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Silver Triflate-Catalyzed or Electrophile-Mediated Tandem Reaction of *N*′-(2-Alkynylbenzylidene)hydrazides with Dimethyl Acetylenedicarboxylate

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Abstract: Different outcomes were generated under different conditions for the tandem reactions of *N*′-(2-alkynylbenzylidene)hydrazides with dimethyl acetylenedicarboxylate (DMAD) catalyzed by silver triflate or in the presence of electrophiles. The unexpected isoquinoline-based azomethine ylides were obtained when the reaction was catalyzed by silver triflate or in the presence of bromine, while the fused 1,2-dihydroisoquinolines were afforded when iodine was employed in the above tandem reactions.

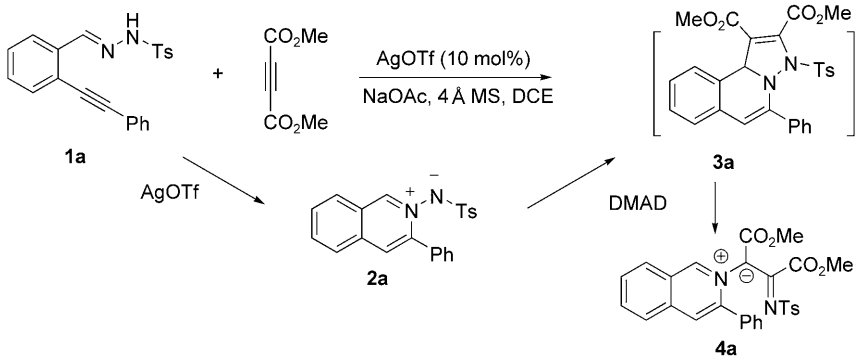
Keywords: *N*′-(2-alkynylbenzylidene)hydrazides; dimethyl acetylenedicarboxylate; electrophiles; silver triflate; tandem reactions

Introduction

Tandem carbon-carbon bond formations are powerful methods for the synthesis of structurally complex molecules from relatively simple starting materials in a convergent way.[1,2] In particular, the development of tandem reactions for the efficient construction of small molecules is an important goal in combinatorial chemistry from the viewpoints of operational simplicity and assembly efficiency. Recently, we have developed efficient methods for the construction of 1,2-dihydroisoquinolines *via* tandem reactions starting from 2-alkynylbenzaldehydes.[3] Following a biological screening it was shown that this kind of compound was active as a PTP1B (protein tyrosine phosphatase) inhibitor (IC_{50}: 4.6 μM). With the expectation to find more active hits as well as part of a continuing effort in our laboratory for the expeditious synthesis of biologically relevant heterocyclic compounds, we started to investigate the possibility to develop novel methods to build up new 1,2-dihydroisoquinoline-based structures. Herein, we disclose our recent efforts for the generation of fused 1,2-dihydroisoquinolines and related *N*-heterocycles *via* tandem cyclization-[3+2] cycloaddition of *N*′-(2-alkynylbenzylidene)hydrazide with dimethyl acetylenedicarboxylate (DMAD) catalyzed by silver triflate or in the presence of electrophiles. Interestingly, different outcomes were generated under the different conditions mentioned above. The unexpected isoquinoline-based azomethine ylides were obtained when the reaction was catalyzed by silver triflate or run in the presence of bromine, while the fused 1,2-dihydroisoquinolines were afforded when iodine was employed in the tandem reactions.

Results and Discussion

The starting materials *N*′-(2-alkynylbenzylidene)hydrazides were easily accessible *via* condensation of 2-alkynylbenzaldehydes with hydrazine. The reaction was initially studied with *N*′-(2-alkynylbenzylidene)-hydrazide **1a** and dimethyl acetylenedicarboxylate (DMAD), which were selected as suitable substrates for reaction development (Scheme 1). We conceived that in the presence of a suitable Lewis acid catalyst, *N*′-(2-alkynylbenzylidene)hydrazide **1a** would be converted to the intermediate **2a**. Subsequently, a further dipolar cycloaddition reaction might occur in the presence of dipolarophiles (such as dimethyl acetylenedicarboxylate), leading to the fused 1,2-dihydroisoquinoline derivatives.[4] To identify the practicability of this proposed route, we started to investigate the possibility for the one-pot tandem electrophilic cycli-



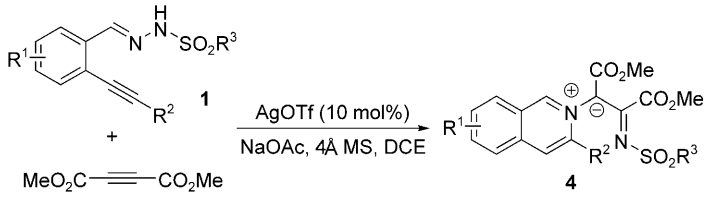
Scheme 1. One-pot tandem reaction of *N*′-(2-alkynylbenzylidene)hydrazide **1a** with dimethyl acetylenedicarboxylate (DMAD).

zation-[3+2] cycloaddition of *N*′-(2-alkynylbenzylidene)hydrazide with dimethyl acetylenedicarboxylate (DMAD).

As described above, in the presence of a Lewis acid, *N*′-(2-alkynylbenzylidene)hydrazide **1a** could be transformed to the intermediate **2a** *via* electrophilic cyclization. At the outset, various Lewis acids were screened and silver triflate (10 mol%) was demonstrated as the best choice when this reaction was performed at 70 °C in dichloroethane (Scheme 1). The reaction went to completion and an almost quantitative yield of product **2a** was generated. Other metal catalysts employed displayed lower yields. For example, an 82% yield of product **2a** was isolated when copper triflate was utilized in the reaction. The starting material *N*′-(2-alkynylbenzylidene)hydrazide **1a** could not be consumed even after 24 h at 70 °C when the reaction was catalyzed by iron(III) chloride or indium(III) triflate. In the silver triflate-catalyzed reaction of *N*′-(2-alkynylbenzylidene)hydrazide **1a**, dimethyl acetylenedicarboxylate (DMAD) was added subsequently. To our delight, the formation of a product was observed although only 15% yield was isolated. Further screening revealed that the yield could be increased to 35% when the one-pot reaction was performed at room temperature. Addition of other Lewis acids as co-catalysts could not improve the result. We finally realized that in the presence of molecular sieves and sodium acetate, the isolated yield of the product could be increased to 70% (Scheme 1). Solvent screening demonstrated that dichloroethane (DCE) was the best choice in the reaction. However, structural identification revealed that the product generated was compound **4a**, instead of the desired fused dihydroisoquinoline **3a**. We also observed a similar transformation for the reaction of 2-alkynylbenzaldoxime, dimethyl acetylenedicarboxylate, and bromine.[5] In the reaction process, an aziridine is generally assumed to be involved in the rearrangement of 4-isoxazoline.[6] Based on these results, we reasoned that a similar approach could be assumed for the conversion of compound **3a** to **4a**. The rearrangement involves homolysis of the N–N bond in compound **3a** and subsequent cyclization to afford the aziridine intermediate. Thermal ring-opening of aziridine could give the unexpected ylide **4a**.[5,6] Under these standard conditions, other Lewis acids were re-examined for the reaction of *N*′-(2-alkynylbenzylidene)hydrazide **1a** with dimethyl acetylenedicarboxylate. Only a small amount of isoquinolinium-2-ylamide **2a** was detected with recovery of the starting material when iron(III) chloride was employed as a catalyst. A 50% yield of product **4a** was obtained when palladium chloride was used as a replacement. Gold(III) chloride as catalyst was found to be effective as well for this transformation (61% yield), while an inferior result (35% yield) was observed when copper triflate was utilized in the reaction.

With this promising result in hands and having defined an efficient catalytic system [silver triflate (10 mol%), dichloroethane, sodium acetate, molecular sieves], the scope of tandem cyclization-[3+2] cycloaddition-rearrangement one-pot reactions of *N*′-(2-alkynylbenzylidene)hydrazide **1** with dimethyl acetylenedicarboxylate was next explored and the results are summarized in Table 1. For most cases, *N*′-(2-alkynylbenzylidene)hydrazide **1** reacted with dimethyl acetylenedicarboxylate catalyzed by silver triflate leading to the corresponding products **4** in good to excellent yields. For instance, reaction of he fluoro-substituted *N*′-(2-alkynylbenzylidene)hydrazide **1b** with dimethyl acetylenedicarboxylate gave rise to the desired product **4b** in 80% yield (Table 1, entry 2). An inferior yield was displayed when the substrate **1c** with an electron-donating group attached on the aromatic ring of *N*′-(2-alkynylbenzylidene)hydrazide was employed in the reaction (45% yield, Table 1, entry 3). When R^2 was replaced by the 4-methoxyphenyl group, reactions also proceeded well to furnish the corresponding products in good yields (Table 1, entries 4 and 5). Similar results were observed when

Table 1. Silver triflate-catalyzed tandem reactions of *N*′-(2-alkynylbenzylidene)hydrazides **1** with dimethyl acetylenedicarboxylate.

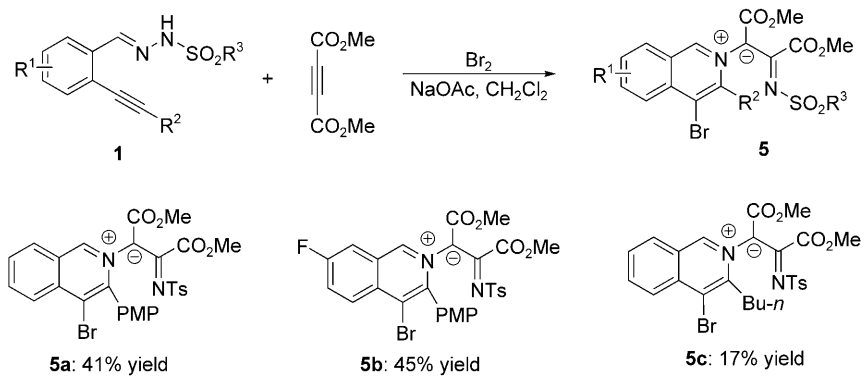


Entry	Substrate **1**	Product **4**	Yield [%][a]
1	**1a**	**4a**	70
2	**1b**	**4b**	80
3	**1c**	**4c**	45
4	**1d**	**4d**	70
5	**1e**	**4e**	83
6	**1f**	**4f**	51
7	**1g**	**4g**	81
8	**1h**	**4h**	65
9	**1i**	**4i**	68

[a] Isolated yield based on *N*′-(2-alkynylbenzylidene)hydrazide **1**. PMP: *p*-methoxyphenyl.

the tosyl group attached on the nitrogen was changed to a phenylsulfonyl group (Table 1, entries 6–9).

Meanwhile, we also tested the tandem reactions *via* an eletrophile-mediated cyclization. The electrophilic cyclization of heteroatomic nucleophiles with tethered alkynes has been well-known for preparing many heterocyclic ring systems.[7–9] Usually, iodine and bromine were used in the reactions since the resulting iodo- or bromo-containing products could be easily transferred to more complex products by palladium-catalyzed cross-coupling reactions. The electrophilic cyclization of *N*′-(2-alkynylbenzylidene)hydrazide in the presence of bromine, iodine, or iodine monochloride was disclosed recently.[9] We found that the reactions of *N*′-(2-alkynylbenzylidene)hydrazide **1** with dimethyl acetylenedicarboxylate (DMAD) in the presence of bromine also gave rise to the expected bromo-containing products **5**, although the yields were lower (Scheme 2). For example, when *N*′-(2-alkynylbenzylidene)hydrazide **1d** was employed as the substrate in the reaction of dimethyl acetylenedicarboxylate with bromine, a 41% yield of compound **5a** was isolated. A similar yield (45%) of product **5b** was observed when substrate **1e** was utilized in this tandem reaction. We



Scheme 2. One-pot tandem reactions of *N*′-(2-alkynylbenzylidene)hydrazides **1**, dimethyl acetylenedicarboxylate, and bromine.

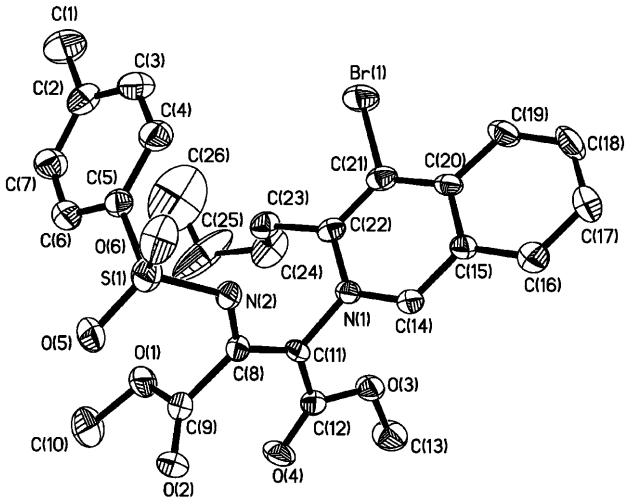


Figure 1. X-ray ORTEP illustration of compound **5c**.

also tried the reaction of *N*′-(2-alkynylbenzylidene)-hydrazide **1j** with an *n*-butyl group attached on the triple bond, and the corresponding product **5c** was generated in 17% yield. The structure of compound **5c** was verified by X-ray diffraction analysis (Figure 1).

Surprisingly, a different outcome was generated when iodine was utilized as a replacement for bromine. Compared with the results obtained in the presence of bromine in the reactions, the sulfonyl group was released during the reaction process. In these iodine-involved reactions, the yields of the corresponding products were dramatically improved (Table 2). For instance, *N*′-(2-alkynylbenzylidene)hydrazide **1a** reacted with dimethyl acetylenedicarboxylate and iodine in the presence of sodium acetate leading to the desired product **6a** in 91% yield (Table 2, entry 1). A similar result was obtained when the fluoro-containing substrate **1b** was used in the reaction (90% yield, Table 2, entry 2). The structure of compound **6b** was also verified by X-ray diffraction analysis (Figure 2). When the phenyl group attached on the triple bond in the *N*′-(2-alkynylbenzylidene)hydrazide **1** was replaced by other groups (such as 4-methoxyphenyl, butyl, cyclopropyl groups), the reactions also proceeded smoothly to furnish the desired products in good yields (Table 2, entries 3–5).

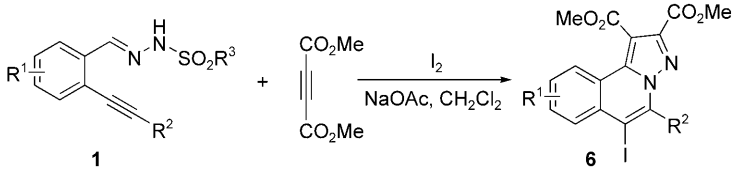
The possible mechanism was also proposed (Scheme 3). As described previously, electrophilic cyclization of *N*′-(2-alkynylbenzylidene)hydrazide **1** with iodine would afford the corresponding isoquinolinium-2-ylamide **7**.[9] This compound subsequently underwent [3+2] cycloaddition in the presence of dimethyl acetylenedicarboxylate (DMAD) leading to the intermediate **8**. Finally, the aromatization occurred to generate the unexpected product **6**.

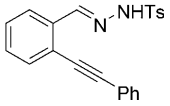
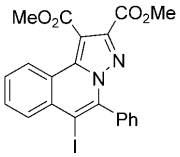
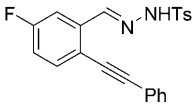
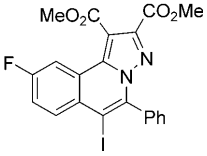
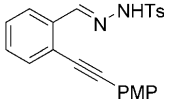
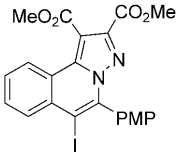
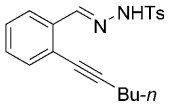
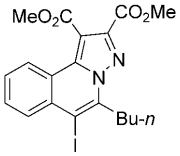
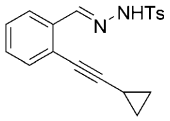
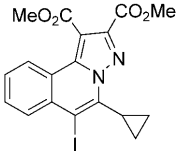
As mentioned above, the iodo-containing products **6** could be easily elaborated *via* palladium-catalyzed cross-coupling reactions. Thus, the palladium-catalyzed reaction of the fused 1,2-dihydroisoquinoline **6c** with phenylboronic acid in DMF-H_2O at room temperature occurred to afford the corresponding product **6f** in 86% yield. Compound **6d** reacted with 4-methoxyphenylacetylene, giving rise to the desired coupling product **6g** in 81% yield (Scheme 4).

Conclusions

In conclusion, we have described an efficient tandem cyclization-[3+2] cycloaddition reaction of *N*′-(2-alkynylbenzylidene)hydrazides with dimethyl acetylenedicarboxylate catalyzed by silver triflate or run in the presence of electrophiles. Different outcomes were generated under the different conditions. The halide-containing products could be further elaborated by palladium-catalyzed cross-coupling reactions to introduce more diversity, which generated the highly functionalized fused 1,2-dihydroisoquinolines. Small library construction as well as biological screening of these small molecules is ongoing, and the results will be reported in due course.

Table 2. One-pot tandem reactions of *N*′-(2-alkynylbenzylidene)hydrazides **1**, dimethyl acetylenedicarboxylate, and iodine.



Entry	Substrate **1**	Product **6**	Yield [%][a]
1	**1a** 	**6a** 	91
2	**1b** 	**6b** 	90
3	**1d** 	**6c** 	76
4	**1j** 	**6d** 	93
5	**1k** 	**6e** 	63

[a] Isolated yield based on *N*′-(2-alkynylbenzylidene)hydrazides **1**. PMP: *p*-methoxyphenyl.

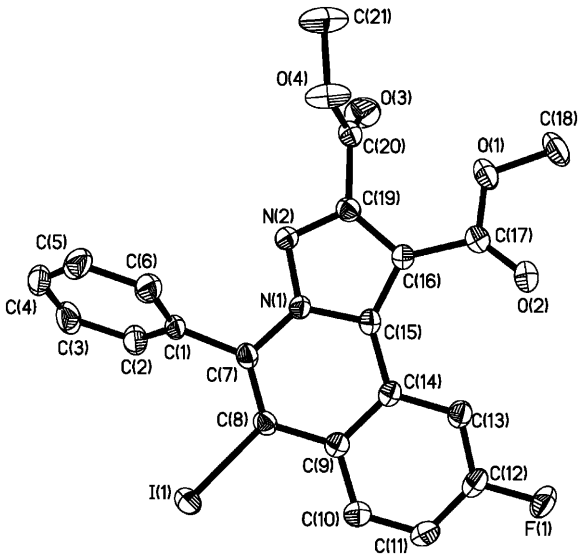
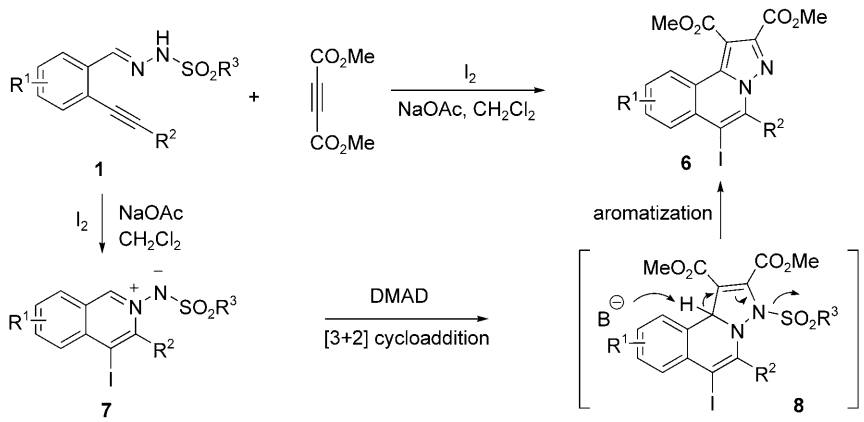


Figure 2. X-ray ORTEP illustration of the fused 1,2-dihydroisoquinoline **6b**.

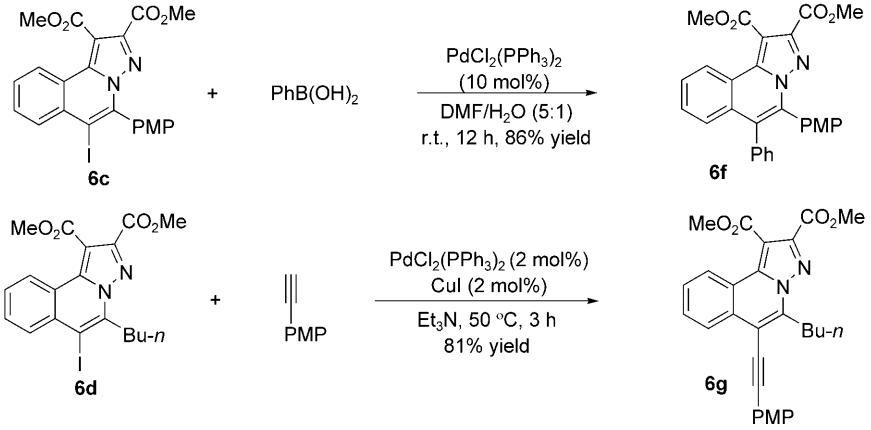
Experimental Section

General Procedure for Silver Triflate-Catalyzed Tandem Reaction of *N*′-(2-Alkynylbenzylidene)-hydrazide 1 with Dimethyl Acetylenedicarboxylate

A mixture of *N*′-(2-alkynylbenzylidene)hydrazide **1** (0.40 mmol, 1.0 equiv.) and silver triflate (10 mol%) in anhydrous dichloroethane (4.0 mL) was stirred at 70 °C for 3 h. Then the mixture was cooled to 0 °C in an ice-water bath, 4 Å MS (100 mg) and sodium acetate (0.48 mmol, 1.2 equiv.) were added. Subsequently, a solution of dimethyl acetylenedicarboxylate (0.80 mmol, 2.0 equiv.) in dichloroethane (2.0 mL) was added dropwise and the mixture was slowly warmed to room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was filtered and the solvent of the filtrate was removed on a rotary evaporator, followed by purification on silica gel which provided the corresponding product **4**.



Scheme 3. Possible mechanism for one-pot tandem reactions of *N*′-(2-alkynylbenzylidene)hydrazides **1**, dimethyl acetylenedicarboxylate, and iodine.



Scheme 4. Synthesis of highly functionalized fused 1,2-dihydroisoquinolines *via* palladium-catalyzed cross-coupling reactions.

Data of a selected example: Compound **4a**; yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.40$ (s, 3H), 3.37 (s, 3H), 3.90 (s, 3H), 7.20 (d, $J = 7.8$ Hz, 2H), 7.24–7.36 (m, 4H), 7.38–7.46 (m, 1H), 7.73 (d, $J = 7.3$ Hz, 2H), 7.87–7.89 (m, 1H), 8.02–8.12 (m, 4H), 9.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.4$, 52.7, 53.4, 126.2, 126.5, 127.0, 127.1, 128.2, 128.8, 129.9, 130.4, 130.5, 131.9, 137.1, 138.6, 141.2, 141.5, 149.7, 154.6, 162.6, 166.3; HR-MS: $m/z = 517.1440$, calcd. for $C_{28}H_{24}N_2O_6S$ $[M+H]^+$: 517.1433.

General Procedure for Tandem Reaction of *N*′-(2-Alkynylbenzylidene)hydrazides 1, DMAD, and Bromine

Bromine (0.48 mmol, 1.2 equiv.) in 2.0 mL of dichloromethane was added dropwise to a mixture of the *N*′-(2-alkynylbenzylidene)hydrazide **1** (0.40 mmol, 1.0 equiv.), and sodium acetate (0.48 mmol, 1.2 equiv.) in dichloromethane (4.0 mL) at 0 °C. Subsequently, a solution of dimethyl acetylenedicarboxylate (DMAD) (0.8 mmol, 2.0 equiv.) in dichloromethane (2.0 mL) was added, and the mixture was slowly warmed to room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with dichloromethane (10 mL), washed with saturated aqueous $Na_2S_2O_3$ (20 mL), dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the corresponding product **5**.

Data of a selected example: Compound **5a**; yield: 41%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H), 3.47 (s, 3H), 3.83 (s, 3H), 3.87 (s, 3H), 6.40–6.70 (br, 1H), 6.90 (d, $J = 6.4$ Hz, 1H), 7.14–7.26 (m, 4H), 7.74 (d, $J = 7.8$ Hz, 2H), 7.95–7.98 (m, 1H), 8.10–8.25 (m, 2H), 8.45 (d, $J = 8.3$ Hz, 1H), 9.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.4$, 51.2, 52.7, 55.2, 113.5, 113.6, 124.1, 124.9, 126.6, 126.7, 127.1, 127.9, 128.9, 130.2, 130.4, 130.8, 131.0, 138.3, 138.4, 141.2, 149.4, 153.9, 161.1, 166.1; HR-MS: $m/z = 625.0672$, calcd. for $C_{29}H_{25}BrN_2O_7S$ $[M+H]^+$: 625.0644.

General Procedure for the Tandem Reaction of *N*′-(2-Alkynylbenzylidene)hydrazides 1, DMAD, and Iodine

Iodine (0.48 mmol, 1.2 equiv.) in 1.0 mL of dichloromethane was added dropwise to a mixture of *N*′-(2-alkynylbenzylidene)hydrazide **1** (0.40 mmol, 1.0 equiv.), and sodium acetate (0.48 mmol, 1.2 equiv.) in dichloromethane (4.0 mL) at 0 °C. Subsequently, a solution of dimethyl acetylenedicarboxylate (DMAD) (0.80 mmol, 2.0 equiv.) in dichloromethane (2.0 mL) was added and the mixture was slowly warmed to room temperature. After completion of the reac-

tion as indicated by TLC, the reaction mixture was diluted with dichloromethane (10 mL), washed with saturated aqueous $Na_2S_2O_3$ (20 mL), dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the corresponding product **6**.

Data of selected example: Compound **6a**; yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.88$ (s, 3H), 4.01 (s, 3H), 7.42–7.44 (m, 2H), 7.54–7.60 (m, 3H), 7.67–7.75 (m, 2H), 8.25 (d, $J = 7.8$ Hz, 1H), 8.87 (d, $J = 8.3$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 52.6$, 52.7, 92.0, 108.1, 123.0, 125.6, 128.7, 129.1, 129.7, 130.2, 130.6, 131.2, 133.5, 137.0, 137.6, 141.0, 144.9, 162.9, 164.8. HR-MS: $m/z = 487.0147$, calcd. for $C_{21}H_{15}IN_2O_4$ $[M+H]^+$: 487.0155. (For details, please see Supporting Information).

CCDC 713190 (**5c**) and CCDC 713191 (**6b**) 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.

Supporting Information

Experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra of all new compounds are available as Suppoprting Iformation.

Acknowledgements

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