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Functionalized 4-Carboxy- and 4-Keto-2,3-dihydropyrroles via Ni(II)-Catalyzed Nucleophilic Amine Ring-Opening Cyclizations of Cyclopropanes

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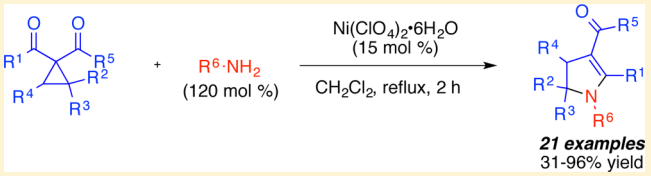
Supporting Information

ABSTRACT: A general synthetic approach to vinylogous 4-carboxy- and 4-keto-2,3-dihydropyrroles is reported using $Ni(ClO_4)_2{\cdot}6H_2O$ as a Lewis acid catalyst for nucleophilic amine ring-opening cyclizations of donor–acceptor (D–A) cyclopropanes. This methodology provided good to excellent yields of functionalized 2,3-dihydropyrroles under milder reaction conditions than previously reported and is amenable to a variety of D–A cyclopropanes and primary amines.



INTRODUCTION

Among nitrogen-containing five-membered heterocycles, 2,3-dihydropyrroles[1,2] (**1**) have garnered significant attention in the literature because of their presence in various natural products and pharmaceutically relevant compounds (Figure 1).[3] They

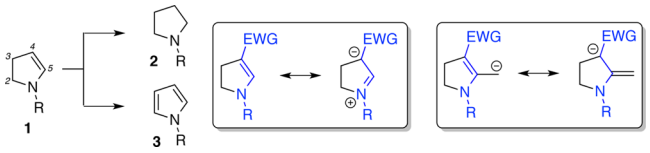


Figure 1. Reactivity of 2,3-dihydropyrroles.

are also extremely versatile synthetic building blocks for the preparation of functionalized pyrrolidines[4] (**2**, their fully reduced counterparts) and pyrroles[5] (**3**, their fully oxidized counterparts). 2,3-Dihydropyrroles can be readily exploited for further functionalization because of the presence of the enamine moiety. Moreover, when an electron-withdrawing group is substituted at the 4-position on the dihydropyrrole, extended conjugation with the enamine is observed, and vinylogous reactivity is possible.

Surprisingly, this type of reactivity has not been reported for dihydropyrroles in the synthetic literature. Thus, at the start of this project, we aimed to address this gap in knowledge by studying the reactivity of vinylogous 2,3-dihydropyrroles. However, we were surprised to find that despite the numerous reported synthetic efforts toward 2,3-dihydropyrroles[6−11] general methods that access vinylogous dihydropyrroles are limited to a handful of examples.[9b,12]

The most general approach to 2,3-dihydropyrroles bearing electron-withdrawing groups in the 4-position involves ring-opening cyclizations of cyclopropyl ketones in the presence of primary amines (Figure 2). Lhommet first reported this approach for donor–acceptor (D–A) cyclopropanes derived

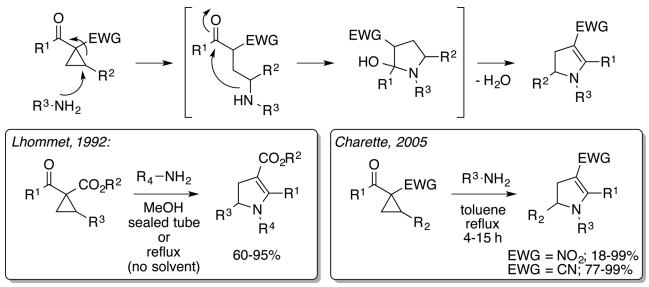


Figure 2. Amine ring-opening cyclizations of cyclopropanes to form 2,3-dihydropyrroles.

from β-ketoesters.[12a] The reactions gave 4-carboxy-dihydropyrroles in modest to good yields but were performed in refluxing methanol in sealed tubes for up to 24 h or using the amine as solvent under reflux (>140 °C) for up to 8 h. Charette reported the use of D–A cyclopropanes derived from α-nitro ketones and α-cyano ketones for the formation of 4-nitro- and 4-cyano-dihydropyrroles, respectively.[12c]

Over the past 5 years, our group has reported several examples of Lewis acid-catalyzed intramolecular ring-opening cyclizations of doubly activated D–A cyclopropanes derived from 1,3-dicarbonyl compounds.[13] Lewis acids have recently been shown to promote ring-opening reactions of D–A cyclopropanes in the presence of amines under milder conditions. In representative examples by Charette[14] and Tang,[15] $Ni(ClO_4)_2{\cdot}6H_2O$ effectively promotes the ring-opening reactions of secondary amines with malonate-derived D–A cyclopropanes to give homoconjugate addition products. As an expansion of our work, we envisaged a milder approach to 4-carboxy-dihydropyrroles via primary amine ring-opening

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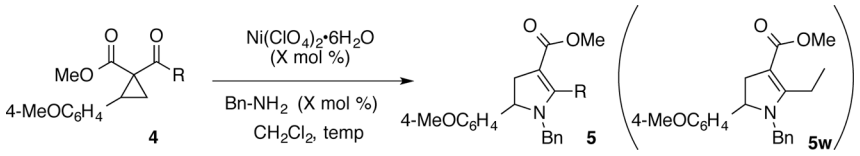
Table 1. Reaction Optimization[a]



entry	R	loading	amine	temp	time (h)	% yield[b]
1	2-propenyl (**4a**)	30 mol %	250 mol %	rt	3	89
2	2-propenyl (**4a**)	30 mol %	200 mol %	rt	3	60
3	2-propenyl (**4a**)	30 mol %	120 mol %	rt	3	50
4	2-propenyl (**4a**)	20 mol %	250 mol %	rt	6	67
5	2-propenyl (**4a**)	15 mol %	250 mol %	rt	>16	50
6	2-propenyl (**4a**)	15 mol %	250 mol %	reflux	1	65[c]
7	2-propenyl (**4a**)	15 mol %	200 mol %	reflux	1	67[c]
8	**2-propenyl (4a)**	**15 mol %**	**120 mol %**	**reflux**	**2**	**80**[c]
9	2-propenyl (**4a**)	5 mol %	250 mol %	reflux	2	47[c]
10	2-propenyl (**4a**)	5 mol %	200 mol %	reflux	2	56[c]
11	phenyl (**4b**)	30 mol %	250 mol %	rt	2	77
12	phenyl (**4b**)	15 mol %	200 mol %	rt	>16	52
13	phenyl (**4b**)	15 mol %	200 mol %	reflux	11	70
14	**phenyl (4b)**	**15 mol %**	**120 mol %**	**reflux**	**2**	**83**

[a]Reactions run with cyclopropane (1 equiv), benzyl amine, and $Ni(ClO_4)_2·6H_2O$ in CH_2Cl_2 according to conditions indicated. [b]Isolated yield after column chromatography. [c]Variable amounts of **5w** were observed.

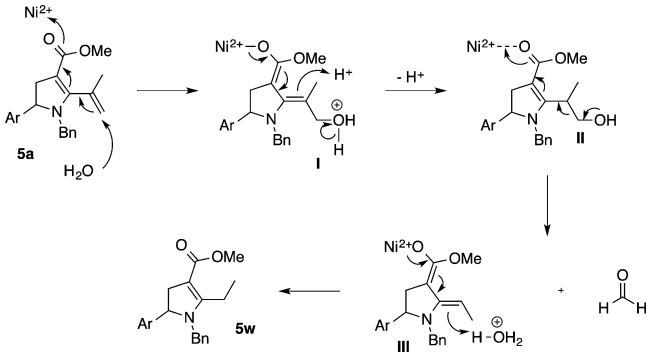
cyclizations of D−A cyclopropanes in the presence of a Lewis acid catalyst. In this article, we report the results of our studies.

RESULTS AND DISCUSSION

Using our previous work as a starting point,[13a] our studies began with alkenyl cyclopropyl ketone **4a** as the model substrate. $Ni(ClO_4)_2·6H_2O$ was selected as the Lewis acid to initiate the reaction optimization because of its demonstrated success in amine-mediated cyclopropane ring-openings.[14,15] Upon treatment of cyclopropane **4a** and benzyl amine (2.5 equiv) in CH_2Cl_2 with $Ni(ClO_4)_2·6H_2O$ (30 mol %) at room temperature, dihydropyrrole **5a** was obtained in 89% yield after 3 h (Table 1, entry 1). Next, the amount of amine was reduced to improve atom economy and overall reaction efficiency. At both 2.0 and 1.2 equiv of benzylamine, decreased product yields were observed (entries 2 and 3). Upon lowering the catalyst loading to 20 mol %, dihydropyrrole **5a** was obtained in 67% yield after 6 h (entry 4). At 15 mol % catalyst, the reaction gave a 50% yield, although it failed to go to completion even after more than 16 h (entry 5). To push the reaction to completion, the reaction was heated at reflux. Within 1 h, the reaction was complete. When the reaction with 15 mol % $Ni(ClO_4)_2·6H_2O$ was set up in CH_2Cl_2 at reflux from the beginning, the reaction was completed within 1 h to give **5a** in 65% yield (entry 6). When the amount of amine was reduced to 2.0 and 1.2 equiv while employing the refluxing conditions, yields of 67 and 80% were obtained within 1 to 2 h (entries 7 and 8).[16] Any attempts to reduce the catalyst loading below 15 mol % failed to provide good product yields (entries 9 and 10). Similarly, changing the solvent has a deleterious effect on overall reaction efficiency and product yields.[17] Thus, the optimum conditions were 15 mol % of $Ni(ClO_4)_2·6H_2O$ with 1.2 equiv of benzylamine in refluxing CH_2Cl_2 or 1,2-dichloroethane.

Unfortunately, variable amounts of the unexpected side product **5w** were observed in all of the reactions at reflux, which accounted for the reduced yields (entries 6−10). As **5a** is an extended Michael acceptor, it is plausible that a molecule of water can undergo a 1,6-addition[18] into the extended π-system (Scheme 1). Proton transfer and isomerization generates

Scheme 1. Proposed Mechanism for Formation of Dihydropyrrole 5w



alcohol **II**, which undergoes loss of formaldehyde and protonation to give side product **5w**.[19] To alleviate this side product issue, the model substrate was changed to cyclopropyl phenyl ketone **4b**. At 30 mol % of $Ni(ClO_4)_2·6H_2O$ with 2.5 equiv of benzylamine, dihydropyrrole **5b** was obtained in 77% yield (Table 1, entry 11). Further experimentation determined the optimal conditions to be 15 mol % of $Ni(ClO_4)_2·6H_2O$ and 1.2 equiv of benzylamine in CH_2Cl_2 at reflux. This gave desired dihydropyrrole **5b** in 83% yield after 2 h (entry 14).

Next, a variety of Lewis acids were screened to find the optimal Lewis acid catalyst (Table 2). Anhydrous $Ni(OTf)_2$ was employed to probe the importance of the water ligands. A reduced yield of 58% was obtained (entry 2). This result supports the catalytic role of the nickel but also suggests the importance of the water for amine exchange. As with Ni(II) hydrates, copper(II) hydrates are known to complex with amines by displacing water molecules.[20] However, when $Cu(ClO_4)_2·6H_2O$ was used as the catalyst, a meager 31% yield was obtained (entry 3). To rule out the possibility that the

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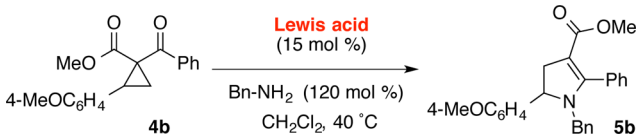
Table 2. Lewis Acid Screening[a]



entry	Lewis acid	time (h)	% yield[b]
1	**$Ni(ClO_4)_2{\cdot}6H_2O$**	**2**	**83**
2	$Ni(OTf)_2$	3	58
3	$Cu(ClO_4)_2{\cdot}6H_2O$	3	31
4	$Li(ClO_4){\cdot}3H_2O$	>16	14
5	$Sc(OTf)_3$	>16	27
6	$In(OTf)_3$	>16	17
7	$Al(OTf)_3$	>16	8
8	$Mg(OTf)_2$	>16	6
9	$Zn(OTf)_2$	>16	5

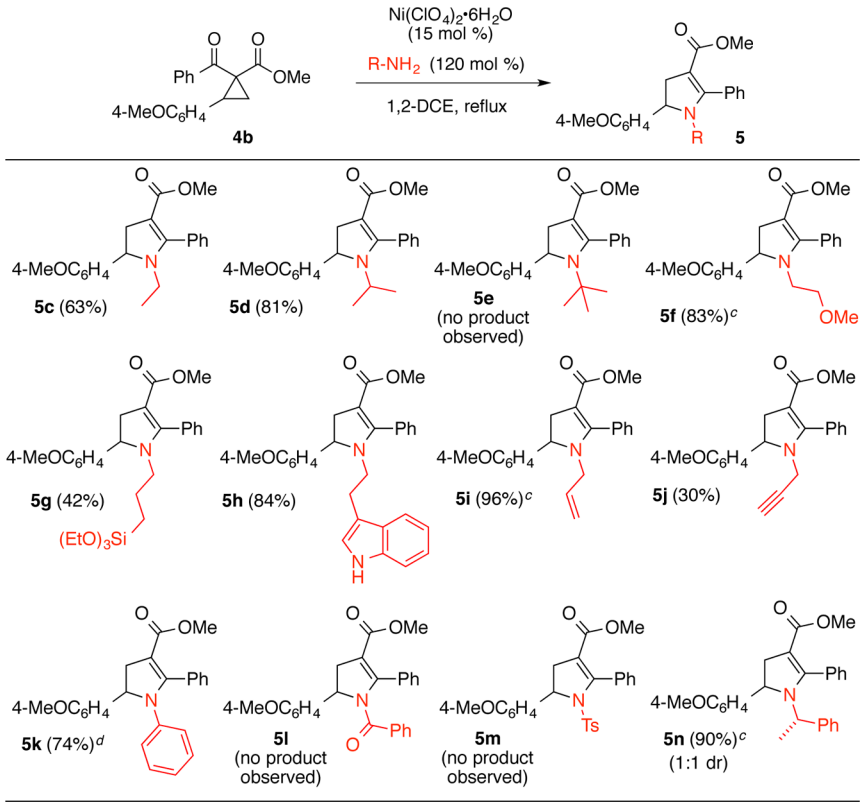
[a]Reactions run with cyclopropane (1 equiv), benzylamine (1.2 equiv), and Lewis acid (15 mol %) in CH_2Cl_2 under reflux. [b]Isolated yields after column chromatography.

ligand is responsible for the observed catalysis, $Li(ClO_4){\cdot}3H_2O$ was employed but only gave 14% yield of **5b** (entry 4). All other catalyst systems (Sc^{3+}, In^{3+}, Al^{3+}, Mg^{2+}, and Zn^{2+}) proved to be highly ineffective, most likely to catalyst deactivation upon amine complexation (entries 5–9). Thus, $Ni(ClO_4)_2{\cdot}6H_2O$ remained the most effective Lewis acid catalyst for this transformation.[21]

To explore reaction generality, other primary amines were employed under the optimized conditions with cyclopropane **4b** (Table 3). Alkyl amines such as ethylamine and isopropylamine readily reacted with **4b** to give dihydropyrroles **5c** and **5d** in 63 and 81%, respectively.[22] However, no reaction to give **5e** was observed with *tert*-butyl amine, which is presumably the result of unfavorable steric interactions that preclude nucleophilic attack. Other functionalized aliphatic amines such as 2-methoxyethan-1-amine and 3-(triethoxysilyl)propan-1-amine also provided their respective dihydropyrroles, **5f** and **5g**, in 83 and 42% yields. Similarly, unprotected tryptamine provided **5h** in 84% yield. Allylamine provided dihydropyrrole **5i** in 96% yield, whereas propargylamine afforded only 30% of **5j** along with a number of byproducts. The poor reaction efficiency is most likely because of competing reactions resulting from coordination of the alkyne π-system with the Ni catalyst.[23] This coordination can influence the electrophilicity of the alkyne π-system as well as reduce the pK_a of the alkynyl hydrogen. Aniline proved to be amenable to the transformation, although the reaction had to be performed at higher temperatures for full conversion to give *N*-aryl dihydropyrrole **5k** in 74% yield. Amines bearing strong electron-withdrawing groups (e.g., acetamide and tosamide) failed to give any measurable dihydropyrrole products even at elevated temperatures because of reduced nucleophilicity.

A chiral amine was also employed in hopes of imparting some diastereocontrol. Disappointingly, when **4b** was treated with (*S*)-1-phenylethan-1-amine, dihydropyrrole **5n** was obtained as a 1:1 diastereomeric mixture in 90% yield. The poor observed selectivity is most likely due to an S_N1-like ring-opening that generates a transient carbocation prior to unbiased nucleophilic attack.

Table 3. Primary Amine Screening[a,b]



[a]Reactions run with cyclopropane (1 equiv), amine (1.2 equiv), and $Ni(ClO_4)_2{\cdot}6H_2O$ (15 mol %) in 1,2-dichloroethane at reflux. [b]Numbers in parentheses represent isolated yields after column chromatography. [c]Reaction run in CH_2Cl_2 under reflux. [d]Reaction run in toluene under reflux.

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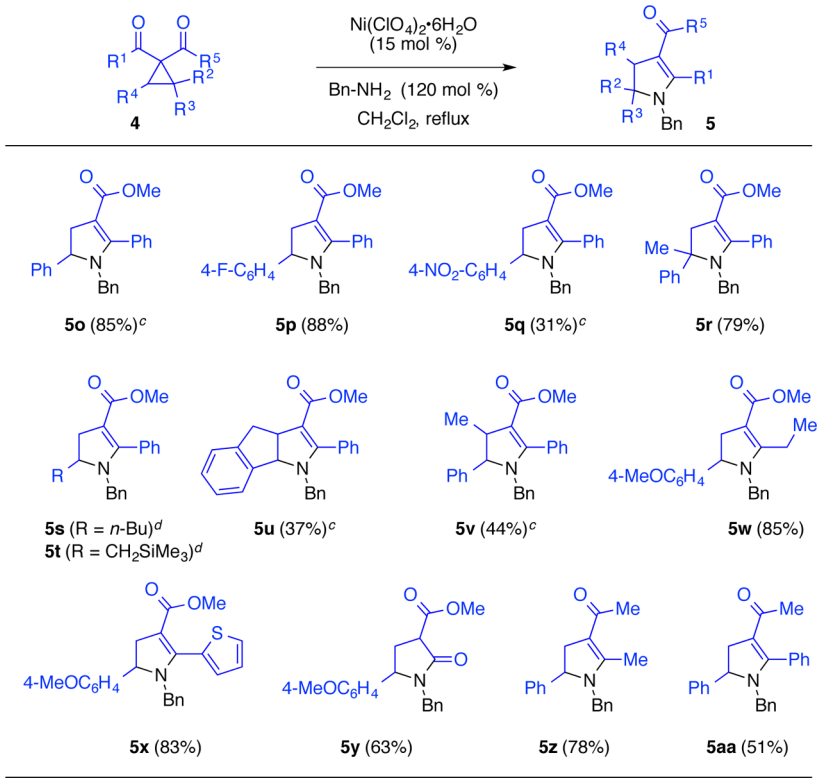
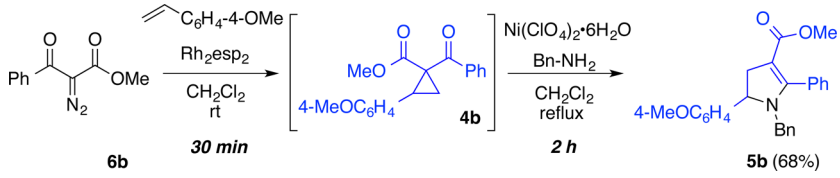
Table 4. Donor–Acceptor Cyclopropane Screening[a,b]



[a]Reactions run with cyclopropane (1 equiv), benzylamine (1.2 equiv), and $Ni(ClO_4)_2·6H_2O$ (15 mol %) in CH_2Cl_2 at reflux for 2 h. [b]Numbers in parentheses represent isolated yields after column chromatography. [c]Reactions performed in toluene under reflux. [d]No desired products observed.

Scheme 2. One-Pot Tandem Cyclopropanation/Amine Ring-Opening Cyclization



The methodology was also applied to the reactions of different D–A cyclopropanes with benzylamine. (Table 4). In the previous reactions, only D–A cyclopropanes bearing a 4-methoxyphenyl substituent as the donor group were explored to help facilitate formation of the dihydropyrroles. When a phenyl substituent was employed instead, dihydropyrrole **5o** was obtained in 85% yield. Similar results were observed for **4p**, where 4-fluorophenyl was the donor and **5p** was generated in 88% yield. When the aromatic substituent bears a strong electron-withdrawing group, the reaction efficiency is reduced, and a low yield of dihydropyrrole **5q** is attained. When a geminal methyl and phenyl group are the donors, the 2,2-disubstituted dihydropyrrole **5r** is observed in 79% yield. D–A cyclopropanes bearing a single alkyl donor do not provide the desired dihydropyrrole products. Cyclopropane **4t**, with a methylene silyl donor substituent, proved incompatible with the reaction conditions because other major products were observed. Cyclopropane **4u** (derived from indene) reacted to give 37% of **5u** in toluene at reflux. No reaction was observed at reduced temperatures. A similar result (44%) was achieved for **5v**, which also contains substituents in both the 2- and 3-positions. Both outcomes appear to be the result of steric effects associated with the amine approaching the sterically congested cyclopropanes.

Cyclopropanes derived from other β-ketoesters were also subjected to the reaction conditions. Dihydropyrrole **5w** was successfully prepared in 85% yield from the corresponding cyclopropyl ethyl ketone. Similarly, the cyclopropyl 2-thienyl ketone afforded desired product **5x** in 83% yield. Alternatively, dimethyl malonate-derived cylopropane **4y** gave pyrrolidin-2-one **5y** in 63% yield upon workup/purification. This result is consistent with observations made by Yamagata.[12b]

1,3-Diketones have not previously been studied in the amine ring-opening cyclizations. To examine their compatibility, cyclopropanes **4z** (from a symmetric 1,3-diketone) and **4aa** (from an unsymmetric 1,3-diketone) were synthesized and treated with benzylamine under the reaction conditions. Cyclopropane **4z** provided its product **5z** in 78% yield. In the case of **4aa** (from the unsymmetric 1,3-diketone), regioisomers are possible. Fortunately, the only product observed is the one that has the phenyl ring in conjugation with the enone π-system (**5aa**).

Given that both the syntheses of the D–A cyclopropanes (via Rh-catalyzed cyclopropanation of alkenes with α-diazo carbonyls) and the dihydropyrroles take place in CH_2Cl_2, a

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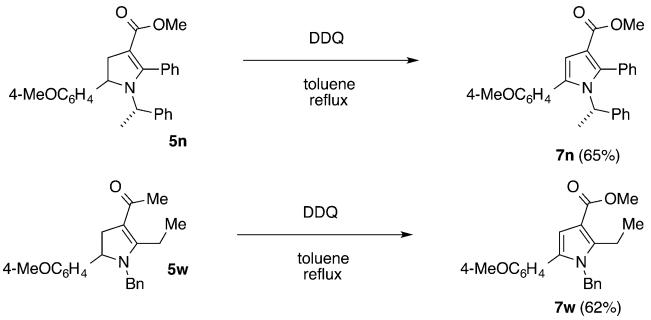
tandem one-pot cyclopropanation/amine ring-opening cyclization was explored (Scheme 2). In a representative example, methyl 2-diazo-3-oxo-3-phenylpropanoate **6b** was first reacted with 4-vinylanisole in the presence of 0.1 mol % Rh_2esp_2 to form cyclopropane **4b**. After 30 min, benzylamine (1.2 equiv) and $Ni(ClO_4)_2{\cdot}6H_2O$ (15 mol %) were added simultaneously, and the reaction mixture was heated at reflux.[24] Desired dihydropyrrole **5b** was obtained in 68% yield, which corresponds to an average of ~82% yield per step.

The 2,3-dihydropyrrole products could be smoothly converted to the corresponding pyrroles in the presence of 1,2-dichloro-5,6-dicyanobenzoquinone (DDQ).[12c,25] For instance, when dihydropyrroles **5n** and **5w** were subjected to DDQ in toluene at reflux, pyrroles **7n** and **7w** were formed in 65 and 62% yields, respectively (Scheme 3). Thus, highly substituted pyrroles are readily accessible using the methodology.

Scheme 3. DDQ-Mediated Conversion of Dihydropyrroles to Pyrroles



In summary, we have developed an efficient and general Ni(II)-catalyzed approach to 4-keto- and 4-carboxy-2,3-dihydropyrroles using activated D–A cyclopropanes under milder conditions than previously reported. The method is amenable to a variety of primary amine nucleophiles as well as substituted D–A cyclopropanes to provide highly substituted dihydropyrroles. Furthermore, the dihydropyrrole products can readily undergo derivatization to serve as building blocks for chemical synthesis. Future work will examine the vinylogous reactivity of these substrates for the efficient synthesis of complex, bioactive molecules.

EXPERIMENTAL SECTION

General Information. Chromatographic purification was performed as flash chromatography with Dynamic Adsorbents silica gel (32–65 μm) and solvents indicated as eluent with 0.1–0.5 bar pressure. For quantitative flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on EMD silica gel 60 F_{254} TLC glass plates. Visualization was accomplished with UV light. Infrared (IR) spectra were obtained using a FTIR with an ATR attachment and by attenuated total reflection (ATR) through a diamond plate. The IR bands are characterized as weak (w), medium (m), and strong (s). Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on a 300 or 500 MHz spectrometer with solvent resonances as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, t = triplet, m = multiplet, and br = broad), coupling constants (Hz), and integration. The accurate mass analyses were run in EI mode using a double-focusing magnetic analyzer at a mass resolution of 10 000 using PFK (perfluorokerosene) as an internal calibrant. Uncorrected melting points were measured with a digital melting-point apparatus.

Synthesis of Cyclopropanes 4. Cyclopropanes **4a**,[13a] **4x**,[13b] **4y**,[26] **4z**,[27] and **4aa**[28] were prepared according to previously reported methods. The remaining cyclopropanes were synthesized according to one of the two following methods.

General Method A. The corresponding alkene (1.0 equiv) was added to a solution Rh_2esp_2 (0.1 mol %) in DCM at 0 °C. After stirring for 5 min, a solution of the α-diazo ester (1.0 equiv) was added in one shot and allowed to stir for 10 min at 0 °C. The ice bath was removed, and the reaction was allowed to warm to room temperature. After 1 h the reaction was quenched with saturated aqueous thiourea and allowed to stir for 30 min. The organic layer was collected, and the aqueous layer was extracted with DCM three times. Then, the organic layer was washed with brine, dried with Na_2SO_4, and concentrated, and column chromatography afforded the desired products.

General Method B. A solution of Grignard reagent (1.5 equiv) was added slowly to a stirred solution of Weinreb amide in THF (10 mL) at 0 °C. The solution was stirred for 5 min at this temperature and then allowed to warm gradually to room temperature. The reaction was monitored by TLC. The solution was then quenched with saturated aqueous ammonium chloride, extracted with Et_2O (three times), washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure.

Methyl 1-Benzoyl-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (4b). According to general method B, a solution of phenyllithium (6.89 mL, 12.4 mmol) was added slowly to a stirred solution of methyl 1-(methoxy(methyl)carbamoyl)-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (2.80 g, 9.55 mmol) in THF (35 mL) at 0 °C to afford **4b** (1.68 g, 57% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.42) as a yellow solid (mp 79–80 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95–7.89 (m, 2H), 7.55–7.49 (m, 1H), 7.46–7.39 (m, 2H), 7.25–7.21 (m, 1H), 6.85–6.80 (m, 2H), 3.73 (s, 3H), 3.52 (t, J = 8.6 Hz, 1H), 3.22 (s, 3H), 2.40 (dd, J = 4.8, 8.1 Hz, 1H), 1.66 (dd, J = 4.8, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.2, 168.7, 158.5, 136.9, 132.7, 129.8, 128.3, 127.9, 126.4, 113.2, 54.8, 51.9, 42.0, 30.0, 20.0. IR: 2951 (s), 2836 (s), 1731 (s), 1674 (s), 1611 (s), 1597 (s), 1580 (s), 1515 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{18}O_4$, 310.1205; found, 310.1202.

Methyl 1-Benzoyl-2-phenylcyclopropane-1-carboxylate (4o). According to general method B, a solution of phenyllithium (1.12 mL, 2.02 mmol) was added slowly to a stirred solution of methyl 1-(methoxy(methyl)carbamoyl)-2-phenylcyclopropane-1-carboxylate (408 mg, 1.55 mmol) in THF (35 mL) at 0 °C to afford **4o** (95.8 mg, 22% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.64) as a yellow solid (mp 91–92 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95–7.90 (m, 2H), 7.59–7.53 (m, 1H), 7.49–7.43 (m, 2H), 7.33–7.29 (m, 3H), 7.28–7.23 (m, 2H), 3.57 (t, J = 8.6 Hz, 1H), 3.24 (s, 3H), 2.45 (dd, J = 4.8, 8.1 Hz, 1H), 1.69 (dd, J = 4.9, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 168.8, 136.9, 134.7, 132.9, 129.0, 128.5, 128.1, 127.2, 52.1, 42.2, 30.6, 20.0. IR: 3058 (s), 3002 (s), 2952 (s), 1728 (m), 1677 (w), 1596 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{16}O_3$, 280.1099; found, 280.1104.

Methyl 1-Benzoyl-2-(4-fluorophenyl)cyclopropane-1-carboxylate (4p). According to general method B, a solution of phenyllithium (1.13 mL, 2.04 mmol) was added slowly to a stirred solution of methyl 2-(4-fluorophenyl)-1-(methoxy(methyl)-carbamoyl)cyclopropane-1-carboxylate (478 mg, 1.70 mmol) in THF (35 mL) at 0 °C to afford **4p** (100 mg, 20% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.54) as a pale yellow solid (mp 93–94 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94–7.89 (m, 2H), 7.59–7.52 (m, 1H), 7.49–7.42 (m, 1H), 7.32–7.24 (m, 2H), 7.02–6.94 (m, 2H), 3.53 (t, J = 8.6 Hz, 1H), 3.25 (s, 3H), 2.41 (dd, J = 5.0, 8.1 Hz, 1H), 1.68 (dd, J = 4.9, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.1, 168.7, 163.5, 160.3, 136.8, 132.9, 130.5, 128.5, 128.1, 114.9, 52.1, 42.1, 29.7, 20.0. IR: 3003 (s), 2952 (s), 1725 (m), 1684 (m), 1597 (s), 1580 (s), 1510 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{15}FO_3$, 298.1005; found, 298.1011.

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Methyl 1-Benzoyl-2-(4-nitrophenyl)cyclopropane-1-carboxylate (4q). According to general method A, to a solution of Rh_2esp_2 (1.90 mg, 2.45 μmol) in DCM was added 4-nitrostyrene (0.31 mL, 2.45 mmol) followed by a solution of methyl 2-diazo-3-oxo-3-phenylpropanoate (500 mg, 2.45 mmol). The reaction was quenched, and column chromatography afforded **4q** (25% EtOAc/hexane, R_f = 0.54) as a white solid (mp 121−122 °C) (47 mg, 6.0% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 7.1 Hz, 1H), 7.64−7.55 (m, 1H), 7.53−7.43 (m, 4H), 3.60 (t, J = 8.5 Hz, 1H), 3.27 (s, 3H), 2.49 (dd, J = 5.0, 8.1 Hz, 1H), 1.77 (dd, J = 5.1, 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3, 168.4, 147.1, 142.7, 136.3, 133.3, 129.9, 128.8, 128.2, 123.3, 52.5, 42.6, 29.7, 19.9. IR: 2952 (s), 2848 (s), 1733 (m), 1676 (m), 1596 (s), 1515 (m) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{18}H_{15}NO_5$, 325.0950; found, 325.0951.

Methyl 1-Benzoyl-2-methyl-2-phenylcyclopropane-1-carboxylate (4r). According to general method A, to a solution of Rh_2esp_2 (2.60 mg, 3.43 μmol) in DCM was added α-methylstyrene (0.45 mL, 3.43 mmol) followed by a solution of methyl 2-diazo-3-oxo-3-phenylpropanoate (700 mg, 3.43 mmol). The reaction was quenched, and column chromatography afforded **4r** (25% EtOAc/hexane, R_f = 0.57) as a white solid (mp 86−87 °C) (595 mg, 59% yield). Diastereomeric ratio: 10:1. Major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12−8.06 (m, 2H), 7.57−7.38 (m, 5H), 7.35−7.27 (m, 2H), 7.26−7.18 (m, 1H), 3.25 (s, 3H), 2.34 (d, J = 4.9 Hz, 1H), 1.75 (d, J = 5.0 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.4, 168.9, 141.2, 136.8, 132.9, 132.2, 128.8, 127.9, 126.7, 51.8, 42.9, 37.6, 25.1, 24.9. IR: 3060 (s), 2997 (s), 2949 (s), 2923 (s), 1724 (m), 1681 (w), 1595 (s), 1578 (s) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{19}H_{18}O_3$, 294.1256; found, 294.1253.

Methyl 1-Benzoyl-2-butylcyclopropane-1-carboxylate (4s). According to general method A, to a solution of Rh_2esp_2 (0.90 mg, 1.22 μmol) in DCM was added n-hexene (0.15 mL, 1.22 mmol) followed by a solution of methyl 2-diazo-3-oxo-3-phenylpropanoate (250 mg, 1.22 mmol). The reaction was quenched, and column chromatography afforded **4s** (25% EtOAc/hexane, R_f = 0.72) as a colorless liquid (124 mg, 39% yield). Diastereomeric ratio: 3:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.81 (m, 3.00), 7.57−7.49 (m, 1.37), 7.47−7.37 (m, 3.09), 3.53 (s, 0.83), 3.51 (s, 2.43), 2.23−2.11 (m, 1.22), 1.67 (dd, J = 4.4, 7.7 Hz, 1.10), 1.60−1.48 (m, 2.83), 1.43−1.29 (m, 5.70), 0.92−0.86 (m, 2.76), 0.84−0.76 (m, 0.91). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.9, 170.6, 137.3, 137.0, 132.7, 132.5, 130.1, 128.4, 128.3, 127.9, 127.3, 77.4, 77.0, 76.6, 52.1, 52.1, 52.0, 38.6, 37.5, 31.1, 29.4, 27.9, 27.0, 26.7, 22.1, 22.1, 22.0, 20.4, 13.8, 13.7. IR: 2955 (s), 2929 (s), 2861 (s), 1730 (m), 1678 (w), 1598 (s), 1581 (s) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{16}H_{20}O_3$, 260.1412; found, 260.1413.

Methyl 1-Benzoyl-2-((trimethylsilyl)methyl)cyclopropane-1-carboxylate (4t). According to general method A, to a solution of Rh_2esp_2 (1.90 mg, 2.45 μmol) in DCM was added allyltrimethylsilane (0.39 mL, 2.45 mmol) followed by a solution of methyl 2-diazo-3-oxo-3-phenylpropanoate (500 mg, 2.45 mmol). The reaction was quenched, and column chromatography afforded **4t** (25% EtOAc/hexane, R_f = 0.72) as a colorless oil (431 mg, 61% yield). Diastereomeric ratio: 3:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89−7.83 (m, 3.00), 7.55−7.50 (m, 1.30), 7.48−7.40 (m, 2.99), 3.53 (s, 1.13), 3.52 (s, 2.94), 2.23−2.16 (m, 1.06), 1.61 (dd, J = 4.3, 7.9 Hz, 1.04), 1.56 (dd, J = 4.3, 7.6 Hz, 0.38), 1.50 (dd, J = 4.5, 9.1 Hz, 0.38), 1.45 (dd, J = 4.4, 9.0 Hz, 1.02), 0.89 (dd, J = 4.4, 14.4 Hz, 1.01), 0.80 (dd, J = 2.7, 14.2 Hz, 0.39), 0.67 (dd, J = 10.7, 14.5 Hz, 1.00), 0.09 (s, 0.90), 0.07 (s, 8.85), 0.03 (s, 3.30). ^{13}C NMR (126 MHz, $CDCl_3$): δ 195.0, 170.7, 172.0, 137.5, 132.8, 132.6, 130.2, 129.2, 128.5, 128.5, 128.5, 128.4, 128.0, 127.6, 127.5, 77.3, 77.0, 76.8, 52.2, 52.1, 39.5, 38.1, 26.9, 24.5, 24.4, 23.8, 21.7, 15.6, 14.3. IR: 2953 (s), 2898 (s), 1727 (m), 1676 (w), 1597 (s), 1581 (s) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{16}H_{22}O_3Si$, 290.1338; found, 290.1333.

Methyl 1-Benzoyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene-1-carboxylate (4u). According to general method A, to a solution of Rh_2esp_2 (1.90 mg, 2.45 μmol) in DCM was added indene (285 mg, 2.45 mmol) followed by a solution of methyl 2-diazo-3-oxo-3-phenylpropanoate (500 mg, 2.45 mmol). The reaction was quenched, and column chromatography afforded **4u** (25% EtOAc/hexane, R_f = 0.58) as a white solid (mp 96−97 °C) (323 mg, 45% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96−7.91 (m, 2H), 7.57−7.51 (m, 1H), 7.48−7.40 (m, 3H), 7.25−7.17 (m, 3H), 3.77−3.73 (m, 1H), 3.68 (s, 1H), 3.41−3.31 (m, 1H), 3.13 (s, 3H), 2.70 (dt, J = 0.9, 6.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7, 167.8, 144.0, 138.7, 137.4, 132.5, 128.3, 127.8, 126.9, 126.3, 124.9, 124.0, 51.6, 44.0, 39.2, 33.4. IR: 3056 (s), 2946 (s), 1728 (m), 1669 (w), 1596 (s), 1579 (s) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{19}H_{16}O_3$, 292.1099, Obs. 292.1105.

Methyl 1-Benzoyl-2-methyl-3-phenylcyclopropane-1-carboxylate (4v). According to general method A, to a solution of Rh_2esp_2 (1.90 mg, 2.45 μmol) in DCM was added β-methylstyrene (0.32 mL, 2.45 mmol) followed by a solution of methyl 2-diazo-3-oxo-3-phenylpropanoate (500 mg, 2.45 mmol). The reaction was quenched, and column chromatography afforded **4v** (25% EtOAc/hexane, R_f = 0.68) as a colorless oil (143 mg, 20% yield). Diastereomeric ratio: 11:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00−7.94 (m, 2H), 7.59−7.53 (m, 1H), 7.52−7.23 (m, 8H), 3.50 (d, J = 9.7 Hz, 1H), 3.41 (s, 3H), 2.11−1.99 (m, 1H), 1.63 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 169.1, 136.8, 133.8, 132.6, 130.1, 129.7, 128.1, 127.3, 126.8, 51.6, 42.3, 33.5, 28.2, 9.7. IR: 3027 (s), 2949 (s), 1737 (s), 1677 (s), 1597 (s), 1580 (s) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{19}H_{18}O_3$, 294.1256; found, 294.1247.

Methyl 2-(4-Methoxyphenyl)-1-propionylcyclopropane-1-carboxylate (4w). According to general method B, a solution of ethyl-magnesium bromide (6.20 mL, 6.14 mmol) was added slowly to a stirred solution of methyl 1-(methoxy(methyl)carbamoyl)-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (1.20 g, 4.09 mmol) in THF (35 mL) at 0 °C to afford **4w** (300 mg, 28% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.58) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11−7.05 (m, 2H), 6.82−6.74 (m, 2H), 3.75 (s, 3H), 3.36 (s, 3H), 3.21 (t, J = 8.6 Hz, 1H), 3.06−2.92 (m, 1H), 2.70−2.56 (m, 1H), 2.16 (dd, J = 4.6, 8.0 Hz, 1H), 1.67 (dd, J = 4.6, 9.1 Hz, 1H), 1.08 (t, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.9, 168.8, 158.7, 129.7, 126.8, 113.4, 55.1, 51.9, 44.2, 35.0, 34.6, 21.5, 8.0. IR: 2938 (s), 2837 (s), 1704 (m), 1612 (s), 1582 (s) cm^{-1}. HRMS (EI) m/z: [M]$^+$ calcd for $C_{15}H_{18}O_4$, 262.1205; found, 262.1204.

Reaction Optimization Procedures. *Procedure for Catalyst and Amine Loading at Varying Temperatures.* To a flask containing the nickel catalyst with the appropriate loading (5, 15, 20, or 30 mol %) and benzylamine with the appropriate loading (120, 200, or 250 mol %) in anhydrous DCM was added either cyclopropane **4a** or **4b**, and the reaction was allowed to go at room temperature or under reflux. The reaction was monitored via TLC, and upon complete disappearance of the starting material, the reaction was dried over $MgSO_4$ and filtered. Column chromatography provided pure desired product **5a** or **5b**.

Procedure for Catalyst Screening. To a flask containing the appropriate catalyst (15 mol %) and benzylamine (120 mol %) in anhydrous DCM was added cyclopropane **4b**, and the reaction was allowed to go under reflux. The reaction was monitored via TLC, and upon complete disappearance of the starting material, the reaction was dried over $MgSO_4$ and filtered. Column chromatography provided pure product **5b**.

Procedure for Solvent Screening. To a flask containing the nickel catalyst (15 mol %) and benzylamine (200 mol %) in the appropriate solvent (THF, Et_2O, toluene, DCE, acetone, or MeCN) was added cyclopropane **4a**, and the reaction was allowed to go under reflux. The reaction was monitored via TLC, and upon complete disappearance of the starting material, the reaction was dried over $MgSO_4$ and filtered. Column chromatography provided pure product **5a**.

Synthesis of Dihydropyrroles. *General Procedure.* The corresponding cyclopropane (1.0 equiv) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (15 mol %) and amine (1.2 equiv) in DCM (4−5 mL) or DCE (4−5 mL) or toluene (4−5 mL) at room temperature. The reaction was allowed to go under reflux. After 2 h, the reaction was dried over $MgSO_4$ and filtered. The organic filtrate

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was concentrated using a rotary evaporator, and column chromatography provided the pure desired products.

*Methyl 1-Benzyl-5-(4-methoxyphenyl)-2-(prop-1-en-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**5a**).* According to the general procedure, cyclopropane **4a** (75 mg, 0.273 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (15.0 mg, 0.041 mmol) and benzylamine (0.04 mL, 0.328 mmol) in DCM (4 mL) to afford **5a** (79.1 mg, 80% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.40) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.25 (m, 3H), 7.15−7.05 (m, 4H), 6.87 (d, J = 8.4 Hz, 2H), 5.37 (s, 1H), 5.12 (s, 1H), 4.61−4.49 (m, 2H), 3.81 (s, 3H), 3.74 (d, J = 15.8 Hz, 1H), 3.65 (s, 3H), 3.30 (dd, J = 12.5, 14.9 Hz, 1H), 2.77 (dd, J = 7.1, 15.1 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 163.7, 159.1, 137.3, 134.5, 128.5, 127.9, 127.3, 117.2, 114.1, 104.9, 93.5, 63.1, 55.2, 50.1, 47.6, 37.5, 22.3. IR: 2946 (s), 1670 (s), 1611 (s), 1567 (s), 1511 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{25}NO_3$, 363.1834; found, 363.1831.

*Methyl 1-Benzyl-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5b**).* According to the general procedure, cyclopropane **4b** (50 mg, 0.161 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (8.80 mg, 0.0241 mmol) and benzylamine (0.02 mL, 0.193 mmol) in DCM (4 mL) to afford **5b** (53.6 mg, 83% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.44) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−7.43 (m, 5H), 7.31−7.25 (m, 5H), 7.03−6.99 (m, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.63 (dd, J = 8.1, 12.3 Hz, 1H), 4.30 (d, J = 15.7 Hz, 1H), 3.86 (s, 3H), 3.69 (d, J = 15.7 Hz, 1H), 3.53 (s, 3H), 3.41 (dd, J = 12.3, 15.2 Hz, 1H), 2.90 (dd, J = 8.1, 15.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 161.8, 159.1, 137.0, 134.6, 132.0, 128.9, 128.4, 128.1, 127.7, 127.3, 114.1, 96.3, 63.1, 55.2, 50.1, 48.3, 38.2. IR: 2946 (s), 2836 (s), 1662 (s), 1610 (s), 1575 (s), 1511 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{26}H_{25}NO_3$, 399.1834; found, 399.1832.

*Methyl 1-Ethyl-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5c**).* According to the general procedure, cyclopropane **4b** (81 mg, 0.261 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (14.3 mg, 0.0391 mmol) and ethylamine (0.16 mL, 0.313 mmol) in DCE (4 mL) to afford **5c** (55.8 mg, 63% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.42) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.30 (m, 7H), 6.92 (d, J = 8.5 Hz, 2H), 4.78 (dd, J = 9.1, 12.0 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H), 3.39 (dd, J = 12.1, 14.9 Hz, 1H), 2.95 (qd, J = 7.2, 14.4 Hz, 1H), 2.83 (dd, J = 9.4, 15.4 Hz, 1H), 2.69 (qd, J = 7.0, 14.4 Hz, 1H), 0.81 (t, J = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 162.3, 159.1, 135.0, 132.5, 128.6, 128.0, 114.0, 96.3, 64.2, 55.2, 50.0, 39.7, 38.5, 12.7. IR: 2947 (s), 1677 (s), 1612 (s), 1572 (s), 1511 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{23}NO_3$, 337.1678; found, 337.1668.

*Methyl 1-Isopropyl-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5d**).* According to the general procedure, cyclopropane **4b** (100 mg, 0.322 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (17.7 mg, 0.0484 mmol) and isopropylamine (0.03 mL, 0.387 mmol) in DCE (5 mL) to afford **5d** (91.7 mg, 81% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.38) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.39 (m, 5H), 7.36−7.30 (m, 2H), 6.89 (d, J = 8.5 Hz, 2H), 4.79 (dd, J = 6.3, 12.2 Hz, 1H), 3.81 (s, 3H), 3.54−3.43 (m, 5H), 2.71 (dd, J = 6.3, 15.2 Hz, 1H), 1.03 (d, J = 6.6 Hz, 3H), 0.70 (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 162.4, 158.6, 138.7, 132.9, 128.8, 128.4, 128.0, 127.1, 113.9, 96.4, 59.7, 55.2, 50.0, 48.2, 40.0, 22.4, 19.7. IR: 2971 (s), 1678 (s), 1612 (s), 1583 (s), 1510 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{25}NO_3$, 351.1834; found, 351.1832.

*Methyl 1-(2-Methoxyethyl)-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5f**).* According to the general procedure, cyclopropane **4b** (75 mg, 0.242 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (13.3 mg, 0.0363 mmol) and 2-methoxyethan-1-amine (0.03 mL, 0.290 mmol) in DCM (5 mL) to afford **5f** (74.1 mg, 83% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.21) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.31 (m, 7H), 6.95−6.89 (m, 2H), 4.88 (dd, J = 8.4, 12.1 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H), 3.42 (dd, J = 11.9, 15.2 Hz, 1H), 3.15 (s, 2H), 3.11−3.01 (m, 1H), 2.90−2.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 162.2, 159.1, 135.1, 132.2, 128.7, 128.0, 114.0, 96.3, 70.3, 65.3, 58.6, 55.2, 50.0, 44.4, 38.5. IR: 2949 (s), 1681 (s), 1611 (s), 1575 (s), 1512 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{25}NO_4$, 367.1627; found, 367.1624.

*Methyl 5-(4-Methoxyphenyl)-2-phenyl-1-(3-(triethoxysilyl)-propyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**5g**).* According to the general procedure, cyclopropane **4b** (75 mg, 0.242 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (13.3 mg, 0.0363 mmol) and 3-(triethoxysilyl)propan-1-amine (0.05 mL, 0.290 mmol) in DCE (5 mL) to afford **5g** (53.2 mg, 42% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.38) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45−7.28 (m, 8H), 6.94−6.87 (m, 2H), 4.76 (dd, J = 8.4, 12.0 Hz, 1H), 3.81 (s, 3H), 3.69 (q, J = 7.0 Hz, 6H), 3.47 (s, 3H), 3.39 (dd, J = 12.1, 15.1 Hz, 1H), 2.87−2.77 (m, 2H), 2.69−2.59 (m, 1H), 1.15 (t, J = 7.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 162.4, 159.1, 135.1, 132.5, 128.7, 128.0, 128.0, 128.0, 114.1, 95.8, 64.5, 58.3, 55.3, 50.1, 47.8, 38.5, 20.9, 18.2, 7.4. IR: 2972 (s), 2926 (s), 1682 (s), 1611 (s), 1573 (s), 1511 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{28}H_{39}NO_6Si$, 513.2359; found, 513.2379.

*Methyl 1-(2-(1H-Indol-3-yl)ethyl)-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5h**).* According to the general procedure, cyclopropane **4b** (100 mg, 0.322 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (17.7 mg, 0.0484 mmol) and tryptamine (62.0 mg, 0.387 mmol) in DCE (5 mL) to afford **5h** (122 mg, 84% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.083) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (br s, 1H), 7.42−7.24 (m, 7H), 7.11 (t, J = 7.6 Hz, 1H), 6.96−6.89 (m, 3H), 6.86−6.81 (m, 1H), 6.72 (d, J = 2.3 Hz, 1H), 4.84 (dd, J = 8.7, 12.0 Hz, 1H), 3.83 (s, 3H), 3.49 (s, 3H), 3.41 (dd, J = 12.1, 15.0 Hz, 1H), 3.27−3.16 (m, 1H), 2.99−2.74 (m, 3H), 2.62−2.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 162.3, 159.2, 136.0, 135.0, 132.3, 128.7, 128.1, 128.1, 128.1, 127.0, 121.9, 119.1, 118.4, 118.4, 114.1, 112.6, 111.0, 96.0, 77.4, 77.0, 76.6, 64.9, 55.3, 50.1, 45.8, 38.5, 23.9. IR: 3273 (s), 2918 (s), 2851 (s), 1658 (m), 1622 (m), 1608 (s), 1567 (s), 1540 (m), 1533 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{29}H_{28}N_2O_3$, 452.2100; found, 452.2104.

*Methyl 1-Allyl-5-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5i**).* According to the general procedure, cyclopropane **4b** (100 mg, 0.322 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (17.7 mg, 0.0484 mmol) and allylamine (0.03 mL, 0.387 mmol) in DCM (5 mL) to afford **5i** (109 mg, 96% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.38) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47−7.34 (m, 5H), 7.32 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 5.57−5.43 (m, 1H), 5.09 (dd, J = 1.0, 10.2 Hz, 1H), 4.95 (dd, J = 1.6, 17.1 Hz, 1H), 4.78 (dd, J = 9.1, 12.0 Hz, 1H), 3.82 (s, 3H), 3.60−3.51 (m, 1H), 3.50 (s, 3H), 3.41 (dd, J = 12.0, 15.2 Hz, 1H), 3.12 (dd, J = 7.5, 16.0 Hz, 2H), 2.87 (dd, J = 9.2, 15.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 161.9, 159.1, 134.5, 133.1, 132.1, 128.7, 128.1, 127.9, 117.7, 114.0, 96.8, 77.4, 77.0, 76.6, 64.0, 55.1, 50.1, 47.5, 38.3. IR: 2944 (s), 2836 (s), 1663 (m), 1611 (m), 1582 (s), 1510 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{23}NO_3$, 349.1678; found, 349.1682.

*Methyl 5-(4-Methoxyphenyl)-2-phenyl-1-(prop-2-yn-1-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**5j**).* According to the general procedure, cyclopropane **4b** (100 mg, 0.322 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (17.7 mg, 0.0484 mmol) and propargylamine (0.02 mL, 0.387 mmol) in DCE (5 mL) to afford **5j** (34.1 mg, 30% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.42) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49−7.35 (m, 7H), 6.93 (d, J = 8.7 Hz, 1H), 4.86 (t, J = 11.5 Hz, 1H), 3.83 (s, 3H), 3.60 (dd, J = 2.4, 17.9 Hz, 1H), 3.51 (s, 3H), 3.34 (dd, J = 11.3, 15.2 Hz, 1H), 3.22 (dd, J = 2.4, 17.9 Hz, 1H), 2.85 (dd, J = 11.6, 15.2 Hz, 1H), 2.20 (t, J = 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 161.0, 159.3, 133.2, 131.9, 128.9, 128.6, 128.1, 114.1, 101.4, 78.3, 72.7, 64.8, 55.3, 50.4, 38.3, 35.7. IR: 3293 (s), 2948 (s), 2836 (s), 1729 (m), 1674 (m), 1612 (m), 1587 (s), 1512 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{21}NO_3$, 347.1521; found, 347.1531.

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*Methyl 5-(4-Methoxyphenyl)-1,2-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5k**).* According to the general procedure, cyclopropane **4b** (75 mg, 0.242 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (13.3 mg, 0.0363 mmol) and aniline (0.03 mL, 0.290 mmol) in toluene (5 mL) to afford **5k** (69.1 mg, 74% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.38) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46−7.41 (m, 2H), 7.39−7.33 (m, 2H), 7.33−7.27 (m, 3H), 7.00−6.81 (m, 5H), 6.62−6.57 (m, 2H), 5.07 (dd, J = 6.2, 11.4 Hz, 1H), 3.81 (s, 3H), 3.65 (dd, J = 11.4, 15.3 Hz, 1H), 3.58 (s, 3H), 2.93 (dd, J = 6.2, 15.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 158.9, 158.0, 142.8, 136.0, 131.7, 129.7, 128.9, 128.2, 127.5, 123.6, 114.1, 101.1, 68.5, 55.2, 50.4, 39.6. IR: 2947 (s), 1686 (s), 1611 (s), 1588 (s), 1571 (s), 1511 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{23}NO_3$, 385.1678; found, 385.1680.

*Methyl 5-(4-Methoxyphenyl)-2-phenyl-1-((S)-1-phenylethyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**5n**).* According to the general procedure, cyclopropane **4b** (75 mg, 0.242 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (13.3 mg, 0.0363 mmol) and (*S*)-1-phenylethan-1-amine (0.04 mL, 0.298 mmol) in DCM (5 mL) to afford **5n** (90.3 mg, 90% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.38) as a colorless oil. Diastereomeric ratio: 1:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55−7.42 (m, 9.00), 7.38−7.28 (m, 2.52), 7.28−7.22 (m, 3.20), 7.14−7.09 (m, 1.95), 7.01−6.95 (m, 3.94), 6.93−6.87 (m, 3.49), 6.61−6.55 (m, 1.54), 4.70−4.49 (m, 2.52), 4.40 (dd, J = 6.1, 12.2 Hz, 0.91), 3.83 (s, 3.01), 3.73 (s, 2.48), 3.51−3.41 (m, 6.66), 3.32 (dd, J = 12.2, 15.3 Hz, 1.04), 2.77−2.62 (m, 1.58), 1.39 (d, J = 7.0 Hz, 2.45), 1.08 (d, J = 7.3 Hz, 2.88). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6, 166.5, 162.5, 162.1, 158.9, 158.2, 141.3, 140.2, 138.5, 137.2, 133.0, 132.6, 129.2, 129.0, 128.5, 128.3, 128.3, 127.7, 127.6, 127.5, 127.4, 127.0, 126.8, 126.2, 114.1, 113.4, 113.3, 98.7, 96.2, 77.6, 77.1, 76.7, 61.3, 60.7, 55.3, 55.3, 54.8, 54.6, 50.3, 50.2, 39.9, 19.4, 16.2. IR: 2943 (s), 1683 (m), 1611 (s), 1583 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{27}NO_3$, 413.1991; found, 413.1995.

*Methyl 1-Benzyl-2,5-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5o**).* According to the general procedure, cyclopropane **4o** (75 mg, 0.242 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (14.7 mg, 0.0402 mmol) and benzylamine (0.04 mL, 0.321 mmol) in toluene (5 mL) to afford **5o** (84.2 mg, 85% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.48) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51−7.25 (m, 13H), 7.01 (dd, J = 1.8, 7.6 Hz, 2H), 4.67 (dd, J = 8.0, 12.3 Hz, 1H), 4.33 (d, J = 15.7 Hz, 1H), 3.70 (d, J = 15.7 Hz, 1H), 3.53 (s, 3H), 3.45 (dd, J = 12.3, 15.3 Hz, 1H), 2.91 (dd, J = 8.0, 15.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 161.9, 142.5, 136.9, 131.9, 128.9, 128.8, 128.4, 128.1, 127.7, 127.6, 127.3, 126.8, 125.8, 96.4, 77.4, 77.0, 76.6, 63.6, 50.1, 48.4, 38.2. IR: 3029 (s), 2946 (s), 1663 (s), 1613 (s), 1579 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{23}NO_2$, 369.1729; found, 369.1722.

*Methyl 1-Benzyl-5-(4-fluorophenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5p**).* According to the general procedure, cyclopropane **4p** (70 mg, 0.235 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (12.9 mg, 0.0352 mmol) and benzylamine (0.03 mL, 0.282 mmol) in DCM (5 mL) to afford **5p** (79.8 mg, 88% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.39) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49−7.43 (m, 5H), 7.32−7.23 (m, 5H), 7.07 (t, J = 8.7 Hz, 2H), 7.00−6.95 (m, 2H), 4.62 (dd, J = 8.1, 12.3 Hz, 1H), 4.29 (d, J = 15.8 Hz, 1H), 3.65 (d, J = 15.7 Hz, 1H), 3.52 (s, 3H), 3.41 (dd, J = 12.3, 15.3 Hz, 1H), 2.85 (dd, J = 8.1, 15.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 163.9, 161.8, 160.6, 138.3, 136.8, 131.8, 129.1, 128.5, 128.2, 127.7, 127.4, 115.8, 115.5, 96.6, 63.0, 50.2, 48.5, 38.4. IR: 2948 (s), 1682 (s), 1610 (s), 1582 (s), 1508 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{22}FNO_2$, 387.1635; found, 387.1626.

*Methyl 1-Benzyl-5-(4-nitrophenyl)-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5q**).* According to the general procedure, cyclopropane **4q** (45 mg, 0.138 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (6.1 mg, 0.0166 mmol) and benzylamine (0.01 mL, 0.133 mmol) in toluene (5 mL) to afford **5q** (14.1 mg, 31% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.32) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, J = 8.6 Hz, 2H), 7.51−7.45 (m, 7H), 7.28−7.23 (m, 3H), 6.98−6.93 (m, 2H), 4.72 (dd, J = 8.1, 12.3 Hz, 1H), 4.33 (d, J = 15.6 Hz, 1H), 3.65 (d, J = 15.4 Hz, 1H), 3.51 (s, 3H), 3.48−3.41 (m, 1H), 2.81 (dd, J = 8.1, 15.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 161.8, 150.0, 147.5, 136.3, 131.4, 129.4, 128.7, 128.6, 128.4, 127.7, 127.7, 124.2, 97.2, 63.1, 50.4, 49.3, 38.5. IR: 3028 (s), 2923 (s), 2853 (s), 1664 (s), 1584 (s), 1518 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{22}N_2O_4$, 414.1580; found, 414.1576.

*Methyl 1-Benzyl-5-methyl-2,5-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5r**).* According to the general procedure, cyclopropane **4r** (75 mg, 0.255 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (14.0 mg, 0.0382 mmol) and benzylamine (0.03 mL, 0.306 mmol) in DCM (5 mL) to afford **5r** (77.3 mg, 79% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.44) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54−7.47 (m, 2H), 7.44−7.28 (m, 8H), 7.19−7.12 (m, 3H), 6.97−6.90 (m, 2H), 4.23 (d, J = 16.5 Hz, 1H), 3.83 (d, J = 16.7 Hz, 1H), 3.49 (s, 3H), 3.22 (q, J = 15.0 Hz, 2H), 1.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 161.6, 145.7, 139.5, 132.5, 128.5, 128.4, 128.2, 128.0, 128.0, 127.3, 126.9, 126.6, 125.6, 95.4, 77.4, 77.0, 76.6, 69.4, 50.1, 47.2, 47.0, 25.8. IR: 3028 (s), 2945 (s), 1732 (s), 1661 (s), 1614 (m), 1580 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{26}H_{25}NO_2$, 383.1885; found,. 383.1877.

*Methyl 1-Benzyl-2-phenyl-1,3a,4,8b-tetrahydroindeno[1,2-b]-pyrrole-3-carboxylate (**5u**).* According to the general procedure, cyclopropane **4u** (75 mg, 0.257 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (14.1 mg, 0.0385 mmol) and benzylamine (0.03 mL, 0.308 mmol) in toluene (5 mL) to afford **5u** (26.9 mg, 37% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.20) as a colorless oil. Diastereomeric ratio: 1:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05−7.95 (m, 5.25), 7.63−7.55 (m, 2.44), 7.51−7.42 (m, 5.91), 7.41−7.14 (m, 26.79), 4.50 (dd, J = 8.8, 18.1 Hz, 2.00), 4.29 (d, J = 5.0 Hz, 0.99), 4.10 (d, J = 5.5 Hz, 0.90), 3.97−3.76 (m, 4.81), 3.66 (s, 3.42), 3.61 (s, 3.50), 3.43−3.23 (m, 5.30), 2.80 (dd, J = 5.2, 15.2 Hz, 1.12), 2.56−2.44 (m, 1.35). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 143.7, 142.0, 141.8, 140.8, 136.8, 133.5, 128.7, 128.3, 127.8, 126.7, 125.0, 124.4, 66.6, 66.4, 57.4, 56.5, 52.4, 50.2, 45.6, 44.9, 35.4, 34.3. IR: 2950 (s), 1734 (s), 1682 (s), 1568 (s), 1512 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{26}H_{23}NO_2$, 381.1729; found, 381.1714.

*Methyl 1-Benzyl-4-methyl-2,5-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (**5v**).* According to the general procedure, cyclopropane **4v** (71 mg, 0.241 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (13.2 mg, 0.0362 mmol) and benzylamine (0.03 mL, 0.290 mmol) in toluene (5 mL) to afford **5v** (40.3 mg, 44% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.51) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52−7.23 (m, 13H), 7.03−6.98 (m, 2H), 4.33 (d, J = 15.7 Hz, 1H), 4.04 (d, J = 5.5 Hz, 1H), 3.70 (d, J = 15.7 Hz, 1H), 3.49 (s, 3H), 3.18−3.08 (m, 1H), 1.28 (d, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 161.4, 142.1, 137.1, 132.1, 129.0, 128.8, 128.5, 128.2, 127.7, 127.5, 127.3, 126.5, 102.2, 71.7, 50.0, 48.4, 45.6, 21.8. IR: 3029 (s), 2949 (s), 1731 (s), 1665 (s), 1570 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{26}H_{25}NO_2$, 383.1885; found, 383.1888.

*Methyl 1-Benzyl-2-ethyl-5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (**5w**).* According to the general procedure, cyclopropane **4w** (44 mg, 0.168 mmol) was added to a stirring solution of $Ni(ClO_4)_2·6H_2O$ (9.20 mg, 0.0252 mmol) and benzylamine (0.02 mL, 0.202 mmol) in DCM (5 mL) to afford **5w** (49.1 mg, 85% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.48) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.25 (m, 3H), 7.13−7.04 (m, 4H), 6.86 (dd, J = 2.1, 6.6 Hz, 2H), 4.55−4.45 (m, 2H), 3.88−3.80 (m, 4H), 3.67 (s, 1H), 3.30−3.16 (m, 2H), 2.70 (dd, J = 7.6, 14.9 Hz, 1H), 2.59−2.45 (m, 1H), 1.22 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 165.9, 159.1, 137.2, 134.7, 128.6, 128.1, 127.3, 127.0, 114.0, 92.8, 63.6, 55.2, 50.0, 49.7, 47.0, 37.4, 19.1, 12.7. IR: 2936 (s), 1699 (s), 1669 (s), 1610 (s), 1577 (s), 1511 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{25}NO_3$, 351.1834; found, 351.1832.

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*Methyl 1-Benzyl-5-(4-methoxyphenyl)-2-(thiophen-2-yl)-4,5-dihydro-1H-pyrrole-3 carboxylate (**5x**).* According to the general procedure, cyclopropane **4x** (80 mg, 0.253 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (13.9 mg, 0.0379 mmol) and benzylamine (0.03 mL, 0.304 mmol) in DCM (5 mL) to afford **5x** (84.2 mg, 83% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.42) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (dd, J = 1.2, 5.1 Hz, 1H), 7.33−7.20 (m, 6H), 7.11 (dd, J = 3.6, 5.1 Hz, 1H), 7.03 (dd, J = 1.8, 7.8 Hz, 2H), 6.91 (dd, J = 2.1, 6.6 Hz, 2H), 4.60 (dd, J = 8.4, 12.3 Hz, 1H), 4.45 (d, J = 15.8 Hz, 1H), 3.83 (s, 2H), 3.71 (d, J = 15.7 Hz, 1H), 3.57 (s, 1H), 3.37 (dd, J = 12.3, 15.6 Hz, 1H), 2.87 (dd, J = 8.5, 15.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 159.1, 154.2, 137.0, 134.4, 131.1, 129.2, 128.4, 128.1, 127.7, 127.4, 127.3, 126.8, 114.1, 98.9, 77.4, 77.0, 76.6, 63.2, 55.2, 50.3, 49.8, 48.6, 38.3. IR: 2944 (s), 2835 (s), 1662 (s), 1596 (s), 1509 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{23}NO_3S$, 405.1399; found, 405.1402.

*Methyl 1-Benzyl-5-(4-methoxyphenyl)-2-oxopyrrolidine-3-carboxylate (**5y**).* According to the general procedure, cyclopropane **4y** (100 mg, 0.378 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (20.8 mg, 0.0568 mmol) and benzylamine (0.05 mL, 0.454 mmol) in DCM (6 mL) to afford **5y** (81 mg, 63% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.11) as a colorless oil. Diastereomeric ratio: 2:1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30−7.22 (m, 5.00), 7.18−7.12 (m, 1.50), 7.08−6.99 (m, 4.73), 6.94−6.86 (m, 3.19), 5.05 (dd, J = 14.5, 19.8 Hz, 1.51), 4.51 (dd, J = 5.7, 8.2 Hz, 0.80), 4.29 (t, J = 7.9 Hz, 0.70), 3.84−3.81 (m, 6.41), 3.80 (s, 2.52), 3.74−3.68 (m, 1.27), 3.65−3.54 (m, 1.53), 3.52−3.42 (m, 1.95), 2.74−2.64 (m, 0.97), 2.63−2.54 (m, 0.68), 2.41−2.32 (m, 0.77), 2.17−2.06 (m, 0.93). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.0, 159.5, 135.7, 131.3, 128.6, 128.1, 127.5, 114.3, 59.5, 59.1, 55.2, 52.6, 48.2, 47.9, 44.5, 32.5, 32.1. IR: 2953 (s), 1739 (s), 1686 (m), 1612 (s), 1586 (s), 1513 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{21}NO_4$, 339.1471; found, 339.1470.

*1-(1-Benzyl-2-methyl-5-phenyl-4,5-dihydro-1H-pyrrol-3-yl)ethan-1-one (**5z**).* According to the general procedure, cyclopropane **4z** (80 mg, 0.396 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (21.7 mg, 0.0594 mmol) and benzylamine (0.05 mL, 0.475 mmol) in DCM (7 mL) to afford **5z** (89.4 mg, 78% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.037) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.27 (m, 6H), 7.23−7.20 (m, 2H), 7.04 (d, J = 7.0 Hz, 2H), 4.61 (dd, J = 7.9, 11.9 Hz, 1H), 4.57 (d, J = 16.5 Hz, 1H), 3.85 (d, J = 16.5 Hz, 1H), 3.33 (ddd, J = 1.1, 12.0, 14.4 Hz, 1H), 2.82 (ddd, J = 1.2, 7.9, 14.3 Hz, 1H), 2.50 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.3, 160.8, 142.0, 136.4, 128.9, 128.8, 128.0, 127.5, 127.0, 127.0, 105.9, 77.3, 77.0, 76.8, 65.0, 47.2, 38.7, 29.0, 13.2. IR: 3028 (s), 2917 (s), 1712 (s), 1621 (m), 1536 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{21}NO$, 291.1623; found, 291.1622.

*1-(1-Benzyl-2,5-diphenyl-4,5-dihydro-1H-pyrrol-3-yl)ethan-1-one (**5aa**).* According to the general procedure, cyclopropane **4aa** (90 mg, 0.341 mmol) was added to a stirring solution of $Ni(ClO_4)_2{\cdot}6H_2O$ (18.7 mg, 0.0511 mmol) and benzylamine (0.04 mL, 0.409 mmol) in DCM (8 mL) to afford **5aa** (60.9 mg, 51% yield) after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.037) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57−7.50 (m, 2H), 7.40−7.28 (m, 9H), 7.27−7.22 (m, 2H), 7.10−7.05 (m, 2H), 4.70−4.55 (m, 2H), 3.93 (d, J = 16.4 Hz, 1H), 3.43 (dd, J = 11.6, 14.8 Hz, 1H), 2.97 (dd, J = 7.9, 14.8 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.3, 162.7, 143.2, 141.5, 136.1, 129.3, 128.8, 128.8, 128.8, 128.0, 127.9, 127.6, 127.2, 127.0, 126.9, 107.2, 77.4, 77.0, 76.6, 65.2, 47.5, 39.0, 14.0. IR: 3059 (s), 3028 (s), 2922 (s), 1712 (s), 1598 (m), 1538 (m) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{23}NO$, 353.1780; found, 353.1769.

Synthesis of Pyrroles. *Methyl (S)-5-(4-Methoxyphenyl)-2-phenyl-1-(1-phenylethyl)-1H-pyrrole-3-carboxylate (**7n**).* DDQ (44.9 mg, 0.198 mmol) was added to a solution of dihydropyrrole **5n** (54.5 mg, 0.132 mmol) in toluene (6.6 mL) to afford pyrrole **7n** (35 mg, 65%) as a colorless oil after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.51). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34−7.27 (m, 3H), 7.20−7.16 (m, 4H), 7.03 (d, J = 8.6 Hz, 2H), 6.84−6.80 (m, 3H), 6.78−6.75 (m, 3H), 6.61 (s, 1H), 5.41 (q, J = 7.2 Hz, 1H), 3.80 (s, 3H), 3.63 (s, 3H), 1.54 (d, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 159.2, 142.1, 139.3, 134.5, 132.7, 131.9, 130.5, 128.1, 128.1, 127.6, 127.0, 126.1, 126.1, 125.6, 125.5, 113.3, 77.3, 77.0, 76.8, 55.2, 54.0, 50.7, 19.4. IR: 2953 (s), 2941 (s), 1702 (m), 1611 (s), 1566 (s), 1533 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{25}NO_3$, 411.1834; found, 411.1836.

*Methyl 1-Benzyl-2-ethyl-5-(4-methoxyphenyl)-1H-pyrrole-3-carboxylate (**7w**).* DDQ (39.6 mg, 0.174 mmol) was added to a solution of dihydropyrrole **5w** (40.8 mg, 0.116 mmol) in toluene (5.8 mL) to afford pyrrole **7w** (25 mg, 62%) as a colorless oil after purification via flash chromatography (25% EtOAc/hexane, R_f = 0.54). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31−7.21 (m, 4H), 7.19−7.15 (m, 2H), 6.89 (d, J = 7.4 Hz, 2H), 6.84−6.80 (m, 2H), 6.60 (s, 1H), 5.11 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 2.87 (q, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 159.2, 142.6, 138.2, 133.7, 130.5, 128.8, 128.8, 127.3, 125.5, 125.0, 113.8, 111.3, 109.5, 77.3, 77.0, 76.8, 55.2, 50.8, 47.4, 19.2, 14.1. IR: 2943 (s), 1713 (m), 1610 (m), 1567 (s) cm^{-1}. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{23}NO_3$, 349.1678; found, 349.1682.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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