Stereoselective Synthesis of (*E*)-3-(Methoxycarbonyl)methylene-1,3-dihydroindol-2-ones by Palladium-Catalyzed Oxidative Carbonylation of 2-Ethynylanilines

Bartolo Gabriele,*[a] Giuseppe Salerno,*[a] Lucia Veltri,[a] Mirco Costa,[b] and Chiara Massera[c]

Keywords: Stereoselective synthesis / Carbonylations / Nitrogen heterocycles / Palladium

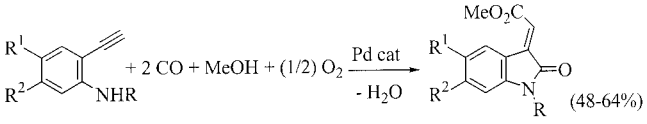
A direct synthesis of (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones **2** by palladium-catalyzed oxidative carbonylation of 2-ethynylanilines **1** is reported. Reactions were carried out in MeOH as the solvent at 50–70 °C in the presence of catalytic amounts of PdI_2 in conjunction with KI under a 4:1 CO/air mixture (20 atm total pressure at 25 °C). When the reaction was applied to 2-alkynylanilines with internal triple bonds, the reaction course changed completely, with formation of carbamates **4**.

Introduction

Palladium-catalyzed oxidative cyclocarbonylation of a substrate bearing a suitably placed nucleophilic group represents an efficient and versatile approach to the one-step synthesis of functionalized heterocycles.[1] We have recently applied our oxidative carbonylation procedure[2] to syntheses of β-lactones,[3,4] γ-lactones,[4] β- and γ-lactams,[5] nitrogen heterocycles,[6] and oxazolidin-2-ones,[7] starting from readily available substrates. We now wish to report a new application of the oxidative carbonylation methodology that allows easy access to 1,3-dihydroindol-2-one derivatives, starting from readily available 2-ethynylanilines.

Results and Discussion

Oxidative carbonylation reactions of 2-ethynylanilines **1** were carried out in MeOH at 50−70 °C in the presence of PdI_2 ($2\cdot10^{-3}-5\cdot10^{-3}$ equiv.) and KI (0.2−0.5 equiv.) under a 4:1 CO/air mixture (20 atm total pressure at 25 °C) and afforded (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones **2** in fair yields [48−64%, Equation (1)]. Lower yields of **2** were consistently obtained if a KI/PdI_2 molar ratio of 10 was used[2] rather than 100. The (*E*) configuration around the double bond of **2a** was confirmed by single-crystal X-ray analysis (Figure 1), the torsion angle C(8)−C(7)−C(9)−C(10) being 179.2(2)°.



1a R = R^1 = R^2 = H
1b R = Bn, R^1 = R^2 = H
1c R = Bu, R^1 = R^2 = H
1d R = H, R^1 = Me, R^2 = H
1e R = H, R^1 = Cl, R^2 = H
1f R = R^1 = H, R^2 = Cl

2a R = R^1 = R^2 = H
2b R = Bn, R^1 = R^2 = H
2c R = Bu, R^1 = R^2 = H
2d R = H, R^1 = Me, R^2 = H
2e R = H, R^1 = Cl, R^2 = H
2f R = R^1 = H, R^2 = Cl

(1)

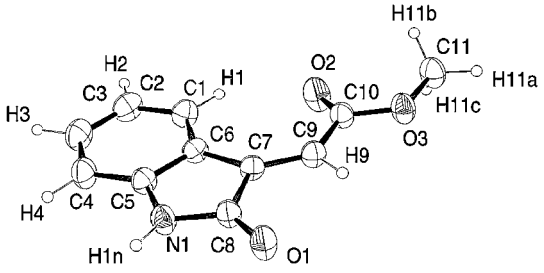


Figure 1. A perspective view and labeling scheme for **2a**; selected bond lengths [Å] and angles [°]: C(5)−N(1) 1.399(2), C(7)−C(9) 1.328(2), C(7)−C(8) 1.521(2), C(8)−O(1) 1.224(2), C(8)−N(1) 1.348(2), C(9)−C(10) 1.474(2), C(10)−O(2) 1.188(2), C(10)−O(3) 1.340(2), C(11)−O(3) 1.439(2), H(1)−O(2) 2.22(2), C(1)···O(2) 3.00(3); C(9)−C(7)−C(6) 136.94(15), C(9)−C(7)−C(8) 118.34(14), C(6)−C(7)−C(8) 104.70(14), C(7)−C(9)−C(10) 127.19(16), C(7)−C(9)−H(9) 118.0(11), C(10)−C(9)−H(9) 114.8(11), O(2)−C(10)−O(3) 123.16(16), O(2)−C(10)−C(9) 126.54(16), O(3)−C(10)−C(9) 110.30(15), C(10)−O(3)−C(11) 115.14(15), C(1)−H(1)···O(2) 134(2)

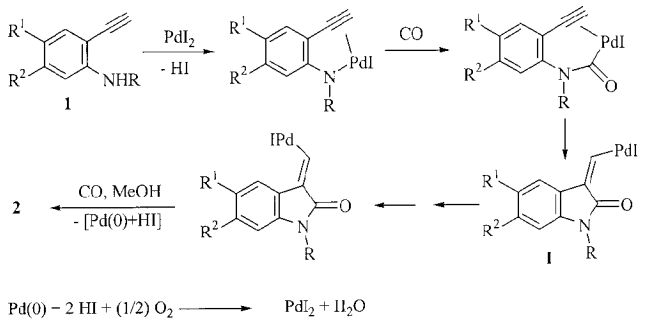
[a] Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy
Fax: (internat.) + 39-0984/492044
E-mail: b.gabriele@unical.it
g.salerno@unical.it
[b] Dipartimento di Chimica Organica e Industriale, Università di Parma, Parco Area delle Scienze, 43100 Parma, Italy
[c] Dipartimento di Chimica Generale e Inorganica Chimica Analitica Chimica Fisica, Università degli Studi di Parma, Centro di studio per la Strutturistica Diffrattometrica del CNR, Parco Area delle Scienze 17A, 43100 Parma, Italy

  1434−193X/01/1224−4607 $ 17.50+.50/0

The 1,3-dihydroindol-2-one moiety is planar, with displacements of the atoms from the least-square plane passing through the nitrogen atom ranging from −0.037(2) to 0.032(2) Å. The bond lengths and angles in the (methoxycarbonyl)methylene fragment indicate extended π-electron delocalization in the C−C−C(O)−O moiety, with significant double bond character in the C(7)−C(9) and C(10)−O(2) bonds. The maximum deviation from the mean plane of the molecule is 0.163(2) Å for O(2). The (*E*) configuration may be stabilized by the intramolecular H(1)···O(2) hydrogen bond. The (*E*) configurations in **2b**−**f** were assigned by comparison of the chemical shifts of the olefinic protons in **2b**−**f** with that of the same proton in **2a**.

Representative results obtained with different ethynylanilines are collected in Table 1. At 70 °C, catalytic efficiencies from 240 to 300 mol of **2** per mol of catalyst used were achieved, with yields of **2** ranging from 48 to 60% (Runs 1, 5, 6). With some substrates, however, better yields of **2** were obtained if the reaction temperature was reduced to 50 °C; the substrate/catalyst molar ratio in such cases was reduced from 500 to 200, in order to compensate for the lower reaction rate at this temperature (Runs 2−4). Small amounts (4%) of methyl [(2-benzylamino)phenyl]propynoate (**3b**), deriving from oxidative monoalkoxycarbonylation of the triple bond, were also detected in the reaction mixture deriving from **1b**.

species, which then inserts into the triple bond (Scheme 1, anionic iodide ligands are omitted for clarity).



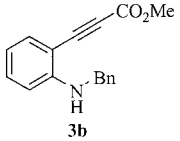
Scheme 1

Formation of an I−Pd−CO_2Me species by reaction between PdI_2, CO, and MeOH followed by triple-bond insertion is another possibility, however (Scheme 2). In any case, triple bond insertion is expected to be *syn*,[2,8] to give vinylpalladium intermediates **I**, **II**, or **III** with (*Z*) stereochemistry. Stereospecific carbonylation of these intermediates would still afford a product with (*Z*) configuration at the double bond, in contrast with the (*E*) stereochemistry actually observed, but no formation of (*Z*) isomers of **2** was

Table 1. Synthesis of (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones **2** by oxidative carbonylation of 2-ethynylanilines **1** in MeOH in the presence of PdI_2 and KI (KI/PdI_2 molar ratio = 100), *p*(CO) = 16 atm, *p*(air) = 4 atm, substrate conc. 0.22 mmol/mL MeOH, *t* = 15 h

Run	**1**	R	R^1	R^2	mol **1**/mol PdI_2	*T* [°C]	Yield of 2 (%)[a]	mol **2**/mol PdI_2
1	**1a**	H	H	H	500	70	60 (53)	300
2	**1b**	Bn	H	H	200	50	55 (50)[b]	110
3	**1c**	Bu	H	H	200	50	49 (45)	98
4	**1d**	H	Me	H	200	50	64 (58)	128
5	**1e**	H	Cl	H	500	70	56 (50)	280
6	**1f**	H	H	Cl	500	70	48 (42)	240

[a] GLC yield (isolated yield) based on starting **1**. Substrate conversion was practically quantitative in all cases. [b] Methyl [(2-benzylamino)-phenyl]propynoate **3b** (4%) was also present in the reaction mixture.



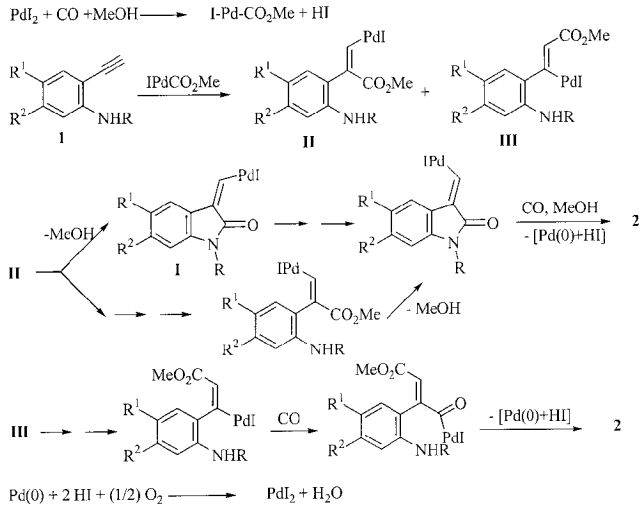
3b

Both ethynylanilines bearing primary amino groups (Runs 1, 4−6) and those bearing secondary amino groups (Runs 2−3) could be used successfully. The reaction did have some limitations, however, since it did not work for substrates bearing strong π-acceptor substituents on the ring (R^1 or R^2 = CN or CO_2Me, for example).

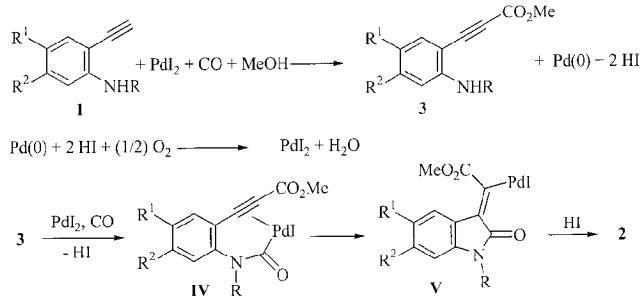
In analogy with what we had previously proposed for the oxidative carbonylation of alkynols to α-(methoxycarbonyl)-methylene-β- and -γ-lactones,[4] formation of **2** can be interpreted as occurring by formation of a carbamoylpalladium

observed even at very low levels of substrate conversion. This result, however, does not rule out the possibility that (*Z*) isomers are formed first, followed by a fast thermal (*Z*) → (*E*) isomerization to give **2**. Isomerization at the vinylpalladium intermediate level (**I**, **II**, or **III**) may also take place. While such an isomerization process is surely possible,[9−14] the occurrence of *complete* isomerization appears rather striking.

A possible alternative mechanism for the formation of **2**, which would directly produce the observed stereochemistry without need of an isomerization step, is shown in Scheme 3. Initial monoalkoxycarbonylation of the triple bond[15] to give **3** might be followed by the intramolecular *syn* triple-bond insertion into the carbamoylpalladium species **IV** formed, as usual, by the reaction between the −NHR group, CO, and PdI_2. The catalytic cycle would ter-



Scheme 2

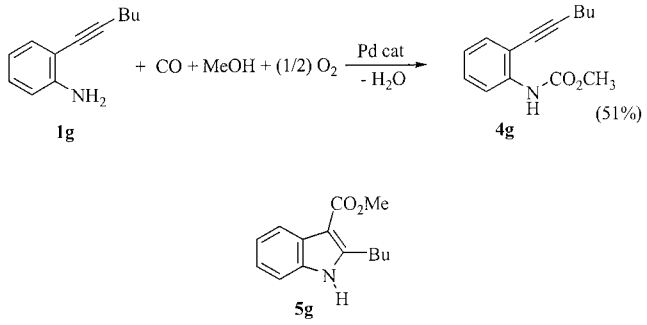


Scheme 3

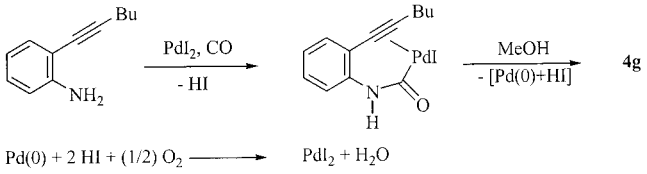
minate with protonolysis of the resulting (methoxycarbonyl)vinylpalladium intermediate **V**.

In order to test the likelihood of such a mechanism, we allowed product **3b** (isolated from the reaction mixture deriving from **1b**) to react under the reaction conditions, and recovered it unchanged. Accordingly, the mechanistic pathway depicted in Scheme 3 does not play a significant role in this reaction. Isomerization of a (*Z*)-vinylpalladium intermediate (**I**, **II**, or **III**) into the corresponding (*E*) isomer followed by methoxycarbonylation (Schemes 1, 2) therefore appears to be a likely explanation for the stereoselective formation of products **2**. It is possible that the (*Z*) → (*E*) isomerization is driven either by a greater stability of the (*E*)-vinylpalladium complex with respect to the (*Z*) isomer or by a higher level of difficulty experienced by the latter in inserting CO.

A different reaction course was followed by substrates bearing internal triple bonds, such as 2-(hex-1-ynyl)aniline (**1g**), which under the usual conditions afforded methyl [2-(hex-1-ynyl)phenyl]carbamate (**4g**) in 51% isolated yield [Equation (2)]. The result shown in Equation (2) is also completely different from that previously obtained in the oxidative carbonylation of **1g** using $PdCl_2$, $CuCl_2$, NaOAc, and K_2CO_3, which provided methyl 2-butyl-1*H*-indole-3-carboxylate (**5g**) in 30% yield.[16]



A possible explanation for the different behavior shown by alkynylanilines such as **1g** with respect to ethynylanilines **1a**−**f** might be as follows. It is likely that triple-bond insertion into the carbamoylpalladium bond is more difficult in the presence of a substituent on the triple bond. This fits with our previous observation that internal alkynes are considerably less reactive than terminal alkynes in PdI_2/KI-catalyzed oxidative dialkoxycarbonylation to give maleic diesters.[2] Consequently, the carbamoylpalladium species may directly undergo nucleophilic displacement by methanol, with formation of **4g** (Scheme 4).



Scheme 4

The reaction reported here is the first example of the synthesis of (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones by a cyclocarbonylation approach. Product **2a** and its corresponding ethyl ester have previously been prepared by Wittig reaction between isatin and the appropriate [(alkoxycarbonyl)methylene]triphenylphosphorane.[17−19] It is noteworthy that even this reaction was completely stereoselective, formation of (*Z*)-3-(alkoxycarbonyl)methylene-1,3-dihydroindol-2-ones consistently not being observed. Compound **2a** (and the corresponding ethyl ester) has found application as a substrate in cycloaddition reactions providing spiro compounds,[18−30] some of which proved useful as intermediates for the synthesis of biologically active molecules.[18,19,21,22,26,28]

Experimental Section

General: Melting points were determined with a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyzer Mod. 1106. ^{1}H NMR and ^{13}C NMR spectra were taken with a Bruker AC300 spectrometer with Me_4Si as internal standard and recorded at 300 MHz and 75 MHz, respectively. Chemical shifts and coupling constants (*J*) are given in ppm (δ) and in Hz, respectively. IR spectra were taken with a Perkin−Elmer Paragon 1000 PC FT-IR spectrometer. Mass spectra were obtained using an HP 5972A GC-

MS apparatus at 70 eV ionization voltage. All reactions were analyzed by TLC on silica gel 60 F_{254} or by GLC using a Shimadzu GC-14A gas chromatograph and capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70−230 mesh).

Preparation of Substrates: Starting materials 2-iodoaniline, 4-methylaniline, 4-chloroaniline, 4-cyanoaniline, methyl 4-aminobenzoate, 4-chloro-3-nitrobenzoic acid, hex-1-yne, benzyl chloride, butyl bromide, trimethylsilylacetylene, and 4-chloro-2-nitroaniline were commercially available and were used without further purification. 2-Ethynylaniline (**1a**) was prepared as described by Cacchi [31]. The same procedure was employed for the preparation of substituted 2-ethynylanilines, starting from the corresponding 2-iodoanilines. 2-(Hex-1-ynyl)aniline (**1g**) was prepared as described in the literature.[32]

***N*-Benzyl-2-ethynylaniline (1b):** This compound was prepared from *N*-benzyl-2-iodoaniline.[33] Yield 1.73 g from 3.0 g of *N*-benzyl-2-iodoaniline (86%). Brown solid, m.p. 36−38 °C. IR (KBr): $\tilde{\nu}$ = 3415 (w), 3290 (m), 3030 (w), 2095 (w), 1601 (m), 1576 (m), 1509 (s), 1452 (m), 1324 (m), 1162 (w), 751 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.41−7.22 (m, 6 H, $CH_2C_6H_5$ + H-3) 7.19−7.11 (m, 1 H, H-5), 6.65−6.58 (m, 1 H, H-4), 6.54 (d, *J* = 8.3, 1 H, H-6), 5.08 (br. s, 1 H, NH), 4.40 (d, *J* = 5.4, 2 H, CH_2Ph), 3.38 (s, 1 H, ≡CH). ^{13}C NMR ($CDCl_3$): δ = 149.34, 138.94, 132.66, 130.39, 128.67, 127.24, 127.16, 116.42, 109.87, 106.23, 83.00, 80.73, 47.59. MS: *m*/*z* = 207 (99) [M^+], 206 (89), 204 (11), 130 (57), 128 (12), 91 (100), 89 (15), 77 (16), 65 (27), 63 (16), 51 (17). $C_{15}H_{13}N$: calcd. C 86.92, H 6.32, N 6.76; found C 87.05, H 6.28, N 6.67.

***N*-Butyl-2-iodoaniline:** This compound was prepared as described in ref.[34] Yield 5.05 g from 6.0 g of 2-iodoaniline (67%, ref.[34] 78%). Yellow oil. IR (film): $\tilde{\nu}$ = 3394 (m), 2955 (s), 2927 (s), 2869 (m), 1590 (s), 1507 (s), 1451 (m), 1317 (m), 1004 (m), 739 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.62 (dd, *J* = 7.8, 1.5, 1 H, H-3), 7.17 (ddd, *J* = 8.3, 7.3, 1.5, 1 H, H-5), 6.52 (dd, *J* = 8.3, 1.5, 1 H, H-6), 6.39 (ddd, *J* = 7.8, 7.3, 1.5, 1 H, H-4), 4.10 (br. s, 1 H, NH), 3.10 (t, *J* = 6.8, 2 H, NCH_2), 1.68−1.57 (m, 2 H, NCH_2CH_2), 1.50−1.36 (m, 2 H, CH_2CH_3), 0.95 (t, *J* = 7.3, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ = 147.42, 138.93, 129.37, 118.27, 110.51, 85.37, 43.88, 31.33, 20.30, 13.86. MS: *m*/*z* = 275 (32) [M^+], 233 (8), 232 (100), 105 (10), 104 (11). $C_{10}H_{14}NI$: calcd. C 43.66, H 5.13, N 5.09; found C 43.75, H 5.17, N 5.04.

***N*-Butyl-2-ethynylaniline (1c):** This compound was prepared from *N*-butyl-2-iodoaniline. Yield 1.3 g from 3.0 g of *N*-butyl-2-iodoaniline (69%). Yellow oil. IR (film): $\tilde{\nu}$ = 3408 (w), 3300 (s), 2957 (s), 2928 (s), 2870 (m), 2095 (w), 1601 (m), 1575 (m), 1509 (s), 1457 (m), 1323 (m), 745 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.31 (dd, *J* = 7.8, 1.5, 1 H, H-3), 7.23−7.15 (m, 1 H, H-5), 6.61−6.54 (m, 2 H, H-4 + H-6), 4.59 (br. s, 1 H, NH), 3.38 (s, 1 H, ≡CH), 3.19−3.10 (m, 2 H, NCH_2), 1.69−1.57 (m, 2 H, NCH_2CH_2), 1.43 (sext, *J* = 7.3, 2 H, CH_2CH_3), 0.96 (t, *J* = 7.3, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ = 149.81, 132.70, 130.40, 115.88, 109.55, 106.09, 82.59, 81.02, 43.22, 31.57, 20.30, 13.88. MS: *m*/*z* = 173 (27) [M^+], 131 (11), 130 (10), 128 (7), 103 (13), 77 (14). $C_{12}H_{15}N$: calcd. C 83.19, H 8.73, N 8.08; found C 83.25, H 8.68, N 8.07.

2-Ethynyl-4-methylaniline (1d): This compound was prepared from 2-iodo-4-methylaniline.[35] Yield 1.62 g from 3.0 g of 2-iodo-4-methylaniline (96%). Orange solid, m.p. 36−37 °C. IR (film): $\tilde{\nu}$ = 3469 (m), 3370 (m), 3284 (s), 2921 (w), 2095 (w), 1625 (s), 1501 (m), 1303 (m), 1245 (s), 816 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.11 (d, *J* = 1.9, 1 H, H-3), 6.91 (dd, *J* = 8.3, 1.9, 1 H, H-5), 6.55 (d, *J* = 8.3, 1 H, H-6), 4.16−4.01 (m, 2 H, NH_2), 3.33 (s, 1 H, ≡CH), 2.17 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ = 146.32, 132.65, 130.99, 126.93, 114.57, 106.66, 82.14, 80.99, 20.14. MS: *m*/*z* = 131 (100) [M^+], 130 (93), 103 (19), 102 (8), 78 (8), 77 (23), 63 (8), 52 (10), 51 (14). C_9H_9N: calcd. C 82.41, H 6.92, N 10.68; found C 82.35, H 6.93, N 10.72.

4-Chloro-2-ethynylaniline (1e): This compound was prepared from 4-chloro-2-iodoaniline.[35,36] Yield 1.43 g from 3.0 g of 4-chloro-2-iodoaniline (80%). Orange solid, m.p. 45−46 °C. IR (KBr): $\tilde{\nu}$ = 3417 (m), 3324 (m), 3286 (m), 2105 (w), 1621 (m), 1614 (m), 1487 (s), 1405 (m), 819 (s), 680 (s), 602 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.26 (d, *J* = 2.4, 1 H, H-3), 7.06 (dd, *J* = 8.8, 2.4, 1 H, H-5), 6.58 (d, *J* = 8.8, 1 H, H-6), 4.26 (br. s, 2 H, NH_2), 3.41 (s, 1 H, ≡CH). ^{13}C NMR ($CDCl_3$): δ = 147.26, 131.79, 130.18, 121.94, 115.49, 107.92, 83.48, 79.48. MS: *m*/*z* = 153 (32) [M^+ + 2], 151 (100) [M^+], 124 (14), 123 (9), 116 (27), 89 (75), 87 (9), 63 (21), 62 (16), 61 (9). C_8H_6ClN: calcd. C 63.38, H 3.99, N 9.24; found C 63.45, H 4.02, N 9.20.

5-Chloro-2-iodoaniline: The procedure described by Sandin and Cairns[37] was employed to prepare 4-chloro-1-iodo-2-nitrobenzene from 11.2 g (65 mmol) of commercially available 4-chloro-2-nitroaniline. This was used for the next step without further purification. A stirred solution of crude 4-chloro-1-iodo-2-nitrobenzene and acetic acid (12 mL) in absolute ethanol (100 mL) was refluxed for 10 min. (***Note:*** It is advisable to use a mechanical stirrer.) Iron powder (26.6 g, 476 mmol) was then added in portions, followed by $FeCl_3{\cdot}6H_2O$ (3 g, 11 mmol), and refluxing was continued for 3 h. After cooling, the mixture was filtered, and the filtrate was diluted with ether. Water was added and the phases were separated. The aqueous layer was extracted with ether and the combined organic phases were dried with Na_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified by column chromatography (SiO_2), with hexane/EtOAc (8:2) as eluent. Yield 8.4 g (51% based on starting 4-chloro-2-nitroaniline). Brown solid, m.p. 40−42 °C. IR (KBr): $\tilde{\nu}$ = 3465 (m), 3371 (m), 1609 (s), 1472 (m), 1408 (m), 1254 (m), 1094 (m), 1011 (m), 901 (m), 845 (m), 787 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.46 (d, *J* = 8.4, 1 H, H-3), 6.65 (d, *J* = 2.2, 1 H, H-6), 6.43 (dd, *J* = 8.4, 2.2, 1 H, H-4), 4.14 (br. s, 2 H, NH_2). ^{13}C NMR ($CDCl_3$): δ = 147.58, 139.43, 119.74, 114.07, 81.10. MS: *m*/*z* = 255 (32) [M^+ + 2], 253 (100) [M^+], 127 (12), 126 (25), 99 (16), 90 (15), 63 (14). C_6H_5ClIN: calcd. C 28.43, H 1.99, N 5.53; found C 28.35, H 2.01, N 5.57.

5-Chloro-2-ethynylaniline (1f): This compound was prepared from 5-chloro-2-iodoaniline. Yield 1.24 g from 3.0 g of 5-chloro-2-iodoaniline (69%). Orange solid, m.p. 58−59 °C. IR (KBr): $\tilde{\nu}$ = 3417 (m), 3325 (m), 3287 (m), 2115 (vw), 1616 (m), 1487 (m), 1405 (m), 887 (m), 819 (s), 679 (s), 605 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.21 (d, *J* = 8.3, 1 H, H-3), 6.67 (distorted d, *J* = 2.0, 1 H, H-6), 6.63 (distorted dd, *J* = 8.3, 2.0, 1 H, H-4), 4.30 (br. s, 2 H, NH_2), 3.40 (s, 1 H, ≡CH). ^{13}C NMR ($CDCl_3$): δ = 149.42, 135.79, 133.56, 117.98, 114.03, 105.10, 83.22, 79.70. MS: *m*/*z* = 153 (32) [M^+ + 2], 151 (100) [M^+], 124 (12), 123 (9), 116 (27), 89 (68), 63 (14), 62 (9). C_8H_6ClN: calcd. C 63.38, H 3.99, N 9.24; found C 63.28, H 3.96, N 9.28.

4-Cyano-2-iodoaniline: A solution of $CaCO_3$ (4.5 g, 45 mmol) in water (12 mL) was added to a solution of 4-cyanoaniline (3.5 g, 30 mmol) in MeOH (40 mL), followed by ICl (4.9 g, 30 mmol). The resulting mixture was stirred at room temp. for 15 h, and then diluted with ether and quenched with water. The aqueous layer was extracted with ether and the combined organic phases were dried with Na_2SO_4. After filtration and removal of the solvent in vacuo,

the residue was purified by column chromatography (SiO_2), with hexane/EtOAc (6:4) as eluent, to give pure 4-cyano-2-iodoaniline (yield 7.1 g, 97%). Its spectroscopic properties agree with those reported.[38]

4-Cyano-2-ethynylaniline: This compound was prepared from 4-cyano-2-iodoaniline. Yield 1.38 g from 3.0 g of 4-cyano-2-iodoaniline (79%). Pale yellow solid, m.p. 105−106 °C. IR (KBr): $\tilde{\nu}$ = 3472 (m), 3359 (m), 3273 (w), 2219 (m), 2096 (w), 1631 (s), 1504 (m), 1331 (m), 910 (m), 818 (s), 692 (s), 617 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.59 (d, *J* = 2.0, 1 H, H-3), 7.38 (dd, *J* = 8.3, 2.0, 1 H, H-5), 6.68 (d, *J* = 8.3, 1 H, H-6), 4.80 (br. s, 2 H, NH_2), 3.46 (s, 1 H, ≡CH). ^{13}C NMR ($CDCl_3$): δ = 151.98, 136.87, 133.59, 119.31, 114.10, 106.77, 99.69, 84.26, 78.29. MS: *m*/*z* = 142 (100) [M^+], 115 (44), 114 (25), 88 (11). $C_9H_6N_2$: calcd. C 76.04, H 4.25, N 19.71; found C 75.93, H 4.24, N 19.83.

2-Iodo-4-(methoxycarbonyl)aniline: A solution of $CaCO_3$ (6.9 g, 69 mmol) in water (20 mL) was added to a solution of methyl 4-aminobenzoate (7.0 g, 40 mmol) in MeOH (62 mL), followed by ICl (7.3 g, 45 mmol). The resulting mixture was allowed to stir at room temp. for 15 h, and then diluted with ether and quenched with water. The aqueous layer was extracted with ether and the combined organic phases were dried with Na_2SO_4. After filtration and removal of the solvent in vacuo, the residue was purified by column chromatography (SiO_2), with hexane/EtOAc (7:3) as eluent, to give pure 4-methoxycarbonyl-2-iodoaniline (yield 10.2 g, 92%). Its spectroscopic properties agree with those reported.[39]

2-Ethynyl-4-(methoxycarbonyl)aniline: This compound was prepared from 2-iodo-4-(methoxycarbonyl)aniline. Yield 1.35 g from 3.0 g of 4-methoxycarbonyl-2-iodoaniline (71%). Pale yellow solid, m.p. 109−110 °C. IR (KBr): $\tilde{\nu}$ = 3441 (w), 3332 (m), 3253 (m), 1696 (s), 1632 (s), 1572 (w), 1507 (w), 1431 (w), 1304 (m), 1263 (m), 1191 (w), 1146 (w), 1101 (w), 765 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.03 (d, *J* = 2.0, 1 H, H-3), 7.81 (dd, *J* = 8.8, 2.0, 1 H, H-5), 6.67 (d, *J* = 8.8, 1 H, H-6), 4.72 (br. s, 2 H, NH_2), 3.85 (s, 3 H, Me), 3.40 (s, 1 H, ≡CH). ^{13}C NMR ($CDCl_3$): δ = 166.48, 152.23, 134.94, 131.85, 119.27, 113.31, 105.82, 82.98, 79.56, 51.74. MS: *m*/*z* = 175 (68) [M^+], 145 (11), 144 (100), 116 (22), 89 (34), 63 (12). $C_{10}H_9NO_2$: calcd. C 68.56, H 5.18, N 8.00; found C 68.67, H 5.15, N 8.06.

2-Iodo-5-(methoxycarbonyl)aniline: This compound was prepared according to ref.[40], starting from 4-amino-3-nitrobenzoic acid.[41] (Overall yield 8.4 g starting from 10.0 g of 4-amino-3-nitrobenzoic acid, 55%.) Yellow solid, m.p. 135−136 °C. IR (KBr): $\tilde{\nu}$ = 3453 (m), 3359 (m), 1714 (s), 1626 (s), 1439 (m), 1421 (m), 1319 (w), 1296 (m), 1248 (s), 1111 (m), 1006 (w), 891 (w), 755 (m) cm^{-1}. ^1H NMR ([D$_6$]DMSO: δ = 7.70 (d, *J* = 8.3, 1 H, H-3), 7.40 (d, *J* = 2.0, 1 H, H-6), 6.89 (dd, *J* = 8.3, 2.0, 1 H, H-4), 5.56 (br. s, 2 H, NH_2), 3.83 (s, 3 H, CO_2Me). ^{13}C NMR ([D$_6$]DMSO): δ = 166.28, 148.89, 138.90, 130.37, 117.92, 114.19, 89.00, 52.00. MS: *m*/*z* = 277 (100) [M^+], 246 (50), 218 (18), 135 (9), 118 (9), 91 (20), 63 (11), 52 (10). $C_8H_8INO_2$: calcd. C 34.68, H 2.91, N 5.06; found C 34.81, H 2.89, N 5.08.

2-Ethynyl-5-(methoxycarbonyl)aniline: This compound was prepared from 2-iodo-5-(methoxycarbonyl)aniline. Yield 1.27 g starting from 3.0 g of 2-iodo-5-(methoxycarbonyl)aniline (67%). Yellow solid, m.p. 108−109 °C. IR (KBr): $\tilde{\nu}$ = 3477 (m), 3377 (m), 3251 (m), 1714 (s), 1633 (s), 1565 (m), 1502 (w), 1435 (m), 1336 (s), 1242 (s), 1107 (m), 985 (w), 880 (w), 763 (m), 709 (w), 647 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.29 (m, 3 H aromatic), 4.41 (br. s, 2 H, NH_2), 3.88 (s, 3 H, CO_2Me), 3.52 (s, 1 H, ≡CH). ^{13}C NMR ($CDCl_3$): δ = 166.78, 148.45, 132.55, 131.32, 118.48, 115.06, 110.74, 84.86, 79.92, 52.20. MS: *m*/*z* = 175 (100) [M^+], 145 (5), 144 (46), 117 (5), 116 (22), 90 (3), 89 (14), 63 (4). $C_{10}H_9NO_2$: calcd. C 68.56, H 5.18, N 8.00; found C 68.45, H 5.21, N 8.03.

Typical Procedure for the Oxidative Carbonylation of 2-Alkynylanilines and Separation of Products: A 250-mL stainless steel autoclave was charged in the presence of air with PdI_2 (3.2 or 7.9 mg, $8.9\cdot10^{-3}$ or 0.022 mmol), KI (148 or 365 mg, 0.89 or 2.2 mmol), and a solution of **1** (4.4 mmol) in MeOH (20 mL). While stirring, the autoclave was pressurized with CO (16 atm) and air (up to 20 atm), then heated at 50 °C or 70 °C for 15 h (see Table 1 for the **1**/PdI_2 molar ratio and the reaction temperature used for each substrate). After cooling, the autoclave was degassed, the solvent was evaporated and the products were separated by column chromatography (SiO_2): **2a** (hexane/EtOAc, 6:4 to 4:6; yield 473 mg, 53%); **2b** and **3b** [hexane/EtOAc, 9:1 to 8:2; order of elution: **3b** (47 mg, 4%), **2b** (645 mg, 50%)]; **2c** (hexane/EtOAc, 9:1 to 8:2; yield 513 mg, 45%); **2d** (hexane/EtOAc, 1:1; yield 554 mg, 58%); **2e** (hexane/EtOAc, 7:3; yield 521 mg, 50%); **2f** (hexane/EtOAc, 7:3; yield 438 mg, 42%); **4g** (hexane/EtOAc, 9:1 to 8:2; yield 518 mg, 51%).

(*E*)-3-(Methoxycarbonyl)methylene-1,3-dihydroindol-2-one (2a): Yield 473 mg starting from 515 mg of **1a** (53%). Orange solid, m.p. 178−180 °C, ref.[18] 170−172 °C. IR (KBr): $\tilde{\nu}$ = 3187 (w), 3159 (w), 1710 (s), 1616 (m), 1463 (m), 1330 (m), 1209 (m), 787 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.59−8.54 (m, 1 H, H-4), 7.91−7.85 (br. signal, 1 H, NH), 7.34 (td, *J* = 7.8, 1.2, 1 H, H-6), 7.07 (td, *J* = 7.8, 1.0, 1 H, H-5), 6.89 (s, 1 H, =CH), 6.88−6.83 (m, 1 H, H-7), 3.89 (s, 3 H, CO_2Me). ^1H NMR ([D$_6$]acetone): δ = 9.83 (br. s, 1 H, NH), 8.50 (ddd, *J* = 7.7, 1.2, 0.7, 1 H, H-4), 7.37 (td, *J* = 7.7, 1.2, 1 H, H-6), 7.03 (td, *J* = 7.7, 1.0, 1 H, H-5), 6.96 (ddd, *J* = 7.7, 1.0, 0.7, 1 H, H-7), 6.71 (s, 1 H, =CH), 3.87 (s, 3 H, CO_2Me). ^{13}C NMR ([D$_6$]acetone): δ = 168.69, 166.71, 145.83, 139.62, 133.69, 129.45, 122.90, 121.41, 121.07, 111.04, 52.42. MS: *m*/*z* = 203 (100) [M^+], 188 (6), 172 (64), 144 (90), 116 (62), 89 (32), 75 (9), 63 (15). $C_{11}H_9NO_3$): calcd. C 65.02, H 4.46, N 6.89; found C 64.83, H 4.49, N 6.93.

(*E*)-1-Benzyl-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-one (2b): Yield 645 mg starting from 910 mg of **1b** (50%). Orange solid, m.p. 106−107 °C. IR (KBr): $\tilde{\nu}$ = 1714 (s), 1608 (m), 1471 (w), 1349 (m), 1206 (s), 1104 (m), 784 (w), 747 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.57 (dd, *J* = 7.8, 1.5, 1 H, H-4), 7.37−7.23 (m, 6 H, Ph + H-6), 7.04 (td, *J* = 7.8, 1.0, 1 H, H-5), 6.99 (s, 1 H, =CH), 6.69 (dd, *J* = 7.8, 1.0, 1 H, H-7), 4.94 (s, 2 H, CH_2Ph), 3.89 (s, 3 H, CO_2Me). ^{13}C NMR ($CDCl_3$): δ = 167.69, 166.10, 145.30, 138.01, 135.55, 132.46, 128.88, 128.85, 127.78, 127.31, 122.90, 122.20, 120.08, 109.20, 52.10, 43.96. MS: *m*/*z* = 293 (39) [M^+], 261 (27), 206 (11), 205 (31), 204 (14), 143 (5), 115 (6), 91 (100), 65 (13). $C_{18}H_{15}NO_3$: calcd. C 73.71, H 5.15, N 4.78; found C 73.82, H 5.13, N 4.80.

(*E*)-1-Butyl-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-one (2c): Yield 513 mg starting from 760 mg of **1c** (45%). Orange solid, m.p. 35−37 °C. IR (film): $\tilde{\nu}$ = 2957 (m), 2871 (w), 1712 (s), 1605 (m), 1467 (m), 1352 (m), 1203 (m), 902 (w), 786 (w), 751 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.56 (ddd, *J* = 7.7, 1.4, 0.7, 1 H, H-4), 7.36 (td, *J* = 7.7, 1.4, 1 H, H-6), 7.05 (td, *J* = 7.7, 1.0, 1 H, H-5), 6.91 (s, 1 H, =CH), 6.83−6.79 (m, 1 H, H-7), 3.87 (s, 3 H, CO_2Me), 3.72 (t, *J* = 7.3, 2 H, NCH_2), 1.72−1.60 (m, 2 H, NCH_2CH_2), 1.46−1.33 (m, 2 H, CH_2CH_3), 0.96 (t, *J* = 7.3, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ = 167.39, 166.16, 145.60, 138.24, 132.43, 128.87, 124.93, 122.61, 121.74, 108.43, 52.10, 39.91, 29.50, 20.18, 13.71. MS: *m*/*z* = 259 (59) [M^+], 228 (14), 217 (20), 216 (65), 203 (15), 188 (23), 186 (24), 185 (100), 172 (21), 171 (18), 157 (23), 156 (15),

144 (19), 143 (34), 130 (17), 129 (78), 128 (34), 116 (23), 115 (20), 102 (17), 101 (15), 89 (13), 59 (12). $C_{15}H_{17}NO_3$: calcd. C 69.48, H 6.61, N 5.40; found C 69.58, H 6.58, N 5.37.

(*E*)-3-(Methoxycarbonyl)methylene-5-methyl-1,3-dihydroindol-2-one (2d): Yield 554 mg starting from 576 mg of **1d** (58%). Orange solid, m.p. 185−187 °C. IR (KBr): $\tilde{\nu}$ = 3184 (m), 1712 (s), 1617 (m), 1475 (w), 1351 (w), 1318 (m), 1213 (m), 1186 (m), 1095 (w), 808 (m), 609 (w) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.70 (br. s, 1 H, NH), 8.20−8.17 (m, 1 H, H-4), 7.21−7.15 (m, 1 H, H-6), 6.76 (dd, *J* = 7.8, 0.5, 1 H, H-7), 6.57 (s, 1 H, =CH), 3.82 (s, 3 H, CO_2Me), 2.27 (s, 3 H, CH_3 at C-5). ^{13}C NMR ([D$_6$]DMSO): δ = 167.73, 165.52, 142.73, 138.60, 133.30, 130.55, 128.36, 119.94, 119.56, 109.99, 52.02, 20.64. MS: *m*/*z* = 217 (100) [M$^+$], 186 (42), 159 (15), 158 (76), 130 (31), 103 (10), 102 (8), 51 (8). $C_{12}H_{11}NO_3$: calcd. C 66.35, H 5.10, N 6.45; found C 66.44, H 5.08, N 6.48.

(*E*)-5-Chloro-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-one (2e): Yield 521 mg starting from 665 mg of **1e** (50%). Orange solid, m.p. 218−220 °C. IR (KBr): $\tilde{\nu}$ = 3180 (w), 1717 (s), 1614 (m), 1455 (m), 1352 (m), 1309 (m), 1219 (s), 1110 (w), 908 (w), 892 (w), 813 (m), 639 (w), 612 (w) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.90 (s, 1 H, NH), 8.32 (dd, *J* = 2.4, 0.5, 1 H, H-4), 7.36 (dd, *J* = 8.3, 2.4, 1 H, H-6), 6.84 (dd, *J* = 8.3, 0.5, 1 H, H-7), 6.58 (s, 1 H, =CH), 3.83 (s, 3 H, CO_2Me). ^{13}C NMR ([D$_6$]DMSO): δ = 167.63, 165.39, 146.28, 137.16, 137.06, 129.32, 121.68, 120.91, 118.34, 110.31, 52.18. MS: *m*/*z* = 239 (32) [M$^+$ +2], 237 (100) [M$^+$], 208 (17), 206 (51), 180 (38), 179 (22), 178 (99), 152 (16), 151 (11), 150 (47), 123 (22), 114 (18), 87 (9), 75 (9). $C_{11}H_8ClNO_3$: calcd. C 55.60, H 3.39, N 5.89; found C 55.72, H 3.41, N 5.85.

(*E*)-6-Chloro-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-one (2f): Yield 438 mg starting from 665 mg of **1f** (42%). Orange solid, m.p. 222−223 °C. IR (KBr): $\tilde{\nu}$ = 3163 (w), 1714 (s), 1609 (m), 1434 (w), 1329 (m), 1210 (s), 1074 (w), 819 (w), 736 (w) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.98 (br. s, 1 H, NH), 8.34 (dd, *J* = 8.3, 0.5, 1 H, H-4), 7.07 (dd, *J* = 8.3, 2.0, 1 H, H-5), 6.88 (dd, *J* = 2.0, 0.5, 1 H, H-7), 6.60 (s, 1 H, =CH), 3.82 (s, 3 H, CO_2Me). ^{13}C NMR ([D$_6$]DMSO): δ = 167.69, 165.42, 146.34, 137.28, 137.12, 129.39, 121.69, 120.86, 118.37, 110.33, 52.24. MS: *m*/*z* = 239 (33) [M$^+$ + 2], 237 (100) [M$^+$], 208 (27), 207 (10), 206 (81), 180 (32), 179 (23), 178 (64), 152 (20), 151 (15), 150 (61), 125 (10), 123 (30), 114 (24), 99 (10), 88 (11), 87 (14), 75 (12), 63 (10), 62 (13). $C_{11}H_8ClNO_3$: calcd. C 55.60, H 3.39, N 5.89; found C 55.69, H 3.38, N 5.91.

Methyl [(2-Benzylamino)phenyl]propynoate (3b): Yield 47 mg starting from 910 mg of **1b** (4%). Orange oil. IR (film): $\tilde{\nu}$ = 3410 (w), 2919 (w), 2209 (m), 1709 (s), 1604 (w), 1574 (w), 1516 (m), 1448 (w), 1431 (w), 1302 (m), 1162 (m), 745 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40 (ddd, *J* = 7.8, 2.0, 0.5, 1 H, H-3), 7.35−7.24 (m, 5 H, Ph), 7.24−7.17 (m, 1 H, H-5), 6.65−6.58 (m, 1 H, H-4), 6.52 (ddd, *J* = 8.3, 1.0, 0.5, 1 H, H-6), 5.26 (t, *J* = 5.9, 1 H, NH), 4.44 (d, *J* = 5.9, 2 H, NCH_2), 3.81 (s, 3 H, CO_2Me). ^{13}C NMR ($CDCl_3$): δ = 154.57, 150.75, 138.48, 134.09, 132.70, 128.71, 127.28, 126.79, 116.64, 110.37, 102.95, 86.94, 84.57, 52.67, 47.25. MS: *m*/*z* = 265 (53) [M$^+$], 250 (13), 232 (15), 207 (18), 206 (66), 205 (17), 204 (52), 188 (54), 128 (31), 91 (100), 65 (14). $C_{17}H_{15}NO_2$: calcd. C 76.96, H 5.70, N 5.28; found C 77.14, H 5.67, N 5.31.

Methyl [2-(Hex-1-ynyl)phenyl]carbamate (4g): Yield 518 mg starting from 760 mg of **1g** (51%). Orange oil. IR (film): $\tilde{\nu}$ = 3395 (m), 2956 (m), 2931 (m), 2871 (w), 2225 (vw), 1743 (s), 1581 (m), 1522 (s), 1453 (s), 1307 (m), 1233 (s), 1212 (s), 1065 (m), 755 (m), cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.15−8.08 (m, 1 H, H-6), 7.44 (br. s, 1 H, NH), 7.34 (dd, *J* = 7.7, 1.7, 1 H, H-3), 7.31−7.23 (m, 1 H, H-5), 6.95 (td, *J* = 7.7, 1.3, 1 H, H-4), 3.79 (s, 3 H, CO_2Me), 2.48 (t, *J* = 6.8, 2 H, ≡CCH_2), 1.68−1.43 (m, 4 H, $CH_2CH_2CH_3$), 0.96 (t, *J* = 7.3, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ = 153.76, 139.02, 131.60, 128.87, 122.38, 117.51, 112.35, 97.71, 75.91, 52.29, 30.83, 22.08, 19.30, 13.55. MS: *m*/*z* = 231 (100) [M$^+$], 216 (10), 199 (12), 198 (17), 189 (20), 188 (13), 184 (20), 174 (36), 172 (32), 170 (26), 158 (11), 157 (18), 156 (76), 144 (20), 143 (28), 131 (13), 130 (85), 129 (21), 128 (25), 115 (22), 102 (17), 101 (13), 77 (15). $C_{14}H_{17}NO_2$: calcd. C 72.70, H 7.41, N 6.06; found C 73.11, H 7.36, N 6.11.

Crystal Structure Determination of (*E*)-3-(Methoxycarbonyl)methylene-1,3-dihydroindol-2-one (2a): Crystal data, data collection, and processing parameters are given in Table 2. Intensity data and cell parameters were recorded at room temperature with a Bruker AXS SMART 1000 single crystal diffractometer (Mo-K_α radiation) equipped with CCD area detector and automatically corrected for absorption using "SMART" software. The structure was solved by direct methods using the program SIR92[42] and refined by full-matrix, least-squares procedures (based on F_o^2), using the SHELX-97 system of crystallographic computer programs.[43] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were located in difference Fourier maps; weighting scheme used in the last cycle of refinement $w = 1/[\sigma^2F_o^2 + (0.0643\ P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Molecular geometry calculations were carried out using the PARST97 program.[44] Drawings were produced by using the ORTEP[45] program. All calculations were carried out with DIGITAL Alpha Station 255 computers at the "Centro di Studio per la Strutturistica Diffrattometrica" of CNR, Parma. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-164269 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for compound **2a**

Empirical formula	$C_{11}H_9NO_3$
Formula mass	203.2
Crystal system	monoclinic
Space group	$P2_1/a$
a [Å]	21.280(5)
b [Å]	11.534(5)
c [Å]	3.955(5)
β [°]	95.06(2)
V [Å^3]	967(1)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.396
μ [cm^{-1}]	1.03
F(000)	424
Crystal size [mm]	0.26 × 0.22 × 0.18
θ range [°]	1.92−28.33
Index ranges	$-27 \le h \le 16$, $-13 \le k \le 14$, $-5 \le l \le 5$
Reflns. collected	5730
Independent reflns.	2160 (R_{int} = 0.0337)
Obsd. reflns. [$I > 2\sigma(I)$]	1216
Data/restr./param.	2160/0/173
Goodness-of-fit on F^2	0.890
Final *R* indices [$I > 2\sigma(I)$]	R_1[a] = 0.0438 wR_2 = 0.0995
R indices (all data)	R_1 = 0.0903, wR_2 = 0.1177
Largest diff peak/hole [eÅ^{-3}]	0.140/−0.161

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Acknowledgments

Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica is gratefully acknowledged (Progetto d'Interesse Nazionale PIN MM03027791_005).

[1] B. Gabriele, G. Salerno, *Cyclocarbonylation*, In: *Handbook of Organopalladium Chemistry for Organic Synthesis* (Ed.: E. Negishi), Wiley, New York, in press.
[2] B. Gabriele, M. Costa, G. Salerno, G. P. Chiusoli, *J. Chem. Soc., Perkin Trans. 1* **1994**, 83−87.
[3] B. Gabriele, M. Costa, G. Salerno, G. P. Chiusoli, *J. Chem. Soc., Chem. Commun.* **1994**, 1429−1430.
[4] B. Gabriele, G. Salerno, F. De Pascali, M. Costa, G. P. Chiusoli, *J. Chem. Soc., Perkin Trans. 1* **1997**, 147−154.
[5] A. Bonardi, M. Costa, B. Gabriele, G. Salerno, G. P. Chiusoli, *Tetrahedron Lett.* **1995**, *36*, 7495−7498.
[6] A. Bacchi, G. P. Chiusoli, M. Costa, C. Sani, B. Gabriele, G. Salerno, *J. Organomet. Chem.* **1998**, *562*, 35−43.
[7] B. Gabriele, G. Salerno, D. Brindisi, M. Costa, G. P. Chiusoli, *Org. Lett.* **2000**, *2*, 625−627.
[8] B. Gabriele, G. Salerno, L. Veltri, M. Costa, *J. Organomet. Chem.* **2001**, *622*, 84−88.
[9] D. Zargarian, H. Alper, *Organometallics* **1991**, *10*, 2914−2921.
[10] P. de Vaal, A. Dedieu, *J. Organomet. Chem.* **1994**, *478*, 121−129.
[11] G. Dyker, A. Kellner, *Tetrahedron Lett.* **1994**, *35*, 7633−7636.
[12] R. A. Gibbs, U. Krishnan, J. M. Dolence, C. D. Poulter, *J. Org. Chem.* **1995**, *60*, 7821−7829.
[13] J. Ji, Z. Wang, X. Lu, *Organometallics* **1996**, *15*, 2821−2828.
[14] A. Arcadi, S. Cacchi, G. Fabrizi, F. Marinelli, P. Pace, *Eur. J. Org. Chem.* **1999**, 3305−3313.
[15] J. Tsuji, M. Takahashi, T. Takahashi, *Tetrahedron Lett.* **1980**, 849−850.
[16] Y. Kondo, F. Shiga, N. Murata, T. Sakamoto, H. Yamanaka, *Tetrahedron* **1994**, *50*, 11803−11812.
[17] H. A. Brandman, *J. Heterocycl. Chem.* **1973**, *10*, 383−384.
[18] E. Wenkert, S. Liu, *Synthesis* **1992**, 323−327.
[19] J. L. Wood, A. A. Holubec, B. M. Stoltz, M. M. Weiss, J. A. Dixon, B. D. Doan, M. F. Shamji, J. M. Chen, T. P. Heffron, *J. Am. Chem. Soc.* **1999**, *121*, 6326−6327.
[20] R. Grigg, L. D. Basanagoudar, D. A. Kennedy, J. F. Malone, S. Thianpatanagul, *Tetrahedron Lett.* **1982**, *23*, 2803−2806.
[21] R. Grigg, *Bull Soc. Chim. Belg.* **1984**, *93*, 593−604.
[22] R. Grigg, M. F. Aly, V. Sridharan, S. Thianpatanagul, *J. Chem. Soc., Chem. Commun.* **1984**, 182−183.
[23] R. Grigg, P. Stevenson, T. Worakun, *J. Chem. Soc., Chem. Commun.* **1985**, 971−972.
[24] R. Grigg, S. Thianpatanagul, V. Sridharan, *J. Chem. Soc., Perkin Trans. 1* **1986**, 1669−1676.
[25] R. Grigg, P. Stevenson, T. Worakun, *Tetrahedron* **1988**, *44*, 2033−2048.
[26] R. Grigg, P. Stevenson, T. Worakun, *Tetrahedron* **1988**, *44*, 2049−2054.
[27] R. Grigg, S. Thianpatanagul, J. Kemp, *Tetrahedron* **1988**, *44*, 7283−7292.
[28] R. Grigg, G. Donegan, H. Q. N. Gunaratne, D. A. Kennedy, J. F. Malone, *Tetrahedron* **1989**, *45*, 1723−1746.
[29] K. Okada, M. Kondo, H. Tanino, H. Kakai, S. Inoue, *Heterocycles* **1992**, *34*, 589−597.
[30] M. Nyerges, L. Gajdics, A. Szoelloesy, L. Toeke, *Synlett.* **1999**, *1*, 111−113.
[31] S. Cacchi, G. Fabrizi, P. Pace, *J. Org. Chem.* **1998**, *63*, 1001−1011.
[32] H. Tokuyama, T. Yamashita, M. T. Reding, Y. Kaburagi, T. Fukuyama, *J. Am. Chem. Soc.* **1999**, *121*, 3791−3792.
[33] Y.-T. Park, I.-H. Lee, Y.-H. Kim, *J. Heterocycl. Chem.* **1994**, *31*, 1625−1629.
[34] A. A. Vitale, A. A. Chiocconi, *J. Chem. Res. (S)* **1996**, 336−337.
[35] W.-J. Xiao, H. Alper, *J. Org. Chem.* **1999**, *64*, 9646−9652.
[36] J. Ezquerra, C. Pedregal, C. Lamas, J. Barluenga, M. Pérez, M. A. García-Martín, J. M. Gonzáles, *J. Org. Chem.* **1996**, *61*, 5804−5812.
[37] R. B. Sandin, T. L. Cairns, *Org. Synth., Coll. Vol. II* **1943**, 604−605.
[38] G. Vaidyanathan, D. J. Affleck, M. R. Zalutsky, *J. Med. Chem.* **1994**, *37*, 3655−3662.
[39] M. L. Hill, R. A. Raphael, *Tetrahedron* **1990**, *46*, 4587−4594.
[40] M. D. Collini, J. W. Ellingboe, *Tetrahedron Lett.* **1997**, *38*, 7963−7966.
[41] A. J. Boulton, P. B. Ghosh, A. R. Katritzky, *J. Chem. Soc. (C)* **1966**, 971−976.
[42] A.Altomare, G. Cascarano, C. Giacovazzo, A. Gualiardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435−436.
[43] G. M. Sheldrick, SHELX-97, *Program for the Solution of Crystal Structures*, University of Göttingen, **1997**.
[44] M. Nardelli, PARST97, updated version of PARST95, *J. Appl. Crystallogr.* **1995**, *28*, 659−659.
[45] Ortep3 in the WinGX suite, L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565−566.

Received June 5, 2001
[O01270]