JOC Article

Synthesis of 4*H*-3,1-Benzoxazines, Quinazolin-2-ones, and Quinoline-4-ones by Palladium-Catalyzed Oxidative Carbonylation of 2-Ethynylaniline Derivatives

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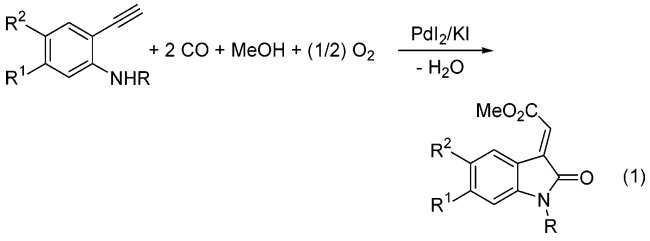
An effective and straightforward approach to the synthesis of 4*H*-3,1-benzoxazines **3** and **4**, quinazolin-2-ones **5**, and quinoline-4-one derivatives **6** and **7** is provided by palladium-catalyzed cyclization−alkoxycarbonylation of variously substituted 2-(trimethylsilanyl)ethynylaniline amide or urea derivatives **2**. Reactions are carried out in 7:1 MeCN/MeOH at 65 or 75 °C in the presence of catalytic amounts of 10% Pd/C in conjunction with Bu_4NI and KF and under 2.4 MPa of a 3:1 mixture of CO and air. Anti and syn 6-*exo*-*dig* cyclization modes account for the formation of the two stereoisomers. Isomerization of the vinylpalladium intermediate may occur as well. Formation of a double carbonylation product **7r** and of a *gem*-dimethoxycarbonylation product **6s**, whose structures have been determined by X-ray diffraction analysis, is justified through an unusual type of rearrangement.

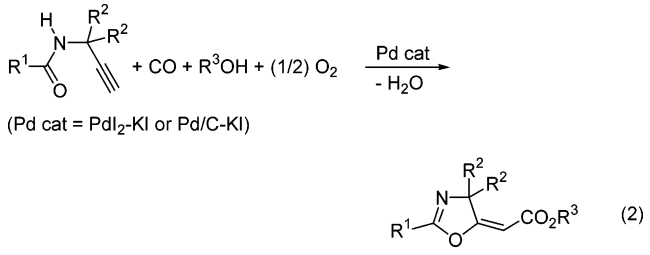
Introduction

The palladium-catalyzed oxidative cyclocarbonylation−alkoxycarbonylation or cyclization−alkoxycarbonylation of acetylenic substrates bearing a suitably placed nucleophilic group allows a simple, atom-economical synthesis of functionalized heterocycles.[1] In particular, we recently reported the first example of the synthesis of (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones starting from 2-ethynylanilines using PdI_2 in conjunction with KI as the catalytic system[1b,2] according to eq 1.[3]

This process is an example of cyclocarbonylation−alkoxycarbonylation; i.e., carbon monoxide is inserted into the cycle and an alkoxycarbonyl group is added to the triple bond.

More recently, we described the synthesis of (*E*)-5-(alkoxycarbonyl)methylene-3-oxazolines from prop-2-ynylamide promoted by the above-mentioned palladium catalytic system (PdI_2−KI or Pd/C−KI) (eq 2).[4]





In this case, intramolecular anti nucleophilic attack by oxygen to the triple bond coordinated to Pd(II) was followed by alkoxycarbonylation, so the overall process corresponded to cyclization−alkoxycarbonylation without CO incorporation into the cycle (Scheme 1).

Under similar conditions, prop-2-ynylureas afforded (*E*)-oxazolines and (*Z*)-cyclic ureas simultaneously depending on whether the cyclization was initiated by oxygen or nitrogen attack to the triple bond respectively (eq 3 and Scheme 2).[5] Bulky and electron-withdrawing groups in the N-bonded R^1 substituent influenced the ratio of the two cyclic products.

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|| Dipartimento di Chimica, Università della Calabria.

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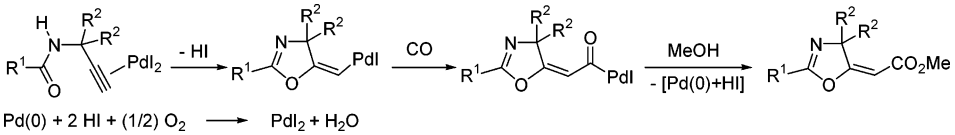

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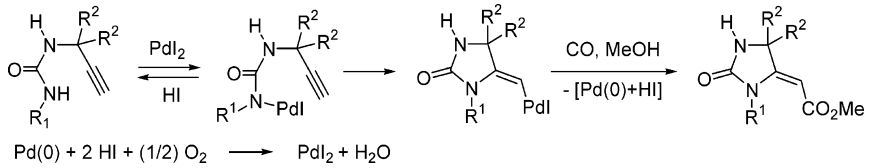

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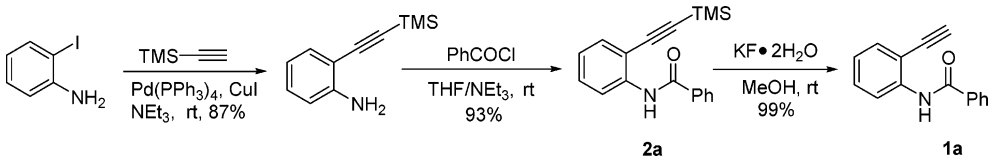
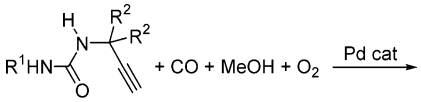
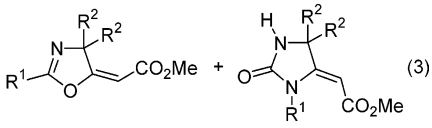






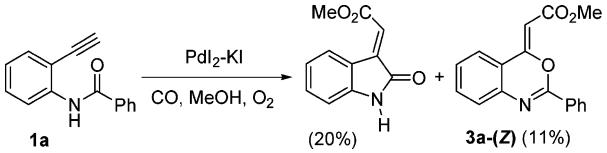
(3)

Our interest in the application of triple-bond oxidative carbonylation methodology[1,2] to the synthesis of heterocycles led us to investigate its application to amides and ureas derived from 2-ethynylanilines. Here we report the results of our research, which allowed a direct access to the synthesis of new 4*H*-3,1-benzoxazine, quinazolin-2-one, and quinoline-4-one derivatives. These nitrogen heterocycles can be used as valuable intermediates for the preparation of dyestuffs[6] and of pharmaceutical products[7] since they exhibit a wide range of biological activity.

Results and Discussion

Synthesis of 1,3-Benzoxazine Derivatives. We began our investigation with *N*-(2-ethynylphenyl)benzamide **1a**, easily prepared starting from 2-iodoaniline through a Cassar−Sonogashira coupling reaction[8] with trimethylsilylacetylene, benzoylation to give *N*-{2-[(trimethylsilanyl)ethynyl]phenyl}benzamide **2a**, and deprotection with KF[9] (Scheme 3).

Oxidative carbonylation of **1a** (3.00 mmol) carried out in MeOH (18 mL) at 60 °C for 30 h in the presence of PdI_2 (0.03 mmol) and KI (0.30 mmol) under a 3:1 CO/air mixture (24 bar total pressure at 25 °C) led to a complete conversion of substrate **1a** with formation of (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-one (about 20% yield) and (*Z*)-4-(methoxycarbonyl)methylene-2-phenyl-*4H*-benzo[*d*][1,3]oxazine **3a-(Z)** (11% yield, eq 4). The (*Z*) configuration around the double bond of **3a-(Z)** was assigned on the basis of ^{1}H, ^{13}C NMR spectroscopy data and ^{1}H−^{1}H NOESY experiments. The two-dimensional spectrum showed a distinct dipolar interaction between the vinylic proton and the aromatic proton at C-5.



(4)

The formation of the dihydroindolone derivative (the same formed from 2-ethynylaniline, see eq 1) could be due to the generation in situ of 2-ethynylaniline by cleavage of the amide bond. Benzoic acid and methyl benzoate were found to be coproducts of the reaction. Better results were observed by working with Pd/C−KI rather than PdI_2−KI. A significantly higher selectivity

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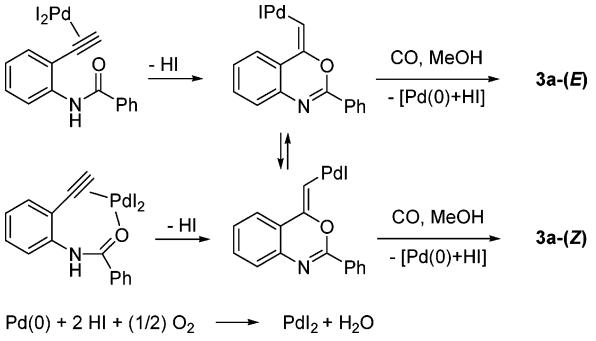
TABLE 1. Oxidative Carbonylation of 2a (3.00 mmol, concentration = 0.187 M) in the Presence of 10% Pd/C (0.03 mmol) (CO/Air = 3:1 (24 bar Total Pressure at 25 °C); Solvent: MeCN/MeOH (7/1 vol/vol 16 mL))

					yield[a] (%)		
run	additives	time (h)	*T* (°C)	conversion[a] (%) of **2a**	of **1a**	of **3a** (*Z* + *E*)	*Z*/*E* mol ratio
1	KI[b]	70	110	71[c]	15	24	22.5:1.5
2	KI[b]+ KF·2H_2O[e]	48	55	98	79	16	15.5:0.5
3	Bu_4NI[d] + KF·2H_2O[e]	15	55	98	34	57	55:2
4	Bu_4NI[d] + KF·2H_2O[e]	15	65	99	5	86	82:4
5	Bu_4NI[d] + KF·2H_2O[e]	24	65	99		91	87:4

[a] Conversions and yields are referred to the starting substrate **2a**; determined by GLC. [b] 0.30 mmol. [c] Substrate **2a** was partially decomposed. [d] 3.00 mmol. [e] 4.50 mmol.

SCHEME 4

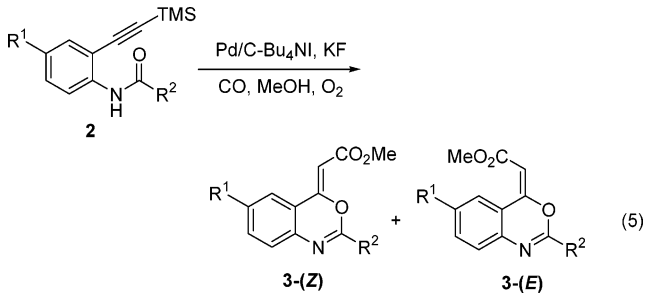


toward product **3a-(*Z*)** (up to 62% yield at total substrate conversion) could be obtained by carrying out the reaction at 60 °C in a 9:1 MeCN/MeOH mixture (to minimize cleavage of the amide bond) with Pd/C−KI as catalyst. Small amounts of the *E* isomer **3a-(*E*)** were also detected in the reaction mixture. Since in the presence of KI−O_2, under the reaction conditions, PdI_2 is formed from Pd−C, its better performance must be due to its gradual solubilization in the reaction mixture.

In a similar way to the formation of oxazolines and cyclic ureas from prop-2-ynamides and prop-2-ynureas (eqs 2 and 3), formation of products **3a** corresponds to cyclization followed by methoxycarbonylation. We have ascertained by stopping the reaction at low conversion that the product distribution was similar to the one achieved at almost complete conversion. This means that products **3a-(*Z*)** and **3a-(*E*)** must derive from different reaction pathways. Predictably, *anti* (as in Scheme 1) and *syn* (as in Scheme 2) 6-*exo*-*dig* cyclization modes can easily account for the formation of the two stereoisomers. Isomerization of the vinylpalladium intermediate,[10] however, cannot be ruled out (Scheme 4).

The reaction did not take place with substrates with an internal triple bond, such as *N*-[2-(phenylethynyl)-phenyl]benzamide. On the other hand, substrates such as **2a**, bearing the triple bond still protected with the TMS group, converted into **1a** and **3a** very slowly, even under more drastic conditions (Table 1, run 1). This latter result showed that desilylation *in situ* of the triple bond, although possible, was not particularly efficient in the presence of the Pd/C−KI system only. Thus, to explore the possibility to achieve the in situ deprotection before cyclization−alkoxycarbonylation, some experiments were carried out using **2a** as substrate in the presence of a fluoride source in addition to the carbonylation catalyst. The addition of KF·2H_2O caused complete desilylation of starting **2a**, but it somewhat inhibited carbonylation (run 2). However, the use of an excess of Bu_4NI in place of KI along with KF·2H_2O eventually led to satisfactory results (run 5).

Under these conditions, the reaction proved to be general for substrates containing different substituents (eq 5). Some representative results are shown in Table 2. The *Z* isomer was consistently found to be the main product, with the exception of **3k** (R^1 = H, R^2 = *p*-MeO_2-CC_6H_4), for which a higher amount of the *E* isomer was actually formed (run 15).



Small amounts (ranging from 2 to 7%) of methyl esters of benzoic acid derivatives coming from the decomposition of the corresponding benzamides were usually detected in the reaction mixtures.

The aromatic ring could bear electron-donating as well as electron-withdrawing groups (runs 7−10); in addition, the carbonyl group could be bonded to variously substituted aryl groups (runs 11−16) as well as vinyl (runs 17−19) and allyl (run 20) substituents. Interestingly, in this latter case, isomerization of the allyl group occurred with formation of the same products obtained starting with crotonamide **2m**. However, simple formamide or acetamide derivatives, as in the case of *N*-{2-[(trimethylsilanyl)-ethynyl]phenyl}formamide (R^2 = H), *N*-{2-[(trimethylsilanyl)ethynyl]phenyl}acetamide (R^2 = CH_3), or *N*-{2-[(trimethylsilanyl)ethynyl]phenyl}trifluoroacetamide (R^2 = CF_3), did not give significant results. Therefore, stabilization of the transition state leading to **3** by conjugation of the carbon−nitrogen double bond with the exocyclic phenyl or vinyl group appears to be a necessary requirement for cyclization to occur.

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TABLE 2. Oxidative Carbonylation of 2a−o (3.00 mmol) in the Presence of 10% Pd/C (0.03 mmol), Bu_4NI (3.00 mmol), $KF{\cdot}2H_2O$ (4.50 mmol) (CO/Air (3/1, 24 bar at 25 °C), *T* 65 °C, Time 24 h, Solvent: MeCN/MeOH (7/1 vol/vol, 16 mL))

run	2	R^1	R^2	conversion[a] (%) of 2	yield[a] (%) of 1	product yield[a] (%) 3-(*Z*)	3-(*E*)
6	**a**	H	Ph	99	4	87 (76)[b]	4
7	**b**	CO_2Me	Ph	98	23	64 (53)	
8	**c**	CN	Ph	99	5	89 (78)	
9	**d**	Cl	Ph	99	4	86 (75)	5
10	**e**	Me	Ph	98	12	75 (64)	5
11	**f**	H	*p*-ClC_6H_4	98	11	67 (55)	4
12	**g**	H	*p*-$O_2NC_6H_4$	98	8	78 (65)	11 (7)
13	**h**	H	*p*-NCC_6H_4	97	9	72 (58)	8 (5)
14	**i**	H	*p*-$MeOC_6H_4$	98	8	74 (62)	
15	**j**	H	*p*-MeC_6H_4	98	8	76 (64)	
16	**k**	H	*p*-$MeO_2CC_6H_4$	98	9	34 (23)	43 (31)
17	**l**	H	$CH{=}CH_2$	99	10	65 (54)	4
18	**m**	H	CH=CHMe	97	12	63 (51)	7 (3)
19	**n**	H	CH=CHPh	98	9	80 (68)	(3)
20	**o**	H	$CH_2CH{=}CH_2$	96	32[c]	44 (32)[d]	2[d]

[a] Conversions and yields are referred to the starting substrate **2**; determined by GLC. [b] Isolated yields are shown in parentheses. [c] Mixture of **1m** and **1o**. [d] R^2 = CH=CHMe in the respective products.

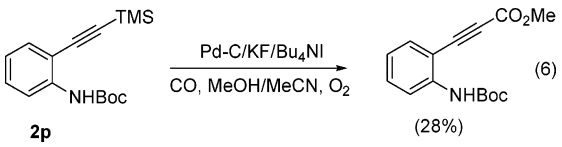
TABLE 3. Oxidative Carbonylation of 2r−u (3.00 mmol), in the Presence 10% Pd−C (0.03 mmol), Bu_4NI (3.00 mmol), $KF{\cdot}2H_2O$ (4.50 mmol) (CO/Air (3/1, 24 bar at 25 °C), *T* 75 °C, Time 24 h, Solvent MeCN/MeOH (7/1 vol/vol, 16 mL))

run	2	R^3	conversion[a] (%) 2	4-(*Z*)[b]	5-(*Z*)[b]	yield (%) 5-(*E*)[b]	6[b]	7[b]
21	**2r**	*n*-Pr	99	54 (45)	9 (5)	11 (6)	23 (15)	
22	**2s**	H	68[c]					(54)
23	**2t**	CH_2Ph	96	79 (68)				
24	**2u**	Ph	99			85 (74)		

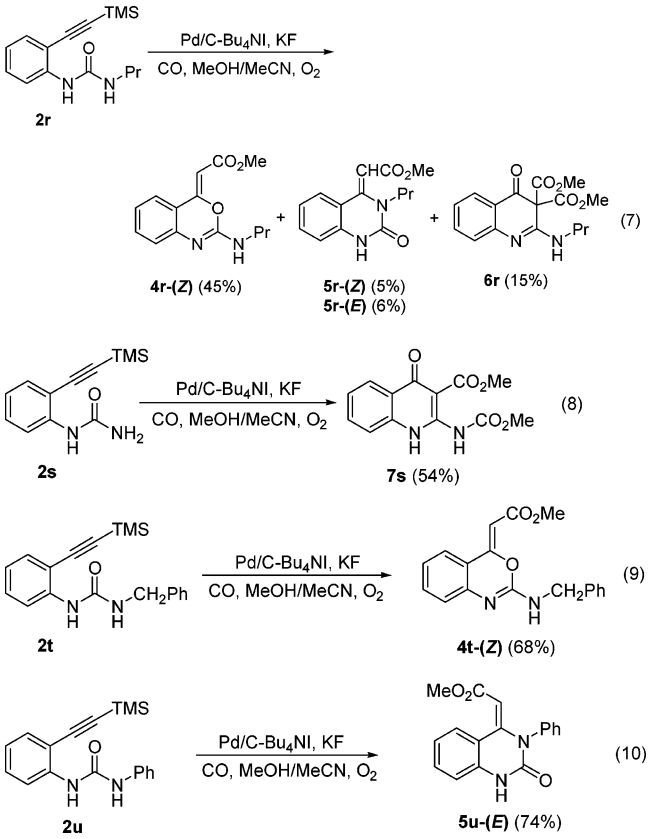
[a] Conversions and yields are referred to the starting substrate **2r**−**u**; determined by GLC. [b] Isolated yields are shown in parentheses. [c] Desilylated **2s** as residual product.

The structure of compound **3i-(*Z*)** was confirmed by single-crystal X-ray analysis (Figure S1, Supporting Information).

Synthesis of Quinazolin-2-one and Quinolin-4-one Derivatives. Other 2-(trimethylsilanyl)ethynylaniline derivatives were tested. The reaction followed a different course with carbamate compounds [R^2 = $OC(Me)_3$ (**2p**)], [R^2 = $OCH_2CH{=}CH_2$ (**2q**)]. A complete desilylation took place with both substrates, and (2-*tert*-butoxycarbonylaminophenyl)propynoic acid methyl ester was obtained (28% yield) with **2p** (eq 6). On the other hand, **2q** afforded a complex mixture of products and its reactivity was not examined further.

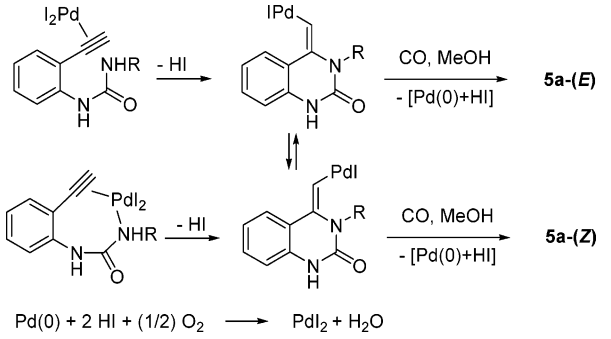


Good results were, however, obtained with ureic derivatives **2r**−**u** (R^2 = NHR^3), which afforded benzoxazine, quinazolin-2-one, and/or quinoline-4-one derivatives (**4**, **5** and **6**, **7**, respectively, eqs 7−10), mainly depending on the nature of group R^3. Thus, when R^3 was an alkyl group such as *n*-propyl, a mixture of **4r**-(*Z*), **5r**-(*Z*), **5r**-(*E*), and **6r** was formed, benzoxazine **4r-*Z*** being the main product (54% yield, eq 7 and run 21, Table 3). When R^3 was hydrogen, product **7s** was obtained exclusively in fair yield (54% yield, eq 8 and run 22). With R^3 = benzyl, only **4t-(*Z*)** was obtained in 79% yield (eq 9 and run 23). On the other hand, when R^3 = Ph, the reaction selectively afforded quinazolin-2-one **5u-(*E*)** (85% yield, eq 10, entry 24), whose structure was confirmed by X-ray analysis (Figure S2, Supporting Information).



In a similar way to the formation of cyclic ureas from prop-2-ynylureas (see Scheme 2), products **5** correspond to nitrogen attack to the triple bond coordinated to Pd(II) followed by methoxycarbonylation. Also in this case, as we have seen in Scheme 4 for oxygen attack leading to benzoxazines, both *anti* and *syn* cyclization modes are

SCHEME 5



possible, and isomerization of the vinylpalladium intermediate may occur as well (Scheme 5).

Interestingly, the reaction of **2r** and **2s** led to the formation of a *gem*-dimethoxycarbonylation product **6r** (23% yield) and of a double carbonylation product **7s** (54% yield), respectively, whose structure were determined by spectroscopic and X-ray analyses (Figure S3 and S4, Supporting Information).

The overall process leading to **6r** and **7s** corresponds to an unusual type of rearrangement that would require further investigation. A reasonable mechanism involving derivative **4r** (*Z* or *E* isomer) or **4s** (not isolated) as starting species may, however, be proposed (Scheme 6) that involves the following steps: (a) reversible MeOH addition to the carbon−nitrogen double bond of **4r** or **4s**; (b) proton shift with cleavage of the C−O bond of the cycle and formation of an enol; (c) nucleophilic attack by the enolic carbon to the carbon−nitrogen double bond with proton shift; (d) elimination of MeOH with formation of an endocyclic double bond; (e) oxidative methoxycarbonylation α to the carbonyl group[11] when R^3 = *n*-Pr, or oxidative methoxycarbonylation of the exocyclic nitrogen when R^3 = H. The presence of the two ureic nitrogen atoms seems to be essential for this rearrangement.

In summary, we have outlined a simple and efficient route for the synthesis of new heterocyclic compounds by in situ deprotection of 2-(trimethylsilanyl)ethynylaniline derivatives followed by cyclization-alkoxycarbonylation. Thus, methoxycarbonylmethylenebenzoxazines were obtained from *N*-aryl or -vinyl substituted amides of 2-ethynylanilines. Using N-substituted ureas derived from 2-ethynylanilines we obtained dihydrobenzoxazine derivatives in the case of N-alkyl and dihydroquinazolinone derivatives in the case of *N*-aryl substituents. Interestingly the unsubstituited ureas of 2-ethynylanilines gave a rearrangement leading to a quinolin-4-one derivative. The methodology thus proved to be quite versatile and allowed the synthesis of molecules not readily accessible by other ways in one step and with good to high yields.

Experimental Section

Preparation of Substrates. Starting materials: 2-iodoaniline, 4-methylaniline, 4-chloroaniline, 4-cyanoaniline, methyl 4-aminobenzoate, (trimethylsilyl)acetylene, benzoyl chloride, 4-chlorobenzoic acid, 4-nitrobenzioc acid, 4-cyanobenzoic acid, *p*-anisic acid, *p*-toluic acid, monomethyl terephthalate, acrylic acid, cinnamic acid, and vinylacetic acid were commercially available and were used without further purification. The respective acid chlorides were obtained through standard procedures.[12] Methyl 3-iodo-4-aminobenzoate,[13] 4-chloro-2-iodoaniline,[14a,b] 4-amino-3-iodobenzenecarbonitrile,[3] 4-methyl-2-iodoaniline[14a] were prepared according to procedures reported in the literature. All the cross-coupling reactions of 2-iodoaniline and substituted 2-iodoanilines with (trimethylsilyl)acetylene were carried out according to reported procedures.[3,14b,15] The crude mixtures of Cassar−Sonogashira reactions were diluted with Et_2O and 0.1 N HCl solution, and phases were separated. The aqueous layer was neutralized with saturated $NaHCO_3$ and extracted with Et_2O, and the collected organic phases were dried over Na_2SO_4. After removal of the solvent in vacuo, crude (trimethylsilanyl)ethynylanilines were caused to react without further purification with acid chlorides according to standard procedures[16] to give amides **1a**, **2a**−**l**,**n**,**o**. Crotonoylamide **2m** was prepared following a procedure reported in the literature.[17]

N-(2-Iodophenyl)formamide,[18] *N*-{2-[(trimethylsilanyl)ethynyl]-phenyl}formamide,[14b,15] *N*-(2-ethynyl-phenyl)acetamide,[19] *N*-(2-ethynyl-phenyl)-2,2,2-trifluoroacetamide,[20] *N*-{2-[(trimethylsilanyl)ethynyl]phenyl}acetamide,[21] *N*-{2-[(trimethylsilanyl)ethynyl]phenyl}-2,2,2-trifluoroacetamide,[22] *N*-[2-phenylethynyl)phenyl]benzamide,[23] (2-trimethylsilanylethynylphenyl)carbamic acid *tert*-butyl ester (**2p**),[24] and (2-trimethylsilanylethynylphenyl)carbamic acid allyl ester (**2q**)[24] were prepared according to procedures reported in the literature.

(2-Trimethylsilanylethynyl-phenyl)urea **2s** was prepared through a standard literature synthesis[25] from 2-(trimethylsilanylethynyl)aniline and sodium cyanate. 1-Propyl-3-(2-trimethylsilanylethynylphenyl)urea **2r**, 1-benzyl-3-(2-trimethylsilanylethynylphenyl)urea **2t**, and 1-phenyl-3-(2-trimethylsilanylethynylphenyl)urea **2u**, were prepared according to general procedures reported in the literture[26] by aminolysis of bis(4-nitrophenyl)carbonate.

The pure substrates were recovered by crystallization from suitable solvents. ^1H and ^{13}C NMR, IR, mass spectra, and elemental analyses confirmed the assigned structures (Supporting Information).

Typical Procedure for the Oxidative Cyclization−Methoxycarbonylation of *N*-(2-Ethynylphenyl)benza-

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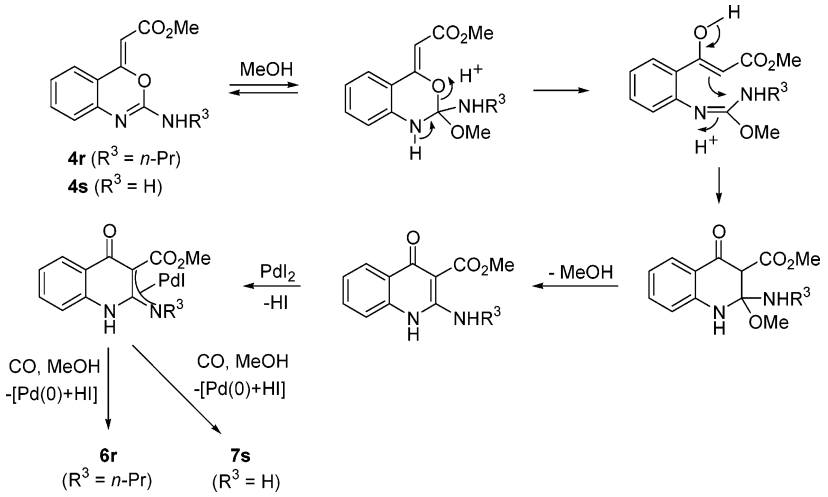
SCHEME 6



mide 1a in the Presence of 10% Pd and KI as Catalytic System. A 125 mL stainless steel autoclave was charged in the presence of air with 10% Pd (0.032 g, 0.03 mmol), KI (0.050 g, 0.30 mmol), and a solution of **1a** (0.663 g, 3.00 mmol) in MeCN/MeOH (9/1 vol/vol 18 mL). The autoclave was pressurized with CO (1.8 Mpa) and air (up to 2.4 Mpa at room temperature) and stirred for 30 h at 60 °C. After cooling, the autoclave was degassed, the solvent was evaporated under vacuum, and product **3a** was separated by column chromatography (SiO_2, hexane/acetone 8:2), yield 0.134 g 48%).

General Procedure for the Deprotection−Oxidative Cyclization−Methoxycarbonylation Reactions of *N*-(2-trimethylsilanylethynylphenyl)amide 2a−o and Urea 2r−u Derivatives. All reactions were carried out in a 125 mL stainless steel autoclave with magnetic stirring. In a typical experiment, the autoclave was charged in the presence of air with amide **2b** (1.05 g, 3.00 mmol), 10% Pd/C (0.032 g, 0.03 mmol), $(Bu)_4NI$ (1.108 g, 3.00 mmol), and $KF{\cdot}2H_2O$ (0.424 g, 4.50 mmol) in MeCN/MeOH (7/1 vol/vol, 16 mL). The autoclave was pressurized with CO (1.8 Mpa) and air (up to 2.4 Mpa at room temperature) and then heated with stirring for 24 h at 65 °C for the amide or 75 °C for urea derivatives, respectively. After cooling, the autoclave was degassed, the solvent was evaporated under vacuum, and the residue was filtered through a short SiO_2 column using CH_2Cl_2 as eluent.

(*Z*)-(2-Phenylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3a-(*Z*): orange solid; mp 117−120 °C; IR (KBr) ν_{max} cm^{-1} 3061 (w), 2947 (w), 1718 (s), 1647 (s), 1610 (m), 1598 (m), 1479 (m), 1276 (m), 1242 (m), 1166 (s), 1127 (m), 1094 (m), 763 (m), 694 (m); ^1H NMR ($CDCl_3$) δ_H 8.50−8.44 (m, 2 H), 7.68−7.62 (m, 1 H), 7.61−7.45 (m, 5 H), 7.36−7.29 (m, 1 H), 5.81 (s, 1 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.3, 156.8, 154.3, 140.5, 133.2, 132.2, 130.5, 128.5, 128.4, 127.9, 127.3, 123.0, 118.6, 89.7, 51.1; MS *m*/*z* 279 (M^+, 100), 248 (24), 234 (31), 221 (18), 206 (33), 192 (17), 165 (33), 103 (27), 89 (17), 77 (20). Anal. Calcd for $C_{17}H_{13}$ NO_3: C, 73.09; H, 4.69; N, 5.02. Found: C, 73.00; H, 4.66; N, 4.93.

(*Z*)-4-Methoxycarbonylmethylene-2-phenyl-4*H*-benzo[*d*][1,3]oxazine-6-carboxylic acid methyl ester 3b-(*Z*): orange-yellow solid; mp 202−205 °C; IR (KBr) ν_{max} cm^{-1} 2950 (w), 1725 (s), 1653 (m), 1597 (m), 1310 (m), 1265 (m), 1240 (m), 1157 (m), 1091 (m), 768 (m), 690 (m); ^1H NMR ($CDCl_3$) δ_H 8.45−8.41 (m, 2 H), 8.27 (d, *J* = 1.8 Hz, 1 H aromatic), 8.12 (dd, *J* = 8.4, 1.8 Hz, 1 H), 7.57−7.47 (m, 3 H), 7.45 (d, *J* = 8.4 Hz, 1 H), 5.87 (s, 1 H, =C*H*CO_2Me), 3.93 (s, 3 H), 3.81 (s, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 164.9, 155.9, 155.7, 144.0, 133.8, 132.7, 130.0, 128.7, 128.6, 128.1, 127.3, 124.8, 118.5, 91.0, 52.4, 51.1; MS *m*/*z* 337 (M^+, 100), 306 (44), 292 (31), 235 (34), 190 (44), 178 (31), 137 (31), 103 (63), 75 (85), 59 (53). Anal. Calcd for $C_{19}H_{15}NO_5$: C, 68.04; H, 3.91; N, 4.15. Found: C, 68.01; H, 3.87; N, 4.12.

(*Z*)-(6-Cyano-2-phenylbenzo[*d*][1,3]oxazin-4-ylidene)-acetic acid methyl ester 3c-(*Z*): pale yellow solid; mp 220−223 °C; IR (KBr) ν_{max} cm^{-1} 2226 (m), 1743 (w), 1695 (s), 1646 (m), 1577 (m), 1517 (m), 1301 (m), 1255 (s), 1174 (m), 1088 (m), 839 (m), 686 (m); ^1H NMR ($CDCl_3$) δ_H 9.16 (d, *J* = 0.9 Hz, 1 H), 8.42 (d, *J* = 8.5 Hz, 1 H), 8.05−8.02 (m, 2 H), 7.59−7.50 (m, 5 H), 5.80 (s, 1 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 164.5, 154.2, 145.3, 143.9, 135.7, 132.8, 129.5, 129.0, 128.8, 128.7, 121.5, 120.7, 117.7, 111.2, 92.2, 51.3; MS *m*/*z* 304 (M^+, 100), 273 (35), 259 (40), 232 (57), 217 (28), 190 (88), 177 (26), 116 (28), 103 (34), 77 (69), 59 (91). Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 71.03; H, 3.98; N, 9.21. Found: C, 70.98; H, 3.94; N, 9.17.

(*Z*)-(6-Chloro-2-phenylbenzo[*d*][1,3]oxazin-4-ylidene)-acetic acid methyl ester 3d-(*Z*): yellow solid; mp 188−191 °C; IR (KBr) ν_{max} cm^{-1} 3086 (m), 1698 (s), 1645 (m), 1608 (m), 1578 (m), 1471 (s), 1283 (s), 1253 (s), 1180 (m), 840 (m), 775 (w), 685 (s); ^1H NMR ($CDCl_3$) δ_H 8.44−8.41 (m, 2 H), 7.58 (d, *J* = 2.2 Hz, 1 H), 7.56−7.49 (m, 3 H), 7.43 (dd, *J* = 8.6, 2.2 Hz, 1 H), 7.38 (d, *J* = 8.6 Hz, 1 H), 5.74 (s, 1 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.1, 155.2, 154.3, 150.0, 139.1, 136.2, 133.4, 129.3, 129.0, 127.8, 123.7, 122.7, 119.7, 90.5, 51.1; MS *m*/*z* 313 (M^+, 100), 282 (18), 268 (31), 240 (30), 226 (21), 199 (26), 191 (22), 139 (15), 120 (18), 105 (16), 77 (33), 59 (30). Anal. Calcd for $C_{17}H_{12}ClNO_3$: C, 65.17; H, 3.86; N, 4.47. Found: C, 65.12; H, 3.84; N, 4.41.

(*Z*)-(6-Methyl-2-phenylbenzo[*d*][1,3]oxazin-4-ylidene)-acetic acid methyl ester 3e-(*Z*): yellow solid; mp 138−141 °C; IR (KBr) ν_{max} cm^{-1} 3066 (w), 2947 (w), 1724 (s), 1650 (m), 1595 (m), 1578 (m), 1496 (w), 1332 (w), 1276 (m), 1194 (s), 1148 (s), 1093 (s), 920 (w), 824 (m), 793 (m), 778 (w), 687 (m); ^1H NMR ($CDCl_3$) δ_H 8.46−8.42 (m, 2 H), 7.56−7.46 (m, 3 H), 7.41−7.34 (m, 3 H), 5.79 (s, 1 H), 3.81 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.3, 156.9, 154.3, 150.0, 139.1, 136.2, 133.4, 129.3, 129.0, 128.2, 123.7, 121.1, 118.2, 89.3, 51.0, 21.7; MS *m*/*z* 293 (M^+, 100), 262 (15), 248 (23), 220 (27), 206 (21), 179 (17), 110 (30), 77 (45), 51 (12). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.69; H, 5.16; N, 4.78. Found: C, 73.63; H, 5.13; N, 4.72.

(*Z*)-[2-(4-Chlorophenyl)benzo[*d*][1,3]oxazin-4-ylidene]-acetic acid methyl ester 3f-(*Z*): pale yellow solid; mp 175−178 °C; IR (KBr) ν_{max} cm^{-1} 2950 (w), 1717 (m), 1652 (s), 1608 (m), 1478 (w), 1278 (m), 1241 (w), 1150 (s), 1123 (m), 1095 (s), 1015 (w), 843 (w), 806 (w), 767 (m), 723 (w); ^1H NMR ($CDCl_3$) δ_H 8.40 (d, *J* = 8.6 Hz, 2 H), 7.65 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.43−7.58 (m, 4 H), 7.34 (td, *J* = 8.0, 1.4 Hz, 1 H), 5.81 (s, 1 H), 3.81 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.2, 156.6, 153.5, 140.3, 138.6, 133.3, 130.4, 129.7, 128.9, 128.2, 127.4, 123.1, 118.5, 89.9, 51.0; MS *m*/*z* 313 (M^+, 100), 282 (29), 268 (40), 240 (40),

199 (40), 139 (28), 120 (54), 89 (40), 76(38), 59 (41). Anal. Calcd for $C_{17}H_{12}ClNO_3$: C, 65.17; H, 3.86; N, 4.47. Found: C, 65.12; H, 3.83; N, 4.42.

(*Z*)-[2-(4-Nitrophenyl)benzo[*d*][1,3]oxazin-4-ylidene]-acetic acid methyl ester 3g-(*Z*): yellow-orange solid; mp 214−216 °C; IR (KBr) ν_{max} cm^{-1} 2954 (w), 1716 (m), 1654 (s), 1613 (m), 1594 (w), 1524 (s), 1347 (m), 1279 (m), 1159 (s), 1127 (m), 1097 (m), 759 (m), 699 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.65 (d, J = 8.9 Hz, 2 H), 8.36 (d, J = 8.9 Hz, 2 H), 7.67 (dd, J = 7.2, 1.3 Hz, 1 H aromatic), 7.60 (td, J = 7.2, 1.4 Hz, 1 H), 7.51 (dd, J = 7.5, 1.3 Hz, 1 H), 7.40 (td, J = 7.5, 1.4 Hz, 1 H), 5.85 (s, 1 H, =C*H*CO$_2$Me), 3.83 (s, 3 H); (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.1, 156.2, 152.3, 150.0, 139.8, 136.2, 133.4, 129.3, 129.0, 127.8, 123.7, 123.1, 118.7, 90.5, 51.1; MS *m*/*z* 324 (M$^+$, 100), 293 (34), 279 (22), 266 (27), 250 (21), 237 (23), 219 (23), 191 (50), 178 (23), 89 (27), 76 (35), 59 (47). Anal. Calcd for $C_{17}H_{12}N_2O_5$: C, 62.95; H, 3.73; N, 8.64. Found: C, 62.91; H, 3.70; N, 8.60.

(*E*)-[2-(4-Nitrophenyl)benzo[*d*][1,3]oxazin-4-ylidene]-acetic acid methyl ester 3g-(*E*): yellow-orange solid; mp 197−199 °C; IR (KBr) ν_{max} cm^{-1} 2952 (w), 1718 (m), 1642 (s), 1611 (m), 1591 (m), 1523 (s), 1348 (s), 1103 (s), 864 (m), 772 (m), 701 (m); ^{1}H NMR ($CDCl_3$) δ_H 9.05 (dd, J = 8.1, 1.2 Hz, 1 H), 8.39 (d, J = 8.8 Hz, 2 H), 8.08 (d, J = 8.8 Hz, 2 H), 7.60 (td, J = 8.1, 1.2 Hz, 1 H), 7.48 (dd, J = 8.0, 1.4 Hz, 1 H), 7.43 (td, J = 8.0, 1.4 Hz, 1 H), 5.90 (s, 1 H), 3.79 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.3, 156.2, 152.6, 145.3, 140.1, 138.6, 135.9, 133.7, 128.7, 128.4, 126.8, 123.5, 119.4, 98.5, 51.4; MS *m*/*z* 324 (M$^+$, 62), 293 (26), 279 (18), 266 (24), 237 (27), 219 (28), 191 (91), 190 (67), 178 (36), 150 (32), 89 (49), 76 (85), 59 (100). Anal. Calcd for $C_{17}H_{12}N_2O_5$: C, 62.95; H, 3.73; N, 8.64. Found: C, 62.90; H, 3.69; N, 8.60.

(*Z*)-[2-(4-Cyanophenyl)benzo[*d*][1,3]oxazin-4-ylidene]-acetic acid methyl ester 3h-(*Z*): yellow-brown solid; 249−251 °C; ν_{max}(KBr)/cm^{-1} 2229 (w), 1716 (s), 1652 (s), 1606 (s), 1280 (m), 1160 (s), 1125 (s), 1097 (m), 850 (m), 818 (m), 757 (m); ^{1}H NMR ($CDCl_3$) δ_H ($CDCl_3$) 8.57 (d, J = 8.5 Hz, 2 H), 7.80 (d, J = 8.5 Hz, 2 H), 7.66 (dd, J = 7.8, 1.3 Hz, 1 H aromatic), 7.58 (td, J = 7.8, 1.3 Hz, 1 H), 7.49 (dd, J = 7.6, 1.3 Hz, 1 H), 7.38 (td, J = 7.6, 1.3 Hz, 1 H), 5.83 (s, 1 H =C*H*CO$_2$-Me), 3.80 (s, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.1, 156.2, 152.5, 139.8, 134.5, 133.4, 132.3, 128.9, 128.8, 127.7, 123.1, 118.7, 118.2, 115.4, 90.4, 51.1; *m*/*z* 304 (M$^+$, 92), 273 (36), 259 (47), 246 (33), 231 (58), 217 (48), 190 (100), 130 (34), 116 (48), 102 (60), 89 (64), 76 (80), 59 (98). Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 71.03; H, 3.98; N, 9.21. Found: C, 70.98; H, 3.94; N, 9.17.

(*E*)-[2-(4-Cyanophenyl)benzo[*d*][1,3]oxazin-4-ylidene]-acetic acid methyl ester 3h-(*E*): yellow-brown solid; 223−225 °C; ν_{max}(KBr)/cm^{-1} 2229 (w), 1716 (s), 1651 (s), 1606 (s), 1280 (m), 1243 (m), 1160 (s), 1126 (s), 1097 (m), 851 (m), 818 (m), 757 (m); ^{1}H NMR ($CDCl_3$) δ_H ($CDCl_3$) 9.03 (dd, J = 8.1, 1.4 Hz, 1 H), 8.28 (d, J = 8.5 Hz, 2 H), 8.00 (d, J = 8.5 Hz, 2 H), 7.51 (td, J = 8.1, 1.0 Hz, 1 H), 7.43 (d, J = 7.6 Hz, H), 7.13 (td, J = 7.6, 1.4 Hz, 1 H), 5.83 (s, 1 H), 3.80 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.2, 156.5, 152.4, 142.3, 134.2, 133.7, 132.1, 130.0, 129.3, 128.2, 126.7, 124.1, 119.4, 118.7, 116.3, 98.3, 51.5; *m*/*z* 304 (M$^+$, 91), 273 (42), 259 (47), 231 (58), 217 (41), 190 (100), 130 (43), 116 (61), 102 (68), 89 (66), 76 (79), 59 (93). Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 71.03; H, 3.98; N, 9.21. Found: C, 70.97; H, 3.94; N, 9.16.

(*Z*)-[2-(4-Methoxyphenyl)benzo[*d*][1,3]oxazin-4-ylidene]acetic acid methyl ester 3i-(*Z*): pale yellow solid: mp 164−167 °C; IR (KBr) ν_{max} cm^{-1} 2974 (w), 2943 (w), 2836 (w), 1716 (m), 1648 (s), 1607 (m), 1592 (m), 1515 (m), 1476 (m), 1245 (m), 1174 (m), 1146 (m), 1124 (m), 839 (m), 768 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.41 (d, J = 9.0 Hz, 2 H), 7.65−7.60 (m, 1 H aromatic), 7.57−7.49 (m, 1 H), 7.46−7.40 (m, 1 H), 7.32−7.25 (m, 1 H), 7.02 (d, J = 9.0 Hz, 2 H), 5.78 (s, 1 H, =C*H*CO$_2$Me), 3.88 (s, 3 H), 3.81 (s, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.4, 162.9, 157.0, 154.3, 140.9, 133.2, 130.3, 127.4, 127.0, 123.0, 119.1, 118.3, 114.0, 89.3, 55.3, 51.0; MS *m*/*z* 309 (M$^+$, 100), 278 (27), 251 (23), 222 (23), 155 (16), 135 (16), 118 (16). Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.88; H, 4.89; N, 4.53. Found: C, 69.82; H, 4.85; N, 4.49.

(*Z*)-(2-*p*-Tolylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3j-(*Z*): orange solid; mp 118−121 °C; IR (KBr) ν_{max} cm^{-1} 2952 (w), 2916 (w), 1726 (s), 1652 (s), 1609 (m), 1599 (m), 1281 (m), 1167 (s), 1127 (m), 1097 (m), 832 (m), 803 (m), 757 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.32 (d, J = 7.7 Hz, 2 H), 7.61−7.56 (m, 1 H), 7.53−7.46 (m, 1 H), 7.44−7.40 (m, 1 H), 7.32−7.23 (m, 3 H), 5.75 (s, 1 H), 3.80 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 165.3, 156.8, 154.5, 142.8, 140.7, 133.1, 129.3, 128.4, 127.7, 127.2, 123.0, 119.2, 118.4, 89.5, 51.0, 21.6; MS *m*/*z* 293 (M$^+$, 100), 262 (26), 248 (29), 235 (23), 220 (28), 204 (20), 179 (18), 119 (20), 110 (32), 89 (21). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.69; H, 5.16; N, 4.78. Found: C, 73.64; H, 5.13; N, 4.73.

(*Z*)-4-(4-Methoxycarbonylmethylene-4*H*-benzo[*d*][1,3]-oxazin-2-yl)benzoic acid methyl ester 3k-(*Z*): lemon-yellow solid; mp 189−191 °C; IR (KBr) ν_{max} cm^{-1} 1716 (s), 1700(m), 1645 (m), 1606 (m), 1274 (m), 1248 (m), 1169 (m), 1093 (s), 771 (m), 708 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.15 (d, J = 8.5 Hz, 2 H), 8.11(d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 1 H), 7.54 (td, J = 8.5, 1.0 Hz, 1 H), 7.35 (d, J = 7.6 Hz, 1 H aromatic), 7.28 (td, J = 7.6, 1.2 Hz, 1 H), 5.74 (s, 1 H, =C*H*CO$_2$Me), 3.92 (s, 3 H), 3.79 (s, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 166.5, 166.3, 156.3, 153.2 140.1, 134.9, 133.2, 129.6, 129.3, 128.4, 127.5, 126.6, 123.0, 118.6, 90.0, 52.2, 51.0; MS *m*/*z* 337 (M$^+$, 56), 306 (21), 292 (18), 279 (12), 264 (20), 219 (15), 191 (38), 163 (31), 137 (100), 109 (82), 102 (36), 96 (59), 89 (82), 76 (83), 59 (85). Anal. Calcd for $C_{19}H_{15}NO_5$: C, 68.04; H, 3.91; N, 4.15. Found: C, 68.00; H, 3.86; N, 4.11.

(*E*)-4-(4-Methoxycarbonylmethylene-4*H*-benzo[*d*][1,3]-oxazin-2-yl)benzoic acid methyl ester 3k-(*E*): lemon-yellow solid; mp 176−179 °C; IR (KBr) ν_{max} cm^{-1} 1717 (s), 1701 (m), 1648 (m), 1612 (m), 1277 (m), 1249 (m), 1170 (m), 1114 (m) 1094 (s), 771 (m), 708 (m); ^{1}H NMR ($CDCl_3$) δ_H 9.02 (dd, J = 8.0, 1.0 Hz, 1 H), 8.16 (d, J = 8.5 Hz, 2 H), 8.07(d, J = 8.5 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1 H), 7.39 (d, J = 7.4 Hz, 1 H), 7.35 (td, J = 8.0, 1.2 Hz, 1 H), 5.82 (s, 1 H), 3.92 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 166.5, 166.2, 158.3, 153.5 141.1, 134.2, 133.5, 132.9, 129.5, 128.2, 127.6, 126.6, 123.0, 118.3, 97.9, 52.2, 51.4; MS *m*/*z* 337 (M$^+$, 91), 306 (39), 292 (37), 264 (30), 219 (27), 191 (48), 163 (37), 137 (100), 109 (70), 96 (53), 89 (73), 76 (76), 59 (64). Anal. Calcd for $C_{19}H_{15}NO_5$: C, 68.04; H, 3.91; N, 4.15. Found: C, 68.01; H, 3.86; N, 4.12.

(*Z*)-(2-Vinylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3l-(*Z*): orange solid; mp 61−63 °C; IR (KBr) ν_{max} cm^{-1} 1711 (s), 1649 (m), 1615 (m), 1603 (m), 1279 (m), 1258 (m), 1148 (s), 1126 (m), 1086 (m), 807 (m), 774 (m), 764 (m); ^{1}H NMR ($CDCl_3$) δ_H 7.52 (d, J = 8.0 Hz, 1 H aromatic), 7.49−7.41 (m, 1 H), 7.30 (d, J = 7.9 Hz, 1 H), 7.27−7.20 (m, 1 H), 6.75 (d, J = 17.3 Hz, 1 H), 6.32 (dd, J = 17.3, 10.7 Hz, 1 H), 5.89 (d, J = 10.7 Hz, 1 H), 5.67 (s, 1 H, =C*H*CO$_2$Me), 3.72 (s, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.1, 156.1, 153.7, 140.2, 133.1, 128.9, 128.2, 127.2, 123.0, 118.6, 112.7, 89.8, 50.9; MS *m*/*z* 229 (M$^+$, 100), 198 (39), 184 (40), 171 (23), 156 (30), 142 (45), 115 (44), 89 (29), 76 (25). Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.10; H, 4.84; N, 6.11. Found: C, 68.03; H, 4.82; N, 6.07.

(*E,Z*)-(2-Propenylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3m-(*Z*) ≡ 3o-(*Z*): orange solid; mp 98−100 °C; IR (KBr) ν_{max} cm^{-1} 2949 (w), 1714 (s), 1684 (s), 1626 (s), 1603 (s), 1471 (m), 1433 (s), 1273 (s), 1142 (m), 1083 (s), 1037 (w), 974 (m), 806 (m), 763 (m); ^{1}H NMR ($CDCl_3$) δ_H 7.59 (d, *J* 7.9, 1 H aromatic), 7.49 (td, J = 7.9, 1.3 Hz, 1 H), 7.41−

7.24 (m, 3 H, 2 H), 6.12 (dq, J = 15.5, 1.6 Hz, 1 H), 5.72 (s, 1 H, =C*H*CO_2Me), 3.81 (s, 3 H), 2.38 (dd, J = 6.8, 1.6 Hz, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.9, 156.3, 154.1, 142.1, 140.2, 133.1, 127.3, 126.9, 123.0, 122.5, 118.4, 89.3, 50.9, 18.7; MS *m*/*z* 243 (M^+, 100), 228 (7), 212 (24), 198 (22), 184 (93), 156 (20), 154 (21), 129 (22), 115 (12), 89 (17), 76 (11), 69 (20), 59 (7). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.11; H, 5.39; N, 5.76. Found: C, 69.06; H, 5.36; N, 5.72.

(*E*,*E*)-(2-Propenylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3m-(*E*) ≡ 3o-(*E*): orange solid; mp 84−86 °C; IR (KBr) ν_{max} cm^{-1} 2949 (w), 1713 (s), 1683 (s), 1626 (s), 1601 (s), 1471 (m), 1431 (s), 1272 (s), 1143 (m), 1083 (s), 974 (m), 806 (m), 763 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.86 (dd, J = 8.5, 1.1 Hz, 1 H), 7.78 (dd, J = 8.1, 1.4 Hz, 1 H), 7.33−7.24 (m, 2 H, 1 H), 7.10 (td, J = 8.5, 1.4 Hz, 1 H), 5.99 (dq, J = 15.4, 1.4 Hz, 1 H), 5.71 (s, 1 H), 3.78 (s, 3 H), 1.94 (dd, J = 6.8, 1.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 167.5, 156.6, 141.5, 135.8, 131.1, 126.6, 126.9, 122.5, 122.3, 121.0, 120.6, 97.1, 52.5, 17.8; MS *m*/*z* 243 (M^+, 89), 228 (12), 212 (28), 198 (23), 184 (100), 156 (25), 154 (22), 129 (25), 89 (19), 69 (24), 59 (11). Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.11; H, 5.39; N, 5.76. Found: C, 69.05; H, 5.35; N, 5.72.

(E,*Z*)-(2-Styrylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3n-(*Z*): orange solid; mp 113−115 °C; IR (KBr) ν_{max} cm^{-1} 2949 (w), 1699 (s), 1645 (s), 1622 (m), 1581 (s), 1465 (m), 1433 (m), 1278 (s), 1260 (m), 1202 (w), 1063 (s), 971 (s), 761 (s), 694 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.03 (d, *J* 16.0 Hz, 1 H), 7.58−7.50 (m, 3 H aromatic), 7.43 (t, *J* 7.4 Hz, 1 H), 7.39−7.29 (m, 4 H), 7.30 (t, *J* 7.3 Hz, 1 H), 6.68 (d, *J* 16.0 Hz, 1 H), 5.69 (s, 1 H, =C*H*CO_2Me), 3.76 (s, 3 H) (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 164.8, 156.0, 154.3, 141.8, 140.5, 135.0, 132.8, 129.7, 128.6, 127.9, 127.6, 126.9, 122.8, 118.9, 118.3, 89.5, 50.8; MS *m*/*z* 305 (M^+, 100), 276 (12), 246 (90), 232 (14), 217 (71), 204 (22), 152 (11), 136 (21), 115 (27), 102 (36), 89 (15), 77 (18), 51 (9). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.73; H, 4.95; N, 4.59. Found: C, 74.68; H, 4.91; N, 4.55.

(*E*,*E*)-(2-Styrylbenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 3n-(*E*): orange solid; mp 95−97 °C; IR (KBr) ν_{max} cm^{-1} 2949 (w), 1698 (s), 1644 (s), 1622 (m), 1580 (s), 1465 (m), 1433 (m), 1278 (s), 1259 (m), 1202 (w), 1063 (s), 971 (s), 761 (s), 694 (m); ^{1}H NMR ($CDCl_3$) δ_H 9.01 (dd, J = 7.9, 0.9 Hz, 1 H), 7.81 (dd, J = 8.0, 1.1 Hz, 1 H), 7.74 (d, J = 15.6 Hz, 1 H), 7.60 (t, J = 8.0 Hz, 1 H), 7.58−7.55 (m, 2 H), 7.39−7.36 (m, 3 H), 7.15 (t, J = 7.9 Hz, 1 H), 6.59 (d, J = 15.6 Hz, 1 H), 5.75 (s, 1 H), 3.72 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 166.4, 158.1, 154.9, 141.6, 139.9, 134.7, 133.3, 129.4, 128.6, 127.8, 127.6, 126.1, 122.9, 118.8, 118.2, 97.3, 51.2; MS *m*/*z* 305 (M^+, 100), 276 (15), 246 (90), 232 (16), 217 (71), 204 (22), 152 (15), 136 (27), 115 (33), 102 (42), 89 (20), 77 (24), 51 (9). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.73; H, 4.95; N, 4.59. Found: C, 74.67; H, 4.91; N, 4.54.

(2-*tert*-Butoxycarbonylaminophenyl)propynoic acid methyl ester: white solid; 84−86 °C; ν_{max}(KBr)/cm^{-1} 3407 (s), 2970 (m), 2210 (w) 1734 (s), 1717 (s), 1707 (s), 1577 (m), 1521 (s), 1452 (s), 1301 (m), 1152 (m); ^{1}H NMR ($CDCl_3$) δ_H ($CDCl_3$) 8.19 (d, J = 8.5 Hz, 1 H), 7.49 (dd, J = 8.5, 1.3 Hz, 1 H), 7.42 (td, J = 8.5, 1.3 Hz, 1 H), 7.16 (bs, 1 H) 7.00 (td, J = 8.5, 0.8 Hz, 1 H), 3.86 (s, 3 H), 1.54 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ_C 154.0, 152.1, 141.5, 133.4, 132.2, 122.2, 118.1, 107.2, 86.8, 82.1, 81.3, 52.8, 28.2; MS *m*/*z* 275 (M^+, 12), 219 (11), 175 (95), 170 (31), 143 (65), 115 (28), 89 (12), 59 (7), 57 (100). Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.43; H, 6.23; N, 5.09. Found: C, 65.38; H, 6.20; N, 5.05.

(*Z*)-(2-Propylaminobenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 4r-(*Z*): yellow orange solid; mp 71−73 °C; IR (KBr) ν_{max} cm^{-1} 3273 (m), 3094 (w), 2956 (w), 1707 (s), 1665 (s), 1607 (s), 1591 (s), 1168 (s), 1063 (m), 810 (m), 757 (m); ^{1}H NMR ($CDCl_3$) δ_H 7.47 (dd, J = 8.0, 1.3 Hz, 1 H aromatic), 7.36 (td, J = 7.4, 1.3 Hz, 1H), 7.07 (d, J = 7.4 Hz, 1 H), 6.99 (td, J = 8.0, 1.2 Hz, 1 H), 5.68 (s, 1 H =C*H*CO_2Me), 5.64 (bs, 1 H), 3.71 (s, 3 H), 3.39 (t, J = 7.1 Hz, 2 H), 1.70−1.55 (m, 2 H), 0.96 (t, J = 7.4 Hz, 3 H); (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.4, 158.0, 151.6, 144.1, 133.3, 124.1, 123.2, 123.1, 115.2, 88.3, 50.8, 43.1, 22.7, 11.3; MS *m*/*z* 260 (M^+, 72), 218 (16), 201 (19), 186 (100), 160 (18), 144 (27), 90 (14), 59 (6). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.20; N, 10.77. Found: C, 64.52; H, 6.17; N,10.74.

(*Z*)-(2-Oxo-3-propyl-2,3-dihydro-1*H*-quinazolin-4-ylidene)acetic acid methyl ester 5r-(*Z*): yellow ochre solid; mp 162−165 °C; IR (KBr) ν_{max} cm^{-1} 3325 (m), 3058 (w), 2945 (w), 1704 (s), 1690 (s), 1602 (s), 1576 (s), 1153 (s), 1075 (m), 799 (m), 755 (m); ^{1}H NMR ($CDCl_3$) δ_H 9.05 (bs, 1 H), 7.57 (d, J = 7.5 Hz, 1 H aromatic), 7.35−7.31 (m, 1 H), 7.07 (td, J = 7.5, 1.1 Hz, 1 H), 6.90 (dd, J = 7.9, 0.9 Hz, 1 H), 5.74 (s, 1 H =C*H*CO_2Me), 4.13 (t, J = 7.1 Hz, 2 H), 3.76 (s, 3 H), 1.64−1.54 (m, 2 H), 0.79 (t, J = 7.4 Hz, 3 H); (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.5, 152.0, 147.1, 135.6, 131.1, 128.5, 126.3, 123.4, 114.7, 96.0, 50.5, 47.1, 20.5, 11.0; MS *m*/*z* 260 (M^+, 28), 229 (15), 218 (74), 201 (26), 187 (100), 160 (40), 145 (15), 131 (15), 116 (20). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.20; N, 10.77. Found: C, 64.51; H, 6.15; N, 10.73.

(*E*)-(2-Oxo-3-propyl-2,3-dihydro-1*H*-quinazolin-4-ylidene)acetic acid methyl ester 5r-(*E*): yellow ochre solid; mp 126−128 °C; IR (KBr) ν_{max} cm^{-1} 3321 (m), 3051 (w), 2955 (w), 1702 (s), 1690 (s), 1602 (s), 1576 (s), 1153 (s), 1075 (m), 799 (m), 755 (m); ^{1}H NMR ($CDCl_3$) δ_H 8.92 (bs, 1 H), 8.08 (dd, J = 8.1, 1.1 Hz, 1 H), 7.38 (td, J = 8.1, 1.3 Hz, 1 H), 7.06 (td, J = 8.0, 1.1 Hz, 1 H), 6.87 (dd, J = 8.0, 1.3 Hz, 1 H), 5.40 (s, 1 H), 3.89 (t, J = 7.4 Hz, 2 H), 3.73 (s, 3 H), 1.83−1.72 (m, 2 H), 0.99 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 167.6, 150.9, 148.4, 136.3, 132.1, 130.1, 127.6, 121.7, 114.1, 94.6, 51.2, 45.8, 19.1, 11.2; MS *m*/*z* 260 (M^+, 25), 229 (17), 218 (77), 201 (22), 187 (100), 160 (43), 145 (12), 131 (11), 116 (22). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.20; N, 10.77. Found: C, 64.55; H, 6.16; N,10.74.

4-Oxo-2-propylamino-4*H*-quinoline-3,3-dicarboxylic acid dimethyl ester (6r): white solid; 177−179 °C; ν_{max}(KBr)/cm^{-1} 3251 (m), 3094 (w), 2956 (w), 1731 (s), 1686 (s), 1661 (s), 1601 (m), 1475 (s), 1327 (s), 1162 (m), 1232 (s), 1071 (m), 811 (m), 756 (m); δ_H ($CDCl_3$) 7.90 (dd, J = 7.7, 1.6 Hz, 1 H), 7.54 (td, J = 8.0, 1.6 Hz, 1 H), 7.23 (dd, J = 8.0, 1.0 Hz, 1 H), 7.07 (td, J = 7.7, 1.0 Hz, 1 H), 5.41 (bs, 1 H), 3.77 (s, 6 H, 2), 3.24 (t, J = 8.4 Hz, 2 H), 1.70−1.58 (m, 2 H), 0.95 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 196.4, 164.8, 153.8, 151.2, 142.9, 137.1, 127.0, 126.5, 123.6, 67.6, 53.9, 43.4, 22.0, 11.2; MS *m*/*z* 318 (M^+, 27), 276 (11), 259 (12), 244 (96), 227 (100), 213 (11), 199 (28), 186 (37), 171 (15), 145 (14), 119 (13), 59 (8). Anal. Calcd for $C_{16}H_{18}N_2O_5$: C, 60.35; H, 5.70; N, 8.80. Found: C, 60.30; H, 5.66; N, 8.76.

2-Methoxycarbonylamino-4-oxo-1,4-dihydroquinoline-3-carboxylic acid methyl ester (7s): white solid; 191−193 °C; ν_{max}(KBr)/cm^{-1} 3502 (m), 3217 (m), 2951 (w), 1723 (s), 1662 (s), 1620 (s), 1581 (s), 1557 (s), 1448 (s), 1399 (s), 1325 (m), 1292 (s), 1232 (s), 1036 (s), 774 (s); δ_H ($CDCl_3$) 12.34 (sb, 1 H), 11.86 (bs, 1 H), 8.34 (d, J = 8.0 Hz, 1 H), 7.58 (td, J = 8.1, 1.3 Hz, 1 H), 7.34 (td, J = 8.0 , 0.9 Hz, 1 H), 7.24 (d, J = 8.1 Hz, 1 H), 3.94 (s, 3 H), 3.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 190.3, 174.8, 170.3, 155.1, 151.8, 135.3, 132.6, 126.9, 125.4, 124.8, 116.9, 53.6, 52.1; MS (EI) *m*/*z* 276 (M^+, absent), 244 (100), 229 (10), 215 (20), 167 (56), 166 (47), 165 (81), 152 (18); (ES) *m*/*z* 277 (M + 1), 263, 245. Anal. Calcd for $C_{13}H_{12}N_2O_5$: C, 56.51; H, 4.38; N, 10.14. Found: C, 56.46; H, 4.36; N, 10.10.

(*Z*)-(2-Benzylaminobenzo[*d*][1,3]oxazin-4-ylidene)acetic acid methyl ester 4t-(*Z*): pale yellow solid; mp 139−141 °C; IR (KBr) ν_{max} cm^{-1} 2934 (w), 1719 (s), 1685 (s), 1604 (m), 1472 (m), 1244 (m), 1150 (s), 1087 (m), 803 (m), 751 (m), 737 (m); ^{1}H NMR ($CDCl_3$) δ_H 7.48 (dd, J = 8.1, 1.4 Hz, 1 H

aromatic), 7.38 (td, $J = 8.1$, 1.2 Hz, 1H), 7.35−7.27 (m, 5 H), 7.09 (d, $J = 8.2$ Hz, 1 H), 7.03 (td, $J = 8.2$, 1.4 Hz, 1 H), 5.73 (bs, 1 H), 5.67 (s, 1 H, =C*H*CO_2Me), 4.62 (s, 2 H), 3.70 (s, 3 H); (the *Z* stereochemistry of the methoxycarbonylmethylene moiety was confirmed by a 2D NOESY experiment); ^{13}C NMR ($CDCl_3$) δ_C 165.4, 157.8, 151.2, 143.8, 136.9, 133.3, 128.6, 127.8, 127.6, 124.4, 123.6, 115.5, 88.7, 50.8, 45.4; MS *m*/*z* 308 (M^+, 38), 249 (63), 145 (81), 132 (13), 106 (15), 91 (100), 65 (12). Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.07; H, 5.19; N,9.05.

(*E*)-(2-Oxo-3-phenyl-2,3-dihydro-1*H*-quinazolin-4-ylidene)acetic acid methyl ester 5u-(*E*): orange solid; mp 223−225 °C; IR (KBr) ν_{max} cm^{-1} 2943 (w), 1698 (s), 1601 (s), 1490 (m), 1445 (m), 1343 (w), 1180 (m), 1140 (s), 1118 (m), 748 (w), 706 (m); ^{1}H NMR ($CDCl_3$) δ_H 9.19 (bs, 1 H), 8.22 (dd, $J = 8.0$, 0.8 Hz, 1 H), 7.58−7.48 (m, 3 H), 7.35 (td, $J = 8.0$, 0.8 Hz, 1 H), 7.30−7.26 (m, 2 H), 7.10 (td, $J = 8.0$, 1.0 Hz, 1 H), 6.76 (d, $J = 8.0$ Hz, 1 H), 4.83 (s, 1 H), 3.62 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ_C 167.2, 150.5, 137.7, 136.5, 132.4, 130.2, 130.0, 128.9, 128.8, 123.3, 122.0, 114.6, 98.3, 51.2; MS *m*/*z* 294 (M^+, 11), 263 (9), 235 (58), 234 (100), 217 (18), 190 (10), 77 (15). Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.79; N, 9.52. Found: C, 69.35; H, 4.77; N, 9.48.

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Supporting Information Available: Structures of **3i**, **5u**, **6s**, and **7r** are shown in Figures S1−S4, respectively. X-ray structural information for **3i**, **5u**, **6s**, and **7r** is collected in Table S1. Spectroscopic characterization of **1a**, **2a**−**u** substrates is reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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