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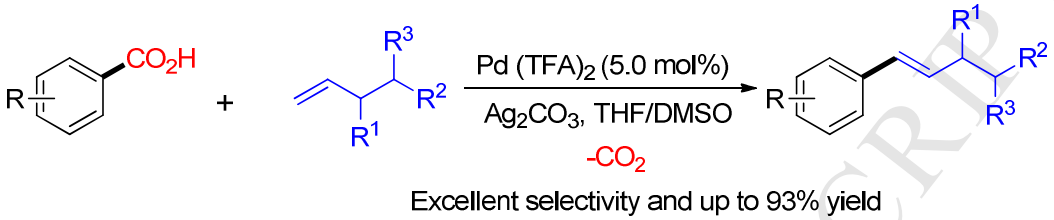
Department of chemistry, Renmin University of China, Beijing 100872, China.



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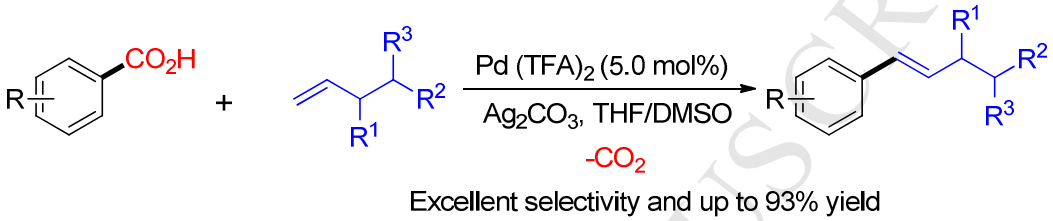

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ABSTRACT

Palladium(II)-catalyzed highly regioselective and stereoselective decarboxylative arylation of unactivated olefins with aryl carboxylic acids has been developed. This method is applicable to a variety of unactivated olefins, including allylamides, long chain functionalized olefins and purely aliphatic olefins, leads to the formation of linear *E*-configured products in high yields. Both electron-rich and electron-deficient aryl carboxylic acids are suitable arylation reagents. It was found that the choice of solvent, catalyst precursor and oxidant had an important influence on reaction efficiency. As a co-solvent and ligand, DMSO is critical to catalysis. This chemistry expands the scope of decarboxylative arylation of olefins with aryl carboxylic acids, and provides a rapid access to useful linear arylation products of unactivated olefins.

1. Introduction

Palladium-catalyzed Heck reaction of aryl halides with olefins has been regarded as one of the most powerful and reliable methods for the formation of carbon-carbon bonds in organic synthesis.[1,2] Although a number of effective palladium catalytic systems demonstrating high reactivities and selectivities have been developed over the past several decades, a major limitation of this chemistry is its strong reliance on the use of halogenated substrates. In recent years, the transition-metal catalyzed decarboxylative cross-coupling reaction has been subjected to extensive investigation in the construction of various C-C and C-X bonds because the readily available, stable and structural diverse carboxylates are employed as the sources of carbon nucleophiles to replace the traditional halides and organometal reagents.[3] In this context, the use of inexpensive, stable and easily accessible aryl carboxylic acids as arylating reagents has attracted increasing research attention.[4-7] In 2002, Myers and co-workers first reported the decarboxylative coupling reaction of arylcarboxylic acids with α,β-unsaturated carbonyls and styrene in 5% DMSO-DMF with $Pd(TFA)_2$ as the catalyst and Ag_2CO_3 as the oxidant, and aryl carboxylic acids have proved to be reliable arylating reagents in these reactions.[8a,b] The subsequent mechanistic studies indicated DMSO functions as both solvent and a ligand.[8c] Following this significant lead, Su and co-workers developed several palladium catalytic systems that could work well for the decarboxylative Heck coupling of arenecarboxylic acids with a variety of olefins, but in the arylation of electronically nonbiased olefins room for improvement in terms of reaction conditions, substrate scope, selectivity and catalyst loading still exists.[9] Recently, Jiang and co-workers realized the $Pd(TFA)_2$-catalyzed highly regioselective decarboxylative coupling reaction of aryl carboxylic acids with electron-rich allylic alcohols to exclusively produce the β-aryl ketones and aldehydes in high yields without detecting the formation of β-arylated allylic alcohol products.[10] More recently, the group of Jana reported two palladium(II) catalytic systems that could catalyze decarboxylative Heck reaction of electron-rich and electron-deficient aryl carboxylic acids with olefins at room temperature, respectively, but the arylation of non-activated olefins is plagued with a higher catalyst loading (20 mol% $Pd(TFA)_2$) and limited substrate scope.[11] Obviously, developing a general and efficient catalytic procedure for selective arylation of unactivated olefins with aryl carboxylic acids remains challenging. In continuing our investigation of selective arylation of unactivated olefins,[12] we became interested in studying the decarboxylative coupling reaction of unactivated olefins with aryl carboxylic acids. Herein we report that the combination of $Pd(TFA)_2$ and Ag_2CO_3 in 5% DMSO-THF could constitute an efficient catalytic system for highly selective arylation of various unactivated olefins with both eletcron-rich and electron-deficient

* Corresponding author. Tel.: +86-10-6251-1528; fax: +86-10-6251-6664; e-mail: 20050062@ruc.edu.cn (L. Xu).

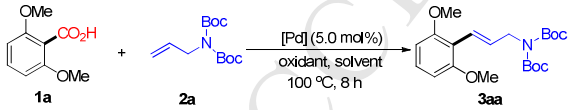
aryl carboxylic acids, and a number of functional groups on both coupling partners were compatible with the reaction conditions.

2. Results and discussion

At the onset of our investigations, the olefination of 2,6-dimethoxybenzoic acid (**1a**) with *N*,*N*-(Boc)$_2$ allylamine **2a** was chosen as the model reaction to screen the optimal reaction conditions (Table 1). With Pd(TFA)$_2$ as the catalyst and Ag_2CO_3 as the oxidant, the effect of different solvents was firstly examined. A solvent screening revealed that DMSO gave the desired product, terminal arylated (*E*)-allylamide **3aa,** in 19% yield with a small amount of the decarboxylative protonation product (4%) (Table 1, entry 7), but only the decarboxylative protonation reaction was observed in other solvents, such as toluene, 1, 4-dioxane, *p*-xylene, THF, CH_3CN and DMF (Table 1, entries 1-6).[13] With an aim to improve the reaction efficiency, the performance of the mixed solvent systems was then evaluated (Table 1, entries 8-13). It was found that a 20:1 mixture of THF/DMSO was the most effective reaction medium, producing **3aa** in 90% yield without the protodecarboxylation being detected (Table 1, entry 10). Notably, although a mixture of toluene/DMSO (20:1) worked well for the arylation of allylic alcohols with aryl carboxylic acids,[10] it only provided **3aa** in a moderate yield (Table 1, entry 8). Varying the amount of DMSO resulted in significantly decreased reactivity (Table 1, entries 14 and 15), suggesting that a specified volume of DMSO is critical for catalysis in this catalytic system.[8,10,14] It is believed that DMSO acts both cosolvent and ligand in this transformation. With THF/DMSO (20/1) as the reaction medium, further optimization showed that employing other palladium precursors diminished the reaction efficiency (Table 1, entries 16-20). Replacing Ag_2CO_3 with other oxidants led to a remarkable drop in yield (Table 1, entries 21-26). Although Su's catalytic systems could work well in the coupling reaction of arenecarboxylic acids with alkyl-substituted olefins,[9] they failed to catalyze the reaction of **1a** and **2a** (Table 1, entries 27 and 28). Moreover, the catalytic system consisting of Pd(TFA)$_2$ and BQ with DMF/DMSO (20:1) as the solvent, reported to be capable of catalyzing the arylation of unactivated olefins with aryl carboxylic acids at room temperature,[11] proved to be completely ineffective in our case (Table 1, entry 29). It should be stressed that in all cases no observation of internal arylation or partial deprotection was made.

Table 1

Optimization of reaction conditions.[a]



Entry	[Pd]	Solvent	Oxidant	**3aa**(%)[b]
1	Pd(TFA)$_2$	toluene	Ag_2CO_3	ND
2	Pd(TFA)$_2$	dioxane	Ag_2CO_3	ND
3	Pd(TFA)$_2$	THF	Ag_2CO_3	ND
4	Pd(TFA)$_2$	CH_3CN	Ag_2CO_3	ND
5	Pd(TFA)$_2$	*p*-xylene	Ag_2CO_3	ND
6	Pd(TFA)$_2$	DMF	Ag_2CO_3	ND
7	Pd(TFA)$_2$	DMSO	Ag_2CO_3	19
8	Pd(TFA)$_2$	toluene/DMSO(20/1)	Ag_2CO_3	65
9	Pd(TFA)$_2$	dioxane/DMSO(20/1)	Ag_2CO_3	40
10	**Pd(TFA)$_2$**	**THF/DMSO(20/1)**	**Ag_2CO_3**	**90**
11	Pd(TFA)$_2$	CH_3CN/DMSO(20/1)	Ag_2CO_3	30
12	Pd(TFA)$_2$	*p*-xylene/DMSO(20/1)	Ag_2CO_3	70
13	Pd(TFA)$_2$	DMF/DMSO(20/1)	Ag_2CO_3	46
14	Pd(TFA)$_2$	THF/DMSO(10/1)	Ag_2CO_3	33
15	Pd(TFA)$_2$	THF/DMSO(30/1)	Ag_2CO_3	28
16	Pd(OAc)$_2$	THF/DMSO(20/1)	Ag_2CO_3	19
17	$PdCl_2$	THF/DMSO(20/1)	Ag_2CO_3	32
18	Pd(PPh$_3$)$_2$Cl$_2$	THF/DMSO(20/1)	Ag_2CO_3	22
19	Pd(PPh$_3$)$_4$	THF/DMSO(20/1)	Ag_2CO_3	12
20	Pd$_2$(dba)$_3$	THF/DMSO(20/1)	Ag_2CO_3	24
21	Pd(TFA)$_2$	THF/DMSO(20/1)	AgOAc	63
22	Pd(TFA)$_2$	THF/DMSO(20/1)	Ag_2O	32
23	Pd(TFA)$_2$	THF/DMSO(20/1)	Ag_2SO_4	6
24	Pd(TFA)$_2$	THF/DMSO(20/1)	Cu(OAc)$_2$	28
25	Pd(TFA)$_2$	THF/DMSO(20/1)	BQ	NR
26	Pd(TFA)$_2$	THF/DMSO(20/1)	O_2(1 atm)	NR
27[c]	Pd(TFA)$_2$	DMSO/DMF/dioxane	BQ	NR
28[d]	Pd(OAc)$_2$	DMF/DMSO(20/1)	O_2(1 atm)	NR
29[e]	Pd(TFA)$_2$	DMF/DMSO(20/1)	BQ	NR

[a] *Reaction conditions*: **1a** (0.2 mmol.), **2a** (0.24 mmol), catalyst (5.0 mol%), base (1.0 mmol), solvent (2.1 ml), 85 °C, 8 h. *E*/*Z* ratio of **3aa** is >99/1 as determined by ^{1}H NMR. When the *Z*-isomer could not be detected, a value of >99/1 was assigned. ND: not detected. NR: no reaction.

[b] Isolated yield.

[c] **1a** (0.2 mmol.), **2a** (0.4 mmol), Pd(TFA)$_2$ (10.0 mol%), BQ (0.24 mmol), 1-AdCO$_2$H (0.8 mmol) and DMSO/DMF/dioxane (2.1 mL, 1:15:5), 120 °C, 1 h.

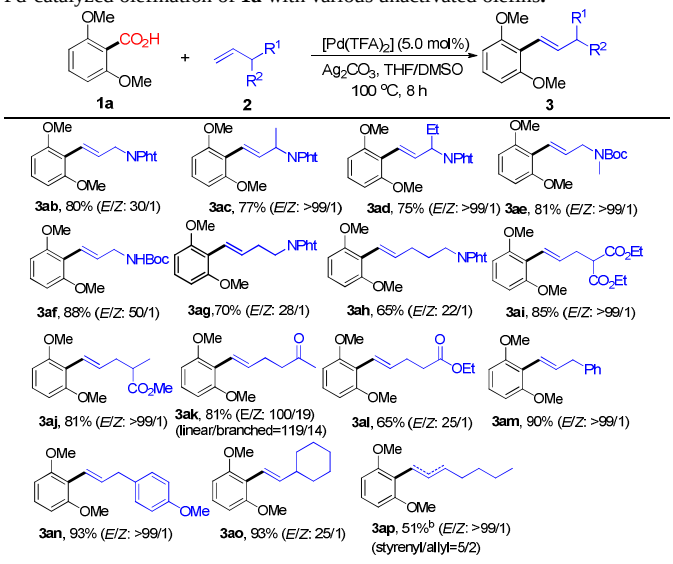
[d] **1a** (0.2 mmol.), **2a** (0.4 mmol), Pd(OAc)$_2$ (10.0 mol%), O_2 (1.0 atm), DMSO/DMF (2.1 mL, 1:20), 120 °C, 10 h.

[e] **1a** (0.2 mmol.), **2a** (0.4 mmol), Pd(TFA)$_2$ (20.0 mol%), BQ (0.4 mmol), DMSO/DMF (3.15 mL, 1:20), 25 °C, 36 h.

With the optimal reaction conditions in hand, we then investigated the generality of this coupling reaction of **1a** with a range of unactivated olefins. As shown in Table 2, **1a** reacted smoothly with *N*,*N*-disubstituted allylamides (**2b**-**2e**) to exclusively afford the corresponding γ-arylated (*E*)-allylamides (**3ab**-**3ae**) in good to excellent yields without the formation of internal regioisomer or cis-isomer, but the presence of α-substituents in allylamide substrates (**2c**,**2d**) slightly impacted the reaction efficiency (**3ac**,**3ad**). The *N*-substituted allyamide **2f** was also reactive, exclusively delivering the corresponding product **3af** in 88% yield. Interestingly, the long chain olefins, 2-(but-3-en-1-yl)isoindoline-1,3-dione (**2g**) and 2-(pent-4-en-1-yl)isoindoline-1,3-dione (**2h**), also successfully engaged in this transformation to produce the products **3ag** and **3ah** in 70% and 65% yields, respectively, and the migration of the C=C double bond along the aliphatic chain and the internal arylation were not observed. The coupling reaction of **1a** with other functionalized olefins (**2i**–**2l**) was also studied. It was found that the olefins **2i, 2j** and **2l** underwent highly regioselective arylation, exclusively affording the arylated products (**3ai**, **3aj**, **3al**) in 65-85% yields. The reaction of **2k** also proceeded smoothly to give the linear arylated product **3ak** as the major products with the Z-isomer and the internal arylated olefin as minor products, but no formation of allylic isomers was detected. Allylbenzene (**2m**) and 1-allyl-4-methoxybenzene (**2n**) displayed excellent reactivity, and the products (**3am**, **3an**) were obtained in excellent yields. Vinylcyclohexane (**2o**) turned out to be a good coupling partner, giving rise to the product **3ap** in 93% yield. Hex-1-ene (**2p**) could also be applied in this transformation, but a mixture of styrenyl product and allylic product was produced.

Table 2

Pd-catalyzed olefination of **1a** with various unactivated olefins.[a]



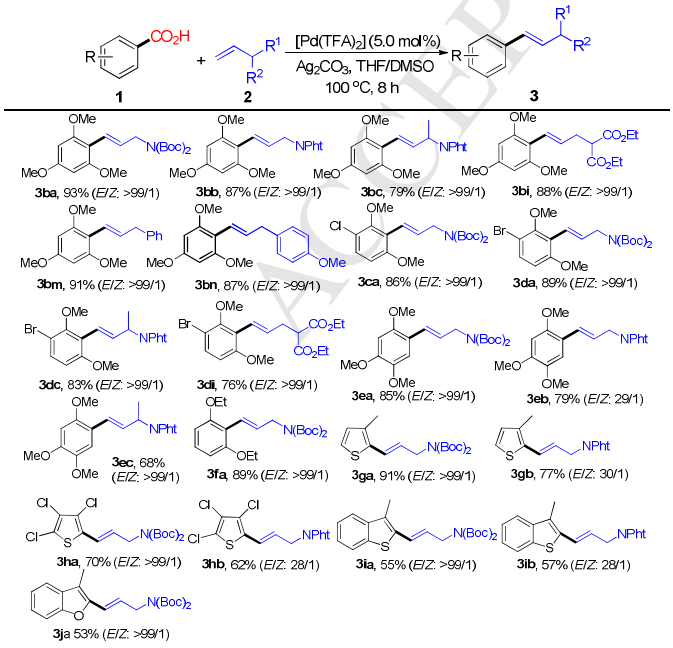
[a] *Reaction conditions*: **1a** (0.2 mmol), **2** (0.24 mmol), $Pd(TFA)_2$ (5.0 mol%), Ag_2CO_3 (0.2 mmol), THF/DMSO (2.1 ml, 20:1), 100 °C, 8 h. Isolated yields. *E*/*Z* ratios of the products were determined by ^{1}H NMR. When the *Z*-isomer could not be detected, a value of >99/1 was assigned.

[b] Reaction time 12 h.

The oxidative cross-coupling reaction was further extended to other aryl carboxylic acids as shown in Table 3. The electron-rich aryl carboxylic acid **1b** proved to be an efficient coupling partner, providing the corresponding (*E*)-arylated allylamide products (**3ba**, **3bb**, **3bc**, **3bi**, **3bm**, **3bn**) in good to excellent yields. Likewise, good results were also achieved in the olefination of electron-rich aryl carboxylic acids **1e** and **1f** (**3ea**, **3eb**, **3ec**, **3fa**). Importantly, the halogenated aryl carboxylic acids **1c** and **1d** could be well applied in this transformation to give the products (**3ca**, **3da**, **3dc**, **3di**) in 76-89% yields, and C-X (X = Cl, Br) bonds remained intact in this process, thereby offering an opportunity for further elaboration.

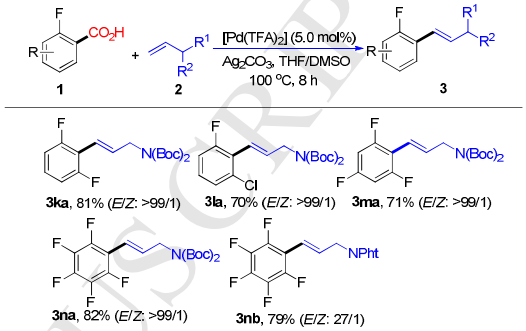
Table 3

Pd-catalyzed coupling reaction of arylcarboxylic acids **1** with unactivated olefins **2**.[a]



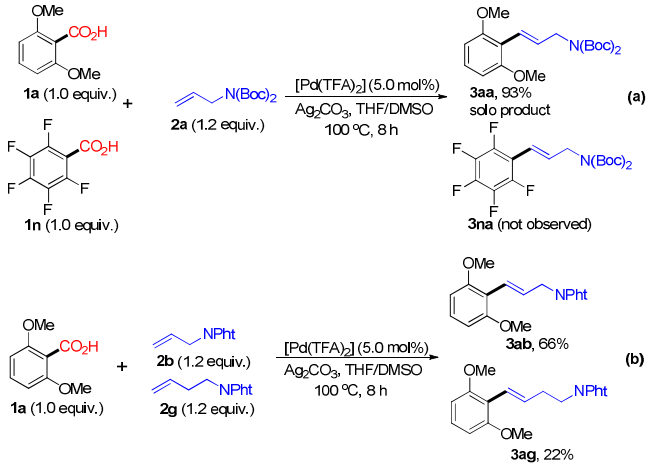
[a] *Reaction conditions*: **1** (0.2 mmol), **2** (0.24 mmol), $Pd(TFA)_2$ (5.0 mol%), Ag_2CO_3 (0.2 mmol), THF/DMSO (2.1 ml, 20:1), 100 °C, 8 h. Isolated yields. *E*/*Z* ratios of the products were determined by ^{1}H NMR. When the *Z*-isomer could not be detected, a value of >99/1 was assigned.

The reaction is not limited to aryl carboxylic acids only; heteroaryl carboxylic acids participated equally well. As can be seen from Table 3, 3-methylthiophene-2-carboxylic acid (**1g**) and 3,4,5-trichlorothiophene-2-carboxylic acid (**1h**) displayed good reactivity to furnish the corresponding products (**3ga**, **3gb**, **3ha**, **3hb**) in high yields. Notably, in the case of **1g**, no C5-olefination was observed. Furthermore, 3-methylbenzo[b]thiophene-2-carboxylic acid (**3i**) and 3-methylbenzofuran-2-carboxylic acid (**3j**) were also reactive, affording the products (**3ia**, **3ib**, **3ja**) in moderate yields. However, under the current conditions, benzoic acid, 2-methoxybenzoic acid and pyridine-2-carboxylic acid completely failed to undergo olefination.



Scheme 1. The coupling reaction of fluorinated aryl carboxylic acids **1** with unactivated olefins **2**.

To further demonstrate the potential of our catalytic system, the olefination of electron-deficient fluorinated aryl carboxylic acids was then examined (Scheme 1). It was found that the coupling reaction of **3k-3m** with **1a** proceeded smoothly under the optimized reaction conditions, affording the desired products (**3ka-3ma**) in good yields. It is worth mentioning that the more electron-deficient 2,3,4,5,6-pentafluorobenzoic acid (**1n**) was also compatible in this transformation, and the products **3na** and **3nb** were isolated in good yields.

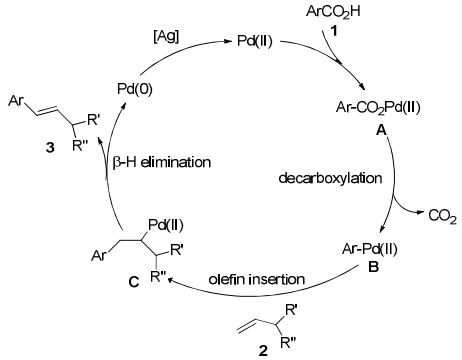


Scheme 2. Intermolecular competition experiments.

To gain insight into the mechanism of this oxidative olefination, the following control experiments were carried out as shown in Scheme 2. The competition reaction between **1a** and **1n** with **2a** under the standard reaction conditions revealed **3aa** to be the sole product, indicating that the more electron-rich substrate was transformed preferentially (Scheme 2a). When an equimolar mixture of **2b** and **2g** underwent coupling reaction with **1a**, the desired products **3ab** and **3ag** were formed in 66% and 22% yields, respectively (Scheme 2b). The higher reactivity observed in the reactions of allylamide **2b** might be attributed to the

preference for chelation between the carbonyl O atom and the Pd atom. A similar chelation effect has also been reported in the arylation of allyl derivatives.[15]

Based on our experimental results and previous reports,[8-11] a plausible mechanism is proposed in Scheme 3. First, coordination of the aryl carboxylic acid **1** to the palladium (II) complex led to the formation of intermediate **A**. The subsequent decarboxylation yielded intermediate **B**, which underwent migratory insertion of the olefin **2** to give intermediate **C**. The following β-H elimination furnished the desired product **3**. Finally oxidation of the Pd(0) species to the Pd(II) complex by the silver salt completed the catalytic cycle.



Scheme 3. Proposed reaction mechanism.

3. Conclusions

In conclusion, we have developed a general and efficient decarboxylative coupling reaction of aryl carboxylic acids with unactivated olefins under Pd(II) catalysis. This method allows for highly regioselective and stereoselective arylation of a diverse of unactivated olefins with differently substituted aryl carboxylic acids to essentially furnish the linear products in good to excellent yields with good functional group tolerance. This methodology offers a valuable complement to the existing decarboxylative olefination of arene carboxylic acids. Further studies to expand the substrate scope and synthetic application of this catalytic process are currently underway in this lab, and will be reported in due course.

4. Experimental section

4.1. General

All experiments were carried out under an atmosphere of nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer (^{1}H 400 MHz and ^{13}C 100.6 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. 3-Chloro-2,6-dimethoxybenzoic acid (**1c**),[16] 3-bromo-2,6-dimethoxybenzoic acid (**1d**),[16] *N*,*N*-(Boc)$_2$-allylamine (**2a**),[17a] 2-allylisoindoline-1,3-dione (**2b**),[17b] 2-(but-3-en-2-yl)isoindoline-1,3-dione (**2c**),[17c] 2-(pent-1-en-3-yl)isoindoline-1,3-dione (**2d**),[17d] *tert*-butyl allyl(methyl)carbamate (**2e**),[17e] *N*-Boc-allylamine (**2f**),[17e] 2-(but-3-en-1-yl)isoindoline-1,3-dione (**2g**)[17f], 2-(pent-4-en-1-yl)isoindoline-1,3-dione (**2h**)[17g], diethyl 2-(but-3-en-1-yl)malonate (**2i**)[17h] and methyl 2-methylpent-4-enoate (**2j**)[17i] were prepared according to the previous reports. All other chemicals were used as received from Aldrich or Acros without further purification.

4.2. General procedure for the decarboxylative arylation of olefins with aryl carboxylic acids

To an oven-dried pressure tube were sequentially added aryl carboxylic acid **1** (0.2 mmol), olefin **2** (0.24 mmol), Pd(TFA)$_2$ (3.33 mg, 5.0 mol%), Ag_2CO_3 (55.2 mg, 0.2 mmol), THF (2.0 mL) and DMSO (0.10 mL) under nitrogen at room temperature. After degassing three times, the reaction mixture was heated at 100 °C for 8 h, and then was cooled to room temperature. Water (20.0 mL) was added, and the mixture was extracted with ethyl acetate (3 × 5.0 mL). The combined organic layer was washed with brine, dried over anhydrious Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluant: hexane/ethyl acetate) to give the pure target product

*4.2.1 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2,6-dimethoxyphenyl)prop-2-en-1-amine (**3aa**)*. White solid, mp: 70-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 18H), 3.82 (s, 6H), 4.33 (dd, *J* = 1.0, 6.5 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.61 (dt, *J* = 6.5, 16.1 Hz, 1 H), 6.85 (d, *J* = 16.2 Hz, 1H), 7.14 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.0, 49.9, 55.6, 82.0, 103.9, 114.1, 123.1, 128.0, 128.8, 152.3, 158.5; HRMS (ESI) calcd. for $C_{21}H_{31}NNaO_6$ [M+Na]$^+$: 416.2044, found: 416.2033.

*4.2.2 (E)-2-(3-(2,6-dimethoxyphenyl)allyl)isoindoline-1,3-dione (**3ab**)*. Yellow solid, mp: 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 6H), 4.47 (dd, *J* = 1.0, 6.7 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 6.72 (dt, *J* = 6.7, 16.1 Hz, 1H), 7.06 (d, *J* = 16.1 Hz, 1H), 7.14 (t, *J* = 8.3 Hz, 1H), 7.71 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.86 (dd, *J* = 3.1, 4.6 Hz, 2H); ^{13}C NMR (100.6MHz, $CDCl_3$) δ 41.7, 55.7, 103.8, 113.5, 123.2, 124.6, 126.4, 128.4, 132.4, 133.8, 158.6, 168.1; HRMS (ESI) calcd. for $C_{19}H_{17}NNaO_4$ [M+Na]$^+$: 346.1050, found: 346.1029.

*4.2.3 (E)-2-(4-(2,6-dimethoxyphenyl)but-3-en-2-yl)isoindoline-1,3-dione (**3ac**)*. Yellow solid, mp: 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (d, *J* = 7.0 Hz, 3H), 3.84 (s, 6H), 5.05-5.13 (m, 1H), 6.53 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 16.2 Hz, 1H), 7.10-7.16 (m, 2H), 7.68 (dd, *J* = 3.1, 5.4 Hz, 2H), 7.82 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.4, 51.0, 55.7, 103.9, 113.6, 122.6, 123.0, 128.3, 131.8, 132.3, 133.7, 158.6, 168.0; HRMS (ESI) calcd. for $C_{20}H_{19}NNaO_4$ [M+Na]$^+$: 360.1206, found: 360.1195.

*4.2.4 (E)-2-(1-(2,6-dimethoxyphenyl)pent-1-en-3-yl)isoindoline-1,3-dione (**3ad**)*. White solid, mp: 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.4 Hz, 3H), 2.02-2.09 (m, 1H), 2.11-2.20 (m, 1H), 3.85 (s, 6H), 4.76-4.82 (m, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 16.2 Hz, 1H), 7.08-7.16 (m, 2H), 7.69 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.83 (dd, *J* = 3.1, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.2, 26.1, 55.7, 57.7, 103.9, 113.7, 123.0, 123.6, 128.3, 130.8, 132.2, 133.7, 158.6, 168.3; HRMS (ESI) calcd. for $C_{21}H_{21}NNaO_4$ [M+Na]$^+$: 374.1363, found: 374.1351.

*4.2.5 (E)-tert-butyl (3-(2,6-dimethoxyphenyl)allyl)(methyl)carbamate (**3ae**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.87 (s, 3H), 3.83 (s, 6H), 3.98 (d, *J* = 8.5 Hz, 2H), 6.50 (m, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 16.1 Hz, 1H), 7.14 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.5, 43.2, 55.3, 55.7, 79.3, 106.2, 114.1, 128.0, 129.2, 129.9, 155.9, 158.4; HRMS (ESI) calcd. for $C_{17}H_{25}NNaO_4$ [M+Na]$^+$: 330.1676, found: 330.1673.

*4.2.6 (E)-tert-butyl (3-(2,6-dimethoxyphenyl)allyl)carbamate (**3af**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s , 9H), 3.83 (s, 6H), 3.91 (d, *J* = 7.3 Hz, 2H), 4.64 (s, 1H), 6.54 (d, *J* = 8.3 Hz, 2H), 6.60 (m, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 7.14 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.4, 44.4, 55.7, 103.7, 103.9, 113.9, 122.1, 128.1, 130.1, 158.4; HRMS (ESI) calcd. for $C_{16}H_{23}NNaO_4$ [M+Na]$^+$: 316.1519, found: 316.1515.

*4.2.7(E)-2-(4-(2,6-dimethoxyphenyl)but-3-en-1-yl)isoindoline-1,3-dione (**3ag**)*. White solid, mp: 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62-2.68 (m, 2H), 3.78 (s, 6H), 3.86 (t, *J* = 7.2 Hz, 2H), 6.51 (d, *J* = 8.3 Hz, 3H), 6.67 (d, *J* = 16.1 Hz, 1H), 7.10 (t, *J* = 6.8 Hz, 1H), 7.70 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.84 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 33.7, 37.9, 55.6, 103.8, 114.5, 123.1, 127.6, 130.3, 132.2, 133.7, 133.8, 158.2, 168.3; HRMS (ESI) calcd. for $C_{20}H_{19}NNaO_4$ $[M+Na]^+$: 360.1206, found: 360.1215.

*4.2.8 (E)-2-(5-(2,6-dimethoxyphenyl)pent-4-en-1-yl)isoindoline-1,3-dione (**3ah**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88-1.94 (m, 2H), 2.31-2.36 (m, 2H), 3.76-3.77 (m, 2H), 3.84 (s, 6H), 6.52-6.60 (m, 3H), 6.67 (d, *J* = 16.2 Hz, 1H), 7.10 (t, *J* = 8.3 Hz, 1H), 7.69 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.83 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.4, 32.2, 37.9, 55.7, 103.7, 103.9, 114.8, 120.8, 123.1, 127.3, 132.2, 133.8, 158.1, 168.4; HRMS (ESI) calcd. for $C_{21}H_{21}NNaO_4$ $[M+Na]^+$: 374.1363, found: 374.1339.

*4.2.9 (E)-diethyl 2-(3-(2,6-dimethoxyphenyl)allyl)malonate (**3ai**)*.[11] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 6H), 2.84 (td, *J* = 1.2, 7.5, Hz, 2H), 3.52 (t, *J* = 7.7 Hz, 1H), 3.83 (s, 6H), 4.22 (dd, *J* = 2.5, 7.2 Hz, 4H), 6.54-6.56 (m, 3H), 6.75 (d, *J* = 16.1 Hz, 1H), 7.13 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 4.1, 34.0, 52.5, 55.7, 61.3, 103.9, 114.4, 123.1, 127.7, 129.8, 158.3, 169.1; HRMS (ESI) calcd. for $C_{18}H_{24}NaO_6$ $[M+Na]^+$: 359.1465, found: 359.1457.

*4.2.10 (E)-methyl 5-(2,6-dimethoxyphenyl)-2-methylpent-4-enoate (**3aj**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.21 (d, *J* = 6.8 Hz, 3H), 2.34 (m, 1H), 2.60 (m, 2H), 3.68 (s, 3H), 3.82 (s, 6H), 6.48 (m, 1H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 7.11 (t, *J* = 8.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.5, 38.8, 39.9, 51.5, 55.7, 104.0, 114.8, 122.3, 127.5, 129.9, 131.6, 158.2; HRMS (ESI) calcd. for $C_{15}H_{20}NaO_4$ $[M+Na]^+$: 287.1254, found: 287.1248.

*4.2.11(E)-6-(2,6-dimethoxyphenyl)hex-5-en-2-one (**3ak**)/(Z)-6-(2,6-dimethoxyphenyl)hex-5-en-2-one (**3ak'**)/5-(2,6-dimethoxyphenyl)hex-5-en-2-one (**3ak''**)* (E/Z=100/19, linear/branched=119/14). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 0.57H) (**3ak'**), 2.10 (s, 0.42H) (**3ak''**), 2.17 (s, 3H) (**3ak**), 2.51 (m, 2.64H) (**3ak**+**3ak'**+**3ak''**), 2.62 (m, 2.30H) (**3ak**+**3ak'**), 3.78 (s, 0.84H) (**3ak''**), 3.83 (s, 1.19H) (**3ak'**), 3.83 (s, 6H) (**3ak**), 4.90 (m, 0.14H) (**3ak''**), 5.31 (m, 0.14H) (**3ak''**), 6.21 (m, 0.19H) (**3ak'**), 6.54 (m, 2.72H) (**3ak**+**3ak'**+**3ak''**) , 6.58 (m, 1.20H) (**3ak**+**3ak'**), 6.66 (d, *J* = 16.2 Hz, 1H) (**3ak**), 7.11 (t, *J* = 8.3 Hz, 1H) (**3ak**), 7.20 (m, 0.34H) (**3ak'**+**3ak''**); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.0, 30.0, 43.7, 55.7, 104.0, 114.6, 121.0, 127.5, 133.1, 158.2, 208.7; HRMS (ESI) calcd. for $C_{14}H_{19}O_3$ $[M+H]^+$: 235.1329, found: 235.1320.

*4.2.12 (E)-ethyl 5-(2,6-dimethoxyphenyl)pent-4-enoate (**3al**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 3H), 2.49-2.53 (m, 2H), 2.56-2.62 (m, 2H), 3.85 (s, 6H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.54-6.59 (m, 3H), 6.72 (d, *J* = 16.1 Hz, 1H), 7.14 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3, 30.1, 34.5, 55.7, 60.3, 104.0, 114.6, 121.1, 127.5, 132.8, 158.2, 173.3; HRMS (ESI) calcd. for $C_{15}H_{20}NaO_4$ $[M+Na]^+$: 287.1254, found: 287.1260.

*4.2.13 (E)-1,3-dimethoxy-2-(3-phenylprop-1-en-1-yl)benzene (**3am**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (d, *J* = 5.3 Hz, 2H), 3.84 (s, 6H), 6.35 (m, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.58 (d, *J* = 8.3 Hz, 2H), 7.16 (m, 2H), 7.25 (m, 2H), 7.33 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.5, 55.9, 103.9, 116.5, 126.0, 126.6, 127.2, 128.3 129.0, 129.5, 138.2 158.3; HRMS (ESI) calcd. for $C_{17}H_{19}O_2$ $[M+H]^+$: 255.1380, found: 255.1369.

*4.2.14 (E)-1,3-dimethoxy-2-(3-(4-methoxyphenyl)prop-1-en-1-yl)benzene (**3an**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (dd, *J* = 1.1, 6.4 Hz, 2H), 3.78 (s, 3H), 3.83 (s, 6H), 6.19 (m, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.57 (d, *J* = 6.8 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 7.21 (m, 2H), 7.16 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.4, 55.3, 55.9, 103.9, 113.7, 116.8, 126.8, 127.1, 128.8, 129.6, 131.0, 158.3, 158.5; HRMS (ESI) calcd. for $C_{18}H_{20}NaO_3$ $[M+Na]^+$: 307.1305, found: 307.1293.

*4.2.15 (E)-2-(2-cyclohexylvinyl)-1,3-dimethoxybenzene (**3ao**)*. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (m , 6H), 1.70 (m, 4H), 2.16 (m, 1H), 3.85 (s, 6H), 6.56 (d, *J* = 8.4 Hz, 2H), 6.61 (m, 1H), 6.67 (d, *J* = 16.4 Hz, 1H), 7.12 (t, *J* = 8.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.2, 26.3, 33.3, 43.0, 55.8, 104.1, 117.6, 127.1, 141.3, 158.2; HRMS (ESI) calcd. for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1693, found: 247.1689.

*4.2.16 (E)-2-(hex-1-en-1-yl)-1,3-dimethoxybenzene (**3ap**) and (E)-2-(hex-2-en-1-yl)-1,3-dimethoxybenzene (**3ap'**)* (ratio= 5/2). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.3, 7.4 Hz, 1.2H) (**3ap'**), 0.92 (t, *J* = 7.2 Hz, 3H) (**3ap**), 1.35 (m, 2H) (**3ap**), 1.46 (m, 2.8H) (**3ap**+**3ap'**), 1.94 (m , 0.8H) (**3ap'**), 2.23 (m, 2H) (**3ap**), 3.34 (s, 0.8H) (**3ap'**), 3.80 (s, 2.4H) (**3ap'**), 3.84 (s, 6H) (**3ap**), 5.38 (m, 0.4H) (**3ap'**), 5.49 (m, 0.4H) (**3ap'**), 6.55 (m, 2.8H) (**3ap**+**3ap'**), 6.60 (m, 1H) (**3ap**), 6.63 (d, *J* = 16.1 Hz, 1H) (**3ap**), 7.09 (t, *J* = 8.3 Hz, 1.4H) (**3ap**+**3ap'**); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0, 22.4, 31.9, 34.5, 55.8, 104.1, 115.2, 119.8, 127.1, 135.9, 158.1; HRMS (ESI) calcd. for $C_{14}H_{21}O_2$ $[M+H]^+$: 221.1536, found: 221.1528.

*4.2.17 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2,4,6-trimethoxyphenyl)prop-2-en-1-amine (**3ba**)*. Colorleess oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 18H), 3.79 (s, 3H), 3.80 (s, 6H), 4.30 (d, *J* = 6.6 Hz, 2H), 6.11 (s, 2H), 6.49 (dt, *J* = 6.6, 16.0 Hz, 1H), 6.77 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.0, 50.1, 55.2, 55.5, 81.9, 90.6, 107.3, 123.2, 126.2, 152.3, 159.3, 160.1; HRMS (ESI) calcd. for $C_{22}H_{33}NNaO_7$ $[M+Na]^+$: 446.2149, found: 446.2138.

*4.2.18 (E)-2-(3-(2,4,6-trimethoxyphenyl)allyl)isoindoline-1,3-dione (**3bb**)*. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.81 (s, 6H), 4.44 (dd, *J* = 0.9, 6.8 Hz, 2H), 6.10 (s, 2H), 6.57 (dt, *J* = 6.8, 16.0 Hz, 1H), 6.98 (d, *J* = 16.0 Hz, 1H), 7.70 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.85 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 41.8, 55.3, 55.7, 90.6, 106.8, 123.1, 123.7, 124.5, 132.4, 133.7, 159.5, 160.4, 168.1; HRMS (ESI) calcd. for $C_{20}H_{19}NNaO_5$ $[M+Na]^+$: 376.1155, found: 376.1148.

*4.2.19 (E)-2-(4-(2,4,6-trimethoxyphenyl)but-3-en-2-yl)isoindoline-1,3-dione (**3bc**)*. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (d, *J* = 7.0 Hz, 3H), 3.81 (s, 3H), 3.83 (s, 6H), 5.02-5.09 (m, 1H), 6.11 (s, 2H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.99 (dd, *J* = 8.0, 16.1 Hz, 1H), 7.68 (dd, *J* = 3.1, 5.4 Hz, 2H), 7.82 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.5, 51.2, 55.3, 55.7, 90.6, 106.8, 122.5, 123.0, 129.2, 132.3, 133.6, 159.5, 160.3, 168.1; HRMS (ESI) calcd. for $C_{21}H_{21}NNaO_5$ $[M+Na]^+$: 390.1312, found: 390.1298.

*4.2.20 (E)-diethyl 2-(3-(2,4,6-trimethoxyphenyl)allyl)malonate (**3bi**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 6H), 2.80 (td, *J* = 1.3, 7.6 Hz, 2H), 3.49 (t, *J* = 7.7 Hz, 1H), 3.82 (s, 6H), 3.82 (s, 3H), 4.19-4.24 (m, 4H), 6.13 (s, 2H), 6.41 (dt, *J* = 7.2, 16.0 Hz, 1H), 6.67 (d, *J* = 16.1 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 34.0, 52.7, 55.3, 55.6, 61.3, 90.7, 107.7, 122.9, 127.2, 159.1, 159.8, 169.2; HRMS (ESI) calcd. for $C_{19}H_{26}NaO_7$ $[M+Na]^+$: 389.1571, found: 389.1575.

*4.2.21 (E)-1,3,5-trimethoxy-2-(3-phenylprop-1-en-1-yl)benzene (**3bm**)*. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (dd, *J* =

1.2, 6.3 Hz, 2H), 3.84 (s, 9H), 6.14-6.24 (m, 4H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.1, 55.3, 55.8, 90.7, 109.3, 113.7, 127.1, 127.3, 128.5, 131.1, 158.4, 158.8, 159.6; HRMS (ESI) calcd. for $C_{18}H_{20}NaO_3$ $[M+Na]^+$: 307.1305, found: 307.1310.

*4.2.22 (E)-1,3,5-trimethoxy-2-(3-(4-methoxyphenyl)prop-1-en-1-yl)benzene (**3bn**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (dd, *J* = 0.9, 6.3 Hz, 2H), 3.81 (s, 3H), 3.85 (s, 9H), 6.20 (s, 2H), 6.21-6.24 (m, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.27-7.29 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.1, 55.3, 55.3, 55.8, 90.7, 109.2, 113.7, 127.1, 127.3, 128.5, 131.1, 158.4, 158.8, 159.4; HRMS (ESI) calcd. for $C_{19}H_{22}NaO_4$ $[M+Na]^+$: 337.1410, found: 337.1419.

*4.2.23 (E)-N,N-bis(tert-butoxycarbonyl)-3-(3-chloro-2,6-dimethoxyphenyl)prop-2-en-1-amine (**3ca**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 18H), 3.75 (s, 3H), 3.81 (s, 3H), 4.34 (d, *J* = 4.1 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 1H), 6.67 (m, 2H), 7.18 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 49.3, 55.8, 60.2, 82.3, 107.5, 120.1, 120.9, 122.1, 128.3, 131.0, 152.3, 154.5, 157.2; HRMS (ESI) calcd. for $C_{21}H_{30}ClNNaO_6$ $[M+Na]^+$: 450.1654, found: 450.1643.

*4.2.24 (E)-N,N-bis(tert-butoxycarbonyl)-3-(3-bromo-2,6-dimethoxyphenyl)prop-2-en-1-amine (**3da**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 18H), 3.75 (s, 3H), 3.82 (s, 3H), 4.37 (dd, *J* = 1.5, 2.9 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 1H), 6.67-6.69 (m, 2H), 7.36 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 49.3, 55.8, 60.2, 82.3, 108.2, 108.8, 121.0, 122.2, 131.1, 131.2, 152.3, 155.5, 157.9; HRMS (ESI) calcd. for $C_{21}H_{30}BrNNaO_6$ $[M+Na]^+$: 494.1149, found: 494.1142.

*4.2.25 (E)-2-(4-(3-bromo-2,6-dimethoxyphenyl)but-3-en-2-yl)isoindoline-1,3-dione (**3dc**).* Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, *J* = 7.0 Hz, 3H), 3.75 (s, 3H), 3.84 (s, 3H), 5.10-5.17 (m, 1H), 6.57 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 16.3 Hz, 1H), 7.08 (dd, *J* = 7.3, 16.2 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.72 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.85 (dd, *J* =3.1, 5.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.8, 19.2, 49.9, 55.9, 60.5, 108.2, 108.8, 121.9, 123.1, 131.5, 132.1, 133.9, 134.0, 158.0, 168.0; HRMS (ESI) calcd. for $C_{20}H_{18}BrNNaO_4$ $[M+Na]^+$: 438.0311, found: 438.0296.

*4.2.26 (E)-diethyl 2-(3-(3-bromo-2,6-dimethoxyphenyl)allyl)malonate (**3di**).* Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 6H), 2.84-2.88 (m, 2H), 3.53 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.83 (s, 3H), 4.18-4.27 (m, 4H), 6.57 (d, *J* = 8.9 Hz, 1H), 6.61-6.63 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 33.7, 52.1, 55.9, 60.2, 61.4, 108.2, 108.9, 121.3, 122.9, 131.0, 131.8, 155.4, 157.8, 168.9; HRMS (ESI) calcd. for $C_{18}H_{23}BrNaO_6$ $[M+Na]^+$: 437.0570, found: 437.0565.

*4.2.27 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2',4',5'-trimethoxyphenyl)prop-2-en-1-amine (**3ea**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 18H), 3.80 (s, 3H), 3.86 (s, 3H), 3.89 (s, 3H), 4.32 (dd, *J* = 1.2, 6.5 Hz, 2H), 6.08 (dt, *J* = 6.5, 15.9 Hz, 1H), 6.49 (s, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.94 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 48.7, 56.0, 56.5, 56.5, 82.3, 97.6, 109.9, 117.6, 123.1, 127.1, 143.3, 149.5, 151.3, 152.4; HRMS (ESI) calcd. for $C_{22}H_{33}NNaO_7$ $[M+Na]^+$: 446.2149, found: 446.2135.

*4.2.28 (E)-2-(3-(2,4,5-trimethoxyphenyl)allyl)isoindoline-1,3-dione (**3eb**).* Yellow solid, mp: 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 3.85 (s, 3H), 3.90 (s, 3H), 4.46 (dd, *J* = 1.2, 6.7 Hz, 2H), 6.16 (dt, *J* = 6.8, 15.9 Hz, 1H), 6.49 (s, 1H), 6.93 (s, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 7.73 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.87 (dd, *J* = 3.0, 5.48 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.3, 56.0, 56.4, 56.6, 97.6, 109.9, 117.0, 120.9, 123.3, 128.5, 132.3, 133.9, 143.3, 149.7, 151.6, 168.1; HRMS (ESI) calcd. for $C_{20}H_{19}NNaO_5$ $[M+Na]^+$: 376.1155, found: 376.1142.

*4.2.29 (E)-2-(4-(2,4,5-trimethoxyphenyl)but-3-en-2-yl)isoindoline-1,3-dione (**3ec**).* Yellow oil ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (d, *J* = 7.0 Hz, 3H), 3.81 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 5.07-5.14 (m, 1H), 6.48 (s, 1H), 6.53 (dd, *J* = 8.1, 16.0 Hz, 1H), 6.92 (d, *J* = 15.5 Hz, 1H), 6.98 (s, 1H), 7.69 (dd, *J* = 3.0, 5.44 Hz, 2H), 7.81 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.3, 49.6, 56.0, 56.5, 56.6, 97.6, 109.7, 117.1, 123.1, 126.1, 126.3, 132.1, 133.8, 143.3, 149.7, 151.5, 168.0; HRMS (ESI) calcd. for $C_{21}H_{21}NNaO_5$ $[M+Na]^+$: 390.1312, found: 390.1294.

*4.2.30 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2,6-diethoxyphenyl)prop-2-en-1-amine (**3fa**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (m , 6H), 1.51 (s , 18H), 4.00 (m, 4H), 4.32 (d, *J* = 6.5 Hz, 2H), 6.51 (d, *J* = 8.2 Hz, 2H), 6.72 (m, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 7.08 (t, *J* = 8.3 Hz 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 28.1, 48.5, 64.1, 82.3, 104.8, 116.2, 128.6, 133.8, 152.4, 158.0; HRMS (ESI) calcd. for $C_{23}H_{35}NNaO_6$ $[M+Na]^+$: 444.2357, found: 444.2345.

*4.2.31 (E)-N,N-bis(tert-butoxycarbonyl)-3-(3-methylthiophen-2-yl)prop-2-en-1-amine (**3ga**).*[12e] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 18H), 2.21 (s, 3H), 4.29 (m, 2H), 5.98 (dt, *J* = 6.4, 15.5 Hz, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.77 (d, *J* = 5.1 Hz, 1H), 7.03 (d, *J* = 5.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 28.1, 48.1, 82.4, 122.6, 124.1, 124.2, 125.5 130.5, 135.3, 152.3; HRMS (ESI) calcd. for $C_{18}H_{27}NNaO_4S$ $[M+Na]^+$: 376.1553, found: 376.1540.

*4.2.32 (E)-2-(3-(3-methylthiophen-2-yl)allyl)isoindoline-1,3-dione (**3gb**).* White solid, mp: 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 4.41 (dd, *J* = 1.1, 7.9 Hz, 2H), 6.00 (dt, *J* = 6.8, 15.5 Hz, 1H), 6.75 (d, *J* = 5.0 Hz, 1H), 6.83 (d, *J* = 15.5 Hz, 1H), 7.02 (d, *J* = 5.0 Hz, 1H), 7.71 (dd, *J* = 3.1, 5.5 Hz, 2H), 7.85 (dd, *J* = 3.1, 5.5 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 39.7, 121.6, 123.1, 123.3, 125.9, 130.5, 132.2, 133.9, 134.7, 167.9; HRMS (ESI) calcd. for $C_{16}H_{13}NNaO_2S$ $[M+Na]^+$: 306.0559, found: 306.0563.

*4.2.33 (E)-N,N-bis(tert-butoxycarbonyl)-3-(3,4,5-trichlorothiophen-2-yl)prop-2-en-1-amine (**3ha**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 18H), 4.32 (dd, *J* = 1.4, 6.2 Hz, 2H), 6.06 (dt, *J* = 6.2, 15.8 Hz,1H), 6.68 (dt, *J* = 1.4, 15.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 47.6, 82.8, 121.3, 121.7, 122.5, 123.6, 127.9, 132.1, 152.1; HRMS (ESI) calcd. for $C_{17}H_{22}Cl_3NNaO_4S$ $[M+Na]^+$: 464.0227, found: 464.0216.

*4.2.34 (E)-2-(3-(3,4,5-trichlorothiophen-2-yl)allyl)isoindoline-1,3-dione (**3hb**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (dd, *J* =1.4, 6.5 Hz, 2H), 6.08 (dt, *J* = 6.5, 15.8 Hz, 1H), 6.82 (dt, *J* = 1.4, 15.8 Hz, 1H), 7.76 (dd, *J* = 3.0, 5.5 Hz, 2H), 7.89 (dd, *J* = 3.0, 5.5 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 39.2, 123.0, 123.3, 123.5, 123.7, 125.4, 131.5, 132.0, 134.0, 134.2, 167.7; HRMS (ESI) calcd. for $C_{15}H_8Cl_3NNaO_2S$ $[M+Na]^+$: 393.9234, found: 393.9228.

*4.2.35 (E)-N,N-bis(tert-butoxycarbonyl)-3-(3-methylbenzo[b]thiophen-2-yl)prop-2-en-1-amine (**3ia**).*[12e] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 18H), 2.41 (s, 3H), 4.38 (dd, *J* = 1.2, 6.3 Hz, 2H), 6.13 (dt, *J* = 6.3, 15.5 Hz, 1H), 6.88 (dt, *J* = 1.3, 15.5 Hz, 1H), 7.30-7.38 (m, 2H), 7.63-7.65 (m, 1H), 7.74-7.76 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.7, 28.1, 48.1, 82.6, 121.7, 122.1, 124.1, 124.3, 124.9, 127.0, 129.4,

135.6, 138.0, 141.0, 152.3; HRMS (ESI) calcd. for $C_{22}H_{29}NNaO_4S$ $[M+Na]^+$: 426.1710, found: 426.1693.

*4.2.36 (E)-2-(3-(3-methylbenzo[b]thiophen-2-yl)allyl)isoindoline-1,3-dione (**3ib**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 4.48 (dd, *J* = 0.7, 4.4 Hz, 2H), 6.13 (dt, *J* = 4.5, 10.3 Hz, 1H), 7.02 (dt, *J* = 0.8, 10.3 Hz, 1H), 7.28-7.33 (m, 2H), 7.61 (dd, *J* = 0.7, 5.6 Hz, 1H), 7.71 (dd, *J* = 0.8, 4.7 Hz, 1H), 7.73 (dd, *J* = 2.0, 3.6 Hz, 2H), 7.87 (dd, *J* = 2.0, 3.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.9, 39.8, 121.9, 122.2, 123.4, 124.1, 124.4, 125.1, 126.2, 130.3, 132.3, 134.1, 135.1, 138.2, 141.0, 168.0; HRMS (ESI) calcd. for $C_{20}H_{15}NNaO_2S$ $[M+Na]^+$: 356.0716, found: 356.0708.

*4.2.37 (E)-N,N-bis(tert-butoxycarbonyl)-3-(3-methylbenzo[b]furan-2-yl)prop-2-en-1-amine (**3ja**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 18H), 2.23 (s, 3H), 4.38 (d, *J* = 6.1 Hz, 2H), 6.37 (m, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 7.19 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 7.9, 28.1, 48.1, 82.3, 110.7, 116.2, 118.7, 119.2, 122.3, 124.6, 125.9, 133.8, 149.6, 152.4; HRMS (ESI) calcd. for $C_{22}H_{29}NNaO_5$ $[M+Na]^+$: 410.1938, found: 410.1927.

*4.2.38 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2,6-difluorophenyl)prop-2-en-1-amine (**3ka**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 18H), 4.34 (d, *J* = 3.7 Hz, 2H), 6.52 (m, 2H), 6.86 (m, 2H), 7.13 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.0, 48.9, 82.5, 111.6, 116.2, 118.3, 128.0, 132.4, 133.8, 152.2; HRMS (ESI) calcd. for $C_{19}H_{25}F_2NNaO_4$ $[M+Na]^+$: 392.1644, found: 392.1630.

*4.2.39 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2-chloro-6-fluorophenyl)prop-2-en-1-amine (**3la**).* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 18H), 4.37 (d, *J* = 5.8 Hz, 2H), 6.45 (m, 1H), 6.61(d, *J* = 16.2 Hz, 1H), 6.97 (m, 1H), 7.10 (m, 1H), 7.16 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 48.7, 82.5, 114.7, 116.2, 122.1, 125.5, 128.1, 128.2, 129.9, 133.4, 152.3; HRMS (ESI) calcd. for $C_{19}H_{25}ClFNNaO_4$ $[M+Na]^+$: 408.1348, found: 408.1333.

*4.2.40 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2,4,6-trifluorophenyl)prop-2-en-1-amine (**3ma**).* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 18H), 4.30 (dd, *J* = 0.8, 6.6 Hz, 2H), 6.13 (s, 2H), 6.50 (dt, *J* = 6.6, 16.1 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.1, 50.1, 81.9, 90.7, 107.4, 123.2, 126.3, 152.3, 159.3, 160.1; HRMS (ESI) calcd. for $C_{19}H_{24}F_3NNaO_4$ $[M+Na]^+$: 410.1550, found: 410.1538.

*4.2.41 (E)-N,N-bis(tert-butoxycarbonyl)-3-(2,3,4,5,6-pentafluorophenyl)prop-2-en-1-amine (**3na**).*[12e] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 18H), 4.35 (d, *J* = 4.6 Hz, 2H), 6.39 (d, *J* = 16.4 Hz, 1H), 6.54 (dt, *J* = 16.4, 5.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.0, 48.5, 82.8, 115.8, 116.2, 133.8, 135.0, 152.1; ^{19}F NMR (376.5 MHz, $CDCl_3$): -163.0 (dt, *J* = 5.5, 14.9 Hz, 2F), -156.4 (t, *J* = 14.8 Hz, 1F). -143.0 (dd, *J* = 5.6, 14.9 Hz, 2F); HRMS (ESI) calcd. for $C_{19}H_{22}F_5NNaO_4$ $[M+Na]^+$: 446.1361, found: 446.1348

*4.2.42 (E)-2-(3-(perfluorophenyl)allyl)isoindoline-1,3-dione (**3nb**).*[12e] White solid, mp: 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (d, *J* = 4.84 Hz, 2H), 6.54 (d, *J* = 16.4 Hz, 1H), 6.60 (dd, *J* = 5.2, 16.4 Hz, 1H), 7.74 (dd, *J* = 3.0, 5.5 Hz, 2H), 7.88 (dd, *J* = 3.0, 5.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.1, 117.6, 123.5, 123.6, 132.0, 132.3, 134.2, 134.3, 167,7; ^{19}F NMR (376.5 MHz, $CDCl_3$): δ -142.4 (dd, *J* = 5.1, 14.4 Hz, 2F), -155.6 (t, *J* = 14.0 Hz, 1F), -162.8 (td, *J* = 4.7, 19.2 Hz, 2F); HRMS (ESI) calcd. for $C_{17}H_8F_5NNaO_2$ $[M+Na]^+$: 376.0367, found: 376.0355.

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