有机化学 DOI: 10.6023/cjoc202203011 研究论文
Chinese Journal of Organic Chemistry ARTICLE

铑催化羧酸原位生成酰氟的脱羰 Suzuki-Miyaura 偶联

刘晓洁[a,b] 徐必平*[,b] 苏伟平*[,a,b]
([a]福州大学化学学院 福建福州 350108)
([b]中国科学院福建物质结构研究所 结构化学国家重点实验室 福建福州 350002)

摘要 联芳基类化合物是非常重要的有机结构, 并且它们广泛存在于药物、功能材料以及天然产物之中. 通过新颖而又独特的反应性, 脱羰反应绕过了脱羧反应, 在芳(杂环)羧酸必须有特定取代基的限制, 逐渐成为羧酸衍生物向联芳基类化合物转化合成中难以忽视的一类方法. 发展了一例铑催化羧酸原位生成酰氟的脱羰 Suzuki-Miyaura 偶联反应, 该方法对芳基羧酸和硼酸有很好的官能团兼容性, 甚至可以用来合成传统方法难以获得的天然产物和修饰药物.
关键词 铑催化; 脱羰交叉偶联; 原位生成; 酰氟

Rhodium-Catalyzed Decarbonylative Suzuki-Miyaura Cross-Coupling via *in-Situ* Generation of Acyl Fluorides from Carboxylic Acids

Liu, Xiaojie[a,b] Xu, Biping*[,b] Su, Weiping*[,a,b]
([a] *College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108*)
([b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002*)

Abstract The biaryl frameworks are momentous organic backbones that are commonly occurred in pharmaceutical, functional materials and natural products. By virtue of the distinctive reactivity through state-of-the-art process, decarbonylative couplings, which have bypassed the restriction to specifically substituted (hetero)aryl carboxylic acids of decarboxylative couplings, gradually become unneglected methods in the conversion of carboxylic acid derivatives. Herein, a rhodium-catalyzed decarbonylative Suzuki-Miyaura cross-coupling via *in-situ* generation strategy of acyl fluorides from carboxylic acids was developed. This protocol shows eminent functional group tolerance with arrays of combinations between carboxylic acid and boronic acid. Furthermore, the reaction offers a new access to those conventionally unattainable biaryl motifs, including natural product and modified drugs.
Keywords rhodium catalysis; decarbonylative cross-coupling; *in-situ* generation; acyl fluorides

1 Introduction

Carboxylic acids are ubiquitous scaffolds that are frequently exploited in organic synthesis. Moreover, their easy manipulation, commercial availability and air stability make them the ideal raw materials for cross-coupling reactions in organic synthesis.[1] Despite tremendous achievements have been made in utilizing carboxylic acids as coupling partners,[2] developing facile and efficient methods to introduce valuable moieties into targeted molecules from inexpensive and readily available carboxylic acids are still highly desirable. In the past few decades, decarbonylative reaction (Figure1a), in which the C—C bond cleaved adjacent to the carbonyl group followed by CO extrusion, has emerged as one of the most attractive approaches where the carboxylic acids were integrated into complex molecules.[3]

However, straightforward decarbonylation from carboxylic acids is challenging because the C(acyl)—O bond in acid is strengthened through the p-π conjugation between the oxygen atom in the hydroxyl group and the carbonyl group. The key is to search the matching low-valent transitional metal catalyst to realize oxidative addition to C(acyl)—X bonds (X=heteroatom) in the activated car-

* Corresponding authors. E-mail: wpsu@fjirsm.ac.cn; xubiping@fjirsm.ac.cn
Received March 3, 2022; revised April 2, 2022; published online April 8, 2022.
Project supported by the National Key Research and Development Program of China (No. 2018FYA0704502), the National Natural Science Foundation of China (Nos. 21931011, 22071241) and the Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (No. 2021ZZ105).
国家重点研发计划(No. 2018FYA0704502)、国家自然科学基金(Nos. 21931011, 22071241)和中国福建光电信息科学与技术创新实验室(闽都创新实验室)(No. 2021ZZ105)资助项目.

boxylic acid. In 1966, it is the first time observed by Tsuji[4] that acid chloride could undergo oxidative addition with chlorotris(triphenylphosphine)rhodium (Wilkinson's catalyst), and afterwards the C(O)-Rh-Cl complex efficiently decarbonylated leading to the corresponding olefins, alkyl or aryl chloride (Figure 1a). Inspired by this pioneering work, acid anhydride[4] and acid chlorides[6] were successively reported to be competent substrates in catalytic decarbonylative coupling reaction in 1969 and 1977, respectively. Because aforementioned activated carboxylic acids are inconveniently to isolate, store and use, as well as easy decomposed by the nucleophilic reagents or moisture, great efforts were soon devoted to developing *in-situ* activation and decarbonylation of carboxylic acid. And the *in-situ* activation strategies through acid anhydrides and acid chlorides were expanded by Gooßen[7] and Nishihara[8]. The decarbonylative coupling of acyl fluorides remains undiscovered until recently in 2018, Schoenebeck group[9] demonstrated that the acyl fluoride was speculated as the suitable precursor for palladium catalyzed decarbonylative trifluoromethylation. Later in the same year, Sanford[10] and Nishihara[11] group also succeeded in nickel catalyzed decarbonylative Suzuki-Miyaura coupling and borylation of carboxylic acyl fluorides. Both of them managed to advert the lengthy preparatory steps in a few examples through the two-step-one-pot's pre-stirring with the fluorinating reagent.

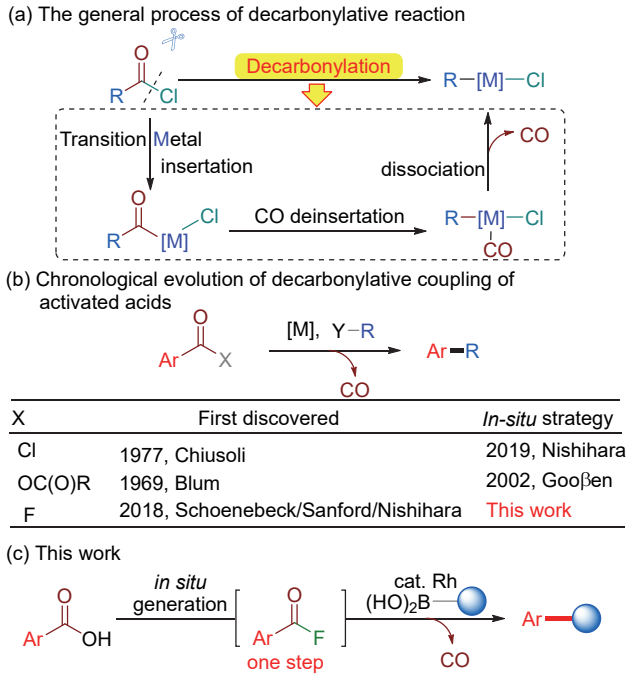


Figure 1 Overview of transition metal mediated decarbonylative coupling reactions

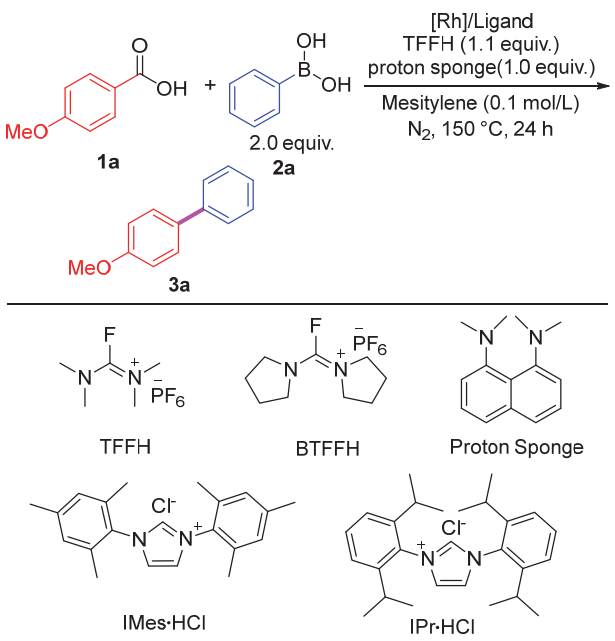
As part of our continuing effort on activation and decarbonylation of carboxylic acid in 2021,[12] we are curious about conceiving novel cross-coupling reactions employing the carboxylic acids. Owing to the appropriate balance between stability and reactivity from moderate electrophilicity of acyl fluorides, they are presumed to be ideal solutions to activate the carbonyl group from acid that was employed in orthogonal transition metal catalyzed reactions.[13] Suzuki-Miyaura coupling, a renowned and robust method to connect carbon-carbon bond for assembling complicated molecules, has recently became hot-topic issue that fascinated numerous chemists.[14] To the best of our knowledge, there is no document describing the rhodium catalyzed decarbonylative Suzuki-Miyaura cross-coupling via *in-situ* generation of acyl fluorides from carboxylic acids, which stimulated us to actualize this envision.

2 Results and discussion

To validate this hypothesis, we initiated the investigation with anisic acid (**1a**) (0.20 mmol) and phenylboronic acid (**2a**) (0.40 mmol) by using rhodium complex as the catalyst. In light of the fact that low-valent rhodium salts exert high capacity of oxidative insertion of C(O)—X bonds (X = heteroatom) in carboxylic acid derivatives, various rhodium complexes with different ligands and counter ions were tested (Entries 1～4), and $[Rh(COD)Cl]_2$ showed best efficiency. Concerns were then turned to find the apt ligand that compromises the demands for oxidative addition of low-valent rhodium as well as reductive elimination of high-valent rhodium. Among the intensive efforts on screening the ligand (Entries 5～14), $P(C_6F_5)_3$ is superior to any other ligands, including N-heterocyclic carbene and diphosphine ligands. The proportion of ligand was also surveyed and the molar ratio 1∶2 (catalyst∶ligand) gives out the best result (Entries 15, 16). According to the literature, BTFFH and K_3PO_4 were powerful fluorinating reagent and base in decarbonylation of acyl fluorides, which exhibited inferior efficiency in this reaction (Entries 17, 18). After extensively and systematically screening of the reaction parameter, the optimized condition for decarbonylative Suzuki-Miyaura biaryl synthesis was finally determined. The reaction proceeded well when using $[Rh(COD)Cl]_2$ as catalyst, $P(C_6F_5)_3$ as the ligand, TFFH (fluoro-*N*,*N*,*N*′,*N*′-tetramethylformamidinium hexafluorophosphate) as the fluorinating reagent, proton sponge as the base under 150 ℃ in mesitylene (0.1 mol/L).

With the optimized reaction conditions established, the scope and generality of decarbonylative Suzuki-Miyaura cross-coupling was explored to verify the reliability of this protocol (Table 2). Undoubtedly, the hydrocarbon substituted aryl carboxylic acid (**3b**～**3f**) went smoothly with phenylboronic acid, including fused polycyclic aromatic scaffolds (**3e**, **3f**). In view of the literature that, the aromatic ether and ester moieties, which are potentially suffered from C—O cleavage under transition metal catalysis,[15] could survive from the reaction with moderate to good yields (**3g**～**3j**). Various polar or coordinative functional groups, such as trifluoromethyl (**3k**), chloro (**3l**), cyano (**3m**) and nitro (**3n**), were well tolerated under the optimized conditions. Moreover, the convertible olefin and

Table 1 Optimization of reaction conditions[a]



Entry	Catalyst (5 mol%)	Ligand	Yield[b]/%
1	$Rh(PPh)_3Cl$	—	32
2	$[Rh(OAc)_2]_2$	—	Trace
3	$[Rh(C_2H_4)_2Cl]_2$	—	7
4	$[Rh(COD)Cl]_2$	—	39
5	$[Rh(COD)Cl]_2$	IMes•HCl (20 mol%)	11
6	$[Rh(COD)Cl]_2$	IPr•HCl (20 mol%)	9
7	$[Rh(COD)Cl]_2$	DPPM (10 mol%)	13
8	$[Rh(COD)Cl]_2$	DPPE (10 mol%)	26
9	$[Rh(COD)Cl]_2$	DPPF (10 mol%)	7
10	$[Rh(COD)Cl]_2$	PPh_3 (20 mol%)	42
11	$[Rh(COD)Cl]_2$	$P(2\text{-furyl})_3$ (20 mol%)	21
12	$[Rh(COD)Cl]_2$	$P(4\text{-}MeOC_6H_5)_3$ (20 mol%)	11
13	$[Rh(COD)Cl]_2$	$P(4\text{-}CF_3C_6H_5)_3$ (20 mol%)	51
14	$[Rh(COD)Cl]_2$	$P(C_6F_5)_3$ (20 mol%)	87 (81)
15[c]	$[Rh(COD)Cl]_2$	$P(C_6F_5)_3$ (20 mol%)	51
16[d]	$[Rh(COD)Cl]_2$	$P(C_6F_5)_3$ (20 mol%)	67
17[e]	$[Rh(COD)Cl]_2$	$P(C_6F_5)_3$ (20 mol%)	84
18[f]	$[Rh(COD)Cl]_2$	$P(C_6F_5)_3$ (20 mol%)	53

[a] The reaction was carried out on the 0.2 mmol scale; [b] Yields were determined by GC analysis using dodecane as an internal standard, and isolated yield is listed in parentheses; [c] 10 mol% $P(C_6F_5)_3$ instead of 20 mol%; [d] 30 mol% $P(C_6F_5)_3$ instead of 20 mol%; [e] BTFFH instead of TFFH. [f] K_3PO_4 instead of proton sponge.

pinacolborane functionality are also endurable in good yield, which provides probability for further modification (Heck reaction and Suzuki-Miyaura reaction. A series of heterocyclic carboxylic acids (**3q**～**3x**) were testified to be competent substrates regardless of the substituted positions, for example benzofuran (**3r**, **3s**) and benzothiophene (**3u**, **3v**). Traditional heterocyclic cores are constructed through multi-step cascade annulative process,[16] however, in this reaction the similar structures are straightforwardly accessed by the combination of 3-quinolinecarboxylic acid and phenyl boronic acid (**3x**). Apart from aryl carboxylic acid, the scope of phenylboronic acid was evaluated with an array of functional groups as well. phenylboronic acids bearing methyl (**4a**), fluoro (**4b**), chloro (**4c**, **4d**) and ester (**4e**), were efficiently used as coupling partner for the biaryl synthesis.

On account of the fact that the cross-coupling reaction ran successfully with simple substituent groups on either reactant, we decide to tack several more challenging but attractive substrates with diverse and concentrated functional groups. The marketed drugs, probenecid (**5a**), adapalene (**5b**) and febuxostat (**5c**), furnished the reaction with satisfactory yield. Considering chromocarb possessing a C(sp^2)-COOH on the 3-position, we reckoned the feasibility that the chromone motif was incorporated into the natural skeleton flavone. Fortunately, the expected natural product flavone (**5d**) was afforded effortlessly with chromocarb in 65% yield, which proved the prominent versatilities and utilities of this method.

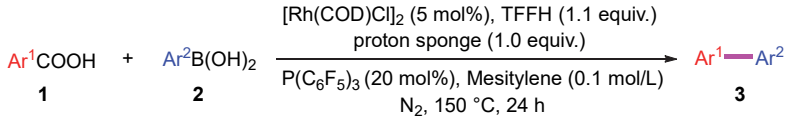
To further explicate the possible reaction intermediate and mechanism, several necessary control experiments were conducted afterwards. The suspected possible intermediate acyl fluoride was detected in 84% yield when **1d** was mixed with fluorinating reagent and base for 4 h, and a comparable yield (72%) of **3d** was isolated through this one-pot two-step strategy (Figure 2A). Then, instead of aryl carboxylic acid, acyl fluoride was directly used under standard condition in the absence of fluorinating reagent, and **3d** was isolated with 68% yield, which corroborates that the inference acyl fluoride is the intermediate (Figure 2B).

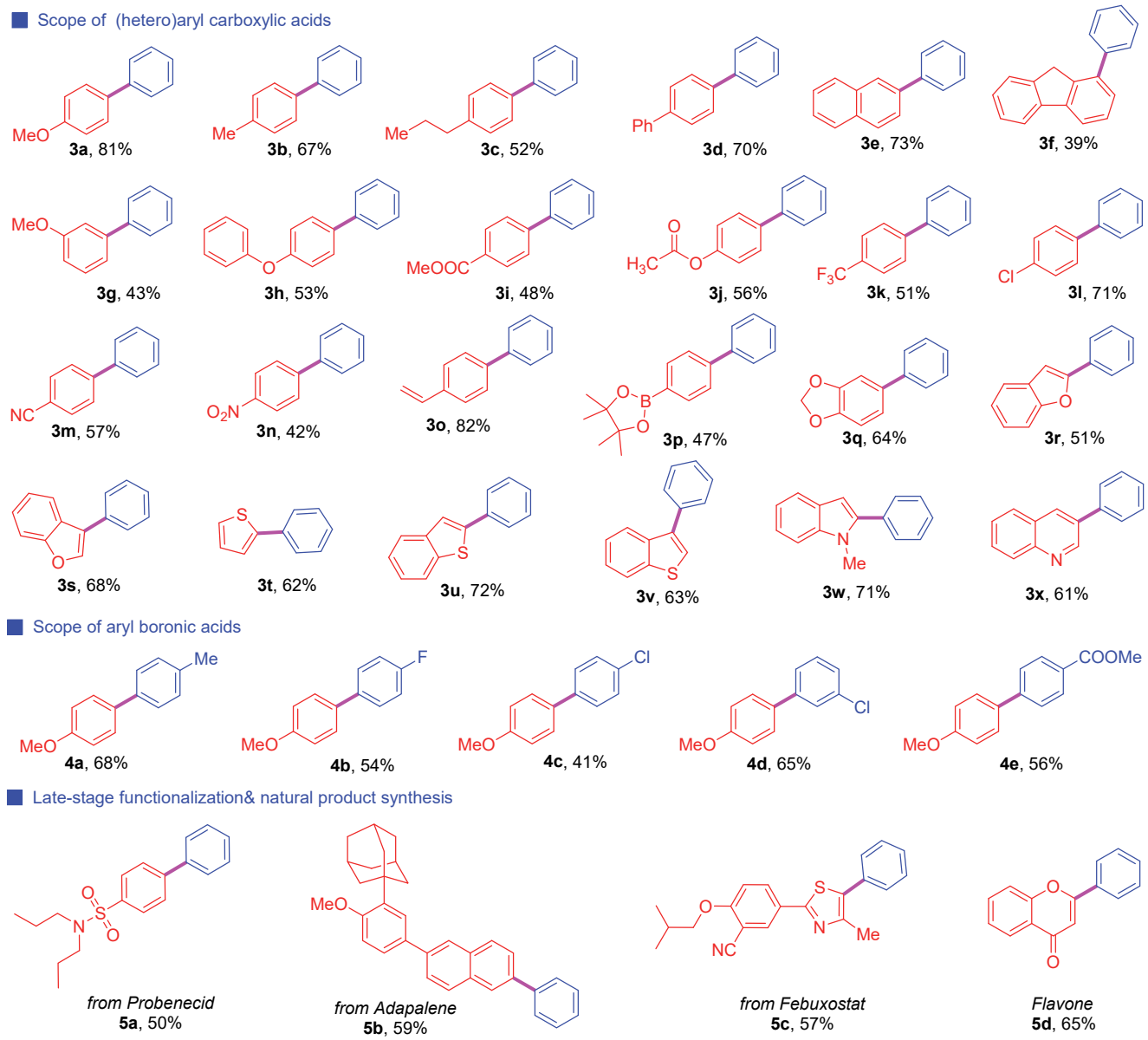
Based on experimental results and previous research,[10,12a] a plausible mechanism was proposed as illustrated in Figure 2. Firstly, the carboxylic acid was *in-situ* converted into the acyl fluoride via nuclephilic deoxygenative fluorination with the aid of TFFH and proton sponge. The catalytic active rhodium complex, formed in the presence of $P(C_6F_5)_3$, subsequently breaks the C(acyl)—F bond through the oxidative addition (**A**). After that, the obtained Ar-C(O)-Rh^{III}-F occurred CO deinsertation giving out the CO coordinated intermediate **B**. Upon extrusion of CO, the phenylboronic acid thereafter coordinates with the generated transmetallation-active Ar-Rh^{III}-F species affording the intermediate **C**. Finally, the desired biaryl product was furnished through the reductive elimination of intermediate **D** after the transmetallation, and the released Rh^{I} catalyst returned to catalytic cycle.

3 Conclusions

In conclusion, a general rhodium-catalyzed decarbonylative Suzuki-Miyaura cross-coupling between aryl carboxylic acid and boronic acid was developed via *in-situ* generation of acyl fluoride strategy. This transformation bears a broad range of scope with high selectivity and good functional group compatibility, including pharmaceutical late-stage functionalizations and natural product synthesis, thus

Table 2 Substrate scopes of aryl carboxylic and boronic acid





providing an alternative access to diversified biaryl synthesis from readily available carboxylic acids and boronic acids.

4 Experimental section

4.1 General information

All reactions were conducted under an atmosphere of nitrogen with dry solvents. Unless otherwise noted, the chemical reagents were purchased from commercial supplies (Accela, Acros Organics, Adamas-beta®, Alfa Aesar, Aladdin, Bide pharmatech, Energy Chemical, TCI Chemicals, Innochem, J&K Chemicals, Laajoo, Leyan, Sigma-Aldrich, Sinocompound and 3A Chemicals) and used directly without further purification. Mesitylene was distilled from metal Na and stored under nitrogen atmosphere. GC-MS data were recorded on Agilent 7820A. Flash chromatography was performed with Sepaflash columns produced by Santai Technologies. NMR spectra were recorded on a Bruker AVANCE 400 or JEOL ECZ400S 400M spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 101 MHz, ^{19}F NMR: 376 MHz) using $CDCl_3$ as solutions. The chemical shift δ was calibrated using tetramethylsilane (TMS, δ 0) for ^{1}H NMR and residual undeuterated solvent ($CDCl_3$,

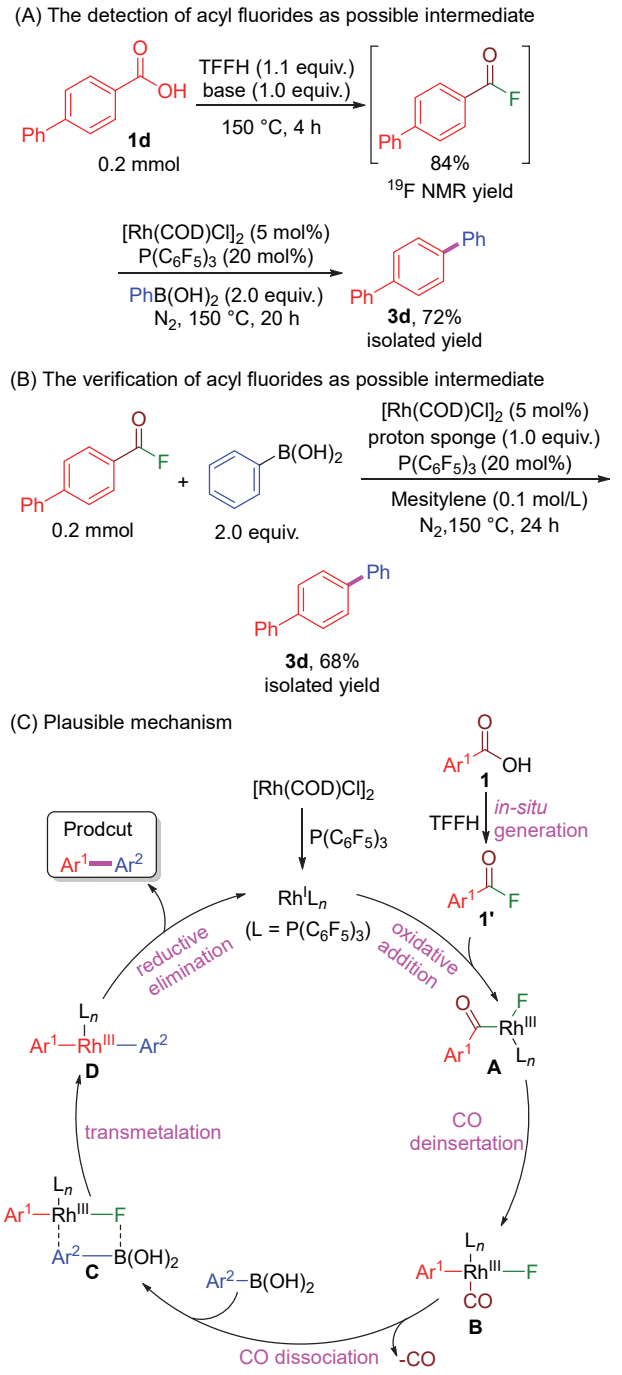


Figure 2 Control experiments and plausible reaction mechanism

δ 77.0) for ^{13}C NMR. HRMS (High resolution mass spectra) were performed by the Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences (Instrument Themo Scientific Q Exactive HF Orbitrap-FTMS, Operated Mode: ESI Positive Ion Mode.).

4.2 General procedures synthesis of compounds 3a～5d

In a nitrogen-filled glovebox, a 35 mL pressure tube equipped with a stir bar was charged with 4-methoxybenzoic acid (30.5 mg, 0.20 mmol), phenylboronic acid (48.8 mg, 0.40 mmol), proton sponge (42.7 mg, 0.20 mmol), fluoro-*N*,*N*,*N*′,*N*′-tetramethylformamidinium hexafluorophosphate (TFFH) (58.1 mg, 0.22 mmol), chloro(1,5-cyclooctadiene)rhodium (I) dimer ((Rh[COD]Cl)$_2$) (5.0 mg, 0.01 mmol) and tris(pentafluorophenyl)phosphine (P(C$_6$F$_5$)$_3$) (21.3 mg, 0.04 mmol), then mesitylene (2.0 mL) was added to the pressure tube via syringe. Later, the reaction mixture was stirred at 150 ℃ for 24 h. After the reaction finished, the mixture was filtered through a short plug of silica gel and washed with 10 mL of ethyl acetate. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel using hexane/ethyl acetate (*V*∶*V*=50∶1) to give compound **3a** as white solid (29.8 mg, 81% yield).

The synthetic procedures of compounds **3b～5d** are the same as that of **3a**.

4-Methoxy-1,1'-biphenyl (**3a**):[17] White solid, 29.8 mg, 81% yield. m.p. 82.1～82.8 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.57～7.51 (m, 4H), 7.44～7.40 (m, 2H), 7.32～7.28 (m, 1H), 6.98 (d, *J*=8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Methyl-1,1'-biphenyl (**3b**):[17] White solid, 22.5 mg, 67% yield. m.p. 43.9～44.3 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.58 (d, *J*=7.1 Hz, 2H), 7.49 (d, *J*=8.1 Hz, 2H), 7.42 (t, *J*=7.6 Hz, 2H), 7.32 (t, *J*=7.4 Hz, 1H), 7.25 (d, *J*=7.9 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 127.0, 21.1.

4-Propyl-1,1'-biphenyl (**3c**):[18] Colorless oil, 22.5 mg, 52% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.54 (d, *J*=7.3 Hz, 2H), 7.47 (d, *J*=8.2 Hz, 2H), 7.38～7.34 (m, 2H), 7.27～7.24 (m, 1H), 7.19 (d, *J*=8.1 Hz, 2H), 2.60～2.56 (m, 2H), 1.69～1.59 (m, 2H), 0.94 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 141.7, 141.1, 138.5, 128.8, 128.6, 126.9, 126.9, 126.9, 37.7, 24.5, 13.9.

1,1':4',1"-Terphenyl (**3d**):[19] White solid, 32.2 mg, 70% yield. m.p. 205.1～205.8 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.68 (m, 4H), 7.66～7.63 (m, 4H), 7.48～7.44 (m, 4H), 7.38～7.34 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.

2-Phenylnaphthalene (**3e**):[17] White solid, 29.8 mg, 73% yield. m.p. 96.6～97.5 ℃; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.03 (s, 1H), 7.90～7.83 (m, 3H), 7.74～7.70 (m, 3H), 7.50～7.45 (m, 4H), 7.38～7.34 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 141.0, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.2, 125.9, 125.8, 125.5.

1-Phenyl-9*H*-fluorene (**3f**):[20] Sticky oil, 18.9 mg, 39% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.80 (dd, *J*=10.7, 7.6 Hz, 2H), 7.55 (d, *J*=7.0 Hz, 2H), 7.50～7.44 (m, 4H), 7.40～7.36 (m, 2H), 7.32～7.27 (m, 2H), 3.95 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ: 143.2, 142.1, 141.5, 141.1, 140.9, 139.1, 128.5, 128.5, 127.4, 127.3, 127.2, 126.8, 126.7, 124.8, 120.0, 118.9, 36.8.

3-Methoxy-1,1'-biphenyl (**3g**):[14] Colorless oil, 15.8 mg, 43% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.58 (d, *J*=7.2 Hz, 2H), 7.43 (t, *J*=7.6 Hz, 2H), 7.37～7.33 (m, 2H), 7.18

(d, J=7.7 Hz, 1H), 7.12 (s, 1H), 6.89 (d, J=8.2, 2.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.9, 142.7, 141.1, 129.7, 128.7, 127.4, 127.2, 119.6, 112.9, 112.6, 55.2.

4-Phenoxy-1,1'-biphenyl (**3h**):[21] White solid, 26.1 mg, 53% yield. m.p. 65.9～66.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56～7.53 (m, 4H), 7.43～7.39 (m, 2H), 7.36～7.29 (m, 3H), 7.12～7.04 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.1, 156.8, 140.5, 136.2, 129.8, 128.8, 128.4, 127.0, 126.9, 123.4, 119.0, 119.0.

Methyl [1,1'-biphenyl]-4-carboxylate (**3i**):[17] White solid, 20.4 mg, 48% yield. m.p. 107.8～108.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12～8.09 (m, 2H), 7.67～7.64 (m, 2H), 7.63～7.61 (m, 2H), 7.49～7.44 (m, 2H), 7.41～7.37 (m, 1H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.0, 145.6, 140.0, 130.1, 128.9, 128.8, 128.1, 127.2, 127.0.

[1,1'-Biphenyl]-4-yl acetate (**3j**):[22] White solid, 23.8 mg, 56% yield. m.p. 80.8～81.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60～7.55 (m, 4H), 7.45～7.41 (m, 2H), 7.37～7.32 (m, 1H), 7.16 (d, J=8.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.6, 150.0, 140.3, 139.0, 128.8, 128.2, 127.3, 127.1, 121.8, 21.2.

4-(Trifluoromethyl)-1,1'-biphenyl (**3k**):[17] White solid, 22.7 mg, 51% yield. m.p. 62.4～63.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69～7.645 (m, 4H), 7.58 (d, J=7.9 Hz, 2H), 7.48～7.44 (m, 2H), 7.41～7.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.7, 139.7, 135.6, 132.7, 129.8, 129.5, 129.2, 129.0, 128.8, 128.7, 128.4, 128.2, 128.0, 127.4, 127.3, 127.2, 125.7, 125.7, 125.7, 125.6, 123.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.3.

4-Chloro-1,1'-biphenyl (**3l**):[17] White solid, 26.8 mg, 71% yield. m.p. 73.2～74.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J=7.3 Hz, 2H), 7.48 (d, J=8.5 Hz, 2H), 7.43～7.36 (m, 4H), 7.35～7.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.0, 139.6, 133.3, 128.9, 128.9, 128.4, 127.6, 127.0.

[1,1'-Biphenyl]-4-carbonitrile (**3m**):[17] White solid, 20.4 mg, 57% yield. m.p. 82.8～83.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74～7.72 (m, 2H), 7.68 (d, J=8.6 Hz, 2H), 7.60～7.57 (m, 2H), 7.51～7.46 (m, 2H), 7.45～7.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.6, 139.1, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9.

4-Nitro-1,1'-biphenyl (**3n**):[18] Light yellow solid, 16.7 mg, 42% yield. m.p. 109.9～110.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, J=8.8 Hz, 2H), 7.72 (d, J=8.8 Hz, 2H), 7.62 (d, J=6.9 Hz, 2H), 7.51～7.42 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.6, 147.0, 138.7, 129.1, 128.9, 127.7, 127.3, 124.0.

4-Vinyl-1,1'-biphenyl (**3o**):[22] White solid, 29.6 mg, 82% yield. m.p. 116.1～116.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60～7.55 (m, 4H), 7.48 (d, J=8.3 Hz, 2H), 7.45～7.41 (m, 2H), 7.35～7.31 (m, 1H), 6.75 (dd, J=17.6, 10.9 Hz, 1H), 5.79 (d, J=17.6 Hz, 1H), 5.27 (d, J=11.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.7, 140.6, 136.6, 136.4, 128.8, 127.3, 127.2, 127.0, 126.6, 113.9.

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**):[23] White soild, 26.3 mg, 47% yield. m.p. 109.1～109.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J=8.2 Hz, 2H), 7.61 (dd, J=8.1, 1.5 Hz, 4H), 7.45～7.41 (m, 2H), 7.37～7.32 (m, 1H), 1.36 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.9, 141.0, 135.2, 128.7, 127.5, 127.2, 126.4, 83.8, 24.9.

5-Phenylbenzo[*d*][1,3]dioxole (**3q**):[24] Colorless oil, 25.4 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, J=7.7 Hz, 2H), 7.39 (t, J=7.4 Hz, 2H), 7.30 (t, J=7.3 Hz, 1H), 7.05 (d, J=9.9 Hz, 2H), 6.87 (d, J=7.9 Hz, 1H), 5.97 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 148.1, 147.0, 140.9, 135.6, 128.7, 126.9, 126.9, 120.6, 108.5, 107.7, 101.1.

2-Phenylbenzofuran (**3r**):[25] White solid, 19.8 mg, 51% yield. m.p. 107.6～109.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J=8.0 Hz, 2H), 7.58 (d, J=7.6 Hz, 1H), 7.52 (d, J=8.0 Hz, 1H), 7.45 (t, J=7.7 Hz, 2H), 7.35 (t, J=7.3 Hz, 1H), 7.30～7.23 (m, 2H), 7.02 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.9, 154.8, 130.4, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.2, 101.3.

3-Phenylbenzofuran (**3s**):[26] Colorless oil, 26.4 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=7.3 Hz, 1H), 7.79 (s, 1H), 7.66～7.64 (m, 2H), 7.55 (d, J=7.7 Hz, 1H), 7.49～7.46 (m, 2H), 7.39～7.29 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.8, 141.3, 132.0, 128.9, 127.5, 127.4, 126.4, 124.5, 123.0, 122.2, 120.4, 111.7.

2-Phenylthiophene (**3t**):[14] White soild, 19.9 mg, 62% yield. m.p. 32.7～33.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J=1.4 Hz, 1H), 7.60 (d, J=1.0 Hz, 2H), 7.39～7.36 (m, 2H), 7.31 (dd, J=3.6, 1.1 Hz, 1H), 7.29～7.25 (m, 2H), 7.09～7.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.4, 134.4, 128.8, 128.0, 127.4, 126.0, 124.8, 123.0.

2-Phenylbenzo[*b*]thiophene (**3u**):[14] White solid, 30.3 mg, 72% yield. m.p. 162.6～164.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=7.7 Hz, 1H), 7.78 (d, J=7.4 Hz, 1H), 7.72 (d, J=7.5 Hz, 2H), 7.55 (s, 1H), 7.43 (t, J=7.6 Hz, 2H), 7.37～7.31 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.5, 141.0, 139.8, 134.6, 129.3, 128.6, 126.8, 124.8, 124.6, 123.9, 122.6, 119.8.

3-Phenylbenzo[*b*]thiophene (**3v**):[26] Colorless oil, 26.5 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94～7.90 (m, 2H), 7.60～7.58 (m, 2H), 7.51～7.47 (m, 2H), 7.42～7.38 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.7, 138.1, 137.9, 136.0, 128.7, 128.7, 127.5, 124.4, 124.3, 123.4, 122.9.

1-Methyl-2-phenyl-1*H*-indole (**3w**):[27] Brown solid, 29.4 mg, 71% yield. m.p. 92.3～93.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J=7.8 Hz, 1H), 7.51 (d, J=6.9 Hz, 2H), 7.46 (dd, J=8.2, 6.6 Hz, 3H), 7.44～7.33 (m, 2H), 7.24 (d, J=6.7 Hz, 1H), 7.14 (t, J=7.5 Hz, 1H), 6.57 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.5, 138.3, 132.8, 129.4, 128.5, 127.9, 127.8, 121.6, 120.4, 119.8, 109.6, 101.6, 31.2.

3-Phenylquinoline (**3x**):[28] Brown solid, 25.0 mg, 61% yield. m.p. 49.5～51.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ:

9.20 (s, 1H), 8.32 (s, 1H), 8.16 (d, J=8.4 Hz, 1H), 7.90 (d, J=8.0 Hz, 1H), 7.75～7.71 (m, 3H), 7.61～7.52 (m, 3H), 7.46～7.43 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.7, 147.1, 137.8, 133.8, 133.4, 129.5, 129.2, 129.1, 128.14, 128.0, 127.4, 127.1, 127.0.

4-Methoxy-4'-methyl-1,1'-biphenyl (**4a**):[28] White solid, 27.0 mg, 68% yield. m.p. 106.1～106.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51～7.43 (m, 4H), 7.21 (d, J=7.7 Hz, 2H), 6.95 (d, J=8.5 Hz, 2H), 3.82 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.6, 114.1, 55.3, 21.0.

4-Fluoro-4'-methoxy-1,1'-biphenyl (**4b**):[29] White solid, 21.8 mg, 54% yield. m.p. 87.0～87.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52～7.45 (m, 4H), 7.13～7.07 (m, 2H), 6.99～6.95 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.3, 160.8, 159.1, 137.0, 132.8, 128.2, 128.2, 128.0, 115.6, 115.4, 114.2, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −116.71.

4-Chloro-4'-methoxy-1,1'-biphenyl (**4c**):[30] White solid, 17.9 mg, 41% yield. m.p. 110.6～111.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.46 (m, 4H), 7.37 (d, J=7.4 Hz, 2H), 6.97 (d, J=7.7 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.3, 139.2, 132.6, 132.4, 128.8, 128.0, 127.9, 114.3, 55.3.

3-Chloro-4'-methoxy-1,1'-biphenyl (**4d**):[17] White solid, 28.4 mg, 65% yield. m.p. 110.3～111.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53～7.49 (m, 3H), 7.42 (d, J=6.8 Hz, 1H), 7.35～7.31 (m, 1H), 7.26 (d, J=8.4 Hz, 1H), 6.97 (d, J=8.5 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.5, 142.6, 134.6, 132.3, 129.9, 128.1, 126.8, 126.6, 124.8, 114.3, 55.3.

Methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate (**4e**):[17] White solid, 27.1 mg, 56% yield. m.p. 170.9～171.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, J=8.4 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H), 7.57 (d, J=8.8 Hz, 2H), 7.00 (d, J=8.8 Hz, 2H), 3.93 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.1, 159.8, 145.2, 132.4, 130.1, 128.3, 128.2, 126.4, 114.3, 55.4, 52.1.

N,*N*-Dipropyl-[1,1'-biphenyl]-4-sulfonamide (**5a**): White solid, 31.7 mg, 50% yield. m.p. 43.8～44.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H), 7.61 (d, J=7.2 Hz, 2H), 7.49～7.45 (m, 2H), 7.42～7.39 (m, 1H), 3.13～3.09 (m, 4H), 1.63～1.54 (m, 4H), 0.89 (t, J=7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 145.1, 139.4, 138.7, 129.1, 129.0, 128.4, 127.6, 127.3, 50.2, 22.1, 11.3; HRMS (ESI) calcd for $C_{18}H_{24}O_2NS$ $[M+H]^+$ 318.1522, found 318.1524.

(3*r*,5*r*,7*r*)-1-(2-Methoxy-5-(6-phenylnaphthalen-2-yl)-phenyl)adamantine (**5b**): White solid, 52.5 mg, 59% yield. m.p. 231.6～232.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J=16.9 Hz, 2H), 7.96～7.92 (m, 2H), 7.77～7.73 (m, 4H), 7.61 (d, J=2.0 Hz, 1H), 7.54 (dd, J=8.3, 1.9 Hz, 1H), 7.49 (t, J=7.6 Hz, 2H), 7.38 (t, J=7.3 Hz, 1H), 6.99 (d, J=8.4 Hz, 1H), 3.89 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.6, 141.1, 139.0, 138.9, 138.1, 133.1, 133.0, 132.4, 128.8, 128.5, 127.3, 127.3, 126.1, 125.9, 125.6, 125.5, 124.7, 112.0, 55.2, 40.6, 37.2 , 37.1, 29.1; HRMS (ESI) calcd for $C_{33}H_{33}O$ $[M+H]^+$ 445.2526, found 445.2534.

2-Isobutoxy-5-(4-methyl-5-phenylthiazol-2-yl)benzonitrile (**5c**): Brown solid, 39.7 mg, 57% yield. m.p. 112.3～113.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, J=2.2 Hz, 1H), 8.05 (dd, J=8.8, 2.2 Hz, 1H), 7.47～7.41 (m, 4H), 7.38～7.34 (m, 1H), 6.98 (d, J=8.9 Hz, 1H), 3.87 (d, J=6.5 Hz, 2H), 2.54 (s, 3H), 2.24～2.14 (m, 1H), 1.09 (d, J=6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.3, 161.7, 148.9, 132.4, 132.0, 131.8, 131.4, 129.1, 128.8, 128.0, 126.8, 115.8, 112.6, 102.7, 77.4, 28.2, 19.1, 16.3; HRMS (ESI) calcd for $C_{21}H_{21}ON_2S$ $[M+H]^+$ 349.1369, found 349.1372.

2-Phenyl-4*H*-chromen-4-one (**5d**):[31] White solid, 28.9 mg, 65% yield. m.p. 92.4～92.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (d, J=8.9 Hz, 1H), 7.92 (d, J=5.4 Hz, 2H), 7.70 (t, J=7.0 Hz, 1H), 7.54 (dd, J=16.2, 7.6 Hz, 4H), 7.42 (t, J=7.5 Hz, 1H), 6.83 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 178.4, 163.3, 156.2, 133.7, 131.7, 131.5, 129.0, 126.2, 125.6, 125.2, 123.9, 118.0, 107.5.

Supporting Information ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of new compounds **3a～5d**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] Rodriguez, N.; Goossen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030.

[2] (a) Goossen, L. J.; Rodriguez, N.; Goossen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100.
(b) Dzik, W. I.; Lange, P. P.; Gooßen, L. J. *Chem. Sci.* **2012**, *3*, 2671.
(c) Larrosa, I.; Cornella, J. *Synthesis* **2012**, *44*, 653.
(d) Fu, Z.; Li, Z.; Xiong, Q.; Cai, H. *Chin. J. Org. Chem.* **2015**, *35*, 984 (in Chinese).
(付拯江, 李兆杰, 熊起恒, 蔡琥, 有机化学, **2015**, *35*, 984.)
(e) Wei, Y.; Hu, P.; Zhang, M.; Su, W. *Chem. Rev.* **2017**, *117*, 8864;

[3] (a) Yang, J.; Deng, M.; Yu, T. *Chin. J. Org. Chem.* **2013**, *33*, 693 (in Chinese).
(杨军, 邓敏智, 于涛, 有机化学, **2013**, *33*, 693.)
(b) Dermenci, A.; Dong, G. *Sci. China Chem.* **2013**, *56*, 685.
(c) Guo, L.; Rueping, M. *Chemistry* **2018**, *24*, 7794.
(d) Zhao, Q.; Szostak, M. *ChemSusChem* **2019**, *12*, 2983.
(e) Wang, Z.; Wang, X.; Nishihara, Y. *Chem.-Asian J.* **2020**, *15*, 1234.
(f) Lu, H.; Yu, T. Y.; Xu, P. F.; Wei, H. *Chem. Rev.* **2021**, *121*, 365.

[4] (a) Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1966**, *88*, 3452.
(b) Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1966**, *7*, 4713.

[5] Blum, J.; Lipshes, Z. *J. Org. Chem.* **1969**, *34*, 3076.

[6] Chiusoli, G. P.; Costa, M.; Pecchini, G.; Cometti, G. *Transition Met. Chem.* **1977**, *2*, 270.

[7] Gooßen, L. J.; Paetzold, J.; Winkel, L. *Synlett* **2002**, 1721.

[8] Wang, Z.; Wang, X.; Ura, Y.; Nishihara, Y. *Org. Lett.* **2019**, *21*, 6779.

[9] Keaveney, S. T.; Schoenebeck, F. *Angew. Chem., Int. Ed.* **2018**, *57*, 4073.

[10] (a) Malapit, C. A.; Bour, J. R.; Brigham, C. E.; Sanford, M. S. *Nature* **2018**, *563*, 100.
(b) Malapit, C. A.; Bour, J. R.; Laursen, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2019**, *141*, 17322.

[11] Wang, Z.; Wang, X.; Nishihara, Y. *Chem. Commun.* **2018**, *54*, 13969.

[12] (a) He, B.; Liu, X.; Li, H.; Zhang, X.; Ren, Y.; Su, W. *Org. Lett.* **2021**, *23*, 4191.
(b) Deng, X.; Guo, J.; Zhang, X.; Wang, X.; Su, W. *Angew. Chem., Int. Ed.* **2021**, *60*, 24510.
[13] (a) Blanchard, N.; Bizet, V. *Angew. Chem., Int. Ed.* **2019**, *58*, 6814.
(b) Ogiwara, Y.; Sakai, N. *Angew. Chem., Int. Ed.* **2020**, *59*, 574.
(c) Karbakhshzadeh, A.; Heravi, M. R. P.; Rahmani, Z.; Ebadi, A. G.; Vessally, E. *J. Fluorine Chem.* **2021**, *248*, 109806.
[14] Fu, L.; Cao, X.; Wan, J.; Liu, Y. *Chin. J. Chem.* **2020**, *38*, 254.
[15] (a) Zarate, C.; Manzano, R.; Martin, R. *J. Am. Chem. Soc.* **2015**, *137*, 6754.
(b) Chatupheeraphat, A.; Liao, H. H.; Srimontree, W.; Guo, L.; Minenkov, Y.; Poater, A.; Cavallo, L.; Rueping, M. *J. Am. Chem. Soc.* **2018**, *140*, 3724.
(c) Malapit, C. A.; Borrell, M.; Milbauer, M. W.; Brigham, C. E.; Sanford, M. S. *J. Am. Chem. Soc.* **2020**, *142*, 5918.
[16] Hu W.; Zhang, Y.; Zhu, H.; Ye, D.; Wang, D. *Green. Chem.* **2020**, *38*, 254.
[17] Zhou, T.; Xie, P. P.; Ji, C. L.; Hong, X.; Szostak, M. *Org. Lett.* **2020**, *22*, 6434.
[18] Aschenaki, A.; Ren, F.; Liu, J.; Zheng, W.; Song, Q.; Jia, W.; Bao, J. J.; Li, Y. *RSC Adv.* **2021**, *11*, 33692.
[19] Zim, D.; Gruber, A. S.; Ebeling, G.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2000**, *2*, 2881.
[20] Sicard, L.; Quinton, C.; Peltier, J. D.; Tondelier, D.; Geffroy, B.; Biapo, U.; Metivier, R.; Jeannin, O.; Rault-Berthelot, J.; Poriel, C. *Chemistry* **2017**, 23, 7719.
[21] Bistri, O.; Correa, A.; Bolm, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 586.
[22] Wójcik, K.; Goux-Henry, C.; Andrioletti, B.; Michał Pietrusiewicz, K.; Framery, E. *Tetrahedron Lett.* **2012**, *53*, 5602.
[23] Shen, N.; Li, R.; Liu, C.; Shen, X.; Guan, W.; Shang, R. *ACS Catal.* **2022**, *12*, 2788.
[24] Hanley, P. S.; Ober, M. S.; Krasovskiy, A. L.; Whiteker, G. T.; Kruper, W. J. *ACS Catal*. **2015**, *5*, 5041.
[25] Nandurkar, N. S.; Bhanushali, M. J.; Bhor, M. D.; Bhanage, B. M. *Tetrahedron Lett*. **2008**, *49*, 1045.
[26] Zou, Y.; Yue, G.; Xu, J.; Zhou, J. S. *Eur. J. Org. Chem*. **2014**, *2014*, 5901.
[27] Lebrasseur, N.; Larrosa, I. *J. Am. Chem. Soc.* **2008**, *130*, 2926.
[28] Santra, S.; Hota, P. K.; Bhattacharyya, R.; Bera, P.; Ghosh, P.; Mandal, S. K. *ACS Catal.* **2013**, *3*, 2776.
[29] Liu, C.; Ni, Q.; Bao, F.; Qiu, J. *Green Chem.* **2011**, 13, 1260.
[30] Zhou, Y.; You, W.; Smith, K. B.; Brown, M. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 3475.
[31] Moon, Y.; Kwon, D.; Hong, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 11333.

(Cheng, F.)

