有机化学 DOI: 10.6023/cjoc202205038 研究论文
Chinese Journal of Organic Chemistry ARTICLE

配体调控钯催化乙烯基环状碳酰胺和异氰酸酯的差异性转化

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摘要 用配体调控策略, 通过钯催化发展了乙烯基环状碳酰胺和异氰酸酯之间的两类差异性转化, 选择性地合成了多取代的共轭二烯脲类化合物和四氢嘧啶酮衍生物. 当反应以 $Pd_2(dba)_3$•$CHCl_3$ (dba: dibenzylideneacetone)为催化剂前体、以单齿配位的 *N*,*N*-二甲基亚磷酰胺(MonoPhos)为配体时, 可以高选择性地得到一系列线性的共轭二烯脲类衍生物; 将配体改为双齿配位的 1,3-双(二苯基膦)丙烷(DPPP)时, 利用相同的原料则能够合成一系列环状的四氢嘧啶酮类化合物. 这一研究通过简便的配体调控策略, 为含氮化合物的多样性合成提供了新方法.
关键词 配体调控; 钯催化; 脲; 烯基碳酰胺; 异氰酸酯

Ligand-Switched Pd-Catalyzed Divergent Transformations of Vinyl Cyclic Carbamates and Isocyanates

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Abstract Synthesis of urea compounds is highly significant for pharmaceutical chemistry, agricultural chemistry, matterials science and organic synthesis. By ultilizing ligands to switch the chemoselectivity, two transformations of vinyl cyclic carbamates and isocyanates were developed to afford linear and cyclic ureas in a controlled manner. When phosphoramidite was used as the monodentate *P*-ligand, a wide range of (*E*)-1,3-diene-substituted linear ureas were produced in high yields and selectivity (21 examples, 51%～95% yields). While, using bidentate biphosphine ligand to replace the phosphoramidite ligand, a variety of highly functionalized vinyl-substitued cyclic ureas, tetrahydro-2-pyrimidinones, were delivered instead starting from the same chemical feedstocks (8 examples, 72%～94% yields). To illusrate the switched chemoselectivity, two possible reaction mechanisms were proposed based on the experiment results and proceeding literatures. The keys of these two reactions, dienylation and annulation, are the *β*-hydride elimination and the *N*-allylic alkylation of ally-Pd species, respectively. It is supposed that the basicity of the ligand will affect the reactivity of π-ally-Pd intermediates toward electrophilic ring closing. It is believed that this research not only enriches the application of vinyl carbamate reagents in organic synthesis, but also provides a new protocol to access significant nitrogen-containing molecules.
Keywords ligand-switched; palladium catalysis; urea; vinyl carbamate; isocyanate

1 Introduction

Vinyl carbamates are a kind of versatile building blocks that are widely utilized as precursors for Pd-catalyzed annulation reactions.[1] In 2000, Hollinshead *et al.*[2] reported a (5＋1) annulation of 5-vinyloxazolidin-2-ones with CO. In 2006, Tunge *et al.*[3] exploited 6-vinyl oxazinanone reagents for Pd-catalyzed asymmetric (4＋2) dipolar annulations with benzylidene lononitriles. In 2013, Ooi *et al.*[4] accomplished a highly enantio- and diastereoselective (3＋2) annulation of 5-vinyloxazolidinones and electro-deficient trisubstituted alkenes. In the recent decade, vinyl carbamate reagents have been widely applied for azaheterocycle synthesis through Pd-catalyzed annulations,[5] while, there were only a few examples on their application in the synthesis of poly-substituted butadienes.[6] To continue our research studies on transition metal catalyzed

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Received May 22, 2022; revised July 25, 2022; published online August 17, 2022.
Project supported by the National Natural Science Foundation of China (Nos. 21822103, 21820102003, 91956201), the Program of Introducing Talents of Discipline to Universities of China (111 Program, No. B17019) and the Natural Science Foundation of Hubei Province (No. 2017AHB047).
国家自然科学基金(Nos. 21822103, 21820102003, 91956201)、高等学校学科创新引智计划(111 计划, No. B17019)和湖北省自然科学基金(No. 2017AHB047)资助项目.

dipolar cycloadditions,[7] herein, we accomplished two kinds of chemoselective transformations of vinyl cyclic carbamates and isocyanates, which were controlled by ligands and afforded linear dienyl and cyclic ureas in good selectivity.

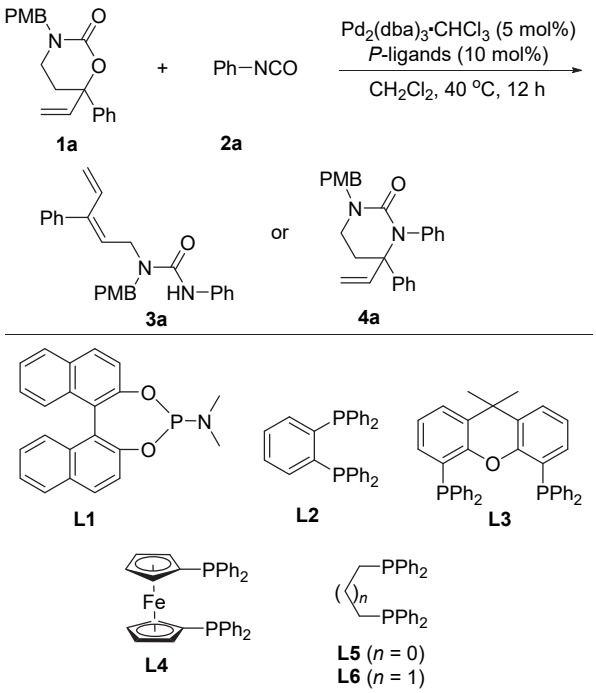
In 2003, Alper *et al.*[8] reported a Pd-catalyzed ring-expansion reaction of 2-vinylpyrrolidines with aryl isocyanates[9] to form seven-membered cyclic ureas. During the study of ligand effect, they found that PPh_3 gave the varied mixture of diene-substituted linear ureas and cyclic ureas which were heavily relied on the electronic characteristics of isocyanates (Scheme 1a). In 2020, we disclosed a Pd-catalyzed enantioselective (8+2) annulation of vinyl carbamates with photogenerated ketenes, affording chiral 10-membered cyclic carbamates with the CO_2 unit remained (Scheme 1a).[10] As a continuation of this work, we planned to develop a similar annulation reaction between the same vinyl carbamates and isocyanates. Out of our expectation, we disclosed two ligand-switched decarboxylative dienylation and (4+2) annulation (Scheme 1c). Different from Alper's work, the chemoselectivity of both reactions can be well controlled by using suitable ligands and configuration of dienene unit was *trans* almost without exception. In addition, different reactivity as 1,4-dipoles was presented here when reacting with isocyanates.

2 Results and discussion

Initially, we started this study with vinyl carbamate **1a** and phenyl isocyanate **2a** as the model substrates to screen different P-ligands. To our delight, the reaction with phosphoramidite ligand **L1** proceeded smoothly to give linear urea **3a** as a sole product in 83% yield and >19∶1 *E*/*Z* (Table 1, Entry 1). Performing the reaction in other solvents, tetrahedron furan or toluene, did not improve the reaction efficiency (Table 1, Entries 2 and 3). Replacement of the Pd catalyst precursor $Pd_2(dba)_3$•$CHCl_3$ (dba: dibenzylideneacetone) with $Pd(OAc)_2$ afforded a largely reduced yield (Table 1, Entry 4, 20% yield). To our delight, reducing the amount of isocyanate **2a** can increase the reaction yield to 92% (Table 1, Entry 5), thus giving the optimal conditions for linear urea products. When bidentate *P*-ligand **L2** was used, a mixture of linear and cyclic ureas **3a** and **4a** was provided in 45% and 28% yields, respectively (Table 1, Entry 6, **3a**/**4a**=1.6/1, *E*/*Z*>19/1 for **3a**). To improve the chemoselectivity of cyclic ureas, a series of biphosphine ligands (**L3**～**L6**) were evaluated (Table 1, Entries 7～10). As a result, biphosphine ligand **L6** stood out as the best choice to afford cyclic urea product **4a** in 91% yield (Table 1, Entry 10).

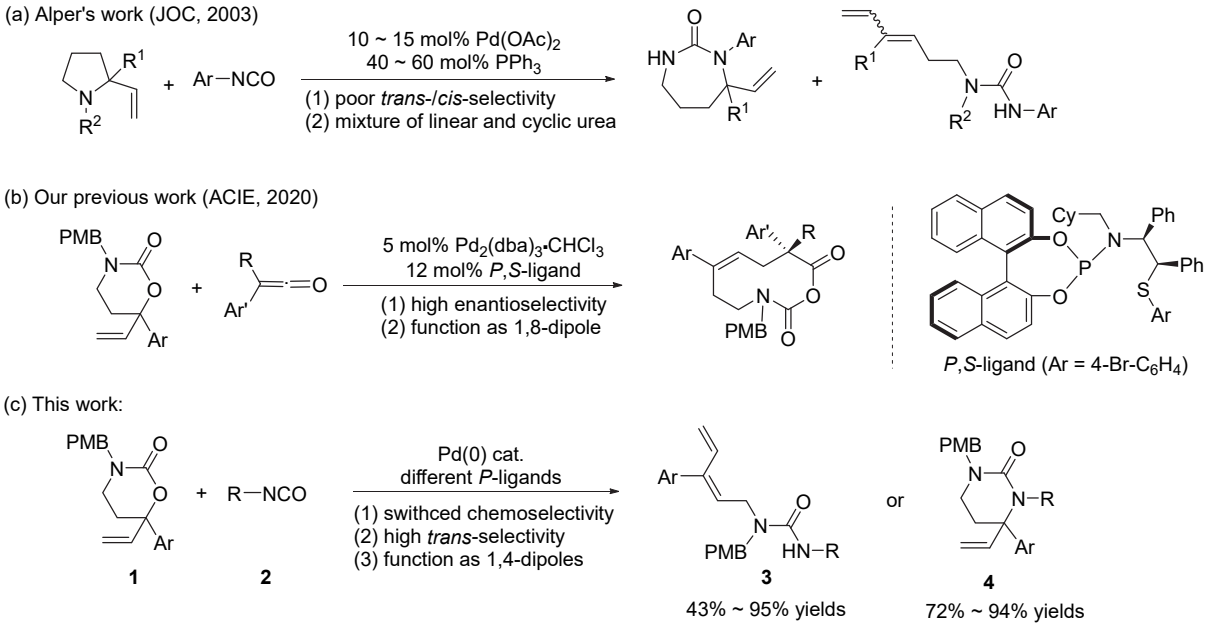
After establishing the optimal conditions, we first examined the substrate scope of Pd-catalyzed dienylation reaction. As summarized in Table 2, the *E*/*Z* selectivity of diene units was not obviously affected by the electronic feature of substituents at the 4-position of the phenyl isocyanates. Both electron-donating and electron-withdrawing groups, such as MeO, Me, Br and CF_3, were well compatible to afford linear urea products in good yields and with excellent selectivity (Table 2, **3a**～**3f**, 71%～95% yields, *E*/*Z* up to >19∶1). Variation of the substitution position was found to affect the stereoselectivity possibly due to the steric hindrance. For example, when isocyanates bearing 2- or 3-substituted phenyl and *α*-naphthyl groups were applied to the standard conditions, corresponding products were delivered in moderate yields and with varied stereoselectivities (Table 2, **3g**～**3j**, 63%～86% yields, *E*/*Z* up to 15∶1). Moreover, though with relatively low activity, alkyl isocyanates were also suitable for this reaction, producing the linear ureas in moderate yields and good stereoselectivities after prolonging reaction time (Table 2, **3k**,

Table 1 Optimization of reaction conditions[a]



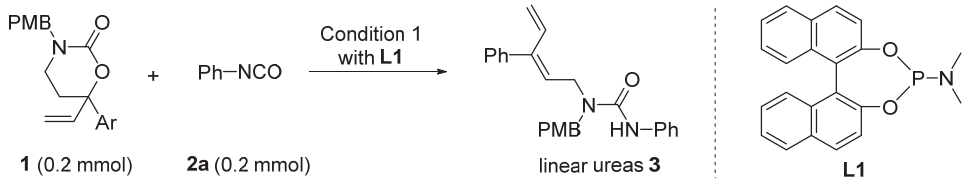
Entry[a]	Ligand	3a		4a
		Yield[b]/%	*E*/*Z*[c]	Yield[b]/%
1[d]	**L1**	83	>19∶1	0
2[d,e]	**L1**	76	>19∶1	0
3[d,f]	**L1**	37	>19∶1	0
4[d,g]	**L1**	20	>19∶1	0
5[d,h]	**L1**	**92**	**>19∶1**	0
6	**L2**	45	>19∶1	28
7	**L3**	6	>19∶1	87
8	**L4**	NR	ND	NR
9	**L5**	16	>19∶1	43
10	**L6**	8	>19∶1	**91**

[a] Unless otherwise stated, the reactions were performed with **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv.), $Pd_2(dba)_3$•$CHCl_3$ (0.005 mmol, 10 mol% Pd), *P*-ligand (0.01 mmol, 10 mol%) and CH_2Cl_2 (2.0 mL) at 40 ℃; [b] Determined by the ^1H NMR analysis of the reaction mixture with dimethyl terephthalate as the internal standard. [c] Determined by the ^1H NMR analysis of the reaction mixture. [d] Using 20 mol% of **L1**. [e] Using tetrahedron furan (2.0 mL) as solvent. [f] Using toluene (2.0 mL) as solvent. [g] Using $Pd(OAc)_2$ (0.01 mmol, 10 mol%) instead of $Pd_2(dba)_3$•$CHCl_3$. [h] Performed with **1a** (0.2 mmol) and **2a** (0.2 mmol, 1.0 equiv.).

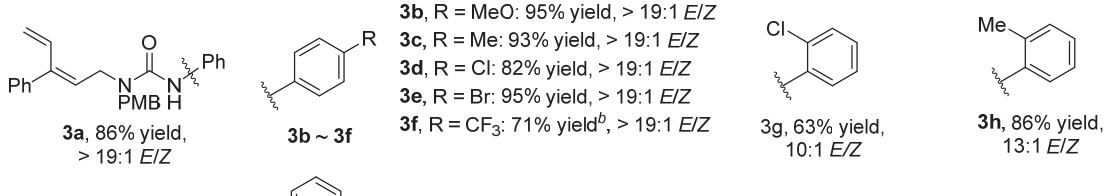


Scheme 1 Ligand-switched transformations of vinyl carbamates and isocyanates (PMB: 4-MeO-benzyl)

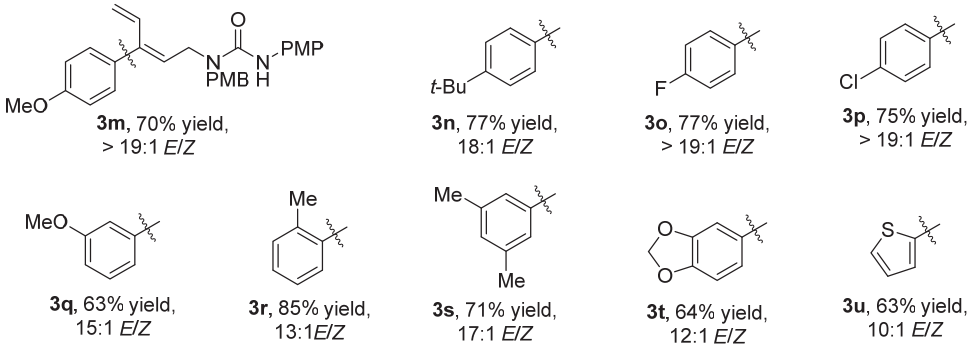
Table 2 Substrate scope of Pd-catalyzed dienylation reaction[a]



Variation of isocyanates



Variation of vinyl carbamates

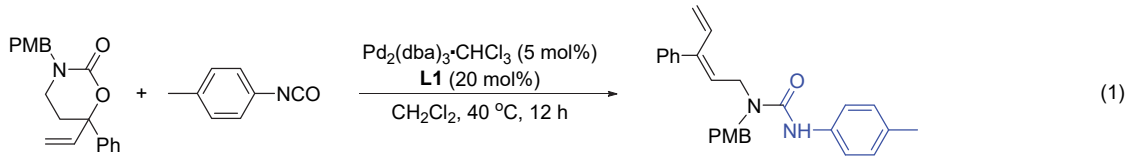


[a] Condition 1: see Entry 5 in Table 1; isolated yields. [b] **1a** (0.2 mmol), **2a** (0.4 mmol). [c] 16 h.

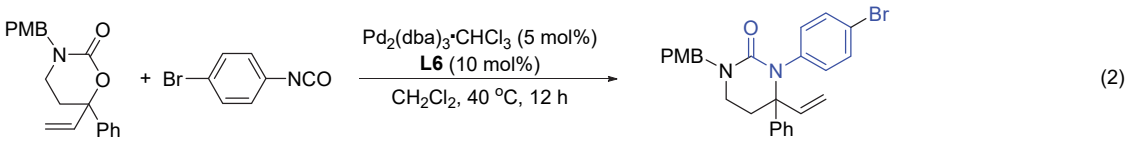
3l, 43%～51% yields, up to 19∶1 *E*/*Z*). In parallel, variation of vinyl carbamates was examined under the standard reaction conditions. As summarized in Table 2, chemoselective transformations of vinyl carbamates and isocyanates leading to corresponding linear ureas **3m**～**3u** in 63%～85% yields and *E*/*Z* up to ＞19∶1.

Furthermore, the generality of Pd-catalyzed decarboxylative (4＋2) annulation of vinyl carbamates was explored with isocyanates under the standard condition 2 using biphosphine ligand **L6**. As highlighted in Table 3, aryl isocyanates with electronically various substituents at the 4-position of benzene ring are applicable to this annulation reaction, affording corresponding cycloadducts in generally good yields (Table 3, **4a**～**4d**, 80%～94% yields). While, alkyl isocyanates failed to be involved in this decarboxylative annulation with isocyanates untouched. Vinyl carbamates having electronically different aryl substituents at the 4- and 3-positions of the benzene ring were also suitable for this catalysis systems. As a result, structurally various cyclic ureas were produced **4e**～**4h** in 72%～85% yields. At the current stage, alkyl-substituted vinyl carbamates are not applicable to both Pd-catalyzed dienylation and annulation reactions. To show the utility of the present methodology, two gram-scale reactions were performed under standard conditions. Desired products **3c** and **4c** can be obtained in 79% yield, *E*/*Z*＞19∶1 and 85% yield, respectively (Eqs. (1), (2)).

Possible reaction mechanisms for these two transformations were outlined in Scheme 2. Initially, the decarboxylation of vinyl carbamate **1a** promoted by the Pd(0) catalyst generates Pd-containing dipolar intermediate **int-I**. Following, a nucleophilic attack of *N*-anion part to isocyanate forms a new dipolar species **int-II**. When the monodentate ligand **L1** is used, a hydrogen migration of **int-II** (path A) proceeds to afford the linear urea product **3a** accompanying the regeneration of Pd(0) catalyst.[8] Alternatively, the mechanism involving the *β*-hydride elimination

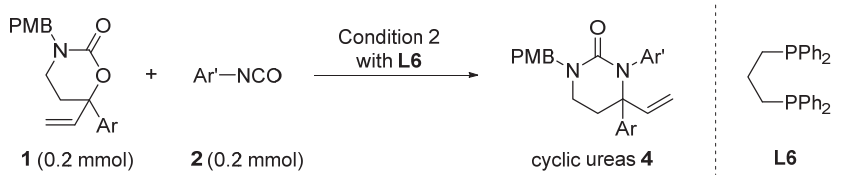


1a: 3.4 mmol **2c**: 3.4 mmol **3c**: 1.1 g, 79% yield, *E*/*Z* > 19:1 (1)

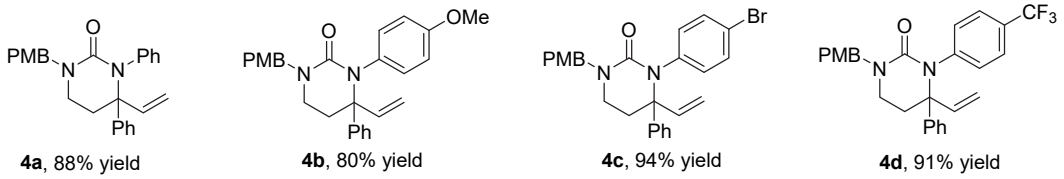


1a: 3.0 mmol **2e**: 6.0 mmol **4c**: 1.2 g, 85% yield (2)

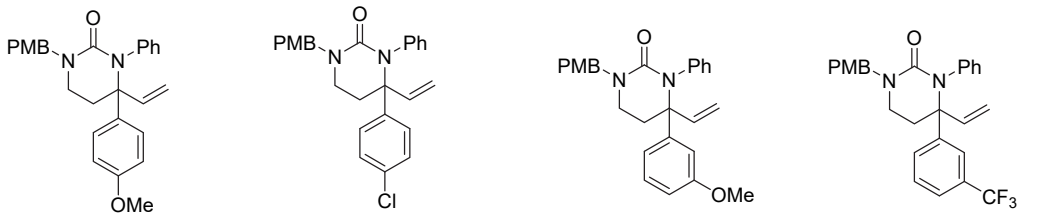
Table 3 Substrate scope of Pd-catalyzed (4＋2) annulation reactions[a]



1 (0.2 mmol) **2** (0.2 mmol) cyclic ureas **4** **L6**

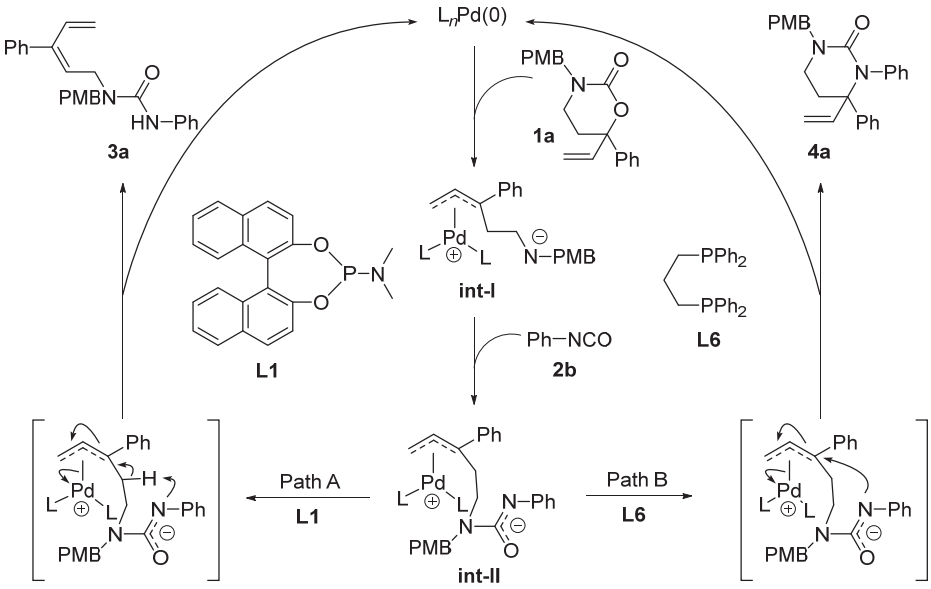


4a, 88% yield **4b**, 80% yield **4c**, 94% yield **4d**, 91% yield



4e, 85% yield **4f**, 85% yield **4g**, 78% yield **4h**, 72% yield

[a] Condition 2: see Entry 10 in Table 1; isolated yields.



Scheme 2 Proposed reaction mechanisms

from an η^1-palladium species cannot be excluded. When the bidentate ligand **L6** is used, a subsequent intramolecular *N*-allylic alkylation (path B) occurs to provide the cyclic urea product **4a**, and regenerates the original Pd(0) catalyst. It seems paths A and B are two competitive processes in the reaction, and the product distribution is controlled by kinetics, depending on the rate difference of β-H elimination and intramolecular allylation. Less electron-donating mono dentate ligands favor β-H elimination, more electron-donating bidentate phosphine ligands can suppress β-H elimination and render the π-allyl Pd species more reactive.[11]

3 Conclusions

In conclusion, we have developed two Pd-catalyzed, ligand-controlled chemoselective transformations of vinyl carbamates and isocyanates. The linear urea products were obtained by utilizing monodentate ligands, whereas the cyclic urea products were obtained in the presence of bidentate ligands. We believe that this study further enriches the application of vinyl carbamates as versatile building blocks in organic synthesis and discloses the important effect ligands on chemoselectivity control.

4 Experimental section

4.1 Instruments and reagents

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200～300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts are reported in delta (δ) units relative to the singlet (δ 0) for tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Varian Mercury 100 MHz with complete proton decoupling spectrophotometer ($CDCl_3$: δ 77.0). ^{19}F NMR spectra were recorded on a Bruker DPX-400 376 MHz spectrophotometer. HRMS was recorded on a Bruker micrOTOFII ESI-TOF using a positive electrospray inonization (ESI^+). Measured values are reported to 4 decimal places of the calculated value.

4.2 Preparation of compound **1**

Substrates (**1a**～**1j**) were prepared according to the reported procedures[10]. Ligands were commercially available.

4.3 General procedure for the synthesis of the **3**

Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3$•$CHCl_3$ (0.01 mmol, 5 mol%), **L1** (0.04 mmol, 20 mol%) and anhydrous dichloromethane (DCM) (2 mL), the resulting solution was stirred for 30 min at room temperature. Then **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.) were added. The resulting solution was stirred at 40 ℃ until complete conversion of **1a** (monitored by thin-layer chromatography (TLC)). The product was purified by flash column chromatography on silica gel (petrol ether/EtOAc, V∶V=20/1～10/1) to give product.

4.4 General procedure for the synthesis of the **4**

Under argon atmosphere, a flame-dried 10 mL Schlenk tube was charged with $Pd_2(dba)_3$•$CHCl_3$ (0.01 mmol, 5 mol%), 1,3-bis(diphenylphosphino)propane (DPPP) (0.02 mmol, 10 mol%) and anhydrous DCM (2 mL). The resulting solution was stirred for 30 min at room temperature. Then **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.) were added. The resulting solution was stirred at 40 ℃ until complete conversion of **1a** (monitored by TLC). The product was purified by flash column chromatography on silica gel (petrol ether/EtOAc, V∶V=5/1～3/1) to give product.

(*E*)-1-(4-Methoxybenzyl)-3-phenyl-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3a**): White solid, 68.5 mg, 86% yield. m.p. 102～105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.07 (m, 10H), 7.00 (s, 1H), 6.91 (d, J=8.3 Hz, 2H), 6.81 (dd, J=17.2, 10.8 Hz, 1H), 6.43 (s, 1H), 5.62 (t, J=7.0 Hz, 1H), 5.44 (d, J=10.8 Hz, 1H), 5.22 (d, J=17.3 Hz, 1H), 4.57 (s, 2H), 4.26 (d, J=7.0 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.23, 155.68, 142.93, 139.14, 131.83, 129.50, 128.90, 128.47, 128.27, 127.70, 126.85, 122.93, 121.28, 119.59, 114.34, 55.36, 50.36, 44.89. HRMS (ESI) calcd for $C_{26}H_{27}N_2O_2$ $[M+H]^+$ 399.2067, found 399.2070.

(*E*)-1-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3b**): White solid, 81.5 mg, 95% yield. m.p. 110～112 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47～7.22 (m, 7H), 7.19 (d, J=8.9 Hz, 2H), 6.89 (d, J=8.5 Hz, 2H), 6.79 (d, J=9.1 Hz, 3H), 6.35 (s, 1H), 5.61 (s, 1H), 5.42 (dd, J=11.0, 1.5 Hz, 1H), 5.20 (dd, J=17.3, 1.5 Hz, 1H), 4.55 (s, 2H), 4.24 (d, J=6.9 Hz, 2H), 3.80 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.17, 156.07, 155.67, 142.78, 140.16, 132.22, 131.88, 129.61, 128.88, 128.49, 128.26, 127.66, 127.03, 121.81, 121.08, 55.53, 55.35, 50.26, 44.81. HRMS (ESI) calcd for $C_{17}H_{29}N_2O_3$ $[M+H]^+$ 429.2173, found 429.2185.

(*E*)-1-(4-Methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)-3-(*p*-tolyl)urea (**3c**): White solid, 82.5 mg, 93% yield. m.p. 113～115 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.21 (m, 6H), 7.17 (d, J=8.2 Hz, 2H), 7.04 (d, J=8.2 Hz, 2H), 6.89 (d, J=8.6 Hz, 2H), 6.78 (dd, J=17.3, 10.8 Hz, 1H), 6.43 (s, 1H), 5.60 (s, 1H), 5.41 (dt, J=10.8, 1.5 Hz, 1H), 5.20 (dd, J=17.3, 1.6 Hz, 1H), 4.55 (s, 2H), 4.23 (d, J=7.0 Hz, 2H), 3.79 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.20, 155.89, 142.84, 140.17, 136.55, 132.50, 131.90, 129.59, 129.39, 128.91, 128.50, 128.26, 127.67, 126.99, 121.12, 119.91, 114.32, 55.35, 50.29, 44.84, 20.78. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_2$ $[M+H]^+$ 413.2224, found 413.2223.

(*E*)-3-(4-Chlorophenyl)-1-(4-methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3d**): White solid, 69.3 mg, 82% yield. m.p. 122～124 ℃; ^{1}H NMR (400 MHz, CDCl3) δ: 7.41～7.09 (m, 10H), 6.91 (d, J=8.6 Hz, 2H), 6.81 (dd, J=17.4, 10.9 Hz, 1H), 6.42 (s, 1H), 5.60 (s, 1H), 5.45 (d, J=10.9 Hz, 1H), 5.23 (d, J=17.3 Hz, 1H), 4.56 (s, 2H), 4.25 (d, J=7.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.29, 155.46, 143.04, 140.01, 137.79, 131.76, 129.28, 128.88, 128.82, 128.44, 128.30, 127.77, 126.62, 121.42, 120.74, 114.38, 55.36, 50.38, 44.90. HRMS (ESI) calcd for $C_{26}H_{26}N_2O_2$ $[M+H]^+$ 455.1502, found 455.1505.

(*E*)-3-(4-Bromophenyl)-1-(4-methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3e**): White solid, 63.4 mg, 66% yield. m.p. 112～114 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53～6.98 (m, 11H), 6.91 (d, J=8.4 Hz, 2H), 6.81 (dd, J=17.3, 10.9 Hz, 1H), 6.42 (s, 1H), 5.60 (t, J=7.0 Hz, 1H), 5.45 (d, J=10.9 Hz, 1H), 5.25 (s, 1H), 4.56 (s, 2H), 4.25 (d, J=7.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.28, 155.40, 143.05, 140.00, 138.32, 131.75, 128.88, 128.44, 128.30, 127.77, 126.61, 121.43, 121.09, 115.29, 114.38, 55.36, 50.36, 44.89. HRMS (ESI) calcd for $C_{26}H_{26}BrN_2O_2$ $[M+H]^+$ 477.1172, found 477.1177.

(*E*)-1-(4-Methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)-3-(4-(trifluoromethyl)phenyl)urea (**3f**): White solid, 65.9 mg, 71% yield. m.p. 106～109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54～7.20 (m, 11H), 6.91 (d, J=8.5 Hz, 2H), 6.82 (dd, J=17.2, 10.8 Hz, 1H), 6.64 (s, 1H), 5.61 (s, 1H), 5.47 (d, J=10.8 Hz, 1H), 5.25 (d, J=17.3 Hz, 1H), 4.58 (s, 2H), 4.26 (d, J=7.1 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.66, 129.10, 128.91, 128.42, 128.33, 127.84, 126.39, 126.15 (q, J=3.1 Hz), 123.0 (q, J=269.1 Hz), 118.76, 114.43, 55.36, 50.49, 44.98; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −61.81. HRMS (ESI) calcd for $C_{27}H_{26}F_3N_2O_2$ $[M+H]^+$ 467.1941, found 467.1944.

(*E*)-3-(2-Chlorophenyl)-1-(4-methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3g**): Colorless oil, 53.5 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (dd, J=8.3, 1.5 Hz, 1H), 7.38～7.17 (m, 9H), 7.07 (s, 1H), 6.90 (d, J=8.6 Hz, 3H), 6.76 (dd, J=17.3, 10.9 Hz, 1H), 5.63 (s, 1H), 5.39 (dt, J=10.9, 1.5 Hz, 1H), 5.17 (dd, J=17.2, 1.5 Hz, 1H), 4.60 (s, 2H), 4.32 (d, J=6.7 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.30, 155.12, 143.23, 140.18, 136.11, 132.25, 129.11, 128.90, 128.77, 128.52, 128.20, 127.63, 127.58, 126.37, 123.08, 122.33, 121.16, 120.68, 114.35, 55.37, 50.40, 45.23. HRMS (ESI) calcd for $C_{26}H_{26}ClN_2O_2$ $[M+H]^+$ 433.1683, found 433.1679.

(*E*)-1-(4-Methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)-3-(*o*-tolyl)urea (**3h**): White solid, 54.3 mg, 66% yield. m.p. 112～115 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, J=8.1 Hz, 1H), 7.43～7.22 (m, 7H), 7.17 (s, 1H), 7.07 (d, J=7.5 Hz, 1H), 7.00～6.88 (m, 3H), 6.79 (dd, J=17.3, 10.9 Hz, 1H), 6.20 (s, 1H), 5.67 (s, 1H), 5.39 (d, J=10.9 Hz, 1H), 5.18 (d, J=17.4 Hz, 1H), 4.58 (s, 2H), 4.34 (d, J=6.8 Hz, 2H), 3.82 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.30, 155.83, 142.88, 140.16, 137.22, 132.06, 130.20, 129.41, 128.67, 128.47, 128.22, 127.62, 127.02, 126.70, 123.48, 122.10, 120.74, 114.40, 55.38, 50.47, 45.32, 17.57. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_2$ $[M+H]^+$ 413.2224, found 413.2222.

(*E*)-3-(3-Chlorophenyl)-1-(4-methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3i**): White solid, 57.1 mg, 66% yield. m.p. 109～113 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (s, 1H), 7.36～7.20 (m, 6H), 7.13 (d, J=8.0 Hz, 1H), 7.08 (t, J=1.5 Hz, 1H), 6.96 (dt, J=7.8, 1.4 Hz, 1H), 6.90 (d, J=8.6 Hz, 2H), 6.80 (dd, J=17.2, 10.8 Hz, 1H), 6.48 (d, J=3.2 Hz, 1H), 5.60 (t, J=7.0 Hz, 1H), 5.46 (d, J=10.8 Hz, 1H), 5.23 (dd, J=17.3, 1.4 Hz, 1H), 4.56 (s, 2H), 4.25 (d, J=7.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.29, 155.34, 143.08, 140.41, 140.02, 134.50, 131.77, 129.78, 129.21, 128.87, 128.46, 128.30, 127.76, 126.53, 122.88, 121.43, 119.59, 117.47, 114.40, 55.36, 50.34, 44.89. HRMS (ESI) calcd for

$C_{26}H_{26}ClN_2O_2$ $[M+H]^+$ 433.1683, found 433.1681.

(*E*)-1-(4-Methoxybenzyl)-3-(naphthalen-1-yl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3j**): White solid, 51.1 mg, 57% yield. m.p. 120～122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (dd, J=22.7, 7.8 Hz, 2H), 7.59 (d, J=8.2 Hz, 1H), 7.49～7.26 (m, 11H), 6.96 (d, J=8.6 Hz, 2H), 6.90～6.74 (m, 2H), 5.76 (t, J=6.8 Hz, 1H), 5.42 (d, J=1.5 Hz, 1H), 5.21 (d, J=17.6 Hz, 1H), 4.66 (s, 2H), 4.42 (d, J=6.8 Hz, 2H), 3.84 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.42, 156.21, 143.11, 140.14, 134.07, 133.81, 132.04, 129.52, 128.92, 128.68, 128.52, 128.28, 127.71, 127.01, 125.92, 125.76, 125.63, 124.23, 121.06, 120.46, 119.73, 114.52, 55.43, 50.67, 45.46. HRMS (ESI) calcd for $C_{30}H_{29}N_2O_2$ $[M+H]^+$ 449.2224, found 449.2228.

(*E*)-3-Butyl-1-(4-methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3k**): Colorless oil, 35.1 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47～7.02 (m, 7H), 6.88 (d, J=8.1 Hz, 2H), 6.73 (dd, J=17.3, 10.9 Hz, 1H), 5.55 (t, J=6.9 Hz, 1H), 5.36 (dd, J=11.0, 1.6 Hz, 1H), 5.14 (d, J=17.3 Hz, 1H), 4.45 (s, 2H), 4.38 (s, 1H), 4.14 (d, J=6.9 Hz, 2H), 3.81 (d, J=1.2 Hz, 3H), 3.45～2.71 (m, 2H), 1.57～1.33 (m, 2H), 1.26 (dd, J=9.3, 5.9 Hz, 2H), 0.86 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.99, 158.35, 142.25, 132.02, 130.03, 128.64, 128.46, 128.14, 127.54, 127.47, 120.35, 114.14, 55.33, 49.96, 44.56, 40.67, 32.24, 20.02, 13.79. HRMS (ESI) calcd for $C_{24}H_{31}N_2O_2$ $[M+H]^+$ 379.2380, found 379.2380.

(*E*)-3-(*tert*-Butyl)-1-(4-methoxybenzyl)-1-(3-phenylpenta-2,4-dien-1-yl)urea (**3l**): Colorless oil, 38.6 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52～7.09 (m, 7H), 6.98～6.81 (m, 2H), 6.73 (dd, J=17.3, 10.9 Hz, 1H), 5.53 (t, J=6.9 Hz, 1H), 5.43～5.28 (m, 1H), 5.13 (dd, J=17.3, 1.6 Hz, 1H), 4.42 (s, 2H), 4.35 (s, 1H), 4.09 (d, J=7.0 Hz, 2H), 3.80 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.95, 157.54, 142.16, 140.41, 132.00, 130.36, 128.74, 128.46, 128.18, 127.87, 127.48, 120.43, 114.11, 55.32, 50.76, 29.49. HRMS (ESI) calcd for $C_{24}H_{31}N_2O_2$ $[M+H]^+$ 379.2380, found 379.2388.

(*E*)-1-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-1-(3-(4-methoxyphenyl)penta-2,4-dien-1-yl)urea (**3m**): White solid, 63.9 mg, 70% yield. m.p. 94～96 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (dd, J=9.0, 2.5 Hz, 2H), 7.21～7.13 (m, 4H), 6.94～6.83 (m, 4H), 6.82～6.70 (m, 3H), 6.34 (s, 1H), 5.57 (t, J=6.8 Hz, 1H), 5.41 (dt, J=10.8, 1.6 Hz, 1H), 5.22 (dd, J=17.3, 1.6 Hz, 1H), 4.55 (s, 2H), 4.21 (d, J=7.0 Hz, 2H), 3.81 (d, J=3.1 Hz, 6H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.22, 159.16, 156.09, 155.66, 142.24, 132.54, 132.27, 132.17, 129.70, 129.54, 128.91, 126.03, 121.78, 121.00, 114.28, 114.09, 113.64, 55.53, 55.34, 55.32, 50.27, 44.89. HRMS (ESI) calcd for $C_{28}H_{31}N_2O_4$ $[M+Na]^+$ 481.2098, found 481.2099.

(*E*)-1-(3-(4-(*tert*-Butyl)phenyl)penta-2,4-dien-1-yl)-1-(4-methoxybenzyl)-3-(4-methoxyphenyl)urea (**3n**): Colorless oil, 75.1 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J=8.3 Hz, 2H), 7.30～7.23 (m, 2H), 7.22～7.15 (m, 4H), 6.89 (d, J=8.6 Hz, 2H), 6.84～6.71 (m, 3H), 6.37 (s, 1H), 5.61 (t, J=6.9 Hz, 1H), 5.42 (d, J=10.8 Hz, 1H), 5.24 (dd, J=17.3, 1.6 Hz, 1H), 4.54 (s, 2H), 4.21 (d, J=6.9 Hz, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.17, 156.11, 155.68, 150.70, 142.59, 137.14, 132.29, 131.99, 129.74, 128.95, 128.04, 126.46, 125.16, 121.80, 121.07, 114.29, 114.11, 55.53, 55.33, 50.27, 44.89, 34.57, 31.36. HRMS (ESI) calcd for $C_{31}H_{37}N_2O_3$ $[M+H]^+$ 485.2799, found 485.2781

(*E*)-1-(3-(4-Fluorophenyl)penta-2,4-dien-1-yl)-1-(4-methoxybenzyl)-3-(4-methoxyphenyl)urea (**3o**): White solid, 68.7 mg, 77% yield. m.p. 80～82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J=8.5 Hz, 2H), 7.23～7.14 (m, 4H), 7.01 (t, J=8.7 Hz, 2H), 6.90 (d, J=8.4 Hz, 2H), 6.78 (dd, J=16.4, 9.9 Hz, 3H), 6.30 (s, 1H), 5.58 (t, J=6.9 Hz, 1H), 5.41 (d, J=10.8 Hz, 1H), 5.16 (d, J=17.6 Hz, 1H), 4.54 (s, 2H), 4.24 (d, J=7.0 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.57, 161.12, 159.22, 156.04, 155.74, 141.71, 136.15 (d, J=3.0 Hz), 132.14, 131.96, 130.12 (d, J=8.0 Hz), 129.47, 128.76, 127.25, 121.89, 120.95, 115.22, 115.01, 114.34, 114.10, 55.52, 55.35, 50.29, 44.84; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −114.75. HRMS (ESI) calcd for $C_{27}H_{28}FN_2O_3$ $[M+H]^+$ 447.2078, found 447.2080.

(*E*)-1-(3-(4-Chlorophenyl)penta-2,4-dien-1-yl)-1-(4-methoxybenzyl)-3-(4-methoxyphenyl)urea (**3p**): Colorless oil, 69.8 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32～7.23 (m, 3H), 7.20～7.12 (m, 4H), 6.92～6.87 (m, 2H), 6.82～6.70 (m, 4H), 6.30 (s, 1H), 5.59 (t, J=6.9 Hz, 1H), 5.40 (dt, J=10.8, 1.5 Hz, 1H), 5.15 (d, J=17.3 Hz, 1H), 4.53 (s, 2H), 4.24 (d, J=6.9 Hz, 2H), 3.80 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.25, 156.01, 155.78, 141.58, 138.63, 133.49, 132.08, 131.74, 129.80, 129.39, 128.70, 128.40, 127.51, 121.92, 121.00, 114.36, 114.11, 55.52, 55.34, 50.33, 44.90. HRMS (ESI) calcd for $C_{27}H_{28}ClN_2O_3$ $[M+H]^+$ 463.1783, found 463.1780.

(*E*)-1-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-1-(3-(3-methoxyphenyl)penta-2,4-dien-1-yl)urea (**3q**): Colorless oil, 57.4 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32～7.15 (m, 4H), 6.94～6.71 (m, 9H), 6.32 (d, J=2.9 Hz, 1H), 5.62 (t, J=7.0 Hz, 1H), 5.42 (d, J=10.9 Hz, 1H), 5.23 (d, J=17.2 Hz, 1H), 4.55 (s, 2H), 4.24 (d, J=7.1 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.95, 157.54, 142.16, 140.41, 132.00, 130.36, 128.74, 128.46, 128.18, 127.87, 127.48, 120.43, 114.11, 55.32, 50.76, 29.49. HRMS (ESI) calcd for $C_{18}H_{31}N_2O_4$ $[M+Na]^+$ 481.2098, found 481.2103.

(*E*)-1-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-1-(3-(*o*-tolyl)penta-2,4-dien-1-yl)urea (**3r**): White solid, 76.3 mg, 86% yield. m.p. 74～76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 1H), 7.18 (dd, J=13.9, 9.0 Hz, 5H), 7.00 (d, J=7.3 Hz, 1H), 6.84 (dd, J=37.7, 8.6 Hz, 6H), 6.38 (s, 1H), 5.44 (s, 1H), 5.27 (d, J=10.5 Hz, 1H), 4.83 (d, J=17.0 Hz, 1H), 4.54 (s, 2H), 4.26 (d, J=7.1 Hz, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.19, 156.09, 155.69, 142.80, 139.76, 135.89, 132.21, 131.33, 129.93, 129.69, 129.53, 128.81, 127.50,

127.44, 125.62, 121.85, 120.08, 114.31, 114.09, 55.52, 55.34, 50.10, 44.17, 19.75. HRMS (ESI) calcd for $C_{28}H_{30}N_2O_3$ $[M+H]^+$ 443.2329, found 443.2346.

(*E*)-1-(3-(3,5-Dimethylphenyl)penta-2,4-dien-1-yl)-1-(4-methoxybenzyl)-3-(4-methoxyphenyl)urea (**3s**): Colorless oil, 64.4 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J=8.6 Hz, 2H), 7.19 (d, J=8.9 Hz, 2H), 6.98～6.68 (m, 8H), 6.32 (s, 1H), 5.58 (t, J=6.9 Hz, 1H), 5.41 (dt, J=10.8, 1.5 Hz, 1H), 5.22 (dd, J=17.2, 1.6 Hz, 1H), 4.55 (s, 2H), 4.22 (d, J=7.0 Hz, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.95, 157.54, 142.16, 140.41, 132.00, 130.36, 128.74, 128.46, 128.18, 127.87, 127.48, 120.43, 114.11, 55.32, 50.76, 29.49. HRMS (ESI) calcd for $C_{29}H_{33}N_2O_3$ $[M+H]^+$ 457.2486, found 457.2488.

(*E*)-1-(3-(Benzo[*d*][1,3]dioxol-5-yl)penta-2,4-dien-1-yl)-1-(4-methoxybenzyl)-3-(4-methoxyphenyl)urea (**3t**): Colorless oil, 60.9 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 1H), 7.21～7.13 (m, 2H), 6.90 (d, J=8.4 Hz, 2H), 6.87～6.67 (m, 7H), 6.29 (s, 1H), 5.96 (s, 2H), 5.56 (t, J=6.9 Hz, 1H), 5.42 (d, J=10.8 Hz, 1H), 5.23 (d, J=17.2 Hz, 1H), 4.54 (s, 2H), 4.21 (d, J=7.0 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.19, 156.03, 155.70, 147.41, 147.13, 142.23, 134.18, 132.18, 132.03, 129.60, 128.83, 126.35, 121.92, 121.81, 121.04, 114.31, 114.10, 108.91, 108.09, 101.09, 55.52, 55.34, 50.30, 44.90. HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5$ $[M+Na]^+$ 495.1890, found 495.1900.

(*E*)-1-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-1-(3-(thiophen-2-yl)penta-2,4-dien-1-yl)urea (**3u**): Colorless oil, 54.4 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (s, 1H), 7.22 (dd, J=4.2, 2.1 Hz, 1H), 7.17 (d, J=9.0 Hz, 2H), 6.99 (d, J=4.2 Hz, 2H), 6.90 (d, J=8.6 Hz, 2H), 6.83～6.75 (m, 3H), 6.68 (dd, J=17.3, 11.0 Hz, 1H), 6.27 (d, J=2.2 Hz, 1H), 5.83 (t, J=6.9 Hz, 1H), 5.55～5.42 (m, 2H), 4.53 (s, 2H), 4.22 (d, J=6.9 Hz, 2H), 3.81 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.21, 156.04, 155.77, 142.71, 135.57, 132.10, 131.68, 129.45, 128.79, 127.24, 126.14, 125.64, 124.91, 122.02, 121.58, 114.35, 114.09, 55.53, 55.35, 50.29, 45.09. HRMS (ESI) calcd for $C_{25}H_{27}N_2O_3S$ $[M+H]^+$ 435.1737, found 435.1740.

1-(4-Methoxybenzyl)-3,4-diphenyl-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4a**): Colorless oil, 70 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J=7.6 Hz, 2H), 7.32～7.15 (m, 7H), 7.11 (d, J=7.4 Hz, 3H), 6.82 (d, J=8.2 Hz, 2H), 5.75 (dd, J=17.3, 10.7 Hz, 1H), 5.39～4.93 (m, 2H), 4.54 (s, 2H), 3.80 (s, 3H), 3.26～3.03 (m, 1H), 2.79 (d, J=4.8 Hz, 1H), 2.52～2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.84, 155.95, 142.26, 141.10, 140.45, 130.13, 129.82, 129.67, 128.24, 128.12, 127.43, 127.35, 126.08, 116.17, 113.74, 66.91, 55.31, 51.23, 41.50, 35.06. HRMS (ESI) calcd for $C_{26}H_{27}N_2O_2$ $[M+H]^+$ 399.2067, found 399.2075.

1-(4-Methoxybenzyl)-3-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4b**): Colorless oil, 68.6 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J=7.6 Hz, 2H), 7.32～7.13 (m, 5H), 7.02 (d, J=8.5 Hz, 2H), 6.82 (d, J=8.4 Hz, 2H), 6.72 (d, J=8.5 Hz, 2H), 5.72 (dd, J=17.4, 10.7 Hz, 1H), 5.31～5.08 (m, 2H), 4.53 (s, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.11 (dd, J=11.3, 5.3 Hz, 1H), 2.78 (d, J=27.1 Hz, 1H), 2.46～2.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.83, 157.64, 156.24, 142.37, 140.60, 133.97, 130.88, 130.16, 129.64, 128.23, 127.34, 127.32, 115.72, 113.73, 113.45, 66.87, 55.32, 55.29, 51.25, 41.40, 34.66. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3$ $[M+H]^+$ 429.2173, found 429.2173.

3-(4-Bromophenyl)-1-(4-methoxybenzyl)-4-phenyl-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4c**): Colorless oil, 89.7 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～7.22 (m, 7H), 7.20 (d, J=8.6 Hz, 2H), 7.02～6.93 (m, 2H), 6.87～6.65 (m, 2H), 5.77 (dd, J=17.4, 10.7 Hz, 1H), 5.34～5.11 (m, 2H), 4.52 (s, 2H), 3.79 (s, 3H), 3.11 (dt, J=11.7, 4.9 Hz, 1H), 2.80 (ddd, J=11.8, 9.7, 4.9 Hz, 1H), 2.44～2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.91, 155.69, 141.82, 140.22, 140.12, 131.34, 131.12, 129.88, 129.66, 128.40, 127.56, 127.33, 119.53, 116.85, 113.78, 67.02, 55.32, 51.31, 41.56, 35.26. HRMS (ESI) calcd for $C_{26}H_{26}BrN_2O_3$ $[M+H]^+$ 477.1172, found 477.1178.

1-(4-Methoxybenzyl)-4-phenyl-3-(4-(trifluoromethyl)-phenyl)-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4d**): Colorless oil, 84.9 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, J=8.3 Hz, 2H), 7.25 (m, 9H), 6.93～6.66 (m, 2H), 5.81 (dd, J=17.4, 10.7 Hz, 1H), 5.49～4.88 (m, 2H), 4.53 (s, 2H), 3.79 (s, 3H), 3.13 (dd, J=11.1, 5.9 Hz, 1H), 3.03～2.69 (m, 1H), 2.33 (dt, J=10.6, 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.94, 155.56, 141.55, 139.90, 129.73, 129.67, 128.46, 127.64, 127.50 (q, J=3.1 Hz), 127.32, 124.97 (q, J=4.0 Hz), 124.13 (q, J=272.7 Hz), 117.33, 113.80, 67.20, 55.30, 51.35, 41.66, 35.63; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.27. HRMS (ESI) calcd for $C_{27}H_{26}FN_2O_3$ $[M+H]^+$ 467.1941, found 467.1950.

1-(4-Methoxybenzyl)-4-(4-methoxyphenyl)-3-phenyl-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4e**): Colorless oil, 68.5 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29～7.14 (m, 6H), 7.13～7.03 (m, 3H), 6.98～6.38 (m, 4H), 5.73 (dd, J=17.4, 10.7 Hz, 1H), 5.37～5.02 (m, 2H), 4.53 (d, J=1.9 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.27～3.05 (m, 1H), 2.82 (ddd, J=11.7, 10.1, 4.8 Hz, 1H), 2.47～2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.83, 158.65, 155.98, 141.10, 140.63, 134.05, 130.15, 129.83, 129.69, 128.61, 128.10, 126.06, 116.03, 113.71, 113.47, 66.50, 55.28, 55.26, 51.22, 41.52, 35.08. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3$ $[M+H]^+$ 429.2173, found 429.2173.

4-(4-Chlorophenyl)-1-(4-methoxybenzyl)-3-phenyl-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4f**): Colorless oil, 73.6 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～7.15 (m, 8H), 7.15～7.00 (m, 3H), 6.83 (d, J=8.6 Hz, 2H), 5.71 (dd, J=17.4, 10.7 Hz, 1H), 5.32～5.02 (m, 2H), 4.70～4.10 (m, 2H), 3.80 (s, 3H), 3.13 (dt, J=11.9, 4.9 Hz, 1H), 2.79 (td, J=11.0, 4.7 Hz, 1H), 2.47～2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.92, 155.78,

140.82, 139.96, 133.24, 129.92, 129.71, 128.86, 128.40, 128.24, 126.28, 116.57, 113.76, 66.58, 55.32, 51.24, 41.40, 35.00. HRMS (ESI) calcd for $C_{26}H_{26}ClN_2O_2$ $[M+H]^+$ 433.1677, found 433.1685.

1-(4-Methoxybenzyl)-4-(3-methoxyphenyl)-3-phenyl-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4g**): Colorless oil, 56.8 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25～7.16 (m, 5H), 7.15～7.07 (m, 3H), 6.99～6.93 (m, 1H), 6.88 (t, J=2.2 Hz, 1H), 6.84～6.72 (m, 3H), 5.73 (dd, J=17.4, 10.7 Hz, 1H), 5.32～5.13 (m, 2H), 4.65～4.39 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 3.12 (dt, J=11.7, 4.8 Hz, 1H), 2.84 (td, J=11.1, 4.6 Hz, 1H), 2.55～1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.52, 158.81, 155.86, 144.14, 141.06, 140.31, 130.10, 129.84, 129.66, 129.19, 128.13, 126.12, 119.80, 116.09, 113.72, 113.66, 112.31, 66.85, 55.28, 55.24, 51.28, 41.54, 34.93. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3$ $[M+H]^+$ 429.2173, found 429.2170.

1-(4-Methoxybenzyl)-3-phenyl-4-(3-(trifluoromethyl)-phenyl)-4-vinyltetrahydropyrimidin-2(1*H*)-one (**4h**): Colorless oil, 89.5 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61～7.52 (m, 2H), 7.48 (d, J=7.7 Hz, 1H), 7.38 (t, J=7.7 Hz, 1H), 7.25～7.15 (m, 4H), 7.13～7.03 (m, 3H), 6.94～6.67 (m, 2H), 5.77 (dd, J=17.4, 10.7 Hz, 1H), 5.46～4.99 (m, 2H), 4.56 (dd, J=88.0, 14.5 Hz, 2H), 3.79 (s, 3H), 3.37～3.03 (m, 1H), 2.80 (ddd, J=11.8, 9.7, 4.8 Hz, 1H), 2.50～2.13 (m, 2H); ^{13}C NMR (400 MHz, CDCl3) δ: 158.91, 155.68, 143.55, 140.76, 139.60, 130.86, 129.82, 129.78, 129.64, 128.79, 128.57 (q, J=34.1 Hz), 128.32, 126.39, 124.36 (q, J=3.1 Hz), 123.90 (q, J=273.7 Hz), 124.16 (q, J=2.0 Hz), 117.01, 113.81, 66.86, 55.28, 51.32, 41.40, 34.82; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.41. HRMS (ESI) calcd for $C_{27}H_{26}F_3N_2O_2$ $[M+H]^+$ 467.1941, found 467.1935.

Supporting Information The ^{1}H NMR and ^{13}C NMR spectra of products **3a**～**3u**, **4a**～**4h** is available free of charge via the Internet at http://sioc-journal.cn/.

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