DOI: 10.1002/ejoc.201402538

Iodine-Mediated Oxidation of Ynamides: A Facile Access to *N*-Monosubstituted α-Ketoamides and α-Ketoimides

Hai Huang,[a] Guangke He,[a] Xiaolin Zhu,[a] Xiaodong Jin,[a] Shineng Qiu,[a] and Hongjun Zhu*[a]

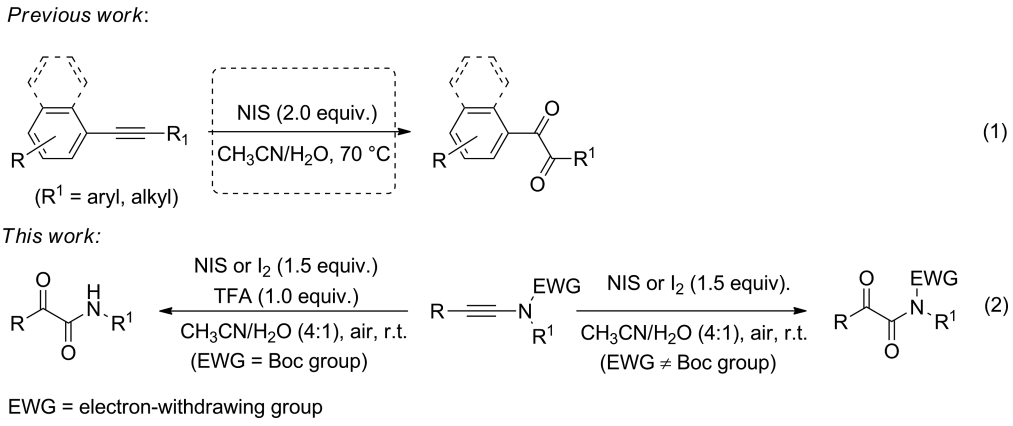
Keywords: Synthetic methods / Iodine / Oxidation / Amides / Alkynes

An efficient iodine-mediated oxidation reaction for ynamides has been developed to produce *N*-monosubstituted α-ketoamides and α-ketoimides. This oxidative method, which exhibits good functional group tolerance, was performed under mild conditions without a metal catalyst.

Introduction

The syntheses of α-ketoamides and their derivatives have attracted considerable attention, because they are biologically active compounds and have widespread applications as versatile building blocks in organic synthesis.[1,2] Various methods have been developed for the syntheses of α-ketoamides, which include the amidation of α-keto acids,[3] the double carbonylation of amines,[4] the oxidation of ynamides,[5] and other chemical transformations.[6] The oxidation of ynamides is a straightforward method to produce α-ketoamides because of the availability of a variety of ynamides.[7] Most of the present oxidation methods, however, are performed in the presence of transition-metal catalysts (e.g., Au and Rh)[5d–5j] and external oxidants.[5f] For instance, Li[5b] reported the Au-catalyzed oxidation of an alkyne by employing diphenyl sulfoxide to produce 1,2-dicarbonyl compounds. However, these oxidative methods have several limitations, such as the need for harsh oxidative conditions, expensive transition-metal catalysts, and high reaction temperatures,[5] thereby restricting their practical applications. Therefore, the development of efficient and convenient methods to synthesize *N*-monosubstituted α-ketoamides and α-ketoimides under mild reaction conditions is necessary.

The use of inexpensive and less toxic iodine-containing reagents is attractive in organic synthesis.[8] Several reports have described the syntheses of α-diketones by using the iodine-mediated oxidation reaction of alkynes.[9] For instance, Zhao and co-workers reported a convenient approach to the preparation of α-diketones that involves the reaction of alkynes with *N*-iodosuccinimide (NIS)/H_2O at 70 °C [see Scheme 1, Equation (1)].[10] Despite these advances, there is no reported example[11] of the synthesis of *N*-monosubstituted α-ketoamides[12] through the direct oxi-



Scheme 1. Iodine-mediated oxidation of ynamides (Boc = *tert*-butoxycarbonyl, TFA = trifluoroacetic acid).

[a] Department of Applied Chemistry, College of Sciences, Nanjing Tech University,
Nanjing 211816, Peoples Republic of China
E-mail: zhuhj@njtech.edu.cn
http://lxy.njtech.edu.cn/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402538.

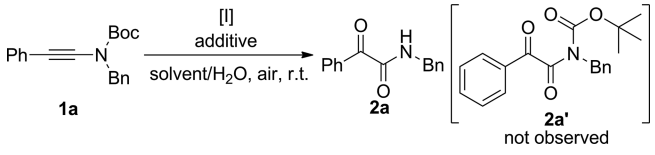
dation of ynamides. Herein, we report a facile and straightforward method based on the iodine/water-mediated oxidation of ynamides to synthesize *N*-monosubstituted α-ketoamides and α-ketoimides [see Scheme 1, Equation (2)].

Results and Discussion

In the initial experiments, *tert*-butyl *N*-benzyl-*N*-(phenylethynyl)carbamate (**1a**)[7d] was treated with NIS and H_2O under N_2. Because of the strong acidic environment during the oxidative process, this reaction afforded the oxidation product *N*-benzyl-2-oxo-2-phenylacetamide (**2a**) in 13% yield by HPLC analysis, instead of the α-ketoimide *tert*-butyl *N*-benzyl-*N*-(2-oxo-2-phenylacetyl)carbamate (**2a′**, see Table 1, Entry 1).[13] The desired product **2a** was obtained in 56% yield when **1a** was stirred with NIS in a mixture of CH_3CN and H_2O in the air (see Table 1, Entry 2). The yield improved from 56 to 80% by decreasing the amount of **1a** (see Table 1, Entry 3). In a control experiment (i.e., without NIS), the target product was not produced (see Table 1, Entry 4). Among the solvents screened, CH_3CN was superior to tetrahydrofuran (THF; 55% yield), 1,4-dioxane (60% yield), *N*,*N*-dimethylformamide (DMF; 43% yield), and dichloromethane (DCM; 22% yield; see Table 1, Entry 3 vs. 5–8). In addition, solvents with poor water solubility, such as DCM, provided unsatisfactory results. Given that amide groups hydrolyze under acidic conditions, TFA was added to the reaction mixture. The target product **2a** was obtained in high yield by using TFA (see Table 1, Entry 9). The employment of 1.5 equiv. of NIS gave the highest yield of **2a** (see Table 1, Entries 9–12). Interestingly, this oxidation reaction was also promoted by using I_2 instead of NIS, and 1.5 equiv. of I_2 was an optimal amount for this transformation (see Table 1, Entry 13).

Employing the optimized reaction conditions (see Table 1, Entry 13), we examined the scope and generality of this transformation by using various ynamides that contained a Boc group (see Table 2). Methyl and bromo substituents on the aryl ring of the ynamide were tolerated and readily gave high yields of the corresponding *N*-monosubstituted α-ketoamide (see Table 2, Entries 2 and 3). Under the optimized reaction conditions, various substrates that contained *ortho*, *meta*, and *para* substituents on the *N*-aryl ring of the ynamide were converted (in moderate to high yields) into the corresponding *N*-monosubstituted α-ketoamides (see Table 2, Entries 4–11). The yields decreased with an electron-withdrawing group at the *meta* position of the *N*-aryl ring (see Table 2, Entries 8–11). *N*-naphthyl-substituted ynamide **1l** was also used in this reaction, and **2l** was produced in a yield of 54% (see Table 2, Entry 12). In addition, a high yield was obtained by using alkyl-substituted ynamide **1m** under the reaction conditions (see Table 2, Entry 13). The structure of **2a** was further confirmed by using single-crystal X-ray structure analysis (see Figure 1).[14]

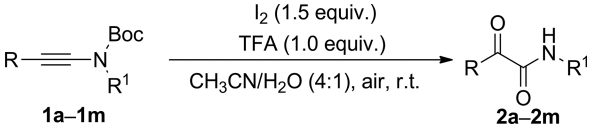
Table 1. Optimization of reaction conditions.[a]



Entry	Solvent	[I] [equiv.]	Additive (equiv.)	*t* [h]	Yield [%]
1	CH_3CN	NIS (1.5)	–	3	13[b,c]
2[c]	CH_3CN	NIS (1.5)	–	3	56
3	CH_3CN	NIS (1.5)	–	3	80
4	CH_3CN	–	–	3	0
5	THF	NIS (1.5)	–	3	55
6	1,4-dioxane	NIS (1.5)	–	3	60
7	DMF	NIS (1.5)	–	4	43
8	DCM	NIS (1.5)	–	12	22
9	CH_3CN	NIS (1.5)	TFA (1.0)	3	95 (93)[d]
10	CH_3CN	NIS (0.5)	TFA (1.0)	3	28
11	CH_3CN	NIS (1.0)	TFA (1.0)	3	57
12	CH_3CN	NIS (2.0)	TFA (1.0)	3	92
13	CH_3CN	I_2 (1.5)	TFA (1.0)	3	94

[a] Reagents and conditions: **1a** (0.2 mmol), NIS or I_2, H_2O (0.5 mL), and solvent (2.0 mL) at room temp. in the air. Unless otherwise noted, yields were determined by HPLC analysis of the crude reaction mixture. [b] H_2O (2.0 equiv.) was used under N_2. [c] **1a** (0.3 mmol) was used. [d] Isolated yield.

Table 2. Iodine-promoted oxidation of ynamides.[a]



Entry	R	R^1	*t* [h]	Product	Isolated yield [%]
1	Ph (**1a**)	Bn	3	**2a**	93
2	*p*-MeC_6H_4 (**1b**)	Bn	3	**2b**	93
3	*p*-BrC_6H_4 (**1c**)	Bn	3	**2c**	90
4	Ph	Ph (**1d**)	5	**2d**	75
5	Ph	*o*-MeC_6H_4 (**1e**)	5	**2e**	83
6	Ph	*m*-MeC_6H_4 (**1f**)	5	**2f**	89
7	Ph	*p*-MeC_6H_4 (**1g**)	5	**2g**	80
8	Ph	*m*-FC_6H_4 (**1h**)	5	**2h**	79
9	Ph	*m*-ClC_6H_4 (**1i**)	5	**2i**	65
10	Ph	*m*-BrC_6H_4 (**1j**)	8	**2j**	59
11	Ph	*m*-$CF_3C_6H_4$ (**1k**)	12	**2k**	57
12	Ph	2-naphthyl (**1l**)	3	**2l**	54
13	*n*-butyl (**1m**)	Ph	4	**2m**	91

[a] Reagents and conditions: ynamide (0.2 mmol), I_2 (1.5 equiv.), TFA (1.0 equiv.), CH_3CN (2.0 mL), H_2O (0.5 mL), room temp., air.

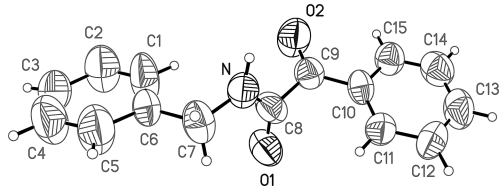
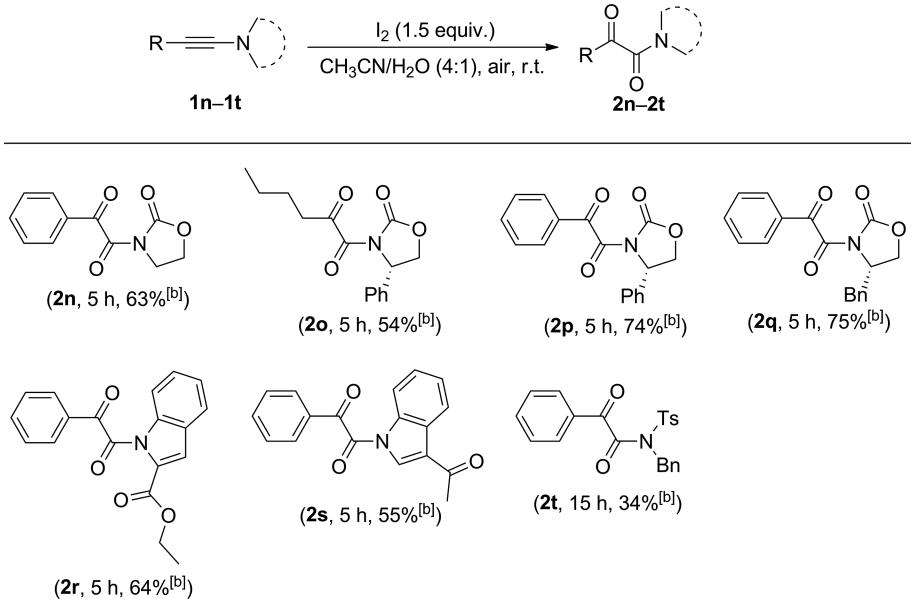


Figure 1. Single-crystal X-ray structure of **2a**.

Table 3. Iodine-promoted oxidation of ynamides without Boc group.[a]

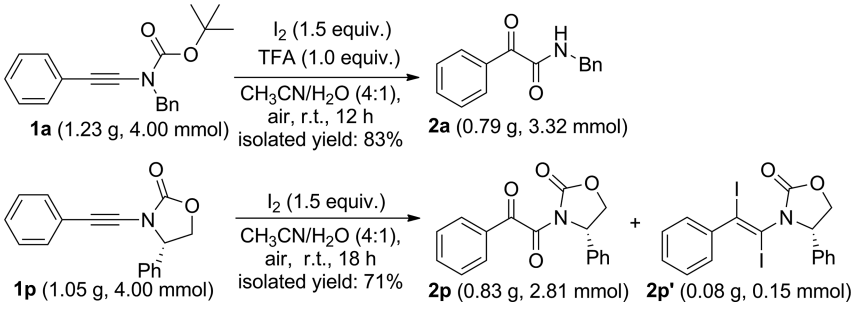


[a] Reagents and conditions: ynamine (0.3 mmol), I_2 (1.5 equiv.), CH_3CN (3.0 mL), H_2O (0.75 mL), room temp., air. [b] Isolated yield.

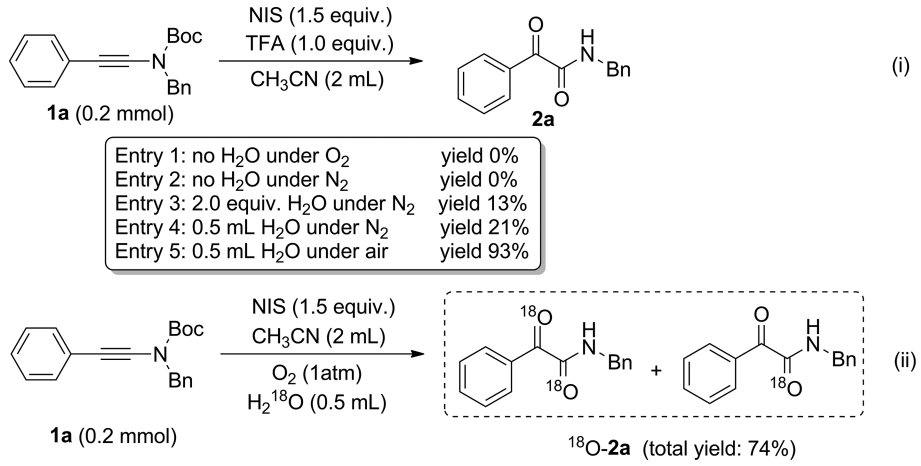
Different alkynamide derivatives that did not contain a Boc group were then investigated (see Table 3). Both *N*-(arylalkynyl)- and *N*-(alkylalkynyl)-substituted oxazolidinones were converted into the corresponding α-ketoimides in moderate yields (see Table 3, Compounds **2n** and **2o**). To examine the steric effects of 4-substituted oxazolidinones, we used (*S*)-4-phenyl-3-(phenylethynyl)oxazolidin-2-one (**1p**) and (*S*)-4-benzyl-3-(phenylethynyl)oxazolidin-2-one (**1q**) as model substrates, which produced the corresponding products in yields of 74 and 75%, respectively (see Table 3, compounds **2p** and **2q**). This indicates that the product yield is affected more by the electronics of the substrates than the steric hindrance of the 4-substituted oxazolidinones. In addition, substituted indoles were also examined, and they could be transformed into the corresponding products in moderate yields (see Table 3, compounds **2r** and **2s**). *N*-Benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (**1t**) was converted into the corresponding α-ketoimide (see Table 3, compound **2t**) with a yield of only 34%, which was possibly because of the strong electron-withdrawing ability of the sulfonyl group.

To demonstrate the synthetic potential of this strategy, **1a** (1.23 g, 4 mmol) and **1p** (1.05 g, 4 mmol) were employed in the reaction under the optimal conditions, which could be scaled up to 4 mmol without a significant decrease in the yield (see Scheme 2). In the large-scale reaction of **1p**, it is noteworthy that alkenyl diiodo intermediate **2p′** was also obtained in 4% isolated yield.

To understand the reaction mechanism, control experiments were conducted by using different amounts of H_2O [see Scheme 3, Equation (i)]. Compound **2a** was not produced under N_2 or O_2 in the absence of H_2O [see Scheme 3, Equation (i), Entries 1 and 2]. Although the reaction did proceed by using different amounts of H_2O in the absence



Scheme 2. Scale-up experiment.



Scheme 3. Experiments for mechanistic study.

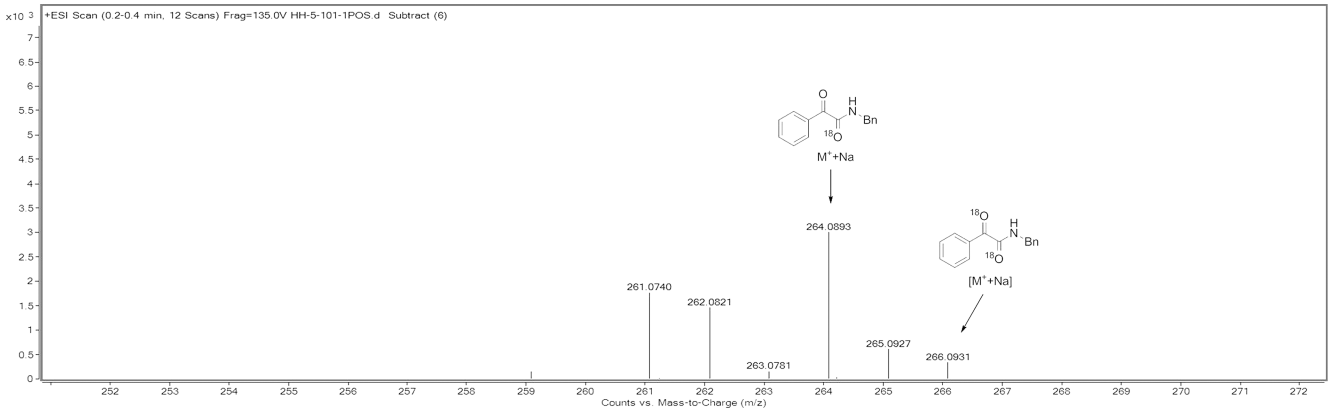


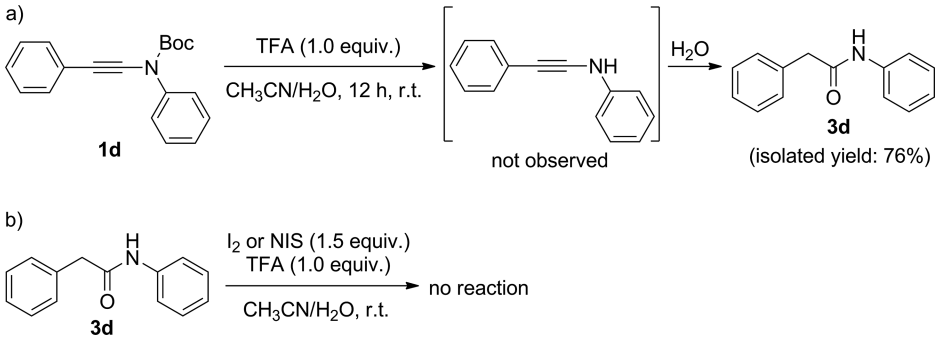
Figure 2. The HR mass spectra of ^{18}O-labeled **2a**.

of oxygen [see Scheme 3, Equation (i), Entries 3 and 4], the desired product was obtained in a relatively low yield. By contrast, the desired product was afforded in 93% yield under the optimized reaction conditions [see Scheme 3, Equation (i), Entry 5]. These results reveal the important role of molecular oxygen and H_2O in this oxidation system. The transformation of **1a** was then investigated by using of $H_2{}^{18}O$ to verify the presence of a double-and single-^{18}O-labeled product. The HR mass spectra showed a signal from a double-^{18}O-labeled product and one from a single-^{18}O-labeled product. The α-ketone moiety of α-ketoamide **2a** can actively undergo oxygen exchange through the hemiketal and $H_2{}^{18}O$, especially under acidic conditions (see Figure 2).[15]

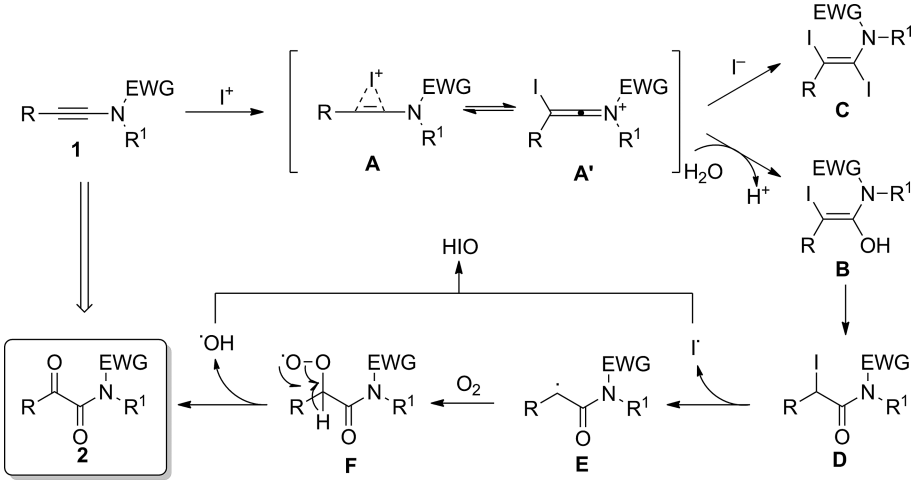
Two control reactions were performed to further understand the mechanism of the oxidative process. The reaction of ynamide **1d** with TFA (1.0 equiv.) in the absence of I_2 or NIS in the air resulted in the formation of amide **3d** in 76% yield, which demonstrates that deprotected ynamides are very sensitive toward hydrolysis[7a] [see Scheme 4, Equation (a)]. Under our optimized reaction conditions for the oxidative process, amide **3d** could not produce the desired α-ketoamide **2d** [see Scheme 4, Equation (b)]. Therefore, the removal of the Boc group could not occur before the oxidation process. It is, however, not easy to determine the point of deprotection under the present reaction conditions.

By employing our experimental results and literature reports, we have proposed a mechanism for this oxidation reaction (see Scheme 5). In the presence of iodine as a weak Lewis acid, **1** can produce iodonium intermediate **A**,[8a] which can undergo a nucleophilic attack by a hydroxy or iodide anion to produce iodoenol intermediate **B**[16] or diiodo compound **C**,[17] respectively. There is a high degree of regioselectivity with the formation of **B** because of the strong electron-donating effect of the nitrogen atom.[18] Through a keto/enol tautomerism, intermediate **B** can then form α-iodo ketone intermediate **D**.[10,19]

Then, radical intermediate **E** and an iodine radical could be generated from **D** through a homolytic cleavage of the C–I bond. Upon treatment with O_2, **E** can be converted into peroxy radical species **F**, which releases a hydroxyl radical to afford α-ketoimides **2**. The hydroxyl radical may combine with the iodine radical to result in the formation of HIO.[20] The further hydrolysis of α-ketoimides **2** under acidic conditions provides the *N*-monosubstituted α-ketoamides.



Scheme 4. Control reactions for mechanistic study.



Scheme 5. Proposed mechanism for this oxidation of ynamides.

Conclusions

We developed a new, efficient, and economical method to synthesize α-ketoamides by using the iodine-mediated oxidation of ynamides in air. This method not only provides a general entry to *N*-monosubstituted α-ketoamides and α-ketoimides but also broadens the application of iodine. Further studies of alkynes and iodine-mediated C–C, C–N, and C–O bond formations are being conducted in our laboratory, and the results will be reported in due course.

Experimental Section

General Methods: Unless otherwise stated, all commercial reagents were used without additional purification. The ^{1}H and ^{13}C NMR spectroscopic data were recorded at 400 and 100 MHz, respectively, with a Bruker Avance DPX spectrometer, and $CDCl_3$ was used as the solvent. The abbreviations that are used to describe the peak patterns are: br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants are reported in Hertz (Hz). Chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ = 0 ppm) for ^{1}H NMR and deuterochloroform (δ = 77.00 ppm) for ^{13}C NMR spectroscopy. Low-resolution and high-resolution mass spectra were obtained by using ESI ionization. Melting points were measured with a micro melting point apparatus. HPLC analysis was performed with a Shimadzu LC-20A high performance liquid chromatograph by using an external standard method. CCDC-991283 (for **2p′**), -991284 (for **2a**) and -993262 (for **2s**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Ynamides Synthesis – Typical Procedure I

***tert*-Butyl *N*-(Phenylethynyl)-*N*-(*o*-tolyl)carbamate (1e):** According to a reported procedure.[7d] To a mixture of *tert*-butyl *o*-tolylcarbamate (1.63 g, 8 mmol), K_3PO_4 (3.21 g, 16 mmol), $CuSO_4{\cdot}5H_2O$ (0.19 g, 0.8 mmol), and 1,10-phenanthroline (0.27 g, 1.6 mmol) in a reaction vial was added a solution of (bromoethynyl)benzene[21] (1.57 g, 8.8 mmol) in toluene (15 mL). The vial was capped and then heated in an oil bath at 85 °C for 18 h, as the progress of the reaction was monitored by TLC analysis. Upon completion, the reaction mixture was cooled to room temperature and diluted with EtOAc. The resulting mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The crude product was purified by flash chromatography on a silica gel column [petroleum ether (PE)/ethyl acetate (EtOAc)] to afford **1e** (1.37 g, 56%) as a yellow solid; m.p. 55–56 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 3 H), 7.29–7.22 (m, 6 H), 2.36 (s, 3 H), 1.52 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 138.4, 135.4, 131.0, 130.9, 128.4, 128.1, 127.5, 127.2, 126.9, 123.5, 83.8, 83.0, 69.3, 28.0, 17.5 ppm. MS (ESI): *m*/*z* (%) = 330 (100) [M + Na]$^+$. IR (KBr): $\tilde{\nu}$ = 3443, 2983, 1725, 1636, 1522, 1370, 1306, 1155, 1006, 857, 762 cm^{-1}. $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 78.42, H 6.73, N 4.39.

***tert*-Butyl *N*-(Phenylethynyl)-*N*-(*m*-tolyl)carbamate (1f):** Yellow solid (0.98 g, 40% yield); m.p. 93–94 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (dd, ^1J = 1.6 Hz, ^2J = 8.0 Hz, 2 H), 7.34 (s, 1 H), 7.32–7.23 (m, 5 H), 7.08 (d, J = 6.8 Hz, 1 H),

2.38 (s, 3 H), 1.57 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 139.5, 138.8, 130.8, 128.6, 128.2, 127.5, 127.3, 125.4, 123.4, 121.8, 83.8, 83.4, 70.0, 28.0, 21.4 ppm. MS (ESI): *m*/*z* (%) = 330 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3412, 2975, 2923, 2257, 1737, 1606, 1490, 1451, 1361, 1290, 1248, 1150, 1043, 852, 758 cm^{-1}. $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 78.16, H 7.02, N 4.31.

***tert*-Butyl *N*-(Phenylethynyl)-*N*-(*p*-tolyl)carbamate (1g):** Yellow solid (1.25 g, 51% yield); m.p. 63–64 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.36 (m, 4 H), 7.31–7.24 (m, 3 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 2.36 (s, 3 H), 1.57 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 137.1, 136.6, 130.8, 129.4, 128.2, 127.3, 124.6, 123.4, 83.9, 83.3, 69.8, 28.0, 21.0 ppm. MS (ESI): *m*/*z* (%) = 330 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3414, 3127, 3058, 2977, 2926, 2251, 1733, 1511, 1365, 1300, 1147, 1006, 755 cm^{-1}. $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 78.33, H 6.92, N 4.58.

***tert*-Butyl *N*-(3-Fluorophenyl)-*N*-(phenylethynyl)carbamate (1h):** Yellow solid (1.42 g, 57% yield); m.p. 33–35 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.27 (m, 8 H), 6.99–6.92 (m, 1 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 141.1, 130.9, 129.8, 129.7, 128.3, 127.6, 123.0, 119.7 (d, *J* = 2.8 Hz), 113.3 (d, *J* = 21.4 Hz), 111.8 (d, *J* = 25.5 Hz), 84.0, 82.7, 70.9, 28.0 ppm. MS (ESI): *m*/*z* (%) = 334 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3415, 3083, 2979, 2930, 2246, 1738, 1601, 1488, 1365, 1292, 1249, 1152, 902, 858, 755 cm^{-1}. $C_{19}H_{18}FNO_2$ (311.35): calcd. C 73.29, H 5.83, N 4.50; found C 73.51, H 5.96, N 4.67.

***tert*-Butyl *N*-(3-Chlorophenyl)-*N*-(phenylethynyl)carbamate (1i):** Yellow solid (1.44 g, 55% yield); m.p. 64–66 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (t, *J* = 2.0 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.41 (dd, ^1J = 2.0 Hz, ^2J = 8.0 Hz, 2 H), 7.35–7.27 (m, 4 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 140.7, 134.3, 130.9, 129.7, 128.3, 127.6, 126.6, 124.6, 123.0, 122.5, 84.0, 82.7, 70.8, 28.0 ppm. MS (ESI): *m*/*z* (%) = 350 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3453, 3111, 3081, 2976, 2930, 2256, 1738, 1588, 1475, 1310, 1287, 1152, 1095, 1023, 781, 751 cm^{-1}. $C_{19}H_{18}ClNO_2$ (327.81): calcd. C 69.62, H 5.53, N 4.27; found C 69.22, H 5.39, N 4.04.

***tert*-Butyl *N*-(3-Bromophenyl)-*N*-(phenylethynyl)carbamate (1j):** Yellow solid (1.48 g, 50% yield); m.p. 65–66 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (t, *J* = 2.0 Hz, 1 H), 7.53–7.48 (m, 1 H), 7.44–7.36 (m, 3 H), 7.34–7.23 (m, 4 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 140.8, 131.0, 130.0, 129.5, 128.3, 127.6, 127.5, 123.0, 122.1, 84.0, 82.7, 70.8, 28.0 ppm. MS (ESI): *m*/*z* (%) = 394 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3452, 3110, 2975, 2254, 1738, 1473, 1308, 1285, 1150, 1021, 863, 750 cm^{-1}. $C_{19}H_{18}ClNO_2$ (327.81): calcd. C 61.30, H 4.87, N 3.76; found C 61.25, H 4.62, N 4.02.

***tert*-Butyl *N*-(Phenylethynyl)-*N*-[3-(trifluoromethyl)phenyl]carbamate (1k):** Yellow solid (1.27 g, 44% yield); m.p. 61–62 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H), 7.80–7.74 (m, 1 H), 7.53–7.48 (m, 2 H), 7.44–7.39 (m, 2 H), 7.35–7.28 (m, 3 H), 1.59 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 140.2, 131.2 (d, *J* = 32.3 Hz), 131.0, 129.3, 128.3, 127.7, 127.4, 123.8 (d, *J* = 270.2 Hz), 123.0 (q, *J* = 4.0 Hz), 122.9, 121.3 (q, *J* = 4.0 Hz), 84.2, 82.5, 71.0, 28.0 ppm. MS (ESI): *m*/*z* (%) = 384 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3414, 3129, 2984, 2254, 1736, 1453, 1397, 1325, 1278, 1157, 1124, 1068, 845, 749 cm^{-1}. $C_{20}H_{18}F_3NO_2$ (361.36): calcd. C 66.48, H 5.02, N 3.88; found C 66.17, H 5.36, N 4.11.

***tert*-Butyl *N*-(Naphthalen-2-yl)-*N*-(phenylethynyl)carbamate (1l):** Yellow solid (1.51 g, 55% yield); m.p. 90–92 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 2.0 Hz, 1 H), 7.88–7.82 (m, 3 H), 7.65 (dd, ^1J = 2.0 Hz, ^2J = 8.8 Hz, 1 H), 7.53–7.45 (m, 2 H), 7.44–7.40 (m, 2 H), 7.33–7.24 (m, 3 H), 1.59 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 137.1, 133.3, 131.8, 130.9, 128.6, 128.2, 127.9, 127.6, 127.4, 126.5, 126.1, 123.3, 122.7, 83.7, 83.6, 70.2, 28.0 ppm. MS (ESI): *m*/*z* (%) = 366 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3414, 3132, 3055, 2978, 2927, 2252, 1736, 1392, 1369, 1289, 1249, 1149, 1022, 855, 754 cm^{-1}. $C_{23}H_{21}NO_2$ (343.42): calcd. C 80.44, H 6.16, N 4.08; found C 80.16, H 6.51, N 4.22.

***tert*-Butyl *N*-(Hex-1-ynyl)-*N*-(phenyl)carbamate (1m):** Colorless oil (0.72 g, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 2 H), 7.38–7.32 (m, 2 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 2.33 (t, *J* = 6.8 Hz, 2 H), 1.58–1.40 (m, 13 H), 0.91 (t, *J* = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 140.2, 128.6, 126.2, 124.5, 82.9, 74.3, 69.2, 31.0, 28.0, 21.9, 18.2, 13.6 ppm. MS (ESI): *m*/*z* (%) = 296 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3415, 3329, 3111, 3062, 2945, 2863, 2256, 1712, 1580, 1523, 1468, 1388, 1300, 1023, 958, 745 cm^{-1}. HRMS (ESI+): calcd. for $C_{17}H_{23}NO_2$ $[M + Na]^+$ 296.1621; found 296.1617.

Oxidation of Ynamides with Boc Group – Typical Procedure II

***N*-Benzyl-2-oxo-2-phenylacetamide (2a):** The reaction of **1a** (61.5 mg, 0.2 mmol), I_2 (75.4 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) was carried out at room temp. for 3 h, as the progress of the reaction was monitored by TLC analysis. Upon completion, the mixture was diluted with 5% Na_2CO_3 solution (10 mL). The resulting mixture was extracted with diethyl ether (3 × 10 mL), and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. The crude product was purified by flash chromatography on a silica gel column (petroleum ether/ethyl acetate) to afford **2a** (44.6 mg, 93% yield) as a light yellow solid; m.p. 125–126 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40–8.33 (m, 2 H), 7.66–7.60 (m, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.42 (br., 1 H), 7.39–7.27 (m, 5 H), 4.57 (d, *J* = 6.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 161.5, 137.1, 134.4, 133.3, 131.2, 128.8, 128.5, 127.9, 127.8, 43.5 ppm. MS (ESI): *m*/*z* (%) = 262 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3248, 3068, 2928, 1697, 1658, 1593, 1546, 1405, 1399, 1216, 1160, 1024, 886, 753 cm^{-1}. $C_{15}H_{13}NO_2$ (239.27): calcd. C 75.30, H 5.48, N 5.85; found C 75.16, H 5.43, N 5.59.

***N*-Benzyl-2-oxo-2-(*p*-tolyl)acetamide (2b):** The reaction of **1b** (63.7 mg, 0.2 mmol), I_2 (75.2 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 3 h afforded **2b** (46.4 mg, 93% yield) as a light yellow solid; m.p. 81–82 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.4 Hz, 2 H), 7.43 (br., 1 H), 7.39–7.25 (m, 7 H), 4.57 (d, *J* = 6.0 Hz, 2 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.0, 161.8, 145.7, 137.1, 131.4, 130.8, 129.2, 128.8, 127.9, 127.8, 43.4, 21.9 ppm. MS (ESI): *m*/*z* (%) = 276 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3272, 3102, 2925, 1677, 1644, 1605, 1565, 1428, 1403, 1228, 1174, 1032, 938, 766 cm^{-1}. $C_{16}H_{15}NO_2$ (253.30): calcd. C 75.87, H 5.97, N 5.53; found C 75.73, H 5.68, N 5.71.

***N*-Benzyl-2-(4-bromophenyl)-2-oxoacetamide (2c):** The reaction of **1c** (74.8 mg, 0.2 mmol), I_2 (74.9 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 3 h afforded **2c** (55.2 mg, 90% yield) as a light yellow solid; m.p. 114–115 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30–8.25 (m, 2 H), 7.66–7.61 (m, 2 H), 7.45 (br., 1 H), 7.40–7.28 (m, 5 H), 4.56 (d, *J* = 6.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

186.3, 161.0, 136.9, 132.7, 132.0, 131.9, 130.2, 128.9, 127.9, 43.5 ppm. MS (ESI): *m*/*z* (%) = 340 (100) $[M + Na]^+$. IR (KBr): ṽ = 3263, 2927, 1659, 1582, 1530, 1398, 1311, 1224, 1066, 931, 797 cm^{-1}. $C_{15}H_{12}BrNO_2$ (318.17): calcd. C 56.62, H 3.80, N 4.40; found C 56.79, H 3.63, N 4.51.

2-Oxo-*N*,2-diphenylacetamide (2d): The reaction of **1d** (60.4 mg, 0.2 mmol), I_2 (76.1 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 5 h afforded **2d** (34.7 mg, 75% yield) as a light yellow solid; m.p. 44–46 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.97 (s, 1 H), 8.45–8.38 (m, 2 H), 7.75–7.62 (m, 2 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.40 (t, *J* = 7.6 Hz, 2 H), 7.20 (t, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.4, 158.8, 136.6, 134.6, 133.0, 131.4, 129.2, 128.5, 125.3, 119.9 ppm. MS (ESI): *m*/*z* (%) = 248 (94) $[M + Na]^+$. IR (KBr): ṽ = 3414, 3230, 1688, 1653, 1590, 1520, 1438, 1366, 1258, 1172, 1032, 922, 752 cm^{-1}. $C_{14}H_{11}NO_2$ (225.25): calcd. C 74.65, H 4.92, N 6.22; found C 74.73, H 4.96, N 5.98.

2-Oxo-2-phenyl-*N*-(*o*-tolyl)acetamide (2e): The reaction of **1e** (63.0 mg, 0.2 mmol), I_2 (75.5 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 5 h afforded **2e** (40.6 mg, 83% yield) as a light yellow solid; m.p. 90–92 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.91 (s, 1 H), 8.44–8.39 (m, 2 H), 7.69–7.62 (m, 1 H), 7.57 (s, 1 H), 7.55–7.46 (m, 3 H), 7.28 (t, *J* = 8.0 Hz, 5 H), 7.02 (d, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.4, 158.8, 139.2, 136.5, 134.6, 133.1, 131.5, 129.0, 128.5, 126.1, 120.5, 117.0, 21.5 ppm. MS (ESI): *m*/*z* (%) = 262 (65) $[M + Na]^+$. IR (KBr): ṽ = 3415, 3234, 1697, 1667, 1587, 1535, 1454, 1400, 1278, 1172, 1041, 890, 745 cm^{-1}. $C_{15}H_{13}NO_2$ (239.27): calcd. C 75.30, H 5.48, N 5.85; found C 75.49, H 5.53, N 6.09.

2-Oxo-2-phenyl-*N*-(*m*-tolyl)acetamide (2f): The reaction of **1f** (61.0 mg, 0.2 mmol), I_2 (75.1 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 5 h afforded **2f** (42.3 mg, 89% yield) as a light yellow solid; m.p. 93–94 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 8.47–8.41 (m, 2 H), 8.12 (d, *J* = 8.0 Hz, 1 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.32–7.22 (m, 2 H), 7.18–7.11 (m, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 158.8, 134.6, 134.5, 133.1, 131.5, 130.7, 128.6, 128.5, 126.9, 125.6, 121.6, 17.6 ppm. MS (ESI): *m*/*z* (%) = 262 (100) $[M + Na]^+$. IR (KBr): ṽ = 3417, 3342, 2980, 1688, 1660, 1593, 1532, 1487, 1279, 1187, 868, 745 cm^{-1}. $C_{15}H_{13}NO_2$ (239.27): calcd. C 75.30, H 5.48, N 5.85; found C 75.16, H 5.61, N 6.11.

2-Oxo-2-phenyl-*N*-(*p*-tolyl)acetamide (2g): The reaction of **1g** (65.2 mg, 0.2 mmol), I_2 (76.4 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 5 h afforded **2g** (40.6 mg, 80% yield) as a light yellow solid; m.p. 114–116 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.44–8.39 (m, 2 H), 7.69–7.62 (m, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 158.7, 135.0, 134.6, 134.0, 133.1, 131.4, 129.7, 128.5, 119.9, 21.0 ppm. MS (ESI): *m*/*z* (%) = 262 (100) $[M + Na]^+$. IR (KBr): ṽ = 3416, 3340, 3059, 3025, 2911, 1694, 1670, 1591, 1536, 1404, 1281, 1167, 987, 819, 741 cm^{-1}. $C_{15}H_{13}NO_2$ (239.27): calcd. C 75.30, H 5.48, N 5.85; found C 75.59, H 5.52, N 5.99.

***N*-(3-Fluorophenyl)-2-oxo-2-phenylacetamide (2h):** The reaction of **1h** (62.3 mg, 0.2 mmol), I_2 (75.6 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 5 h afforded **2h** (38.2 mg, 79% yield) as a light yellow solid; m.p. 97–98 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 8.44–8.39 (m, 2 H), 7.72–7.64 (m, 2 H), 7.52 (t, *J* = 8.0 Hz, 2 H), 7.37–7.30 (m, 2 H), 6.94–6.87 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.9, 163.0 (d, *J* = 243.9 Hz), 158.8, 138.0 (d, *J* = 10.7 Hz), 134.8, 132.8, 131.5, 130.3 (d, *J* = 9.1 Hz), 128.6, 115.3 (d, *J* = 3.0 Hz), 112.1 (d, *J* = 21.8 Hz), 107.4 (d, *J* = 26.5 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.76 ppm. MS (ESI): *m*/*z* (%) = 266 (100) $[M + Na]^+$. IR (KBr): ṽ = 3345, 3107, 1691, 1654, 1594, 1540, 1446, 1401, 1296, 1270, 1159, 1132, 867, 775 cm^{-1}. $C_{14}H_{10}FNO_2$ (243.24): calcd. C 69.13, H 4.14, N 5.76; found C 69.26, H 4.51, N 6.00.

***N*-(3-Chlorophenyl)-2-oxo-2-phenylacetamide (2i):** The reaction of **1i** (65.8 mg, 0.2 mmol), I_2 (75.3 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 5 h afforded **2i** (34.0 mg, 65% yield) as a light yellow solid; m.p. 120–121 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1 H), 8.44–8.38 (m, 2 H), 7.87 (t, *J* = 2.0 Hz, 1 H), 7.70–7.64 (m, 1 H), 7.56–7.49 (m, 3 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.20–7.15 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.9, 158.8, 137.7, 134.9, 134.8, 132.8, 131.5, 130.2, 128.6, 125.3, 120.0, 117.9 ppm. MS (ESI): *m*/*z* (%) = 282 (100) $[M + Na]^+$. IR (KBr): ṽ = 3417, 3347, 3149, 1689, 1661, 1592, 1539, 1403, 1278, 1174, 737 cm^{-1}. $C_{14}H_{10}ClNO_2$ (259.69): calcd. C 64.75, H 3.88, N 5.39; found C 64.89, H 4.01, N 5.16.

***N*-(3-Bromophenyl)-2-oxo-2-phenylacetamide (2j):** The reaction of **1j** (77.2 mg, 0.2 mmol), I_2 (76.1 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 8 h afforded **2j** (37.1 mg, 59% yield) as a light yellow solid; m.p. 113–115 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1 H), 8.44–8.39 (m, 2 H), 8.01 (t, *J* = 2.0 Hz, 1 H), 7.71–7.66 (m, 1 H), 7.66–7.55 (m, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.36–7.31 (m, 1 H), 7.29–7.23 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.8, 158.7, 137.8, 134.8, 132.8, 131.5, 130.5, 128.6, 128.3, 122.9, 122.8, 118.3 ppm. MS (ESI): *m*/*z* (%) = 326 (46) $[M + Na]^+$. IR (KBr): ṽ = 3414, 3340, 3058, 2933, 1692, 1677, 1594, 1432, 1380, 1323, 1214, 1143, 1083, 960, 784 cm^{-1}. $C_{14}H_{10}BrNO_2$ (304.14): calcd. C 55.29, H 3.31, N 4.61; found C 55.43, H 3.21, N 4.83.

2-Oxo-2-phenyl-*N*-[3-(trifluoromethyl)phenyl]acetamide (2k): The reaction of **1k** (72.5 mg, 0.2 mmol), I_2 (74.6 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 12 h afforded **2k** (33.5 mg, 57% yield) as a light yellow solid; m.p. 89–90 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.13 (s, 1 H), 8.45–8.40 (m, 2 H), 8.08 (s, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.71–7.65 (m, 1 H), 7.53 (t, *J* = 8.0 Hz, 3 H), 7.46 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.7, 158.9, 137.1, 134.9, 132.8, 131.8, 131.5, 129.8, 128.6, 122.9, 121.8 (q, *J* = 3.7 Hz), 116.7 (q, *J* = 3.6 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.78 ppm. MS (ESI): *m*/*z* (%) = 316 (100) $[M + Na]^+$. IR (KBr): ṽ = 3413, 3344, 3061, 1694, 1664, 1597, 1538, 1446, 1334, 1273, 1165, 1117, 1071, 997, 889, 743 cm^{-1}. $C_{15}H_{10}F_3NO_2$ (293.24): calcd. C 61.44, H 3.44, N 4.78; found C 61.36, H 3.71, N 4.67.

***N*-(Naphthalen-2-yl)-2-oxo-2-phenylacetamide (2l):** The reaction of **1l** (68.6 mg, 0.2 mmol), I_2 (75.8 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 4 h afforded **2l** (29.8 mg, 54% yield) as a light yellow solid; m.p. 143–144 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.14 (s, 1 H), 8.46–8.43 (m, 3 H), 7.86 (dd, ^1J = 4.0 Hz, ^2J = 8.8 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 7.70–7.64 (m, 1 H), 7.60 (dd, ^1J = 2.0 Hz, ^2J = 8.8 Hz, 2 H), 7.56–7.42 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.3, 158.9, 134.7, 134.0, 133.7, 133.0, 131.5, 131.0, 129.1, 128.6, 127.9, 127.6, 126.8, 125.5, 119.5, 117.1 ppm. MS (ESI): *m*/*z* (%) = 298 (39) $[M + Na]^+$. IR (KBr): ṽ = 3416, 3338, 3135, 3050, 1668, 1663, 1597, 1541, 1505, 1399, 1276, 1226, 852,

741 cm^{-1}. $C_{18}H_{13}NO_2$ (275.31): calcd. C 78.53, H 4.76, N 5.09; found C 78.71, H 4.76, N 5.17.

2-Oxo-*N*-phenylhexanamide (2m): The reaction of **1m** (56.2 mg, 0.2 mmol), I_2 (74.8 mg, 0.3 mmol), TFA (15 μL), and CH_3CN/H_2O (4:1, 2.5 mL) at room temp. for 3 h afforded **2m** (38.3 mg, 91% yield) as a light yellow solid; m.p. 84–85 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (s, 1 H), 7.65 (d, J = 7.6 Hz, 2 H), 7.38 (t, J = 7.6 Hz, 2 H), 7.18 (t, J = 7.6 Hz, 1 H), 3.02 (t, J = 7.2 Hz, 2 H), 1.70–1.60 (m, 2 H), 1.45–1.34 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 157.5, 136.3, 129.2, 125.2, 119.7, 36.1, 25.4, 22.2, 13.8 ppm. MS (ESI): *m*/*z* (%) = 228 (25) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3415, 3329, 3111, 3062, 2945, 2863, 1719, 1684, 1599, 1543, 1492, 1443, 1388, 1048, 911, 759 cm^{-1}. $C_{12}H_{15}NO_2$ (205.26): calcd. C 70.22, H 7.37, N 6.82; found C 70.52, H 7.62, N 7.08.

Oxidation of Ynamides without Boc Group – Typical Procedure III

1-(2-Oxooxazolidin-3-yl)-2-phenylethane-1,2-dione (2n): The reaction of **1n** (57.0 mg, 0.3 mmol), I_2 (111.3 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) was carried out at room temp. for 5 h, as the progress of the reaction was monitored by TLC analysis. Upon completion, the mixture was diluted with 5% Na_2CO_3 solution (10 mL). The resulting mixture was extracted with diethyl ether (3 × 10 mL), and the combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. The crude product was purified by flash chromatography on a silica gel column (petroleum ether/ethyl acetate) to afford **2n** (41.7 mg, 63% yield) as a white solid; m.p. 149–150 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 7.2 Hz, 2 H), 7.66 (t, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H), 4.62 (t, J = 8.0 Hz, 2 H), 4.18 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.8, 166.4, 153.0, 134.8, 132.3, 129.3, 129.0, 64.0, 40.9 ppm. MS (ESI): *m*/*z* (%) = 242 (55) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3415, 3069, 2924, 2853, 1787, 1690, 1468, 1396, 1239, 1201, 1125, 1025, 966, 716 cm^{-1}. $C_{11}H_9NO_4$ (219.20): calcd. C 60.27, H 4.14, N 6.39; found C 60.31, H 4.19, N 6.15.

(*S*)-1-(2-Oxo-4-phenyloxazolidin-3-yl)hexane-1,2-dione (2o): The reaction of **1o** (71.2 mg, 0.3 mmol), I_2 (114.2 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) at room temp. for 5 h afforded **2o** (43.5 mg, 54% yield) as a white solid; m.p. 63–64 °C (*n*-hexane/ethyl acetate). $[\alpha]_D^{20}$ = +71.5 (c = 0.78, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.32 (m, 5 H), 5.39 (dd, ^1J = 4.4 Hz, ^2J = 8.8 Hz, 1 H), 4.86 (t, J = 8.8 Hz, 2 H), 4.41 (dd, ^1J = 4.4 Hz, ^2J = 8.8 Hz, 1 H), 2.79–2.62 (m, 2 H), 1.71–1.60 (m, 2 H), 1.43–1.31 (m, 2 H), 0.91 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 166.8, 153.7, 137.1, 129.4, 129.3, 125.9, 72.0, 56.5, 38.9, 24.3, 22.0, 13.7 ppm. MS (ESI): *m*/*z* (%) = 298 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3425, 3112, 3024, 2948, 2903, 1788, 1676, 1501, 1438, 1332, 1302, 1123, 1001, 836, 740 cm^{-1}. $C_{15}H_{17}NO_4$ (275.30): calcd. C 65.44, H 6.22, N 5.09; found C 65.30, H 6.51, N 5.18.

(*S*)-1-(2-Oxo-4-phenyloxazolidin-3-yl)-2-phenylethane-1,2-dione (2p): The reaction of **1p** (77.3 mg, 0.3 mmol), I_2 (111.2 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) at room temp. for 5 h afforded **2p** (64.3 mg, 74% yield) as a white solid; m.p. 127–128 °C (*n*-hexane/ethyl acetate). $[\alpha]_D^{20}$ = +37.4 (c = 1.01, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.2 Hz, 2 H), 7.62 (t, J = 7.6 Hz, 1 H), 7.51–7.40 (m, 7 H), 5.53 (dd, ^1J = 4.0 Hz, ^2J = 8.8 Hz, 1 H), 4.88 (t, J = 9.2 Hz, 1 H), 4.44 (dd, ^1J = 4.0 Hz, ^2J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.3, 165.9, 153.2, 137.4, 134.7, 132.3, 129.5, 129.3, 129.0, 126.0, 71.9, 56.6 ppm. MS (ESI): *m*/*z* (%) = 318 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3441, 3012, 2948, 1756, 1692, 1544, 1438, 1369, 1334, 1223, 1115, 1022, 924, 745 cm^{-1}. $C_{17}H_{13}NO_4$ (295.29): calcd. C 69.15, H 4.44, N 4.74; found C 69.51, H 4.13, N 5.15.

(*S*)-1-(4-Benzyl-2-oxooxazolidin-3-yl)-2-phenylethane-1,2-dione (2q): The reaction of **1q** (84.5 mg, 0.3 mmol), I_2 (113.6 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) at room temp. for 5 h afforded **2q** (70.7 mg, 75% yield) as a white solid; m.p. 121–123 °C (*n*-hexane/ethyl acetate). $[\alpha]_D^{20}$ = +75.3 (c = 1.01, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2 H), 7.69–7.63 (m, 1 H), 7.53 (t, J = 8.0 Hz, 2 H), 7.42–7.35 (m, 2 H), 7.35–7.21 (m, 3 H), 4.86–4.78 (m, 1 H), 4.42 (t, J = 9.2 Hz, 1 H), 4.34 (dd, ^1J = 3.6 Hz, ^2J = 9.6 Hz, 1 H), 3.55 (dd, ^1J = 3.6 Hz, ^2J = 13.6 Hz, 1 H), 2.99 (dd, ^1J = 9.6 Hz, ^2J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.5, 166.6, 153.0, 134.7, 134.3, 132.4, 129.5, 129.3, 129.2, 129.0, 127.7, 68.1, 54.1, 37.6 ppm. MS (ESI): *m*/*z* (%) = 332 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3441, 3131, 2923, 1790, 1691, 1597, 1451, 1398, 1368, 1237, 1122, 1005, 740 cm^{-1}. $C_{18}H_{15}NO_4$ (309.32): calcd. C 69.89, H 4.89, N 4.53; found C 69.63, H 5.12, N 4.71.

Ethyl [1-(2-Oxo-2-phenylacetyl)-1*H*-indol-2-yl]carboxylate (2r): The reaction of **1r** (85.1 mg, 0.3 mmol), I_2 (119.8 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) at room temp. for 5 h afforded **2r** (60.5 mg, 64% yield) as a white solid; m.p. 103–104 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, J = 8.4 Hz, 1 H), 8.19–8.14 (m, 2 H), 7.71–7.64 (m, 2 H), 7.60–7.50 (m, 3 H), 7.44 (s, 1 H), 7.38 (t, J = 7.2 Hz, 1 H), 4.13 (q, J = 7.2 Hz, 2 H), 1.21 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 185.1, 165.2, 161.6, 138.6, 134.1, 133.2, 130.5, 129.6, 128.6, 128.5, 127.9, 124.9, 122.7, 118.4, 116.0, 61.8, 14.0 ppm. MS (ESI): *m*/*z* (%) = 344 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3343, 3116, 2983, 2932, 1692, 1680, 1548, 1444, 1397, 1340, 1267, 1205, 1143, 1044, 938, 753 cm^{-1}. $C_{19}H_{15}NO_4$ (321.33): calcd. C 71.02, H 4.71, N 4.36; found C 71.56, H 4.49, N 4.70.

1-(3-Acetyl-1*H*-indol-1-yl)-2-phenylethane-1,2-dione (2s): The reaction of **1s** (78.1 mg, 0.3 mmol), I_2 (112.5 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) at room temp. for 5 h afforded **2s** (48.3 mg, 55% yield) as a white solid; m.p. 167–168 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.50–8.36 (m, 2 H), 8.13–8.08 (m, 2 H), 7.93 (s, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.59 (t, J = 8.0 Hz, 2 H), 7.52–7.44 (m, 2 H), 2.51 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 187.5, 164.0, 135.9, 135.7, 132.2, 131.1, 130.4, 129.3, 127.6, 126.7, 126.3, 123.6, 123.0, 116.2, 27.9 ppm. MS (ESI): *m*/*z* (%) = 314 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3168, 2958, 2901, 1701, 1680, 1621, 1533, 1498, 1402, 1333, 1287, 1234, 1121, 1022, 878, 746 cm^{-1}. $C_{22}H_{19}NO_4S$ (393.46): calcd. C 74.22, H 4.50, N 4.81; found C 74.21, H 4.72, N 4.61.

***N*-Benzyl-2-oxo-2-phenyl-*N*-tosylacetamide (2t):** The reaction of **1t** (107.3 mg, 0.3 mmol), I_2 (114.2 mg, 0.45 mmol), and H_2O (0.75 mL) in CH_3CN (3 mL) at room temp. for 5 h afforded **2t** (39.7 mg, 34% yield) as a white solid; m.p. 90–92 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.66–7.60 (m, 1 H), 7.50 (t, J = 7.6 Hz, 2 H), 7.31–7.20 (m, 7 H), 4.98 (s, 2 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.7, 167.5, 145.6, 134.6, 134.4, 134.3, 132.8, 129.8, 129.6, 128.8, 128.5, 128.0, 127.8, 48.2, 21.7 ppm. MS (ESI): *m*/*z* (%) = 416 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3423, 3102, 3028, 1690, 1670, 1593, 1371, 1213, 1163, 1088, 1059, 931, 714 cm^{-1}. $C_{22}H_{19}NO_4S$ (393.46): calcd. C 67.16, H 4.87, N 3.56; found C 67.01, H 4.59, N 3.37.

Large-Scale Reaction of Ynamide with Boc Group: The reaction of **1a** (1.25 g, 4 mmol), I_2 (1.53 mg, 6.0 mmol), TFA (0.3 mL), and CH_3CN/H_2O (4:1, 40 mL) was carried out at room temp. for 12 h, and the progress of the reaction was monitored by TLC analysis. Upon completion, the reaction mixture was then diluted by the

addition of 5% Na_2CO_3 solution (15 mL), and the resulting mixture was extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Filtration and concentration gave the crude product, which was purified by chromatography on silica gel (PE/EtOAc, 10:1) to afford **2a** (0.79 g, 83% yield) as a white solid.

Large-Scale Reaction of Ynamide without Boc Group: The reaction of **1p** (1.05 g, 4 mmol), I_2 (1.45 g, 6.0 mmol), and CH_3CN/H_2O (4:1, 40 mL) was carried out at room temp. for 18 h, as the progress of the reaction was monitored by TLC analysis. Upon completion, the reaction mixture was then diluted by the addition of 5% Na_2CO_3 solution (15 mL), and the resulting mixture was extracted with Et_2O (3× 20 mL). The combined organic extracts were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Filtration and concentration gave the crude product, which was purified by chromatography on silica gel (PE/EtOAc, 2:1) to afforded **2p** (0.83 g, 71% yield) as a white solid and (*S*,*E*)-3-(1,2-diiodo-2-phenylethenyl)-4-phenyloxazolidin-2-one (**2p′**, 0.08 g, 4% yield) as a white solid; m.p. 118–119 °C (*n*-hexane/ethyl acetate). $[a]_D^{20}$ = +10.5 (*c* = 1.02, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.61 (m, 2 H), 7.49–7.43 (m, 3 H), 7.32–7.25 (m, 4 H), 7.11–7.06 (m, 2 H), 5.05 (dd, ^1J = 8.8 Hz, ^2J = 10.4 Hz, 1 H), 4.74 (t, *J* = 9.2 Hz, 1 H), 4.46 (dd, ^1J = 8.8 Hz, ^2J = 10.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 144.7, 133.8, 129.7, 129.1, 128.9, 128.8, 128.6, 128.4, 101.0, 93.5, 69.6, 63.8 ppm. MS (ESI): *m*/*z* (%) = 540 (100) $[M + Na]^+$. IR (KBr): $\tilde{\nu}$ = 3418, 3139, 3054, 1777, 1617, 1387, 1331, 1277, 1205, 1096, 1023, 868, 757 cm^{-1}. $C_{17}H_{13}I_2NO_4$ (549.10): calcd. C 39.49, H 2.53, N 2.71; found C 39.53, H 2.76, N 2.56.

Reaction Mechanism Studies

Entry 1: Starting material **1a** was dried in vacuo over P_2O_5 for 1 d. CH_3CN was freshly distilled from CaH_2 under N_2. After distillation, the anhydrous CH_3CN was stored in a bottle over molecular sieves (4 Å). An oven-dried Schlenk tube with a magnetic stirrer bar was purged with oxygen, and **1a** (61.2 mg, 0.2 mmol), NIS (67.4 mg, 0.3 mmol), TFA (15 μL), and dry CH_3CN (2.0 mL) were added. The resulting solution was stirred at room temp. for 3 h, and then the mixture was diluted to 50 mL by the addition of CH_3CN. The yield was determined by HPLC analysis using the external standard method.

Entry 2: An oven-dried Schlenk tube with a magnetic stirrer bar was purged with nitrogen, and **1a** (60.9 mg, 0.2 mmol), NIS (67.9 mg, 0.3 mmol), TFA (15 μL), and dry CH_3CN (2.0 mL) were added. The resulting solution was stirred at room temp. for 3 h, then the mixture was diluted to 50 mL by the addition of CH_3CN. The yield was determined by HPLC analysis using the external standard method.

Entry 3: An oven-dried Schlenk tube with a magnetic stirrer bar was purged with nitrogen, and **1a** (61.6 mg, 0.2 mmol), NIS (66.8 mg, 0.3 mmol), H_2O (7.2 μL), TFA (15 μL), and dry CH_3CN (2.0 mL) were added. The resulting solution was stirred at room temp. for 3 h, and then the mixture was diluted to 50 mL by the addition of CH_3CN. The yield was determined by HPLC analysis using the external standard method.

Entry 4: An oven-dried Schlenk tube with a magnetic stirrer bar was purged with nitrogen, and **1a** (61.3 mg, 0.2 mmol), NIS (67.6 mg, 0.3 mmol), H_2O (0.5 mL), TFA (15 μL), and dry CH_3CN (2.0 mL) were added. The resulting solution was stirred at room temp. for 3 h, and then the mixture was diluted to 50 mL by the addition of CH_3CN. The yield was determined by HPLC analysis using the external standard method.

^{18}O-Labeling Experiments with 1a: An oven-dried Schlenk tube with a magnetic stirrer bar was purged with oxygen, and **1a** (61.3 mg, 0.2 mmol), NIS (67.6 mg, 0.3 mmol), $H_2{}^{18}O$ (0.5 mL), and dry CH_3CN (2.0 mL) were added. The resulting solution was stirred at room temp. for 3 h, and then the mixture was analyzed by HRMS. The product was purified by chromatography on a silica gel column and then analyzed by HRMS.

***N*,2-Diphenylacetamide (3d):** The reaction of **1d** (296.3 mg, 1 mmol), TFA (74 μL), and CH_3CN/H_2O (4:1, 10 mL) was carried out at room temp. for 12 h, as the progress of the reaction was monitored by TLC analysis. Upon completion, the reaction was diluted by the addition of 5% Na_2CO_3 solution (15 mL), and the resulting mixture was extracted with Et_2O (3× 20 mL). The combined organic extracts were washed with brine (5 mL) and dried with anhydrous Na_2SO_4. Filtration and concentration gave the crude product, which was purified by chromatography on a silica gel column (PE/EtOAc, 5:1) to afford **3d**[22] (162.2 mg, 76% yield) as a white solid; m.p. 116–117 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, *J* = 8.0 Hz, 4 H), 7.36–7.30 (m, 3 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.16 (s, 1 H), 7.08 (t, *J* = 7.6 Hz, 2 H), 3.72 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 137.6, 134.4, 129.5, 129.2, 128.9, 127.7, 124.4, 119.8, 44.8 ppm. HRMS (ESI+): calcd. for $C_{14}H_{13}NO$ $[M + Na]^+$ 234.0889; found 234.0884.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra of all compounds and X-ray crystal structures of **2p′** and **2s**.

Acknowledgments

The authors greatly acknowledge the financial support, in part, from the Natural Science Foundation of Jiangsu Provincial Universities (grant number 12KJB150011), the Jiangsu Provincial Technology Support Program (grant number BE2012363), and the Postgraduate Innovation Fund of Jiangsu Province (2013, CXZZ13_0459).

[1] a) D. K. Leahy, S. K. Pack, *Org. Process Res. Dev.* **2013**, *17*, 1440–1444; b) H. Dai, L. Gao, Y. Yang, J. Li, J. Cheng, J. Li, R. Wen, Y. Peng, J. Zheng, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 7440–7443; c) R. Gopalakrishnan, C. Kozany, S. Gaali, C. Kress, B. Hoogeland, A. Bracher, F. Hausch, *J. Med. Chem.* **2012**, *55*, 4114–4122; d) J. F. Kadow, Y. Ueda, N. A. Meanwell, T. P. Connolly, T. Wang, C. Chen, K. S. Yeung, J. Zhu, J. A. Bender, Z. Yang, D. Parker, P.-F. Lin, R. J. Colonno, M. Mathew, D. Morgan, M. Zheng, C. Chien, D. Grasela, *J. Med. Chem.* **2012**, *55*, 2048–2056; e) S. Alvarez, R. Alvarez, H. Khanwalkar, P. Germain, G. Lemaire, F. Rodríguez-Barrios, H. Gronemeyer, A. R. D. Lera, *Bioorg. Med. Chem.* **2009**, *17*, 4345–4359; f) Y. Chen, Y. Zhang, H. Zhang, D. Liu, M. Gu, J. Li, F. Wu, X. Zhu, J. Li, F. Nan, *J. Med. Chem.* **2006**, *49*, 1613–1623; g) G. M. Dubowchik, J. L. Ditta, J. J. Herbst, S. Bollini, A. Vinitsky, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 559–562.

[2] a) G. R. Boyce, J. S. Johnson, *Angew. Chem. Int. Ed.* **2010**, *49*, 8930–8933; b) J. Xiao, H. Zhang, S. Liang, J. Ren, H. Yang, X. Chen, *J. Org. Chem.* **2013**, *78*, 11577–11583; c) G. Wang, A. Zhou, J. Wang, R. Hu, S. Yang, *Org. Lett.* **2013**, *15*, 5270–5273; d) J. H. Park, Y. R. Lee, S. H. Kimb, *Tetrahedron* **2013**, *69*, 9682–9689; e) D. Tomita, K. Yamatsugu, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 6946–6948; f) Z. Duan, J. Han, P. Qian, Z. Zhang, Y. Wang, Y. Pan, *Org. Biomol. Chem.* **2013**, *11*, 6456–6459; g) R. Raghunathan, E. Kumarasamy, A. Iyer, A. Ugrinov, J. Sivaguru, *Chem. Commun.* **2013**, *49*, 8713–8715; h) L. Tian, X. Hu, Y. Li, P. Xu, *Chem. Commun.* **2013**, *49*, 7213–7215; i) A. Rahmati, T. Kenarkoohi,

H. R. Khavasi, *ACS Comb. Sci.* **2012**, *14*, 657–664; j) Q. Ren, J. Huang, L. Wang, W. Li, H. Liu, X. Jiang, J. Wang, *ACS Catal.* **2012**, *2*, 2622–2625; k) C. Cassani, P. Melchiorre, *Org. Lett.* **2012**, *14*, 5590–5593; l) H. Zhu, J. Ling, P. Xu, *J. Org. Chem.* **2012**, *77*, 7737–7743; m) M. Zhao, M. Chen, W. Tang, D. Wei, T. Dai, M. Shi, *Eur. J. Org. Chem.* **2012**, 3598–3606; n) J. Sun, Y. Sun, H. Gao, C. Yan, *Eur. J. Org. Chem.* **2012**, 1976–1983.

[3] a) T. Igarashi, E. Tayama, H. Iwamoto, E. Hasegaw, *Tetrahedron Lett.* **2013**, *54*, 6874–6877; b) R. P. Singh, J. M. Shreeve, *J. Org. Chem.* **2003**, *68*, 6063–6065; c) L. Yang, D. Wang, Z. Huang, M. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 10390–10391; d) F. Heaney, J. Fenlon, P. McArdle, D. Cunningham, *Org. Biomol. Chem.* **2003**, *1*, 1122–1132; e) F. R. Bou-Harndan, J. L. Leighton, *Angew. Chem. Int. Ed.* **2009**, *48*, 2403–2406; *Angew. Chem.* **2009**, *121*, 2439.

[4] a) M. Genelot, N. Villandier, A. Bendjeriou, P. Jaithong, L. Djakovitch, V. Dufaudz, *Catal. Sci. Technol.* **2012**, *2*, 1886–1893; b) J. Liu, R. Zhang, S. Wang, W. Sun, C. Xia, *Org. Lett.* **2010**, *12*, 1321–1324; c) A. Szilagyi, R. Farkas, A. Petz, L. Kollar, *Tetrahedron* **2009**, *65*, 4484–4489; d) A. Takacs, A. Petz, L. Kollar, *Tetrahedron* **2008**, *64*, 8726–8730; e) I. J. S. Fairlamb, S. Grant, P. M. Cormack, J. Whittall, *Dalton Trans.* **2007**, 859–865; f) P. Acs, E. Muller, G. Rangits, T. Lorand, L. Kollar, *Tetrahedron* **2006**, *62*, 12051–12056; g) P. W. Miller, N. J. Long, A. J. D. Mello, R. Vilar, J. Passchier, A. Gee, *Chem. Commun.* **2006**, 546–548; h) M. Iizuka, Y. Kondo, *Chem. Commun.* **2006**, 1739–1741; i) E. Muller, G. Peczely, R. S. Foldes, E. Takacs, G. Kokotos, E. Bellis, L. Kollar, *Tetrahedron* **2005**, *61*, 797–802.

[5] a) Z. F. Al-Rashid, W. L. Johnson, R. P. Hsung, Y. Wei, P.-Y. Yao, R. Liu, K. Zhao, *J. Org. Chem.* **2008**, *73*, 8780–8784; b) C. Xu, M. Xu, Y. Jia, C. Li, *Org. Lett.* **2011**, *13*, 1556–1559; c) K. Schank, H. Beck, G. Himbert, *Synthesis* **1998**, 1718–1720; d) P. W. Davies, A. Cremonesi, N. Martin, *Chem. Commun.* **2011**, *47*, 379–381; e) A. Mukherjee, R. B. Dateer, R. Chaudhuri, S. Bhunia, S. N. Karad, R.-S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 15372–15375; f) R. Liu, G. N. Winston-McPherson, Z. Yang, X. Zhou, W. Song, I. A. Guzei, X. Xu, W. Tang, *J. Am. Chem. Soc.* **2013**, *135*, 8201–8204; g) R. B. Dateer, K. Pati, R.-S. Liu, *Chem. Commun.* **2012**, *48*, 7200–7202; h) D. Vasu, H.-H. Hung, S. Bhunia, S. A. Gawade, A. Das, R. Liu, *Angew. Chem. Int. Ed.* **2011**, *50*, 6911–6914; i) K. Wang, R. Ran, S. Xiu, C. Li, *Org. Lett.* **2013**, *15*, 2374–2377; j) L. Yang, K. Wang, C. Li, *Eur. J. Org. Chem.* **2013**, 2775–2779; k) Z. F. Al-Rashid, R. P. Hsung, *Org. Lett.* **2008**, *10*, 661–663; l) H. Li, J. E. Antoline, J. H. Yang, Z. F. Al-Rashid, R. P. Hsung, *New J. Chem.* **2010**, *34*, 1309–1316.

[6] a) Z. Zhang, J. Su, Z. Zha, Z. Wang, *Chem. Commun.* **2013**, *49*, 8982–8984; b) C. Zhang, X. Zong, L. Zhang, N. Jiao, *Org. Lett.* **2012**, *14*, 3280–3283; c) A. Y. Shawa, C. R. Denning, C. Hulme, *Tetrahedron Lett.* **2012**, *53*, 4151–4153; d) M. Lamani, K. R. Prabhu, *Chem. Eur. J.* **2012**, *18*, 14638–14642; e) C. Zhang, Z. Xu, L. Zhang, N. Jiao, *Angew. Chem. Int. Ed.* **2011**, *50*, 11088–11092; f) W. Mai, H. Wang, Z. Li, J. Yuan, Y. Xiao, L. Yang, P. Mao, L. Qu, *Chem. Commun.* **2012**, *48*, 10117–10119; g) X. Zhang, L. Wang, *Green Chem.* **2012**, *14*, 2141–2145.

[7] a) K. A. DeKorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2010**, *110*, 5064–5106; b) G. Evano, A. Coste, K. Jouvin, *Angew. Chem. Int. Ed.* **2010**, *49*, 2840–2859; *Angew. Chem.* **2010**, *122*, 2902; c) J. A. Mulder, K. C. M. Kurtz, R. P. Hsung, *Synlett* **2003**, *10*, 1379–1390; d) F. M. Istrate, A. K. Buzas, I. D. Jurberg, Y. Odabachian, F. Gagosz, *Org. Lett.* **2008**, *10*, 925–928.

[8] For select reviews about the iodine-containing reagent: a) Y. Yamamoto, A. Gridnev, N. T. Patil, T. Jin, *Chem. Commun.* **2009**, 5075–5087; b) M. J. Mphahlele, *Molecules* **2009**, *14*, 4814–4837; c) P. Finkbeiner, B. J. Nachtsheim, *Synthesis* **2013**, *45*, 979–999; d) H. Togo, S. Iida, *Synlett* **2006**, *14*, 2159–2175.

[9] a) M. S. Yusybov, V. D. Filimonov, *Synthesis* **1991**, 131–132; b) M. Chen, Q. Zhao, D. She, M. Yang, H. Hui, G. Huang, *J. Chem. Sci.* **2008**, *119*, 347–351; c) S. Matsumoto, H. Shibata, M. Akazome, *J. Org. Chem.* **2013**, *78*, 1650–1654; d) K. Sakthivel, K. Srinivasan, *Eur. J. Org. Chem.* **2013**, 3386–3396; e) K. Sakthivel, K. Srinivasan, *Eur. J. Org. Chem.* **2011**, 2781–2784; f) D. Chen, G. Song, A. Jia, X. Li, *J. Org. Chem.* **2011**, *76*, 8488–8494.

[10] M. Niu, H. Fu, Y. Jiang, Y. Zhao, *Synthesis* **2008**, 2879–2882.

[11] During the preparation of our manuscript, a closely related paper about using NIS/dimethyl sulfoxide (DMSO) as oxidants to prepare α-ketoimides became available online. For details, see: T. Chikugo, Y. Yauchi, M. Ide, T. Iwasawa, *Tetrahedron* **2014**, *70*, 3988–3993.

[12] For select examples, see: a) Z. Wang, M. Bois-Choussy, Y. Jia, J. Zhu, *Angew. Chem. Int. Ed.* **2010**, *49*, 2018–2022; *Angew. Chem.* **2010**, *122*, 2062; b) Y. Jia, M. Bois-Choussy, J. Zhu, *Angew. Chem. Int. Ed.* **2008**, *47*, 4167–4172; *Angew. Chem.* **2008**, *120*, 4235; c) Y. X. Jia, M. Bois-Choussy, J. Zhu, *Org. Lett.* **2007**, *9*, 2401–2404; d) D. G. Barrett, V. M. Boncek, J. G. Catalano, D. N. Deaton, A. M. Hassell, C. H. Jurgensen, S. T. Long, R. B. McFadyen, A. B. Miller, L. R. Miller, J. A. Payne, A. Ray, V. Samano, L. M. Shewchuk, F. X. Tavares, K. J. Wells-Knecht, D. H. Willard Jr., L. L. Wright, H. Zhou, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3540–3546; e) L. Feng, M. Liu, Y. Chai, B. Wang, Y. Zhang, K. Lv, Y. Guan, H. Guo, C. Xiao, S. Zhang, *Eur. J. Med. Chem.* **2011**, *46*, 341–348; f) K. Manley, I. Clarina, J. J. Bergh, J. P. Petzer, *Bioorg. Med. Chem.* **2011**, *19*, 261–274; g) R. Sabet, M. Mohammadpour, A. Sadeghi, A. Fassihi, *Eur. J. Med. Chem.* **2010**, *45*, 1113–1118; h) P. Diaz, J. Xu, F. Astruc-Diaz, H. M. Pan, D. L. Brown, M. Naguib, *J. Med. Chem.* **2008**, *51*, 4932–4947.

[13] J. J. Park, Y.-H. Kima, C. Kim, J. Kang, *Tetrahedron Lett.* **2011**, *52*, 3361–3366.

[14] Crystal data for **2a**: $C_{15}H_{13}NO_2$, M = 239.26, orthorhombic, space group *Pbca*, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0770, wR_2 = 0.1510, R indices (all data): R_1 = 0.1938, wR_2 = 0.1914, a = 10.077(2) Å, b = 9.2150(18) Å, c = 27.358(6) Å, V = 2540.5(9) Å^3, T = 293 K, Z = 8, reflection measured/independent: 4609/2339 (R_{int} = 0.103), number of observations [$I > 2\sigma(I)$]: 929, parameters: 163.

[15] C. Zhang, N. Jiao, *J. Am. Chem. Soc.* **2010**, *132*, 28–29.

[16] a) J. Barluenga, M. A. Rodriguez, P. J. Campos, *J. Org. Chem.* **1990**, *55*, 3104–3106; b) T. Muraki, M. Yokoyama, H. Togo, *J. Org. Chem.* **2000**, *65*, 4679–4684.

[17] A. O. Terent'ev, D. A. Borisov, I. B. Krylov, G. I. Nikishin, *Synth. Commun.* **2007**, *37*, 3151–3164.

[18] a) G. He, Q. Zhang, H. Huang, S. Chen, Q. Wang, D. Zhang, R. Zhang, H. Zhu, *Eur. J. Org. Chem.* **2013**, 6979–6989; b) M. Ide, Y. Yauchi, T. Iwasawa, *Eur. J. Org. Chem.* **2014**, 3262–3267; c) G. He, S. Chen, Q. Wang, H. Huang, Q. Zhang, D. Zhang, R. Zhang, H. Zhu, *Org. Biomol. Chem.* **2014**, *12*, 5945–5953.

[19] Z. Chen, H. Jiang, X. Pan, Z. He, *Tetrahedron* **2011**, *67*, 5920–5927.

[20] S. Li, Z. Li, Y. Yuan, Y. Li, L. Zhang, Y. Wu, *Chem. Eur. J.* **2013**, *19*, 1496–1501.

[21] H. Hofmeister, K. Annen, H. Laurent, R. Wiechert, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 727–729; *Angew. Chem.* **1984**, *96*, 720.

[22] L. U. Nordstrøm, H. Vogt, R. Madsen, *J. Am. Chem. Soc.* **2008**, *130*, 17672–17673.

Received: May 5, 2014
Published Online: September 24, 2014

