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Aerobic Oxidative Olefination of Benzamides with Styrenes Catalyzed by a Moderately Electron-Deficient CpRh(III) Complex with a Pendant Amide

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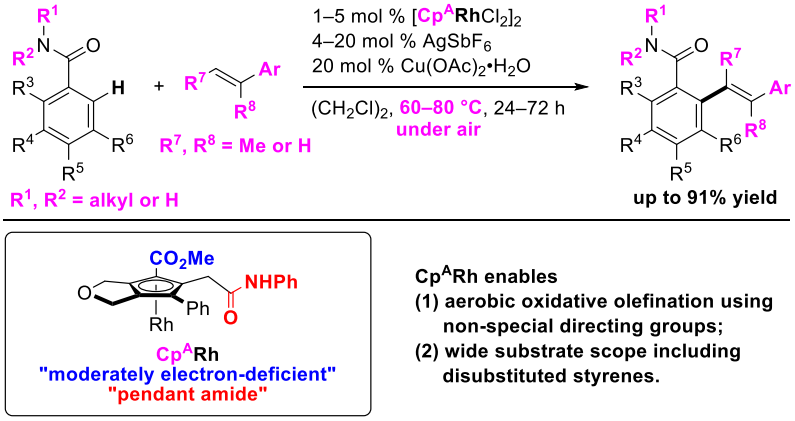


ABSTRACT: It has been established that a newly developed moderately electron-deficient cyclopentadienyl (Cp)-Rh(III) complex, bearing ester and pendant amide moieties on the Cp ring [Cp^{A}Rh(III)], is able to catalyze the aerobic oxidative olefination of benzamides, bearing non-special carbamoyl groups, with styrenes including disubstituted ones at relatively low temperature (60–80 °C). The presence of both the ester and pendant acidic *N*-phenylcarbamoyl moieties on the Cp^A ligand play important roles in facilitation of the catalysis without sacrificing thermal stability of the complex.

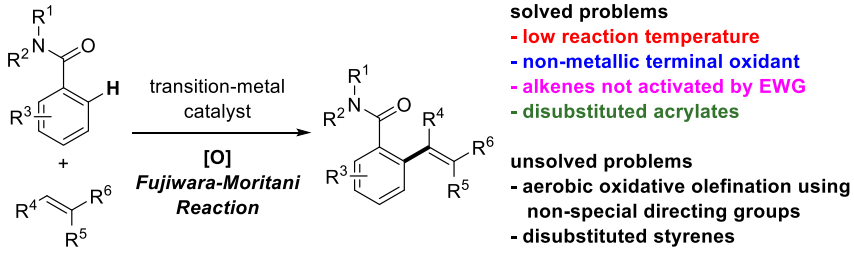
INTRODUCTION

The transition-metal catalyzed oxidative C–H olefination of arenes with olefins (i.e., the Fujiwara-Moritani and oxidative Heck reactions) are atom- and step-economical methods for the synthesis of substituted styrenes.[1,2] In particular, the use of directing groups realized regioselective ortho-directed transformations.[3] In this area, benzamides are commonly investigated substrates and a number of amide-directed oxidative olefinations catalyzed by a Cp*Rh(III) complex has been reported (Scheme 1).[4] However, there are limitations on the reaction conditions and substrate scope of these transformations. In terms of the reaction conditions, high reaction temperature and a stoichiometric amount of a metal oxidant are typically required. In terms of the substrate scope, the use of styrenes giving stilbenes generally results in lower yields than the use of activated alkenes bearing electron-withdrawing groups. Additionally, the use of disubstituted alkenes is scarce.

In 2010, the neutral pentamethylcyclopentadienyl (Cp*)-Rh(III) complex-catalyzed oxidative olefination of benzamides was first reported using acrylates and a stoichiometric amount of a silver oxidant at 110 °C.[4a] A single example using styrene was demonstrated, while the yield of the corresponding stilbene derivative was moderate. The use of a cationic Cp*Rh(III) complex broadened the scope of styrenes and improved the yields of stilbene products; however, a stoichiometric amount of a copper(II) oxidant and the high reaction temperature (120 °C) were still required.[4b] Subsequently, the low-temperature (60 °C) C–H olefination of benzamides with styrenes was reported, but the *N*-methoxycarbamoyl group was necessary as an oxidizing-directing group.[4c] Recently, the aerobic oxidative olefination of benzamides was achieved at 80 °C, even when styrenes were employed, but the highly acidic *N*-pentafluorophenylcarbamoyl directing group was necessary.[4e] Therefore, the aerobic oxidative olefination of benzamides bearing non-special carbamoyl groups with styrenes remains a challenge.[5] Following the above Rh-catalyzed reactions, Ru,[4d,6,7] Ir,[8] Co,[9] and Pd[10]-catalyzed variants were reported, and the use of $Pd(OAc)_2$ enabled the oxidative olefination-cyclization of benzamides with styrenes at 90 °C using O_2 as a terminal oxidant. However, the directing group was still limited to the *N*-methoxycarbamoyl group.[8b]

Furthermore, usable disubstituted alkenes in the previously reports were limited to electron-deficient acrylate derivatives, and so the aerobic oxidative olefination using disubstituted styrenes is highly challenging.[5,7] In this paper, we have established that a newly developed moderately electron-deficient CpRh(III) complex bearing ester and pendant amide moieties on the Cp ring is able to catalyze the aerobic oxidative olefination of benzamides with styrenes, including disubstituted ones, at relatively low temperature (60–80 °C).

Scheme 1. Oxidative Olefinations of Benzamides

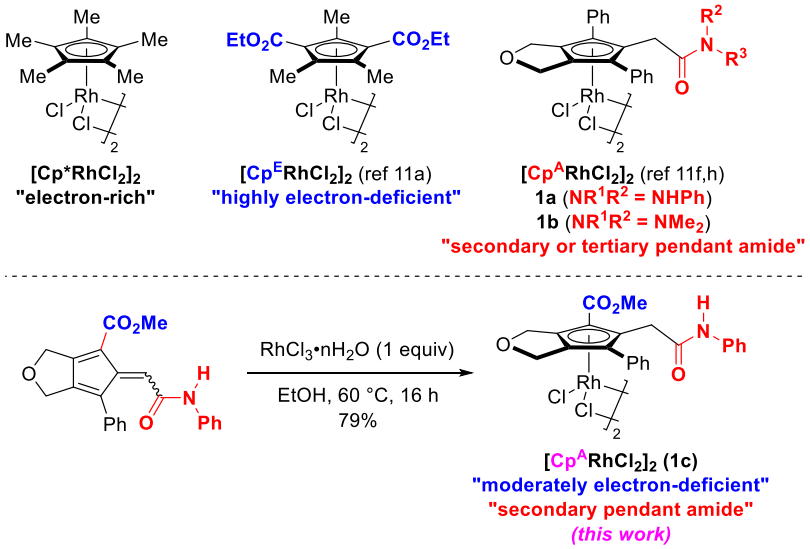


	EWG more reactive alkenes	Ar less reactive olefins	R^4 R^6 R^5
Li (2010)[4a] $[Cp^*RhCl_2]_2$,110 °C Ag_2CO_3 (2 equiv)	74–96% (>10 examples)	42% (1 examples)	–
Glorius (2011)[4b] $[Cp^*RhCl_2]_2$, $AgSbF_6$, 120 °C $Cu(OAc)_2$ (2.1 equiv)	95%	60–86% (>10 examples)	**76%** (R^4 = Me, R^5 = H, R^6 = CO_2Me) **49%** (R^4 = H, R^5 = Me, R^6 = CO_2Me)
Glorius (2011)[4c] $[Cp^*RhCl_2]_2$, CsOPiv, **60 °C** **NR^1R^2 = NHOMe**	74%	62–99% (>20 examples)	–
Lu, Yu (2015)[4e] $[Cp^*RhCl_2]_2$, NaOPiv, **80 °C** **O_2 in air** **NR^1R^2 = NHC_6F_5**	73–92% (>10 examples)	64–79% (3 examples)	–
Hii (2016)[8b] $Pd(OAc)_2$, $Cu(OAc)_2$•H_2O, **90 °C** **O_2** **NR^1R^2 = NHOMe**	–	17–72% (>20 examples)	–

Our research group previously developed modified CpRh(III) complexes through the reductive complexation of $RhCl_3$ with substituted fulvenes (Scheme 2).[11–13] These complexes exhibited high catalytic activities in various C–H functionalizations.[11] For example, a highly electron-deficient Cp^ERh(III) complex bearing two ester moieties on the Cp ring catalyzed the aerobic oxidative annulation and olefination of anilides with various alkynes and alkenes, respectively, including unactivated ones, under ambient conditions.[11a–e] Subsequently, Cp^ARh(III) complex **1a** bearing a pendant *N*-phenylcarbamoyl

moiety on the Cp ring also catalyzed the aerobic oxidative annulation of acetanilide with diphenylacetylene under ambient conditions.[11f] We believe that increasing electrophilicity of the Cp^{E}Rh(III) complex[11a,13] and contribution of intramolecular C–H extraction by the pendant acidic *N*-phenylcarbamoyl moiety of **1a** accelerate the C–H cleavage. Interestingly, Cp^{A}Rh(III) complex **1b** bearing a pendant *N*,*N*-dimethylcarbamoyl moiety on the Cp ring catalyzed not the usual [4+2] annulation but the unusual formal Lossen rearrangement/[3+2] annulation of *N*-pivaloyl benzamides with alkynes. Coordination of the pendant *N*,*N*-dimethylcarbamoyl moiety to rhodium may accelerate ring contraction rearrangement.[11h]

Scheme 2. Modified CpRh(III) Complexes

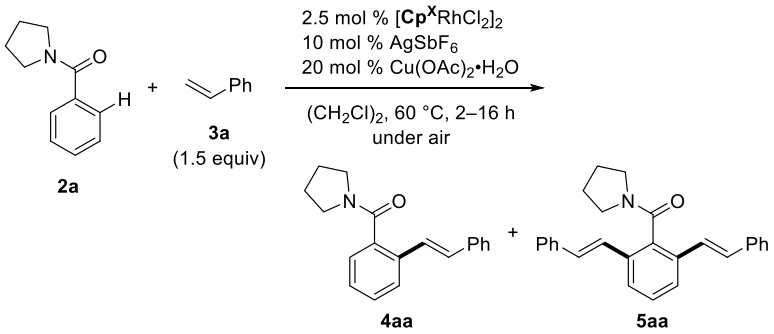


RESULTS AND DISCUSSION

Thus, we attempted the oxidative olefination of pyrrolidine-based benzamide **2a** with styrene (**3a**) by using these modified CpRh(III) complexes as well as the Cp*Rh(III) complex in the presence of $AgSbF_6$/$Cu(OAc)_2$•H_2O co-catalysts in 1,2-dichloroethane at 60 °C under air. Interestingly, the use of our modified CpRh(III) complexes afforded the desired olefinated product **4aa** in significantly higher yields than the use of the Cp*Rh(III) complex (Table 1, entry 1 vs. entries 2–4). The electron-deficient Cp^{E}Rh complex exhibited the highest catalytic activity (entry 2), and Cp^{A}Rh(III) complex **1a** bearing a pendant *N*-phenylcarbamoyl moiety exhibited higher catalytic activity than Cp^{A}Rh(III) complex **1b** bearing a pendant *N*,*N*-dimethylcarbamoyl moiety (entry 3 vs, entry 4). As the Cp^{Cy}Rh complex bearing

two phenyl groups[13,14] showed lower activity than **1a** and **1b** (entry 5), the pendant amide moiety certainly improve the catalytic activity. Subsequently, we synthesized moderately electron-deficient $Cp^{A}Rh(III)$ complex **1c** bearing both the ester and pendant *N*-phenylcarbamoyl moieties on the Cp ring to increase the electrophilicity of the complex (Scheme 2). Pleasingly, the use of **1c** increased the yield of **4aa** to 60% (entry 6). Although further screening of counter anions, additives (Table S1), and solvents (Table S2) failed to improve the yield of **4aa**, elevation of the reaction temperature to 80 °C improved the yield to 79% (entry 7). Instead, a prolonged reaction time and high catalyst loading did also improve the yield to 85% (entries 8 and 9). Under the same conditions, the use of the highly electron-deficient $Cp^{E}Rh(III)$ complex did not improve the yield of **4aa**, because of generation of doubly olefinated **5aa** (entry 10). In terms of the total yield, $Cp^{E}Rh(III)$ resulted in the lower yield than **1c** presumably due to its instability at 60 °C [entry 9 (93%) vs. entry 10 (78%)].[15]

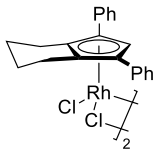
Table 1. Optimization of Reaction Conditions[a]



entry	[Rh₂]	time (h)	yield (%)[b]	
			4aa	**5aa**
1	$[Cp^{*}RhCl_2]_2$	2	15	<3
2	$[Cp^{E}RhCl_2]_2$	2	57	5
3	**1a**	2	42	<3
4	**1b**	2	32	<3
5	$[Cp^{Cy}RhCl_2]_2$	2	22	<3
6	**1c**	2	60	4
7[c]	**1c**	2	79	<3
8	**1c**	2	63	4
9[d]	**1c**	16	85 (90[e])	8
10[d]	$[Cp^{E}RhCl_2]_2$	16	56	22

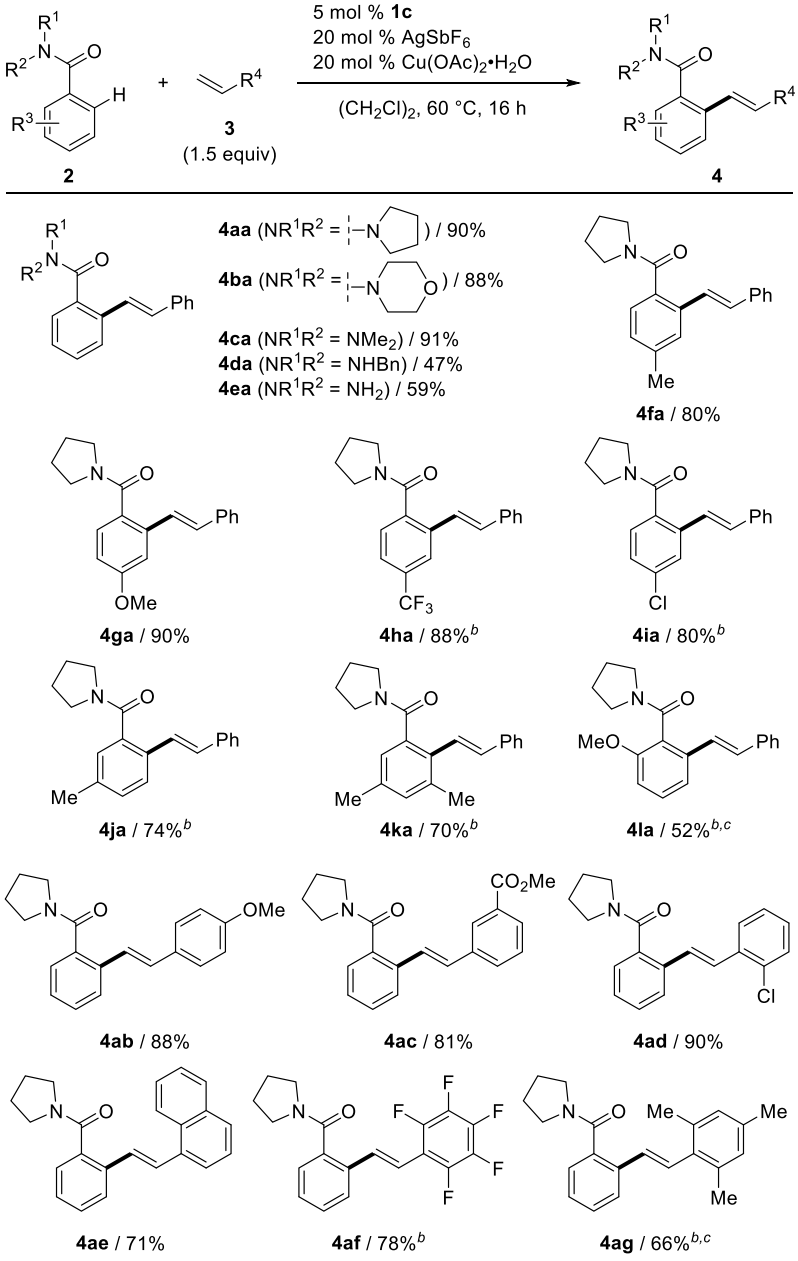
[a] $[Cp^{X}RhCl_2]_2$ (0.0025 mmol), $AgSbF_6$ (0.010 mmol), $Cu(OAc)_2•H_2O$ (0.020 mmol), **2a** (0.100 mmol),

3a (0.150 mmol), and $(CH_2Cl)_2$ (0.5 mL) were used. [b] Determined by ^1H NMR spectroscopy. [c] At 80 °C. [d] **1** (5 mol %, 0.0050 mmol) and $AgSbF_6$ (20 mol %, 0.020 mmol) were used. [e] Isolated yield for the reactions using **1c** (0.010 mmol), $AgSbF_6$ (0.040 mmol), $Cu(OAc)_2•H_2O$ (0.040 mmol), **2a** (0.200 mmol), **3a** (0.300 mmol), and $(CH_2Cl)_2$ (1.0 mL).



$[Cp^{Cy}RhCl_2]_2$

Scheme 3. Scope of Benzamides and Styrenes[a]

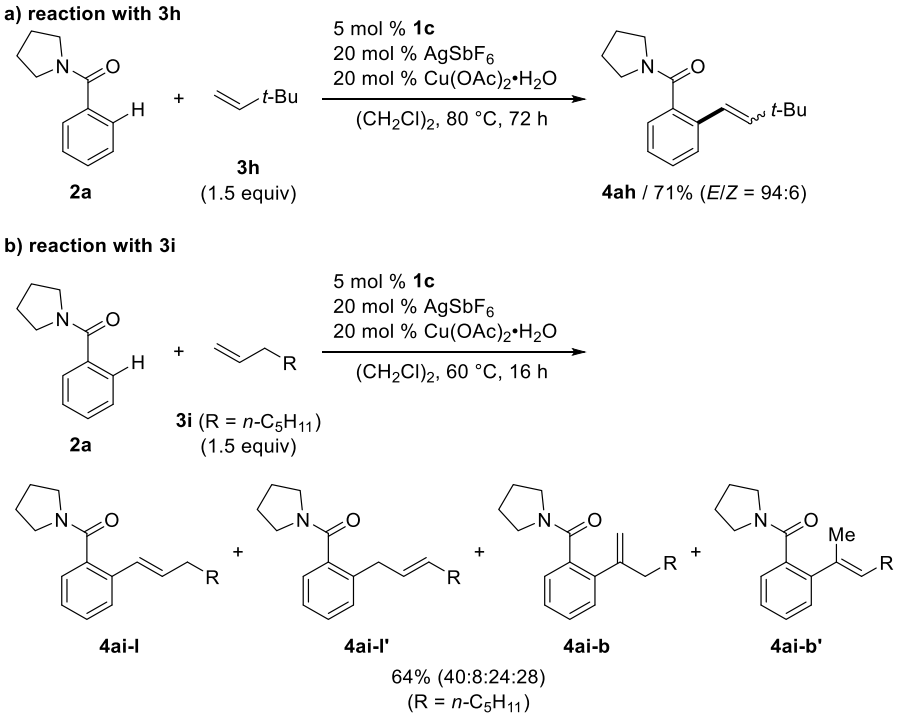


[a] **1c** (0.010 mmol), $AgSbF_6$ (0.040 mmol), $Cu(OAc)_2•H_2O$ (0.040 mmol), **2** (0.200 mmol), **3** (0.300 mmol), and $(CH_2Cl)_2$ (1.0 mL) were used. [b] For 72 h. [c] At 80 °C.

The substrate scope of the reaction was then examined, as shown in Scheme 3. In terms of the amide-directing group, not only tertiary (**2a**–**c**) but also secondary (**2d**) and primary (**2e**) amides were applicable, although the yields were moderate. In addition, various electron-donating (**2f** and **2g**) and electron-withdrawing (**2h** and **2i**) substituents were tolerated at the para-position of the benzene ring. In the reaction of meta-substituted benzamide **2j**, the olefination proceeded selectively at the sterically vacant position. Fortunately, less reactive 3,5-disubstituted **2k** and ortho-substituted **2l** could be employed, although high temperature (80 °C) and/or prolonged reaction time (72 h) were required. In terms of the styrenes, electronically and sterically diverse ones (**3b**–**g**) reacted with **2a** to give the corresponding products **4ab**–**ag** in high yields. Notably, extremely bulky *ortho*-disubstituted styrene **3g**, which has not been explored in the previously reported oxidative olefinations, could also be applicable to the present Cp^ARh catalysis.

The reactions of aliphatic alkenes were also investigated. Bulky 3,3-dimethyl-1-butene (**3h**) that was unusable in our previously reported Cp^ERh(III)-catalyzed olefination of anilides[11c] reacted with **2a** at 80 °C to give olefinated product **4ah** in 71% yield (Scheme 4a). Less bulky 1-octene (**3i**) also reacted with **2a** under the same conditions to give the corresponding oxidative olefination products in good yields, but a mixture of linear/branch and double bond isomers were generated with low selectivity (Scheme 4b).

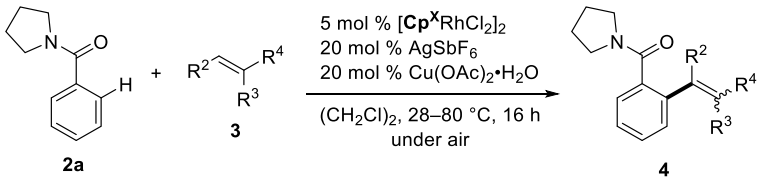
Scheme 4. Olefination with Aliphatic Alkenes

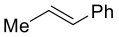
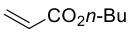
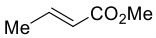
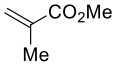


This successful use of bulky and less reactive **3g** and **3h** prompted our investigation into the use of less reactive disubstituted alkenes. To our delight, 1,2-disubstituted styrene **3j** reacted with **2a** to give **4aj** accompanied by its isomer **4aj'** in moderate yield (Table 2, entry 1). Elevation of the reaction temperature to 80 °C improved the total yield (entry 2, left column). Not only **3j** but also 1,1-disubstituted styrene **3k** equally employed to give **4ak** in good yield (entry 3, left column). Under the conditions, the use of the Cp^E and Cp* ligands afforded **4aj** and **4ak** in lower yields (entries 2 and 3, middle and right columns), especially in the reactions of far less coordinative **3j** (entry 2). The reactions of mono- and disubstituted acrylates **3l**–**n** with **2a** were also catalyzed by **1c** to give **4al**–**an** at room temperature in higher yields than the use of the Cp^ERh(III) and Cp*Rh(III) catalysts (entries 4–6). The reactions of **2a** with acrylate **3l** and crotonate **3m** were also catalyzed by **1c** to give **4al** and **4am** at room temperature in higher yields than the use of the Cp^ERh(III) and Cp*Rh(III) catalysts (entries 4 and 5). In these reactions, (*E*)-trisubstitued alkenes were generated as sole or major isomers (76–100% selectivity). However, the reaction of **2a** with methacrylate **3n** at room temperature afforded disubstituted alkene **4an'** (allylation product) as a major isomer. This disubstituted alkene **4an'** may be a kinetic product, thermodynamically

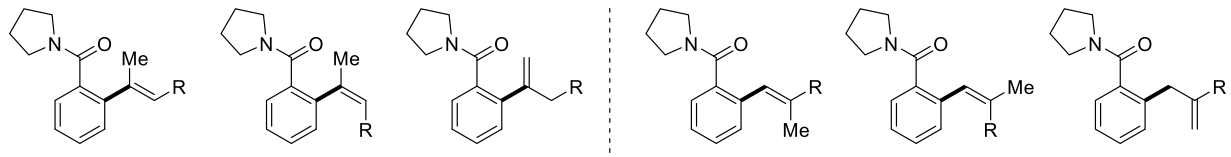
stable (*E*)-trisubstituted alkene **4an** was generated as a major isomer at elevated temperature (80 °C). Finally, the reactions of (*E*)- and (*Z*)-stilbenes with **2a** were also tested, but no reaction was observed even at the elevated temperature of 80 °C.

Table 2. Scope of Disubstituted Alkenes and Ligand-Effects[a]



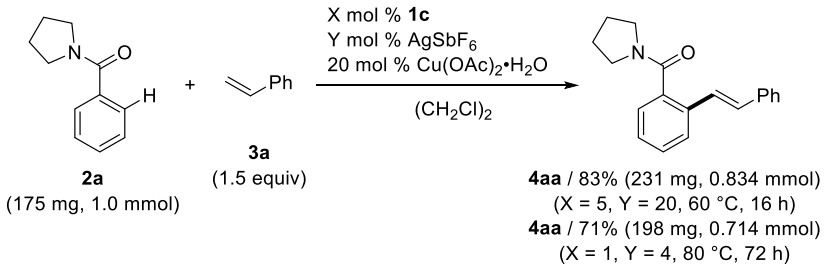
entry	**3**	temp. (°C)	% yield [ratio of (*E*)-**4**/(*Z*)-**4**/**4'**][b] Cp^A (**1c**)	Cp^E	Cp*
1	 **3j**	60	**54**[c] (85:7:8)	–	–
2		80	**74**[c] (85:12:3)	17 (77:4:19)	21 (89:11:0)
3	 **3k**	80	**72**[c] (76:16:8)	64 (66:20:14)	35 (55:37:8)
4	 **3l**	28	**90**[c] [(*E*)-only]	82 [(*E*)-only]	19 [(*E*)-only]
5	 **3m**	28	**77**[c] (82:18:0)	70 (84:14:2)	56 (82:18:0)
6	 **3n**	28	**57**[c] (16:14:70)	52 (15:15:70)	<3 (–)
7		80	**81**[c] (58:27:15)	–	–

[a] $[Cp^XRhCl_2]_2$ complexes (0.0050 mmol), $AgSbF_6$ (0.020 mmol), $Cu(OAc)_2•H_2O$ (0.020 mmol), **2a** (0.100 mmol), **3** (0.150 mmol), and $(CH_2Cl)_2$ (0.5 mL) were used. [b] Determined by ^1H NMR. The products were obtained as a mixture of *E*/*Z* stereoisomers **4** and regioisomers **4'** as shown below. [c] The yields are isolated yields using **1c** (0.010 mmol), $AgSbF_6$ (0.040 mmol), $Cu(OAc)_2•H_2O$ (0.040 mmol), **2a** (0.200 mmol), **3** (0.300 mmol), and $(CH_2Cl)_2$ (1.0 mL).



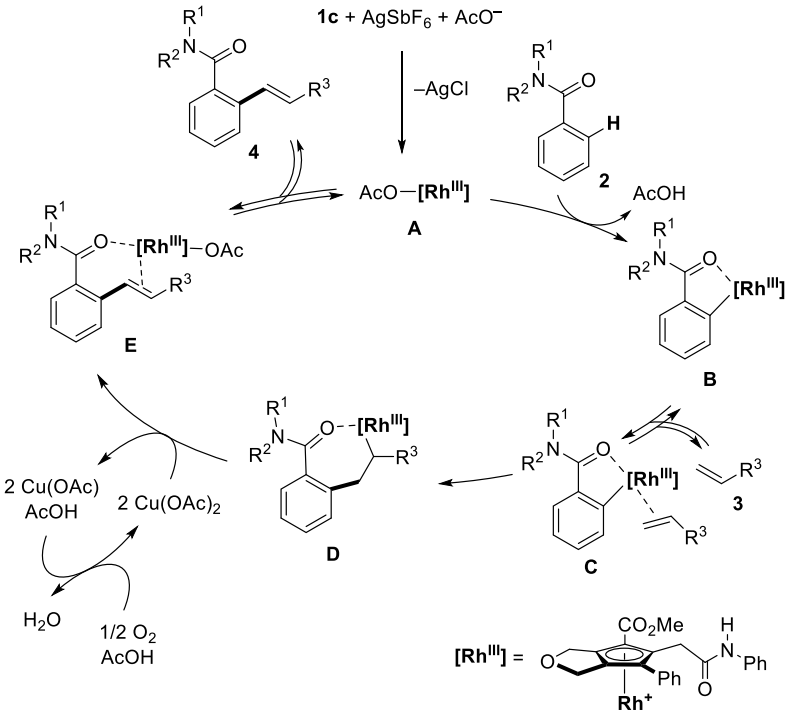
Preparative scale reactions (Scheme 5) were also conducted, giving **4aa** without any significant decrease in yield. Although high temperature (80 °C) was necessary, the low catalyst loading reaction (1 mol % **1c**) proceeded to give **4aa** in satisfactory yield.

Scheme 5. Preparative Scale Reactions



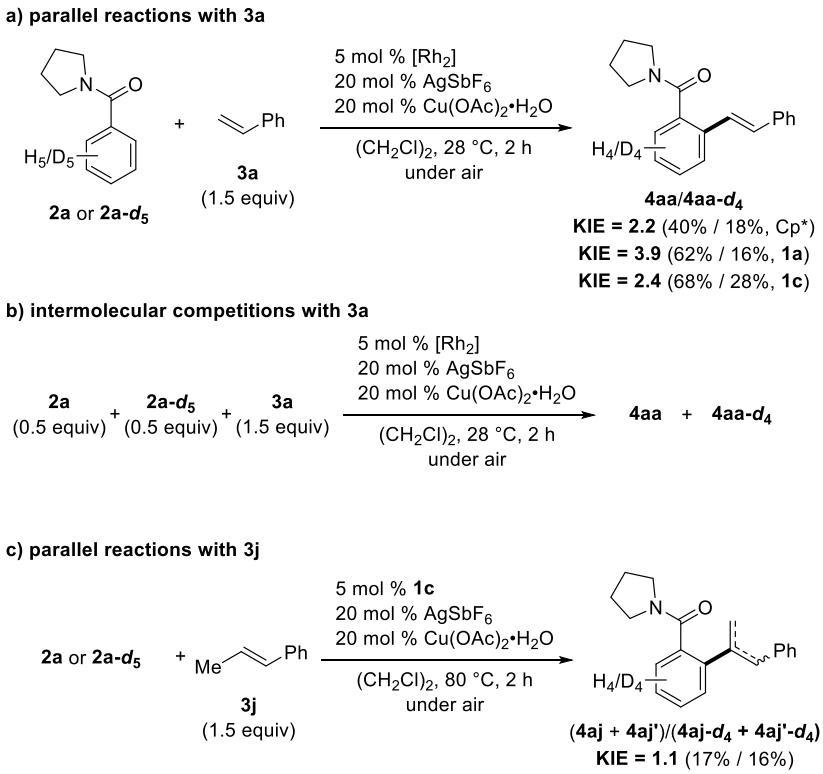
Based on previous reports,[4] a plausible reaction mechanism was proposed as outlined in Scheme 6. First, the catalytically active rhodium(III) acetate **A** generated from **1c**, $AgSbF_6$, and an acetate anion reacts with **2** to form rhodacycle **B** via an electrophilic concerted metalation-deprotonation pathway. Subsequent alkene coordination and insertion afford rhodacycle **D** via **C**. β-Hydride elimination and oxidation with a Cu(II) oxidant afford product **4**-coordinating rhodium(III) acetate **E**. Finally, dissociation of the product **4** regenerates the catalytically active species **A**.

Scheme 6. Plausible Reaction Mechanism



To explore the effect of the Cp ligand on the catalytic cycle, deuterium kinetic isotope effects (KIEs) of the olefination of **2a** with **3a** were measured by the two parallel reactions (Scheme 7a) and the intermolecular competition reactions (Scheme 7b) using the Cp* and Cp^A (**1a** and **1c**) Rh(III) complexes as the catalysts. We found that the reactions using the Cp*Rh(III) complex resulted in the significantly different KIE values (2.2 vs. 4.9), while no significant H/D exchange of the recovered **2a**-d_5 with H_2O was observed in the parallel reactions (Scheme S1). These observations suggest that not only the irreversible C–H cleavage step but other rate-limiting steps may also exist in the Cp*Rh(III)-based catalysis.[15] In contrast, in the reactions using **1a** and **1c**, no significant KIE difference was observed between the two measurements (3.9 vs. 5.8 using **1a**, 2.4 vs. 3.0 using **1c**), which suggests that not only the C–H bond cleavage step but also the other rate-limiting steps may be accelerated by the pendant amide moiety of the Cp^ARh(III) catalyst.

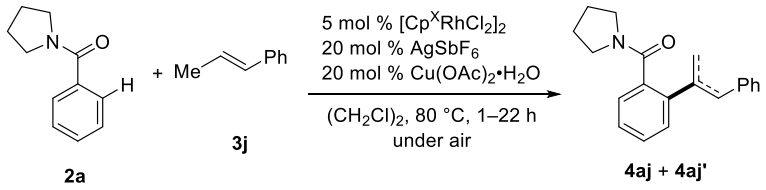
Scheme 7. Deuterium Kinetic Isotope Effects



Thus, the roles of the ester and amide moieties of **1c** may be the followings. The ester moiety accelerates the C–H bond cleavage even with a weakly coordinating directing group and the alkene insertion due to the electron-deficient nature of the rhodium center.[5] On the other hand, the pendant secondary amide moiety accelerates the C–H bond cleavage by intramolecular C-H extraction, and controls the coordination equilibrium of substrates and products by its hemilabile coordination to rhodium, which facilitates the alkene coordination and product dissociation giving intermediates **C** and **A**, respectively.[16]

In the reaction of far less coordinative 1,2-disubstituted styrene **3j**, the alkene coordination and insertion steps would be more rate-limiting than the C–H cleavage step. Indeed, the parallel reactions using **3j** resulted in no KIE (Scheme 7c). In this reaction, **1c** showed the significantly higher catalytic activity than the $Cp^{E}Rh(III)$ complex (Table 2, entry 2). Time course of these reactions revealed that **1c** is significantly more stable than the $Cp^{E}Rh(III)$ complex at 80 °C (Scheme 8, Figure 1),[17] which accounts for the high catalytic activity of **1c**. The pendant acidic *N*-phenylcarbamoyl moiety on the Cp^{A} ligand may accelerate the C–H cleavage without introducing two ester moieties that cause low thermal stability of the complex.

Scheme 8. Reaction Profiles for Oxidative Olefination of 2a with 3j



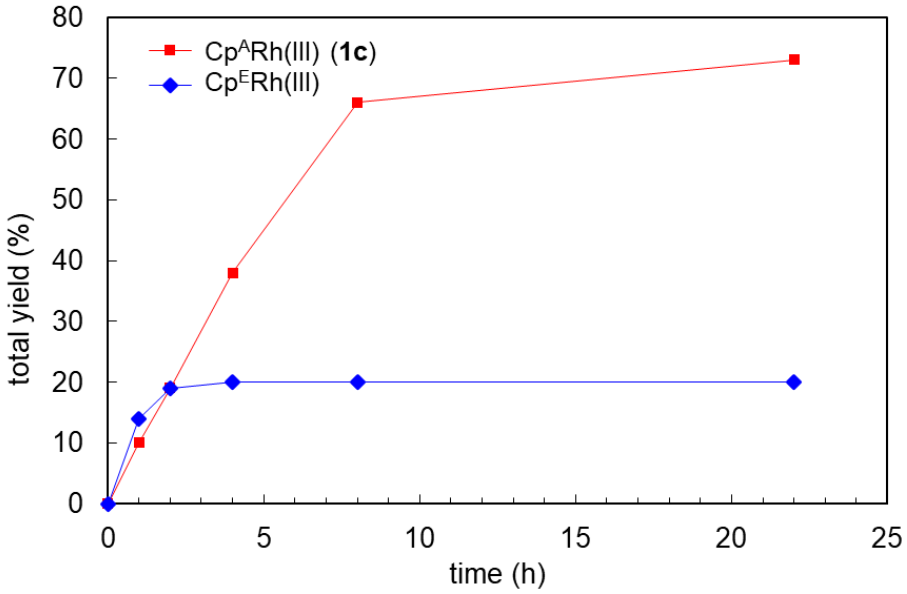


Figure 1. Reaction profiles for the oxidative olefination of **2a** with **3j** in the presence of complex **1c** (red square) or $[Cp^ERhCl_2]_2$ (blue diamond). The total yields of (*E*/*Z*)-**4aj** and **4aj'** are shown.

CONCLUSION

In conclusion, we have established that a newly developed moderately electron-deficient cyclopentadienyl (Cp)-Rh(III) complex, bearing ester and pendant amide moieties on the Cp ring [$Cp^ARh(III)$], is able to catalyze the aerobic oxidative olefination of benzamides, bearing non-special carbamoyl groups, with styrenes including disubstituted ones at relatively low temperature (60–80 °C). The presence of both the ester and pendant acidic *N*-phenylcarbamoyl moieties on the Cp^A ligand play important roles in facilitation of the catalysis without sacrificing thermal stability of the complex. Future works will include the further application of the $Cp^ARh(III)$ complex in the problematic C–H bond functionalization reactions.

EXPERIMENTAL SECTION

General: Anhydrous $(CH_2Cl)_2$ (No. 28,450-5) was obtained from Aldrich used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. Rh(III) complexes **1a**,[11f] **1b**,[11f] $[Cp^ERhCl_2]_2$,[11a] $[Cp^{Cy}RhCl_2]_2$,[13] benzamides **2a**,[18] **2b**,[18] **2f**,[18] **2g**,[18] **2h**,[18] **2i**,[18] **2j**,[18] **2k**,[19] **2l**,[20] and alkene **3c**[21] were prepared according to the literature procedures. All other reagents were obtained from commercial sources and used as received. ^1H and $^{13}C\{^1H\}$ NMR data were collected on a Bruker AVANCE III HD 400 (400 MHz) at ambient temperature. HRMS data were obtained on a Bruker micrOTOF Focus II. All reactions were carried out in oven-dried glassware with magnetic stirring. An oil bath was used for the reactions that require heating (60 °C or 80 °C).

Methyl -5-[2-oxo-2-(phenylamino)ethylidene]-6-phenyl-3,5-dihydro-1*H*-cyclo-penta[*c*]furan-4-carboxylate: Segphos (12.2 mg, 0.0200 mmol) and $[Rh(cod)_2]BF_4$ (8.1 mg, 0.0200 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at room temperature (28 °C) for 10 min. H_2 was introdced to the resulting solution in a Schlenk tube. After stirring at room temperature (28 °C) for 30 min, the resulting mixture was concentrated and dissolved in $(CH_2Cl)_2$ (0.5 mL). To the solution were added a solution of 2-cyclopropylidene-*N*-phenylacetamide[11f] (38.2 mg, 0.220 mmol) in $(CH_2Cl)_2$ (0.5 mL) and methyl 4-[(3-phenylprop-2-yn-1-yl)oxy]but-2-ynoate[22] (45.6 mg, 0.200 mmol) in $(CH_2Cl)_2$ (1.0 mL) in this order and the resulting mixture was stirred at 40 °C for 16 h. The resulting solution was concentrated and purified by a silica gel preparative TLC (eluent: EtOAc), which furnished the title compound (42.3 mg, 0.113 mmol, 57% isolated yield, *E*/*Z* = 77:23) as an orange amorphous. ^1H NMR ($CDCl_3$, 400 MHz) of (*E*)-isomer: δ 7.87 (s, 1H), 7.58 (s, 1H), 7.47–6.95 (m, 9H), 4.86 (s, 2H), 4.69 (s, 2H), 3.79 (s, 3H); ^1H NMR ($CDCl_3$, 400 MHz) of (*Z*)-isomer: δ 8.24 (s, 1H), 7.61 (s, 1H), 7.47–6.95 (m, 8H), 6.72 (s, 1H), 4.86 (s, 2H), 4.71 (s, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 163.3, 163.3, 163.2, 149.9, 148.0, 146.0, 136.8, 133.9, 133.3, 132.4, 129.8, 129.3, 129.0, 128.9, 128.6, 128.3, 127.9, 127.7, 124.5, 119.9, 119.8, 113.4, 68.2, 67.9, 66.3, 60.3, 51.7, 51.4; HRMS (ESI) calcd for $C_{23}H_{19}NNaO_4$ $[M+Na]^+$ 396.1206, found 396.1216.

Cp^ARh Complex 1c: To a solution of $RhCl_3$•*n*H_2O (39.15 wt% Rh, 29.4 mg, 0.113 mmol) in EtOH (1.0 mL) was added a solution of methyl 5-[2-oxo-2-(phenylamino)ethylidene]-6-phenyl-3,5-dihydro-1*H*-cyclo-penta[*c*]furan-4-carboxylate (42.3 mg, 0.113 mmol, *E*/*Z* = 77:23) in EtOH (1.0 mL) and the mixture was stirred at 60 °C for 16 h. The resulting mixture was concentrated under reduced pressure and the residue was diluted with CH_2Cl_2 (2.0 mL) and filtered. The filtrate was poured into *n*-hexane (10.0 mL) and the resulting precipitates were collected, washed with Et_2O (2.0 mL) twice and dried under vacuum to give **1c** (50.1 mg, 0.0446 mmol, 79% isolated yield) as a red solid. Mp >300 °C; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.59 (br, 2H), 7.73–7.71 (m, 4H), 7.51–7.42 (m, 10H), 7.30–7.26 (m, 4H), 7.09–7.05 (m, 2H), 4.73 (d, 13.9 Hz, 2H), 4.57 (d, 12.8 Hz, 2H), 4.43–4.40 (m, 4H), 4.23 (d, 16.8 Hz, 2H), 3.82 (s, 6H), 3.66 (d, 16.8 Hz, 2H); ^{13}C{^{1}H} NMR (CD_3CN, 100 MHz) δ 166.1, 165.1, 139.0, 130.5, 130.3, 129.5, 129.43, 129.36, 128.0, 124.6, 110.7, 109.5, 69.1, 66.5, 65.8, 53.5, 34.7; HRMS (ESI) calcd for $C_{23}H_{19}ClNNaO_4Rh$ $[M-HCl+Na]^+$ 533.9950, found 533.9950.

Representative procedure for rhodium-catalyzed oxidative olefination (Table 1, entry 12): To a Schlenk flask was added $AgSbF_6$ (13.6 mg, 0.0400 mmol), complex **1c** (11.0 mg, 0.0100 mmol), $Cu(OAc)_2$•H_2O (8.0 mg, 0.0400 mmol), **2a** (35.0 mg, 0.200 mmol), **3a** (31.2 mg, 0.300 mmol), and $(CH_2Cl)_2$ (1.0 mL) in this order. The mixture stirred at 60 °C under air for 16 h. The resulting mixture was diluted with diethyl ether, filtered through a silica gel pad, and washed with EtOAc. The solvent was concentrated under reduced pressure and the residue was purified by a preparative TLC (toluene/EtOAc = 1:1) to give **4aa** (49.9 mg, 0.180 mmol, 90% yield) as a colorless oil and **5aa** (6.15 mg, 0.0162 mmol, 8% yield).

Procedure for preparative scale reactions (Scheme 5): To a Schlenk flask was added $AgSbF_6$ (13.6 mg, 0.0400 mmol), complex **1c** (11.0 mg, 0.0100 mmol), $Cu(OAc)_2$•H_2O (8.0 mg, 0.0400 mmol), **2a** (175 mg, 1.00 mmol), **3a** (156 mg, 3.00 mmol), and $(CH_2Cl)_2$ (1.0 mL) in this order. The mixture stirred at 80 °C under air for 72 h. The resulting mixture was diluted with diethyl ether, filtered through a silica gel pad, and washed with EtOAc. The solvent was concentrated under reduced pressure and the

residue was purified by a preparative TLC (toluene/EtOAc = 1:1) to give **4aa** (198 mg, 0.714 mmol, 71% yield).

(*E*)-Pyrrolidin-1-yl(2-styrylphenyl)methanone (4aa): Colorless oil; 49.9 mg, 0.180 mmol, 90% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 7.8 Hz, 1H), 7.49–7.46 (m, 2H), 7.41–7.24 (m, 5H), 7.19–7.08 (m, 2H), 3.70 (t, J = 7.0 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 1.96–1.77 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.5, 137.1, 137.0, 133.7, 131.1, 129.1, 128.7, 128.0, 127.7, 126.7, 126.5, 125.7, 125.3, 48.3, 45.6, 26.0, 24.6; HRMS (ESI) calcd for $C_{19}H_{19}NNaO$ $[M+Na]^+$ 300.1359, found 300.1379.

{2,6-Di[(*E*)-Styryl]phenyl}(pyrrolidin-1-yl)methanone (5aa): Colorless oil; 6.15 mg, 0.0162 mmol, 8% yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, J = 7.8 Hz, 2H), 7.50–7.548 (m, 4H), 7.39–7.33 (m, 5H), 7.29–7.26 (m, 2H), 7.12 (s, 4H), 3.76 (t, J = 7.0 Hz, 2H), 3.02 (t, J = 6.8 Hz, 2H), 1.95–1.88 (m, 2H), 1.80–1.74 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 168.6, 137.1, 136.1, 134.0, 131.4, 128.9, 128.7, 128.0, 126.8, 125.2, 124.6, 47.7, 45.4, 25.9, 24.7; HRMS (ESI) calcd for $C_{27}H_{25}NNaO$ $[M+Na]^+$ 402.1828, found 402.1802.

(*E*)-Morpholino(2-styrylphenyl)methanone (4ba): Colorless oil; 52.2 mg, 0.176 mmol, 88% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, J = 7.9 Hz, 1H), 7.49–7.47 (m, 2H), 7.42–7.25 (m, 6H), 7.17–7.07 (m, 2H), 3.91–3.74 (br, 4H), 3.51–3.50 (br, 2H), 3.20 (t, J = 4.8 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.7, 136.8, 134.8, 134.2, 131.6, 129.4, 128.8, 128.2, 127.8, 126.7, 126.7, 125.7, 125.0, 70.0, 66.9, 47.4, 42.1; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_2$ [M+Na]+ 316.1308, found 316.1316.

(*E*)-*N*,*N*-Dimethyl-2-styrylbenzamide (4ca)[6b]: Colorless oil; 45.7 mg, 0.182 mmol, 91% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 7.8 Hz, 1H), 7.49–7.47 (m, 2H), 7.40–7.24 (m, 6H), 7.10 (s, 2H), 3.16 (s, 3H), 2.79 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 171.1, 137.1, 135.9, 134.0, 131.2, 129.1, 128.7, 128.0, 127.7, 126.7, 126.6, 125.6, 125.2, 38.6, 34.8.

(*E*)-*N*-Benzyl-2-styrylbenzamide (4da)[23]: Colorless solid; 29.2 mg, 0.0930 mmol, 47% isolated yield; Mp 119.8–120.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 7.9 Hz, 1H), 7.49 (dd, J = 7.6 Hz, 1.1 Hz, 1H), 7.43–7.24 (m, 13H), 7.01 (d, J = 16.2 Hz, 1H), 6.19 (br, 1H), 4.62 (d, J = 5.9 Hz, 2H);

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.3, 138.2, 137.0, 135.50, 135.48, 131.6, 130.3, 128.8, 128.7, 128.0, 127.9, 127.8, 127.6, 127.5, 126.8, 126.2, 125.9, 44.1.

(*E*)-2-Styrylbenzamide (4ea)[4b]: Colorless solid; 25.9 mg, 0.118 mmol, 59% isolated yield, reaction time: 72 h; Mp 189.5–190.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 7.70 (d, *J* = 7.8 Hz, 1H), 7.59–7.44 (m, 5H), 7.38–7.26 (m, 4H), 7.07 (d, *J* = 16.3 Hz, 1H), 5.87 (br, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 171.3, 137.0, 135.9, 134.3, 131.7, 130.7, 128.7, 128.1, 127.9, 127.5, 126.9, 126.5, 126.1.

(*E*)-(4-Methyl-2-styrylphenyl)(pyrrolidin-1-yl)methanone (4fa): Colorless oil; 46.4 mg, 0.159 mmol, 90% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 7.42–7.39 (m, 3H), 7.29–7.25 (m, 2H), 7.21–7.16 (m, 1H), 7.13–7.00 (m, 4H), 3.61 (t, *J* = 7.0 Hz, 2H), 3.05 (t, *J* = 6.7 Hz, 2H), 2.32 (s, 3H), 1.88–1.80 (m, 2H), 1.76–1.67 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* 169.7, 138.9, 137.3, 134.4, 133.6, 130.7, 128.7, 128.5, 127.9, 126.7, 126.5, 1276.2, 125.5, 48.4, 45.6, 26.0, 24.6, 21.4; HRMS (ESI) calcd for $C_{20}H_{21}NNaO$ $[M+Na]^+$ 314.1515, found 314.1522.

(*E*)-(4-Methoxy-2-styrylphenyl)(pyrrolidin-1-yl)methanone (4ga): Colorless oil; 55.2 mg, 0.180 mmol, 90% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 7.49–7.46 (m, 2H), 7.37–7.33 (m, 2H), 7.28–7.26 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.17 (d, *J* = 16.2 Hz, 1H), 7.08 (d, *J* = 16.2 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.87 (s, 3H), 3.68 (t, *J* = 7.0 Hz, 2H), 3.14 (t, *J* = 6.7 Hz, 2H), 1.95–1.88 (m, 2H), 1.83–1.77 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* 169.5, 160.1, 137.1, 135.5, 131.2, 130.0, 128.7, 128.1, 128.0, 126.7, 125.5, 113.5, 110.6, 55.4, 48.5, 45.7, 26.0, 24.7; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$ 330.1465, found 330.1470.

(*E*)-Pyrrolidin-1-yl[2-styryl-4-(trifluoromethyl)phenyl]methanone (4ha): Colorless solid; 60.5 mg, 0.176 mmol, 88% isolated yield, reaction time: 72 h; Mp 120.0–120.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) *δ* 7.93 (s, 1H), 7.55–7.53 (m, 1H), 7.50–7.48 (m, 2H), 7.42–7.35 (m, 3H), 7.32–7.26 (m, 1H), 7.21–7.12 (m, 2H), 3.71 (t, *J* = 7.0 Hz, 2H), 3.11 (t, *J* = 6.7 Hz, 2H), 1.98–1.91 (m, 2H), 1.87–1.78 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) *δ* 168.1, 140.0, 136.5, 134.7, 133.0, 131.4 (q, *J* = 32.5 Hz), 128.9, 128.5, 127.1, 126.9, 124.2 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 123.8, 122.7 (q, *J* = 3.8 Hz), 48.3, 45.7, 26.0, 24.5; HRMS (ESI) calcd for $C_{20}H_{18}F_3NNaO$ $[M+Na]^+$ 368.1233, found 368.1238.

(*E*)-(4-Chloro-2-styrylphenyl)(pyrrolidin-1-yl)methanone (4ia): Colorless oil; 49.9 mg, 0.160 mmol, 80% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, J = 1.8 Hz, 1H), 7.48–7.46 (m, 2H), 7.38–7.34 (m, 2H), 7.31–7.22 (m, 3H), 7.15–7.06 (m, 2H), 3.69 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 6.7 Hz, 2H), 1.97–1.90 (m, 2H), 1.86–1.79 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 168.5, 136.6, 135.7, 135.3, 135.1, 132.4, 128.8, 128.4, 127.9, 127.6, 126.9, 125.6, 124.0, 48.4, 45.7, 26.0, 24.6; HRMS (ESI) calcd for $C_{19}H_{18}ClNNaO$ $[M+Na]^+$ 334.0969, found 334.0973.

(*E*)-(5-Methyl-2-styrylphenyl)(pyrrolidin-1-yl)methanone (4ja): Colorless oil; 43.2 mg, 0.148 mmol, 74% isolated yield, reaction time: 72 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 2H), 7.28–7.25 (m, 2H), 7.20–7.16 (m, 1H), 7.12–7.10 (m, 1H), 7.07–6.96 (m, 3H), 3.62 (t, J = 7.0 Hz, 2H), 3.06 (t, J = 6.8 Hz, 2H), 2.28 (s, 3H), 1.89–1.82 (m, 2H), 1.77–1.70 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.7, 137.8, 137.3, 137.0, 130.8, 130.1, 129.9, 128.7, 127.7, 127.0, 126.6, 125.6, 125.3, 48.3, 45.6, 26.0, 24.6, 21.1; HRMS (ESI) calcd for $C_{20}H_{21}NNaO$ $[M+Na]^+$ 314.1515, found 314.1519.

(*E*)-(3,5-Dimethyl-2-styrylphenyl)(pyrrolidin-1-yl)methanone (4ka): Colorless solid; 43.0 mg, 0.140 mmol, 70% isolated yield, reaction time: 72 h; Mp 120.0–120.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45–7.43 (m, 2H), 7.35–7.31 (m, 2H), 7.26–7.22 (m, 1H), 7.15 (d, J = 16.4 Hz, 1H), 7.02–6.99 (m, 2H), 6.83 (t, J = 16.4 Hz, 1H), 3.55 (t, J = 6.6 Hz, 2H), 3.08 (t, J = 6.4 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.81–1.70 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 170.5, 137.7, 137.3, 137.0, 136.6, 133.4, 131.6, 130.1, 128.7, 127.7, 126.4, 125.2, 124.5, 47.9, 45.6, 25.9, 24.5, 21.0, 20.6; HRMS (ESI) calcd for $C_{21}H_{23}NNaO$ $[M+Na]^+$ 328.1672, found 328.1658.

(*E*)-(2-Methoxy-6-styrylphenyl)(pyrrolidin-1-yl)methanone (4la): Colorless oil; 31.9 mg, 0.104 mmol, 52% isolated yield, reaction temperature: 80 °C, reaction time: 72 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52–7.46 (m, 2H), 7.35–7.22 (m, 5H), 7.14–7.04 (m, 2H), 6.85–6.81 (m, 1H), 3.84 (s, 3H), 3.81–3.74 (m, 1H), 3.70–3.64 (m, 1H), 3.17–3.11 (m, 1H), 3.09–3.03 (m, 1H), 1.98–1.75 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 167.1, 155.5, 137.1, 135.1, 131.4, 129.5, 128.7, 127.9, 126.8, 126.6,

125.1, 117.8, 109.9, 55.9, 47.4, 45.3, 25.8, 24.7; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$ 330.1465, found 330.1453.

(*E*)-[2-(4-Methoxystyryl)phenyl](pyrrolidin-1-yl)methanone (4ab): Colorless oil; 54.0 mg, 0.176 mmol, 88% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, J = 7.9 Hz, 1H), 7.43–7.34 (m, 3H), 7.29–7.24 (m, 2H), 7.09–6.99 (m, 2H), 6.90–6.87 (m, 2H), 3.82 (s, 3H), 3.70 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 6.7 Hz, 2H), 1.96–1.89 (m, 2H), 1.84–1.77 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.6, 159.6, 136.8, 134.0, 130.6, 130.0, 129.1, 128.0, 127.3, 126.4, 125.5, 123.2, 114.2, 55.3 48.3, 45.6, 26.0, 24.6; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$ 330.1465, found 330.1448.

Methyl (*E*)-3-[2-(pyrrolidine-1-carbonyl)styryl]benzoate (4ac): Colorless oil; 54.5 mg, 0.162 mmol, 81% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13–8.12 (m, 1H), 7.95–7.92 (m, 1H), 7.69–7.65 (m, 2H), 7.44–7.36 (m, 2H), 7.34–7.30 (m, 2H), 7.25–7.11 (m, 2H), 3.94 (s, 2H), 3.71 (t, J = 7.0 Hz, 2H), 3.14 (t, J = 6.7 Hz, 2H), 1.98–1.78 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.4, 166.9, 137.5, 137.1, 133.3, 130.8, 130.7, 130.1, 129.2, 128.9, 128.8, 128.0, 127.9, 126.6 126.5, 125.9, 52.2, 48.4, 45.7, 26.0, 24.6; HRMS (ESI) calcd for $C_{21}H_{21}NNaO_3$ $[M+Na]^+$ 358.1398, found 358.1414.

(*E*)-[2-(2-Chlorostyryl)phenyl](pyrrolidin-1-yl)methanone (4ad): Colorless oil; 56.4 mg, 0.181 mmol, 90% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, J = 7.9 Hz, 1H), 7.62 (dd, J = 7.7 Hz, 1.7 Hz, 1H), 7.49 (d, J = 16.2 Hz, 1H), 7.42–7.36 (m, 2H), 7.34–7.28 (m, 2H), 7.27–7.17 (m, 2H), 7.15 (d, J = 16.2 Hz, 1H), 3.69 (t, J = 7.0 Hz, 2H), 3.14 (t, J = 6.7 Hz, 2H), 1.967–1.79 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.4, 137.2, 135.3, 133.5, 133.5, 129.8, 129.2, 128.8, 128.1, 128.0, 127.1, 127.0, 126.8, 126.5, 126.2, 48.4, 45.6, 26.0, 24.6; HRMS (ESI) calcd for $C_{19}H_{18}ClNNaO$ $[M+Na]^+$ 334.0969, found 334.0958.

(*E*)-{2-[2-(Naphthalen-1-yl)vinyl]phenyl}(pyrrolidin-1-yl)methanone (4ae): Colorless amorphous; 46.4 mg, 0.142 mmol, 71% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 8.0 Hz, 1H), 7.91–7.85 (m, 2H), 7.82–7.77 (m, 2H), 7.70 (d, J = 7.1 Hz, 1H), 7.56–7.38 (m, 4H), 7.34–7.33 (m, 2H), 7.21 (d, J = 16.0 Hz, 1H), 3.68 (t, J = 7.0 Hz, 2H), 3.17 (t, J = 6.7 Hz, 2H), 1.93–1.77 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.5, 137.2, 134.8, 134.0, 133.7, 131.4, 129.2, 128.7, 128.41,

128.38, 128.35, 127.9, 126.6, 126.22, 126.16, 125.9, 125.7, 123.9, 123.7, 48.4, 45.6, 26.0, 24.6; HRMS (ESI) calcd for $C_{19}H_{18}NNaO$ $[M+Na]^+$ 350.1515, found 350.1503.

(*E*)-{2-[2-(Perfluorophenyl)vinyl]phenyl}(pyrrolidin-1-yl)methanone (4af): Colorless solid; 57.3 mg, 0.156 mmol, 78% isolated yield, reaction time: 72 h; Mp 121.2–121.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, J = 7.5 Hz, 1H), 7.48–7.32 (m, 4H), 6.98 (d, J = 16.7 Hz, 1H), 3.70 (t, J = 7.0 Hz, 2H), 3.15 (t, J = 6.7 Hz, 2H), 2.01–1.83 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 168.9, 146.2–146.0 (m), 143.7–143.5 (m), 141.4–141.1 (m), 139.2–138.6 (m), 137.9, 136.8–136.4 (m), 134.1 (td, 12.4 Hz, 2.4 Hz), 132.7, 129.3, 129.1, 126.6, 125.6, 114.9, 112.3 (td, 20.9 Hz, 4.2 Hz), 48.4, 45.6, 26.0, 24.6; HRMS (ESI) calcd for $C_{19}H_{14}F_5NNaO$ $[M+Na]^+$ 390.0888, found 390.0876.

(*E*)-Pyrrolidin-1-yl[2-(2,4,6-trimethylstyryl)phenyl]methanone (4ag): Colorless oil; 42.2 mg, 0.132 mmol, 66% isolated yield, reaction temperature: 80 °C, reaction time: 72 h; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, J = 7.9 Hz, 1H), 7.40–7.36 (m, 1H), 7.31–7.25 (m, 2H), 7.11 (d, J = 16.5 Hz, 1H), 6.89 (s, 2H), 6.66 (d, J = 16.6 Hz, 1H), 3.62 (t, J = 6.9 Hz, 2H), 3.15 (t, J = 6.7 Hz, 2H), 1.95–1.78 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.5, 137.0, 136.6, 136.1, 134.1, 133.7, 130.5, 129.4, 129.0, 128.8, 127.6, 126.2, 125.5, 48.6, 45.5, 25.9, 24.6, 21.1, 21.0; HRMS (ESI) calcd for $C_{22}H_{25}NNaO$ $[M+Na]^+$ 342.1828, found 342.1847.

(*E*/*Z*)-[2-(3,3-Dimethylbut-1-en-1-yl)phenyl](pyrrolidin-1-yl)methanone (4ah): The title compounds were isolated as a mixture of (*E*)-**4ah** and (*Z*)-**4ah** [(*E*)-**4ah**:(*Z*)-**4ah**= 94:6]. Colorless oil; 36.3 mg, 0.141 mmol, 71% isolated yield, reaction time: 72 h; ^{1}H NMR ($CDCl_3$, 400 MHz) (*E*)-**4ah**: δ 7.47–7.45 (m, 1H), 7.32–7.22 (m, 3H), 6.33 (dd, J = 16.1 Hz, 1H), 6.22 (d, J = 16.1 Hz, 1H), 3.67–3.60 (m, 2H), 3.08 (d, J = 6.7 Hz, 2H), 1.96–1.90 (m, 2H), 1.86–1.79 (m, 2H), 1.09 (s, 9H); partial protons of (*Z*)-**4ah**: 6.36 (d, J = 12.8 Hz, 1H), 5.60 (d, J = 12.9 Hz, 1H), 3.20 (d, J = 6.7 Hz, 2H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.8, 144.7, 136.5, 134.3, 128.9, 127.0, 126.2, 125.9, 121.7, 47.9, 45.5, 33.6, 31.0, 29.5, 26.0, 24.7; HRMS (ESI) calcd for $C_{17}H_{23}NNaO$ $[M+Na]^+$ 280.1672, found 280.1662.

(*E*)-[2-(Oct-1-en-1-yl)phenyl](pyrrolidin-1-yl)methanone (4ai-l), (*E*)-[2-(oct-2-en-1-yl)phenyl](pyrrolidin-1-yl)methanone (4ai-l'), [2-(oct-1-en-2-yl)phenyl](pyrrolidin-1-yl)methanone (4ai-b) and (*E*)-[2-(oct-2-en-2-yl)phenyl](pyrrolidin-1-yl)methanone (4ai-b'): The title compounds were isolated as a mixture of **4ai-l**, **4ai-l'**, **4ai-b**, and **4ai-b'** [**4ai-l**/**4ai-l'**/**4ai-b**/**4ai-b'** = 40:8:24:28]. Colorless oil; 36.7 mg, 0.129 mmol, 64% isolated yield, reaction time: 72 h; ^{1}H NMR ($CDCl_3$, 400 MHz) of **4ai-l**: δ 7.48 (d, J = 7.8 Hz, 1H), 7.34–7.19 (m, 3H), 6.40 (d, J = 15.8 Hz, 1H), 6.23 (dt, J = 15.6 Hz, 6.9 Hz, 1H), 3.68–3.56 (m, 2H), 3.21–3.08 (m, 2H), 2.21–2.09 (m, 2H), 1.97–1.78 (m, 4H), 1.47–1.24 (m, 8H), 0.92–0.83 (m, 3H); ^{1}H NMR ($CDCl_3$, 400 MHz) of **4ai-l'**: δ 7.34–7.19 (m, 4H), 5.57–5.43 (m, 2H), 3.68–3.56 (m, 2H), 3.43–3.36 (m, 4H), 3.21–3.08 (m, 2H), 1.97–1.78 (m, 4H), 1.47–1.24 (m, 6H), 0.92–0.83 (m, 3H); ^{1}H NMR ($CDCl_3$, 400 MHz) of **4ai-b**: δ 7.34–7.19 (m, 4H), 5.11 (d, J = 1.4 Hz, 1H), 5.05 (br, 1H), 3.68–3.56 (m, 2H), 3.21–3.08 (m, 2H), 2.38 (t, J = 7.5 Hz, 2H), 1.97–1.78 (m, 4H), 1.47–1.24 (m, 8H), 0.92–0.83 (m, 3H); ^{1}H NMR ($CDCl_3$, 400 MHz) of **4ai-b'**: 7.34–7.19 (m, 4H), 5.57–5.43 (m, 1H), 3.68–3.56 (m, 2H), 3.21–3.08 (m, 2H), 2.21–2.09 (m, 2H), 1.99 (s, 3H), 1.97–1.78 (m, 4H), 1.47–1.24 (m, 6H), 0.92–0.83 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 170.29, 169.9, 169.8, 149.3, 142.2, 140.1, 136.25, 136.22, 136.18, 134.13, 134. 05, 134.0, 132.4, 131.44, 131.37, 129.7, 129.5, 129.3, 128.94, 128.86, 128.80, 128.75, 128.7, 128.1, 127.9, 127.3, 127.2, 126.9, 126.7, 126.6, 126.5, 126.4, 126.12, 126.09, 126.07, 125.84, 125.80, 125.7, 114.2, 48.6, 48.4, 48.13, 48.08, 45.50, 45.48, 45.38, 45.36, 36.6, 36.2, 33.2, 32.8, 32.5, 31.73, 31.70, 31.6, 31.5, 31.4, 30.8, 29.33, 29.30, 29.2, 29.1, 29.0, 28.9, 28.7, 28.2, 27.3, 25.99, 25.96, 25.95, 24.6, 24.55, 24.52, 22.62, 22.60, 22.57, 22.5, 17.2, 14.09, 14.06, 14.0; HRMS (ESI) calcd for $C_{19}H_{27}NNaO$ $[M+Na]^+$ 308.1985, found 308.1981.

(*E*/*Z*)-[2-(2-Phenylprop-1-en-1-yl)phenyl](pyrrolidin-1-yl)methanone (4aj) and [2-(2-Phenylallyl)phenyl](pyrrolidin-1-yl)methanone (4aj'): The title compounds were isolated as a mixture of (*E*)-**4aj**, (*Z*)-**4aj**, and **4aj'** [(*E*)-**4aj**/(*Z*)-**4aj**/**4aj'** = 40:38:22]. The stereochemistry of **4aj** was determined by the comparison of ^{1}H NMR spectrum with *N*,*N*-diisopropyl-2-(2-phenylprop-1-en-1-yl)benzamide.[24] The structure of **4aj'** was determined by ^{1}H NMR of partial protons and the result of hydrogenation as shown below. Colorless oil; 42.0 mg, 0.144 mmol, 72% isolated yield, reaction tem-

perature: 80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) of (*E*)-**4aj**: δ 7.48–7.15 (m, 9H), 6.859–6.856 (m, 1H), 3.63 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 6.7 Hz, 2H), 2.22 (d, *J* = 1.4 Hz, 3H), 2.00–1.75 (m, 4H); ^{1}H NMR ($CDCl_3$, 400 MHz) of (*Z*)-**4aj**: δ 7.48–7.15 (m, 6H), 7.08 (td, *J* = 11.2, 0.96 Hz, 1H), 6.94 (td, *J* = 11.6, 1.09 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.49 (s, 1H), 3.68 (t, *J* = 7.0 Hz, 2H), 3.20 (t, *J* = 6.7 Hz, 2H), 2.20 (d, *J* = 1.5 Hz, 3H), 2.00–1.75 (m, 4H); ^{1}H NMR ($CDCl_3$, 400 MHz) of **4aj'**: δ 7.48–7.15 (m, 9H), 5.41 (d, *J* = 1.3 Hz, 1H), 5.00 (d, *J* = 1.4 Hz, 1H), 3.93 (s, 2H), 3.65–3.61 (m, 2H), 3.12–3.07 (m, 2H), 2.00–1.75 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) of the mixture of (*E*)-**4aj**, (*Z*)-**4aj**, and **4aj'** δ 169.7, 169.64, 169.60, 146.9, 143.2, 141.6, 140.9, 140.3, 138.7, 138.2, 137.8, 137.7, 136.1, 134.6, 134.1, 130.5, 130.0, 129.7, 128.8, 128.5, 128.39, 128.36, 128.25, 128.18, 128.0, 127.51, 127.45, 127.1, 126.4, 126.3, 126.2, 126.1, 126.0, 125.8, 124.7, 123.4, 114.7, 48.7, 48.3, 48.0, 45.5, 45.4, 38.4, 26.8, 26.1, 26.04, 25.96, 24.60, 24.58, 24.5, 17.4; HRMS (ESI) calcd for $C_{20}H_{21}NNaO$ $[M+Na]^+$ 314.1515, found 314.1511.

Hydrogenation of a mixture of 4aj and 4aj': To a solution of a mixture of (*E*)-**4aj**, (*Z*)-**4aj**, and **4aj'** (29.1 mg, 0.100 mmol, (*E*)-**4aj**/(*Z*)-**4aj**/**4aj'** = 40:38:22) in CH_2Cl_2 (1.0 ml) was added Pd/C (21.3 mg, 5 wt% Pd) in CH_2Cl_2 (1.0 ml). H_2 was introduced to the resulting suspension in a Schlenk tube. The mixture stirred at room temperature (28 °C) for 16 h. The resulting mixture was filtered, concentrated under reduced pressure, and purified by a preparative TLC (hexane/acetone = 2:1) to give [2-(2-Phenylpropyl)phenyl](pyrrolidin-1-yl)methanone (27.9 mg, 0.0951 mmol, 95% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27–7.12 (m, 9H), 3.66 (*J* = 7.0 Hz, 2H), 3.13–2.98 (m, 3H), 2.93–2.77 (m, 2H), 1.98–1.74 (m, 4H), 1.24 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.7, 147.0, 137.8, 137.3, 130.5, 128.5, 128.3, 127.1, 126.01, 125.99, 48.5, 45.5, 42.3, 41.1, 26.0, 24.6, 21.3; HRMS (ESI) calcd for $C_{20}H_{23}NNaO$ $[M+Na]^+$ 316.1672, found 316.1672.

(*E*/*Z*)-[2-(1-Phenylprop-1-en-2-yl)phenyl](pyrrolidin-1-yl)methanone (4ak, Table 2) and [2-(3-Phenylandprop-1-en-2-yl)phenyl](pyrrolidin-1-yl)methanone (4ak' , Table 2): The title compounds were isolated as a mixture of (*E*)-**4ak**, (*Z*)-**4ak**, and **4ak'** [(*E*)-**4ak**/(*Z*)-**4ak**/**4ak'** = 85:12:3]. The stereochemistry of **4ak** was determined by the comparison of ^{1}H NMR spectrum with (*E*)-*N*,*N*-dimethyl-2-(1-

phenylprop-1-en-2-yl)benzamide.[25] The structure of **4ak'** was determined by ^{1}H NMR of partial protons and the result of hydrogenation as shown below. Colorless oil; 43.2 mg, 0.148 mmol, 74% isolated yield, reaction temperature: 80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) of (*E*)-**4ak**: δ 7.40–7.17 (m, 9H), 6.61 (s, 1H), 3.59 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 6.6 Hz, 2H), 2.243–2.240 (m, 3H), 1.92–1.70 (m, 4H); ^{1}H NMR ($CDCl_3$, 400 MHz) of (*Z*)-**4ak**: δ 7.40–7.17 (m, 4H), 7.09–7.02 (m, 3H), 6.93–6.91 (m, 2H), 6.46 (s, 1H), 3.44 (t, *J* = 7.0 Hz, 2H), 2.67 (br, 2H), 2.243–2.240 (m, 3H), 1.92–1.70 (m, 2H), 1.43–1.34 (m, 2H); ^{1}H NMR ($CDCl_3$, 400 MHz) of **4ak'**: δ 7.40–7.17 (m, 9H), 5.19 (s, 1H), 5.01 (d, *J* = 1.4 Hz, 1H), 3.72 (s, 2H), 3.61–3.58 (m, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 1.92–1.70 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 170.0, 168.7, 142.2, 140.8, 138.9, 137.9, 137.7, 137.0, 136.4, 136.1, 130.2, 130.1, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 128.22, 128.18, 127.9, 127.4, 127.2, 126.90, 126.87, 126.8, 126.7, 126.5, 126.2, 126.0, 48.3, 48.2, 45.6, 45.4, 43.2, 27.8, 26.0, 25.9, 24.5, 24.2, 19.1; HRMS (ESI) calcd for $C_{20}H_{21}NNaO$ $[M+Na]^+$ 314.1515, found 314.1516.

Hydrogenation of a mixture of 4ak and 4ak': To a solution of a mixture of (*E*)-**4ak**, (*Z*)-**4ak**, and **4ak'** (29.1 mg, 0.100 mmol, (*E*)-**4ak**/(*Z*)-**4ak**/**4ak'** = 85:12:3) in CH_2Cl_2 (1.0 ml) was added Pd/C (21.3 mg, 5 wt% Pd) in CH_2Cl_2 (1.0 ml). H_2 was introduced to the resulting suspension in a Schlenk tube. The mixture stirred at room temperature (28 °C) for 16 h. The resulting mixture was filtered, concentrated under reduced pressure, and purified by a preparative TLC (hexane/acetone = 2:1) to give [2-(1-Phenylpropan-2-yl)phenyl](pyrrolidin-1-yl)methanone (27.4 mg, 0.0934 mmol, 93% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.34 (m, 2H), 7.21–7.07 (m, 7H), 3.66–3.56 (m, 2H), 3.18–2.92 (m, 3H), 2.80–2.68 (m, 1H), 2.39 (br, 1H), 1.91–1.84 (m, 2H), 1.77–1.69 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 169.7, 143.1, 141.1, 137.5, 129.2, 128.9, 128.1, 126.6, 126.0, 125.8, 125.7, 48.4, 45.4, 44.3, 38.9, 26.0, 24.6, 22.2; HRMS (ESI) calcd for $C_{20}H_{23}NNaO$ $[M+Na]^+$ 316.1672, found 316.1671.

Butyl (*E*)-3-[2-(pyrrolidine-1-carbonyl)phenyl]acrylate (4al, Table 2)[6b]: Colorless oil; 53.9 mg, 0.179 mmol, 90% isolated yield; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.66–7.62 (m, 1H), 7.44–7.37 (m, 2H), 7.36–7.31 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.69 (t, *J*

= 7.0 Hz, 2H), 3.09 (t, *J* = 6.7 Hz, 2H), 2.01–1.82 (m, 4H), 1.71–1.64 (m, 2H), 1.47–1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 168.5, 166.6, 141.1, 138.5, 130.8, 130.2, 129.3, 126.8, 126.7, 120.6, 64.5, 48.5, 45.7, 30.7, 26.0, 24.5, 19.2, 13.7.

(*E*/*Z*)-Methyl 2-methyl-3-[2-(pyrrolidine-1-carbonyl)phenyl]acrylate (4am) and Methyl 2-[2-(pyrrolidine-1-carbonyl)benzyl]acrylate (4am'): The title compounds were isolated as a mixture of (*E*)-**4am**, (*Z*)-**4am**, and **4am'** [(*E*)-**4am**/(*Z*)-**4am**/**4am'** = 1:3:96]. The stereochemistry of 4am was determined by the comparison of ^{1}H NMR spectrum with butyl 3-[2-(diethylcarbamoyl)phenyl]-2-methylacrylate.[4b] Colorless oil; 31.1 mg, 0.114 mmol, 57% isolated yield, reaction temperature: 28 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) of 4am': δ 7.32–7.19 (m, 4H), 6.22 (br, 1H), 5.53 (q, *J* = 1.4 Hz, 1H), 3.72 (s, 2H), 3.70 (s, 3H), 3.61 (t, *J* = 7.0 Hz, 2H), 3.14 (t, *J* = 6.7 Hz, 2H), 1.98–1.91 (m, 2H), 1.87–1.80 (m, 2H); ^{1}H NMR ($CDCl_3$, 400 MHz) of (*E*)-4am: δ 7.68 (s, 1H), 7.32–7.19 (m, 4H), 3.79 (s, 3H), 3.63–3.59 (m, 2H), 3.16–3.13 (m, 2H), 2.04 (d, *J* = 1.5 Hz, 3H), 1.98–1.91 (m, 2H), 1.87–1.80 (m, 2H); ^{1}H NMR ($CDCl_3$, 400 MHz) of (*Z*)-4am: δ 7.32–7.19 (m, 4H), 6.86 (s, 1H), 3.89 (s, 3H), 3.63–3.59 (m, 2H), 3.16–3.13 (m, 2H), 2.07 (d, *J* = 1.6 Hz, 3H), 1.98–1.91 (m, 2H), 1.87–1.80 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.2, 139.0, 137.8, 135.2, 130.3, 128.9, 126.9, 126.5, 126.1, 51.8, 48.8, 45.4, 35.2, 26.0, 24.6; HRMS (ESI) calcd for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.1257, found 296.1253.

(*E*/*Z*)-Methyl 3-[2-(pyrrolidine-1-carbonyl)phenyl]but-2-enoate (4an): The title compounds were isolated as a mixture of (*E*)-**4an** and (*Z*)-**4an** [(*E*)-**4an**:(*Z*)-**4an** = 81:19]. The stereochemistry of **4an** was determined by the comparison of ^{1}H NMR spectrum with butyl 3-[2-(diethylcarbamoyl)phenyl]but-2-enoate.[4b] Colorless oil; 42.0 mg, 0.154 mmol, 77% isolated yield, reaction temperature: 28 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) of (*E*)-**4an**: δ 7.40–7.27 (m, 4H), 5.93 (q, *J* = 1.3 Hz, 1H), 3.73 (s, 3H), 3.60–3.53 (m, 2H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.49 (d, *J* = 1.4 Hz, 3H), 1.96–1.76 (m, 4H); ^{1}H NMR ($CDCl_3$, 400 MHz) of (*Z*)-**4an**: δ 7.40–7.27 (m, 3H), 7.11–7.09 (m, 1H), 5.90 (q, *J* = 1.4 Hz, 1H), 3.60–3.55 (m, 2H), 3.53 (s, 3H), 3.34 (t, *J* = 6.6 Hz, 2H), 2.27 (d, *J* = 1.4 Hz, 3H), 1.96–1.76 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) of the mixture of (*E*)-**4an** and (*Z*)-**4an**: δ 169.1, 168.8, 166.8, 165.8, 157.8, 155.9, 140.7, 139.6, 136.1, 135.2, 129.1, 128.9, 128.4, 128.0, 127.2, 126.9, 126.9, 126.3, 119.2, 117.3, 51.1,

50.8, 48.8, 48.5, 45.6, 45.5, 28.0, 26.2, 26.0, 24.5, 24.4, 19.8; HRMS (ESI) calcd for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.1257, found 296.1271.

Deutrium kinetic isotope effect for parallel reaction of 2a with 3a (Scheme 7a): The reaction was carried out according to the general procedure using $AgSbF_6$ (6.8 mg, 0.020 mmol), complex **1c** (5.5 mg, 0.0050 mmol), $Cu(OAc)_2•H_2O$ (4.0 mg, 0.020 mmol), **2a** (17.5 mg, 0.100 mmol), **3a** (15.6 mg, 0.150 mmol), and $(CH_2Cl)_2$ (0.5 mL) at 28 °C for 2 h, which furnished **4aa** (18.9 mg, 0.0681 mmol, 68% yield).

Deutrium kinetic isotope effect for parallel reaction of 2a-*d*$_5$ with 3a (Scheme 7a): The reaction was carried out according to the general procedure using $AgSbF_6$ (6.8 mg, 0.020 mmol), complex **1c** (5.5 mg, 0.0050 mmol), $Cu(OAc)_2•H_2O$ (4.0 mg, 0.020 mmol), **2a-*d*$_5$** (18.0 mg, 0.100 mmol), **3a** (15.6 mg, 0.150 mmol), and $(CH_2Cl)_2$ (0.5 mL) at 28 °C for 2 h, which furnished **4aa-*d*$_4$** (7.79 mg, 0.0277 mmol, 28% yield) and revovered **2a-*d*$_5$** (11.8 mg, 0.0656 mmol, 65% recov.)

Deutrium kinetic isotope effect for intermolecular competition of 2a and 2a-*d*$_5$ with 3a (Scheme 7b): The reaction was carried out according to the general procedure using $AgSbF_6$ (6.8 mg, 0.020 mmol), complex **1c** (5.5 mg, 0.0050 mmol), $Cu(OAc)_2•H_2O$ (4.0 mg, 0.020 mmol), **2a** (8.8 mg, 0.0500 mmol), **2a-*d*$_5$** (9.0 mg, 0.0500 mmol), **3a** (15.6 mg, 0.150 mmol), and $(CH_2Cl)_2$ (0.5 mL) at 28 °C for 2 h, which furnished a mixture of **4aa** and **4aa-*d*$_4$** (10.8 mg, 0.0388 mmol, 39% yield, **4aa**/**4aa-*d*$_4$** = 75:25).

Deutrium kinetic isotope effect for parallel reaction of 2a with 3f (Scheme 7c): The reaction was carried out according to the general procedure using $AgSbF_6$ (6.8 mg, 0.020 mmol), complex **1c** (5.5 mg, 0.0050 mmol), $Cu(OAc)_2•H_2O$ (4.0 mg, 0.020 mmol), **2a** (17.5 mg, 0.100 mmol), **3f** (17.7 mg, 0.150 mmol), and $(CH_2Cl)_2$ (0.5 mL) at 80 °C for 2 h, which furnished **4af** (4.80 mg, 0.0173 mmol, 17% yield).

Deutrium kinetic isotope effect for parallel reaction of 2a-*d*$_5$ with 3f (Scheme 7c): The reaction was carried out according to the general procedure using $AgSbF_6$ (6.8 mg, 0.020 mmol), complex **1c** (5.5 mg, 0.0050 mmol), $Cu(OAc)_2•H_2O$ (4.0 mg, 0.020 mmol), **2a-*d*$_5$** (18.0 mg, 0.100 mmol), **3f** (17.7

mg, 0.150 mmol), and $(CH_2Cl)_2$ (1.0 mL) at 80 °C for 2 h, which furnished **4af-*d*$_4$** (4.53 mg, 0.0161 mmol, 16% yield).

Reaction profiles for oxidative olefination of 2a with 3f (Figure 1): To a Schlenk flask was added $AgSbF_6$ (13.6 mg, 0.0400 mmol), complex **1c** or $[Cp^ERhCl_2]_2$ (0.0100 mmol), $Cu(OAc)_2•H_2O$ (8.0 mg, 0.0400 mmol), **2a** (35.0 mg, 0.200 mmol), **3f** (31.2 mg, 0.300 mmol), diethyl terephthalate (38.8 mg, 0.200 mmol, internal standard) and $(CH_2Cl)_2$ (1.0 mL) in this order. Aliquots (~0.1 mL) from the mixture were removed at 1, 2, 4, 8, and 22 hour intervals. Each aliquot wasdiluted with diethyl ether, filtered through a silica gel pad, and washed with EtOAc. The filtrate was analyzed by ^{1}H NMR spectroscopy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Table S1, Scheme S1, and copies of ^{1}H and ^{13}C{^{1}H} NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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