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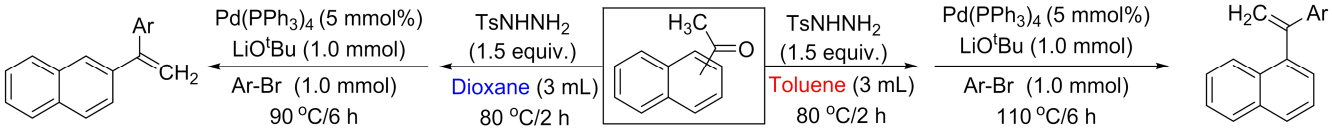

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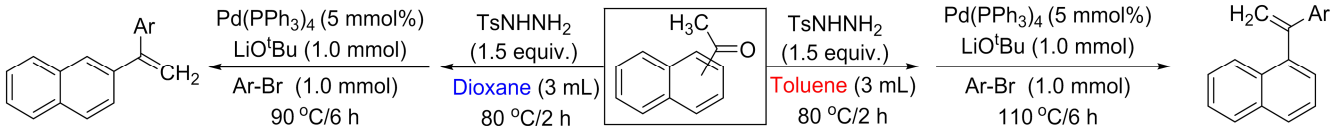

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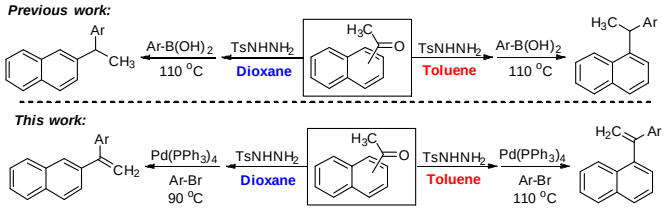
ABSTRACT

In this study, an one-pot two-step Pd-catalyzed reductive eliminate between acetyl naphthalene derivatives, tosylhydrazide, and aryl halide, affording substituted 1(or 2)-(1-phenylvinyl)naphthalene in moderate-to-excellent yields, was reported. Notably, solvent played a crucial role in the coupling of 1-acetyl naphthalene derivatives (toluene) or 2-acetyl naphthalene derivatives (1, 4-dioxane) as starting materials. Meanwhile, the scope of this one-pot coupling reaction was extended to 1(or 2)-naphthaldehyde substrates. Importantly, the catalytic system can be employed on a wide variety of substrates with good functional group tolerance. This protocol could also be particularly useful for the synthesis of olefins-substituents hydroxyl compounds.

1. Introduction

Substituted olefins are one of the versatile functional groups and intermediates in organic synthesis owing to their unique reaction properties[1]. Among the known synthetic routes to obtain the diarylethylene skeleton, the Mizoroki–Heck and the Wittig reactions are the most popular methods[2]. In addition, other related synthetic protocols were also reported[3-11]. Naphthyl-substituted olefins as an important member of this family have attracted considerable attention[12]. Very limited methods, especially those involving the naphthyl-substituted terminal olefins, have been developed for the synthesis of these type of products[13]. Thus, new methodologies for the efficient synthesis of this type of skeleton are highly desired. Transition-metal catalyzed cross-coupling reactions have been developed as an efficient approach for the synthesis of olefins[14]. However, these methods are often limited by sensitive/or expensive organometallic reagents, catalysts, and ligands, narrow substrate scopes, and so on.

Recently, *N*-tosylhydrazones proven to be highly versatile synthetic intermediates have attracted considerable interest in a variety of research fields[15]. In 2007, Barluenga *et al.* reported a palladium-catalyzed coupling reaction between *N*-tosylhydrazone and aryl halides for the preparation of polysubstituted olefins[16]. Subsequently, Barluenga's group and other groups investigated a series of palladium-catalyzed coupling reactions of different *N*-tosylhydrazone substrates with aryl halides to synthesize various substituted olefins[17]. In 2010, Wang *et al.* reported the Pd-catalyzed reaction of *N*-tosylhydrazones and arylboronic acids, providing olefin derivatives[18]. Meanwhile, they also reported the Pd(0)-catalyzed cross-coupling reactions of diazirines with aryl halides, affording a series of substituted olefins[19]. In 2015, Chen *et al.* reported olefin preparation via the palladium-catalyzed oxidative de-azotative and de-sulfitative internal cross-coupling of sulfonylhydrazones[20]. Based on our previous reports[21], herein, we envisioned a new approach for the synthesis of naphthyl-substituted terminal olefins by Pd-catalyzed one-pot coupling of acetylnaphthalene and tosylhydrazide with aryl halides(**Scheme 1**).



Scheme 1. One-pot coupling of acetylnaphthalene, $TsNHNH_2$ with aryl halide or arylboronic acids.

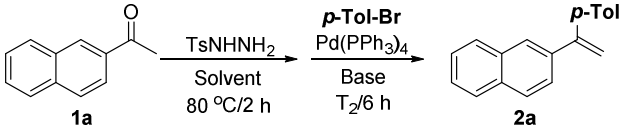
2. Results and Discussion

2.1. Optimization of the reaction conditions

Initially, *β*-acetylnaphthalene (0.5 mmol) and 4-bromotoluene (1.0 mmol) were used as the reactants for model reaction in the presence of tosylhydrazide (1.5 equiv) using $Pd(PPh_3)_4$ (5 mol%) as the catalyst, LiO^tBu (1.0 mmol) as the base, and 1,4-dioxane as the solvent, affording 80% yield of the desired product. The same reaction using $Pd(OAc)_2/PCy_3{\cdot}HBF_4$ as the catalyst instead of $Pd(PPh_3)_4$ afforded 66% yield of the desired product. Further,

the effects of bases on the reaction were investigated (Table 1). K_2CO_3, K_3PO_4, KOH, and Cs_2CO_3 gave lower yields in the range 40–72% (Entries 2–6). Moreover, solvent screening showed dioxane to the best solvent (Entries 7–10). In the presence of nitrogen (N_2) atmosphere, the product was obtained in 78% yield (Entry 10). The reaction proceeded more efficiently at high temperatures, and high yield was obtained when the temperature was increased up to 110 °C (Entry 11). Based on these observations, the optimized reaction conditions are as follows: dioxane as solvent, temperature 80 °C and reaction time(T_2) 6 h at 90 °C; and LiO^tBu as base.

Table 1. Optimized reaction conditions[a]



Entry	Base	Solvent	T_2(°C)	Yield (%)[b]
1	LiO^tBu	Dioxane	90	80/66[c]
2	K_2CO_3	Dioxane	90	56
3	K_3PO_4	Dioxane	90	66
4	KOH	Dioxane	90	40
5	Cs_2CO_3	Dioxane	90	72
6	LiO^tBu	Toluene	90	49
7	LiO^tBu	CH_3CN	90	58
8	LiO^tBu	DMF	90	72
9	LiO^tBu	DMSO	90	70
10	LiO^tBu	Dioxane	110	79
11[d]	LiO^tBu	Dioxane	90	78

[a] Reaction conditions: (i) 0.5 mmol *β*-acetylnaphthalene, 0.75 mmol tosylhydrazide, 3 mL solvent, 80 °C, 2 h; (ii) 1.0 mmol 4-bromotoluene, 2.0 equivalents base, 5 mol% catalyst, 90-110 ºC, 6 h.

[b] Isolated yield.

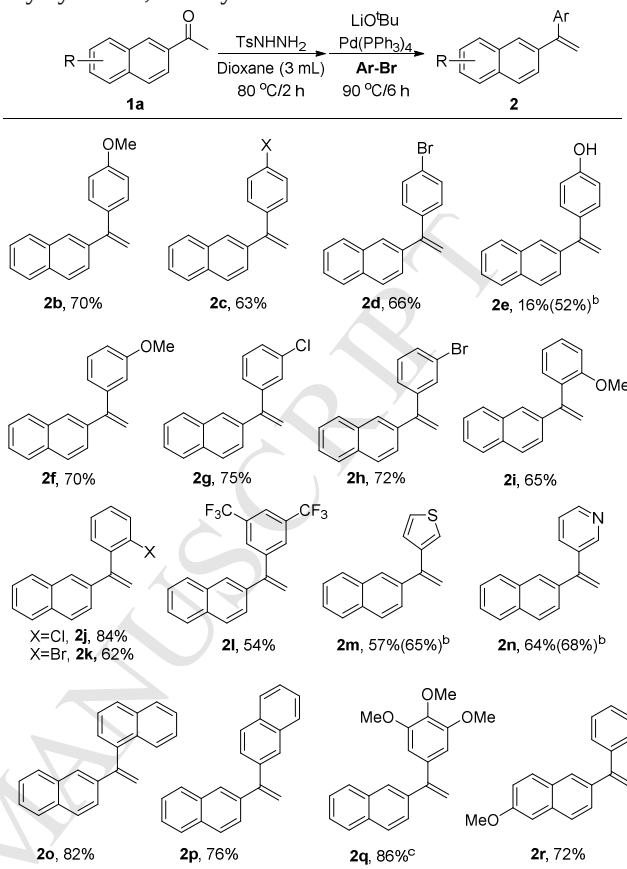
[c] 5 mol% $Pd(OAc)_2$ and 10 mol% PCy_3•HBF_4 as catalyst.

[d] N_2 protection.

2.2. Scope and limitations of substrates

With the optimized reaction conditions in hand, the scope of the reaction was then studied, and the results are depicted in Table 2. The electronic and steric nature of the substituents on the aryl halides did not significantly affect the reaction. The reaction worked well with both electron-donating substituents, such as a methoxy group (**2b**, **2f**, and **2i**) with similar results in different positions, and with electron-withdrawing substituents such as chlorine (**2c**, **2g**, **2j**) and bromine (**2d**, **2h**, and **2k**) groups, and these substituents were tolerated in the reaction conditions, which is advantageous for further transformations. However, the reaction of **2e** with a powerful electron-donating hydroxyl substituent at the para-position was relatively complicated and sluggish, affording only 16% of the desired product. The transformation worked for the substrate bearing CF_3 (**2l**) substituent; 2-bromonaphthalene (**2p**) and 1-bromonaphthalene (**2o**) also exhibited excellent substrate, affording 82% and 76% overall yields of the desired products, respectively. Identically, halogenated aromatic heterocycles such as 3-bromothiophene (**2m**) and 3-bromopyridine (**2n**) also showed moderate yields of 57% and 64%, respectively. Notably, when 5-bromo-1,2,3-trimethoxybenzene was used as a reaction partner, the desired product (**2q**) was obtained in 86% yield. The coupling reaction of 6-OMe substituted *β*-acetylnaphthalene and 1-bromo-2-fluorobenzene also led to the product **2r** in 72% yield. Using the *β*-acetylnaphthalene *N*-tosylhydrazone as substrates helped to improve the yields in some cases.

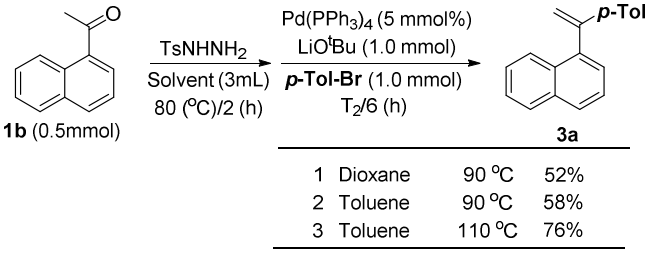
Table 2. One-pot reductive eliminating of *β*-acetylnaphthalene, tosylhydrazide, and aryl halide [a].



[a] Reaction conditions: (i) 0.5 mmol *β*-acetylnaphthalene, 0.75 mmol tosylhydrazide, 3 mL dioxane, 80 °C(T_1), 2 h; (ii) 1.0 mmol aryl bromide, 2.0 equivalents LiO^tBu, 5mol% $Pd(PPh_3)_4$, 90 ºC(T_2), 6 h. The yields of isolated products are given;

[b] *β*-Acetylnaphthalene *N*-tosylhydrazone was used;

[c] t = 2 h.

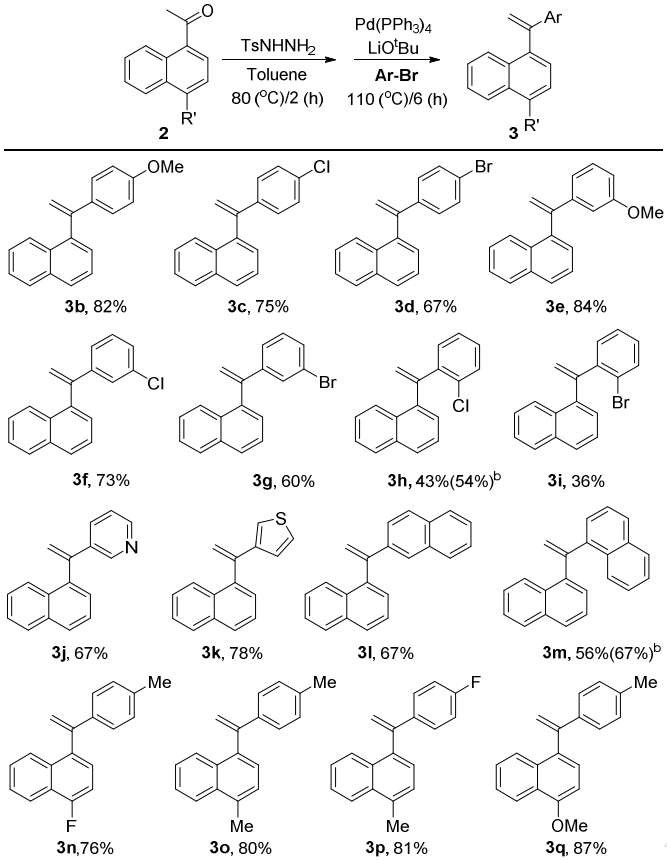


Scheme 2. The effect of solvent and temperature on the reaction of *α*-acetyl naphthalene, $TsNHNH_2$, with 4-bromotoluene.

Then, the scope of the substrates was expanded to α-acetylnaphthalene; however, the above-mentioned catalytic system was not found to be suitable for α-acetylnaphthalene. Therefore, reoptimization of the reaction conditions of α-acetylnaphthalene susbstrate was necessary(**Scheme 2**). Subsequently, *α*-acetylnaphthalene and 4-bromotoluene were selected as the substrates to further investigate the effects of other factors, including solvents and reaction temperature. Solvent is an important factor in the catalysis. When toluene was used as the primary solvent, 58% yield of the desired product **3a** was obtained. 1,4-Dioxane gave relatively low yields of the reaction products. Meanwhile, the reaction proceeded more efficiently at

high-temperature, i.e., when the temperature was increased up to 110 °C, the highest yield up to 76% was obtained.

Table 3. One-pot reductive eliminating of *α*-acetylnaphthalene, tosylhydrazide, and aryl halide [a].

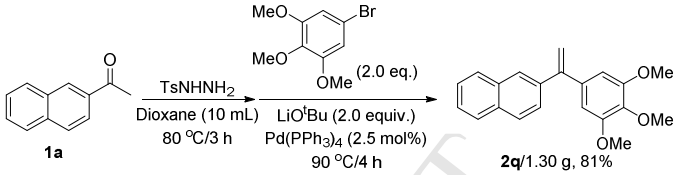


[a] Reaction conditions: (i) 0.5 mmol *α*-acetylnaphthalene, 0.75 mmol tosylhydrazide, 3 mL toluene, 80 °C, 2 h; (ii) 1.0 mmol aryl bromide, 2.0 equivalents LiO^tBu, 5 mol% $Pd(PPh_3)_4$, 110 ºC, 6 h;

[b] *α*-Acetylnaphthalene *N*-tosylhydrazone was used.

The scope of substrates was then investigated with this catalytic system under the optimized reaction conditions. As listed in Table 3, in general, most of the aryl halides reacted smoothly, affording the desired products in moderate to excellent yields. Seemingly, electron-donating group have a significant effect on the reaction. For example, aryl bromides with a methoxy group afforded the products **3b** and **3e** in 82% and 84% yield, respectively. Furthermore, naphthyl bromides, **3g** and **3i,** also afforded 67% and 56% yields, respectively. In addition, halogenated aromatic heterocycles such as 3-bromopyridine (**3j**) and 3-bromothiophene (**3k**) also reacted successfully, furnishing the desired products in 78% and 67% yields, respectively; however, aryl bromides (**3c**, **3d**, **3f**–**3i**) such as 1, 2-dibromobenzene, 1,4-dibromobenzene, 1,3-dibromobenzene, 4-bromochlorobenzene, 3-bromochlorobenzen, 2-bromochlorobenzene with electron-withdrawing groups afforded the corresponding products in low to moderate yields. The coupling of 1-bromonaphthalene and 2-bromonaphthalene as substrates also led to the products **3k** and **3l** in 67% and 56% yields, respectively. It is particularly gratifying that the reactions of α-acetylnaphthalene derivatives containing electron-donating group such as methoxyl and methyl substituents exclusively afforded the corresponding products **3o**-**3q** in the yields of 80-87%, and the reaction with 4-F substituent also furnished the desired product in 76% yield(**3n**). Using the *α*-acetylnaphthalene *N*-tosylhydrazone as substrates helped to improve the yields in some cases.

To demonstrate the practical usefulness of this reaction, a gram-scale experiment was carried out with *β*-acetylnaphthalene **1a** and 5-bromo-1, 2, 3-trimethoxybenzene. The gram-scale experiment gave comparable result (**Scheme 3**).



Scheme 3. A gram-scale synthesis of products **2q**.

3. Conclusions

To summarize, a simple and efficient method for the synthesis of olefins *via* Pd-catalyzed reductive elimination of aryl halide with *N*-tosylhydrazones *in situ* was developed, affording the corresponding target molecules in moderate to excellent yields. Moreover, the desired *N*-tosylhydrazones were not isolated, and the reaction was carried out in two steps one-pot directly to form the olefins derivatives. Potential substrates for this reaction are diverse, exhibiting a superior functional-group tolerance. Notably, this protocol was also found to be suitable for the synthesis of olefins-substituted hydroxyl compounds. Further studies to explore this reaction system to other related reactions are currently underway in our laboratory.

4. Experimental Section

4.1. Materials and instruments

Chemicals were obtained commercially and used as received. NMR spectra were recorded on a Bruker DPX–400 spectrometer using TMS as the internal standard. EI–Mass spectrum was measured on a LC/Q–TOF MS (Micromass, England) All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60–90 °C), unless otherwise noted. Acetylnaphthalene and its derivatives, and aryl bromides were of analytical grade quality, purchased from Adamas-beta Pharmaceuticals, Inc.

4.2. General procedure for Pd-catalyzed one-pot two-step reaction of acetylnaphthalene, N-tosylhydrazide with aryl halide

Acetylnaphthalene (0.5 mmol) and tosylhydrazide (0.75 mmol) were taken in 3 mL of solvent in in a reaction tube, and the resulting reaction mixture was stirred at 80 ºC for 2 h. Lithium tert-butoxide (1.5 mmol) and appropriate aryl bromide (1.0 mmol) were added to the reaction mixture. The system was heated under reflux at 90 ºC for 6 h with stirring. After the completion of the reaction, the reaction mixture was allowed to cool to room temperature. Dichloromethane and a saturated solution of $NaHCO_3$ were added to the cooled reaction mixture, and the layers were separated. The aqueous phase was re-extracted thrice with dichloromethane. The combined organic extract was washed with a saturated solution of $NaHCO_3$, followed by brine, dried over anhydrous $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the crude products thus obtained were purified by column chromatography on silica gel.

*4.3. 2-(1-(4-chlorophenyl)vinyl)naphthalene [**2c**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.71 (m, 4H), 7.53 – 7.42 (m, 3H), 7.32 (s, 4H), 5.60 (s, 1H), 5.53 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.11, 140.11, 138.53, 133.83, 133.39, 133.15, 129.81, 128.57, 128.31, 127.99, 127.75, 127.43,

126.42, 126.32, 115.34. HRMS (ESI) m/z calcd for $C_{18}H_{14}Cl^+$ $(M+H)^+$ 265.0778, found 265.0784.

*4.4. 2-(1-(4-bromophenyl)vinyl)naphthalene [**2d**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 3H), 7.74 (s, 1H), 7.51 – 7.42 (m, 5H), 7.27 – 7.23 (m, 3H), 5.60 (d, *J* = 0.8 Hz, 1H), 5.53 (d, J = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.15, 140.59, 138.44, 133.38, 133.15, 131.53, 130.15, 128.31, 128.00, 127.75, 127.44, 126.43, 126.33, 126.30, 122.02, 115.38. HRMS (ESI) m/z calcd for $C_{18}H_{14}Br^+$ $(M+H)^+$ 309.0273, found 309.0273.

*4.5. 4-(1-(naphthalen-2-yl)vinyl)phenol [**2e**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 4H), 7.51 – 7.43 (m, 3H), 7.40-7.34 (m, 5H), 5.59 (d, *J* = 1.2 Hz, 1H), 5.54 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.18, 141.64, 139.02, 133.42, 133.10, 128.52, 128.37, 128.32, 127.94, 127.82, 127.73, 127.42, 126.54, 126.29, 126.15, 114.98. HRMS (ESI) m/z calcd for $C_{18}H_{15}O^+$ $(M+H)^+$ 247.1117, found 247.1115.

*4.6. 2-(1-(3-chlorophenyl)vinyl)naphthalene [**2g**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.50 – 7.35 (m, 4H), 7.33 – 7.19 (m, 3H), 5.60 (d, *J* = 0.8 Hz, 1H), 5.53 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.02, 143.54, 134.35, 133.39, 133.16, 129.61, 128.55, 128.34, 128.03, 128.00, 127.75, 127.44, 126.70, 126.42, 126.34, 126.27, 115.91. HRMS (ESI) m/z calcd for $C_{18}H_{14}Cl^+$ $(M+H)^+$ 265.0779, found 265.0780.

*4.7. 2-(1-(3-bromophenyl)vinyl)naphthalene [**2h**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.54 (t, *J* = 1.6 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.31 – 7.26 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 0.8 Hz, 1H), 5.53 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.93, 143.83, 138.28, 133.38, 133.16, 131.42, 130.92, 129.90, 128.34, 128.04, 127.75, 127.44, 127.17, 126.43, 126.34, 126.24, 122.59, 115.97. HRMS (ESI) m/z calcd for $C_{18}H_{14}Br^+$ $(M+H)^+$ 309.0273, found 309.0274.

*4.8. 2-(1-(2-methoxyphenyl)vinyl)naphthalene [**2i**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 3H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.53 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.38 – 7.33 (m, 1H), 7.30 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.01 (td, *J* = 7.6, 1.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.85 (d, *J* = 1.2 Hz, 1H), 5.41 (d, *J* = 1.2 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.29, 147.09, 138.62, 133.49, 132.98, 131.49, 129.23, 128.38, 127.67, 127.63, 126.02, 125.80, 125.49, 124.87, 120.78, 116.12, 111.38, 55.74. HRMS (ESI) m/z calcd for $C_{19}H_{17}O^+$ $(M+H)^+$ 261.1274, found 261.1269.

*4.9. 2-(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)naphthalene [**2l**]*

White solide,, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 6H), 7.73 (d, J = 1.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (dd, J = 8.8, 2.0 Hz, 1H), 5.77 (s, 1H), 5.64 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.94, 143.85, 137.22, 133.42, 133.36, 131.84, 128.54, 128.48, 128.39, 127.84, 127.55, 126.74, 125.77, 124.81, 122.10, 121.75, 117.77. HRMS (ESI) m/z calcd for calcd for $C_{20}H_{12}F_6^+$ $(M)^+$ 366.0838, found 366.0841.

*4.10. 3-(1-(naphthalen-2-yl)vinyl)pyridine [**2n**]*

Brown solide,, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 6H), 7.73 (d, *J* = 1.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.77 (s, 1H), 5.64 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.94, 143.85, 137.22, 133.42, 133.36, 131.84, 128.54, 128.48, 128.39, 127.84, 127.55, 126.74, 125.77, 124.81, 122.10, 121.75, 117.77. HRMS (ESI) m/z calcd for calcd for $C_{20}H_{12}F_6^+$ $(M)^+$ 366.0838, found 366.0841.

*4.11. 2-(1-(2-fluorophenyl)vinyl)-6-methoxynaphthalene [**2r**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 9.8 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.49 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.21 – 7.14 (m, 1H), 7.13 – 7.04 (m, 3H), 5.85 (d, *J* = 1.2 Hz, 1H), 5.46 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.35 (d, *J* = 248.3 Hz), 158.00 , 144.21 , 135.88 , 134.31 , 131.77 (d, *J* = 3.6 Hz), 129.91 , 129.59 (d, *J* = 14.5 Hz), 129.51 (d, *J* = 8.1 Hz), 128.86 , 126.87 , 125.97 , 125.44 , 124.12 (d, *J* = 3.7 Hz), 119.09 , 116.81 (d, *J* = 2.1 Hz), 115.96 (d, *J* = 22.3 Hz), 105.79 , 55.46 . HRMS (ESI) m/z calcd for $C_{19}H_{16}FO^+$ $(M+H)^+$ 279.1179, found 279.1188.

*4.12. 1-(1-(4-chlorophenyl)vinyl)naphthalene [**3c**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.39 (m, 3H), 7.35 – 7.29 (m, 1H), 7.22 – 7.21 (m, 4H), 5.95 (d, *J* = 1.2 Hz, 1H), 5.39 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.37, 139.65, 139.35, 133.84, 133.69, 131.80, 128.69, 128.40, 128.33, 128.05, 127.40, 126.35, 126.14, 125.92, 125.58, 116.80. HRMS (ESI) m/z calcd for $C_{18}H_{14}Cl^+$ $(M+H)^+$ 265.0778, found 265.0779.

*4.13. 1-(1-(3-methoxyphenyl)vinyl)naphthalene [**3e**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.43 – 7.39 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 1H), 6.91 – 6.86 (m, 2H), 6.81 – 6.76 (m, 1H), 5.96 (d, *J* = 1.6 Hz, 1H), 5.38 (d, J = 1.6 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.74, 148.32, 142.76, 139.80, 133.80, 132.00, 129.46, 128.28, 128.10, 127.33, 126.52, 126.00, 125.79, 125.51, 119.53, 116.65, 112.97, 112.71, 55.31. HRMS (ESI) m/z calcd for $C_{19}H_{17}O^+$ $(M+H)^+$ 261.1274, found 261.1263.

*4.14. 1-(1-(3-bromophenyl)vinyl)naphthalene [**3g**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.31 (m, 6H), 7.16 (dt, *J* = 8.0, 1.6, 1.2 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 5.96 (d, *J* = 1.2 Hz, 1H), 5.42 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.23, 143.44, 139.04, 133.86, 131.77, 130.80, 130.04, 129.52, 128.41, 127.46, 126.29, 126.20, 125.94, 125.62, 125.55, 122.83, 117.72. HRMS (ESI) m/z calcd for $C_{18}H_{14}Br^+$ $(M+H)^+$ 309.0273, found 309.0275.

*4.15. 1-(1-(2-bromophenyl)vinyl)naphthalene [**3i**]*

Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 6H), 7.73 (d, *J* = 1.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.77 (s, 1H), 5.64 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.94, 143.85, 137.22, 133.42, 133.36, 131.84, 128.54, 128.48, 128.39, 127.84, 127.55, 126.74, 125.77, 124.81, 122.10, 121.75, 117.77. HRMS (ESI) m/z calcd for calcd for $C_{20}H_{12}F_6^+$ $(M)^+$366.0838, found 366.0841.

*4.16. 3-(1-(naphthalen-1-yl)vinyl)pyridine [**3j**]*

Brown solide, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.49 (d, *J* = 4.0 Hz, 1H), 7.87 (dt, *J* = 8.0, 1.2, 0.8 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.35 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 5.51 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.86, 147.91, 145.58, 138.55, 136.78, 134.04, 133.90, 131.60, 128.57, 128.50, 127.48, 126.30, 126.14, 126.00, 125.58, 123.34, 118.03.

HRMS (ESI) m/z calcd for $C_{17}H_{14}N^+$ $(M+H)^+$ 232.1121, found 232.1121.

*4.17. 3-(1-(naphthalen-1-yl)vinyl)thiophene [**3k**]*

White solide, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 8.0 Hz, 3H), 7.56 – 7.47 (m, 3H), 7.41 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.35 – 7.29 (m, 2H), 6.81 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 5.35 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.37, 143.15, 139.92, 133.76, 131.89, 128.27, 128.04, 126.71, 126.46, 125.99, 125.85, 125.69, 125.53, 123.37, 116.98, 115.06. HRMS (ESI) m/z calcd for $C_{16}H_{13}S^+$ $(M+H)^+$ 237.0732, found 237.0733.

*4.18. 1-fluoro-4-(1-(p-tolyl)vinyl)naphthalene [**3n**]*

White solide, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.21 (m, 1H), 7.20 – 7.11 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 5.92 (d, *J* = 1.2 Hz, H), 5.30 (d, *J* = 1.2 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.57, 147.60, 138.27, 137.79, 136.14, 133.29, 129.25, 128.55, 127.44, 126.89, 126.62, 126.09, 123.93, 120.78, 115.83, 109.03, 21.27. HRMS (ESI) m/z calcd for $C_{19}H_{16}F^+$ $(M+H)^+$ 263.1231, found 263.1231.

*4.19. 1-methyl-4-(1-(p-tolyl)vinyl)naphthalene [**3o**]*

White solide, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.34 – 7.30 (m, 4H), 7.22 – 7.18 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 1.6 Hz, 1H), 5.30 (d, *J* = 1.6 Hz, 1H), 2.71 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.38, 138.54, 138.50, 137.56, 134.18, 132.86, 132.08, 129.18, 128.47, 127.24, 126.99, 126.64, 126.33, 125.62, 124.39, 115.33, 21.27, 19.70. HRMS (ESI) m/z calcd for $C_{20}H_{19}^+$ $(M+H)^+$ 259.1481, found 259.1482.

*4.20. 1-(1-(4-fluorophenyl)vinyl)-4-methylnaphthalene [**3p**]*

White solide, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.46 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 7.38 – 7.19 (m, 5H), 6.91 (t, *J* = 8.7 Hz, 2H), 5.88 (d, *J* = 1.3 Hz, 1H), 5.34 (d, *J* = 1.3 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.45 (d, *J* = 247.1 Hz), 147.51, 137.92 , 137.42 (d, *J* = 3.3 Hz), 134.41 , 132.83 , 131.78 , 128.30 (d, *J* = 8.0 Hz), 126.96 , 126.25 , 125.63 , 124.40 , 115.87 (d, *J* = 1.7 Hz), 115.23 (d, *J* = 21.6 Hz), 19.60. HRMS (ESI) m/z calcd for $C_{19}H_{16}F^+$ $(M+H)^+$ 263.12306, found 263.12305.

*4.21. 1-methoxy-4-(1-(p-tolyl)vinyl)naphthalene [**3q**]*

White solide, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.29 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 1H), 6.80 (d, *J* =7.6 Hz, 1H), 5.88 (d, *J* = 1.6 Hz, 1H), 5.30 (d, *J* = 1.6 Hz, 1H), 4.00 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.29, 148.27, 138.76, 137.51, 132.89, 132.46, 129.15, 128.45, 127.28, 126.69, 126.45, 125.77, 125.09, 122.18, 115.26, 103.39, 55.64, 21.26. HRMS (ESI) m/z calcd for $C_{20}H_{19}O^+$ $(M+H)^+$ 275.1430, found 275.1430.

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References and notes

1. (a) Franssen, N.; Reek, H.; de, B. *Chem. Soc. Rev.* **2013**, *42*, 5809-5832. (b) Kress, S.; Blechert, S. *Chem. Soc. Rev.* **2012**, *41*, 4389-4408. (c) Demonceau, A.; Dragutan, I.; Dragutan, V.; Le, G. P. *Curr. Org.Synth.* **2012**, *9*, 779-790. (d) Feng, X.; Du, H. *Asian J. Org. Chem.* **2012**, *1*, 204-213. (e) Morzycki, J. W. *Steroids* **2011**, *76*, 949-966.
2. Heck R.F.; Nolley, J.P. *J. Org. Chem.* **1972**, *37*, 2320-2322.
3. Lei, C.; Yip, Y. J.; Steve Zhou, J. *J. Am. Chem. Soc*. **2017**, *139*, 6086-6089.
4. (a) Patel, H.A.; Patel A.L.; Bedekar, A.V.; *Appl. Organometal. Chem.* **2015**, *29*, 1-6; (b) Christophe, D.; Wang, D.; Salmon, L.; Laetitia, E.; Labrugere, C.; Jaime, R.; Didier, A. *ChemCatChem.* **2015**, *7*, 303-308; (c) Liu, X.; Zhao X.H.; Lu, M. *Catal Lett.* **2015**, *145*, 1549-1556; (d) Mamidala, R.; Mukundam, V.; Dhanunjayarao, K.; Venkatasubbaiah, K. *Dalton Trans.* **2015**, 44, 5805-5809; (e) Shen, C.; Shen, H.Y.; Yang, M.; Xia C.C.; Zhang, P.F. *Green Chem.* **2015**, *17*, 225-230.
5. (a) Meijere, A.; Meyer, F.E. *Angew. Chem. Int. Ed.* **1995**, *33*, 2379-2411; (b) Beletskaya I. P.; Cheprakov, A.V. *Chem. Rev.* **2000**, *100*, 3009-3066; (c) Amatore C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314-321.
6. Shirakawa, E.; Watabe, R.; Murakami, T.; Hayashib, T. *Chem. Commun.* **2013**, *49*, 5219-5221.
7. Zhang, M.N.; Jia, T.Z.; Yin, H.L.; Carroll, P.J.; Schelter E.J.; Walsh, P.J. *Angew. Chem. Int. Ed.* **2014**, *53*, 10755-10758; *Angew. Chem.* **2014**, *126*, 10931-10934.
8. Tanaka, S.; Mori, A.; *Eur. J. Org. Chem.* **2014**, *2014*, 1167-1171.
9. Richmond, E.; Moran, J. *J. Org. Chem.* **2015**, *80*, 6922-6929.
10. Fu, S.M.; Chen, N.Y.; Liu, X.F.; Shao, Z.H.; Luo, S.P.; Liu, Q. *J. Am. Chem. Soc.* **2016**, *138*, 8588-8594.
11. Zhong, J.J.; Liu, Q.; Wu, C.J.; Meng, Q.Y.; Gao, X.W.; Li, Z.J.; Chen, B.; Tung, C.H.; Wu, L.Z. *Chem. Commun.* **2016**, *52*, 1800-1803.
12. (a) Kos, T.; Strissel, C.; Yagci, Y.; Nugay, T.; Nuyken, O. *European Polymer Journal* **2005**, *41*, 1265-1271.(b) Zhang, G. F.; Wang, H. F.; Aldred, M. P.; Chen, T.; Chen, Z.; Meng, X.; Zhu, M.; *Chemistry of Materials* **2014**, *26*, 4433-4446. (c) Braun, D.; Platzek, U.; Hefter, H. J., *Chemische Berichte* **1971**, *104*, 2581-2587. (d) Zhou, J.; Chang, Z.; Jiang, Y.; He, B.; Du, M.; Lu, P.; Hong, Y.; Kwok, H. S.; Qin, A.; Qiu, H.; Zhao, Z.; Tang, B. Z., *Chem. Commun*. **2013**, *49*, 2491-2493.(e) Li, H. H.; Jin, Y.; Wang, J.; Tian, S., *Organic & Biomolecular Chemistry* 2009, 7, 3219-3221.(f) Zhou, J; Chang, Z.; Jiang, Y.; He, B.; Du, M.; Lu, P.; Hong, Y.; Kwok, H.; Qin, A.; Qiu, H. Z.; Tang, B. Z.; Chem. Commun. **2013**, *49*, 2491-2493.(g) Gao, M.; Wu, Y.; Chen, B.; He, B.; Nie, H.; Li, T.; Wu, F.; Zhou, W.; Zhou, J.; Zhao, Z. *Polymer Chemistry* **2015**, *6*, 7641-7645.
13. (a) Dhandapani G.; Govindasamy S.; *Org. Lett.* **2014**, *16*, 3856-3859. (b) Tan, H.; Houpis, I.; Liu, R.; Wang, Y.; Chen, Z. *Org. Lett.* **2015**, *17*, 3548-3551. (c) Anders L. H.; Jean-Philippe E.; Thomas M. G.; and Troels S. *J. Org. Chem.* **2009**, *74*, 3536-3539. (d) Maddali L. N. R.; Deepak N. J.; and Varadhachari V. *Eur. J. Org. Chem.* **2009**, 4300-4306. (e) Zou, Y.; Qin, L.; Ren, X.; Lu, Y.; Li, Y.; and Zhou, J. *Chem. Eur. J.* **2013**, 19, 3504-3511. (f) Zhao, X.; Wu, G.; Yan, C.; Lu, K.; Li, H.; Zhang, Y.; and Wang, J.; *Org. Lett.* **2010**, 12, 5580-5583.
14. (a) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486-7500. (b) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236-247.(c) Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 11577-11585. (d) Jiao, J.; Nakajima,K.; Nishihara, Y. *Org. Lett.* **2013**, *15*, 3294-3297. (e) Jin, W. W.; Du, W. M.; Yang, Q.; Yu, H. F.; Chen, J. P.; Yu, Z. K. *Org. Lett.* **2011**, *13*, 4272-4275. (f) Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560-572. (g) Barluenga, J.; Escribano, M.; Aznar, F.; Valdes, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 6856-6859. (h) Jiao, J.; Hyodo, K.; Hu, H.; Nakajima, K.; Nishihara, Y. *J. Org. Chem.* **2014**, *79*, 285-295. (i) Ye, S.; Yang, X.; Wu, J. *Chem. Commun.* **2010**, *46*, 2950-2952. (j) Sun, C. L.; Wang, Y.; Zhou, X.; Wu, Z. H.; Li, B. J.; Guan, B. T.; Shi, Z. J. *Chem. Eur. J.* **2010**, *16*, 5844-5847.
15. (a) J. Robin F., Varinder K. A.; Javier de V. *Eur. J. Org. Chem.* **2005**, 2005, 1479-1492. (b) Barluenga J.; Valdés, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 7486-7500; (c) Shao Z. and Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560-572; (d) Xu. K.; Shen. C.; Shan. S. *Chin. J. Org. Chem.* **2015**, *35*, 294-308; (e) Liu, Z.; Zhang, Y.; Wang, J. *Chin. J. Org. Chem.* **2013**, *33*, 687-692. (f) Xiao, Q.; Zhang, Y.;

Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236-247. (g) Zhang, Y.; Wang, J.; *Top Curr Chem* **2012**, *327*, 239-270;

16. Barluenga, J.; Moriel, P.; Valdés, C.; Aznar, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5587-5590.
17. (a) Barluenga, J.; Tomes-Gamasa, M.; Aznar, F.; Valdés, C. *Adv. Synth. Catal.* **2010**, *352*, 3235-3240. (b) Tréguier, B.; Hamze, A.; Provot, O.; Jean-Daniel B.; Alami, M. *Tetrahedron Letters* **2009**, *50* 6549-6552. (c) Barluenga, J.; Escribano, M.; Aznar, F.; Valdés, Carlos. *Angew. Chem.* **2010**, *122*, 7008-7011. (d) Barluenga, J.; Tomes-Gamasa, M.; Moriel, P.; Aznar, F.; Valdés, C. *Chem. Eur. J.* **2008**, *14*, 4792-4795. (e) Barluenga, J.; Escribano, M.; Moriel, P.; Aznar, F.; Valdés, C. *Chem. Eur. J.* **2009**, *15*, 13291-13294. (f) Barluenga, J.; Tomes-Gamasa, M.; Moriel, P.; Aznar, F.; Valdés, C. *Chem. Eur. J.* **2010**, *16*, 12801-12803. (g) Barluenga, J.; Florentino, L.; Aznar, F.; Valdés, C. *Org. Lett.* **2011**, *13*, 510-513. (h) Brachet, E.; Hamze, A.; Peyrat, J.; Brion, J.; Alami, M. *Org. Lett.* **2010**, *12*, 4042-4045. (i) Ganapathy D.; and Sekar, G. *Org. Lett.* **2014**, *16*, 3856-3859. (j) Zhang, Z.; Liu, Y.; Gong, M.; Zhao, X.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2010**, *49*, 1139-1142.
18. Zhao, X.; Jing, J.; Lu, K.; Zhang Y.; Wang, J. *Chem. Commun.* **2010**, *46*, 1724-1726.
19. Zhao, X.; Wu, G.; Yan, C.; Lu, K.; Li, H.; Zhang, Y.; Wang, J. *Org. Lett.* **2010**, *12*, 5580-5583.
20. Tan, H.; Houpis, I.; Liu, R.; Wang, Y.; and Chen, Z. *Org. Lett.* **2015**, *17*, 3548-3551.
21. (a) Shen, X.; Gu, N.N.; Liu, P.; Ma, X.W.; Xie, J.W.; Liu, Y.; He, L.; Dai, B. *RSC Adv.* **2015**, *5*, 63726-63731; (b) Shen, X.; Gu, N.N.; Liu, P.; Ma, X.W.; Xie, J.W.; Liu, Y.; Dai, B. Chin. J. Chem. **2016**, *34*, 1033-1038; (c) Shen, X.; Liu, P.; Liu, Y.; Liu, Y.; Dai, B. Tetrahedron **2017**, *73*, 785-793; Liu, Y.; Liu, P.; Liu, Y.; and Wei, Y. *Chin. J. Chem.* **2017**, *35*, 1141-1148.

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