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$K_2S_2O_8$-HFIP synergistically promoted *para*-selective sp^3 C–H bond diarylation of glycine esters†

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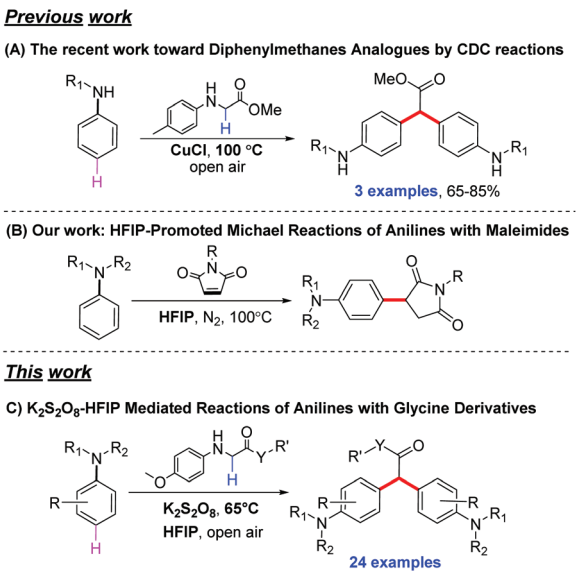
A metal-free $K_2S_2O_8$-HFIP synergistically promoted double Friedel–Crafts alkylation between a glycine derivative and *N*-substituted aniline was developed to efficiently synthesize diarylmethane derivatives with high *para*-selectivity. The reaction proceeded smoothly in the absence of any metal and ligand, and exhibited a good tolerance of functional groups.

Introduction

The geminal diaryl functionality featuring indoles, anilines, or other electro-rich aryls is frequently found in alkaloid natural products (*e.g.* streptindole, arundine, vibrindole A) and in many pharmaceutically and biologically important compounds[1] with representative agents including muscarinic antagonists like fesoterodine[2] and tolterodine (Detrol),[3] antidepressants such as sertraline (Zoloft)[4] and nomifensine,[5] and the phosphodiesterase type 4 inhibitor CDP-840.[6] Owing to their intriguing biological activities, many studies have reported on the synthesis of diarylmethane derivatives.[7a,b] The most common methods involve condensation of electron-rich arenes with aldehydes/ketones or imines.[7c–g] Transition-metal catalyzed coupling methods between diazo compounds and electron-rich[8] or pre-functional aryl substrates (*e.g.* boronic acid,[9] boroxines,[10] halides,[11] or siloxanes[12]) have also been developed.

The direct cross-dehydrogenative coupling (CDC) reaction between two hydrocarbons has been considered as one of the most fundamental strategies to construct C–C bonds which avoid pre-functionalization of substrates.[13] Many impressive results in the arylation of sp^3 carbon centers have been achieved through the CDC reaction.[14] Glycines, the simplest and the most inexpensive natural amino acids, are abundant chemical feedstock and have become important building blocks to form novel and complex organic molecules[15] since the pioneering study of Li.[16] A double alkylation reaction of glycines with different arenes has emerged as an alternative route to synthesize the geminal diarylmethanes. The synthesis of 3,3′ bisindolylmethanes has been well established by diarylation of the sp^3 C–H bond with indoles *via* transition metal-,[17] organo-,[18] photo-,[19] and radical cation[1h] catalyzed reactions as well as other methods.[20] However, few methods have been developed for diarylation of the sp^3 C–H bond in esters with electron-rich arenes. Most recently, Chandrasekharam and co-workers[17] reported a Cu-catalyzed double Friedel–Crafts (FC) alkylation reaction between glycine derivatives and limited aniline substrates at 100 °C (Scheme 1A).

Transition metal-free C–H coupling has always attracted much attention[21] and remains to be highly desirable for the construction of diarylmethane derivatives. Very recently, we have demonstrated an effective and concise Michael reaction of *N*,*N*-disubstituted anilines as C(sp^2)–H nucleophiles with maleimides as electrophiles in 1,1,1,3,3,3-hexafluoro-2-propa-



Scheme 1 Protocols for sp^3 C–H bond arylation.

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nol (HFIP) with no need for any additional metal catalysts or reagents (Scheme 1B).[22] Inspired by these results, we envisaged that a HFIP-promoted double FC alkylation reaction between glycine derivatives and anilines would result in the straightforward formation of diarylmethane derivatives. Herein, we report an efficient transition metal-free $K_2S_2O_8$-HFIP synergistically promoted double FC alkylation of *N*-substituted anilines with phenylglycine esters under mild conditions (Scheme 1C).

Results and discussion

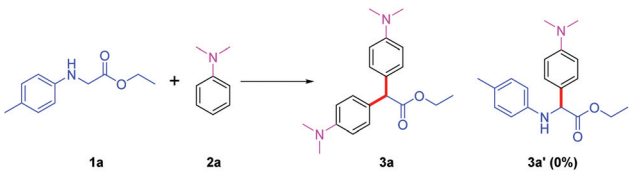
Our initial investigation began with a double FC alkylation reaction of 4-methylphenylglycines **1a** with *N*,*N*-dimethyl aniline **2a** in HFIP under an O_2 atmosphere at 50 °C for 12 h (Table 1, entry 1). However, no reaction occurred. Potassium persulfate ($K_2S_2O_8$) has emerged as a cost-effective, suitable inorganic oxidant for a wide array of oxidative transformations.[21b] When we added $K_2S_2O_8$ to our reaction, only the desired diarylated product **3a** was expectedly obtained in an isolated yield of 32% with *para*-selectivity (entry 2) and no mono-FC alkylation by-product **3a′** (Table 1) was observed from TLC plates. The yield was unchanged under open air (entry 3). To our delight, it improved to 56% at 65 °C (entry 4). Optimization of an equivalent ratio of aniline **2a** and $K_2S_2O_8$ provided the best proportion (3 : 2) in an excellent yield (88%) (entries 3–10).

Later, replacing the oxidant with $Na_2S_2O_8$, DTBP, TBHP, *m*-CPBA, H_2O_2, oxone, or $NaIO_4$, was found to be ineffective in affording **3a** in a better yield (entries 11–17). Additionally, changing the reaction solvent did not show any improvement either. Notably, alcohol solvents, TFE and methanol, were significantly superior to non-alcohol solvents (*e.g.* DMSO, THF, DMF, 1,4-dioxane, and $CHCl_3$) in this transformation (entries 18–24), but still less efficient than HFIP (entry 8), which highlights the importance of alcohol solvents in the transformation.

We also optimized the substitutions on phenylglycine esters **1** under the optimal reaction conditions in hand (Table 2). The yield was decreased when the methyl group in the phenylglycine esters was switched from the *para* to *ortho* or *meta* position (**1a–c**), maybe due to the formation of self-dimeric byproducts.[23] Removal of the methyl group (**1d**) also lowered the yield. To our delight, electro-donating groups (**1a** and **1e**) were found to be more effective than electro-withdrawing groups (**1f–j**) in affording **3a** with a high yield. Finally, ethyl (4-methoxyphenyl)glycinate (**1e**) achieved **3a** in the highest yield (93%) and thus was used for further analysis of substrate scope.

With the optimal reaction conditions in hand, we focused our attention on the aniline substrate scope of the $K_2S_2O_8$-mediated double FC reaction in HFIP under open flask conditions. A range of electron-rich anilines were thus converted under the optimized conditions (Scheme 2). Overall, most of the aniline substrates were readily converted into the corresponding CDC reaction products with high *para*-selectivity and

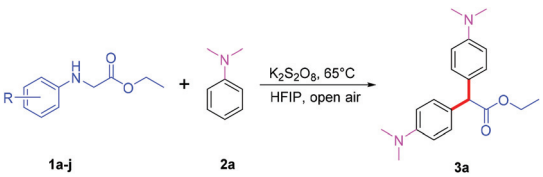
Table 1 Optimization of reaction conditions[a]



Entry	Eq. (**2a**)	Oxidant	Eq. (oxidant)	Temp/ °C	Solvent	Yield[b] (%)
1[c]	2	—	—	50	HFIP	–[d]
2[c]	2	$K_2S_2O_8$	1	50	HFIP	32
3	2	$K_2S_2O_8$	1	50	HFIP	31
4	2	$K_2S_2O_8$	1	65	HFIP	56
5	3	$K_2S_2O_8$	1	65	HFIP	54
6	2	$K_2S_2O_8$	2	65	HFIP	69
7	3	$K_2S_2O_8$	1	65	HFIP	83
8	3	$K_2S_2O_8$	2	65	HFIP	88
9	3	$K_2S_2O_8$	3	65	HFIP	70
10	4	$K_2S_2O_8$	2	65	HFIP	78
11	3	$Na_2S_2O_8$	2	65	HFIP	31
12	3	DTBP	2	65	HFIP	6
13	3	TBHP	2	65	HFIP	10
14	3	*m*-CPBA	2	65	HFIP	56
15	3	H_2O_2	2	65	HFIP	20
16	3	Oxone	2	65	HFIP	44
17	3	$NaIO_4$	2	65	HFIP	53
18	3	$K_2S_2O_8$	2	65	TFE	71
19	3	$K_2S_2O_8$	2	65	CH_3OH	47
20	3	$K_2S_2O_8$	2	65	DMSO	21
21	3	$K_2S_2O_8$	2	65	DMF	17
22	3	$K_2S_2O_8$	2	65	THF	13
23	3	$K_2S_2O_8$	2	65	1,4-Dioxane	6
24	3	$K_2S_2O_8$	2	65	$CHCl_3$	19

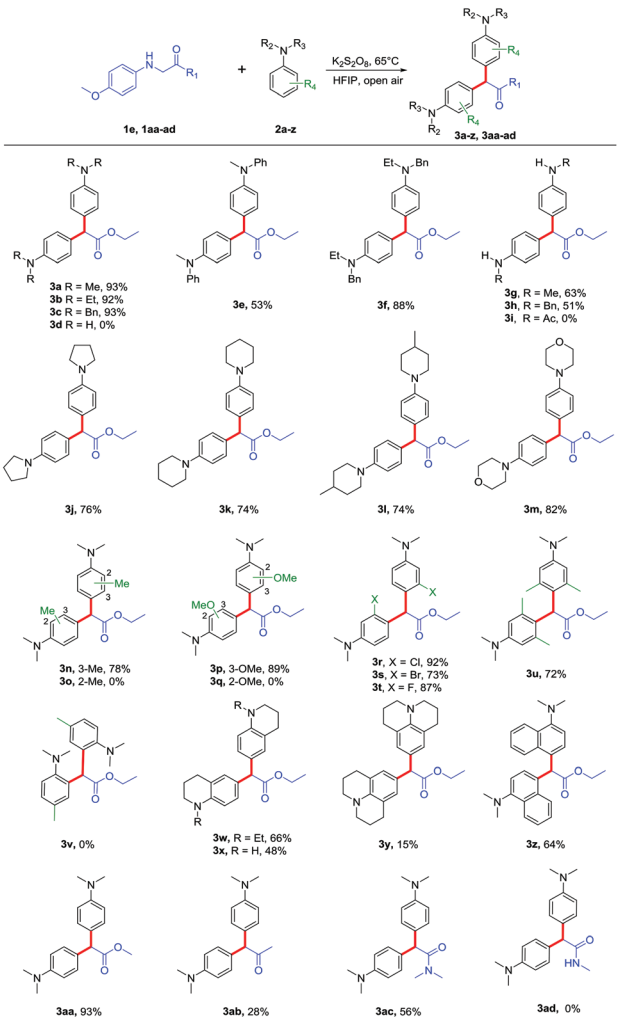
[a] Standard reaction conditions: **1a** (0.25 mmol), **2a**, oxidant, solvent (2.0 mL), open air, 65 °C for 12 h. [b] The isolated yield of **3a** is based on **1a**. [c] Under O_2. [d] No reaction. $Na_2S_2O_8$, sodium persulfate; DTBP, di-*tert*-butyl peroxide; TBHP, *tert*-butyl hydroperoxide; *m*-CPBA, 3-chloroperbenzoic acid; H_2O_2, hydrogen peroxide; $NaIO_4$, sodium periodate; TFE, 2,2,2-trifluoroethanol.

Table 2 Optimization of phenylglycines (**1**)[a]



No.	R	Yield[b] (%)	No.	R	Yield[b] (%)
1a	4-Me	88%	**1f**	4-Br	37%
1b	3-Me	43%	**1g**	4-Cl	—[c]
1c	2-Me	51%	**1h**	4-F	—[d]
1d	H	30%	**1i**	3-Br	—[c]
1e	4-OMe	93%	**1j**	2-Br	—[c]

[a] Standard reaction conditions: **1a–j** (0.25 mmol), **2a** (0.75 mmol), $K_2S_2O_8$ (0.50 mmol), HFIP (2.0 mL), open air, 65 °C for 12 h. [b] The isolated yield is based on **1a–j**. [c] Complex mixtures and no desired product. [d] No reaction.



Scheme 2 Scope and limitation for *N*-substituted aniline substrates (**2**). Standard reaction conditions: **1e** or **1aa–ad** (0.25 mmol), **2a–z** (0.75 mmol), $K_2S_2O_8$ (0.50 mmol), HFIP (2.0 mL), open air, 65 °C for 12 h. Isolated yields are shown.

good to excellent isolated yields. Aniline derivatives with acyclic moieties (**2a–c** and **2e–f**) could be smoothly transformed into the desired products **3a–c** and **3e–f** with good yields. For example, *N*,*N*-diethylaniline (**2b**) and *N*,*N*-dibenzylaniline (**2c**) reacted well with ethyl (4-methoxyphenyl)glycinate (**1e**) and gave the corresponding double *para*-substituted products **3b** and **3c** in 91% and 81% yields, respectively. Although the primary aniline **2d** unsuccessfully converted into **3d** due to the potential azo reaction,[24] secondary amines such as *N*-methylaniline (**2g**) and *N*-benzylaniline (**2h**) successfully converted into the corresponding *para* alkylated products **3g** and **3h**, respectively.

Disappointingly, the reaction of acetanilide (**2i**) failed to provide the corresponding product **3i**. Aniline derivatives with cyclic moieties (**2j–2m**) could also be smoothly transformed into the desired products **3j–3m** with good yields (74–82%). For example, 4-phenylmorpholine (**2m**) reacted well with 4-methoxyphenylglycine ester (**1e**) to give the corresponding double *para*-substituted product **3m** in an 82% yield. Furthermore, when we investigated the *N*,*N*-dimethylaniline bearing either electron-donating groups (**2n**, **2p**, **2u**) or electron-withdrawing groups (**2r–t**) on the 3-position of the phenyl ring, the corresponding *gem*-diarylacetic derivatives **3n**, **3p**, and **3r–u** were isolated in good yields (72–92%) and *para*-selectivities. Moreover, compound **3p** was crystallized, and the X-ray analysis unambiguously established the observed regioselectivity (Fig. 1).

Unexpectedly, *N*,*N*-dimethylanilines with acyclic electron-donating groups on the 2-position of the phenyl ring (**2o** and **2q**) failed to provide the expected products (**3o** and **3q**, Scheme 2). Moreover, if the *para*-position was blocked, no *ortho* substitution was observed likely due to the strong steric effect, *e.g.*, when *N*,*N*,4-trimethylaniline (**2v**) was used as a substrate. However, anilines cyclizing the substitution on the 2-position, such as *N*-ethyltetrahydroquinoline (**2w**), free tetrahydroquinoline (**2x**), and julolidine (**2y**), all smoothly gave the corresponding double *para* alkylated products (**3w–3y**) in low to good yields (15–66%). Similarly, the reaction of *N*,*N*-dimethyl-1-naphthylamine (**2z**) gave the C4-substituted product **3z** in a 64% yield under the standard reaction conditions.

The scope of this reaction with respect to the functional group of phenylglycines was further investigated (Scheme 2). To our satisfaction, the reactions of phenylglycines having methyl ester (**1aa**) and *N*,*N*-dimethylamide (**1ac**) functionalities readily furnished the desired products **3aa** and **3ac** in 93% and 56% yields, respectively, with the expected *para*-selectivity. And the reaction also tolerated phenylglycine acetone (**1ab**) in a 28% yield. Disappointingly, the reaction of secondary amide **1ad** failed to provide the corresponding products **3ad**.

To have a better understanding of this transformation, control experiments were conducted. The reaction of **1aa** and **2a** under a nitrogen atmosphere was also investigated [Scheme 3, eqn (1)]; the desired product **3aa** was achieved in a yield comparable to that in the open air (90% *vs.* 93%), indicating that oxygen is not crucial for the reaction. When 5 equiv. of tetramethylpiperidin-1-oxyl (TEMPO), a radical scavenger, was added into the reaction system under optimized conditions, the yield of the coupling product **3aa** was dramatically

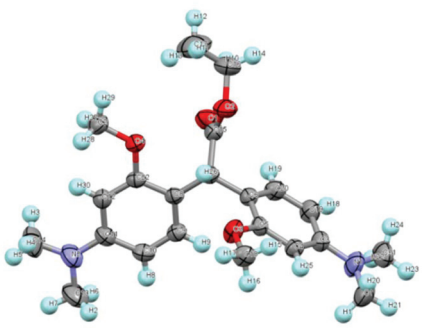
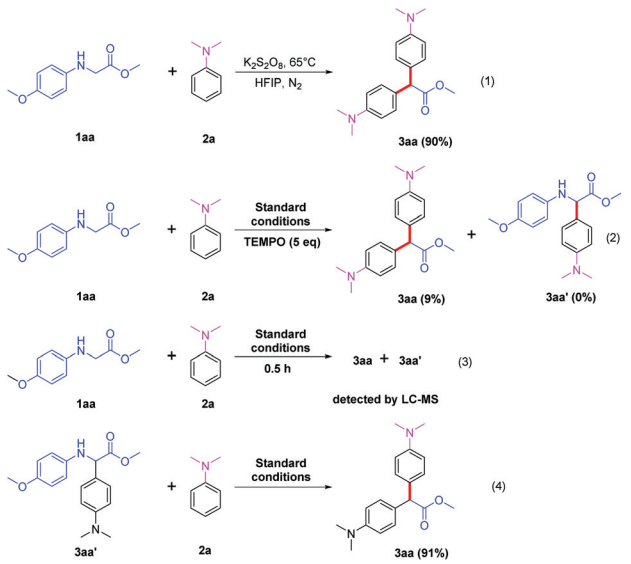


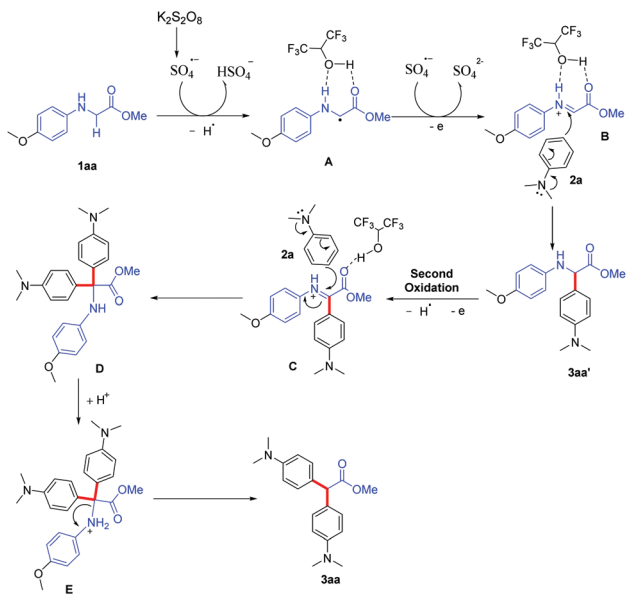
Fig. 1 X-ray crystal of **3p**.



Scheme 3 Control experiments.

decreased from 93% to 9%, and no mono-FC alkylation product **3aa′** was detected [eqn (2)]. This result suggests that the reaction may undergo a radical mechanism. Moreover, intermediate **3aa′** could be detected by LC-MS in the reaction mixture of **1aa** and **2a** under the standard reaction conditions by stopping the reaction after a short time (0.5 h) [eqn (3)]. Furthermore, we proved that the detectable intermediate **3aa′** can provide the same product **3aa** in a 91% yield when subjected to standard reaction conditions [eqn (4)].

On the basis of the control experiments and previous work, a plausible reaction mechanism for the present $K_2S_2O_8$–HFIP synergistically promoted double FC dialkylation reactions is depicted in Scheme 4. The initial step of the reaction is probably the decomposition of $K_2S_2O_8$ to generate the sulfate radical anion ($SO_4^{\bullet-}$), which abstracts a hydrogen atom from **1aa** to afford a free radical **A** stabilized by the push–pull effect.[1h,25] The subsequent one electron oxidation by $SO_4^{\bullet-}$ offers an intermediate **B**, followed by nucleophilic addition with **2a** leading to the intermediate **3aa′** with the aid of H-bond activation of phenylglycine derivatives by HFIP. Subsequently, a second oxidation of compound **3aa′** occurs to form another iminium intermediate **C**, followed by nucleophilic addition with **2a** and elimination of the aniline,[1h,26] finally leading to the product **3aa**.



Scheme 4 Proposed reaction pathway.

Conclusions

In summary, we developed a robust $K_2S_2O_8$–HFIP synergistically promoted FC dialkylation reaction of a glycine derivative with *N*-substituted aniline, which provides a straightforward access to diarylmethane derivatives. The reaction proceeds for a wide range of substrates with high *para*-selectivity, and the desired diversified products are obtained in good to excellent isolated yields overall. It is notable that the reaction tolerates a range of functional groups and performs well in the absence of any transition metal and ligand.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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