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The Coupling of Tertiary Amines with Acrylate Derivatives via Visible-Light Photoredox Catalysis

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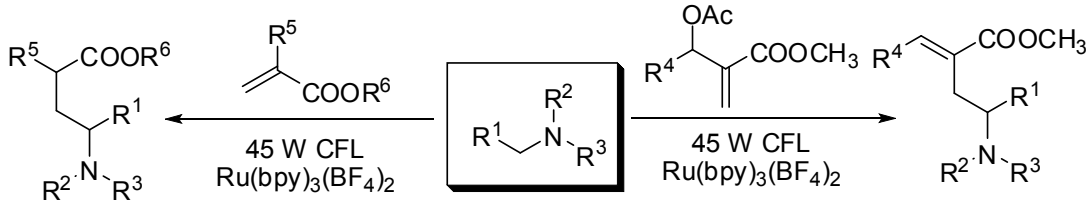
ABSTRACT:



Catalyzed by $Ru(bpy)_3(BF_4)_2$, the photoredox coupling of tertiary amines with acrylate derivatives including Baylis-Hillman adducts under visible light irritation was successfully established. The scope of the substrates was broad and thus an array of γ-aminobutyric ester derivatives was obtained in moderate to good yields.

Recently visible light photoredox catalysis attracted much attention due to the rich resource of visible light, its environment friendly and high efficiency.[1] After having

kept silence for about one century since sponsored by Ciamician,[2] reports about the visible light photoredox catalysis showed a sudden development from 2008, which exhibited powerful ability in organic synthesis and material chemistry.[3] Under photoredox catalysis, especially Ir or Ru complexes, organic dye catalysts,[4,5] several types of novel chemical transformations through the *in situ* active radical intermediates were established. Some groundbreaking literatures have reported the unusual chemical reactions induced by photoredox catalysis, especially carbon-carbon formation reactions.

The direct sp^3 C-H functionalization adjacent to a nitrogen atom of tertiary amine has become one of the most important methods to synthesize more complex tertiary amine compounds,[6] which could be expediently achieved through the oxidation of tertiary amines and subsequent coupling with appropriate reagents. Lots of oxidative systems could achieve this goal.[6] Among, photoredox catalytic oxidation of tertiary amines is an efficient method and some advanced amine derivatives with potential biological activity have been synthesized in simple ways.[7] Generally, the path for the photoredox oxidation of tertiary amine firstly to form amine radical cation which subsequently loses a hydrogen atom to generate an electrophilic iminium ion or loses a proton to generate a nucleophilic α-aminoalkyl radical is accepted.

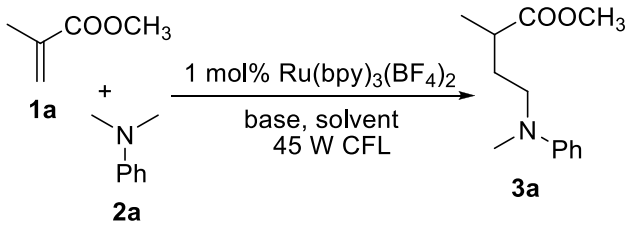
While the research of the iminium ion routes has been drawn much attention,[8] the study of α-aminoalkyl radicals is limited for the reason that they could be easily oxidized to form the iminium ions.[9] Under photoredox catalysis, the nucleophilic coupling of α-aminoalkyl radicals to electron-deficient substrates such as cyanoarene,

α,β-unsaturated derivative, isocyanate and etc. was recently reported, and arrays of diverse structure tertiary amines were synthesized.[10] As far as *α,β*-unsaturated derivatives were concerned, the coupling of *α,β*-unsaturated ketones, *α,β*-unsaturated diesters with tertiary amines were fully investigated. However, due to their easy oligomerization, research of *α,β*-unsaturated monoesters under the photoredox radical conditions was very rare. Nishibayashi reported the sole example of ethyl crotonate participating in this radical coupling reaction.[10b] Under the photoredox conditions employed by Yu and Bian, methyl acrylate failed to react with *N,N*-dimethylaniline to give the coupling or cyclization product.[10d] Herein we report a detailed investigation on the photoredox coupling of acrylate derivatives and tertiary amines, which supply an efficient method for the synthesis of γ-aminobutyric ester derivatives.

Initially, methyl methacrylate **1a** and *N,N*-dimethylaniline **2a** were selected as model substrates to examine the optimal reaction condition. Catalyzed by 1 mol% $Ru(bpy)_3(BF_4)_2$, the desired photoredox coupling product could be isolated in 39% yield along with some oligomerized compounds under the irradiation of 45 W compact fluorescent lamp in DMSO (Table 1, entry 1). Checked by ^1H NMR spectrum, the oligomerized compounds should be the radical coupling of one molecule of **2a** with two to four molecules of **1a**. The efficiency of photoredox catalysts such as $Ru(bpy)_3Cl_2$ and $[Ir(ppy)_2bpy]BF_4$ were poor (Table 1, entries 2-3). Almost no desired product was detected when $Ir(ppy)_3$ was used as the catalyst (Table 1, entry 4). To our delight, irradiation of 1 equiv. of **1a** with 1.5 equiv. of **2a** catalyzed by 1 mol% $Ru(bpy)_3(BF_4)_2$ in NMP under N_2 atmosphere resulted in the product in 56%

yield (Table 4, entry 5). Increasing the amount of **2a**, the yield was not significantly improved (Table 1, entry 6). The control experiment showed that no desired coupling product was observed in the absence of photocatalyst or light.

Table 1. Oxidative Coupling Optimization of Acrylates with *N*,*N*-Dimethylaniline[a]

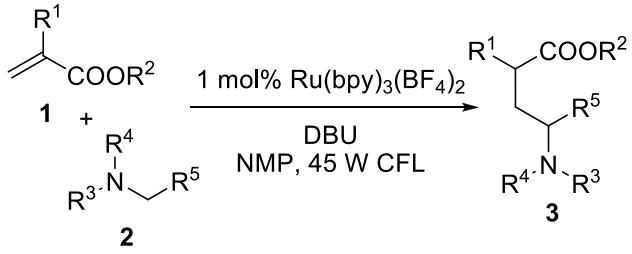


entry	catalyst	solvent	base	yield/%[b]
1	$Ru(bpy)_3(BF_4)_2$	DMSO	NaOAc	39
2	$Ru(bpy)_3Cl_2$	DMSO	NaOAc	35
3	$[Ir(ppy)_2bpy]BF_4$	DMSO	NaOAc	36
4	$Ir(ppy)_3$	DMSO	NaOAc	trace
5[c]	$Ru(bpy)_3(BF_4)_2$	NMP	DBU	56
6[d]	$Ru(bpy)_3(BF_4)_2$	NMP	DBU	60

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), $Ru(bpy)_3(BF_4)_2$ (0.01 mmol), base (1 mmol), solvent (4 mL), 12 hrs, 45 W compact fluorescent lamp irradiation under N_2 atmosphere and r.t. [b] Isolated yield based on **1a**. [c] 1.5 mmol of **2a**; [d] 2 mmol of **2a**.

Different anilines and acrylates were subjected to the optimal reaction conditions. Reacting with the methyl methacrylate, several anilines were successfully used and the corresponding products were obtained in moderate yields (Table 2, entries 4-7). However the yields were low when methyl acrylate or ethyl acrylate were used as the substrates due to the severe oligomerization (Table 2, entries 2-3).

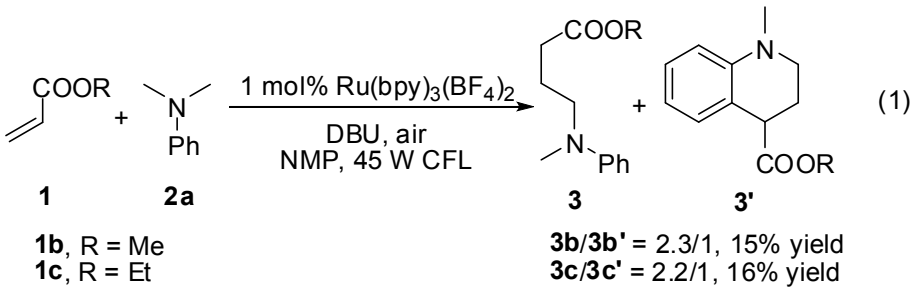
Table 2. Scope of Acrylates with Tertiary Amines[a]



Entry	R^1, R^2	R^3, R^4, R^5	Yield (%)[b]
1	Me, COOMe (**1a**)	Ph, Me, H (**2a**)	56 (**3a**)
2	H, COOMe (**1b**)	Ph, Me, H (**2a**)	31 (**3b**)
3	H, COOEt (**1c**)	Ph, Me, H (**2a**)	29 (**3c**)
4	Me, COOBu (**1d**)	Ph, Me, H (**2a**)	45 (**3d**)
5	Me, COOMe (**1a**)	4-ClC_6H_4, Me, H (**2b**)	37 (**3e**)
6	Me, COOMe (**1a**)	4-$CH_3OC_6H_4$, Me, H **(2c)**	40 (**3f**)
7	Me, COOMe (**1a**)	*N*-phenylpyroridine (**2d**)	60 (**3g**)[c]

[a] Reaction conditions: **1** (1 mmol), **2** (1.5 mmol), $Ru(bpy)_3(BF_4)_2$ (0.01 mmol), DBU (1 mmol), DMSO (4 mL), 12 hrs, 45 W compact fluorescent lamp irradiation under N_2 atmosphere and r.t. [b] Isolated yield based on **1**. [c] dr = 1:1.

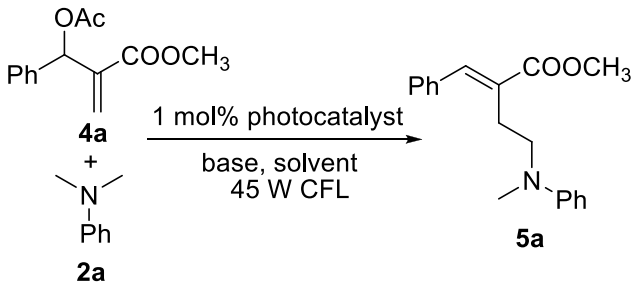
In the presence of oxygen, a radical addition/cyclization process was observed although the yield is very low (eq. 1). Because of the same R_f value of addition and cyclization product on TLC, the reaction mixture could not be separated and purified by column chromatography on silica gel. Determined by GC-MS and ^1H NMR spectra, the ratio of the addition/cyclization product could be determined.



Baylis-Hillman adducts are important intermediates and widely used in organic synthesis.[11] In order to expand the scope of the substrate, the reaction was applied to Baylis-Hillman adducts. Initially, the reaction of 2-(acetoxy(phenyl)methyl)acrylate

4a with *N,N*-dimethylaniline **2a** was examined (Table 3). Firstly, catalyzed by $Ru(bpy)_3Cl_2$, use of CH_3CN as a solvent and K_2CO_3 as a base, it was found that the oxidative coupling product was isolated in 14% yield (Table 3, entry 1). Changing the base K_2CO_3 to NaOAc, Na_2CO_3, Cs_2CO_3 revealed that the final base gave a slight better result with 28% yield (Table 3, entries 2-4). Based on these, Except DCE, the attempts on other solvents such as toluene, THF, DMF, NMP, EtOAc almost gave disappointing result (Table 3, entry 5). The performance of $Ir(ppy)_3$, $[Ir(ppy)_2bpy]PF_6$, $[Ir(ppy)_2bpy]BF_4$, $Ru(bpy)_3(PF_6)_2$ was not efficient (Table 3, entries 6-9). It revealed that the combination of $Ru(bpy)_3(BF_4)_2$, NaOAc as a base and DMSO as a solvent was most effective and the desired product can be obtained in 67% isolated yield (Table 3, entry 11). Replacing the acetate of Baylis-Hillman to Boc group could not promote the result. Notably, control experiment showed that no desired product was detected in the absence of visible light or photocatalyst (Table 3, entries 12-13). In the absence of base, just trace product was detected by TLC (Table 3, entry 14).

Table 3. Oxidative Coupling Optimization of Baylis-Hillman Acetates with *N,N*-Dimethylaniline[a]



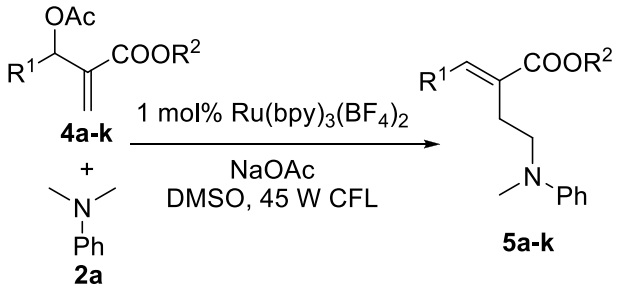
entry	catalyst	base	solvent	yield[f]
1	$Ru(bpy)_3Cl_2$	K_2CO_3	MeCN	14
2	$Ru(bpy)_3Cl_2$	Na_2CO_3	MeCN	5

3	$Ru(bpy)_3Cl_2$	Cs_2CO_3	MeCN	28
4	$Ru(bpy)_3Cl_2$	NaOAc	MeCN	5
5[b]	$Ru(bpy)_3Cl_2$	Cs_2CO_3	DCE	32
6	$Ir(ppy)_3$	K_2CO_3	MeCN	trace
7[c]	$[Ir(ppy)_2bpy]PF_6$	Cs_2CO_3	DCE	19
8[c]	$[Ir(ppy)_2bpy]BF_4$	Cs_2CO_3	DCE	22
9	$Ru(bpy)_3(PF_6)_2$	K_2CO_3	MeCN	trace
10[b]	$Ru(bpy)_3 (BF_4)_2$	Cs_2CO_3	DCE	39
11[d]	$Ru(bpy)_3(BF_4)_2$	NaOAc	DMSO	67
12[d]	-	NaOAc	DMSO	0
13[d,e]	$Ru(bpy)_3(BF_4)_2$	NaOAc	DMSO	0
14[d]	$Ru(bpy)_3(BF_4)_2$	-	DMSO	trace

[a] Reaction conditions: **4a** (0.5 mmol), **2a** (1 mmol), photocatalyst (0.005 mmol), base (1.5 mmol), solvent (2 mL), 24 hrs, 45 W compact fluorescent lamp irradiation under N_2 and room temperature until otherwise noted; [b] 1 mmol of **2a**, 1 mmol of base; [c] 0.6 mmol of **2a**, 0.5 mmol of base; [d] 0.6 mmol of **2a,** 0.6 mmol of base. [e] In the dark. [f] Isolated yield based on **4a**.

Then the scope of the substrate was examined. Baylis-Hillman acetates containing substituents such as methyl, isopropyl and methoxy on the aryl rings underwent the reaction smoothly (Table 4, entries 2-4). No obvious steric effect was observed (Table 4, entries 4-6). For substrates with halogenated phenyl rings, the desired products were isolated in modest yields (Table 4, entries 7-8). While furyl substituted Baylis-Hillman acetate was introduced, the reaction was also successfully performed (Table 4, entry 9). The reaction of ethyl 2-(acetoxy(phenyl)methyl)acrylate proceeded elegantly to give **5k** in 62% yield (Table 4, entry 11).

Table 4. Scope of Baylis-Hillman acetates[a]



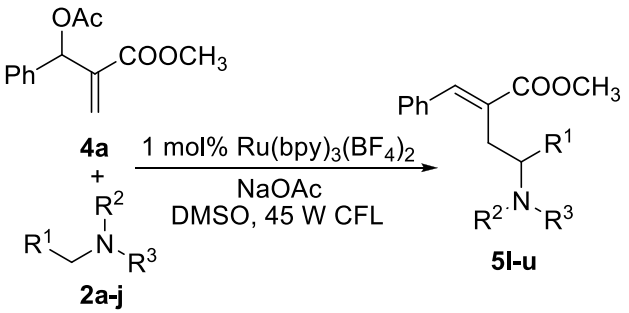
entry	R^1, R^2	yield (%)[b]
1	Ph, Me (**4a**)	67 (**5a**)
2	4-MeC_6H_4, Me (**4b**)	76 (**5b**)
3	4-$Pr^iC_6H_4$, Me (**4c**)	73 (**5c**)
4	4-$MeOC_6H_4$, Me (**4d**)	74 (**5d**)
5	3-$MeOC_6H_4$, Me (**4e**)	60 (**5e**)
6	2-$MeOC_6H_4$, Me (**4f**)	74 (**5f**)
7	4-FC_6H_4, Me (**4g**)	54 (**5g**)
8	4-ClC_6H_4, Me (**4h**)	44 (**5h**)
9	2-furyl, Me (**4i**)	57 (**5i**)
10	Pr^n, Me (**4j**)	43 (**5j**)
11	Ph, Et (**4k**)	62 (**5k**)

[a] Reaction conditions: **4a-k** (0.5 mmol), **2a** (0.6 mmol), $Ru(bpy)_3(BF_4)_2$ (0.005 mmol), NaOAc (0.6 mmol), DMSO (2 mL), 6 hrs, 45 W compact fluorescent lamp irradiation under N_2 atmosphere and r.t. [b] Isolated yield based on **4a-k**.

Next, a variety of tertiary amines were tried (Table 5). While the 4-chloro-*N*,*N*-dimethylaniline gave good results, the 3-chloro-*N*,*N*-dimethylaniline afforded the corresponding product only in 34% yield for unknown reason (Table 5, entries 1-2). The *N*,*N*-dimethylanilines bearing with Br or F atom also gave good yields (Table 5, entries 3-4). For *N*,*N*-dimethylanilines with an electron-donating group on the phenyl rings, the desired products were obtained in modest yields (Table 5, entries 5-6). *N*,*N*-diethylaniline and *N*-methyl-*N*-phenylaniline also participated in the reaction to give the corresponding products in moderate yields (Table 5, entries 7-8). The desired product was isolated in 65% yield when cyclic *N*-phenylpyroridine

was used (Table 5, entry 9). It was very glad to find that the aliphatic tertiary amine ethyl diisopropylamine could give addition product in reasonable yield (Table 5, entry 10).

Table 5. Scope of Tertiary Amines[a]



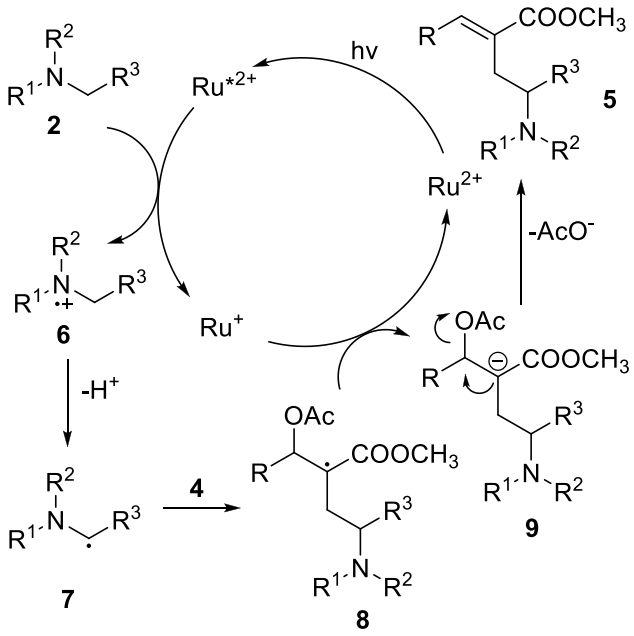
entry	R^1, R^2, R^3	yield(%)[b]
1	H, Me, 4-ClC_6H_4 (**2b**)	71 (**5l**)
2	H, Me, 3-ClC_6H_4 (**2e**)	34 (**5m**)
3	H, Me, 4-FC_6H_4 (**2f**)	57 (**5n**)
4	H, Me, 4-BrC_6H_4 (**2g**)	74 (**5o**)
5	H, Me, 4-MeC_6H_4 (**2h**)	63 (**5p**)
6	H, Me, 4-$MeOC_6H_4$ (**2c**)	58 (**5q**)
7	H, Ph, Ph (**2i**)	45 (**5r**)
8	Me, Et, Ph (**2j**)	51 (**5s**)
9	*N*-phenylpyroridine (**2d**)	65 (**5t**)
10[c]	Me, Pr^i, Pr^i (**2k**)	25 (**5u**)

[a] Reaction conditions: **4a** (0.5 mmol), **2b-k** (0.6 mmol), $Ru(bpy)_3(BF_4)_2$ (0.005 mmol), NaOAc (0.6 mmol), DMSO (2 mL), 45 W compact fluorescent lamp irradiation under N_2 and room temperature; see experimental section for details. [b] Isolated yield based on **4a**. [c] $[Ir(ppy)_2bpy]BF_4$ as photocatalyst.

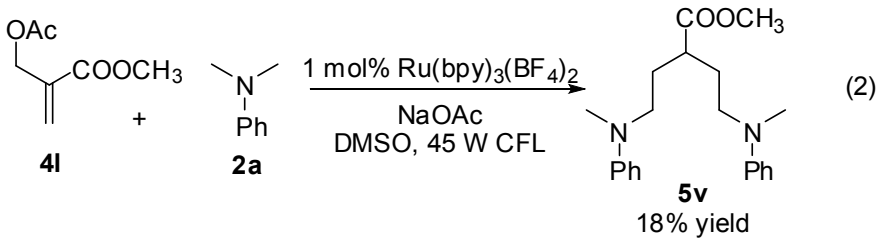
On the basis of literatures[1] and the aforementioned experimental results, a plausible reaction pathway is proposed in Scheme 1. Upon irradiation, Ru^{2+} is excited to provide Ru^{*2+}, which is then reductively quenched by **2** to produce Ru^+ and amine radical cation **6** via single electron transfer oxidation. The amine radical cation **6** can

be deprotonated by NaOAc to generate the tertiary α-amino carbon radical **7**, which can react with Baylis-Hillman acetate **4** to produce the alkyl radical **8**. The key intermediate alkyl anion **9** was generated from the reduction of **8** by photocatalyst (Ru^{+}) which itself was oxidized to initial photocatalyst (Ru^{2+}). Subsequently, elimination of AcO^{-} from the alkyl anion **9** formed the unsaturated γ-aminobutyric ester derivative **5**.

Scheme 1. Possible Mechanism

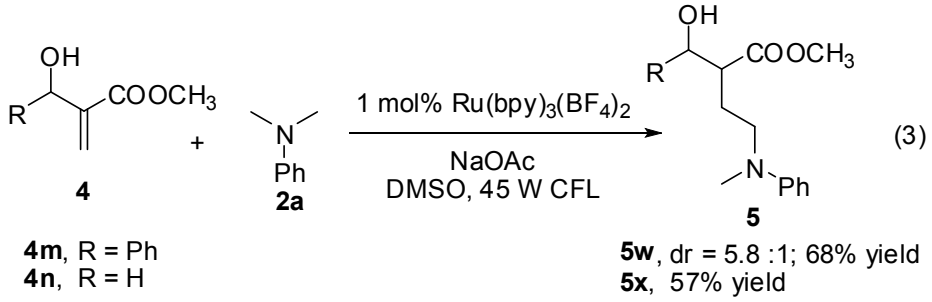


In case of simple methyl 2-(acetoxymethyl)acrylate **4l**, the double coupling product **5v** was obtained, which indicated that **4l** could react with two molecules of *N,N*-dimethylaniline **2a** (eq 2). Because **4l** was oligomerized easily or AcO^{-} was more difficult to leave, the yield of **5v** was very low although considerable reaction conditions were screened.



(2)

Finally, the reactions of Baylis-Hillman alcohols with *N,N*-dimethylaniline **2a** were investigated. The normal corresponding addition products were obtained in the presence of the hydroxyl group (eq 3). The dr ratio of product **5w** is about 5.8:1.



(3)

In summary, we have developed an efficient method for the synthesis of γ-aminobutyric ester derivatives via visible-light-promoted addition of α-aminoalkyl radicals to acrylates or Baylis-Hillman derivatives. The advantages of reaction are mild condition, broad scope of substrates. This reaction expands the synthetic application of α-aminoalkyl radicals under visible-light photoredox catalysis.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out under dry nitrogen atmosphere until otherwise noted. Solvents were dried by the general methods, and degassed before use. Baylis-Hillman acetates **4a~l**[12,13], Baylis-Hillman alcohols **4m~n**[12] and tertiary amines **2b~c**[14]**, 2e~h**[14], **2i**[15], **2d**[16] were prepared according to literature. Photoredox catalysts $Ir(ppy)_3$[17,18], $[Ir(ppy)_2bpy]PF_6$[19,20], $[Ir(ppy)_2bpy]BF_4$[19,10b], $Ru(bpy)_3(PF_6)_2$[21], $Ru(bpy)_3Cl_2$[22], $Ru(bpy)_3(BF_4)_2$[21] were

prepared according to literature. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 500 MHz instrument with TMS as internal standard. Low-resolution MS was obtained using EI or ESI ionization. HRMS was obtained using ESI ionization by TOF LC/MS. GC-MS spectra were obtained using normal analysis method, which MS spectra were obtained using EI ionization.

General Procedure for Synthesis of 3 under N_2. In a typical procedure: In a 10 mL two-necked round-bottom flask were placed acrylate **1** (1 mmol), DBU (152 mg, 1 mmol), $Ru(bpy)_3(BF_4)_2$ (7.4 mg, 0.01 mmol, 1 mol%) under N_2, and then amine **2** (0.6 mmol) and NMP (4 mL) were added. The reaction mixture was placed at a distance of about 5 cm from a 45 W compact fluorescent lamp (Arrow BHSL 45) and stirred at room temperature. After 12 hrs, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and H_2O (20 mL). The layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers washed with H_2O (2 x 10 mL), then were dried over Na_2SO_4. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (20/1) as the eluent to give the pure product **3**.

*Methyl 2-methyl-4-(methyl(phenyl)amino)butanoate (**3a**):* 123 mg, 56% Yield; Yellow oil; IR (thin film): 2950, 2360, 1735, 1600, 1507, 1460, 1370, 1194, 1172, 990, 748, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 2H), 6.79 – 6.66 (m, 3H), 3.70 (s, 3H), 3.42 – 3.29 (m, 2H), 2.94 (s, 3H), 2.58 – 2.47 (m, 1H), 2.05 – 1.93 (m, 1H), 1.77 – 1.65 (m, 1H), 1.24 (d, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 176.7, 149.2, 129.2, 116.3, 112.3, 51.6, 50.7, 38.3, 37.3, 30.5, 17.5; MS (ESI): ($[M+H]^+$) 222.1; HRMS (ESI) calcd for $C_{13}H_{20}NO_2$ ($[M+H]^+$) 222.1494, found 222.1498.

*Methyl 4-(methyl(phenyl)amino)butanoate (**3b**)*:[23] 65 mg, 31% Yield; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.77 – 6.69 (m, 3H), 3.69 (s, 3H), 3.40 – 3.35 (m, 2H), 2.95 (s, 3H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.98 – 1.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 149.3, 129.2, 116.3, 112.3, 51.9, 51.6, 38.3, 31.3, 22.2; MS (EI): 207, 176, 146, 132, 120, 104, 91, 77, 69, 59, 51, 42, 28, 15.

*Ethyl 4-(methyl(phenyl)amino)butanoate (**3c**)*:[24] 64 mg, 29% Yield; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.78 – 6.69 (m, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.36 (m, 2H), 2.95 (s, 3H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 149.3, 129.2, 116.3, 112.3, 60.4, 52.0, 38.3, 31.6, 22.2, 14.2; MS (EI): 221, 176, 146, 132, 120, 104, 91, 77, 69, 59, 51, 42, 28, 15.

*Butyl 2-methyl-4-(methyl(phenyl)amino)butanoate (**3d**)*: 119 mg, 45% Yield; Yellow oil; IR (thin film): 2960, 2935, 2874, 1731, 1600, 1507, 1464, 1372, 1177, 748, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 6.77 – 6.67 (m, 3H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.43 – 3.28 (m, 2H), 2.93 (s, 3H), 2.55 – 2.45 (m, 1H), 2.03 – 1.92 (m, 1H), 1.76 – 1.66 (m, 1H), 1.66 – 1.56 (m, 2H), 1.45 – 1.35 (m, 2H), 1.23 (d, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.33, 149.2, 129.2, 116.3, 112.3, 64.3, 50.7, 38.3, 37.5, 30.7, 30.5, 19.2, 17.6, 13.7; MS (ESI):

([M+H]$^+$) 264.2; HRMS (ESI) calcd for $C_{16}H_{26}NO_2$ ([M+H]$^+$) 264.1964, found 264.1969.

*Methyl 4-((4-methoxyphenyl)(methyl)amino)-2-methylbutanoate (**3e**):* 92 mg, 37% Yield; Yellow oil; IR (thin film): 2950, 2832, 1735, 1514, 1463, 1361, 1179, 1040, 816 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 – 6.82 (m, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 3.68 (s, 3H), 3.28 – 3.22 (m, 2H), 2.85 (s, 3H), 2.56 – 2.47 (m, 1H), 2.00 – 1.90 (m, 1H), 1.71 – 1.61 (m, 1H), 1.21 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 151.8, 144.3, 114.8, 55.8, 51.9, 51.5, 39.0, 37.3, 30.4, 17.4; MS (ESI): ([M+H]$^+$) 252.2; HRMS (ESI) calcd for $C_{14}H_{22}NO_3$ ([M+H]$^+$) 252.1600, found 252.1600.

*Methyl 4-((4-chlorophenyl)(methyl)amino)-2-methylbutanoate (**3f**):* 103 mg, 40% Yield; Yellow oil; IR (thin film): 2974, 2950, 2878, 1733, 1597, 1503, 1461, 1375, 1193, 1040, 810 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 2H), 6.62 (d, *J* = 8.3 Hz, 2H), 3.68 (s, 3H), 3.38 – 3.25 (m, 2H), 2.90 (s, 3H), 2.53 – 2.45 (m, 1H), 2.00 – 1.90 (m, 1H), 1.72 – 1.62 (m, 1H), 1.22 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 147.7, 128.9, 121.1, 113.4, 51.6, 50.8, 38.4, 37.2, 30.3, 17.5; MS (ESI): ([M+H]$^+$) 256.1; HRMS (ESI) calcd for $C_{13}H_{19}ClNO_2$ ([M+H]$^+$) 256.1104, found 256.1101.

*Methyl 2-methyl-3-(1-phenylpyrrolidin-2-yl)propanoate (**3g**):* 140 mg, 60% Yield, 1:1 dr; **Diastereomer 1:** White solid, m.p. 34-37 °C; IR (thin film): 2969, 2950, 1735, 1599, 1506, 1460, 1363, 1196, 1164, 747, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.12 (m, 2H), 6.79 – 6.56 (m, 3H), 3.78 (s, 3H), 3.71 – 3.64 (m, 1H), 3.50 –

3.38 (m, 1H), 3.23 – 3.10 (m, 1H), 2.65 – 2.47 (m, 1H), 2.31 – 2.17 (m, 1H), 2.11 – 1.92 (m, 3H), 1.88 – 1.76 (m, 1H), 1.39 – 1.26 (m, 1H), 1.23 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 147.3, 129.2, 115.6, 111.9, 56.8, 51.6, 48.3, 37.3, 37.0, 30.1, 23.3, 18.7; MS (ESI): ($[M+H]^+$) 248.2; HRMS (ESI) calcd for $C_{15}H_{22}NO_2$ ($[M+H]^+$) 248.1651, found 248.1662. **Diastereomer 2:** Yellow oil; IR (thin film): 2969, 2950, 2876, 1736, 1598, 1505, 1460, 1365, 1193, 1161, 747, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, J = 8.5, 7.4 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.1 Hz, 2H), 3.84 – 3.78 (m, 1H), 3.62 (s, 3H), 3.46 – 3.40 (m, 1H), 3.20 – 3.13 (m, 1H), 2.14 – 2.04 (m, 1H), 2.04 – 1.93 (m, 2H), 1.85 – 1.75 (m, 3H), 1.30 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 147.1, 129.2, 115.6, 111.9, 56.5, 51.5, 48.3, 37.3, 36.8, 30.3, 23.4, 17.2; MS (ESI): ($[M+H]^+$) 248.2; HRMS (ESI) calcd for $C_{15}H_{22}NO_2$ ($[M+H]^+$) 248.1651, found 248.1659.

General Procedure for Synthesis of 3 under air. In a 10 mL two-necked round-bottom flask were placed acrylate **1** (1 mmol), DBU (152 mg, 1 mmol), $Ru(bpy)_3(BF_4)_2$ (7.4 mg, 0.01 mmol, 1 mol%) under air, and then amine **2** (0.6 mmol) and NMP (2 mL) were added. The reaction mixture was placed at a distance of about 5 cm from a 45 W compact fluorescent lamp (Arrow BHSL 45) and stirred at room temperature. After 12 hrs, the reaction mixture was purified by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (20/1) as the eluent to give the mixture products of **3** and **3'**.

*A mixture of methyl 4-(methyl(phenyl)amino)butanoate (**3b**) and methyl 1-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylate (**3b'**):* 29 mg, 15% Yield,

3b/**3b'**=2.3/1; Yellow oil; **3b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.77 – 6.69 (m, 3H), 3.69 (s, 3H), 3.40 – 3.35 (m, 2H), 2.95 (s, 3H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.98 – 1.89 (m, 2H); **3b':** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 6.69 – 6.64 (m, 2H), 3.81 (t, *J* = 5.0 Hz, 1H), 3.73 (s, 3H), 3.45 – 3.40 (m, 1H), 3.23 – 3.17 (m, 1H), 2.93 (s, 3H), 2.35 – 2.28 (m, 1H), 2.13 – 2.04 (m, 1H).

*A mixture of ethyl 4-(methyl(phenyl)amino)butanoate (**3c**) and ethyl 1-methyl-1,2,3,4-tetrahydroquinoline-4-carboxylate (**3c'**):* 36 mg, 16% Yield, **3c**/**3c'**=2.2/1; Yellow oil; **3c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.78 – 6.69 (m, 3H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.36 (m, 2H), 2.95 (s, 3H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); **3c':** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 2H), 6.69 – 6.62 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.79 (t, *J* = 5.1 Hz, 1H), 3.46 – 3.41 (m, 1H), 3.23 – 3.17 (m, 1H), 2.94 (s, 3H), 2.34 – 2.27 (m, 1H), 2.13 – 2.05 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

General Procedure for Synthesis of 5. In a typical procedure: In a 10 mL two-necked round-bottom flask were placed Baylis-Hillman acetate or alcohol **4** (0.5 mmol), NaOAc (49.2 mg, 0.6 mmol), $Ru(bpy)_3(BF_4)_2$ (3.7 mg, 0.005 mmol, 1 mol%) under N_2, and then amine **2** (0.6 mmol) and DMSO (2 mL) were added. The reaction mixture was placed at a distance of about 5 cm from a 45 W compact fluorescent lamp (Arrow BHSL 45) and stirred at room temperature. After 6 hrs, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and H_2O (20 mL). The layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers washed with H_2O (2 x 10 mL), then were dried over Na_2SO_4.

Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (20/1) as the eluent to give the pure product **5**.

*(E)-Methyl 2-benzylidene-4-(methyl(phenyl)amino)butanoate (**5a**):* 99 mg, 67% Yield; Light yellow oil; IR (thin film): 3058, 3025, 2948, 2821, 1713, 1600, 1505, 1434, 1373, 1256, 1195, 1128, 748, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.42 – 7.34 (m, 5H), 7.21 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.74 – 6.63 (m, 3H), 3.88 (s, 3H), 3.55 – 3.48 (m, 2H), 2.92 (s, 3H), 2.84 – 2.77 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 148.8, 141.1, 135.5, 130.6, 129.1, 128.8, 128.6, 128.5, 116.2, 112.2, 52.1, 51.9, 38.0, 24.8; MS (ESI): ($[M+H]^+$) 296.2; HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ ($[M+H]^+$) 296.1651, found 296.1645.

*(E)-Methyl 4-(methyl(phenyl)amino)-2-(4-methylbenzylidene)butanoate (**5b**):* 117 mg, 76% Yield; Light yellow solid, m.p. 34-36 °C; IR (thin film): 3025, 2948, 1715, 1600, 1505, 1435, 1372, 1256, 1128, 747, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.16 (m, 4H), 6.72 (d, *J* = 7.6 Hz, 3H), 3.88 (s, 3H), 3.57 – 3.49 (m, 2H), 2.95 (s, 3H), 2.88 – 2.79 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.75, 148.8, 141.1, 138.7, 132.6, 129.7, 129.3, 129.1, 128.9, 116.2, 112.2, 52.0, 51.8, 38.0, 24.8, 21.3; MS (ESI): ($[M+H]^+$) 310.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_2$ ($[M+H]^+$) 310.1807, found 310.1814.

*(E)-Methyl 2-(4-isopropylbenzylidene)-4-(methyl(phenyl)amino)butanoate (**5c**):* 112 mg, 73% Yield; Yellow oil; IR (thin film): 3025, 2960, 2870, 1709, 1600, 1506, 1435, 1373, 1256, 1195, 1129, 748, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.22 (m, 4H), 6.82 – 6.67 (m, 3H), 3.89 (s, 3H), 3.60

– 3.49 (m, 2H), 3.05 – 2.91 (m, 1H), 2.98 (s, 3H), 2.87 – 2.80 (m, 2H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 149.6, 148.9, 141.1, 133.0, 129.7, 129.2, 129.1, 126.7, 116.2, 112.3, 52.1, 51.9, 38.1, 34.0, 24.9, 23.9; MS (ESI): ($[M+H]^+$) 338.2; HRMS (ESI) calcd for $C_{22}H_{28}NO_2$ ($[M+H]^+$) 338.2120, found 338.2139.

*(E)-Methyl 2-(4-methoxybenzylidene)-4-(methyl(phenyl)amino)butanoate (**5d**):* 121mg, 74% Yield; Light yellow solid, m.p. 62-64 °C; IR (thin film): 3025, 2949, 2837, 1705, 1603, 1510, 1435, 1355, 1255, 1176, 1128, 749, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.78 – 6.69 (m, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.58 – 3.50 (m, 2H), 2.96 (s, 3H), 2.88 – 2.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 159.9, 148.9, 140.7, 130.7, 129.2, 128.4, 127.9, 116.2, 114.0, 112.3, 55.3, 52.0, 51.8, 38.1, 24.8; MS (ESI): ($[M+H]^+$) 326.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_3$ ($[M+H]^+$) 326.1756, found 326.1766.

*(E)-Methyl 2-(3-methoxybenzylidene)-4-(methyl(phenyl)amino)butanoate (**5e**):* 97 mg, 60% Yield; Yellow oil; IR (thin film): 3025, 2948, 2837, 1709, 1599, 1506, 1487, 1373, 1248, 1131, 1127, 750, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.42 – 7.35 (m, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.22 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.98 (dd, *J* = 12.4, 7.9 Hz, 2H), 6.74 – 6.64 (m, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.55 – 3.49 (m, 2H), 2.94 (s, 3H), 2.81 – 2.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 157.3, 148.7, 137.6, 130.5, 129.9, 129.3, 129.1, 124.5, 120.2, 115.9, 111.9, 110.6, 55.4, 51.9,

51.9, 37.9, 24.8; MS (ESI): ($[M+H]^+$) 326.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_3$ ($[M+H]^+$) 326.1756, found 326.1756.

*(E)-Methyl 2-(2-methoxybenzylidene)-4-(methyl(phenyl)amino)butanoate (**5f**):* 120 mg, 74% Yield; Yellow oil; IR (thin film): 3025, 2949, 2835, 1708, 1600, 1506, 1434, 1372, 1245, 1195, 1128, 748, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.74 – 6.65 (m, 3H), 3.88 (s, 3H), 3.81 (s, 3H), 3.55 – 3.47 (m, 2H), 2.93 (s, 3H), 2.86 – 2.79 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 159.7, 148.8, 141.0, 136.9, 130.8, 129.6, 129.1, 121.1, 116.1, 114.3, 114.0, 112.1, 55.2, 52.1, 51.9, 38.0, 24.8; MS (ESI): ($[M+H]^+$) 326.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_3$ ($[M+H]^+$) 326.1756, found 326.1770.

*(E)-Methyl 2-(4-fluorobenzylidene)-4-(methyl(phenyl)amino)butanoate (**5g**):* 85 mg, 54% Yield; Yellow oil; IR (thin film): 3025, 2949, 2886, 1709, 1600, 1508, 1436, 1373, 1228, 1196, 1128, 749, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.34 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 2H), 7.08-7.03 (m, 2H), 6.75 – 6.64 (m, 3H), 3.88 (s, 3H), 3.55 – 3.49 (m, 2H), 2.92 (s, 3H), 2.83 – 2.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 163.6, 161.6, 148.7, 140.0, 131.5, 130.8, 130.7, 130.6, 129.2, 116.4, 115.7, 115.5, 112.2, 52.2, 51.8, 38.2, 24.7; MS (ESI): ($[M+H]^+$) 314.2; HRMS (ESI) calcd for $C_{19}H_{21}FNO_2$ ($[M+H]^+$) 314.1556, found 314.1553.

*(E)-Methyl 2-(4-chlorobenzylidene)-4-(methyl(phenyl)amino)butanoate (**5h**):* 73 mg, 44% Yield; Yellow solid, m.p. 44-46 °C; IR (thin film): 3026, 2949, 2886, 1712, 1600, 1506, 1490, 1434, 1372, 1253, 1196, 1129, 1090, 749, 693 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$) δ 7.73 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.22 (t, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 2H), 3.88 (s, 3H), 3.54 – 3.48 (m, 2H), 2.91 (s, 3H), 2.81 – 2.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 148.7, 139.8, 134.4, 133.9, 131.2, 130.1, 129.2 128.8, 116.4, 112.2, 52.2, 51.8, 38.2, 24.8; MS (ESI): ($[M+H]^+$) 330.1; HRMS (ESI) calcd for $C_{19}H_{21}ClNO_2$ ($[M+H]^+$) 330.1261, found 330.1267.

*Methyl 2-(furan-2-ylmethylene)-4-(methyl(phenyl)amino)butanoate (**5i**):* 80 mg, 57% Yield (*E*/*Z*=63/27); Yellow oil; IR (thin film): 3025, 2949, 2885, 1712, 1633, 1600, 1506, 1434, 1365, 1258, 1210, 1128, 747, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.3 Hz, 0.63H), 7.47 (s, 0.63H), 7.43 (d, *J* = 1.6 Hz, 0.37H), 7.32 – 7.22 (m, 2H), 6.93 (d, *J* = 3.4 Hz, 0.37H), 6.88 (d, *J* = 7.8 Hz, 1.13H), 6.75 (dd, *J* = 18.2, 7.7 Hz, 1.87H), 6.64 (d, *J* = 3.3 Hz, 0.63H), 6.56 (s, 0.37H), 6.54 – 6.51 (m, 0.63H), 6.47 – 6.44 (m, 0.37H), 3.855 (s, 1.13H), 3.851 (s, 1.87H), 3.61 – 3.48 (m, 2H), 3.10 – 3.06 (m, 1.26H), 3.05 (s, 1.87H), 2.98 (s, 1.13H), 2.70 – 2.61 (m, 0.74H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 168.5, 151.5, 150.5, 148.9, 148.7, 144.4, 143.1, 129.2, 129.1, 126.8, 126.5, 126.1, 124.9, 116.3, 116.0, 113.2, 112.1, 112.0, 52.6, 52.1, 51.9, 51.7, 38.5, 38.0, 32.8, 25.3; MS (ESI): ($[M+H]^+$) 286.1; HRMS (ESI) calcd for $C_{17}H_{20}NO_3$ ($[M+H]^+$) 286.1443, found 286.1452.

*(E)-Methyl 2-(2-(methyl(phenyl)amino)ethyl)hex-2-enoate (**5j**):* 56 mg, 43% Yield; Light yellow oil; IR (thin film): 3025, 2958, 2872, 1709, 1600, 1507, 1435, 1365, 1373, 1278, 1251, 1198, 1145, 748, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.72 (t, *J* = 7.2 Hz,

1H), 3.80 (s, 3H), 3.48 – 3.37 (m, 2H), 2.98 (s, 3H), 2.64 – 2.55 (m, 2H), 2.23 – 2.13 (m, 2H), 1.54 – 1.43 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 148.8, 144.6, 129.3, 129.2, 116.0, 112.0, 51.9, 51.7, 38.3, 30.6, 24.1, 22.1, 13.9; MS (ESI): ($[M+H]^+$) 262.2; HRMS (ESI) calcd for $C_{16}H_{24}NO_2$ ($[M+H]^+$) 262.1807, found 262.1814.

*(E)-Ethyl 2-benzylidene-4-(methyl(phenyl)amino)butanoate (**5k**):* 96 mg, 62% Yield; Yellow oil; IR (thin film): 3059, 3025, 2979, 2903, 2820, 1705, 1600, 1507, 1447, 1372, 1254, 1194, 1129, 748, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.43 – 7.34 (m, 5H), 7.22 (t, J = 7.9 Hz, 2H), 6.70 (d, J = 7.5 Hz, 3H), 4.35 (q, J = 7.1 Hz, 2H), 3.57 – 3.48 (m, 2H), 2.93 (s, 3H), 2.86 – 2.77 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 148.8, 140.9, 135.6, 130.8, 129.1, 128.8, 128.5, 128.4, 116.1, 112.1, 61.0, 51.9, 38.0, 24.6, 14.3; MS (ESI): ($[M+H]^+$) 310.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_2$ ($[M+H]^+$) 310.1807, found 310.1810.

*(E)-Methyl 2-benzylidene-4-((4-chlorophenyl)(methyl)amino)butanoate (**5l**):* 117 mg, 71% Yield; Yellow oil; IR (thin film): 3054, 3025, 2949, 1713, 1630, 1597,1504, 1434, 1373, 1196, 1129, 810, 764, 702, 629 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.30 (m, 2H), 7.12 (d, J = 8.9 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 3.52 – 3.43 (m, 2H), 2.88 (s, 3H), 2.81 – 2.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 147.3, 141.3, 135.5, 130.4, 128.9, 128.7, 128.6, 128.5, 120.1, 113.2, 52.1, 51.9, 38.2, 24.6; MS (ESI): ($[M+H]^+$) 330.1; HRMS (ESI) calcd for $C_{19}H_{21}ClNO_2$ ($[M+H]^+$) 330.1261, found 330.1258.

*(E)-Methyl 2-benzylidene-4-((3-chlorophenyl)(methyl)amino)butanoate (**5m**):* Reation time is 18 hrs; 56 mg, 34% Yield; Yellow oil; IR (thin film): 3025, 2949, 2821, 1712, 1594, 1561, 1495, 1434, 1371, 1258, 1199, 1130, 987, 761, 702, 683 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.32 (m, 3H), 7.09 (t, *J* = 8.1 Hz, 1H), 6.70 – 6.62 (m, 2H), 6.52 (d, *J* = 7.0 Hz, 1H), 3.90 (s, 3H), 3.53 – 3.47 (m, 2H), 2.89 (s, 3H), 2.82 – 2.77 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 149.8, 141.5, 135.4, 135.1, 130.1, 130.0, 128.7, 128.63, 128.60, 115.9, 111.9, 110.2, 52.2, 51.7, 38.1, 24.7; MS (ESI): ($[M+H]^+$) 330.1; HRMS (ESI) calcd for $C_{19}H_{21}ClNO_2$ ($[M+H]^+$) 330.1261, found 330.1275.

*(E)-Methyl 2-benzylidene-4-((4-fluorophenyl)(methyl)amino)butanoate (**5n**):* 90 mg, 57% Yield; Yellow oil; IR (thin film): 3025, 2950, 2821, 1709, 1517, 1435, 1356, 1256, 1227, 1169, 1128, 1085, 816, 766, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 – 7.32 (m, 5H), 6.94 – 6.87 (m, 2H), 6.65 – 6.54 (m, 2H), 3.87 (s, 3H), 3.51 – 3.43 (m, 2H), 2.88 (s, 3H), 2.82 – 2.74 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 156.2, 154.4, 145.5, 141.1, 135.5, 130.5, 128.8, 128.6, 128.5, 115.5, 115.4, 113.4, 113.3, 52.5, 52.1, 38.5, 24.5; MS (ESI): ($[M+H]^+$) 314.2; HRMS (ESI) calcd for $C_{19}H_{21}FNO_2$ ($[M+H]^+$) 314.1556, found 314.1563.

*(E)-Methyl 2-benzylidene-4-((4-bromophenyl)(methyl)amino)butanoate (**5o**):* 138 mg, 74% Yield; Yellow oil; IR (thin film): 3025, 2999, 2821, 1716, 1590, 1497, 1374, 1256, 1194, 1129, 1085, 808, 761, 700, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 7.27 – 7.23 (m, 2H), 6.50 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.50 – 3.43 (m, 2H), 2.87 (s, 3H), 2.82 – 2.74 (m, 2H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 168.5, 147.7, 141.4, 135.5, 131.8, 130.4, 128.7, 128.6, 128.5, 113.7, 108.0, 52.1, 51.8, 38.2, 24.6; MS (ESI): ($[M+H]^+$) 374.1; HRMS (ESI) calcd for $C_{19}H_{21}BrNO_2$ ($[M+H]^+$) 374.0756, found 374.0768.

*(E)-Methyl 2-benzylidene-4-(methyl(p-tolyl)amino)butanoate (**5p**):* 98 mg, 63% Yield; Yellow oil; IR (thin film): 3025, 2948, 2821, 1712, 1619, 1521, 1434, 1355, 1255, 1190, 1127, 1085, 804, 766, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.44 – 7.35 (m, 5H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 3.54 – 3.45 (m, 2H), 2.91 (s, 3H), 2.85 – 2.76 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 146.8, 141.0, 135.6, 130.7, 129.7, 128.9, 128.6, 128.5, 125.5, 112.7, 52.2, 52.1, 38.2, 24.6, 20.2; MS (ESI): ($[M+H]^+$) 310.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_2$ ($[M+H]^+$) 310.1807, found 310.1803.

*(E)-Methyl 2-benzylidene-4-((4-methoxyphenyl)(methyl)amino)butanoate (**5q**):* 94 mg, 58% Yield; Yellow oil; IR (thin film): 3024, 2949, 2904, 2832, 1713, 1630, 1514, 1435, 1356, 1245, 1128, 1084, 1039, 816, 766, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.45 – 7.29 (m, 5H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 3.49 – 3.41 (m, 2H), 2.87 (s, 3H), 2.81 – 2.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 151.6, 143.8, 140.9, 135.6, 130.7, 128.9, 128.6, 128.5, 114.8, 114.4, 55.8, 52.9, 52.1, 38.6, 24.5; MS (ESI): ($[M+H]^+$) 326.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_3$ ($[M+H]^+$) 326.1756, found 326.1749.

*(E)-Methyl 2-benzylidene-4-(diphenylamino)butanoate (**5r**):* 81 mg, 45% Yield; White solid, m.p. 95-97 °C; IR (thin film): 3058, 3024, 2950, 2926, 1707, 1589, 1494, 1435, 1369, 1245, 1218, 1193, 1110, 749, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ

7.79 (s, 1H), 7.31 (dt, *J* = 12.4, 4.8 Hz, 5H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 4H), 7.00 (t, *J* = 7.3 Hz, 2H), 3.98 – 3.92 (m, 2H), 3.90 (s, 3H), 3.00 – 2.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 147.6, 141.1, 135.3, 129.9, 129.3, 129.0, 128.5, 128.5, 121.3, 121.0, 52.2, 51.3, 25.6; MS (ESI): ($[M+H]^+$) 358.2; HRMS (ESI) calcd for $C_{24}H_{24}NO_2$ ($[M+H]^+$) 358.1807, found 358.1800.

*(E)-Methyl 2-benzylidene-4-(ethyl(phenyl)amino)pentanoate (**5s**):* 82 mg, 51% Yield; Yellow oil; IR (thin film): 3058, 3023, 2972, 2871, 1716, 1596, 1504, 1435, 1375, 747, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.31 (m, 3H), 7.19 (dd, *J* = 8.8, 7.2 Hz, 2H), 6.74 – 6.64 (m, 3H), 4.29 – 4.19 (m, 1H), 3.82 (s, 3H), 3.14 – 2.96 (m, 2H), 2.92 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.80 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 148.3, 140.4, 135.8, 131.3, 129.0, 128.5, 128.2, 116.2, 113.7, 53.2, 52.0, 37.6, 31.3, 18.0, 14.3; MS (ESI): ($[M+H]^+$) 324.2; HRMS (ESI) calcd for $C_{21}H_{26}NO_2$ ($[M+H]^+$) 324.1964, found 324.1967.

*(E)-Methyl 3-phenyl-2-((1-phenylpyrrolidin-2-yl)methyl)acrylate (**5t**):* 104 mg, 65% Yield; Yellow oil; IR (thin film): 3058, 3024, 2949, 2874, 2841, 1712, 1597, 1505, 1435, 1367, 1259, 1225, 1118, 991, 747, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.32 (m, 3H), 7.22 (t, *J* = 7.9 Hz, 2H), 6.70 – 6.61 (m, 3H), 4.04 – 3.95 (m, 1H), 3.91 (s, 3H), 3.30 (t, *J* = 8.2 Hz, 1H), 3.09 (dd, *J* = 16.0, 8.7 Hz, 1H), 2.96 (dd, *J* = 13.4, 4.4 Hz, 1H), 2.68 (dd, *J* = 13.4, 10.0 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.76 – 1.69 (m, 1H), 1.69 – 1.56 (m, 2H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 168.8, 147.1, 141.6, 136.0, 131.34, 129.2, 128.8, 128.6, 128.2, 115.4, 111.9, 57.7, 52.1, 48.0, 29.5, 29.2, 23.0; MS (ESI): ($[M+H]^+$) 322.2; HRMS (ESI) calcd for $C_{21}H_{24}NO_2$ ($[M+H]^+$) 322.1807, found 322.1809.

*(E)-Methyl 2-benzylidene-4-(diisopropylamino)pentanoate (**5u**):* Reation time is 24 hrs; 38 mg, 25% Yield; Yellow oil; IR (thin film): 3025, 2962, 2869, 1715, 1447, 1435, 1396, 1365, 1264, 1189, 774, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.44 – 7.37 (m, 4H), 7.34 – 7.29 (m, 1H), 3.82 (s, 3H), 3.27 – 3.17 (m, 1H), 3.07 – 2.94 (m, 2H), 2.78 – 2.71 (m, 1H), 2.68 – 2.61 (m, 1H), 0.98 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.6 Hz, 6H), 0.88 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 138.9, 136.3, 133.2, 129.3, 128.4, 128.1, 51.9, 49.2, 44.3, 34.2, 23.5, 22.4, 20.4; MS (ESI): ($[M+H]^+$) 304.2; HRMS (ESI) calcd for $C_{19}H_{30}NO_2$ ($[M+H]^+$) 304.2277, found 304.2287.

*Methyl 4-(methyl(phenyl)amino)-2-(2-(methyl(phenyl)amino)ethyl)butanoate (**5v**):* 30 mg, 18% Yield; Yellow oil; IR (thin film): 3025, 2949, 1732,1600, 1506, 1449, 1371, 1193, 991, 748, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 4H), 6.76 – 6.68 (m, 6H), 3.70 (s, 3H), 3.40 – 3.26 (m, 4H), 2.91 (s, 6H), 2.51 – 2.43 (m, 1H), 2.03 – 1.93 (m, 2H), 1.83 – 1.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 149.2, 129.2, 116.5, 112.4, 51.6, 50.8, 41.0, 38.3, 29.3; MS (ESI): ($[M+H]^+$) 341.2; HRMS (ESI) calcd for $C_{21}H_{29}N_2O_2$ ($[M+H]^+$) 341.2229, found 341.2234.

*Methyl 2-(hydroxy(phenyl)methyl)-4-(methyl(phenyl)amino)butanoate (**5w**):* 107 mg, 68% Yield, 5.8:1 dr; **Major diastereoisomer:** Colorless oil; IR (thin film): 3482, 3029, 2949, 1732,1600, 1507, 1452, 1435, 1364, 1193, 1035, 750, 701 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 7.23 – 7.15 (m, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 4.84 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 3.32 – 3.23 (m, 1H), 3.23 – 3.14 (m, 1H), 2.88 (s, 1H), 2.86 – 2.80 (m, 1H), 2.80 (s, 3H), 1.95 – 1.85 (m, 1H), 1.66 – 1.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 149.1, 141.5, 129.1, 128.7, 128.3, 126.5, 116.5, 112.5, 75.4, 51.9, 50.8, 38.1, 26.3; MS (ESI): ($[M+H]^+$) 314.2; HRMS (ESI) calcd for $C_{19}H_{24}NO_3$ ($[M+H]^+$) 314.1756, found 314.1749. **Minor diastereoisomer:** Colorless oil; IR (thin film): 3479, 3028, 2950, 1732,1600, 1506, 1453, 1371, 1201, 1168, 1035, 749, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.33 – 7.28 (m, 1H), 7.24 – 7.17 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 2H), 5.05 (d, *J* = 5.3 Hz, 1H), 3.62 (s, 3H), 3.35 – 3.26 (m, 1H), 3.26 – 3.17 (m, 1H), 2.94 (s, 1H), 2.82 – 2.74 (m, 4H), 2.07 – 1.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 149.3, 141.4, 129.1, 128.4, 127.8, 126.0, 116.6, 112.7, 74.1, 51.8, 51.3, 50.6, 38.1, 24.1; MS (ESI): ($[M+H]^+$) 314.2; HRMS (ESI) calcd for $C_{19}H_{24}NO_3$ ($[M+H]^+$) 314.1756, found 314.1761.

*Methyl 2-(hydroxymethyl)-4-(methyl(phenyl)amino)butanoate (**5x**):* 67 mg, 57% Yield; Colorless oil; IR (thin film): 3444, 3025, 2951, 2883, 1732,1600, 1507, 1436, 1372, 1194, 1037, 750, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 6.78 – 6.70 (m, 3H), 3.83 – 3.77 (m, 2H), 3.74 (s, 3H), 3.46 – 3.32 (m, 2H), 2.93 (s, 3H), 2.69 – 2.61 (m, 1H), 2.42 (s, 1H), 2.02 – 1.92 (m, 1H), 1.89 – 1.79 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 149.2, 129.2, 116.8, 112.7, 63.3, 51.9, 50.8, 45.4, 38.4, 25.6; MS (ESI): ($[M+H]^+$) 238.1; HRMS (ESI) calcd for $C_{13}H_{20}NO_3$ ($[M+H]^+$) 238.1443, found 238.1440.

ASSOCIATED CONTENT

Supporting Information

Spectroscopic data for all products **3a-g** and **5a-x** (PDF version). This material is available free of charge via the internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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