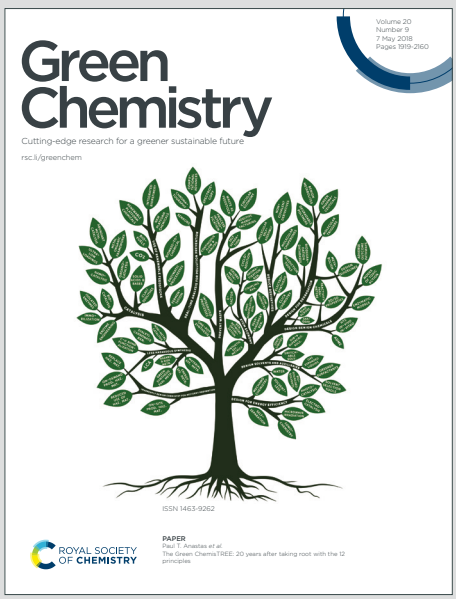
View Article Online
View Journal

Green Chemistry

Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: K. Li, Y. Jiang, K. Xu, C. Zeng and B. Sun, *Green Chem.*, 2019, DOI: 10.1039/C9GC01474H.



Electrochemically Dehydrogenative C-H/P-H Cross-Coupling: Effective Synthesis of Phosphonated Quinoxalin-2(1*H*)-ones and Xanthenes

Ke-Jing Li,[1,2] Yang-Ye Jiang,[2] Kun Xu, [2] Cheng-Chu Zeng*[1,2] and Bao-Guo Sun[1]

[1] *Beijing advanced innovation center for food nutrition and human health, School of Food and Chemical Engineering, Beijing Technology and Business University, Beijing 100048, China*

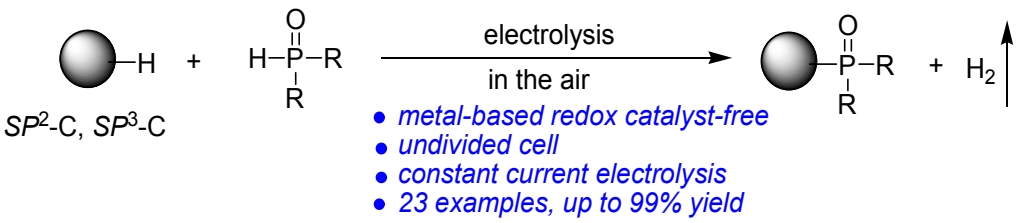
[2] *Beijing Key Laboratory of Environmental and Viral Oncology, College of Life Science & Bioengineering, Beijing University of Technology, Beijing 100124, China. Corresponding author: zengcc@bjut.edu.cn*

Abstract:

An efficient electrochemical approach for the C(sp^2)-H phosphonation of quinoxalin-2(1*H*)-ones and C(sp^3)-H phosphonation of xanthene has been developed. The chemistry was performed in an undivided cell under constant current conditions and features wide range of substrates, up to 99% yield as well as transition-metal catalyst- and external oxidant-free, thereby providing a straightforward approach for the dehydrogenative C-H/P-H cross-coupling. In addition, control experiments disclose that some of the reactions may involve a radical pathway.

Key words: Electrochemically dehydrogenative cross-coupling, oxidative phosphonation, quinoxalin-2(1*H*)-ones, xanthene

Graphical Abstract:



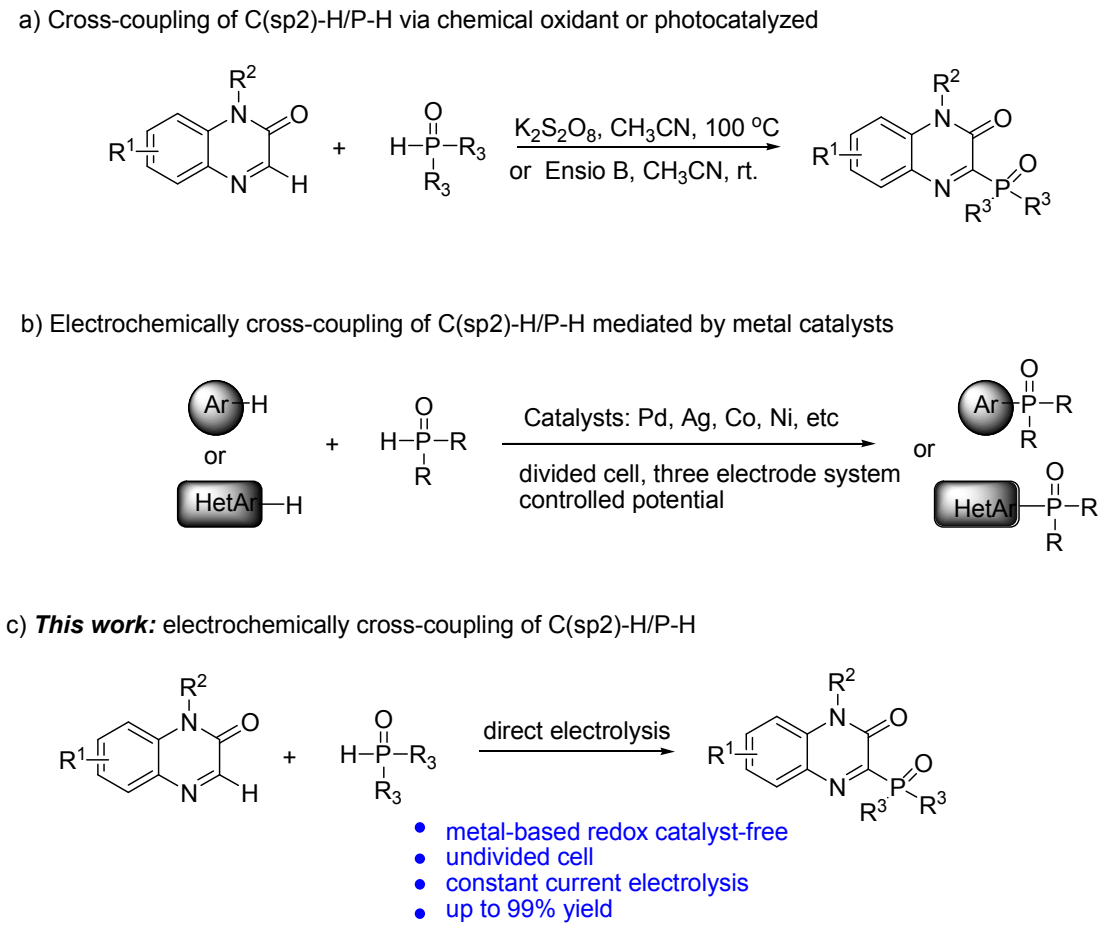
View Article Online
DOI: 10.1039/C9GC01474H

Introduction

The efficient construction of diverse C-P bonds is of great important since organophosphorus compounds exists widely in agrichemicals, organic ligands, material and bioactive compounds. [1] The reactions of trialkyl phosphite with an electrophilic alkyl halide at elevated temperature are the most traditional pathway to construct a C(sp^3)-P bond, [2] whereas, transition metal based catalysts (such as palladium, [3] copper, [4] manganese, [5] and silver [6]) have been widely employed to form various C(sp^2)-P bonds. Recently, owing to the intrinsic sustainability and green chemistry character, visible light-induced photoredox catalysis has also been extensively applied in the formation of various C-P bonds. [7] On the other hand, quinoxalin-2(1*H*)-one, especially 3-substituted quinoxalin-2(1*H*)-ones are broadly existed in natural products and bioactive compounds [8] due to their antibacterial, [8a] antiviral [8b-c] and anticancer properties. [8d-e] As a result, the synthesis of 3-phosphonated quinoxalin-2(1*H*)-ones has attracted much attention. In this context, Cui and coworkers reported the phosphonation of quinoxalin-2(1*H*)-ones under transition-metal-free conditions using 3.0 equiv of $K_2S_2O_8$ as oxidant at elevated temperature (Scheme 1a).[9] Alternatively, Kim et al developed a visible light photoredox-catalyzed phosphorylation of quinoxalin-2(1*H*)-ones with diphenylphosphine oxide (Scheme 1a). [10] Nevertheless, these protocols suffer from the use of excess amounts of oxidizing reagents, as well as the limited substrate scopes.

Organic electrosynthesis, which utilizes traceless electrons as the clean reactants, has been recognized as a green synthetic tool since electrons produce no waste in contrast with chemical redox reagents. [11] The past decade has witnessed an increasing interest in organic electrosynthesis that expanded the toolbox of organic chemists for green synthesis.[12] A variety of electroorganic reactions for C-C,[13] C-N,[14] C-O [15] and C-S [16] bonds formation have been developed under environmentally-friendly conditions. Despite these advances, electrochemically dehydrogenative C-H/P-H cross coupling is less studied. Budnikova and coworkers first reported the elegant electrochemical phosphorylation of arenes and coumarins catalyzed by transition metal complex, such as bimetallic catalyst system $MnCl_2$bpy/$Ni(BF_4)_2$bpy [17a] or bpy$CoCl_2$

(Scheme 1b). [17b] Later on, silver-based catalysts were employed for the electrochemical phosphorylation of azole derivatives [17c] and caffeine [17d] (Scheme 1b). These transition metal catalyzed electrochemical phosphorylations were performed in three-electrode divided cell under controlled potential conditions, which is not suitable for scale-up, especially for industrial preparation. Moreover, the electrolysis efficiency is not excellent due to the strong coordination of phosphorus reagents with the metal catalyst.[18] In addition, as far as we know, the electrochemical C(sp3)-P formation has not been reported.



Scheme 1. Cross-coupling of C(sp2)-H/P-H

In continuation to our interests in electrochemical C-H functionalization,[19] we herein reported an efficient intermolecular electrochemical cross-coupling of quinoxalin-2(1*H*)-one with H-phosphonates and H-phosphine oxides to obtain 3-phosphonated quinoxalin-2(1*H*)-ones (Scheme 1c). The protocol could also extend to

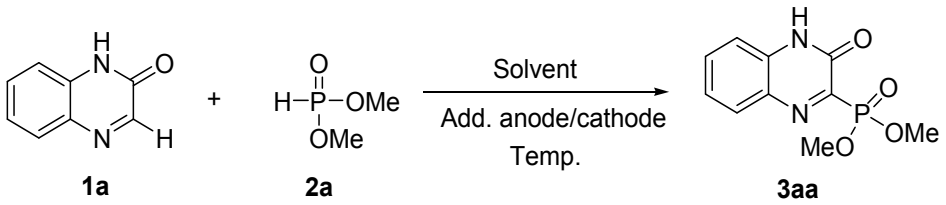
the C(sp^3)-H phosphonation of xanthene. To the best of our knowledge, this is the first example of electrochemical C-H phosphonation without the utilization of transition metal redox catalyst (direct electrolysis). This protocol features mild reaction conditions, wide scope of P-H and C-H sources, avoiding the utilization of transition metal catalysts and excess oxidant. The last but not the least, the procedure is carried out in an undivided cell under galvanostatic conditions.

Results and discussion

We initiated our studies by using quinoxalinone, **1a,** and dimethyl phosphonate, **2a,** as model substrates to identify the optimal reaction conditions. As shown in Table 1, when constant current electrolysis (CCE) of **1a** and **2a** was performed in an undivided cell equipped with two graphite plates as anode and cathode at 80 ^{o}C, the 3-phosphonated product **3aa** was isolated in 59% yield (entry 1). Encouraged by this result, different solvents were firstly screened. The results disclosed that CH_3CN was preferable among the solvents detected, since CH_3OH gave 20% yield of **3aa** (46% yield based on the recovery **1a**), and other solvents (such as DCE and DMF) led to a trace amount of **3aa** (entries 2-4). In the course of the electrolysis, we observed that an intermediate **4aa** (see Scheme 3 for its structure) generated initially and it transformed to **3aa** with the electricity passing. Based on this observation, we envisioned that the presence of a base might assist this conversion. However, only trace of **3aa** was detected and most of the starting material **1a** was recovered when K_2CO_3, NaOH, Na_2CO_3, Cs_2CO_3 or $NaHPO_4$ were added as the additives (entries 5-9). Then, acetic acid was added as an additive and the yield of **3aa** also decreased to 43% (Entry 10). Subsequently, the effect of current density on the reaction was examined. It was found that increasing the current density to 5 mA/cm^2 or 10 mA/cm^2 resulted in lower yields of **3aa** compared with that at 3 mA/cm^2 (entries 11-12 *vs* 1). The exploration of effect of the electrode on the reaction disclosed that changing the anodic material from graphite to platinum resulted in reduced yield (50%) along with longer reaction time (Entry 13). Conversely, the platinum cathode, instead of graphite, improved the yield of **3aa** to 75% (Entry 14). In addition, a slightly decreased yield of **3aa** was observed

when nickel sheet was used as the cathode (Entry 15). These results should be rational due to the low over-potential of Pt cathode for the hydrogen evolution. Delightedly, the yield of **3aa** enhanced from 75% to 83% when the ratio of **1a** to **2a** increased from 1:1.1 to 1:2 (entries 14 *vs* 16). A further increase to 1:4 did not improve the yield of **3aa** (entries 16 *vs* 17). Further evaluating the reaction temperature indicated that 40 °C was superior and the desired product **3aa** was obtained in 90% yield since **3aa** was obtained in lower yields and longer time when the reaction was performed at 80 °C or 25 °C (entries 18 *vs* 16, 19). In addition, it was observed that, $LiClO_4$ is superior since **3aa** was obtained in trace amount or much lower yield when *n*-Bu_4NBF_4, *n*-Bu_4NPF_6, or *n*-Bu_4NClO_4 were applied as the electrolytes (entries 20-22). Notably, without electricity, **3aa** was not produced (entry 23), thereby revealing that electricity plays an essential role for this reaction. Based on the results mentioned above, we concluded that the optimal reaction conditions call for constant current electrolysis at a constant current of 3 mA/cm^2, in an undivided cell equipped with a graphite plate anode and a platinum cathode, using 0.1 M $LiClO_4/CH_3CN$ as solvent at 40 °C.

Table 1. Condition optimization for the C(sp2)-H phosphonation of quinoxalinone [a]



1a **2a** **3aa**

Entry	**1a**:**2a**	Temp. (°C)	Solvent	Additive (equiv.)	Electrodes	Yield (%) [b]
1	1:1.1	80	CH_3CN	-	C(+)/C(-)	59
2[d]	1:1.1	60	CH_3OH	-	C(+)/C(-)	20 (46)[c]
3	1:1.1	80	DCE	-	C(+)/C(-)	Trace
4	1:1.1	80	DMF	-	C(+)/C(-)	Trace
5	1:1.1	80	CH_3CN	K_2CO_3(2)	C(+)/C(-)	Trace
6	1:1.1	80	CH_3CN	NaOH(2)	C(+)/C(-)	Trace
7	1:1.1	80	CH_3CN	Na_2CO_3(2)	C(+)/C(-)	Trace
8	1:1.1	80	CH_3CN	Cs_2CO_3(2)	C(+)/C(-)	Trace
9	1:1.1	80	CH_3CN	$NaHPO_4$(2)	C(+)/C(-)	Trace

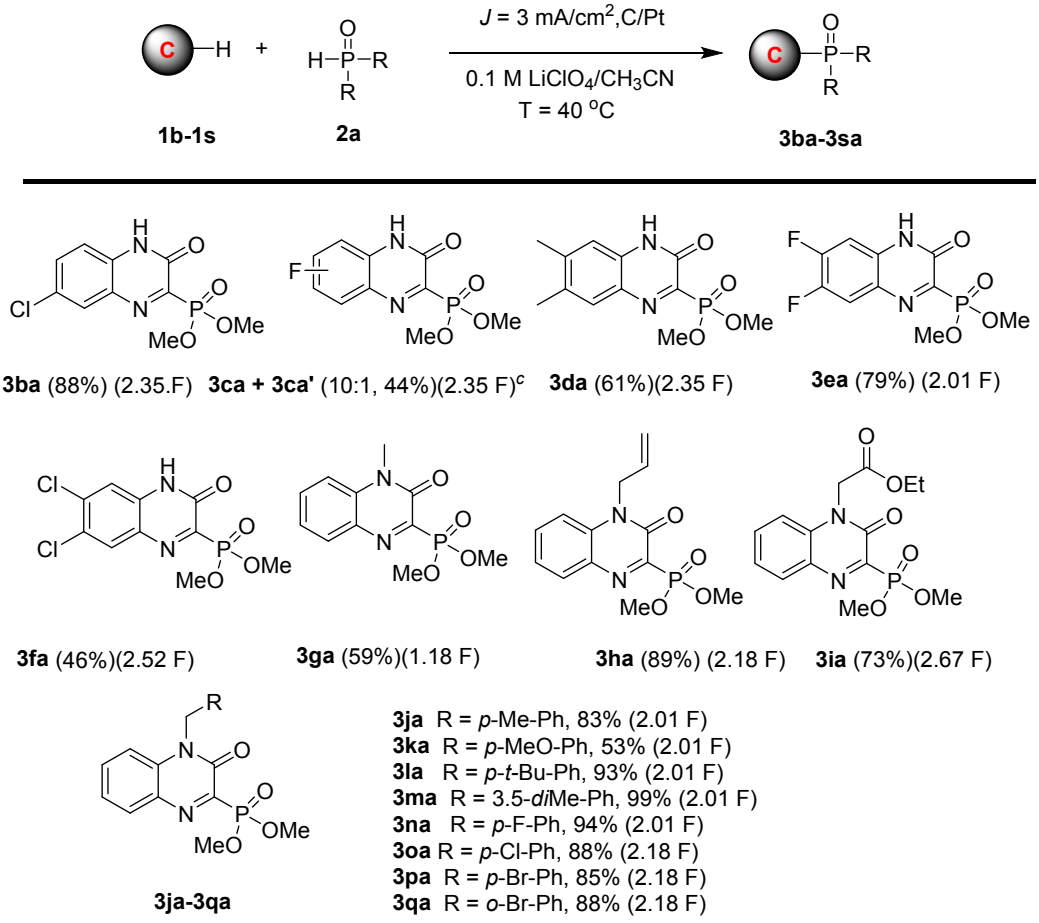
10	1:1.1	80	CH_3CN	HOAc(2)	C(+)/C(-)	43
11[e]	1:1.1	80	CH_3CN	-	C(+)/C(-)	53
12[f]	1:1.1	80	CH_3CN	-	C(+)/C(-)	39
13	1:1.1	80	CH_3CN	-	Pt(+)/C(-)	50
14	1:1.1	80	CH_3CN	-	C(+)/Pt(-)	75
15	1:1.1	80	CH_3CN	-	C(+)/Ni(-)	70
16	1:2	80	CH_3CN	-	C(+)/Pt(-)	83
17	1:4	80	CH_3CN	-	C(+)/Pt(-)	83
18	1:2	40	CH_3CN	-	C(+)/Pt(-)	90 (2.35 F)
19	1:2	rt	CH_3CN	-	C(+)/Pt(-)	82
20[g]	1:2	40	CH_3CN	-	C(+)/Pt(-)	Trace
21[h]	1:2	40	CH_3CN	-	C(+)/Pt(-)	Trace
22[i]	1:2	40	CH_3CN	-	C(+)/Pt(-)	34
23	1:2	40	CH_3CN	-	-	0

[a] Reaction conditions: **1a** (1 mmol) and **2a** in 10 mL of solvent, undivided cell, current density of 3 mA/cm^2, 0.1 M $LiClO_4$ as supporting electrolyte.
[b] Isolated yield.
[c] Recovery yield.
[d] 0.1 M *n*-Bu_4NBF_4 as electrolyte.
[e] J = 5 mA/cm^2, 4.5 h.
[f] J = 10 mA/cm^2, 1.5 h.
[g] 0.1 M *n*-Bu_4NBF_4 as electrolyte.
[h] 0.1 M *n*-Bu_4NPF_6 as electrolyte.
[i] 0.1 M *n*-Bu_4NClO_4 as electrolyte .

With the optimized reaction conditions in hand, we then studied the scope and the generality of the protocol by examining the reactions of a plethora of quinoxalinones **1** with dimethyl phosphonate **2a**. As shown in Figure 1, the corresponding products **3aa**-**3qa** were obtained in up to 99% yield under the standard electrochemical conditions. It was found that when quinoxalinones substituted by single electron-withdrawing groups, such as chloro and fluoro groups, corresponding **3ba** and **3ca** were afforded in 88% and 87% yields, respectively. For dimethyl- and difluoro-quinoxalinones, the yield decreased slightly to 61% (**3da**) and 79% (**3ea**), respectively. However, in the case of 6,7-dichloro substituted **2f**, the corresponding **3fa** was afforded with a lower yield, which is consistent with the results from the literature report. [9] *N*-substituted quinoxalinones, such as *N*-methyl-, *N*-allyl-, *N*-acetate- and *N*-benzyl-protected derivatives, also proceeded smoothly to give the corresponding products **3ga-3qa** in moderate to high yields. It is worthy of noting that when *N*-allyl quinoxalinone (**1h**)

was subjected to reaction with **2a**, the cross-coupling took place only at the electron-deficient C=N bonds, instead of C=C bond, to give the phosphonated product **3ha** in 89% yield, thereby demonstrating a good chemoselectivity.

Figure 1. Substrate scope with respect to quinoxalinone [a,b]



[a] Reaction conditions: **1a** (1 mmol) and **2a** (2 mmol) in 10 mL of CH_3CN, undivided cell, current density of 3 mA/cm^2, 0.1 M $LiClO_4$ as supporting electrolyte, graphite as an anode and platinum net as a cathode, 40 °C.

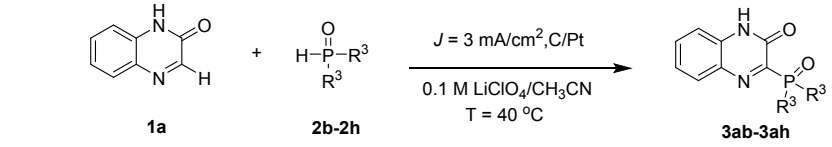
[b] Isolated yield.

[c] **1a** (0.5 mmol) and **2a** (1 mmol).

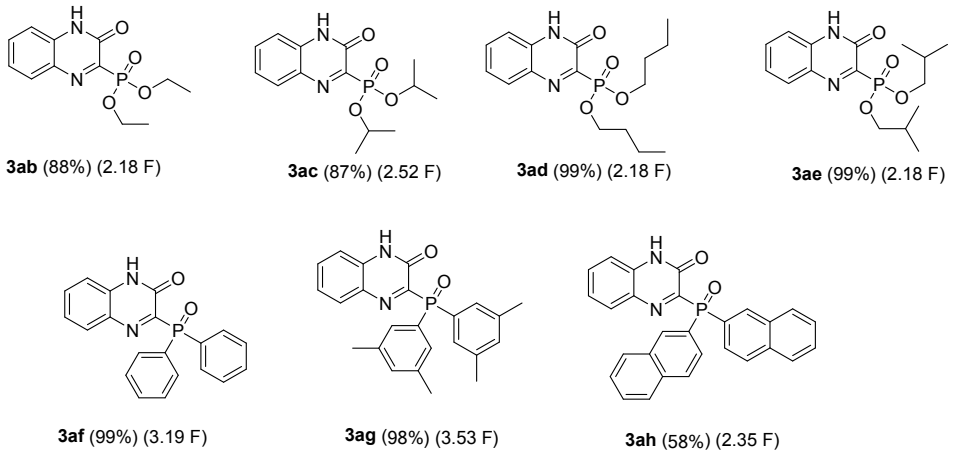
Next, the scope of phosphorus source **2** were investigated and the results were summarized in Figure 2. Phosphonates bearing various groups could react with **1a** to afford the corresponding products in excellent yield under the standard conditions. For example, diethyl-, diisopropyl-, dibutyl- and diisobutylphosphonates gave corresponding **3ab, 3ac, 3ad** and **3ae** in 88%, 87%, 99% and 99% yields, respectively.

Moreover, changing the phosphorus resource from phosphonates to diarylphosphine oxide, the target products could also obtained. As shown in Figure 2, when diarylphosphine oxides **2f**, **2g** and **2h** were subjected to reaction with **1a** under the standard conditions, the corresponding adducts **3af, 3ag** and **3ah** were afforded in 99%, 98% and 58% yields, respectively.

Figure 2. Substrate scope of phosphorus source [a,b]



1a **2b-2h** **3ab-3ah**



3ab (88%) (2.18 F) **3ac** (87%) (2.52 F) **3ad** (99%) (2.18 F) **3ae** (99%) (2.18 F)

3af (99%) (3.19 F) **3ag** (98%) (3.53 F) **3ah** (58%) (2.35 F)

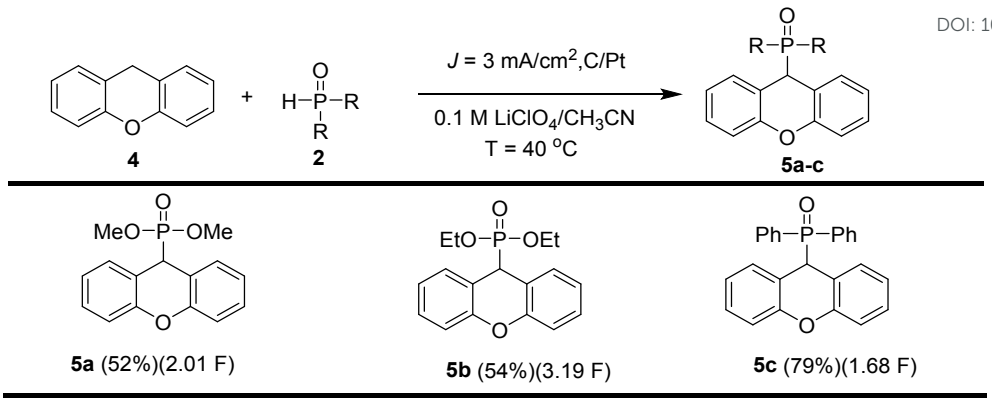
[a] Reaction conditions: **1a** (1 mmol) and **2** (2 mmol) in 10 mL of solvent, undivided cell, current density of 3 mA/cm^2, 0.1 M $LiClO_4$ as supporting electrolyte, graphite as an anode and platinum net as a cathode, 40 ^{o}C.

[b] Isolated yield.

It is worthy of noting, to the best of our knowledge, there is no reported protocols suitable not only for the C(sp2)-H phosphonylation, but also for the C(sp3)-H phosphonylation under the same reaction conditions. To our delighted, our protocol could also be applied to C(sp^3)-H phosphonation. As shown in Figure 3, when xanthene, **4**, was subjected to electrolysis in the presence of P-H sources under the standard conditions, the reaction worked smoothly and afforded the corresponding adducts **5a**, **5b** and **5c** in 52%, 54% and 79% yields, which further demonstrated the compatibility of our electrochemical protocol.

Figure 3. C(sp^3)-H phosphonation of xanthene [a,b]

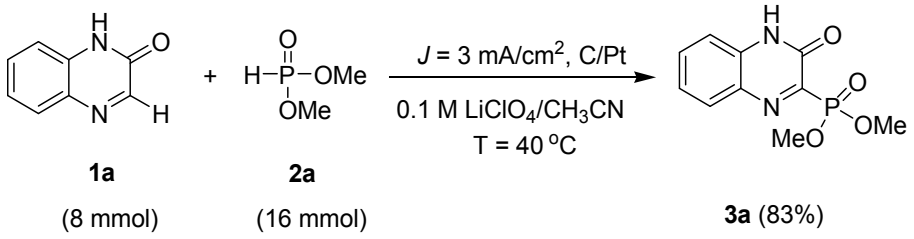
View Article Online
DOI: 10.1039/C9GC01474H



[a] Reaction conditions: **4** (1 mmol) and **2** (2 mmol) in 10 mL of solvent, undivided cell, current density of 3 mA/cm^2, 0.1 M $LiClO_4$ as supporting electrolyte, graphite as an anode and platinum net as a cathode, 40 °C.

[b] Isolated yield.

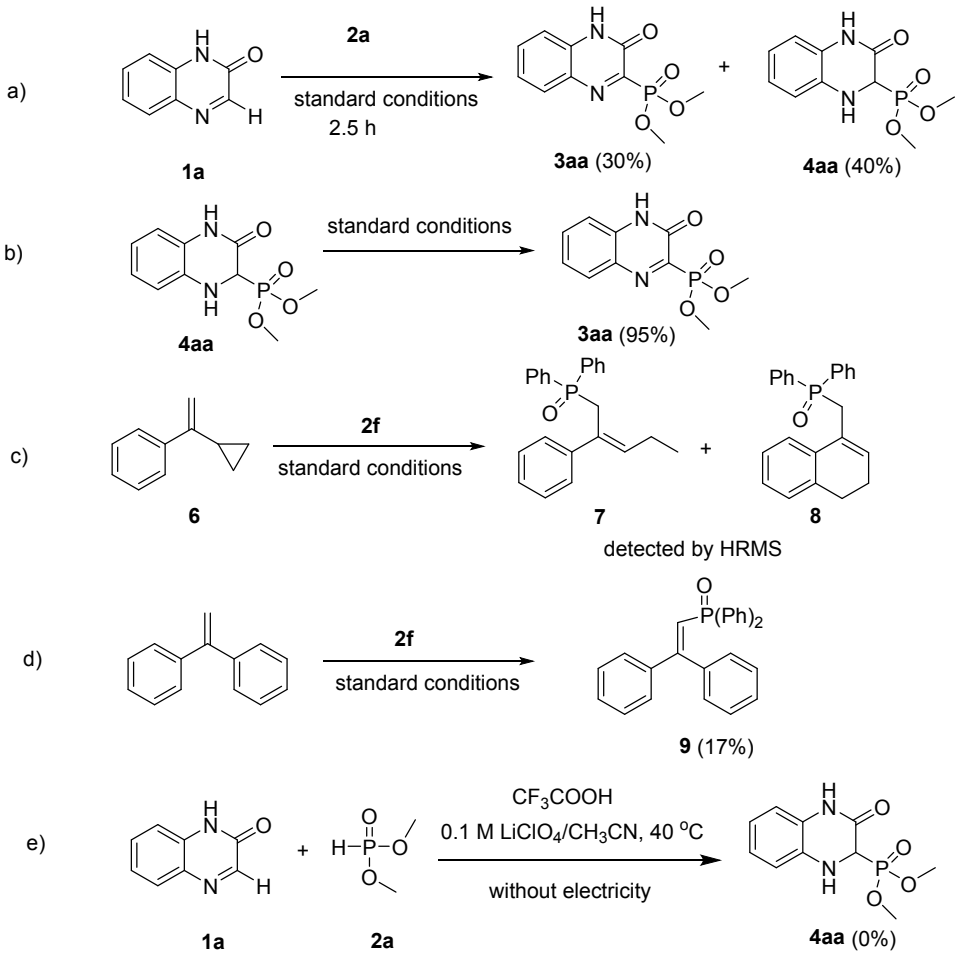
To verify the practicability of the protocol, a scaled-up reaction was carried out. As illustrated in Scheme 2, when 8.0 mmol of quinoxalinone **1a** was allowed to react with dimethyl phosphonate **2a** under the standard conditions, 83% yield of the corresponding product **3a** was isolated, without losing the reaction efficiency.



Scheme 2. Scaling up

In order to better understand the reaction mechanism, controlled experiments were performed. Initially, when the electrochemical cross-coupling of **1a** with **2a** was terminated after passing 2.5 hours of charge, a mixture of **3aa** (in 30% yield) and **4aa** (40% yield) were afforded (Scheme 3a). Moreover, the isolated **4aa** could transfer to **3aa** in 95% yield under the standard conditions (Scheme 3b). These results indicate that **4aa** should be a key intermediate of the cross-coupling reaction. Next, when 1-(1-cyclopropylvinyl)benzene, **6**, was subjected to electrolysis with diphenylphosphine oxide **2f** under the standard conditions, a mixture of ring-opening addition products **7** and **8** was detected by HRMS (Scheme 3c). This radical clock experiment discloses that

the reaction involves a radical pathway, which was further demonstrated by the generation of **9** from the reaction of 1,1-diphenylethene with **2f** under the standard electrochemical conditions (Scheme 3d). In addition, the reaction of **1a** and **2a** in the presence of CF_3COOH in an undivided cell without electricity didn't give intermediate **4aa**, which rules out the formation of **4aa** is from the reaction of protonated **1a** with **2a** (Scheme 3e).



Scheme 3. Control Experiments

Cyclic voltammetry analysis was also performed to understand the possible mechanism (see SI for the detail). As listed in Table 2, the oxidation potentials of substrate **1a** and **2a** are 1.55 V and 1.92 V vs $Ag/AgNO_3$ (0.1 M in CH_3CN), respectively. Intermediate **4aa** exhibits two oxidation peaks at 0.59 V and 1.63 V vs $Ag/AgNO_3$ (0.1 M in CH_3CN), which discloses that **4aa** easily undergo oxidation reaction at anode or by air atmosphere. In the case of xanthene, **4**, whose peak potential

is 1.29 V, much lower than that of **2a.** This result indicates that a different pathway may proceed for the reaction of xanthene and **2a**.

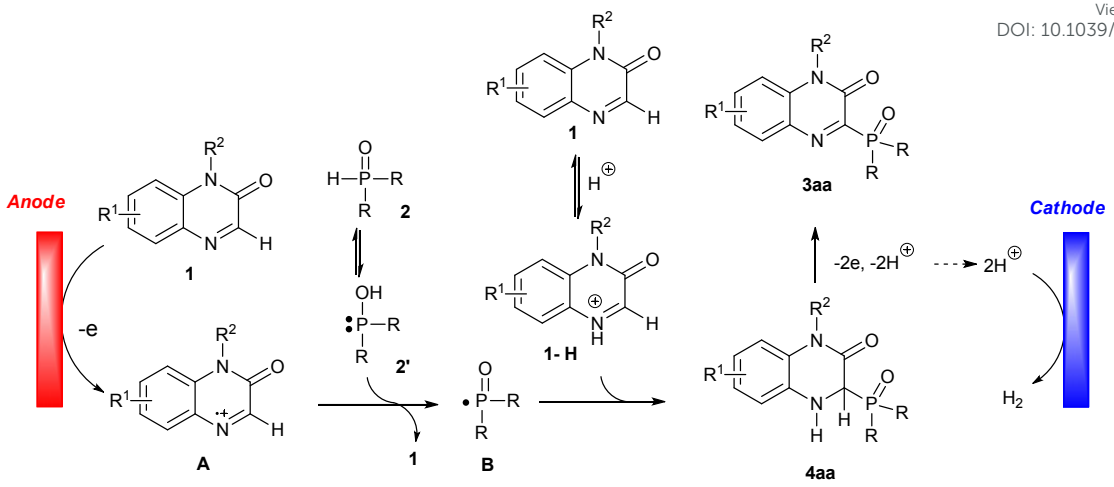
Table 2. Potentials of related compounds

Comp.	P_{ox}^1 (V)	P_{ox}^1 (V)	Comp.	P_{ox}^1 (V)	P_{ox}^1 (V)
1a	1.55	-	**4aa**	0.59	1.63
2a	1.92	-	**4**	1.29	-
3aa	1.86	-	**5a**	1.53	2.00

Conditions for cyclic voltammetry: Related compounds (5.0 mmol) in $LiClO_4$ (0.1 M) in CH_3CN using Pt working electrode, Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrode at 100 mV/s scan rate.

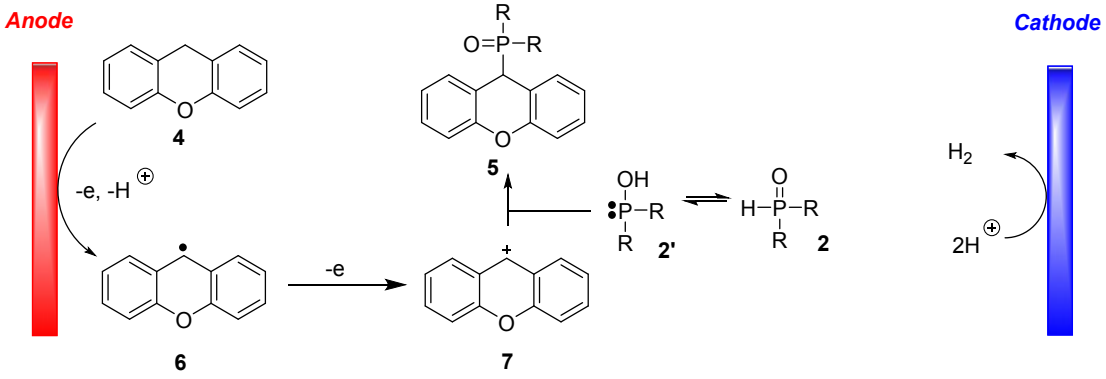
Based on the above experiments and literature studies, [8,9,17] a radical pathway for electrochemically oxidative phosphonation of quinoxaline-2(1*H*)-one reaction was proposed. As illustrated in Scheme 4, the anodic oxidation of quinoxaline-2(1*H*)-one **1** gives intermediate **A.** Since the low oxidation potential gap (1.55 V vs 1.92 V) between **1a** and **2a**, intermediate **A** may undergo homogeneous electron transfer with H-phosphonates or H-phosphine oxides to generate phosphorus-centered radical **B,** along with the regeneration of **1**. Radical **B** then carry out radical addition to carbon-nitrogen double bond of the protonated quinoxaline-2(1*H*)-one **1-H** to afford **4aa**. Further anodic oxidation and deprotonation of **4aa** affords the target product **3aa**. Simultaneously, proton is reduced at the cathode to generate molecular hydrogen which was detected by GC analysis (see ESI for details).

View Article Online
DOI: 10.1039/C9GC01474H



Scheme 4. Possible pathway for the electrochemical oxidative phosphonation of quinoxaline-2(1*H*)-ones

On the other hand, based on CV results and our previous work, [19f] a different pathway may proceed for the anodic cross-coupling of xanthene with phosphonate **2**. Since the much lower oxidation of xanthene than H-phosphonates (1.29 V vs 1.92 V for **2a**), xanthene is initially oxidized to the benzylic carbon radical. Followed by further oxidation, a benzylic carbocation is formed, which then react with **2'** to get the desired products **5** (Scheme 5).



Scheme 5. Possible pathway for the electrochemical oxidative phosphonation of xanthene

Conclusion

In summary, we have developed an efficient electrochemical method for the oxidative phosphonation of quinoxaline-2(1*H*)-one through dehydrogenative C(sp^2)-

View Article Online
DOI: 10.1039/C9GC01474H

H/P-H cross-coupling. Compared with the previous reports, this method has a broader range of substrates and up to 99% yield, with H-phosphonates and H-phosphine oxides as the phosphorus sources. This protocol can also be utilized for C(sp^3)-H/P-H cross-coupling of xanthene. Furthermore, this protocol avoids utilizing transition metal-based catalysts, external stoichiometric oxidants and additives, providing a sustainable and atom economical approach for the 3-phosphonated quinoxalin-2(1*H*)-ones.

Experimental

Instruments and reagents

All melting points were measured with an electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded using a 400 MHz or 300 MHz (400 MHz ^{1}H frequency, 100 MHz ^{13}C frequency; 300 MHz ^{1}H frequency, 75 MHz ^{13}C frequency). Chemical shifts are given as δ values (internal standard: TMS). Coupling constants are reported in Hz. The chemical shifts were referenced to signals at 7.28 ppm. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). All starting materials and solvents were obtained from commercial sources and used without further purification. Products were purified by chromatography on silica gel (petroleum ether/EtOAc or dichloromethane/methanol). The starting quinoxalin-2(1*H*)-ones were prepared according to known procedure.

Typical procedure for the synthesis of 3-Phosphonated Quinoxalin-2(1*H*)-ones

An undivided cell was equipped with a carbon anode (2.0×1.5 cm^2) and a platinum net (2.0×1.5 cm^2) and connected to a DC regulated power supply. To the cell was added the quinoxalinone (1 mmol), phosphate or phosphorus oxide (2 mmol) and 10 mL of 0.1 M $LiClO_4/CH_3CN$. The mixture was electrolyzed using constant current conditions (3 mA/cm^2) at 40 ^oC under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the quinoxalinone), the solvent was removed under reduced pressure. The residue was purified by column

View Article Online
DOI: 10.1039/C9GC01474H

chromatography on silica gel (petroleum ether/EtOAc or dichloromethane/methanol) to afford the desired pure product. The current density was calculated with the part of the electrode submerged into the electrolyte solution which described above (anode (2.0×1.5 cm^2) and a platinum net (2.0×1.5 cm^2)). The gap between the two electrodes was fixed in 1 cm.

Dimethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3aa)[9]

Primrose yellow solid; 229.0 mg; Yield 90%; m.p.: 156-158 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.86 (d, J = 11.2 Hz, 6H), 7.33-7.38 (m, 2H), 7.63-7.67 (m, 1H), 7.88 (d, J = 8.0 Hz, 1H), 12.84 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 54.5 (d, JCP = 6.0 Hz), 116.3, 124.3, 130.3, 132.0 (d, JCP = 25.5 Hz), 133.1 (d, JCP = 3.0 Hz), 133.4, 153.7 (d, JCP = 223.5 Hz), 154.5 (d, JCP = 31.5 Hz).

Dimethyl (3-oxo-1,2,3,4-tetrahydroquinoxalin-2-yl)phosphonate (4aa)[9]

White solid; 102.4 mg; Yield 40%; m.p.: 153-156 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.51 (d, J = 10.8 Hz, 3H), 3.64 (d, J = 10.8 Hz, 3H), 4.48 (d, J = 14.7 Hz, 1H), 6.28 (s, 1H), 6.54-6.60 (m, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.74-6.78 (m, 2H), 10.45 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 53.5 (dd, JCP = 13.5, 6.0 Hz), 55.2 (d, JCP = 132.8 Hz), 113.9, 115.2, 118.3, 123.4, 125.9, 133.1, 162.3 (d, JCP = 1.5 Hz).

Dimethyl (7-chloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ba)

Primrose yellow solid; 254.0 mg; Yield 88%; m.p.: 177-181 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.92 (d, J = 10.8 Hz, 6H), 7.37 (d, J = 8.8 Hz, 1H), 7.70 (dd, J = 8.8, 2.4 Hz, 1H), 7.97 (d, J = 2.4 Hz, 1H), 12.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 54.7 (d, JCP = 6.0 Hz), 118.0, 127.9, 129.1, 132.2 (d, JCP = 6.0 Hz), 132.5, 133.2, 154.3 (d, JCP = 26.0 Hz), 155.2 (d, JCP = 228.0 Hz). HRMS (ESI) m/z calculated for $C_{10}H_{10}ClN_2O_4P$ $(M+H)^+$ 289.0139, Found 289.0138.

Dimethyl (6-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca) and dimethyl (7-fluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ca')

Yellow solid; 119.7 mg; Yield 44%; m.p.: 127-131 °C; ^{1}H NMR for (3ca) (400 MHz, DMSO-d_6) δ 3.87 (d, J = 11.2 Hz, 6H), 7.36-7.40 (m, 1H), 7.61 (td, J = 8.8 Hz, 2.8 Hz,

1H), 7.39 (td, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.48-7.51 (m, 1H), 7.65 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 12.74 (s, 1H); 7.78 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 12.89 (s, 1H). ^{1}H NMR for (3ca') (400 MHz, DMSO-d_6) δ 3.86 (d, *J* = 10.8 Hz, 6H), 7.06 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.25 (td, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.95-7.99 (m, 1H), 12.89 (s, 1H); ^{13}C NMR for (3ca) and (3ca') (100 MHz, DMSO-d_6) δ 54.5 (d, *JCP* = 6.0 Hz), 54.6 (d, *JCP* = 7.0 Hz), 102.1 (d, *JCF* = 26.0 Hz), 112.6 (d, *JCF* = 24.0 Hz), 115.1 (d, *JCF* = 22.0 Hz), 117.9 (d, *JCF* = 9.0 Hz), 121.7 (d, *JCF* = 24.0 Hz), 130.1, 130.3, 132.0 (d, *JCF* = 11.0 Hz), 132.2 (d, *JCF* = 11.0 Hz), 133.0 (d, *JCF* = 12.0 Hz), 133.4, 154.2 (d, *JCP* = 31.0 Hz), 155.3 (d, *JCP* = 219.0 Hz), 158.3 (d, *JCF* = 239.0 Hz), 164.4 (d, *JCF* = 250.0 Hz). HRMS (ESI) m/z calculated for $C_{10}H_{10}FN_2O_4P$ $(M+H)^+$ 273.0435, Found 273.0432.

Dimethyl (6,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3da)[9]

Yellow solid; 172.2 mg; Yield 61%; m.p.: 188-191 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.27 (s, 3H), 2.31 (s, 3H), 3.86 (d, *J* = 11.2 Hz, 6H), 7.06 (s, 1H), 7.60 (s, 1H), 12.65 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.2, 20.5, 54.5 (d, *JCP* = 6.0 Hz), 116.1, 129.8, 130.6 (d, *JCP* = 25.0 Hz), 131.2 (d, *JCP* = 3.0 Hz), 133.3, 143.8, 151.9 (d, *JCP* = 225.0 Hz), 154.6 (d, *JCP* = 32.0 Hz).

Dimethyl (6,7-difluoro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ea)

Grey solid; 229.1 mg; Yield 79%; m.p.: 155-159 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.85 (d, *J* = 10.8 Hz, 6H), 7.21-7.25 (m, 1H), 7.98-8.03 (m, 1H), 12.96 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 54.6 (d, *JCP* = 6.0 Hz), 104.1 (d, *JCF* = 23.0 Hz), 117.9 (d, *JCF* = 19.0 Hz), 128.3 (dd, *JCF* = 26.0 Hz, *JCP* = 10.0 Hz), 131.1 (d, *JCF* = 11.0 Hz), 146.5 (dd, *JCF* = 243.0 Hz, 14.0 Hz), 152.2 (dd, *JCF* = 202.0 Hz, 15.0 Hz), 154.05 (d, *JCP* = 224.0 Hz), 154.14 (d, *JCP* = 31.0 Hz). HRMS (ESI) m/z calculated for $C_{10}H_9F_2N_2O_4P$ $(M+H)^+$ 291.0341, Found 291.0345.

Dimethyl (6,7-dichloro-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3fa)[9]

Yellow solid; 148.1 mg; Yield 46%; m.p.: 207-210 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.87 (d, *J* = 11.2 Hz, 6H), 7.50 (s, 1H), 8.17 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 54.7 (d, *JCP* = 6.0 Hz), 117.4, 126.1, 131.18, 131.23 (d, *JCP* = 26.0 Hz), 133.0 (d, *JCP* = 3.0 Hz), 135.4, 154.1 (d, *JCP* = 31.0 Hz), 155.5 (d, *JCP* = 223.0 Hz).

Dimethyl (4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ga)

Yellow solid; 158.2 mg; Yield 59%; m.p.: 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 4.06 (d, J = 11.2 Hz, 6H), 7.37-7.44 (m, 2H), 7.70 (t, J = 7.6 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9 (d, *JCP* = 1.0 Hz), 54.6 (d, *JCP* = 6.0 Hz), 114.0, 124.1, 131.8 (d, *JCP* = 1.0 Hz), 132.8 (d, *JCP* = 26.0 Hz), 133.2, 133.9 (d, *JCP* = 3.0 Hz), 152.0 (d, *JCP* = 230.0 Hz), 154.1 (d, *JCP* = 32.0 Hz). HRMS (ESI) m/z calculated for $C_{11}H_{13}N_2O_4P$ $(M+H)^+$ 269.0686, Found 269.0690.

Dimethyl (4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ha)

Yellow solid; 261.7 mg; Yield 89%; m.p.: 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (d, J = 11.2 Hz, 6H), 4.91-4.92 (m, 2H), 5.20-5.25 (m, 1H), 5.29-5.32 (m, 1H), 5.88-5.98 (m, 1H), 7.28-7.42 (m, 2H), 7.63-7.67 (m, 1H), 8.00 (dd, J = 8.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.4 (d, *JCP* = 1.0 Hz), 54.7 (d, *JCP* = 6.0 Hz), 114.5, 118.8, 124.1, 130.1, 131.8, 132.9 (d, *JCP* = 26.0 Hz), 133.1, 133.2 (d, *JCP* = 3.0 Hz), 152.1 (d, *JCP* = 230.0 Hz), 153.7 (d, *JCP* = 32.0 Hz). HRMS (ESI) m/z calculated for $C_{13}H_{15}N_2O_4P$ $(M+H)^+$ 295.0842, Found 295.0843.

Ethyl 2-(3-(dimethoxyphosphoryl)-2-oxoquinoxalin-1(2H)-yl)acetate (3ia)[9]

White solid; 248.3 mg; Yield 73%; m.p.: 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 4.05 (d, J = 10.8 Hz, 6H), 4.25 (q, J = 14.4 Hz, 2H), 5.03 (s, 2H), 7.12 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 43.2 (d, *JCP* = 1.0 Hz), 54.6 (d, *JCP* = 6.0 Hz), 62.2, 113.5, 124.4, 132.0 (d, *JCP* = 2.0 Hz), 132.8 (d, *JCP* = 26.0 Hz), 133.1 (d, *JCP* = 3.0 Hz), 133.3, 152.0 (d, *JCP* = 231.0 Hz), 153.6 (d, *JCP* = 33.0 Hz), 166.6.

Dimethyl (4-(4-methylbenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ja)

Yellow oily; 297.2 mg; Yield 83%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.23 (s, 3H), 3.91 (d, J = 10.8 Hz, 6H), 5.45 (s, 2H), 7.14 (q, J = 19.2 Hz, 4H), 7.42 (t, J = 8.0 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.65-7.70 (m, 1H), 7.95-7.97 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.1, 45.1, 54.7 (d, *JCP* = 6.0 Hz), 116.0, 124.6, 127.3, 129.8, 131.5, 132.78 (d, *JCP* = 26.0 Hz), 132.83, 133.5 (d, *JCP* = 3.0 Hz), 133.8, 137.2, 152.4 (d, *JCP* = 227.0 Hz), 154.1 (d, *JCP* = 32.0 Hz). HRMS (ESI) m/z calculated for

View Article Online
DOI: 10.1039/C9GC01474H

$C_{18}H_{19}N_2O_4P$ $(M+H)^+$ 359.1155, Found 359.1154.

Dimethyl (4-(4-methoxybenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ka)

Yellow oily; 198.2 mg; Yield 53%; ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.09 (d, J = 10.8 Hz, 6H), 5.43 (s, 2H), 6.83-6.86 (m, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.34-7.37 (m, 2H), 7.54-7.59 (m, 1H), 7.99 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.4, 54.7 (d, JCP = 6.0 Hz), 55.3, 114.4, 114.7, 124.1, 126.7, 128.6, 131.9, 133.0, 133.1 (d, JCP = 27.0 Hz), 133.0, 133.3 (d, JCP = 3.0 Hz), 152.3 (d, JCP = 230.0 Hz), 154.3 (d, JCP = 32.0 Hz), 159.2. HRMS (ESI) m/z calculated for $C_{18}H_{19}N_2O_5P$ $(M+H)^+$ 375.1104, Found 375.1102.

Dimethyl (4-(4-(tert-butyl)benzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3la)

Light gray solid; 372.1 mg; Yield 93%; m.p.: 192-194 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 4.10 (d, J = 11.2 Hz, 6H), 5.47 (s, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.33-7.39 (m, 4H), 7.56-7.60 (m, 1H), 8.01 (d, JCP = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.5, 45.5 (d, JCP = 2.0 Hz), 54.7 (d, JCP = 7.0 Hz), 114.8 (d, JCP = 1.0 Hz), 124.1, 125.9, 126.9, 131.6, 131.8 (d, JCP = 1.0 Hz), 133.0 (d, JCP = 24.0 Hz), 133.2, 133.4 (d, JCP = 3.0 Hz), 150.9, 152.2 (d, JCP = 231.0 Hz), 154.2 (d, JCP = 32.0 Hz). HRMS (ESI) m/z calculated for $C_{21}H_{25}N_2O_4P$ $(M+H)^+$ 401.1625, Found 401.1635.

Dimethyl (4-(3,5-dimethylbenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ma)

Yellow solid; 368.4 mg; Yield 99%; m.p.: 186-188 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 6H), 3.99 (d, J = 11.2 Hz, 6H), 5.46 (s, 2H), 6.81 (s, 2H), 6.85 (s, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.41-7.45 (m, 1H), 7.60-7.64 (m, 1H), 8.03 (dd, J = 8.0 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 46.7, 55.2 (d, JCP = 6.0 Hz), 115.8, 124.5, 125.1, 129.6, 131.8, 133.0 (d, JCP = 3.0 Hz), 133.7 (d, JCP = 26.0 Hz), 134.2, 134.3, 138.7, 148.7 (d, JCP = 232.0 Hz), 155.6 (d, JCP = 33.0 Hz). HRMS (ESI) m/z calculated for $C_{19}H_{21}N_2O_4P$ $(M+H)^+$ 373.1312, Found 373.1319.

Dimethyl (4-(4-fluorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3na)

Yellow oily; 340.4 mg; Yield 94%; ^1H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, J = 10.8 Hz,

6H), 5.47 (s, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 7.27-7.32 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.2, 54.7 (d, *JCP* = 6.0 Hz), 114.5, 115.9, 116.1, 124.3, 129.0 (d, *JCF* = 8.0 Hz), 130.4 (d, *JCP* = 3.0 Hz), 132.0, 133.0 (d, *JCP* = 19.0 Hz), 133.2, 152.3 (d, *JCP* = 231.0 Hz), 154.2 (d, *JCP* = 33.0 Hz), 162.3 (d, *JCF* = 245.0 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{16}FN_2O_4P$ $(M+H)^+$ 363.0904, Found 363.0897.

Dimethyl (4-(4-chlorobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3oa)

Yellow solid; 332.7 mg; Yield 88%; m.p.: 56-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (d, *J* = 11.2 Hz, 6H), 5.46 (s, 2H), 7.22-7.32 (m, 5H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.56-7.60 (m, 1H), 8.02 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.2 (d, *JCP* = 1.0 Hz), 54.7 (d, *JCP* = 6.0 Hz), 114.5, 124.3, 128.6, 129.2, 132.0, 133.0 (d, *JCP* = 26.0 Hz), 133.04 (d, *JCP* = 3.0 Hz), 133.2, 133.8, 152.3 (d, *JCP* = 231.0 Hz), 154.1 (d, *JCP* = 32.0 Hz). (1 carbon is missing due to overlapping) HRMS (ESI) m/z calculated for $C_{17}H_{16}ClN_2O_4P$ $(M+H)^+$ 379.0609, Found 379.0604.

Dimethyl (4-(4-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3pa)

Yellow solid; 358.7 mg; Yield 85%; m.p.: 61-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, *J* = 10.8 Hz, 6H), 5.45 (s, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.3, 54.7 (d, *JCP* = 7.0 Hz), 114.5, 121.9, 124.3, 128.9, 132.0 (d, *JCP* = 1.0 Hz), 132.1, 133.0 (d, *JCP* = 26.0 Hz), 133.03 (d, *JCP* = 3.0 Hz), 133.2, 133.7, 152.3 (d, *JCP* = 230.0 Hz), 154.1 (d, *JCP* = 32.0 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{16}BrN_2O_4P$ $(M+H)^+$ 423.0104, Found 423.0103.

Dimethyl (4-(2-bromobenzyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3qa)

Yellow solid; 371.4 mg; Yield 88%; m.p.: 110-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (d, *J* = 11.2 Hz, 6H), 5.57 (s, 2H), 6.76-6.78 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.17 (t, *J* = 3.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.64-7.67 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.1, 54.8 (d, *JCP* = 6.0 Hz), 114.8, 122.5, 124.4, 127.0, 128.1, 129.4, 131.9, 133.0 (d, *JCP* = 3.0 Hz), 133.02

(d, *JCP* = 26.0 Hz), 133.1, 133.4, 152.4 (d, *JCP* = 231.0 Hz), 154.2 (d, *JCP* = 33.0 Hz). (1 carbon is missing due to overlapping) HRMS (ESI) m/z calculated for $C_{17}H_{16}BrN_2O_4P$ $(M+H)^+$ 423.0104, Found 423.0099.

(2,2-diphenylvinyl)diphenylphosphine oxide (3ra)

Yellow solid; 64.6 mg; Yield 17%; m.p.: 136-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 18.4 Hz, 1H), 7.09-7.16 (m, 3H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.32-7.38 (m, 8H), 7.40-7.42 (m, 3H), 7.68-7.73 (m, 4H). HRMS (ESI) m/z calculated for $C_{26}H_{21}OP$ $(M+H)^+$ 381.1403, Found 381.1404.

Dimethyl (9H-xanthen-9-yl)phosphonate (3sa)

White solid; 150.8 mg; Yield 52%; m.p.: 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (d, *J* = 10.8 Hz, 6H), 4.51 (d, *J* = 24.8 Hz, 1H), 7.08-7.12 (m, 4H), 7.25-7.30 (m, 2H), 7.33-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0 (d, *JCP* = 140.0 Hz), 53.7 (d, *JCP* = 7.0 Hz), 116.7 (d, *JCP* = 4.0 Hz), 117.0 (d, *JCP* = 8.0 Hz), 123.4 (d, *JCP* = 4.0 Hz), 128.9 (d, *JCP* = 3.0 Hz), 130.1 (d, *JCP* = 5.0 Hz), 152.3 (d, *JCP* = 5.0 Hz). HRMS (ESI) m/z calculated for $C_{15}H_{15}O_4P$ $(M+H)^+$ 291.0781, Found 291.0779.

Diethyl (9H-xanthen-9-yl)phosphonate (3ta)

Yellow oily; 171.7 mg; Yield 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 6H), 3.89 (m, 4H), 4.50 (d, *J* = 24.8 Hz, 1H), 7.09-7.13 (m, 4H), 7.26-7.31 (m, 2H), 7.37-7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3 (d, *JCP* = 6.0 Hz), 40.4 (d, *JCP* = 140.0 Hz), 63.1 (d, *JCP* = 7.0 Hz), 116.6 (d, *JCP* = 3.0 Hz), 117.3 (d, *JCP* = 9.0 Hz), 123.2 (d, *JCP* = 3.0 Hz), 128.7 (d, *JCP* = 3.0 Hz), 130.2 (d, *JCP* = 4.0 Hz), 152.4 (d, *JCP* = 5.0 Hz). HRMS (ESI) m/z calculated for $C_{17}H_{19}O_4P$ (M+H)+ 319.1094, Found 319.1106.

Diphenyl(9H-xanthen-9-yl)phosphine oxide (3ua)

Primrose yellow solid; 301.8 mg; Yield 79%; m.p.: 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (d, *J* = 18.0 Hz, 1H), 6.86-6.91 (m, 4H), 6.97-6.99 (m, 2H), 7.15-7.20 (m, 2H), 7.35 (td, *J* = 7.6 Hz, 2.8 Hz, 4H), 7.49-7.57 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.3 (d, *JCP* = 64.0 Hz), 116.4 (d, *JCP* = 2.0 Hz), 116.9 (d, *JCP* = 5.0 Hz), 123.0 (d, *JCP* = 2.0 Hz), 128.1, 128.2, 128.7 (d, *JCP* = 3.0 Hz), 128.9 (d, *JCP* = 95.0 Hz), 130.3 (d, *JCP* = 4.0 Hz), 132.1 (d, *JCP* = 3.0 Hz), 132.2, 132.3, 152.6 (d, *JCP* =

4.0 Hz). HRMS (ESI) m/z calculated for $C_{25}H_{19}O_2P$ $(M+H)^+$ 383.1195, Found 383.1196.

Diethyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ab)[9]

Yellow solid; 248.2 mg; Yield 88%; m.p.: 175-178 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.32 (t, J = 6.8 Hz, 6H), 4.22-4.29 (m, 4H), 7.34-7.39 (m, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 12.77 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 16.8 (d, *JCP* = 6.0 Hz), 63.8 (d, *JCP* = 6.0 Hz), 116.3, 124.2, 130.3, 131.9 (d, *JCP* = 25.0 Hz), 133.2, 133.3, 154.1 (d, *JCP* = 224.0 Hz), 154.5 (d, *JCP* = 32.0 Hz).

Diisopropyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ac)[9]

Primrose yellow solid; 269.8 mg; Yield 87%; m.p.: 178-181 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.35 (dd, J = 6.0 Hz, 4.8 Hz, 12H), 4.78-4.86 (m, 2H), 7.34-7.40 (m, 2H), 7.64-7.68 (m, 1H), 7.85 (d, J = 8.0 Hz, 1H), 12.73 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 23.9 (d, *JCP* = 6.0 Hz), 24.5 (d, *JCP* = 3.0 Hz), 72.3 (d, *JCP* = 7.0 Hz), 116.2, 124.3, 130.2, 131.9 (d, *JCP* = 26.0 Hz), 133.1 (d, *JCP* = 3.0 Hz), 133.3, 154.3 (d, *JCP* = 32.0 Hz), 154.5 (d, *JCP* = 224.0 Hz).

Dibutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ad)[9]

Yellow solid; 334.8 mg; Yield 99%; m.p.: 91-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 6H), 1.46-1.55 (m, 4H), 1.76-1.83 (m, 4H), 4.40 (q, J = 13.8 Hz, 4H), 7.38-7.42 (m, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.59-7.63 (m, 1H), 7.96 (d, J = 8.0 Hz, 1H), 12.87 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.7, 18.8, 32.6 (d, *JCP* = 6.0 Hz), 67.8 (d, *JCP* = 6.0 Hz), 116.5, 124.5, 130.4, 132.2 (d, *JCP* = 3.0 Hz), 132.7 (d, J_{CP} = 25.0 Hz), 132.9, 152.8 (d, *JCP* = 228.0 Hz), 156.0 (d, *JCP* = 32.0 Hz).

Diisobutyl (3-oxo-3,4-dihydroquinoxalin-2-yl)phosphonate (3ae)[9]

Primrose yellow solid; 334.7 mg; Yield 99%; m.p.: 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.4 Hz, 12H), 2.01-2.04 (m, 2H), 4.10 (s, 4H), 7.35 (t, J = 7.6 Hz, 1H), 7.49-7.59 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.8 (d, *JCP* = 1.0 Hz), 29.3 (d, *JCP* = 6.0 Hz), 73.9 (d, *JCP* = 6.0 Hz), 116.4, 124.5, 130.5, 132.1 (d, *JCP* = 3.0 Hz), 132.6, 132.8 , 152.9 (d, *JCP* = 229.0 Hz), 156.1 (d, *JCP* = 31.0 Hz).

3-(diphenylphosphoryl)quinoxalin-2(1H)-one (3af)[9]

Yellow solid; 342.6 mg; Yield 99%; m.p.: 256-258 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32-7.37 (m, 2H), 7.50-7.55 (m, 4H), 7.58-7.61 (m, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.77-7.82 (m, 4H), 12.74 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 116.4, 124.2, 128.8 (d, *JCP* = 12.0 Hz), 130.4, 131.8 (d, *JCP* = 9.0 Hz), 132.2 (d, *JCP* = 2.0 Hz), 132.5 (d, *JCP* = 20.0 Hz), 132.8, 133.4, 133.5, 154.6 (d, *JCP* = 24.0 Hz), 157.5 (d, *JCP* = 126.0 Hz).

3-(bis(3,5-dimethylphenyl)phosphoryl)quinoxalin-2(1*H*)-one (3ag)

Yellow solid; 394.1 mg; Yield 98%; m.p.: 251-254 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.29 (s, 12H), 7.20 (s, 2H), 7.31-7.39 (m, 6H), 7.64 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 12.67 (s, 1H). HRMS (ESI) m/z calculated for C24H23N2O2P $(M+H)^+$ 403.1570, Found 403.1578.

3-(di(naphthalen-2-yl)phosphoryl)quinoxalin-2(1H)-one (3ah)

Yellow solid; 258.7 mg; Yield 58%; m.p.: 281-284 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.32 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.58-7.72 (m, 6H), 7.88 (t, J = 9.2 Hz, 2H), 7.98-8.05 (m, 4H), 8.08 (d, J = 8.0 Hz, 2H), 8.54 (d, J = 14.0 Hz, 2H), 12.77 (s, 1H). HRMS (ESI) m/z calculated for $C_{28}H_{19}N_2O_2P$ $(M+H)^+$ 447.1257, Found 447.1266.

Acknowledgements

This work was supported by grants from the National Key Technology R&D Program (2016YFD040080) and the National Natural Science Foundation of China (No. 21871019).

References:

[1] *(a)* C. S. Demmer, N. K. Larsen, L. Bunch, *Chem. Rev.*, 2011, **111,** 7981; *(b)* J. L. Montchamp, *Accounts. Chem. Res.*, 2014, **47,** 77; *(c)* M. F. Mady, M. A. Kelland, *Energ. Fuel.*, 2017, **31,** 4603; *(d)* V. Ntatsopoulos, K. Macegoniuk, A. Mucha, S. Vassiliou, L. Berlicki, *Eur. J. Med. Chem.*, 2018, **159,** 307; *(e)* N. Llorente, H. Fernández-Pérez, J. L. Núñez-Rico, L. Carreras, A. Martínez-Carrión, E. Iniesta, A. Romero-Navarro, A. Martínez-Bascuñana, A. Vidal-Ferran, *Pure. Appl. Chem.*,

View Article Online
DOI: 10.1039/C9GC01474H

2019, **91,** 3.

[2] *(a)* A. K. Bhattacharya, G. Thyagarajan, *Chem. Rev.*, 1981, **81,** 415; *(b)* A. Jasiak, G. Mielniczak, K. Owsianik, M. Koprowski, D. Krasowska, J. Drabowicz, *J. Org. Chem.*, 2019, **84,** 2619; *(c)* X. T. Ma, Q. Xu, H. Li, C. L. Su, L. Yu, X. Zhang, H. E. Cao, L. B. Han, *Green Chem.*, 2018, **20,** 3408.

[3] *(a)* T. Hirao, T. Masunaga, Y. Ohshiro, T. Agawa, *Synthesis-Stuttgart.*, 1981, **1,** 56; *(b)* E. A. Mikhalitsyna, E. S. Podyacheva, A. D. Averin, I. P. Beletskaya, *J. Porphyr. Phthalocya.*, 2018, **22,** 603; *(c)* J. Y. Dong, L. Liu, X. Y. Ji, Q. Shang, L. X. Liu, L. B. Su, B. Chen, R. F. Kan, Y. B. Zhou, S. F. Yin, L. B. Han, DOI: 10.1021/acs.orglett.9b00922. *(d)* R. Jójárt, S. Pécsy, G. Keglevich, M. Szécsi, R. Rigó, C. Özvegy-Laczka, G. Kecskeméti, E. Mernyák, *Beilstein J. Org. Chem.*, 2018, **14,** 2838.

[4] *(a)* H. Singh, T. Sahoo, C. Sen, S. M. Galani, S. C. Ghosh, *Catal. Sci. Technol.*, 2019, **9,** 1691; *(b)* H. Lee, J. Yun, *Org. Lett.*, 2018, **20,** 7961; *(c)* J. Wang, J. Li, Y. Y. Wei, J. Y. Yang, C. D. Huo, *Org. Chem. Front.*, 2018, **5,** 3534; *(d)* K. N. Li, X. X. Shao, L. Tseng, S. J. Malcolmson, *J. Am. Chem. Soc*., 2018, **140,** 598.

[5] *(a)* G. Y. Zhang, C. K. Li, D. P. Li, R. S. Zeng, A. Shoberu, J. P. Zou, *Tetrahedron. Lett.*, 2016, **72,** 2972; *(b)* H. Lim, V. Datilus, R. Teriak, P. Chohan, P. Kaur, *Tetrahedron Lett.*, 2017, **58,** 1480; *(c)* D. Yamamoto, H. Ansai, J. Hoshino, K. Makino, *Chem. Pharm. Bull.*, 2018, **66,** 873; *(d)* J. Xu, X. Q. Li, Y. Z. Gao, L. L. Zhang, W. Z. Chen, H. Fang, G. Tang, Y. F. Zhao, *Chem. Commun.*, 2015, **51,** 11240.

[6] *(a)* S. Mahdjoub, R. Boulcina, M. Yildirim, S. Lakehal, H. Boulebd, A. Debache, *Synthetic. Commun.*, 2018, **48,** 2366; *(b)* X. X. Su, F. Yang, Y. S. Wu, Y. J. Wu, *Org. Biomol. Chem.*, 2018, **16,** 2753; *(c)* E. O. Yurko, T. V. Gryaznova, K. V. Kholin, V. V. Khrizanforova, Y. H. Budnikova, *Dalton. T.*, 2018, **47,** 190; *(d)* R. W. Shen, J. L. Yang, M. Zhang, L. B. Han, *Adv. Synth. Catal.*, 2017, **359,** 3626.

[7] B. G. Cai, J. Xuan, W. J. Xiao, *Sci. Bull.*, 2019, **64,** 337.

[8] *(a)* X. Y. Qin, X. Hao, H. Han, S. J. Zhu, Y. C. Yang, B. B. Wu, S. Hussain, S. Parveen, C. J. Jing, B. Ma, C. J. Zhu, *J. Med. Chem.*, 2015, **58,** 1254; *(b)* S. A. M.

El-Hawash, N. S. Habib, M. A. Kassem, *Arch. Pharm.*, 2006, **339,** 564; *(c)* S. A. Galal, S. H. M. Khairat, F. A. F. Ragab, A. S. Abdelsamie, M. M. Ali, S. M. Soliman, J. Mortier, G. Wolber, H. I. E. Diwani, *Eur. J. Med. Chem.*, 2014, **86,** 122; *(d)* M. I. Shahin, D. A. Abou El Ella, N. S. M. Ismail, K. A. M. Abouzid, *Bioorg. Chem.*, 2014, **56,** 16; *(e)* M. Weïwer, J. Spoonamore, J. Q. Wei, B. Guichard, N. T. Ross, K. Masso, W. Silkwort, S. Dandapan, M. Palmer, C. A. Scherer, A. M. Stern, S. L. Schreiber, B. Munoz, *ACS. Med. Chem. Lett.*, 2012, **3,** 1034.

[9] M. Gao, Y. Li, L. J. Xie, R. Chauvin, X. L. Cui, *Chem. Commun.*, 2016, **52,** 2846.

[10] Y. Kim, D. Y. Kim, *Tetrahedron Lett.*, 2018, **59,** 2443.

[11] For the detailed discussion of organic electrosynthesis as the green synthetic tool, see: *(a)* H. J. Schäfer, *C. R. Chim.*, 2011, **14**, 745; *(b)* B. A. Frontana-Uribe, R. Daniel Little, J. G. Ibanez, A. Palma, R. Vasquez-Medrano, *Green Chem.*, 2010, **12**, 2099.

[12] For reviews on organic electrosynthesis, see: *(a)* M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.*, 2017, **117,** 13230; *(b)* Y. Y. Jiang, K. Xu, C. C. Zeng, *Chem. Rev.*, 2018, **118,** 4485; *(c)* Q. L. Yang, P. Fang, T. S. Mei, *Chin. J. Chem.*, 2018, **36,** 338; *(d)* A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes, S. R. Waldvogel, *Angew. Chem. Int. Ed.*, 2018, **57,** 5594; *(e)* J. I. Yoshida, A. Shimizu, R. Hayashi, *Chem. Rev*., 2018, **118,** 4702; *(f)* R. Francke, R. D. Little, *Chem. Soc. Rev*., 2014, **43,** 2492; *(g)* M. D. Kärkäs, *Chem. Soc. Rev.*, 2018, **47,** 5786; *(h)* Z. H. Ye, F. Z. Zhang, Chin. J. Chem., 2019, **37,** 513; *(i)* J. B. Chen, S. D. Lv, S. Y. Tian, *Chem. Sus. Chem.*, 2019, **12,** 115.

[13] *(a)* Y. Y. Gao, Y. Wang, J. Zhou, H. B. Mei, J. L. Han, *Green Chem.*, 2018, **20,** 58; *(b)* Q. Q. Wang, K. Xu, Y. Y. Jiang, Y. G. Liu, B. G. Sun, C. C. Zeng, *Org. Lett.*, 2017, **19,** 5517; *(c)* D. T. Yang, M. H. Zhu, Z. J. Schiffer, K. Williams, X. J. Song, X. H. Liu, K. Manthiram, *ACS Catal.*, 2019, **9,** 4699; *(d)* W. J. Kong, L. H. Finger, J. C. A. Oliveira, L. Ackermann, *Angew. Chem. Int. Ed.*, 2019, **58,** 6342;

(e) N. Fu, Y. F. Shen, A. R. Allen, L. Song, A. Ozaki, S. Lin, *ACS Catal.*, 2019, **9,** 746.

[14] *(a)* M. L. Feng, S. Q. Li, H. Z. He, L. Y. Xi, S. Y. Chen, X. Q. Yu, *Green Chem.*, 2019, **21,** 1619; *(b)* Y. Yu, Y. Yuan, H. L. Liu, M. He, M. Z. Yang, P. Liu, B. Y. Yu, X. C. Dong, A. W. Lei, *Chem. Commun.*, 2019, **55,** 1809; *(c)* Y. Adeli, K. M. Huang, Y. J. Liang, Y. Y. Jiang, J. Z. Liu, S. Song, C. C. Zeng, N. Jiao, *ACS Catal.*, 2019, **9,** 2063; *(d)* X. H. Chang, Q. L. Zhang, C. Guo, *Org. Lett.*, 2019, **21,** 10; *(e)* S. Zhang, L. Li, M. Xue, R. Zhang, K. Xu, C. Zeng, *Org. Lett.*, 2018, **20**, 3443; *(f)* S. Tang, S. Y. Wang, Y. C. Liu, H. J. Cong, A. W. Lei, *Angew. Chem. Int. Ed.*, 2018, **57,** 4737.

[15] *(a)* S. Zhang, L. Li, J. Zhang, J. Zhang, M. Xue, K. Xu, *Chem. Sci.*, 2019, **10,** 3181; *(b)* J. A. Marko, A. Durgham, S. L. Bretz, W. Liu, *Chem. Commun.*, 2019, **55,** 937; *(c)* F. Wang, M. Rafiee, S. S. Stahl, *Angew. Chem. Int. Ed.*, 2018, **57,** 6686; *(d)* A. Shao, N. Li, Y. Gao, J. Zhan, C. W. Chiang, A. W. Lei, *Chin. J. Chem.*, 2018, **36,** 619; *(e)* X. Z. Tao, J. J. Dai, J. Zhou, J. Xu, H. J. Xu, *Chem. Eur. J.*, 2018, **24,** 6932; *(f)* S. Zhang, L. J. Li, H. Q. Wang, Q. Li, W. M. Liu, K. Xu, C. C. Zeng, *Org. Lett.*, 2018, **20,** 252.

[16] *(a)* C. L. Song, K. Liu, X. Dong, C. W. Chiang, A. W. Lei, *Synlett.*, 2019, **30,** 1149; *(b)* Y. Wang, L. L. Deng, X. C. Wang, Z. G. Wu, Y. Wang, Y. Pan, *ACS Catal.*, 2019, **9,** 1630; *(c)* D. D. Li, S. B. Li, C. Peng, L. J. Lu, S. C. Wang, P. Wang, Y. H. Chen, H. J. Cong, A. W. Lei, *Chem. Sci.*, 2019, **10,** 2791; *(d)* Y. Wang, L. L. Deng, H. B. Mei, B. N. Du, J. L. Han, Y. Pan, *Green Chem.*, 2018, **20,** 3444; (e) D. Liu, H. X. Ma, P. Fang, T. S. Mei, *Angew. Chem. Int. Ed.*, 2019, **58,** 5033.

[17] *(a)* M. N. Khrizanforov, S. O. Strekalova, K. V. Kholin, V. V. Khrizanforova, M.K. Kadirov, T.V. Gryaznova, Y.H. Budnikova, *Catal. Today.*, 2017, **279,** 133; *(b)* M. Khrizanforov, S. Strekalova, V. Khrizanforova, A. Dobrynin, K. Kholin, T. Gryaznova, V. Grinenko, A. Gubaidullin, M. K. Kadirov, Y. Budnikova, *Top. Catal.*, 2018, **61,** 1949; *(c)* E. O. Yurko, T. V. Gryaznova, K. V. Kholin, V. V. Khrizanforova, Y. H. Budnikova, *Dalton. T.*, 2018, **47,** 190; *(d)* E. O. Yurko, T. V. Gryaznova, Y. H. Budnikova, *Phosphorus. Sulfur.*, DOI:

View Article Online
DOI: 10.1039/C9GC01474H

10.1080/10426507.2018.1541897.

[18] Y. H. Budnikova, O. G. Sinyashin, *Russ. Chem. Rev.*, 2015, **84,** 917.

[19] *(a)* C. C. Sun, K. Xu, C. C. Zeng, *ACS. Sustainable Chem. Eng.*, 2019, **7,** 2255; *(b)* M. H. Luo, Y. Y. Jiang, K. Xu, Y. G. Liu, B. G. Sun, C. C. Zeng, *Beilstein J. Org. Chem.*, 2018, **14,** 499; *(c)* S. Liang, K. Xu, C. C. Zeng, H. Y. Tian, B. G. Sun, *Adv. Synth. Catal.*, 2018, **360,** 4266; *(d)* Y. Y. Jiang, G. Y. Dou, K. Xu, C. C. Zeng, *Org. Chem. Front.*, 2018, **5,** 2573; *(e)* K. J. Li, K. Xu, Y. G. Liu, C. C. Zeng, B. G. Sun, *Adv. Synth. Catal*., 2018, **360,** 1; *(f)* M. Y. Lin, K, Xu, Y. Y. Jiang, Y. G. Liu, B. G. Sun, C. C. Zeng, *Adv. Synth. Catal*., 2018, **360,** 1665; *(g)* F. Lian, C. C. Sun, K. Xu, C. C. Zeng, *Org. Lett.*, 2019, **21,** 156.