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Catalytic C–C Coupling of Diazo Compounds with Arylboronic Acids: Using Surface Modified Sewage Sludge as Catalyst

Zhipeng Zhang^{1,3 \perp}, Yang Yu^{2,4 \perp}, Yuxing Xie³, Timothy Hughes,⁴ Jun Xu,⁵ Fei Huang^{*3} and He Huang^{*,1,3}

A green, mild and efficient synthesis of diarylmethines via sewage sludge-derived carbonaceous materials (SW) by perchloric acid catalyzed coupling reactions between diazo compounds and arylboronic acids was developed. The reaction shows a high level of functional tolerance and broad substrate scope. Furthermore, the highly selective 1,2-alkyl shift products were furnishend through the sterically demanding R⁴, R⁵ migration of diazo compounds (3-diazochromanone). The structures of 1,2-shift products have been further confirmed by single-crystal X-ray analysis. Significantly, the systhesis of the core structures of darifenacin (clinical drug for overactive bladder syndrome, OAB) and diclofensine (stimulant drug showing antidepressant and monoamine reuptake inhibitor activity) further demonstrated the efficacy and synthetic potential of this method.

Introduction

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Diarylacetates¹ are ubiquitous subunits which present in therapeutically important marketed drugs, bioactive molecules and natural products (Fig. 1). In this area, darifenacin is used for the treatment of overactive bladder syndrome.² BPA-COOH is a bioactive molecule which exhibits antiproliferative activity against MCF-7 cell lines.³ Bromophenol derivative is one of the natural products from the red alga, numerous recent studies have shown that they have anti-inflammatory, anti-oxidative and anti-tumorigenic activities.⁴

In view of the medicinal applications, green and highly efficient synthesis of diarylacetate derivatives has attracted much attention. Classical syntheses of diarylacetate derivatives suffer from the use of toxic reagents,^{5a} multi-step reactions^{5b} and harsh reaction conditions.^{5c} Based on these classic methods, new synthetic methods have been gradually developed. Such as transition-metal catalyzed direct arylation of aryl acetate derivatives^{6a-b} or α -halo aryl acetate derivatives,^{6c} as well as tandem cross-coupling of ethyl diazoacetate (EDA) (Scheme 1a).^{6d} Diazo compounds could also be used for the synthesis of diarylacetate derivatives through C-H bond functionalization with phenols (Scheme 1b)⁷ or

coupling with ArSi(OMe)₃ and ArSnMe₃ (Scheme 1c).⁸ These transformations provide effective methods to afford diarylacetate derivatives, but developing greener and sustainable methods for these transformations have always been a serious challenge. Boronic acid derivatives are stable, nontoxic, and easily available, becoming popularity within the synthetic organic chemistry.⁹ Most recently, an alternative synthesis of diarylacetates were accomplished via C-C coupling of diazo compounds with arylboronic acids (Scheme 1d). These transformations often need transition-metal catalysts,10 such as Pd^{10a} or Rh^{10b-d}, as well as the strong base (ⁱPr₂NH)¹¹ or other additive¹² (CF₃TMS^{6c,12a} or NH₄Cl^{12b}). With this context, we wonder whether the cheaper and ubiquitous sewage sludge-derived carbonaceous materials (SW) could be used as a greener catalyst for these transformations. This work, surface modified SW-I will be used as valuable and greener catalyst for C-C coupling without using additional base or addictive (Scheme 1e).



Fig. 1 Diarylacetate group in biologically active compounds.

- [1] School of Biology and Biological Engineering, South China University of Technology, Guangzhou, 510006, China.
- [2] School of Environmental Science and Engineering, Nanjing Tech University, Nanjing, 211816, China.
- [3] School of Food Science and Pharmaceutical Engineering, Nanjing Normal University, Nanjing, 210023, China.
- [4] Manufacturing, CSIRO, Clayton, Victoria 3169, Australia.
- [5] Aba Chemicals Corporation, Shanghai, 200063, China.
- [⊥]These authors contributed equally to this work.

Email: huangfei0208@yeah.net; huang_h@njnu.edu.cn

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Scheme 1. Synthesis of diarylacetates.

Wastewater is one of the most abundant residues which derives from industry and domestic activities.¹³ Sewage sludge is a major by-product generated in wastewater treatment. The main contaminants of sewage sludge are proteins, carbohydrates, heavy metals, pathogenic bacteria and other inorganic or organic pollutants, presenting a high risk to the environment.¹⁴ So far, traditionally sewage sludge has been disposed in landfill sites or use as fertilizer.¹⁵ On the other hand, the sewage sludge could be also activated by thermal or chemical activation methods. The latter method involves the impregnation of waste sludge with a salt, acid or base.¹⁶ Notably, carbonization of sewage sludge under the pyrolysis to produce sewage sludge-derived carbonaceous materials (SW) has been a sustainable method for appropriate use of sewage sludge. Because of its greener, low cost and catalytically active characteristics, which could be used as adsorbents for air pollution, organic pollutants and heavy metals.¹⁷ Further, it also could be used as a beneficial catalyst for degradation of organic wastewater or even for preparation of the surfactants, microp lastics, sewage sludge biochar (SSBC) and nanoparticles.¹⁸ Currently, Luque groups¹⁹ have reported that sewage sludge material would be also used for the selective oxidation of isoeugenol to vanillin. We reasonably envisioned whether SW can be used as advanced and high-activity catalyst for organic synthesis. In this paper, we reported SW-I catalyzed C-C coupling reactions of diazo compounds with arylboronic acids. SW was treated by HClO₄, HCl, H₂SO₄, H₃PO₄, HNO₃ NaOH respectively, we called them SW- I (HClO₄), SW-II (HCl), SW-III (H_2SO_4), SW-IV (H_3PO_4), SW-V (HNO₃) and SW-VI (NaOH)¹⁷, common soil also treated by HClO₄, and we called Soil- I (HClO₄)¹⁷. (see the SI for details).

Results and discussion

SW-catalyzed C-C couplings of diazo compounds with arylboronic acids. At the beginning of this study, ethyl 2-diazo-

			DC	DI. 10.1039/DOC	3C0031/L
		+ , H	conditions		
	1a	2a		3a	
Entry	Catalyst	1a:2a	Solvent	Temp.	Yield ^b
		(equiv)		(°C)	(%)
1	—	1:1.5	DCE	70	trace
2	SW^c	1:1.5	DCE	70	19
3	SW-II ^c	1:1.5	DCE	70	23
4	SW-Ⅲ ^c	1:1.5	DCE	70	20
5	$SW-IV^c$	1:1.5	DCE	70	25
6	SW-V ^c	1:1.5	DCE	70	22
7	$SW-VI^c$	1:1.5	DCE	70	23
8	$HClO_4^d$	1:1.5	DCE	70	12
9	SW-I ^c	1:1.5	DCE	70	56
10	SW- I	1:1.5	DCE	70	59
11	SW-I ^e	1:1.5	DCE	70	45
12	SW- I	1:1.5	DMF	70	19
13	SW- I	1:1.5	Toluene	70	35
14	SW- I	1:1.5	1,4-dioxane	70	28
15	SW- I	1:1.5	CH₃CN	70	25
16	SW- I	1:1.5	DCE	60	47
17	SW- I	1:1.5	DCE	reflux	45
18	SW- I	1:1.6	DCE	70	61
19	SW- I	1:1.7	DCE	70	55
20	SW- I	1:1.4	DCE	70	51
21 ^f	SW- I	1:1.6	DCE	70	46

Table 1. Screening the optimum conditions for the synthesis of 3a^a

^aConditions: **1a** (0.5 mmol), **2a**, catalyst (50 mg), solvent (5 mL), 0.1 MPa air, 6 h; symbol "-" means no catalyst. ^bIsolated yields. ^c75 mg. ^dHClO₄ (2 mg). ^e25 mg. ^fSW-I reusing one time, 10 h.

2-phenylacetate 1a and phenylboronic acid 2a were chosen as the model substrates to optimize the reaction conditions (Table 1). We found that the reaction did not occur in the absence of SW catalyst (entry 1), and a variety of SWs (SW-SW-V) produced the C-C coupling product 3a (entries 2-6) with low yield (less than 25%). We considered that the base might accelerate the transformation and promote the yield.¹¹ SW-VI (SW treated by NaOH) was used as a catalyst, reducing the yield to 23% (entry 7). Besides, using HClO₄ as only catalyst, it also could not give a satisfactory yield (entry 8), indicating that this reaction was not caused by acid. By contrast, when SW-I (SW treated by HClO₄) was used as a catalyst, the yield could remarkably improve to 56% in DCE at 70 °C for 6 h (entry 9). It should be noted that the addition of transition-metal and base were not required-the reactions proceeded simply by heating both reagents in DCE and SW- I . This promising result encouraged us to screen the other reaction variables (entries 10-16). When the amount of the catalyst was reduced to 50 mg, the yield was improved to 59% (entry 10). However, the yield could not be improved when the amount of the catalyst was reduced to 25 mg (entry 11). Further, solvent screen suggested that DCE was optimum for this transformation (entry 10). The reaction also proceeded at lower or higher temperature, the conversion was noticeable decrease (entries 16-17). Moreover, increasing the quantity of Published on 27 April 2020. Downloaded by Université de Paris on 4/27/2020 8:29:56 AM

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2a (1.6 equiv) could improve the yield to 61% (entry 18), and further increasing or decreasing the amount of **2a** could not improve yield (entries 19-20). Based on the above results (see the SI for more details: Table S1), the optimum conditions for this C-C coupling reaction were identified as DCE at 70 °C for 6 h, SW- I (50 mg) as catalyst, **1a:2a** (equiv) = 1:1.6 (entry 17). Might because of the diazo compound **1a** is so active that it is easy to form self-coupling product²⁰ or other uncertain by-products under this catalytic system, only giving the corresponding product **3a** in 61% isolated yield. Further, the catalyst could be reused and furnish the desired product **3a** in 46% yield (entry 21).

With the optimized reaction conditions in hand, we then inspected the reaction scope of arylboronic acids, summarizing in Scheme 2. Significantly, the reaction exhibits a high level of functional group tolerance, affording the desired arylation products in moderate to good yields. A series of paraelectron-withdrawing substituted groups were compatible, furnishing the products (3b-d) in good yields (70-83%). Meanwhile, halide groups (F, Cl, Br and I) were tolerated, giving the corresponding products (3e-h) in moderate yields (41-60%). However, the electron-donating groups inhibited the transformation, furnishing the corresponding products (3i-j) in low yields (29-43%). Above results suggested that an obvious electronic effect could influence on the activity of the reaction. Moreover, a series of meta- and ortho-substituted phenylboronic acids were also compatible, affording the corresponding products (3k-n). Formation of the 3f (56%), 3k (53%), 3m (35%) and 3j (43%), 3l (41%), 3n (5%, GC yield) indicated that steric hindrance had an obvious effect on the transformation of ortho-substituted phenylboronic acids. Surprisingly, strong sterically hindered naphthalen-2-ylboronic acid could be well tolerated, giving the



product **3o** in good yield (65%). Further, the reaction also allowed the use of heterocycle-containing pyrimidin-5-ylboronic acid to furnish heterocycle-aryl esters **3p** in good yields (69%), which might be used as scaffold for drug discovery.^{9d,21} Interestingly, CH₃CN could be used as the greener solvent and give the desired products (**3c-d**) in good yield (63-70%).



Scheme 3. Scope of diazo compounds^{*a*}. ^{*a*}Conditions: **1** (0.5 mmol), **2c** (0.8 mmol), SW- I (50 mg), DCE (5 mL), 0.1 MPa air, 6 h. ^{*b*}Isolated yields. ^{*c*}12 h. ^{*d*}GC yield with mesitylene as the internal standard. ^{*e*}CH₃CN as the solvent (5 mL)

Next, the reactions of various substituted diazo compounds with (4-acetylphenyl)boronic acid 2c were examined, as illustrated in Scheme 3. The reaction showed a remarkably broad scope of applicability with diazo compounds. The electron-donating or -withdrawing groups at para-positions of the phenyl ring on R¹ were tolerated, affording the corresponding products (3r-3x) in moderate to good yields (55-81%). It should be noted that the reaction of 1b, might be attributed to the strong electron absorption of substituted group CF₃, was sluggish and required 12 h, affording the C-C coupling product 3r in reduced yield (55%). Besides, might due to the low selectivity of the nitrogen heterocycles for this catalytic system, ethyl 2-diazo-2-(pyridin-3-yl) acetate 1i could only give the product 3y in low GC yield (9%). Ethyl diazoacetate 1j (EDA) was also tolerated and gave the product 3z in good yield (64%). Meanwhile, methyl 2-diazo-2phenylacetate (1k) or chlorine (1l-n) at different positions of the phenyl ring moiety of 1 could work well and provide the

products (**3z1-z4**) in good to excellent yields (61-85%). Further, other esters such as allyl, benzyl and isobutyl ester variants were also compatible and afforded the products (**3z5-z7**) in good yields (72-80%). Fascinatingly, when CH₃CN was used as the greener solvent, the corresponding product **3z2** and **3z6** were obtained in good yields (72% and 62%).

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Dihydroisoflavone is one of the flavonoids which could interfere with different biological processes in human organism.²² Numerous recent studies have shown that it can use clinically for anti-inflammatory, anti-oxidative, antitumorigenic and reducing the risk of cardiovascular disease (anti-diabetic, anti-anxiety, anti-depressant properties).²³ With this context, we expected to synthesize the core structure of dihydroisoflavone under standard conditions. Interestingly, the 1,2-shift product 4a was obtained without observation of the expected product 3ct (Scheme 4). Thus, we inferred that the diazo compound 1t might undergo 1,2-methyl migration to form 1,2-shift product 4a.24 With this mind, we next evaluated the 1,2-shift of diazo compounds 1t-1z. As shown in Scheme 5, the reactions proceeded smoothly under the standard conditions, efficiently giving the highly selective 1,2-alkyl shift products (4a-4d) in good to excellent yields (74%-85%). Interestingly, cycloalkyl could also be migrated, affording the corresponding products (4e-4g) in good yields (58%-75%).



Scheme 4. The synthesis of core structure of dihydroisoflavone.^{*a,b*} ^{*a*}Conditions: **1t** (0.5 mmol), **2c** (0.8 mmol), SW- I (50 mg), DCE (5 mL), 0.1 MPa air. ^{*b*}Isolated yields.



Scheme 5. 1,2-shift products of chromanone.^{*a,b*} ^{*a*}Conditions: 1 (0.5 mmol), SW- I (50 mg), DCE (5 mL), 0.1 MPa air. ^{*b*}Isolated yields.

To evaluate the practical utility of the SW- I catalyst, a gramscale reaction of 1p (1.26 g, 5 mmol) and 2c (1.31 g, 8 mmol) was carried out with SW- I (500 mg) under the optimum conditions,

affording 1.34 g of the desired product **3z6** in 78% isolated yield (Scheme 6). In addition, we envisaged the synthesis/log the core structures of darifenacin (clinical drug for overactive bladder syndrome, OAB)² and diclofensine (stimulant drug having antidepressant and monoamine reuptake inhibitor activity).²⁵ Synthesis began from the SW- I -catalyzed coupling of diazo compound **1k** with phenylboronic acid **2a** under the optimized conditions, affording the target product methyl 2,2-diphenylacetate **3z8**. After several steps of reaction, the core structures of darifenacin **5** and diclofensine **6** were obtained, as shown in Fig.2 (see the SI for more details: Fig. S2).



Scheme 6. A gram-scale reaction



Fig. 2 Synthesis of the core structures of darifenacin and diclofensine.

Mechanistic investigations. A precise reaction mechanism of SW-I -catalyzed C-C coupling reaction is unclear. At the beginning of the study, the effect of substituents on the phenyl ring of arylboronic acids was explored, the results are shown in Scheme 7. The resulting product ratios of **3d** and **3l** suggested that the electron-withdrawing group could promote the reaction, while the electron-donating substituent inhibit the transformation. This also follows the result that (*para*-methoxyphenyl) boronic acid **2i** afford the C-C coupling product **3i** in lower yield. This might due to that the electron-withdrawing group could facilitate the coordination of the electron-rich diazo carbon atom to the electron-deficient boron center, then, improving the yield.^{12b}



Scheme 7. $\operatorname{SW-}\,I\,$ catalyzed C-C coupling: effect of the substituents.

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It is reported that the C-C coupling reaction depends strongly on the ease of formation of the zwitterionic intermediate, and the Lewis acidity of boron is an important factor to form zwitterionic intermediate.^{12a} Conventional boronic acids, in which two oxygen atoms decrease the boron Lewis acidity, especially do not couple with diazo compounds.12a,26 The electron density of boron was decreased, thereby increasing Lewis acidity of boron.²⁷ Thus, we speculated whether a certain interaction could decrease the electron density of boron or reduce the coordination between hydroxyl groups and boron in boronic acid, thereby increasing the boron Lewis acidity so as to protonate the diazo compounds and generate zwitterionic intermediate, finally promoting the C-C coupling reaction. According to relevant literature reported that the hydrogen bonding might lead to C-H functionalization and form C-C bond products.^{7a} We wondered whether the C-C coupling reactions were related to hydrogen bonding interaction between the hydroxy group of arylboronic acid and SW- I.

Table 2. XRF analysis of elements in $\rm SW$ and $\rm SW\mathchar`-I$

Chemical	SW	SW-I	
composition	(Wt%)	(Wt%)	
С	13.800	12.180	
Na ₂ O	1.154	1.016	
MgO	2.490	1.527	
AI_2O_3	15.207	15.043	
Si ₂ O	46.269	58.201	
P ₂ O ₅	2.059	0.458	
SO ₃	1.377	1.396	
Cl	0.166	3.815	
K ₂ O	1.796	2.123	
CaO	9.683	1.018	
TiO ₂	0.618	0.720	
Cr_2O_3	0.047	0.040	
MnO	0.109	0.040	
Fe ₂ O ₃	5.050	2.308	
CuO	0.027	0.029	
ZnO	0.087	0.032	
Rb₂O	0.009	0.011	
SrO	0.029	0.011	
Y ₂ O ₃	0.003	0.002	
ZrO ₂	0.021	0.021	

With this mind, NMR titration experiments were carried out.^{7a,28} We found that the single ¹H resonance of hydroxy group was shifted downfield and showed a broad singlet when more SW- I was added with *p*-tolylboronic acid (see the SI for details: Fig. S4a-c). The broad singlet might be associated with a relatively slow exchange rate between the free form and that bound to the anion $(ClO_4 \cdot) p$ -tolylboronic acid.²⁸ The above results indicated that the predominant interaction between *p*-tolylboronic acid and SW- I was hydrogen bonding. Thus, we could infer that C-C coupling reaction might due to the hydrogen bonding between SW- I and hydroxy group of arylbronic acid. Besides, the PH value of SW- I (SW was surface modified by HClO₄) is 6-7 (see the SI for details: Table S2), indicating that the SW- I is not strong acid. To further demonstrate that the hydrogen bonding is not caused by acids. The

NMR titration experiments with different acids were carried out (Fig. S5a, S5d-e). It was found that the single: hydrox p or p out (Fig. S5a, S5d-e). It was found that the single: hydrox p or p out (Fig. S5a, S5d-e). It was found that the single: hydrox p or p out (Fig. S6a) and p -tolylboronic acid was shifted upfield when HCl or HClO₄ was added. These results also support that the hydrogen bond in this catalytic system is caused by SW- I and arylbronic acid, not causing by acid. Furthermore, according to the results of NMR titration experiments of SW- I and acids, we wondered whether the SW- I might act as a Lewis or Bronsted base. Then, the NMR titration experiments of different bases were evaluated (Fig. S6). The results showed that the single ¹H resonance of hydroxy group was shifted downfield when Et₃N or Pr_2 NH was added with p-tolylboronic acid. The single ¹H resonance was shifted consistent with that observed for SW- I and in the opposite direction with acids. The results supported our inference that SW- I might act as a Lewis or Bronsted base.



Fig. 3 Properties of $SW\mathcal{SW-I}$. (a, b) SEM and EDS elemental mapping images.

To gain further mechanistic insight, we should get a better understanding of SW catalysts. Then, XRF (X-ray fluorescence) and EDS (Energy Dispersive Spectrometer, noran) were used to analyze the element content of SW catalysts (Table 2). It is obviously that the SW- I is rich in SiO₂ and Al₂O₃. Apart from C and Cl atoms, the traditional-metals Fe and Cu (Fe and Cu could be used for metal carbene insertion reaction),²⁹ as well as Zn, Mn, Mg, Na etc. are also present. Further, the morphology and structure of SW- I catalyst were observed by SEM (scanning electron microscopy). As shown in Fig. 3a, it shows roughness surface. EDS mapping images of the bright dot indicate that C, O, Al, Cl, Fe and Na atoms are homogeneously distributed within the whole granule of SW-I (Fig. 3b). The presence of O and Cl atoms prove that anion (ClO₄-) might present in SW-I, which also consistent that SW- I was prepared with SW treated by HClO₄.

Based on the above results, we wondered whether the surface modification was the main factor due to the activity of SW- I ,

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whether this transformation followed the metal carbene process, or whether this transformation was related to SW-I potentially acting as a Lewis or Brønsted base. So some control experiments were carried out, as shown in Table 3. The results showed that in the presence of a variety of metals could not give the product 3a in satisfactory yield (entries 1-6). Interestingly, the reaction essentially did not occur in the presence of transition metals Fe and Cu (Fe and Cu could be used for metal carbene insertion reaction), indicating that this transformation might not follow the metal carbene process (entry 2, entry 4). Even with all the metals added together, the reaction also could hardly proceed (entry 7). Moreover, addition of NaClO₄ or NaClO₄ with other metals (entries 8-9) did not improve the yields of 3a. These results also suggested that the elements in SW-I, which might not the main factor for the cause of the reaction. However, when Soil-I (common soil was surface modified by HClO₄) was used, the yield of **3a** was increased (entry 10), but also lower than SW-I (entry 11). Based on the characterization and comparison of the Soil-I and SW- I (Table S4, Fig. 3 and Fig. S8), we could infer that the surface modification of SW-I and soil might be the main factor due to the difference catalytic activity of the two catalysts. Meanwhile, when SW and HClO₄ were directly added together, or just adding HClO₄, both processes could not improve the yield (entry 12, Table 1, entry 8). The results further indicated the importance of SW surface modification to the reaction, and also supported that the C-C coupling reaction was not caused by acid. The NMR titration experiments suggested that SW-I might act as a Lewis or Brønsted base. We have screened different bases, the positive results supported our inference that SW-I might act as a base and cause the reaction (entries 13-15). This is also consistent with the articles reported that bases could be used for C-C coupling or arylation reactions.11,30

Table 3. Screening of catalytic sites for 3a.^a

		ОН В ОН	Catalysts		.0	
	1a	2a		3a		
Entry	Cat	alyst	Wt	(mg)	Yield ^b (%)	
1	Al ₂ O ₃		10)	21	
2	FeCl ₃		3	3		
3	Fel ₂		3		14	
4	CuCl ₂		3		NR	
5	MnCl ₂ ^c		3		10	
6	ZnCl ₂ ^c		3		40	
7	Al_2O_3 +FeCl_3+Fel_2+ MnCl_2+ZnCl_2+CuCl_2		10+3+3+ 3+3+3		ND	
/					INK	
8	NaClO ₄		10		11	
9	NaClO ₄ +FeCl ₃		10-	10+3		
10	Soil-I		50)	39	
11	SW-I		50		90	
12	SW+HClO ₄		50+2		8	
13	K ₃ PO ₄		30		45	
14	Et₃N		5		37	
15	15 ⁱ Pr ₂ NH		5		51	
^a Conditions: 1a (0.5 mmol), 2a (0.8 mmol), DCE (5 mL), 0.1 MPa air,70						

°C, 6 h. ^bGC yield with mesitylene as the internal standard. View Article Online

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Combining the above results, the reaction mechanism was proposed (Fig. 4).³⁰ Starting with the intermediate **A** which was formed by the hydrogen bonding between SW- I and arylboronic acid.^{28,31} The hydrogen bonding between arylboronic acid and SW-I might decrease the electron density of boron or reduce the coordination between hydroxyl groups and boron in arylboronic acids, thereby increasing the boron Lewis acidity. On the other hand, since the SW- I act as a Lewis or Bronsted base, it can enhance the acidity of boron. Then, the boron of intermediate **A** may have the proper acidity to form the zwitterionic intermediate **B**.^{12a,27,30} The aryl group on zwitterionic intermediate **B** was migrated with releasing molecular nitrogen as the leaving group, giving intermediate **C**. Finally, protodeboronation of the intermediate **C** would afford the desired C-C coupling product **3**,³⁰ releasing SW- I and achieving catalytic cycle.



Fig. 4 Proposed mechanism

Conclusion

In summary, this is the first example of the surface modification of sewage sludge-derived carbonaceous materials by perchloric acid as greener catalyst for C-C coupling of diazo compound with arylboronic acids. Typically, the reactions proceeded under mild conditions, with good substrate scope, and ease in further transformations. Moreover, we have also developed a simple method for preparing the 1,2-shift products of chromanone from 3diazochromanone. It should be noted that this work might provide new avenues to catalyst research and give an alternative strategy for the selection of catalysts in organic chemistry.

Experimental

Preparation of SW catalysts.

The surface of SW was modified by different kinds of acids or bases to gain SW catalysts. SW was prepared by using municipal sewage sludge from wastewater treatment plant (WWTP) in China. Sewage sludge was dried to constant weight at 105 °C and carbonized at 600 °C for 4 h under a heating rate of 3 °C min⁻¹ and a high purity nitrogen (99.999 wt%) flow of 500 mL min⁻¹. After the furnace had cooled to room temperature, SW was obtained. Different kinds of acids or bases were used to treat the SW. In the acid or base treatment process, 50 mL of SW were produced by immersing carbonized SW with the same volume of HClO₄ (35.4 wt%), HCl (20.5 wt%), H₂SO₄ (63.4 wt%), H₃PO₄ (45.4 wt%), HNO₃ (40.5 wt%) and NaOH (39.5 wt%) for 24 h for 24 h, respectively. Then, SW- I (HClO₄), SW- II (HCl), SW-Ⅲ (H₂SO₄), SW-Ⅳ (H₃PO₄), SW-Ⅴ (HNO₃) and SW-Ⅵ (NaOH) were washed with deionized water until the pH of the washing water reached 6-7 and the recovered solids were dried at room temperature. Soil- I (common soil treated by HClO₄) was prepared by the same method of $\operatorname{SW-}\ensuremath{I}$.

Catalyst characterization.

X-ray Fluorescence (XRF, Magix 601) and Energy Dispersive Spectrometer (EDS, noran) were used to analyse the element content in the SW catalysts. The morphology and microstructure of SW- I catalyst were examined by scanning electron microscope (SEM, HITACHI S4800) and transmission electron microscopy (TEM, JSM7500F).

General experimental procedures.

A typical procedure for the synthesis of α-diazoesters^{24b,32} (1) – Synthesis of 1a: DBU (2.24 mL, 15 mmol) was added slowly to a stirred solution of ethyl 2-phenylacetate (sm1a 1.59 mL, 10.0 mmol) and tosylazide (sm2, 2.42 mL, 11.0 mmol) in the CH₃CN (20 mL) at 0 °C. Then, it was placed in microwave reactor that was heated to 40 °C (400 W, monitored by IR temperature sensor) and maintained at this temperature for 30-40 min. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous solution of NH₄Cl (5 mL), extracted with CH₂Cl₂ (3 × 30 mL), washed with brine (3 × 30 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give the product. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/AcOEt, 10:1) to afford the corresponding ethyl-2-diazo-2phenylacetate 1a as a yellow liquid (1.65 g, 87%).

A typical C-C coupling reaction procedure (3). Synthesis of 3a: A mixture of SW- I (50 mg), Phenylboronic acid (2a, 98 mg, 0.8 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 6 h. After filtrating, the filtrate was dissolved in DCM (20 mL). The DCM layer was washed with water (3×20 mL) and brine (3×20 mL). Then, the organic layer was dried over anhydrous Na₂SO₄ and concentrated to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding **3a** as a colorless liquid (73 mg, 61%).

A typical procedure for 1,2-shift products of chromanone (4). Synthesis of 4a: A mixture of SW-I (50 mg), 3-diazo-2,2-dimethylchroman-4-one (1t, 101 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under 0.1 Mpa air for 1 h, then the resulting mixture was stirred at 70 °C for 6 h. After filtrating and removing solvent in vacuum the product was purified by flash

chromatography with petroleum ether (60-90 °C)/AcQEt_A(10:1), ite afford the corresponding **4a** as a white solid (65 fild, 75%), GC00317D **Data availability.** The X-ray crystallographic structures for compounds **4b** reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC 1975819 for **4b**. (http://www.ccdc.cam.ac.uk/data_request/cif). The authors declare that all other relevant data supporting the findings of this study are available within the article and its Supplementary Information files.

Conflicts of interest

There are no conflicts to declare.

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