): δ_{H} 0.98-1.04 (6H, m, 2 CH_3), 1.49-1.68 (8H, m, 4 CH_2), 2.79 (2H, t, J 7.2 Hz, CH_2), 2.91 (2H, t, J 7.7 Hz, CH_2), 7.22 (1H, t, J 7.1 Hz, Ar-H), 7.40-7.46 (2H, m, Ar-H), 7.69 (1H, d, J 8.1 Hz, Ar-H), 12.3 (1H, s, NH). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 14.0, 14.2, 23.2, 23.4, 26.8, 28.7, 31.7, 32.2, 116.4, 120.2, 122.1, 124.3, 129.0, 131.4, 137.4, 147.5, 164.1 (C=O). Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}$ (257.37): C, 79.33; H, 9.01; N, 5.44. Found: C, 79.60; H, 9.13; N, 5.58.

6-Methoxy-3,4-dipropyl-2(1H)-quinolinone (3d): Brown solid, mp 157-158 °C (Ref.⁶⁷ 158-161 °C); IR (ν_{max} , cm^{-1}) 1650 (C=O). ^1H NMR (300 MHz, CDCl_3): δ_{H} 1.09 (3H, t, J 7.3 Hz, CH_3), 1.11 (3H, t, J 7.3 Hz, CH_3), 1.60-1.70 (4H, m, 2 CH_2), 2.75-2.78 (2H, m, CH_2), 2.84-2.88 (2H, m, CH_2), 3.88 (3H, s, OCH_3), 7.08-7.12 (2H, m, Ar-H), 7.34-7.37 (1H, m, Ar-H), 12.1 (1H, s, NH). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 14.9, 15.0, 23.0, 23.4, 29.5, 31.3, 56.0, 107.4, 117.7, 117.8, 121.1, 132.0, 132.3, 147.1, 155.1, 164.0 (C=O). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ (259.34): C, 74.10; H, 8.16; N, 5.40. Found: C, 74.38; H, 8.29; N, 5.57.

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