Graphical Abstract

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ARTICLE INFO

Article history:

Received

Received in revised form

Accepted

Available online

Cobalt

Oxidative cou

Alkenylation

Catalysis

C-H activation

pling

ABSTRACT

The utility of Cp*Co(III)-catalysts was expanded to oxidative C-C bond-forming reaction. *In situ*-generated Cp*Co(III)-catalyst, rather than a preformed cationic Cp*Co(III)-complex, was effective. Oxidative alkenylation of benzamides and acetanilide with ethyl acrylate proceeded with silver acetate as a stoichiometric oxidant, giving products in up to 93% yield.

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1. Introduction

Functionalization of ubiquitous unreactive C-H bonds has attracted considerable attention in the field of organic synthesis.¹ The C-H functionalization process provides new opportunities for developing atom-² and step-economical³ synthetic routes of natural products, biologically active compounds, functional organic materials, and other useful organic molecules. Regio- and chemoselective activation of a specific C-H bond among numerous C-H bonds in a molecule is essential for this purpose. Directing group-assisted C-H bond activation under transition metal catalysis is the most successful and widely used strategy, and various catalysts have been developed over the last two decades. Among them, cationic Cp*Rh(III) complexes are widely applied for various oxidative as well as redox neutral C-C, C-N, and other C-X bond-forming reactions.⁴ Despite their high catalytic activity and broad reaction scope, however, the use of expensive rhodium metal has disadvantages for future application in large-scale synthesis. Thus, the development of an alternative catalyst with readily available base metal sources is highly desirable.⁵⁻⁷ Since our report on the utility of a cationic Cp*Co(III)-arene complex **1a** in 2013 (Fig. 1),⁸ we and others have attempted to broaden the scope of Cp*Co(III)-catalysis.^{9,10} Cp*Co(III) complexes were successfully applied for a variety of redox neutral C-C and C-N bond formations. Cp*Co(III) was found to be superior to Cp*Rh(III) in some nucleophilic addition

reactions^{9b} as well as in some formally nucleophilic substitution reactions.^{10b} On the other hand, there are no reports of oxidative C-C bond-forming reactions with external oxidants under Cp*Co(III)-catalysis.¹¹ Studies of oxidative C-H functionalizations are, therefore, important toward broadening the scope of Cp*Co(III)-catalysis. Herein, we demonstrate oxidative alkenylation of arenes with ethyl acrylate. The appropriate cationic Cp*Co(III) complex promoted the alkenylation reaction in the presence of silver oxidant, affording products in up to 93% yield.

Fig. 1. Structures of Cp*Co(III)-complexes **1a** and **1b**.

2. Results and discussion

Transition metal-catalyzed oxidative alkenylation reactions of arenes, especially those using Pd, Rh, and Ru-catalysts, have been studied extensively.^{12,13} Thus, we selected the reaction of arenes and acrylate as a model reaction to evaluate the feasibility

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of oxidative C-C bond-forming processes under Cp*Co(III)-catalysis. Optimization studies of benzamide **2a** and ethyl acrylate **3** are summarized in Table 1. Our original cationic Cp*Co(III)-arene complex **1a** gave trace, if any, amounts of the desired product **4a** in the presence of silver acetate as a stoichiometric oxidant (entry 1). On the other hand, *in situ*-generated Co(III)-catalyst by mixing Cp*Co(CO)I₂ **1b** and AgPF₆ gave the product in 54% yield. The selection of the counter ion affected the reactivity of the Co(III)-catalyst, and AgSbF₆ afforded the best reactivity among silver salts screened (entries 2-6). The results were not improved by the use of any other oxidants screened. The use of benzoquinone as an oxidant led to only trace amounts of the product (entry 7). Cu(OAc)₂, which is often used for oxidative reactions under Cp*Rh(III)-catalysis, resulted in a lower yield than AgOAc (entry 8, 48%). We assume that the selection of a suitable oxidant is important for efficient catalyst turnover to regenerate catalytically active Cp*Co(III), while suppressing undesirable catalyst de-activation from the relatively unstable Cp*Co(I) species. Ag₂CO₃ also resulted in a low yield (entry 9, 16%), possibly because the acetate ion is important to efficiently assist the C-H activation step. The reaction proceeded smoothly even at 40 °C, but resulted in a slightly lower yield (entry 10, 73%). Thus, we selected the conditions in entry 6 as optimum for oxidative alkenylation. Negative control experiments in entries 11-15 suggested that the use of the well-defined cationic Cp*Co(III)-catalyst is required for present C-H functionalization.

Table 1. Optimization studies of Cp*Co(III)-catalyzed oxidative alkenylation.

Entry	Co-cat. (x mol%)	Ag-salt (2x mol%)	Oxidant (y equiv)	Temp (°C)	Yield ^a (%)
1	1a (10)	none	AgOAc (2.5)	60	trace
2	1b (10)	AgPF ₆ (20)	AgOAc (2.5)	60	54
3	1b (10)	AgOTf (20)	AgOAc (2.5)	60	60
4	1b (10)	AgNTf ₂ (20)	AgOAc (2.5)	60	72
5	1b (10)	AgBF ₄ (20)	AgOAc (2.5)	60	74
6	1b (10)	AgSbF ₆ (20)	AgOAc (2.5)	60	84 (80) ^b
7	1b (10)	AgSbF ₆ (20)	BQ (1.3)	60	trace
8	1b (10)	AgSbF ₆ (20)	Cu(OAc) ₂ (2.5)	60	47
9	1b (10)	AgSbF ₆ (20)	Ag ₂ CO ₃ (1.3)	60	16
10	1b (10)	AgSbF ₆ (20)	AgOAc (2.5)	40	73
11	none	AgSbF ₆ (20)	AgOAc (2.5)	60	0
12	CoI ₂ (10)	AgSbF ₆ (20)	AgOAc (2.5)	60	0
13	Co(OAc) ₂ (10)	none	AgOAc (2.5)	60	0
14	Co(acac) ₃ (10)	none	AgOAc (2.5)	60	0
15	Co(NH ₃) ₆ Cl ₃ (10)	none	AgOAc (2.5)	60	0

^a Yield of **4a** determined by ¹H NMR analysis of crude mixture with an internal standard.

^b Isolated yield of **4a** after purification by silica gel column chromatography.

We then investigated the scope and limitations of Cp*Co(III)-catalyzed oxidative alkenylation reactions. The scope of

benzamides is summarized in Table 2. Various functional groups at the *para*-position, such as Me, MeO, F, Br, CF₃, NO₂, and CO₂Me, were compatible (**4b-4h**, 73-93%), while phenol and aniline units (**4i** and **4j**) gave complex mixtures of byproducts. Substituents at the *meta*-position also gave the products in good yield (**4k** and **4l**). Good regioselectivity with *meta*-substituted substrates can be explained based on the steric factor. C-H metalation occurred selectively at the sterically less hindered position. With an *ortho*-substituted substrate, the reactivity decreased significantly, and product **4m** was obtained in only 33% yield. The *ortho*-substituent would destabilize a planar metalacyclic intermediate due to steric repulsion. In addition to other benzamide derivatives **4n** and **4o**, the C-H bond of thiophenyl unit was also functionalized, albeit in moderate yield (**4p**, 52%). As shown in Scheme 1, acetanilide (**5**) also reacted with ethyl acrylate, although 20 mol % of Cp*Co(III) was required to obtain product **6** in 61% yield.

Table 2. Cp*Co(III)-catalyzed oxidative alkenylation of benzamides.^a

4a : X = H, 80%	4f : X = CF ₃ , 73%	
4b : X = Me, 77%	4g : X = NO ₂ , 78%	
4c : X = MeO, 82%	4h : X = CO ₂ Me, 76%	
4d : X = F, 77%	4i : X = OH, messy	
4e : X = Br, 93%	4j : X = NH ₂ , messy	
4k : X = Me, R = Me, 70%	4l : X = Br, R = <i>t</i> Bu, 75%	
4m : 33%		
4n : 79%	4o : 75%	4p : 52%

^a Reaction was run using **4** (0.10 mmol) and **3** (0.15 mmol). Isolated yields of **4** after purification by silica gel column chromatography are shown in Table 2.

Scheme 1. Cp*Co(III)-catalyzed oxidative alkenylation of acetanilide **5**.

A plausible catalytic cycle is shown in Fig. 2. Initial halide abstraction from Cp*Co(CO)I₂ **1b** by AgSbF₆ in the presence of the AgOAc would form a neutral Cp*Co(III)(OAc)₂ complex, which would be a resting complex. On the basis of our previous mechanistic studies,^{9b} we speculate that mono-cationic [Cp*Co(III)(OAc)]⁺ **I** would be a catalytically active species. We

assume that the concentration of the catalytically active species would be different depending on silver salts, which led to the reactivity difference observed in Table 1, entries 2-6. A key C-H bond activation step to afford metalacycle **II** would proceed via concerted metalation-deprotonation (CMD)¹⁴ assisted by the acetate ion. Insertion into acrylate (**III**), followed by β -hydride elimination and reductive elimination, would afford product **4**, AcOH, and Cp*Co(I). Oxidation of Cp*Co(I) by silver salt regenerated the Cp*Co(III)-catalyst.

Fig. 2. Plausible catalytic cycle.

3. Conclusion

In conclusion, we report the first successful application of a Cp*Co(III)-catalyst to oxidative C-H alkenylation with an external oxidant, thereby expanding the utility of Cp*Co(III)-catalysis. The present protocol can be further improved, however, with regard to the use of precious silver salt as a stoichiometric oxidant and the limited substrate scope. Additional studies to improve the Cp*Co(III)-catalyzed oxidative process, including the use of environmentally benign oxidant, are ongoing in our group.

4. Experimental Section

4.1. General Procedure (Table 2)

To a dried screw-capped vial were added benzamide **2** (0.10 mmol), ethyl acrylate **3** (0.15 mmol), **1b** (4.8 mg, 0.01 mmol), AgSbF₆ (6.8mg, 0.02 mmol), AgOAc (41.7 mg, 0.25 mmol) and 1,2-dichloroethane (1.0 mL) under Ar atmosphere. The vial was capped and the mixture was heated at 60 °C for 13 h with stirring. After the mixture was cooled to room temperature, saturated EDTA·2Na aq. was added following dilution with CH₂Cl₂. Organic layer was separated and aqueous layer was extracted with CH₂Cl₂ (x 2). Combined organic layers were dried over Na₂SO₄. After filtration and evaporation, obtained crude mixture was purified by silica gel column chromatography (CH₂Cl₂/EtOAc) to give product **3**.

4.1.1. (E)-Ethyl 3-(2-(methylcarbamoyl)phenyl)acrylate (**4a**).

A colorless solid; IR (KBr) ν 3085, 2979, 1714, 1703, 1635, 1557, 1270, 1048, 980, 767 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.31 (t, J = 7.3 Hz, 3 H), 2.99 (d, J = 4.6 Hz, 3H), 4.23 (q, J = 7.3 Hz, 2H), 5.98 (brs, 1H), 6.35 (d, J = 16.0 Hz, 1H), 7.34-7.50 (m, 3H), 7.59 (s, J = 7.3 Hz, 1H), 7.96 (d, J = 16.0 Hz,

1H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.4, 27.0, 60.7, 120.9, 127.2, 127.7, 129.9, 130.4, 132.8, 137.3, 141.9, 166.6, 169.5; HRMS (ESI): m/z calculated for C₁₃H₁₅NNaO₃⁺ [M+Na]⁺: 256.0944, found: 256.0956.

4.1.2. (E)-Ethyl 3-(5-methyl-2-(methylcarbamoyl)phenyl)acrylate (**4b**).

A colorless solid; IR (KBr) ν 2982, 1714, 1643, 1550, 1317, 1178, 1037, 976, 862 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.32 (t, J = 5.5 Hz, 3 H), 2.38 (s, 3H), 3.00 (d, J = 4.1 Hz, 3H), 4.23 (q, J = 5.5 Hz, 2H), 5.78 (brs, 1H), 6.36 (d, J = 12.4 Hz, 1H), 7.19 (d, J = 6.4 Hz, 1H), 7.34-7.42 (m, 2H), 8.00 (d, J = 12.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.4, 21.4, 27.0, 60.7, 120.7, 127.8, 127.8, 130.6, 132.9, 134.5, 140.5, 142.3, 166.7, 169.5; HRMS (ESI): m/z calculated for C₁₄H₁₇NNaO₃⁺ [M+Na]⁺: 270.1101, found: 270.1092.

4.1.3. (E)-Ethyl 3-(5-methoxy-2-(methylcarbamoyl)phenyl)acrylate (**4c**).

A colorless solid; IR (KBr) ν 2985, 2942, 1715, 16641, 1625, 1546, 1314, 1293, 1228, 1182, 1034, 974, 862 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.32 (t, J = 7.3 Hz, 3 H), 2.98 (d, J = 5.0 Hz, 3H), 3.83 (s, 3H), 4.24 (q, J = 7.3 Hz, 2H), 5.88 (brs, 1H), 6.33 (d, J = 16.7 Hz, 1H), 6.89 (dd, J = 2.3, 8.7 Hz, 1H), 7.06 (d, J = 2.3 Hz, 1H), 7.43 (d, J = 8.7 Hz, 1s) 8.02 (d, J = 16.5 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.4, 27.1, 55.6, 60.8, 112.2, 115.4, 121.1, 129.5, 129.7, 135.0, 142.3, 161.0, 166.6, 169.2; HRMS (ESI): m/z calculated for C₁₄H₁₇NNaO₄⁺ [M+Na]⁺: 286.1050, found: 286.1054.

4.1.4. (E)-Ethyl 3-(5-fluoro-2-(methylcarbamoyl)phenyl)acrylate (**4d**).

A colorless solid; IR (KBr) ν 3082, 2984, 1721, 1635, 1558, 1321, 1182, 1034, 971, 855 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.30 (t, J = 6.8 Hz, 3 H), 2.99 (d, J = 5.0 Hz, 3H), 4.24 (q, J = 6.8 Hz, 2H), 5.95 (brs, 1H), 6.34 (d, J = 16.5 Hz, 1H), 7.04 (ddd, J = 2.8, 8.7, 8.7 Hz, 1H), 7.25 (dd, J = 2.8, 10.1 Hz, 1H), 7.44 (dd, J = 6.0, 8.7 Hz, 2H), 7.91 (d, J = 16.5 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.4, 27.1, 60.9, 113.9 (d, J = 22.9 Hz), 116.8 (d, J = 22.9 Hz), 122.1, 130.6 (d, J = 9.5 Hz), 133.4 (d, J = 2.9 Hz), 135.5 (d, J = 7.6 Hz), 140.8 (d, J = 2.9 Hz), 163.5 (d, J = 254.7 Hz), 166.3, 168.6; HRMS (ESI): m/z calculated for C₁₃H₁₄FNNaO₃⁺ [M+Na]⁺: 274.0850, found: 274.0844.

4.1.5. (E)-Ethyl 3-(5-bromo-2-(methylcarbamoyl)phenyl)acrylate (**4e**).

A colorless solid; IR (KBr) ν 3079, 2975, 2935, 1719, 1642, 1561, 1316, 1190, 1032, 979, 862 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.32 (t, J = 7.5 Hz, 3 H), 3.00 (d, J = 5.2 Hz, 3H), 4.23 (q, J = 7.5 Hz, 2H), 5.88 (brs, 1H), 6.36 (d, J = 16.0 Hz, 1H), 7.34 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.74 (s, 1H) 7.90 (d, J = 16.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.4, 27.1, 60.1, 122.1, 124.1, 124.7, 129.3, 130.1, 132.7, 134.9, 135.8, 140.5, 166.2, 168.5; HRMS (ESI): m/z calculated for C₁₃H₁₄BrNNaO₃⁺ [M+Na]⁺: 334.0049, found: 334.0050.

4.1.6. (E)-Ethyl 3-(2-(methylcarbamoyl)-5-(trifluoromethyl)phenyl)acrylate (**4f**).

A colorless solid; IR (KBr) ν 3084, 2974, 1717, 1642, 1551, 1337, 1292, 1159, 1122, 1042, 989, 924, 843 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.33 (t, J = 6.9 Hz, 3 H), 3.04 (d, J = 4.6 Hz, 3H), 4.24 (q, J = 6.9 Hz, 2H), 5.88 (brs, 1H), 6.45 (d, J =

16.0 Hz, 1H), 7.57-7.65 (m, 2H), 7.85 (s, 1H) 7.94 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 27.1, 61.0, 122.6, 123.5 (q, J = 273.4 Hz), 124.1 (q, J = 3.8 Hz), 126.3 (q, J = 22.9 Hz), 128.4, 132.5 (q, J = 32.9 Hz), 133.7; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 324.0818, found: 324.0818.

4.1.7. (E)-Ethyl 3-(2-(methylcarbamoyl)-5-nitrophenyl)acrylate (4g).

A colorless solid; IR (KBr) ν 3085, 2977, 1713, 1643, 1556, 1522, 1352, 1282, 1040, 989, 825 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.31 (t, J = 7.3 Hz, 3 H), 3.03 (d, J = 5.0 Hz, 3H), 4.26 (q, J = 7.3 Hz, 2H), 6.14 (brs, 1H), 6.50 (d, J = 16.5 Hz, 1H), 7.62 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 16.5 Hz, 1H), 8.19 (d, J = 8.7 Hz, 1H) 8.43 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 27.2, 61.2, 122.1, 123.7, 124.2, 134.7, 139.4, 142.3, 148.8, 165.9, 167.5; HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$: 301.0795, found: 301.0791.

4.1.8. (E)-Methyl 3-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-(methylcarbamoyl)benzoate (4h).

A colorless solid; IR (KBr) ν 3082, 2988, 2954, 1721, 1644, 1551, 1320, 1252, 1184, 1032, 976, 866, 760 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.32 (t, J = 7.2 Hz, 3 H), 3.02 (d, J = 4.8 Hz, 3H), 3.94 (s, 3H), 4.25 (q, J = 7.2 Hz, 2H), 6.07 (brs, 1H), 6.46 (d, J = 16.0 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 16.0 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 8.35 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 27.1, 52.7, 60.9, 122.1, 122.1, 127.9, 128.4, 130.6, 131.9, 133.2, 140.8, 140.9, 166.0, 166.4, 168.6; HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{17}\text{NNaO}_5^+$ $[\text{M}+\text{Na}]^+$: 314.0999, found: 314.0993.

4.1.9. (E)-Ethyl 3-(4-methyl-2-(methylcarbamoyl)phenyl)acrylate (4k).

A colorless solid; IR (KBr) ν 2979, 1715, 1639, 1604, 1541, 1309, 1272, 1178, 1030, 977, 822 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.30 (t, J = 7.3 Hz, 3 H), 2.35 (s, 3H), 3.00 (d, J = 5.0 Hz, 3H), 4.22 (q, J = 7.3 Hz, 2H), 5.88 (brs, 1H), 6.32 (d, J = 16.0 Hz, 1H), 7.29-7.37 (m, 2H), 7.48 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 21.4, 27.0, 60.7, 119.9, 127.2, 128.4, 129.9, 131.1, 137.3, 140.4, 141.8, 166.8, 169.6; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{17}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 270.1101, found: 270.1104.

4.1.10. (E)-Ethyl 3-(4-bromo-2-(tert-butylcarbamoyl)phenyl)acrylate (4l).

A colorless oil; IR (neat) ν 3065, 2973, 1714, 1641, 1541, 1312, 1263, 1178, 1097, 1041, 976, 895, 816 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.31 (t, J = 7.3 Hz, 3 H), 1.47(s, 9H), 4.24 (q, J = 7.3 Hz, 2H), 5.64 (brs, 1H), 6.35 (d, J = 16.5 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.52 (dd, J = 2.3, 7.8 Hz, 1H), 7.57 (s, J = 2.3 Hz, 1H), 7.85 (d, J = 16.5 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 28.8, 52.7, 60.8, 121.3, 124.0, 128.5, 130.7, 131.2, 133.1, 140.0, 140.7, 166.3, 166.7; HRMS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{20}\text{BrNNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 376.0519, found: 376.0520.

4.1.11. (E)-Ethyl 3-(3-methyl-2-(methylcarbamoyl)phenyl)acrylate (4m).

A colorless oil; IR (neat) ν 2980, 1710, 1638, 1543, 1313, 1233, 1090, 1039, 979, 867, 790 cm^{-1} ; ^1H NMR (CDCl_3 , 400

MHz) δ 1.31 (t, J = 7.3 Hz, 3 H), 2.34 (s, 3H), 3.04 (d, J = 5.0 Hz, 3H), 4.22 (q, J = 7.3 Hz, 2H), 5.72 (brs, 1H), 6.38 (d, J = 16.0 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.28 (dd, J = 7.8, 7.8 Hz, 1H), 7.70 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 19.3, 26.8, 60.7, 120.8, 124.0, 129.3, 131.7, 121.9, 135.6, 138.2, 141.6, 166.7, 169.8; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{17}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 270.1101, found: 270.1102.

4.1.12. (E)-Ethyl 3-(3-(methylcarbamoyl)naphthalen-2-yl)acrylate (4n).

A colorless solid; IR (KBr) ν 2981, 1715, 1644, 1622, 1551, 1304, 1177, 1033, 976, 863, 758 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.33 (t, J = 7.3 Hz, 3 H), 3.05 (d, J = 5.0 Hz, 3H), 4.26 (q, J = 7.3 Hz, 2H), 6.14 (brs, 1H), 6.44 (d, J = 16.5 Hz, 1H), 7.50-7.57 (m, 2H), 7.76-7.87 (m, 2H), 7.91 (s, 1H), 8.01 (s, 1H), 8.23 (d, J = 16.5 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.5, 27.1, 60.7, 120.8, 127.6, 127.7, 127.8, 127.9, 128.2, 128.4, 130.4, 133.0, 133.6, 134.4, 142.5, 166.7, 169.5; HRMS (ESI): m/z calculated for $\text{C}_{17}\text{H}_{17}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 306.1101, found: 306.1105.

4.1.13. (E)-Ethyl 3-(2-(tert-butylcarbamoyl)phenyl)acrylate (4o).

A colorless oil; IR (neat) ν 3063, 2971, 1712, 1639, 1538, 1314, 1177, 1094, 1042, 977, 879, 764 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.33 (t, J = 7.3 Hz, 3 H), 1.49 (s, 9H), 4.26 (q, J = 7.3 Hz, 2H), 5.55 (brs, 1H), 6.39 (d, J = 16.0 Hz, 1H), 7.36-7.50 (m, 3H), 7.59 (s, J = 7.4 Hz, 1H), 7.98 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 28.9, 52.4, 60.7, 120.8, 127.0, 127.7, 130.0, 130.1, 132.3, 138.7, 142.0, 166.6, 168.3; HRMS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{20}\text{BrNNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 298.1414, found: 298.1423.

4.1.14. (E)-Ethyl 3-(2-(methylcarbamoyl)thiophen-3-yl)acrylate (4p).

A colorless solid; IR (neat) ν 2979, 1707, 1632, 1536, 1244, 1178, 1037, 987, 867, 774 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.33 (t, J = 6.9 Hz, 3 H), 3.01 (s, 3H), 4.26 (q, J = 6.9 Hz, 2H), 6.33 (d, J = 16.5 Hz, 1H), 5.84 (brs, 1H), 7.29 (d, J = 5.5 Hz, 1H), 7.33 (d, J = 5.5 Hz, 1H), 8.26 (d, J = 16.5 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.5, 27.2, 60.8, 121.7, 127.0, 127.2, 136.4, 136.5, 138.6, 162.8, 162.9; HRMS (ESI): m/z calculated for $\text{C}_{11}\text{H}_{13}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 262.0508, found: 262.0513.

4.1.15. (E)-Ethyl 3-(2-(acetamidophenyl)acrylate (6) (Scheme 2).

To a dried screw-capped vial were added acetanilide **5** (0.10 mmol), ethyl acrylate **3** (0.15 mmol), **1b** (9.6 mg, 0.02 mmol), AgSbF_6 (13.6mg, 0.04 mmol), AgOAc (41.7 mg, 0.25 mmol) and 1,2-dichloroethane (1.0 mL) under Ar atmosphere. The vial was capped and the mixture was heated at 60 °C for 13 h with stirring. After the mixture was cooled to room temperature, saturated $\text{EDTA}\cdot 2\text{Na}$ aq. was added following dilution with CH_2Cl_2 . Organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (x 2). Combined organic layers were dried over Na_2SO_4 . After filtration and evaporation, obtained crude mixture was purified by silica gel column chromatography ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$) to give product **6**. A colorless solid; IR (KBr) ν 2978, 1712, 1659, 1537, 1455, 1302, 1270, 1045, 971, 764, 743 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.33 (t, J = 7.6 Hz, 3 H),

2.23 (s, 3H), 4.26 (q, $J = 7.6$ Hz, 2H), 6.39 (d, $J = 16.0$ Hz, 1H), 7.20 (m, 1H), 7.29-7.43 (m, 2H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.70-7.90 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.4, 24.4, 60.9, 120.9, 125.3, 126.0, 127.3, 127.7, 130.9, 136.0, 139.4, 166.9, 169.0; HRMS (ESI): m/z calculated for $\text{C}_{13}\text{H}_{15}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 256.0944, found: 256.0936

Acknowledgments

This work was supported by ACT-C from JST, Grant-in-Aid for Scientific Research on Innovative Areas from MEXT and the Naito foundation. Y.S. thanks JSPS fellowship.

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