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镍催化芳基碳酸酯和芳基氨基磺酸酯与环烯烃的 Heck 反应

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摘要 报道了一种高效的镍催化芳基碳酸酯和芳基氨基磺酸酯的惰性 C—O 键与环烯烃的 Heck 反应. 带有各种官能团的萘基、杂环以及苯基碳酸酯均能在由二价镍、PhBPE 配体和还原性金属锌组成的催化体系中顺利反应.
关键词 镍; Heck 反应; 芳基碳酸酯; 芳基氨基磺酸酯

Nickel-Catalyzed Heck Reaction of Cycloalkenes with Inert C—O Bonds of Aryl Carbonates and Aryl Sulfamates

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Abstract An efficient nickel-catalyzed Heck reaction of cycloalkenes with inert C—O bonds of aryl carbonates and sulfamates has been developed. Naphthyl, heterocycles and simple phenyl substituted carbonates with various functional groups are compatible with the catalytic systems comprising Ni(II), PhBPE ligand and reductive metal Zn.
Keywords nickel; Heck reaction; aryl carbonates; aryl sulfamates

1 Introduction

In recent years, cheap nickel-catalyzed transformations to build carbon-carbon and carbon-heteroatom bonds have emerged as an important research top in the synthetic organic chemistry community.[1] In this realm, employing relatively inert C—O electrophiles as coupling partners in nickel catalysis systems has attracted considerable attention due to the abundance and diversity of the O-based starting materials in natural products and synthetic chemicals.[2] In many cases, the high C—O bond strength in phenols is detrimental to the oxidative addition process. Thus, various O-protecting groups (phosphates, sulfonates, ethers, and carboxylates, etc.) have been introduced to adjust reactivity of the C—O bond.[3]

Given the facile installation and stability, aryl carbonates have been widely used as protecting groups in organic synthesis.[4] The use of a protecting group such as carbonates as aryl electrophiles in nickel-catalyzed cross-couplings presents potentially significant advantages in complex molecule synthesis.[5] In fact, the studies on the activation of C—O bonds of aryl carbonates are still limited. In 2009, Garg *et al.*[6] reported the first nickel-catalyzed Suzuki-Miyaura coupling of aryl carbonates with arylboronic acids (Scheme 1a). It is frustrating that only a small range of naphthyl carbonates examples can undergo the catalytic systems. Subsequently, Kuwano and Shimizu[7] reported that a limited number of phenyl carbonates can be also used as coupling partners in nickel-catalyzed Suzuki-Miyaura reactions via the adjustment of catalytic systems. Rueping *et al.*[8] developed a new and practical nickel-catalyzed alkylation of 2-naphthyl carbonate with B-alkyl-9-BBNs (Scheme 1b). Inert C_{Ar}—O activation by nickel-palladium hetero-bimetallic nanoparticles are reported for *N*-heterocycles directing group-assisted Suzuki-Miyaura reactions of 2-benzo[d]oxazolyl aryl carbonates with aryl boronic acids (Scheme 1c).[9] In 2017, A nickel-catalyzed methodology for the transformation of 2-naphthyl carbonate to primary naphthalen-2-amine via C—O bond cleavage was described (Scheme 1d).[10] Typically, these nickel-catalyzed cross-coupling reactions of aryl carbonates via inert C—O bond activation feature

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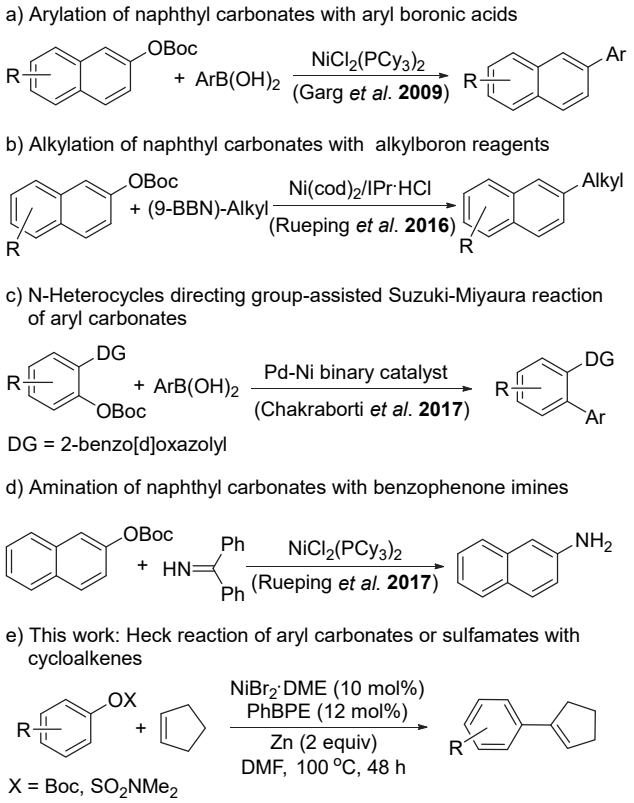
clearly limited substrate scope. Therefore, the development of more efficient and practical catalytic system for the C—O bond activation of aryl carbonates, especially simple phenyl carbonates with various functional groups, would be highly desirable and valuable.



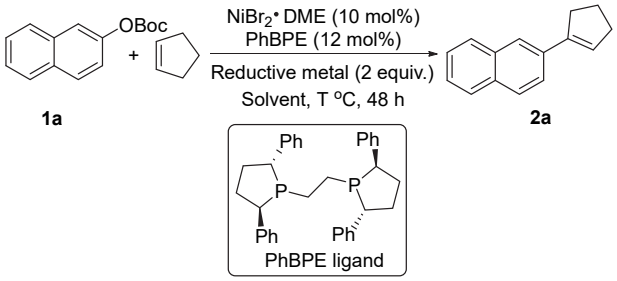
Scheme 1 Evolution of transition metal-catalyzed cross-coupling of inert C—O bonds of aryl carbonates

Catalytic Mizoroki-Heck reactions are commonly used today to prepare biologically active molecules, medicines, and organic functional materials.[11] In typical Heck reactions of acyclic olefins, conjugated isomers are formed as the main products.[12] For cyclic olefins, aryl insertion and sequential *syn* β-hydrogen elimination leads to non-conjugated isomers,[13] representing the basis of asymmetric Heck reactions.[14] The elegant contributions from Gaunt, Barber, and Zhou have disclosed catalytic Heck reactions that could realize the formation of conjugated arylcycloalkenes using copper, palladium or nickel salts as catalysts.[15] Herein, we would like to report nickel-catalyzed Heck reaction of cycloalkenes with aryl carbonates, affording conjugated aryl alkenes in complete vinylic selectivity (Scheme 1e). It is worth noting that aryl sulfamates can also be used as aryl electrophiles to undergo the Heck transformation.

2 Results and discussion

Our study commenced with the Heck reaction of *tert*-butyl naphthalen-2-yl carbonate **1a** with cyclopentene as the model reaction (For details, see Table 1 and Tables S1～S7 in ESI). The desired Heck product **2a** could be obtained in 85% yield by using 10 mol% $NiBr_2$•DME as the catalyst, 12 mol% chiral 1,2-bis(2,5-diphenylphospholano)ethane (PhBPE) as the ligand and 2 equiv. of zinc dust as the reductive metal in *N*,*N*-dimethylformamide (DMF) at 100 °C for 48 h (Table 1, Entry 1). In this reaction, conjugated **2a** was generated as sole isomer and non-conjugated isomers can not be detected. Unlike classic Heck reactions, no bases were necessary and excess zinc dust could also reduce nickel hydride to nickel(0) species (Table 1, Entries 2～3). Other common reductive metals such as manganese, magnesium, iron, and lithium were ineffective on the transformation (Table 1, Entries 4～6 and Table S2). A further solvent screening revealed that the aprotic polar solvents were necessary and DMF was superior to dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMA) (Table 1, Entries 7～11). Furthermore, this transformation afforded a decreased yield when the temperature was increased from 100 °C to 110 °C. Small amount of naphthalene and naphthalen-2-ol were detected by GC-MS as by-products (Table 1, Entries 12～14). Nickel(II) salts of chloride and iodide can also form the active nickel(0) catalyst with Ph-BPE in the presence of reductive Zn (Table S5, Entries 1 and 3). However, no desired product **2a** was detected when $Ni(cod)_2$ was used as the catalyst (Table S5, Entry 6).

Table 1 Optimization of reaction conditions[a]

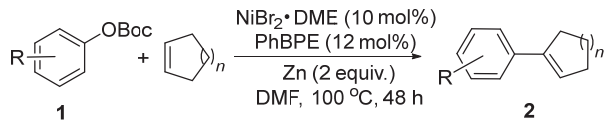


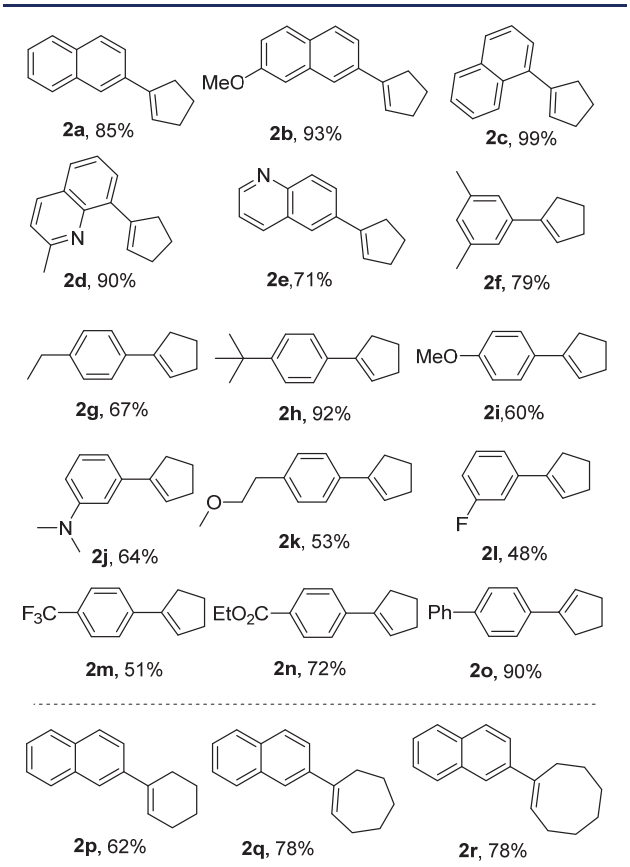
Entry	Reductive metal	Solvent	*T*/°C	Yield[b]/%
1	Zn	DMF	100	85
2[c]	Zn	DMF	100	40
3[d]	Zn	DMF	100	68
4	Mn	DMF	100	0
5	Mg	DMF	100	0
6	Fe	DMF	100	0
7	Zn	Dioxane	100	0
8	Zn	Toluene	100	0
9	Zn	DCE	100	0
10	Zn	DMSO	100	64
11	Zn	DMA	100	72
12	Zn	DMF	90	36
13	Zn	DMF	110	64
14	Zn	DMF	120	62

[a] Reaction conditions: **1a** (0.1 mmol), cyclopentene (0.30 mmol, 3 equiv.), $NiBr_2$•DME (10 mol%), PhBPE (12 mol%), and reductive metal (2 equiv.) in solvent (0.5 mL) for 48 h under an N_2 atmosphere. [b] GC yields. [c] 20 mol% Zn was used. [d] 1 equiv. of Zn was used.

With the optimized conditions in hand, our attention focused on a study of the scope of substituted *tert*-butyl aryl carbonates **1** with cycloalkenes. Both naphthalenyl carbonates and hetero-atoms substituted naphthalenyl carbonates underwent the Heck transformation smoothly to afford the desired products in good to excellent yields (Table 2, **2a**～**2e**). Common aryl carbonate substituents containing electron-donating groups such as methyl, ethyl, *tert*-butyl, methoxy and dimethylamino on the phenyl ring can successfully react with cyclopentene to give the corresponding Heck products in good yields (Table 2, **2f**～**2k**). Electron-withdrawing groups including fluorine, trifluoromethyl, and esters can also be tolerated in this Heck reaction, but only moderate yields of the desired products was obtained along with the arenes generated as the main side products (Table 2, **2l**～**2n**). Moreover, [1,1'-biphenyl]-4-yl *tert*-butyl carbonate coupled with cyclopentene to afford 4-(cyclopent-1-en-1-yl)-1,1'-biphenyl **2o** in 90% yield. When other cycloalkenes were tested, cyclohexene, cycloheptene and cyclooctene were compatible in this Ni/PhBPE catalytic system, and corresponding products were obtained in good yields (Table 2, **2p**～**2r**). Substituted cyclopentenes and cyclohexenes had lower reactivity in this transformation owing to steric effect.

Table 2 Scope of aryl carbonates with cycloalkenes[a]

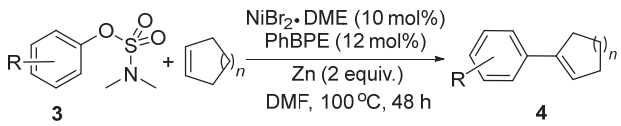


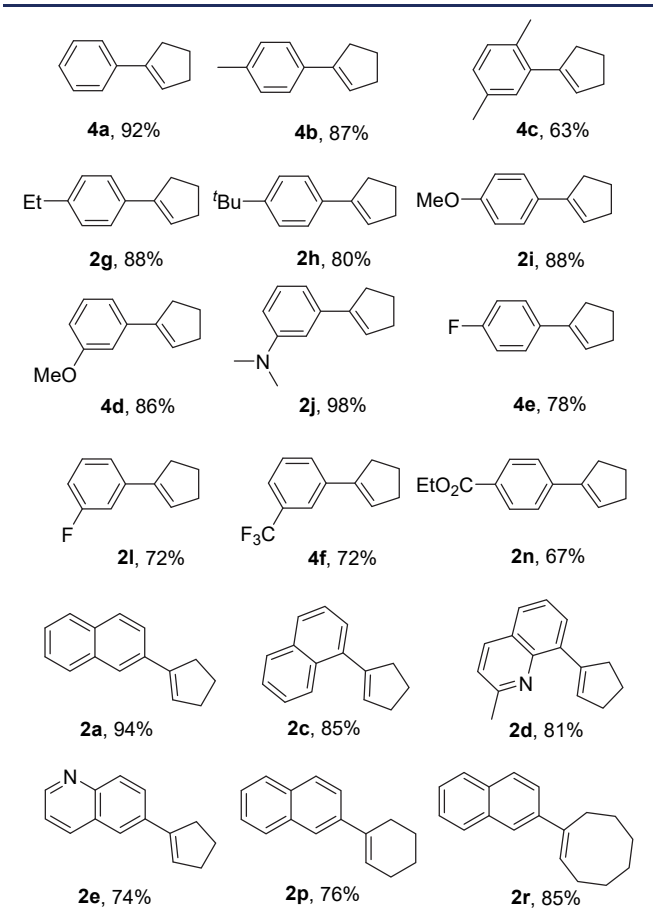


[a] Reaction conditions: **1** (0.2 mmol), cycloalkenes (0.6 mmol, 3 equiv.), $NiBr_2$• DME (10 mol%), PhBPE (12 mol%), and Zn (2 equiv.) in DMF for 48 h under an N_2 atmosphere. Isolated yields.

To our delight, we found that the nickel catalyst ligated by PhBPE can also be used to activate the inert C—O bonds of aryl sulfamates (Table 3). Unlike aryl carbonates, aryl sulfamates containing both electron-donating and electron-withdrawing groups on phenyl ring moiety showed satisfactory reactivity and afforded the desired Heck products in excellent yields in most cases (Table 3, **4a**～**4d**, **2g**～**2j**). Naphthalenyl and quinolyl sulfamates can also undergo the Heck process smoothly. In addition, other cycloalkenes such as cyclohexene and cyclooctene were compatible with the current nickel-catalyzed Heck reaction in good yields (Table 3, **2q** and **2r**).

Table 3 Scope of aryl sulfamates[a]

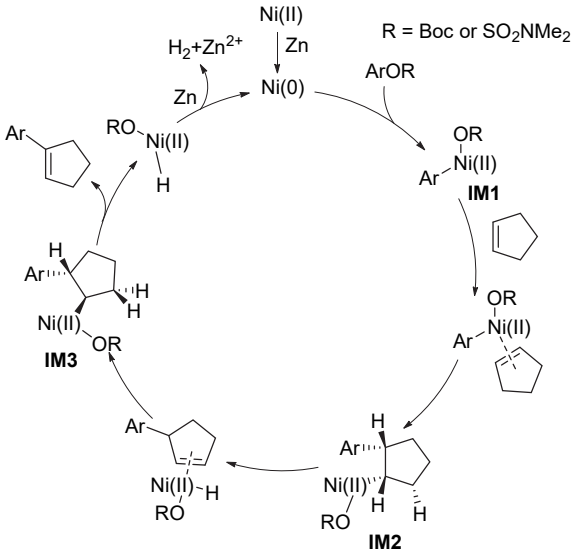




[a] Reaction conditions: **3** (0.2 mmol), cycloalkenes (0.6 mmol, 3 equiv.), $NiBr_2$• DME (10 mol%), PhBPE (12 mol%), and Zn (2 equiv.) in DMF for 48 h under an N_2 atmosphere. Isolated yields.

On the basis of our previous work on nickel-catalyzed Heck reaction[15a] and other related literature reports,[15b]

we envision a Ni(0)/Ni(II) catalytic cycle[14a] outlined in Scheme 2. First, Ni(II) was reduced to Ni(0). The ArNi(II) intermediate **IM1** was formed through the oxidative addition of aryl electrophile to Ni(0). The *syn* insertion of **IM1** with cyclopentene afforded the intermediate **IM2**, which would undergo a *syn* β-hydride elimination to give Ni(II)H species and non-conjugated cycloalkenes. Ni(II)H species can live long enough in the absence of base to coordinated with the generated non-conjugated cycloalkenes to afford **IM3**. After another *syn* β-hydride elimination, the desired conjugated cycloalkenes was formed, and the Ni(II)H species was reduced by Zn to release Ni(0) and H_2.



Scheme 2 Proposed mechanisms

3 Conclusions

In conclusion, we have demonstrated an efficient nickel-catalyzed Heck reaction of cycloalkenes with inert C—O bonds of aryl carbonates and sulfamates. A series of aryl carbonates and sulfamates show good reactivity and outstanding functional group tolerance under the catalytic systems comprising Ni(II), PhBPE ligand and reductive metal Zn. Studies of the application of this methodology are currently underway.

4 Experimental section

4.1 General information

All NMR spectra were acquired on Bruker AV 600 MHz or BBF 400 MHz NMR spectrometers. ^{1}H NMR chemical shifts were recorded relative to $SiMe_4$ (δ 0.00) or residual protiated solvents ($CDCl_3$ δ: 7.26); ^{13}C NMR chemical shifts were recorded relative to solvent resonance ($CDCl_3$ δ: 77.16).

Unless noted otherwise, commercially available chemicals were used as received without purification. Toluene and 1,4-dioxane were distilled from sodium under nitrogen and was stored over activated 4 Å molecular sieve beads. Dichloroethane (DCE), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO) were distilled from CaH_2 under nitrogen and was stored over activated 4 Å molecular sieve beads. Aryl carbonates[6] and sulfamates[16] were synthesized from phenols according to the literature procedures. The GC internal standard, *n*-$C_{12}H_{26}$ was degassed with nitrogen and dried over activated 4 Å molecular sieve beads before use. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI).

4.2 Procedure for Heck reaction of aryl carbonates with cycloalkenes

A typical procedure: In a nitrogen-filled glove box, $NiBr_2$•DME (6.2 mg, 0.02 mmol, 10 mol%), PhBPE (12.2 mg, 0.024 mmol, 12 mol%), Zn dust (26.4 mg, 0.4 mmol, 2 equiv) and DMF (1.0 mL) were added to a 10-mL reaction tube. After stirring at room temperature for 15 min, aryl carbonates (0.2 mmol, 1 equiv.), cycloalkenes (0.6 mmol, 3 equiv.) were added. The reaction mixture was stirred at 100 °C for 48 h. The reaction mixture was cooled to room temperature and then extracted with Et_2O. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatograph on directly.

1-(2-Naphthyl)cyclopentene (**2a**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84～7.71 (m, 5H), 7.49～7.43 (m, 2H), 6.37～6.34 (m, 1H), 2.89～2.84 (m, 2H), 2.65～2.59 (m, 2H), 2.14～2.07 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.6, 134.3, 133.8, 132.7, 128.2, 127.8, 127.7, 127.1, 126.2, 125.6, 124.4, 124.2, 33.7, 33.3, 23.5; GC-MS (EI) *m/z*: 194.2.

2-(1-Cyclopentenyl)-7-methoxynaphthalene (**2b**): The product was isolated by flash chromatography (EtOAc/petroleum ether, *V*/*V*=1/150) as colorless oil. 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 7.67 (s, 1H), 7.64 (s, 1H), 7.55 (dd, *J*=6.8, 1.6 Hz, 1H), 7.12 (d, *J*=2.4 Hz, 1H), 7.09 (dd, *J*=6.4, 2.4 Hz, 1H), 6.33～6.32 (m, 1H), 3.92 (s, 3H), 2.85～ 2.80 (m, 2H), 2.61～2.57 (m, 2H), 2.11～2.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.0, 142.8, 135.0, 134.9, 129.2, 128.2, 127.6, 127.2, 123.3, 122.2, 118.3, 106.4, 55.5, 33.7, 33.4, 23.6. HRMS (ESI) calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1279, found 225.1281.

1-(1-Naphthyl)cyclopentene (**2c**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18～8.15 (m, 1H), 7.86～7.84 (m, 1H), 7.74 (d, *J*=8.0 Hz, 1H), 7.49～7.46 (m, 2H), 7.43 (t, *J*=7.6 Hz, 1H), 7.36 (d, *J*=6.8 Hz, 1H), 5.95～5.94 (m, 1H), 2.85～2.80 (m, 2H), 2.67～2.63 (m, 2H), 2.14～2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.4, 137.3, 134.0, 131.6, 130.7, 128.5, 127.2, 126.0, 125.8, 125.7, 125.4, 124.8, 37.9, 33.9, 24.0; GC-MS (EI) *m/z*: 194.2.

8-(1-Cyclopentenyl)-2-methylquinoline (**2d**): The product was isolated by flash chromatography (EtOAc/petro-

leum ether, *V*/*V*=1/20) as colorless oil. 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J*=8.4 Hz, 1H), 7.62 (d, *J*=7.6 Hz, 2H), 7.41 (t, *J*=8.0 Hz, 1H), 7.27 (d, *J*=8.4 Hz, 1H), 7.08～7.06 (m, 1H), 3.05～3.00 (m, 2H), 2.76 (s, 3H), 2.71～2.65 (m, 2H), 2.11～2.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.2, 146.3, 141.3, 136.6, 135.6, 133.4, 128.3, 126.9, 126.6, 125.4, 121.5, 36.3, 34.3, 25.8, 23.3. HRMS (ESI) calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1283, found 210.1288.

1-(6-Quinolinyl)cyclopentene (**2e**):[15a] The product was isolated by flash chromatography (EtOAc/ petroleum ether, *V*/*V*=1/20) as colorless oil. 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.84(dd, *J*=2.4, 1.6 Hz, 1H), 8.12 (d, *J*=8.4 Hz, 1H), 8.02 (d, *J*=8.8 Hz, 1H), 7.93 (dd, *J*=6.8, 2.0 Hz, 1H), 7.67 (d, *J*=1.6 Hz, 1H), 7.37 (q, *J*=4.0 Hz, 1H), 6.39～6.37 (m, 1H), 2.85～2.80 (m, 2H), 2.63～2.57 (m, 2H), 2.12～2.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.8, 147.8, 141.9, 136.3, 135.1, 129.2, 128.6, 128.5, 128.1, 123.7, 121.4, 33.7, 33.3, 23.5. HRMS (ESI) calcd for $C_{14}H_{14}N$ $[M+H]^+$ 196.1126, found 196.1130.

1-(3,5-Dimethylphenyl)cyclopentene (**2f**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (s, 2H), 6.88 (s, 1H), 6.16～6.15 (m, 1H), 2.73～2.68 (m, 2H), 2.55～2.51 (m, 2H), 2.32 (s, 6H), 2.06～1.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.7, 137.8, 136.9, 128.7, 125.9, 123.6, 33.4, 23.5, 21.5; GC-MS (EI) *m/z*: 172.1.

1-(*p*-Ethylphenyl)cyclopentene (**2g**):[15a] The product was isolated by flash chromatography (hexanes) as colorless oil. 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J*=8.0 Hz, 2H), 7.15 (d, *J*=8.0 Hz, 2H), 6.15～6.13 (m, 1H), 2.73～2.68 (m, 2H), 2.64 (q, *J*=8.0 Hz, 2H), 2.55～2.50 (m, 2H), 2.06～1.98 (m, 2H), 1.24 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.1, 142.4, 134.5, 127.9, 125.7, 125.3, 33.5, 33.4, 28.7, 23.5, 15.8; GC-MS (EI) *m/z*: 172.1.

1-(*p*-*t*-Butylphenyl)cyclopentene (**2h**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.39～7.38 (m, 2H), 7.35～7.33 (m, 2H), 6.15～6.13 (m, 1H), 2.72～2.68 (m, 2H), 2.54～2.50 (m, 2H), 2.03～1.98 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.9, 142.4, 134.2, 125.42, 125.40, 125.3, 34.6, 33.5, 33.4, 31.5, 23.6; GC-MS (EI) *m/z*: 200.1.

1-(*p*-Methoxyphenyl)cyclopentene (**2i**):[15a] The product was isolated by flash chromatography (Et_2O/petroleum ether, *V*/*V*=1/80) as colorless oil. 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40～7.36 (m, 2H), 6.87～6.84 (m, 2H), 6.06～6.04 (m, 1H), 3.81 (s, 3H), 2.71～2.66 (m, 2H), 2.54～2.49 (m, 2H), 2.05～1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.8, 142.0, 129.9, 126.9, 124.1, 113.8, 55.4, 33.5, 33.4, 23.5; GC-MS (EI) *m/z*: 174.0.

N,*N*-Dimethyl 1-(*m*-aminophenyl)cyclopentene (**2j**): The product was isolated by flash chromatography (EtOAc/petroleum ether, *V*/*V*=1/50) as colorless oil. 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (t, *J*=8.0 Hz, 1H), 6.86～6.82 (m, 2H), 6.65 (dd, *J*=8.2, 2.4 Hz, 1H), 6.16～6.15 (m, 1H), 2.96 (s, 6H), 2.74～2.71 (m, 2H), 2.54～2.50 (m, 2H), 2.04～2.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 150.9, 143.4, 137.9, 129.0, 125.9, 114.8, 111.9, 110.3, 40.9, 33.6, 33.5, 23.6; GC-MS (EI) *m/z*: 187.2. HRMS (ESI) calcd for $C_{13}H_{18}N$ $[M+H]^+$ 188.1439, found 188.1436.

1-(Cyclopent-1-en-1-yl-4-(2-methoxyethyl)benzene (**2k**): The product was isolated by flash chromatography (hexanes) as colorless oil. 53% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.37 (d, *J*=8.4 Hz, 2H), 7.17 (d, *J*=7.8 Hz, 2H), 6.15～6.13 (m, 1H), 3.59 (t, *J*=7.2 Hz, 2H), 3.35 (s, 3H), 2.88 (t, *J*=7.2 Hz, 2H), 2.70～2.67 (m, 2H), 2.53～2.50 (m, 2H), 2.03～1.98 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.3, 137.6, 135.0, 128.9, 125.7, 125.6, 73.8, 58.8, 36.1, 33.5, 33.3, 23.5; GC-MS (EI) *m/z*: 202.1. HRMS (ESI): calcd for $C_{14}H_{19}O$ $[M+H]^+$203.1436, found 203.1440.

1-(*m*-Fluorophenyl)cyclopentene (**2l**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28～7.23 (m, 1H), 7.21～7.19 (m, 1H), 7.12～7.09 (m, 1H), 6.92～6.88 (m, 1H), 6.21～6.20 (m, 1H), 2.70～2.66 (m, 2H), 2.55～2.51 (m, 2H), 2.05～2.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.2 (d, J_{C-F}=245.4 Hz), 141.7 (d, J_{C-F}=2.0 Hz), 139.3 (d, J_{C-F}=8.1 Hz), 129.7 (d, J_{C-F}=8.1 Hz), 127.8, 121.4 (d, J_{C-F}=3.0 Hz), 113.6 (d, J_{C-F}=21.2 Hz), 112.4 (d, J_{C-F}=22.2 Hz), 33.5, 33.3, 23.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −114.0; GC-MS (EI) *m/z*: 162.0.

1-(*p*-Trifluoromethylphenyl)cyclopentene (**2m**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J*=8.0 Hz, 2H), 7.52 (d, *J*=8.0 Hz, 2H), 6.31～6.30 (m, 1H), 2.75～2.69 (m, 2H), 2.58～2.54 (m, 2H), 2.09～2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.6, 140.4 (q, J_{C-F}=1.0 Hz), 129.1, 128.7 (q, J_{C-F}=32.3 Hz), 125.8, 125.3 (q, J_{C-F}=4.0 Hz), 124.7 (q, J_{C-F}=272.7 Hz), 33.6, 33.2, 23.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.4; GC-MS (EI) *m/z*: 212.0.

1-(*p*-Ethoxycarbonylphenyl)cyclopentene (**2n**):[15a] The product was isolated by flash chromatography (EtOAc/ petroleum ether, *V*/*V*=1/20) as colorless oil. 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J*=8.4 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 2H), 6.34～6.32 (m, 1H), 4.37 (q, *J*=7.2 Hz, 2H), 2.75～2.70 (m, 2H), 2.58～2.53 (m, 2H), 2.08～2.00 (m, 2H), 1.39 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.7, 142.0, 141.3, 129.8, 129.3, 128.7, 125.5, 61.0, 33.8, 33.2, 23.4, 14.5; GC-MS (EI) *m/z*: 216.2.

4-(Cyclopent-1-en-1-yl)-1,1'-biphenyl (**2o**): The product was isolated by flash chromatography (petroleum ether) as colorless oil. 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.61 (d, *J*=7.8 Hz, 2H), 7.56 (d, *J*=8.4 Hz, 2H), 7.52 (d, *J*=8.4 Hz, 2H), 7.44 (t, *J*=7.8 Hz, 2H), 7.34 (t, *J*=7.2 Hz, 1H), 6.25～6.23 (m, 1H), 2.76～2.73 (m, 2H), 2.57～2.54 (m, 2H), 2.07～2.02 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.2, 141.0, 139.6, 136.0, 128.9, 127.3, 127.1,

127.1, 126.5, 126.1, 33.6, 33.3, 23.5; GC-MS (EI) *m/z*: 220.1. HRMS (ESI) calcd for $C_{17}H_{17}$ $[M+H]^+$ 221.1330, found 221.1324.

1-(2-Naphthyl)cyclohexene (**2p**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82～7.77 (m, 4H), 7.62 (dd, J=8.0, 1.6 Hz, 1H), 7.47～7.41 (m, 2H), 6.32～6.30 (m, 1H), 2.57～2.54 (m, 2H), 2.30～2.27 (m, 2H), 1.88～1.84 (m, 2H), 1.75～1.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.0, 136.6, 133.8, 132.6, 128.2, 127.7, 127.6, 126.1, 125.7, 125.5, 124.0, 123.3, 27.6, 26.2, 23.3, 22.4; GC-MS (EI) *m/z*: 208.2.

1-(2-Naphthyl)cycloheptene (**2q**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82～7.73 (m, 4H), 7.52 (dd, J=12.0, 4.0 Hz, 1H), 7.47～7.39 (m, 2H), 6.27 (t, J=8.0 Hz, 1H), 2.74～2.71 (m, 2H), 2.38～2.32 (m, 2H), 1.91～1.85 (m, 2H), 1.74～1.69 (m, 2H), 1.64～1.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.1, 142.4, 133.7, 132.4, 131.2, 128.1, 127.7, 127.6, 126.1, 125.4, 125.0, 123.9, 32.93, 32.88, 29.2, 27.1, 27.0; GC-MS (EI) *m/z*: 222.1.

2-(Cyclooct-1-en-1-yl)naphthalene (**2r**): The product was isolated by flash chromatography (petroleum ether) as colorless oil. 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82～7.76 (m, 4H), 7.62 (d, J=8.4 Hz, 1H), 7.46～7.40 (m, 2H), 6.20～6.19 (t, J=8.4 Hz, 1H), 2.76～2.74 (m, 2H), 2.38～2.34 (m, 2H), 1.71～1.63 (m, 4H), 1.59～1.57 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 140.4, 140.2, 133.7, 132.5, 128.8, 128.1, 127.8, 127.6, 126.1, 125.5, 124.7, 124.1, 30.2, 29.6, 28.4, 27.7, 27.1, 26.3; GC-MS (EI) *m/z*: 236.2. HRMS (ESI) calcd for $C_{18}H_{21}$ $[M+H]^+$ 237.1643, found 237.1640.

4.3 Procedure for Heck reaction of aryl sulfamates with cycloalkenes

A typical procedure: In a nitrogen-filled glove box, $NiBr_2$•DME (6.2 mg, 0.02 mmol, 10 mol%), PhBPE (12.2 mg, 0.024 mmol, 12 mol%), Zn dust (26.4 mg, 0.4 mmol, 2 equiv) and DMF (1.0 mL) were added to a 10-mL reaction tube. After stirring at room temperature for 15 min, aryl sulfamates (0.2 mmol, 1 equiv.), cycloalkenes (0.6 mmol, 3 equiv) were added. The reaction mixture was stirred at 100 °C for 48 h. The reaction mixture was cooled to room temperature and then extracted with Et_2O. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph on directly.

1-Phenylcyclopentene (**4a**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J=8.0 Hz, 2H), 7.31～7.28 (m, 2H), 7.22～7.17 (m, 1H), 6.18～6.17 (m, 1H), 2.72～2.68 (m, 2H), 2.54～2.50 (m, 2H), 2.05～1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.6, 137.0, 128.4, 126.9, 126.2, 125.7, 33.5, 33.3, 23.5; GC-MS (EI) *m/z*: 144.2.

1-(*p*-Methylphenyl)cyclopentene (**4b**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 6.14～6.13 (m, 1H), 2.74～2.68 (m, 2H), 2.56～2.49 (m, 2H), 2.35 (s, 3H), 2.07～1.98 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.4, 136.6, 134.2, 129.1, 125.6, 125.2, 33.44, 33.37, 23.5, 21.3; GC-MS (EI) *m/z*: 158.0.

1-(2,5-Dimethylphenyl)cyclopentene (**4c**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (d, J=8.0 Hz, 1H), 7.03 (s, 1H), 6.98 (d, J=8.0 Hz, 1H), 5.78～5.75 (m, 1H), 2.70-2.65 (m, 2H), 2.56-2.50 (m, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 2.04-1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.6, 138.2, 135.0, 132.4, 130.5, 129.2, 128.8, 127.4, 36.8, 33.7, 23.9, 21.1, 20.8; GC-MS (EI) *m/z*: 172.1.

1-(*m*-Methoxyphenyl)cyclopentene (**4d**):[15a] The product was isolated by flash chromatography (Et_2O/petroleum ether, V/V=1/80) as colorless oil. 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (t, J=8.0 Hz, 1H), 7.04 (d, J=7.6 Hz, 1H), 6.98～6.97 (m, 1H), 6.77 (dd, J=5.6, 2.4 Hz, 1H), 6.19～6.17 (m, 1H), 3.81 (s, 3H), 2.72～2.67 (m, 2H), 2.55～2.49 (m, 2H), 2.05-1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.7, 142.5, 138.4, 129.3, 126.7, 118.4, 112.3, 111.5, 55.3, 33.5, 33.4, 23.5; GC-MS (EI) *m/z*: 174.2.

1-(*p*-Fluorophenyl)cyclopentene (**4e**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.35 (m, 2H), 6.98～6.94 (m, 2H), 6.08～6.06 (m, 1H), 2.67～2.63 (m, 2H), 2.51～2.47 (m, 2H), 2.02～1.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.0 (d, J_{C-F}=246.4 Hz), 141.5, 133.2 (d, J_{C-F}=4.0 Hz), 127.2 (d, J_{C-F}=8.0 Hz), 125.9 (d, J_{C-F}=2.0 Hz), 115.2 (d, J_{C-F}=19.2 Hz), 33.53, 33.50, 23.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −115.8; GC-MS (EI) *m/z*: 162.0.

1-(*m*-Trifluoromethylphenyl)cyclopentene (**4f**):[15a] The product was isolated by flash chromatography (petroleum ether) as colorless oil. 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (m, 1H), 7.61 (d, J=8.0 Hz, 1H), 7.48～7.40 (m, 2H), 6.29～6.27 (m, 1H), 2.75～2.71 (m, 2H), 2.59～2.55 (m, 2H), 2.10～2.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.5, 137.7, 130.9 (q, J_{C-F}=31.3 Hz), 128.83 (q, J_{C-F}=1.0 Hz), 128.81, 128.3, 124.4 (q, J_{C-F}=272.7 Hz), 123.5 (q, J_{C-F}=4.0 Hz), 122.4 (q, J_{C-F}=4.0 Hz), 33.6, 33.3, 23.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −62.7; GC-MS (EI) *m/z*: 212.2.

Supporting Information The condition optimization and the ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of all products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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