有机化学 DOI: 10.6023/cjoc201805022 研究论文
Chinese Journal of Organic Chemistry ARTICLE

钌(III)催化的芳烃室温邻位羟甲基化反应

张 勇 杨中振 余昕玲 程 旭 李伟剑
郭令妹 海 俐 郭 丽* 吴 勇*
(四川大学华西药学院 成都 610041)

摘要 开发了一种通过钌(III)催化的 N-导向碳氢活化反应来直接合成羟甲基化芳烃衍生物的新方法. 该方法的底物适用范围广泛, 室温条件下即可以较高收率制得目标产物. 为化学结构中含有羟甲基的生物活性化合物的合成提供了新的思路.

关键词 碳氢活化; 多聚甲醛; 羟甲基化; 室温

Room Temperature Ru(III)-Catalyzed *ortho*-Hydroxymethylation of Arenes

Zhang, Yong Yang, Zhongzhen Yu, Xinling Cheng, Xu Li, Weijian
Guo, Lingmei Hai, Li Guo, Li* Wu, Yong*
(*Key Laboratory of Drug-Targeting of Education Ministry and Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University, Chengdu 610041*)

Abstract Direct synthesis of the hydroxymethylated arene derivatives via ruthenium(III)-catalyzed nitrogen atom directed C—H activation is described. The reaction proceeds smoothly at room temperature and generates the corresponding products in moderate to excellent yields. Meanwhile, it has a broad substrate scope and opens up an attractive avenue for the application of direct hydroxymethylation in the synthesis of biologically active compounds.

Keywords C—H activation; paraformaldehyde; hydroxymethylation; room temperature

1 Introduction

Hydroxymethylated arenes are one of the most important and widely occurring structural units in many natural products and biologically active compounds (Figure 1).[1] They are rifely existed in a variety of drug molecules. For example, salbutamol sulfate[1a] is a β_2-adrenoceptor agonist that was first launched by GlaxoSmithKline (GSK) in 1968 for the treatment of asthma (Figure 1). In 2002, it was commercialized for the prevention of chronic obstructive pulmonary disease (COPD). Salmeterol,[1b] marketed and manufactured by GSK in 1990, was also used in the maintenance and prevention of asthma symptoms (Figure 1). Fesoterodine fumarate,[1c] a muscarinic antagonist developed by Schwarz Pharma, was first launched in the U.K. in 2008, followed by E.U. approval for the treatment of urinary urge incontinence and overactive bladder (OAB) (Figure 1). Oxamniquine,[1d] sold under the brand name Vansil among others, is a medication used to treat schistosomiasis due to *Schistosoma mansoni* (Figure 1). Because of their enormous value in pharmaceuticals, a variety of methods have been developed to synthesize the substituted hydroxymethylated arenes over the past several decades.[2~14] Common starting materials include the benzyl grignard reagents,[2] benzoic acids,[3] benzaldehydes,[4] aryl esters,[5] benzyl halides,[6] benzoyl chlorides,[7] 1,2-diphenylethylene,[8] benzamides,[9] benzonitriles,[10] benzyl ethers,[11] potassium benzyltrifluoroborate,[12] iodobenzene[13] and benzylamine.[14] However, all these reported methods suffer from one or more drawbacks such as multiple steps, harsh reaction conditions, low yields of products, poor functional group tolerance, and the use of expensive or toxic reagents (*eg* CO gas). Therefore, the development of a more milder, convenient, high yields

* Corresponding authors. E-mail: guoli@scu.edu.cn; wyong@scu.edu.cn
Received May 9, 2018; revised July 31, 2018; published online Septemer 5, 2018.
Project supported by the National Natural Science Foundation of China (Nos. 81373259, 81573286, 81602954).
国家自然科学基金(Nos. 81373259, 81573286, 81602954)资助项目.

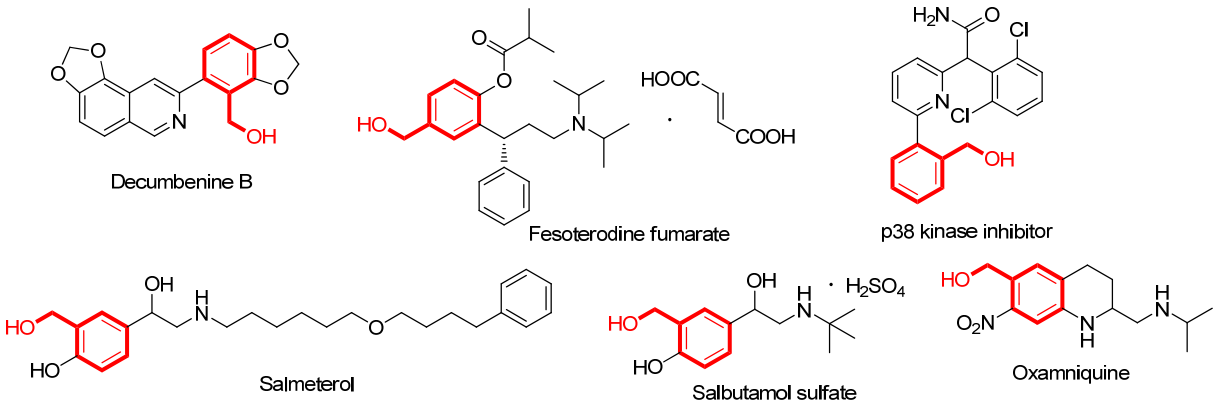


Figure 1 Hydroxymethylated arenes as core structures in natural products and biologically active compounds

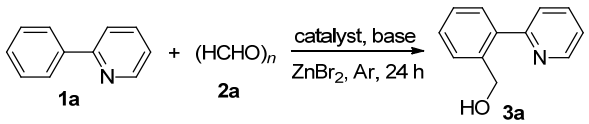
synthetic method to access hydroxymethylated arenes is still highly necessary.

On the other hand, paraformaldehyde, as an infinite solid form of formaldehyde, has been widely used to install a hydroxymethyl group into various substrates.[15~17] It can also be used as a methylene block,[18] CO source,[19] hydrogen donor or acceptor,[20] formylation[21] and methylation reagent[22] in the presence of metal or organocatalysis. Since the discovery of its structure about 100 years ago,[23] paraformaldehyde has become a very important raw material for the chemical industry due to its advantages in low-cost, stability and low toxicity.[24] Last year, the group of Ding[25] reported an efficient Ru(II)-catalyzed regioselective direct hydroxymethylation using paraformaldehyde as the hydroxymethylating reagent via C—H activation. Zhou and co-workers[26] disclosed a Ru(II)-catalyzed site-selective C—H hydroxy-methylation of arenes with formalin as the hydroxymethylating reagent. Recently, we[27] developed a novel and efficient method for the total synthesis of natural product decumbenine B. With this method, decumbenine B could be easily synthesized from commercially available materials by only five steps with an overall yield of 26.1%.[27] After further research, we found that Ru(III) has better catalytic activity than Ru(II) in the synthesis of hydroxymethylated arenes. Here, we report on our progress in achieving direct Ru(III)-catalyzed regioselective hydroxy-methylation of arenes via room temperature C—H activation. In comparison with the two well-established methods of Ding and Zhou groups, our work can be conducted at room temperature with good to excellent yields.

2 Results and discussion

At the beginning of our investigation, the optimization of reaction conditions was focused on a variety of reaction parameters by using 2-phenylpyridine (**1a**) as a model substrate. After extensive screenings, we were pleased to find that $RuCl_3•xH_2O$ was the optimal catalyst for the synthesis of **3a** (Table 1, Entries 1～7). Among the various bases examined, $ZnMe_2$ turned out to be the best choice, while others, such as NaOH, *t*-BuOK, Cs_2CO_3 and AcOK, were less effective (Table 1, Entries 7～11). Further research

Table 1 Optimization of reaction conditions[a]



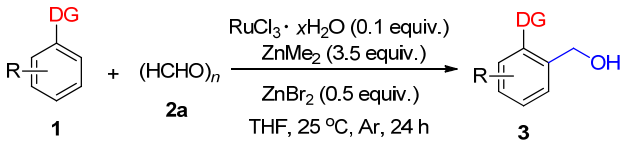
Entry	Catalyst	Base (equiv.)	Temp./℃	Yield[b]/%
1	$MnBr(CO)_5$	$ZnMe_2$ (2.0)	100	63
2	$[RuCl_2(p\text{-cymene})]_2$	$ZnMe_2$ (2.0)	100	61
3	$Cp^*Rh(MeCN)_3(SbF_6)_2$	$ZnMe_2$ (2.0)	100	Trace
4	$Cp^*Co(MeCN)_3(SbF_6)_2$	$ZnMe_2$ (2.0)	100	Trace
5	Cp^*IrCl_2	$ZnMe_2$ (2.0)	100	N.R[m]
6	$AuCl(PPh_3)_2$	$ZnMe_2$ (2.0)	100	N.R[m]
7	$RuCl_3•xH_2O$	$ZnMe_2$ (2.0)	100	69
8	$RuCl_3•xH_2O$	NaOH (2.0)	100	6
9	$RuCl_3•xH_2O$	*t*-BuOK (2.0)	100	11
10	$RuCl_3•xH_2O$	Cs_2CO_3 (2.0)	100	13
11	$RuCl_3•xH_2O$	AcOK (2.0)	100	N.R[m]
12	$RuCl_3•xH_2O$	$ZnMe_2$ (2.0)	60	65
13	$RuCl_3•xH_2O$	$ZnMe_2$ (2.0)	25	64
14	$RuCl_3•xH_2O$	$ZnMe_2$ (3.0)	25	74
15	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	83
16	$RuCl_3•xH_2O$	$ZnMe_2$ (4.0)	25	79
17	$RuCl_3•xH_2O$ (0.05 equiv.)	$ZnMe_2$ (3.5)	25	43
18	$RuCl_3•xH_2O$ (0.2 equiv.)	$ZnMe_2$ (3.5)	25	80
19[c]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	77
20[d]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	84
21[e]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	N.R[m]
22[f]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	82
23[g]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	61
24[h]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	71
25[i]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	36
26[j]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	21
27[k]	$RuCl_3•xH_2O$	$ZnMe_2$ (3.5)	25	47
28[l]	$RuCl_3$	$ZnMe_2$ (3.5)	25	85

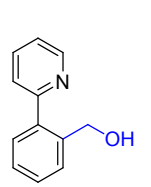
[a] Reaction conditions: **1a** (1 mmol), **2a** (5 mmol), catalyst (0.1 mmol), base (2 mmol), $ZnBr_2$ (1 mmol), THF (1 mL), Ar, 24 h; [b] Isolated yield; [c] $ZnBr_2$ (1.5 mmol); [d] $ZnBr_2$ (0.5 mmol); [e] $ZnBr_2$ (0 mmol); [f] **2a** (10 mmol); [g] **2a** (3 mmol); [h] in DCE; [i] in DMF; [j] in DMSO; [k] in MeCN; [l] in anhydrous THF; [m] No Reaction.

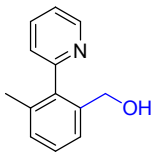
indicated that temperature was not important for this transformation. The yield of **3a** did not decrease significantly when the reaction temperature cooling to 25 ℃ (Table 1, Entries 12, 13). For the optimization of the amounts of $ZnMe_2$, $RuCl_3$•xH_2O, $ZnBr_2$ and **2a** used in the model reaction, 3.5, 0.1, 0.5 and 5 equiv. were found to be adequate, as neither larger nor smaller amount showed better yields (Table 1, Entries 14～23). Increasing the amount of **2a** to 10 equiv. did not produce the disubstituted product, and the yield did not differ significantly (Table 1, Entry 22). When the reaction was allowed to proceed in different solvents, an optimal yield of 84% was obtained in THF (Table 1, Entries 20, 24～27). Notably, no obvious difference can be found when the reaction was catalyzed by $RuCl_3$ in anhydrous THF (Table 1, Entry 28). Therefore, as observed in this study, the optimized conditions for the synthesis of **3a** proved to be 2-phenylpyridine (1 mmol), **2a** (5 mmol), $RuCl_3$•xH_2O (0.1 mmol), $ZnMe_2$ (3.5 mmol), $ZnBr_2$ (0.5 mmol) in THF at 25 ℃.

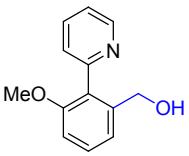
In order to evaluate the versatility of this novel method, we applied the procedure to the hydroxymethylation of a wide range of arenes. The results are summarized in Table 2. A host of 2-arylpyridines bearing either the electron-donating groups, such as methyl, methoxy and *tert*-butyl, or the electron-withdrawing groups, such as halogen and trifluoromethyl, were well tolerated during the course of the reaction, providing the desired compounds **3a**～**3m** in good to excellent yields (Table 2). The results showed that electron-donating groups could improve the reaction yields. In addition to the pyridine group, products **3p**～

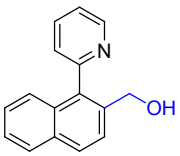
Table 2 Substrate scope[a]

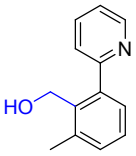


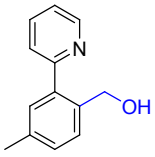

3a, 84%b

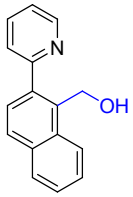

3b, 87%b

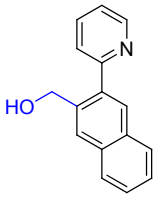

3c, 96%[b]

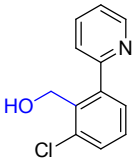

3d, 84%[b]

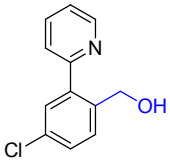

3e, 15%[b]

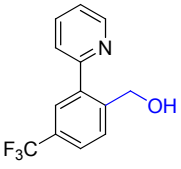

3e', 73%[b]

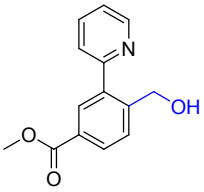

3f, 9%[b]

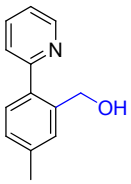

3f', 74%[b]

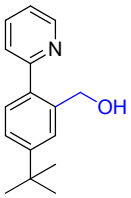

3g, 37%[b] (71%)[c]

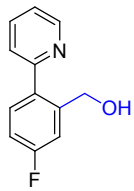

3g', 40%[b] (71%)[c]

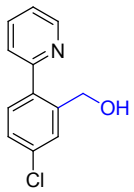

3h, 62%[b] (39%)[c]

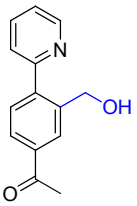

3i, 71%[b] (54%)[c]

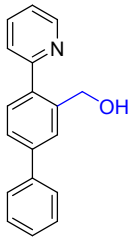

3j, 71%[b]


3k, 88%[b]

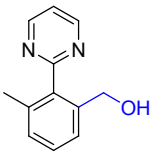

3l, 72%[b] (70%)[c]

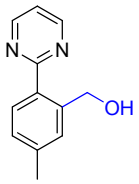

3m, 63%[b] (90%)[c]

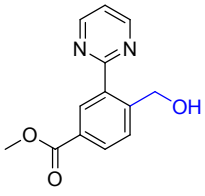

3n, 44%[b]

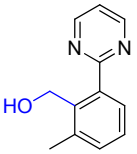

3o, 74%[b]

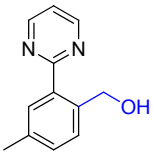

3p, 58%[b] (72%)[c]

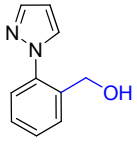

3q, 77%[b]

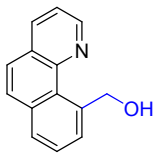

3r, 52%[b]

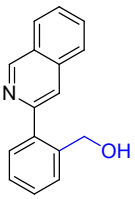

3s, 40%[b] (34%)[c]


3t, 27%[b]


3t', 54%[b]


3u, 80%[b] (67%)[c]


3v, 57%[b] (58%)[c]


3w, 75%[b]

[a] Reaction conditions: **1** (1 mmol), **2a** (5 mmol), $RuCl_3$•xH_2O (0.1 mmol), $ZnMe_2$ (3.5 mmol), $ZnBr_2$ (0.5 mmol), THF (1 mL), Ar, 24 h; [b] Isolated yield; [c] conversion rates are listed in the square brackets; [d] yield determined by ^1H NMR spectroscopy.

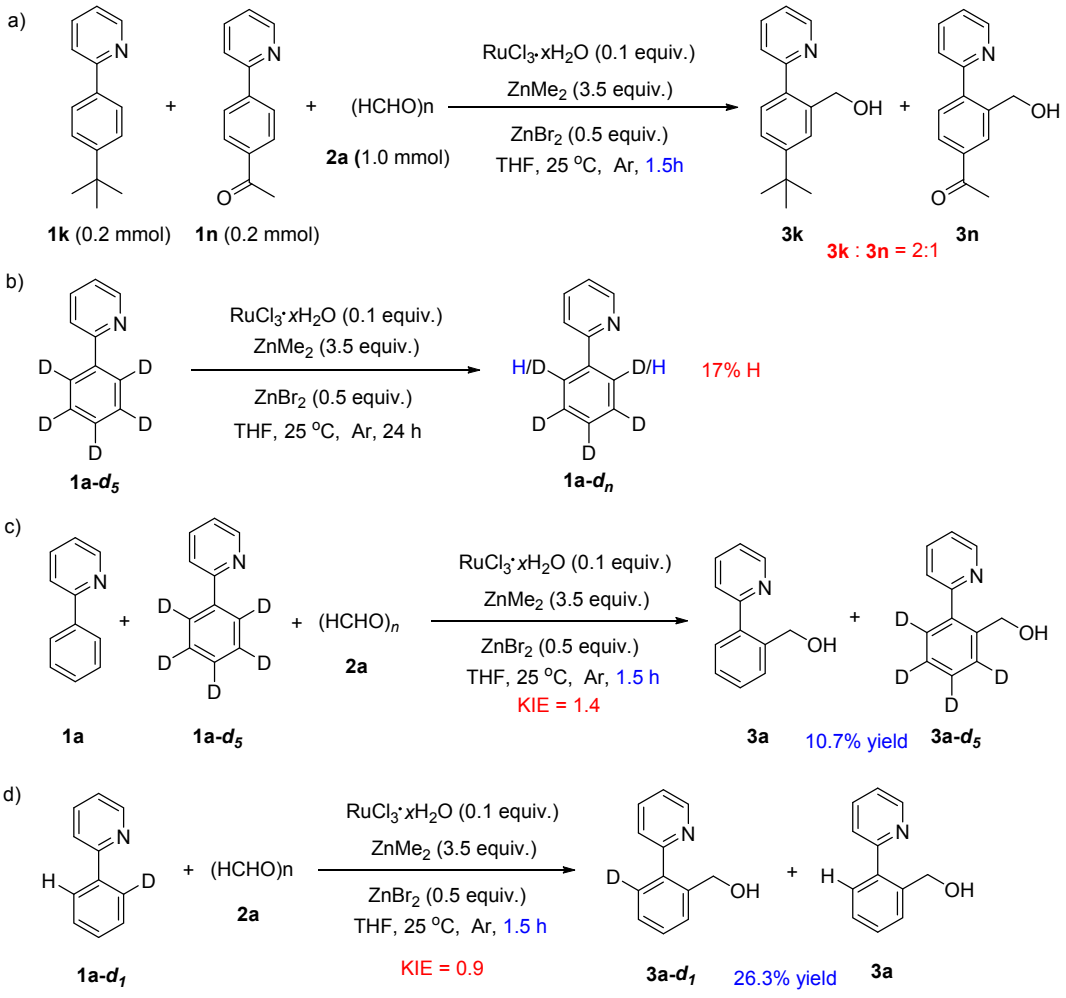
3w that have other directing groups, such as pyrimidine, parazole and isoquinoline, could also be obtained in moderate to good yields. Besides, synthetically useful naphthyl, biphenyl and benzo[*h*]quinoline were also tolerated in this method, giving **3d**～**3f'**, **3o** and **3v** in good yields. Furthermore, a variety of functional groups such as ether, halogen, trifluoromethyl, ester and carbonyl were well-suited for this reaction (Table 2).

It is worth to note that when the benzene ring has a substituent at the meta position, the reaction becomes more complicated due to the possibility of regioisomers (**3e**～**3i**, **3s**～**3t'**). In general, when the substituent had stronger steric hindrance with the *ortho* position, it was more likely to obtain the 6-substitution products (**3e**～**3f'**, **3t**～**3t'**). Likewise, when the steric hindrance was weaker, slightly more 2-substitution products could be obtained (**3g**∶**3g'**=1∶1.06). In addition to the steric hindrance, it was also found that the electron-withdrawing groups could further enhance the regioselectivity of the reaction, leaving only the 6-substitution products (**3h**～**3i**, **3s**).

To obtain some insight into the mechanism, we conducted competing experiments by using 2-phenylpyridines with different electronic substituents (Scheme 1a). Electron-rich arene **1k** reacted faster than electron-deficient arene **1n**, and this showed that C—H activation went through an electrophilic metalation pathway, which is consistent with the previous results.[26] Then, to further probe the nature of the C—H activation step, deuterium-labeling experiments were carried out. The sole treatment of **1a-*d*$_5$** under the reaction conditions clearly indicated an obvious D-H exchange solely occurring at the *ortho* positions of **1a-*d*$_5$** (Scheme 2b). The ruthenium-catalyzed C—H hydroxymethylation of isotopically labeled substrates led to a minor kinetic isotope effect (KIE) of k_H/k_D = 1.4 and k_H/k_D = 0.9 for the inter- and intra-molecular KIE, respectively (Scheme 1, c～d). These data indicate that the C—H bond cleavage may not be the rate-limiting step. All the above results are similar to the previous reports.[25,26]

3 Conclusions

In summary, a novel and efficient method for the *ortho*-hydroxymethylation of arenes via Ru(III)-catalyzed C—H activation has been developed. Mild and cheap commercially available reagents, wide scope of substrates and moderate to excellent yields are the main merits of this reaction. Further studies for other applications of this novel method are ongoing in our laboratory. We anticipate that



Scheme 1 Control experiments for the reaction mechanism

this work would open up a new direction for the synthesis of biologically active compounds that have hydroxylmethyl groups.

4 Experimental section

4.1 General Information

Unless otherwise noted, all reactions were carried out in oven-dried reaction vessels with sealed tube under argon. Solvents were purified and dried according to standard methods prior to use. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light. The product purification was done using silica gel column chromatography. Thin layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2 mm), while column chromatography characterization was performed with silica gel (100～200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 or 600 MHz and ^{13}C NMR spectra were recorded at 100 or 150 MHz. Commercial reagent were purchased from Best-reagent (Homepage: http://www.best-reagent.com) and Astatech Chemical Technology Co., Ltd. (Homepage: http://www.astabiochem.com). All reagents were directly used without further purification.

4.2 General procedure for the synthesis of compound 3

To a 15 mL oven-dried tube was added $ZnBr_2$ (0.3 mmol, 67.6 mg), $RuCl_3$•xH_2O (0.06 mmol, 10 mol%, 15.3 mg), THF (2.0 mL), 2-phenylpyridine (**1a**, 0.6 mmol, 93.1 mg), paraformaldehyde (**2a**, 3.0 mmol, 90.1 mg) and Me_2Zn (2.1 mmol, 1.0 mol•L^{-1} in toluene, 2.1 mL) sequentially under argon. The tube was sealed and stirred at room temperature for 24 h. After completion, the reaction mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with ethyl acetate (10 mL×3). Then the organic layer was dried with anhydrous sodium sulfate, concentrated *in vacuo* and purified by silica gel column chromatography (petroleum/ethyl acetate, V∶V=10∶1) to provide the product **3a** (pale brown oil) in 84% yield.

(2-(Pyridin-2-yl)phenyl)methanol (**3a**):[25,26] Yield 84%, pale brown oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.66 (d, J=4.4 Hz, 1H), 7.92 (t, J=7.6 Hz, 1H), 7.64 (d, J=7.6 Hz, 1H), 7.59 (d, J=7.6 Hz, 1H), 7.51～7.33 (m, 4H), 5.37 (t, J=5.6 Hz, 1H), 4.50 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.45, 148.95, 140.22, 139.84, 136.50, 136.02, 130.19, 128.73, 127.53, 125.62, 122.33, 64.37.

(3-Methyl-2-(pyridin-2-yl)phenyl)methanol (**3b**):[25,26] Yield 87%, pale yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.69 (d, J=4.2 Hz, 1H), 7.81 (t, J=7.8 Hz, 1H), 7.40 (d, J=7.8 Hz, 1H), 7.36～7.30 (m, 3H), 7.27～7.23 (m, 1H), 4.58 (br s, 1H), 4.22 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.45, 148.95, 140.22, 139.84, 136.50, 136.02, 130.19, 128.73, 127.53, 125.62, 122.33, 64.37, 20.69.

(3-Methoxy-2-(pyridin-2-yl)phenyl)methanol (**3c**): Yield 96%, pale yellow solid, m.p. 104～106 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.61 (d, J=4.4 Hz, 1H), 7.82 (t, J=7.6 Hz, 1H), 7.42～7.30 (m, 3H), 7.18 (d, J=7.6 Hz, 1H), 7.01 (d, J=8.2 Hz, 1H), 5.04 (t, J=5.6 Hz, 1H), 4.15 (d, J=5.6 Hz, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.32, 160.61, 153.98, 147.08, 141.18, 134.20, 132.82, 131.01, 127.23, 124.43, 114.99, 66.00, 60.75; HRMS calcd for $C_{13}H_{13}N$- NaO_2 $[M+Na]^+$ 238.0838, found 238.0843.

(1-(Pyridin-2-yl)naphthalen-2-yl)methanol (**3d**):[25] Yield 84%, pale white solid, m.p. 140～142 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.75 (d, J=4.2 Hz, 1H), 8.00 (d, J=8.4 Hz, 1H), 7.98～7.93 (m, 2H), 7.77 (d, J=8.4 Hz, 1H), 7.55～7.42 (m, 3H), 7.39 (t, J=8.4 Hz, 1H), 7.23 (d, J=8.4 Hz, 1H), 5.18 (t, J=5.4 Hz, 1H), 4.53～4.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.30, 149.10, 138.04, 136.86, 136.68, 133.41, 131.91, 129.52, 128.47, 127.97, 126.93, 126.72, 125.98, 125.50, 122.89, 64.52.

(2-Methyl-6-(pyridin-2-yl)phenyl)methanol (**3e**): Yield 15%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (d, J=4.4 Hz, 1H), 7.84 (dt, J=8.0, 1.6 Hz, 1H), 7.60 (d, J=8.0 Hz, 1H), 7.35～7.27 (m, 4H), 4.46 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.18, 148.28, 141.17, 138.47, 138.08, 137.50, 131.37, 128.16, 127.75, 123.96, 122.21, 59.51, 19.93; HRMS calcd for $C_{13}H_{13}NNaO$ $[M+Na]^+$ 222.0889, found 222.0892.

(4-Methyl-2-(pyridin-2-yl)phenyl)methanol (**3e'**): Yield 73%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, J=4.8 Hz, 1H), 7.84 (dt, J=8.0, 1.6 Hz, 1H), 7.63 (d, J=8.0 Hz, 1H), 7.38 (d, J=8.0 Hz, 1H), 7.35 (s, 1H), 7.32 (t, J=6.4 Hz, 1H), 7.23 (d, J=8.0 Hz, 1H), 4.44 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 158.66, 148.83, 138.97, 137.41, 137.21, 136.33, 130.34, 129.15, 128.87, 124.07, 122.38, 61.56, 20.83. HRMS calcd for $C_{13}H_{13}NNaO$ $[M+Na]^+$ 222.0889, found 222.0892.

(2-(pyridin-2-yl)naphthalen-1-yl)methanol (**3f**): Yield 9%, off-white solid. m.p. 105～107 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.74 (d, J=4.4 Hz, 1H), 8.39 (d, J=8.0 Hz, 1H), 8.01～7.92 (m, 4H), 7.80 (d, J=8.0 Hz, 1H), 7.67～7.59 (m, 2H), 7.59～7.49 (m, 1H), 5.31 (t, J=5.2 Hz, 1H), 4.85 (d, J=5.2 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 158.76 (d, J=3.0 Hz), 149.56, 149.23, 138.10, 136.75, 134.51, 133.25, 132.44, 128.38 (d, J=13.5 Hz), 127.96 (d, J=12.0 Hz), 127.67 (d, J=12.0 Hz), 126.65 (d, J=13.5 Hz), 126.33, 125.05, 122.49, 57.68. Compounds **3f** and **3f'** are inseparable mixture, which was analyzed by ^{1}H NMR in DMSO-d_6.

(3-(Pyridin-2-yl)naphthalen-2-yl)methanol (**3f'**): Yield 74%, off-white solid. m.p. 105～107 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.69 (d, J=4.0 Hz, 1H), 8.09 (s, 1H), 8.03 (s, 1H), 8.01～7.92 (m, 3H), 7.76 (d, J=7.6 Hz, 1H), 7.59～7.49 (m, 2H), 7.48～7.40 (m, 1H), 5.52 (t, J=6.0 Hz, 1H), 4.68 (d, J=6.0 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 158.70 (d, J=3.0 Hz), 148.98, 148.67, 138.53, 137.57, 137.48, 132.88, 132.07, 129.19 (d, J=16.5 Hz), 128.09 (d, J=13.5 Hz), 127.58 (d, J=13.5 Hz),

126.79 (d, J=16.5 Hz), 126.23, 124.26, 122.56, 62.10.

(2-Chloro-6-(pyridin-2-yl)phenyl)methanol (**3g**):[26] Yield 37%, pale yellow solid. m.p. 89～92 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.69 (d, J=4.4 Hz, 1H), 7.96 (t, J=7.6 Hz, 1H), 7.75 (d, J=7.6 Hz, 1H), 7.56 (d, J=7.6 Hz, 1H), 7.50～7.39 (m, 3H), 5.28 (t, J=5.6 Hz, 1H), 4.50 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.66, 148.28, 142.41, 137.76, 137.55, 135.86, 130.37, 128.78, 123.99, 122.74, 59.79.

(4-Chloro-2-(pyridin-2-yl)phenyl)methanol (**3g'**):[26] Yield 40%, pale yellow solid. m.p. 63～65 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.67 (d, J=4.4 Hz, 1H), 7.92 (t, J=7.6 Hz, 1H), 7.68 (d, J=7.6 Hz, 1H), 7.63 (d, J=7.6 Hz, 1H), 7.54～7.46 (m, 2H), 7.46～7.34 (m, 1H), 5.37 (s, 1H), 4.50 (d, J=3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.02, 148.41, 141.57, 138.96, 137.93, 133.85, 132.69, 130.07, 129.26, 123.97, 122.91, 64.03.

(2-(Pyridin-2-yl)-4-(trifluoromethyl)phenyl)methanol (**3h**): Yield 62%, pale brown solid. m.p. 48～52 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.70 (d, J=4.4 Hz, 1H), 7.95 (t, J=7.6 Hz, 1H), 7.88 (d, J=8.0 Hz, 1H), 7.82 (d, J=8.0 Hz, 1H), 7.77 (s, 1H), 7.71 (d, J=7.6 Hz, 1H), 7.50～7.41 (m, 1H), 5.48 (t, J=5.6 Hz, 1H), 4.62 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 156.81, 149.32, 145.17, 139.40, 137.37, 128.83, 127.76 (q, J=32.0 Hz), 126.06, 125.81, 125.15, 124.34, 123.09, 60.96; HRMS calcd for $C_{13}H_{10}F_3NNaO$ $[M+Na]^+$ 276.0607, found 276.0611.

Methyl 4-(hydroxymethyl)-3-(pyridin-2-yl)benzoate (**3i**): Yield 71%, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.69 (d, J=4.0 Hz, 1H), 8.07～7.98 (m, 2H), 7.94 (t, J=7.6 Hz, 1H), 7.79 (d, J=7.6 Hz, 1H), 7.67 (d, J=7.6 Hz, 1H), 7.48～7.40 (m, 1H), 5.45 (t, J=5.6 Hz, 1H), 4.61 (d, J=5.6 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 166.41, 157.57, 149.47, 146.16, 139.16, 137.59, 130.52, 129.35, 128.57, 124.38, 123.12, 114.49, 61.36, 52.61; HRMS calcd for $C_{14}H_{13}NNaO_3$ $[M+Na]^+$ 266.0788, found 266.0792.

(5-Methyl-2-(pyridin-2-yl)phenyl)methanol (**3j**):[25,26] Yield 71%, pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.63 (d, J=4.2 Hz, 1H), 7.85 (t, J=7.8 Hz, 1H), 7.62 (d, J=7.8 Hz, 1H), 7.44 (d, J=7.8 Hz, 1H),7.34～7.29 (m, 2H), 7.23 (d, J=7.8 Hz, 1H), 4.45 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.31, 148.05, 140.27, 139.47, 137.60, 137.04, 132.06, 130.18, 128.87, 123.75, 122.05, 64.81, 21.20.

(5-(*tert*-Butyl)-2-(pyridin-2-yl)phenyl)methanol (**3k**): Yield 88%, pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.64 (d, J=4.4 Hz, 1H), 7.90 (t, J=7.6 Hz, 1H), 7.67～7.59 (m, 2H), 7.46～7.34 (m, 3H), 5.47 (t, J=5.6 Hz, 1H), 4.50 (d, J=5.6 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 158.60, 151.05, 148.79, 139.90, 137.28, 136.34, 129.61, 125.64, 124.11 , 124.02, 122.27, 62.14, 34.59, 31.30; HRMS cald for $C_{16}H_{19}NNaO$ $[M+Na]^+$ 264.1359, found 264.1365.

(5-Fluoro-2-(pyridin-2-yl)phenyl)methanol (**3l**):[25] Yield 72%, pale brown oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.65 (d, J=4.4 Hz, 1H), 7.90 (t, J=7.6 Hz, 1H), 7.60 (d, J=7.6 Hz, 1H), 7.51 (t, J=7.6 Hz, 1H), 7.43～7.33 (m, 2H), 7.19 (t, J=7.6 Hz, 1H), 5.44 (t, J=5.6 Hz, 1H), 4.54 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.04 (d, J_{C-F}=248.3 Hz), 158.35 (s), 148.20 (s), 142.93 (d, J_{C-F}=6.9 Hz), 137.80 (s), 135.98 (d, J_{C-F}=3.4 Hz), 132.00 (d, J_{C-F}=8.3 Hz), 123.87 (s), 122.41 (s), 117.97 (d, J_{C-F}=21.0 Hz), 114.93 (d, J_{C-F}=21.0 Hz), 64.37.

(5-Chloro-2-(pyridin-2-yl)phenyl)methanol (**3m**): Yield 63%, pale white solid. m.p. 92～94 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.67 (d, J=4.8 Hz, 1H), 7.92 (t, J=7.6 Hz, 1H), 7.66 (s, 1H), 7.63 (d, J=7.6 Hz, 1H), 7.51 (d, J=7.6 Hz, 1H), 7.4～7.38 (m, 2H), 5.46 (t, J=5.6 Hz, 1H), 4.56 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.30, 154.07, 147.99, 142.37, 142.29, 138.39, 136.50, 132.60, 131.87, 129.08, 127.71, 65.94; HRMS calcd for $C_{12}H_{10}ClNNaO$ $[M+Na]^+$ 242.0343, found 242.0348.

1-(3-(Hydroxymethyl)-4-(pyridin-2-yl)phenyl)ethan-1-one (**3n**):[25] Yield 44%, pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.70 (d, J=4.4 Hz, 1H), 8.21 (s, 1H), 7.99～7.91 (m, 2H), 7.69 (d, J=7.6 Hz, 1H), 7.62 (d, J=7.6 Hz, 1H), 7.45 (t, J=7.6 Hz, 1H), 5.44 (t, J=5.6 Hz, 1H), 4.59 (d, J=5.6 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.65, 158.11, 148.39, 144.13, 140.81, 137.96, 137.46, 131.31, 130.51, 127.92, 124.26, 123.09, 64.55, 26.89.

(4-(Pyridin-2-yl)-[1,1'-biphenyl]-3-yl)methanol (**3o**): Yield 74%, pale white solid. m.p. 83～85 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.68 (d, J=4.4 Hz, 1H), 7.97～7.86 (m, 2H), 7.77～7.64 (m, 4H), 7.59 (d, J=7.6 Hz, 1H), 7.50 (t, J=7.6 Hz, 2H), 7.45～7.35 (m, 2H), 5.52 (t, J=5.6 Hz, 1H), 4.61 (d, J=5.6 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 158.19, 148.97, 141.06, 140.27, 139.94, 137.99, 137.31, 130.47, 129.21, 127.85, 126.90, 126.86, 125.40, 124.11, 122.50, 61.81. HRMS calcd for $C_{18}H_{15}NNaO$ $[M+Na]^+$ 284.1046, found 284.1051.

(2-(Pyrimidin-2-yl)phenyl)methanol (**3p**):[25,26] Yield 58%, pale brown oil. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.93 (d, J=4.8 Hz, 1H), 7.92 (d, J=7.8 Hz, 1H), 7.66 (d, J=7.8 Hz, 1H), 7.54～7.44 (m, 2H), 7.39 (t, J=7.8 Hz, 1H), 5.22 (br s, 1H), 4.76 (d, J=5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.16, 157.20, 140.76, 137.60, 131.61, 131.43, 130.98, 128.41, 119.09, 64.86.

(3-Methyl-2-(pyrimidin-2-yl)phenyl)methanol (**3q**): Yield 77%, pale yellow solid. m.p. 96～100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.92 (d, J=4.8 Hz, 2H), 7.41～7.30 (m, 3H), 7.30～7.27 (m, 1H), 4.31 (s, 2H), 3.26 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 171.64, 162.42, 145.18, 142.44, 139.94, 133.48, 133.25, 129.21, 124.70, 65.95, 24.57; HRMS calcd for $C_{12}H_{12}N_2NaO$ $[M+Na]^+$ 223.0842, found 223.0838.

(5-Methyl-2-(pyrimidin-2-yl)phenyl)methanol (**3r**): Yield 52%, pale yellow solid. m.p. 87～90 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (d, J=4.8 Hz, 2H), 8.11 (d, J=8.4 Hz, 1H), 7.31～7.27 (m, 3H), 4.59 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 165.95, 157.68,

142.21, 139.79, 133.90, 130.88, 129.01, 127.76, 119.48, 62.40, 21.50. HRMS calcd for $C_{12}H_{12}N_2$- NaO $[M+Na]^+$ 223.0842, found 223.0838.

Methyl 4-(hydroxymethyl)-3-(pyrimidin-2-yl)benzoate (**3s**): Yield 40%, white solid. m.p. 134～137 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.97 (d, J=4.8 Hz, 2H), 8.60 (s, 1H), 8.09 (d, J=8.4 Hz, 1H), 7.90 (d, J=8.4 Hz, 1H), 7.52 (t, J=4.8 Hz, 1H), 5.39 (t, J=5.4 Hz, 1H), 4.92 (d, J=5.4 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 166.38, 164.97, 157.88, 148.05, 136.39, 131.46, 130.57, 128.39, 128.18, 120.12, 62.02, 52.63; HRMS calcd for $C_{13}H_{12}N_2NaO_3$ $[M+Na]^+$267.0740, found 267.0747.

(2-Methyl-6-(pyrimidin-2-yl)phenyl)methanol (**3t**): Yield 27%, pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.95 (d, J=4.8 Hz, 2H), 7.59～7.55 (m, 1H), 7.52～7.49 (m, 1H), 7.31～7.28 (m, 2H), 4.80 (t, J=6.4 Hz, 1H), 4.56 (d, J=6.4 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 167.02, 157.73, 139.48, 138.75, 138.21, 136.58, 131.98, 128.89, 127.54, 58.18, 19.78. Compound **3t** and **3t'** are inseparable mixture, which was analyzed by ^{1}H NMR in DMSO-d_6.

(4-Methyl-2-(pyrimidin-2-yl)phenyl)methanol (**3t'**): Yield 54%, pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.93 (d, J=4.8 Hz, 2H), 7.77 (s, 1H), 7.54 (d, J=8.0 Hz, 1H), 7.48 (t, J=4.8 Hz, 1H), 7.34～7.31 (m, 1H), 5.20 (t, J=6.0 Hz, 1H), 4.72 (d, J=6.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 166.07, 157.69, 139.33, 136.58, 136.22, 131.29, 130.72, 128.58, 119.69, 62.16, 21.06.

(2-(1*H*-Pyrazol-1-yl)phenyl)methanol (**3u**):[25,26] Yield 80%, yellow oi. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.12 (s, 1H), 7.74 (s, 1H), 7.66 (d, J=7.2 Hz, 1H), 7.50～7.43 (m, 1H), 7.42～7.39 (m, 2H), 6.51 (d, J=1.8 Hz, 1H), 5.29 (t, J=5.6 Hz, 1H), 4.43 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.83, 139.90, 135.59, 132.02, 130.20, 129.03, 128.35, 123.85, 107.33, 62.81.

Benzo[h]quinolin-10-ylmethanol (**3v**):[25,26] Yield 57%, white solid. m.p. 116～118 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.07 (br s, 1H), 8.50 (d, J=8.0 Hz, 1H), 8.04～7.95 (m, 3H), 7.91 (d, J=8.0 Hz, 1H), 7.81～7.64 (m, 2H), 5.93 (t, J=6.4 Hz, 1H), 5.40 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.91, 146.63, 139.80, 137.19, 135.72, 130.67, 129.91, 129.50, 129.15, 128.29, 128.06, 125.48, 121.42, 66.93.

(2-(Isoquinolin-3-yl)phenyl)methanol (**3w**): Yield 75%, white solid. m.p. 102～104 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.40 (s, 1H), 8.17 (d, J=8.0 Hz, 1H), 8.06 (s, 1H), 8.03 (d, J=8.0 Hz, 1H), 7.82 (t, J=7.6 Hz, 1H), 7.71 (t, J=7.6 Hz, 1H), 7.64 (d, J=7.6 Hz, 1H), 7.58 (d, J=7.6 Hz, 1H), 7.45 (t, J=7.2 Hz, 1H), 7.40 (t, J=7.2 Hz, 1H), 5.38 (t, J=6.0 Hz, 1H), 4.59 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.34, 156.68, 145.60, 144.13, 141.04, 136.08, 135.04, 133.41, 133.32, 132.78, 132.71, 132.13, 132.05, 132.03, 125.06, 66.75.

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

References

[1] (a) Collin, D. T.; Hartley, D.; Jack, D.; Lunts, L. H.; Press, J. C.; Ritchie, A. C.; Toon, P. *J. Med. Chem.* **1970**, *13*, 674.
(b) Schachter, E. N. *Drugs Today* **2010**, *46*, 911.
(c) Gomelsky, A.; Dmochowski, R. R. *Drugs Today* **2010**, *46*, 81.
(d) Filho, R. P.; de Souza Menezes, C. M.; Pinto, P. L.; Paula, G. A.; Brandt, C. A.; da Silveira, M. A. *Bioorg. Med. Chem.* **2007**, *15*, 1229.
(e) Zhang, J. S.; Zhu, D. Y.; Hong, S. H. *Phytochemistry* **1995**, *39*, 435.

[2] Select example: Bouveault, L. *Bull. Soc. Chim. Fr.* **1903**, *29*, 1051.

[3] Select example: Mettler, C. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1745.

[4] (a) Vavon, G. *Anal. Chim.* **1914**, *1*, 144.
(b) Raber, D. J.; Guida, W. C.; Shoenberger, D. C. *Tetrahedron Lett.* **1981**, *22*, 4077.

[5] (a) Nystrom, R. F.; Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 3245.
(b) Santaniello, E. *J. Org. Chem.* **1981**, *46*, 4584.
(c) Brown, H. C.; Choi, Y. M. *Synthesis* **1981**, 439.

[6] (a) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *Synthesis* **1981**, 793.
(b) Chemla, F.; Normant, J. *Tetrahedron Lett.* **1995**, *36*, 3157.
(c) Hu, Y. L.; Jiang, H.; Zhu, J.; Lu, M. *New J. Chem.* **2011**, *35*, 292.

[7] (a) Raber, D. J.; Guida, W. C. *J. Org. Chem.* **1976**, *41*, 690.
(b) Santaniello, E.; Fiecchi, A.; Manzocchi, A.; Ferraboschi, P. *J. Org. Chem.* **1983**, *48*, 3074.

[8] Flippin, L. A.; Gallagher, D. W.; Jalali-Araghi, K. *J. Org. Chem.* **1989**, *54*, 1430.

[9] (a) Kamochi, Y.; Kudo, T. *Chem. Lett.* **1993**, *9*, 1495.
(b) Fisher, G. B. *J. Org. Chem.* **1994**, *59*, 6378.

[10] Kamitanaka, T.; Yamamoto K.; Matsuda, T. *Tetrahedron* **2008**, *64*, 5699.

[11] (a) Wu, Y. Q. *Tetrahedron Lett.* **2000**, *41*, 2847.
(b) Reddy, M. A. *New. J. Chem.* **2001**, *25*, 359.
(c) Cadot, C. *Tetrahedron Lett.* **2002**, *43*, 1839.
(d) Markovic, D.; Vogel, P. *Org. Lett.* **2004**, *6*, 2693.

[12] Molander, G. A.; Cavalcanti, L. N. *J. Org. Chem.* **2011**, *76*, 623.

[13] (a) Kawamoto, T. *Org. Lett.* **2013**, *15*, 2144.
(b) Molla, R. A. *Green Chem.* **2016**, *18*, 4649.

[14] Khusnutdinova, J. R.; Milstein, Y. B-D. *Angew. Chem., Int. Ed.* **2013**, *52*, 6269.

[15] Hydroxymethylation of carbonyl substrates see: (a) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 235.
(b) Torii, H.; Nakadai, M.; Ishihara, K.; Saito S.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1983.
(c) Kuhl N.; Glorius, F. *Chem. Commun.* **2011**, *47*, 573.
(d) Shirakawa, S.; Ota, K.; Terao S. J.; Maruoka, K. *Org. Biomol. Chem.* **2012**, *10*, 5753.

[16] Reductive hydroxymethylation of allenes, alkenes and alkynes see:
(a) Ngai, M.-Y.; Skucas, E.; Krische, M. J. *Org. Lett.* **2008**, *10*, 2705.
(b) Sam, B.; Montgomery, T. P.; Krische, M. J. *Org. Lett.* **2013**, *15*, 3790.
(c) Kopfer, A.; Sam, B.; Breit B.; Krische, M. J. *Chem. Sci.* **2013**, *4*, 1876.
(d) Bausch, C. C.; Patman, R. L.; Breit, B.; Krische, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 5687.

[17] Hydromethoxylation of boronic acids see: (a) Yamamoto, T.; Zhumagazin, A.; Furusawa, T.; Tanaka, R.; Yamakawa, T.; Oe Y.; Ohta, T. *Adv. Synth. Catal.* **2014**, *356*, 3525.
(b) Kawamoto, T.; Fukuyama, T.; Ryz, I. *J. Am. Chem. Soc.* **2012**, *134*, 875.
(c) Kawamoto, T.; Ryu, I. *Chimia* **2012**, *66*, 372.

[18] (a) Maruyama, K.; Kubo, K.; Toda, Y.; Kawase, K.; Mashino, T.; Nishinaga, A. *Tetrahedron Lett*. **1995**, *36*, 5609.
(b) Khan, A.; Zheng, R.; Kan, Y.; Ye, J.; Xing J.; Zhang, Y. J. *Angew*. *Chem*., *Int*. *Ed*. **2014**, *53*, 6439.
(c) Xie, Y.; Hu, J.; Wang, Y.; Xia, C.; Huang, H. *J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 20613.
(d) Zhang, G.; Gao, B.; Huang, H. *Angew*. *Chem*., *Int*. *Ed*. **2015**, *54*, 7657-7661.
[19] (a) Morimoto, T.; Fujioka, M.; Fuji, K.; Tsutsumi K.; Kakiuchi, K. *J*. *Organomet*. *Chem*. **2007**, *692*, 625.
(b) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *ChemCatChem* **2014**, *6*, 2805.
(c) Kusumoto, S.; Tatsuki T.; Nozaki, K. *Angew*. *Chem*., *Int*. *Ed*. **2015**, *54*, 8458.
[20] (a) Pyo, A.; Kim, S.; Kumar, M. R.; Byeun, A.; Eom, M. S.; Han, M. S.; Lee, S. *Tetrahedron Lett*. **2013**, *54*, 5207.
(b) Heim, L. E.; Schloer, N. E.; Choi, J.-H.; Prechtl, M. H. G. *Nat*. *Commun*. **2014**, *5*, 3621.
(c) Suenobu, T.; Isaka, Y.; Shibata, S.; Fukuzumi, S. *Chem*. *Commun*. **2015**, *51*, 1670.
[21] (a) Saidi, O.; Bamford, M. J.; Blacker, A. J.; Lynch, J.; Marsden, S. P.; Plucinski, P.; Watson, R. J.; Williams, J. M. J. *Tetrahedron Lett*. **2010**, *51*, 5804.
(b) Zhang, J.; Hong, S. H. *Org*. *Lett*. **2012**, *14*, 4646.
(c) Lee, H.; Kang, B.; Lee, S.-I.; Hong, S. H. *Synlett* **2015**, 1077.
[22] (a) Watanabe, Y.; Yamamoto, M.; Mitsudo, T.-A.; Takegami, Y. *Tetrahedron Lett*. **1978**, *19*, 1289.
(b) Man, N. Y. T.; Li, W.; Stewart, S. G.; Wu, X.-F. *Chimia* **2015**, *69*, 345.
[23] Li, W. F.; Wu, X. F. *Adv*. *Synth*. *Catal*. **2015**, *357*, 3393.
[24] Cheng, X. F.; Wang, H. M.; Xiao, F. H.; Deng, G. J. *Green Chem*. **2016**, *18*, 5773.
[25] Zhang, G. F.; Li, Y.; Xie, X. Q.; Ding, C. R. *Org*. *Lett*. **2017**, *19*, 1216.
[26] Wu, Y. X.; Zhou, B. *ACS Catal*. **2017**, *7*, 2213.
[27] Zhang, Y.; Yang, Z. Z.; Guo, L. M.; Li, W. J.; Cheng, X.; Wang, X. L.; Wang, Q. T.; Hai, L.; Wu, Y. *Org*. *Chem*. *Front*. **2018**, *5*, 1604.

(Zhao, C.)

