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Transition Metal-Free Oxidative Cross-Coupling Reaction of Activated Olefins with *N*-Alkyl Amides

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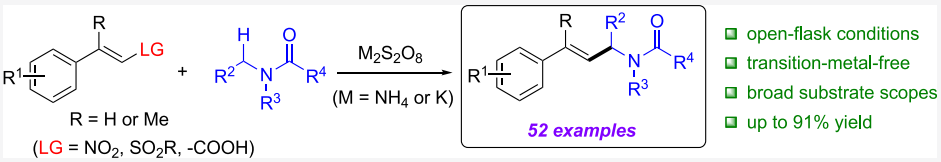

ABSTRACT: The $K_2S_2O_8$-mediated transition metal-free oxidative cross-coupling reaction of activated olefins with *N*-alkyl amides was developed, and the reaction gave *N*-allylic amides in moderate to good yield. This reaction protocol was suitable for different kinds of activated olefins.

INTRODUCTION

The oxidative cross-coupling reactions have been developed to be a powerful tool for the construction of various chemical bonds owing to high atom economy and sustainable chemical process.[1] Among them, oxidative R^1-H/R^2-H cross-dehydrogenative coupling (CDC) reaction with air or O_2 as the oxidant is an ideal approach because C−H nucleophiles exist extensively in nature and water is the only byproduct.[2] However, oxidative R^1-H/R^2-X (or R^2-M) cross-coupling reaction is still an alternative strategy for some bond formation, even though it generates considerable useless byproducts.[3]

N-alkyl amides are an important class of oxidative coupling synthon,[4] and this synthon has been successfully used in construction of chemical bonds, such as C−C,[5] C−N,[6] and C−O.[7] In the presence of oxidants, *N*-alkyl amides could be used as radical precursors to generate the α-amide radical or radical cations via losing one or two electrons,[5−8] and then, the active amide radical couples with other reaction partners to form diverse α-C functionalization amides. In spite of these great achievements, the ideal oxidative CDC reaction between sp^2 C−H of terminal alkenes and $\alpha-C(sp^3)-H$ of *N*-alkyl amides to form allylic amides was still a challenge because of the potential polymerization of terminal alkenes (Scheme 1a).

A compromise strategy was to utilize activated olefins as radical acceptors, such as the reported cinnamic acids or alkenyl sulfones, which couples with *N*-alkyl amides to form *N*-allylic amides in the presence of metals[9] or photocatalysts[10] (Scheme 1b,c). Moreover, arylacetylene as a coupling partner to react with amides was also developed, although this reaction could give *E*/*Z*-*N*-allylic amides (Scheme 1d).[11] *N*-allylic amides are prevalent in natural products[12] and as a synthetic precursor for construction of other useful molecules.[13] Hence, more convenient and efficient methods (such as transition metal-free and open-flask conditions) to access *N*-allylic amides are still desired.

In continuation of our research on metal-catalyzed cross-coupling[14] and oxidative cyclization reactions,[15] herein, we disclosed a transition metal-free oxidative coupling reaction of activated olefins (including nitro-olefins, cinnamic acids, and alkenyl sulfones) with *N*-alkyl amides.

RESULTS AND DISCUSSION

(*E*)-(2-Nitrovinyl)benzene (**1a**) was chosen as an activated olefin to react with *N*,*N*-dimethylacetamide (DMA, **2a**) for our initial study, and the results are summarized in Table 1. First, the reaction was performed by using 3 equiv of *tert*-butyl hydroperoxide (TBHP) as an oxidant,[16] and the expected product **3aa** was obtained with 24% isolated yield (entry 1). In general, the *tert*-butyl hydroperoxide (TBAI)/TBHP[17] reaction system was popular for oxidative C−H bond functionalization. However, 20 mol % TBAI along with TBHP had no improvement for the yield of reaction (entry 2). Then, a preliminary screening of the oxidants was conducted. Some common oxidants such as di-*tert*-butyl peroxide (DTBP), $K_2S_2O_8$, $PhI(OAc)_2$, $(NH_4)_2S_2O_8$, and radical initiators including benzoic peroxyanhydride (BPO), azodiisobutyronitrile (AIBN), and 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) were tested (entries 3−9). Notably, using $K_2S_2O_8$ as an oxidant at 100 °C gave the best yield of **3aa** (entry 4, 87%). Altering the temperature of the reaction led no further improvements (entries 10, 11). Different solvents such as CH_3CN, DCE, EtOH, toluene, DMSO, and EtOAc were

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Scheme 1. Synthesis of *N*-Allylic Amides

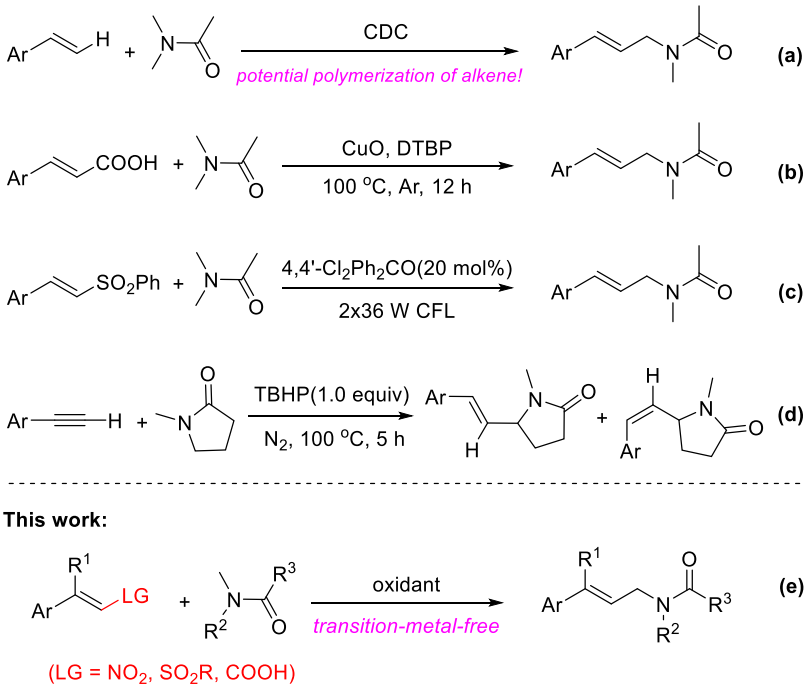
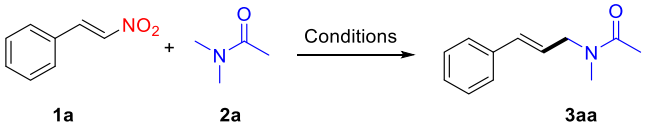


Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

entry	oxidant	solvent	additive	temp (°C)	yield[b] (%)
1	TBHP	DMA		100	24
2[c]	TBHP	DMA	TBAI[c]	100	22
3	PhI(OAc)2	DMA		100	44
4	**$K_2S_2O_8$**	**DMA**		**100**	87
5	DTBP	DMA		100	trace
6	BPO	DMA		100	61
7	AIBN	DMA		100	21
8	DDQ	DMA		100	n.r
9	$(NH4)2S_2O_8$	DMA		100	82
10	$K_2S_2O_8$	DMA		110	73
11[d]	$K_2S_2O_8$	DMA		80	59
12	$K_2S_2O_8$	CH_3CN		100	51
13	$K_2S_2O_8$	EtOH		100	n.r
14	$K_2S_2O_8$	DCE		100	19
15	$K_2S_2O_8$	toluene		100	26
16	$K_2S_2O_8$	EtOAc		100	25
17	$K_2S_2O_8$	DMSO		100	21
18	$K_2S_2O_8$	DMA	HOAc	100	17
19	$K_2S_2O_8$	DMA	K_2CO_3	100	81
20[e]	$K_2S_2O_8$	DMA		100	59

[a]Reaction Conditions: **1a** (0.2 mmol), **2a** (2 mL as solvent), oxidant (0.6 mmol), additive (0.4 mmol), under air, and 0.5 h. [b]Isolated yield based on **1a**. [c]20 mmol % of additives. [d]Stirred for 2 h. [e]0.4 mmol $K_2S_2O_8$ was used, n.r = no reaction. TBHP: *tert*-Butyl hydroperoxide; TBAI: tetrabutylammonium iodide; DTBP: di-*tert*-butyl peroxide; BPO: benzoic peroxyanhydride; DDQ: 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile; and AIBN: azodiisobutyronitrile.

introduced to reduce the amount of DMA (the ratio to DMA was 1:1), but no better result was achieved (entries 12−17). Moreover, the addition of acidic or basic additives did not improve the yield (entries 18, 19), and lowering the amount of oxidants also led to a decreased yield of **3aa** (entry 20).

With the optimized condition in hand (Table 1, entry 4), the scope of this reaction was subsequently examined (Table 2). In summary, all substrates proceeded fast and gave the target products in moderate to good yields. First, an array of (*E*)-(2-nitrovinyl)benzenes **1** with different electron-withdrawing groups (−F, −Cl, −Br, and −CN) substituted on different positions (ortho-, meta-, and para-) of the phenyl ring reacted with DMA provided the corresponding products in good yields (**3ba**−**3ja**, 81%−90%). Moreover, electron-donating group (−Me and −OMe)-substituted nitroalkenes also gave moderate yields (**3fa**, 71%; **3ja**, 70%). Next, the scope of amides including NMP, pyrrolidone, and DMF was also tested for this reaction. As for NMP, the desired *N*-allylic amide was formed in moderate yield and the amount of oxidants was increased to 4 equiv (**3ab**−**3mb**, 74−84%). Pyrrolidone was also suitable for this reaction and gave the corresponding products with good yield (up to 91% for **3id**). However, lower yields were observed, while DMF was used as an amide partner, probably because of side reactions of the CHO group (**3ac**, 51%; **3bc**, 53%).

On the other hand, α-alkyl nitroalkenes were also tested for substrate scope (Table 3). It was found that the reactions were completed within only 20 min by using $(NH_4)_2S_2O_8$ as oxidants at 75 °C. However, the reactions yielded two isomer products for all cases. For example, when (*E*)-(1-nitroprop-1-en-2-yl)benzene (**4a**) was used to react with DMA, (*E*)-*N*-methyl-*N*-(3-phenylbut-2-en-1-yl)acetamide **5a** and *N*-methyl-*N*-(3-phenylbut-3-en-1-yl)acetamide **5a′** were obtained in a mixed yield of 88% with the ratio at 0.86−0.14 because there is an equilibrium between **4a** and **4a′**, especially in polar DMF or DMA solvent.[18] Therefore, α-alkyl nitroalkenes (**4**/**4′**) with different substitute groups were also tested, and the ratios of the two isomeric products changed with different substituents

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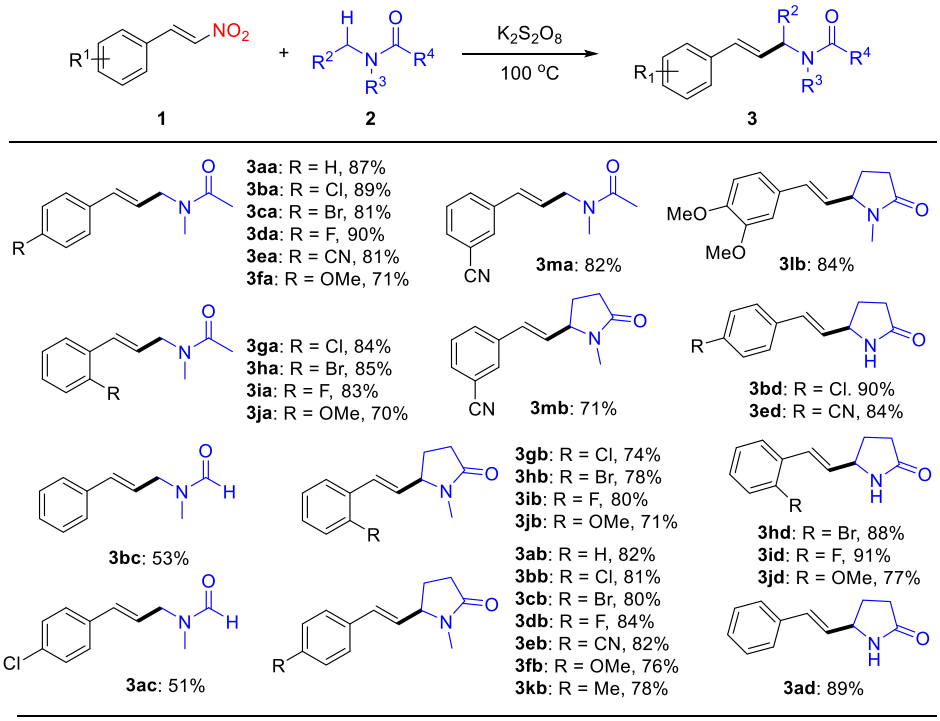
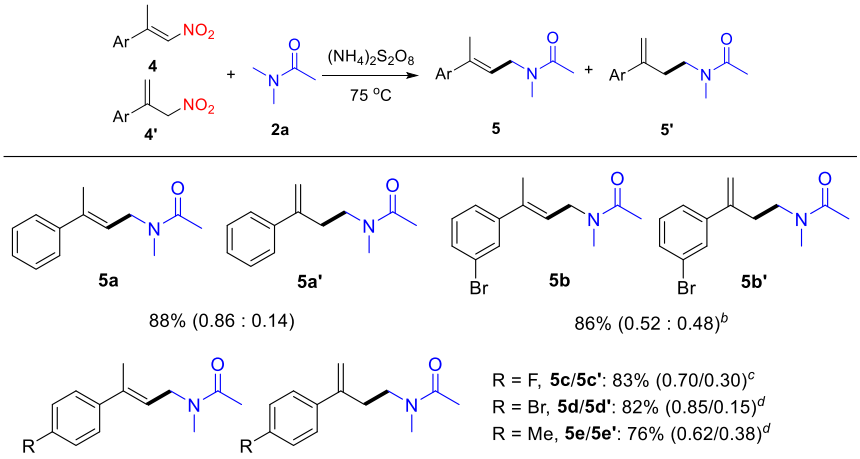
Table 2. Substrate Scope of Nitroalkenes and Amides[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (3 mL as solvent), $K_2S_2O_8$ (0.6 mmol), 100 °C for 0.5 h, when NMP used as a reactant, the amount of $K_2S_2O_8$ is 0.8 mmol.

Table 3. Substrate Scope of α-Nitroalkenes and DMA[a]



[a]Reaction conditions: **4** (0.2 mmol), **2** (2 mL as solvent), $(NH_4)_2S_2O_8$ (0.6 mmol), 75 °C for 0.5 h. The ratio of isomers of reactants. [b]**4b**:**4b′** = 87%:13%. [c]**4c**:**4c′** = 93%:7%. [d]**4d**:**4d′** (**4e**:**4e′**) = 99%:1%; all the ratios were detected by ^{1}H NMR.

on the α-alkyl nitroalkenes and ratios of the isomers of reactants.

Because −SO_2Ar and −COOH are also good leaving groups,[19,20] we further expanded this transition metal-free oxidative condition to cinnamic acids and alkenyl sulfones. Pleasantly, the expected *N*-allylic amides could be obtained from both cinnamic acids and alkenyl sulfones. In this case, an appropriate amount of base such as sodium carbonate or *t*-BuOK must be added to improve the reactions, and the reaction results are summarized in Table 4.

To gain insights into mechanism of this oxidative cross-coupling reaction, some control experiments were conducted (Scheme 2). First, when styrene was chosen as the reaction partner under optimal reaction conditions, fast polymerization of styrene happened and only trace product was detected (Scheme 2a). In the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl, a radical scavenger, the formation of products was totally inhibited, which revealed that the reaction might undergo a radical process (Scheme 2b). If β-methylstyrene served as the reaction partner, the corresponding product **5a** or **5a′** was hard to be detected (Scheme 2c). At the same time, the reaction of isomeric α-alkyl nitro-olefin (**4a′**) could give product **5a′** as the major product under standard reaction conditions (Scheme 2d), and prolongation of the reaction time did not change the ratio of the products, which revealed that the formation of the regioisomers (**5a**) could be started from

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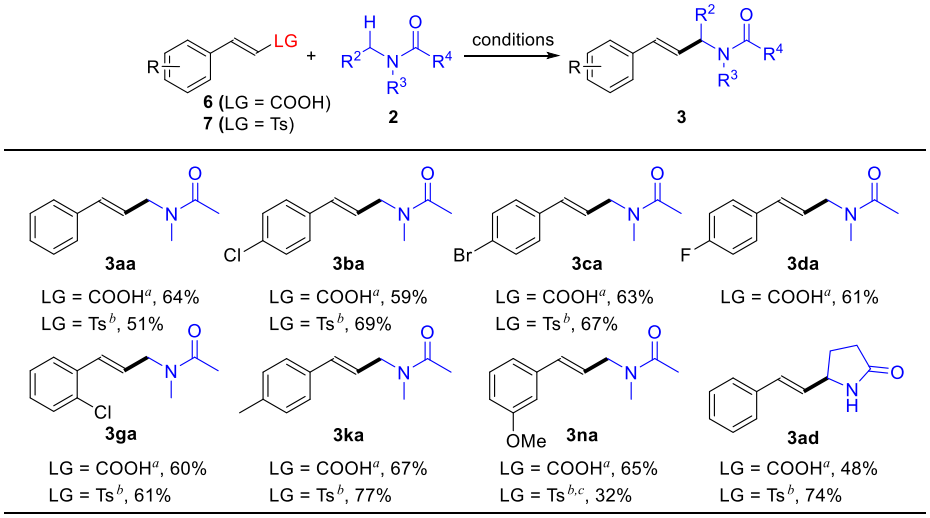
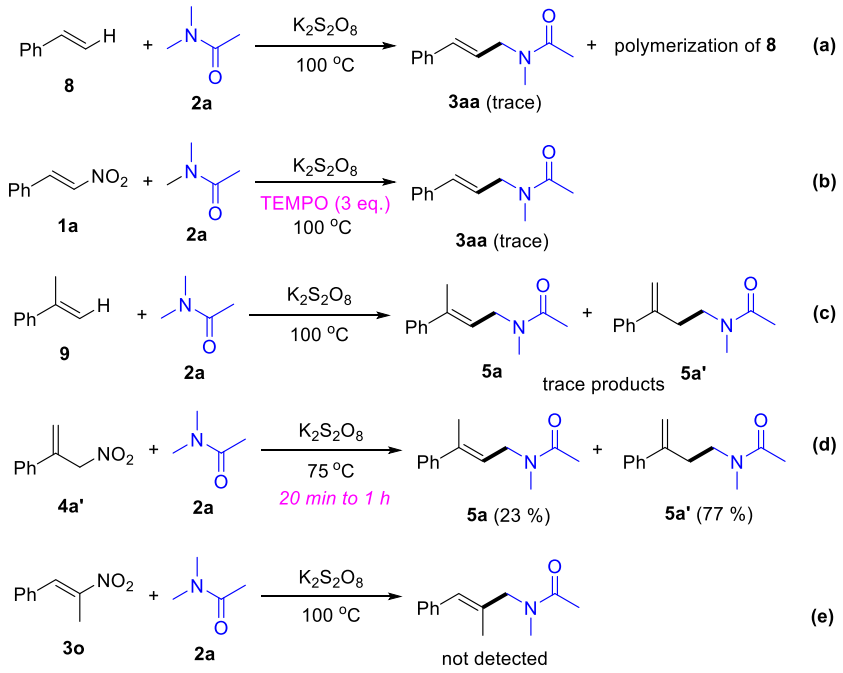
Table 4. Scope of Other Activated Olefins

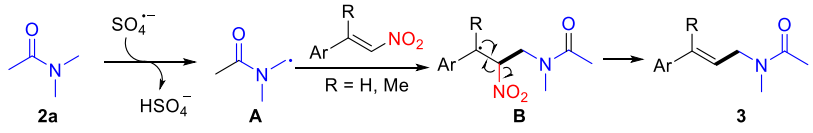


[a]Reaction Conditions: **5** (0.2 mmol), **2** (2 mmol), K_2CO_3 (0.6 mmol), $K_2S_2O_8$ (0.6 mmol), toluene (2.5 mL), and H_2O (0.5 mL), stirred at 90 °C for 0.5 h under air. [b]Reaction Conditions: **5** (0.2 mmol), **2** (2 mL as solvent), *t*-BuOK (0.8 mmol), and $(NH_4)_2S_2O_8$ (0.6 mmol), stirred at 110 °C for 0.5 h under air.

Scheme 2. Control Experiments



Scheme 3. Plausible Mechanism



the original isomers of starting materials. When using (*E*)-(2-nitroprop-1-en-1-yl)benzene (**3o**) as a reactant, no product was detected (Scheme 2e).

Based on abovementioned experiments and previous results,[13] a plausible mechanism was proposed (Scheme 3). Potassium peroxodisulfate generated peroxodisulfate radicals first and subsequently abstracted a hydrogen atom from the α−C−H bond of DMA to form amide radical species **A**. Then, the amide radical addition to olefins resulted in formation of the alkyl radical species **B**. If there was an alkyl group, it was easy to be formed, which was in accordance with lower reaction temperature and shorter reaction time. Finally, **B** was converted to the product **3** with the departure of the leaving group.

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In conclusion, we developed a transition metal-free oxidative coupling reaction between activated olefins and *N*-alkyl amides. Besides simple and mild reaction conditions, the method could give *N*-allylic amides in moderate to good yields. This protocol was suitable for different activated olefins, which supplied some alternative strategies for the accomplishment of *N*-allylic amides.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all chemicals used in the experiments were obtained from commercial sources and used directly without further treatment. Thin-layer chromatography (TLC) was performed with the detection of compounds with UV light. Flash column chromatography purification of the products was accomplished on silica gel (200−300 mesh). Petroleum ether (PE) (60−90 °C) and ethyl acetate (EA) were used as eluents for silica gel chromatography. Melting points for all solid products were measured on an X-4A melting point apparatus without correction. ^{1}H and ^{13}C NMR spectra were recorded at 22 °C on a Bruker AV 400 and 600 MHz spectrometers with tetramethylsilane as an internal standard, respectively. ^{1}H and ^{13}C chemical shifts in NMR spectra were referenced, relative to signals of $CDCl_3$ (δ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). High-resolution mass spectra (HRMS) were acquired on Waters Acquity UPLC Class I/Xevo G2Q-TOF. The activated olefins were synthesized according to the literatures: α-alkyl nitroalkenes,[18] nitroalkenes,[21a] and vinyl sulfones.[21b]

General Procedure for Oxidative Coupling Reaction between Amides and Nitroalkenes. A mixture of (*E*)-(2-nitrovinyl)benzene (**1a**) (0.2 mmol) and $K_2S_2O_8$ (0.6 mmol) in 2 mL of DMA was stirred under air in a 10 mL dried tube at 100 °C (oil bath). After the reaction was completed (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 15 mL). The organic layer was washed with saturated brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude products, which was purified by flash column chromatography using 100−200 mesh silica gel and a mixture of petroleum ether and EA (v/v = 1:1) as eluents to afford the desired products.

General Procedure for Oxidative Coupling Reaction between Amides and α-Alkyl Nitroalkenes. To a 10 mL dried tube with a magnetic bar, (*E*)-(1-nitroprop-1-en-2-yl)benzene (**4a**) (0.2 mmol) was loaded and 2 mL of DMA was added, followed by the addition of $(NH_4)_2S_2O_8$ (0.6 mmol). The reaction mixture was allowed to stir at 75 °C (oil bath) for 0.5 h. After the reaction was completed (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 15 mL). The organic layer was washed with saturated brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude products, which was purified by flash column chromatography using 100−200 mesh silica gel and a mixture of petroleum ether and EA (v/v = 3:1) as eluents to afford the desired products **3aa**.

General Procedure for Oxidative Coupling Reaction between Amides and Vinyl Sulfones. To a 10 mL dried tube with a magnetic bar, (*E*)-1-methyl-4-(styrylsulfonyl)benzene **6a** (0.2 mmol) and *t*-BuOK (0.6 mmol) were loaded and 2 mL of DMA was added, followed by the addition of $(NH_4)_2S_2O_8$ (0.6 mmol). The mixture was stirred at 110 °C (oil bath) for 0.5 h. After the reaction was completed (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 15 mL). The organic layer was washed with saturated brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude products, which was purified by flash column chromatography using 100−200 mesh silica gel and a mixture of petroleum ether and EA (v/v = 3:1) as eluents to afford the desired products **3aa.**

General Procedure for Oxidative Coupling Reaction between Amides and Cinnamic Acids. To a 10 mL dried tube with a magnetic bar, cinnamic acid **7a** (0.2 mmol) and Na_2CO_3 (0.6 mmol) were loaded and 1.5 mL of toluene, DMA (2.0 mmol), and 0.7 mL of water were added, followed by the addition of $K_2S_2O_8$ (0.6 mmol). The reaction mixture was allowed to stir at 90 °C (oil bath) for 0.5 h. After the reaction was completed (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 15 mL). The organic layer was washed with saturated brine (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude products, which was purified by flash column chromatography using 100−200 mesh silica gel and a mixture of petroleum ether and EA (v/v = 3:1) as eluents to afford the desired products **3aa**.

Gram Scale for the Synthesis of *N*-Allylic Amides 3aa. A mixture of (*E*)-(2-nitrovinyl)benzene **1a** (1.04 g, 7 mmol) and $K_2S_2O_8$ (5.68 g, 21 mmol) in 20 mL of DMA was stirred under air in a 50 mL flask at 100 °C (oil bath) for 40 min. Refer to the general procedure above to get **3aa** (0.97 g, 72.8%) as a pale-yellow oil.

Characterization Data. *N*-cinnamyl-*N*-methylacetamide (**3aa**)[11] was obtained as pale-yellow oil (32.9 mg, 87%); purification by silica gel chromatography (R_f = 0.19 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.41−7.19 (m, 5H), 6.48 (dd, *J* = 15.8, 9.8 Hz, 1H), 6.20−6.07 (m, 1H), 4.18−4.12 (m, 1H), 4.08−4.05 (m, 1H), 2.99 (s, 1.4H), 2.98 (s, 1.6H), 2.14 (s, 1.4H), 2.13 (s, 1.6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.8, 170.4, 136.5, 136.0, 132.7, 131.7, 128.6, 128.5, 127.9, 127.6, 126.3, 126.0, 124.5, 123.6, 52.5, 49.2, 35.4, 33.4, 21.8, 21.2 ppm.

(*E*)-*N*-(3-(4-chlorophenyl)allyl)-*N*-methylacetamide (**3ba**)[9] was obtained as pale-yellow oil (39.8 mg, 89%); purification by silica gel chromatography (R_f = 0.14 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.28 (s, 2H), 7.26 (d, *J* = 1.6 Hz, 2H), 6.41 (dd, *J* = 16.0, 8.5 Hz, 1H), 6.16−6.04 (m, 1H), 4.14−4.11 (m, 1H), 4.06−4.03 (m, 1H), 2.98 (s, 1.7H), 2.96 (s, 1.3H), 2.12 (s, 1.3H), 2.12 (s, 1.7H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.5, 135.0, 134.5, 133.6, 133.2, 131.3, 130.4, 128.8, 128.6, 127.6, 127.5, 125.3, 124.4, 52.5, 49.2, 35.5, 33.5, 21.8, 21.3 ppm.

(*E*)-*N*-(3-(4-bromophenyl)allyl)-*N*-methylacetamide (**3ca**) was obtained as pale-yellow oil (43.4 mg, 81%); purification by silica gel chromatography (R_f = 0.19 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.46−7.40 (m, 2H), 7.24−7.20 (m, 2H), 6.40 (dd, *J* = 16.0, 8.3 Hz, 1H), 6.18−6.07 (m, 1H), 4.15−4.09 (m, 1H), 4.07−4.01 (m, 1H), 2.97 (d, *J* = 8.0 Hz, 3H), 2.12 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.4, 135.5, 135.0, 131.7, 131.6, 131.3, 130.4, 127.8, 127.8, 125.4, 124.5, 121.7, 121.3, 52.4, 49.2, 35.5, 33.4, 21.7, 21.2 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{15}BrNO$, 268.0332; found, 268.0330.

(*E*)-*N*-(3-(4-fluorophenyl)allyl)-*N*-methylacetamide (**3da**)[9] was obtained as colorless oil (37.3 mg, 90%); purification by silica gel chromatography (R_f = 0.19 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.36−7.28 (m, 2H), 7.03−6.96 (m, 2H), 6.43 (dd, *J* = 15.8, 9.6 Hz, 1H), 6.08−6.00 (m, 1H), 4.12 (d, *J* = 6.4 Hz, 1H), 4.04 (d, *J* = 4.2 Hz, 1H), 2.98 (s, 1.6H), 2.96 (s, 1.4H), 2.13 (s, 1.4H), 2.11 (s, 1.6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.4, 161.0, 132.7, 132.3, 131.5, 130.5, 127.9 (d, *J* = 6.3 Hz), 127.8 (d, *J* = 6.3 Hz), 124.3 (d, *J* = 2.2 Hz), 123.4 (d, *J* = 2.2 Hz), 115.6 (d, *J* = 15.1 Hz), 115.4 (d, *J* = 15.0 Hz), 52.5, 49.2, 35.5, 33.4, 21.8, 21.3 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{15}FNO$, 208.1132; found, 208.1128.

(*E*)-*N*-(3-(4-cyanophenyl)allyl)-*N*-methylacetamide (**3ea**)[9] was obtained as yellow oil (34.7 mg, 81%); purification by silica gel chromatography (R_f = 0.21 eluent: PE/EA = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.59−7.54 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 6.45 (dd, *J* = 16.0, 5.5 Hz, 1H), 6.31−6.24 (m, 1H), 4.16−4.12 (m, 1H), 4.10−4.08 (m, 1H), 2.99 (s, 1.8H), 2.95 (s, 1.2H), 2.11 (s, 1.8H), 2.10 (s, 1.2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.5, 140.9, 140.4, 132.4, 132.3, 130.5, 129.6, 128.7, 127.9, 126.8, 126.7, 118.8, 118.7, 111.0, 110.6, 52.3, 49.1, 35.7, 33.6, 21.7, 21.2 ppm.

(*E*)-*N*-(3-(4-methoxyphenyl)allyl)-*N*-methylacetamide (**3fa**)[9] was obtained as pale-yellow oil (31.1 mg, 71%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.32−7.27 (m, 2H), 6.85 (t, *J* = 8.2 Hz, 2H), 6.41 (dd, *J* = 16.0, 12.0 Hz, 1H), 6.05−5.91 (m, 1H), 4.13−4.10 (m, 1H), 4.04−4.01 (m, 1H), 3.80 (s, 1.5H), 3.79 (s, 1.5H), 2.97 (s, 1.5H),

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2.96 (s, 1.5H), 2.13 (s, 1.5H), 2.11 (s, 1.5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.4, 159.4, 159.2, 132.3, 131.2, 129.3, 128.8, 127.6, 127.5, 122.3, 121.3, 114.1, 113.9, 55.3, 55.2, 52.6, 49.3, 35.3, 33.4, 21.8, 21.3 ppm.

(*E*)-*N*-(3-(2-chlorophenyl)allyl)-*N*-methylacetamide (**3ga**) was obtained as pale-yellow oil (37.6 mg, 84%); purification by silica gel chromatography (R_f = 0.25 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.53−7.46 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.27−7.12 (m, 2H), 6.86 (d, *J* = 15.8 Hz, 1H), 6.16−6.04 (m, 1H), 4.17 (d, *J* = 6.4 Hz, 1H), 4.08 (d, *J* = 5.6 Hz, 1H), 3.01 (s, 1.7H), 2.99 (s, 1.3H), 2.15 (s, 1.3H), 2.13 (s, 1.7H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.5, 134.7, 132.8, 129.7, 129.6, 128.9, 128.8, 128.6, 128.5, 127.5, 126.9, 126.9, 126.8, 126.7, 52.7, 49.3, 35.5, 33.4, 21.8, 21.3 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{15}ClNO$, 224.0837; found, 224.0839.

(*E*)-*N*-(3-(2-bromophenyl)allyl)-*N*-methylacetamide (**3ha**) was obtained as pale-yellow oil (45.6 mg, 85%); purification by silica gel chromatography (R_f = 21 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.57−7.42 (m, 2H), 7.25 (d, *J* = 10.0 Hz, 1H), 7.15−7.03 (m, 1H), 6.80 (dd, *J* = 15.8, 4.4 Hz, 1H), 6.11−5.97 (m, 1H), 4.19−4.13 (m, 1H), 4.10−4.04 (m, 1H), 3.00 (s, 1.7H), 2.98 (s, 1.3H), 2.14 (s, 1.3H), 2.12 (s, 1.7H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.5, 136.4, 136.2, 132.8, 132.8, 131.3, 131.0, 129.1, 128.9, 127.6, 127.5, 127.5, 127.1, 127.1, 126.8, 123.5, 123.4, 52.5, 49.2, 35.4, 33.4, 21.7, 21.3 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{15}BrNO$, 268.0332; found, 268.0332.

(*E*)-*N*-(3-(2-fluorophenyl)allyl)-*N*-methylacetamide (**3ia**) was obtained as pale-yellow oil (34.4 mg, 83%); purification by silica gel chromatography (R_f = 0.21 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.41 (q, *J* = 7.2, 6.8 Hz, 1H), 7.18 (d, *J* = 11.8 Hz, 1H), 7.13−6.98 (m, 2H), 6.61 (t, *J* = 14.8 Hz, 1H), 6.27−6.14 (m, 1H), 4.15 (d, *J* = 6.4 Hz, 2H), 4.06 (d, *J* = 5.2 Hz, 1H), 2.98 (s, 1.6H), 2.97 (s, 1.4H), 2.13 (s, 1.4H), 2.12 (s, 1.6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.5, 161.3, 158.8, 129.2 (d, *J* = 8.5 Hz), 128.9 (d, *J* = 8.5 Hz), 127.6 (d, *J* = 3.6 Hz), 127.3 (d, *J* = 3.6 Hz), 127.2 (d, *J* = 4.6 Hz), 126.5 (d, *J* = 5.4 Hz), 124.9 (d, *J* = 3.8 Hz), 124.6, 124.3, 124.1 (d, *J* = 3.6 Hz), 124.0 (d, *J* = 3.5 Hz), 115.9, 115.7, 115.7, 115.5, 52.8, 49.5, 35.5, 33.4, 21.7, 21.3 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{12}H_{15}FNO$, 208.1132; found, 208.1132.

(*E*)-*N*-(3-(2-methoxyphenyl)allyl)-*N*-methylacetamide (**3ja**)[9] was obtained as pale-yellow oil (30.7 mg, 70%); purification by silica gel chromatography (R_f = 0.22 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.26−7.17 (m, 1H), 6.99−6.82 (m, 2H), 6.81 (dd, *J* = 16.0, 12.4 Hz, 1H), 6.19−6.08 (m, 1H), 4.18−4.12 (m, 1H), 4.08−4.02 (m, 1H), 3.84 (d, *J* = 1.6 Hz, 3H), 2.97 (d, *J* = 2.0 Hz, 3H), 2.13 (d, *J* = 10.8 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.4, 156.7, 156.5, 129.0, 128.7, 127.7, 127.1, 127.0, 126.8, 125.5, 125.1, 125.0, 124.2, 120.6, 110.8, 110.8, 55.4, 55.4, 53.1, 49.6, 35.3, 33.3, 21.8, 21.3 ppm.

(*E*)-*N*-methyl-*N*-(3-(*p*-tolyl)allyl)acetamide (**3ka**)[9] was obtained as colorless oil (31.3 mg, 77%); purification by silica gel chromatography (R_f = 0.22 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.29−7.23 (m, 2H), 7.12 (t, *J* = 8.2 Hz, 2H), 6.44 (dd, *J* = 15.8, 10.8 Hz, 1H), 6.13−6.03 (m, 1H), 4.13 (d, *J* = 6.4 Hz, 1H), 4.04 (d, *J* = 5.2 Hz, 1H), 2.97 (s, 3H), 2.34 (s, 1.6H), 2.33 (s, 1.4H), 2.14 (s, 1.5H), 2.12 (s, 1.5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.8, 170.4, 137.8, 137.5, 133.7, 133.2, 132.7), 131.6, 129.3, 129.2, 126.2, 126.2, 123.4, 122.5, 52.6, 49.2, 35.3, 33.4, 21.8, 21.3, 21.1 ppm.

(*E*)-*N*-(3-(3-cyanophenyl)allyl)-*N*-methylacetamide (**3ma**) was obtained as pale-yellow oil (35.1 mg, 82%); purification by silica gel chromatography (R_f = 0.22 eluent: PE/EA = 1:3); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.62−7.37 (m, 4H), 6.43 (dd, *J* = 16.0, 4.0 Hz, 1H), 6.26−6.14 (m, 1H), 4.16−4.13 (m, 1H), 4.10−4.07 (m, 1H), 2.99 (s, 1.8H), 2.96 (s, 1.2H), 2.12 (s, 1.8H), 2.11 (s, 1.2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.7, 170.6, 137.7, 137.3, 131.1, 130.8, 130.5, 130.4, 130.1, 129.8, 129.7, 129.5, 129.3, 129.3, 127.5, 126.8, 118.6, 118.5, 112.8, 112.6, 52.3, 49.1, 35.7, 33.5, 21.7, 21.2 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{13}H_{15}N_2O$, 215.1179; found, 215.1180.

(*E*)-*N*-(3-(3-methoxyphenyl)allyl)-*N*-methylacetamide (**3na**)[9] was obtained as pale-yellow oil (28.5 mg, 65%); purification by silica gel chromatography (R_f = 0.23 eluent: PE/EA = 1:3); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.25−7.19 (m, 1H), 6.99−6.92 (m, 1H), 6.90 (s, 1H), 6.85−6.75 (m, 1H), 6.44 (dd, *J* = 15.6, 12.2 Hz, 1H), 6.19−6.06 (m, 1H), 4.14 (d, *J* = 6.4 Hz, 1H), 4.05 (d, *J* = 4.8 Hz, 1H), 3.81 (d, *J* = 5.2 Hz, 3H), 2.98 (d, *J* = 2.8 Hz, 3H), 2.13 (d, *J* = 4.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 170.8, 170.4, 159.8, 159.8, 138.0, 137.5, 132.6, 131.5, 129.6, 129.5, 124.9, 124.0, 119.0, 118.9, 113.6, 113.5, 111.7, 111.4, 55.2, 55.2, 52.5, 49.2, 35.4, 33.5, 21.8, 21.3 ppm.

(*E*)-1-methyl-5-styrylpyrrolidin-2-one (**3ab**)[9] was obtained as colorless oil (33.0 mg, 82%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.42−7.25 (m, 5H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.01 (dd, *J* = 15.8, 8.6 Hz, 1H), 4.14−4.02 (m, 1H), 2.78 (s, 3H), 2.55−2.24 (m, 3H), 1.89−1.77 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 175.1, 135.9, 133.0, 128.9, 128.7, 128.2, 126.5, 63.0, 30.0, 27.9, 25.7 ppm.

(*E*)-5-(4-chlorostyryl)-1-methylpyrrolidin-2-one (**3bb**) was obtained as pale-yellow oil (38.2 mg, 81%); purification by silica gel chromatography (R_f = 0.13 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.28 (d, *J* = 12.4 Hz, 4H), 6.51 (d, *J* = 15.8 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.5 Hz, 1H), 4.14−4.02 (m, 1H), 2.77 (s, 3H), 2.54−2.23 (m, 3H), 1.87−1.76 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 134.3, 133.8, 131.7, 129.5, 128.8, 127.7, 62.8, 29.9, 27.9, 25.6 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{13}H_{15}ClNO$, 236.0837; found, 236.0840.

(*E*)-5-(4-bromostyryl)-1-methylpyrrolidin-2-one (**3cb**) was obtained as pale-yellow oil (44.8 mg, 80%); purification by silica gel chromatography (R_f = 0.13 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.01 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.16−3.97 (m, 1H), 2.77 (s, 3H), 2.53−2.24 (m, 3H), 1.91−1.75 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 134.8, 131.8), 131.7, 129.7, 128.0, 122.0, 62.8, 29.9, 28.0, 25.6 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{13}H_{15}BrNO$, 280.0332; found, 280.0333.

(*E*)-5-(4-fluorostyryl)-1-methylpyrrolidin-2-one (**3db**) was obtained as pale-yellow oil (36.8 mg, 84%); purification by silica gel chromatography (R_f = 0.15 eluent: PE/EA = 1:1); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.37−7.33 (m, 2H), 7.01 (t, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 5.92 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.12−4.02 (m, 1H), 2.77 (s, 3H), 2.51−2.24 (m, 3H), 1.88−1.77 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 163.8, 161.3, 132.0, 131.7, 128.6 (d, *J* = 2.2 Hz), 128.1 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 21.6 Hz), 62.8, 29.9, 27.9, 25.7 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{13}H_{15}FNO$, 220.1132; found, 220.1131.

(*E*)-4-(2-(1-methyl-5-oxopyrrolidin-2-yl)vinyl)benzonitrile (**3eb**) was obtained as a pale-yellow solid (37.1 mg, 82%); mp 88−91 °C; purification by silica gel chromatography (R_f = 0.14 eluent: PE/EA = 1:3); ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.15 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.15−4.07 (m, 1H), 2.76−2.74 (m, 3H), 2.48−2.24 (m, 3H), 1.87−1.75 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 174.9, 140.2, 132.8, 132.4, 131.0, 126.9, 118.6, 111.2, 62.4, 29.6, 27.9, 25.3 ppm. HRMS (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{15}N_2O$, 227.1179; found, 227.1180.

(*E*)-5-(4-methoxystyryl)-1-methylpyrrolidin-2-one (**3fb**) was obtained as a pale-yellow solid (35.2 mg, 76%); mp 56−59 °C; purification by silica gel chromatography (R_f = 0.13 eluent: PE/EA = 1:1) ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 15.6 Hz, 1H), 5.84 (dd, *J* = 15.6, 8.6 Hz, 1H), 4.07−3.99 (m, 1H), 3.79 (d, *J* = 1.2 Hz, 3H), 2.75 (s, 3H), 2.48−2.23 (m, 3H), 1.87−1.73 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 159.5, 132.4, 128.6, 127.7, 126.5, 114.0, 63.0, 55.2, 30.0, 27.8, 25.8 ppm. HMSR (ESITOF) *m*/*z*: $[M + H]^+$ calcd for $C_{14}H_{18}NO_2$, 232.1332; found, 232.1321.

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(*E*)-5-(2-chlorostyryl)-1-methylpyrrolidin-2-one (**3gb**) was obtained as pale-yellow oil (34.9 mg, 74%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.55−7.46 (m, 1H), 7.37−7.34 (m, 1H), 7.25−7.13 (m, 2H), 6.95 (d, *J* = 15.6 Hz, 1H), 5.99 (dd, *J* = 15.6, 8.6 Hz, 1H), 4.22−4.02 (m, 1H), 2.79 (s, 3H), 2.57−2.23 (m, 3H), 1.92−1.77 (m, 1H). ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 134.1, 133.1, 131.7, 129.8, 129.3), 129.1, 126.9, 126.9, 62.8, 29.9, 27.9, 25.5 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{15}ClNO$, 236.0837; found, 236.0840.

(*E*)-5-(2-bromostyryl)-1-methylpyrrolidin-2-one (**3hb**) was obtained as pale-yellow oil (43.7 mg, 78%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59−7.44 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.17−7.07 (m, 1H), 6.91 (d, *J* = 15.6 Hz, 1H), 5.95 (dd, *J* = 15.6, 8.6 Hz, 1H), 4.22−4.02 (m, 1H), 2.80 (s, 3H), 2.51−2.27 (m, 3H), 1.91−1.78 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 135.9, 133.0, 131.9, 131.9, 129.4, 127.6, 127.1, 123.6, 62.7, 29.9, 278.0, 25.5 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{15}BrNO$, 280.0332; found, 280.0333.

(*E*)-5-(2-fluorostyryl)-1-methylpyrrolidin-2-one (**3ib**) was obtained as pale-yellow oil (35.1 mg, 80%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.29−7.19 (m, 1H), 7.15−7.00 (m, 2H), 6.71 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.8, 8.6 Hz, 1H), 4.13−4.07 (m, 1H), 2.78 (s, 3H), 2.54−2.25 (m, 3H), 1.89−1.78 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 161.5, 159.0, 131.6 (d, *J* = 5.0 Hz), 129.4 (d, *J* = 8.4 Hz), 127.6 (d, *J* = 3.5 Hz), 125.5 (d, *J* = 3.4 Hz), 124.2 (d, *J* = 3.6 Hz), 123.7 (d, *J* = 12.2 Hz), 115.8 (d, *J* = 22.0 Hz), 63.2, 29.9, 27.9, 25.6. ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{15}FNO$, 220.1132; found, 220.1148.

(*E*)-5-(2-methoxystyryl)-1-methylpyrrolidin-2-one (**3jb**) was obtained as pale-yellow oil (32.8 mg, 71%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.44−7.40 (m, 1H), 7.29−7.19 (m, 1H), 6.97−6.84 (m, 3H), 6.02 (dd, *J* = 15.6, 8.7 Hz, 1H), 4.14−4.00 (m, 1H), 3.85 (s, 3H), 2.78 (s, 3H), 2.51−2.23 (m, 3H), 1.90−1.76 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 156.8, 129.4, 129.2, 127.9, 127.0, 124.8, 120.6, 110.9, 63.4, 55.4, 30.1, 27.8, 25.8 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{18}NO_2$, 232.1332; found, 232.1321.

(*E*)-1-methyl-5-(4-methylstyryl)pyrrolidin-2-one (**3kb**) was obtained as pale-yellow oil (33.6 mg, 78%); purification by silica gel chromatography (R_f = 0.21 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.17−7.10 (m, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.12−3.99 (m, 1H), 2.76 (s, 3H), 2.33 (d, *J* = 5.8 Hz, 6H), 1.88−1.73 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 175.0, 138.0, 133.0, 132.8, 129.3, 127.7, 126.4, 63.0, 30.0, 27.8, 25.7, 21.1 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{18}NO$, 216.1383; found, 216.1380.

(*E*)-5-(3,4-dimethoxystyryl)-1-methylpyrrolidin-2-one (**3lb**) was obtained as a pale-yellow solid (43.9 mg, 84%); mp 66−70 °C; purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 6.90 (d, *J* = 6.4 Hz, 2H), 6.82−6.78 (m, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 5.85 (dd, *J* = 16.0, 8.6 Hz, 1H), 4.09−3.99 (m, 1H), 3.88 (d, *J* = 1.2 Hz, 3H), 3.85 (d, *J* = 1.2 Hz, 3H), 2.75 (s, 3H), 2.48−2.23 (m, 3H), 1.87−1.74 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 174.9, 149.1, 149.0, 132.6, 128.8, 126.7, 119.8, 111.0, 108.7, 62.9, 55.8, 55.8, 29.9, 27.8, 25.7 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{20}NO_3$, 262.1438; found, 262.1430.

(*E*)-3-(2-(1-methyl-5-oxopyrrolidin-2-yl)vinyl)benzonitrile (**3mb**) was obtained as a pale-yellow solid (32.1 mg, 71%); mp 57−60 °C; purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.63 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.6, 8.2 Hz, 1H), 4.16−4.06 (m, 1H), 2.76 (s, 3H), 2.50−2.26 (m, 3H), 1.88−1.78 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 174.9, 137.1, 131.8, 131.2, 130.5, 130.5, 129.9, 129.5, 118.4, 112.8, 62.5, 29.7, 28.0, 25.4 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{15}N_2O$, 227.1179; found, 227.1176.

N-cinnamyl-*N*-methylformamide (**3ac**)[10] was obtained as colorless oil (17.9 mg, 51%); purification by silica gel chromatography (R_f = 0.36 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.13 (d, *J* = 21.0 Hz, 1H), 7.41−7.24 (m, 5H), 6.54 (dd, *J* = 16.0, 4.4 Hz, 1H), 6.14−6.05 (m, 1H), 4.11 (d, *J* = 6.6 Hz, 1H), 4.00 (d, *J* = 6.2 Hz, 1H), 2.91 (d, *J* = 23.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 162.7, 162.3, 136.2, 135.8, 133.6, 128.7, 128.6, 128.1, 127.8, 126.4, 126.4, 123.9, 123.2, 51.6, 46.1, 34.1, 29.5 ppm.

(*E*)-*N*-(3-(4-chlorophenyl)allyl)-*N*-methylformamide (**3bc**) was obtained as colorless oil (22.2 mg, 53%); purification by silica gel chromatography (R_f = 0.29 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.12 (d, *J* = 18.0 Hz, 1H), 7.28 (s, 2H), 7.27 (s, 2H), 6.48 (dd, *J* = 16.0, 5.6 Hz, 1H), 6.12−6.02 (m, 1H), 4.12−4.06 (m, 1H), 4.01−3.95 (m, 1H), 2.93 (s, 1.4H), 2.87 (s, 1.6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 162.7, 162.4, 134.7, 134.4, 133.8, 133.4, 132.3, 132.2, 128.8, 128.7, 127.6, 127.6, 124.6, 123.9, 51.5, 46.1, 34.2, 29.6 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{11}H_{13}ClNO$, 210.0680; found, 210.0676.

(*E*)-5-styrylpyrrolidin-2-one (**3ad**)[9] was obtained as a white solid, (33.3 mg, 89%); mp 71−75 °C; purification by silica gel chromatography (R_f = 0.25 eluent: PE/EA = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.39−7.29 (m, 4H), 7.29−7.20 (m, 1H), 6.53 (d, *J* = 15.8 Hz, 2H), 6.12 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.32 (q, *J* = 6.4 Hz, 1H), 2.45−2.32 (m, 3H), 1.97−1.86 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.4, 136.0, 131.0, 129.8, 128.6, 127.9, 126.4, 56.5, 30.0, 28.4 ppm.

(*E*)-5-(4-chlorostyryl)pyrrolidin-2-one (**3bd**) was obtained as a white solid (39.9 mg, 90%); mp 106−108 °C; purification by silica gel chromatography (R_f = 0.29 eluent: PE/EA = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.31−7.26 (m, 2H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.25 (s, 1H), 6.10 (dd, *J* = 15.8, 7.2 Hz, 1H), 4.32 (q, *J* = 6.8 Hz, 1H), 2.47−2.30 (m, 3H), 2.00−1.84 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.5, 134.5, 133.6, 130.5, 129.8, 128.8, 127.7, 56.4, 30.0, 28.3 ppm. HRMS (ESITOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{12}H_{12}ClNNaO$, 244.0500; found, 244.0499.

(*E*)-4-(2-(5-oxopyrrolidin-2-yl)vinyl)benzonitrile (**3ed**) was obtained as a white solid (35.7 mg, 84%); mp 73−76 °C; purification by silica gel chromatography (R_f = 0.19 eluent: PE/EA = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0 6.8 Hz, 1H), 4.40−4.29 (m, 1H), 2.45−2.28 (m, 3H), 1.89 (q, *J* = 8.8, 6.8 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.7, 140.6, 133.9, 132.3, 129.0, 126.9, 118.7, 110.9, 56.0, 29.8, 27.9 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{13}N_2O$, 213.1022; found, 213.1021.

(*E*)-5-(2-bromostyryl)pyrrolidin-2-one (**3hd**) was obtained as colorless oil (39.8 mg, 88%); purification by silica gel chromatography (R_f = 0.18 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.58−7.45 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.17−7.08 (m, 1H), 6.89 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 7.6 Hz, 1H), 5.91 (s, 1H), 4.44−4.34 (m, 1H), 2.48−2.33 (m, 3H), 2.02−1.90 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.6, 135.9, 132.9, 132.7, 129.9, 129.2, 127.5, 127.1, 123.6, 56.4, 30.0, 28.2 ppm. HRMS (ESITOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{12}H_{12}BrNNaO$, 287.9994; found, 287.9998.

(*E*)-5-(2-fluorostyryl)pyrrolidin-2-one (**3id**) was obtained as a white solid (37.4 mg, 91%); mp 108−111 °C; purification by silica gel chromatography (R_f = 0.27 eluent: PE/EA = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.45−7.37 (m, 1H), 7.24−7.16 (m, 1H), 7.12−6.97 (m, 2H), 6.67 (d, *J* = 16.0 Hz, 2H), 6.21 (dd, *J* = 16.0, 7.4 Hz, 1H), 4.37−4.30 (m, 1H), 2.45−2.30 (m, 3H), 1.92 (d, *J* = 4.2 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.4, 161.4, 159.0, 132.6 (d, *J* = 5.0 Hz), 129.2 (d, *J* = 8.4 Hz), 127.5 (d, *J* = 3.6 Hz), 124.1 (d, *J* = 3.6 Hz), 123.8 (d, *J* = 12.1 Hz), 123.5, 115.7 (d, *J* = 22.1 Hz), 56.7, 29.9, 28.3 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{13}FNO$, 206.0976; found, 206.0972.

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(*E*)-5-(2-methoxystyryl)pyrrolidin-2-one (**3jd**) was obtained as pale-yellow oil (33.5 mg, 77%); purification by silica gel chromatography (R_f = 0.13 eluent: PE/EA = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.40 (d, *J* = 6.0 Hz, 1H), 7.28−7.19 (m, 1H), 6.94−6.80 (m, 3H), 6.13 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.04 (s, 1H), 4.39−4.27 (m, 1H), 3.84 (s, 3H), 2.45−2.31 (m, 3H), 2.00−1.87 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 178.2, 156.7, 130.4, 129.1, 127.0, 126.1, 124.9, 120.6, 110.8, 57.0, 55.4, 30.0, 28.6 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{16}NO_2$, 218.1176; found, 218.1152.

(*E*)-*N*-methyl-*N*-(3-phenylbut-2-en-1-yl)acetamide (**5a**) was obtained as colorless oil (35.8 mg, 88%); purification by silica gel chromatography (R_f = 0.08 eluent: PE/EA = 3:1); the ratio of vinyl/allyl is about 0.86:0.14; ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.48−7.26 (m, 5.6H), 5.75−5.66 (m, 1H), 5.38−5.35 (m, 0.2H), 5.11 (s, 0.2H), 4.21 (d, *J* = 6.9 Hz, 1H), 4.08 (d, *J* = 6.5 Hz, 1H), 3.49−3.43 (m, 0.2H), 3.39−3.34 (m, 0.2H), 2.97 (d, *J* = 9.2 Hz, 3H), 2.91 (s, 0.5H), 2.78 (s, 0.4H), 2.15−2.07 (m, 6H), 2.02 (s, 0.3H), 1.91 (s, 0.3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.4, 142.9, 142.4, 138.5, 138.4, 128.6, 128.4, 128.2, 127.5, 127.1, 125.9, 125.9, 125.7, 125.6, 123.0, 122.6, 49.2, 45.1, 35.4, 33.2, 21.8, 21.5, 16.0, 15.9 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_3H_{18}NO$, 204.1383; found, 204.1384.

(*E*)-*N*-(3-(3-bromophenyl)but-2-en-1-yl)-*N*-methylacetamide (**5b**) was obtained as colorless oil (48.5 mg, 86%); purification by silica gel chromatography (R_f = 0.08 eluent: PE/EA = 3:1); ratio of vinyl/allyl is about 0.52:0.48; ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.60−7.46 (m, 2H), 7.44−7.27 (m, 4H), 7.25−7.13 (m, 2H), 5.75−5.64 (m, 1H), 5.36 (d, *J* = 10.8 Hz, 0.9H), 5.13 (s, 0.9H), 4.18 (d, *J* = 6.9 Hz, 1H), 4.06 (d, *J* = 6.4 Hz, 1H), 3.46−3.41 (m, 1H), 3.37−3.32 (m, 0.8H), 2.96 (d, *J* = 14.3 Hz, 3H), 2.90 (d, *J* = 7.1 Hz, 2.7H), 2.76−2.68 (m, 2H), 2.11 (d, *J* = 9.5 Hz, 3H), 2.06 (s, 3H), 2.02 (s, 1.8H), 1.92 (s, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.4, 170.4, 144.9, 144.3, 143.3, 142.6, 142.0, 137.1, 130.8, 130.4, 130.3, 130.1, 130.0, 129.9, 129.8, 129.7, 129.0, 128.8, 124.6, 124.4, 124.3, 124.2, 123.9, 122.8, 122.5, 122.4, 116.1, 115.1, 49.5, 49.1, 47.4, 45.1, 36.8, 35.6, 34.0, 33.2, 33.1, 32.7, 21.8, 21.8, 21.5, 21.0, 16.0, 15.8 ppm. HRMS (ESITOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{16}BrNNaO$, 304.0307; found, 304.0307.

(*E*)-*N*-(3-(4-fluorophenyl)but-2-en-1-yl)-*N*-methylacetamide (**5c**) was obtained as colorless oil (36.7 mg, 83%); purification by silica gel chromatography (R_f = 0.06 eluent: PE/EA = 3:1); the ratio of vinyl/allyl is about 0.70:0.30; ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.45−7.39 (m, 0.8H), 7.33 (m, 2.4H), 7.04−6.96 (m, 3H), 5.69−5.58 (m, 1H), 5.29 (d, *J* = 1.2 Hz, 0.4H), 5.09 (d, *J* = 4.2 Hz, 0.4H), 4.18 (d, *J* = 7.0 Hz, 1H), 4.09−4.02 (m, 1H), 3.49−3.29 (m, 0.8H), 2.98 (s, 2H), 2.94 (s, 1H), 2.90 (d, *J* = 9.9 Hz, 1.2H), 2.77−2.65 (m, 0.8H), 2.13 (s, 1.3H), 2.10 (s, 1.7H), 2.08−2.06 (m, 3H), 2.02 (s, 0.6H), 1.90 (s, 0.6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.5, 163.2, 160.8, 137.4, 127.6, 127.5, 127.2 (d, *J* = 1.5 Hz), 127.1 (d, *J* = 1.5 Hz), 122.8, 122.4, 115.3, 115.2, 115.1, 115.0 (d, *J* = 1.9 Hz), 114.8, 83.8, 49.1, 47.6, 45.2, 36.8, 35.5, 34.2, 33.7, 33.2, 33.0, 21.8, 21.7, 21.4, 16.2, 16.0 ppm. HRMS (ESITOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{16}FNNaO$, 244.1108; found, 244.1108.

(*E*)-*N*-(3-(4-bromophenyl)but-2-en-1-yl)-*N*-methylacetamide (**5d**) was obtained as colorless oil (46.3 mg, 82%); purification by silica gel chromatography (R_f = 0.06 eluent: PE/EA = 3:1); the ratio of vinyl/allyl is about 0.85:0.15; ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.49−7.38 (m, 2.4H), 7.32 (d, *J* = 8.6 Hz, 0.2H), 7.27−7.22 (m, 2.3 H), 5.74−5.63 (m, 1H), 5.35 (d, *J* = 9.1 Hz, 0.2H), 5.15−5.11 (m, 0.2H), 4.18 (d, *J* = 6.9 Hz, 1H), 4.05 (d, *J* = 6.4 Hz, 1H), 3.46−3.38 (m, 0.2H), 3.37−3.31 (m, 0.2H), 2.96 (d, *J* = 14.0 Hz, 3H), 2.90 (d, *J* = 9.7 Hz, 0.6H), 2.75−2.65 (m, 0.4H), 2.15−2.04 (m, 6H), 1.98 (s, 0.4H), 1.91 (s, 0.2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.4, 141.7, 141.2, 137.3, 131.7, 131.4, 131.4, 131.2, 127.6, 127.5, 127.3, 127.3, 123.6, 123.2, 121.4, 121.0, 35.6, 33.2, 21.8, 21.5, 15.9, 15.8 ppm. HRMS (ESITOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{16}BrNNaO$, 304.0307; found, 304.0307.

(*E*)-*N*-methyl-*N*-(3-(p-tolyl)but-2-en-1-yl)acetamide (**5e**) was obtained as colorless oil (33 mg, 76%); purification by silica gel chromatography (R_f = 0.09 eluent: PE/EA = 3:1); the ratio of vinyl/allyl is about 0.62:0.38; ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.35 (d, *J* = 8.2 Hz, 0.7H), 7.28 (m, 2.5H), 7.14 (q, *J* = 8.7, 7.9 Hz, 3.2H), 5.73−5.63 (m, 1H), 5.36−5.33 (m, 0.6H), 5.06 (s, 0.6H), 4.20 (d, *J* = 7.0 Hz, 1H), 4.07 (d, *J* = 6.4 Hz, 1H), 3.47−3.41 (m, 0.6H), 3.38−3.32 (m, 0.6H), 2.96 (d, *J* = 7.5 Hz, 3H), 2.91 (d, *J* = 1.6 Hz, 1.8H), 2.78−2.70 (m, 1.2H), 2.37−2.31 (m, 4.8H), 2.12 (d, *J* = 13.0 Hz, 3H), 2.09−2.06 (m, 3H), 2.03 (s, 0.8H), 1.92 (s, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$-*d*): δ 170.4, 170.3, 145.4, 144.3, 139.9, 139.5, 138.3, 138.1, 137.7, 137.3, 136.9, 129.3, 129.1, 129.0, 128.9, 125.8, 125.7, 125.5, 125.5, 122.1, 121.8, 114.1, 113.1, 49.7, 49.2, 47.7, 45.0, 37.0, 35.4, 34.2, 33.2, 33.1, 33.0, 21.9, 21.8, 21.5, 21.1, 21.1, 21.0, 21.0, 16.0, 15.9 ppm. HRMS (ESITOF) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{20}NO$, 218.1539; found, 218.1539.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02837.

Optimization of the reaction Conditions for α-alkyl nitroalkenes, vinyl sulfones, and cinnamic acids with DMA, coupling constants of all compounds, ratio of vinyl/allyl of compounds **5**, and ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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