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Rhodium(III)-Catalyzed Directed *ortho*-C−H Bond Functionalization of Aromatic Ketazines via C−S and C−C Coupling

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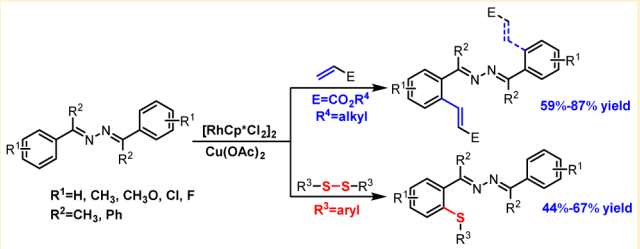
Supporting Information

ABSTRACT: Described herein is a convenient and efficient method for sulfuration and olefination of aromatic ketazines via rhodium-catalyzed oxidative C−H bond activation. A range of substituted substrates are supported, and a possible mechanism is proposed according to experimental results of kinetic isotopic effect, reversibility studies, and catalysis of rhodacycle intermediate **c1**.



INTRODUCTION

Transition-metal-catalyzed directed sp^2 C−H activation, which occurs based on directing groups, has emerged as a powerful tool for the functionalization of various arenes with advantages of step- and atom-economy, high selectivity, and efficiency, providing an alternative to traditional transformations.[1] In recent years, rhodium-catalyzed directed sp^2 C−H bond activation has been broadly exploited and used for its excellent catalysis and good tolerance of functional groups.[2] In the catalytic activation, directing groups such as pyridine, oxime, and hydrazone, which have proved to be viable directing groups with "C═N" as substructure, always play an important role.[3] Ketazine derivatives, most of which were used in a wide range of agricultural chemicals, medicines, and materials, have the generic substructure "−C═N−N═C−" that proved to be an effective directing group by Huang et al. and others.[4] In addition, aryl sulfides, generally prepared under harsh reaction conditions with the need for prefunctionalized partners, are common structures in natural products with biological activity widely used in medicines and materials.[5] Therefore, on the basis of related reports and the importance of ketazines, introducing Rh-catalyzed directed C−H activation to functionalization of ketazines with sulfides or other partners should be attractive and feasible. Herein, we report a study of sulfuration and olefination of aromatic ketazines with disulfides and acrylates catalyzed by $[RhCp^*Cl_2]_2$ ($Cp^* = C_5Me_5$) as catalysts via directed C−H activation under mild conditions. This study also shows a range of substituted substrates, a possible mechanism that rhodacycle **4** is the key intermediate in the catalytic cycle, and a kinetic test which identifies the rate-determining step for this transformation.

RESULTS AND DISSCUSSION

With the reaction of acetophenone azine (**1a**, 1.0 equiv) with diphenyl disulfide (**2a**, 1.2 equiv) as a model, we initiated our studies by examining the effects of several silver salts (12%) that could activate the Rh catalyst via antichloration toward the reaction in THF (2 mL) at 60 °C for 24 h, using 1:4 $[RhCp^*Cl_2]_2$ (3%) as catalyst (entries 1−5, Table 1). It suggested that silver salts played a crucial role in the reaction efficiency by the results of that the desired product **3a** was not observed under conditions without silver salts added, and AgOTf was optimal with product **3a** in 41% yield. According to screening oxidants for the coupling, we found that oxidants were required and $Cu(OAc)_2$ worked best in the catalytic system than others (entries 6−11, Table 1). Among the set of representative solvents, DCE was found to be optimal (entries 12−15, Table 1). By increasing the amounts of catalyst and silver salt, respectively, to 5 mol % and 20 mol %, the optimal conditions were determined with the isolated 56% yield of product **3a** (entry 16, Table 1) and used as standard conditions in the following studies. Additionally, on the basis of the effects of additives (S10, Supporting Information), it was found that chloride abstraction is required for catalyst turnover in the coupling with disulfides, and the anion of silver salts has an impact on the catalyst turnover.

With an optimized catalytic system in hand, we proceeded to evaluate the generality of the standard reaction conditions with a range of substrates, as shown in Table 2. The results showed that electron-donating substrates, affording products **3b** and **3c** in yields of 66% and 67%, showed better activity than electron-withdrawing substrates in the catalytic system. According to the contrast between products **3c** and **3f**, it suggested that *para*-substituted substrates had higher efficiency than *meta*-substituted substrates. The lower yield of product **3g**, obtained from the substrate with a phenyl substituent on ketazine, revealed the steric property that substrates with large substituents on ketazine tended to form a (*Z*)-configuration, which was unable to direct C−H activation.

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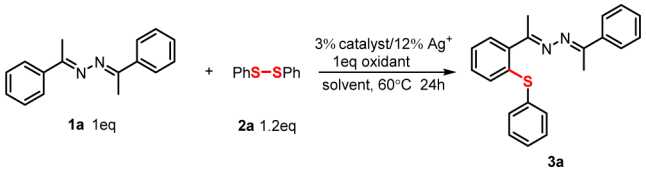
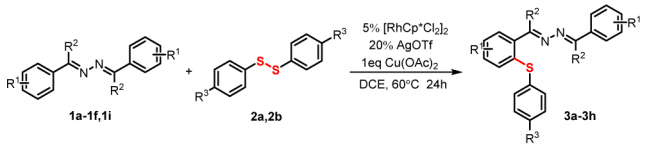
Table 1. Coupling of Acetophenone Azine (1a) with Diphenyl Disulfide (2a) under Various Conditions[a,b]

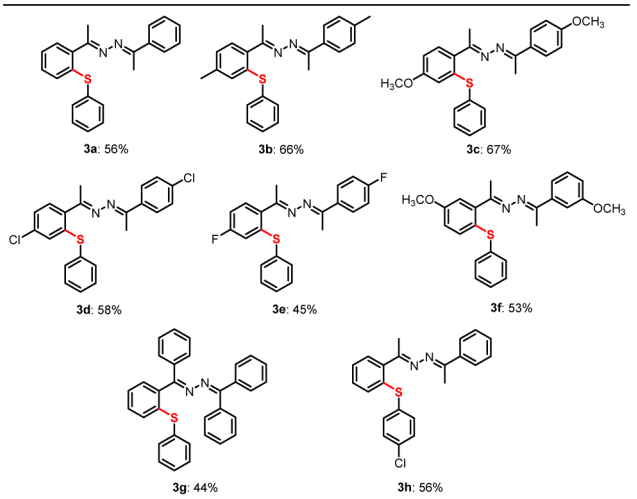


entry	catalyst	oxidant	solvent	3a yield (%)
1	$[RhCp^*Cl_2]_2$ /$AgSbF_6$	$Cu(OAc)_2$	THF	16
2	$[RhCp^*Cl_2]_2$/AgOAc	$Cu(OAc)_2$	THF	~5
3	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	THF	41
4	$[RhCp^*Cl_2]_2$/AgOTs	$Cu(OAc)_2$	THF	35
5	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$	THF	trace
6	$[RhCp^*Cl_2]_2$/AgOTf	$CuCl_2$	THF	22
7	$[RhCp^*Cl_2]_2$/AgOTf	$AgNO_3$	THF	13
8	$[RhCp^*Cl_2]_2$/AgOTf	AgOAc	THF	trace
9	$[RhCp^*Cl_2]_2$/AgOTf	Ag_2CO_3	THF	trace
10	$[RhCp^*Cl_2]_2$/AgOTf	O_2	THF	~5
11	$[RhCp^*Cl_2]_2$/AgOTf	none	THF	~5
12	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	toluene	27
13	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	MeOH	12
14	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	DCE	46
15	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	MeCN	18
16[c]	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	DCE	56
17[d]	$[RhCp^*Cl_2]_2$/AgOTf	$Cu(OAc)_2$	DCE	54

[a]Conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (1.2 equiv), catalyst/Ag^+ (3 mol %/12 mol %), solvent (2 mL), 60 °C, 24 h, all the oxidants (1.0 equiv). [b]Yields (<10%) estimated by TLC; isolated yields estimated by weighing. [c]Catalyst/Ag^+ (5 mol %/20 mol %). [d]Catalyst/Ag^+ (5 mol %/20 mol %), $Cu(OAc)_2$ (2.0 equiv).

Table 2. Coupling of Aromatic Ketazines with Disulfides[a,b]

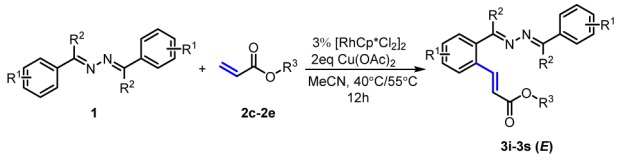


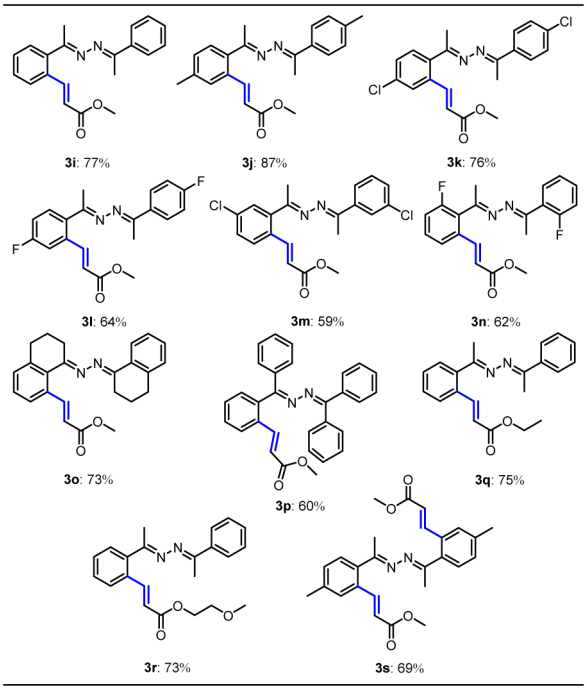


[a]Reaction conditions presented by entry 16 in Table 1. [b]Isolated yields given unless otherwise noted.

In addition to disulfides, acrylates also worked as a coupling partner in *ortho*-functionalization of aromatic ketazines and emerged more efficient than disulfides under the conditions without silver salt in MeCN (2 mL) at 40/55 °C for 12 h (Table 3). In these reactions, substrates bearing diverse

Table 3. Coupling of Aromatic Ketazines with Alkenes[a,b,c]





[a]Conditions: **1** (0.1 mmol, 1.0 equiv), **2** (1.2 equiv), $[RhCp^*Cl_2]_2$ (3 mol %), MeCN (2 mL), 40 °C/55 °C, 12 h, $Cu(OAc)_2$ (2.0 equiv) as oxidant. [b]Only the (*E*)-configuration afforded, isolated yields given. [c]All products obtained at 40 °C, except for **3a**, **3l**−**3n**, and **3s** obtained at 55 °C.

substituents at different positions all coupled smoothly with acrylates, affording products **3i**−**3s** in yields of 60−87%. Like the coupling with disulfides, the coupling with acrylates also showed effects of electronic property, steric property, and substituted position. Electron-donating and *para*-substituted substrates were converted preferentially in the catalytic system compared with others. Substrates with large substituents on ketazine gave products **3o** and **3p** in lower yields of 73% and 60%. In all these cases, only the (*E*)-configuration of products was observed. Clearly, all of the coupling reactions via C−H activation occurred at the *ortho*-position on aryl, which demonstrated the key role of the directing group. In contrast, benzylidene azine as substrate failed to deliver a sulfuration or olefination product, which probably revealed that the long distance between the directing N atom and C atom on the activation site, which resulted from bond angles, blocked metalation−cyclization of the substrate with the Rh catalyst.[6]

Subsequently, mechanism experiments were carried out with disulfides as a template. On the basis of the competition experiment, the chemoselectivity of the rhodium catalysis was further understood. Essentially, in accord with yield data of products, the result that the electron-donating substituted substrate was converted preferentially to product **3b** revealed

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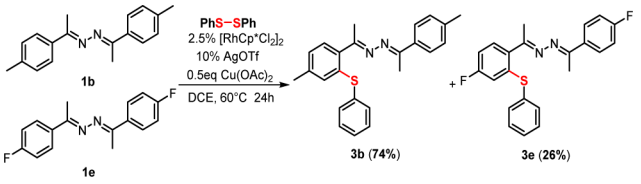
the effect of the electronic property (Scheme 1). The result also suggested that C−H activation probably followed the electrophilic aromatic substitution (EAS) rather than concerted metalation−deprotonation.[7]

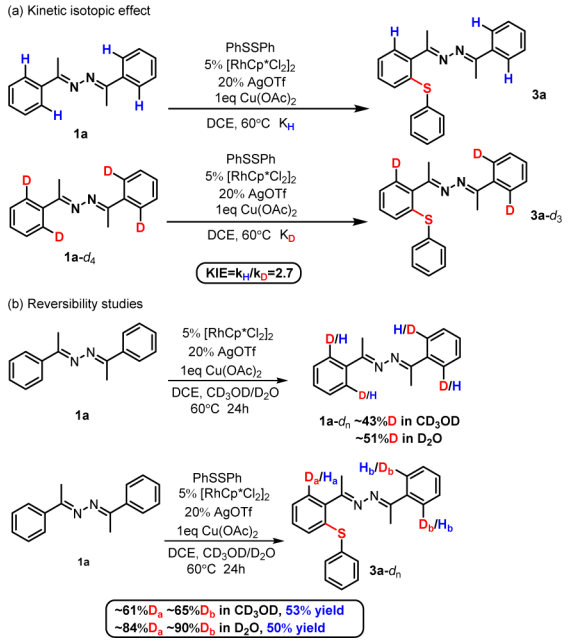
Scheme 1. Competition Experiment[a,b]



[a]The substrate ratio was determined to be 1:1. [b]Percentage in bracket estimated by ^{1}H NMR meaning the proportion of each product in total, not the yield.

Further mechanistic studies showed that the kinetic isotope effect (KIE), which was measured to be 2.7 by using two parallel reactions, revealed a reaction involving a rate-limiting C−H bond activation (Scheme 2a).[8] Additionally, an H/D

Scheme 2. Deuterium Experiments[a]

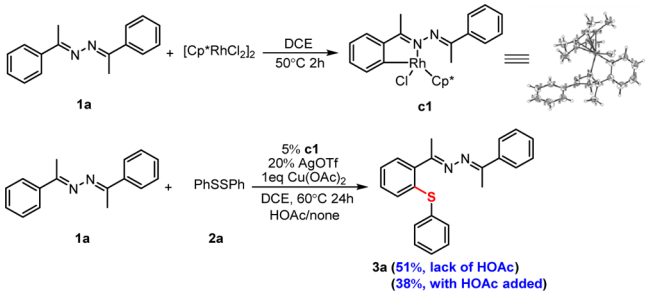


[a]Deuteration rate estimated by ^{1}H NMR.

exchange experiment, under the standard conditions with CD_3OD/D_2O as proton donor and in the absence of diphenyl disulfide, was carried out to examine the reversibility of C−H activation. By the results that H/D exchange of substrate **1a** was remarkably observed, C−H activation was determined to be reversible (Scheme 2b). Similarly, under the standard conditions with CD_3OD/D_2O added, H/D exchange of product **3a** was also observed, which revealed the reversibility of migratory insertion of the S−S bond into the C−Rh bond (Scheme 2b) (note that some deuterium protons (D_b) of **3a**-d_n resulted from Rh-catalyzed C−H activation rather than migratory insertion).

Under the satndard conditions in the absence of diphenyl disulfide and additives, the rhodacycle **c1** was afforded by the reaction of the Rh catalyst with acetophenone azine (Scheme 3). Subsequently, we examined the catalysis of rhodacycle **c1** in the reaction (Scheme 3). Because of the fact that the process of

Scheme 3. Catalysis of Rhodacycle Intermediate c1[a]

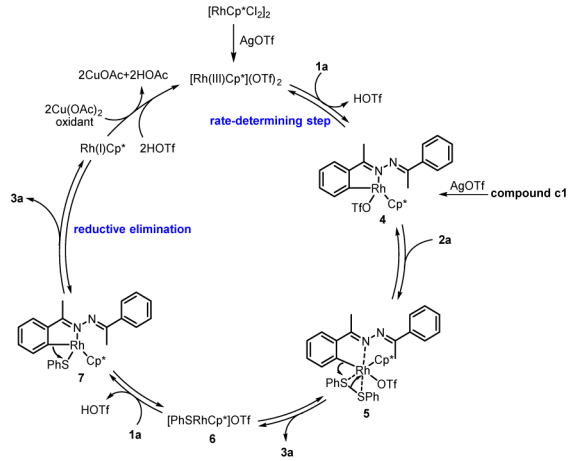


[a]HOAc as proton donor for the loss of HCl resulting from isolating **c1**.

separating rhodacycle **c1** resulted in a lack of protons, the reaction system with rhodacycle **c1** instead of $[RhCp^*Cl_2]_2$ requested HOAc for proton supplement, which afforded product **3a** in 38% yield. Surprisingly, the reaction afforded product **3a** as well with only rhodacycle **c1** subjected to the standard conditions instead of $[RhCp^*Cl_2]_2$, and the yield of **3a** in this reaction was consistent with it in a typical reaction. Under this, we inferred that the PhS^- fragment, which was delivered by cleavage of the S−S bond, could combine Rh(III) rather than a proton to form the phenylthio-coordination Rh complex.

On the basis of these studies, a reasonable catalytic cycle for diphenyl disulfide sketched in Scheme 4 is proposed. We

Scheme 4. Mechanism Proposal[a]



[a]In the catalytic cycle, due to the rate-determining step, $[Rh(III)Cp^*](OTf)_2$ is formed first, and then it reacts with substrate **1a** to form the rhodacycle intermediate **4**. In contrast, in the mechanism experiment, as the previously prepared compound **c1** is separately subjected to catalytic system, the rhodacycle **4** could be formed from compound **c1** and AgOTf.

hypothesize that a proposed catalytic cycle initiates with the formation of the rhodacycle intermediate **4** via Rh(III)-catalyzed C−H activation.[9] After the disulfide combines with Rh(III) by coordination, with formation of a C−S bond and a S−Rh bond, product **3a** and Rh(III) complex **6** are delivered by insertion of the S−S bond into the C−Rh bond. The Rh(III) complex **6** proceeds with catalysis toward the coupling reaction

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to form the rhodacycle **7** via C−H activation. Then, another molecule of **3a** and Rh(I)Cp* are formed from rhodacycle intermediate **7** by reductive elimination.[10] Finally, Rh(I) is oxidized to Rh(III) by external oxidant $Cu(OAc)_2$. In this catalytic cycle, 1 equiv of disulfide **2a** is converted into 2 equiv of product **3a** with just 1 equiv of $Cu(OAc)_2$ required, demonstrating that there is little difference in yield between 1 and 2 equiv of $Cu(OAc)_2$ employed (entries 16, 17, Table 1). In addition, according to the study on balance of the materials (S8−S10, Supporting Information), we identified [Rh]/AgOTf as the key role that the stalled reaction with other materials remaining, which resulted from inactivation of the Rh catalyst, can be restarted by fresh [Rh]/AgOTf.

CONCLUSION

In summary, we have developed an effective methodology to achieve the direct *ortho*-functionalization of aromatic ketazines with aryl disulfides and acrylates via Rh-catalyzed C−H activation and studied the mechanism for C−S coupling in some detail by experiments of KIE, H−D exchange, substrate competition, and catalysis of Rh(III) complex intermediate **c1**. This methodology, which, especially for *ortho*-olefination of aromatic ketazines, is attractive with the low loading of Rh catalyst, mild reaction temperature, high yield, and only the (*E*)-configuration of products obtained, supports a range of differently substituted substrates and shows good chemoselectivity. Morever, the method for *ortho*-olefination exhibits tolerance of mono- or diolefination. The above features should lead to many applications, especially derivation and modification of aromatic organics with the generic "C═N" as substructure.

EXPERIMENTAL SECTION

General Information. All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. HPLC grade DCE and MeCN were used directly. $[RhCp^*Cl_2]_2$ was purchased from commercial sources, stored, and weighed in an argon-filled glovebox. AgOTf was purchased from commercial sources and also stored and manipulated in the glovebox. All other chemicals were obtained from local suppliers or synthesized according to the literature procedures. ^1H, ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ (with tetramethylsilane as internal standard) solution on a 500/300 MHz NMR spectrometer. High-resolution mass spectra were obtained via ESI/EI mode with a TOF mass analyzer. Column chromatography was performed on silica gel (300−400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

Preparation of Alkyl Disulfides and Alkenes. Alkyl disulfides and alkenes were purchased from commercial sources and used without further purification.

Preparation of Aromatic Ketazines 1a−1k. Aromatic ketazines **1a−1k** were prepared following a published procedure.[11]

(1E,2E)-1,2-Bis(1-phenylethylidene)hydrazine ***1a***.[12] Bright yellow solid, 1.77 g, 75% yield; (PE/EtOAc 20:1, R_f 0.67); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.89−7.92 (m, 4H), 7.38−7.43 (m, 6H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 157.8, 138.5, 129.7, 128.4, 126.7, 15.1; MS (EI), *m*/*z* (% relative intensity): 236.1 ($[M]^+$, 29), 221.1 ($[M - CH_3]^+$, 100).

(1E,2E)-1,2-Bis(1-(p-tolyl)ethylidene)hydrazine ***1b***.[12] Bright yellow solid, 2.06 g, 78% yield; (PE/EtOAc 20:1, R_f 0.57); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.80−7.81 (m, 4H), 7.20−7.22 (m, 4H), 2.38 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 157.8, 139.7, 135.9, 129.1, 126.6, 21.4, 15.0; MS (EI), *m*/*z* (% relative intensity): 264.1 ($[M]^+$, 28), 249.0 ($[M - CH_3]^+$, 100).

(1E,2E)-1,2-Bis(1-(4-methoxyphenyl)ethylidene)hydrazine ***1c***.[12] Yellow solid, 1.95 g, 66% yield; (PE/EtOAc 20:1, R_f 0.21); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.86−7.89 (m, 4H), 6.93−6.95 (m, 4H), 3.85 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 160.8, 157.4, 131.4, 128.1, 113.7, 55.4, 14.8; MS (EI), *m*/*z* (% relative intensity): 296.1 ($[M]^+$, 50), 281.0 ($[M - CH_3]^+$, 100).

(1E,2E)-1,2-Bis(1-(4-chlorophenyl)ethylidene)hydrazine ***1d***.[12] Light yellow solid, 2.03 g, 68% yield; (PE/EtOAc 20:1, R_f 0.64); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.83−7.85 (m, 4H), 7.37−7.39 (m, 4H), 2.30 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 151.3, 136.8, 135.8, 128.6, 128.0, 14.9; MS (EI), *m*/*z* (% relative intensity): 306.0 ($[M + 2]^+$, 1), 304.0 ($[M]^+$, 7), 291.0 ($[M + 2 - CH_3]^+$, 34), 288.9 ($[M - CH_3]^+$, 100).

(1E,2E)-1,2-Bis(1-(4-fluorophenyl)ethylidene)hydrazine ***1e***.[12] Bright yellow solid, 1.72 g, 63% yield; (PE/EtOAc 20:1, R_f 0.53); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.88−7.92 (m, 4H), 7.07−7.11 (m, 4H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 163.8 (d, J = 250.6 Hz, CF), 157.4, 134.6, 128.6 (d, J = 7.6 Hz, CN), 115.3 (d, J = 21.4 Hz, CH), 15.0; MS (EI), *m*/*z* (% relative intensity): 272.0 ($[M]^+$, 28), 257.0 ($[M - CH_3]^+$, 100).

(1E,2E)-1,2-Bis(1-(3-methoxyphenyl)ethylidene)hydrazine ***1f***.[13] Bright yellow solid, 1.56 g, 53% yield; (PE/EtOAc 20:1, R_f 0.32); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.51−7.52 (m, 2H), 7.43−7.46 (m, 2H), 7.32 (t, J = 8.0 Hz, 2H), 6.95−6.97 (m, 2H), 3.85 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 159.7, 157.3, 139.9, 129.3, 119.3, 115.7, 111.7, 55.4, 15.2; MS (EI), *m*/*z* (% relative intensity): 296.1 ($[M]^+$, 31), 281.1 ($[M - CH_3]^+$, 100).

(1E,2E)-1,2-Bis(1-(3-chlorophenyl)ethylidene)hydrazine ***1g***. Yellow solid, 1.43 g, 48% yield; (PE/EtOAc 20:1, R_f 0.68); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.90−7.92 (m, 2H), 7.75−7.77 (m, 2H), 7.37−7.40 (m, 2H), 7.33−7.36 (m, 2H), 2.30 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 157.3, 140.0, 134.5, 129.7, 129.6, 126.8, 124.8, 15.1; MS (EI), *m*/*z* (% relative intensity): 306.0 ($[M + 2]^+$, 1), 304.0 ($[M]^+$, 8), 291.0 ($[M + 2 - CH_3]^+$, 32), 288.9 ($[M - CH_3]^+$, 100). Anal. Calcd for $C_{16}H_{14}Cl_2N_2$: C, 62.97; H, 4.62; Cl, 23.23; N, 9.18. Found: C, 63.06; H, 4.56; Cl, 23.44; N, 8.94.

(1E,2E)-1,2-Bis(1-(2-fluorophenyl)ethylidene)hydrazine ***1h***. White solid, 1.52 g, 56% yield; (PE/EtOAc 20:1, R_f 0.39); ^1H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.73−7.76 (m, 2H), 7.49−7.53 (m, 2H), 7.29−7.33 (m, 4H), 2.23 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 160.6 (d, J = 250.6 Hz, CF), 155.5, 131.9 (d, J = 7.6 Hz, CH), 130.3, 127.1 (d, J = 11.3 Hz, CH), 125.0, 116.8 (d, J = 22.7 Hz, CH), 18.4; MS (EI), *m*/*z* (% relative intensity): 272.1 ($[M]^+$, 50), 257.0 ($[M - CH_3]^+$, 100). Anal. Calcd for $C_{16}H_{14}F_2N_2$: C, 70.58; H, 5.18; F, 13.95; N, 10.29. Found: C, 70.38; H, 4.96; F, 14.52; N, 10.14.

1,2-Bis(diphenylmethylene)hydrazine ***1i***.[12] White solid, 1.88 g, 52% yield; (PE/EtOAc 20:1, R_f 0.46); ^1H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.45−7.50 (m, 5H), 7.34−7.42 (m, 10H), 7.29−7.31 (m, 5H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.5, 137.9, 135.6, 130.4, 129.4, 129.3, 128.8, 128.5; MS (EI), *m*/*z* (% relative intensity): 283.1 ($[M - Ph]^+$, 100), 180.1 ($[M - Ph_2CN]^+$, 41).

(1E,2E)-1,2-Bis(3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine ***1j***.[12] Yellow solid, 1.45 g, 50% yield; (PE/EtOAc 20:1, R_f 0.58); ^1H NMR (500 MHz, DMSO-d_6), δ (ppm): 8.16−8.18 (m, 2H), 7.32−7.35 (m, 2H), 7.23−7.28 (m, 4H), 2.80 (t, J = 6.0 Hz, 4H), 2.69 (t, J = 6.0 Hz, 4H), 1.81−1.86 (m, 4H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 157.0, 141.0, 132.8, 130.1, 129.2, 126.7, 125.4, 29.6, 27.3, 22.2; MS (EI), *m*/*z* (% relative intensity): 288.1 ($[M]^+$, 100), 259.1 (32).

(1E,2E)-1,2-Dibenzylidenehydrazine ***1k***.[14] Bright yellow solid, 1.56 g, 75% yield; (PE/EtOAc 20:1, R_f 0.66); ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.65 (s, 2H), 7.82−7.84 (m, 4H), 7.40−7.44 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm): 162.1, 134.2, 131.3, 128.9, 128.7; MS (ESI), *m*/*z*: $[M + H]^+$ 209.3.

General Procedures for Synthesis of 3a−3h. To a 13 × 150 mm test tube equipped with magnetic stirrer were added **1a** (23.7 mg, 0.1 mmol, 1.0 equiv), **2a** (26.1 mg, 0.12 mmol, 1.2 equiv), AgOTf (5.1 mg, 0.02 mmol, 20%), and $Cu(OAc)_2$ (20.0 mg, 0.1 mmol, 1.0 equiv). The test tube was transferred to a glovebox, and then $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 5%) was further added. The test tube was sealed with a rubber septum and removed from the glovebox. A DCE (2 mL) solution was injected into the test tube via syringe. The reaction mixture was placed in a preheated oil bath and stirred for 24 h at 60 °C, during which time a constant checking by TLC was performed.

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J. Org. Chem. 2015, 80, 10457−10463

Subsequently, the reaction mixture was filtered over Celite. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel with 15:1 PE/EtOAc as the eluent to afford the product **3a** in 56.4% yield as a yellow solid. Experimental procedures for synthesizing **3b**−**3h** were the same as that for product **3a**.

(1E,2E)-1-(1-Phenylethylidene)-2-(1-(2-(phenylthio)phenyl)ethylidene)hydrazine ***3a***. Yellow solid, 19.4 mg, 56% yield; (PE/EtOAc 15:1, R_f 0.62); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.90−7.93 (m, 2H), 7.60−7.62 (m, 1H), 7.46−7.47 (m, 3H), 7.32−7.42 (m, 7H), 7.10−7.12 (m, 1H), 2.28 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.6, 158.2, 140.1, 138.3, 135.7, 135.5, 132.6, 131.3, 130.3, 130.1, 129.9, 129.5, 128.9, 128.3, 127.1, 18.5, 15.5. One signal is missing due to overlap; MS (ESI), m/z: $[M + H]^+$ 345.3, $[M + Na]^+$ 367.3; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{22}H_{21}N_2S$: 345.1420, found 345.1416.

(1E,2E)-1-(1-(4-Methyl-2-(phenylthio)phenyl)ethylidene)-2-(1-(p-tolyl)ethylidene)hydrazine ***3b***. Yellow solid, 24.6 mg, 66% yield; (PE/EtOAc 15:1, R_f 0.66); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.81 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.33−7.42 (m, 5H), 7.27 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 6.95 (s, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.6, 158.2, 140.0, 139.4, 137.7, 136.0, 135.6, 135.0, 132.2, 131.8, 130.1, 129.51, 129.46, 128.1, 128.0, 127.0, 21.4, 21.2, 18.5, 15.4; MS (ESI), m/z: $[M + H]^+$ 373.3, $[M + Na]^+$ 395.3; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{24}H_{25}N_2S$: 373.1733, found 373.1728;

(1E,2E)-1-(1-(4-Methoxy-2-(phenylthio)phenyl)ethylidene)-2-(1-(4-methoxyphenyl)ethylidene)hydrazine ***3c***. Yellow solid, 27.1 mg, 67% yield; (PE/EtOAc 15:1, R_f 0.51); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.94 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.46−7.52 (m, 5H), 7.06 (d, J = 9.0 Hz, 2H), 6.93 (dd, J = 8.5, 2.5 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H), 2.38 (bs, 6H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 161.2, 160.0, 159.8, 158.7, 138.7, 135.1, 133.9, 131.3, 131.1, 130.9, 130.2, 128.9, 128.6, 115.6, 114.2, 111.3, 55.7, 55.6, 17.8, 15.6; MS (ESI), m/z: $[M + H]^+$ 405.4, $[M + Na]^+$ 427.3; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{24}H_{25}N_2O_2S$: 405.1631, found 405.1626.

(1E,2E)-1-(1-(4-Chloro-2-(phenylthio)phenyl)ethylidene)-2-(1-(4-chlorophenyl)ethylidene)hydrazine ***3d***. Yellow solid, 23.4 mg, 58% yield; (PE/EtOAc 15:1, R_f 0.55); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 8.00 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.51−7.59 (m, 7H), 7.41 (dd, J = 8.5, 2.0 Hz, 1H), 6.93 (s, 1H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.2, 158.0, 139.7, 137.0, 136.9, 135.2, 134.4, 134.2, 134.0, 131.2, 130.5, 129.5, 128.9, 128.8, 128.5, 126.1, 18.0, 15.6; MS (ESI), m/z: $[M + H]^+$ 413.2; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{22}H_{19}Cl_2N_2S$: 413.0641, found 413.0635.

(1E,2E)-1-(1-(4-Fluoro-2-(phenylthio)phenyl)ethylidene)-2-(1-(4-fluorophenyl)ethylidene)hydrazine ***3e***. Yellow solid, 17.6 mg, 45% yield; (PE/EtOAc 15:1, R_f 0.46); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 8.03−8.06 (m, 2H), 7.76 (dd, J = 8.5, 6.0 Hz, 1H), 7.50−7.57 (m, 5H), 7.35 (t, J = 8.5 Hz, 2H), 7.19 (td, J = 8.5, 2.5 Hz, 1H), 6.67 (dd, J = 10.5, 2.5 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 163.7 (d, J = 248.2 Hz, CF), 162.5 (d, J = 248.9 Hz, CF), 159.3, 158.1, 140.4 (d, J = 7.8 Hz, CH), 134.7 (d, J = 2.1 Hz, CH), 134.5, 134.3, 134.0, 131.7 (d, J = 8.8 Hz, CH), 130.5, 129.5, 129.4, 115.9, 115.7, 115.5, 113.2 (d, J = 21.7 Hz, CH), 18.0, 15.7; MS (ESI), m/z: $[M + H]^+$ 381.3, $[M + Na]^+$ 403.2; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{22}H_{19}F_2N_2S$: 381.1232, found 381.1227.

(1E,2E)-1-(1-(5-Methoxy-2-(phenylthio)phenyl)ethylidene)-2-(1-(3-methoxyphenyl)ethylidene)hydrazine ***3f***. Yellow solid, 21.5 mg, 53% yield; (PE/EtOAc 15:1, R_f 0.41); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.29−7.43 (m, 6H), 7.13−7.22 (m, 4H), 7.02−7.05 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.18 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.7, 159.3, 157.3, 144.9, 139.7, 138.2, 136.6, 130.0, 129.7, 129.0, 126.7, 122.6, 119.5, 116.12, 116.06, 115.0, 112.0, 56.0, 55.6, 19.3, 15.3. One signal is missing due to overlap; MS (ESI), m/z: $[M + H]^+$ 405.5, $[M + Na]^+$ 427.5; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{24}H_{25}N_2O_2S$: 405.1631, found 405.1627.

(E)-1-(Diphenylmethylene)-2-(phenyl(2-(phenylthio)phenyl)-methylene)hydrazine ***3g***. Yellow solid, 21.0 mg, 44% yield; (PE/EtOAc 15:1, R_f 0.56); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.72−7.80 (m, 5H), 7.62 (t, J = 7.5 Hz, 3H), 7.38−7.54 (m, 13H), 7.33−7.35 (m, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.5, 137.9, 137.5, 135.6, 133.2, 130.4, 130.1, 129.4, 129.3, 129.0, 128.8, 128.5. Some signals are missing due to overlap; MS (ESI), m/z: $[M + H]^+$ 469.3, $[M + Na]^+$ 491.3; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{32}H_{25}N_2S$: 469.1733, found 469.1726.

(1E,2E)-1-(1-(2-((4-Chlorophenyl)thio)phenyl)ethylidene)-2-(1-phenylethylidene)hydrazine ***3h***. Yellow solid, 20.5 mg, 56% yield; (PE/EtOAc 15:1, R_f 0.48); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.95−7.97 (m, 2H), 7.67−7.68 (m, 1H), 7.50−7.52 (m, 5H), 7.40−7.43 (m, 4H), 7.19−7.21 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 159.6, 158.4, 140.3, 138.2, 135.1, 134.8, 134.0, 133.0, 131.6, 130.4, 130.1, 129.6, 128.9, 127.4, 127.1, 18.5, 15.5; MS (ESI), m/z: $[M + H]^+$ 379.3, $[M + Na]^+$ 401.3; HRMS (ESI), m/z: $[M + H]^+$ calculated for $C_{22}H_{20}ClN_2S$: 379.1030, found 379.1026.

General Procedures for Synthesis of 3i−3s. To a 13 × 150 mm test tube equipped with magnetic stirrer was added **1a** (23.7 mg, 0.1 mmol, 1.0 equiv) and $Cu(OAc)_2$ (40.0 mg, 0.2 mmol, 2.0 equiv). The test tube was transferred to a glovebox, and then $[RhCp^*Cl_2]_2$ (1.9 mg, 0.003 mmol, 3%) was further added. The test tube was sealed with a rubber septum and removed from the glovebox. A MeCN (2 mL) solution of **2a** (10.9 μL, 0.12 mmol, 1.2 equiv) was injected into the test tube via syringe. The reaction mixture was placed in a preheated oil bath and stirred for 12 h at 40 °C, during which time a constant checking by TLC was performed. Subsequently, the reaction mixture was filtered over Celite. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel with 8:1 PE/EtOAc as the eluent and triethylamine in a small amount as stabilizer to afford the product **3i** in 78.2% yield as a yellow solid. Experimental procedures for synthesizing **3j**−**3s** were the same as that for product **3i**.

Methyl (E)-3-(2-((E)-1-(((E)-1-Phenylethylidene)hydrazono)ethyl)-phenyl)acrylate ***3i***. Yellow solid, 24.7 mg, 77% yield; (PE/EtOAc 8:1, R_f 0.59); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 8.08 (d, J = 16.0 Hz, 1H), 7.94−7.96 (m, 2H), 7.86 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.48−7.56 (m, 5H), 6.54 (d, J = 16.0 Hz, 1H), 3.72 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 167.1, 160.1, 158.9, 144.6, 140.4, 138.2, 132.8, 130.5, 130.4, 129.6, 129.1, 128.9, 128.1, 127.1, 118.7, 51.9, 19.0, 15.4; MS (E.I.), m/z: $[M]^{\bullet+}$ 320.2, $[M - CH_3CO_2]^{\bullet+}$ 261.2; HRMS (EI), m/z: $[M]^+$ calculated for $C_{20}H_{20}N_2O_2$: 320.1525, found 320.1528.

Methyl (E)-3-(5-Methyl-2-((E)-1-(((E)-1-(p-tolyl)ethylidene)-hydrazono)ethyl)phenyl)acrylate ***3j***. Yellow solid, 30.1 mg, 87% yield; (PE/EtOAc 8:1, R_f 0.61); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.07 (d, J = 15.9 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.67 (s, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 15.9 Hz, 1H), 3.71 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 167.2, 160.1, 159.0, 145.0, 140.1, 139.2, 137.7, 135.6, 132.7, 131.1, 129.5, 129.1, 128.5, 127.1, 118.3, 51.9, 21.4, 21.2, 18.7, 15.2; MS (E.I.), m/z: $[M]^{\bullet+}$ 348.1, $[M - CH_3CO_2]^{\bullet+}$ 289.2; HRMS (EI), m/z: $[M]^+$ calculated for $C_{22}H_{24}N_2O_2$: 348.1838, found 348.1833.

Methyl (E)-3-(5-Chloro-2-((E)-1-(((E)-1-(4-chlorophenyl)ethylidene)hydrazono)ethyl)phenyl)acrylate ***3k***. Yellow oil, 29.5 mg, 76% yield; (PE/EtOAc 8:1, R_f 0.55); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.94−8.01 (m, 4H), 7.68 (d, J = 8.4 Hz, 1H), 7.52−7.60 (m, 3H), 6.64 (d, J = 16.2 Hz, 1H), 3.72 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (76 MHz, DMSO-d_6), δ (ppm): 166.8, 159.6, 158.2, 143.1, 138.7, 136.8, 135.1, 134.9, 134.3, 130.9, 130.0, 128.9, 127.7, 120.0, 51.9, 18.7, 15.2. One signal is missing due to overlap; MS (E.I.), m/z: $[M]^{\bullet+}$ 388.0, $[M - CH_3CO_2]^{\bullet+}$ 329.0; HRMS (EI), m/z: $[M]^+$ calculated for $C_{20}H_{18}Cl_2N_2O_2$: 388.0745, found 388.0742.

Methyl (E)-3-(5-Fluoro-2-((E)-1-(((E)-1-(4-fluorophenyl)ethylidene)hydrazono)ethyl)phenyl)acrylate ***3l***. Yellow oil, 22.7 mg,

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64% yield; (PE/EtOAc 8:1, R_f 0.49); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.98−8.04 (m, 3H), 7.69−7.77 (m, 2H), 7.39 (td, J = 8.5, 2.6 Hz, 1H), 7.30 (t, J = 8.8 Hz, 2H), 6.64 (d, J = 15.9 Hz, 1H), 3.72 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 167.0, 163.7 (d, J = 248.0 Hz), 162.5 (d, J = 247.3 Hz), 159.8, 158.4, 143.3, 136.9, 135.4 (d, J = 8.2 Hz), 134.7, 131.5 (d, J = 8.4 Hz), 129.5 (d, J = 8.4 Hz), 120.1, 117.3 (d, J = 21.6 Hz), 115.8 (d, J = 21.7 Hz), 114.6 (d, J = 22.7 Hz), 52.0, 18.9, 15.4; MS (E.I.), m/z: $[M]^{\bullet+}$ 356.1, $[M - CH_3CO_2]^{\bullet+}$ 297.1; HRMS (EI), m/z: $[M]^+$ calculated for $C_{20}H_{18}F_2N_2O_2$: 356.1336, found 356.1339.

Methyl (E)-3-(4-Chloro-2-((E)-1-(((E)-1-(3-chlorophenyl)ethylidene)hydrazono)ethyl)phenyl)acrylate ***3m***. Yellow oil, 22.9 mg, 59% yield; (PE/EtOAc 8:1, R_f 0.45); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.87−8.01 (m, 4H), 7.73 (s, 1H), 7.48−7.56 (m, 3H), 6.56 (d, J = 15.9 Hz, 1H), 3.71 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 167.0, 159.2, 157.8, 143.1, 141.8, 140.1, 135.0, 133.9, 131.7, 130.8, 130.3, 130.0, 129.6, 128.8, 126.7, 125.9, 119.5, 52.0, 18.9, 15.4; MS (E.I.), m/z: $[M]^{\bullet+}$ 388.0, $[M - CH_3CO_2]^{\bullet+}$ 329.0; HRMS (EI), m/z: $[M]^+$ calculated for $C_{20}H_{18}Cl_2N_2O_2$: 388.0745, found 388.0751.

Methyl (E)-3-(3-Fluoro-2-((E)-1-(((E)-1-(2-fluorophenyl)ethylidene)hydrazono)ethyl)phenyl)acrylate ***3n***. Yellow oil, 21.8 mg, 62% yield; (PE/EtOAc 8:1, R_f 0.41); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.75−7.81 (m, 3H), 7.50−7.56 (m, 2H), 7.41 (t, J = 9.0 Hz, 1H), 7.30−7.34 (m, 2H), 6.68 (d, J = 15.5 Hz, 1H), 3.73 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 166.7, 160.5 (d, J = 249.5 Hz), 160.3 (d, J = 244.8 Hz), 156.1, 155.2, 141.4, 134.7, 132.0 (d, J = 7.9 Hz), 131.0 (d, J = 8.7 Hz), 130.3, 128.3 (d, J = 15.8 Hz), 127.0 (d, J = 11.8 Hz), 125.0, 123.6, 121.0, 117.6 (d, J = 21.8 Hz), 116.8 (d, J = 22.2 Hz), 52.1, 20.1, 18.7; MS (E.I.), m/z: $[M]^{\bullet+}$ 356.1, $[M - CH_3CO_2]^{\bullet+}$ 297.1; HRMS (EI), m/z: $[M]^+$ calculated for $C_{20}H_{18}F_2N_2O_2$: 356.1336, found 356.1334.

Methyl (E)-3-((E)-8-(((E)-3,4-Dihydronaphthalen-1(2H)-ylidene)hydrazono)-5,6,7,8-tetrahydronaphthalen-1-yl)acrylate ***3o***. Yellow solid, 27.1 mg, 73% yield; (PE/EtOAc 8:1, R_f 0.57); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.36 (d, J = 15.6 Hz, 1H), 8.19 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 6.9 Hz, 1H), 7.23−7.41 (m, 5H), 6.30 (d, J = 15.9 Hz, 1H), 3.72 (s, 3H), 2.75−2.83 (m, 8H), 1.76−1.87 (m, 4H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 167.4, 159.3, 158.2, 148.1, 143.1, 141.3, 134.6, 133.0, 132.7, 130.3, 130.1, 129.5, 129.2, 127.3, 126.7, 125.6, 116.9, 51.8, 30.6, 29.6, 28.6, 27.9, 22.3, 22.0; MS (E.I.), m/z: $[M]^{\bullet+}$ 372.2, $[M - CH_3CO_2]^{\bullet+}$ 313.1; HRMS (EI), m/z: $[M]^+$ calculated for $C_{24}H_{24}N_2O_2$: 372.1838, found 372.1839.

Methyl (E)-3-(2-((E)-((Diphenylmethylene)hydrazono)(phenyl)methyl)phenyl)acrylate ***3p***. Yellow solid, 26.6 mg, 60% yield; (PE/EtOAc 8:1, R_f 0.52); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.02−8.05 (m, 1H), 7.49−7.55 (m, 5H), 7.22−7.43 (m, 13H), 7.14−7.17 (m, 1H), 6.64 (d, J = 15.9 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 166.8, 161.2, 160.3, 142.2, 137.7, 137.6, 137.2, 135.3, 131.9, 131.0, 130.72, 130.68, 129.5, 129.1, 128.8, 128.54, 128.48, 127.9, 127.1, 119.7, 52.0; MS (E.I.), m/z: $[M]^{\bullet+}$ 444.1, $[M - CH_3CO_2]^{\bullet+}$ 385.1; HRMS (EI), m/z: $[M]^+$ calculated for $C_{30}H_{24}N_2O_2$: 444.1838, found 444.1834.

Ethyl (E)-3-(2-((E)-1-(((E)-1-Phenylethylidene)hydrazono)ethyl)phenyl)acrylate ***3q***. Yellow solid, 24.9 mg, 75% yield; (PE/EtOAc 8:1, R_f 0.58); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 8.07 (d, J = 16.0 Hz, 1H), 7.94−7.95 (m, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.0, 1.0 Hz, 1H), 7.53 (td, J = 7.5, 1.5 Hz, 1H), 7.47−7.50 (m, 4H), 6.52 (d, J = 16.0 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 166.7, 160.0, 158.8, 144.4, 140.4, 138.2, 132.9, 130.4, 129.6, 129.1, 128.9, 128.0, 127.1, 119.0, 60.5, 18.9, 15.4, 14.7. One signal is missing due to overlap; MS (E.I.), m/z: $[M]^{\bullet+}$ 334.2, $[M - CH_3CH_2CO_2]^{\bullet+}$ 261.2; HRMS (EI), m/z: $[M]^+$ calculated for $C_{21}H_{22}N_2O_2$: 334.1681, found 334.1687.

2-Methoxyethyl (E)-3-(2-((E)-1-(((E)-1-Phenylethylidene)hydrazono)ethyl)phenyl)acrylate ***3r***. Yellow solid, 26.4 mg, 73% yield; (PE/EtOAc 8:1, R_f 0.54); ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 8.12 (d, J = 16.0 Hz, 1H), 7.97−7.99 (m, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.51−7.59 (m, 5H), 6.58 (d, J = 16.0 Hz, 1H), 4.30 (t, J = 4.5 Hz, 2H), 3.61 (t, J = 4.5 Hz, 2H), 3.30 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6), δ (ppm): 166.7, 160.0, 158.9, 144.8, 140.4, 138.2, 132.8, 130.44, 130.40, 129.6, 129.1, 128.9, 128.1, 127.1, 118.7, 70.3, 63.6, 58.5, 18.9, 15.4; MS (E.I.), m/z: $[M]^{\bullet+}$ 364.2, $[M - CH_3OC_2H_4CO_2]^{\bullet+}$ 261.2; HRMS (EI), m/z: $[M]^+$ calculated for $C_{22}H_{24}N_2O_3$: 364.1787, found 364.1785.

Dimethyl 3,3′-(((1E,1′E)-Hydrazine-1,2-diylidenebis(ethan-1-yl-1-ylidene))bis(5-methyl-2,1-phenylene))(2E,2′E)-diacrylate ***3s***. Yellow solid, 29.7 mg, 69% yield; (PE/EtOAc 8:1, R_f 0.49); ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.08 (d, J = 15.9 Hz, 2H), 7.68 (s, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.51 (d, J = 15.9 Hz, 2H), 3.71 (s, 6H), 2.39 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (76 MHz, DMSO-d_6), δ (ppm): 167.0, 160.7, 144.8, 139.3, 137.5, 132.6, 131.0, 129.1, 128.4, 118.3, 51.8, 21.1, 19.0; MS (E.I.), m/z: $[M]^{\bullet+}$ 432.2, $[M - CH_3CO_2]^{\bullet+}$ 373.1; HRMS (EI), m/z: $[M]^+$ calculated for $C_{26}H_{28}N_2O_4$: 432.2049, found 432.2041.

Mechanistic Experiments. The operation of mechanistic experiments including kinetic isotopic effect, reversibility studies, competition experiment, and catalysis of rhodacycle intermediate **c1**, described in the Supporting Information, is similar to the operation of synthesizing **3a** with some different reagents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01154.

Experimental procedures, crystallographic data for compound **c1**, and ^{1}H and ^{13}C NMR spectra for substrates and products (PDF)

Crystallographic data for compound **c1** (CIF)

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Notes

The authors declare no competing financial interest.

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