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Direct oxidative coupling of *N*-acyl pyrroles with alkenes by ruthenium(II)-catalyzed regioselective C2-alkenylation†

Weiqiang Chen,[a] Hui-Jing Li,*[a,b] Qin-Ying Li[a,b] and Yan-Chao Wu *[a,b]

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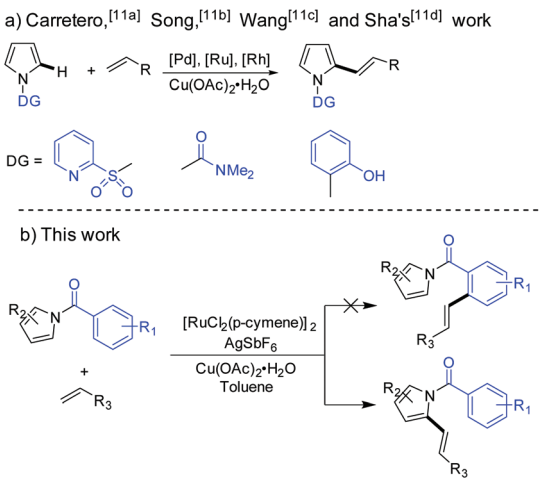
Ruthenium(II)-catalyzed oxidative coupling by C2-alkenylation of *N*-acyl pyrroles with alkenes has been described. The acyl unit was found to be an effective chelating group for the activation of aryl C–H bonds *ortho* to the directing group. The alkenylation reaction of benzoyl pyrroles occurred regioselectively at the C2-position of the pyrrole ring, without touching the benzene ring. The reaction provides exclusively monosubstituted pyrroles under the optimized conditions. Disubstituted pyrroles could be obtained using higher loadings of the ruthenium(II)-catalyst and the additives.

Introduction

Over the past few decades, transition-metal-catalyzed organic reactions through C–H bond cleavage have received considerable interest[1–4] as a powerful and straightforward approach for their synthetic applications in materials science,[5] natural products and pharmaceuticals.[6] Employing transition-metal-catalyzed C–H activation in the synthesis of vinylarene derivatives has attracted much attention in recent years. Considering the subtle differences in the intrinsic reactivity of C–H bonds at different positions of pyrroles, common solutions for controlling regioselectivity involve optimizing the electronic/steric properties,[7] solvents,[8] ligands,[9] and directing groups.[10,11] Among these protocols, utilization of the proximate effect by coordination of a functional group to the metal center is often used as a promising activation strategy to achieve regioselective C–H bond functionalizations at the *ortho*-position. For pyrrole derivatives, the use of directing groups on the nitrogen atom has been effective for C2-alkenylation (Scheme 1a). Carretero reported an efficient palladium(II)-catalyzed regioselective C2-alkenylation of pyrroles bearing an *N*-(2-pyridyl)sulfonyl protecting group.[11a] Song and Wang developed a selective ruthenium(II)-catalyzed direct C2-alkenylation of indoles and pyrroles assisted by an *N*-dimethylcarbamoyl group.[11b,c] Shortly afterwards, Sha reported a rhodium(III)-catalyzed C2-alkenylation of unactivated indoles and pyrroles utilizing hydroxy as a directing group.[11d] Meanwhile, aromatic esters, aryl ketones, benzamides and acylsilanes were also employed as chelating groups for the activation of aryl C–H bonds at the *ortho* position under ruthenium or rhodium catalysis, according to ref. 12 and based on other reports.[13] Prabhu reported a regioselective alkenylation of indole derivatives at the C2-position using the benzoyl group as a directing group.[14] Given the importance of the acyl group, which behaves as a directing group for ruthenium(II)-catalyzed functionalization, for the different behaviours of the directing groups,[15] another very attractive platform for developing a new selective C–H activation strategy is the *N*-acyl pyrrole skeleton, which widely exists in natural products and biomolecules



Scheme 1 Directing group-controlled regioselectivity in C2-alkenylation.

[a]School of Marine Science and Technology, Harbin Institute of Technology, 2 Weihai Road, Weihai 264209, P. R. China. E-mail: ycwu@iccas.ac.cn
[b]Weihai Institute of Marine Biomedical Industrial Technology, Wendeng District, Weihai 264400, P. R. China

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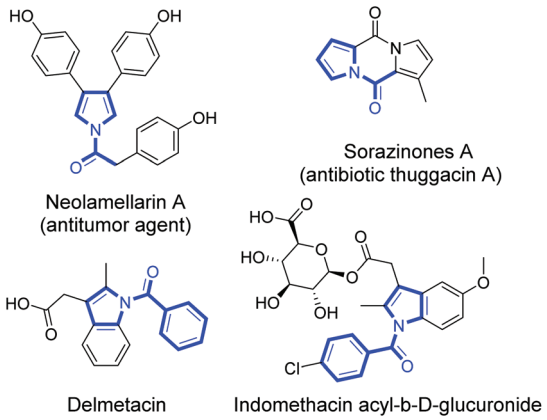


Fig. 1 Selected medicinal and bioactive molecules containing *N*-acyl pyrrole skeletons.

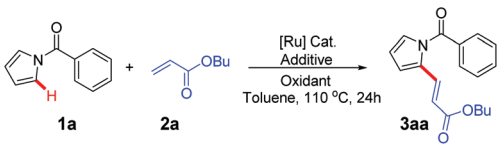
(Fig. 1),[16] and organic compounds containing such pyrrole functional groups are used in various organic reactions.[17] In light of the recent work on C–H functionalization under ruthenium catalysis, it is highly desirable to extend the approach to ruthenium-catalyzed C–H activation processes. With this background and based on previous reports on ruthenium catalysis, we wanted to know whether the ruthenium-catalyzed oxidative C2-alkenylation of benzoyl pyrroles takes place on the pyrrole or benzene rings. We would like to report herein that the above C2-alkenylation reaction occurred only on the pyrrole rings and not on the benzene rings (Scheme 1b).

Results and discussion

The reaction of phenyl(1*H*-pyrrol-1-yl)methanone (**1a**) with butyl acrylate (**2a**) was used as a probe for evaluating the reaction conditions, and the representative results are summarized in Table 1. Initially, substrates **1a** and **2a** were reacted in the presence of different ruthenium catalysts (0.05 equiv.) and $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv.) in toluene at 110 °C for 24 h under an argon atmosphere (1 atm). No C2-alkenylation product **3aa** was obtained with the use of $Ru(PPh_3)_3Cl_2$, $RuH_2(PPh_3)_4$, $Ru(COD)Cl_2$, $Ru_3(CO)_{12}$, and RuCl[(*R*,*R*)-Tsdpen](*p*-cymene) as the catalyst in combination with $Cu(OAc)_2{\cdot}H_2O$ (entries 1–4, and 7). When $[RuCl_2(CO)_3]_2$ and $[RuCl_2(p\text{-cymene})]_2$ were used as the catalyst under the same conditions, C2-alkenylation product **3aa** was obtained in 16% and 29% yields, respectively (entries 5 and 6). Furthermore, other oxidants such as $K_2S_2O_8$ and $PhI(OAc)_2$ did not promote the reaction (entries 8 and 9). In order to further increase the yield, various silver salts were tested as additives in combination with $[RuCl_2(p\text{-cymene})]_2$ and $Cu(OAc)_2{\cdot}H_2O$ under otherwise identical conditions. The C2-alkenylation product **3aa** was obtained in low yields with the use of Ag_2CO_3, Ag_3PO_4, AgF, and AgOAc as the additives (entries 12, 14, 15, and 17). No conversion was observed when $AgNO_3$ was employed (entry 13). In contrast, AgOTf, $AgSbF_6$ and $AgBF_4$ were the relatively effective additives for this oxidative coupling by C–H alkenylation (entries 10, 11, and 16). The yield of **3aa** slightly decreased when the loading of $Cu(OAc)_2{\cdot}H_2O$ was increased from 1.0 equiv. to 1.5 equiv. (entry 18). In addition, when substrates **1a** and **2a** were reacted in the presence of $[RuCl_2(p\text{-cymene})]_2$ or a mixture of $AgSbF_6$ and $Cu(OAc)_2{\cdot}H_2O$, no C2-alkenylation product **3aa** was obtained (entries 19 and 20). However, $AgSbF_6$ was chosen as the additive in our investigations because it gave the best yield. Therefore, the optimal reaction conditions were determined to be $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv.), $AgSbF_6$ (0.10 equiv.), and $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv.) in toluene at 110 °C for 24 h under an argon atmosphere (1 atm).

After establishing the optimal reaction conditions, the scope and limitation of this ruthenium(II)-catalyzed direct oxidative C2-alkenylation reaction was subsequently investigated, and the representative results are summarized in Table 2. Alkenes **2a–d** reacted well with phenyl(1*H*-pyrrol-1-yl)methanone (**1a**) in the presence of $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv.), $AgSbF_6$ (0.10 equiv.), and $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv.) in toluene at 110 °C for 24 h under an argon atmosphere (1 atm) to afford exclusively the C2-alkenylation products **3aa–ad** in 71–81% yields. The C2-alkenylation product **3ae** was obtained in only a moderate yield with the use of a relatively sterically hindered alkene **2e** as the substrate, indicating that the steric factor may

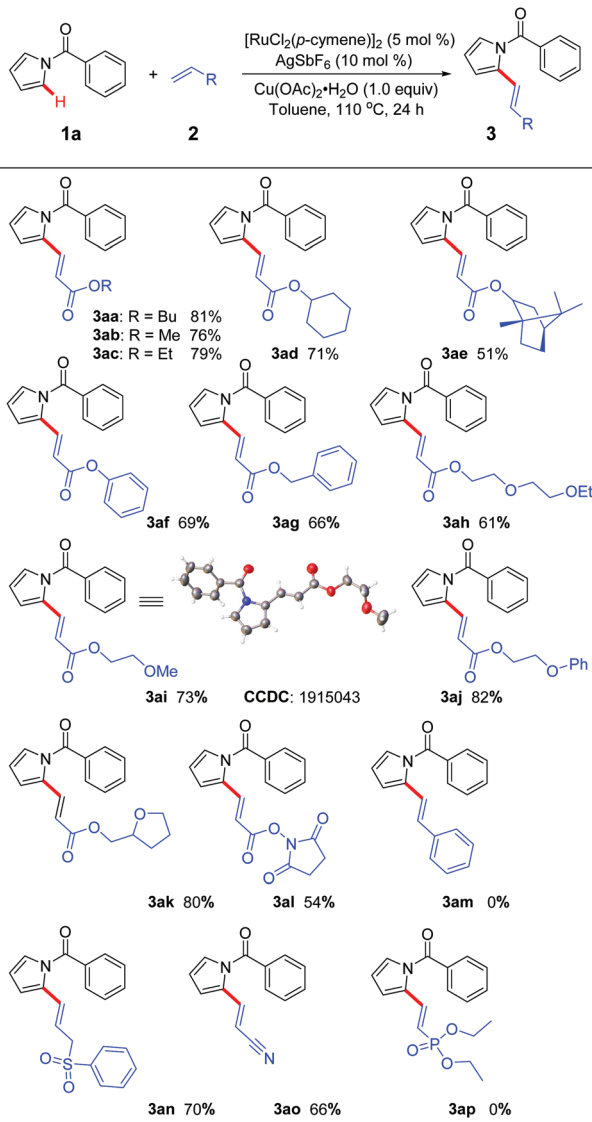
Table 1 Optimization of the reaction conditions for **3aa**[a]



Entry	[Ru] Cat.	Additive	Oxidant	Yield[b] (%)
1	$Ru(PPh_3)_3Cl_2$		$Cu(OAc)_2{\cdot}H_2O$	0
2	$RuH_2(PPh_3)_4$		$Cu(OAc)_2{\cdot}H_2O$	0
3	$Ru(COD)Cl_2$		$Cu(OAc)_2{\cdot}H_2O$	0
4	$Ru_3(CO)_{12}$		$Cu(OAc)_2{\cdot}H_2O$	0
5	$[RuCl_2(CO)_3]_2$		$Cu(OAc)_2{\cdot}H_2O$	16
6	$[RuCl_2(p\text{-cymene})]_2$		$Cu(OAc)_2{\cdot}H_2O$	29
7	RuCl[(*R*,*R*)-Tsdpen](*p*-cymene)		$Cu(OAc)_2{\cdot}H_2O$	0
8	$[RuCl_2(p\text{-cymene})]_2$		$K_2S_2O_8$	<5
9	$[RuCl_2(p\text{-cymene})]_2$		$PhI(OAc)_2$	12
10	$[RuCl_2(p\text{-cymene})]_2$	AgOTf	$Cu(OAc)_2{\cdot}H_2O$	66
11	$[RuCl_2(p\text{-cymene})]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	81
12	$[RuCl_2(p\text{-cymene})]_2$	Ag_2CO_3	$Cu(OAc)_2{\cdot}H_2O$	18
13	$[RuCl_2(p\text{-cymene})]_2$	$AgNO_3$	$Cu(OAc)_2{\cdot}H_2O$	0
14	$[RuCl_2(p\text{-cymene})]_2$	Ag_3PO_4	$Cu(OAc)_2{\cdot}H_2O$	26
15	$[RuCl_2(p\text{-cymene})]_2$	AgF	$Cu(OAc)_2{\cdot}H_2O$	21
16	$[RuCl_2(p\text{-cymene})]_2$	$AgBF_4$	$Cu(OAc)_2{\cdot}H_2O$	45
17	$[RuCl_2(p\text{-cymene})]_2$	AgOAc	$Cu(OAc)_2{\cdot}H_2O$	<5
18[c]	$[RuCl_2(p\text{-cymene})]_2$	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	69
19	$[RuCl_2(p\text{-cymene})]_2$			0
20		$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	0

[a] General conditions: [Ru] Cat. (0.01 mmol), additive (0.02 mmol), oxidant (0.20 mmol), *N*-acyl pyrrole (**1a**, 0.20 mmol), and alkene (**2a**, 0.40 mmol) in toluene (2.0 mL) at 110 °C for 24 h under an argon atmosphere (1 atm). [b] Isolated yields. [c] [Ru] Cat. (0.01 mmol), additive (0.02 mmol), oxidant (0.30 mmol), in toluene (2.0 mL) at 110 °C for 24 h under an argon atmosphere (1 atm).

Table 2 Evaluation of alkenes for the C2-alkenylation reaction[a,b]

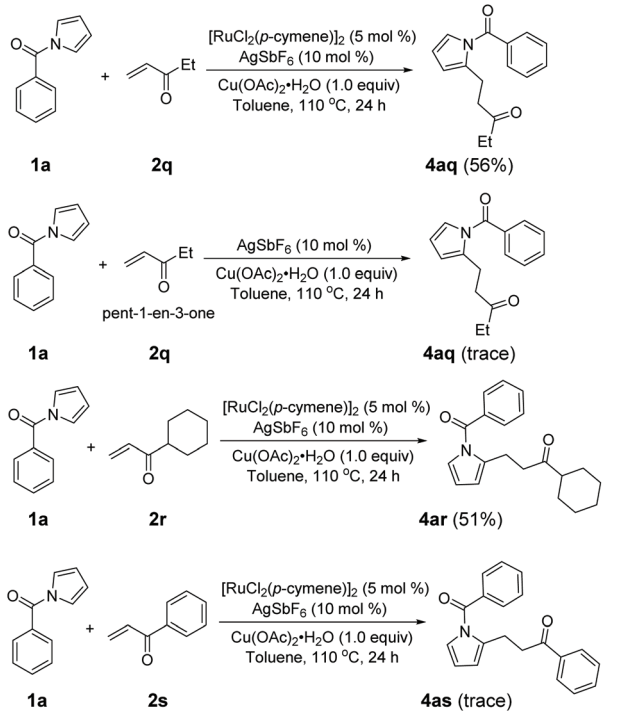


[a] General conditions: $[RuCl_2(p\text{-cymene})]_2$ (0.01 mmol), $AgSbF_6$ (0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.20 mmol,), phenyl(1*H*-pyrrol-1-yl)methanone (**1a**, 0.20 mmol), and alkene (**2a**, 0.40 mmol) in toluene (2.0 mL) at 110 °C for 24 h under an argon atmosphere (1 atm). [b] Isolated yields.

effect the complexation of the double bond to the metal center. Alkenes **2f** and **2g** reacted with **1a** under the standard conditions to give C2-alkenylation products **3af** and **3ag** in 69% and 66% yields, respectively. Some other types of alkenes **2h–l** have also been investigated, and the C2-alkenylation products **3ah–al** were obtained in moderate to good yields under the standard reaction conditions. Unfortunately, the reaction was complex when styrene (**2m**) was used as the substrate, and the expected pyrrole product was not obtained, indicating that non-activated styrene derivatives are not suitable substrates. Electrophilic alkenes including sulfone, nitrile, and phosphonate were investigated next, and alkenes **2n** and **2o** reacted smoothly with phenyl(1*H*-pyrrol-1-yl)methanone (**1a**) to give C2-alkenylation products **3an** and **3ao** in satisfactory yields. When alkene **2p** was reacted with phenyl(1*H*-pyrrol-1-yl)methanone (**1a**), C2-alkenylation product **3ap** was not obtained under the standard conditions.

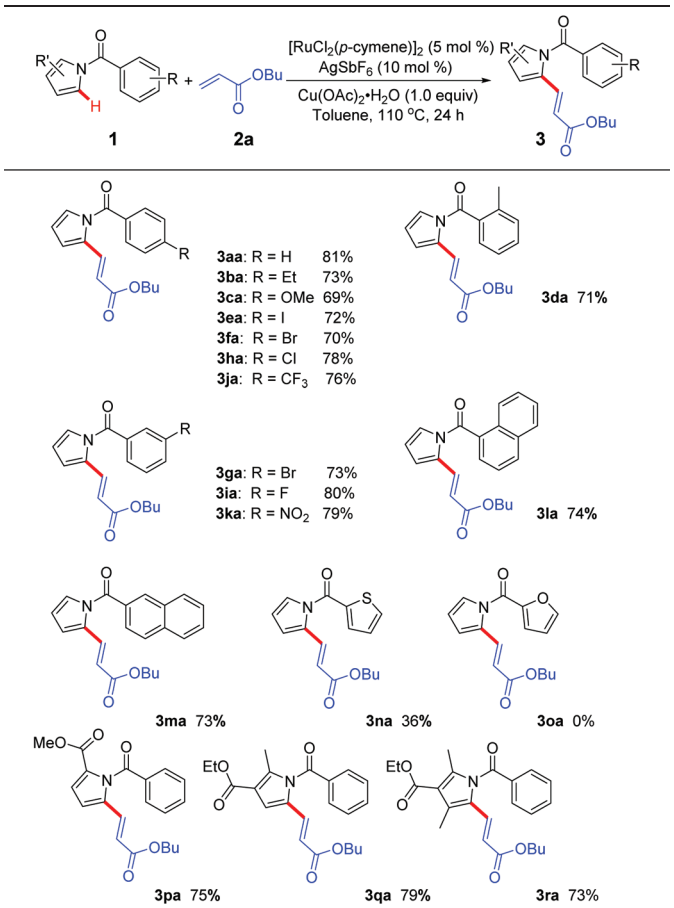
Interestingly, 1,4-addition product **4aq** was obtained in 56% yield by treating *N*-acyl pyrrole **1a** with pent-1-en-3-one (**2q**) under the above-mentioned standard conditions (Scheme 2). When the reaction was performed in the absence of $[RuCl_2(p\text{-cymene})]_2$, under otherwise same conditions, 1,4-addition product **4aq** was obtained only in trace amounts, indicating that the transformation occurs via a transition-metal-mediated C–H activation reaction. α,β-Unsaturated ketone **2r** reacted uneventfully with *N*-acyl pyrrole **1a** to afford adduct **4ar** in 51% yield. When a deactivated α,β-unsaturated ketone **2s** was used, trace amounts of 1,4-addition product **4as** were obtained and the starting materials were recovered.[18]

Next, the scope of the direct oxidative alkenylation of differently substituted *N*-acyl pyrroles **1** was investigated, and the results are shown in Table 3. This coupling reaction turned out to be a versatile reaction, as the alkenylation could tolerate various functional groups. *N*-Acyl pyrroles **1b–d**, each bearing an electron-donating group, smoothly underwent oxidative coupling by the alkenylation reaction in the presence of $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv.), $AgSbF_6$ (0.10 equiv.), and $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv.) in toluene at 110 °C for 24 h under an argon atmosphere (1 atm) to generate C2-alkenylation products **3ba–da** in 69%–73% yields. With their *meta*/*para*-position bearing sensitive functional groups such as I, Br, Cl and F, *N*-acyl pyrroles **1e–i** were well-tolerated substrates for the oxi-



Scheme 2 1,4-Addition reaction of *N*-acyl pyrrole **1a** with α,β-unsaturated ketones **2q–s**.

Table 3 Evaluation of *N*-acyl pyrroles for the C2-alkenylation reaction[a,b]



[a] General conditions: $[RuCl_2(p\text{-cymene})]_2$ (0.01 mmol), $AgSbF_6$ (0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.20 mmol), *N*-acyl pyrrole (**1a**, 0.20 mmol), and alkene (**2a**, 0.40 mmol) in toluene (2.0 mL) at 110 °C for 24 h under an argon atmosphere (1 atm). [b] Isolated yields.

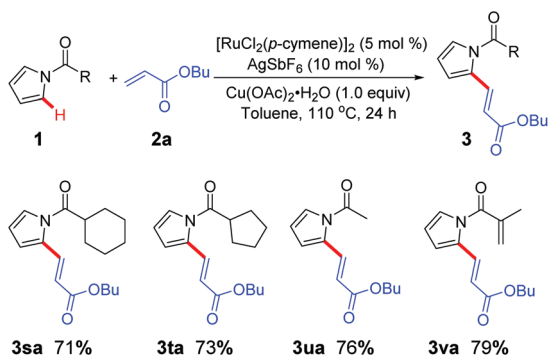
dative alkenylation reaction to afford C2-alkenylation products **3ea–ia** in good yields. The reaction of butyl acrylate (**2a**) with *N*-acyl pyrroles **1j** and **1k**, each bearing an electron-withdrawing group, CF_3 or NO_2, on the aromatic ring proceeded well under the standard conditions to generate C2-alkenylation products **3ja** and **3ka** in 76% and 79% yields, respectively. *N*-Acyl pyrroles **1l** and **1m**, each bearing a naphthyl group, reacted smoothly with butyl acrylate (**2a**) to give C2-alkenylation products **3la** and **3ma** in 74% and 73% yields, respectively. From the experimental results, it was found that electron-withdrawing or electron-donating groups on the benzene ring do not have a significant impact on the reactivity. Thiophene- and furan-containing *N*-acyl pyrroles **1n** and **1o** have also been investigated, and only substrate **1n** could convert to the corresponding product **3na** in a low yield. The reaction of butyl acrylate (**2a**) with 2-substituted pyrrole **1p** proceeded well under the standard conditions to generate C2-alkenylation product **3pa** in 75% yield, and no C4-alkenylation product was obtained. When 2,3-disubstituted pyrrole **1q** was subjected to standard conditions, C2-alkenylation product **3qa** was obtained exclusively. 2,3,4-Trisubstituted pyrrole **1r** has also been investigated, which reacted with **2a** to give C2-alkenylation product **3ra** in 73% yield, without being influenced by the steric factor effect.

To our delight, when alkene **2a** reacted with cyclohexyl(1*H*-pyrrol-1-yl)methanone (**1s**) under the optimized reaction conditions, the desired C2-alkenylation product **3sa** was obtained in 71% yield (Scheme 3), indicating the great synthetic value of this protocol. Subsequently, several other *N*-acyl pyrroles **1t–v** were also investigated, affording C2-alkenylation products **3ta–va** in good yields.

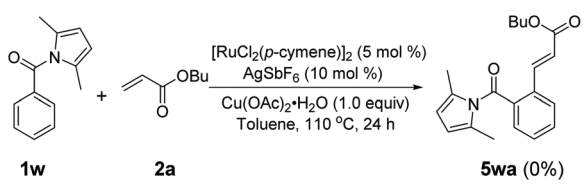
To further evaluate the regioselectivity of the C2-alkenylation reaction, 2,5-disubstituted *N*-acyl pyrrole **1w** was subjected to the procedure and no reaction occurred, reflecting an excellent regioselectivity of the alkenylation at the pyrrole C2-position (Scheme 4). The product outcome of the catalysis indicates that the C–H bond functionalization occurring in pyrrole is due to the fact that the C–H bond in the pyrrole ring is more acidic than in the benzene ring.[19]

The C2,C5-double alkenylated product **6aa** was also obtained in 61% yield using higher loadings of $[RuCl_2(p\text{-cymene})]_2$, $AgSbF_6$ and $Cu(OAc)_2{\cdot}H_2O$ (*i.e.*, 10 mol% *versus* 5 mol%, 20 mol% *versus* 10 mol%, and 2.0 equiv. *versus* 1.0 equiv., respectively, Scheme 5 and Table 2). We were pleased to find that the current catalytic system could be successfully applied to *N*-benzoyl indole (Scheme 6). Under the optimized conditions, indole cleanly produced the C2-alkenylation product **8aa** in 80% yield.

To demonstrate the further utility of our synthesis, we attempted elaboration of the alkenylated product **3ab**. As can

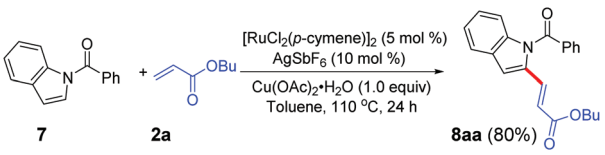


Scheme 3 Substrate scope with respect to *N*-acyl pyrroles.

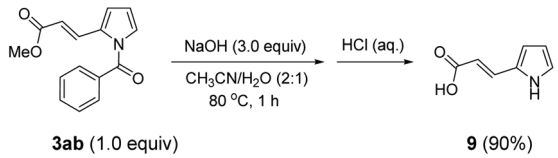


Scheme 4 Investigation of the alkenylation reaction of 2,5-disubstituted *N*-acyl pyrrole **1w** with alkene **2a**.

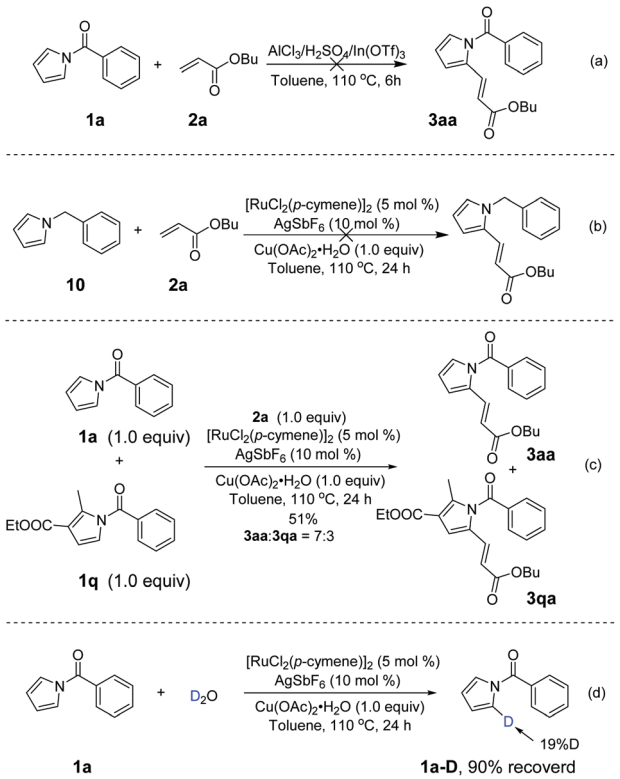
Scheme 5 The coupling of pyrrole **1a** with butyl acrylate (**2a**).



Scheme 6 The coupling of indole **7** with butyl acrylate (**2a**).



Scheme 7 Deprotection and hydrolysis of the C2-alkenylation product **3ab**.

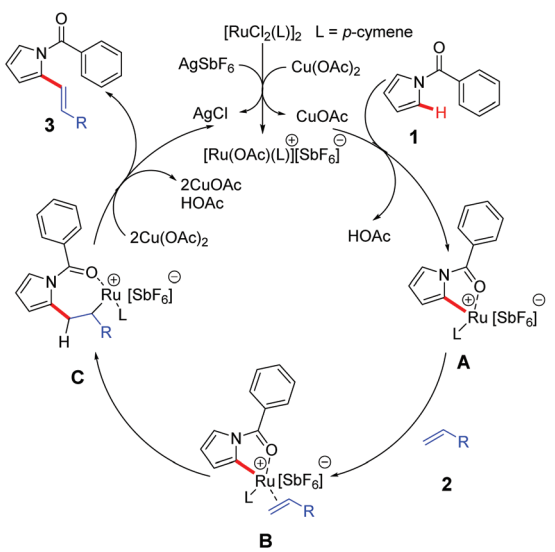


Scheme 8 Verification experiments.

be seen from Scheme 7, deprotection and hydrolysis was readily achieved by heating **3ab** with NaOH to furnish the debenzoylated pyrrole derivative of acrylic acid **9**. This product **9** is a very useful intermediate, which can be transformed into a variety of bioactive molecules.[20]

The reaction mechanism of this oxidative coupling by the C2-alkenylation reaction was studied next, and the representative results are illustrated in Scheme 8. In order to check whether the reaction was a Friedel–Crafts alkylation or not, phenyl(1*H*-pyrrol-1-yl)methanone (**1a**) was reacted with butyl acrylate (**2a**) in the presence of $AlCl_3$, H_2SO_4, or $In(OTf)_3$ (0.50 equiv.) in toluene at 110 °C for 6 h under an argon atmosphere (1 atm), but C2-alkenylation product **3aa** was not obtained (Scheme 8a). When 1-benzyl-1*H*-pyrrole **10** was reacted with butyl acrylate (**2a**) under standard conditions, no reaction occurred, indicating that the mechanism is chelation-controlled with an acyl unit as the directing group (Scheme 8b). The inter-molecular competition experiment was also conducted using different pyrroles **1a** and **1q**. Alkenylation of **1a** and **1q** with alkene **2a** in a one-pot fashion revealed the electron-rich substrate **1a** to be preferentially functionalized (Scheme 8c), which is in good agreement with the electrophilic activation mode. Considering the remarkable activity of the cationic ruthenium(II) catalyst, its mode of action in this alkenylation reaction was studied next. When *N*-acyl pyrrole **1a** was subjected to standard conditions in the presence of D_2O, H/D scrambling was observed in **1a**, thereby indicating a reversible C–H cyclometalation reaction (Scheme 8d).

On the basis of these experimental results and previous reports,[10–15,21] a plausible mechanism for oxidative coupling by the C2-alkenylation reaction of *N*-acyl pyrroles **1** with alkenes **2** is illustrated in Scheme 9. First, the catalytically active species $[Ru(OAc)(L)][SbF_6]$ is generated from the reaction of $[RuCl_2(p\text{-cymene})]_2$, $AgSbF_6$ and $Cu(OAc)_2{\cdot}H_2O$ by the elim-



Scheme 9 Mechanism for the oxidative coupling by C2-alkenylation of *N*-acyl pyrroles with alkenes.

ination of chloride ions. Intramolecular C–H bond activation at the *ortho*-position of the pyrrole ring occurs to give a five-membered ruthenacycle intermediate **A** accompanied by the release of acetic acid. The coordination of the intermediate **A** with alkene **2** produces intermediate **B**, and further intramolecular insertion of alkene **2** into the Ru–C bond generates intermediate **C**. Subsequently, β-hydride elimination of the intermediate **C** occurs to give the desired C2-alkenylation product **3**. Finally, a catalytically active species is regenerated in the presence of a copper(II) salt, which is then used in another catalytic cycle.

Conclusions

In summary, we have developed a ruthenium(II)-catalyzed regioselective C–H activation of the pyrrole C2-position with alkenes leading to the formation of 2-substituted alkenylation pyrrole derivatives. The regioselectivity of the current alkenylation reaction has been achieved by employing acyl as the directing group. This protocol provides a straightforward method for the preparation of valuable vinyl pyrroles, a structural motif for a large number of functional materials, natural products, and biomolecules. Further mechanistic investigations on the applications of this method are in progress.

Experimental

General information

All reactions were carried out under an argon atmosphere unless otherwise noted. Dichloromethane and toluene were distilled prior to use under a nitrogen atmosphere. Silica gel (200–300 mesh) was used for flash chromatography. *N*-acyl pyrroles were prepared according to the literature procedures.[1] Formyl chloride, alkenes, and other reagents were purchased from commercial sources and used directly. High-resolution mass spectra (HRMS) were recorded using an Electrothermal LTQ-Orbitrap mass spectrometer. Melting points were measured using Gongyi X-5 microscopy digital melting point apparatus and were uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer with $CDCl_3$ as the solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ (δ = 7.26) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. Coupling constants (J) are quoted in Hz. NMR data of the known compounds are in agreement with the literature values. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m).

General procedure for the synthesis of *N*-acyl pyrroles[22]

Benzoyl chloride (20.0 mmol) was added dropwise to a stirred solution of pyrrole (1.71 g, 25.6 mmol), triethylamine (2.60 g, 25.6 mmol) and DMAP (260 mg, 2.1 mmol) in dry dichloromethane (30 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred until the end of the reaction. The reaction mixture was then diluted with Et_2O, washed with 1 M HCl (30 mL), saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried over Na_2SO_4 and filtered. The volatiles were removed *in vacuo* and the residue was subjected to flash column chromatography to give *N*-acyl pyrroles.

Phenyl(1*H*-pyrrol-1-yl)methanone (1a). Synthesis was carried out according to the general procedure, and compound **1a** was obtained in 91% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.29 (d, J = 1.6 Hz, 2H), 6.35 (d, J = 1.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 167.7, 133.2, 132.2, 129.4, 128.4, 121.2, 113.1. These spectral data correspond to previously reported data.[22a]

(4-Ethylphenyl)(1*H*-pyrrol-1-yl)methanone (1b). Synthesis was carried out according to the general procedure, and compound **1b** was obtained in 90% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, J = 7.6 Hz, 2H), 7.34–7.30 (m, 4H), 6.34 (s, 2H), 2.75 (q, J = 7.4 Hz, 2H), 1.29 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.7, 149.2, 130.5, 129.8, 127.9, 121.3, 112.9, 28.9, 15.2. These spectral data correspond to previously reported data.[22c]

(4-Methoxyphenyl)(1*H*-pyrrol-1-yl)methanone (1c). Synthesis was carried out according to the general procedure, and compound **1c** was obtained in 93% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, J = 8.4 Hz, 2H), 7.29 (t, J = 2.0 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.34 (t, J = 2.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.1, 163.0, 132.0, 125.2, 121.3, 113.8, 112.7, 55.5. These spectral data correspond to previously reported data.[22b]

(1*H*-Pyrrol-1-yl)(*o*-tolyl)methanone (1d). Synthesis was carried out according to the general procedure, and compound **1d** was obtained in 90% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44–7.39 (m, 2H), 7.30 (t, J = 6.6 Hz, 2H), 7.15 (s, 2H), 6.31 (d, J = 1.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.2, 136.4, 133.7, 130.8, 130.7, 127.8, 125.5, 120.6, 113.4, 19.3. These spectral data correspond to previously reported data.[22b]

(4-Iodophenyl)(1*H*-pyrrol-1-yl)methanone (1e). Synthesis was carried out according to the general procedure, and compound **1e** was obtained in 87% yield as a white solid after purification by silica gel column chromatography. mp 69–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 1.8 Hz, 2H), 6.36 (t, J = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.9, 137.7, 132.5, 130.9, 121.1, 113.4, 99.6. These spectral data correspond to previously reported data.[22d]

(4-Bromophenyl)(1*H*-pyrrol-1-yl)methanone (1f). Synthesis was carried out according to the general procedure, and compound **1f** was obtained in 86% yield as a white solid after purification by silica gel column chromatography. mp 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70–7.64 (m, 4H), 7.27 (t, J = 2.2 Hz, 2H), 6.38 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ (ppm): 166.7, 132.0, 131.8, 131.0, 127.2, 121.1, 113.4. These spectral data correspond to previously reported data.[22e]

(3-Bromophenyl)(1*H*-pyrrol-1-yl)methanone (1g). Synthesis was carried out according to the general procedure, and compound **1g** was obtained in 87% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (s, 1H), 7.77–7.68 (m, 2H), 7.42 (t, J = 7.8 Hz, 1H), 7.28 (s, 2H), 6.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.1, 135.2, 135.1, 132.3, 130.0, 127.9, 122.6, 121.1, 113.6. These spectral data correspond to previously reported data.[22c]

(4-Chlorophenyl)(1*H*-pyrrol-1-yl)methanone (1h). Synthesis was carried out according to the general procedure, and compound **1h** was obtained in 83% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.25 (t, J = 2.4 Hz, 2H), 6.36 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 138.7, 131.5, 130.9, 128.8, 121.1, 113.4. These spectral data correspond to previously reported data.[22c]

(3-Fluorophenyl)(1*H*-pyrrol-1-yl)methanone (1i). Synthesis was carried out according to the general procedure, and compound **1i** was obtained in 80% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54–7.44 (m, 3H), 7.33–7.28 (m, 1H), 7.27 (t, J = 2.2 Hz, 2H), 6.36 (t, J = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.2, 163.5, 161.0, 135.2, 135.1, 130.3, 130.2, 125.2, 125.1, 121.1, 119.4, 119.2, 116.7, 116.4, 113.5. These spectral data correspond to previously reported data.[22c]

(1*H*-Pyrrol-1-yl)(4-(trifluoromethyl)phenyl)methanone (1j). Synthesis was carried out according to the general procedure, and compound **1j** was obtained in 80% yield as a yellow solid after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 2.2 Hz, 2H), 6.38 (t, J = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.4, 136.6, 134.0, 133.7, 129.7, 125.6, 125.5, 124.8, 122.1, 121.1, 113.8. HRMS (ESI) m/z: calcd for $C_{12}H_8F_3NNaO$ $[M + Na]^+$: 262.0450, found: 262.0456.

(3-Nitrophenyl)(1*H*-pyrrol-1-yl)methanone (1k). Synthesis was carried out according to the general procedure, and compound **1k** was obtained in 80% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (s, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.27 (s, 2H), 6.44 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.2, 148.0, 134.9, 134.8, 129.9, 126.7, 124.3, 121.0, 114.2. These spectral data correspond to previously reported data.[22f]

Naphthalen-1-yl(1*H*-pyrrol-1-yl)methanone (1l). Synthesis was carried out according to the general procedure, and compound **1l** was obtained in 80% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 8.0 Hz, 1H), 7.96–7.92 (m, 2H), 7.67–7.65 (m, 1H), 7.59–7.52 (m, 3H), 7.22 (s, 2H), 6.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.6, 133.4, 131.4, 131.2, 130.4, 128.4, 127.6, 126.9, 126.7, 125.0, 124.4, 121.0, 113.4. These spectral data correspond to previously reported data.[22g]

Naphthalen-2-yl(1*H*-pyrrol-1-yl)methanone (1m). Synthesis was carried out according to the general procedure, and compound **1m** was obtained in 83% yield as a white solid after purification by silica gel column chromatography. mp 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.27 (s, 1H), 7.98–7.92 (m, 3H), 7.82 (d, J = 8.4 Hz, 1H), 7.66–7.58 (m, 2H), 7.36 (s, 2H), 6.39 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.8, 134.9, 132.2, 130.7, 130.4, 129.1, 128.5, 128.4, 127.9, 127.1, 125.5, 121.4, 113.1. These spectral data correspond to previously reported data.[22c]

(1*H*-Pyrrol-1-yl)(thiophen-2-yl)methanone (1n). Synthesis was carried out according to the general procedure, and compound **1n** was obtained in 80% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77–7.76 (m, 1H), 7.72–7.71 (m, 1H), 7.47 (t, J = 2.4 Hz, 2H), 7.20–7.18 (m, 1H), 6.38 (t, J = 2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.6, 135.8, 134.0, 133.3, 127.7, 121.0, 113.2. These spectral data correspond to previously reported data.[22c]

Furan-2-yl(1*H*-pyrrol-1-yl)methanone (1o). Synthesis was carried out according to the general procedure, and compound **1o** was obtained in 82% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69–7.66 (m, 3H), 7.43–7.42 (m, 1H), 6.63–6.62 (m, 1H), 6.36 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.5, 146.7, 146.5, 121.2, 120.7, 113.2, 112.4. These spectral data correspond to previously reported data.[22c]

Methyl 1-benzoyl-1*H*-pyrrole-2-carboxylate (1p). Synthesis was carried out according to the general procedure, and compound **1p** was obtained in 81% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (d, J = 6.8 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.23–7.22 (m, 1H), 7.07–7.06 (m, 1H), 6.30 (t, J = 3.2 Hz, 1H), 3.57 s, (3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.2, 160.6, 133.5, 133.3, 129.8, 128.6, 127.7, 126.0, 121.2, 110.6, 51.5. HRMS (ESI) m/z: calcd for $C_{13}H_{11}NNaO_3$ $[M + Na]^+$: 252.0631, found: 252.0636.

Ethyl 1-benzoyl-2-methyl-1*H*-pyrrole-3-carboxylate (1q). Synthesis was carried out according to the general procedure, and compound **1q** was obtained in 75% yield as a white solid after purification by silica gel column chromatography. mp 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 6.75 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.6 Hz, 1H), 4.31 (q, J = 7.0 Hz, 2H), 2.81 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.3, 164.9, 139.1, 133.4, 133.1, 130.1, 128.6, 121.9, 117.2, 111.2, 60.0, 14.4, 13.4. HRMS (ESI) m/z: calcd for $C_{15}H_{15}NNaO_3$ $[M + Na]^+$: 280.0944, found: 280.0941.

Ethyl 1-benzoyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (1r). Synthesis was carried out according to the general procedure, and compound **1r** was obtained in 79% yield as a yellowish oil after purification by silica gel column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 6.53 (s, 1H), 4.31 (q, J = 7.0 Hz, 2H), 2.77 (s, 3H), 2.16 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.1, 165.6, 139.6, 133.7, 132.8, 129.9, 128.5, 121.6, 120.2, 117.2, 59.8, 14.3, 13.9, 12.5. HRMS (ESI) m/z: calcd for $C_{16}H_{17}NNaO_3$ $[M + Na]^+$: 294.1101, found: 294.1106.

Cyclohexyl(1*H*-pyrrol-1-yl)methanone (1s). Synthesis was carried out according to the general procedure, and compound **1s** was obtained in 80% yield as a white solid after purification by silica gel column chromatography. mp 54–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 (t, J = 2.0 Hz, 2H), 6.29 (t, J = 2.4 Hz, 2H), 2.96–2.89 (m, 1H), 1.97–1.85 (m, 4H), 1.76–1.58 (m, 3H), 1.43–1.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.8, 118.9, 112.9, 42.8, 29.6, 25.6, 25.5. These spectral data correspond to previously reported data.[22e]

Cyclopentyl(1*H*-pyrrol-1-yl)methanone (1t). Synthesis was carried out according to the general procedure, and compound **1t** was obtained in 81% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34(s, 2H), 6.29 (t, J = 2.4 Hz, 2H), 3.42–3.34 (m, 1H), 2.02–1.97 (m, 4H), 1.84–1.75 (m, 2H), 1.72–1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.8, 119.2, 112.8, 43.0, 30.5, 26.1. HRMS (ESI) m/z: calcd for $C_{10}H_{13}NNaO$ $[M + Na]^+$: 186.0889, found: 186.0891.

1-(1*H*-Pyrrol-1-yl)ethan-1-one (1u). Synthesis was carried out according to the general procedure, and compound **1u** was obtained in 82% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (s, 2H), 6.30 (t, J = 2.2 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.7, 119.3, 113.2, 22.3. These spectral data correspond to previously reported data.[22h]

2-Methyl-1-(1*H*-pyrrol-1-yl)prop-2-en-1-one (1v). Synthesis was carried out according to the general procedure, and compound **1v** was obtained in 80% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30 (t, J = 2.2 Hz, 2H), 6.31 (t, J = 2.4 Hz, 2H), 5.70 (d, J = 1.2 Hz, 1H), 5.52 (s, 1H), 2.11 (t, J = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.5, 138.6, 123.0, 120.5, 113.1, 19.8. HRMS (ESI) m/z: calcd for C_8H_9NNaO $[M + Na]^+$: 158.0576, found: 158.0573.

(2,5-Dimethyl-1*H*-pyrrol-1-yl)(phenyl)methanone (1w). Synthesis was carried out according to the general procedure, and compound **1w** was obtained in 80% yield as a yellowish oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 5.87 (s, 2H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.1, 135.6, 133.1, 130.3, 130.1, 128.6, 110.1, 14.6. HRMS (ESI) m/z: calcd for $C_{13}H_{13}NNaO$ $[M + Na]^+$: 222.0889, found: 222.0893.

(1*H*-Indol-1-yl)(phenyl)methanone (7). Synthesis was carried out according to the general procedure, and compound **7** was obtained in 82% yield as a white solid after purification by silica gel column chromatography. mp 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.45 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 6.8 Hz, 2H), 7.62 (t, J = 8.0 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.0 Hz, 1H), 7.35 (d, J = 6.8 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 135.9, 135.0, 131.8, 130.7, 129.1, 128.5, 127.5, 124.8, 123.9, 120.8, 116.3, 108.5. HRMS (ESI) m/z: calcd for $C_{15}H_{11}NNaO$ $[M + Na]^+$: 244.0733, found: 244.0737.

General procedure for direct oxidative coupling between *N*-acyl pyrroles and alkenes

A Schlenk reaction tube equipped with a magnetic stir bar was charged with $[RuCl_2(p\text{-cymene})]_2$ (0.05 equiv., 0.01 mmol), $AgSbF_6$ (0.10 equiv., 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv., 0.20 mmol), *N*-acyl pyrroles **1** (1.0 equiv., 0.2 mmol) and alkenes **2** (2.0 equiv., 0.4 mmol) in toluene (2.0 mL). The tube was sealed under argon and heated to 110 °C with stirring for 24 h. After cooling down, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (ethyl acetate/petroleum ether mixtures).

Butyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3aa). Synthesis was carried out according to the general procedure, and compound **3aa** was obtained in 81% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (d, J = 16.0 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.02–7.01 (m, 1H), 6.84 (d, J = 3.2 Hz, 1H), 6.28–6.24 (m, 2H), 4.16 (t, J = 6.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.45–1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 167.0, 134.1, 133.3, 133.1, 132.2, 130.1, 128.6, 126.6, 116.8, 115.7, 111.9, 64.2, 30.7, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{19}NNaO_3$ $[M + Na]^+$: 320.1257, found 320.1263.

Methyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ab). Synthesis was carried out according to the general procedure, and compound **3ab** was obtained in 76% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.02 (s, 1H), 6.85 (s, 1H), 6.29–6.25 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 167.3, 134.4, 133.2, 133.1, 132.1, 130.1, 128.6, 126.7, 116.3, 115.8, 111.9, 51.5. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}NNaO_3$ $[M + Na]^+$: 278.0788, found 278.0791.

Ethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ac). Synthesis was carried out according to the general procedure, and compound **3ac** was obtained in 79% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.02 (d, J = 2.8 Hz, 1H), 6.85 (d, J = 3.6 Hz, 1H), 6.28–6.24 (m, 2H), 4.22 (q, J = 7.2 Hz, 2H), 1.3 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.8, 166.9, 134.2, 133.4, 133.1, 132.2, 130.1, 128.6, 126.6, 116.9, 115.7, 111.9, 60.3, 14.3. HRMS (ESI) m/z: calcd for $C_{16}H_{15}NNaO_3$ $[M + Na]^+$: 292.0944, found 292.0951.

Cyclohexyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ad). Synthesis was carried out according to the general procedure, and compound **3ad** was obtained in 71% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H

NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.02 (d, J = 2.0 Hz, 1H), 6.84 (d, J = 3.2 Hz, 1H), 6.28–6.24 (m, 2H), 1.89–1.86 (m, 2H), 1.75–1.72 (m, 2H), 1.56–1.23 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.8, 166.3, 133.8, 133.4, 133.1, 132.3, 130.1, 128.6, 126.5, 117.5, 115.6, 111.9, 72.5, 31.7, 25.5, 23.8. HRMS (ESI) m/z: calcd for $C_{20}H_{21}NNaO_3$ $[M + Na]^+$: 346.1414, found 346.1409.

(1*S*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl(*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ae). Synthesis was carried out according to the general procedure, and compound **3ae** was obtained in 51% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.03–7.02 (m, 1H), 6.85 (d, J = 3.2 Hz, 1H), 6.28–6.22 (m, 2H), 4.78–4.75 (m, 1H), 1.87–1.77 (m, 2H), 1.74–1.71 (m, 1H), 1.60–1.52 (m, 2H), 1.25–1.21 (m, 2H), 1.03 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.4, 133.8, 133.5, 133.0, 132.2, 130.0, 128.6, 126.6, 117.5, 115.6, 111.9, 80.9, 48.9, 47.0, 45.1, 38.8, 33.7, 27.1, 20.1, 20.0, 11.5. HRMS (ESI) m/z: calcd for $C_{23}H_{25}NNaO_3$ $[M + Na]^+$: 386.1727, found 386.1731.

Phenyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3af). Synthesis was carried out according to the general procedure, and compound **3af** was obtained in 69% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, J = 16.0 Hz, 1H), 7.78 (d, J = 6.8 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.09–7.07 (m, 1H), 6.97 (d, J = 3.2 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 6.33 (t, J = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 165.3, 150.8, 135.9, 133.2, 133.1, 131.9, 130.1, 129.3, 128.7, 127.1, 125.6, 121.7, 116.5, 115.6, 112.1. HRMS (ESI) m/z: calcd for $C_{20}H_{15}NNaO_3$ $[M + Na]^+$: 340.0944, found 340.0941.

Benzyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ag). Synthesis was carried out according to the general procedure, and compound **3ag** was obtained in 66% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 6.8 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.38–7.33 (m, 5H), 7.04–7.03 (m, 1H), 6.86 (d, J = 3.2 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 6.28 (t, J = 3.4 Hz, 1H), 5.22 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.7, 136.2, 134.7, 133.3, 133.1, 132.1, 130.1, 128.6, 128.5, 128.2, 128.1, 126.7, 116.3, 115.9, 111.9, 66.1. HRMS (ESI) m/z: calcd for $C_{21}H_{17}NNaO_3$ $[M + Na]^+$: 354.1101, found 354.1106.

2-(2-Ethoxyethoxy)ethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ah). Synthesis was carried out according to the general procedure, and compound **3ah** was obtained in 61% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 6.8 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.03–7.02 (m, 1H), 6.85 (d, J = 3.2 Hz, 1H), 6.33–6.27 (m, 2H), 4.34 (t, J = 5.0 Hz, 2H), 3.76 (t, J = 4.8 Hz, 2H), 3.69–3.67 (m, 2H), 3.61–3.59 (m, 2H), 3.53 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.8, 134.6, 133.3, 133.1, 132.2, 130.1, 128.6, 126.7, 116.4, 115.9, 111.9, 70.7, 69.8, 69.3, 66.7, 63.6, 15.1. HRMS (ESI) m/z: calcd for $C_{20}H_{23}NNaO_5$ $[M + Na]^+$: 380.1468, found 380.1491.

2-Methoxyethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3ai). Synthesis was carried out according to the general procedure, and compound **3ai** was obtained in 73% yield as a pale yellow solid after purification by silica gel column chromatography. Mp: 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.03–7.01 (m, 1H), 6.85 (d, J = 3.2 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 6.28 (t, J = 3.4 Hz, 1H), 4.33 (t, J = 4.8 Hz, 2H), 3.65 (t, J = 4.6 Hz, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 166.9, 134.7, 133.3, 133.1, 132.1, 130.1, 128.6, 126.7, 116.3, 115.9, 111.9, 70.6, 63.4, 59.0. HRMS (ESI) m/z: calcd for $C_{17}H_{17}NNaO_4$ $[M + Na]^+$: 322.1050, found 322.1054.

2-Phenoxyethyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3aj). Synthesis was carried out according to the general procedure, and compound **3aj** was obtained in 82% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.04–7.03 (m, 1H), 6.97–6.93 (m, 3H), 6.86 (d, J = 3.2 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 6.28 (t, J = 3.4 Hz, 1H), 4.53 (t, J = 5.0 Hz, 2H), 4.22 (t, J = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 166.8, 158.7, 134.9, 133.2, 133.1, 132.1, 130.1, 129.5, 128.6, 126.7, 121.1, 116.0, 114.6, 111.9, 65.9, 62.7. HRMS (ESI) m/z: calcd for $C_{22}H_{19}NNaO_4$ $[M + Na]^+$: 384.1206, found 384.1201.

(Tetrahydrofuran-2-yl)methyl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl) acrylate (3ak). Synthesis was carried out according to the general procedure, and compound **3ak** was obtained in 80% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, J = 16.0 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.02–7.01 (m, 1H), 6.85 (d, J = 3.6 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 6.27 (t, J = 3.4 Hz, 1H), 4.26–4.23 (m, 1H), 4.20–4.08 (m, 2H), 3.93–3.88 (m, 1H), 3.82–3.78 (m, 1H), 2.06–1.86 (m, 3H), 1.69–1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 166.8, 134.6, 133.3, 133.1, 132.1, 130.0, 128.6, 126.7, 116.3, 115.8, 111.9, 76.6, 68.4, 66.4, 28.0, 25.6. HRMS (ESI) m/z: calcd for $C_{19}H_{19}NNaO_4$ $[M + Na]^+$: 348.1206, found 348.1210.

2,5-Dioxopyrrolidin-1-yl (*E*)-3-(1-benzoyl-1*H*-pyrrol-2-yl)acrylate (3al). Synthesis was carried out according to the general procedure, and compound **3al** was obtained in 54% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.36 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 6.8 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.11–7.10 (m, 1H), 7.02 (d, J = 3.6 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 6.33 (t, J = 3.4 Hz, 1H), 2.86 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.4, 168.5, 162.0, 139.1, 133.3, 133.0, 131.4, 130.1, 128.7, 128.1, 117.8, 112.3, 109.2, 25.6. HRMS (ESI) m/z: calcd for $C_{18}H_{14}N_2NaO_5$ $[M + Na]^+$: 361.0795, found 361.0800.

(*E*)-Phenyl(2-(3-(phenylsulfonyl)prop-1-en-1-yl)-1*H*-pyrrol-1-yl) methanone (3an). Synthesis was carried out according to the general procedure, and compound **3an** was obtained in 70% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.63–7.59 (m, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 6.90 (d, J = 15.6 Hz, 1H), 6.85–6.84 (m, 1H), 6.57 (d, J = 3.2 Hz, 1H), 6.19 (t, J = 3.4 Hz, 1H), 6.00–5.93 (m, 1H), 3.95–3.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.0, 138.5, 133.7, 133.6, 133.2, 132.8, 129.9, 129.6, 129.1, 128.5, 128.4, 124.7, 114.3, 113.0, 111.5, 60.6. HRMS (ESI) m/z: calcd for $C_{20}H_{17}NNaO_3S$ $[M + Na]^+$: 374.0821, found 374.0823.

(*E*)-3-(1-Benzoyl-1*H*-pyrrol-2-yl)acrylonitrile (3ao). Synthesis was carried out according to the general procedure, and compound **3ao** was obtained in 66% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, J = 16.4 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.06–7.05 (m, 1H), 6.86 (d, J = 3.6 Hz, 1H), 6.29 (t, J = 3.4 Hz, 1H), 5.70 (d, J = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.7, 140.0, 133.3, 132.9, 131.2, 130.0, 128.7, 127.5, 118.5, 116.0, 112.1, 94.0. HRMS (ESI) m/z: calcd for $C_{14}H_{10}N_2NaO$ $[M + Na]^+$: 245.0685, found 245.0689.

Butyl (*E*)-3-(1-(4-ethylbenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ba). Synthesis was carried out according to the general procedure, and compound **3ba** was obtained in 73% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 1.6 Hz, 1H), 6.83 (d, J = 2.8 Hz, 1H), 6.27–6.23 (m, 2H), 4.16 (t, J = 6.6 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.45–1.35 (m, 2H), 1.28 (t, J = 7.6 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.6, 167.0, 150.2, 134.1, 132.0, 130.6, 130.4, 128.1, 126.6, 115.5, 111.6, 64.1, 30.7, 28.9, 19.1, 15.1, 13.7. HRMS (ESI) m/z: calcd for $C_{20}H_{23}NNaO_3$ $[M + Na]^+$: 348.1570, found 348.1573.

Butyl (*E*)-3-(1-(4-methoxybenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ca). Synthesis was carried out according to the general procedure, and compound **3ca** was obtained in 69% yield as a pale yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, J = 16.0 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 3.2 Hz, 1H), 6.28–6.23 (m, 2H), 4.16 (t, J = 6.6 Hz, 2H), 3.89 (s, 3H), 1.68–1.61 (m, 2H), 1.44–1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.0, 167.1, 163.7, 134.0, 132.7, 132.0, 126.5, 125.3, 116.4, 115.3, 113.9, 111.5, 64.2, 55.6, 30.7, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{19}H_{21}NNaO_4$ $[M + Na]^+$: 350.1363, found 350.1366.

Butyl (*E*)-3-(1-(2-methylbenzoyl)-1*H*-pyrrol-2-yl)acrylate (3da). Synthesis was carried out according to the general procedure, and compound **3da** was obtained in 71% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.19 (d, J = 16.0 Hz, 1H), 7.45–7.41 (m, 1H), 7.37 (d, J = 6.8 Hz, 1H), 7.29 (t, J = 6.6 Hz, 2H), 6.81 (t, J = 2.8 Hz, 2H), 6.27 (d, J = 16.0 Hz, 1H), 6.22 (t, J = 3.4 Hz, 1H), 4.17 (t, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.70–1.63 (m, 2H), 1.46–1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.4, 167.0, 136.9, 134.3, 133.9, 132.0, 131.2, 131.0, 128.2, 126.1, 125.7, 117.2, 116.0, 112.3, 64.2, 30.7, 19.4, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{19}H_{21}NNaO_3$ $[M + Na]^+$: 334.1414, found 334.1410.

Butyl (*E*)-3-(1-(4-iodobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ea). Synthesis was carried out according to the general procedure, and compound **3ea** was obtained in 72% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, J = 16.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 6.98–6.97 (m, 1H), 6.84 (d, J = 3.2 Hz, 1H), 6.29–6.24 (m, 2H), 4.17 (t, J = 6.8 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.0, 166.9, 137.9, 133.8, 132.6, 132.2, 131.3, 126.2, 117.1, 115.8, 112.2, 100.8, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) m/z: Calcd for $C_{18}H_{18}INNaO_3$ $[M + Na]^+$: 446.0224, found 446.0220.

Butyl (*E*)-3-(1-(4-bromobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3fa). Synthesis was carried out according to the general procedure, and compound **3fa** was obtained in 70% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, J = 16.0 Hz, 1H), 7.67–7.62 (m, 4H), 6.97 (d, J = 2.4 Hz, 1H), 6.84 (d, J = 3.2 Hz, 1H), 6.29–6.24 (m, 2H), 4.16 (t, J = 6.6 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.35 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.7, 166.9, 133.8, 132.2, 132.1, 132.0, 131.5, 128.2, 126.2, 117.1, 115.8, 112.2, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{18}BrNNaO_3$ $[M + Na]^+$: 398.0362, found 398.0366.

Butyl (*E*)-3-(1-(3-bromobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ga). Synthesis was carried out according to the general procedure, and compound **3ga** was obtained in 73% yield as a pale yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, J = 16.0 Hz, 1H), 7.89 (t, J = 1.8 Hz, 1H), 7.77–7.74 (m, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 6.99–6.98 (m, 1H), 6.85 (d, J = 3.6 Hz, 1H), 6.30–6.25 (m, 2H), 4.17 (t, J = 6.6 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.1, 166.9, 136.0, 135.2, 133.8, 132.8, 132.3, 130.1, 128.5, 126.2, 122.7, 117.2, 116.0, 112.4, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{18}BrNNaO_3$ $[M + Na]^+$: 398.0362, found 398.0360.

Butyl (*E*)-3-(1-(4-chlorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ha). Synthesis was carried out according to the general procedure, and compound **3ha** was obtained in 78% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, J = 16.0 Hz, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 6.99–6.98 (m, 1H), 6.85 (d, J = 3.2 Hz, 1H), 6.30–6.24 (m, 2H), 4.17 (t, J = 6.8 Hz, 2H), 1.69–1.62 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.6, 166.9, 139.7, 133.8, 132.2, 131.6, 131.5, 129.0, 126.2, 117.1, 115.8, 112.2, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{18}ClNNaO_3$ $[M + Na]^+$: 354.0867, found 354.0863.

Butyl (*E*)-3-(1-(3-fluorobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ia). Synthesis was carried out according to the general procedure, and compound **3ia** was obtained in 80% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, J = 16.0 Hz, 1H), 7.56–7.46 (m, 3H), 7.37–7.32 (m, 1H), 7.01–7.00 (m, 1H), 6.86 (d, J = 3.2 Hz, 1H), 6.31–6.25 (m, 2H), 4.18 (t, J = 6.6 Hz, 2H), 1.70–1.63 (m, 2H), 1.46–1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.4, 166.9, 163.6, 161.1, 135.4, 135.3, 133.9, 132.3, 130.5, 130.4, 126.3, 125.8, 125.7, 120.3, 120.1, 117.2, 117.1, 116.9, 116.0, 112.3, 64.3, 30.8, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{18}FNNaO_3$ $[M + Na]^+$: 338.1163, found 338.1160.

Butyl (*E*)-3-(1-(4-(trifluoromethyl)benzoyl)-1*H*-pyrrol-2-yl) acrylate (3ja). Synthesis was carried out according to the general procedure, and compound **3ja** was obtained in 76% yield as a pale yellow solid after purification by silica gel column chromatography. Mp: 38–39 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, J = 16.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 6.94–6.93 (m, 1H), 6.86 (d, J = 3.2 Hz, 1H), 6.31–6.27 (m, 2H), 4.18 (t, J = 6.8 Hz, 2H), 1.70–1.62 (m, 2H), 1.46–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.5, 166.8, 136.7, 134.6, 134.3, 133.8, 132.5, 130.2, 126.1, 125.7, 125.7, 125.6, 125.6, 124.7, 122.0, 117.5, 116.1, 112.6, 64.3, 30.7, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{19}H_{18}F_3NNaO_3$ $[M + Na]^+$: 388.1131, found 388.1133.

Butyl (*E*)-3-(1-(3-nitrobenzoyl)-1*H*-pyrrol-2-yl)acrylate (3ka). Synthesis was carried out according to the general procedure, and compound **3ka** was obtained in 79% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.60 (t, J = 1.8 Hz, 1H), 8.51–8.48 (m, 1H), 8.11–8.09 (m, 1H), 8.04 (d, J = 16.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 6.95–6.94 (m, 1H), 6.89 (d, J = 3.2 Hz, 1H), 6.35 (t, J = 3.4 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.8 Hz, 2H), 1.70–1.62 (m, 2H), 1.46–1.36 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.8, 166.3, 148.1, 135.4, 135.0, 133.5, 132.6, 130.0, 127.4, 125.8, 124.8, 117.8, 116.3, 113.1, 64.4, 30.7, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{18}N_2NaO_5$ $[M + Na]^+$: 365.1108, found 365.1106.

Butyl (*E*)-3-(1-(1-naphthoyl)-1*H*-pyrrol-2-yl)acrylate (3la). Synthesis was carried out according to the general procedure, and compound **3la** was obtained in 74% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.29 (d, J = 16.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.98–7.92 (m, 2H), 7.67–7.65 (m, 1H), 7.57–7.52 (m, 3H), 6.86 (d, J = 3.2 Hz, 1H), 6.81–6.80 (m, 1H), 6.31 (d, J = 16.0 Hz, 1H), 6.20 (t, J = 3.4 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 1.70–1.63 (m, 2H), 1.46–1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.9, 166.9, 134.4, 133.5, 132.3, 132.2, 131.4, 130.5, 128.5, 127.8, 127.7, 126.9, 126.6, 124.7, 124.4, 117.3, 116.1, 112.3, 64.3, 30.7, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{22}H_{21}NNaO_3$ $[M + Na]^+$: 370.1414, found 370.1410.

Butyl (*E*)-3-(1-(2-naphthoyl)-1*H*-pyrrol-2-yl)acrylate (3ma). Synthesis was carried out according to the general procedure, and compound **3ma** was obtained in 73% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (s, 1H), 8.10 (d, J = 16.0 Hz, 1H), 7.97–7.92 (m, 3H), 7.84–7.81 (m, 1H), 7.67–7.58 (m, 2H), 7.10–7.09 (m, 1H), 6.89 (d, J = 2.8 Hz, 1H), 6.32–6.28 (m, 2H), 4.16 (t, J = 6.6 Hz, 2H), 1.67–1.60 (m, 2H), 1.43–1.34 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.8, 167.0, 135.3, 134.1, 132.3, 132.1, 131.7, 130.4, 129.2, 128.8, 128.6, 127.9, 127.2, 126.7, 125.6, 116.8, 115.7, 111.9, 64.2, 30.7, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{22}H_{21}NNaO_3$ $[M + Na]^+$: 370.1414, found 370.1411.

Butyl (*E*)-3-(1-(thiophene-2-carbonyl)-1*H*-pyrrol-2-yl)acrylate (3na). Synthesis was carried out according to the general procedure, and compound **3na** was obtained in 36% yield as a pale orange oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, J = 16.0 Hz, 1H), 7.78–7.77 (m, 1H), 7.71–7.70 (m, 1H), 7.34–7.33 (m, 1H), 7.20–7.18 (m, 1H), 6.85 (d, J = 3.6 Hz, 1H), 6.32 (t, J = 3.6 Hz, 1H), 6.26 (d, J = 16.0 Hz, 1H), 4.17 (t, J = 6.8 Hz, 2H), 1.69–1.63 (m, 2H), 1.45–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.0, 161.7, 136.6, 135.2, 134.8, 133.7, 132.0, 128.0, 126.0, 116.8, 115.5, 112.0, 64.3, 30.7, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{16}H_{17}NNaO_3S$ $[M + Na]^+$: 326.0821, found 326.0823.

Methyl (*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-1*H*-pyrrole-2-carboxylate (3pa). Synthesis was carried out according to the general procedure, and compound **3pa** was obtained in 75% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63–7.59 (m, 3H), 7.45 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 15.6 Hz, 1H), 7.03 (d, J = 4.0 Hz, 1H), 6.77 (d, J = 4.0 Hz, 1H), 6.33 (d, J = 15.6 Hz, 1H), 4.11 (t, J = 6.8 Hz, 2H), 3.61 (s, 3H), 1.64–1.57 (m, 2H), 1.39–1.30 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.5, 166.2, 160.1, 135.1, 134.6, 133.8, 130.9, 129.8, 129.0, 127.4, 119.9, 118.3, 111.5, 64.5, 51.8, 30.6, 19.0, 13.6. HRMS (ESI) m/z: calcd for $C_{20}H_{21}NNaO_5$ $[M + Na]^+$: 378.1312, found 378.1316.

Ethyl (*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (3qa). Synthesis was carried out according to the general procedure, and compound **3qa** was obtained in 79% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68–7.64 (m, 3H), 7.48 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 15.6 Hz, 1H), 7.09 (s, 1H), 6.06 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.0 Hz, 2H), 4.04 (t, J = 6.6 Hz, 2H), 3.45 (s, 3H), 1.58–1.51 (m, 2H), 1.36 (t, J = 7.0 Hz, 3H), 1.32–1.25 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.8, 166.6, 164.3, 139.9, 135.1, 133.2, 132.1, 130.7, 129.3, 129.2, 115.9, 115.6, 113.8, 64.1, 60.1, 30.6, 19.0, 14.3, 13.6, 13.0. HRMS (ESI) m/z: calcd for $C_{22}H_{25}NNaO_5$ $[M + Na]^+$: 406.1625, found 406.1629.

Ethyl (*E*)-1-benzoyl-5-(3-butoxy-3-oxoprop-1-en-1-yl)-2,4-dimethyl-1*H*-pyrrole-3-carboxylate (3ra). Synthesis was carried out according to the general procedure, and compound **3ra** was obtained in 73% yield as a yellow oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$)

δ (ppm): 7.67–7.63 (m, 3H), 7.46 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 16.0 Hz, 1H),5.69 (d, J = 16.4 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.04 (t, J = 6.6 Hz, 2H), 2.43 (d, J = 2.8 Hz, 6H), 1.59–1.52 (m, 2H), 1.38 (t, J = 7.0 Hz, 3H), 1.34–1.27 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.8, 167.0, 165.2, 140.3, 135.0, 133.3, 131.4, 130.6, 129.2, 127.8, 119.1, 115.5, 115.3, 64.2, 60.0, 30.6, 19.1, 14.4, 13.7, 13.2, 12.1. HRMS (ESI) m/z: calcd for $C_{23}H_{27}NNaO_5$ $[M + Na]^+$: 420.1781, found 420.1787.

Butyl (*E*)-3-(1-(cyclohexanecarbonyl)-1*H*-pyrrol-2-yl)acrylate (3sa). Synthesis was carried out according to the general procedure, and compound **3sa** was obtained in 71% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (d, J = 16.0 Hz, 1H), 7.28–7.27 (m, 1H), 6.70 (d, J = 4.0 Hz, 1H), 6.28 (t, J = 3.4 Hz, 1H), 6.20 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 2.96–2.91 (m, 1H), 1.98–1.94 (m, 2H), 1.89–1.85 (m, 2H), 1.69–1.64 (m, 4H), 1.44–1.39 (m, 6H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.5, 167.1, 135.5, 132.1, 123.0, 117.3, 115.3, 112.5, 64.2, 44.1, 30.8, 29.6, 25.6, 25.5, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{18}H_{25}NNaO_3$ $[M + Na]^+$: 326.1727, found 326.1730.

Butyl (*E*)-3-(1-(cyclopentanecarbonyl)-1*H*-pyrrol-2-yl)acrylate (3ta). Synthesis was carried out according to the general procedure, and compound **3ta** was obtained in 73% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (d, J = 16.0 Hz, 1H), 7.30–7.29 (m, 1H), 6.69 (d, J = 3.6 Hz, 1H), 6.27 (t, J = 3.4 Hz, 1H), 6.20 (d, J = 16.0 Hz, 1H), 4.17 (t, J = 6.8 Hz, 2H), 3.43–3.35 (m, 1H), 2.01–1.96 (m, 4H), 1.83–1.75 (m, 2H), 1.70–1.63 (m, 4H), 1.46–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.5, 167.0, 135.5, 132.2, 123.3, 117.2, 115.2, 112.4, 64.2, 44.3, 30.8, 30.6, 26.1, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{17}H_{23}NNaO_3$ $[M + Na]^+$: 312.1570, found 312.1573.

Butyl (*E*)-3-(1-acetyl-1*H*-pyrrol-2-yl)acrylate (3ua). Synthesis was carried out according to the general procedure, and compound **3ua** was obtained in 76% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.32 (d, J = 16.0 Hz, 1H), 7.21–7.20 (m, 1H), 6.71 (d, J = 3.2 Hz, 1H), 6.28 (t, J = 3.4 Hz, 1H), 6.22 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.8 Hz, 2H), 2.59 (s, 3H), 1.71–1.63 (m, 2H), 1.47–1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.2, 167.0, 135.1, 132.2, 123.8, 117.6, 115.4, 112.8, 64.3, 30.8, 24.2, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{13}H_{17}NNaO_3$ $[M + Na]^+$: 258.1101, found 258.1103.

Butyl (*E*)-3-(1-methacryloyl-1*H*-pyrrol-2-yl)acrylate (3va). Synthesis was carried out according to the general procedure, and compound **3va** was obtained in 79% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.04 (d, J = 16.0 Hz, 1H), 7.18–7.17 (m, 1H), 6.80 (d, J = 3.2 Hz, 1H), 6.25 (t, J = 3.4 Hz, 1H), 6.22 (d, J = 16.0 Hz, 1H), 5.80 (d, J = 1.6 Hz, 1H), 5.59 (s, 1H), 4.18 (t, J = 6.8 Hz, 2H), 2.12 (s, 3H), 1.71–1.63 (m, 2H), 1.47–1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.7, 167.0, 139.5, 134.2, 131.7, 125.9, 125.5, 116.7, 115.8, 111.8, 64.3, 30.8, 19.4, 19.2, 13.7. HRMS (ESI) m/z: calcd for $C_{15}H_{19}NNaO_3$ $[M + Na]^+$: 284.1257, found 284.1254.

1-(1-Benzoyl-1*H*-pyrrol-2-yl)pentan-3-one (4aq). Synthesis was carried out according to the general procedure, and compound **4aq** was obtained in 56% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 6.77 (t, J = 2.4 Hz, 1H), 6.11 (d, J = 2.8 Hz, 2H), 3.24 (t, J = 7.4 Hz, 2H), 2.82 (t, J = 7.4 Hz, 2H), 2.45 (q, J = 7.2 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 210.6, 169.3, 136.0, 134.3, 132.3, 129.7, 128.4, 123.4, 112.8, 110.6, 42.1, 35.9, 23.0, 7.8. HRMS (ESI) m/z: calcd for $C_{16}H_{17}NNaO_2$ $[M + Na]^+$: 278.1151, found 278.1154.

3-(1-Benzoyl-1H-pyrrol-2-yl)-1-cyclohexylpropan-1-one (4ar). Synthesis was carried out according to the general procedure, and compound **4ar** was obtained in 51% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, J = 6.8 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 6.77 (t, J = 2.6 Hz, 1H), 6.10 (d, J = 2.8 Hz, 2H), 3.21 (t, J = 7.4 Hz, 2H), 2.85 (t, J = 7.4 Hz, 2H), 2.39–2.32 (m, 1H), 1.85–1.75 (m, 4H), 1.38–1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 213.1, 169.3, 136.2, 134.3, 132.3, 129.7, 128.4, 123.4, 112.8, 110.5, 50.8, 40.4, 28.4, 25.8, 25.7, 22.9. HRMS (ESI) m/z: calcd for $C_{20}H_{23}NNaO_2$ $[M + Na]^+$: 332.1621, found 332.1616.

Dibutyl 3,3′-(1-benzoyl-1*H*-pyrrole-2,5-diyl)(2*E*,2′*E*)-diacrylate (6aa). Synthesis was carried out according to the general procedure, and compound **6aa** was obtained in 61% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70–7.65 (m, 3H), 7.49 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 16.0 Hz, 2H), 6.82 (s, 2H), 6.18 (d, J = 16.0 Hz, 2H), 4.08 (t, J = 6.6 Hz, 4H), 1.61–1.54 (m, 4H), 1.37–1.28 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.2, 166.5, 135.0, 134.0, 133.6, 132.0, 130.8, 129.1, 117.4, 114.0, 64.3, 30.6, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{25}H_{29}NNaO_5$ $[M + Na]^+$: 446.1938, found 446.1932.

Butyl (*E*)-3-(1-benzoyl-1*H*-indol-2-yl)acrylate (8aa). Synthesis was carried out according to the general procedure, and compound **8aa** was obtained in 80% yield as a colorless oil after purification by silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, J = 7.6 Hz, 2H), 7.67–7.60 (m, 2H), 7.52–7.47 (m, 3H), 7.34 (d, J = 8.0 Hz, 1H), 7.26–7.18 (m, 2H), 7.10 (s, 1H), 6.33 (d, J = 16.0 Hz, 1H), 4.12 (t, J = 6.8 Hz, 2H), 1.64–1.57 (m, 2H), 1.41–1.31 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.2, 166.2, 138.2, 136.1, 134.8, 134.3, 133.4, 130.1, 128.9, 128.7, 125.4, 123.4, 121.3, 119.0, 114.6, 110.7, 64.4, 30.6, 19.1, 13.7. HRMS (ESI) m/z: calcd for $C_{22}H_{21}NNaO_3$ $[M + Na]^+$: 370.1414, found: 370.1410.

Conflicts of interest

There are no conflicts to declare.

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