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Room-Temperature Palladium-Catalyzed Intramolecular Oxidative Aminocarbonylation of Vinylic C(sp^2)–H Bonds with Amines and CO

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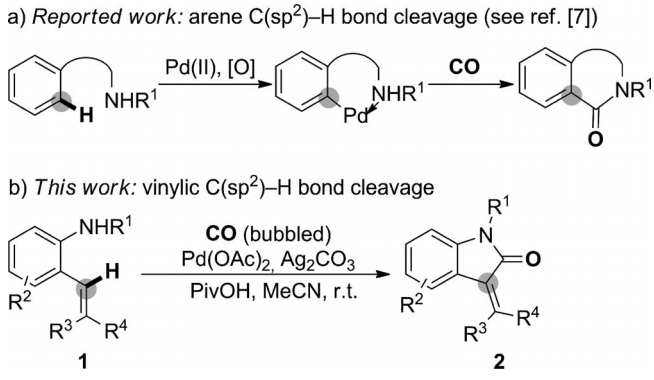
A new, mild route to access 3-methyleneindolin-2-ones is presented that proceeds through a room-temperature, palladium-catalyzed intramolecular oxidative aminocarbonylation of alkenes with amines and CO. This method represents a new aminocarbonylation strategy by employing an oxidative functionalization of a vinyl C(sp^2)–H bond.

Introduction

Carbonylation is an important reaction because of its broad applications in organic synthesis and industry and for incorporating carbonyl groups into organic molecules.[1–7] Of its numerous applications, the transition-metal-catalyzed carbonylation of organic molecules,[1–6] which include organohalides,[2] alkynes,[3] and alkenes[4–6] as well as some special compounds with C(sp^2)–H bonds,[7] with amines and CO has proven extremely effective for the synthesis of amides. However, methods for the transition-metal-catalyzed (often by Pd) aminocarbonylation of alkenes with amines and CO still face a huge challenge because of the dicarbonylation of amines and the amination of alkenes with amines prior to aminocarbonylation, and thus successful examples of aminocarbonylation are quite rare.[4–6] To the best of our knowledge, the only reported approach of an intramolecular aminocarbonylation of alkenes with amines and CO involves a Pd^0-catalyzed process,[6] which is achieved by cleavage of the carbon–carbon π bond of the alkenes and transformation of the carbon–carbon double bond into a carbon–carbon σ bond.[6] Therefore, it would be a highly desirable synthetic technique to develop new, mild routes for the aminocarbonylation of alkenes.

Recently, elegant methods were established for the palladium-catalyzed intramolecular oxidative aminocarbonylation of aryl C(sp^2)–H bonds with amines and CO (see Scheme 1, a).[7] During the process, the C(sp^2)–Pd^{II}←N complexation occurred through the insertion of Pd^{II} into the aryl C(sp^2)–H bond followed by the coordination with the amine prior to this insertion of CO. We reasoned that vinylic C(sp^2)–Pd^{II}←N complexation might readily form under similar conditions, as a vinylic C(sp^2)–H bond is more reactive than an aryl C(sp^2)–H bond. This complex would then be treated with CO to access the aminocarbonylation product. Herein, we report a room-temperature, palladium-catalyzed intramolecular oxidative aminocarbonylation of alkenes with amines and CO by using Ag_2CO_3 as the oxidant and PivOH (Piv = pivaloyl) as the promoter (see Scheme 1, b). This method represents both a new example of the direct oxidative aminocarbonylation of vinylic C(sp^2)–H bonds and a straightforward way to prepare 3-methyleneindolin-2-ones,[8] which are motifs that are found in many natural products and bioactive compounds.[9]



Scheme 1. Pd-catalyzed C–H aminocarbonylation.

Results and Discussion

To test our hypothesis, (*E*)-*N*-methyl-2-styrylaniline (**1a**) was employed for the reaction with CO, $Pd(OAc)_2$, and the oxidants (see Table 1). Gratifyingly, treatment of substrate **1a** with CO, $Pd(OAc)_2$, and $Cu(OAc)_2$ in HOAc at 100 °C afforded the desired product **2a** in 72% yield (see Table 1, Entry 1). Screening the amount of $Pd(OAc)_2$ revealed that

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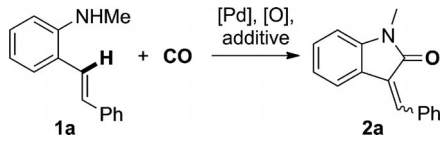
Table 1. Screening optimal conditions.[a]



Entry	[Pd]	Oxidant [equiv.]	Additive [equiv.]	Solvent	% Yield[b]
1	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	–	HOAc	72
2[c]	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	–	HOAc	53
3[d]	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	–	HOAc	73
4	$PdCl_2$	$Cu(OAc)_2$ (2)	–	HOAc	66
5[e]	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	–	MeCN	34
6[e]	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	–	DMF	trace
7[e]	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	–	toluene	26
8	$Pd(OAc)_2$	$Cu(OAc)_2$ (2)	PivOH (5)	MeCN	78
9	$Pd(OAc)_2$	$CuCl_2$ (2)	PivOH (5)	MeCN	trace
10	$Pd(OAc)_2$	AgOAc (2)	PivOH (5)	MeCN	80
11	$Pd(OAc)_2$	Ag_2CO_3 (2)	PivOH (5)	MeCN	82
12[f]	$Pd(OAc)_2$	Ag_2CO_3 (2)	PivOH (5)	MeCN	85 (1:1.3)
13[f]	$Pd(OAc)_2$	Ag_2CO_3 (2)	PivOH (0.1)	MeCN	36

[a] Reagents and conditions: **1a** (0.3 mmol), CO (bubbled), [Pd] (5 mol-%), oxidant, additive, and solvent (2 mL) at 100 °C for 12 h. [b] Isolated % yield. *Z* and *E* isomers were separated, and the *Z*/*E* ratio is given in parenthesis. [c] $Pd(OAc)_2$ (2 mol-%). [d] $Pd(OAc)_2$ (10 mol-%). [e] Some byproducts, as a result of the amination of the alkene with the amine, were detected by GC–MS analysis. [f] At room temperature.

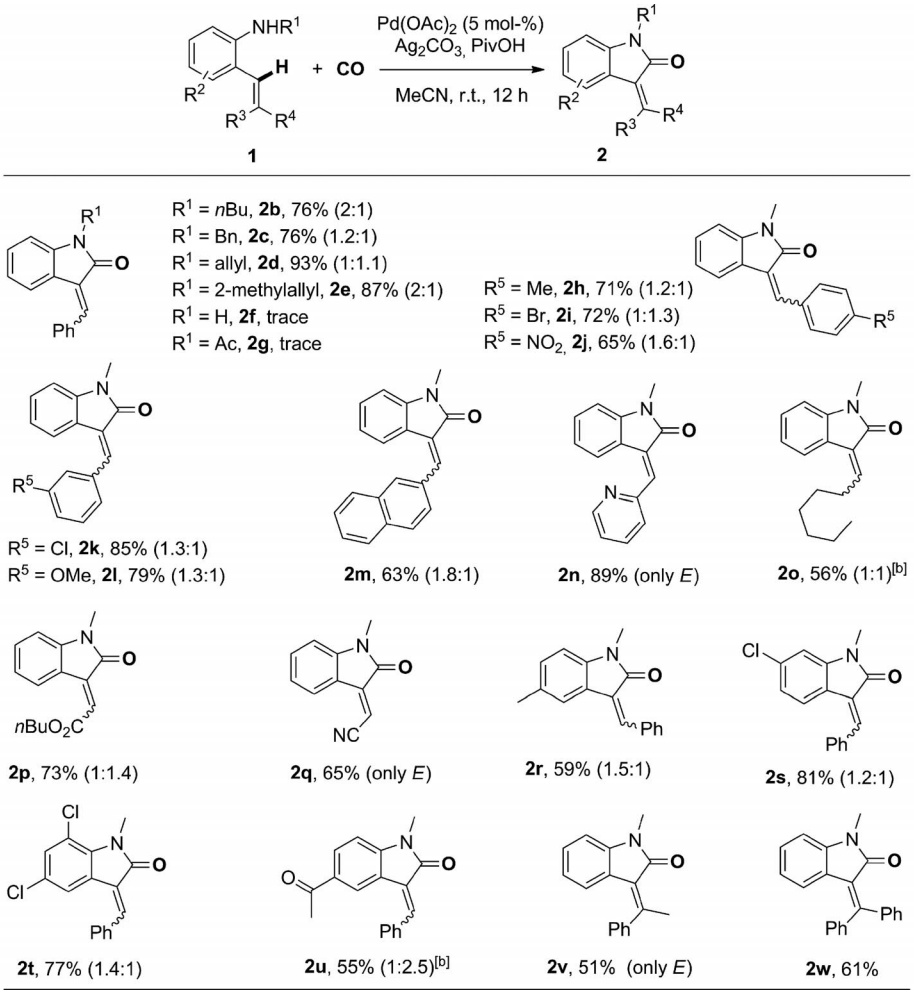
5 mol-% $Pd(OAc)_2$ was viable for the reaction (see Table 1, Entries 1–3). $PdCl_2$ as a catalyst was also highly reactive, albeit the yield was slightly lower (see Table 1, Entry 4). Encouraged by the results, the solvents MeCN, *N*,*N*-dimethylformamide (DMF), and toluene were subsequently examined, but they were less effective than HOAc. Moreover, the reaction in DMF was completely sluggish (see Table 1, Entries 1 vs. 5–7). Interestingly, the addition of PivOH improved the reaction, and 5 equiv. PivOH gave the best results (see Table 1, Entry 8). Some other oxidants, which include $CuCl_2$, AgOAc, and Ag_2CO_3, were investigated (see Table 1, Entries 9–11). Surprisingly, the reaction that employed $CuCl_2$ as the oxidant, which was previously reported as an efficient oxidant for amination-carbonylation transformations,[5] resulted in no detectable amount of product **2a** (see Table 1, Entry 9). Interestingly, the results showed that changing the oxidant to either AgOAc or Ag_2CO_3 also gave a good yield (see Table 1, Entries 10 and 11). Notably, substrate **1a** was consumed completely at room temperature in 12 h to provide product **2a** in 85% yield with an isolated *Z*/*E* ratio of 1:1.3 (*Z* and *E* isomers were separated by silica gel column chromatography with hexane/ethyl acetate as the eluent, see Table 1, Entry 12).[10] However, the yield of **2a** was lowered sharply when the reaction was carried out with 0.1 equiv. PivOH (see Table 1, Entry 13).

As shown in Table 2, 2-vinylanilines **1b**–**1w** were subjected to the optimal reaction conditions.[10] Initially, the effect of the substituent on the nitrogen atom of (*E*)-2-styrylanilines **1b**–**1g** was investigated in the presence of CO, $Pd(OAc)_2$, Ag_2CO_3, and PivOH to give products **2b**–**2g**. Substrates **1b**–**1e**, which contain *n*Bu, Bn, allyl, or 2-methylallyl groups on the nitrogen atom, furnished the corresponding products **2b**–**2e** in good yields. Unfortunately, both the free NH_2-substituted substrate **1f** and the *N*-Ac-substituted substrate **1g** were inert under the reaction conditions (i.e., products **2f** and **2g**). Gratifyingly, several substituents that include an aryl, alkyl, ester, or CN group at the terminal alkene were well tolerated to give products **2h**–**2q**. For examples, (*E*)-*N*-methyl-2-vinylanilines **1h**–**1m**, which have either electron-rich or electron-deficient aryl groups at the terminal alkene, underwent the reaction with CO smoothly to afford the corresponding products **2h**–**2m** in moderate yields. Significantly, some functional groups such as the Br, Cl, or pyridin-2-yl groups were tolerated under the optimal conditions (i.e., to give products **2i**, **2k** and **2n**), thereby making this methodology more useful to organic synthesis.[9] Electron-poor alkenes **1p** and **1q** still afforded satisfactory yields (i.e., products **2p** and **2q**). Notably, only the (*E*) isomer **2q** was produced from substrate **1q**, which contained a CN group. The reason for this may be the interaction of the CN donor directed towards the palladium center.

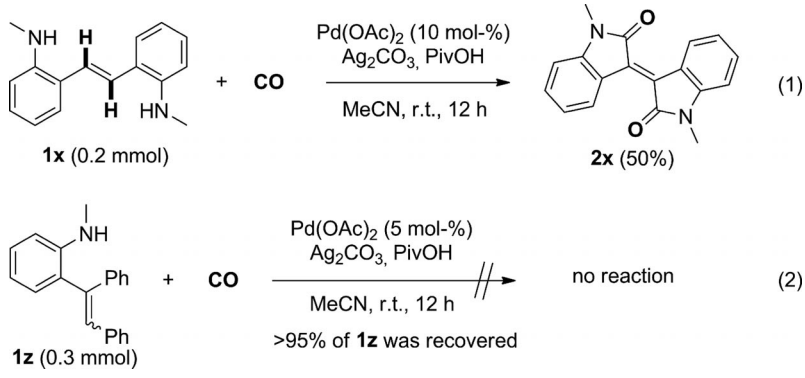
We next set out to examine substituents on the aromatic ring of the aniline moiety, and the screening revealed that Me-, Cl-, and acetyl-substituted anilines **1r**–**1u** were compatible under the optimal conditions to give products **2r**–**2u**. For instance, (*E*)-*N*,4-dimethyl-2-styrylaniline (**1r**) provided the desired product **2r** in 59% yield. Anilines **1s** and **1t** that contain a Cl group or two Cl groups, respectively, also gave the corresponding products **2s** and **2t** in good yields. The optimal conditions were also compatible with substrates **1v** and **1w** that contained two substituents at the terminal alkene to provide products **2v** and **2w** in 51 and 61% yields, respectively.

Interestingly, (*E*)-2,2′-(ethene-1,2-diyl)bis(*N*-methylaniline) (**1x**) performed the aminocarbonylation twice to provide the two indolin-2-one rings, a unit in some bioactive molecules and dyes,[11] of product **2x** in 50% yield [see

Table 2. Scope of 2-vinylanilines (**1**).[a]



[a] Reagents and conditions: **1** (0.3 mmol), CO (bubbled), $Pd(OAc)_2$ (5 mol-%), Ag_2CO_3 (2 equiv.), PivOH (5 equiv.), and MeCN (2 mL) at room temperature for 12 h. The *Z* and *E* isomers were separated, and the *Z*/*E* ratio is given in parenthesis. [b] The *Z*/*E* ratio was determined by ^{1}H NMR analysis.

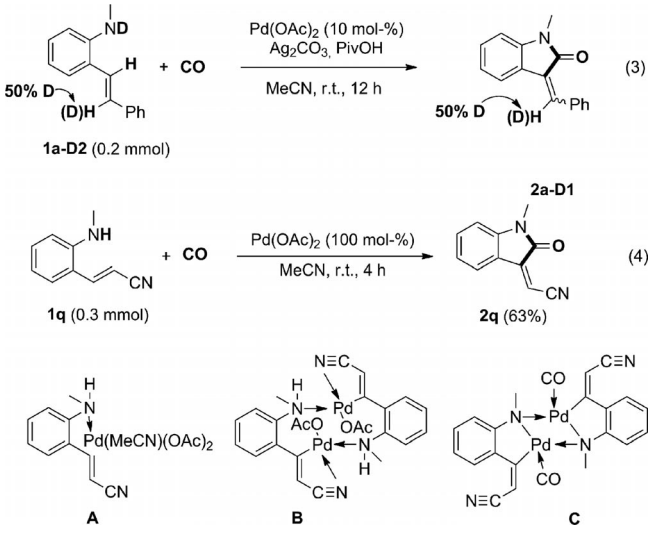


Scheme 2. Carbonylation of other substrates.

Scheme 2, Equation (1)]. However, our attempt at the aminocarbonylation of 2-(1,2-diphenylvinyl)-*N*-methylaniline (**1z**) failed [see Scheme 2, Equation (2)].

To understand the mechanism, a deuterium labeling experiment was performed [see Scheme 3, Equation (3)]. The amount of deuterium at the terminal alkene remained unchanged upon the complete conversion of deuterium-substituted substrate **1a-D2** into product **2a-D1**. These results suggest there is a different mechanism taking place from the reported mechanism proposed by Alper.[6] Interestingly, the reaction of **1q** with CO was carried out with 1 equiv. of $Pd(OAc)_2$ for 4 h without the oxidant and acid to provide

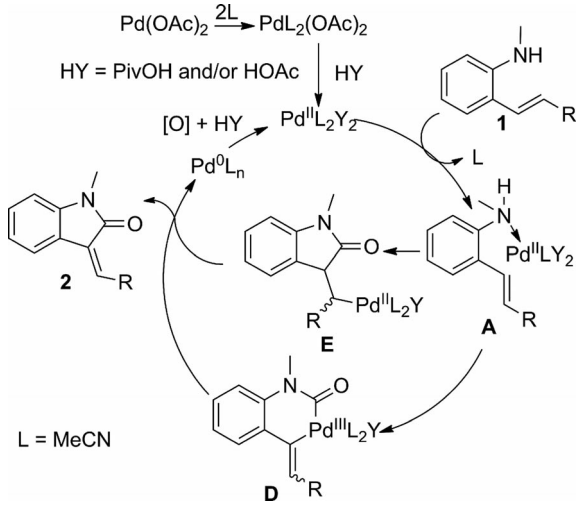
only the (*E*) isomer of **2q** in 63% yield [see Scheme 3, Equation (4)]. The selectivity of the reaction with substrate **1q** was elucidated by HRMS (high resolution mass spectrometry) analysis after 1 h of reaction time (see Figure S1 in Supporting Information). According to these results, the three Pd-containing intermediates **A**–**C** were involved (see Scheme 3), which implies that there is an interaction of the CN donor that is directed towards the palladium center.



Scheme 3. Control experiments.

Although product **2a** was obtained in 85% yield by using 5 equiv. of PivOH, the yield was reduced to 36% by using 0.1 equiv. of PivOH (see Table 1, Entries 12 and 13). Moreover, only 34% yield was obtained in the absence of the acids (see Table 1, Entry 5), and 78% yield was achieved in the presence of HOAc (see Table 1, Entry 1). These results imply that the acidic conditions favor the reaction by helping to remove the hydrogen atom of the amine and exchanging $^{-}$OAc from $PdL_2(OAc)_2$ with $PivO^{-}$ to make the Pd species more active and enhance the yields.

Consequently, the possible mechanism outlined in Scheme 4 is proposed on the basis of the present results and the reported mechanisms.[1–7] Initially, $Pd(OAc)_2$ coordinates with MeCN to yield the $PdL_2(OAc)_2$ complex (L = MeCN), and then an exchange with the acid HY (PivOH) leads to the more active PdL_2Y_2 species. The nitrogen atom in substrate **1** can readily complex with the PdL_2Y_2 species to afford intermediate **A**.[6,7] Subsequently, two of the following pathways may take place: (i) sequential reactions of the amine with CO and the insertion of the PdL_2Y_2 species into the vinyl C–H bond of intermediate **A** to give Pd^{III} intermediate **D**[7] or ii) sequential reactions of the amine with CO and an oxidative Heck reaction to form intermediate **E**.[6c] Finally, the reductive elimination of either intermediate **D** or **E** affords both product **2** and the Pd^0L_n species. The deuterium labeling experiment displayed in Scheme 3, Equation (3) does not support the latter pathway because no exchange takes place between the hydrogen and deuterium atoms.



Scheme 4. Possible mechanism.

Conclusions

In summary, we have illustrated a new, mild protocol for the synthesis of 3-methyleneindolin-2-ones by using a palladium-catalyzed intramolecular oxidative aminocarbonylation of alkenes with amines and CO at room temperature. This present method was achieved by the direct aminocarbonylation of the vinyl C(sp^2)–H bond and provides a new access to bioactive 3-methyleneindolin-2-ones.

Experimental Section

General Methods: All materials and solvents were purchased from commercial suppliers and used without additional purification. IR measurements were performed with a FTIR SHIMADZU DR-8000 spectrometer that was fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. The ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Bruker DRX-500 spectrometer (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) or a Bruker DRX-400 spectrometer (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz). The NMR samples were dissolved in $CDCl_3$ unless otherwise noted. High resolution mass spectra were recorded with a Bruker microTOF-QII (ESI) spectrometer. Preparative thin layer chromatography was performed on silica gel plates with PF254 indicator. Flash column chromatography was performed with silica gel 60N unless otherwise noted.

Typical Experimental Procedure for the Room-Temperature Palladium-Catalyzed Oxidative Intramolecular Aminocarbonylation: To a flask (10 mL) were added 2-vinylaniline **1** (0.3 mmol), $Pd(OAc)_2$ (5 mol-%), Ag_2CO_3 (2 equiv.), PivOH (5 equiv.), and MeCN (2 mL). Then, CO was bubbled through a tube into the mixture, and the reaction was stirred at room temperature for 12 h until there was complete consumption of starting material as monitored by TLC and/or GC–MS analysis. Upon completion, the reaction mixture was washed with brine, and the aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate, 5:1) to afford the desired product **2**. Caution: Carbon monoxide (CO) is a colorless, tasteless, and highly poisonous gas.

3-Benzylidene-1-methylindolin-2-one (2a):[31,8j] (*Z*/*E*, 1:1.3). Data for (*Z*) isomer: yellow solid; m.p. 95.4–96.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.5 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 2 H), 7.47–7.41 (m, 3 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 3.27 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 142.4, 137.0, 133.8, 131.9, 130.4, 128.9, 128.2, 126.1, 124.4, 121.8, 118.9, 107.8, 25.9 ppm. IR (KBr): $\tilde{\nu}$ = 1716, 1658, 1504 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 235 (100) $[M]^+$, 207 (18), 159 (42), 117 (9). Data for (*E*) isomer: yellow solid; m.p. 106.5–107.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.65–7.61 (m, 3 H), 7.48–7.41 (m, 3 H), 7.26 (t, *J* = 8.0 Hz, 1 H), 6.87 (t, *J* = 8.0 Hz, 1 H), 6.82 (d, *J* = 7.5 Hz, 1 H), 3.28 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4, 144.2, 137.1, 134.9, 129.7, 129.4, 129.3, 128.6, 127.2, 122.7, 121.7, 121.1, 108.1, 26.1 ppm. IR (KBr): $\tilde{\nu}$ = 1716, 1658, 1504 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 235 (100) $[M]^+$, 207 (21), 159 (45), 117 (12).

3-Benzylidene-1-butylindolin-2-one (2b): (*Z*/*E*, 2:1). Data for (*Z*) isomer: yellow solid; m.p. 171.6–173.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.5 Hz, 2 H), 7.54–7.53 (m, 2 H), 7.46–7.39 (m, 3 H), 7.29–7.26 (m, 1 H), 7.05 (t, *J* = 8.5 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 3.77 (t, *J* = 7.5 Hz, 2 H), 1.72–1.66 (m, 2 H), 1.45–1.39 (m, 2 H), 0.96 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0, 141.9, 137.0, 133.8, 131.9, 130.4, 128.8, 128.2, 126.2, 124.5, 121.6, 119.0, 108.1, 39.7, 29.7, 20.3, 13.8 ppm. IR (KBr): $\tilde{\nu}$ = 1763, 1629, 1546 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 277 (82) $[M]^+$, 234 (100), 206 (50), 178 (24). HRMS (ESI): calcd. for $C_{19}H_{20}NO$ $[M + H]^+$ 278.1556; found 278.1589. Data for (*E*) isomer: yellow solid; m.p. 158.7–159.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (s, 1 H), 7.65–7.61 (m, 3 H), 7.48–7.40 (m, 3 H), 7.26–7.23 (m, 1 H), 6.88–6.83 (m, 2 H), 3.79 (t, *J* = 7.5 Hz, 2 H), 1.73–1.67 (m, 2 H), 1.45–1.41 (m, 2 H), 0.97 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4, 143.7, 137.1, 135.1, 129.7, 129.4, 129.2, 128.6, 127.3, 122.8, 121.5, 121.3, 108.4, 39.8, 29.7, 20.2, 13.8 ppm. IR (KBr): $\tilde{\nu}$ = 1763, 1629, 1546 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 277 (85) $[M]^+$, 234 (100), 206 (48), 178 (26).

1-Benzyl-3-benzylideneindolin-2-one (2c):[31,8j] (*Z*/*E*, 1.2:1). Data for (*Z*) isomer: yellow solid; m.p. 187.3–188.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 7.5 Hz, 2 H), 7.59 (s, 1 H), 7.54 (d, *J* = 7.0 Hz, 1 H), 7.48–7.42 (m, 3 H), 7.34–7.28 (m, 4 H), 7.26–7.23 (m, 1 H), 7.18 (t, *J* = 7.0 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 4.99 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 141.5, 137.4, 136.2, 133.8, 132.0, 130.5, 128.8, 128.7, 128.3, 127.5, 127.3, 125.8, 124.4, 121.9, 119.0, 108.8, 43.6 ppm. IR (KBr): $\tilde{\nu}$ = 1759, 1644, 1576 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 311 (68) $[M]^+$, 206 (11), 165 (24), 91 (100). Data for (*E*) isomer: yellow solid; m.p. 153.6–154.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.67–7.62 (m, 3 H), 7.50–7.45 (m, 3 H), 7.35–7.30 (m, 4 H), 7.28–7.25 (m, 1 H), 7.14 (t, *J* = 8.0 Hz, 1 H), 6.84 (t, *J* = 8.0 Hz, 1 H), 6.72 (d, *J* = 8.0 Hz, 1 H), 5.00 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 143.3, 137.6, 136.0, 134.9, 132.0, 129.7, 129.6, 129.3, 128.8, 128.7, 128.6, 127.5, 127.3, 122.8, 121.8, 109.2, 43.7 ppm. IR (KBr): $\tilde{\nu}$ = 1759, 1644, 1576 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 311 (70) $[M]^+$, 206 (14), 165 (27), 91 (100).

1-Allyl-3-benzylideneindolin-2-one (2d): (*Z*/*E*, 1:1.1). Data for (*Z*) isomer: yellow solid; m.p. 157.4–158.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.0 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 2 H), 7.46–7.41 (m, 3 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 6.81 (d, *J* = 7.5 Hz, 1 H), 5.91–5.83 (m, 1 H), 5.26–5.20 (m, 2 H), 4.41 (d, *J* = 4.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7, 141.5, 137.3, 133.8, 131.9, 131.6, 130.5, 128.8, 128.2, 125.9, 124.4, 121.8, 119.0, 117.3, 108.6, 42.2 ppm. IR (KBr): $\tilde{\nu}$ = 1767, 1654, 1538 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 261 (100) $[M]^+$, 232 (15), 184 (27), 165 (38). HRMS (ESI): calcd. for $C_{18}H_{16}NO$ $[M + H]^+$ 262.1246; found 262.1258. Data for (*E*) isomer: yellow solid; m.p. 136.7–137.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (s, 1 H), 7.64 (t, *J* = 7.5 Hz, 3 H), 7.48–7.40 (m, 3 H), 7.25–7.21 (m, 1 H), 6.88–6.82 (m, 2 H), 5.91–5.85 (m, 1 H), 5.28–5.22 (m, 2 H), 4.43–4.42 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.1, 143.4, 137.3, 134.9, 131.6, 129.6, 129.5, 129.2, 128.6, 127.0, 122.8, 121.7, 121.2, 117.4, 109.0, 42.3 ppm. IR (KBr): $\tilde{\nu}$ = 1767, 1654, 1538 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 261 (100) $[M]^+$, 232 (18), 184 (30), 165 (41).

3-Benzylidene-1-(2-methylallyl)indolin-2-one (2e): (*Z*/*E*, 2:1). Data for (*Z*) isomer: yellow solid; m.p. 186.1–188.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.0 Hz, 2 H), 7.56 (s, 1 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.45–7.40 (m, 3 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 6.80 (d, *J* = 7.5 Hz, 1 H), 4.92 (s, 1 H), 4.87 (s, 1 H), 4.33 (s, 2 H), 1.75 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9, 141.8, 139.4, 137.3, 133.8, 132.0, 130.5, 128.8, 128.2, 125.8, 124.3, 121.8, 118.9, 112.2, 108.8, 45.6, 19.9 ppm. IR (KBr): $\tilde{\nu}$ = 1765, 1637, 1585 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 275 (100) $[M]^+$, 258 (49), 206 (19), 165 (30). HRMS (ESI): calcd. for $C_{19}H_{18}NO$ $[M + H]^+$ 276.1383; found 276.1386. Data for (*E*) isomer: yellow solid; m.p. 170.3–171.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.65 (t, *J* = 8.0 Hz, 3 H), 7.48–7.42 (m, 3 H), 7.23–7.20 (m, 1 H), 6.89–6.82 (m, 2 H), 4.95 (s, 1 H), 4.90 (s, 1 H), 4.35 (s, 2 H), 1.77 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 143.6, 139.2, 137.4, 135.0, 129.7, 129.5, 129.4, 128.6, 127.0, 122.7, 121.7, 121.1, 112.4, 109.2, 45.9, 19.9 ppm. IR (KBr): $\tilde{\nu}$ = 1765, 1637, 1585 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 275 (100) $[M]^+$, 258 (52), 206 (22), 165 (32).

1-Methyl-3-(4-methylbenzylidene)indolin-2-one (2h):[31,8j] (*Z*/*E*, 1.2:1). Data for (*Z*) isomer: yellow solid; m.p. 128.4–129.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.0 Hz, 2 H), 7.53–7.51 (m, 2 H), 7.29–7.25 (m, 3 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 6.80 (d, *J* = 7.5 Hz, 1 H), 3.28 (s, 3 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 142.1, 141.1, 137.2, 132.1, 131.2, 129.0, 128.5, 125.1, 124.6, 121.7, 118.7, 107.8, 25.9, 21.7 ppm. IR (KBr): $\tilde{\nu}$ = 1747, 1660, 1540 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 249 (100) $[M]^+$, 248 (79), 158 (49), 123 (17). Data for (*E*) isomer: yellow solid; m.p. 118.6–119.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.69 (d, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.26 (t, *J* = 8.0 Hz, 3 H), 6.89 (t, *J* = 8.0 Hz, 1 H), 6.82 (d, *J* = 7.5 Hz, 1 H), 3.28 (s, 3 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.6, 144.1, 139.9, 137.5, 132.0, 129.5, 129.4, 129.3, 126.4, 122.6, 121.7, 121.3, 108.1, 26.1, 21.5 ppm. IR (KBr): $\tilde{\nu}$ = 1747, 1660, 1540 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 249 (100) $[M]^+$, 248 (82), 158 (48), 123 (15).

3-(4-Bromobenzylidene)-1-methylindolin-2-one (2i):[12a] (*Z*/*E*, 1:1.3). Data for (*Z*) isomer: yellow solid; m.p. 144.3–145.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.43 (s, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 7.06 (t, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 3.27 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 142.4, 135.4, 133.4, 132.7, 131.5, 129.2, 126.7, 124.9, 124.1, 121.9, 119.0, 108.0, 25.9 ppm. IR (KBr): $\tilde{\nu}$ = 1759, 1645, 1536 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 315 (88) $[M + 2]^+$, 313 (88) $[M]^+$, 158 (100), 117 (51). Data for (*E*) isomer: yellow solid; m.p. 121.5–122.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.61–7.55 (m, 3 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.83 (t, *J* = 8.0 Hz, 1 H), 3.28 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.3, 144.4, 135.5, 133.9, 131.9, 130.8,

130.1, 127.8, 123.7, 122.7, 121.9, 120.9, 108.3, 26.2 ppm. IR (KBr): $\tilde{\nu}$ = 1759, 1645, 1536 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 315 (86) $[M + 2]^+$, 313 (86) $[M]^+$, 158 (100), 117 (55).

1-Methyl-3-(4-nitrobenzylidene)indolin-2-one (2j):[12a] (*Z*/*E*, 1.6:1). Data for (*Z*) isomer: red solid; m.p. 187.6–189.1 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.5 Hz, 2 H), 8.26 (d, *J* = 7.0 Hz, 2 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.51 (s, 1 H), 7.35 (t, *J* = 7.0 Hz, 1 H), 7.09 (t, *J* = 7.5 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 3.27 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.6, 147.9, 143.0, 139.8, 133.0, 132.2, 130.2, 129.6, 123.4, 123.3, 122.2, 119.7, 108.3, 26.0 ppm. IR (KBr): $\tilde{\nu}$ = 1788, 1675, 1569 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 280 (24) $[M]^+$, 250 (41), 207 (100), 158 (26). Data for (*E*) isomer: red solid; m.p. 167.6–168.5 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 9.0 Hz, 2 H), 7.80–7.78 (m, 3 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 6.90 (t, *J* = 8.0 Hz, 1 H), 6.85 (d, *J* = 7.5 Hz, 1 H), 3.29 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.7, 147.9, 144.8, 141.8, 133.3, 130.9, 130.0, 129.9, 124.0, 122.9, 122.1, 120.3, 108.6, 26.3 ppm. IR (KBr): $\tilde{\nu}$ = 1788, 1675, 1569 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 280 (26) $[M]^+$, 250 (45), 207 (100), 158 (28).

3-(3-Chlorobenzylidene)-1-methylindolin-2-one (2k): (*Z*/*E*, 1.3:1). Data for (*Z*) isomer: yellow solid; m.p. 106.9–108.4 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.35 (s, 1 H), 8.14–8.12 (m, 1 H), 7.51 (d, *J* = 7.5 Hz, 1 H), 7.44 (s, 1 H), 7.39–7.35 (m, 2 H), 7.31 (t, *J* = 7.5 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 6.82 (d, *J* = 7.5 Hz, 1 H), 3.28 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9, 142.6, 135.4, 135.0, 134.1, 131.4, 130.2, 129.9, 129.4 (2 C), 127.4, 124.0, 122.0, 119.1, 108.0, 26.0 ppm. IR (KBr): $\tilde{\nu}$ = 1745, 1689, 1539 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 271 (34) $[M + 2]^+$, 269 (99) $[M]^+$, 204 (21), 158 (100), 117 (23). HRMS (ESI): calcd. for $C_{16}H_{13}ClNO$ $[M + H]^+$ 270.0680; found 270.0681. Data for (*E*) isomer: yellow solid; m.p. 80.4–81.6 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.76 (s, 1 H), 7.61 (s, 1 H), 7.54–7.50 (m, 2 H), 7.41–7.40 (m, 2 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 6.90 (t, *J* = 7.5 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 3.28 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.2, 144.5, 136.8, 135.0, 134.7, 130.2, 130.0, 129.4, 129.0, 128.3, 127.3, 122.8, 122.0, 120.7, 108.3, 26.2 ppm. IR (KBr): $\tilde{\nu}$ = 1745, 1689, 1539 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 271 (36) $[M + 2]^+$, 269 (96) $[M]^+$, 204 (25), 158 (100), 117 (26).

3-(3-Methoxybenzylidene)-1-methylindolin-2-one (2l): (*Z*/*E*, 1.3:1). Data for (*Z*) isomer: yellow solid; m.p. 106.9–108.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 8.64 (d, *J* = 8.0 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.36–7.26 (m, 2 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 3.92 (s, 3 H), 3.28 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 159.5, 142.3, 137.1, 135.2, 129.1, 128.9, 126.2, 125.2, 124.4, 121.8, 118.9, 117.6, 115.8, 107.9, 55.5, 26.0 ppm. IR (KBr): $\tilde{\nu}$ = 1745, 1689, 1539 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 271 (34) $[M + 2]^+$, 269 (99) $[M]^+$, 204 (21), 158 (100), 117 (23). HRMS (ESI): calcd. for $C_{16}H_{13}ClNO$ $[M + H]^+$ 270.0680; found 270.0681. Data for (*E*) isomer: yellow solid; m.p. 80.4–81.6 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.21–7.15 (m, 2 H), 7.08 (s, 1 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 6.81 (t, *J* = 8.0 Hz, 1 H), 6.75 (t, *J* = 8.0 Hz, 1 H), 3.76 (s, 3 H), 3.20 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 159.6, 144.2, 137.0, 136.2, 129.8, 129.7, 127.3, 122.9, 121.8, 121.7, 121.1, 115.4, 114.2, 108.1, 55.3, 26.1 ppm. IR (KBr): $\tilde{\nu}$ = 1745, 1689, 1539 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 271 (36) $[M + 2]^+$, 269 (96) $[M]^+$, 204 (25), 158 (100), 117 (26).

1-Methyl-3-(naphthalen-2-ylmethylene)indolin-2-one (2m): (*Z*/*E*, 1.8:1). Data for (*Z*) isomer: yellow solid; m.p. 213.4–215.2 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 8.46 (d, *J* = 8.0 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.85–7.80 (m, 2 H), 7.61 (s, 1 H), 7.52–7.45 (m, 3 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 6.76 (d, *J* = 7.5 Hz, 1 H), 3.24 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 142.2, 137.0, 134.1, 133.0, 132.9, 131.5, 129.1, 128.8, 128.6, 127.6, 127.5, 127.4, 126.2, 126.0, 124.4, 121.8, 118.8, 107.8, 25.9 ppm. IR (KBr): $\tilde{\nu}$ = 1749, 1648, 1563 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 285 (100) $[M]^+$, 207 (16), 158 (35), 142 (15). HRMS (ESI): calcd. for $C_{20}H_{16}NO$ $[M + H]^+$ 286.1226; found 286.1229. Data for (*E*) isomer: yellow solid; m.p. 178.6–181.5 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 8.00 (s, 1 H), 7.92–7.85 (m, 3 H), 7.72 (d, *J* = 8.5 Hz, 1 H), 7.68–7.66 (m, 1 H), 7.55–7.53 (m, 2 H), 7.28–7.25 (m, 1 H), 6.88–6.82 (m, 2 H), 3.30 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.5, 144.3, 137.1, 133.6, 133.0, 132.4, 129.8, 129.3, 128.4, 128.2, 127.8, 127.3, 127.2, 126.7, 126.4, 122.7, 121.8, 121.2, 108.2, 26.2 ppm. IR (KBr): $\tilde{\nu}$ = 1749, 1648, 1563 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 285 (100) $[M]^+$, 207 (18), 158 (37), 142 (19).

(*E*)-1-Methyl-3-(pyridin-2-ylmethylene)indolin-2-one (2n):[12b] Yellow solid; m.p. 113.7–114.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.00 (d, *J* = 7.5 Hz, 1 H), 8.85 (d, *J* = 4.5 Hz, 1 H), 7.76 (t, *J* = 8.0 Hz, 1 H), 7.72 (s, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.33–7.27 (m, 2 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 3.28 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.0, 153.8, 149.5, 144.8, 136.5, 134.4, 130.4, 129.1, 127.8, 123.5, 122.1 (2 C), 121.5, 107.6, 26.2 ppm. IR (KBr): $\tilde{\nu}$ = 1764, 1655, 1534 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 236 (70) $[M]^+$, 208 (64), 158 (100), 130 (40).

3-Heptylidene-1-methylindolin-2-one (2o): (*Z*/*E*, 1:1). Data for mixture of (*Z*) and (*E*) isomers: yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 4.0 Hz, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.07–7.02 (m, 2 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 3.24 (s, 3 H), 2.70–2.65 (m, 2 H), 1.68–1.62 (m, 2 H), 1.46–1.39 (m, 2 H), 1.33–1.31 (m, 4 H), 0.89 (t, *J* = 4.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.0, 143.6, 142.4, 128.7, 127.5, 123.4, 122.4, 122.0, 108.0, 31.6, 29.4, 29.2, 28.6, 26.0, 22.6, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 1749, 1648, 1563 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 243 (91) $[M]^+$, 174 (90), 161 (100), 145 (62). HRMS (ESI): calcd. for $C_{16}H_{22}NO$ $[M + H]^+$ 244.1696; found 244.1688.

Butyl 2-(1-Methyl-2-oxoindolin-3-ylidene)acetate (2p):[13] (*Z*/*E*, 1:1.4). Data for (*Z*) isomer: yellow solid; m.p. 162.5–163.7 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.5 Hz, 1 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 6.99 (t, *J* = 7.5 Hz, 1 H), 6.62 (d, *J* = 7.5 Hz, 1 H), 4.68 (s, 1 H), 4.17–4.13 (m, 1 H), 4.00–3.96 (m, 1 H), 3.04 (s, 3 H), 1.50–1.43 (m, 2 H), 1.22–1.19 (m, 2 H), 0.83 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.2, 170.4, 144.2, 132.4, 129.4, 125.8, 125.3, 122.8, 122.5, 107.6, 64.6, 30.5, 26.0, 18.8, 13.6 ppm. IR (KBr): $\tilde{\nu}$ = 1718, 1654, 1571 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 259 (43) $[M]^+$, 186 (55), 159 (100), 130 (54). Data for (*E*) isomer: yellow solid; m.p. 184.8–185.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 7.5 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.91 (s, 1 H), 6.79 (d, *J* = 7.5 Hz, 1 H), 4.27 (t, *J* = 6.5 Hz, 2 H), 3.23 (s, 3 H), 1.75–1.69 (m, 2 H), 1.49–1.41 (m, 2 H), 0.97 (t, *J* = 6.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.6, 165.8, 145.9, 137.8, 132.4, 128.7, 122.8, 122.5, 119.8, 108.1, 65.0, 30.6, 26.2, 19.1, 13.7 ppm. IR (KBr): $\tilde{\nu}$ = 1718, 1654, 1571 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 259 (41) $[M]^+$, 186 (52), 159 (100), 130 (52).

(*E*)-2-(1-Methyl-2-oxoindolin-3-ylidene)acetonitrile (2q):[14] Yellow solid; m.p. 232.7–233.4 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.13 (t, *J* = 7.5 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 6.32 (s, 1 H), 3.23 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.2, 145.6, 143.5, 133.7, 124.9, 123.2, 119.2, 116.1, 108.8, 97.5, 26.3 ppm. IR (KBr): $\tilde{\nu}$ = 1756,

1672, 1569 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 184 (100) $[M]^+$, 155 (96), 130 (34), 114 (19).

3-Benzylidene-1,5-dimethylindolin-2-one (2r): (*Z*/*E*, 1.5:1). Data for (*Z*) isomer: yellow solid; m.p. 143.5–145.1 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.5 Hz, 2 H), 7.50 (s, 1 H), 7.46–7.40 (m, 3 H), 7.34 (s, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 6.69 (d, *J* = 7.5 Hz, 1 H), 3.24 (s, 3 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.2, 140.2, 136.6, 133.9, 131.9, 131.2, 130.3, 129.3, 128.2, 126.3, 124.3, 119.7, 107.6, 25.9, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 1776, 1653, 1586 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 249 (100) $[M]^+$, 220 (27), 172 (64), 123 (26). HRMS (ESI): calcd. for $C_{17}H_{16}NO$ $[M + H]^+$ 250.1226; found 250.1231. Data for (*E*) isomer: yellow solid; m.p. 127.1–128.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.64 (d, *J* = 7.5 Hz, 2 H), 7.49–7.42 (m, 4 H), 7.07 (d, *J* = 7.5 Hz, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 3.26 (s, 3 H), 2.22 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.5, 142.1, 136.8, 135.1, 131.1, 130.1, 129.4, 129.3, 128.6, 127.4, 123.4, 121.1, 107.9, 26.2, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 1776, 1653, 1586 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 249 (100) $[M]^+$, 220 (29), 172 (67), 123 (28).

3-Benzylidene-6-chloro-1-methylindolin-2-one (2s):[8j] (*Z*/*E*, 1.2:1). Data for (*Z*) isomer: yellow solid; m.p. 167.3–168.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.29–8.27 (m, 2 H), 7.45–7.41 (m, 5 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 6.66 (d, *J* = 8.0 Hz, 1 H),3.20 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 140.6, 138.4, 133.4, 132.1, 130.9, 128.3, 128.3, 127.2, 125.7, 125.0, 119.3, 108.7, 26.0 ppm. IR (KBr): $\tilde{\nu}$ = 1765, 1643, 1556 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 271 (34) $[M + 2]^+$, 269 (100) $[M]^+$, 268 (66), 192 (58), 164 (22). Data for (*E*) isomer: yellow solid; m.p. 152.6–153.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.62–7.58 (m, 3 H), 7.51–7.45 (m, 3 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 3.26 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 142.6, 138.8, 134.4, 130.0, 129.3, 129.2, 128.8, 127.0, 126.2, 122.7, 122.4, 108.9, 26.2 ppm. IR (KBr): $\tilde{\nu}$ = 1765, 1643, 1556 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 271 (36) $[M + 2]^+$, 269 (100) $[M]^+$, 268 (69), 192 (55), 164 (23).

(*Z*)-3-Benzylidene-5,7-dichloro-1-methylindolin-2-one (2t): (*Z*/*E*, 1.4:1). Data for (*Z*) isomer: yellow solid; m.p. 193.7–194.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.28–8.26 (m, 2 H), 7.46–7.43 (m, 4 H), 7.31 (s, 1 H), 7.15 (s, 1 H), 3.57 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 139.5, 136.5, 133.1, 132.4, 131.4, 129.9, 128.3, 127.9, 127.1, 123.8, 117.6, 115.6, 29.0 ppm. IR (KBr): $\tilde{\nu}$ = 1787, 1608, 1512 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 306 (19) $[M + 3]^+$, 305 (69) $[M + 2]^+$, 304 (68) $[M + 1]^+$, 303 (100) $[M]^+$, 302 (85), 226 (49), 134 (24). HRMS (ESI): calcd. for $C_{16}H_{12}Cl_2NO$ $[M + H]^+$ 304.0362; found 304.0364. Data for (*E*) isomer: yellow solid; m.p. 176.5–177.9 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H), 7.58–7.56 (m, 2 H), 7.51–7.46 (m, 4 H), 7.19 (s, 1 H), 3.65 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 140.2, 138.6, 134.1, 130.9, 130.2, 129.1, 128.9, 127.1, 125.4, 124.8, 121.2, 116.0, 29.7 ppm. IR (KBr): $\tilde{\nu}$ = 1787, 1608, 1512 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 306 (16) $[M + 3]^+$, 305 (65) $[M + 2]^+$, 304 (70) $[M + 1]^+$, 303 (100) $[M]^+$, 302 (82), 226 (46), 134 (20).

5-Acetyl-3-benzylidene-1-methylindolin-2-one (2u): (*Z*/*E*, 1:2.5). Data for mixture of (*Z*) and (*E*) isomers: yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.0 Hz, 0.55 H), 8.27 (s, 0.71 H), 8.18 (s, 0.28 H), 7.94 (d, *J* = 9.0 Hz, 1.65 H), 7.67 (d, *J* = 7.0 Hz, 1.73 H), 7.51–7.46 (m, 3 H), 6.89–6.85 (m, 1 H), 3.33 (s, 3 H), 2.63 (s, 0.86 H), 2.44 (s, 2.16 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.9, 196.5, 168.8, 147.9, 146.0, 138.9, 134.4, 133.5, 132.2, 131.5, 131.4, 131.0, 130.9, 130.4, 130.2, 129.4, 128.8, 128.4, 126.2, 124.7, 124.6, 123.0, 121.1, 118.8, 107.8, 107.2, 26.4, 26.2 ppm. IR (KBr): $\tilde{\nu}$ = 1787, 1608, 1512 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 277 (62) $[M]^+$, 262 (100), 207 (23), 165 (17). HRMS (ESI): calcd. for $C_{18}H_{16}NO_2$ $[M + H]^+$ 278.1237; found 278.1241.

(*E*)-1-Methyl-3-(1-Phenylethylidene)indolin-2-one (2v):.[15] Yellow solid; m.p. 161.4–162.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.44 (m, 3 H), 7.29–7.26 (m, 3 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 6.75 (d, *J* = 7.6 Hz, 1 H), 6.63 (t, *J* = 7.6 Hz, 1 H), 6.13 (d, *J* = 7.6 Hz, 1 H), 3.28 (s, 3 H), 2.81 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 154.9, 143.0, 142.3, 129.2, 128.3, 128.1, 126.5, 123.4, 122.8, 122.6, 121.3, 107.4, 25.7, 22.9 ppm. IR (KBr): $\tilde{\nu}$ = 1758, 1674, 1565 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 249 (100) $[M]^+$, 172 (21), 132 (59), 117 (28).

3-(Diphenylmethylene)-1-methylindolin-2-one (2w):[15] Yellow solid; m.p. 214.6–215.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 3 H), 7.37–7.31 (m, 7 H), 7.15 (t, *J* = 7.5 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.68 (t, *J* = 7.5 Hz, 1 H), 6.42 (d, *J* = 7.5 Hz, 1 H), 3.20 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 154.5, 143.3, 141.3, 139.9, 129.9, 129.3, 129.1, 129.0, 128.9, 128.7, 127.8, 124.2, 123.2, 123.1, 121.3, 107.6, 25.8 ppm. IR (KBr): $\tilde{\nu}$ = 1758, 1674, 1565 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 311 (98) $[M]^+$, 310 (100), 234 (30), 165 (16).

1,1′-Dimethyl-[3,3′-biindolinylidene]-2,2′-dione (2x):[11a,11b] Yellow solid; m.p. 173.6–175.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.21 (d, *J* = 8.0 Hz, 2 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.07 (t, *J* = 7.6 Hz, 2 H), 6.78 (d, *J* = 7.6 Hz, 2 H), 3.29 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 145.2, 133.4, 132.4, 129.8, 122.4, 121.6, 107.6, 26.1 ppm. IR (KBr): $\tilde{\nu}$ = 1784, 1683, 1552 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 290 (100) $[M]^+$, 262 (43), 233 (45), 207 (38).

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for indolin-2-one products **2**.

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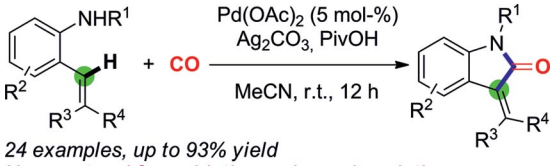

A general, room-temperature route to 3-methyleneindolin-2-ones is presented that is achieved by a palladium-catalyzed intramolecular oxidative aminocarbonylation of vinylic C(sp^2)–H bonds with amines and CO.

Keywords: Nitrogen heterocycles / Palladium / Carbonylation / Amines / Reaction mechanisms

