A one-pot oxidative decarboxylation–Friedel-Crafts reaction of acyclic α-amino acid derivatives activated by the combination of iodobenzene diacetate/iodine and iron dust†

Renhua Fan,* Weixun Li and Bing Wang*

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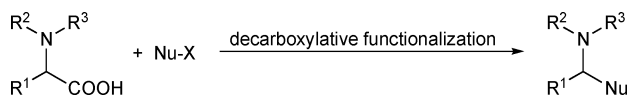
An efficient one-pot oxidative decarboxylation–Friedel-Crafts reaction of acyclic α-amino acid derivatives with electron-rich aromatic compounds is reported. The reaction is activated by the combination of iodobenzene diacetate, iodine and iron dust, resulting in a mild and simple reaction system. The use of iron avoids the oxidation of aromatic compounds, and *in situ* generation of Fe(III) salts to promote the Friedel-Crafts reaction avoids the use of the highly hygroscopic $FeCl_3$.

Introduction

The radical decarboxylation of organic carboxylic acids accompanied by simultaneous replacement by a nucleophile is an extremely useful and selective procedure in organic synthesis.[1] α-Amino acids are known to undergo oxidative decarboxylation with lead tetraacetate,[2] silver(I) acetate/peroxydisulfate,[3] trichloroisocyanuric acid,[4] *N*-bromosuccinimide,[5] potassium permanganate in concentrated sulfuric acid,[6] copper(II) bromide–lithium *tert*-butoxide,[7] *N*-chloro-*p*-toluenesulfonamide sodium,[8] dimethyl dioxirane,[9] and iodosobenzene diacetate/iodine.[10] Although considerable progress has been made, decarboxylative functionalization of α-amino acids, which would open an additional route to amines, remains to be investigated (Scheme 1).



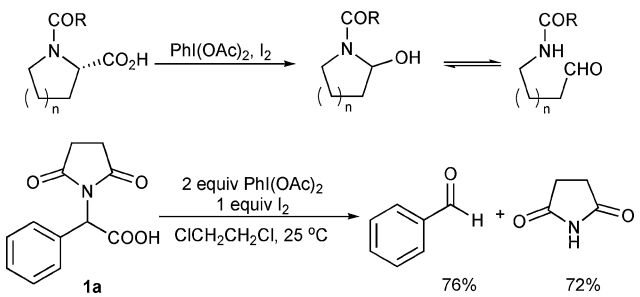
Scheme 1 Oxidative decarboxylative functionalization of α-amino acid derivatives.

Suárez *et al.* reported the oxidative decarboxylation of α-amino acids for the generation of *N*-acyliminium ions and their nucleophilic trapping with heteroatomic or carbon nucleophiles.[10b] Only cyclic α-amino acid derivatives were used as the substrates for the decarboxylation–oxidation–alkylation reactions. As a part of our development of the synthetic application of amines in the presence of hypervalent iodine,[11] we report herein the results regarding the one-pot oxidative decarboxylation–Friedel-Crafts reaction of acyclic α-amino acid derivatives activated by the combination of iodobenzene diacetate/iodine and iron dust.

Results and discussion

Since electron-rich aromatic compounds as well as α-amino acids are reactive toward hypervalent iodine species,[12] central to the implementation of this strategy is the realization of a process to oxidize the α-amino acid that would not affect sensitive aromatic compounds. A one-pot stepwise procedure might be suitable for our proposed oxidative decarboxylation–Friedel-Crafts reaction.

To undergo the subsequent Friedel-Crafts reaction, generation of a stable and reactive intermediate from the oxidative decarboxylation of α-amino acid is required. Suárez *et al.* found that the reaction of cyclic α-amino acids with $PhI(OAc)_2$ and I_2 gave γ- or ω-amino aldehydes and hemiaminals as the products, which are stable, but ought to be reactive enough to undergo the subsequent alkylation reactions.[10a] In our initial test, treatment of acyclic 2-phenylglycine derivative **1a** with $PhI(OAc)_2$ and I_2 in $ClCH_2CH_2Cl$ resulted in high yields of benzaldehyde and succinimide, which failed to undergo Friedel-Crafts reaction with 1,3,5-trimethoxybenzene in the presence of $BF_3{\cdot}Et_2O$ (Scheme 2).



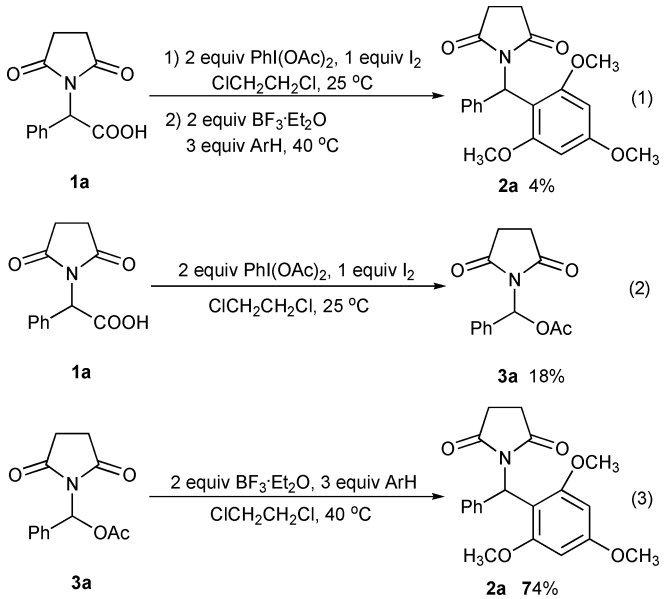
Scheme 2 Oxidative decarboxylation of acyclic 2-phenylglycine derivative **1a**.

It was, however, surprising to find that the expected product **2a** was obtained in 4% yield from the one-pot stepwise oxidative decarboxylation–Friedel-Crafts reaction [Scheme 3, Eq. (1)]. Further investigation indicated that compound **3a**, with an *O*-acetyl-*N*,*O*-acetal structure, was generated besides benzaldehyde and succinimide in the decarboxylation reaction [Scheme 3, Eq. (2)], and that this underwent Friedel-Crafts reaction to afford **2a** in good yield [Scheme 3, Eq. (3)]. Similar *N*,*O*-acetals have been prepared by the electrochemical oxidative decarboxylation of α-amino acids.[13]

A proposed reaction pathway for the one-pot oxidative decarboxylation–Friedel-Crafts reaction is outlined in Scheme 4.

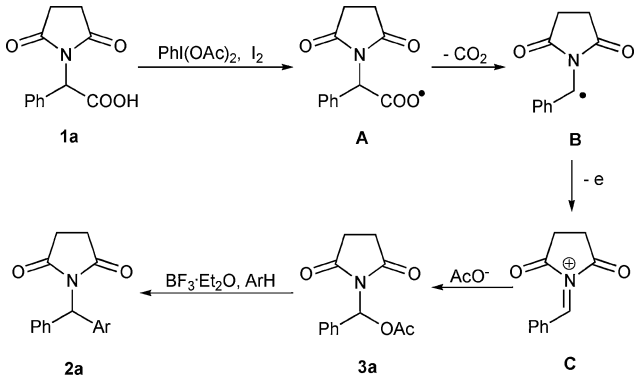
Department of Chemistry, Fudan University, 220 Handan Road, Shanghai, 200433, China. E-mail: rhfan@fudan.edu.cn; Fax: +86 21 6510 2412; Tel: +86 21 6564 3462

† Electronic supplementary information (ESI) available: General experimental information, characterization data. See DOI: 10.1039/b815227f



Scheme 3 Oxidative decarboxylation and Friedel-Crafts reaction of acyclic 2-phenylglycine derivative **1a**.

In the presence of $PhI(OAc)_2$ and iodine, which work as the radical precursor,[12c,d] 2-phenylglycine derivative **1a** is converted into a carboxyl radical intermediate **A**. The carboxyl radical decomposes to carbon dioxide and an alkyl radical **B**, which is a very easily oxidizable species. After further oxidation, an iminium ion intermediate **C** is formed. The trapping of intermediate **C** with acetate gives rise to *O*-acetyl-*N*,*O*-acetal **3a**, while the hydrolysis of intermediate **C** affords benzaldehyde and succinimide. In the presence of $BF_3{\cdot}Et_2O$, *O*-acetyl-*N*,*O*-acetal **3a** is activated to regenerate the iminium ion **C**, which undergoes the aza-Friedel-Crafts reaction[14,15] to give rise to the corresponding oxidative decarboxylation–Friedel-Crafts reaction product **2a**.

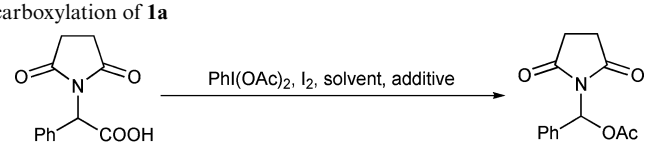


Scheme 4 Proposed reaction pathway for the one-pot oxidative decarboxylation–Friedel-Crafts reaction.

Further optimization of decarboxylation conditions was shown in Table 1. The best ratio of substrate, $PhI(OAc)_2$ and iodine was 1:2:3, with which the reaction time could be shortened to 2 h and the yield of **3a** increased to 35% (Table 1, entry 5). To inhibit the deleterious hydrolysis of iminium ion **C**, 4 Å molecular sieves were added to the oxidative decarboxylation reaction, increasing the yield of **3a** to 46% (Table 1, entry 7). To promote the trapping of intermediate **C** with acetate, acetic acid was introduced into the oxidative decarboxylation reaction. As a result a higher yield of **3a** (86%) was obtained when 8 equivalents of acetic acid was used (Table 1, entry 9). The reaction proceeded with variable efficiency in CH_2Cl_2 and EtOAc, but no **3a** was formed when DMF, THF, and toluene were used as the solvent (Table 1, entries 11–15).

Various Lewis and protic acids were examined to promote the aza-Friedel-Crafts reaction of **3a**, and $FeCl_3$ was found to be better than $BF_3{\cdot}Et_2O$.[16] However, the use of $FeCl_3$ led to variable yields of **2a**, which might be caused by the high hygroscopicity of $FeCl_3$.[17] As a comparison, a control experiment with $FeCl_2$ failed in the Friedel-Crafts reaction. Further investigation indicated that the

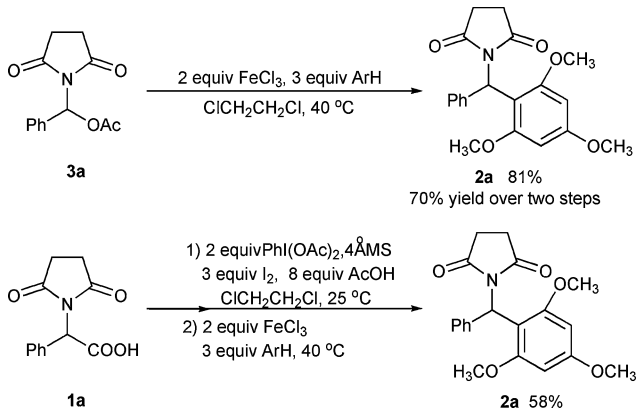
Table 1 Optimization of oxidative decarboxylation of **1a**



Entry	$PhI(OAc)_2$ (equiv)	I_2 (equiv)	Solvent	Additive (equiv)	Yield (%)[a]
1	1	1	$ClCH_2CH_2Cl$	—	6
2	2	1	$ClCH_2CH_2Cl$	—	18
3	3	1	$ClCH_2CH_2Cl$	—	17
4	2	2	$ClCH_2CH_2Cl$	—	21
5	2	3	$ClCH_2CH_2Cl$	—	35
6	2	4	$ClCH_2CH_2Cl$	—	28
7	2	3	$ClCH_2CH_2Cl$	4 Å MS	46
8	2	3	$ClCH_2CH_2Cl$	4 Å MS, AcOH (4)	66
9	2	3	$ClCH_2CH_2Cl$	4 Å MS, AcOH (8)	86
10	2	3	$ClCH_2CH_2Cl$	4 Å MS, AcOH (12)	76
11	2	3	CH_2Cl_2	4 Å MS, AcOH (8)	64
12	2	3	EtOAc	4 Å MS, AcOH (8)	47
13	2	3	DMF	4 Å MS, AcOH (8)	0
14	2	3	toluene	4 Å MS, AcOH (8)	0
15	2	3	THF	4 Å MS, AcOH (8)	0

[a] Isolated yield based on **1a**.

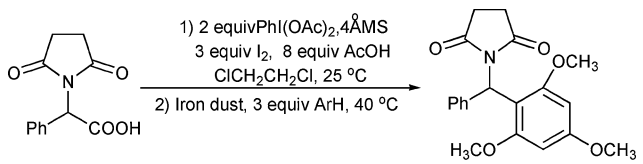
yield of product from the one-pot oxidative decarboxylation–Friedel-Crafts reaction was lower than the total yield of the two-step reaction (Scheme 5). Some oxidation products of 1,3,5-trimethoxybenzene were isolated as the by-products because of the existence of excess oxidants [$PhI(OAc)_2$ and I_2].



Scheme 5 $FeCl_3$ catalyzed Friedel-Crafts reaction of **3a**.

These results prompted us to investigate the possibility of using iron dust for the one-pot oxidative decarboxylation–Friedel-Crafts reaction; iron could consume the excess oxidants to avoid oxidation of the aromatic compounds. Moreover, the *in situ*-generated Fe(III) salts could promote the Friedel-Crafts reaction to avoid the use of the highly hygroscopic $FeCl_3$.

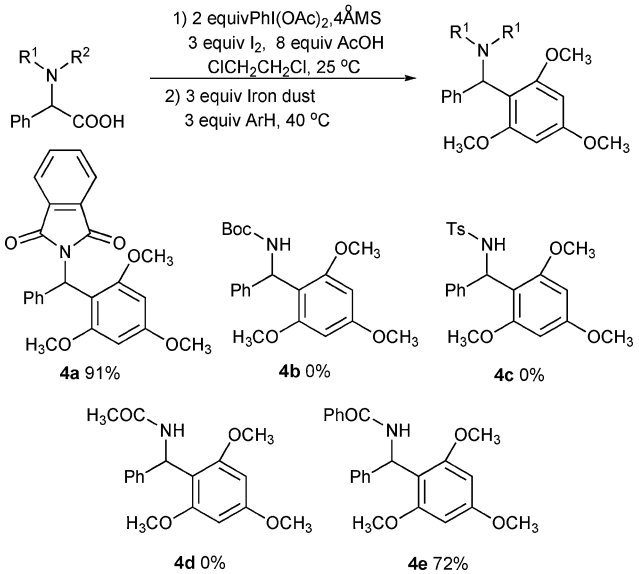
As shown in Scheme 6, the solution of **1a** was treated with $PhI(OAc)_2$ and I_2 at room temperature. After decarboxylation reaction, iron dust and 1,3,5-trimethoxybenzene were added to the reaction mixture, and the reaction was then allowed to stir at 40 °C. When 1 or 2 equivalents of iron dust were used, only low yields of product **2a** were obtained. When the amount of iron dust was increased to 3 equivalents, the expected product was isolated in 87% yield. Further increase of the amount of iron dust did not improve the yield. No double Friedel-Crafts reaction product, which is generally formed in the aza-Friedel-Crafts reaction of aromatic imines,[18] was isolated from the one-pot oxidative decarboxylation–Friedel-Crafts reaction of **1a**.



Scheme 6 One-pot oxidative decarboxylation–Friedel-Crafts reaction using iron dust.

The scope of oxidative decarboxylation–Friedel-Crafts reaction with respect to the aromatic compounds was then investigated. Reactions of electron-rich aromatic compounds with alkoxy substitutions proceeded smoothly, and gave rise to the corresponding products in moderate to good yields (Table 2, entries 1–7). Electron-withdrawing substitution on methoxybenzene inhibited the reaction (Table 2, entry 8). Mesitylene was also effective, but the reaction only gave the product in a moderate yield (Table 2, entry 9). When *o*- and *p*-xylene were employed, the one-pot reactions proceeded sluggishly and resulted in low yields of the products. The corresponding products could be obtained in moderate yields when the reactions were carried out in two steps (Table 2, entries 9–11). The reaction with *N*,*N*-dimethylaniline was very complex, and no isolable amount of product was formed (Table 2, entry 12). Reactions with heteroaromatic compounds were also examined (Table 2, entries 13–16). The reaction with furan proceeded smoothly, and afforded the product in good yield. In the case of thiophene, a low yield was obtained. Pyridine and indole were found to be sensitive to the reaction conditions, and complex product mixtures were observed.

The influence of the nitrogen protecting group was studied (Scheme 7). Under the same condition, the reaction of phthalimide derivative proceeded smoothly, and gave rise to the corresponding product **4a** in 91% yield. However, when *tert*-butyl carbamate, sulfonamide, acetamide, and benzamide derivatives were employed, only the reaction of benzamide derivative afforded the corresponding product.



Scheme 7 The influence of the nitrogen protecting group of 2-phenylglycine derivative.

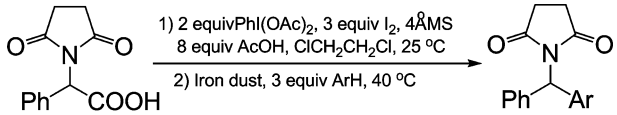
The reaction of leucine derivatives was then investigated (Scheme 8). The oxidative decarboxylation of the corresponding succinimide and phthalimide derivatives proceeded smoothly, but the resulted *N*,*O*-acetals did not undergo the subsequent Friedel-Crafts reaction under the same conditions. The one-pot oxidative decarboxylation–Friedel-Crafts reaction of benzamido leucine gave rise to the expected product **5e** in 57% yield.

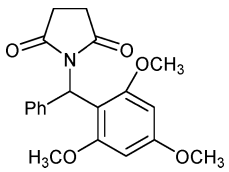
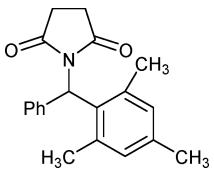
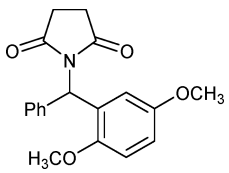
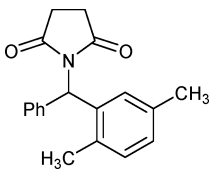
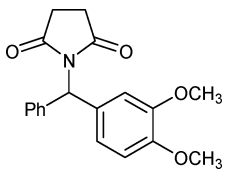
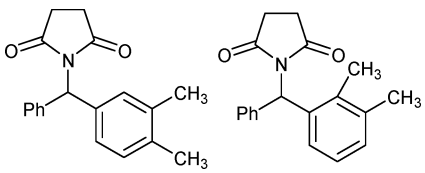
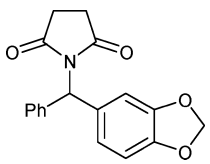
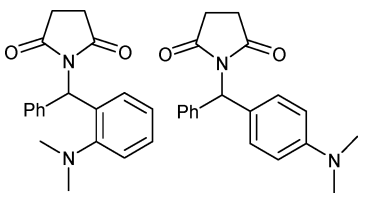
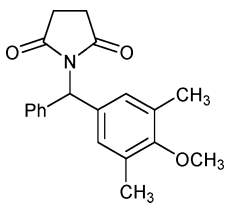
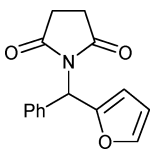
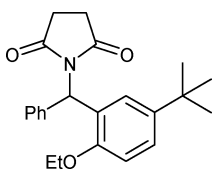
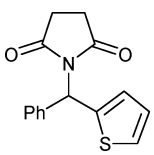
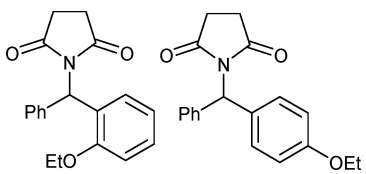
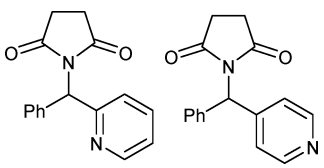
The synthetically relevant deprotection of product **4a** to afford the corresponding diaryl methylamine **6a** can be cleanly achieved under the Ing-Manske condition (Scheme 9).[19]

Conclusions

In summary, we report here an efficient one-pot oxidative decarboxylation–Friedel-Crafts reaction of acyclic α-amino acid

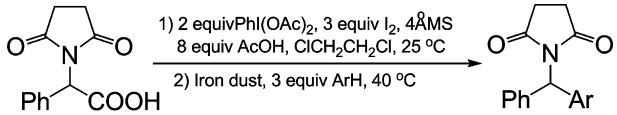
Table 2 One-pot oxidative decarboxylation–Friedel-Crafts reaction of **1a** with aromatic compounds

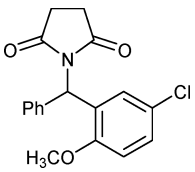
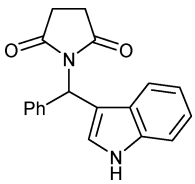


Entry	Product **2**	Yield (%)[a]	Entry	Product **2**	Yield (%)[a]
1		**2a** 87	9		**2i** 50 (75)[c,d]
2		**2b** 78	10		**2j** 12 (57)[c,d]
3		**2c** 88	11		**2k** 13 (61)[c,d] (80:20)[b]
4		**2d** 70	12		**2l** 0
5		**2e** 65	13		**2m** 70
6		**2f** 77	14		**2n** 37
7		**2g** 55[b] (55:45)	15		**2o** 0

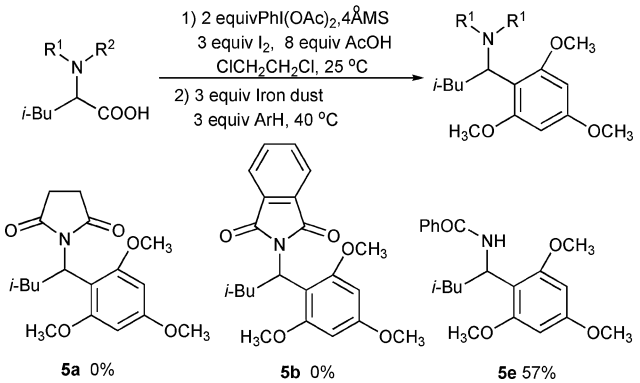
derivatives activated by the combination of iodobenzene diacetate/iodine and iron dust. The use of iron avoids the oxidation of aromatic compounds, and *in situ* generation of Fe(III) salts to promote the Friedel-Crafts reaction avoids the use of the highly hygroscopic $FeCl_3$, resulting in a mild and simple reaction system. The scope, mechanism, synthetic application, and asymmetric reaction (using tartaric derivatives as the protecting groups) are ongoing and will be reported in due course.

Table 2 One-pot oxidative decarboxylation–Friedel-Crafts reaction of **1a** with aromatic compounds

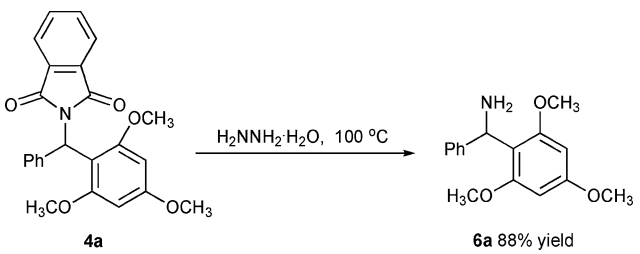


Entry	Product **2**	Yield (%)[a]	Entry	Product **2**	Yield (%)[a]
8		**2h** 0	16		**2p** 0

[a] Isolated yield based on **1a**. [b] Determined by ^{1}H NMR. [c] Reaction carried out in two steps: after the oxidative decarboxylation, the corresponding intermediate **3** was isolated, and then treated with 3 equivalents of iron dust and 3 equivalents of ArH in $ClCH_2CH_2Cl$ at 40 °C. [d] Isolated yield over two steps based on **1**.



Scheme 8 One-pot oxidative decarboxylation–Friedel-Crafts reaction of leucine derivatives.



Scheme 9 Deprotection of product **4a**.

Experimental section

General comments

All reactions were performed in test tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60 Å pore size, 32–63 μm, standard grade). Analytical thin–layer chromatography was performed using glass plates precoated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received.

Oxidative decarboxylation of 1a

A mixture of **1a** (93 mg, 0.4 mmol), 4 Å molecular sieves (100 mg) and $PhI(OAc)_2$ (258 mg, 0.8 mmol) in $ClCH_2CH_2Cl$ (3 mL) was stirred at room temperature for 30 min, and then was treated with I_2 (305 mg, 1.2 mmol) and AcOH (192 mg, 3.2 mmol). The reaction was allowed to stir at room temperature until the disappearance of **1a**. The reaction was quenched with saturated $Na_2S_2O_3$, and extracted by ethyl acetate (20 mL × 3). The organic layer was dried over Na_2SO_4. After concentration in vacuo, the residue was purified by column chromatography on silica gel (20% ethyl acetate in hexanes) to provide the desired product 2,5-dioxopyrrolidin-1-yl)(phenyl)methyl acetate (**3a**) in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.45 (s, 1H), 7.38–7.34 (m, 3H), 2.71 (s, 4H), 2.20 (s, 3H); ^{13}C NMR δ 175.1, 169.3, 134.5, 129.2, 128.5, 126.6, 75.2, 28.1, 20.8; IR (neat cm^{-1}): ν = 3011, 2963, 1752, 1708, 1605, 1458, 1387; HRMS calcd for $C_{13}H_{13}NNaO_4$ ([M + Na]$^+$): 270.0742, found: 270.0751.

$FeCl_3$-catalyzed Friedel-Crafts reaction of 3a with 1,3,5-trimethoxybenzene

A solution of **3a** (74 mg, 0.3 mmol) in $ClCH_2CH_2Cl$ (3 mL) was treated with 1,3,5-trimethoxybenzene (151 mg, 0.9 mmol) and $FeCl_3$ (97 mg, 0.6 mmol). The reaction was stirred at 40 °C until the disappearance of **3a**. The reaction was quenched with 4% HCl aqueous solution, and extracted by ethyl acetate (20 mL × 3). The organic layer was dried over Na_2SO_4, and was concentrated in vacuo. The residue was purified by column chromatography on silica gel (20% ethyl acetate in hexanes) to provide the desired product 1-(phenyl-(2,4,6-trimethoxyphenyl)methyl)-pyrrolidine-2,5-dione (**2a**) in 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.10 (m, 5H), 6.79 (s, 1H), 6.12 (s, 2H), 3.79 (s, 3H), 3.63 (s, 6H), 2.63 (s, 4H); ^{13}C NMR δ 176.7, 161.0, 159.8, 138.6, 127.7, 127.4, 126.6, 106.6, 91.2, 55.9, 55.3, 51.5, 28.2; IR (neat cm^{-1}): ν = 2937, 1705, 1606, 1454,

1391, 1121; HRMS calcd for $C_{20}H_{21}NNaO_5$ ([M + Na]$^+$): 378.1318, found: 378.1326.

General procedure for one-pot oxidative decarboxylation–Friedel-Crafts reaction

A mixture of **1** (0.4 mmol), 4 Å molecular sieves (100 mg) and $PhI(OAc)_2$ (258 mg, 0.8 mmol) in $ClCH_2CH_2Cl$ (3 mL) was stirred at room temperature for 30 min, and then was treated with I_2 (305 mg, 1.2 mmol) and AcOH (192 mg, 3.2 mmol). The reaction was allowed to stir at room temperature until the disappearance of **1** (about 2 h). Iron dust (67 mg, 1.2 mmol) and ArH (1.2 mmol) were added into the reaction mixture, and the resulting reaction was allowed to stir at 40 °C. Upon completion as shown by TLC (about 3 h), the reaction was quenched with 4% HCl aqueous solution, and extracted with ethyl acetate (20 mL × 3). The organic layer was washed with saturated $Na_2S_2O_3$, and then dried over Na_2SO_4. After concentration in vacuo, the residue was purified by column chromatography on silica gel (20% ethyl acetate in hexanes) to provide the desired product. The characterization data is available in the ESI†.

2-(Phenyl(2,4,6-trimethoxyphenyl)methyl)isoindoline-1,3-dione (4a). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76–7.75 (m, 2H), 7.66–7.64 (m, 2H), 7.26–7.20 (m, 5H), 7.00 (s, 1H), 6.12 (s, 2H), 3.78 (s, 3H), 3.61 (s, 6H); ^{13}C NMR δ (ppm) 168.1, 161.1, 159.8, 139.2, 133.7, 132.2, 127.8, 127.4, 126.6, 123.0, 107.0, 91.1, 90.6, 55.9, 55.3, 50.6; IR 2937, 1771, 1716, 1606, 1495, 1389 cm^{-1}; HRMS calcd for $C_{24}H_{21}NNaO_5$ ([M + Na]$^+$): 426.1318, found: 426.1334.

***N*-(Phenyl(2,4,6-trimethoxyphenyl)methyl)benzamide (4e).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 9.6 Hz, 1H), 7.83-781 (m, 2H), 7.47–7.40 (m, 3H), 7.29–7.13 (m, 6H), 6.19 (s, 2H), 3.80 (s, 9H); ^{13}C NMR δ 166.27, 160.8, 158.8, 142.8, 135.1, 131.3, 128.6, 128.1, 127.0, 126.5, 126.4, 110.2, 91.5, 56.1, 55.4, 47.4; IR (neat cm^{-1}): v = 3445, 2938, 1661, 1510, 1332, 1204 cm^{-1}; HRMS calcd for $C_{23}H_{23}NNaO_4$ ([M + Na]$^+$): 400.1525, found: 400.1524.

***N*-(3-Methyl-1-(2,4,6-trimethoxyphenyl)butyl)benzamide (5e).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.99 (m, 2H), 7.43–7.39 (m, 3H), 6.12 (s, 2H), 5.54 (d, J = 6.9 Hz, 1H), 4.40 (t, J = 7.2 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 6H), 1.87-1.90 (m, 1H), 1.20–1.25 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 163.5, 160.8, 159.6, 130.8, 128.2, 128.6, 110.7, 91.2, 89.5, 63.5, 55.9, 55.3, 33.4, 18.1, 17.3; IR (neat cm^{-1}): v = 2958, 2927, 1608, 1465, 1419, 1152, 1025 cm^{-1}; HRMS calcd for $C_{21}H_{27}NNaO_4$ ([M + Na]$^+$): 380.1838, found: 380.1834.

Deprotection of product 4a

A mixture of **4a** (101 mg, 0.25 mmol) in hydrazine monohydrate (2 mL) was stirred at 100 °C for 24 h. The hydrazine monohydrate was removed in vacuo, and the residue was purified by column chromatography on silica gel (5% MeOH inCH_2Cl_2) to provide the desired product phenyl-(2,4,6-trimethoxyphenyl)-methanamine (**6a**)[20] in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.14 (m, 5H), 6.12 (s, 2H), 5.71 (s, 1H), 3.79 (s, 3H), 3.73 (s, 6H), 3.23 (br, 2H).

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