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C–H Activation

Rhodium-Catalyzed Vinylic C–H Functionalization of Enol Carbamates with Maleimides

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Abstract: The rhodium(III)-catalyzed direct C–H functionalization of enol carbamates with a range of maleimides is described. With the assistance of the carbamoyl directing group, this reaction provides biologically relevant succinimide compounds by proceeding through a C–Rh addition and subsequent protonation pathway.

Introduction

Cyclic imides have been recognized as crucial structural cores of a number of organic molecules such as bioactive natural products, pharmaceuticals, and functional materials.[1] The succinimide motif is of particular interest because of its prevalence in natural products such as palasimide[2] and salfredin (Figure 1).[3] In addition, the succinimide scaffold is the central functional unit of many drugs such as phensuximide,[4] thalidomide,[5] and lurasidone[6] as well as new drug candidates that have interesting bioactivity.[7] Furthermore, synthetic derivatives such as pyrrolidines and γ-lactams, derived from the reduction of succinimides, are also found in biologically active molecules, which makes these derivatives relevant for drug development in the pharmaceutical industry.[8]

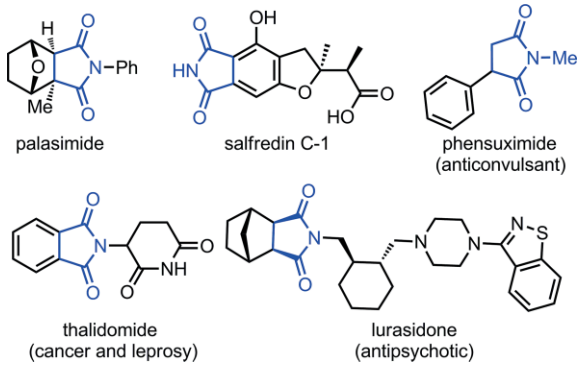
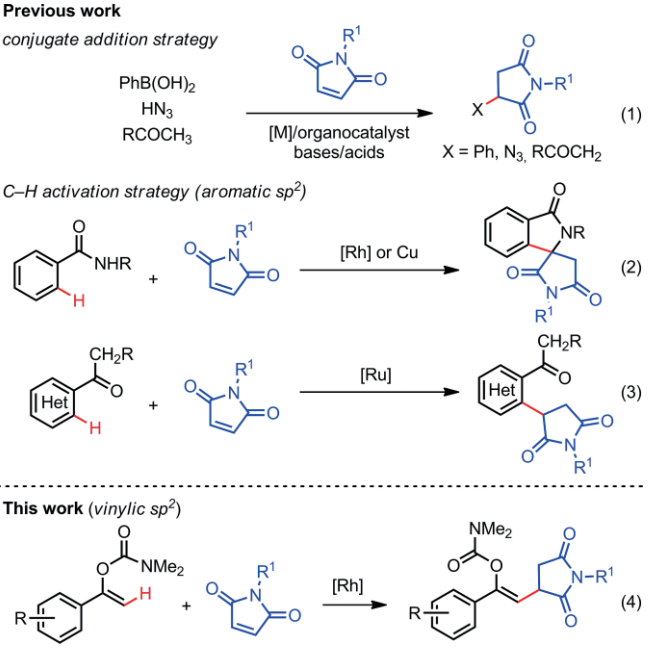


Figure 1. Natural products and pharmaceuticals that contain succinimide scaffolds.

The 1,4-addition reaction of carbon nucleophiles to electron-deficient alkenes such as α,β-unsaturated ketones is a straightforward strategy for the construction of new carbon–carbon bonds.[9] In sharp contrast, the conjugate addition of nucleophiles to maleimides in organic synthesis has been less explored.[10] For instance, metal complexes, organocatalysts, and acids/bases have been used for coupling nucleophiles, such as arylboronic acids,[10a–10c] ketones,[10d–10g] and hydrazoic acids,[10h] with maleimides [Scheme 1, Equation (1)].



Scheme 1. Coupling reactions using maleimides.

With the development of catalytic C–H bond functionalizations, the C–H olefination reaction has evolved into a powerful tool for C–C bond formation.[11] Regardless of the versatility of C–H olefination, however, these transformations are mostly limited to terminal olefins. Only few examples of C–H olefinations of internal olefins have been reported for the formation of the corresponding Heck-type products. For instance, Glorius showed a single example of the Rh-catalyzed oxidative Heck-type reaction of benzamides with internal olefins to afford ole-

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finated products.[12a] Antonchick reported the oxidative coupling reaction of quinones and maleic esters with chromones and flavones under rhodium catalysis.[12b] Recently, Li also described the oxidative cross-coupling reaction of benzamides with quinones by using a Rh^{III} catalyst.[12c] However, maleimides as internal olefins have rarely been reported in the C–H activation event. In 2012, Zhu demonstrated the first example of the C–H olefination of *N*-benzoylsulfonamides with maleimides followed by a cyclization reaction to afford the corresponding spiro adducts under Rh catalysis.[12d] In addition, Hirano and Miura developed a synthetic protocol for the formation of spirosuccinimides from benzamides and maleimides by using a Cu-mediated 8-aminoquinoline-directed C–H cleavage strategy [Scheme 1, Equation (2)].[12e] In contrast to Zhu's study, a single example of a Heck-type product from the reaction of benzamides and maleimides under Rh^{III} catalysis was reported by Hong.[12f] Very recently, Prabhu disclosed the Ru^{II}-catalyzed C–H alkylation of acetophenones[12g] and *N*-benzoylindoles[12h] with maleimides by using ketones as directing groups to give arylated succinimides [Scheme 1, Equation (3)].

Enol carbamates have been recognized as integral structural motifs of pharmaceuticals and agrochemicals and have also served as versatile synthons in organic transformations.[13] However, the catalytic C–H functionalization of enol carbamates has rarely been exploited.[14] Our continued efforts on rhodium-catalyzed C–H functionalizations of aromatic compounds[15] prompted us to explore the reaction of enol carbamates with maleimides [Scheme 1, Equation (4)].

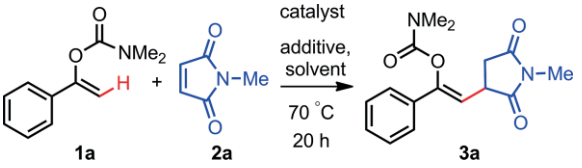
Results and Discussion

Our initial study began by investigating the coupling between 1-phenylvinyl *N*,*N*-dimethylcarbamate (**1a**) and *N*-methylmaleimide (**2a**) under rhodium catalysis (Table 1). Fortunately, the reaction of **1a** and **2a** in the presence of 2.5 mol-% of $[RhCp^*Cl_2]_2$ (Cp* = pentamethylcyclopentadienyl), 10 mol-% of $AgSbF_6$, and 2 equiv. of $Cu(OAc)_2$ in 1,2-dichloroethane (DCE) at 70 °C for 20 h afforded the desired product **3a** in 44 % yield (Table 1, Entry 1). After the further screening of solvents and additives, we found either pivalic acid (PivOH) or acetic acid to be the most effective in the reaction (Table 1, Entries 2–9). Surprisingly, a change in the loading amount of $AgSbF_6$ to 20 mol-% resulted in a remarkable improvement of the catalytic reactivity to give **3a** in 80 % yield (Table 1, Entry 10). Other catalysts such as $[CoCp^*(CO)I_2]$ and $[Ru(p\text{-cymene})Cl_2]_2$ were found to be less effective (Table 1, Entries 11 and 12). In addition, decreased amounts of PivOH afforded lower yields of **3a** (Table 1, Entries 13 and 14). Further control experiments revealed that a cationic rhodium complex in the presence of PivOH is very crucial to promote the coupling of **1a** and **2a** (Table 1, Entries 15–20).

To examine the substrate scope and limitations, a broad range of enol carbamates were screened in the coupling reaction with **2a** (Scheme 2). First, we examined substrates with different carbamate groups, which smoothly participated in the coupling to give **3b**–**3d** in moderate yields. Enol carbamates **1e**–**1m**, which contained either an electron-rich or electron-deficient group on the aromatic ring, successfully participated in the alkylation process to give the corresponding products **3e**–**3m**. Notably, this transformation showed good tolerance towards alkyl-substituted enol carbamate **1n** to provide **3n** in 51 % yield. In addition, trisubstituted enol carbamate **1o** and heteroaryl enol carbamate **1p** underwent the coupling reaction in low to moderate yields. Finally, bis(enol) carbamate **1q** afforded bis(succinimide) **3q** in 78 % yield.

To further evaluate the scope of this process, the coupling of various maleimides **2b**–**2l** with enol carbamate **1a** was examined under the optimal reaction conditions (Scheme 3). Gratifyingly, *N*-alkyl, *N*-aryl, and unprotected maleimides **2b**–**2g** were favored in the coupling reaction to afford the desired products **4b**–**4g** in good to high yields. However, *N*-allylmaleimide **2h** displayed low reactivity. In addition, *N*-carbonylated maleimides **2i** and **2j** were also found to be less reactive. Notably, this reaction readily proceeded with maleimide **2k**, which was derived from its corresponding amino acid, to chemoselectively furnish **4k** in 83 % yield with a diastereomeric ratio of 1:1. In addition,

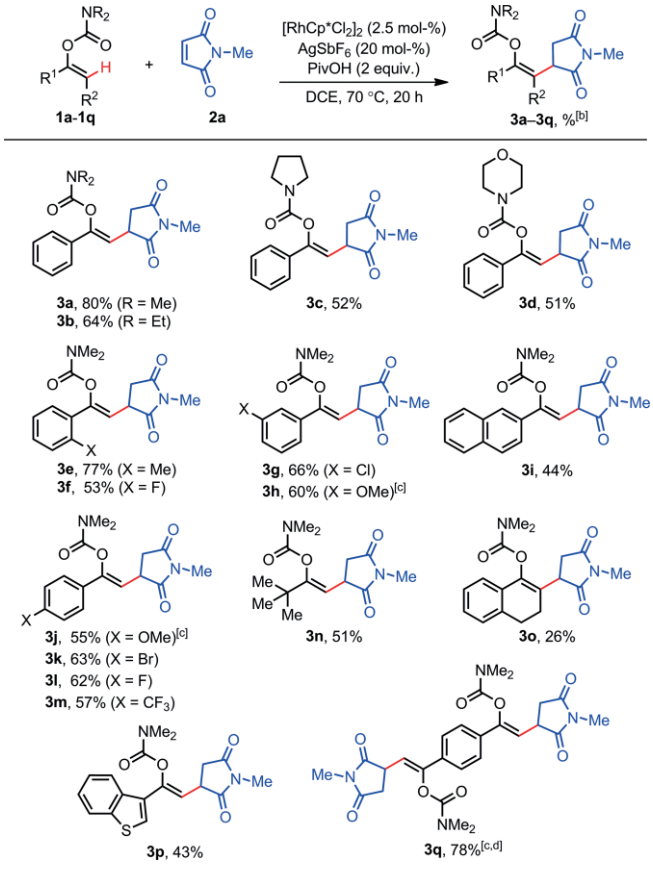
Table 1. Selected optimization of reaction conditions.[a]



1a **2a** **3a**

Entry	Catalyst	Additive [equiv.]	Solvent	% Yield[b]
1	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), $Cu(OAc)_2$ (2)	DCE	44
2	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), $Cu(OAc)_2$ (2)	MeOH	35
3	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), $Cu(OAc)_2$ (2)	THF[c]	30
4	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), $Cu(OAc)_2$ (2)	*t*AmOH[c]	trace
5	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), $Cu(OAc)_2$ (2)	dioxane	17
6	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), PivOH (2)	DCE	61
7	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), Mes-CO_2H[c] (2)	DCE	44
8	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), AcOH (2)	DCE	59
9	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.1), CsOPiv (2)	DCE	trace
10	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.2), PivOH (2)	DCE	80
11[d]	$[CoCp^*(CO)I_2]$	$AgSbF_6$ (0.2), PivOH (2)	DCE	12
12	$[Ru(p\text{-Cy})Cl_2]_2$[c]	$AgSbF_6$ (0.2), PivOH (2)	DCE	36
13	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.2), PivOH (1)	DCE	65
14	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.2), PivOH (0.5)	DCE	28
15	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.2)	DCE	trace
16	$[RhCp^*Cl_2]_2$	PivOH (2)	DCE	trace
17	–	$AgSbF_6$ (0.2)	DCE	n.r.[c]
18[d]	$[RhCp^*(MeCN)_3][SbF_6]_2$	$AgSbF_6$ (0.1), PivOH (2)	DCE	78
19	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.2), NaOAc (0.5)	DCE	trace
20	–	–	DCE	n.r.

[a] Reagents and conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (2.5 mol-%), additive (quantity noted above), and solvent (1 mL) under air at 70 °C for 20 h in pressure tubes. [b] Isolated yield determined after flash column chromatography. [c] THF = tetrahydrofuran, Am = amyl, Mes = mesityl, *p*-Cy = *para*-cymene, n.r.: no reaction. [d] Catalyst (5 mol-%) was used.

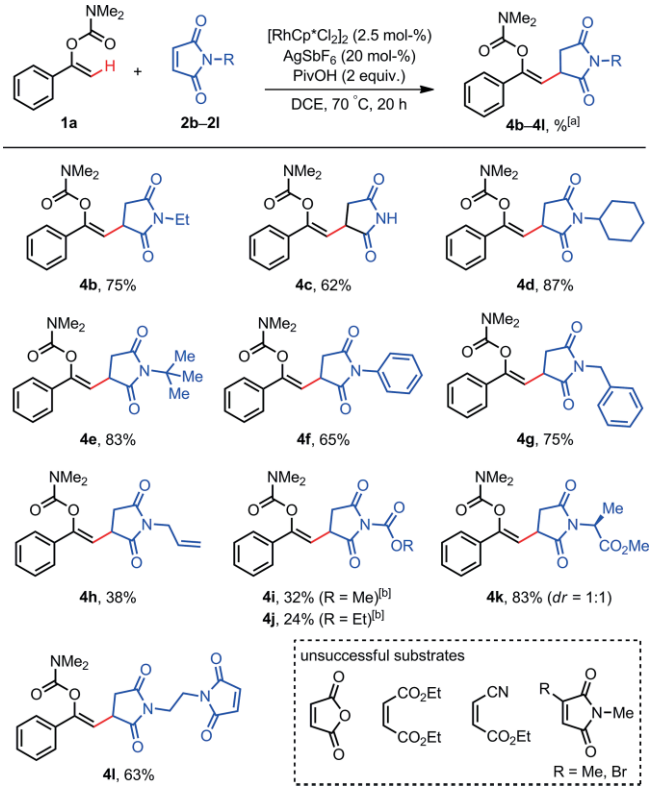


Scheme 2. Scope of enol carbamates. Reagents and conditions: **1a**–**1q** (0.2 mmol), **2a** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol-%), $AgSbF_6$ (20 mol-%), PivOH (2 equiv.), and DCE (1 mL) under air at 70 °C for 20 h in pressure tubes. [a] Isolated yield determined after flash column chromatography. [b] $[RhCp^*Cl_2]_2$ (5 mol-%) and $AgSbF_6$ (40 mol-%) were used. [c] **2a** (0.8 mmol, 4 equiv.) was used.

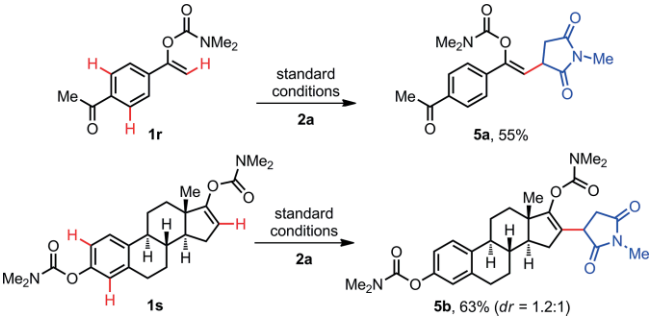
this transformation showed high monoselectivity in the coupling of **2l** with **1a** to give **4l**, the remaining maleimide moiety of which offers versatile synthetic functionality for further elaboration by using other cross-coupling reactions. In contrast, other substrates such as maleic anhydride, dimethyl maleate, ethyl (*Z*)-3-cyanoacrylate, and C-3-substituted maleimides were unreactive in this transformation.

To determine the site selectivity between aromatic and vinylic C–H bonds, we treated **1r**, which has both ketone and carbamate directing groups, with **2a** under the standard reaction conditions (Scheme 4). To our delight, the vinylic C–H functionalization took place to afford **5a** in 55 % yield along with 32 % of the recovered starting material **1r**. In addition, this site selectivity was observed during the late-stage functionalization of bioactive estrone derivative **1s**, which contains both phenol and enol carbamates to furnish **5b** in 63 % yield with a diastereomeric ratio of 1.2:1.

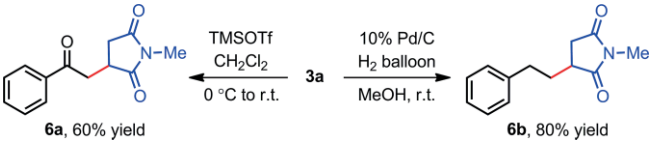
To highlight the synthetic utility of succinimide-containing enol carbamates, the cleavage of the carbamate group of **3a** by using trimethylsilyl triflate (TMSOTf) was performed to afford ketone adduct **6a** in 60 % yield (Scheme 5).[16] Further reductive cleavage of the enol carbamate moiety gave the corresponding product **6b** in 80 % yield.



Scheme 3. Scope of maleimides. Reagents and conditions: **1a** (0.2 mmol), **2b**–**2l** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol-%), $AgSbF_6$ (20 mol-%), PivOH (2 equiv.), and DCE (1 mL) under air at 70 °C for 20 h in pressure tubes. [a] Isolated yield determined after flash column chromatography. [b] $[RhCp^*Cl_2]_2$ (5 mol-%) and $AgSbF_6$ (40 mol-%) were used.

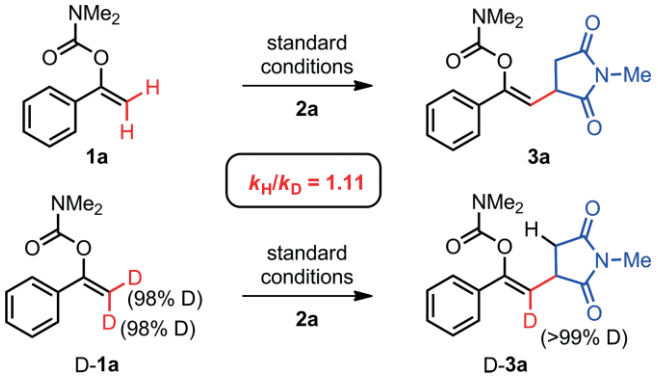


Scheme 4. Site selectivity and late-stage functionalization.



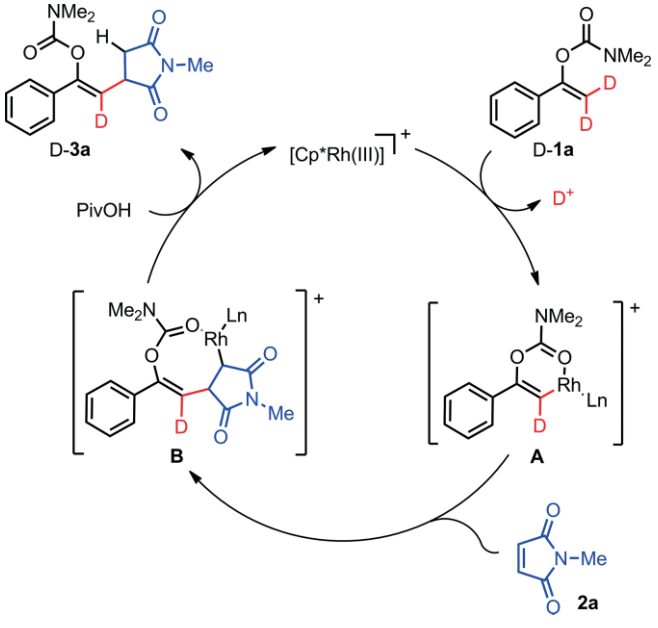
Scheme 5. Synthetic transformation of coupling product.

To gain some insight into the mechanistic, two parallel reactions of **1a** and deuterio-**1a** with **2a** under the standard reaction conditions were conducted. Experiments showed a kinetic isotope effect (k_H/k_D) of 1.11 (see Supporting Information for details), which suggests that the C–H cleavage might not be involved in the rate-determining step (Scheme 6).



Scheme 6. Kinetic isotope effect (KIE) experiments.

A plausible reaction mechanism is outlined in Scheme 7. The coordination of a cationic Rh^{III} catalyst and subsequent cleavage of the vinylic C–H bond of deuterio-**1a** affords six-membered rhodacycle intermediate **A**, which upon coordination of **2a** and migratory insertion delivers eight-membered rhodacycle species **B**.[17] Finally, protonation by PivOH takes place to generate alkylated product **3a**, and the active Rh^{III} complex further recycles through the catalytic pathway. It should be noted that the β-H elimination reaction, which would have led to the corresponding Heck-type product, was not observed because of the absence of a *syn*-planar β-hydrogen atom relative to the Rh atom.



Scheme 7. Plausible reaction mechanism.

Conclusions

In summary, we described the rhodium(III)-catalyzed direct C–H alkylation reaction of enol carbamates with maleimides to afford biologically important succinimide-containing enol carbamates. These transformations have been applied to a wide range of substrates, and typically proceed with excellent levels of chemoselectivity as well as with high functional group tolerance. Further synthetic transformations reveal that the enol carbamate group of products can readily be converted into other useful functionalities.

Experimental Section

Typical Procedure for the Reaction of Enol Carbamates with Maleimides (3a–3q, 4b–4l, 5a, and 5b): To an oven-dried sealed tube charged with 1-phenylvinyl *N*,*N*-dimethylcarbamate (**1a**, 38.2 mg, 0.2 mmol, 1 equiv.), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol-%), $AgSbF_6$ (13.7 mg, 0.02 mmol, 20 mol-%), and pivalic acid (40.8 mg, 0.4 mmol, 2 equiv.) were added 1-methyl-(1*H*)-pyrrole-2,5-dione (**2a**, 44.4 mg, 0.4 mmol, 2 equiv.) and DCE (1 mL). The reaction mixture was allowed to stir at 70 °C for 20 h and then diluted with EtOAc (3 mL). The resulting mixture was concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc, 2:1) to afford **3a** (48.4 mg, 80 % yield).

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (3a): Light brown sticky oil (48.4 mg, 80 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.35–7.30 (m, 3 H), 5.83 (d, *J* = 8.0 Hz, 1 H), 3.85–3.80 (m, 1 H), 3.14 (s, 3 H), 3.07 (t, *J* = 9.6 Hz, 1 H), 3.02 (s, 3 H), 2.96 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.1, 153.3, 150.7, 134.5, 128.9, 128.5, 124.7, 112.1, 38.2, 36.8, 36.5, 35.5, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2927, 1777, 1693, 1494, 1434, 1384, 1279, 1157, 1118, 1048, 1028, 955, 862, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{16}H_{18}N_2O_4$ $[M]^+$ 302.1267; found 302.1265.

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Diethylcarbamate (3b): Brown sticky oil (42.3 mg, 64 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 8.4, 2.0 Hz, 2 H), 7.35–7.29 (m, 3 H), 5.83 (d, *J* = 8.0 Hz, 1 H), 3.83–3.77 (m, 1 H), 3.52–3.44 (m, 2 H), 3.31 (q, *J* = 7.2 Hz, 2 H), 3.05 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.02 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.6 Hz, 1 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.15 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.1, 152.7, 150.7, 134.7, 128.8, 128.5, 124.8, 112.1, 42.1, 41.8, 38.2, 35.5, 25.0, 14.4, 13.2 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 2931, 1778, 1696, 1473, 1420, 1381, 1279, 1256, 1221, 1152, 1116, 1054, 1002, 960, 752 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{22}N_2O_4$ $[M]^+$ 330.1580; found 330.1581.

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Pyrrolidine-1-carboxylate (3c): Brown solid (34.1 mg, 52 %); m.p. 58.9–62.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 8.4, 2.0 Hz, 2 H), 7.34–7.29 (m, 3 H), 5.84 (d, *J* = 8.0 Hz, 1 H), 3.87–3.82 (m, 1 H), 3.58 (t, *J* = 7.2 Hz, 2 H), 3.41 (t, *J* = 6.4 Hz, 2 H), 3.05 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.01 (s, 3 H), 2.72 (dd, *J* = 18.4, 5.6 Hz, 1 H), 2.03–1.89 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 176.2, 151.6, 150.5, 134.6, 128.8, 128.5, 124.8, 112.1, 46.6, 46.5, 38.3, 35.5, 25.8, 25.0, 24.9 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2876, 1776, 1694, 1405, 1382, 1278, 1224, 1173, 1117, 1078, 1026, 954, 866, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{20}N_2O_4$ $[M]^+$ 328.1423; found 328.1424.

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Morpholine-4-carboxylate (3d): Brown sticky oil (35.1 mg, 51 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.33 (m, 5 H), 5.82 (d, *J* = 8.4 Hz, 1 H), 3.84–3.78 (m, 1 H), 3.74–3.65 (m, 6 H), 3.50 (br. s, 2 H), 3.07 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.02 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.5, 176.0, 152.2, 150.6, 134.3, 129.1, 128.6, 124.7, 112.4, 66.6, 66.5, 45.0, 44.2, 38.2, 35.5, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2923, 2855, 1778, 1697, 1495, 1428, 1384, 1360,

1277, 1220, 1113, 1068, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{20}N_2O_5$ $[M]^+$ 344.1372; found 344.1373.

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-*o*-tolylvinyl Dimethylcarbamate (3e): Brown sticky oil (48.7 mg, 77 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.2 Hz, 1 H), 7.21–7.19 (m, 1 H), 7.16–7.13 (m, 2 H), 5.35 (d, *J* = 8.4 Hz, 1 H), 3.87–3.81 (m, 1 H), 3.08 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.01 (d, *J* = 3.6 Hz, 6 H), 2.86 (s, 3 H), 2.68 (dd, *J* = 18.4, 5.6 Hz, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.2, 153.1, 151.2, 135.9, 135.0, 130.4, 129.1, 128.8, 125.6, 115.3, 38.0, 36.5, 36.3, 35.7, 25.0, 20.1 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2855, 1778, 1697, 1487, 1433, 1383, 1279, 1221, 1157, 1117, 1036, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{17}H_{20}N_2O_4$ $[M]^+$ 316.1423; found 316.1426.

(*Z*)-1-(2-Fluorophenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)-vinyl Dimethylcarbamate (3f): Brown sticky oil (34.0 mg, 53 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (td, *J* = 8.8, 1.6 Hz, 1 H), 7.28–7.26 (m, 1 H), 7.13–7.02 (m, 2 H), 5.88 (d, *J* = 8.4 Hz, 1 H), 3.88–3.83 (m, 1 H), 3.09 (s, 3 H), 3.05–2.96 (m, 4 H), 2.93 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6, 176.1, 159.5 (d, $J_{C,F}$ = 249.9 Hz), 153.3, 145.8 (d, $J_{C,F}$ = 3.4 Hz), 130.2 (d, $J_{C,F}$ = 8.7 Hz), 128.1 (d, $J_{C,F}$ = 2.3 Hz), 124.1 (d, $J_{C,F}$ = 3.6 Hz), 122.7, 116.6 (d, $J_{C,F}$ = 8.2 Hz), 116.2 (d, $J_{C,F}$ = 22.5 Hz), 38.2, 36.7, 36.4, 35.5, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2855, 1779, 1697, 1612, 1488, 1435, 1384, 1280, 1220, 1156, 1117, 1049, 753 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{16}H_{17}FN_2O_4$ $[M]^+$ 320.1172; found 320.1169.

(*Z*)-1-(3-Chlorophenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (3g): Brown sticky oil (44.5 mg, 66 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (s, 1 H), 7.29–7.24 (m, 3 H), 5.82 (d, *J* = 8.0 Hz, 1 H), 3.83–3.77 (m, 1 H), 3.12 (s, 3 H), 3.04 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.0 (s, 3 H), 2.94 (s, 3 H), 2.67 (dd, *J* = 18.0, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.5, 175.9, 153.2, 149.5, 136.5, 134.6, 129.8, 128.9, 125.0, 122.9, 113.5, 38.2, 36.8, 36.5, 35.3, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 2855, 1779, 1697, 1594, 1566, 1434, 1384, 1280, 1221, 1157, 1117, 1048, 865, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{16}H_{17}ClN_2O_4$ $[M]^+$ 336.0877; found 336.0877.

(*Z*)-1-(3-Methoxyphenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (3h): Yellow solid (39.9 mg, 60 %); m.p. 148.2–149.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 5.6 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.96 (s, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 5.86 (d, *J* = 8.0 Hz, 1 H), 3.87–3.84 (m, 1 H), 3.82 (s, 3 H), 3.17 (s, 3 H), 3.10 (dd, *J* = 18.4, 9.2 Hz, 1 H), 3.05 (s, 3 H), 2.99 (s, 3 H), 2.73 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.1, 159.6, 153.3, 150.5, 136.0, 129.6, 117.2, 114.3, 112.4, 110.6, 55.2, 38.2, 36.8, 36.5, 35.5, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2854, 2352, 1777, 1696, 1600, 1579, 1487, 1433, 1384, 1281, 1159, 1118, 1038, 955, 877, 755 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{17}H_{20}N_2O_5$ $[M]^+$ 332.1372; found 332.1375.

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-(naphthalen-2-yl)vinyl Dimethylcarbamate (3i): Brown sticky oil (31.0 mg, 44 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.79 (m, 4 H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.48–7.47 (m, 2 H), 5.96 (d, *J* = 8.0 Hz, 1 H), 3.91–3.85 (m, 1 H), 3.21 (s, 3 H), 3.09 (dd, *J* = 18.4, 9.2 Hz, 1 H), 3.04 (s, 3 H), 2.98 (s, 3 H), 2.75 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.2, 153.4, 150.8, 133.4, 133.0, 131.9, 128.4, 127.6, 126.5, 126.4, 124.1, 122.5, 112.7, 38.3, 36.8, 36.5, 35.5, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 2926, 2855, 1778, 1695, 1598, 1433, 1382, 1354, 1279, 1221, 1156, 1127, 1047, 954, 864, 817, 753 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{20}H_{20}N_2O_4$ $[M]^+$ 352.1423; found 352.1425.

(*Z*)-1-(4-Methoxyphenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (3j): Yellow sticky oil (36.5 mg, 55 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.8 Hz, 2 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 5.70 (d, *J* = 8.4 Hz, 1 H), 3.83–3.77 (m, 4 H), 3.12 (s, 3 H), 3.04 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.01 (s, 3 H), 2.95 (s, 3 H), 2.68 (dd, *J* = 18.4, 5.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 176.2, 160.1, 153.4, 150.5, 127.1, 126.2, 113.9, 110.3, 55.2, 38.2, 36.7, 36.4, 35.6, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 2853, 1777, 1696, 1607, 1511, 1434, 1383, 1280, 1248, 1158, 1115, 1027, 827, 756 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{17}H_{20}N_2O_5$ $[M]^+$ 332.1372; found 332.1375.

(*Z*)-1-(4-Bromophenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (3k): Brown sticky oil (48.0 mg, 63 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.8 Hz, 2 H), 5.82 (d, *J* = 8.0 Hz, 1 H), 3.83–3.77 (m, 1 H), 3.13 (s, 3 H), 3.06 (dd, *J* = 18.4, 9.2 Hz, 1 H), 2.99 (s, 3 H), 2.95 (s, 3 H), 2.68 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.5, 176.0, 153.2, 149.9, 133.7, 131.7, 126.4, 123.0, 112.8, 38.2, 36.8, 36.5, 35.4, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2854, 1779, 1696, 1588, 1486, 1434, 1383, 1280, 1157, 1115, 1072, 1007, 812, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{16}H_{17}BrN_2O_4$ $[M]^+$ 380.0372; found 380.0371.

(*Z*)-1-(4-Fluorophenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (3l): Brown sticky oil (39.7 mg, 62 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 2 H), 7.04–6.99 (m, 2 H), 5.75 (d, *J* = 8.0 Hz, 1 H), 3.83–3.78 (m, 1 H), 3.13 (s, 3 H), 3.06 (dd, *J* = 18.0, 9.2 Hz, 1 H), 3.01 (s, 3 H), 2.95 (s, 3 H), 2.68 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.1, 163.0 (d, $J_{C,F}$ = 247.4 Hz), 153.3, 149.9, 130.8 (d, $J_{C,F}$ = 3.3 Hz), 126.7 (d, $J_{C,F}$ = 8.2 Hz), 115.6 (d, $J_{C,F}$ = 21.8 Hz), 112.0, 38.1, 36.8, 36.4, 35.4, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 3073, 2926, 1779, 1694, 1603, 1508, 1435, 1385, 1281, 1232, 1154, 1119, 829, 756 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{16}H_{17}FN_2O_4$ $[M]^+$ 320.1172; found 320.1175.

(*Z*)-2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-[4-(trifluoromethyl)phenyl]vinyl Dimethylcarbamate (3m): Brown sticky oil (42.2 mg, 57 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 8.4 Hz, 2 H), 5.91 (d, *J* = 8.0 Hz, 1 H), 3.88–3.82 (m, 1 H), 3.15 (s, 3 H), 3.08 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.02 (s, 3 H), 2.96 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.3, 175.9, 153.1, 149.5, 138.1, 138.0, 130.7 (q, $J_{C,F}$ = 32.6 Hz), 127.9, 125.6 (q, $J_{C,F}$ = 3.9 Hz), 125.0, 122.4 (q, $J_{C,F}$ = 270.5 Hz), 114.3, 38.2, 36.8, 36.5, 35.3, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2854, 1779, 1697, 1617, 1435, 1387, 1322, 1281, 1159, 1110, 1067, 1013, 955, 823, 755 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{17}H_{17}F_3N_2O_4$ $[M]^+$ 370.1140; found 370.1142.

(*Z*)-3,3-Dimethyl-1-(1-methyl-2,5-dioxopyrrolidin-3-yl)but-1-en-2-yl Dimethylcarbamate (3n): Colorless sticky oil (28.8 mg, 51 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.22 (d, *J* = 8.0 Hz, 1 H), 3.56–3.51 (m, 1 H), 3.02 (s, 3 H), 2.99–2.92 (m, 7 H), 2.55 (dd, *J* = 18.4, 5.6 Hz, 1 H), 1.08 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 176.6, 159.3, 153.4, 109.2, 38.3, 36.7, 36.5, 36.3, 35.5, 27.8, 24.9 ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2934, 2872, 1779, 1696, 1435, 1384, 1279, 1160, 1120, 1055, 955, 756 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{14}H_{22}N_2O_4$ $[M]^+$ 282.1580; found 282.1581.

2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-3,4-dihydronaphthalen-1-yl Dimethylcarbamate (3o): Yellow sticky solid (17 mg, 26 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.14 (m, 2 H), 7.12–7.10 (m, 1 H), 7.07–7.05 (m, 1 H), 3.97–3.93 (m, 1 H), 3.15 (s, 3 H), 3.07–3.00 (m, 4 H), 2.99 (s, 3 H), 2.89 (t, *J* = 8.0 Hz, 2 H), 2.70 (dd, *J* = 18.8, 5.2 Hz, 1 H), 2.31 (t, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.3, 176.5, 153.8, 143.8, 135.6, 130.7, 128.0, 127.3, 126.5, 121.9, 121.0, 41.5, 36.8, 36.4, 34.2, 27.5, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 2931, 1776, 1698, 1434, 1387, 1278, 1185, 1117, 1074, 767 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{20}N_2O_4$ $[M]^+$ 328.1423; found 328.1424.

(*Z*)-1-(Benzo[*b*]thiophen-3-yl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (3p): Yellow sticky solid (30.8 mg, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.2 Hz, 1 H), 7.83 (d, *J* = 7.2 Hz, 1 H), 7.53 (s, 1 H), 7.42–7.33 (m, 2 H), 5.77 (d, *J* = 8.0 Hz, 1 H), 3.92–3.89 (m, 1 H), 3.15 (dd, *J* = 17.2, 7.6 Hz, 1 H), 3.10 (s, 3 H), 3.03 (s, 3 H), 2.90 (s, 3 H), 2.75 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.2, 176.1, 153.3, 146.4, 140.3, 136.4, 131.5, 125.9, 124.6, 122.9, 122.7, 114.6, 38.1, 36.7, 36.5, 35.6, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 2929, 1776, 1697, 1434, 1385, 1281, 1160, 1126, 1055, 955, 756 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{18}N_2O_4S$ [M]$^+$ 358.0987; found 358.0984.

(1*Z*,1′*Z*)-1,4-Phenylenebis[2-(1-methyl-2,5-dioxopyrrolidin-3-yl)ethene-1,1-diyl] Bis(dimethylcarbamate) (3q): Yellow solid (82.1 mg, 78 %); m.p. 130.2–135.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 4 H), 5.85 (d, *J* = 8.4 Hz, 2 H), 3.85–3.79 (m, 2 H), 3.14 (s, 6 H), 3.09–3.03 (m, 2 H), 3.02 (s, 6 H), 2.96 (s, 6 H), 2.70 (dd, *J* = 18.0, 5.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6, 176.1, 153.2, 150.1, 135.0, 125.0, 112.8, 38.2, 36.8, 36.5, 35.4, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 2932, 1713, 1701, 1466, 1436, 1389, 1279, 1167, 1118, 755 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{26}H_{30}N_4O_8$ [M]$^+$ 526.2064; found 526.2067.

(*Z*)-2-(1-Ethyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4b): Yellow sticky oil (47.5 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 2 H), 7.35–7.28 (m, 3 H), 5.83 (d, *J* = 7.9 Hz, 1 H), 3.84–3.78 (m, 1 H), 3.59 (q, *J* = 7.2 Hz, 2 H), 3.15 (s, 3 H), 3.04 (dd, *J* = 18.3, 9.4 Hz, 1 H), 2.96 (s, 3 H), 2.68 (dd, *J* = 18.3, 5.6 Hz, 1 H), 1.18 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 176.1, 153.6, 150.9, 134.8, 129.1, 128.7, 125.0, 112.4, 38.4, 37.0, 36.7, 35.7, 34.2, 13.2 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 2935, 1774, 1696, 1494, 1443, 1398, 1346, 1262, 1223, 1157, 1124, 1048, 753 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{17}H_{20}N_2O_4$ [M]$^+$ 316.1423; found 316.1424.

(*Z*)-2-(2,5-Dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4c): Pale yellow solid (35.7 mg, 62 %); m.p. 151.9–154.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (br. s, 1 H), 7.42 (dd, *J* = 8.2, 1.8 Hz, 2 H), 7.35–7.29 (m, 3 H), 5.85 (d, *J* = 8.1 Hz, 1 H), 3.91–3.87 (m, 1 H), 3.15 (s, 3 H), 3.08 (dd, *J* = 18.5, 9.5 Hz, 1 H), 2.97 (s, 3 H), 2.77 (dd, *J* = 18.5, 5.9 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.8, 176.0, 153.6, 151.1, 134.7, 129.2, 128.8, 125.0, 111.9, 39.8, 37.0, 36.9, 36.7 ppm. IR (KBr): $\tilde{\nu}$ = 3214, 3082, 2925, 1783, 1710, 1494, 1446, 1395, 1345, 1266, 1165, 758 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{15}H_{16}N_2O_4$ [M]$^+$ 288.1110; found 288.1107.

(*Z*)-2-(1-Cyclohexyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4d): Yellow oil (64.5 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.37–7.28 (m, 3 H), 5.82 (d, *J* = 7.7 Hz, 1 H), 4.03–3.95 (m, 1 H), 3.78–3.73 (m, 1 H), 3.15 (s, 3 H), 3.01 (dd, *J* = 18.2, 9.4 Hz, 1 H), 3.03–2.94 (m, 4 H), 2.63 (dd, *J* = 18.2, 5.8 Hz, 1 H), 2.19–2.11 (m, 2 H), 1.83–1.80 (m, 2 H), 1.66–1.57 (m, 3 H), 1.36–1.18 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 176.3, 153.6, 150.8, 134.9, 129.0, 128.7, 125.0, 112.8, 52.1, 38.2, 37.0, 36.7, 35.6, 29.1, 28.8, 26.1, 26.0, 25.2 ppm. IR (KBr): $\tilde{\nu}$ = 2929, 2856, 1771, 1696, 1446, 1393, 1371, 1259, 1187, 1157, 1051, 983, 753 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{21}H_{26}N_2O_4$ [M]$^+$ 370.1893; found 370.1895.

(*Z*)-2-(1-*tert*-Butyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4e): Yellow oil (57.2 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.36–7.29 (m, 3 H), 5.83 (d, *J* = 7.7 Hz, 1 H), 3.72–3.66 (m, 1 H), 3.15 (s, 3 H), 2.96–2.89 (m, 4 H), 2.57 (dd, *J* = 18.0, 6.3 Hz, 1 H), 1.58 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.8, 177.2, 153.7, 150.6, 135.0, 129.0, 128.7, 125.0, 113.1, 58.8, 38.6, 37.0, 36.7, 36.1, 28.6 ppm. IR (KBr): $\tilde{\nu}$ = 2933, 1775, 1699, 1446, 1394, 1342, 1263, 1158, 1052, 755 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{19}H_{24}N_2O_4$ [M]$^+$ 344.1736; found 344.1738.

(*Z*)-2-(2,5-Dioxo-1-phenylpyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4f): Brown sticky oil (47.4 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.44 (m, 4 H), 7.41–7.37 (m, 1 H), 7.35–7.30 (m, 5 H), 5.96 (d, *J* = 7.6 Hz, 1 H), 4.05–3.99 (m, 1 H), 3.24 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.15 (s, 3 H), 2.97 (s, 3 H), 2.90 (dd, *J* = 18.4, 6.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.5, 175.0, 153.4, 150.9, 134.5, 131.8, 129.1, 129.0, 128.6, 126.3, 124.8, 112.0, 38.4, 36.8, 36.5, 35.6 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 2927, 2855, 1778, 1706, 1597, 1496, 1445, 1382, 1262, 1157, 1051, 862, 756, 697 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{21}H_{20}N_2O_4$ [M]$^+$ 364.1423; found 364.1420.

(*Z*)-2-(1-Benzyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4g): Dark brown sticky oil (56.8 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 4 H), 7.33–7.30 (m, 6 H), 5.82 (d, *J* = 8.0 Hz, 1 H), 4.68 (s, 2 H), 3.86–3.81 (m, 1 H), 3.11 (s, 3 H), 3.07 (dd, *J* = 18.4, 9.2 Hz, 1 H), 2.95 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.3, 175.7, 153.3, 150.7, 135.6, 134.5, 129.0, 128.9, 128.6, 128.5, 127.9, 124.7, 112.0, 42.6, 38.2, 36.7, 36.4, 35.4 ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2925, 2854, 1777, 1699, 1495, 1432, 1394, 1324, 1282, 1162, 1122, 1069, 1014, 754 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{22}H_{22}N_2O_4$ [M]$^+$ 378.1580; found 378.1577.

(*Z*)-2-(1-Allyl-2,5-dioxopyrrolidin-3-yl)-1-phenylvinyl Dimethylcarbamate (4h): Brown sticky oil (25.0 mg, 38 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H), 7.36–7.30 (m, 3 H), 5.85–5.82 (m, 1 H), 5.81–5.75 (m, 1 H), 5.27–5.22 (m, 1 H), 5.21–5.18 (m, 1 H), 4.14 (d, *J* = 6.0 Hz, 2 H), 3.88–3.82 (m, 1 H), 3.15 (s, 3 H), 3.08 (dd, *J* = 18.4, 9.6 Hz, 1 H), 2.97 (s, 3 H), 2.71 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$): δ = 177.1, 175.6, 153.4, 150.8, 134.6, 130.6, 129.0, 128.6, 124.8, 118.6, 112.1, 41.1, 38.2, 36.8, 36.5, 35.5 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2854, 1775, 1701, 1494, 1391, 1333, 1265, 1160, 757 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{20}N_2O_4$ [M]$^+$ 328.1423; found 328.1419.

Methyl (*Z*)-3-[2-(Dimethylcarbamoyloxy)-2-phenylvinyl]-2,5-dioxopyrrolidine-1-carboxylate (4i): Yellow sticky oil (22.2 mg, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 2 H), 7.35–7.33 (m, 3 H), 5.86 (d, *J* = 8.0 Hz, 1 H), 4.0 (s, 3 H), 3.94–3.88 (m, 1 H), 3.18–3.11 (m, 4 H), 2.96 (s, 3 H), 2.82 (dd, *J* = 18.4, 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 171.3, 153.2, 151.4, 148.7, 134.3, 129.2, 128.6, 124.8, 111.0, 55.0, 38.6, 36.8, 36.5, 35.8 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 2925, 2854, 1814, 1768, 1722, 1495, 1439, 1394, 1323, 1254, 1160, 1058, 757 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{17}H_{18}N_2O_6$ [M]$^+$ 346.1165; found 346.1166.

Ethyl (*Z*)-3-[2-(Dimethylcarbamoyloxy)-2-phenylvinyl]-2,5-dioxopyrrolidine-1-carboxylate (4j): Brown sticky oil (17.3 mg, 24 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 2 H), 7.36–7.32 (m, 3 H), 5.86 (d, *J* = 8.0 Hz, 1 H), 4.44 (q, *J* = 7.1 Hz, 2 H), 3.93–3.87 (m, 1 H), 3.17–3.10 (m, 4 H), 2.96 (s, 3 H), 2.82 (dd, *J* = 18.6, 6.6 Hz, 1 H), 1.41 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 171.6, 153.4, 151.5, 148.3, 134.5, 129.3, 128.8, 125.0, 111.3, 65.1, 38.8, 37.0, 36.7, 36.0, 14.1 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2855, 1809, 1765, 1717, 1494, 1394, 1325, 1239, 1153, 1026, 861, 753 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{20}N_2O_6$ [M]$^+$ 360.1321; found 360.1320.

Methyl (2*S*)-2-(3-{(*Z*)-2-[(Dimethylcarbamoyl)oxy]-2-phenylvinyl}-2,5-dioxopyrrolidin-1-yl)propanoate (4k): Yellow sticky oil (62.1 mg, 83 %, *dr* 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.0 Hz, 2 H), 7.36–7.31 (m, 3 H), 5.84 (dd, *J* = 7.9, 3.2 Hz, 1 H), 4.83

(q, *J* = 7.2 Hz, 1 H), 3.94–3.87 (m, 1 H), 3.74 (s, 3 H), 3.16 (s, 3 H), 3.11 (dq, *J* = 18.4, 2.8 Hz, 1 H), 2.97 (s, 3 H), 2.74 (dq, *J* = 18.4, 2.8 Hz, 1 H), 1.58 (d, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.9, 176.8, 175.2, 169.8, 169.7, 153.6, 151.0, 134.7, 129.2, 128.8, 125.0, 112.2, 112.1, 53.0, 48.4, 48.4, 38.4, 37.0, 36.7, 35.7, 35.6, 14.7, 14.5 ppm. IR (KBr): $\tilde{\nu}$ = 2926, 1779, 1708, 1446, 1392, 1261, 1161, 1119, 758 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{19}H_{22}N_2O_6$ $[M]^+$ 374.1478; found 374.1483.

(*Z*)-2-{1-[2-(2,5-Dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)ethyl]-2,5-dioxopyrrolidin-3-yl}-1-phenylvinyl Dimethylcarbamate (4l): Light yellow sticky oil (51.9 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.1 Hz, 2 H), 7.36–7.30 (m, 3 H), 6.67 (s, 2 H), 5.82 (d, *J* = 8.4 Hz, 1 H), 3.83–3.72 (m, 5 H), 3.15 (s, 3 H), 3.04–2.96 (m, 4 H), 2.62 (dd, *J* = 18.4, 5.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0, 176.4, 171.0, 153.6, 150.8, 134.8, 134.4, 129.1, 128.7, 125.0, 112.3, 38.2, 38.1, 37.0, 36.7, 36.1, 35.6 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 2855, 1775, 1700, 1495, 1435, 1393, 1358, 1322, 1150, 1060, 827, 753, 697 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{21}H_{21}N_3O_6$ $[M]^+$ 411.1430; found 411.1433.

(*Z*)-1-(4-Acetylphenyl)-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)vinyl Dimethylcarbamate (5a): Colorless sticky solid (37.8 mg, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 5.96 (d, *J* = 8.0 Hz, 1 H), 3.88–3.82 (m, 1 H), 3.15 (s, 3 H), 3.07 (dd, *J* = 18.4, 8.4 Hz, 1 H), 3.02 (s, 3 H), 2.96 (s, 3 H), 2.71 (dd, *J* = 18.4, 5.6 Hz, 1 H), 2.58 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.3, 177.4, 175.9, 153.1, 149.9, 138.9, 137.0, 128.6, 124.8, 114.4, 38.3, 36.8, 36.5, 35.3, 26.6, 25.1 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1779, 1707, 1689, 1435, 1385, 1359, 1266, 1159, 1116, 1047, 756 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{18}H_{20}N_2O_5$ $[M]^+$ 344.1372; found 344.1370.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-16-(1-methyl-2,5-dioxopyrrolidin-3-yl)-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diyl Bis(dimethylcarbamate) (5b): Light yellow solid (66.0 mg, 63 %, *dr* 1.2:1); m.p. 120.0–125.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.8 Hz, 1 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 6.80 (s, 1 H), 3.74–3.71 (m, 0.57 H, diastereomeric), 3.65–3.62 (m, 0.43 H, diastereomeric), 3.07 (s, 3 H), 3.05–2.90 (m, 13 H), 2.86–2.84 (m, 2 H), 2.66–2.57 (m, 1 H), 2.33–2.27 (m, 2 H), 2.16–1.96 (m, 2 H), 1.87–1.80 (m, 2 H), 1.71–1.69 (m, 2 H), 1.60–1.50 (m, 2 H), 1.43–1.41 (m, 1 H), 0.96 (s, 1.64 H, diastereomeric), 0.89 (s, 1.32 H, diastereomeric) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.6, 177.1, 176.7, 157.6, 157.1, 155.1, 153.9, 153.7, 149.2, 137.3, 137.1, 125.7, 121.7, 120.6, 120.5, 118.7, 52.1, 51.8, 45.8, 44.3, 44.2, 39.4, 38.6, 36.8, 36.7, 36.6, 36.4, 36.38, 36.30, 33.9, 33.5, 33.2, 33.1, 29.7, 29.2, 28.5, 26.7, 25.7, 24.8, 15.8, 15.1 ppm. IR (KBr): $\tilde{\nu}$ = 2932, 1743, 1701, 1486, 1436, 1389, 1279, 1187, 1065, 759 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{29}H_{37}N_3O_6$ $[M]^+$ 523.2682; found 523.2682.

Cleavage of an Enol Carbamate Group by Using TMSOTf: To an oven-dried sealed tube charged with **3a** (60.5 mg, 0.2 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was added TMSOTf (88.9 mg, 0.4 mmol, 2 equiv.) at 0 °C under N_2. The reaction mixture was allowed to stir at room temperature for 3 h. The resulting mixture was quenched with H_2O (10 mL), and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with H_2O and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc, 5:1) to afford the corresponding ketone **6a** (27.5 mg, 60 % yield).

1-Methyl-3-(2-oxo-2-phenylethyl)pyrrolidine-2,5-dione (6a): Colorless sticky oil (27.5 mg, 60 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.0 Hz, 2 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 3.62 (dd, *J* = 18.5, 3.5 Hz, 1 H), 3.43 (dd, *J* = 18.5, 7.5 Hz, 1 H), 3.26–3.23 (m, 1 H), 3.04 (s, 3 H), 3.01 (t, *J* = 9.0 Hz, 1 H), 2.44 (dd, *J* = 18.0, 5.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.7, 179.7, 176.5, 135.8, 133.7, 128.7, 127.9, 38.9, 35.7, 34.7, 24.9 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 2922, 1775, 1682, 1596, 1436, 1384, 1280, 1125, 1017, 758 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{13}H_{13}NO_3$ $[M]^+$ 231.0895; found 231.0894.

Reductive Cleavage of an Enol Carbamate Group: To a stirred solution of **3a** (60.5 mg, 0.2 mmol, 1 equiv.) in MeOH (1 mL) was added 10 % Pd/C (21.3 mg, 0.02 mmol, 10 mol-%). The reaction mixture was stirred under a hydrogen balloon for 24 h and then concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc, 3:1) to afford **6b** (35.0 mg, 80 % yield).

2-(1-Methyl-2,5-dioxopyrrolidin-3-yl)-1-phenylethane (6b): Light yellow oil (35.0 mg, 80 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.27 (m, 2 H), 7.21–7.17 (m, 3 H), 2.95 (s, 3 H), 2.83–2.67 (m, 4 H), 2.36 (dd, *J* = 17.3, 3.8 Hz, 1 H), 2.29–2.22 (m, 1 H), 1.84–1.76 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.0, 176.6, 140.4, 128.7, 128.6, 126.5, 39.3, 34.5, 33.2, 33.0, 24.9 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2853, 1774, 1694, 1434, 1381, 1277, 1122, 955 cm^{-1}. HRMS (quadrupole, EI): calcd. for $C_{13}H_{15}NO_2$ $[M]^+$ 217.1103; found 217.1100.

Experimental Procedure and Characterization Data for the Preparation of Deuterio-1a: To an oven-dried round-bottom flask charged with sodium hydride (60 % suspension in oil, 400 mg, 10.0 mmol) was added $[D_6]$DMSO (8 mL) at room temperature. The reaction mixture was stirred at 50 °C for 2 h, and the resulting mixture was cooled to room temperature. To the reaction mixture was added dropwise a solution of $[D_3]$acetophenone (0.99 g, 8 mmol) in $[D_6]$DMSO (1 mL) over 10 min, and the resulting mixture was further stirred at room temperature for 30 min. To this mixture was added dropwise a solution of dimethylcarbamoyl chloride (1.08 g, 10.0 mmol) in $[D_6]$DMSO (1 mL) at room temperature over 10 min. The reaction mixture was stirred overnight and then quenched with D_2O (10 mL). The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc, 6:1) to afford deuterio-**1a** (0.485 g, 32 % yield). ^{1}H NMR analysis showed a mixture of three products d_2-**1a**/(*E*)-d_1-**1a**/(*Z*)-d_1-**1a**, 96:2:2; colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 2 H), 7.37–7.28 (m, 3 H), 5.41 (s, 0.02 H), 5.02 (s, 0.02 H), 3.12 (s, 3 H), 2.98 (s, 3 H) ppm.

Kinetic Isotope Effect (KIE) Experiments: To an oven-dried sealed tube charged with 1-phenylvinyl *N*,*N*-dimethylcarbamate (**1a**, 38.2 mg, 0.2 mmol, 1 equiv.), $[RhCp^*Cl_2]_2$ (2.5 mol-%), $AgSbF_6$ (20 mol-%), and PivOH (2 equiv.) in DCE (1 mL) were added *N*-methylmaleimide (**2a**, 44.4 mg, 0.4 mmol, 2 equiv.) and bromobenzene (157.0 mg, 5 equiv.) as an internal standard. In another reaction tube, deuterio-**1a** (98 % D, 38.6 mg, 0.2 mmol, 1 equiv.) was used instead of **1a**. The two reactions were allowed to stir at 70 °C. An aliquot of each reaction mixture was removed at 10, 20, 30, 40, and 50 min intervals. The corresponding yield of product for each sample was determined by GC analysis (bromobenzene as an internal standard). A kinetic isotope effect value (k_H/k_D) of 1.11 was observed.

D-3a: Yellow sticky solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 1 H), 7.35–7.28 (m, 3 H), 3.84–3.80 (m, 1 H), 3.14 (s, 3 H), 3.09–3.02 (m, 4 H), 2.96 (s, 3 H), 2.70 (dd, *J* = 18.4, 5.6 Hz, 1 H) ppm.

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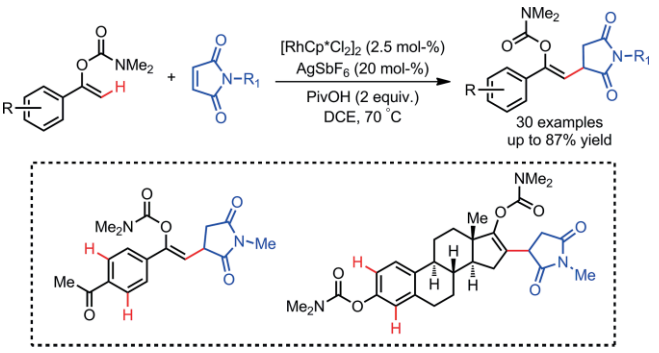
C–H Activation



The rhodium(III)-catalyzed direct C–H alkylation of enol carbamates with a range of maleimides is described. With the assistance of the carbamoyl directing group, this reaction provides biologically relevant succinimide compounds by proceeding through a C–Rh addition and subsequent protonation pathway.

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