Tetrahedron xxx (xxxx) xxx

Contents lists available at ScienceDirect

Tetrahedron

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# C($sp^2$)-C($sp^2$) Suzuki cross-coupling of arylammonium salts catalyzed by a stable Pd—NHC complex

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ARTICLE INFO

*Article history:*
Received 23 June 2021
Received in revised form
26 August 2021
Accepted 30 August 2021
Available online xxx

*Keywords:*
Pd-NHC complex
Suzuki reaction
Ammonium salt
C—N bond activation

ABSTRACT

We have developed the Suzuki-Miyaura cross-coupling of aryl ammonium salts via C—N bond activation catalyzed by an easily prepared and bench-stable palladium-N-heterocyclic carbene complex. The reaction proceeded well under mild conditions with phenylboronic acid, pinacol ester or anhydride and provided yields of products up to 97% with good functional group compatibility. The direct arylation of arylamine can be performed by a two-step one-pot process and the protocol can be performed on the gram scale.

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## 1. Introduction

Transition-metal-catalyzed cross-coupling reactions, such as Suzuki—Miyaura [1], Heck [2], Stille [3], Kumada [4], Negishi [5], Hiyama [6], and Sonogashira [7] reactions are highly practical approaches for the formation of C—C bonds. Among these cross-coupling reactions, the Suzuki—Miyaura reaction has been proven to be the most attractive method to form the C—C bond, because organoboron reagents involved in the reaction have air- and moisture-stability, good functional group tolerance, low toxicity and wide availability [8].

Electrophiles employed in the Suzuki reaction are principally aryl halides and oxygen-containing compounds, such as triflates, mesylates/tosylates and phosphates [9]. Recently, the nitrogen-containing electrophilic partners have been developed due to the abundance of C—N bonds in organic intermediates, therapeutic drugs, and organic materials [10]. Among them, the research of using quaternary ammonium salts as coupling partners has attracted considerable attention.[10g] Quaternary ammonium salts are not only air and thermally stable, but only readily available through quaternization of a large variety of tertiary aryl/alkyl amines [11]. Until now, the coupling reaction of trimethylammonium salts has been successfully applied in Kumada [12], Negishi [13], Still [14], Suzuki [15], Buchwald—Hartwig [16], Sonogashira [17] and other cross-couplings [18]. Although several approaches on the C($Sp^2$)-C($Sp^3$) cross-coupling of benzyl trimethylammonium salts with boronic acids have been developed [15b-15f], only one method on the C($Sp^2$)-C($Sp^2$) cross-coupling of aryl trimethylammonium salts was reported by Macmillan until now (Scheme 1) [15a]. In Macmillan's reaction, the extremely air-sensitive and thermally unstable Ni(COD)$_2$ was employed as the catalyst, so it would be interested to develop an alternative approach for the Suzuki coupling of arylammonium salts using an air-stable, robust, and user-friendly catalyst.

Herein, we describe the Suzuki reaction of aryltrimethylammonium salts with phenylboronic acid, anhydride and ester via C—N bond activation catalyzed by a well-defined and stable Pd—NHC complex in good to excellent yields.

## 2. Results and discussion

In our previous work, we found that the stable and well-defined Pd—NHC complex, SIPr-PdCl$_2$-Py (Fig. 1) was an effective catalyst for the Sonogashira reaction of trimethylammonium salts, suggesting that the Pd(0)-NHC readily inserts into the C—N bond of phenylammonium via oxidation addition.[17] Triggered by this work, we envisaged that the Pd—NHC complex could be effective for the Suzuki cross-coupling of aryl quaternary ammonium salt, as Pd

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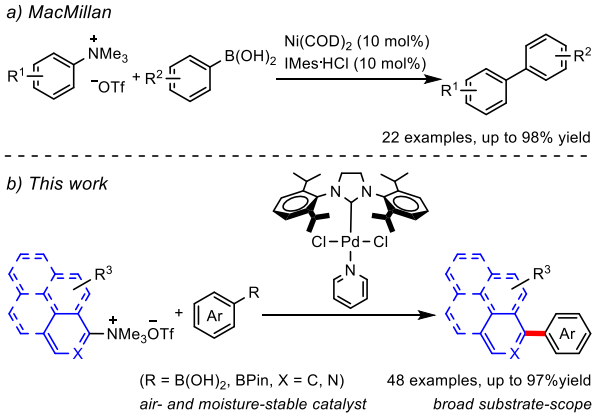
https://doi.org/10.1016/j.tet.2021.132431
0040-4020/© 2021 Published by Elsevier Ltd.

Please cite this article as: H. Tang, M. Liu, M. Zhu *et al.*, C($sp^2$)-C($sp^2$) Suzuki cross-coupling of arylammonium salts catalyzed by a stable Pd—NHC complex, Tetrahedron, https://doi.org/10.1016/j.tet.2021.132431




**Scheme 1.** C($sp^2$)-C($sp^2$) Suzuki cross-coupling of aryltrimethylammonium salts via C–N bond activation.

catalysts have been successfully employed in a wide range of Suzuki coupling reaction through transmetalation with aryl boronic acids. Therefore, our investigation into the Suzuki reaction of arylammonium salts started with *N*,*N*,*N*-trimethylnaphthalen-1-aminium triflate (**1**), phenylboronic acid (**2**) and a series of stable Pd catalyst. It was gratifying to note that the desired product, 1-phenylnaphthalene (**3**) was obtained in 42% of yield when SIPr-$PdCl_2$-Py (5 mol%) was employed (Table 1, entry 1). However, when less electron-rich IPr-$PdCl_2$-Py was used, the yield of **3** decreased nearly 30% (Table 1, entry 2). In the cases of commercially available $Pd(PPh_3)_2Cl_2$, $PdCl_2$ or $Pd(OAc)_2$ with the addition of the phosphine ligand $PCy_3$, $PPh_3$, dppe, dppf, Xphos, *t*-BuXphos and Ruphos, only less than 20% of **3** were observed (Table 1, entries 3–11). $PdCl_2$ with the N-heterocycle carbene (NHC) ligand SIPr or IPr provided less than 30% of **3** (Table 1, entries 10–11). Because a large amount of *N*,*N*-dimethylnaphthalen-1-amine decomposed from **1** was detected by GC-MS in the reaction mixture, the amount of **1** was raised to 2 equivalent, which led to 53% of **3** (Table 1, entry 14). The amount of catalyst loading and base slightly influence the reaction, and 73% of **3** was afforded when doubling the amount of SIPr-$PdCl_2$-Py to 10 mol% and *t*-BuONa to 2 equivalent (Table 1, entries 15–16). Subsequently, the screening of bases indicates that **3** could be afforded in 79% yield when CsF was employed, while the yield of **3** was generally lower than 55% when other bases were used (Table 1, entries 17–22). Finally, different solvents were also screened, and the highest yield was observed with THF used as the solvent (Table 1, entries 23–27). It was found that elevating the reaction temperature would facilitate the reaction, and the highest reaction yield was reached at 80 °C in 86% (Table 1, entries 28–30).

With the optimized reaction conditions in hand, the scope and generality of the ammonium Suzuki reaction was explored. A wide range of boronic acids were chosen to react with arylammonium salt **1** (Table 2, **3**–**29**). Various substituted phenyl boronic acid bearing either electron-donating or electron-withdrawing group could be successfully converted to the corresponding phenylnaphthalene in good to excellent yields. There was no obvious steric effect when the phenylboronic acid had a group in the *ortho* position (Table 2, **20**–**22**). Various useful functional groups, such as thioether, trimethylsilyl, trifluoro, ether, fluoro, cyano, nitro, ester, keto, amide and vinyl groups were well tolerated to provide desired coupling products in good to high yields (Table 2, **6**–**7**, **9**–**17** and **24**). However, Cl substitution on the phenylboronic acid interfered with the reaction and resulted in a low yield of **12** (36%). It is assumed that the chloride reacted competitively with ammonium salt **1** in the reaction of phenylboronic acid, which was confirmed by formation of a large amount of biphenyl in the one-pot reaction of phenylchloride, phenylboronic acid and **1** under the same conditions. The reaction of naphthylboronic acid with **1** proceeded well and 1,1′-binaphthalene (Table 2, **23**) was obtained in 80% of yield. Moreover, heterocyclic boronic acids, such as dibenzofuran, dibenzothiophene, thiophene, benzodioxole and pyridine are applicable to this system, and the corresponding reactions with **1** provided the desired products in moderate to good yields (Table 2, **25**–**29**).

Furthermore, a few arylammonium triflates were examined in the Suzuki reaction of methylphenylboronic acid (Table 3). The trimethylammonium triflate with a fused aromatic ring could partake in this reaction smoothly (Table 3, **30**–**32**). For example, 2-indolyltrimethylammonium triflate smoothly reacted with 4-methylbenzeneboronic acid to give 95% of **30**. Both methoxy-substituted electron-rich and cyano-substituted electron-deficient 1-naphthyltrimethylammonium triflates showed good activity in the reaction (Table 3, **31**–**32**). The electron-deficient 2-pyridyltrimethylammonium triflate smoothly reacted with 4-methylbenzeneboronic acid to afford **33** in 90% yield. Unfortunately, in the Suzuki reaction of phenyltrimethylammonium triflate, only *N*,*N*-dimethylaniline decomposed from the ammonium salt was observed without any cross-coupling product (Table 3, **34**). The better activity of naphthyl group over phenyl group in quaternary ammonium salt was observed in the C–P cross coupling reaction of ammonium salt [19]. When *N*,*N*-dimethyl-*N*-phenyl-1-naphthyldimethylammonium triflate was employed in the reaction, the coupling product **4** was exclusively generated in 75% yield, suggesting that the reaction proceeded selectively at the side of naphthyl group. The protocol is applicable to benzyl ammonium salt as well, and 76% yield of **35** was isolated with benzyldimethylammonium triflate.

Furthermore, the arylboronic acid can be replaced by arylboronic acid ester in this protocol. In the reaction of arylboronic acid pinacol ester with **1**, the corresponding products were efficiently obtained with moderate to good yields (Table 4). However,

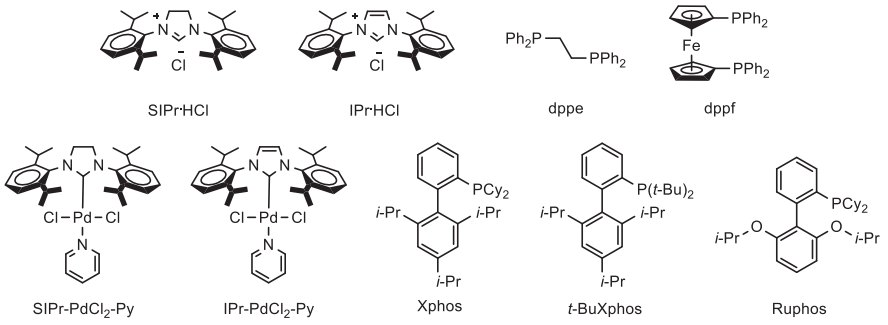
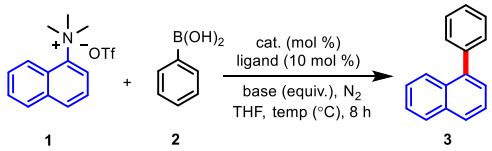



**Fig. 1.** Structure of Pd–NHC complexes and NHC Ligands.

**Table 1**
Optimization of the reaction conditions[a].




| Entry[a] | Cat. (mol%) | Ligand | 1 (equiv) | Base (eq.) | Temp (°C) | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | SIPr-$PdCl_2$-Py (5) | | 1 | *t*-BuONa (1.5) | 60 | 42 |
| 2 | IPr-$PdCl_2$-Py (5) | | 1 | *t*-BuONa (1.5) | 60 | 14 |
| 3 | $Pd(PPh_3)_2Cl_2$ (5) | $PPh_3$ | 1 | *t*-BuONa (1.5) | 60 | trace |
| 4 | $Pd(OAc)_2$ (5) | $PPh_3$ | 1 | *t*-BuONa (1.5) | 60 | trace |
| 5 | $Pd(OAc)_2$ (5) | dppe | 2 | *t*-BuONa (1.5) | 60 | 13 |
| 6 | $Pd(OAc)_2$ (5) | dppf | 2 | *t*-BuONa (1.5) | 60 | 17 |
| 7 | $Pd(OAc)_2$ (5) | Xphos | 2 | *t*-BuONa (1.5) | 60 | 14 |
| 8 | $Pd(OAc)_2$ (5) | *t*-BuXphos | 2 | *t*-BuONa (1.5) | 60 | 15 |
| 9 | $Pd(OAc)_2$ (5) | Ruphos | 2 | *t*-BuONa (1.5) | 60 | 13 |
| 10 | $PdCl_2$ (5) | $PPh_3$ | 1 | *t*-BuONa (1.5) | 60 | trace |
| 11 | $PdCl_2$ (5) | $PCy_3$ | 1 | *t*-BuONa (1.5) | 60 | trace |
| 12 | $PdCl_2$ (5) | SIPr · HCl | 1 | *t*-BuONa (1.5) | 60 | 29 |
| 13 | $PdCl_2$ (5) | IPr · HCl | 1 | *t*-BuONa (1.5) | 60 | 10 |
| 14 | SIPr-$PdCl_2$-Py (5) | | 2 | *t*-BuONa (1.5) | 60 | 53 |
| 15 | SIPr-$PdCl_2$-Py (10) | | 2 | *t*-BuONa (1.5) | 60 | 65 |
| 16 | SIPr-$PdCl_2$-Py (10) | | 2 | *t*-BuONa (2) | 60 | 73 |
| 17 | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 60 | 79 |
| 18 | SIPr-$PdCl_2$-Py (10) | | 2 | $Cs_2CO_3$ (2) | 60 | 35 |
| 19 | SIPr-$PdCl_2$-Py (10) | | 2 | $K_3PO_4$ (2) | 60 | 24 |
| 20 | SIPr-$PdCl_2$-Py (10) | | 2 | *t*-BuOK (2) | 60 | 55 |
| 21 | SIPr-$PdCl_2$-Py (10) | | 2 | *t*-BuOLi (2) | 60 | 10 |
| 22 | SIPr-$PdCl_2$-Py (10) | | 2 | $K_3PO_4 \cdot 3H_2O$ (2) | 60 | 42 |
| 23[c] | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 60 | 73 |
| 24[d] | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 60 | 53 |
| 25[e] | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 60 | 6 |
| 26[f] | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 60 | 6 |
| 27[g] | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 60 | 39 |
| 28 | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 70 | 81 |
| 29 | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 80 | 86 |
| 30 | SIPr-$PdCl_2$-Py (10) | | 2 | CsF (2) | 90 | 85 |

[a] Conditions: **1** (1–2 equiv.), **2** (0.2 mmol), catalyst (5–10 mol%), ligand (10 mol%), base (1.5–2 equiv.), THF (1 mL), 60–90 °C under $N_2$ atmosphere, unless noted otherwise.
[b] HPLC yield with *N*-phenylbenzamide as the internal standard.
[c] Dioxane as the solvent.
[d] DMF as the solvent.
[e] *i*-PrOH as the solvent.
[f] $CH_3CN$ as the solvent.
[g] Toluene as the solvent.

compared to the reaction with boronic acid, the slightly decreased yield was observed in the reaction with pinacol ester (Table 4, **36**–**41** and **44**–**48**). For example, the reaction of **1** with 2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane achieved 81% yield of **40** (Table 4, **40**). The yield is slightly low compared with that of the reaction with (4-fluorophenyl)boronic acid (Table 2, **11**, 91%). Both electron-withdrawing group and electron-donating group on pinacol esters were none notable effective in the reaction, moreover, many sensitive groups, even aldehyde could be tolerated in the reaction (**43**). Although ortho-, meta-, and para-methoxyphenylboronic acid pinacol esters reacted smoothly with **1** to give coupling products in good yields, yields of ortho and para product are slightly reduced, showing steric effect in the reaction (**44**–**46**). Heterocyclic boronic acid pinacol esters, such as thiophene and furan are applicable in the reaction (**48**–**49**). Finally, phenylboronic anhydride can also be used in this protocol, affording 1-phenylnaphthalene (**50**) in 87% yield (Scheme 2).

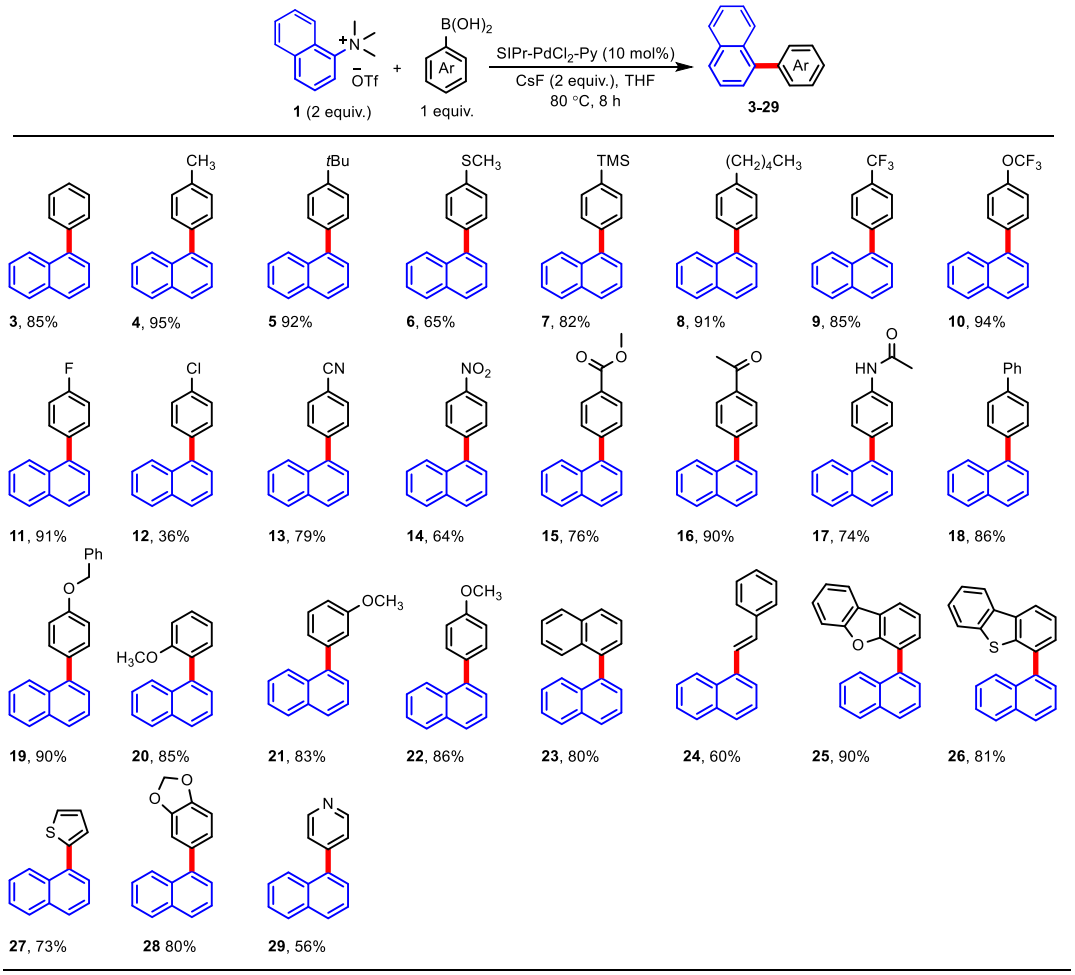
To demonstrate the practicality of the protocol, amine was directly used in a two-step one-pot process. Dimethylnaphthylamine can be converted to **3** in an 80% overall yield via methylation by methyl triflate followed by the Pd-catalyzed Suzuki reaction with phenylboronic acid (**2**). In the reaction, 1-naphthyltrimethylammonium triflate was prepared in-situ and then used directly without isolation and purification (Scheme 3). Moreover, 0.66 g of **3** in 81% yield was obtained when the reaction scale was increased 8-fold to 4 mmol of **2** and 8 mmol of **1** (Scheme 4). These yields in two-step one-pot and scale-up reactions are comparable with the yield of the small-scale one-step reaction (Table 2, **3**).

Based on our previous investigation [17], a possible mechanism for this transformation is shown in Scheme 5. First, the oxidative addition of SIPr-Pd(0)-Py **A** which is generated in situ, with trimethylbenzylicammonium salt **I** produced intermediate **B** and released trimethylamine. Then intermediate **B** converted to a new complex **C** by a transmetalation with boronic acid **II**. Finally, the cross coupling product **III** was obtained upon reductive elimination of **C**.

## 3. Conclusion

In summary, we have developed a palladium-catalyzed Suzuki coupling of ammonium triflates with arylboronic acids, anhydride and pinacol ester through C–N bond cleavage. The readily available palladium catalyst is air- and moisture-stable, and the reaction

**Table 2**
The Suzuki cross-coupling of arylboronic acids with **1**.




Reaction conditions: SIPr-$PdCl_2$-Py (0.10 mmol), boronic acid (0.50 mmol), ammonium triflate **1** (1.0 mmol) and CsF (1 mmol) in THF (2.5 mL) at 80 °C for 8 h under $N_2$ atmosphere.

proceeded well under mild conditions providing yields of products up to 97%. This reaction has a broad scope of organoboron substrates, and exhibits good functional group compatibility Moreover, the direct arylation of arylamine can be performed by a two-step one-pot process without isolation of the ammonium salt and the protocol can be performed on the gram scale.

Compared to the reported Ni catalyst system [15a], the Pd–NHC catalyst is user-friendly and easy to handle, however, the Pd–NHC is ineffective with simple phenyl trimethylammonium triflate in the Suzuki coupling, showing limited substrate scope with aryl ammonium salts.

## 3.1. Experimental section

### 3.1.1. General information

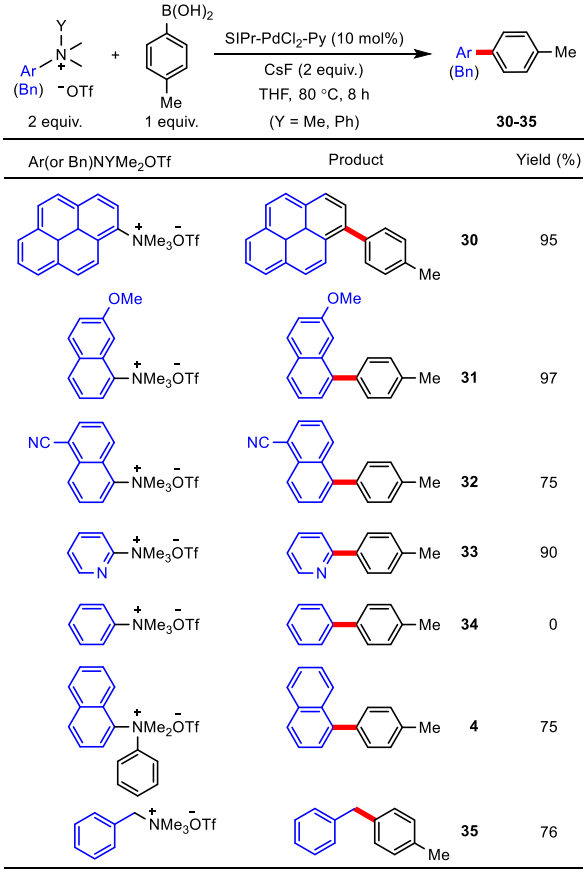
All manipulations were carried out under a nitrogen atmosphere. All anhydrous solvents were collected from the VAC Solvent Purifier instrument. *N,N,N*-trimethylpyren-1-ammonium trifluoromethanesulfonate was prepared according to the following procedure and the other aryltrimethylammonium trifluoromethanesulfonates were prepared according to the literature procedure [19]. NHC–Pd complexes were prepared according to our previous procedure [20]. All other substrates and reagents were purchased from Energy Chemical and used as received. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a Bruker AV400 spectrometer with chemical shift values relative to the solvent residue. HRMS was recorded on a Bruker solarix 9.4T. HPLC was performed on an Agilent 1200 series with 256 nm UV detector using a liquid chromatography column that purchased from Agela Technologies Innoval ODS-P. Melting points were detected by microscope melting point apparatus.

### 3.1.2. The synthesis of *N,N,N*-trimethylpyren-1-aminium trifluoromethanesulfonate

Methyltriflate (0.28 mL, 2.40 mmol) was added dropwise into a solution of *N,N*-dimethyl-1-pyrenamine (0.4902 g, 2 mmol) in DCM (5 mL) in an 8 mL of vial. After the reaction was stirred overnight at room temperature, $Et_2O$ (10 mL) was added into the mixture. The precipitate was filtered and washed by $Et_2O$ (3 × 5 mL), and the product was collected as a white solid.

Yield: 0.65 g (80%). White solid. M.p. 203–204 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.92 (d, $J$ = 9.7 Hz, 1H), 8.65 (d, $J$ = 8.9 Hz,

**Table 3**
The Suzuki cross-coupling of arylammonium triflates with *p*-methylphenylboronic acid.




Reaction conditions: SIPr-$PdCl_2$-Py (0.10 mmol), methylphenylboronic acid (0.50 mmol), arylammonium triflate (1.0 mmol) and CsF (1 mmol) in THF (2.5 mL) at 80 °C for 8 h under $N_2$ atmosphere.

1H), 8.58–8.48 (m, 4H), 8.39 (d, $J$ = 8.8 Hz, 1H), 8.33 (d, $J$ = 8.8 Hz, 1H), 8.29–8.22 (m, 1H), 4.09 (s, 9H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 139.5, 132.9, 131.2, 130.3, 130.0, 129.6, 128.1, 128.0, 127.5, 127.4, 126.1, 125.7, 124.1, 122.8, 122.2, 119.8, 58.4. HRMS-APCI (*m/z*): Calcd for $[M\text{-OTf}]^+$ $C_{19}H_{19}N^+$, 260.1434; found, 260.1437.

### 3.1.3. General procedure for the Suzuki reaction

THF (2.5 mL) was injected into the mixture of ammonium salts (1 mmol), boronic acid (0.5 mmol), SIPr-$PdCl_2$-Py (0.05 mmol) and CsF (1 mmol) in a Schleck tube under $N_2$ atmosphere. After stirring for 8 h at 80 °C, the mixture was concentrated via reduced pressure. Finally, the residue was purified by flash chromatography on silica gel with an eluent to afford the target compound.

### 3.1.4. Data for products of the Suzuki reaction

*3.1.4.1. 1-phenylnaphthalene (3) [21].* Eluent (PE). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J$ = 9.4 Hz, 2H), 7.89 (d, $J$ = 8.2 Hz, 1H), 7.59–7.42 (m, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.5, 134.0, 131.8, 130.3, 128.48, 128.47, 127.8, 127.4, 127.1, 126.24 (2C), 126.0, 125.6. HRMS-APCI (*m/z*): Calcd for $[M+H]^+$ $C_{16}H_{13}^+$, 205.1012; found, 205.1009.

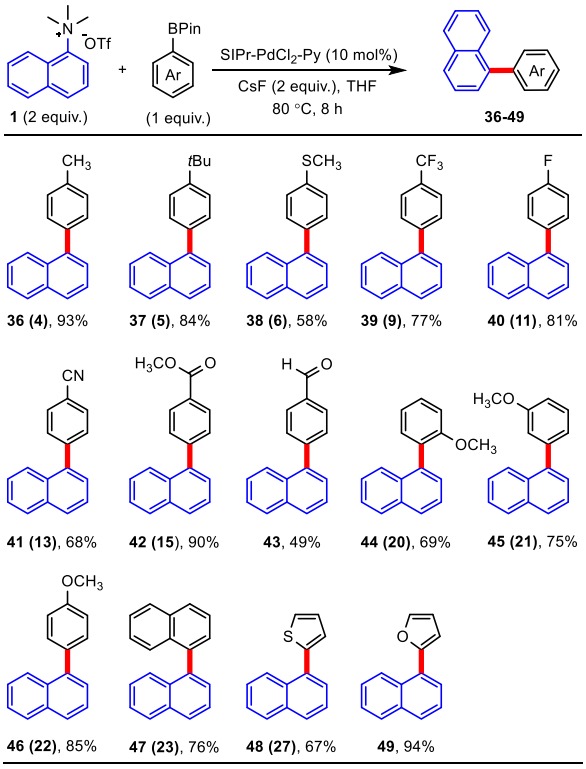
*3.1.4.2. 1-(p-tolyl)naphthalene (4) [22].* Eluent (PE). White solid. M.p. 52–53 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98–7.90 (m, 2H), 7.87 (d, $J$ = 8.3 Hz, 1H), 7.59–7.48 (m, 2H), 7.47–7.40 (m, 4H), 7.33 (d, $J$ = 7.8 Hz, 2H), 2.48 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.4, 138.0, 137.1, 134.0, 131.9, 130.1, 129.1, 128.4, 127.6, 127.0, 126.2, 126.1, 125.8, 125.5, 21.4. HRMS-APCI (*m/z*): Calcd for $[M+H]^+$ $C_{17}H_{15}^+$, 219.1168; found, 219.1157.

*3.1.4.3. 1-(4-(tert-butyl)phenyl)naphthalene (5).* Eluent (PE). White solid. M.p. 90–91 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, $J$ = 7.2 Hz, 1H), 7.92 (d, $J$ = 7.6 Hz, 1H), 7.87 (d, $J$ = 8.0 Hz, 1H), 7.58–7.50 (m, 4H), 7.50–7.41 (m, 4H), 1.44 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.3, 140.4, 137.9, 134.0, 131.9, 129.9, 128.4, 127.6, 127.1, 126.3, 126.0, 125.8, 125.6, 125.3, 34.8, 31.6. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{20}H_{21}^+$, 261.1638; found, 261.1633.

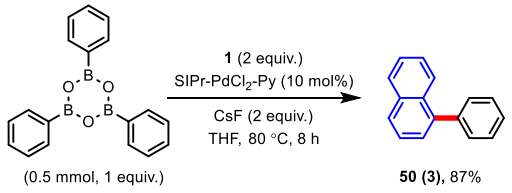
*3.1.4.4. methyl(4-(naphthalen-1-yl)phenyl)sulfane (6).* Eluent (PE). White solid. M.p. 91–92 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J$ = 8.0 Hz, 2H), 7.86 (d, $J$ = 8.4 Hz, 1H), 7.57–7.47 (m, 2H), 7.47–7.37 (m, 6H), 2.57 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.7, 137.6, 134.0, 131.7, 130.6, 128.5, 127.8, 127.0, 126.6, 126.2, 126.0, 125.9, 125.5, 16.0. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{15}S^+$, 251.0889; found, 251.0881.

*3.1.4.5. trimethyl(4-(naphthalen-1-yl)phenyl)silane (7).* Eluent (PE). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, $J$ = 7.6 Hz, 1H),

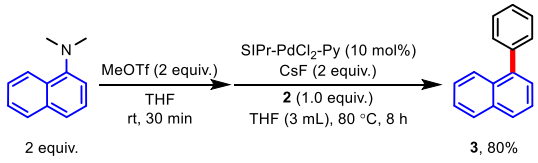
**Table 4**
The cross-coupling of arylboronic acid pinacol ester with **1**.



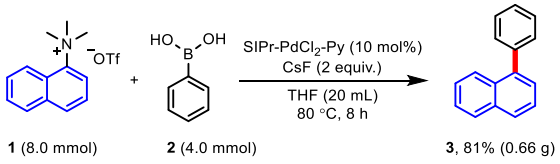

Reaction conditions: **1** (1.0 mmol), SIPr-PdCl$_2$-Py (0.10 mmol), arylboronic acid pinacol ester (0.50 mmol), CsF (1.0 mmol) in THF (2.5 mL) at 80 °C for 8 h under $N_2$ atmosphere.



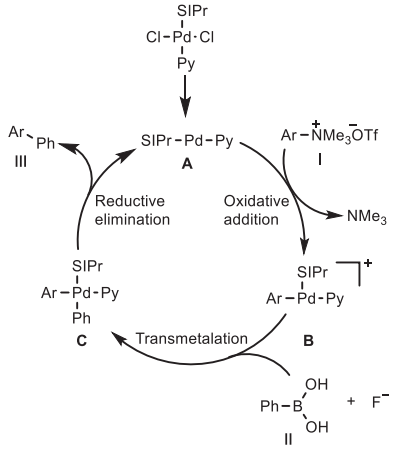

**Scheme 2.** Suzuki cross-coupling of phenylboronic anhydride with **1**.




**Scheme 3.** The two-step one-pot process.




**Scheme 4.** The gram-scale reaction.




**Scheme 5.** The proposed reaction mechanism.

7.97 (d, $J$ = 8.0 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 1H), 7.79–7.69 (m, 2H), 7.63–7.53 (m, 4H), 7.49 (m, 2H), 0.43 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.3, 140.4, 139.3, 134.0, 133.4, 131.7, 129.6, 128.4, 127.8, 127.1, 126.2, 126.1, 125.9, 125.5, −0.8. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{19}H_{21}Si^+$, 277.1407; found, 277.1415.

*3.1.4.6. 1-(4-pentylphenyl)naphthalene (8).* Eluent (PE). White solid. M.p. 77–78 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J$ = 8.4 Hz, 1H), 7.95 (d, $J$ = 8.0 Hz, 1H), 7.89 (d, $J$ = 8.0 Hz, 1H), 7.62–7.51 (m,

2H), 7.51–7.44 (m, 4H), 7.36 (d, $J$ = 8.0 Hz, 2H), 2.76 (t, $J$ = 8.0 Hz, 2H), 1.86–1.71 (m, 2H), 1.51–1.42 (m, 4H), 1.05–0.97 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$)) δ 142.1, 140.5, 138.2, 134.0, 131.9, 130.1, 128.4, 128.4, 127.5, 127.0, 126.3, 126.0, 125.8, 125.5, 35.9, 31.8, 31.4, 22.8, 14.2. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{21}H_{23}^+$, 275.1794; found, 275.1802.

*3.1.4.7. 1-(4-(trifluoromethyl)phenyl)naphthalene (9) [22].* Eluent (PE). White solid. M.p. 48–49 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, $J$ = 8.6 Hz, 2H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 2H), 7.64 (d, $J$ = 7.6 Hz, 2H), 7.61–7.52 (m, 2H), 7.51–7.46 (m, 1H), 7.44 (dd, $J$ = 6.8, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.6 (d, $^4J_{C\text{-}F}$ = 1.4 Hz), 138.9, 133.9, 131.4, 130.5, 129.6 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 128.6, 128.5, 127.2, 126.6, 126.2, 125.6, 125.5, 125.4 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.5 (q, $^1J_{C\text{-}F}$ = 270.6 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ −62.28. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{17}H_{12}F_3^+$, 273.0886; found, 273.0879.

*3.1.4.8. 1-(4-(trifluoromethoxy)phenyl)naphthalene (10).* Eluent (PE). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J$ = 8.0 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 1H), 7.89 (d, $J$ = 8.0 Hz, 1H), 7.60–7.52 (m, 4H), 7.52–7.47 (m, 1H), 7.44 (dd, $J$ = 7.0, 1.4 Hz, 1H), 7.38 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.7 (q, $^2J_{C\text{-}F}$ = 1.5 Hz), 139.6, 138.9, 134.0, 131.6, 131.5, 128.5, 128.2, 127.2, 126.5, 126.1, 125.8, 125.5, 120.91, 120.8 (q, $^1J_{C\text{-}F}$ = 255.7 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ −57.62; HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{17}H_{12}F_3O^+$, 289.0835; found, 289.0830.

*3.1.4.9. 1-(4-fluorophenyl)naphthalene (11) [22].* Eluent (PE). White solid. M.p. 71–72 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, $J$ = 8.4, 1.2 Hz, 1H), 7.86 (t, $J$ = 8.8 Hz, 2H), 7.57–7.50 (m, 1H), 7.54–7.46 (m, 1H), 7.50–7.40 (m, 3H), 7.40 (dd, $J$ = 7.2, 1.2 Hz, 1H), 7.23–7.15 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $^1J_{C\text{-}F}$ = 244.9 Hz), 139.3, 136.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 134.0, 131.8, 131.7 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 128.5, 128.0, 127.2, 126.3, 126.0, 125.9, 125.5, 115.3 (d, $^2J_{C\text{-}F}$ = 21.2 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ −115.47; HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{16}H_{12}F^+$, 223.0981; found, 223.0985.

*3.1.4.10. 1-(4-chlorophenyl)naphthalene (12) [23].* Eluent (PE). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, $J$ = 8.0 Hz, 1H), 7.88–7.83 (m, 2H), 7.56–7.52 (m, 1H), 7.52–7.42 (m, 6H), 7.40 (dd, $J$ = 7.2, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.1, 133.9, 133.5, 131.6, 131.5, 128.6, 128.5, 128.1, 127.1, 126.4, 126.1, 126.0, 125.8, 125.5. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{16}H_{12}Cl^+$, 239.0622; found, 239.0622.

*3.1.4.11. 4-(naphthalen-1-yl)benzonitrile (13) [24].* Gradient eluting (PE → PE/EtOAc (40/1)). White solid; M.p. 76–77 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J$ = 7.6 Hz, 2H), 7.79 (d, $J$ = 8.3 Hz, 3H), 7.61 (d, $J$ = 8.2 Hz, 2H), 7.60–7.50 (m, 2H), 7.52–7.43 (m, 1H), 7.41 (dd, $J$ = 7.1, 1.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.8, 138.3, 133.9, 132.2, 131.1, 130.9, 128.9, 128.7, 127.1, 126.8, 126.3, 125.4, 125.3, 119.0, 111.3. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{17}H_{12}N^+$, 230.0964; found, 230.0960.

*3.1.4.12. 1-(4-nitrophenyl)naphthalene (14) [25].* Gradient eluting: PE → PE/EtOAc (10/1); White solid. M.p. 131–132 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40–8.32 (m, 2H), 7.95 (dd, $J$ = 8.0, 3.2 Hz, 2H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.71–7.64 (m, 2H), 7.61–7.50 (m, 2H), 7.54–7.44 (m, 1H), 7.44 (dd, $J$ = 6.8, 1.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147. 8, 147.3, 137.9, 133.9, 131.1, 131.0, 129.1, 128.7, 127.2, 126.9, 126.4, 125.4, 125.3, 123.7; HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{16}H_{12}NO_2^+$, 250.0863; found, 250.0859.

*3.1.4.13. methyl 4-(naphthalen-1-yl)benzoate (15) [26].* Gradient eluting: PE → PE/EtOAc (40/1). White solid; M.p. 66–67 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, $J$ = 8.4 Hz, 2H), 7.92 (dd, $J$ = 10.4, 8.2 Hz, 2H), 7.86 (d, $J$ = 8.0 Hz, 1H), 7.59 (d, $J$ = 8.0 Hz, 2H), 7.57–7.53 (m, 1H), 7.53–7.49 (m, 1H), 7.48–7.42 (m, 2H), 3.99 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.2, 145.7, 139.3, 133.9, 131.4, 130.2, 129.7, 129.2, 128.5, 128.4, 127.1, 126.5, 126.1, 125.7, 125. 5, 52.3. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{18}H_{15}O_2^+$, 263.1067; found, 263.1062.

*3.1.4.14. 1-(4-(naphthalen-1-yl)phenyl)ethan-1-one (16) [22].* Gradient eluting: PE → PE/EtOAc (50/1). White solid. M.p. 98–99 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, $J$ = 8.4 Hz, 2H), 7.92 (t, $J$ = 9.4 Hz, 2H), 7.86 (d, $J$ = 8.4 Hz, 1H), 7.61 (d, $J$ = 8.4 Hz, 2H), 7.58–7.50 (m, 2H), 7.49–7.40 (m, 2H), 2.69 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 197.9, 145.9, 139.1, 136.1, 133.9, 131.3, 130.4, 128.5, 128.48, 128.46, 127.0, 126.5, 126.1, 125.7, 125. 5, 26.8. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{18}H_{15}O^+$, 247.1117; found, 247.1113.

*3.1.4.15. N-(4-(naphthalen-1-yl)phenyl)acetamide (17).* Gradient eluting: PE → PE/EtOAc (1/1). White solid. M.p. 205–206 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, $J$ = 9.2 Hz, 2H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.67 (d, $J$ = 8.0 Hz, 1H), 7.54–7.46 (m, 4H), 7.45–7.37 (m, 3H), 7.23 (d, $J$ = 7.6 Hz, 1H), 2.17 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.7, 141.7, 139.8, 138.0, 133.9, 131.6, 129.0, 128.4, 127.9, 127.0, 126.2, 126.0, 125.9, 125.4, 121.6, 119.1, 24.7. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{18}H_{16}NO^+$, 262.1226; found, 262.1221.

*3.1.4.16. 1-([1,1′-biphenyl]-4-yl)naphthalene (18) [27].* PE. White solid. M.p. 149–150 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J$ = 8.8 Hz, 1H), 7.94 (d, $J$ = 7.6 Hz, 1H), 7.90 (d, $J$ = 8.0 Hz, 1H), 7.79–7.66 (m, 4H), 7.64–7.45 (m, 8H), 7.43–7.38 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.3, 134.0, 139.9, 134.0, 131.8, 130.6, 129.0, 128.5, 127.9, 127.5, 127.3, 127.1, 127.1, 126.2, 126.2, 126.0, 125. 6. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{22}H_{17}^+$, 281.1325; found, 281.1329.

*3.1.4.17. 1-(4-(benzyloxy)phenyl)naphthalene (19).* Gradient eluting: PE → PE/EtOAc (40/1). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, $J$ = 13.4, 8.2 Hz, 2H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.57–7.48 (m, 4H), 7.47–7.40 (m, 6H), 7.40–7.35 (m, 1H), 7.12 (d, $J$ = 8.8 Hz, 2H), 5.17 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.3, 140.0, 137.2, 134.0, 133.6, 132.0, 131.3, 128. 8, 128.4, 128.2, 127.7, 127.5, 127.1, 126.2, 126.1, 125.8, 125.5, 114. 8, 70.3. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{23}H_{19}O^+$, 311.1430; found, 311.1427.

*3.1.4.18. 1-(2-methoxyphenyl)naphthalene (20) [28].* Gradient eluting: PE → PE/EtOAc (100/1). White solid. M.p. 98–99 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, $J$ = 9.0 Hz, 2H), 7.62 (d, $J$ = 8.8 Hz, 1H), 7.56 (t, $J$ = 7.6 Hz, 1H), 7.53–7.38 (m, 4H), 7.33 (dd, $J$ = 7.4, 1.8 Hz, 1H), 7.16–7.02 (m, 2H), 3.72 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4, 137.1, 133.6, 132.3, 132.1, 129.7, 129.1, 128.3, 127.8, 127.4, 126.6, 125.8, 125.7, 125.5, 120.7, 111.1, 55.7. HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{17}H_{15}O^+$, 235.1117; found, 235.1120.

*3.1.4.19. 1-(3-methoxyphenyl)naphthalene (21) [29].* Gradient eluting: PE → PE/EtOAc (100/1). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, $J$ = 8.8 Hz, 1H), 7.94 (d, $J$ = 8.4 Hz, 1H), 7.90 (d, $J$ = 8.4 Hz, 1H), 7.60–7.49 (m, 2H), 7.52–7.40 (m, 3H), 7.16–7.08 (m, 2H), 7.06–6.99 (m, 1H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.6, 142.3, 140.2, 133.9, 131.7, 129.4, 128.4, 127.8, 126.9, 126.2, 126.2, 125.9, 125.5, 122.7, 115.8, 113.0, 55.4; HRMS-APCI ($m/z$): $[M+H]^+$ Calcd for $C_{17}H_{15}O^+$, 235.1117; found, 235.1119.

*3.1.4.20. 1-(4-methoxyphenyl)naphthalene (22) [22].* Gradient eluting: PE → PE/EtOAc (100/1). White solid; M.p. 115–116 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96–7.89 (m, 2H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.55–7.47 (m, 2H), 7.47–7.40 (m, 4H), 7.09–7.01 (m, 2H), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.1, 140.1, 134.0, 133.3, 132.0, 131.3, 128.4, 127.5, 127.4, 126.2, 126.1, 125.8, 125.5, 113.9, 55.5; HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{15}O^+$, 235.1117; found, 235.1122.

*3.1.4.21. 1,1′-binaphthalene (23) [29].* PE. White solid. M.p. 159–160 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, $J$ = 8.4, 3.6 Hz, 4H), 7.66–7.58 (m, 2H), 7.57–7.46 (m, 4H), 7.44 (d, $J$ = 7.2 Hz, 2H), 7.35–7.28 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.6, 133.7, 133.0, 128.3, 128.0, 128.0, 126.7, 126.1, 125.9, 125.5; HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{20}H_{15}^+$, 255.1168; found, 255.1163.

*3.1.4.22. (E)-1-styrylnaphthalene (24).* Gradient eluting: PE → PE/EtOAc (100/1). White solid. M.p. 199–200 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, $J$ = 7.2 Hz, 1H), 7.97–7.88 (m, 2H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.78 (d, $J$ = 7.2 Hz, 1H), 7.64 (d, $J$ = 7.2 Hz, 2H), 7.61–7.49 (m, 3H), 7.44 (t, $J$ = 7.4 Hz, 2H), 7.34 (t, $J$ = 7.3 Hz, 1H), 7.19 (d, $J$ = 16.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.8, 135.2, 133.9, 131.9, 131.5, 128.9, 128.8, 128.2, 127.9, 126.8, 126.2, 127.0, 126.0, 125.8, 123.9, 123.8; HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{15}^+$, 231.1168; found, 231.1171.

*3.1.4.23. 4-(naphthalen-1-yl)dibenzo[b,d]furan (25).* PE. White solid. M.p. 105–106 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, $J$ = 7.8 Hz, 2H), 8.02–7.94 (m, 2H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.70–7.61 (m, 2H), 7.59–7.48 (m, 3H), 7.48–7.34 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.4, 154.3, 134.7, 133.9, 132.0, 129.4, 128.6, 128.5, 128.0, 127.3, 126.3, 126.3, 126.0, 125. 6, 125.1, 124.6, 124.5, 123.0, 122.9, 120.8, 120.1, 112.1; HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{22}H_{15}O^+$, 295.1117; found, 295.1113.

*3.1.4.24. 4-(naphthalen-1-yl)dibenzo[b,d]thiophene (26).* PE. White solid. Mp: 118–119 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25 (t, $J$ = 8.0 Hz, 2H), 7.98 (dd, $J$ = 8.0, 4.4 Hz, 2H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.70–7.58 (m, 4H), 7.56–7.41 (m, 4H), 7.38 (t, $J$ = 7.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.9, 138.3, 136.0, 135.9, 135.7, 134.0, 131.4, 128.7, 128.5, 128.4, 127.1, 126.9, 126.3, 126.2, 126.1, 125.6, 124.8, 124.5, 122.9, 121.9, 120.8; HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{22}H_{15}S^+$, 311.0889; found, 311.0883.

*3.1.4.25. 2-(naphthalen-1-yl)thiophene (27) [30].* PE. Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.33–8.17 (m, 1H), 7.97–7.90 (m, 1H), 7.89 (d, $J$ = 8.0 Hz, 1H), 7.62 (d, $J$ = 6.8 Hz, 1H), 7.58–7.49 (m, 3H), 7.47 (dd, $J$ = 5.2, 1.2 Hz, 1H), 7.30 (d, $J$ = 3.2 Hz, 1H), 7.23 (dd, $J$ = 5.2, 3.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.9, 134.0, 132.6, 132.0, 128.5, 128.5, 128.3, 127.5, 127.4, 126.6, 126.1, 125.9, 125.8, 125.4. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{14}H_{11}S^+$, 211.0576; found, 211.0569.

*3.1.4.26. 5-(naphthalen-1-yl)benzo[d][1,3]dioxole (28) [24].* Gradient eluting: PE → PE/EtOAc (100/1). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $J$ = 8.4 Hz, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.87 (d, $J$ = 8.0 Hz, 1H), 7.57–7.47 (m, 2H), 7.51–7.39 (m, 2H), 7.04–6.93 (m, 3H), 6.06 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.0, 140.0, 134.8, 134.0, 131.9, 128.4, 127.7, 127.0, 126.13, 126.11, 125.9, 125.5, 123.6, 110.8, 108.4, 101.2. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{13}O_2^+$, 249.0910; found, 249.0915.

*3.1.4.27. 4-(naphthalen-1-yl)pyridine (29) [30].* Gradient eluting: DCM → DCM/MeOH (50/1). White solid. M.p. 94–95 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, $J$ = 6.4 Hz, 2H), 8.00–7.91 (m, 2H), 7.82 (d, $J$ = 8.4 Hz, 1H), 7.62–7.48 (m, 5H), 7.44 (dd, $J$ = 7.0, 1.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.4, 147.7, 136.6, 133.9, 130.6, 129.7, 128.8, 127.3, 127.2, 126.6, 125.9, 125.5, 124.9. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{15}H_{12}N^+$, 206.0964; found, 193.1018.

*3.1.4.28. 1-(p-tolyl)-3a1,5a1-dihydropyrene (30).* PE. White solid. M.p. 70–71 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.25–8.15 (m, 4H), 8.10 (s, 1H), 8.01 (dd, $J$ = 15, 7.8 Hz, 3H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.40 (d, $J$ = 8.0 Hz, 2H), 2.52 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.9, 137.1, 131.6, 131.1, 130.6, 130.6, 129.2, 128.7, 127.8, 127.6, 127.5, 127.4, 126.1, 125.5, 125.2, 125.12, 125.08, 124.9, 124.8, 21.4. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{23}H_{17}^+$, 293.3885; found, 293.3879.

*3.1.4.29. 7-methoxy-1-(p-tolyl)naphthalene (31) [31].* Gradient eluting: PE → PE/EtOAc (100/1). White solid. M.p. 90–91 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J$ = 8.8 Hz, 1H), 7.84–7.79 (m, 1H), 7.48 (d, $J$ = 8.0 Hz, 2H), 7.45–7.41 (m, 2H), 7.39–7.32 (m, 3H), 7.23 (dd, $J$ = 9.0, 2.6 Hz, 1H), 3.82 (s, 3H), 2.51 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.9, 139.1, 138.2, 136.9, 132.9, 129.91, 129.86, 129.5, 129.2, 127.6, 127.3, 123.3, 118.4, 104.7, 55.3, 21.4. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{17}O^+$, 249.1274; found, 249.1268.

*3.1.4.30. 5-(p-tolyl)-1-naphthonitrile (32).* Gradient eluting: PE → PE/EtOAc (40/1). Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, $J$ = 8.4 Hz, 1H), 8.18 (d, $J$ = 8.8 Hz, 1H), 7.92 (dd, $J$ = 6.8, 1.2 Hz, 1H), 7.73 (dd, $J$ = 8.4, 7.2 Hz, 1H), 7.55 (dd, $J$ = 7.2, 1.2 Hz, 1H), 7.46 (dd, $J$ = 8.6, 7.0 Hz, 1H), 7.38–7.30 (m, 4H), 2.47 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.7, 136.7, 132.9, 132.7, 131.8, 131.6, 130.0, 129.3, 128.6, 128.2, 125.0, 124.6, 118.2, 110.5, 21.4. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{18}H_{14}N^+$, 244.1121; found, 244.1116.

*3.1.4.31. 2-(p-tolyl)pyridine (33) [28].* Gradient eluting: PE/EtOAc (20/1) → PE/EtOAc (5/1). White solid; M.p. 107–108 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.73–8.65 (m, 1H), 7.91 (d, $J$ = 8.4 Hz, 2H), 7.77–7.66 (m, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.23–7.15 (m, 1H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.6, 139.1, 136.8, 136.6, 129.6, 126.9, 121.9, 120.46, 21.4. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{12}H_{12}N^+$, 170.0964; found, 170.0959.

*3.1.4.32. 1-benzyl-4-methylbenzene (35) [15b].* Eluent: PE. Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 2H), 7.25–7.17 (m, 3H), 7.11 (s, 4H), 3.97 (s, 2H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.2, 135.7, 129.3, 129.0, 128.9, 128.6, 126.1, 41.7, 21.1; HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{14}H_{15}^+$, 183.1168; found, 183.1172.

*3.1.4.33. 4-(naphthalen-1-yl)benzaldehyde (43) [29].* Gradient eluting: PE → PE/EtOAc (40/1). White solid; M.p. 67–68 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.02 (d, $J$ = 8.2 Hz, 2H), 7.93 (t, $J$ = 8.0 Hz, 2H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 8.2 Hz, 2H), 7.60–7.51 (m, 2H), 7.50–7.43 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.3, 137.0, 133.5, 132.2, 132.0, 130.3, 129.6, 129.1, 128.2, 127.7, 127.4, 126.5, 125.7, 125.6, 125.4, 120.6, 111.7, 55.6. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{17}H_{13}O^+$, 233.0966; found, 233.0955.

*3.1.4.34. 2-(naphthalen-1-yl)furan (49) [31].* PE. Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, $J$ = 7.2 Hz, 1H), 7.98–7.91 (m, 1H), 7.89 (d, $J$ = 8.4 Hz, 1H), 7.80 (dd, $J$ = 7.2, 1.2 Hz, 1H), 7.68 (d, $J$ = 1.6 Hz, 1H), 7.64–7.53 (m, 3H), 6.79 (d, $J$ = 3.2 Hz, 1H), 6.64 (dd, $J$ = 3.2, 1.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.6, 142.5, 134.1, 130.5, 128.7, 128. 7, 128.6, 126.7, 126.3, 126.0, 125. 7, 125.4, 111.5, 109.3. HRMS-APCI (*m/z*): $[M+H]^+$ Calcd for $C_{14}H_{11}O^+$, 195.0810; found, 195.0801.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgement

We are grateful to the National Natural Science Foundation of China (22171110 and 21571087) for the financial support.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132431.

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